Thermodynamic analysis of electrodialysis

by

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Submitted to the Department of Mechanical Engineering
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in Mechanical Engineering

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2017

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Abstract

The work presented in this thesis is motivated by the water and energy problems our world faces today. Desalination can help alleviate the problem of water shortage by increasing the supply of fresh water. However, for desalination to play a major role in the future, it needs to be done in a sustainable manner. Significant progress towards making desalination technologies sustainable can be made by decreasing their energy consumption. This can be done with the help of a better understanding of the thermodynamics of desalination technologies.

In this thesis, we present a thermodynamic analysis of electrodialysis (ED). ED is a desalination technology with many applications, and has shown promise in desalinating brackish water and in concentrating high-salinity brines. In order to better understand how the energetic performance of this technology can be improved, we first study the sources of entropy generation at different salinities, and locate areas where possible improvements need to be made under different operating conditions.

In the second part, we define a fair set of constraints to allow a fair comparison between different system sizes, designs, and operating conditions. We study the trade-offs governing the optimal channel height and velocity for brackish-water desalination and for high-salinity brine concentration. In addition, we study the minimum costs associated with the different system sizes, and we compare the differing trends in brackish-water and high-salinity applications. Further, we report optimal values of system size, current density, length, velocity, and cost for the two applications at different unit fixed costs and energy costs.

In the third part, we study possible improvements to the energy efficiency of electrodialysis through the use of two electric stages with different voltages, and through the operation using a counterflow configuration. We first look at how a two-stage ED system should be operated for optimal energy efficiency. We then quantify the effect of operating under two voltages in brackish-water desalination and in high-salinity brine concentration. This is done at systems sizes that are shown to be cost effective at different unit fixed costs and energy costs. Finally, we quantify the effect of operating ED in counterflow for the same applications.

In the final part, we study the optimal operation of a batch ED system for the
desalination of brackish water and seawater, and for the concentration of high-salinity brine. We compare three processes: operation under constant voltage, constant current, and constant entropy generation. We then study the effect of improved operation on the energy consumption and on the system cost of batch ED at different fixed-to-energy cost ratios. It is shown that significant improvements to energy consumption and cost can be made through better system operation, especially in the seawater desalination application.

Thesis Supervisor: John H. Lienhard V
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Acknowledgments

I thank my advisor, Professor John Lienhard, for giving me the chance to visit the group as an undergraduate student, and for his support and guidance during my time at MIT. I thank my committee members, Professor Jongyoon Han and Professor Rohit Karnik, for their assistance in guiding this work.

I thank Prakash Narayan for being a great mentor and friend since I first visited MIT 6 years ago. I also thank Professor Syed Zubair for the constant encouragement.

I thank my co-authors, Daniel Farhat for his invaluable contribution to the work presented in Chapter 3, and Kishor Nayar for his work on Chapters 3 and 4. I thank past and present members of the Lienhard Research Group for making our lab a great place to work, and for contributing to this work through their constant feedback.

Words cannot express how grateful I am for the support from my family, my girlfriend, Ruth, and my friends.

Finally, I would like to thank the Kuwait Foundation for the Advancement Sciences (KFAS) for their financial support through Project No. P31475EC01.
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Nomenclature

Acronyms
AEM  anion-exchange membrane
CEM  cation-exchange membrane
MS   Maxwell-Stefan

Symbols
A   effective cell-pair area [m²]
\(a\) activity [-]
\(C\) cost [$/m³ product]
\(c^*\) normalized cost [($/m³ product)/($/kWh)]
\(c\) concentration [mol/m³]
\(D\) diffusion coefficient of salt [m²/s]
\(D_{ij}\) Maxwell-Stefan diffusion coefficient for species \(i\) and \(j\) [m²/s]
\(F\) Faraday constant, 96,487 [C/mol]
\(f\) driving force [J/mol-m-K]
\(f\) friction factor [-]
\(h\) channel height [m]
\(i\) current density [A/m²]
\(i\) annual interest rate [-]
\(i_{lim}\) limiting current density [A/m²]
\(J\) molar duty [mol/s]
\(j\) molar flux [mol/m²-s]
\(K_e\) cost of electricity [$/W-s]
\( K_m \) fixed cost per unit cell-pair area per unit time [\$/m^2-s]  
\( K_{m,0} \) fixed cost per unit cell-pair area per unit time at time 0 [\$/m^2-s]  
\( k_m \) mass transfer coefficient [m/s]  
\( L \) effective stack length [m]  
\( L \) phenomenological coefficient [J-m-s/K-mol^2]  
\( L_s \) salt permeability [m/s]  
\( L_w \) water permeability [mol/m^2-s-bar]  
\( M \) molar mass [g/mol]  
\( m \) molality [mol/kg]  
\( N \) molar flow rate [mol/s]  
\( N_{cp} \) number of cell pairs [-]  
\( P \) absolute pressure [Pa]  
\( P \) power consumption [W]  
\( Q \) volumetric flow rate [m^3/s]  
\( R \) universal gas constant, 8.3145 [J/mol-K]  
\( \text{Re} \) Reynolds number, Eq. B.5 [-]  
\( r_{CP} \) total cell-pair resistance [\( \Omega \cdot m^2 \)]  
\( r \) electric resistance [\( \Omega \cdot m^2 \)]  
\( r \) cost ratio, Eq. 3.9 [W/m^2]  
\( S \) salinity [g/kg]  
\( S \) entropy [J/K]  
\( S_{\text{gen}} \) entropy generation rate [W/K]  
\( S_{\text{gen, equip}} \) entropy generation rate of the equivalent equipartitioned system [W/K]  
\( S_{\text{gen, imbalance}} \) entropy generation rate due to the imbalance [W/K]  
\( \dot{S}_{\text{gen}} \) volumetric rate of entropy generation [W/m^3-K]  
\( \dot{S}_{\text{gen}} \) entropy generation rate per unit area [W/m^2-K]  
\( Sc \) Schmidt number, Eq. B.6 [-]  
\( Sh \) Sherwood number, Eq. B.1 [-]  
\( T \) absolute temperature [K]  
\( T_s \) salt transport number [-]
$T_w$  water transport number [-]
$t$  time [s]
$U$  internal energy [J]
$V$  Volume [$m^3$]
$V$  voltage [V]
$V_1^*$  voltage of the first stage divided by that of the single-stage system [-]
$V_{1,P}^*$  normalized first-stage voltage that minimizes power consumption [-]
$V_{1,Var(i)}^*$  normalized first-stage voltage that minimizes the variance of the current density [-]
$V_{1,Var(\gamma_{gen})}^*$  normalized first-stage voltage that minimizes the variance of rate of entropy generation [-]
$v$  velocity (at the product outlet) [m/s]
$\dot{W}$  work input [W]
$W$  stack width [m]
$x$  spacial coordinate [m]
$z$  charge number

**Greek**

$\Delta$  difference or change
$\delta$  diffusion layer thickness [m]
$\nabla$  gradient
$\varepsilon$  spacer volume fraction [-]
$\Phi$  electric potential [V]
$\gamma$  mean molal (or molar) activity coefficient [-]
$\mu$  dynamic viscosity [Pa-s]
$\mu_i$  electrochemical potential of ion $i$ [J/mol]
$\mu_s$  chemical potential of the salt [J/mol]
$\mu_w$  chemical potential of water [J/mol]
$\pi$  osmotic pressure [bar]
$\tau$  plant life [years]
\( \tau_{\text{process}} \) batch process time [s]
\( \mu^0 \) chemical potential at the reference state [J/mol]
\( \Xi \) equipartition factor [-]
\( \xi_i \) current utilization rate [-]
\( \xi_V \) voltage utilization rate [-]
\( \rho \) density [kg/m³]

Subscripts
- avg average
- C concentrate
- co co-ion
- cou counter-ion
- cp cell-pair
- D diluate
- i ion \( i \)
- m at membrane interface
- s salt
- w water

Superscripts
- m in membrane
- s in solution
Chapter 1

Introduction

The work presented in this thesis is motivated by the water and energy problems our world faces today. According to the World Health Organization and UNICEF, 663 million people still lacked access to safe water in 2015 [8], and, according to a study by the 2030 Water Resources Group, the world’s demand for water is expected to outstrip supply by 40% by 2030 under the business-as-usual scenario [9]. Desalination is one possible solution to the problem of low supply of fresh water given that it can treat various feed waters that would otherwise not be usable. As shown in Fig. 1-1, the installed desalination capacity has been increasing rapidly over the past four decades. If desalination is to play a major role in the supply of fresh water, it has to be done sustainably in a world threatened by climate change.

Reducing the energy consumption of desalination technologies is essential to making these technologies sustainable. In addition, making desalination systems more energy efficient helps in reducing their overall costs. This is important if these technologies are to play a role in improving the access to clean water outside of the developed world.

To be able to reduce the energy consumption of desalination systems, it is essential to study the thermodynamics underpinning these systems. By combining the First and Second Laws of thermodynamics, as detailed in Appendix A, the following
expression for the energy consumption of a desalination process can be reached:

$$\dot{W} = \dot{W}_{\text{least}} + T\dot{S}_{\text{gen}}$$ (1.1)

where $\dot{W}$ is the work input into the system, $\dot{W}_{\text{least}}$ is the least work of separation, which is only a function of the inlet and outlet states and is independent of the process, $T$ is the temperature of the system, and $\dot{S}_{\text{gen}}$ is the rate of entropy generation. Studying the energetic losses in a system, which are represented by the entropy generation, is the first step in reducing these losses. In fact, the thermodynamic analysis of a desalination technology helps answer the following questions: how big are the losses? where do they occur? what is the nature of these losses, and what is causing them? and the ultimate goal: how do we reduce the system losses? and what should we focus on improving under different conditions?

In this thesis, this framework is applied to electrodialysis (ED), which is a desalination technology that takes in a work input in the form of an electric current that flows between two electrodes. These two electrodes are separated by fluid channels, which are bounded by cation-exchange and anion-exchange membranes placed in
alternating order, as shown in Fig. 1-2. A cation-exchange membrane (CEM) preferentially lets cations through, and an anion-exchange membrane (AEM) preferentially lets anions through. This configuration, along with the applied voltage, results in the stream flowing in half of the channels becoming more dilute and the stream in the other half becoming more concentrated. The diluate and concentrate streams leave the ED stack in alternating order.

Figure 1-2: Schematic diagram representing the operating principle of electrodialysis.

ED has many applications in the food and beverage industry. Some of the products manufactured using ED include dairy goods, wine, fruit juice, and sugar [10]. ED is widely used for the desalination of brackish water [11–19]. In addition, it has been used for the concentration of seawater [20, 21] or reverse-osmosis brine for salt production [11, 22, 23].

In Chapter 2, we study the sources of entropy generation at different salinities, and locate areas where possible improvements need to be made under different operating conditions. In addition, we study the effect of the channel height, membrane thickness, and cell-pair voltage on the specific rate of entropy generation. We express the second-law efficiency of ED as the product of current and voltage utilization rates, and study its variation with current density. Further, we define the useful voltage that is used beneficially for separation. We derive the rate of entropy generation that is due to the passage of ions through a voltage drop, and we investigate whether
voltage drops themselves can provide a good estimate of entropy generation.

In Chapter 3, we first define a set of constraints that allows a fair comparison between different system sizes, designs, and operating conditions. We then study the design and operation of ED for brackish-water desalination and for high-salinity brine concentration for a fixed system size. The set of variables that determine the power consumption of a fixed-size system is reduced to include only the channel height and the velocity, with all the other design and operation variables depending on these two variables. After studying the minimization of power consumption for a fixed system size, the minimum costs associated with the different system sizes are studied, and the differing trends in brackish-water and high-salinity applications are compared. Finally we present the effect of the cost modeling parameters on the trends of the optimal system size, current density, length, velocity, and cost for the two applications studied.

When comparing ED configurations of the same size and for the same application, the conditions for the use of the theorem of equipartition of entropy generation, first proposed by Tondeur and Kvaalen [24], are satisfied. The theorem states that, for a given system size, and for a given total duty, which is the quantity transported, the rate of entropy generation is minimized when its spatial and/or temporal variance is minimized. Details on equipartition of entropy generation are presented in Section 4.2, and the theorem is used extensively in Chapters 4 and 5.

In Chapter 4, we study possible improvements to the energy efficiency of electrodialysis through the use of two electric stages with different voltages, and through the operation in counterflow configuration. We first look at how a two-stage ED system should be operated. In particular, we look at how the voltages and current densities should be chosen. In addition, we quantify the effect of operating under two voltages in brackish-water desalination and in high-salinity brine concentration. This is done at systems sizes that are shown to be cost effective. Finally, we quantify the effect of operating ED in counterflow for the same applications. This is done by comparing the performance of counterflow systems to parallel-flow systems of the same size and for the same application.
In Chapter 5, we study the optimal operation of a batch ED system for the desalination of brackish water and seawater, and for the concentration of high-salinity brine. We compare three processes: operation under constant voltage, constant current, and constant entropy generation. We then study the effect of improved operation on the energy consumption and on the system cost of batch ED at different cost ratios.
Chapter 2

Entropy generation analysis of electrodialysis

2.1 Introduction

Although ED has been in the market for decades, few studies have examined the thermodynamics of ED systems. McGovern et al. [19] defined thermodynamic metrics for efficiency and productivity, and they studied the local cost of desalination for different applications. Koter [25] studied the effect of channel height, diffusion layer thickness, membrane transport number, diluate salinity, and current density on the current efficiency and energy efficiency of the ED system.

Evaluating the thermodynamics of ED system, especially the causes of irreversibility (or entropy generation), is essential to improving the energy efficiency of these systems. Entropy generation analysis can be thought of as a diagnosis of the system. It locates and quantifies the losses in the system under different operating conditions. This identifies the major sources of losses that should be tackled in order to improve the energy efficiency of the system. This analysis also determines which part of the electrical work input is used beneficially (i.e., for the purpose of separation) and which part is simply dissipated and why. Reducing the entropy generation in a system results in a direct reduction in its energy consumption as seen in the following
equation, which is derived in detail in A:

\[ \dot{W} = \dot{W}_{\text{least}} + T \dot{S}_{\text{gen}} \]  

(2.1)

where \( \dot{W} \) is the work input into the system, \( \dot{W}_{\text{least}} \) is the least work of separation, \( T \) is the temperature of the system, and \( \dot{S}_{\text{gen}} \) is the rate of entropy generation.

In this chapter, we study the sources of entropy generation in an ED system, and we look at how the magnitudes of these losses vary at different operating conditions. This analysis guides the improvement of the technology at different salinities. In addition, we look at possible improvements to the system by studying the effect of channel height and membrane thickness. We study the effect of the cell pair voltage on the entropy generation in the system. Also, we define a useful voltage (that which contributes to ion separation) and compare voltage drops to entropy generation in order to determine whether voltage drops can be used to estimate the system losses.

### 2.2 Existing electrodialysis models

Several approaches to modeling electrodialysis can be found in the literature. Lee et al. [12] and Tsiakis and Papageorgiou [17] make several assumptions that are only valid for brackish water desalination, and model a complete electrodialysis desalination plant without examining the details of ion transport. The simplifying assumptions used in these papers are not valid when modeling the desalination of high-salinity feeds.

Fidaleo and Moresi [26] use a model based on the Nernst-Planck equations. This approach inherently assumes an ideal solution, which is not valid at high salinity. In addition, the model neglects kinetic coupling between the different components in the solution. The authors, however, manage to model the operation of ED up to a salinity of around 90 g/kg. They accomplish this by defining a water transport number that estimates the kinetic coupling between water and salt, and they empirically fit several membrane parameters in the range of the desired operation.
McGovern et al. [4] use the same approach and manage to model a multi-stage ED system operating in batch mode. The membrane parameters are empirically fitted at different salinities so that the model can predict the performance in a wide salinity range, reaching 192 g/kg.

Ortiz et al. [27] use a similar approach to model a single-stage batch ED system used in treating brackish water. The main idea behind these models [4, 26, 27] is that the flux of salt through the membranes can be divided into two parts: migration, which is proportional to the applied current density, and diffusion, which is proportional to the concentration difference across the membrane. Similarly, the water flux is assumed to be a result of migration, where water is dragged by the moving ions, and osmosis, which is proportional to the difference in osmotic pressure across the membrane.

Tedesco et al. [28, 29] extend the Nernst-Planck equation to the membrane, and model the water transport through the membrane using the Maxwell-Stefan equation.

Kraaijeveld et al. [5] use a Maxwell-Stefan-based approach to model the use of ED in the desalination of a solution of NaCl-HCl, and Pintauro and Bennion [30] measure the Maxwell-Stefan (MS) diffusion coefficients of NaCl in a Nafion membrane. The MS model is the most accurate model for concentrated solutions in the presence of electrostatic forces [31, 32]. Unlike the Nernst-Planck model, the MS model does not assume the solution is ideal. In addition, the Maxwell-Stefan-based model captures electro-osmosis through the membrane naturally through kinetic coupling, whereas the Nernst-Planck-based model requires a separate fitting parameter in the form of a water transport number to capture that effect. In addition, the MS equation is the more general expression, and simplifies to the Nernst-Planck equation if we neglect kinetic coupling by limiting the forces felt by each species to those exerted by the solvent, and if, in addition, we assume that the solution is ideal.

From a different perspective, the MS equation writes the expression for flux in a fashion consistent with the theory of irreversible thermodynamics. The phenomenological coefficients in irreversible thermodynamics and the MS diffusion coefficients can in fact be theoretically related to one another [32–34]. It has been shown, however,
that the MS coefficients are less dependent on composition (total dissolved solids, as well as the different ions present) than are the phenomenological coefficients [35].

According to Fidaleo and Moresi [26], the Nernst-Planck-based model is more appropriate to model the performance of a specific system given that the fitting parameters are easier to measure. However, given that the goal of the present chapter is the thermodynamic analysis of ED, we will use the MS model because it is closer to fundamental equations and better captures the true driving forces. That said, the results presented in this chapter have been qualitatively replicated by the present authors using the Nernst-Planck-based model, and are not specific to the MS model.

2.3 Modeling

As explained in the previous section, the model that is the closest to the fundamentals, and that is valid at high salinities, is that based on the MS equations as reported by Kraaijeveld et al. [5]. The major components of the model that will be used in the proposed research are presented in detail in Appendix B. In this chapter, the change in salinity along an ED stack is not modeled, and the focus is on the local level, which can be modeled at a single location with one pair of salinities.

2.4 Calculating entropy generation

The volumetric rate of entropy generation from transport can be written as

$$ s_{gen}'' = \sum_k \nabla F_k \cdot J_k \quad (2.2) $$

where $J_k$ is the flux of the extensive property, $X_k$:

$$ J_k = \frac{1}{A} \frac{dX_k}{dt} \quad (2.3) $$
Table 2.1: The driving forces for different extensive properties, where $F_k$ is defined by Eq. 2.4.

<table>
<thead>
<tr>
<th>Extensive property, $X_k$</th>
<th>Driving force, $\nabla F_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal energy, $U$</td>
<td>$\nabla \left( \frac{1}{T} \right)$</td>
</tr>
<tr>
<td>Volume, $V$</td>
<td>$\nabla \left( \frac{P}{T} \right)$</td>
</tr>
<tr>
<td>Number of moles of species $j$, $N_j$</td>
<td>$\nabla \left( \frac{-\mu_j}{T} \right)$</td>
</tr>
</tbody>
</table>

where $A$ is area, and $t$ is time. $\nabla F_k$ is the driving force associated with $X_k$ (also called affinity, conjugate force, or generalized force), and $F_k$ is defined as

$$ F_k = \frac{\partial S}{\partial X_k} \tag{2.4} $$

where $S$ is the total entropy. The driving forces for different extensive properties are shown in Table 2.1. These equations can be derived from first principles as shown by Callen [36] and Bejan [37].

The volumetric rate of entropy generation due to diffusion then is

$$ \dot{s}''_{\text{gen}} = \sum_k \nabla \left( \frac{-\mu_k}{T} \right) \cdot J_k \tag{2.5} $$

and the volumetric rate of entropy generation due to fluid flow is

$$ \dot{s}''_{\text{gen}} = -\frac{Q}{A} \cdot \nabla \frac{P}{T} \tag{2.6} $$

The expression for the total entropy generation rate of the entire channel was expressed by Bejan [38] as:

$$ \dot{S}_{\text{gen}} = \frac{Q \Delta P}{T} \tag{2.7} $$

where $Q$ is the volumetric flow rate, $\Delta P$ is a positive pressure drop, and $T$ is the temperature. The calculation of the pressure drop is shown in B.1.1.
2.5 Sources of entropy generation in electrodialysis

In this section, we study the different sources of entropy generation in ED and we look at how the contribution of each source varies with the salinities of the concentrate and diluate channels. Total entropy generation is divided by location: CEM and AEM membranes, concentrate and diluate channels, and the diffusion films between each membrane and the bulk of the channel. In order to be able to compare the operation of ED under different salinities, we fixed the value of the electric current to 75 A/m², which was below the limiting current at the lowest concentration studied. The current was fixed instead of the voltage because losses in an electric system are mostly rate dependent, and, therefore, a fixed current would result in a better comparison.

Given that salinity varies along the length of an ED stack, the effect of a salinity pair can only be isolated by studying the entropy generation rate locally. At given concentrate and diluate salinities, channel height, and membrane characteristics, the entropy generation rate can be calculated locally on a per unit area basis without the need to specify the length of the system or update the salinities using a mass balance.

2.5.1 Effect of salinity on the spatial distribution of entropy generation

In an ED cell pair, the concentrate and the diluate have different salinities at most locations. To simplify the presentation of results, only three concentrate-to-dilulate salinity ratios are presented: 1, 2, and 3. At a salinity ratio of 1, both salinities are set to the same value and are varied from 2 g/kg to 150 g/kg. The division of the entropy generation between the different sources is presented in Fig. 2-1. At low salinities, most of the entropy is generated in the fluid channels as a result of the high electric resistivity of low-salinity solutions. This phenomenon is well understood in ED, and possible solutions, such as the use of conductive spacers [39, 40], have been proposed. At higher salinities, the resistivity of the solutions decreases and the membranes become the dominant sources of entropy generation. In fact, the entropy generation rate inside the membranes is a weak function of salinity, and salinity affects
the distribution of entropy generation by changing the resistivity of the solutions.

![Figure 2-1: The division of the entropy generation by source at different salinities. $h = 1$ mm in both channels, and $Sh = 18$. $Sc = S_D$.](image)

We can conclude from this graph that the design of channels and spacers is very important at low salinity but not as important at high salinity. For example, at 100 g/kg, around 80% of the losses occur in the membranes which means that targeting the channels can at most decrease the losses by 20%. In reality, the improvement will be much less than the full reversible (lossless) limit, which means that any significant improvement of the energetic performance of a high-salinity system has to be directed at the membranes. Similarly, any significant improvement at low salinity has to be directed at the fluid channels. The dashed line at 21 g/kg indicates the salinity at which the major source of entropy generation switches from the channels to the membranes. This specific salinity is only valid for this particular system, but can provide a general estimate to what is meant by low salinity and high salinity.

Figure 2-2 shows the division of the entropy generation by source for: a) a concentrate-to-diluate salinity ratio of 2; and b) a ratio of 3. As was the case for a salinity ratio of 1, the fluid channels are the dominant source of losses at low salin-
ity, and the membranes dominate at high salinity. There two main differences between the results presented in Fig. 2-2 and those presented in Fig. 2-1. The first is that the diluate channel generates more entropy than the concentrate channel, which is expected given the difference in their concentrations. The second is that more entropy is generated in the membranes than for the case with equal concentrations. This is because the higher salinity difference results in more osmosis and diffusion. This last point can be seen by comparing the fraction of entropy that is generated in the dilute channel for a ratio of 2 and a ratio of 3. It can be seen that, at the same diluate salinity, the dilute channel constitutes a bigger portion of the total entropy generation at the lower salinity ratio, and the membranes generate more entropy for the higher concentrate-to-dilute salinity ratio.

Figure 2-2: The division of the entropy generation by source at different salinities. $h = 1$ mm in both channels, and $Sh = 18$. a) $S_C = 2S_D$, and b) $S_C = 3S_D$. 

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2.5.2 Viscous losses in electrodialysis

The previous section was limited to study of entropy generation due to transport in the direction through the membranes. If the goal is to improve the energetic performance of the entire system by tackling only these sources, entropy generation due to lateral transport has to be the dominant fraction of the total entropy generation. Figure 2-3 shows that, at current densities used in most practical applications, most of the entropy generation is indeed due to transport, and not to viscous effects. The fraction of losses due to viscous effects becomes very small at high currents, which means that significant energetic improvements can be made by focusing on reducing the losses due to transport. For these results, the velocity was set to 10 cm/s, and the channel height was set to 1 mm, which are typical values for ED systems. In addition, entrance effects were neglected to enable a location-independent study of viscous losses. This is an acceptable approximation given that the correlations used are for channels with spacers, and that a typical ED stack length is much larger than the channel height. Further, looking at the rate of entropy generation per unit area enables the calculation of local viscous losses without the need to integrate over a stack length. We note here that these results show the entropy generation due to viscous effects inside the stack. In reality, more losses also occur inside the pump, manifolding, and the piping. An inefficient pump would obviously increase the importance of hydraulic losses.

The choice of velocity affects the viscous losses much more than it affects the transport losses. The chosen velocity of 10 cm/s in Fig. 2-3 is on the higher end of typical ED velocities, and the conclusion that transport losses dominate is not affected by going to slightly higher velocities. Decreasing the channel height decreases the transport losses and increases the viscous losses, thereby decreasing the fraction of the total entropy generation that is due to transport. Given that high-salinity systems are operated at high current densities, the only situation in Fig. 2-3 for which viscous losses are significant is at low salinity. However, at low salinities, the decrease in channel height results in an increase in the limiting current density, and higher current densities counter viscous losses. This is how brackish water ED systems
Figure 2-3: The fraction of the total entropy generation that is due to transport at different current densities. This fraction can be referred to as a modified Bejan number [2].

2.5.3 Effect of channel height

In an ED cell pair treating low-salinity water, most of the losses occur in the fluid channel. The area resistance of the fluid channel is the product of the resistivity of the solution and the channel height. Given that the concentration of the fluid in the channel is set by the application, we can only vary the channel height to reduce the resistance. Figure 2-4 shows the effect of the channel height on the entropy generation normalized per mole of salt removed. The system simulated has a concentrate salinity, $S_C$, equal to 2 g/kg and a diluate salinity, $S_D$ equal to 1 g/kg. The volumetric flow rate of the system is kept constant to keep the capital costs of the different systems constant (i.e., the same membrane area per unit feed), which means that the product of bulk velocity and channel height is kept constant. The velocity is
set to the typical value of 10 cm/s at the typical channel height of 1 mm. The total entropy generated is divided into entropy generated through mass transport (in the direction through the membrane) and entropy generated through viscous losses (fluid flow along the membrane). The entropy generation due to transport increases linearly with increasing channel height, due to the increased channel resistance, and the entropy generation due to viscous effects decreases quadratically with increasing channel height, as can be shown from the equations in B.1.1. The two opposing effects result in the total specific entropy generation having a clear minimum. The numbers presented in this graph are dependent on the system modeled, but this result frames the design of the optimal channel height as a balance between electric resistance and pumping power. At low salinity, the balance is delicate, as seen in Fig. 2-4. At high salinity, given the low resistivity of the channels, the viscous losses are important and a higher channel height is preferred. In real system design, the objective function will be the total power consumption, which is the sum of the power consumed by the ED stack to desalinate and the pumping power. Inefficient pumps and highly saline solutions push the optimal design to wider channels.

2.5.4 Effect of membrane thickness

At high salinity, most of the losses occur inside the membranes. Just like the channel height, we can think of the membrane electric resistance as being proportional to the membrane thickness. Figure 2-5 shows the variation of specific entropy generation with the membrane thickness for two systems: one with a small difference in salinity and the other with a large difference. For the system at low salinity difference, decreasing the membrane thickness decreases the total entropy generated in the system. This is not the case at the high salinity difference, where decreasing the membrane thickness results in a significant increase in entropy generation. The high salinity difference results in high driving forces for osmosis and diffusion across the membranes. This is shown in Fig. 2-6, where membrane thickness does not have a strong effect on the salt and water fluxes for the system at the low salinity difference. As for the system with the higher salinity difference, decreasing the membrane thickness from
1 mm to 0.35 mm increases the water flux by around 50% and greatly decreases the salt flux.

The conclusion from this result is that a thinner membrane thickness is beneficial only if the salinity difference is kept low or if the water permeability is greatly decreased. Although a thin membrane reduces the electric resistance, it also reduces the resistance to mass transport through diffusion and osmosis. These effects only become significant when the driving forces are high enough. At low salinity difference, energetic considerations motivate a thinner membrane, and the optimal membrane thickness is then determined by how thin the membrane can be while still remaining robust and tolerating cleaning.

2.6 Minimizing entropy generation in ED

In this section, we study the effect of the cell pair voltage on the entropy generation in the ED system. The required energy input is minimized when the entropy generation
Figure 2-5: The effect of membrane thickness on the specific entropy generation. $i = 75 \text{ A/m}^2$

Figure 2-6: The effect of membrane thickness on salt and water fluxes through the membrane. $i = 75 \text{ A/m}^2$
in the system is minimized, and more of the work input goes into achieving the goal of ED, which is the transfer of salt from the diluate channel to the concentrate channel.

2.6.1 Can the process be reversible?

Figure 2-7 shows that the total entropy generation rate due to transport is minimized when the two ionic fluxes through the membrane are equal, or, in other words, when there is no electric current. Even though the minimum total flux (in absolute value) occurs at around 0.055 V, entropy is still generated in the two channels because of the passage of current. An interesting trend that is apparent from this figure is that the applied voltage can never result in both ionic fluxes being 0. The applied voltage can set the flux of the counter-ion to 0 because it acts in the direction opposite to the chemical potential driving force, such that the net driving force for the counter-ion can be set to 0. The applied voltage, however, cannot set the flux of the co-ion to 0. In the CEM modeled here, diffusion will cause the co-ion to flow in the negative direction, and the applied voltage will also drive the co-ion in that direction. Similarly, the applied voltage can never block osmosis because the voltage actually results in an electro-osmotic water flow in the same direction as that of osmosis. Therefore, we can conclude that an ED stack with different concentrations in the diluate and concentrate channels cannot result in a reversible process at any applied voltage because there will always be fluxes of ions and water which cannot be stopped by the applied voltage. The only reversible systems would be either one with equal diluate and concentrate concentrations or one using perfectly perm-selective membranes (which do not allow the passage of co-ions) which also blocked the passage of water molecules, with the applied voltage in both systems set such that the flux of the counter-ion is infinitely small. 

1The applied voltage that results in no current flow is that equal and opposite to that faced by the membrane due to being subject to different activities. For a single membrane, this voltage can be supplied by reversible electrodes placed in the solutions adjacent to the membrane. The potential difference between the two electrodes is only due to the difference in the activities of the solutions and will be equal and opposite to that of the membrane, resulting in no net potential drop.
2.6.2 How should the voltage be set?

Figure 2-8 shows the variation of specific entropy generation with cell pair voltage. Focusing first on the entropy generation due to diffusion and migration, we see that it is minimized at a voltage close to that which results in no electric current flow. The results reported in the figure start at the lowest voltage which results in a positive salt flux, and the reason for the apparent singularity at low cell-pair voltage is that the initial salt flux is very small. This initial decrease of specific entropy generation due to diffusion and migration can also be explained by looking at the efficiency of the system, which will be done in Section 2.7. This figure shows that from an energetic perspective, the ED stack should be operated at the voltage that is just large enough to overcome the electric potential generated by having different concentrations in the two channels. An explicit expression for this voltage is derived in Section 2.7.

Figure 2-8 also shows the variation of the specific entropy generation due to viscous effects. The velocity and stack geometry are not varied, therefore the total viscous
Figure 2-8: The effect of voltage of the specific entropy generation in an ED cell pair. $S_D = 35\ \text{g/kg}$ and $S_C = 40\ \text{g/kg}$.

losses are constant. The decreasing specific rate of viscous entropy generation is due to the increasing salt flux with increasing voltage. This shows that even though the energy input to the stack is minimized when the current is zero, the pumping power still needs to be considered. The figure shows an optimal operating voltage specific to this case, but the competing effects of voltage on transport losses and viscous losses are general: for each case, there exists a cell pair voltage that minimizes the total specific rate of entropy generation.

In addition, we should consider the required membrane area. The modeling in this work focuses on local entropy generation. A real ED system, however, needs to remove a specific amount of salt. At small current density (and salt fluxes), large membrane surfaces are required to remove a specific amount of salt. The specific ED-stack power input is minimized at close to the lowest possible voltage, while the capital costs are minimized at the highest possible voltage: the optimal operating voltage has to be determined through an economic analysis, which factors in the
price of electricity, the price of membranes, and other capital costs.

2.7 Second-law efficiency

As shown in detail in A, the least work to take $J_s dA$ of salt from a concentrate of salinity $S_C$ to a diluate salinity of $S_D$ can be written as:

$$W_{\text{least}} = J_s \Delta \mu_s dA$$ (2.8)

where $J_s$ is the salt flux and $\Delta \mu_s$ is the difference in salt chemical potential between the concentrate and diluate channels and is positive. The salt flux can be written as a function of the current density by defining the current utilization rate, $\xi_i$, which, for a binary salt, is defined as

$$\xi_i = \frac{F J_s}{i}$$ (2.9)

which can at best be equal to 1.

We can then define a second-law efficiency as:

$$\eta = \frac{W_{\text{least}}}{W_{\text{electric}}} = \frac{\xi_i \Delta \mu_s}{F V_{\text{CP}}}$$ (2.10)

where the actual work input is:

$$W_{\text{electric}} = i V_{\text{CP}} dA = \frac{F J_s}{\xi_i} V_{\text{CP}} dA$$ (2.11)

From Eq. 2.10 we can also back out a 'useful voltage', which represents the voltage actually used for separation rather than for overcoming losses:

$$V_{\text{useful}} = \frac{\Delta \mu_s}{F} = 2 \frac{RT}{F} \ln \frac{\gamma_{i,C} m_C}{\gamma_{i,D} m_D}$$ (2.12)

where $\gamma_{i}$ is the mean molal activity coefficient, and $m$ is the molality. This expression, like the Nernst equation for electrodes, simply relates the required electric potential drop to the salt activities in the two channels. The same expression can also be
reached by setting the entropy generation in the membranes to be zero. For each membrane, the driving force for the counter-ion is set to zero, which allows us to write the required membrane potential drop as a function of the activities of the counter-ion in the two channels. Summing the two membrane potential drops results in the expression for useful voltage reached above.

From Eq. 2.10, we can then define a voltage utilization rate, $\xi_V$, which is the ratio of the useful voltage to the applied voltage:

$$\xi_V = \frac{V_{\text{useful}}}{V_{\text{CP}}} = \frac{\Delta \mu_s}{FV_{\text{CP}}}$$

(2.13)

The expression for efficiency can then be written as the product of the current and voltage utilization rates:

$$\eta = \xi_i \xi_V$$

(2.14)

Figure 2-9 shows the effect of the current density on the efficiency and on the current and voltage utilization rates. The current utilization rate increases with increasing current density. This can be explained by looking at the expression for salt flux as described by Fidaleo and Moresi [26]:

$$J_s = \frac{t_s i}{F} - L_s \Delta c$$

(2.15)

where $t_s$ is the cell-pair salt transport number, with $t_s \leq 1$, and $L_s$ is the permeability, which is a proportionality constant for diffusion from the concentrate to the diluate. Both factors are independent of the current density. The current utilization rate can be expressed as:

$$\xi_i = t_s - \frac{FL_s \Delta c}{i}$$

(2.16)

The current utilization rate starts with negative values at very low current density, and converges to $t_s$ as $i$ becomes large enough. When the concentration difference between the two channels is small, the salt flux is directly proportional to the current density, and the voltage that results in no salt flux also results in no current flow.

Using the MS equations, it can be shown that the voltage losses in the channels
Figure 2-9: The effect of current density on efficiency, current utilization rate, and voltage utilization rate at: a) $S_D = 1 \text{ g/kg}$ and $S_C = 2 \text{ g/kg}$; and b) $S_D = 35 \text{ g/kg}$ and $S_C = 70 \text{ g/kg}$.

including the diffusion films) and in the membranes (other than the useful voltage) are purely ohmic losses due to friction between the different ions, the solvent, and the membranes. The diffusion film also adds to the resistance by reducing the concentration and conductivity in the diluate channel such that the additional resistance becomes significant when the system is operating near the limiting current density.

Another type of voltage loss is the additional voltage that has to be spent above the useful voltage due to concentration polarization. Concentration polarization results in a higher concentrate concentration next to the membrane, $c_{G,m}$, and a lower diluate concentration on the other side of the membrane, $c_{D,m}$. As a result, the minimum voltage that has to be applied to overcome this concentration difference, at zero current, is then similar to the expression in Eq. 2.12, with the updated activities to reflect the concentrations just outside the membranes. Figure 2-10 shows that there are no potential drops in the channels and films when there is no current flow, and the useful voltage is the only potential drop.

The cell-pair voltage can then be written as the sum of the useful voltage, the
ohmic losses, and the contribution of concentration polarization described above:

\[ V_{CP} = V_{useful} + r_{CP}i + 2 \frac{RT}{F} \ln \frac{c_{C,m}c_D}{c_{D,m}c_C} \]  

(2.17)

where it is assumed that the activity coefficients do not vary greatly with the concentration changes due to concentration polarization. Equation 2.17 explains the variation of the voltage utilization rate with current density. As shown in Fig. 2-9, the voltage utilization rate starts at a value of 1 when there is no net salt flux, and decreases as the current density increases. In addition, the voltage utilization rate decreases faster in the first case, where the concentrate and diluate salinities are lower and the cell-pair resistance is higher.

Figure 2-10: The electric potential profile for a diluate at 35 g/kg and a concentrate at 40 g/kg at: a) 0 A/m²; and b) 75 A/m².

As shown in the first case presented in Fig. 2-9, when the concentration difference between the concentrate and diluate channels is small, the current utilization rate increases rapidly and reaches a high value even at low current density. A system with a small concentration difference can, therefore, achieve a high efficiency when it is operated at low current density that is high enough to result in a high current utilization rate. By comparing the two cases shown in Fig. 2-9, it is clear that the higher concentration difference requires going to higher current densities to achieve high current utilization rates. However, going to high current densities decreases the voltage utilization rate, and, as a result, systems with a large salinity difference
cannot achieve high efficiency values regardless of the operating current density.

The expression for efficiency defined in Eq. 2.10 includes losses due to non-perfect current and voltage utilization rates. A third type of loss that does not feature in Eq. 2.10 is that due to water transport, which reduces the volume of the diluate and dilutes the concentrate. When the goal is to desalinate, the required amount of diluate and its salinity are set. In this case, a system with significant osmosis and electro-osmosis requires the desalination of a larger diluate stream, which translates into a larger work input to remove a larger amount of salt, and a combination of larger channels (more electrical losses) and a larger pumping requirement. When the goal is to concentrate a stream (for zero-discharge desalination or salt production), this type of loss requires the removal of larger amounts of salt, which translates into higher energy requirements.

McGovern et al. [19] included the effect of water flux in their definition of efficiency. In deriving our definition of efficiency, we set salt removal as the goal of the energy input, whereas McGovern et al. [19] set the change in free energy as the goal of the process. The effect of the water flux on the efficiency is similar to that of diffusion: both are stronger when the concentration difference is larger, and both are independent of current, and so their effect decreases with increasing current density.

Finally, we can relate efficiency to the rate of entropy generation:

\[ \eta = \frac{\dot{W}_{\text{least}}}{W_{\text{electric}}} = \frac{\dot{W}_{\text{least}}}{\dot{W}_{\text{least}} + TS_{\text{gen, transport}}} \]  

(2.18)

where \( S_{\text{gen, transport}} \) is the rate of entropy generation due to the transport in the direction perpendicular to the membranes. In this expression, the viscous losses are not considered because we are looking at the efficiency of the local separation process. The efficiency is maximized when the rate of entropy generation due to transport is minimized. The effect of the current density on the efficiency, presented above, helps explain the initial decrease in the rate of specific entropy generation at low cell-pair voltage shown in Fig. 2-8. At low voltage (or current density), the low current utilization rate decreases the efficiency, and also increases the specific rate of entropy
generation. Hence, the voltage that minimizes the specific rate of entropy generation due to transport is slightly larger than \( V_{\text{useful}} \), with higher concentration differences requiring larger voltages.

### 2.8 Using voltage drops to estimate losses

In this section, we link voltage drops to the entropy generation rate, and look into whether voltage drops are a good approximation of losses. It has been shown in Section 2.4 that the volumetric entropy generation rate can be calculated as follows

\[
\dot{s}'''' = \sum_k \nabla \left( \frac{-\mu_k}{T} \right) \cdot J_k
\]  

(2.2)

In the direction perpendicular to the membrane,

\[
\dot{s}'''' = -\frac{1}{T} \left( J_+ \frac{d\mu_+}{dx} + J_- \frac{d\mu_-}{dx} + J_0 \frac{d\mu_0}{dx} \right)
\]  

(2.19)

In the simple case where the concentrations do not vary with space, for example at a central location in the channels outside the diffusion layer, we can write:

\[
\dot{s}'''' = -\frac{F}{T} (J_+ - J_-) \frac{d\Phi}{dx} = - \frac{i}{T} \frac{d\Phi}{dx}
\]  

(2.20)

Integrating along \( x \), we get the entropy generation rate per unit area:

\[
\dot{s}'''' = -\frac{i \Delta \Phi}{T}
\]  

(2.21)

In the absence of concentration gradients, diffusion and osmosis are also absent, and fluxes are only driven by electro-migration and electro-osmosis. In these cases, all of the entropy generation is due to the current flowing across an electric potential drop, as shown above. However, when osmosis and diffusion occur due to chemical potential differences, more or less entropy is generated than that accounted for by only considering the electric driving force. In the cases where the concentration gradient...
contributes positively to the driving force (i.e., the gradient in the concentration increases the salt flux), the actual entropy generation rate will be higher than that calculated using only the current. One such example is the diffusion layer, which enhances the salt flux. The opposite happens inside the membranes, where the applied electric potential must overcome the chemical potential gradient. In that case, the concentration gradient drives the salt from the concentrate to the diluate, whereas the applied electric field drives the salt in the direction that desalinates the diluate. The resulting entropy generation rate is then smaller than that predicted by just considering that generated by the flow of current through a voltage drop.

Given that, for a specific location along the ED stack, the current density is the same in the membranes, channels, and diffusion films, Eq. 2.21 can be used to convert a voltage drop to a rate of entropy generation. In the following analysis, we look at whether voltage drops can be used to estimate the total local rate of entropy generation. As described above, Eq. 2.21 captures the full rate of entropy generation only in the bulk of the channels where there are no concentration gradients. Figure 2-11 shows that using the total voltage drop in Eq. 2.21 does not result in a good approximation of the actual entropy generation rate in the films and membranes. This is consistent with the fact that not the entire voltage drop is necessarily a loss, such as in the membrane, and not every loss is necessarily captured by the voltage drop, such as in the diffusion films. In fact, the voltage drop across a membrane consists of a useful voltage drop and a voltage loss due to the resistance of the membrane:

\[ V_{\text{loss}} = V - V_{\text{useful}} \]  

(2.22)

In the presence of concentration gradients, going from Eq. 2.19 to Eq. 2.20 involves neglecting the following terms:

\[-\frac{1}{T} \left( J_{\text{cou}} RT \frac{d \ln a_{\text{cou}}}{dx} + J_{\text{co}} RT \frac{d \ln a_{\text{co}}}{dx} + J_{\text{w}} \frac{d \mu_{\text{w}}}{dx} \right) \]  

(2.23)

where the subscripts 'cou' and 'co' refer to the counter-ion and the co-ion, respectively. As shown in Fig. 2-11, neglecting all of these terms results in a poor estimate of the
actual rate of entropy generation. By neglecting the losses due to water transport (the third term in Eq. 2.23), and by assuming perfectly perm-selective membranes, we can rewrite Eq. 2.19 as:

$$\dot{s}_{gen}^{''} \approx -\frac{J_{cou} d\mu_{cou}}{T} dx$$

(2.24)

and Eq. 2.21 as

$$\dot{s}_{gen}^{''} \approx -\frac{iV_{mod}}{T}$$

(2.25)

where

$$V_{mod} = \frac{\Delta \mu_{cou}}{z_{cou}F} = \Delta \Phi_{total} + \frac{RT}{z_{cou}F} \Delta \ln a_{cou}$$

(2.26)

Equation 2.26 can be thought of as a generalized expression for Eq. 2.22, where the term ‘loss’ is dropped in favor of the term ‘modified’ so that the same definition can be extended to the diffusion layer, where the modified voltage, as defined in the equation above, is greater than the actual voltage drop because the concentration gradient adds to the driving force.

As shown in Fig. 2-11, using the modified voltage drop results in much better matching with the total entropy generation rate. However, when the concentration difference is large, osmosis and diffusion are no longer negligible, and, as a result, even the modified voltage is not always a good approximation of entropy generation. The expression only becomes acceptable at higher currents as the relative importance of osmosis and diffusion is reduced. Generally speaking, this condition is achieved when the current utilization rate, $\xi_i$, is close to 1. Using the modified voltage in general results in a good approximation of the losses in the system, but it does not capture the water flux and the effect of diffusion on the ionic fluxes. Ideally, the full expression of entropy generation should be used to guide the improvements of the system, but if a simpler expression is required, only the modified voltage expression should be used because the actual voltage will result in poor estimates.
2.9 Conclusions

In this chapter, we have looked at entropy generation in an ED system and studied its variation with salinity. The second-law efficiency was written as the product of current and voltage utilization rates. A useful voltage was defined, and the different sources of losses were characterized. We also linked voltage drops to entropy generation and investigated whether voltage drops can be used to approximate system losses.

The major conclusions from this work are the following:

1. At low salinity, most of the entropy is generated inside the fluid channels. In this case, efforts to decrease energy consumption should be focused on transport in the channels.

2. At high salinity, most of the entropy is generated inside the membranes. Decreasing the membrane electrical resistance is key to better performance at high salinity.

3. Thinner membranes can decrease entropy generation and energy consumption. However, thinner membranes also decrease the resistances to diffusion and osmosis, which means that the overall effect is beneficial only when the driving
forces for these modes of transport are small, or when the membranes are very resistant to the passage of co-ions and water.

4. At high enough current density, most of the entropy is generated from salt and water transport, and not through viscous losses.

5. Given a specified volumetric flow rate, there exists an optimal channel height that minimizes the local entropy generation from transport and viscous effects.

6. Second-law efficiency is maximized, and specific entropy generation due to salt and water transport is minimized, at a voltage slightly larger than the useful voltage, with higher concentration differences requiring larger voltages. However, from a total energy efficiency perspective, the optimal voltage should minimize total entropy generation, including that from viscous losses.

7. A modified voltage which approximates the complete driving force to salt transport should be used in approximating entropy generation. These approximations are only valid at high enough current when osmosis and diffusion become relatively less important.
Chapter 3

Optimal design and operation of electrodialysis for brackish-water desalination and for high-salinity brine concentration

3.1 Introduction

Despite the large number of studies published on ED, only a small number of these has analyzed the optimal design and operation of ED systems, with the bulk of the work being focused on brackish-water desalination. Select studies on the optimal design and operation of ED systems are described below.

Sonin and Isaacson [41] presented a dimensional analysis of a general electrochemical system where fluid flow enhanced the limiting current density. They presented two conditions for optimal hydrodynamic design, which they defined as the choice of the channel geometry and the flow speed in the channels. The first condition required operating at a low-enough current density such that the system is operated without concentration polarization. The second condition required a velocity low enough for the pumping cost to be much smaller than the capital costs of the system. They
also stated that the channel height should always be minimized. They applied this dimensional analysis to the example of brackish-water ED to determine the optimal spacer design and to identify areas for improvement.

Hattenbach et al. [42] studied the effects of the flow velocity and the channel height on the cost of electrodialysis. They reported that velocity affected the pumping power and the limiting current density while the channel height affected both the pumping power and the ED stack power. The current was always set to 70% of the limiting current density, so that the velocity set the operating current and the required membrane area. They concluded that the channel height should be minimized, and they specified a range of velocities that minimized the total cost.

Nikonenko et al. [43] minimized the system cost by varying the channel height and the stack voltage, but they fixed the length of the system and did not vary the velocity as an independent variable. They concluded that the channel height should be small and that the velocity should be large so that the required area and the ED power consumption are decreased.

Lee et al. [12] set the applied current density to a fixed fraction of the limiting current density. They concluded that the cost of desalination of brackish water using ED is minimized at the highest possible limiting current density. However, as will be shown later in this chapter, this conclusion was reached only because Lee et al. did not include the pumping power in their cost calculation.

Tsiakis et al. [17] accounted for pumping power in their optimization, but they also set the operating current at a fixed fraction of the limiting current density.

Choi et al. [44] determined the optimal current density based on capital costs, maintenance costs, ED stack power, and pumping power. However, they studied a batch system that operated at a fixed circulating velocity.

While the studies described above have studied the effect of select parameters on the design of ED systems, none of them comprehensively included the effects of all the important variables on the optimal design of ED systems. Thus, important trade-offs between variables were missed. For example, in several studies, the ratio of the applied current density to the limiting current density was kept constant, leading
to the trade-off between ED power consumption and pumping power being poorly captured. Additionally, in some studies, the length of the system or the flow velocity was held constant, limiting the optimization possible. This has led to an incomplete understanding of how ED systems should be designed and operated. In this chapter, we present a set of constraints that allows a fair comparison of the different designs and operating points, and that does not hold any design variables constant, which is essential to fully optimize ED systems, and to reach general conclusions. The approach presented is applied to brackish-water desalination and to high-salinity brine concentration. The constraints needed for a fair comparison between different designs and operating points are discussed in detail in Section 3.2 while the analytical ED models used in our analysis are discussed in Section 3.3.

### 3.2 Constraints for a fair comparison between different designs and operating points

In order to determine the optimal design and operation of an ED system, it is essential to decide on a set of system constraints that results in a fair comparison between the different designs and operating points. In deciding on these constraints, we can think about a general desalination or water treatment system which takes in a fixed amount of feed at a fixed salinity and is required to treat this feed to result in a fixed flow rate of product at a set salinity. Allowing different systems to treat different amounts of feeds with different recoveries or different product quality would result in an unfair comparison between these systems. In this study, we consider two different applications of ED: a) brackish-water desalination which takes a feed at 3 g/kg, and desalinates it to a product at 0.35 g/kg with a recovery of 80%; and b) high-salinity brine concentration which takes in seawater-desalination brine at 70 g/kg (e.g., the discharge from reverse osmosis or multi-stage flash) and concentrates it to 200 g/kg such that the diluted stream leaves at 35 g/kg, which represents the salinity of seawater. We note that setting the inlet and outlet stream salinities also sets the
recovery, which in this case is around 21%.

Figure 3-1 shows the configurations used and the specified inlet and outlet salinities. In the brackish-water application, the brine is recirculated to ensure high recovery. In addition, the channel height and the flow rate in the concentrate and diluate channels are the same. These two constraints determine the amount of brine that is recirculated. A species balance is performed where mixing occurs to calculate the concentrate salinity at the stack inlet. In the brine-concentration application, the channel height is the same in the two channels, but the flow rates need to be different to result in the set recovery ratio. Additional details on the configurations used are presented in B.8.

![Diagram of brackish-water desalination and high-salinity brine concentration configurations.]

Figure 3-1: Configurations and salinities used in the two cases studied.

After setting the general constraints for a fair comparison, we look at the variables that influence the cost and performance of the system. To better understand the effect of the design and operation of the system on its energetic performance, we first study the different designs and operating points at a fixed system size, i.e., a fixed total membrane area. We assume that the fixed costs of the system are directly proportional to the membrane area, which means that fixing the membrane area sets the fixed costs of the system. This condition means that, when comparing different systems with the same area, it is only important to study their power consumption.
The performance and cost of an ED system are fully determined by the following variables: the feed and product salinities, $S_{\text{feed}}$ and $S_{\text{product}}$, the feed and product flow rates, $Q_{\text{feed}}$ and $Q_{\text{product}}$, the cell-pair area, $A$, the length of the stack, $L$, the width of the stack, $W$, the number of cell pairs, $N_{cp}$, the product flow velocity at the outlet, $v$, the channel height (the distance between two membranes), $h$, and the applied voltage, $V$, with some of these variables being dependent on others in the set. These variables are shown in Fig. 3-2. We note that membrane properties affect the system performance and cost, and should ideally be considered in the optimization of system performance. In this chapter, however, we use only one set of ion-exchange membranes for each application, and we focus on the analysis of the design and operation variables listed above.

![Diagram of a cell pair and a stack of cell pairs.](image)

**Figure 3-2:** Schematic diagrams of a cell pair and a stack of $N_{cp}$ cell pairs. $V$ is the applied voltage, $L$ is the stack length, $W$ is the stack width, and $h$ is the channel height.

We start by reiterating that the inlet and outlet flow rates and salinities are set by the application and will be the same for all the systems studied in each of the two applications. In addition, we first study the operation of systems with the same area. This leaves us with the following set of variables: $\{L, W, N_{cp}, v, h, V\}$. Further, we note that when the following variables are set, $\{L, W, N_{cp}, v, h\}$, only one voltage results in the required product salinity, which means that the voltage can be considered as a dependent variable and does need to be considered as an operating variable.
The stack power consumption can be expressed as:

\[ P_{\text{stack}} = V_{\text{tot}} i_{\text{avg}} A_{\text{cp}} \]  \hspace{1cm} (3.1)

where \( V_{\text{tot}} \) is the total applied voltage, \( i_{\text{avg}} \) is the area-averaged current density, and \( A_{\text{cp}} \) is the cell-pair area. For a system with one cell pair, \( V_{\text{tot}} = V_{\text{cp}}, A_{\text{cp}} = LW_{\text{tot}} \), and the stack power consumption is

\[ P_{\text{stack}} = V_{\text{tot}} i_{\text{avg}} A_{\text{cp}} = V_{\text{cp}} i_{\text{avg}} LW_{\text{tot}} \]  \hspace{1cm} (3.2)

For a system with \( N_{\text{cp}} \) cell pairs, \( V_{\text{tot}} = N_{\text{cp}} V_{\text{cp}}, A_{\text{cp}} = LW_{\text{cp}} \), and the power consumption is

\[ P_{\text{stack}} = V_{\text{tot}} i_{\text{avg}} A_{\text{cp}} = N_{\text{cp}} V_{\text{cp}} i_{\text{avg}} LW_{\text{cp}} \]  \hspace{1cm} (3.3)

Equations 3.2 and 3.3 show that, as long as \( W_{\text{tot}} = WN_{\text{cp}} \), the number of cell pairs does not change the power consumption. The number of cell pairs, \( N_{\text{cp}} \), contributes to the power consumption either through the voltage or through the cell-pair area. If the electric circuits of the two cases are analyzed, it can be shown that the system with \( N_{\text{cp}} \) cell pairs places the cell pairs in series, whereas the system with one cell pair effectively places \( N_{\text{cp}} \) cell pairs in parallel, such that the current density in the two cases is the same.

Combining \( W \) and \( N_{\text{cp}} \) into one variable results in the system performance depending only on the following variables: \( \{L, N_{\text{cp}} W, v, h\} \). These four variables are interdependent, such that only two of them can be independent. We can write the following expression for the product flow rate:

\[ Q_{\text{product}} = vh \left( N_{\text{cp}} W \right) \]  \hspace{1cm} (3.4)

and the following expression for the total cell-pair area:

\[ A = L \left( N_{\text{cp}} W \right) \]  \hspace{1cm} (3.5)
We initially considered setting the length and width of the system as the independent variables, but results showed that the best independent variables to vary were the channel height and the flow velocity because they have the strongest direct effects on the power consumption. The stack power consumption strongly depends on the channel height, and the pumping power depends strongly on the velocity.

In summary, for a system of fixed area, we study the effects of the velocity and the channel height on the total power consumption. Setting these two independent variables fully determines the system design and operation as discussed in detail in this section. After studying the design and operation of a system of fixed area, we move towards modeling the costs of the different system sizes (each operated at the optimal channel height and velocity) to be able to find the optimal system size. In addition, all of the results in this work are normalized to systems resulting in 1 m$^3$/s of product. This normalization allows calculation of the system size, power consumption, and cost required for any capacity of production, with the design and operation variables such as the channel height, the velocity, and the length left unchanged for different production capacities.

3.3 Modeling

The modeling required to calculate the costs associated with an ED system consists of two parts. The first is the prediction of the performance of the electrodialysis system under different designs and operating conditions, and the second is the determination of the cost of these systems.

3.3.1 Modeling electrodialysis

The main goal of the electrodialysis model is to calculate the current density and the salt and water fluxes that result from an applied voltage. The voltage can be related to the current density by dividing the electric circuit into several resistances.
and electric potential drops in series:

\[ V_{cp} = (r_{bulk,C} + r_{bulk,D}) i + \Delta \Phi_{CEM} + \Delta \Phi_{AEM} + \sum_{j=1}^{4} \Delta \Phi_{film,j} \]  

(3.6)

where \( i \) is the current density. \( r_{bulk,C} \) and \( r_{bulk,D} \) are the bulk resistances in the concentrate and diluate channels, respectively. The bulk resistances are calculated from experimental data on conductivity [45-47]. \( \Delta \Phi_{CEM} \) and \( \Delta \Phi_{AEM} \) are the electric potential drops across the membranes, including the associated Donnan potentials at each interface, and \( \Delta \Phi_{film,j} \) is the electric potential drop in each of the four diffusion films between the membrane and the bulk.

To include the effect of the velocity on the performance of electrodialysis, the stagnant film model is used, and the thickness of the diffusion film, \( \delta \), is calculated from the Sherwood number correlation developed by Kuroda et al. [48], as presented in B.1. The concentration and electric potential profiles inside the diffusion films are calculated using the Maxwell-Stefan model as described in B.3. These profiles include the concentration in the solution at each membrane interface.

The membranes characterized by Kraaijeveld et al. [5] are only appropriate for brackish-water applications, and, as a result, the Maxwell-Stefan-based model is only used to predict the transport of salt and water through the membranes in the brackish-water desalination case. The details of this model have been laid out in previous studies [5,49], and the major points of the model are summarized in B.4. In modeling high-salinity brine concentration, the model developed by Fidaleo and Moresi [26] is used with coefficients measured by McGovern et al. [4] at high salinity. The major points of this model are summarized in B.5. One of the outputs of these models is the current density, which is used in the calculation of the stack power consumption.

The calculated salt and water fluxes are used to modify the quantities of salt and water flowing through each channel. The electrodialysis stack is discretized and the finite-difference method is used to maintain a species balance, as described in B.8.

In addition to predicting the performance of an electrodialysis stack, we need to calculate the pumping power required to ensure the flow of the solutions through the
stack. A pumping efficiency of 70% is assumed, and the friction factor correlation developed by Kuroda et al. [48] is used to ensure coherence between the effects of the spacer on mass-transfer enhancement and friction losses. The details of these calculations are presented in B.1.

### 3.3.2 Cost modeling

To calculate the cost of an electrodialysis system, the fixed costs are assumed to be proportional to the system size represented by the effective cell-pair area (not covered by the spacer). In addition, it is assumed that the operating costs consist only of the energy costs associated with the stack power consumption and the pumping power. As a result of these two assumptions, we can express the total cost of the system as follows:

\[
C = K_m A + K_e P
\]  

(3.7)

where \(K_m\) is the fixed cost per unit effective cell-pair area per unit time, \(A\) is the effective cell-pair area, \(K_e\) is the cost of electricity, and \(P\) is the total power consumption, which is the sum of stack power consumption and pumping power. The minimization of the total cost is a trade-off between the fixed costs and the operating costs. Equation 3.7 can be divided by the cost of electricity, \(K_e\) to get a normalized cost:

\[
c^* = \frac{C}{K_e} = r A + P
\]  

(3.8)

where \(r\) is the cost ratio:

\[
r = \frac{K_m}{K_e}
\]  

(3.9)

Equation 3.8 shows that, given the optimal power consumption at each system size, the determination of the optimal system size is only a function of the ratio of the two cost factors, \(r\). In addition, the normalized cost can be calculated without requiring specific values of \(K_m\) and \(K_e\). This is beneficial because these costs vary greatly by location, and it is difficult to determine with any certainty what value of \(K_m\) should be used. In this chapter, we focus on the framework that should be used for
the optimization of ED systems, and we study the different trade-offs that need to be understood in the optimization of these systems. The results of this study are general, and can be used for any values of $K_m$ and $K_e$.

As an example of how the normalization results presented in the following sections should be interpreted, we provide a sample calculation of the cost ratio, $r$. Table 3.1 shows typical values of the variables needed to calculate the cost ratio. The interest rate, $i$, and the plant life, $\tau$, are required to amortize the capital expenses:

$$K_m = \frac{K_{m,0}}{\frac{i}{\tau} \left[1 - \left(\frac{1}{1+i}\right)^\tau\right]} \quad (3.10)$$

where $K_{m,0}$ is the present value of the equipment costs.

Table 3.1: The variables used in the cost modeling examples in the following sections [4]. The resulting cost ratio is $r = 134 \text{ W/m}^2$.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost of electricity, $K_e$</td>
<td>$0.15$/kWh</td>
</tr>
<tr>
<td>Present value of equipment costs, $K_{m,0}$</td>
<td>$1,500$/m$^2$ effective cell pair</td>
</tr>
<tr>
<td>Rate of return on capital, $i$</td>
<td>10%</td>
</tr>
<tr>
<td>Plant life, $\tau$</td>
<td>20 years</td>
</tr>
</tbody>
</table>

3.4 Design and operation of a system of fixed size:  
Effect of channel height and fluid velocity on energy consumption

In this section, we study the effect of the channel height and the fluid velocity on the power consumption of systems of fixed membrane area. It must be noted here that, as a result of our assumption that the fixed costs of the system are proportional to the membrane area (Section 3.3.2), minimizing the power consumption of a system
of fixed size also results in the lowest possible total costs.

Figure 3-3 shows the effect of channel height and velocity on the energy consumption of a fixed-size ED system, where the energy consumption is obtained by dividing the power consumption by the volumetric flow rate of the product.

### 3.4.1 Effect of channel height on energy consumption

We focus first on the effect of the channel height. Equation 3.6 shows that the stack energy consumption increases with the channel height, given that the channel resistances are directly proportional to their height. In addition, Fig. 3-3 shows that the lowest channel height results in the lowest total energy consumption. Even though going to a smaller channel height results in higher pumping power, the velocity can be decreased enough to make the increase in pumping power smaller than the decrease in stack power consumption. This is consistent with previous studies in the literature [41, 42]. Whenever the power consumption is reported to be minimized at a value of channel height that is higher than the lowest value possible, it is because the velocity is not treated as an independent variable, and the increase in pumping power is larger than the decrease in stack power consumption [43].

### 3.4.2 Effect of fluid velocity on energy consumption

As shown in Fig. 3-3, high velocities result in significant pumping requirements, which increases the total energy consumption. This effect pushes the optimal velocity downwards. The total energy consumption decreases with decreasing velocity until low velocities are reached and the stack energy consumption increases significantly.

Fluid velocity affects the stack consumption through its effect on the mass transfer coefficient, or the thickness of the diffusion film, $\delta$, in the stagnant film model, where a higher velocity leads to a thinner diffusion film. As shown in Fig. 3-4, a larger diffusion film results in stronger concentration polarization, which has two negative effects. The first is that, for the same current density, a thicker diffusion film results in a larger change in concentration between the bulk concentration and the concentration at the
interface. This is due to the fact that the slope of the concentration inside the diffusion layer is directly proportional to the current density. The change in concentration at the membrane interface, $\Delta c$, that is associated with having a different diffusion layer thickness is shown in Fig. 3-4. This effect results in a larger trans-membrane concentration difference, which leads to stronger diffusion and osmosis. With more osmosis and diffusion, more salt needs to be transported to result in the set outlet salinities. This results in a higher total current, which is directly proportional to the amount of salt transported. The second effect is that, in the diluate channel, a thicker diffusion film results in a lower concentration inside the film, which increases the stack resistance. The difference between the two concentration profiles is shown in red in Fig. 3-4. The increase in stack resistance becomes very significant when the system is operated at close to limiting current density, and the concentration close
to the membrane becomes close to zero. This effect is shown in the $i-V$ curves at two different velocities in Fig. 3-5. The concentrations are set to those at the end of the stack and are not varied. A higher voltage needs to be applied to result in the same current density when the velocity is lower. In the results reported in Fig. 3-3, a current density of around 400 A/m$^2$ is required to result in the specified outlet salinity. At that current density, the voltage needs to be around 5% higher for the lower velocity. In addition, the higher velocity allows the system to reach a higher limiting current density, as evidenced by the difference between the two asymptotes.

![Figure 3-4: Schematic diagram showing the effect of the diffusion film thickness, $\delta$, on concentration polarization for two velocities under the same current density.](image)

Table 3.2 shows the changes in stack power, voltage, current, and resistance that result from going from a velocity of 1 cm/s to a velocity of 0.1 cm/s, and summarizes the causes for these changes.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Change</th>
<th>Cause of the change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stack power consumption, $P_{\text{stack}}$</td>
<td>+6.6%</td>
<td>increase in voltage and current</td>
</tr>
<tr>
<td>Voltage, $V$</td>
<td>+5.2%</td>
<td>increase in current and resistance</td>
</tr>
<tr>
<td>Total current, $I$</td>
<td>+1.3%</td>
<td>increase in diffusion and osmosis</td>
</tr>
<tr>
<td>Stack resistance, $\Omega$</td>
<td>+3.9%</td>
<td>lower concentrations inside films</td>
</tr>
</tbody>
</table>

Table 3.2: Effect of decreasing the velocity from 1 cm/s to 0.1 cm/s for the full system with $h = 0.5$ mm, and with the system size that is modeled in Fig. 3-3.
3.4.3 Optimal channel height and velocity for high-salinity brine concentration and brackish-water desalination

The design and operation of a brackish-water desalination system should follow the same guidelines as those described above for the brine concentration case: as shown in Fig. 3-6, the channel height should be made as small as possible, and the velocity should be just high enough to decrease the effect of concentration polarization. The velocity should be increased until the increase in the required pumping power becomes equal to the decrease in stack power consumption.

We notice two differences between the two applications. The first is that, for brackish-water desalination, the lowest achievable velocity is dictated by the limiting current density, which explains why the curves do not go below relatively high velocities, and why the thickness of \( h = 1 \) mm cannot be used for this system size and this velocity range. The second is that the increase in stack power consumption close to the limiting current is not as high as that in the brine concentration case. This
is because the total stack resistance is higher in brackish-water desalination and is not strongly influenced by the diffusion film. In addition, the velocity in the brackish application is higher, and the resulting diffusion film is thinner, which means that the increase in film resistance has a smaller effect on the total stack resistance.

Figure 3-6: Effect of channel height and velocity on the energy consumption of a fixed-size ED system for brackish-water desalination. The solid line indicates the total energy consumption, the dashed line indicates the stack energy consumption, and the difference between the two lines is the pumping energy consumption. The simulated membrane area is the one that leads to the lowest total cost in the Section 3.5.

3.5 Minimizing the total cost of ED for brackish-water desalination: Trade-off between ED system size, stack power, and pumping power

The previous section discussed how to design and operate a system of fixed size. In this section, we look at how the system size should be chosen to minimize the total cost of brackish-water ED desalination. This is primarily achieved by finding
the average current density that accounts for the trade-off between ED stack capital costs, ED stack power consumption, and pumping power. Increasing the average current density decreases the ED capital costs while increasing ED operating costs. Given that brackish-water ED is constrained by low limiting current densities, the fluid velocity within the stack needs to be increased to achieve higher limiting current densities. This results in pumping power playing an important role in the trade-off that determines the optimal system size. The details of this analysis are presented in the paragraphs below.

3.5.1 Choice of channel height and velocity

Equation 3.8 shows that, given the minimum power consumption at each membrane area, only the ratio $r$ is required to determine the optimal system size. For each system size, the channel height and the velocity have to be set to result in the lowest power consumption. As mentioned in Section 3.4, the channel height should be set to the smallest value achievable. This minimum is limited by practical difficulties in designing sealing frames and spacers [42]. For the following results, the channel height is set to 0.5 mm, which is a thickness already used in actual systems [4]. In addition, for each system size, the velocity is set such that the total power consumption is minimized.

3.5.2 Effect of the average current density on system costs

Figure 3-7 shows the variation of the normalized cost of water production with the average current density. Average current density can be thought of as a measure of the inverse of the system size. As the system size decreases, the same amount of salt needs to be removed through a smaller area, which results in a higher average current density. This explains why fixed costs decrease as the average current density increases. As predicted by Eq. 3.6, the stack power consumption increases with the average current density. The fixed costs of the system dominate at low current density, which pushes the system operation to higher current densities. Due to the
low concentration in the diluate channel, the limiting current density is low, and the velocity needs to be increased to increase the limiting current density, as shown in Fig. 3-5. The increased limiting current density comes with the cost of a higher pumping power, which determines how much the operating current can be increased before the increase in energy costs starts outweighing the decrease in fixed costs. It is this trade-off between fixed costs and energy costs (both stack and pumping energy) that determines the optimal operating current density and system size.

Figure 3-7: Normalized cost of a brackish-water desalination system which desalinates a feed from 3 g/kg at 80% recovery and produces 1 m³/s of product at 0.35 g/kg. r = 134 W/m².

Figure 3-8 shows the variation of the applied current density and the limiting current density at the outlet of the ED stack, as well as their ratio, with the average current density. As expected, the applied current density at the outlet of the system varies linearly with the average current density. The current density at the outlet is much smaller than the average given that it is the smallest current density anywhere in the stack because it occurs at the point with the lowest diluate concentration. The limiting current density must increase with the average current density in order
to allow the higher current densities to be reached. We note that applied current density is only equal to the limiting current density for systems with an average current density higher than around 200 A/m². For systems with a smaller average current density, more pumping power is spent than is necessary to achieve a limiting current density equal to the applied current density. This is the case because the velocity in those cases is small, and the excess pumping power is smaller than the savings in stack power consumption due to operating away from the limiting current regime, as explained in Section 3.4. As the applied current density increases, the velocity needs to be increased to result in a limiting current density that is at least equal to the applied current density. At these high velocities, the savings in ED stack consumption no longer justify the excess pumping power, and the velocity is just high enough to allow the operation under the applied current. As explained in Section 3.4, this trade-off between pumping power and stack power consumption determines how far from the limiting current density the system should be operated. For a cost ratio
equal to 134 W/m², the applied current density at the outlet of the stack is equal to around 94% of the limiting current density. This number is strongly dependent on the relationship between pumping power and stack power consumption, which is a result of the spacer design and the resulting Sherwood number and friction factor relations.

3.5.3 Impact of optimization of velocity and system size on system costs

In this section, we highlight the benefit of optimization by looking at the impact that deviations of velocity and system size from their optimal values have on system costs. In Table 3.3, the increase in cost due to improper operation and sizing is quantified. First, we look at the effect that deviations in velocity have on the final costs of the system. For every system size, the velocity is set to 50% larger than the optimal velocity at that size. The minimum cost is 6% higher than that obtained using the optimal velocity. At a velocity 50% lower than the optimal velocity, the cost increases by 33%, a very significant increase. This is because a low velocity results in a low limiting current density, which limits the average current density and leads to unnecessarily large systems.

Next, we look at the effect that deviations in system size have on the final costs. Using the cost numbers presented in Fig. 3-7, the cost increases by 9% when a system that is oversized by 50% is used. When a system 40% smaller than the optimal size is used, the cost increases by 38%, a significant increase. In addition, these numbers show the effect of having only one variable being suboptimal, with the other being optimized. We can expect the cost numbers to be even worse when no optimization is performed. This shows the importance of choosing the optimal velocity and system size for the minimization of the cost of brackish-water desalination.
Table 3.3: Effect of operating away from the optimal velocity and the optimal system size in the brackish-water desalination application. $r = 134 \text{ W/m}^2$.

<table>
<thead>
<tr>
<th>Deviation from the optimal</th>
<th>Resulting increase in cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Velocity increase of 50%</td>
<td>+6%</td>
</tr>
<tr>
<td>Velocity decrease of 50%</td>
<td>+33%</td>
</tr>
<tr>
<td>System size increase of 50%</td>
<td>+9%</td>
</tr>
<tr>
<td>System size decrease of 40%</td>
<td>+38%</td>
</tr>
</tbody>
</table>

3.5.4 Optimal operating conditions at different cost ratios

The results shown above are for a cost ratio equal to 134 W/m$^2$. Given that the minimum power consumption was calculated for a range of system sizes, the cost ratio can be varied, and the optimal operating points can be determined at each cost ratio. Figure 3-9(a) shows the variation of the optimal effective cell-pair area and average current density with the cost ratio, $r$. As expected, as the ratio increases, the relative importance of the fixed costs increases, and the optimal system size becomes smaller. As shown in Fig. 3-9(b), making the system smaller requires increasing the limiting current density, which results in a higher velocity at higher cost ratios. Equations 3.4 and 3.5 can be combined by eliminating $N_{cp} W$ to result in the following equation:

$$L = \frac{Ahv}{Q_{product}}$$

Equation 3.11 shows that the length, $L$, is the product of the velocity, $v$, and the area, $A$. Figure 3-9(b) shows that the decreasing area and the increasing velocity result in an increase in the optimal length with the cost ratio. We note that the membrane areas and the lengths reported are the effective area and length, and that real systems usually employ spacers which result in only around 65% of the total area being used effectively [4, 50, 51], so we expect the physical membrane area of these systems to be approximately 50% larger than the effective values reported above. We also note that the reported cost modeling is not dependent on the spacer shadow factor because
it uses the effective cell-pair area. By using the effective area in the cost modeling, we ensure that the results presented in this work are not dependent on the spacer shadow factor. For a given shadow factor, the total membrane area and the physical stack length can be calculated from the effective values presented above.

Figure 3-10 shows that the ratio of the applied current density to the limiting current density increases with increasing cost ratio. This can be explained by the increase of the average current density with increasing cost ratio (shown in Fig. 3-9(a)), and the analysis of the trends reported in Fig. 3-8. In addition, the optimal limiting-current ratio strongly depends on the cost ratio, and it is not sufficient to use a general ratio as is commonly done in the literature.

Finally, the normalized cost of water production can be expressed as a function of the cost ratio $r$. For any cost ratio (calculated based on local cost numbers), Fig. 3-11 gives the cost of producing 1 m$^3$/s of water at 0.35 g/kg and at a recovery of 80% starting with a feed at 3 g/kg. The normalized cost is then easily multiplied by the local cost of electricity expressed in $$/kWh to give the actual cost of water production, which for the cost numbers reported in Table 3.1 is around $0.3 per m$^3$ of product.
Figure 3-9: Effect of the cost ratio on the system size and on design and operation variables for brackish-water desalination.
Figure 3-10: Variation of the ratio of operating current to limiting current with the cost ratio for brackish-water desalination.

Figure 3-11: Variation of the normalized cost with the cost ratio for brackish-water desalination.
3.6 Minimizing the total cost of ED for high-salinity brine concentration: Limited effect of pumping

In this section, we study the cost minimization of ED for high-salinity brine concentration. As in Section 3.5, the channel height is set to 0.5 mm, and, for every system size, the velocity is chosen such that the power consumption is minimized.

3.6.1 Effect of average current density on system costs

Figure 3-12 shows the variation of the costs associated with brine concentration with the average current density, which is inversely proportional to the system size. The fixed costs, which are proportional to the system size, are inversely proportional to the average current density. In addition, the stack power consumption is linearly proportional to the average current density. This is consistent with the fact that the dominant resistance at high salinity is that of the membranes [49], which is assumed constant. Further, the pumping cost is negligible for all system sizes. As shown in Fig. 3-13, the limiting current density is fairly high because of the high concentrations, and, as a result, high velocities are not needed to increase the limiting current density. The trade-off between fixed costs and stack energy costs is what determines the optimal system size and optimal average current density without any influence from the pumping costs.

3.6.2 Impact of optimization of velocity and system size on system costs

In this section, we highlight the benefit of optimization by looking at the impact that deviations of velocity and system size from their optimal values have on system costs. In Table 3.4, the increase in cost due to improper operation and sizing is quantified. It can be seen that, in brine concentration, velocity affects the system cost much less than in brackish-water desalination (Table 3.3). A 50% deviation in velocity from the optimal value results in only a 2%-3% increase in the system cost.
Figure 3-12: Normalized cost of a high-salinity desalination system which concentrates a feed of 70 g/kg and produced 1 m³/s of product at 200 g/kg.

This follows from the fact that, in brine concentration, velocity has a low effect on ED stack power consumption, and, near the optimal velocity, the pumping power is negligible, as shown in Fig. 3-12. That said, even a 2% increase in total cost may be significant when designing large plants. System size, however, significantly affects the costs. When a system is undersized by 50%, the cost increases by 22%. Oversizing increases costs to a lesser extent, with a system 50% larger than optimal increasing costs by 7%. These numbers show that it is important to properly size an ED brine-concentration system and to operate it under the optimal average current density, and that undersizing a system (i.e., operating under a higher than optimal current density) has a higher penalty on costs than oversizing.

3.6.3 Optimal operating conditions at different cost ratios

Figure 3-14(a) shows the variation of the optimal cell-pair area and the average current density with the cost ratio, \( r \). As discussed in Section 3.5, the higher cost ratio
increases the relative importance of fixed costs, and pushes the optimum towards lower areas and higher current densities. The required cell-pair area and average current density are both higher in brine concentration than in brackish-water desalination because of the much higher quantity of salt to be transported in taking a feed from 70 g/kg to 200 g/kg than in taking a feed from 3 g/kg to 0.35 g/kg.

Figure 3-14(b) shows the variation of the velocity and stack length with the cost ratio. The velocity here is at the outlet of the concentrate, and, given the low system recovery of around 21%, the velocity at the outlet of the diluate channel is around 4 times higher. Given the high water transport in brine concentration, the flow rates change significantly over the length of the system. This variation in velocity should be kept in mind when interpreting these results. The optimal velocity increases with the cost ratio. At higher cost ratios, the average current density is higher, and, as a result, the relative importance of stack power consumption compared to pumping power is higher. This pushes the optimal velocity upwards as explained in Section 3.4.
Table 3.4: Effect of operating away from the optimal velocity and the optimal system size in the brine-concentration application. \( r = 134 \text{ W/m}^2 \).

<table>
<thead>
<tr>
<th>Deviation from the optimal</th>
<th>Resulting increase in cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Velocity increase of 50%</td>
<td>+2%</td>
</tr>
<tr>
<td>Velocity decrease of 50%</td>
<td>+3%</td>
</tr>
<tr>
<td>System size increase of 50%</td>
<td>+7%</td>
</tr>
<tr>
<td>System size decrease of 50%</td>
<td>+22%</td>
</tr>
</tbody>
</table>

The stack length decreases with the cost ratio because the decrease in area is more significant than the increase in velocity, as explained by Eq. 3.11.

Figure 3-15 shows the normalized cost of producing 1 m\(^3\)/s of a saline solution at 200 g/kg at a recovery of 21%, starting with a feed at 70 g/kg. The normalized cost can be multiplied by the local cost of electricity to give the total cost. This set of results serves to generalize the analysis, and allows the estimation of the optimal membrane area, average current density, velocity, length, and cost of brine concentration under different cost scenarios. For the cost numbers presented in Table 3.1, the cost of brine concentration is around $11 per m\(^3\) of product at 200 g/kg.
Figure 3-14: Effect of the cost ratio on the system size and on design and operation variables for high-salinity brine concentration.
3.7 Conclusions

In this chapter, a fair set of constraints was developed to thoroughly study the optimal design and operation of ED systems both for brackish-water desalination and for high-salinity brine concentration. The major conclusions from this work are the following:

1. The channel height should always be minimized. The reduction in the channel height also results in a reduction in stack length, so future improvements that lead to decreasing the channel height will also result in a decrease in the optimal stack length.

2. The optimal velocity is determined by a trade-off between pumping power and ED stack power consumption. It should be small enough to reduce pumping power, but just high enough to increase the limiting current density and to limit concentration polarization.

3. The ratio of the operating current density to the limiting current density in
brackish-water desalination is determined by a trade-off between pumping power and ED stack power consumption. This ratio is dependent on the spacer design and on the cost factors.

4. In the desalination of brackish water, the optimal system size is determined by a trade-off between fixed costs on one end, and pumping power and stack power consumption on the other end.

5. In high-salinity brine concentration, the optimal system size is determined by a trade-off between fixed costs and stack power consumption. Pumping costs are negligible because the system operates far from the limiting current regime.

In addition, optimal values of effective cell-pair area, average current density, velocity, effective stack length, ratio of operating current density to limiting current density, and cost have been presented as a function of the cost ratio, $r$, which includes the effects of the different cost factors that vary greatly with location and possibly with time.
Chapter 4

On the merits of using multi-stage and counterflow electrodialysis for reduced energy consumption

4.1 Introduction

The cost of ED can be decreased through the reduction of its power consumption. One way power consumption can be decreased is by increasing the system size\textsuperscript{1}. The trade-off that exists between the costs related to the system size and the energy costs is well understood, and the choice of system size is determined through cost minimization, as was done in Chapter 3 for the use of ED for brackish-water desalination and high-salinity brine concentration.

\textsuperscript{1}Increasing ED’s system size decreases the power consumption only up to a certain critical size. The increase in area decreases the average salt flux, which reduces the rate of entropy generation, as shown in Eq. 4.6. However, in ED, there are losses in the form of osmosis and diffusion that also increase with the system size. At the critical system size, the marginal increase in area increases the losses due to osmosis and diffusion more than it decreases the losses due to the sought-after salt flux.
4.1.1 Reducing energy consumption using the theorem of equipartition of entropy generation

A less commonly employed concept is that, for heat and mass transfer systems of fixed size, additional operation flexibility can also reduce power consumption. This can be explained by the theorem of equipartition of entropy generation, which was first introduced by Tondeur and Kvaalen [24]. This theorem states that, given a fixed duty (total quantity to be transported) and a fixed system size, the optimal configuration is that which minimizes the spatial or temporal variance in the rate of entropy generation. A more physical way of thinking about this concept is by considering the distribution of the available area. By better distributing the rate of entropy generation, the driving force is also better distributed (when flux is a linear function of the driving force), and more area is allocated to the part of the system where the driving force is higher. Thus, in a poorly equipartitioned system, part of the available area is wasted on sections where the driving force is very small, resulting in low fluxes.

4.1.2 Equipartition through the use of multiple stages and of counterflow operation

One way to achieve better equipartition of entropy generation is by operating the system under multiple stages. Staging results in additional degrees of freedom, which, even at a fixed system size, can lead to improvements in the system’s energy efficiency. The idea of multi-staging has been previously applied to multiple desalination technologies such as humidification-dehumidification [52-55], membrane distillation [56], and reverse osmosis [57]. In the case of ED, each stage can be operated at a different voltage to better control the distribution of the flux. This is referred to in the literature as ‘electric staging’ of ED systems. In this chapter, we use the term ‘multi-staging’ to exclusively imply ‘electric staging’.

Another way to better distribute the driving force over the available area is by operating a heat or mass exchanger in a counterflow configuration. In the case of ED,
this can serve to better distribute the concentration profiles over the length of the system, which might lead to improvements to the system’s energy consumption.

Few studies have looked at the operation of ED under multiple voltages or in counterflow configurations. Tsiakis and Papageorgiou [17] modeled ED systems with multiple hydraulic and electric stages. The conditions at each stage were optimized numerically to minimize total system costs. Turek [58] studied a counterflow two-stage ED seawater desalination system and reported energy and cost numbers. Ryabtsev et al. [59] implemented a two-stage desalination system. The first stage was operated under a constant current density, and the second stage was operated under a constant voltage. Tanaka [60] presented a multi-stage ED computer model that combines multiple stacks in series. McGovern et al. [61, 62] used a counterflow ED system coupled with reverse osmosis to decrease the costs of water production.

Even though these ideas have been previously presented in the literature, there has not been a detailed study on how to make the best use of multi-stage ED, and on the effect of these configurations on the performance of ED systems. In particular, there has been no mention of how current densities (or voltages) in each stage should be chosen, or how two-stage ED compares to single-stage ED, and how counterflow ED compares to parallel-flow ED.

In this chapter, we study possible improvements to the energy efficiency of electrodialysis through the use of two electric stages, and through the operation in counterflow configuration. We start by introducing some ideas from the literature that are necessary to explain the results that follow, such as the theorem of equipartition of entropy generation [24] and the concept of the equipartition factor [63]. We then look at how a two-stage ED system should be operated for optimal energy efficiency. In addition, we quantify the energetic benefits of two-staging in cost-effective brackish-water desalination and high-salinity brine concentration ED systems. Finally, we study the effect of operating in counterflow on these two applications.
4.2 Equipartition of entropy generation

In this section, we present some concepts that are necessary to interpret the results presented in this study. A good starting point is to present the motivation behind trying to reduce the rate of entropy generation. For a desalination system with fixed inlet and outlet flow rates and salinities, reducing the rate of entropy generation reduces the system's power consumption:

\[ P = P_{\text{least}} + T_0 \dot{S}_{\text{gen}} \]  

where the least power, \( P_{\text{least}} \), is only a function of the inlet and outlet states and is fixed. \( T_0 \) is the temperature (of the environment and of the system), and \( \dot{S}_{\text{gen}} \) is the rate of entropy generation. The derivation of the equation above involves combining the First and Second Laws of thermodynamics, and can be found in Appendix A.

As mentioned in Section 4.1, an important concept in the reduction of entropy generation is that of equipartition of entropy generation, first introduced by Tondeur and Kvaalen [24]. For a given system size operated continuously at steady state, and for a given total duty, the rate of entropy generation is minimized when its spatial variance is minimized. This theorem can be proven by using the Cauchy-Schwarz inequality when the phenomenological coefficient, \( L \), which is the proportionality constant between the flux and the driving force, is assumed constant in the following relationship:

\[ j = Lf \]  

where \( j \) is the flux and \( f \) is the associated driving force, defined as

\[ f \equiv \nabla \left( \frac{\partial S}{\partial X} \right) \]  

where \( S \) is the entropy, and \( X \) is the quantity being transported (e.g., the number of moles of a species).

The local rate of entropy generation per unit volume is the product of the flux
and the driving force:

$$\dot{S}_{\text{gen}}'' = jf = Lj^2 = \frac{f^2}{L} \tag{4.4}$$

When $L$ is constant, the variance of the rate of entropy generation is minimized when the variance of the driving force and that of the flux are minimized.

Johannessen et al. [64] have shown that, even when $L$ is not constant, the total rate of entropy generation is minimized when the variance of the entropy generation is minimized. In their study, minimizing the variance of the driving force led to a very similar total rate of entropy generation even though the temperature profiles in the heat exchanger were different. The explanation they provide for this result is that the variation of the entropy generation around its minimum is flat.

As a result of the theorem of equipartition of entropy generation, the total rate of entropy generation can be divided into two parts. The first part is the rate that arises if the variance of rate of entropy generation is set to zero, and which Thiel et al. [63] refer to as the rate of entropy generation of the equivalent equipartitioned system, $\dot{S}_{\text{gen, equip}}$. The second part is the rate of entropy generation that arises due to the imbalance in the distribution of the rate of entropy generation, $\dot{S}_{\text{gen, imbalance}}$. We can write:

$$\dot{S}_{\text{gen, total}} = \dot{S}_{\text{gen, equip}} + \dot{S}_{\text{gen, imbalance}} \tag{4.5}$$

For a given transport area, $A$, and a given duty, $J$, which is transported over a distance $h$, $\dot{S}_{\text{gen, equip}}$ is constant. For a constant phenomenological coefficient, $L$, we can write:

$$\dot{S}_{\text{gen, equip}} = \int \dot{S}_{\text{gen}}'' \, dV = j\bar{f}hA = \frac{J^2h}{LA} \tag{4.6}$$

where $\bar{f}$ is the mean driving force, and $\bar{j}$ is the mean flux:

$$\bar{j} = L\bar{f} = \frac{J}{A} \tag{4.7}$$

As a result, for a fixed system size and a fixed phenomenological coefficient, changing the distribution of the flux through better use of operating degrees of freedom only affects the rate of entropy generation due to imbalance, $\dot{S}_{\text{gen, imbalance}}$. 

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The extent of the performance improvement that arises from better operation is captured by the equipartition factor, $\Xi$, as defined by Thiel et al. [63]:

$$\Xi \equiv \frac{\dot{S}_{\text{gen, equip}}}{\dot{S}_{\text{gen, total}}}$$

(4.8)

If a very large fraction of the total rate of entropy generation is simply due to a large mean flux, resulting in a high equipartition factor, no significant improvements to the system performance can be made by better distributing the rate of entropy generation. In other words, even if the system operation is changed to result in zero variance of the rate of entropy generation, the total rate of entropy generation does not change greatly, and the performance is barely affected. A low equipartition factor means that a significant fraction of the total rate of entropy generation is due to a poor distribution of the flux, which means that significant improvements can be made without increasing the system size if the variance is decreased through better operation. We note that it is difficult to calculate the equipartition factor when the phenomenological coefficient is not constant without fully modeling the equipartitioned system.

### 4.2.1 Applying the theorem of equipartition of entropy generation to ED systems

We now apply the objective of equipartition of entropy generation to ED systems. The local rate of entropy generation that arises from the transport of a single species is the product of the species flux and its driving force. For the transport of $n$ species, the rate of entropy generation per unit area can be written as [36, 37, 49]:

$$\dot{S}_{\text{gen}} = \sum_{i}^{n} j_i \Delta \left( \frac{-\mu_i}{T} \right)$$

(4.9)

where $j_i$ is the flux of species $i$, $\mu$ is the electrochemical potential, and $T$ is the absolute temperature. As explained in detail in C, some approximations can be made, and
Eq. 4.9 can be simplified to result in the following expression:

$$\delta' = j_s \left( \frac{F V_{cp} - \Delta \mu_s}{T} \right)$$

(4.10)

where $j_s$ is the salt flux, $F$ is the Faraday constant, $V_{cp}$ is the cell-pair voltage, and $\Delta \mu_s$ is the difference in the salt chemical potential between the concentrate and the diluate. In addition, it is helpful to think about the flux in terms of the current density, which is easier to measure in practical systems:

$$i \approx F j_s$$

(4.11)

where the current utilization rate is assumed to be very close to 1. We note that Eq. 4.10 and Eq. 4.11 are only used to give a clearer picture of how entropy generation can be related to current density and voltage, and that, in the calculated results presented in this chapter, the full expression for entropy generation, Eq. 4.9, is used.

For an electrodialysis system, the quantity transported (or the “duty”) is the total rate of salt transport in mol/s. If the phenomenological coefficient linking the salt flux to the driving force is assumed constant, equipartition of entropy generation would state that the variances of the driving force and the flux need to be minimized. However, in ED $L$ is not constant because the stack resistance can be a strong function of the concentrations, which are changing over the length of the system. When the assumption of a constant $L$ breaks down, no single operating point can at once minimize the variances of the flux, the driving force, and the rate of entropy generation. The effect of a varying $L$ on equipartition of entropy generation in ED is investigated in Section 4.4.

### 4.3 Modeling

In this section, we present summarize the components of the ED models used. In addition, we present the system configuration and constraints, and a brief overview of the solution method.
4.3.1 Local transport

At any location in an ED stack, given the cell-pair voltage and the diluate and concentrate concentrations, we can calculate the local species fluxes and the current density as detailed in Appendix B.

In modeling brackish-water desalination, we use the Maxwell-Stefan-based model developed by Kraaijeveld et al. [5], presented in B.4. The membranes characterized by Kraaijeveld et al. [5] are not suitable for high-salinity applications, so the model developed by Fidaleo and Moresi [26] is used to model the brine-concentration application, as is detailed in B.5.

4.3.2 System constrains and configuration

To be able to compare the power consumption of the different operating points, the system size is held constant. As was done in Chapter 3, the fixed costs of the system are assumed to depend only on its size, represented by the total cell-pair membrane area. In addition, the feed flow rate and salinity, and the product flow rate and salinity are kept constant to allow a fair comparison between the different operating points.

When the area of a single-stage system is fixed, there is only one voltage that results in the set outlet salinities. In a two-stage system, the total available area is divided between two stages, each operated at a different voltage, as shown in Fig. 4-1. Because the total area is fixed, setting the fraction of area that goes into the first stage automatically sets the fraction that goes into the second, resulting in one degree of freedom. By choosing the voltage of the first stage, $V_1$, as the second degree of freedom, the voltage of the second stage, $V_2$, is set because the outlet salinities are fixed.

The degree of brine recirculation is determined by the set recovery. Given that the volumetric flow rates of the two streams are affected by water transport, only the outlet streams of the stack are fixed. For this reason, the system is solved starting at the outlets, and using species balance to build the concentration and current density
profiles to get to the inlets. At the inlets, species balance is performed to check that the solution is correct.

In studying the effect of multi-staging and counterflow operation, it is not necessary to consider pumping power because it can be assumed constant. This is possible because the velocity, length of stack, and channel height are held constant, and entry effects are negligible compared to the pressure loss in the stack, as was shown in Chapter 3. The velocity is fixed to values determined in Chapter 3.

4.4 The optimal operation of a two-stage ED system

Operating a system of fixed total area under two voltages results in two degrees of freedom: the fraction of the area that goes into the first stage, and the voltage of the first-stage. In this section, we look at how these two variables should be chosen to result in the best energetic performance.

4.4.1 Effect of the voltage of the first stage on power consumption

First, we study the effect of $V_1$ on the energy consumption of the system. This is done by dividing the total length equally between the two stages. In this section, a feed of brackish water at 3 g/kg is desalinated to result in a product at 0.35 g/kg at a recovery of 80%. To magnify the effect of two-staging, a large system is modeled: the stack length is 5 m, double the cost-effective value calculated for this application at a cost ratio of 134 W/m$^2$ in Chapter 3. A channel height value of 0.5 mm and a velocity of 18 cm/s are also taken from Chapter 3.
As shown in Fig. 4-2(a), there exists a value of the first-stage voltage that minimizes the stack power consumption. As shown in Fig. 4-2(b), this is the same value that minimizes the total rate of entropy generation, as expected from Eq. 4.1. For this case, the reduction in power consumption is around 5% compared to the single-stage system.

As shown in Fig. 4-3, the voltage of the first stage affects the performance of the system by changing the distribution of the current density. As the first-stage voltage increases, more salt is transported in the first stage and less in the second. The voltage that yields the lowest power consumption, indicated by the vertical dashed line, yields a better distribution of current density between the first and the second stage than the single-stage system represented by a normalized first-stage voltage of 1. This also yields a better spatial distribution of the rate of entropy generation. In fact, as shown in Fig. 4-4, the voltage that minimizes power consumption and total entropy generation, $V_{1,P}$, is equal to that which minimizes the variance of the rate of entropy generation, $V_{1,\text{Var}(\dot{\varsigma}_{\text{gen}})}^*$, and is higher than the first-stage voltage that minimizes the variance of the current density, $V_{1,\text{Var}(\dot{i})}^*$:

$$V_{1,P} = V_{1,\text{Var}(\dot{\varsigma}_{\text{gen}})}^* > V_{1,\text{Var}(\dot{i})}^*$$

where the first-stage voltage is normalized by the single-stage voltage:

$$V_1^* = \frac{V_1}{V_{\text{single}}} \quad (4.12)$$

Thus, a single-stage system is that corresponding to a normalized first-stage voltage of 1.

This result is consistent with the conclusion by Johannessen et al. [64] that, for a system with a varying phenomenological coefficient, the rate of entropy generation is what fundamentally needs to be equipartitioned, and not the flux or the driving force. In this case, minimization of the variance of the current density results in a power consumption that is 1.6% higher than the optimal. The variances of the three quantities are minimized at the same operating point only when the phenomenological
Figure 4-2: The effect of the voltage of the first stage on the power consumption of a two-stage system. The first-stage voltage, the power, and the entropy generation are normalized by their single-stage values. $S_{\text{feed}} = 3 \, \text{g/kg}$.
Figure 4-3: The effect of the voltage of the first stage on the average current density in each stage. The first-stage is normalized by the single-stage voltage. $S_{\text{feed}} = 3 \text{ g/kg}$.

Figure 4-4: The effect of the voltage of the first stage on the variance of the current density, the variance of the rate of entropy generation, and the average current density for brackish-water desalination where osmosis and diffusion are negligible. The variables are normalized by their single-stage values. $S_{\text{feed}} = 3 \text{ g/kg}$.
coefficient is constant.

To better illustrate how the voltage of the first stage lowers the total rate of entropy generation, the current density and entropy generation profiles of the optimal two-stage system are compared to those of the single-stage system in Fig. 4-5. The single-stage system does not make good use of the membrane area towards the end of the stack because the current density is low. To compensate for the low current density at the end of the stack, the single-stage voltage has to be set to a high value, which results in a high current density at the inlet of the stack. The two-stage system overcomes this problem by having a low voltage in the first stage, and a higher voltage in the second stage, ensuring a better distribution of the current density and of the entropy generation rate, and a better usage of the available membrane area. This results in the reduction of the required power consumption.

4.4.2 Effect of osmosis and diffusion on the optimal operation of two-stage ED

In some ED applications, the concentration difference between the concentrate and diluate channels can be large, resulting in significant losses due to osmosis and diffusion. In such cases, when the inlet and outlet salinities and flow rates are fixed, different operating conditions can result in different rates of osmosis and diffusion. In the case of a two-stage system, a higher voltage in the first stage results in a faster increase in the difference in concentration between the concentrate and the diluate channels. A higher concentration difference in the second stage over the same membrane area results in more osmosis and diffusion, which in turn result in a larger amount of salt that needs to be removed from the diluate to the concentrate, and a larger required current. The increasing average current density with increasing first-stage voltage is shown in Fig. 4-6 for the desalination of a feed from 35 g/kg to 1 g/kg at a recovery of 70% and a system length of 12 m. By contrast, the average current density in the case shown in Fig. 4-4 was constant for the full range of the first-stage voltage.
Figure 4-5: The distribution of the current density and of the rate of entropy generation along the length of the stack for a single-stage system and for the optimal two-stage system. In this case, operating under two voltages results in a 5% reduction in power consumption compared to the single-stage system. $S_{\text{feed}} = 3 \text{ g/kg.}$
Figure 4-6: The effect of the voltage of the first stage on the average current density. The variables are normalized by their single-stage values. $S_{\text{feed}} = 35 \text{ g/kg}$.

The variation of the current with the first-stage voltage violates the condition of fixed duty that is required by the theorem of equipartition of entropy generation. As a result, as shown in Fig. 4-7, the voltage that minimizes power consumption and total entropy generation, $V_{1,P}^*$, is lower than the voltage that minimizes the variance of the rate of entropy generation, $V_{1,\text{Var}(\dot{s}_{\text{gen}})}^*$:

$$V_{1,P}^* < V_{1,\text{Var}(\dot{s}_{\text{gen}})}^*$$

As shown by Eq. 4.5, the total rate of entropy generation can be thought of as consisting of two parts. The first, due to the average of the flux, is minimized when the current is minimized, and this behavior favors a lower value of the first-stage voltage. The second part, due to the imbalance in the system, is minimized when the variance of the entropy generation is minimized. As a result of these two effects, the voltage that minimizes the total rate of entropy generation is lower than that which minimizes the variance of the rate of entropy generation when osmosis and diffusion are non-negligible. In the case studied in Fig. 4-7, the optimal first-stage voltage is
closer to that which minimizes the variance of the current density.

In summary, in the absence of osmosis and diffusion, the voltage of the first stage should be set such that the variance of the rate of entropy generation is minimized. When osmosis and diffusion are non-negligible, the optimal first-stage voltage is smaller than that which minimizes the variance of the rate of entropy generation because a smaller first-stage voltage results in lower osmotic and diffusive losses, and in a lower duty. The optimal operating point is determined by the trade-off between the reduction in duty and the reduction in the variance of the rate of entropy generation.

4.4.3 Effect of the distribution of area between the two stages on power consumption

Next, we turn to the effect of the distribution of area between the two stages on the power consumption. We consider the desalination of a feed from 35 g/kg to 1 g/kg at a recovery of 70% at a system length of 12 m. At each division of area, the voltage of the first stage is set such that the power consumption is minimized. The distribution
of the available area provides an additional degree of freedom which can be used to decrease the total rate of entropy generation for a fixed system size.

Figure 4-8 shows that the total power consumption is minimized when around 80% of the total area is used in the first stage, which is the distribution of area that also minimizes the variance of rate of entropy generation and the average current density. The power consumption is reduced by 29% compared to the single-stage system, and by 7% compared to the two-stage system with equal distribution of area between the two stages. The reduction in power consumption compared to the single-stage system is significant because the modeled desalination application is highly favorable to multi-staging due to its small equipartition factor, as defined in Eq. 4.8. The wide range of salinity covered by the system ensures a large change in resistance and current density over the length of the system, which, at a fixed voltage, results in a large variability in the rate of entropy generation. In addition, a large system size results in a lower rate of entropy generation that is due to the average flux (see Eq. 4.6), and magnifies the effect of multi-staging on the system energy consumption, as explained in Section 4.2.

In addition, the choice of the first-stage length can serve to decrease the average current density. The average current density is decreased by around 3% for a first-stage fraction of around 70%. This is an indication that the choice of the distribution of area can decrease osmosis and diffusion by making the available area smaller when the salinity difference between the two streams is large, which is close to the outlet of the system. Even with the same inlet and outlet salinities, the operation of the system dictates the distribution of the available area between the different parts of the process.

The optimal first-stage fraction of around 80% is specific to the system modeled in this section. Different inlet and outlet salinities have yielded first-stage fractions between 50% and 80%, with the applications with a higher salinity range yielding a larger first stage.
Figure 4-8: The effect of the distribution of area between the two stages on the power consumption, the variance of the current density, the variance of the rate of entropy generation, and the average current density. The variables are normalized by their single-stage values. $S_{\text{feed}} = 35$ g/kg.

4.5 The benefits of multi-staging in brackish-water desalination and in high-salinity brine concentration

In the previous section, large systems were modeled to magnify the effects of two-staging in order to be able to study how a two-stage system should be operated. In this section, we quantify the benefits of multi-staging for system sizes that are cost-effective, and for ED applications that are already in use. We expect the benefits of multi-staging to increase with increasing system size, so it is important to choose cost-effective system sizes, which are smaller than those modeled in the previous section.

We study the effect of multi-staging on two applications: a) the desalination of a brackish-water feed from 3 g/kg to 0.35 g/kg at a recovery of 80%, and b) the concentration of highly-saline brine from 70 g/kg to 200 g/kg at a recovery of 21%.
The first application is for the production of drinking water from brackish water, where the brine stream is recirculated to ensure high recovery. The second application is part of a salt production process, which uses as feed the brine outlet of a typical seawater desalination system. The recovery is set such that the diluate stream leaves the system at 35 g/kg, which is considered to match the salinity of seawater for convenience of discharge. The configuration used in the first application is the same as in Fig. 4-1. The configuration of the second application does not employ brine recirculation, and instead the flow rates of the diluate and concentrate channels have different values so as to produce the required recovery.

In Chapter 3, a cost model was used to determine the system size at which total costs are minimized for a single-stage system. In this section, we study the effect of operating under two voltages at the previously determined cost-effective system sizes and operating conditions such as the velocity. For each system size, the voltage of the first stage, and the division of area between the first and second stage are set such that the power consumption is minimized.

### 4.5.1 The effect of multi-staging on brackish-water desalination

At a cost ratio of 134 W/m² (see Section 3.3.2) and for a channel height of 0.5 mm, the optimal effective length for this application is 2.5 m and the optimal velocity is 18 cm/s as shown in Section 3.5. As shown in Fig. 4-9, at the cost-optimal length of 2.5 m, operating under two voltages only reduces the power consumption by less than 1%, and the improvement in the energetic performance reaches less than 6% at a length of 5 m, which is double the cost-optimal length. The effect of multi-staging is not large because fixed costs are very high; and, as shown in Chapter 3, the ED system is operated close to the limiting current density, which means that the system size that minimizes the total costs is fairly small. A small system size results in a large rate of entropy generation that is due to the average flux, which reduces the importance of the rate of entropy generation that is due to the variance of the flux.
In other words, the cost-optimal ED system for brackish-water desalination has a high equipartition factor, and, even if the variance in the rate of entropy generation is minimized, the total rate of entropy generation does not vary greatly.

Figure 4-9: The effect of the length of the system on the power consumption of single-stage and two-stage systems for brackish-water desalination. The cost-optimal length for the single-stage system is 2.5 m.

The results presented in Fig. 4-9 are for a cost ratio, \( r \), equal to 134 W/m². If the cost ratio is reduced fivefold (to \( r = 26 \) W/m²), operating under two voltages at the cost-optimal system size reduces the power consumption by slightly less than 5%. For two-stage operation to yield a significant reduction in power consumption and costs, the fixed costs of ED need to be much smaller relative to electricity costs than are those reported in Table 3.1.

4.5.2 The effect of multi-staging on high-salinity brine concentration

The effect of multi-staging is even lower in the brine concentration application. As shown in Fig. 4-10, operating under two voltages barely reduces the power consump-
tion. In fact, the improvement is less than 2% for a length of 10 m, which is around 50% larger than the cost-optimal length of 6.6 m.

![Graph showing the effect of length on the equipartition factor and variance](image)

Figure 4-10: The effect of the length of the system on the equipartition factor, the ratio of two-stage to single-stage power consumption, and on the variance of single-stage and two-stage systems for high-salinity brine concentration. The cost-optimal length for the single-stage system is 6.6 m.

The stack resistance at high salinity is dominated by the membrane resistance, as shown in Chapter 2, which does not vary greatly with salinity. We can therefore approximate the equipartition factor by assuming a constant resistance, and Eq. 4.8 can be written as a function of the current density:

\[ \Xi \approx \frac{j^2}{l^2} \]  

(4.13)

where the numerator is the square of the average current density, and the denominator is the average of the square of the current density. As explained in Section 4.5.1, the high capital costs relative to energy costs push the optimum towards smaller systems and higher energy consumption, which explains why the equipartition factor for this application in the range of the cost-optimal system size is very high, as shown in Fig. 4-10.
Even though operating under two voltages significantly decreases the variance of the current density, as shown in Fig. 4-10, this decrease in variance barely affects the total rate of entropy generation, which is mostly due to the average of the flux, and not its variance, as shown by the high equipartition factor.

At first, a ratio of two-stage to single-stage power consumption that is lower than the equipartition factor seems contradictory. The equipartition factor sets the limit on the amount by which the total rate of entropy generation can be decreased if the entropy generation due to the imbalance, \( \dot{S}_{\text{gen, imbalance}} \), is set to zero. However, it is also assumed that the entropy generation due to the mean will not change. In this case, the amount of salt that needs to be removed decreases slightly due to the decrease in osmosis and diffusion, which means that even the rate of entropy generation due to the mean decreases, which explains why the improvement in performance is slightly larger than the maximum predicted by the equipartition factor.

The effect of multi-staging in the high-salinity case is lower than that in the brackish-water case. This can be explained by a higher equipartition factor in the brine-concentration application. At high salinity, the dominant resistance is that of the membranes, which does not vary greatly with salinity. This means that the variation of the concentrations along the stack affects the total resistance much less than in brackish-water applications, resulting in a lower variance of the rate of entropy generation. In addition, the entropy generation is much higher in the brine-concentration application because a lot more salt is being removed to take a feed from 70 g/kg to 200 g/kg than in taking a feed from 3 g/kg to 0.35 g/kg, resulting in a higher \( \dot{S}_{\text{gen, equip}} \).

Finally, even if the cost ratio is reduced from 134 W/m² to around 40 W/m², the two-stage system at the cost-optimal size only reduces the power consumption by 2% relative to the single-stage system. In summary, current electrodialysis fixed costs need to be greatly reduced relative to the cost of electricity for two-staging to have significant effects on the power consumption of ED.

The effect of multi-staging on the energetic performance of cost-effective ED systems is summarized in Table 4.1.
Table 4.1: Summary of the effect of two-staging on the energetic performance of cost-effective ED systems for brackish-water desalination and high-salinity brine concentration.

<table>
<thead>
<tr>
<th>Application</th>
<th>Cost ratio [W/m²]</th>
<th>Reduction of power consumption due to two-staging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brackish-water desalination</td>
<td>134</td>
<td>&lt;1%</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>5%</td>
</tr>
<tr>
<td>High-salinity brine concentration</td>
<td>134</td>
<td>&lt;1%</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2%</td>
</tr>
</tbody>
</table>

4.6 Counterflow electrodialysis

In this section, we study the effect of operating in counterflow on the performance of ED systems. Operating in counterflow is expected to improve the distribution of the concentration difference. In a parallel flow ED system, the concentrations are close (or equal) at the inlet, and diverge as salt is transported from the diluate to the concentrate channel. In a counterflow system, the concentrations of the two streams are high on one end, and low at the other.

4.6.1 Brackish-water desalination

First, we look at the effect of operating in counterflow on the performance of a brackish-water desalination system. We compare a counterflow system to a parallel-flow system with the same inlets and outlets and with the same system dimensions. By setting these constraints we can compare the energy consumption of the two systems fairly. In addition, we neglect any trans-membrane pressure drop that might arise from the operation in counterflow mode, which means that we are calculating a performance limit of the counterflow system, with practical systems yielding a lower performance due to leakage.

Figure 4-9 shows that operating in counterflow reduces the power consumption relative to the parallel-flow system by around 3-4%. We note that this improvement
can be divided between a decrease in the required voltage, and a decrease in the total current, which represents the total amount of salt removed, and which quantifies the effects of osmosis and diffusion. In the brackish-water desalination application, the voltage is decreased by around 3% compared to the parallel-flow operation, which is due to a better distribution of the chemical potential difference, whereas the current is only decreased by less than 1%, which means that operating in counterflow does not greatly reduce osmosis and diffusion in this application. Operating in counterflow reduces the voltage that is required to overcome the concentration difference, and results in a better distribution of the rate of entropy generation, thus reducing the required power consumption by directly affecting the required voltage.

Figure 4-11: The effect of the length of the system on the power consumption of parallel flow and counterflow ED systems for brackish-water desalination.

If the system length is increased to 15 m, a very significant size, a 6% reduction in power consumption can be achieved relative to the parallel-flow configuration. This shows that the effect of operation in counterflow increases with increasing system size. This is due to having a lower equipartition factor when the system size is increased.

For operation of counterflow to be preferred over operation in parallel flow, this improvement in performance would need to be greater than the negative effects that
arise from operating in counterflow, including leakage through the membrane due to the resulting trans-membrane pressure difference, the additional strain on the membranes, and the increased piping complexity.

4.6.2 High-salinity brine concentration

The effect of operating in counterflow is even lower in the brine-concentration application. As shown in Fig. 4-12, operating in counterflow reduces the variance in the current density by up to 98%, but only reduces the power consumption by 2.5% at a length of 10 m. This again is a result of the very high equipartition factor, which is due to operating at high current density (small system size) and low variability in the resistance along the stack. In addition, even for the brine concentration application, operating in counterflow reduces the total current by less than 1%, which means that it does not have a great effect on diffusion and osmosis.

4.6.3 Differences between ED systems and heat exchangers

An ED stack, which can be thought of as a mass exchanger, has some significant differences from a heat exchanger. In a heat exchanger, we can think of the heat flux as being proportional to a temperature difference. By operating in counterflow, we make the streamwise distribution of the temperature difference more uniform, such that the temperature difference in no location along the exchanger is too small, as would happen in parallel flow, as shown in Fig. 4-13. By contrast, the driving force in an ED system is the difference in the electrochemical potential of the salt between the two streams, as shown in Eq. 4.10. Given that these systems are small and operate at high current densities, the contribution of the chemical potential difference to the electrochemical potential difference is small, as shown in Fig. 4-13. As a result, the variance of the chemical potential difference is small compared to the mean electrochemical potential difference, and a better distribution of the concentration difference does not have a great effect on performance. If ED fixed costs are reduced relative to energy costs, larger systems can be used and counterflow ED
Figure 4-12: The variation of the power consumption and variance of the current density with system length for a single-stage system, a two-stage system, and a counterflow single-stage system.
will have a bigger effect on the performance because the chemical potential difference forms a larger fraction of the applied voltage.

![Diagram showing temperature, chemical potential, and electrochemical potential profiles in parallel and counterflow configurations.](image)

Figure 4-13: Qualitative temperature profile in a heat exchanger, and chemical potential, and electrochemical potential profiles in an ED stack in parallel flow and in counterflow.

### 4.7 Conclusions

In this chapter, we studied the effect of multi-staging ED and of operating ED in counterflow for brackish-water desalination and high-salinity brine concentration. We have shown that, in the absence of process-dependent losses such as osmosis and diffusion, the voltages in a multi-stage system should be set such that the spatial variance of the entropy generation rate is minimized, as predicted by the theorem of equipartition of entropy generation. When osmotic and diffusive losses are non-negligible, the total amount of salt that needs to be transported depends on the process, and equipartition of entropy generation is not enough to determine the optimal operating point because the condition of fixed duty does not hold. In such cases, the opti-
mal first-stage voltage is determined by the trade-off between the reduction in duty and the reduction in the variance of the rate of entropy generation. In addition, the distribution of area between the two stages is another variable that can be used to decrease the power consumption by further decreasing the duty and the variance of the entropy generation rate.

Cost-effective ED systems tend to be small and are operated at high current density because of their high fixed costs relative to their energy costs. This results in a large rate of entropy generation that is due to the mean flux, which corresponds to a high equipartition factor. For system sizes that are cost effective, operating under two voltage does not have a big effect on the power consumption in brackish-water desalination and in high-salinity brine concentration because the entropy generation that can be saved through the minimization of its spatial variance is a small fraction of the total rate of entropy generation. For these same reasons, operating in counterflow does not result in a significant decrease in power consumption compared to operating in parallel flow. When one considers the negative effects of operating in counterflow, the prospects become even less promising, if not negative.

If a large membrane area is used, and the stack resistance varies greatly over the length, the amount of entropy generation that is due to imbalance, $\dot{S}_{\text{gen,imbalance}}$, can be significant. It was shown that, in such cases, operating in two-stages can result in a significant reduction in a system's energy consumption (up to 29%). Future work on improving the energy efficiency of ED systems should therefore focus on reducing $\dot{S}_{\text{gen,equip}}$ as defined in Eq. 4.6, which can be done by decreasing the stack resistance or by decreasing ED fixed costs to allow the use of larger systems. This would allow the improved operation of ED to results in significant benefits.
Chapter 5

Optimal operation of batch electrodialysis for reduced energy consumption

5.1 Introduction

In Chapter 4, we looked at how an ED system’s energy consumption can be decreased through better operation by two-staging and by operating in counterflow. In this chapter, we study the operation of ED in batch mode.

Few studies in the literature have looked at the optimal operation of a batch ED system. Below, we consider some of these studies.

Parulekar [65] studied five possible operating profiles of a batch ED system, including constant-current and constant-voltage operation. The values of the applied current and voltage were determined by minimizing the sum of the stack energy consumption and the pumping energy, such that the process time and the final diluate salinity were not held constant.

Rohman et al. [66] modeled a batch ED system operating under constant current, and studied the effects of various parameters on the process time and energy consumption. In another study, Rohman and Aziz [67] made use of dynamic optimization to
determine the optimal processes for different objective functions.

In a study by Lee et al. [68], a batch ED system is operated under constant current until a pre-determined concentration is reached, where the operation is switched to constant voltage. Tran et al. [69] used a batch ED system to treat RO concentrate, and operated the ED system at constant current density. Tanaka [70] modeled a constant-voltage batch ED system and determined that it can consume less energy than reverse osmosis at low salinities. Yan et al. [71] studied the effects of several parameters by operating a batch ED system under a constant voltage.

In fact, it is common for a batch ED system to be operated at constant voltage [27, 70-75], or constant current [44, 66, 68, 69]. This is usually done without a justification of which regime to operate under, and without a comparison between the different operating regimes.

As shown in Section 4.2, for a system of fixed size and fixed duty, the optimal process is that which minimizes the variance of the rate of entropy generation, as shown by Tondeur and Kvaalen [24] for a system with a constant phenomenological coefficient, and as shown by Johannessen et al. [64] for a system with a varying coefficient. In Chapter 4, this conclusion was verified for a two-stage ED system with a fixed duty, where the power consumption was minimized at the first-stage voltage that minimized the variance in the rate of entropy generation (see Fig. 4-4). In addition, it was shown that, in the presence of non-negligible osmosis and diffusion, when the inlet and outlet salinities and flow rates are fixed, the duty depends on the process, and equipartition of entropy generation cannot be used to determine the optimal operating point. In fact, it was shown that the optimal operating point balances between the reduction in the duty and the reduction in the variance of the entropy generation.

A batch ED system can be thought of as a continuously staged system, where the applied voltage can be varied with time to result in the best energetic performance. The infinite number of degrees of freedom means that many processes can achieve the set desalination requirements. However, it is difficult to numerically simulate all the possible processes, and it is difficult to run some of these processes in practice.
For these reasons, only specific processes are considered in this chapter. Based on the results presented in Chapter 4, and based on the common processes used in the literature, we investigate the following processes: a) fixed-voltage operation, b) fixed-current operation, and c) operation at fixed entropy generation.

In the first part of the chapter, we study the energy consumption of the different processes at different system sizes, represented by the product of the process time and the cell-pair area. We then look at how these different operating points affect the stack energy consumption and the non-pumping costs at various cost factors by using a simple cost model.

5.2 Modeling

As mentioned in the previous chapters, when comparing the energy efficiency of different operating points, it is important to ensure a fair set of constraints. The systems being compared need to have the same application, which entails having the same inlet and outlet salinities and flow rates. In addition, it is important to fix the size of the systems being compared to ensure that only the operating conditions are varied. Any change in these constraints between the systems being compared results in having an inconclusive comparison. It might be that a system appears more efficient because it is treating water to a lesser extent or in smaller quantities, or because it is using more capital. In the case of a batch ED system, we fix the initial volume and salinity of the feed, and the final volumes (determined by the recovery) and salinities of the concentrate and the diluate tanks, shown in Fig. 5-1.

![Figure 5-1: Schematic diagram showing the batch configuration.](image-url)
Given that the process affects the rates of osmosis and diffusion, we do not know the initial division of the feed volume between the concentrate and diluate tanks. For this reason, the numerical simulation starts with the final state, where the volumes and concentrations are set, and solves the species balances with time until the initial state is reached. For example, for a constant-voltage process, given the application and the system size, there is only one voltage which results in the required salinities. Starting with the final state, a value of the voltage is guessed, and species balance is performed until the end of the process time. The guessed value is updated until the initial feed salinity is reached. By solving in the reverse direction, we only need to guess the voltage, whereas, by starting with the initial state, we also need to guess the division of the volume of the feed between the two tanks that leads to the set recovery.

At each step of the process, given the concentrations in the two tanks, we can determine the species fluxes using the models detailed in Appendix B. We assume that the stack length is small such that the concentrations do not vary with space, and only vary with time. If the size and shape of the stack are known, the optimal velocity at any point in time is determined by the trade-off between stack power consumption and pumping power, as was shown in Chapter 3. Given that the concentrations change with time, the velocity can be varied to minimize the total power consumption. We expect the optimal velocity in the diluate channel to increase as the concentration decreases. In this chapter, however, the velocity is held constant in each application and is equal in the two channels, so the pumping power is the same between the three processes that are compared. For this reason, and because the pumping power depends strongly on the size and shape of the stack, the pumping power is not considered in this chapter, and the different processes are compared based on the stack power consumption at each system size.

Further, as was done in the previous chapters, the electrodes are not modeled because ED systems consist of a large number of cell pairs, and the electrode potential is small compared to the total applied voltage. Finally, the temperature is assumed to not vary with space or time, and is equal to the ambient temperature.
When an ED system is operated in batch mode, the size of the system is determined by the product of the cell-pair area and the process time. These two quantities are equivalent because the spatial variation of the concentrations is neglected. A system with an effective cell-pair area $A_1$ and process time $\tau_{\text{process},1}$ has the same production rate and energy consumption as a system with area $A_2$ and process time $\tau_{\text{process},2}$ if

$$A_1 \tau_{\text{process},1} = A_2 \tau_{\text{process},2}$$

Given that a unit of m$^2$s is not very intuitive, the system size is replaced by the following expression of the minimum average current density:

$$i_{\text{mean, min}} = \frac{FV_f (c_i - c_f)}{A \tau_{\text{process}}}$$  (5.1)

where $F$ is the Faraday constant, $V_f$ is the final volume of the product, and $c_i$ is the initial concentration. We note here that this expression assumes perfect membranes (no water or co-ion transport). This is done so that Eq. 5.1 is a true indicator of the system size regardless of the process. When two processes with the same system size result in a different duty due to osmosis and diffusion, they both have the same value of the average current density calculated using Eq. 5.1.

### 5.3 Equipartition of entropy generation in batch electrodialysis

As explained in Chapter 4, the theorem of equipartition of entropy generation, developed by Tondeur and Kvaalen [24], states that, for a system of fixed size and fixed duty, the total rate of entropy generation is minimized when the spatial and/or temporal variance of the entropy generation is minimized. Tondeur and Kvaalen [24] extend the condition to the minimization of the variance of the flux and the variance of the driving force. This is possible because the phenomenological coefficient, $L$, which relates the flux to the driving force is assumed constant. In fact, Tondeur and
Kvaalen [24] prove the theorem by starting with the assumption of constant $L$, and by using the Cauchy-Schwarz inequality.

In an ED system, the electric resistance of the stack changes because of the changing concentrations. As a result, the relationship between salt flux and driving force is not constant, which means that the variances of the flux, the driving force, and the rate of entropy generation are not minimized at the same operating point. In addition, the salt flux in ED is limited by the limiting current density, which does not have the same value throughout the process because of the changing diluate concentration. Finally, in some ED applications, there are operation-dependent losses in the form of osmosis and back-diffusion. This places the condition of constant inlet and outlet salinities and flow rates at odds with the condition of fixed total duty. In this section, we look at how each of these points affects the optimal operation of ED, and we compare the operation of ED under constant voltage to better operating regimes.

5.3.1 Effect of having a varying phenomenological coefficient on the optimal operation of ED

In a batch ED system, the concentrations of the diluate and concentrate channels vary with time, which causes the stack resistance, and with it the phenomenological coefficient linking the salt flux to the driving force to vary. A varying phenomenological coefficient, $L$, means that the variance of the entropy generation is not minimized at the same operating points that minimize the variance of the flux and the variance of the driving force. In Section 4.4.1, we showed that, in the absence of osmosis and diffusion, the power consumption is minimized when the variance of the rate of entropy generation is minimized. In this section, we investigate the effect of operation under constant entropy generation and constant current density on the performance of a batch ED system, and we compare these regimes to a constant-voltage operation. The application considered in this section is that of the desalination of brackish water from 3 g/kg to 0.35 g/kg at a recovery of 80%.

Figure 5-2 shows the improvement in energy consumption of operation at constant
current and at constant entropy generation relative to a constant-voltage operation at different system sizes, where the system size can be thought of as inversely proportional to the average current density. As shown in Fig. 5-2, the energy consumption of a fixed-current operation is not the same as that of a fixed-entropy-generation operation. This difference arises from having a stack resistance that varies with time. In addition, operation under constant entropy generation outperforms the constant-current operation, which means that, for a system of varying phenomenological coefficient, the spatial and temporal equipartition should be that of entropy generation and not of flux. This is consistent with the mathematical proof reported by Johannessen et al. [64], which generalizes the theorem of equipartition of entropy generation to systems of varying resistance, and is consistent with the results reported in Section 4.4.1. For practical purposes, the local rate of entropy generation per unit area can be estimated by that due to current flowing across a resistive loss, as shown in Chapter 2 for systems with negligible diffusion and osmosis:

\[
\dot{S}_{\text{gen}}^{''} = \frac{r_{\text{stack}} i^2}{T}
\]  

(5.2)

where \( r_{\text{stack}} \) is the stack ohmic resistance, \( i \) is the current density, and \( T \) is the temperature.

Further, as shown in Fig. 5-2, the effect of improved operation increases with increasing system size. This can be explained by looking back at Eq. 4.5. A larger system size, or a lower average current density, yields a lower \( \dot{S}_{\text{gen, equip}} \). As a result, the same decrease in \( \dot{S}_{\text{gen, imbalance}} \) has a larger effect on the total rate of entropy generation when the system size is larger.

5.3.2 Effect of limiting current density on the optimal operation of ED

A possible constraint that might arise in the optimal operation of ED is that related to the limiting current density. When the diluate concentration in ED is low, concentration polarization causes the concentration at the membrane interface to reach
zero, as explained in Chapter 3, which limits the current density that can be achieved. In a constant-current batch ED system, the highest applied current density is limited by the lowest limiting current in the process, which is set by the final diluate concentration (the lowest concentration).

This constraint on the highest current density sets the limit on the smallest possible system size that can be used for constant-current operation. The system sizes that allow a constant-current operation are shown using a solid line in Fig. 5-2, and the transition to a dashed line occurs when the smallest possible system size is reached. For the system sizes represented by a dashed line, the process can be divided into two parts. The system is initially operated at constant current. When the set current density is larger than 90% of the local limiting current density, the remainder of the process is operated at 90% of the local limiting current density, where the limiting
current density is estimated using the following expression:

\[ i_{\text{lim}} \approx \frac{2D_{\text{Na}^+, \text{H}_2\text{O}} F C_D}{\delta} \]  

(5.3)

where \( D_{\text{Na}^+, \text{H}_2\text{O}} \) is the diffusivity of the sodium ion in water because the chloride ion has a higher diffusivity and does not limit the diffusion, as shown in Table B.1. The same operating procedure is applied to operation under a constant entropy generation rate. The variation of current density and entropy generation with time for the smallest simulated system size is shown in Fig. 5-3 for operation at constant voltage, at partially constant current, and at partially constant entropy generation.

At this small system size, constant-voltage operation outperforms the operation at partially constant current by 2% and yields a similar energy consumption as the partially constant entropy generation profile because it results in a smooth entropy generation profile, as shown in Fig. 5-3(b), which is made possible by the changing stack resistance. When the rate of entropy generation cannot be held constant with time, its variance should be minimized, and the partially fixed profile is not necessarily the one with the smallest variance.

5.3.3 Effect of osmosis and diffusion on the optimal operation of ED

A third point to consider in the optimal operation of ED is the presence of osmosis and diffusion. The magnitudes of osmosis and diffusion depend on the system size, and on the profiles of the diluate and concentrate concentrations, which are set by the application and by the system operation.

If a batch ED system with the same inlet and outlet concentrations is operated differently, the total rates of osmosis and diffusion could change. As shown in Fig. 5-4, a system operated under constant voltage results in the largest total difference between the two concentration profiles, followed by the constant-entropy system and the constant-current system. As a result, osmosis and diffusion, and the total amount of salt that needs to be transported, are the smallest in the constant-current operation.
Figure 5-3: Current density and entropy generation profiles of the three processes: constant voltage, partially constant current, and partially constant entropy generation. The dashed lines indicate that the system is operated at 90% of the local limiting current density.
The total current in the constant-current operation is 0.8\% lower than that in the constant-entropy-generation operation, and 3.5\% lower than that in the constant-voltage operation. As a result, the condition of fixed duty is no longer satisfied when the inlet and outlet salinities and flow rates are set, and the theorem of equipartition of entropy generation cannot be used.

Figure 5-4: Concentration profiles of the three processes: constant voltage, constant current, and constant entropy generation. \( S_{\text{feed}} = 35 \text{ g/kg.} \)

In fact, Fig. 5-5 shows that the constant-current system outperforms the constant-entropy-generation system for average current densities lower than around 164 A/m\(^2\). The difference between the energy consumption of two increases when the average current density decreases and the system size increases because of increased osmosis and diffusion. The current density and entropy generation profiles for an average current density of 164 A/m\(^2\) are shown in Fig. 5-6. Even though the entropy generation rate is much better balanced when entropy generation is constant, the fact that the fixed-current operation can achieve the same application by removing 0.8\% less salt results in the same total energy consumption for the two operating points. As the system size is increased, the effect of the increased duty dominates and operation at constant current outperforms the operation at constant entropy generation.
In a batch process where we can control the voltage at every point in time, there are many process paths that can achieve the set desalination requirements. These processes can be divided into equal-duty groups. In each of these groups, because the condition of fixed duty is satisfied, equipartition of entropy generation can be used, and the process with the lowest energy consumption is the one with the lowest variance of the rate of entropy generation. From each of these equal-duty groups, we are left with the best process, which leaves us with a subset of processes, each with a different combination of duty and variance of the rate of entropy generation. All of these processes can achieve the required desalination application and use the same system size, which means that we can compare them based on their energy consumption. The best process among this subset is the one that balances between a low duty and a low variance of the rate of entropy generation as was shown in Fig. 4-7 for a two-stage system. In this chapter, however, we only consider the three processes previously outlined.

![Graph](image)

Figure 5-5: The effect of the average current density on the reduction in energy consumption relative to a constant-voltage operation for a constant-current process and for a process at constant entropy generation. Osmosis and diffusion are significant in this application. $S_{\text{feed}} = 35 \text{ g/kg}$. 

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Figure 5-6: Current density and entropy generation profiles of the three processes at the cross-over average current density of 164 A/m². At lower values of the average current density, the constant-current operation outperforms operation at constant entropy generation. $S_{feed} = 35$ g/kg.
In this section, we have shown that the presence of osmosis and diffusion moves the optimal operating point away from perfect equipartition of entropy generation. Equipartition of entropy generation minimizes the rate of entropy generation that is due to imbalance, as defined in Eq. 4.5, but it also increases the rate of entropy generation of the equipartitioned system by increasing the total duty, which means that the theorem of equipartition of entropy generation alone is not sufficient to optimize the operation of ED when osmosis and diffusion are present.

5.4 Effect of improved operation on energy consumption and system cost

In this section, we look at the reductions in energy consumption and in cost that are gained by going from constant-voltage operation to operation at constant current and at constant entropy generation. The possible improvements in performance due to better operation greatly depend on the system size, with larger systems yielding larger improvements because of lower equipartition factors. It is therefore important to determine the system sizes that are cost effective. To do this, we use the cost model introduced in Chapter 3. We assume that all the fixed costs are proportional to the system size, represented by the product of the effective cell-pair area and the process time. For a continuously operated system, we calculated the cost rate of producing a flow rate of 1 m$^3$/s, which results in cost numbers having the unit of $$/m^3$. For batch systems, the process time, $\tau_{\text{process}}$, is varied, and the rate of production is 1 m$^3$/$\tau_{\text{process}}$. By multiplying the previous expression of cost by the process time, which is an indicator of system size, we get the following expression for cost:

$$C = K_m A \tau_{\text{process}} + K_e E$$

(5.4)

where $C$ is the cost of producing 1 m$^3$, $K_m$ is the amortized fixed cost per unit cell-pair area, $A$ is the cell-pair area, $K_e$ is the cost of electricity, and $E$ is the energy input required to produce 1 m$^3$ of product. As was done in the previous chapters,
the cost is normalized by the cost of electricity to result in the following expression:

\[ c^* = \frac{C}{K_e} = rA_{\text{process}} + E \]  

which shows that the optimal system size is only a function of the cost ratio, \( r \), where

\[ r = \frac{K_m}{K_e} \]

At each value of the cost ratio, \( r \), the optimal system size, \( (A_{\text{process}})_{\text{opt}} \), is determined for each of the processes, and at those system sizes the energy and cost savings by going from a constant-voltage process to operation at constant current and at constant entropy generation are calculated for three different applications, summarized in Table 5.1. In choosing the concentration of sodium chloride that is equivalent to seawater, the total salinity is held constant to fix the amount of salt that needs to be removed.

Table 5.1: Summary of the conditions of the three applications studied.

<table>
<thead>
<tr>
<th>Application</th>
<th>Initial salinity [g/kg]</th>
<th>Final salinity [g/kg]</th>
<th>Recovery ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brackish-water desalination</td>
<td>3</td>
<td>0.35</td>
<td>80</td>
</tr>
<tr>
<td>Partial seawater desalination</td>
<td>35</td>
<td>1</td>
<td>70</td>
</tr>
<tr>
<td>High-salinity brine concentration</td>
<td>70</td>
<td>200</td>
<td>21</td>
</tr>
</tbody>
</table>

In Chapter 3, it was determined based on data from the literature that current fixed costs and electricity prices result in a cost ratio of around 134 W/m². As shown in Table 5.2, constant current and constant entropy generation cannot be achieved in brackish-water desalination at this cost ratio because of limiting current density, and, as a result, operating under a partially constant current is worse than a fixed-voltage operation, and operating under a partially constant entropy generation yields a similar performance to fixed-voltage operation. As shown in Fig. 5-3, the current density and entropy generation profiles for constant-voltage operation at this system size are close to linear, and yield an acceptable temporal variance compared to the partially constant current and entropy generation profiles.
Table 5.2: Improvements in energy consumption and system costs compared to a system at constant voltage for a cost ratio of $r = 134 \text{ W/m}^2$.

<table>
<thead>
<tr>
<th>Application</th>
<th>Improvement in energy consumption [%]</th>
<th>Improvement in cost [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brackish-water desalination</td>
<td>Constant $i$</td>
<td>Constant $\dot{s}_{\text{gen}}$</td>
</tr>
<tr>
<td>Partial seawater desalination</td>
<td>-2\textsuperscript{1}</td>
<td>&lt;1\textsuperscript{2}</td>
</tr>
<tr>
<td>High-salinity brine concentration</td>
<td>12.5</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>Constant $\dot{s}_{\text{gen}}$</td>
<td>Constant i</td>
</tr>
<tr>
<td></td>
<td>&lt;1\textsuperscript{3}</td>
<td>5</td>
</tr>
</tbody>
</table>

Better operation yields an energy reduction of 13.5% in the seawater desalination application, and also a non-pumping cost reduction of around 6%. At this system size, operation at constant current and at constant entropy generation can be achieved without being constrained by the limiting current density. In the brine-concentration case, the improvements at this cost ratio are negligible. As explained in Chapter 4, the equipartition factor for this case is very high. This is because the average current density is very high, and the dominant resistance is that of the membranes, which does not vary greatly with salinity.

A question that arises at this point is: what if ED fixed costs could be decreased? Table 5.3 shows the energy and cost improvements at a cost ratio of 26 W/m$^2$, a five-fold decrease from the previously considered cost ratio. At this decreased cost ratio, significant improvements happen in seawater desalination, where energy consumption is decreased by 30%, and non-pumping costs are reduced by 15%. Brackish-water desalination sees a non-pumping cost improvement of 5%, which is no longer negligible, and better operation of brine concentration yields a minor cost improvement of 2%.

From the results presented in this section, we can conclude that operation under constant entropy generation or constant current is necessary in the use of ED for seawater desalination. This improved operation can yield significant energy and cost improvements, especially when the relative importance of fixed costs with respect to energy costs is decreased. The improvements seen from better operation

\textsuperscript{1} partially constant current density due to the limiting current density
\textsuperscript{2} partially constant entropy generation due to the limiting current density
\textsuperscript{3} constant entropy generation calculated without osmosis and diffusion
Table 5.3: Improvements in energy consumption and system costs compared to a system at constant voltage for a cost ratio of $r = 26 \text{ W/m}^2$.

<table>
<thead>
<tr>
<th>Application</th>
<th>Improvement in energy consumption [%]</th>
<th>Improvement in cost [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Constant $i$</td>
<td>Constant $s_{gen}$</td>
</tr>
<tr>
<td>Brackish-water desalination</td>
<td>31</td>
<td>8</td>
</tr>
<tr>
<td>Partial seawater desalination</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>High-salinity brine concentration</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

of brackish-water desalination can also be significant at lower cost ratios, especially when operation is not constrained by the limiting current density. Better operation of high-salinity brine concentration results in minor improvements, which can be explained by the very high equipartition factor for this application.

5.5 Conclusions

In this chapter, we investigated the application of the equipartition of entropy generation to batch ED systems. The major conclusions from this chapter are the following:

1. The varying stack resistance in ED results in equipartition of entropy generation being different from equipartition of flux. It was shown that, in the absence of osmosis and diffusion, operation under constant entropy generation performs better than constant-current operation.

2. Osmosis and diffusion in ED are process-dependent losses. As a result, changing the operation of a fixed-size and fixed-application system where these losses are important results in a change in its duty, which means that the conditions for equipartition of entropy generation are violated. In these cases, the optimal operation balances between the minimization of the total salt flux (or the duty) and equipartition of entropy generation.

3. Significant improvements in energy consumption and cost can be achieved by better operating batch ED systems if unit fixed costs are decreased relative
to the cost of electricity. Between the three applications studied, seawater desalination shows the greatest room for process improvement.

In practice, it might be difficult to control for constant rate of entropy generation, and the practical choices available are limited to constant-current operation or constant-voltage operation. In this chapter, we have shown that constant-current operation is always energetically better than constant-voltage operation, and the difference between the two increases with system size. To achieve constant-current operation, the current density can be initially set using Eq. 5.1, which is a function of the amount of salt that needs to be removed and the available process time and membrane area. The current density can then be tweaked to account for losses like imperfect current utilization rate, osmosis, and diffusion. When the system size is small, and the required current density is above the lowest limiting current density, constant-current operation is not possible. In such cases, constant-voltage operation might outperform operation at a partially constant current.
Chapter 6

Summary and recommendations

In this thesis, we have studied the energetic losses that occur in electrodialysis. A simplified version\(^1\) of Eq. 4.5 can be used as an overview of this work:

\[
\dot{S}_{\text{gen}} = \frac{F^2}{T} \left( \frac{\text{Chapter 2}}{\text{Chapter 3}} \right) \frac{J^2}{A} + \dot{S}_{\text{gen, imbalance}} \quad (6.1)
\]

In Chapter 2, we have shown that improvements to the energy consumption of electrodialysis need to focus on different components at different salinities. In the low salinity range, most of the losses occur in the fluid channels, so improvements need to focus on decreasing the channel height, which acts as a major ohmic loss. In the high salinity range, improvements to the membranes are essential in reducing the energy consumption. Reducing the membrane thickness has to be done while keeping in mind that the membrane thickness also acts as a resistance to losses such as osmosis and diffusion.

In Chapter 3, we have determined the trade-offs that should govern the choice of the fluid velocity, and through a simple cost model, we have provided typical value of the average current density, the system size, the velocity, the stack length, and the cost as a function of the cost ratio. These values can be used as initial guidelines in the design of future ED systems.

\(^1\)the stack resistance and the duty are assumed constant
In Chapters 4 and 5, we have shown how the process design of ED systems can improve their energy efficiency. This can be done by operating continuously under multiple voltages, by operating in counterflow, and by operating in batch mode. We have shown how equipartition of entropy generation can be applied to ED systems, and how this framework is affected by the presence of process-dependent losses such as osmosis and diffusion. In addition, we have shown that, for process design to result in significant improvements, the fraction of the total entropy generation that occurs because of non-process related losses (the first term on the right-hand side of Eq. 6.1) needs to be much smaller than our estimate of today’s cost-effective systems.

This final point guides the major recommendation for the improvement of ED systems going forward. Given the high fixed costs of today’s ED systems, energy improvements should focus first on the reduction in losses outlined in Chapter 2. In addition, future work needs to focus on reducing the fixed costs of ED systems, which would allow the usage of larger systems in a cost-effective manner. Only when these improvements occur, will the process improvements described in Chapter 4 and 5 become significant.

Finally, the ideas behind this analysis can also be applied to other separation processes. It is beneficial to divide the losses into the parts outlined in Eq. 6.1 above, and then proceeding to study where the losses occur at the local level, before moving towards improving the process design by using equipartition of entropy generation.
Appendix A

Derivation of least work

We can derive the expression for the least work required to remove salt from a low concentration to a high concentration by studying the control volume shown in Fig. A-1. We assume that the amount of salt removed is small enough to not result in a change in the salinities of the streams: \( J_s dA \ll \dot{N} \). This condition is required to be able to calculate the least work required for two specific salinities: \( c_C \) and \( c_D \).

We can write the first law of thermodynamics for the control volume shown in Fig. A-1:

\[
J_s dA (\bar{h}_C - \bar{h}_D) = \dot{W} + \dot{Q}
\]

(A.1)

where \( J_s dA \) is the amount of salt removed, \( \bar{h} \) is the molar specific enthalpy, \( \dot{W} \) is the work input, and \( \dot{Q} \) is the heat input from a source temperature, \( T \), equal to that of the system, which is assumed at constant temperature.

We can also write the second law of thermodynamics:

\[
J_s dA (\bar{s}_C - \bar{s}_D) = \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}}
\]

(A.2)

where \( \bar{s} \) is the molar specific entropy, and \( \dot{S}_{\text{gen}} \) is the rate of entropy generation.

We can multiply the second equation by the temperature, \( T \), and subtract it from the first equation, and get an expression for the work input as a function of the
Figure A-1: Schematic diagram of the control volume used for calculating the least work required to transport $J_s dA$ of salt from a stream of concentration of $c_D$ to a stream of concentration of $c_C$.

chemical potential difference, $\Delta \mu_s$, and the rate of entropy generation:

$$\dot{W} = J_s dA \left[ (\dot{h}_C - T \dot{s}_C) - (\dot{h}_D - T \dot{s}_D) \right] + T \dot{S}_{gen} = J_s dA \Delta \mu_s + T \dot{S}_{gen} \quad (A.3)$$

The smallest work input is required when there is no entropy generation:

$$\dot{W}_{least} = J_s \Delta \mu_s \, dA \quad (2.8)$$

and

$$\dot{W} = \dot{W}_{least} + T \dot{S}_{gen} \quad (2.1)$$
Appendix B

Modeling

In this section, we present the different components of the models used.

B.1 Hydrodynamics

An ideal ED model would accurately model the fluid dynamics inside the channels. In other words, the ideal model would solve the Navier-Stokes equations coupled with the salt transport equations and Poisson's equation. However, this set of equations is very complex and requires a numerical solution, which would limit the scope of the simulation to a small section of the channel without any regard to what is happening at the level of the complete system; this also makes it very difficult to model the fluxes with the appropriate boundary conditions across the membranes. The major effect of fluid flow on the performance of ED is that it enhances the mass transfer by making the boundary layer thinner. This effect can be captured by using the stagnant film theory as is commonly used in modeling ED [4, 5, 26, 27]. This model assumes that the fluid inside the channel is very well mixed, except for a thin boundary layer of thickness $\delta$ that is adjacent to each membrane. The thickness, $\delta$, can be calculated using the Sherwood number, Sh, which is the dimensionless number representing the mass transfer coefficient. Previous attempts of empirically measuring the Sherwood number can be found in the literature [41, 76]. In this thesis, we use the correlation
developed by Kuroda et al [48]:

\[
\text{Sh} = \frac{k_m D_e}{D} = 0.25 \text{ Re}^{\frac{1}{2}} \text{ Sc}^{\frac{1}{3}} \tag{B.1}
\]

where \( k_m \) is the mass transfer coefficient, \( D_e \) is the effective diameter, \( D \) is the diffusivity, \( \text{Re} \) is the Reynolds number, and \( \text{Sc} \) is the Schmidt number. This correlation is based on the effective diameter, \( D_e \), and the thickness of the diffusion film is calculated from the following relation

\[
\delta = \frac{D_e}{\text{Sh}} \tag{B.2}
\]

The effective diameter is defined as

\[
D_e = \frac{2hW (1 - \epsilon_s)}{h + W} \tag{B.3}
\]

where \( h \) is the channel height, \( W \) is the channel width, \( \epsilon_s \) is the volume fraction inside the channel. Given that \( W \gg h \)

\[
D_e = 2h (1 - \epsilon_s) \tag{B.4}
\]

and

\[
\text{Re} = \frac{\rho v D_e}{\mu (1 - \epsilon_s)} = \frac{2 \rho v h}{\mu} \tag{B.5}
\]

The Schmidt number is defined as

\[
\text{Sc} = \frac{\mu}{\rho D} \tag{B.6}
\]

where \( \mu \) is the dynamic viscosity, \( \rho \) is the density, and \( D \) is the diffusion coefficient.

Figure B-1 shows the boundary layer thickness, \( \delta \), and the channel height, \( h \).
B.1.1 Pressure drop calculation

We can write the pressure drop inside the ED channel as

$$ \Delta P = 4f \frac{L \rho v^2}{D_e} \quad (B.7) $$

The correlation by Kuroda et al. [48] is used to calculate the friction factor:

$$ f = k_f R e^{-\frac{1}{2}} \quad (B.8) $$

where $k_f$ is a spacer property also defined by Kuroda et al. In this thesis, we use the properties of spacer A where $k_f = 9.6$ and $\epsilon_s = 0.2$.

In addition, the entrance pressure drop is calculated using correlations developed by Sadri and Floryan [77], but is negligible compared to the friction losses over the length of the stack because $L \gg h$.

B.2 Electric potential profile

The voltage of the cell pair is equal to the sum of all the voltage drops in the cell pair

$$ V_{CP} = (r_{bulk,C} + r_{bulk,D}) i + \Delta \Phi_{CEM} + \Delta \Phi_{AEM} + \Sigma_{j=1}^{3} \Delta \Phi_{film,j} \quad (B.9) $$

where $i$ is the current density, and $r_{bulk,C}$ and $r_{bulk,D}$ are the bulk resistances in the concentrate and diluate channels, respectively, and are calculated from experimental data on conductivity [45–47]. The calculation of the electric potential drops in the
membranes, $\Delta \Phi_{CEM}$ and $\Delta \Phi_{AEM}$, and in each of the four films, $\Delta \Phi_{film,i}$ is described in the following sections. We note that the Donnan potential drops are included in the membrane potential drops given that we treat the interface a part of the membrane.

### B.3 Transport inside the diffusion film

Each Maxwell-Stefan (MS) equation can be thought of as a force balance, where the driving force on a species is equal to the friction forces exerted on this species by the other species present inside the solution:

$$-\frac{c_i}{RT} \nabla \mu_i = \frac{1}{RT} \sum_{j=1}^{n} K_{ij} (v_i - v_j) = \sum_{j=1}^{n} \frac{c_i c_j}{c_{tot} D_{ij}} (v_i - v_j) \quad (B.10)$$

where $D_{ij}$ are the MS diffusion coefficients, defined according to the above equation. $K_{ij}$ is a friction factor, $v_i$ is the velocity of species $i$, averaged over all the particles of the same species, and $\mu_i$ is the electrochemical potential of species $i$:

$$\mu_i = RT \ln a_i + z_i F \Phi + \mu_i^0 \quad (B.11)$$

where $a_i$ is the activity of species $i$, $\Phi$ is the electric potential, and $\mu_i^0$ is the chemical potential at the reference state. We can replace the velocity by the mole flux of the species, $j_i = c_i v_i$, and rearrange the MS equation:

$$-c_i \nabla \ln a_i - \frac{z_i c_i F}{RT} \nabla \Phi = \sum_{j=1}^{n} \frac{c_j j_i - c_i j_j}{c_{tot} D_{ij}} \quad (B.12)$$

For a system of $n$ species, we have $n-1$ independent MS equations, as the MS equation of the $n^{th}$ species can be obtained from the first $n-1$ MS equations using the Gibbs-Duhem equation, and is therefore not independent.

In describing the electric potential profile, the more fundamental equation linking the electric potential to the charges of the ions is Poisson's equation. In the regions where the Laplacian of the electric potential, $\nabla^2 \Phi$, is not great, this equation reduces
to the electroneutrality equation:

\[ \sum_i z_i c_i = 0 \]  \hspace{1cm} (B.13)

The only region where this condition fails is in the electric double layer, which occurs at the interface between the solution and the membrane and has a thickness between 1 and 10 nm [32]. However, we can consider the electric double layer as part of the interface and treat it separately from the solution where we can use the electroneutrality equation. A thorough discussion on the validity of the electroneutrality equation is given by Newman and Thomas-Alyea [32].

Inside the diffusion film, there are three species (anion, cation, and water), which results in two independent Maxwell-Stefan (MS) equations. These equations are used to calculate the concentration and electric potential profiles inside the diffusion films. These profiles give the concentration at each membrane interface, and the film potential drops in Eq. 3.6. The two MS equations for a binary salt are shown below:

\[ -c \nabla \ln a_+ - \frac{cF}{RT} \nabla \phi = \frac{c_j^+ - j_+}{c_{tot} D_+} + \frac{c_+ - c_j^+}{c_{tot} D_{w+}} \]  \hspace{1cm} (B.14)

\[ -c \nabla \ln a_- + \frac{cF}{RT} \nabla \phi = \frac{c_j^- - j_-}{c_{tot} D_-} + \frac{c_- - c_j^-}{c_{tot} D_{w-}} \]  \hspace{1cm} (B.15)

Equations B.14 and B.15 are added:

\[ -c (\nabla \ln a_+ + \nabla \ln a_-) = \frac{c w j^+ - c j^+}{c_{tot} D_{w+}} + \frac{c w j^- - c j^-}{c_{tot} D_{w-}} \]  \hspace{1cm} (B.16)

For sodium chloride,

\[ a = a_+ a_- = \gamma_+ c_+ \gamma_- c_- = (\gamma_\pm c) \]  \hspace{1cm} (B.17)

We combine Equations B.17 and B.16 and rearrange:

\[ -c \nabla \ln a = \frac{c_w}{c_{tot} D_{w+}} j^+ + \frac{c_w}{c_{tot} D_{w-}} j_- - \frac{c}{c_{tot}} \left( \frac{1}{D_{w+}} + \frac{1}{D_{w-}} \right) j_w \]  \hspace{1cm} (B.18)
We then subtract equations B.14 and B.15:

\[-c (\nabla \ln a_+ - \nabla \ln a_-) - 2 \frac{cF}{RT} \nabla \phi = 2c \frac{j_+ - j_-}{c_{\text{tot}} D_{+-}} + \frac{c w j_+ - c j_+}{c_{\text{tot}} D_{w+}} - \frac{c w j_- - c j_-}{c_{\text{tot}} D_{w-}} \quad (B.19)\]

We assume \( \gamma_+ \approx \gamma_- \) such that

\[\nabla \ln a_+ - \nabla \ln a_- = \nabla \ln \frac{a_+}{a_-} = \nabla \ln \frac{\gamma_+}{\gamma_-} \approx 0 \quad (B.20)\]

Eq. B.19 is rearranged:

\[-2 \frac{cF}{RT} \nabla \phi = \left( \frac{2c}{c_{\text{tot}} D_{+-}} + \frac{c w}{c_{\text{tot}} D_{w+}} \right) j_+ - \left( \frac{2c}{c_{\text{tot}} D_{+-}} + \frac{c w}{c_{\text{tot}} D_{w-}} \right) j_- - \frac{c}{c_{\text{tot}}} \left( \frac{1}{D_{w+}} - \frac{1}{D_{w-}} \right) j_w \quad (B.21)\]

To summarize, the equations describing the concentration and potential profiles inside the boundary layer are the following:

\[-c \nabla \ln a = \frac{c w}{c_{\text{tot}} D_{w+}} j_+ + \frac{c w}{c_{\text{tot}} D_{w-}} j_- - \frac{c}{c_{\text{tot}}} \left( \frac{1}{D_{w+}} + \frac{1}{D_{w-}} \right) j_w \quad (B.18)\]

\[-2 \frac{cF}{RT} \nabla \phi = \left( \frac{2c}{c_{\text{tot}} D_{+-}} + \frac{c w}{c_{\text{tot}} D_{w+}} \right) j_+ - \left( \frac{2c}{c_{\text{tot}} D_{+-}} + \frac{c w}{c_{\text{tot}} D_{w-}} \right) j_- - \frac{c}{c_{\text{tot}}} \left( \frac{1}{D_{w+}} - \frac{1}{D_{w-}} \right) j_w \quad (B.21)\]

Given the guessed values of the fluxes, Eq. B.18 can be used to first calculate the concentration profile, and then Eq. B.21 can be used to calculate the potential profile.

The MS model has a major advantage in describing the transport inside the diffusion films. This model allows the integration of the concentration profile, which is important to be able to model the curvature of the \( i-V \) curves presented in Fig. 3-5. Simply calculating the change in concentration between the bulk and the membrane is enough to estimate the limiting current density, but it does not account for the gradual increase in the film resistance as the operating current density gets closer to the limiting current density.
In addition, we note that the concentration in the diluate channel reaches zero close to the CEM. This is because the diffusion coefficient of Na\(^+\) is lower than that of Cl\(^-\), as shown in Table B.1. Given the assumption of the same diffusion layer thickness on both sides of the channel, the effect of concentration polarization is stronger near the CEM.

Table B.1: The diffusion coefficients outside the membranes as reported by Kraaijeveld et al. [5]. Original data from Chapman [6] and Mills and Lobo [7]. \(c\) is the solution concentration in mol/m\(^3\).

<table>
<thead>
<tr>
<th>Components</th>
<th>Diffusivity ([10^{-9} \text{ m}^2/\text{s}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+), H(_2)O</td>
<td>1.333</td>
</tr>
<tr>
<td>Cl(^-), H(_2)O</td>
<td>2.033</td>
</tr>
<tr>
<td>Na(^+), Cl(^-)</td>
<td>0.0015 (c^{0.65})</td>
</tr>
</tbody>
</table>

B.4 Modeling of the transport through the membranes using the Maxwell-Stefan-based model

Given the applied voltage and the bulk concentrations in the diluate and concentrate channels, we can calculate the ionic and water fluxes. The first step is to guess 5 fluxes in the cell pair: \(j_{+,.CEM}, j_{-,CEM}, j_{w,CEM}, j_{+,AEM},\) and \(j_{w,AEM}\). The sixth flux, \(j_{-,AEM}\), can be calculated through conservation of charge:

\[
i = F (j_{+,CEM} - j_{-,CEM}) = F (j_{+,AEM} - j_{-,AEM}) \tag{B.22}\]

Given all the fluxes, we can use two independent MS equations inside each diffusion film to build the concentration and electric potential profiles. The two MS equations can be rearranged, and, using the fourth order Runge-Kutta method, the concentration profile can be calculated. The concentration profile and a second combination of the MS equations can then be used to build the electric potential profile.
At the interface, we assume that each species that exists in both media is in thermodynamic equilibrium:

\[ \mu_i^m = \mu_i^s \]  \hspace{1cm} (B.23)

where \( \mu_i^m \) is the electrochemical potential inside the membrane, and \( \mu_i^s \) is that inside the solution:

\[ RT \ln a_i^m + z_i F \phi^m = RT \ln a_i^s + z_i F \phi^s \]  \hspace{1cm} (B.24)

The equilibrium equations for the cation and anion can be rearranged to give the following expression for the Donnan potential:

\[ \Delta \phi_{\text{Donnan}} = \phi^m - \phi^s = \frac{RT}{z_i F} \ln \frac{a_i^s}{a_i^m} \]  \hspace{1cm} (B.25)

Equating the resulting Donnan potential for the two ions results in the following equations:

\[ \frac{a_i^s a_+^s}{a_i^m a_-^m} = 1 \]  \hspace{1cm} (B.26)

\[ \frac{c_+^m c_-^m}{c_+^s c_-^s} = \frac{\gamma_{+m}^2}{\gamma_{-m}^2} \]  \hspace{1cm} (B.27)

where the activity coefficient inside the membrane, \( \gamma_{\pm}^m \), can be determined experimentally [5]. We note that the activity coefficient is for the salt, and that there is no need for the activity coefficients of the separate ions as the equation above only uses the product of the activities. Equation B.27 can be combined with the electroneutrality equation inside the membrane, which is the same as Eq. B.13 and includes the membrane fixed charge. Combining the electroneutrality equation with Eq. B.27 allows the calculation of the concentrations of the co-ion and counter-ion inside the membrane. Once the ionic concentrations inside the membrane are known, Eq. B.25 can be used to calculate the Donnan potential at each interface. The two expressions of Eq. B.25 can be averaged to cancel out the activity coefficient of the separate ions.
by assuming that $\gamma_+ = \gamma_-:

$$
\Delta \phi_{\text{Donnan}} = \frac{\Delta \phi_{\text{Donnan},+} + \Delta \phi_{\text{Donnan},-}}{2} \approx 0.5 \frac{RT}{F} \ln \frac{c_{m_+}^{\text{m}}}{c_{m_+}^{\text{m}}} \tag{B.28}
$$

The MS equations are used to model the salt and water transport through the membranes. One difference between the equations used inside the membrane and those used in the diffusion film is that the fixed charge of the membrane is added as a new species. In addition, the diffusion coefficients are different inside the membrane. Also, the membrane velocity (or flux) is set to 0 because the membrane is stationary [5]. Given that we do not have the activities of the different species inside the membrane away from the surface, we can apply the MS equations by treating the membrane as one finite difference and taking the differences between the two sides of the membrane where the properties are known. In addition, we can use average values of the concentrations at the two surfaces of the membrane to approximate the concentration at the center of the membrane. At steady state, the fluxes of salt and water through the membrane are equal to those in the adjacent diffusion layers. We assume that heat is dissipated fast enough to keep the systems studied at a constant temperature, $T$.

We can write three independent MS equations for each membrane because we have four species:

$$
-c_+ \nabla \ln a_+ - \frac{c_+ F}{RT} \nabla \phi = \frac{c_{-} j_+ - c_+ j_-}{c_{\text{tot}} D_{+}} + \frac{c_{w} j_+ - c_+ j_w}{c_{\text{tot}} D_{w+}} + \frac{c_{m} j_+}{c_{\text{tot}} D_{m+}} \tag{B.29}
$$

$$
-c_- \nabla \ln a_- + \frac{c_- F}{RT} \nabla \phi = \frac{c_{+} j_- - c_- j_+}{c_{\text{tot}} D_{-}} + \frac{c_{w} j_- - c_- j_{w}}{c_{\text{tot}} D_{w-}} + \frac{c_{m} j_-}{c_{\text{tot}} D_{m-}} \tag{B.30}
$$

The MS equation applied to water is:

$$
-c_w \nabla \ln a_w = \frac{c_{+} j_{w} - c_w j_+}{c_{\text{tot}} D_{w+}} + \frac{c_{-} j_{w} - c_w j_-}{c_{\text{tot}} D_{w-}} + \frac{c_{m} j_{w}}{c_{\text{tot}} D_{mww}} \tag{B.31}
$$
where the left-hand side is the driving force associated with the water flux, and the right-hand side is the sum of the friction forces acting on the water by the cation, the anion, and the membrane, respectively. The concentrations are taken as the average of those on either end of the membrane, but just inside the membrane. The gradient on the left-hand side is calculated as one difference between the two sides of the membrane divided by the thickness of the membrane, without further discretization of the membrane.

The three MS equations can be rearranged, and one of the resulting equations can be used to calculate the electric potential drop across the membrane, and the other two equations can be used as checks on the guessed fluxes. In addition, we can calculate the difference between the set voltage and the sum of all the voltage drops in the system, which should be set to 0. We have 2 MS equations in each membrane, and the cell-pair voltage equation, totaling 5 equations where all the quantities are known. We can write these 5 equations in the form

\[ f(j) = 0 \]  

which is the function we need to solve by guessing the fluxes, \( j \). The roots of the function, i.e. the correct fluxes, are then calculated iteratively using MATLAB's \textit{fsolve} function.

### B.4.1 Validation of the Maxwell-Stefan-based model

The Maxwell-Stefan-based modeling used in this thesis is based on the work done by Kraaijeveld et al. [3, 5], which also reports experimental results and measured diffusion coefficients. To validate our model with the reported experimental results, we also modeled a solution of HCl-NaCl. Given that the electrode equations used in that work were not very clear, we used the reported experimental values of the current density. Instead of setting the cell-pair voltage, we set the current density to the experimental value. Given the experimental current density, the model is used to determine the fluxes of the different ions and that of the water. This resulted in
very good matching between our model and the reported concentrations, as shown in Fig. B-2 and Fig. B-3. The variation of the concentrations with time is a direct result of all the fluxes, which means that the transport through the membranes is modeled accurately.

Figure B-2: Validation of the model using experiments from the literature [3]. The symbols represent experimental values and the solid lines represent the modeling results.

Ideally, we should also be able to validate the resistance network by comparing the total calculated voltage to that measured in the same experiments. However, given that this was not possible, this part of the modeling was verified by comparing the film resistances to those calculated using experimental values of resistivity. In addition, the membrane voltage difference is calculated from the MS equations used to determine the fluxes through the membranes. Given that the fluxes through the membranes are predicted accurately, as discussed above, we can safely assume that
the calculated membrane voltage drop is also accurate, especially given that the 3 MS equations in each membrane need to be solved simultaneously to get the fluxes, and two of them need to be combined to result in the membrane voltage drop. For additional assurance, the calculated membrane resistances were compared to typical values reported in the literature and were found to be within the appropriate range.

Figure B-3: Validation of the model using experiments from the literature [3]. The symbols represent experimental values and the solid lines represent the modeling results.
B.5 Modeling of the transport through the membranes using the Nernst-Planck-based model

The Nernst-Planck-based model developed by Fidaleo and Moresi [26] is used to calculate the salt and water fluxes through the membranes in the concentration of high-salinity brines. The salt flux in this model is assumed to be a result of electro-migration and diffusion:

$$ j_s = \frac{T_s i}{F} - L_s (c_{s,C,m} - c_{s,D,m}) $$

(B.33)

and the water flux is a result of electro-osmosis and osmosis:

$$ j_w = \frac{T_w i}{F} + L_w (\pi_{C,m} - \pi_{D,m}) $$

(B.34)

where the subscript ‘s’ denotes the salt, the subscript ‘w’ denotes the water, $J$ is the molar flux, $i$ is the current density, $c_{s,C,m}$ is the salt concentration at the membrane interface in the concentrate channel, $\pi_{D,m}$ is the osmotic pressure at the membrane interface in the diluate channel, $T_s$ is the salt transport number, and $L$ is the permeability. The transport numbers and permeabilities of salt and water used in this thesis were measured at high salinity by McGovern et al. [4].

The fluxes inside the membranes are the same as those inside the adjacent diffusion films. The use of the MS equations inside the diffusion films involves the fluxes of each of the different species, whereas the model used to predict the transport through the membranes only uses the cell-pair salt and water fluxes. In matching the two sets of fluxes, the AEM and CEM are assumed to have the same transport and permeability numbers: the salt flux is the same in the two membranes, and the amount of current density carried by the counter-ion is the same in the two membranes. This allows the matching of the fluxes inside the diffusion films and those inside the membranes.

Finally, the potential drop across the membranes is calculated as the sum of the
membrane ohmic potential drops and the Donnan potential:

$$\Delta \Phi_{CEM} + \Delta \Phi_{AEM} = (r_{CEM} + r_{AEM}) i + \frac{\Delta \mu_s}{F} = (r_{CEM} + r_{AEM}) i + 2 \frac{RT}{F} \ln \gamma_{\pm,cm_{C,m}}$$

where $\gamma_{\pm}$ is the mean molal activity coefficient, and $m$ is the molality. The resistances of the membranes, $r_{CEM}$ and $r_{AEM}$, were measured experimentally by McGovern et al. [4]. The membrane characteristics used in this model are presented in Section B.6. The validation of this model with experimental data from McGovern et al. [4] is shown in Fig. B-4.

![Graphs showing specific process time and specific energy consumption](image)

(a) Specific process time, which is a measure of system size defined and reported by McGovern et al. [4].

(b) Specific energy consumption.

Figure B-4: Validation of the high-salinity model using experimental data from McGovern et al. [4]. Each stage is a batch system which takes the diluate from a given salinity to another set salinity.

### B.6 System characteristics

#### B.6.1 Characteristics of the membranes used for brackish-water desalination.

The diffusion coefficients inside the membranes are presented in Table B.2, and the membrane characteristics are presented in Table B.3.
Table B.2: The diffusion coefficients inside the membranes (in $10^{-10}$ m$^2$/s), measured and calculated by Kraaijeveld et al. [5].

<table>
<thead>
<tr>
<th>Components</th>
<th>61 CZL 386</th>
<th>204 UZL 386</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$, Cl$^-$</td>
<td>0.24</td>
<td>0.19</td>
</tr>
<tr>
<td>Na$^+$, H$_2$O</td>
<td>3.12</td>
<td>0.75</td>
</tr>
<tr>
<td>Na$^+$, Membrane</td>
<td>0.31</td>
<td>0.16</td>
</tr>
<tr>
<td>Cl$^-$, H$_2$O</td>
<td>1.81</td>
<td>5.12</td>
</tr>
<tr>
<td>Cl$^-$, Membrane</td>
<td>0.31</td>
<td>0.51</td>
</tr>
<tr>
<td>H$_2$O, Membrane</td>
<td>2.49</td>
<td>4.93</td>
</tr>
</tbody>
</table>

Table B.3: Membrane characteristics measured by Kraaijeveld et al. [5]. $c$ is the solution concentration in mol/L.

<table>
<thead>
<tr>
<th>Membrane property</th>
<th>61 CZL 386</th>
<th>204 UZL 386</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity [mol/m$^3$ wet membrane]</td>
<td>1690</td>
<td>1827</td>
</tr>
<tr>
<td>Thickness [mm]</td>
<td>0.563</td>
<td>0.551</td>
</tr>
<tr>
<td>Density of wet membrane, $\rho_m$ [kg/m$^3$]</td>
<td>1167.5 - 7.5c + 7.5c$^2$</td>
<td>1100.0 + 15.0c</td>
</tr>
<tr>
<td>Salt activity coefficient, $\gamma_{\pm}^m$ [-]</td>
<td>0.57 + 0.28c</td>
<td>0.56 + 0.29c</td>
</tr>
<tr>
<td>Water content [%]</td>
<td>30.17 - 0.83c</td>
<td>33.38 - 1.42c</td>
</tr>
</tbody>
</table>

Water concentration inside the membrane is calculated from the water content and membrane density

\[
c_w^m = \frac{\%H_2O \times \rho_m}{100M_w} \quad (B.36)
\]
B.6.2 Characteristics of the membranes used for high-salinity brine concentration.

The membrane characteristics measured by McGovern et al. [4] and used in this work are for the Neosepta AMX-SB and CMX-SB membranes, and are listed below:

\[ r_{\text{CEM}} = r_{\text{AEM}} = 3.5 \times 10^{-4} \Omega \text{ m}^2 \quad (B.37) \]

\[ T_s = -4 \times 10^{-6} S_D^2 + 4 \times 10^{-5} S_D + 0.96 \quad (B.38) \]

\[ T_w = -4 \times 10^{-5} S_C^2 - 1.9 \times 10^{-5} S_C + 11.2 \quad (B.39) \]

\[ L_s = 2 \times 10^{-12} S_D^2 - 3 \times 10^{-10} S_D + 6 \times 10^{-8}[\text{m/s}] \quad (B.40) \]

\[ L_w = 5 \times 10^{-4} S_C^{-0.416}[\text{mol/m}^2\text{-s-bar}] \quad (B.41) \]

B.7 Thermophysical properties

The complexity of the model used increases greatly with the presence of additional species. For this reason, it was decided to only model a binary salt. A solution of sodium chloride was chosen as the electrolyte because experimental data on the diffusion coefficients and activity coefficient of sodium chloride inside the membranes were found in the literature [5]. In addition, sodium chloride is the major component in seawater, and the most recent property correlations of seawater [78] show close agreement with those of sodium chloride [79]. Further, sodium chloride serves as an acceptable substitute in estimating the properties of certain high-salinity waters [80]. When considering the scaling potential in the system, it is important to model the solution of interest. However, we expect the trends in power consumption, which are
the focus of this thesis, to be captured by the use of solutions of sodium chloride. The properties of sodium chloride were taken from an implementation by Thiel et al. [80, 81] of Pitzer’s equations [82–87]. The properties used in our calculations are the solution density, the mean molal activity coefficient, the water activity, and the osmotic pressure.

B.8 Species balance

The models presented in Sections B.3, B.4, and B.5 allow the calculation of the fluxes of the species and the current density at a given location along the stack. These fluxes are used to update the concentrations and flow rates along the stack. The length of the stack is discretized into sufficiently small elements, and the finite-difference method is used to perform a species balance on each channel. We provide the example of the conservation of salt in the diluate channel:

$$N_{s,i+1} = N_{s,i} - j_{s} dA$$

(B.42)

where $N_{s,i}$ is the molar rate of salt in mol/s in element $i$, $j_{s,i}$ is the salt flux through the cell pair (two membranes), and $dA$ is the finite area associated with the element.

Given the inlet and outlet salinities and flow rates, and given the dimensions of a stack ($A, L, W, h$), and the velocity at the product outlet, the required applied voltage needs to be determined.

In the brackish-water desalination case, the feed flow rate is given, but its division between the concentrate and the diluate channel needs to be such that the product flow rate is equal to 1 m$^3$/s. By contrast, the flow rates at the outlet of the stack can both be known by forcing the condition that the concentrate outlet volumetric flow rate be equal to that of the product. This is consistent with having the same channel height and velocity in the two channels. Given the flow rates and salinities at the outlet of stack, and by guessing a value of the applied voltage, the concentrations and flow rates in the two channels can be calculated using a species balance until
the inlet of the stack is reached. At the inlet, the calculated diluate concentration is compared to the set inlet concentration, and the voltage guess is updated using the bisection method until convergence is reached. The node where mixing occurs before the concentrate inlet is used to check that the species are conserved and that there are no errors in the procedure.

In the high-salinity brine concentration case, a similar approach is followed. The outlet flow rates and salinities are known. The voltage is guessed and the concentrations and flow rates in the two channels are calculated until the inlet is reached. At the inlet, the diluate and concentrate concentrations must be equal to the feed concentration. This condition is used to update the applied voltage using the bisection method until convergence is reached.

A similar usage of finite differences is used to model batch operation, which is discretized in time as opposed to space.
Appendix C

Simplified driving force in electrodialysis

The local rate of entropy generation per unit area is the sum of the entropy generated by all the species:

\[ \dot{s}_{\text{gen}}'' = \sum_{i}^{n} j_i \Delta \left( \frac{-\mu_i}{T} \right) \]  

where \( j_i \) is the flux of species \( i \), \( T \) is the temperature, and \( \mu_i \) is the electrochemical potential of species \( i \):

\[ \mu_i = RT \ln a_i + z_i F \Phi \]  

where \( a_i \) is the activity of species \( i \), and \( \Phi \) is electric potential. For a binary salt, the species present are the cation, the anion, and the water. To obtain a simple expression, we assume perfectly perm-selective membranes, and we ignore water transport. The cation flux goes from the center of the diluate channel, denoted by the subscript "D", to the center of concentrate channel \( C_1 \) and the anion flux goes from the diluate channel to the concentrate channel \( C_2 \), as shown in Fig. C-1.

The two concentrate channels are at the same concentration, but at different electric potentials. We can write:

\[ \dot{s}_{\text{gen}}'' = j_{+,-\text{CEM}} \left[ RT \ln \frac{a_{+D}}{a_{+,C}} + F (\Phi_{D} - \Phi_{C_2}) \right] \frac{1}{T} + j_{-,\text{AEM}} \left[ RT \ln \frac{a_{-,D}}{a_{-,C}} - F (\Phi_{D} - \Phi_{C_1}) \right] \frac{1}{T} \]  

\[ \text{(C.2)} \]
where $\Phi_D$ is the electric potential in the diluate channel.

For perfectly perm-selective membranes:

$$j_s = j_{+,\text{CEM}} = j_{-,\text{AEM}} \quad \text{(C.3)}$$

and

$$s''_{\text{gen}} = j_s \left[ F \left( \Phi_{C_1} - \Phi_{C_2} \right) - (\mu_{s,C} - \mu_{s,D}) \right] \frac{1}{T} = j_s \left( \frac{FV_{cp} - \Delta \mu_s}{T} \right) \quad \text{(4.10)}$$

where $\mu_s$ is the chemical potential of the salt. Even though the salt is neutral, the use of ion-exchange membranes results in the salt being driven by the electrochemical potential difference. This is clear from how ED uses an applied voltage to move salt from the diluate to the concentrate channel.

Eq. 4.10 is only valid for perfectly perm-selective membranes without water transport, and is used to provide a simpler expression of entropy generation as a function of physical variables such as the cell-pair voltage. In the results shown in this thesis, we use the full expression of the local rate of entropy generation expressed in Eq. 4.9, which includes the effects of osmosis and diffusion.
Bibliography


