# CONVERSION OF CO2 AND SALINE WATER TO VALUE-ADDED CHEMICALS AND DESALINATED WATER

by

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#### Abstract

Two electrochemical approaches that simultaneously convert carbon dioxide and high salinity brines to desalinated water and value-added chemicals in the form of inorganic acids and carbonate salts were demonstrated. In the first method, a multi-compartment electrodialysis cell module using anion exchange and cation exchange membranes, and a Pt/Ir-coated Ti anode and Ti mesh cathode was used to produce HCl and NaHCO<sub>3</sub> products from a carbonic acid and sodium chloride solution. Under an applied voltage inorganic carbon salts and acids were produced. A mathematical model for this electrodialysis cell configuration was developed to better understand limitations within the cell which were not available from experimental data including concentration profiles within the intra-membrane channels.

In the second method, a first of a kind 5-compartment electrochemical cell including an anode, cathode and three electro-dialytic compartments was used. Water was converted to oxygen and protons at the anode while gaseous O<sub>2</sub> and CO<sub>2</sub> were converted to bi(carbonate) or hydroxide ions at the cathode. The three central electrodialysis compartments combine the ions present in the saline water with the products of the anode and cathode to produce value-added chemicals and desalinated water. A custom-built electrochemical cell with an active area of 3.24 cm<sup>2</sup> containing an array of two anion and cation exchange membranes each, Pt/C catalyzed cathode and titanium anode electrodes were used. The cell was investigated to understand the different factors affecting cell performance. Increasing concentrations of hydrochloric acid and bi(carbonate)/hydroxide salts was observed in the respective compartments over 24-hour periods of testing. Current efficiencies of alkaline (bicarbonate, carbonate or hydroxide) ions and proton production were as high as 71% and 96%, respectively. Polarization losses across the different compartments of the

electrochemical cell were mapped to determine the source of overpotentials with different gas compositions. The new electrochemical cell platform is scalable and was used to successfully desalinate and convert carbon dioxide to chemicals. The process shows considerable commercial potential and has been scaled-up to a commercial module for deployment with different industrial operations within the oil and gas, and mining sectors.

### Lay Summary

An innovation for the simultaneous conversion of different brines and carbon dioxide produced during industrial operations to re-usable water and chemicals was developed. The work focused on demonstrating the first of a kind technology and investigating fundamental limitations. Conventional technologies treat either carbon dioxide or brines separately with the treatment being a cost in both cases. Instead, simultaneous treatment of carbon dioxide and brines in a combine technology allows for the production of chemicals and re-usable water resulting in value being created for the user. The technology has various industrial applications and is currently being commercialized by Mangrove Water Technologies Ltd.

## Preface

This thesis is original and independent work by the author, Mohammad Saad Dara. I was responsible for most of the work in this thesis including but not limited to:

- All design of the 5-compartment electrochemical cell.
- All design of experiments and testing methodologies including reference electrodes.
- Experiments for collection of data in all chapters.
- Data analysis of all experimental work.
- Preparation of electrodes, membranes, and experimental set-up.
- All writing within the thesis and majority of the writing of the published papers.
- GHG and economic analysis.

Part of the work performed in this thesis was performed by co-op students under my direct supervision. These students included Joseph English, Rubenthran Govindarajan and Meghan Ho.

The following chapters of the thesis have been published in the corresponding peer-reviewed papers:

- Chapter 3: Dara, S., Lindstrom, M, English, J, Bonakdarpour, A, Wetton, B, Wilkinson, D.P.
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- Chapter 4 and 5: Dara, S., Bonakdarpour, A., Ho, M., Govindarajan, R. & Wilkinson, D. P. Conversion of saline waste-water and gaseous carbon dioxide to (bi)carbonate salts, hydrochloric acid and desalinated water for on-site industrial utilization. *React. Chem. Eng.* (2019) doi:10.1039/c8re00259b.

The results of this study have been presentated at the following conferences:

- Banff Venture Forum 2018.
- o 232<sup>nd</sup> ECS Meeting, Washington, DC

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# List of Symbols

a	Activity
А	Electrode Area (cm <sup>2</sup> )
Св	Bulk concentration of the electroactive species (mol/cm <sup>3</sup> )
$C_R^*$	Reactant concentration at the catalyst surface (mol/cm <sup>3</sup> )
D	Diffusion Coefficient (cm <sup>2</sup> /s)
E	Electrochemical Potential (V)
E°	Standard Electrode Potential (V)
$E^{\circ}_{cell}$	Standard Cell Potential (V)
F	Faraday constant (96485 C mol <sup>-1</sup> )
G	Gibbs Free Energy (kJ)
Н	Enthalpy (kJ)
Ι	Current (A)
i	Current density (mA/cm <sup>2</sup> )
iL	Limiting current density (A/cm <sup>2</sup> )
<i>i</i> <sub>o</sub>	Exchange current density (A/cm <sup>2</sup> )
k <sub>m</sub>	Mass Transfer Coefficient (m/s)
n	Number of electrons involved in the electrode process
Р	Pressure (kPa)
Р	Power density (mW/cm <sup>2</sup> )
P <sub>1</sub> ,P <sub>2</sub>	Pressure at state 1, Pressure at state 2 (kPa)
R	Ideal gas constant (8.314 J K <sup>-1</sup> mol <sup>-1</sup> ) or general resistance (Ohm)
R <sub>xyz</sub>	Resistance of appropriate component (ohms)

S	Entropy (kJ)
s	Stoichiometric Coefficient
Т	Temperature (K)
t	Time (seconds)
V	Voltage (V)
Φ	Cell efficiency (dimensionless)
$lpha_{ m a}$	Anodic charge transfer coefficient (dimensionless)
$lpha_{ m c}$	Cathodic charge transfer coefficient (dimensionless)
η	Overpotential (Tafel equation)

# Glossary

ССМ	Catalyst Coated Membrane
CERC	Clean Energy Research Centre
CHBE	Chemical and Biological Engineering
ED	Electrodialysis
ERA	Emissions Reduction Alberta
GDL	Gas Diffusion Layer
MEA	Membrane Electrode Assembly
MPL	Micro-porous Layer
NSERC	Natural Sciences and Engineering Research Council
OCV	Open Circuit Voltage
ORR	Oxygen Reduction Reaction
PGM	Precious Group Metal
PTFE	Polytetrafluoroethylene
ТРВ	Triple Phase Boundary
TPS	Triple Phase Site
UBC	University of British Columbia

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# Dedication

Jo Ammi, Abbu & Muna

### **Chapter 1: Introduction**

Management of freshwater consumption, brine production and greenhouse gas (GHG) emissions pose significant challenges for different industrial sectors including mining, chemical processes, and oil & gas operations. While scarcity and reduced reliability of freshwater resources have reduced the water available for industrial use, increasing regulations and fewer opportunities for safe disposal of industrial brines have increased the complexity of managing water flows to and from industrial sites. Consequently, these macro-drivers have resulted in an increased need for reuse of brine or brackish water within industry<sup>1–3</sup>. At the same time, mitigating carbon emissions associated with industrial operations is also receiving increased attention. Currently, carbon dioxide emissions from industrial processes account for about 21% of the global anthropogenic carbon emissions, which are widely considered to be one of the primary causes of global warming<sup>4</sup>.

Solutions for both saline water management and carbon emissions exist, as discussed below. However, these solutions have traditionally focused on treating carbon emissions and saline water management separately and as pollutants to be managed. The focus of this work was to develop a new approach that simultaneously converts brines and carbon dioxide to value.

#### **1.1 Desalination technologies**

Desalination options for industrial processes can be categorized into either thermal/phase-change or membrane based processes<sup>5–7</sup>. Thermal based desalination processes use heat through various sources (e.g., fossil fuels, solar, waste-heat, etc.) to evaporate and consequently condense water to produce a highly pure desalinated water stream. Membrane based desalination processes use different varieties of membranes and modes of operation to desalinate water.

Thermal desalination processes include multi-stage flash, multiple effect boiling, and solar stills for humidification/dehumidification<sup>8</sup>. Multi-stage flash distillation operates by using multiple counter-current heat exchangers to evaporate the water in multiple stages and collect the condensate to produce desalinated water<sup>9</sup>. Multiple effect boiling uses multiple evaporators to boil the water in multiple stages with each evaporator at a lower pressure than the previous stage<sup>9</sup>. Solar still humidification uses solar energy inside an enclosed container to evaporate and condense water on a second surface of the container to produce a desalinated water stream<sup>9</sup>. Thermal based desalination technologies have been technically successful and have been deployed in many applications but are considered to be both capital and energy intensive<sup>10,11</sup>. In addition, these processes tend to be inefficient in terms of energy consumption and suffer from corrosion and scaling issues.

Membrane-based technologies include membrane distillation, reverse osmosis and electro-dialysis and rely on different methods of operation. Membrane distillation is a thermally driven process in which a hydrophobic membrane (e.g., polyvinylidene fluoride membranes or polypropylene membranes) is subjected to a temperature gradient<sup>12,13</sup>. The liquid water is repelled by the membrane while the membrane pores (~  $0.2 - 1 \mu m$ ) allow the passage of water vapor. Reverse osmosis (RO), which is the most commonly used desalination process globally, utilizes semipermeable membranes and pressure differentials to separate various different ions and molecules from a waste-water stream<sup>14</sup>. In addition to these physical methods, electrodialysis is also used for desalination of brackish water. Electrodialysis is an electrochemical membrane separation technique that uses ion-selective membranes as a physical barrier through which ions are transported away from a feed solution under the application of an external electric potential<sup>15</sup>. All of these membrane-based desalination technologies, however, suffer, to some extent, from scaling and fouling of their membrane components, and utilize expensive electrical energy<sup>16-18</sup>.

While several options for desalination processes exist, these technologies are: i) an added-cost for the end-user, ii) produce a concentrated waste-stream, which requires disposal, and iii) are highly energy intensive. However, all desalination technologies produce a waste-concentrate stream which still requires disposal. The handling of the concentrated waste for disposal can often make the process uneconomic while the high-energy intensity of desalination options also contributes to the carbon dioxide emissions from industrial processes.

#### **1.2** CO<sub>2</sub> emissions mitigation technologies

Approaches to the reduction of carbon emissions have included: i) transition to low carbon or noncarbon producing processes (e.g., renewable energy technologies)<sup>19</sup>, ii) CO<sub>2</sub> capture and sequestration<sup>20,21,30–37,22–29</sup>, and iii) conversion of CO<sub>2</sub> to useful products.

Carbon dioxide sequestration occurs in one of two ways; abiotic, through chemical and physical processes, and biotic, using organisms that remove carbon dioxide from the atmosphere. Both abiotic and biotic processes may occur naturally or through managed interventions. The focus here is on managed abiotic processes. Some examples of managed abiotic processes include oceanic injection, geological injection or carbon dioxide scrubbing and mineral carbonation.

Oceanic injection of carbon dioxide involves a high purity carbon dioxide stream to be injected deep into the ocean where the carbon dioxide may remain stable<sup>22</sup>. This may be performed by

injecting deep into the ocean from ships or pumping the carbon dioxide into a depression in the ocean. However, for this to be successful the carbon dioxide must be injected as a liquefied stream which requires significant energy and cost<sup>38</sup>. Furthermore, carbon dioxide injection may have adverse effects on deep sea life and the stability of the technique still needs to be validated<sup>39</sup>.

Geological sequestration of carbon dioxide involves capture and transport of the carbon dioxide to suitable sites where it may be stored in suitable geological formations. Examples of suitable geological formations include stable rock strata, coal-seams, old oil wells or saline aquifers<sup>24,25</sup>. Old oil wells have also been used as a source for depleting carbon dioxide and extracting remaining oil in a technique known as enhanced oil recovery<sup>26</sup>. However, similar to oceanic injection, the reliability, economics and stability of geological sequestration are yet to be validated<sup>38</sup>.

Carbon dioxide may also be sequestered in a mineralized form in a process mimicking natural phenomena. Here, a high purity carbon dioxide stream is combined with highly basic minerals like magnesium and calcium to form geologically and thermodynamically stable mineral carbonates<sup>27–29</sup>. While reserves of highly basic mineral reserves are large enough to remove carbon dioxide for a long time the reaction rates are slow. The reaction rates may be increased with the use of catalysts and reaction conditions, but this is both economically and energy intensive<sup>40</sup>.

In recent years, the use of carbon dioxide as a reactant feed for production of fuels and/or chemicals has received more attention. In particular, a number of approaches, including the conversion of carbon dioxide through electrochemical<sup>31–34</sup>, photo-chemical<sup>35</sup> or chemical<sup>36</sup> means have been reported.

Electrochemical approaches have included electroreduction of CO<sub>2</sub> to formates or formic acid<sup>41–</sup><sup>44</sup>, oxalates or oxalic acid<sup>45</sup>, ethylene<sup>46</sup>, liquid fuels including methanol<sup>47–49</sup>, or synthesis gas in the form of carbon monoxide and hydrogen<sup>50</sup>. Electrochemical conversion of carbon dioxide has also been demonstrated in a fuel cell where a selective catalyst was used to convert carbon dioxide to carbonate ions which act as the charge transfer species<sup>51</sup>. In these approaches, carbon dioxide undergoes an electro-reduction reaction at the cathode of the electrochemical reactor. In each case, the operating conditions, catalyst composition and reactor design determine the composition of product(s), conversion efficiencies and energy requirements. Although these electrochemical approaches have, in general, been technically successful, they rely on zero-carbon emitting sources of power to be a net-carbon negative process.

#### 1.3 Project goals

The goal of this thesis was to develop and demonstrate a process for the combined conversion of brines and carbon dioxide to value added chemicals and recovering desalinated water for industrial use. The work focused on evaluating two approaches:

1. Electrodialysis for the conversion of dissolved CO<sub>2</sub> and brine: The approach involves the use of a multi-compartment electrodialysis cell with an alternating pattern of anion-and cation-exchange membranes as summarized in Figure 1.1.



Figure 1.1: Electrodialysis cell for the conversion of dissolved CO<sub>2</sub> and brine.

A feed brine containing ions which are to be removed is provided to one feed compartment and carbon dioxide dissolved in water or other high carbon dioxide solubility solvents is provided in the form of carbonates (e.g.,  $CO_3^{2-}$ ,  $HCO_3^{-}$ ) to a second feed compartment. The ion exchange membranes are configured in such a manner that the transport of cations and anions from the feed chambers produces carbonates (e.g., NaHCO<sub>3</sub>) and acids (e.g., HCl or other acid) or other products in separate chambers. The removal of the ions present in the feed streams results in a dilute purified stream and a concentrated product stream leaving the cell. The result is the electrolyte is concentrated in some compartments and purified in others.

2. Electrolysis for the conversion of gaseous CO<sub>2</sub> and brine: This method involves a multicompartment electrolyzer which operates on the fundamental scientific principles shown in Figure 1.2a and 1.2b. Air is fed to the cathode of the electrolyzer where the application of an external voltage across the electrodes produces hydroxide ions. At the anode, water oxidation is used to generate protons. A saline or brine feed stream (e.g., basal aquifer water, lithium chloride) containing ions (e.g., Na<sup>+</sup>, Li<sup>+</sup>, Cl<sup>-</sup>) which are to be removed is provided to a separate compartment in between the anode and cathode. Under an externally applied voltage the anions and cations present in the saline water move towards the anode and cathode, respectively. A strategic pattern of anion and cation selective membranes is used to prevent back-transport of the ions leading to the concentration of a base (e.g., sodium hydroxide) and an acid (e.g., hydrochloric acid) while desalinating the feed saline stream. Overall, the system is fed with a mixture of air, and saline water and produces desalinated water, a base, and an acid. The resulting hydroxide produced, as shown in Figure 1.2a, can be used to convert carbon dioxide to a mineralized carbonate or bicarbonate form (e.g., lithium carbonate, sodium carbonate, etc.) externally with the use of a scrubber. As an example, sodium hydroxide is used to convert carbon dioxide to sodium bicarbonate (1.1) or sodium carbonate (1.2) by:

$$NaOH + CO_2 \rightarrow NaHCO_3 \tag{1.1}$$

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$$
(1.2)

Alternatively, the carbon dioxide could be provided directly to the cathode where it could be electrochemically converted to carbonate or other ions as shown in Figure 1.2b. However, for this to occur, a selective catalyst for the conversion of  $CO_2$  would likely be required. An example of a selective catalyst for use in such an application is reported by Vega et. al<sup>51</sup>. The development of a selective catalyst for use in such a system was not a focus of this work.

The objectives of the work were to:

- Demonstrate the feasibility of the two aforementioned approaches;
- Identify limitations and factors affecting performance of the two aforementioned approaches;
- Demonstrate production of chemicals at industrially relevant fluxes;
- Demonstrate flexibility of the approach to different brine and carbon dioxide concentrations.



# Anion selective membrane Cation selective membrane

Figure 1.2: Electrolysis based approach for the conversion of different gases and brine to value-added chemicals and desalinated water.

#### **1.4** Use of brines for production of chemicals

While the recent focus on using carbon dioxide as a feedstock has started to demonstrate that carbon dioxide can be an asset and not just a pollutant that requires management, similar approaches for brine management are less common and not widely reported. An option to produce chemicals from brines is to use conventional chlor-alkali technology to produce sodium hydroxide and chlorine gas<sup>52</sup>. The reactions for a chlor-alkali cell are as follows:

Anode: 
$$2\text{Cl}^{-} \rightarrow \text{Cl}_{2} + 2\text{e}^{-}$$
  
Cathode:  $2\text{H}_{2}\text{O} + 2\text{e}^{-} \rightarrow 2\text{OH}^{-}$   
 $E^{\circ} = -0.83 \text{ V}$  (1.3)  
(1.4)

The chlorine gas can then be combusted with hydrogen from an external source or from the cathode to produce concentrated hydrochloric acid while the sodium hydroxide can be used to externally capture carbon dioxide with a scrubber. This approach can have some advantages as it allows for high concentrations of hydrochloric acid (as high as 40 wt.%) and sodium hydroxide (32 wt.%) to be produced. However, this approach is limited for several reasons:

1. Chlor-alkali requires high sodium chloride concentrations: Typically, chlor-alkali plants require the feed sodium chloride to have a concentration as high as 30 wt.% NaCl for the reaction at the anode to produce chlorine gas. As the brine becomes weaker, more oxygen is generated at the anode from the oxidation of water instead of chlorine as water oxidation occurs before chlorine production (water oxidation occurs at 1.23 V) resulting in reduced efficiency of the cell and process. This means that strong brines are preferred, and this limits the potential of this option as most industrial brines are significantly weaker. For industrial brines, significant concentration will be required to achieve the desired feed sodium chloride concentrations.

- 2. Depleted brine still has significant salt content: In addition to requiring high concentrations of sodium chloride, chlor-alkali cells produce a depleted brine that is approximately 20-22 wt.% NaCl. This means a significant amount of salt remains in the depleted brine. This depleted brine must be treated before it can be processed within the cell again. The treatment requires increasing the concentration up to the feed NaCl concentration and removal of dissolved chlorine gas from the brine. Both add costs and complexity to the system.
- 3. Production and handling of chlorine gas at industrial sites is problematic: Chlorine is a known toxic chemical with special production and handling requirements. Industrial sites that produce brines often have lengthy permitting requirements and stringent safety standards. The production of chlorine at these sites, e.g., at a mining site, is likely to face significant resistance due to the added hazards.
- 4. Hydrogen management and combustion is an additional cost: Hydrogen gas is produced at the cathode when hydroxide ions are generated through water reduction. The hydrogen gas would normally be vented in a chlor-alkali plant but still requires safe management due to the explosive nature of the hydrogen. However, when considering the production of chlorine gas through the combustion of hydrogen and chlorine, the management of hydrogen is of even more importance. The source of hydrogen for the combustion can either be an external source in which case there will be an additional cost to the process, or it can be hydrogen produced at the cathode. If hydrogen produced at the cathode is to be used for the combustion reaction, then the hydrogen will need to be treated to remove any moisture or other particles from the cell before combustion. Further, the chlorine gas will also need to be treated to remove moisture and oxygen

prior to combustion due to the explosive nature of a chlorine, hydrogen, and oxygen mixture.

5. Materials of selection for corrosive chemicals: The production of high concentrations of chlorine gas, hydrochloric acid and sodium hydroxide requires special materials of construction for not just the cell but also the plant which can further increase costs of the system.

These challenges limit the possibility of using conventional chlor-alkali type cells to produce desalinated water and chemicals as several additional process units, complex process schemes, special materials of construction and additional safety hazards need to be considered.

#### **1.5** Significance and novelty

The work presented here demonstrates a first-of-a-kind electrochemical approach where a 5compartment electrochemical cell with a gaseous fed cathode which was developed in-house is used to simultaneously address CO<sub>2</sub> emissions, and water use and treatment. This approach also provides a significantly simpler method to produce chemicals and desalinated water than conventional electrochemical routes as discussed earlier (i.e., chlor-alkali). Rather than treating each issue separately, the new process addresses both issues simultaneously while producing beneficial by-products. A simple modular and scalable process that combines waste CO<sub>2</sub> and produced water/brine inputs in one module through electrodialysis to produce high value products (such as HCl and carbonate salts) for on-site utilization and desalinated water for reuse is demonstrated. Although electrodialysis is used for such industrial applications as desalination and electro-deionization, a multi-compartment electrochemical cell that combines a gaseous or gas diffusion cathode, and electrodialysis compartments has not been reported before. The use of electrodialytic compartments allows for the use of weak brines not possible with conventional electrolytic cells while the gas diffusion cathode allows for the cell to have a lower voltage requirement and eliminates the production of explosive hydrogen. This allows the cell to have a higher recovery rate of the salt and reduces the complexity of the overall system. Successful industrial scale application of the proposed process has the potential to significantly alleviate issues of brine management, and chemical supply and logistics by converting the brines and  $CO_2$  to chemicals for on-site utilization. This would reduce the amount of brine requiring disposal and chemicals needing to be trucked to site for use.

#### 1.6 Thesis Layout

Chapter 1 provides background information and introductory material including literature review for the work discussed in this thesis.

Chapter 2 provides the necessary experimental details for the experimental work discussed in this thesis including the apparatus used.

In Chapter 3, an electrodialysis based method for the conversion of carbon dioxide in a dissolved aqueous solution and brine to desalinated water and chemicals is demonstrated. A mathematical model for the approach is also developed. The model is used to discuss the limitations of the approach.

In Chapter 4, a 5-compartment electrochemical cell with an oxygen depolarized cathode is demonstrated to produce hydrochloric acid and sodium hydroxide from brine and oxygen. The 5-compartment electrochemical cell is used to further investigate the performance of the different compartments of the electrochemical.

In Chapter 5, carbon dioxide is introduced to the cathode of the 5-compartment electrochemical cell demonstrated in Chapter 4. The effect of carbon dioxide being provided to the cathode is investigated. Long-term tests to demonstrate the build-up of chemicals and the depletion of brine are performed. A material and energy balance for the testing is developed.
Chapter 6 and 7 discuss the GHG reductions and the economic value proposition of the 5compartment electrochemical cell in relation to the costs of incumbent options for industrial applications.

# **Chapter 2: Background**

Electrochemical cells are characterized into either galvanic or electrolytic cells. Galvanic cells are electrochemical systems where the electrochemical reactions occur spontaneously resulting in chemical energy being converted into electrical energy. Electrolytic cells, on the other hand, are electrochemical systems where the electrochemical reaction does not occur spontaneously. Instead, an externally applied voltage that is greater than the open-circuit voltage of the cell is used to drive the chemical reactions in an electrolytic cell. Therefore, electrical energy is converted to chemical energy in an electrolytic cell. Further, the anode and cathode of an electrolytic cell are positive and negative, respectively, with oxidation occurring at the anode and reduction occurring at the cathode. The electrode and electrochemical reactions of a galvanic cell are opposite to that of an electrolytic cell. Both electrolysis and electrodialysis are electrolytic processes and the fundamental operation requires the application of an external voltage for the electrochemical reactions to occur. As such, the next section attempts to provide enough detail of the fundamental operating principles for electrodialysis and the cell components so that the reader may have a good base for understanding the work performed in this thesis.

#### 2.1 Fundamentals of electrochemistry

## 2.1.1 Characterization of electrochemical cells

Electrolytic cells follow the basic laws of electrochemistry where a reaction always occurs between an oxidized (Ox) and reduced (Red) species at an electrode/electrolyte interface. At this interface, a reaction proceeds by either liberation or consumption of electron(s). When a voltage is applied, electrons flow in an external circuit from the anode to the cathode resulting in electrical energy being converted to chemical energy. The voltage required for this reaction to occur can be related to the summation of Gibbs free energy of formation of the oxidized ( $\Delta G_{f,Ox}^{\circ}$ ) and reduced ( $\Delta G_{f,Red}^{\circ}$ ) species involved in the cell:

$$\Delta G_{cell}^{\circ} = \sum \Delta G_{f,Red}^{\circ} - \sum \Delta G_{f,Ox}^{\circ}$$
(2.1)

The Gibbs free energy change of the cell is related to the standard (298 K, 1 atm) reversible cell potential,  $E^{\circ}_{cell}$  by the expression:

$$\Delta G_{cell}^{\circ} = -nFE_{cell}^{\circ}$$
(2.2)

where n is the number of electrons transferred in the reaction and F is Faraday's constant equal to 96485 Coulombs/mol. The change in the cell's Gibbs free energy will be positive as the system moves from a more "stable" state to a less "stable" state and thus its reversible cell potential will be negative. The overall reaction is a combination of the anodic and cathodic half-cell reactions. As in all cases of electrochemistry, where absolute single electrode potentials do not exist, potentials are measured against some arbitrary value, i.e., half-cell reactions must be measured against some reference electrode. The reference electrode itself though has its own potential which is measured against the standard hydrogen electrode (SHE), which is given a value of 0 V. A list of some common reference electrode potentials can be found in Table 2.1.

Abbreviation	Half-cell Reaction	Potential (V vs. SHE)	Electrolyte
Hg/Hg <sub>2</sub> SO <sub>4</sub>	$\begin{array}{rcl} Hg_2SO_{4(s)} \ + \ 2e\ \rightarrow \ 2Hg_{(l)} \ + \\ SO_4^{2\ } \end{array}$	0.67	Sat'd K <sub>2</sub> SO <sub>4</sub>
Cu/ CuSO <sub>4</sub>	$Cu^{2+} + 2e- \rightarrow Cu_{(s)}$	0.32	Sat'd CuSO <sub>4</sub>
SCE	$Hg_2Cl_{2(s)} + 2e \rightarrow 2Hg_{(l)} + Cl^{-}$	0.24	Sat'd KCl
Ag/AgCl	$AgCl_{(s)} + e \rightarrow Ag_{(s)} + Cl^{-}$	0.20	Sat'd KCl
Hg/HgO	$\begin{array}{c} HgO_{(s)} + H_2O + 2e - \rightarrow Hg_{(l)} + \\ 2OH^- \end{array}$	0.14	1 M NaOH
SHE	$2H^+ + e^- \rightarrow H_{2(g)}$	0.00	$[H^+] = 1 M$

Table 2.1: List of commonly used reference electrodes.

## 2.1.2 Electrochemical Cell Potential

Electrolytic cells are complex systems with many factors affecting their operating voltage. It would be expected that the voltage required for a reaction to occur should equal the theoretical equilibrium cell voltage,  $E_{cell}^{\circ}$ . However, this is seldom the case because of losses in the electrochemical cell due to different mechanisms. These losses are a result of many factors, including but not limited to electrode design, catalyst loading, flow channel design, operating temperature, pressure compression, membrane conductivity, and solution conductivity. This is particularly important in a multi-compartment cell such as the one proposed in this work where each compartment contributes to the voltage required for the reaction to occur.

These losses are termed overpotential and can apply to an electrolytic or galvanic cell. Overpotential refers to the amount of extra energy, i.e., voltage, that is required compared to what would be predicted by thermodynamic values for the reaction to occur. There are three main mechanisms that lead to overpotential; kinetic or activation overpotentials, ohmic overpotentials, and concentration or mass-transport overpotentials. These can be written in terms of the cell potential as follows:

$$E_{cell} = E_{cell}^{\circ} - |\eta_{c,a}| - |\eta_{a,a}| + IR_{membranes} + IR_{solution} - |\eta_{solution,mt}| - |\eta_{c,mt}| - |\eta_{a,mt}| (2.3)$$

where  $|\eta_{c,a}|$  is cathodic activation overpotential,  $|\eta_{a,a}|$  is anodic activation overpotential,  $|\eta_{c,mt}|$  is the cathodic mass-transport overpotential,  $|\eta_{a,mt}|$  is the anodic mass transport overpotential,  $|\eta_{solution,mt}|$  is the mass-transport overpotential associated with each solution, I is the operating current in Amps, R<sub>membranes</sub> is the resistance of each membrane in ohms, and R<sub>solution</sub> is the resistance of each solution.

## 2.1.3 Cell performance characterization

The performance of an electrolytic cell can be evaluated by the development of characteristic polarization curves which can help identify and illustrate cell overpotentials due to the different mechanisms. The different overpotentials - activation, ohmic, mass-transport – are dominant in three distinct regions of the polarization curve as shown in Figure 2.1.



Current Density (A/cm<sup>2</sup>)

Figure 2.1: Schematic showing the different regions of a characteristic polarization curve for an electrolytic

cell.

## 2.1.4 Activation Overpotential

The Butler-Volmer equation defines the activation overpotential in terms of the temperature, T, current density, i, and the reaction mechanism with the following relationships,

$$i = i_o \left[ exp\left(\frac{\alpha_a F}{RT} \eta_s\right) - exp\left(\frac{\alpha_c F}{RT} \eta_s\right) \right]$$
(2.4)

$$\alpha_a = (1 - \beta_s)n \tag{2.5}$$

$$\alpha_c = \beta_s n \tag{2.6}$$

where  $\beta_s$  is the symmetry factor describing which of the anodic or cathodic processes is favoured,  $\alpha_a$  and  $\alpha_c$  are the charge transfer coefficients, n is the number of electrons transferred in the rate determining step,  $\eta_s$  is the overpotential in V, F is Faraday's constant (96485 Coulombs/mole), R is the ideal gas constant, T is temperature in K and  $i_o$  is the exchange current density in A/m<sup>2</sup>. The Butler-Volmer equation is represented graphically as shown in Figure 2.2.



Figure 2.2: Graphical representation of the Butler-Volmer equation.

Here, the region,  $|\eta_s| \ge 50 \text{ mV}$ , has a linear approximation and is represented by the Tafel equation,

$$|\eta_s| = b(\log|i|) + a$$
(2.7)

$$b = \frac{2.303RT}{\alpha F} \tag{2.8}$$

$$a = b(\log i_o) \tag{2.9}$$

For cathodic processes,  $|\eta_s| = -\eta_{s,c}$ ;  $\alpha = \alpha_c$ ;  $|i| = -i_c$  while for anodic processes,  $|\eta_s| = \eta_{s,a}$ ;  $\alpha = \alpha_a$ ;  $|i| = i_a$ . Under activation control, when the concentration of the reactant can be assumed to be the same at both the electrode surface and bulk solution the Tafel slope, b, and intercept, a, are used to indicate the effectiveness of electrode design at lowering the activation overpotential as low as possible. An electrode with a low Tafel slope, b, and a high exchange current density, i<sub>o</sub>, are desired. Exchange current density is defined as "the rate of exchange between the reactant and product states at equilibrium". It includes several terms and can be written in the form:

$$i_o = nFc_R^* e^{-\frac{\Delta G^\dagger}{RT}} \tag{2.10}$$

where  $c_R^*$  is the reactant surface concentration and  $\Delta G$  † is the activation barrier. Successful electrode design minimizes activation overpotentials by having a high exchange current density,  $i_o$ . Strategies for reducing activation overpotentials include:

- 1. Increasing reactant concentration which linearly increases exchange current density
- 2. Decreasing the activation barrier by using catalysts that have a high exchange current density associated with the desired reaction
- Increasing temperature to provide more thermal energy to the reactants which increases the exchange current density
- 4. Increasing the number of potential reaction sites. As the reaction occurs on a surface area basis increasing the surface area of the catalyst but keeping the geometric area constant can have a large impact on the exchange current density.

#### 2.1.5 Ohmic Overpotential

Ohmic overpotentials refer to voltage losses due to the resistance of all the electronic and ionic components in the system and can be written as an equation in the form,

$$iR_{cell} = i \sum_{n} R_n = i \sum_{n} \frac{\tau}{\kappa A}$$
(2.11)

where  $R_{cell}$  is the overall cell resistance in ohms,  $\tau$  is the thickness of the component in cm,  $\kappa$  is the specific conductivity of the component in S/cm and A is the geometric area in cm<sup>2</sup>.

The conductivity of ion-exchange membranes used in this work is dependent on the ion being conducted and the hydration levels of the membrane, which in turn is dependent on temperature. The conductivity of each membrane is usually reported by the manufacturers and can be used to calculate the voltage loss associated with the specific membrane.

In addition to the membranes, a significant amount of voltage loss is also associated with the liquid solutions in-between the membranes or at the anode. As such, losses associated with the conductivity of the solutions should also be considered. The conductivity of each solution is dependent on temperature, concentration, inerts and void fraction. A binary ionic solution that completely dissociates can be shown as follows,

$$A_{s+}B_{s-} \to s_{+}A^{z+} + s_{-}B^{z-}$$
 (2.12)

For dilute solutions with a concentration less than 1 mol/dm<sup>3</sup>, the specific conductivity of the solution,  $\kappa_s$ , can be expressed as follows,

$$\kappa_s = F^2 \sum_j z_j^2 u_j^2 C_j^2 \tag{2.13}$$

where  $z_j$  is the charge of species j,  $u_j$  is the ionic mobility of species j in m<sup>2</sup>mol/Js and  $C_j$  is the concentration of species j in mol/m<sup>3</sup>.

When concentrated solutions are used ion-ion interactions can have a large effect on solution conductivity. This dependence of conductivity,  $\kappa$ , on concentration is described by the Casteel-Amis equation,

$$\kappa = \kappa'_{max} \left(\frac{c}{c'_{max}}\right)^x exp\left[y(C - C'_{max})^2 - \frac{x}{c'_{max}}(C - C'_{max})\right]$$
(2.14)

$$\kappa'_{max} = \kappa_{max1} + \kappa_{max2}T \tag{2.15}$$

$$C'_{max} = C_{max1} + C_{max2}T \tag{2.16}$$

where *C* is wt.%,  $C_{max1}$  and  $C_{max2}$  are tabulated wt.% constants,  $\kappa_{max1}$  and  $\kappa_{max2}$  are tabulated conductivity constants in mS/cm, and *x* and *y* are tabulated constants. Some strategies for reducing ohmic losses include:

- 1. Increasing the temperature to improve conductivity.
- 2. Using supporting electrolytes to improve the conductivity of the solution.

The presence of inert voids also influences the conductivity of solutions. These voids may include gas bubbles and dispersed solids. The conductivity of the solution can be estimated using either the Maxwell equation for void fraction,  $\varepsilon < 0.6$ ,

$$\kappa / \kappa_o = 1 - \varepsilon / 1 + \frac{\varepsilon}{2} \tag{2.17}$$

or from the Meredith-Tobias equation for void fraction,  $\varepsilon > 0.6$ ,

$$\kappa / \kappa_0 = 8(1 - \varepsilon)(2 - \varepsilon)/(4 + \varepsilon)(4 - \varepsilon)$$
 (2.18)

where  $\kappa_o$  and  $\kappa$  are the specific conductivity in the absence and presence of voids, respectively, in S/m.

#### 2.1.6 Mass-transport Overpotential

Anode and cathode reactions take place on the surface of the catalyst at the electrode. When current densities get sufficiently high the reactant is not able to diffuse to the catalyst surface fast enough to sustain the reactant consumption rate. Therefore, a concentration gradient between the bulk reactant concentration,  $C_{bulk}$ , and the concentration at the electrode surface,  $C_{surface}$ , develops. This limits the current density that can be achieved within an electrochemical cell. The concentration overpotential,  $\eta_{conc}$ , can be expressed by the following relationships,

$$\eta_{conc} = \frac{RT}{nF} \sum_{j} \ln \left( 1 - \frac{i}{i_{l,j}} \right)$$
(2.19)

$$i_{l,j} = \frac{nF}{s_j} k_{m,j} C_{bulk,j} \tag{2.20}$$

where  $i_{l,j}$  is the limiting current of species j in A/cm<sup>2</sup>,  $s_j$  is the stoichiometric coefficient of species j in mol/cm<sup>3</sup>. It is important to note here that in a multi-compartment electrochemical cell such as the one used in this work or even conventional electrodialysis cells, the mass transport overpotential is not only related to the electrodes but also to diffusion of the various ions through the membrane and solutions. In such a cell, the ion with the lowest concentration in the boundary layer next to the respective surface, i.e., diffusion next to the membrane or electrode, will control the performance of the entire cell. As such, when the cell enters the mass transport regime, it is important to differentiate between the different compartments to understand which is controlling performance. Effective strategies for reducing mass transport overpotentials include:

- 1. Increasing the concentration of the bulk solution;
- 2. Increasing the flow-rate of the reactants to improve mass transport;
- 3. Utilizing turbulence promoters to create turbulent flow resulting in better transport;
- 4. Increasing the temperature of the solution to increase the conductivity of the solution.

## 2.1.7 Cell efficiency

Cell performance is essentially evaluated through measuring current densities for a given voltage or vice versa. While cell performance can be investigated through the development of characteristic polarization curves, this performance means little without understanding the efficiency of the cell with respect to the amount of product generated or the amount of reactant consumed. The cell efficiency is defined as:

$$\phi = \frac{c_f v_f - c_i v_i}{n_{dot} t} \tag{2.21}$$

Where  $\emptyset$  is cell efficiency,  $C_i$  and  $C_f$  are the initial and final concentration of the solution in mol/m<sup>3</sup>,  $V_i$  and  $V_f$  are the initial and final volume of the concentration in m<sup>3</sup>, respectively, *t* is time in seconds and  $n_{dot}$  is the expected molar consumption or production rate of the reactant or product in moles per second, respectively, and calculated by Faraday's law:

$$n_{dot} = I/nF \tag{2.22}$$

Where I is the total cell current in Amps, n is the number of moles of electron per moles of reactant or product consumed or produced, and F is Faraday's constant equal to 96,485 Coulombs per mole of electrons.

The efficiency of the cell is affected by many factors including:

- Depletion of salt: The amount of salt removed from the solution treated should be directly correlated to the amount of current supplied to the cell.
- Production of acid: Protons are generated at the anode and combine with the anions within the salt solution to produce an acid. The amount of acid generated should match the amount of salt removed under ideal operation.

• Production of base: Hydroxide ions generated at the cathode will combine with the cations within the salt solution to produce a base. The amount of base generated should match the amount of salt removed under ideal operation.

The amount of salt removed from the solution, and the amount of acid and base generated will depend significantly on different factors including:

- Membrane type: Not all anion and cation exchange membranes have the same performance. Certain membranes will allow ions to be conducted more easily allowing for higher concentrations to be achieved but at the expense of permselectivity (described in more detail in 2.3.3) allowing the co-ions to migrate across the membrane leading to a lower amount of product being produced. The overall power required to produce the products can therefore be higher.
- Product acid and base concentrations: The back migration of the products to the salt compartments increases as concentrations of the products increases leading to lower efficiency at higher concentrations, e.g., the efficiency of increasing the concentration from 1 wt.% HCl to 2 wt.% HCl will not be the same as increasing the same amount from 6 wt.% HCl to 7 wt.% HCl.
- Treated salt concentration: Salt removal efficiency of the system is reduced versus the expected amount from the current provided to the system as the amount of salt removed increases and the concentration of the salt is decreased due to increased back migration of the products under a larger concentration gradient. This will become increasingly worse as the product concentrations increase for the same concentration of salt.
- Salt type: In addition to the salt concentration the type of salt can also play an important role in cell efficiency. For example, sulfate based salts can have lower efficiency as they

can attach to the positive ammonium functional groups of anion exchange groups to create a sulfonic acid group (NH<sub>4</sub><sup>+</sup>-SO<sub>4</sub><sup>2-</sup>  $\rightarrow$  NH<sub>3</sub>-SO<sub>3</sub><sup>-</sup>) which can act as a site to conduct protons or positive ions back from the product side to the feed salt side. However, this does not occur with all ions. This is likely to occur with multi-charge ionic species (e.g., SO<sub>4</sub><sup>2-</sup>) and not with single-charge ionic species (e.g., Cl<sup>-</sup>) as the multi-charge ionic species will create an excess negative on the site while the single-charge ionic species will make the site neutral.

## 2.2 Electrodialysis in detail

#### 2.2.1 Principles and methods of electrodialysis

Electrodialysis uses ion-exchange membranes which allow ions to permeate under an externally applied voltage resulting in a concentrated solution of the ions and a depleted solution of the ions on either side of the ion-exchange membrane. Conventional or passive dialysis – as opposed to electrodialysis – is a commonly used technique which uses semi-permeable membranes to remove or reduce the concentration of a solute. In passive dialysis, a solute will move from an area of high concentration to an area of low concentration resulting in the concentration being lowered in one area and increased in another. Most commonly, this technique is used with membranes that only allow a specific type of molecule to be transported resulting in the recovery of the molecule in a dilute solution and separating the molecule from other molecules present in the original solution. Electrodialysis builds on this approach by using ion-exchange membranes which theoretically only allow charged species to be transport and using voltage to remove the charge from one side to another.

The fundamental operating principle of electrodialysis, as shown in Figure 2.3, rely on alternating anion exchange membranes (AEM) and cation exchange membranes (CEM). Feed streams containing anions and cations are supplied to the membrane stack where migration of the ions occurs under the electric potential gradient created by the electrochemical reactions at the electrodes or by the potential when no reaction occurs. Electrodialysis is generally carried out using a multi-compartment electrodialyzer where multiple sets of ion-exchange membranes are repeated in-between the anode and cathode which are at each end of the electrodialyzer. The most common electrochemical reactions at the electrodes are as follows:

Anode: $H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2$	-1.23 V vs. SHE	(2.23)
$2OH^{-} \rightarrow \frac{1}{2}O_{2} + 2H_{2}O + 2e^{-}$	-0.40 V vs. SHE	(2.24)
Cathode: $2H^+ + 2e^- \rightarrow H_2$	0.00 V	(2.25)
$2H_2O + 2e^- \rightarrow 2OH^- + H_2$	-0.83 V vs. SHE	(2.26)



Figure 2.3: Principle of electrodialysis using ion-exchange membranes.

The anions present in solution travel towards the anode through an AEM while the cations travel towards the cathode through a CEM. In theory, 100% of the current transferred within the cell should correlate with the AEM only conducting anions and the CEM only conducting cations. In practice, a small amount of the current transferred by an AEM will be by cations (instead of anions) and for a CEM will be by anions (instead of cations) moving the opposite way of the intended

operation. A highly effective membrane may prevent this from happening but at the expense of other important properties such as increased resistance. The AEM and CEM are separated with the use of a spacer which allows the solution to flow between them. The spacer is also used to create turbulence in the stream to improve mass transfer. The removal of the ionic species present in the feed streams results in a dilute stream and a concentrated product stream leaving the cell in alternate compartments.

Electrodialysis is a versatile technology which can be used in several ways and configurations where the pattern or the number of ion-exchange membranes can be changed to achieve a variety of objectives. Electrodialysis cells have been shown to be cost effective for desalination purposes<sup>11</sup>. They have been shown to have many applications including industrial saline water treatment<sup>53</sup>, brackish water treatment<sup>54</sup>, and acid and alkali production<sup>55</sup>. Electrodialysis removal rates of 65% for bicarbonate, 91% for hardness, 72% for chloride, and 89% for sulphate have been reported<sup>56</sup>. A number of studies have shown that the energy costs of electrodialysis are lower than other conventional methods like ion resin exchange<sup>56–58</sup>.

Electrodialysis has been shown to be able to produce acids and bases in a salt splitting process with the use of bipolar membranes though industrial applications have been relatively limited with most applications to date having been performed at the lab or pilot scale<sup>53,59</sup>. The success of this technique is however based on the use of expensive and complex bipolar membranes capable of splitting water within the membrane to produce the conjugate acid and base. Furthermore, the base/caustic solution produced is limited to a low concentration due to the instability of bipolar membranes (usually unstable over pH 12-13) at high pH and over limiting current densities<sup>60,61</sup>. It

is also possible to sequester the carbon dioxide in a mineralized form by combining with the produced base.

Electrodialysis cells have also been shown to be used to recover caustic scrubbing solvents used to capture carbon dioxide from a flue gas stream<sup>62</sup>. Here, the sodium hydroxide solution was regenerated with the use of bipolar membranes and carbon dioxide separated into a purified stream. This technique is suited for applications of carbon dioxide scrubbing with solvents which need to be regenerated to remove the carbon dioxide.

While electrodialysis cells have been shown to have a variety of uses as discussed above they also do have a fundamental limit with respect to the salinity levels that can be achieved. As electrodialysis cells rely on voltage to transport ions from one side of a membrane to another, they inherently require the presence of charged ions in solution for the reaction to occur. As the concentration of ions in solution decreases, the resistance of the solution increases and less current can be transported. Further, as the concentration of ion tends to zero the voltage required will increase to infinity. Essentially, this means that electrodialysis cells cannot produce pure water but a depleted solution which will always have some number of ions present in solution. Practically, an electrodialysis cell can be used to achieve concentrations below 2,000 ppm as NaCl.

#### 2.2.2 Electrodialyzer

The core of the electrodialysis process is the electrodialyzer with purpose-selected ion-exchange membranes. In general, the ion-exchange membranes with strongly acidic cationic (e.g., sulfonic - SO<sub>3</sub><sup>-</sup>) and strongly alkaline (e.g., ammonium - NH<sub>4</sub><sup>+</sup>) anionic exchange groups are used for the

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cation and anion exchange membranes, respectively. The exchange groups not only provide conductivity for the appropriate counter ion but also act as a repellant to the ions with the same charge as the exchange group allowing for concentration and depletion of the salt solution, e.g., a sulfonic acid group, which is negatively charged, provides conductivity for cations such as protons or sodium ions, but also acts as a repellant to anions such as chloride or hydroxide due to the same charge on both the exchange group and the counter ion. The ion exchange membranes can be modified to be impermeable or allow for permeation of specific ions. However, this is usually quite challenging and comes at the cost of reduced conductivity of the membrane.

Different electrodialyzer designs have been proposed with for example the ion-exchange membranes spirally wound or more commonly arranged in a planar manner. In both cases, the ion-exchange membranes must have a suitable spacer in-between alternating membrane to allow enough liquid flow in between the membranes. An example of a planar design electrodialyzer is the filter-press electrodialyzer as shown in Figure 2.4<sup>163</sup>. A well-designed electrodialyzer should have low energy consumption, low manufacturing costs, high efficiencies, be easy to operate and have low maintenance requirements. The energy consumption of the electrodialyzer can be reduced by using low resistance ion-exchange membranes without compromising mass transport or pressure drops through the compartment. The cost of the electrodialyzer is dependent on the materials of construction, and the normalized gasket area and production costs in relation to the membrane active area. For example, an electrodialyzer with a small active area will have higher machining and gasket costs normalized to the membrane active area. On the other hand, a

<sup>&</sup>lt;sup>1</sup> Figure used with permission from Elsevier.

significantly larger electrodialyzer may have lower normalized machining and gasket costs but the materials of construction may have a higher cost due to the need for higher strength and flexibility materials required to support the design. There is likely to be an optimum design and size of the electrodialyzer that balances the different factors.



a. Desalting cell; b. concentrating cell; c. manifold; d. slot; e. fastening frame; f. feeding frame; g. cation exchange membrane; h.



Figure 2.4: Basic structure of a filter-press electrodialyzer.

## 2.2.3 Limiting current density

Ions usually have a higher mobility within the membrane than they do in solution. As such, a boundary layer develops next to the surface of the membrane as the ions are transported through the membrane faster than they can diffuse to the membrane surface. This results in mass transport limitations developing at the membrane surface at sufficiently high current densities. The current density at which this begins to occur is the limiting current density for the system. At current densities higher than the limiting current density water splitting can occur at the surface of the membrane resulting in the production of protons or hydroxide ions. The protons or hydroxide ions will then permeate through the membrane depending on whether the membrane is an anion or cation exchange membrane. This can result in a change of pH of the solution which can impact the solubility of ions within the solution and cause precipitation at the membrane surface. This can cause issues within the electrodialysis cell and reduce the current efficiency of the system as energy is now being used for transporting proton and/or hydroxide ions.

The limiting current density is usually observed on a current-voltage polarization curve for an electrodialyzer and is shown later in the next sections. The limiting current density of the electrodialyzer can be increased by using turbulence promoters in-between the alternating membrane. The turbulence promoters are usually comprised of some plastic mesh that is chemically and thermally stable in the solution being treated with hexagonal or honeycomb mesh designs usually used. The use of turbulence promoters can disrupt the flow of the solution which reduces the thickness of the boundary layers at the surface of the membrane resulting in improved mass transport to the membrane surface.

#### 2.3 Ion-exchange membranes

## 2.3.1 Properties and operating considerations of ion-exchange membranes

Ion-exchange membranes are designed to conduct ions from one side to another resulting in a net transfer of charge. However, the operation of the membrane is never as simple and several phenomena have been observed when ion-exchange membranes have been used in electrodialysis, electrolysis or even fuel cell applications. It is important to understand and consider these phenomena when operating a system that uses ion-exchange membranes. The following section aims to provide important background information regarding the use of ion-exchange membranes within the proposed system.

Evaluation of the properties of the ion-exchange membrane is vital to proper operation of any industrial operation that utilizes ion-exchange membranes. The following section provides important background regarding the properties of ion-exchange membranes and certain phenomena that are observed during operation that are important to the understanding of the project and work completed within this thesis. However, the discussion is limited to describing the properties of the membranes and does not elaborate on the methods and experiments that may be used to determine these properties. Several references are available to the reader if these are required<sup>15,64,65</sup>.

#### 2.3.2 Ion-exchange capacity

Different ion-exchange membranes contain different ion-exchange groups to provide conductivity for the counter-ions. Most commonly, sulfonic acid or carboxylic acid groups provide conductivity for cations in a cation exchange membrane while quaternary ammonium or tertiary amino groups

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provide conductivity for the anions in an anion exchange membrane. The species and the amount of these ion-exchange groups within the membrane determine the properties of the ion-exchange membrane. The amount of ion-exchange groups within the membrane is referred to as the membrane's ion-exchange capacity and is reported as milligram equivalent per gram of membrane (meq.g<sup>-1</sup>) as either dry or wet weight and with or without supporting fabric. Higher ion-exchange capacity membranes are desired. Table 1.2 summarizes the ion-exchange capacity of several commercially available membranes.

#### 2.3.3 Permselectivity of ion-exchange membranes

The permselectivity of an ion-exchange membrane is one of its most important properties. The permselectivity of the membrane describes the ability of the membrane to discriminate between counter-ions and co-ions, i.e., the membrane's ability to differentiate between anions and cations. During operation charge is transferred by the ion-exchange membrane. The amount of charge transferred by the membrane corresponds to the amount of current being passed through the cell. Ideally, all the charge transferred by the ion-exchange membrane should be counter-ions, i.e., a cation exchange membrane should only transfer cations and an anion exchange membrane should only transfer anions. However, in actual operations 100% of the charge passed through a CEM should be cations. However, in actual operation a large portion of the charge passed through the CEM will be cations moving towards the anode. The sum of the cations moving towards the cathode and anions moving towards the anode will equal the total charge pass through the membrane and should be equal to the current being passed through the cell. The permselectivity of the ion-exchange

membrane describes the amount of charge transferred by the counter-ion in comparison to the total amount of charge moved during operation, i.e., the amount of charge being passed by the CEM being cations and the amount of charge being passed by the AEM being anions. The permselectivity of the membrane is usually represented as a percentage or as a decimal ranging from 0 to 1 with a perfectly permselective membrane that only transports counter-ions having a permselectivity of 100% or 1. The permselectivity of the membrane may be reported as the transport number relative to a specific counter-ion for a given solution. Examples of the permselectivity of some chosen membranes from different manufacturers is summarized in Table 2.2. It is possible to create a membrane with a very high permselectivity, but this usually comes at the cost of increased membrane resistance. Therefore, for actual operation a trade-off between permselectivity and membrane resistance needs to be made with the intended operation of the membrane dictating which is preferred.

Manufacturer	Membrane name &	Transport number	Ion-exchange
	type	and solution	capacity meq/g
PC-Cell*	PC MVK – CEM	> 0.97 KCl	N/A
PC-Cell*	PC MVA – AEM	> 0.97 KCl	N/A
Fumatech†	FKB – CEM	0.98-0.99 NaCl	1.2-1.3
Fumatech <sup>†</sup>	FAB – AEM	0.94-0.97 NaCl	1.0-1.1
Fumatech <sup>†</sup>	FAA-3 – AEM	0.94-0.96 NaCl	1.4-1.6

Table 2.2: Transport number for some chosen anion and cation exchange membranes.

\* See PC-Cell data sheet in Appendix A.

† See Fumatech website

(https://www.fumatech.com/EN/Membranes/Water+treatment/Products+fumasep/)

This property of the membrane can be further expanded to determine the membrane's selectivity to specific counter-ions in a mixed salt system. For example, a mixed sodium and potassium chloride salt may be processed in an electrodialyzer. In this case, both sodium and potassium ions will be conducted by the ion-exchange membrane. It is possible to determine the permselectivity of the membrane to the sodium or potassium ion as desired. However, these values are not normally reported and should be measured through experimental methods.

# 2.3.4 Ionic resistance of ion exchange membranes

Along with permselectivity, the electrical resistance is also an important property of an ionexchange membrane. The resistance is normally measured in resistance per unit area, e.g.,  $\Omega cm^2$ . The resistance of the membrane depends both on the ion-exchange capacity of the membrane as well as the mobility of the counter-ion within the membrane exchange groups. Due to this, the resistance of the membrane is highly dependent on the species of the counter-ions as well as the concentration of the solution the membrane is operating in, as different counter-ions and concentrations of solutions affect the swelling of the membrane. Table 2.3<sup>66</sup> summarizes the electrical resistance of different membranes with different solutions while Figure 2.5<sup>66</sup> shows the resistance of different membranes with increasing concentration of sodium hydroxide. The resistance of the membrane is also dependent on other factors. These include temperature where an increase in temperature of the electrolyte solution decreases the resistance of the membrane. The ion-exchange membranes are often supported with additional fabric which can result in changes in the resistance of the membrane due to increased thickness or tortuosity of the membrane. For these reasons, the resistance of the membrane is normally reported versus some standard solution and temperature. Generally, membranes with high ion-exchange capacity and high water content have the lowest resistance.

Membrane	HCI	NaCl	KCl	MgCl <sub>2</sub>	CaCl <sub>2</sub>	NaCl- CaCl2
NEOSEPTA CL-25T	0.3	2.8	1.7	9.2	7.1	5.1
AMFion C-310	0.5	3.5	2.1	9	7.4	6.4
Ionac MC-3470	0.9	6.3	4.1	04.2	11.7	10.5

Table 2.3: Change in electrical resistance (Ωcm<sup>2</sup>) of cation exchange membrane with ionic forms.



Figure 2.5: Change in electrical resistance of Nafion® membranes and specific resistance of sodium hydroxide solution with concentration of sodium hydroxide.<sup>2</sup>

<sup>&</sup>lt;sup>2</sup> Figure used with permission from the Royal Society of Chemistry.

#### 2.3.5 Water transport

During operation, an ion-exchange membrane should only allow counter-ions to pass through it. However, diffusion of low molecular weight electrolytes (e.g., sulfuric acid at the anode) and nonelectrolytes (e.g., water, non-aqueous solvents) can occur due to the difference in concentration on either side of the membrane. For the purposes of this thesis, water is the major component of concern as all solutions are provided in aqueous media. Water transport occurs through the membrane through two phenomena – osmotic and electro-osmotic water transport.

Osmotic water transport across the membrane is the result of a difference in concentration on either side of the membrane. During electrodialysis osmotic water transport causes water from the dilute side of the membrane to move towards the concentrated side of the membrane. The osmotic water transport through the membrane is related to the ion-exchange capacity, i.e., the number of ion-exchange groups within the membrane. Higher ion-exchange capacity membranes have lower osmotic water transport.

Electro-osmotic water transport occurs when a potential is applied and is a result of the water being transported across the membrane as part of the hydration shell of the counter ions being transported. Electro-osmotic water transport depends on both the ionic solution and operating conditions as well as the membrane, as it is related to the hydration shell of the counter-ions being transported. Figure 2.6 shows electro-osmotic water transport for different salts as a function of concentration and illustrates the large variation in the amount of water transported through electro-osmotic water transport. Electro-osmotic water transport. Electro-osmotic water transport.

concentration differences on either side of the membrane exist. It is important to consider the concentration of the solution under operation when using ion-exchange membranes in electrodialysis type applications and determining electro-osmotic water transport. A more dilute boundary layer can form on the surface of the ion-exchange membrane in an electro-dialysis based as the ions may not be able to move sufficiently quickly from the bulk solution to the surface of the membrane. In this scenario, the electro-osmotic water transport can be much higher than what would be expected based on the concentration of the solution.



Figure 2.6: Change in electro-osmotic water with concentration of different salt solutions. Cation exchange membrane: MK-40; measured at low current density to reduce concentration polarization.<sup>3</sup>

<sup>&</sup>lt;sup>3</sup> Figure used with permission from the Royal Society of Chemistry.

## 2.3.6 Membrane swelling

Ion-exchange membranes expand or swell when in water or other solvents with the degree of swelling depending on many factors including ion-exchange capacity, type of ion-exchange groups, reinforcement cross-linking, ionic form, pH, and temperature among many other factors. The swelling of the membrane can significantly affect membrane performance as it affects several properties of the membrane including conductivity and mechanical strength. The membrane conductivity is significantly affected through hydration of the membrane. A membrane that has not been sufficiently hydrated may have a low number of active sites but a membrane that has swelled too much may have expanded so much that the ion-exchange sites are too far apart resulting in a lower conductivity as well. In addition, it is important for proper use that the membranes be properly equilibrated with the operating ions and solutions before being installed in an electrodialysis type system as the swelling will result in changes in dimension of the membrane. Tearing or micro-tears resulting in leaks through the membrane can occur if a fully expanded membrane that has not equilibrated is installed in the cell. It is also possible that as the membrane expands later inside the cell it will affect gap between the membranes and create pressure differentials affecting flow.

## 2.3.7 Chemical and thermal stability

Membrane stability is an important consideration when using ion-exchange membranes in an electrodialysis type application. The chemical stability of the membranes is of significant importance within the context of this work as the membrane is exposed to different pH on either side and potential contaminant within the brine. Further, thermal and mechanical stability of the

ion-exchange membranes is also important to consider as this will limit the operating conditions of the cell.

Chemical stability of the ion-exchange membranes within acid and base solutions is dependent on the type of polymer used for the backbone of the membrane. Generally, hydrocarbon- based anion and cation exchange membranes are stable in dilute concentrations of inorganic acids such as hydrochloric, sulfuric, and nitric acid and lower strengths of sodium hydroxide. Generally, the stability of the membranes is poorer in caustic solutions than in acidic solutions. Further, the stability of any reinforcing backing layers that provide mechanical support to the main polymer backbone should also be considered to prevent degradation of the backing layer resulting in membrane failure. More importantly, the presence of any oxidizing agents can result in much quicker degradation of the membrane. Oxidizing agents such as chlorine are known to severely decompose the membrane matrix even at ppm level concentrations. On the other hand, ionexchange membranes are stable in contact with reducing agents.

The thermal stability of cation-exchange membranes is usually much higher than that of anionexchange membranes. Cation-exchange membranes such as Nafion have been shown to be stable to 120°C while the stability of anion-exchange membranes can depend on the ionic form of the membrane. Anionic membranes in the chloride form may be stable up to 80°C while they may only be stable up to 60°C in the hydroxide form. The stability of the reinforcing fabric or any backing layers should also be considered when determining the stability of the ion-exchange membranes with respect to temperature.

## 2.4 Gas diffusion electrodes

A portion of this work uses a gas diffusion electrode (GDE) within the electrochemical cell which to the best of our knowledge has not been reported in a multi-compartment electrodialysis or electrolysis cell. The electrodes for the cell provide the catalyst sites where the electrochemical reactions take place. However, other components are required to ensure proper operation of the electrodes. Usually the catalyst is applied onto a gas diffusion layer (GDL) or on another microporous layer (MPL) applied on to the GDL. The GDL serves several important functions in any electrochemical cell which include:

- Providing access for the reactants to reach the catalyst layer;
- Provide access for any products to be removed from the catalyst layer;
- Provide an electrical connection between the catalyst sites and flow plates so electrons may be able to travel in an external circuit;
- Act as a heat conductor to conduct heat to or away from the electrode;
- Provide mechanical support to the MEA so it does not sag into the flow channels.
- The following properties are therefore required in a GDL to serve these functions:
- The GDL must be porous to ensure reactant access as well as product removal. Furthermore, pore size is important as the catalyst nanoparticles must be supported by the GDL. Often a micro-porous layer (MPL) or an electrode backing layer with different properties is applied to the GDL depending on its purpose.
- The GDL must have good electrical and thermal conductivity.
- The GDL should also be rigid enough to support the MEA but with sufficient flexibility to ensure good electrical contact with the flow plates.

Carbon fiber-based materials have normally been best suited for use as the GDL though Teflon layers integrated with nickel or other metal meshes have been used in electrolysis-based applications. The catalyst required for the respective reaction is usually applied to the GDL or to the MPL on the GDL by means of creating a catalyst ink of the required composition. The catalyst ink consists of the catalyst particles in a solution of water, some solvent (e.g., iso-propanol) and some binding agent (e.g., Nafion® ionomer, Teflon, etc.). The catalyst ink is then applied to the GDL by painting, spraying, printing, or scraping. The MPL may be added to the GDL in a similar manner. This catalyst layer, the MPL (if present) and GDL together comprise the gas diffusion electrode (GDE). The GDE within this work acts as the cathode where the oxygen reduction reaction occurs to produce hydroxide ions.

#### 2.4.1 The Oxygen Reduction Cathode

Electrochemical reduction of oxygen to hydroxide ions requires oxygen, water, and electrons (see equation 2.24) to all be present at the catalyst site. Therefore, this active catalyst site necessarily must be connected electrically to an external circuit and ionically to the ionomer or electrolyte that transports the hydroxide ions to the cathode. Furthermore, this catalyst site must be adjacent to a pore that allows oxygen transport to it. This intersecting point is known as the triple phase site (TPS)<sup>67</sup>. Usually, the number of TPS is limited by the ionic connection between the membrane and the catalyst. This leads to most of the TPS existing only in a thin film adjacent to the membrane and catalyst not immediately next to the membrane is not utilized.

Previous commercial attempts at utilizing the oxygen reduction cathode in electrolysis type applications have relied on the transport of cations to the cathode as shown in Figure 2.7 for example in an oxygen depolarized cathode (ODC) chlor-alkali cell<sup>68</sup>. To date, a full-scale commercial chlor-alkali plant using an oxygen cathode has not been commissioned. However, Uhde-Bayer, Covestro and De-Nora have developed oxygen cathodes for use in chlor-alkali type systems and succeeded in scaling up the process for commercial applications. The advantage of this approach over conventional chlor-alkali electrolysis is the approximately 25% lower energy consumption of the process due to the lower voltage required. This approach is especially attractive for areas where electricity costs are high.

ODC-chlor-alkali cell use a cation exchange membrane to conduct the cation and produce a liquid caustic solution is produced on the surface of the cathode, e.g., sodium hydroxide. In this application, the structure of the gas diffusion electrode is critical to operation of the system. The GDE must prevent flooding of the catalyst sites by the liquid caustic solution as the oxygen will not be able to diffuse to a flooded catalyst site thus preventing the reaction from occurring. However, this must be balanced with providing enough water to the catalyst sites as well as enough solution to allow for conductivity of ions (sodium or hydroxide) as both are necessary reactants in the reaction. Therefore, Covestro and De-Nora have used a highly hydrophobic layer on the catalyst layer to prevent the liquid from flooding the catalyst site while the porosity of the catalyst layer is carefully managed to allow for water vapor to diffuse to the catalyst site. The amount of water vapor can be increased by increasing the temperature of the cell. While this addresses the issues of flooding of the site, two additional issues are raised with this approach. First, as water vapor and oxygen are both gases, increasing the amount of water vapor reduces the partial pressure of the oxygen which increases the activation losses of the reaction. Second, the use of a highly hydrophobic layer can both reduce the ionic conductivity as well as electrical conductivity of the

electrode. Due to all these factors, the design of the oxygen reduction reaction is a very fine balance between GDL porosity, catalyst layer hydrophobicity, temperature and providing electrical conductivity of the electrode among other factors as shown in Figure 2.8a. Some of these issues can be mitigated through the addition of an ion-exchange membrane as shown in Figure 2.8b which can help reduce the amount of flooding of the catalyst site by the liquid solution making the design of the GDE somewhat simpler and potentially expanding the number of triple phase sites. The addition of the membrane can also help manage the hydrostatic pressure on the electrode in commercial scale electrochemical cells.

Unlike conventional ORR GDEs, the work performed in this thesis instead relies on transporting the anions (hydroxide, bicarbonate, or carbonate) produced at the cathode through an anion exchange membrane to a separate compartment as shown in Figure 1.2. This alleviates some of the issues of conventional ORR GDEs as the anion exchange membrane prevents the catalyst site from being flooded by the liquid caustic solution. The water can be provided to the catalyst sites by either providing a humidified air or oxygen stream and/or it may diffuse through the anion exchange membrane to the catalyst layer. However, the GDE must be in proper contact with the anion exchange membrane to maximize the ion conductivity at the catalyst layer by increasing the number of triple phase sites. This can be achieved by carefully managing the catalyst-membrane interface through pressure within the cell or by bonding the catalyst layer to the membrane itself. The most used catalyst for the oxygen reduction reaction (ORR) is carbon supported Pt or Pt black without a support. Usually 10-40 by wt.% Pt supported on C is best suited for the ORR. Catalyst loadings of the Pt in the catalyst layer should be around 0.2-0.4 mg/cm<sup>2</sup> to ensure good performance. Though the amount of catalyst used can be increased further it is unnecessary as it

is only the active catalyst surface area that is important. Increasing the mass of catalyst does not necessarily increase the active surface area. Hot-pressing the cathode to the membrane and/or adding ionomer to the catalyst layer are approaches that can be used to improve the utilization of the catalyst layer. During hot-pressing the cathode is compressed with the catalyst layer facing the membrane at a temperature that is higher than the glass-point temperature of the membrane. At this temperature ionomer which was added to the catalyst ink when it was applied to the GDL becomes fluid-like and bonds to the anion-exchange membrane. This provides improved ion conductivity by creating an ionomer extension away from the membrane into the catalyst layer. Usually an ionomer composition of 20-30% in the catalyst ink is best for this purpose. Higher ionomer compositions may result in the catalyst layer losing electrical conductivity.



Figure 2.7: Conventional chlor-alkali cell for producing sodium hydroxide and chlorine gas; 2. Chlor-alkali cell with an oxygen depolarized cathode for producing sodium hydroxide and chlorine gas; a – Anode; b – cation exchange membrane; c – hydrogen evolving cathode; d – oxygen depolarized cathode.<sup>4</sup>

<sup>&</sup>lt;sup>4</sup> Figure used with permission from Springer Science and Business Media.


a)

b)

[\_\_\_\_\_] Mainly active electrode surface area



Figure 2.8: Schematic showing the triple-phase site in an oxygen depolarized cathode and; a) the narrow operating range of the catalyst without a membrane; b) reduced flooding and more expanded operating range with an ion-exchange membrane.

## **Chapter 3: Experimental**

The experimental work performed in this thesis was performed in two different electro-chemical cells;

- 1. The electrodialysis experiments and modeling work which is the subject of Chapter 4 is described in section 3.1 of this chapter. This work focused on the conversion of carbonic acid as opposed to the gas phase conversion of carbon dioxide.
- 2. All other experimental work performed within this thesis which focused on the conversion of carbon dioxide in the gas phase and was performed in the electro-chemical cell reported in section 3.2.

## 3.1 Electrodialysis cell for conversion of carbonic acid and saline water

*Electrodialysis cell:* Experimental demonstration of the treatment and conversion of dissolved carbon dioxide (carbonic acid) and saline water into chemicals was performed in a commercially available, bench-top, four chamber electrodialysis cell acquired from PC-*Cell* Gmbh, shown in Figure 3.1. The cell is provided by PC-Cell under the name PC-64004 name. The cell has an active membrane area of 64 cm<sup>2</sup> and an intra-membrane gap of 0.75 mm. The anode and cathode electrodes were comprised of Pt-coated and Ir-coated titanium mesh, respectively. Schematic and instructions for assembling the PC-Cell can be acquired from PC-Cell.

*Membrane configuration for 64 cm<sup>2</sup> PC-Cell:* The membranes were configured as shown Figure 3.2. All membranes used in the 64 cm<sup>2</sup> electrodialysis cell were supplied by PC-Cell. The membranes were pre-treated by storing in a salt solution of the relevant ion for at least 24 hours. The membranes used to conduct the different ions are summarized in Table 3.1. While there are

numerous membranes available for this purpose, the choice of membranes used (see Table 3.1) was based on the manufacturer's recommendations for the different ions and solutions. Development of polarization curves and modeling work performed used PC-MVK, PC-SK and PC-MVA membranes. For longer-term tests at constant voltage the PC-MVA membrane was replaced with a PC-Acid 60 membranes due to its lower proton leakage.



Figure 3.1: Picture of the 64 cm<sup>2</sup> PC-Cell for conversion of carbonic acid and saline water to chemicals

through electrodialysis.

Table 3.1: Summary of membranes used in the 64cm<sup>2</sup> PC-Cell for the relevant ions and the solutions for pre-

#### treatment of the membranes.

Ion	Membrane type	Membrane name	Pre-treatment
			solution
Proton	Acidic sulfonic CEM	PC SK	Deionized water
Sodium	Acidic sulfonic CEM	PC MVK	5 wt.% NaCl
Bicarbonate	Alkaline ammonium AEM	PC MVA	0.5 M NaHCO <sub>3</sub>

Chloride	Alkaline ammonium AEM	PC Acid 60	5 wt.% NaCl
Nitrate	Alkaline ammonium AEM	PC Acid 60	0.5 M NaNO <sub>3</sub>



Figure 3.2: Schematic of membrane configuration used in the 64 cm<sup>2</sup> PC-Cell.

*Testing conditions:* Carbon dioxide was continuously bubbled in deionized water during operation to maintain sufficient ionic species in the carbonic acid stream. In all cases the saline stream to be treated consisted of 1 M NaCl. Raw brines are likely to contain additional components such as divalent ions, transition metal ions, inorganic anions and organics. All of these can affect the performance of the cell. This is discussed later in more detail. The anode and cathode compartments were fed a 1 M sulfuric acid solution to facilitate oxygen and hydrogen generation. All streams were supplied to the cell at a flow rate of 5 ml/min to ensure a sufficient molar flow rate is maintained at the highest current densities. The addition of sulfuric acid improves

conductivity and minimizes voltage losses at the electrodes thus allowing a better understanding of the ion transport voltage within the cell.

*Performance characterization:* Electrochemical cell performance is most commonly measured through the development of characteristic polarization curves which show the relationship between applied voltage and current density<sup>69</sup>. Characteristic polarizations curves were developed to test the performance of the electrochemical reactor under different conditions with the electrochemical cell being operated in single-pass mode. The polarization curves were developed through potentio-static testing at varying voltages with the current density recorded once the current response had stabilized to within 2 mA/cm<sup>2</sup> and held constant for a period of at least 3 minutes. The cell was operated for periods of time up to 12 hours at different applied cell potentials in the range of 0 to 7 volts.

*Long-term testing to show chemical production:* Demonstration of production of chemicals was performed by operating the electrochemical cell at constant voltage for a period of 24 hours with 1 liter of each solution being recycled continuously. The product NaHCO<sub>3</sub> and HCl streams were provided with an initial concentration of 5 mM NaHCO<sub>3</sub> and 10 mM HCl, respectively.

## **3.2** Electrolytic cell for conversion of gaseous carbon dioxide and saline water

A custom-built electrochemical cell designed by the author as shown in Figure 3.3 was used to demonstrate conversion of gaseous carbon dioxide and treatment of saline water into chemicals.

*Cell dimensions, active area, and assembly:* All dimensions of the cell can be found in Appendix C. The overall active area of the cell was 3.24 cm<sup>2</sup>.

*Anode preparation:* The anode consisted of a mixed metal oxide coated titanium electrode acquired from Metakem GmbH (Type G). The anode was placed onto the titanium anode flow plate and had dimensions of 3 cm x 3 cm.



Figure 3.3: Picture of the custom built electrochemical cell for gas phase conversion of carbon dioxide and desalination of saline water.

*Cathode preparation:* the cathode used for testing varied with the test being carried out. A gas diffusion electrode (GDE) or a catalyst coated membrane (CCM) was used. Both the CCM and GDE were prepared using a using a fully automated spray coater available at 4-D Labs at Simon Fraser University. The spray-coater model is Sono-Tek ExactaCoat while the nozzle model used is the Ultrasonic Accumist. The spray coater is equipped with a heated vacuum table which was used to heat the membrane or gas diffusion layer to a temperature of 95°C to evaporate the solvents used to prepare the catalyst ink.

• *Catalyst coated membrane preparation:* The catalyst layer consisted of an 85 wt.% catalyst (20% Pt on Vulcan XC-72, Alfa-Aesar) and 15 wt.% ionomer (EES HMT-PMBI ionomer,

Ionomr Innovations Inc.) in an aqueous methanol solution and was spray coated on the anion exchange membranes (Fumasep FAB thickness 100-130  $\mu$ m, Fumatech®). The catalyst loading on the membrane was approximately 0.5 mg<sub>Pt</sub>/cm<sup>2</sup>. Different membranes were used for the preparation of the CCM including those available from PC-Cell GmbH and Fumatech. However, these membranes suffered from incompatibility issues between the ionomer and the membrane. The Fumatech FAB membrane was found to be relatively more stable and showed reliable adhesion of the catalyst layer to the membrane.

- Gas diffusion electrode: The catalyst layer consisted of a 85 wt.% catalyst (20% Pt on Vulcan XC-72, Alfa-Aesar) catalyst and 15 wt.% ionomer (EES HMT-PMBI ionomer, Ionomr Innovations Inc.) in an aqueous methanol solution and was spray coated on to a Sigracet 25-BC gas diffusion layer.
- *Electrode structure:* The electrode comprised of three layers of carbon fiber paper (TGP-H-090 non-WP, Toray®) with either the gas diffusion electrode or the CCM resting on top of it. The catalyst layer was in contact with the anion exchange membrane.

*Electrode flow plates:* Serpentine flow fields were machined into the titanium anode plate (99% titanium, Superior Alloy Technologies) and graphite cathode plates (high temperature conductive graphite, McMaster-Carr) to provide the reactants to the electrodes and remove the products. The flow channels had dimensions of 1 mm (width)  $\times$  1 mm (depth). The flow plates had separate flow manifolds machined to provide solutions to the central compartment. Engineering drawings of the electrode flow plates can be found in Appendix C.

Membranes, cell spacers, and configuration: The spacers were aligned to the flow manifolds to ensure flow would only be provided to the correct compartment. The spacers were arranged in a strategic manner to ensure that each spacer not only acted to provide solutions to the appropriate compartment but also to either allow solutions to pass through without mixing or to block a solution and divert into the correct compartment as shown in Appendix C. The membrane gap was maintained with the use of spacers cut from a silicone rubber sheet (HT-6220, Stockwell Elastomerics) with a thickness of 0.032 inches and an active open area of 3.24 cm<sup>2</sup> for fluid flow. The spacers were also used to provide manifolds for providing liquid flow to the different compartments. The membranes were supported with the use of porous glass filter paper (1.6 µm particle retention, Fisher Scientific) which was used to fill the 3.24 cm<sup>2</sup> area within the silicone rubber spacer. Table 3.2 summarizes all the membranes used for the experiments. The membranes were pre-treated by storing in a salt solution of the relevant ion for at least 24 hours. The choice of membranes used was based on the manufacturer's recommendations for the different ions and solutions. The cell was assembled as shown in Figure 3.4 and Figure 3.5. The membrane configuration of the cell is summarized Figure 3.6.

Table 3.2: Summary of membranes used in the custom built electrolytic cell	for the relevant ions and the
solutions for pre-treatment of the membranes	

Ion	Membrane type	Membrane name	Pre-treatment
		(manufacturer)	Solution
Proton	Acidic sulfonic PEM	Nafion 117 (Nafion®)	Deionized water
Sodium	Acidic sulfonic CEM	PC MVK (PC-Cell)	5 wt.% NaCl
Carbonate,	Alkaline ammonium AEM	FAB (Fumatech)	0.5 M NaHCO <sub>3</sub>
Bicarbonate,		FAA3-pk 130	
Hydroxide		(Fumatech)	
		PC-Acid 60 (PC-Cell)	
Chloride	Alkaline ammonium AEM	PC MVA (PC-Cell)	5 wt.% NaCl
		PC Acid 60 (PC-Cell)	



Figure 3.4: Schematic showing the components for cell assembly for the custom-built electrochemical cell.



Figure 3.5: Picture of components for the custom-built electrochemical cell.



Figure 3.6: Schematic of membrane and reference electrode configuration for the custom-built electrochemical cell.

*Other cell components:* Gold plated copper current collectors, a titanium anode plate and a graphite cathode plate were used within the cell assembly. A nitrogen bladder was used to provide compression pressure to the cell (20-30 psi) to reduce contact resistance within the cell.

*Reference electrode measurements:* A voltage profile across the cell was developed to better understand the voltage losses within the cell using reference electrodes. An Ag/AgCl (Leak-free Ag/AgCl, Harvard Apparatus) reference electrode was placed at the entrance of the three central compartments with ionic contact made through the flowing solutions as shown in Figure 3.6. The

voltage profile was developed by measuring the reference voltage of each of these reference electrodes versus the anode. This measurement can then be used to extract voltage losses between the different compartments and for the cathode. All reference electrode measurements were taken once the cell current density had stabilized to within 2 mA/cm<sup>2</sup> per minute. Example calculations of how reference electrode data measurements and calculations are shown in Appendix D.

*Performance characterization:* Characteristic polarizations curves were developed to test the performance of the electrochemical reactor under different conditions with the electrochemical cell being operated in single-pass mode. The polarization curves were developed through potentiostatic testing at varying voltages with the current density recorded once the current response had stabilized to within 2 mA/cm<sup>2</sup> and held constant for a period of at least 3 minutes. All performance characterization curves were repeated a minimum of three times with the reported data corresponding to the average of at least two tests. The data for the individual tests comprising the average results can be found in Appendix E. Averaging the data for multiple tests allows the effect of day to day variation in testing to be reduced and trends to be viewed more easily. The variation in the data through this method was small enough that the comparisons of the different graphs was always valid, i.e., the effect of changing parameters was always larger than the variation in the data. The electrochemical cell was provided with some initial solutions of the product during development of polarization curves to negate the effect of changing concentrations during the testing and reported with the results. The overall testing conditions are summarized in Table 3.3.

*Long-term testing:* Demonstration of production of chemicals was performed by operating the electrochemical cell at constant voltage for a period of 24 hours with 1 liter of each solution being

recycled continuously. However, the cathode feed gas was operated in a single-pass mode with the composition of gas varied depending on the test. Due to issues of stability of the catalyst layer in the CCM all long-term testing was performed using GDEs described earlier. While the FAB CCM is stable during short-term polarization tests it was found that longer term tests resulted in the catalyst layer becoming detached from the membrane and becoming bonded to the gas diffusion layer. This is likely to do with incompatibility between the ionomer and membranes with the compression pressure resulting in some adherence of the catalyst layer to the gas diffusion layer. The current density of the cell was measured continuously throughout the 24 hours. The overall testing conditions are summarized in Table 3.3.

 Table 3.3: Summary of testing conditions for the gas-phase conversion of carbon dioxide and desalination of saline water.

	Polarization curves	Long-term testing
Gas composition and flow rate	Composition varied at 50 ml/min (CO <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub> )	
Gas pressure 5 psi		osi
Saline stream Varied concentrations of NaCl		rations of NaCl
Acid compartment	Varied concentrations of Na <sub>2</sub> SO <sub>4</sub> or HCl at 5 ml/min	
Base compartment	Varied concentrations Na <sub>2</sub> SO <sub>4</sub> , NaOH, NaHCO <sub>3</sub> at 5 ml/min	
Anode electrolyte and flow rate	0.1 M H <sub>2</sub> SO <sub>4</sub>	at 5 ml/min
Temperature	25	°C
Compression pressure	2	25 si

## 3.3 System setup, equipment, and ion analysis

System setup: A schematic and picture of the system are shown in Figure 3.7.

*Electrochemical performance characterization and long-term testing:* All electrochemical measurements were performed using a Biologic SP-150 potentiostat with a current and voltage collection frequency of 3 Hz.

*Liquid and gas flow controllers:* The flow rate of all liquid feeds was controlled with the use of peristaltic pumps (Masterflex L/S 600 RPM, Cole-Parmer Inc.) The gas flow rates were controlled during the experiments using panel-mount flow meters (Gilmont Instruments, Cole-Parmer).



Figure 3.7: Schematic of the testing setup for the custom-built electrochemical cell.

*Ion analysis:* The streams fed to the ED system were sampled at regular intervals, analyzed for the relevant ions and the pH was measured. Analysis of chloride ions was performed by ion chromatography (350 ppm detection limit, Dionex Ion Chromatograph ICS-900 with an AS22-FAST column). Bicarbonate ion analysis was performed by titration of the solution with 10 mM hydrochloric acid (37% concentration, 99.9% purity, Fisher-Scientific) using a pH meter (pH5+ meter, Oakton) to determine neutralization points. Details of determination of hydrochloric acid 63

by titration can be found in Vogel's "Textbook of Quantitative Chemical Analysis" <sup>70</sup>. Sodium ion analysis was performed by inductively coupled plasma – optical emissions spectroscopy (ICP-OES).

# Chapter 4: Conversion of saline water and dissolved carbon dioxide to value added chemicals and desalinated water

Electrodialysis is a process which utilizes ion selective membranes in the presence of an electrochemical potential to remove ionic species from a liquid stream. Electrodialysis cells have been shown to be cost effective for desalination purposes <sup>11</sup> for many applications including industrial saline water treatment <sup>53</sup>, brackish water treatment <sup>54</sup>, and acid and alkali production <sup>55</sup> with high removal rates for different ions <sup>56</sup>. A number of studies have shown that the energy costs of electrodialysis are lower than other conventional methods like ion resin exchange<sup>56–58</sup>. The fundamental operating principle of electrodialysis requires the feed solution to have ions present which are to be removed. As such the removal of carbon dioxide with the use of electrodialysis requires the carbon dioxide to be provided as an ionic species. This can be accomplished by dissolving the carbon dioxide in water to create carbonic acid. Carbonic acid at equilibrium dissociates into carbonate and bicarbonate ions which can then be removed through electrodialysis.

**Hypothesis:** The focus of this chapter is to investigate the use of a multi-compartment electrodialysis system with a strategic pattern of anion exchange membranes (AEM) and cation exchange membranes (CEM) to simultaneously remove carbon dioxide in a mineralized form and desalinate saline water. A feed water stream (e.g., brine, seawater, or waste-water) containing ionic species, which are to be removed, are provided to one feed compartment and carbon dioxide dissolved in water or other high carbon dioxide solubility solvents is provided in the form of carbonates (e.g.,  $CO_3^{2-}$ ,  $HCO_3^{-}$ ) to a second feed compartment. An applied voltage with an appropriate configuration of membranes can be used to transport cations and anions from the feed

chambers to produce carbonate (e.g., NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>) and acids (e.g., HCl or other acid) or other products in separate chambers. The membranes (AEM and CEM) are separated with the use of a spacer which allows the solutions to flow between them and create turbulence in the stream to improve mass transfer. The basic operation of this electrodialysis approach is shown in a schematic in Figure 4.1. The electrochemical reactions at the electrodes should be the electrolytic water decomposition reactions (oxygen evolution reaction) and the reduction reaction to hydrogen, which can be summarized as follows:

Anode:  $H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2$  -1.23 V vs. SHE (4.1)

Cathode: $2H^+ + 2e^- \rightarrow H_2$	0.00 V	(4.2)	)
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Figure 4.1: Schematic showing the basic operation within the electrodialysis cell to simultaneously remove

dissolved CO<sub>2</sub> and desalinate saline solutions.

### 4.1 Experimental results for proof of concept and modeling comparison.

The objective of the experiments was to show an increase in the concentration of hydrochloric acid and bicarbonate ions under a constant applied cell voltage. Preliminary testing in the 64 cm<sup>2</sup> PC-Cell (described in section 3.1) over 12 hours successfully demonstrated the proof of concept of this new approach. Figure 4.2c shows the cell current density and the applied potential vs. the duration of the experiment. The cell achieved a stable current density of approximately 1.5 mA/cm<sup>2</sup>. Figures 4.2a and 4.2b show clear evidence to produce carbonate salts and acids, respectively. The pH and ion concentrations in both the product hydrochloric acid compartment and the product NaHCO<sub>3</sub> compartment agree with the expected results based on Faraday's law. The pH of the hydrochloric acid solution decreased from 2 to 1.3 over the 12-hour period in agreement with the Faradaic predictions. The concentration of the chloride ion increased from 10 mM to about 52 mM, which corresponds to a pH of 1.30 but is slightly lower than the Faradaic predicted concentration of 54 mM. A similar Faradaic concentration change is observed in the product NaHCO<sub>3</sub> chamber, where sodium ion concentration increased to approximately 40 mM while the bicarbonate ion concentration increased to 42 mM over the 12-hour period.

While these results show that the approach is technically feasible, the current density and thus the ion flux rates are very low for any practical applications. The low current densities measured were considered to be due to the high solution resistance within the electrodialysis cell chambers and not the electrodes. To confirm this, the electrodialysis cell was operated as a water electrolysis cell with the chambers removed and just a CEM placed between the electrodes. A comparison of the electrodialysis cell and the electrolytic cell polarization curves is shown in Figure 4.3. While the electrolysis cell achieved current densities well in excess of 600 mA/cm<sup>2</sup> at 2.5 V (full range not

shown in Figure 4.3), the electrodialysis cell's current density did not exceed 1.25 mA/cm<sup>2</sup> even at 7 V. This high resistance was determined to be due to mass transport limitations associated with the low solubility of  $CO_2$  in water and the poor dissociation of carbonic acid in water. Carbon dioxide dissolution in water produces carbonic acid (H<sub>2</sub>CO<sub>3</sub>) with a saturation concentration of about 40 mM and a pH of approximately 3.9. However, under equilibrium most of this dissolved carbon dioxide exists as  $CO_{2(aq)}$  according to the following equilibrium, and is dependent on pH <sup>71–73</sup> with HCO<sub>3</sub><sup>-</sup> being the prevalent species in solutions with a pH of 8-9 and  $CO_3^{2-}$  dominating in solutions with a pH greater than 12:

$$\text{CO}_{2(g)} \rightarrow \text{CO}_{2(aq)}$$
 (4.3)

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

$$(4.4)$$

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+ + HCO_3^-$$
(4.5)

$$HCO_3^- + H_2O_{(1)} \rightleftharpoons H_3O^+ + CO_3^{2-}$$
 (4.6)

As carbonic acid weakly dissociates, less than 1% of the dissolved  $CO_2$  is usually converted to ions such as  $HCO_3^-$  or  $CO_3^{2-72}$ . Low performance due to limitations in the carbonic acid chamber can be easily shown by replacing the carbonic acid chamber feed with nitric acid, which is similar in molecular weight and charge to bicarbonate ions but dissociates easily providing a much higher concentration of ions (HNO<sub>3</sub> has saturation concentrations in excess of 15 M). Figure 4.3 shows a comparison between the operation of the electrodialysis cell with carbonic acid and different concentrations of nitric acid. All electrodialysis cell polarization curves shown in Figure 4.3 were fed a 50 mM product acid (HCl) and 50 mM product salt (NaHCO<sub>3</sub> or NaNO<sub>3</sub>) to reduce the effect of changing concentrations which can affect the cell performance. In general, current densities achieved with nitric acid were much higher than those obtained with carbonic acid and reached the levels of the electrolysis mode alone. Cell limiting current densities experimentally observed for nitric acid as shown in Figure 4.3 are roughly linear with inlet nitric acid concentration. Maximum current densities achieved with nitic acid concentrations of 1 mM, 50 mM and 100 mM were 0.5 mA/cm<sup>2</sup>, 5 mA/cm<sup>2</sup> and 11 mA/cm<sup>2</sup>, respectively. At 1,000 mM HNO<sub>3</sub> the current density achieved for the electrodialysis cell was 15 mA/cm<sup>2</sup> at 3 V. These results clearly show that increasing the concentration of the ionic carbonate/bicarbonate species in the feed chamber is extremely important to improve the performance of the cell.



Figure 4.2: Proof-of-concept results for a carbonic acid and saline water fed electrodialysis cell showing production of acid and carbonate salts over time. All samples were taken from the bottles for each stream.



Figure 4.3: Comparison of polarization curves of the ED cell operated as an electrolytic cell, with dissolved carbon dioxide feed (carbonic acid) and with different concentrations of nitric acid fed in the dissolved CO2 chamber.

The short term experiment to demonstrate production of salts and acid was repeated in the electrodialysis with nitric acid instead of carbonic acid for a period of 3 hours. The feed salt consisted of a 1 M sodium chloride solution while a 100 mM feed nitric acid solution was provided to the cell. The product salt and acid solutions were composed of only deionized (DI) water initially. A potential of 3 V was applied across the cell. The results of these measurements are summarized in Figure 4.4. The pH of the product acid chamber (HCl) decreased from a pH of 6.60 to 1.65 while the concentration of chloride ions measured was slightly lower than the expected value for this pH as shown in Figure 4.4c. The concentration of the sodium and nitrate ions in the product salt chamber (NaNO<sub>3</sub>), as shown in Figure 4.4b, increased from 0 mM to 19 mM and 22

mM, respectively, over 3 hours of testing. These changes in concentration are similar to those expected from Faraday's law. Figure 4.4a shows that the change in pH of the nitric acid feed chamber follows the same trend that would be expected from Faraday's law. Figure 4.4 also shows the electrodialysis cell achieved a current density of approximately 3 mA/cm<sup>2</sup> which compares with the polarization curves where a HNO<sub>3</sub> concentration of 20 mM achieves performance in between 10 mM (1 mA/cm<sup>2</sup>) and 50 mM (5 mA/cm<sup>2</sup>). These experimental electrodialysis results show that dissolved carbon dioxide and salt removal can be coupled to produce other chemicals. The current density, resistance, and ion fluxes are mainly limited by the liquid phase carbonate/bicarbonate concentration and diffusion in the chambers. Section 4.2 discussing the results of the modeling provides further insight on these limitations.



Figure 4.4: Electrodialysis cell testing with 0.1 M HNO3 and 1 M NaCl feed showing production of

hydrochloric acid and nitrate salts.

#### 4.2 Development of the model

A mathematical model of some of the experimental aspects was developed to further understand the performance limitations of this electrodialysis approach and to assess future designs. The model was developed by providing a nitric acid feed instead of the carbonic acid feed. Modelling of this feed is simpler and a clearer match to the experimental results in this case can be obtained due to the absence of the dynamic equilibrium that exists with carbonic acid.

#### 4.2.1 Fit to Electrolysis Polarization and External Resistance

Detailed modelling of the electrolysis in the electrodes of the electrodialysis cell is difficult and not central to the current project. However, the voltage losses at the electrodes which are primarily kinetic in origin, are significant and therefore must be considered when matching the model to experimental results. An empirical fit to the experimental polarization curve for the isolated electrolysis system, shown in Figure 4.3 as "Electrolytic Cell", can be made as follows:

$$V(i) = 7.1 \times 10^{-4}i + 1.54 + \frac{\ln i}{12.0}$$
(4.7)

where V is in volts and i is the current density in  $A/m^2$ .

## 4.2.2 Resistances in Membranes and non-Limiting Channels

The membranes in the device were considered as having fixed resistances. The manufacturer reports the PC-MVA AEM used for transport of chloride and nitrate ions has a resistivity of  $2 \times 10^{-3} \Omega \text{ m}^2$  while the PC-SK CEM used for sodium transport has a resistivity of  $2.5 \times 10^{-4} \Omega m^2$ . The resistances of the end proton exchange membranes (Figure 3.1) are included in the fit for the polarization curve for the electrolysis cell. The membranes in the non-limiting channels (channels

other than the nitric acid or carbonic acid channels) are assumed to have fixed resistance based on their input concentrations. There is some error associated with this assumption as the concentration changes during operation. However, this error was reduced by feeding some initial concentration (usually 5-50 mM) of the product into the product chambers as discussed below.

The literature values for the ionic diffusivities are reported in Table 3.1 below<sup>74</sup> and the standard theory for ionic resistance of dilute solutions <sup>75</sup>, resistances can be computed by

$$R_{\Omega} = \frac{WRT}{(D_{-} + D_{+})F^{2}C}$$
(4.8)

where  $W = 7.5 \times 10^{-4}$  m is the channel width, R is the deal gas constant, T = 300 K is the temperature, F is Faraday's constant, and C is the channel inlet concentration. This gives resistances of:

1 M NaCl channel: 
$$6.1 \times 10^{-5} \Omega m^2$$
  
50 mM NaNO<sub>3</sub> channel:  $1.2 \times 10^{-3} \Omega m^2$   
50 mM HCl channel:  $3.7 \times 10^{-4} \Omega m^2$ .

Table 4.1: Literature values for the ionic diffusivities of different ions at infinite dilution used in the

calculation.

Ion	Diffusivity (× 10 <sup>-9</sup> m <sup>2</sup> /s)
NO <sub>3</sub> -	2
$\mathrm{H}^+$	9
Na <sup>+</sup>	1.3
Cl	2
HCO <sub>3</sub> -	1.2
CO3 <sup>2-</sup>	0.9

Summing the internal membrane and non-limiting channel resistances provides a total resistivity of

$$R_{\Omega} = 6.5 \times 10^{-3} \Omega \, m^2 \tag{4.9}$$

For the channel that limits the current (nitric or carbonic acid), concentrations tend to zero at one of the membranes and result in current densities that vary strongly along the length of the channel. This is the subject of the model developed in the next section.

## 4.2.3 Detailed Nitric Acid Channel Model

The steady state molar concentration c(x, y) and electric field  $\varphi(x, y)$  in the nitric acid channel (Figure 4.5) was modeled under an applied device voltage U. Here c is the concentration of both nitrate ions and protons due to electro-neutrality; x is the cross-channel coordinate with x = 0 adjacent to the nitrate selective membrane and x = W the proton selective membrane; y = 0 is the down channel coordinate with y = 0 the nitric acid inlet and y = L = 0.08 m the outlet. Following the procedure of Newman and Thomas-Alyea<sup>75</sup>, the conservation of ionic species using the Nernst-Planck equations is:

$$vc_y = -J_x$$
 proton conservation (4.10)  
 $uc_y = -K$  pitrate concernation (4.11)

$$vc_y = -\kappa_x$$
 intrate conservation (4.11)

where v is the channel velocity and J(x,y) and K(x,y) are the cross channel molar fluxes of protons and nitrate, respectively, given by

$$J = -D_{H+} \left(\frac{Fc}{RT}\varphi_x + c_x\right) \tag{4.12}$$

$$K = -D_{NO3-} \left( -\frac{Fc}{RT} \varphi_x + c_x \right) \tag{4.13}$$

In (4.10) and (4.11) the down channel fluxes have been neglected which is justified by the large aspect ratio of the channel length to  $L/W \gg 1$ . Note that (4.10) and (4.11) can be combined to show that J – K is a constant for each position along the channel y. The proportionality constant is equal to zF and related to the local current density by Faraday's law at that position y along the channel. Since K(W, y) = 0, see (4.13), +FJ(W, y) is used to represent the current density at each y. At every y, the model matches the given cell voltage to the sum of voltage drops from the nitric acid channel and the resistive losses from other channels and membranes (4.9) and the electrochemical reaction. This is written mathematically in (4.13) below.

Inlet conditions  $c(x, y) = c_0$  are given, where  $c_0$  is the inlet molar concentration. Conditions on the membranes x = 0 and x = W are given as follows:

$$K(W, y) = 0$$
 no nitrate passes through the cation selective membrane (4.14)

$$J(0, y) = 0$$
 no protons pass through the anion selective membrane (4.15)

$$\varphi(W, y) = 0$$
 reference voltage (4.16)

$$U - \varphi(0, y) - R_{\Omega} FJ(W, y) - V(+FJ(W, y)) = 0$$
(4.17)

where in (4.17)  $R_{\Omega}$  is the resistance from (4.9), V(i) is the polarization curve for electrolysis and the external resistance in (4.7), and the expression +FJ(W,y) is one of the equivalent expressions for the local current density. Equations (4.10) and (4.11), together with the expressions (4.12) and (4.13) for the fluxes, the inlet conditions, and the four boundary conditions, above represent a solvable problem for c and  $\varphi$ . However, the expression is of unusual mixed character as it has a component that is a parabolic problem in y coupled to a boundary value problem in x at each y. The equations are scaled and solutions are approximated numerically. Details can be found in the supplementary material for the manuscript. The numerical implementation is done in the MATLAB environment.



Figure 4.5: Schematic showing the nitric acid channel and the characteristic length for the model.

#### 4.2.4 Effect of Turbulent Flow in the Channel Model

The electrodialysis cell uses mesh spacers in-between channels to keep the membranes apart, promote mass transfer and reduce concentration polarization phenomena. The use of spacers heuristically does two relevant things to channel flow in this problem: (i) it increases the diffusivity and (ii) it makes the velocity profile more uniform except in a boundary layer near the channel walls. The channel velocity, v, has been assumed to be constant rather than parabolic across the channel width as would be expected for laminar flow to reflect the second property. One could consider a constant multiple for the diffusivities as a fitting parameter to describe the nature of the induced turbulence, however, this was not required in modelling the experimental results.

### 4.3 **Results of the Model**

The MATLAB code that is used to generate Figures 4.6 and 4.7 is included Appendix B. Figure 4.6a shows the quality of the empirical fit to the experimental polarization curve for the isolated electrolysis system. The parameters in Figure 4.6a are empirical parameters representing a mix of reactions, but taken as a single charge transfer electrochemical process, they correspond to an exchange current density of  $10^{-8}$ A/m<sup>2</sup> and a charge transfer coefficient of 0.31. These are reasonable parameters for the sluggish electrolysis reaction. The fitted resistivity of  $7 \times 10^{-4} \Omega m^2$  includes the sulfuric acid channels, the proton exchange membrane, and external resistance in the circuit.

The comparison of the numerical to the experimental (Figure 4.3) polarization results in Figure 4.6b is quite good. It should be noted that the limiting current observed in the experiments and in the model is not the stoichiometric limit from the inlet reactants. For example, an inlet flow rate of 10 mM nitric acid at 5 ml/min at full consumption corresponds to a current density of

$$\frac{5 \times 10^{-3} \text{l/min} \times 10^{-2} \text{ mol/l} \times 96845 \text{ C/mol}}{60 \text{ s/min} \times 64 \times 10^{-4} \text{m}^2} \approx 12.6 \frac{\text{A}}{\text{m}^2} = 1.26 \text{ mA/cm}^2$$

The model and the experimental results agree that the limiting current with these operating conditions is  $1.0 \ mA/cm^2$ . Identifying the onset of the transport limitations of desired ions is one of the main questions of interest for the application. That the model can correctly identify this limiting current is a strong validation of it.



Figure 4.6: a) Fit of the electrolytic region; b) Comparison of the experimental and model results for the nitric acid polarization curves.

The model also provides some details of the performance of the test cell that are not available from experiments. A schematic of the model geometry for the nitric acid channel and the local current density profile in y is shown in Figure 4.7a. The average of the current density in Figure 4.7a is

what is plotted on the polarization curve in Figure 4.6b at V = 2.2 volts. This results in a large variation in current density from inlet to outlet. At inlet, the ionic concentration is higher and so can carry more current at limiting conditions than at the outlet where the ionic concentration is lower. A similar phenomenon has been observed in hydrogen fuel cells<sup>76</sup>. A contour plot of the concentration c(x,y) is shown in Figure 4.7b and it can be seen that the ionic concentration c tends to zero at the anion selective membrane. This occurs since the nitrate ions diffuse less easily than protons and so they experience mass transport limits first.





Figure 4.7: a) Current density profile near limiting current in the feed nitric acid chamber, Inset: Schematic of the electrodialysis geometry for the nitric acid channel; b) Simulated nitric acid concentration in the channel geometry near limiting current.

## 4.3.1 Discussion of the Carbonic Acid Channel

The experimentally observed current density of  $1.1 \text{ mA/cm}^2$  at maximum voltage is more than the stoichiometric limit of the inlet ion concentration. However, the current is much less than the stoichiometric limit of dissolved CO<sub>2</sub>. Dissociation of CO<sub>2(aq)</sub> is clearly relevant to the calculation of the limiting current and there are also clearly diffusion limitations.

Attempts to model the carbonic acid channel qualitatively using the same approach as for nitric acid in the previous section, including the dissociation reactions (4.18) below, led to computed limiting currents much lower than those observed experimentally. Details of our model and computations can be found in the Appendices. As the flow and diffusion model for nitric acid show good agreement with experiments, the discrepancy is assumed to be a result of the assumptions regarding the dissociation process.

Simple estimates on the behavior in the carbonic acid channel can be made by considering the equilibrium between the different carbon dioxide species that exist in an aqueous solution. Dissolved CO<sub>2</sub> flows into the carbonic acid channel with a pH of 3.9 giving  $[H^+] = 1.23 \times 10^{-4}$  M. The overall chemical equilibrium reaction is as follows:

$$\begin{array}{ccc} k_1 & k_3 \\ H_2 O + C O_2 \rightleftharpoons H_2 C O_3 \rightleftharpoons H^+ + H C O_3^- \\ k_2 & k_4 \end{array}$$

$$(4.18)$$

with  $k_1 = 0.04 \text{ s}^{-1}$ ,  $k_2 = 18 \text{ s}^{-1}$ ,  $k_3 = 10^7 \text{ s}^{-1}$ ,  $k_4 = 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \text{ }^{77,78}$  such that at equilibrium, the concentration of  $CO_2 = 0.034 \text{ M}$ ,  $H_2CO_3 = 7.56 \times 10^{-5} \text{ M}$ , and  $HCO_3^- = 1.23 \times 10^{-4} \text{ M}$ .

## 4.3.2 Model Assumptions and Equations

The current densities considered experimentally are on the order of  $1.4 \text{ mA/cm}^2$ . The system has two stoichiometric current limits: one for inlet ion concentration and the other for total CO<sub>2</sub> content. The inflow of 5 m*l*/min and the inlet bicarbonate concentration above are stoichiometrically equivalent to a current density of

$$\frac{5 \times 10^{-3} \text{l/min}}{60 \text{ s/min}} \times \frac{1.23 \times 10^{-4} \text{ mol/l}}{\times 64 \times 10^{-4} \text{m}^2} \times \frac{96500 \text{ C}}{\text{mol}} \approx 1.55 \times 10^{-2} \frac{\text{mA}}{\text{cm}^2}$$

This is two orders of magnitude smaller than the observed limiting currents at maximum voltage so it can be assumed that there is significant dissociation of dissolved  $CO_2$  in the stream. If the stoichiometric equivalent of all the  $CO_2$  in the stream is considered, the experimental limiting current density is calculated to be

$$\frac{5 \times 10^{-3} \text{l/min}}{60 \text{ s/min}} \times \frac{0.034 \frac{\text{mol}}{\text{l}}}{\times 64 \times 10^{-4} \text{m}^2} \times \frac{96500 \text{ C}}{\text{mol}} \approx 4.27 \frac{\text{mA}}{\text{cm}^2}$$

This overestimates the observed current but is in the same order of magnitude. To distinguish between the possible limiting factors of diffusion losses and dissociation rates, a case in which the CO<sub>2</sub> concentration remains at the inlet concentration (high inlet flow rate) and that it dissociates at the maximum rate and all the bicarbonate ions produced generate current is considered. The current in this idealized case would be

$$0.034 \frac{\text{mol}}{\text{l}} \times 0.04/\text{s} \times 7.5 \times 10^{-4} \text{m} \times \frac{96500 \text{ C}}{\text{mol}} \approx 9.84 \frac{\text{mA}}{\text{cm}^2}$$

using only the limiting reaction rate  $K_1$  above. This calculation shows that the current is not limited by the dissociation rate of carbonic acid to bicarbonate or carbonate ions but rather that the limitations are from diffusion.

#### 4.4 Conclusions

An electrodialysis-based method that accepts saline water and  $CO_2$  in the form of carbonic acid and converts them to hydrochloric acid and bicarbonate salts was demonstrated. Testing showed that the approach was limited due to the low conductivity of the feed carbonic acid solution. A mathematical model was developed to provide further insight into the limitations of this approach. Mathematical modeling indicated that limitations due to the low conductivity of the solution were likely due to the diffusion and mobility of the anionic carbonate/bicarbonate species rather than the slow dissociation rate of carbonic acid. This is due to the low concentration of dissolved carbon dioxide within water. For this approach to be successful, the concentration of carbon dioxide within the feed must be increased. Some possible way to achieve this include:

- Amine scrubbers such as diethanolamine or monethanolamine<sup>79,80</sup> can be used to scrub carbon dioxide. Aqueous solutions of these amines can be used to capture carbon dioxide as a mineralized form as a carbamate (H<sub>2</sub>NCOO<sup>-</sup>) or (bi)carbonate<sup>81</sup>. The amine is then regenerated through temperature or pressure changes which releases the carbon dioxide as a purified gas. The regeneration, however, can be energy intensive, corrosive and can degrade unit operations within the system. While this is a known and mature technology, it is unsuitable for use within the electrodialysis cell as amines or other organic ions can cause degradation of ion-exchange membranes. Further, as the bicarbonate or carbamate would be removed out of the amine solution, it would be replaced by a chloride or another anion from the brine. This would result in the amine solution not being suitable for continued use for further conversion of carbon dioxide.
- Use of catalysts to increase the hydration reaction of carbon dioxide to carbonic acid. Nickel nanoparticles have been reported to catalyze the reversible hydration of carbon

dioxide to carbonic acid at room temperature and atmospheric pressure. This could offer a potential opportunity to increase the concentration of carbonic acid within the solution with the nickel nanoparticles being easily removed from solution as they are both water insoluble and magnetic. However, this approach is still likely to be limited as it would only increase the amount of carbonic acid in solution but would not increase the amount of carbon dioxide that is present in solution<sup>73</sup>.

The next stage of this work is focused on advancing this approach and improving carbon dioxide removal rates by converting the  $CO_2$  to a mineralized species from the gas phase.
# **Chapter 5: Oxygen depolarized cathode for hydroxide production for**

## investigation of individual cell compartments

### 5.1 **Baseline experiments**

**Hypothesis:** The five-compartment electrochemical cell as shown in Figure 5.1 consists of an anode, cathode, a saline feed compartment, a product acid compartment, and a product base compartment. Each of these compartments should contribute to losses in performance through different mechanisms of kinetic, ohmic and mass-transport. The overall performance losses within the cell are likely to be due to the electrolysis compartments, i.e., the anode and cathode compartments, and the different ions within the system as follows:

- Anode electrolysis and proton transport: The protons will contribute to cell performance losses due to kinetic losses from the production of protons from the water oxidation reaction at the anode, and ohmic losses from proton transport within the anolyte, proton transport through the cation exchange membrane and then proton transport within the product acid compartment.
- Chloride: losses associated with the chloride ion should be from ohmic losses due to transport within the feed sodium chloride solution, transport within the chloride conducting anion exchange membrane and transport in the product acid compartment.
- Sodium: like the chloride ion, losses associated with the sodium ion should be ohmic losses associated with transport within the sodium conducting cation exchange membrane, the feed sodium chloride and product base solutions.
- Cathode reduction and hydroxide, carbonate and/or bicarbonate anion transport: losses associated with the basic ions should be kinetic losses due to the electrochemical or

chemical production of the basic ion at the cathode, and ohmic losses due to the transport of the basic ion from the catalyst surface to the membrane, transport within the membrane and transport through the product base solution.



Figure 5.1: 5-compartment electrochemical cell being operated with an oxygen reduction cathode, water oxidation anode and sodium chloride feed.

Each of the above ions and their associated losses contribute to the overall performance of the cell. A key aspect of this work is to demonstrate and understand the conversion of carbon dioxide at the cathode. For this to be accomplished, it is important to first understand the factors that affect the performance of each of the compartments, i.e., the anode, cathode, feed sodium chloride, product acid, and product base compartments.

#### 5.2 Baseline testing with oxygen

The five-compartment electrochemical cell was operated with an oxygen feed as a baseline to understand each of the other compartments. In effect, this is a five-compartment electrolytic cell with an oxygen depolarized cathode. A gas diffusion electrode as described in the "Experimental" section was used for all testing results reported within this chapter. The anodic and cathodic reactions are as follows:

Anode:	$\mathrm{H_2O} \rightarrow \mathrm{2H^+} + \mathrm{2e^-} + \mathrm{\frac{1}{2}O_2}$	1.23 V vs. SHE	(5.1)
Cathode:	$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$	0.40 V vs. SHE	(5.2)

Figure 5.2 shows an average (solid black squares) and the different runs comprising the average (solid gray squares) of the cell polarization testing with a 1 M NaCl feed at a flow rate of 5 ml/min and humidified oxygen feed at a flow rate of 50 ml/min. The product acid and base compartments were initiated with 50 mM HCl and 50 mM NaOH, respectively, at a flow rate of 5 ml/min. The different membranes used in the cell assembly are summarized in Table 5.1. The anode was provided with a 0.1 M H<sub>2</sub>SO<sub>4</sub> solution as the anolyte at a flow rate of 5 ml/min. The average cell resistance (entire cell including all compartments and current collectors) was measured to be 13.9  $\Omega$ . The average polarization of the cell showed significant variation between the different runs with the current density varying by ~± 30% at the highest operating voltage. The reasons for this are discussed in more detail later in this chapter.

The overall polarization (experimental and calculated) curve shows characteristics of a kinetic region at lower current densities and an ohmic region beginning at about 5 mA/cm<sup>2</sup> while no mass transport region is observed. As expected, (based on half-cell reactions 5.1 and 5.2) a current is first observed after the applied cell voltage is above the theoretical minimum voltage requirement of 0.83 V. The cell current density was observed to increase with increasing voltage and achieved an average current density of ~146 mA/cm<sup>2</sup> at an applied cell voltage of 7 V. The cell voltage was not increased beyond this due to limits on the equipment. Over the voltage range up to 7V, the cell should not become convectively mass transport limited as there should be sufficient reactants available for the reaction as compartment concentrations are at least an order of magnitude higher than stoichiometry. At a current density of 146 mA/cm<sup>2</sup> and an active cell area of 3.24 cm<sup>2</sup>, the salt depletion in the central compartment would not exceed ~6% of the incoming solution while the oxygen flow rate is also in excess of 100 at a flow rate of 50 ml/min oxygen.

 Table 5.1: Summary of membranes used for conducting different ions and the corresponding pre-treatment solution.

lon	Membrane type	Membrane name	Pre-treatment
		(manufacturer)	solution
Proton	Acidic sulfonic PEM	Nafion 117 (Nafion <sup>®</sup> )	Deionized water
Sodium	Acidic sulfonic CEM	PC MVK (PC-Cell)	5 wt.% NaCl
		Nafion <sup>®</sup> 117 (Dupont)	
Hydroxide	Alkaline ammonium AEM	FAB (Fumatech)	0.5 M NaHCO <sub>3</sub>
Chloride	Alkaline ammonium AEM	PC MVA (PC-Cell)	5 wt.% NaCl



Figure 5.2: Cell performance and reference electrode voltages for a 5-compartment cell fed with a 1 M NaCl solution and pure oxygen stream. Membranes used are as follows – Fumatech FAB for hydroxide ions, PC-MVK for sodium ions, PC-MVA for chloride ions, and Nafion for protons.

Figure 5.2 also shows the calculated polarization of the cell with increasing current density based on the conductivity of the different ions and the membranes, a gap thickness of 1 mm for each of the compartments, and the anode and cathode voltage losses as measured by the reference electrode. The actual cell polarization appears to have significantly higher voltage losses associated with it than expected through calculated overpotential and resistance losses alone. The cell reference electrode data shown in Figure 5.2 is helpful in explaining the additional voltage losses. The "Reference: Anode – Acid" data corresponds to losses associated with the proton from the anode to the hydrochloric acid compartment including the proton conducting membrane. Over the 7 V of the cell operation the loss in voltage associated with the proton only increased by 17 mV from 1.15 V to 1.32 V. The "Reference: Acid – Salt" data corresponds to voltage losses associated with the chloride ion. The overall change in voltage for the chloride ion is 700 mV over the polarization range. The "Reference: Salt – Base" corresponds to voltage losses associated with the sodium ion which contributes to the cell performance significantly more than any of the other ions with a voltage loss of approximately 3,900 mV. Finally, the "Reference: Base – Cathode" data shows the voltage loss associated with the kinetics of the oxygen reduction reaction for hydroxide production and transport of the hydroxide ion to the product base solution including through the membrane. The overall voltage loss for the hydroxide ion is 912 mV.

While each of the ions contributes to cell performance losses, the sodium ion controls the performance of the cell the most. This should be expected as the sodium ion has the lowest conductivity of  $50 \ge 10^{-4} \ m^2S/mol$  compared to chloride ( $76 \ge 10^{-4} \ m^2S/mol$ ), protons ( $350 \ge 10^{-4} \ m^2S/mol$ ) and hydroxide ( $199 \ge 10^{-4} \ m^2S/mol$ ). However, while in effect, the sodium ion is the rate-determining step within this system, the additional voltage loss associated with this ion is significantly higher than expected. As such resistance of the membrane and likely diffusion-based mass transport losses associated with the sodium ion are likely contributing to controlling cell performance. It is also possible that the sodium conducting membrane has a significantly lower conductivity than reported. Based on this testing, cell performance improvements can be expected

by improving convective, diffusion and migration-based voltage losses associated with the sodium ion. Further investigation should help identify how cell performance can be improved.

Figure 5.3 shows the individual cell tests across 4 days with assembling and disassembling of the cells and new solutions to determine reproducibility were averaged to generate the data in Figure 5.2. The variability in cell polarization reproducibility is quite large with the current density at 7 V ranging from 120 mA/cm<sup>2</sup> to 179 mA/cm<sup>2</sup>. This is an approximately  $\pm$ 20% difference in polarization with an average current density achieved of 146 mA/cm<sup>2</sup>. Within the cell assembly the different compartments and ions contribute to this variability in performance. The reference electrode data shown in Figure 5.3b – 5.3e shows the variability in the performance for each of the ions within the cell assembly as follows:

- Figure 5.2b ("Anode-acid") is the performance of the proton and shows that an overall variation in performance of ~220 mV can occur at higher current densities of the polarization curve.
- Figure 5.2c shows voltage losses associated with the chloride ion can vary by as much as 600 mV at higher current densities under the same testing conditions.
- Figure 5.2d shows voltage losses associated with the sodium ion can vary by as much as 1,000 mV at higher current densities.
- Figure 5.2e shows voltage losses associated with the hydroxide ion can vary by as much as 700 mV at higher current densities.

This data is illustrative of the large variation in cell performance and provides an important benchmark to better understand the parametric testing that follows in this chapter.







Figure 5.3: Summary of reproducibility of polarization testing on different days with different components for 1 M NaCl showing a) overall cell polarization; b) reference voltage for the anode and proton; c) reference voltage for the chloride ions; d) reference voltage for the sodium ion; and e) reference voltage for the cathode and hydroxide ions.

#### 5.3 Effect of changing sodium chloride concentration

The effect of feed sodium chloride concentration on cell performance was investigated to better understand the voltage losses associated with the saline feed compartment. Characteristic polarization curves for a five-compartment cell assembly as before for different sodium chloride concentrations and a constant feed of pure oxygen at the cathode, and initial concentrations of 50 mM NaOH in the product base compartment, 50 mM HCl in the acid compartment and 0.1 M H<sub>2</sub>SO<sub>4</sub> at the anode were developed. The results of the testing are shown in Figure 5.4a-d which show the cell polarizations, and the reference electrode voltage associated with the chloride ion, sodium ion and the hydroxide. The results are an average of at least 3 tests for each concentration.

Figure 5.4a shows that cell performance significantly improves as sodium chloride concentration is increased from 0.2 M sodium chloride to 2 M sodium chloride. The highest current density achieved with 0.2 M sodium chloride of 50 mA/cm<sup>2</sup> is more than quadrupled to 233 mA/cm<sup>2</sup> for 2 M sodium chloride at 7 V. Based on the conductivity of sodium chloride, increasing sodium chloride concentration from 0.2 M to 2 M should improve the overall cell voltage by approximately 11 mV at a current density of 50 mA/cm<sup>2</sup>. However, Figure 5.4a shows the observed improvement in cell voltage at a 50 mA/cm<sup>2</sup> is 4,500 mV. While, increased electrolyte concentration has been shown to reduce membrane resistance<sup>82</sup>, the improved resistance is unlikely to be of this magnitude. This provides further evidence that the cell performance is not just controlled by cell resistance.

A closer look at the reference electrode measurements for the different compartments seems to confirm the initial observation that cell performance is controlled by the central saline fed compartment, and more specifically by the sodium ion, i.e., the largest contribution to the cell voltage losses is due to the central compartment. Figure 5.4c shows how the voltage loss associated with the chloride ion changes as sodium chloride concentration is increased. The large difference in performance for the chloride ion (5.4c "Acid-salt") versus the sodium ion (5.4d "Salt-base") is especially illustrative of the factors affecting cell performance. Increasing sodium chloride concentration from 0.2 M to 0.5 M reduces the voltage loss associated with the chloride ion by almost 500 mV at 50 mA/cm<sup>2</sup>. This is significantly higher than the variability of 200 mV that is

observed in the performance of the chloride ion in Figure 5.3c at the same current density. Further increase of the sodium chloride concentration to 1 M NaCl and 2 M NaCl improves the performance of the chloride ion with the voltage losses continuing to decrease. In addition, the change in performance from 0.2 M NaCl to 0.5 M NaCl indicates that the chloride ion is mass transport limited at the lower sodium chloride concentration. As the salt depletion at this current density is not significant compared to the bulk concentration – depletion of salt is approximately 0.0017 mol/s while the molar flow rate is an order of magnitude higher at 0.0167 mol/s, this mass transport limitation at 0.2 M NaCl is likely not convective but rather due to diffusion in the boundary layer or due to limitations within the membrane.

Figure 5.4d shows the performance of the sodium ion in the cell as the sodium chloride concentration is changed. At 50 mA/cm<sup>2</sup> the sodium ion contributes approximately 2,500 mV of voltage loss when 0.2 M NaCl is fed to the cell but this loss is reduced to 900 mV and only 90 mV when 0.5 M NaCl and 2 M NaCl is provided to the cell, respectively. Like chloride ion performance, the sodium ion appears to be mass transport limited at 0.2 M NaCl and largely controlling the performance of the entire cell. Unlike the chloride ion which does not appear to be mass transport limited at sodium chloride concentrations higher than 0.5 M NaCl, the sodium ion appears to continue to control cell performance with improvements in voltage loss associated with the sodium ion performance being largely responsible for improving cell performance. It is also important to note here that as sodium chloride concentration and cell current density increase the overall voltage loss associated with the sodium ion relative to the total cell voltage applied continues to remain the same for 0.2, 0.5 and 1 M NaCl and only slightly improves for 2 M NaCl as seen in Figure 5.5a which shows the overall voltage loss for the sodium ion versus the applied

cell voltage. This is an indication that the cell improvements observed with increasing sodium chloride concentration are related to the improvements associated with the chloride ion and not the sodium ion. Further, the lack of improvement in voltage loss for the sodium ion with increasing salt concentration is not due to convective or diffusion-based limitations but are likely due to transport of the sodium ion within the membrane. The resistance of sulfonic acid based cation exchange membranes such as Nafion 117 has also been shown to increase when exposed to alkaline solutions<sup>83</sup>. It is likely that the additional resistance associated with the sodium ion is due to a higher resistance of the membrane due to the high pH in the base compartment.

Figure 5.4e shows the effect of increasing sodium chloride concentration also improves the overall current density that can be achieved at the cathode. However, the overall voltage loss associated with the hydroxide ion increases over the total 7 V applied on the cell increases with sodium chloride concentration and cell current density from 1.5 V to 2.1 V as shown in both Figure 5.3d and Figure 5.4b. This appears to indicate that with increasing current density the cathode performance becomes increasingly limited. This is likely related to the cathodic reaction, cathode catalyst layer, or the interface between the cathode and the membrane. Some explanations for this limited cathode performance follow:

- A lower partial pressure of the oxygen or water at the catalyst site. It is possible that the reaction becomes constrained at higher current densities due to a lack of oxygen or water for the reaction.
- Drying of the catalyst layer leading to poor conductivity of the hydroxide ion within the ionomer-based catalyst layer is an additional possibility. The cathodic reaction (equation 5.2) requires water to be consumed for the reaction to be sustained. It is possible that drying

of the ionomer in the catalyst layer occurs at higher at higher current densities amounts of water are consumed. This is likely to lead to an increase in the resistance of the catalyst layer and reduces the number of triple phase sites available for the reaction to occur leading to poorer performance of the cathode and lower production of the hydroxide ion.

• Poor ionic conductivity between the catalyst layer and the hydroxide ion conducting membrane: A thin layer of solution can exist between the cathode and the hydroxide ion conducting membrane since the anion exchange membrane and the GDE are not bonded together. The conductivity of the solution at this interface will increasingly contribute to voltage losses as higher current densities are achieved resulting in performance losses at the cathode.

The next sections focus on investigation to determine other factors which affect the performance of the cell.









Figure 5.4: Effect of feed sodium chloride concentration on cell performance showing a) cell polarization; b) reference electrode voltage for the chloride ion; c) reference electrode voltage for the sodium ion; and d) reference electrode voltage for the cathode and hydroxide ion. Data for individual runs can be found in

Figure E.1.



Figure 5.5: Effect of feed sodium chloride concentration on cell performance showing the voltage loss as a function of applied cell assembly voltage associated with a) chloride ions; and b) sodium ions.

#### 5.4 Effect of increasing sodium hydroxide concentration

It is important to understand how the performance of the cell changes under operation as the concentration of the sodium hydroxide increases. To investigate the effect of the concentration of the product base solution on cell performance a five compartment cell assembly with a constant feed of pure oxygen at the cathode, 1 M NaCl solution in the saline feed compartment, and initial concentrations 50 mM HCl in the acid compartment, 0.1 M  $H_2SO_4$  at the anode, and different NaOH concentrations was operated. Figure 5.6a shows that cell performance improves as the sodium hydroxide concentration in the base compartment is increased. A cell current density of 146 mA/cm<sup>2</sup> is observed at a cell voltage of 7 V when 50 mM NaOH is provided to the base compartment. The observed cell current density increases to 232 mA/cm<sup>2</sup> at a total cell voltage of 7 V when 1 M NaOH is provided to the base compartment. For a sodium hydroxide conductivity of 249 x 10<sup>-4</sup> m<sup>2</sup>S/mol, cell current density of 150 mA/cm<sup>2</sup> and a gap thickness of 1 mm the voltage improvement due to reduced solution resistance in the base compartment for an increase in sodium hydroxide concentration from 50 mM to 1 M NaOH is 1.14 V. However, the observed improvement in cell voltage in Figure 5.6a for a 150 mA/cm<sup>2</sup> for increasing NaOH concentration from 50 mM to 1 M is approximately 1.8 V. This is an indication that cell performance improvement is affected by other factors in addition to the resistance losses associated with solution resistance.

Figure 5.6b and 5.6c show the reference electrode voltages for the chloride and sodium ions, respectively. The difference in performance for the chloride ion that is observed in Figure 5.6b does not display any observable trend and is largely due to variation in cell performance. Figure

5.6c appears to show sodium ion performance improving with an increase in sodium hydroxide concentration. The overall voltage loss improvement for the sodium ion associated with an increase in sodium hydroxide concentration from 50 mM to 1 M NaOH at a current density of 150 mA/cm<sup>2</sup> is approximately 1.2 V which is comparable to the expected improvement of 1.14 V due to reduced resistance in the base compartment with increasing sodium hydroxide concentration. However, the voltage loss contributed by the sodium ion as a function of applied cell voltage is comparable for all sodium hydroxide concentrations as shown in the inset of Figure 5.7.

Figure 5.6d shows the reference electrode voltage associated with the hydroxide ion and the cathode. It can be observed that the performance associated with the hydroxide ion significantly improves with an overall increase in sodium hydroxide. An approximately 500 mV improvement in voltage loss is observed at 150 mA/cm<sup>2</sup> for an increase in sodium hydroxide concentration from 50 mM NaOH to 1 M NaOH. Furthermore, the voltage loss contributed by the hydroxide ion as a function of total cell voltage is also reduced. This indicates that increasing sodium hydroxide concentration improves the performance of the cell by not only improving solution resistance but also improving the performance of the cathode. This is likely associated with improved hydroxide ion concentration at the interface between the cathode catalyst layer and ion-exchange membrane as shown in Figure 5.8. This is an indication that further improvements in cell performance can be expected with improved contact between the cathode catalyst layer and the membrane between the cathode and the base compartment. Finally, this shows that the likely reason for reduced cathode performance with increasing sodium chloride concentration, i.e., increasing current densities in the testing in Figures 5.4e and 5.5b is the conductivity of the hydroxide ion at the membrane cathode interface.







Figure 5.6: Effect of increasing sodium hydroxide concentration on cell performance showing a) cell polarization; b) reference electrode voltage for the chloride ions; c) reference electrode voltage for the sodium ions; d) reference electrode voltage for the cathode-base. Data for the individual polarization curves can be found in Figure E.2.



Figure 5.7: Effect of feed sodium hydroxide concentration on cell performance showing the voltage loss as a function of applied cell assembly voltage associated with the chloride, sodium and hydroxide ions.



Figure 5.8: Schematic showing how sodium hydroxide may interact at the catalyst membrane interface to

improve catalyst layer and membrane hydration and conductivity.

#### 5.5 Effect of different membranes on cell performance

As previous results have demonstrated cell performance is largely controlled by the performance of the compartments containing the sodium and hydroxide ions. Losses associated with the resistance of the hydroxide and sodium ion were found to be higher than expected from membrane and solution resistance alone. Different membranes for both the sodium and hydroxide ions were investigation to further understand cell performance. The cell was operated with a constant feed of pure oxygen at the cathode, 1 M NaCl solution in the saline feed compartment, and initial concentrations of 50 mM NaOH in the product base compartment, 50 mM HCl in the acid compartment, and 0.1 M H<sub>2</sub>SO<sub>4</sub> at the anode with different combinations of membranes as summarized in Table 5.2. Figure 5.9 compares cell performance for different combinations of membrane and solutions of the solution is the configuration used in this chapter for all previous results.

Table 5.2: Summary of the different membranes used for testing sodium and hydroxide ion with results

shown	in	Figure	5.9.
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	Hydroxide ion	Sodium ion (base-salt)
	(cathode-base)	
Baseline ("FAB-PCMVK")	Fumatech FAB	PC Cell MVK
Combination 1 ("FAB-N117")	Fumatech FAB	Nafion® 117
Combination 2 ("FAA3-PCMVK")	Fumatech FAA3-pk130	PC Cell MVK

Figure 5.9a shows that cell performance improved with both Combination 1 and Combination 2, as shown in Table 5.2, compared to the baseline case. Figures 5.9b shows the voltage as a function of current density while Figure 5.9c shows the voltage as a function of total applied cell voltage associated with the sodium ion. Figures 5.9d shows the voltage as a function of current density

while Figure 5.9e shows the voltage as a function of total applied cell voltage associated with the hydroxide ion. In Combination 1, the sodium conducting PC Cell MVK membrane was changed to a Nafion 117 membrane. Cell performance was observed to improve significantly with an increase in cell current density at 6 V from 59 mA/cm<sup>2</sup> to 93 mA/cm<sup>2</sup> and 84 mA/cm<sup>2</sup> to 126 mA/cm<sup>2</sup> for saline feeds of 0.5 M NaCl and 1 M NaCl, respectively.

Figure 5.9b shows that changing the sodium conducting membrane significantly improves the performance of the sodium ion. This is expected as the resistance of the PC-Cell MVK membrane of 600  $\Omega$ cm (according to manufacturer specifications) is significantly higher than that of Nafion  $117^{84}$  which is between  $90 - 111 \ \Omega$ cm for sodium chloride solutions. For a Nafion 117 membrane with a thickness of 117 microns, the voltage loss associated with the membrane at 100 mA/cm<sup>2</sup> would be expected to be 0.11 - 0.13 V whereas the voltage loss associated with the PC-MVK membrane with a thickness of 100 microns at the same current density would be expected to be 0.6 V. Figure 5.9c shows that the total voltage loss associated with the sodium ion does not change for different sodium chloride concentrations but is significantly reduced for Nafion 117 in comparison to PC-MVK. This confirms that transport of the sodium ion within the sodium conducting membrane significantly affects cell performance. However, differences in membrane conductivity do not explain differences in performance alone. For a Nafion 117 membrane with a thickness of 117 microns, the voltage loss associated with the membrane at 100 mA/cm<sup>2</sup> would be expected to be 0.11 - 0.13 V whereas the voltage loss associated with the PC-MVK membrane with a thickness of 100 microns at the same current density would be expected to be 0.6 V. The observed voltage difference across this membrane of approximately 1.3-1.4 V is significantly higher than the calculated difference of approximately 0.5 V at 100 mA/cm<sup>2</sup> as seen in Figure 5.9b.

It is unlikely that this is due to convective or diffusion mass transport effects related to the membrane surface or other reasons as no mass transport region is observed over the testing window. Instead, the simplest explanation for this is that the actual membrane resistance during operation is likely higher than the reported resistances due to a variety of reasons including membrane swelling, actual membrane thickness, and differences in pH and sodium ion concentration on either side of the membrane.

Figure 5.9d shows that changing the hydroxide membrane also significantly improves performance of the hydroxide ion. This corresponds with expected results as the Fumatech FAB membrane is a low proton crossover membrane specialized to build-up acid concentrations while the Fumatech FAA-3 is an electrodialysis membrane specialized to facilitate anion transport. Low proton crossover membranes are anion conducting membranes tend to have a higher resistance resulting in lowered anion transport. As such, the Fumatech FAB membrane has a higher resistance of between 5-9  $\Omega$ cm<sup>2</sup> compared to 1.8-4  $\Omega$ cm<sup>2</sup> for the Fumatech FAA-3 when the membranes are in the chloride form. Figure 5.9e shows that the voltage loss associated with the hydroxide ion as a function of total applied cell voltage is reduced when the Fumatech FAB membrane is changed to Funatech FAA-3 membrane with the performance improvements appearing to be largely ohmic. The measured difference in voltage loss between the two membranes during the test was approximately 0.8-0.9 V. At 100 mA/cm<sup>2</sup>, the voltage loss associated with the FAB membrane is 0.5-0.9 V while the voltage loss associated with FAA-3 membrane is 0.18-0.4 V resulting in an expected difference of 0.32-0.4 V if the membranes were conducting chloride ions. The resistance of the membrane can vary significantly depending on the ion being conducted and membrane swelling among other things, e.g., the FAB membrane in the SO<sub>4</sub><sup>2-</sup> form has a reported resistance

of 10-20  $\Omega$ cm<sup>2</sup> as opposed to 5-9  $\Omega$ cm<sup>2</sup>. As such, the higher than expected voltage loss observed is highly likely due to the differences in membrane conductivity for hydroxide ions.

Figures 5.9c and 5.9e also show the effect of changing the hydroxide ion and sodium ion conducting membrane on the performance of the sodium ion and hydroxide ion, respectively, and vice versa. Figure 5.9c shows that changing the hydroxide ion conducting membrane from FAB to FAA3 does not affect the voltage loss associated with the sodium ion. On the other hand, Figure 5.9e shows that performance of the hydroxide ion is adversely affected when the sodium ion performance improves with the change of the sodium ion conducting membrane from PC-MVK to Nafion 117. This was observed earlier as well with a 50 mM NaOH solution in the product base compartment where the improvements associated with the sodium chloride feed adversely affect the performance as current density increases for the sodium ion due to the poor performance of the FAB membrane, i.e., previously the sodium ion was more limiting but as its performance is improved the hydroxide as ion starts to become more limited as the membrane is the same as the baseline case.







Figure 5.9: Effect of different membrane combinations as summarized in Table 5.2 on cell performance showing a) cell polarization; b) reference electrode voltage for the chloride ion; c) reference electrode voltage for the sodium ion; and d) reference electrode voltage for the cathode and hydroxide ions. Different runs to calculate the average polarization are shown in Figure E.3 in Appendix E.

### 5.6 Conclusions

The results of testing in this chapter demonstrated that several factors are important to the performance of the cell assembly to produce hydroxide ion. These factors can be summarized as follows:

- Sodium chloride concentration is an important factor in the performance of the cell as low concentrations of sodium chloride or the salt can cause the cell to become mass transport limited.
- Sodium ion performance was found to be the rate-limiting step in most of the tests performed in this chapter with the sodium conducting membrane experiencing significantly higher losses than expected from membrane conductivity alone.
- The choice of membrane is extremely important to the overall performance of the cell with the performance of the hydroxide ions and sodium ions being the most affected. In particular, the membrane-electrode interface at the cathode is critical to the performance of the hydroxide ions. The membrane should be sufficiently conductive to the anion being conducted, reduce water transport through the membrane to avoid flooding while also making sufficient contact with the electrode to maximize the number of active triple phase sites, i.e., oxygen, water and electrons must all have access to the sites to ensure the reaction in Equation 5.2 can occur.

## **Chapter 6: Impact of cathode gas composition on cell performance.**

**Hypothesis:** This chapter focuses on demonstrating and investigating the conversion of carbon dioxide in the gaseous phase at the cathode in a 5-compartment electrochemical cell. Unlike in the previous chapter, where the cathode was only provided with a humidified oxygen stream, the work in this chapter introduced carbon dioxide with the oxygen stream at the cathode. The aim here was to show that a gaseous stream, in this case carbon dioxide, could be converted to an anionic species to be conducted by an anion exchange membrane and combined with the cations removed from the salt compartment. This approach can be modified with the use of an appropriate catalyst to convert the carbon dioxide to different chemical species or for the treatment of other gases that can produce an anionic species. The most likely chemical reactions when carbon dioxide is used in this system with a non-selective catalyst are:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{6.1}$$

$$OH^{-} + CO_2 \rightarrow HCO_3^{-} \tag{6.2}$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{6.3}$$

Under operation, all three anionic species of hydroxide, bicarbonate and carbonate should exist and will be transported through the anion selective membrane based on their mobility (i.e., how quickly the ion travels) and operating conditions (e.g., CO<sub>2</sub> flow rate, cell voltage, membrane type, etc.) Preferred production of one species or the other can occur by changing the amount of carbon dioxide gas provided. For example, a significantly higher than stoichiometric amount of carbon dioxide provided to the system will result in the production of bicarbonate ions as all hydroxide ions could be consumed. Alternatively, at a hydroxide production rate which is more than twice the carbon dioxide molar flow rate only carbonate ions should be produced. The overall goal of this chapter is to demonstrate:

- That carbon dioxide gas can be converted to carbonate and/or bicarbonate ions;
- That the carbonate and/or bicarbonate ions are can be transported through the anion selective membrane;
- That the transported carbon and/or bicarbonate ions can be combined with cations from the feed salt stream.

In addition, the work performed attempted to investigate the effects of introducing carbon dioxide gas to the system on cell performance with respect to current density, voltage, and cell resistance.

### 6.1 Effect of carbon dioxide composition on cell performance

Figure 6.1 shows cell polarizations and potential differences across the different compartments for different cathode gas compositions. Polarization measurements were also performed with nitrogen to study the impact of oxygen dilution since nitrogen is inert and does not interact with the hydroxide ions. The potential differences shown in Figures 6.1b-d indicate the transport overpotentials associated with relevant ions migrating across a membrane. For instance,  $E_{Acid} - E_{salt}$  (Figure 6.1b) represents the potential losses due to transport of Cl<sup>-</sup> across the anion membrane separating the salt and acid chambers. The reference electrode measurements for the anode and proton transport have been omitted as these were found not to affect the performance and are not relevant to the discussions here.

Increasing the concentration of nitrogen at the cathode reduces the current density of the cell as shown Figure 6.1a by up to approximately 8% at the highest nitrogen concentration at 7V. This

slight decrease in performance is due to the reduced partial pressure of oxygen leading to thermodynamic losses related to the Nernst potential (4 mV loss for 50% oxygen partial pressure). Partial evidence for this can be seen in the reference electrode measurements shown in Figures 6c-d. Figure 6c shows a slight gain of the potential differences between the salt and base compartment while no changes are observed for the other compartments with pure oxygen and different dilution levels with nitrogen.

Introducing carbon dioxide to the cathode gas leads to larger cell overpotentials than dilution with nitrogen alone (Figure 6.1a). The increase in potentials is observed across both the cathode-base and the salt-base compartments. This implies that the loss in performance is due to both the cathodic losses and transport of the sodium ion from the saline feed to the base compartment. The loss in performance of the cathode can be due to: i) lowered partial pressure of oxygen, ii) poisoning of the catalyst layer by carbon dioxide where the carbon dioxide preferentially adsorbs on the catalyst surface preventing the oxygen reduction reaction from occurring or iii) lower mobility (i.e., diffusion, and migration under a voltage gradient) of (bi)carbonate ions that are being transported to the base compartment. While lowering of oxygen partial pressure (as observed with the introduction of nitrogen) does reduce the cell performance slightly, it does not account for all the losses observed. CO<sub>2</sub> Poisoning of the platinum in the catalyst layer is a possibility that could potentially contribute to losses in performance; however, its impact is much lower than CO poisoning. It is worth mentioning that gas chromatograph (GC) measurements showed no presence of produced CO.



Figure 6.1: Effect of different cathode compositions on the a) polarization curves of the cell, and potential drops across the b) acid – salt, c) salt – base and d) cathode – base compartments. Different runs to calculate the average polarization are shown in Figure E.4 and E.5 in the Appendix.

 Table 6.1: Summary of the calculated slope for the different gas compositions for the cathode-base

Gas Composition		Measured Slope	
O <sub>2</sub>	CO <sub>2</sub>	N2	$(m\Omega \ cm^2)$
100 %	0	0	0.011
90 %	10 %	0	0.019
90 %	0	10 %	Experiment not performed
75 %	25 %	0	0.021
75 %	0	25 %	0.014
50 %	50 %	0	0.023
50 %	0	50 %	0.015
20 %	80 %	0	Experiment not performed
20 %	0	80 %	0.015

polarization losses.

The likely reason for the cell losses is the lower mobility of the (bi)carbonate ions compared to hydroxide ions. Carbon dioxide reacts with hydroxide ions at the cathode resulting in the formation of bicarbonate and carbonate ions which migrate in parallel with the unconverted hydroxide ions to the base compartment. Bicarbonate ions (mobility of  $4.59 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ , conductivity of 45 m<sup>2</sup> S mol<sup>-1</sup>) and carbonate ions (mobility of  $7.18 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ , conductivity of  $139 \text{ m}^2 \text{ S} \text{ mol}^{-1}$ ) are less mobile and less conductive (in water at 298 K) than hydroxide ions (mobility of  $20.6 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ , conductivity of  $199 \text{ m}^2 \text{ S} \text{ mol}^{-1}$ ) and lead to higher ohmic losses the within the membrane conducting these ions. The mobility of the ion depends on different factors including the charge of the ion, the hydration shell of the ion, the size of the ion as well as the medium in which the ion exists (e.g., ion-exchange membrane or solution) and as such under the same conditions will largely follow the above trend. This can also be observed in Figure 6.1d where the
slope of the reference electrode measurements (voltage vs. current density) increases with increasing carbon dioxide concentration indicating an increase in the resistance of this compartment. Table 6.1 shows the slopes of the data shown in Figure 6.1d obtained by linear regression and normalized by the geometric surface area of the membranes for each of the gas compositions examined. The normalized resistances were higher than pure oxygen when nitrogen was used in the cathode gas feed but did not increase with increasing concentration of nitrogen. However, the normalized slopes increased when carbon dioxide was used, and in addition, increased with increasing carbon dioxide concentration. These results show that the lower mobility and conductivity of (bi)carbonate ions are important factors in the observed increases in the cell potential, in addition to the relatively minor losses due to partial pressure effects.

While losses in performance at the cathode can be explained due to the introduction of carbon dioxide, the reasons for losses in the voltage performance of the sodium ion are less clear as the carbon dioxide does not interact with the solutions being provided to the saline feed compartment. However, these losses are likely due to the fundamental requirements of charge neutrality related to ionic mobility and the changes in the voltage gradient with a change in potential. In this electrochemical cell, while the compartments are ostensibly independent of each other, changes in ion transport and potential from one compartment to another will indirectly affect the other compartments. Therefore, an increase in the ohmic resistance of the cathode-base compartment, because of the lower mobility/conductivity of the (bi)carbonate ions, and/or an increase in cathode overpotential affects the transport of other ions in the other compartments as well. This can be observed in the increased resistance losses of the saline feed-base compartment (Figure 6.1c). In this work we have shown that this coupled transport/potential phenomenon is largely due to the

loss of performance for the cathode-base compartment. This effect can be observed, for example, in the data shown in Figure 6b, where transport of the chloride ions which do not interact with the (bi)carbonate ions is also affected.

#### 6.2 Baseline Experiment: Production of HCl and NaOH with oxygen and sodium chloride

The efficiency of the cell with respect to the amount of chemicals produced is just as important as the cell voltage and current density. Therefore, longer term operation to increase the concentration of the chemicals and comparing with the expected increase is an important element of better understanding this cell configuration. In its simplest form, the cell is operated with oxygen and sodium chloride with protons and hydroxide ions produced at the anode and cathode, respectively. This is achieved by providing humidified air or oxygen to the cathode and water to the anode where the following reactions occur:

Anode: $H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2$ 1.23 V vs. SHE(6.4)Cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ 0.40 V vs. SHE(6.5)

Under an applied potential, sodium and chloride ions present in the saline water stream migrate towards the cathode and anode, respectively. Chloride ions and the protons, transported from the anodic compartment, produce hydrochloric acid while the sodium ions combine with the  $OH^-$  to produce sodium hydroxide in separate compartments. Figure 6.2 shows the results of a potentio-static test (3 V, 24 hours) using initial feeds of sodium sulfate and sodium chloride (see Table 5.2) for the base and acid compartments, respectively. Sodium sulfate and sodium chloride were used as they allow the system to be operated with conductivity of sodium in the base and chloride ions

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in the acid compartment but have a neutral pH allowing for a better resolution of concentration changes during operation.

	Long-term testing
Gas flow rate	50 ml min <sup>-1</sup> with
	different compositions
Saline stream	1 M NaCl
Acid compartment initial	50 mM NaCl
feed	
Base compartment initial	50 mM Na <sub>2</sub> SO <sub>4</sub>
feed	
Anode electrolyte	0.1 M H <sub>2</sub> SO <sub>4</sub>
Temperature	21°C
Cell compression pressure	25 psi

Table 6.2: Summary of initial concentrations for the different compartments for long-term testing.

The observed current density of the cell improved during the 24 h test period to approximately 41 mA cm<sup>-2</sup> (Figure 6.2a). The initial (< 1 h) improvements in cell current density are associated with electrode (e.g., hydration of the ionomer), membrane (e.g., hydration of the membrane) and cell conditioning (e.g., removal of any bubbles in between the membranes). Further improvements in the current density (> 1 h) are related to the reduced resistance in the cell because of the increasing concentrations of the acid and base compartments. Figure 6.2a also shows the improvements in the measured cell resistance during the 24-hour testing period.

The pH of the acid compartment decreased from an initial value of 3.23 to a final value of 1.37. Overall, the increase in the acidity of the acid compartment followed the expected trend from Faraday's law over 24 hours. The agreement between the observed and expected changes in the Cl<sup>-</sup> concentration is even better. Some of the discrepancy between the measured and expected pH values is attributed to the loss of acid through the anion exchange membrane to the saline feed compartment which corresponds to the observed pH decrease from 5.72 to 1.95 in the saline feed compartment. After correcting for this loss of protons to the saline compartment, a measured pH value of 1.27 for the acidic compartment is obtained. This result corresponds well with the expected value of  $1.17 \pm 0.10$ . Figure 6.2b shows the measured and expected production of hydrochloric acid (i.e., changes in the H<sup>+</sup> and Cl<sup>-</sup> concentrations) in the acid compartment after correction of proton leakage through the chloride conducting membrane.

The increase in the pH of the base compartment closely follows the expected trend. Titration of the base solution with 10 mM hydrochloric acid showed that the base compartment solution had a concentration of 64 mM of hydroxide corresponding to a pH value of 12.80 after the 24-hour test period. This matches with the pH value of 12.76 obtained by direct measurement; however, it is lower than the expected pH value of 13 from Faraday's law. This is due to the loss of hydroxide ions to the saline compartment through the sodium conducting membrane. However, a corresponding increase of the alkalinity of the saline compartment was not observed as the basic ions that are transported over are neutralized by protons that have come through the chloride conducting membrane due to the permselectivity of the membrane. The current efficiency of the cell for hydroxide conversion is  $\approx 64\%$ . The sodium ion concentration in the base compartment also increased and followed the expected Faradaic trend within the experimental errors of  $\pm 5$  mM. Figure 6.2c shows the measured and expected concentration of sodium hydroxide in the base compartment.



Figure 6.2: Proof-of-concept testing in a 3.24 cm<sup>2</sup> cell with humidified oxygen feed at the cathode. a) Current density and cell resistance during the 24-hour testing period; b) Changes in pH and chloride ion concentration in the acid compartment; c) Change in pH, sodium ion and hydroxide concentrations in the base compartment. Cell potential = 3 V, cathode feed = humidified O<sub>2</sub>, anode feed = water.

#### 6.3 Production of carbonate salts and hydrochloric acid

When carbon dioxide is introduced to the cathode gas feed, it reacts with the hydroxide ions generated at the cathode according to:

$$OH^- + CO_2 \rightarrow HCO_3^- \tag{6.6}$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{6.7}$$

The amount of bicarbonate (or carbonate) produced can be controlled by the amount of carbon dioxide provided to the system but all three ions are likely to be present in solution under equilibrium when a hydroxide-producing catalyst is used. However, with a selective catalyst (e.g.,  $Ca_2Ru_2O_{7-y}$ ) only carbonate ions may be produced:

$$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$$
 (6.8)

In principle, this approach can be expanded to the use of other catalysts to produce other chemicals such as formate or oxalate-based salts. The method can be generalized to treat other types of gases at either electrode leading to a powerful electrolysis/electrodialysis configuration suited for the simultaneous electro-synthesis of desirable chemicals and purification of input streams.

Figure 6.3 shows the results of potentio-static measurements performed at 3 V for a period of 24 hours. Initial concentrations as summarized in Table 5.2 were provided to all compartments. Figure 6.3a shows the increasing trend of the current density (up to 32 mA cm<sup>-2</sup>) for the 24-hour test period. As in the baseline case (i.e., no CO<sub>2</sub>), improvements in cell current density are associated with the reduction of the cell's ohmic resistance as the product concentration in the acid and base compartments increases. The pH of the acid compartment decreased from an initial value of 3.16 to a final value of 1.44. As in the baseline case (Figure 6.2), the overall trend for the pH decrease closely follows that of Faraday's law. However, the final pH (= 1.44) showed a slight deviation 128

from that of the expected value  $(1.28 \pm 0.10)$ . Loss of protons to the saline feed compartment corresponds to 6 mM HCl approximately. Accounting for this loss of acid to the saline compartment would result in an expected pH of the acid compartment of about 1.38, closer to the expected value. Figure 3b shows the measured and expected amounts of hydrochloric acid in the acid compartment after correcting for proton leakage through the chloride conducting anion exchange membrane.

The sodium ion concentration in the base compartment increased and matched within the variability ( $\pm$  5 mM) of experimentation, sampling, and analysis of the test to the expected sodium ion concentration. Figure 6.3c shows the measured concentration of the different ions in the base compartment. The base compartment in this experiment is not comprised only of sodium hydroxide but rather a combination of sodium carbonate, bicarbonate, and hydroxide solutions (equations (2), (3), (4)). When  $CO_2$  is present in the cathodic gas stream, (bi)carbonate ions produced will buffer the base compartment leading to a lower pH than one would expect based on a hydroxide-only pH scale which is shown in Figure 6.3c. The base solution consisted of 24 mM of OH<sup>-</sup>, 7.5 mM of HCO<sub>3</sub><sup>-</sup> and 13 mM of  $CO_3^{2-}$  ions according to titration results after 24 hours. This corresponds to a total monovalent charge of approximately 57.5 mM of anions. The equivalent number of anions would be about 73 mM of anions if all electrons were used in electroreduction of oxygen to OH<sup>-</sup>. It is likely that some hydroxide and/or (bi)carbonate ions are transported to the saline compartment and subsequently neutralized by the protons as in the baseline case. This corresponds to a cathodic current efficiency of approximately 71% for the 24hour duration of the experiment.



Figure 6.3: Proof-of-concept testing in a 3.24 cm<sup>2</sup> cell with a humidified oxygen and carbon dioxide feed at the cathode; a) Current density and cell resistance during the 24-hour testing period; b) Changes in pH and chloride ion concentration in the acid compartment c) changes in pH, sodium ion, hydroxide, and carbonate ion concentrations in the base compartment. Cell potential = 3 V, cathode feed = humidified O<sub>2</sub>/CO<sub>2</sub>, anode feed = 0.1 M sulfuric acid.

#### 6.4 Impact of cathode gas composition on production of carbonate and bicarbonate salts

Figure 6.4 shows the measured and expected concentrations of different ions after 24 hours of potentio-static experiments under different cathode gas compositions and cell potentials. In general, the measured chloride concentration in the hydrochloric acid compartment corresponded with the expected concentration through Faraday's law. The pH change once corrected for acid leakage to the salt compartment also corresponded to the expected trend from Faraday's law. Figure 6.4b shows the measured and expected concentrations of the sodium and alkaline anions (hydroxide, bicarbonate, and carbonate) in the base compartment. As in the earlier cases, the concentration of the sodium ions followed the trend with the expected concentrations (i.e., Faradaic concentrations) for the different gas compositions and cell potential experiments studied. On the other hand, the production of the alkaline anions is lower than the expected production. These experiments clearly demonstrate that by tuning the cathodic gas composition ( $CO_2/O_2$ ), control of the product concentrations is possible. The chemical reactions between carbon dioxide and hydroxide ions shown in equations (3)-(5) imply that when excess carbon dioxide is present with respect to hydroxide ions, more bicarbonate ions than carbonate ions are formed. Alternatively, when hydroxide ions are present more than carbon dioxide more carbonate ions are produced in solution. This does not generally happen, because some of the hydroxide also transfers across the AEM to the base compartment. However, increasing the carbon dioxide concentration and thus exposing more of the hydroxide to carbon dioxide leads to more hydroxide ions reacting with carbon dioxide. At the higher cell potential of 6 V, a significantly higher ratio of hydroxide is transported across the AEM membrane compared to bicarbonate and carbonate ions. This is most likely due to the higher flux and thus quicker transport of the hydroxide ions at a higher

voltage reducing the amount of time available for the hydroxide ion to react with the carbon dioxide to produce bicarbonate and carbonate ions.



Figure 6.4: Products of electrolysis experiments summary of chemical concentrations for testing at 3 V and 6 V for different gas compositions after 24 hours of testing; a) Difference in expected and measured pH and chloride ion concentration in the acid compartment; b) Difference in expected and measured concentration of sodium and alkaline ions in the base compartment.

## 6.5 Conclusions

The work in this chapter demonstrated and investigated a 5-compartment electrochemical cell for the conversion of carbon dioxide and sodium chloride to chemicals and desalinated water. A nonselective platinum catalyst was used to demonstrate the conversion of carbon dioxide to a mineralized species in the form of carbonate and bicarbonate salts by reacting the carbon dioxide chemically with the hydroxide ions produced through electrochemical reduction of oxygen. The carbon dioxide is converted by chemically reacting with hydroxide ions produced at the cathode through electrochemical reduction of oxygen.

The 5-compartment electrochemical cell demonstrated the production of acids and bases. Parametric testing of the cell in this chapter determined that the performance of the cell is lowered when carbon dioxide is introduced at the cathode in comparison to when the cell is operated with only oxygen or a mixture of oxygen and nitrogen where only hydroxide is produced. Introducing carbon dioxide to the cathode gas led to larger cell overpotentials than dilution with nitrogen alone suggesting that losses in performance were not only because of lowered partial pressure of oxygen at the cathode. In addition to increase in overpotential related to lowered partial pressure, cell overpotential losses increased when carbon dioxide is introduced to cathode due to the lower mobility of the (bi)carbonate ions produced when carbon dioxide reacts with the hydroxide ions. This increase was also observed in the increased resistance of the cell when carbon dioxide was provided to the cell in comparison to when only oxygen or a mixture of oxygen and nitrogen was provided to the cell. Long-term testing was also performed to demonstrate the build-up of chemicals within the cell. The cell was operated with different amounts of carbon dioxide at the cathode and at different voltages. Production of sodium hydroxide, carbonate, bicarbonate, and hydrochloric acid was successfully demonstrated. However, the system was found to have efficiency losses as the produced acid and base were found to have some leakage through the anion and cation exchange membranes, respectively. This issue was exacerbated as higher concentrations of the products were produced and is likely to limit the ultimate concentration of products that can be produced through this approach.

# **Chapter 7: Greenhouse gas analysis for the system**

The increasing amounts of greenhouse gases (GHGs) emitted to the atmosphere and their resulting impact on climate has become one of the largest technological and environmental challenge faced by the world. This has also increased the need for analysis, monitoring and sensing of carbon emissions to better quantify and understand how different processes affect the overall carbon cycle. As such, objectively analysing the GHG fluxes at different levels is vital to understanding the potential impact or benefit a technology may have over a process. This chapter focusses on a greenhouse gas analysis of the electrochemical system where carbon dioxide is converted to a mineralized form as carbonate.

For the purposes of the greenhouse gas analysis the following were considered as potential benefits the system could offer:

- Conversion of carbon dioxide to value-added chemicals for on-site utilization: the system converts waste-carbon dioxide to carbonate or bicarbonate salts for use in different applications.
- Control salinity of brine and desalinate water for on-site utilization: the desalinated water can be used allowing for recycling of brine and reducing the need to source and transport fresh water to a site.
- Eliminate or reduce brine management requirements: The system offers benefits associated with elimination of brine management including treatment and disposal of saline water by allowing the desalinated water to be recycled into operations.
- Eliminate or reduce the need for chemicals to be produced off-site: the production of chemicals on-site also eliminates the need to source and transport chemicals.

The conversion of wastes produced to value for on-site utilization eliminates or significantly reduces the need for processes within the supply and operations chain and could result in an overall reduction in greenhouse gas emissions.

### 7.1 Carbon sinks and sources for the system

The GHG analysis is based on a system throughput of 1,000 m<sup>3</sup>/day of saline water which is to be desalinated. A mass and energy balance of a 1,000 m<sup>3</sup>/day system and the system assumptions is shown in Table 7.1. The overall carbon sinks for such a system are:

- CO<sub>2</sub> consumed within the system: The overall capability of the system to remove carbon dioxide is dependent on the mineralized salt being produced, the volume of brine treated and the total salinity of the brine. On a molar basis, twice as much carbon dioxide can be removed as sodium bicarbonate compared to sodium carbonate but the analysis only considers sodium carbonate production. Sodium carbonate can act as a carbon sink where the CO<sub>2</sub> is mineralized in the form of carbonate salts at ~0.42 kg<sub>CO2</sub>/kg of carbonate salts. Sodium bicarbonate can act as a carbon sink where the CO<sub>2</sub> is mineralized in the form of bicarbonate salts at ~0.52 kg<sub>CO2</sub>/kg of bicarbonate salts.
- Brine management: Desalinated water produced is assumed to be used on-site. A treatment module of 1,000 m<sup>3</sup> per day capability would eliminate the carbon emissions associated with transport to a disposal site and downhole disposal of 1,000 m<sup>3</sup> per day of saline water.
- Chemical demand management: The sodium carbonate and hydrochloric acid produced while desalinating water and converting the carbon dioxide are assumed to be able to offset the need to produce these salts elsewhere thus reducing carbon emissions.

Greenhouse gas emissions created by the system are:

• Electrochemical reactor power consumption: The system relies on electrical power to operate the reactor units. This is likely to be the largest component of GHG emissions associated with the system. It is assumed that electrical power comes from a source with a carbon emissions factor of 0.45 kg<sub>CO2</sub>/kWh is used.

Constants	Value	Units	Notes
HCI (mW)	36.50	g/mol	Hydrochloric acid molecular weight
NaOH (mW)	40.00	g/mol	Sodium hydroxide molecular weight
CO2 (mW)	44.01	g/mol	Carbon dioxide molecular weight
Na2CO3	105.98	g/mol	Sodium carbonate molecular weight
NaCl (mW)	58.44	g/mol	Sodium chloride molecular weight
F	96,485	C/mol	Faraday's constant for electrochemical calculations
n	1		For use in Faraday's law calculations
Inputs	Value	Units	Notes
Initial TDS	20,000	mg/L	Assumed sodium chloride concentration
Throughput	1,000	m³/day	Assumed volume to be treated
Throughput	6,289	BPD	Volume in barrels
TDS removed	90%		Assumed salt content removed
TDS removed	18,000	mg/L	Calculated TDS removed
Final TDS	2,000	mg/L	Final TDS after treatment
Total salt removed	18,000,000	g	Total mass of NaCl removed
Total salt removed	0.308	mol/L	Moles of NaCl removed per liter of brine treated
Total salt removed	308,008	mol per day	Total moles of NaCl removed per day
Total CO2 required	154,004	mol per day	2NaOH + CO2> Na2CO3 + H2O
Total CO2 converted	6,778	kg/day	Total mass of CO <sub>2</sub> required to consume sodium hydroxide produced
System performance	Value	Units	Notes
Total salt removed	308,008	mols/day	As sodium ion concentration
Cell efficiency	75%		Faradaic calculation - 75% efficiency
l (Faradaic)	458,613.77	Amps	Total current required
Voltage	6	V	Corresponding cell voltage for current density
Power	2,751.68	kW	P = voltage x current
Cell current density	125	mA/cm <sup>2</sup>	Assumed current density

Table 7.1: Material and energy balance for a 1,000 m<sup>3</sup> per day system desalinating a 20,000 mg/l NaCl brine.

Cell area required	403.58	m²	Electrochemical active area required
System Outputs	Value	Units	Notes
Soda Ash Produced	16,321	kg/day	Mass produced based on number of moles
HCl Produced	11,242	kg/day	Mass produced based on number of moles
Mangrove System Outputs	Value	Units	Notes
Mangrove System Outputs Na2CO3 (25wt%)	<b>Value</b> 65,285	Units kg/day	Notes Mass of dilute chemical produced
Mangrove System Outputs Na2CO3 (25wt%) HCl (10wt%)	Value 65,285 112,423	Units kg/day kg/day	Notes Mass of dilute chemical produced Mass of dilute chemical produced

#### 7.2 Baseline for analysis

The baseline for greenhouse gas analysis was a site where the status-quo was as follows:

- Brine disposal: brine produced on-site during activities is transported by truck to a downhole disposal site an average of 900 kms away with trucking emissions of brine having a carbon emissions factor of 100.1 gCO<sub>2</sub>/tonne (Environmental Defense Fund Green Freight Handbook).
- **Production of chemicals:** The system converts carbon dioxide into carbonate and/or bicarbonate salts. The system also produces hydrochloric acid as a by-product. It is assumed that both the carbonate/bicarbonate salt and hydrochloric acid are chemicals that can be utilized on-site and do not require transport to another site. The on-site generation of these chemicals also eliminates the need for an equivalent amount of these chemicals to be produced elsewhere. Carbon dioxide emissions intensity of 0.441 kgCO<sub>2</sub>E/kg sodium carbonate/bicarbonate and 0.079 kgCO<sub>2</sub>E/kg hydrochloric acid are used based on LCA values from the Ecoinvent database. Further, the chemicals need to be shipped 1,500 km to site for use which is avoided when the chemicals are produced from wastes on-site.

#### 7.3 GHG Emissions and water consumptions reduction enabled by the system

The analysis of the overall system using grid electrical power is shown in Table 7.2. The analysis considers carbon dioxide being converted to sodium carbonate. Each 1,000 m<sup>3</sup> per day system that converts carbon dioxide and desalinates 1,000 m<sup>3</sup> of brine to desalinated water, sodium carbonate and hydrochloric acid under the assumptions of the material and energy balance in Table 7.1 would:

 Create carbon emissions equivalent to 8,395 tonnesCO<sub>2</sub>/year assuming a carbon emissions factor for grid electricity consumption of 0.45 kgCO<sub>2</sub>/kWh.

Reduce greenhouse gas emissions equivalent to 30,219 tonnesCO<sub>2</sub>/year through:

- Conversion of carbon dioxide to carbonate salt;
- Eliminating the need for transport and disposal of brine;
- Eliminating the need for production of carbonate salts and hydrochloric acid.

On a normalized basis, under these assumptions the technology can reduce:

- GHG emissions equivalent to 0.08 tCO<sub>2</sub>E per m<sup>3</sup> of brine treated;
- Reduce freshwater consumption by 0.84 m<sup>3</sup> per m<sup>3</sup> of water treated.

Table 7.2: Summary of GHG reductions enabled by the on-site conversion of brines and carbon dioxide to chemicals and desalinated water for use.

Emissions associated with baseline		eline	Notes
Water disposal amount	1,000	m³ per day	Assumed treatment throughput
Trucking distance	900	km	Assumed distance to disposal site
			161.8 gCO2E/t-mile - http://business.edf.org/files/2014/07/EDF-
E.F. Trucking	100.1	gCO2E/t-km	Green-Freight-Handbook.pdf
Trucking weight	1,000	tonnes per day	Based on volume of water to be disposed
Hydrochloric purchased (32 wt.%)	35,132	kg per day	Based on equivalent amount produced by Mangrove - see Table 1
Soda ash purchased (dry)	16,321	kg per day	Based on equivalent amount produced by Mangrove - see Table 1
E.F. HCl production	0.079	kgCO2E per kg HCl	Ecoinvent database
		kgCO2E per kg	
E.F. Na2CO3 production	0.441	Na2CO3	Ecoinvent database
Chemical trucking distance	1,500	km	Assumed chemical transportation trucking distance
Trucking weight of chemicals	51	tonnes per day	Based on assumed HCl and NaOH amounts
Brine trucking emissions	90	tCO2E per day	Calculated emissions
HCl production emissions	1	tCO2E per day	Calculated emissions
Soda ash production emissions	7	tCO2E per day	Calculated emissions
Chemical trucking emissions	8	tCO2E per day	Calculated emissions
Total emissions for baseline	106	tCO2E per day	Total calculated emissions
Emissions associated with Mangrove's system		e's system	Notes
Water treatment amount	1,000	m³ per day	Assumed treatment throughput
Carbon dioxide converted	-7	tonnes per day	
Mangrove energy	66,040	kWh per day	Based on energy required in Table 1
HCl produced	35,132	kg per day	Based on material and energy balance in Table 1
Soda ash produced	16,321	kg per day	Based on material and energy balance in Table 1
Desalinated water produced	844.31	m³ per day	Based on material and energy balance in Table 1
E.F Electricity	0.45	kgCO2E/kWh	SDTC CO2 electricity emissions factor for natural gas
Electrical emissions	30	tCO2E	
Mangrove emissions	23	tCO2E per day	Calculated emissions
			142

Emissions and water usage reduction			Notes
Emissions reduction	83	tCO2E per day	Overall emissions reduction
Emissions reduction	30,219	tCO2E per year	Overall emission reduction for a 1,000 m <sup>3</sup> per day system
Fresh water consumption reduced	844	m³ per day	Overall water consumption reduction
			Overall water consumption reduction for a 1,000 m <sup>3</sup> per day
Fresh water consumption reduced	308,174	m <sup>3</sup> per year	system
Emissions reduction	0.08	tCO2E per m <sup>3</sup> treated	Normalized emissions reduction
Fresh water consumption reduced	0.84	m <sup>3</sup> /m <sup>3</sup> water treated	Normalized freshwater consumption reduction

# **Chapter 8: Economic Analysis**

The strength of the proposed technology is in its flexible nature where it can be utilized in different ways depending on the application. The technology offers an end-user the ability to convert their brines to value added chemicals for on-site utilization and avoid the costs of brine disposal. Different salts processed through the technology can be used to produce their conjugate acids and bases. For example, a sodium chloride brine will produce sodium hydroxide and hydrochloric acid while a lithium sulfate brine will produce lithium hydroxide and sulfuric acid.

For an end-user, the value of the technology is dependent on any supply chain operations that can be eliminated or replaced which may include:

- Storage and transport of the brine that is used as the feedstock and/or chemicals that are produced by the technology;
- Any process units related to the conversion of the brine to the produced chemicals.

This can vary greatly by application but in general the technology will have the greatest value in applications where:

- Saline water or waste salt management, disposal, or treatment is of vital importance;
- The chemicals produced by the technology (acids and bases) can be consumed on-site;
- The chemicals produced from the salt are of significant value with a large difference in the value of the brine and the produce acid and base;
- The chemicals produced can be consumed at low concentrations without requiring additional process units to increase concentration, i.e., less than 15 wt.% acid and base;
- The feed saline water or waste-salt has minimal pre-treatment requirements.

For the purposes of discussion here, it is assumed that the technology is utilized in an application where:

- A sodium chloride brine used as the feed to the electrochemical cell requires disposal;
- The hydrochloric acid and sodium hydroxide produced do not need to be transport to or away from the site and can be consumed at the site.

An overall material and energy balance for the technology is shown in Table 8.1 for:

- A 1,000 m<sup>3</sup> per day treatment system;
- Removing 90% of the salinity from an initial brine concentration of 20,000 mg/l sodium chloride;
- An assumed cell performance of 125 mA/cm<sup>2</sup> at 6 V.

Inputs		Units	Notes
Initial TDS	18,000	mg/L	Assumed water composition at site
Throughput	1,000	m³/day	Volume throughput
Total salt removed	18,000,000	g	
CO2 required	6,778	kg/day	
Mangrove System Performance		Units	Notes
Total salt removed	308,008	mols/day	Assuming sodium chloride solution
Voltage	6	V	Applied cell voltage
Power	2,751.68	kW	Total system power required
Cell current density	125	mA/cm²	Target cell current density
Mangrove System Outputs		Units	Notes
Soda Ash (25 wt.%)	65,285	kg/day	Mass of dilute chemical produced
HCl (10 wt.%)	112,423	kg/day	Mass of dilute chemical produced
			Minus water used to build chemical
Desalinated water	844	m³/day	concentration

Table 8.1: Summary of material and energy balance for a 1,000 m<sup>3</sup> per day system.

The economics of the technology are determined by current density and voltage of the electrochemical reactor which control the energy requirements (OPEX) and the active area of the

cell (CAPEX). Durability of the membranes and electrodes are related to the frequency of replacement and affect the OPEX of the cell. Figure 8.1 compares the electrical cost of the technology providing the equivalent services to incumbent alternatives available for saline water management (electrodialysis, reverse osmosis, or disposal) in combination with trucking chemicals to site for use. Figure 8.1 shows that the technology could offer the most economic option available as:

- There is no disposal cost associated with the technology as the desalinated water produced can be consumed;
- Chemicals produced on-site and on-demand from waste eliminate the need to bring chemicals to site.

The amount of chemicals purchased is based on the equivalent amount of hydrochloric acid and sodium hydroxide produced by the technology as summarized in the material and energy balance in Table 8.1 and list of assumptions in Table 8.2. Assumptions in Table 8.2 for chemical pricing and disposal are based on delivered rates at Canadian mining sites. This analysis did not consider the affect of other contaminants on the cost of the technology and instead assumed that pre-treatment requirements are similar for Electrodialysis and Reverse Osmosis. Hardness in the form of divalent ions (e.g., calcium, magnesium) is likely to be present in the brines from naturally occurring aquifers. These species have a potential to foul the membrane through precipitation and likely need to be removed prior to entering the electrochemical cell. Some level of pre-treatment will also be required for both Electrodialysis and Reverse Osmosis which are likely similar to what is required for this technology. On the other hand, Disposal of the brines has no pre-treatment requirements and as such has more certainty around operating costs.



Figure 8.1: Comparison of the 5-compartment electrochemical cell with incumbent options to provide

desalinated water and sodium hydroxide and hydrochloric acid.

Assumptions		Units	Notes
Throughput	1,000	m <sup>3</sup> per day	Assumed
TDS removed	18,000		Design basis from material and energy balance
Disposal cost	\$ 9.43	per m³	Equivalent to \$1.50 per barrel
HCl amount	11 <i>,</i> 867	kg/day	Equivalent HCl produced based on TDS removed
			Equivalent NaOH produced based on TDS
NaOH amount	13 <i>,</i> 005	kg/day	removed
HCl cost	\$ 450	per ton	Delivered price in Alberta
NaOH cost	\$ 600	per ton	Delivered price in Alberta

Table 8.2: List of assumptions used to compare the technology versus incumbent options available.

Electricity price	\$ 0.07	per kWh	Assumed price	
Electrodialysis				
			Per 1,000 mg/l; "Desalination - A National	
Energy consumption	0.5	kWh/m³	Perspective"	
Water recovery	60%		"Desalination - A National Perspective"	
Reverse Osmosis				
Energy consumption	6	kWh/m³	"Desalination - A National Perspective"	
Water recovery	40%		"Desalination - A National Perspective"	



Figure 8.2: Sensitivity analysis showing how the value created changes for this technology versus conventional ED, Chemicals Purchase and Disposal as shown in Figure 8.1.

Figure 8.2 shows a Tornado plot that summarizes how the value created by the technology versus the Electrodialysis and Chemicals Purchase (Figure 8.1) option changes as different assumptions in Figure 8.2 are changed by different amounts. The variance change for each assumption is summarized in Figure 8.2, e.g., a change in 25% for HCl Price means that the lower value of \$22.03 for value created was calculated for a HCl Price of \$337.5 per ton HCl while the upper

bound value of \$29.94 corresponds to a HCl Price of \$562.5 per ton HCl. The value created is the difference in the cost of the technology in this work and the cost of the incumbent option of Electrodialysis and Chemicals Purchase. Figure 8.1 shows that as each variable changes the value created either increases (green) or decreases (orange) versus the baseline case of ~\$25.98 per m<sup>3</sup> brine treated. The baseline of \$25.98 per m<sup>3</sup> brine treated is based on the assumptions of the analysis in Figure 8.1. The analysis shows that the price of hydrochloric acid and sodium hydroxide have the most impact on the overall value created while Cell Efficiency has the least effect on the value create among the variables chosen here.

# **Chapter 9: Summary and Conclusions**

The overall objective of the thesis was to develop a process for the simultaneous conversion of carbon dioxide and saline water to chemicals and desalinated water. Two electrochemical approaches were developed and investigated as follows:

- Electrodialysis of carbonic acid and brine: Carbon dioxide dissolved in deionized water to produce carbonic acid and a sodium chloride brine was provided to a multi-compartment electrodialysis cell with ion exchange membranes configured in a strategic pattern. The cell successfully demonstrated that this approach could be used to produce carbonates (e.g., NaHCO<sub>3</sub>) and acids (e.g., HCl or other acid). However, the current densities of the approach were found to be too low to have much commercial use. A mathematical model to investigate the cell was developed. The mathematical model illustrated that the limiting compartment within the cell was the carbonic acid channel. It was hypothesized that the carbonic acid channel was limiting performance due to the low solubility of carbon dioxide in water, the slow dissociation of dissolved carbonate ions. Analysis of the model showed that the performance of the cell was limited due to the low mobility of the carbonate and/or bicarbonate ions and not because of the dissociation of dissolved carbonic acid or the low solubility of carbonic acid.
- Electrolytic cell with gaseous carbon dioxide and brine: A first of a kind 5-compartment electrolytic cell with a gaseous cathode was developed. This cell attempted to overcome all potential issues associated with the carbonic acid channel. Unlike the earlier approach, the carbon dioxide was provided to the cathode as a gaseous feed while the electro-dialytic compartments for the removal of sodium chloride remained the same. At the cathode, the 150

carbon dioxide reacts with hydroxide ions generated through the oxygen reduction reaction to produce bicarbonate or carbonate ions which along with any unconverted hydroxide ions are transported through an anion exchange membrane and combine with transported cations present in the saline water to remove the carbon dioxide as a mineralized species. Anions present in the saline water are combined with protons generated at the anode to produce an acid. Thus, inputs of saline water, carbon dioxide and oxygen, and electricity are converted to desalinated water, a base, and an acid.

Given the novelty of the cell, parametric studies were performed to investigate the performance of each of the different compartments with oxygen where only hydroxide ions are produced. The parametric study demonstrated:

- Brine concentration is an important factor in the performance of the cell as low concentrations of brine can cause the cell to become mass transport limited. This has important implications with respect to commercial operation of the cell as it will effectively limit the brine concentrations that can be treated with this cell as well as the final concentration of brine that can be achieved within the cell.
- The choice of membrane is extremely important to the overall performance of the cell with the performance of the hydroxide ions and sodium ions being the most affected.
- The sodium ion was found to be the rate-limiting step in most of the tests with the sodium conducting cation exchange membrane experiencing significantly higher losses than expected from membrane conductivity alone. This was determined to be most likely due to the loss in conductivity of cation exchange membranes when exposed to caustic

solutions. For commercial applications, the resistance of the membrane and their stability in highly caustic solutions should be an important consideration of cell design.

• For the hydroxide ion, the membrane-electrode interface at the cathode is critical to the performance of the hydroxide ions. The membrane should be sufficiently conductive to the anion being conducted, reduce water transport through the membrane to avoid flooding while also making sufficient contact with the electrode to maximize the number of active triple phase sites, i.e., oxygen, water and electrons must all have access to the sites to ensure the oxygen reduction reaction occurs. Any scale-up to commercial scale levels will need to replicate these conditions and ensure that the cathode-membrane interface optimizes wetting of the catalyst layer, oxygen partial pressure, hydrostatic pressure at scale, and electrical contact for successful operation.

The cell was then operated with a mixture of carbon dioxide and oxygen provided to the cathode. Parametric testing was performed with different mixtures of carbon dioxide and oxygen, and nitrogen and oxygen to better understand performance of the cell. The parametric testing demonstrated that cell performance was lowered when carbon dioxide was introduced to the cathode. This occurs due to two main reasons:

- (Bi)carbonate ions have a lower mobility than hydroxide ions and are more difficult to transport through the membrane and the solution than hydroxide ions. This results in increased resistance of the cell.
- The partial pressure of oxygen is lowered when carbon dioxide or another gas that is not involved in the oxygen reduction reaction is introduced at the cathode. This results in increased over-potential losses at the cathode. To a certain extent, even humidification of

the oxygen with water vapor can contribute to this. As such, when carbon dioxide can only be converted through a chemical reaction as opposed to an electrochemical reaction it would be better to only produce hydroxide ions by not introducing carbon dioxide to the cathode. The carbon dioxide can be then be converted using an external caustic scrubber to (bi)carbonate ions. This may increase the complexity and cost of the system. However, it is likely that the higher current densities that could be achieved with using oxygen to produce hydroxide ions only would mean that the electrochemical cell and stack is smaller resulting in cost savings that are likely more than the cost of the scrubber.

Long-term testing of the 5-compartment electrochemical cell with different compositions of carbon dioxide, oxygen and nitrogen at different voltages was also performed to demonstrate the build-up of chemicals. Results of the testing include:

- Hydroxide, carbonate, and bicarbonate-based salts can be produced with this approach when carbon dioxide is used in the system. The amount of hydroxide, carbonate or bicarbonate can be controlled by the amount of carbon dioxide that is provided to the system. This can be done both within the electrochemical cell or externally with a scrubber. However, control of the desired species is likely to be much greater in an external scrubber as opposed to within the electrochemical cell.
- Production of the hydrochloric acid was successfully demonstrated. Some loss of the hydrochloric acid into the feed brine compartment was observed as the pH of the brine compartment was found to increase in acidity as the test progressed. Loss of the hydroxide, carbonate or bicarbonate ions to the brine compartment also occurs. However, this is not observed as the leakage of the acid is higher resulting in neutralization of the base.

- The anion and cation exchange membranes allow some back migration of the acid and base produced resulting in loss of the product and lowered cell efficiency. The back-migration also results in the re-production of the salt that has been removed from the feed brine resulting in more energy required to desalinate in addition to loss of the product. Leakage through the membranes is higher at higher concentrations of the products and lower concentrations of the brine and is likely to limit the commercial applications of the technology. There is likely a point at which the back migration through the membranes equals the removal of the salt from the feed brine resulting in no increase in concentration of the products or decrease of the salt amount in the feed brine compartment. This point will be different for different salts, products, membranes, current density, and voltage.
- Leakage of products through one membrane will affect the performance of the other compartments as well. For example, once hydrochloric acid has permeated to the brine compartment it will be transported to the base compartment where it will further reduce the concentration of the base produced through neutralization. The opposite with caustic is also true. This effectively means that a membrane that is not effective at building concentration of one product will also reduce the concentration of the second product, i.e., a membrane that allows a lot of acid will contribute to poor performance of not just the acid but also of the base and vice versa.

GHG analysis for the 5-compartment electrolytic cell was performed. The GHG analysis showed that the technology has the potential to enable a reduction in overall carbon emissions. The potential for significant carbon emissions reductions is higher when waste brines that would normally require disposal are converted to chemicals and the chemicals produced are consumed on-site where they are produced. In this scenario, the avoided trucking of brines for disposal, and chemicals to site for use are the major contributors to carbon emissions reduction. The carbon emissions reductions are possible even when a carbon emitting electrical source is used for the electrical energy and will be higher when a non-carbon emitting electrical source is used for the electrical energy of the electrochemical cell.

The work performed in this thesis developed a first-of-a-kind 5-compartment electrochemical cell that combined concepts of electrodialysis with a gas diffusion cathode. In particular, the use of the gas diffusion electrode in an electrodialysis cell is not a simple engineering problem as it requires careful control of several parameters to optimize reactant supply, ion conductivity, electron conductivity, hydrophobicity and contact between the electrode and membrane. Further, unlike in a conventional electrochemical cell where the anode and cathode catalysts are on either side of the same membrane, this work used a half membrane electrode assembly at the anode and cathode. The in-house designed 5-compartment electrochemical cell also had important design considerations regarding flow of reactants, materials of selection, compression and sealing.

The work performed in the thesis has been scaled up to a commercial scale pilot reactor and a field demonstration of the approach is planned soon. This approach has particularly relevant industrial applications in areas where saline water and waste-gases are present, and where the chemicals and desalinated water produced can be used on-site. The approach is particularly suited for industrial applications such as oil and gas production, mining, or treatment of brine rejects. Industries which require desalination and have a need for the produced chemicals would greatly benefit as the costs of water treatment could be offset through the value in the produced chemicals creating an economic incentive for reclamation and re-use of water and utilization of carbon dioxide.

The concept is flexible to the production of other salts of chemicals that can be formed through the reduction of carbon dioxide with different catalysts. These chemicals could, for example, include the production of formate or oxalate salts. Furthermore, the concept can also be used to treat gases other than carbon dioxide to produce other chemicals. These may, for example, include the treatment of nitrous or sulfur oxides to produce nitrate or sulfide-based salts.

## **Chapter 10: Future Work and Recommendations**

The work performed in the thesis successfully demonstrated the technical feasibility but several important areas require development for the technology to achieve commercialization. This includes:

- Developing better understanding of crossover or loss of products into other compartments: The work in this thesis has shown that produced acid and base are lost to the other compartments. The factors affecting the amount of acid and base lost are unclear at this time and can include concentration of the products and membrane type. However, other factors such as current density, cell voltage, flow rates or temperature are also likely to affect the loss of the products. Parametric testing to better understand these is recommended.
- Scale-up to commercial scale electrochemical cell: The technology has been demonstrated at the bench-scale and some work has been performed by Mangrove Water Technologies on a 5,000 cm<sup>2</sup> electrochemical cell. The scale-up work still requires development to advance the technology. This is not a simple undertaking and will likely need to proceed in stages. However, the most important aspect of the scale-up is the height of the electrochemical cell. Any scale-up effects of the cell will show up most in the height of the cell where additional effects of hydrostatic pressure and/or flow rate will be exacerbated. Therefore, it is recommended that an intermediate size cell which has the same height as that expected for a full-size cell is developed for further study.
- Design of flow channels for the central compartments: The mass transport of sodium and chloride ions will likely become limiting as the brine is depleted and the concentration lowered. This will result in reduced current densities or high voltage losses and will be 157

worse in a large cell where additional constraints around flow rates and velocity will be encountered. Therefore, the incorporation of flow channels within the central compartments could be helpful in improving the mass transport within the central compartments. In addition, the use of flow channels if designed correctly could also be helpful in a more uniform pressure profile across the cell improving contact of the gas diffusion electrode with both the membrane and the cathode plate. However, the flow channel design and any benefits associated with this should be carefully examined in relation to the loss of active membrane area.

- Improvement of turbulence within the brine compartment to improve mass transport: A second method to improve the mass transport within the brine compartment is to use turbulence promoters within the channels. Glass filter paper was used in this work to promote turbulence but a more appropriate plastic mesh that simultaneously allows pressure transfer and flow in between the membranes is recommended to be used. For scale-up purposes, the turbulence promoters could also be specifically designed for the application. The design of the turbulence promoters for use at the commercial scale-cell could involve computational fluid dynamics and modelling to better understand the design of the turbulence promoter and maximize the mass transfer coefficient.
- Computational fluid dynamics (CFD) and modeling to better understand cell design at the commercial scale: CFD or other modeling techniques can be an important tool to better understand different effects within the cell, especially at large scale. These modeling techniques could be used to better understand flow regimes, concentration changes, mass transport coefficients or voltage drops within the cell that may not be available from experiments. This can be especially helpful to understand the effects at low brine
concentrations and to help with better design of the cell components including turbulence promoters, flow channels, gas diffusion layers or cell geometry.

- Gas diffusion electrode design to reduce flooding of the cathode: A critical element affecting performance of the cell is the cathode. This will be even more important as the cell is scaled-up. Managing the issue of the gas diffusion electrode becoming flooded with water will be especially important. The oxygen reduction reaction will be impeded as the cathode becomes flooded with water and the water reduction reaction will start to increase. This has two important implications. First, it will increase the overall voltage of the cell and benefits of using an oxygen cathode which has a lower cell voltage will begin to be lost due to a mixed potential at the cathode. Secondly, the production of hydrogen will result in a potentially explosive atmosphere being created at the cathode due to the presence of oxygen, hydrogen, and a catalyst. This will prevent the cell being operated at higher voltages and may limit overall current densities that can be achieved. As such, the design of the cathode to effectively prevent flooding is an important element to be investigated. The design may include among other aspects bi-layer electrode designs, hydrophobic coatings, or multi-porous layers.
- Development of the gas diffusion electrode for use at scale with air: The reaction at the cathode requires oxygen. Providing pure oxygen to the cathode from a commercial perspective is likely to be expensive and will increase the complexity of the system. The use of an air at the cathode will have some drawbacks given the lower concentration and partial pressure of oxygen in air. Improving the design of the gas diffusion electrode to be able to operate with air without an appreciable loss in performance will be important for commercialization of the technology.

- Cell design improvements to operate the system with air: Cell design is also important to improving the performance of the cathode with respect to operating the cell with air. One potential opportunity may be to use an open pocket design for the cathode where the cathode is exposed to the atmosphere. Previously, Lam et. al performed work on a passive air breathing direct methanol cell in the Wilkinson research group. Similar designs could be utilized for this technology but with the added design change of convective flow of air. This may also have advantages regarding any hydrogen that is produced in the cell. An open cathode design will likely have less of a possibility of an explosive atmosphere being built-up in the cell and flow rates of the air could be controlled to ensure that the lower explosive limit of hydrogen is not exceeded.
- Investigation of contaminants: The work performed in this thesis demonstrated operation
  of the technology with sodium chloride. However, application of the technology in a realworld setting is likely to occur in industrial settings where the brines are unlikely to have
  only one component. Mining, or oil and gas operations are likely to have significant other
  components present that will interact with the membranes. The level of these contaminants
  and compositions of brines varies significantly with total dissolved solids content randing
  from a few thousand ppm to as much as 200,000 ppm and typically includes various alkali
  metals, alkaline earth metals, transition metals, non-metallic species and inorganic species
  among other various compounds. Some of these may adversely affect the membranes used.
  The presence of hardness causing cations such as calcium, magnesium or strontium or low
  solubility cations may be especially problematic for the cation conducting membrane next
  to the base compartment. Ions with low solubility in alkaline environments will precipitate
  on the cation conducting membrane adjacent to the base compartment resulting in ion-

conducting sites becoming blocked. This will increase cell ionic resistance and affect cell performance. The presence of organic molecules and dissolved hydrocarbons will also be problematic. Organic molecules and hydrocarbons often cause severe degradation of polymeric membranes by dissolving them but can also increase resistance by becoming permanently attached to the ion-exchange sites reducing the overall conductivity of the membrane. Extended exposure of the membrane to these contaminants will result in the membranes becoming irreversibly damaged increasing overall operating costs. As such, the effect of these contaminants on the performance of the cell and durability studies on the membrane with extended exposure of these contaminants is important to understand. It is important to understand the effect of these contaminants on cell performance, membrane active area requirements and membrane lifetime which directly affect the operating and capital cost requirements of the technology.

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## Appendices

Appendix A Appendix A - Properties of chosen membranes

## PCA Ion Exchange Membranes: Technical Data Sheet



	Mineral Acid	Series	Organic Anion	Series		Standard Ser	ies	Standard Series w/o reinforcement	
	PC Acid 60	PC Acid 100	PC 100 D	PC 200 D	PC 400 D	PC SA	PC SK	PC SFA	PC SFC
General use	monovalent acid (HCl/ HNO₃/HF)	sulphuric acid	small organic anions	medium organic anions	large organic anions	standard desalination	standard desalination	low cost	low cost
Membrane type	strongly alkaline	strongly alkaline	strongly alkaline	strongly alkaline	strongly alkaline	strongly alkaline	strongly acidic	strongly alkalino	strongly acidic
	ammonium	ammonium	ammonium	ammonium	ammonium	ammonium	sulfonic acid	ammonium	sulfonic acid
Transference number KCl (0.1 / 0.5 N) <sup>a)</sup> Acid (0.7/3 N) <sup>b)</sup>	>0.95 0.55	0.41	>0.94	>0,91 > 0.9 °)	>0,86	>0,95	>0,95	>0,95	>0,94
Resistance / $\Omega$ cm <sup>2</sup>	~ 2		~ 5	~ 2	~ 10	~ 1.8	~ 2.5	~ 1	~1
Water content (wt%)	~ 17	~ 19	~ 50	~ 40	~ 48	~ 14	~ 9	~ 24	~ 21
lon exch. capacity Strong basic (meq·g <sup>-1</sup> ): Weak basic (meq·g <sup>-1</sup> ):	ca 1.14 ca 0.45	ca 0.57 ca 0.37	ca 1.2 ca 0.7	ca 1.24 ca 0.56	ca 0.66 ca 0.35	n/a	n/a	n/a	n/a
Burst strenght /kg·cm <sup>-2</sup>	4 - 5	4 - 5	4 - 5	4 - 5	4 - 5	4-5	4-5		
Maximum operating Temperature / °C	60	40	50	50	40	60	50	60	50
Thickness / µm	160-200	160-200	180-220	180-220	160-200	180-220	160-200	50-120*	15-50*
Reinforcement <sup>d)</sup>	Polyester	Polyester	Polyester	Polyester	Polyester	Polyester	Polyester	none	none
lonic form as shipped	Cl.	Cl.	Cl	Cl	Cl	Cl.	Na⁺	Cl.	Na⁺

<sup>a)</sup> calculated from potentiometric measurements <sup>b)</sup> observed current efficiencies <sup>c)</sup> Gluconate <sup>d)</sup> Optional reinforcements: Polyamide, Polyetheretherketone (only for some types available)

\* adjusted to customers wishes

## PCA Ion Exchange Membranes: Technical Data Sheet



	Mineral Acid	Series	Monovaler	nt selective	Series		Standard Se	eries	End membr	anes
	PC AV 100	PC Acid 100 PEEK	PC MVA	PC FH	PC MVK	PC VK	PC AV	PC MV	PC SC	PC MF
Internal Code	#59(-0)	#65(-Q)	#56(-P)	#34(8)	#57(N)	#63(R)	#38(-8)	#41 (2)	#58(K)	#61(P)
General use	mineral acids	sulphuric acid	Monovalen t anion selective	Proton selective	Monovalent cation selective	Monovalent cation selective	standard desalination	standard desalination	End membrane	End membrane (fluorinated)
Membrane type	strongly alkaline	strongly alkaline	strongly alkaline	strongly acidic	strongly acidic	strongly acidic	strongly alkaline	strongly acidic	strongly acidic	strongly acidic
	ammonium	ammonium	ammoniu m	sulfonic acid	sulfonic acid	sulfonic acid	ammonium	sulfonic acid	sulfonic acid	sulfonic acid
Transference number KCl (0.1 / 0.5 N) <sup>a)</sup> Acid (0.7/3 N) <sup>b)</sup>	>0.95		>0.97		>0,97		>0.96	>0.96	>0.94	>0.95
Resistance / Ω cm²	~ 5-20 (acid)		~ 20	~ 0.3			~ 2.5	~ 3	~ 9	~ 1-3
lon exch. capacity Strong basic (meq·g <sup>-1</sup> ): Weak basic (meq·g <sup>-1</sup> ): strong acidic (meq·g <sup>-1</sup> ):										
Burst strenght /kg·cm <sup>·2</sup>	2		2	2	3		4	4	15	10
Maximum operating Temperature / °C	40	60	40	40	40	45	40	40	40	65
Thickness / µm	130	80	110	150	100	180	130	130	400	440
Reinforcement <sup>d)</sup>	PVC	PEEK	PVC	Polysulfon Ø	PVC	Polyester	PVC	PVC	PVC	PTFE
lonic form as shipped	Cl <sup>-</sup>	Cl <sup>.</sup>	Cl.	H.	Na⁺	Na⁺	Cl-	Na⁺	Na⁺	H⁺

Figure A.1: Properties of chosen anion and cation and cation exchange membranes available from PC-Cell.

	Туре	Reinforcement	Thickness	IEC	Selectivity	Specific area resistance	Stability
			hw	meq/g	%	Ωcm <sup>2</sup>	pH
			Standard Gr	rade Membrane	15		
FAS	anion	none	10-50	1.6-1.8	94-97	0.4-0.8	1-14
FKS	cation	none	10-50	1.3-1.4	98-99	0.9-1.9	1-14
FKS	cation	polyester	75-130	0.8-1.2	98-99	2.0-4.5	1-9
FAS	anion	polyester	75-130	1.0-1.4	92.97	2.0-3.0	1-9

		Membra	nes for Electrodia	lysis with Bipol	ar Membranes		
FAB	anion	PEEK	100-130	1.0-1.1	94-97	4-7	1-14
FKB	cation	PEEK	100-130	1.2-1.3	98-99	4-6	1-14
FBM	bipolar	PEEK	180-200	-	-	-	1-14

			Special Gro	ade Membranes			
FAD	anion	polyester	75-90	1.5-1.7	>85	0.4-0.8	1-9
FKD	cation	PEEK	75-90	1.2-1.4	>94	1.0-1.2	1-14
FAP	anion	PEEK/PTFE	130-160	1.1-1.3	>91	1.1-1.3	1-11
FAA-3	anion	PEEK	100-130	1.4-1.6	94-96	1.9-2.5	1-14
FKL	cation	PEEK	100-130	1.0-1.2	98-99	6-10	1-14
FAA-3	anion	none	10-50	1.9-2.1	92-95	0.2-0.7	1-14
FKE	cation	none	10-50	1.4-1.5	98-99	0.3-0.9	1-14

Figure A.2: Properties of chosen anion and cation exchange membranes available for Fumatech.

Appendix B - MATLAB Code for modeling

```
Nitric acid model Matlab code
% MATLAB script nitric main.m
00
% Supplementary Material for:
% "Conversion of Waste Water and Carbon Dioxide into Value-Added
     Chemicals by Electrodialysis"
9
% by Saad Dara, Michael Lindstrom, Joseph English, Arman
Bonakdarpour,
% Brian Wetton, and David Wilkinson}
00
% Code written by Brian Wetton, wetton@math.ubc.ca
% August 29, 2016
00
% Calls the function nitric Ysolve.m in another file
% Computes scaled concentration and potential in the nitric acid
channel
% of the generalized dialysis system described in the
manuscript. It is
% set with default parameters to compute the 10mM inlet nitric
acid
% case with system voltage 2.2, reproducing the figures in the
paper.
00
% Numerical paremeters
Ny = 200; % M in the written notes
hy = 1/Ny; % Delta Y in the written notes
Nx = 200; % N in the written notes
hx = 1/Nx; % Delta X in the written notes
% Physical constants
Dp = 9e-9; % H+ diffusivity m^2/s
Dm = 2e-9; % HNO3- diffusivity m^2/s
F = 96485; % Faraday constant
R = 8.314; % Ideal gas Constant
% System parameters
W = 0.75e-3; % channel width m
L = 0.08; % channel length m
offset = 18.38/11.97; % Offset to voltage of electrolysis fit
logfactor = 1/11.97; % multiple of natural log of current in
fit
```

```
Romega = 72e-4;
% External resistivity Ohm/m^2.
% Includes the resistivty from the electrolysis fit
% Operating conditions
c0 = 10; % inlet concentration Moles/m^3
U = 2.2; % cell voltage
T = 300; % Temperature in K
v = 1.4e-3; % inlet velocity m/s (5ml/min)
% Dimensionless numbers
A = L^*Dp/W^2/v; % Dimensionless number
delta = Dm/Dp; % ratio of diffusivities, D in the written notes
% Put these numbers (and one more below) into a structure for
passing
% to the update solve function, nitric Ysolve
param.Romega = Romega;
param.hy = hy;
param.Nx = Nx;
param.hx = hx;
param.A = A;
param.U = U;
param.delta = delta;
param.R = R;
param.T = T;
param.F = F;
param.offset = offset;
param.logfactor = logfactor;
% Initial conditions
% y=0 concentrations are normalized to value 1
cvec = zeros(Nx+2, Ny+1);
c = zeros(Nx+2, 1) + 1;
sol.c = c;
cvec(:, 1) = c;
% Solve for consistent phi0 at y=0
% At y=0, with C constant, the channel current is B phi0
B = Dp*c0*F/W;
param.B = B;
% U = R*T/F*phi0 + Romega*B*phi0 + offset + logfactor*ln(B*phi0)
% Use scalar Newton's method to find phi0
phi0= 1;
tol = 1e-8;
resid = 2 \times tol;
```

```
while resid > tol
    res = R*T/F*phi0 + Romega*B*phi0 + offset +
logfactor*log(B*phi0)-U;
    resid = abs(res);
    dres = R*T/F + Romega*B + logfactor/phi0;
    phi0 new = phi0 - res/dres;
    if phi0 new < 0 % to handle stray Newton steps
        phi0 = phi0/2;
    else
        phi0 = phi0 new;
    end
end
% potential is linear at inlet
sol.phi = (1-(((1:Nx+2)-1.5)*hx)')*phi0;
phivec = zeros(Nx+2, Ny);
current = zeros(1, Ny);
% march from inlet to outlet doing the update Newton solve in
the
% function nitrc Ysolve
00
% Keep dimensional current and scaled concentration for later
plotting
for j=1:Ny
    sol = nitric Ysolve(sol,param);
    current(j) = sol.current;
    cvec(:, j+1) = sol.c;
    phivec(:,j) = sol.phi;
    % pause(1)
end
% Plot output of solver
y1 = linspace(0, 1, Ny+1);
y^2 = linspace(hy, 1, Ny);
x= linspace(-hx/2,1+hx/2,Nx+2);
% Contour plot of scaled concentration
figure(1)
hold off
contour(x,y1,cvec','LineWidth',2);
colorbar;
title('Contour lines of scaled concentration', 'Fontsize', 18)
text(0.45,0.9,'outlet','Fontsize',18)
text(0.45,0.1,'inlet','Fontsize',18)
getframe;
```

```
% Plot of local current density
figure(2)
hold off
plot(y2,current,'k-','LineWidth',2)
title('Current Density Profile', 'Fontsize',18)
ylabel('Local Current density A/m^2','Fontsize',18)
xlabel('Scaled y','Fontsize',18)
getframe;
avgI = sum(current)/Ny;
voltage = U;
fprintf('Voltage: %10.4e, Average current (A/m^2): %10.4e \n',
...
voltage, avgI)
```

```
function [ sol ] = nitric Ysolve( sol, param)
% Function called by nitric main
% Finds the residual in the 2N+4 discrete equations described in
the
8
     written supplementary material
% Finds the Jacobian matrix (sensitivities) at the current
estimate
% Corrects with Newton's method
% Iterates to convergence of the nonlinear system
% Returns approximate solution at the next discrete channel
location
%fprintf('\n')
c = sol.c;
c0 = c;
phi = sol.phi;
hy = param.hy;
hx = param.hx;
Nx = param.Nx;
A = param.A;
U = param.U;
delta = param.delta;
Romega = param.Romega;
B = param.B;
R = param.R;
T = param.T;
F = param.F;
offset = param.offset;
logfactor = param.logfactor;
% There are 2(Nx+2) unknowns, Nx+2 c values followed by Nx+2 phi
values
Ntot = 2*Nx+4;
tolerance = 1e-10;
residual = 2*tolerance;
while residual > tolerance
    res = zeros(Ntot, 1);
    Jac = sparse(Ntot, Ntot);
    % first equation voltage balance
```

```
current = -(c(Nx+1)+c(Nx+2))*(phi(Nx+2)-phi(Nx+1))/2/hx -
. . .
        (c(Nx+2)-c(Nx+1))/hx;
    current = B*current;
    res(1) = R*T/F*(phi(1)+phi(2))/2 +Romega*current + offset +
. . .
        logfactor*log(current)-U;
    Jac(1, Nx+3) = R*T/F/2;
    Jac(1, Nx+4) = R*T/F/2;
    dcurrentdCNx1 = 1/hx*(-(phi(Nx+2)-phi(Nx+1))/2+1);
    Jac(1, Nx+1) = (B*Romega+B*logfactor/current)*dcurrentdCNx1;
    dcurrentdCNx2 = 1/hx*(-(phi(Nx+2)-phi(Nx+1))/2-1);
    Jac(1, Nx+2) = (B*Romega+B*logfactor/current)*dcurrentdCNx2;
    dcurrentdPhi = 1/hx*(c(Nx+1)+c(Nx+2))/2;
    Jac(1, Ntot-1) =
(B*Romega+B*logfactor/current)*dcurrentdPhi;
    Jac(1, Ntot) = -(B*Romega+B*logfactor/current)*dcurrentdPhi;
    % Nx+2 equation is phi = 0 at x = 1;
    res(Nx+2) = phi(Nx+1) + phi(Nx+2);
    Jac(Nx+2,Ntot-1) = 1;
    Jac(Nx+2,Ntot) = 1;
    Nx+3 equation is c phi x + c x = 0 at x=0
    res(Nx+3) = (c(1)+c(2))*(phi(2)-phi(1))/2 + c(2)-c(1);
    Jac(Nx+3, 1) = (phi(2)-phi(1))/2-1;
    Jac(Nx+3, 2) = (phi(2)-phi(1))/2+1;
    Jac(Nx+3, Nx+3) = -(c(1)+c(2))/2;
    Jac(Nx+3, Nx+4) = (c(1)+c(2))/2;
    \% Ntot (last) equation is c phi x - c x = 0 at x=1
    res(Ntot) = (c(Nx+1)+c(Nx+2))*(phi(Nx+2)-phi(Nx+1))/2 -
c(Nx+2)+c(Nx+1);
    Jac(Ntot, Nx+1) = (phi(Nx+2)-phi(Nx+1))/2+1;
    Jac(Ntot, Nx+2) = (phi(Nx+2)-phi(Nx+1))/2-1;
    Jac(Ntot, Ntot-1) = -(c(Nx+1)+c(Nx+2))/2;
    Jac(Ntot, Ntot) = (c(Nx+1)+c(Nx+2))/2;
    % Now iterate over the interior equations
    for i=2:Nx+1
        res(i) = -(c(i+1)+c(i))*(phi(i+1)-phi(i))/2 + ...
            (c(i)+c(i-1))*(phi(i)-phi(i-1))/2- ...
            (c(i+1)-2*c(i)+c(i-1)) + 1/A*(c(i) - c0(i))/hy*hx^{2};
        Jac(i, i-1) = (phi(i) - phi(i-1))/2 - 1;
        Jac(i, i+1) = -(phi(i+1)-phi(i))/2-1;
        Jac(i,i) = (phi(i)-phi(i-1))/2-(phi(i+1)-phi(i))/2+2
+1/A/hy*hx^2;
```

```
Jac(i,i+Nx+1) = -(c(i)+c(i-1))/2;
        Jac(i, i+Nx+3) = -(c(i+1)+c(i))/2;
        Jac(i, i+Nx+2) = (2*c(i) + c(i-1)+c(i+1))/2;
        res(i+Nx+2) = delta*(c(i+1)+c(i))*(phi(i+1)-phi(i))/2 -
. . .
            delta*(c(i)+c(i-1))*(phi(i)-phi(i-1))/2- ...
            delta^{((i+1)-2c(i)+c(i-1))} + 1/A^{((i))} -
c0(i))/hy*hx^2;
        Jac(i+Nx+2,i-1) = (-(phi(i)-phi(i-1))/2-1)*delta;
        Jac(i+Nx+2,i+1) = ((phi(i+1)-phi(i))/2-1)*delta;
        Jac(i+Nx+2,i) = (-(phi(i)-phi(i-1))/2+(phi(i+1)-
phi(i))/2+2)*delta ...
            +1/A/hy*hx^2;
        Jac(i+Nx+2,i+Nx+1) = (c(i)+c(i-1))/2*delta;
        Jac(i+Nx+2,i+Nx+3) = (c(i+1)+c(i))/2*delta;
        Jac(i+Nx+2,i+Nx+2) = -(2*c(i) + c(i-1)+c(i+1))/2*delta;
    end
    residual = max(abs(res));
    % fprintf('%d \n', residual)
   update = Jac\res;
   c = c-update(1:Nx+2);
   phi = phi-update(Nx+3:Ntot);
end
sol.c = c;
sol.phi = phi;
sol.current = current;
```

Appendix C - Electrochemical Cell Drawings



Figure C.1: Dimensions of the anode and cathode electrode plates used in the 5-compartment cell.



Figure C.2: Dimensions of the spacer used in the 5-compartment electrochemical cell.

Appendix D - Sample reference electrode measurements and calculations

	А	В	С	D	E	F	G	н	1	J	к	L	М	N
1														
2		Voltage (V)	0	1	1.5	2	2.5	3	3.5	4	4.5	5	6	7
3		Resistance (ohms)	4.65											
4		Current (mA) Run 1	0	0.1	10	55	101	158	212	263	315	360	459	566
5		Current Density (mA/cm <sup>2</sup> )	=C4/3.24	=D4/3.24	=E4/3.24	=F4/3.24	=G4/3.24	=H4/3.24	=14/3.24	=J4/3.24	=K4/3.24	=L4/3.24	=M4/3.24	=N4/3.24
6														
7		Anode-Acid			1.19	1.19	1.2	1.22	1.24	1.27	1.28	1.31	1.33	1.35
8		Anode-Salt			1.39	1.47	1.54	1.6	1.66	1.73	1.77	1.87	2.09	2.28
9	Measured	Anode-Carbonate			1.39	1.76	2.19	2.66	3.13	3.57	4.05	4.48	5.44	6.17
10		Carbonate-Cathode			0.09	0.22	0.28	0.32	0.34	0.41	0.44	0.47	0.55	0.79
11		Total vs. Ag/AgCl			=SUM(E9:E10)	=SUM(F9:F10)	=SUM(G9:G10)	=SUM(H9:H10)	=SUM(I9:I10)	=SUM(J9:J10)	=SUM(K9:K10)	=SUM(L9:L10)	=SUM(M9:M10)	=SUM(N9:N10)
12														
13		Acid-carbonate			=E9-E7	=F9-F7	=G9-G7	=H9-H7	=19-17	=J9-J7	=K9-K7	=L9-L7	=M9-M7	=N9-N7
14	Calculated	Acid-Salt			=E8-E7	=F8-F7	=G8-G7	=H8-H7	=18-17	=J8-J7	=K8-K7	=L8-L7	=M8-M7	=N8-N7
15		Salt-Carbonate			=E9-E8	=F9-F8	=G9-G8	=H9-H8	=19-18	=J9-J8	=K9-K8	=L9-L8	=M9-M8	=N9-N8
16														

Figure D.1: Example showing how the polarization curve data including reference electrodes was measured, recorded and calculated.

Appendix E - Data for calculation of averages of polarization curves



Figure E.1: Summary of the different polarization curves for different sodium chloride concentrations for Figure 5.4-5.5.



Figure E.2: Summary of the different polarization curves for different sodium chloride concentrations for Figure 5.6.



Figure E.3: Summary of the different polarization curves for different membrane combinations for 1 M NaCl as shown in Figure 5.9.



Figure E.4: Summary of the different polarization curves for different carbon dioxide compositions as shown in Figure 6.1.



Figure E.5: Summary of the different polarization curves for different nitrogen compositions as shown in Figure 6.1.