MASTER

An experimental and numerical study of ion and water fluxes through a cation-selective membrane at high current densities

Oppers, N.A.W.

Award date:
2014

Link to publication
An experimental and numerical study of ion and water fluxes through a cation-selective membrane at high current densities

N.A.W. Oppers
July 2014

Supervisors:
S. Moshtari Khah
dr. ir. J. van der Schaaf
prof. dr. ir. J.C. Schouten

External committee member:
dr. ir. M.T. de Groot

Department of Chemical Engineering and Chemistry
Laboratory of Chemical Reactor Engineering
Summary

Information on the behavior of a membrane chlor-alkali electrochemical cell at high current density is required in order to intensify this cell for the development of a container sized, transportable ‘Plug and Produce’ electrochemical production unit of approximately 10,000 tons chlorine per year. Unfortunately, the behavior of cation selective membranes at current densities higher than 5 kA·m⁻² has not yet been investigated and there are no adequate models available to accurately predict its behavior. Therefore, this study aims to gain insight in the behavior of these membranes at elevated current density and concentration of which their investigated ranges are 2-20 kA·m⁻² and 10-32 wt%, respectively. The transport of ions and water through the membrane and its potential drop are investigated experimentally and validated by means of a numerical model. The use of chlorine is avoided for safety reasons and simplicity, thereby resulting in a system with aqueous NaOH solutions as the anolyte and the catholyte.

The model is based on the Nernst-Planck approach in which an extended form for the water flux is used and the osmotic pressure is proven to be negligible. Furthermore, expressions are derived for the non-linear potential gradient and the relation between the electrolyte interface concentration as a function of the membrane interface concentration for a monovalent system. Both equations can be used for a multicomponent system. Moreover, a sensitivity analysis was performed to verify which parameters have the largest influence on the model output. It revealed that the diffusion coefficient is the most important parameter to be optimized.

The reproducibility of the experiments was considered sufficient and their trends were as expected, except for one experiment performed at 20 kA·m⁻² in which the membrane selectivity diminished from approximately 0.74 at 10 kA·m⁻² to approximately 0.44. Based on the selectivity analysis, the model was optimized to resemble the reproducibility experiments, which were performed at 10 kA·m⁻² and 10 wt%. This optimization resulted in a good fit at current densities up to 10 kA·m⁻², but failed to predict the diminished selectivity drop at 20 kA·m⁻².

The model was unable to accurately predict the experimental results at varying concentration. This is attributed to the fact that the parameter optimization was performed for a single concentration and the obtained diffusion coefficients are actually concentration and temperature dependent. Consequently, their effects should be investigated and incorporated in the model before aiming to implement non-ideality or extend it to a multicomponent system.

The membrane potential drop requires special attention since the model underestimates its output by nearly an order of magnitude. One should evaluate the potential gradient by investigating the convective term and the diffusion coefficients in more detail in which it has been shown that the potential drop is enhanced by reducing the channel diameter and the diffusion coefficients. Moreover, one could incorporate tortuosity effects in order to reduce the convective term, thereby increasing the potential drop as well.
**List of contents**

1) Introduction .............................................................................................................................................. 6  
   1.1 Objective....................................................................................................................................... 7  

2) Literature overview................................................................................................................................... 8  
   2.1 The membrane chlor-alkali cell ............................................................................................. 8  
   2.2 Current efficiency ......................................................................................................................... 8  
   2.3 Membrane structure ...................................................................................................................... 9  
   2.4 Theoretical models of transport through the membrane .......................................................... 11  
   2.5 Concentration profile at the membrane interface........................................................................ 14  

3) Experimental section .............................................................................................................................. 18  
   3.1 Nafion® ........................................................................................................................................ 18  
   3.2 Experimental setup...................................................................................................................... 18  
   3.3 Current efficiency and flux experiments ..................................................................................... 19  
   3.4 Outline of the experiments.......................................................................................................... 21  

4) Numerical section................................................................................................................................... 22  
   4.1 Model assumptions and simplifications ...................................................................................... 22  
   4.2 Nernst-Planck model................................................................................................................... 22  
   4.3 Initial conditions ........................................................................................................................... 24  
   4.4 Boundary conditions ................................................................................................................... 24  
   4.5 Grid definition............................................................................................................................. 25  
   4.6 Input parameters.......................................................................................................................... 25  

5) Experimental results and discussion....................................................................................................... 28  
   5.1 General remarks .......................................................................................................................... 28  
   5.2 Reproducibility ........................................................................................................................... 28  
   5.3 Nafion N1110 versus a bilayer membrane .................................................................................. 32  

6) Nernst-Planck model results ................................................................................................................... 34  
   6.1 Verification of neglecting the osmotic pressure.......................................................................... 34  
   6.2 Parameter sensitivity analysis and model optimization ............................................................ 35  
   6.3 Evaluation of the water flux equation .......................................................................................... 40  
   6.4 Additional remarks...................................................................................................................... 41
7) Model comparison with experimental results ........................................................................................................................................... 42
   7.1 The influence of concentration on the flux and transport numbers ........................................................................................................ 42
   7.2 The influence of current density on the flux and transport numbers ..................................................................................................... 43
   7.3 Evaluating the membrane potential drop ........................................................................................................................................... 45
8) Conclusions and recommendations .......................................................................................................................................................... 48
Acknowledgements .................................................................................................................................................................................. 50
List of symbols ......................................................................................................................................................................................... 52
References .............................................................................................................................................................................................. 54
Appendix A: Derivation of the Maxwell-Stefan approach and the Nernst-Planck approach ............................................................ 56
Appendix B: Derivation of the extended NP approach ............................................................................................................................ 58
Appendix C: Derivation of Ohm’s law when neglecting the diffusion and convective term ........................................................................ 59
Appendix D: Prove that the potential gradient cannot be constant ........................................................................................................... 60
Appendix E: Derivation of the osmotic pressure gradient .......................................................................................................................... 61
Appendix F: Pitzer activity model parameters and equations .................................................................................................................... 62
Appendix G: Derivation of the concentration jump based on the Donnan equilibrium theory .............................................................. 64
Appendix H: Hydrogen safety limits .............................................................................................................................................................. 67
Appendix I: Setup dimensions and equipment information ......................................................................................................................... 68
Appendix J: Experimental method of the current efficiency and flux experiments ...................................................................................... 69
Appendix K: Outline of the performed experiments ................................................................................................................................. 71
Appendix L: Empirical correlations ................................................................................................................................................................. 73
Appendix M: Model code .................................................................................................................................................................................. 76
Appendix N: Sensitivity analysis, preliminary results ............................................................................................................................... 87
Appendix O: Absolute tolerance values used in the sensitivity analysis simulations ................................................................................. 89
Appendix P: Experimental temperature results ........................................................................................................................................... 91
1) Introduction
Chlorine and caustic soda are considered among the top 10 chemicals produced worldwide\cite{1} with their global production capacities in 2012 being 58 million tonne and 63 million tonne\cite{2}, respectively. They both have various industrial applications, which are described thoroughly by O’Brien et al.\cite{1} Caustic finds its main uses in the pulp and paper industry and the production of numerous organics and inorganics. Moreover, it is used for water treatment and, for example, in: petroleum and natural gas operations; the food industry; and the production of soap, detergents, and aluminium.\cite{1,3} A schematic of the uses of chlorine is depicted in Figure 1. PVC and titanium dioxide are the most important products within the organic and inorganic chemicals production involving chlorine, respectively. In addition, chlorine is extensively used for water treatment and in the pulp and paper industry.\cite{1,4}

Chlorine and caustic soda are produced by the chlor-alkali process in which 1.1 ton of caustic soda and 28 kg of hydrogen are produced together with the production of 1 ton of chlorine.\cite{3} There are basically three different chlor-alkali technologies available: the diaphragm, the mercury and the membrane cell technology of which the latter is considered the current state of the art.\cite{1} It has gained interest over the last decades since it has a lower energy consumption, a higher caustic purity and a lower environmental impact compared to the other cell technologies.\cite{5} The environmental aspect is of special importance because diaphragm and mercury cell are fading out due to their use of hazardous asbestos and mercury, respectively.

![Figure 1: The chlorine tree.\cite{4}](image-url)
The need for a relatively low environmental impact chlor-alkali process, due to which the interest has shifted towards the use of membrane cells, has not been the only societal issue that recently influenced the chlor-alkali sector. Discussion about the safety of transporting large amounts of chlorine in public has resulted in governmental restrictions that forbid such transport. Therefore, process development for the on-site production of chlorine is of great interest for the industry.

Whereas conventional production sites are comparable with the size of a soccer field, the SPINCHAL project focuses on the development of a container-sized, transportable ‘Plug and Produce’ electrochemical production unit of approximately 10,000 tons chlorine per year. This production unit is based on the membrane chlor-alkali cell technology in which a back to back cation-selective membrane, such as Nafion®, can be used.

Although Nafion® membranes have been subject of investigation in several studies, the behavior of the components in these membranes and their behavior at elevated current densities (5-100 kA·m⁻²) and at high concentrations (~32 wt%) is still not yet fully understood. Particularly, intensification of the chlor-alkali process with respect to a high operational current density is of interest since this might be economically beneficial if power consumption does not increase too much and the membrane selectivity towards sodium ions remains sufficiently high.

1.1 Objective

This research study aims to develop a numerical model describing the transport of ions and water through a single layer cation-selective membrane containing sulfonate groups (Nafion®) for its use in a membrane chlor-alkali cell. Emphasis is put on the behavior of Nafion® regarding its selectivity for sodium ion transfer at high current densities (up to 20 kA·m⁻²) and at high concentrations (up to 32 wt%). The model will be based on the Nernst-Planck approach and validated qualitatively and quantitatively by means of experimental data. Model validation will be performed with respect to the flux of the components, the selectivity of the membrane towards sodium ions, and the potential drop over the membrane.

It should be noted that this study focuses on the simplified case in which the numerical model is constructed for and experiments are performed with a system containing only aqueous sodium hydroxide, i.e. a system without chlorine. However, the model will be constructed such that it can be easily extended to a multicomponent system.

The next chapter provides theoretical background information on the membrane chlor-alkali cell, the current efficiency in such cell, the membrane structure, and the fundamentals of modelling ion transport in such a system. Chapter 3 provides data about the Nafion® membrane and describes the experimental setup and the performed experiments. Chapter 4 provides the translation of the system into the numerical model along with accompanying assumptions and simplifications. The general experimental and numerical results are presented and discussed in chapter 5 and 6, respectively. Next, their results on varying the concentration and current density are presented and validated in chapter 7. Finally, the conclusions and recommendations are stated in chapter 8.

---

1 Nafion® behavior at current densities between 20 and 100 kA·m⁻² is not investigated in this study due to limitations of the experimental setup.
2) Literature overview

2.1 The membrane chlor-alkali cell
As stated in chapter 1, the membrane chlor-alkali process is the current state of the art electrolysis process in which chlorine can be produced by using a back to back cation-selective membrane. A schematic representation of this process is shown in Figure 2. It depicts an anode and a cathode compartment, which are separated by a cation selective membrane. Saturated brine enters the anode compartment in which it depletes due to selective transport of sodium ions through the membrane and the production of chlorine gas. At the other side of the membrane, an aqueous solution of 30 wt% caustic soda enters the cathode compartment in which its weight percentage increases to 33 wt% due to the aforementioned sodium transport and the production of hydrogen. The corresponding reactions at the anode and the cathode are depicted by Scheme 1 and Scheme 2, respectively.

![Figure 2: Scheme of the membrane chlor-alkali process.](image)

**Scheme 1:** Reaction at the anode.

\[ 2Cl^- \rightarrow Cl_2 + 2e^- \]

**Scheme 2:** Reaction at the cathode.

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]

2.2 Current efficiency
The current efficiency, i.e. the selectivity of the membrane towards the transport of sodium ions, is of high importance for effective operation. One aims to prevent transport of chloride ions from the anolyte to the catholyte as well as back migration of hydroxide ions because in both cases the less valuable components hypochlorite and chlorate will be formed.
Equation 1 describes the current efficiency by means of the transport number, which is defined as the fraction of the current carried by the sodium ions. When rewriting the equation, one can conclude that it can be calculated via the fluxes of the ions as well. In addition, it is evident that the summation of the transport numbers of all ionic species should equal unity, as shown by Equation 2. It should be noted that several different definitions are used in literature and, therefore, a direct comparison of the transport numbers mentioned in this report with literature data is not always allowed.

\[
CE = S_{Na} = t_{Na} = \frac{t_{Na} \Delta n_{Na} F}{It} = \left( \sum_{i} N_{i} \right) \left( \sum_{i} t_{i} \right)
\]

Equation 1

\[
\frac{N_{Na}}{\sum_{i} N_{i}} = 1
\]

Equation 2

Where CE equals the current efficiency [-], \(S_i\) equals the selectivity of species \(i\) [-], \(t_i\) equals the transport number of species \(i\) [-], \(\Delta n_i\) equals the number of moles of species \(i\) transferred [mol], \(F\) equals the Faraday constant [C·mol\(^{-1}\)], \(I\) equals the current [A], \(t\) equals the time [s], and \(N_i\) equals the molar flux of species \(i\) [mol·m\(^{-2}\)·s\(^{-1}\)].

### 2.3 Membrane structure

Typical membranes used in the membrane cell consist of a polymer perfluorinated backbone with ionic groups, usually sulfonate or carboxylate groups. Single layer or bilayer membrane structures are commercially available. The latter consists either of two layers with different ionic groups or with the same ionic groups but with a different ion exchange capacity (IEC), which is defined as the number of moles of ionic groups per gram of polymer. Although the electrical resistance of sulfonate membranes is lower than the electrical resistance of carboxylate membranes, they are more sensitive for back migration of hydroxyl ions at high caustic concentrations. Consequently, bilayer membranes with a sulfonic layer on the anolyte side and a small carboxylate layer on the catholyte side render the highest current efficiency.

Two important physical properties of a cation selective membrane are its IEC and its ability to absorb water. The reciprocal value of the IEC is the equivalent weight (EW), which is commonly used to describe the type of the membrane. The water content is usually expressed in mol H\(_2\)O per mol SO\(_3\)\(^-\) and depends on: the membrane pretreatment, the EW of the membrane, the temperature, and the nature and concentration of the electrolyte. It is usually higher for sulfonate membranes and increases with decreasing EW, increasing temperature, and decreasing electrolyte concentration.

The structure of the membranes, particularly Nafion\textsuperscript{®}, has been subject of investigation in numerous studies and different geometries are proposed. A well-known geometry for Nafion\textsuperscript{®} was proposed by Gierke et al. and is referred to as the cluster-network model. This model is shown in Figure 3 and depicts hydrophilic clusters with a diameter of 4 nm, which are separated by hydrophilic channels with a diameter of 1 nm.\[1][8] Although Duan et al. obtained a similar spacing between the clusters ranging from 5 to 6 nm by means of small angle X-ray scattering (SAXS), they state that the narrow channels proposed by Gierke et al. are inconsistent with water sorption and hydraulic permeability data. Based on their calculations, the channel diameter is approximately 2.5 nm.\[9]
A different model was presented by Schmidt-Rohr et al.\textsuperscript{[10]} They propose a water-channel model with cylindrical inverted micelles forming long parallel channels. Contradictory to the cluster-network model, they state that the ‘ionomer peak’, present in the SAXS analysis, is fully attributed to these channels. In addition, they state that Nafion\textsuperscript{®} with an EW of 1100 has a backbone crystallinity between 5 and 20\%, which acts as physical crosslinks providing the required mechanical strength of the membrane. A schematic of the suggested water-channel model is provided in Figure 4. Furthermore, they state that hydrated channels (20 vol\%) have a diameter between 1.8 and 3.5 nm with an average diameter of 2.4 nm, which is similar to the value found by Duan et al.

The tortuosity of the membrane channels has been studied by Zhao et al.\textsuperscript{[11]} They have shown that the tortuosity decreases from 20 at a water uptake (\(\lambda\)) of 0.5 mol H\(_2\)O/mol SO\(_3\)- to approximately 2 at a water uptake > 5 mol H\(_2\)O/mol SO\(_3\). Furthermore, results of Zhao et al. suggest that there are two hydration layers present when Nafion\textsuperscript{®} is equilibrated in water, as depicted by Figure 5. The first layer forms between 0 < \(\lambda\) < 4 and corresponds with water which strongly interacts with the ionic groups. The second layer forms at \(\lambda\) > 4 and has considerably less interaction with the ionic groups.
An important aspect, which has to be evaluated when describing the microscopic structure of charged channels, is whether or not a potential gradient will occur due to the formation of a Debye double layer. A Debye double layer is characterized by the Debye length, which is the distance from a charged surface at which charge separation is no longer present. Strathmann provides data for the Debye length for different electrolyte concentrations up to 0.1M. For a monovalent electrolyte, the Debye length decreases rapidly from 30.4 nm for a $1\cdot10^{-4}$ M solution to 1 nm for a $1\cdot10^{-1}$ M solution. Consequently, with a channel diameter of $\sim 2.4$ nm, a potential drop in the radial direction should be present when the concentration of the electrolyte is sufficiently high ($>1\cdot10^{-1}$ M). However, Burton reports that a hydrated sodium ion has a diameter of 1.58 nm, which is very large compared to the channel diameter. Although one can argue whether the hydration factor of sodium ions decreases in the channel, thereby decreasing the hydrated diameter of the ion, it seems to be peculiar to state that there are multiple layers present in the radial direction of the channel. Consequently, it is hard to believe that there is a potential gradient present in the radial direction. The nature of this nanoscale system requires a study on molecular dynamics in order to achieve insight on the exact structure of an electrolyte solution in a cation selective membrane. Unfortunately, as far as is known, this is unavailable.

2.4 Theoretical models of transport through the membrane
Appropriate mass transport models are required for the prediction of ion transport inside the membrane at industrial operating conditions at equilibrium. This mass transfer can be modeled using either the Nernst-Planck (NP) or the Maxwell-Stefan (MS) approach, which are presented schematically on a molecular level in Figure 6. While the MS approach accounts for the interactions of different species, the NP approach neglects them. Therefore, the NP approach is considered to be only valid for systems of dilute concentrations.
The MS approach originates from the law of conservation of momentum and the irreversible thermodynamics theory.\[^{14}\] Its derivation is presented in Appendix A. One has attempted to model the membrane cell with the MS approach, but the unavailability of accurate Maxwell-Stefan diffusivities is a recurring issue.\[^{15}\][\(^{16}\)] Consequently, the composed model in this study is based on the NP approach for simplicity, thereby neglecting that the electrolytes in the industrial membrane cell electrolyzer are actually highly concentrated. This approach is presented by Equation 3 and is derived from the MS approach as described in Appendix A.

\[ N_i = -D_i \nabla C_i - z_i D_i C_i \frac{F}{RT} \nabla \phi + C_i \nu \]  
Equation 3

Where \( D \) equals the diffusion coefficient \([\text{m}^2 \cdot \text{s}^{-1}]\), \( C \) equals the concentration \([\text{mol} \cdot \text{m}^{-3}]\), \( z \) equals the valence of species \( i \) \([-]\), \( R \) equals the universal gas constant \([\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]\), \( T \) equals the temperature \([\text{K}]\), \( \phi \) equals the potential \([\text{V}]\), and \( \nu \) equals the convective volume flux \([\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}]\).

In the NP equation, there are three terms that contribute to ion transfer; namely, a diffusion term, a potential term and term reflecting the convective flow of aqueous caustic soda. These terms are represented by the first three terms on the right hand side of Equation 3, respectively. The convective term consists of two factors; namely, transfer due to osmotic pressure and due to electro-osmotic effects. This is governed by the convective volume flux (Equation 4), which is commonly referred to as the Schlögl equation.\[^{17}\][\(^{18}\)] Furthermore, Schlögl mentioned a relation for the hydrodynamic permeability based on its derivation via the Hagen-Poiseulle equation, see Equation 5.\[^{17}\]

\[ v = d_h \left( z_m C_m F \nabla \phi - \nabla P \right) \]  
Equation 4

\[ d_h = \frac{d_c^2 \varepsilon_{\text{void}}}{32 \eta} \]  
Equation 5

Where \( d_h \) equals the hydrodynamic permeability \([\text{s} \cdot \text{kg} \cdot \text{m}^{-3}]\), \( z_m \) equals the valence of the ionic groups in the membrane \([-]\), \( C_m \) equals the concentration of the ionic groups in the membrane \([\text{mol} \cdot \text{m}^{-3}]\), \( P \) equals the pressure \([\text{Pa}]\), \( d_c \) equals the channel diameter \([\text{m}]\), \( \varepsilon_{\text{void}} \) equals the void fraction \([\text{m}_{\text{void}}^3 \cdot \text{m}_M^{-3}]\), and \( \eta \) equals the dynamic viscosity \([\text{Pa} \cdot \text{s}]\).

One could obtain an intermediate approach of the NP and the MS model by still using the non-ideal form of the driving force (Equation A5) instead of its diluted form (Equation A12). In this case, only the Maxwell-Stefan diffusivities are omitted by assuming Equation A10 and Equation A11. Solving the remaining set of equations results in this extended form of the NP approach, see Equation 6. The derivation of this equation is presented in Appendix B.

\[ N_i = -D_i \left( C_i \frac{\nabla \ln (\gamma_i)}{\nabla C_i} + 1 \right) \nabla C_i + \frac{C_i}{C_{\text{tot}}} D_i \nabla C_{\text{tot}} - z_i D_i C_i \frac{F}{RT} \nabla \phi + C_i \nu \]  
Equation 6

Where \( \gamma \) equals the activity coefficient \([-]\).

Literature data and model validation based on the NP approach is executed mostly at concentrations up to 32 wt% and at relatively low current densities (0 to 5 kA \cdot m^{-2}).\[^{5}\][\(^{19}\)][\(^{20}\)] Chen et al.\[^{20}\] focus on the chloride and chlorate levels in the 32 wt% caustic product. They use Ohm’s law for the potential gradient (Equation 7) with the conductivity being only dependent on temperature. The validity of Ohm’s law with the conductivity being only dependent on temperature is debatable since it is also concentration dependent.\[^{11}\]
\[ \frac{d \varphi}{dz} = -\frac{J}{\kappa} \]  
\text{Equation 7}

Where \( z' \) equals the length scale parameter [m], \( J \) equals the current density \([\text{A} \cdot \text{m}^{-2}]\) and \( \kappa \) equals the membrane conductivity \([\Omega^{-1} \cdot \text{s}^{-1}]\)

In literature, Equation 8 is commonly used for the conductivity.\(^{[12][21]}\) However, the validity of Equation 7 is still debatable since it can be derived that this relation is obtained for the case of no convection and no concentration gradient, see Appendix C. Therefore, back substitution of Equation 7 into Equation 3 is not suitable in the general case when the diffusion and convective term are included.

\[ \kappa = \sum \left( z_i^2 D_i C_i \frac{F^2}{RT} \right) \]  
\text{Equation 8}

One can omit the use of Ohm’s law when considering electroneutrality in the system, which is presented in Equation 9 and Equation 10 for the solution and the membrane phase, respectively. The electroneutrality condition provides an additional degree of freedom due to which the potential gradient can be determined as a function of the other terms of the NP equation. This is done by Bouzek et al.\(^{[5][19]}\), although they do not specifically mention the correlation between the potential gradient and the other terms in the NP equation. Besides considering electroneutrality, they use the aforementioned Schlögl equation to describe the convective flow. Moreover, they assume laminar electrolyte flow, ideal behavior of the solutions, incompressibility of the liquid phase, and a constant concentration of evenly distributed ionic groups in the membrane. The major disadvantage from the model of Bouzek et al.\(^{[5][19]}\) is that it assumes steady state and, therefore, requires accurate initial guesses in order to avoid convergence errors.

\[ \sum_{i=1}^{n} z_i C_i = 0 \]  
\text{Equation 9}

\[ \sum_{i=1}^{n} z_i C_i + z_m C_m = 0 \]  
\text{Equation 10}

The potential gradient cannot be linear since this conflicts with the electroneutrality condition as is proven in Appendix D. A non-linear potential gradient, in which the electroneutrality condition is still obeyed, can be obtained via a relation between the current density and the fluxes of the ionic species (Equation 11).\(^{2}\) Substitution of Equation 3 in this equation results after a few rearrangements in the expression for the non-linear potential gradient (Equation 12).

\[ J = F \sum_{i=1}^{n} z_i N_i + \epsilon \frac{\partial E}{\partial t} \approx F \sum_{i=1}^{n} z_i N_i \]  
\text{Equation 11}

\[ \nabla \varphi = \frac{J}{F} + \sum_{i=1}^{n} z_i D_i \nabla C_i + \sum_{i=1}^{n} z_i C_i d_i \nabla P \]  
\text{Equation 12}

\[ \sum_{i=1}^{n} z_i C_i d_i z_m C_m F - \sum_{i=1}^{n} z_i^2 D_i C_i \frac{F}{RT} \]

Where \( \epsilon \) equals the permittivity \([\text{F} \cdot \text{m}^{-1}]\) and \( E \) equals the electric field \([\text{V} \cdot \text{m}^{-1}]\).

\(^{2}\) The displacement current, which describes the change of the electric field in time, is neglected.
The osmotic pressure gradient for non-ideal electrolytes can be described by Equation 13 and is derived from the equilibrium of the chemical potential between an electrolyte at position $i_{i+1}$ and position $i_i$, as is described in more detail in Appendix E.

$$\nabla P = -RTV C_{H_2O} \ln \left( \frac{y_{i_{i+1}}^{i_{i+1}} H_2O \Delta y_{i_{i+1}}^{i_{i+1}}}{y_{i_i}^{i_i} H_2O \Delta y_{i_i}^{i_i}} \right)$$

Equation 13

Where $x$ equals the mole fraction [-].

Along with the transport of ionic species, there is a flux of water through the membrane. This water flux physically comprises the transport due to: water diffusion, hydrated ions, drag forces, and osmotic pressure. Most research on the topic of water transport through membranes focuses on proton exchange membrane fuel cells (PEMFC), which differ from the membrane cell for caustic production in a sense that it has a catalyst layer in the membrane and a gaseous phase on one side of the membrane. Therefore, their model equations cannot be directly applied for the caustic production membrane cells. In this study, it is attempted to model the water flux based on an equation similar to Equation 3, which is presented in Chapter 4.

### 2.5 Concentration profile at the membrane interface

There is a concentration gradient present in the solution near the membrane interface. This gradient is investigated in several studies and is schematically depicted in Figure 7. A distinction is made between an electroneutral diffuse layer (DL) and an electrically charged double layer (EDL). The latter is caused by the ionic groups in the membrane.

![Figure 7: The concentration gradient at the solution-membrane interface.][26]

Mathematically, the double layer region can be described by the Donnan equilibrium theory. It describes the jump in potential and activity of an ionic species at the solution-membrane interface, which is schematically depicted in Figure 8. Consequently, the electrolyte interface activity refers to the activity at the DL-EDL interface. The Donnan potential ($\varphi_{Don}$) can be calculated either via the activity of a positive species or a negative species as described by Equation 14. It contains the osmotic pressure difference, which is described by Equation 15.

$$\varphi_{Don} = \varphi^{M,0} - \varphi^{A,\text{int}} = \frac{1}{z_i F} \left( RT \ln \left( \frac{a_i^{A,\text{int}}}{a_i^{M,0}} \right) - \bar{V} \Delta \Pi \right)$$

Equation 14

Where $a_i$ equals the activity of species $i$ [-], $\bar{V}$ equals the partial molar volume $[m^3\cdot mol^{-1}]$, $\Delta \Pi$ equals the osmotic pressure difference [Pa].

---

3 Note that the concentration gradient in the diffuse layers and in the membrane is most likely non-linear in reality and that the potential will not be constant in the solution or in the membrane.
Activity can be expressed in terms of molality or in terms of concentration (Equation 16). Activity models for electrolyte systems are commonly based on molality. An example of such activity model is the Pitzer model, which is able to provide activity coefficients for electrolyte bulk solutions\cite{31}\cite{32} as well as electrolyte solutions\cite{33} in membranes if values for the interaction parameters are known. Fortunately, parameters for caustic solutions are available and are provided in Appendix F together with the Pitzer model equations. Molality is related to concentration via Equation 17. It contains the caustic density and the water weight fraction, which are both concentration dependent as well.

\[ a_i = \gamma_i x_i = \frac{\gamma_i m_i}{m_{\text{tot}}} = \frac{\gamma_i C_i}{C_{\text{tot}}} \]  
\[ m_i = \frac{C_i}{\rho_{\text{sol}} w_f H_2O} \]  

Where \( m \) equals the molality [mol·kg\(_{H_2O}\)^{-1}], \( \rho \) equals the density [kg·m^{-3}] and \( w_f \) equals the weight fraction [-].

Equation 18 is obtained after simplification of Equation 14 for a system containing only Na\(^+\) and OH\(^-\).\footnote{12} Unfortunately, extension to a multicomponent system via this derivation is not straightforward without the use of certain assumptions.

\[ C_{Na}^{M,0} = \frac{C_m + \sqrt{C_m^2 + 4 \left(C_{Na,\text{int}}^{A,0} \right)^2 \left(\gamma_{\text{Na}^+}^{M,0} \gamma_{\text{OH}^-}^{M,0} \right)/ \left(\gamma_{\text{Na}^+}^{A,\text{int}} \gamma_{\text{OH}^-}^{A,\text{int}} \right)}}{2} \]  

\footnote{In order to obtain Equation 18, it is assumed that \( e^{\frac{\mu_{\text{int, tot}} \Delta \Pi}{RTz_e V_i}} \approx 1 \)}
Higa et al. neglect the second term on the right hand side of Equation 14, which represents the osmotic contribution. After rearrangement of the remaining formula, a relation between the solution interface activity and the membrane interface activity of an ionic species is obtained, see Equation 19.\footnote{Instead of concentration, one could also write molality.} It includes the Donnan equilibrium constant, $K$, which is equal for all ionic species. Furthermore, the electroneutrality condition in the electrolyte and the membrane for a monovalent system are presented in Equation 20a and Equation 20b, respectively.

$$\frac{\gamma_i^{M,0} C_i^{M,0}}{\gamma_i^{A,int} C_i^{A,int}} = e^{\left(\frac{-Fz_i \phi_{Don}}{RT}\right)} = K^z_i \quad \text{Equation 19}$$

$$\sum_i N^A,\text{int}_i C^A,\text{int}_i \text{,pos} = \sum_i N^A,\text{int}_i C^A,\text{int}_i \text{,neg} \quad \text{Equation 20a}$$

$$\sum_i N^A,\text{int}_i C^A,\text{int}_i \text{,pos} - C_m^A = \sum_i N^A,\text{int}_i C^A,\text{int}_i \text{,neg} \quad \text{Equation 20b}$$

Via Equation 20a, one can obtain a relation between the concentration at the solution interface as a function of the concentration at the membrane interface. Similarly, one can obtain a relation between the concentration at the membrane interface as a function the concentration at the solution interface via Equation 20b. Their derivations for a monovalent multicomponent system are presented in Appendix G. For a system containing only $\text{Na}^+$ and $\text{OH}^-$, Equation 21 and Equation 18 are obtained from these derivations and it can be shown that they are equal, which is described in Appendix G as well.

$$C_{Na^+}^{A,\text{int}} = \sqrt[3]{\frac{\gamma_{Na^+}^{M,0} C_{Na^+}^{M,0} \gamma_{OH^-}^{M,0} C_{OH^-}^{M,0}}{\gamma_{Na^+}^{A,\text{int}} \gamma_{OH^-}^{A,\text{int}}}} \quad \text{Equation 21}$$

The boundary condition of the model requires the electrolyte interface concentration to be described as a function of the membrane interface concentration. Unfortunately, the commonly used derivation, which is based on Equation 20b, cannot be easily rearranged in the case of a multicomponent system in order to fulfill this requirement. Consequently, the relation obtained via Equation 20a is preferred.
3) Experimental section

3.1 Nafion®
A commercially available DuPon® Nafion® PFSA membrane, Nafion N1110, was used for the experiments. Its properties are provided in Table 1.[34] Before each experiment, the membrane was pretreated by means of overnight equilibration in a caustic solution of the same concentration as the concentration used during the experiment. Consequently, the membrane was ensured to be in the sodium and swollen state before starting the experiment.

<table>
<thead>
<tr>
<th>Property</th>
<th>Nafion N1110</th>
</tr>
</thead>
<tbody>
<tr>
<td>EW [g polymer/mol SO₃⁻]</td>
<td>1100</td>
</tr>
<tr>
<td>Thickness [m]</td>
<td>254·10⁻⁶</td>
</tr>
<tr>
<td>Dry state density [g·m⁻³]</td>
<td>1.97·10⁶</td>
</tr>
<tr>
<td>Expansion [%]</td>
<td>10</td>
</tr>
<tr>
<td>Swollen state density [g·m⁻³]</td>
<td>1.79·10⁶</td>
</tr>
</tbody>
</table>

3.2 Experimental setup
For safety reasons, all experiments were performed with an aqueous NaOH solution as the anolyte and the catholyte; i.e. the use of chlorine was prevented. Therefore, the reaction at the anode corresponding with the operating conditions is described by Scheme 3.

\[
4OH^- \rightarrow O_2 + 2H_2O + 4e^-
\]

The experimental setup is schematically depicted in Figure 9. The anolyte compartment (A) is shown on the left and the cathode compartment (C) on the right. They each contain an outer shell in which oil is circulated. This oil flows through a heating bath by which the temperature of the solutions is controlled. In addition, a thermometer (T) is used to monitor the temperature inside the catholyte compartment. Furthermore, each compartment is provided with a cooler in order to prevent evaporation of water and make the system closed for the water balance. In the cooler of the catholyte compartment, nitrogen (N₂) is used to dilute the formed hydrogen during reaction in order to ensure safe operation. The nitrogen flow is controlled via a flow meter and is set according to the safety data provided by NASA.[35] More details about the required nitrogen flow are provided in Appendix H.

The membrane is positioned between the two compartments by using a clamp and rubber O-rings. The potential drop over the membrane is measured via Ag/AgCl reference electrodes (RE), which are positioned in Luggin capillaries. In order to improve mass transfer at the solution side near the membrane interface and decrease the boundary layer effect, the anolyte and catholyte are separately circulated by using a pump. Moreover, in each circulation loop, a thermometer is placed in a flow cell to monitor the temperature of the electrolytes before they enter the compartments close to the membrane. In addition, the flow cells are closed with rubber septic caps to be able to take samples for titration. A list of the dimensions of the setup and the equipment information is provided in Appendix I.

---

6 Expansion corresponds with the transition from 50% relative humidity at 296 K to water soaked at 296 K.[34]
The input and output parameters of the setup are described in Table 2. The details on how each output parameter is obtained are provided in Table I2.

### Table 2: Input and output parameters of the experiments.

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>Output parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat bath temperature [°C]</td>
<td>Temperature catholyte compartment [°C]</td>
</tr>
<tr>
<td></td>
<td>Temperature anolyte flow cell [°C]</td>
</tr>
<tr>
<td></td>
<td>Temperature catholyte flow cell [°C]</td>
</tr>
<tr>
<td>Current density [kA·m⁻²]</td>
<td>Voltage over the electrodes [V]</td>
</tr>
<tr>
<td></td>
<td>Voltage over the membrane [V]</td>
</tr>
<tr>
<td>Anolyte and Catholyte [wt%]</td>
<td>Anolyte and Catholyte [wt%]</td>
</tr>
<tr>
<td>Anolyte weight [g]</td>
<td>Anolyte weight [g]</td>
</tr>
<tr>
<td>Catholyte weight [g]</td>
<td>Catholyte weight [g]</td>
</tr>
</tbody>
</table>

### 3.3 Current efficiency and flux experiments

The influence of current density and concentration on the current efficiency and component fluxes was investigated by performing experiments in which a certain current density was applied for a sufficient period of time allowing the anolyte and catholyte concentrations to change. Furthermore, the temperature was aimed to remain constant during the experiment. Beforehand, the compartments were filled with an equal, weighed amount of anolyte and catholyte, which were taken from a single NaOH solution with a known concentration. This solution was prepared from a 50 wt% stock solution. The final concentration and weight of the electrolytes were determined by taking samples for titration and weighing the...

---

7 50 wt% NaOH in H₂O: Sigma-Aldrich, product number 415413-4L, CAS number 1310-73-2
electrolytes at the end of the experiment. All titrations were performed in triplicate with a 0.1 M HCl solution\(^8\) and under an argon atmosphere in order to prevent absorption of CO\(_2\). The potential drop over the membrane was measured via reference electrodes and is corrected for the potential drop due to the electrolyte resistance. The detailed experimental method of the current efficiency and flux experiments is provided in Appendix J.

From the weight and concentration data and the mass balance in the system, the transport numbers and the fluxes of the components were obtained via Equation 22 and Equation 23, respectively.\(^7\) For water, the flux with respect to the sodium flux is calculated, thereby indicating the relative amount of water transport with respect to the sodium ions. This is described by Equation 24.

\[
t_i = \frac{\Delta w_i F}{M_{w_i} I t}
\]

Equation 22

\[
N_i = \frac{\Delta w_i}{M_{w_i} A \perp t}
\]

Equation 23

\[
T_{H_2O} = \frac{\Delta w_{H_2O} M_{Na^+}}{\Delta w_{Na^+} M_{H_2O}}
\]

Equation 24

Where \(\Delta w_i\) equals the weight difference of species \(i\) [g], \(M_{w_i}\) equals the molecular weight of species \(i\) [g·mol\(^{-1}\)], \(A \perp\) equals the area perpendicular to the flow direction (i.e. the membrane cross-sectional area), and \(T_{H_2O}\) equals the relative water transport number [-].

The mass balance is depicted in Figure 10 and described by Scheme 4 and Scheme 5 for the anolyte and the catholyte, respectively. The mass balance accounts for mass loss due to: reaction at the electrodes, the evaporation of water, samples which were taken, and possible leakage near the membrane. The latter might occur when the membrane is not perfectly sealed by the clamp.

\[8\] 0.1 M HCl: TitrPUR\textsuperscript{®}, product number 1.09060.1000, CAS number 7647-01-0
3.4 Outline of the experiments

The industrial and experimental operating conditions are described in Table 3. Since the emphasis of the experiments is on the effect of high current densities and concentrations, the temperature influence on the current efficiency and flux was not investigated. In order to verify the reproducibility of the experiments, four experiments were performed at a current density of 10 kA·m⁻² and a concentration of 10 wt%. Afterwards, the current density and concentration were varied, with their values being 2, 6, 10, 20 kA·m⁻² and 10, 15, 32 wt%, respectively. A detailed description of the experiments is provided in Appendix K and the main results are explained in chapter 5.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Industrial value</th>
<th>Experimental value/range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [°C]</td>
<td>88-94</td>
<td>See Table K5</td>
</tr>
<tr>
<td>Pressure [bar]</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Current density [kA·m⁻²]</td>
<td>3-5</td>
<td>2, 6, 10, 20</td>
</tr>
<tr>
<td>Caustic concentration [wt%]</td>
<td>30-32</td>
<td>10, 15, 32</td>
</tr>
</tbody>
</table>
4) Numerical section
The PDEPE solver of MATLAB R2013b was used to model the mass transport through the membrane. This solver is able to cope with one-dimensional, unsteady state partial differential equations. Although the unsteady state solution is not of interest in this study, it is used as a method to obtain the steady state solution. The advantage compared to a steady state solver for differential and algebraic equations is that numerical convergence errors, caused by inaccurate initial guesses of parameters, are prevented. These convergence errors were an issue in the model of Bouzek et al.[15][19]

4.1 Model assumptions and simplifications
The following assumptions and simplifications were used in the model:
- The system is at constant temperature corresponding to the experimental steady state temperature;
- The system is at constant pressure;
- The pressure contribution is neglected in the derivation of the Donnan equilibrium constant;
- The potential gradient in the radial direction is neglected;
- The concentration of H2O at the anolyte and membrane interface are set equal;
- The diffusion coefficient is set equal for all non-stationary species in the preliminary simulations;
- The components behave ideally;
- The sulfonate groups are stationary and evenly distributed throughout the membrane;
- The membrane consists of uniform, cylindrical channels;
- The membrane does not swell, i.e. the IEC, void fraction and polymer density are constant;
- The sulfonate groups are considered to be fully present in the void fraction of the membrane;
- Tortuosity effects are neglected;
- Experimental data was used to obtain empirical relations for the bulk concentrations as a function of time.

4.2 Nernst-Planck model
In the system of investigation, there are three species able to migrate through the membrane: Na+, OH− and H2O. As mentioned in paragraph 2.4, the NP equation is derived from the generalized Maxwell-Stefan equations by using the assumption of a dilute system, which results in Equation 3. Since electroneutrality should hold in the membrane solution (Equation 10), one can model the transport of n-1 species by using the continuity equation (Equation 25) in which the NP equation can be substituted and the source term (σ) equals zero in the system of investigation.

\[
\frac{dC_i}{dt} = \sigma - \nabla \left( N_i \right) \quad \text{Equation 25}
\]

Although the presence of potential and concentration gradients due to the formation of a Debye double layer in the radial direction is not indisputable, see paragraph 2.3, membrane transport is only modeled in the longitudinal direction of the channels (z-direction). Moreover, the model is made dimensionless with respect to this direction by using Equation 26a, which results in Equation 26b and Equation 26c for the NP flux and Schlögl, respectively. Substitution of Equation 26b in Equation 25 results in Equation 27 and Equation 28 for Na+ and H2O, respectively. Since there are only two non-stationary ions in this system, OH− is modeled via the electroneutrality condition.

\[
\frac{z}{\delta_M} = z \quad \text{Equation 26a}
\]
\[
N_i = \left( -D_i \frac{dC_i}{dz} - z_i D_i C_i \frac{F}{RT} \frac{d\phi}{dz} + v C_i \delta_M \right) \frac{1}{\delta_M} \quad \text{Equation 26b}
\]
\[
\frac{v}{\delta_M} = \frac{d_h}{\delta_M} \left( \frac{z_m C_{m} F d\varphi}{dz} - \frac{dP}{dz} \right) 
\]

Equation 26c

\[
\delta_M \frac{dC_{Na^+}}{dt} = \frac{d}{dz} \left( D_{Na^+} \frac{dC_{Na^+}}{dz} - z_{Na^+} D_{Na^+} C_{Na^+} \frac{F d\varphi}{RT dz} - \nu C_{Na^+} \delta_M \right) \frac{1}{\delta_M} 
\]

Equation 27

\[
\delta_M \frac{dC_{H2O}}{dt} = \frac{d}{dz} \left( D_{H2O} \frac{dC_{H2O}}{dz} - \nu C_{H2O} \delta_M \right) \frac{1}{\delta_M} 
\]

Equation 28

Where \( \delta_M \) equals the membrane thickness [m], and \( z \) equals the dimensionless length scale parameter [-].

The convective term in Equation 28 accounts for the amount of water transported together with the convective flux of sodium ions. However, water transport by means of hydrated sodium ions, which are transported by means of diffusion or potential forces, is not accounted for. In order to include this water transfer, it is suggested to add two terms to this equation, see Equation 29.

\[
\delta_M \frac{dC_{H2O}}{dt} = \frac{d}{dz} \left( D_{H2O} \frac{dC_{H2O}}{dz} - \nu C_{H2O} \delta_M + hf_{Na^+} \sum_{i=1}^{n} D_{Na^+} \frac{dC_{Na^+}}{dz} \right) \frac{1}{\delta_M} 
\]

Equation 29

Where \( hf \) equals a hydration factor for the diffusional and potential contributions of \( Na^+ \) to the transport of water [-].

In summary, Equation 20b, Equation 27 and Equation 28 are used to model the transport of \( OH^- \), \( Na^+ \) and \( H_2O \) in the membrane, respectively. The potential gradient (Equation 12) reduces to Equation 30 when using the Equation 20b.

\[
\frac{d\varphi}{dz} = \frac{J \delta_M}{F} + z_{Na^+} D_{Na^+} \frac{dC_{Na^+}}{dz} + z_{OH^-} D_{OH^-} \frac{dC_{OH^-}}{dz} + z_{SO_3^-} C_{SO_3^-} d_h \frac{dP}{dz} 
\]

Equation 30

Equation 30 and the convective volume flux (Equation 4) both contain the osmotic pressure gradient, which can be neglected according to literature since its contribution is small compared to the other terms.\(^{[14]}\) Note that this assumption was already made in the derivation of the Donnan equilibrium constant. In order to verify whether the osmotic pressure drop can indeed be neglected, the two terms in the Schlögl equation were evaluated for the ideal and non-ideal case of the osmotic pressure. In order to determine the pressure gradient in the non-ideal case, an empirical relation of the water activity coefficient was used based on experimental data from Stokes, which is presented in Appendix L.\(^{[36]}\)

It is complicated to implement the osmotic pressure equation directly into the model since it includes the logarithm of the water activity at two consecutive longitudinal positions. Therefore, an indirect method was used to compare the osmotic pressure term with the potential term. First, the model was run without the osmotic pressure and the order of magnitude of the logarithm was determined from its resulting water concentration profile. Then, the osmotic pressure drop was implemented in the model in which a multiplication factor of this order of magnitude was used in order to account for the logarithm. Finally, the resulting water concentration profile was used to determine the osmotic pressure contribution.
4.3 Initial conditions
The unsteady state values are not of interest in this study; consequently, a rough estimate of the initial values is sufficient. The concentration of Na\(^+\) is simply set equal to the concentration of the sulfonate groups. The sulfonate concentration is calculated via Equation 31 and the value for the polymer density is assumed to be constant and equal to the value of the swollen polymer density mentioned in Table 1. Due to electroneutrality, the initial OH\(^-\) concentration is set to zero. The initial water concentration is based on an empirical correlation of water uptake data from O’Brien et al. The influence of temperature on the water uptake is not taken into account. As a result, the obtained correlation is only dependent on the caustic concentration. It is presented in Appendix L.

\[
C_{S\text{O}_3} = \frac{\rho_{pol} \text{IEC}}{\epsilon_{\text{void}}}
\]

Equation 31

4.4 Boundary conditions
The boundary conditions of Na\(^+\) and H\(_2\)O are set via the requirement that the flux on the solution side should be equal to the flux on the membrane side as is shown in Equation 32a and Equation 32b for the left and right side of the membrane, respectively. Note that the membrane fluxes are multiplied with the void fraction in order to ensure equal units for both fluxes. In the case of Na\(^+\), the concentration at the solution interface is eliminated by insertion of Equation 21 (the Donnan equilibrium) and in the case of H\(_2\)O, it is assumed that the concentration at the anolyte and membrane interface are equal. Similar to the membrane OH\(^-\) concentration, its concentration at the boundary is set by electroneutrality.

\[
k_{AM} \left( C_i^{A,\text{bulk}} - C_i^{A,\text{int}} \right) = \left( -D_i \frac{dC_i^{M,0}}{dz} - z_i D_i C_i^{M,0} \frac{F}{RT} \frac{d\varphi}{dz} + vC_i^{M,0} \delta_M \right) \frac{1}{\delta_M} \frac{A_{\text{void}}}{A_M}
\]

Equation 32a

\[
k_{CM} \left( C_i^{C,\text{int}} - C_i^{C,\text{bulk}} \right) = \left( -D_i \frac{dC_i^{M,\delta}}{dz} - z_i D_i C_i^{M,\delta} \frac{F}{RT} \frac{d\varphi}{dz} + vC_i^{M,\delta} \delta_M \right) \frac{1}{\delta_M} \frac{A_{\text{void}}}{A_M}
\]

Equation 32b

Where \(k_{AM}\) and \(k_{CM}\) equal the anolyte to membrane and membrane to catholyte mass transfer coefficient \([\text{m}_{\text{sol}} \text{m}^{-2}\text{s}^{-1}]\), respectively.

Alternatively, one could describe the system such that the boundary conditions are set as the bulk electrolyte concentrations by modeling the diffusion layer on the electrolyte side via the NP approach. The boundary condition itself would become numerically easier to solve and the mass transfer coefficients, which are now implemented as educated guesses, will be omitted. More importantly, the activity coefficients at the solution interface are unknown, but are still present in Equation 21. Consequently, one avoids an additional assumption if one would aim to implement non-ideality within the adjusted system setup. A disadvantage of this setup is that it requires knowledge on the relative thickness of the diffusion layers compared to the membrane thickness, which is dependent on the flow pattern in the diffusion layers. Moreover, the concentration jump should be implemented at the grid points corresponding to the electrolyte-membrane interfaces, as depicted in Figure 11. For more information on this model setup, the reader is referred to Bouzek et al.\cite{5,19}
4.5 Grid definition

Gradients near the boundary are large; consequently, the grid point settings for the dimensionless length scale parameter are separated in a logarithmic layer of 0.01 at both boundaries and a linear grid in the center of the membrane. In total, the dimensionless length scale parameter is defined by 52 grid points of which the first 6 and final 6 are logarithmic. A linear grid point settings is used for the time parameter.

4.6 Input parameters

The input parameters of the model are presented in Table 4. The initial values for the diffusion coefficient, the void fraction, and the solution to membrane mass transfer coefficients were introduced as estimated constants based on literature values or simply as educated guesses. The influence of these parameters on the model output parameters and their optimum value with respect to the results of the reproducibility experiments are described in paragraph 6.2. Besides these input parameters, an empirical correlation is used for the water uptake as a function of NaOH concentration, which is provided in Appendix L.

Since the experiments are performed in batch mode for the anolyte and catholyte, their bulk concentrations change in time. Consequently, the experimental data as a function of time is used as input for the boundary conditions in order to be able to properly validate the model with the experiments.
Table 4: Input parameters used in the model.

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>Value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>T [°C]</td>
<td>-</td>
<td>Value corresponding with experiments</td>
</tr>
<tr>
<td>C (anolyte and catholyte) [wt%]</td>
<td>-</td>
<td>Value corresponding with experiments</td>
</tr>
<tr>
<td>J [A·m⁻²]</td>
<td>-</td>
<td>Value corresponding with experiments</td>
</tr>
<tr>
<td>t [s]</td>
<td>-</td>
<td>Value corresponding with experiments</td>
</tr>
<tr>
<td>η [Pa·s]</td>
<td>-</td>
<td>Value corresponding with experiments</td>
</tr>
<tr>
<td>z(Na⁺, OH⁻, H₂O, SO₃⁻) [-]</td>
<td>1, -1, 0, -1</td>
<td>Based on data from Solvay Chemicals[37]</td>
</tr>
<tr>
<td>R [J·K⁻¹·mol⁻¹]</td>
<td>8.3145</td>
<td></td>
</tr>
<tr>
<td>F [C·mol⁻¹]</td>
<td>96485</td>
<td></td>
</tr>
<tr>
<td>Mw NaOH [g·mol⁻¹]</td>
<td>39.997</td>
<td></td>
</tr>
<tr>
<td>Mw H₂O [g·mol⁻¹]</td>
<td>18.015</td>
<td></td>
</tr>
<tr>
<td>IEC [mol SO₃⁻·gₚol⁻¹]</td>
<td>9.09·10⁻⁴</td>
<td>DuPont[34]</td>
</tr>
<tr>
<td>δₕ [m]</td>
<td>254·10⁻⁵</td>
<td>DuPont[34]</td>
</tr>
<tr>
<td>Swollen state density [g·m⁻³]</td>
<td>1.79·10⁶</td>
<td>DuPont[34]</td>
</tr>
<tr>
<td>D [m²·s⁻¹]</td>
<td>1·10⁻⁹</td>
<td>Educated guess</td>
</tr>
<tr>
<td>ε void [mᵢₚ₀³·mᵢₚ⁻³]</td>
<td>0.2</td>
<td>Schmidt-Rohr et al.[10] and Zhao et al.[11]</td>
</tr>
<tr>
<td>kₐM &amp; kₐCM (Na⁺) [m·s⁻¹]</td>
<td>1·10⁴</td>
<td>Educated guesses</td>
</tr>
<tr>
<td>kₐM &amp; kₐCM (H₂O) [m·s⁻¹]</td>
<td>1·10⁴</td>
<td>Educated guesses</td>
</tr>
<tr>
<td>hf [-]</td>
<td>-</td>
<td>This parameter was implemented after</td>
</tr>
<tr>
<td></td>
<td></td>
<td>performing the sensitivity analysis</td>
</tr>
</tbody>
</table>
5) Experimental results and discussion

Several general remarks on the experimental operations and the reproducibility of the experiments are described in this chapter. Moreover, a comparison between the Nafion membrane and a bilayer membrane is made. The experimental results of varying the current density and concentration are discussed together with the model validation in chapter 7.

5.1 General remarks

At first, an attempt was made to perform a real-time, indirect measurement of the anolyte and catholyte concentration via their conductivities by using a conductivity meter, see Table I3. Unfortunately, the conductivity depends significantly on the temperature as well and the temperature fluctuations during the experiments cause a real-time, indirect relation between the conductivity and the concentration to be inaccurate. Therefore, the concentration was determined by means of titration instead.

Another point of attention is the distance between the Luggin capillary and the membrane. One aims to keep this distance as small as possible since the relative error of the membrane potential drop increases with increasing distance due to the electrical resistance by the electrolyte. However, the membrane deforms at the operating conditions under investigation and one must ensure that the membrane does not touch the capillaries because it will cause the electric field to change. As a result, the measured membrane potential drop will be significantly lower than its actual value in case of no contact.

A third general observation was that the temperature of the electrolytes rises significantly at the operating conditions under investigation, even when the heat bath was set to a value below ambient temperature. This is due to heat production by reaction and electrical friction forces. Consequently, experiments cannot be performed at ambient temperature with the current setup and a gradual temperature increase in the beginning of the experiment (~0-30 min) cannot be avoided if one would start the experiment at ambient temperature.

5.2 Reproducibility

Four experiments were performed in order to investigate the reproducibility of the experiments, see Appendix K. The fluxes and transport numbers were obtained from the mass balances in the compartments and are depicted in Figure 12 and Figure 13, respectively. The fluxes and transport numbers, obtained from the anolyte and catholyte mass balance, would be equal in the case of perfect experimental operation. However, as can be seen from these figures, there is a mismatch between the anolyte and the catholyte mass balance; especially the Na\(^+\) flux of experiment 2 and 4 deviate significantly. This mismatch can be partially explained by the inaccuracy of the titrations, which is depicted in Figure 14 and shows that the obtained Na\(^+\) weight at the end of the experiment is nearly equal to the value of the lower 95% confidence level based on the titration inaccuracy only. Although one can conclude that the mismatch is partially caused by the titration inaccuracy, it cannot statistically explain the observed trend that the final weight is always lower than its initial weight. It is believed that operational mass loss was causing this statistical discrepancy since a few grams weight loss from initial batches of approximately 700g would already cause a similar discrepancy. More specifically, drainage of the electrolytes into beakers might be the reason for the mass loss since no closed container was used, which probably resulted in minor spillage and water evaporation. The latter depends of course significantly on the temperature of the solution at the moment of drainage. From this perspective, it would be better to wait with draining until the solution would be cooled until ambient temperature. However, the solutions were drained directly at the end of the experiment because there might still be mass transfer by means of the concentration gradient and osmotic pressure when the voltage meter is switched off.
Figure 12: Na⁺, H₂O, and OH⁻ flux results of the reproducibility experiments based on the anolyte and catholyte mass balance (top left, top right and bottom, respectively). Initial concentration: 10 wt%, current density: 10 kA·m⁻², anolyte flow cell temperature at steady state: ~ 45°C, 1 O-ring used per membrane side, time: 360 minutes.

Figure 13: Na⁺ transport number (left) and relative H₂O transport number (right) of the reproducibility experiments based on the anolyte and catholyte mass balance. Initial concentration: 10 wt%, current density: 10 kA·m⁻², anolyte flow cell temperature at steady state: ~ 45°C, 1 O-ring used per membrane side, time: 360 minutes.
Figure 14: Na\(^+\) mass balance for the reproducibility experiments together with their 95% confidence level based on the titration inaccuracy. Initial concentration: 10 wt\%, current density: 10 kA·m\(^{-2}\), anolyte flow cell temperature at steady state: ~ 45°C, 1 O-ring used per membrane side, time: 360 minutes.

The membrane potential drop was measured and the corresponding reproducibility results are depicted in Figure 15. These experiments were performed with only one O-ring on each side of the membrane. Apparently, the resulting Luggin capillary to membrane distance together with the membrane deformation caused the membrane to occasionally touch the capillaries. This was the case during experiment 2 and 3 and is reflected by a lower membrane potential drop. Therefore, the actual membrane potential drop is presented by experiment 1 and 4 and they show a similar profile. For subsequent experiments, two O-rings were used on each side of the membrane in order to ensure that the membrane would not touch the capillaries. Another observation is that the membrane potential drop decreases in time, which is explained by its dependence on temperature: a higher temperature results in a lower potential drop.

Figure 15: Reproducibility results of the membrane potential drop. Initial concentration: 10 wt\%, current density: 10 kA·m\(^{-2}\), anolyte flow cell temperature at steady state: ~ 45°C, 1 O-ring used per membrane side, time: 360 minutes.
The temperature was measured in the flow cells and in the catholyte compartment. As depicted by Figure 16, the temperature increases significantly from ambient temperature in the beginning of the experiments to a certain steady state temperature at the end of the experiments. In order to minimize this temperature fluctuation, the electrolytes were preheated during subsequent experiments to a temperature which was approximately 5 °C below the obtained steady state temperature. The catholyte compartment temperature profile of experiment 2 deviates from the other experiments during the first 180 minutes. This was related to the fact that the pump was not switched on at the beginning of the experiment due to a manual error. Furthermore, the temperature between the catholyte in the compartment and in the flow cell differs slightly and the actual temperature of the solution near the membrane would be a value in between. The steady state temperature of the catholyte in the flow cell was used as input for model validation. Moreover, the temperature difference between the anolyte and catholyte are considered negligible.

Figure 16: Temperature profiles of the reproducibility experiments: temperature in the catholyte compartment (top left), temperature in the catholyte flow cell (top right) and temperature in the anolyte flow cell (bottom). Initial concentration: 10 wt%, current density: 10 kA·m⁻², 1 O-ring used per membrane side, time: 360 minutes.

Overall, it can be concluded that the reproducibility of the experiments with respect to the fluxes, membrane selectivity, membrane potential drop, and temperature is sufficient. On average, experiment 1 and 3 seem to render the most constant transport numbers and fluxes; therefore, the average of their results are used as the experimental result for the corresponding operating conditions in the remainder of this report.
5.3 Nafion N1110 versus a bilayer membrane

The performance of a bilayer membrane was also investigated in order to verify its benefit with respect to increased selectivity of the membrane. The same operating conditions were used as with the reproducibility experiments. As depicted in Figure 17, the OH\(^-\) flux is significantly lower, which confirms the higher resistance of the bilayer membrane towards back migration of OH\(^-\). As a consequence of this reduced flux, the resistance for mass transfer towards the catholyte compartment is reduced as well, which results in an increased Na\(^+\) and H\(_2\)O flux. Therefore, the selectivity towards Na\(^+\) and the relative water transport are significantly higher for the bilayer membrane, as depicted by Figure 18. The membrane potential profiles are depicted in Figure 19 and indicate that the potential drop is slightly higher for the bilayer membrane. This is as expected as well since the resistance of this membrane is higher.

![Figure 17: Na\(^+\), H\(_2\)O, and OH\(^-\) flux results of the Nafion and the bilayer experiment based on the anolyte and catholyte mass balance (top left, top right and bottom, respectively). Initial concentration: 10 wt\%, current density: 10 kA-m\(^-2\), anolyte flow cell temperature at steady state: ~ 45°C, 1 O-ring used per membrane side, time: 360 minutes.](image-url)
Figure 18: Na\(^+\) transport number (left) and relative H\(_2\)O transport number (right) of the Nafion and the bilayer experiment based on the anolyte and catholyte mass balance. Initial concentration: 10 wt\%, current density: 10 kA·m\(^{-2}\), anolyte flow cell temperature at steady state: \(~45^\circ\)C, 1 O-ring used per membrane side, time: 360 minutes.

Figure 19: Membrane potential drop of the Nafion and the bilayer experiment. Initial concentration: 10 wt\%, current density: 10 kA·m\(^{-2}\), anolyte flow cell temperature at steady state: \(~45^\circ\)C, 1 O-ring used per membrane side, time: 360 minutes.
6) Nernst-Planck model results
The model was first constructed for the ideal case of the NP equation as described in paragraph 4.1 in which the Schlögl equation is given by Equation 4 and the continuity equation for water by Equation 28. First, the osmotic pressure contribution is evaluated. Then, a parameter sensitivity analysis was performed in order to determine the most influential parameters which were entered as educated guesses. Based on this analysis and these parameters, the model was optimized to describe the experimental results of the reproducibility experiments. Afterwards, the water transport was evaluated by introducing the proposed extended form of the NP flux (Equation 29). The obtained final model code is provided in Appendix M.

6.1 Verification of neglecting the osmotic pressure
Figure 20 depicts the osmotic pressure contribution for anolyte-catholyte systems of 24-32 wt% and 4-32 wt%. For these systems, the following graphs are shown: the water concentration profiles in the case of no pressure gradient, ideal pressure gradient and non-ideal pressure gradient; the ideal and non-ideal logarithm of the pressure gradient based on water concentration output in the case of no pressure gradient; and the relative pressure contribution in the Schlögl equation in the ideal and non-ideal case.

The water concentration profiles change more significantly when the concentration between the anolyte and the catholyte becomes larger. Moreover, the logarithm graphs show a profile which seems random at first, but they originate from the relatively steep gradients of the water concentration. Therefore, it can be concluded that the pressure contribution becomes larger when the concentration gradient increases. Since the anolyte and catholyte concentrations in this study differ not more than 4.3 wt%, it can be concluded that the relative contribution of the osmotic pressure gradient can be safely neglected.
Figure 20: Anolyte-catholyte systems of 24-32 wt% (left) and 4-32 wt% (right) depicting: the water concentration profiles in the case of no pressure gradient, ideal pressure gradient and non-ideal pressure gradient (top); the ideal and non-ideal logarithm of the pressure gradient based on water concentration output in the case of no pressure gradient (middle); and the relative pressure contribution in the Schlögl equation in the ideal and non-ideal case (bottom). Additional model input: $D_{Na}=D_{OH}=1 \cdot 10^{-9}$ m$^2$·s$^{-1}$, $d_c = 2.4 \cdot 10^{-9}$ m, $\varepsilon_{void} = 0.2$, and $k_{AM}=k_{MC}=1 \cdot 10^{-4}$ m·s$^{-1}$, $J = 10$ kA·m$^{-2}$, $T = 45^\circ$C, and $t = 360$ min.

6.2 Parameter sensitivity analysis and model optimization

In the model, the following parameters are implemented as educated guesses: the diffusion coefficient, the void fraction, the channel diameter, and the solution to membrane mass transfer coefficients. Preliminary simulation results are presented in Appendix N and reveal that the diffusion coefficient has the largest
effect on all of the investigated output parameters ($t_{\text{Na}}$, $T_{\text{H}_2\text{O}}$, and $\phi$). The channel diameter has a significant effect on the model output as well, while the influence of the void fraction and the mass transfer coefficients is relatively low. Therefore, the influence of the diffusion coefficient was investigated first. Based on those results, the influence of the channel diameter was investigated. The influence of the void fraction and the mass transfer coefficients was not investigated in more detail.

It should be mentioned that the preliminary simulations were not able to run with the standard tolerance values. Only when increasing the absolute tolerance value by a few orders of magnitude, the model resulted in profiles in which fluctuations remained limited and the flux on the left side of the membrane was (nearly) equal to the flux on the right side of the membrane. The absolute tolerance value of each preliminary simulation is reported in Appendix N. The absolute tolerance values for the other simulations in this section are reported in Appendix O.

6.2.1 The influence of the diffusion coefficient

While the diffusion coefficient was assumed equal for all species during the preliminary simulations, a distinction was made between the diffusion coefficient of $\text{Na}^+$ and $\text{OH}^-$ for the detailed analysis since it is generally believed that $\text{OH}^-$ diffuses faster in electrolyte systems due to the hopping mechanism. Moreover, the diffusion coefficient is affected by concentration and temperature. Although it actually decreases with increasing concentration and decreasing temperature, it is not accounted for in this study. Unfortunately, literature data on diffusion coefficients in membrane solutions is not readily available. O’Brien et al. reports that the $\text{Na}^+$ diffusion coefficient in membranes at 5M NaOH (~17 wt%) is in the order of $1 \cdot 10^{-10}$ m$^2$s$^{-1}$ and at 11M NaOH (~32 wt%) in the order of $1 \cdot 10^{-10}$ m$^2$s$^{-1}$.[1] Similar values are reported by Yeager et al. for the highly concentrated caustic solutions.[39] For the sensitivity analysis, the diffusion coefficients of $\text{Na}^+$, $\text{OH}^-$ were varied between $1 \cdot 10^{-10}$ m$^2$s$^{-1}$ and $4 \cdot 10^{-9}$ m$^2$s$^{-1}$ and the diffusion coefficient of $\text{H}_2\text{O}$ was kept constant at a value of $1 \cdot 10^{-9}$ m$^2$s$^{-1}$. Besides the $\text{Na}^+$ transport number, the relative $\text{H}_2\text{O}$ transport number, and the membrane potential drop, the fluxes and concentrations of the species were evaluated.

The concentration profiles of $\text{Na}^+$ and $\text{H}_2\text{O}$ are depicted in Figure 21 for $\text{Na}^+$ diffusion coefficients of $1 \cdot 10^{-10}$ and $5 \cdot 10^{-10}$ m$^2$s$^{-1}$. The profiles for a $\text{Na}^+$ diffusion coefficient of $1 \cdot 10^{-9}$ m$^2$s$^{-1}$ were similar to the profiles at $5 \cdot 10^{-10}$ m$^2$s$^{-1}$; consequently, they were not shown. In addition, the concentration profiles of $\text{OH}^-$ are not discussed since they had equal slope and trend as the profiles of $\text{Na}^+$, i.e. they only showed a lower value corresponding with the concentration of the sulfonic groups.

Although the anolyte bulk concentration of $\text{H}_2\text{O}$ is higher than its catholyte bulk concentration, the anolyte interface concentration of $\text{H}_2\text{O}$ is lower than its catholyte interface concentration. This originates from the diffusion layer, which causes the anolyte interface concentration to be lower than its bulk concentration and the catholyte interface concentration to be higher than its bulk concentration, as previously depicted in Figure 8. Moreover, different concentrations at the left and right boundary of the membrane are obtained for different $\text{OH}^-$ diffusion coefficients. This can be explained by the fact that the flux is different at different $\text{OH}^-$ diffusion coefficients.

Interestingly, an optimum was found in most water concentration profiles. Since its flux on the left and right side of the membrane were found to be equal (neglecting little numerical fluctuations in some cases), it is considered that this optimum was mathematically required in order to obtain the same flux.

9 Standard relative and absolute tolerance values are $1 \cdot 10^{-3}$ and $1 \cdot 10^{-6}$, respectively. For all simulations, the standard relative tolerance value was used.
everywhere in the membrane. The physical reasoning behind this optimum is unknown and the profile might deviate in reality. Another peculiar observation is that the Na\(^+\) and H\(_2\)O concentration profiles deviate from the more logical, gradually increasing profile at OH\(^-\) diffusion coefficients smaller than ~7\(\times\)10\(^{-10}\) m\(^2\)·s\(^{-1}\). Further evaluation of other parameters reveals that the model output at this small OH\(^-\) diffusion coefficient does not match the experimental data, as will be discussed next. Therefore, these deviating profiles are considered to be misrepresentative.

Figure 21: Na\(^+\) and H\(_2\)O concentration profiles for the sensitivity analysis at different diffusion coefficients (left and right graphs, respectively). Top and bottom graphs correspond with a Na\(^+\) diffusion coefficient of 1\(\times\)10\(^{-10}\) and 5\(\times\)10\(^{-10}\) m\(^2\)·s\(^{-1}\).

Additional model input: initial anolyte and catholyte concentration = 10 wt\%, \(d_c=2.4\times10^{-9}\) m, \(\varepsilon_{void}=0.2\), and \(k_{AM}=k_{MC}=1\times10^{-4}\) m·s\(^{-1}\), \(J=10\) kA·m\(^{-2}\), \(T=45^\circ\)C, and \(t=360\) min.

Figure 22 depicts the Na\(^+\) and H\(_2\)O fluxes and the Na\(^+\) transport number and relative H\(_2\)O transport number. It reveals that the fluxes and Na\(^+\) transport number are significantly depending on both diffusion coefficients. Only the relative water transport number seems to be affected only merely by the OH\(^-\) diffusion coefficient. The Na\(^+\) flux and transport number increase with increasing Na\(^+\) diffusion coefficient but decrease with increasing OH\(^-\) diffusion coefficient. The latter effect is caused by the diffusion dependent term in the denominator of the potential gradient (Equation 30). This causes the potential gradient to reduce; consequently, the potential and convective term of Na\(^+\) and OH\(^-\) reduce as well. However, the increased OH\(^-\) diffusion coefficient contributes positively to the flux of OH\(^-\) as well. Therefore, its flux reduces less than the flux of Na\(^+\) and the selectivity drops. The decreased water flux with increasing diffusion coefficients is caused by the same reduction of the potential gradient.
According to the results in Figure 22, the model resembles the experimental values best with the Na\(^+\) and OH\(^-\) diffusion coefficients being approximately 1·10\(^{-10}\) m\(^2\)·s\(^{-1}\) and 2.5·10\(^{-9}\) m\(^2\)·s\(^{-1}\), respectively. It should be noted that this is just a numerical optimization, which does not necessarily result in their real values. Although a trend was observed that lower diffusion coefficients enlarge the potential drop, no simulation resulted in a potential drop that matches the experimental value, as depicted by Figure 23.

**Figure 22:** Na\(^+\) and H\(_2\)O fluxes (top) and Na\(^+\) transport number and relative H\(_2\)O transport number (bottom) for the sensitivity analysis at different diffusion coefficients. Additional model input: initial anolyte and catholyte concentration = 10 wt\%, d\(_c\) = 2.4·10\(^{-9}\) m, ε\(_\text{void}\) = 0.2, and k\(_{AM}\) = k\(_{MC}\) = 1·10\(^{-4}\) m·s\(^{-1}\), J = 10 kA·m\(^{-2}\), T = 45\(^\circ\)C, and t = 360 min.

**Figure 23:** Membrane potential drop at different diffusion coefficients. Additional model input: initial anolyte and catholyte concentration = 10 wt\%, d\(_c\) = 2.4·10\(^{-9}\) m, ε\(_\text{void}\) = 0.2, and k\(_{AM}\) = k\(_{MC}\) = 1·10\(^{-4}\) m·s\(^{-1}\), J = 10 kA·m\(^{-2}\), T = 45\(^\circ\)C, and t = 360 min.
6.2.2 The influence of the channel diameter

From paragraph 6.2.1, it was concluded that the best match with the experimental values was obtained with a Na\(^+\) and OH\(^-\) diffusion coefficient of \(1 \cdot 10^{-10}\) m\(^2\)·s\(^{-1}\) and \(2.5 \cdot 10^{-9}\) m\(^2\)·s\(^{-1}\), respectively. These values were used in the simulations in which the channel diameter was varied. The average channel diameter of 2.4 nm, as used in the previous simulations, and its range (between 1.8 and 3.5 nm) were based on the data from Schmidt-Rohr et al.\(^{[10]}\). This range was considered for the sensitivity analysis of the channel diameter. Another conclusion of the diffusion coefficient sensitivity analysis was that the model did not resemble the measured membrane potential drop. Since the first term in the denominator of the potential drop has a second order dependency on the channel diameter, it is expected that decreasing this diameter will result in an increased potential drop.

The concentration profiles of the simulations with varying channel diameter are omitted since they were similar to the profiles depicted in paragraph 6.2.1. The results on the Na\(^+\) and H\(_2\)O fluxes and the Na\(^+\) transport number and relative H\(_2\)O transport number are depicted in Figure 24. The graphs show that the influence of the channel diameter is significant. As expected, the fluxes increase with increasing channel diameter. Because this effect is the highest for H\(_2\)O and the lowest for OH\(^-\), the Na\(^+\) transport number and relative H\(_2\)O transport number increase as well.

![Graphs showing Na\(^+\) and H\(_2\)O fluxes and Na\(^+\) transport number and relative H\(_2\)O transport number as a function of channel diameter.](image)

Figure 24: Na\(^+\) and H\(_2\)O fluxes (top) and Na\(^+\) transport number and relative H\(_2\)O transport number (bottom) for the channel diameter sensitivity analysis. Additional model input: initial anolyte and catholyte concentration = 10 wt%, D\(\text{Na}^+\) = \(1 \cdot 10^{-10}\) m\(^2\)·s\(^{-1}\), D\(\text{OH}^-\) = \(2.5 \cdot 10^{-9}\) m\(^2\)·s\(^{-1}\), \(\varepsilon_{\text{void}}\) = 0.2, and \(k_{\text{AM}} = k_{\text{MC}} = 1 \cdot 10^{-4}\) m·s\(^{-1}\), \(J = 10\) kA·m\(^{-2}\), \(T = 45^\circ\text{C}\), and \(t = 360\) min.
Although the membrane potential drop enhances with decreasing channel diameter, this effect is not enough to reach its experimental value within the investigated range. The tortuosity of the membrane is another parameter which has a similar effect on the model and this parameter is currently neglected. It would only appear as a reciprocal multiplication factor in the convective term since reported diffusion coefficients were taken from experiments. Therefore, tortuosity is already taken into account for the diffusion and potential term. Since the effect would be similar to decreasing the channel diameter, its influence is not investigated at the moment.

Figure 25: Membrane potential drop at different channel diameters. Additional model input: initial anolyte and catholyte concentration = 10 wt%, $D_{Na} = 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $D_{OH} = 2.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $\varepsilon_{void} = 0.2$, and $k_{AM} = k_{MC} = 1 \times 10^{-4} \text{ m s}^{-1}$, $J = 10 \text{ kA m}^{-2}$, $T = 45^\circ \text{C}$, and $t = 360 \text{ min}$.

One could opt to optimize all parameters at once instead of performing consecutive selectivity analysis, thereby being able to optimize the model such that it will better reflect reality. However, combined optimization of multiple parameters will not be considered in this study. Since the literature value of the channel diameter is believed to better reflect reality compared to the diffusion coefficients, the optimum model conditions remained as obtained in paragraph 6.2.1.

6.3 Evaluation of the water flux equation

In paragraph 4.1, an extended form of the water continuity equation was proposed (Equation 29). Recall that the additional terms in this equation resulted from the principle that Na\(^+\) should be present in the hydrated form and that this type of transport by means of the diffusion and the potential term of the Na\(^+\) flux was not accounted for in the equation resulting from the generally used NP equation (Equation 28). Implementing these additional terms could be of importance when attempting to describe the real behavior of the system. Therefore, their influence is investigated for different hydration factors (1-12).

The evaluation of the extended water flux is performed despite the fact that the numerical optimization of the diffusion coefficients already resulted in matching values for the $H_2O$ flux and its relative transport number since it is not certain whether the obtained diffusion coefficients resemble the actual diffusion coefficients. Moreover, it has been shown that the channel diameter has a significant effect on the model output.

Figure 26 shows the simulation results for the $H_2O$ flux and its relative transport number. The other parameters were not considered since the additional terms in the water flux do not affect them. With these terms, the flux of water logically increases and this effect is more pronounced with increasing hydration factor. Moreover, it is observed that the model resembles the experimental data up to a hydration factor of
approximately 7. In addition, implementing the extended form of water transport does not seem to have a negative effect on the model stability. Consequently, it is retained within the model for the detailed model validation, which is described in the next chapter. The value for the hydration factor for this validation is chosen to be 4.

![Figure 26: H₂O flux and its relative transport number as a function of the hydration factor. Additional model input: initial anolyte and catholyte concentration = 10 wt%, D_{Na} = 1 \cdot 10^{-10} \text{ m}^2\cdot\text{s}^{-1}, D_{OH} = 2.5 \cdot 10^{-9} \text{ m}^2\cdot\text{s}^{-1}, d_c = 2.4 \cdot 10^{-9} \text{ m}, \varepsilon_{\text{void}} = 0.2, and k_{AM} = k_{MC} = 1 \cdot 10^{-4} \text{ m} \cdot \text{s}^{-1}, J = 10 \text{ kA} \cdot \text{m}^{-2}, T = 45^\circ\text{C}, and t = 360 \text{ min.}]

6.4 Additional remarks

As mentioned in paragraph 6.2, the stability of the model requires attention, especially if one attempts to extend the model by implementing non-ideality or additional species. The model was even incapable to cope properly with an empirical correlation for the density of the electrolyte solutions as an input for the bulk concentrations, which in principle is not a major adjustment. Therefore, numerical instability of the model is expected when one would try to extend the model. For example, implementing non-ideality by introducing the Pitzer model for the activity coefficients will probably be difficult since it depends on the density as well.

Direct comparison with literature model data is not straightforward due to differently defined system setups and operating conditions. For example: Bouzek et al. have investigated the membrane cell with the following operating conditions: a current density between 0 and 2500 A/m², a brine concentration of 5M in the anolyte, and a NaOH solution of 13M in the catholyte. Nevertheless, the concentration and flux profiles seems to match roughly. However, they have obtained a potential drop which is somewhat higher while the current density is lower compared to this study and it is unclear whether it indeed could reflect the experiments sufficiently.
7) Model comparison with experimental results

The optimized parameter input from the sensitivity analysis was used for the simulations at different concentrations and current densities. It is presented in Table 5. Additional model input is based on the experimental conditions, which are summarized together with their corresponding absolute tolerance values in Table 6. More information on the experimental conditions is provided in Appendix K.

Table 5: Model input based on the optimized parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{\text{Na}}$ [m$^2$·s$^{-1}$]</td>
<td>$1 \cdot 10^{-10}$</td>
</tr>
<tr>
<td>$D_{\text{OH}}$ [m$^2$·s$^{-1}$]</td>
<td>$2.5 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>$\epsilon_{\text{void}}$ [m$^{3}$·m$^{-3}$]</td>
<td>0.2</td>
</tr>
<tr>
<td>$k_{\text{AM}}$ &amp; $k_{\text{CM}}$ [m$^{-1}$]</td>
<td>$1 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$d_c$ [m]</td>
<td>$2.4 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>hf [-]</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 6: Outline of the model validation simulations and their absolute tolerance values.

<table>
<thead>
<tr>
<th>Validation of experiment [#]</th>
<th>Current density [kA·m$^{-2}$]</th>
<th>Concentration [wt%]</th>
<th>AbsTol [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2</td>
<td>10</td>
<td>$1 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>7,8</td>
<td>6</td>
<td>10</td>
<td>$1 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>1,3</td>
<td>10</td>
<td>10</td>
<td>$1 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>10</td>
<td>$1 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>10,11</td>
<td>10</td>
<td>15</td>
<td>$1 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>32</td>
<td>$1 \cdot 10^{-5}$</td>
</tr>
</tbody>
</table>

7.1 The influence of concentration on the flux and transport numbers

Figure 27 and Figure 28 depict the experimental and model results of the fluxes and transport numbers as a function of NaOH concentration. The $\text{Na}^+$ flux decreases with increasing concentration, which is expected since mass transfer is reduced due to a decreased membrane water content. Consequently, it is logical that the H$_2$O and OH$^-$ flux decrease as well with increasing NaOH concentration. Furthermore, the selectivity decreases because the increase in OH$^-$ concentration is relatively higher than the increase in $\text{Na}^+$ concentration due to the presence of the fixed groups.

The model simulations based on the preliminary base case (Appendix N) cover these trends quite well, albeit with a slightly different slope of decay. Moreover, it overestimates the flux of $\text{Na}^+$ and H$_2$O and underestimates the flux of OH$^-$. As concluded from the sensitivity analysis, the optimized case with respect to the reproducibility experiments (10 wt%, 10 kA·m$^{-2}$) match the output parameters very well. In addition, it describes the water flux better than the base case. However, the obtained fluxes of the ionic species are significantly lower at higher concentrations, which is most likely attributed to the low Na$^+$ diffusion coefficient. Due to the mismatch of the fluxes of the ionic species, the transport numbers deviate as well. It can be concluded that the optimization is only valid for a small range of concentrations and that each experiment requires its own combination of input values for the diffusion coefficients and other parameters. Consequently, it is advised to further investigate the dependency of the diffusion coefficients on concentration and temperature.

---

10 Average values for the experimental fluxes and transport numbers were used as model input in case the experiment was performed in duplicate.
Figure 27: Na⁺, H₂O, and OH⁻ flux as a function of concentration (top left, top right and bottom, respectively). Additional model input: \( hf = 4 \), \( D_{Na} = 1 \times 10^{-10} \, m^2 \cdot s^{-1} \), \( D_{OH} = 2.5 \times 10^{-9} \, m^2 \cdot s^{-1} \), \( d_c = 2.4 \times 10^{-9} \, m \), \( \varepsilon_{void} = 0.2 \), and \( k_{AM}=k_{MC}=1 \times 10^{-4} \, m \cdot s^{-1} \), \( J = 10 \, kA \cdot m^{-2} \), \( t = 360 \, min \), and \( T=T_{SS} \) (see Table K5).

Figure 28: Na⁺ transport number (left) and relative H₂O transport number (right) as a function of concentration. Additional model input: \( hf = 4 \), \( D_{Na} = 1 \times 10^{-10} \, m^2 \cdot s^{-1} \), \( D_{OH} = 2.5 \times 10^{-9} \, m^2 \cdot s^{-1} \), \( d_c = 2.4 \times 10^{-9} \, m \), \( \varepsilon_{void} = 0.2 \), and \( k_{AM}=k_{MC}=1 \times 10^{-4} \, m \cdot s^{-1} \), \( J = 10 \, kA \cdot m^{-2} \), \( t = 360 \, min \), and \( T=T_{SS} \) (see Table K5).

7.2 The influence of current density on the flux and transport numbers
Figure 29 and Figure 30 depict the experimental and model results of the fluxes and transport numbers as a function of current density. Up to a current density of at least 10 kA·m⁻², the experimental data shows that fluxes increase more or less linearly with increasing current density. A remarkable result is observed...
for the experiment performed at 20 kA·m⁻². At this current density, the Na⁺ flux increased only slightly compared to the value at 10 kA·m⁻² and the flux of H₂O suddenly dropped from ~0.4 mol·m⁻²·s⁻¹ to ~0.1 mol·m⁻²·s⁻¹. More importantly, the OH⁻ flux rose tremendously from approximately -0.025 mol·m⁻²·s⁻¹ to approximately -0.115 mol·m⁻²·s⁻¹. Its absolute value was even higher than the Na⁺ flux; consequently, it caused the Na⁺ transport number to become smaller than 0.5. It can be concluded that the membrane’s ability for Na⁺ transport is limited and that this limit is reached at this high current density. In order to fulfill the fixed current density, OH⁻ is forced to back migrate through the membrane, thereby losing its selectivity towards Na⁺. It should be mentioned that this experiment was performed only once and it is advised to repeat the experiment in order to verify its reproducibility.

The optimization model clearly shows a better match with the experimental data than the base case simulation results. It captures the experimental values very well, except for the experiment performed at 20 kA·m⁻². Consequently, it can be concluded that the model is not able to predict the loss of membrane selectivity at high current densities. However, it is able to predict the membrane behavior at relatively low current densities (up to 10 kA·m⁻²). Although this is only verified for one concentration, it is concluded that the current density does not have an effect on the model accuracy and, therefore, on the diffusion coefficients. One should, however, verify this conclusion if one manages to optimize the model for various concentrations.

Figure 29: Na⁺, H₂O, and OH⁻ flux as a function of current density (top left, top right and bottom, respectively). Na⁺, H₂O, and OH⁻ flux as a function of current density (top left, top right and bottom, respectively). Additional model input: hf = 4, initial anolyte and catholyte concentration = 10 wt%, D鈩 = 1·10⁻¹⁰ m²·s⁻¹, D鈴 = 2.5·10⁻⁹ m²·s⁻¹, d鈩 = 2.4·10⁻⁹ m, ε_void = 0.2, and k鈩=k鈴=1·10⁻⁴ m·s⁻¹, t = 360 min, and T=T鈲 (see Table K5).
Figure 30: \( \text{Na}^+ \) transport number (left) and relative \( \text{H}_2\text{O} \) transport number (right) as a function of current density. Additional model input: \( h_f = 4 \), initial anolyte and catholyte concentration = 10 wt\%, \( D_{\text{Na}} = 1 \times 10^{-10} \text{ m}^2\text{s}^{-1} \), \( D_{\text{OH}} = 2.5 \times 10^{-9} \text{ m}^2\text{s}^{-1} \), \( d_c = 2.4 \times 10^{-9} \text{ m} \), \( \epsilon_{\text{void}} = 0.2 \), and \( k_{\text{AM}} = k_{\text{MC}} = 1 \times 10^{-4} \text{ m}\text{s}^{-1} \), \( t = 360 \text{ min} \), and \( T = T_{\text{SS}} \) (see Table K5).

### 7.3 Evaluating the membrane potential drop

As already mentioned in paragraph 5.2, the membrane potential drop depends on temperature, which was not perfectly constant during the experiments. Appendix P provides the temperature profiles of the performed experiments and shows that even the steady state temperatures of the experiments were not equal. Consequently, the experimental steady state membrane potential drop values presented in this section cannot be qualitatively compared. In other words, only rough trends are evaluated. The results are depicted in Figure 31 and show that the potential drop becomes larger with increasing NaOH concentration and current density (neglecting the data point at 20 kA\( \cdot \text{m}^{-2} \)). The latter makes perfectly sense when considering Ohm’s law (Equation 7) for simplicity. Considering the fact that the conductivity has an optimum between 15 and 20 wt\% at a temperature between 40 and 50 °C\(^1\), one would expect that the membrane potential drop shows similar behavior; however, this is not the case.

The observed equilibrium temperature was used as the input value for the simulations, see Appendix K. Although the model optimization resulted in a slightly higher potential drop, its values are nearly an order of magnitude smaller than the experimental values. It is questionable whether the experimental values can be reached by simply optimizing the parameters while still maintaining a good fit with the other membrane properties. One could try to further optimize the model in order to match the experimental potential drop by evaluating the convective term together with the diffusion coefficients. A higher potential drop is obtained with a decreased convective term and decreased diffusion coefficients. The former could be obtained with a decreased channel diameter and by incorporating tortuosity effects.
Figure 31: Membrane potential drop as a function of concentration (left) and current density (right). Membrane potential drop as a function of concentration (left) and current density (right). Additional model input: $h_f = 4$, initial anolyte and catholyte concentration = 10 wt% (right), $D_{Na} = 1 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, $D_{OH} = 2.5 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, $d_{c} = 2.4 \cdot 10^{-9} \text{ m}$, $\varepsilon_{\text{void}} = 0.2$, and $k_{AM} = k_{MC} = 1 \cdot 10^{-7} \text{ m} \cdot \text{s}^{-1}$, $J = 10 \text{ kA} \cdot \text{m}^{-2}$ (left), $t = 360 \text{ min}$, and $T = T_{SS}$ (see Table K5).
8) Conclusions and recommendations

It is advised to perform a molecular dynamics study to investigate the behavior of the ions and water within the membrane channels in more detail since the membrane dimensions suggest the presence of a Debye double layer while sodium hydration data suggest that this is rather peculiar. Whether or not this layer is present, may affect the conceptual thoughts on the ion and water behavior in these nanoscale systems as well as the required model setup.

An overview of the model equations based on the MS and NP approach has been presented in which the equations for the NP approach are derived for the ideal, diluted system and for the case where the driving force is considered to be non-ideal. Moreover, it has been shown that Ohm’s law is not generally valid as the potential gradient in the NP equation and it has been numerically proven that the potential gradient cannot be linear since this conflicts with the electroneutrality condition. Therefore, an expression for the non-linear potential gradient has been derived from the relation between the current density and the fluxes of the ionic species.

The Donnan equilibrium theory and the electroneutrality condition in the electrolyte were used to derive an equation for the electrolyte interface concentration as a function of the membrane interface concentration for a monovalent system. This derivation is easy to implement for a multicomponent system, whereas the commonly used equation, based on the direct use of the Donnan potential equation or on the derivation obtained from the electroneutrality in the membrane, are not. While the Donnan equilibrium is currently used within the boundary of the model, one could also aim to model the diffusion layer of the electrolytes by means of the NP approach. Consequently, the boundary condition could simply be set by the bulk electrolyte concentrations and the use of the estimated mass transfer coefficients in the diffusion layer is omitted. Moreover, the additionally required assumption for the unknown activity coefficient at the electrolyte interface is omitted if non-ideality would be implemented in the model. However, one requires information about the relative thickness of the diffusion layers and the membrane layer when modeling the diffusion layers as well. In addition, one has to verify whether the concentration and potential jump at the interface will be easy to implement.

Several empirical correlations are obtained from literature data. A correlation for the water activity as a function of molality was used in the numerical evaluation of the osmotic pressure drop. Furthermore, a correlation for the water content as a function of concentration was implemented in the model and used to calculate the initial water concentration in the membrane. Unfortunately, it was not succeeded to implement the correlation for the NaOH density as a function of weight percent and temperature in the model for the bulk electrolyte concentrations since this yielded an unstable model. However, this correlation was used in the calculations of the experimental flux and transport number results.

During the experiments, it was noticed that the temperature of the electrolytes rises significantly in the beginning of the experiment, which makes it difficult to directly obtain a steady state temperature. Another important observation from the experiments is that there is a mismatch between the mass balances based on the anolyte and the catholyte, which resulted most likely from operational mass losses. In addition, observed membrane deformation caused the membrane to touch the Luggin capillaries when the distance between them became too small. This resulted in an unrealistic membrane potential drop and this distance was therefore increased.

The reproducibility with respect to the fluxes, membrane selectivity, membrane potential drop, and temperature is sufficient. Moreover, their results with varying concentration and current density are as expected, except for the experiment performed at 20 kA·m⁻². At this current density, the membrane
appeared to have lost its selectivity. It should be mentioned that this experiment was performed only once and it is advised to repeat the experiment in order to verify its reproducibility. The comparison between Nafion and the bilayer membrane showed that the latter indeed has a better selectivity.

The composed model was based on the ideal NP approach in which the osmotic pressure was proven to be negligible at the operating conditions under investigation. The sensitivity analysis revealed that the diffusion coefficient is the most important parameter to be optimized, followed by the channel diameter. Unfortunately, the model was not able to run at the standard tolerance values and became unstable quite easily when replacing constants with empirical correlations or when changing several parameters too much. Therefore, implementing non-ideality or adding additional species will probably result in model instabilities as well. Despite the obtained instability at low tolerance values, a proposed extended NP equation for the water flux was successfully implemented without further reducing the instability and it is believed to better describe the physical behavior of the membrane.

The preliminary and the optimized model were validated with the experimental data. The preliminary model covers the experimental trends quite well. However, it was observed that its Na\(^+\) and the H\(_2\)O flux were overestimated and its OH\(^-\) flux was underestimated; consequently, the transport numbers showed a correlated deviation. Although the optimized model is not capable to predict the membrane selectivity drop at high current densities, it resembles the experimental results at current densities up to 10 kA-m\(^{-2}\) very well. Moreover, it is not capable to accurately predict the experimental results at varying concentration. This is attributed to the fact that the parameter optimization was performed for a single concentration and the obtained diffusion coefficients are not optimal for other concentrations. In fact, they are concentration and temperature dependent, which is not accounted for in the model. Consequently, their effects should be investigated and incorporated in the model. Further optimization could also be performed by investigating the combined effects of the diffusion coefficient and the other parameters, for example, the channel diameter.

The membrane potential drop requires special attention since the model underestimates its output by nearly an order of magnitude. One should evaluate the potential gradient by investigating the convective term and the diffusion coefficients in more detail in which it has been shown that the potential drop is enhanced by reducing the channel diameter and diffusion coefficients. Moreover, one could incorporate tortuosity effects in order to reduce the convective term, thereby increasing the potential drop as well.

In general, more experiments and simulations at different concentrations and current densities could be performed to strengthen the conclusions on the observed trends. It is advised not to implement non-ideality before the model is further optimized with respect to the diffusion coefficients and the convective term. Finally, if one manages to obtain a stable model, which sufficiently resembles the experimental data, one could try to extend the model to a multicomponent system including chlorine and extend it to a bilayer membrane.
Acknowledgements

First of all, I want to thank my daily supervisor, Shohreh Moshtari Khah, for her supervision on the lab and for her input in the numerous discussions on the model and experimental results. Moreover, I am grateful for the gained insight on various aspects of the project during the many fruitful meetings I had with her and John van der Schaaf. I also want to thank Jaap Schouten and Thijs de Groot, who provided me with nice suggestions during several intermediate meetings.

In general, I have enjoyed the friendly atmosphere within the SCR group in which everyone is in for a nice conversation. Furthermore, I appreciate it a lot that everyone is willing to help when requested. In particular, I want to thank Michiel de Beer and Paola Granados Mendoza for providing me with the literature data I requested and Carlo Buijs, Peter Lipman, and Eric van Herk for their assistance with the experimental setup.
## List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Activity [-]</td>
</tr>
<tr>
<td>A</td>
<td>Area [m²]</td>
</tr>
<tr>
<td>B</td>
<td>Factor comprising the inverse of the binary diffusion coefficient [s·m⁻²]</td>
</tr>
<tr>
<td>C</td>
<td>Concentration [mol·m⁻³]</td>
</tr>
<tr>
<td>CE</td>
<td>Current efficiency [-]</td>
</tr>
<tr>
<td>d</td>
<td>Diameter [m]</td>
</tr>
<tr>
<td>d_h</td>
<td>Hydrodynamic permeability [s·kg·m⁻³]</td>
</tr>
<tr>
<td>d_i</td>
<td>Driving force for mass diffusion [m⁻¹]</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient [m²·s⁻¹]</td>
</tr>
<tr>
<td>D_0</td>
<td>Binary Maxwell-Stefan diffusivity [m²·s⁻¹]</td>
</tr>
<tr>
<td>E</td>
<td>Electric field [V·m⁻¹]</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant [C·mol⁻¹]</td>
</tr>
<tr>
<td>F_i</td>
<td>External body force [J·mol⁻¹]</td>
</tr>
<tr>
<td>hf</td>
<td>Hydration factor for the diffusional and potential contributions of Na⁺ to the transport of water [-]</td>
</tr>
<tr>
<td>I</td>
<td>Current [A]</td>
</tr>
<tr>
<td>J</td>
<td>Current density [A·m⁻²]</td>
</tr>
<tr>
<td>J_i</td>
<td>Molar diffusion flux relative to the molar average velocity [mol·m⁻²·s⁻¹]</td>
</tr>
<tr>
<td>k</td>
<td>Mass transfer coefficient [m_mol⁻³·m²·s⁻¹]</td>
</tr>
<tr>
<td>K</td>
<td>Donnan equilibrium constant [-]</td>
</tr>
<tr>
<td>m</td>
<td>Molality [mol·kg⁻¹]</td>
</tr>
<tr>
<td>M_w</td>
<td>Molecular weight [g·mol⁻¹]</td>
</tr>
<tr>
<td>n</td>
<td>Number of moles [mol]</td>
</tr>
<tr>
<td>N</td>
<td>Flux [mol·m⁻²·s⁻¹]</td>
</tr>
<tr>
<td>N_i</td>
<td>Molar flux of species i referred to a stationary coordinate reference frame [mol·m⁻²·s⁻¹]</td>
</tr>
<tr>
<td>P</td>
<td>Pressure [Pa]</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant [J·mol⁻¹·K⁻¹]</td>
</tr>
<tr>
<td>S</td>
<td>Selectivity [-]</td>
</tr>
<tr>
<td>t</td>
<td>Time [s]</td>
</tr>
<tr>
<td>t_i</td>
<td>Transport number of component i [-]</td>
</tr>
<tr>
<td>T</td>
<td>Temperature [K]</td>
</tr>
<tr>
<td>u_i</td>
<td>Velocity of diffusion of species i [m·s⁻¹]</td>
</tr>
<tr>
<td>v</td>
<td>Convective volume flux [m³·m⁻²·s⁻¹]</td>
</tr>
<tr>
<td>V</td>
<td>Partial molar volume [m³·mol⁻¹]</td>
</tr>
<tr>
<td>w</td>
<td>Weight [g]</td>
</tr>
<tr>
<td>wf</td>
<td>Weight fraction [-]</td>
</tr>
<tr>
<td>x</td>
<td>Mol fraction [-]</td>
</tr>
<tr>
<td>z</td>
<td>Length scale parameter [m]</td>
</tr>
<tr>
<td>z_i</td>
<td>Dimensionless length scale parameter [-]</td>
</tr>
<tr>
<td>z_v</td>
<td>Valence [-]</td>
</tr>
</tbody>
</table>

### Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ</td>
<td>Activity coefficient [-]</td>
</tr>
<tr>
<td>δ</td>
<td>Thickness [m]</td>
</tr>
<tr>
<td>Δ</td>
<td>Difference [-]</td>
</tr>
<tr>
<td>ε</td>
<td>Permittivity [F·m⁻¹]</td>
</tr>
<tr>
<td>ε void</td>
<td>Void fraction [m_void³·m_mol⁻³]</td>
</tr>
<tr>
<td>η</td>
<td>Viscosity [Pa·s]</td>
</tr>
<tr>
<td>κ</td>
<td>Membrane conductivity [Ω⁻¹·m⁻¹]</td>
</tr>
<tr>
<td>λ</td>
<td>Water content [mol H₂O/mol SO₃⁻]</td>
</tr>
<tr>
<td>μ</td>
<td>Chemical potential [J·mol⁻¹]</td>
</tr>
<tr>
<td>μ⁰</td>
<td>Chemical potential of a pure species [J·mol⁻¹]</td>
</tr>
<tr>
<td>π</td>
<td>Osmotic pressure [Pa]</td>
</tr>
<tr>
<td>ρ</td>
<td>Density [kg·m⁻³]</td>
</tr>
<tr>
<td>σ</td>
<td>Source term [mol·m⁻³·s⁻¹]</td>
</tr>
<tr>
<td>φ</td>
<td>Potential [V]</td>
</tr>
<tr>
<td>φ_i</td>
<td>Volume fraction [-]</td>
</tr>
<tr>
<td>ω</td>
<td>Mass fraction [-]</td>
</tr>
</tbody>
</table>

### Subscripts and superscripts

- 0: Left side of the membrane
- ⊥: Perpendicular
- A: Anolyte
- AM: Anolyte to membrane
- bulk: Bulk phase
- c: Channel
- C: Catholyte
- Don: Donnan
- H₂O: Water
- i,j,k,n: Component i,j,k,n
- ii: Grid point
- Ion: Ion
- Int: Interface
- m: Membrane ionic groups
- M: Membrane
- MC: Membrane to catholyte
- Na⁺: Sodium
- OH⁻: Hydroxide
- pol: Polymer
- pos: Positive ions
- P: Pressure
- SO₃⁻: Sulfonate groups
- sol: Solution
- SS: Steady state
- tot: Total
- T: Temperature
- void: Void phase
- δ: Right side of the membrane
References


[18] Schlögl R.(1966), Membrane Permeation in Systems far from Equilibrium, Berichte der Bunsengesellschaft, Bd. 70, Nr. 4, 400 - 414


[34] DuPont Fuel Cells, DuPont™ Nafion® PFSA Membranes, 2009,
Appendix A: Derivation of the Maxwell-Stefan approach and the Nernst-Planck approach

The MS approach originates from the law of conservation of momentum and the irreversible thermodynamics theory, which result in the generalized Maxwell-Stefan equations (Equation A1) and the generalized driving force (Equation A2), respectively. Equation A1 describes the interaction of species \( i \) with other species. In the case of an electrolyte system, the external body force \( (F_i) \) of Equation A2 is described by Equation A3. Moreover, the chemical potential \( (\mu) \) for a system at constant temperature and pressure is described by Equation A4.

\[
d_i = -\sum_{j=1}^{n} \frac{x_i x_j (u_i - u_j)}{D_{ij}} = \sum_{j=1}^{n} x_i N_j - x_j N_i = \sum_{j=1}^{n} x_i J_j - x_j J_i
\]

Equation A1

\[
C_{\text{tot}} RT d_i = C_i \nabla r_i \mu_i + (\varphi_i - \omega_i) \nabla P - \left( C_i F_i - \omega_i \sum_{j=1}^{n} C_j F_j \right)
\]

Equation A2

\[
F_i = -z_i F \nabla \varphi
\]

Equation A3

\[
\mu_i = \mu_0^i + RT \ln \left( \gamma_i x_i \right)
\]

Equation A4

Where \( d_i \) equals the driving force for mass diffusion \([m^{-1}]\), \( u_i \) equals the velocity of diffusion of species \( i \) \([m \cdot s^{-1}]\), \( N_i \) equals the molar flux of species \( i \) referred to a stationary coordinate reference frame \([mol \cdot m^{-2} \cdot s^{-1}]\), \( D_{ij} \) equals the binary Maxwell-Stefan diffusivity \([m^2 \cdot s^{-1}]\), \( J_i \) equals the molar diffusion flux relative to the molar average velocity \([mol \cdot m^{-2} \cdot s^{-1}]\), \( \mu \) equals the chemical potential \([J \cdot mol^{-1}]\), \( \varphi_i \) equals the volume fraction \([-]\), \( \omega_i \) equals the mass fraction \([-]\), \( F_i \) equals an external body force \([J \cdot mol^{-1}]\), and \( \mu_0^i \) equals the chemical potential of a pure species \([J \cdot mol^{-1}]\). Indices \( i, j \), \( T \) and \( P \) denote the species \( i \), species \( j \), temperature and pressure, respectively.

When neglecting the pressure gradient, substituting Equation A3 and Equation A4 into Equation A2 and making use of the electroneutrality condition (Equation 9), one obtains Equation A5 after a few rearrangements. Note that the gradient of the chemical potential of a pure species equals zero.

\[
d_i = x_i \nabla \ln \left( \gamma_i x_i \right) + z_i x_i \frac{F}{RT} \nabla \varphi
\]

Equation A5

An alternative form of Equation A1 is obtained by introducing a reference velocity for one of the species \( (v) \) via Equation A6. Consequently, the flux of that species, usually the solvent velocity, becomes zero. The result is described by Equation A7 with parameter \( B \) described by Equation A8 and Equation A9. These equations reduce to Equation A10 and Equation A11 for dilute electrolyte systems. Moreover, Equation A5 reduces to Equation A12. Finally, the NP equation (Equation 3) is obtained after combining equations A6, A7, A10, A11 and A12.[14]

\[
J_i = N_i - C_i v
\]

Equation A6

\[
C_{\text{tot}} d_i = -\sum_{j=1}^{n-1} B_{ij} J_j
\]

Equation A7

\[
B_{ii} = \sum_{k=1}^{n} \frac{x_k}{D_{ik}} \quad i = 1, 2, \ldots, n-1
\]

Equation A8
\[ B_{ij}^* = -\frac{x_i}{D_{ij}} \quad i \neq j = 1, 2, \ldots, n - 1 \]  
\hspace{1cm} \text{Equation A9}

\[ B_{ii}^n = \frac{1}{D_i} \]  
\hspace{1cm} \text{Equation A10}

\[ B_{ij}^n = 0 \]  
\hspace{1cm} \text{Equation A11}

\[ \mathbf{d}_i = \nabla x_i + z_i x_i \frac{F}{RT} \nabla \phi \]  
\hspace{1cm} \text{Equation A12}

\[ N_i = -D_i \nabla C_i - z_i D_i C_i \frac{F}{RT} \nabla \phi + C_i \nu \]  
\hspace{1cm} \text{Equation 3}

B equals a factor comprising the inverse of the binary diffusion coefficient \([s \cdot m^{-2}]\).
Appendix B: Derivation of the extended NP approach
Recall equations A5 – A7 and equations A10 and A11. Combining these equations results in Equation B1. Equations B2 – B4 are obtained when evaluating the first term on the right hand side of Equation B1. Finally, after substituting Equation B4 into Equation B1, one obtains Equation 6.

\[ d_i = x_i \nabla \ln \left( \frac{\gamma_i}{x_i} \right) + z_i x_i \frac{F}{RT} \nabla \phi \]  
\[ J^n_i = N_i^n - C_i \nu \]  
\[ C_{tot} d_i = -\sum_{j=1}^{n-1} B_j^n J^n_j \]  
\[ B^n_i = \frac{1}{D_i} \]  
\[ B^n_j = 0 \]  
\[ N_i = -C_i D_i \nabla \left( \ln \left( \frac{\gamma_i}{C_i} \right) \right) - C_i D_i z_i \frac{F}{RT} \nabla \phi + C_i \nu \]  
\[ -C_i D_i \nabla \left( \ln \left( \frac{\gamma_i}{C_i} \right) \right) = -C_i D_i \nabla \ln \left( \gamma_i C_i \right) + C_i D_i \nabla \ln \left( C_{tot} \right) \]  
\[ -C_i D_i \nabla \left( \ln \left( \frac{\gamma_i}{C_i} \right) \right) = -D_i \left( C_i \frac{\nabla \ln \left( \gamma_i \right)}{\nabla C_i} + C_i \frac{\nabla \ln \left( C_i \right)}{\nabla C_i} \right) \nabla C_i + C_i D_i \frac{\nabla \ln \left( C_{tot} \right)}{\nabla C_{tot}} \nabla C_{tot} \]  
\[ -C_i D_i \nabla \left( \ln \left( \frac{\gamma_i}{C_i} \right) \right) = -D_i \left( C_i \frac{\nabla \ln \left( \gamma_i \right)}{\nabla C_i} + 1 \right) \nabla C_i + C_i \frac{C_i D_i}{C_{tot}} \nabla C_{tot} \]  
\[ N_i = -D_i \left( C_i \frac{\nabla \ln \left( \gamma_i \right)}{\nabla C_i} + 1 \right) \nabla C_i + C_i \frac{C_i D_i}{C_{tot}} \nabla C_{tot} - z_i D_i C_i \frac{F}{RT} \nabla \phi + C_i \nu \]
Appendix C: Derivation of Ohm’s law when neglecting the diffusion and convective term

Substitution of the NP flux (Equation 3) in the current density equation (Equation 11) and neglecting the displacement current, results in Equation C1.

\[ N_i = -D_i \nabla C_i - z_i D_i C_i \frac{F}{RT} \nabla \phi + C_i \nu \]  
Equation 3

\[ J = F \sum (z_i N_i) + \epsilon \frac{\partial E}{\partial t} \approx F \sum (z_i N_i) \]  
Equation 11

\[ J = F \sum \left( z_i \left( -D_i \nabla C_i - z_i D_i C_i \frac{F}{RT} \nabla \phi + C_i \nu \right) \right) \]  
Equation C1

Neglecting the diffusion and convection term, results in Equation C2.

\[ J = F \sum \left( z_i \left( -z_i D_i C_i \frac{F}{RT} \nabla \phi \right) \right) \]  
Equation C2

Rearranging Equation C2 results in Equation C3 in which the conductivity is given by Equation 8. Due to the previous neglect of the diffusion and convection term, one may not substitute Equation C3 into Equation 3.

\[ \nabla \phi = -\frac{J}{\sum \left( z_i^2 D_i C_i \frac{F^2}{RT} \right)} = -\frac{J}{\kappa} \]  
Equation C3

\[ \kappa = \sum \left( z_i^2 D_i C_i \frac{F^2}{RT} \right) \]  
Equation 8
Appendix D: Prove that the potential gradient cannot be constant

Recall the NP equation and the electroneutrality condition in the membrane. The latter requires Equation D1 to be valid as well. Furthermore, the assumption that the sulfonate concentration is constant requires that the summation of the diffusional flux of the positive charges equals the summation of the diffusional flux of the negative charges. In other words, the total diffusional flux of charges is equal to zero, see Equation D2. An additional requirement of the system is that the flux on the left side of the membrane should equal the flux on the right side of the membrane, as shown by Equation D3.

\[
N_i = -D_i \nabla C_i - z_i D_i C_i \frac{F}{RT} \nabla \phi + C_i \gamma 
\]

Equation 3

\[
\sum_{i=1}^{n} z_i C_i + z_m C_m = 0
\]

Equation 10

\[
\sum_{i=1}^{n} z_i C_i^0 = \sum_{i=1}^{n} z_i C_i^\delta
\]

Equation D1

\[
\sum_{i=1}^{n} z_i D_i \nabla C_i = 0
\]

Equation D2

\[
N_i^0 = N_i^\delta
\]

Equation D3

Recall the current density equation:

\[
J = F \sum_{i=1}^{n} z_i N_i
\]

Equation 11

When neglecting the convective term and combining Equation 3 and Equation 11, Equation D4 and Equation D5 are obtained for the left and right side of the membrane, respectively.

\[
\frac{J}{F} = - \left( \sum_{i=1}^{n} z_i D_i \nabla C_i^0 + \sum_{i=1}^{n} z_i^2 D_i C_i^0 \frac{F}{RT} \nabla \phi \right)
\]

Equation D4

\[
\frac{J}{F} = - \left( \sum_{i=1}^{n} z_i D_i \nabla C_i^\delta + \sum_{i=1}^{n} z_i^2 D_i C_i^\delta \frac{F}{RT} \nabla \phi \right)
\]

Equation D5

Combining Equation D4 and Equation D5 and omitting the diffusion terms due to Equation D2, one obtains Equation D6 after a few rearrangements and by considering the potential gradient to be constant. This equation deviates from Equation D1 by the diffusion coefficients and, more importantly, by the order of the charge valence. The latter causes a change in sign for the negative ions in these equations. Therefore, the potential gradient must be non-linear in order to satisfy both the electroneutrality condition and the fact that the flux on the left and right side of the membrane for each component must be equal.

\[
\sum_{i=1}^{n} z_i^2 D_i C_i^0 = \sum_{i=1}^{n} z_i^2 D_i C_i^\delta
\]

Equation D6
Appendix E: Derivation of the osmotic pressure gradient

The equilibrium between the chemical potential between an electrolyte at position ii+1 and position ii is shown in Equation E1 and can be rewritten to obtain Equation E4 with Equation E2 and Equation E3 as intermediate results. By introducing the water concentration as the reciprocal of its molar volume one obtains Equation 13.

\[
\mu^{\text{ii}}_{\text{H}_2\text{O}}(x^{\text{ii}}_{\text{H}_2\text{O}}; p) = \mu^{\text{ii+1}}_{\text{H}_2\text{O}}(x^{\text{ii+1}}_{\text{H}_2\text{O}}, p + \Pi) \quad \text{Equation E1}
\]

\[
\mu^{\text{0}}_{\text{H}_2\text{O}}(p) + RT \ln \left( \gamma^{\text{ii}}_{\text{H}_2\text{O}} x^{\text{ii}}_{\text{H}_2\text{O}} \right) = \mu^{\text{0}}_{\text{H}_2\text{O}}(p + \Pi) + RT \ln \left( \gamma^{\text{ii+1}}_{\text{H}_2\text{O}} x^{\text{ii+1}}_{\text{H}_2\text{O}} \right) \quad \text{Equation E2}
\]

\[
\mu^{\text{0}}_{\text{H}_2\text{O}}(p) + RT \ln \left( \gamma^{\text{ii}}_{\text{H}_2\text{O}} x^{\text{ii}}_{\text{H}_2\text{O}} \right) = \mu^{\text{0}}_{\text{H}_2\text{O}}(p) + \int_{p}^{p+\Pi} V_m dp + RT \ln \left( \gamma^{\text{ii+1}}_{\text{H}_2\text{O}} x^{\text{ii+1}}_{\text{H}_2\text{O}} \right) \quad \text{Equation E3}
\]

\[
\int_{p}^{p+\Pi} V_m dp = -RT \ln \left( \frac{\gamma^{\text{ii+1}}_{\text{H}_2\text{O}} x^{\text{ii+1}}_{\text{H}_2\text{O}}}{\gamma^{\text{ii}}_{\text{H}_2\text{O}} x^{\text{ii}}_{\text{H}_2\text{O}}} \right) \quad \text{Equation E4}
\]

\[
\nabla P = -RT \nabla C_{\text{H}_2\text{O}} \ln \left( \frac{\gamma^{\text{ii+1}}_{\text{H}_2\text{O}} x^{\text{ii+1}}_{\text{H}_2\text{O}}}{\gamma^{\text{ii}}_{\text{H}_2\text{O}} x^{\text{ii}}_{\text{H}_2\text{O}}} \right) \quad \text{Equation 13}
\]
Appendix F: Pitzer activity model parameters and equations

The Pitzer model for the estimation of activity coefficients of electrolytes in aqueous solutions is given by the following set of equations. Values for the model interaction parameters are provided in Table F1. Note that in this appendix \( I \) equals the ionic strength of the solution [mol/kg \( H_2O \)].\[^{32}\]

\[
\ln(\gamma_{NaOH}) = \left| z_{Na^+} z_{OH^-} \right| f^\gamma + mb_{NaOH}^{\beta} + m^2 c_{NaOH}^{\gamma} \]

\[
I = 1/2 \sum_{i} m_i z_i^2
\]

\[
f^\gamma = -A_{\phi}\left[ \frac{I^{0.5}}{1 + bI^{0.5}} + \frac{2}{b} \ln(1 + bI^{0.5}) \right]
\]

\[
B_{NaOH}^{\beta} = 2\beta_{NaOH}^{(0)} + 2\beta_{NaOH}^{(1)} \left( 1 - e^{-\alpha I^{0.5}} \right) \left( 1 + \alpha I^{0.5} - 0.5 \alpha^2 I \right)
\]

\[
c_{NaOH}^{\gamma} = \frac{3c_{NaOH}^{\phi}}{2}
\]

Table F1: Interaction parameters of the Pitzer model in the NaOH solution.

<table>
<thead>
<tr>
<th>Interaction parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) [-]</td>
<td>2</td>
</tr>
<tr>
<td>b [-]</td>
<td>1.2</td>
</tr>
<tr>
<td>( A_{\phi} ) [-]</td>
<td>0.392</td>
</tr>
<tr>
<td>( B_{NaOH}^{(0)} ) [-]</td>
<td>0.0864</td>
</tr>
<tr>
<td>( B_{NaOH}^{(1)} ) [-]</td>
<td>0.253</td>
</tr>
<tr>
<td>( C_{NaOH}^{\phi} ) [-]</td>
<td>0.0044</td>
</tr>
</tbody>
</table>

The Pitzer model for the estimation of activity coefficients of electrolytes in ion selective membranes is given by the following set of equations. Values for the model interaction parameters, which are nonzero, are provided in Table F2.\[^{33}\]

\[
\ln(\gamma_M) = z_M^2 F + \sum_{a} m_a (2B_{Ma} + ZC_{Ma}) + \sum_{c} m_c (2\Phi_{Me} + \sum_{a} m_a \psi_{Ma}) + \sum_{a<ca} m_a m_c \psi_{Ma} + z_M \sum_{c} m_c m_a C_{ca}
\]

\[
\ln(\gamma_X) = z_X^2 F + \sum_{c} m_c (2B_{cX} + ZC_{cX}) + \sum_{a} m_a (2\Phi_{Xa} + \sum_{c} m_c \psi_{Xa}) + \sum_{a<ca} m_a m_c \psi_{Xa} + z_X \sum_{c} m_c m_a C_{ca}
\]

\[
I = 1/2 \sum_{i} m_i z_i^2
\]
\[ Z = \sum_i m_i |z_i| \]

\[ F = f^\gamma + \sum_c \sum_a m_c m_a B_{ca} + \sum_{c\neq c} \sum_a m_c m_c \Phi_{cc}^\gamma + \sum_{a\neq a} m_a m_a \Phi_{aa}^\gamma \]

\[ f^\gamma = -A_{\phi} \left[ \frac{I^{0.5}}{1 + bI^{0.5}} + \frac{2}{b} \ln(1 + bI^{0.5}) \right] \]

\[ B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 I^{0.5}) + \beta_{MX}^{(2)} g(\alpha_2 I^{0.5}) \]

\[ g(x) = \frac{2[1-(1-x)e^{-x}]}{x^2} \]

\[ x = \alpha I^{0.5} \]

\[ B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \Phi_{MX}^{(a\beta)} \Phi_{MX}^{(a\gamma)} + \beta_{MX}^{(2)} \Phi_{MX}^{(a\delta)} \Phi_{MX}^{(a\gamma)} \]

\[ g'(x) = -\frac{2[1-(1+x+0.5x^2)e^{-x}]}{x^2} \]

\[ C_{MX} = \frac{C^\phi}{2z_c z_{1.5}} \]

\[ \Phi_{cc}^\phi = \Phi_{cc} + i\Phi_{cc}^\gamma \]

Table F2: Interaction parameter for the Pitzer model in the cation selective membrane.

<table>
<thead>
<tr>
<th>Interaction parameter</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_1 ) [-]</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b [-]</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_{\phi} ) [-]</td>
<td>0.392</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B^{(0)} ) [-]</td>
<td>0.0864</td>
<td>0.07031</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B^{(1)} ) [-]</td>
<td>0.253</td>
<td>-11.0268</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C^\phi ) [-]</td>
<td>0.0044</td>
<td>-0.00362</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Phi_{aa} ) [-]</td>
<td>0.17011</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \psi_{aa\beta\gamma} )</td>
<td></td>
<td>-0.01134</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix G: Derivation of the concentration jump based on the Donnan equilibrium theory

Derivation of the solution interface concentration as a function of the membrane interface concentration

Recalling the Donnan equilibrium equation in which the osmotic contribution is neglected, Equation 19, one can obtain Equation G1 and Equation G2 for the positive and negative species, respectively.

\[
\frac{\gamma_i^{M,0}C_i^{M,0}}{\gamma_i^{A,\text{int}}C_i^{A,\text{int}}} = e^\left(-\frac{Fz_i\phi_{\text{Don}}}{RT}\right) = K^{z_i}
\]

Equation 19

\[
C_{i,\text{pos}}^{A,\text{int}} = \frac{\gamma_i^{M,0}C_i^{M,0}}{\gamma_i^{A,\text{int}}} \frac{1}{K}
\]

Equation G1

\[
C_{i,\text{neg}}^{A,\text{int}} = \frac{\gamma_i^{M,0}C_i^{M,0}}{\gamma_i^{A,\text{int}}} K
\]

Equation G2

Recalling the electroneutrality in the solution, Equation 20a, and combining this equation with Equation G1 and Equation G2, one obtains Equation G3. After rearrangement of the latter, an expression for K is obtained, see Equation G4.

\[
\sum_{i}^N m C_{i,\text{int}}^{A,\text{int}} = \sum_{i}^N m C_{i,\text{int}}^{A,\text{int}}
\]

Equation 20a

\[
\sum_{i}^N m \frac{\gamma_i^{M,0}C_i^{M,0}}{\gamma_i^{A,\text{int}}} K = \sum_{i}^N m \frac{\gamma_i^{M,0}C_i^{M,0}}{\gamma_i^{A,\text{int}}} K
\]

Equation G3

\[
K = \sqrt{\frac{\sum_{i}^N m \gamma_i^{M,0}C_i^{M,0}}{\gamma_i^{A,\text{int}}}} \frac{1}{\sqrt{\sum_{i}^N m \gamma_i^{M,0}C_i^{M,0}}}
\]

Equation G4

Substitution of Equation G4 in Equation G1 and Equation G2 results in the general equation for the positive ions (Equation G5) and negative ions (Equation G6), respectively. For a system of only Na\(^+\) and OH\(^-\), Equation G5 and Equation G6 reduce to Equation 21.

\[
C_{i,\text{pos}}^{A,\text{int}} = \frac{\gamma_i^{M,0}C_i^{M,0}}{\gamma_i^{A,\text{int}}C_i^{A,\text{int}}} \frac{1}{K}
\]

Equation G5
Derivation of the membrane interface molality as a function of the solution interface molality

From Equation 19, one can obtain Equation G7 and Equation G8 for the positive and negative species, respectively.

\[ C_{M,0}^{i_{pos}} = \frac{\gamma_{i,\text{pos}}^{M,0} C^{M,0}_{i_{pos}}}{\gamma_{i,\text{neg}}^{M,0}} K \]  
Equation G7

\[ C_{M,0}^{i_{neg}} = \frac{\gamma_{i,\text{neg}}^{A,\text{int}} C_{i,\text{int}}^{A,\text{int}}}{\gamma_{i,\text{neg}}^{M,0}} \frac{1}{K} \]  
Equation G8

Recalling the electroneutrality in the membrane, Equation 20b, and combining this equation with Equation G7 and Equation G8, one obtains Equation G9. After rearrangement of the latter, a quadratic expression for K is obtained, see Equation G10. This quadratic expression can be solved resulting in Equation G11.

\[ \sum_{i} N_{\text{im}}^{A,\text{int}} \gamma_{i,\text{pos}}^{A,\text{int}} C^{A,\text{int}}_{i_{pos}} - C_{m} = \sum_{i} N_{\text{im}}^{A,\text{int}} C^{A,\text{int}}_{i_{neg}} \]  
Equation 20b

\[ \sum_{i} N_{\text{im}}^{A,\text{int}} C^{A,\text{int}}_{i_{pos}} - C_{m} K = \sum_{i} N_{\text{im}}^{A,\text{int}} C^{A,\text{int}}_{i_{neg}} \frac{1}{K} \]  
Equation G9

\[ \sum_{i} N_{\text{im}}^{A,\text{int}} C^{A,\text{int}}_{i_{pos}} - C_{m} K^2 - K C_{m} K - \sum_{i} N_{\text{im}}^{A,\text{int}} C^{A,\text{int}}_{i_{neg}} = 0 \]  
Equation G10

\[ K = \frac{C_{m} \pm \sqrt{C_{m}^2 + 4 \sum_{i} N_{\text{im}}^{A,\text{int}} C^{A,\text{int}}_{i_{pos}} N_{\text{im}}^{A,\text{int}} C^{A,\text{int}}_{i_{neg}}}}{2 \sum_{i} N_{\text{im}}^{A,\text{int}} C^{A,\text{int}}_{i_{pos}} \gamma_{i,\text{pos}}^{M,0}} \]  
Equation G11

Substitution of Equation G11 in Equation G7 and Equation G8 results in in the general equation for the positive ions (Equation G12) and negative ions (Equation G13), respectively. For a system of only Na\(^+\) and OH\(^-\), Equation G12 reduces to Equation 18.
\[ C^{-M,0}_{i,\text{pos}} = \frac{\gamma^{A,\text{int}}_{i,\text{pos}} C_{i,\text{pos}}^{A,\text{int}}}{\gamma^{M,0}_{i,\text{pos}}} C_m + \sqrt{C_m^2 + 4 \sum_{i=1}^{N_{\text{int}}} \frac{\gamma^{A,\text{int}}_{i,\text{pos}} C_{i,\text{pos}}^{A,\text{int}}}{\gamma^{M,0}_{i,\text{pos}}} \sum_{i=1}^{N_{\text{int}}} \frac{\gamma^{A,\text{int}}_{i,\text{neg}} C_{i,\text{neg}}^{A,\text{int}}}{\gamma^{M,0}_{i,\text{neg}}}} \]  

Equation G12

\[ C^{-M,0}_{i,\text{neg}} = \frac{\gamma^{A,\text{int}}_{i,\text{neg}} C_{i,\text{neg}}^{A,\text{int}}}{\gamma^{M,0}_{i,\text{neg}}} C_m + \sqrt{C_m^2 + 4 \sum_{i=1}^{N_{\text{int}}} \frac{\gamma^{A,\text{int}}_{i,\text{pos}} C_{i,\text{pos}}^{A,\text{int}}}{\gamma^{M,0}_{i,\text{pos}}} \sum_{i=1}^{N_{\text{int}}} \frac{\gamma^{A,\text{int}}_{i,\text{neg}} C_{i,\text{neg}}^{A,\text{int}}}{\gamma^{M,0}_{i,\text{neg}}}} \]  

Equation G13

\[ C^{-M,0}_{\text{Na}} = \frac{C_m + \sqrt{C_m^2 + 4 \left(C_{\text{Na}}^{A,\text{int}}\right)^2 \gamma^{A,\text{int}}_{\text{Na}} \gamma^{A,\text{int}}_{\text{OH}} \gamma^{A,\text{int}}_{\text{Na}} \gamma^{A,\text{int}}_{\text{OH}}}}{2} \]  

Equation 18

Prove that Equation 18 and Equation 21 are equal

After substitution of the electroneutrality condition in the membrane in Equation 18, one obtains Equation 21 with Equation G14 and Equation G15 as intermediate results.

\[ C^{-M,0}_{\text{Na}} = \frac{\sqrt{\left(C_{\text{Na}}^{M,0}\right)^2 - C_{\text{Na}}^{M,0} C_m}}{2} \]  

Equation 21
Appendix H: Hydrogen safety limits

A ternary diagram describing the flammable and nonflammable region of several H\textsubscript{2}/air/diluent mixture is depicted in Figure H1.\textsuperscript{[35]} Data obtained after translating this graph into the amount of N\textsubscript{2} required for safe operation for different current density is described in Table H1.

![Ternary diagram showing flammable and nonflammable regions of H\textsubscript{2}/air/diluent mixtures with N\textsubscript{2}, He, CO\textsubscript{2}, and H\textsubscript{2}O diluents.]

**Figure H1**: Effects of N\textsubscript{2}, He, CO\textsubscript{2}, and H\textsubscript{2}O diluents on flammability limits of H\textsubscript{2} in air at 101.3 kPa. Effects of N\textsubscript{2}, He, and CO\textsubscript{2} are at 298K and H\textsubscript{2}O at 422K.\textsuperscript{[35]}

**Table H1**: The required N\textsubscript{2} flow for different current densities in order to guarantee safe operation.

<table>
<thead>
<tr>
<th>I [A]</th>
<th>J [A-m\textsuperscript{-2}]</th>
<th>H\textsubscript{2} formed [cm\textsuperscript{3}·s\textsuperscript{-1}]</th>
<th>Nitrogen flow required [dm\textsuperscript{3}·min\textsuperscript{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>200</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>0.31</td>
<td>1000</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>0.63</td>
<td>2000</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>1.57</td>
<td>5000</td>
<td>0.19</td>
<td>0.23</td>
</tr>
<tr>
<td>3.13</td>
<td>9963</td>
<td>0.38</td>
<td>0.45</td>
</tr>
<tr>
<td>3.14</td>
<td>10000</td>
<td>0.38</td>
<td>0.45</td>
</tr>
<tr>
<td>4.71</td>
<td>15000</td>
<td>0.58</td>
<td>0.68</td>
</tr>
<tr>
<td>6.28</td>
<td>20000</td>
<td>0.77</td>
<td>0.90</td>
</tr>
<tr>
<td>7.85</td>
<td>25000</td>
<td>0.96</td>
<td>1.13</td>
</tr>
<tr>
<td>12.57</td>
<td>40000</td>
<td>1.54</td>
<td>1.80</td>
</tr>
<tr>
<td>12.72</td>
<td>40500</td>
<td>1.56</td>
<td>1.82</td>
</tr>
<tr>
<td>15.71</td>
<td>50000</td>
<td>1.92</td>
<td>2.25</td>
</tr>
<tr>
<td>31.42</td>
<td>100000</td>
<td>3.85</td>
<td>4.50</td>
</tr>
</tbody>
</table>
Appendix I: Setup dimensions and equipment information

Dimensions of several parts of the setup are described in Table I1. In addition, the equipment used during the experiments is described in Table I2. Although the conductivity meter was not used in the final setup since the accuracy was not sufficient to measure the electrolyte concentration via the conductivity, its type is described in Table I3 for completeness.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber O-ring thickness [m]</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Rubber O-ring inner area [m$^2$]</td>
<td>$2 \times 10^{-2}$</td>
</tr>
<tr>
<td>Anolyte compartment diameter [m]</td>
<td>$9.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>Anolyte compartment membrane outlet diameter [m]</td>
<td>$2 \times 10^{-2}$</td>
</tr>
<tr>
<td>Catholyte compartment diameter [m]</td>
<td>$9.44 \times 10^{-2}$</td>
</tr>
<tr>
<td>Catholyte compartment membrane outlet diameter [m]</td>
<td>$2 \times 10^{-2}$</td>
</tr>
<tr>
<td>Pump speed [rpm]</td>
<td>223</td>
</tr>
</tbody>
</table>

Table I2: Equipment used during the experiments.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Equipment type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage meter for electrodes</td>
<td>TDK-LAMBDA GEN 750W</td>
</tr>
<tr>
<td>Voltage meter for membrane</td>
<td>KEITHLEY 175 Autoranging Multimeter</td>
</tr>
<tr>
<td>Reference electrodes</td>
<td>QIS Type No. QM710X Ser No. 36546/003 (Filled with 3M KCl saturated with AgCl)</td>
</tr>
<tr>
<td>Pump</td>
<td>WATSON MARLOW 503U</td>
</tr>
<tr>
<td>Heat bath</td>
<td>LAUDA Ecoline StaRedition 003</td>
</tr>
<tr>
<td>Heat bath temperature controller</td>
<td>LAUDA Ecoline StaRedition E100</td>
</tr>
<tr>
<td>Thermometer (cathode compartment)</td>
<td>Traceable® Thermometer VWRI 620-2080</td>
</tr>
<tr>
<td>Thermometer data loggers (in flow cells)</td>
<td>Lascar Electronics EL-USB-TC K-Type Data Logger using Easylog USB software</td>
</tr>
<tr>
<td>Mass balance for titration samples</td>
<td>Sartorius MC1 Analytic AC 210 S</td>
</tr>
<tr>
<td>Mass balance for weighing solutions</td>
<td>Sartorius P14 (I8100P)</td>
</tr>
<tr>
<td>Autoburet</td>
<td>SCHOTT GERÄTE T82/50</td>
</tr>
</tbody>
</table>

Table I3: Equipment used for the conductivity measurements.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Equipment type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity meter</td>
<td>Thermo Scientific Orion Star A212 Benchtop Conductivity Meter</td>
</tr>
<tr>
<td>Conductivity cell</td>
<td>Orion 018020MD Conductivity Cell</td>
</tr>
</tbody>
</table>
Appendix J: Experimental method of the current efficiency and flux experiments

Caustic solution preparation
Prepare a caustic batch solution of desired concentration by adding 50 wt% caustic soda stock solution\(^{11}\) and demiwater into a container, which is placed in an ice bath in order to remove the heat produced when adding water to the caustic solution. Stir the solution for ~30 minutes and titrate in triplicate to determine its exact concentration.

Membrane pre-treatment
The membrane should be equilibrated overnight in a caustic solution of the same concentration as the concentration used for the experiment in order to ensure that the membrane is in the sodium and swollen state.

Startup of the system
1. Put the equilibrated membrane between the rubber O-rings and place it between the anolyte and catholyte compartment. Ensure that the clamp is firmly fixed to prevent leakage.
2. Place a beaker underneath the membrane to collect solution in case there is some leakage.
3. Weigh an equal amount of anolyte and the catholyte (~700g each) in separate beakers and partially fill the Luggin capillaries with the corresponding solution and fasten them to their compartments.
4. Put catholyte thermometer in place, turn on the cooling water and make sure that the tubes are properly attached to the flow cells by using clamps.
5. Pour the remainder of the solutions in the corresponding compartments and capillaries. The height of the compartment and the capillaries do not have to be equal at this stage.
6. Start the pump in order to partially fill the flow cells to be able to determine the remaining weight after draining the system.
7. Stop the pump, empty the flow cells and drain the compartments in the same beakers by removing the tubes from flow cells into the beakers. Empty the Luggin capillaries in the corresponding beakers as well.
8. Determine the weight of the solutions after drainage.
9. Attach the tubes back to the flow cells.
10. Rinse the reference electrodes with demiwater (they are stored in a 3M KCl solution) and dry them with a cotton cloth. Then, install them in the capillaries.
11. Pour the solutions in their capillaries and compartments again and weigh the empty beakers to determine the weight of the solution left behind in the beakers. Make sure that the height of the solution in the capillary and the compartment are nearly equal.
12. Put the electrodes in place and turn on the heat bath to preheat the solution until a desired temperature. More details on preheating the solution and the temperature settings during the experiments are provided in Appendix K.
13. Turn on the nitrogen flow to flush the gaseous phase above the catholyte.
14. Set the flow cell thermometers to the desired setting by using the Easylog USB software and install them in the flow cells. In this study, the thermometers were set to measure the temperature every minute.
15. Start the pump.
16. Properly connect the voltage meters to the electrodes and the reference electrodes.

\(^{11}\) 50 wt% NaOH in H\(_2\)O: Sigma-Aldrich, product number 415413-4L, CAS number 1310-73-2
17. Turn on the power supply of the voltage meter for the electrodes and set the desired current density.
18. When the desired temperature has been reached, write down the initial values for the voltage drop over the reference electrodes, the temperature in the catholyte compartment and the temperature of the heat bath.
19. Start the experiment by applying the current.

**During the measurement**

In principle, data is only required at the end of the experiment since the electro-osmotic effect should result in a linear concentration change. However, osmotic pressure and diffusion might cause the concentration change to become nonlinear and their influence might become visible when the concentration difference becomes significant. In addition, the temperature might not be perfectly constant, which also influences mass transfer and the potential drop. The latter effect follows from the dependency of the electrolyte conductivity on temperature.

Collect data at fixed moments in time (see Appendix K) by writing down:
- The voltage between the reference electrodes;
- The voltage between the electrodes;
- The temperature in the catholyte compartment;
- The temperature of the heat bath.

In addition, take samples of the anolyte and catholyte halfway the experiment (see Appendix K) and determine their concentrations via titrations in triplicate.

**At the end of the experiment**

1. Take samples of the anolyte and catholyte for titration in triplicate.
2. Turn of the voltage meters, heat bath and the pump.
3. Disconnect the voltage meters from the electrodes and reference electrodes.
4. Remove the reference electrodes and rinse them with demiwater. Store them in the 3M KCl solution.
5. Disconnect the tubes from the flow cells and empty the compartments in the same beakers. Make sure that the flow cells are emptied as well. Empty the Luggin capillaries in the corresponding beakers as well.
6. Weigh the beakers in order to determine the final weight.
7. Turn of the nitrogen flow and the cooling water.
8. Remove the electrodes, catholyte thermometer and flow cell thermometers and wash them with water.
9. Store the data of the flow cell thermometers on a computer by using the Easylog USB software.
10. Remove the membrane, wash it with demiwater.
11. Wash the O-rings and Luggin capillaries with water and put them back in place.
12. Clean the system once with water and once with demiwater. Make sure that the flow cells are cleaned completely as well.
13. Remove the O-rings and Luggin capillaries and wash them with demiwater.
Appendix K: Outline of the performed experiments

Table K1 presents the settings of the four reproducibility experiments and Table K2 presents the settings for the experiment with the bilayer membrane. They were performed for six hours at a current density of 10 kA·m⁻², a concentration of 10 wt% and the heat bath was set at 4°C. One O-ring of 1mm was used on each side of the membrane in order to properly close the system. Table K3 and Table K4 present the experiments in which the current density and the concentration were varied, respectively. Furthermore, the temperature settings during these experiments are presented by Table K5.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>J [kA·m⁻²]</th>
<th>C₅₀OH [wt%]</th>
<th>Run time [hours]</th>
<th>O-rings used on each side [#]</th>
<th>Heat bath temperature [°C]</th>
<th>Anolyte weight [g]</th>
<th>Catholyte weight [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>1</td>
<td>4 at t=0</td>
<td>679.3</td>
<td>679.8</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>1</td>
<td>4 at t=0</td>
<td>676.4</td>
<td>674.1</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>1</td>
<td>4 at t=0</td>
<td>685.3</td>
<td>686.5</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>1</td>
<td>4 at t=0</td>
<td>685.3</td>
<td>686.3</td>
</tr>
</tbody>
</table>

Table K2: Outline of the performed experiments with the bilayer membrane.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>J [kA·m⁻²]</th>
<th>C₅₀OH [wt%]</th>
<th>Run time [hours]</th>
<th>O-rings used on each side [#]</th>
<th>Heat bath temperature [°C]</th>
<th>Anolyte weight [g]</th>
<th>Catholyte weight [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>1</td>
<td>4 at t=0</td>
<td>684.6</td>
<td>684.4</td>
</tr>
</tbody>
</table>

Table K3: Outline of the performed experiments with current density variation.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>J [kA·m⁻²]</th>
<th>C₅₀OH [wt%]</th>
<th>Run time [hours]</th>
<th>O-rings used on each side [#]</th>
<th>Anolyte weight [g]</th>
<th>Catholyte weight [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2</td>
<td>10</td>
<td>20</td>
<td>2</td>
<td>688.4</td>
<td>688.2</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>10</td>
<td>6</td>
<td>2</td>
<td>665.1</td>
<td>665.0</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
<td>10</td>
<td>6</td>
<td>2</td>
<td>687.3</td>
<td>687.1</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>1</td>
<td>679.3</td>
<td>679.8</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>1</td>
<td>684.5</td>
<td>686.5</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>10</td>
<td>3</td>
<td>2</td>
<td>684.9</td>
<td>685.7</td>
</tr>
</tbody>
</table>

Table K4: Outline of the performed experiments with concentration variation.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>J [kA·m⁻²]</th>
<th>C₅₀OH [wt%]</th>
<th>Run time [hours]</th>
<th>O-rings used on each side [#]</th>
<th>Anolyte weight [g]</th>
<th>Catholyte weight [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>1</td>
<td>679.3</td>
<td>679.8</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>1</td>
<td>684.5</td>
<td>686.5</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>15</td>
<td>6</td>
<td>2</td>
<td>690.9</td>
<td>690.9</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>15</td>
<td>6</td>
<td>2</td>
<td>694.7</td>
<td>694.7</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>32</td>
<td>6</td>
<td>2</td>
<td>768.6</td>
<td>769.4</td>
</tr>
</tbody>
</table>

12 During this experiment, the pump was started only after 180 minutes instead of at the beginning of the experiment due to a manual error.
Table K5: Heat bath settings during the experiments.

*Steady state temperature

<table>
<thead>
<tr>
<th>Experiment [#]</th>
<th>At time [min]</th>
<th>Catholyte temperature [°C]</th>
<th>Heat bath set to [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>21.4</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>44°</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>20.9</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>44.5°</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>21.1</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>44.5°</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>21.1</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>43.5°</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>22.1</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>44°</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>43.5</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>45.3</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>45.0</td>
<td>52.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>44.2</td>
<td>54.0</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>43.8</td>
<td>56.0</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>40°</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>44.1</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>45.4</td>
<td>41.0</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>42.7</td>
<td>43.5</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>43.5</td>
<td>45.0</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>41.7</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>43°</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>40.0</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>45.6</td>
<td>45.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>45.0</td>
<td>49.0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>44°</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>42.5</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>66°</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>43.5</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>47.9</td>
<td>38.0</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>47.2</td>
<td>36.0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>45.5°</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>43.2</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>47.8</td>
<td>35.0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>45°</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>42.5</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46°</td>
<td></td>
</tr>
</tbody>
</table>
Appendix L: Empirical correlations

Water activity and water activity coefficient as a function of NaOH molality
The empirical correlation for the water activity as a function of NaOH molality is based on data from Stokes and presented in Scheme L1.\cite{36} This correlation can be translated into a correlation of the water activity coefficient as a function of water mole fraction, which is presented by Scheme L2. The $R^2$ of these correlations equal 1.0000 and their parity plots are depicted in Figure L1. The numerical values deviate from their experimental values at water activities below approximately 0.16, which correspond to a molality above 19 mol NaOH/mol H$_2$O (44 wt%). Since 32 wt% is the maximum concentration used in this study, the correlation is sufficient.

Scheme L1: Empirical correlation of the water activity as a function of caustic molality.

$$a_{H_2O} = 0.93973927 + 1.437009 \times 10^{-2} m_{NaOH} - 1.269655 \times 10^{-2} m_{NaOH}^2 + 8.932 \times 10^{-4} m_{NaOH}^3 - 2.468 \times 10^{-5} m_{NaOH}^4 + 2.5 \times 10^{-7} m_{NaOH}^5$$

Scheme L2: Empirical correlation of the water activity coefficient as a function of water mole fraction.

$$\gamma_{H_2O} = -320.9457 + 1989.3457 x_{H_2O} - 4850.6232 x_{H_2O}^2 + 5809.8415 x_{H_2O}^3 - 3414.2246 x_{H_2O}^4 + 787.5484 x_{H_2O}^5$$

Figure L1: Parity plots for the water activity and the water activity coefficient.
Water uptake as a function of NaOH concentration
The empirical correlation for the water uptake as a function of NaOH concentration is based on data from O’Brien et al. and presented in Scheme L3.\textsuperscript{[1]} The $R^2$ of the correlation equals 0.9998 and its parity plot is depicted in Figure L2.

\textbf{Scheme L3: Empirical correlation of the water uptake as a function of caustic concentration.}

\[ \lambda_{H_2O} = 22.629 - 1.7038C_{NaOH} + 0.104C_{NaOH}^2 - 0.0032C_{NaOH}^3 \]

![Figure L2: Parity plot for the water uptake.](image)

Density as a function of NaOH concentration and temperature
The empirical correlation for the density as a function of NaOH concentration and temperature is based on data from Perry et al.\textsuperscript{[38]} in which the correlation for the density of pure water as a function of temperature is provided by McCutcheon et al.\textsuperscript{[40]} The obtained correlation is presented in Scheme L4. Parity plots for the density at several temperatures are depicted in Figure L3.

\textbf{Scheme L4: Empirical correlation of the density as a function of NaOH concentration and temperature.}

\[ \rho_{NaOH} = (\rho_{H_2O} + \rho_{1 wt\%NaOH} + \rho_{2 wt\%NaOH}^2 + \rho_{3 wt\%NaOH}^3 + \rho_{4 wt\%NaOH}^4) \]

\[ \rho_{H_2O} = 1 - \frac{(T + 288.9414)}{(508929.2(T + 68.12963))(T - 3.9863)^2} \]

\[ \rho_1 = 1.1730 \cdot 10^{-2} - 6.1448 \cdot 10^{-5} T + 7.1696 \cdot 10^{-7} T^2 - 2.4706 \cdot 10^{-9} T^3 \]

\[ \rho_2 = -1.3651 \cdot 10^{-5} + 2.5358 \cdot 10^{-6} T - 2.2820 \cdot 10^{-8} T^2 - 1.1360 \cdot 10^{-10} T^3 + 1.3025 \cdot 10^{-12} T^4 \]

\[ \rho_3 = 9.0073 \cdot 10^{-8} - 6.2449 \cdot 10^{-8} T + 8.6787 \cdot 10^{-10} T^2 - 3.2763 \cdot 10^{-12} T^3 \]

\[ \rho_4 = -3.7737 \cdot 10^{-9} + 4.9870 \cdot 10^{-10} T - 6.9570 \cdot 10^{-12} T^2 + 2.6590 \cdot 10^{-14} T^3 \]
Figure L3: Parity plots for the density at different temperatures. Top graph: $T = 20^\circ$C, middle graph: $T = 60^\circ$C, bottom graph $T = 80^\circ$C.
Appendix M: Model code

The constructed model, which uses the pdepe solver, contains 5 m-files. The NP.m file is the main file containing the solver and the calculations used afterwards to obtain several parameters, which are then plotted by this file as well. The 4 additional files are initpar.m, NPic.m, NPbc.m, and NPpde.m. They contain the input parameters and grid definition, the initial conditions, the boundary conditions, and the continuity equations, respectively.

```matlab
NP.m
par=initpar;

options=odeset('RelTol',1e-3,'AbsTol',1e-5); %Default settings: RelTol=1e-3, AbsTol=1e-6
m=0;
sol=pdepe(m,@NPpde,@NPic,@NPbc,par.z,par.t,options,par);

C1=sol(:,:,1);              %Na concentration [mol/m3]
C2=sol(:,:,2);              %OH concentration [mol/m3]
C3=sol(:,:,3);              %H2O concentration [mol/m3]
Ctot=C1+C2+C3+par.CSO3;     %Total concentration including the sulfonate groups [mol/m3]

% Pressure gradient, potential gradient and Schlogl equation for the left side of the membrane.
dPdzl=0;
dphidzl=(par.J*par.deltam/(par.F)+(par.zi(1)*par.D(1)*(sol(1:101,2,1) -
    sol(1:101,1,1))/par.zstep+par.zi(2)*par.D(2)*(sol(1:101,2,2) -
    sol(1:101,1,2))/par.zstep)+(par.zi(1)*sol(1:101,1,1)+par.zi(2)*sol(1:101,1,2))*par.dh.*dPdzl)./(par.F*(
    par.zi(1)*sol(1:101,1,1)+par.zi(2)*sol(1:101,1,2))*par.dh*par.zSO3*par.CSO3-
    (par.zi(1)^2*sol(1:101,1,1)*par.D(1)+par.zi(2)^2*sol(1:101,1,2)*par.D(2))/(par.R*par.T)));
vl=par.dh/par.deltam*(par.zSO3*par.CSO3*par.F*dphidzl-dPdzl); %Convective mass flux [m3/(m2*s)], (Schlogl equation)

% Pressure gradient, potential gradient and Schlogl equation for the right side of the membrane.
dPdzr=0;
dphidzr=(par.J*par.deltam/(par.F)+(par.zi(1)*par.D(1)*(sol(1:101,52,1) -
    sol(1:101,51,1))/par.zstep+par.zi(2)*par.D(2)*(sol(1:101,52,2) -
    sol(1:101,51,2))/par.zstep)+(par.zi(1)*sol(1:101,52,1)+par.zi(2)*sol(1:101,52,2))*par.dh.*dPdzr)./(par.F*
    (par.zi(1)*sol(1:101,52,1)+par.zi(2)*sol(1:101,52,2))*par.dh*par.zSO3*par.CSO3-
    (par.zi(1)^2*sol(1:101,52,1)*par.D(1)+par.zi(2)^2*sol(1:101,52,2)*par.D(2))/(par.R*par.T)));
```
vr=par.dh/par.deltam*(par.zSO3*par.CSO3*par.F*dphidzr-dPdzr); %Convective mass flux [m3/(m2*s)], (Schlogl equation)

% Fluxes at the membrane sides [mol/(m2mem*s)]
NNal=-(par.D(1)*(sol(1:101,2,1)-
    sol(1:101,1,1))/par.zstep+sol(1:101,1,1)*par.D(1)*par.zi(1)*par.F/(par.R*par.T).*dphidzl-
    sol(1:101,1,1).*vl*par.deltam)/par.deltam);
NNar=-(par.D(1)*(sol(1:101,52,1)-
    sol(1:101,51,1))/par.zstep+sol(1:101,52,1)*par.D(1)*par.zi(1)*par.F/(par.R*par.T).*dphidzr-
    sol(1:101,52,1).*vr*par.deltam)/par.deltam);
NOHl=-(par.D(2)*(sol(1:101,2,2)-
    sol(1:101,1,2))/par.zstep+sol(1:101,1,2)*par.D(2)*par.zi(2)*par.F/(par.R*par.T).*dphidzl-
    sol(1:101,1,2).*vl*par.deltam)/par.deltam);
NOHr=-(par.D(2)*(sol(1:101,52,2)-
    sol(1:101,51,2))/par.zstep+sol(1:101,52,2)*par.D(2)*par.zi(2)*par.F/(par.R*par.T).*dphidzr-
    sol(1:101,52,2).*vr*par.deltam)/par.deltam);

% Water flux NP
% NH2Ol=(-(par.D(3)*(sol(1:101,2,3)-sol(1:101,1,3))/par.zstep-sol(1:101,1,3).*vl*par.deltam)/par.deltam);
% NH2Or=(-(par.D(3)*(sol(1:101,52,3)-sol(1:101,51,3))/par.zstep-
    sol(1:101,52,3).*vr*par.deltam))/par.deltam);
% Water flux extended NP
NH2Ol=-(par.D(3)*(sol(1:101,2,3)-sol(1:101,1,3))/par.zstep-
    sol(1:101,1,3).*vl*par.deltam+par.hf*(par.D(1)*(sol(1:101,2,1)-
    sol(1:101,1,1))/par.zstep+sol(1:101,1,1)*par.D(1)*par.zi(1)*par.F/(par.R*par.T).*dphidzl))/par.deltam);
NH2Or=-(par.D(3)*(sol(1:101,52,3)-sol(1:101,51,3))/par.zstep-
    sol(1:101,52,3).*vr*par.deltam+par.hf*(par.D(1)*(sol(1:101,52,1)-
    sol(1:101,51,1))/par.zstep+sol(1:101,52,1)*par.D(1)*par.zi(1)*par.F/(par.R*par.T).*dphidzr))/par.deltam);

% Transport numbers and selectivity
% tNa=NNal*par.F/par.J;   %Transport number of Na+ [-]
tOH=-NOHl*par.F/par.J;  %Transport number of OH- [-]
tH2O=NH2Ol*par.F/par.J; %Transport number of Na+ [-]
TH2O=tH2O./tNa;         % Relative transport number of water [-]

% Membrane potential drop

77
\[ \text{dphidz} = \frac{(\text{par.J} \times \text{par.deltam} / (\text{par.F}) + (\text{par.zi(1)} \times \text{sol(1:101,1:52,1)} + \text{par.zi(2)} \times \text{sol(1:101,1:52,2)}) \times \text{par.dh} \times \text{par.dPdz})}{(\text{par.F} \times ((\text{par.zi(1)} \times \text{sol(1:101,1:52,1)} + \text{par.zi(2)} \times \text{sol(1:101,1:52,2)}) \times \text{par.dh} \times \text{par.zSO3} \times \text{par.CSO3} - (\text{par.zi(1)} \times \text{sol(1:101,1:52,1)} \times \text{par.D(1)} + \text{par.zi(1)} \times \text{sol(1:101,1:52,1)} \times \text{par.D(2)}) / (\text{par.R} \times \text{par.T})))}; \]

% Additional output data used for the determination of the contribution of the osmotic pressure gradient
% CwaterSS=sol(101,1:52,3); % Output data steady state water concentration
% CtotalSS=(sol(101,1:52,1)+sol(101,1:52,2)+sol(101,1:52,3)+par.CSO3); % Output data steady state total concentration
% Potential_gradientSS=dphidz(101,1:52); % Steady state potential gradient

% Integration of dphidz via first order Taylor series: \( f(x+dx) = f(x) + f'(x) \times dx \)
for i=1,
    phi(i)=0;
end
for ii=(2:52),
    phi(ii)=phi(ii-1)+(dphidz(101,ii)+dphidz(101,ii-1))/2*(z(ii)-z(ii-1));
end

% Graphs for the concentrations (1,2,3,4), fluxes (5,6,7), membrane potential drop (8), transport numbers (9,10), water relative transport number (11), potential gradient (12)
figure, clf
subplot(3,4,1)
plot(par.z,sol(1,:,1),'r')
hold on
plot(par.z,sol(10,:,1),'g')
plot(par.z,sol(40,:,1),'b')
plot(par.z,sol(80,:,1),'c')
plot(par.z,sol(100,:,1),'m')
ylabel('C_{Na^+} \ [mol \cdot m^{-3}_{void}]')
xlabel('z')

subplot(3,4,2)
plot(par.z,sol(1,:,2),'r')
hold on
plot(par.z,sol(10,:,2),'g')
plot(par.z,sol(40,:,2),'b')
plot(par.z,sol(80,:,2),'c')
plot(par.z,sol(100,:,2),'m')
ylabel('N_{H_{2}O} [mol*m^{-2}*s^{-1}]')
xlabel('t')
legend('Nl_{H_{2}O}','Nr_{H_{2}O}')

subplot(3,4,8)
plot(par.z,phi,'y')
ylabel('dphi [V]')
xlabel('z')
legend('Taylor series 1st order')

subplot(3,4,9)
plot(par.t,tNa,'r')
hold on
plot(par.t,tOH,'y')
ylabel('transport number [-]')
xlabel('t')
legend('t_{Na^{+}}','t_{OH^{-}}')

subplot(3,4,10)
plot(par.t,tH2O,'r')
ylabel('water transport number [-]')
xlabel('t')

subplot(3,4,11)
plot(par.t,TH2O,'r')
ylabel('water relative transport number [-]')
xlabel('t')

subplot(3,4,12)
plot(par.z,dphidz(101,:),'r')
ylabel('dphi/dz [V]')
xlabel('z')
legend('model data')
% Grid definition for t and z
Nloggrid=5;
Nlingrid=40;
brayer=0.01;
par.z=zeros(1,2*Nloggrid+2); %Creates 1 row of 2*Nloggrid+2 zeros --> [0 0 0 0 0 0 0 0 0 0 0 0]
par.z(1,2*Nloggrid+2)=1; %Makes the (2*Nloggrid+2)th zero equal to 1 --> [0 0 0 0 0 0 0 0 0 0 0 1]
power=linspace(-10,log10(brayer*0.99),Nloggrid); %Creates Nloggrid points with values from -10 to log10(brayer*0.99) with stepsize=(-10-log10(brayer*0.99))/(Nloggrid-1) -->  -10.0000   -8.0011   -6.0022
   -4.0033   -2.0044
for ii=1:Nloggrid,
    par.z(1,ii+1)=10^power(ii); %Gives values at position 2 3 4 5 6
    par.z(1,2*Nloggrid+2-ii)=1-10^power(ii); %Gives values at position 7 8 9 10 11. These 2 lines give
par.z=[0 1.0000e-10 9.9749e-09 9.9499e-07 9.9249e-05 0.0099 0.9901 0.9999 1.0000 1.0000 1.0000 1]
end
par.z=[par.z(1,1:Nloggrid+1),linspace(brayer,1-brayer,Nlingrid),par.z(1,Nloggrid+2:2*Nloggrid+2)]; %First 6 and last 6 grid points according to previous par.z. The 40 middel points increase linearly with stepsize=(1-2*brayer)/(Nlingrid-1) with starting value at the 7th grid point being brayer.
par.t=linspace(0,21600,101);
par.zstep=1e-10; %Stepsize at the boundaries
par.zsteplin=(1-2*brayer)/(Nlingrid-1); %Stepsize for the linear part of the grid

% Real constants
par.zi=[1;-1;0]; %Charge numbers for Na+, OH-, and H2O [-]
par.zSO3=-1; %Charge number for SO3- [-]
par.R=8.3145; %Gas constant [J/(K*mol)]
par.F=96485; %Faraday constant [C/mol]
par.MwNaOH=39.997; %Molecular weight NaOH [g/mol]
par.MwH2O=18.015; %Molecular weight H2O [g/mol]

% Input parameters
par.TC=46; %Temperature [°C]
par.T=par.TC+273.15; %Temperature [K]
par.D=[1*1e-10,2.5*1e-9,1*1e-9]; %Diffusion coefficient [m2/s]
par.epsvvoid=0.2; %Void fraction [m3void/m3membrane]
par.kAMNa=1e-4; %Mass transfer coefficient at the anolyte side [m/s]
par.kMCNa=1e-4; %Mass transfer coefficient at the catholyte side [m/s]
par.kAMH2O=1e-4; %Water mass transfer coefficient at the anolyte side [m/s]
par.kCMH2O=1e-4; %Water mass transfer coefficient at the catholyte side [m/s]
par.J=10000; %Current density [A/m²]
par.hf=4; %Hydration factor for the extended NP water flux [-]

% Viscosity based on experimental conditions and data from Solvay Chemicals (steady state temperatures of the experiments were used)
% % Experiment 10 wt% 10kA/m² (average of experiment 1 and 3, performed at 06-03-2014 and 25-03-2014, respectively)
% par.visc=1.047e-3;
% % Experiment 10 wt% 6kA/m² (average of experiment 7 and 8, performed at 18-04-2014 and 23-04-2014, respectively)
% par.visc=1.036e-3;
% % Experiment 15 wt% 10kA/m² (average of experiment 10 and 11, performed at 21-04-2014 and 25-04-2014, respectively)
% par.visc=1.446e-3;
% % Experiment 10 wt% 2kA/m² (experiment 6, performed at 29-04-2014)
% par.visc=1.114e-3;
% % Experiment 10 wt% 20kA/m² (experiment 9, performed at 06-05-2014)
% par.visc=6.981e-4;
% Experiment 32 wt% 10kA/m² (experiment 12, performed at 13-05-2014)
par.visc=5.959e-3;

%Constants of Nafion N1110 (sulfonic groups)
par.deltam=254e-6; %Membrane thickness [m]
par.rhopol=1.79e6; %Membrane density in swollen conditions for 0M NaOH [g/m³ membrane]
par.IEC=1/1100; %Ion exchange capacity [mol/g polymer]
par.dchannel=2.4e-9; %Channel diameter [m]
par.dh=par.dchannel^2*par.epsvoid/32/par.visc; %Hydrodynamic permeability of the membrane [s·m³/kg]

%Parameters as a function of other constants
par.CSO3=par.IEC*par.rhopol/par.epsvoid; %Concentration of SO₃⁻ groups [mol/m³ void]
par.dPdz=0; %Pressure gradient [kg/(m²·s²)]

% Bulk concentrations as a function of time according to the experimental results
% % Experiment 10 wt% 10kA/m² (average of experiment 1 and 3)
% par.CNaA0=2747.4; %Initial concentration of sodium in the anolyte [mol/m³]
% par.CH2OA0=54775; %Initial concentration of water in the anolyte [mol/m3]
% par.CH2OCo=54773; %Initial concentration of water in the catholyte [mol/m3]
% par.CNaA0=2753.7; %Initial concentration of sodium in the anolyte [mol/m3]
% par.CNaC0=2757.8; %Initial concentration of sodium in the catholyte [mol/m3]
% % Experiment 10 wt% 6kA/m2 (average of experiment 7 and 8)
% par.CNaA0=2745.8; %Initial concentration of sodium in the anolyte [mol/m3]
% par.CH2OA0=54762; %Initial concentration of water in the anolyte [mol/m3]
% par.CNaCo=2747.8; %Initial concentration of sodium in the catholyte [mol/m3]
% par.CH2OC0=54761; %Initial concentration of water in the catholyte [mol/m3]
% % Experiment 15 wt% 10kA/m2 (average of experiment 10 and 11)
% par.CNaA0=4297.1; %Initial concentration of sodium in the anolyte [mol/m3]
% par.CH2OA0=54282; %Initial concentration of water in the anolyte [mol/m3]
% par.CNaCo=4299.2; %Initial concentration of sodium in the catholyte [mol/m3]
% par.CH2OC0=54281; %Initial concentration of water in the catholyte [mol/m3]
% % Experiment 10 wt% 2kA/m2 (experiment 6)
% par.CNaA0=2740.8; %Initial concentration of sodium in the anolyte [mol/m3]
% par.CH2OA0=54853; %Initial concentration of water in the anolyte [mol/m3]
% par.CNaCo=2768.1; %Initial concentration of sodium in the catholyte [mol/m3]
% par.CH2OC0=54848; %Initial concentration of water in the catholyte [mol/m3]
% % Experiment 10 wt% 20kA/m2 (experiment 9)
% par.CNaA0=2697.6; %Initial concentration of sodium in the anolyte [mol/m3]
% par.CH2OA0=54163; %Initial concentration of water in the anolyte [mol/m3]
% par.CNaCo=2719.7; %Initial concentration of sodium in the catholyte [mol/m3]
% par.CH2OC0=54158; %Initial concentration of water in the catholyte [mol/m3]
% % Experiment 32 wt% 10kA/m2 (experiment 12)
% par.CNaA0=10655; %Initial concentration of sodium in the anolyte [mol/m3]
% par.CH2OA0=50288; %Initial concentration of water in the anolyte [mol/m3]
% par.CNaCo=10676; %Initial concentration of sodium in the catholyte [mol/m3]
% par.CH2OC0=50270; %Initial concentration of water in the catholyte [mol/m3]
% % Initial concentrations
par.lambda=-0.0032*(par.CNaA0/1E3)^3+0.104*(par.CNaA0/1E3)^2-1.7038*(par.CNaA0/1E3)+22.629; % Water content as a function of NaOH concentration [mol H2O/mol Na2SO4] Based on data from Chlor-Alkali Handbook fig 4.8.3 (translated into an empirical formula)
par.Cinit=zeros(size(par.z,2),3);
par.Cinit(:,1)=par.CSO3+par.Cinit(:,2); %Concentration of Na+ ions [mol/m3void]
par.Cinit(:,2)=0; %Concentration of OH- ions [mol/m3void] (Assumption which might not be valid at high concentration, but reliable unsteady state profiles are not of interest.)
par.Cinit(:,3)=par.CSO3*par.lambda; %Water concentration [mol/m3void]

NPic.m
function C0 = NPic(z,par)

ii=1;
while par.z(1,ii)<z,
    ii=ii+1;
end
C0 = par.Cinit(ii,:);

return

NPbc.m
function [pl,ql,pr,qr] = NPbc(zl,Cl,zr,Cr,t,par)
% % Experiment 10 wt% 10kA/m2 (average of experiment 1 and 3)
% par.CNaA=-1.8732*t/60+par.CNaA0; %Concentration of sodium in the anolyte [mol/m3]
% par.CH2OA=0.3548*t/60+par.CH2OA0; %Concentration of water in the anolyte [mol/m3]
% par.CNaC=1.6949*t/60+par.CNaC0; %Concentration of sodium in the catholyte [mol/m3]
% par.CH2OC=-0.4321*t/60+par.CH2OC0; %Concentration of water in the catholyte [mol/m3]
%
% % Experiment 10 wt% 6kA/m2(average of experiment 7 and 8)
% par.CNaA=-1.2225*t/60+par.CNaA0; %Concentration of sodium in the anolyte [mol/m3]
% par.CH2OA=0.2466*t/60+par.CH2OA0; %Concentration of water in the anolyte [mol/m3]
% par.CNaC=1.2128*t/60+par.CNaC0; %Concentration of sodium in the catholyte [mol/m3]
% par.CH2OC=-0.2988*t/60+par.CH2OC0; %Concentration of water in the catholyte [mol/m3]
%
% % Experiment 15 wt% 10kA/m2(average of experiment 10 and 11)
% par.CNaA=-1.5931*t/60+par.CNaA0; %Concentration of sodium in the anolyte [mol/m3]
% par.CH2OA=0.5554*t/60+par.CH2OA0; %Concentration of water in the anolyte [mol/m3]
% par.CNaC=1.5814*t/60+par.CNaC0; %Concentration of sodium in the catholyte [mol/m3]
% par.CH2OC=-0.6341*t/60+par.CH2OC0; %Concentration of water in the catholyte [mol/m3]
% % Experiment 10 wt% 2kA/m2(experiment 6)
% par.CNaA=-0.4345*t/60+par.CNaA0; %Concentration of sodium in the anolyte [mol/m3]
% par.CH2OA=0.0841*t/60+par.CH2OA0; %Concentration of water in the anolyte [mol/m3]
% par.CNaC=0.5145*t/60+par.CNaC0; %Concentration of sodium in the catholyte [mol/m3]
% par.CH2OC=-0.1326*t/60+par.CH2OC0; %Concentration of water in the catholyte [mol/m3]

% % Experiment 10 wt% 20kA/m2(experiment 9)
% par.CNaA=-2.6054*t/60+par.CNaA0; %Concentration of sodium in the anolyte [mol/m3]
% par.CH2OA=0.5328*t/60+par.CH2OA0; %Concentration of water in the anolyte [mol/m3]
% par.CNaC=2.9288*t/60+par.CNaC0; %Concentration of sodium in the catholyte [mol/m3]
% par.CH2OC=-0.7498*t/60+par.CH2OC0; %Concentration of water in the catholyte [mol/m3]

% Experiment 32 wt% 10kA/m2(experiment 12)
par.CNaA=-1.5221*t/60+par.CNaA0; %Concentration of sodium in the anolyte [mol/m3]
par.CH2OA=1.2485*t/60+par.CH2OA0; %Concentration of water in the anolyte [mol/m3]
par.CNaC=1.4359*t/60+par.CNaC0; %Concentration of sodium in the catholyte [mol/m3]
par.CH2OC=-1.2208*t/60+par.CH2OC0; %Concentration of water in the catholyte [mol/m3]

%Based on fluxNa(sol-int)=fluxNa(mem) with Donnan in which CNaA=COHA is assumed
CNaAintm=Cl(1);                         %Na+ left side membrane interface concentration.
CNaAint=sqrt(Cl(1)^2-Cl(1)*par.CSO3);   %Na+ anolyte interface concentration. At t=0 Cl(1)=par.CSO3 and the
% interface concentration at the interface is 0
NNal=par.kAMNa*(par.CNaA-CNaAint);
COHl=-(par.zi(1)*Cl(1)+par.zSO3*par.CSO3)/par.zi(2);
NH2Ol=par.kAMH2O*(par.CH2OA-Cl(3));   %Assuming that the water concentration at the solution interface is
% equal to the membrane interface

CNaCintm=Cr(1);                         %Na+ right side membrane interface concentration.
CNaCint=sqrt(Cr(1)^2-Cr(1)*par.CSO3);   %Na+ catholyte interface concentration. At t=0 Cr(1)=par.CSO3 and the
% interface concentration at the interface is 0
NNar=par.kMCNa*(CNaCint-par.CNaC);
COHr=-(par.zi(1)*Cr(1)+par.zSO3*par.CSO3)/par.zi(2);
NH2Or=par.kCMH2O*(Cr(3)-par.CH2OC);   %Assuming that the water concentration at the solution interface is
% equal to the membrane interface

pl=[NNal;Cl(2)-COHl;NH2Ol];
ql=[par.epsvoid; 0; par.epsvoid];
pr=[NNar;Cr(2)-COHr;NH2Or];
function \[\text{c, f, s} = \text{NPpde}(z, t, C, \text{DCDz}, \text{par})\]

% Pressure gradient, potential gradient and Schlogl equation.
\[dPdz=0;\]
\[dphidz=(\text{par.J*par.deltam/(par.F)}+\text{par.zi(1)*par.D*DCDz(1)+par.zi(2)*par.D*DCDz(2)})+(\text{par.zi(1)*C(1)+par.zi(2)}\times\text{par.zi(2)})*\text{par.dh}\times dPdz) / (\text{par.F*((par.zi(1)*C(1)+par.zi(2)*C(2))}\times\text{par.dh}\times\text{par.zSO3}\times\text{par.CSO3}} - \text{par.zi(1)^2*C(1)*par.D+par.zi(2)^2*C(2)*par.D)/(par.R*par.T)});\]
\[v=\text{par.dh}\times\text{par.deltam*par.zSO3}\times\text{par.CSO3*par.F*dpdz-dPdz}); \quad \% \text{Convective mass flux [m3/(m2*s)}\], \quad \text{(Schlogl equation)}\]
\[c(1) = \text{par.deltam};\]
\[f(1) = \text{(par.D*DCDz(1)+C(1)*par.D*par.zi(1)*par.F)/(par.R*par.T)}*dphidz-v*C(1)*\text{par.deltam}) / \text{par.deltam};\]
\[f(1)=-N(1) [\text{mol/m^2/s}];\]
\[s(1) = 0;\]
\[c(2) = 0;\]
\[f(2) = 0;\]
\[s(2) = C(2)+\text{(par.zi(1)*C(1)+par.zSO3*par.CSO3)}/\text{par.zi(2)};\]
\[c(3) = \text{par.deltam};\]
\[f(3) = \text{(par.D*DCDz(3)-v*C(3)*par.deltam)}/\text{par.deltam}; \quad \% f(3)=-N(3) [\text{mol/m^2/s}] \text{ Water flux NP}\]
\[f(3) = \text{(par.D*DCDz(3)}-\text{v*C(3)*par.deltam+par.hf*(par.D*DCDz(1)+C(1)*par.D*par.zi(1)*par.F)/(par.R*par.T)*dpdz)}) / \text{par.deltam};\]
\[f(3)=-N(3) [\text{mol/m^2/s}] \text{ Water flux extended NP}\]
\[s(3) = 0;\]
\[\text{return}\]
Appendix N: Sensitivity analysis, preliminary results

A few simulations were performed in which the diffusion coefficient, the void fraction, the channel diameter, and the solution to membrane mass transfer coefficients were varied within a set range. Their corresponding model output was compared to a defined base case comprising initial guesses for these parameters together with the input corresponding with the operating conditions of the reproducibility experiments mentioned in Table K1. The initial values and reasonable ranges are presented in Table N1.

The evaluated model output parameters are: the Na\(^+\) transport number, the relative water transport number and the membrane potential drop. The result of the base case is presented in Table N2 together with the experimental values. Since the model was not able to run with the standard tolerance values, the absolute tolerance value used for the simulation is mentioned as well. The base case Na\(^+\) transport number is higher than its experimental value, while the relative water transport number and the membrane potential drop are lower.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial guess</th>
<th>Investigated range</th>
</tr>
</thead>
<tbody>
<tr>
<td>D ([m^2 \cdot s^{-1}])</td>
<td>(1 \cdot 10^{-9})</td>
<td>(1 \cdot 10^{-10} - 5 \cdot 10^{-9})</td>
</tr>
<tr>
<td>(\varepsilon_{\text{void}} \left[ m_{\text{void}}^3 \cdot m_M^{-3}\right])</td>
<td>0.2</td>
<td>0.18 - 0.22</td>
</tr>
<tr>
<td>(k_{\text{AM}} &amp; k_{\text{CM}} \left[ m \cdot s^{-1}\right])</td>
<td>(1 \cdot 10^{-4})</td>
<td>(5 \cdot 10^{-5} - 5 \cdot 10^{-4})</td>
</tr>
<tr>
<td>(d_c \left[ m\right])</td>
<td>(2.4 \cdot 10^{-9})</td>
<td>(2.0 \cdot 10^{-9} - 2.8 \cdot 10^{-9})</td>
</tr>
</tbody>
</table>

Table N2: Experimental, base case model and optimized model results.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Input value</th>
<th>(t_{\text{Na}})</th>
<th>(T_{\text{H2O}})</th>
<th>(\phi)</th>
<th>AbsTol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>Anolyte based</td>
<td>-</td>
<td>0.757</td>
<td>6.09</td>
<td>-0.567</td>
</tr>
<tr>
<td></td>
<td>Catholyte based</td>
<td>-</td>
<td>0.724</td>
<td>5.27</td>
<td>-0.567</td>
</tr>
<tr>
<td>Base case</td>
<td>D ([m^2 \cdot s^{-1}])</td>
<td>(1 \cdot 10^{-9})</td>
<td>0.950</td>
<td>2.667</td>
<td>-0.045</td>
</tr>
<tr>
<td></td>
<td>(\varepsilon_{\text{void}} \left[ m_{\text{void}}^3 \cdot m_M^{-3}\right])</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(k_{\text{AM}} &amp; k_{\text{CM}} \left[ m \cdot s^{-1}\right])</td>
<td>(1 \cdot 10^{-4})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(d_c \left[ m\right])</td>
<td>(2.4 \cdot 10^{-9})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Although the model stability is an issue, a preliminary parameter sensitivity analysis was performed on the estimated parameters. Only one parameter was varied per simulation, so combined effects, which might occur when varying multiple parameters simultaneously, are not investigated. Furthermore, the diffusion coefficient was assumed to be equal for all non-stationary species. The analysis results are presented in Table N3 by showing the absolute and relative difference between the steady state simulation results corresponding with the input value mentioned in this table and the simulation with the initial guesses as the model input. Moreover, the absolute tolerance value, corresponding to the case where the model was the most stable, is presented in Table N3 as well.

The model results reveal that the diffusion coefficient has the largest effect on all of the investigated output parameters (\(t_{\text{Na}}, T_{\text{H2O}}\), and \(\phi\)). The channel diameter also a significant effect on the model output, while the influence of the void fraction and the mass transfer coefficients is relatively low.
Table N3: Preliminary results of the parameter sensitivity analysis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Input value</th>
<th>$\Delta t_{Na}$</th>
<th>$\Delta t_{Na}$ [%]</th>
<th>$\Delta T_{H2O}$</th>
<th>$\Delta T_{H2O}$ [%]</th>
<th>$\Delta \phi$ [V]</th>
<th>$\Delta \phi$ [%]</th>
<th>AbsTol []</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D \ [m^2 \cdot s^{-1}]$</td>
<td>$1 \cdot 10^{-10}$</td>
<td>0.087</td>
<td>9.19</td>
<td>2.871</td>
<td>107.67</td>
<td>-0.059</td>
<td>130.71</td>
<td>$1 \cdot 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$5 \cdot 10^{-10}$</td>
<td>0.050</td>
<td>5.23</td>
<td>1.086</td>
<td>40.73</td>
<td>-0.021</td>
<td>46.7</td>
<td>$1 \cdot 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$4 \cdot 10^{-9}$</td>
<td>-0.149</td>
<td>-15.72</td>
<td>-1.57</td>
<td>-58.90</td>
<td>0.029</td>
<td>-65.11</td>
<td>$1 \cdot 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$5 \cdot 10^{-9}$</td>
<td>-0.186</td>
<td>-19.58</td>
<td>-1.70</td>
<td>-63.73</td>
<td>0.032</td>
<td>-71.31</td>
<td>$1 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$\varepsilon_{void} \ [m_{void}^3 \cdot m_{M}^{-3}]$</td>
<td>0.18</td>
<td>0.0056</td>
<td>0.59</td>
<td>-0.234</td>
<td>-8.79</td>
<td>0.0037</td>
<td>-8.18</td>
<td>$1 \cdot 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>-0.0055</td>
<td>-0.58</td>
<td>0.223</td>
<td>8.34</td>
<td>-0.0035</td>
<td>7.73</td>
<td>$1 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$k_{AM} \ &amp; k_{CM} \ [m \cdot s^{-1}]$</td>
<td>$5 \cdot 10^{-5}$</td>
<td>-0.0083</td>
<td>-0.87</td>
<td>0.0006</td>
<td>0.02</td>
<td>0.00016</td>
<td>-0.35</td>
<td>$1 \cdot 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$5 \cdot 10^{-4}$</td>
<td>0.0067</td>
<td>0.71</td>
<td>0.0179</td>
<td>0.67</td>
<td>-0.00011</td>
<td>0.24</td>
<td>$1 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$d_c \ [m]$</td>
<td>$2 \cdot 10^{-9}$</td>
<td>0.0170</td>
<td>-1.79</td>
<td>0.5435</td>
<td>-20.38</td>
<td>-0.0057</td>
<td>12.55</td>
<td>$1 \cdot 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$2.8 \cdot 10^{-9}$</td>
<td>0.0148</td>
<td>1.56</td>
<td>0.4863</td>
<td>18.24</td>
<td>0.0053</td>
<td>-11.70</td>
<td>$1 \cdot 10^{-3}$</td>
</tr>
</tbody>
</table>
Appendix O: Absolute tolerance values used in the sensitivity analysis simulations

The absolute tolerance values are presented in Table O1, Table O2, and Table O3 for the sensitivity analysis simulations of the diffusion coefficients, the channel diameter, and the model extension of the H₂O flux. These values represent the lowest tolerance value at which the model was still providing stable results.

### Table O1: Absolute tolerance values of the diffusion coefficient sensitivity analysis simulations.

<table>
<thead>
<tr>
<th>( D_{Na} ) [m²s⁻¹]</th>
<th>( D_{OH} ) [m²s⁻¹]</th>
<th>AbsTol [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1·10⁻¹⁰</td>
<td>1·10⁻¹⁰</td>
<td>1·10⁻²</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>2·10⁻¹⁰</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>3·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>4·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>5·10⁻¹⁰</td>
<td>1·10⁻⁵</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>6·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>7·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>8·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>9·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>1·10⁻⁹</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>2·10⁻⁹</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>3·10⁻⁹</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>1·10⁻¹⁰</td>
<td>4·10⁻⁹</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>5·10⁻¹⁰</td>
<td>5·10⁻¹⁰</td>
<td>1·10⁻¹</td>
</tr>
<tr>
<td>5·10⁻¹⁰</td>
<td>6·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>5·10⁻¹⁰</td>
<td>7·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>5·10⁻¹⁰</td>
<td>8·10⁻¹⁰</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>5·10⁻¹⁰</td>
<td>9·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>5·10⁻¹⁰</td>
<td>1·10⁻⁹</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>5·10⁻¹⁰</td>
<td>2·10⁻⁹</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>5·10⁻¹⁰</td>
<td>3·10⁻⁹</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>5·10⁻¹⁰</td>
<td>4·10⁻⁹</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>1·10⁻⁹</td>
<td>8·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>1·10⁻⁹</td>
<td>9·10⁻¹⁰</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>1·10⁻⁹</td>
<td>1·10⁻⁹</td>
<td>1·10⁻¹</td>
</tr>
<tr>
<td>1·10⁻⁹</td>
<td>2·10⁻⁹</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>1·10⁻⁹</td>
<td>3·10⁻⁹</td>
<td>1·10⁻²</td>
</tr>
</tbody>
</table>

### Table O2: Absolute tolerance values of the channel diameter sensitivity analysis simulations.

<table>
<thead>
<tr>
<th>( d_c ) [m]</th>
<th>AbsTol [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8·10⁻⁹</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>2.1·10⁻⁹</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>2.4·10⁻⁹</td>
<td>1·10⁻⁵</td>
</tr>
<tr>
<td>2.7·10⁻⁹</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>3.1·10⁻⁹</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>3.5·10⁻⁹</td>
<td>1·10⁻⁴</td>
</tr>
</tbody>
</table>
Table O3: Absolute tolerance values of the hydration factor sensitivity analysis simulations.

<table>
<thead>
<tr>
<th>hf [-]</th>
<th>AbsTol [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>2</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>3</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>4</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>6</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>8</td>
<td>1·10⁻³</td>
</tr>
<tr>
<td>10</td>
<td>1·10⁻⁴</td>
</tr>
<tr>
<td>12</td>
<td>1·10⁻³</td>
</tr>
</tbody>
</table>
Appendix P: Experimental temperature results

The anolyte flow cell, catholyte flow cell and catholyte compartment temperature profiles of the experiments are depicted in Figure P1.

Figure P1: The temperature profiles for experiments 1 - 12. Experiments 1-5 were performed at 10 wt%, 10 kA·m\(^{-2}\) 360 minutes and 1 O-ring was used per membrane side. Experiment 6 was performed at 10 wt%, 2 kA·m\(^{-2}\) 1200 minutes and 2 O-rings were used per membrane side. Experiments 7 and 8 were performed at 10 wt%, 6 kA·m\(^{-2}\) 360 minutes and 2 O-rings were used per membrane side. Experiment 9 was performed at 10 wt%, 20 kA·m\(^{-2}\) 180 minutes and 2 O-rings were used per membrane side. Experiments 10 and 11 were performed at 15 wt%, 10 kA·m\(^{-2}\) 360 minutes and 2 O-rings were used per membrane side. Experiment 12 was performed at 32 wt%, 10 kA·m\(^{-2}\) 360 minutes and 2 O-rings were used per membrane side.
Figure P2 (continued): The temperature profiles for experiments 1 - 12. Experiments 1-5 were performed at 10 wt%, 10 kA·m⁻² 360 minutes and 1 O-ring was used per membrane side. Experiment 6 was performed at 10 wt%, 2 kA·m⁻² 1200 minutes and 2 O-rings were used per membrane side. Experiments 7 and 8 were performed at 10 wt%, 6 kA·m⁻² 360 minutes and 2 O-rings were used per membrane side. Experiment 9 was performed at 10 wt%, 20 kA·m⁻² 180 minutes and 2 O-rings were used per membrane side. Experiments 10 and 11 were performed at 15 wt%, 10 kA·m⁻² 360 minutes and 2 O-rings were used per membrane side. Experiment 12 was performed at 32 wt%, 10 kA·m⁻² 360 minutes and 2 O-rings were used per membrane side.