

École polytechnique de Louvain

Experimental study of different shaped nanopores in a porous silicon cathodic exchange membrane for reverse electrodialysis

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ABSTRACT

In the context of blue energy harvesting in a reverse electrodialysis cell, the shape of the nanopores of the ion exchange membrane is a key parameter for its efficiency. In this work, the impact of porous silicon pore topology is investigated using numerical simulation and the results are validated using experimental tests.

The initial numerical simulations confirms that smaller pore radii imply better selectivity, while osmotic current increases for larger pores. Based on these results, three topologies are selected for an in depth study: conical pore, pencil-shaped pore with 70:30 ratio (i.e. 70% of the length being cylindrical and the rest conical) and pencil-shaped pore with a 50:50 ratio.

The numerical simulations show that, although the conical pore offers a better selectivity and membrane potential, the corresponding internal resistance increases and therefore reduces the current flow. The Membranes with pencil-shaped pores are a trade-off between the excellent selectivity of conical pores and the higher current flow of cylindrical pores.

Both membranes are then tested experimentally. Membranes with conical pores give maximum power densities of 1.8 mW/m^2 (four to five times higher than those with cylindrical pores). Membranes with pencil-shaped pores show similar selective performance and slightly lower electrical resistance.

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ACRONYMS AND NOTATIONS

Acronyms

PRO	Pressure Retarded Osmosis
RED	Reverse ElectroDialysis
IEM	Ion Exchange Membrane
EDL	Electrical Double Layer
KCl	Potassium chloride
NaCl	Sodium chloride
AEM	Anionic Exchange Membrane
CEM	Cathodic Exchange Membrane
CMOS	Complementary Metal-Oxide-Semiconductor
MEMS	MicroElectroMechanical Systems
SOI	Silicon On Insulator
PSi	Porous Silicon
WINFAB	Wallonia Infrastructure for Nano FABrication
HF	Hydrofluoric acid
SEM	Scanning Electron Microscope
LPCVD	Low Pressure Chemical Vapor Deposition
HMDS	hexamethyldisilazane
RF	Radio Frequency
SiO₂	Silicon dioxide
UV	Ultra violet
WEC	Wedge Error Compensation
TMAH	tetramethylammonium
RIE	Reactive Ion Etching
ICP-RIE	Induced Coupled Plasma Reactive Ion Etching
BHF	Buffered Hydrofluoric acid
Al	Aluminium
KOH	Potassium Hydroxide
DRIE	Deep Reactive Ion Etching
IV curves	Current-voltage curves
DI	DeIonized
IPA	IsoPropyl Alcohol, Isopropanol

Notations

- ϵ_0 : Vacuum permittivity = $8.85 \times 10^{-12} [F/m]$
- k_b : Boltzmann's constant = $1.38 \times 10^{-23} [m^2 kgs^{-2} K^{-1}]$
- F : Faraday's constant = $95\,485 [sAmol^{-1}]$
- R : Universal gas constant = $8.314 [JK^{-1}mol^{-1}]$
- T : Absolute temperature = $300 [K]$
- λ_D : Debye length = $10\text{-}20 [nm]$

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CHAPTER 1

INTRODUCTION

1.1 Context

Nowadays, fossil energy sources are declining, while the climate issues they cause are on the rise. So it's important to focus more closely on renewable energies such as solar, wind or water energy. The latter is referred to as blue energy. This energy can be harvested via reverse electrodialysis, in which the concentration gradient between two saline solutions is exploited. The efficiency of such a method depends crucially on the ion exchange membrane between the two solutions.

Most membranes available on the market these days are made from polymers, but these are difficult to integrate with CMOS¹. It has consequently become interesting to look into silicon membranes, since silicon can be easily integrated into CMOS and its porosification is known and controllable. Porous silicon is manufactured by electrochemical etching of monocrystalline Si. This method results in nanopores penetrating the silicon. The properties of these channels determine the membrane's selectivity and performance.

The porous silicon membranes considered give maximum power densities between 0.1 and 3.5 mW/m^2 . This may seem low, but typical sensor power consumption ranges between 0.5 mW and 5 W . Hence it is conceivable that such membranes could be used to fully or partially power such a system [1].

¹Complementary Metal-Oxide-Semiconductor

1.2 Master thesis objectives

In an attempt to improve this recovered power density, the pore topology of the ion exchange membranes will be studied. As explained above, porous silicon is chosen as the membrane material because of the ease with which its porosification can be controlled. Pore topology has a significant influence on membrane performance.

To this end, numerical simulations will be carried out to find the optimum pore topology. The three topologies considered are: conical pores and two different pencil pores. To produce these pores, a single-layer study will be carried out prior to the manufacture of the final membranes. Once the membranes are manufactured in WINFAB², their I-V curves are measured in the WELCOME³ laboratory to determine the membrane potential and the current flowing through it. Based on these two measurements, the selectivity and maximum power density of the membrane are determined.

Therefore, the main objective of this work is to study numerically and experimentally the characteristics and potential benefits of the three topologies mentioned above.

1.3 Master thesis outlines

This master thesis is arranged as follows :

- **Chapter 2 : State of the art** summarizes the key concepts that are important for a complete understanding of this work.
- **Chapter 3 : Materials and methods** presents the methodology to fabricate and determine the properties of porous silicon membranes.
- **Chapter 4 : Study of optimal pore topology and anodization for porous silicon membrane** explains the design process of the porous silicon membrane. The reflexion which led to the choice of the topologies as well as the methodology to achieve them are detailed herein.
- **Chapter 5 : Experimental results** gathers the scientific findings and discussion on the impact of pore topology on the reverse electrodialysis (RED) efficiency. Some perspectives for other improvements of the efficiency are proposed.
- **Chapter 6 : Conclusion** summarizes the main results obtained in the course of this work.

²Wallonia Infrastructure for Nano FABrication

³Wallonie ELeCtronics & COmmunication Measurements

CHAPTER 2

STATE OF THE ART

2.1 Blue energy

Blue energy, also known as osmotic power, is a way to create electricity by using the gradient of concentrations between two solutions separated by a semipermeable membrane. This renewable energy source could allow to create up to 2.3 MJ of Gibbs energy with 1m^3 of fresh water and salted water without any fuel cost nor carbon dioxide emission [2]. Figure 2.1 shows an example of the natural cycle of water used for different sources of salinity gradient power [3], [4].

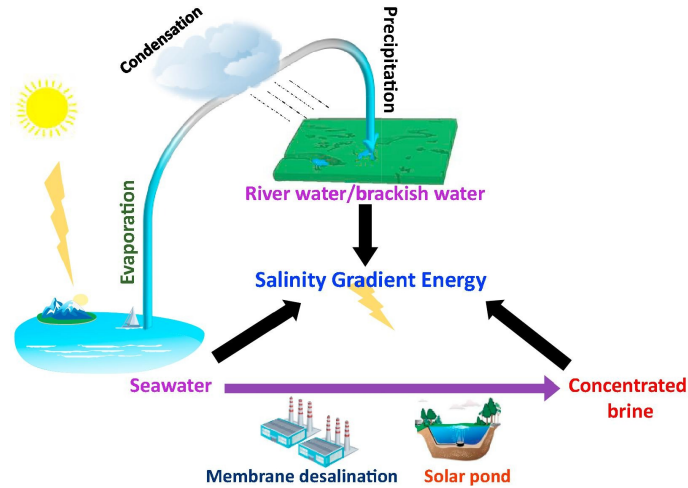


Figure 2.1: Example of the continuous use of salinity gradient energy. Extracted from [5].

That being said, blue energy does have negative aspects. For instance, its waste product i.e. the water with an intermediate salinity, called brackish water, has to be released somewhere. Ecosystems are generally designed to live in a freshwater or seawater environment, not in between. To be sure not to damage either system, the resulting water should be dumped at the embouchures involving significant water transport.

There are different ways to recover this energy. The two most advanced ones are Pressure Retarded Osmosis (PRO) and Reverse Electrodialysis (RED). PRO is the most developed method to this date and it is based on the mechanical principle represented on figure 2.2. The ion free water will pass through the membrane to balance the concentrations of the solutions. This movement creates a difference of pressure which is used to turn the turbines. This method is active as it requires a continuous pumping to bring new water in the system. The second method (RED) relies on electrochemical reactions to transform an ionic current into an electric current. This one is detailed in the following section (2.2) and used throughout this study. There are other methods but they will not be detailed in this work.

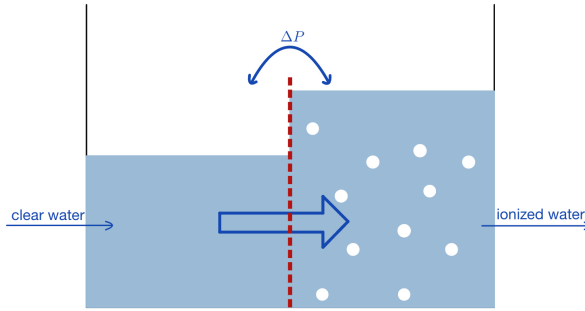


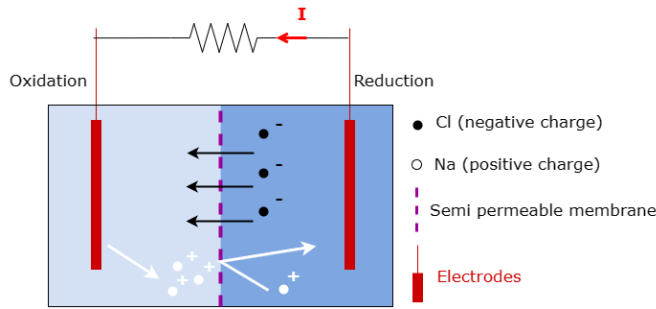
Figure 2.2: PRO method schematic

2.2 Working principle of reverse electrodialysis

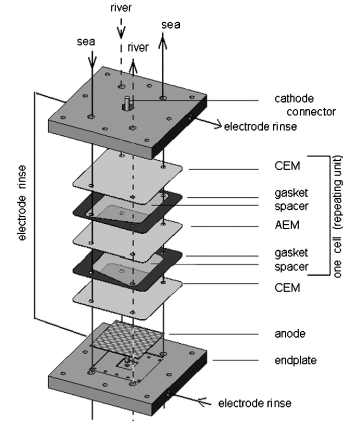
RED is a way to transform ionic current into electric current. This mechanism takes advantage of the natural tendency of solutions to balance concentrations. The system shown in figure 2.3a is constituted as follows: two solutions (clear water and salt water) are in a closed system, separated by a selective membrane called ion exchange membrane (IEM). The difference in ion concentrations generates an ion flow and the selective membrane allows to select which type of ion will go through the membrane.

These ions then generate redox reactions at the two electrodes each immersed in one of the two solutions. The circuit is closed by a charge placed between the two electrodes and the current passing through this charge is then recovered. A system like this one provides a very low energy source compared to batteries for instance which can provide up to hundreds of Wh/kg [6]. To date, only 0.6 Wh/kg are recoverable with a RED system [2]. These figures imply that such a power supply process could only be used in tiny electronics MEMs with low power consumption need.

If one would want to use it for higher power demands, the system would need to be optimized. The efficiency of the system will depend on the pumping method (to bring the water into the system), the ion concentration on both sides of the IEM and the selectivity (i.e. property to let one type of ions go through or not) of the membrane.



(a) Schematic of the RED system



(b) Schematic of a single cell. Extracted from [7]

It is important to note that by stacking and alternating membranes of opposite permeability, one can obtain a much increased electrochemical potential. One can see in figure 2.3b a reverse electrodialysis stack with one cell. By stacking several of these cells one can obtain a power density of 0.93 W/m² which was the best reported result in 2009 by stacking 50 cells of 10cm x 10cm each [7].

2.3 Selective membrane

2.3.1 Donnan exclusion

The permselectivity of an IEM is its selectivity to the transport of ions of opposite charges. It is due to the Donnan equilibrium which is developed as follows [8] [1].

Considering an IEM and an adjacent electrolyte solution, the medium inside the membrane and solution are different. Therefore an ion has different interactions with both. The equilibrium depends on the chemical potential and electrical potential and is reached when the electrochemical potential of all ions is equal in the two different phases. At equilibrium, for each ion :

$$v_i^m = v_i^s = \mu_i^m + z_i F \varphi^m = \mu_i^s + |z_i| F \varphi^s \quad (2.1)$$

Where m and s stand for membrane and solution (respectively), v_i is the electrochemical potential of the component i , μ_i the chemical potential, z_i the charge of ion i , F the Faraday constant and φ is the electrical potential.

Figure 2.4c shows that the Donnan potential (φ_D) is the electrical potential between the membrane and the adjacent solution. From this definition and equation 2.1, it gives :

$$\varphi_{Don} = \varphi^m - \varphi^s = \frac{1}{|z_i| F} (\mu_i^s - \mu_i^m) \quad (2.2)$$

It is interesting to develop the gradient of chemical potential to have a more explicit expression of the Donnan potential. The total change of the ion i between the membrane and the adjacent solution is given by :

$$\Delta\mu_i = \mu_i^s - \mu_i^m = V_i \Delta p + RT \ln \frac{a_i^s}{a_i^m} \quad (2.3)$$

Where V_i is the partial molar volume, Δp the pressure difference between the two mixtures, R the gas constant, T the absolute temperature and a_i is the activity of component i . This concentration gradient (and consequently the Donnan potential) depends on the salt concentration as shown in figure 2.4b. This means that for different solution concentrations the Donnan potential is different.

Combining equation 2.2 and 2.3, the complete expression of the Donnan potential between the membrane and a solution is given :

$$\varphi_{Don} = \frac{1}{|z_i| F} [RT \ln \frac{a_i^s}{a_i^m} + V_i (p^s - p^m)] \quad (2.4)$$

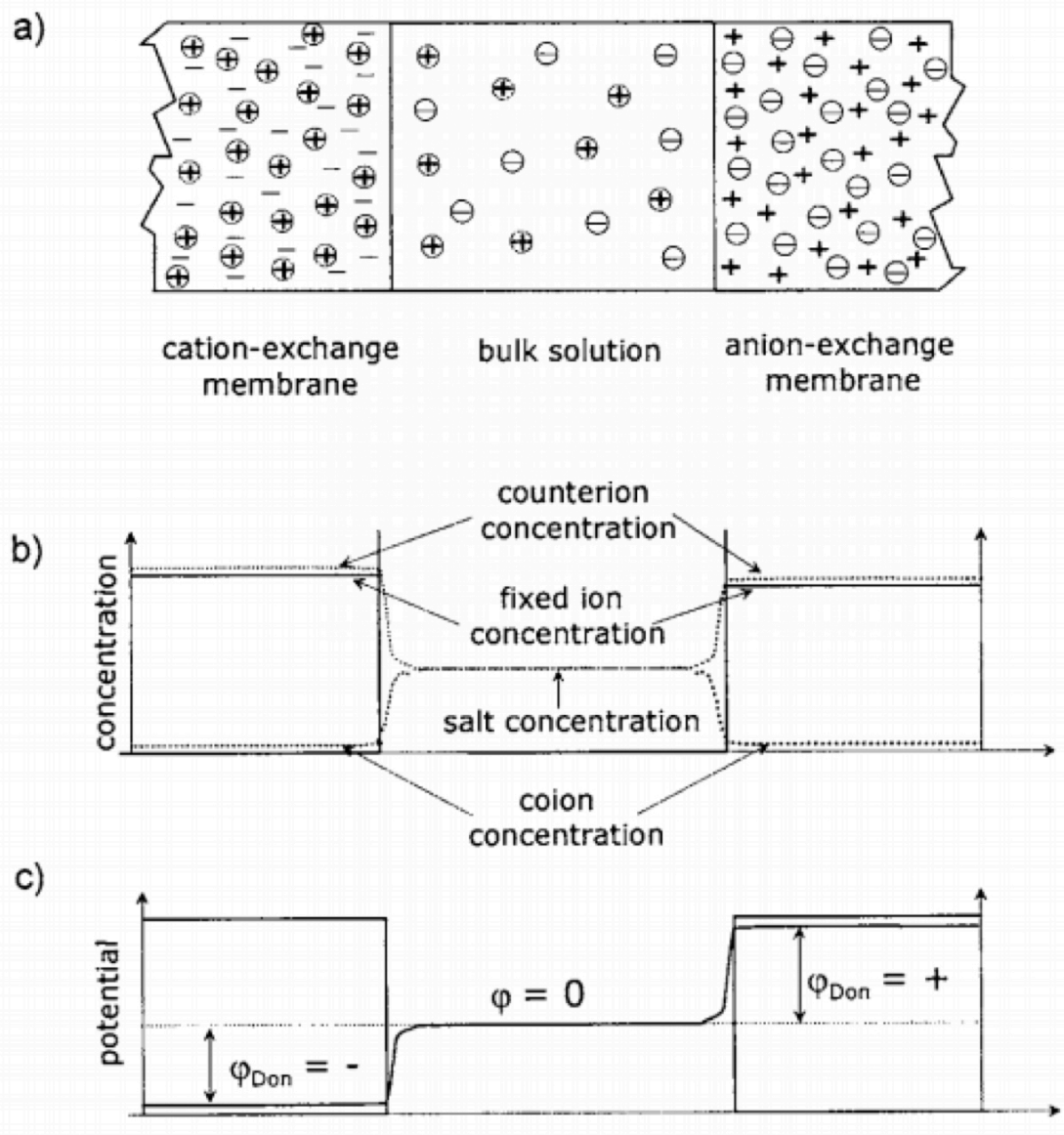


Figure 2.4: a) Visual representation of a bulk solution adjacent to a CEM and AEM. b) Distribution of ions in the different regions. c) Donnan potential in the different regions. Extracted from [8].

At equilibrium, no net transport of ions takes place between the membrane and the solution. This means that the concentration gradient driving force is counter-balanced by another driving force : the Donnan potential.

When a membrane is surrounded by two different solutions, the membrane potential is found by assembling the two respective Donnan potential.

The Donnan equilibrium (and permselectivity) depends on :

- Concentration of the fixed ions (proportional)
- Concentration of the electrolyte solution (inversely proportional)
- Valence of the co-ions (inversely proportional)
- Affinity of the IEM with the counter-ions.

2.3.2 Type of ion exchange membrane

An ion exchange membrane (IEM) is a semi-permeable membrane that excludes a specific type of ions. An efficient IEM has a high permselectivity, a low electrical resistance and a great mechanical and chemical stability [9].

Type of selectivity :

An IEM can either be cationic (CEM) or anionic (AEM). Figure 2.5 shows the structure of a polymer based CEM. Fixed anions are on the polymer matrix and they are surrounded by mobile cations (called counter-ions). The co-ions (mobile anions) are almost completely excluded because their electrical charge is the same as the fixed ions. Therefore, in an ideal CEM, only cations are able to transfer through the membrane.

For AEM, it is the same principle but with fixed cations resulting in an exclusion of the cation co-ions [9].

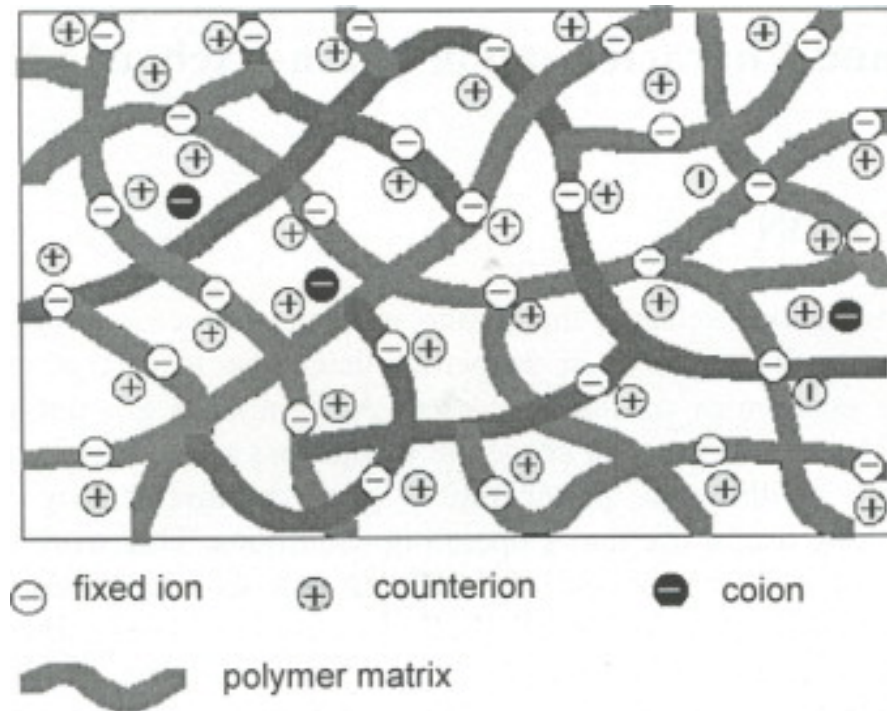


Figure 2.5: Schematic drawing illustrating the structure of a cation-exchange membrane. Extracted from [9].

Type of material :

The selective membranes can be either made from polymer or from inorganic material. **Polymer based membranes** are very appreciated as they do not cost much (between 0.2 and 5 \$/cm² [10]). They are also very versatile as their properties depends on the chosen monomer. When such a membrane is immersed into water, the charges are poorly attached to the polymer chains therefore allowing mobility of the counter-ions.

However, these membranes suffer from diverse factors which usually come with time. For instance, depending on the polymer and the solution, it will be damaged by chemical degradation. One should also take the swelling into account when using these membranes as the water always finds its way through the polymer structure.

Additionally, polymer membranes are not easily integrable with CMOS and MEMS technologies. The following type of membrane can overcome these problems.

Inorganic based membranes can be made out of aluminum vanadate, strontium tungstoarsenate, porous alumina, porous silicon and others but this work will mainly focus on porous silicon. As said before, these membranes will suffer less

from chemical degradation and swelling. However, these materials are more fragile and the IEM efficiency is generally reduced [11] [12] [13] [14] [15].

2.3.3 Electrical double layer

When a solid surface and a conductive fluid come in contact, an electrical double layer (EDL) appears. Several models have been developed over time to explain this double layer. Figure 2.6 shows the 3 main models considered to date : Helmholtz, Gouy-Chapman and Stern model.

The **Helmholtz** model considers that the double layer has two layers of opposite charge separated by a fixed distance.

The **Gouy-Chapman** model considers that the layer is not rigid but diffuse. This allowed to explain that the EDL is impacted by the applied voltage as well as the ionic concentration.

As the second model is based on assumptions that do not accurately represent reality, the **Stern** model is introduced, combining the main ideas of the two previous models.

According to Stern, the double layer is divided into several parts.

- The first, called the Stern layer, is defined as the space between the charge on the surface itself (φ_b) and the almost compact layer of counter-ions close to the surface (Helmholtz vision).
- The second layer is called the diffuse layer. It is composed of the remaining counter-ion charges in diffuse form. In this layer, the electrostatic attraction that brings the counter-ions closer to the surface is combined with the thermal agitation that moves them away to it (Gouy Chapman's vision).

Stern considers that the electrical potential is a linear function of the distance to the surface in the Stern layer and that the function becomes exponential in the diffuse layer until electrostatic equilibrium is reached in the solution at the centre of the channel (φ_s). The potential in the imaginary plane between the stern and the diffuse layer is called the zeta potential (φ_i or ζ in literature). It can be used to estimate the double layer's charge degree.

Assuming that the solution of the potential φ at a distance x from the surface is mainly governed by the Gouy-Chapman solution, this profile is exponentially decreasing :

$$\varphi = \zeta e^{-x/\lambda_D} \quad (2.5)$$

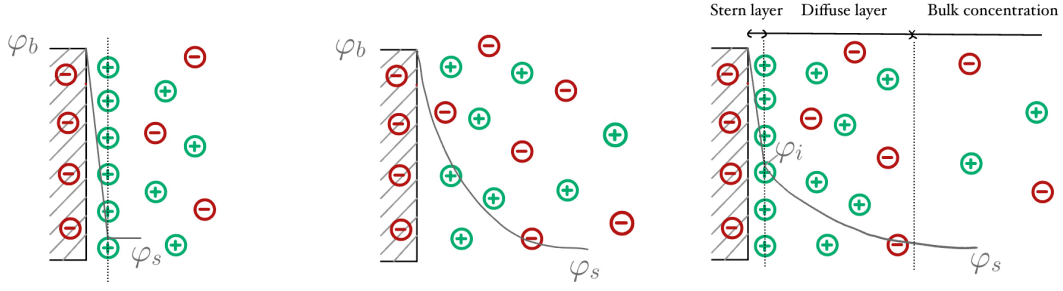


Figure 2.6: a) Helmholtz double layer mode. b) Gouy-Chapman double layer model. c) Stern double layer model. Inspired by [16].

Where x is the distance from the surface and λ_D the Debye length. The Debye length represents the range for which the net electrostatic effect of a charged ion persists in electrolytes solution. It is given by

$$\lambda_D = \sqrt{\frac{\epsilon k_b T}{\sum_i C_{i0} q_i^2}} \quad (2.6)$$

Where ϵ is the permittivity ($\simeq 80\epsilon_0$ for water), k_b the Boltzmann's constant, T the absolute temperature, C_{i0} the ionic concentration of species i outside of the double layer and q_i the charge of the ion species i .

This length is inversely proportional to the ionic concentration. For example, for a saline solution (NaCl) at room temperature, the Debye length is 9.6 nm for a concentration of 1mM, whereas it is 30.4 nm for a concentration of 0,1mM.

2.3.4 Permselectivity of nanopores

As a reminder, the permselectivity of an IEM is its selectivity to the transport of ions of opposite charges.

When a pore is filled with an electrolyte solution, the double layer forms over a thickness of λ_D as explained in the previous section. Figure 2.7 shows the cross-section of such a pore and how it is affected by the surface potential for different radii of the pore. If the pore radius is relatively large compared to the Debye length, the solution in the middle of the channel is not affected. In this case, electro osmotic flow is more often studied.

However, if the pore radius approaches the Debye length, the electrical potential within the pore cannot reach the bulk potential (φ_s). This phenomenon of the

potential spanning the entire cross-section of the pore is called EDL overlap. By imposing a pore radius at the Debye length, EDL overlap takes place and the pore is enriched in counter-ions. This facilitates their mobility and makes it more difficult for the co-ions to move, so the flow is (mainly) composed of counter-ions. Therefore the nanopore becomes more selective and permselectivity increases.

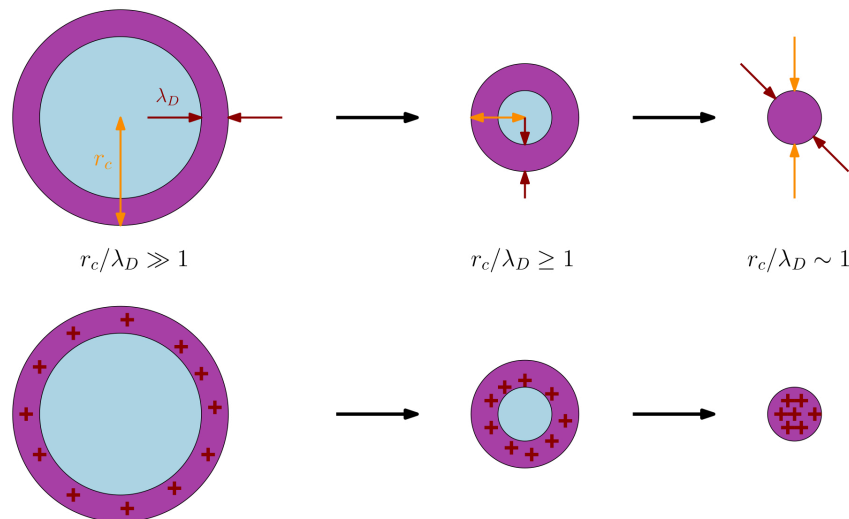


Figure 2.7: Selectivity through Debye length diameter pores. Extracted from [1].

2.4 Equivalent electrical circuit of a RED cell

An IEM in a RED cell can be modeled as a voltage source with an internal resistance in series as shown in figure 2.8. The total electromotive force generated in RED, is the Open Circuit Voltage ($OCV=V$). When no current flows through the membrane this measured voltage is the membrane potential (E_{diff}). The internal resistance R_i , is composed of the Ohmic resistance, the non-Ohmic resistance and the resistance of the electrode system. The Ohmic resistance is mainly due to the resistance of the membranes and feed compartments. The non-Ohmic resistance can be measured using electrochemical impedance spectroscopy and is influenced by diffusion and the electrical double layer. The resistance of the electrode system is due to the Nernst voltage [1].

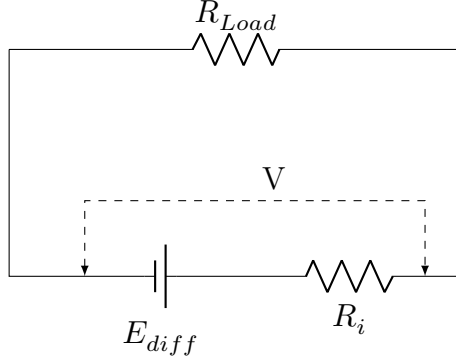


Figure 2.8: Equivalent electrical circuit of a RED cell with a load.

From equation 2.7 and 2.8, the power generated in a RED cell with an IEM is found. V is the voltage seen by the load (also called OCV), I is the current going through the elements of the circuit and R_{load} is the resistance of the load.

$$E_{diff} = V - IR_i \quad (2.7)$$

$$P_{IEM} = VI \quad (2.8)$$

$$P_{IEM} = E_{diff}^2 \frac{R_{load}}{(R_{load} + R_i)^2} \quad (2.9)$$

The maximal power density and the transference number are two of the IEM properties often used to quantify the efficiency of a RED cell.

Maximal power density

The power generation is maximal when the load resistance matches the internal resistance ($R_{load} = R_i$). Generally, to determine membranes efficiency, power densities are used so the maximal power generated is divided by the surface of the membrane (A).

$$P_{max} = \frac{1}{A} \frac{E_{diff}^2}{4R_i} \quad (2.10)$$

The power density has to be specified along with its RED conditions as they impact the open circuit voltage and internal resistance. Table 2.1 gathers the power density of different membranes with their condition found in the literature.

Research in micro scaled RED have been made. Kim and Duan [17] reached a maximum power density of 7.7 W/m^2 using nano-channels of silica and potassium

chloride (KCl). In Winfab, porous silicon is studied and reached power densities of $0.32 \text{ mW}/\text{m}^2$ using sodium chloride (NaCl) in concentration 0.1 and 0.01 M [1].

Transference number

The transference number (t_+) is defined as the ratio of the electric current derived from the cation to the total electric current. A t_+ close to 1 (0) implies that the current is mainly due to cations (resp. anions) in motion and $t_+ = 0.5$ means that the membrane is not selective at all [30].

$$t_+ = \frac{I_{cation}}{I_{cation} + I_{anion}} \quad (2.11)$$

From equations 2.7 and 2.11, the membrane potential can be expressed as in equation 2.12. Due to this relation between E_{diff} and t_+ , it is possible to experimentally describe a membrane's selectivity with the voltage measures using 2.13.

$$E_{diff} = (1 - 2t_+) \frac{RT}{zF} \ln\left(\frac{\gamma_{CH}C_H}{\gamma_{CL}C_L}\right) \quad (2.12)$$

$$t_+ = \frac{1}{2} - \frac{zF}{2RT} \frac{E_{diff}}{\ln\left(\frac{\gamma_{CH}C_H}{\gamma_{CL}C_L}\right)} \quad (2.13)$$

The permselectivity is determined by the ratio of the flux of specific components to the total mass flux through the membrane under a given force [9].

$$\alpha = \frac{t_{cou}^m - t_{co}}{t_{co}} \quad (2.14)$$

Where *cou* and *co* stand for counterion and co-ion and t^m represents the transference number inside the membrane.

Table 2.2 gathers the properties of commercial and tailor-made homogeneous IEMs. In Winfab, porous silicon with SiO_2 membrane reached a permselectivity of 64.12 % using a 0.1 M and 0.01M NaCl solutions.

Membrane	Produtor	A [cm^2]	$\delta[\mu\text{m}]$	N	Electrolyte	Electrode	v [cm/s]	$P_{d,max}$ [W/m^2]	Ref.
FAD/FKD	FunasTech, GmbH, Germany	10×10	82	50	0.05M $\text{K}_4\text{Fe}(\text{CN})_6$, 0.05M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.25M NaCl	$\text{Ti} - \text{RuO}_2/\text{IrO}_2$	4.2	6.7 (60°C)	[18]
FKS/EAS		10×10	30–40	5	0.025M $\text{K}_3\text{Fe}(\text{CN})_6$, 0.025M $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.25M NaCl	$\text{Ti} - \text{RuO}_2/\text{IrO}_2$	0.56	2.2	[19]
FKD and FAD		10×10	40–80	25	0.25M NaCl	$\text{Ti} - \text{RuO}_2/\text{IrO}_2$	58.3	1.17	[20]
Neosepta ACS/CMS	Tokuyama Inc., Japan	10×10	120–200	5	0.1M $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1M $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.5M NaCl	$\text{Ti} - \text{RuO}_2/\text{IrO}_2$	4.2	3.8	[21]
Neosepta CMX/AMX		10×10	134–164	2–30	0.25M NaCl	Capacitive electrodes ($\text{Ti} - \text{Pt}$ with activated C)	1.7	0.95	[22]
Selention AMV/CMV	Asahi Glass, Japan	10×10	110–150	5	0.25M NaCl	$\text{Ti} - \text{RuO}_2/\text{IrO}_2$	58.3	1.18	[23]
AEM/CEM	Fujifilm, Netherlands	10×10	114–129	25	0.3M $\text{K}_3\text{Fe}(\text{CN})_6$, 0.3 M $\text{K}_4\text{Fe}(\text{CN})_6$ and 2.5M NaCl	$\text{Ti} - \text{Ru}/\text{Ir}$ mesh	1	1.06	[24]
T1 CEM/T1 AEM		6.5×6.5	115	10	0.1 M $\text{K}_4\text{Fe}(\text{CN})_6$ / 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$ with 0.25 M NaCl	$\text{Ti}/\text{Ru} - \text{Ir}$ mesh	0.92	0.7	[25]
Heterogeneous AEM/CEM	Hangzhou Qianqiu Inc., China	10×10	40–80	5	0.25 M NaCl	$\text{Ti} - \text{RuO}_2/\text{IrO}_2$	58.3	1.05	[26]
AEM/CEM		25×75	205–294	25	0.05 M $\text{K}_4\text{Fe}(\text{CN})_6$, 0.05 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.25 M NaCl	$\text{Ti} - \text{RuO}_2/\text{IrO}_2$	2.5	0.83	[27]
Ralex CMH- PES/AMH-PES	MEGA, Czech Republic	5×5	580±25	5	0.05 M $\text{K}_3\text{Fe}(\text{CN})_6$, 0.05 M $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.25 M NaCl	$\text{Ti} - \text{Pt}$ mesh	16	0.65	[28]
PC-SK and PC-SA	PCCell, Germany	8×8	90–130	10	0.6 M NaCl	Ti coated with Pt	3.5	0.33	[29]

Table 2.1: RED power densities and conditions reported in literature. A is the active membrane area, δ the thickness, N the number of cell pairs, v the flow velocity and $P_{d,max}$ the maximal power density. Extracted from [5].

Membrane	Type	$\delta[\mu m]$	$\alpha[\%]$	$R_a[\Omega cm^2]$	$SR[\Omega cm]$	Ref.
Qianqiu	AEM	294	86.3	2.85	97	[31]
PECH B-2	AEM	77	87.2	0.94	122	[32]
Neosepta AMX	AEM	160-180	90.7	2.35	138	[31]
IMD-40-PAES	AEM	64	94.35	1.65	258	[33]
KIER-CEM1	CEM	26	97.8	0.34	131	[34]
Qianqiu CEM	CEM	205	98.8	1.97	96	[32]
Neosepta CMX	CEM	140-200	99	2.91	171	[31]

Table 2.2: Properties of different IEMs. δ is the thickness, α the permselectivity, R_a the area resistance and SR the specific resistance. Extracted from [1].

2.5 Parameters influencing the IEM's properties

Many researchers have tried to quantify the effect of different parameters on the IEM properties, either experimentally or by numerical simulation. This section explains the most relevant findings in literature [2] [1] [35] [36] [37] [38].

2.5.1 Surface charge density

Surface charge density (σ) does not affect EDL overlap directly but rather the permselectivity. The total number of counter-ions must be equal to the total surface charge in order to have equilibrium. Therefore, increasing σ also increases the number of counter-ions while decreasing the number of co-ions. As counter-ions are the main charge carrier, it also increases the osmotic current by lowering the electrical resistance. This increases the maximal power density of the IEM [35].

Surface charge density depends on the material and is also a function of the pH. It is inversely proportional to the Debye length which depends on temperature and ionic strength of the solution [1].

2.5.2 Ionic strength

As explained before, ionic strength or concentration of ions in the solution impacts the surface charge density. More importantly, it impacts the Debye length which determines the thickness of the EDL. It is inversely proportional, therefore for a lower concentration, the EDL will be thicker [1].

The ratio of concentrations of the two used solutions impacts proportionally the membrane's potential following equation 2.12. This ratio is also said to improve

the ionic current for asymmetric geometries with a smaller section placed at the end of the channel [35] [36].

A bigger ratio also means a bigger driving force. This increases the electrical conductance of the channel, thus decreasing its electrical resistance. Electrical conductivity also improves with higher concentrations of electrolytes because in that case the EDL is shrunk compared to a lower concentration. Therefore more ions, whatever the species, are able to pass through the channel. However, impact on electrical resistance is less significant for lower concentrations.

The transference number depends on the ratio of concentrations but is also impacted via the changes in the Debye length. The latter is inversely proportional to the concentration.

There is a trade-off between the concentrations chosen and the ratio between these concentrations. A bigger ratio leads to better performances but the selectivity is better for lower concentrations [2] [35].

2.5.3 Temperature

As the temperature rises, the Debye length and surface charge density increase. This means that the number of counter-ions in the pore is higher, which improves selectivity. Temperature also has an impact on ion mobility, since the liquid's viscosity decreases [1].

2.5.4 Applied potential

C.R. Martin and Al did a study on how to change the permselectivity with an applied voltage. By applying a potential to the surface of a gold pore, ion become attracted towards that surface.

For a negative applied voltage, an excess of electron appears on the pore's surface. Thus, cations can be transported whereas anions are excluded from the channel [38].

2.5.5 Pore geometry

Radius

As the radius of the pore decreases, the transference number approaches 1 (or 0 depending if the IEM is cathodic or anionic respectively). For smaller radius, the membrane potential increases in absolute value [2].

Length

The selectivity and membrane potential improve for a longer channel. However, a longer channel also means a higher electrical resistance [2].

Figure 2.9 shows the impact of the radius and length's channel on the transference number and the membrane potential. Note that these results are for an alumina pore, meaning that the membrane is an AEM. In this case, an improving t_+ implies that it approaches 0.

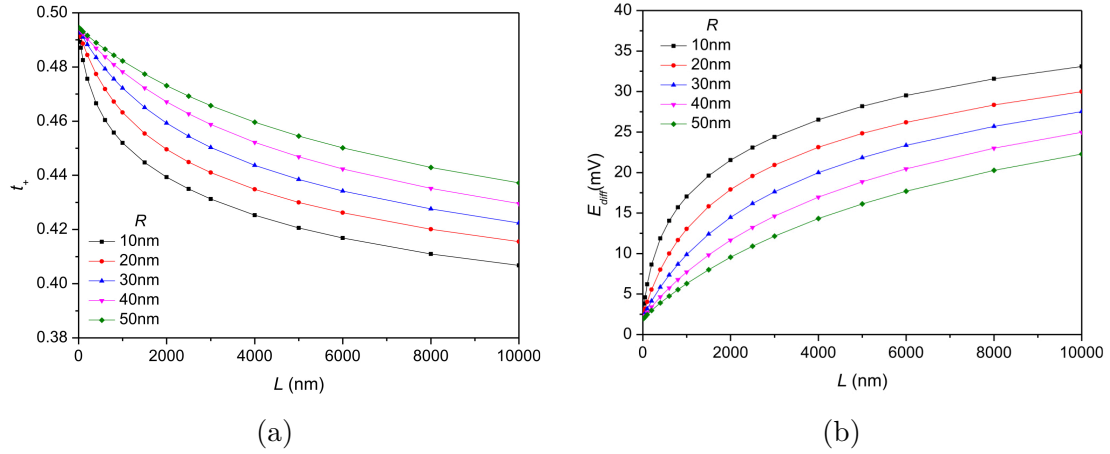


Figure 2.9: Impact of the radius and length's pore on a) the transference number, b) the membrane potential. Extracted from [2].

An optimal channel length-diameter combination exist thanks to the trade-off between selectivity and permeability [36].

Porosity and tortuosity

The porosity of a membrane is the ratio between the total pore volume and the apparent volume. This is further explained in section 3.1.3. A higher porosity means that there are more channels in which the ions can be transported. This means that in order to optimize the power density, the porosity has to be maximal. However, the more the substrate is perforated, the less bulk stands in the material to give it its structural resistance. For a porous material for instance, a too high porosity leads to an excessive fragility of the membrane [1].

The tortuosity is a parameter quantifying how straight the wall of the pore are. As it increases, the ions have a longer distance to travel. In numerical simulation,

it is generally assumed to be equal to 1 but in experimental results, it becomes a difficult parameter to measure.

2.5.6 Conical pores

As seen in the previous sections, several factors are responsible for the efficiency of energy harvesting. Figure 2.10 shows an example of a conical pore where different factors are involved. The difference in concentrations imposes a non-uniform EDL along the length of the channel. The difference in radii at the ends of the pore ensures that the selectivity is respected on the small side and does not reduce the flow of ions too much or obstruct them on the large side. It can be seen that if the orientation of the pore is reversed, the overlap and ion flow are reduced [37].

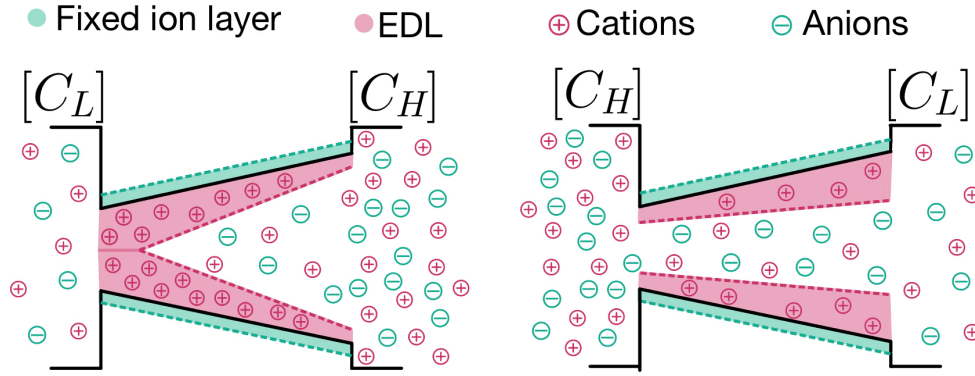


Figure 2.10: Schematic representation of EDL overlap depending on the orientation of the asymmetric pore. Left is the complete overlap of the EDL when the smaller tip of the nanochannel is adjacent to the low concentration solution. Right is a non sufficient EDL to overlap when the smaller tip is adjacent to the high concentration solution. Inspired by [37].

2.6 Conclusion and thesis objectives

Over the years, researchers have tried to improve the membranes used in reverse electrodialysis in order to maximise the system's efficiency. Many different membranes (mainly polymer) are already on the market, but these are prone to chemical degradation and swelling. Additionally, these are not very compatible with CMOS technologies. Therefore, it is important to look into inorganic solutions and try to bring their performance as close as possible to that of polymer membranes.

In this work, PSi was chosen as the inorganic material because it is already often used for CMOS processes and its porosification is easily controllable. As an additional advantage, its manufacturing process is fairly well known in Winfab. In order to optimise the properties of these membranes, different geometries will be studied.

Conical pores have already been studied with other materials or only via simulation in the case of PSi. In this work, a verification of the simulations and experimental results will be presented for conical pores. Then in order to try to find a trade-off between the electrical and mechanical resistance of the membrane while keeping the potential benefits of the cone, pencil shaped pores will be studied in simulation as well as experimentally.

CHAPTER 3

MATERIALS AND METHODS

3.1 Porous silicon

3.1.1 History of porous silicon

In 1956, a married couple named the Uhlirs, accidentally discovered porous silicon at Bell Laboratories. They were looking for a way to electrochemically machine silicon wafers for use in microelectronics. Instead of getting a smooth and uniform surface, they found holes propagating mostly in the $\langle 100 \rangle$ direction in the results of their experiment.

At that time, the interest for such a material did not really exist and it is only in the 70's and 80's that scientists have again looked at the subject for its very interesting spectroscopic properties. In those days, some were trying to integrate porous silicon (PSi) films to circuit technology while others were studying PSi for the oxide layer for SOI structures.

Moreover, porous silicon has a different quantum behavior than bulk silicon. This revived the interest for this material in the eyes of all scientists in the early 90s. At room temperature, PSi can produce an emission above the band gap of silicon (in bulk form).

Since then, porous silicon has been used to create optoelectronic devices, but these had too many chemical and mechanical weaknesses. Through the years the problems regarding the chemical stability were solved and since this material is compatible with conventional silicon microfabrication, many applications were born such as biomedical sensors (particle diffusion in porous capsules), optics and electronics such as this work [39].

3.1.2 Fabrication of porous silicon

In order to generate porous silicon, a silicon wafer has to be etched electrochemically in an electrolyte solution containing hydrofluoric acid (HF). This method is called anodization. The electrochemistry element is needed in this case because without it, the passive chemical dissolution would be very slow. The reason for such a slow passive reaction is the hydrides on the surface which passivate it and therefore limit the speed of the corrosion. Adding electricity to the system speeds up the reaction.

Figure 3.1 represents the set-up for the anodization. One can see that two electrodes are needed : the anode, also called the "working electrode", is the silicon electrode and is the most important because it is where the oxidation occurs thus removing the electrons of the solution. The other electrode is the cathode, also called the "counter-electrode", it is made out of platinum and it supplies the electrons. The reduction occurs at the counter-electrode. Together these electrodes keep a neutrality of charges and complete the electrical circuit.

If one wanted to measure the current simultaneously with the potential of such an electrochemical reaction, one could use a three-electrodes cell. The idea is to add a high impedance reference electrode connected into a specialized feed-back circuit to the two-electrodes set-up [39].

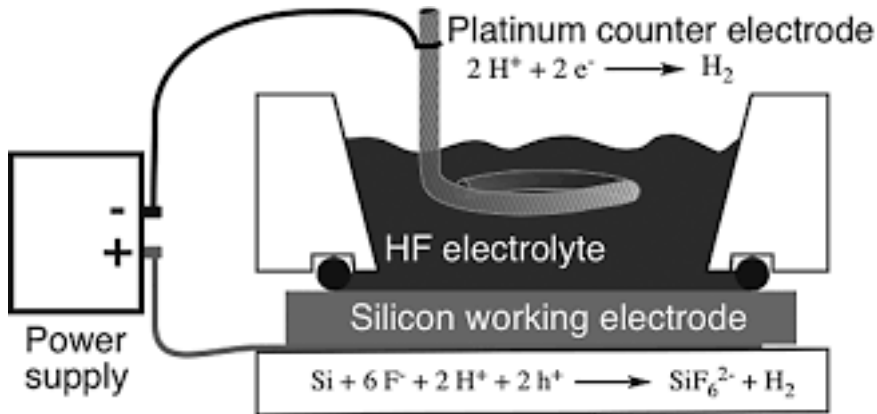
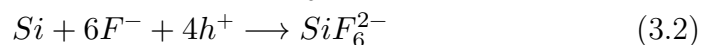
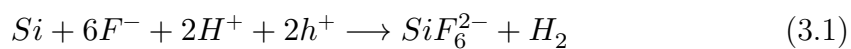


Figure 3.1: Schematic of a two-electrode electrochemical cell. Extracted from [39].

Electrochemical reactions in the silicon system

When performing anodization, two reactions can occur : a two-electron (eq. 3.1) or a four-electron (eq. 3.2) electrochemical oxidation of silicon. Whether one reaction will happen instead of the other is mainly depending on the current density.



For a lower current density, the holes (h^+) are essentially located at the tip of the pore but as the current density increases the etching begins on the lateral sides of the pore because the anodic etching is limited by ion diffusion resulting in larger pores and thinner walls. Figure 3.2 illustrates how past a certain threshold, the diameter of each pore becomes too great and the pores merge until forming a nearly uniform plane of etching. This phenomenon is called electropolishing and it occurs when equation 3.2 dominates.

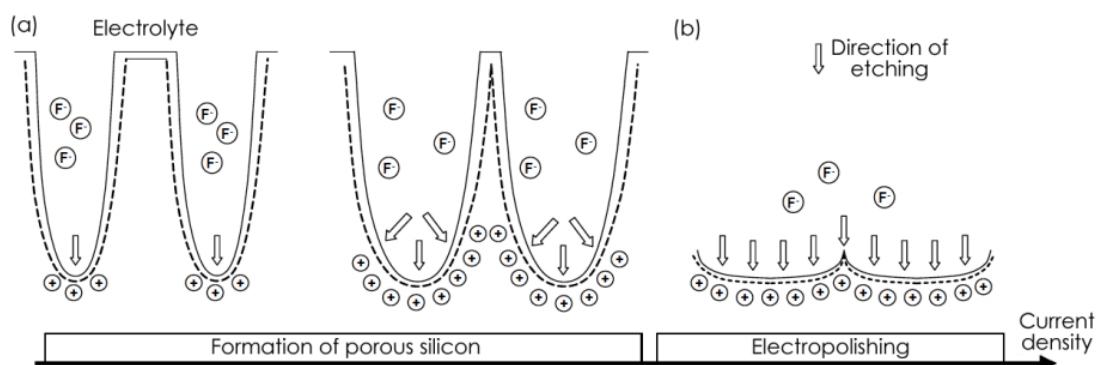


Figure 3.2: Impact of increasing current density on pore formation. Extracted from [40].

Figure 3.3 shows the curve of the current density (J) versus applied potential (V) and the different regimes of the reaction.

- First the porous Si formation regime where the current density increases exponentially with the applied voltage. In this regime, the pore formation is easily controllable as well as the etch rate.
- Second is the transition regime where the increase seems more linear. In this regime, pores continue their formation but the surface is slightly etched at the same time.

- Eventually there is the electropolishing regime where the current density will first decrease and then increase again but much more slower then in the other regimes.

The threshold between these regimes is mainly defined by the ratio between current density and HF concentration. In this work, the electropolishing and the transition region are avoided as much as possible [39], [40], [41] and [42].

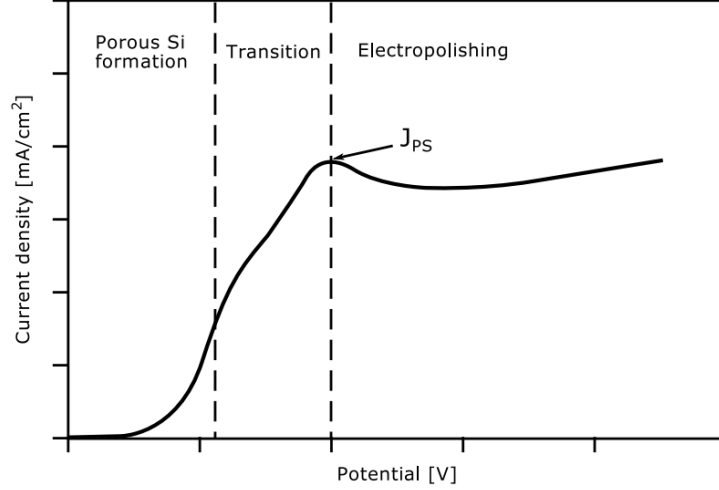


Figure 3.3: J-V curve for electrochemical etch of silicon with HF. Extracted from [39].

In reality, many parameters come into play for the formation of porous silicon and to this day all the ins and outs of this mechanism are not yet known. However we can learn the general trends from literature. The table 3.1 shows the impact of some parameters on the anodization.

Increase of	Porosity	Etching rate	Critical current
HF concentration	Decreases	Decreases	Increases
Current density	Increases	Increases	-
Anodization time	Increases	Almost constant	-
Temperature	-	-	Increases
Wafer doping (p-type)	Decreases	Increases	Increases
Wafer doping (n-type)	Increases	Increases	-

Table 3.1: Effect of anodization parameters on PSi formation. Inspired by [41], [43].

3.1.3 Morphology

Density

As the porous material contains holes, its density is lower than the bulk material it is made of. It is important to take into account the open or closed nature of the pores, thus here are the definitions used in this work.

- **true density** : Density of the material excluding pores and void. In this case 2.33 mg/l for the silicon.
- **bulk density** : Density of the material including pores, voids, and closed or inaccessible pores. It is always smaller than true density and is calculated as the product of the sample mass with the space it takes.
- **apparent density** : Density of the material including closed and inaccessible pores. It is often measured with a known volume of a liquid in which the sample is placed. The liquid only penetrates accessible pores or pores big enough for the probe molecule to penetrate. This means that the sample and the probe molecule can be measured at the same time.

Porosity

Porosity is defined as the ratio between the total pore volume and the apparent volume. Depending on the method used, total pore volume can vary and therefore one has to distinguish open porosity to closed porosity [39].

- **Open porosity** : the volume of pores accessible to a given probe molecule.
- **Closed porosity** : the volume of pores that are inaccessible to the probe molecule.
- **Total porosity** : open + closed porosity. The total volume of pores whether they are accessible or not.

Closed porosity can occur if the material has been (passively or actively) oxidized but also for other reasons such as an additional deposition for instance. One has to keep in mind that open porosity is only relative to a certain molecule and that it will be different for smaller molecule. Porosity is therefore strongly related to the pore size.

Pore size

PSi is categorized by its pore size :

- **Micropores** : diameter smaller the 2 *nm*.

- **Mesopores** : diameter between 2 *nm* and 50 *nm*.
- **Macropores** : diameter greater than 50 *nm*.

A nanostructure is defined as smaller than 100 nm. As all the diameter are well below this threshold, the three categories of pores can be classified as nanopores. However, in litterature one can find pores with a diameter close to a micron and these pores are called macropores.

As said before, the morphology of P*Si* depends mainly on the current density but it also depends on the initial wafer chosen : highly doped wafers will tend to give meso to micropores [39].

3.1.4 Transitional layer

When initiating anodization, a thin layer (generally less than 200 nm) is formed : the transitional layer in which pores are dense but small (less than 10 nm). Figure 3.4 shows that many of these pores end their journey in this layer whereas the others expand in diameter and grow in depth in the silicon bulk.

In this work, such a layer is not desirable. Indeed all these smaller or unfinished pores decrease the volume of solution that can enter the P*Si* when immersed into a solution.

To avoid such an heterogeneous layer, one can make a first electrochemical etching for a short amount of time, then use KOH to remove this layer while leaving "indents" of the right diameter to guide the following anodization.

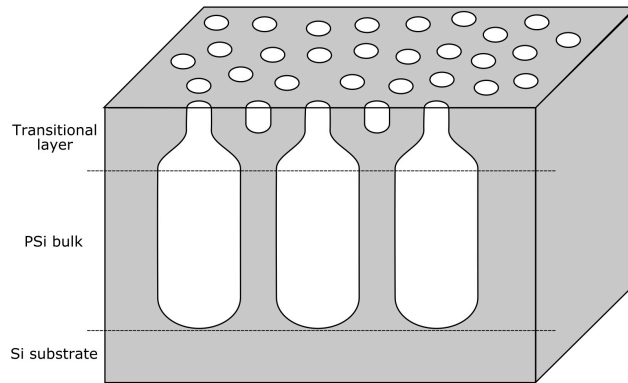


Figure 3.4: Schematic of the transitional layer, porous silicon layer and bulk layer. Extracted from [42].

3.1.5 Characterization of porous silicon

In this section, one can find the different tools used to characterize porous silicon viewed from the top or in a cross sectional view.

Interferometer

The interferometer is a surface characterization instrument. Using light reflection, it is possible to estimate the thickness of thin layers fairly accurately.

Originally, the Michelson interferometer splits a single beam from a coherent light source into two identical beams. Each beam then follows its own individual optical path before being reunited to reach a detector. The distance travelled by each beam results in a phase difference between them. This phase difference creates the interference pattern between the identical waves identified by the detector.

In this work, the interferometer is used to study the etching rate of anodization. A precise etching rate allows to obtain the targeted thickness [44].

Scanning electron microscope

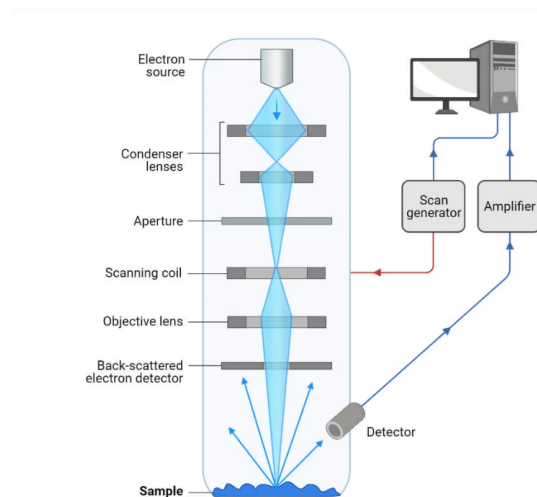


Figure 3.5: SEM working principle. Extracted from [45].

Since 1930, electron microscopy has evolved and led to scanning electron microscopy (SEM). The principle is to use back-scattered and reflected electrons to recreate a high resolution image of the analyzed surface. Figure 3.5 is a schematic of the working principle of a SEM. A source of electrons produces them under the effect of heat and a voltage applied between 1 and 40kV accelerates them. The beam of electrons is shaped by the lenses, which condense and direct the beam. The high-energy electrons arriving on the surface under study are called primary electrons.

Due to their kinetic energy, these cause the appearance of low-energy secondary electrons. In general, secondary electrons are used to determine morphology, while backscattered electrons provide information on the composition of the elements in the specimen. When the electrons enter the detector, a scintillator converts the impact into an electric current via flashes of light due to the scintillator's fluorescent nature. The electrical current recovered is then amplified and processed to recreate the image of the specimen being studied.

One of the main advantages of the SEM is that the sample does not need to be treated to be observed. Nevertheless, one should pay attention when studying microbial specimen as the SEM works in a vacuum environment. Also, oxidation must be taken care of as it will result in a drift of the electron beam and therefore a decline in the image quality [46] [45].

The SEM enables detailed images to be captured to analyse the distribution of pore diameters and membrane porosity using image processing software (ImageJ¹). The top view images such as figure 3.6a are used to determine the pore size radius and porosity on the PSi surface. Cross sectional images such as figure 3.6b provide the pore radius on the other side of the PSi as well as its depth.

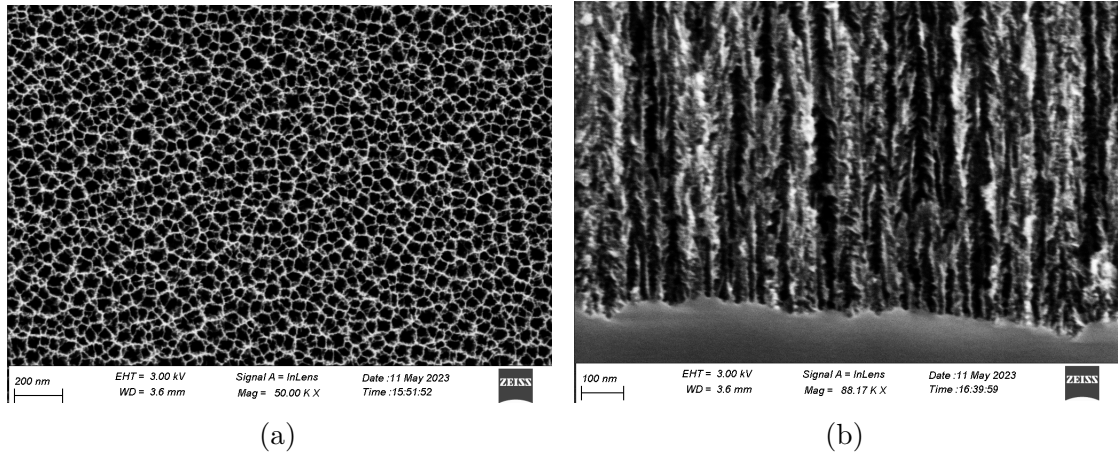


Figure 3.6: SEM images used in ImageJ to analyse the porosification parameters. a) Top view and b) cross sectional view.

3.2 Porous silicon membranes

3.2.1 Process

The process used for this work is the one developed by Roselien Vercauteren [47]. The initial wafer is double polished and doped with p++ 0.8-0.9 [$m\Omega/cm$]. A first oxidation takes place before depositing a polysilicon layer. This is then carved according to a mask visible on the figure 3.9b. The same mask is used on the backside, this time using aluminium deposition. Next comes the anodizing process explained in section 3.1.2. The process ends with a second oxidation prior to carving out the silicon from the back until reaching the membranes in order to

¹The methodology is explained in appendix 7.1

release them. This section explains each stage of the process in more detail. Each step corresponds to a number in the process flow on figure 3.7.

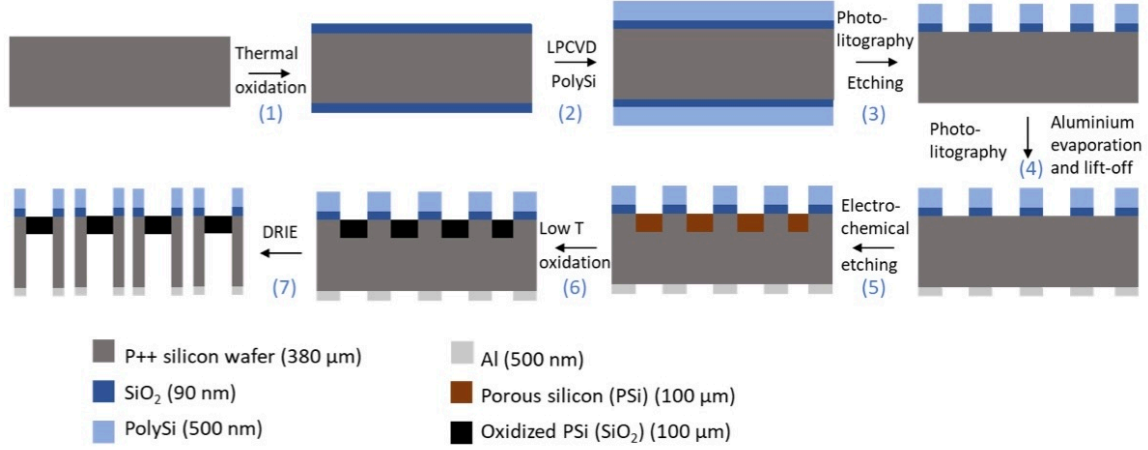


Figure 3.7: Process flow of a PSi membrane. Extracted from [47].

- **Wafer choice :**

The crystal orientation, the type of dopant and the resistivity are parameters playing on the morphology of the membrane. Indeed, the $\langle 100 \rangle$ orientation is used for the porous material, otherwise the holes would not be vertical but would spread at an angle of 45° for a $\langle 110 \rangle$ for example [39]. Regarding doping, a highly doped wafer with Boron is preferred because as said before a higher doped wafer tends to have meso or micropores. The resistivity measurement allows to assess if an oxide layer is present by measuring with the 4 point probe and comparing the result with the theory. Table 3.2 gathers the specifications of the wafers purchased from Sil'tronix (France) used in this work.

Specification	Prime CZ
Diameter	3" (76.2 ± 0.3 mm)
Type & dop	P-Bore
Orientation	$\langle 100 \rangle \pm 0.5^\circ$
Resistivity	$0.0008\text{-}0.0009$ Ω/cm
Thickness	380 ± 10 μm
Surface	Double side polished

Table 3.2: Specifications of the wafers

- **Thermal oxidation (1) :**

Oxidation can occur naturally. This is not desirable as the deposition of polysilicon will be neither controlled nor uniform. Since oxidation is inevitable, wet oxidation allows to know exactly which oxidation layer is present. In the process used in this work 110 nm are deposited at 750 °C in the KOYO thermo system 1. The thickness of this layer can be checked by ellipsometry.

- **Low pressure chemical vapor deposition (LPCVD) of polysilicon (2):**

The chemical vapor deposition represented on figure 3.8 works as follows: the material is conveyed in gaseous form, then adsorbed on the surface. These molecules then react on the surface and the by-products are released and pumped away. This technique is made at low pressure to have a uniform film by limiting the reactions in gas phase. The high temperature used lead to a film deposition also on the walls of the furnace meaning that the reaction rate will not be the same for each region of the wafer. This problem can be handled with temperature control by separating the furnace in zones with different temperatures.

In this case, 500 nm of polysilicon is deposited on both sides of the wafer by decomposition of silane at 620°C in the KOYO thermo system 2 [48].

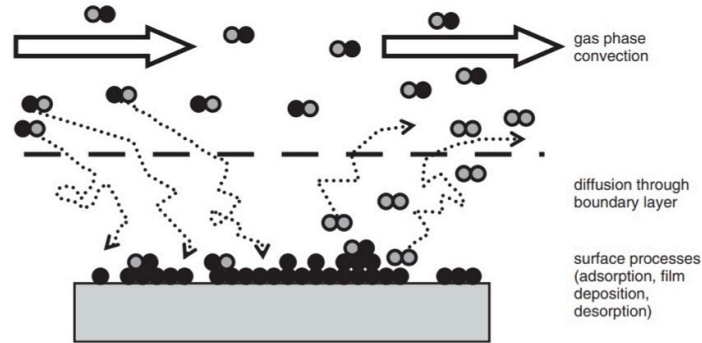


Figure 3.8: Chemical vapor deposition process. Extracted from [49].

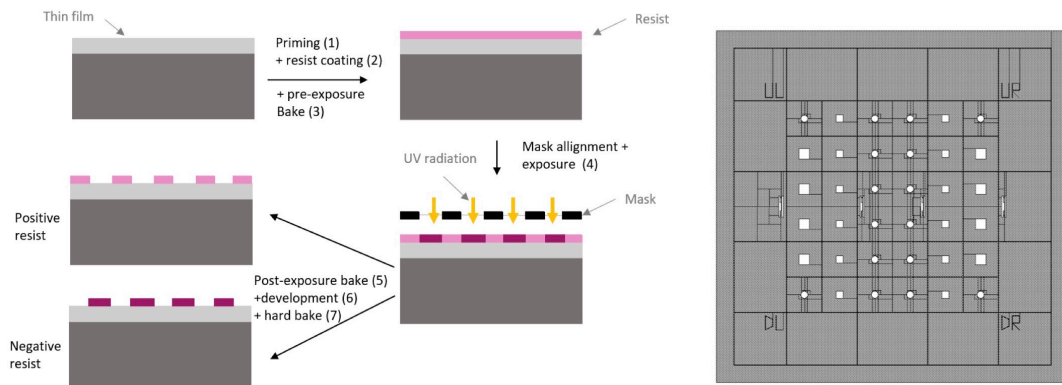
- **Positive lithography (3):**

In figure 3.9a, one can see the general process flow of a photolithography. It is a microfabrication technique used to pattern resist on the wafer according to a predefined mask. Afterwards an etching step or a deposition one can be made following the pattern created.

Lithography can be either positive or negative depending on the reaction of the exposed parts. If the regions of resist are made solid (resp. dissolvable) during exposure, then it is the unexposed (resp. exposed) parts that will dissolve during development. This is defined as a negative (resp. positive) lithography.

In this work's process, the wafer is cleaned after the LPCVD step. A layer of hexamethyldisilazane (HMDS) is added to improve the adhesion between the polysilicon thin film and the resist. This is done with vapor during 40 minutes at 120°C. After that, the resist (AZMIR 701) is spin coated and soft baked at 90 °C for 90 seconds.

Then the wafer and the mask are placed in the SUSS coater gamma which uses a hard contact and automatic wedge error compensation (WEC) to expose the wanted pattern with a 170 [mJ/cm^3] UV light. A post exposure bake at 110°C for 90 seconds is made, then the pattern is developed in tetramethylammonium (TMAH) for 60 seconds to dissolve the exposed regions and this step ends with a hard bake at 120°C for 90 seconds. Figure 3.9b shows the mask used in this work.



(a) General process flow of photolithography. Extracted from [41].

(b) Print of the PSi membrane mask. Extracted from [47]

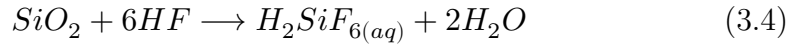
- **RIE etching + BHF bath (3):**

This step is the one that allows to transfer the pattern in the polysilicon layer and to remove the layer of this same material on the backside of the wafer. This is done by reactive ion etching (RIE) also called plasma etching. The wafer is placed in a vacuumed chamber and a radio frequency (RF) field is applied to excite the reactive gasses flowing. This leads to a bombardment of the wafer with a much higher etching rate for the vertical direction than the horizontal. This results in almost perfectly vertical walls.

One can use Fluorine to break the chemical bonds in the polysilicon layer as the halogen to silicon bonds are stronger.

Most specifically, this step is made by Induced coupled plasma reactive ion etching (ICP-RIE). The difference between these two processes is that it is possible to decouple ion current and ion energy applied to the wafer thanks to an ICP RF power source added to the cathode responsible for the DC bias [50].

Right after the ICP-RIE, the wafer is placed in a buffered hydrofluoric acid (BHF) bath to remove any remaining layer of oxide. Indeed the silicon dioxide (SiO_2) dissolves in HF following the equation 3.4



- **Negative lithography (4):**

The mask on the back side has to be already on the wafer when doing the anodization otherwise the membranes would break under the mechanical stresses the following steps imply. Unlike the first lithography, this one is negative. This means that the exposed parts will be solidified during the exposure. The same mask is used as on the front side. Again, first a layer of HMDS is applied for adhesion (120°C for 40 minutes) and then the resin is spin-coated. It is very important to align the mask correctly to the front surface pattern in order to release correctly the membranes.

- **Aluminium evaporation (4):**

Aluminium has been chosen because of its properties such as its chemical resistance to SiF_6 (useful as selectivity in DRIE step) but also because its deposition is relatively easy.

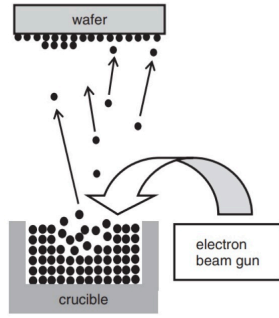


Figure 3.10: Electron beam evaporation.
Extracted from [49].

A 300 nm layer of aluminium (Al) deposition is made with electron beam evaporation. The whole mechanism takes place in a high vacuum chamber where the crucible containing the aluminum, the wafer and the electron beam gun are located. The latter emits electrons by Joules effect and accelerates them with a high voltage. These electrons hit the crucible sending the aluminum particles on the wafer with a high kinetic energy. The higher the vacuum, the less the electrons will collide with each other and the more they will follow a straight path between the source and target.

Finally, the wafer is bathed in acetone for the lift-off. The Al deposition that was made onto the resist is removed along with it, leaving only the aluminum layer in direct contact with the substrate.

- **Anodization (5):**

The principle of porosification has already been explained in section 3.1.2.

- A first anodization step is carried out, which is short enough just to prime the pores. For each batch of membrane this step lasts 30 seconds with a current density being the initial value for the real anodization.
- The sacrificial layer is removed with a 1 M potassium hydroxide (KOH) bath.
- The pores are continued according to the current density settings entered in the scripts governing the voltage source². It is mainly on this step that the optimization will be studied in this work.

- **Low temperature dry oxidation (6):**

Once again, the oxide layer should be as controlled as possible. Therefore a low temperature dry oxidation is made to be able to take this layer into account. Indeed, after the anodization, oxidation can lead to closed porosity and thus a lower efficiency. The mechanical weakness of the membranes requires lower temperature than the first oxidation. This oxidation takes 1 hour at 250 °C with a 1.5 L/min O_2 and 1.2 L/min N_2 flows and also allows to use an etch-stop in the next step.

²These scripts are described in section 4.2.1.

- **DRIE on the backside (7):**

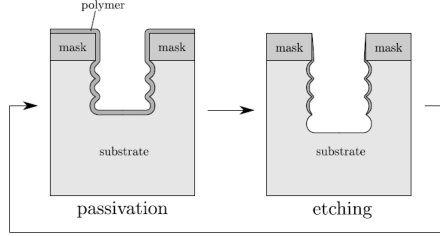


Figure 3.11: Bosch process steps. Extracted from [51].

In order to recover the membranes, the entire silicon substrate under the porous silicon (PSi) must be removed. To do this, deep reactive ion etching (DRIE) is used. More precisely the BOSCH process. Since this type of etching is isotropic, it is necessary to proceed in two alternating steps as shown on figure 3.11. First the surface is etched with SiF_6 and then comes the passivation step with C_4F_8 which will protect the walls from the next SiF_6 step.

As a reminder, the Al layer allows the etching to happen only where the membranes are located.

This step is performed in the Oxford Plasmalab System 100 under the parameters explicated in table 3.3. Around 330 cycles are performed to be able to etch circa 330 μm of Si and release the membranes.

	Etching	Passivation
Duration	13s	6s
SiF_6 flow	120sscm	1sscm
C_4F_8 flow	1sscm	150 sscm
RF power	30W	10W
ICP power	1500 W	1500 W
Temperature	-10°C	-10°C
Pressure	20mTorr	20mTorr

Table 3.3: Parameters used for the DRIE

- **Debond and clean (not shown):**

To release the membranes, the wafer is placed in a beaker with acetone and left there for 10 minutes. Once the dies debonded, they have to be cleaned with new acetone, methanol and water. To be certain that no residue of C_4F_8 is left, the dies are placed in the barrel with an O_2 plasma of 100W for 10 minutes.

3.2.2 Electrical characterization

As explained in section 2.4, the membrane potential (E_{diff}) and current flowing through the membrane (I) are needed to determine a P*Si* membrane efficiency. The following section describes the experimental set-up and its modelling.

Experimental set-up

The set-up that is used to determine the selectivity of the membrane as well as the power one can retrieve from a RED system is described as follows.

The cell (**l**) contains two reservoirs for the two solutions (**b** and **i**) which have different concentrations. These are separated by the membrane (**j**) under test. The two compartments are independent and are reunited with four screws. Two O-rings between each of the reservoirs and the membrane ensure that no solution gets out of the system.

Two pairs of electrodes are used.

- The first is the working (**h**) and counter (**d**) electrodes made of silver chloride. A voltage is applied between these electrodes leading to a current going through the membrane.
- The second is the reference electrodes (**a** and **g**). These are silver chloride electrodes kept in a KCl solution (**c**) and terminated by a frit (**k**). As both electrodes are in the same solution (KCl), the additional voltage drop due to the concentration difference is negligible. Which is not the case if normal working electrodes had been used.

The working and reference electrodes are connected to a Keithley Model 2400 Series SourceMeter (**e**) and to a Model DMM7510 digital multimeter (**f**) respectively. A computer is connected to the latter through GPIB-USB cables and connectors. The synchronization between the two instruments and definition of the parameters regulating the voltage sweep on the working electrode are set in a matlab code. Figure 3.12 shows all these elements and their connections. It is important to note that the positive electrodes will always be placed in the high concentration solution.

For each membrane, two pairs of concentrations were tested: $10^{-2}/10^{-3}$ and $10^{-3}/10^{-4}$ *M*. For each pair, two tests were carried out: the first with the front face towards the high concentration and the second towards the low concentration. For a membrane with symmetrical pores, the only minor impact should be due to the irregularities introduced by the DRIE, but otherwise it should be possible to observe a difference between the two tests. Each situation (membrane-concentrations-direction of the membrane) is tested three times.

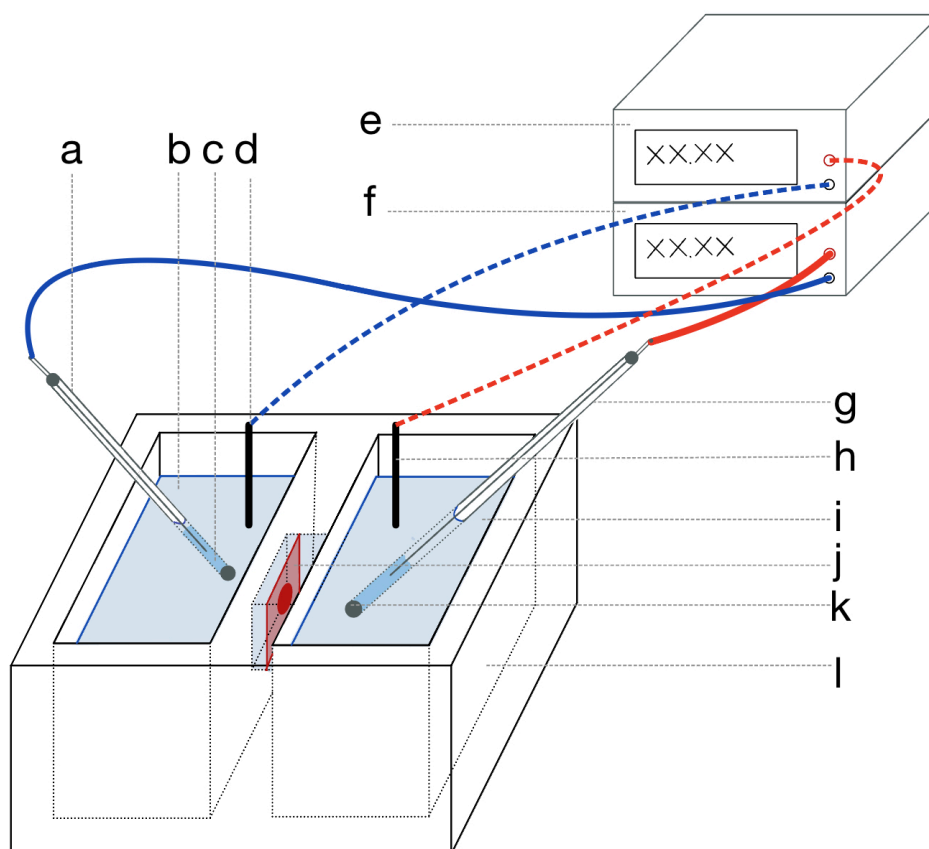


Figure 3.12: Schematic representing the experimental set-up for measuring through working and reference electrodes the potential of a membrane in a RED system.

- a** : Negative reference electrode
- b** : Low concentration NaCl solution
- c** : KCl solution
- d** : Counter electrode
- e** : Keithley Model 2400 Series SourceMeter
- f** : Model DMM7510 digital multimeter
- g** : Positive reference electrode
- h** : Working electrode
- i** : High concentration NaCl solution
- j** : PSi CEM
- k** : frit
- l** : RED cell

Equivalent electrical circuit

Figure 3.13 represents the equivalent electrical circuit when a potential is applied between the working electrode and the counter electrode. The measured voltage is the potential between the reference electrodes. $E_{potential}$ is the true potential of the membrane, R_{mem} and R_{water} represents the resistance of the membrane and water respectively and i is the current going through the membrane due to the applied voltage on the working electrodes.

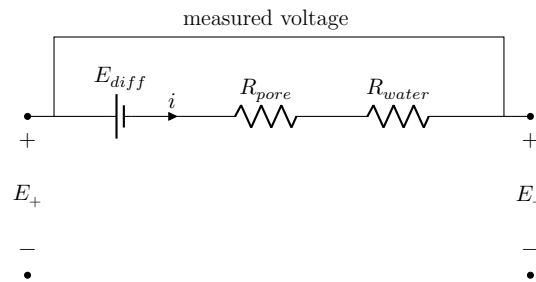


Figure 3.13: Equivalent electrical circuit of the experimental set-up with the working and reference electrodes.

One can note that the circuit is represented as a quadripole. It is because E_+ and E_- include the potential drop related to the redox reactions which varies with concentration (C) and activity(γ) of the ions in solution. Note that this potential also depends on the temperature (T), the number of transferred electrons in the half equation (z) and is proportional to the ratio of the universal gas constant ($R = 8,314\ 462\ 1\ [Jmol^{-1}K^{-1}]$) and the Faraday constant ($F = 96\ 485\ [Cmol^{-1}]$).

$$\begin{aligned} E_+ - E_- &= E_{applied} + E_{redox+} - E_{redox-} \\ &= E_{applied} - E_{redox} \end{aligned} \quad (3.5)$$

$$E_{redox} = \frac{RT}{zF} \ln\left(\frac{\gamma_H C_H}{\gamma_L C_L}\right) \quad (3.6)$$

Therefore, the potential at the working are not the same in the two different solutions. The voltage potential gradient is composed of the applied potential with an additional redox potential given by equation 3.6. Where H and L are referring to the high and low concentration solutions respectively.

The membrane potential (E_{diff}) is determined by measuring the open circuit voltage with the reference electrodes. When the current flowing through the membrane is equal to zero, the measured voltage is E_{diff} as the voltage drops due to the resistances are also equal to zero.

Current-voltage curve

As mentioned in section 3.2.2, a matlab code synchronize the source meter and multimeter. The voltage sweep is done between -150 mV and 50 mV with a step of 5 mV every 0.2 seconds. For a visibility convenience, the curve represents the current as a function of the opposite of the applied voltage so that the curve of interest is in the first quadrant.

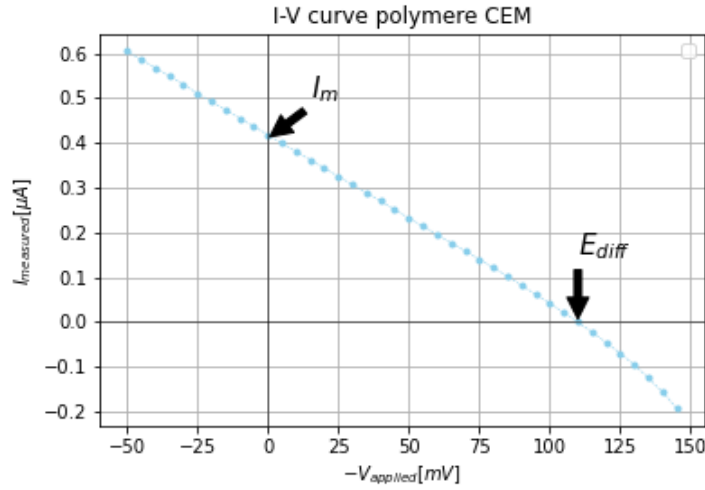


Figure 3.14: I-V curve of a polymer cathodic exchange membrane with the points of interest E_{diff} and $I_{membrane}$ highlighted.

The zero to the x-axis is the open circuit voltage when no current flows through the membrane. This is the membrane potential (E_{diff}). The zero to the y-axis gives the current flowing passively through the membrane (I_m). The slope represents $-1/R_{cell}$, knowing that R_{cell} is the resistance of the membrane and the water in series. From these informations and using equations 3.7 and 3.8, one can find the maximal power of the membrane as well as its transference number (i.e. selectivity).

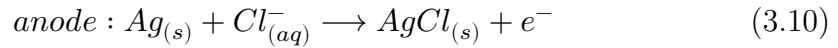
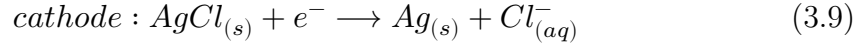
$$P_{max} = \frac{E_{diff}^2}{4R_{cell}} \quad (3.7)$$

$$t_+ = \frac{1}{2} - \frac{zF}{2RT} \frac{E_{diff}}{\ln(\frac{\gamma_H C_H}{\gamma_L C_L})} \quad (3.8)$$

Choice of electrodes

The choice of electrodes is a very important factor in the efficiency of the system. To transform the ionic current into an electric current, a redox reaction needs to take place. This depends on the concentrations and ions in solution, as well as the choice of electrodes. Electrodes without opposing reactions lead to the production of gas, which would create problematic bubbles on the surface of the membrane, as well as a loss of energy. For this reason, the pairs of electrodes (reference and working) are both active electrodes with opposing reactions [52].

In the system presented in figure 3.12, the ions in solutions are sodium (Na) and Chlore (Cl). The reference electrodes and working electrodes are silver chloride (Ag/AgCl) so the half reactions involved are the following :



The working electrodes were fabricated in WINFAB cleanroom as follows. An electroplating on a pure silver wire of silver chloride is made by applying a 10 $[mA/cm^2]$ current density through the silver wire inside a 0.1 M HCl bath while using a platinum wire as a cathode. If the procedure is successful, a black deposit appears on the silver wire.

As far as the working electrodes are concerned, the procedure ends here. However, the reference electrodes are then placed in a tube filled with 1 M KCl, which ends with a frit. The margin of error of such an electrode is around one millivolt [1], [53].

Figure 3.15a represents the I-V curves for two different pairs of working electrodes. One can see that the quality of these electrodes impacts a lot the results. Indeed, depending on the deposit and activity of the electrodes, the efficiency of the system will vary. All the tests were made with the same pair of working electrodes and alternating the cathode and the anode in order to prevent that one will end up with no deposit.

As said before, the working electrode will induce an additional voltage drop depending on the concentration in which they are. This shift can be seen in figure 3.15b. Therefore, the IV curves analyzed in this work are measured with the reference electrodes which ignore this redox potential.

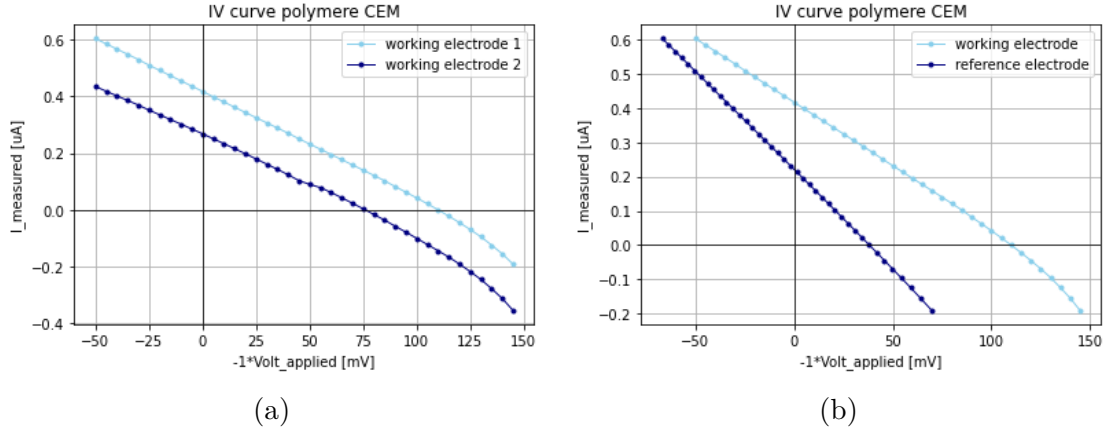


Figure 3.15: **a)** I-V curves for two different sets of working electrodes. **b)** I-V curves for working vs reference electrodes.

	Working electrode 1	Working electrode 2	Reference electrode
$E_{diff}[mV]$	107	70	38
$I[\mu A]$	0.42	0.27	0.22

Table 3.4: Results of the different IV curves in figure 3.15a and 3.15b.

3.3 Conclusion

In this chapter, Porous Silicon was described. First its history was told, and then its fabrication and the parameters that influence it were explained. In order to better understand the design explained in the next section, the key factors affecting the porosity, density and pore size (i.e. morphology) of porous silicon and the transition layer were discussed. The main instruments used to characterize PSi during this work were presented and finally the process for creating PSi membranes in WINFAB was detailed step by step.

With regard to the electrical characterisation of the membrane, the equivalent circuit and experimental set-up, as well as the choices made for the latter, provide a better understanding of the results that will be presented in the following sections. These are based on the IV curves from which the membrane potential (E_{diff}) and the current passing through the membrane (I) can be determined.

The main goal of this section was to explain how to obtain these measurements and how to use them to obtain the figure of merits : the maximal power density (P_{max}) and transference number (t_+).

CHAPTER 4

STUDY OF OPTIMAL PORE TOPOLOGY AND ANODIZATION FOR PSI MEMBRANE.

In this section, the optimal pore topology and the recipes used to obtain it are studied to optimize the membrane's properties.

Firstly, numerical simulations are used to identify the key parameters affecting membrane efficiency. Three pore types are considered in this work. Conical pores are studied and compared to the literature. Secondly, different pencil shaped pores are introduced aiming to have the same selectivity properties as the conical pores with lower electrical resistance.

Having decided on the pore types studied during this work, a single layer study is carried out to confirm the anodizing chosen parameters and obtain controlled topologies. Finally, these chosen parameters are detailed.

4.1 Numerical simulation

In order to better design the membranes, the effects of different geometries of a single pore separating two saline water tanks of different concentrations are studied using COMSOL Multiphysics 5.4 [1]. Assuming that the behaviour of a membrane can be simulated by a multitude of pores in parallel, this study allows the identification of trends and the understanding of the influence of pore topology parameters on the membrane efficiency.

4.1.1 Numerical modelisation

To describe ion transport correctly, continuum dynamics can be used. More precisely, the modified full Poisson-Nernst-Planck equation as in equation 4.1 can be used. Please note that this description is only valid for pore scales larger than 5 nm [17].

$$\mathbf{J}_i = \mathbf{J}_i^e + \mathbf{J}_i^D + \mathbf{u}C_i = -\frac{z_i F}{RT} D_i C_i \nabla \phi - D_i \nabla C_i + \mathbf{u}C_i \quad (4.1)$$

where $\mathbf{J}_i$ is the molar flux, $\mathbf{J}_i^e$ the electromigration, $\mathbf{J}_i^D$ the diffusion flux, $\mathbf{u}$ the velocity vector, C_i the molar concentration of the i th ion species, z_i the valence, F the Faraday constant, R the gas constant, T the absolute temperature, D_i the diffusivity and ϕ the electrostatic potential.

It is important to note that molar flux is composed of electromigration, diffusion and convection.

The electrostatic potential needs to be developed to have an explicit expression for the electromigration term. The electrical potential is given by the Poisson equation :

$$\nabla^2 \phi = -\frac{\rho_e}{\epsilon_r \epsilon_0} = -\frac{F \sum_i z_i C_i}{\epsilon} \quad (4.2)$$

Regarding the convection term, the velocity vector $\mathbf{u}$ needs to be explicitated. The motion of incompressible solution is due to applied potential and pressure gradient as shown in equation 4.3. But in this particular case, this $\mathbf{u}$ term is negligible, given that the pressures on either side of the pore are equal and that the electroosmotic effect is very weak (10-100mV).

$$0 = -\nabla p + \mu \nabla^2 \mathbf{u} + F \sum_i z_i \nabla \phi \quad (4.3)$$

In a steady-state solution where no chemical reaction happens, the continuity equation 4.4 applies.

$$\nabla \cdot \mathbf{J}_i = 0 \quad (4.4)$$

As the ions species are in motion, an electrical current density is produced.

$$\mathbf{i} = F \sum_i z_i \mathbf{J}_i = -\nabla \phi \sum_i \frac{z_i^2 F^2}{RT} D_i C_i - F \sum_i z_i D_i \nabla C_i + F \mathbf{u} \sum_i z_i C_i \quad (4.5)$$

$$I = \int_A i dA \quad (4.6)$$

In order to obtain the electrical current going through the pore, this current density has to be integrated over the cross-sectional area of the channel as in equation 4.6.

4.1.2 Geometry of the problem

The first studied topology is a cylindrical pore as it is the easiest to study simulation wise. Figure 4.2 shows the numerical domain as well as the boundary conditions used to complete the I-V curves. It is considered that :

- There is no pressure gradient so each tank has a pressure set to zero.
- By setting the low and high concentration to the two reservoirs, the direction of the current flowing in the pore is settled.

While the potential would be imposed via electrodes in a real set-up, for reasons of simplicity the potential is applied to the walls of the containers. Note that the positive potential should be on the high concentration side.

Concerning the conditions on the pore walls, the potential depends on the electric double layer as explained in section 2.3.3. Thanks to the symmetry, only half of the nanopore has to be simulated . The current integration is done in the middle of its length.

Figure 4.1 shows the mesh used for the numerical simulation. In order to have a better perception of the physical events occurring in the nanopore, the elements are finer around the charged surface.

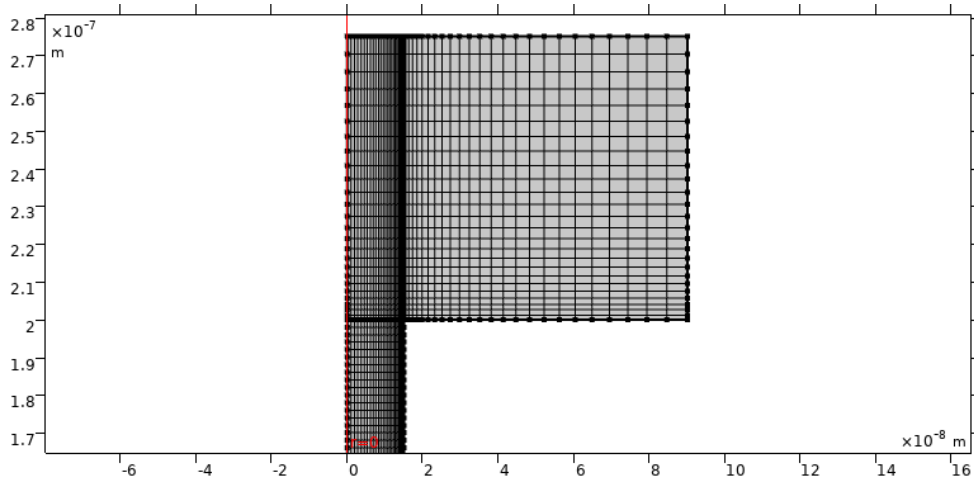
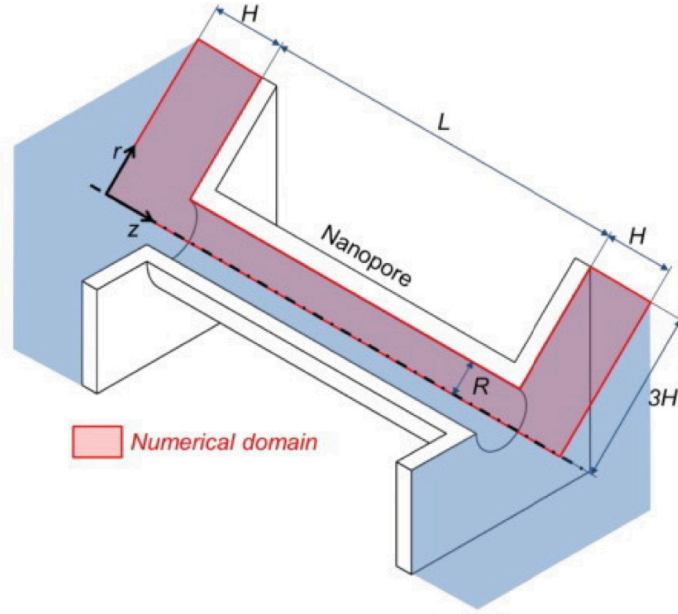
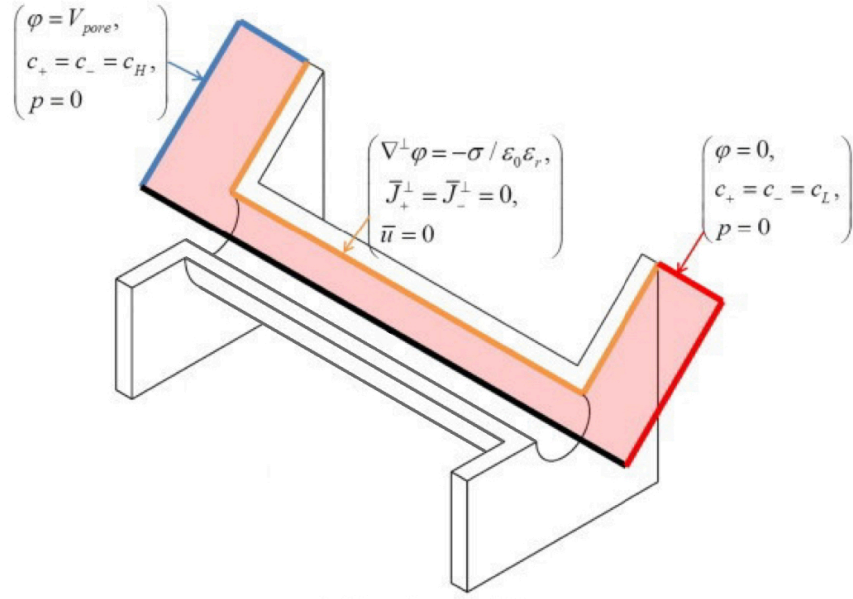


Figure 4.1: Mesh used for the numerical simulation.



(a) Numerical domain



(b) Boundary conditions

Figure 4.2: Numerical domain and boundary conditions for a nanopore with reservoirs on either side. Taken from [2] [1].

4.1.3 Numerical results

The numerical study simulates a cylindrical nanopore separating two tanks of KCl solution with different solutions. The main advantage of KCl is that these ions have very similar diffusion coefficient allowing to consider them equal and ignore the impact of these coefficient on the ion transport and electrical potential. This following study is made with the typical parameters in table 4.1 [2].

Pore radius	R	15 <i>nm</i>
Pore length	L	200 <i>nm</i>
Surface charge density	σ	-0.03 <i>C/m²</i>
Lowest concentration	C_L	1 <i>mM</i>
Highest concentration	C_H	10 <i>mM</i>
Cation diffusion coefficient	D_+	2.032e-9 <i>m²/s</i>
Anion diffusion coefficient	D_-	2.032e-9 <i>m²/s</i>
Relative permittivity (of water)	ϵ_r	80
Temperature	T	273.15 <i>°K</i>

Table 4.1: Typical input values for the numerical study in COMSOL.

Parameters influence

The first parameter studied is the pore radius. Figure 4.3 shows the IV curves for different possible radii of a cylindrical pore. A smaller pore will have a higher resistance which is inversely proportional to the IV curve slope. Tighter pores also have the advantage of better selectivity due to the overlap of the double layer. As explained in section 2.3, the closer the radius is to the Debye length, the more effective the selectivity is. As a reminder, electric potential and selectivity are linked by the equation 4.7. As expected from literature, selectivity decreases as the radius increases as shown on figure 4.4.

$$t_+ = 0.5 - \frac{zF}{2RT} \frac{E_{diff}}{\ln(\frac{\gamma_H C_H}{\gamma_L C_L})} \quad (4.7)$$

Several other parameters can affect the IV curves and therefore, by extension, the transference number and maximal power density. Figure 4.5a and 4.5b show the impact of the channel length and surface charge density on the IV curves. As much as these parameters are interesting the main focus of this work is on the radius impact. Corresponding to the literature (see 2.5.5), here are the main observations made for these parameters:

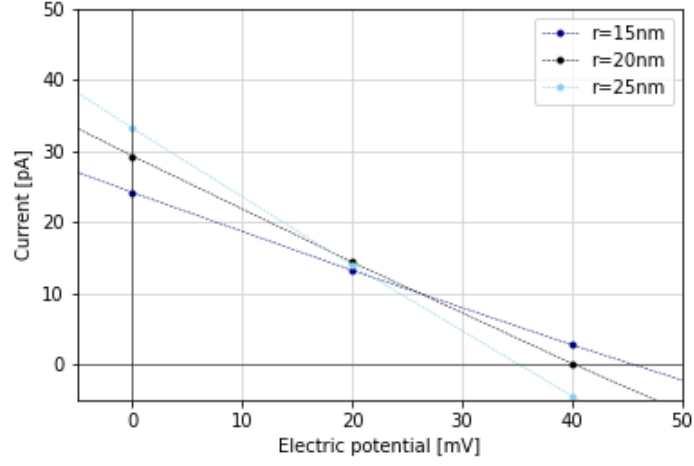


Figure 4.3: I-V curves for different radii between 15 and 25nm, other parameters are in table 4.1. The slope of these I-V curves is $1/R_{pore}$.

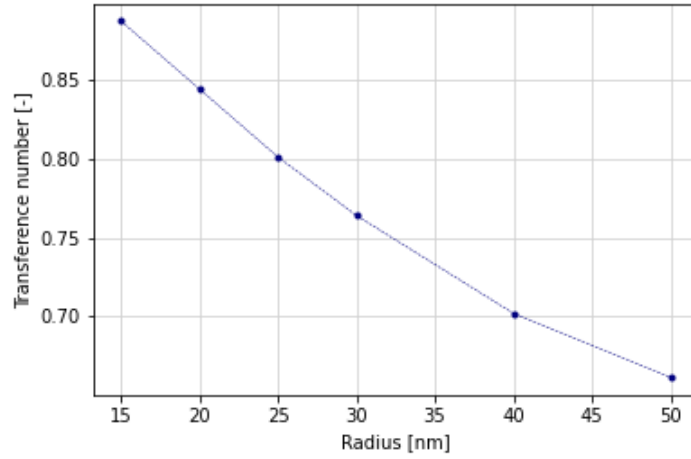


Figure 4.4: Transference number as a function of the pore radius.

- Increasing the length of the pore increases its resistance. Thus the slope of the IV curve decreases.
- A very small decrease in E_{diff} is observed with increasing length of the channel. Consequently, the transference number decreases.
- Increasing the surface charge density increases the number of counter-ions in the channel and therefore the osmotic current increases.
- A smaller radius leads to a higher membrane potential and better selectivity.
- A bigger radius leads to a higher osmotic flow as the ions have more room to be transported.

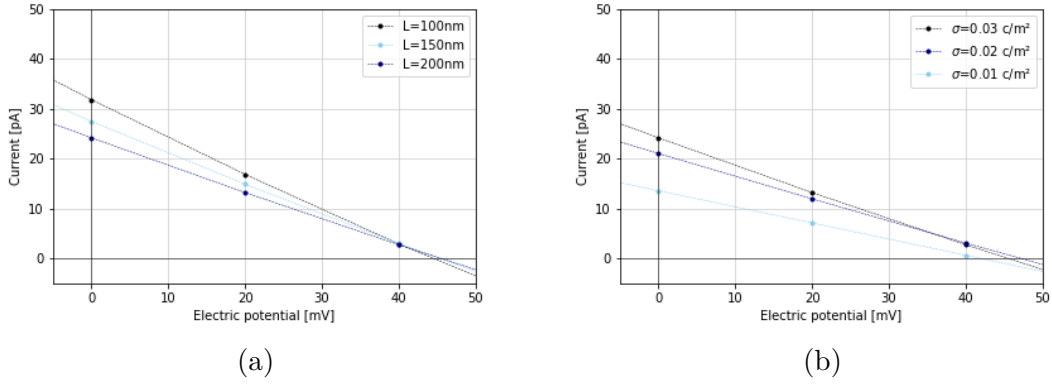


Figure 4.5: I-V curves for different a) channel length, b) surface charge density. Others parameters are in table 4.1.

Conical pores

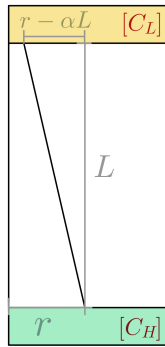


Figure 4.6: Geometrical impact of factor a on the pore topology.

A first approach to understanding the behavioral changes of conical pores is to compare their I-V curves with those of cylindrical pores. A factor a or α is introduced into the geometry of the problem in order to determine the slope of the pore walls. Figure 4.6 gives a visual representation of how a is defined.

For this shape study, the bigger end of the nano pore is fixed to 15 nm and the other end is determined via the a factor. The other parameters are the same as table 4.1.

The black curve in Figure 4.7 represents the case of a cylindrical pore ($a=0$). As the smaller radius tightens the membrane potential and the electrical resistance increase. The osmotic current is also impacted as the shrinking of the pore diameter allows less ions to be transported. There is a trade-off between the selectivity and the ionic current. The maximal power density decreases because the electrical resistance is bigger but the transference number increases because the EDL overlap is stronger.

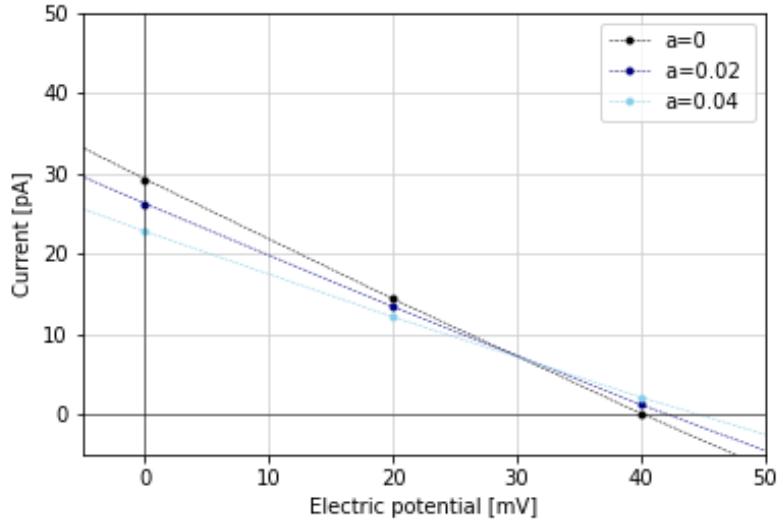


Figure 4.7: I-V curves for a cylindrical pore ($a=0$) and for conical pores with different size on the low concentration side.

EDL overlap

As a reminder, Debye length depends on concentration as seen in the following equation (4.8). Figure 4.8a and 4.8b show the EDL overlap when the lower concentrated solution is adjacent to the smaller end of the nano channel or the bigger end (respectively). In both figure, the non-uniformity of the EDL is visible and confirms the fact that the EDL is as thick as the Debye length. The color scale shows the concentration of anions in mol/m^3 . Therefore, when it is very low (represented as blue), this means that the flow is mainly made of counter-ions. The less anions in the channel, the more selective it is. These figures show that the conical pore is more selective in the first case than in the second because its EDL overlap is stronger.

$$\lambda_D = \sqrt{\frac{\epsilon k_b T}{\sum_i C_{i0} q_i^2}} \quad (4.8)$$

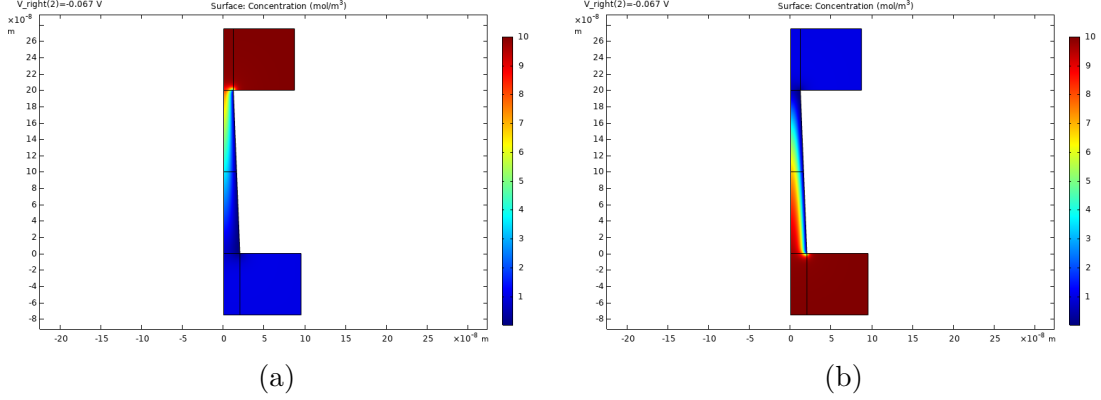


Figure 4.8: Concentration of anions in the nano channel when a) the lower concentration is at the smaller end, b) the higher concentration is at the smaller end.

Pencil pores

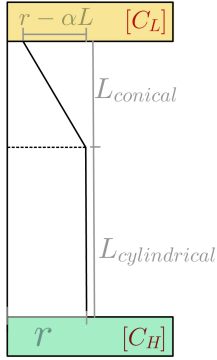


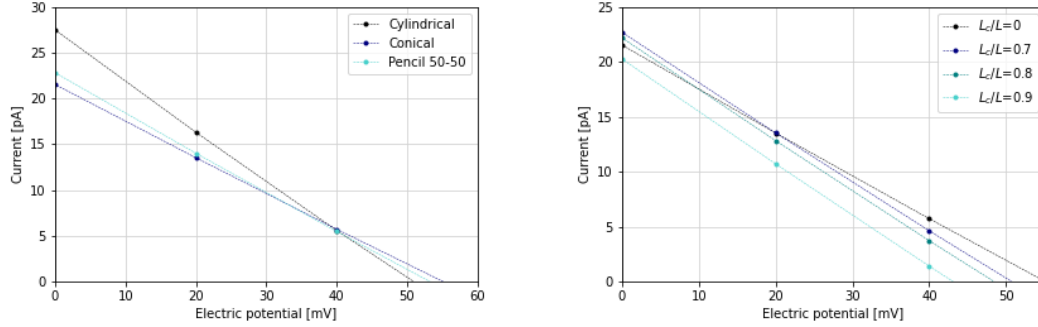
Figure 4.9: Geometrical impact of the proportion on the pore topology.

As explained before, a smaller pore will have a greater electrical resistance. It is then interesting to study other geometries that have potentially the same selectivity characteristics as the conical pores but which have a possibly lower resistance. For instance, such a geometry can be the pencil topology shown in figure 4.9. The first part of the pore is cylindrical and the second is conical.

The proportion between these two parts can be an important factor in performance. In fact, the bigger the proportion of cylindrical part, the lower the resistance. But in order to have a more mechanically resistant membrane, smaller pores with less porosity are desired.

Figure 4.10a shows the curves for the different topologies studied in this work. Compared with a cylindrical pore, the conical pore offers greater selectivity and membrane potential, but its electrical resistance reduces the maximum power density. According to numerical simulations, pencil pores should offer a trade-off between a better resistance than conical pores and a better selectivity than cylindrical pores.

When choosing the cylindrical/conical length ratio, figure 4.10b shows that beyond a certain threshold, the pencil pore is no longer beneficial. For this reason, in this work, the cylindrical part will never exceed 70%. As explained above, there is a trade-off between electrical and mechanical resistance when it comes to the pencil topology. To try and quantify the impact on these resistances, the work will focus on two different proportions: 50-50% and 70-30%.



(a) I-V curves for the three types of topologies studied in this work. (b) I-V curves for different ratio between the cylindrical length and total length.

Figure 4.10: The bigger radius is 15 nm and the α factor is 0.04. Other parameters are in table 4.1.

4.2 Study of anodization step on Si single layer

The membrane process is carried out on one complete wafer at a time. To avoid wasting a wafer and unnecessarily repeating the lithography steps etc, it is interesting to carry out tests on pieces of untreated Si substrate (which will be referred to as a 'single layer'). As well as avoiding waste, by studying the anodization on the single layer, the bulk of Si under the PSi makes it possible to transversely cut the sample. Therefore, cross-section SEM images can be obtained to analyze the topology of the pore along its entire length and get a better idea of the diameter of the pores at the end of the anodization.

PSi is a material too brittle to be able to carry out this analysis on membranes. With the latter, only top-view images of its front and back surfaces can be analyzed. However, it is complicated to obtain clear images of the back surface because of drift, probably due to DRIE residues. A single layer study is therefore the only possible way of analyzing the chosen parameters with sufficient accuracy.

4.2.1 Process automatization

As explained in section 3.1.2, current density is a very important factor that can be easily manipulated to change pore diameter. In all the cases studied, a first anodization for the sacrificial layer is made with the same current density as for the real anodization. After removing the sacrificial layer with KOH, two different scripts are considered to generate the necessary current densities to form the nanopores. A visual representation of the scripts results are represented in appendix 7.2.

Current source for cylindrical pores

In the case of cylindrical pores (and the cylindrical part of the pencil pores), the first script called "etch_stop" is used. Its parameters are :

- The desired current density which determines the radius of the pores.
- The number of cycles which determines the thickness of the membrane.
- The etching-stop distribution of the cycle. The stop stage allows the solution to slightly homogenize. In all cases, this proportion is 10 seconds of etching for 2 seconds of stop.

Current source for conical pores

In the case of conical pores (and the conical part of the pencil pores), the parameters of the script called "linear_etch_stop" are :

- The initial current density which determines the large radius of the pore.
- The final current density which determines the small radius of the pore.
- The desired thickness.
- The number of cycles

In these cases, the desired thickness and the number of cycles both determine the etch-stop ratio proportionally (i.e. the longer the current is applied, the longer the stop time).

4.2.2 Experimental acquired knowledge

Effet of maximal current density

To quantify the impact of applied current density on pore size, several single-layer tests were carried out. Figure 4.11a shows the values obtained. The relationship resembles a linear regression of equation $R[nm] = 0.17J[A/cm^2] + 4.04$. The first idea was to make the bigger radius of the pores as large as possible to allow a maximum volume of solution to penetrate the pores. However, care must be taken not to fall into electropolishing (see section 3.1.2).

Additionally, detachments have been observed for current densities greater than 100 mA/cm^2 . Sometimes these are laminar, like a skin peeling off, or sometimes they result from cracks due to the fragility (increasing because of the large porosity which is linked to high current density) of the porous material, as in figure 4.11b.

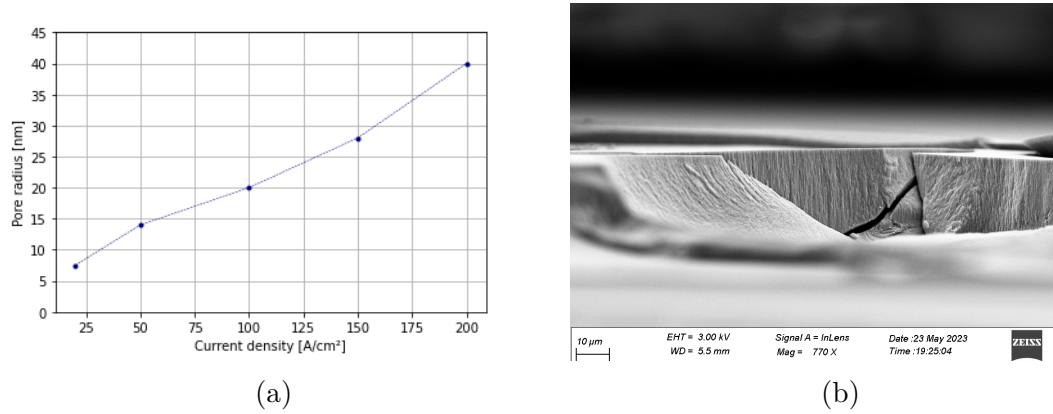


Figure 4.11: **a)** Relation between imposed current density and obtained pore radius. **b)** Detachment of the PSi resulting from cracks due to an excessive current density ($I_{init} = 150 \text{ mA/cm}^2$, $I_{end} = 50 \text{ mA/cm}^2$, thickness = $50 \text{ }\mu\text{m}$ and cycles = 150).

Effect of etch rate

The first tests for the cylindrical (part of) pores were carried out using the etch rate by R. Vercauteren in Winfab for her process [47]. However, after a few single layer observations, this proved to be erroneous for the wafers used as the PSi thicknesses were always different from those targeted. This could be due to a difference in doping or due to the fact that etch rate depends on the current density and it could differ a little from this work's experiments [39]. To rectify this problem, a quick analysis of the etch rate using the ellipsometer enabled us to determine the etch rate, which is 0.63 /cycle for a density of 100 mA/cm^2 instead of 0.24 as before.

Regarding the conical pores, the script takes the desired etch depth and divides it by the specified number of cycles. For each cycle, the etch time is computed based on a linear approximation of the etch rate as a function of the current density. The stop time is adapted proportionally : if the etch time is greater than 10 seconds then another stop time of 2 seconds is added. This linear approximation was made in the Winfab with R. Hanus.

Effect of minimal current density

The minimum current densities for the second script were also tested. A lower current density means a smaller radius and therefore a stronger EDL overlap. Furthermore, the porosity is proportional to the current density. Having a small porosity allows a better mechanical resistance.

However, when the density was too close to zero, the desired PSi thickness was always erroneous despite the etch rate correction. This phenomenon is probably due to the fact that at low current densities, there are now insufficient electrons to continue anodising and thus obtain the correct thickness. This error occurs at densities below 20 mA/cm^2 .

Choice of parameters

Based on the effect mentioned above, the parameters are selected as follows:

- The minimal current density is set to 20 mA/cm^2 to ensure the proper thickness of the PSi. This density corresponds to a diameter of 15 nm which is sufficient to obtain the EDL overlap as the Debye length is around $10\text{-}20 \text{ nm}$.
- The maximal current density is set to 100 mA/cm^2 to avoid detachment problems and electropolishing. This density corresponds to a diameter of 40 nm .
- The number of cycles depends directly on the script used as explained previously.
- The thickness is set to $50 \text{ }\mu\text{m}$. As explained in section 4.1.3, the electrical resistance of the channel is proportional to its length. Additionally, detachment and cracks were more frequently observed for longer pores. Indeed the origin of cracks can be explained by a critical thickness depending on the Youngs modulus of the Si, porosity and the pore radius. Over this critical

thickness, the breaks in the membrane are very probable. Therefore, a minimal length is desired. However, PSi is a very delicate matter and a too thin membrane will break too easily. This thickness seemed a good trade-off.

4.3 Conclusion

In conclusion, after analyzing the impact of parameters by numerical simulation and verifying the recipes used for the anodization step, three different membrane topologies are made : conical, pencil with 70% in cylindrical and 30% in conical and pencil with a 50-50 proportion of cylindrical/conical shape. The membranes are fabricated following the scripts explained in section 4.2.1. The details of the anodization steps for each topology are described in appendix 7.2.

Based on literature and the numerical simulation made in this section, the conical pores should give a better selectivity and membrane potential than cylindrical pores. It should be possible to observe an asymmetry when the solutions are exchanged because the overlap will be weaker when the smaller radius is adjacent to the higher concentration solution as explained in section 4.1.3. Pencil membranes should give the same selectivity results as conical membranes, while reducing pore resistance.

CHAPTER 5

EXPERIMENTAL RESULTS

5.1 Characterization of PSi

Before anodizing a complete wafer, the three recipes were tested and adjusted on pieces of doped Si wafer. SEM and ImageJ analysis were used to obtain the distributions of the large diameters of the nanopores (d_{front}), the small diameters (d_{back}), the thickness obtained and the porosity of the membrane which are gathered in table 5.1.

The top view images such as figure 5.1a can be utilized to calculate d_{front} by taking the smallest diameter of the pores, as well as the porosity by calculating the proportion of perforated surface area to total surface area.

Cross-section images such as figure 5.1b and 5.2 are used to obtain the depth of the PSi and the d_{back} (more information on the procedure in appendix 7.1).

	d_{front}	d_{back}	$depth$	$porosity$
Conical	38 nm	13 nm	51 μm	54.8%
Pencil 70-30	39 nm	11.5 nm	52 μm	52.8%
Pencil 50-50	44 nm	14 nm	50 μm	61.3%

Table 5.1: Membrane characteristics distributions obtained by ImageJ.

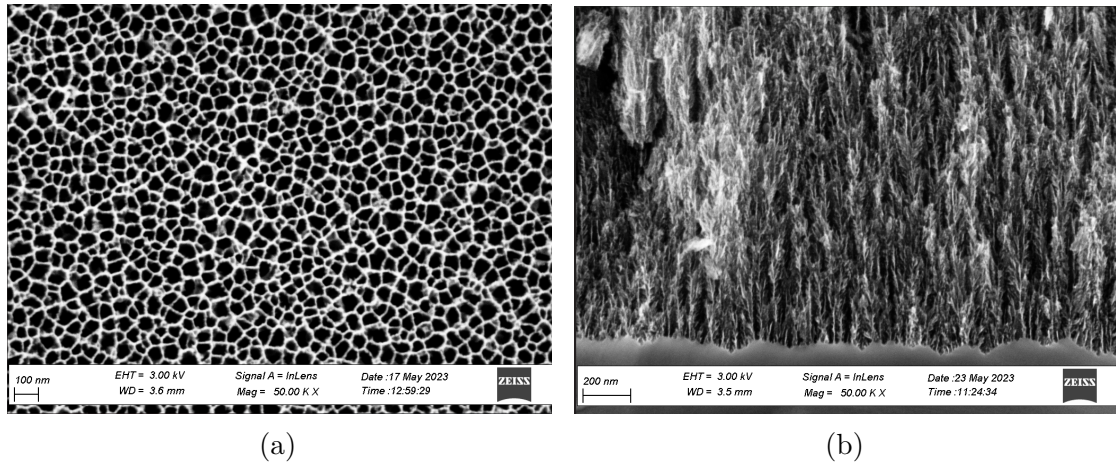


Figure 5.1: SEM images of PSi results for pencil 70-30 parameters. a) is the top view, b) the cross sectional zoomed on the smaller end of the pores.

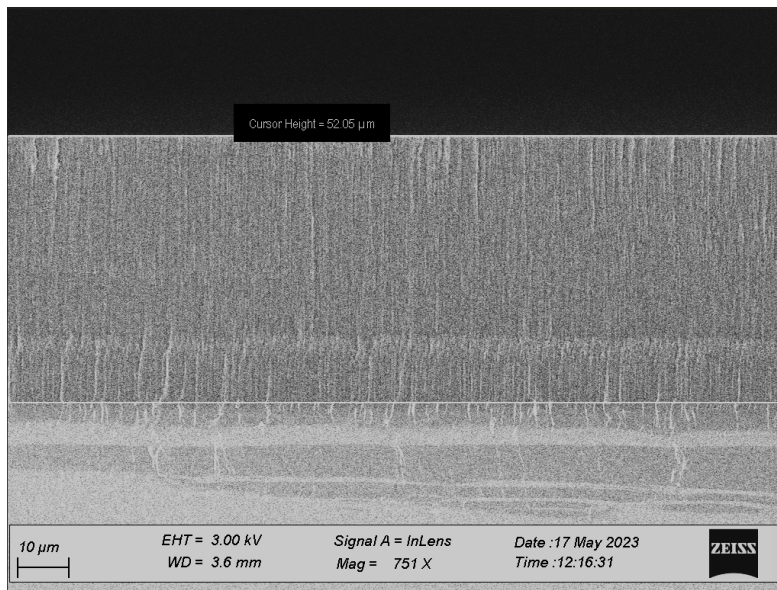


Figure 5.2: SEM images of PSi results for pencil 70-30 parameters. The general cross sectional view to measure the thickness.

5.2 I-V curves

For each topology considered (the three mentioned in the previous section as well as the cylindrical one for reference¹), 3 membranes were used (within the limit of what was left after breaking, cracks etc).

For each membrane, four situations are studied:

- **Situation 1** : $[C_H] = 1 \text{ mM}$ facing front and $[C_L] = 0.1 \text{ mM}$ facing back (fig. 5.3a)
- **Situation 2** : $[C_H] = 1 \text{ mM}$ facing back and $[C_L] = 0.1 \text{ mM}$ facing front (fig. 5.3b)
- **Situation 3** : $[C_H] = 10 \text{ mM}$ facing front and $[C_L] = 1 \text{ mM}$ facing back (fig. 5.3a)
- **Situation 4** : $[C_H] = 10 \text{ mM}$ facing back and $[C_L] = 1 \text{ mM}$ facing front (fig. 5.3b)

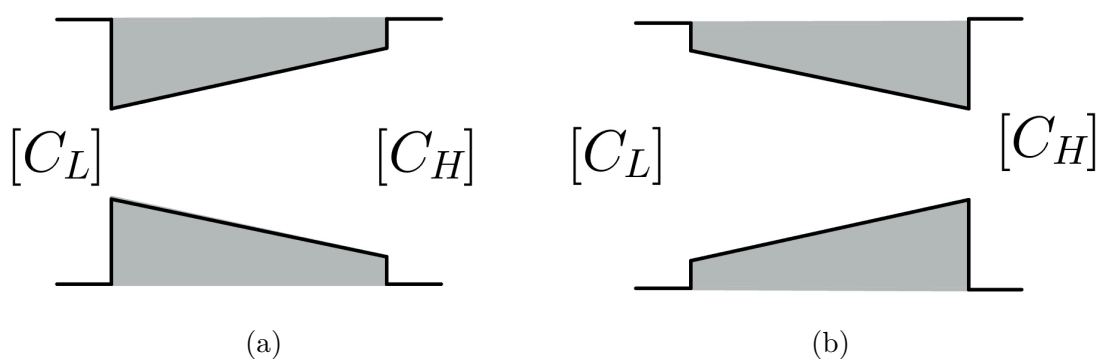


Figure 5.3: Schematic representation of situation a) 1 and 3, b) 2 and 4. The bigger radius side is the front of the membrane.

Where the electrolyte used is NaCl dissolved in deionized (DI) water. Each of these situations is measured three times to analyze the impact of time on the set-up and for repeatability. The first situation is the ideal situation to study selectivity as the double layer will be thicker with lower concentrations and the orientation of the membrane leads to a better overlap.

As a reminder from section 3.2.2, the equivalent circuit of such a membrane can be modelled by a voltage source in series with an internal resistance. The charac-

¹The cylindrical ones were made by Romain Hanus on the same substract and with the same process except for the anodization step.

teristics of the membrane are determined from the measurements obtained (E_{diff} and I_m) from the experimental set-up explained in section 3.2.2.

The **resistance** of the cell (which corresponds to the resistance of the water and the membrane in series) can be found by taking the inverse of the slope of the I-V curve.

The maximum **power** that can be generated using the membrane is obtained according to the equation (3.7) and for clarity of results this power is divided by the area of the membrane ($4mm^2$ for square membrane and $3.14mm^2$ for the round ones) to obtain a result in $[W/m^2]$.

Finally t_+ is found using equation 4.7, assuming that γ_H and γ_L are considered equal to 1 (true for low concentrations [54]) with a concentration ratio of 10. Care must be taken to the potential used for the transference number equation. Indeed one must subtract $12mV$ to the measured potential to obtain the potential of the membrane. This is because the sodium and chloride ions do not have the same diffusion coefficient (more information on this in section 5.3.3). However, the I-V curves in the next section are the raw measurement without subtracting the $12mV$.

5.2.1 Repeatability and standard deviations

Figure 5.4 shows the I-V curves for tests carried out consecutively on a conical membrane in the same situation (the first). Approximately two minutes separate each measurement. It can be seen that the difference between the curves is not very significant: around $8mV$ for the membrane potential and $0.05\mu A$ for the current.

In order to obtain the general standard deviations, the standard deviation of the three measurements for each situation of each membrane has been calculated. The resulting values are averaged to obtain the mean standard deviation of the potential which is $1.332mV$ and the average standard deviation of the current which is $0.015\mu A$.

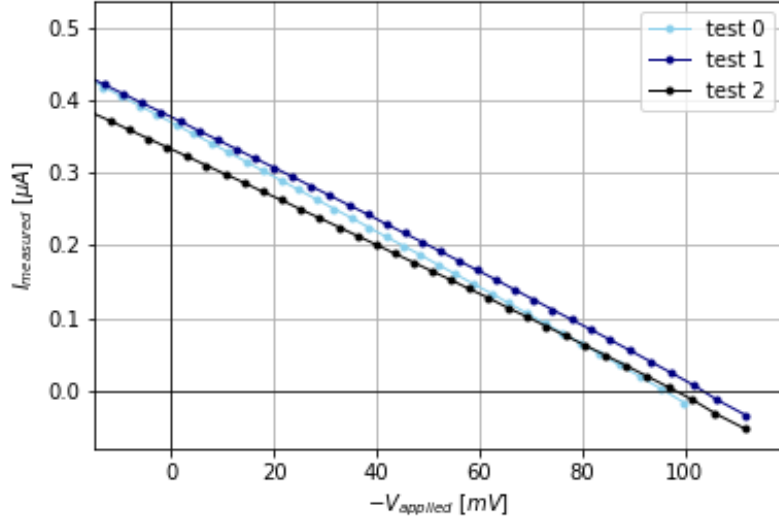


Figure 5.4: I-V curves measured in succession for the a conical membrane in situation 1.

	$E_{diff}[mV]$	$I[\mu A]$	$R_{cell}[k\Omega]$	$P[mW/m^2]$
<i>test 0</i>	-97	0.37	264.9	2.86
<i>test 1</i>	-105	0.38	279.4	3.15
<i>test 2</i>	-99	0.33	298.1	2.61

Table 5.2: Properties of the membrane for situation 1 for the three different measures in figure 5.4.

5.2.2 Asymmetry of the EDL overlap

When comparing the curves for a conical membrane in the two possible directions as in figure 5.5, it can be seen that there is a shift between the two curves leading to a 60 mV difference for E_{diff} . The electrical resistances are very close as the curves seem to be parallel.

This experimentally shows the asymmetry of the double layer as already shown in section 4.1.3 numerically.

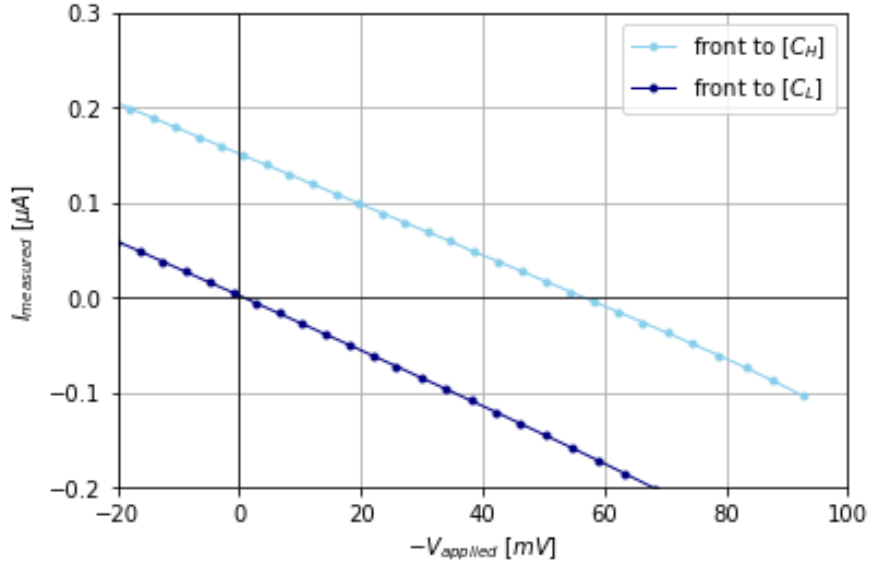


Figure 5.5: I-V curves for a conical membrane with concentrations at 1 mM and 0.1 mM (situation 1 and 2)

	$E_{diff}[mV]$	$I[\mu A]$	$R_{cell}[k\Omega]$	$P[mW/m^2]$
<i>Situation 1</i>	-56.4	0.15	372.62	0.67
<i>Situation 2</i>	-0.063	0.0001	346.7	9.55e-4

Table 5.3: Properties of the membrane for situation 1 and 2 in figure 5.5.

However, when working with higher concentrations such as in figure 5.6, two observations can be made :

- The measured voltage are less significant at these concentrations than in the cases considered above.
- The difference between the two curves is of the same order of magnitude as the standard deviations calculated for the repeatability.

This shows experimentally that the EDL overlap is weaker when using higher concentrations.

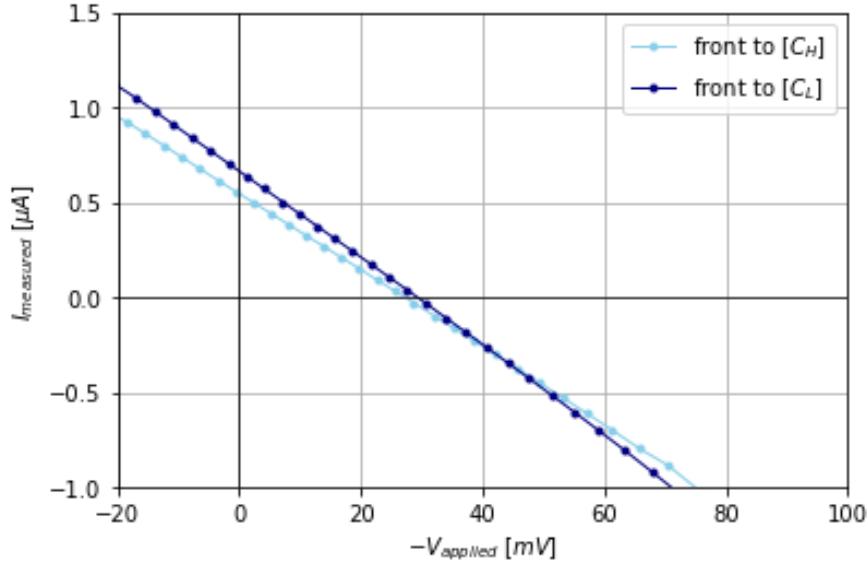


Figure 5.6: I-V curves for a conical membrane with concentrations at 10 mM and 1 mM (situation 3 and 4)

	$E_{diff}[mV]$	$I[\mu A]$	$R_{cell}[k\Omega]$	$P[mW/m^2]$
<i>Situation 3</i>	-27.08	0.55	49.48	1.18
<i>Situation 4</i>	-28.8	0.66	43.6	1.51

Table 5.4: Properties of the membrane for situation 3 and 4 in figure 5.6.

5.2.3 Topology impact

Figure 5.7 shows the I-V curves for a cylindrical, conical and pencil membrane (70-30). The 50-50 pencil membranes are not shown in the figure as there were concerns about the uniformity of the PSi (more information on this in section 5.3.4). These are taken from the results in the ideal situation for studying selectivity (situation 1).

It can be seen that the conical membrane performs better generally than the cylindrical one. However, its slope indicates that its resistance is greater even though it is thinner than the cylindrical membrane.

With regard to the pencil membrane, its performance is comparable if not better than the one of the conical membrane. It has a steeper slope showing the (admittedly slight) decrease in resistance.

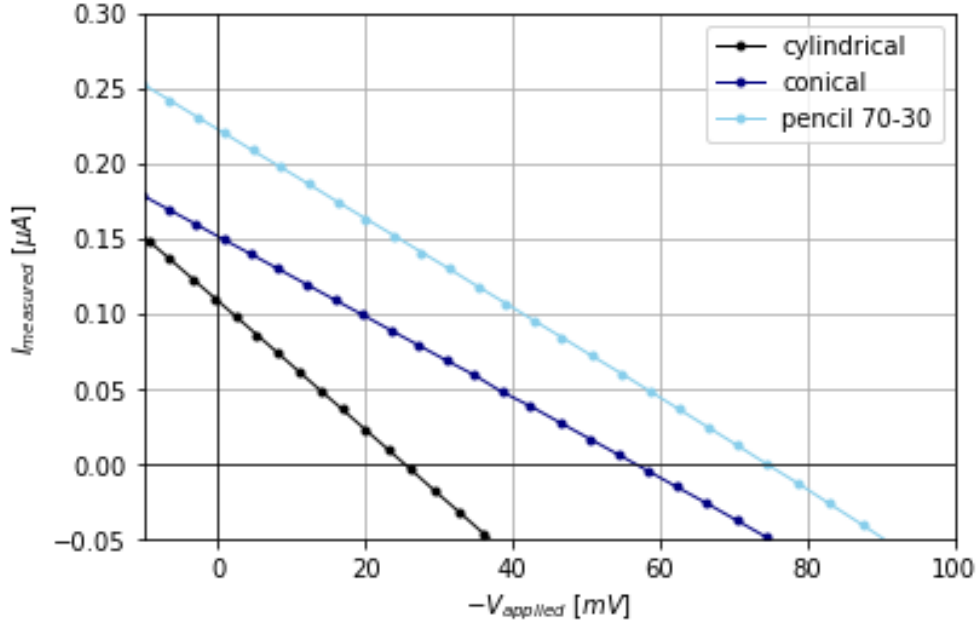


Figure 5.7: I-V curves for a membrane with cylindrical nanopore, with conical nanopores and pencil shaped nanopores with a proportion of 70-30%. Used concentrations are $C_H=0.1 \text{ mM}$ and $C_L=1 \text{ mM}$ (situation 1).

	$E_{diff}[mV]$	$I[\mu A]$	$R_{cell}[k\Omega]$	$P[mW/m^2]$
<i>Cylindrical</i>	-25.19	0.108	232.27	0.21
<i>Conical</i>	-56.4	0.15	372.62	0.677
<i>Pencil 70-30</i>	-74.62	0.22	335.22	1.32

Table 5.5: Properties of the membranes (cylindrical, conical and pencil 70-30) for situation 1 in figure 5.7.

5.2.4 Summary

Table 5.6 gathers the means of the results for the first and third situation of each topology (as they are supposed to be the optimal situations). Appendix 7.3 shows the complete results for each membrane.

Membrane	C_H & C_L	$E_{diff}[mV]$	σ_{OCV}	$I[\mu A]$	σ_I	$R_{cell}[k\Omega]$	$P[mW/m^2]$	$t_+[-]$
cylindrical	1 & 0.1 mM	-35.48	3.66	0.149	0.014	248.402	0.355	0.94
	10 & 1 mM	-11.43	0.26	0.338	0.012	33.568	0.246	0.716
conical	1 & 0.1 mM	-79.23	2.15	0.26	0.011	320.65	1.8	1.34
	10 & 1 mM	-23.87	0.94	0.503	0.019	47.177	0.96	0.83
pencil 70-30	1 & 0.1 mM	-80.152	10.94	0.259	0.04	317.18	1.55	1.35
	10 & 1 mM	-51.545	2.54	0.985	0.026	52.27	3.6	1.087
pencil 50-50	1 & 0.1 mM	-43.79	14.7	0.1435	0.045	299.73	0.475	1.015
	10 & 1 mM	6.11	0.85	0.281	0.046	21.762	0.136	0.55

Table 5.6: Mean of results for each topology in situation 1 and 3 (membrane in the right direction to theoretically have the best EDL overlap).

These results show that membrane performance is a trade-off between selectivity and diffusion. Lower concentrations will give a better membrane potential (and therefore better selectivity) but they will also imply a lower current and a higher resistance. When higher concentrations are used, the overlap of the double layer is no longer sufficient to overpower the diffusion phenomenon.

Comparing the performance of the different topologies, it can be seen that conical membranes have better E_{diff} than cylindrical ones, while having comparable currents. As expected, pencil-shaped membranes have similar characteristics to conical ones. This is especially true for 70-30 pencil membranes.

Normally, the transfer number is assumed to be between 0 and 1. It is physically impossible for it to exceed this range, as can be encountered in the results above. The reason for this error is discussed in the next section.5.3.3

5.3 Discussion

5.3.1 Process limitations

The stages that have the greatest impact on process errors are the choice of wafer, the anodizing stage and, above all, the DRIE.

By **choosing the wafer**, one also chooses the dependency between the current density and the topology of the porous material. Using wafers that are more doped than those used in this work will result in a higher porosity (more pores/cm² for the same current density applied). A higher porosity means more ionic current but the electropolishing limit will be lower. The range of values that can be used is therefore narrower, which reduces the choice and ease of adjusting pore size. More importantly, a higher porosity means also that the mechanical resistance of the membrane is lower as the material becomes more brittle. There is a trade-off between a better current and a stronger membrane with an easier control on pore radius.

The main problem with **anodizing** is that the current density is assumed to be uniform. Although it is done with an electrode having the same surface area as the wafer and being very finely meshed, the PSi may not be homogeneous. In fact, for one of the wafers (pencil 50-50), SEM showed that a third of the membranes appeared to have non-uniform characteristics on their surface. In some regions of each corrupted membranes, the pores were smaller, less homogeneous and not as closely spaced. The images 5.8a and 5.8b show the resulting topology after anodization of a membrane but in different local area of this membrane. The images do not show the cause of this heterogeneity but it is very likely that it is due to a non-uniform current density.

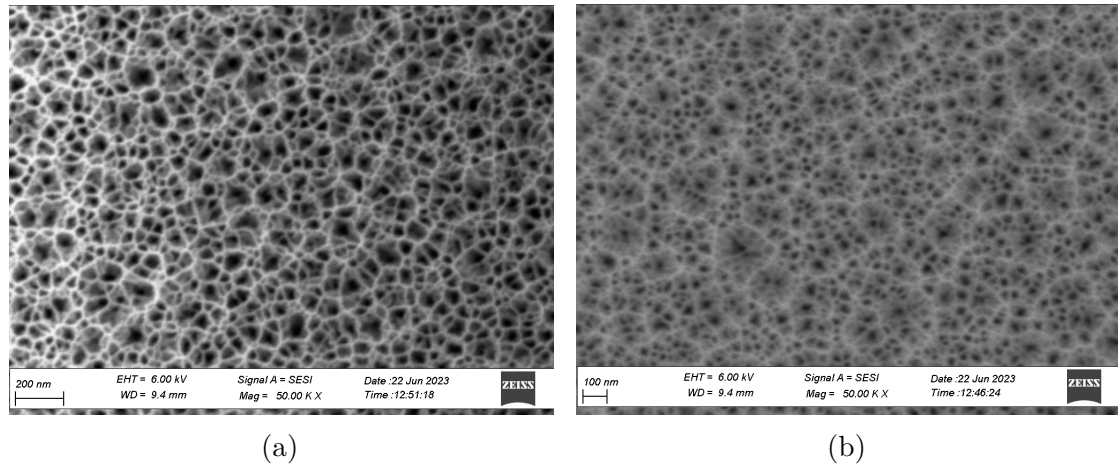


Figure 5.8: Top view SEM images of a membrane after the anodization. a) shows the expected results and b) shows what happened on certain locations of the membrane.

The stage that complicates the whole process the most is the **DRIE**. Since the entire wafer is introduced into the chamber and the BOSCH process is not homogeneous on the wafer, the membranes are not released at the same time. When this is the case, either the process is continued in small numbers of cycles to release as many membranes as possible at a time (this was done for conical membranes) or, as soon as some membranes are released, the membranes are debonded and cleaned. All the remaining unreleased membranes need to be glued back individually onto a dummy wafer or an aluminium plate and passed through the oxford in small numbers.

Obviously, the success rate and precision of the membrane thickness is much better in the second case, but in addition to the amount of time involved, risk of breaking is increased with the added steps of manipulation required. For instance, the membranes are cleaned with acetone, methanol and lastly IPA, as these lead to the least tension inside the pore when drying due to their lower surface tension compared to water. This means that a membrane has to be manipulated at least three additional times for each try in the Oxford.

Another issue associated with the DRIE is the cleanness of the surface released on the back. Indeed, from the SEM images done on the back as figure 5.9, the number of 'freed' pores seems lower than expected. There are two possible explanations for this. Firstly, porosity decreases with the current density applied. Secondly, the DRIE leaves residues from its passivation on the membrane, which plug up some of the holes. These also cause a lot of drift in the SEM images because they are very poor conductors. This drift makes it impossible to take sufficiently magnified images to study the pore size distribution. Therefore, one has to rely on the results found in the single layer study for the smaller diameter distribution.

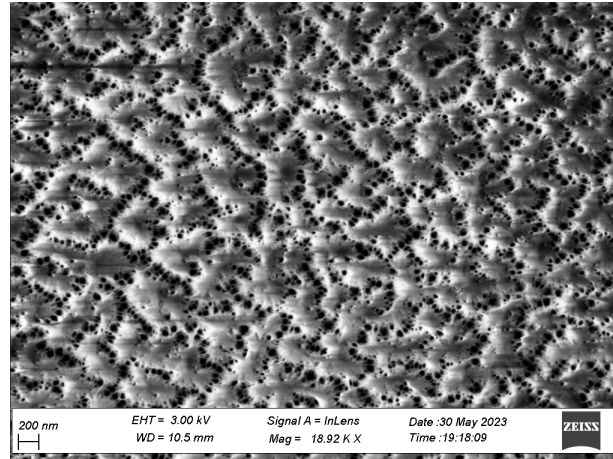


Figure 5.9: SEM images of the back of the membrane after DRIE and release.

The other steps are less problematic but must also be taken into account. For example, the oxidation and deposition stages always have a margin of error on the thickness of the added layer. In addition, the resolution of the lithographies needs to be taken into account (which can be done by looking at the quality marks). In this case, as the mask is not very detailed, this shouldn't be too limiting, unlike the **alignment** between the two masks, which is very important if the membrane is to be released correctly.

The success rate of this process is fairly low. Of the 96 potential membranes to be tested, only around forty managed to get out of the WINFAB without breaking. Since these membranes are very thin, they are likely to break. Then, 25 membranes broke during the experimental measurements: cracks appeared (when there were none right after the DRIE), no current was flowing, sometimes it was more a case of detachment (the membrane separated from the die as a whole and could be seen floating in one of the tanks). One solution could be to do thicker membranes but then it means that a detachment of the P*Si* (as in figure 4.11b) is more probable. Another solution would be to reduce the current density used to have smaller pores and a lower porosity, therefore decreasing the hollow volume of the membrane. However, these solutions both increase the membrane resistance (thus decreasing the maximal power).

5.3.2 Error analysis and repeatability

The general standard deviation of the **membrane potential** calculated in section 5.2.1 is of the same order of magnitude as the margin of error of the reference electrodes : 1mV (see section 3.2.2). Errors due to the precision of the multimeter used can be rejected or at least ignored because its resolution reaches the nanovolt range [55].

However, the cables used introduce electrical noise in the millivolt range. (This noise was defined by measuring the voltage with the cables at no load).

The **current** is imposed in the closed electrical circuit via the voltage source on the working electrodes. A voltage ranging from -150 to 50 mV with a step of 5mV is imposed between these electrodes. From this voltage, the redox reactions transform the electric current into an ionic current. Tracing the charge path from the positive electrode, a first potential drop due the half reaction at the cathode electrode, then the membrane potential and the electrical resistance of the saline solutions and finally the other half reaction from the anode electrode (opposite to the one at the cathode). Note that the two half reaction potentials are not equal because the concentrations are different, so they cannot be considered to cancel each other out.

This potential has an impact on the electromigration factor in the equation 4.1 and therefore directly on the current. The accuracy of the voltage source is 0.6 mV , which corresponds to variations in the order of 1 fA for the current [56]. This is not enough to explain the standard deviation of the current, which is in the nanoampere range.

There are other possible hypotheses to explain this phenomenon:

Process variations :

The manufacturing process does not produce identical membranes between wafers or even on the same wafer. Whether during porosification, deposition, oxidation or (D)RIE steps, differences in thickness or porosity appear. This is beyond our control and to describes their impact, the number of tests would have to be multiplied, but this was not possible in the time available.

Diffusion :

The resulting characterization values of the PSi in table 5.1 are distributions. This means that although the average of the radii should ensure that the double layer is overlapped, in reality this will not necessarily be the case for all the nanopores. This implies that even if the selectivity of certain pores was 1, anions could still pass through less selective pores. Through the phenomenon of osmosis, the solutions will tend to equilibrate. If the system were studied over a much longer period of time, the two solutions would end up with equal concentrations and zero current.

In the 2 minutes between each test, it is possible that the concentrations will slightly equilibrate, leading to a decrease in the current obtained over time. However, Appendix 7.3 shows that a decrease in current over time is not necessarily the case for all membranes.

One plausible reason for this is that the reference electrodes discharge into the water (very slowly). In fact, the solution in which they are kept is 3 M KCl. When they are immersed in 1 mM NaCl, there is a strong gradient and some of the ions will pass into the solution. As a result, there are more ions in the solution for the current.

Bubbles :

When solutions are poured into the cell reservoirs, air bubbles sometimes remain trapped on the surface of the membrane. The largest bubbles, visible to the human eye, are removed by pushing solution onto the membrane with a pipette. However, some bubbles may remain unseen. Since air is an electrical insulator, these bubbles prevent the entire surface from being used, leading to erroneous results.

Noise induced by the working electrodes :

Because of the half-reactions that occur at the electrodes, these do not remain exactly the same throughout all the measurements. In fact, after a long period of time it should be possible to observe growth of the deposit on the negative electrode, while the positive electrode gradually shrinks. This is why, during the experiments, they were regularly exchanged. However, this process is fairly slow. Given that milliamperes are used for about ten minutes to create these electrodes, the microampere effect should be relatively innocuous. Nevertheless, this phenomenon remains another source of noise: electrochemical noise.

EDL formation :

It has also been suggested that the reason for the current fluctuations is that the formation of the double layer is not instantaneous. However, it would appear that the double layer is formed in the order of microseconds, which is much smaller than the delay between two applied voltages (0.2 seconds), making this hypothesis untenable [57].

Time of penetration :

A final hypothesis is that water has cohesive properties. This could mean that water does not necessarily enter all the pores, or at least not immediately, as long as the stress exerted on it does not exceed its surface tension. Unused pores are equivalent to infinite resistances in parallel to those representing used pores. Over time, it is conceivable that water will be forced into previously unused pores, leading to changes in the measured current [58].

5.3.3 Selectivity analysis

Parasitic potential due to diffusion coefficient

As explained in the results, in order to calculate the transference number, 12 *mV* must be subtracted from the measured voltage to obtain the true membrane potential. The explanation is that as the diffusion coefficients are different, Cl will diffuse faster than Na. In other words: for a Cl that passes through the membrane, the Na has not yet arrived. As a result, there is an excess negative charge on one side. Because of this, an electric field is gradually created to slow down this imbalance of charges. At equilibrium, the current created by this difference in coefficients is compensated by the potential that can be measured (12 *mV*).

By developing the equation 4.6 and considering $i=0$ ($J_{Na} = J_{Cl}$), one can find the equation for this 'parasitic' potential :

$$\Delta\phi = \frac{D_{Cl^-} - D_{Na^+}}{D_{Cl^-} + D_{Na^+}} \frac{RT \ln([C_H]/[C_L])}{F} \quad (5.1)$$

In the case of NaCl solution, $D_{Na^+} = 1.334\text{e-}9$ and $D_{Cl^-} = 2.032\text{e-}9$, a potential of 12 *mV* is obtained.

Transference number

As a reminder, t_+ is defined as follows :

$$t_+ = \frac{I_{cation}}{I_{cation} + I_{anion}} \quad (5.2)$$

$$t_+ = 0.5 - \frac{zF}{2RT} \frac{E_{diff}}{\ln(\frac{\gamma_H C_H}{\gamma_L C_L})} \quad (5.3)$$

It is physically impossible for it to be greater than 1, which indicates that there must be an error in the measurements or in the hypothesis. The only parameters in 5.3 are E_{diff} and the ratio of activities and concentrations.²

As far as E_{diff} is concerned, it is unlikely that this is the source of the error. In fact, reference electrodes are used to avoid having the potential of the different redox reactions in action and the parasitic potential due to the different diffusion coefficient is subtracted in order to have the real potential of the membrane.

²Theoretically temperature is also a parameter but all the measurements were made in Welcome lab at 25 °C.

However errors can still occur as explained in the error analysis (section 5.3.2). The margin of error on the membrane potential value is most likely related to the multimeter used, which is far too small to explain the entire transference number error.

Concerning the ratio, its impact is much greater, since it is exponential. In the calculations, this ratio is considered to be equal to 10. To avoid imprecision errors, instead of assuming they are equal to 1, the activity coefficients (γ_i) should be calculated as follows [59] :

$$\log(\gamma_{i(l)}) = \frac{-0.511\sqrt{I_s}}{1 + \sqrt{I_s}} \quad (5.4)$$

Where $I_s = 0.5 \sum_{i=1}^2 c_i z_i^2$ is the ionic strength (equal to 1 in this work).

Since the ions in solution have the same valency (with opposite signs) the activity coefficients are considered to be equal and it is sufficient to calculate this coefficient for the different concentrations ($\gamma_{10^{-4}} = 0.989$, $\gamma_{10^{-3}}=0.965$, $\gamma_{10^{-2}}=0.9$). The ratio between the coefficient should be 0.975 and 0.93 for the situation with lower set of concentrations and higher set (respectively) instead of one.

In addition to this approximation error on the activity coefficient, the most likely cause is human error. The solutions at the various concentrations were made in the laboratory from 5M NaCl. This means that the volume needed to obtain a very low concentration is infinitesimally small. To limit human error, volumes of 2l for each concentration were prepared.

This means that for the 0.1 *mM* (resp. 1 *mM*, 10 *mM*) concentration, 0.04 (resp. 0.4, 4) millilitres of the 5M solution are needed. DI water was added in significant volumes (2, 1.9996 and 1.996 l) to reach the two litres aimed. Given that the test tubes used to measure water have a margin of error of 5 μl , that the micropipettes used in the laboratory only reach down to 20 μl and taking into account the possibility of human error, the accuracy of the concentration is very low.

To try and quantify the concentration better, the conductivity of the solutions can be studied. According to the literature, for concentrations lower than 0.1 *M* the regression of the concentration as a function of the conductivity can be considered linear [60][61]. However, the only solutions with guaranteed concentrations are those at 5 *M*³ and 0 (DI water). A calibrated 0.1 *M* solution would be needed to

³And yet, two different bottles of this purchased solution were measured and gave different conductivities

give the most appropriate linear regression, and by measuring the conductivity of the solutions, the exact concentrations could be found.

Figure 5.10 shows the log linear regression of conductivity against concentration. This curve is only experimental, but may enable a better estimation of the concentrations of the manufactured solutions which should be 0.1, 1 and 10 *mM*. According to this linear regression, these should be equal to 0.097 mM , 0.58 mM and 9.4 mM.

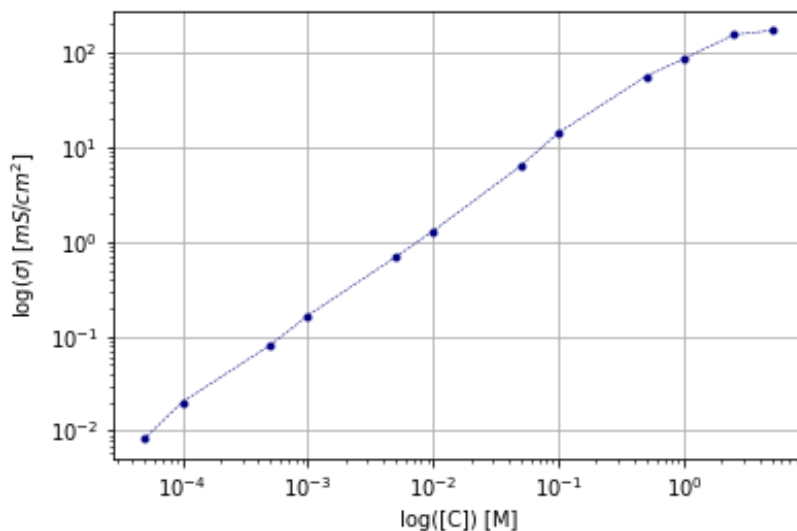


Figure 5.10: Linear regression of conductivity over concentration in both logarithmic scales. $\sigma = 0.14[C] - 6.03e^{-5}$

When combining the errors of activity coefficient and concentration values, the ratios used in equation 5.3 are 5.83 (for situation 1 and 2) and 15.64 (for situation 3 and 4). The corrected transference number are detailed for each membrane in appendix 7.3. Table 5.7 gathers the mean of non-outliers t_+ for the different membranes in their optimal situation of test.⁴

⁴The mean of non outliers t_+ is made considering only the values between 0 and 1 of each calculated t_+ .

In agreement with the simulation results, E_{diff} and t_+ are always better when concentrations are lower. However, these values can not be truly trusted. Indeed the number of outliers is very important. The most plausible explanation for this is the apparition of bubbles on the membrane surface. Therefore the fact that the selectivity is supposed to be better for the cylindrical pores might be due to a fortunate placing of bubbles. If not, these errors can still come from errors of measurement, human error, etc.

Membrane	C_H & C_L	$E_{diff, corrected}$	$t_{+, corrected}$
cylindrical	1 & 0.1 mM	-47.48	0.95
	10 & 1 mM	-23.43	0.63
conical	1 & 0.1 mM	-91.23	0.63
	10 & 1 mM	-35.87	0.615
pencil 70-30	1 & 0.1 mM	-92.152	Only outliers
	10 & 1 mM	-63.545	0.982
pencil 50-50	1 & 0.1 mM	-55.79	0.635
	10 & 1 mM	-5.89	0.543

Table 5.7: Corrected transference number for the different topologies.

5.3.4 Topology analysis

Conical membrane improvement with respect to cylindrical membrane

Confirming the literature and simulations, conical membranes did indeed give higher membrane potentials than cylindrical ones with currents of the same range. Also, as expected, the equivalent resistance is bigger for a conical membrane because at higher radius more current is able to flow through the pore. The orders of magnitude are not so different because the work is carried out at low concentrations (see section 2.5.2). Combined, these two facts lead to an average power that is 4 to 5 times greater for conical membranes.

It should be noted that for the cylindrical pore membrane, the thickness aiming to be 100 μm instead of 50 μm like all the other membranes, its resistance needs to be scaled so that it is comparable to that created for this work. Theoretically, the resistance of the cylindrical pores should be halved because it is linear with the length of the nanopores [62]. Meaning the difference between the obtained power would be less important. However, given the margin of error on the thickness due to the DRIE, there is no way of knowing exactly how thick they are.

Although the transference number values are probably wrong, the error is the same for all values (if it comes from the concentration/activity ratio). This means that the increase in t-values between cylindrical and conical membranes would still be similar to that shown in table 5.6.

Pencil membranes improvement with respect to conical membranes

A first analysis is done for the pencil membrane 70-30 and the last topology will be briefly discussed.

The aim of the pencil membranes was to achieve the same electrical performance as the conical type, but with a larger penetration volume and lower electrical resistance. Results showed that this objective was reached. There is even a slight increase in power performance.

The fact that the difference between the electrical resistances is so small is probably due to the fact that it is assumed to be less significant at low concentrations, as in this work. However, it is also possible that this difference is negligible because the thickness and difference between the radii is small enough to neglect the impact of the topology on the resistance.

As it is often the case in this field, the advantages come with disadvantages. Higher current density for anodizing means not only larger pores but also greater porosity. This means that there is little bulk Si left to give the material a solid body. The more porous the PSi, the more brittle it is. Experimentally, it turned out that the membranes that broke the most were in fact the conical ones (it was expected to be the pencil shaped 70-30 as it is less thick than the cylindrical but has the largest proportion of cylindrical part). One hypothesis is linked to the release technique. Indeed, the number of cycles used for the DRIE on this particular wafer was not chosen to release the first membrane, as was the case for the other wafers, but to release as many membranes as possible. This means that there is no real way of knowing the thickness of the membranes and that the majority of them have probably been over-etched, making the membranes weaker. Figure 5.11 shows a crack in the membrane after DRIE, many membranes were also broken during the experiments.

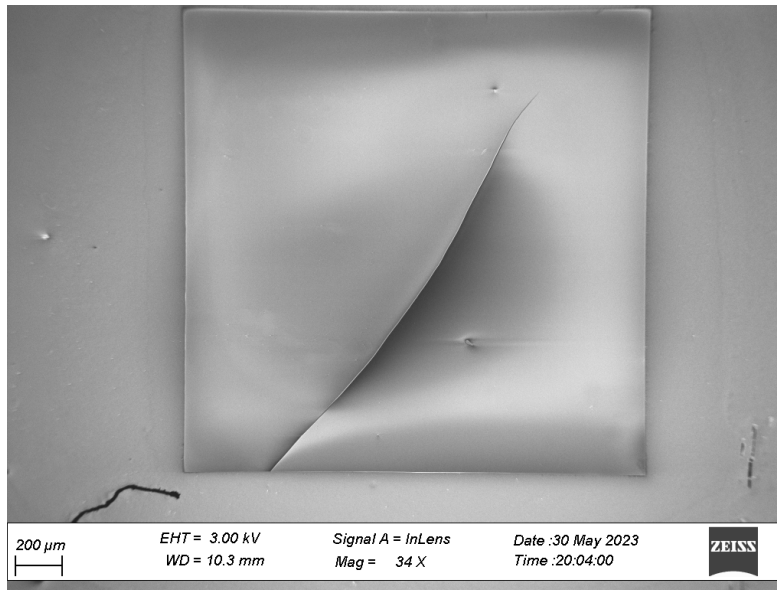


Figure 5.11: SEM image of a conical membrane after DRIE. A large crack crosses the surface.

Concerning the pencil 50-50 membranes, it was supposed to prove that the equivalent resistance should be between the conical and the pencil 70-30 's one. However, the results obtained do not correspond to expected results (same order than conical and pencil 70-30). This could be explained by the phenomenon explained in section 5.3.1 for the unusual inhomogeneity on this particular wafer. Some fraction of the membrane surface almost seemed to have clogged pores which lead to a less efficient membrane.

Another (less likely) hypothesis is the following. For the DRIE of the 70-30 and 50-50 wafer, a problem has arisen with the Oxford. The 50-50 membranes could be released (some of them) until the end, but when the wafer of the 70-30 membranes was etched, after circa 300 cycles all the membranes turned black. This is supposed to mean that the membranes are released, but the fact that they were all released at the same time and all at once seemed too odd. After removing the wafer in question from the Oxford, it turned out that there were problems with the plasma of the machine.

Although it would seem that the 70-30 membranes should have been more affected, since in fact the membranes had not yet been released, when the Oxford was repaired, the black deposit on it was removed and the membranes were released intact. However, the 50-50 membranes had already been released, but under unknown conditions. It's possible that a modified recipe (due to the technical problem) led to additional problems on the back side.

5.3.5 Concentration impact

As expected, higher concentrations gave higher currents. However, since the Debye length is inversely proportional to concentration, double-layer overlap (and hence selectivity) is no longer as effective. As explained in section 2.5.2, membrane resistance is also impacted by concentration.

Altogether, this results in maximum powers of the same order of magnitude for both sets of concentrations. However, to maintain such a power density due to the concentration gradient, a pumping system must be used to keep the solutions from chemically equilibrate.

5.4 Future works for improvement

5.4.1 Process upgrade

The main bottleneck of the process is the DRIE. In order to remove all the residues that seem to clog a part of the pores, it might be interesting to study the etching of the back of the wafer with the Corial 210IL, the STS 340 or the electrotech ET340 instead of the Oxford Plasmalab100.

All these equipments are available in WINFAB, and could be used. Even if their etching is anisotropic, they could be used to remove the last nanometers along with the passivation residus of the ICP-RIE Oxford chamber.

Another idea on the process topic would be to develop a new mask to make smaller membranes. This way the smaller membranes would be less likely to break.

5.4.2 Choice of solutions

As explained in section 5.3.3, a parasitic potential due to the difference of diffusion coefficient appeared in this work. By using Potassium chloride (KCl) solution, this problem would be solved as potassium and chloride have diffusion coefficients considered equal. Furthermore, the results would be more coherent with the numerical simulations (made with KCl).

Another important parameter is the concentration ratio. Smaller concentrations were chosen in this work to have the best EDL overlap possible. However, a bigger ratio would decrease the margin of error on the transference number. It would be interesting to study the same results with a concentration of 0.1 mM and 10 mM. The overlap should be as efficient at the lower concentration while ensuring better results.

Indeed, the Debye length for a concentration of 0.1 mM is 30 nm which is over the 15 nm diameter of the pore. Whereas, at the bigger end of the pore, where the concentration would be 10 mM , λ_D is 3 nm . Knowing that the bigger radius is supposed to be around 40 nm , this means that the ions have at least 34 nm where they can enter easily.

However, as the concentration is higher, the impact on the electrical resistance is more pronounced. Additionally, such a large concentration gradient implies a greater membrane resistance [35]. The trade-off between a higher concentration ratio and the resistance it implies should be studied.

5.4.3 Other topologies

Intuitively, it might seem that if the aim is to have a layer with smaller pores, all you have to do is leave the sacrificial layer in place. However, the problem with the sacrificial layer is that it is by nature uncontrollable and many pores end up with no opening.

Another idea proposed by R. Hanus and R. Vercauteren is to study stratified PSi. An alternation between layers whose pore size ensures selectivity and others with larger pores in order to absorb cracks and other defects. For the anodizing step, it has been shown in WINFAB that such a topology can be achieved in a single layer, but membranes have not yet been tested. Figure 5.12 shows stratified PSi on single layer. The cracks and detachment are successfully stopped by the 'absorption' layer. The results should be close to those of the conical topology. It would be interesting to assess the impact of reducing the current linearly or block-wise, and to see whether one of the two situations leads to fewer dead-end pores.

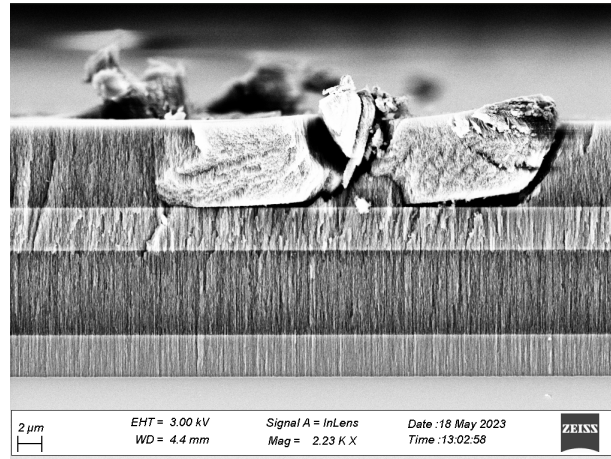


Figure 5.12: Crack stopped by stratified PSi

5.4.4 Noise

For broken membranes, an oscillation current around zero still appears. These oscillations are due to noise : thermal and electrochemical noise. The latter is usually described as stochastic pulses of current generated by sudden film rupture, crack propagation, discrete events involving metal dissolution, etc. Because the working electrode used in this work are homemade, this noise depends on the deposit on the electrodes [63] [1].

Better control over the manufacture of working electrodes and electrochemical noise would be highly beneficial.

5.4.5 Surface charge density

As explained in the literature and shown in the numerical simulation, the surface charge density can be highly beneficial. Indeed, changing σ increases the current flowing through the membrane without impacting the electrical resistance nor the EDL overlap. This parameter was not studied in this work as the focus was mainly on the topology influence but it would be very interesting to combine these two parameters. For instance, H. Dartoomi and Al. figured that adding a soft layer to increase the surface charge density was beneficial for every geometry of nanopore [35].

Many other research have been made, mostly in numerical simulation but the main challenge would be to study the adhesion of this soft layer in practice and its fabrication.

5.4.6 Experimental set-up

Despite all the corrections made to restore a logical transference number, some errors remain. A series of tests would have to be carried out to verify each hypothesis and each method of measurement in order to understand in greater depth where the error comes from. For instance, it would be necessary to find a way of ensuring that there are no more bubbles on the surface of the membrane.

5.5 Conclusion

In this section P*Si* was characterized. The targeted radii of 40 and 15 *nm* were reached as well as the 50 μm thickness.

Then, I-V curves of membranes made with this P*Si* were analyzed. From this, the figure of merits were calculated: the maximum power that can be withdrawn from the membrane in this set-up and the number of transference. Conical pores resulted in maximal power density five times greater than the cylindrical ones. However, unknown errors prevents us to conclude anything on the transference number.

The impact of error, overlap of the double layer and topologies were analysed and attempted to be explained.

- The averaged standard deviation for the measured voltage is 1.332 *mV* and for the current is 0.05 μA .
- An asymmetry appears when comparing the I-V curves for situations with opposite direction. However, this asymmetry is insignificant for higher concentrations, proving that the asymmetry is due to the EDL overlap.
- The topology which appeared to have the best performance for selectivity and power density is the pencil shaped. This matches the hypothesis made with numerical simulations.

Finally, ideas for future work were proposed. One of the main ideas would be to do the same experiments as in this work but with higher concentration ratio. For instance 0.1 and 10 *mM*. Additionally, only few different geometries were studied in this work but many other possibilities exist. Eventually, a study of a practical use of a soft layer to increase the surface charge density would be highly beneficial.

CHAPTER 6

CONCLUSION

The objectives of this work were to study numerically and experimentally the characteristics and potential benefits of membrane with conical pores and with pencil shaped pores in two different proportions (70-30 and 50-50).

Reverse electrodialysis is a renewable method to retrieve blue energy. It relies on electrochemical reactions to transform ionic current in electrical current in saline solutions. RED efficiency depends on the pumping system, the ions concentrations on both sides of the membrane and the membrane characteristics which was the main interest in this study.

There are different kinds of ion exchange membrane (IEM), depending on their selectivity (CEM or AEM) or their material (polymer or inorganic). PSi is easily integrable with CMOS and does not suffer chemical degradation such as the polymer IEM. Additionally, the control that the anodization offers on the porous morphology is an undeniable advantage when trying to create different shapes. Therefore, the membranes considered in this work are CEM in PSi.

The efficiency of the membrane is influenced by different parameters but the main interest of this work was the pore radius impact. According to literature, there is a trade-off between the selectivity caused by a smaller radius and a higher ionic current for a larger radius. The conical shaped pore is introduced as it might benefit from both advantages. In an attempt to maximise all the profits, the pencil pore shape is proposed as it might offer the same properties as conical pores, but with potentially lower internal resistance.

The CEM made out of PSi were fabricated in WINFAB cleanroom. As the electrical characterization set-up was explained, the importance of the reference electrodes has been highlighted. Indeed these allow to ignore the different redox potentials at each electrode and only measure the potential due to the membrane, the pore resistance and the water resistance.

In order to propose a proper topology, a numerical study of the parameters has been made, followed by a study of the anodization on a single layer of Si. The impact of the length, surface charge density and radius of the pore matched the literature as well as the behavior of a conical pore. Regarding the pencil shaped pore, the hypothesis of its benefits proved to be a trade-off between the selectivity of a conical pore and the higher ionic current of a cylindrical pore.

After several trials, the chosen parameters to obtain the conical and pencil shaped pore are 20 mA/cm^2 and 100 mA/cm^2 respectively for the minimal and maximal current densities and a channel length of $50 \text{ }\mu\text{m}$.

The key findings of this study are the following:

- The targeted topologies were reached with pore diameters of 40 nm and 13 nm on each side with a membrane thickness very close to $50 \text{ }\mu\text{m}$.
- The I-V curves measured showed that the asymmetry of the EDL overlap was more significant for lower concentrations proving that the EDL overlap is weaker when using higher concentrations.
- The main study was on the topology impact. Cylindrical pore membranes in PSi can retrieve up to a few mW/m^2 . The conical membranes reached four to five times greater power densities. Pencil shaped pores gave similar results in selectivity as well as power densities.

However, many improvements of the RED efficiency can be made. For instance, it would be interesting to revisit the experimental set-up by changing the concentration ratio and study if the selectivity would still be ensured while increasing the osmotic current. Another idea would be to change the surface charge density by adding a soft layer on the nanopore surface to experimentally quantify its impact.

Nevertheless, optimizing the efficiency of a RED system through the pore topology is a promising path that is still full of possibilities. For instance, it would be interesting to compare the conical pores to a stratified PSi.

CHAPTER 7

APPENDIX

7.1 ImageJ computation

ImageJ is a multi-platform, free and open source image processing and analysis software developed by the National Institutes of Health in 1997. It is written in Java and allows functions to be added via plugins and macros [64]. This section explains how the distributions for the PSi characterisation are obtained.

Top view images allow to determine the diameter at the bigger end of the nanopores and the initial porosity. Please note that this porosity changes along the membrane as it is a function of the current density. The porosity only gives us a mere idea of how many pores are probably in the membrane.

Figure 7.1a and 7.1b show the image taken with the SEM and the binary filter applied with ImageJ. To obtain the porosity, the ratio between the black area and total area is taken. To calculate the distribution of the front diameter, the software can detect the outlines of the pores from the binary image. The minimum Feret distance (smallest diameter of the pore) is calculated. A verification of the outliers (pore that fused together or wrong outline) is made and the mean of these Feret diameter is taken as the distribution of the front diameter.

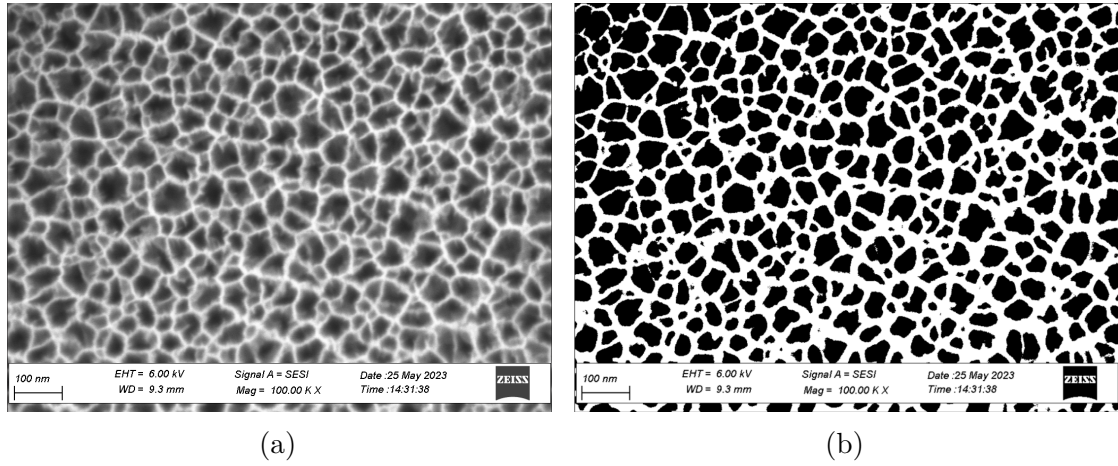


Figure 7.1: Top view SEM images of a membrane after the anodisation. a) shows the raw SEM image and b) shows the binary filter applied by ImageJ.

Cross sectional images allow to determine the thickness of the membrane and the diameter at the end of the P*Si*. To get the thickness, ImageJ is not needed. Indeed as in figure 7.2, it can be measured directly with the SEM. However to calculate the diameter distribution, ImageJ needs to have line on which it can plot the binary results. This line is represented in red on figure 7.3a and the resulting profile plot is in figure 7.3b. From these values, a mean of diameter can be obtained.

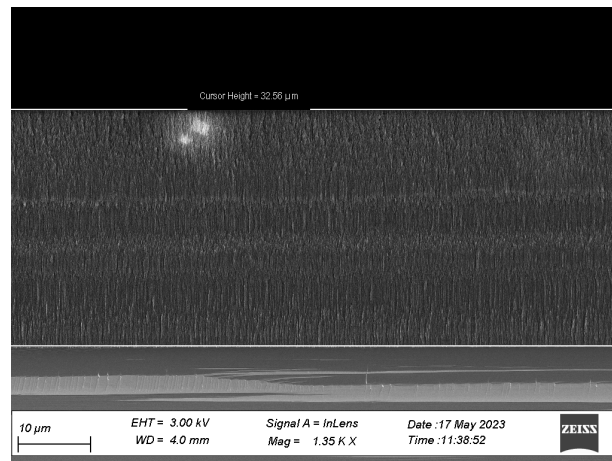


Figure 7.2: Cross sectional view of P*Si* to measure its thickness.

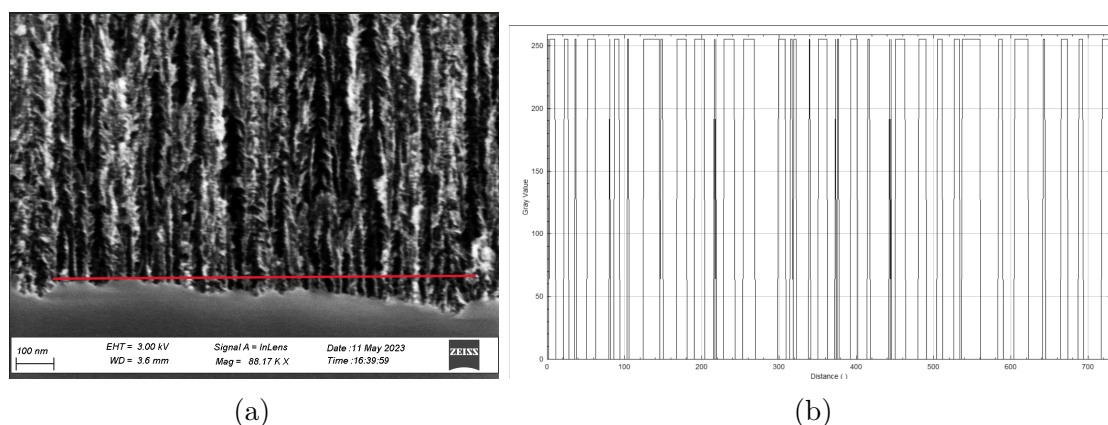


Figure 7.3: Top view SEM images of a membrane after the anodisation. a) shows the raw SEM image and b) shows the binary filter applied by ImageJ.

Even if ImageJ offers a more precise analysis of the PSi characteristics than a human approximation via SEM images, it is important to keep in mind that human error is still introduced in the software. Indeed, the threshold for the binary filter is chosen to best fit the original image but ultimately, it is not possible to be sure that it is exactly the correct threshold.

7.2 Anodization steps for each topology.

Conical membranes anodisation was made following these steps :

1. Sacrificial layer :
 $J = 100mA/cm^2$, $A = 2.229cm^2$, $t = 30seconds$ + removal of this layer with KOH
2. Linear current density :
 $J_{init} = 100mA/cm^2$, $J_{end} = 20mA/cm^2$, $depth = 50\mu m$, $\#cycles = 334$,
 $A = 2.229cm^2$

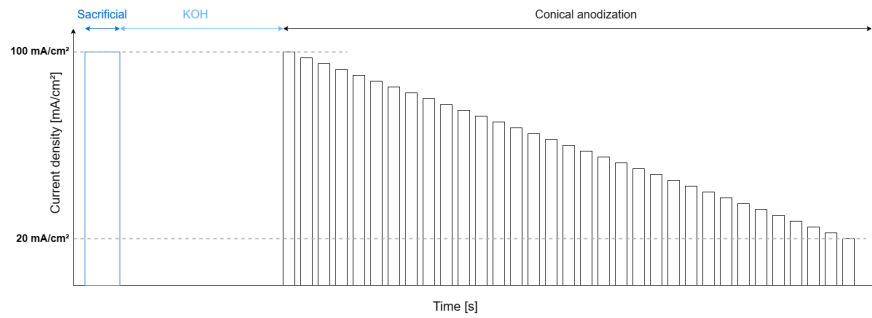


Figure 7.4: Schematic representation of the scripts current density output for the conical pores. The etch-stop ratio might be approximately represented for the conical anodization.

Pencil 70-30 membranes anodization was made following these steps :

1. Sacrificial layer :
 $J = 100mA/cm^2$, $A = 2.229cm^2$, $t = 30seconds$ + removal of this layer with KOH
2. Constant current density :
 $J_{cylindrical} = 100mA/cm^2$, $depth = 35\mu m$, $\#cycles = 62$, $A = 2.229cm^2$
3. Linear current density :
 $J_{init} = 100mA/cm^2$, $J_{end} = 20mA/cm^2$, $depth = 15\mu m$, $\#cycles = 100$,
 $A = 2.229cm^2$

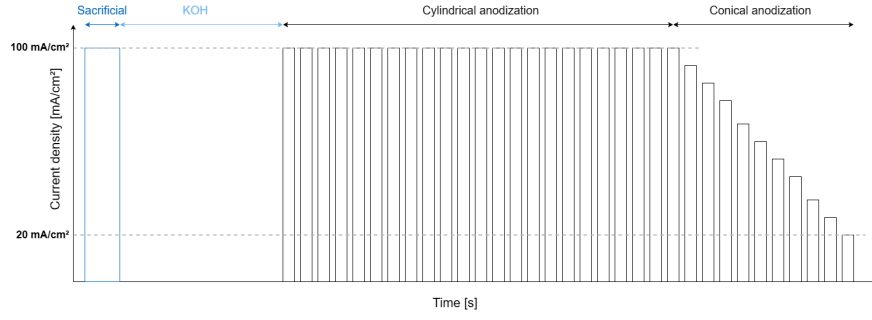


Figure 7.5: Schematic representation of the scripts current density output for the pencil shaped 70-30 pores. The etch-stop ratio might be approximately represented for the conical anodization.

Pencil 50-50 membranes anodization was made following these steps :

1. Sacrificial layer :
 $J = 100\text{mA}/\text{cm}^2$, $A = 2.229\text{cm}^2$, $t = 30\text{seconds}$ + removal of this layer with KOH
2. Constant current density :
 $J_{\text{cylindrical}} = 100\text{mA}/\text{cm}^2$, $\text{depth} = 25\mu\text{m}$, $\#\text{cycles} = 43$, $A = 2.229\text{cm}^2$
3. Linear current density :
 $J_{\text{init}} = 100\text{mA}/\text{cm}^2$, $J_{\text{end}} = 20\text{mA}/\text{cm}^2$, $\text{depth} = 25\mu\text{m}$, $\#\text{cycles} = 185$, $A = 2.229\text{cm}^2$

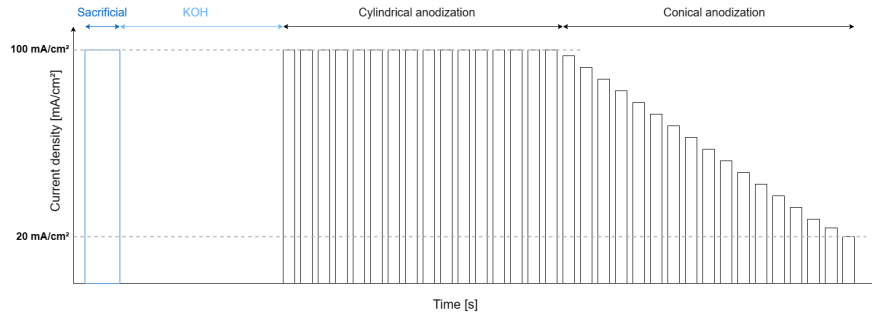


Figure 7.6: Schematic representation of the scripts current density output for the pencil shaped 50-50 pores. The etch-stop ratio might be approximately represented for the conical anodization.

Where J is the current density during the sacrificial layer, A the area accessible to HF for the anodization ¹, t the time of the sacrificial etching, J_{init} the current density at which the anodization starts, J_{end} the current density where the linear decrease ends. The linear decrease is made in $\#cycle$ steps.

¹This means the sum of all the membranes surfaces and spaces between the dies to separate them. The value is calculated by analysing a picture of a wafer after the anodization step in ImageJ and computing the area of black surface(PSi).

7.3 Detailed membrane results

Table 7.1, 7.2, 7.3, 7.4 gather the measured voltage and current for each membrane. The resistance is obtained by taking the inverse of the slope of the iv curve and the power is computed using equation 3.7. In these tables, the transference number is computed using the measured voltage meaning that the additional voltage due to the diffusion coefficient difference is still taken into account.

For conical membranes, it seems like v1[]1 is actually broken as the results are very different from what expected but close to results for a membrane with no selectivity. For v1o1, it is also the case but only when using bigger concentrations. This could mean that the membrane broke when changing the solutions.

For the pencil 70-30 membrane, the last two situation could not be studied on the last membrane as it broke when changing the solutions and no other membrane was left to carry the experiment on.

For the pencil 50-50, some very strange results occur. It might be because of the presence of bubbles on the surface as discussed in discussion.

For cylindrical membranes, not all the tests were made as it was only to have a reference to compare to.

For a test to avoid being an outlier for the transference number, its measured voltage must be between -29.5mV and 53.5mV (-52.75mV and 76.75 mV) for the lower (resp. higher) set of concentrations. Note that for all voltage higher than 12 mV it means that the membrane has an opposite ion selectivity as predicted (AEM instead of CEM). This could also be considered as an outlier.

Membrane	Concentrations	Direction	Time	$E_{diff}[mV]$	$I_m[\mu A]$	$R_{cell}[k\Omega]$	$P_{max}[nW]$	$t_{+corrected}$
v1o1	10-3vs10-4	up	1	-97	0.37	264.9	9	1.81
			2	-105	0.38	279.4	9.9	1.9
			3	-99	0.33	298.1	8.2	1.83
		down	1	6	0.02	302.7	0.031	0.58
			2	5.2	0.017	297	0.023	0.58
			3	4.8	0.016	293	0.02	0.59
	10-2 vs 10-3	up	1	2.55	0.07	38.1	0.04	0.573
			2	3.2	0.08	36.8	0.07	0.57
			3	3.5	0.1	35.9	0.08	0.56
		down	1	7	0.21	33.5	0.37	0.54
			2	7.2	0.22	32.5	0.4	0.54
			3	7.2	0.22	32.3	0.4	0.54
v1□1	10-3 vs 10-4	up	1	0.48	0.002	228	0.0002	0.64
			2	1.3	0.006	213	0.002	0.63
			3	2.72	0.013	205	0.009	0.61
		down	1	11	0.062	177	0.17	0.51
			2	12.13	0.078	154	0.23	0.5
			3	12.37	0.08	146	0.26	0.49
	10-2 vs 10-3	up	1	10.63	0.5	21.3	1.32	0.51
			2	10.74	0.49	21.9	1.3	0.51
			3	10.77	0.47	23.01	1.26	0.51
		down	1	10.11	0.61	16.5	1.54	0.514
			2	9.8	0.56	17.3	1.4	0.517
			3	9.68	0.53	18.1	1.29	0.518
v1o4	10-3 vs 10-4	up	1	-56.4	0.15	372.62	2.13	1.32
			2	-56.87	0.16	357.7	2.2	1.33
			3	-61.12	0.17	351.2	2.65	1.38
		down	1	-0.063	0.0001	346.7	3e-6	0.645
			2	-1.1	0.003	342.4	8.8e-4	0.657
			3	-8.02	0.024	334.1	0.048	0.74
	10-2 vs 10-3	up	1	-27.08	0.55	49.48	3.7	0.802
			2	-23.12	0.49	46.8	2.85	0.802
			3	-21.41	0.47	45.25	2.53	0.758
		down	1	-28.8	0.66	43.6	4.75	0.81
			2	-26.04	0.61	42.08	4.03	0.79
			3	24.42	0.59	41.12	3.62	0.4

Table 7.1: Conical membrane properties

Membrane	Concentrations	Direction	Time	$E_{diff}[mV]$	$I_m[\mu A]$	$R_{cell}[k\Omega]$	$P_{max}[nW]$	$t_{+corrected}$
w3o4	10-3vs10-4	up	1	-74.62	0.22	335.22	4.15	1.544
			2	-83.45	0.27	310.25	5.61	1.65
			3	-101.85	0.33	301.76	8.6	1.87
		down	1	11.74	0.037	319.77	0.107	0.5
			2	4.31	0.013	316.01	0.0147	0.59
			3	-1.0133	0.003	314.32	8.17e-4	0.65
	10-2 vs 10-3	up	1	-54.81	1.005	54.543	13.77	1.01
			2	-50.35	0.961	52.4	12.1	0.981
			3	-47.84	0.93	51.13	11.1	0.962
		down	1	-50.07	1.13	44.29	14.15	0.98
			2	-46.3	1.08	42.63	12.5	0.95
			3	-44.69	1.066	41.91	11.9	0.938
w3[]6	10-3 vs 10-4	up	1	-68.63	0.178	384.92	3.06	1.47
			2	-78.55	0.222	353.17	4.36	1.59
			3	-110.1	0.335	328.33	9.23	1.97
		down	1	37.78	0.114	330.07	1.08	0.19
			2	29.17	0.088	331.25	0.642	0.3
			3	22.4	0.067	331.65	0.38	0.37
	10-2 vs 10-3	up	1	-54.97	1.035	53.1	14.22	1.017
			2	-51.7	1	51.7	12.93	0.99
			3	-49.6	0.98	50.77	12.11	0.975
		down	1	-44.23	0.99	44.323	11.03	0.93
			2	-40.28	0.94	42.45	9.55	0.9
			3	-38.75	0.93	41.74	8.99	0.89
w3o5	10-3 vs 10-4	up	1	-62.77	0.23	276.03	3.56	1.4
			2	-69.8	0.25	277.56	4.38	1.48
			3	-71.6	0.25	287.4	4.46	1.5
		down	1	10.21	0.03	341.56	0.076	0.52
			2	7.76	0.023	335.95	0.045	0.55
			3	5.59	0.016	332.06	0.0235	0.57

Table 7.2: Pencil 70-30 membrane properties

Membrane	Concentrations	Direction	Time	$E_{diff}[mV]$	$I_m[\mu A]$	$R_{cell}[k\Omega]$	$P_{max}[nW]$	t_+
w4[]6	10-3vs10-4	up	1	-14.38	0.05	283.22	0.18	0.82
			2	-45.32	0.16	284.06	1.8	1.2
			3	-74.47	0.23	325.42	4.26	1.54
		down	1	24.58	0.126	194.8	0.775	0.348
			2	23.7	0.144	164.39	0.85	0.36
			3	22.62	0.148	152.684	0.838	0.372
	10-2 vs 10-3	up	1	6.4	0.306	20.91	0.49	0.54
			2	3.51	0.171	20.45	0.15	0.56
			3	1.4	0.06	21.16	0.023	0.58
		down	1	27.58	0.58	47.3	4.02	0.38
			2	27.5	0.58	46.94	4.03	0.38
			3	27.62	0.59	46.8	4.07	0.38
w4[]3	10-3 vs 10-4	up	1	5.6	0.04	129.37	0.06	0.55
			2	6.64	0.058	114.66	0.096	0.56
			3	6.31	0.057	109.5	0.091	0.57
		down	1	51.01	0.119	425.49	1.53	0.03
			2	53.95	0.13	413.82	1.75	-0.005
			3	56.42	0.137	411.89	1.93	-0.035
	10-2 vs 10-3	up	1	7.51	0.365	20.58	0.68	0.53
			2	8.23	0.418	19.705	0.86	0.53
			3	8.15	0.39	20.96	0.79	0.53
		down	1	15.19	0.31	49	1.17	0.475
			2	14.65	0.3	48.44	1.1	0.48
			3	14.19	0.297	47.78	1.05	0.48
w4o3	10-3 vs 10-4	up	1	3.43	0.014	240.21	0.0122	0.6
			2	-5.51	0.025	217.072	0.035	0.71
			3	-40.98	0.134	306.25	1.37	114
		down	1	65.95	0.15	437.23	2.49	-0.15
			2	61.1	0.144	423.73	2.2	-0.09
			3	55.92	0.137	407.88	1.92	-0.03
	10-2 vs 10-3	up	1	6.38	0.25	25.3	0.4	0.54
			2	6.67	0.28	23.58	0.47	0.54
			3	6.79	0.29	23.215	0.49	0.54
		down	1	4.99	0.31	15.72	0.39	0.55
			2	4.35	0.245	17.77	0.267	0.56
			3	4.65	0.25	18.35	0.294	0.55

Table 7.3: Pencil 50-50 membrane properties

Membrane	Concentrations	Direction	Time	$E_{diff}[mV]$	$I_m[\mu A]$	$R_{cell}[k\Omega]$	$P_{max}[nW]$	t_+
RH1	10-3vs10-4	up	1	-25.19	0.108	232.27	0.68	0.95
			2	-31.04	0.132	234.61	1.02	1.01
			3	-37.45	0.158	236.717	1.48	1.09
		down	1	-9.87	0.03	320.418	0.076	0.76
			2	-4.83	0.016	303.33	0.02	0.7
			3	-4.12	0.014	298.146	0.014	0.69
	10-2 vs 10-3	up	1	-11.17	0.32	34.316	0.91	0.679
			2	-11.53	0.34	33.983	0.98	0.68
			3	-11.82	0.35	33.617	1.038	0.68
		down	1	-14.46	0.415	34.855	1.5	0.7
			2	-10.95	0.332	32.99	0.908	0.677
			3	-8.63	0.27	31.646	0.59	0.66
RH2	10-3 vs 10-4	up	1	-31.78	0.147	215.69	1.17	1.02
			2	-37.33	0.172	216.4	1.61	1.09
			3	-43.21	0.196	220.189	2.12	1.165
		down	1	-25.14	0.089	280.747	0.56	0.95
			2	-23.86	0.087	273.947	0.52	0.93
			3	-23.5	0.087	269.91	0.93	0.283
RH3	10-3 vs 10-4	up	1	-47.53	0.2	283.273	2.37	1.21
			2	-49.002	0.201	243.3	2.46	1.23
			3	-50.72	0.205	246.82	2.6	1.25

Table 7.4: Cylindrical membrane properties

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