FROM SMALL TO BIG ION TRANSPORT AT INTERFACES

Anne M. Benneker

DISSERTATION

From small to big:

Ion transport at interfaces

Van klein naar groot:

Iontransport nabij grensvlakken

by Anne M. Benneker

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PROEFSCHRIFT

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en

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(...)

I am sure that I have not lived in vain.

*We have done our task,
and we can leave the world with the conviction
that we leave it better than we found it.*

- Aletta Jacobs (1854 - 1929)

Physician, feminist, suffragette

Preface

When the well is dry, we know the worth of water.

- Benjamin Franklin (1706 - 1790)
Scientist, Philosopher and Statesman

All people are equal. All people are equal in their need for clean water to sustain life. However, access to clean water is one of the largest inequalities threatening the world population nowadays [1–3]. Access to clean drinking water is scarce in large parts of the world [4, 5] and the sources are often not reliable [6]. In the past few decades clean water availability for domestic use has increased immensely, but there are still large regions of the world where more than 20% of the population has no access to clean, safe drinking water [1, 6]. On the other hand, overall water stress has increased due to an increased world population [2, 7]. In total, in 2015, one in ten people only have access to water from unprotected sources [6]. Primarily, this affects women and girls who have to travel great distances for the retrieval of drinking water for their families [1], posing a threat to their education and development [8]. In most of western Europe, a tap can be opened on demand to continuously obtain clean drinking water, although even this is not guaranteed for the future since the demand for water is currently growing faster than the increase in production capacity [4, 9].

Clean water is not only required for domestic use but is also essential in agriculture and for the production of energy and our consumer products [8, 10, 11]. In almost all industrial processes, water is used at some stage of the production for a chemical reaction, to cool, to dilute or to wash process streams [12]. Through international trade, water inequalities in the world can be reduced. However, the current trade levels are not sufficient to provide for water equality around the world [13, 14].

Water scarcity is one of the drivers of large scale migration [15–17], imposing dilemmas worldwide. Throughout history, many border skirmishes have been fought over water and water scarcity still threatens the stability of many regions, indicating that water scarcity is a possible catalyst for conflicts in the future [17–20]. As a result of this, political, economic and war refugees are migrating around the world in search of a better future for themselves and their children. At the same time, countries are restricting border access in response to this increasing migrant population [21, 22] which only enhances the degree of misery from this situation. No direct solutions are provided for the problems at the origin of these migration patterns. Consumption of food and energy in so-called ‘developed countries’ is increasing [23], and consumption in fast growing economies, such as China, India and countries alike, is increasing at an even faster pace [23–25]. This enhanced consumption places a larger stress on the world’s resources [8, 26, 27] and will only lead to more migration if no sustainable solution for attending peoples needs is provided in the coming decades.

This can lead us to the conclusion that the production of clean water is one of the most important challenges on earth, as is also identified by the UN and the H2020 program of the European Union [28, 29]. A challenge that we are able to tackle, if we all agree on the urgency of this problem. Political choices

have to be made in ensuring clean drinking water for the future generations, even though they might not always be the popular decisions in the short term. We all need to dare to speak out for the interest of the world and all its people, not only for those of us lucky enough to be born in countries of relative wealth. More research should be conducted to enhance efficiency of water cleaning processes, the re-use of water and the optimum usage of water in agricultural and industrial applications. Efficient water purification processes should be made available to all people, worldwide. In my view this should be the top priority of policy makers everywhere, since providing clean water to all people is one of the most important steps in resolving a lot of the world's current and future challenges. To paraphrase the 18th century statesman Benjamin Franklin; as we know the value of water, we should prevent the well from drying.

To produce drinking water, contaminants such as bacteria, viruses and dissolved salts must be removed. The most efficient water production processes are based on membrane separations of these contaminants from water [30, 31]. Reverse osmosis (RO) utilizes a pressure gradient to push water through a reverse osmosis membrane (with sub-nanometer pores), while the solutes are retained by the membrane. Another example is electrodialysis (ED), which uses electric fields over stacks of cation and anion exchange membranes to purify water. ED is a suitable technique for smaller scale desalination of brackish feed streams, for instance in rural areas, but is not as energy efficient when compared to RO processes for large scale, high concentration desalination plants (yet) [32].

In ED, selective ion transport towards and through the membrane is important in achieving an efficient process. Ion transport in the vicinity of a membrane is a result of combined diffusion, electromigration and advection. In industrial ED processes, the operational range is limited by the limited diffusion of ions through a stagnant boundary layer at the membrane. If this transport can be enhanced, for instance by convection in the direction of the membrane, ED efficiency can increase. In this research, convective transport at a charge selective interface as a result of local net charges inside the solution has been investigated in a variety of systems. Experiments and theoretical investigations on various length scales for the effect of various parameters such as temperature and geometry were carried out.

The understanding of ion transport adjacent to charge selective interfaces is important for applications other than electrodialysis as well. Another large challenge for society at the present is the production of power/storage of energy, preferably with an as low as possible impact on the environment and climate. Fuel cells are widely applied for the storage and transport of energy and rely on ion transport through a membrane for their operation [33–35]. Apart from this, ion selective interfaces are also used in solid-state applications, such as sensors, actuators [36] or ion selective electrodes [37]. The knowledge gained in this work

can be of potential relevance for these fields as well, as the fundamentals of ion transport investigated here are also applicable to these systems.

The work presented in this thesis is only a small step in understanding the complex transport phenomena at charge selective interfaces and certainly is at most a drop in the bucket of solving the worldwide water scarcity issue. The fundamental insights gained in this work are part of my attempt to contribute to a world in which all people have equal chances, through potentially alleviating even the smallest amount of water stress by improving efficiency of electrodialysis processes and other processes relying on ion transport phenomena. This thesis represents my tiny contribution to try to make the world a better place, and that is all any of us can do. The insights on the concepts and possible further investigations have definitely made working on this project worthwhile for me.

References

- [1] World Health Organization, *Safely managed drinking water - thematic report on drinking water 2017*, Geneva, Switzerland (2017).
- [2] M. Kummu, P. J. Ward, H. de Moel, and O. Varis, *Is physical water scarcity a new phenomenon? Global assessment of water shortage over the last two millennia*, Environ. Res. Lett. **5**, 034006 (2010).
- [3] A. J. McMichael, S. Friel, A. Nyong, and C. Corvalan, *Global environmental change and health: impacts, inequalities and the health sector*, BMJ **336**, 191 (2008).
- [4] F. R. Rijsberman, *Water scarcity: Fact or fiction?*, Agricultural Water Management **80**, 5 (2006), special Issue on Water Scarcity: Challenges and Opportunities for Crop Science.
- [5] S. L. Postel, *Entering an era of water scarcity: The challenges ahead*, Ecological Applications **10**, 941 (2000).
- [6] World Health Organization and United Nations Children's Fund (UNICEF), *Progress on drinking water, sanitation and hygiene: 2017 update and SDG baselines*, Geneva, Switzerland (2017).
- [7] C. J. Vörösmarty *et al.*, *Global threats to human water security and river biodiversity*, Nature **467**, 555 (2010).
- [8] M. W. Rosegrant and S. A. Cline, *Global food security: Challenges and policies*, Science **302**, 1917 (2003).
- [9] European Commission, *Addressing the challenge of water scarcity and droughts in the European Union*, Brussels, Belgium (2007).
- [10] A. Y. Hoekstra and M. M. Mekonnen, *The water footprint of humanity*, Proc. Natl. Acad. Sci. **109**, 3232 (2012).

- [11] G. Olsson, *Water, energy and food interactions - Challenges and opportunities*, Front. Environ. Sci. Eng. **7**, 787 (2013).
- [12] M. A. Maupin, J. F. Kenny, S. S. Hutson, J. K. Lovelace, N. L. Barber, and K. S. Linsey, *Estimated use of water in the United States in 2010*, U.S. Geological Survey Circular 1405 (2010).
- [13] J. A. Carr, D. A. Seekell, and P. D’Odorico, *Inequality or injustice in water use for food?*, Environ. Res. Lett. **10**, 024013 (2015).
- [14] D. A. Seekell, P. D’Odorico, and M. L. Pace, *Virtual water transfers unlikely to redress inequality in global water use*, Environ. Res. Lett. **6**, 024017 (2011).
- [15] R. Black, S. R. G. Bennett, S. M. Thomas, and J. R. Beddington, *Climate change: Migration as adaptation*, Nature **478**, 447 (2011).
- [16] The Government Office for Science, *Foresight: Migration and Global Environmental Change*, London, England (2011).
- [17] R. Reuveny, *Climate change-induced migration and violent conflict*, Polit. Geogr. **26**, 656 (2007).
- [18] P. H. Gleick, *Water and Conflict: Fresh water resources and international security*, Int. Secur. **18**, 79 (1993).
- [19] T. F. Homer-Dixon, *Environmental scarcities and violent conflict: Evidence from cases*, Int. Secur. **19**, 5 (1994).
- [20] N. P. Gleditsch, K. Furlong, H. Hegre, B. Lacina, and T. Owen, *Conflicts over shared rivers: Resource scarcity or fuzzy boundaries?*, Polit. Geogr. **25**, 361 (2006).
- [21] DRC Middle East and North Africa regional office, *Closing borders, shifting routes: Summary of regional migration trends middle east*, Danish Refugee Council (2016).
- [22] A. Mohdin, *These are the routes being closed off to refugees fleeing into Europe*, Quartz (2016).
- [23] U.S. Energy Information Administration, *International Energy Outlook 2017*, (2017).
- [24] N. Alexandratos and J. Bruinsma, *World agriculture towards 2030/2050: the 2012 revision*, ESA Working paper No. 12-03. Rome (2012).
- [25] J. Kearney, *Food consumption trends and drivers*, Philos. Trans. R. Soc. B Biol. Sci. **365**, 2793 (2010).
- [26] M. Elferink and F. Schierhorn, *Global demand for food is rising. Can we meet it?*, Harv. Bus. Rev. (April 2016).
- [27] C. J. Vörösmarty, P. Green, J. Salisbury, and R. B. Lammers, *Global water resources: Vulnerability from climate change and population growth*, Science **289**, 284 (2000).
- [28] Water Environment European Commission, *Water is for life: How the water framework directive helps safeguard Europe’s resources*, Luxembourg (2010).
- [29] United Nations, *Transforming our world: the 2030 agenda for sustainable*

- development*, Resolution adopted by General Assembly on 25 september 2015 (2015).
- [30] M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas, and A. M. Mayes, *Science and technology for water purification in the coming decades*, Nature **452**, 301 (2008).
 - [31] F. Macedonio, E. Drioli, A. A. Gusev, A. Bardow, R. Semiat, and M. Kurihara, *Efficient technologies for worldwide clean water supply*, Chem. Eng. Process. Process Intensif. **51**, 2 (2012).
 - [32] H. Strathmann, *Electrodialysis, a mature technology with a multitude of new applications*, Desalination **264**, 268 (2010).
 - [33] P. Grimes, *Historical pathways for fuel cells. The new electric century*, Proc. Annu. Batter. Conf. Appl. Adv. 41 (2000).
 - [34] B. Smitha, S. Sridhar, and A. A. Khan, *Solid polymer electrolyte membranes for fuel cell applications - A review*, J. Memb. Sci. **259**, 10 (2005).
 - [35] M. Winter and R. J. Brodd, *What are batteries, fuel cells, and supercapacitors?*, Chem. Rev. **104**, 4245 (2004).
 - [36] M. Shahinpoor, Y. Bar-Cohen, J. O. Simpson, and J. Smith, *Ionic polymer-metal composites (IPMCs) as biomimetic sensors, actuators and artificial muscles - a review*, Smart Mater. Struct. **7**, R15 (1998).
 - [37] E. Bakker, P. Bühlmann, and E. Pretsch, *Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics*, Chem. Rev. **97**, 3083 (1997).

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Summary

This thesis combines numerical, theoretical and experimental investigations of charge transport through and near ion selective interfaces, for electrodialysis applications. Electrodialysis (ED) is typically used industrially for the de-ionization of process streams and the desalination of brackish water. In ED, alternating cation and anion selective interfaces are placed in a DC electric field, which causes ions to migrate towards their counter electrode. As a result of the transport through the charge selective interface, ion depleted and enriched streams are formed within the ED stack. A depletion boundary layer establishes at the membrane interface as a result of the difference in the magnitude of transport of ions in the membrane and the solution. At low applied potentials (in the “Ohmic regime”), the number of ions transported increases with increasing applied potential according to Ohm’s law. In the so-called “limiting current regime”, diffusive ion transport through the depletion boundary layer is limiting the total charge transport in the system. Increasing the applied potential difference results in the transition towards the “overlimiting current regime”, in which the boundary layer breaks down as a result of the electric field acting on an extended space charge that develops at the membrane interface.

Different aspects of charge transport in these three different current regimes are discussed. In particular, the influence of temperature and temperature differences in ED systems and the influence of interface geometry are the subject of investigation, primarily by a combination of experimental and numerical investigations of ED systems. Microscopic observations are combined with simple numerical simulations in order to understand the macroscopic transport characteristics in these systems. A general introduction on charge transport, ion selective interfaces and the theory behind the influence of geometry and temperature on system behaviour is given in **Chapter 1**.

The influence of temperature differences on charge transport through electrically gated cation selective nanochannels is investigated numerically (**Chapter 2**) using a non-isothermal formulation of the Poisson-Nernst-Planck and Navier-Stokes equations. Nanochannels are charge selective as a result of their characteristic length scale, which is in the order of the size of the electric double layer. In this work, both uniform and tapered nanochannels were simulated. Joule heating and viscous dissipation were found to be negligible at relevant field strengths

and ion concentrations at which ion selectivity was maintained. In isothermal systems, the selectivity of the nanochannel is reduced when the temperature is increased, as a result of increased co-ion transport through the nanochannel. This increased co-ion transport is a result of the increased ion diffusivity and decreased viscosity of the solution. For the same reasons, the total current is enhanced if the temperature increased. More interestingly, it is found that the selectivity of the cation selective nanochannels is enhanced when a temperature gradient is applied in the same direction as the electric field. In this situation, the diffusivity of the ions on the hot “inlet” side of the nanochannel is enhanced when compared to the diffusivity of the ions on the colder “outlet” side of the nanochannel. Apart from that, the viscosity of the solution on the inlet side is lower than the viscosity on the outlet side as a result of the temperature differences. These combined effects on diffusivity and viscosity result in enhanced selective transport through the nanochannels. If the direction of the temperature gradient is reversed, the opposite interactions yield a lower overall selectivity of the nanochannel when compared to a low temperature isothermal case. Tapered nanochannels are of interest as diodes since they show rectification of current as a function of the direction of the applied electric field. For tapered nanochannels, the selectivity is mostly determined by the minimal size of the nanochannel. Since the average height of the nanochannels is kept constant, the tapered nanochannels show a slightly higher selectivity, albeit at lower total currents. The temperature gradient enhances the rectification of tapered nanochannels, which is of possible use in sensing applications.

The results of these numerical investigations motivated the experimental investigations of the effect of temperature gradients in lab-scale electrodialysis stacks. First (**Chapter 3**), the effect of temperature and temperature gradients is investigated in the industrially relevant Ohmic regime in which the current is linearly increasing with increasing potential. Four different temperature configurations are investigated in both ED and reverse electrodialysis (RED) operation of a commercially available RED-stack with a cross-flow feed configuration, employing Neosepta® CMX (cation exchange membranes) and Neosepta® AMX (anion exchange membranes). In RED, two feed streams of different salinity are fed to the stack and as a result of the concentration gradient an ionic current is established through the membranes, which can be harvested as electric work. The efficiency of the ED process is enhanced (by $\sim 15\%$ when increasing the feed temperature from $20\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$) with increasing temperature, meaning lower power is required to achieve the same separation degree. It was postulated from the numerical results in nanochannels that imposing a temperature gradient could lead to enhanced ion-selectivity. However, no significant difference in ED efficiency was measured between the two temperature gradient cases. This is attributed to operation in the Ohmic regime, in which the effect of the depletion boundary

layer is relatively small, and the significant heat conduction in the experimental system. The total efficiency for the ED process is increased by $\sim 9\%$ if only one of the feed streams is heated to $40\text{ }^{\circ}\text{C}$. For the operation in RED mode, the same overall conclusion can be drawn. At elevated constant temperature, the obtainable gross power density is increased by $\sim 38\%$ when the feed streams are heated from $20\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$, as a result of increased diffusivity of the ions in solution. The direction of an imposed temperature gradient has no significant effect, while it was expected that heating the more dilute “river” water feed stream would enhance the obtainable power density when compared to heating the concentrated “sea” water. For both cases, the gross power density was increased by $\sim 25\%$. However, the heat required to increase the feed temperature greatly exceeds the gained power, which implies that this is only feasible if waste heat is used. This indicates that the total efficiency of both ED and RED processes can be enhanced by increasing the temperature of the feed streams, which can be established by low grade waste heat.

In the limiting current regime, the effect of temperature and temperature gradients is expected to be enhanced, since in this regime the diffusive transport through the ion depletion boundary layer is determining the total transport in the system. To investigate this, experiments are conducted in the limiting current regime and co-flow configuration (**Chapter 4**) using a different commercial lab-scale ED stack (FUMATECH, Germany BWT GmbH) with their FKS (cation exchange) and FAS (anion exchange) membranes. Two different feed configurations are measured, a monovalent KCl/NaCl feed and a mixture of both KCl/NaCl and MgCl_2 . In the limiting current regime, the direction of the temperature does yield a significant difference in the obtained current at a fixed applied potential. For the monovalent NaCl solution, the case in which the diluted stream is heated yields a higher total current ($\sim 7\%$) than the case in which the concentrate stream is heated, which is in line with the expectations based on our numerical investigations in the nanochannel system. The difference in obtained current is also reflected in an enhanced degree of separation for the case in which the dilute stream is heated, although the differences are minor. For the mixture, the effect of imposing temperature gradients is even more interesting, as the diffusivity of the different ions has a different response to temperature. The competitive transport between Mg^{2+} and the monovalent K^+ and Na^+ ions results in a different influence of temperature on these systems. The transport of divalent ions is enhanced with respect to the transport of monovalent ions if the temperature of the dilute stream is heated, which implies that temperature gradients can be of use in enhancing the selective transport of multivalent to monovalent ions in these systems.

For ED stacks, operation is limited generally to the Ohmic regime in order to maximize efficiency. In order to study the development of boundary layers

and their role in the onset of the overlimiting current, we have developed a new investigation platform based on charge selective hydrogels in a microfluidic device (**Chapter 5**). Visualization of the ion depletion zone and the microfluidic flows yielding additional ion transport towards the interface can be done using microfluidic systems that contain a charge selective interface. Six parallel channels are separated by alternating cation and anion exchange hydrogels, that are patterned *in-situ* using a capillary line pinning technique. The hydrogels have been characterized for performance as charge selective interfaces by measuring the permselectivity, area resistance and charge density. Desalination of low concentration feed streams was obtained using these microfluidic devices. Ion depletion zones are visualized using charged fluorescent dyes that mimic the behaviour of the ions in the system. Combining these visualization and outlet concentration measurements, we have a proof-of-principle demonstration of the functionality of our microfluidic ED stack. This system can then be used as a mimic of an ED stack, in which the development of ion depletion zones and electrokinetic flows can be visualized.

The hydrogel patterning method allows for the fabrication of charge selective interfaces with different geometries (**Chapter 6**). Three different hydrogel geometries were investigated, a homogeneous interface and two different heterogeneous interfaces. It was found that, as a result of the electric field distribution, charge transport through the heterogeneous hydrogels is enhanced when compared to the transport through the homogeneous hydrogels. Already in the Ohmic regime, tangential components of the electric fields arise adjacent to the microchannel walls and hydrogel interface, causing an electro-osmotic fluid motion towards the charge selective interface. This additional transport towards the interface results in larger currents through the interface and a more efficient operation of the device. The development of ion depletion zones in systems without imposed flow is visualized qualitatively using fluorescence intensity microscopy, while it is quantitatively measured using fluorescent lifetime image microscopy (FLIM). The absence of imposed flow allows us to decouple the development of ion depletion zones and electrokinetically induced flows from the cross flow through the channels. The development of ion depletion zones depends on the geometry of the hydrogels, as in the heterogeneous configurations there is pinning of the ion depletion zones at the plane between the hydrogel and the channel wall. In the homogeneous hydrogel, this pinning of the ion depletion zones does not take place and the depletion zones move along the charge selective interface. Our approach allows for a rapid investigation of different membrane topologies on overall ion transport performance.

The influence of geometry on the development of ion depletion zones and electrokinetically induced flows was also investigated in a more conventional microfluidic device containing charge selective nanochannels. The nanochannels

have a characteristic length of 20 nm, while the microfluidic channels are $70 \times 20 \mu\text{m}$. In experiments using a charged fluorescent dye to track the ion concentration and particles for fluid flow tracking, vortex speeds over 1.5 mm/s are found in the vicinity of the nanochannels (**Chapter 7**). Three different nanochannel distributions are investigated, yielding information on the interplay of geometry, the electric field and charge transport. Ion depletion zones are observed at the nanochannels, and are developing as a function of time. Nanochannels further away from the driving electrodes show less ion depletion in their vicinity when compared to the nanochannels close to the electrodes. The confined geometry plays an important role, as large portions of a membrane interface can be unused which would represent a significant process inefficiency. Vortex formation is observed adjacent to the nanochannels in all different geometries, but is also dependent on the location of the nanochannels with respect to the driving electrodes.

In the final chapter of this thesis (**Chapter 8**) a short reflection on the research that is presented is given, including some suggestions for improvements on the numerical and experimental investigations and further research. The implications of this research for electrodialysis systems and analogous applications such as fuel cells are also described. The influence of temperature and more importantly temperature gradients on charge transport can be of use in enhancing the selective transport ions and reducing the required power in ED processes. Using gradients in permittivity or conductivity at the charge selective interface can enhance the convective transport of solute towards the membrane, resulting in increased currents and therefore process efficiency in for example desalination or concentrating waste streams.

Samenvatting

Dit proefschrift combineert numeriek, theoretisch en experimenteel onderzoek naar ladingstransport door en bij ionselectieve grensvlakken, voor toepassingen in elektrodialyse. Elektrodialyse (ED) wordt in de industrie gebruikt voor het de-ioniseren van processtromen en de ontzouting van brak water. Voor ED worden kation en anion uitwisselingsmembranen afwisselend onder een elektrische gelijkspanning geplaatst, waardoor de ionen naar de elektrode met tegengestelde lading worden getransporteerd. Doordat de ionen worden tegengehouden door membranen met een gelijke lading worden er ontzoute en geconcentreerde stromen gevormd in de ED stack. In het “Ohmse regime”, bij relatief laag aangelegde spanningen, wordt het aantal getransporteerde ionen lineair verhoogd als de potentiaal verhoogd wordt. Bij voldoende hoog aangelegde spanning vormt zich een stagnante, ontzoute grenslaag aan het membraanoppervlak door het verschil in transportsnelheid van ionen in de oplossing en het membraan. Diffusief transport door deze ontzoute grenslaag limiteert het ladingstransport door het ED systeem in het zogenoemde “limiterende stroomdichtheid regime”. In dit regime groeit de stroomdichtheid niet meer lineair als functie van de aangelegde spanning. Door de aangelegde spanning nog verder te verhogen wordt het “overlimiterende stroomdichtheid regime” bereikt. In dit regime wordt de ontzoute grenslaag verstoord doordat het elektrisch veld werkt op een vergrote niet ladingsneutrale zone die zich ontwikkelt aan het membraanoppervlak.

Verschillende aspecten van ladingstransport in deze drie verschillende regimes worden behandeld in dit proefschrift. In het bijzonder worden de invloed van temperatuur, temperatuurverschillen en de invloed van oppervlaktegeometrie onderzocht, door een combinatie van experimenteel en numeriek onderzoek aan ED systemen. Microscopische observaties worden gecombineerd met simpele numerieke simulaties om het macroscopische ladingstransport in deze systemen te begrijpen. Een algemene introductie over ladingstransport, ladingsselectieve grensvlakken en de theorie achter de invloed van oppervlaktegeometrie en temperatuur op het systeemgedrag is beschreven in **Hoofdstuk 1**.

De invloed van temperatuurverschillen op ladingstransport door kationselectieve nanokanalen is numeriek onderzocht door een niet isotherme formulering van de Poisson-Nernst-Planck en Navier-Stokes vergelijkingen (**Hoofdstuk 2**). Nanokanalen zijn ladingsselectief doordat hun karakteristieke lengte de ordegrootte

van de elektrische dubbellaag heeft. In dit hoofdstuk worden zowel uniforme als asymmetrische nanokanalen gesimuleerd. Verwarming door de elektrische stroom die door het nanokanaal gaat (Joule opwarming) en viskeuze dissipatie van warmte zijn verwaarloosbaar bij relevante elektrische veldsterktes en bij ionconcentraties waarbij het nanokanaal nog ladingselectief is. In isotherme systemen wordt de selectiviteit van het nanokanaal lager als de temperatuur verhoogd wordt, doordat er een hoger transport van co-ionen door het nanokanaal is. Dit verhoogde transport van co-ionen is een resultaat van de verhoogde diffusiviteit van ionen en de verlaagde viscositeit van de oplossing. Om dezelfde redenen is de totale elektrische stroom hoger bij hogere temperatuur. Nog interessanter is dat de selectiviteit van het nanokanaal hoger wordt als er een temperatuurgradient aangelegd wordt in dezelfde richting als het elektrisch veld. In deze situatie wordt de diffusiviteit van ionen aan de warme “ingaaende” kant van het nanokanaal verhoogd in vergelijking met de diffusiviteit van ionen aan de koude “uitgaande” kant van het nanokanaal. Daarnaast wordt ook de viscositeit aan de ingaande kant verlaagd in vergelijking met de viscositeit aan de uitgaande kant door het opgelegde temperatuurverschil. Gecombineerd zorgen deze effecten voor een toename in het selectieve ladingstransport door het nanokanaal. Als de richting van de temperatuurgradiënt wordt veranderd, zorgen de tegenovergestelde interacties voor een lagere ladingselectiviteit van het nanokanaal in vergelijking met de isotherme situatie. Asymmetrische nanokanalen zijn interessant als diode omdat hierin rectificatie van de stroom plaatsvindt als de richting van het elektrisch veld veranderd wordt. In deze asymmetrische nanokanalen wordt de selectiviteit vooral bepaald door de minimale grootte van het nanokanaal. Omdat in ons onderzoek de gemiddelde grootte van het nanokanaal gelijk gehouden wordt zijn de asymmetrische nanokanalen meer ladingselectief dan de symmetrische kanalen, maar is de totale stroom door het kanaal ook lager. Een temperatuurgradiënt vergroot de rectificatie van asymmetrische nanokanalen, wat mogelijk gebruikt kan worden in toepassingen zoals iondetectie.

De resultaten van dit numerieke onderzoek motiveerden experimenteel onderzoek naar de effecten van temperatuurgradiënten op een labschaal elektrolyse stack. In eerste instantie (**Hoofdstuk 3**) is het effect van temperatuur en temperatuurgradiënten in het industrieel relevante Ohmse regime onderzocht. Vier verschillende temperatuurconfiguraties zijn onderzocht in zowel ED als omgekeerde ED (RED) modus van een commercieel beschikbare RED-stack met een dwarsstroom vloeistof voedingsconfiguratie, gebruikmakend van commerciële Neosepta® CMX (kation uitwisselingsmembranen) en Neosepta® AMX (anion uitwisselingsmembranen). Voor RED worden twee voedingsstromen met verschillend zoutgehalte aan de stack gevoed, waarbij door het concentratieverschil een ionische stroom door de membranen ontstaat. Deze ionische stroom kan als elektrische energie gewonnen worden. Het rendement van het ED proces wordt verhoogd

als de temperatuur verhoogd wordt, met ongeveer 15% als de temperatuur van 20 °C tot 40 °C wordt verhoogd, wat betekent dat minder vermogen nodig is om dezelfde scheiding te bewerkstelligen. Op basis van de numerieke resultaten met nanokanalen was een hogere ladingselectiviteit verwacht wanneer er een temperatuurgradiënt was aangelegd. Er is echter geen significant verschil in ED rendement gemeten tussen de configuraties waarbij een temperatuurgradiënt is aangelegd. Dit kan verklaard worden doordat er in het Ohmse regime gemeten werd, waar het effect van de ontzoute grenslaag relatief klein is. Daarnaast is er een goede warmteoverdracht in het systeem, waardoor de daadwerkelijke temperatuurverschillen kleiner zijn dan de ingaande temperatuurverschillen. Het rendement van het ED proces is met $\sim 9\%$ verhoogd als één van de voedingsstromen is opgewarmd tot 40 °C. Dezelfde conclusie kan getrokken worden voor de experimenten in RED-modus. De gewonnen elektrische energie wordt met $\sim 38\%$ verhoogd als de temperatuur van de voedingsstromen wordt verhoogd van 20 °C naar 40 °C door een verhoogde diffusiviteit van ionen in de oplossing. De richting van een opgelegde temperatuurgradiënt had geen significant effect op het systeemgedrag, terwijl er was verwacht dat het verwarmen van het laagzoute “rivierwater” een verhoging in de elektrische energie zou opleveren in vergelijking met de situatie waarin het hoogzoute “zeewater” verwarmd zou worden. Voor beide richtingen van de temperatuurgradiënt is de gewonnen elektrische energie met ongeveer 25% verhoogd. Deze resultaten laten zien dat het rendement van zowel ED als RED processen verhoogd kan worden door de temperatuur van de voedingsstromen te verhogen. Wel moet overwogen worden dat de energie die nodig is om de voedingsstromen te verwarmen vele malen groter is dan de energie die bespaard kan worden door het gebruik van een verhoogde temperatuur, waardoor het toepassen van deze resultaten alleen uitvoerbaar is als de stromen worden opgewarmd met afvalwarmte.

Verwacht wordt dat het effect van temperatuur en temperatuurgradiënten in het limiterende stroomdichtheid regime groter is omdat in dit regime diffusie door de ontzoute grenslaag limiterend is voor het iontransport door het systeem. Om dit te onderzoeken zijn experimenten gedaan in het limiterende stroomdichtheid regime onder gelijkstroom configuratie (**Hoofdstuk 4**). Deze experimenten zijn gedaan in een andere commercieel verkrijgbare labschaal ED-stack (FUMATECH, Germany BWT GmbH) met de bijbehorende FKS (kation uitwisseling) en FAS (anion uitwisseling) membranen. Er is gemeten met twee verschillende voedings-samenstellingen, een voeding met enkel monovalente KCl/NaCl zouten en een mengsel van mono- en divalente ionen KCl/NaCl en $MgCl_2$. In het limiterende stroomdichtheid regime maakt een verschil in de richting van de opgelegde temperatuurgradiënt een significant verschil in de verkregen elektrische stroom bij een constante opgelegde potentiaal. Voor experimenten met de monovalente ionen in oplossing levert de situatie waarin de ontzoute voedingsstroom is verwarmd

een hogere totale elektrische stroom ($\sim 7\%$ hoger) dan de situatie waarin de geconcentreerde voedingsstroom is verwarmd. Dit resultaat komt overeen met de verwachtingen gebaseerd op het numerieke onderzoek aan ladingsselectieve nanokanalen. Het verschil in gemeten stroom heeft ook een effect op de totale ontzouting van de stroom als de ontzoute stroom verwarmd is, ook al zijn deze effecten klein. Nog interessanter is het effect van temperatuurgradiënten op metingen met een mengsel van mono- en divalente ionen, omdat de diffusiviteit van de verschillende ionen op een verschillende manier afhangt van temperatuur. Het competitief transport tussen de Mg^{2+} en de monovalente K^+ en Na^+ resulteert in een veranderde invloed van temperatuur op het systeem. Het transport van de divalente ionen is verhoogd in vergelijking met het transport van monovalente ionen als de ontzoute stroom is opgewarmd. Dit impliceert dat het toepassen van een temperatuurgradiënt gebruikt kan worden om de scheiding tussen divalente en monovalente ionen te vergemakkelijken.

In de industrie wordt de exploitatie van ED-stacks vaak gelimiteerd tot het Ohmse regime om de efficiëntie zo hoog mogelijk te houden. Om de ontwikkeling van ontzoute grenslagen en de rol van deze grenslaag in het ontstaan van het overlimiterende stroomdichtheid regime te bestuderen is er een nieuw microfluidisch platform ontwikkeld, gebaseerd op ladingsselectieve hydrogels (**Hoofdstuk 5**). In dit systeem kunnen de ontzoute grenslaag en de ontstane microfluidische stromingen gevisualiseerd worden. Zes parallelle kanalen worden gescheiden door afwisselende kation en anion selectieve hydrogels, die *in-situ* gevormd worden. De hydrogels zijn gekarakteriseerd voor hun gebruik als ladingsselectieve grensvlakken door de permselectiviteit, weerstand en ladingsdichtheid te meten. Met dit platform hebben we voedingsstromen met een relatief lage zoutconcentratie kunnen ontzouten, terwijl ook de ontwikkeling van de ontzoute grenslagen gevisualiseerd werd door een negatief geladen fluorescente kleurstof toe te voegen aan de voeding. Deze fluorescente kleurstof bootst het gedrag van de negatieve ionen in het systeem na. Door de visualisatie te combineren met metingen van de uitgaande ionconcentraties hebben we de functionaliteit van onze microfluidische ED-stack kunnen aantonen. Dit systeem kan gebruikt worden als imitatie van een ED-stack waarin we de ontwikkeling van ontzoute grenslagen en elektrokinetische stromen kunnen visualiseren.

Door het *in-situ* vormen van de hydrogels kunnen ladingsselectieve grensvlakken met verschillende geometrieën gemaakt worden, zoals beschreven in **Hoofdstuk 6**. Drie verschillende hydrogelgeometrieën zijn onderzocht; een homogeen grensvlak en twee verschillende heterogene grensvlakken. Door de vervorming van het elektrisch veld door de heterogene hydrogels wordt het ladingstransport in deze systemen vergroot in vergelijking met het transport in heterogene systemen. Al in het Ohmse regime ontstaan er componenten van het elektrisch veld parallel aan het grensvlak, die resulteren in een elektro-osmotische vloeistofstroom richting

het ladingselectieve grensvlak. Deze vloeistofstroom zorgt voor een aanvullend transport van ionen naar het grensvlak waardoor er grotere elektrische stromen door het grensvlak ontstaan en het rendement van het systeem verhoogd wordt. Het ontstaan van ontzoute grenslagen is gevisualiseerd in systemen zonder opgelegde vloeistofstroom door fluorescentie microscopie en gekwantificeerd door “fluorescence lifetime microscopy (FLIM)”. Door de afwezigheid van een opgelegde vloeistofstroom kunnen de ontwikkeling van de grenslaag en elektrokinetische vloeistofstromen ontkoppeld worden van de dwarsstromen door het kanaal. De ontwikkeling van ontzoute zones is afhankelijk van de geometrie van de hydrogels. In de heterogene configuraties is worden de ontzoute zones vastgepind aan het oppervlak tussen de hydrogel en de kanaalwand. In het homogene systeem worden de ontzoute zones niet vastgepind en kunnen ze vrij over het ladingselectieve oppervlak bewegen. Deze aanpak maakt het mogelijk om snel en gemakkelijk het ladingstransport voor verschillende membraantopologieën te onderzoeken.

De invloed van geometrie op de ontwikkeling van ontzoute zones en de elektrokinetische vloeistofstromen is ook onderzocht in een meer conventioneel microfluidisch systeem waarin ladingselectieve nanokanalen het membraan representeren (**Hoofdstuk 7**). Onze nanokanalen hebben een karakteristieke lengte van 20 nm en de microfluidische kanalen die door de nanokanalen gescheiden worden zijn $70 \times 20 \mu\text{m}$. Een geladen fluorescente kleurstof is gebruikt om de ionconcentratie in het systeem te meten terwijl polystyrene deeltjes gebruikt zijn om de vloeistofstroom te volgen. Wervelingssnelheden van meer dan 1.5 mm/s zijn gemeten nabij de nanokanalen. Er zijn drie verschillende distributies van nanokanalen onderzocht, die informatie opleverden over de wisselwerking tussen geometrie, elektrisch veld en het ladingstransport. Ontzoute zones worden gevormd nabij de nanokanalen and ontwikkelen zich als een functie van tijd. Nanokanalen die verder van de elektroden geplaatst zijn hebben minder ontzouting in hun nabijheid dan nanokanalen dichterbij de elektroden. De begrenzendende geometrie van het microfluidisch systeem speelt een belangrijke rol omdat grote gedeelten van het ladingselectieve oppervlak ongebruikt kunnen blijven, wat leidt tot een significant verlies van procesefficiëntie. Wervelingen ontstaan nabij nanokanalen in alle verschillende geometrieën, maar de snelheid en grootte van deze wervelingen is afhankelijk van de locatie van de nanokanalen ten opzichte van de elektroden.

In het laatste hoofdstuk van dit proefschrift (**Hoofdstuk 8**) wordt een korte reflectie op het gepresenteerde werk gegeven, inclusief een aantal aanbevelingen en verbeteringen met betrekking tot de numerieke en experimentele onderzoeken en suggesties voor verder onderzoek. De implicaties van dit onderzoek voor elektrodialyse systemen en analoge toepassingen zoals brandstofcellen zijn ook beschreven. De invloed van temperatuur en, belangrijker, temperatuurgradiënten op ladingstransport zouden gebruikt kunnen worden om het selectief transport van ionen te bevorderen en hiermee de benodigde elektrische energie voor ED

processen te verminderen. Het gebruik van gradiënten in conductiviteit en permittiviteit op het ladingsselectieve oppervlak kan het convectief transport van de ionoplossing naar het membraan verhogen, waardoor er een grotere elektrische stroom ontstaat en de efficiëntie van het proces verhoogd kan worden, in bijvoorbeeld ontzoutingsprocessen.

CHAPTER 1

Transport phenomena near charge selective interfaces

1.1 Introduction

If a salt is dissolved in a polar solvent, it (partially) dissociates into positive cations and negative anions. Since ions possess a fixed charge, they are responsive to gradients in electric potential and they can be manipulated by imposing an electric field over the solution. Ions can also diffuse through a solution as a result of local concentration gradients. The total flux of ions through a solution as a result of these gradients can be described by the Nernst-Planck equation, as will be discussed in Section 1.5. Selective ion transport can be established by using charge selective interfaces, which preferably allow one type of ions (either positive or negative) to be transported. Ion selective interfaces have a multitude of applications, for instance in fuel cells [1], analytical chemistry, sensors [2] and in the human body.

Electrodialysis (ED) is a well-established technique that can be employed in demineralization and preconcentration of brackish feed streams such as river water and industrial waste streams [3–5]. Prior to the introduction of membrane based desalination techniques, desalination was mostly done using thermal techniques that require relatively large amounts of energy. Electrodialysis using ion selective membranes was developed in the 1940s [6, 7], when the concept of utilizing a stack of cell pairs with alternating anion (AEM) and cation (CEM) exchange membranes was conceived. Development of stable, low resistance ion exchange membranes resulted in practical application of the ED process in the 1950s. In the following decades, both companies and governments of different countries invested in research and development of industrial ED processes, resulting in commercial scale ED demineralization plants [3, 8, 9].

In electrodialysis processes, an electric potential is applied over a stack of alternating cation and anion exchange membranes, as is schematically shown in Figure 1.1. The inter-membrane distance is in the order of $\sim 100 - 2000 \mu\text{m}$ [5, 10, 11], obtained by positioning a spacer between the membranes. Aqueous feed solutions containing dissolved salts are pumped through the membrane compartments and an electric potential is applied at the electrodes in the outermost compartments. The electrode compartments are usually flushed using a reversible electrolyte pair to suppress gas formation as a result of electrode reactions. As a result of the electromigration of ions in the electric field, cations move towards the cathode and anions move towards the anode. Ion selective membranes selectively block either anions or cations from transporting towards the electrode, resulting in alternating concentrated and diluted compartments [5, 11–13].

The combination of one AEM and CEM, together with their adjoining concentrate and dilute compartments, is called a cell pair. In industrial applications of electrodialysis a stack typically contains 100 - 200 cell pairs between a pair of electrodes but this number can be as high as 2000 [5, 11]. Charge transport in the

Figure 1.1 — Schematic representation of an electrodialysis (ED) stack, in which equiconcentrated feed streams are separated into a concentrated and diluted stream under the influence of an externally applied electric field. The electrode compartments are often flushed with a redox solution (orange arrows), providing electrons for charge transport and to avoid gas formation.

system can be divided into three main parts: (i) ion transport in the electrolyte, (ii) ion transport through the membrane and (iii) electron transport through the wires and electrodes [5, 14]. Commercial membranes are highly charged and thus exhibit a low electrical resistance. As the membrane and electrodes have a low resistance to charge transport, the main limitation in electrodialysis systems is often the resistance of the electrolyte solution. Particularly, at low ion concentrations this resistance to charge transport is significant and imposes a challenge in efficient operation of ED processes.

In aqueous electrolyte solutions the bulk of the solution is electrically neutral, meaning that there is no net charge density in the fluid [15, 16]. This electroneutrality condition implies that the sum of all charges in the system, arising from a certain concentration c of ions with a valence z should be zero in the bulk over all N species (Equation 1.1).

$$\sum_{i=1}^N z_i c_i = 0 \quad (1.1)$$

In thin regions near a charged boundary (in the order of the Debye length, see section 1.2.2) the solution is not electroneutral, as the ions screen the fixed charge

Figure 1.2 — Ion concentration profile at a cation exchange membrane (CEM). A boundary layer of increased ion concentration forms at the enriched (cathodic) side of the membrane where the local concentration at the membrane $c_{m,c}$ is increased when compared to the bulk c_b . At the depleted (anodic) side of the CEM a boundary layer with decreased ion concentration forms ($c_{m,d}$).

of the boundary. Equation 1.1 holds for aqueous solutions and implies that there is no electric body force on the liquid bulk in an electric field [15, 17].

Electrodialysis processes utilize the difference in transport numbers of ions in the solution when compared to the transport numbers of ions in membranes [12, 18]. The transport number τ of a certain species i is defined as the fraction of the total current that is carried by species i and thus, as a result of the electroneutrality condition $\tau_+ + \tau_- = 1$ holds [19–21]. In an ionic solution transport numbers of both anions τ_- and cations τ_+ are similar while in, for example, a cation selective membrane $\bar{\tau}_+ \gg \bar{\tau}_-$. The bars indicate transport numbers in the membrane, while transport numbers in the solution are displayed without a bar. For cation selective membranes $\bar{\tau}_+ > \tau_+$ and for anion selective membranes $\bar{\tau}_- > \tau_-$. As a result of the difference in transport numbers, in combination with the application of an electric potential, a concentrated layer will form on one side of the membrane and a diluted layer will form on the opposite side of the membrane, schematically shown in Figure 1.2.

The permselectivity of an ion exchange membrane is the extent to which the membrane is selective for transport of one charge and blocks the transport of the opposite charge and is defined based on the transport numbers. In Equation 1.2, the definition of the permselectivity of a cation exchange membrane is shown [12, 19]. If $\alpha_c = 1$ the membrane is perfectly cation selective, while if $\alpha_c = 0$ there is no selectivity for cations.

$$\alpha_c = \frac{\bar{\tau}_+ - \tau_+}{1 - \tau_+} = \frac{\bar{\tau}_+ - \tau_+}{\tau_-} \quad (1.2)$$

As the resistance of the electrolyte solutions in the stack limits the ion transport in the system, ED is only practical for solutions with relatively high inlet

concentrations (between 1500 - 10,000 ppm, i.e. 25.7 mM to 171.1 mM NaCl [3]). However, beyond certain concentrations (higher than $\sim 10,000$ ppm), the power consumption of ED processes increases significantly and scaling on the concentrated side of the membrane occurs which makes it unattractive for large scale sea water desalination [12]. The power consumption in ED scales linearly with both current and applied potential, meaning that for high concentration feed streams the required current is increased to such extent that ED is not feasible in comparison to other techniques such as reverse osmosis. Currently, ED is primarily applied in the production of potable water from brackish water sources and the concentration of sea water [10, 22]. Other typical applications are the demineralization of whey and nonfat milk for food and animal feed applications and treatment of industrial wastes [5].

1.2 Charge selective interfaces

For the selective transport of ions, charge selective materials are required. Commercial membranes used in industrial ED processes are usually dense polymeric membranes with fixed charged groups in the polymer chain [23, 24]. This fixed group can either have a positive or negative charge, resulting in a selectivity of the membrane towards the other ion. Apart from these membranes, nanoporous materials such as nanochannels in glass, porous silicon, ZIFs or MOFs can also be applied as charge selective interface at lower salt concentrations [25, 26]. For these nanoporous (sometimes with sub-nanometer pores) materials, size exclusion as well as exclusion based on double layer overlap (see section 1.2.2) and dielectric exclusion contributes to the charge selectivity of the material.

1.2.1 Ion exchange membranes

Ion exchange membranes can be fabricated of a large variety of either organic, inorganic or hybrid materials and are charge selective because of functional groups being present in their chemical structure [23, 27]. These functional groups can be either acidic or basic in nature, which yields the membrane to be either cation or anion selective. Cation exchange membranes have negatively charged functional groups that allow the passage of positively charged counter ions. Anion exchange membranes, on the contrary, have positively charged functional groups that allow for the transport of negatively charged counter ions. Ion exchange membranes are micro-structured in nature, require a high permselectivity, a low electric resistance and typically have a hydrocarbon or fluorocarbon polymeric backbone. They are charge selective because of Donnan exclusion of ions with the same charge as the functional end groups inside the membrane material [28].

For the description of the transport phenomena in ion exchange membranes, the

Figure 1.3 — The concentration profile through a cation exchange membrane in equilibrium with two perfectly mixed compartments of unequal ion concentration (upper part) and the resulting potential distribution ψ in the solution (lower part). Not to scale. The membrane potential is established through the Donnan potentials at both membrane-solution interfaces and the diffusion potential through the membrane. Note that in this case, there is no external electric field applied.

theory of Teorell, Meyer and Sievers (TMS Theory) [29–31] is often applied [21]. This theory describes the important parameters and transport mechanisms in membranes when there is no applied current (no external electric field is applied) and is based on the Nernst-Planck equation and the derived Donnan equilibrium [28, 32].

The Donnan equilibrium theory is based on the chemical potentials of the components inside the solution, which are, by definition, equal in equilibrium. As a result of this requirement for the electrochemical potentials, a potential difference between the membrane and adjacent solutions ($\bar{\psi} - \psi$) arises. This Donnan potential E_{Don} can be calculated by equalizing the chemical potentials of species i in the membrane and the solution. Note that $E_{Don} < 0$ on one side of the membrane while $E_{Don} > 0$ on the other side. This results in Equation 1.3, in which z_i is the charge number, F is the Faraday constant, R is the gas constant, T is the absolute temperature, a_i is the activity of species i in the solution and $\bar{a}_i$ is the activity in the membrane. π is the osmotic pressure resulting from the water swelling of the membrane and V_i is the partial molar volume of ion i [24, 33, 34].

$$E_{Don} = \bar{\psi} - \psi = \frac{1}{z_i F} \left(RT \ln \frac{a_i}{\bar{a}_i} - \pi V_i \right) \quad (1.3)$$

Transport of ions inside the membrane is based on diffusion, driven by con-

centration gradients or the application of an external field [35, 36]. Owing to the charged groups present in the membrane, diffusion of counter ions through the membrane is much larger than the diffusion of co-ions. As a result there is a separation of charges and therefore in equilibrium an electric potential will arise between solutions with different ionic concentrations separated by a charge selective interface. This potential is called the diffusion potential or concentration potential [24], and can be calculated using Equation 1.4. In this equation, $\bar{c}_m$ is the fixed concentration of ion exchange groups inside the membrane, while $c_{i,1}$ and $c_{i,2}$ are the concentrations on the concentrate and dilute side of the membrane. The relative mobility of ions inside the membrane $\bar{u}$ is calculated using the diffusivity $\bar{D}$ of both ions inside the membrane [21].

$$E_{\text{diff}} = -\frac{RT}{F}\bar{u} \ln \frac{\sqrt{\bar{c}_m^2 + 4c_{i,2}^2} + \bar{u}\bar{c}_m}{\sqrt{\bar{c}_m^2 + 4c_{i,1}^2} + \bar{u}\bar{c}_m} \quad (1.4)$$

where

$$\bar{u} = \frac{\bar{D}_+ - \bar{D}_-}{\bar{D}_+ + \bar{D}_-} \quad (1.5)$$

The total potential difference between the two solutions adjacent to the membrane is by definition equal for all species in the solution and is called the membrane potential. This membrane potential (Equation 1.6) is the sum of the Donnan potentials on both sides of the membrane and the diffusion potential in the membrane, shown in Figure 1.3 [24, 36]. For monovalent salt solutions (e.g. NaCl), instead of using $\bar{u}$ we rewrite these to the transport numbers $\bar{\tau}$ using $\bar{\tau}_+ = \bar{D}_+ / (\bar{D}_+ + \bar{D}_-)$. When the system is in equilibrium, the membrane potential can be calculated by Equation 1.6, which is based on the activity coefficients (or concentrations for sufficiently diluted systems) of the ions present in the compartments adjacent to the membrane. For ideally permselective ($\bar{\tau}_i = 1$ for either positive or negative ions) membranes this equation reduces to the Nernst equation.

$$E_m = -\bar{\tau}_+ \frac{RT}{z_+ F} \ln \left(\frac{a_{+,1}}{a_{+,2}} \right) + \bar{\tau}_- \frac{RT}{z_- F} \ln \left(\frac{a_{-,1}}{a_{-,2}} \right) \quad (1.6)$$

Note that this membrane potential arises solely due to a difference in chemical potentials of the species present in the solution and that no external electric field is considered here. Also, this simplified equation is only valid for membranes with a high charge density where the diffusion potential is small. In typical commercial ion exchange membranes, which have charge densities of approximately 5 M [37], this is the case and the diffusion potential can be neglected.

Apart from electrolyte transport, there is also transport of non-charged solvent

(in ED this is most typically water) through the membrane. This transport does not influence the potential distribution in the solution directly, but it has an influence on the ion concentrations inside the solutions [12, 18, 24]. As a result of the concentration gradient, an osmotic pressure gradient occurs resulting in an osmotic flow of solvent towards the compartment of higher concentration reducing the concentration gradient. Electro-osmotic transport (see Section 1.4.1) of solvent, in which the solvent is transported alongside the counter ions present in the membrane as a result of an electric field, also yields a lower overall concentration gradient. Solvent transport through an ion exchange membrane is usually undesirable since it reduces the driving force for transport or reduces the efficiency of the separation of charges [33].

1.2.2 Nanoporous materials

Most solid surfaces have a surface charge, which is screened by ions of the opposite charge (counter ions) when placed in an electrolyte solution (Figure 1.4(a)) [17, 26, 38]. At the solid surface, an electric potential ψ is present as a result of the surface charge (see Figure 1.4(b)). By screening the surface charges, the ions decrease the local electric potential in the fluid to zero and there is local charge neutrality at a finite distance from the wall. The Stern model provides a description of the potential inside the fluid as a function of the distance from the wall.

The Stern model proposes a combination of the previously developed Helmholtz and Gouy-Chapman models [39, 40]. Adjacent to the charged surface, there is the so-called Stern layer (also referred to as Helmholtz layer) in which the counter ions are adsorbed to the surface. The Stern layer has a size in the order of the length scale of the effective size of the hydrated screening ions, which is on the order of 0.3 nm. Outside of this layer, there is a diffuse layer in which the ions can be treated as being point charges in a solution (as was done in the Gouy-Chapman model). A slipping plane occurs between the inner Stern layer and the diffuse layer. At this slipping plane, the local potential is equal to the experimentally measurable ζ -potential. Therefore, this value is generally treated as the value of the surface potential. The diffuse region can be orders of magnitude larger than the Stern layer and is, amongst other factors, a function of the ionic strength of the solution. Outside the so-called electrical double layer (EDL), which consists of both the Stern layer and the diffusive layer, the local electric potential in the solution reduces to zero and in the bulk electroneutrality is restored.

An indication of the characteristic length of the double layer is called the Debye length (κ^{-1} or λ_D) and can be calculated using equation 1.7 [17, 26, 38] where $\epsilon_r\epsilon_0$ is the permittivity of the medium k_B is Boltzmann's constant, T is the temperature, e the elementary charge, z ion valency and n is the concentration of

Figure 1.4 — Charge distribution in a 1:1 electrolyte solution adjacent to a solid surface, according to the Stern model. Figure 1.4(a) shows a schematic of the distribution of ions in the solution with the Stern layer of counter ions directly at the negatively charged wall. The slipping plane, at which the ζ -potential is defined is separating the Stern layer from the diffuse layer. In figure 1.4(b) the absolute potential in the solution is plotted. The Debye length, an indicator of the size of the electrical double layer is indicated by λ_D . The total electric double layer (EDL) is completed by the diffuse layer, in which the cation concentration is still slightly higher than the anion concentration. Figure 1.4(c) schematically shows the concentrations of anions and cations in the vicinity of the negatively charged wall. In the bulk, outside of the diffuse layer concentrations of anions and cations are such that there is no net space charge and the solution is electrically neutral.

ionic species (in mole/m³).

$$\lambda_D = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{\sum e^2 z_i^2 n_i}} \quad (1.7)$$

From this equation, it follows that for lower ionic strengths, the size of the double layer is larger than for solutions with high ionic strength. Inside the electrical double layer, there is an excess of counter ions when compared to co-ions (Figure 1.4(c)). When two walls with wall charges of equal sign are spaced in the order of two Debye lengths (or shorter), co-ions will mainly be excluded from the created void as they are somewhat excluded from the electrical double layer [41]. This results in charge selectivity of the pore for ions with a charge opposite to the wall charge. When the ionic strength of the electrolyte is increased, the Debye length is decreased and the pore can lose its charge selectivity.

Nanopores, nanochannels or nanoslots all have at least one dimension that is in the order of (tens of) nanometers, making them charge selective at low ion concentrations [42–50]. For a 1 mM monovalent salt solution, the Debye length is 10 nm, while it drops to 3 nm when the concentration is increased to 10 mM. Typical nanochannel sizes in experimental systems are in the order of tens of nanometers [42, 51], and nanoporous networks can have pore sizes down to a few nanometers [52, 53].

1.2.3 Ion exchange membranes in microfluidic systems

Experimental observations of concentration and velocity profiles are of high importance in understanding the transport phenomena adjacent to charge selective interfaces. For *in-situ* investigation of concentration and flow profiles, optical access to the system under investigation is extremely convenient. Local ion depletion zones at the charge selective interfaces can be indicated using a charged dye, while the convection in the system can be tracked using fluorescent particles. As the typical length scale at which these ion depletion zones and fluid flows occur is in the order of $\sim 20 - 100 \mu\text{m}$ [18, 54, 55], microfluidic systems are useful for experimental investigations. Several microfluidic platforms containing a charge selective material have been developed in the recent years. Typically, these systems consist of two (or more) microfluidic channels (in for instance glass, silicon or PDMS) with dimensions in the order of $100 \mu\text{m}$, interconnected by a charge selective barrier. For this charge selective barrier different materials have been applied such as prefabricated, polymeric membranes with a fixed charge [56, 57], microfluidically patterned charged polymeric membranes (e.g. Nafion) [58–62] or nanoporous materials [42, 48, 63–66].

Different aspects of the development of ion depletion zones and electroconvection have been investigated in these systems. The onset, growth and characteristic

length of ion depletion zones have been measured as a function of time [47, 67], applied voltage [68–70], channel dimensions [71] and solution properties such as pH and ion concentration [42, 72]. Electroconvective flows and vortices have been observed under various conditions in these systems [49, 61, 66, 73, 74]. Vortices are usually visualized by means of particle tracking inside the fluid, but can also be indicated by visualization using a (charged) fluorescent dye. Several comprehensive reviews have discussed these experimental investigations and their important results in detail [44, 54, 55]. Since all these experimental systems have different dimensions, dominating resistances and operating conditions, it is difficult to directly compare the experimental results from the different systems.

1.3 Ion transport at charge selective interfaces

The amount of ions transferred through a membrane can be quantified by measuring the electric current that is going through a system when an electric potential is applied. The total current I is related to the amount of transported ions J [mol/s] through the Faraday constant, $F = eN_A = 9.65 \times 10^4$ C/mol, and the valence z [–] of the different ion species i transported through Equation 1.8 [12, 15, 19, 75, 76]. The ion flux J_i consists of electromigration, diffusion and convection¹ fluxes, as described by the Nernst-Planck equation. To calculate the current density (usually denoted as i) through the membrane, the total measured current is simply divided by the membrane area available for transport A [m²].

$$I = F \sum_i z_i J_i \quad (1.8)$$

If the driving force for ion transport (the electric potential V) is increased while the resistance to this transport R is kept constant, following Ohm’s law (Equation 1.9) a higher flux of ions is expected and therefore a higher current should be measured.

$$V = IR \quad (1.9)$$

The resistance in ED systems consists of the resistance in the membrane and the resistance in the electrolyte solution, in series such that the total resistance is the sum of the different resistances [5]. For systems with highly conductive membranes and fairly dilute electrolyte solutions, the resistance in the solution is higher and determines the resistance of the total system as the different resistances are in series. The electrical resistivity ($\rho = R \cdot (l/A)$, in which l is the length and A the specific area of the material) of an electrolyte solution is the reciprocal of

¹ In transport phenomena (and throughout this thesis), convection is the term used for transport by the bulk motion of the fluid and used as synonymous to advection [77]

Figure 1.5 — Schematic representation of the relation between the current and the potential in an electrodialysis stack. At low applied potentials, the current increases linearly with an increasing driving force following Ohm’s law (region I). In the so-called limiting current regime (region II) the current is nearly constant as ion transport in this region is limited by diffusive ion transport through the depletion boundary layer. Above a certain potential an overlimiting current (region III) is observed, indicating the additional transport of ions through the membrane.

the conductivity σ , which scales with the ion concentration and ion mobility (ν) in the solution as per Equation 1.10.

$$\sigma = \frac{1}{\rho} = F^2 \sum_i z_i^2 \nu_i c_i \quad (1.10)$$

The ion mobility is directly related to the ion diffusivity D through the Nernst-Einstein equation, $\nu_i = D_i/RT$ and is a measure of the ease of transport of ions in the solution. If concentration gradients are established in the system, Ohm’s law will not hold as a result of additional diffusive ion transport in the system contributing to the total current [76].

For ED (and other electrolyte) systems, when the measured current is plotted against the driving potential, a characteristic shaped IV-curve is obtained [78–81]. A schematic example of such a curve is drawn in Figure 1.5, in which three distinct regions can be identified. In the first region (I), at relatively low applied potentials, the current linearly increases with increasing applied potential following Ohm’s law indicating a constant resistance in the system. At elevated potentials, the current reaches a plateau region (II) in which the total current is not increasing linearly with increasing field strength but is instead nearly constant or weakly increasing. In this region, the resistance to charge transport increases as a result

of the formation of an ion depletion zone adjacent to the membrane. Upon further increase of the driving potential, in the so-called overlimiting current regime (III), additional current is measured indicating the additional transport of ions through the charge selective interface. Commercial electrodialysis processes are operated at current densities in which charge transport through the solution is in the Ohmic regime, as this yields the highest energy efficiency [5].

1.3.1 Ion concentration polarization

To be able to understand the characteristic shape of such an IV-curve, we have to zoom in on the ion transport in a thin stagnant layer ($\sim 20 \mu\text{m}$) adjacent to the membrane. When an electric potential is applied perpendicular to a membrane immersed in an electrolyte solution, ions in the solution will migrate towards the electrode with opposite charge [81]. If we take the example of a cation exchange material (CEM) immersed in an ionic solution (as schematically shown in Figure 1.6), upon application of the electric field anions will migrate towards the positively charged anode, and cations will migrate towards the negatively charged cathode. The CEM blocks the transport of anions, while it conducts the cations. As a result of this, anions will be enriched on the cathodic side of the membrane (Figure 1.6, left) and because of the resulting potential distribution, the cations will distribute accordingly, resulting in local charge neutrality in the boundary layer. For cations, the transport number in the CEM is higher than the transport number in solution, yielding a depletion layer (of thickness δ) on the anodic side of the membrane (Figure 1.6, right). Again, anions are distributed accordingly as a result of the resulting potential distribution adjacent to the membrane and there is local neutrality in the boundary layer [12, 55, 82, 83]. Note that these boundary layers are typically orders of magnitude larger than the electrical double layer, in which the distribution of anions and cations is not equal and there is a net charge in the solution. The simultaneous development of an ion enriched zone and an ion depleted zone on the different sides of the membrane is called ion concentration polarization.

Diffusive fluxes of both anions and cations develop, with the local concentration gradient in the boundary layer as the driving force for this transport. The boundary layer thickness δ (indicated by the dotted lines in Figure 1.6) increases with time until ionic fluxes match and is dependent on the hydrodynamics of the flow adjacent to the membrane, the transport numbers of ions in solution and membrane and the desired current density through the membrane [83].

1.3.2 Limiting current

In steady state, a concentration gradient is established in the boundary layers adjacent to the membrane interface. By assuming a stagnant boundary layer, we neglect any possible ion transport by convection. For both the membrane

and the solution, the flux of cations J_i is described by adding a diffusive and an electromigration flux, as per the Nernst-Planck equation [84–86]. This results in Equation 1.11, in which τ_i and $\bar{\tau}_i$ are the ion transport numbers in the solution and membrane respectively, i is the current density, D and $\bar{D}$ are the diffusion coefficients of the cation in the solution and the membrane, δ is the thickness of the stagnant boundary layer and d is the thickness of the membrane. Δc_{bl} is the concentration difference inside the boundary layer, while Δc_m is the concentration difference in the membrane. For the flux through the boundary layer, electromigration and diffusion act in the same direction, while in the membrane diffusion opposes electromigration [16, 19, 83].

$$J_i = \frac{\tau_i i}{z_i F} + \frac{D \Delta c_{bl}}{\delta} = \frac{\bar{\tau}_i i}{z_i F} - \frac{\bar{D} \Delta c_m}{d} \quad (1.11)$$

Since electromigration is the dominant ion transport process within the membrane, $\bar{D} \Delta c_m / d \ll \bar{\tau}_i i / F$, then Δc_{bl} can be rewritten to be the difference between

Figure 1.6 — Schematic representation of ion concentration polarization at a cation exchange membrane (CEM). As a result of the electric field anions and cations are migrating in opposite directions J_{migr} . At the CEM, anions are blocked, resulting in a local increase of ion concentration c while cations are conducted by the membrane, resulting in a local decrease of ion concentration at the anodic side of the membrane. Due to the developed concentration gradients, diffusive fluxes J_{diff} of both ions are established alongside the electromigrative fluxes. Local ion concentration is indicated by the thick black lines, the dashed lines indicate the situation in which the developed boundary layer δ is completely stagnant. The influence of the electrical double layer (EDL) at the membrane is not represented here, since the length scales are usually different by orders of magnitude.

the bulk concentration c_b and the concentration at the membrane c_m , so that:

$$i = \frac{z_i F D}{\bar{\tau}_i - \tau_i} \frac{c_b - c_m}{\delta} \quad (1.12)$$

In the limiting situation, the concentration at the membrane interface vanishes yielding $c_m = 0$. With these assumptions, the Peers equation is obtained for the limiting current density in the system as a result of concentration polarization at the membrane[78]:

$$i_{\text{lim}} = \frac{z_i F D}{\bar{\tau}_i - \tau_i} \frac{c_b}{\delta} \quad (1.13)$$

The limiting current density can be experimentally determined by IV-characterization of membrane systems. The limiting current density of experimental systems is externally influenced by the temperature, temperature gradients, the membrane selectivity and flow conditions. By changing these parameters, the onset of the limiting current regime can be shifted, yielding more favourable operating conditions. The development of ion concentration polarization near membranes is unfavourable for the transport of ions, but ultimately it cannot be avoided beyond a certain point as it is an intrinsic result of the selectivity of the membrane. Ion concentration polarization can be suppressed by enhanced mixing of the boundary layer, which usually is accomplished by increasing the feed flow rate and usage of functional spacers in the system [11, 12].

1.3.3 Overlimiting current

Upon increase of the driving potential, a current higher than the theoretical limiting current can be measured in ED systems, as was depicted in Figure 1.5. Since the current is a result of the transport of charge carriers, an increased amount of charge carriers are transported through the membrane in the overlimiting current regime. Different theoretical [78, 82, 87–98], and experimental [44, 45, 68, 70, 71, 99–104] explanations for the overlimiting current have been proposed and investigated. In reality, the overlimiting current regime is usually established through a combination of the different mechanisms and the dominant mechanism is dependent on the system properties and operating conditions [105–107].

Water splitting

Water splitting is induced by an electrical potential gradient, usually in combination with a reaction promoting surface [78, 104, 108–111]. In polymeric membrane systems, the membrane itself is the surface at which this reaction takes place as the charged end groups promote the reaction. As a result of the depletion layer and the low local ion concentration, the local electric potential gradient is sufficient to induce the water splitting reaction given by Equation 1.14. Since

the presence of H^+ and OH^- shifts the local $p\text{H}$ of the solution, water splitting can be experimentally observed by measuring the $p\text{H}$ at the membrane or in the outlet streams [12].

Additional charge carriers in the form of OH^- and H^+ are formed in the water splitting reaction, resulting in a measurable increase in current. This contribution to the total current is not desirable in ED since it does not contribute to the separation of desired ions in the solution. The mobility of hydroxide and hydronium ions is higher than the mobility of all common ions in the solution [112], yielding these ions to be transported favourably over the salt ions in solution. In ED processes using bipolar membranes, in which a salt is converted into its corresponding acid and base (for instance the production of NaOH and HCl from a NaCl solution), the water splitting reaction is required and promoted at the bipolar membrane interface [113, 114]. In most systems, however, the contribution of water splitting is found to account for a minor contribution in the additional charge carriers [12, 115].

A secondary effect of water splitting is the exaltation effect [93, 94], in which the ions generated at the membrane attract ions of the opposite charge towards the membrane. For instance, if at a cation exchange membrane water is split into hydroxide and hydronium, the hydronium will migrate through the membrane leaving the hydroxide to cause a negative space charge at the membrane interface. Cations in the solution are attracted by this negative charge near the membrane, causing an additional flux of ions towards the membrane. Theoretical and numerical modeling of this phenomenon has shown that there is an increased ion flux through the charge selective interface when water is split, along the flux of water ions [111]. Current induced membrane discharge as a result of water self-ionization results in the loss of selectivity of the membrane and also can result in an overlimiting current [97].

Gravitational convection

When ion concentration polarization occurs at the membrane interface, local differences in density are arising owing to the ion concentration differences. In the earth's gravitational field, these density differences can result in convective flows [92, 99, 116]. If the density gradient is along the gravitational field and the ion depleted zone (having a lower density) is below the ion enriched zone, Rayleigh-Bénard instabilities arise if the Rayleigh number Ra is above the critical Rayleigh number Ra_c [117]. The Rayleigh number is defined as the ratio of the buoyancy forces to the viscous forces and is mainly dependent on the density difference (as a result of the concentration difference Δc) and the characteristic

length L of the system. $Ra = \frac{M\Delta cgL^3}{\eta D}$ in which M is the molar mass of the solute, g is the gravitational constant and η is the viscosity of the solvent. If the density gradient is perpendicular to the gravitational field, convective mixing will always occur. The critical Rayleigh number depends on the system parameters, but is usually in the order of $Ra_c = 1000 - 2000$ [117]. By this convective mixing, additional ions are transported from the bulk solution towards the charge selective interface resulting in additional current through the interface. Additionally, the boundary layer thickness δ is reduced by the convective mixing.

In systems containing dilute salt solutions the effect of gravitational convection is small as a result of the relatively small density differences that can arise. In systems with small dimensions, since the Rayleigh number scales with L^3 , the effect of gravitational convection is usually small. For higher salt concentrations and relatively large systems gravitational convection can be a significant contributor to the overlimiting current [87, 103, 118]. Imposing a temperature gradient in the membrane system can also yield gravitational convection as a result of the arising density differences [119], which might be of use in the promotion of convective fluid mixing adjacent to a membrane. In this case, gravitational convection can be significant in systems containing a low salt concentration.

Electroconvection

Another form of convective mixing adjacent to the membrane interface is electroconvection (EC), which is a result of the interplay of the electric field and a local space charge inside the solution [82, 88]. A net space charge can be developed when local potential gradients are high enough, locally breaking the electroneutrality condition and resulting in an effective charge on the solution. The applied electric field will act on this charge, causing the fluid to move and convective mixing in the this charged boundary layer, schematically shown in Figure 1.8. This convection yields an additional transport of ions towards the ion selective interface, increasing the current through this interface. Electroconvection has been experimentally found to be the most common origin of the overlimiting current in dilute solutions [87, 99, 105], and therefore will be expanded upon in the following sections.

1.4 Electroconvection at charge selective interfaces

Fundamental understanding of (electro)convective transport adjacent to charge selective interfaces is important in the description of phenomena happening in the boundary layer adjacent to the interface. In section 1.3.1 and 1.3.2, the boundary layer was described as a thin stagnant layer adjacent to the membrane and convection was only introduced briefly as a possible explanation for the

observed overlimiting current regime. Contributions of electro-osmosis through the membrane and other fluid flow perpendicular to the membrane interface were neglected in the description of charge transport and the calculations of the limiting current. For commercial operation of ED processes, the assumption of a thin, stagnant boundary layer adjacent to the membrane usually holds as a result of the imposed flow in the direction parallel to the membranes [120] and the operating range being below the onset of the limiting current regime. In systems without imposed flow, the contribution of electro-osmosis and electroconvection to the charge transport becomes more significant.

1.4.1 Electro-osmosis

Electro-osmosis is the movement of an ion containing fluid relative to a stationary charged surface as a result of an applied electric field. This phenomenon was described first in 1809, when F.F. Reuss demonstrated that water migrated through porous clay under the application of an electric field without the application of an external pressure gradient [121–123].

In the electrical double layer (which was described in Section 1.2.2), there is an unbalanced distribution of ions as counter ions are screening the fixed wall charge of the material that is immersed in the liquid. The concentration of counter ions is exceeding the concentration of co-ions (see Figure 1.4), resulting in a space charge being present in the double layer. When an electric field is applied tangential to the wall, the ions in the solutions will start to migrate towards the electrode with opposite charge. In the bulk, where cation and anion concentrations are equal and the space charge is zero, there is no net force on the fluid. In the electrical double layer, there is a net charge in the fluid resulting in a unidirectional flow toward the electrode of opposite charge, as is schematically depicted for an ionic solution adjacent to a negatively charged wall in Figure 1.7 [34, 124–126].

The fluid is dragged along as a result of viscous drag and an electro-osmotic flow (EOF) adjacent to the wall is established. Due to the no-slip condition at the wall, the velocity of the fluid will increase from zero to the maximum velocity over the width of the space charge region adjacent to the wall. Since the width of the double layer, in which the velocity gradient is present, is usually small when compared to the channel dimensions, the flow profile of EOF is a plug flow profile through the channel. This also means that most of the resulting EOF is shear-free since nearly all the viscous dissipation takes place inside the charged double layer [17, 125].

For steady state EOF past a planar homogeneously charged surface, the theoretic electro-osmotic velocity is dependent on the applied external field in the direction of the flow E_x , the wall potential ζ , the viscosity of the medium η and electric permittivity of the medium $\epsilon_r \epsilon_0$. The electro-osmotic velocity can be obtained by solving Stokes equation ($\mu \nabla^2 u = \epsilon_r \epsilon_0 \nabla^2 \psi E$) using the relevant

Figure 1.7 — The concept of electro-osmotic flow at a charged wall. The applied electric field is acting on the (positive) space charge in the electric double layer (EDL), resulting in a fluid movement. The space charge is indicated by the color, where white indicates a zero net charge and blue indicates a positive net charge. The cations in the EDL screening the negatively charged wall (see section 1.2.2) are attracted by the negatively charged cathode. Water is drawn by these cations as a result of viscous drag, which results in a net convective flow with velocity u_{eo} [m/s] towards the cathode. All shear stress is dissipated between the slipping plane (indicated by the dotted line) and the neutral bulk, resulting in a plug flow velocity profile in the bulk.

system boundary conditions (at the wall, $u = 0$ and $\psi = \zeta$ while in the bulk, $u = u_{eo}$ and $\psi = 0$) which results in the Helmholtz-Smoluchowski equation [127];

$$u_{eo} = -\frac{\epsilon_r \epsilon_0 \zeta}{\eta} E_x \quad (1.15)$$

For this equation to apply, the channel width a should be much larger than the Debye length λ_D , there should be no concentration gradient along the width of the channel and the surface conduction contribution should be negligible compared to the bulk [128]. For channels with a small diameter (when $a \gg \lambda_D$) the electro-osmotic contribution to the total flow becomes significant.

In ED, electro-osmosis in the membrane pores results in water being transported through the membrane alongside the transport of ions. This water transport reduces the efficiency of the separation as it reduces the concentration of the concentrate while it increases the concentration in the dilute stream. By tuning the material properties of the membrane, this water transport can be minimized [34].

1.4.2 Electro-osmosis of the second kind

In the description of concentration polarization and the emergence of the limiting current density, charge neutrality outside of the electric double layer was given

as a result of the potential distribution in the solution. For the understanding of electro-osmosis of the second kind [95, 96] (or induced charge electro-osmosis [129, 130]), this charge neutrality is not necessarily present [131]. In this type of electroconvection, a space charge outside the equilibrium double layer is induced by the application of an external electric field [82, 95, 129, 130]. This electric field will in turn act on the induced charge in the solution, resulting in convective motion of the fluid.

The emergence of an extended space charge region in the vicinity of a charge selective interface under the application of an electric field is the result of different spatial distributions of counter ions and co-ions in the diffusive boundary layer, as described by the Poisson-Boltzmann equation [95]. By increasing the current above the limiting current, the electroneutral diffusion boundary layer (DBL, not to be confused with the diffuse layer in the electric double layer) is reduced while the space charge region adjacent to the membrane is increased in size, resulting in a non-equilibrium situation, see Figure 1.8(b) [90, 132]. In the extended space charge (ESC) region, the concentration of cations (c_+) and anions (c_-) are not equal. The non-equilibrium extended space charge region has a much larger dimension (up to 10 μm in size) than the equilibrium electrical double layer (usually in the order of tens of nm) [82, 96].

If there is a tangential component of the electric field acting on this space charge, the fluid will exhibit an induced convective motion. The tangential component of the electric field can emerge, amongst others, from inhomogeneities in the membrane interface, a not perfectly flat membrane surface or local concentration differences in the solution adjacent to the membrane [88, 95, 106]. The tangential component of the electric field results in a tangential component of the fluid flow adjacent to the membrane, referred to as non-equilibrium electro-osmotic slip [88, 133] disturbing the diffusion boundary layer. As a result of this induced flow, pressure gradients build up in the system which induce vortical movement of the fluid, as is schematically shown in Figure 1.8(c). These vortices mix the extended space charge region with part of the diffusion boundary layer and result in convective transport of ions towards the membrane interface. In systems with a periodic heterogeneity at the membrane interface and a perpendicular applied electric field, this will result in the formation of counter-rotating vortex pairs since the heterogeneities will bend the electric field in opposite directions [42, 98, 134].

1.4.3 Electroconvection at membranes

On perfectly flat, homogeneous membranes, electroconvection only emerges above a critical voltage in the form of electrokinetic instabilities (electro-osmosis of the second kind) which result from an induced inhomogeneity in the solution at the membrane such as a concentration or pressure gradient [88], since there is no intrinsic tangential component of the electric field (Figure 1.9(a)). On the

Figure 1.8 — Simplified schematic of electro-osmosis of the second kind near a cation exchange membrane (CEM). The electromigration force on the cations is towards the cathode (left), while the electromigration force on the anions is towards the anode (right). (a) As a result of the selective ion transport through the interface a concentration gradient is developing in the diffusion boundary layer (DBL), resulting in diffusive forces on cations and anions towards the CEM. When the current is lower than the limiting current, an equilibrium situation in which a constant flux of ideally only cations is transported through the membrane. (b) At elevated local field strengths, an extended space charge (ESC) layer develops at the membrane interface, in which the cation concentration (solid line) is higher than the anion concentration (dotted line). The applied electric field acts on this space charge. (c) As a result of the forces acting on the space charge, vortices are emerging. These vortices mix the ESC and yield an additional supply of ions towards the membrane.

Figure 1.9 — Electric field distribution (indicated by the arrows) in (a) homogeneous and (b) heterogeneous membrane interface in a perfectly homogeneous electrolyte. In a homogeneous system, the field lines are parallel to each other from the anode to cathode and no electric field component tangential to the membrane is arising. In heterogeneous membranes with a conductivity gradient, the electric field lines are bent resulting in a tangential component present at the membrane interface.

contrary, for heterogeneous membranes (or membranes with a curvature) at any voltage an electroconvective contribution will emerge at the membrane interface, in the form of a electro-osmotic flow of the first kind. At heterogeneous charge selective interfaces, a non-normal component of the electric field is intrinsically present [101], as is schematically depicted in Figure 1.9(b). As a result of the curvature in the electric field and the existence of the double layer on the charge selective interface, an electro-osmotic movement is induced along the membrane interface. This electro-osmotic fluid movement enhances the onset of fluid flow in the bulk solution and promotes ion transport towards the charge selective interface and could be of use in ED stacks. By structuring of membranes, the interplay between the electric field and the membrane can be optimized, to optimize the efficiency of ion transport processes [134].

More recently, an equilibrium electroconvective instability at charge selective interfaces was introduced [135]. In this mechanism a discontinuity of the electrochemical potential of the counter ions at the membrane interface is responsible for the development of the instability. For this type of electroconvection, no extended space charge is required for the formation of the fluid movement.

1.5 Governing equations

In the previous sections, different aspects of mass and momentum transport in aqueous systems adjacent to charge selective interfaces have been introduced. To be able to mathematically describe the transport of ions in the solution adjacent to a charge selective interface a coupled set of equations describing the mass transport, electric field distribution and momentum transport is required.

For the description of mass transport and more specifically the ion transport

in the system the Nernst-Planck (NP) equation can be formulated [84–86]. Ion transport in the fluid can occur in three different ways; (i) convection, (ii) migration in the electric field and (iii) diffusion as a result of a concentration or temperature gradient. Assuming a dilute solution with a relatively low concentration c_i without any temperature gradients, the Nernst-Planck equation reads:

$$\mathbf{J}_i = c_i \mathbf{u} - \nu_i z_i F c_i \nabla V - D_i \nabla c_i \quad (1.16)$$

The velocity $\mathbf{u}$ consists of components perpendicular and tangential to the membrane interface. In our description of charge transport, the flux perpendicular to the membrane is of interest. Convection in the direction perpendicular to the membrane with velocity u consists of both gravitational and electro-convection and is usually minimal in traditional ED stacks. Convection in the direction tangential v to the membrane, as a result of the cross flow velocity of the fluid through the stack is much larger. In these circumstances, the only significant contribution to convective ion transport through the membrane is electro-osmosis through the membrane which is negligible in comparison to the other terms of the Nernst-Planck equation [120]. If the convective term is neglected, the concentration profile in the boundary layer adjacent to the membrane reduces to a linear profile as indicated by the dashed line in Figure 1.6. Migration is a result of the electric potential V driving ions with a certain charge z_i and mobility $\nu_i = D_i/RT$ through the system. Diffusion results from a concentration gradient ∇c_i in the system, and is expressed by Fick's law in which the diffusivity of the ions D_i [m^2/s] is incorporated. Diffusivity is assumed to be independent of concentration in this equation, which holds for dilute binary systems. As there is a conservation of charge in the system, the continuity equation (Equation 1.17) is also applicable to the system.

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{J}_i \quad (1.17)$$

To be able to solve this equation to obtain ion fluxes and concentrations, some additional equations describing the distribution of potential V and the velocity field $\mathbf{u}$ are required. For the description of the potential distribution, the Poisson equation (Equation 1.18) applies. In this equation, $\rho_e = eN_A(c_+ - c_-)$ [C/m^3] is the electric charge density as a result of the (potentially) non-equal concentrations of cations (c_+) and anions (c_-) where $e = 1.609 \times 10^{-19}$ C is the elementary charge and $N_A = 6.022 \times 10^{23}$ #/mol is Avogadro's number. $\epsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of a vacuum and ϵ_r [–] is the relative permittivity of the medium.

$$\nabla \cdot (\epsilon_r \epsilon_0 \nabla V) = -\rho_e \quad (1.18)$$

For the description of the velocity field, the incompressible Navier-Stokes equation that describes the conservation of momentum in a fluid is used (Equation 1.19) [136]. In ion transport systems there are external body forces, such as the electrical body force $\rho_e \mathbf{E}$ resulting from space charges in the system and the gravitational force $\rho_m \mathbf{g}$, as a result of density gradients in the system. These body forces are balanced by the conservation of momentum through a (viscous) diffusion term $\nabla \cdot (\mu \nabla \mathbf{u})$ and a pressure gradient ∇p in the system. μ [kg/(s m)] is the viscosity of the fluid, ρ_m [kg/m³] is the density of the fluid and $\mathbf{g}$ [m/s²] is the gravitational field.

$$\rho_m \left[\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right] = -\nabla p + \nabla \cdot (\mu \nabla \mathbf{u}) + \rho_e \mathbf{E} + \rho_m \mathbf{g} \quad (1.19)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (1.20)$$

For aqueous systems, incompressibility is generally assumed ($\rho_m = \text{constant}$) so that Equation 1.20 holds as the continuity equation. If salt concentration gradients are sufficiently large to cause gradients in density, the Boussinesq approximation [137] is used.

With the combination of the Poisson, Nernst-Planck and Navier-Stokes equations the transport of mass and momentum can be described, as well as the electric field distribution. A full solution of the electric, velocity and ion concentration fields can be obtained by numerically solving these equations assuming velocities are lower than the speed of sound. Important implicit assumptions in these equations are the absence of temperature gradients in the system and the absence of the formation of heat in the system in general. For the description of these effects, an additional energy balance can be formulated (Equation 1.21), in which k [W/(m K)] is the thermal conductivity of the liquid, c_p [J/(kg K)] is the specific heat of the solution and a source term resulting from Joule heating $\mathbf{i} \cdot \mathbf{E}$ is introduced. For membranes, $\mathbf{i}$ and $\mathbf{E}$ are not necessarily in the same direction (meaning you can have “negative” Joule heating as well) and overall Joule heating will only be relevant for high currents or high electric field strengths.

$$\rho_m c_p \mathbf{u} \cdot \nabla T = \nabla \cdot (k \nabla T) + \mathbf{i} \cdot \mathbf{E} \quad (1.21)$$

Now that we have a complete mathematical description of the system of interest, the influence of different boundary conditions and environmental variables can be investigated. Many numerical studies [51, 56, 88, 90, 128, 132, 138–148] have been conducted and have shown the possible development of electroconvection and gravitational convection in the fluid layer adjacent to a charge selective interface, resulting in an increased ion flux through the membrane.

1.5.1 Influence of temperature and temperature gradients

In the governing equations introduced here, physical properties of both the ions and the solvent, such as diffusivity, thermal conductivity and viscosity are required for a meaningful solution. These properties are usually available in literature for common species and at ambient conditions. However, most of these properties are dependent on environmental variables such as temperature and pressure [149] and thus the process conditions are of (a potentially large) influence on the resulting concentration and velocity profiles.

If the temperature in the system is increased, the diffusivity of ions is increased while the viscosity of the solution is decreased [149]. As a result of this, the resistance to charge transport, both through electromigration and convection is reduced and higher currents can be obtained when the driving potential is kept constant. At higher temperatures the limiting current density is therefore increased [120], which can be experimentally measured. Gradients in temperature also affect the system and cause gradients in viscosity, permittivity and diffusivity inside the system. If the temperature in electrodialysis systems is changed, this will thus alter charge transport in the system [150], as well as the solvent transport. In general, at higher temperatures an increased flux of ions is expected as a result of the lower viscosity and higher diffusivity of ions in the solution and the subsequent effect of this in the Nernst-Planck equation [151, 152].

Apart from having an influence on the properties of the solvent and the solute, the temperature can also have an influence on the membrane. Membrane resistance is reduced as a function of temperature [153], and membrane permselectivity generally reduces with increasing temperature as well [154]. The diffusion of ions inside the membrane is increasing with temperature, as was the case for the diffusion of ions in the solution [155, 156]. For the conductivity of Nafion membranes [157], an optimum temperature is found, while the water content and diffusivity of the membrane is a function of temperature as well [157, 158].

Thermodiffusion and thermo-osmosis

In non-isothermal systems, a thermodiffusion (or thermophoretic) ion flux is established through the membrane as a result of the temperature gradient [159–161]. These effects are particularly significant at low applied potentials and can enhance the ion transport in electrodialysis systems. The thermodiffusive flux yields a thermoelectric potential difference [162–164], which is small in comparison to a typical applied potential, but can be significant in the case of large temperature differences or small applied electric fields. To describe thermodiffusive transport, a species thermodiffusion coefficient $D_{T,i}$ is required [159], which is incorporated

in the Nernst-Planck equations, yielding Equation 1.22.

$$\mathbf{J}_i = c_i \mathbf{u} - \nu_i z_i F c_i \nabla V - D_i \nabla c_i - D_{T,i} \nabla T \quad (1.22)$$

Additionally, a temperature gradient can induce a thermo-osmotic flux of solvent at and through the membrane interface [159, 165–167]. In this phenomenon, fluid moves as a result of an imposed temperature gradient, so that the total entropy of the system is increased [168]. The flux of solvent is increased linearly with the imposed temperature gradient and is usually small when compared to the electro-osmotic water flux [169]. The direction and magnitude of the thermo-osmotic transport are dependent on the system and membrane properties, and the thermo-osmotic water transport number t_w is different for all systems [168].

1.6 Scope and outline of this thesis

To describe macro-scale behaviour of electrodialysis systems, fundamental understanding of the phenomena happening in the microscopic boundary layer is crucial. In this research, electrohydrodynamic phenomena in the vicinity of charge selective interfaces are investigated at the microscopic scale with the goal of relating to the macro-scale performance. Using a combination of experiments on different length scales and numerical modelling of simple systems, different aspects of charge transport in the different operating regimes of ED are investigated.

In the first part of this thesis, the influence of temperature (gradients) on charge transport is investigated both numerically and experimentally. In the second part of this thesis, different microfluidic systems containing charge selective interfaces are developed to investigate the influence of membrane geometry and flow configurations on ion transport. Electrical characterization is done for all systems and ion concentrations are measured using various techniques. For visualization of transport phenomena in these different microfluidic systems, multiple experimental techniques are applied, such as fluorescence microscopy, particle tracking and fluorescent lifetime imaging.

Chapter 2 describes the development of a model consisting of non-isothermal Poisson-Nernst-Planck (PNP) and Navier-Stokes (NS) equations. With this model, we investigate the influence of temperature and temperature gradients on ion selectivity of symmetric and asymmetric nanochannels. Selectivity of these nanochannels is found to be enhanced if a temperature gradient is aligned with the applied electric field and the asymmetry of the nanochannel. This lead to the idea of investigating the effect of temperature gradients experimentally, as is described in **Chapter 3** and **Chapter 4**. In these chapters, two different lab scale electrodialysis set-ups have been used in order to investigate the effect of temperature and temperature gradients under varying conditions in electrodialysis

stacks. The effect of temperature and temperature gradients on ion transport in the Ohmic regime of both ED and reverse electrodialysis processes is investigated in **Chapter 3**. Higher efficiencies are found at elevated temperatures, but there was no significant effect of the temperature gradient on the separation of ions in the Ohmic regime. The influence of temperature and temperature gradients on ED in the limiting regime is discussed in **Chapter 4**, where we also investigate what the influence of temperature is on ED utilizing a mixture of mono- and divalent ions. Contrary to the Ohmic results, the boundary layer that occurs in the limiting current regime is sensitive to temperature gradients. System efficiency is found to be dependent on the direction of the temperature gradient in the limiting current regime. Competitive transport between mono- and divalent ions is enhanced when temperature gradients are applied.

The development of a microfluidic electrodialysis platform containing alternating anion and cation exchange hydrogels is described in **Chapter 5**. In this chapter, the proof-of-principle of this platform is described, showing that we are able to obtain concentrated and diluted streams from our device. These devices can be used for visualization of ion concentration profiles and the different modes of transport. In **Chapter 6**, we utilized this platform in order to investigate the influence of hydrogel geometry and therefore the electric field distribution on the resulting ion depletion zones and transport phenomena. We have compared three different geometries of the hydrogel pattern, to be able to distinguish between heterogeneous and homogeneous interfaces. The geometry is found to be of large influence, as a result of the existence of inhomogeneous electric fields in systems with local conductivity and permittivity gradients. These inhomogeneous fields give rise to an electro-osmotic contribution of ions towards the charge selective hydrogels, increasing the total ion transport in the system.

In **Chapter 7** a glass based microfluidic system containing charge selective nanochannels is employed for the investigation of the effect of confinement on electrohydrodynamic effects near a charge selective interface. Flow patterns are visualized using microparticles and local flow velocities in electrokinetic vortices are measured. The size of the ion depletion zones is reduced with increased distance from the driving electrodes, as a result of the highly reduced local electric potential further from the electrodes. Vortex growth and local flow velocity are highly dependent on the location of the nanochannels in the applied electric field. This has implications for the fabrication of microfluidic devices and the interpretation of experimental results in which the electric field is not applied normally to the charge selective interface, as well as for the performance of ED stacks.

Chapter 8 is a discussion of the implications of this work for the field of membrane science and provides an outlook on interesting questions for future research directions. Different charge selective interfaces such as porous silicon

and highly ordered 3D nanostructures are of interest for the investigation of the influence of geometry on charge transport. Simple experimental systems for the investigation of temperature gradients in charge selective capillaries are proposed. Implications of this work for charge transport in fuel cells and sensing applications are discussed as well.

References

- [1] M. Winter and R. J. Brodd, *What are batteries, fuel cells, and supercapacitors?*, Chem. Rev. **104**, 4245 (2004).
- [2] E. Bakker, P. Bühlmann, and E. Pretsch, *Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics*, Chem. Rev. **97**, 3083 (1997).
- [3] J. Wilson, B. Cooke, W. Mandersloot, and S. Wiechers, The electrodialysis process in *Demineralization by electrodialysis*, edited by J. Wilson (Butterworths Publications LTD, 1962), pp. 1–47.
- [4] R. Lacey, Basis of Electromembrane Processes in *Industrial processing with membranes*, edited by R. Lacey and S. Loeb (Wiley-Interscience, 1972), pp. 3–20.
- [5] H. Strathmann, *Electrodialysis, a mature technology with a multitude of new applications*, Desalination **264**, 268 (2010).
- [6] K. H. Meyer and W. Straus, *La perméabilité des membranes VI. Sur le passage du courant électrique à travers des membranes sélectives*, Helvetica Chimica Acta **23**, 795 (1940).
- [7] E. Manegold and C. Kalauch, *Über kapillarsysteme: XXII die Wirksamkeit verschiedener Reinigungsmethoden (Filtration, Dialyse, Elektrolyse und Ihre Kombinationen)*, Kolloid-Z **86**, 93 (1939).
- [8] J. Powell and M. Guild, Salinity problems in the arid zones: Field operation of electric membrane equipment for water desalinating in *Proceedings of the Teheran symposium*, edited by UNESCO (1961), pp. 363–370.
- [9] A. T. Fane, R. Wang, and Y. Jia, Membrane technology: Past, present and future in *Membrane and desalination technologies*, edited by L. K. Wang, J. P. Chen, Y.-T. Hung, and N. K. Shamma (Springer, 2011), pp. 1–45.
- [10] W. A. McRae, Electroseparations, electrodialysis in *Kirk-Othmer Encyclopedia of Chemical Technology*,
- [11] Y. Tanaka, Chapter 12: Electrodialysis in *Ion exchange membranes*, 2nd ed., edited by Y. Tanaka (Elsevier, Amsterdam, 2015), pp. 255 – 293.
- [12] L. Shaffer and M. Mintz, Chapter 6: Electrodialysis in *Principles of desalination*, edited by K. Spiegler (Academic Press, 1966), pp. 199 – 289.
- [13] S. Tuwiner, Chapter 13: Electrodialysis in *Diffusion and membrane tech-*

- nology*, edited by S. Tuwiner (Reinhold Publishing Corporation, 1962), pp. 237 – 286.
- [14] P. Długołęcki, P. Ogonowski, S. J. Metz, M. Saakes, K. Nijmeijer, and M. Wessling, *On the resistances of membrane, diffusion boundary layer and double layer in ion exchange membrane transport*, J. Memb. Sci. **349**, 369 (2010).
 - [15] V. Levich, Chapter 6: Passage of Current Through Electrolytic Solutions in *Physicochemical hydrodynamics*, 2nd ed., edited by L. Scriven (Prentice-Hall, Inc., 1962), pp. 231 – 371.
 - [16] R. Probstein, Chapter 3: Equations of Change in *Physicochemical hydrodynamics: An introduction*, 2nd ed., edited by R. Probstein (John Wiley & Sons, Inc., 1994), pp. 31–51.
 - [17] R. Probstein, Chapter 6: Solutions of Electrolytes in *Physicochemical hydrodynamics: An introduction*, 2nd ed., edited by R. Probstein (John Wiley & Sons, Inc., 1994), pp. 165 – 207.
 - [18] N. Lakshminarayanaiah, Chapter 5: Phenomena due to an Applied Electric Field in *Transport phenomena in membranes*, edited by N. Lakshminarayanaiah (Academic Press, Inc., 1969), pp. 224 – 292.
 - [19] N. Lakshminarayanaiah, Chapter 3: Basic Principles in *Transport phenomena in membranes*, edited by N. Lakshminarayanaiah (Academic Press, Inc., 1969), pp. 58 – 128.
 - [20] S. Tuwiner, Chapter 4: Electrolytes in *Diffusion and membrane technology*, edited by S. Tuwiner (Reinhold Publishing Corporation, 1962), pp. 77 – 90.
 - [21] Y. Tanaka, Chapter 3: Theory of Teorell, Meyer, and Sievers (TMS Theory) in *Ion exchange membranes*, 2nd ed., edited by Y. Tanaka (Elsevier, Amsterdam, 2015), pp. 67 – 73.
 - [22] H. Strathmann, Membrane Separation Processes in *Ullmann's encyclopedia of industrial chemistry* (Wiley-VCH Verlag GmbH & Co. KGaA, 2000).
 - [23] Y. Tanaka, Chapter 1: Preparation of Ion Exchange Membranes in *Ion exchange membranes*, 2nd ed., edited by Y. Tanaka (Elsevier, Amsterdam, 2015), pp. 3 – 28.
 - [24] F. Helfferich, Chapter 8: Ion Exchange Membranes in *Ion exchange*, Dover ed., edited by F. G. Helfferich (Dover Publications, 1995), pp. 339 – 420.
 - [25] R. B. Schoch, J. Han, and P. Renaud, *Transport phenomena in nanofluidics*, Rev. Mod. Phys. **80**, 839 (2008).
 - [26] H.-C. Chang, Chapter 2: Classical Equilibrium Theory Due to Surface Charges in *Electrokinetically driven microfluidics and nanofluidics*, edited by H.-C. Chang and L. Yeo (Cambridge University Press, 2010), pp. 35 – 75.
 - [27] T. Xu, *Ion exchange membranes: State of their development and perspective*, J. Memb. Sci. **263**, 1 (2005).

- [28] F. G. Donnan, *Theorie der Membrangleichgewichte und membranpotentiale bei vorhandensein von nicht dialysierenden Elektrolyten. ein Beitrag zur physikalisch-chemischen Physiologie.*, Zeitschrift für Elektrochemie und angewandte physikalische Chemie **17**, 572 (1911).
- [29] K. H. Meyer and J.-F. Sievers, *La perméabilité des membranes I. Théorie de la perméabilité ionique*, Helvetica Chimica Acta **19**, 649 (1936).
- [30] K. H. Meyer and J.-F. Sievers, *La perméabilité des membranes. II. Essais avec des membranes sélectives artificielles*, Helvetica Chimica Acta **19**, 665 (1936).
- [31] T. Teorell, *An attempt to formulate a quantitative theory of membrane permeability*, Proc. Soc. Exptl. Biol. **33**, 282 (1935).
- [32] F. Donnan, *Die genaue Thermodynamik der Membrangleichgewichte*, Zeitschr. Phys. Chem. **168A**, 369 (1934).
- [33] T. Sata, Chapter 2: Theory of Membrane Phenomena in Ion Exchange Membranes in *Ion exchange membranes: Preparation, characterization, modification and application*, edited by T. Sata (Royal Society of Chemistry, 1962), pp. 7–33.
- [34] Y. Tanaka, Chapter 2: Fundamental Properties of Ion Exchange Membranes in *Ion exchange membranes*, 2nd ed., edited by Y. Tanaka (Elsevier, Amsterdam, 2015), pp. 29 – 65.
- [35] S. Tuwiner, Chapter 9: Diffusion within membranes in *Diffusion and membrane technology*, edited by S. Tuwiner (Reinhold Publishing Corporation, 2002), pp. 170 – 179.
- [36] N. Lakshminarayanaiah, Chapter 4: Membrane Phenomena due to a Gradient of Chemical or Electrochemical Potential in *Transport phenomena in membranes*, edited by N. Lakshminarayanaiah (Academic Press, Inc., 1969), pp. 129 – 223.
- [37] A. H. Galama, J. W. Post, M. A. Cohen Stuart, and P. M. Biesheuvel, *Validity of the Boltzmann equation to describe Donnan equilibrium at the membrane-solution interface*, J. Membr. Sci. **442**, 131 (2013).
- [38] G. Barnes and I. R. Gentle, Chapter 9: The liquid-solid interace: adsorption; colloids in *Interfacial science: An introduction*, 2nd ed., edited by G. Barnes and I. R. Gentle (Oxford University Press, 2011), pp. 242 – 288.
- [39] O. Stern, *Zur theorie der elektrolytischen doppelschicht*, Z. Electrochem. **30**, 508 (1924).
- [40] D. C. Grahame, *The electrical double layer and the theory of electrocapillarity*, Chemical Reviews **41**, 441 (1947).
- [41] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal dispersions* (Cambridge University Press, Cambridge; New York, 1989).
- [42] S. J. Kim, Y.-C. Wang, J. H. Lee, H. Jang, and J. Han, *Concentration polarization and nonlinear electrokinetic flow near a nanofluidic channel*,

- Phys. Rev. Lett. **99**, 044501 (2007).
- [43] H.-C. Chang and G. Yossifon, *Understanding electrokinetics at the nanoscale: A perspective.*, Biomicrofluidics **3**, 12001 (2009).
 - [44] H.-C. Chang, G. Yossifon, and E. A. Demekhin, Nanoscale electrokinetics and microvortices: How microhydrodynamics affects nanofluidic ion flux in *Annu. Rev. Fluid Mech.*, edited by S. H. Davis and P. Moin (2012), Vol. 44, pp. 401–426.
 - [45] G. Yossifon, P. Mushenheim, Y.-C. Chang, and H.-C. Chang, *Eliminating the limiting-current phenomenon by geometric field focusing into nanopores and nanoslots*, Phys. Rev. E **81**, 046301 (2010).
 - [46] G. Yossifon and H.-C. Chang, *Changing nanoslot ion flux with a dynamic nanocolloid ion-selective filter: Secondary overlimiting currents due to nanocolloid-nanoslot interaction*, Phys. Rev. E **81**, 066317 (2010).
 - [47] Q. Yu and Z. Silber-Li, *Measurements of the ion-depletion zone evolution in a micro/nano-channel*, Microfluid. Nanofluidics **11**, 623 (2011).
 - [48] S. Yu, T.-J. Jeon, and S. M. Kim, *Active micromixer using electrokinetic effects in the micro/nanochannel junction*, Chem. Eng. J. **197**, 289 (2012).
 - [49] Y. Green and G. Yossifon, *Dynamical trapping of colloids at the stagnation points of electro-osmotic vortices of the second kind*, Phys. Rev. E **87**, 033005 (2013).
 - [50] C. Lee, C. Cottin-Bizonne, A. L. Biance, P. Joseph, L. Bocquet, and C. Ybert, *Osmotic flow through fully permeable nanochannels*, Phys. Rev. Lett. **112**, 244501 (2014).
 - [51] A. M. Benneker, H. D. Wendt, R. G. H. Lammertink, and J. A. Wood, *Influence of temperature gradients on charge transport in asymmetric nanochannels*, Phys. Chem. Chem. Phys. **19**, 28232 (2017).
 - [52] P. Searson, *Porous silicon membranes*, Appl. Phys. Lett. **59**, 823 (1991).
 - [53] S. Sukas, R. M. Tiggelaar, G. Desmet, and H. J. G. E. Gardeniers, *Fabrication of integrated porous glass for microfluidic applications*, Lab Chip **13**, 3061 (2013).
 - [54] S. J. Kim, Y.-A. Song, and J. Han, *Nanofluidic concentration devices for biomolecules utilizing ion concentration polarization: theory, fabrication, and applications*, Chem. Soc. Rev. **39**, 912 (2010).
 - [55] T. A. Zangle, A. Mani, and J. G. Santiago, *Theory and experiments of concentration polarization and ion focusing at microchannel and nanochannel interfaces.*, Chem. Soc. Rev. **39**, 1014 (2010).
 - [56] R. Kwak, P. Van Sang, K. M. Lim, and J. Han, *Shear flow of an electrically charged fluid by ion concentration polarization: Scaling laws for electroconvective vortices*, Phys. Rev. Lett. **110**, 114501 (2013).
 - [57] R. Kwak, V. S. Pham, and J. Han, *Sheltering the perturbed vortical layer of electroconvection under the shear flow*, J. Fluid. Mech. **813**, 799 (2017).

- [58] M. Kim, M. Jia, and T. Kim, *Ion concentration polarization in a single and open microchannel induced by a surface-patterned perm-selective film*, Analyst **138**, 1370 (2013).
- [59] S. J. Kim, S. H. Ko, K. H. Kang, and J. Han, *Direct seawater desalination by ion concentration polarization*, Nat. Nanotechnol. **5**, 297 (2010).
- [60] B. D. MacDonald, M. M. Gong, P. Zhang, and D. Sinton, *Out-of-plane ion concentration polarization for scalable water desalination.*, Lab Chip **14**, 681 (2014).
- [61] P.-H. Chiu, C.-C. Chang, and R.-J. Yang, *Electrokinetic micromixing of charged and non-charged samples near nano-microchannel junction*, Microfluid. Nanofluidics **14**, 839 (2013).
- [62] B. Gumuscu, A. S. Haase, A. M. Benneker, M. A. Hempenius, A. van den Berg, R. G. H. Lammertink, and J. C. T. Eijkel, *Desalination by electro-dialysis using a stack of patterned ion-selective hydrogels on a microfluidic device*, Adv. Funct. Mater. **26**, 8685 (2016).
- [63] Y.-C. Wang, A. L. Stevens, and J. Han, *Million-fold preconcentration of proteins and peptides by nanofluidic filter.*, Anal. Chem. **77**, 4293 (2005).
- [64] P. Mao and J. Han, *Massively-parallel ultra-high-aspect-ratio nanochannels as mesoporous membranes.*, Lab Chip **9**, 586 (2009).
- [65] E. Choi, K. Kwon, D. Kim, and J. Park, *An electrokinetic study on tunable 3D nanochannel networks constructed by spatially controlled nanoparticle assembly.*, Lab Chip **15**, 512 (2014).
- [66] A. M. Benneker, J. A. Wood, P. A. Tsai, and R. G. H. Lammertink, *Observation and experimental investigation of confinement effects on ion transport and electrokinetic flows at the microscale*, Sci. Rep. **6**, 37236 (2016).
- [67] J. C. De Valena, R. M. Wagterveld, R. G. H. Lammertink, and P. A. Tsai, *Dynamics of microvortices induced by ion concentration polarization*, Phys. Rev. E. **92**, 031003(R) (2015).
- [68] S. M. Rubinstein, G. Manukyan, A. Staicu, I. Rubinstein, B. Zaltzman, R. G. H. Lammertink, F. Mugele, and M. Wessling, *Direct observation of a nonequilibrium electro-osmotic instability*, Phys. Rev. Lett. **101**, 236101 (2008).
- [69] S. J. Kim, S. H. Ko, R. Kwak, J. D. Posner, K. H. Kang, and J. Han, *Multi-vortical flow inducing electrokinetic instability in ion concentration polarization layer*, Nanoscale **4**, 7406 (2012).
- [70] I. Cho, G. Y. Sung, and S. J. Kim, *Overlimiting current through ion concentration polarization layer: hydrodynamic convection effects.*, Nanoscale **6**, 4620 (2014).
- [71] S. Nam, I. Cho, J. Heo, G. Lim, M. Z. Bazant, D. J. Moon, G. Y. Sung, and S. J. Kim, *Experimental verification of overlimiting current by surface*

- conduction and electro-osmotic flow in microchannels, *Phys. Rev. Lett.* **114**, 114501 (2015).
- [72] C.-C. Chang, C.-P. Yeh, and R.-J. Yang, *Ion concentration polarization near microchannel-nanochannel interfaces: Effect of pH value*, *Electrophoresis* **33**, 758 (2012).
- [73] S. Hanasoge and F. J. Diez, *Vortex chain formation in regions of ion concentration polarization*, *Lab Chip* **15**, 3549 (2015).
- [74] S. J. Kim, L. D. Li, and J. Han, *Amplified electrokinetic response by concentration polarization near nanofluidic channel*, *Langmuir* **25**, 7759 (2009).
- [75] F. Helfferich, Chapter 7: Electrochemical properties in *Ion exchange*, Dover ed., edited by F. G. Helfferich (Dover Publications, 1995), pp. 323 – 338.
- [76] R. Probstein, Chapter 2: Transport in Fluids in *Physicochemical hydrodynamics: An introduction*, 2nd ed., edited by R. Probstein (John Wiley & Sons, Inc., 1994), pp. 9 – 30.
- [77] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Chapter 17: Diffusivity and the Mechanisms of Mass Transport in *Transport phenomena (second edition)*, 2nd ed., edited by R. B. Bird, W. E. Stewart, and E. N. Lightfoot (John Wiley & Sons, Inc., New York, 2002), pp. 533–536.
- [78] A. M. Peers, *General discussion*, *Discuss. Faraday Soc.* **21**, 124 (1956).
- [79] D. Cowan and J. Brown, *Effect of turbulence on limiting current in electro-dialysis cells*, *Ind. Eng. Chem.* **51**, 1445 (1959).
- [80] W. Kooistra, *Characterization of Ion Exchange Membranes by Polarization Curves*, *Desalination* **2**, 139 (1967).
- [81] K. S. Spiegler, *Polarization at ion exchange membrane-solution interfaces*, *Desalination* **9**, 367 (1971).
- [82] I. Rubinstein and L. Shtilman, *Voltage against current curves of cation exchange membranes*, *J. Chem. Soc., Faraday Trans. 2* **75**, 231 (1979).
- [83] Y. Tanaka, Chapter 6: Concentration Polarization in *Ion exchange membranes*, 2nd ed., edited by Y. Tanaka (Elsevier, Amsterdam, 2015), pp. 101 – 121.
- [84] W. Nernst, *Zur Kinetik der in Lösung befindlichen Körper*, *Zeitschr. Phys. Chem.* **2U**, 613 (1888).
- [85] W. Nernst, *Die elektromotorische Wirksamkeit der Ionen*, *Zeitschr. Phys. Chem.* **4U**, 129 (1889).
- [86] M. Planck, *Ueber die Potentialdifferenz zwischen zwei verdünnten Lösungen binärer Electrolyte*, *Annalen der Physik* **276**, 561 (1890).
- [87] I. Rubinstein, E. Staude, and O. Kedem, *Role of the membrane surface in concentration polarization at ion-exchange membrane*, *Desalination* **69**, 101 (1988).
- [88] I. Rubinstein and B. Zaltzman, *Electro-osmotically induced convection at a*

- permselective membrane*, Phys. Rev. E **62**, 2238 (2000).
- [89] I. Rubinstein, B. Zaltzman, and I. Lerman, *Electroconvective instability in concentration polarization and nonequilibrium electro-osmotic slip*, Phys. Rev. E **72**, 011505 (2005).
- [90] I. Rubinstein and B. Zaltzman, *Extended space charge in concentration polarization.*, Adv. Colloid Interface Sci. **159**, 117 (2010).
- [91] V. J. Frilette, *Electrogravitational transport at synthetic ion exchange membrane surfaces*, J. Phys. Chem. **61**, 168 (1957).
- [92] B. Gavish and S. Lifson, *Membrane polarisation at high current densities*, J. Chem. Soc., Faraday Trans. 1 **75**, 463 (1979).
- [93] Y. I. Kharkats, *Theory of the exaltation effect and the effect of correlation exaltation of migration current*, J. Electroanal. Chem. **105**, 97 (1979).
- [94] Y. I. Kharkats and A. V. Sokirko, *Theory of the effect of migration current exaltation taking into account dissociation-recombination reactions*, J. Electroanal. Chem. **303**, 27 (1991).
- [95] S. S. Dukhin, *Electrokinetic phenomena of the second kind and their applications*, Adv. Colloid Interface Sci. **35**, 173 (1991).
- [96] N. A. Mishchuk and P. V. Takhistov, *Electroosmosis of the second kind*, Colloids Surfaces A: Physicochem. Eng. Asp. **95**, 119 (1995).
- [97] M. B. Andersen, M. van Soestbergen, A. Mani, H. Bruus, P. M. Biesheuvel, and M. Z. Bazant, *Current-induced membrane discharge*, Phys. Rev. Lett. **109**, 108301 (2012).
- [98] E. V. Dydek, B. Zaltzman, I. Rubinstein, D. S. Deng, A. Mani, and M. Z. Bazant, *Overlimiting current in a microchannel*, Phys. Rev. Lett. **107**, 118301 (2011).
- [99] V. I. Zabolotsky, V. V. Nikonenko, and N. D. Pismenskaya, *On the role of gravitational convection in the transfer enhancement of salt ions in the course of dilute solution electrodialysis*, J. Memb. Sci. **119**, 171 (1996).
- [100] J. J. Krol, M. Wessling, and H. Strathmann, *Concentration polarization with monopolar ion exchange membranes: Current-voltage curves and water dissociation*, J. Memb. Sci. **162**, 145 (1999).
- [101] J. Balster, M. H. Yildirim, D. F. Stamatialis, R. Ibanez, R. G. H. Lammertink, V. Jordan, and M. Wessling, *Morphology and microtopology of cation-exchange polymers and the origin of the overlimiting current*, J. Phys. Chem. B **111**, 2152 (2007).
- [102] R. Kwak, G. Guan, W. K. Peng, and J. Han, *Microscale electrodialysis: Concentration profiling and vortex visualization*, Desalination **308**, 138 (2013).
- [103] F. Maletzki, H.-W. Rosler, and E. Staude, *Ion transfer across electrodialysis membranes in the overlimiting current range: Stationary voltage current characteristics and current noise power spectra under different conditions*

- of free convection*, J. Memb. Sci. **71**, 105 (1992).
- [104] R. Simons, *Water splitting in ion exchange membranes*, Electrochim. Acta **30**, 275 (1985).
 - [105] V. V. Nikonenko, N. D. Pismenskaya, E. I. Belova, P. Sistat, P. Huguet, G. Pourcelly, and C. Larchet, *Intensive current transfer in membrane systems: Modelling, mechanisms and application in electrodialysis*, Adv. Colloid Interface Sci. **160**, 101 (2010).
 - [106] V. V. Nikonenko, A. V. Kovalenko, M. K. Urtenov, N. D. Pismenskaya, J. Han, P. Sistat, and G. Pourcelly, *Desalination at overlimiting currents: State-of-the-art and perspectives*, Desalination **342**, 85 (2014).
 - [107] V. I. Zabolotsky, V. V. Nikonenko, N. D. Pismenskaya, E. V. Laktionov, M. K. Urtenov, H. Strathmann, M. Wessling, and G. H. Koops, *Coupled transport phenomena in overlimiting current electrodialysis*, Sep. Purif. Technol. **14**, 255 (1998).
 - [108] T. R. E. Kressman and F. L. Tye, *The effect of current density on the transport of ions through ion-selective membranes*, Discuss. Faraday Soc. **21**, 185 (1959).
 - [109] R. Simons, *The origin and elimination of water splitting in ion exchange membranes during water demineralisation by electrodialysis*, Desalination **28**, 41 (1979).
 - [110] K. N. Mani, *Electrodialysis water splitting technology*, J. Memb. Sci. **58**, 117 (1991).
 - [111] C. P. Nielsen and H. Bruus, *Transport-limited water splitting at ion-selective interfaces during concentration polarization*, Phys. Rev. E **89**, 042405 (2014).
 - [112] P. Vanysek, Ionic conductivity and diffusion at infinite dilution in *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (2003), pp. 5.76 – 5.77.
 - [113] K. Nagasubramanian, F. P. Chlanda, and K. J. Liu, *Use of bipolar membranes for generation of acid and base - an engineering and economic analysis*, J. Memb. Sci. **2**, 109 (1977).
 - [114] A. Bazinet, L. Lamarche, and D. Ippersiel, *Bipolar-membrane electrodialysis: application of electrodialysis in food industry*, Trends Food Sci. Technol. **9**, 107 (1998).
 - [115] Y. Tanaka, Chapter 7: Water Dissociation in *Ion exchange membranes*, 2nd ed., edited by Y. Tanaka (Elsevier, Amsterdam, 2015), pp. 123 – 159.
 - [116] N. D. Pismenskaya, V. V. Nikonenko, E. I. Belova, G. Y. Lopatkova, P. Sistat, G. Pourcelly, and K. Larshe, *Coupled convection of solution near the surface of ion-exchange membranes in intensive current regimes*, Russ. J. Electrochem. **43**, 307 (2007).
 - [117] E. Cussler, Chapter 4: Free Convection in *Diffusion - mass transfer in fluid*

- systems*, second edition ed., edited by E. Cussler (Cambridge University Press, Cambridge, 1997), pp. 356 – 367.
- [118] J. C. de Valença, A. Kurniawan, R. M. Wagterveld, J. A. Wood, and R. G. H. Lammertink, *Influence of Rayleigh-Bénard convection on electrokinetic instability in overlimiting current conditions*, Phys. Rev. Fluids **2**, 033701 (2017).
- [119] T. Lohaus, N. Herkenhoff, R. Shankar, and M. Wessling, *Feed flow patterns of combined Rayleigh-Bénard convection and membrane permeation*, J. Mem. Sci. (2017).
- [120] Y. Tanaka, Chapter 9: Limiting Current Density in *Ion exchange membranes*, 2nd ed., edited by Y. Tanaka (Elsevier, Amsterdam, 2015), pp. 199 – 214.
- [121] F. F. Reuss, *Sur un nouvel effet de l'électricité galvanique*, Mémoires de la Société Impériale des Naturalistes de Moscou **2**, 327 (1809).
- [122] G. Wiedemann, *Ueber die Bewegung von Flüssigkeiten im Kreise der geschlossenen galvanischen Säule*, Annalen der Physik **163**, 321 (1852).
- [123] S. Wall, *The history of electrokinetic phenomena*, Curr. Opin. Colloid Interface Sci. **15**, 119 (2010).
- [124] S. Tuwiner, Chapter 8: Structure and Properties of Membranes in *Diffusion and membrane technology*, edited by S. Tuwiner (Reinhold Publishing Corporation, 1962), pp. 152 – 179.
- [125] H.-C. Chang and L. Yeo, Chapter 3: Electro-Osmotic Transport in *Electrokinetically driven microfluidics and nanofluidics*, edited by H.-C. Chang (Cambridge University Press, 2010), pp. 76 – 127.
- [126] V. Levich, Chapter 9: Motions of Particles in Electrolytic Solutions in *Physicochemical hydrodynamics*, 2nd ed., edited by L. Scriven (Prentice-Hall, Inc., 1962), pp. 472 – 531.
- [127] M. von Smoluchowski, *Contribution to the theory of electro-osmosis and related phenomena*, Bull. Int. Acad. Sci. Cracovie **3**, 184 (1903).
- [128] C. P. Nielsen and H. Bruus, *Concentration polarization, surface currents, and bulk advection in a microchannel*, Phys. Rev. E **90**, 043020 (2014).
- [129] T. M. Squires and M. Z. Bazant, *Induced-charge electro-osmosis*, J. Fluid Mech. **509**, 217 (2004).
- [130] M. Z. Bazant and T. M. Squires, *Induced-charge electrokinetic phenomena: Theory and microfluidic applications*, Phys. Rev. Lett. **92**, 066101 (2004).
- [131] H.-C. Chang and L. Yeo, Chapter 6: DC Nonlinear electrokinetics due to field-induced double layer polarization in *Electrokinetically driven microfluidics and nanofluidics*, edited by H.-C. Chang (Cambridge University Press, 2010), pp. 184 – 250.
- [132] C. L. Druzgalski, M. B. Andersen, and A. Mani, *Direct numerical simulation of electroconvective instability and hydrodynamic chaos near an ion-selective surface*, Phys. Fluids **25**, 110804 (2013).

-
- [133] I. Rubinstein and B. Zaltzman, *Electro-osmotic slip of the second kind and instability in concentration polarization at electrodialysis membranes*, Math. Models Methods Appl. Sci. **11**, 263 (2001).
 - [134] J. C. de Valena, *Overlimiting current properties at ion exchange membranes* (thesis) (Universiteit Twente, 2017).
 - [135] I. Rubinstein and B. Zaltzman, *Equilibrium electroconvective instability*, Phys. Rev. Lett. **114**, 114502 (2015).
 - [136] C. L. M. H. Navier, *Mmoire sur les lois du mouvement des fluides*, Mem. Acad. Sci. Inst. Fr **6**, 389 (1823).
 - [137] E. A. Spiegel and G. Veronis, *On the Boussinesq approximation for a compressible fluid*, Astrophysical Journal **131**, 442 (1959).
 - [138] M. K. Urtenov, A. M. Uzdenova, A. V. Kovalenko, V. V. Nikonenko, N. D. Pismenskaya, V. I. Vasil’eva, P. Sistat, and G. Pourcelly, *Basic mathematical model of overlimiting transfer enhanced by electroconvection in flow-through electrodialysis membrane cells*, J. Memb. Sci. **447**, 190 (2013).
 - [139] E. Karatay, C. L. Druzgalski, and A. Mani, *Simulation of chaotic electrokinetic transport: Performance of commercial software versus custom-built direct numerical simulation codes*, J. Colloid Interface Sci. **446**, 67 (2015).
 - [140] E. A. Demekhin, V. S. Shelistov, and S. V. Polyanskikh, *Linear and nonlinear evolution and diffusion layer selection in electrokinetic instability*, Phys. Rev. E **84**, 036318 (2011).
 - [141] S. M. Davidson, M. Wessling, and A. Mani, *On the dynamical regimes of pattern-accelerated electroconvection*, Sci. Rep. **6**, 22505 (2016).
 - [142] V. S. Pham, Z. Li, K. M. Lim, J. K. White, and J. Han, *Direct numerical simulation of electroconvective instability and hysteretic current-voltage response of a permselective membrane*, Phys. Rev. E **86**, 046310 (2012).
 - [143] E. A. Demekhin, N. V. Nikitin, and V. S. Shelistov, *Direct numerical simulation of electrokinetic instability and transition to chaotic motion*, Phys. Fluids **25**, 122001 (2013).
 - [144] E. A. Demekhin, N. V. Nikitin, and V. S. Shelistov, *Three-dimensional coherent structures of electrokinetic instability*, Phys. Rev. E **90**, 013031 (2014).
 - [145] H. C. Chang, E. A. Demekhin, and V. S. Shelistov, *Competition between Dukhin’s and Rubinstein’s electrokinetic modes*, Phys. Rev. E **86**, 046319 (2012).
 - [146] A. Mani and M. Z. Bazant, *Deionization shocks in microstructures*, Phys. Rev. E **84**, 061504 (2011).
 - [147] J. Schiffbauer and G. Yossifon, *Role of electro-osmosis in the impedance response of microchannel-nanochannel interfaces*, Phys. Rev. E **86**, 056309 (2012).
 - [148] J. A. Wood, A. M. Benneker, and R. G. H. Lammertink, *Temperature effects*

- on the electrohydrodynamic and electrokinetic behaviour of ion-selective nanochannels*, J. Phys. Condens. Matter **28**, 114002 (2016).
- [149] Fluid Properties *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (2003), pp. 6.1–6.197.
- [150] S. Tseng, Y.-M. Li, C.-Y. Lin, and J.-P. Hsu, *Salinity gradient power: influences of temperature and nanopore size*, Nanoscale **8**, 2350 (2016).
- [151] M. Tedesco, E. Brauns, A. Cipollina, G. Micale, P. Modica, G. Russo, and J. Helsen, *Reverse electrodialysis with saline waters and concentrated brines: A laboratory investigation towards technology scale-up*, J. Memb. Sci. **492**, 9 (2015).
- [152] A. Daniilidis, D. A. Vermaas, R. Herber, and K. Nijmeijer, *Experimentally obtainable energy from mixing river water, seawater or brines with reverse electrodialysis*, Renew. Energy **64**, 123 (2014).
- [153] E. Fontananova, W. Zhang, I. Nicotera, C. Simari, W. van Baak, G. Di Profio, E. Curcio, and E. Drioli, *Probing membrane and interface properties in concentrated electrolyte solutions*, J. Memb. Sci. **459**, 177 (2014).
- [154] Y. Ji and G. M. Geise, *The role of experimental factors in membrane permselectivity measurements*, Ind. Eng. Chem. Res. **56**, 7559 (2017).
- [155] H. L. Yeager and B. Kipling, *Ionic diffusion and ion clustering in a perfluorosulfonate ion-exchange membrane.*, J. Phys. Chem. **83**, 1836 (1979).
- [156] H. L. Yeager and A. Steck, *Cation and water diffusion in nation ion exchange membranes: Influence of polymer structure*, J. Electrochem. Soc. **128**, 1880 (1981).
- [157] P. C. Rieke and N. E. Vanderborgh, *Temperature dependence of water content and proton conductivity in polyperfluorosulfonic acid membranes*, J. Memb. Sci. **32**, 313 (1987).
- [158] Q. H. Guo, P. N. Pintauro, H. Tang, and S. O'Connor, *Sulfonated and crosslinked polyphosphazene-based proton-exchange membranes*, J. Memb. Sci. **154**, 175 (1999).
- [159] Y. Kobatake and H. Fujita, *Osmotic flows in charged membranes. II. Thermo-osmosis*, J. Chem. Phys. **41**, 2963 (1964).
- [160] A. Würger, *Transport in charged colloids driven by thermoelectricity*, Phys. Rev. Lett. **101**, 108302 (2008).
- [161] S. Duhr and D. Braun, *Why molecules move along a temperature gradient*, Proc. Natl. Acad. Sci. **103**, 19678 (2006).
- [162] G. Hills, P. Jacobs, and N. Lakshiminarayanaiah, *Non-isothermal membrane potentials*, Nature **179**, 96 (1957).
- [163] T. Ikeda, *Thermal membrane potential*, J. Chem. Phys. **28**, 166 (1958).
- [164] M. Tasaka, *Thermal membrane potential and thermoosmosis across charged membranes*, Pure & Appl. Chem. **58**, 1637 (1986).
- [165] M. S. Dariel and O. Kedem, *Thermoosmosis in semipermeable membranes*,

- J. Phys. Chem. **79**, 336 (1975).
- [166] K. D. Sandbakk, A. Bentien, and S. Kjelstrup, *Thermoelectric effects in ion conducting membranes and perspectives for thermoelectric energy conversion*, J. Memb. Sci. **434**, 10 (2013).
- [167] M. Tasaka, T. Mizuta, and O. Sekiguchi, *Mass transfer through polymer membranes due to a temperature gradient*, J. Memb. Sci. **54**, 191 (1990).
- [168] V. M. Barragan and S. Kjelstrup, *Thermo-osmosis in membrane systems*, J. Non-Equilibrium Thermodyn. **42**, 217 (2017).
- [169] R. P. Rastogi, K. Singh, and B. Misra, *Themo-osmosis and electro-osmosis of water and electrophoresis of suspensions in water*, Desalination **3**, 32 (1967).

CHAPTER 2

Temperature effects on ion transport in charge selective nanochannels

Abstract — Charge selective nanochannels are used for a variety of applications, such as nanofluidic sensing devices, energy conversion applications and as mimics for conventional membrane systems. In this chapter, we numerically investigate the influence of an applied temperature difference over both uniform (symmetric) and tapered (asymmetric) nanochannels on the resulting charge transport and flow behaviour. Using a temperature-dependent formulation of the coupled Poisson-Nernst-Planck and Navier-Stokes equations, various nanochannel geometries and the influence of temperature on the system behaviour are investigated. Temperature has a large influence on the ion transport, as the diffusivity of ions and viscosity of the solution are strongly affected by temperature. We find that applying a temperature gradient (from high to low) along the electric field and from the large to the small nanochannel inlet enhances the selectivity of the channels even further, while a temperature gradient countering the electric field reduces the selectivity of the nanochannel. Current rectification is enhanced in asymmetric nanochannels if a temperature gradient is applied, independent of the direction of the temperature difference. The degree of rectification depends on the direction of the temperature gradient with respect to the channel geometry and the electric field direction. The enhanced selectivity of nanochannels due to applied temperature gradients could result in more efficient operation in energy harvesting or desalination applications as well as more conventional membrane processes.

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2.1 Introduction

Nanochannels with a characteristic dimension in the order of the Debye length are charge selective due to charge exclusion of co-ions, based on the wall charge of the channel. Ion selective nanochannels [1–3] and nanoslits [4, 5] are a well-established investigation platform, both in experimental and numerical studies of charge transport and electrokinetic effects, in order to improve understanding of various applications [6], such as desalination [7], mixing [8, 9] and energy harvesting [10–13]. Many different aspects of ion and fluid transport in and near nanochannels have been experimentally investigated, amongst which were the effect of pH [14, 15], temperature [16] and concentration gradients [2]. Nanochannels have well-defined fabrication tolerances which is advantageous for characterizing their behaviour when compared to membranes, which typically possess larger pore size distributions and have a more complicated chemical structure. The disadvantages of using nanochannels are the relatively small obtainable currents (down to the pA range) and time consuming fabrication methods [17, 18].

In addition to uniform nanochannels, asymmetric, tapered or conical shaped nanochannels are interesting for different applications, for use as diodes, as mimic to the gating functions of biological ion channels and for microscale energy conversion or nanofluidic sensing devices [19–21]. Different experimental studies have been conducted on geometrically asymmetric nanochannels in which the nanochannel surface characteristics [22, 23] or the environmental conditions such as pH [24] and temperature [25] have been successfully controlled and studied [26, 27], showing amongst others a rectification of the current [28–30]. This rectification implies that changing the the direction of the applied potential gradient (optionally accompanied by other gradients, such as pH or ion concentration) yields a different overall resistance of the nanochannel. As the rectification ratio (the ratio of the resistances between the different electric field directions) is influenced by the distribution of the surface charges and hydrophobicity gradients inside the nanochannel, a gradient in pH across nanochannel can enhance or suppress the rectification degree of the channel [19, 21]. Measured currents are increased if the temperature of the surrounding electrolyte is increased (under isothermal conditions), independent of the direction of the electric field [25].

Theoretical frameworks for the description of electrokinetic transport phenomena in uniform nanochannels range from analytical solutions in 1D [31, 32] to numerical 2D and 3D solutions of the combined Poisson-Nernst-Planck (PNP) and Navier-Stokes (NS) equations [33, 34]. Numerical investigation of transport in and near nanofluidic channels has yielded information on, amongst others, concentration polarization [35] and micromixing [36]. Nanochannel characteristics that are of crucial importance are wall ζ -potential/wall charge and size [37, 38], which can be easily varied in numerical studies when compared to experimental

systems. The scale difference between nanochannels and microscale reservoirs yields additional numerical difficulty, as one should account for the entrance and exit effects of the nanochannels [39]. There is a large variation in hydrodynamic resistance, as well as electric field focusing towards the nanochannels yielding curved electric field lines in the channels and strong velocity gradients [40].

Ion current rectification inside tapered nanochannels has been simulated widely, using different formulations of the Poisson-Nernst-Planck equations [41–45], indicating that tailor made nanochannels show potential as diodes, which has also been demonstrated in experiments [24]. As the degree of double layer overlap varies along the length of these tapered nanochannels, the transport of ions through these channels is altered when compared to uniform channels. The electric field normal to the nanochannel wall will have a higher magnitude in the more narrow part of the channel, locally affecting the transport of ions and influencing the selectivity of the channels. The contribution of electro-osmotic flow (EOF) to ion current rectification in tapered channels was found to be significant at high voltages for channels with high overlap of Debye layers [46].

If a temperature gradient is applied over a charge selective interface in an electrolyte solution, a potential difference arises [47, 48], which can be harvested as electrical work. Applying temperature gradients to experimental nanochannel systems can be challenging, but can yield information on transport mechanisms in macro-systems such as electrodialysis membrane stacks. In comparison to the large breadth of both experimental and theoretical work on ion selective nanochannels, the role of temperature gradients is relatively unexplored. Investigation has focused primarily on heat transfer in charged microchannels and the role this plays in induced electro-osmotic flows. For example, Chen (2009) studied the development of temperature profiles in micro- and nanochannels with a thin double layer at low potentials using a Poisson-Boltzmann framework considering Joule heating (JH) as the primary heat source while neglecting viscous dissipation based on order of magnitude considerations [49]. The results demonstrated the importance of temperature on the resulting electro-osmotic flow (EOF) and friction factors for pure EOF, as well as EOF with pressure gradients, finding that viscous dissipation became comparable to JH for channels smaller than 50 nm. This work also demonstrated the importance of accounting for the temperature-dependence of physical properties, as significant deviations could be observed assuming a constant value. Shi *et al.* (2008) used the Lattice-Boltzmann method to describe non-isothermal electro-osmotic flows again with a Poisson-Boltzmann type distribution, concluding that for channels less than 100 nm in diameter viscous dissipation effects will become dominant compared with JH, dependent upon the salt concentration in the bulk [50]. The role of temperature gradients in the double layer and how this coupled to thermoelectric effects was studied theoretically recently by Ghonge *et al* [51], using a Poisson-Nernst-Planck

approach, indicating that Soret and thermoelectric effects could be significant for the case of electrohydrodynamic flow in a nanochannel with an imposed wall temperature gradient along the longitudinal channel axis. The contribution of JH was neglected versus viscous dissipation based on an order of magnitude analysis, although in a micro/nanojunction system the electric field constriction and enhancement due to the ion distribution may result in conditions where the Joule heat contribution could be significant. However, the role of temperature and temperature gradients in nanochannels on the resulting ion selectivity, fluxes and induced flow profiles in the case of double layer overlap or high surface charges/wall potentials has not been examined in depth.

In this research, we numerically investigate the effect of applied temperature gradients on charge transport through both uniform and asymmetric nanochannels containing a 1:1 monovalent electrolyte KCl solution using a non-isothermal formulation of the Poisson-Nernst-Planck with Navier-Stokes equations. In particular, nanochannels with a large overlap of the double layer are of interest, as the role of imposed temperature gradients, viscous dissipation and Joule heating for charge selective nanochannels has not yet been explored in detail. We compare charge selectivity, total flux and resulting rectification between uniform and asymmetric nanochannels with temperature gradients, as well as coupling to the applied electric field direction in these systems.

2.2 Theoretical background

The Debye length, the characteristic size of the electric double layer on a wall in an electrolyte solution, is defined as $\kappa^{-1} = \sqrt{(\epsilon_r \epsilon_0 k_B T) / (\sum e^2 z_i^2 n_i)}$, where $\epsilon_r \epsilon_0$ is the permittivity (dielectric constant) of the medium, k_B is Boltzmann's constant, T is the temperature in K, e the elementary charge, z is the ion valency and n is the number of ions per unit of volume [52]. We use the situation where $T = T_0$ as our reference case. In nanochannel systems, the degree of overlap of Debye layers is thus dependent on the ion concentration and the characteristic size of the nanochannel. If the height of the nanochannel changes with length (as schematically shown in Figure 2.1), this will have an effect on the local overlap of Debye layers, which may influence the selectivity of the nanochannel and thus influence the degree of separation and charge transport.

2.2.1 Model framework

In order to simulate the influence of various temperature related effects on transport in ion selective media, a model framework based on a non-isothermal formulation of the steady-state Poisson-Nernst-Planck equations coupled with the Navier-Stokes equations was formulated. This framework (or variations of

Figure 2.1 — Schematic illustration of the simulation geometry, which consists of two micro-reservoirs connected through an asymmetric nanochannel with a half-height h_l at the left side, decreasing to a half-height h_r at the right side. Temperature, potential and concentration in the microchannels are varied in the different cases investigated. In our simulations, $\varphi_R = 0$ and $\varphi_L = [-300V_{th}, 300V_{th}]$.

it) has been employed successfully by a number of scientists to describe the resulting ion transport and induced fluid flows (electro-osmotic and otherwise) [43, 53]. Depending on the salt concentration and electric field strength, significant deviations from assuming Poisson-Boltzmann type description of the boundary layer can be expected, which motivates the use of a PNP approach [49, 53].

In our model, the electric potential is split into two terms; the applied potential φ and the induced electrokinetic potential ψ , scaled against $V_{th} = k_B T / e$, as described in [54]. This is effective for numerically resolving the coupling of the electric field to ion concentration due to the relative scale difference in these potentials. The applied potential can be on the order of volts while a constant surface charge or potential would result in potentials on the order of tens of millivolts. This approach is modified slightly to include a temperature-dependent permittivity, as gradients in permittivity will affect the electric field profile which correspondingly affects the body forces on the liquid in the form of dielectric stresses (resulting in electrothermal flows) [51, 55]. This yields the following equations for description of the electric field, where c_1 and c_2 represent the cation and anion concentration respectively, which are scaled against the reservoir bulk concentration c_0 . ε_r is the temperature dependent permittivity which is scaled against the permittivity at $T_0 = 293$ K using a linear function of dimensionless temperature, which is a good approximation between the applied temperatures of 293 and 313 K [56, 57]. $L_{ref} = h$, where h is the average channel height, holds for scaling of the spatial dimensions:

$$\nabla \cdot (\varepsilon_r \nabla \varphi) = 0 \quad (2.1)$$

$$\nabla \cdot (\varepsilon_r \nabla \psi) = -\frac{1}{2} (\kappa L_{ref})^2 (c_1 - c_2) \quad (2.2)$$

$$\mathbf{E} = -\nabla(\varphi + \psi) \quad (2.3)$$

Temperature dependence of the different physical properties are listed in the Appendix of this chapter. We consider the case of a 1:1 electrolyte, KCl. This electrolyte was selected because of similar diffusivities of both K^+ and Cl^- ions, and similar responses of diffusivity to temperature of these ions [58]. Using the dimensionless Nernst-Planck equations we can describe the transport as a result of convection, diffusion and electromigration:

$$\text{Pe}_{c_i} \mathbf{u} \cdot \nabla c_i - \nabla \cdot \left(D_i \nabla c_i + \frac{z_i D_i c_i}{1 + \theta} \nabla(\varphi + \psi) \right) = 0 \quad (2.4)$$

Temperature dependence of ion diffusivity (D_i) was taken into account, while it was considered independent of concentration in the considered range. The Soret effects in our system were studied by using dimensionless ionic heat of transport coefficients for potassium and chloride, but found to be negligible in comparison to the other transport mechanisms. $\theta = (T - T_0)/T_0$ is the dimensionless temperature and Pe_{c_i} is the Péclet number (for mass transfer, both for anion and cation), which is evaluated at the reference temperature T_0 . The influence of temperature on the density of the solvent, water, was neglected as a temperature increase from 293 to 313 K results in a 0.6% change in density. Viscosity changes with 35% in this temperature range, which motivates treating viscosity as being temperature dependent [59]. The fluid was therefore treated as being incompressible, which simplifies both the continuity equation and the expression for viscous dissipation. For description of the fluid hydrodynamics, the dimensionless Navier-Stokes equations with a temperature dependent viscosity (μ) are applied and a contribution of the Coulomb force ($\mathbf{f}_C$) and electrothermal force ($\mathbf{f}_{\text{ETF}}$) is taken into account where Re , the Reynolds number, is evaluated at the reference temperature:

$$\text{Re}(\mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \nabla \cdot (\mu \nabla \mathbf{u}) + \mathbf{f}_C + \mathbf{f}_{\text{ETF}} \quad (2.5)$$

$$\mathbf{f}_C = \frac{k_B T_0 c_0 L_{\text{ref}}}{\mu_0 u_0} (c_1 - c_2) \mathbf{E} \quad (2.6)$$

$$\mathbf{f}_{\text{ETF}} = -\frac{\varepsilon_0 \varepsilon_{r,0} V_{\text{ref}}^2 L_{\text{ref}}}{2\mu_0 u_0} |\mathbf{E}|^2 \nabla \varepsilon_r \quad (2.7)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (2.8)$$

While developing the model, we have tested the contributions of Coulomb and dielectric forces on the fluid flow. The dielectric (electrothermal) forces

were found to be insignificant compared to the Coulomb force in this work for both symmetric and asymmetric channels, despite the tapered geometry causing larger field gradients. The bending of the electric field does induce a non-zero contribution to the dielectric forces, but the magnitude is still negligible when compared to the Coulomb forces in the system. Therefore, these forces were neglected in the remainder of this research. This also holds for the contribution of Soret diffusion, which was negligible compared to electromigration and diffusion at potentials that are of interest for charge transport. While the dielectric force was negligible in this case, we note that this may not be the case for other geometries with larger geometric effects. We have neglected the potentially large effect from temperature-dependent ζ -potentials by choosing a constant wall potential, treating the system as an effective gated dielectric as in line with previous work [38, 60], due to the large amount of uncertainty in the precise temperature-dependence of solid ζ -potentials [61].

To close the system of equations, a dimensionless energy balance is formulated (equation 2.9), in which we assumed the heat capacity to be constant in the considered temperature range, while the thermal conductivity k was considered to be dependent on temperature (albeit weakly) and Pe_θ is the thermal Péclet number.

$$Pe_\theta \mathbf{u} \cdot \nabla \theta = \nabla \cdot (k \nabla \theta) + q_d + q_{jh} \quad (2.9)$$

The sources of heat generation in the system that are considered in our initial models are Joule heating (equation 2.10) through the dissipation of current into heat and viscous dissipation (equation 2.11). Joule heating was evaluated based on the conduction current with the applied electric field, neglecting the contribution of convective current dissipation and the induced electric field along the nanochannel wall based on an order of magnitude analysis [49, 62];

$$q_{jh} = \left(\frac{\sigma_0 V_{\text{ref}}^2}{\rho C_p T_0 u_0 L_{\text{ref}}} \right) \sigma |\nabla \varphi|^2 \quad (2.10)$$

For an incompressible fluid, the contribution of the viscous dissipation on the total heat production can be simplified and non-dimensionalized as shown in equation 2.11;

$$q_d = \frac{2u_0\mu_0\mu}{\rho C_p T_0 u_0 L_{\text{ref}}} \left[\left(\frac{\partial u}{\partial x} \right)^2 + \left(\frac{\partial v}{\partial y} \right)^2 + \frac{1}{2} \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right)^2 \right] \quad (2.11)$$

2.2.2 Simulation details

In this study, we use a 2D model (COMSOL Multiphysics 5.2) to investigate the effects of non-uniformity of the nanochannels and temperature gradients on

charge transport. The general geometry is depicted in Figure 2.1, where we can vary the nanochannel height and asymmetry ratio $\alpha = h_l/h_r$. The electric field and temperature gradient are applied in the adjacent microchannels. For every asymmetry ratio we investigated four different cases; two isothermal cases (at 293 K and 313 K) and two temperature gradient cases in which the direction of the temperature gradient with respect to the nanochannel is altered. In the temperature gradient cases, one reservoir wall is kept at 293 K while the other is at 313 K, resulting in a difference of 20 K. For all models, $c_0 = 1 \times 10^{-5}$ M, corresponding to a Debye length of 95 nm at $T = T_0$ on each nanochannel wall, which was chosen to ensure Debye layer overlap in the 100 nm channel. The applied potential is varied from -300 to 300 V_{th}, which corresponds to electric field strengths of $\sim -1.02 \times 10^6$ to $\sim 1.02 \times 10^6$ V/m in physical dimensions. The sign of the electric field, as well as the direction of the temperature gradient, is expected to have an influence on the charge transport, as in asymmetric channels we expect current rectification to occur. Three different asymmetry ratios were considered, in which α is 1, 3 and 9 respectively, while the average channel height h was kept constant at 100 nm. The nanochannel is considered to have a constant wall potential of -50 mV, which can be considered as a realistic potential in the case of a gated dielectric [43].

If we state that the electric field and temperature gradient are aligned, this indicates that both high T and high φ are on the same side of the nanochannel, either left or right. In all our simulations, the largest nanochannel inlet is on the left side of the geometry ($h_l \geq h_r$, see Figure 2.1). This means that if we state that the temperature, electric field and geometry are aligned, the high T and high φ are also applied at the left side of the nanochannel. If, in our figures, the electric potential is negative, this means that the potential on the left side is grounded and the potential is applied in the right reservoir.

The channel length is 500 dimensionless units, which corresponds to $2.5 \mu\text{m}$ in physical dimensions. The connected microchannels are also 500 dimensionless units in both width and height. We confirmed that this is sufficient to treat the reservoir boundary conditions as far-field, by inspection of the resulting concentration profiles. The nanochannel is mapped using 40×2000 quadrilateral elements, in which we operated a symmetric distribution and a maximum element ratio of 10. The microchannels were meshed using quadrilateral elements, decreasing in size closer to the nanochannel entrance and the boundaries of the system, with mesh independence confirmed for the different geometries and applied potentials by examination of the selectivity and ion fluxes.

2.3 Results and discussion

2.3.1 Heat sources

In our initial simulations, the induced heating effects of Joule heating and viscous dissipation are considered in the case $\alpha = 1$ and reservoirs of equal temperatures. Local heating effects, especially from corner effects could potentially give rise to different local physical properties of the solution. This would affect the resulting electro-osmotic flows and induce additional forces upon the fluid in the form of dielectric stresses. Viscous dissipation can be significant in nanochannels, giving rise to large temperature gradients which affect the induced electro-osmotic flows within the channel [51]. However, in those cases the nanochannel was considered as an isolated system without accounting for thermal contact with a much larger reservoir. We have investigated the maximum possible local heating in the nanochannel for the symmetric channels under isothermal conditions and various applied potentials. It was found that for the concentrations considered the maximum local heating of approximately 3 K occurs at high applied electric field strengths (and relatively high ionic strengths), at which all selectivity of the nanochannel is lost. Compared to the electric field strength, thermophoretic effects (Soret) are negligible, and electrothermal flow contributions are negligible compared to the Coulombic force. At low electric field strengths viscous dissipation accounts for most of the heating, while at high field strengths Joule heating is dominant. However, neither of these effects was able to generate large local temperature gradients as the convective/diffusive heat transport towards the reservoirs was sufficient to suppress localized gradients in temperature. As we found no significant heating in the initial isothermal symmetric cases, we have neglected the contributions of Joule heating and viscous dissipation in the remainder of the simulations.

2.3.2 Symmetric nanochannels

From our simulations, we obtain the flux of both cations J_1 and anions J_2 and we are therefore able to calculate the total current ($J_1 - J_2$) and the selectivity (J_1/J_2) of the nanochannels. J_i is obtained by averaging the total flux, consisting of the diffusive and electrophoretic flux, over the reservoir wall. The influence of temperature on current rectification ($(J_1 - J_2)_+/(J_1 - J_2)_-$), in which the + and - are indicating the different directions of the electric field, in the nanochannels is investigated for both symmetric and asymmetric nanochannels. Current rectification indicates a preferential transport direction of ions through the nanochannel [19].

For symmetric channels with an aspect ratio of $\alpha = 1$ the total current and selectivity as a function of applied potential are shown in Figure 2.2. As the channels are symmetric, only the interplay of the directions of the electric field

Figure 2.2 — Total current (a) and selectivity (b) in symmetric nanochannels with $\alpha = 1$ under different temperature configurations. Asymmetry of the current and selectivity with respect to the applied potential indicates current rectification in this system. Dashed lines are for visualization purposes only.

and temperature gradient are of importance. The total current through the nanochannel is highest for the isothermal case at high temperature, while the total current is lowest for the isothermal case at low temperature. The case in which a temperature gradient is applied yields intermediate total currents, although at low electric field strengths, the current is comparable to the high temperature isothermal case. For ion selectivity, the case in which a temperature gradient is applied yields the highest values for positive electric field strengths, while it yields the lowest selectivity in the case of a negative electric field strength. The maximum of the selectivity is shifted for the case in which a temperature gradients is imposed. The high temperature isothermal case yields consistently lower selectivity than the low temperature isothermal case.

This response of the system to the applied temperature settings can be explained by the sensitivity of the physical properties to temperature. For higher temperatures, the diffusivity of ions is enhanced, which in turn enhances the conductivity of the solution at these conditions, yielding less resistance to charge transport. The diffusivity of both investigated ions is $\sim 55\%$ higher at 313 K when compared to 293 K, meaning that the conductivity is also significantly higher. This means that in hot reservoirs, the ions are transported more easily than in cold reservoirs, which effectively acts as a barrier for anions to move into the nanochannel on the cold side via diffusion or electromigration and as an enhancement for cations to enter on the hot side of the nanochannel. These effects result in a higher ion selectivity for the cases in which the anions are transported from a cold reservoir, either when the other reservoir is hot or cold. The higher selectivity can be mainly attributed to the reduced transport of co-ions.

If we take a closer look on the local fluid velocity inside the nanochannel, we find an increased velocity for the case in which the temperature gradient is applied along the electric field, when compared to the isothermal cases. The isothermal case at low temperature yields significantly lower velocities than both other configurations. This can be explained by comparison of the average Coulomb force in the channel and the decreased viscosity of the fluid at higher temperatures. The viscosity of the solution is reduced by 35% when temperature is increased from 293 K to 313 K, yielding a higher electro-osmotic velocity inside the nanochannel.

Current rectification (Figure 2.3) in the symmetric nanochannel only occurs in the case of an applied temperature gradient and is most pronounced at low electric field strengths. The rectification factor is up to 1.4 in the channels that we have simulated, which is not as high as values that have been reported for asymmetric nanochannels [22, 26]. This can be attributed to the relatively small size of our nanochannels in relation to the Debye length. However, if we increase the channel height, selectivity of the nanochannels is lost and they lose their function as a charge selective interface.

Figure 2.3 — Current rectification in the symmetric nanochannel as a result of an imposed temperature gradient. Rectification is calculated by dividing the total current for the positive applied electric field by the total current for the negative applied electric field at equal strengths. Lines are for visualization purposes only.

2.3.3 Asymmetric nanochannels

Figure 2.4(a) shows the total current through the nanochannel as a function of applied potential for the four different temperature configurations in a channel with an asymmetry ratio of 3. Just as was the case for symmetric nanochannels, the total (absolute) current is highest for the isothermal case at high temperatures, as the diffusivity of both co-ions and counter ions is enhanced at enhanced temperatures. Likewise, the absolute current is lowest for the isothermal case at low temperatures. The cases in which there is a temperature difference show intermediate currents. The case in which the electric field and the temperature gradient are aligned yields the highest current, as the high temperature enhances cation diffusivity. As the nanochannel is cation selective, the enhancement of cation transport towards the channel will result in a higher overall current through the channel, which would be flipped for the case of anion selective materials.

In Figure 2.4(b) the influence of temperature gradients on the selectivity of the nanochannel is shown. Selectivity is highest at low field strengths, as at higher field strengths the transport of all ions is enhanced, including the counterions which reduces the selectivity of the channel. The direction of the potential at which the highest selectivity occurs is dependent on the interplay of the temperature gradients with the geometry. For the isothermal cases, the low temperature case

Figure 2.4 — Total current (a) and selectivity (b) in asymmetric nanochannels with $\alpha = 3$ under different temperature configurations. Asymmetry of the current and selectivity with respect to the applied potential indicates current rectification in this system. Dashed lines are for visualization purposes only.

shows the higher selectivity when compared to the higher temperature case, as a result of the lower relative diffusivity of anions (compared to cation diffusivity) at lower temperatures. Selectivity can be enhanced with a temperature gradient, and this enhancement is dependent on the interplay between the direction of the temperature gradient and the direction of the electric field with respect to the nanochannel geometry. The largest enhancement in selectivity is obtained for the case in which the high temperature is on the large inlet of the nanochannel and the temperature gradient is aligned with the electric field, so where high T , high φ and high h are all on the same side of the channel. If the electric field is flipped (corresponding to negative potentials in Figure 2.4(b)), the case with the opposite temperature gradient yields the highest selectivity, again when the temperature gradient is aligned with the electric field (low T , low φ and high h at the same side). This indicates that if the temperature is enhanced in the reservoir where cations are depleted, the selectivity of the nanochannel is enhanced, independent of the inlet characteristic length of the nanochannel, meaning that the enhanced diffusivity of ions has a large influence on the selectivity of the channel. In particular, the relatively low diffusivity of anions (compared to cations) at lower temperatures enhances the selectivity as this reduces the transport of co-ions through the channel, as was the case in symmetric channels. If the temperature gradient counters the electric field gradient, the selectivity of the nanochannel is reduced, as a result of enhanced relative diffusivity of anions in the cathodic reservoir, which enhances transport of these anions through the nanochannel.

If we compare the current rectification, which is defined by the ratios of the total current for the different directions of the electric field and shown in Figure 2.5, we see that for the isothermal cases, the total rectification is very similar in both quantitative and qualitative behaviour and does not exceed a rectification of 1.2 throughout the range of applied potentials. The absolute value of rectification is relatively low as we are working at relatively low ion concentrations to have a good selectivity of the nanopore. With increasing field strength the degree of rectification is reduced and at very high field strengths there is no significant rectification observed, just as there was no significant selectivity at these field strengths. For the cases where a temperature gradient is applied, this behaviour is altered and the rectification is increased. The field strength at which the rectification is the highest is shifted to higher potentials when a temperature gradient is applied. For the case where the high temperature is on the smaller nanochannel inlet this is most pronounced, with rectification factors over 1.5 at low field strengths. This enhanced rectification is mainly attributed to the increase of selectivity for the cases in which a temperature gradient is applied, which was a result of the enhanced diffusivity and viscosity at high temperature. For the case with higher asymmetry ratios $\alpha = 9$, the rectification is enhanced slightly for all temperature configurations in comparison to the case where $\alpha = 3$. This

Figure 2.5 — Current rectification for the four different temperature configurations at different field strengths for the case $\alpha = 3$. Rectification is calculated by dividing the total current for the positive applied electric field by the total current for the negative applied electric field at equal strengths. Lines are for visualization purposes only.

is attributed to the enhanced asymmetry of the nanochannel. The quantitative behaviour of the nanochannel with larger degree of asymmetry is similar to the behaviour shown in Figure 2.5.

In asymmetric nanochannels, the degree of Debye layer overlap is not constant throughout the channel. In our model, we have defined the Debye layer as such that there is overlap at the location where the channel height is 1 dimensionless unit, which for the asymmetric nanochannels is in the middle of the channel, while in the symmetric channel the Debye layers are overlapping throughout the entire channel. However, as a result of the constricted inlet (or outlet) of the asymmetric nanochannels, selectivity is enhanced when increasing the aspect ratio of the channel. This indicates that the minimum size of the channel (degree of Debye layer overlap) is very important in the determination of nanochannel selectivity. However, many other factors, such as a variation of wall potential and pH [19] could be of high importance as well and not investigated here. The interplay of minimum channel size and the resulting local field strength and the implications of this for channel selectivity are interesting for further detailed analysis.

By investigating the individual terms of the Nerst-Planck equation (eq. 2.4), we are able to determine the contributions of convective, diffusive and electromigration flux to the total current. In general, the convective flux has the dominant

contribution to the total cation flux, at all modeled field strengths. Convection within the nanochannel is a result of electro-osmotic movement of the fluid. For low to moderate applied electric field strengths the convective flux of ions is increasing with increasing field strength. At sufficiently large applied potentials (above $50 V_{th}$), the convective contribution to the total flux decreases again as a result of lower selectivity of the channel, which results in a smaller cation concentration in the channel and thus less cations being transported by convection. The anion flux as a result of convective ion transport is increasing with increasing applied potentials. For anions, however, there is no maximum in the convective flux found at moderate field strengths, as the concentration of anions in the nanochannel is increasing at higher potentials. The electromigration flux of both cations and anions is increasing with increasing applied potential because this is directly proportional to the electric field strength. For high field strengths, the electromigration flux accounts for a significant contribution in the total current for both cations and anions, as it grows faster than the convective flux. However, at these high field strengths the selectivity of the nanochannel has dropped significantly and current rectification is reduced as both cations and anions are free to pass through the channel.

2.4 Conclusion

In this chapter, we have demonstrated that temperature gradients can enhance selectivity and current rectification in nanochannels through the use of numerical simulations based on a non-isothermal PNP-NS framework. For symmetric cation selective nanochannels, the selectivity of the nanochannel is enhanced when a temperature gradient is applied along the electric field gradient, so when the depleted reservoir has a high temperature. Selectivity of the asymmetric nanochannels is enhanced if the electric field and temperature gradient are aligned with the nanochannel asymmetry. This enhancement was found to result primarily from increased diffusivity of both cations and anions at elevated temperatures and the subsequent enhancement of transport of ions along the electric field. For asymmetric nanochannels, current rectification occurs also without temperature gradients, but this is significantly enhanced when a temperature difference is applied over the nanochannel. Most interesting is that if the direction of the temperature gradient, the electric field and the decrease in nanochannel height are aligned, the enhancement in selectivity and rectification is enhanced over 50%. Channels with higher aspect ratios show a higher ion selectivity and rectification, as a result of a higher degree of Debye layer overlap. Implementing temperature gradients in an experimental nanochannel system would be challenging, but temperature gradients can be applied, or be present, in macro-scale membrane

systems.

This work was done using KCl, an electrolyte in which both anion and cation are monovalent and have similar diffusivities and temperature dependence of diffusivity. Extension of this work towards multivalent ions or other ions with different diffusivities and responses of diffusivity to temperature can yield interesting mechanisms for the selective removal of mono- or multivalent ions from salt solutions. Temperature gradients within the Debye layer can be of interest in a fundamental study on how this affects the electro-osmotic flow inside nanoporous materials, as well as the effect of temperature dependence of the ζ -potential of the channel wall [63], which we have neglected in this study by assuming a constant wall potential.

In general, in ion transport systems such as electrodialysis (ED), thermophoretic transport is not significant when compared to transport as a result of a concentration gradient or a potential gradient [47]. However, a temperature gradient can yield significant beneficial effects on the ion transport in these systems, if applied alongside an electric potential. This is of interest in many different systems, for instance in enhancing pre-concentration in micro-nanosystems and for understanding fundamental ion transport mechanisms. As the selectivity is increasing, a lower potential would be required to obtain the same degree of desalination in ED systems, which is of interest as it reduces energy requirements in desalination processes. This work motivates the experimental investigation of the influence of temperature and temperature gradients on macro-scale electrodialysis systems. The results of these investigations are written in chapter 3 and 4 of this thesis.

References

- [1] S. J. Kim, L. D. Li, and J. Han, *Amplified electrokinetic response by concentration polarization near nanofluidic channel*, *Langmuir* **25**, 7759 (2009).
- [2] C. Lee, C. Cottin-Bizonne, A. L. Biance, P. Joseph, L. Bocquet, and C. Ybert, *Osmotic flow through fully permeable nanochannels*, *Phys. Rev. Lett.* **112**, 244501 (2014).
- [3] A. M. Benneker, J. A. Wood, P. A. Tsai, and R. G. H. Lammertink, *Observation and experimental investigation of confinement effects on ion transport and electrokinetic flows at the microscale*, *Sci. Rep.* **6**, 37236 (2016).
- [4] G. Yossifon, P. Mushenheim, Y.-C. Chang, and H.-C. Chang, *Eliminating the limiting-current phenomenon by geometric field focusing into nanopores and nanoslots*, *Phys. Rev. E* **81**, 046301 (2010).
- [5] G. Yossifon and H.-C. Chang, *Changing nanoslot ion flux with a dynamic nanocolloid ion-selective filter: Secondary overlimiting currents due to nanocolloid-nanoslot interaction*, *Phys. Rev. E* **81**, 066317 (2010).

- [6] P. Abgrall and N. T. Nguyen, *Nanofluidic devices and their applications.*, Anal. Chem. **80**, 2326 (2008).
- [7] C. C. Lai, C. J. Chang, Y. S. Huang, W. C. Chang, F. G. Tseng, and Y. L. Chueh, *Desalination of saline water by nanochannel arrays through manipulation of electrical double layer*, Nano Energy **12**, 394 (2015).
- [8] S. Yu, T.-J. Jeon, and S. M. Kim, *Active micromixer using electrokinetic effects in the micro/nanochannel junction*, Chem. Eng. J. **197**, 289 (2012).
- [9] P.-H. Chiu, C.-C. Chang, and R.-J. Yang, *Electrokinetic micromixing of charged and non-charged samples near nano-microchannel junction*, Microfluid. Nanofluidics **14**, 839 (2013).
- [10] R. Chein, C. Liao, and H. Chen, *Thermodynamic reversibility analysis of electrokinetic energy conversion in nanofluidic channels*, Nanoscale Microscale Thermophys. Eng. **14**, 75 (2010).
- [11] D. K. Kim, C. Duan, Y. F. Chen, and A. Majumdar, *Power generation from concentration gradient by reverse electrodialysis in ion-selective nanochannels*, Microfluid. Nanofluidics **9**, 1215 (2010).
- [12] C. C. Chang and R. J. Yang, *Electrokinetic energy conversion in micrometer-length nanofluidic channels*, Microfluid. Nanofluidics **9**, 225 (2010).
- [13] S. Tseng, Y.-M. Li, C.-Y. Lin, and J.-P. Hsu, *Salinity gradient power: Influences of temperature and nanopore size*, Nanoscale **8**, 2350 (2016).
- [14] Z. Meng, Y. Chen, X. Li, Y. Xu, and J. Zhai, *Cooperative effect of pH-dependent ion transport within two symmetric-structured nanochannels*, ACS Appl. Mater. Interfaces **7**, 7709 (2015).
- [15] C.-C. Chang, C.-P. Yeh, and R.-J. Yang, *Ion concentration polarization near microchannel-nanochannel interfaces: Effect of pH value*, Electrophoresis **33**, 758 (2012).
- [16] M. Taghipoor, A. Bertsch, and P. Renaud, *Temperature sensitivity of nanochannel electrical conductance*, ACS Nano **9**, 4563 (2015).
- [17] J. L. Perry and S. G. Kandlikar, *Review of fabrication of nanochannels for single phase liquid flow*, Microfluid. Nanofluidics **2**, 185 (2006).
- [18] D. Mijatovic, J. C. T. Eijkel, and A. van den Berg, *Technologies for nanofluidic systems: top-down vs. bottom-up - a review*, Lab Chip **5**, 492 (2005).
- [19] W. Guo, Y. Tian, and L. Jiang, *Asymmetric ion transport through ion-channel-mimetic solid-state nanopores*, Acc. Chem. Res. **46**, 2834 (2013).
- [20] Y. Kong, X. Fan, M. Zhang, X. Hou, Z. Liu, J. Zhai, and L. Jiang, *Nanofluidic diode based on branched alumina nanochannels with tunable ionic rectification*, ACS Appl. Mater. Interfaces **5**, 7931 (2013).
- [21] Z. Zhang, X. Y. Kong, K. Xiao, Q. Liu, G. Xie, P. Li, J. Ma, Y. Tian, L. Wen, and L. Jiang, *Engineered asymmetric heterogeneous membrane: A concentration-gradient-driven energy harvesting device*, J. Am. Chem. Soc. **137**, 14765 (2015).

-
- [22] X. Hou, H. Dong, D. Zhu, and L. Jiang, *Fabrication of stable single nanochannels with controllable ionic rectification*, *Small* **6**, 361 (2010).
- [23] M. Ali, B. Schiedt, R. Neumann, and W. Ensinger, *Biosensing with functionalized single asymmetric polymer nanochannels*, *Macromol. Biosci.* **10**, 28 (2010).
- [24] Z. Guo, J. Wang, J. Ren, and E. Wang, *pH-Reversed ionic current rectification displayed by conically shaped nanochannel without any modification*, *Nanoscale* **3**, 3767 (2011).
- [25] R. T. Perera, R. P. Johnson, M. A. Edwards, and H. S. White, *The Effect of the Electric Double Layer on the Activation Energy of Ion Transport in Conical Nanopores*, *J. Phys. Chem. C* **119**, 24299 (2015).
- [26] L. Cao, W. Guo, Y. Wang, and L. Jiang, *Concentration-gradient-dependent ion current rectification in charged conical nanopores*, *Langmuir* **28**, 2194 (2012).
- [27] K. Xiao, P. Li, G. Xie, Z. Zhang, L. Wen, and L. Jiang, *Fabrication and ionic transportation characterization of funnel-shaped nanochannels*, *RSC Adv.* **6**, 55064 (2016).
- [28] W. J. Lan, M. A. Edwards, L. Luo, R. T. Perera, X. Wu, C. R. Martin, and H. S. White, *Voltage-rectified current and fluid flow in conical nanopores*, *Acc. Chem. Res.* **49**, 2605 (2016).
- [29] R. B. Schoch, J. Han, and P. Renaud, *Transport phenomena in nanofluidics*, *Rev. Mod. Phys.* **80**, 839 (2008).
- [30] D. Woermann, *Electrochemical transport properties of a cone-shaped nanopore: high and low electrical conductivity states depending on the sign of an applied electrical potential difference*, *Phys. Chem. Chem. Phys.* **5**, 1853 (2003).
- [31] A. Mani, T. A. Zangle, and J. G. Santiago, *On the propagation of concentration polarization from microchannel nanochannel interfaces Part I: Analytical model and characteristic analysis*, *Langmuir* **25**, 3898 (2009).
- [32] F. H. J. Van Der Heyden, D. Stein, and C. Dekker, *Streaming currents in a single nanofluidic channel*, *Phys. Rev. Lett.* **95**, 9 (2005).
- [33] X. Jin, S. Joseph, E. N. Gatimu, P. W. Bohn, and N. R. Aluru, *Induced electrokinetic transport in micro-nanofluidic interconnect devices.*, *Langmuir* **23**, 13209 (2007).
- [34] S. Movahed and D. Li, *Electrokinetic transport through nanochannels*, *Electrophoresis* **32**, 1259 (2011).
- [35] T. A. Zangle, A. Mani, and J. G. Santiago, *On the propagation of concentration polarization from microchannel - nanochannel interfaces Part II: Numerical and experimental study*, *Langmuir* **25**, 3909 (2009).
- [36] H. Hadidi and R. Kamali, *Numerical simulation of a non-equilibrium electrokinetic micro/nano fluidic mixer*, *J. Micromech. Microeng.* **26**, 035019 (2016).

- [37] A. Szymczyk, H. Zhu, and B. Balannec, *Pressure-driven ionic transport through nanochannels with inhomogenous charge distributions*, *Langmuir* **26**, 1214 (2010).
- [38] M. Tagliazucchi and I. Szleifer, *Salt pumping by voltage-gated nanochannels*, *J. Phys. Chem. Lett.* **6**, 3534 (2015).
- [39] H.-C. Chang, G. Yossifon, and E. A. Demekhin, *Nanoscale Electrokinetics and Microvortices: How Microhydrodynamics Affects Nanofluidic Ion Flux in Annu. Rev. Fluid Mech.*, edited by S. H. Davis and P. Moin (2012), Vol. 44, pp. 401–426.
- [40] W. S. Koegler and C. F. Ivory, *Focusing proteins in an electric field gradient*, *J. Chromatogr. A* **726**, 229 (1996).
- [41] J. Wang, M. Zhang, J. Zhai, and L. Jiang, *Theoretical simulation of the ion current rectification (ICR) in nano-pores based on the Poisson-Nernst-Planck (PNP) model*, *Phys. Chem. Chem. Phys.* **16**, 23 (2014).
- [42] H. S. White and A. Bund, *Ion current rectification at nanopores in glass membranes*, *Langmuir* **24**, 2212 (2008).
- [43] C. Zhao, Y. Song, and C. Yang, *Induced-charge electrokinetics in a conducting nanochannel with broken geometric symmetry: Towards a flexible control of ionic transport*, *Phys. Fluids* **27**, 012003 (2015).
- [44] Q. Liu, Y. Wang, W. Guo, H. Ji, J. Xue, and Q. Ouyang, *Asymmetric properties of ion transport in a charged conical nanopore*, *Phys. Rev. E* **75**, 051501 (2007).
- [45] C. Wei, A. J. Bard, and S. W. Feldberg, *Current rectification at quartz nanopipet electrodes*, *Anal. Chem.* **69**, 4627 (1997).
- [46] Y. Ai, M. Zhang, S. W. Joo, M. A. Cheney, and S. Qian, *Effects of electroosmotic flow on ionic current rectification in conical nanopores*, *J. Phys. Chem. C* **114**, 3883 (2010).
- [47] M. Tasaka, *Thermal membrane potential and thermosmosis across charged membranes*, *Pure & Appl. Chem.* **58**, 1637 (1986).
- [48] M. Tasaka, T. Mizuta, and O. Sekiguchi, *Mass transfer through polymer membranes due to a temperature gradient*, *J. Memb. Sci.* **54**, 191 (1990).
- [49] C.-H. Chen, *Thermal transport characteristics of mixed pressure and electroosmotically driven flow in micro-and nanochannels with joule heating*, *J. Heat Transfer* **131**, 022401 (2009).
- [50] Y. Shi, T. Zhao, and Z. Guo, *Lattice Boltzmann simulation of thermal electroosmotic flows in micro/nanochannels*, *J. Comput. Theor. Nanosci.* **5**, 236 (2008).
- [51] T. Ghonge, J. Chakraborty, R. Dey, and S. Chakraborty, *Electrohydrodynamics within the electrical double layer in the presence of finite temperature gradients*, *Phys. Rev. E* **88**, 053020 (2013).
- [52] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal dispersions*

- (Cambridge University Press, Cambridge; New York, 1989).
- [53] C. C. Chang and R. J. Yang, *A perspective on streaming current in silica nanofluidic channels: Poisson-Boltzmann model versus Poisson-Nernst-Planck model*, J. Colloid Interface Sci. **339**, 517 (2009).
 - [54] K. Kim, H. S. Kwak, and T.-H. Song, *A numerical model for simulating electroosmotic micro- and nanochannel flows under non-Boltzmann equilibrium*, Fluid Dyn. Res. **43**, 041401 (2011).
 - [55] B. G. Hawkins and B. J. Kirby, *Electrothermal flow effects in insulating (electrodeless) dielectrophoresis systems*, Electrophoresis **31**, 3622 (2010).
 - [56] U. Kaatze, *Complex permittivity of water as a function of frequency and temperature*, J. Chem. Eng. Data **34**, 371 (1989).
 - [57] J. A. Wood, B. Zhang, M. R. Tomkins, and A. Docoslis, *Numerical investigation of AC electrokinetic virus trapping inside high ionic strength media*, Microfluid. Nanofluidics **3**, 547 (2007).
 - [58] G. C. Benson and A. R. Gordon, *A reinvestigation of the conductance of aqueous solutions of potassium chloride, sodium chloride, and potassium bromide at temperatures from 15 to 45C*, J. Chem. Phys. **13**, 473 (1945).
 - [59] E. W. Lemmon, M. O. McLinden, and D. G. Friend, in *NIST Chemistry webbook, NIST Standard reference database*, edited by P. J. Linstrom and W. G. Mallard (National Institute of Standards and Technology, Gaithersburg MD, 20899, USA, 1998), Vol. 69.
 - [60] G. Pardon and W. van der Wijngaart, *Modeling and simulation of electrostatically gated nanochannels*, Adv. Colloid Interface Sci. **199-200**, 78 (2013).
 - [61] R. Venditti, X. Xuan, and D. Li, *Experimental characterization of the temperature dependence of zeta potential and its effect on electroosmotic flow velocity in microchannels*, Microfluid. Nanofluidics **2**, 493 (2006).
 - [62] P. M. Coelho, M. A. Alves, and F. T. Pinho, *Forced convection in electroosmotic/Poiseuille micro-channel flows of viscoelastic fluids: Fully developed flow with imposed wall heat flux*, Microfluid. Nanofluidics **12**, 431 (2012).
 - [63] M. Dietzel and S. Hardt, *Flow and streaming potential of an electrolyte in a microchannel with an axial temperature gradient*, J. Fluid Mech. **813**, 1060 (2013).

Appendix

Temperature dependence of physical properties

Permittivity data was obtained from Kaatze (1989) [56]. The diffusion coefficients are based on molar conductivity data of Benson and Gordon [58] and converted to diffusion coefficients by $D_i = (RT\Lambda)/(z^2F^2)$. Viscosity and thermal conductivity were obtained from the NIST Chemistry Webbook [59]. All values are 1 at T_0 of 293 K and increase or decrease with θ , dimensionless temperature $(T - T_0)/T_0$.

$$\varepsilon_r = 1 - 1.2984\theta$$

$$D_1 = 1 + 8.4585\theta$$

$$D_2 = 1 + 8.8466\theta$$

$$\mu = \exp(-6.46\theta)$$

$$k = 1 + 0.8098\theta$$

Boundary conditions for simulations

The boundary conditions below are used for the corresponding boundaries as shown in Figure 1.

AB

Dirichlet/Constant value for φ , θ and c_i

$$\varphi = V_0/V_{\text{ref}} \text{ or } 0$$

$$\theta = \theta_{\text{left}}$$

$$c_i = 1$$

Zero flux for ψ

$$\mathbf{n} \cdot (\varepsilon_r \nabla \psi) = 0$$

Open boundary for velocity

$$[-p\mathbf{I} + \mu \nabla \bar{u}]\mathbf{n} = 0$$

BC and FG

Symmetry/No normal velocity component

Insulating/Zero flux for θ , c_i , φ and ψ

CD and EF

No-slip for velocity ($\bar{u} = 0$)

Insulating/Zero flux for θ and c_i

DE

$$\psi = V_{\text{wall}}/V_{\text{ref}}$$

No-slip for velocity ($\bar{u} = 0$)

Insulating/Zero flux for θ , c_i and φ

GH

Dirichlet/Constant value for φ , θ and c_i

$$\varphi = V_0/V_{\text{ref}} \text{ or } 0$$

$$\theta = \theta_{\text{right}}$$

$$c_i = 1$$

Zero flux for ψ

$$\mathbf{n} \cdot (\varepsilon_r \nabla \psi) = 0$$

Open boundary for velocity

$$[-p\mathbf{I} + \mu \nabla \bar{u}]\mathbf{n} = 0$$

AH

Symmetry conditions

CHAPTER 3

Effect of temperature gradients on (reverse) electrodialysis in the Ohmic regime

Abstract — Electrodialysis (ED) and reverse electrodialysis (RED) are processes for the production of desalinated water (ED) and power (RED). Temperature of the feed streams can strongly influence the performance of both processes. In this chapter, commercial membranes are used for the investigation of temperature and temperature gradients on ED and RED processes. We find that the energy required for ED processes can be reduced by 9% if the temperature of one of the feed streams is increased by 20 °C, while maintaining the charge selectivity of the membranes. The direction of the temperature gradient did not have a significant influence on the efficiency and selectivity of ED in the Ohmic regime. In RED, we find an increase in obtained gross power density over 25% for the process when one feed stream is heated to 40 °C instead of 20 °C. This work experimentally demonstrates that utilization of low-grade waste heat from industrial processes can yield significant reduction of energy costs in ED processes, or result in higher power densities for RED systems where the increase in temperature of a single feed stream already yields significant efficiency improvements.

This chapter is based on the publication

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3.1 Introduction

Electrodialysis is a technique applied on industrial scale for the deionization of aqueous feed streams. In electrodialysis (ED), a membrane stack containing alternating anion (AEM) and cation exchange membranes (CEM) is used for the selective transport of ions by applying a potential gradient over the system [1]. Anions will be transported through the AEM and blocked by the CEM, while for the cations the opposite is true, resulting in an ion enriched (concentrate) and an ion depleted (diluate) stream at the outlet of the stack [2]. ED is applied on an industrial scale in the treatment of aqueous solutions for various applications such as desalination for drinking water, nitrate removal, salt removal from protein and sugar solutions and the deionization of whey [1]. In commercial systems, ED is operated in the so-called Ohmic regime, to prevent concentration polarization and minimize pressure drops in the solution adjacent to the membrane [3].

In reverse electrodialysis (RED), as the name suggests, the opposite is occurring as the energy of mixing two streams with different inlet salt concentrations is harvested in a membrane stack. RED processes can be of use at natural points where two streams containing different salt concentrations are contacting, such as for instance river estuaries (low salt concentration) in the sea (high salt concentration) [4–7], or in hypersaline brines [4]. RED processes are currently being tested at lab and pilot plant scales [8].

Both ED and RED have been studied extensively in the past decades [1, 9–11], regarding membrane selectivity and optimizing flow patterns adjacent to the membranes as two prominent goals for improving the efficiency of both processes. Typically, most commercial membranes exhibit a selectivity above 90% [10]. Ion transport from the liquid phase to the membrane is of large influence on the efficiency of ED and RED, and partially determines the required or obtained power. Transport can be enhanced by continuously mixing the solution in order to reduce the development of an ion depleted boundary layer or by enhancing the transport of ions in the solution. Optimization of the flow patterns can be achieved using profiled membranes or spacers [12–14]. In both ED and RED, there is transport of water as a result of the osmotic gradient. This water transport results in a drastic reduction in efficiency of the process [15], most significantly in ED processes. For cation exchange membranes, the direction of the water transport in systems where only a temperature gradient is applied (no applied potential gradient) depends on the coupling between the electrolyte and the water [16–18]. If only an osmotic gradient is present, water transport will be from the solution with a low salt concentration towards the higher salt concentrations, therefore in the opposite direction of ion transport [16]. In addition to osmosis, there is water transport as a result of electro-osmotic flows, in which the water is transported alongside the ions that are moving as a result of the electric field.

In ED, the direction of electro-osmotic transport of water is the same as the osmotic water transport, while in RED they are in opposite directions [19]. The efficiency losses as a result of water transport are reported to increase with increasing concentration differences and increasing temperature in the system [15, 20]. Elevated temperatures can yield additional limitations in the process, such as the degradation of the membrane material and the precipitation of low solubility compounds on the membranes [21]. Conversely, elevated temperatures might yield a lower energy requirement for the ED process [22] and can enhance the obtainable power from RED processes [10].

When a temperature gradient is applied over a membrane separating two solutions of equal salt concentration, a thermal membrane potential is measured, indicating a thermoelectric effect over the membrane [23–26], which can be harvested as electric work [24, 27, 28], similar to the RED principle. Additionally, a thermo-osmotic water flux might be established [18, 29, 30], of which the direction is dependent on the membrane at hand [16]. It is stressed that this temperature gradient does not necessarily result in the development of a concentration gradient over the membrane [25]. If, in addition to the temperature gradient a potential or concentration gradient is applied over the membrane, the selective transport of ions might be enhanced by the coupling of effects resulting from temperature gradients with the other transport phenomena in the system. When the temperature gradient in ED is applied in the same direction as the electric field, the relative flux of counter ions can be enhanced when compared to the co-ion flux, increasing the efficiency of the separation of ions from the solution [31]. The total ionic current can be increased if temperature gradients or elevated temperatures are applied over the membrane, as a result of the increased diffusivity of ions in the solution [31, 32]. Experimental [33, 34] and theoretical [35] investigations have shown that elevated temperatures are beneficial for the obtainable power density in RED systems with highly saline feed solutions, albeit at isothermal conditions. The effect of temperature gradients in realistic ED and RED set-ups also containing a salt or potential gradient have, to the best of our knowledge, not been investigated experimentally. These situations are interesting for applications where there is a natural temperature gradient between two inlet feed streams, e.g. where a river meets a sea, or for industrial plants that deal with low-grade waste heat. Moreover, applying a temperature gradient vs. isothermal operation may reduce the negative side-effects of high temperature operations, such as scaling and increased water transport [21].

Many industrial plants have to deal with low-grade waste heat resulting from their production processes [36]. Most of the waste heat is found in food, tobacco, pulp and paper, basic metals and non-metallic minerals industries, which has large potentials to be re-used. Usually, waste heat with high temperatures is considered as most valuable, as this can provide energy most easily for other

processes [37]. Low temperature waste heat (streams with a temperature up to 100 °C) is mostly used in the food and tobacco industry, but is widely available [37]. If waste heat can be used for heating feed streams of ED and RED plants, the energy efficiency of these processes can theoretically be enhanced.

In this chapter, we experimentally study the effect of imposed temperature gradients in ED and RED systems. We measure the required power for desalination in ED in the industrially relevant Ohmic regime, as well as the obtained power density from the RED system under various temperature settings. The temperature settings are chosen as such that they are obtainable by utilizing waste heat for heating the feed streams. Additionally, we measure ion concentrations to investigate the effect of temperature gradients on the selectivity of membranes and the efficiency of the ED system. Our experiments show that we can enhance the energy efficiency of ED systems by working with temperature gradients and at elevated temperatures, and improve the power density of RED systems in the same manner. The selectivity for ion transport remained constant, meaning there was no loss of membrane selectivity and functionality at elevated temperatures. These results show the potential use of waste heat to improve either desalination or power generation in ED and RED processes.

3.2 Experimental details

Experiments were performed using a cross-flow RED stack, with an active area of $10 \times 10 \text{ cm}^2$, provided by REDstack BV (The Netherlands). The two feed inlet streams are perpendicular to each other, resulting in a relatively high heat transfer between the two streams which are in cross-flow configuration. Four cell pairs consisting of commercially available cation and anion exchange membranes with an intermembrane distance (channel height) of $260 \text{ }\mu\text{m}$ were assembled in the stack. The membranes used are Neosepta® CMX and Neosepta® AMX (obtained from Eurodia, France), which are punched to size using an in-house built mold. The $260 \text{ }\mu\text{m}$ thick spacers with a free volume fraction of 0.726 and a free surface fraction of 0.476 were provided by Deukum GmbH (Germany). End-plates were tightened using screws and the side plates of the RED stack were sealed. Electrical measurements are done using a Metrohm Autolab PGSTAT302N equipped with a FRA module (Metrohm Autolab, The Netherlands), which is controlled by NOVA 2.0 software. Current or potential was applied through Pt coated Ti electrodes (provided by Magneto Special Anodes BV, The Netherlands), located in the stack end plates.

Both ED and RED experiments are done at four different temperature configurations; (1) isothermal at 20 °C, (2) feed 1 at 20 °C, feed 2 at 40 °C, (3) feed 1 at 40 °C, feed 2 at 20 °C and (4) isothermal at 40 °C, as is summarized in Table 3.1.

Table 3.1 — Tested temperature configurations in ED and RED experiments

Case	T_D (river) [°C]	T_C (sea) [°C]
Cold Isotherm	20	20
Hot Concentrate	20	40
Hot Diluate	40	20
Hot Isotherm	40	40

Feed solutions were kept at the desired temperatures using two Julabo F12-ED Refrigerated - Heating Circulators. The system was allowed to settle to thermal equilibrium and outlet temperatures were measured using AMA-digit ad 15th thermometers (Amarell, Germany) during the electrical measurements.

All measurements are done at a constant flow rate of 50 mL/min, which corresponds to a flow speed (linear flow velocity) of 0.81 cm/s in the compartments. Flow was pumped using peristaltic pumps (Cole-Parmer) and flow pulsations were suppressed using in-house built pulsation dampeners. The flow rate was controlled using an in-house built flow meter (TCO, University of Twente, The Netherlands), containing a McMillan Co. 101 flo-sen flow sensor. The membrane packing was ensured by applying an 0.1 bar overpressure on the electrolyte stream (flow rate was adjusted accordingly), using a simple needle valve.

3.2.1 Electrodialysis

For experiments in the electrodialysis (ED) mode a feed solution of 1 g/L NaCl (0.017 M) is pumped through all compartments of the stack. The electrolyte used in ED mode contained 0.017 M NaCl and 0.1 M $K_4Fe(CN)_6$ and 0.1 M $K_3Fe(CN)_6$ as the redox pair. Both depleted and enriched outlet streams are recycled into the feed container, which is continuously mixed using aquarium mixers (Wavereef® Auto Top Off System, Single Level Sensor WIC-01S, obtained from Aquaria Veldhuis BV, The Netherlands). The system was allowed to equilibrate in temperature before measurements were started.

Constant current measurements (chronopotentiometry) are done at a current of 0.15 A, corresponding to 15 A/m², which was confirmed to be in the Ohmic regime of this stack (by measuring IV responses) to avoid any influences of concentration polarization on the measurements as the goal of these experiments was the investigation of temperature gradients in the Ohmic regime. The required potential to sustain this current is measured for 600 seconds.

Samples are taken during the measurements to evaluate the salt concentrations in the outlet streams by means of ion chromatography (IC). Conductivity of inlet and outlet streams was monitored during the experiments using a WTW Cond 3310 conductivity meter equipped with a WTW Tetracon 325 sensor (WTW, Germany), to check if depletion and enrichment of the streams is as expected.

Anion concentrations were quantified with IC (Metrosep A Supp 16 - 150/4.0 column on a Metrohm 850 Professional IC). Cation concentrations were measured with IC as well (Metrosep C6 - 150/4.0 column on a Metrohm 850 Professional IC).

3.2.2 Reverse electrodialysis

Reverse electrodialysis experiments were done with model solutions of 30 g/L NaCl (0.513 M, “sea water”) and 1 g/L NaCl (0.017 M, “river water”) through the different compartments. The electrolyte used in RED mode contained 0.25 M NaCl and 0.1 M $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$ as the redox pair. No recycling of the outlet streams is done in these experiments, as the salt gradient would be reduced during the measurement. The pressure drop in both sea and river water streams was monitored between the inflow and the outflow of the solutions, using a differential pressure meter (Endress + Hauser Deltabar S, Germany).

Different parameters were measured during a single RED measurement. Open circuit voltage (OCV) was measured prior and after the stack resistance measurements (both AC and DC mode). The total stack resistance is a result of the Ohmic resistance (resulting from the resistance of the feed streams and the membranes) and the non-Ohmic resistance (caused by concentration changes due to ionic transport). To be able to uncouple the Ohmic resistance from the total stack resistance, measurements in AC mode are required. In AC measurements there is no net ionic current due to the alternating direction, which eliminates the non-Ohmic effects in the system[34]. For determination of the Ohmic stack resistance, alternating currents with a frequency between 1 and 10 kHz are applied, while measuring the impedance. Total stack resistance is measured in DC mode (direct current, 17 steps of 40 s each, from 0 to 40 A/m² and back), and the non-Ohmic resistance is calculated as the difference between the total and Ohmic resistance of the stack. A blank measurement is done to determine the resistance of the electrolyte and the outer CMX membrane, in which no salt solutions are fed.

3.3 Results and discussion

3.3.1 Temperature profile development in the system

In our measurements, we controlled the inlet temperature of both feed streams and measured the outlet temperatures. For the non-isothermal cases, we found that the cold feed stream (independent of its composition) had a higher outlet temperature ($\sim 32^\circ\text{C}$) than the outlet of the hot feed stream ($\sim 28^\circ\text{C}$). This indicates a high amount of heat exchange between the two streams, as was expected. Note that we measure the average outlet temperatures of both streams,

and are not able to record local temperatures inside the stack. For isothermal systems, both hot and cold, the outlet temperatures of both streams were equal. For the low temperature isothermal cases, the streams showed a slight increase in temperature, from 20 °C to ~ 22 °C, while for the isothermal high temperature case, the outlet streams were cooled down from 40 °C to ~ 32 °C due to the temperature of the surroundings of ~ 25 °C. Heat is conducted well through our, mostly steal, membrane stack. Thermal insulation is present around the reservoir and the feed tubes towards the stack, but not the total stack. Thermal insulation of the total stack would prevent leakage of heat, but also inhibit our visual observations of the bubble formation in the stack as a result of the elevated temperatures.

In order to estimate the local temperature profile within the stack, the following partial differential equations (eq. 3.1) were solved in MATLAB using polynomial collocation with a Chebyshev polynomial basis [38]. This model is a simple extension of the existing cross flow heat exchange temperature profile model to include heat losses to the environment from both the cold and hot streams [39]. By measuring both the in- and outlet temperatures of the stack we obtain an estimate of the heat losses to the surroundings which are taking into account in our model. In this approach, the heat losses/gains from the environment are approximated as being proportional to the temperature difference between each respective stream (river/sea) and the environment (treated as a constant wall temperature). Qualitatively similar results are obtained from the 2D analytical solution without heat loss, particularly with respect to the average temperature difference between the hot and cold streams at any given point in the stack [39].

$$\begin{aligned}\frac{\partial T_C}{\partial x} &= \frac{kA}{mC_pXY}(T_H - T_C) + \frac{hA}{mC_pXY}(T_{\text{wall}} - T_C) \\ \frac{\partial T_H}{\partial y} &= \frac{-kA}{mC_pXY}(T_H - T_C) + \frac{hA}{mC_pXY}(T_{\text{wall}} - T_H)\end{aligned}\quad (3.1)$$

In Equation 3.1 k is the overall heat transfer coefficient between hot and cold streams, h is the heat transfer coefficient to the environment, A the heat exchange area, m is the mass of fluid in the respective stream (in this case equal for hot and cold and equal to the flow rate multiplied by residence time), C_p the heat capacity and X and Y represent the length of the x and y path respectively. hA is estimated based on the measured values for the in- and outlet temperatures, together with our relevant system parameters, and is found to be $hA = 3 \text{ J} \cdot \text{m/K}$. kA is estimated based on the flow rate in our system and assumed to be $2.35 \text{ J} \cdot \text{m/K}$. Using these values, a local temperature profile within the stack can be

Figure 3.1 — Dimensionless temperature profiles inside the stack, resulting from numerical calculations of local temperatures. Temperature in the hot stream, θ_H (a) (flow from bottom to top, as indicated by arrow) and temperature in the cold stream, θ_C (b) (flow from left to right, indicated by arrow) as a function of location in the stack. (c) Local dimensionless temperature difference ($\theta_H - \theta_C$) between hot and cold streams, indicating a positive temperature gradient in all locations of the stack.

estimated. The average outlet temperatures are compared with the experimentally measured outlet temperatures and are in good agreement.

Results from this model are shown in Figure 3.1, which shows the dimensionless temperatures, $\theta = (T - T_{C,in}) / (T_{H,in} - T_{C,in})$, with T as the local temperature, $T_{H,in}$ and $T_{C,in}$ as the respective hot and cold inlet temperatures, in the hot and cold streams along with the difference. From our model, we can predict a temperature gradient in the same direction at all locations in the stack (see Figure 3.1(c)). At the outlets, the temperature difference is dramatically reduced when

Figure 3.2 — Potential required to obtain a constant current of 15 A/m^2 in ED mode in the different temperature configurations. Lines are for indication purposes only. Error bars are standard deviation between the measurements

compared to the difference in inlet temperatures. From the temperature profiles one can see that the cold stream is heated mostly at the side at the inlet of the hot stream, left in Figure 3.1(b). The hot stream is, as is expected, cooled down the most at the inlet side of the cold stream, seen in the bottom of Figure 3.1(a).

3.3.2 Electrodialysis

Six measurements were done at every temperature configuration shown in Table 3.1. During the first three measurements no samples were taken to not disturb the flow patterns in the system, while samples were taken during the additional measurements. Results of the constant current measurements ($I = 0.15 \text{ A}$ which corresponds to a current density of 15 A/m^2), for which the potential was recorded, are shown in Figure 3.2. As can be observed, there is a distinct difference between the different temperature configurations, as is expected. The highest potential is required for measurements with an isothermal low temperature, while the lowest potential is required for measurements with an isothermal high temperature. The cases in which there is a temperature gradient applied require a moderate potential for the same current, but no significant difference between the two directions of the temperature gradient was measured. The variance between the different measurement runs (six per temperature configuration), were very small (a relative error of $\sim 2\%$ at maximum).

The settling time for the potential to become stable is ~ 20 s, after which the potential becomes very stable. This indicates that we are in the Ohmic regime and the current is still linearly dependent on the potential that is applied, which was also confirmed by an IV-sweep of the total stack, where the transition from the Ohmic regime towards the limiting regime is observed around 0.24 A (24 A/m^2).

Most of the drop in required potential for the transport of current can be explained by the altered diffusivity of ions at higher temperatures. If the temperature of the feed is higher, the diffusivity (and therefore the conductivity) of the solution is increased, and thus the resistance of the total stack is reduced. The conductivity of the solution is increased by approximately 27% [40] at 40°C , which is also approximately the drop in required potential. Surprisingly, our potential measurements did not show a significant difference between the measurements in which a temperature gradient was applied, which we mainly attribute to the efficient heat transfer between the different flow compartments leading to a smaller gradient vs. inlet conditions, as was discussed in the previous section.

To establish if the imposed temperature (gradient) has an influence on the selectivity of the membranes or the ratio between cation and anion fluxes, samples were taken of both streams during the measurements after the potential stabilized (around $t = 300$ s). Both cation and anion concentrations in these streams were measured, results are shown in Figure 3.3. For cations, there were significant concentrations of Na^+ and K^+ in the outlet streams. The presence of K^+ is a result of cation exchange with the electrolyte, in which K^+ is the main cation. The inlet concentration that was measured is slightly higher than the feed concentration of salt at the start of the experiments (0.020 M versus 0.017 M), which is also contributed to the flux of ions from the electrolyte towards the salt solution. The total inlet cation concentration (measured at the end of all experiments) is compared to the total outlet cation concentration, consisting of both measured cations. In the anion analysis only Cl^- ions were found to be present in the solution. The total average concentration of the outlet streams was increased, also as a result of a concentration gradient between the electrolyte solution and the feed solutions, which results in leakage of the ions towards the salt solutions.

No significant difference in the outlet ion concentrations for the different temperature configurations was found. This indicates that there is no significant loss of selectivity of the membranes in the case of elevated temperatures and temperature gradients, but also no enhancement. We attribute this to the fact that we operate in the commercially relevant Ohmic regime, where we only expect minimal changes for the different configurations depending on how close to the limiting plateau the system is operated. The absence of concentration polarization inhibits any differences in ion transport between the different temperature

Figure 3.3 — Outlet concentrations of both ions for the different cases and streams. Error bars are the standard deviation between three measurement samples. The dashed line is the inlet concentration of 0.020 M, which is measured after all measurements are finished.

configurations to play a significant role in the process under these conditions. Surprisingly, the temperature (gradients) do not significantly influence the water transport through the membranes either, which is unlike expectations based on previous results [16]. This is beneficial for the efficiency of the process and enables the application of temperature gradients in commercial systems. Cation concentrations are consistently higher than anion concentrations (in both depleted and enriched streams) which is attributed to the preferential leaking of cations from the electrolyte to the feed solution through the outer CMX membranes and the existence of additional anions in the system which are not measured in IC measurements, such as HCO_3^- . With the in- and outlet concentrations (c_{in} and c_{out}), the so called desalination degree $(1 - c_{\text{out}}/c_{\text{in}}) \times 100\%$ [41] can be calculated, yielding a desalination degree of $\sim 35\%$ for cations for all cases. The desalination degree is similar for all configurations (as was expected due the equal current that was applied for all configurations), as the outlet concentrations are not significantly different for the different configurations.

Another indicator is the current efficiency of desalination;

$$CE = \frac{zFQ_f(c_{\text{in}} - c_{\text{out}})}{NI} \times 100\% \quad (3.2)$$

where Q_f is the diluate flow rate (m^3/s), F is Faraday's constant, z the ion

valency, N is the number of cell pairs and I is the current (A). This current efficiency is an indicator of the amount of current that is being used for effective ion transport. A current efficiency lower than 100% indicates the undesired transport of additional charge carriers (such as H^+ or OH^-) or the existence of shortcut currents in the system. For our measurements, the current efficiency is $\sim 100\%$, for both cations and anions, indicating that all current is used for selective transport of Na^+ and Cl^- ions. This high value is a result of measuring in the Ohmic regime, in which there are no significant limitations in ion transport and water splitting is not significant. Enhancing the diffusivity in the diluted channel is not of larger influence than enhancing the diffusivity in the enriched channel, which is contrary to our expectations [16, 31]. At higher currents, in the so-called limiting and overlimiting current regime [1, 42], we expect the current efficiency to change for the different temperature configurations as a result of the increased diffusivity of the ions at higher temperatures. In the limiting current regime, concentration polarization over the membrane results in an enhanced resistance for ion transport, limited by the (diffusive) transport of ions towards the membrane. If temperature is increased in this case, the transport of ions towards the interface is enhanced, resulting in a higher current efficiency.

The total power ($P = UI$) required for desalination can be calculated for the different temperature configurations. As the current was kept constant, the only variable in this equation is the required potential U (Figure 3.2). This potential was highest for the low temperature isothermal case and lowest for the high temperature isothermal case. Based on the average potential required in the steady state of our 50 mL/min measurements, the power required for the low temperature isothermal case is highest ($P = 58.7$ mW) and is reduced by $\sim 15\%$ for the high temperature isothermal case ($P = 50.1$ mW). The cases in which there is a temperature gradient require intermediate power ($\sim P = 53.5$ mW for both cases). Thus, heating up one of the feed streams reduces the required power by $\sim 9\%$, independent on the composition of the hot stream. As the depletion and enrichment of the different ions did not differ between the different cases, it can be concluded that pre-heating of (one of the) feed streams for ED processes can reduce the power input in these processes. The heat that it would require to increase the feed temperature of both streams accounts to 140 W, and is significantly higher than the reduction in electric power that is obtained. However, process plants usually need to cool down process streams before they can be discharged into rivers, and the ED process efficiency can potentially be enhanced by utilizing this waste heat for increasing the temperature of the feed streams [36, 37]. Of course, the effects of elevated temperatures on membrane fouling and lifetime should be investigated in more detail as well before any conclusions on improving efficiency through implementation can be drawn.

For fundamental understanding of the effect of temperature on the formation

of ion concentration polarization and transport through the depletion zone, ED experiments in the limiting or overlimiting current regime would be of interest. However, experimental implementation of this in this RED stack set-up is problematic due to bubble formation at higher temperatures and intensive currents, resulting in a non-stable system for measurements. In the next chapter of this thesis, a different ED stack is used for the investigation of temperature gradients in ED in the limiting current regime at lower temperatures which might alleviate these problems.

3.3.3 Reverse electrodialysis

From the measurements in RED mode, the gross power density (GPD in W/m^2) can be calculated using the measured current (I) and potential (U), which is corrected for the resistance of the electrolyte by subtraction of U_{blank} and the total membrane area inside the four cell pairs (A).

$$GPD = \frac{I(U - U_{\text{blank}})}{A} \quad (3.3)$$

The calculated GPD as function of current density is plotted in Figure 3.4 for the different temperature configurations. As expected, the maximum GPD is increased for the cases in which at least one of the feed streams has an elevated inlet temperature. In the most extreme case, the total maximum GPD is increased with almost 38% (from 0.68 W/m^2 at $T = 20 \text{ }^\circ\text{C}$ to 0.94 W/m^2 at $T = 40 \text{ }^\circ\text{C}$), while if only one stream is heated the total maximum GPD is increased by over 25% to 0.85 W/m^2 . The current density at which this maximum GPD is found is also shifting when temperatures are increased in the system, which is beneficial for the total energy that can be harvested from the RED stack.

Measured and fitted (from IV data) values for the open circuit voltage (OCV in V) are reported in Table 3.2. The OCV is the potential difference over the membrane stack as a result of the imposed ion concentration gradients, when there is no applied current and no losses due to concentration gradients in the system. For the low temperature isothermal case, the measured OCV is 0.60 V and it increases when a temperature gradient is applied, just as is expected. Consistently, the measured OCV is slightly higher than the fitted OCV, as this results from fitting with data points at the other applied currents. The measured OCV values can be compared to theoretical values that are expected for a stack of four cell pairs, based on the Nernst equation;

$$E = \frac{RT}{zF} \alpha_{\text{CEM}} \ln\left(\frac{\gamma_c c_c}{\gamma_d c_d}\right) + \frac{RT}{zF} \alpha_{\text{AEM}} \ln\left(\frac{\gamma_c c_c}{\gamma_d c_d}\right) \quad (3.4)$$

using the activity coefficients of the ions in both concentrate and diluate streams (γ_c and γ_d , see Appendix A), the ion concentrations (c_c and c_d), the operating

Figure 3.4 — Gross power density as function of the applied current density in the RED stack for different temperature configurations. The maximum GPD increases with increasing temperature, while the current density at which this maximum occurs also shifts upwards. Lines are for indication purposes only. Errors are calculated using the propagation of errors.

temperature (T) and the universal gas constant (R). The effect of temperature on the activity coefficients for 1:1 salts was treated as negligible in this temperature range, as per previous results [43]. For an actual cell, this potential has to be corrected for the non-perfect permselectivity of the membranes, in our case using the correction factors $\alpha_{\text{CEM}} = 0.907$ and $\alpha_{\text{AEM}} = 0.970$, obtained from the membrane manufacturer.

For simplicity, we have calculated the expected Nernst potential at both 20 and 40 °C, and have not incorporated the temperature gradient in the Nernst equation, as the thermoelectric potential generated by the temperature gradient is expected to be on the order of a few mV at most [24, 25]. At $T = 20$ °C the expected cell potential is 0.146 V (compared to a measured cell potential of 0.150 V), while at $T = 40$ °C this potential is increased to 0.161 V (measured cell potential of 0.155 V). The differences in measured and predicted values can be explained by slight variations in the temperature during experiments, yielding an overestimation of the cell potential at high temperatures and an underestimation of the cell potential at low temperatures.

Another important parameter for RED is the electrical resistance of the stack, as this determines the efficiency of the system and the potential power generation with it. The total impedance of the stack can be split into an Ohmic and a non-Ohmic

part. The Ohmic resistance of the stack consists of both AEM and CEM resistance, as well as the resistances in the feed streams, $R_{\text{Ohmic}} = R_{\text{CEM}} + R_{\text{AEM}} + R_{\text{RW}} + R_{\text{SW}}$ and can be measured using the AC mode of the potentiostat, while the total resistance is measured in DC mode. The non-Ohmic resistance can be calculated as the difference between the measured total and Ohmic resistance. All resistances are shown in Table 3.2, and it is clear that the total resistance of the stack goes down with increasing temperature. This mostly is a result from a lower Ohmic resistance, which results from the increased diffusivity of ions in both feed streams (reduction of R_{RW} and R_{SW}) and thus the enhanced ion transport in the solutions. For example, at the average temperature in the stack for inlet temperatures of $T_{\text{D}} = T_{\text{C}} = 40$ °C, the river water resistance is decreased by approximately 27% [40] and a similar value is expected for the sea water [44]. The resistance of CMX and AMX membranes is also expected to decrease by approximately this amount based on previous literature [45] and this is also the observed percent reduction in the total Ohmic resistance for the isothermal hot system vs. an inlet of 20 °C for both channels. The non-Ohmic resistance of the stack increases with an increase of temperature in the stack due to higher capacitive effects of the solution at higher temperatures. As a result of this, a larger concentration gradient is developed in the direction of the flow because of the larger charge transport in these cases, which results in a higher non-Ohmic resistance in the system [46].

The net power density (NPD, shown in Figure 3.5) that can be obtained with the RED stack can be calculated using the GPD and the losses that are present as a result of pressure drops over the effluent channels. The pressure drop was measured to be 25 mbar on average, and the applied flow rate was 50 mL/min

Table 3.2 — Open circuit voltages and stack resistances for different temperature configurations. Our stack consisted of four cell pairs. Errors in directly measured values are standard deviations, errors of calculated values are standard errors (given between brackets).

	$T_{\text{D}} = T_{\text{C}} = 20$ °C	$T_{\text{D}} = 20$ °C, $T_{\text{C}} = 40$ °C
OCV _{meas} [V]	0.60 (5.8×10^{-4})	0.61 (1.5×10^{-3})
OCV _{fit} [V]	0.57 (2.5×10^{-3})	0.59 (2.1×10^{-3})
R_{total} [Ω]	1.59 (1.1×10^{-2})	1.38 (8.7×10^{-3})
R_{Ohmic} [Ω]	1.56 (3.5×10^{-2})	1.30 (1.7×10^{-2})
$R_{\text{Non-Ohmic}}$ [Ω]	0.03 (7.0×10^{-4})	0.08 (1.2×10^{-3})
	$T_{\text{D}} = 40$ °C, $T_{\text{C}} = 20$ °C	$T_{\text{D}} = T_{\text{C}} = 40$ °C
OCV _{meas} [V]	0.62 (5.8×10^{-4})	0.62 (1.5×10^{-3})
OCV _{fit} [V]	0.59 (2.0×10^{-3})	0.60 (2.0×10^{-3})
R_{total} [Ω]	1.39 (8.7×10^{-3})	1.33 (8.4×10^{-2})
R_{Ohmic} [Ω]	1.29 (1.6×10^{-3})	1.19 (6.1×10^{-3})
$R_{\text{Non-Ohmic}}$ [Ω]	0.10 (6.4×10^{-4})	0.14 (8.9×10^{-3})

Figure 3.5 — Maximum gross and net power density for the different temperature configurations.

(a linear flow velocity of 0.81 cm/s) for both compartments. We did not find a significant change in pressure drop for the different temperature configurations. The net power density is highest for the case where there is a high temperature, indicating that by heating the inlet streams, the efficiency of the RED stack can be enhanced.

3.4 Conclusion

In this chapter, we have investigated the effect of imposed temperature gradients on ED and RED performance. We have experimentally demonstrated that the power input for electrodialysis processes for desalinating sea water can be reduced by ~ 15% if the temperature of the inlet streams are increased from 20 °C to 40 °C. The selectivity of the used commercial membranes and the degree of desalination are not significantly affected if the temperature is increased. An imposed temperature gradient over the membranes in the stack did also increase the desalination efficiency, since the power input was reduced by ~ 9%, although we measured no significant influence of the direction of the imposed temperature gradient in combination with the direction of the electric field in the Ohmic regime. The reduced power input can be attributed mainly to reduced stack resistance as a result of elevated diffusivity of the ions caused by an elevated temperature. This indicates that by using low-grade waste heat to heat even a single inlet stream

in an ED process, the total required power to produce desalinated water can be decreased. Heating only one of the streams can also potentially reduce the negative effects of working at elevated temperatures, such as scaling and fouling [21].

In reverse electrodialysis, the gross power density was increased with $\sim 38\%$ as a result of an increased temperature from $20\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$. If a temperature gradient is imposed, the GPD increased by $\sim 25\%$. The Ohmic resistance of the stack decreases for higher temperatures, which results in a higher obtainable current and thus a higher gross power density. The current density at which the maximum power density is obtained is shifted upwards with increasing temperature. No significant difference in power generation was determined based on the direction of the temperature gradient at the conditions studied, although this may not be the case when considering mixtures including multivalent ions or if membrane permselectivity is changing with temperature.

It is important to note that if streams are to be heated up by anything other than waste heat, the energy cost for heating the feed streams is substantially higher than the benefit that can be gained in ED or RED operations. Other challenges for the practical implementation of elevated temperatures and temperature gradients arise from the physical properties of the system. At higher temperatures, the nucleation of gas bubbles within the stack is enhanced because of the lower solubility of gases at high temperatures, resulting in a higher overall resistance and a decreased performance of the stack. Also, as a result of the elevated temperature, the characteristic IV-curve of the stack will shift, as the transition to the limiting regime takes place at a higher voltage. Apart from that, the effect of temperature on other effects such as fouling [47, 48] and membrane lifetime [49] should be investigated in more detail.

In our experiments, heat transfer in between both feed streams was relatively high (as a result of flow configuration and the small compartments), resulting in small effects of the imposed temperature gradient on ion transport phenomena. We therefore can mainly conclude on the effect of operating ED and RED at higher temperatures. In the next chapter, a different flow configuration will be applied to investigate the effect of temperature gradients in more detail.

As we were measuring in the Ohmic regime, the effect of temperature on ion concentration polarization was minor. However, in the limiting and overlimiting current regimes, the effect of temperature may be more significant, as it increases the diffusivity of the ions in solution and thus can potentially enhance transport in the boundary layer at the membrane [31]. Apart from that, the reduced viscosity at higher temperatures might result in a thinner boundary layer, also reducing the resistance of ion transport near the membrane. Thermoelectroconvection, an instability created by local Joule heating near a charge selective interface [50], can also be of influence in these systems. In ED operation, this might result in

significant differences in current efficiency and desalination degree as function of the applied temperature (gradient). Therefore, operation at higher currents is interesting for investigation of temperature effects on ion transport in the vicinity of membranes.

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References

- [1] H. Strathmann, *Electrodialysis, a mature technology with a multitude of new applications*, Desalination **264**, 268 (2010).
- [2] F. G. Helfferich, *Ion Exchange* (McGraw-Hill, 1962).
- [3] W. A. McRae, Electroseparations, electrodialysis in *Kirk-Othmer Encyclopedia of Chemical Technology*,
- [4] G. L. Wick, *Power from salinity gradients*, Energy **3**, 95 (1978).
- [5] R. E. Lacey, *Energy by reverse electrodialysis*, Ocean Eng. **7**, 1 (1980).
- [6] R. Pattle, *Production of electric power by mixing fresh and salt water in the hydroelectric pile*, Nature **174**, 660 (1954).
- [7] J. N. Weinstein and F. B. Leitz, *Electric power from differences in salinity: The dialytic battery*, Science **191**, 557 (1976).
- [8] J. W. Post, C. H. Goeting, J. Valk, S. Goinga, J. Veerman, H. V. M. Hamelers, and P. J. F. M. Hack, *Towards implementation of reverse electrodialysis for power generation from salinity gradients*, Desalin. Water Treat. **16**, 182 (2010).
- [9] J. W. Post, H. V. M. Hamelers, and C. J. N. Buisman, *Energy recovery from controlled mixing salt and fresh water with a reverse electrodialysis system*, Environ. Sci. Technol. **42**, 5785 (2008).
- [10] P. Długolecki, A. Gambier, K. Nijmeijer, and M. Wessling, *Practical potential of reverse electrodialysis as process for sustainable energy generation.*, Environ. Sci. Technol. **43**, 6888 (2009).
- [11] J. G. Hong, B. Zhang, S. Glabman, N. Uzal, X. Dou, H. Zhang, X. Wei, and Y. Chen, *Potential ion exchange membranes and system performance in reverse electrodialysis for power generation: A review*, J. Memb. Sci. **486**, 71 (2015).

-
- [12] D. A. Vermaas, M. Saakes, and K. Nijmeijer, *Power generation using profiled membranes in reverse electrodialysis*, J. Memb. Sci. **385-386**, 234 (2011).
- [13] S. Pawlowski, V. Geraldès, J. G. Crespo, and S. Velizarov, *Computational fluid dynamics (CFD) assisted analysis of profiled membranes performance in reverse electrodialysis*, J. Memb. Sci. **502**, 179 (2016).
- [14] D. A. Vermaas, M. Saakes, and K. Nijmeijer, *Enhanced mixing in the diffusive boundary layer for energy generation in reverse electrodialysis*, J. Memb. Sci. **453**, 312 (2014).
- [15] W. J. van Egmond, M. Saakes, S. Porada, T. Meuwissen, and C. J. N. Buisman, *The concentration gradient flow battery as electricity storage system: Technology potential and energy dissipation*, J. Power Sources **325**, 129 (2016).
- [16] M. Tasaka, T. Hirai, R. Kiyono, and Y. Aki, *Solvent transport across cation-exchange membranes under a temperature difference and under an osmotic-pressure difference*, J. Memb. Sci. **71**, 151 (1992).
- [17] S. Kim and M. M. Mench, *Investigation of temperature-driven water transport in polymer electrolyte fuel cell: Thermo-osmosis in membranes*, J. Memb. Sci. **328**, 113 (2009).
- [18] K. D. Sandbakk, A. Bentien, and S. Kjelstrup, *Thermoelectric effects in ion conducting membranes and perspectives for thermoelectric energy conversion*, J. Memb. Sci. **434**, 10 (2013).
- [19] J. Veerman, R. M. de Jong, M. Saakes, S. J. Metz, and G. J. Harmsen, *Reverse electrodialysis: Comparison of six commercial membrane pairs on the thermodynamic efficiency and power density*, J. Memb. Sci. **343**, 7 (2009).
- [20] W. J. van Egmond, U. K. Starke, M. Saakes, C. J. N. Buisman, and H. V. M. Hamelers, *Energy efficiency of a concentration gradient flow battery at elevated temperatures*, J. Power Sources **340**, 71 (2017).
- [21] A. Moura Bernardes, M. A. S. Rodrigues, and J. Z. Ferreira, in *Electrodialysis and water reuse: Novel approaches* (Springer Berlin Heidelberg, 2014), pp. 11–23.
- [22] F. B. Leitz, M. A. Accomazzo, and W. A. McRae, *High temperature electrodialysis*, Desalination **14**, 33 (1974).
- [23] G. J. Hills, P. W. M. Jacobs, and N. Lakshiminarayanaiah, *Non-isothermal membrane potentials*, Nature **179**, 96 (1957).
- [24] T. Ikeda, *Thermal membrane potential*, J. Chem. Phys. **28**, 166 (1958).
- [25] M. Tasaka, *Thermal membrane potential and thermoosmosis across charged membranes*, Pure & Appl. Chem. **58**, 1637 (1986).
- [26] M. Tasaka, T. Mizuta, and O. Sekiguchi, *Mass transfer through polymer membranes temperature gradient due to a*, J. Memb. Sci. **54**, 191 (1990).
- [27] K. Hanaoka, R. Kiyono, and M. Tasaka, *Thermal membrane potential across anion-exchange membranes in KCl and KIO₃ solutions and the transported*

- entropy of ions*, J. Memb. Sci. **82**, 255 (1993).
- [28] B. B. Sales, O. S. Burheim, S. Porada, V. Presser, C. J. N. Buisman, and H. V. M. Hamelers, *Extraction of energy from small thermal differences near room temperature using capacitive membrane technology*, Environ. Sci. Technol. Lett. **1**, 356 (2014).
- [29] M. S. Dariel and O. Kedem, *Thermoosmosis in semipermeable membranes*, The Journal of Physical Chemistry **79**, 336 (1975).
- [30] V. M. Barragán and S. Kjelstrup, *Thermo-osmosis in membrane systems: A review*, Journal of Non-Equilibrium Thermodynamics **42**, 217 (2017).
- [31] J. A. Wood, A. M. Benneker, and R. G. H. Lammertink, *Temperature effects on the electrohydrodynamic and electrokinetic behaviour of ion-selective nanochannels*, J. Phys. Condens. Matter **28**, 114002 (2016).
- [32] S. Tseng, Y.-M. Li, C.-Y. Lin, and J.-P. Hsu, *Salinity gradient power: influences of temperature and nanopore size*, Nanoscale **8**, 2350 (2016).
- [33] M. Tedesco, E. Brauns, A. Cipollina, G. Micale, P. Modica, G. Russo, and J. Helsen, *Reverse electrodialysis with saline waters and concentrated brines: A laboratory investigation towards technology scale-up*, J. Memb. Sci. **492**, 9 (2015).
- [34] A. Daniilidis, D. A. Vermaas, R. Herber, and K. Nijmeijer, *Experimentally obtainable energy from mixing river water, seawater or brines with reverse electrodialysis*, Renew. Energy **64**, 123 (2014).
- [35] M. Janssen, A. Härtel, and R. Van Roij, *Boosting capacitive blue-energy and desalination devices with waste heat*, Phys. Rev. Lett. **113**, 268501 (2014).
- [36] L. E. Bell, *Cooling, heating, generating power, and recovering waste heat with thermoelectric systems*, Science **321**, 1457 (2008).
- [37] S. Brückner, S. Liu, L. Miró, M. Radspieler, L. F. Cabeza, and E. Lävemann, *Industrial waste heat recovery technologies: An economic analysis of heat transformation technologies*, Appl. Energy **151**, 157 (2015).
- [38] J. A. C. Weideman and S. C. Reddy, *A MATLAB differentiation matrix suite*, ACM Trans. Math. Softw. **26**, 465 (2000).
- [39] A. M. Binnie and E. G. C. Poole, in *Mathematical Proceedings of the Cambridge Philosophical Society*, Cambridge Univ. Press (1937), No. 03, pp. 403–411.
- [40] G. C. Benson and A. R. Gordon, *A reinvestigation of the conductance of aqueous solutions of potassium chloride, sodium chloride, and potassium bromide at temperatures from 15 to 45°C*, J. Chem. Phys. **13**, 473 (1945).
- [41] M. B. Sik Ali, A. Mnif, B. Hamrouni, and M. Dhahbi, *Electrodialytic desalination of brackish water: Effect of process parameters and water characteristics*, Ionics **16**, 621 (2010).
- [42] V. V. Nikonenko, A. V. Kovalenko, M. K. Urtenov, N. D. Pismenskaya, J. Han, P. Sistat, and G. Pourcelly, *Desalination at overlimiting currents:*

- State-of-the-art and perspectives*, Desalination **342**, 85 (2014).
- [43] L. F. Silvester and K. S. Pitzer, *Thermodynamics of electrolytes. X. Enthalpy and the effect of temperature on the activity coefficients*, Journal of Solution Chemistry **7**, 327 (1978).
- [44] M. Hayashi, *Temperature-electrical conductivity relation of water for environmental monitoring and geophysical data inversion*, Environ. Monit. Assess. **96**, 119 (2004).
- [45] P. Dhugolecki, P. Ogonowski, S. J. Metz, M. Saakes, K. Nijmeijer, and M. Wessling, *On the resistances of membrane, diffusion boundary layer and double layer in ion exchange membrane transport*, J. Memb. Sci. **349**, 369 (2010).
- [46] A. Cipollina and G. Micale, *Sustainable energy from salinity gradients* (Woodhead Publishing, 2016).
- [47] G. Grossman and A. A. Sonin, *Membrane fouling in electrodialysis: A model and experiments*, Desalination **12**, 107 (1973).
- [48] D. A. Vermaas, D. Kunteng, M. Saakes, and K. Nijmeijer, *Fouling in reverse electrodialysis under natural conditions*, Water Res. **47**, 1289 (2013).
- [49] A. Collier, H. Wang, X. Zi Yuan, J. Zhang, and D. P. Wilkinson, *Degradation of polymer electrolyte membranes*, Int. J. Hydrogen Energy **31**, 1838 (2006).
- [50] E. A. Demekhin, S. Amiroudine, G. S. Ganchenko, and N. Y. Khasmatulina, *Thermoelectroconvection near charge-selective surfaces*, Phys. Rev. E **91**, 063006 (2015).
- [51] R. Weast, D. Lide, M. Astle, and W. Beyer, *Handbook of Chemistry and Physics*, 76 ed. (CRC press, 1989).

Appendix

Table 3.3 — Activity coefficients (at 25 °C) used for calculation of Nernst potential in RED [51]

Ion	Concentration [M]	γ_i
Na ⁺	0.5	0.6137
Cl [−]	0.5	0.6509
Na ⁺	0.017	0.8734
Cl [−]	0.017	0.8777

CHAPTER 4

Effect of temperature gradients on electrodialysis in the limiting current regime

Abstract — Temperature gradients in electrodialysis (ED) stacks can potentially enhance the efficiency of charge separation and the selective transport of ions. We investigated temperature gradients in the Ohmic regime in the previous chapter. In this chapter, the effect of temperature gradients in the limiting current regime is investigated, where diffusion of ions towards the membrane determines the rate of transport and temperature gradients will have potentially the largest influence. Commercial ion exchange membranes (FAS and FKS, FUMATECH, Germany) are used for the investigation of temperature gradients in the limiting current regime. In contrast to the Ohmic regime, we find that heating the diluted stream increases the current obtained (at a constant applied potential) when compared to heating the concentrate stream in systems containing monovalent K^+ and Na^+ ionic solutions. For mixtures of mono- and divalent ions, the temperature gradient has a larger influence on the selectivity of the separation. If the desalted stream is heated, divalent Mg^{2+} ions show a higher transport than the monovalent K^+ and Na^+ ions, while the total current is only slightly lowered at the same driving potential. This is due to the enhanced competitive transport of the mono- and divalent ions under the application of a temperature gradient and the influence of temperature on the interaction between the different ions and the membrane. These results show the potential application of temperature gradients to enhance the selective separation of mono- and divalent ions.

4.1 Introduction

The number of ions transported in electrodialysis (indicated by the measured current) increases linearly (following Ohm's law) with increasing driving potential difference, until there is a mismatch between the supply and removal rates of ions at the membrane interface [1, 2]. A depleted boundary layer at the membrane interface develops at elevated field strengths. Ion transport through this boundary layer, which is dictated by diffusion and electromigration, limits the total transport of ions in the system. As a result, a system specific so-called "limiting current density" is observed for all electrodialysis systems, in which the efficiency of the process is reduced since the required power ($P = UI$, where I is the current through and U is the potential over the stack) is increasing while the ionic current is stable. To increase the process efficiency and to be able to operate at higher current densities, the enhancement of selective ion transport in electrodialysis has been of interest for many years [3]. Enhancing the membrane selectivity can be of interest, but nowadays commercial membranes have a permselectivity of over 90% [4] and enhancing this would only yield minor improvements on the overall process. Most research focuses on mixing the fluid in the stack by means of profiled membranes [5, 6], ion conducting spacers that reduce the electrical resistance of the dilute channel [7, 8] or turbulence promoting spacers [9–11] to increase the supply of ions towards the membrane interface.

The total flux of ions ($\mathbf{J}_i$) through the boundary layer towards the membrane for dilute systems can be described by the Nernst-Planck equation (Equation 4.1). The ion transport consists of advection via the flow velocity $\mathbf{u}$, diffusion as a result of a concentration gradient ∇c_i and a molecular ion diffusivity D_i or similarly, through a temperature gradient ∇T with diffusivity $D_{T,i}$, an electromigration flux resulting from the local electric potential gradient ∇V , the ionic mobility ν_i , charge z_i and Faraday's constant F .

$$\mathbf{J}_i = \mathbf{J}_{i,\text{conv}} + \mathbf{J}_{i,\text{migr}} + \mathbf{J}_{i,\text{diff}} = c_i \mathbf{u} - \nu_i z_i F c_i \nabla V - D_i \nabla c_i - D_{T,i} \nabla T \quad (4.1)$$

Temperature has a large influence on the physical properties of an ionic solution, and thus influences the total flux as described by Equation 4.1. For instance, the diffusivity D_i and mobility ν_i of ions in solution increase with increasing temperature, while the viscosity of the solution decreases with increasing temperature [12]. Since $D_i \sim T/\eta$ and $\nu_i \sim D_i/RT$, temperature has a larger influence on the diffusivity than on the electric mobility. If the temperature in electrodialysis systems is altered, the charge transport characteristics in the system will therefore be changes [13]. In general, at higher temperatures, an increased flux of ions is expected as a result of the enhanced ionic mobility and diffusivity of ions in the solution and the subsequent effect of this on the different terms of the Nernst-Planck equation [14, 15]. Membrane resistance reduces as a function of

increasing temperature, most pronounced at temperatures above 30 °C [16]. A thermodiffusive flux (known as the Soret effect) due to a temperature gradient ∇T and the thermodiffusion coefficient $D_{T,i}$ should be considered in non-isothermal systems [17]. While many studies have focused on the role of temperature in isothermal experiments, fewer have investigated the effect of temperature gradients on the charge transport in electrodialysis systems [18].

The combined effect of temperature gradients, (induced) potential gradients and developing concentration gradients in electrodialysis yields a complicated interplay of effects, opening up a rich field of investigation. Temperature gradients in the membrane directly influence the ion flux through the contribution of thermodiffusive transport yielding a thermoelectric potential difference [19–21] and can induce thermo-osmotic water transport across ion exchange membranes [17, 22–24]. The direction and magnitude of the thermo-osmotic water transport are dependent on both membrane and system properties, and the thermo-osmotic water transport number is different for all experimental systems [22]. Additionally, a temperature gradient can theoretically enhance the selectivity of the separation process as a result of reducing the non-desired co-ion transport through the membrane [25]. By heating the ion depleted stream, diffusive ion transport inside this stream can be enhanced compared to the transport in the enriched stream. This enhances the diffusive transport of counter-ions towards the membrane in the dilute stream, while the relative diffusive transport of co-ions in the concentrate stream is reduced. Since the diffusion boundary layer is most important in the limiting current regime, the effect of temperature and temperature gradients is expected to be most pronounced in this regime.

The separation of divalent from monovalent ions is of interest for industrial desalination [26–28], for instance in systems where heavy metals have to be selectively removed and in water softening by exchanging divalent ions with monovalent ions [29, 30]. Electrodialysis is one of the techniques that is promising for this separation [31, 32]. Competitive charge transport between mono- and divalent ions changes the ion flux through a membrane if a mixture is present versus a pure salt solution [33]. In a mixture, the relative flux of monovalent Na^+ was drastically reduced by the addition of divalent Mg^{2+} or Ca^{2+} ions, while the effect of adding Na^+ on the Mg^{2+} flux was minor. The temperature dependence of the diffusivity is slightly different for all ions and can influence the selectivity of the ED process for di- or monovalent ions. In general, at higher temperatures, the relative differences between the diffusivity of the different ions are enhanced [34] resulting in altered transport characteristics. Unequal temperatures in the concentrate and diluate stream can, through these different relative diffusivities, theoretically yield more selective transport of these ions relative to one another. Temperature can also have an effect on the interaction between the different ions and the membrane. For example, the ion hydration radius affects the interaction

with the membrane and this radius is dependent on temperature.

In the previous chapter, the effect of temperature and temperature gradients in the industrially relevant Ohmic regime was investigated, where it was found that increasing the temperature of (one of the) feed streams enhances the efficiency of ED processes [18]. However, the direction of the applied temperature gradient did not have a significant influence on the selectivity and the reduction in required power for the ED process in the Ohmic regime. This is expected to be different for operation in the limiting regime, as in this regime the diffusion of ions plays a crucial role in the overall ion transport and the limiting current i_{lim} scales directly with D_i . In this chapter, the influence of temperature and temperature gradients on charge transport in electrodialysis systems in the limiting current regime is investigated. The effect of temperature gradients on the individual ion transport and overall currents is investigated in systems containing either or both mono- and divalent ions. It should be noted that the efficiency of the ED process in the limiting regime will be lower than the efficiency in the Ohmic regime, since the boundary layers present in the limiting regime increase the total resistance of the stack. An elevated temperature (or temperature gradient) can only shift the onset of the limiting current regime, allowing operation at higher potentials and current densities, but not increasing the efficiency of the separation. However, the fundamental investigation of ion transport in the limiting current regime is of interest as knowledge on this regime can be applied in the enhancement of ion separation and yields more insights in the physical background of electrodialysis processes.

4.2 Experimental details

A lab scale, commercially available electrodialysis stack with an active area of $10 \times 10 \text{ cm}^2$ (FUMATECH BWT GmbH, Germany) was used for all measurements. This stack is different from the stack used in the previous chapter. The stack consists of three cell pairs, composed of three FAS-PET-100 (AEM) and four FKS-PET-100 (CEM) membranes spaced with ED-100-4CS PVC ($600 \mu\text{m}$) spacers, all obtained from FUMATECH BWT GmbH, Germany. Before composing the stack, membranes are pre-treated by placing them in 0.5 M KOH overnight and flushing them with 0.017 M KOH to ensure exchange of all native ions in the membrane for K^+ and OH^- , which are ions that are present in the experimental system. The membrane stack is assembled and secured by screwing the end-plates containing the electrodes in a metal framework. The stack is flushed overnight with the desired feed solution to equilibrate the ion composition in the membranes. The stack is operated in a vertical co-flow configuration, feeding the compartments from bottom to top to ensure a constant compartment fluid volume. In the co-flow

configuration, there is less overall heat transfer than for experiments in cross-flow configuration, so we are able to maintain the temperature gradient over a larger part of the system.

To check if membrane permselectivity is affected by the increased temperature, we measured the membrane potential after the electrodialysis experiments, using a standard two compartment measurement [35] set-up at 0.1 M and 0.5 M KCl. By comparing the measured potential to the theoretical potential, $V_t = \frac{RT}{zF} \ln \frac{\gamma_c c_c}{\gamma_d c_d}$, the permselectivity of the membrane can be estimated. In this equation, γ_c and γ_d are the activity coefficients of the electrolyte in the different compartments.

Both IV-sweeps and chronoamperometric measurements are conducted in this work. IV-sweeps are performed to investigate the effect of temperature and temperature gradients on the characteristic shape of the IV-curve. The onset and magnitude of the limiting current regime can be determined by these measurements. For the investigation of the effect of temperature gradients on the charge transport through the boundary layer, and the effect of this on the desalination and selective transport of mono- and divalent ions, chronoamperometric measurements are conducted in the limiting current regime. In these measurements a constant potential is applied and the resulting current is measured. Ion concentrations of the dilute and concentrate stream are measured for the chronoamperometric measurements.

All measurements are done at a flow rate of 50 mL/min in both the dilute and concentrate stream, which corresponds to a linear flow speed of 0.46 cm/s and a residence time of ~ 22 s. Flow was pumped using peristaltic pumps (Cole-Palmer) and pulsations are suppressed by in-house build pulsation dampeners. The flow rate was controlled using an in-house built flow meter (TCO, University of Twente, The Netherlands), containing a McMillan Co. 101 flo-sen flow sensor. To ensure membrane packing, an 0.1 bar overpressure was applied to the electrolyte stream by adjusting the flow rate accordingly.

Different feed solutions are used for the different sets of measurements. Ionic strength is kept constant for all measurements, to be able to directly compare our measurement results. For measurements with NaCl, we use a model solution of 6.7 mM, which is corresponding to typical concentrations of river water in the Netherlands [36]. The electrode compartments are flushed with 6.7 mM K_2SO_4 as a redox solution for avoiding Cl_2 gas formation. We choose this relatively low electrolyte concentration to prevent osmotic water transport from the feed to the electrode rinse. For the measurements with $MgCl_2$, the concentration was 3.35 mM so that the ionic strength of the mono- and divalent solutions are equal. For the measurements with a mixture of mono- and divalent ions we use 3.35 mM NaCl and 1.68 mM $MgCl_2$, once again keeping the ionic strength constant and minimizing the osmotic pressure difference with the electrolyte solution. Outlet flows are recycled into a 20 L feed tank, which is continuously

stirred using aquarium mixers (Wavereef® Auto Top Off System, Single Level Sensor WIC-01S, obtained from Aquaria Veldhuis B.V., The Netherlands).

Experiments are carried out at four different temperature configurations; (1) isothermal at 5 °C, (2) dilute at 5 °C, concentrate at 25 °C, (3) dilute at 25 °C, concentrate at 5 °C and (4) isothermal at 25 °C. When we indicate the dilute or concentrate stream, this of course is an indicator of the stream leaving the stack, as the inlet concentrations of both streams are equal. Feed solutions are kept at the desired temperature by two Julabo F12-ED Refrigerated - Heating Circulators. Prior to all measurements, the system was allowed to reach thermal equilibrium. Both in- and outlet temperatures of both feed streams are constantly monitored using AMA-digit ad 15th thermometers (Amarell, Germany).

All electrical characterization of the system is done using a Metrohm Autolab PGSTAT302N (Metrohm, The Netherlands) which is controlled by NOVA 2.0 software. In the IV-sweeps, we first measure the open circuit potential of the system and afterwards apply currents between 0 and 0.2 A with steps of 0.01 A to the system. The system is allowed to settle for 30 seconds, which corresponds to ~ 1.5 residence times. After 30 seconds, the potential required to obtain the current is measured and the applied current is increased. At experimental times above 600 s the system becomes unstable due to gas formation. For the chronoamperometric measurements, a constant potential of 5 V is applied and the resulting current is measured for 500 seconds. This potential is confirmed to be in the limiting current regime based on the IV-sweeps.

During the chronoamperometric measurements, samples are collected for evaluating ion concentration by means of ion chromatography (IC). Anion concentrations were quantified with IC (Metrosep A Supp 16 - 150/4.0 column on a Metrohm 850 Professional IC). Cation concentrations were measured with IC as well (Metrosep C6 - 150/4.0 column on a Metrohm 850 Professional IC).

4.3 Results and Discussion

The membrane permselectivity was found to be independent of temperature in the range between 5 °C and 40 °C, with a value of 0.98 for all configurations for the cation exchange membrane. The selectivity of the anion exchange membrane dropped from 0.98 at a temperature of 25 °C to 0.93 at a temperature of 40 °C, but was constant in the range between 5 °C and 25 °C, in which we performed our ED experiments. We note that outside of the temperature range that was tested here, the permselectivity of the membrane may show larger changes [37]. No significant water transport was observed during the permselectivity measurements, indicating that the temperature has no influence on water transport through our commercial membranes.

After our measurements, we found K^+ to be present in our in- and outlet streams. This is a result of leakage of K^+ ions from the electrolyte solution in the electrode compartments towards the feed solution through the outer two cation exchange membranes. Na^+ and Mg^{2+} are exchanged with K^+ . This also holds for the measurements with $MgCl_2$ as a feed, in which Na^+ ions are present as a result of exchange with the membrane and the electrolyte. The cation composition of the feed (c_F) was measured for all configurations using additional IC measurements (Table 4.1). In the remainder of this work, we will focus on the measurements with only monovalent ions (NaCl feed in Table 4.1) and the intended mixture of mono- and divalent ions (Mix in Table 4.1). For the interpretation of the measurements we take the effect of both K^+ and Na^+ into account when discussing monovalent ions.

Table 4.1 — Actual feed cation concentrations, percentages of monovalent and divalent cations and amount of positive charge with their standard deviation for the different salt compositions.

	NaCl	$MgCl_2^\dagger$	Mix
c_{F,Na^+} [mmol/L]	5.53 ± 0.04	0.60 ± 0.01	2.93 ± 0.01
c_{F,K^+} [mmol/L]	1.24 ± 0.02	0.18 ± 0.001	1.11 ± 0.01
$c_{F,Mg^{2+}}$ [mmol/L]	0	2.82 ± 0.04	1.41 ± 0.02
Monovalent cations [%]	100 ± 0.1	21.6 ± 0.04	74.2 ± 0.3
Divalent cations [%]	0 ± 0	78.4 ± 0.04	25.8 ± 0.3
$\Sigma z_j F c_j$ [C/L]	6.53 ± 0.06	6.19 ± 0.01	6.45 ± 0.04

[†] Standard deviation is based on two measurements

4.3.1 IV-characterization

For all systems and temperature configurations IV-sweeps were conducted, in order to determine the onset of the limiting current regime and investigate the influence of temperature/temperature gradients on the characteristics of the ED system. The highest current densities were measured for systems with the highest temperature and lowest current densities were measured for systems with the lowest temperatures, as was expected. The measurements for the NaCl and the mixed solution containing both Mg^{2+} and Na^+ are shown in Figure 4.1. The total current density was approximately 30% higher for the hot isothermal case (red line) when compared to the cold isothermal case (blue line) for the NaCl measurements. For the measurements of the mixture, the hot isothermal case also has an enhanced current density of 30% when compared to the cold isothermal case. This increase in current density between the two isothermal matches with the expected increase in ion diffusivity for a temperature increase of 20 °C [34]. The

transition into the limiting current regime is shifted to a lower applied potential at higher temperatures and the limiting current density is higher, as is expected because of the enhanced transport of ions at a higher temperature [38].

As can be observed, at high field strengths for both cases slightly higher current densities are measured in the situation in which the concentrate stream is heated, which is in contrast to our expectations. We expected that heating the dilute stream would increase the overall current density since the transport main limitations for diffusive ion transport occur in this stream. However, the measured difference between the two different temperature gradient configurations is too small to be significant in these IV-sweeps, especially at low to moderate field strengths and for the measurement of the mixture. A possible explanation for this is the short times for which the current is measured (30 s), which, after the chronoamperometric measurements that will be presented in the next section, turned out to be a time at which the measured current was not yet stable. IV-sweeps with a longer waiting time per potential were done, but were found to be unstable at high measurement times.

The temperature increase from Joule heating as a result of the current through the system can be estimated using $\Delta T = P/(\phi_m c_p)$, in which $P = UI$ is the input power, $\phi_m = 50$ g/s is the mass flow rate through the system and $c_p = 4.2$ J/(gK) is the specific heat of the fluid. Joule heating is estimated to be negligible, as at the highest measured potentials ($U = 10$ V) and currents ($I = 0.2$ A), the temperature increase estimated in this way is 0.01 K. The different relative diffusivities of ions in the solution is also expected to have an influence on the total current density that is measured [33].

The transition towards the limiting current regime is sharpest in the pure NaCl measurements, occurring around a potential of 2 V with a corresponding current of 4 A/m², for the cold isothermal case. For the mixture, the onset of the limiting current regime is shifted to ~ 3 V, and a higher value of the current (~ 6 A/m²). The thickness of the diffusion boundary layer δ can be estimated through the Peers equation (Equation 4.2) [39], in which z_i is the charge number, F is the Faraday constant, D_i the diffusivity of the ions, $\bar{\tau}_i$ and τ_i are the relative ion transport numbers inside the membrane and the solution and c_b is the bulk ion concentration. We have $\bar{\tau}_i = 0.98$ for our commercial membranes at the low concentrations present in our system and we assume the relative transport of both cation and anion in the solution to be equal so that $\tau_i = 0.5$, although in reality the transport numbers of the different ions in solution are slightly different [40]. However, for our order of magnitude estimation of the boundary layer thickness, the effect of changing τ_i is minor.

$$i_{\text{lim}} = \frac{z_i F D_i c_b}{\bar{\tau}_i - \tau_i \delta} \quad (4.2)$$

Figure 4.1 — IV-characterization of the ED stack. (a) for 6.7 mM NaCl as a feed solution and (b) for the mixed feed of 3.35 mM NaCl and 1.68 mM MgCl_2 . The shaded area indicates the standard error between the measurements, lines are for visualization purposes only.

By using our measured limiting current densities and taking $\bar{\tau}_i - \tau_i = 0.48$, we find a thickness in the order of hundreds of micrometers, which is in good comparison to boundary layer thicknesses found in similar systems [41, 42].

For the measurements of the mixture, Figure 4.1(b), an inflection point can be observed in the Ohmic region (around 2 V), after which the slope is increased and thus the resistance of the system decreases at these voltages. This inflection is attributed to the preferential transport of divalent ions at low current densities [32, 43] resulting from an enhanced electrostatic interaction between divalent ions and the membrane. The transport of monovalent ions is reduced due to electrostatic repulsion between the Na^+ and Mg^{2+} . At higher current densities, the contribution of this additional attraction is of lesser influence and the transport of monovalent ions is enhanced by the larger electric driving force (higher ΔV) overcoming the electrostatic forces.

4.3.2 Chronoamperometric measurements

From the IV-sweeps we conclude that applying a potential of 5V in the chronoamperometric measurements is sufficient to ensure operation in the limiting current regime, but to not be in the overlimiting regime. Samples are taken for all these measurements to be able to measure the ion concentrations in the dilute and concentrate streams and to investigate the influence of temperature gradients on the transport of the different ions in the system. In Figure 4.2, the current is plotted as a function of time for (a) the NaCl and (b) the mixed MgCl_2 and NaCl. The system requires $\sim 150\text{s}$ (over five times the liquid residence time) to stabilize, after which a constant current is measured. This implies that when doing the IV-sweeps, the measured potential is not the equilibrium potential since for those experiments a hold time of 30 seconds per applied potential was used in order to avoid system instability at larger hold times (over the total IV-sweep). The measured current is highest (7.9 A/m^2 for NaCl, 10.7 A/m^2 for the mixture) for the isothermal case at 25°C and lowest (5.7 A/m^2 and 8.4 A/m^2 respectively) for the isothermal case at 5°C for all different feed compositions, as was expected. In contrast to our previous work, where measurements were done in the Ohmic regime [18] and the IV-sweeps in the current, here we are able to measure a difference between the two temperature gradient cases. In the limiting current regime the diffusion boundary layer is more developed compared to the Ohmic regime, resulting in a larger influence of temperature on the ion transport. Measurements for the monovalent salts are very reproducible, having a small standard error ($\sim 2\%$). For the measurements of the pure NaCl and MgCl_2 solutions (not shown here, the general trend is similar to NaCl) feed, the measured current is higher ($\sim 7\%$) for the case when the dilute stream is heated when compared to the concentrate stream and this is most pronounced for the NaCl case, see Figure 4.2 (a). For the mixture, the higher current is measured

Figure 4.2 — It-characterization of the ED stack for all feed compositions. (a) Feed is 6.7 mM NaCl, with as inset a close-up of the first 50 s. (b) Feed is 3.35 mM NaCl and 1.68 mM MgCl_2 . Error bars are the standard error between the measurement runs.

for the case in which the concentrate stream is heated, although the difference between these two temperature configurations is generally small (between 2 and 6%).

For the NaCl measurements, the IV-characterization and chronoamperometric measurements are seemingly contradictory. In the IV-sweeps the case in which the concentrate stream was heated yielded the highest currents, but in the chronoamperometric measurements higher currents are observed when the dilute stream is heated. However, initially this was also the case for the chronoamperometric measurements, see inset of Figure 4.2(a). After $\sim 30 - 40$ s, the current for the hot concentrate case drops below the current measured for the case with a hot dilute stream. We attribute this to the development of the diffusion boundary layer, which is not in equilibrium at shorter times. The boundary layer is calculated to be in the order of hundreds of micrometers in the channel of $600 \mu\text{m}$, and the concentration profile in this boundary layer is not established at the start of the measurements. When the steady state concentration profile in the boundary layer is developed, the current through the system becomes stable. In the measurements with a mixed feed in Figure 4.2(b), higher current is measured when heating the concentrate stream, which is contrary to our expectations. This is possibly due to a different response of the mono- and divalent ions to the temperature [33]. Together with the competitive transport of these ions at different temperature configurations, this could lead to a higher current when the concentrate stream is heated when compared to the case in which the dilute stream is heated, most pronounced when the diffusivity of the divalent ions is less dependent on temperature than the diffusivity of the monovalent ions. This was confirmed by the measurements of ion concentrations of all outlet streams, as is described in the next sections.

From the measured currents and Equation 4.2, we can identify the influence of different parameters on the current. The boundary layer thickness δ is dependent on the viscosity (and density) of the liquid, and can thus be influenced by the temperature of the stream. The flow rate and compartment geometry, have not changed between the measurements. The permselectivity of the membrane was found to be independent of temperature in the range applied in our measurements ($5 - 25^\circ\text{C}$). Apart from that, the diffusivity D_i changes with changing temperature. The difference in measured current (27 to 39%) can be compared with the difference in diffusivity of the different ions over the applied feed temperature range, which is roughly doubled for all ions (see appendix [34, 44]). The ED system containing n cell pairs can be described as a series of electrical resistances, resulting in a total resistance $R_{\text{tot}} = 2 * R_{\text{elec}} + R_{\text{CEM}} + [R_{\text{dil}} + R_{\text{AEM}} + R_{\text{conc}} + R_{\text{CEM}}]_n$, which is dependent on the resistance of the electrolyte compartments (R_{elec}), the resistance of the membranes (R_{CEM} and R_{AEM}) and the resistance of the dilute and concentrate compartments (R_{dil} and R_{conc}). There is one additional

CEM shielding the first cell pair from the electrolyte solution, which shows up separately in the equation. The resistance of the membranes is typically in the order of $10^5 \Omega/\text{m}^2$ and the resistance of the electrolyte and salt solutions can be calculated using $R = \rho/(lA)$ in which $\rho = 1/\sigma$. The conductivity of the solution, $\sigma = F^2 \sum z_i^2 \nu_i c_i$, depends on the ion concentration c_i and charge z_i and the ionic mobility $\nu_i = D_i/RT$ which depends on the diffusivity D_i and temperature. If we take the difference in diffusivity at different temperatures into account we can calculate the change in resistance of the solution. For instance, considering Cl^- and K^+ , at $T = 298 \text{ K}$ and an inlet concentration of 6.7 mM the diffusivity of these ions is $\sim 2.0 \times 10^{-9} \text{ m}^2/\text{s}$, yielding a resistance of $R = 1.65 \times 10^6 \Omega/\text{m}^2$. At a lower temperature of $T = 278 \text{ K}$ and the same feed concentration the diffusivity is $\sim 1.05 \times 10^{-9} \text{ m}^2/\text{s}$ yielding a resistance of $R = 3.05 \times 10^6 \Omega/\text{m}^2$. The resistance of the solutions is higher than the resistance of the membranes and electrolyte and thus contribute most to the total resistance in the system. Decreasing the temperature of the solution by 20 degrees increases the resistance of the electrolyte solution by 85 %. From this, we can identify that the change in D_i is large enough to account for the change in measured current, even if the actual change in temperature are less than the inlet temperature differences due to heat transfer between the dilute and concentrate stream.

Cation concentrations have been measured for all different measurement configurations, and are shown in Figure 4.3 for the NaCl and mixed feed. In this figure, the outlet concentrations for all ions are given relative to their inlet concentrations that were analyzed for all experiments as well (see Table 4.1). As was discussed previously, K^+ ions are present in the system as a result of ion exchange with the electrolyte solution (K_2SO_4). In contrast to our previous results in the Ohmic regime, we do find differences in the relative outlet concentrations for the different temperature configurations. We can define an average relative separation based on the concentrate $c_{j,C}$ and dilute stream $c_{j,D}$ outlet concentrations when compared to the inlet concentrations $c_{j,F}$, as $\frac{1}{2}((1 - c_{j,D}/c_{j,F}) + (c_{j,C}/c_{j,F} - 1))$. For all measurements, the cold isothermal case yields the lowest degree of separation for all present ions (an average relative separation of $\sim 26\%$ in the NaCl measurements, $\sim 40\%$ for the mixture), while the hot isothermal case yields the highest degree of separation (average relative separation of $\sim 43\%$ in NaCl, $\sim 56\%$ for the mixture). This is in line with the currents that were measured, as higher currents imply a larger transport of ions. These measurements also indicate that there is no significant influence of temperature on water splitting in our system under these operating conditions, as the enhanced separation is in agreement with the increased current. For the cases with an applied temperature gradient, the difference in outlet concentrations is smaller. For the NaCl feed, the case in which the dilute stream is heated has an average separation of 35%, while heating the concentrate stream yields a separation of 33%. For the mixture, the opposite is

Figure 4.3 — Relative outlet concentrations (to feed concentrations) for all cations at the different temperature configurations, for the measurements with only NaCl (a) and the mixed NaCl and MgCl₂ feed (b). Relative concentrations of the individual cations as well as the total cation concentration are given. Concentrate concentrations are above the $c_j/c_{j,F} = 1$ line, while dilute concentrations are below this line. The error is the standard deviation between the measurements. Note the different values on the axis.

the case, here the case with the heated dilute stream yields a lower (43%) average separation than the case with a heated concentrate stream (46%). This again is consistent with the measured difference in currents for these different settings and can be explained by the increased competitive transport of ions in the case of the mixture.

Water transport as a result of an osmotic gradient is expected to be minor in our system since the commercial membranes have a high resistance to water transport and we have only small osmotic pressures (maximum of 0.17 bar for a concentration difference of 6.7 mM) in our system due to the low absolute salt concentrations in our system. In our set-up we cannot directly quantify the water transport, but based on the measured concentration differences we assume the role of osmotic, thermo-osmotic and electro-osmotic water transport to be minor. Taking typical total water transport numbers ($t_w \approx 10$) [45, 46], the water transport can be estimated as $\frac{t_w M_w}{F} \int I dt$, in which M_w is the molecular weight of water. For our system, this is estimated to be ~ 0.1 g per chronoamperometric measurement of 500 seconds. The amount of NaCl ions transported as a result of this water transport is 6.7×10^{-7} mol in total (1.34×10^{-9} mol/s), corresponding to a current of 1.3×10^{-4} A (calculated using Faraday's constant), is negligible to the ionic current as a result of the imposed electric field (Figure 4.2) indicating that the thermodiffusive contribution (the last term of Equation 4.1) is negligible.

From our ion concentration measurements (see Figure 4.3), we find that in the case of temperature gradients the degree of separation of Na^+ and K^+ differs from the separation of Mg^{2+} . In the mixture, the monovalent ions are separated to a lesser extent when the desalinated stream is heated when compared to the heating of the concentrated stream. This indicates that for the temperature configuration where the dilute stream is heated in a mixture of mono- and divalent ions there is competitive transport that reduces the transport of monovalent ions. For the Mg^{2+} ions, there is no reduced transport observed when changing the direction of the temperature gradient. This implies that the competitive transport of divalent ions [32] is more significant in the case of a hot diluted stream. The total charge transport is then reduced by the reduction in transport of monovalent ions, resulting in a lower current measured at this configuration.

With the measured current I , concentrations $c_{i,in}$ and $c_{i,out}$, Faraday's constant F and the dilute flow rate Q_f , the current efficiency η_{curr} of the membrane stack containing N cell pairs can be calculated using Equation 4.3 [47]. Based on our measurements we find the highest current efficiency for the hot isothermal cases, which means that apart from obtaining the highest current, the power in this case is also used most efficiently for the selective transport of ions.

$$\eta_{curr} = \frac{Q_f F \sum (z_i (c_{i,in} - c_{i,out}))}{NI} \quad (4.3)$$

The current efficiency is not significantly dependent on the direction of the temperature gradient. Current efficiency for the NaCl feed ranges from 69% (for the cold isothermal case) to 100% (for the hot isothermal case). This high efficiency indicates that for the high isothermal case there is no significant concentration polarization. This is a result of the increased diffusion of ions at the elevated temperature and is an indication that increasing the temperature is a useful strategy in enhancing the obtainable current in ED systems. For the mixture the efficiency is $\sim 83\%$ for all temperature configurations, except for the hot isothermal case, where the efficiency is 88%. The current efficiency of the mixture is therefore not dependent on the temperature configuration, but higher degrees of desalination can be obtained when working with a temperature gradient. This shows that the increased selective transport of ions is of more significance than the possibly increased water transport at elevated temperatures and temperature gradients.

The relative efficiency for the separation of Mg^{2+} when compared to the separation of Na^+ and K^+ is enhanced when the dilute stream is heated, albeit with a relatively small magnitude. The direction of the temperature gradient has an influence on the relative transport of Mg^{2+} when compared to the transport of K^+ and Na^+ . If the dilute stream is heated the transport of monovalent ions is inhibited while the transport of the divalent ions is not impacted, resulting in a more selective transport of divalent ions for this temperature configuration. This is presumed to be a result of the competitive ion transport between the mono- and divalent ions [32, 33, 48], both in the solution and the membrane, inhibiting the transport of monovalent ions towards and through the membrane at this configuration. The flux of Na^+ ions was found to decrease significantly when Mg^{2+} was also present in the feed stream [33], since Mg^{2+} can monopolize the transfer sites (yielding a possible partial charge inversion) in the membrane and can thus suppress the transport of monovalent ions. The temperature gradient can enhance this, as the hydrated radii of the different ions are changing with temperature, yielding a different degree of polarization at different temperatures. Mg^{2+} ions are already relatively polarized when compared to the other ions in the system [33], yielding a higher affinity of these ions with the cation exchange membrane. The hydration of Na^+ and K^+ ions increases more with temperature than the hydration of Mg^{2+} ions [49], meaning that at a higher temperature the relative polarization of the Mg^{2+} is increased, enhancing the transport of these ions over the monovalent ions. This effect is most pronounced for the case in which the dilute channel temperature is increased.

4.4 Conclusion

In this chapter, we investigated the influence of temperature gradients on charge transport in electrodialysis in the limiting current regime. It was found that temperature gradients can enhance the total ion transport in the system when operated in the limiting current regime. Higher currents, and thus an increased flux of ions, are measured when temperature in (one of) the streams is increased. For a feed of only monovalent ions, the efficiency of the ED process is increased when the dilute stream is heated, since the main diffusive resistance is located in this compartment. This is in contrast to the application of temperature gradients in electrodialysis in the Ohmic regime, where the direction of the temperature gradient had no significant influence on the process efficiency [18]. The direction of the temperature gradient did not significantly enhance separation of monovalent ions.

Experiments were also done for mixtures of mono- and divalent cations. In this case, the influence of the direction of the temperature gradient on the measured current was lower. The selectivity favored the separation of divalent ions when the dilute stream was heated. This is attributed to competitive transport of the mono- and divalent ions that is influenced by their different response on temperature. Apart from an altered ratio in diffusivities in the solution, the polarization of the different ions has a different response to temperature. Increasing the temperature enhances the relative polarization of Mg^{2+} , resulting in a higher affinity of these ions towards the membrane and an enhanced transport of these multivalent ions. This work demonstrates that other gradients, such as temperature, can be applied in order to tune selectivity without having to change other operating parameters, such as the system geometry, spacers and flow rate. Our results can be of potential use in the improvement of separation of mono- and divalent ions by electrodialysis under temperature gradients.

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References

- [1] C. Forgacs, N. Ishibashi, J. Leibovitz, J. Sinkovic, and K. S. Spiegler, *Polarization at ion-exchange membranes in electrodialysis*, Desalination **10**, 181 (1972).

- [2] K. S. Spiegler, *Polarization at ion exchange membrane-solution interfaces*, Desalination **9**, 367 (1971).
- [3] H. Strathmann, A. Grabowski, and G. Eigenberger, *Ion-exchange membranes in the chemical process industry*, Ind. Eng. Chem. Res. **52**, 10364 (2013).
- [4] P. Długolecki, A. Gambier, K. Nijmeijer, and M. Wessling, *Practical potential of reverse electrodialysis as process for sustainable energy generation*, Environ. Sci. Technol. **43**, 6888 (2009).
- [5] V. I. Zabolotskii, S. A. Loza, and M. V. Sharafan, *Physicochemical properties of profiled heterogeneous ion-exchange membranes*, Russ. J. Electrochem. **41**, 1053 (2005).
- [6] J. Balster, D. F. Stamatialis, and M. Wessling, *Membrane with integrated spacer*, J. Memb. Sci. **360**, 185 (2010).
- [7] O. Kedem, *Reduction of polarization in electrodialysis by ion-conducting spacers*, Desalination **16**, 105 (1975).
- [8] O. Kedem and Y. Maoz, *Ion conducting spacer for improved ED*, Desalination **19**, 465 (1976).
- [9] J. M. Chiapello and M. Bernard, *Improved spacer design and cost reduction in an electrodialysis system*, J. Memb. Sci. **80**, 251 (1993).
- [10] F. Li, W. Meindersma, A. B. De Haan, and T. Reith, *Novel spacers for mass transfer enhancement in membrane separations*, J. Memb. Sci. **253**, 1 (2005).
- [11] J. Balster, I. Pünt, D. F. Stamatialis, and M. Wessling, *Multi-layer spacer geometries with improved mass transport*, J. Memb. Sci. **282**, 351 (2006).
- [12] D. R. Lide, *CRC Handbook of Chemistry and Physics*, (2003).
- [13] S. Tseng, Y.-M. Li, C.-Y. Lin, and J.-P. Hsu, *Salinity gradient power: Influences of temperature and nanopore size*, Nanoscale **8**, 2350 (2016).
- [14] M. Tedesco, E. Brauns, A. Cipollina, G. Micale, P. Modica, G. Russo, and J. Helsen, *Reverse electrodialysis with saline waters and concentrated brines: A laboratory investigation towards technology scale-up*, J. Memb. Sci. **492**, 9 (2015).
- [15] A. Daniilidis, D. A. Vermaas, R. Herber, and K. Nijmeijer, *Experimentally obtainable energy from mixing river water, seawater or brines with reverse electrodialysis*, Renew. Energy **64**, 123 (2014).
- [16] E. Fontananova, W. Zhang, I. Nicotera, C. Simari, W. van Baak, G. Di Profio, E. Curcio, and E. Drioli, *Probing membrane and interface properties in concentrated electrolyte solutions*, J. Memb. Sci. **459**, 177 (2014).
- [17] Y. Kobatake and H. Fujita, *Osmotic flows in charged membranes. II. Thermo-osmosis*, J. Chem. Phys. **41**, 2963 (1964).
- [18] A. M. Benneker, T. Rijnaarts, R. G. Lammertink, and J. A. Wood, *Effect of temperature gradients in (reverse) electrodialysis in the Ohmic regime*, Journal of Membrane Science **548**, 421 (2018).

-
- [19] G. Hills, P. Jacobs, and N. Lakshminarayanaiah, *Non-isothermal membrane potentials*, *Nature* **179**, 96 (1957).
- [20] T. Ikeda, *Thermal membrane potential*, *J. Chem. Phys.* **28**, 166 (1958).
- [21] M. Tasaka, *Thermal membrane potential and thermoosmosis across charged membranes*, *Pure & Appl. Chem.* **58**, 1637 (1986).
- [22] V. M. Barragán and S. Kjelstrup, *Thermo-osmosis in membrane systems: A review*, *Journal of Non-Equilibrium Thermodynamics* **42**, 217 (2017).
- [23] K. D. Sandbakk, A. Bentien, and S. Kjelstrup, *Thermoelectric effects in ion conducting membranes and perspectives for thermoelectric energy conversion*, *J. Memb. Sci.* **434**, 10 (2013).
- [24] M. S. DarieI and O. Kedem, *Thermoosmosis in semipermeable membranes*, *J. Phys. Chem.* **79**, 336 (1975).
- [25] J. A. Wood, A. M. Benneker, and R. G. H. Lammertink, *Temperature effects on the electrohydrodynamic and electrokinetic behaviour of ion-selective nanochannels*, *J. Phys. Condens. Matter* **28**, 114002 (2016).
- [26] B. Van Der Bruggen, A. Koninckx, and C. Vandecasteele, *Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration*, *Water Res.* **38**, 1347 (2004).
- [27] M. Sadrzadeh, A. Razmi, and T. Mohammadi, *Separation of monovalent, divalent and trivalent ions from wastewater at various operating conditions using electrodialysis*, *Desalination* **205**, 53 (2007).
- [28] N. Kabay *et al.*, *Effect of feed characteristics on the separation performances of monovalent and divalent salts by electrodialysis*, *Desalination* **158**, 95 (2003).
- [29] R. K. Nagarale, G. S. Gohil, and V. K. Shahi, *Recent developments on ion-exchange membranes and electro-membrane processes*, *Adv. Colloid Interface Sci.* **119**, 97 (2006).
- [30] N. Kabay, M. Demircioglu, E. Ersöz, and I. Kurucaovali, *Removal of calcium and magnesium hardness by electrodialysis*, *Desalination* **149**, 343 (2002).
- [31] N. Kabay, H. Kahveci, Ö. Ipek, and M. Yüksel, *Separation of monovalent and divalent ions from ternary mixtures by electrodialysis*, *Desalination* **198**, 74 (2006).
- [32] A. H. Galama, G. Daubaras, O. S. Burheim, H. H. Rijnaarts, and J. W. Post, *Seawater electrodialysis with preferential removal of divalent ions*, *J. Memb. Sci.* **452**, 219 (2014).
- [33] L. Firdaous, J. P. Malérial, J. P. Schlumpf, and F. Quéméneur, *Transfer of monovalent and divalent cations in salt solutions by electrodialysis*, *Sep. Sci. Technol.* **42**, 931 (2007).
- [34] Y.-H. Li and S. Gregory, *Diffusion of ions in sea water and in deep sea sediments*, *Geochim. Cosmochim. Acta*, 1974 **38**, 703 (1973).
- [35] P. Długołęcki, P. Ogonowski, S. J. Metz, M. Saakes, K. Nijmeijer, and M.

- Wessling, *On the resistances of membrane, diffusion boundary layer and double layer in ion exchange membrane transport*, J. Memb. Sci. **349**, 369 (2010).
- [36] RIWA - Vereniging van Rivierwaterbedrijven, *Jaarrapport 2015 De Rijn*, (2015).
- [37] Y. Ji and G. M. Geise, *The role of experimental factors in membrane permselectivity measurements*, Ind. Eng. Chem. Res. **56**, 7559 (2017).
- [38] Y. Tanaka, Chapter 9: Limiting Current Density in *Ion exchange membranes*, 2nd ed., edited by Y. Tanaka (Elsevier, Amsterdam, 2015), pp. 199 – 214.
- [39] A. M. Peers, *General discussion*, Discuss. Faraday Soc. **21**, 124 (1956).
- [40] J. J. Krol, M. Wessling, and H. Strathmann, *Concentration polarization with monopolar ion exchange membranes: Current-voltage curves and water dissociation*, J. Memb. Sci. **162**, 145 (1999).
- [41] P. Sistat, A. Kozmai, N. Pismenskaya, C. Larchet, G. Pourcelly, and V. Nikonenko, *Low-frequency impedance of an ion-exchange membrane system*, Electrochim. Acta **53**, 6380 (2008).
- [42] J.-H. Choi, J.-S. Park, and S.-H. Moon, *Direct measurement of concentration distribution within the boundary layer of an ion-exchange membrane*, J. Colloid Interface Sci. **251**, 311 (2002).
- [43] A. Chapotot, G. Pourcelly, and C. Gavach, *Transport competition between monovalent and divalent cations through cation-exchange membranes. Exchange isotherms and kinetic concepts*, J. Memb. Sci. **96**, 167 (1994).
- [44] G. C. Benson and A. R. Gordon, *A reinvestigation of the conductance of aqueous solutions of potassium chloride, sodium chloride, and potassium bromide at temperatures from 15 to 45°C*, J. Chem. Phys. **13**, 473 (1945).
- [45] A. Zlotorowicz, R. V. Strand, O. S. Burheim, O. Wilhelmsen, and S. Kjelstrup, *The permselectivity and water transference number of ion exchange membranes in reverse electrodialysis*, J. Memb. Sci. **523**, 402 (2017).
- [46] P. Długolecki, B. Anet, S. J. Metz, K. Nijmeijer, and M. Wessling, *Transport limitations in ion exchange membranes at low salt concentrations*, J. Memb. Sci. **346**, 163 (2010).
- [47] M. Sadrzadeh and T. Mohammadi, *Treatment of sea water using electrodialysis: Current efficiency evaluation*, Desalination **249**, 279 (2009).
- [48] A. Chapotot, G. Pourcelly, and C. Gavach, *Transport competition between monovalent and divalent cations through cation-exchange membranes. exchange isotherms and kinetic concepts*, Journal of Membrane Science **96**, 167 (1994).
- [49] E. R. Nightingale, *Phenomenological theory of ion solvation. Effective radii of hydrated ions*, J. Phys. Chem. **63**, 1381 (1959).

Appendix

Diffusion coefficients for ions

Figure 4.4 — Temperature dependence of diffusivity of the different ions used in the experiments, extracted from experimental data reported elsewhere. [34, 44]

CHAPTER 5

Desalination by electrodialysis using a stack of ion selective hydrogels on a microfluidic device

Abstract — We report a new microfluidic device for the separation of charged species using anion and cation exchange hydrogels. The capillary line pinning technique we applied enables *in situ* fabrication of alternating anion and cation exchange hydrogels that are placed in confined compartments. Adjacent enriched and depleted streams were obtained in continuous operation when a potential difference was applied over the hydrogel stack. The desalination performance of the microchip was demonstrated at different salt concentrations (0.01–1 mM NaCl), potentials (10–100 V), current densities (3–7 A/m²) and liquid flow rates (0–5 μ L/min). We show that the microchip was able to remove approximately 75% of the salt initially present in the depleted outlet streams for an inlet concentration of 1 mM sodium chloride. Besides desalination, the microchip allows the visualization of ion transport in the ion selective hydrogels. It can therefore be used to study the interplay of transport phenomena at the electrolyte-hydrogel interface during the desalination process.

This chapter is based on the publication

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5.1 Introduction

Membrane stacks are widely used for electrodialysis (ED) and reverse electrodialysis (RED) in macro-scale systems [1–3]. Alternating cation (CEM) and anion selective membranes (AEM) are stacked with spacers to allow a flowing electrolyte solution between the membranes. When an electric field is applied to this system, the anions in the electrolyte solution will migrate towards the anode, while the cations migrate towards the cathode. However, anions and cations will be blocked by the CEM and AEM, respectively, resulting in the formation of alternating depleted and enriched flow streams. When the applied electric field strength is increased, the ion transport rate and therefore the current in the system will rise, until a critical point is reached. Beyond this point, the system enters the well-known limiting current regime [4], where the current no longer increases with electric field strength and the energy efficiency of the ion separation process is reduced. In this regime, a boundary depletion layer is formed in which the major resistance for ion transport is located. Upon further increase of the electric field strength, the overlimiting current regime can be reached, resulting in the transport of additional ions obtained through either water splitting or hydrodynamic effects [5, 6]. Water splitting can also lead to a developing pH profile in the membrane that can give rise to a change in membrane charge density. The hydrodynamic and ion transport phenomena can result in a loss of performance for macro-scale ED systems [7–9].

Thanks to the advances in micro-fabrication techniques, ion selective materials have been integrated in microfluidic platforms, increasing the number of experimental investigations of the aforementioned phenomena [10–16]. Microfluidic desalination systems have been applied for two purposes. First, microfluidics has been used for downscaling the electrodialysis process in order to obtain more insight into the ion transport phenomena that occur at the micro-scale [17]. Kim *et al.* used two microchannels separated by a Nafion membrane, which was fabricated using micro-stamping, to observe multiple vortical flows inside the ion concentration polarization layer [14]. Kwak *et al.* fabricated a polydimethylsiloxane (PDMS) microchip consisting of externally mounted commercial ion exchange membranes for visualization of concentration and liquid flow profiles in the Ohmic, limiting, and overlimiting current regimes [15]. Second, microfluidics has been used to manufacture miniaturized electrodialysis devices for application purposes. Recently, *in situ* fabrication of (hybrid) membranes by photolithography in glass microchips has been demonstrated for DNA preconcentration [12] and for micro-scale pH regulation by splitting water [13]. In other work, solvent evaporation was used for *in situ* fabrication of ion selective membranes in a PDMS microchip for inducing ion concentration polarization in order to preconcentrate proteins [16].

The aforementioned methods for incorporation of membranes in microfluidic systems pose challenges in terms of robustness, consistency and ease of fabrication. For example, photolithography techniques bring alignment problems, while evaporation bears the risk of damaging the membranes. Integration of pre-fabricated membranes in microfluidic chips can lead to liquid leakage [18]. Incorporation of patterned Nafion nanojunctions into microfluidic PDMS systems [12] is a well known alternative, and leakage problems can be tackled using enhanced bonding between PDMS and the Nafion [19]. *In situ* fabrication of membranes in microchips is an alternative, but is difficult when using, for instance, interfacial polymerization [20]. Charged hydrogels provide an alternative to membranes, and hydrogels have been successfully incorporated in microfluidic devices in the past [13, 21]. Previously, the capillary line pinning technique was introduced for controllable patterning of hydrogels in microchips [22]. Hydrogels are therefore promising candidates for studying the hydrodynamic and ion transport phenomena in microfluidic devices, as they provide an ion selective and hydrophilic matrix, which is versatile, inexpensive and tailorable [13, 21].

In this work, we present a microfluidic device consisting of a stack of alternately patterned and oppositely charged hydrogel patches fabricated by capillary line pinning for investigation of electrodialysis phenomena. To the best of our knowledge, the use of such a platform has not been demonstrated or investigated before. As a proof of principle, periodic hydrogel patches were used to obtain alternating diluted and enriched parallel streams under different flow rates and applied potential differences. By using a negatively charged fluorescent dye, this platform also allowed us to study ion transport through the hydrogels as well as salt concentration fluctuations and ion concentration polarization (ICP) in the microchannels. The ability to visualize charge transport in the hydrogels helps to obtain a better understanding of the hydrodynamic and ion transport phenomena that occur in ED and RED systems.

5.2 Experimental details

5.2.1 Microchip and hydrogel fabrication

SU-8 masters of the polydimethylsiloxane (PDMS) microchips, see Figure 5.1(a), were fabricated in the MESA⁺ cleanroom facility at the University of Twente. The masters consisted of two layers of SU-8. The width of the microchannels and the pillars was 700 μm and 1720 μm , respectively. The first layer contained the pillar layout has a measured thickness of 67.5 μm (Bruker Dektak, Germany). The second layer contained both pillar and capillary barrier layouts with a width of 2.0 μm and a thickness of 7.5 μm (see Figure 5.1(b) and the appendix Figure 5.8).

Figure 5.1 — (a) Image of the assembled microchip. (b) Schematic illustration of the membrane stack consisting of alternating rows of positively charged anion exchange hydrogels (AEHs, in green) and negatively charged cation exchange hydrogels (CEHs, in red). (c) Schematic representation of the desalination process in our chip.

The microchips were fabricated by assembling a PDMS layer with a microscope slide. PDMS precursor was prepared, degassed, poured onto the master and cured. The cured PDMS was peeled off from the master and treated with oxygen plasma to ensure irreversible bonding with the microscope slide. All microchannels, pillars, capillary barriers, inlets and outlets were structured in the PDMS layer. Figure 5.1(a) shows an assembled microchip with PDMS pillars and capillary barriers. All hydrogel compartments (each with a size of $200 \times 500 \mu\text{m}$) in a specific row are connected with each other via microchannels.

All hydrogel solutions (each with a volume of $500 \mu\text{L}$) were degassed at 7 kPa vacuum for 15 min immediately prior to use. To avoid the presence of dust particles, all hydrogel precursors were prepared in a nitrogen environment in a flow hood by blending 20% v/v of acrylamide/bis (19:1) (BioRad), 15% w/v N,N'-bis(2-hydroxyethyl)ethylenediamine (bis, Sigma-Aldrich), 10% w/v of 2,2-dimethoxy-2-phenylacetophenone (DMPA, Invitrogen) and 5% w/v of ammonium persulfate solutions (Invitrogen). For the anion exchange hydrogels (AEH), 1% v/v [2-(methacryloyloxy)ethyl]trimethylammonium chloride solution (METC, Sigma-Aldrich), and for the cation exchange hydrogels (CEH) 1% w/v 3-sulfopropyl

acrylate potassium salt (SPAP, Sigma-Aldrich) was added to the acrylamide/bis mixture. As the crosslinking reaction is inhibited by oxygen, the patterning and polymerization processes were performed in a nitrogen environment.

Figure 5.2 outlines the microchip fabrication and hydrogel patterning process. A detailed explanation of the capillary pinning technique has been reported by Gümüşcü *et al.* [22]. After the degassing process, approximately 0.5 μL of the AEH and CEH solutions was alternately pipetted into the parallel rows by capillary action. The hydrogel precursor remained contained between the PDMS pillars due to capillary pinning at the barriers. The patterned precursors were subsequently exposed to UV light at 400 mW/cm² for 3 min. Microchips containing CEHs and AEHs were immersed in a 0.1 mM NaCl solution at room temperature. Each microchip contained six microchannels, which were connected to each other via the alternating rows of AEHs and CEHs as shown in Figure 5.1(b).

5.2.2 Characterization of hydrogels

Scanning electron microscopy. Thin films of polymerized hydrogels were casted on a glass surface and freeze-dried for 2 days. Samples were kept in a vacuum chamber overnight and subsequently coated with a 5 nm layer of chromium using an E5000 sputter coater (Bio-Rad). Scanning electron microscopy (SEM) images were taken using a FEI Sirion HR-SEM.

FTIR and XPS. Fourier transform infrared spectroscopy (FTIR) spectra were measured with a Bruker ALPHA (Bruker Optics) using an attenuated total reflectance attachment. Polymerized hydrogels were freeze-dried for 2 days in Eppendorf tubes and kept in a vacuum chamber overnight. Dried samples were directly analysed without any further sample preparation. For X-ray photoelectron spectroscopy (XPS), 1 g of both polymerized AEH and CEH was freeze-dried for 2 days in Eppendorf tubes and kept in a vacuum chamber overnight. Dried samples were analysed using a Quantera SXM (Physical Electronics).

Ion exchange capacity. The ion exchange capacity (IEC) is the amount of charged groups in the hydrogel and is measured by titration [23]. For the titration of the AEH, 0.7 g of the hydrogel was immersed in a 3 M NaCl solution (Sigma-Aldrich) for 3 days at room temperature to exchange all counter ions in the AEH for Cl⁻. After rinsing it with deionized water, the chloride ions were replaced by sulfate ions by immersing the hydrogel into a 1.5 M Na₂SO₄ solution for 3 hours. The Na₂SO₄ solution was refreshed every hour of the experiment and the collected solutions were titrated with a 0.1 M AgNO₃ solution. The required volume of AgNO₃ was recorded. The hydrogel was dried in a vacuum oven at 60 °C for 48 hours and its dry weight was recorded for IEC calculations. A similar procedure was followed to determine the IEC of the CEH. 0.7 g of the CEH was immersed in a 1 M HCl solution to exchange all counter-ions for H⁺. The hydrogel was then

Figure 5.2 — Photolithography, soft lithography and chip assembly procedures. The schematics on the first two lines illustrate the photolithography process. The schematics on the third line present the soft lithography process. The fourth line depicts the chip assembly and patterning procedure. The blue dashed line indicates the position of the cross sectional area.

rinsed with deionized water and immersed in a 2 M NaCl solution for 3 hours to replace the hydrogen ions for sodium ions. The NaCl solution was refreshed every hour and the collected solutions were titrated with a 0.1 M NaOH solution. The hydrogel was dried in a vacuum oven. All experiments were repeated three times.

Water swelling. Water swelling of the hydrogels was determined by immersion in deionized water and subsequent drying in a vacuum oven. The degree of water swelling S was calculated using the following equation: $S = (W_s - W_d)/W_d$. Here, W_s and W_d represent the weight W of the swollen (s) hydrogels and the dried (d) hydrogels. Also the swelling degree of the polymerized hydrogels was tested: 2 mL of bulk hydrogel after polymerization was immersed in 50 mL deionized water for 72 hours, and patterned hydrogels on chip were immersed in deionized water for 16 hours.

Permselectivity. The permselectivity of the hydrogel is a measure of the capability of the hydrogel to discriminate between anions and cations. An in-house built two-compartment plexiglass cell was used for the permselectivity experiments. The charged bulk hydrogel was located in between the two compartments. By using a peristaltic pump, one of the compartments was filled with a 0.1 M NaCl solution, while the other compartment was filled with a 0.5 M NaCl solution. Both solutions were recirculated continuously during the measurement and kept at 25 °C using a thermostatic bath. Two reference calomel electrodes were used to measure the electric potential over the hydrogel by connecting the system to a potentiostat (Metrohm Autolab PGSTAT302N) for monitoring the changes in voltage over the hydrogel. The apparent permselectivity $\alpha = \Delta V_{\text{meas}}/\Delta V_{\text{theor}}$ was calculated for both AEH and CEH separately using the ratio of the measured potential difference ΔV_{meas} over the theoretical potential difference ΔV_{theor} for an ideal permselective membrane. The theoretical potential difference, consisting of both the Donnan and diffusion potential and is described by the theory of Teorell, Meyer and Sievers [24], was calculated using the Nernst equation $\Delta V_{\text{theor}} = (RT)/(zF) \ln(\gamma_1 c_1/\gamma_2 c_2)$. Here, R is the gas constant, T the temperature, z the electrochemical valence and F the Faraday constant [25]. The salt concentrations and activity coefficients of the two solutions are indicated by c_i and γ_i , where γ_i denotes the mean activity coefficient for an aqueous NaCl solution at 25 °C as obtained from [26].

Membrane resistivity. The area resistances of both AEH and CEH were measured using an in-house built six-compartment plexiglass cell. In the experiments, a 0.1 M NaCl solution was used and the voltage drop ΔV over the hydrogel was recorded for an applied current density I/A . Here, I is the current through the membrane with area A . The resistivity R_ρ of each hydrogel, after baseline correction by performing a blank run, was given by the slope of the potential difference versus current density curve. Thus, $R_\rho = (A\Delta V)/(Id)$, d being the thickness of the hydrogel. The resistivity of the hydrogel is directly related to the ion exchange capacity and the mobility of ions inside the hydrogel.

Electrodialysis experiments. The desalination performance of the microchip was investigated using solutions with different NaCl concentrations (0.01, 0.1 and 1 mM) containing 5 μ M Alexa Fluor 488 Cadaverine (ThermoFisher Scientific), which is a negatively charged fluorescent dye. This dye was utilized to qualitatively determine the local ion concentration in the microchannels. Gold coated copper electrodes were placed in the outer two microchannels adjacent to the hydrogels. An electrical potential or current was applied by a Keithley 2450 Source Meter, controlled by a home-built LabVIEW program. The fluorescent dye was visualized using a Hamamatsu ORCA-Flash4.0 LT camera mounted on an inverted Zeiss Axiovert 40 MAT microscope. The liquid flow was supplied to the microchip using six Harvard Picoplus programmable syringe pumps and six Braun Omnifix-F 1 mL syringes. The samples were collected separately at the outlet of each microchannel. The conductivity of the samples was measured using a potentiostat (BioLogic SP300) combined with an in-house made interdigitated electrode sensor. By using a calibration curve, the outlet stream salt concentrations could be obtained from the measured impedance (see the appendix, Figure 5.9).

5.3 Results and discussion

5.3.1 Characterization of hydrogels

In the appendix (Figure 5.10), the molecular structures of the charged monomers (METC and SPAP) photopolymerized with acrylamide and bis are shown. The free radicals yielded by DMPA start the crosslinking process by randomly associating with acrylamide, bis and the METC or SPAP monomers or polymer chains, which eventually become polymerized in the region that is illuminated with UV-light. The photopolymerization process has previously been explained in detail [27]. The SEM images indicate that the hydrogels obtained after photopolymerization were homogeneous (see the appendix Figure 5.11).

METC and SPAP are suitable monomers to obtain charge selective interfaces

Table 5.1 — Bulk material characteristics of cross-linked METC and SPAP polymers, with the 95% confidence interval of the mean indicated. Except for the resistivity and permselectivity, all measurements have been repeated three times.

	AEH (METC)	CEH (SPAP)
Swelling S in deionized water [%]	460 $\pm$ 10	450 $\pm$ 10
Ion exchange capacity IEC [mmol/g _{dry}]	1.95 $\pm$ 0.45	0.64 $\pm$ 0.09
Charge density CD [mmol/g _{H₂O}]	0.43 $\pm$ 0.10	0.14 $\pm$ 0.02
Resistivity R_p [Ω cm] (single meas.)	310	470
Permselectivity α [%] (single meas.)	29	26

for electrodialysis, because they permanently have a positive and negative charge density, respectively, which is *pH* independent in the range of *pH* 2–12 [28, 29]. In addition, the hydrolytic stability of METC and SPAP polymers enables charge based separations in electrodialysis microchips [28, 29]. In some previous studies, both charged monomers are shown to be super-absorbents, which results in strong swelling behaviour [30, 31]. In this work, the swelling behaviour was suppressed by increasing the cross-linking density and the amount of uncharged monomers. We measured water swelling of the bulk METC and SPAP polymers as $460 \pm 10\%$ for METC and as $450 \pm 10\%$ for SPAP after drying the bulk materials in a vacuum oven (Table 5.1). The high swelling degree indicates the ability of the hydrogels to absorb water in high contents, which is related to the hydrophilic nature of the polyacrylamide backbone. Note that directly after photopolymerization, the hydrogels already have a high water content. By immersing the hydrogels in deionized water directly after photopolymerization, the additional swelling of the bulk hydrogels was measured to be 15% and 16% for AEH and CEH, respectively. Both hydrogels showed identical swelling behaviour in the microchip as well, as shown in the appendix (Figure 5.8). In addition, immersed hydrogels are expected to swell less in salt solutions than in deionized water [32]. The reason is that hydrogel swelling decreases with increasing ion concentration, as the charged side groups present in the hydrogels are increasingly screened by the ions in the salt solution [33, 34]. However, we operate at relatively low salt concentrations and expect a significant amount of hydrogel swelling during our desalination experiments. This results in a lower effective charge density of the hydrogels under the experimental conditions.

The presence of crosslinker and SPAP or METC was verified using FTIR. The FTIR spectra shown in Figure 5.3 indicate the presence of SPAP sulfonate groups from S=O stretching bands at 982 and 1043 cm^{-1} and a SO_2 symmetric stretching absorption at 1178 cm^{-1} [35]. A relatively weak absorption at 1170 cm^{-1} was ascribed to N–CH₃ stretching of METC repeat units [35]. C–N stretching absorption in general are known to be weak [35, 36]. We measured the FTIR spectra of the corresponding monomers to confirm the location of the peaks observed in the polymers (see the appendix Figure 5.12).

We also analysed the chemical composition of the hydrogels using XPS to verify the presence of either METC or SPAP. The atomic ratios of carbon, nitrogen, oxygen, sulphur, chlorine and potassium are given in Table 5.2. METC and SPAP polymers were compared with PA polymer for the evaluation of the atomic percentage changes. For the METC polymer, the amount of carbon atoms remained the same, despite the fact a slight increase was expected [36]. In agreement with the expected composition, the nitrogen atom content remained the same and oxygen content increased. The detection of chloride clearly indicates that charged N^+ groups were present [37, 38]. In the SPAP hydrogel the content

Figure 5.3 — FTIR spectra of polyacrylamide (PA), METC + PA (anion exchange hydrogel) and SPAP + PA (cation exchange hydrogel) are shown.

Table 5.2 — XPS results for polyacrylamide (PA), the positively charged hydrogel (PA + METC) and the negatively charged hydrogel (PA + SPAP).

Element (%)	C(1s) 283 eV	N(1s) 399 eV	O(1s) 529 eV	S(2p) 164 eV	Cl(2p) 200 eV	K(2p) 293 eV
PA	64.6	16.3	18.7	—	—	—
PA + METC	64.4	16.3	20.1	—	0.5	—
PA + SPAP	62.1	16.1	20.3	1.2	—	0.1

of carbon atoms decreased, which could be an experimental artefact. On the other hand, as expected, the amount of nitrogen atoms remained constant. The increased amount of oxygen atoms can be attributed to the high oxygen content of the SPAP monomer [36]. The presence of sulfonate groups was validated by the detection of sulphur and potassium atoms. However, potassium was present in a lower amount than expected. These atoms might be out of the scanning range due to the orientation of the charged groups on the polymer film.

Table 5.1 shows some material characteristics of the anion exchange (METC) and cation exchange (SPAP) hydrogels. Compared to commercially available ion exchange membranes [39, 40], METC exhibited a comparable and SPAP a low ion exchange capacity. When considering the charge density, we found that both hydrogels, in comparison to commercially available membranes (for example, Neosepta AMX has a charge density of 4.8 M and Neosepta CMX has a charge

density 5.7 M [41]), have a low number of charged groups per gram of water. We attribute this to the high water content inside the polymeric meshes of the hydrogels. This can explain the moderate permselectivity of both hydrogels, as the permselectivity of an ion selective membrane is related to its charge density [25, 39, 40]. Both anion and cation exchange hydrogels are therefore not fully selective for the counter ions, which has an adverse effect on the desalination efficiency. However, low salt concentrations lead to a decreased screening of the charged groups present in the hydrogels, thereby promoting charge separation [25]. To demonstrate the successful functioning of the platform, we therefore performed the desalination experiments using a salt concentration of maximum 1 mM NaCl. This concentration is two orders of magnitude smaller than the salt concentrations of 0.1 M/0.5 M, which are commonly used in permselectivity measurements, and thus the apparent charge density of the hydrogels in the desalination experiments may differ as a result of the altered swelling behaviour at different ionic strengths. The resistivity of the hydrogels is larger than that of a typical commercial membrane which has an area resistance of $3 \Omega \text{ cm}^2$ and a membrane thickness of $150 \mu\text{m}$, resulting in a resistivity of $200 \Omega \text{ cm}$ for the membrane [39, 40]. The relatively high resistivity of our hydrogels (1.5 to 2.5 times larger, see Table 5.1) is related to their low charge density, giving rise to a low concentration of mobile counter ions.

5.3.2 Desalination - Proof of principle experiments

When filling the microfluidic channels with electrolyte solution and applying a gradually increasing potential ($\Delta V = 0\text{--}3 \text{ V}$), we observed migration of the fluorescent dye (and thus presumably of the ions) into the hydrogels. A concentration of $5 \mu\text{M}$ of Alexa Fluor 488 Cadaverine was utilized. This negatively charged fluorescent dye is considered to be *pH* insensitive in the range we are interested in and has a low degree of photobleaching [42]. As expected, the AEHs were observed to have a high fluorescence intensity, as they absorb the negatively charged fluorescent dye as a counter ion to a much greater extent than the CEHs, in which the dye is the co-ion and is mostly excluded from the hydrogel.

To test whether the stack of charged hydrogels can be used for desalination purposes, we filled all microchannels with a diluted salt solution (0.1 mM NaCl) and did not impose any flow through the microchannels. Upon application of a potential difference, depletion zones of the fluorescent dye formed adjacent to the hydrogels in the expected microchannels (which are channels 1, 3 and 5 as shown in Figure 5.1(b)), while the average fluorescence intensity in the enriched microchannels increased. Snapshots of this observation are shown in the appendix (Figure 5.13). These observations indicate that the hydrogels are charge selective and that they can be used for desalination.

IV-sweeps were performed to determine the characteristic Ohmic, limiting and

Figure 5.4 — IV characteristics for different salt concentrations at flow rates of $3 \mu\text{L}/\text{min}$. In (a), the absolute current I is plotted as a function of the potential difference ΔV . The measured currents strongly depend on the salt concentration and scale accordingly. In (b), the currents are normalized by the maximum current (measured at $\Delta V = 50$ V) of the corresponding experiment. The graphs, in particular those for 0.1 and 1 mM, show that around a potential difference of approximately $\Delta V = 6$ V and $\Delta V = 22$ V, the slope changes. This indicates where the boundaries between the Ohmic, limiting and overlimiting current regimes are roughly located.

overlimiting current regimes, which are well known for ion selective membrane systems [2, 4, 8, 9]. These measurements were performed for different NaCl concentrations (0.01, 0.1 and 1 mM) and flow rates (2, 3, 5 and 10 $\mu\text{L}/\text{min}$). Relatively low salt concentrations were used to avoid the possible adverse effects occurring at high current densities (*e.g.* extensive electrode reactions or gas formation). The applied voltage was ramped up with steps of 1 V, with a speed of 10 seconds per voltage step. Figure 5.4 shows the IV-curves for different salt concentrations. We observed higher currents for higher salt concentrations, indicating that the current in the Ohmic regime is proportional to the ion concentration in the liquid. The maximum current, which is reached at the highest potential difference of $\Delta V = 50$ V in the overlimiting current regime, does not precisely scale one to one with the salt concentration. A possible explanation for this is the water splitting reaction at the electrodes, which consumes part of the power supplied to the system as well and produces charged species that will be transported through the system.

Normalization of the current I by the maximum current I_{max} of the corresponding experiment indicates that for all concentrations the transport behaviour is similar. At a potential difference of approximately $\Delta V = 6$ V, ion transport transitions from the Ohmic to the limiting current regime. At a potential difference of roughly $\Delta V = 22$ V, the overlimiting current regime starts. Calculation of the derivative $dI/d\Delta V$ shows that at these points the slope of the $I(\Delta V)$ -curve changes, indicating a change in the transport characteristics. Although the data is relatively noisy, the transition points are apparent from the curves for 0.1 and 1 mM NaCl. The fluctuations in current decreased with increasing salt concentration. Different flow rates did not lead to significant differences in the measured currents. This can possibly be attributed to incomplete depletion of ions in the diluted streams, implying that there are still ions available for charge transport through the hydrogels for all flow rates.

For elevated voltages ($\Delta V > 10$ V) we observed the development of ion depletion zones in the depleted microchannels. A local increase in fluorescence intensity was observed in the enriched microchannels, indicating the existence of locally higher salt concentrations. As shown in Figure 5.5(a), the depletion zones were observed to grow in size with increasing applied voltage and distance from the inlet. Figure 5.5(b) shows that for $\Delta V > 25$ V vortices were formed in the depletion zones. Potentially due to the discontinuous nature of the hydrogel patches – we have an alternating pattern of charge selective hydrogels and PDMS in our system – the vortices did not migrate in the direction of the imposed flow as reported by Kwak *et al.* [15]. In our heterogeneous system, there is a tangential component of the electric field with respect to the membrane interface, resulting in electro-osmotic flow at the channel walls. As a result of this, the ion depletion zones are “pinned” at the hydrogel surface, as will be elaborated upon in Chapter 6. At the upstream

Figure 5.5 — Fluorescence images showing the formation of ion depleted and enriched zones in the depleted (D) and enriched (E) microchannels for two constant potential measurements. A 0.1 mM NaCl solution containing 5 μM Alexa Fluor 488 Cadaverine (the fluorescent dye) was flushed through the microchip at 3 $\mu\text{L}/\text{min}$. The experiments were performed at a constant potential difference of (a) $\Delta V = 20\text{ V}$ and (b) $\Delta V = 30\text{ V}$. The bright coloured hydrogel is the anion exchange hydrogel (METC) and the dark coloured one is the cation exchange hydrogel (SPAP).

edge of each hydrogel patch, in the depletion zone, a high fluorescence intensity was observed. This suggests that near those points the local salt concentration was larger than in the rest of the depletion zones. The mixing of the electrolyte solution next to the PMDS pillars by the vortices could explain this behaviour, as this mixing increases the ion concentration near the PDMS pillar and consequently also near the upstream edge of each hydrogel. Charge transport is thus affected by the heterogeneity of the ion concentration at the hydrogel interface and could even enhance it when compared to a homogeneous ion selective membrane, as previously discussed in the literature [43].

To quantify the desalination performance of the microchip, we performed experiments in which we applied a constant potential in the range of 0–100 V or a constant current in the range of 3–7 μA , which corresponds to a current density in the range of 12–28 A/m^2 (here, the area is defined as the hydrogel surface area per channel wall). The resulting currents and potentials were measured to confirm that there is charge transport through the hydrogel patches.

A 1 mM NaCl solution (supplemented with 5 μM Alexa Fluor 488 Cadaverine) was pumped through the microchannels at a flow rate of either 3 or 5 $\mu\text{L}/\text{min}$. The conductivities of the solutions collected at the channel outlets were measured, and the salt concentration were estimated accordingly, under the assumption that the only salt in the system is NaCl and no significant charge carriers are

Figure 5.6 — NaCl concentrations of the solutions collected at the channel outlets for (a) constant potential measurements ($\Delta V = 70$ V) for different flow rates (3 and 5 $\mu\text{L}/\text{min}$), and for (b) constant current measurements with different currents (3, 5 and 7 μA , corresponding to current densities of 12.2, 20.3 and 28.4 A/m^2) for a fixed flow rate (3 $\mu\text{L}/\text{min}$). The error bars indicate the 95% prediction bounds. Channel 2 and 4 represent the ion enriched channels, while channel 3 and 5 are the ion depleted channels.

added as a result of water splitting. As expected, the effluent streams from the microchannels were either salt enriched or depleted in an alternating pattern.

In Figure 5.6(a) the measured outlet salt concentrations (inferred from conductivity measurements of the outlet flows) are shown for constant potential experiments for two different flow rates (3 and 5 $\mu\text{L}/\text{min}$). When the flow rate was increased, the residence time and therefore the charge separation decreased. Only the outlet streams of the microchannels 2 to 5 were taken into account. In the outer two microchannels 1 and 6, containing the electrodes and both facing only an anion exchange hydrogel (see Figure 5.1), the solution is not necessarily either enriched or depleted because of ions generated by electrode reactions.

In Figure 5.7(a), the current I is plotted as a function of time t for a fixed potential difference of $\Delta V = 70\text{ V}$ and a flow rate of 3 $\mu\text{L}/\text{min}$. This data corresponds to the results shown for 3 $\mu\text{L}/\text{min}$ in Figure 5.6(a). Figure 5.7(a) demonstrates that the average current during this experiment was 7.7 μA (31.3 A/m^2) at steady state. Based on this current, the total transport was calculated to be 4.8×10^{13} ions per second, while 6.0×10^{13} ions entered each channel per second. Based on this calculation, we expect a desalination degree of 80%. This is twice as high as the measured value of 40% for 3 $\mu\text{L}/\text{min}$, as Figure 5.6(a) shows. The deviation between the measured and expected desalination degree could be attributed to the low permselectivity of the hydrogels, which leads to non-selective ion transport in addition to selective ion transport. Additional effects reducing the desalination degree are hydrogel swelling which reduces the charge density and possibly overcoming the Donnan potential at high field strengths, causing ion leakage at these fields.

In Figure 5.6(b), the salt concentrations of the outlet streams are shown for three different applied currents, *i.e.* for 3, 5, and 7 μA (12.2, 20.3 and 28.4 A/m^2). The data shows that the outlet concentrations did not change when increasing the current I . Because the transport rate of charge carriers is proportional to the current, we would expect to see a difference in the degree of desalination. For all three currents, however, 75% of the initially present salt was removed in the desalinated streams. This suggests that 75% is the maximum desalination degree that is achievable with these devices. Since the ion concentration is estimated from conductivity measurements, the presence of ions other than Na^+ and Cl^- is neglected. At large field strengths and currents, if water splitting is occurring, this would yield an underestimation of the desalination degree.

A valuable property of our microfluidic electrodialysis platform is that it enables real-time visualization of ion transport adjacent to and through the hydrogels using a fluorescent dye. This helps in obtaining a better understanding of the relevant ion transport phenomena in and at charge selective interfaces. As the curve in Figure 5.7(a) shows, approximately 600 seconds were required before the system reached steady state. We observe that at the very first instance ($t < 10$

Figure 5.7 — The design of the microfluidic electrodialysis platform allows visualization of ion transport in the hydrogels between the salt enriched (E) and depleted (D) channels. In (a) the current I is plotted as function of time t for a fixed potential difference of $\Delta V = 70 \text{ V}$ and flow rate of 3 $\mu\text{L}/\text{min}$. Before reaching steady state, the change in current can be related to transport in the hydrogel, as indicated by the (b) fluorescence images of the dye in the hydrogels (1 mM NaCl solution with 5 μM Alexa Fluor 488 Cadaverine). It took about 600 s before the intensity, and thus presumably the dye and ion concentration, in the hydrogels was constant.

s), the current decreased. This could indicate the build-up of a concentration boundary layer. Subsequently the current was increasing, reaching a (local) maximum at 250 s. Inspection of the fluorescence images for this experiment, given in Figure 5.7(b), shows that the fluorescence distribution can be related to the charge transport through the hydrogels. Directly after applying a potential difference, a high concentration of negatively charged fluorescent dye was observed near the interface of the anion exchange METC-hydrogel with the salt depleted channel. This cluster of fluorescent dye migrated towards the enriched channel in approximately 250 seconds. Comparison with the current profile in Figure 5.7(a) shows that at that moment, the current reached a (local) maximum. Subsequently, the fluorescence slowly approached a constant intensity distribution, reaching steady state after approximately 600 s. Note that not only in the positively charged anion exchange hydrogel (AEH) the fluorescence intensity and thus the dye concentration increased, but also in the negatively charged cation exchange SPAP-hydrogel (CEH). This indicates that, in line with the measured permselectivity of the bulk polymers, the ion selectivity of the hydrogels was not perfect. The dye concentration, however, was clearly larger in the AEH than in the CEH.

5.4 Conclusion

Alternatingly patterned anion and cation exchange hydrogels were fabricated in a PDMS microchip using capillary barriers. The chemical composition of the hydrogels was tailored to obtain a suitable balance between the degree of swelling and the charge density. The material properties were characterized, and the ion exchange hydrogels showed ion selective permeation, based on their ion exchange capacity, permselectivity and resistivity. We demonstrated that the hydrogels can be used for desalination of water with salt concentrations up to 1 mM NaCl at various flow rates (0–5 $\mu\text{L}/\text{min}$), applied potentials (0–100 V), and current densities (12–28 A/m^2). We obtained alternating dilute and concentrated streams at the channel outlets of the microchips. We measured a desalination degree of 40% for an inlet concentration of 1 mM NaCl, an applied potential difference of $\Delta V = 70$ V and a flow rate of 3 $\mu\text{L}/\text{min}$. The maximum desalination degree obtained was 75%.

The separation can be enhanced by increasing the total length of the hydrogel-liquid interface, by increasing the residence time of the solution in the microchannels, or by optimizing the hydrogel properties like the charge density. This would allow desalination of salt solutions with higher concentrations, without the need to apply large potential differences. Our approach might therefore be promising for the development of processes related to water desalination [44], sample

pre-treatment [45] and high-focusing of proteins [46].

By utilizing a charged fluorescent dye, we could visualize the ion concentration in the electrodialysis device. The fluorescence images revealed that ion depleted boundary layers are formed near the ion exchange hydrogels when a potential difference ΔV is applied. When $\Delta V > 25$ V, we observed the formation of vortices, enhancing convective transport towards the hydrogels in the overlimiting current regime. The desalination platform described here also enables visualization of charge transport through the hydrogels, which can contribute to a better understanding of the transport phenomena in electrodialysis processes. The simple fabrication method allow us to design a variety of hydrogel geometries, which can be studied to investigate the influence of geometry on charge transport, which is the subject of the next chapter.

References

- [1] H. Strathmann, *Electrodialysis, a mature technology with a multitude of new applications*, Desalination **264**, 268 (2010).
- [2] V. V. Nikonenko, N. D. Pismenskaya, E. I. Belova, P. Sistat, P. Huguet, G. Pourcelly, and C. Larchet, *Intensive current transfer in membrane systems: modelling, mechanisms and application in electrodialysis*, Adv. Colloid Interfac. **160**, 101 (2010).
- [3] M. Tedesco, H. V. M. Hamelers, and P. M. Biesheuvel, *Nernst-Planck transport theory for (reverse) electrodialysis: I. Effect of co-ion transport through the membranes*, J. Membr. Sci. **510**, 370 (2016).
- [4] R. W. Baker, in *Membrane technology and applications* (John Wiley & Sons, Chichester, 2004).
- [5] M. B. Andersen, M. van Soestbergen, A. Mani, H. Bruus, P. M. Biesheuvel, and M. Z. Bazant, *Current-induced membrane discharge*, Phys. Rev. Lett. **109**, 108301 (2012).
- [6] I. Rubinstein and B. Zaltzman, *Convective diffusive mixing in concentration polarization: from Taylor dispersion to surface convection*, J. Fluid Mech. **728**, 239 (2013).
- [7] F. Maletzki, H.-W. Rösler, and E. Staude, *Ion transfer across electrodialysis membranes in the overlimiting current range: stationary voltage current characteristics and current noise power spectra under different conditions of free convection*, J. Membr. Sci. **71**, 105 (1992).
- [8] E. Belashova, N. Melnik, N. Pismenskaya, K. Shevtsova, A. Nebavsky, K. Lebedev, and V. Nikonenko, *Overlimiting mass transfer through cation-exchange membranes modified by Nafion film and carbon nanotubes*, Electrochim. Acta **59**, 412 (2012).

- [9] V. V. Nikonenko, A. V. Kovalenko, M. K. Urtenov, N. D. Pismenskaya, J. Han, P. Sistat, and G. Pourcelly, *Desalination at overlimiting currents: state-of-the-art and perspectives*, *Desalination* **342**, 85 (2014).
- [10] J. H. Lee, Y.-A. Song, and J. Han, *Multiplexed proteomic sample preconcentration device using surface-patterned ion-selective membrane*, *Lab Chip* **8**, 596 (2008).
- [11] S. J. Kim, S. H. Ko, K. H. Kang, and J. Han, *Direct seawater desalination by ion concentration polarization*, *Nat. Nanotechnol.* **5**, 297 (2010).
- [12] H. Kim, J. Kim, E.-G. Kim, A. J. Heinz, S. Kwon, and H. Chun, *Optofluidic in situ maskless lithography of charge selective nanoporous hydrogel for DNA preconcentration*, *Biomicrofluidics* **4**, 043014 (2010).
- [13] L.-J. Cheng and H.-C. Chang, *Microscale pH regulation by splitting water*, *Biomicrofluidics* **5**, 046502 (2011).
- [14] S. J. Kim, S. H. Ko, R. Kwak, J. D. Posner, K. H. Kang, and J. Han, *Multi-vortical flow inducing electrokinetic instability in ion concentration polarization layer*, *Nanoscale* **4**, 7406 (2012).
- [15] R. Kwak, G. Guan, W. K. Peng, and J. Han, *Microscale electrodialysis: concentration profiling and vortex visualization*, *Desalination* **308**, 138 (2013).
- [16] M. Kim, M. Jia, and T. Kim, *Ion concentration polarization in a single and open microchannel induced by a surface-patterned perm-selective film*, *Analyst* **138**, 1370 (2013).
- [17] T. A. Zangle, A. Mani, and J. G. Santiago, *Theory and experiments of concentration polarization and ion focusing at microchannel and nanochannel interfaces*, *Chem. Soc. Rev.* **39**, 1014 (2010).
- [18] S. Park, T. D. Chung, and H. C. Kim, *Ion bridges in microfluidic systems*, *Microfluid. Nanofluid.* **6**, 315 (2009).
- [19] M. H. Pham and D. P. Barz, *Bonding Nafion® with polydimethylsiloxane: A versatile approach towards ion-exchange membrane microfluidic devices*, *J. Memb. Sci.* **537**, 310 (2017).
- [20] Y. Zhang, N. E. Benes, and R. G. H. Lammertink, *Visualization and characterization of interfacial polymerization layer formation*, *Lab Chip* **15**, 575 (2015).
- [21] D. Hlushkou, R. Dhopeswarkar, R. M. Crooks, and U. Tallarek, *The influence of membrane ion-permeability on electrokinetic concentration enrichment in membrane-based preconcentration units*, *Lab Chip* **8**, 1153 (2008).
- [22] B. Gumuscu, J. G. Bomer, A. van den Berg, and J. C. T. Eijkel, *Large scale patterning of hydrogel microarrays using capillary pinning*, *Lab Chip* **15**, 664 (2015).
- [23] H. Strathmann, *Ion-exchange membrane separation processes* (Elsevier, Amsterdam, 2004).
- [24] Y. Tanaka, Chapter 3: Theory of Teorell, Meyer, and Sievers (TMS Theory) in

- Ion exchange membranes*, 2nd ed., edited by Y. Tanaka (Elsevier, Amsterdam, 2015), pp. 67 – 73.
- [25] T. Sata, *Ion exchange membranes: preparation, characterization, modification and application* (Royal Society of Chemistry, Cambridge, 2004).
- [26] *CRC handbook of chemistry and physics*, 76th ed., edited by D. R. Lide (CRC Press, Boca Raton, 1995).
- [27] B. Gumuscu, J. G. Bomer, A. van den Berg, and J. C. T. Eijkel, *Photopatterning of hydrogel microarrays in closed microchips*, *Biomacromolecules* **16**, 3802 (2015).
- [28] W. Zhao, P. Fonsny, P. FitzGerald, G. G. Warr, and S. Perrier, *Unexpected behavior of polydimethylsiloxane/poly(2-(dimethylamino)ethyl acrylate) (charged) amphiphilic block copolymers in aqueous solution*, *Polym. Chem.* **4**, 2140 (2013).
- [29] M. Balastre, S. J. Kostka, and M. McMillan, U.S. patent application no. 14/527,812, 2015.
- [30] V. V. Khutoryanskiy, Z. S. Nurkeeva, G. A. Mun, A. D. Sergaziyev, Z. Ryskalieva, and J. M. Rosiak, *Polyelectrolyte complexes of soluble poly-2-[(methacryloyloxy)ethyl]trimethylammonium chloride and its hydrogels with poly(acrylic acid)*, *Eur. Polym. J.* **39**, 761 (2003).
- [31] S. Scognamillo, V. Alzari, D. Nuvoli, J. Illescas, S. Marceddu, and A. Mariani, *Thermoresponsive super water absorbent hydrogels prepared by frontal polymerization of N-isopropyl acrylamide and 3-sulfopropyl acrylate potassium salt*, *J. Polym. Sci. A Polym. Chem.* **49**, 1228 (2011).
- [32] P. M. Biesheuvel, A. P. van Loon, R. Raangs, H. Verweij, and C. Dirksen, *A prototype osmotic tensiometer with polymeric gel grains*, *Eur. J. Soil Sci.* **51**, 355 (2000).
- [33] S. Durmaz and O. Okay, *Acrylamide/2-acrylamido-2-methylpropane sulfonic acid sodium salt-based hydrogels: synthesis and characterization*, *Polymer* **41**, 3693 (2000).
- [34] O. Okay, General Properties of Hydrogels in *Hydrogel sensors and actuators: Engineering and technology*, edited by G. Gerlach and K.-F. Arndt (Springer-Verlag, Berlin, Heidelberg, 2010), pp. 1–14.
- [35] E. Pretsch, P. Bühlmann, and M. Badertscher, *Structure determination of organic compounds* (Springer-Verlag, Berlin, 2009).
- [36] Y.-L. Ji, Q.-F. An, Q. Zhao, W.-D. Sun, K.-R. Lee, H.-L. Chen, and C.-J. Gao, *Novel composite nanofiltration membranes containing zwitterions with high permeate flux and improved anti-fouling performance*, *J. Membr. Sci.* **390-391**, 243 (2012).
- [37] G. Beamson and D. Briggs, *High resolution XPS of organic polymers: the Scienta ESCA300 database* (John Wiley & Sons, Chichester, 1992).
- [38] P. Cardiano, P. G. Mineo, F. Neri, S. Lo Schiavo, and P. Piraino, *A new*

- application of ionic liquids: hydrophobic properties of tetraalkylammonium-based poly(ionic liquid)s*, J. Mater. Chem. **18**, 1253 (2008).
- [39] T. Xu, *Ion exchange membranes: state of their development and perspective*, J. Membr. Sci. **263**, 1 (2005).
- [40] P. Długolecki, K. Nymijer, S. Metz, and M. Wessling, *Current status of ion exchange membranes for power generation from salinity gradients*, J. Membr. Sci. **319**, 214 (2008).
- [41] A. H. Galama, J. W. Post, M. A. Cohen Stuart, and P. M. Biesheuvel, *Validity of the Boltzmann equation to describe Donnan equilibrium at the membrane-solution interface*, J. Membr. Sci. **442**, 131 (2013).
- [42] N. Panchuk-Voloshina, R. P. Haugland, J. Bishop-Stewart, M. K. Bhalgat, P. J. Millard, F. Mao, W.-Y. Leung, and R. P. Haugland, *Alexa dyes, a series of new fluorescent dyes that yield exceptionally bright, photostable conjugates*, J. Histochem. Cytochem. **47**, 1179 (1999).
- [43] S. M. Davidson, M. Wessling, and A. Mani, *On the dynamical regimes of pattern-accelerated electroconvection*, Sci. Rep. **6**, 22505 (2016).
- [44] K. N. Knust, D. Hlushkou, R. K. Anand, U. Tallarek, and R. M. Crooks, *Electrochemically mediated seawater desalination*, Angew. Chem. Int. Edit. **52**, 8107 (2013).
- [45] P. Kubáň, A. Šlampová, and P. Boček, *Electric field-enhanced transport across phase boundaries and membranes and its potential use in sample pretreatment for bioanalysis*, Electrophoresis **31**, 768 (2010).
- [46] R. S. Foote, J. Khandurina, S. C. Jacobson, and J. M. Ramsey, *Preconcentration of proteins on microfluidic devices using porous silica membranes*, Anal. Chem. **77**, 57 (2005).

Appendix

Figure 5.8 — Phase contrast microscopy images of SPAP (red) and METC (green) hydrogels (a) after fabrication, prior to injection of deionized water into the microchannels, (b) after 1.5 hours in water and (c) after 16 hours in water. The hydrogels are artificially coloured based on grey scale differences.

Figure 5.9 — Calibration curve of the impedance Z as a function of the NaCl concentration c . The fitting is performed on a log-log scale to ensure that the experimental data is normally distributed around the calibration curve. The data points for 0.01 and 0.02 mM are omitted, as they clearly fall outside the linear range. This improves the reliability of the calibration curve. The minimum concentration we measured was always larger than 0.1 mM. The dashed lines form the 95% prediction bounds. As the calibration line gives $\log_{10}(Z)$ as function of $\log_{10}(c)$, on an absolute scale the size of the error depends on the concentration, and the errors are not symmetric around the determined concentration.

Figure 5.10 — Molecular structures of (a) the various monomers, (b) METC + polyacrylamide, the anion exchange hydrogel, and (c) SPAP + polyacrylamide, the cation exchange hydrogel.

Figure 5.11 — SEM images of the hydrogels: (a) polyacrylamide, (b) METC + polyacrylamide and (c) SPAP + polyacrylamide.

Figure 5.12 — FTIR spectra of the METC and SPAP monomers. For METC, there is a peak at 1178 cm^{-1} for C–N stretching. For SPAP, the peaks at 982 and 1043 cm^{-1} denote the presence of R–SO₃–groups .

Figure 5.13 — Fluorescence images showing ion concentration polarization in the microchip. A 1 mM NaCl solution with $5\text{ }\mu\text{M}$ of NaAlexa Fluor 488 Cadaverine (the fluorescent dye) was injected into the microchip and an IV-sweep up to 3 V was applied. The experiments were performed under an increasing electric field without liquid flow.

CHAPTER 6

Enhanced ion transport using geometrically structured charge selective interfaces

Abstract — The microfluidic platform containing charged hydrogels presented in the previous chapter is used to investigate the effect of geometry on charge transport in electrodialysis applications. The influence of heterogeneity on ion transport is determined by electrical characterization and fluorescence microscopy of three different hydrogel geometries and compared with numerical simulations. We found that electro-osmotic transport of ions towards the hydrogel is enhanced in heterogeneous geometries, as a result of the inhomogeneous electric field in these systems. This yields higher ionic current densities for equal applied potentials when compared to homogeneous geometries. The contribution of electro-osmotic transport is present in all current regimes, including the Ohmic regime. We also found that the onset of the overlimiting current is positively influenced by the increased heterogeneity in hydrogel shape, owing to the non-uniform electric field distribution in these systems. Pinning of ion depletion and enrichment zones is observed in the heterogeneous hydrogel systems, due to electro-osmotic flows and electrokinetic instabilities. Our platform is highly versatile for the rapid investigation of the effects of membrane topology on general electrodialysis characteristics, including the formation of ion depletion zones on the micro-scale and the onset of the overlimiting current.

6.1 Introduction

Electrodialysis (ED) is an established technique in water deionization, using a stack of alternating anion and cation selective membranes [1]. Under the application of an electrical potential, ions migrate towards their counter electrode and are selectively blocked by cation and anion exchange membranes (CEM/AEM), resulting in the formation of desalinated and concentrated streams. Ion transport towards the membrane often limits the currents at which these processes are being operated in industry. At increasing field strengths diffusive transport becomes limiting, causing concentration polarization. The current reaches a limiting value, which reduces the efficiency of the process and prohibits economic operation. At elevated field strengths, the well-known overlimiting current regime arises as a result of induced electrokinetic flows at the membrane interface [2–4]. In this overlimiting current regime, current starts increasing again because the concentration polarization layer is broken down by the convective movement of the fluid.

Ions migrate along the electric field lines because of their charge. In systems with a homogeneous charge selective interface, electric field lines are homogeneously distributed as well. In systems with local conductivity, permittivity or permselectivity gradients an inhomogeneous field arises. This can happen due to heterogeneous charge selective interfaces, for example patterned [5, 6] or structured [7] membranes. Since a driving force for ion transport tangential to the membrane arises, the distorted electric field gives rise to the formation of electro-osmotic flows (EOF) at the charged walls of the system, starting from the Ohmic regime. In the overlimiting current regime, this tangential component acts on the emerging extended space charge and enhances the formation of electrokinetic instabilities (EKI) [8]. The increased rate of ion transport can potentially yield a higher overall efficiency in electrodialysis (ED) processes in the Ohmic regime or reduce the limiting current plateau region by reducing the onset voltage for the overlimiting current regime. The influence of membrane geometry on the efficiency of ED systems has been of interest for several studies [9, 10] with the purpose of yielding more energy-efficient processes. Most of these studies have focused on the macro-scale effects of membrane topology on ED performance parameters, such as resistance and the onset of the limiting and overlimiting current regime in large scale systems [11, 12]. For fundamental understanding of the influence of membrane geometry on charge transport, visualization of the ion concentration profiles adjacent to the membrane is crucial [13, 14]. Pinning of ion depletion zones and vortices at heterogeneities on the membrane has been experimentally observed [15] and numerically studied [16]. Microfluidic platforms enable optical access to the membrane surface and can be manipulated easily for the investigation of several aspects of charge transport adjacent to a charge

selective surface [17–25].

In the previous chapter, a microfluidic platform using charge selective hydrogels for the microscopic investigation of ion transport in electrodialysis systems was introduced [26]. Hydrogels are versatile materials that can easily be patterned with different geometries on the micro-scale. Therefore, hydrogels can be used to build micro-ED systems for rapid investigation of the influence of geometry on ion transport which can be applied in large scale electrodialysis systems. In our micro-scale electrodialysis system, six adjacent microchannels are separated by alternating anion exchange hydrogels (AEH) and cation exchange hydrogels (CEH). This allows us to microscopically observe concentration profiles and depletion zones adjacent to the hydrogel compartments. The previous chapter was a proof-of-principle of using patterned and charged hydrogels for microfluidic investigation of ion transport phenomena in electrodialysis. In this chapter, we investigate the influence of hydrogel geometry on the development of ion depletion zones and the IV-characteristics. Fluorescence microscopy and fluorescence lifetime microscopy (FLIM) are used for the visualization of ion concentration profiles. This demonstrates the role of hydrogel geometry on the formation and pinning of ion depletion zones. These experiments give insight into the interplay of membrane topology and performance. We show that transport of ions through the hydrogel is enhanced with increasing heterogeneity in hydrogel shape, as was predicted based on numerical simulations [16].

6.2 Experimental details

6.2.1 Microchip fabrication

The microchips consist of a polydimethylsiloxane (PDMS, Dow Corning) layer on a microscope slide (see Figure 6.1(a)). The PDMS layer contains microfluidic channels, capillary barriers, inlets and outlets and was fabricated using standard soft lithography techniques. Microchip designs included three different geometrical shapes: (1) Continuous hydrogel compartments (Figure 6.1(c)) supported with capillary barriers with dimensions of $16100 \times 1720 \mu\text{m}$ (width, length), which will be referred to as full, homogeneous hydrogels. (2) Pillars ($700 \mu\text{m}$ wide) and five hydrogel compartments with dimensions of $700 \times 1720 \mu\text{m}$ (Figure 6.1(d)), which will be referred to as symmetric or rectangular heterogeneous hydrogels. (3) Five trapezoidal, asymmetric heterogeneous hydrogel compartments (width varying from $300 \mu\text{m}$ to $1725 \mu\text{m}$) generated by PDMS pillars with $600 \times 500 \mu\text{m}$ (width, length) placed with a zigzag pattern at angles of 20° (Figure 6.1(e)). The height of microchannels and capillary barriers was $75 \mu\text{m}$ and $7.5 \mu\text{m}$, respectively, while the microchannel width was $700 \mu\text{m}$ for all geometries. The details of the fabrication of the chip and the preparation of the hydrogels were given in the

Figure 6.1 — Microfluidic desalination chip. (a) Gold-coated copper electrodes are placed in the outer microchannels and a salt solution is flowed through all microchannels. (b) Schematic representation of the microchip, alternating anion and cation exchange hydrogels (AEH and CEH) are patterned in between the microchannels. An electric potential can be applied using the electrodes placed in the outer channels, resulting in alternating depleted and concentrated streams. Three different geometries are under investigation, (c) 'full' homogeneous hydrogels, where the entire microchannel wall consists of hydrogels, (d) symmetric heterogeneous hydrogels, where PDMS pillars partially block the microchannel wall and (e) asymmetric 'trapezoidal' heterogeneous hydrogels, in which the hydrogels have a trapezoidal shape.

previous chapter.

All microchips consist of six parallel microchannels connected through alternating AEH and CEH, as depicted in Figure 6.1(b). The liquid flow is supplied to the individual channels using six programmable Harvard Picoplus syringe pumps connected to Tygon flexible plastic tubing (0.01" inner diameter) and Braun Omnifix-F 1 mL syringes.

Two gold-coated copper electrodes are placed in the two outside microchannels and electrical characterization of the system is performed using an Autolab PGSTAT204 potentiostat (Metrohm, the Netherlands). To avoid bubble formation at the electrodes and minimize water splitting, the maximum applied potential was limited to 10 V. For the electrical characterization of the system, IV-sweeps are

performed with steps of 0.05 V and a scan rate of 0.01 V/s. In all microchannels, a cross flow (with a channel flow rate between 2 and 9 $\mu\text{L}/\text{min}$) is applied for all IV-sweeps. This yields a linear flow velocity between $\sim 635 \mu\text{m}/\text{s}$ and $\sim 2900 \mu\text{m}/\text{s}$, corresponding to fluid residence times between 10 and 2.2 seconds in the part of the microchip containing charge selective hydrogels. The total residence time in the microchip is approximately three times larger due to in- and outlet sections that do not contain any hydrogel surface. Chronoamperometric (measuring the current as a function of time at a fixed potential) and chronopotentiometric (measuring the potential as a function of time at a fixed current) measurements are done at these flow conditions as well. For visualization experiments, chronoamperometric and chronopotentiometric measurements are conducted while microscopy images are taken, without the application of flow in the microchannels.

6.2.2 Fluorescence Microscopy

All six microchannels were flushed with electrolyte solutions of NaCl. For the fluorescence experiments, solutions with 0.1 mM NaCl were used, containing 5 μM Alexa Fluor 488 Cadaverine (ThermoFisher Scientific) as a fluorescent dye (ex/em 490/525nm). The Alexa dye is *pH* insensitive in the range applied (*pH* 4 - 10) [27], has a negative charge and therefore qualitatively mimics the behaviour of negative ions yielding information on the formation of ion depletion zones in the system. Prior to visualization experiments, the electrolyte flow through all microchannels was stopped to enable investigation of ion depletion in a stagnant system, where concentration polarization is maximized. The fluorescent dye was visualized using a Hamamatsu ORCA-Flash4.0 LT camera mounted on an inverted Zeiss Axiovert 40 MAT microscope.

6.2.3 Fluorescence-Lifetime Imaging Microscopy

For quantification of the local ion concentrations as a function of time, fluorescence-lifetime imaging (FLIM) was used. The fluorescence-lifetime of a dye can be dependent on the environmental conditions such as *pH*, local electric potential or solute concentration [28], however independent on the concentration of the dye. The lifetime of the dye used in our study, Lucigenin (ThermoFisher Scientific), is dependent on the local Cl^- concentration [29], and we are therefore able to quantify the local ion concentrations inside the microchannels. The lifetime of Lucigenin is linearly dependent on the Cl^- concentration between 0.2 mM and 1 mM (see Figure 6.6 in the appendix for calibration curve). We used a background electrolyte concentration of 0.5 mM NaCl, enabling quantification in both the concentrated and the diluted microchannels.

Fluorescence lifetime was measured using a LI-FLIM system (Lambert Instruments, Groningen, The Netherlands) working in the frequency domain at a modulation frequency of 5 MHz and a phase angle of 30 degrees, equipped with a

modulated TRiCAM and a modulated LED of wavelength 460 nm (3 W). The equipment is mounted on a Zeiss Axio Vert.A1 inverted microscope (Zeiss, Germany). An identical light path was used in all measurements to ensure the validity of the measurements. The lifetime is calculated based on a reference measurement of the lifetime of Lucigenin without a background electrolyte, measured in the same light path configuration.

6.3 Results and discussion

6.3.1 Electrical characterization

IV-sweeps were performed using 0.1 mM NaCl at a feed flow rate of 3 $\mu\text{L}/\text{min}$ in at least two different microchips for all geometries. As seen in Figure 6.2(a), current is the highest when the trapezoidal heterogeneous hydrogels are used, and lowest for the full homogeneous hydrogels. On chip reproducibility was high (standard deviation <5 %), but the reproducibility between different chips was lower, yielding large standard deviations for the IV characteristics observed in Figure 6.2(a). In the Ohmic regime (up to ~ 2 V, see inset of Figure 6.2(a)), the highest currents are measured for both heterogeneous hydrogels, even though they have a lower total area. We attribute this to the presence of electro-osmotic contributions to the flow (EOF) at even the lowest voltages in heterogeneous systems. This EOF is a result of the tangential component in the electric field, shown in Figure 6.3. Apart from that, in the heterogeneous structures, the depletion zone is not growing into the microchannel to the same extent as at the homogeneous hydrogel. Due to the channel heterogeneity, the depletion zone is discontinuous along the channel wall, breaking down the growth of the depleted area into the channel. Inside the depletion zone, the potential drop is much larger than in the ion rich zones as a result of the lower conductivity. When the depletion zone is larger, this thus requires a larger driving potential to induce the same total current. At moderate voltages, the resistance of the system to charge transport seems to reduce as the applied potential is increased, especially for the trapezoidal hydrogels. At higher voltages, the variance in the measurements for the trapezoidal hydrogels is large. We attribute this behaviour to transitioning into the overlimiting current regime and the variable onset of this regime between different microchips that were tested. In the overlimiting regime, electrokinetic instabilities may lead to turbulent mixing, which results in variations in current [13, 30]. In the trapezoidal geometry, more than in the others, the initial contribution of EOF along the channel walls influences the development of the ion depletion zones. The slightest change in configuration is expected to yield a deviation in IV-curve characteristics. This effect is less pronounced for the symmetric heterogeneous and homogeneous hydrogels, as the

Figure 6.2 — (a) IV-sweeps for all different geometries, at a flow rate of $3 \mu\text{L}/\text{min}$ and an inlet concentration of 0.1 mM NaCl . Error bars indicate standard deviation between measurements. (b) Average steady state current density at an applied potential of 8 V as a function of flow rate, obtained by dividing the total current by the active hydrogel area for the different geometries. For the measured absolute currents and the calculation of hydrogel areas, see appendix Figure 6.7.

initial component of the EOF is smaller. The onset for the overlimiting current regime for these geometries is then at a higher voltage.

Current was measured as a function of time at different feed flow rates and a feed concentration of 0.1 mM NaCl. The current was averaged over 180 s for all systems, after reaching a steady state. In our system, we defined the onset of steady state as the time after which the current was not monotonically increasing or decreasing. The highest currents were measured for the asymmetric trapezoidal hydrogels. The absolute current as a function of flow rate is measured at an applied potential of 8 V, and is shown in Figure 6.7 in the appendix. The asymmetric trapezoidal hydrogels show the highest absolute current for all flow rates and are less prone to a reduction in current as a function of flow rate. We attribute the decrease in current as a function of flow rate to not overcoming the limiting current regime at higher flow rates when homogeneous and rectangular heterogeneous hydrogels were used. In the chips with trapezoidal hydrogels, the overlimiting current regime is reached at all flow rates. To make a more fair comparison, the current per hydrogel area (A/m^2) in the different microchips should be compared, as shown in Figure 6.2(b). For the asymmetric trapezoidal hydrogels, the average width of the hydrogel is taken as a reference for the active hydrogel area (see appendix for calculations of the area). Since the full homogeneous hydrogels have the highest surface area per channel, the current density in this geometry is lowest. For both heterogeneous (trapezoidal and rectangular) hydrogels, the total exchange area is lower, resulting in higher current densities when compared to the full homogeneous hydrogel. This indicates a more efficient use of hydrogel area in these configurations.

For all electrical measurements it is confirmed that the supply of ions is larger than the theoretical removal of ions as a result of the electric field and the obtained currents. Even for the lowest flow rates ($2 \mu\text{L}/\text{min}$) and hypothetical currents up to $0.6 \mu\text{A}$ (which is the highest current measured in this work) at this flow rate, not all ions will be removed from the feed, so this is not a limiting factor in our experiments.

From the combined IV and chronopotentiometric measurements, we conclude that the asymmetric trapezoidal hydrogels enhance charge transport when compared to full homogeneous hydrogels. This enhancement occurs in all regimes: Ohmic, limiting and overlimiting. To explain this behaviour, the potential distribution in the microchannels is modeled for all geometries. The results are shown in Figure 6.3. These plots are obtained using COMSOL Multiphysics, in which the electric field is solved using the Poisson equation. For the homogeneous geometry (Figure 6.3(a)), there is no initial gradient of the electric field in the direction tangential to the hydrogel surface, while for both heterogeneous geometries there is a tangential component present immediately after applying a potential (Figure 6.3(b-c)). The tangential component gives rise to an electro-osmotic flow

Figure 6.3 — Modeled potential distribution and electric field lines inside the microfluidic channels, (a) for homogeneous hydrogels (b) for symmetric heterogeneous hydrogels and (c) for asymmetric heterogeneous hydrogels.

(EOF) adjacent to the microchannel wall, yielding an additional transport of ions towards the hydrogel. Using the local electric field strength E_x obtained from these simulations, the magnitude of this EOF can be estimated for both heterogeneous geometries, using the Smoluchowski equation [31], $u_{eo} = \frac{\epsilon_r \epsilon_0 \zeta}{\eta} E_x$. With a ζ -potential of -100 mV [32, 33], a viscosity η of 8.9×10^{-4} Pa $\cdot$ s and a relative permittivity $\epsilon_r \epsilon_0 = 7 \times 10^{-10}$ F/m the expected velocity of EOF is estimated to be between ~ 100 $\mu\text{m/s}$ and ~ 200 $\mu\text{m/s}$ at the PDMS pillars between the hydrogel patches for an overall applied potential of 5 V. This EOF is enhanced by the heterogeneous nature of the surface charge as well, as PDMS is negatively charged and the AEHs are positively charged this will also drive EOF mixing. Apart from that, the contrast between the CEHs and the PDMS surface charge will also play a role in driving EOF [16, 34, 35]. Electric field distortion from the geometric patterning couples to this and can enhance the overall EOF mixing in the system.

The local field strength is higher for the trapezoidal hydrogels than for the rectangular heterogeneous hydrogels ($\sim 10\%$), resulting in slightly higher EOF velocities for this geometry. The difference in shape (and hydrogel curvature) also affects the general flow profile and the driving of the EOF. This EOF is present in all regimes, including the Ohmic and limiting. Already in the Ohmic regime, this yields a contribution of EOF to the charge transport in the heterogeneous

geometries increasing the transport of ions towards the hydrogels. The direction of EOF is dependent on the local direction of the electric field at the and is thus of opposite sign on either side of the hydrogels. This induces electro-osmotic mixing in the boundary layer, reducing concentration polarization and enhancing the effective ion transport. Additionally, the tangential component of the electric field and the presence of EOF enhances the onset of EKI and microfluidic mixing in the ion depletion zones after the development of an extended space charge.

6.3.2 Ion concentration profiles

To gain more understanding of the influence of geometry on ion transport, ion concentration profiles are monitored as a function of time and applied potential or current. All concentration profiles shown here are measured without the application of external cross flow, in order to decouple the effect of concentration polarization from the imposed flow.

Fluorescence Microscopy

Fluorescence microscopy is often used as an indicator of local ion concentrations and in observing the development of ion depletion zones [24, 25]. The fluorescent dye is negatively charged and thus mimics the behaviour of the anions inside the solution. In Figure 6.4 the fluorescence microscopy images of the three different geometries are shown. Positively charged AEHs contain relatively high

Figure 6.4 — Fluorescence intensity profiles for (a) homogeneous hydrogels, (b) for symmetric heterogeneous hydrogels and (c) for asymmetric heterogeneous hydrogels as a function of time with an applied potential of 9 V, without the application of cross flow. Anion exchange hydrogels (indicated by the green markers) are bright as a result of the negatively charged fluorescent dye, cation exchange hydrogels (red markers) are less bright. Depletion zones are developing adjacent to the hydrogels after the application of an electric field, yielding different patterns for the three geometries.

concentrations of the negatively charged fluorescent dye and appear bright. For all images, the electric field is applied from top (positive electrode) to bottom (negative electrode), as is indicated in Figure 6.4(a). This configuration leads to ion depletion adjacent to the hydrogels in the diluted microchannels, as can also be observed from the fluorescence intensity profiles inside the microchannels. Depletion zones are formed in all different hydrogel geometries and grow as a function of time.

The ion depletion zones form in a different manner because the geometry of the hydrogel has an influence on the distribution of the electric field and thus alters the behaviour of charge transport for the different geometries. For the homogeneous hydrogels (Figure 6.4(a)), initially a depletion boundary layer forms at the hydrogel interface and grows into the microchannel until breaking down in small circular ion depletion zones moving along the hydrogel interface (from 27.5 s). Then, the smaller depletion zones merge into larger zones that are still moving (with no preferential direction) along the hydrogel interface. The direction of this movement is dependent on the local charge distribution in the solution. Concentrated solution plugs remain between the large depletion zones (from $t = 100$ s). There are nearly no initial heterogeneities in the electric field distribution in homogeneous geometries and thus no initial contribution of EOF on the ion transport is present. Therefore, initially a stagnant concentration polarization layer forms and covers the entire membrane interface. Upon the development of ion depletion zones and an extended space charge adjacent to the hydrogel interfaces, the electric field is distorted in the homogeneous system as well, resulting in EKI and the movement of fluid and depletion zones at the hydrogel interface. Our experimental observations are in general agreement with the numerical predictions reported by Davidson *et al.* for similar geometric configurations [16].

In both microchips with a heterogeneous hydrogel geometry, depletion zones form in a more controlled manner as pinning of depletion zones occurs at the hydrogel edges. A local zone of increased concentration is formed at both edges between the PDMS pillar and the hydrogel, while the depletion zone continues growing at the hydrogel interface. Near rectangular heterogeneous hydrogels, first small depletion zones form adjacent to the hydrogel interface, and merge into two larger depletion zones that are pinned at the hydrogel surface. These depletion zones grow as a function of time, until ions are fully depleted in the entire microchannel. The channel outside of the hydrogels (beginning and ends of the microchannel, as can be seen from Figure 6.4(b) at 210 s), still contains a higher concentration of ions when compared to the depletion zones. The zones of high concentration are locally pinned to the edge between the hydrogel and the PDMS. At this point, the current is reduced to a lower steady value, indicating a steady flux of ions through the hydrogels. Similar behaviour can be observed in the heterogeneous trapezoidal hydrogels, where a local pinning of high concentration

at the hydrogel edges and depletion zones form as a function of time. However, at the smaller hydrogel borders, there is only one depletion zone forming while at the larger border multiple smaller depletion zones are formed. These small zones merge into larger depletion zones (around $t = 40$ s) until the ions in entire microchannel are fully depleted at $t = 200$ s.

From the experiments with fluorescent dye, we can observe some of the fluid movement, especially at the planes of discontinuous conductivity (the edges between the hydrogel and the PDMS pillars) and we can compare the ion depletion zones to numerical predictions of similar systems that also included the development of fluid flow [16, 36]. Particle seeding of the flow was not successful as the polystyrene beads stick to the hydrogel surface and can move electrophoretically through the hydrogels and with that distort the system under investigation. We expect, based on these numerical predictions and previous experiments in microfluidic systems [13, 37] that vortex formation occurs also within the depletion zones observed in the current system.

The observed movement of the enriched zones pinned to the hydrogel edge can be explained by the combined effect of EOF adjacent to the microchannel walls and the electric field working on the extended space charge adjacent to the hydrogel surface. As was explained in Section 6.3.1, EOF is present in our system as a result of the negative surface charge of PDMS and a tangential component of the electric field. The surface is screened by cations present in the Debye layer. These cations migrate along the electric field lines towards the low potential sink, and drag along the liquid which results in an electro-osmotic flow in the microchannels. For this EOF to establish itself, there should be a component of the electric field in the direction along the channel walls. As was shown, this component arises in systems with a heterogeneous distribution of hydrogels, since the electric field is non-homogeneous through local changes in conductivity and permittivity at the wall in such systems. Electrokinetic instabilities (EKI) can also occur from the development of a local space charge that is a result of the selective charge transport through the hydrogel [38], which is also influenced by the shape of the electric field lines. At the cation selective interface, a negative space charge develops and results in a fluid movement inside the electric field, directed towards the middle of the microchannel. The combination of this EOF and EKI lead to the pinning of high concentration plugs at the interface between the PDMS and the hydrogel in both heterogeneous geometries.

Fluorescence-Lifetime Imaging Microscopy

To quantify the ion concentration inside the microchannels, we combined FLIM with chronoamperometric and chronopotentiometric measurements. After setting a potential or current, images are captured to measure the ion concentration in the

microchannels as a function of time. Typical results of the FLIM measurements are shown for the different geometries in Figure 6.5, the fluorescence-lifetime of the dye is converted to Cl^- concentration via a calibration curve (see Figure 6.6 in the appendix). These chronopotentiometric measurements were done at a constant current of $0.5 \mu\text{A}$. Note that while the dye concentration does not influence the measurement of the lifetime, the dye concentration must be high enough to yield a sufficient signal in order to measure lifetime. In FLIM, the positively charged AEHs show a signal since the Lucigenin dye is negatively charged, the negative CEHs do not show any signal during the measurement. Measuring the ion concentration inside of the AEHs is not possible, since this concentration is higher than the maximum range for calibration.

For all geometries, the Cl^- concentration increases in the upper channel, while it decreases in the lower channel, as is expected based on the configuration of the electric field (see Figure 6.5(a)). The negatively charged fluorescent dye was eventually depleted in the depleted channel, resulting in the loss of signal from

Figure 6.5 — Local Cl^- concentrations in both depleted and enriched microchannel in chronopotentiometric measurements at a constant current of $0.5 \mu\text{A}$, measured with FLIM for (a) homogeneous hydrogels, (b) for symmetric heterogeneous hydrogels and (c) for asymmetric heterogeneous hydrogels. CEHs are indicated by the red markers and are not yielding a signal, while AEHs are indicated by the green markers and show a signal since the negatively charged Lucigenin is present in these hydrogels as well. The fluorescent dye is also depleted from the depleted channel, resulting in the loss of signal in this channel at elevated times. In the upper channel, the increase in local concentration can be followed as a function of time.

this channel (most pronounced at the longest times). The behaviour observed in the FLIM measurements is similar to the results of fluorescence microscopy measurements, which confirms that fluorescence measurements are a good indicator for qualifying ion concentration profiles inside microfluidic systems. However, both the spatial and time resolution of our FLIM system is not sufficient to detect the development of local depletion zones in our relatively small system in sufficient detail to draw firm conclusions. Fluorescence microscopy has shown that the time scale of this development is in the order of seconds while recording one FLIM frame takes 13 seconds in our system.

The increase of ion concentration in the enriched microchannels can be measured as a function of time for all different geometries. An example of such a result is shown in the appendix (Figure 6.8). However, the space and time resolution of the FLIM method yield a high variance in the measurements, resulting in uncertainties in the actual local value of concentration. In general, as observed in the electrical characterization, the system with the heterogeneous trapezoidal hydrogels shows the fastest charge transport and the highest final concentrations inside the enriched channel. As expected, the enrichment is most pronounced at high potentials and currents, yielding the highest final concentrations in the enriched channel.

6.4 Conclusion

In this study, we investigated the effect of geometry on ion transport through charge selective interfaces. Our platform is versatile and can be easily adjusted to test various geometries, as the PDMS molds can be designed in any desired shape and size. Using capillary line pinning of hydrogels we are able to produce charge selective interfaces in a large variety of shapes which are of interest for determination of the influence of geometry on ED stack performance.

Comparing quantitative (FLIM) and qualitative (fluorescence) concentration measurements, we have found that the use of fluorescence microscopy as an indication for the ion concentration yields a good description of the local concentrations in microfluidic systems. Fluorescence imaging generally has better time and space resolution than FLIM and is a more simple experimental method yielding advantages for the investigation of fast developing systems such as our platform. FLIM was useful to confirm that our simple dye fluorescence measurements are representative of the ion behaviour in the system.

By electrical characterization and imaging of concentration profiles of systems with different hydrogel geometries, we found that a heterogeneous charge selective interface can enhance the charge transport in the system, as the heterogeneity induces tangential components to the electric field acting on charges in the solution

and causing an electro-osmotic flow in the microchannels. This electro-osmotic flow is present in all current regimes, including the Ohmic regime and thus enhances ion transport to the hydrogels even in this regime. The electro-osmotic contribution to the flow induces an enhanced vortex fluid movement in heterogeneous hydrogel systems, mixing the depletion boundary layer and supplying additional ions to the interface. When comparing two different heterogeneous geometries, the trapezoidal hydrogels show a higher charge transport as a result of the larger tangential electric field in this system when compared to the rectangular heterogeneous hydrogels. In systems containing homogeneous charge selective interfaces, initially there is no tangential component in the electric field. After the development of an extended space charge at the membrane interface, a tangential component does occur. This means that there is a delayed mixing of the boundary layer when compared to the heterogeneous systems. Our results are in agreement with theoretical predictions on the formation of ion depletion zones in similar systems [6, 16]. We also found that in heterogeneous systems, pinning of the ion depletion zones and vortexes occurs at the plane of discontinuous conductivity, showing a local increase in ion concentration in the microchannel above the non-permeable pillars.

References

- [1] H. Strathmann, *Electrodialysis, a mature technology with a multitude of new applications*, Desalination **264**, 268 (2010).
- [2] I. Rubinstein and L. Shtilman, *Voltage against current curves of cation exchange membranes*, J. Chem. Soc. Faraday Trans. **2 75**, 231 (1979).
- [3] J. J. Krol, M. Wessling, and H. Strathmann, *Concentration polarization with monopolar ion exchange membranes: Current-voltage curves and water dissociation*, J. Memb. Sci. **162**, 145 (1999).
- [4] V. V. Nikonenko, A. V. Kovalenko, M. K. Urtenov, N. D. Pismenskaya, J. Han, P. Sistat, and G. Pourcelly, *Desalination at overlimiting currents: State-of-the-art and perspectives*, Desalination **342**, 85 (2014).
- [5] S. A. Mareev, V. S. Nichka, D. Y. Butylskii, M. K. Urtenov, N. D. Pismenskaya, P. Y. Apel, and V. V. Nikonenko, *Chronopotentiometric response of an electrically heterogeneous permselective surface: 3D modeling of transition time and experiment*, J. Phys. Chem. C **120**, 13113 (2016).
- [6] V. I. Zabolotskii, V. V. Nikonenko, M. K. Urtenov, K. a. Lebedev, and V. V. Bugakov, *Electroconvection in systems with heterogeneous ion-exchange membranes*, Russ. J. Electrochem. **48**, 692 (2012).
- [7] J. Balster, M. H. Yildirim, D. F. Stamatialis, R. Ibanez, R. G. H. Lamertink, V. Jordan, and M. Wessling, *Morphology and microtopology of cation-exchange polymers and the origin of the overlimiting current*, J. Phys.

- Chem. B **111**, 2152 (2007).
- [8] I. Rubinstein and B. Zaltzman, *Electro-osmotically induced convection at a permselective membrane*, Phys. Rev. E **62**, 2238 (2000).
 - [9] S. Pawlowski, V. Geraldes, J. G. Crespo, and S. Velizarov, *Computational fluid dynamics (CFD) assisted analysis of profiled membranes performance in reverse electrodialysis*, J. Memb. Sci. **502**, 179 (2016).
 - [10] V. S. Pham, Z. Li, K. M. Lim, J. K. White, and J. Han, *Direct numerical simulation of electroconvective instability and hysteretic current-voltage response of a permselective membrane*, Phys. Rev. E **86**, 046310 (2012).
 - [11] M. Wessling, L. G. Morcillo, and S. Abdu, *Nanometer-thick lateral poly-electrolyte micropatterns induce macroscopic electro-osmotic chaotic fluid instabilities.*, Sci. Rep. **4**, 4294 (2014).
 - [12] M. C. Martí-Calatayud, D. C. Buzzi, M. García-Gabaldón, A. M. Bernardes, J. A. S. Tenório, and V. Pérez-Herranz, *Ion transport through homogeneous and heterogeneous ion-exchange membranes in single salt and multicomponent electrolyte solutions*, J. Memb. Sci. **466**, 45 (2014).
 - [13] J. C. de Valença, R. M. Wagterveld, R. G. H. Lammertink, and P. A. Tsai, *Dynamics of microvortices induced by ion concentration polarization*, Phys. Rev. E **92**, 031003(R) (2015).
 - [14] S. M. Rubinstein, G. Manukyan, A. Staicu, I. Rubinstein, B. Zaltzman, R. G. H. Lammertink, F. Mugele, and M. Wessling, *Direct observation of a nonequilibrium electro-osmotic instability*, Phys. Rev. Lett. **101**, 236101 (2008).
 - [15] J. de Valença, *Overlimiting current properties at ion exchange membranes*, Ph.D. thesis, 2017.
 - [16] S. M. Davidson, M. Wessling, and A. Mani, *On the dynamical regimes of pattern-accelerated electroconvection*, Sci. Rep. **6**, 22505 (2016).
 - [17] P. Kim, S. J. Kim, J. Han, and K. Y. Suh, *Stabilization of ion concentration polarization using a heterogeneous nanoporous junction*, Nano Lett. **10**, 16 (2010).
 - [18] I. Cho, G. Y. Sung, and S. J. Kim, *Overlimiting current through ion concentration polarization layer: hydrodynamic convection effects*, Nanoscale **6**, 4620 (2014).
 - [19] R. Kwak, G. Guan, W. K. Peng, and J. Han, *Microscale electrodialysis: Concentration profiling and vortex visualization*, Desalination **308**, 138 (2013).
 - [20] S. J. Kim, Y.-C. Wang, J. H. Lee, H. Jang, and J. Han, *Concentration polarization and nonlinear electrokinetic flow near a nanofluidic channel*, Phys. Rev. Lett. **99**, 044501 (2007).
 - [21] S. Hanasoge and F. J. Diez, *Vortex chain formation in regions of ion concentration polarization*, Lab Chip **15**, 3549 (2015).
 - [22] J. de Jong, R. G. H. Lammertink, and M. Wessling, *Membranes and mi-*

- crofluidics: a review*, Lab Chip **6**, 1125 (2006).
- [23] S. Yu, T.-J. Jeon, and S. M. Kim, *Active micromixer using electrokinetic effects in the micro/nanochannel junction*, Chem. Eng. J. **197**, 289 (2012).
 - [24] T. A. Zangle, A. Mani, and J. G. Santiago, *Theory and experiments of concentration polarization and ion focusing at microchannel and nanochannel interfaces*, Chem. Soc. Rev. **39**, 1014 (2010).
 - [25] H.-C. Chang, G. Yossifon, and E. A. Demekhin, *Nanoscale Electrokinetics and Microvortices: How Microhydrodynamics Affects Nanofluidic Ion Flux in Annu. Rev. Fluid Mech.*, edited by S. H. Davis and P. Moin (2012), Vol. 44, pp. 401–426.
 - [26] B. Gumuscu, A. S. Haase, A. M. Benneker, M. A. Hempenius, A. van den Berg, R. G. H. Lammertink, and J. C. T. Eijkel, *Desalination by electrodialysis using a stack of patterned ion-selective hydrogels on a microfluidic device*, Adv. Funct. Mater. **26**, 8685 (2016).
 - [27] N. Panchuk-Voloshina, R. P. Haugland, J. Bishop-Stewart, M. K. Bhalgat, P. J. Millard, F. Mao, W. Y. Leung, and R. P. Haugland, *Alexa dyes, a series of new fluorescent dyes that yield exceptionally bright, photostable conjugates.*, J. Histochem. Cytochem. **47**, 1179 (1999).
 - [28] J. R. Lakowicz, H. Szmajnski, K. Nowaczyk, K. W. Berndt, and M. Johnson, *Fluorescence lifetime imaging.*, Anal. Biochem. **202**, 316 (1992).
 - [29] J. Biwersi, B. Tulk, and A. S. Verkman, *Long-wavelength chloride-sensitive fluorescent indicators*, Anal. Biochem. **219**, 139 (1994).
 - [30] V. V. Nikonenko, N. D. Pismenskaya, E. I. Belova, P. Sistat, P. Huguet, G. Pourcelly, and C. Larchet, *Intensive current transfer in membrane systems: Modelling, mechanisms and application in electrodialysis*, Adv. Colloid Interface Sci. **160**, 101 (2010).
 - [31] C. J. van Oss, *Electrical Double Layer Interactions Interfacial forces aqueous media, second ed.* (CRC Press, 2006), pp. 51–69.
 - [32] X. Ren, M. Bachman, C. Sims, G. P. Li, and N. Allbritton, *Electroosmotic properties of microfluidic channels composed of poly(dimethylsiloxane)*, J. Chromatogr. B Biomed. Sci. Appl. **762**, 117 (2001).
 - [33] A. Sze, D. Erickson, L. Ren, and D. Li, *Zeta-potential measurement using the Smoluchowski equation and the slope of the current-time relationship in electroosmotic flow*, J. Colloid Interface Sci. **261**, 402 (2003).
 - [34] A. D. Stroock and G. M. Whitesides, *Controlling flows in microchannels with patterned surface charge and topography*, Acc. Chem. Res. **36**, 597 (2003).
 - [35] F. Tian, B. Li, and D. Y. Kwok, *Tradeoff between mixing and transport for electroosmotic flow in heterogeneous microchannels with nonuniform surface potentials*, Langmuir **21**, 1126 (2005).
 - [36] C. L. Druzgalski, M. B. Andersen, and A. Mani, *Direct numerical simulation of electroconvective instability and hydrodynamic chaos near an ion-selective*

- surface*, Phys. Fluids **25**, 110804 (2013).
- [37] A. M. Benneker, J. A. Wood, P. A. Tsai, and R. G. H. Lammertink, *Observation and experimental investigation of confinement effects on ion transport and electrokinetic flows at the microscale*, Sci. Rep. **6**, 37236 (2016).
- [38] M. Bazant and T. Squires, *Induced-charge electrokinetic phenomena: Theory and microfluidic applications*, Phys. Rev. Lett. **92**, 066101 (2004).
- [39] J. Lakowicz, *Principles of fluorescence spectroscopy*, 3rd ed. (Springer, New York, 2013).

Appendix

FLIM calibration

For the quantification of the Cl^- concentration in the microchannels by fluorescence-lifetime imaging microscopy (FLIM), a calibration curve for is constructed. A modified Stern-Volmer equation [39] (Equation 6.1, where τ is the measured lifetime, c is the concentration and A , f and K are fitting parameters) can be used to fit the concentration over the measured concentration range from 0.01 to 10 mM.

$$\tau = A \left(1 - \frac{1}{\frac{1}{fKc} + \frac{1}{f}} \right) \quad (6.1)$$

Figure 6.6 — Calibration curve for FLIM measurements. The lifetime of the fluorescent dye is dependent on the local chloride concentration.

This fit is shown in Figure 6.6, where one can observe that especially for higher concentrations the spread in measurements is large. Therefore, we are only measuring in the linear regime between 0.2 and 1 mM (shown in the inset of Figure 6.6), resulting in a higher accuracy in our estimations, also based on the resulting normal probability plots of both fits. For the linear fit ($\tau = a \cdot c_{\text{Cl}} + b$) we found the $a = -3.942 \pm 0.154$ and $b = 18.04 \pm 0.1$ (95% confidence intervals).

Current and current density

The measured absolute current for the different geometries at different flow rates is shown in Figure 6.7. For a comparison between the different geometries, the current density is a better measure.

Figure 6.7 — Absolute current as a function of flow rate for the three different hydrogel geometries.

For calculation of the current density (Figure 6.2 in this chapter) from the absolute current, the hydrogel area for all different geometries is required. This is calculated using the width (w_1 and w_2) and height (h) of the hydrogels in the channels and the number of patches (n), per Equation 6.2. The values of the different dimensions are shown in Table 6.1.

$$S = nh(\frac{w_1 + w_2}{2})$$

(6.2)

Table 6.1 — Hydrogel dimensions

Configuration	n	$h[\mu\text{m}]$	$w_1[\mu\text{m}]$	$w_2[\mu\text{m}]$
Trapezoidal heterogeneous	5	67.5	295	1725
Rectangular heterogeneous	5	67.5	690	690
Homogeneous	1	67.5	16100	16100

FLIM results

Figure 6.8 — Example of quantitative result of the FLIM measurements. Lines are for visualization purposes only.

In our FLIM measurements, we obtain a quantification of local Cl^- concentration as function of time for all locations where there is a fluorescence signal. Especially in the enriched channel this is valuable as here the enrichment of ions can be monitored. In the depleted channel, the fluorescent dye is depleted as well, as it has a negative charge. Therefore, results shown here are only the enriched channels.

By averaging the lifetime along the center of the enriched channel for all times, we can see the development of the ion concentration in time. These developments can be compared for the different geometries. However, the standard deviation between the different measurements and the variance in concentration in the channel yields a large uncertainty in the measured values of concentration. We can plot the average concentration in the upper channel as a function of time for all different configurations of hydrogel and applied current or potential.

An example of such a measurement is shown in Figure 6.8, where the FLIM results of chronopotentiometric measurements in heterogeneous, rectangular hydrogel chips are shown. In this figure, the error bars are not shown for ease of reading the figure. Especially at lower times, the error bars are overlapping. What can be observed is that as a function of time the concentration in the concentrated channel is increasing, as is expected. It seems that this is happening faster for higher applied currents, which would also be according to expectations, but no

firm conclusions can be drawn from this based on the confidence intervals of the measurements.

The only conclusion that can be drawn based on the FLIM measurements is that the Cl^- concentration in the enriched channel is increasing as a function of time, for all geometries and all applied currents and voltages. No quantification of the transport rate of ions can be done based on these measurements, since the confidence intervals are too large to draw unambiguous conclusions.

CHAPTER 7

Confinement effects on ion transport and electrokinetic flows at the micro-scale

Abstract — Electrokinetic effects adjacent to charge selective interfaces (CSI) have been experimentally investigated in microfluidic platforms in order to gain understanding on underlying phenomena of ion transport at elevated applied voltages. We experimentally investigate the influence of geometry and multiple array densities of the CSI on concentration and flow profiles in a microfluidic set-up using nanochannels as the CSI. The distribution of the electric field has a large influence on the charge transport and can be observed in microfluidic devices. Particle tracking obtained under chronoamperometric measurements shows the development of vortices in the microchannel adjacent to the nanochannels. We found that the direction of the electric field and the potential drop inside the microchannel have a large influence on the ion transport through the interface, for example by inducing wall electro-osmotic flow. Electric field distortion can result in inefficient use of the CSI as the local potential is much lower than the applied potential. Multiple vortices are observed adjacent to the CSI, growing in size and velocity as a function of time and dependent on their location in the microfluidic device. Local velocities inside the vortices are measured to be more than 1.5 mm/s. Vortex speed, as well as flow speed in the channel, are dependent on the geometry of the CSI and the distance from the electrode.

This chapter is based on the publication

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7.1 Introduction

Ion selective membranes are important for a variety of applications, such as water desalination, energy harvesting and in biological systems [1–3]. Ion transport phenomena near membranes have been of interest for many decades and electrokinetic effects associated with ion selective membranes have been investigated widely in the recent years [4–7]. Due to the development of micro- and nanoscale fabrication methods, numerous microfluidic experiments on electrokinetic phenomena adjacent to charge selective interfaces (CSIs) have been conducted [8, 9]. The advantages of microfluidic systems include the control of the imposed flow, which is mostly in the laminar regime, the ease of handling and the small volumes required for experimenting. Most importantly, the optical access and visualization techniques available for microfluidic systems are especially beneficial for the fundamental understanding of ion transport phenomena taking place on the microscopic interface in macroscopic systems.

Investigations of microfluidic charge selective systems typically consist of two or more micro-scale channels which are interconnected through a charge selective layer [10, 11]. This charge selective layer can be a membrane, such as Nafion [9, 10], or a medium providing charge selectivity through double layer overlap, such as nanochannels [12, 13]. The driving voltage is typically applied through electrodes located relatively far from the membrane interface. Due to the many different geometries and materials employed as CSI, the electrical measurements typically cannot be compared to each other directly [11–15]. Observations of ion concentration polarization (ICP) regions using charged fluorescent dyes have yielded information on the size of ion depletion zones as function of applied voltage [12] and the formation of multiple depletion zones in charged membrane systems [11, 16]. Local electric field strengths have been measured using electrodes inserted in the depleted microchannel [17], showing that the local electric field strength in the depletion zone is high as a result of the depletion of charge carriers. In a similar way, the local ion concentration was measured in a dead-end channel with a Nafion membrane [18].

Vortex formation has been both predicted from numerical research and experimentally observed in the overlimiting current regime (OLC) adjacent to a CSI for different geometries and applied electric fields. Many numerical studies have been executed on the prediction of these fluid flows, with different proposed explanations for the occurrence of the OLC regime [5, 19–21], depending on geometry and other system parameters. Experimentally, vortex structures and depletion zones associated with vortex-like rolls have been observed in multiple microfluidic systems [7, 8, 18, 22–24], using particles and dyes. These results have shown the presence of multiple vortices in the vicinity of the CSI, but not the formation of these vortices and their growth as function of time in detail

for microfluidic systems. In larger systems, the vortex size and speed grow in time, up to a velocity of $80 \mu\text{m/s}$ and a size of $1000 \mu\text{m}$ as a function applied current density [22, 25]. These hydrodynamic vortices can be utilized for creating micromixers in lab-on-a-chip applications [21, 26, 27], as they enhance mixing in a laminar system.

Often, in microfluidic systems and numerical simulations in particular, the assumption is made that the electric field is in the same overall direction as the ion transport through the charge selective interface [19, 20]. The majority of experimental papers simplify these relationships of the local electric field variations and the difference between the applied and induced local electric fields to provide order of magnitude or scaling law interpretations [12, 18]. However, the nature of most microfluidic systems does not necessarily provide such a normal electric field as a result of the distortion of electric field lines through the geometry of the microchannels. In numerical research, the applied field is also typically assumed to be normal to the CSI for numerical simplification. In this chapter, we experimentally show that this electric field distribution has a significant contribution to the observed phenomena and membrane performance, by using different geometries of the charge selective interface. Concentration profiles are obtained using fluorescent dyes and particle tracking experiments are done for observation of flow patterns and speeds inside the microchannels. These experiments show that the direction of the electric field and small distortions in this, have a large influence on the ion transport through and near charge selective interfaces.

All solids placed in an electrolyte solution obtain a surface charge, which induces an electric potential distribution inside the liquid. Ions present in the solution will re-distribute according to this potential, yielding an electric double layer (EDL) adjacent to the surface. The size of the EDL is dependent on the ionic strength of the surrounding solution and becomes larger for lower ionic strengths. The characteristic size of the EDL is described by the Debye length, $\lambda_d = \sqrt{(\epsilon_r \epsilon_0 k_B T) / (\sum e^2 z_i^2 n_i)}$, where $\epsilon_r \epsilon_0$ is the dielectric permittivity of the medium, k_B is Boltzmann's constant, T is the temperature (in K), e the elementary charge, z is the ion valency and n is the concentration of ionic species (in mole/m³) [28]. If two walls are spaced in the order of this Debye length ($\mathcal{O}(10 \text{ nm})$ for 1 mM NaCl solution) or less, co-ions are largely excluded from the resulting channel due to the overlapping EDL, resulting in selective ion transport of counter ions through this channel. An advantage of nanochannels over the use of classical membranes such as Nafion is their defined geometry and the controllability of the interface.

When an electric field is applied over a CSI in an ionic solution, counter ions will migrate through the interface, towards their attracting electrode. Co-ions will drift towards the interface on the opposite side, but are blocked by the membrane, yielding a local increase in ion concentration at the interface and ICP

Figure 7.1 — Schematic representation of a CSI in ionic solution under the application of an electric field. Depletion of both anions (yellow) and cations (red) at the interface occurs in the limiting current regime, yielding a transport limitation in the diffusive layer (indicated by the background color gradient). Diffusive, drift and drag forces on the different ions and water result in fluid vortices as time proceeds. Before any potential or current is applied the ions are distributed evenly in the solution adjacent to the CSI (a). After the application of an electric field over the CSI an ion depletion zone is forming at the anodic side of the charge selective interface, while different forces are acting on the ions and water molecules in the solution (b). After proceeding of time, the combination of these forces (in combination with the absence of ions in the vicinity of the CSI) results in vortices forming adjacent to the CSI and within the boundary layer (c).

over the membrane. Upon increase of the electric field, the depletion zone will grow into the solution and diffusion of ions through this zone will become the limiting step in the charge transport, yielding the well-known limiting current in the IV-curves [5]. For a cation selective interface, the depletion zone will be on the anodic side of the interface and an enrichment zone is formed on the cathodic side. As a result of these concentration gradients and local potential gradients in the system, electro-osmosis, (di)electrophoresis and diffusiophoresis will become more pronounced. At elevated field strengths, an extended space charge is formed outside of the electric double layer [29, 30]. The high local electric field strengths (as a result of low local ion concentrations) will act on

this space charge, yielding fast hydrodynamic developments inside the confined microchannel, as schematically depicted in Figure 7.1. In this figure, as function of time, the development of hydrodynamic vortices is schematically shown. At $t = 0$ s, there are no concentration gradients in the system (a). Upon application of an electric field a concentration gradient forms, shown in Figure 7.1(b), which results in diffusive forces acting on both cations and anions. The applied electric field imposes a drift force on the cations towards the membrane. These forces cause movement of the ions, which in turn drag along the surrounding water molecules. These combined drift, diffusion and drag forces result in fluid movement in the vicinity of the CSI, where local concentration gradients result in tangential components of the electric field. As a result of these tangential components of the electric field in the electrically non-neutral parts of the ionic solution, a tangential force near the CSI arises and vortices are formed, shown in Figure 7.1(c). These electrohydrodynamic effects affect the diffusion limited layer adjacent to the CSI and contribute to the transition from the limiting towards the overlimiting regime in the IV-curve [31].

Velocities of classical electro-osmotic flows (EOF) are a function of the applied external field E_∞ , the dielectric permittivity of the medium $\epsilon_r\epsilon_0$, viscosity η and the wall zeta potential ζ and can be described by the Smoluchowski equation [32], $u_{eo} = -(\epsilon_r\epsilon_0/\eta)\zeta E_\infty$. Velocities that are observed as a result of the concentration gradients are reported to be orders of magnitude higher than the predicted value for conventional wall EOF [12, 17].

7.2 Experimental details

In our experiments, we used nanochannels with a characteristic dimension of ~ 20 nm in depth as charge selective medium. The salt solutions used are between 0.1 and 1 mM NaCl, corresponding to a Debye length λ_d of 30 and 9.6 nm, respectively. Two microchannels (70 μm in width, 20 μm in depth) are connected through 50 μm long nanochannels with a width and depth of 2 μm and ~ 20 nm respectively. The dimensions of these nanochannels are measured by white-light interferometry. Different distributions of nanochannels between the microchannels have been used, as shown in Figure 7.2(b), in (I) there is a single patch of 10 nanochannels (spaced 3 μm), in (II) there are $n = 50$ of these patches (spaced 135 μm) and in (III) there are 1660 nanochannels (all spaced 3 μm). Chips are fabricated using wet etching of the nanochannels in glass, applying a sacrificial chrome-gold layer which is removed after wet etching of the microchannels. Access holes are powder blasted before thermally bonding two glass wafers. The glass has a negative surface charge, resulting in cation selective nanochannels. More details on the fabrication method can be found in the appendix.

Figure 7.2 — (a) Schematic design of micro/nanofluidic devices. Two microfluidic channels are interconnected by nanochannels. Fluid access holes are connecting the microchannels to liquid reservoirs on the chip holes. Potential is applied through silver electrodes that are placed in off-chip liquid reservoirs, while the resulting current is measured. (b) Three different distributions of nanochannels between the two microchannels are used, type I, II and III. In type I, a single patch of ten nanochannels is in the middle of the microchannels. In type II, $n = 50$ patches of ten nanochannels are connecting the microchannels, patch numbering is indicated for this chip type. In type III, a full array of 1660 nanochannels is connecting microchannels.

The microchips were placed in a dedicated chip holder and flushed with the desired salt solution for at least 30 minutes using a syringe pump, by first flushing one of the microchannels to make sure that all nanochannels are filled by capillary forces and afterwards flushing both channels. After flushing, the fluid reservoirs in the chip holder were filled with the desired solution and the liquid was allowed to equilibrate inside the microchannels in the absence of any pressure gradients. To monitor ion concentrations, 0.1 mM NaCl solutions containing an additional 5 μ M Alexa Fluor 488 Cadaverine were used. For the visualization of the flow fields, 0.05 wt% fluorescent polystyrene particles with a diameter of 1.0 μ m were

added to the solution.

Electric potential was applied by a Keithley 2450 Source Meter, controlled by an in-house built LabVIEW program. Silver electrodes were placed in all four fluidic reservoirs and a constant potential was applied to both electrodes connecting the upper microchannel while keeping the other two grounded, or vice versa. During these chronoamperometric measurements, resulting current and applied potential were recorded. Fixed potentials between 0 and 100 V were applied for all geometries. Due to the presence of the charge selective nanochannels the electric field lines are distorted with respect to the channels. We have confirmed this by a simple COMSOL Multiphysics model of type I chips, from which we illustrate how the electric field lines bend in the vicinity of the nanochannels. Movies were recorded using a Zeiss Axiocam 105 Color (for fluorescent dyes) and a Hamamatsu ORCA-Flash4.0 LT (for particle tracking) camera, mounted on an inverted Zeiss Axiovert 40 MAT microscope.

7.3 Results and discussion

Typical chronoamperometric responses of the different systems are shown in Figure 7.3. A fast decay of current as function of time is observed for all configurations of nanochannels. This indicates that the ions available for transport become depleted from the CSI and that there is a strongly reduced transport of charged species through the nanochannels as time proceeds. Usually *IV*-curves are reported, as opposed to chronoamperometric (*I* versus *t*) measurements [12, 15, 31, 33, 34]. When current as a function of time has been reported, researchers have observed similar decaying behaviour for current as function of time for a fixed applied voltage [7, 16]. The standard deviation (error bars) in measured current is in the order of $\sim 20\%$ relative standard deviation, which is in line with previous literature for nanochannels [35].

In our experimental system the electric field is distorted as a result of the presence of the CSI, yielding a growing resistance for ion transport as depletion zones are growing (as explained in the next section). An interesting note is the absence of an initial diffusive time scale, as electro-osmotic flows on the walls are present from the start of the measurements. The nanochannel conductivity and selectivity are extremely sensitive on their geometry. Due to the fabrication tolerance of our nanochannels, the quantitative electrical response for chips of the same type shows relatively large differences. However, the qualitative behaviour as shown in Figure 7.3 is found for all chips. On-chip reproducibility of the *IV* and *I-t* data was relatively good, with a relative error of 4%, 20% and 46% for the measurements under 100, 50 and 10 V respectively. The large error for the 10 V measurement is due to the relatively small currents ($\mathcal{O}(\text{nA})$). The

Figure 7.3 — Typical chronoamperometric response for nanochannel chips as function of applied electric field strength. These results were obtained by a type II (see Figure 7.2) chip. Current decays as a function of time, for all applied potentials. Error bars are based on SD for multiple runs.

fabrication tolerance of nanochannels is large as a result of the non-uniformity of the wet-etching process and cannot be measured quantitatively for all chips due to their small width. We measured the depth of a nanosized patch on different parts of the wafer before bonding, resulting in a difference in nanochannel depth of $\sim 50\%$ for different locations on the wafer. This results in a large deviation in area available for ion transport, which in turn yields large variations in the values of the measured currents if we compare different chips with the same geometry.

7.3.1 Electric field distribution

Due to the location of the driving electrodes, the local driving potential for the ion transport through the nanochannels is much smaller than the applied potential. The electric field lines are locally distorted yielding a non-normal electric field adjacent to the nanochannels. This is a result of the nature of microfluidic systems, in which there are relatively long channels, which usually have corners that distort the flow and electric field, as stated before [17, 27, 31]. Therefore, the electric field strength cannot be assumed to be constant over all nanochannels and can certainly not be assumed as equal to the applied electric field strength.

For confirmation of the proposed mechanism and the local electric fields, a simple quasi-3D model was built in COMSOL Multiphysics using the Electric Currents package. In Figure 7.4 the resulting local electric potential in both the

Figure 7.4 — Local electric potential inside the microchannels of type II chips with an applied potential of 50 V in the anodic reservoirs, modeled in COMSOL Multiphysics. Distance 0 μm is the position of the first nanochannel patch, in total seven patches are represented in this figure. The first five patch locations are indicated by the arrows.

anodic and cathodic channel is shown. Before reaching the CSI, the local electric potential has reduced dramatically, yielding a relatively small driving force for ion transport through the CSI. The potential drop in the microchannel is a result of the length of the channels before the CSI is reached. It can easily be observed that the driving potential for the first patch is higher than for the second patch, and so on. From the fifth patch, the driving potential becomes negligibly small. This simplified model supports our hypothesis that the length of the microchannels has a large influence on the distribution of the electric field, which in its turn has a dramatic effect on the transport of ions through the nanochannels and the performance of the CSI. Placing the electrodes much closer to the CSI would reduce this effect, as has been noted for simpler geometries [31]. These findings are also in line with the work of Green *et al.*, who demonstrated the importance of the microchannel resistance for simpler microchannel/nanochannel geometries [36].

7.3.2 Concentration profiling

To mimic the behaviour of ions, a charged fluorescent dye is added to the salt solution. In our case, we used the Alexa Fluor 488 Cadaverine (ex/em 490/525 nm), which has a negative charge and is *pH* independent in the measurement

Figure 7.5 — Intensity profiles of Alexa (negatively charged) for different chip geometries (geometry I (a), II (b) and III (c)) upon the application of a driving potential of 50 V. Both channels contain a 0.1 mM NaCl solution, seeded with 5 μM Alexa fluorescent dye, the positive potential is applied in the upper channel for all geometries. Low intensity zones can be observed adjacent to the nanochannels in the anodic channel, indicating that locally the salt concentration is low.

range ($4 < \text{pH} < 10$) [37]. Typical ion concentration profiles are presented in Figure 7.5 for the three different geometries under investigation. For geometry I, Figure(a), we observe a gradual growth of the ion depletion zone on the anodic side of the CSI, similar to the observations of Kim *et al.* [12] The size of the depletion zone grows as function of time. Growth speed increases with increasing electric field strength. From this figure, it can be observed that the zone does not grow equally fast in both directions, which we attribute to a difference in local electric field, which might be the result of electrode placement, a slight pressure difference in the two reservoirs or bubble formation during the experiment.

Results for type II chips are shown in Figure 7.5(b). The field of view contains the first arrays of nanochannels on the left side of the chip. Wave patterns of ion depletion are developing in the vicinity of the patches of nanochannels, and growing in time until the depleted zone spans the entire width of the microchannel. The waves are forming as a result of the preferential direction of the transport of ions near the nanochannels and the interplay with the electric field which bends towards the nanochannels. It can be observed that the depletion above the patch closest to the electrode is faster and more intense than depletion above the patches further from the driving electrodes. This is a result of the local driving potential, which is drastically reduced along the microchannel towards the patches of nanochannels, as was shown in the previous section. The behaviour observed is symmetric, as on the other end of the array of patches the same wave patterns are observed in a mirrored direction towards the other electrode (not shown in Figure 7.5(b), as a result of the limited field of view of our camera in comparison to the total geometry, but was visually observed to be symmetric). This results in a plug of ionic solution being trapped between two zones depleted of ions, where there is no driving force for ion transport due to the reduction of the electric field strength at this location in the chip.

For chips of type III, only one depletion wave was formed at each end of the CSI, see Figure 7.5(c). In this system, symmetric behaviour was also observed (again not shown due to the limited field of view of our camera), resulting in a trapped plug of ion containing solution above the CSI, which seems unaffected by the imposed electric field. This indicates that the potential drop is located over just a portion of the nanochannels and microchannel before the arrays, leaving most of the CSI unused in the transport of ions as there is no driving potential for the transport. We note that this is likely the result of the local perpendicular direction of the electric field, which can also occur in larger membrane systems as a result of a small perturbation in the membrane surface [5].

Figure 7.6 — Dye intensity profiles (that mimic the local ion concentration) above different patches as function of time, for applied potentials of 10 V (a), 50 V (b) and 100 V (c). Patch 1 is the first patch from the electrode (as indicated in Figure 7.2, patch 6 is the sixth. We averaged the dye intensity above the different patches as a function of time from different experimental runs to obtain these profiles.

Influence of nanochannel configuration

Using the type II chips, we see clear local differences in dye intensity and its decrease as function of time and applied voltage for the different patches of nanochannels. In Figure 7.6, the average intensity of the dye in the channel above three patches in the field of view is plotted as function of time for three different applied voltages. The patch closest to the driving electrode (patch 1, see numbering in Figure 7.2) shows the fastest decay in local intensity, while the patch furthest from the electrode (patch 6) shows a significantly slower decay of intensity. A clear difference can also be observed for the different applied potentials, showing that for an applied voltage of 10 V and 50 V, the patches further from the electrode are not completely depleted of dye at higher times. This reduced dye intensity indicates a lower local ion concentration above patches closer to the electrode, resulting in a higher local electric field strength. Similar behaviour is observed for chips of type III, in which a depletion zone is forming on both sides of the array of nanochannels, but a plug of ion containing solution is trapped above the center of the CSI.

In our system, the electric field lines are distorted significantly in the vicinity of the CSI, due the geometry of the microchips. As a result of this and the local concentration differences, the local electric field strength and the potential drop over the nanochannels is not constant for all patches. This results in a reduction of ion transport through the channels further away from the electrodes, as there is a smaller driving electric potential remaining for the charge transport at these channels. As a result, the local concentration above the patches in the center of the chip stays higher compared to the local concentration above the outer patches. Experimentally we observe that this effect is more pronounced for lower applied electric fields and that for higher applied electric fields a larger number of patches of show transportation of ions. For an applied voltage of 100 V, all patches in the field of view are depleted from dye, although further from the electrode dye is still present above the patches. The electric potential is reduced across all patches, showing that for a higher starting potential, more patches are affected by the electric field and play a role in ion transport. This can also explain the reduction in measured current, as was shown in Figure 7.3, which flattens out after the depletion zones have been fully established as there is a constant diffusive supply of ions towards the patches that are still influenced by the electric field.

pH effects

One of the possible mechanisms for overlimiting current is the formation of additional charge carriers, as a result of water splitting in the vicinity of the CSI [6]. This would yield protons and hydroxyl ions, which establish a *pH* gradient in the system. To test if a *pH* gradient near nanochannels is developed in the

Figure 7.7 — Pattern formation under the application of a 50V electric field type II chips, with Alexa (left), Fluorescein (middle) and Rhodamine B (right) as indicative dyes for ion concentration and pH gradients. Alexa and Fluorescein are negatively charged, while Rhodamine B is uncharged. Fluorescein and Rhodamine B are known to be pH dependent in the measurement range, while Alexa is pH independent. Similar wave patterns are formed for both negative dyes, while no changes are observed in the intensity of the Rhodamine B experiments. This is an indication that no significant pH effects are influencing our measurements at this scale.

system, we repeated the experiments with Fluorescein (495/517 nm), which is negatively charged and pH dependent and Rhodamine B (543/565 nm) which has no to a very slight charge, and is pH dependent in our measurement range. As can be observed from Figure 7.7, the quantitative behaviour of the Alexa and Fluorescein (both negatively charged) dye is similar, while for Rhodamine B (no charge) no gradients in intensity are observed. This indicates that the observed effects for the Alexa dye are a result of the negative charge of the fluorophore, and thus can serve as an indication of the local ion concentration. The Rhodamine B experiments did not show any alteration in intensity upon application of an electric field, which, together with the Fluorescein measurements can lead to the conclusion that there are no significant pH changes in the vicinity of the CSI in our system. This indicates that water splitting is not significantly occurring in this system, and no additional charge carriers are produced near the nanochannels under these conditions.

7.3.3 Fluid flow and vortex dynamics

To be able to follow the fluid flow profiles inside the microchannels, fluorescent particles are seeded in the feed solution. Movies in which the flow is clearly visualized for the three different geometries can be found online [38]. Typical frame rates for the capturing of the particle movement are between 100 and 150 fps, which at higher times and developed flow is too low for taking clear particle images. These frame rates are the highest possible for the system, as a result of light intensity required to maintain an acceptable image quality. This prohibits automated particle tracking or PIV, but particles can be tracked manually. In all

experiments no external pressure was applied, yielding negligible flows before the electric potential was applied.

For geometry I, we observe two fast developing vortices in the anodic channel upon the application of the electric potential of 50 V. The vortices grow into the channel at first instance, but are being pressed onto the microchannel bottom walls at later times, which can be observed from Movie 1 [38]. The size and speed of the vortices is growing as a function of time, just as the depletion zone was growing as function of time. Electro-osmotic instabilities (EOI) occur as a result of the extended space charge near the nanochannels (due to the concentration polarization) and the action of the non-uniform electric field on these regions [19]. The observed effect is an interplay between electro-osmotic flows near the walls, electro-osmotic instabilities in the vicinity of the nanochannel and dielectrophoretic/diffusiophoretic forces.

In chips of type II, vortices are observed in the anodic channel above several patches as can be observed in Movie 2 and Figure 7.8. Upon application of the electric field, Movie 2 shows the formation of vortices in the anodic channel above five patches under the application of a 50 V potential, where the right end of the nanochannel arrays is imaged, patch n-5 to patch n. The vortex on the n-th patch (closest to the electrode on the right side of the channel) shows the fastest development and the largest final speed and size. This vortex extends significantly in the channel towards the driving electrode, while the vortices on the other patches stay relatively small and adjacent to their nanochannel patch. The vortices that are formed show a suppression towards the lower microchannel wall, just as type I chips. In the cathodic channel, movement of particles towards the nanochannels is observed, where they are retained by size exclusion forming particle cakes on the microchannel wall. At the walls between the patches particle movement in the direction of the expected EOF for a negative glass surface is observed. The chip shows symmetric behaviour, as was the case for the concentration profiles, on the other side (above patch 1 to 5) also vortices have been observed directed towards the other electrode. Vortex speeds and sizes grow as a function of time and applied voltage.

This is also true for the observations in experiments with type III chips, in which a single vortex is growing on each end of the CSI in the anodic channel (see Movie 3 [38] for one side of the CSI). More generally, these experiments indicate that a (small) distortion of the electric field and the magnitude of the residual field strength in membrane systems has a high influence on the efficiency of the membrane. A small distortion in this field can result in reduced capacity of the total membrane as part of the membrane is not contributing to the transport of ions.

The total fluid movement in the different geometries is a result of different forces acting on the ions, particles and liquid present in the system. EOF is present

Figure 7.8 — Fluid flow development over time for type II chips. Only patch 1 and 2 are in the field of view. vortices are observed above the different patches, and are growing in speed and size as a function of time. Regions of electro-osmotic flow (EOF) and electro-osmotic instabilities (EOI) are indicated.

in both the anodic and cathodic channel, but is countered by different induced flows in both channels. In the anodic channel, the EOF becomes negligibly small in comparison to the flow as a result of the local non-electroneutrality in the depletion zones. We observe no net flow in the expected direction of EOF in the anodic channel in our experiments. In the cathodic channel, the EOF is countered by the electrophoretic (EP) mobility of the particles and ions inside the flow. Flow in the direction of the EOF was experimentally observed near the channel walls, but in the center of the channel the flow is dominated by the EP flow, as can be observed from the movies [38].

Quantification of observed flows

As stated, the detailed analysis of the obtained particle tracking images is done manually. Images were loaded into MATLAB and particles were tracked by identifying one and following it over multiple (up to 1000) frames to get local velocities inside and outside the vortices. We track particle clusters, as these can be unambiguously identified in every frame because of their characteristic larger size than single particles. We should note that we can only measure the velocity in the x and y-plane, and not the velocity in the z-direction. Hence, we only report the speed, which is defined as $s = \sqrt{\Delta x^2 + \Delta y^2} / \Delta t$. The reported speed can be considered as a slight underestimation of the actual particle speed, since the z-component is neglected.

Anodic channel. In type I chips, two vortices are formed, which are confined towards the lower microchannel wall and span approximately half of the microchannel width. The speed measured in these vortices is increasing with increasing electric field and time from application of this field. Maximum speeds inside the vortices are $\sim 600 \mu\text{m/s}$, $\sim 900 \mu\text{m/s}$ and $\sim 1000 \mu\text{m/s}$ for applied electric fields of 20, 40 and 50V respectively. These speeds are much larger than the flow speeds that would arise as a result of pure Smoluchowski EOF and similar to estimates by Kim *et al.* [12] Inside the vortices the flow is not dominated by EOF, but by EOI.

For type II chips, the vortex speed for the vortex closest to the driving electrodes is measured to be $\sim 500 \mu\text{m/s}$ for a 10 V potential difference and $\sim 1500 \mu\text{m/s}$ for 50 V. The second patch has a significantly lower vortex speed, around $\sim 600 \mu\text{m/s}$ for an applied voltage of 50 V. The speed decreased for the patches further from the electrode, as can also be observed in Movie 2 [38]. This again indicates that the patches further from the electrode are not contributing as much in the phenomena taking place as the patches closest to the electrode. The absence of vortices above patches in the center of the microfluidic device also indicate that no significant transport is taking place there and thus that the entire CSI is not used optimally.

Flow speed in the channel above the suppressed vortices (in type II chips) is also dependent on the distance from the electrode. Particles are accelerated significantly as they cross the vortices from subsequent patches towards the driving electrodes. The measured speed of the fluid above the vortex on patch 3 is $\sim 150 \mu\text{m/s}$, above patch 2 this speeds up to $\sim 575 \mu\text{m/s}$ and from the first patch on towards the electrode the speed is increased to $\sim 1125 \mu\text{m/s}$. The speed of the flow on the anodic upper channel wall which is not covered by the vortex, is measured to be $\sim 200 \mu\text{m/s}$, also in the direction of the driving electrode. The flow in the anodic channel opposes the expected direction of EOF in the channel, indicating that the EOF is negligibly small in the anodic channel as a result of electrostatic forces on the extended space charge and to a lesser extent electrophoretic forces in this channel.

Cathodic channel. The flow profile in the cathodic channel shows typical behaviour of EOF in combination with EP. The speed on the channel walls is directed towards the grounded electrodes, in the expected direction for EOF, while the flow in the center of the channel is directed away from the electrode and towards the CSI, in the expected direction for EP.

The speed of the flow on the side wall was measured to be $\sim 120 \mu\text{m/s}$ in the direction of the EOF before the first patch for an applied electric potential of 50 V. Between the patches the speed on the wall is $\sim 50 \mu\text{m/s}$. These speeds significantly reduce when the vortices are at full speed in the anodic channel. The speed in the center of the channel was measured to be $\sim 200 \mu\text{m/s}$, in the direction opposing the EOF before the first patch, reducing to $\sim 80 \mu\text{m/s}$ after the second patch. This speed decreased with increasing distance from the electrode.

The maximum EOF was calculated, using the Smoluchowski equation, to be $\sim 400 \mu\text{m/s}$, using a ζ -potential of -30 mV [39] and an electric field strength of 20 kV/m (which is the maximum applied field strength). The electrophoretic mobility of particles with a relatively small electric double layer can be calculated using Hückel's equation [32], $\mu = \zeta\epsilon/(6\pi\eta)$, which in combination with electric field strength of 20 kV/m gives a predicted EP velocity of the particles of $\sim 37 - 55 \mu\text{m/s}$ if we assume the ζ -potential of the particles to be between -75 and -50 mV [28, 40]. If EOF would only be countered by EP, the net direction of the particles would still be towards the electrodes, which is not observed experimentally. However, due to the symmetry of the chips and continuity, we expect a pressure-driven flow in the direction opposing the EOF on the walls [41], which adds to the movement of fluid towards the nanochannel patches. We attribute the observed particle speed in the center of the channel to a combination of EP and EOF driven flows, resulting in a velocity that is higher than the single EOF and EP velocities. On the walls, the EOF, in the direction of the electrodes, is countered by the EP of the particles towards the nanochannels, which yield an experimental underestimation of the pure EOF on the wall. The orders of

magnitude for these predicted flows are comparable to the orders of magnitude that we measured experimentally.

7.4 Conclusion

In this chapter, we have shown that the local electric field strength inside a microchannel has a large influence on the efficiency of charge selective interfaces between these channels. Due to the nature of most microfluidic systems, the electric field is not necessarily distributed normally with respect to the CSI, yielding strong localized potential gradients and concentration gradients. The resulting electrokinetic instabilities are largely influenced by the drop in field strength with increasing distance from the electrodes. Results show that much of the membrane in our microchannel/nanochannel array system is not used efficiently, due to a combination of local distortions in the electric field as well as significant potential drop in the microchannel. These local distortions in the field and relatively large distance of the electrodes to the CSI are potential pitfalls inherent to microfluidic devices that should be considered when interpreting results. Small distortions yield a tangential wall component of the electric field to arise, resulting in different directions of EOF in the system. Large differences arise in fluid velocities above the different patches, the fastest vortices are observed closer to the electrodes. For macroscopic membrane systems, these problems may be less pronounced but distortions in the applied electric field could potentially have a strong influence on the membrane performance.

In the investigated nanochannel systems, local pH changes near the nanochannel entrances have not been observed which indicates that the vortex mechanism is entirely based on salt exclusion from the nanochannel arrays. Fluid movement is observed adjacent to the CSI in a limiting current regime in the depletion zones forming above the membrane. Flow speeds of $\mathcal{O}(\text{mm/s})$ have been observed, both in vortices and the flows adjacent to the developing vortices. Large differences in the vortex speed and dynamics were observed between the various geometries, further stressing the importance of the interplay of geometry and electrokinetic effects at the micro-scale.

References

- [1] B. E. Logan and M. Elimelech, *Membrane-based processes for sustainable power generation using water*, *Nature* **488**, 313 (2012).
- [2] M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas, and A. M. Mayes, *Science and technology for water purification in the coming decades*, *Nature* **452**, 301 (2008).

- [3] Z. Jia, B. Wang, S. Song, and Y. Fan, *Blue energy: Current technologies for sustainable power generation from water salinity gradient*, Renewable Sustainable Energy Rev. **31**, 91 (2014).
- [4] T. A. Zangle, A. Mani, and J. G. Santiago, *Theory and experiments of concentration polarization and ion focusing at microchannel and nanochannel interfaces*, Chem. Soc. Rev. **39**, 1014 (2010).
- [5] I. Rubinstein and B. Zaltzman, *Electro-osmotically induced convection at a permselective membrane*, Phys. Rev. E **62**, 2238 (2000).
- [6] V. V. Nikonenko, A. V. Kovalenko, M. K. Urtenov, N. D. Pismenskaya, J. Han, P. Sistat, and G. Pourcelly, *Desalination at overlimiting currents: State-of-the-art and perspectives*, Desalination **342**, 85 (2014).
- [7] S. M. Rubinstein, G. Manukyan, A. Staicu, I. Rubinstein, B. Zaltzman, R. G. H. Lammertink, F. Mugele, and M. Wessling, *Direct observation of a nonequilibrium electro-osmotic instability*, Phys. Rev. Lett. **101**, 236101 (2008).
- [8] H.-C. Chang, G. Yossifon, and E. A. Demekhin, *Nanoscale Electrokinetics and Microvortices: How Microhydrodynamics Affects Nanofluidic Ion Flux in Annu. Rev. Fluid Mech.*, edited by S. H. Davis and P. Moin (2012), Vol. 44, pp. 401–426.
- [9] S. J. Kim, Y.-A. Song, and J. Han, *Nanofluidic concentration devices for biomolecules utilizing ion concentration polarization: theory, fabrication, and applications*, Chem. Soc. Rev. **39**, 912 (2010).
- [10] S. J. Kim, S. H. Ko, K. H. Kang, and J. Han, *Direct seawater desalination by ion concentration polarization*, Nat. Nanotechnol. **5**, 297 (2010).
- [11] R. Kwak, V. S. Pham, K. M. Lim, and J. Han, *Shear flow of an electrically charged fluid by ion concentration polarization: Scaling laws for electroconvective vortices*, Phys. Rev. Lett. **110**, 114501 (2013).
- [12] S. J. Kim, Y.-C. Wang, J. H. Lee, H. Jang, and J. Han, *Concentration polarization and nonlinear electrokinetic flow near a nanofluidic channel*, Phys. Rev. Lett. **99**, 044501 (2007).
- [13] Q. Yu and Z. Silber-Li, *Measurements of the ion-depletion zone evolution in a micro/nano-channel*, Microfluid. Nanofluid. **11**, 623 (2011).
- [14] C.-C. Chang, C.-P. Yeh, and R.-J. Yang, *Ion concentration polarization near microchannel-nanochannel interfaces: Effect of pH value*, Electrophoresis **33**, 758 (2012).
- [15] G. Yossifon and H.-C. Chang, *Changing nanoslot ion flux with a dynamic nanocolloid ion-selective filter: Secondary overlimiting currents due to nanocolloid-nanoslot interaction*, Phys. Rev. E **81**, 066317 (2010).
- [16] R. Kwak, G. Guan, W. K. Peng, and J. Han, *Microscale electrodialysis: Concentration profiling and vortex visualization*, Desalination **308**, 138 (2013).
- [17] S. J. Kim, L. D. Li, and J. Han, *Amplified electrokinetic response by concen-*

- tration polarization near nanofluidic channel*, *Langmuir* **25**, 7759 (2009).
- [18] S. J. Kim, S. H. Ko, R. Kwak, J. D. Posner, K. H. Kang, and J. Han, *Multi-vortical flow inducing electrokinetic instability in ion concentration polarization layer*, *Nanoscale* **4**, 7406 (2012).
 - [19] E. V. Dydek, B. Zaltzman, I. Rubinstein, D. S. Deng, A. Mani, and M. Z. Bazant, *Overlimiting current in a microchannel*, *Phys. Rev. Lett.* **107**, 236101 (2011).
 - [20] C. L. Druzgalski, M. B. Andersen, and A. Mani, *Direct numerical simulation of electroconvective instability and hydrodynamic chaos near an ion-selective surface*, *Phys. Fluids* **25**, 110804 (2013).
 - [21] M. Z. Bazant and T. M. Squires, *Induced-charge electrokinetic phenomena*, *Curr. Opin. Colloid Interface Sci.* **15**, 203 (2010).
 - [22] J. C. de Valena, R. M. Wagterveld, R. G. H. Lammertink, and P. A. Tsai, *Dynamics of microvortices induced by ion concentration polarization*, *Phys. Rev. E* **92**, 031003 (2015).
 - [23] Y. Green and G. Yossifon, *Dynamical trapping of colloids at the stagnation points of electro-osmotic vortices of the second kind*, *Phys. Rev. E* **87**, 033005 (2013).
 - [24] S. Hanasoge and F. J. Diez, *Vortex chain formation in regions of ion concentration polarization*, *Lab Chip* **15**, 3549 (2015).
 - [25] S. M. Davidson, M. Wessling, and A. Mani, *On the dynamical regimes of pattern-accelerated electroconvection*, *Sci. Rep.* **6**, 22505 (2016).
 - [26] P.-H. Chiu, C.-C. Chang, and R.-J. Yang, *Electrokinetic micromixing of charged and non-charged samples near nano-microchannel junction*, *Microfluid. Nanofluid.* **14**, 839 (2013).
 - [27] S. Yu, T.-J. Jeon, and S. M. Kim, *Active micromixer using electrokinetic effects in the micro/nanochannel junction*, *Chem. Eng. J.* **197**, 289 (2012).
 - [28] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal dispersions* (Cambridge University Press, Cambridge; New York, 1989).
 - [29] I. Rubinstein and L. Shtilman, *Voltage against current curves of cation exchange membranes*, *J. Chem. Soc. Faraday Trans. 2* **75**, 231 (1979).
 - [30] S. S. Dukhin, *Electrokinetic phenomena of the second kind and their applications*, *Adv. Colloid Interface Sci.* **35**, 173 (1991).
 - [31] G. Yossifon, P. Mushenheim, Y.-C. Chang, and H.-C. Chang, *Eliminating the limiting-current phenomenon by geometric field focusing into nanopores and nanoslots*, *Phys. Rev. E* **81**, 046301 (2010).
 - [32] C. J. van Oss, *Interfacial forces aqueous media, second ed.* (CRC Press, 2006), pp. 51–69.
 - [33] I. Cho, G. Y. Sung, and S. J. Kim, *Overlimiting current through ion concentration polarization layer: hydrodynamic convection effects*, *Nanoscale* **6**, 4620 (2014).

- [34] S. J. Kim and J. Han, *Self-sealed vertical polymeric nanoporous-junctions for high-throughput nanofluidic applications*, Anal. Chem. **80**, 3507 (2008).
- [35] S. Nam, I. Cho, J. Heo, G. Lim, M. Z. Bazant, D. J. Moon, G. Y. Sung, and S. J. Kim, *Experimental verification of overlimiting current by surface conduction and electro-osmotic flow in microchannels*, Phys. Rev. Lett. **114**, 114501 (2015).
- [36] Y. Green, R. Eshel, S. Park, and G. Yossifon, *Interplay between nanochannel and microchannel resistances*, Nano Lett. **6**, 2744 (2016).
- [37] N. Panchuk-Voloshina, R. P. Haugland, J. Bishop-Stewart, M. K. Bhargat, P. J. Millard, F. Mao, W. Y. Leung, and R. P. Haugland, *Alexa dyes, a series of new fluorescent dyes that yield exceptionally bright, photostable conjugates*, J. Histochem. Cytochem. **47**, 1179 (1999).
- [38] A. M. Benneker, J. A. Wood, P. A. Tsai, and R. G. H. Lammertink, *Supplementary information: Observation and experimental investigation of confinement effects on ion transport and electrokinetic flows at the microscale*, doi:10.1038/srep37236 .
- [39] Y. Gu and D. Li, *The ζ -potential of glass surface in contact with aqueous solutions*, J. Colloid Interface Sci. **226**, 328 (2000).
- [40] B. R. Midmore and R. J. Hunter, *The effect of electrolyte concentration and co-ion type on the zeta-potential of polystyrene lattices*, J. Colloid Interface Sci. **122**, 521 (1988).
- [41] R. G. H. Lammertink, S. Schlautmann, G. A. J. Besselink, and R. B. M. Schasfoort, *Recirculation of nanoliter volumes within microfluidic channels*, Anal. Chem. **76**, 3018 (2004).

Appendix

Chip fabrication

For the fabrication of the chips used in the experiments we cleaned glass wafers in HNO_3 before priming them with HMDS. To be able to align the nanochannels with the microchannels, we first etched alignment marks on the blank wafers before etching the nanochannels. Standard photolithography was applied for the marks, and the backside of the wafer was protected with foil before glass etching in BHF for 8 minutes. After stripping of the resist wafers were cleaned in HNO_3 again before applying the photolithography for the nanochannels. Nanochannels were etched for 30 seconds in BHF, after which the resist was stripped and the dimensions of the nanochannels were measured using a White Light Interferometer (Bruker WLI Gontour GT-I). After cleaning the wafers in HNO_3 again and drying them on a hot plate of 150 °C immediately a chrome (15 nm) and gold (150 nm) layer was sputtered on the wafers. This layer prevents further etching of the nanochannels in the further process steps. After sputtering, immediately photolithography for the microchannels is applied on the wafer. Gold and chrome are removed from the microchannel locations using dedicated etchants and backside foil is applied again before glass etching. In a 25% BHF solution the microchannels are etched into the glass until they are 20 μm deep, which is indicated by size indicators elsewhere on the wafer. For the powder blasting of via-holes a photosensitive foil is applied on the backside of the wafer. Access holes are aligned and the foil is developed after which holes can be powder blasted. The foil is removed in a solution of CaCO_3 , placed in an ultrasonic bath. The wafer is completely cleaned and particles are removed in an ultrasonic bath using acetone. The sacrificial chrome-gold layer is removed using the dedicated etchant and the wafer is cleaned before pre-bonding it to a cleaned glass wafer. The wafers are thermally bonded overnight before they are diced.

Reflections and perspectives

*People generally see what they look for,
and hear what they listen for.*

- Harper Lee
To kill a Mockingbird (1960)

This thesis describes research on ion transport at different charge selective interfaces and on different length scales. The work combines numerical and experimental investigations of charge transport through and near ion selective interfaces, primarily for electrodialysis applications. In electrodialysis, ion transport limitations in the boundary layer determine the operational range of the process. Different approaches to reduce and understand the factors that influence these transport limitations have been investigated, by altering temperature and applying temperature gradients and changing the membrane geometry. The experimental and numerical results presented in this thesis have implications for research in (amongst others) the fields of membrane technology, fuel cells and microfluidics. The outcome of this research relates to possible long-term applications in industrial electrodialysis processes, or other chemical processes which rely on charge transport in which the enhancement of charge transport can be established using imposed temperature differences or differences in system topology.

Reflections

The influence of temperature

Numerical modeling of a non-isothermal formulation of the Poisson-Nernst-Planck and Navier-Stokes equations was done to study the effect of temperature (gradients) on ion transport through charge selective nanochannels (*Chapter 2*). The influence of the direction of temperature and electric potential gradients on the charge transport was investigated for both symmetric and asymmetric nanochannels. We found that the selectivity of symmetric nanochannels can be enhanced by applying a temperature gradient in the direction opposite to the charge transport, so that the depleted reservoir has a higher temperature. In this way, the ions that are selectively transported through the nanochannel have a higher diffusivity on the depleted side, while the ions that are ideally blocked by the channel have a relatively low diffusivity on the enriched side, since diffusivity scales with temperature. This results in enhanced transport of ions on the depleted side when compared to the enriched side. For asymmetric nanochannels, applying a temperature gradient along the electric field and along the asymmetry direction of the nanochannel enhances the selectivity of the channels even further, while a temperature gradient countering the electric field reduces the selectivity of the nanochannel. To avoid complications of the variation of ζ -potential with temperature, we assumed gated walls and therefore constant wall potentials. In most membrane systems, the ζ -potential or surface charge density will however be dependent on the temperature [1, 2], and it is therefore of interest to investigate the influence of temperature gradients on nanochannel systems with a ζ -potential

that is temperature dependent. Preliminary numerical investigations showed that over the temperature range applied here, changes in ζ -potential did not show any large changes in the overall behaviour of the system.

These numerical results motivated experiments on lab-scale electrodialysis systems in which a temperature gradient was imposed. First, experiments were conducted in the, industrially most relevant, Ohmic regime using an electrodialysis stack containing commercial cation and anion exchange membranes (*Chapter 3*). The influence of temperature and temperature gradients on both electrodialysis and reverse electrodialysis were investigated. As a result of measuring in the Ohmic regime (in which the diffusion boundary layer is not limiting the ion transport) and due to heat transfer within the system and to the surroundings, no significant differences in charge transport are measured for the two different directions of the temperature gradient. However, the power required for electrodialysis is reduced by 9% if one of the feed streams is heated from 20 °C to 40 °C, while the total reduction in required power is 15% if both feed streams are heated to 40 °C. The increased temperature did not have a negative influence on the selectivity of the charge transport. For reverse electrodialysis, the obtainable gross power density was increased by 25% when one of the feed streams was heated by 20 °C. No significant difference was found when changing the direction of the temperature gradient. When heating both feed streams from 20 °C to 40 °C, the gross power density was increased by 38%. These results indicate the possible application of low grade waste heat from industrial processes to enhance the ion transport in electrodialysis processes. Since the heat required for increasing the feed temperature is much larger than the gained power, using any other heat source than waste heat is not feasible.

Theoretically, the temperature gradients should have a larger impact on systems that are operated in the limiting current regime. In this regime the ion transport is limited by diffusive transport of ions through a depletion boundary layer that is developed at the diluted side of the charge selective interface. Temperature has a large influence on the diffusivity of ions, and thus an increased temperature should enhance the ion transport, most notably when the dilute stream is heated. This was experimentally investigated using a lab-scale, commercially available electrodialysis stack (*Chapter 4*). In contrast to the measurements in the Ohmic regime, there was a significant difference in ion transport when the direction of the temperature gradient was changed. It was found that when heating the dilute stream from 5 °C to 25 °C, the ion transport was enhanced by 2 to 6% when compared to heating the concentrate stream, as the resistivity of the stream is decreased with increasing temperature. In the measurements in the Ohmic regime, this decrease in resistivity of the dilute stream was of smaller influence. The total power consumption to obtain the same degree of desalination is thus reduced when heating the dilute stream. Heating both streams by 20 °C enhanced the ion

transport even further, as was the case for the experiments in the Ohmic regime. More interestingly, the selective transport of divalent over monovalent cations was enhanced as a result of this temperature gradient. This can be of use in the separation of divalent ions (for instance Mg^{2+} and Ca^{2+}) from sea water, as they impose scaling and precipitation problems in water treatment plants.

In both of these experimental investigations, heat transfer between the two different streams was significant, reducing the theoretical effect of the temperature gradient. Different, thicker, membranes that have lower thermal conductivity such as RALEX® could be of use to reduce the heat transfer in the system, although these would have a slightly higher electrical resistance which can possibly reduce the total current. However, since the resistance of the membrane is typically much lower than the resistance in the solution, this increase in resistance may be negligible.

To gain a more fundamental understanding, investigation of the influence of temperature differences in microfluidic ion transport systems is of interest as well. In these systems, it is important that temperature can locally be controlled and measured. In the experiments conducted in this work, the local temperature gradients were not controlled and heat transfer between the hot and cold stream was large, since at the outlet of the stack the temperature of both streams was similar. Local temperature differences in smaller systems can be established using Peltier elements [3–5], that can either heat or cool a certain part of the system. Local temperature can be measured using temperature sensitive dyes by either fluorescence microscopy or fluorescent lifetime imaging [6, 7] and is of interest in combination with the imaging of local ion concentrations.

Another, much simpler, experiment to investigate the influence of temperature on the charge transport would be the connection of two macro-scale reservoirs by a charged capillary at salt concentrations where there is Debye layer overlap inside the capillary. The temperature of the macro-scale reservoirs can be controlled relatively easy and as the reservoirs are not directly connected, the heat transfer between the reservoirs is minimized. Additionally, the reservoirs can be thermally insulated and the capillary as well as if optical access is not required. For macroscopic investigation of the total current through the capillary, electrodes can be placed in the reservoirs for applying and recording of potential and current as a function of temperature gradients.

The influence of geometry

The detailed experimental investigation of electroconvection at the interface benefits from optical access to the microscopic boundary layer adjacent to a charge selective interface. To this end, microfluidic devices are used. A microfluidic device containing an alternating series of patterned, charged hydrogels was developed to mimic the behaviour of an electrodialysis stack (*Chapter 5*). The

permselectivity and resistance of the hydrogels are measured using conventional membrane characterization techniques. In terms of membrane performance, the hydrogels have poor characteristics compared to conventional cation and anion exchange membranes, as the charge density is low as a result of the high water content of the hydrogels. Swelling increases the interstitial volume between the charged groups, reducing the permselectivity of the hydrogels and makes application for desalination unfeasible except for very low salt concentrations (~ 1 mM and lower). This system is a versatile platform for the investigation of charge transport at selective interfaces, since the fabrication method allows for a wide range of hydrogel geometries to be investigated. Our microfluidic device is able to desalinate low concentration feed streams (up to 1 mM) to a desalination degree of 75%. Increasing the charge density of the hydrogels by adding a larger amount of charged groups to the structure would theoretically enable desalination of feed streams with higher concentration, but also yields additional problems in terms of hydrogel swelling. This is a common problem for microfluidic systems with membranes, for instance Nafion based chips have adhesion and swelling problems as well. By adding a negatively charged fluorescent molecule to the solution, ion depletion zones can be observed. Electroconvective vortices are developing at the hydrogel interfaces, especially at high voltages. These devices provide a highly versatile platform for the investigation of ion transport near and through the charge selective interface.

Using this microfluidic platform, the influence of geometry on ion transport was investigated. Three different hydrogel geometries were tested to investigate the influence of surface heterogeneities on the development of ion depletion zones and vorticity (*Chapter 6*). Ion concentration profiles are qualitatively investigated using a negatively charged fluorescent dye, while for the quantification of the Cl^- concentration the fluorescence lifetime of a chloride sensitive dye is measured. Surface heterogeneities were found to induce an electro-osmotic contribution to the ion transport, as a result of the non-uniform electric field that is induced by the local conductivity and permittivity changes in the system. This electro-osmotic contribution to the charge transport towards the interface results in higher currents for systems with a surface heterogeneity, which is interesting for the application in industrial electrodialysis systems as it implies that geometric structuring alone can be useful for increasing the effective conductivity in the Ohmic regime. This shifts the onset of the limiting current regime to higher field strengths and shortens the plateau length in the characteristic IV-curve. To increase the understanding of the influence of the distorted field lines on the charge transport, an additional geometry in which heterogeneous hydrogels are present is of high interest. In this geometry, shown in Figure 7.9(b), the alternating hydrogel patches would be shifted with respect to each other. In this way more electric field lines have a tangential component, as can be seen from the potential

Figure 7.9 — (a) One microfluidic channel from the heterogeneous hydrogel chip configuration used in this work (*Chapter 6*), in which the cation and anion exchange hydrogels (indicated in respectively red and green) are aligned. The electric field on the right is solved using the Poisson equation in COMSOL Multiphysics (b) New geometry for the hydrogel chips, in which the location of the hydrogels is shifted with respect to each other. In this configuration, the tangential components of the electric field are larger (see potential distribution and field lines on the right) and thus a larger contribution of electro-osmotic flow to the total charge transport is expected.

distributions (simulated with COMSOL Multiphysics) on the right of the figure. These tangential components of the electric field will act on the charged interface of the hydrogels and the PDMS walls, which can generate electro-osmotic flow contributions to the ion transport already from the Ohmic regime.

Charge selective nanochannels are used for the investigation of the development of electrokinetic flows in the vicinity of a membrane, in which a non-normal electric field is applied (*Chapter 7*). Nanochannels with a characteristic length of 20 nm are connecting two microchannels with dimensions of $70 \times 20 \mu\text{m}$. Particles are added to the solution to track the development of electro-osmotic flows and electrokinetic instabilities. The influence of the geometry in combination with the applied electric field is shown to be significant. Microfluidic vortices with speeds over 1.5 mm/s are experimentally found to arise in the ion depletion zones adjacent to the nanochannel interface. These speeds are significantly higher than the expected velocities for pure electro-osmotic flow, which are in the order of $400 \mu\text{m/s}$ and indicate the presence of electrokinetic instabilities at the nanochannels. The development of the vortex size, speed and flow speed inside the channel are dependent on the geometry of the charge selective interface and the distance from the driving electrodes. In our nanochannel systems, the electric field is not normal with respect to the charge selective interface as a result of the microchannel

configuration. In most numerical approaches, the field is initially directed normal to the interface [8–11]. To be able to compare experimental systems with widely available numerical simulations, a different chip design in which the electric field is normal to the charge selective interface would be desired.

All visualization and analysis of the development of hydrodynamic vortices were done without the application of cross flow, while in actual ED systems cross flow is always present. This motivates experiments with an imposed cross flow adjacent to the charge selective interface, although experimental difficulties, such as bubbles forming at the electrode that are then transported through the microfluidic channels, are a challenge that should be sufficiently tackled.

The results of these investigations on the influence of geometry on charge transport (*Chapter 5 - 7*) pique curiosity and motivate additional experimental and numerical investigations on similar systems. As was previously indicated, the investigation of the influence of geometry on the charge transport is of high interest, as this might yield more efficient charge transport, resulting from the additional electro-osmotic transport of ions [8, 12–14]. Both numerical investigations of charge transport in heterogeneous systems, as experimental verification of the concepts are of importance to enhance the understanding of the interplay between electric field, charge selective interface and non-conducting regions.

Experimental techniques

Quantification of local ion concentrations inside the charge selective material would be of interest for the understanding of the coupling of the transport in the solution with the transport inside the membrane. Our hydrogel platform provides both optical access to the charge selective material and the solution and would thus be suitable to study the influence of transport in the membrane on the ion transport outside of the membrane.

As the systems under investigation are typically non-steady, fast developing processes, conventional techniques for the tracking of flow fields such as μ -PIV [15] are not suitable [16]. In μ -PIV, a velocity is measured based on a number of image pairs, as the concentration of tracer particles is limited by the required optical transparency of the solution. To resolve the total velocity field, multiple images are required, which greatly reduces the time resolution of the technique. Therefore, different particle tracking algorithms are of use for the study of the development of electrokinetic flows and vortices at the micro-scale. Rigorous algorithms for the analysis of the measured particle locations are not widely available [16], but are of interest for the measurement of electrokinetic flows as observed in the experiments in this work.

FLIM (used in *Chapter 6*) is a promising technique for the quantification of local concentration, temperature and *pH* [17], but also suffers from a poor frame rate and spatial resolution with respect to the dynamics of the phenomena under

investigation [18, 19]. An improved frame rate can be obtained using optical delay of the obtained images [20], but this technique is non-trivial and not widely available. It is however very interesting to use a pH sensitive dye for the tracking of water splitting in and around the charge selective interface. If a dye sensitive to ion concentration at concentrations in the range of the charge density of the hydrogel would be developed, this would yield the possibility to track the ion concentration (as a function of location, and possibly time) inside the charge selective interface and match this with the known descriptions of ion distribution in membranes.

Different charge selective interfaces

In the experiments described in this work, three different types of charge selective materials were utilized, namely (*i*) commercial, dense polymeric membranes, (*ii*) *in-situ* patterned charged polymeric hydrogels and (*iii*) cation selective nanochannels. All of these materials have their own advantages and drawbacks in the microfluidic investigation of the formation of ion depletion zones and hydrodynamics.

The use of commercial membranes in microfluidic systems is challenging as the fabrication of leak-free systems with an incorporated polymeric membrane that also provide optical access to the membrane interface is non-trivial [21]. Hydrogels that are patterned after sealing the device are less prone to leakage, however the bonding between device and hydrogels can be enhanced as well [22]. Drawbacks of using hydrogels are the relatively poor membrane characteristics and the ability of charged particles to transport through the hydrogel structure, which inhibits the efficient use of particles for particle fluid tracking in these systems. In systems using etched nanochannels, the typical total currents that are measured are small, as a result of the small cross sectional dimensions of the nanochannels. This requires the use of highly sensitive measuring equipment and shielding of the system to outside disturbances, which is impractical providing that optical access to the system is required for the investigations.

Therefore, the use of other types of charge selective interfaces in microfluidic systems is of interest. Colloidal crystals [23] consist of nanoparticles that are assembled to form a crystalline structure. The interstitial space between these nanoparticles can be on the nanometer length scale, such that a network of nano-sized pores is formed within the colloidal crystal. The formation of these crystals can be by self-assembly [24, 25], template-assisted assembly [26] or external field assisted assembly (either by a gravity, temperature, electric or magnetic field) [27–29]. Using different particle sizes, the size of the interstitial space can be controlled and tuned, yielding charge selective interfaces with different characteristic length scales. Such a system was previously developed [30], in which capillary forces are used to ensure *in-situ* assembly on the desired location. By using electric

Figure 7.10 — SEM images of a nanoporous structure fabricated using a direct laser writing technique in photoresist on a glass slide. Preliminary fabrication of these structures was conducted using a Nanoscribe Photonic Professional DLW system in the *MESA+* Cleanroom at the University of Twente.

fields to assist the assembly of nanoparticles, an enhanced control over the formed structures can be obtained. Using a liquid depositing system to directly place the colloidal suspension on the desired location in a non-bonded chip is another option to control the formation of the crystals. Crack and defect free fabrication of these colloidal crystals is challenging but important since microscopic defects result in the loss of charge selectivity of these colloidal crystals. However, intentionally imposing defects to the structure can be a mimic of leaky membranes [31], which is of interest for experimental investigations as well.

Another option for the fabrication of a nanostructured material is the *in-situ* polymerization of a photosensitive material using mask-less photolithography [32]. Two-photon polymerization is used to write a pre-defined structure into a low viscosity photoresist by direct laser writing (DLW). Preliminary experiments using a Photonic Professional DLW system (Nanoscribe, Germany) yielded promising results for the fabrication of nanoporous structures within fluidic devices. In this system, the sample is moved on a programmable positioning system which is mounted on an inverted Zeiss Axiovert microscope with an auto-focus/interface finding system. The resolution of this method is dependent on the numerical aperture of the objective used in the DLW procedure [32].

Using this method different designs of nanoporous structures can be made. A result of such a structure on a microscope slide is shown in Figure 7.10. By polymerizing directly from the glass surface, the structure is fixed to the location on the glass slide. In preliminary tests of writing these structures inside microfluidic channels we were able to fabricate these structures as well, but development

of the photoresist and removal of non-polymerized resist remains a challenge. However, the development of these structures in chip has been demonstrated in different chip materials such as silicon, glass and PDMS based chips [32–34]. The versatility of both chip and structure design with this method opens up a range of possibilities for the investigation of the effects of membrane structure and flow confinement on charge transport.

A third, also promising range of materials are nanoporous materials such as anodized alumina [35, 36], ZIFs and MOFs [37, 38] or porous silicon [39–41]. Porous silicon can be fabricated in a microfluidic chip using an anodization technique developed at the University of Twente [42]. Porous silicon is formed on a highly doped p-type silicon wafer with (100) orientation, that are covered with a silicon rich silicon nitride (SiRN) layer. The SiRN layer is required to have a unidirectional growth of the porous silicon in the desired direction. After etching microchannels into the wafer, the porous silicon can be formed in the layer between the microchannels. The wafer is anodized in an aqueous hydrogen fluoride solution, using a platinum counter electrode. This anodization results in the formation of nanopores in the structures that are etched in the silicon wafer [42]. If the etching process is sufficiently long, the pores from both sides of the structure are interconnecting, yielding a highly nanoporous material between the etched microchannels. This material is charge selective as a result of the surface charge of the silicon, and the small characteristic size of the pores, as was the case for the etched nanochannels. An advantage of using this porous silicon is the high surface area of this porous material, and thus the high expected ionic currents through these materials when compared to single nanochannels. The fabrication method allows for different interface and reservoir geometries, resulting in a promising platform for the investigation of confinement effects on the formation of depletion zones and electrokinetic vortices.

Perspectives

The numerical and experimental results in this work have implications for different fields of research and industry that focus on the (selective) transport of ions. The main focus of this thesis was the investigation of the effect of temperature and geometry on the ion transport in electrodialysis applications, including the underlying physical principles that cause system dependence on these variables.

The influence of temperature gradients

The influence of temperature on charge transport observed in this work is mainly a result of the change of physical properties of the different ions with temperature. For the nanochannel systems that were investigated numerically, these

differences provided an enhancement in nanochannel selectivity. For the conical shaped nanochannels, the ion current rectification was enhanced by imposing a temperature gradient. However, other effects resulting from the temperature gradient such as Soret-effects [43, 44] were found to be minor at relevant field strengths (at which ion selectivity is maintained and currents are measured). Many other numerical and experimental studies were done on the influence of different parameters such as pH , surface charge and surface heterogeneity [45–48] on the behaviour of nanochannels and nanopores. For fundamental understanding of the influence of temperature and temperature gradients on transport through these nanochannels, experimental investigations are desirable. If visualization of the ion depletion and enrichment zones is desired, a microfluidic system is of interest. As stated, the control of temperature in such nano/microfluidic systems is non-trivial [49], but could possibly be achieved by employing local heating and cooling using for instance Peltier elements [3]. The other option, using a charge selective capillary between to macro-scale reservoirs of which the temperature is controlled, seems more feasible, but potentially lacks the option of easy visualization of the ion depletion zones.

Our experimental results on lab-scale electrodialysis systems with commercial membranes show that the influence of temperature on total transport is more pronounced than the enhancement of selectivity. The increased temperature does not have a negative influence on the selectivity of the membranes, which makes the application of low grade waste heat [50, 51] for the enhancement of electrodialysis processes possible. However, the increase in efficiency is much lower than the amount of energy that should be supplied to the system so if heating is done with anything other than waste heat, this is unfeasible.

For other fields of research, such as fuel cell chemistry and sensing applications, these results are interesting as there are analogous transport mechanisms in these systems. As the local production of heat in fuel cells changes the temperature, the charge transport in these systems is influenced by the resulting temperature differences. If the location of the heat dissipation can be imposed, the ion transport can be enhanced, which can potentially enhance the fuel cell efficiency. In sensing applications that rely on ionic transport, the temperature and possible temperature gradients arising from operation can have an influence on the charge transport in the system and thus on the reliability of the sensors. For calibration of such systems, these effects should be considered.

As a result of Joule heating, local temperature gradients inside membrane systems can arise, so no application of an external temperature gradient is required. These temperature gradients can yield a thermoelectrokinetic instability, that results in fluid mixing at the interface [10]. The instability is a result of the induced non-uniformity of the electrical conductivity in the electrolyte resulting from the temperature gradient, and is numerically modeled to investigate the influence

of this instability on the total ionic current through the interface [52]. This mechanism is thus fundamentally different from the conventional Rayleigh-Bénard instabilities (described as gravitational convection/instability in the introduction), which results from differences in liquid density [53, 54]. To experimentally confirm this thermoelectrokinetic instability, local temperature measurements alongside the measurements of current and flow profile in microfluidic or millifluidic systems are of high importance.

The influence of geometry

The influence of geometry on total ion transport was found to be significant for different microfluidic systems that were investigated. Electro-osmotic surface flows are emerging as a result of tangential components of the electric field adjacent to the charge selective interface. These electro-osmotic additions to the total charge transport can enhance the charge transport through the system and possible even induce the development of low speed convective vortices in the membrane system before onset of the overlimiting current regime. The influence of geometry on flow profile [55–57] has been investigated in many different systems, but the contribution of the electric field distortion to the added charge transport is often overlooked in membrane research. In all of these investigations, the implementation of a spacer or profiled membrane will change the electric field distribution, yielding additional electro-osmotic transport mechanisms.

These experimental results have implications for charge transport in large-scale electrodialysis plants, as a small distortion of the electric field can lead to altered charge transport. When conductivity and permittivity gradients arise in the system, inhomogeneities in the electric field result in an altered transport of ions in the system [58]. The knowledge gained here can be used to enhance the charge transport towards membranes by using gradients of permittivity in the membrane material. Additional theoretical investigations on the optimal design in which the current density is optimized should be conducted before testing this on large-scale systems. Changing the membrane topology by having a structured membrane also changes the charge transport characteristics in the system [14] and does not sacrifice in membrane surface area. This can potentially enhance the ion transport towards the charge selective interface even further.

In a broader perspective, non-uniform electric fields can be applied for the enhancement of transport in the boundary layer in the chemical industry. Concentration polarization is important in many systems apart from electrodialysis [59], such as electrocatalysis, mixing and liquid pumping. The knowledge on concentration polarization phenomena, including the interplay of the electric field with gradients in polarizability of the surface is thus of use in many other fields of research. Process intensification by using microfluidic reactors is of interest [60, 61]. In these reactors, the application of electric fields and electrokinetic

mixing for the enhancement of transport is a realistic approach. In such systems, non-uniform electric fields can be a result of local conductivity changes of both the solution and the surrounding system boundaries.

The most immediate applications of the results obtained in this work are for the microfluidic mixing of samples in lab-on-a-chip applications. In many of these applications, mixing is challenging [62] and the development of turbulent promoters is a broad field of research [63, 64]. Electrokinetically induced vortices yield relatively high speeds in microsystems, that can effectively mix solutions in these typically laminar systems. Similar to induced charge electro-osmosis (that is applied for mixing in microsystems) [65, 66], these gradients in local permittivity can induce significant fluid motion [67–70]. Insights from this field of induced charge electro-osmosis can be applied in the research field of electrokinetic instabilities, since the principles and applications are very similar. Using changes in local conductivity, permittivity or wall potential, non-uniform electro-osmotic flows can be established, resulting in mixing of the fluid. Controllability of the electrokinetic instabilities and the influence of for instance electric field strength and topology on the degree of mixing are of interest for further research.

References

- [1] R. Venditti, X. Xuan, and D. Li, *Experimental characterization of the temperature dependence of zeta potential and its effect on electroosmotic flow velocity in microchannels*, Microfluid. Nanofluidics **2**, 493 (2006).
- [2] B. J. Kirby and E. F. Hasselbrink, *Zeta potential of microfluidic substrates: 1. Theory, experimental techniques, and effects on separations*, Electrophoresis **25**, 187 (2004).
- [3] F. J. Disalvo, *Thermoelectric cooling and power generation*, Science **285**, 703 (1999).
- [4] G. Maltezos, M. Johnston, and A. Scherer, *Thermal management in microfluidics using micro-Peltier junctions*, Appl. Phys. Lett. **87**, 154105 (2005).
- [5] G. Velte Casquillas *et al.*, *Fast microfluidic temperature control for high resolution live cell imaging*, Lab Chip **11**, 484 (2011).
- [6] C. Paviolo, A. H. A. Clayton, S. L. Mcarthur, and P. R. Stoddart, *Temperature measurement in the microscopic regime: A comparison between fluorescence lifetime- and intensity-based methods*, J. Microsc. **250**, 179 (2013).
- [7] C. E. Estrada-Pérez, Y. A. Hassan, and S. Tan, *Experimental characterization of temperature sensitive dyes for laser induced fluorescence thermometry*, Rev. Sci. Instrum. **82**, 074901 (2011).
- [8] I. Rubinstein and B. Zaltzman, *Electro-osmotically induced convection at a permselective membrane*, Phys. Rev. E **62**, 2238 (2000).

- [9] C. L. Druzgalski, M. B. Andersen, and A. Mani, *Direct numerical simulation of electroconvective instability and hydrodynamic chaos near an ion-selective surface*, Phys. Fluids **25**, 110804 (2013).
- [10] E. N. Kalaydin, N. Y. Ganchenko, G. S. Ganchenko, N. V. Nikitin, and E. A. Demekhin, *Thermoelectrokinetic instability and salt superconcentration near permselective electric membranes*, Phys. Rev. Fluids **2**, 114201 (2017).
- [11] V. I. Zabolotskii, V. V. Nikonenko, M. K. Urtenov, K. A. Lebedev, and V. V. Bugakov, *Electroconvection in systems with heterogeneous ion-exchange membranes*, Russ. J. Electrochem. **48**, 692 (2012).
- [12] J. Balster, M. H. Yildirim, D. F. Stamatialis, R. Ibanez, R. G. H. Lammertink, V. Jordan, and M. Wessling, *Morphology and microtopology of cation-exchange polymers and the origin of the overlimiting current*, J. Phys. Chem. B **111**, 2152 (2007).
- [13] S. M. Davidson, M. Wessling, and A. Mani, *On the dynamical regimes of pattern-accelerated electroconvection*, Sci. Rep. **6**, 22505 (2016).
- [14] J. C. de Valença, *Overlimiting current properties at ion exchange membranes* (thesis) (Universiteit Twente, 2017).
- [15] J. G. Santiago, S. T. Wereley, C. D. Meinhart, D. J. Beebe, and R. J. Adrian, *A particle image velocimetry system for microfluidics*, Exp. Fluids **25**, 316 (1998).
- [16] K. Shinohara, Y. Sugii, A. Aota, A. Hibara, M. Tokeshi, T. Kitamori, and K. Okamoto, *High-speed micro-PIV measurements of transient flow in microfluidic devices*, Meas. Sci. Technol. **15**, 1965 (2004).
- [17] J. R. Lakowicz, H. Szmajdzinski, K. Nowaczyk, K. W. Berndt, and M. Johnson, *Fluorescence lifetime imaging*, Anal. Biochem. **202**, 316 (1992).
- [18] W. Becker, *Fluorescence lifetime imaging - techniques and applications*, J. Microsc. **247**, 119 (2012).
- [19] H. C. Gerritsen, M. A. H. Asselbergs, A. V. Agronskaia, and W. G. J. H. M. Van Sark, *Fluorescence lifetime imaging in scanning microscopes: Acquisition speed, photon economy and lifetime resolution*, J. Microsc. **206**, 218 (2002).
- [20] A. V. Agronskaia, L. Tertoolen, and H. C. Gerritsen, *High frame rate fluorescence lifetime*, J. Phys. D: Appl. Phys. **36**, 1655 (2003).
- [21] S. Park, T. D. Chung, and H. C. Kim, *Ion bridges in microfluidic systems*, Microfluid. Nanofluidics **6**, 315 (2009).
- [22] M. H. Pham and D. P. J. Barz, *Bonding Nafion® with polydimethylsiloxane: A versatile approach towards ion-exchange membrane microfluidic devices*, J. Memb. Sci. **537**, 310 (2017).
- [23] M. Trau, D. A. Saville, and I. A. Aksay, *Field-induced layering of colloidal crystals*, Science **272**, 706 (1996).
- [24] M. Grzelczak, J. Vermant, E. M. Furst, and L. M. Liz-Marzán, *Directed self-assembly of nanoparticles*, ACS Nano **4**, 3591 (2010).

-
- [25] E. Rabani, D. R. Reichman, P. L. Geissler, and L. E. Brus, *Drying-mediated self-assembly of nanoparticles*, Nature 271 .
- [26] Y. Yin, Y. Lu, B. Gates, and Y. Xia, *Template-assisted self-assembly: A practical route to complex aggregates of monodispersed colloids with well-defined sizes, shapes, and structures*, J. Am. Chem. Soc. **123**, 8718 (2001).
- [27] K. Zahn and G. Maret, *Two-dimensional colloidal structures responsive to external fields*, Curr. Opin. Colloid Interface Sci. **4**, 60 (1999).
- [28] M. Sullivan, K. Zhao, C. Harrison, R. H. Austin, M. Megens, A. Hollingsworth, W. B. Russel, Z. Cheng, T. Mason, and P. M. Chaikin, *Control of colloids with gravity, temperature gradients, and electric fields*, J. Phys. Condens. Matter **15**, S11 (2003).
- [29] S. J. Koh, *Strategies for controlled placement of nanoscale building blocks*, Nanoscale Res. Lett. **2**, 519 (2007).
- [30] E. Choi, K. Kwon, D. Kim, and J. Park, *An electrokinetic study on tunable 3D nanochannel networks constructed by spatially controlled nanoparticle assembly*, Lab Chip **15**, 512 (2014).
- [31] E. V. Dydek and M. Z. Bazant, *Nonlinear dynamics of ion concentration polarization in porous media: The leaky membrane model*, AIChE J. **59**, 3539 (2013).
- [32] J. van t Oever, N. Spannenburg, H. Offerhaus, D. van den Ende, J. Herek, and F. Mugele, *In-chip direct laser writing of a centimeter-scale acoustic micromixer*, J. Micro/Nanolithography, MEMS, MOEMS **14**, 023503 (2015).
- [33] L. Amato, Y. Gu, N. Bellini, S. M. Eaton, G. Cerullo, and R. Osellame, *Integrated three-dimensional filter separates nanoscale from microscale elements in a microfluidic chip*, Lab Chip **12**, 1135 (2012).
- [34] M. H. Olsen, G. M. Hjortø, M. Hansen, Ö. Met, I. M. Svane, and N. B. Larsen, *In-chip fabrication of free-form 3D constructs for directed cell migration analysis*, Lab Chip **13**, 4800 (2013).
- [35] W. Lee, R. Ji, U. Gösele, and K. Nielsch, *Fast fabrication of long-range ordered porous alumina membranes by hard anodization*, Nat. Mater. **5**, 741 (2006).
- [36] O. Jessensky, F. Müller, and U. Gösele, *Self-organized formation of hexagonal pore arrays in anodic alumina*, App. Phys. Lett. **72**, 1173 (1998).
- [37] A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O’Keeffe, and O. M. Yaghi, *Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks*, Acc. Chem. Res. **43**, 58 (2010).
- [38] L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, and J. T. Hupp, *Metal-organic framework materials as chemical sensors*, Chem. Rev. **112**, 1105 (2012).
- [39] P. Searson, *Porous silicon membranes*, Appl. Phys. Lett **59**, 823 (1991).
- [40] T. Leïchl and D. Bourrier, *Integration of lateral porous silicon membranes*

- into planar microfluidics*, Lab Chip **15**, 833 (2015).
- [41] R. M. Tiggelaar, V. Verdoold, H. Eghbali, G. Desmet, and J. G. E. Gardeniers, *Characterization of porous silicon integrated in liquid chromatography chips*, Lab Chip **9**, 456 (2009).
- [42] S. Sukas, R. M. Tiggelaar, G. Desmet, and J. G. E. Gardeniers, *Fabrication of integrated porous glass for microfluidic applications*, Lab Chip **13**, 3061 (2013).
- [43] S. Duhr and D. Braun, *Why molecules move along a temperature gradient*, Proc. Natl. Acad. Sci. **103**, 19678 (2006).
- [44] Y. Kobatake and H. Fujita, *Osmotic flows in charged membranes. II. Thermo-osmosis*, J. Chem. Phys. **41**, 2963 (1964).
- [45] X. Hou, Y. Liu, H. Dong, F. Yang, L. Li, and L. Jiang, *A pH-gating ionic transport nanodevice: Asymmetric chemical modification of single nanochannels*, Adv. Mater. **22**, 2440 (2010).
- [46] M. Ali, B. Schiedt, R. Neumann, and W. Ensinger, *Biosensing with functionalized single asymmetric polymer nanochannels*, Macromol. Biosci. **10**, 28 (2010).
- [47] Z. Guo, J. Wang, J. Ren, and E. Wang, *pH-Reversed ionic current rectification displayed by conically shaped nanochannel without any modification*, Nanoscale **3**, 3767 (2011).
- [48] R. T. Perera, R. P. Johnson, M. A. Edwards, and H. S. White, *The effect of the electric double layer on the activation energy of ion transport in conical nanopores*, J. Phys. Chem. C **119**, 24299 (2015).
- [49] V. Miralles, A. Huerre, F. Malloggi, and M.-C. Jullien, *A review of heating and temperature control in microfluidic systems: Techniques and applications*, Diagnostics **3**, 33 (2013).
- [50] L. E. Bell, *Cooling, heating, generating power, and recovering waste heat with thermoelectric systems*, Science **321**, 1457 (2008).
- [51] S. Brückner, S. Liu, L. Miró, M. Radspieler, L. F. Cabeza, and E. Lävemann, *Industrial waste heat recovery technologies: An economic analysis of heat transformation technologies*, Appl. Energy **151**, 157 (2015).
- [52] E. A. Demekhin, S. Amiroudine, G. S. Ganchenko, and N. Y. Khasmatulina, *Thermoelectroconvection near charge-selective surfaces*, Phys. Rev. E **91**, 063006 (2015).
- [53] E. Karatay, C. L. Druzgalski, and A. Mani, *Simulation of chaotic electrokinetic transport: Performance of commercial software versus custom-built direct numerical simulation codes*, J. Colloid Interface Sci. **446**, 67 (2015).
- [54] J. C. de Valença, A. Kurniawan, R. M. Wagterveld, J. A. Wood, and R. G. H. Lammertink, *Influence of Rayleigh-Bénard convection on electrokinetic instability in overlimiting current conditions*, Phys. Rev. Fluids **2**, 033701 (2017).

-
- [55] S. Pawlowski, T. Rijnaarts, M. Saakes, K. Nijmeijer, J. G. Crespo, and S. Velizarov, *Improved fluid mixing and power density in reverse electrodialysis stacks with chevron-profiled membranes*, J. Memb. Sci. **531**, 111 (2017).
- [56] V. S. Pham, Z. Li, K. M. Lim, J. K. White, and J. Han, *Direct numerical simulation of electroconvective instability and hysteretic current-voltage response of a permselective membrane*, Phys. Rev. E **86**, 046310 (2012).
- [57] S. Pawlowski, V. Geraldes, J. G. Crespo, and S. Velizarov, *Computational fluid dynamics (CFD) assisted analysis of profiled membranes performance in reverse electrodialysis*, J. Memb. Sci. **502**, 179 (2016).
- [58] M. Wessling, L. G. Morcillo, and S. Abdu, *Nanometer-thick lateral poly-electrolyte micropatterns induce macroscopic electro-osmotic chaotic fluid instabilities*, Sci. Rep. **4**, 4294 (2014).
- [59] N. A. Mishchuk, *Polarization of systems with complex geometry*, Curr. Opin. Colloid Interface Sci. **18**, 137 (2013).
- [60] T. van Gerven and A. Stankiewicz, *Structure, energy, synergy, time - The fundamentals of process intensification*, Ind. Eng. Chem. Res. **48**, 2465 (2009).
- [61] J.-C. Charpentier, *Process intensification by miniaturization*, Chem. Eng. Technol. **28**, 255 (2005).
- [62] J. M. Ottino and S. Wiggins, *Introduction: mixing in microfluidics*, Phil. Trans. R. Soc. Lond. A **362**, 923 (2004).
- [63] K. Ward and Z. H. Fan, *Mixing in microfluidic devices and enhancement methods*, J. Micromech. Microeng. **25**, 094001 (2015).
- [64] E. A. Mansur, Y. Mingxing, W. Yundong, and D. Youyuan, *A State-of-the-Art Review of Mixing in Microfluidic Mixers*, Chinese J. Chem. Eng. **16**, 503 (2008).
- [65] M. Z. Bazant and T. M. Squires, *Induced-charge electrokinetic phenomena: Theory and microfluidic applications*, Phys. Rev. Lett. **92**, 066101 (2004).
- [66] T. M. Squires and M. Z. Bazant, *Breaking symmetries in induced-charge electro-osmosis and electrophoresis*, J. Fluid Mech. **560**, 65 (2006).
- [67] J. A. Levitan, S. Devasenathipathy, V. Studer, Y. Ben, T. Thorsen, T. M. Squires, and M. Z. Bazant, *Experimental observation of induced-charge electro-osmosis around a metal wire in a microchannel*, Colloids Surfaces A: Physicochem. Eng. Asp. **267**, 122 (2005).
- [68] H. Zhao and H. H. Bau, *Microfluidic chaotic stirrer utilizing induced-charge electro-osmosis*, Phys. Rev. E **75**, 066217 (2007).
- [69] A. J. Pascall and T. M. Squires, *Induced charge electro-osmosis over controllably contaminated electrodes*, Phys. Rev. Lett. **104**, 088301 (2010).
- [70] S. M. Davidson, M. B. Andersen, and A. Mani, *Chaotic induced-charge electro-osmosis*, Phys. Rev. Lett. **112**, 128302 (2014).

Acknowledgements

I liked working with smart people.

- Katherine Johnson
Research mathematician at NASA

This thesis started with the phrase ‘All people are equal’, which I do believe to be true, but in reality this does not mean that all people have equal opportunities. Being born in the Netherlands at the end of the 20th century has granted me privileges, which I did not earn through any of my own effort, but for them I am eternally grateful. For me, going to school and being educated was something that was not even in question. I did not have to give up school to care for my siblings, I did not have to give up school to make a living for my parents. My society allowed me to pursue the highest possible education in the subject of my choice. All doors were open, many different paths for personal development were laid-out, and I was able to make my own decisions to shape my own future. In many parts of the world, education, especially for girls, is not self-evident and motivation for personal development is barely-existent. Even in the Netherlands, a mere 150 years ago, women were not allowed to study at universities. With this in mind, I feel very lucky for the opportunities that I have had and I hope that in the near future the place where you are born does not determine your chances in life and that all people will have the opportunities that I had to develop themselves.

With that said, of course for me personally, I’ll paraphrase Napoleon, the pig from *Animal Farm* (George Orwell, 1945), by saying “All people are equal but some people are more equal than others”. Finishing this thesis would not have been possible without the help of many people, and I would not be the person I am today without my colleagues, friends and family.

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About the author

Anne Benneker was born on July 22, 1989 in Oldenzaal, the Netherlands. After graduating high school at C.S.G. Reggesteyn in Nijverdal, she started studying Chemical Engineering at the University of Twente. She was active in many committees at the university, amongst others in organizing a three week study tour to China and as a member of the University Council. During her studies she also gained some teaching experience as a teaching assistant in different subjects. For her Bachelor's thesis (2010) she conducted research on bouncing and walking droplets on a

vibrating bath in the Physics of Fluids group of Prof. Detlef Lohse.

After finishing her Bachelor of Science she continued studying Chemical Engineering with a specialization in Process Engineering at the same university. She did an internship in 2012 on the capture of CO₂ at the CO₂ Technology Center Mongstad in Norway, which is a collaboration between Gassnova, Statoil, Sasol and Shell. The subject of her graduation project was the process intensification of the industrial DADPM process, operated by Huntsman B.V. in the Netherlands. This work was done in the Sustainable Process Technology group under the supervision of Louis van der Ham and Prof. Henk van den Berg.

After obtaining her Master of Science degree in 2013 she started her PhD in the Soft matter, Fluidics and Interfaces group of Prof. Rob Lammertink at the University of Twente with Jeffery Wood as her supervisor. The research focused on the hydrodynamics involved in selective transport of ions in electrodialysis applications. Experimental investigations of such systems were done at different length scales, for the investigation of the influence of temperature and geometry on charge transport. The results of this work are presented in this thesis. During the course of her PhD she was appointed as a lecturer in Chemical Engineering in the Sustainable Process Technology group, where she is currently working.

Next to her work she volunteers as a teacher of 'De Digitale Topschool', an on-line school for primary school children, she reads to infants with language deficiencies and she is active as a campaigner and board member of a local political party. In her spare time she likes sports such as swimming, running and cycling, as well as reading novels and travelling.

Scientific Output

List of publications

- submitted* **A.M. Benneker**, J. Klomp, R.G.H. Lammertink and J.A. Wood *Influence of temperature gradients on mono- and divalent ion transport in limiting current electrodialysis*, submitted to *Desalination*
- 2018 **A.M. Benneker**, B. Gümüşcü, E.G.H. Derckx, R.G.H. Lammertink, J.C.T. Eijkel and J.A. Wood, *Efficient determination of geometric effects on ion transport through charge selective materials*, accepted for publication in *Lab on a Chip*
- 2018 **A.M. Benneker**, T. Rijnaarts, R.G.H. Lammertink and J.A. Wood *Effect of temperature gradients in (reverse) electrodialysis in the Ohmic regime* J. Mem. Sci. **548** 421 (2018)
- 2017 **A.M. Benneker**, H.D. Wendt, R.G.H. Lammertink and J.A. Wood, *Influence of temperature gradients on charge transport in asymmetric nanochannels*, Phys. Chem. Chem. Phys **19** 28232
- 2016 B. Gümüşcü*, A.S. Haase*, **A.M. Benneker***, M.A. Hempenius, A. van den Berg, R.G.H. Lammertink and J.C.T. Eijkel, *Desalination by electrodialysis using a stack of patterned ion-selective hydrogels on a microfluidic device*, Adv. Func. Mater. **26** 8685
- 2016 **A.M. Benneker**, J.A. Wood, P.A. Tsai and R.G.H. Lammertink *Observation and experimental investigation of confinement effects on ion transport and electrokinetic flows at the microscale*, Sci. Rep. **6** 37236
- 2016 J.A. Wood, **A.M. Benneker** and R.G.H. Lammertink, *Temperature effects on the electrohydrodynamic and electrokinetic behaviour of ion-selective nanochannels*, J. Phys. Condens. Matter **28** 114002
- 2016 **A.M. Benneker**, A.G.J. van der Ham, B. de Waele, A.J. Zeeuw and H. van den Berg, *Design and intensification of the industrial DADPM process*, Chem. Eng and Proc.: Process Intensification, **109** 39

Selected conference presentations

- 2017 **A.M. Benneker**, B. Gümüşcü, A.S. Haase, J.A. Wood, J.C.T. Eijkel and R.G.H. Lammertink, *Microfluidic desalination on a chip: Influence of geometry*, Oral presentation at 91st ACS Colloid & Surface Science Symposium, New York (USA)
- 2017 **A.M. Benneker**, J.A. Wood, P.A. Tsai and R.G.H. Lammertink, *Geometric effects on electrohydrodynamics near ion-selective nanochannels*, Oral presentation at 91st ACS Colloid & Surface Science Symposium, New York (USA)
- 2015 **A.M. Benneker**, J.A. Wood, P.A. Tsai and R.G.H. Lammertink, *Electrohydrodynamic effects near ion selective nanochannels: An experimental study*, Oral presentation at IFPEN Microfluidics: From laboratory tools to process development conference, Paris (France)
- 2014 **A.M. Benneker**, E. Karatay, R.G.H. Lammertink and P.A. Tsai, *Electrokinetic microflows at charge selective nano-junctions*, Oral presentation at 10th European Fluid Mechanics Conference, Copenhagen (Denmark)

Ion transport is crucial in many applications such as desalination and fuel cells. This thesis describes fundamental investigations on the effect of temperature and permittivity gradients on ion transport at charge selective interfaces for electrodialysis systems. Numerical and experimental investigations on different length scales were combined to investigate charge transport in the characteristic Ohmic, limiting and overlimiting current regimes of electrodialysis systems. Temperature gradients can enhance the selective transport of ions through changing ionic diffusivity. In systems with permittivity gradients at the charge selective interface, an immediate electro-osmotic flow is induced even in the Ohmic regime. This can greatly enhance ion transport towards the interface, without having to operate in overlimiting current conditions. The results of this work have implications in numerous processes dependent on ion transport phenomena such as fuel cells and desalination and yields fundamental insights into the nature of charge transport.