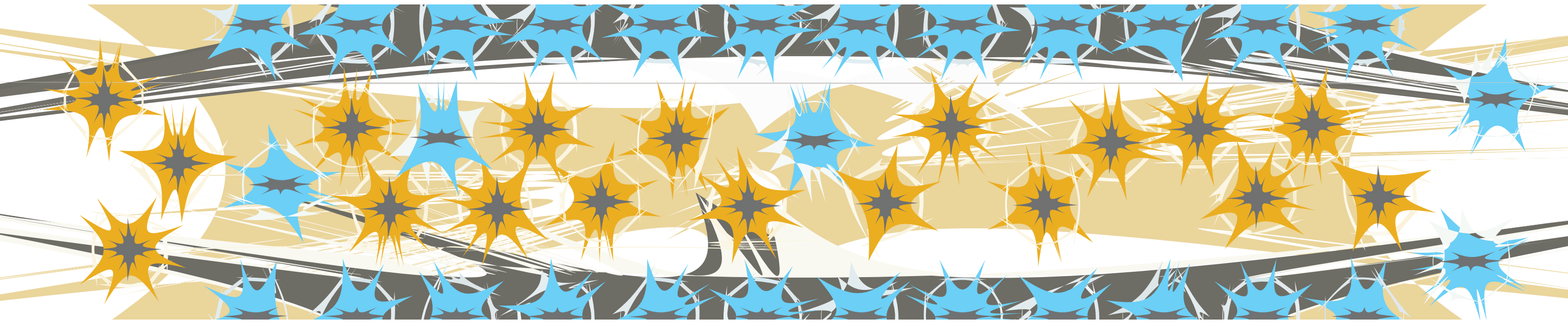
Bachelor's Thesis



Experimental investigation of the overlimiting current in a micro-nanochannel system

Opportunities and pitfalls

Maaike Annelien Sikkink
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Department
Bachelor Program Chemical Engineering
Soft matter, Fluidics and Interfaces group
Faculty of Science and Technology
University of Twente, Enschede, The Netherlands

Committee
A. M. Benneker MSc.
Dr. J.A. Wood
Prof.Dr.Ir. R.G.H Lammertink
Prof. Dr. G. Mul

UNIVERSITY OF TWENTE.

Abstract

The investigation of Ion Concentration Polarization (ICP) phenomena has become more and more interesting due to the implications for desalination and other important industrial operations. The ability to relatively carefully control and analyze the transport of ions using charge selective interfaces, from cation or anion selective membranes to ion-selective nanochannels, is widely studied. In literature there is already a lot of numerical analysis on ICP phenomena in a system with a perm-selective interface. In this research, ICP was studied using an array of nanochannels between microchannels. Firstly, the experimental system was optimized to achieve reliable experimental results. The optimization of the set-up was done by testing applied voltages, different measurement/equilibration time and many other factors. The outcomes have shown that despite several optimization steps the results remain difficult to reproduce. However, due to the comparison of the theoretical conductance and the experimental conductance it was shown that the nanochannels are not behaving unexpectedly from a surface charge point of view. Recommendations for a re-design are provided.

Contents

1 Introduction

1.1 Background

In the last ten years Ion Concentration Polarization (ICP) phenomena became more and more interesting for different applications due to the progress in fabrication of micro- and nanofluidic devicesf [1]. Applications based on this phenomena can be for instance; water desalination [2, 3], bio-analytical sensors [4] and fuel cells [5].

The mathematics of these phenomena through perm-selective membranes have already been described by Nernst in 1904. Detailed theoretical and experimental investigations have become of interest again because of the ability to relatively carefully control and analyse transport of ions on nanoscale which has broad implications for the ability to improve performance in a number of the previously mentined applications [1]. The Nernst-Planck equations consider ion transport only due to diffusion and electromigration. This results in a linear concentration profile in the ion depletion zone and as a result an Ohmic and limiting current [6]. However by increasing the voltage, a further increase of the current beyond the limiting current called the over-limiting current can be observed [7].

The exact origin and implications of this over-limiting current are unknown [8]. However in literature there are some mechanisms proposed to be the cause of this remarkable phenomenon. One of them is the dissociation of water whereby the higher concentration of ions could make it possible to observe a higher current [9]. Another proposed mechanism is the formation of a vortex flow caused by the applied electrical field close by the perm-selective membrane surface acting on the local non-electroneutrality. This will nullify the linear concentration profile in the ion depletion zone and therefore abolish the velocity limiting factor of the ions which perhaps will lead to a higher current [10].

In this bachelors assignment instead of a conventional membrane, nanochannels are used as the charge selective interface. Nanochannels are charge selective due to their characteristic dimensions, as the small dimensions of the nanochannels provide overlapping Debye layers and in this way cause exclusion of the co-ion [11]. These small channels are well-defined structures, which make them easier to be described and therefore very useful for fundamental research.

1.2 Scope

In literature a lot of numerical analyses have already been done in the field of ion concentration polarization in micro-nanofluidic devices [12–16] nonetheless the experimental results are lacking for many systems of interest, particularly for how fluid flow in nanochannel arrays can be manipulated to control performance. However, to achieve reliable results the experimental system used should be running as optimal as possible. Therefore the optimization of the experimental system will be the main goal of this research, which includes:

- Minimizing external influences
- Optimization of the set-up
- Optimization of the measurement method

2 Theoretical Background

2.1 Ion Concentration Polarization

Ion Concentration Polarization phenomena occur after applying an electric field over a stream of electrolyte that is divided by a charge selective interface (CSI). The exact behaviour of Ion Concentration Polarisation depends on the specific system in which it appears, but in general the following will happen:

The electric field will make the positive ions migrate towards the anode and the negative ions to the cathode. This flow through an specific area caused by an applied electric field is called a drift flux. Besides this drift flux the movement of ions can also occur due to concentration gradients referred to as diffusion flux. However, positive or negative ions will be blocked by the charge selective interface because it allows only one of the two to pass. This leads to an enrichment of the blocked ions on one side of the interface and depletion of the passed species on the other side of the interface. It is schematically shown in figure 1.

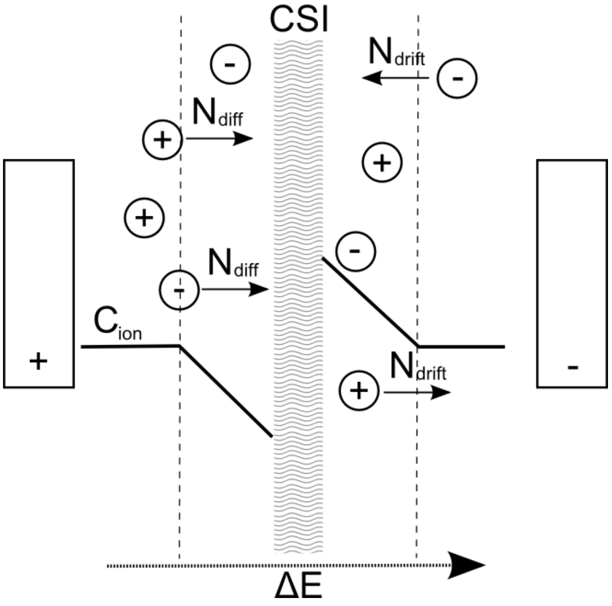

Figure 1: Schematic representation of Ion Concentration Polarization through a cation selective material. N_{diff} *and* N_{drift} *are respectively the diffusion flux and the drift flux. The black lines with* C_{ion} *represent the concentration of the passing ions. [17]*

Nernst discussed in 1904 the mathematics of the above described phenomenon. With the help of the Nernst-Planck equations a formula can be derived which described the behaviour of the current through Ion Concentration Polarization in a simplified system [18]:

$$I = I_0 \left[1 - e^{-\frac{z_- V}{k_B T}} \right] \tag{1}$$

In which I is the current, I_0 is the limiting current, z the charge of the species, V the voltage, k_B the Boltzmann constant and T the temperature. This formula can be used to illustrate the behaviour of the limiting current and can be used to predict the magnitude of the limiting current in more complicated systems.

2.2 Behaviour of the current

Rested on the classical theories and experimental results when applying a higher electric field, thus a higher voltage, over a charge selective interface which separates an electrolyte the behaviour of current is shown in figure 2.

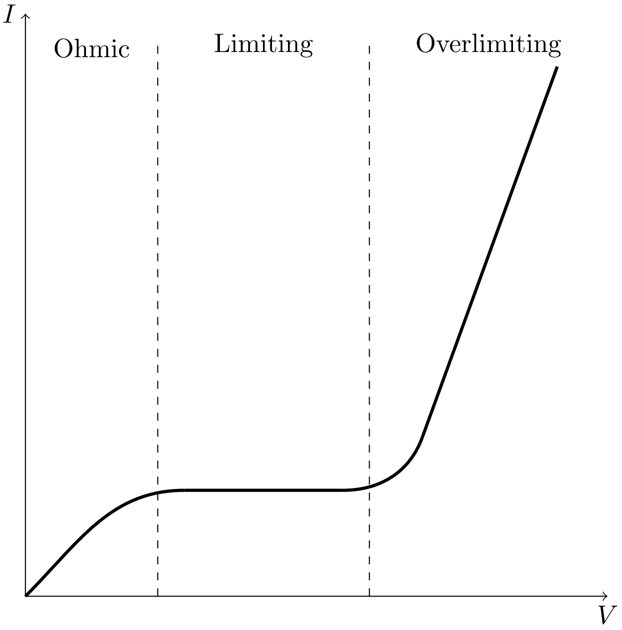

Figure 2: Schematic representation of the behaviour of a current in a system where there is an electric field applied over a stream of electrolyte is divided by a charge selective interface. The three regions ohmic, limiting and overlimiting can be recognized.

In the graph shown above it is possible to define three regions: ohmic, limiting and overlimiting. These three regions will be explained in the next three paragraphs.

2.2.1 Region I: Ohmic

In the first region the current follows Ohm's law. This means that at this point there is no depletion or enrichment of the positive and negative ions on either side of the charge selective interface and therefore the current is developing linear with respect to the applied voltage. This phenomenon can be described by the Ohms law in which the resistance of the ions in the solution encounter from the water molecules and the surface charge of the charge selective interface. The resistance further depends on the temperature, chemical nature, homogeneity and on the size and shape of the ions [19].

2.2.2 Region II: Limiting

In the second region it can be seen that by increasing the voltage it does not result in further increase of the current. This behaviour of the current is called limiting.

It is caused by the earlier explained Ion Concentration Polarization. So, looking back at figure 1 it can be seen that a certain point the concentration of the ions that can pass the charge selective interfaces becomes zero at the surface of the interface. A diffusion layer will be formed and the transport in this diffusion becomes limiting. So despite of making the voltage higher no further increase in the current is found [3, 6]. In other words, the resistance in the membrane will become smaller than the resistance in the diffusion layer:

$$R_{\text{membrane}} < R_{\text{diffusion}} \tag{2}$$

The behaviour of the current can also be explained by looking at equation 1 derived from the Nernst-Planck equations. By increasing the voltage, the exponential term approaches zero as the exponent increases in magnitude (and is negative). And this means the current I gets ultimately the same value as the limiting current I_0.

2.2.3 Region III: Overlimiting

In the last region the current gets to the point that it become to be a so called over-limiting current. Even though the theory around the Ion Concentration Polarization phenomena predicts that the end stage of the current should be limited, in experiments the current can still exceeds this limiting value once voltage is further increased beyond a certain threshold. It can be seen in figure 2 that the current is significant increasing after the limiting value.

The exact mechanisms for the overlimiting current are quite complicated and involve many different effects. However there are some mechanism proposed in literature which are shown in figure 3.

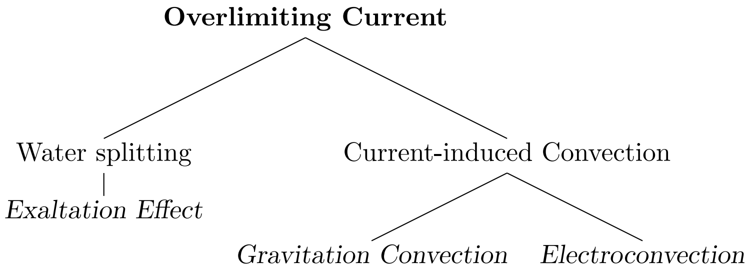

Figure 3: Mechanisms proposed in literature for the overlimiting current

Watersplitting
Already in the late sixties and early seventies one of the first explanations proposed in literature was watersplitting at the depleted membrane surface [9,20,21]. It is schematicaly shown in figure 4. The new formed charge carriers would be the reason for the increasing current. The existence of these ions was proven by measuring the change in pH of the solutions surrounding by the used membrane. Nevertheless, it was in different researches experimentally shown that not a significant part of the current increase after the limited value could be due to the extra protons generated by the water splitting reaction [20].

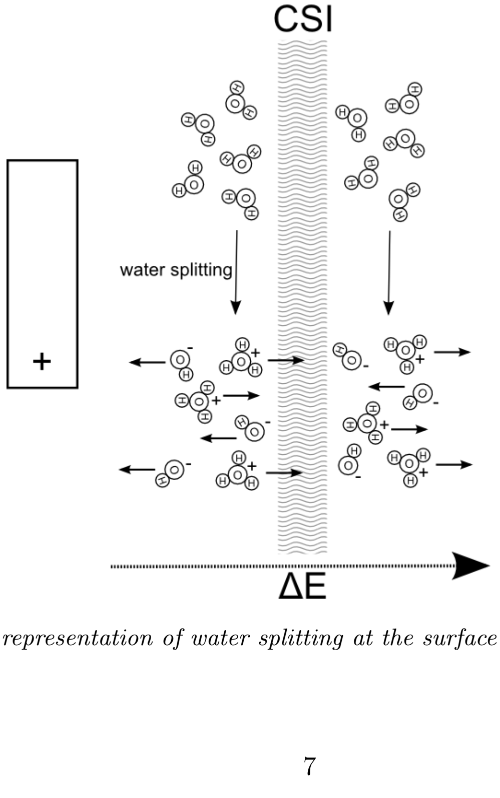

Figure 4: The schematic representation of water splitting at the surface of the charge selective interface [22]

Another, however less evident mechanism of the overlimiting current as a result of water splitting, is the exaltation effect. The H^+ and OH^- ions generated in the depleted region by water splitting will attract the opposite charged ions towards the interface and making it possible to transfer more ions through the charge selective interface. [23, 24]

Current-induced convection

It is believed that current-induced convection, which is coupled with the flowing of current, is a more effective mechanism for the increasing current [8]. Current-induced convection will cause agitation of the solution by the formation of vortexes due to the convection. These vortexes are the reason for the elimination of the diffusion layer and therefore the increase in current.

In literature there are two types of current-induced convection proposed [25, 26].The first one is gravitational convection. This kind of convection is caused by gradients in concentration and/or temperature causing density changes. Temperature changes are caused due to Joule heating and thermal effects of the water splitting reaction. Heat is then absorpt in the water splitting reaction and generated in the recombination reaction [8].

The second type is electroconvection [1,10]. Electroconvection is current-induced volume transport due to charge gradients in the depleted zone near to the interface, which arises when an electric field is imposed through the charged solution. Due to local charge gradients, the imposed electrical field will act on the liquid adjacent to the surface as shown in figure 5. A drift force will act on the ions dragging along the liquid in regions of increased charge density, resulting in the formation of liquid flows. In order to remain continuity of the fluid, vortex structures arise. As a result of local concentration gradients the Debye layer extends from the nanochannel into the microchannel.

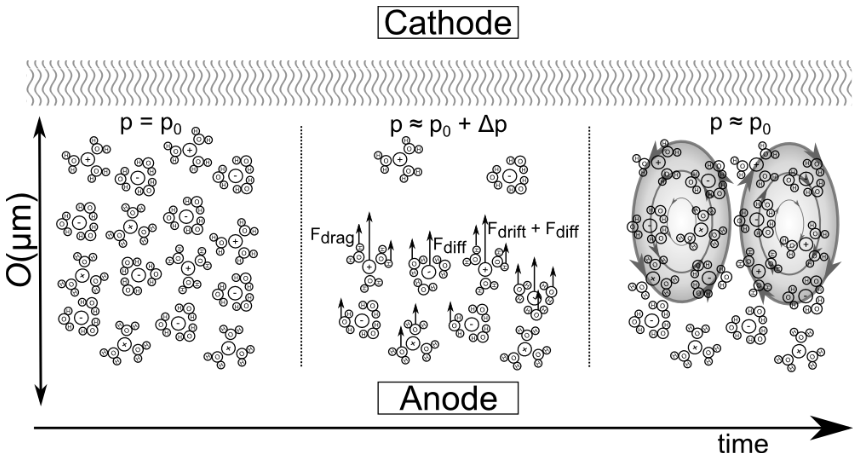

Figure 5: Schematic representation of the forming of electroconvection. On the left side the initial state of ions adjacent to the interface are shown. In the middle the depletion layer is formed causing gradients in the charge density. Then the imposed electric field will act on the ions, which drag along liquid, towards the interface, resulting in vortical flow as shown at the right side of the figure. [27]

Which current-induced convection is dominating in the region of the overlimiting current can be tested by eliminating one of the two types of convection. This can be accomplished by putting the set-up horizontal in the Earths gravitation field so that the gravitational convection is cancelled out. At higher (>0.1 M) concentrations gravitational convection has quite some influence on the overlimiting current [16]. However, at lower concentrations (<0.001 M) and elevated flow rates ($> 0.1\ cm\ s^{-1}$) it seems that gravitational convection has far less influence on the transport of ions through the charge selective interface at higher voltages [13, 26, 28]. However, it is important to keep in mind that these findings were based on measurements in different systems.

2.3 Charge Selective Interface

For the previous described phenomena to appear a charge selective interface is necessary. In this research nanochannels are used to create an interface with the correct properties. These nanochannels become charge selective because the double layer thickness is non-negligible compared with the width of the nanochannels [12, 29]. In other words when the Debye layers overlap with each other in a nanochannel it will cause the exclusion of either positive or negative ions, which one will pass depends on the charge of the walls of the nanochannels.

If the walls of the channels are negative they will be screened by positive ions. If the solution has a high concentration the ionic strength will be high and therefore the Debye Layers will be small and will not overlap. In this way there is no exclusion of one of the ions, so the channels wont be charge selective. However, if the solutions has a low concentration the ionic strength will be low and the Debye layers can overlap. It will cause the exclusion of the negative ions and the inclusion of the positive ions. Hence the channels are charge selective for positive ions. It is schematically shown in figure 6.

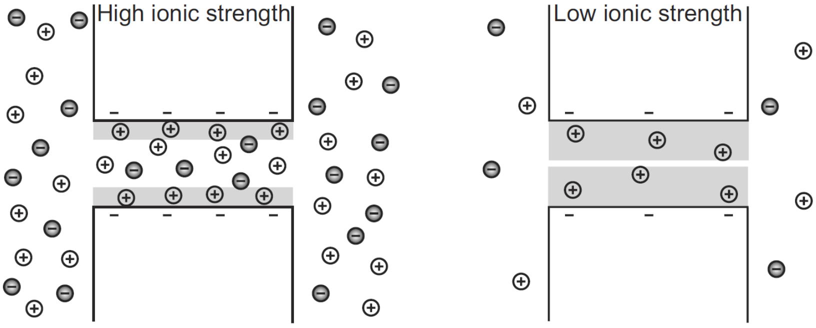

Figure 6: At high ionic strength the electrical double layer is small allowing positive and negative ions to pass. At low ionic strength the electrical double layer is broad and only one of the two can pass. [30]

2.3.1 Debye Length

The double layer thickness is also called the Debye Length and is derived from combining the Boltzmann distribution and the Poisson equation and applying the Debye-Hückel approximation [31]. This results eventually in the following relation for the potential as function of the distance from the wall (x):

$$\phi = \phi_0 \cdot e^{-\kappa x} \tag{3}$$

Where κ is defined by:

$$\kappa^2 = \frac{2e^2 N_A}{kT\epsilon_r\epsilon_0} \cdot I \tag{4}$$

And I is the ionic strength defined by:

$$I = \frac{1}{2}\sum c_i z_i^2 \tag{5}$$

The Debye length is the reciprocal of :

$$\text{Debye Length} = \kappa^{-1} \tag{6}$$

When the distance is equal to the Debye Length the potential has dropped to e^{-1} of the surface potential. Also it can be seen from these equations that if the concentration of the solution gets higher the ionic strength gets higher, nonetheless according to above equations the Debye Length gets in the end smaller.

3 Experimental Background

In the field of Ion Concentration Polarization in nano-micro devices not a lot of experimental work is done. In this chapter the set-up used in research is discussed and after this what is done in this field with the use of nanochannels as charge selective interface.

3.1 Set-ups

The research is primarily done in special fabricated chips which are constructed of some main components. These components are the base of the chip, the charge selective interface and the chosen electrolyte.

Base of the Cip
The most common used material for the chip in this field of experimental work is polydimethylsioxane (PDMS) [3, 32–34]. It is a mineral-organic polymer of the siloxane family and has as advantages that it is transparant at optical frequenties, it bond tightly with glass after simple plasma treatment, it is gas permeable, it is inexpensive and it is easy to mold. Difficulties of using PDMS are the limitation of the integration of electrodes or resistors and the aging of the material. [35]

Another used material for the base of the chip is glass. In literature there are different kinds of glass mentioned like amorphous silica [36] and soda lime glass [37]. A advantage of glass is that it electronics can be more easily installed. However drawbacks of this material for nano-microdevices is that the fabrication takes considerable time and the material is quit fragile.

Charge Selective Interface
One of the most important components of the chip is the charge selective interface, because this is the main part of the set-up which will causes the Ion Concentration Polarisation to take place. Roughly the interfaces can be divided into two categories, membranes and etched nanochannels.

The membranes are dominating the field for the last years. A frequentely used membrane is the so called Nafion mebrane [3, 33, 34, 38]. It is a sulfonated tetrafluorethylene based fluoropolymer-copolymer. The sulfonic acid groups causes the membrane to be cation selective, because protons can jump from one acid group to another. Other membranes, however less used, are Pyrex [39], MA-40/MK-40 [28] and amorphous silica [36].

Nonetheless the dimensions of the previous named membranes can be less controlled and this can give difficulties by comparing theories and experimental results. In principle a solution for this can be to use etched nanochannels. These nanochannels can be etched relatively precisely in different kind of glass, for instance silica [40] or soda lime glass [37]. For instance, this offers over specific degree of Debye Layer overlap and the investigation of the spacing between parallel nanochannel on the developed electroosmotic flows.

Electrolyte
Another condition for Ion Concentration Polarisation to take place is the presence of an electrolyte. Because of the similar mobilities of K^+ and Cl^- 1 mM of KCl is generally used as the charge carrier in order to simplify the analysis and interpretation. [37, 39–41]

In case of the use of a polymer membrane, like the Nafion membrane, which contains functional groups it is necessary to use a buffer which maintains to keep the pH to a constant level so that the charge selectivity of the membrane don't change.

3.2 Previous Work

3.2.1 Validation of the perm-selective nanochannels

Around 1998 it was confirmed experimentally that nanochannels became charge selective due to a negatively charged membrane and the ionic strength of the buffer used [42]. This finding caused the next generation of experiments which focus on the unique properties of these nanochannels to realize efficient separations. [43]

To further investigate the charge selectivity of the nanochannels a large amount of research has been carried out using dyes with different properties, such as valence and pH/temperature sensitivity. It was found that by a negative charged wall the more negatively charged molecules exhibit faster mobilities through the system than less negatively charged or neutral molecules which provides a mechanism for separation [44]. In other experiments it was seen that the area averaged electroosmotic velocity within the channels decreased as the width of double layer increased [32, 45]. [43]

In later work primarily solutions of sodium- or potassium chloride were used, because of the more easy comparison between the numerical studies and experimental outcomes. There are several studies done on the charge selective nanochannels with these solutions and they all shown perm-selectivity of the channels with the use of one or an array of nanochannels, investigating for conductance or other properties [41, 46, 47].

3.2.2 Ion Concentration Polarisation

Due to the relatively simple procedure for fabrication of the chips with a Nafion membrane a large amount experimental research about the Ion Concentration Polarisation phenomena are perfomed with this kind of membrane. For instance the investigations of multiple vortex instabilities inside the ICP layer [1], the mixing performance of nano-microchannel devices [33] and the effect of an external hydrodynamic convective flow on the ohmic-limting-overlimting current behaviour [34]. However the nanopores in Nafion membranes are hard to define due to the way they are fabricated and therefore the use of etched nanochannels can can provide clarity by allowing for precise control of the pore size.

In 2007 an article was published which claimed to be the first to experimental microscopic study on the nonlinear electrokinetic flow generated by nanochannels. To explore this phenomenon in more detail, the concentration and electrokinetic flow pattern inside and outside the ion-depletion region were visualized by tracking the fluorescent nano-particles and also there were current measurements performed to examine the relationship between overlimiting current and the nonlinear electrokinetic mixing. [7] Later on there were more articles published on the forming of the ion depletion and enrichment zone [48, 49] and the remarkable overlimiting current behaviour [15, 50, 51].

Nonetheless there could be a lot more done experimentally on this subject, because even relatively simple experiments on studying systematically the effect of concentration and valency of salt on the current-voltage characteristics and how this couples into the number/spacing between individual nanochannels in a nanochannel array has not been carried out.

4 Materials and Methods

4.1 Initial Set-up

The set-up consists of two parts. The chip is the part where in principal the Ion Concentration Polarisation phenomena should take place and the chip holder allows for recording measurements, which can be electrical or visual observations.

4.1.1 Chip

Design of the chip
In Figure 7, the design of the chip Type 1 is shown. In the middle of the chip the nanochannels are placed with a microchannel at both sides. The nanochannels are placed between the two blue lines. The microchannels are attached to four reservoirs which will be filled with the electrolyte solution. There are also some electrodes and other electrical equipment integrated in the chip however these were not used as they are integrated for use in AC impedance measurements and this thesis focused on DC measurements.

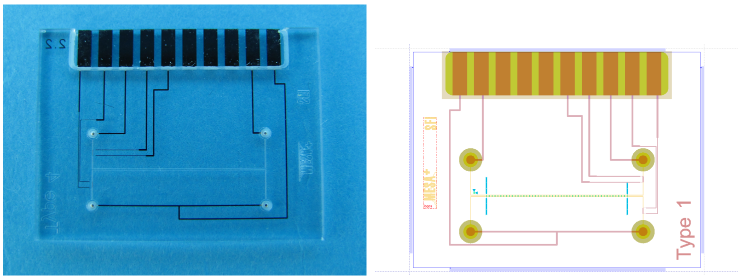

Figure 7: The microchip used to perform the experiments with. On the left side a real picture of the chip is shown and on the right side a schematical representation.

The microchannels have a width of 50-70 micrometers and a depth of 10-20 micrometers. The width of the microchannels depend on the depth of the microchannels due to the nature of the etch process. By etching the channel there was aimed for a depth of 10 micrometers. There are 500 nanochannels etched in the glass with a width of 2 micrometer, a depth of 20 nanometer and a length of 100 micrometer.

Fabrication of the Chip
The chips were fabricated in the MESA+ Nanolab cleanroom facilities. The nanochannel patterns were applied to a glass wafer by standard photolithography and wet etched using BHF. A sacrificial Cr/Au layer was sputtered on the wafer including the nanochannels, before applying photolithography of the microchannels on this layer sacrificial layer. After etching of the microchannels using HF, the sacrificial Cr/Au layer is removed and fluidic access holes and opening for the electrode connectors are powder blasted. On the opposite wafer, electrodes are fabricated by first wet etching of their structures and then sputtering of the electrode material (Ti/Pt) onto the wafer. The surplus electrode material is removed with the photoresist by a metal lift off procedure and electrode patches and connections are remaining. Both wafers are aligned prior to bonding and thermally bonded overnight at an 600 ^{o}C oven.

4.1.2 Chipholder

The chip is placed in a chipholder which is shown in figure 8. The chipholder consist of two parts whereby the upper part is screwed on the lower part. The chip is placed in the notch of the lower part. The four reservoirs on the chip are connected to the four outside reservoirs of the upper part. In each of these four reservoirs an platinum electrode is placed which is bent to a 90 degrees angle and fixed with some tape. The electrodes are placed directly in the reservoir to avoid any gas build up issues from the placement of the previous on-chip electrodes.The electrodes are then connected by alligator clips to the sourcemeter.

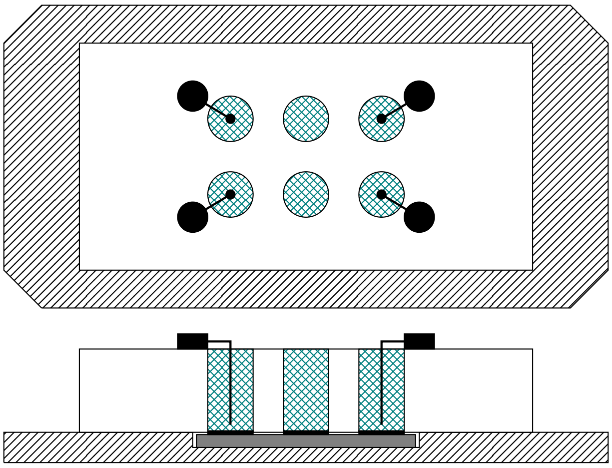

Figure 8: Schematic representation of the chipholder.

4.2 Methods

Preperation
The electrolyte of choice is sodium chloride, which is a strong electrolyte, with various concentrations. A stock solution of 1 mmol/L was used to make subsequent solutions by serial dilution. Before the actual measurement the chip has to be flushed with the relevant solution. The flushing is done with a syringe pump (Harvard Apparatus PicoPlus) at a flowrate of 50 μL/min. After flushing of the channels they are inspected for any airbubbles, using optical microscopy (Axiocam 105 color, Carl Zeis Microscopy GmhB) with a 50x magnification.

Measurements
Subsequently the chip holder is set into place and the outermost reservoirs of chipholder are filled with 140 μL of the solution with the same concentration which was flushed with. Next the sourcemeter (Keithly 2450 Sourcemeter) is connected and the settings for the meter are set through a modified program in labview [52]. The voltage range for these experiments goes from 0 to 200 voltage, the current measurements per voltage range from 20 to 100 items, the waiting time between each measurement per voltage range from 50 to 500 and the waiting time after each measured voltage range form 500 to 5000 milliseconds. To make the results instantly visible the measured current is plotted against te applied voltage with help of a program in matlab, which averages the twenty measured currents per voltage.

5 Results and Discussion

5.1 Base Case

The first measurements were done with the system and settings mentioned in the previous chapter with a 1 mmol/L sodium chloride solution.

5.1.1 Results

There results of the first three measurements are shown in figure 9. The number of measurements per voltage, the waiting time between each measurement per voltage and the waiting time between each measurement per voltage are changed in between the measurements in a measurement series.

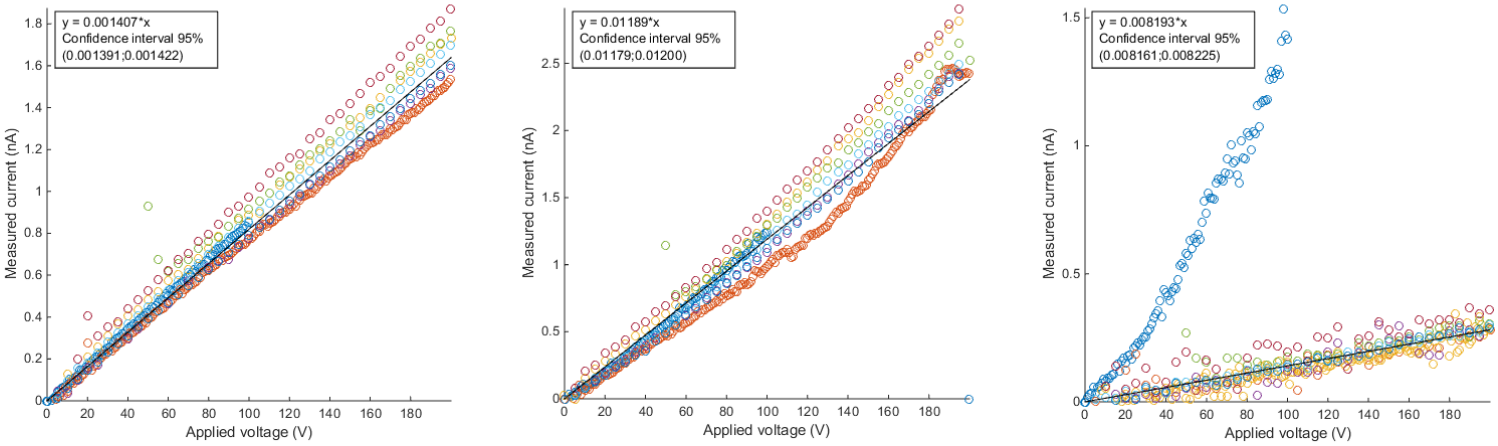

Figure 9: First three IV-measurements with a 1 mmol/L sodium chloride solution. The blue measurement in the third graph has not been taken in to account in the fitting and the 95% confidence interval

It can be seen that there is a large measurement to measurement variation between series. The 95% confidence intervals don't overlap with each other which indicates that the results are really noisy and not reliable. However, the measurements are relatively consistent within one series and don't seem to change by varying the waiting times and measurements per voltage.

5.1.2 Statistics

To check if the values of the current that were measured per voltage weren't dominated by noises produced by the source meter an statistical analysis was performed. It was done with the help of a standard function of Matlab which show graphically if the values are normal distributed. The analysis was done for the 50 voltage of the first measurement serie with 40,10 and 100 measurements per voltage. The outcomes are shown in figure 10 on the next page.

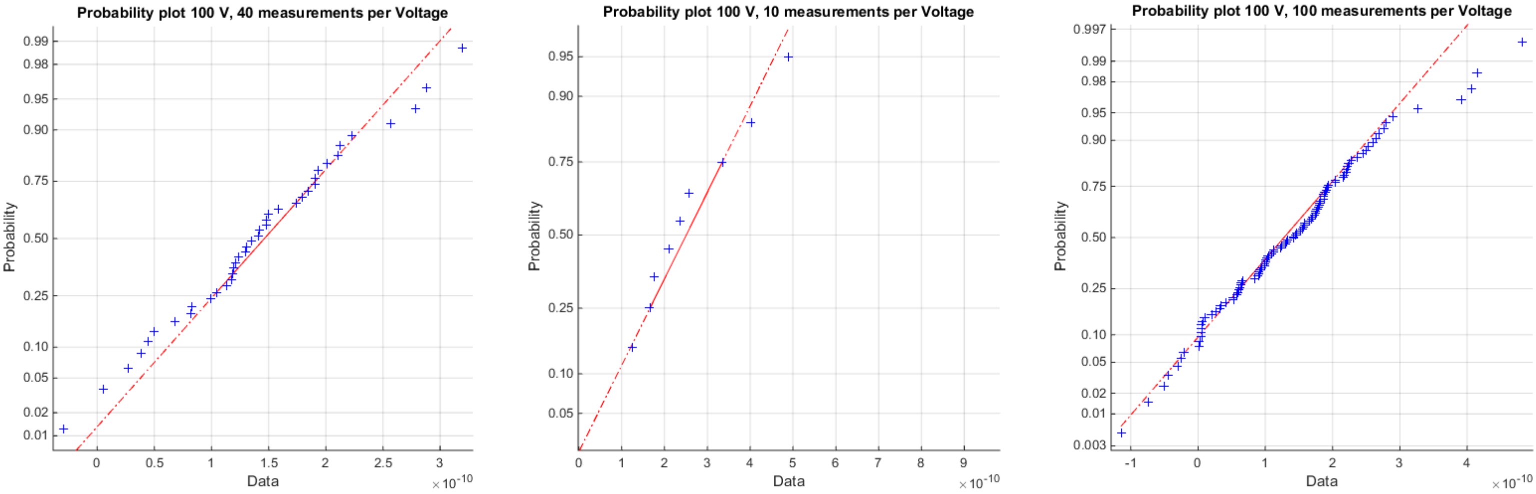

Figure 10: Probability plot of three IV-measurements with a 1 mmol/L sodium chloride solution with different numbers of measurements per voltage, namely 40, 10 and 100.

If most of the values lay on the diagonal the conclusion can be drawn that the values are normally distributed. As can be seen in figure 10 almost all of the values are on the line and it can be concluded that there is no significant bias from the machine, the error at each voltage is randomly distributed with a mean of zero.

5.2 Experimental Adjustments

As seen in figure 9 the measurements between the measurement series aren't reproducible, therefore different optimizations have been done on different parts of the set-up, minimization of the influences of external factors and improvement of the measurement method.

5.2.1 External Influences

Contaminations
Because of the small dimensions of the system the influence of a bit of dust can be huge. It can for instance clog the nanochannels or disturb the flow patterns. To prevent this from happening the lab where the measurements were taken place has been cleaned, because there was a lot of dust and dirt gathered in the whole lab. Besides of dust also remaining salt on the chip and in the chip holder can disturb the measurements as it can cause a concentration gradient. Consequently the chip and chip holder were more often cleaned by leaving the chip soaking in demiwater overnight and rinsing the reservoirs of the chip holder after the measurements.

Vibrations
By an accidental drop of a heavy object on the same table as the set-up it was seen that the drop has direct influence on the measurements. In figure 11 two measurements with a 0.1 mmol/L sodium chloride solutions are shown. One of the measurements was done while it was very noisy and busy in the lab and even at some point a very heavy object fell on the table. The other measurement is done shortly after the first one, but without all the noise and vibrations.

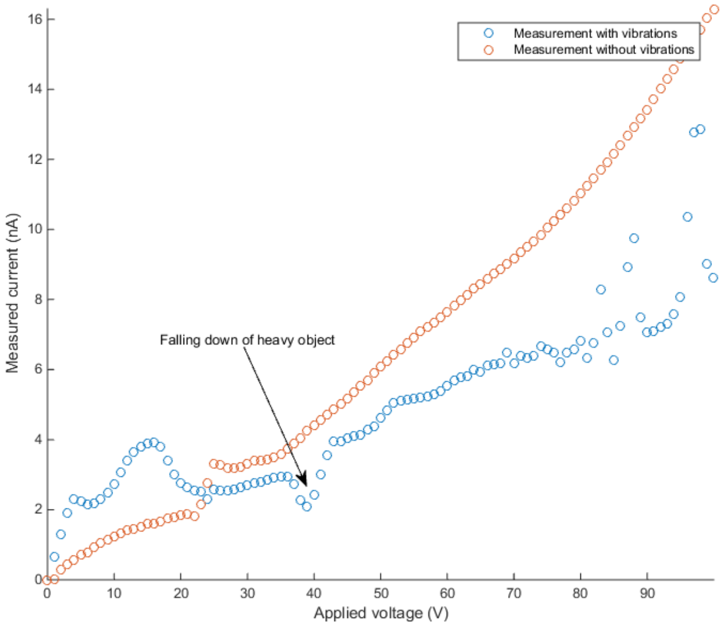

Figure 11: Two IV-measurements with a 0.1 mmol/L sodium chloride solution whereby on of the measurements were done with a lot of vibrations and the other one without

It seems that the system is very sensitive to vibrations of for instance a radio, singing in the lab or falling of objects on the table were the measurements took place. Some of the experiments were therefore performed on a vibration-free table and in an enclosed space.

Temperature

Between the different measurements in a measurement series the presence of air bubbles in the system was checked with the microscope. The microscope uses a lamp to make a clear picture and this lamp gets warmer and warmer by leaving it on for a longer period of time, which heats the liquid. This leads to faster emergence of air bubbles but also causes temperature gradients in the system, which can also induce fluid forces.

5.2.2 Set-up

Electrodes

The first measurements were done with the electrodes folded in a ninety degree angle and placed with one side into the reservoirs while being fixed to the chip holder with tape. The electrodes were then connected to the source meter by alligator clips. The consequences of this kind of set-up are that the electrodes quite easily can break and move every time the chip holder has to be (re)moved.

For fixing the electrodes at the same place the tape was replaced with a screw-ring connection, whereby the electrode is clamped between the ring and the screw. The side of the electrode that is not placed into the reservoir is connected to the source meter by micro-grabbers The electrodes in the reservoirs are in this way fixed but the connection of the micro-grabbers and the electrodes aren't and because of this broke a few times. This leads to the last adjustment on the fixation of the electrodes by soldering the ends of the electrodes to other wires and connecting these wires to the source meter using the the micro-grabbers In this way the electrodes are completely fixed and can't break due to moving the chip holder

Wires

The wires were checked if they were broken by measuring the resistance of the wire and it was found that three of the four wires or the connecting micro-crocodile clip were not working correctly. It was discovered during the ordering of the new wires that the reason that the old ones broke was due to the limiting voltage range of the wires of 50 Volts. In order to ensure no damage occurred, further experiments were limited to a maximum of 50 Voltage.

5.2.3 Measurement Method

Relaxation of the System

In the initial measurement method the measurements followed each other up directly, this has as consequence that the systems gets no time to relax and get back in it's initial state. In other words it is possible that after just one measurement there is a total enrichment and depletion of the ions at either side of the membrane and by directly starting the second measurement afterwards there are less ions available. To prevent this from happening it was calculated that the systems needs one minute to relax back to the original state, however to be sure this time was increased to five minutes.

Reservoirs

The reservoirs of the chip holder were initial filled with a simple plastic five milliliter piper, however it was found out that after the filling a little layer of air between the chip and the solution in the reservoirs remained whereby there is no contact between the solution in the reservoirs of the chip and the reservoirs of the chip holder and the reservoirs cannot be considered to be infinite. To have enough pressure to break to little film of air the reservoirs have been filled with the help of a 1000 μL finnpipet of thousand microliter.

Another disadvantage of filling the reservoirs at the initial way is that the technique is quite sensitive to pipetting and has direct influence on the accuracy and reliability. This could potentially lead to flows from hydrostatic sources, which can be significant in the case of nanochannels. It was seen that by not filling the reservoirs equally it has influence on the measurements probably because of an imposed driving force which will lead of imbalance since the reservoirs are not the same size as ions accumulate. To prevent this from happening all the reservoirs were filled with the same amount of solution, namely 140 μL.

5.2.4 Verification of improved system

To do the verification of the improved system the first results are compared to the last results using a solution of sodium chloride with a concentration of 1 mmol/L.

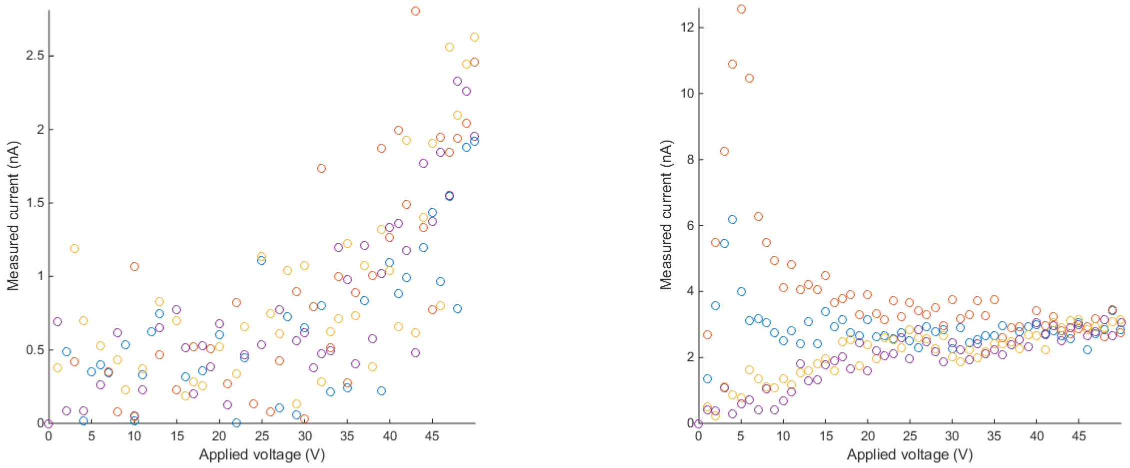

Figure 12: Two IV-measurements with a 1 mmol/L sodium chloride solution after al the adaptations to the system

It can be seen that these measurements also differ a lot in between the measurement series. However in the graph on the left it can be seen that also the measurements in the series are not consistent. The measurements in the other graph are quit more consistent but show a large bump in the beginning. This is a phenomena that also described and observed in literature and is often explained as being an stabilization bump from ions adsorbing on the negatively charged surface and this being a time-dependent phenomena [15].

The last experiments are therefor looking quit a bit more non reproducible than the first measurements, however one of the major drawbacks of these measurements are that the chip was not connected to the four reservoirs. There is a possibility that the first three measurements only have measured the resistance of the source meter and the chipholder.

5.3 Other Results

5.4 Behaviour of the current

Althought the measurements in between the series and sometimes even in the same measurement serie were difficult to reproduce, some expected trends regarding the different concentration and therefore different measures of overlapping Debye Layers have been seen. It was very hard to quantify the degree of nonlinearity for the low and medium overlapping Debye Lengths because the results were to noisy and a precise line can't be drawn. The findings are summarized in table 1 and a example graph for high overlapping Debye Lengths is shown in Figure 13.

Table 1: Summary of the behaviour of the current by different measures of overlapping Debye Layers

Overlapping Debye Lengths	Behaviour of the current
High	*Ohmic, limiting and overlimiting*
Medium	*Nonlinear*
Low	*Linear*

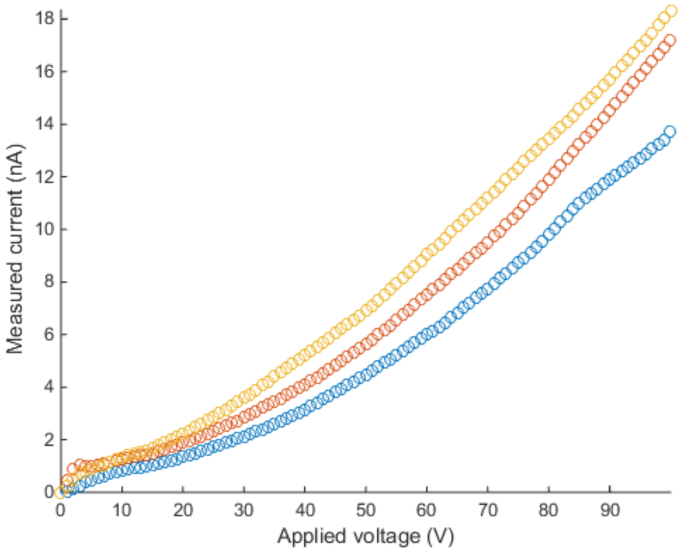

Figure 13: The trend for high overlapping Debye layers showing Ohmic, limiting and overlimiting current behaviour

5.4.1 Checking Nanochannels

To check if the nanochannels aren't the problem the empirical and the theoretical conductance of the nanochannels are compared. The measured conductance was obtained by inverting the resistance of the system. The theoretical conductance was calculated by summing up the conductance of the bulk and the conductance of the effective surface in the nanochannel. The effective surface charge in the nanochannels is formed by the layer of counterions against the surface of the nanochannels .

$$G_{theoretical} = G_{bulk} + G_{surface} \tag{7}$$

$$G_{theoretical} = n_{channels}\sigma_{solution}\frac{A_{channel}}{L_{channel}} + z\mu_{Na^+}\sigma_{surface}\frac{w_{channel}}{L_{channel}} \tag{8}$$

The $n_{channels}$ are the number of nanochannels in the system, the $\sigma_{solution}$ is the conductivity of the solutions, the $A_{channel}$ is the surface area of the cross-sectional area of the channels, the $L_{channel}$ is the length of the channels, the z is the valence of the electrolyte, μ_{Na^+} is the mobility of the sodium ions, $\sigma_{surface}$ is the conductivity of the surface and $w_{channel}$ is the width of the channel.

Subsequently the theoretical conductance and emperical conductance were plot against each other. The outcome is shown in figure 14.

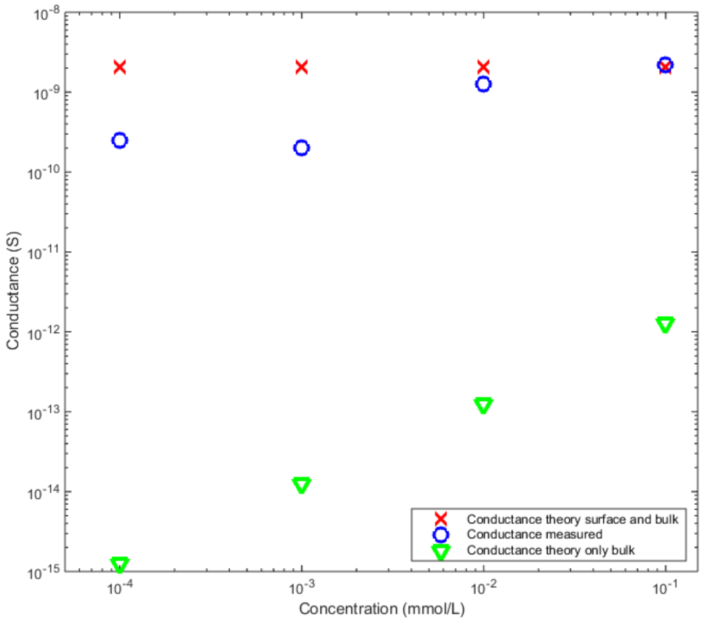

Figure 14: Comparison of measured conductance with the theoretical predicted conductance. When only bulk is taken into account a large underestimation of conductance can be observed, while conductance are in nice agreement when both surface and bulk conduction are considered.

It can be seen that if only the theoretical bulk conductance is taken into account the value is significantly lower than the measured conductance. However if the theoretical conductance consist of the conductance of the bulk and the conductance of the effective surface in the nanochannel the measured an the theoretical conductance are in the same order of magnitude. To obtain this the value of the surface charge lays between 0.5-1.5 mC/m^2, which is on the low end but not unrealistic for a silicia surface [53]. This indicates that there is in all probability nothing major wrong with the nanochannels and they are functioning correctly.

5.5 Possible explanations

As seen in the verification of the improved system the measurements are at that point still not quite stable and there are maybe some other possible explanations for it. One of them could be water splitting at random nucleation points in the system which causes local pH differences and thereby random vortexes which influences the ion flux.

Another explanation could by the influence of the integrated electrodes on the chip. These integrated electrodes are asymmetric placed on the chip which can result in local electrical field gradients when applying an electric field which can also cause random vortexes which influences the ion flux.

The voltages applied to the system causes a current, but can also cause Joule heating due to the resistance of the system. This Joule heating will result in temperature gradients which also will lead to the forming of vortexes which influences the ion flux.

With the help of the microscope it can be seen if there is any dirt in the reservoirs or microchannels, however it is hard to check if the nanochannels are being partially clogged which can also have an effect at the way the current behaved.

It can be imagined that if all these possibilities or even just one are taken place in the system it gets very complicated and the results will be harder to interpret or even be compared to models.

6 Conclusion

The main goal of this research was to optimize the experimental system used to investigate the behaviour of the overlimiting current in a micro-nanochannel system. The first IV-measurements showed results that were quite noisy and unreliable, because of the large measurement to measurement variation between the series. However this was not caused by the bias from the source meter because probability plots have shown that the measurements per voltages are normally distributed.

To make the results more reliable some experimental adjustments on the system were made. The external influences were minimized by first preventing the contamination of the system due to the cleaning of the lab, the chipholder and the chip. Then the influence of vibrations on the measurement was decreased by putting the set-up on a vibration-free table and last the influence of the temperature on the forming of airbubbles was minimized by using reducing the time of using the microscope. Next the set-up was optimized by making a better fixation for the electrodes on the chipholder by using a screw-ring connection and replace the broken wires. Last the measurement method was adjusted by by filling the reservoirs with a 1000 μL finnpipet in such a way that there isn't a air layer formed between the reservoirs of the chip and the chipholder. Also the reservoirs were equally filled with 140 μL sodium chloride solution to prevent the emergence of a driving force.

Despite of al these optimizations at the verification of the improved system the measurements still differed a lot between the measurement series and even within one measurement series. Nonetheless during the optimization some trends have been seen regarding the behaviour of the current and the measure of overlap of the Debye Layers. If the overlapping of the Debye Layers is high the behaviour of the current became first Ohmic, then limiting and as last overlimiting, if the overlapping is medium or low the behaviour of the current became respectivitly nonlinear and linear.

It was shown that the inconsistency of the results weren't caused by problems with the nanochannels, because after comparison of the empirical and the theoretical conductance the surface charge of the nanochannels was find to be 0.5-1.5 mC/m^2, which is quite realistic.

Some other explanations for the inconsistent results are water splitting at random nucleation points in the system, the local electrical field gradients caused by the asymmetric on chip electrodes and Joule heating due the resistance of the system which all will cause random formation of vortexes in the systems which will lead to unpredictable ion fluxes. But they have to be investigated in more detail, before any conclusions can be drawn.

7 Recommendations

In order to get a better understanding of the reasons for the inconsistent results of this investigation more research is required. The phenomena which can arise in the used set-up are very complex and investigating them in the current set-up will be quite difficult. However the water splitting at random nucleation points in the system is the only explanation that can be relatively easy tested by looking at the local pH differences. It can be done by the optical comparison of two kinds of dyes whereby one of them is pH sensitive and the other isn't. Examples of such dyes are AlexaFluor (pH-insensitive) and Fluorescein (pH-sensitive). Another possible method is FLIM (Fluorescent Lifetime Imaging Microscopy), in which the lifetime of probe molecules is measured.

Because of the very difficult troubleshooting of the current set-up it will be almost impossible to do in a reasonable amount of time the actual experimental investigation of the overlimiting current in this micro-nanochannel device. Therefore it can be recommended to make a new simpler design whereby the knowledge gained in this research are taken into account.

One of the weaker points in the current system is the connection between the reservoirs which are on the chip and the reservoirs of the chipholder. This connection can be improved by making a new set-up whereby the whole reservoir is integrated in one device. In this way both the reservoirs and the chip can be flushed to eliminate any air and are definitely connected to each other.

Another thing that can be recommended is to not use chips with integrated electrodes on the chip while using external ones because the electrodes on the chip can result in local electrical field gradients which can influence the behaviour of the current.

In the present used set-up the dimensions of the microchannels are very large with respect to the dimensions of the nanochannels, which maybe can result in lower ion fluxes through the nanochannels. When considering to building a new chip it can be recommended to take the ratio between the micro- and nanochannels into account. This can for instance be done by making a broad nanoslit instead of a nanochannel.

Also, the number of nanochannels etched in the current chip is quite high , namely 500, and the channels themselves are quite low (low fluxes), which increases the complexity of the system. Decreasing the amount of channels might result in a less complex system whereby the results can be better evaluated. A disadvantage can be that the ion flux through the nanochannel decrease, however this can be solved by making the nanoslots wider.

At this moment if there are any air bubbles formed during a measurement in the chip the air can't get out of the system. This can be prevented by using the material PDMS with a integrated nanochannels of glass.

When future measurements are performed with the new system it can be recommended to start with low voltages to suppress the Joule heating due to the resistance of the system. In this way the influence of Joule heating will be suppressed while testing the set-up, making it a bit less complicated.

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