

École polytechnique de Louvain

Harvesting blue energy using porous silicon

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List of Abbreviations

AEM	Anion exchange membrane
ALD	Atomic layer deposition
CAPMIX	Capacitive mixing
CEM	Cation exchange membrane
CP	Concentration polarisation
CVD	Chemical vapour deposition
DBL	Diffusion boundary layer
DRIE	Deep reactive ion etching
EDL	Electric double layer
EIS	Electrochemical impedance spectroscopy
IEM	Ion exchange membrane
IOT	Internet of things
LPCVD	Low-pressure chemical vapour deposition
MCU	Micro-controller unit
MEB	Mixing entropy batteries
OCV	Open circuit voltage
PECVD	Plasma enhanced chemical vapour deposition
PRO	Pressure retarded osmosis
PSi	Porous silicon
PZC	Point of zero charge
RED	Reverse electro-dialysis
RIE	Reactive ion etching
SEM	Scanning electron microscopy
SGP	Salinity gradient power
SMU	Source/monitor units
TEM	Transmission electron microscope
UCL	Université Catholique the Louvain-la-neuve
VPD	Vapour pressure difference utilization

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Outline master's thesis

The increase of autonomous nodes for the Internet of Things (IoT) leads to an increasing demand for sustainable and compact energy sources in order to supply them. A typical power requirement for future nodes is in the range of 100 μW and less. In this field, it is also important to reduce the environmental footprint and avoid fossil fuels.

Emerging as a concept in the 1970's, the so-called "blue energy" or "salinity gradient power" is harvesting the free energy released during the mixing of waters with different saline concentrations. For instance, the mixing of freshwater and seawater near estuaries can be harvested with devices implementing this concept. This clean and green energy is not producing any waste.

Several approaches have been proposed to collect the blue energy. Most of them are based on semi-permeable or ionic-conducting membranes. This thesis will be investigating the use of porous silicon as specific embodiment for the salt/fresh water separation and mixing control.

Porous silicon is obtained by the electrochemical etching of monocrystalline silicon. This step is well-known in the micro and nanofabrication cleanrooms of UCL (WINFAB) and results in nanochannels perforating the silicon substrate. The objective of the thesis will be targeted at fabricating and characterizing porous silicon membranes, and perform surface treatments to change the conducting properties of the substrate. A test bench will be set up to test the energy harvesting of different membranes and various electrode configurations.

According to the interest of the student, the thesis may also include the development of the circuit-equivalent battery model with the parameters influencing the energy harvesting device's performances.

Chapter 1

Harvesting energy from salted water

In this chapter, the concept of the "internet of thing" or IoT is presented and more specially about the sensors part and their consumption. The problem of self sustainable sensors is then discussed and the energy harvesting solution explored. One of the environmental energy sources that could be used to generate energy is found in the concentration difference between fresh and salted water. Finally, one of the most advanced techniques to harvest this environmental is presented.

1.1 Internet of things, where devices meet the internet

In this section, a brief description of the IoT and its concepts are presented.

1.1.1 The big network

It was in 1999 that the first effort to connect objects (things) through the internet was made[1], with the concept of creating a network that could link-up physical devices with the help of sensors and software through intelligent interfaces. During the same year, Kevin Ashton introduced a term "Internet of Things" (IoT) to describe a system in which physical objects could be related to the sensors and the internet[2]. Day-by-day the world is changing and IoT along with it. Iot services can now collect requested data from different sources and transfer it to the other devices and systems automatically: it goes beyond machine-to-machine (M2M) interaction. Thus, it became possible to solve business tasks and personal issues with ease and flexibility.

Nowadays, our lives, both professional and personal, are a part of the digitized world. The Internet of things is the extension of Internet connectivity into physical devices and everyday objects [3]. The devices, embedded with electronics, internet connectivity, and other forms of hardware (such as sensors), can communicate and interact with others over the Internet, and they can be remotely monitored and controlled as schematically shown in Figure 1.1. Some report predict that the number of connected IoT devices is expected to increase up to 26 to 35 billion by 2020[4, 5].

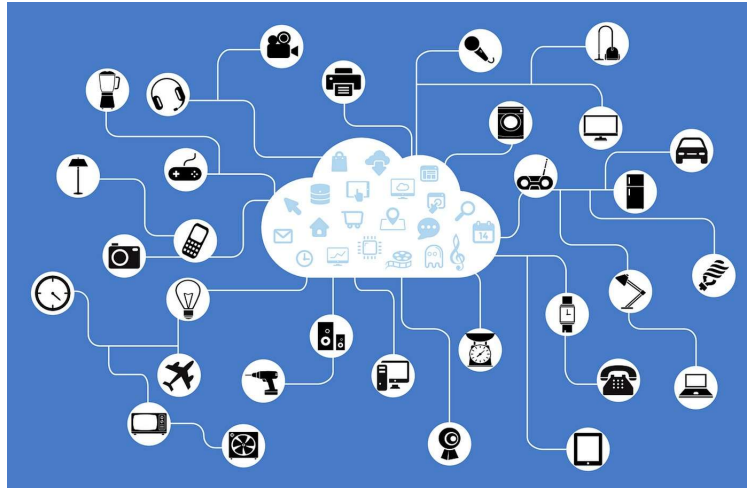


Figure 1.1: Schematis of IoT. Each "thing", called a node, interacts with its environnement and others nodes by collecting and sending data. Taken from [6].

IoT can be seen as a sensor network with sensor nodes connected between them. The sensors nodes consist of sensing, data processing, and communicating component, taking advantage of the sensors networks idea[7]. The sensor network is more usually modelled with a sensor model, as shown in Figure 1.2, consisting of a large number of sensor nodes deployed over a large geographic area or sensing field and one base station or sink node [8].

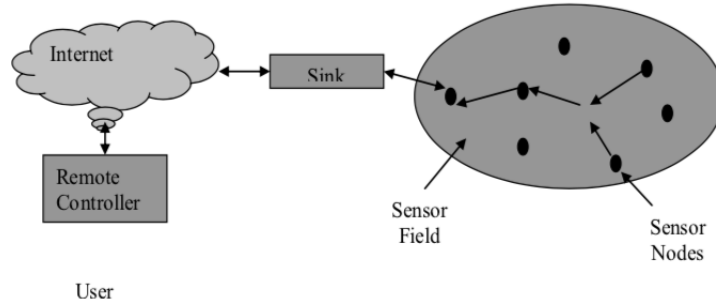


Figure 1.2: Wireless Sensor Network Model. Reproduced from [8].

The emergence of smart IoT devices will continue to grow in applications as diverse as fitness, automotive, medical arenas and house. Despite their broad difference in usage, a similar architecture is shared between sensors nodes or motes designs. As shown in Figure 1.3, power-management circuits and energy transducers are used as the power supply to the load, while micro-controller units (MCUs) wirelessly transmit sensor data to data aggregators, other node, systems, or even tablets and smartphones in the wireless sensor network which can then communicate to a remote controller, via the Internet, recolted data [9].

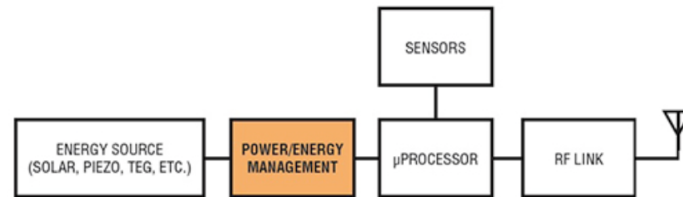


Figure 1.3: Box representation of the different part of a sensor node. Reproduced from [9].

1.1.2 Typical sensors consumption in IoT

In the near future, expectation for millions of smart sensors pushing data to the IoT depend on successful deployment of MCU-based wireless sensor nodes capable of operating for years without battery replacement. Yet, the possibility for engineers to achieve a "zero power" design depends on careful attention to low-power operation of RF transceivers and MCUs, both while sitting idle between measurements and during active sensor-data collection [9].

In a typical IoT smart sensor application, power consumption is divided between sensing, processing and sending data. However, a node is not constantly sensing and sending data and it might sit idle for long periods of time between peak periods

of activity. Consequently, the power demand profile of a node exhibits high periodic peak power periods separated by long periods of lower power operation as shown in Figure 1.4. It is interesting to note that most of the power consumption is due to relatively extended time of operation of wireless communications within these peaks. In fact, it has been shown the power consumption for transmitting one bit may be as high as executing a few thousands instructions [8].

In the case where idle time largely dominates peak-period duration, for example with slow-changing data, the low power consumption of the system can easily represent the largest part of power loss over time [9].

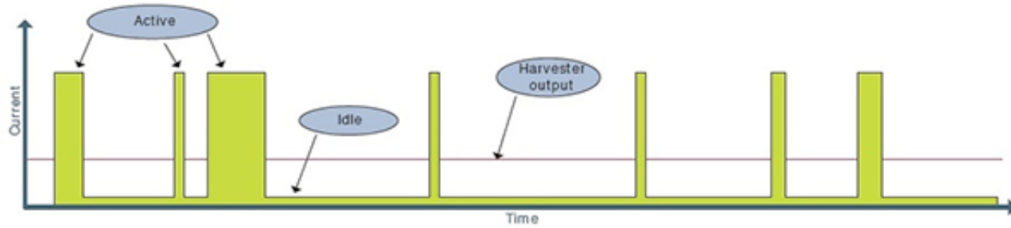


Figure 1.4: Typical power consumption over time of a sensor. Reproduced from [9].

Regarding the energy consumption of the sensing part, it depends on specific sensor category. The typical energy consumption of sensing subsystem is shown in Table 1.1. As mentioned above, this part is in many cases insignificant with respect to the energy consumed by the communication subsystem and the processing [8, 10].

Sensor Type	Power Consumption
low-power GPS	5 W
Motion detection	4 W
Gas	500 mW-800 mW
Acoustic	500 mW
Pressure	10 mW-15 mW
Humidity	3 mW-15 mW
Acceleration	10 mW
Temperature	0.5 mW-10 mW

Table 1.1: Sensor types and typical power consumption [11, 8, 10, 12, 13].

1.2 The need for alternatives energy ressources

The challenge behind truly pervasive smart spaces is energy sustainability. Traditionally, non-rechargeable limited-capacity batteries are used for wireless

sensor networks (WSNs), the backbone of many smart spaces, in order to meet energy sustainability while being non-intrusive. Although many efforts are made to improve and prolong the system lifetime by maintaining the system performance under energy-efficient requirements, maintenance cost remains a huge charge in WSNs due to the short batteries life-time.

A promising solution concerning energy reduction and the issue of energy sustainability related to the limited battery in WSNs is renewable energy technologies such as energy harvester and more specifically micro-scale energy harvesting systems. The concept of micro-scale energy harvesting systems as opposed to macro-scale energy harvesting systems (such as solar or wind farms) is defined as [11]: *Micro-scale Energy Harvesting Systems are small low power devices which have energy harvesting subsystems capable of harvesting energy from the surrounding environment to fully or partially power the whole system, hence attain almost perpetual system lifetime.*

Micro-scale energy harvesting systems offers many advantages such as energy sustainability, environmental friendliness, energy scalability, low maintenance cost, diversity etc. . Ideally these would enable to prolong the lifetime of a WSN (perpetually), there remain, however, important problem. It starts to become quite a challenge to realize such sustainable micro-scale energy harvesting system considering the unstable nature of environmental energy sources in addition with the variable demanding requirements of applications, the heterogeneity in energy harvesting systems, size and cost[11].

The choice of a feasible energy source(s) depends on the size constraint, the location where sensors are deployed, cost and power demand. Any energy source in the surrounding environment that has the potential to be converted into useful energy for powering partly or totally sensor networks in smart spaces is considered as energy harvesting sources. Table 1.2 shows different energy sources for energy harvesting, their source type, and typical harvesting power.

Energy source	Type	Typical power
Outdoor solar light	Natural	100mW/cm ² (outdoor)
Indoor solar light	Artificial/natural	100μW/cm ² (artificial light) 10mW/cm ² (filtered solar light)
Ambient radio frequency	Artificial	0.001μW/cm ² (Wifi) 0.1μW/cm ² (GSM)
Thermoelectric	Artificial	60μW/cm ²
Vibration	Artificial	4μW/cm ³ (human motion) 800μW/cm ³ (machines)
Ambient airflow	Natural/artificial	1mW/cm ²
Acoustic noise	Natural/artificial	960nW/cm ³

Table 1.2: Energy harvesting sources. Reproduced from [11].

Finally, it is important to understand that micro-scale energy harvesters are not mean to replace batteries, but rather support to prolong their lifetime. In fact, in Figure 1.4, peak power demand of some motes can be higher than the available ambient energy source, thus still requiring use of energy storage.

Nevertheless, the values in Table 1.2 shows that micro-scale energy harvesting system are good potential energy source for low power sensors (Temperature, acceleration, humidity ...) and general sensor boards since their power range matches (Table 1.1 and 1.2). Medium (acoustic, magnetic ...) and maybe high power sensors (GPS, motion detection ...) could also be supported by micro-scale energy harvester but a more sophisticated control would be required.

1.3 Harvesting energy from salted water and Reverse electrolysis

In this section, a form of energy based on salinity concentration difference is introduced. First, its potential in term of energy capacity is developed and compared to other form of known energy. Then, a membrane based applications, called the reverse electrolysis or RED, is described. Finally, a novel way of producing membranes for RED is presented.

1.3.1 Salinity gradient power and Techniques for harvesting the blue energy

Salinity Gradient Power (SGP) or Salinity gradient energy, also referred to as 'Blue Energy', is generated by converting the chemical potential between a

diluted and a concentrated salt solutions into useful energy such as electrical and mechanical energy [14]. It is a clean, sustainable energy source and the process itself does not produce any toxic gas emissions. Theoretically, 2.3 MJ of Gibbs free energy can be generated by mixing 1 m³ of freshwater with a large volume of seawater [15]¹. Consequently, compared to other electrical energy storage, the power density of salinity gradient energy is rather small as shown in Table 1.3. This makes salinity gradient power based battery applications hardly feasible. However, one of the advantages of salinity gradient power is the quantity of salted and fresh water around the world.

Systems	Specific energy (Wh/kg)	Energy density (Wh/L)
Pumped hydroelectric storage	0.5-1.5	0.5-1.5
Salinity gradient energy	0.6	0.6
Battery		
Lead acid	30-50	50-80
Li-ion	75-200	200-500
Fuel cell	800-10000	500-30000
Solar fuels	800-100 000	500-10 000

Table 1.3: Specific energies and energy densities of electrical energy storage systems [15]. More data in [15].

River and seawater are the most common sources for the salt solutions, but there are many potential other resources of SGP. For example, natural sources (e.g. the Dead Sea) or brine solutions from anthropogenic sources (solar ponds, industrial streams), saline wastewater from industrial processes or domestic source, etc.

Compared to other marine-based energy source, the unexploited estuarial SGP is the second largest next to ocean waves (see Table 1.4[14]), with an estimated maximum global potential of 2.6 TW. The one from wastewater discharged into an ocean is estimated to be 18 GW as an example. If we consider only the most relevant water bodies, an extractable part around 2000 TWh/year of gross global potential of salinity gradient energy estimated at 27,000TWh/year is possible. This is more than 10% of the total global potential of renewable energy resources [14]. Many parameters are expected to influence this estimation, depending on technical and operational factors, such as efficiency, flow rate, temperature, recovery rate, salinity levels and other aspects, including ecological and legal constraints. With

¹ $\Delta G = G_{s+f} - (G_f + G_s)$

the present technique, the available part of the total global potential of SGP for extraction is estimated at 0.98 TW [14].

Marine renewable energy resources	Driving force	Global potential (TW)
Salinity gradient energy	Salinity difference	2.6
Thermal energy conversion	Temperature difference	2.0
Ocean waves	Kinetic energy transfer	2.7
Tides	Water flow and Gravitational forces	0.03
Ocean currents	Temperature difference and water flow	0.005

Table 1.4: Comparison of salinity gradient energy global potential with other marine renewable energy resources[14].

SGP can be exploited continuously unlike intermittent wind and solar energy sources. The concept of SGP as a renewable energy resource is illustrated in Fig. 1.5 with an example of the natural water cycle showing the mixing with each other of river water, brackish water, seawater or brine as SGP. What is

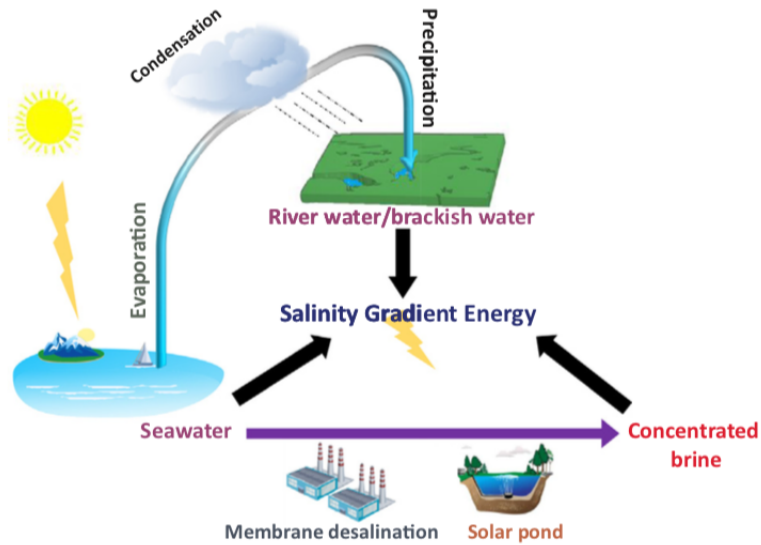


Figure 1.5: The natural water cycle illustrating the possibility of continuous exploitation of SGP; concentrated brine can be obtained from anthropogenic sources like seawater desalination plants and/or solar evaporators (ponds) [14]

There exist different technologies that can generate SGP. Reverse Electrodialysis

(RED) and pressure retarded osmosis (PRO) are two membrane-based technologies. However, RED is based on the diffusion of ions through ion exchange membranes to generate SGP in a closed electrical circuit, while PRO is based on the pressure difference created by the transfer of water due to the concentration imbalance. The pressure difference is then used to operate a turbine in a external circuit. Microbial RED is variant of the classical RED technology. In the latter, electrode are used to close the electrical circuit by the mean of redox reactions. However, due to thermodynamically unfavourable electrode reactions, electrode over-potentials create significant energy losses and as a consequence a large number of stacked cells² must be used to have significant energy recovery. In an Microbial RED, this can be avoided through oxidation of organic matter by exoelectrogenic bacteria on the anode and oxygen reduction on the cathode[16].

The precedent technologies are based on membrane separating the solutions, but there are also others technologies producing SGP which do not use membrane, such as mixing entropy batteries (MEB)[17], capacitive mixing (CAPMIX)[18] and vapour pressure difference utilization (VPD)[19]. The most advanced stage of development technologies are the two promising membrane-based technologies PRO and RED. As these two technologies relies on membrane, their application is strongly based on the cost, energy efficiency, and lifetime of the membranes themselves.

1.3.2 Principle of reverse electrodialysis

A typical RED unit operated on two solutions of different salinity is illustrated fig. 1.6. In RED, cation exchange membranes³ (CEMs) and anion exchange membranes⁴ (AEMs) stacked in a alternate fashion create a series of adjacent high concentration compartments (HCCs) and low concentration compartments (LCCs)[14]. An electrochemical potential is generated by salinity gradient and charge segregation, induced by ion exchange membranes (IEMs). An electrical current is created toward an external circuit by the conversion of the resulting ionic flux into electricity by a redox reaction occurring at the electrodes. Use of appropriate electrode rinse solutions and proper selection of electrode materials can maintain a low overpotential of the electrode[14, 20]. In this configuration, the RED stack can be seen as a classical fuel cell: as the concentrations between the high and low compartments equilibrate, the electrochemical potential and the electrical current both decrease down to zero. However, if the stacks of high and low concentration compartments is fed with salted and fresh water respectively by

²A cell is composed of 2 ions exchange membranes, one for cations and the other for anions, one diluted salt solution and one concentrated salt solution.

³CEM is a membrane that has a strong tendency to let pass cations and block anions.

⁴AEM is a membrane that has a strong tendency to let pass anions and block cations.

an external source, the RED stack is no longer considered as a battery, but as an energy harvester.

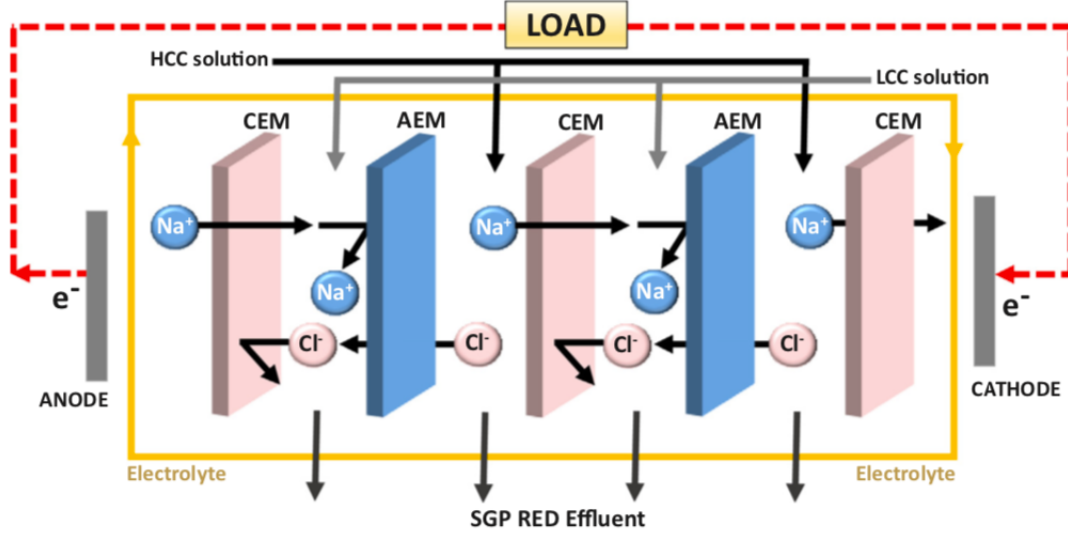


Figure 1.6: Schematic illustration of a RED stack: the electrochemical potential is generated when feeding each high concentration compartment (HCC) and low concentration compartment (LCC) created by aligning alternatively a CEM and an AEM. The salinity gradient drives the selective transport of ions across the membranes towards electrodes where a redox reaction allows continuous generation of electricity. Reproduced from[14].

The following development for the RED principles are based on [14]. Two adjacent IEMs constitute a single ‘cell’ (sometimes called a ‘cell pair’), consisting of an anion exchange membrane (AEM), a low concentration compartment (LCC), a cation exchange membrane (CEM) and a high concentration compartment (HCC) as shown in Figure 1.7. A RED stack usually includes a large number of cells.

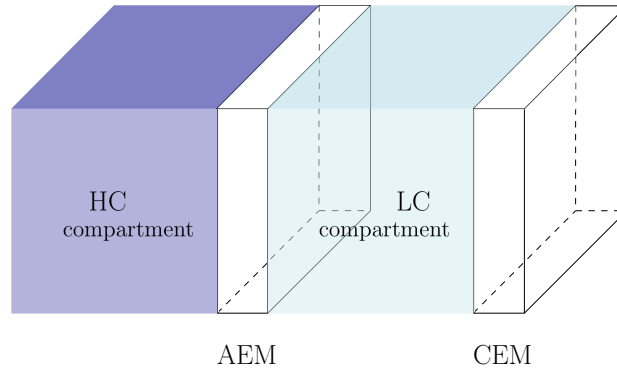


Figure 1.7: Two adjacent IEMs constitute a single ‘cell’, consisting of an anion exchange membrane (AEM), a low concentration compartment (LCC), a cation exchange membrane (CEM) and a high concentration compartment (HCC).

The total electromotive force generated in RED, which is the sum of the Nernst potential over each cell, is the Open Circuit Voltage (OCV), theoretically calculated by the Nernst equation [14]:

$$OCV = \frac{NRT}{F} \left[\frac{\alpha_{CEM}}{z_{ct}} \ln \frac{\gamma_{c,ct} C_c}{\gamma_{d,ct} C_d} + \frac{\alpha_{AEM}}{z_{an}} \ln \frac{\gamma_{c,an} C_c}{\gamma_{d,an} C_d} \right] \quad (1.1)$$

where N is the number of membrane pairs (cell pairs), α is the permselectivity of the ion exchange membrane, subscripts ‘an’ and ‘ct’ stand for ‘anion’ and ‘cation’, respectively. OCV is mainly dependent on the membrane permselectivity, the concentration gradient and the valence of the transported ions. The membrane permselectivity (α) represents the ability of the material to selectively transport only counter-ions (i.e. cations in CEMs or anions in AEMs) and to exclude co-ions (i.e. anions in CEMs or cations in AEMs), which explains why a low permselective membrane will show a lower OCV.

Theoretically, a potential of about 0.12V, 0.16V and 0.2V can be generated from a pair of IEMs (considering 100% permselective membranes) by mixing brine (5 M NaCl)/seawater (0.5 M NaCl), sea water (0.5 M NaCl)/river water (0.017 M NaCl) and brine (5 M NaCl)/ brackish water (0.1 M NaCl), respectively. But in real IEMs, the value of the permselectivity will be lower than 100%, reducing the OCV.

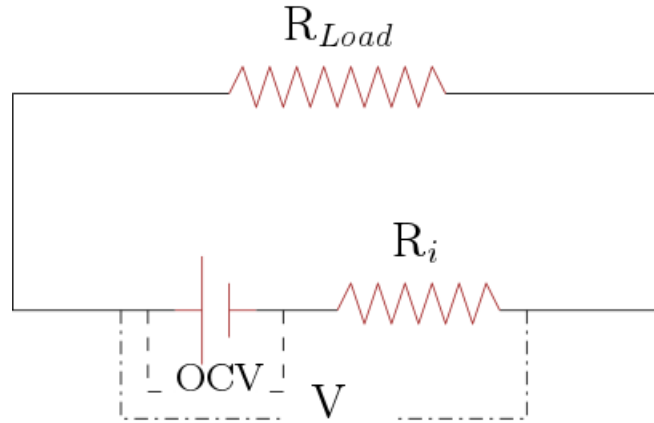


Figure 1.8: Equivalent electrical circuit for a RED stack of cell with a load. The stack of cell is represented by a source voltage OCV with an internal resistance R_i .

For an ideal RED stack working in the ohm's regime (see Chapter 4), the equivalent electrical circuit for the stacks of cell is a resistance in series with a voltage source as shown in Figure 1.8, with an open circuit voltage equal to the OCV, given by (1.1). The maximum power density $P_{d,max}$ (W/m²: Watt per m² of total membrane area) is obtained when the load resistance equals the internal stack resistance ($R_{Load} = R_i$):

$$P_{d,max} = \frac{OCV^2}{4AR_i}, \quad (1.2)$$

where A (m²) is the active membrane area and R_i the internal stack resistance.

The ultimate objective of a RED operation is to achieve the highest possible value of net power density. It is important to note that net power density depends on several parameters related to the intrinsic electrochemical performance of IEMs, stack configuration (number of cell pairs, channel length), hydrodynamics, nature of available saline streams (ionic composition, the presence of foulants). More specifically, in eq. (1.2), $P_{d,max}$ depend on OCV^2 and R_i , which need to be maximized and minimized respectively in order to achieve the highest maximal power density possible. Regarding the membrane properties, this can be done with a high permselectivity α combine with a low electrical resistance.

1.3.3 Power generation with RED

One of the key parameter in any energy harvester is power density, which is the case also for RED. Other parameters such as internal stack resistance are also interesting for the system design. Many factors influence the maximal power density such as the membrane properties, the feed characteristics (composition and

concentration) and operating conditions (flow velocity and temperature). Thus, a value for the power density in a RED design must always be associated with the RED conditions. Table 1.5 summarizes some power density values alongside the RED conditions from the relevant literature[14].

Many effort have already been made to improve the performance of RED in the past, but mostly at the lab scale. Large-scale RED advances and scale-up is limited. Nevertheless, in the Netherlands, the first 5 kW RED pilot plant was operated by REDstack BV together with Frisia Zout BV (a European salt company) [27]. On October 2013, still in Netherlands, a first real-world RED pilot plant with a capacity of 50 kW started to be build [28, 27]. The idea of the installed RED pilot plant was to mix fresh water (0.2–0.5 g/L NaCl) from Lake Issel and salt water (28g/L NaCl) from the Wadden Sea/North Sea to generate electricity [28]. By 2020, the upscale target is to generate 1 MW while investigating on improvement of the stack design [27].

Another pilot-scale RED system was developed and demonstrated in Italy under an EU-FP7 REAPower project in 2014 [29, 30, 31]. Equipped with 125 cell pairs and and active area of 50 m² (44×44 cm²) (Figure 1.9), the first tests of the RED pilot plant with saturated brine (4–5 M NaCl) and artificial brackish water (0.03 M NaCl) resulted in a maximum output power of 65 W [30]. In 2016, a further scaled-up was planned to produce a nominal power capacity of 1kW, ($\simeq$ 700 with artificioal solutions), but a 50% decrease in power density was observed when using real solutions.

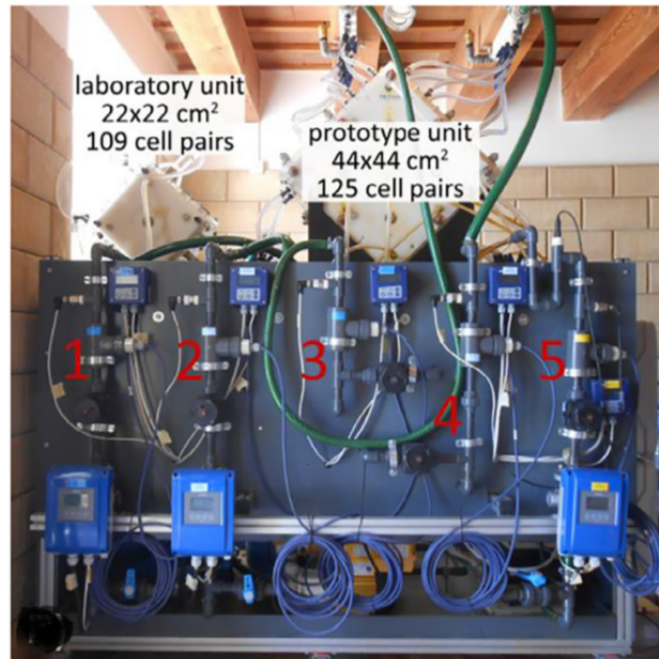


Figure 1.9: RED pilot plant installed at Ettore-Infersa Saltworks in Marsala (Trapani, Italy) with 125 cells and 44×44 cm² single membrane area.

Reproduced from [30].

Membrane	A (cm ²)	N	Electrolyte	Electrode	Power $P_{d,max}$ (W/m ²)	Ref.
PC-SK and PC-SA (PCCell, Germany)	8×8	10	~ 0.6M NaCl	Ti coated ith Pt	~ 0.33	[21]
Neosepta AMX/CMX (Tokuyama Co., Japan)	10×10	4	0.5M NaCl	Ti-RuO ₂ /IrO ₂	0.8	[22]
Neosepta CMX/AMX (Tokuyama Co., Japan)	10×10	2-30	0.25M NaCl	Capacitive electrodes (Ti-Pt with activated carbon)	~0.95	[23]
Selemon AMV/CMV (Asahi Glass, Japan)	10×10	5	~0.25 NaCl	Ti-RuO ₂ /IrO ₂	1.18	[24]
FKS/FAS (FumaTech GmbH, Germany)	10×10	5	0.025 M K ₃ Fe(CN) ₆ , 0.025 M K ₄ Fe (CN) ₆ and 0.25 M NaCl	Ti-RuO ₂ /IrO ₂	2.2	[25]
FumasTech FAD/FKD (GmbH, Germany)	10×10	50	0.05 M K ₄ Fe(CN) ₆ , 0.05 M K ₃ Fe (CN) ₆ and 0.25 M NaCl	Ti-RuO ₂ /IrO ₂	6.7 (60°C)	[26]

Table 1.5: RED conditions and power densities reported in the literature on testing and optimization. Spacer type, spacing distance between two membrane and speed of the feed solution not detailed for more clarity. More detailed information in [14].

Thus, in order to turn RED into a competitive technology for power generation, there is still a set of important questions/challenges which deserve special attention. Such fields of research are related to fluid dynamics (profiled membranes, stack arrangement) and stability against fouling of the membrane when using natural saline streams (sea and river water), membrane properties (electric resistance and permselectivity) and its cost [14]. The main advantages of RED is that it is a clean and an inherently sustainable technology. However, this technology is limited by the cost and performance of membranes. For example, a low resistance membranes cost is still high (above 94 euro /m²) [32, 33]. Technical requirements for RED applications are not met by cheap membranes, mainly due to a lack of low resistance. To overcome the current limitations, development and design of new IEMs with high permselectivity and low resistance at an affordable cost need to be the first target in advanced technological innovations of RED[14].

1.3.4 Micro-scale energy harvesting RED

Most of the current IEMs share a similar homogeneous polymer based structure (see next Chapter). However, another kind of membrane has recently attracted interest. These membranes consist of nano-structured membrane materials with similar properties to homogeneous membranes. However, the charge selectivity origin between the two membranes rely on different interaction mechanisms between the membrane and the solution.

This nano-structuration is interesting regarding the possibility of alternative energy sources using miniaturized electrical devices [34, 35]. Kim and Duan [35] used silica nano-channels fabricated by a standard semiconductor manufacturing process (reactive ion etching) and demonstrated the possibility of harnessing salinity gradient energy. The nano-structured silica made of 10 nanochannels (Figure 1.10) was placed between two potassium chloride solutions with varying concentrations achieving a power output of 2.89 pW, corresponding to a maximum P_d of about 7.7 W/m²(77mW/cm²). Such power density is 10 times larger than some of the power density achieved with homogeneous IEM (see Table 1.5). With nano-channels length of 0.14 mm and channel height of 4 nm, such a system is called a ‘Nanofluidic Reverse Electrodialysis System (NFRED)’[35].

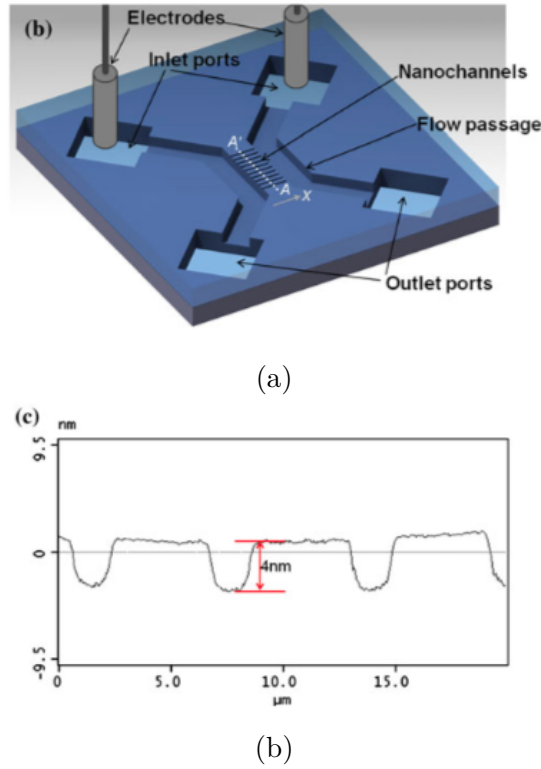


Figure 1.10: (a) Schematic diagram of the fabricated chip for reverse-electrodialytic energy conversion used by Kim and Duan [35]. (b) Surface profile of the nanochannels along line A-A' ($H = 4 \text{ nm}$)

An output power of 26 pW has been achieved by Guo et al. [36] using a single nanopore device. They proposed track-etched nanopores embedded in polyimide membranes and showed that the power density can approach a value between 2 and 260 mW/cm² if a pore density of 10^8 to 10^{10} nanopores/cm² are assumed for parallel nanopores. However, in order to drive microsystems such as low-power circuitry for wireless systems or biomedical implant devices [12, 13] (see also Table 1.1), the power generation reported in previous studies is not sufficient enough, despite the recent improvement. One of the reason is that forming ion-selective structures with a high pore density on a large scale is a difficulty that conventional track-etching and lithographic processes used in previous studies face.

There exist, however, solution that has been proposed by some authors to overcome this difficulty such as anodic oxidation technique of aluminum in an acidic electrolyte. Byeong Dong Kang et al. [15] have been able to produce an alumina nano-pore array and experimentally obtained a power density of 9.9 W/m² (99 mW/cm²) using alumina nano-pore array (10^{11} pores/cm²). This kind of alumina nano-pore array coated with silica (see Figure 1.11) have also been used

to generate power up to 542 nW in [37]. The experimental of Juwan Kim et al.[37] is shown in Figure 1.12.

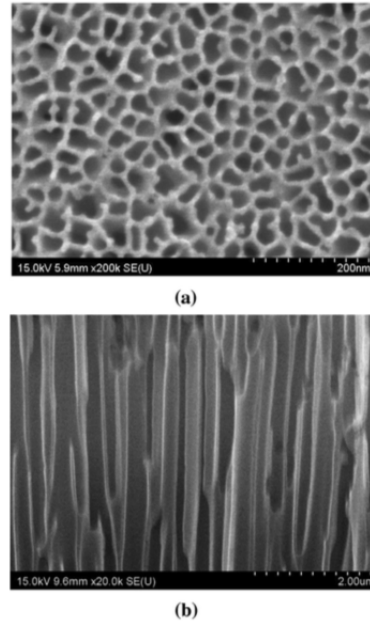


Figure 1.11: SEM images of alumina membranes obtained in [37]. (a) Top view and (b) cross-sectional view.

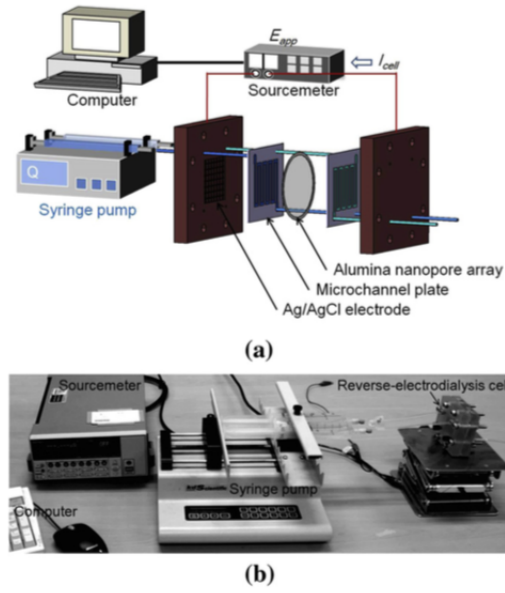


Figure 1.12: Experimental setup of Juwan Kim et al. [37] for energy harvesting from a reverse electrodialysis cell (a) schematic diagram of the experimental set-up (b) photograph of the experimental setup.

To sum-up, the potential increase in efficiency for RED applications with membranes based on nano-pores and nano-channels is promising, but the materials and drilling methods limit their wide applications. Therefore, challenge remains to increase the production efficiency of nano-structured membranes and substantial improvement are needed to advance applications in the future.

1.4 Conclusion

In this chapter, the concept of IoT and its structure has been presented. Important part of the network nodes are the sensors, and their number are set to keep increasing in the near future. With the current limitations of the batteries, the Global warming and the availability of fossil fuel resources, development of efficient energy harvesters is required. Salinity gradient power is one kind of renewable energy sources that in theory is completely CO₂ free and less subject to the variability of the external factor such as sun, wind etc. Different techniques exist to harness this energy source, RED being the most advanced one. However, in order to maximize the power density, improvements of ion exchange membrane properties are required. In this context, nano-structured such as a nano-channel and a nano-pore are promising for RED applications, but manufacturing processes

able to produce a large number/density of these structure on one membrane are needed to obtain reasonable power density.

1.5 Objectives of the thesis

In this thesis, the purpose will be to fabricated nano-porous silicon based membrane with different surface treatments (SiO_2 , HfO_2 and Al_2O_3), to analyse and compare experimentally their performances in a RED set-up. The next chapter is focused on the description of nano structured ion exchange membrane. First the physical principle of the Donnan exclusion is explained, then the origin of the ion perm-selectivity in a nano-pore is described. In the third chapter, a numerical model for the transport of ions in a charged nano-scale pore is presented, and numerical results discussed.

In the fourth Chapter, the process flow for fabricating the membrane is described, as well as the experimental methods to characterize the membrane. In the fifth Chapter, the experimental measurements are presented and interpreted based on the previous Chapters. Finally, a conclusion of the thesis will be made, and future work proposed.

Chapter 2

Ion exchange membrane: General aspects, physical interpretations and state of the art

In this chapter, the structure and properties of nano-porous ion exchange membrane are described. In a first time, homogenous IEMs are covered, then the Donnan exclusion and the double electric layer are physically explained before describing nano-porous IEMs. Finally, some methods to obtain nano-porous structure, and more specifically porous silicon, are presented.

2.1 Homogeneous Ion exchange membrane: Structure, Donnan exclusion and permselectivity

An ion-exchange membrane is a semi-permeable membrane that transports certain dissolved ions, while blocking other ions or neutral molecules[38]. Ion-exchange membranes are therefore electrically conductive and are used in a number of processes which are rather different in their practical application, their technical relevance and basic concept. However, in all these processes, the membrane will impact the control on the transport of ionic species. such as a selective separation of ionic species from a mixture with neutral components[38].

Based on their application, three major classifications can be made for ion-exchange membrane separation processes[38]:

- Mass separation processes such as Donnan and diffusion dialysis, electrodialysis and electrodialysis with bipolar membranes.
- Chemical synthesis processes such as the hydrogen and oxygen production by water electrolysis and the chlorine-alkaline electrolysis.

- Energy conversion and storage processes such as electrical batteries and fuel cells.

All ion-exchange membrane separation processes are based on the same fundamental principle, which is the coupling of the transport of electrical charges (or equivalently an electrical current) with a transport of mass [38].

Important examples of ion-exchange membranes include the anion exchange membranes used in certain alkaline fuel cells to transport OH^- anions and the proton-exchange membranes, that transport H^+ cations.

2.1.1 Structure of homogeneous IEM

An ion-exchange membrane is generally made of organic or inorganic polymer with charged (ionic) side groups, such as ion-exchange resins. In a cation-exchange membrane, there is an electrical equilibrium between the fixed negative charges and mobile cations in the interstices of the polymer as indicated in Figure 2.1. In a cation-exchange membrane, the mobile anion are referred to counterion.

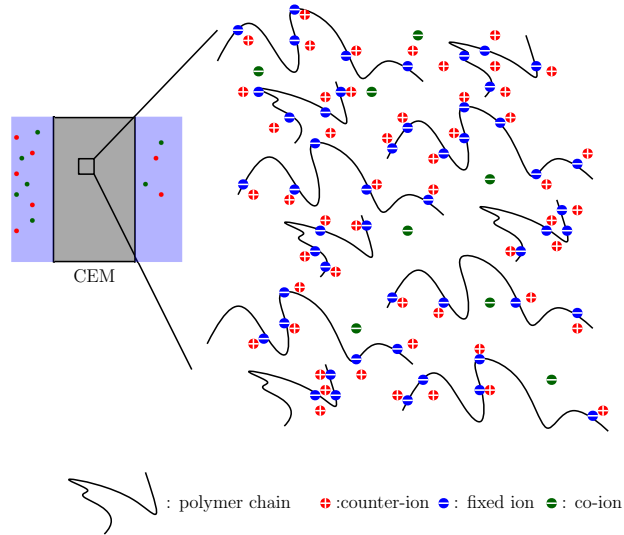


Figure 2.1: Schematic drawing illustrating the structure of a cation-exchange membrane.

The mobile anions are referred to as co-ions. A more or less complete exclusion of these co-ions from the polymer matrix is present because of the electrical charge which is identical to that of the fixed ions. This type of exclusion is called Donnan exclusion (see below)[38]. When a flux of ions goes through the membrane, cations are responsible for most of the conductivity because there are the majority mobile

species. Anion-exchange membranes are just the opposite of cation-exchange membrane.

Note that in the polymer-based IEM category, heterogeneous membranes are also possible. These membranes involves most often highly crystallized polymer with ionic groups fixed on a side chain. Crystalline areas formed by the linear fluorocarbon polymer and separated by amorphous, highly hydrophilic domains formed by the side chains with the ionic groups, make these membrane quite heterogeneous on a microscopic scale[38] as shown in Figure 2.2. Because of their different structure, swelling and transport properties are different than homogeneous membrane but will not be covered in this thesis.

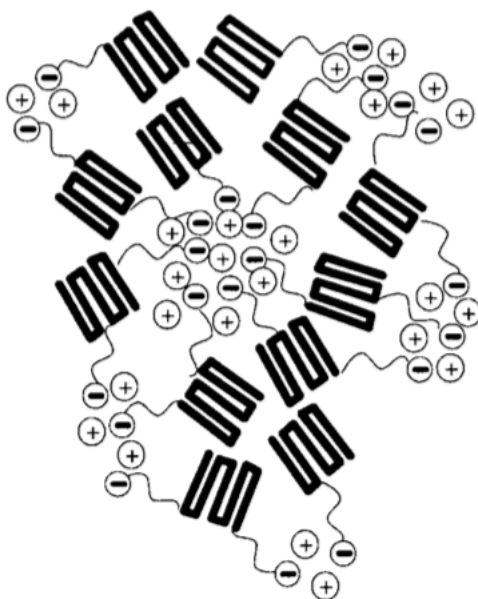


Figure 2.2: Schematic drawing illustrating the structure of the fluorocarbon polymers based membranes showing the crystalline polytetrafluorethylene region and the negatively fixed charges on the vinyl ether linkages. Reproduced from [38].

2.1.2 Donnan exclusion and permselectivity: Thermodynamics considerations

The selectivity of an ion-exchange membrane to the transport of ions of opposite charges is called its permselectivity (quantify the strength of the exclusion of the co-ions from the membrane phase). It is due to a Donnan equilibrium and not due to an electrostatically excluding specific charged species[38] or a physically blocking. In the following part of the section, the origins of the donnan exclusion are explained in term of thermodynamics, which will help to understand the different

parameters influencing the permselectivity. The developments are based on [38].

First consider an ion-exchange membrane and an adjacent electrolyte solution. As the medium inside the membrane is different as the one in the solution, an ion will feel a different interaction depending is in the membrane or in the solution. This is expressed through the concept of chemical potential or electrochemical potential in case of charged components (i.e. ions). An ion-exchange membrane and an adjacent electrolyte solution will be in equilibrium if the electrochemical potentials of all ions in the two phases are equal. Thus, for each ion in equilibrium:

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

Here μ_i and ν_i are the chemical and the electrochemical potential of the component i , φ is the electrical potential, F is the Faraday constant and z_i the charge of ion i . The superscripts m and s refer to the membrane and to the solution, respectively. Thus, the electrochemical potential of an ion is composed of two additive terms, the first is the chemical potential and the second is the electrical potential multiplied by the Faraday constant and the valence of the ion.

The electrical potential difference between the membrane and the adjacent solution is then

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

where φ_{Don} is called the Donnan potential. In order to have a more explicit expression of φ_{Don} , the difference in chemical potential ($\mu_i^s - \mu_i^m$) need to be developed. For this, we can temporally consider two mixtures separated by some wall. Any imbalances between the two mixtures can initiate a transport of components from one mixture to the other. The gradient in the chemical potential μ across the wall between two mixtures is the driving force for the transport of a component through the wall from one mixture into the other. Its change of a component i in a real mixture at isothermal conditions is given by

$$d\mu_i = \bar{V}_i dp + RT d \ln a_i, \quad (2.3)$$

where $\bar{V}_i$ is the partial molar volume, a_i the activity of the component¹ i , p the pressure, T the absolute temperature and R the gas constant. Assuming perfect equilibrium within each mixture, the total change for a component i in one mixture to another is given by:

$$\Delta\mu_i = \mu_i' - \mu_i'' = \bar{V}_i \Delta p + RT \ln \frac{a_i'}{a_i''}, \quad (2.4)$$

where (') and (") refer to the two mixtures separated by the wall, with Δp the pressure difference between the two mixtures. Now going back to the case with the

¹The mole fraction X and the activity a are related by the activity coefficient γ : $a_i = \gamma_i X_i$.

membrane in contact a solution, we rename mixture ' as the solution s and " as the membrane m . Introducing eq. (2.4) into eq. (2.2), this gives

$$\varphi_{Don} = \varphi^m - \varphi^s = \frac{1}{|z_i|F} \left[RT \ln \frac{a_i^s}{a_i^m} + \bar{V}_i(p^s - p^m) \right]. \quad (2.5)$$

Note that $p^m - p^s = \Delta\pi$ is also referred to as swelling pressure. The swelling pressure can be considered as the osmotic pressure difference between the solution and the membrane phase. The osmotic pressure difference $\Delta\pi$ can be calculated from the water activity (a_w) in the membrane and in the solution.

The Donnan potentials between a cat- and an anion-exchange membrane and an adjacent bulk solution is illustrated in Figure 2.3. The concentrations of mobile and fixed anions and cations is also shown.

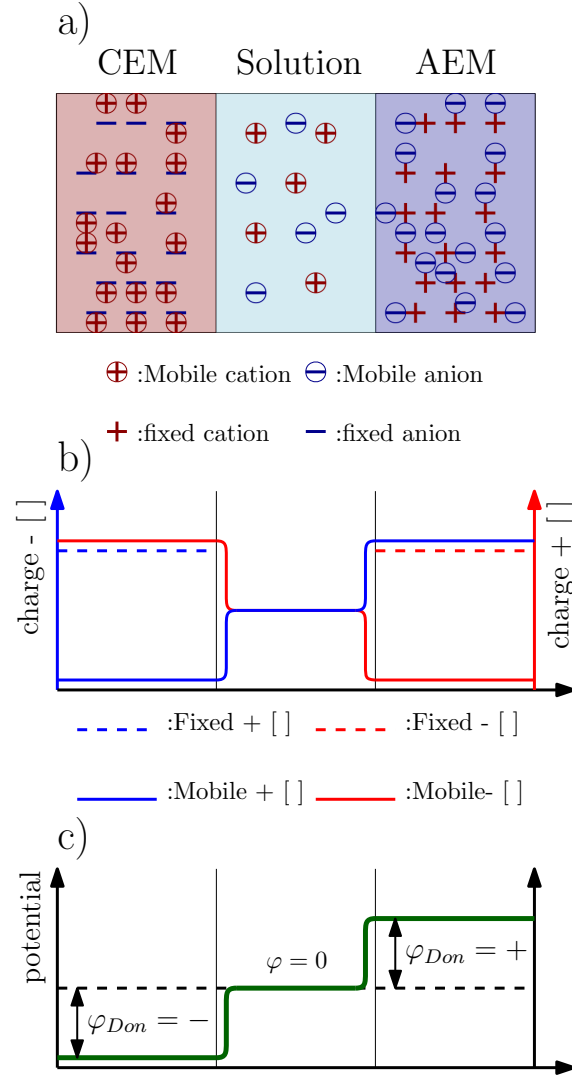


Figure 2.3: Schematic drawing illustrating the distribution of ions between a bulk solution and a cat- and anion-exchange membrane and the Donnan potentials between the membranes and the bulk solution. Reproduced from [38].

In Figure 2.3(b), at the interface membrane solution, steep gradients in the ion concentration are present due to the high fixed ions concentrations in the IEMs. These steep gradients at the interface act as driving force for the transport of coions into the membrane and counterions from the membrane into the solution. Since the solution and the membrane are in equilibrium no net transport of ions between the membrane and the solution takes place. This means that the concentration gradient driving force is counter-balanced by a driving force acting in opposite direction. This driving force is the Donnan potential as illustrated in Figure 2.3(c), which is

due to a difference in the activity of the ions in solution and in the membrane as seen in eq. (2.5).

Another interpretation can be made if we consider for example a mobile anion in a CEM or in the adjacent solution. First, because the system is in equilibrium, it is electrically neutral. Second, since there is a high concentration of fixed negative charged in the CEM compared to the concentration of anion in the solution, there must be a high concentration of mobile cation in the CEM compared to the solution. The fixed negative charge attracts the mobile cation by creating a favourable negative potential, which is the Donnan potential.

To obtain a completely permselective membrane the coions should completely be excluded from the membrane phase. This exclusion is referred to as Donnan exclusion. One could calculate the concentration of co-ions in the membrane numerically or analytically (assuming some simplifications) based on eq. (2.5) and the relation between the activity and the mole fraction. One would find that the Donnan equilibrium and thus the selectivity of an ion-exchange membrane depends on:

- the concentration of the fixed ions,
- the valence of the coions,
- the concentration of the electrolyte solution
- the affinity of the ions-exchange material with respect to the counterions.

One important conclusion is that the permselectivity of an ion-exchange membrane increases with increasing concentration of the fixed ions with decreasing electrolyte solution concentration and with decreasing chemical valence of the co-ions.

2.1.3 Tailor-made homogeneous membranes

The most desired properties of ion-exchange membranes are [38]:

- high permselectivity: an ion-exchange membrane should be highly permeable for counterions, but impermeable to coions,
- low electrical resistance: under the driving force of an electrical potential gradient, the permeability for the counterions should be as high as possible,
- good mechanical stability: the membrane should be mechanically strong. It should also have a low degree of swelling or shrinking in transition from dilute to concentrated ionic solutions,

- high chemical and thermal stability: the membrane should be stable and in the presence of oxidizing agents and over the entire pH-range.

Most of these requirements are reached by many of today's available membranes. Especially the Nation-type² cation-exchange membrane has received a considerable amount of attention in the chlorine-alkaline electrolyses and in electrodialysis as well as a proton conductor for proton exchange membrane (PEM) fuel cells because of its excellent thermal and mechanical stability.

Homogeneous ion-exchange membranes can be prepared with 3 different techniques[39, 40]:

- Polymerization or polycondensation of monomers; at least one of them must contain a moiety that either is or can be made anionic or cationic groups, respectively.
- Introduction of anionic or cationic moieties into a preformed solid film.
- Introduction of anionic or cationic moieties into a polymer, such as polysulfone, followed by dissolving the polymer and casting it onto a film.

Different parameters determine the properties of homogeneous ion-exchange membranes such as the hydrophobic or hydrophilic character of the matrix polymer, the density of the polymer network, the type and concentration of the charges in the polymer and the morphology of the membrane itself.

Regarding the requirement of optimal IEMs for RED application such as presented in 1.3.2, a high permselectivity above 95% , a low electrical resistance below $1\Omega\text{cm}^2$, acceptable mechanical and chemical stability are required [14]. In electrochemical process like fuel cells, IEM are specifically tailored to have a high conductivity and chemical stability, because of the strongly acidic environment in fuel cells. For RED, the requirement are less strong, since the IEMs will operate in a neutral environment (pH~5-7) with mostly Na^+ and Cl^- as ionic species. Basically, a high permselective and moderate mechanical properties are required, thus thin IEMs with no reinforcement are chosen for RED. Properties of some commercial and tailor-made homogeneous IEMs for potential applications in RED are shown in Table 2.1[14].

²<https://en.wikipedia.org/wiki/Nafion>

Membrane	Type	$\delta(\mu\text{m})$	α (%)	$R_a(\Omega\text{cm}^2)$	SR(Ωcm)	Ref.
Qianqiu AEM	AEM	294	86.3	2.85	97	[41]
PECH B-2	AEM	77	87.2	0.94	122	[42]
Neosepta AMX	AEM	160-180	90.7	2.35	138	[41]
IMD-40-PAES	AEM	64	94.35	1.65	258	[43]
KIER-CEM1	CEM	26	97.8	0.34	131	[44]
Qianqiu CEM	CEM	205	98.8	1.97	96	[42]
Neosepta CMX	CEM	140-200	99.0	2.91	171	[41]

Table 2.1: Properties of commercial and tailor-made IEMs for potential applications in RED. δ is the thickness, α the permselectivity, R_a the area resistance and SR the specific resistance. More detailed information in [14].

2.2 Permselectivity through nanostructuration

In this section, a novel way based on nano-structuration to create ion-exchange membrane is presented. The origin of permselectivity in charged nano-pores is explained and parameters influencing the properties of porous IEMs detailed. first, the concept of double charged is described, then the importance of working at the nano-scale is developed.

2.2.1 Double charge layer

When a dielectric solid (e.g., a fused-silica capillary, Figure 2.4a) is in contact with a liquid electrolyte (e.g., a dilute aqueous NaCl solution) an electrical double layer (EDL) develops at the solid-liquid interface due to ionizable groups of the material (e.g., dissociation of silanol groups in the above example: $\equiv \text{Si-OH} + \text{H}_2\text{O} \rightleftharpoons \text{Si-O}^- + \text{H}_3\text{O}^+$, Figure 2.4b) or by ions adsorbing on its surface[45][46].

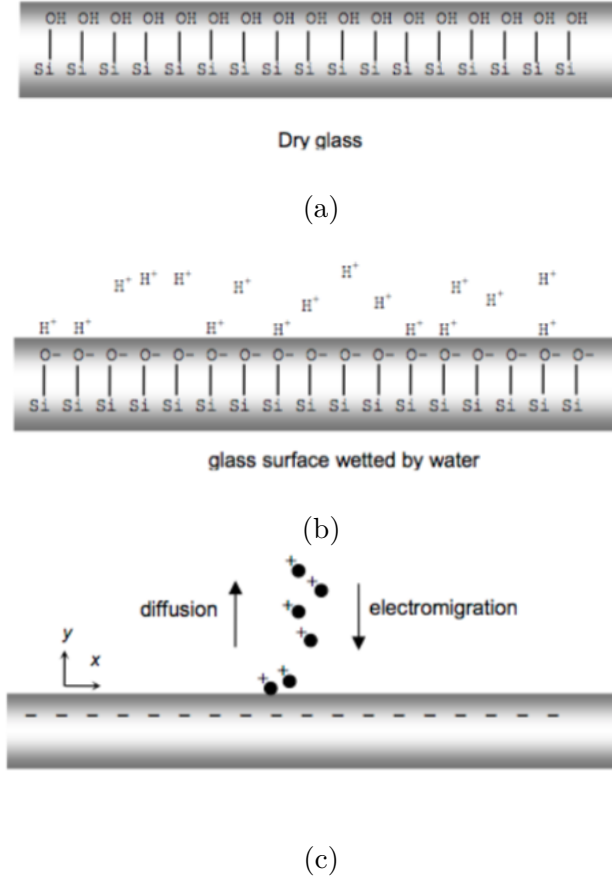


Figure 2.4: Surface ionization between silanol groups and water. (b) Dissociation of silanol groups in the above. (c) Formation of an electrical double layer by equilibrium between electromigration and diffusion. Reproduced from [46].

Several models exist to describe this electrical double layer. The Helmholtz model is the first model that has been proposed. It postulates that all counter-ions necessary to neutralize a charged surface are aligned in a single parallel layer at a certain distance from the membrane surface, which is determined by the radius of the hydrated or unhydrated counterion. Similarly as a parallel plate capacitor, the potential decreases linearly away from the charge surface and a potential difference $\Delta\varphi$ can be calculated base on the surface charge density:

$$\Delta\varphi = \frac{4\pi d}{\varepsilon}\sigma, \quad (2.6)$$

where ε is the permittivity, σ the surface charge density and d the thickness of the double layer (e.i. the thickness of the capacitor).

However, the Hemholtz model is far too simple. For example, it neglects the thermal motion of the solution. Louis Georges Gouy in 1910 and David Leonard Chapman in 1913 both observed that the capacitance of the double layer was dependent on the applied voltage to the surface and the ionic concentration [38]. In the Gouy-Chapman model, a diffuse model is introduced for the double layer. The total number of counter-ions in this double layer is still equal to the fixed charge of the surface, but their distribution now results from the equilibrium between electro-migration and diffusion. Assuming several assumptions, it can be shown [46] that the approximate solution for the potential φ at a distance x from the surface follows a decreasing exponential:

$$\varphi = \zeta e^{-x/\lambda_D}, \quad (2.7)$$

where ζ is the "zeta"-potential of the liquid/solid interface ($\zeta \simeq -0.1\text{V}$ for water on glass) and λ_D is the Debye length. The Debye length is given by

$$\lambda_D = \sqrt{\frac{\varepsilon k_B T}{\sum_i n_{i0} z_i^2}}, \quad (2.8)$$

with k_B the Boltzmann's constant, T the absolute temperature of the solution, n_i the concentration of the ionic species i in the bulk far from the surface and z_i the net of ions i . It represents the scale of the length required for a group of ions to screen the effect of a charge carrier (e.g., a charge surface) or equivalently the scale of how far charge carrier's net electrostatic effect persists in electrolytes solution. For an electrolyte at $n_{i0} = 1\text{mM} = 6 \times 10^{23} \text{ ions/m}^3$ with $\varepsilon_{\text{water}} \simeq 78\varepsilon_0$, $\lambda_D \simeq 13 \times 10^{-9}\text{m}$.

In eq. 2.8, the surface charge density does not appear, suggesting that it does not influence the exponential decrease for the potential. In fact, this is only a consequence of the approximations made in the model. First of all, the model is studied with the electric potential and a "zeta"-potential has been introduced to reflect the charge surface, but no relation between the "zeta"-potential and the surface charge density is given. Secondly, the exponential decrease is valid as long as the Hückel's approximation is met, which assumes that the thermal energy $k_b T$ is large compare to the electrostatic interaction $z\varphi$, so for values of $\varphi \ll 25\text{e}-3\text{V}$ at ambient temperature and single charged ions. This basically assumes that the concentration of ions depends linearly on the potential rather than exponentially as given by the Maxwell-Boltzmann distribution. This assumption is already false for water on glass for example. Nevertheless, the Debye length is still the length at which the potential is expected to significantly vary.

The Debye length is an important parameter as it will be one of the determinant factor for nano-structured IEMs. One important property of the Debye length is that it decreases as the concentration of ions increases. The interpretation is that

more charge are available to screen the surface charge, thus the electrostatic effect persists on a shorter distance. Note, however, that this behaviour is only valid at low concentration (ca. below 0.1 M for most electrolyte solution) [47]. Above this concentration this concentration, the Debye length does not longer decrease with concentration but increases [47]. This happens typically when the Debye length decreases below the hydrated ions diameter (above ca. 0.1M).

Finally, there exists another model for the double charge layer which is the mostly used one. In the the Gouy-Chapman model, ions are considered as punctual charges and can be as close as possible to the charge surface. Thus Otto Stern suggested a combination of the Helmholtz model with the Gouy-Chapman model. In Stern's model, some ions adhere to the surface as suggested by Helmholtz, constituting an internal Stern layer, while some ions form a Gouy-Chapman diffuse layer. Consequently, as shown in Figure 2.5, the variation of the potential decreases linearly close to the surface as in a plane capacitor, until it reaches the "zeta"-potential and then decreases exponentially following eq. (2.7). Thus, in this model, ψ_0 and ψ_d are used to indicate the potential at $x = 0$ and $x = d$ from the solid-liquid interface, where d is the thickness of the Stern layer, instead of ζ .

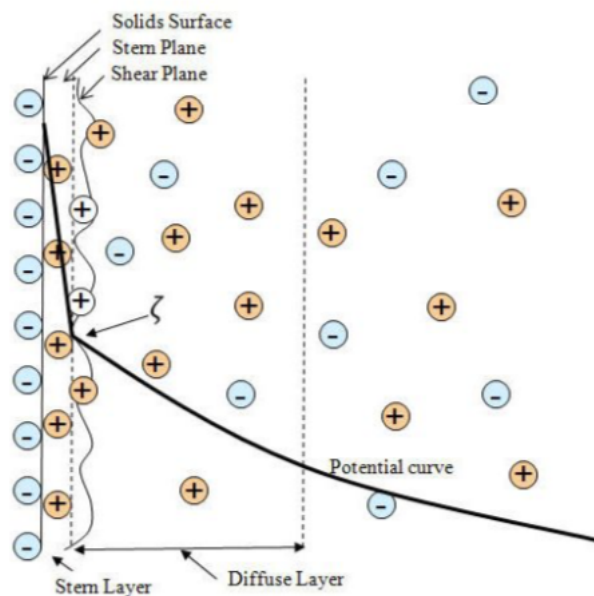


Figure 2.5: Variation of the electric potential in the double electric charged layer, based on the Gouy-Chapman-Stern model. Taken from [48].

2.2.2 Permselective nano-structures

In recent years, solid-state nano-fluidic channels, i.e., nano-pores, have been demonstrated experimentally to serve as ion-selective membranes for small reverse electrodialysis systems [15, 35, 45, 49, 50, 51, 52, 53, 34]. In homogeneous membrane, due to an exclusion of mobile co-ions by the membrane fixed charges, counter-ions are the majority mobile ions in the membrane, thus the ionic flux is mostly constituted of counter-ions. In some way, the diffusion of counter-ions is increased while the diffusion of co-ions is decreased.

If we consider the case of a pore filled with an electrolyte solution, the inner wall of the pore will charge as explained earlier and an electrical double layer will form like an annulus of thickness λ_D in the inner wall of the pore. If the pore radius r_c is large compared to the Debye length λ_D ($r_c \gg \lambda_D$), then the bulk solution inside the pore is not affected by the surface charge because the wall potential is screened on the scale of the Debye length. Situations with $r_c \gg \lambda_D$ have found application. For example, if an electric field is applied along the pore axis, the ions in the EDL will start to accelerate because of the electrostatic force. Due to viscous effect, the liquid in the EDL is driven also and rapidly the whole liquid volume inside the pore is driven. This effect is called electro-osmotic flow and has been used for pumping fluid in microfluidic application[48]. A benefit of using EOF is that biochemical and chemical species can be transported over relatively long distances, while hydrodynamic dispersion being very limited compared to classic pressure driven flow[45].

If, however, the EDL thickness becomes comparable to the capillary radius (r_c), that is, as the microfluidic channel ($\lambda_D \ll r_c$) becomes a nanofluidic channel ($\lambda_D \simeq r_c$), the local electrical potential cannot reach bulk potential ψ_{bulk} as it drops rapidly with distance from the solid surface towards the center of the channel. The electrical potential (of the same sign as the surface potential) now prevails over the whole channel or pore cross-section and the nanopore enriches counterions and excludes co-ions: the nanopore as a whole becomes ion-permselective, by a process sometimes referred to as *EDL overlap*. At electrochemical equilibrium the tendency of counterions to leave the nanochannel and that of the co-ions to enter it, i.e., tendency of ionic species to level out the chemical potential gradients, is balanced by an electrical phase boundary potential (the so-called Donnan potential)[45]. The transition from charge-nonselective to charge-selective behaviour is illustrated in Figure 2.6a.

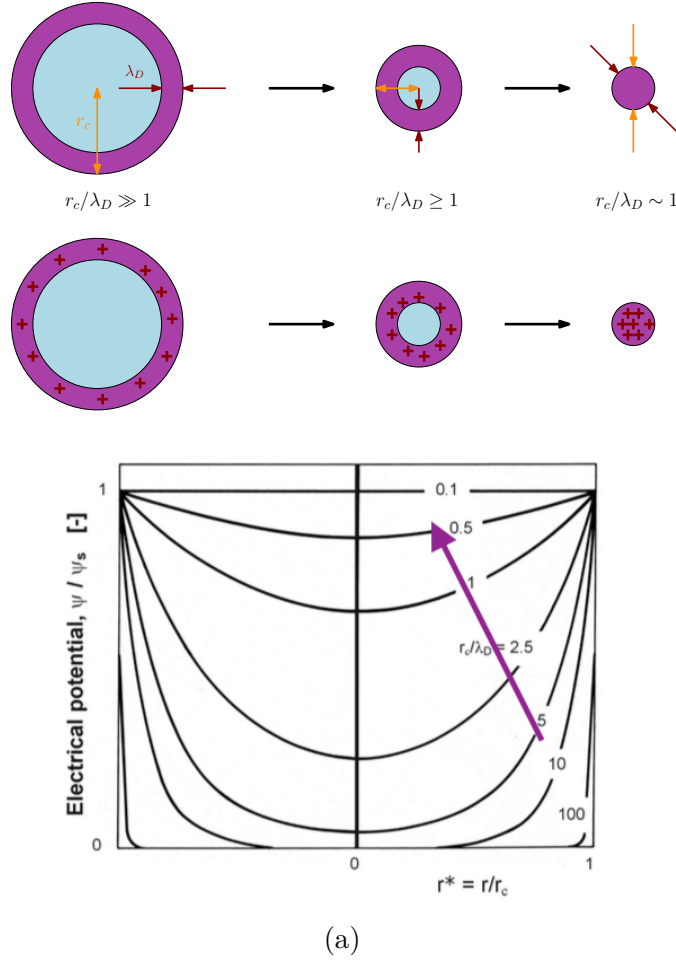


Figure 2.6: (a) Overlap of the EDL when $r_c \rightarrow \lambda_D$. (b) Cross-sectional distribution of electrical potential in a channel (normalized by the surface potential $\psi_s = \psi_0$) for different values of r_c/λ_D , radius over Debye length. Reproduced from [45].

It is interesting to note that this ion permselective properties is present in many systems. Either it is present as whole, e.g., in the form of the membrane geometry presented above in Figure 2.7a, or via discrete and local ion-permselective domains in materials which at a macroscopic scale would not present charge-selective properties, but start to develop charge selectivity when nanostructure e.g. in the form of fixed beds of micrometer-sized, mesoporous particles. For example, in the intraparticle and intraskeleton mesopores of particulate and monolithic materials, ion-permselectivity also develops as shown in Figure 2.7c. This kind of materials are also employed in separation science, particularly liquid chromatography. More information on nano-structures and nano-composite materials used for applications requiring charge selectivity can be found in [40].

In each of this case, *EDL overlap* is what makes the system charge selective. This appears when one of the dimension of the system becomes comparable to the Debye length. Thus, the important factor in each system is the ratio between the critical dimension of interest and the Debye length. For a nanopore, this is ratio of the pore radius and the Debye length, R_p/λ_D . For a bed of particles this is half of the interparticle distance over the Debye length, $(D_p/2)/\lambda_D$. For an opened channel, this is the ratio of the channel height and the Debye length, H/λ_D . Each situation is represented in Figure 2.7 and 2.8.

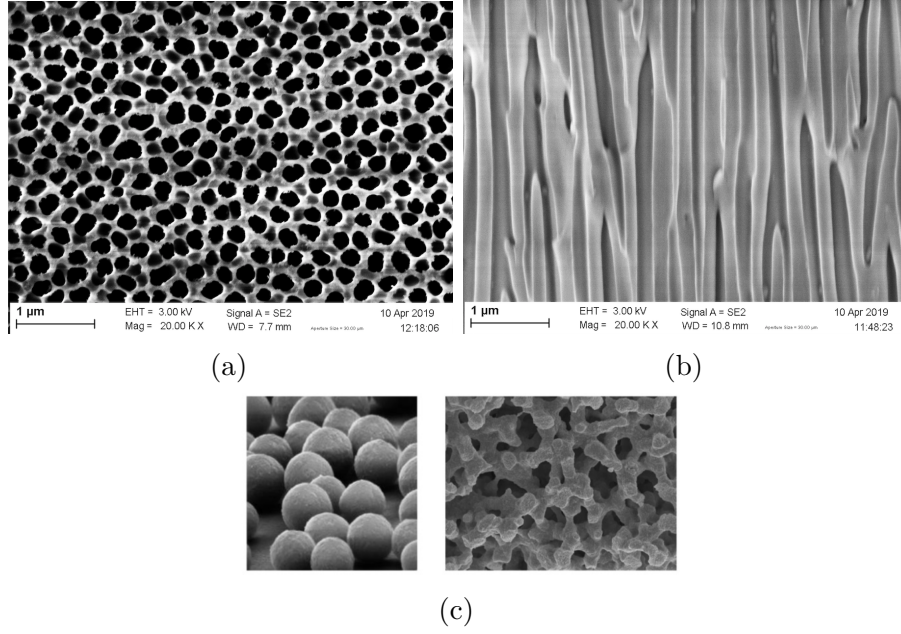


Figure 2.7: SEM images of an AAO ion exchange membrane with 20nm pore size. (a) Top view. (b) Side view. (c) Scanning electron micrographs of sphere packings and monolith taken from[45]. No scale available.

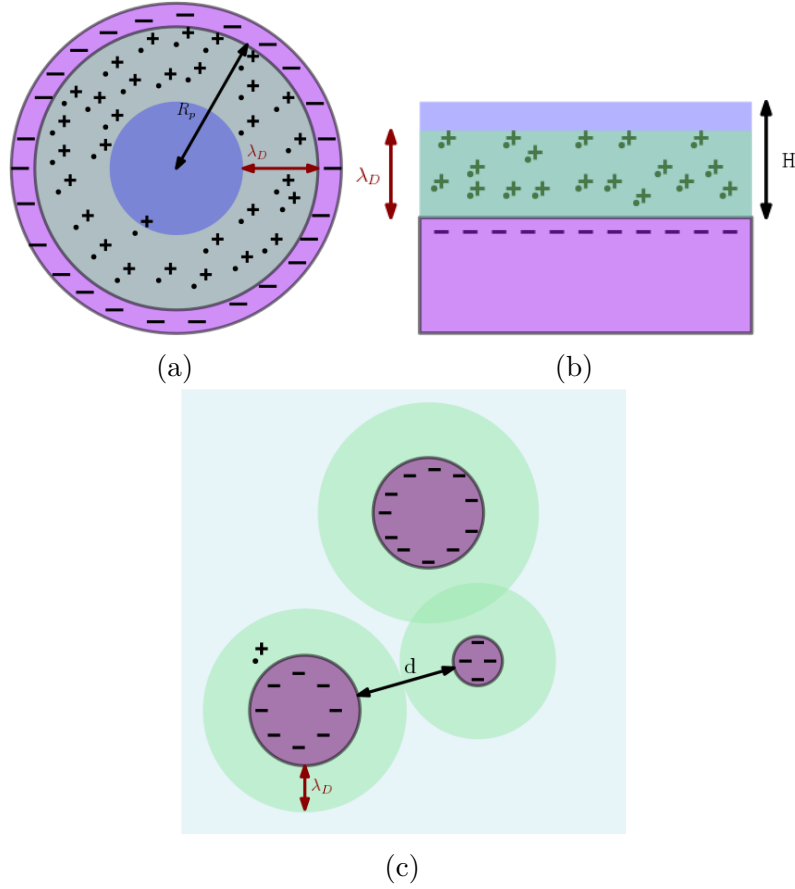


Figure 2.8: Schematic representation of nano-structured in contact with an electrolyte fluid. (a) Nano-pore. (b) Plane surface. (c) Fixed beds of micrometer-sized sphere.

In conclusion, by reducing the diameter of the pore down to the Debye scale, an enrichment of counter-ions inside the pore occurs due to an *EDL overlap*. Similarly to the homogeneous IEM, the mobility inside the pore (or homogeneous membrane) is increased for counter-ions and reduced for co-ions. Thus, the ionic flux inside the pore (homogeneous membrane) is mostly made of counter-ion, as desired.

2.2.3 Parameters influencing the properties of the properties of nano-porous IEMs

When discussing about the parameters influencing the properties of nano-porous IEMs, they can be either parasitic external factors or either controlled parameters. This categorisation depends on the applications in which the properties of nano-porous IEMs. For a RED application, stable conditions (temperature, pH, ...) are

mostly required since a stable energy output is most often desired. However, there are applications where a control on the selectivity of the pore is desired, such as in the field of iontronics [54].

The surface charge density parameter: surface structure and influence of pH

In homogeneous membrane, the permselectivity increases if the concentration of the fixed ions increases as it has been explained in 2.1.2. Similarly in nano-porous membrane, the permselectivity originates due to an enrichment of counterions and exclusion of co-ions. Even though the value of surface charge density of the pore does not affect the EDL overlap³, it directly influences the permselectivity. Indeed, the concentration of counterions in the pore is such that the total number of counterions is equals to the total surface charge. Thus, increasing the surface charge density increases the concentration of counter-ions, and decreases the concentration of co-ions: permselectivity increases[15].

Furthermore, when a membrane is placed between two electrolytic solutions of different concentration like in RED, ionic transport through the membrane is dominated by counter-ions, which are the main charge carrier in the pore. Thus, increasing the surface charge density will have the effect of decreasing the electrical resistance of the pore because the number of charge carrier increases with the surface charge density [15]. In addition, in the numerical model, next section, the only true material parameter is the surface charge density of the pore. It is then clear that this parameter need to be well known and controlled.

First of all, it is important to understand how this surface charge appears. In 2.2.1, for the case of a silica-water interface, dissociation of silanol groups into the water was used to explain an apparition of negative charge on the surface. However, the situation could be an apparition of positive charge if some hydrogen of the hydronium ion adsorb onto the surface. Such behaviour is called amphoteric⁴ surface ionization. This example emphasizes the fact that the apparition of charge on the surface such as SiO_2 , but also HfO_2 , Al_2O_3 and other oxides surface, is due to different reaction between the oxides surface and the electrolytic water.

Most of the metallic oxide found in nature have a crystalline structure. Finite volume of metallic oxides in vacuum such as alumina have clean surfaces with atoms that have unsatisfied bonds as shown in Figure 2.10a. When the metallic oxides is immersed in water or exposed to ambient air (there always at least 15% relative humidity), a reaction between the surface and the water produces surface

³As long as there is a charge density.

⁴In chemistry, an amphoteric compound is a ion or molecule that can react both as a base and as an acid [55]

hydroxyl groups (denoted M-OH) as shown in Figure 2.10b [56]. Several types of surface hydroxyl groups are possible, the primary difference between them is the number of metallic ions to which the hydroxide is coordinated[56]. Figure 2.9 shows an example for a silica surface.

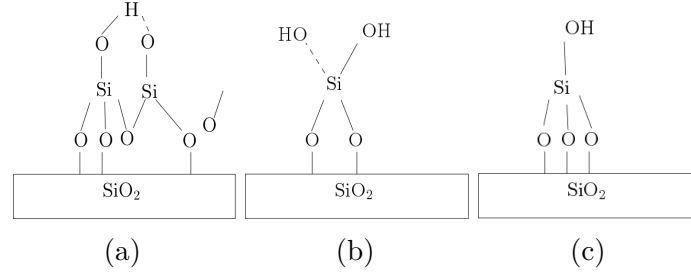
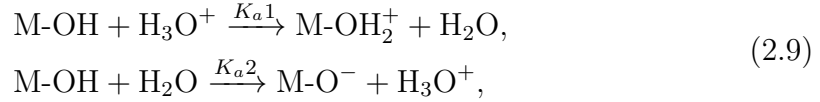


Figure 2.9: Schematic presentation of three types of silanol groups occurring on silica surfaces: (a) vicinal, (b) geminal silanols, and (c) isolated silanols. Reproduced from [57].

A single amphoteric site surface hydroxyl group reacts with acid and base at high and low pH, respectively, via surface ionization reactions as follows[56]:



resulting in either a positively charged surface (M-OH_2^+) as in Figure 2.10c, or a negatively charged surface (M-O^-) as in Figure 2.10d.

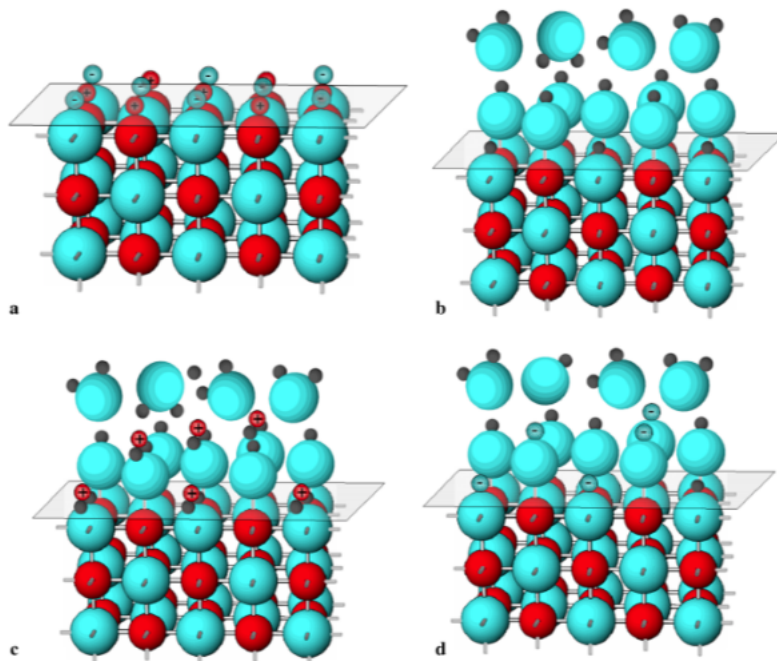


Figure 2.10: Schematic representation of the surface of metal oxides. The blue spheres represent oxygen, the red spheres a metal cation and the small gray spheres represent hydrogen. (a) In vacuum, (b) in water or ambient air, (c) at pH below the PZC and (d) pH above the PZC. Taken from [56].

The amphoteric behaviour also implies that there is a pH at which the net charge on the surface is zero because the majority of surface sites are neutral (M–OH). This particular pH is known as the point of zero charge or PZC. At a pH above or below the PZC, the particle’s surfaces become negatively (M–O[−]) or positively (M–OH₂⁺) charged due to the reaction with either base (OH[−]) or acid (H⁺), respectively. Figure 2.11 shows how the concentration of surface sites changes with pH. The PZC is determined by the values of the surface ionization reaction constants (Ka1 and Ka2) and depend upon the particular type of material (for example Al₂O₃, SiO₂, TiO₂, etc.)

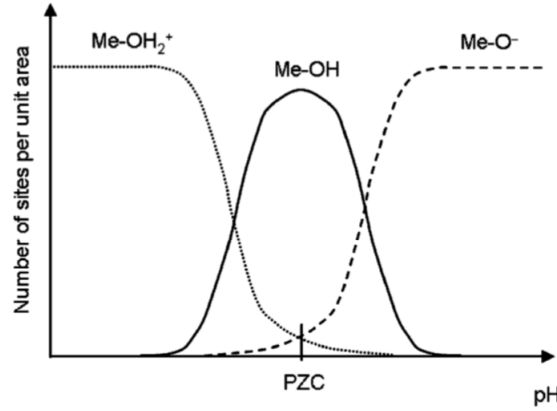


Figure 2.11: Number density per unit area of neutral (Me-OH), positive (Me-OH₂⁺) and negative (Me-O⁻) surface sites as a function of pH. Taken from [56].

Different methods are possible to determine the surface charge density σ_s . One of them is by a potentiometric acid-base titration of oxides which provides a direct measure of net proton surface charge density [58, 56]. This method gives accurate value as long as there is no specific affinity between the surface and the ions of the background electrolyte, which could then adsorb. The surface charge formation should also be the result of the total acid or base consumption only and no any other acid-base reactions, like dissolution, hydrolysis, take place. By determining the net proton excess at different pH, the surface charge density is also known as a function of the pH, because the net proton excess amount and the surface charge density σ are proportional (by a factor F , the Faraday constant).

Approximate analytical models also exist, such as the Gouy-Chapman equation which gives a relation between the density of charge in the diffusive layer as a function of the diffusive potential (the "zeta"-potential). With some assumption [58] (e.g. $\psi_0 = \psi_d$, $\psi_d < 25\text{mV}$), the surface charge density σ_s can be determined,

$$\sigma_s = \varepsilon_0 \varepsilon_r \kappa \psi_0 = \varepsilon_0 \varepsilon_r \kappa \psi_d, \quad (2.10)$$

where $\kappa = 1/\lambda_D$ and ψ_0 the potential of the solid-liquid interface. This equation shows that the surface charge density is inversely proportional to the Debye length, and thus depend on the temperature and the ionic strength of the solution also. This equation gives good approximations, but the "zeta"-potential (ψ_d) is required. The most frequently used methods for determining the ζ potentials and IEPs⁵ (isoelectric points) of single crystal planes and macroscopic surfaces are fitting diffuse layer potentials from surface force apparatus and atomic force microscopy (AFM) data and Streaming potential measurements[56]. Others techniques based

⁵This is the pH where the "zeta"-potential is zero.

on electro-osmotic flows can also be used. By imposing a voltage difference across the pore and by measuring the water flow, the "zeta"-potential can be determined.

Numerical models also exist, such as the combined chemical and electrostatic models [58] or more recently the surface complexation models (SCMs) which are the most used. For example, a simple 1D model on a spherical silica particle has been implemented by Murat Barisik et al. [59] on COMSOL®.

Ionic strength and temperature

The ionic strength or equivalently the concentration of ions in the solution will have an impact on the properties of the membrane. As seen in eq. (2.10), the surface charge density is expected to vary with the ionic strength. However, the major impact of the ionic strength is on the Debye length (2.8). For example, when charged pore is placed between two electrolyte solutions of different concentrations, the Debye length is expected to vary along the pore channel since the ions will diffuse and so the concentration varies. Thus, varying the concentration at the entry of the pore will results in different selectivity.

The temperature is also influencing the properties of the membrane. In fact, the temperature affects many parameters such as the Debye length, but also the "zeta"-potential. Indeed, based on the Gouy-Chapman approximation eq. (2.10), one would expect the surface charge density to decrease since $\sigma_s \propto \lambda^{-1} \propto T^{-1/2}$, but Junho Hwang et al. [34] have experimentally observed that the surface charge density increased with temperature, meaning the "zeta"-potential has increased. Increasing the temperature results in a increase in the Debye length and in the surface charge density, meaning more counter-ions are present in the pore, increasing their ionic conductance (i.e. increasing the selectivity of the pore). In addition, an increase in temperature means a decrease in the liquid viscosity, leading to an increase in the ion mobility. These effects of temperature is shown in Figure 2.12. Note, however, that bubbles nucleation on the surface of the mesopores is induced with further increase in the temperature, decreasing the ion conductance[34].

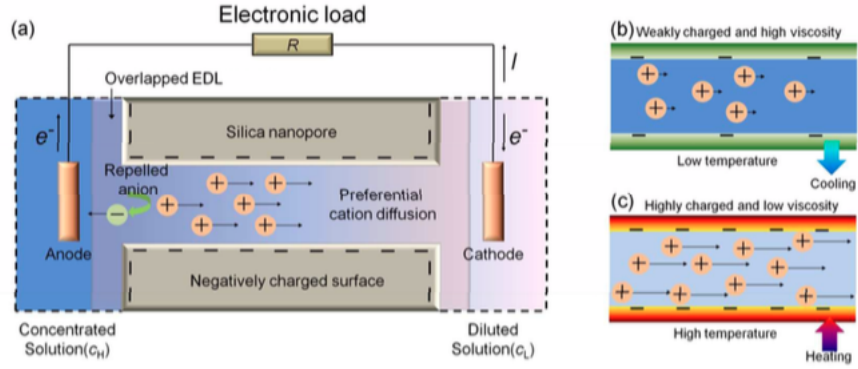


Figure 2.12: Schematic diagrams of (a) preferential cation diffusion across a negatively charged silica mesopore between two reservoirs containing diluted and concentrated solutions, respectively. Cation transport characteristics at (b) low and (c) high temperature. Taken from [34].

Porous structure and pore geometry

The structure of the porous medium has also an impact on the ionic transport through the membrane. Regarding the diffusion of ionic species, the situation is different if an ion diffuses in the bulk solution or in a porous structure, the diffusion coefficient is impacted by the porous structure. Several factors need to be taken into account when tailoring a membrane. First, the porosity ϵ of the membrane needs to be as high as possible in order to have the highest ionic flux possible. Then, the tortuosity τ ($\tau \geq 1$) of the pore needs to be as close as possible to the straight cylinder, $\tau = 1$, so that the distance an ion travels in the membrane is the shortest possible with no "turns".

Numerically, the simplest way to account for the porous structure is by using an effective diffusion coefficient given by

$$D_{eff,i} = D_i \delta, \quad (2.11)$$

where D_i is the macroscopic diffusion coefficient of the ionic species i and $\delta = \epsilon/\tau$ is a scale factor, accounting for the porosity ϵ and the tortuosity τ of the porous medium.

However, this effective diffusion coefficient only accounts for the effect along the membrane and this homogenised picture does not account for inhomogeneities across the cells. The pore space connectivity is also an important parameter to consider [60]. For example, in the case where the membrane is just a stack of parallel pores with no connectivity between them, as soon as one pore is blocked on one of its sides (e.g., dust), the whole pore is not contributing any more to the

transport of ions. But in the case where a connectivity exists between the pores (e.g., like a pipe system), an ion can still find a way to travel through the membrane. Unfortunately, it is difficult to account for this effect with an effective diffusion coefficient.

Regarding the pore geometry, it can have an impact on the properties of the membrane. For example, conical shaped nanopore have been shown numerically by Hung-Chun et al. [50] to impact the transport properties of ions through the nanopore such that more better performance are obtained when diffusion of ions is from the base side of the cone the tip side. As shown in Figure 2.13, this is due to an enhancement of the EDL overlap effect when the low concentration compartment is situated on the tip side of the cone (the lower the concentration, the larger the the Debye length).

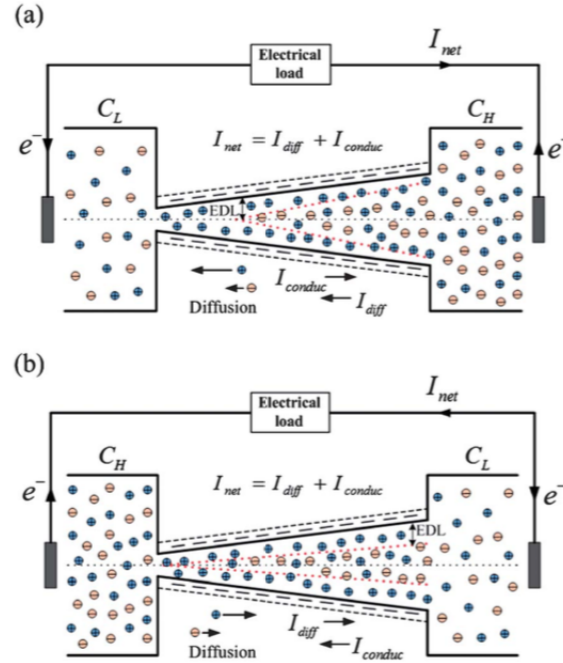


Figure 2.13: Schematic representation of power generation in negatively-charged conical nanopore as a result of reverse electrodialysis (RED). Taken from [50].

Applied potential

Charles R. Martin et al.[49] have been able to control the permselectivity property of gold nanopore with an applied voltage on the membrane. When immersed in an electrolytic solution, since gold is a metal that does not oxidize in standard conditions, no electric double charge layer appears. However, cation

or anion will be attracted toward the surface of the gold pore when a potential is applied to it. As shown in Figure 2.14, at negative applied potentials, the nanotubule membrane shows ideal cation permselectivity ⁶, whereas at positive applied potentials the membrane shows ideal anion permselectivity. This selectivity occurs because excess electrons are present on the walls of the pore at negative applied potentials. Consequently, cations are transported and anions are excluded by the membrane. The induced selectivity is only due to the applied potential as long as the the anions used do not adsorb to gold because to not influence the excess charge on the surface.

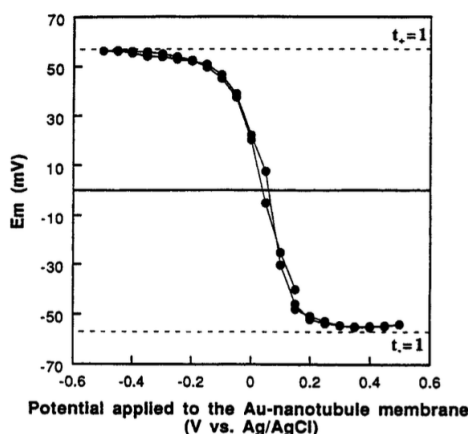


Figure 2.14: Variation of E_m with potential applied to the membrane composed of gold nanopore immersed between two KF solutions. Taken from [49].

2.2.4 Methods for producing nano-structured selective material

It has been introduced in the first Chapter that nano-structures material such as nano-pore and nano-channel have the potential to offer more efficient IEMs for RED applications. Nano-pore and nano-channel can usually be made following three major methods: ion beam sculting, transmission electron microscopy (TEM) drilling, and electrical pulse fabrication [40]. Despite that these methods allow to reach high resolution (down to the nanometer), they are not suitable for large production and are often too expensive to be widely used [40].

A more promising nano-structured material for practical use in RED applications are nano-porous material. Byeong Dong Kang et al. [15] and Juwan Kim [37] both

⁶A transference number for the cation $t_+ = 1$ means the whole ionic flux is composed of cation only

used alumina nano-pore arrays as the IEM for their RED set-up and obtained a power density higher than power density obtained with homogeneous IEMS (see 1.3.4). These alumina nano-pore arrays are obtained in an acidic electrolyte by anodic oxidation of aluminum [61]. It results columnar hexagonal cells where each cell contains a cylindrical, uniformly sized nanopores ranging from 4 to 200 nm in diameter centred in it. According to the temperature and composition of the electrolyte solution, the high pore density (10^{11} pores/cm²) can be controlled. More detailed information can be found in [61].

The advantages of the anodization method over drilling methods are the large surface of membrane with a tunable high pore density that can be produced at once and the ease of manufacturing. In this work, the motivation is to produce a similar nano-porous membrane but using silicon as the structural basis.

2.3 Porous silicon

It was unintentionally that in 1956, Arthur Uhlir Jr. and Ingeborg Uhlir discovered porous silicon during their work on silicon wafers machining [62]. Under specific conditions they observed that small holes appeared instead of the uniformly polished silicon [63]. However, it was only after the discovery of photo luminescence properties of porous silicon (PSi) at room temperature in the early 1990s that it has found practical uses. Improvement of the manufacturing process has made PSi a valuable material for many applications such as drug delivery and biosensing thanks to its biocompatibility, tunable pore morphology, large surface and ease of manufacturing [64, 65].

At the UCL, porous silicon had been studied in previous work related to biosensing [66, 67] and its manufacturing process is well mastered. Thus, porous silicon is the main material used in this work.

2.3.1 Manufacturing process

The detailed information about the manufacturing process of PSi can be found in [66, 67]. Most commonly, PSi is prepared through anodization, or electrochemical etching of monocrystalline silicon wafers in HF-based electrolyte solutions. The process is depicted in Figure 2.15. In a two electrodes configuration silicon, acting as the working electrode or anode, is oxidised while protons are reduced at the anode, often made of platinum. The electrolyte solution separating the two electrode is hydrofluoric acid (HF) with a surfactant, most often ethanol. It helps the electrolyte to penetrate the pore by reducing the surface tension. Finally, a potential between the two electrodes is applied to start the porosification. The process is usually run in galvanostatic mode to control the current density.

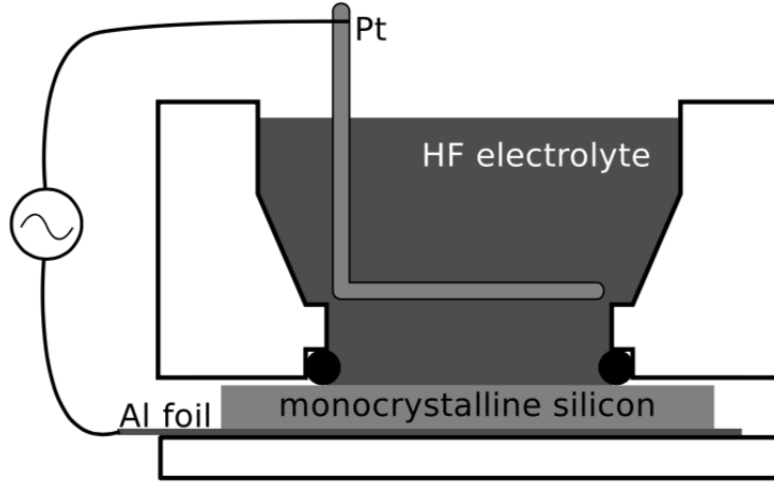
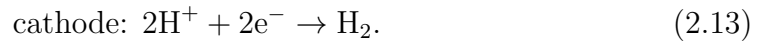
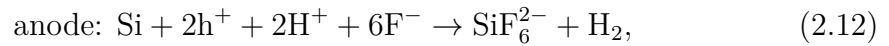


Figure 2.15: Schematic of the electrochemical etching cell used in this work for the PSi formation. The monocrystalline silicon sample is introduced in the cell with an aluminum foil on the back side for the electrical contact, while the front side, sealed with a Viton® O-ring, is in contact with the HF-based electrolyte. The cell is made out of Teflon. The electrochemical cell is completed by immersing a platinum electrode. Taken from [67].

Doped silicon, either n, n+, p, p+ or p++, can be used to form PSi. During the start of the process, due to the applied electric field, band holes are attracted to the surface. Nucleophiles such as F^- first, and H^+ ions from H_2O secondly target holes that reaches a silicon atom of the surface for nucleophilic attack. A reactions where hydrogen molecules are released and Si-F bonds progressively formed, as detailed by the two half reaction:



Porous silicon is then considered as a results two contributions. On one hand, from the direct dissolution of silicon by the acid HF, and on the other hand, by the dissolution of silicon oxide previously formed. Different possible mechanisms have been described to explain the formation of pore. For example, during the formation and propagation of pore, an enhanced electric field is present for pores with a sharp tip, attracting more even mores holes for the half reactions (2.12). Hole diffusion is then the limiting factor for this process.

The manufacturing parameters have an important impacts on the pore formation. Depending on the current density, another reaction can take place. For example,

electro-polishing is observed if the current is too high or the concentration of HF too low. In this case, an oxide layer is formed, ending the porosification process, because the F^- are replaced by water and HF diffusion is dominated by holes diffusion. Consequently, silicon on the surface is uniformly dissolved, resulting in a smooth surface (i.e. electro-polishing). The different regimes of electrochemical oxidation of silicon are presented on the I-V curve Figure 2.16 for silicon in an HF electrolyte. For low voltage, where the current increases exponentially, pore formation occurs. Electro-polishing occurs for high voltage where the current remains constant. The transition region happens between the pores formation and electro-polishing zones with the formation of a non-uniform porous layer. This I-V curve depends on the dopant concentration and type and on HF concentration. Usually, highly p-type wafers with crystalline orientation are used in the literature to manufacture PSi samples.

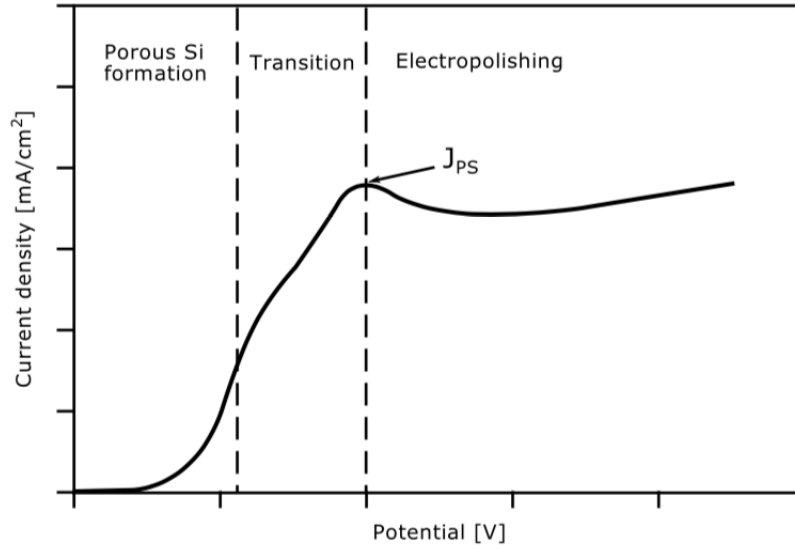


Figure 2.16: Typical IV curve for the electrochemical etching of p-type silicon in an HF electrolyte with the regimes of porous silicon formation, electropolishing and transition region delimited, and the current density value J_{PS} above which no more porous silicon is formed. Taken [67].

2.3.2 Structure and morphology of porous silicon

Fabrications parameters such as concentration and dopent type, HF concentration, current density, etc. influence the morphology and structure of PSi [66, 67]. Three features mainly characterized PSi morphology: pore depth, pore diameter and porosity. The pore size is generally the first feature to be taken into account

since most often the pore diameter is used to classified P*Si* as defined by International Union of Pure and Applied Chemistry (IUPAC)[68]. Pore are then classified following:

- micropores have a diameter inferior to 2 nm
- mesopores have a diameter comprised between 2 and 50 nm
- macropores have a diameter superior to 50 nm

Because the morphology, and thus the pore size, porosity and layer depth, is dependent on the P*Si* formation parameters, prediction of the parameters needed for a wanted porosity or pore size cannot be made with a formula. The most efficient way to achieve the the fabrication of the desired features remains to experiment and characterize the sample and then fin the tune the parameters. Nevertheless, some trends can be observed when specific parameters are varied for the evolution of the morphology.

Current density is known to mainly influence the growth rate and the pore size [66, 67]. A larger current density leads to larger pore formation and a larger growth rate. A larger depth is thus obtained for the same anodization time.

For the HF concentration, smaller pores are obtained for a higher HF concentration. Additionnaly, the shape of the IV curve is also influenced by the HF concentration. An decrease in HF concentration has the opposite effect of increasing the current regarding the growth rate. As we get closer to the regime of transition for the porous silicon formation by decreasing the HF concentration, the growth rate is increased.

Pore depth, or layer thickness, is the the second feature to be taken into account. The thickness of the porous film is directly correlated to the etching time. Indeed, doubling the etching time will results in porous later thickness also doubled for a constant current. Note that this might not be true for large depth as HF concentration will be impacted by the possible limited transport of ions in the pores, thus influencing the the growth rate.

Porosity is the third morphological feature of interest. The definition of the the IUPAC for the porosity is "the ratio of the total pore volume V_p to the apparent volume V " [68]. A further distinction is made by definition the close and open porosity. Open porosity is defined as " the volume of pores accessible by a probe molecule" and close porosity as " the volume of inaccessible pores to the probe molecule". As the total porosity is the sum of both porosity, the characterization methods may influenced its value. Finally, the current density can also influence the porosity. At any time during the pore formation, the current density is directly reflected by the porosity, therefore the higher the current density, the larger the porosity

2.4 Conclusion

In this chapter, a physical explanation about the permselectivity of IEM and charged nano-pore has been developed. First, the permselectivity of homogeneous polymer-based membrane has been made based on their internal structure. Due to fixed charge in the matrix of the membrane, an exclusion of co-ions is present, which is called the Donnan exclusion. Thus the majority mobile ionic species in the membrane are counter-ions, explaining the permselectivity of IEM. The permselectivity of a membrane depends on several parameters, such as the concentration of fixed charges in the membrane.

Second, the properties of selectively transport counter-ions has been shown in a charged pore. This is observed when 2 conditions are met: the surface of the pore charges itself in the solution, creating a double charge layer over a scale determined by the Debye length, and when the pore cross-dimension is on the order of the Debye length such that an *EDL overlap* is present. Consequently, the pore will be filled mainly by ions of opposite charge (counter-ions) to the surface charge of the pore and will exclude ions with the same charge (co-ions). The ionic flux will then mainly be composed of counter-ions, and the pore will show selective properties.

Chapter 3

Numerical simulation for the ionic transport

In this chapter, a model focused on the ionic transport inside a charged nanopore is described. First, important quantities computed with the simulation are described. Second, the model is introduced and the assumptions behind it detailed. Then, values for the surface charge density are proposed. Finally, numerical results for different important parameters are analysed.

3.1 Numerical model for ions transport

Transport of ions inside a charged nanopore can be modelled numerically with the modified full Poisson-Nernst-Planck (PNP) equations. Ion transport in nanofluidic channels is analyzed using continuum dynamics, as the continuum dynamics equations are known to be an adequate description of ion transport for length scales larger than 5 nm [35]. The molar flux of the i th ion species is composed of the electromigration J_i^e , diffusion flux J_i^D and convection,

$$\mathbf{J}_i = \mathbf{J}_i^e + \mathbf{J}_i^D + \mathbf{u}C_i = -\frac{z_i F}{RT} D_i C_i \nabla \varphi - D_i \nabla C_i + \mathbf{u}C_i, \quad (3.1)$$

where the subscript i denotes 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, C_i the molar concentration and $\mathbf{u}$ the velocity vector. If motion of the fluid is neglected (i.e. $\mathbf{u} = 0$), the equation is reduced to the Nernst-Planck equation.

For steady state solution and assuming no chemical reaction (no species generation or consumption), the governing equation for the transport of the i th species from the species conservation of mass is given as:

$$\nabla \cdot \mathbf{J}_i = 0. \quad (3.2)$$

Motion of the incompressible solution is generated by the electric potential and pressure gradient and can be described by the modified Navier-Stokes equation for creeping flow (Reynolds number $\text{Re} \simeq 10^{-5} - 10^{-3}$) and the continuity equation:

$$0 = -\nabla p + \mu \nabla^2 \mathbf{u} + F \sum_i z_i \nabla \varphi, \quad (3.3)$$

and

$$\nabla \cdot \mathbf{u} = 0, \quad (3.4)$$

where p is the pressure and μ the viscosity. As seen in eq. 3.3, motion of fluid can be either induced by a gradient potential of electric force. Usually in when studying the ionic conductance, the pressure is set to zero every where and the motion of fluid is only induced for an electric force. This kind of flow is name electro-osmotic flow.

An electrical current density is produced by the motion of the ions species,

$$\mathbf{i} = F \sum_i z_i \mathbf{J}_i = -\nabla \varphi \sum_i \frac{z_i^2 F^2}{RT} D_i C_i - F \sum_i z_i D_i \nabla C_i + F \mathbf{u} \sum_i z_i C_i. \quad (3.5)$$

The total electrical current through the nanopore is then simply integrated over the cross-sectional area of the pore as $I = \int_A i dA = Fz \int_A (J_+ - J_-) dA$, where A is the cross-sectional area of the channel and $|z_+| = |z_-| = z$ considered in this study.

The electrical potential is given by the Poisson equation i.e.,

$$\nabla^2 \varphi = -\frac{\rho_e}{\epsilon_r \epsilon_0}, \quad (3.6)$$

where ϵ_0 is the permittivity of vacuum, and ϵ_r is the dielectric constant of the electrolyte solution. The net charge density is given as $\rho_e = F \sum_i z_i C_i$.

The simplest geometry that can be studied is a cylindrical pore. The numerical domain for a cylindrical pore is represented in Figure 3.1 as well as the boundary conditions. Two kind of numerical test can be performed: determination of (i) the diffusion potential under zero current condition (i.e., open circuit voltage) and of (ii) the electrical current–voltage in the RED mode. Different types of boundary conditions are imposed for the kind of tests.

In the calculations of the diffusion potential, the boundary conditions are given by

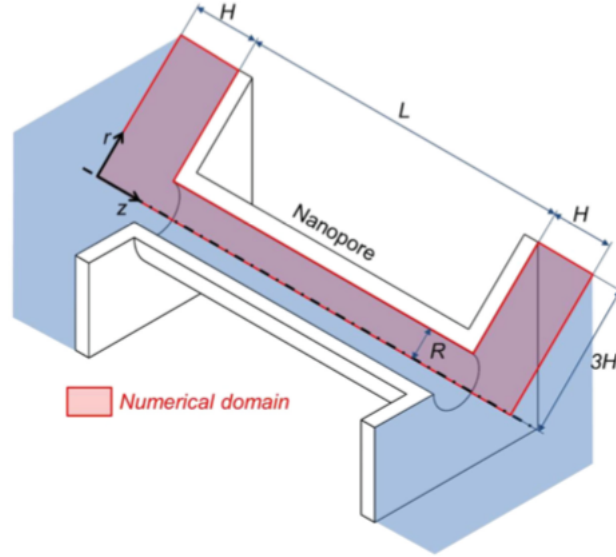
$$\begin{aligned} \text{left} \quad C_i &= C_L, & \mathbf{n} \cdot \nabla \varphi &= 0, \\ \text{right} \quad C_i &= C_R, & \varphi &= \varphi_R. \end{aligned} \quad (3.7)$$

For the other numerical test (current–voltage relationship), the Neumann boundary condition for the Poisson equation is replaced by the Dirichlet boundary condition. Thus, the boundary conditions becomes

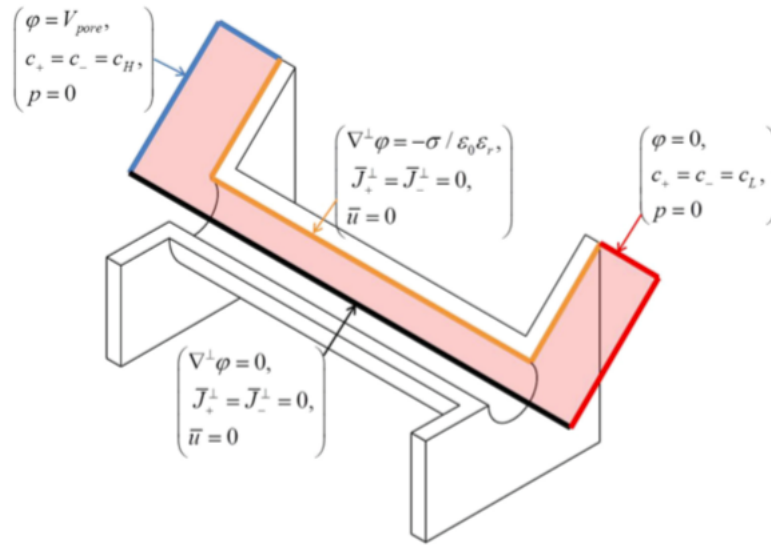
$$\begin{aligned} \text{left} \quad C_i &= C_L, & \varphi &= \varphi_L, \\ \text{right} \quad C_i &= C_R, & \varphi &= \varphi_R. \end{aligned} \quad (3.8)$$

In every simulation, no pressure difference is considered:

$$\begin{aligned} \text{left} \quad p &= 0, \\ \text{right} \quad p &= 0. \end{aligned} \tag{3.9}$$



(a) Numerical domain



(b) Boundary conditions

Figure 3.1: Numerical domain and boundary conditions for a nanopore with reservoirs on either side[15].

Due to the geometrical symmetry of the nanopore, only half of physical domain is needed for the computational domain, reducing the computational cost. The center line of the nanopore and reservoir now require a symmetric boundary condition. The boundary conditions at the pore surfaces are

$$\mathbf{n} \cdot \mathbf{J}_i = 0, \quad \mathbf{n} \cdot \nabla \varphi = -\frac{\sigma}{\epsilon_r \epsilon_0}, \quad (3.10)$$

where $\mathbf{n}$ denotes the unit normal vector of the boundary surface, σ the surface charge density of the pore surfaces.

3.2 Surface charge density

As explained in 2.2.3, the surface charge density of the nano-pore inner wall surface is an important parameter for the ion-selective properties, but its experimental determination can be difficult and depends on the method used. What is more, most of the values for the surface charge density are for planar surface of nano-particle. It has been shown also been shown [59, 69] that the curvature and the size of the nano-particle impacts the surface charge density. Unfortunately in this work, it has not been possible to determined experimentally the surface charge density for the three oxides (SiO_2 , HfO_2 and Al_2O_3). Determination of this parameter in a nano-pore as a function of the pore geometry and solution properties is important and a more specific study on the way to improve surface charge density for membrane in RED application would be interesting in the future.

Consequently, values obtained for planar surface or nano-particle are not necessarily correct values for nano-pore. An approximative method based on the numerical model proposed above has been proposed in [15], where the surface charge density is varied in order to match the experimental data. However, the numerical model is based on several assumptions and represents an ideal visualisation of the transport of ions in the nano-pore. Thus, values obtained with this methods should only be considered as qualitative.

In this work, the main target is to characterise nano-porous silicon membrane with 3 different oxides surface: SiO_2 , Al_2O_3 and HfO_2 . The sign of the surface charge density is specific to each material and can be determined based on the their PZC (see Figure 2.11). Values from the literature for the PZC of the three oxides studied in this work are listed in Table 3.1.

The solution that will be used during the experiment is NaCl in deionized (DI) water. The pH of such solution is around 7 (neutral) at 25 °C. The pH can be slightly lower than 7 if the concentration of CO_2 in the air increases. This is because water exposed to air contains dissolved carbon dioxide (as for oxygen), which can also react with the water to form carbonic acid, making the water more

acid. However, this reaction is usually minimal [70]. In this work, a pH around 6-7 is assumed. Consequently, as seen in Table 3.1, at a pH around 6-7, the surface charge density of Al_2O_3 will be positive, negative for SiO_2 and slightly positive for HfO_2 .

	[71]	[72]	[73]	[74](NaCl)	[74](KC)	[74](NaCl)
Al_2O_3	9.2	9.1(α)	9			
SiO_2	2	1.8	2.2			
HfO_2				7.6	7.6	7.4

Table 3.1: PZC Values of Oxides from Different Sources. Reproduced from[74].

In the literature, the surface charge density is on the order of 1 to 10 $\mu\text{C}/\text{cm}^2$ for nano-particle oxide and oxide surface in water depending on the pH, the solution and the electrolyte[59, 69, 75, 76]. Values around -2 $\mu\text{C}/\text{cm}^2$ to -4 $\mu\text{C}/\text{cm}^2$ are found for spherical silica bed[59, 69] at in water at pH 6-7, +4 $\mu\text{C}/\text{cm}^2$ to 10 $\mu\text{C}/\text{cm}^2$ for alumina[76] and $<+2$ $\mu\text{C}/\text{cm}^2$ for HfO_2 .

3.3 The importance of the transference number

3.3.1 Definition

Different quantities can be analysed such as the current-voltage curve for different input parameters. One important quantity that can be studied is the open circuit voltage E_{OCV} . But before this, the transference number of the ion i must be defined. Its expression is given by

$$t_i = \frac{z_i J_i}{\sum_j z_j J_j}, \quad (3.11)$$

where J_i is the total flux of the ionic species i , z_i the valence charge of the ionic species i and I the electrical current. For a system with only 2 ionic species (e.g. Na^+ and Cl^-), $i = +$ or $i = -$. The transference number t_i can take value between 0 and 1, 1 meaning the total ionic flux is made only by the ionic species i and 0 that the ionic species does not contribute to the total ionic flux. The average transference number $\bar{t}_i$ is equal to

$$\bar{t}_i = \frac{z_i \bar{J}_i}{\sum_j z_j \bar{J}_j}, \quad (3.12)$$

where the bar indicates average quantities. The following approximations can be made for the average transference number $\bar{t}_i \simeq \frac{I_i}{I_{total}}$.

3.3.2 The open-circuit voltage

The open circuit voltage E_{OCV} is related to the transference number and the concentration of each solution through

$$E_{OCV} = (2t_+ - 1) \frac{RT}{zF} \ln \frac{\gamma_{C_H} C_H}{\gamma_{C_L} C_L}, \quad (3.13)$$

where γ_i is the mean activity coefficient. Its expression can be derived based on thermodynamics as detailed in the next Chapter. It results from the difference Donnan potential across the membrane and in mobility between cation and anion in the IEM (here nano-channel) (see next chapter).

In the case where we have two ionic species of opposite charge, if we have a membrane with no selective properties and assuming both ions diffuse at the same rate (i.e. same diffusion coefficient), then the transference number for each species becomes $t_+ = t_- = 0.5$, and $E_{OCV} = 0$. No power is extractable in this case. This example also shows that the transference number can also be interpreted as a ratio of molar conductivity. Numerically, by determining the OCV, the transference number for the cation can be determined as

$$t_+ = \frac{1}{2} - \frac{zF}{2RT} \frac{E_{OCV}}{\ln \frac{\gamma_{C_H} C_H}{\gamma_{C_L} C_L}} \quad (3.14)$$

3.3.3 Efficiency of RED applications

In the case where the nano-pore in Figure 3.1 is connected to an external load, the electrical circuit can be modelled as schematically shown in Figure 3.2, assuming the nano-pore can be viewed as a voltage source E_{OCV} with some internal resistance R_{pore} .

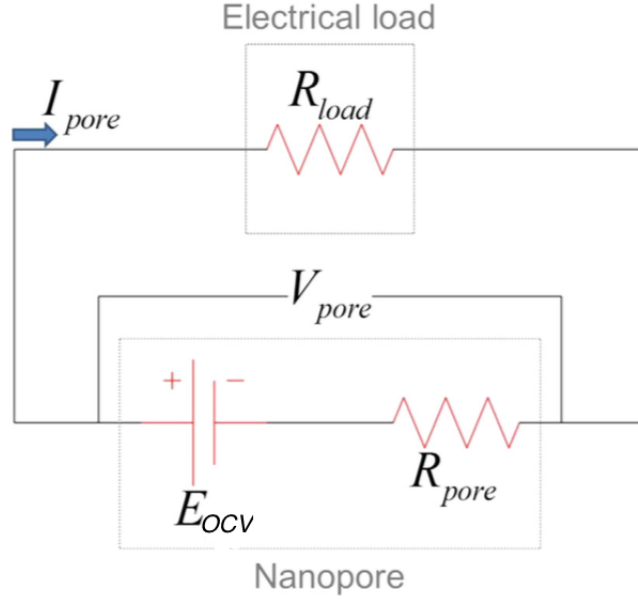


Figure 3.2: Equivalent electrical circuit for the charged nanopore separating two solutions of different concentration [15].

Based on this electrical equivalent circuit, the electric potential generated in the nanopore, V_{pore} , is given as

$$V_{pore} = E_{OCV} - R_{pore}I_{pore}, \quad (3.15)$$

and the power generated by the pore when a load is connected to the circuit is given by

$$P_{pore} = E_{OCV}^2 \frac{R_{pore}}{(R_{pore} + R_{load})^2}. \quad (3.16)$$

The maximal power generated is given when the load matches the resistance of the pore

$$P_{pore,max} = \frac{E_{OCV}^2}{4R_{load}^2}. \quad (3.17)$$

The energy conversion efficiency η of the system in Figure 3.2 is defined in [15] as the ratio of the output energy (electrical energy) to the input energy (Gibbs free energy of mixing):

$$\eta = \frac{V_{pore}I_{pore}}{RT \ln \left(\frac{\gamma_{CH}C_H}{\gamma_{CL}C_L} \right) \int (J_+ + J_-)dA}, \quad (3.18)$$

where $\int (J_+ + J_-)dA$ is the number of ions transported through the nano-pore per unit time. Using $I = \int_A i dA = Fz \int_A (J_+ - J_-)dA$ and the approximation

$\int J_+ dA / \int J_- dA \simeq t_+ / (1 - t_+)$, the efficiency is then given by

$$\eta = \frac{(1 - 2t_+)V_{pore}}{\frac{RT}{zF} \ln \left(\frac{\gamma_{C_H} C_H}{\gamma_{C_L} C_L} \right)}. \quad (3.19)$$

The efficiency corresponding to the maximal power generation is found when $V_{pore} = E_{OCV}/2$, which gives

$$\eta_{max,W} = \frac{(1 - 2t_+)^2}{2}. \quad (3.20)$$

The last relation shows that the efficiency at maximal power generation is 50% for a perfectly ion-selective nano-pore. This also shows the importance of the transference number.

3.4 Numericals results

The numerical results are obtained using COMSOL Multiphysics©5.4. Typical parameters used in the numerical study are presented in Table 3.2. Sodium chloride in water is considered as the solution. The mesh of the numerical simulation is also shown in Figure 3.3.

Radius R	length L	σ_s	C_L	C_H	D_+	D_-	ϵ_r
10 nm	100 nm	10 mC/m ²	0.01 M	0.001 M	1.334e-9 m ² /s	2.032e-9m ² /s	80

Table 3.2: Typical set of values used for the numerical simulation.

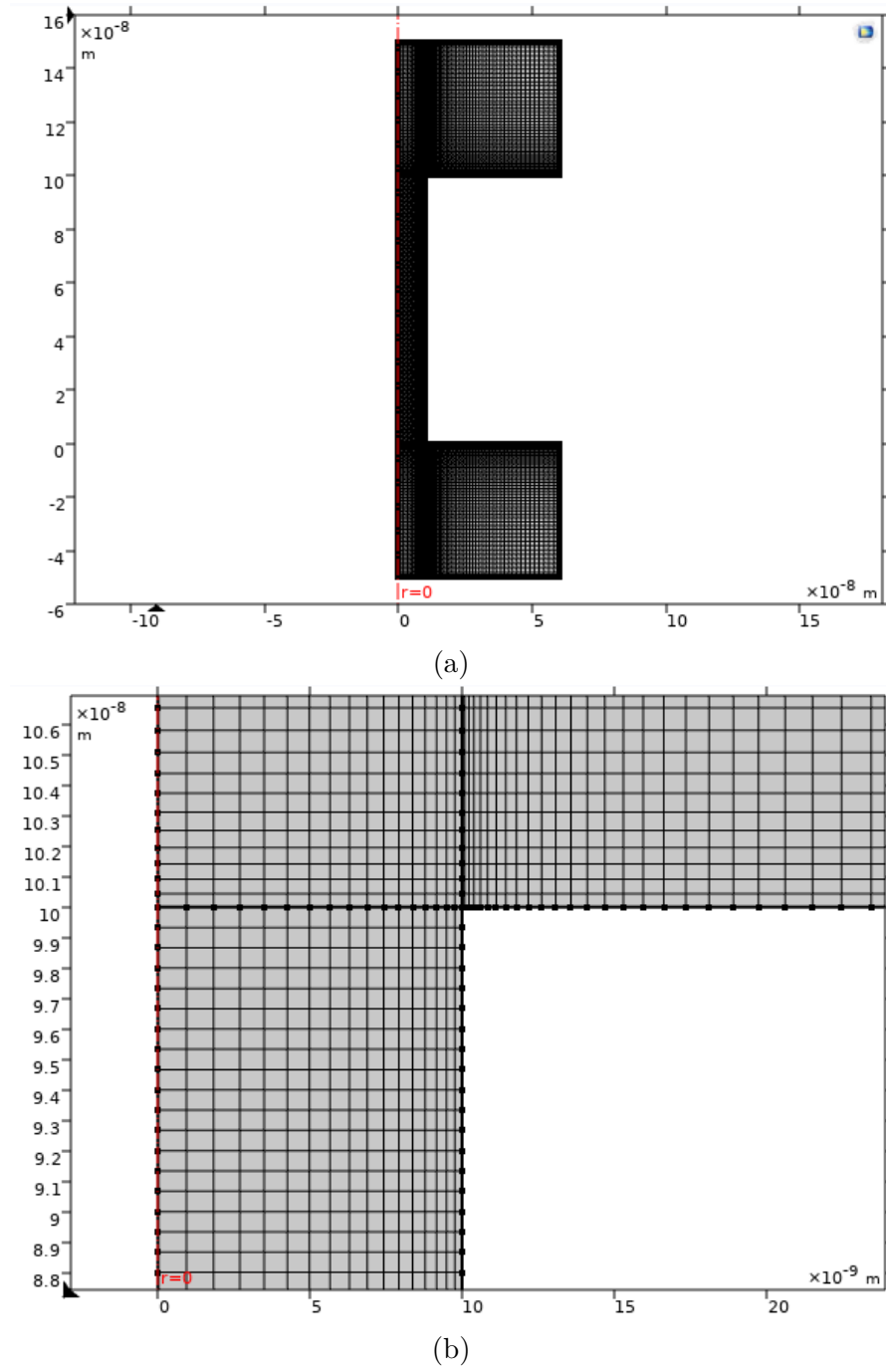


Figure 3.3: (a) Mesh used for the numerical simulations. (b) The mesh is thinner closer to the charged surface in order to capture the correct physical phenomenon. Number of degree of Freedom=105105.

Typical results for a IV curve and the power generated are shown in Figure 3.5 for the specified parameters in Table 3.2. For a positive surface charge density, the majority carrier in the pore are the anions. Following the convention in Figure 3.4, a positive current indicates a net flux of anions toward from the high concentration compartment to the low concentration compartment.

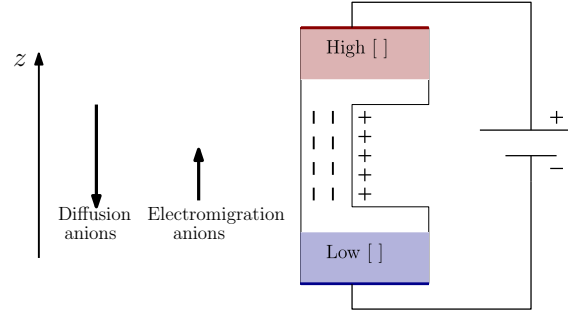
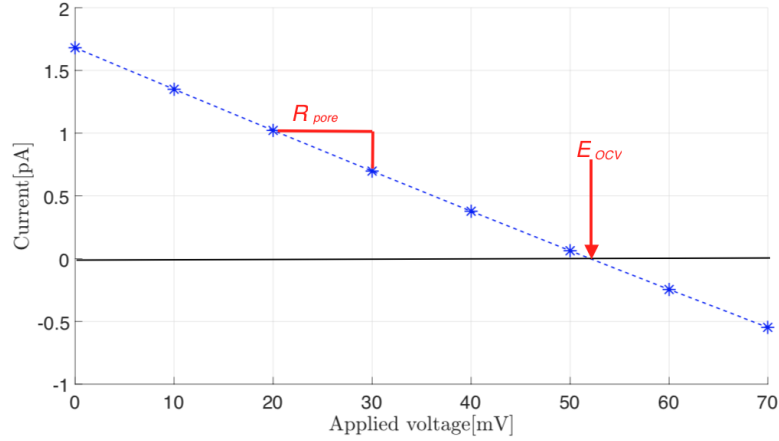


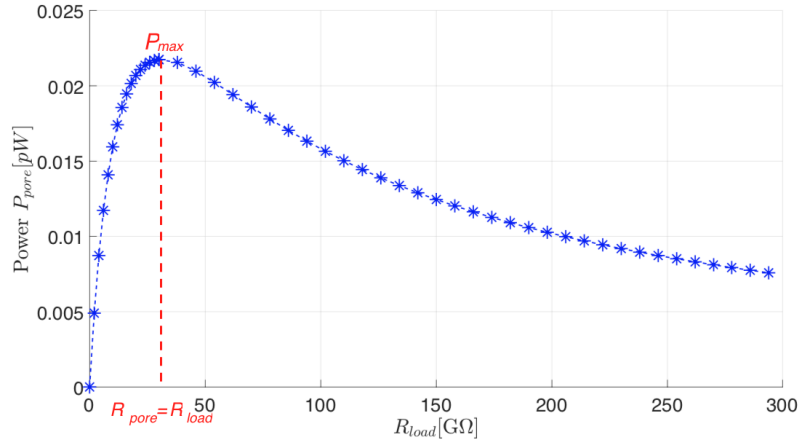
Figure 3.4: Schematic of the charged nano-pore separating two solutions of different concentration with an applied potential. The current here is positive because the main carrier are anions and they diffuse from top to bottom.

As seen in Figure 3.5a, the net current going through the nano-pore follows a linear behaviour with the voltage applied across the pore. A linear regression can be made to fit the data and the slope is related to the resistance of the nano-pore. Note that the slope is negative because the applied voltage acts against the flux of anions. This resistance is not an intrinsic property of the nano-pore, such as the conductivity, but a consequence of the charge surface influencing the distribution of ions inside the pore.

When no current is going through the nano-pore, the voltage obtained is equal to E_{OCV} because it is as the circuit is opened. From the linear regression, a value of $R_{pore} = 31.37 \text{ G}\Omega$ and $E_{OCV} = 52.2 \text{ mV}$ are found, which gives a transference number for the cations $t_+ = 0.0610$ based on eq. (3.14) with $\gamma_L = 1$ and $\gamma_H = 0.997$ [77]. The transference number is close to 0 because the current is mostly transported by anions with a positive surface charge density.



(a)



(b)

Figure 3.5: (a) Typical I-V curve for a nano-pore with $R = 10\text{nm}$, $L = 100\text{nm}$, $\sigma_s = 0.01\text{C/m}^2$, $C_H = 0.01\text{M}$ and $C_L = 0.001\text{M}$. (b) Typical power generation curve for a nano-pore with $R_{pore} = 31.37\text{ G}\Omega$ and $E_{OCV} = 52.2\text{ mV}$.

3.4.1 Influence of the surface charge density

Numerical simulations for the current potential curves at different positive surface charge density are shown in Figure 3.6 and the corresponding transference number in Figure 3.7. As it can be seen, as the slope of the IV curve increases in absolute value as the surface charge density increases, meaning the resistance decreases. When the surface charge density increases in absolute value, more counter-ions are present in the pore to insure electrostatic equilibrium. As counter-ions are the main carrier for the electrical current, the resistance decreases with an increase in surface charge density.

The second observation is the decrease in the output circuit voltage decreases with a decrease in the surface charge density. Because the selectivity and thus the output circuit voltage originate in a Donnan exclusion, the more charge on the pore (ie. fixed charges for homogeneous membranes), the stronger the Donnan effect and thus the output circuit voltage increases. This is reflected in Figure 3.7, where the transference number for the cation decreases with an increase of the surface charge density, meaning the membrane becomes more selective to anions.

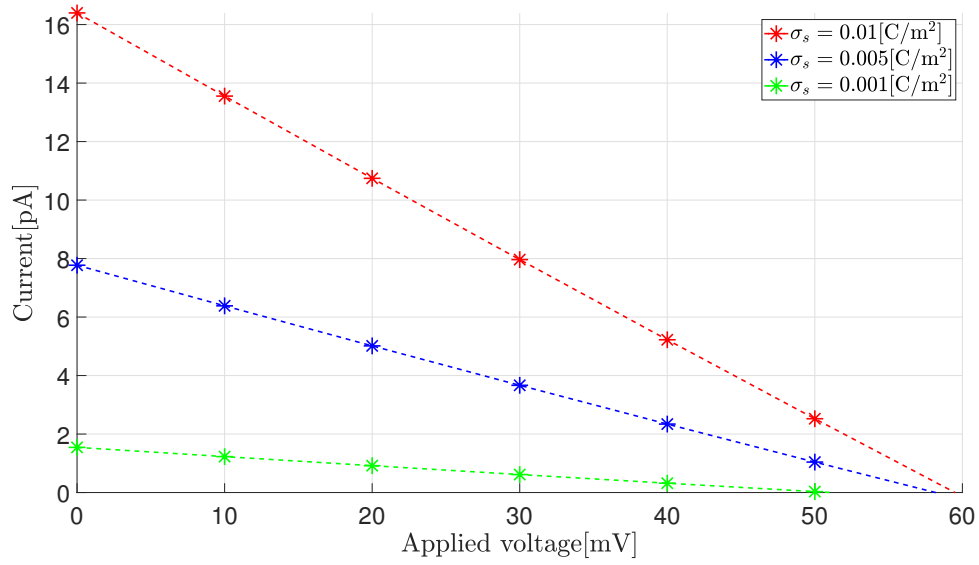


Figure 3.6: Typical current potential curves of nanopores for various surface charge densities. ($R = 10\text{nm}$, $L = 100\text{nm}$, $\sigma_s = 0.01\text{C/m}^2$, $C_H = 0.01\text{M}$ and $C_L = 0.001\text{M}$).

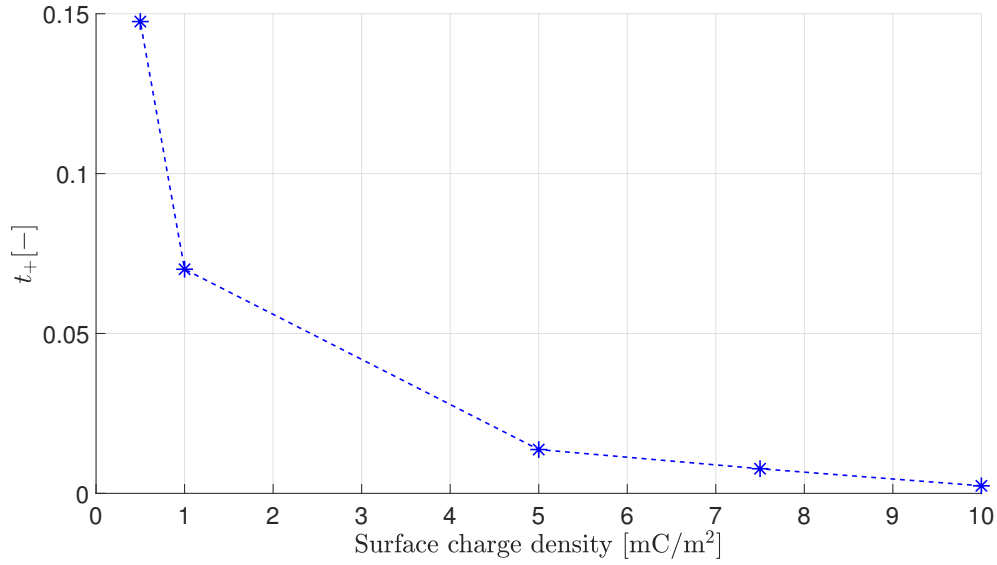


Figure 3.7: Transference numbers for various surface charge densities. ($R = 10\text{nm}$, $L = 100\text{nm}$, $\sigma_s = 0.01\text{C/m}^2$, $C_H = 10\text{mM}$ and $C_L = 1\text{mM}$).

3.4.2 Influence of the pore radius

Numerical simulations for the current potential curves at different pore radius are shown in Figure 3.8 and the corresponding positive transference number in Figure 3.9. The first observation is when the pore radius is increased, the slope of the IV curve increases in absolute values, meaning the resistance decreases. Similarly to a classical resistor, when the area is increased, more flux (ie. current) can go through the nano-pore. This is visible in Figure 3.8 at low voltage.

The second observation is a decrease in the output circuit voltage with an increase in the pore radius. This is a direct consequence of the finite size of the electric double layer. As the pore size increases the *EDL overlap* is weakened as shown in Figure 2.6, and the ion-selective properties of the pore decreases. This is clearly visible with an increase of the positive transference number with an increase of the pore radius as shown in Figure 3.9.

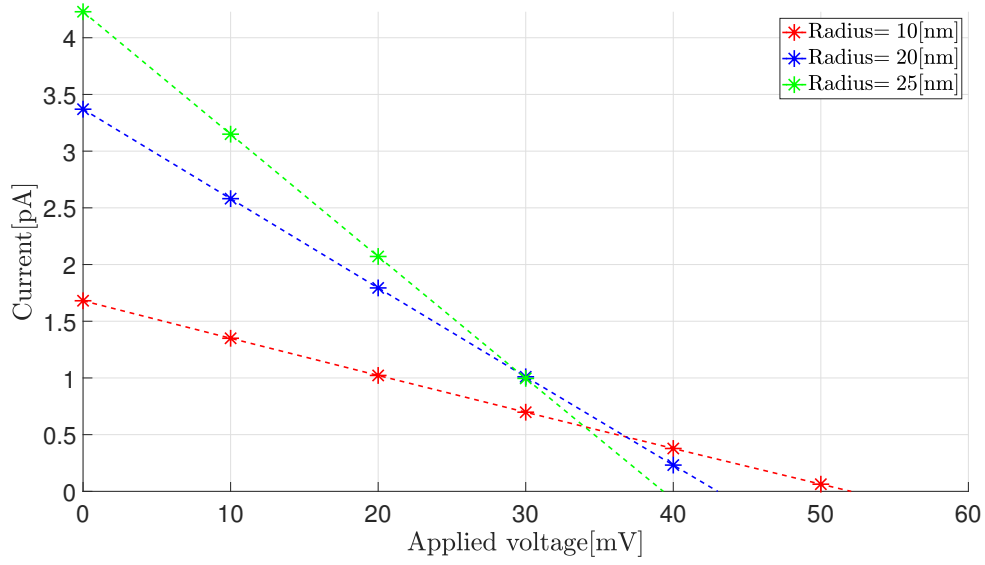


Figure 3.8: Typical current potential curves of nanopores for various surface charge densities. ($L = 100\text{nm}$, $\sigma_s = 0.001\text{C/m}^2$, $C_H = 10\text{mM}$ and $C_L = 1\text{mM}$).

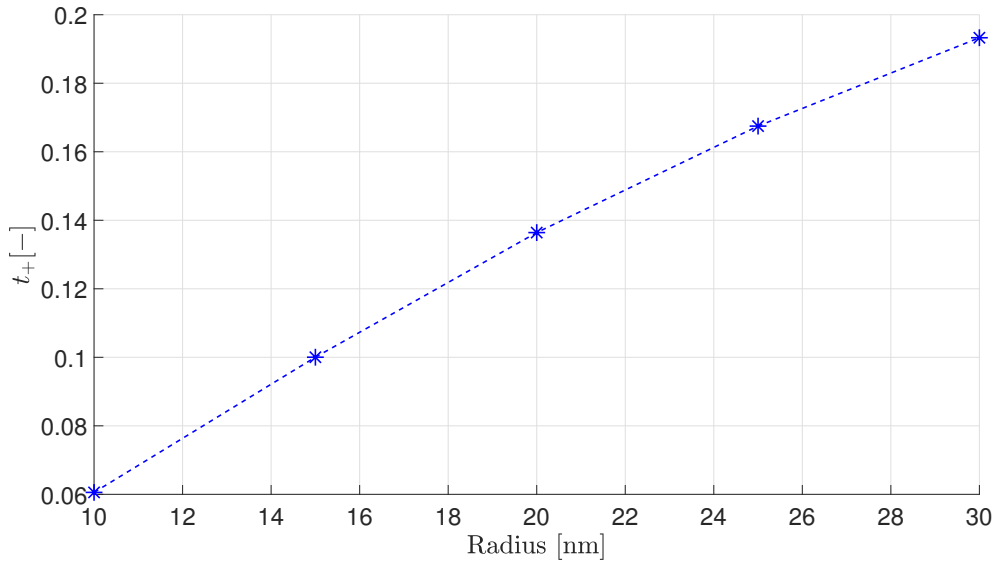


Figure 3.9: Transference numbers for various surface charge densities. ($L = 100\text{nm}$, $\sigma_s = 0.001\text{C/m}^2$, $C_H = 10\text{mM}$ and $C_L = 1\text{mM}$).

3.4.3 Influence of the pore length

Numerical simulations for the current potential curves at different pore length are shown in Figure 3.10 and the corresponding positive transference number in Figure 3.11. The first observation is that an increase in the pore length increases the pore resistance similarly to a classical resistor. In the present case, by keeping the concentration difference between the two compartments unchanged, an increase in the pore length actually leads to a decrease in gradient potential, thus the driving force of the flux is decreased.

The second observation is that the positive transference number decreases with an increase in the pore length (Figure 3.11). This means the pore becomes more selective to negative charge. When the length is increased, the reduction in the fluxes is more detrimental for cations than anions because the channel is anion-selective.

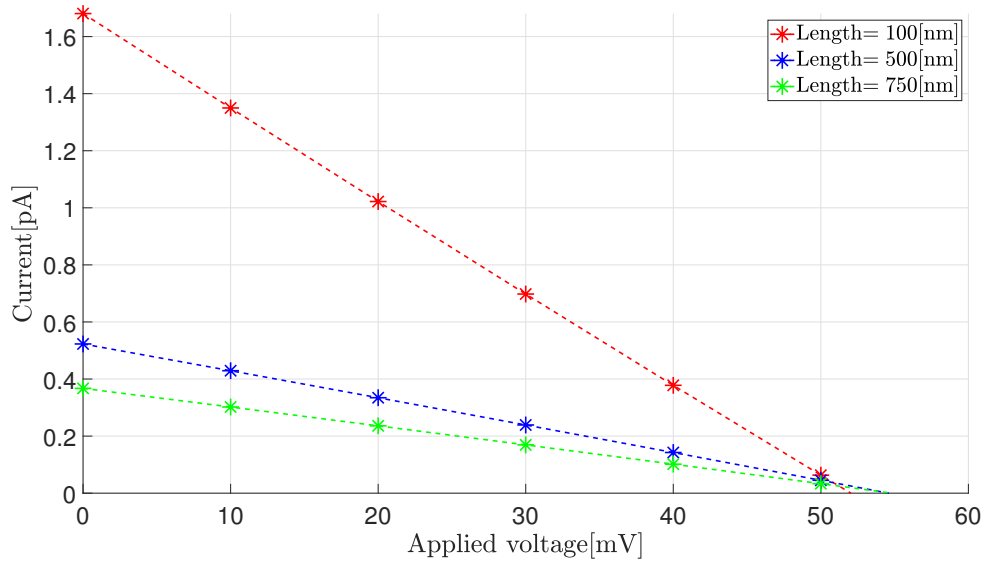


Figure 3.10: Typical current potential curves of nanopores for various surface charge densities. ($R = 10\text{nm}$, $\sigma_s = 0.001\text{C/m}^2$, $C_H = 10\text{mM}$ and $C_L = 1\text{mM}$).

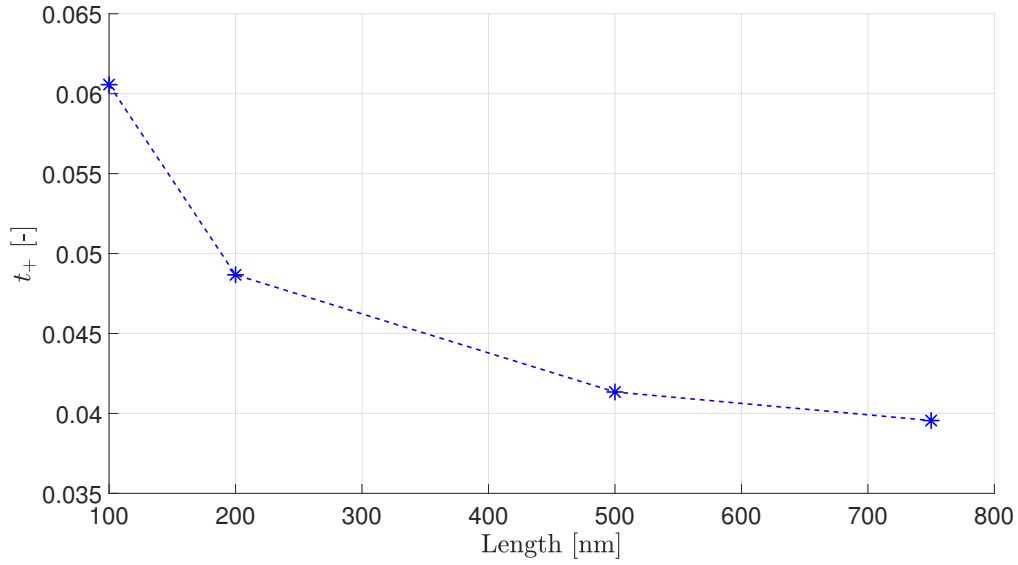


Figure 3.11: Transference numbers for various surface charge densities. ($R = 10\text{nm}$, $\sigma_s = 0.001\text{C/m}^2$, $C_H = 10\text{mM}$ and $C_L = 1\text{mM}$).

3.4.4 Influence of the high concentration compartment

Numerical simulations for the current potential curves at different high concentration values are shown in Figure 3.12 and the corresponding positive transference number in Figure 3.13. The first observation is that the resistance of the nano-pore decreases with an increases in the high concentration. As the concentration of ions increases, the number of carrier in the nano-pore also increases, resulting in a higher current for the same applied voltage.

The second observation is that the positive transference number increases with an increases in the high concentration. This is a consequence of the dependence of the EDL to the concentration (see eq. (2.8)): as the concentration is increased, the EDL overlapp is decreased on the high concentration side of the pore. The EDL overlapp becomes effective only after a certain distance from the pore entrance, and it is as an ion sees a shorter ion-selective nano-pore. The positive transference number thus increases (ie the pore become less anion-selective) as seen in figure 3.13.

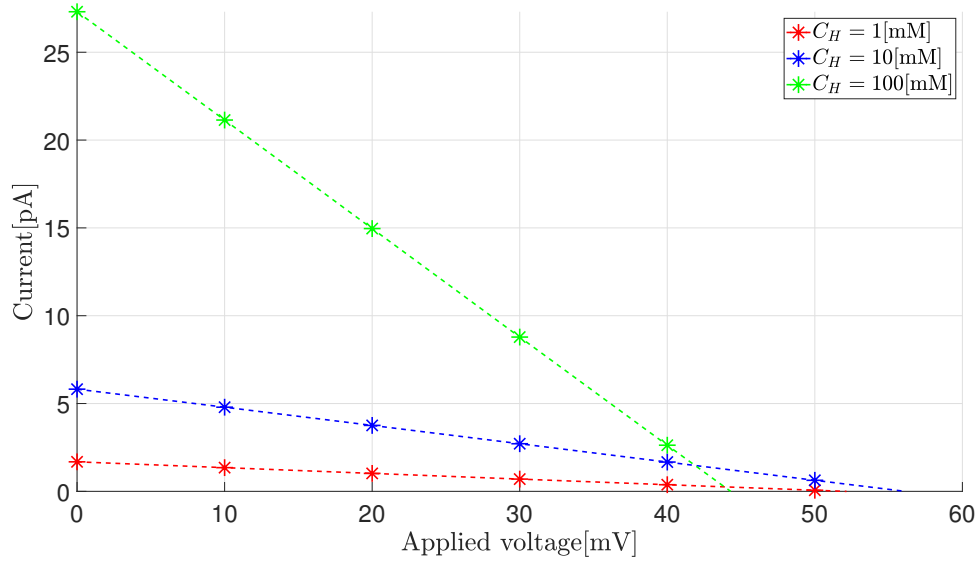


Figure 3.12: Typical current potential curves of nanopores for various surface charge densities. ($R = 10\text{nm}$, $L = 100\text{nm}$, $\sigma_s = 0.001\text{C/m}^2$ and $C_L = 1\text{mM}$).

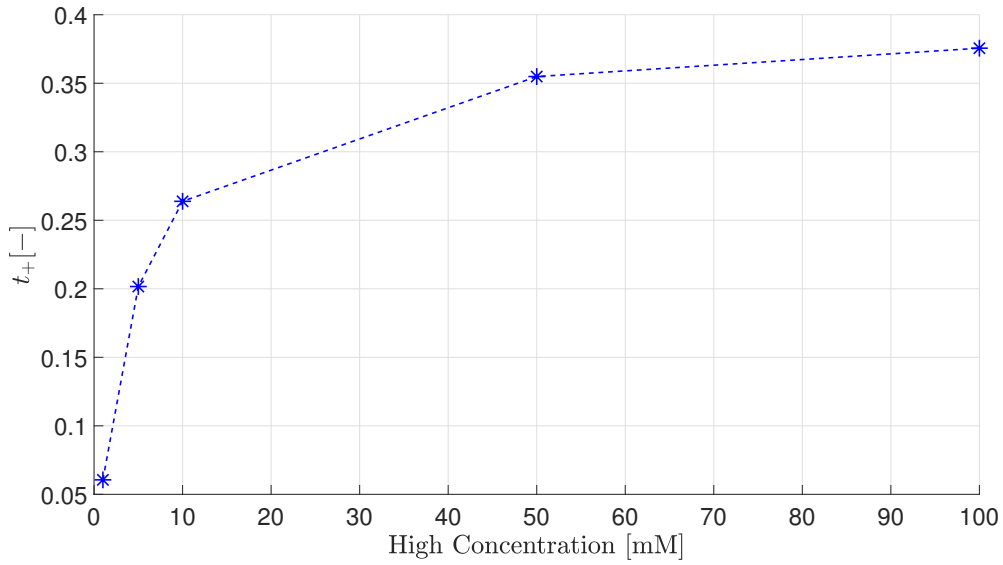


Figure 3.13: Transference numbers for various surface charge densities. ($R = 10\text{nm}$, $L = 100\text{nm}$, $\sigma_s = 0.001\text{C/m}^2$ and $C_L = 1\text{mM}$).

3.4.5 Influence of the low concentration compartment

Numerical simulations for the current potential curves at different low concentration values are shown in Figure 3.14 and the corresponding positive transference number in Figure 3.15. The first observation is that resistance increase with a decrease in the low concentration. The same explanation as for the dependence of the resistance with the high concentration can be made here.

The second observation is the increase of the positive transference number with the low concentration. Once again, the same explanation as the one made for the high concentration dependence can be made here.

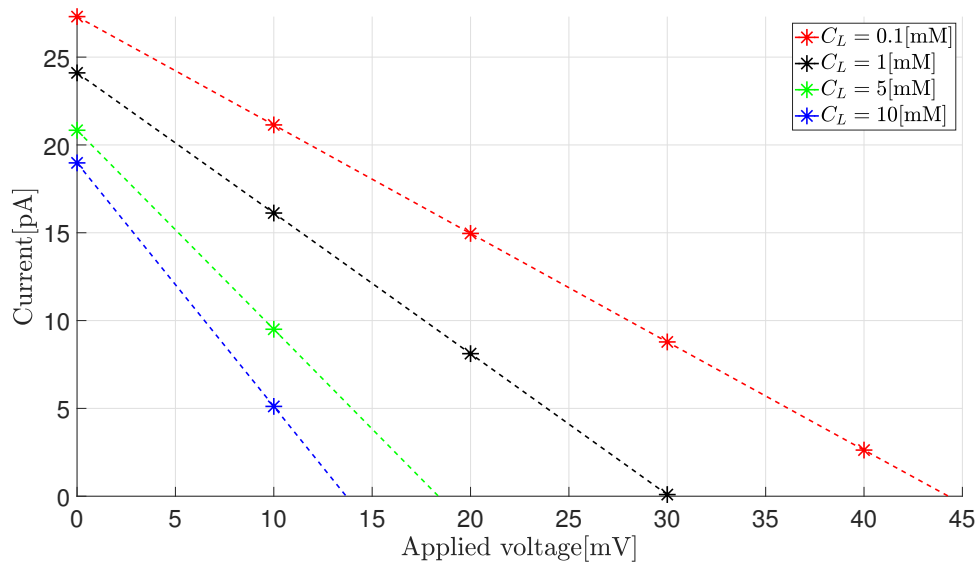


Figure 3.14: Typical current potential curves of nanopores for various surface charge densities. ($R = 10\text{nm}$, $L = 100\text{nm}$, $\sigma_s = 0.001\text{C/m}^2$ and $C_H = 10\text{mM}$).

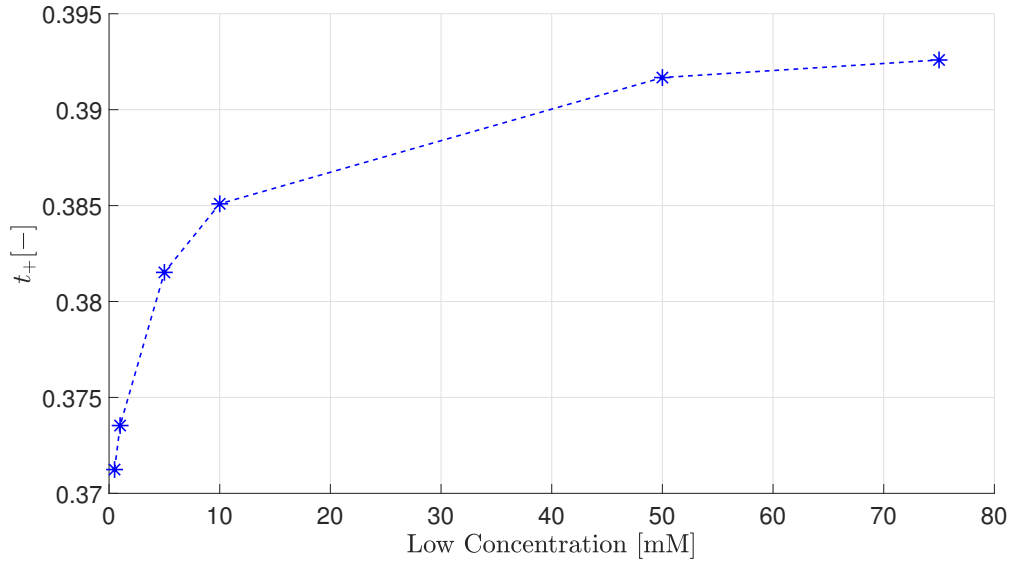


Figure 3.15: Transference numbers for various surface charge densities. ($R = 10\text{nm}$, $L = 100\text{nm}$, $\sigma_s = 0.001\text{C/m}^2$ and $C_H = 10\text{mM}$).

3.5 Conclusion

In this chapter, a numerical models for the ionic transport in charge nano-pore has been presented. Based on the Nernst-Planck equations coupled with the Poisson's equation, ion-selective properties of nano-pore can be studied. The interaction at the solid-interface is represented with a surface charge density parameter. Because of the electrostatic interaction between the ions and the charged surface, a selective property appears inside the nano-pore. This selectivity is impacted by different parameters, such as the surface charge density, the pore dimensions and the concentrations in each compartment. The maximal power that can be generated is influenced by the choice of these parameters. The maximal efficiency of the process only depends on the transference number. Increasing the surface charge density while keeping the other parameters constant results in better selective properties and more current at a given applied voltage.

Chapter 4

Tailor made Silicon ion exchange membrane: Materials and methods of characterization

In this chapter, the materials and methods used for the fabrication and characterisation of PSi as permselective membrane are presented. The first part is dedicated at the process for porous silicon membranes manufacturing and a second part to the description of the different characterization techniques. Finally, the experimental set-up is detailed.

4.1 Porous silicon samples fabrication

The membrane fabrication process in this work is depicted in Figure 4.1. Each step has been carried out in the Winfab cleanroom of UCL. The manufacturing process of PSi proposed in this work is based on several previous works done at the UCL and is well mastered[66, 67]. The purpose of the manufacturing process is to obtain a mechanically stable PSi to use in saline solution as an IEM for RED. Different manufacturing process have been tested in [66] to obtain stable membranes. In this work, the membrane thickness can be chosen thicker than for the membrane used for the biosensor in [66] to further increase the mechanical stability.

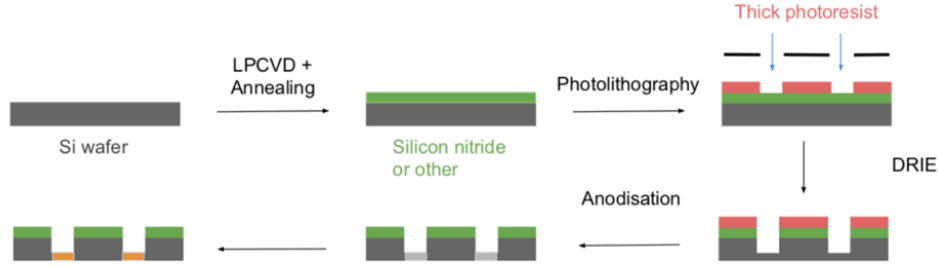


Figure 4.1: Process flow steps for the fabrication of PSi used in this work. The last step is either an ALD or a thermal oxidation.

The silicon wafers used are double side polished $\langle 100 \rangle$ -oriented highly boron p++ wafers. Wafers have a resistivity between 0.8 and 0.9 m Ω cm. They have a diameter of 3 inches (sin7.62cm) and are 380 μ m. The first step of the manufacturing process is a standard cleaning to remove all organic contaminants using sulphuric peroxide mixture, also called Piranha. The composition of the solution is H₂SO₄ (97%) and H₂O₂ (30%) in the proportion 5:2 v:v. Wafers are immersed in this bath for 20 minutes. Then the wafers are plunged in a solution of HF (2%) for 15 seconds and rinse after for 5 min. After the HF bath, the wafers are plunged in a dionised water bath with a N₂ flux for another 10 minutes. Finally, the wafers are placed in a rincer-dryer for eight minutes.

4.1.1 Deposition of silicon nitride

The first step consists in the deposition of a layer of silicon nitride on the front side of the wafer using a plasma enhanced chemical vapor deposition technique (PECVD). In chemical vapour decomposition (CVD) techniques, a source gas of material is brought near a surface where it reacts to form layer. The substrate surface is usually heated to activate the reaction. The source gas can either be caused by thermal decomposition (thermal CVD) or by a glow discharge to create a plasma. LPCVD is another chemical vapour deposition using pressure smaller than the atmospheric pressure [66]. Deposition rates with LPCVD are lower than with PECVD, but the lower pressure helps to avoid gas-phase reactions and improve the thickness uniformity and homogeneity of the deposited layer. LPCVD also implies that both side of the wafer will have a deposition layer.

The purpose of the silicon nitride is to give a protective layer for silicon against HF during anodization, as it is only slowly etched by the acid. In this work, PECVD was used instead of LPCVD because a good ohmic contact was required for the anodization step. A 420nm thick layer of silicon nitride (Si₃N₄) was deposited on wafers front side at 320°C during 20 minutes in the PECVD chamber of an

Oxford Plasmalab System 100. The deposition parameters are presented in Table 4.1. Then, an annealing was applied to the wafers in a horizontal oven at 900°C under N₂ atmosphere (flow of 1L/min) at least three hours. This last step allows to desorb hydrogen and obtain stoichiometric silicon nitride Si₃N₄.

Duration	SiH ₄ flux	NH ₃ flux	N ₂ flux	RF flux	Temperature	Pressure
20	500 sccm	10 sccm	750 sccm	30 W	320 °C	800 mTorr

Table 4.1: Parameters of a PECVD process for the deposition of 420nm thick silicon nitride layer in an Oxford Plasmalab System 100.

4.1.2 Photolithography

Once silicon nitride covers the wafer front, a photoresist is next coated on the wafer to perform photolithography. Photolithography consist in exposing specific areas of the resist with mostly UV light, in order to transfer patterns. In this work, a positive resist is applied on the front side. The AZ MIR701 thin resist is used to then pattern the silicon nitride underneath.

First, hexamethyl disilazane vapour (HDMS) is primed on the wafer, in order to render the surface hydrophobic, preventing moisture condensation. This step promotes the photoresist adhesion. Then photolithography is carried ou in two steps. First, the photoresist is applied on the front side using spin coating at 300 rpm with an acceleration of 600 rpm/s during 30 seconds. Next, the remaining solvent is evaporated with a bake at 90°C for 90 seconds. To avoid a non-uniform resist thickness a smooth surface water surface is required. This side is then exposed to I-line 365 nm UV lighth at 130mJ/cm² in split exposure (5 seconds mask on, 5 seconds mask off) with a Karl Süss MA6 equipment using the mask in Figure 4.2. and annealed during 90 seconds at 110°C. Finally, a bake at 120°C during 120 seconds is performed. Coating, baking and development are executed with a Karl Süss Gamma 80 coater.

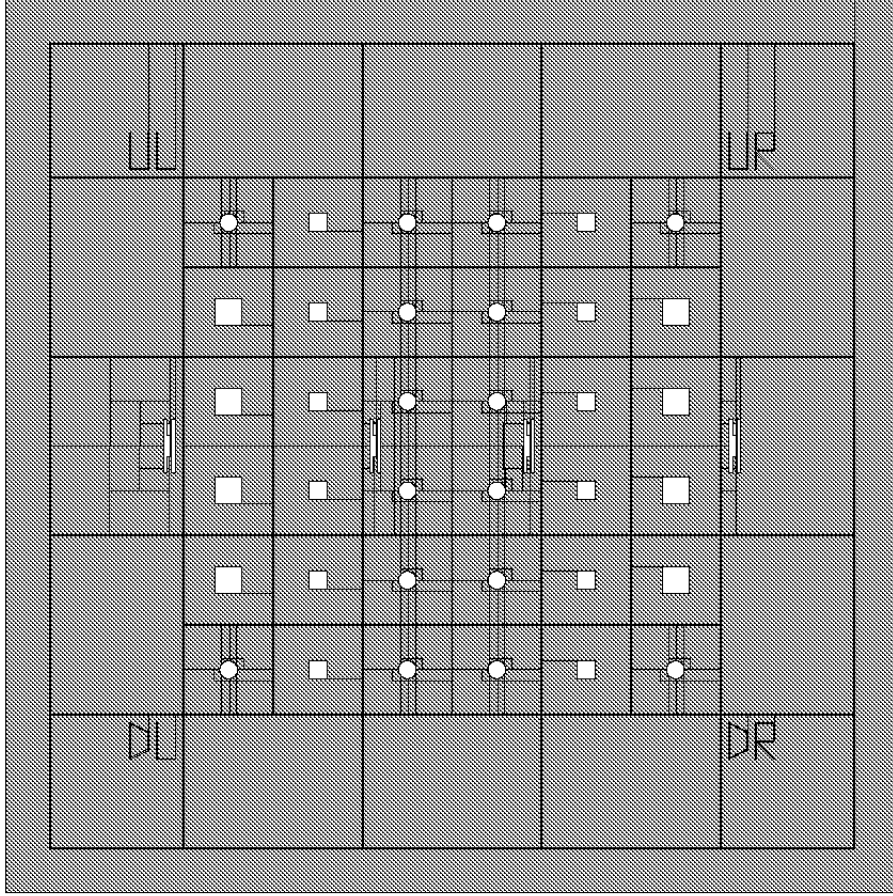


Figure 4.2: Mask used for photolithography used in this work. Large and small patterns (squares and circles) are 2 and 1 mm wide respectively.

4.1.3 Etch of silicon nitride and silicon bulk

In order to etch important depths of silicon, deep-reactive-ion plasma etching is used. Both the silicon nitride layer and the bulk silicon are etched to end up with a membrane approximatively $45\mu\text{m}$ thick. Thicker membranes are more stable, but then realisation of fine pores is much more difficult from a technical point of view with anodization [78].

The process consists of repetitive cycle composed of gas deposition and etch [66]. The first step is the gas deposition where CHF_3 is used to deposit a fluorocarbon polymer to act as a passivation layer on all surfaces. In the second step, a SF_6 plasma is created, which first remove the passivation layer on horizontal surfaces and then etch the exposed silicon, while the walls remain protected.

The origin of the plasma is a time-varying RF source, based on an ICP-RIE

(inductively coupled plasma) technology. A total of 225 cycles, performed in an Oxford ICP-RIE in batches of 50 cycles to allow the tool to cool down, are carried out in order to etch approximately $335\mu\text{m}$ of silicon. The parameters of the DRIE cycle used in this work are presented in Tables 4.2.

	Deposition	Etch
Duration	6s	13s
SF ₆ flux	1 sccm	10 sccm
CHF ₃ flux	159 sccm	1 sccm
RF power	10 W	30 W
ICP power	2000 W	1500 W
Temperature	-10°C	-10°C
Pressure	20 mTorr	20 mTorr

Table 4.2: Recipe used for DRIE experiments.

4.1.4 Electrochemical etching

The principle of porous silicon manufacturing has been described in Section 2.3. For the membrane fabrication, the electrochemical etching is carried out in a Teflon single-bath cell (Figure 4.3) with an HF.(49%):ethanol (3:1 v:v) electrolyte. The bottom part contains a piece of aluminium foil to ensure the electrical contact between the sample and the working electrode, while the opening in the top part of the cell is used for the counter-electrode in platinum immersed in the electrolyte. The sample is maintained with an O-ring in Viton® 2.4 mm wide and of 4.3 mm internal diameter, which also seals the cell. The opening is 0.145 cm^2 and the cell can contain 5 mL of electrolyte.

Before the etching step to produce the PSi, each sample was etched to produce a thin sacrificial layer which was then removed. Using the same electrolyte mentioned above, the sacrificial layer was produced with a current density of 200 mA/cm^2 during 30 seconds. After removing the electrolyte and rinsing with isopropanol (IPA) the cell, the sacrificial layer is removed by immersing the sample in a 2M KOH solution. The silicon is then rinsed with deionised water and IPA once the reaction with the KOH has occurred. Then, the anodisation of the silicon can start by pouring the electrolyte in the bath and applying a current density. Once the etch has ended, the electrolyte is removed from the cell which is rinsed with IPA and subsequently dried with N₂.



(a)



(b)

Figure 4.3: Teflon single-bath small cell used for electrochemical etching. Left : bottom part with aluminium contact. Right : top part with O-ring of 4.3 mm internal diameter and 2.4 mm wall width.

The electrode shape is shown in Figure 4.4. In order to have an uniform current density over the membrane surface, the electrode forms a circle shape. Since the anodization depends on the current density, a non-uniform current density leads to a non-uniform porosification over the membrane surface.



Figure 4.4: Shape of platinum counter-electrode used for electrochemical etching. The circle is around 2.3 mm.

The current density used in this work are presented in Table 4.3. For large thickness, during the anodization process, the reduction in HF concentration with depth becomes significant and leads to a porosity gradient and possible mechanical instabilities [66]. Thus, to reduce the effect of variation in HF concentration with depth, the principle of etch-stop was used. The current is stop during a short period of time to allow the HF electrolyte to diffuse inside the pore.

current density [mA/cm ²]	Etch step duration [s]	Stop step duration [s]	number of cycle	Surface
150	5	2	200	Al ₂ O ₃
100	7	2	250	SiO ₂

Table 4.3: Current densities used in this work. Etch and break steps durations are added.

4.1.5 Surface treatment: atomic layer deposition and oxidation

The purpose of this work was to analyse the use of PSi in a RED set-up for different surface treatments: SiO_2 , HfO_2 and Al_2O_3 .

Pore surface with HfO_2 and Al_2O_3 were obtained by atomic layer deposition. In this technique, sequential and self-limiting surface reactions involving usually two gas precursors are used to obtain highly conformal thin films with a thickness control to the Angstrom [66].

Thermal-ALD was used to coat PSi with Al_2O_3 at 100°C in a Fiji F200 ALD reactor from Veeco/CNT. The two precursors were water vapour and trimethylaluminium (TMA). In the first half cycle, a pulse of 0.3 second of TMA is sent. Then to give time for the first react precursors to a waiting time of 120 seconds is made and ends with a purge of 360 seconds to remove by-products and unadsorbed precursor. The second half cycle follows the same pattern for vapour and same duration time, excepted for the pulse which is 0.1 second. The full-cycle was repeated 75 times. For HfO_2 , the two precursors used were tetrakis(dimethylamido)hafnium (TDMAH) and water vapour. Excepted for a longer pulse of TDMAH of 0.5 seconds in the first half-cycle, the same parameters than for the Al_2O_3 ALD were used.

The last surface treatment made was SiO_2 . Silicon naturally reacts with the oxygen present in the air to form an oxide layer a few Angstrom [79], preventing for further oxidation of the silicon underneath. This layer can be further increased by a thermal oxidation. This was carried on in a MOS oven with a 1.8 L/min flux of O_2 and 0.5 L/min of N_2 , with a temperature ramping up $5^\circ/\text{min}$ to 300°C for one hour.

4.2 Techniques for the experimental characterization

In this section, the different measurements method that will be used to characterize the membrane performances/properties are described. Two characteristics are determined, the membrane resistance and the permselectivity. Two methods are described for the determination of the membrane resistance: DC measurement and impedance spectroscopy.

4.2.1 Membrane resistance: DC measurement

The resistance $[\Omega]$ or the area resistance $[\Omega\text{m}^2]$ of ion-exchange membranes can be determined by direct current (DC) measurements. In DC measurements, the membrane is placed in a test cell which consists of two compartments containing

the test solution separated by the membrane, as shown in Figure 4.5. Usually, four electrodes are used, one pair to apply an potential and the other pair to measure the voltage drop across the membrane, as shown in Figure 4.5. The first pair of electrodes is composed of a working electrode and a counter electrode, while the other pair is composed of two reference electrodes.

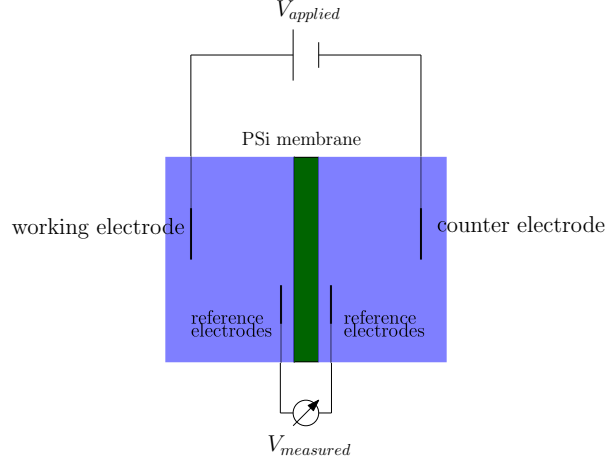


Figure 4.5: Schematic of the set-up for DC measurement.

The resistance can be obtained from the slope of the current-voltage curve. An estimation of the membrane resistance in a DC situation is obtained by subtracting the total resistance with and without the membrane. The total resistance is given by:

$$R_{m+s} = \frac{V_{measured}}{I}, \quad (4.1)$$

and the membrane resistance is

$$R_m = R_{m+s} - R_s. \quad (4.2)$$

Here R is the resistance, I the current and U is the voltage drop measured between the two reference electrode. Subscripts $m + s$, m and s refer to the membrane and the solution resistance, the membrane resistance and the solution resistance respectively.

In the evaluation of the membrane resistance with DC measurement, an important effect is actually neglected. When applying a DC electric field, a coupled mass and charge transport takes place through charge-selective membranes and an electrical current can be measured. Because of the difference in ion transport number between the solution phase and the membrane, an effect called concentration polarisation (CP) leads to the building up of diffusion boundary layers

(DBLs) at the membrane surface [45]. These layers typically have thicknesses in the micrometers range (e.g $300\mu\text{m}$)[45].

As shown in Figure 4.6, depletion and enrichment zone appear across the membrane, forming the diffusion boundary layers. The formation of diffusion boundary layers (DBLs) due to the passage of the ionic current impact the resistance of the solution near the membrane since in the depleted zone, ionic concentration is reduced. A consequence of this is the over-estimation of the membrane resistance, because the CP effect is removed when the measurement are taken without the membrane.

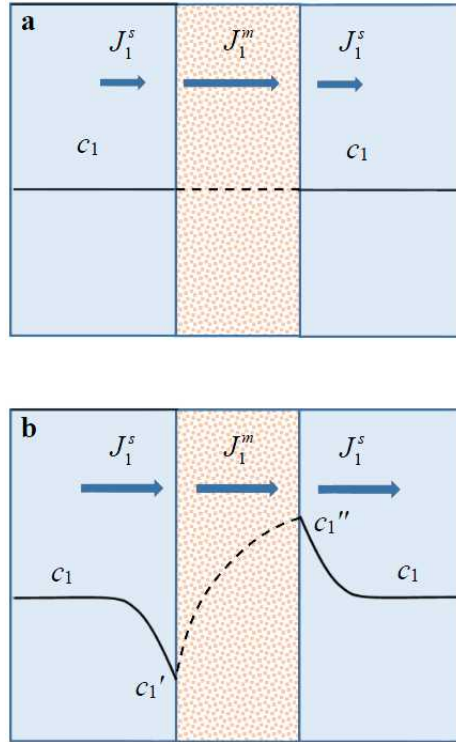


Figure 4.6: Fluxes and concentration profiles in a membrane and the surrounding solutions. In (a), a driving force is applied to a system initially at equilibrium: the flux of a selectively permeating species in the membrane, J_1^m , is higher than its flux in solution, J_1^s . Higher flux in the membrane causes decreasing concentration at the upstream membrane/solution interface, and increasing concentration at the downstream interface (b). Concentration gradients gives rise to diffusion transport, which increases the total flux in solution and decreases the flux in the membrane.

In steady state, $J_1^s = J_1^m$. Reproduced from [80].

As shown in Figure 4.7a, a decrease in the ionic concentration (ion-permselectivity of the membrane increases, cf. 2.2.3) and an increase of the applied field strength

(electrical current through the membrane increases) results to steeper concentration gradients in the CP zones (i.e. the two DBLs). An Ohm's law for the current-voltage behaviour is expected at sufficiently low field strengths (zone 1 in Fig. 4.7b). However, with increasing field strength, a maximum in the current density, known as the *limiting current density* in the classical description of CP, is reached (zone 2 in Fig. 4.7b). This is due to the concentrations of ions being reduced toward zero in the depleted CP zone. Note that the overlimiting region (zone 3 in Fig. 4.7b) cannot be explained with the classical description CP, but will not be detailed in this work. More information can be found in [45].

The CP effect is related to the formation of concentration gradients and affects the estimation of the membrane resistance. One way usually to limit this effect is by vigorous stirring because it will reduce the thickness of the depleted CP zone [81, 14]. In this case, the estimation of the membrane resistance depends on the stirring. In this work, stirring is not directly controlled, but a consequence of the feeding from the pump.

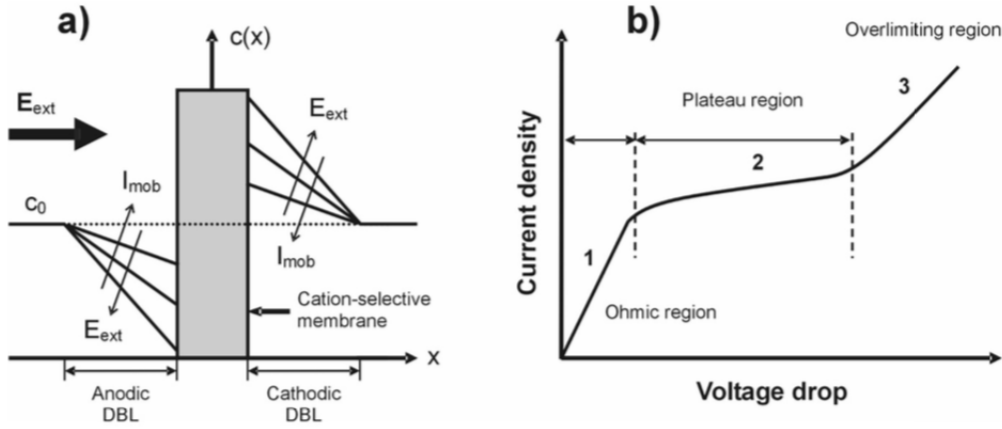


Figure 4.7: (a) Electrical field-induced E_{ext} concentration polarization (CP) at the interface between an ion-permselective, here CEM, and the adjacent solutions. I_{mob} is the mobile ionic strength and c_0 the bulk concentration of electrolyte. (b) Characteristic regions of the current-voltage curve for a CEM. Reproduced from [45].

4.2.2 Membrane resistance: impedance spectroscopy

In general, direct current method are used to measure cells or membranes resistance[82, 37, 83]. However, as it has been explain in the section below, the existence of double layer and the diffusion boundary layer add resistances that cannot be distinguished from the individual membrane resistance. Thus, another

method based on the frequency response of the system under an applied alternative current can be used in order to distinguish individual contributions of the different phenomena occurring at the membrane surface

It is a power-full technique for studying electrical properties of materials and can provide more information on the structural and functional characteristics of membrane systems. The basic principle of EIS is to apply a sinusoidal current or voltage on the system at a given frequency and to measure the voltage drop across the system as well. The impedance Z of the system at a given frequency can then be determined. An important aspect of EIS is the use of an equivalent electrical circuit to represent the electrochemical system under study (e.g. ion exchange membrane). Thus, an analytical expression for the impedance can be determined and by fitting of the experimental values obtained, distinct values for the membrane resistance are obtained. Consequently, a key step in EIS measurement is the determination of an equivalent electrical.

Different equivalent electrical circuit exist to model the electrical response of IEM and most of them has been studied for homogeneous polymer based IEM [82, 81, 84, 85, 86]. The most commonly is can be found in [82] and is described in the below.

When a membrane is placed in a salt solution, because of different effects (CP and EDL) appearing in the solution adjacent to the membrane, in addition to the pure membrane resistance R_M (Figure 4.8a), several resistances need to be taken into account. For homogeneous polymer based IEM, because of the fixed charges inside the membrane structure, opposite charges are attracted to the membrane and form a thin layer in the order of the nanometers (Debye length). This layer also exists for porous-IEM since the surface also charged itself when placed in a salt solution. This layer is represented in Figure 4.8b by a capacitor C in parallel with a resistor R_{DL} . The last layer modelled is the diffusion boundary layers (DBLs) resulting from the passage of the passage of a current through the membrane (Figure 4.8c). Classically, a capacitor leads to a phase shift of 90° which is independent of the frequency. However, for the DBLs, at each specific frequency, a difference phase shift is observed. This non-ideal responses cannot be represented with a pure capacitor, but instead it is represented with a constant phase element Q , which represents a non-ideal capacitor to obtain a better fit. The electrical equivalent circuit is represented in Figure 4.9a as well as a typical Nyquist diagram from the circuit in Figure 4.9b.

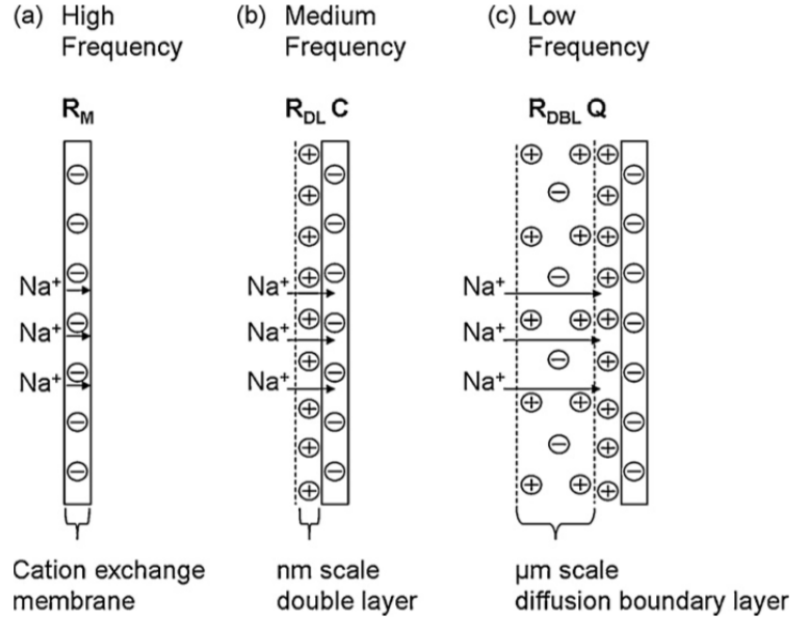


Figure 4.8: Phenomena occurring in the cation exchange membrane and in the layer adjacent to the membrane at different regime. R_M is the membrane resistance, R_{DL} or R_{EDL} is the resistance of the ionic transfer from the solution through the electric double layer into the membrane, C is the capacitance of the electric double charge layer, R_{DBL} is the diffusion boundary layer resistance and Q is the constant phase element representing a non-ideal capacitor of the diffusion boundary layer. Taken from [82].

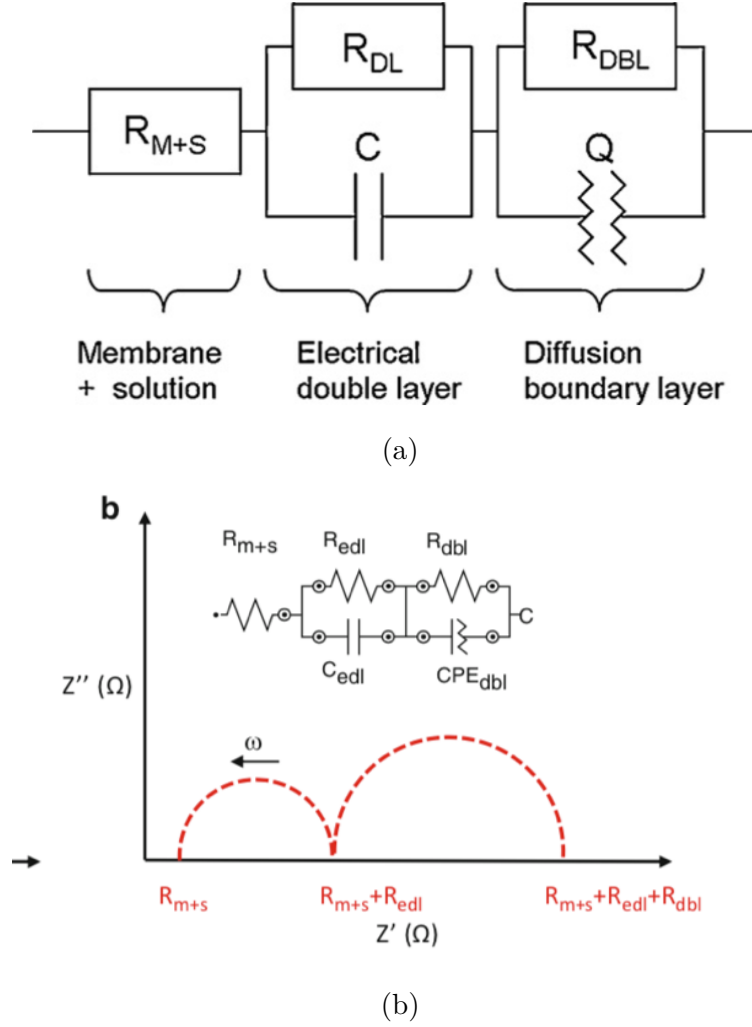


Figure 4.9: (a) Equivalent circuit modelling an IEM. The membrane and solution resistance (R_{M+S}) is represented by a resistor. The ionic transfer resistance through the electrical double layer R_{DL} and capacitance C can be represented by a resistor and a capacitor connected in parallel. The diffusion boundary layer resistance R_{DBL} and capacitance Q can be represented by a resistor and constant phase element connected in parallel. Taken from [82] (b) Typical Nyquist diagram for the electrical circuit presented in (a).

The equivalent electrical circuit can only be used with resistor and capacitor as long as the ohmic behaviour can be assumed. This imposes to be lower than the limiting current density. It is difficult to obtain a good estimation for the limiting current density as it depends on the many factor such as the stirring flow, distance between two IEMs, the concentration of the solution etc, and complex model can

only give an approximation of it [81].

An estimation is given in [85]:

$$i_{lim} = \frac{DFc_0}{(t_1^m - t_1)\delta}, \quad (4.3)$$

with the electrolyte diffusion coefficient $D = 2D_1D_2/(D_1 + D_2)$, F the Faraday constant, c_0 the electrolyte concentration, t_1^m the transference number in the membrane, t_1 the transference number in the solution and δ the thickness of the DBL. Subscript 1 indicates the first ionic species (e.g. Na^+) and subscript 2 the second ionic species (e.g. Cl^-). In cation exchange membrane, T_1^m is usually close to 1. In the solution, the transference number can be approximated by $t_i = D_i/(D_1 + D_2)$.

Assuming the BDL is on the order of the micrometer range ($\sim 170\mu\text{m}$) [85], $D_+ = 1.3e - 9 \text{ m}^2/\text{s}$ for Na^+ , $D_- = 2e - 9 \text{ m}^2/\text{s}$ for Cl^- , $T_1^m = 1$ and $c_0 = 0.01\text{M}$, the limiting current density $i_{lim} \sim 30 \text{ A/m}^2$ or $i_{lim} \sim 3 \text{ mA/cm}^2$, a value close to what is found in the literature [86].

4.2.3 Membrane permselectivity

The permselectivity α of a membrane is determined by the ratio of the flux of specific components to the total mass flux through the membrane under a given driving force [38]:

$$\alpha = \frac{t_{cou}^m - t_{cou}}{t_{co}}, \quad (4.4)$$

where t_i is the transference number of the ionic species i , subscript *cou* stands for counter-ion, *co* for co-ions and t_i^m indicate the transference number of species i inside the membrane. The transport number for the ionic species i is given in (3.11).

Two methods exists to evaluate the permselectivity of the membrane. The first one, the dynamic method, is based on the evaluated of the different ionic flux. For this, the increase and decrease of concentration across the membrane are measured as well as the amount of current passing through the membrane. With this method, the total flux of ions (electro-osmotic and osmotic) are taken into account and the 'true' permselectivity is obtained. This method, however, is affected by the concentration polarization and is rather time consuming.

The second method, the static method, is faster and more simple to effectuate. In the situation where a IEM separates two electrolyte solutions of different concentrations, the method is based on the measurement of the potential gradient across the membrane.

For a completely permselective membrane, the potential across the membrane is given by the difference in the Donnan potential:

$$\varphi_{m,cp} = \varphi_{Don,1} - \varphi_{Don,2}, \quad (4.5)$$

where φ is the potential, subscript 1 and 2 refer to the different solutions across the membrane, m for the membrane and cp to completely permselective. Assuming several approximations, such as negligible osmotic flow between the two solutions small concentration gradients across the membrane phase, valence charge equal to 1, etc. [38], base on (2.5), the membrane potential $\varphi_{m,cp}$ then is given by

$$\varphi_{m,cp} = \frac{RT}{|z_i| F} \ln \frac{a_{s,1}}{a_{s,2}} \quad (4.6)$$

If the membrane is not completely permselective, some co-ions can permeate the membrane. Because counter-ions permeate more easily in the membrane, for each co-ion going able to permeate the membrane, a larger quantity of counter-ions have already permeated the membrane. An imbalanced in charge build-up and create a potential across the membrane, called the diffusion potential φ_{diff} . The membrane is then given by

$$\varphi_m = \varphi_{diff} + \varphi_{Don,1} - \varphi_{Don,2}. \quad (4.7)$$

Based on the same approximations as for the completely permselective membrane, the membrane can be expressed by

$$\varphi_m = (t_{cou}^m - t_{co}^m) \frac{RT}{|z_i| F} \ln \frac{a_{s,1}}{a_{s,2}} = (2t_{cou}^m - 1) \frac{RT}{|z_i| F} \ln \frac{a_{s,1}}{a_{s,2}} \quad (4.8)$$

As it can be seen in the expression for φ_m , the transference number y_i appears. Thus, by rearranging the different terms, the membrane permselectivity can be expressed as

$$\alpha = \frac{\frac{\varphi_m}{\varphi_{m,cp}} + 1 - 2t_{cou}}{2t_{co}}. \quad (4.9)$$

The transport number number in the solution can be approximated with

$$t_i \simeq \frac{D_i}{\sum_j D_j}, \quad (4.10)$$

with D_i the diffusion coefficient of the ionic species i . For example, for KCl, $D_{K^+} = 1.957 \times 10^{-9} \text{ m}^2/\text{s}$ and $D_{Cl^-} = 2.032 \times 10^{-9} \text{ m}^2/\text{s}$ so that $t_{cou} \simeq t_{co} \simeq 0.5$ and the permselectivity is then given by

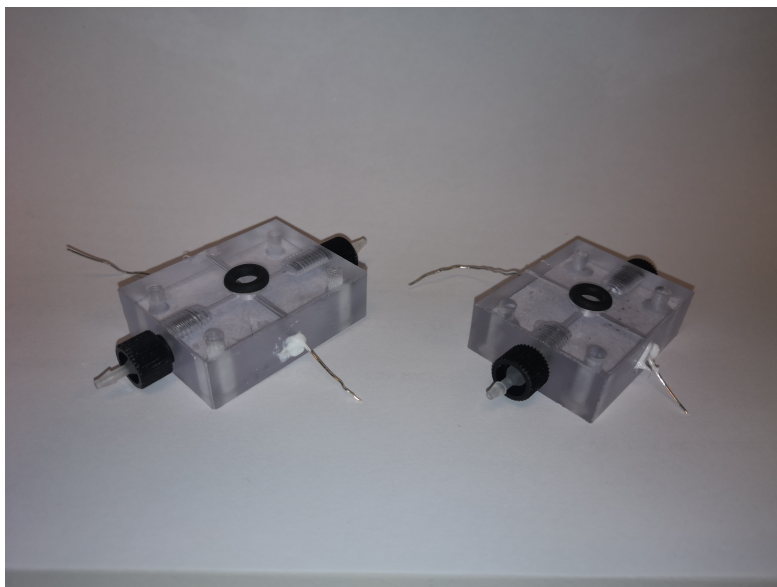
$$\alpha \simeq \frac{\varphi_m}{\varphi_{m,cp}}. \quad (4.11)$$

For a membrane separated with concentration of 0.5 and 1 mol/L of KCl, at 25°C, $\varphi_{m,cp} = 0.0158\text{V}$ [38].

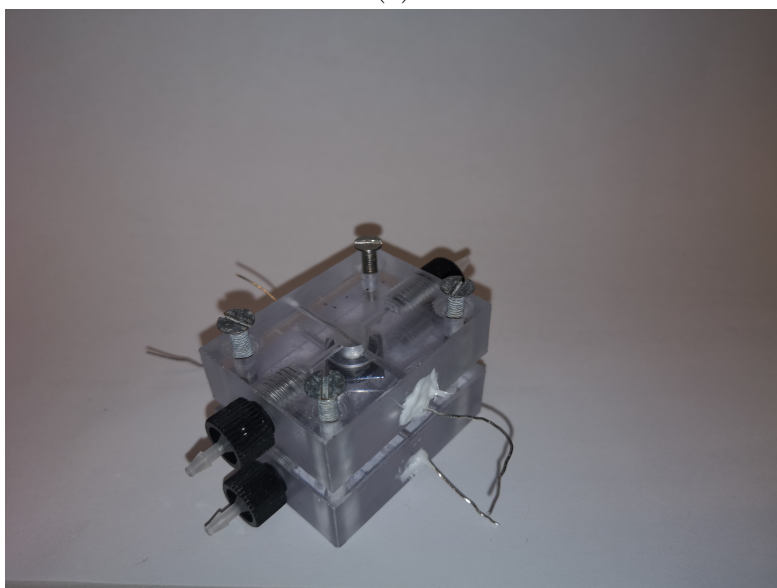
Consequently, by measuring the membrane potential φ_m , the membrane permselectivity can be evaluated. The set-up used is the same as in Figure 4.5. Note that the static method only give an apparent permselectivity which is higher than the real permselectivity because osmotic and electroosmotic flows are neglected [38]. However, issues linked to concentration polarization effects are avoided.

4.3 Experimental set-up

For the different measurements, a fluidic cell has been tailor made. It is shown in Figure 4.10. It consists of two chambers filled with water of different salt concentrations and separated by the porous Silicon IEM. The two chambers are held together by four screws. Two O-rings are placed across the membrane to lock it and avoid any water leakage. Two small holes are used for the electrodes, and two others small holes are used for the reference electrodes. Each chamber can be fed with external solutions reservoirs by using an external pump. The



(a)



(b)

Figure 4.10: Fluidic cell used in this work to performed the different experimental measurements.

In this work, the electrolyte is pure NaCl dissolved in deionized water (DI water). The external pump is a Gibson©minipuls 3 peristaltic pump. The pair of working/counter electrode are made of Ag/AgCl and the other pair is also made of Ag/AgCl. The choice of the electrode is explained below. the full set-up is shown

in Figure 4.11.

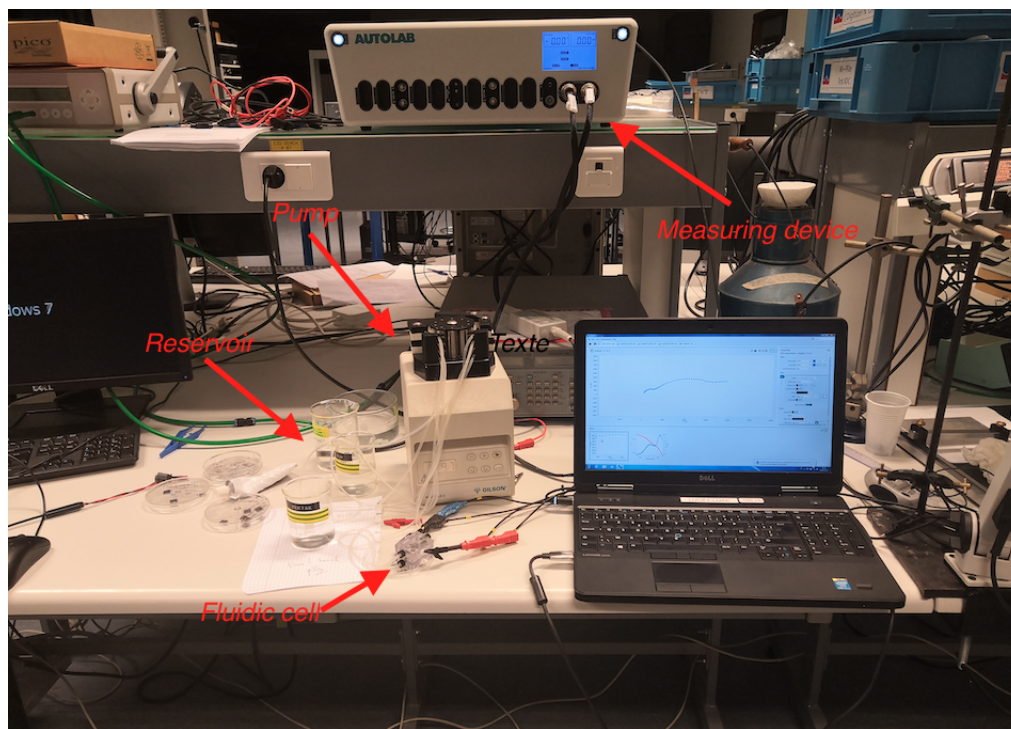


Figure 4.11: Experimental set-up used in this work.

4.3.1 Choice of the electrodes

Because the current is transported by ions inside the cell, redox reactions are required to transform this ionic current in a electron current. The choice of the electrodes system (ES) is a key component and determined the type of electrochemical reactions taking placed inside the cell [20], but others aspects are important for it operation: reversibility, energy consumption, etc.

At least four parts constitute the electrode system : (i) electrodes, (ii) anolyte and catholyte, (iii) outer membranes and (iv) recirculation system for the electrode rinse solution. Figure 4.12 show an example of a RED stack with only one cell. In principle, an 'ionic' short-circuit of the RED stack can be caused by the recirculation system of the electrode rinse solution. However, this can be reduced/neglected provided that the internal resistance of the stack is much lower than the resistance of this recirculation system. This can be achieved by applying relatively long tubes to the recirculating system[20].

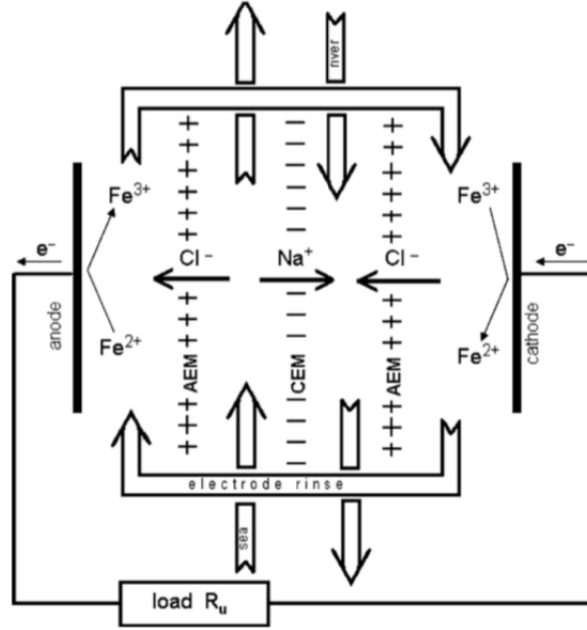


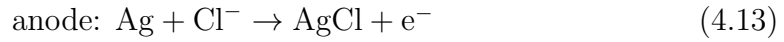
Figure 4.12: Electrode system equipped with inert electrodes with a reversible redox couple containing $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions in a NaCl-HCl supporting electrolyte. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is kept constant by recirculation the combined anolyte and catholyte through the electrode compartments. Taken from [20].

Two groups can be used to classify the electrode systems: with or without opposite electrode reactions [20]. First, for systems with opposite electrode reactions, no net chemical reaction is present and have a zero equilibrium voltage. Consequently, there is no energy consumption from the electrode system and only a few cells in the RED are required to generate electrical energy with such an electrode system. In addition, there is no gas production and no loss of chemicals due to the recirculating electrode rinse. Depending on the redox processes taking place, the electrodes can either play active role or be inert. With active electrodes, one electrode is dissolving and the other is growing. In order to increase the electrode system lifetime and avoid to mechanically perform the periodical interchange of anode and cathode, the direction of the electrical current, and so the redox processes, should be inverted periodically. With inert electrodes, these drawbacks are avoided because of the homogeneous redox couple (e.g. Figure 4.12) taking place.

Second, the system without opposite electrodes reactions are the systems with gas generation. These reactions lead to a loss of energy, production of electricity is only possible if a significant number of cells is used to overcome the cell equilibrium voltage. This can be solved on a laboratory scale by using a small number of cells together with an external power supply[20].

In this work, the electrolyte is dissolved NaCl. Due to the constraints of the experimental set-up, the cathode and anode cannot be separated by outer-membranes. Consequently, only electrodes with redox reactions taking place in the NaCl electrolyte solution are possible for the power generation. As only two closed chamber are used in the set-up (see Figure 4.10), gas production from redox reaction cannot be used otherwise formation of bubbles inside the chambers would start and compromise the experiment. Thus, the second type of electrodes reactions mentioned above cannot be used.

Consequently, a pair of Ag/AgCl active electrodes with opposite reactions are chosen in this work. The half reaction are given by



This electrodes are fabricated at WINFAB cleanroom using the preparation in [87]. An electroplating on a pure silver wire of silver chloride is made. For this, a current density of 10 mA/cm² through the silver wire inside a 0.1M HCL bath is made with a platinum as the cathode is made. During the electrolysis a black deposit is formed on the silver as shown in Figure 4.13. The electrode is kept in tube compartment filled with 1 M KCl.

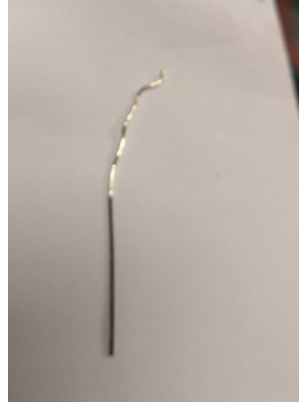


Figure 4.13: Ag/AgCl electrode obtained by electroplating. The black deposit is composed of AgCl.

4.3.2 Measuring devices

In order to make the measurement, two measuring devices are used. The first is a 4156C Precision Semiconductor Parameter Analyzer, a highly accurate laboratory bench top solution for advanced device characterization. This device allows to measure very low electrical current with a high precision (lowest resolution

to 1 femtoamp) as well as low voltage (lowest resolution: 0.2 microvolt). The basic principles of the measurement are based on the electrical circuit, called a source/monitor units (SMU), represented in Figure 4.14. To measure a current, the SMU un applies a potential difference over the device to analyse and the current going through the ammeter, in series with the voltage source, is measured. For a voltage measurement, a current is applied and a voltmeter in parallel to the current source measure the voltage drop. Thus, a SMU performs a two point measurement and only two electrodes are used. Membrane potential and IV measurement can be made both on this device.

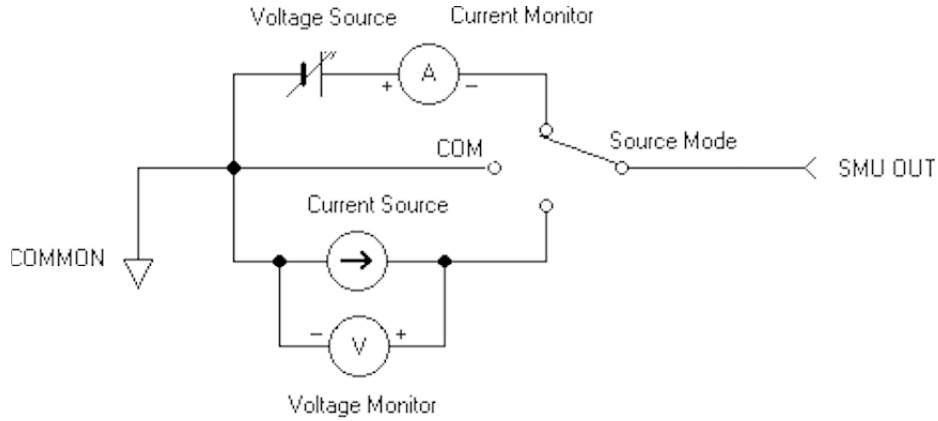


Figure 4.14: Diagram of a simplified electrical circuit for a source/monitor units.

The second device is a metrohm©potentiostat/galvanostat. This device is usually used in the electrochemical industry such as for the characterization of Li-ion battery [88]. It will be used for the electrochemical impedance spectroscopy measurement.

Chapter 5

Experimental results

In this chapter, the experimental results for the PSi membranes as IEM in a RED system are presented. First, the membrane characteristic are detailed. Then the experimental results are discussed. Finally, future works are proposed to improve the performance of the PSi membranes as IEM for RED applications.

5.1 Membranes characteristics

A PSi membrane is shown in Figure 5.1. In order to determine the geometrical properties of the membranes, SEM images of the surface of the PSi have been obtained. SEM images of a membrane surface with SiO_2 are shown in Figure 5.2 and with an ALD of Al_2O_3 in Figure 5.3. Unfortunately, no PSi membranes with an ALD of HfO_2 has been tested.

The pore density as well as the pore diameter are computed on average using image processing methods based on the SEM image of the membrane. The characteristics for the the two membranes in Figure 5.2 and 5.3 are detailed in Table 5.1. Note that these values are dependant on the image processing method (e.g. ability to discriminate between the inside of the pore (black) and the wall of the pore (white) and might vary more than expected. Nevertheless, it can be seen that the pore diameter is on the order of tens of nanometer, which is required for obtaining ion-selective properties in water.

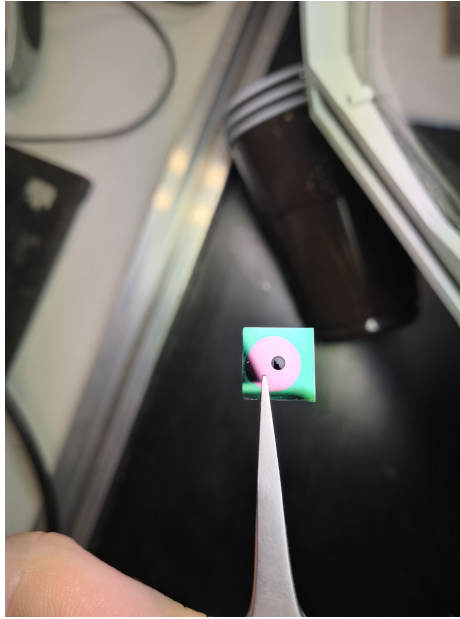
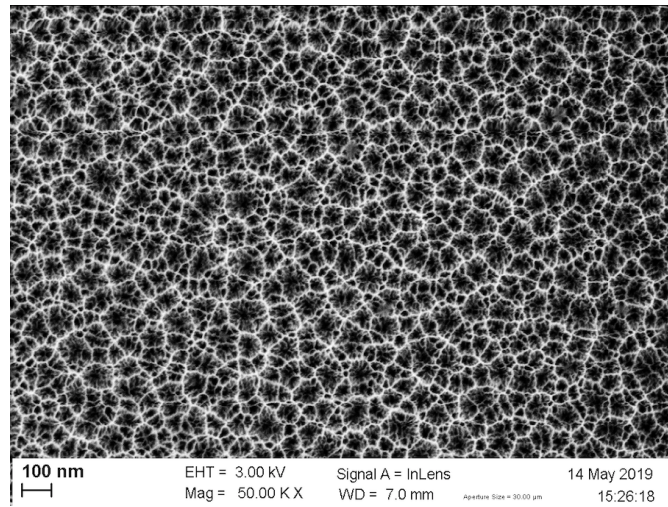


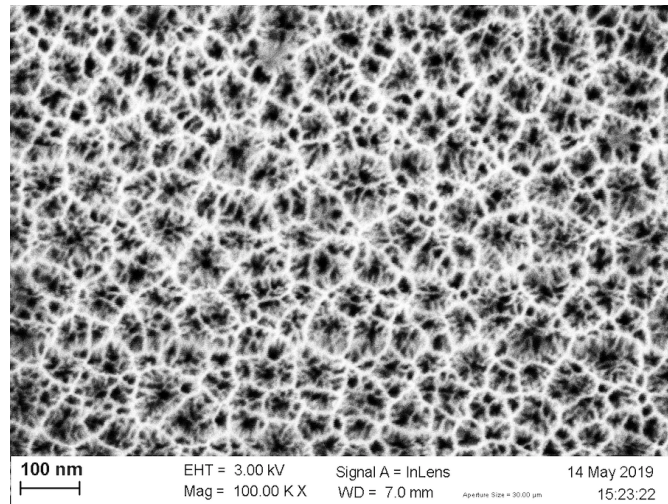
Figure 5.1: PSi membrane obtained in the Winfab cleanroom. The black disk is the membrane, with a diameter of 1mm.

Surface treatment	Pore density [pores/ μm^2]	pore size [nm]	Thickness [μm]	Figure
SiO_2	~ 500	$12 \pm 5 \text{ nm}$	45	5.2
Al_2O_3	~ 300	$15 \pm 8 \text{ nm}$	45	5.3

Table 5.1: Characteristics of the membrane studied in this work.

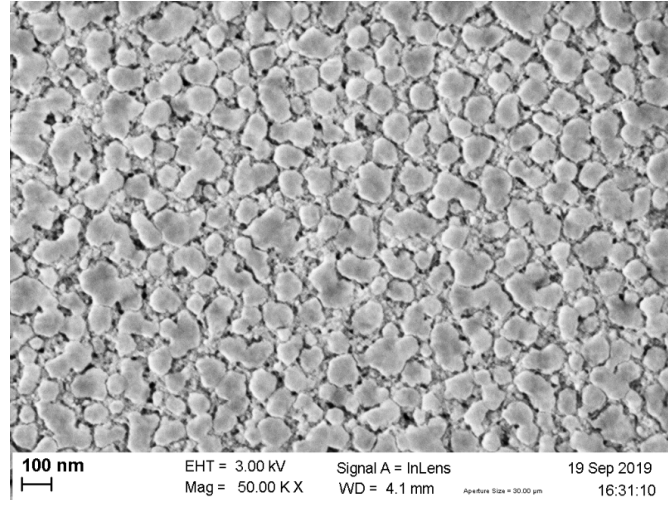


(a)

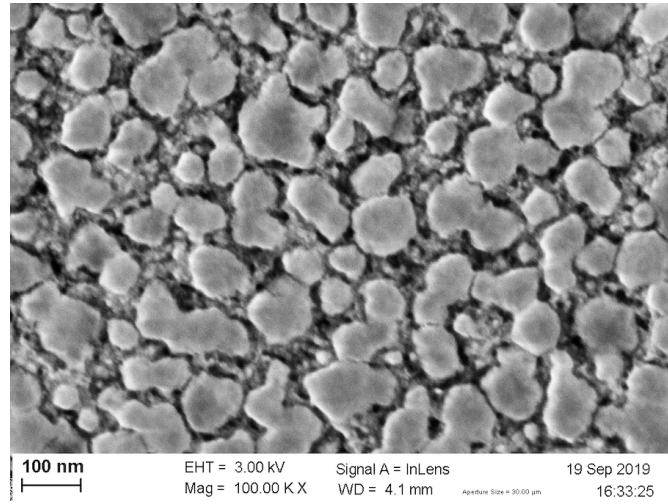


(b)

Figure 5.2: SEM images of a PSi after a thermal oxidation to obtain SiO_2 .



(a)



(b)

Figure 5.3: SEM images of a PSi after an ALD of Al_2O_3 .

5.2 IV curve and open-circuit voltage measurements

For the IV curve, the system applied a potential across the membrane and the resulting current is measured. Since the cell is electrically closed with electrode with redox reaction, an unequal voltage drops in different electrolyte concentrations

at the electrode must be considered, with expression given by

$$E_{redox} = \frac{RT}{zF} \ln \left(\frac{\gamma_H C_H}{\gamma_L C_L} \right), \quad (5.1)$$

and the electrical circuit can be represented as in Figure 5.4. The potential across the membrane V_{cell} is then given by

$$V_{cell} = V_{app} - E_{redox} = E_{OCV} - R_{cell}I_{cell}. \quad (5.2)$$

Thus, we need to subtract the voltage drop of the electrode to the applied voltage otherwise we would overestimate the membrane across the cell. The values for E_{redox} for the the different concentration use in this work are presented in Table 5.2.

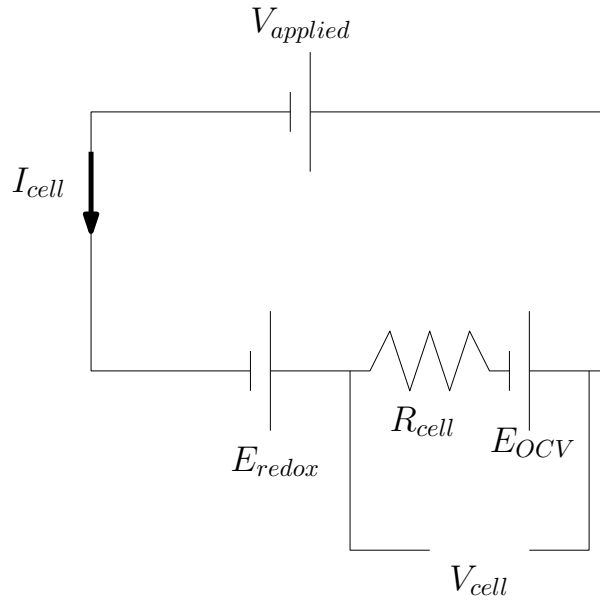


Figure 5.4: Equivalent electrical circuit of the fluidic cell under an applied potential. $V_{applied}$ is the applied potential from the source metre, E_{redox} represents the unequal voltage drop across the electrode system, E_{OCV} represents the potential across the membrane, R_{cell} represents the electrical resistance of the membrane and the solution and V_{cell} is the voltage across the fluidic cell.

C_H/C_L [M]	γ_H [-]	γ_L [-]	E_{redox} [mV]
0.1/0.01	0.748	0.907	54.5
0.01/0.001	0.907	0.962	58.0
1/0.01	0.6507	0.907	110.5

Table 5.2: Voltage drop for the electrode for different concentrations. Values for the activities from [89, 90].

For the open circuit voltage, the measure was repeated over time at given steps until a stable values was obtained. The total time of measurement was 90 seconds, with a total of 20 steps.

5.2.1 PSi with SiO₂

Membrane 1

Unfortunately for the first membrane, measurement could only be performed once because the membrane broke during the manipulation. The mean value for the open circuit voltage measured without any applied voltage is $E_{OCV} = 13.9\text{mV}$ and the standard deviation is 0.16 mV. The experimental data for the IV curve are shown in Figure 5.5. A linear regression is also shown. The slope of the linear regression give $-1/R_{cell}$, and $V_{cell} = E_{OCV}$ for $I_{cell} = 0$. The corresponding values are listed in Table 5.3. Nota that R_{cell} is the resistance of the membrane and the solution.

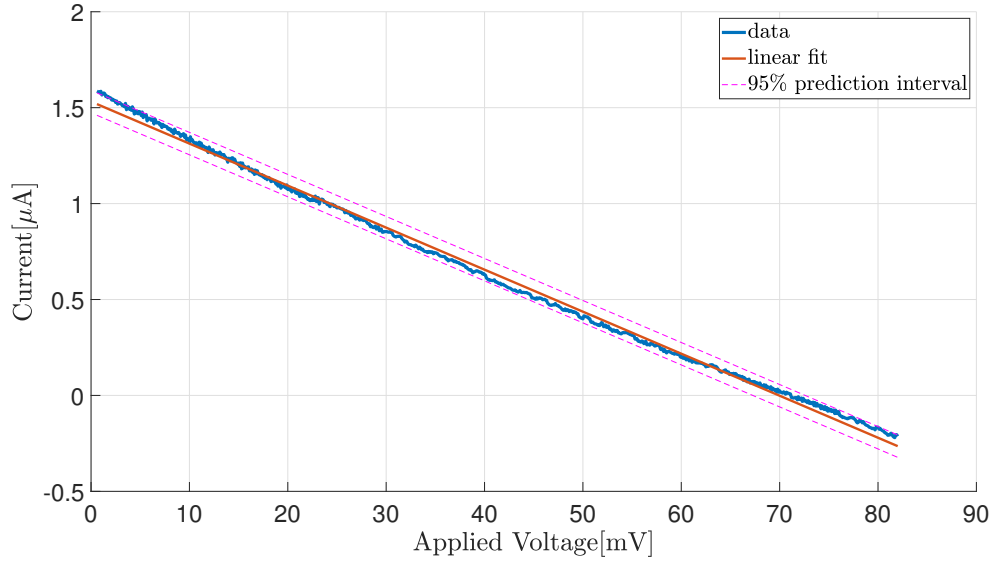


Figure 5.5: PSi membrane with SiO_2 separated by two solutions of $C_H = 0.1\text{M}$ and $C_L = 0.01\text{M}$.

Area[mm ²]	$R_{cell}[\Omega]$	$R_a[\Omega\text{cm}^2]$	$E_{OCV}[\text{mV}]$	t_+	α
4	4.56e4	1.82e3	15.2	0.6387	0.2774

Table 5.3: Properties of the membrane for $C_H = 0.1\text{M}$ and $C_L = 0.01\text{M}$. R_a is the area resistance of the membrane, E_{OCV} the output circuit voltage, t_+ the positive transference number and α the permselectivity. Results from the linear regression.

As it can be seen in Table 5.3, the membrane has a positive transference number t_+ greater than 0.5, meaning the majority carrier are cations, which was expected because we were using SiO_2 which has a negative surface charge density. However, its permselectivity is rather low compare to polymer membranes in Table 2.1.

Based on the values above, the maximal power that can be generated using this membrane can be computed

$$P_{max} = \frac{E_{OCV}^2}{4R_{cell}}, \quad (5.3)$$

which gives a maximal power of 1.2 nW and a power density of 0.32 mW/m² for a membrane of 4 mm².

Membrane 2

The mean value for the open circuit voltage measured without any applied voltage

is $E_{OCV} = 23.4\text{mV}$ and the standard deviation is 0.349 mV . The experimental data for the IV curve are shown in Figure 5.6. A linear regression is also shown and the membrane characteristic listed in Table 5.4.

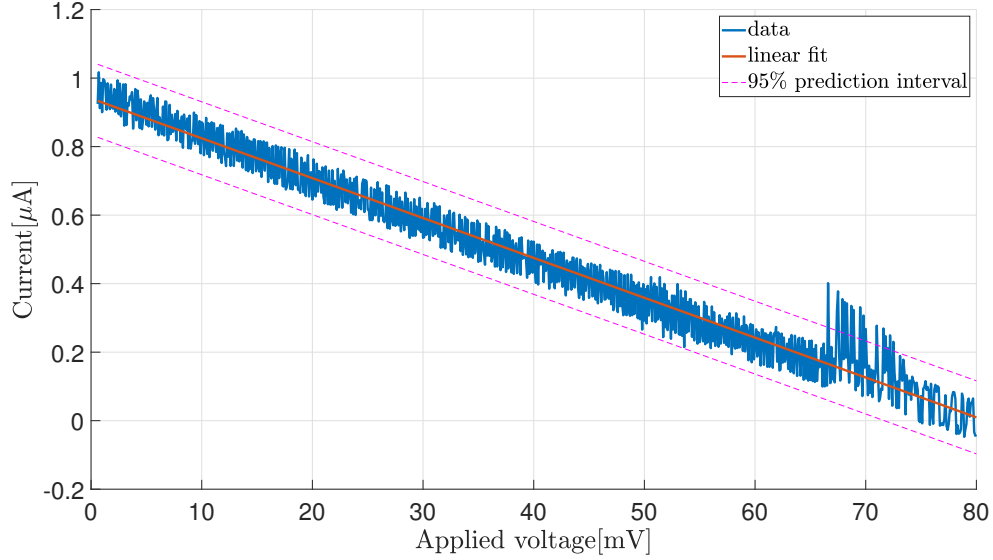


Figure 5.6: PSi membrane with SiO_2 separated by two solutions of $C_H = 0.1\text{M}$ and $C_L = 0.01\text{M}$.

Area[mm ²]	$R_{cell}[\Omega]$	$R_a[\Omega\text{cm}^2]$	$E_{OCV}[\text{mV}]$	t_+	α
pi/4	8.5925e4	674.85	26.1	0.7382	0.5664

Table 5.4: Properties of the membrane for $C_H = 0.1\text{M}$ and $C_L = 0.01\text{M}$. R_a is the area resistance of the membrane, E_{OCV} the output circuit voltage, t_+ the positive transference number and α the permselectivity. Results from the linear regression.

Based on the values above, the maximal power that can be generated using this membrane can be computed, which gives a maximal power of 1.98 nW and a power density of 2.5 mW/m^2 for a membrane of $\text{pi}/4\text{ mm}^2$.

Experimental results for different concentrations have been performed. As it can be seen in Figure 5.7, the same conclusion as in the one made for the numerical simulations can be made 3.4.4. As the high concentration is increased, the number of carrier in the nano-pore also increases, resulting in a higher current for the same applied voltage.

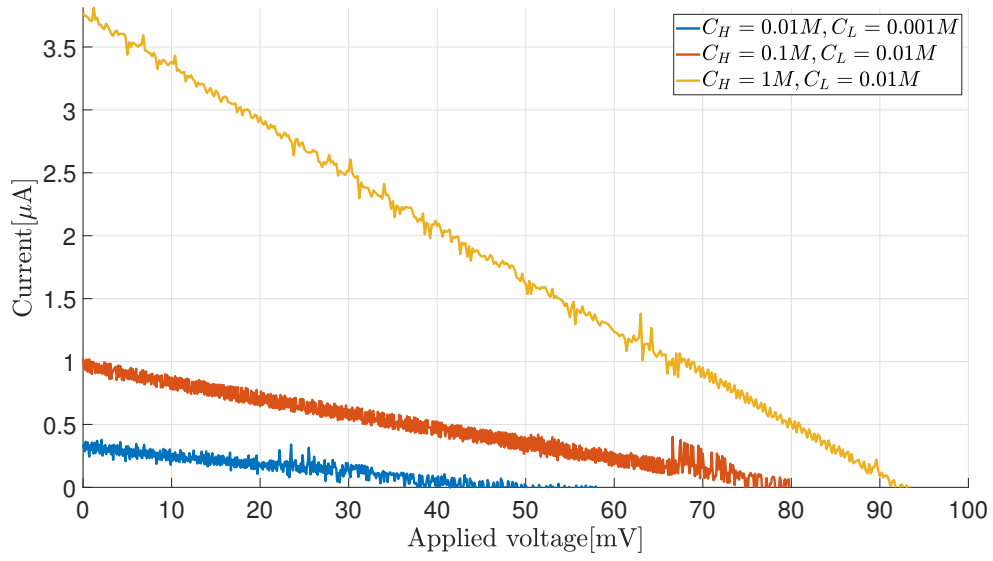


Figure 5.7: PSi membrane with SiO_2 separated by two solutions of various concentrations.

Membrane 3

The experimental data for the IV curve are shown in Figure 5.8. A linear regression is also shown and the membrane characteristic listed in Table 5.5.

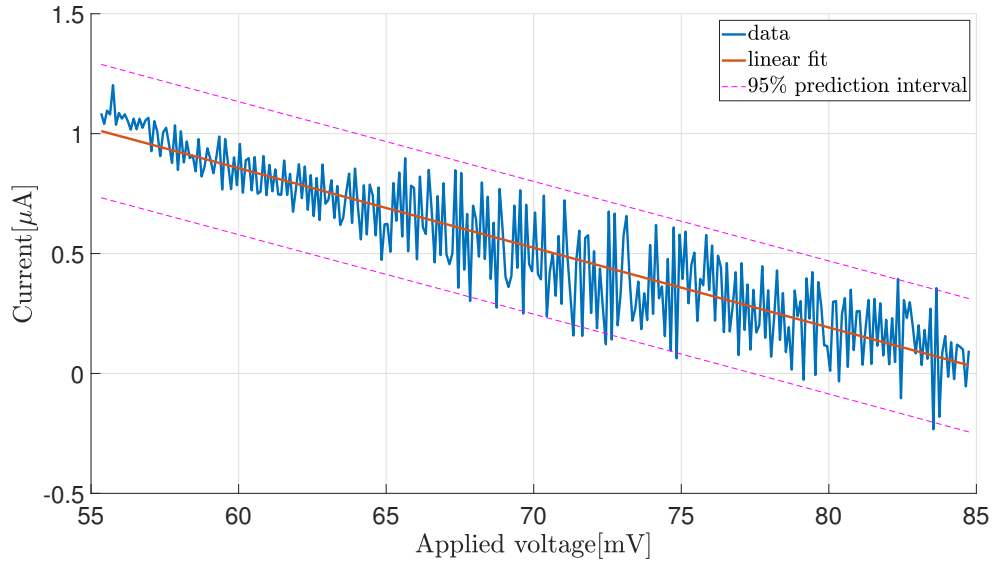


Figure 5.8: PSi membrane with SiO_2 separated by two solutions of $C_H = 0.1\text{M}$ and $C_L = 0.01\text{M}$.

Area[mm ²]	$R_{cell}[\Omega]$	$R_a[\Omega\text{cm}^2]$	$E_{OCV}[\text{mV}]$	t_+	α
pi/4	8.5925e4	674.85	31	0.7834	0.6412

Table 5.5: Properties of the membrane for $C_H = 0.1\text{M}$ and $C_L = 0.01\text{M}$. R_a is the area resistance of the membrane, E_{OCV} the output circuit voltage, t_+ the positive transference number and α the permselectivity. Results from the linear regression.

Based on the values above, the maximal power that can be generated using this membrane can be computed, which gives a maximal power of 7.99 nW and a power density of 10.2 mW/m² for a membrane of pi/4 mm².

5.2.2 PSi with Al_2O_3

When the PSi membranes with an ALD of Al_2O_3 have been tested, no linear behaviour was recovered and the current was oscillation around zero as shown in Figure 5.9. This indicates that no net flux ionic flux is going through the membrane. These oscillations correspond to noise, mostly thermal noise and electrochemical noise [91, 92, 93]. Electrochemical noise for Ag/AgCl electrode in electrolyte such as NaCl can have a noise level up to a few mV [94]. The electrochemical noise is usually described by stochastic pulses of current generated by sudden film rupture, crack propagation, discrete events involving metal dissolution, etc. [94]. The

electrochemical noise in our can be important considering that the electrode have been home made.

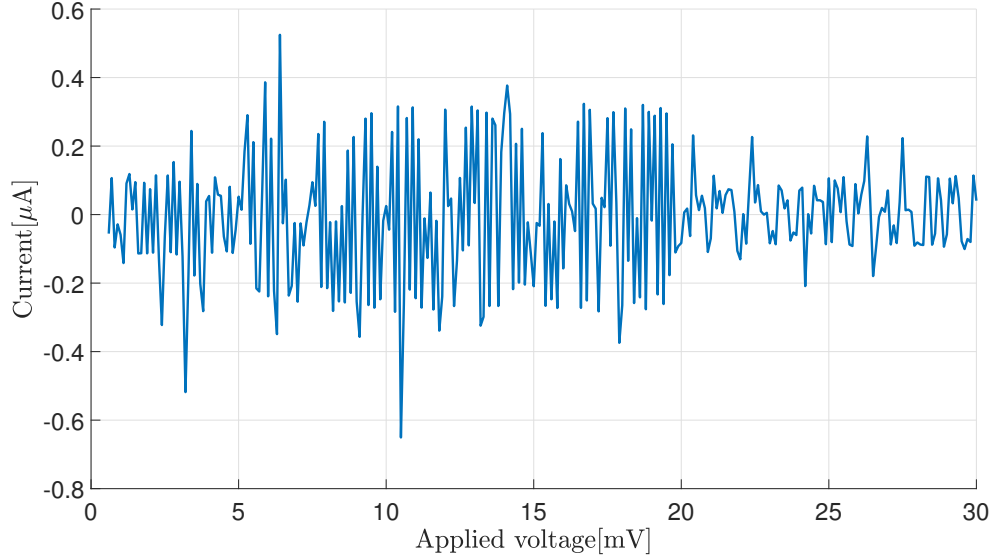


Figure 5.9: PSi membrane with Al_2O_3 separated by two solutions of $C_H = 0.1\text{M}$ and $C_L = 0.01\text{M}$.

The reason why there is no current through the membrane can be due two effects. First, during the manufacturing process, the removal of the sacrificial layer has not been complete. As shown in Figure 5.10, when no sacrificial is etched before the bulk etching, a thin layer recovered pore more open, more round and with thinner walls underneath. Thus, if an ALD is made on the samples, the pore of the thin layer will be rapidly blocked.

The second effects is due to the ALD step. If at some level inside the membrane thickness the pore size is reduced, an ALD would further reduce the pore size and in the worst case block it. Because of the thickness of the membrane used in this work, it is more complex to obtain a uniform pore size along the thickness of the PSi, and thus the ALD can be dramatic.

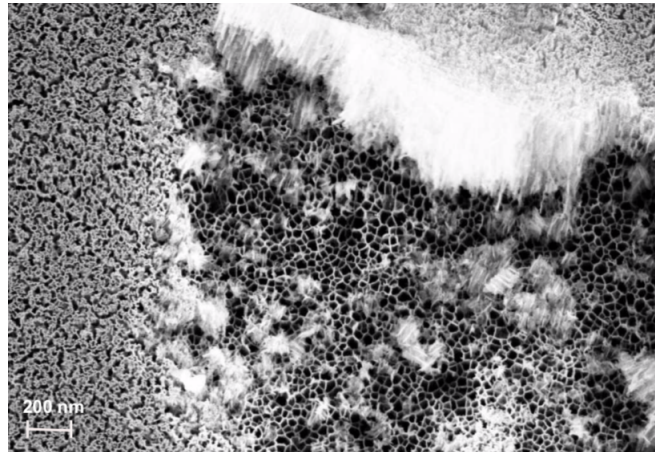
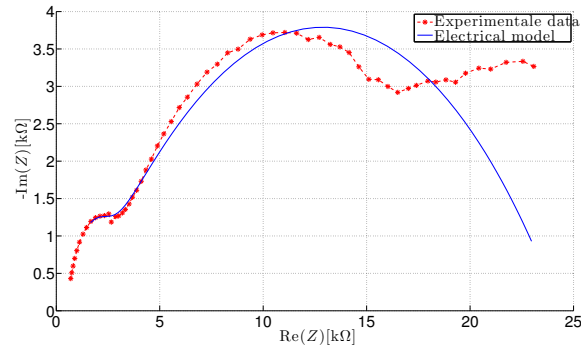


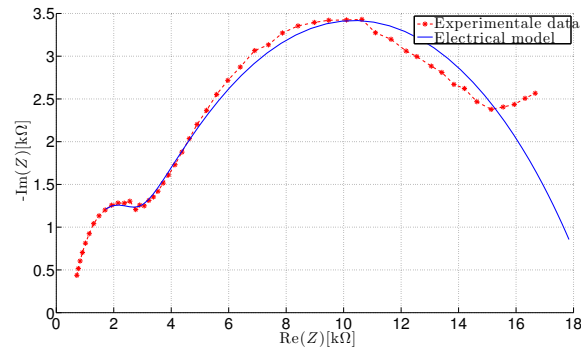
Figure 5.10: Top view SEM image of a PSi single layer etched at 150 mA/cm². A thin layer is peeled off, so that the pores below are visible. Taken from [66].

5.3 Electrochemical spectroscopy impedance measurements

5.3.1 PSi with SiO₂, membrane 2



(a)



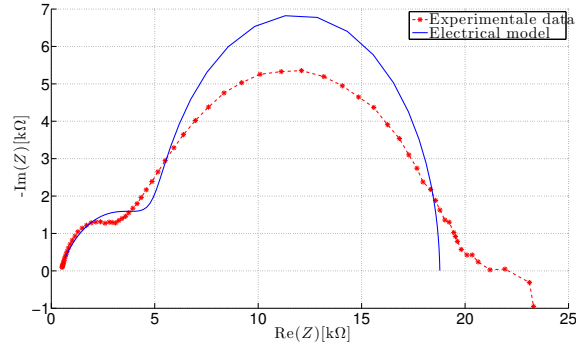
(b)

Figure 5.11: Electrochemical impedance spectroscopy in galvanostatic mode with a DC current density $I_{DC} = 5e - 5A/m^2$, an AC signal with $I_{rms} = 5e - 51/m^2$ and $C_H = C_L = 0.1M$. (a) First run and (b) second run after a full recycling of the solution.

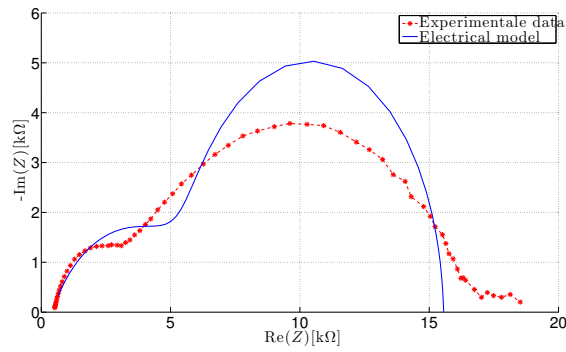
Following the convention in Figure 4.9, the fitted values from the Autolab program are given in Table 5.6.

run	R_{m+s}	R_{edl}	R_{dbl}	C_{edl}	CPE_{edl}
1	269 Ω	1.17 k Ω	22.9 k Ω	919 nF	55.8 $\mu\Omega$, n=0.404
2	696 Ω	1.46 k Ω	16.9 k Ω	696 nF	46.1 $\mu\Omega$, n=0.489

Table 5.6



(a)



(b)

Figure 5.12: Electrochemical impedance spectroscopy in galvanostatic mode with a DC current density $I_{DC} = 1e - 6 \text{ A/m}^2$, an AC signal with $I_{rms} = 5e - 51/\text{m}^2$ and $C_H = C_L = 0.1\text{M}$. (a) First run and (b) second run after a full recycling of the solution.

run	R_{m+s}	R_{edl}	R_{dbl}	C_{edl}	CPE_{edl}
1	431 Ω	13.3 k Ω	5.05 k Ω	33.2 μF	5.44 $\mu\Omega, n=0.657$
2	413 Ω	9.47 k Ω	5.68 k Ω	42.7 μF	6.57 $\mu\Omega, n=0.636$

Table 5.7: Properties of the membrane for $C_H = 0.1\text{M}$ and $C_L = 0.01\text{M}$. R_a is the area resistance of the membrane, E_{OCV} the output circuit voltage, t_+ the positive transference number and α the permselectivity. Results from the linear regression.

5.4 Future works for improvement of PSi as IEM

5.4.1 Homogeneity of the porous layer

It has been observed that the membrane were not fully porosified on some region of the membrane surface. This has a negative impact on its properties, such as its surface resistance which is higher than what we would have with a fully porosified membrane. Two effects can explain this observation.

The first effect that can explain the observation is the non-uniform current density resulting from the position and shape of the electrode [66]. As it has been explained in 2.3.2, the current density influence the growth rate and the pore size. Consequently, a non-uniform current density will lead to a gradient in the porosity, as shown in Figure 5.13. The electrode used in this work has already a shape that limit the gradient in the current density, but improvement can still be made.

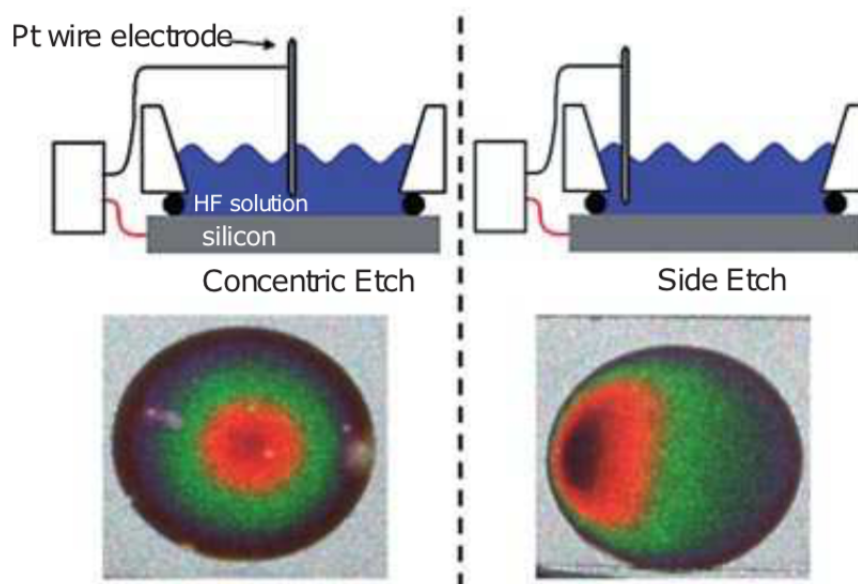


Figure 5.13: Schematics and photographs of two counter-electrode configurations and the resulting samples. On the left, the platinum wire electrode is centered while the electrode is closer to the edge, on the right. The colour gradient reflects the porosity of the PSi.

The second effect, which is often a consequence of the first one, is that once the first pore has been released on both side of the membrane, the porosification of the other pores decreases. During the electrochemical etching, the current is transported by ions. When no pore is opened on both side of the membrane, the

electrolyte is forced to react with the silicon. However, once the first pore has been opened, a path of low resistance is now there for the ions. Similarly to resistors in parallel, the ions will choose preferentially the path of low resistance. This leads to a decrease of the current density going through the bulk silicon, which reduces the grow rate of the pore formation.

A solution to this problem has been proposed in this work. It consists in placing a sacrificial silicon wafers between the membrane and the aluminium contact (see Figure 4.3). This way, once the first pore is opened, the resistance of the overall membrane doesn't decrease because the ions still faced the sacrificial silicon wafers. This allows the porosification uniform as long as the sacrificial silicon wafers has no pore fully etched. The membrane obtained this way were fully porosified, however, they were all damaged at certain areas as shown in Figure 5.14.

An explanation for this could be that due to the large contact surface between the two silicon wafers, the surface tension between the two surfaces due to the presence of residual solution in the pore would have created too much stresses when the PSi was removed from the electrochemical cell.

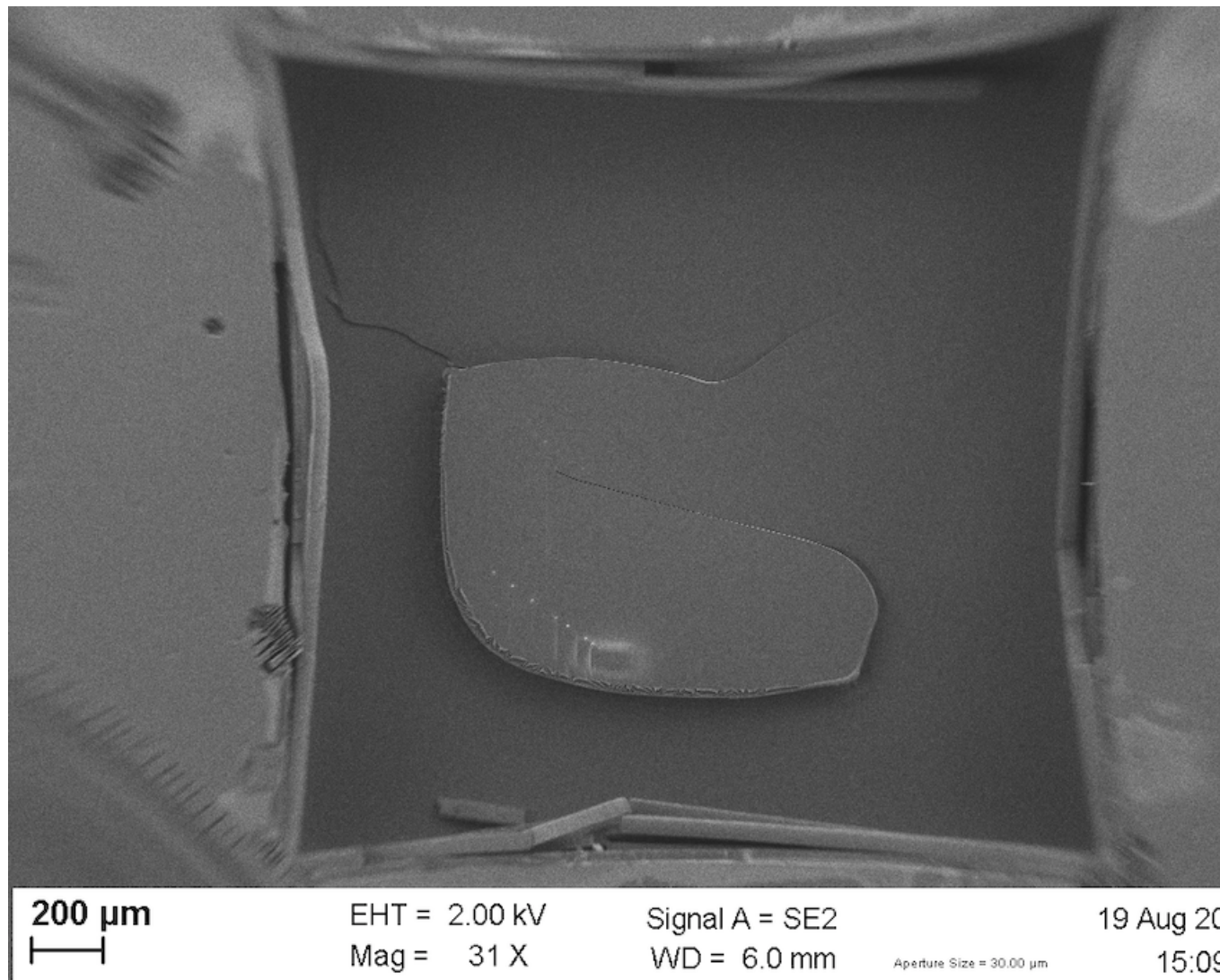


Figure 5.14: SEM image of PSi obtained using a sacrificial silicon wafer. Part of the membrane has been peeled off from the silicon structure.

5.4.2 Experimental set-up

The design of the fluidic cell can be changed to improve the measurement and the manipulation of the different components. Amongst the different factors impacting the measurements, the presence of bubbles was the most dramatic. The peristaltic pump was the main factor importing bubbles into the cell.

Mixing was not controlled in the cell, but was only a consequence of the pumping. What is more, the effects such as the formation of diffusion layers that we want to

decrease appear in the solution adjacent to the membrane. However, in the design of the fluidic cell used in this work, the mixing resulting from the pumping was made far from the membrane. Another design would help to improve this aspect, but also others aspects such as an easier control over the shape and position of the electrode in the cell

5.4.3 Study of the surface charge density of nanopore

In this work, it has not been possible to determine experimentally the surface charge density in a nano-pore. It would be interesting to propose a standard process to determine this value, as its impacts on the selective properties is important as shown in 3.4.1. It would also help to understand which materials or methods are best suited to obtain the highest charge density in a given set of working conditions.

5.4.4 Reduction of the noise

As it has been seen in the experimental data, noise is present. This noise mostly comes from the fluidic cell and more specifically from the electrodes. Better manufacturing of the electrodes, as well as the use of a real reference electrode instead of a pseudo-electrode could help to reduce the noise level.

5.5 Conclusion

In this chapter, the experimental results have been presented. A permselective behaviour has been demonstrated on the PSi membrane with a SiO_2 surface treatment. Power density in the range mW/m^2 can be harvested using these membranes. Membranes with an ALD of Al_2O_3 did not demonstrate permselective properties. This is most likely associated to pores blocked within the membrane.

Chapter 6

Conclusion

In this project, the objective was to fabricate and characterize porous silicon membranes, and perform surface treatments to change the conducting properties of the substrate.

In the first chapter, the concept of energy harvesting from saline solution was presented. One of the techniques is the reverse electrodialysis, which is based on membranes that selectively transport the ions. These membranes have a huge impact on the efficiency of process, and improvements are required to make RED interesting technology. In this view, nano structured material have been tested as potential high efficient selective membrane. However, despite their interesting properties, there is still a lack of manufacturing process able to produce these nano-structure in a large number on a single membrane. The purpose of the work was to propose and study porous silicon membranes as potential ion exchange membrane.

In the second chapter, the physical origin of the selective properties of nano-structure material was described. It results from the presence of charge on the surface of the material, affecting locally the distribution of charges and the ionic transport. The surface charge originates from the interaction between a solution and the surface of the material in contact with. Based on this principles, nano-porous material such as porous silicon make good candidates for large nano-structure selective membrane.

In the third chapter, a numerical model has been proposed to study the selective properties of a single charge nano-pore. Different geometrical parameters affect the selective property of the nano-pore, but the more important parameter is the surface charge density.

In the fourth chapter, the process flow to produce porous silicon with different surface treatment has been detailed. Porous silicon can be obtained with an electrochemical etching. Membranes have been manufactured in the Winfab cleanroom. Then, the different methods to characterise the membranes as ion

selective membranes have been explained.

Finally in the fifth chapter, the different experimental results have been presented. The possibility to use Porous silicon as ion permselective membrane is promising, with a power density up to a few mW/m^2 . It also opens the possibility to use PSi for iontronics applications, which could be an advantage over other classical polymer membrane as PSi can be manufactured at very small scales. However, many challenges still need to be addressed, such as improving the manufacturing process to obtain more stable membrane with a uniform porosified membrane. Nevertheless, harvesting the blue energy with PSi is a promising technology.

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