Pencil shape pores in porous silicon membrane toward improved efficiencies in reverse electrodialysis energy harvesting system

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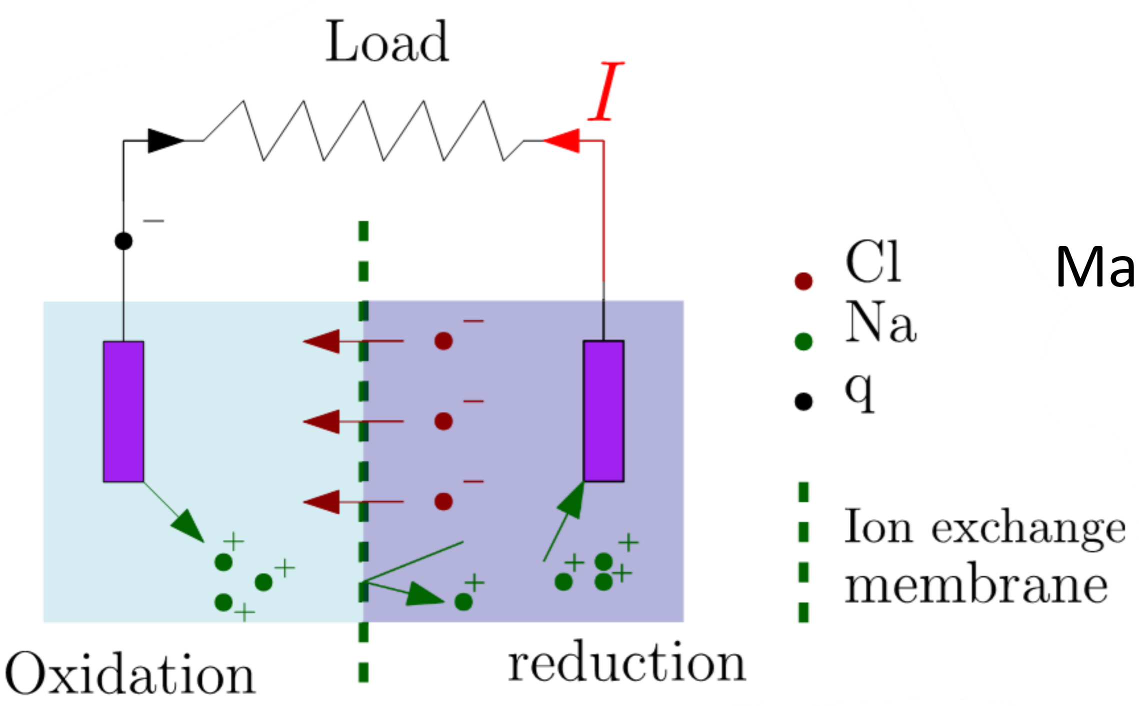
Reverse electrodialysis: harvesting blue energy (Gibbs Free energy)

RED cell



Based on **ion selective membranes (IEM):**

- High ionic selectivity ➔ High E_{diff} (~ tens of mV)
- Low membrane ionic resistance (R_{cell}) ➔ High I_{cell}

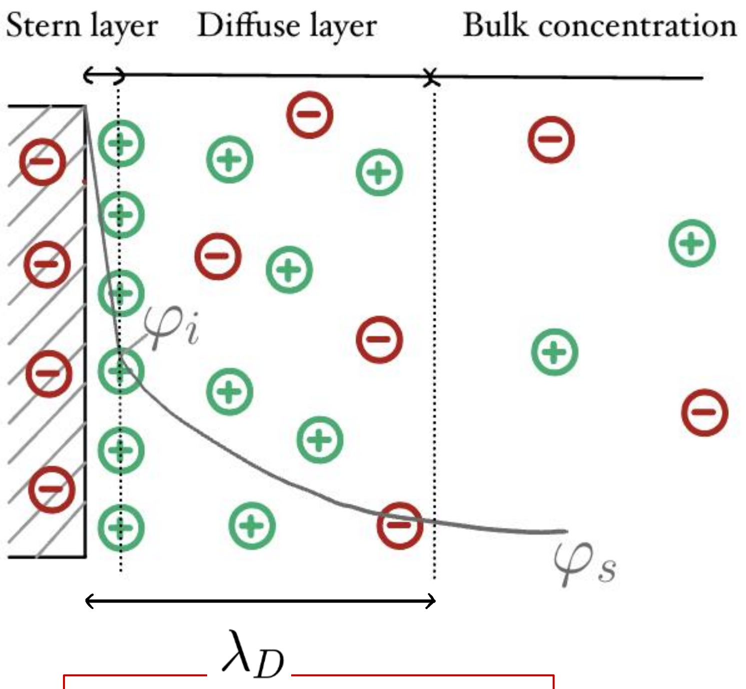
Maximal power:

- $P_{max} = \frac{E_{diff}^2}{R_{cell}} \sim$ a few W/m^2 (literature or commercial IEM)

Direct integration of RED for small, low consumption power system ?
(e.g., sensors, MEMS, IoT nodes, …)
➔ Requires **effective** **integrable** membrane

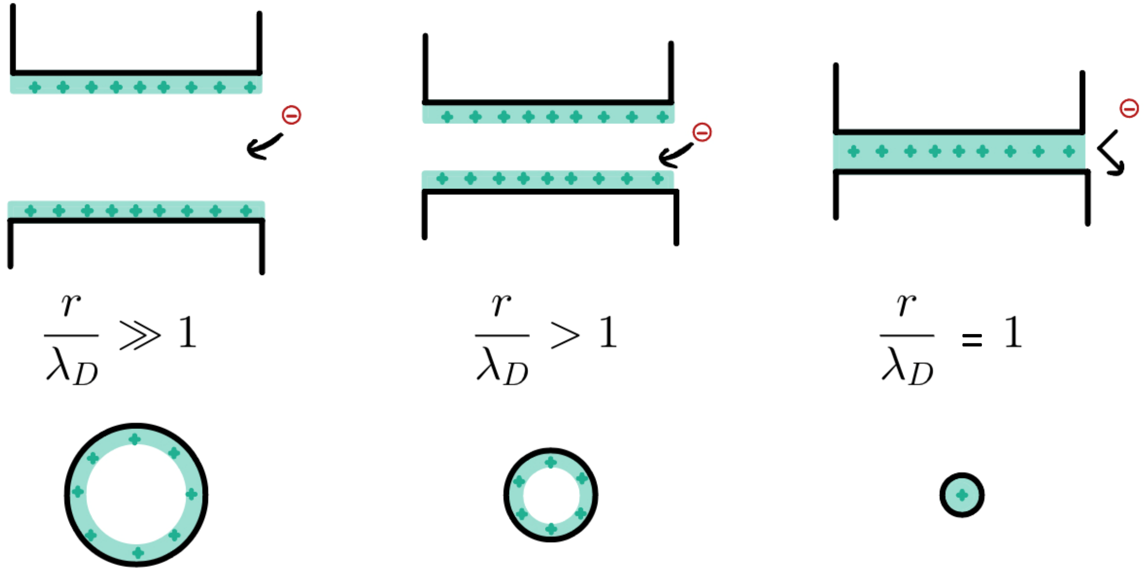
Selectivity through EDL overlap and Debye length

Electrical double layer (EDL)



$$\lambda_D \propto \sqrt{\frac{1}{C_i}}$$

Electrical double layer overlap



- C_i = 1mM → λ_D ~ 10 nm
- C_i = 0.1 mM → λ_D ~ 30 nm

Good selectivity with nanopores → Low resistivity p++ substrates chosen for these pore size

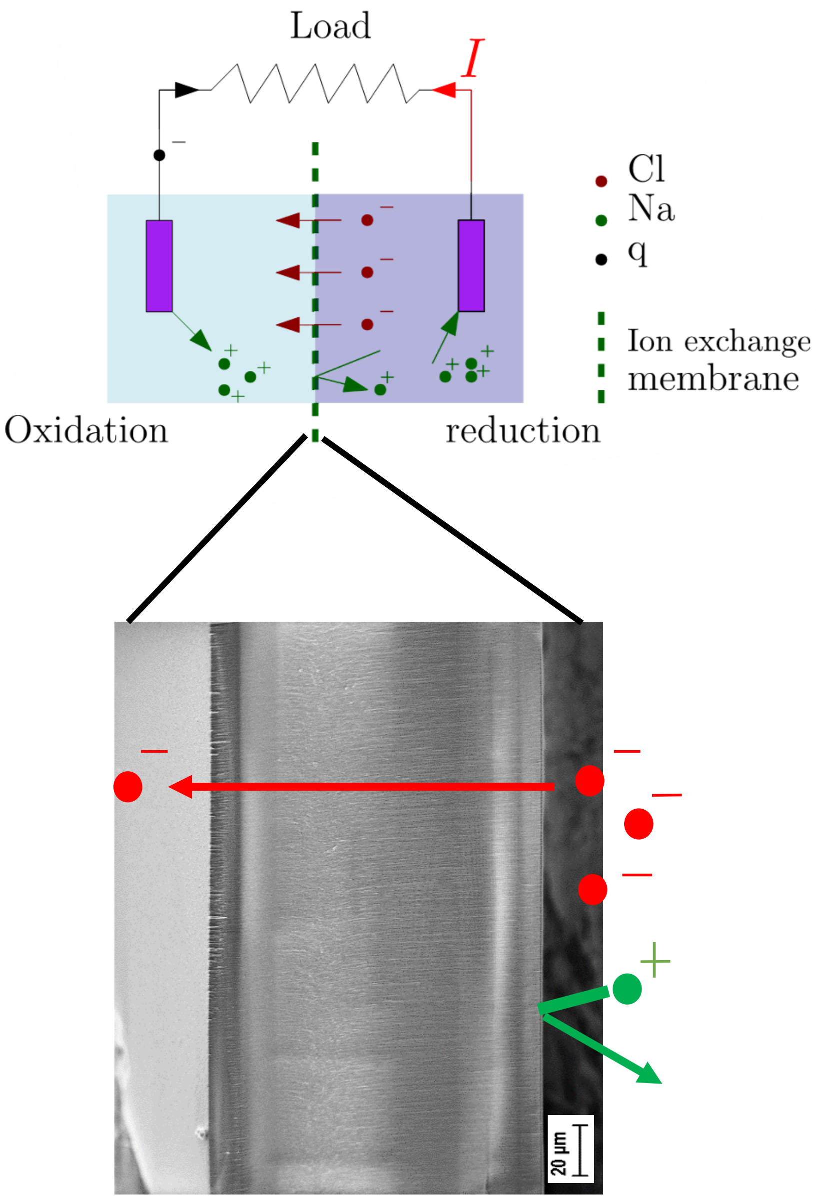
Porous silicon as ion exchange membrane

Polymer based membrane	Inorganic Based membrane (Porous silicon)
Very selective	Generally less selective
Well known	Recent study
Adaptable	Topology controlable
Chemical degradation	Less chemical degradation
Less stable in time	More stable in time
	Easily integrable with CMOS

a few W/m^2 on full membrane

Tens of W/m^2 shown
BUT not on macroscopic membranes
(single nanopore study)

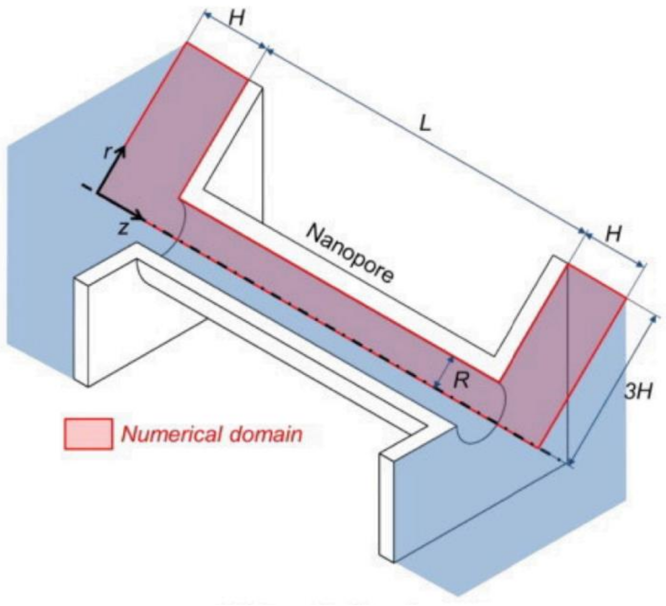
Motivation : full membrane in Si



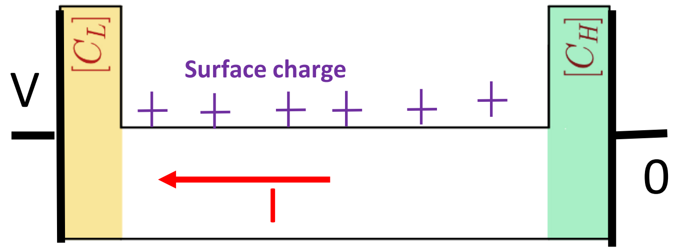
PSi membrane - side view

Numerical study of selective properties of single nanopore

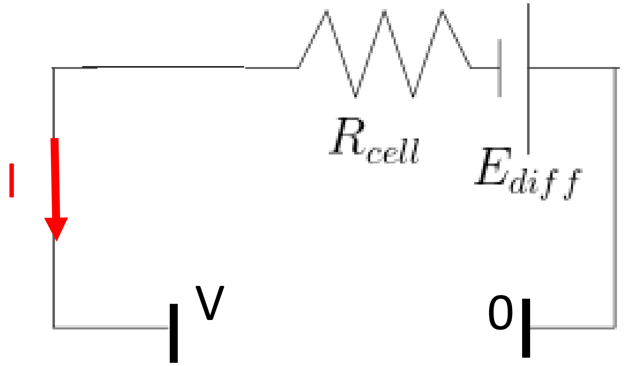
Numerical domain:
2D axysymmetric
half pore



Schematic of the model

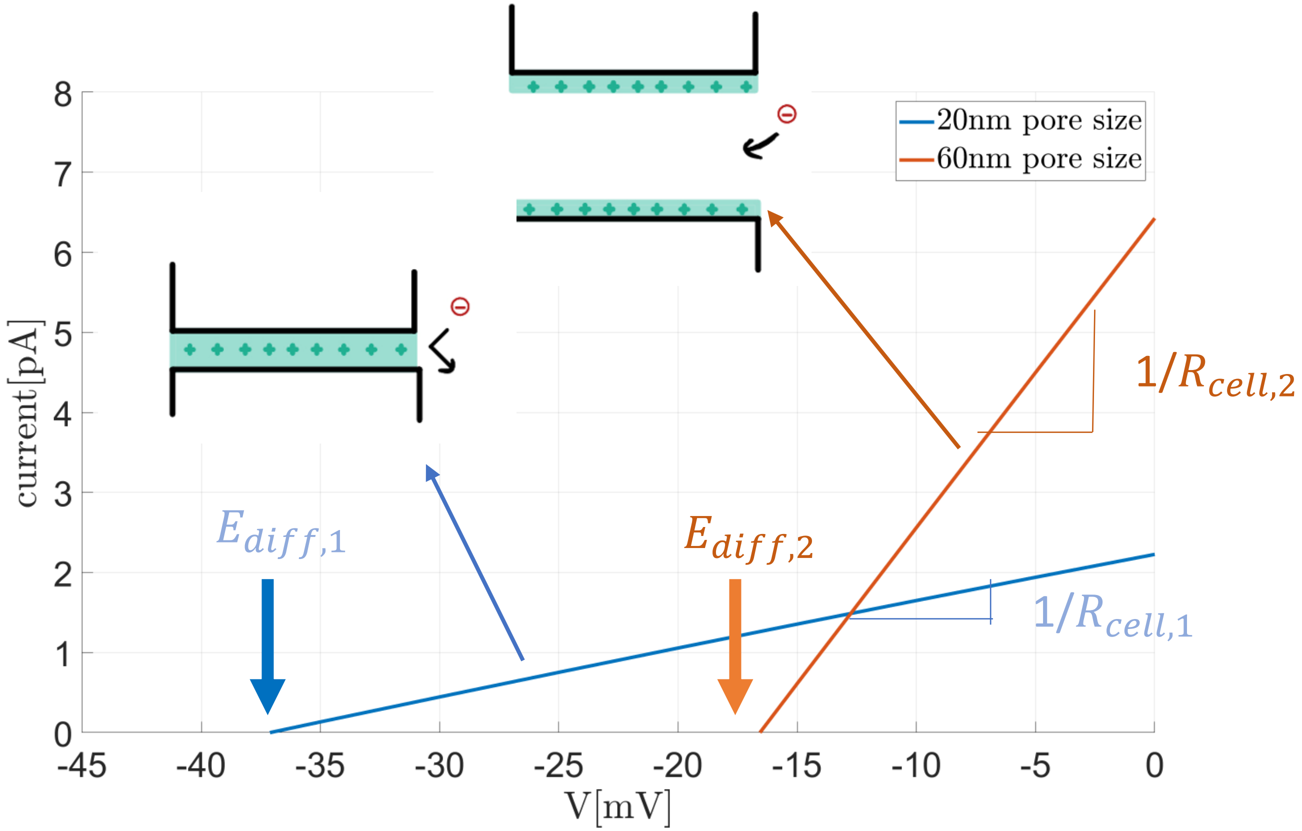


Electrical equivalent
circuit of the models



Numerical study of selective properties of single nanopore

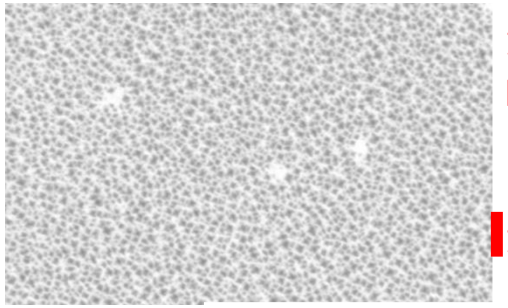
Numerical results for [LC]=0.1mM KCl, [HC]=1mM KCl



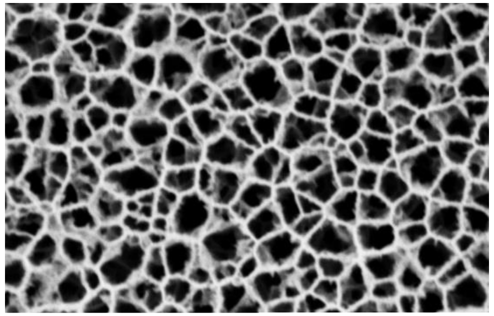
- Smaller pore radius→ higher E_{diff}: $E_{diff,1} > E_{diff,2}$
- Larger pore radius→ lower resistance R_{cell}: $R_{cell,2} < R_{cell,1}$

Trade-off between selectivity and resistance !

Experimental I-V test on membrane with different pore size

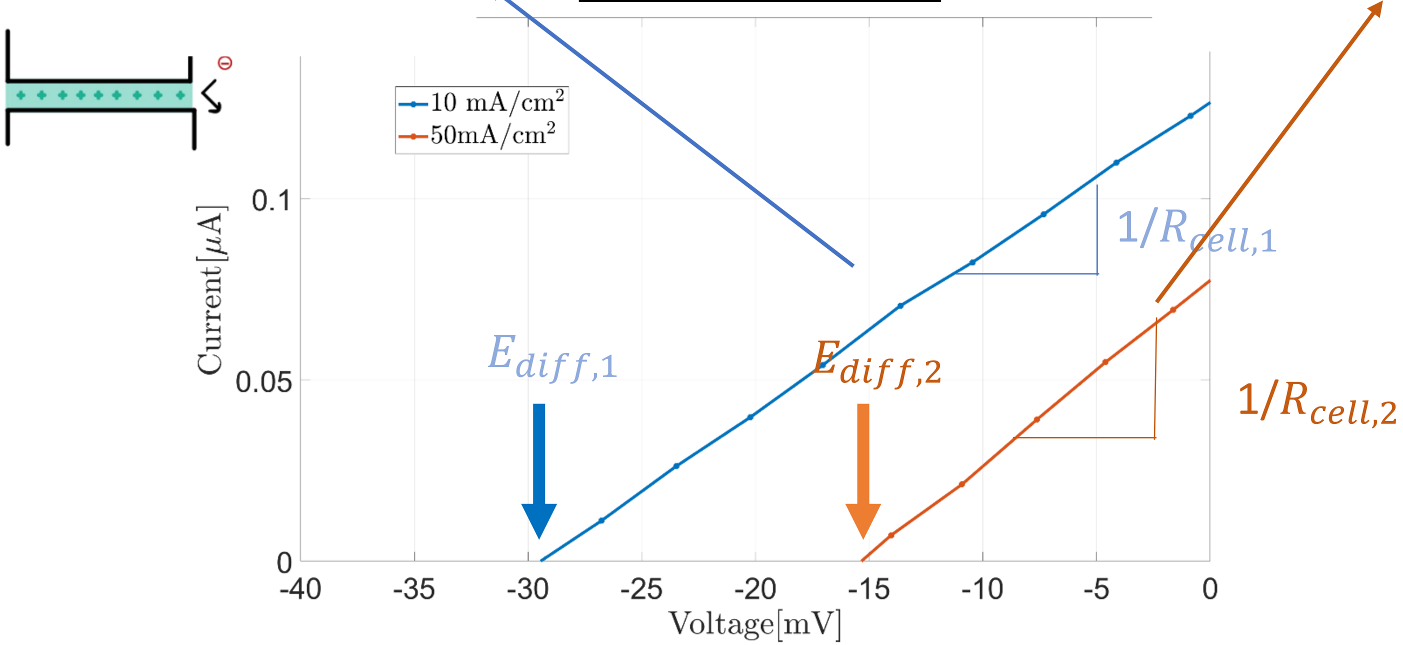


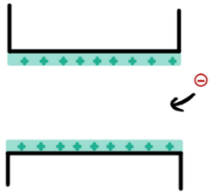
$10mA/cm^2$
R~20nm
100nm



$50mA/cm^2$
R~60nm
100nm

Experimental results





Parameter:

Membrane thickness:

~ **25** µm (10 mA/cm^2)

~ **35** µm (50 mA/cm^2)

Ionic solutions:

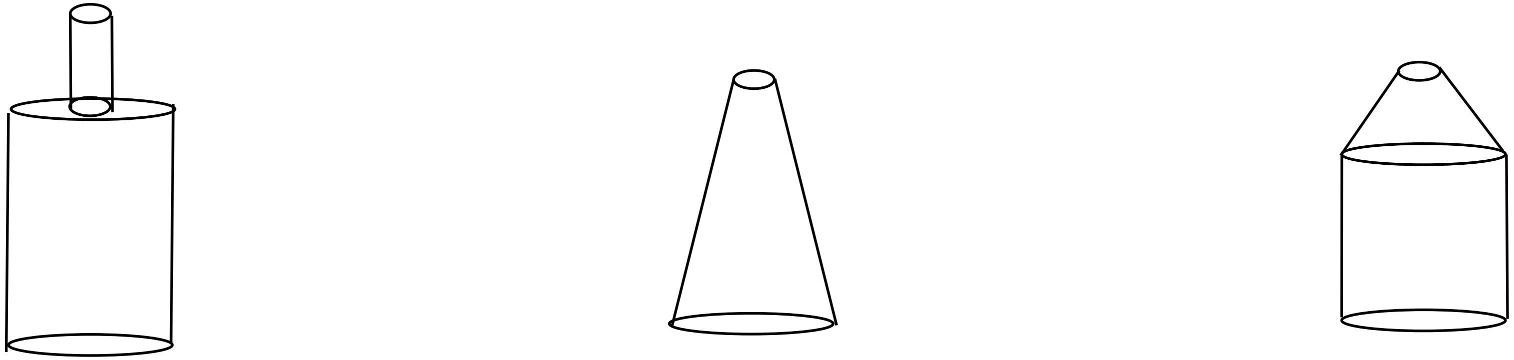
[KCl] ~ 0.5 mM *vs.* [KCl] ~ 1mM

- **Similar trends with the numerical results**
- Lower 'short circuit current' for $50mA/cm^2$ associated to pore opening and membrane thickness control issues with DRIE during the membrane released

➔ How to benefit from the advantages of both pore size ?

Pore shape variation: finding a good trade-off

- Different shapes possibles….

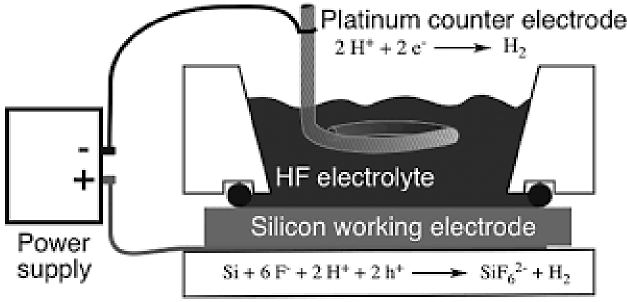


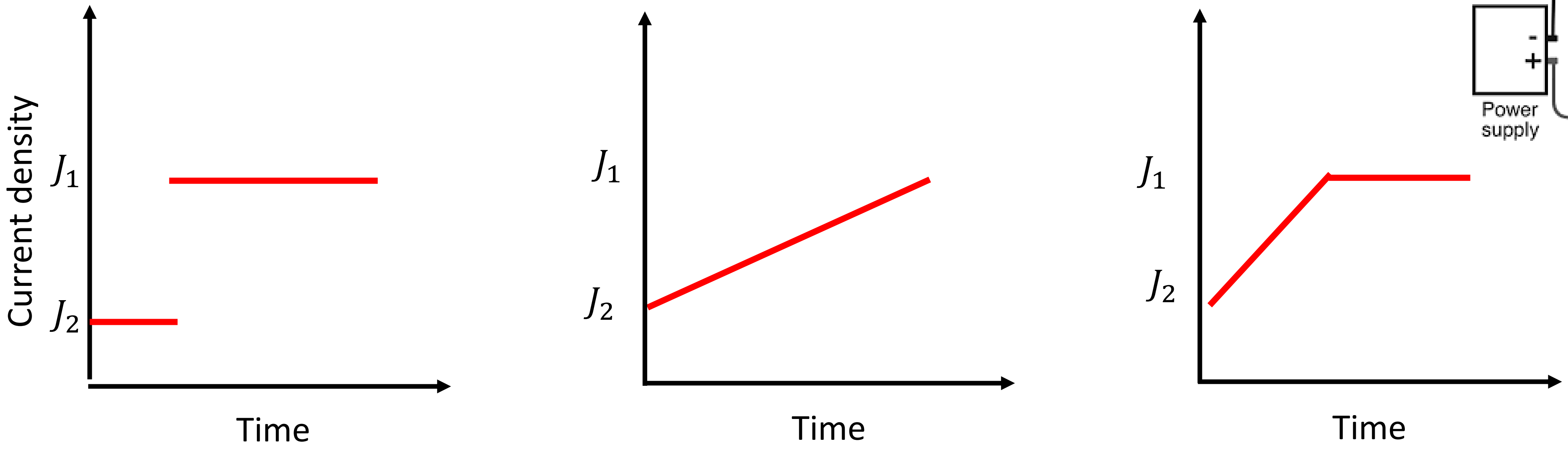
STEP CONICAL PENCIL

Small pore radius
=High selectivity

Larger pore radius
=Low resistance

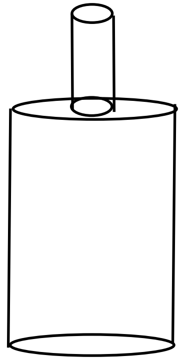
- … obtained by monitoring the current density during porosification of the substrate





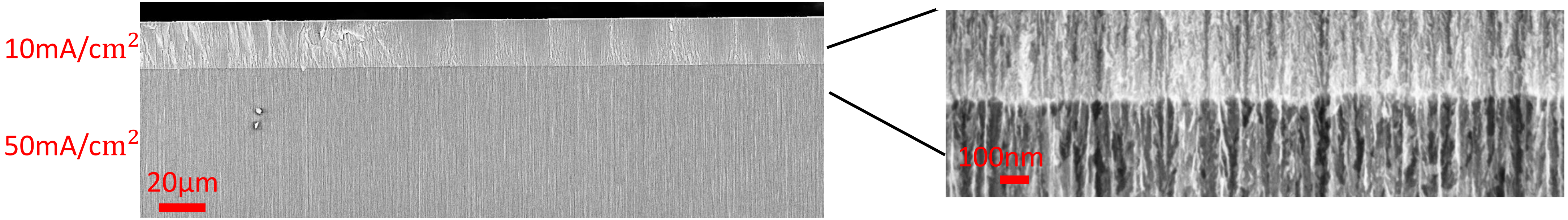
Control of the pore size along the thickness with the applied current density

Psi membrane with varying pore shapes

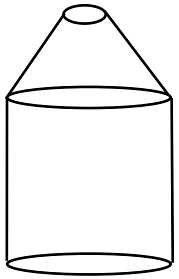


STEP

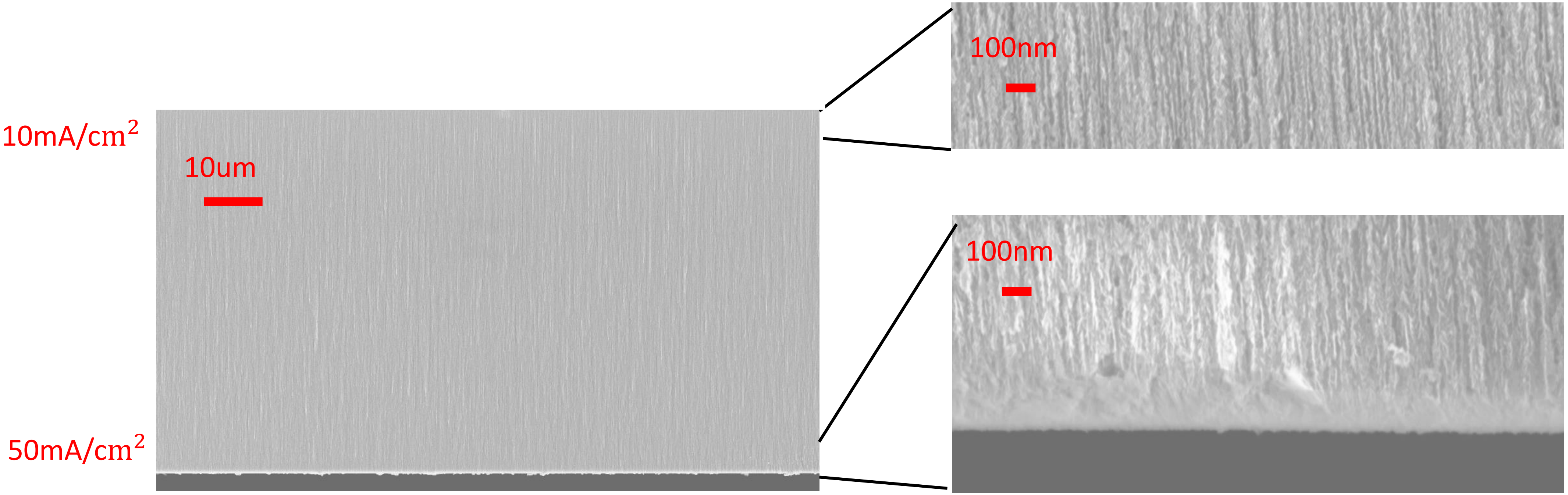
Membrane STEP-Side view



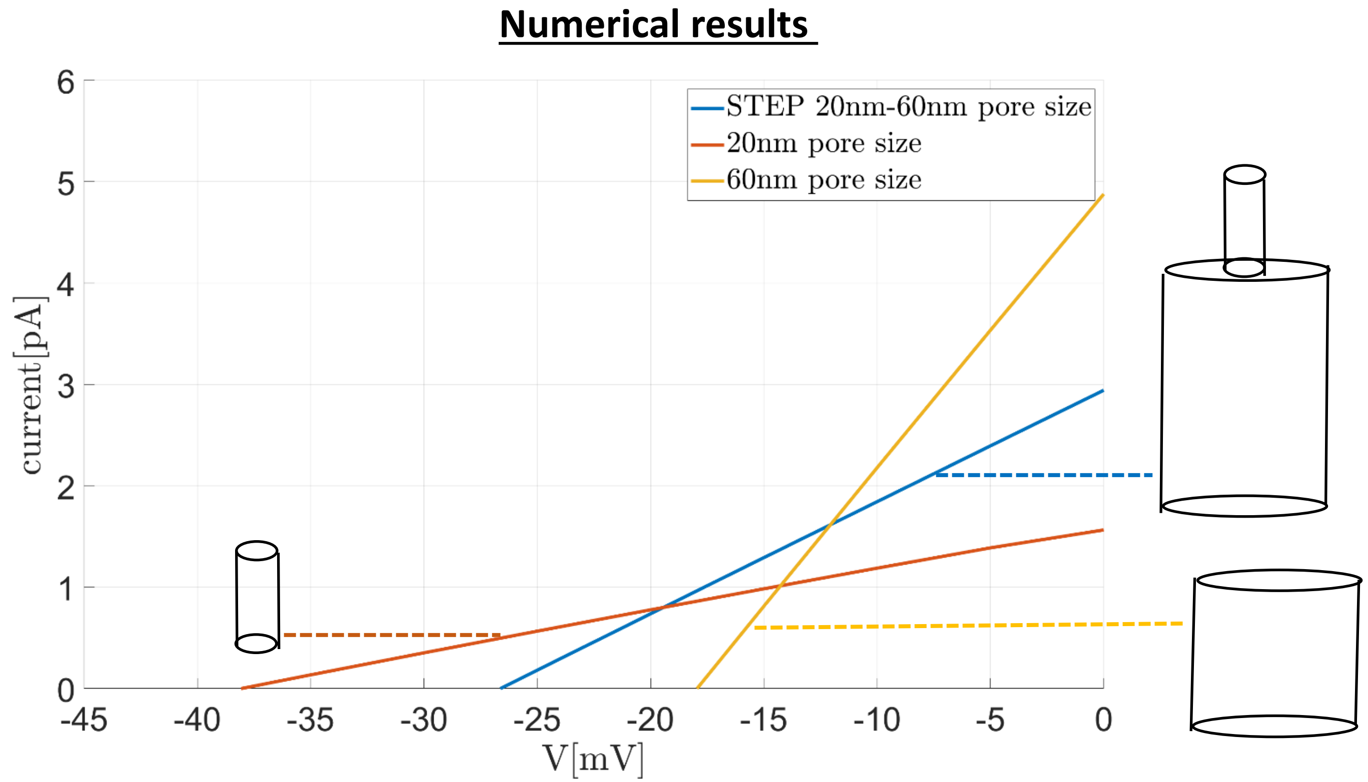
Membrane PENCIL-Side view



PENCIL



Numerical comparison 'step' pores *vs*. conical pores



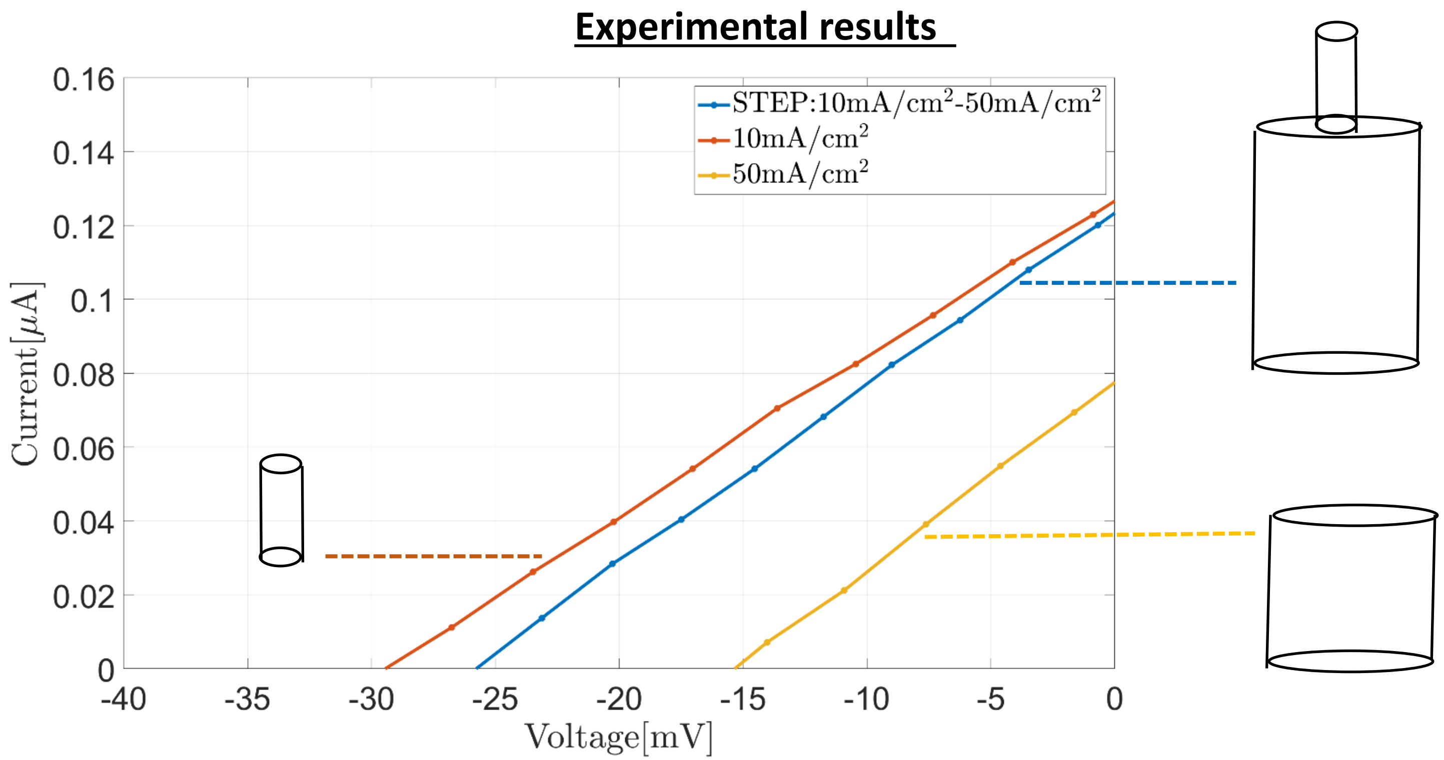
Numerical I-V test on:

- 1 step with 20% 20 nm and 80% 60 nm pore size
- 1 cylindrical 20 nm
- 1 cylindrical 60 nm
- Same length: **600 nm**
- Ionic solution: : [KCl] = 0.1 mM vs [KCl] = 1 mM

Numerical results:

- E_{diff} 'step' intermediate between E_{diff} 20nm and E_{diff} 50nm
- Similar conclusion for resistance 'step'

Comparison 'step' pores with conical pores



Experimental I-V test on:

- 3 membranes with different current density (1 step shape, 2 cylindrical shape)
- 50mA/cm^2: **35 µm thick**
- 10mA/cm^2: **25 µm thick**
- STEP: **70 µm thick**
- Ionic solutions: [KCl] ~ 0.5 mM *vs.* [KCl] ~ 1 mM

Experimental results:

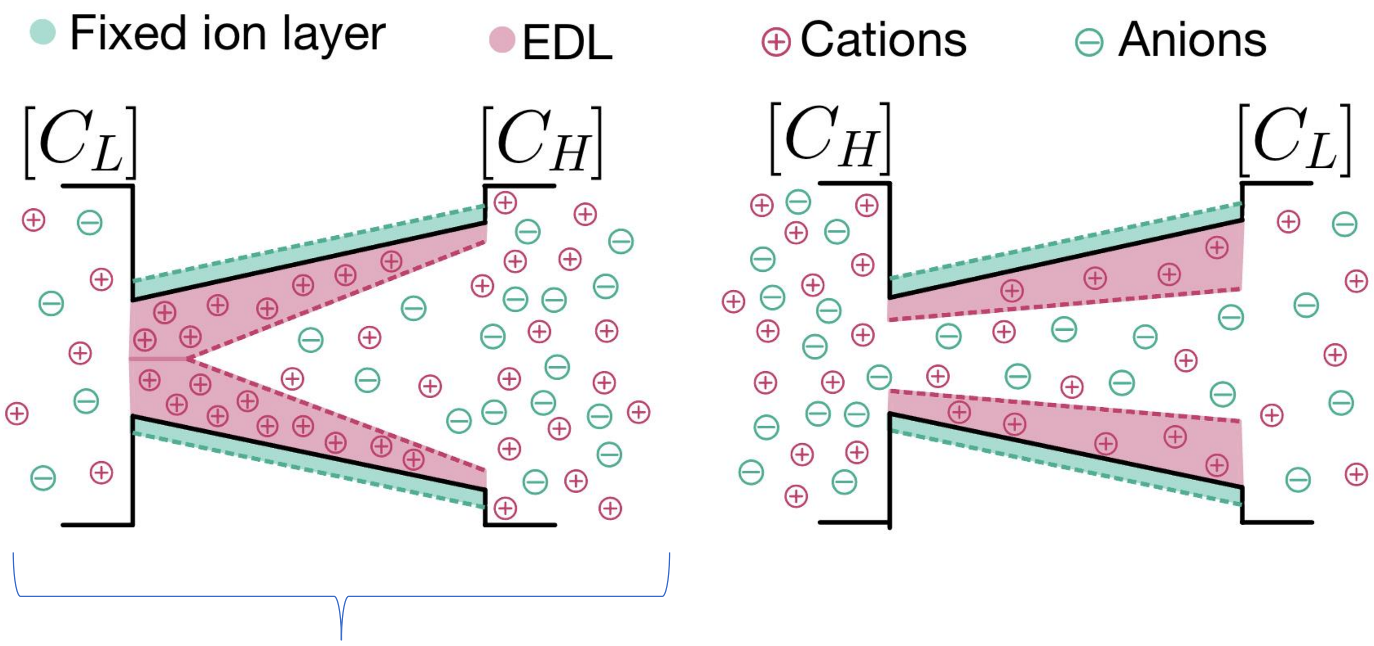
- E_{diff} 'step' intermediate between E_{diff} 20 nm and E_{diff} 50 nm
- Similar conclusion for resistance 'step'
- **One to one comparison not straighforward as thickness is not similar between the membranes !**

Asymmetric selective property

Benefits of varying pore size membrane:

- Similar selectivity as pores with small pore radius
- BUT lower resistance than with small pore radius

Side effects: asymmetry of selectivity

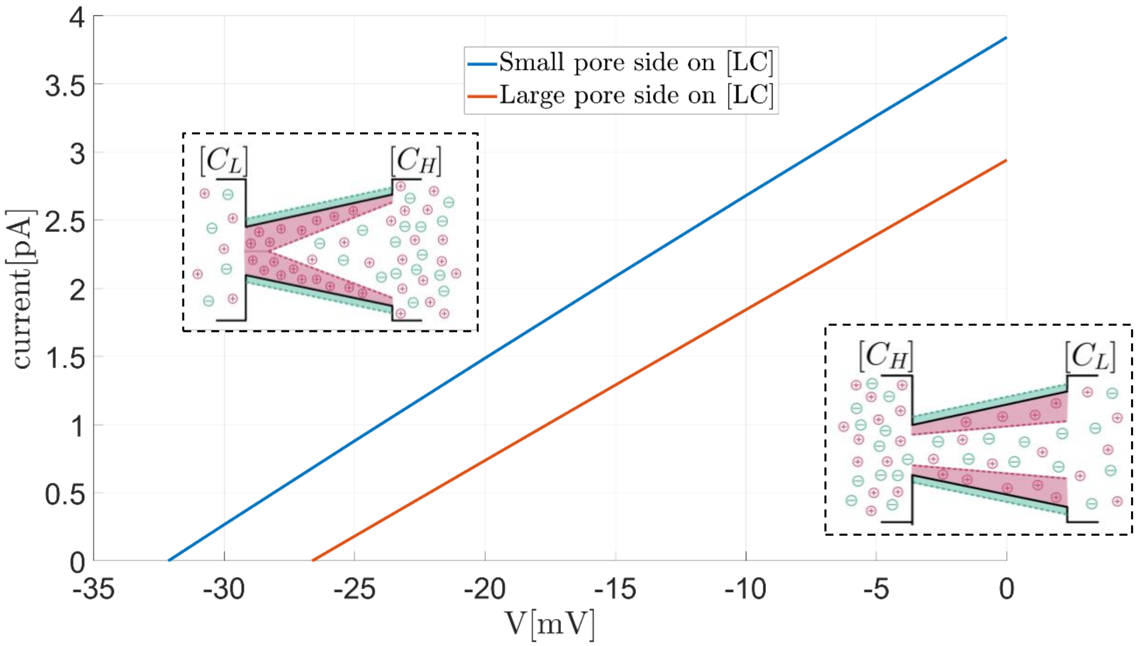


Ideal selectivity situation

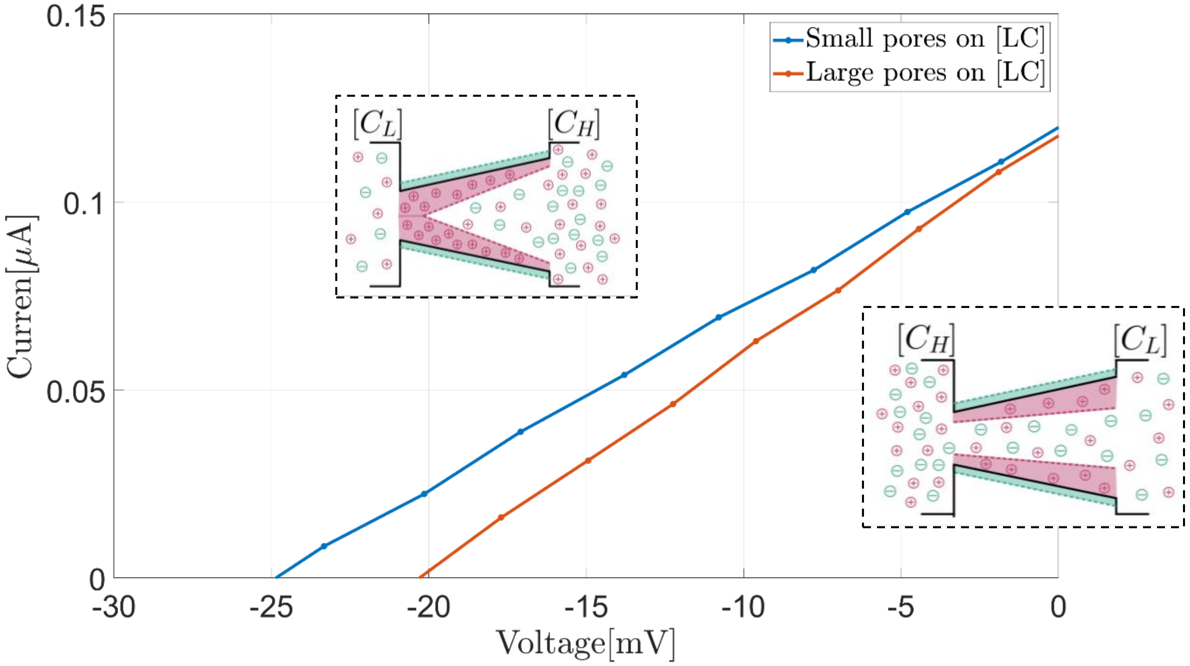
→ Can be used to control if the pores are cylindrical of with varying pore size along the thickness

EDL overlap asymmetry verification- ‘Step’ membrane

Numerical results on the same pore



Experimental results on the same membrane



Numerical results:

- E_{diff} is worst when the large pore side is exposed to the low concentration side (EDL overlap worst)
- Resistance is still relatively higher in the worst case even though EDL overlap is weaker
- Asymetric selective property

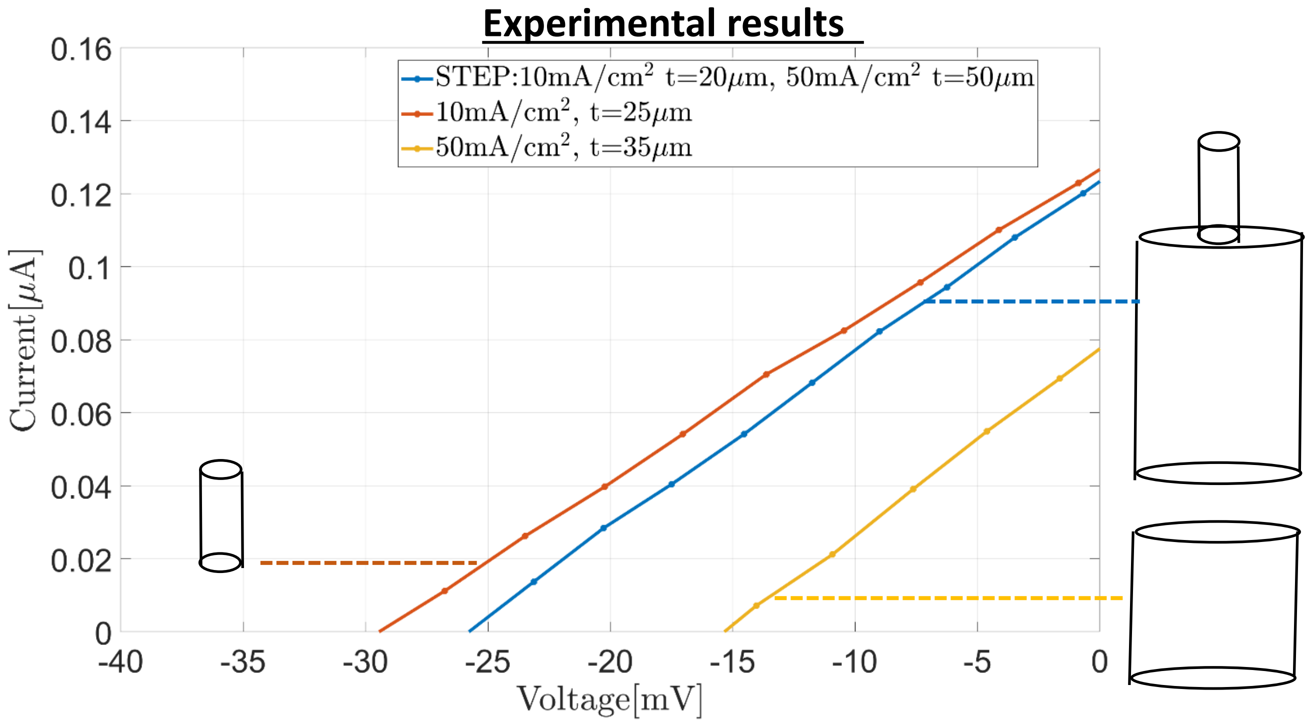
Experimental results:

- E_{diff} is worst when the large pore side is exposed to the low concentration side (EDL overlap worst)
- Resistance is relatively lower in the worst case
- Asymetric selective property

What about the power comparison ?

Max power:

$$P_{max} = \frac{E_{diff}^2}{R_{cell}}$$

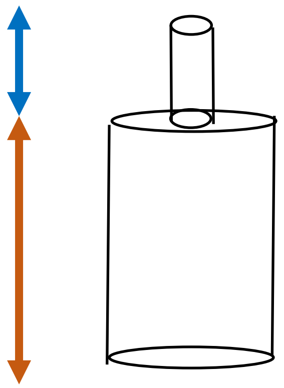


Experimental results:

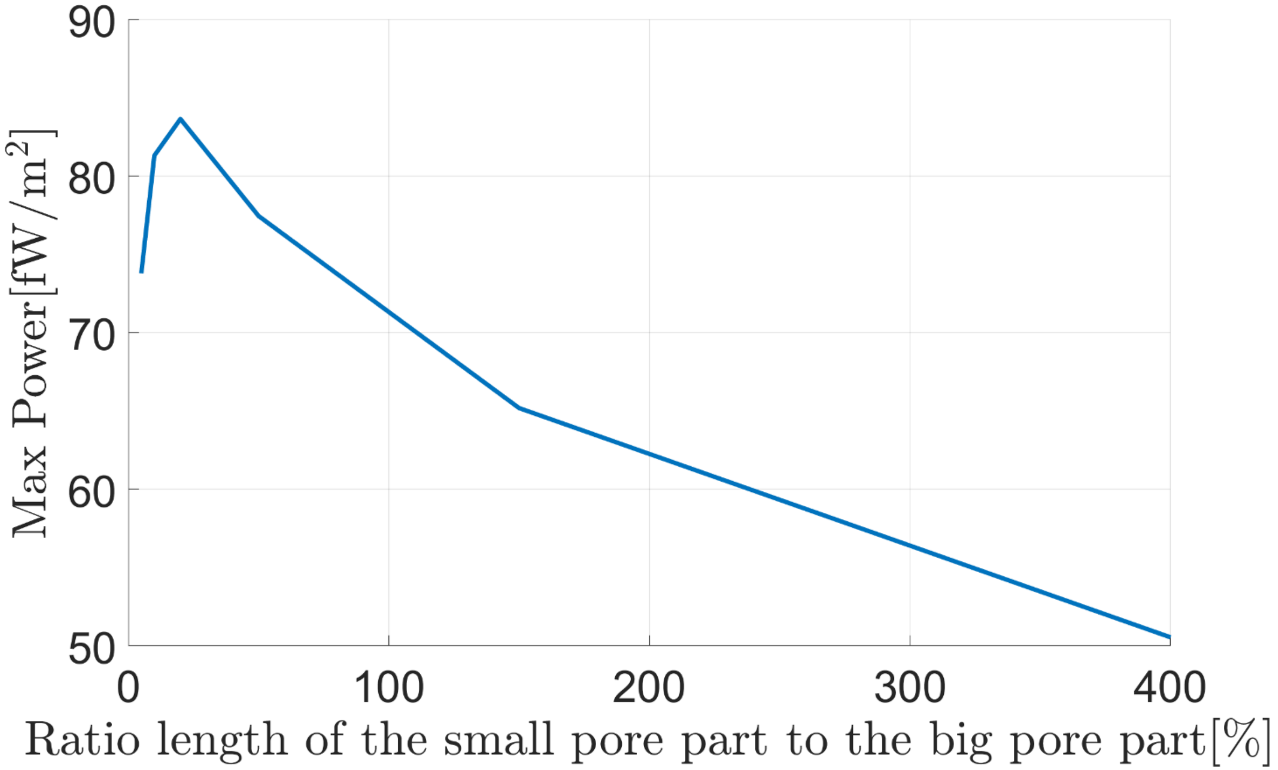
- Maximal power :
  - 60 nm: $P_{max} = 0.29$ nW
  - STEP: $P_{max} = 0.792$ nW
  - 20 nm: $P_{max} = 0.93$ nW
- Maximal power density (3.14 mm^2 membrane)
  - 60 nm: $P_{max,d} = 0.0922\ mW/m^2$
  - STEP: $P_{max,d} = 0.252\ mW/m^2$
  - 20 nm: $P_{max,d} = 0.297\ mW/m^2$

Improved resistance from 'STEP' does not compensate the loss in E_{diff} here.
BUT, based on the thickness, **we can extrapolate improved perfomances for the STEP membrane**

Finding the best ratio using simulations



STEP

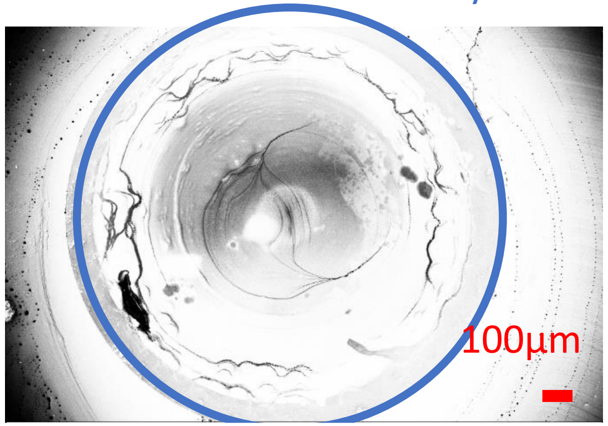


For each of the three shapes, we can report such optimum sizing

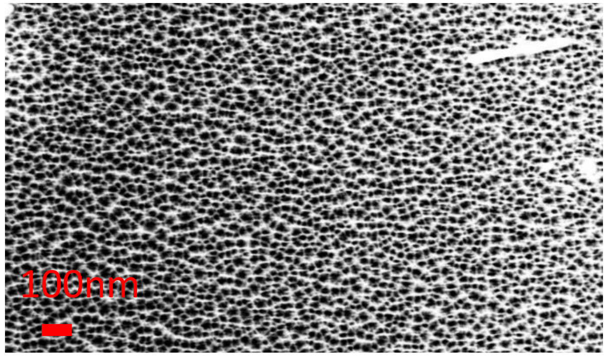
Few issues…

- Membrane released issue with DRIE:
  - non uniform release of the membrane back side with DRIE: surface area underestimated
  - Membrane substrate support etched: mechanical issues
  - Porous layer (oxydized) slighly affected by the plasma during the release

Back side membrane not uniformly released

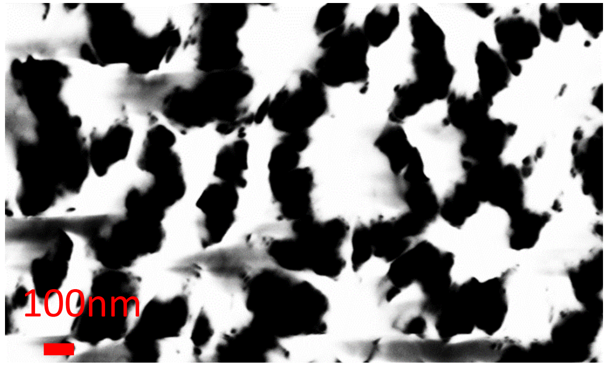


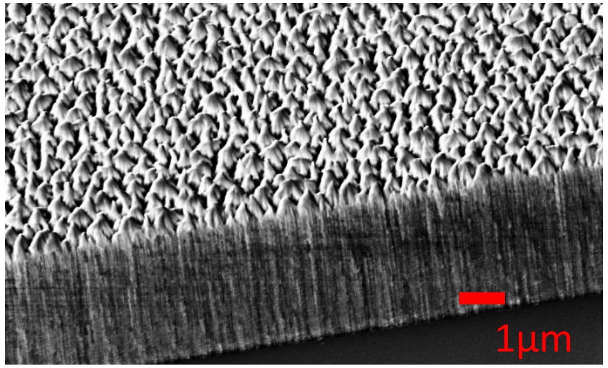
Top view Psi 50mA/cm^2



DRIE

Top view and side Psi 50mA/cm^2 after 3 cycles DRIE

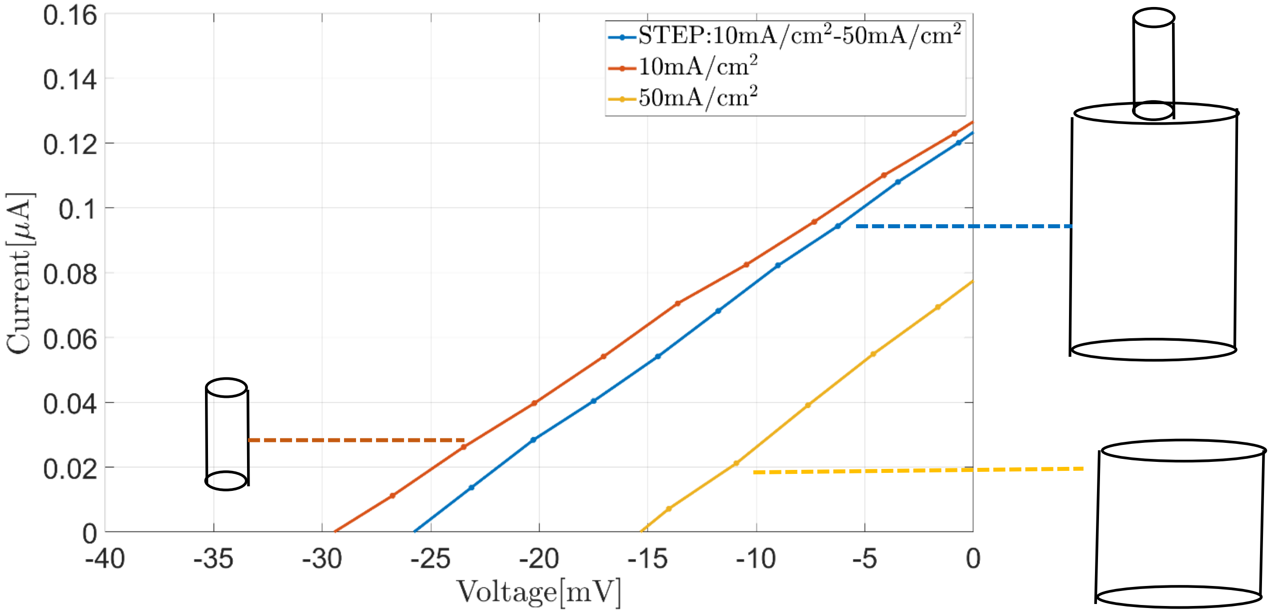




- Porosification:
  - Branching of pores not taken into account in the simulations
  - Closed pores

Conclusion

- **PSi** membrane as ion exchange membranes **(IEM)** has been demonstrated
- The versality of **PSi properties** allows for **improvement for the net power** output for reverse electrodialysis system
- Connecting smaller pores with larger pores on the same membrane to benefit from the **higher selective property** with the **lower resistance** respectively, can increase the net output power of Psi membrane



Experimental results

Future work

- Process of fabrication optimization
  - Increase pore size variation while avoiding membrane lift off
  - Pore membrane release (DRIE)
- Surface charge density impact
  - Atomic layer deposition of other material (Al_2O_3,Hf_2O)
- Numerical study
  - Study and comparison of the different shapes
  - Optimisation of the pore dimension

Thank you for your attention !

Any questions ?

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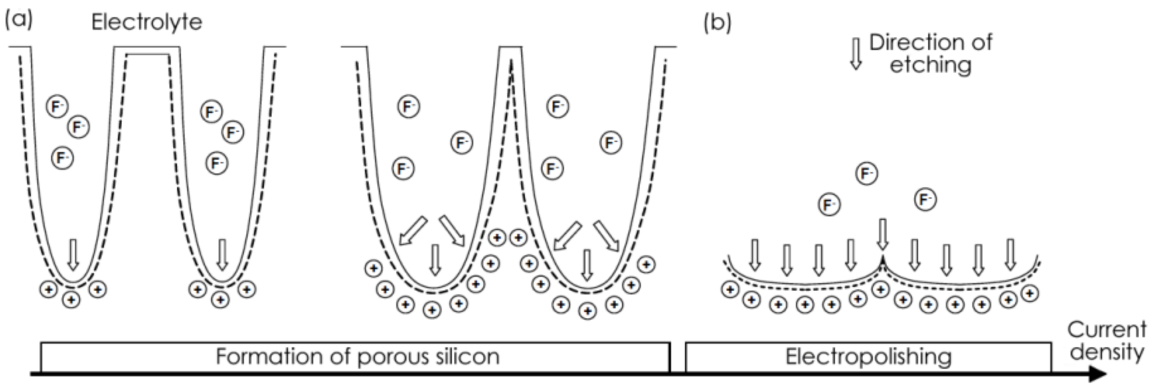
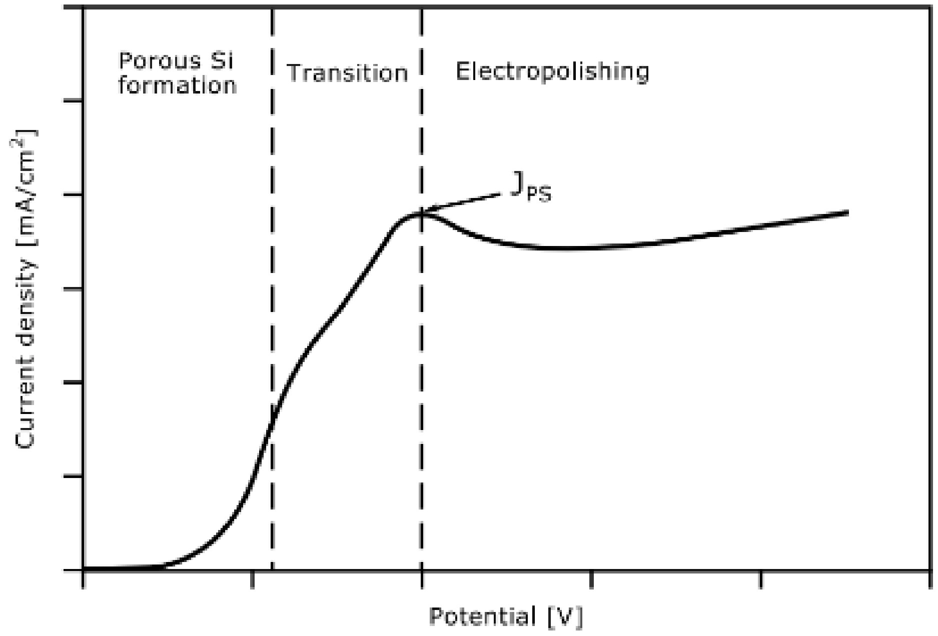
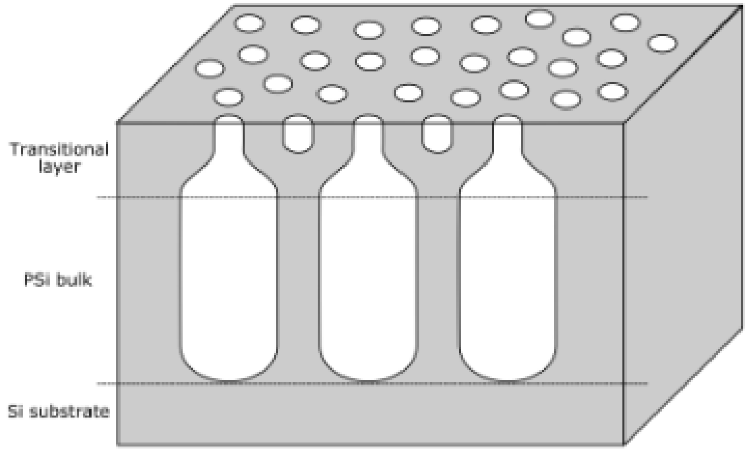


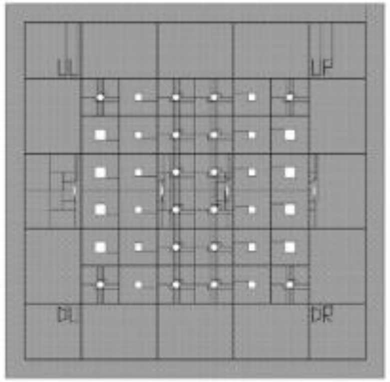


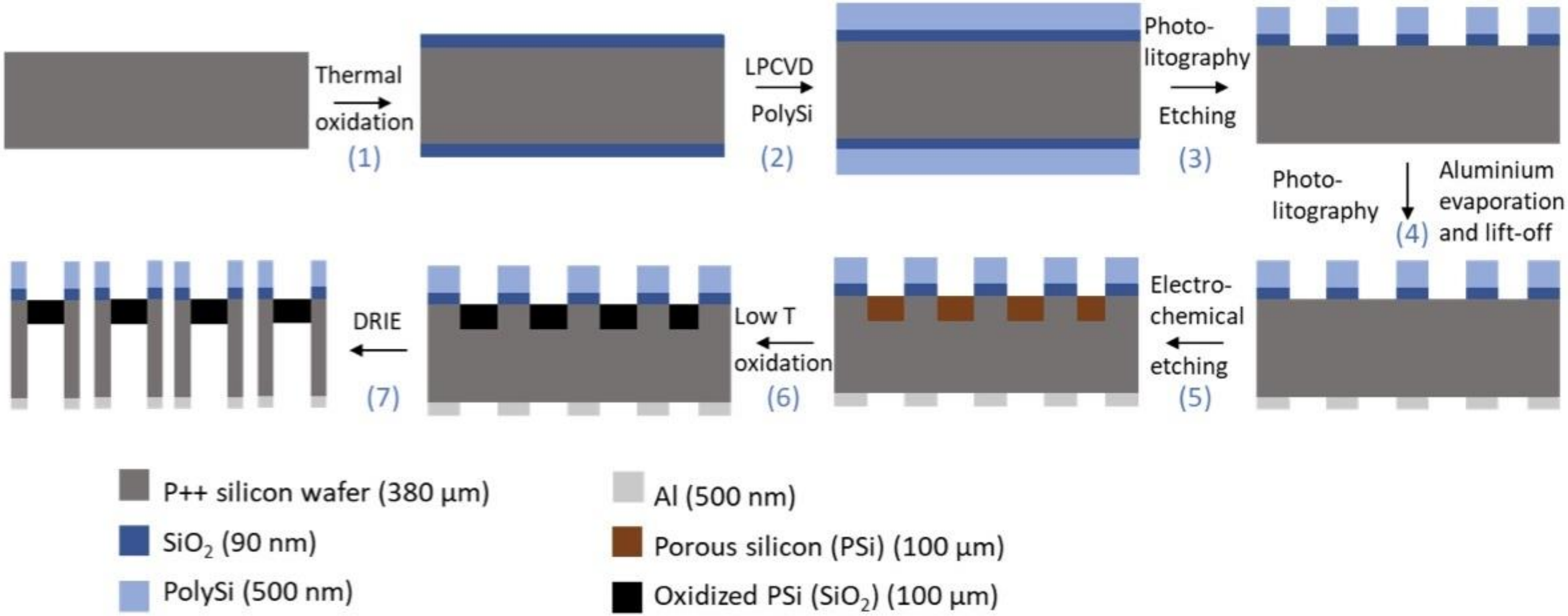
Increase of	Porosity	Etching rate	Critical current
HF concentration	Decreases	Decreases	Increases
Current density	Increases	Increases	-
Anodization time	Increases	Almost constant	-
Temperature	-	-	Increases
Wafer doping (p-type)	Decreases	Increases	Increases
Wafer doping (n-type)	Increases	Increases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



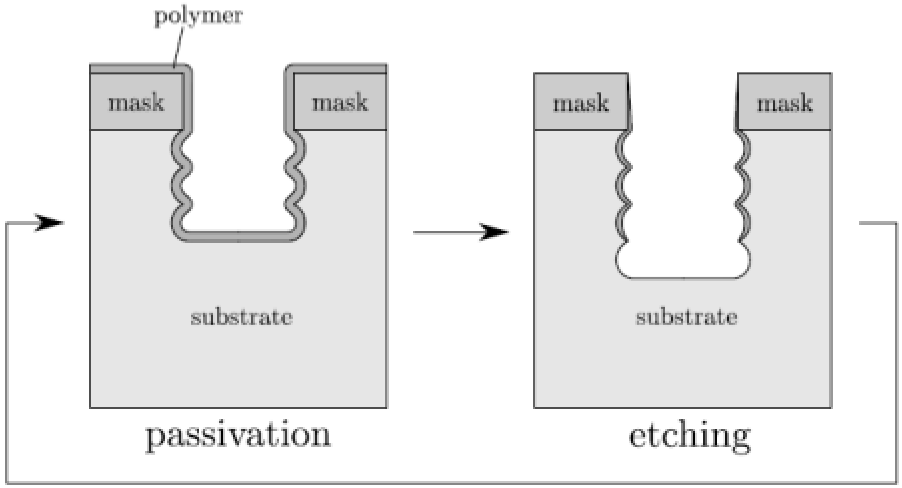
- Substrate: Si p++ boron, 0.8-0.9m Ω.cm
- Current density range: 100mA/cm^2→ 20mA/cm^2

Additional support : process

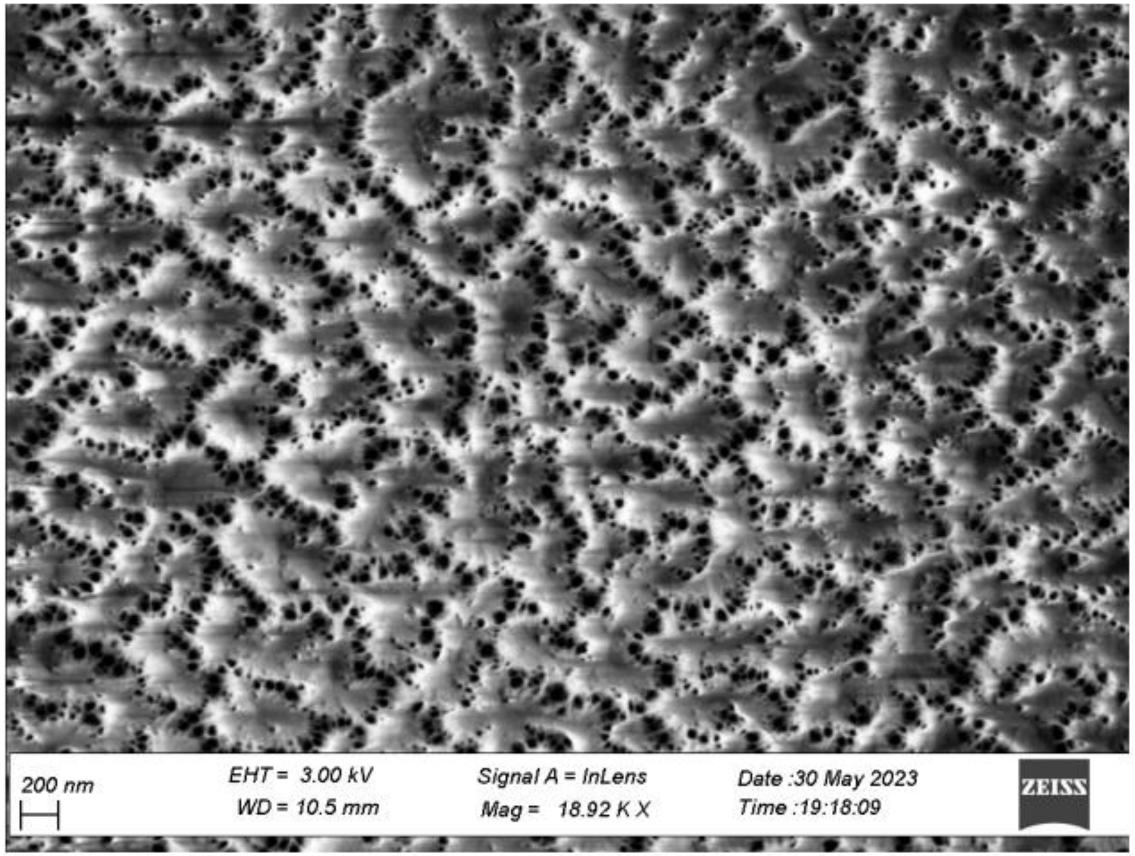




DRIE



	Etching	Passivation
Duration	13s	6s
SF_6 flow	120sscm	1sscm
C_4F_8 flow	1sscm	150 sscm
RF power	30W	10W
ICP power	~~1500 W~~	~~1500 W~~
Temperature	-10°C	-10°C
Pressure	20mTorr	20mTorr



Rectification Diffusion coefficient

- Nernst potential : 1 ion

$$E_{redox} = \frac{\mathrm{RT}}{z\mathrm{F}} ln(\frac{\gamma_H C_H}{\gamma_L C_L})\ (1\text{-}2t_+)$$

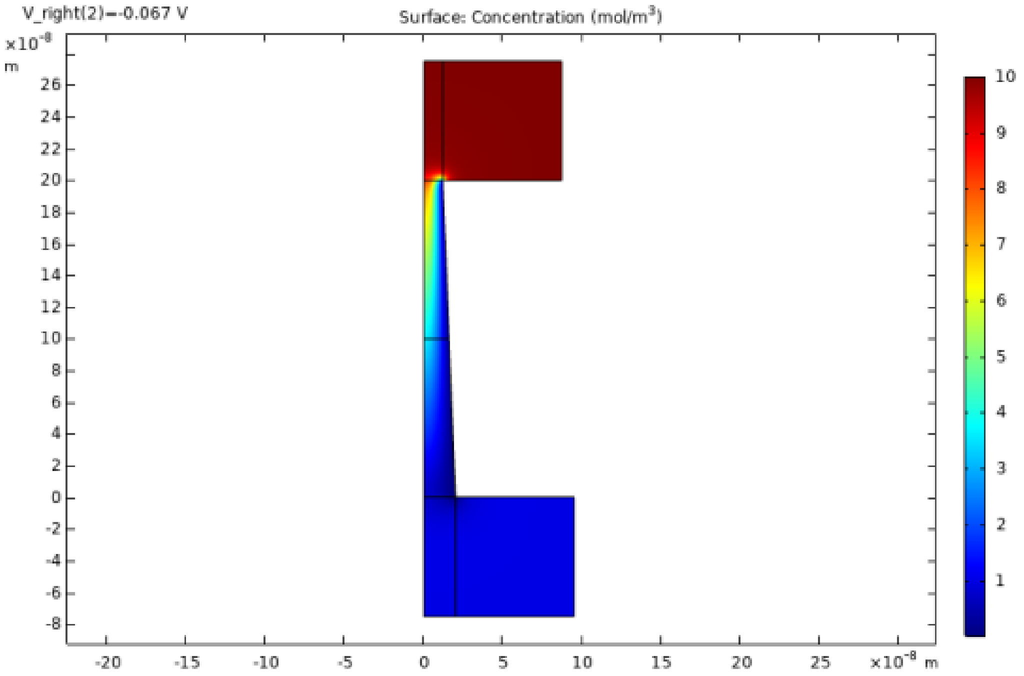
- Nernst modified : 2 ions

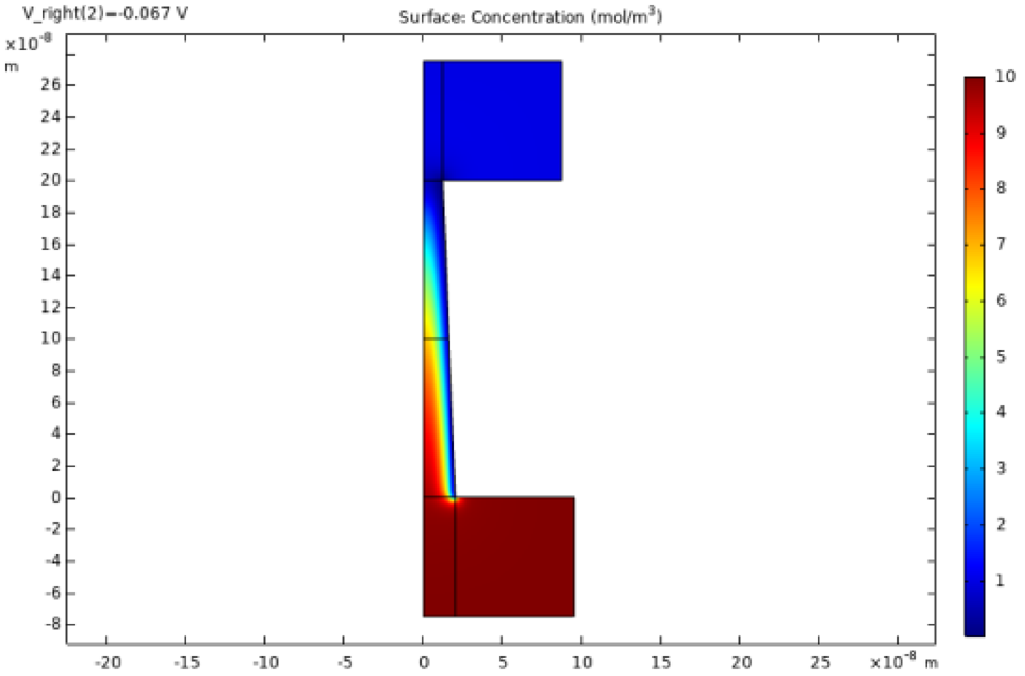
$$E_{redox} = \frac{\mathrm{RT}}{z\mathrm{F}} ln(\frac{\gamma_H C_H}{\gamma_L C_L})\ (1\text{-}2t_+ + \frac{D_{Cl^-} - D_{Na^+}}{D_{Cl^-} + D_{Na^+}})$$

- Constant field equation : As many ions but need of permselectivity

$$E_m = \frac{RT}{F} \ln \left(\frac{\sum_i^n P_{M_i^+}[M_i^+]_{\mathrm{out}} + \sum_j^m P_{A_j^-}[A_j^-]_{\mathrm{in}}}{\sum_i^n P_{M_i^+}[M_i^+]_{\mathrm{in}} + \sum_j^m P_{A_j^-}[A_j^-]_{\mathrm{out}}} \right)$$

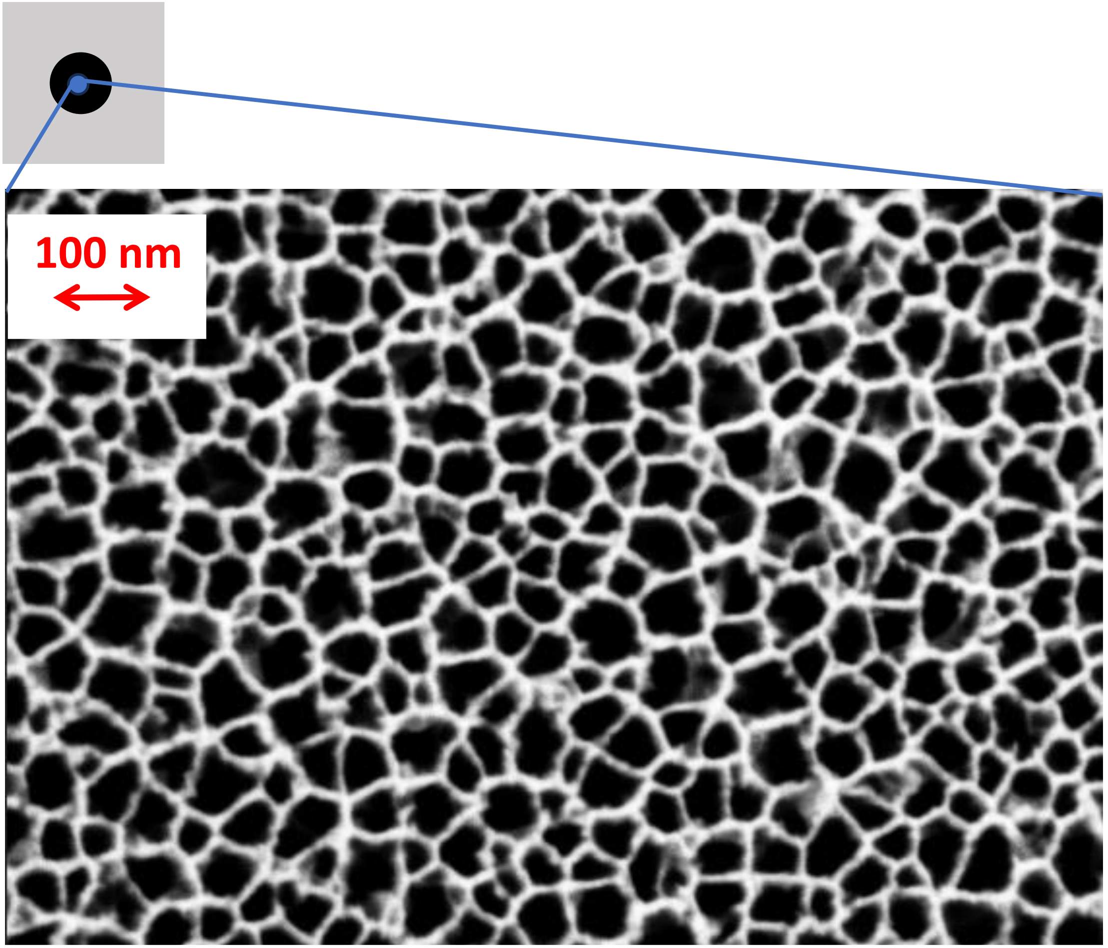
Concentration of anion in mol/m³
Blue = flow mainly due to cation = selectivity



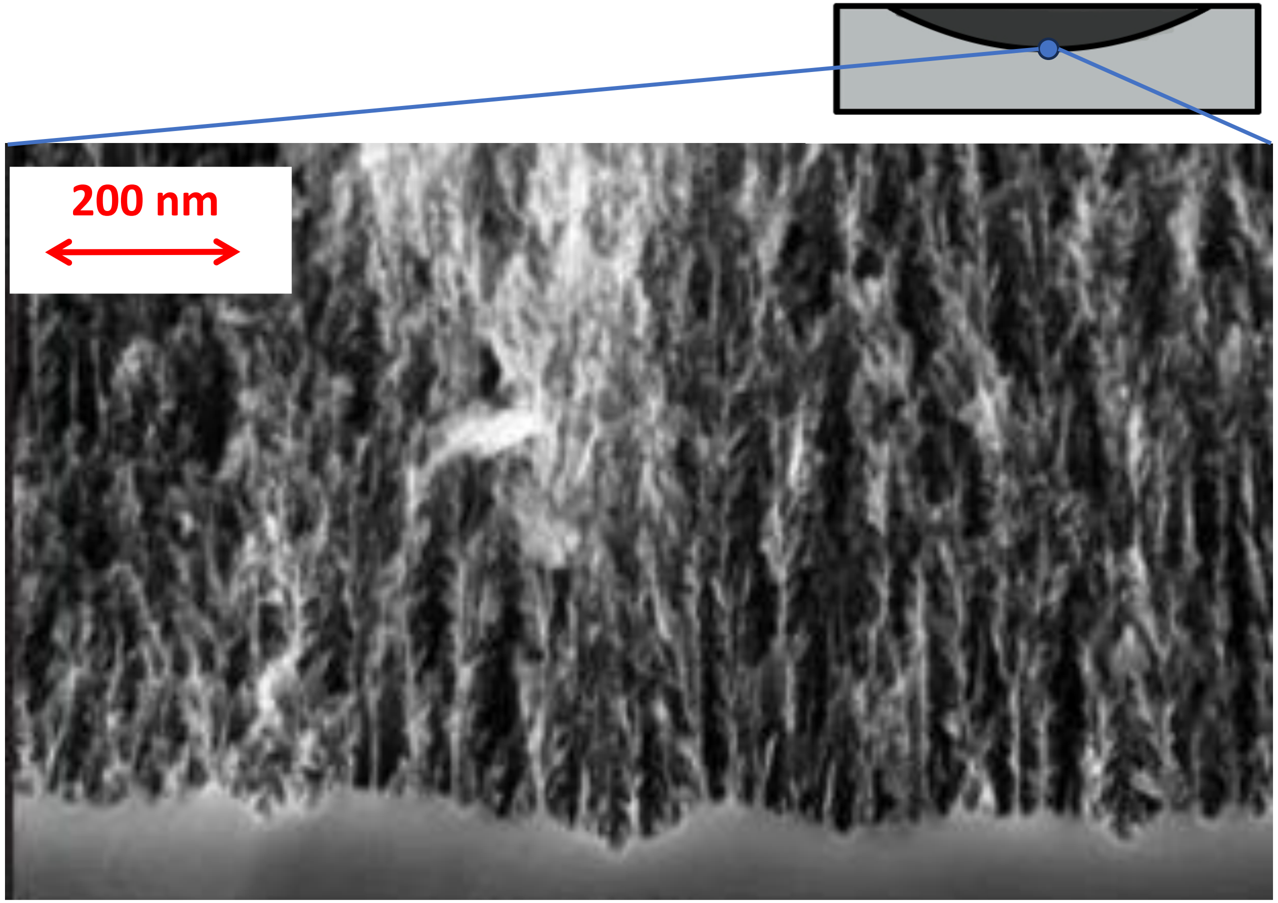


Choice of parameter in single layer

- The minimal current density is set to 20 mA/cm^2 to ensure the proper thickness of the PSi. This density corresponds to a diameter of 15 nm which is sufficient to obtain the EDL overlap as the Debye length is around 10-20 nm.
- The maximal current density is set to 100 mA/cm^2 to avoid detachment problems and electropolishing. This density corresponds to a diameter of 40 nm.
- The number of cycles depends directly on the script used as explained previously.
- The thickness is set to 50 μm. As explained in section 4.1.3, the electrical resistance of the channel is proportional to its length. Additionally, detachment and cracks were more frequently observed for longer pores.



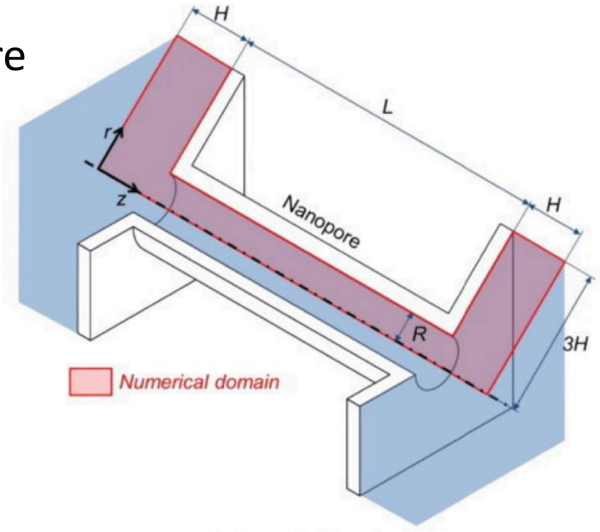
Top view SEM image of PSi



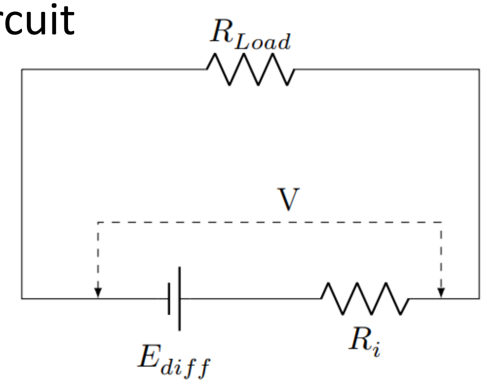
Cross sectional view SEM image of PSi

Simulation model

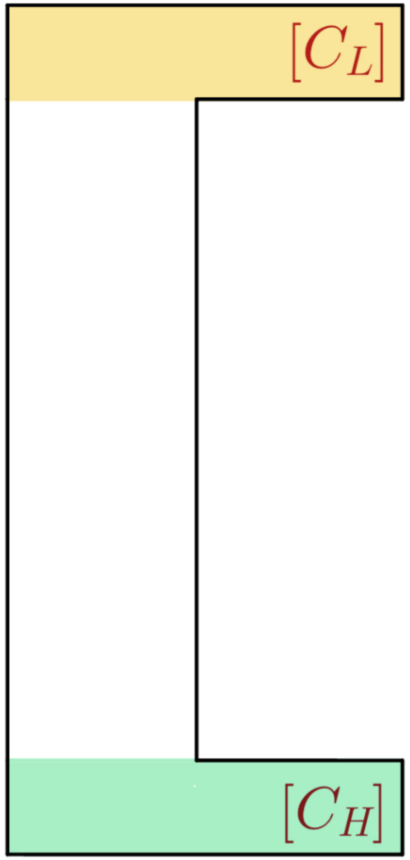
- Domain: 2D half pore



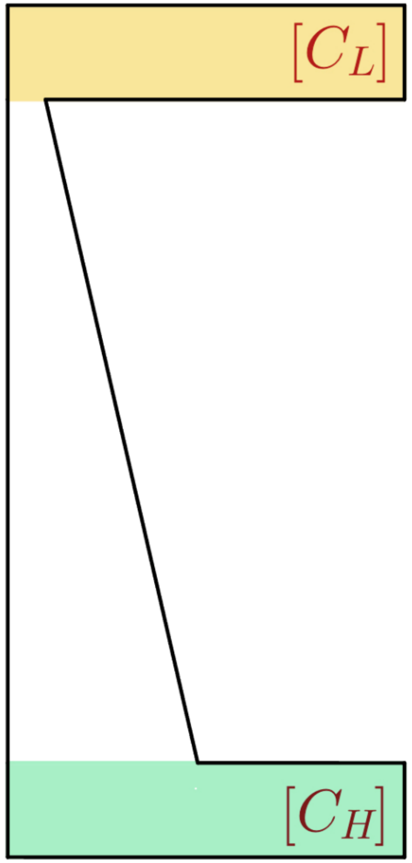
- Equivalent electrical circuit



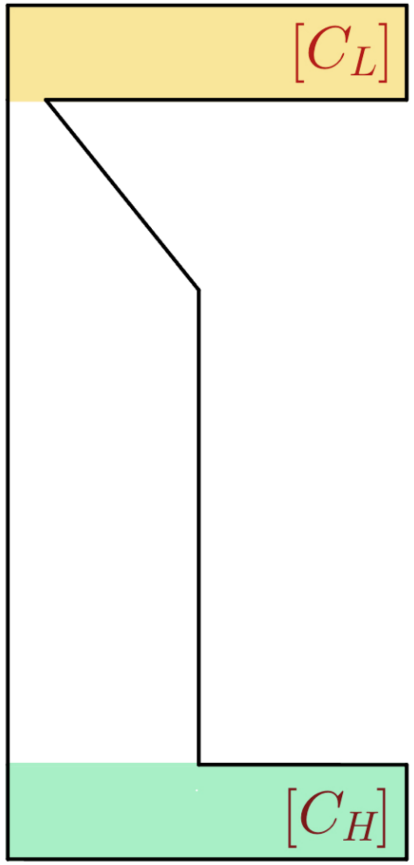
Cylindrical



Conical



Pencil



μRED/nRED with nano-structured material

Salinity ratio	Nanochannels/nanopores type	Power density (W/m^2)	Reference	Year
1000	Track-etched conical nanopore	20-2600	[10]	2010
1000	Track-etched conical nanopore	8.3-14.3	[6]	2011
1000	Nanochannels formed by packed nanoparticles	2.82	[22]	2013
1000	Nanochannels formed by packed nanoparticles	0.02	[23]	2015
1000	Silica nanochannels	7.7	[5]	2010
50	Hybrid membrane of coating BCP on PET substrate with conical nanochannels	0.35	[47]	2015
50	Nanochannels in graphene oxide	0.77	[48]	2016
30	Polyelectrolyte coated anodic aluminium oxide	0.017	[24]	2016
10	Silica coated Anodic alumina nanopores	0.007	[25]	2013
10	Silica coated on alumina substrate	0.001	[26]	2016

Single of limited number of nanopore → low net energy

Membrane with large density of nanopores → higher net energy

Surface material silica often used

Need for porous membranes for realistic energy supply