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

6ièmes journées SemiConducteurs et Oxyde Poreux

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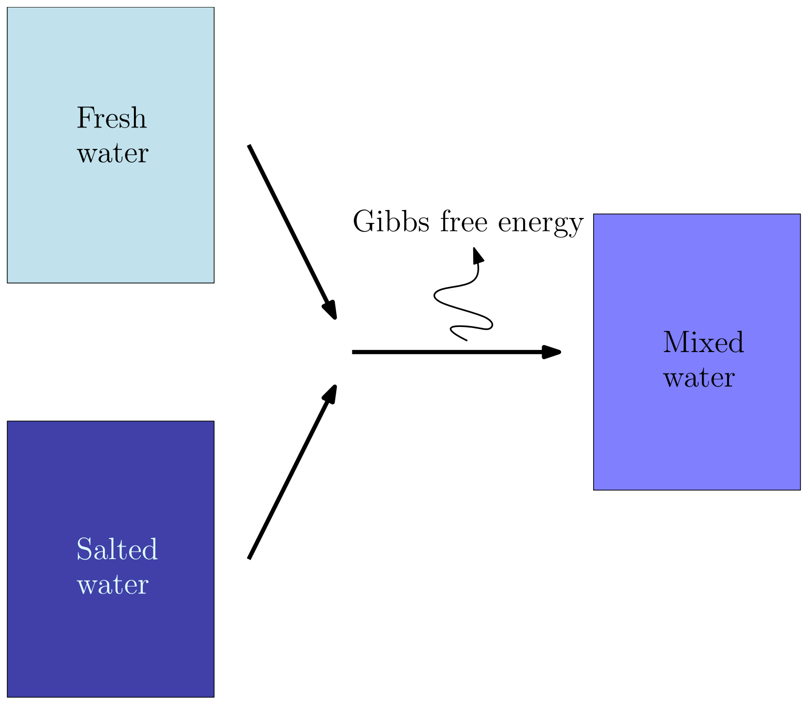
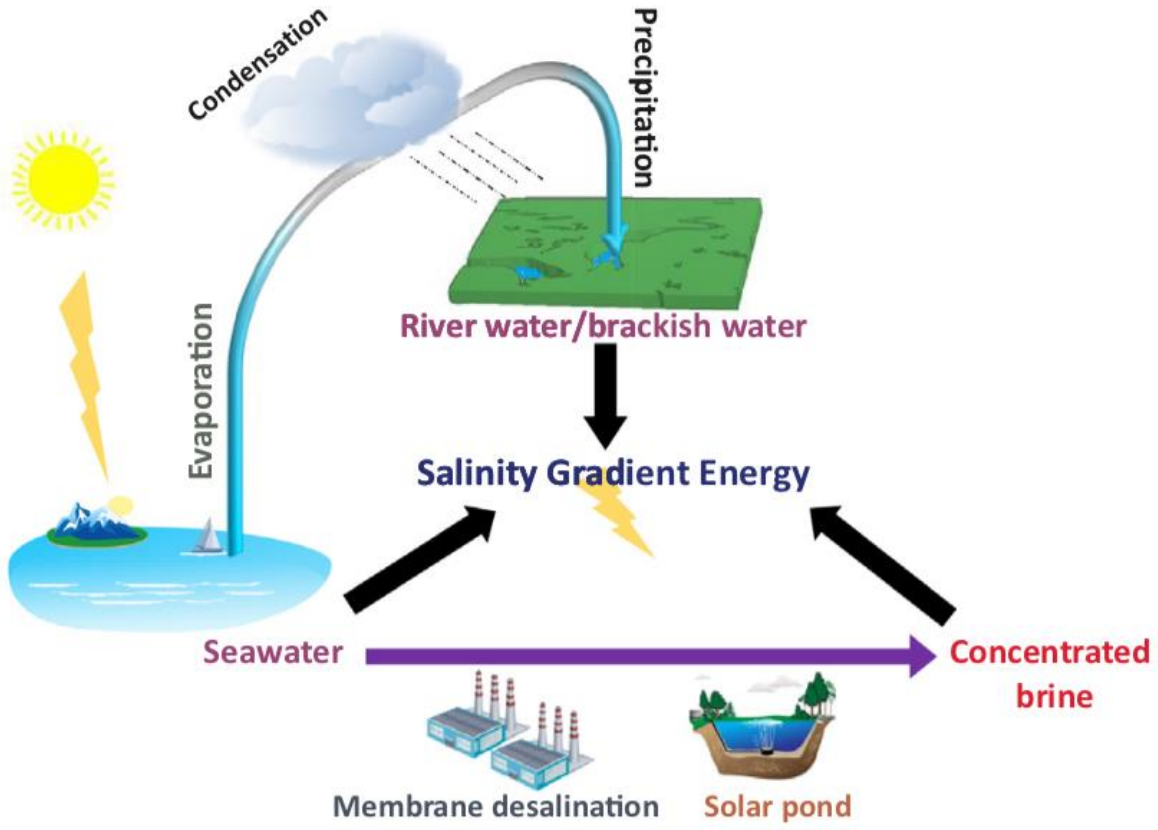
UCLouvain

icteam

Blue energy

Theoretically: $1\mathrm{m}^3$ fresh water+ salted water→ 2.3 MJ of Gibbs free energy, continuously with no CO_2 production!

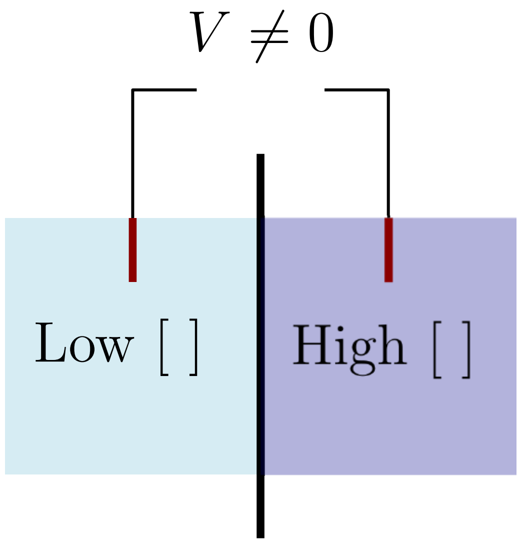




Large quantities available and renewable management possible

RED principle

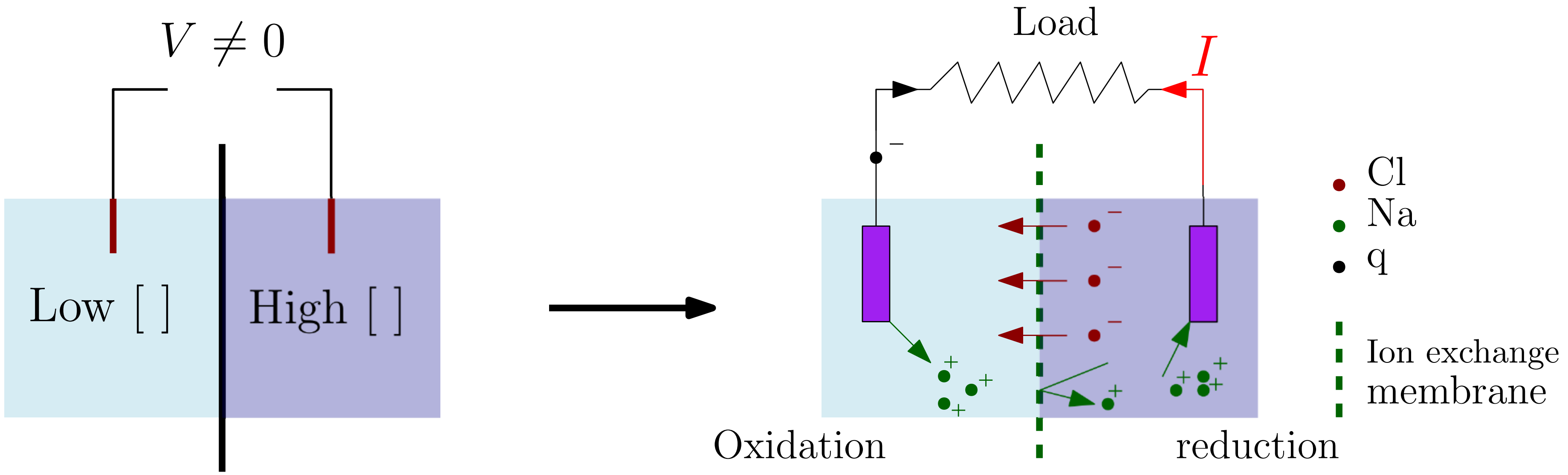
- Reverse electrodialysis: harvesting blue energy (Gibbs Free energy)

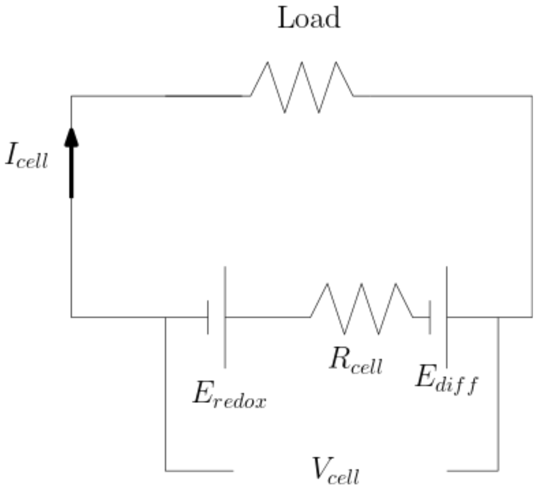


V=tens of mV

RED principle

- Reverse electrodialysis: harvesting blue energy (Gibbs Free energy)





Technology based on **ion selective membranes**

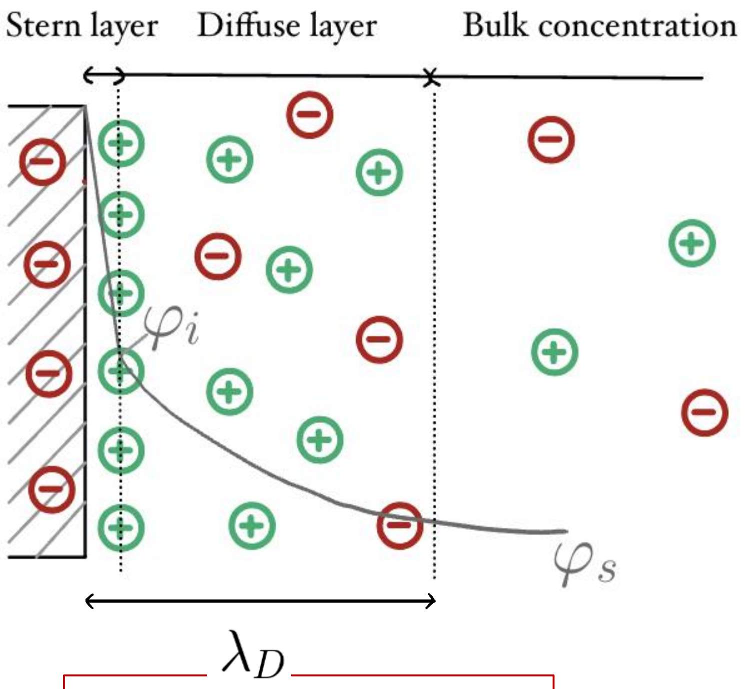
- High selectivity=high Ediff
- Low membrane ionic resistance=high *I*cell

Porous silicon 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

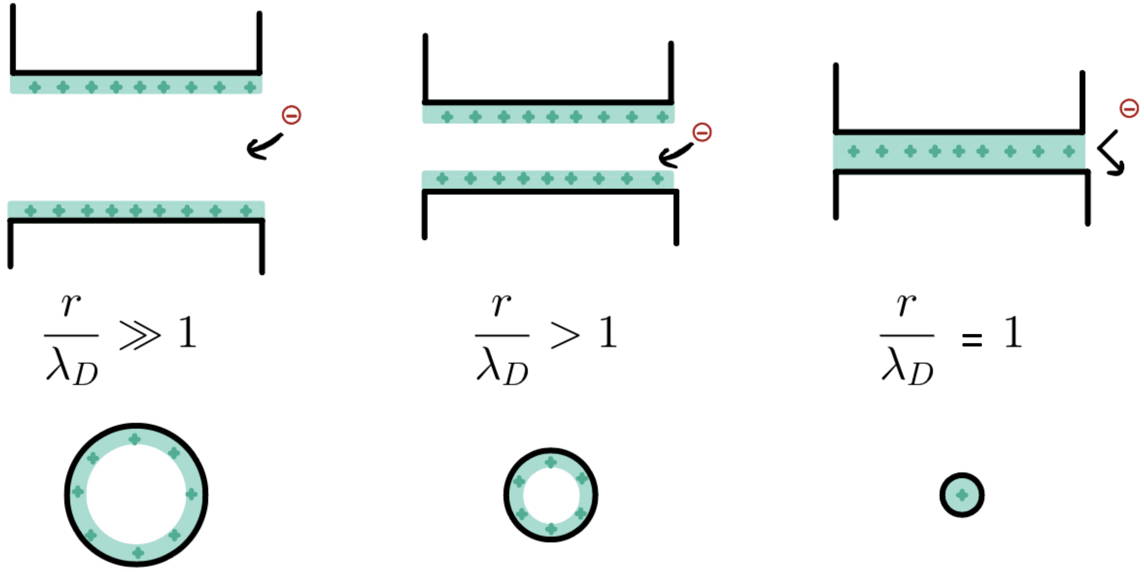
Selectivity through EDL overlap and Debye length

Electrical double layer (EDL)



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

Electrical double layer overlap



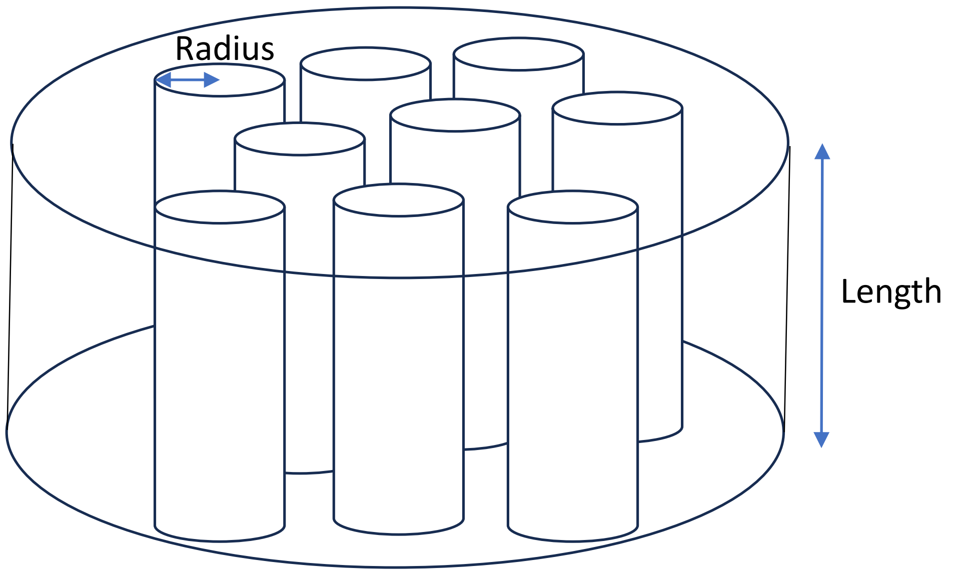
- C_i = 1mM → λ_D ~ 10 nm
- C_i = 0.1 mM → λ_D ~ 30 nm

Good selectivity with nanopores

Trade-off between selectivity and current

Radius ↗

- Selectivity ↘
- R_{elec} ↘
- Ionic current ↗



Length ↗

- R_{elec} ↗
- R_{meca} ↗

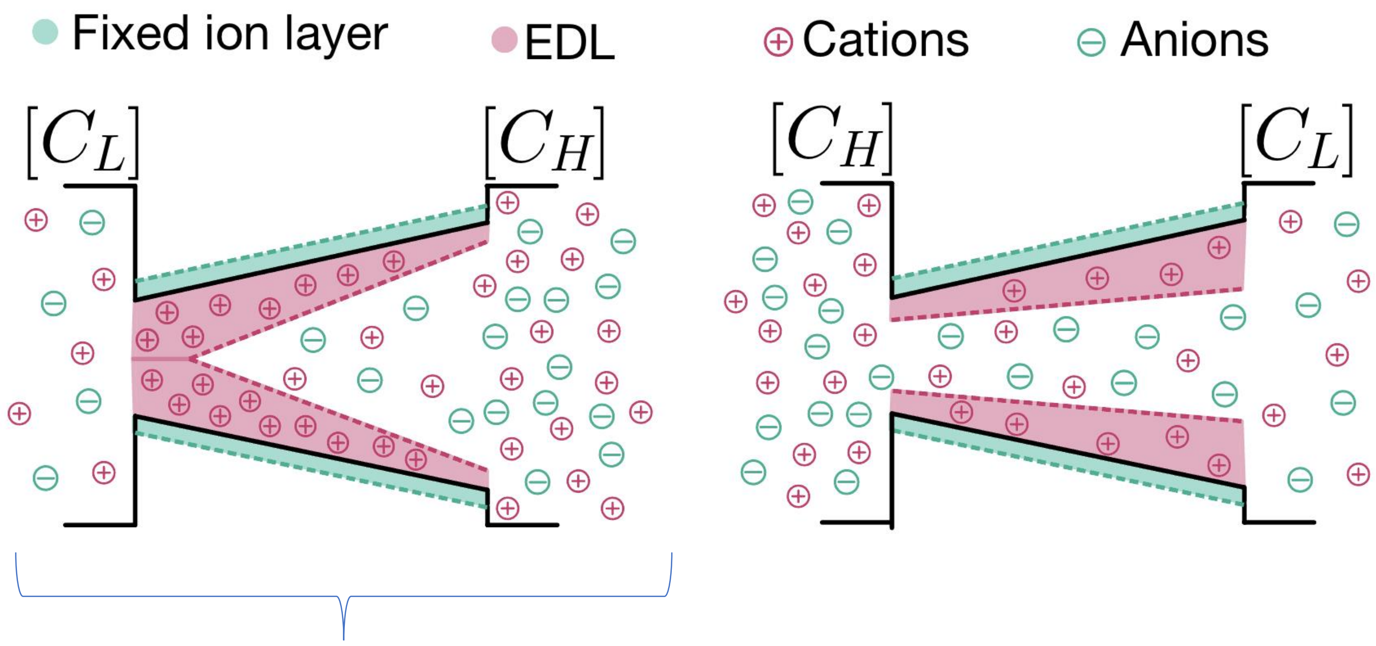
How to obtain selective, efficient and strong membranes?

Conical pores compared to smaller radius cylindrical pores

Potential of conical pores :

- Similar selectivity
- Higher ionic current
- Lower R_{elec}
- Weaker membrane

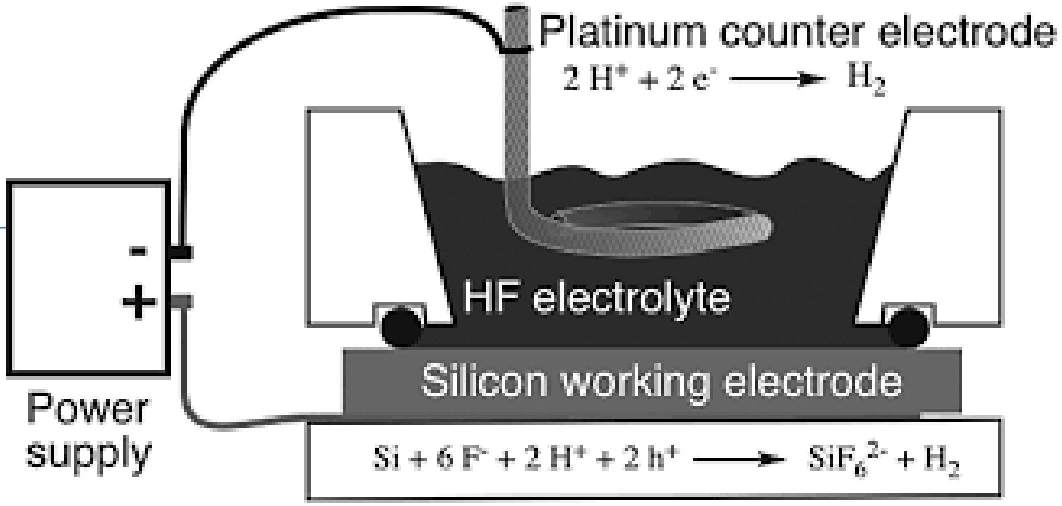
Theoretical asymmetry of EDL overlap:



Ideal selectivity situation

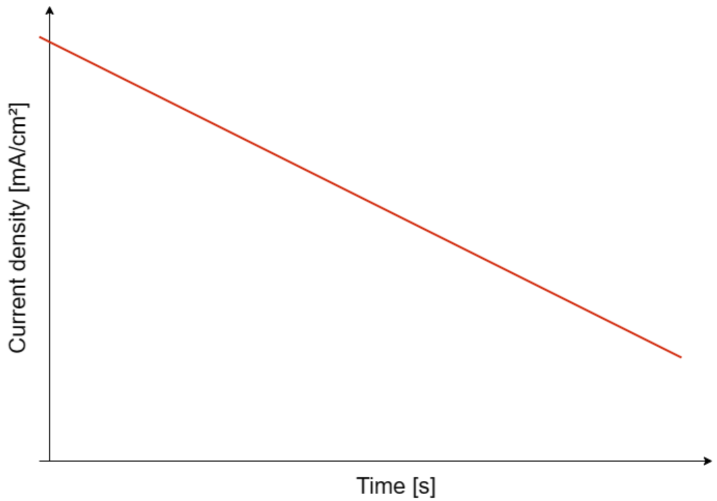
Fabrication of conical pores in porous silicon

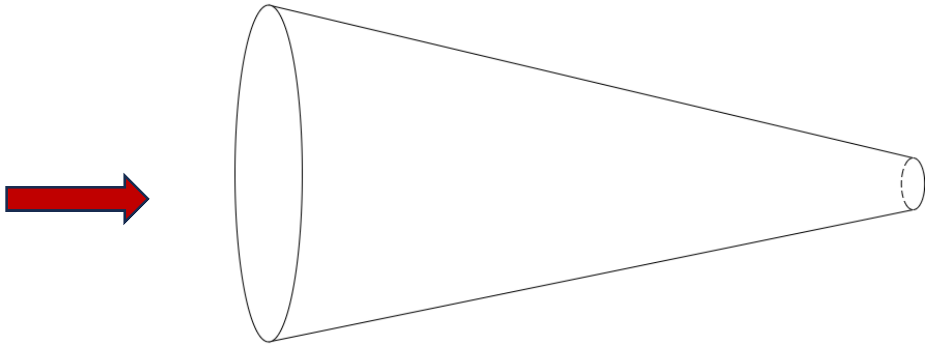
Schematic of a two-electrode electrochemical cell [2]



Influence of :

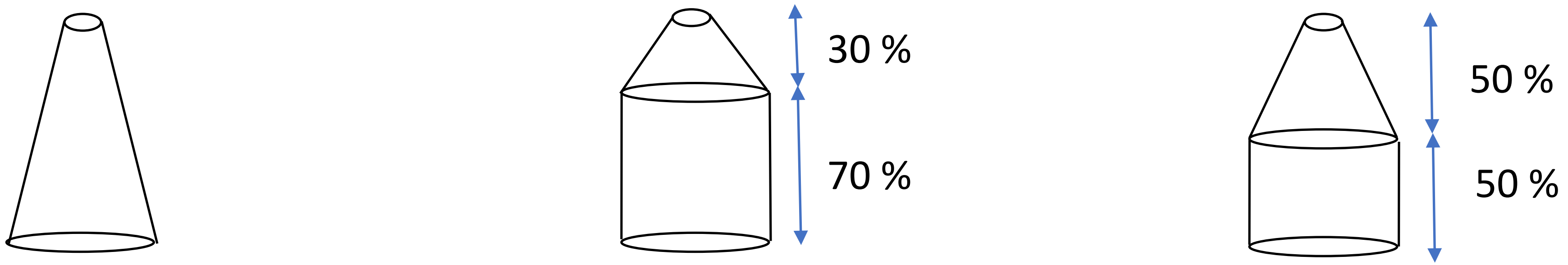
- Current density
  - Pore radius
  - Porosity
- Number of cycles
  - Membrane thickness





Conical shape pore

Main objective : study three different membrane topologies

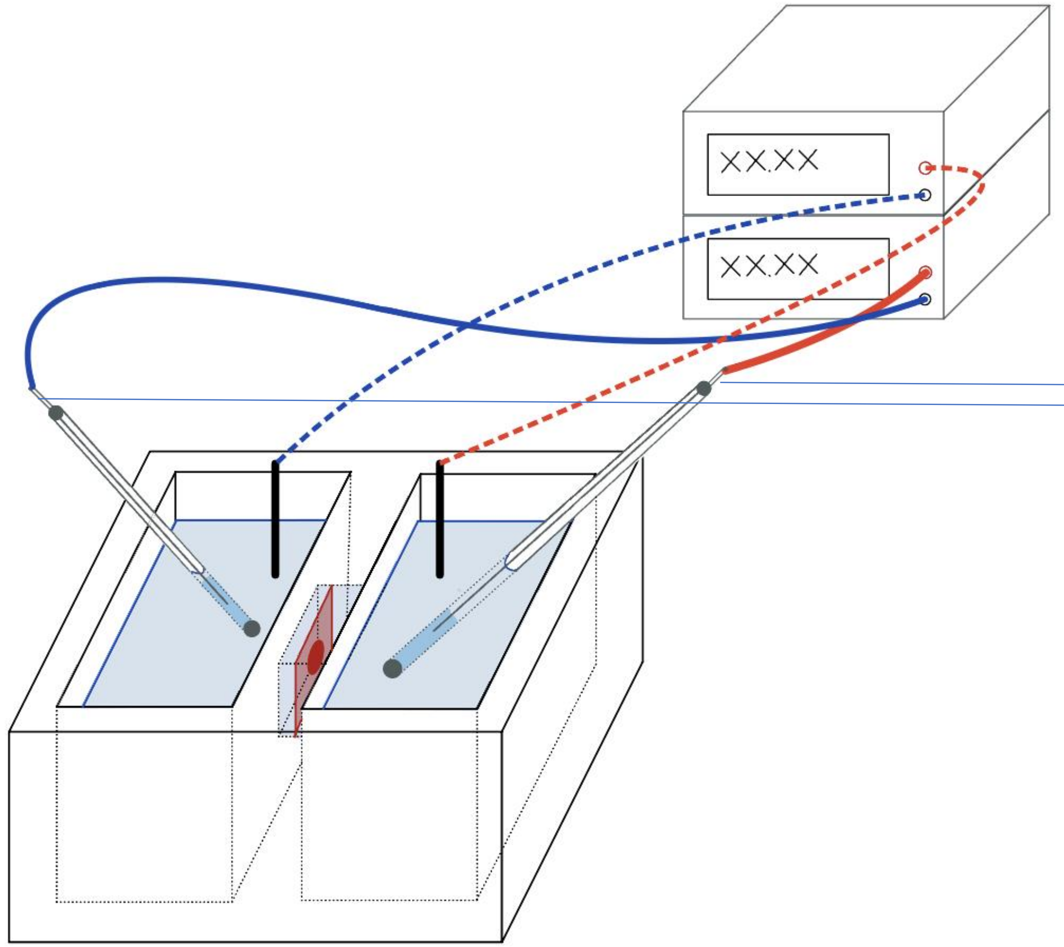


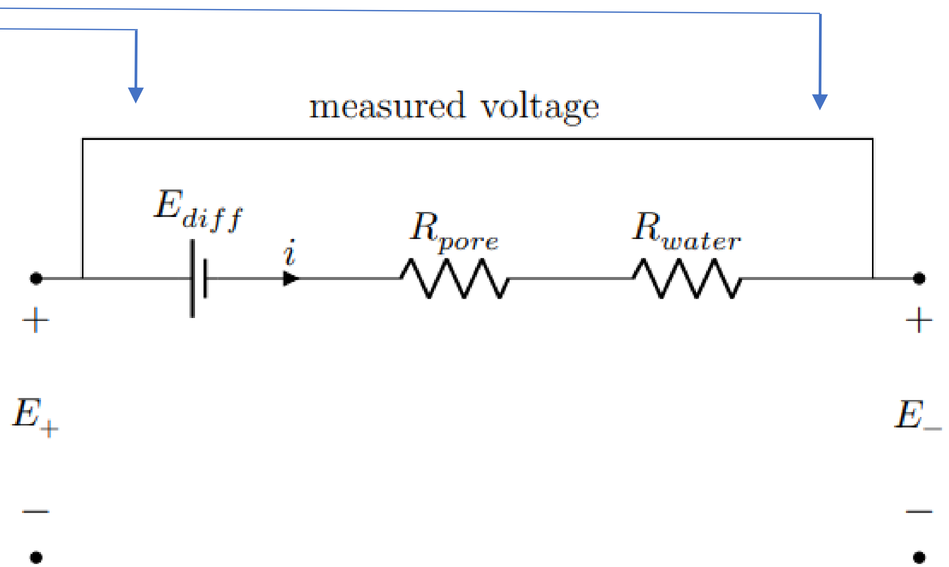
	CONICAL	PENCIL 70-30	PENCIL 50-50
Selectivity	✓	✓	✓
R_{elec}	✗	✓	✓
R_{meca}	✓	✗	✓

Experimental set-up

4 situations : 3 measures each

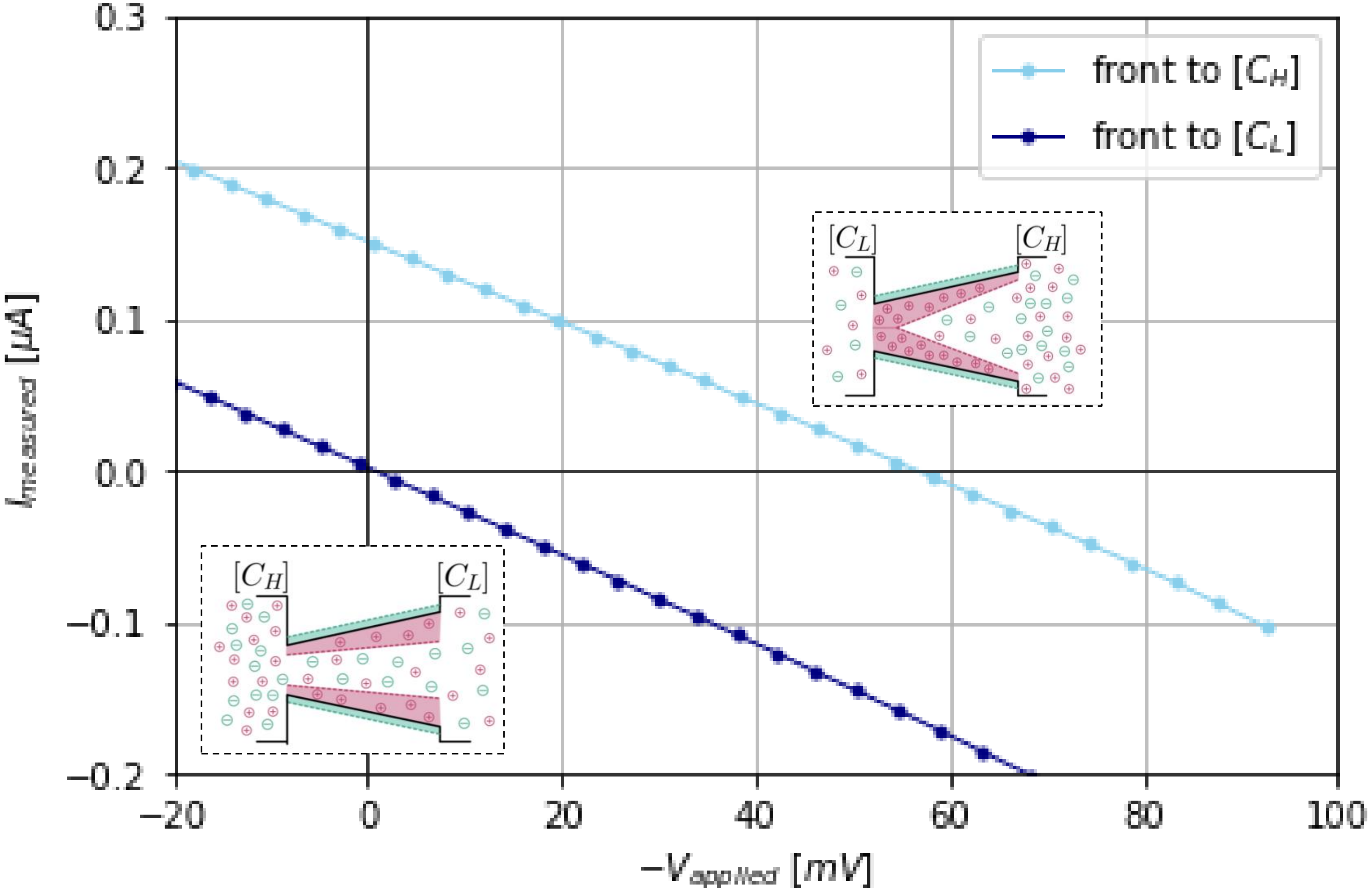
- 0.1 mM vs 1 mM : ideal
- 0.1 mM vs 1 mM : inverse
- 1 mM vs 10 mM : ideal
- 1 mM vs 10 mM : inverse





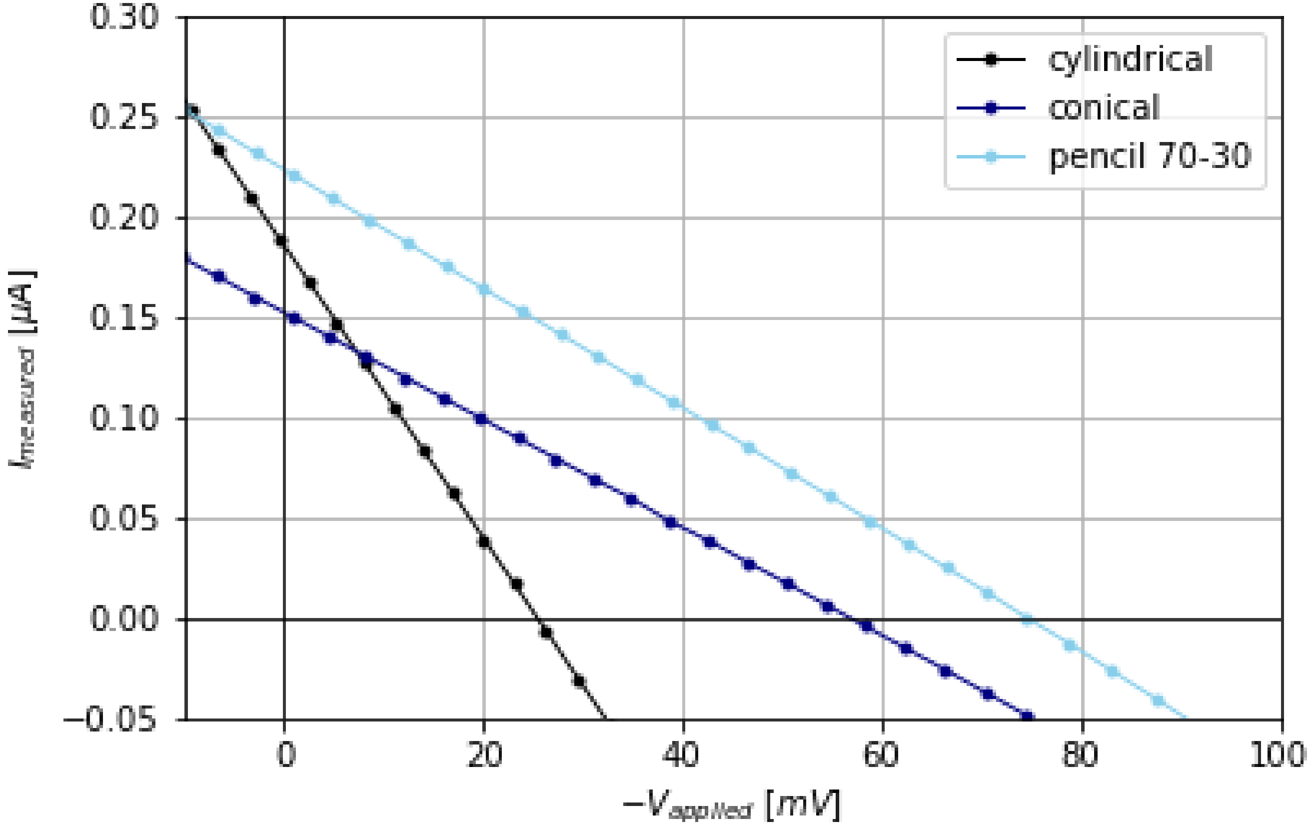
EDL overlap asymmetry

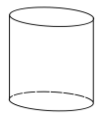
I-V curves for a conical membrane with concentrations at 1 mM and 0.1 mM



Topology impact : Maximal power density

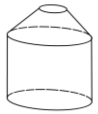
Experimental results for different topologies





0.42 mW/m²

0.677 mW/m²



1.32 mW/m²

➢ $P_{max,cyl} < P_{max,conic} < P_{max,pencil}$

Important findings

PSi CEM
few mW/m²

CONICAL
Trade-off
selectivity-current

PENCIL
Best performance

Pore geometry is an effictive parameter to improve RED efficiency

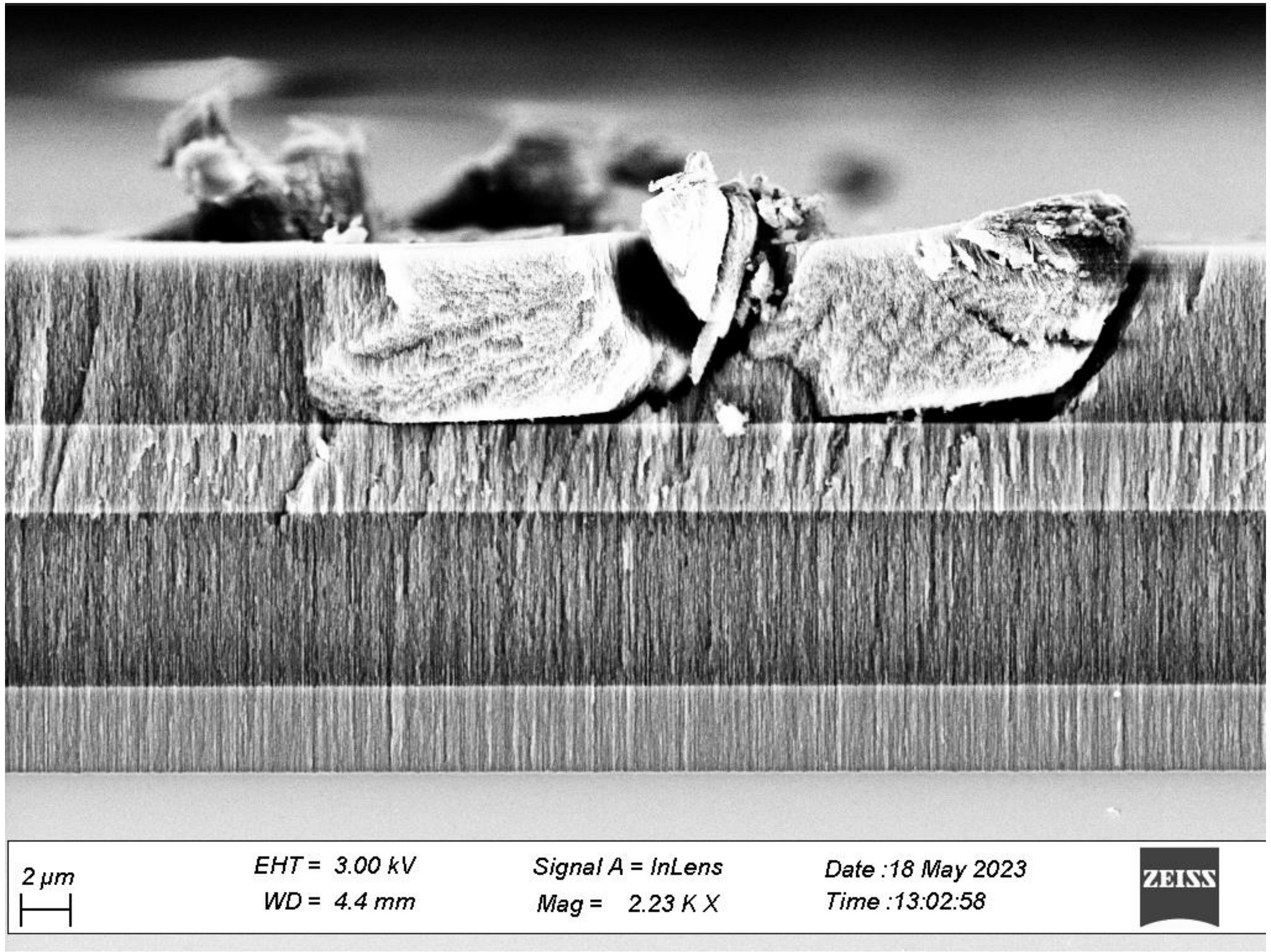
Futur works ideas

- Process of fabrication update
  - Porosification
  - Membrane release (DRIE)
- Surface charge density
  - Different material
  - Soft layer deposition [4]
  - Atomic layer deposition
- Other topologies

Futur works ideas

- ➢ Process of fabrication update
  - Porosification
  - Membrane release
- ➢ Surface charge density
  - Different material
  - Soft layer deposition [4]
  - Atomic layer deposition
- ➢ Other topologies

Cross sectional view of stratified PSi



Thank you for your attention !

Any questions ?

PSi CEM
few mW/m²

CONICAL
Trade-off
selectivity-current

PENCIL
Best performance

Pore geometry is an effictive parameter to improve RED efficiency

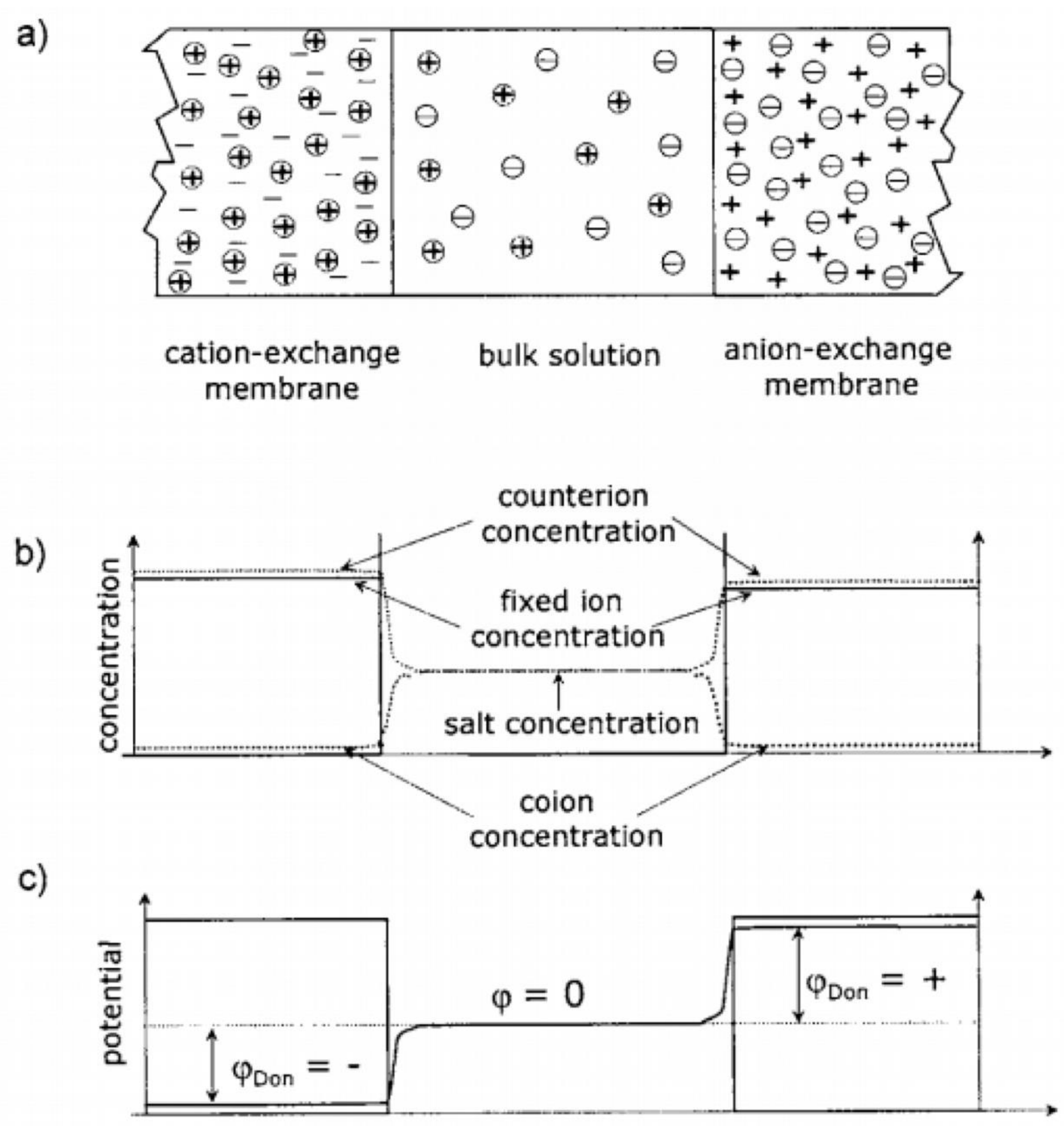
Bibliography

[1] R. Hanus, “Harvesting blue energy using porous silicon,” Ph.D. dissertation, Ecole polytechnique de Louvain, Université catholique de Louvain, 2019.

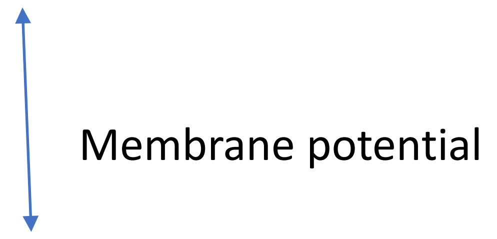
[2] M. J. Sailor, Porous Silicon in Practice. Wiley, 2011

[3] G. Scheen, “Metal electrode integration and palladium nanoparticule functionalization on a miniaturized macroporous silicon chemiresistor,” Ph.D. dissertation, Ecole polytechnique de Louvain, Université catholique de Louvain, 2015

[4] H. Dartoomi, M. Khatibi, and S. N. Ashrafizadeh, “Importance of nanochannels shape on blue energy generation in soft nanochannels,” Electrochimica Acta, vol. 431, p. 141175, 2022. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0013468622013329



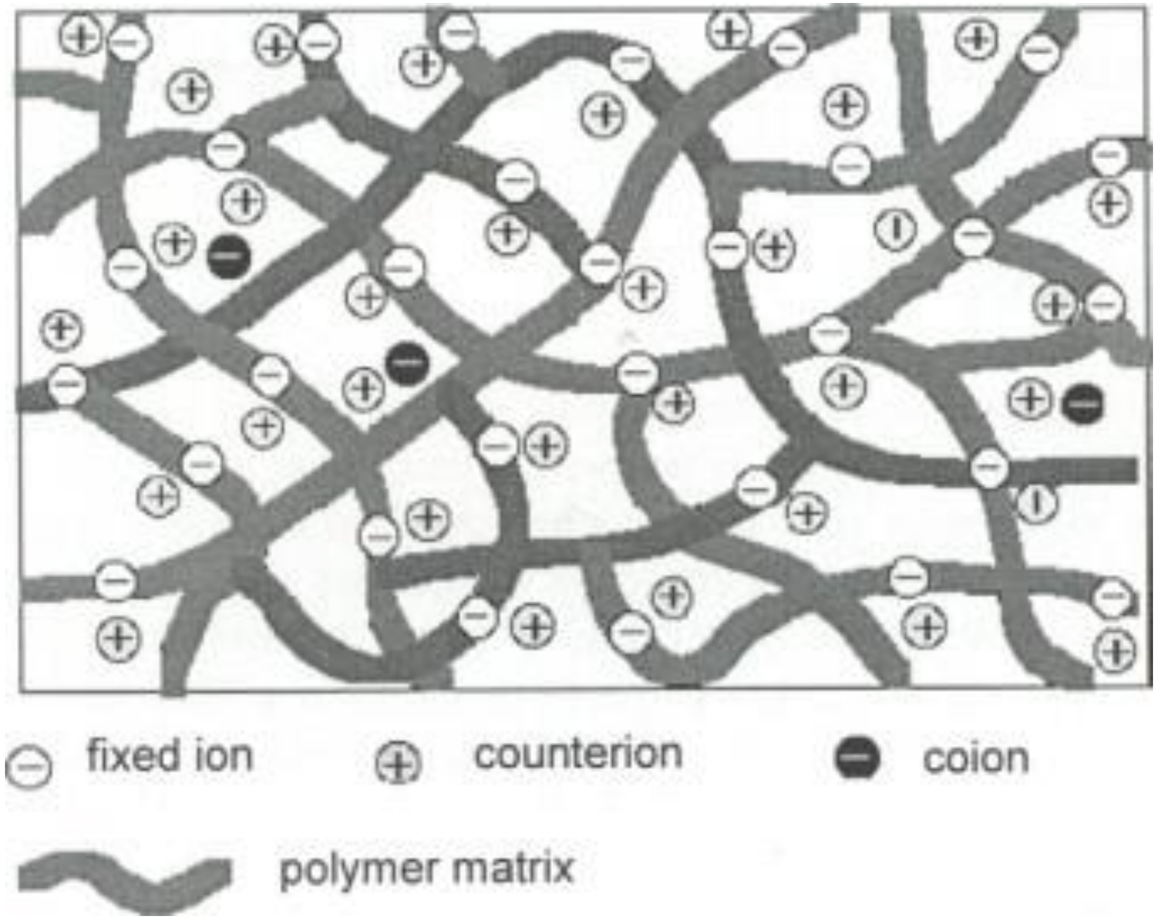
a)
cation-exchange membrane
bulk solution
anion-exchange membrane
b)
concentration
counterion concentration
fixed ion concentration
salt concentration
coion concentration
c)
potential
φ = 0
φDon = +
φDon = -



Membrane potential

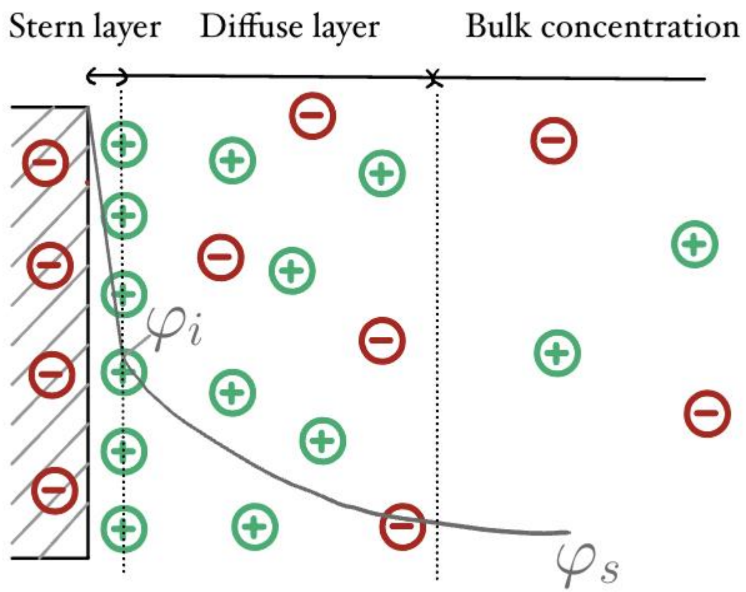
Polymer

Amount of counterion attached adaptable



PSi

Amount of counterion liberated depends on EDL



Commercial IEM

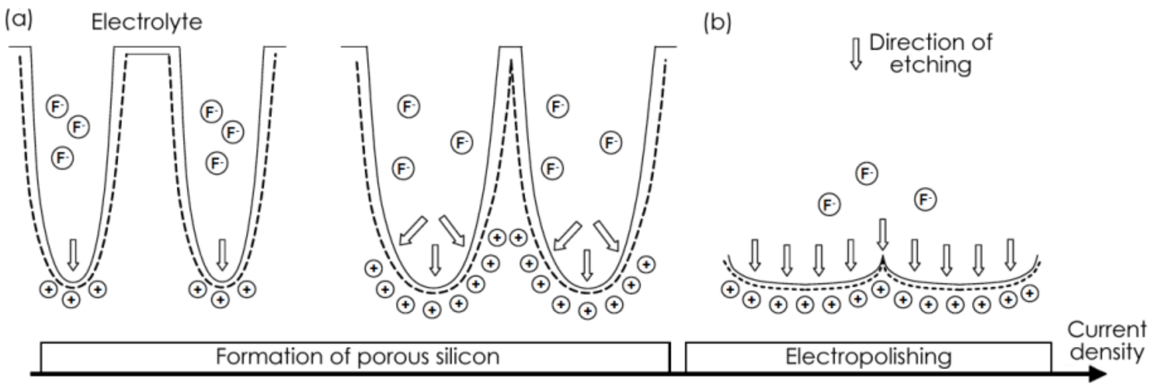
- Power : 0.3-4 W/m^2
- Selectivity : Up to 99%

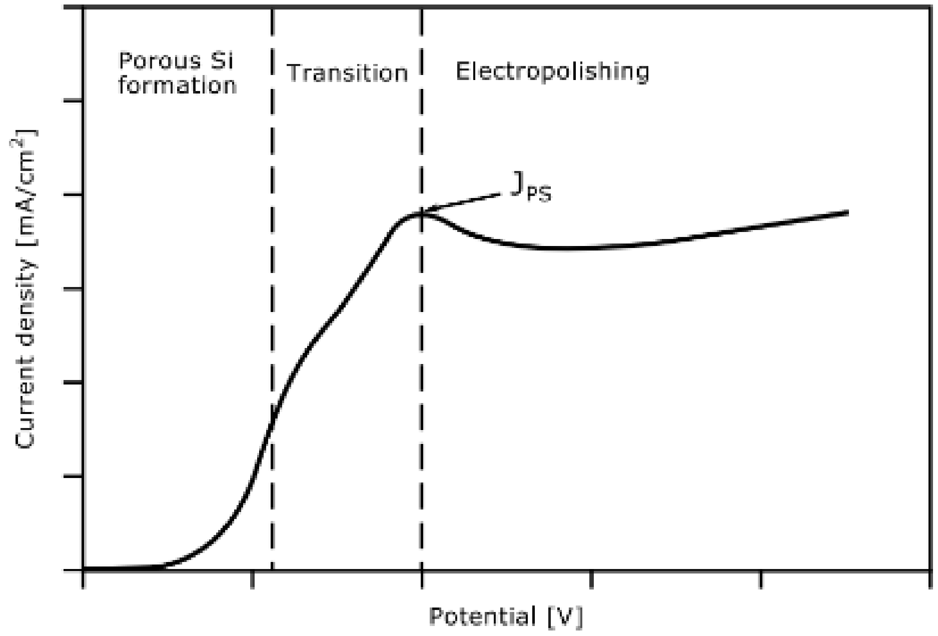
PSi cylindrical IEM

- Power : ~ 0.3 W/m^2
- Selectivity : 60-70%

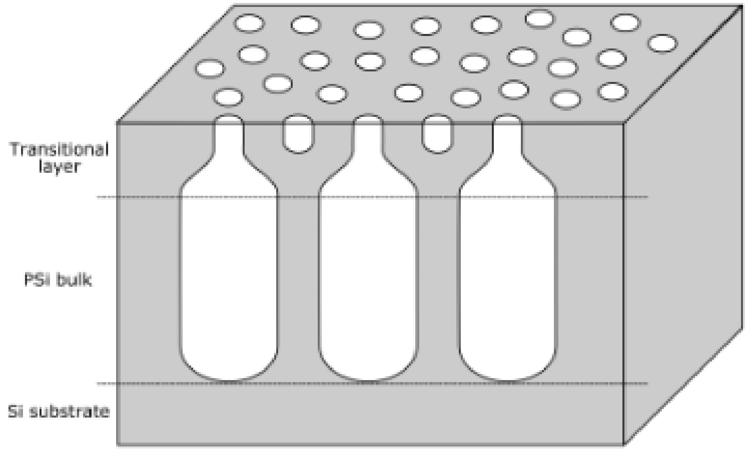
Pore parameters influence

Increasing of	Selectivity	Resistance	Current
Length of the pore	Decrease	Increase	Decrease
Radius of the pore	Increase	Decrease	Increase
Surface charge density	-	-	Increase
Concentration ratio	-	Increase	Increase
Concentration	Decrease	Decrease	Increase



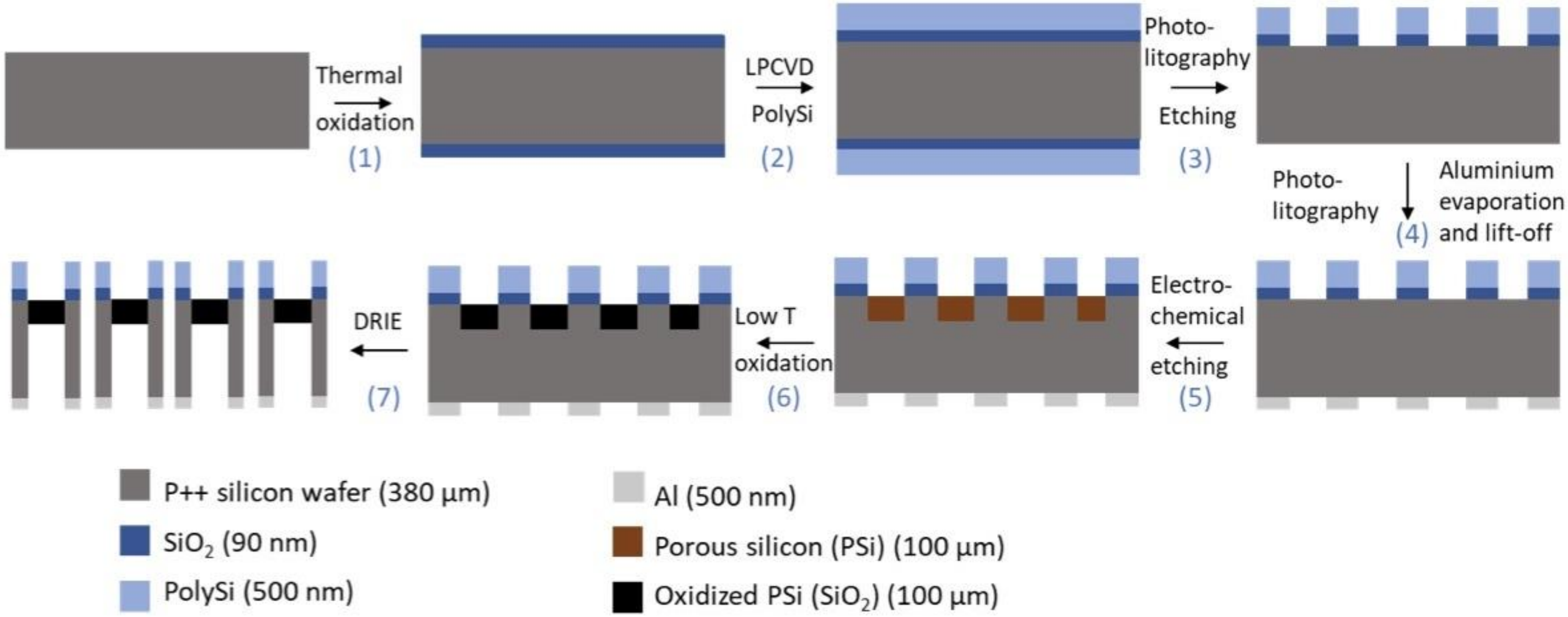


Increase of	Porosity	Etching rate	Critical current
HF concentration	Decreases	Decreases	Increases
Current density	Increases	Increases	-
Anodization time	Increases	Almost constant	-
Temperature	-	-	Increases
Wafer doping (p-type)	Decreases	Increases	Increases
Wafer doping (n-type)	Increases	Increases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

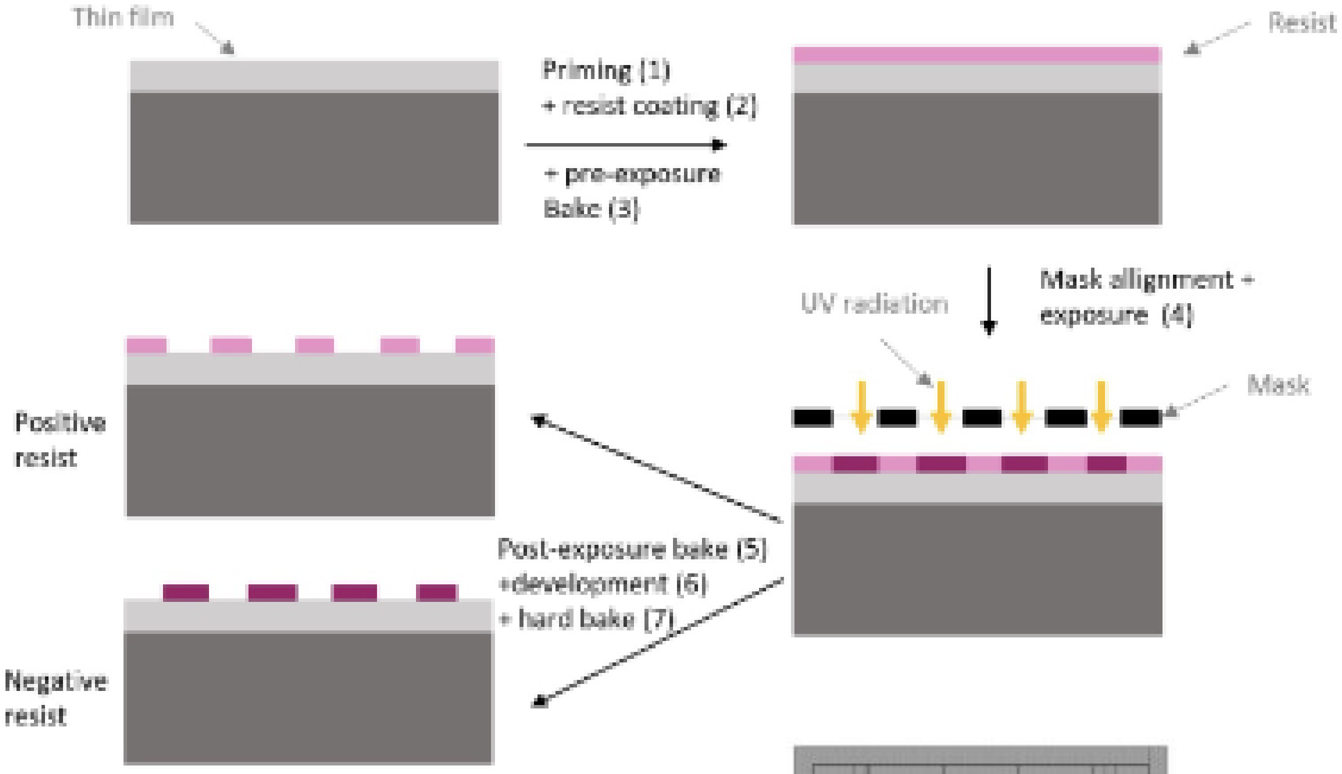


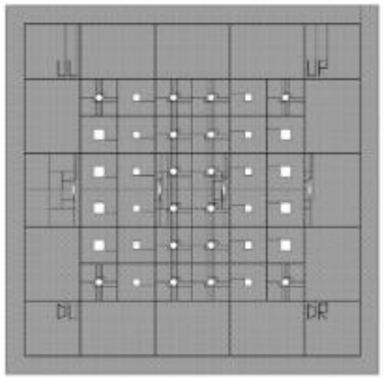
- Substrate: Si p++ boron, 0.8-0.9m Ω.cm
- Current density range: 100mA/cm^2→ 20mA/cm^2

Additional support : process

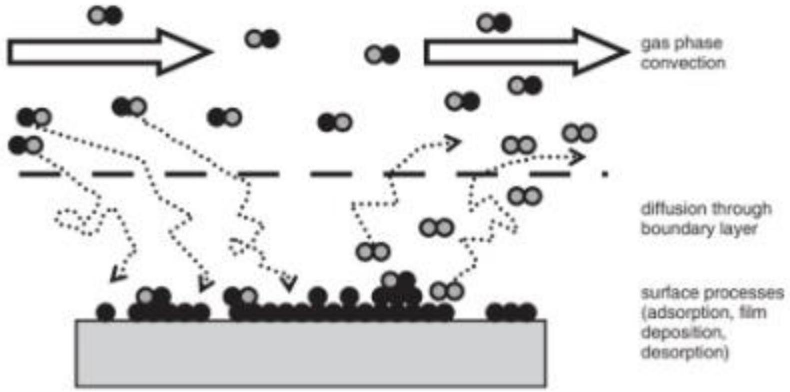


Lithographie

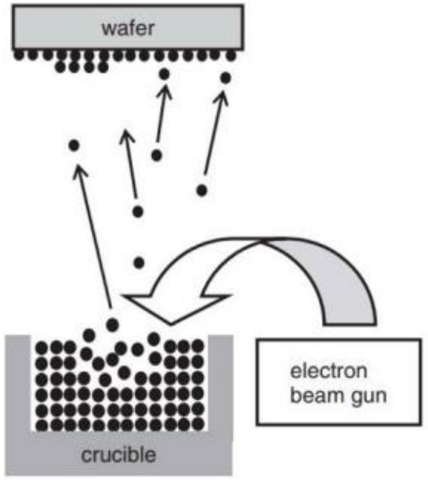




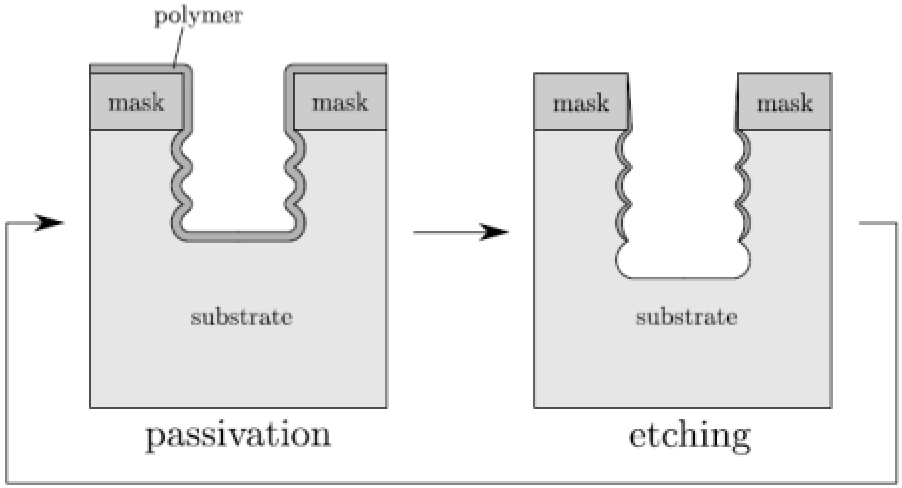
LPCVD



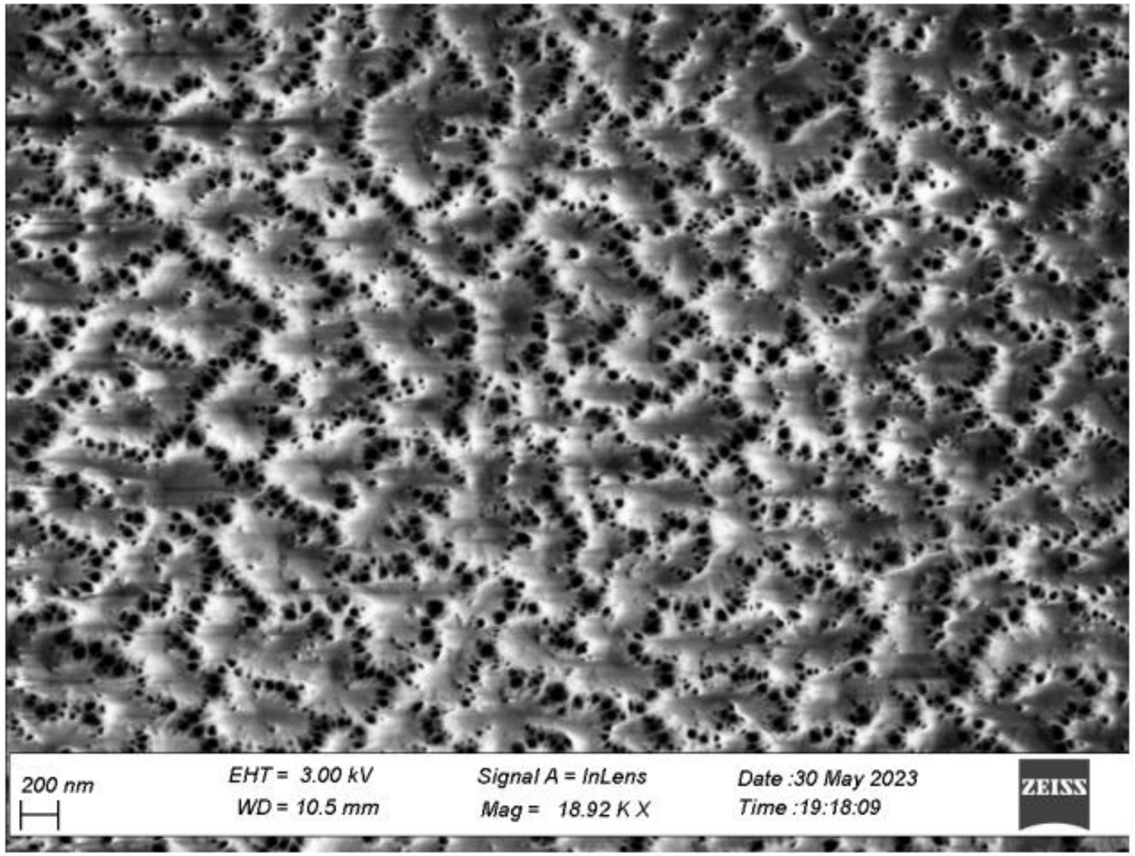
Alu e-beam



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

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

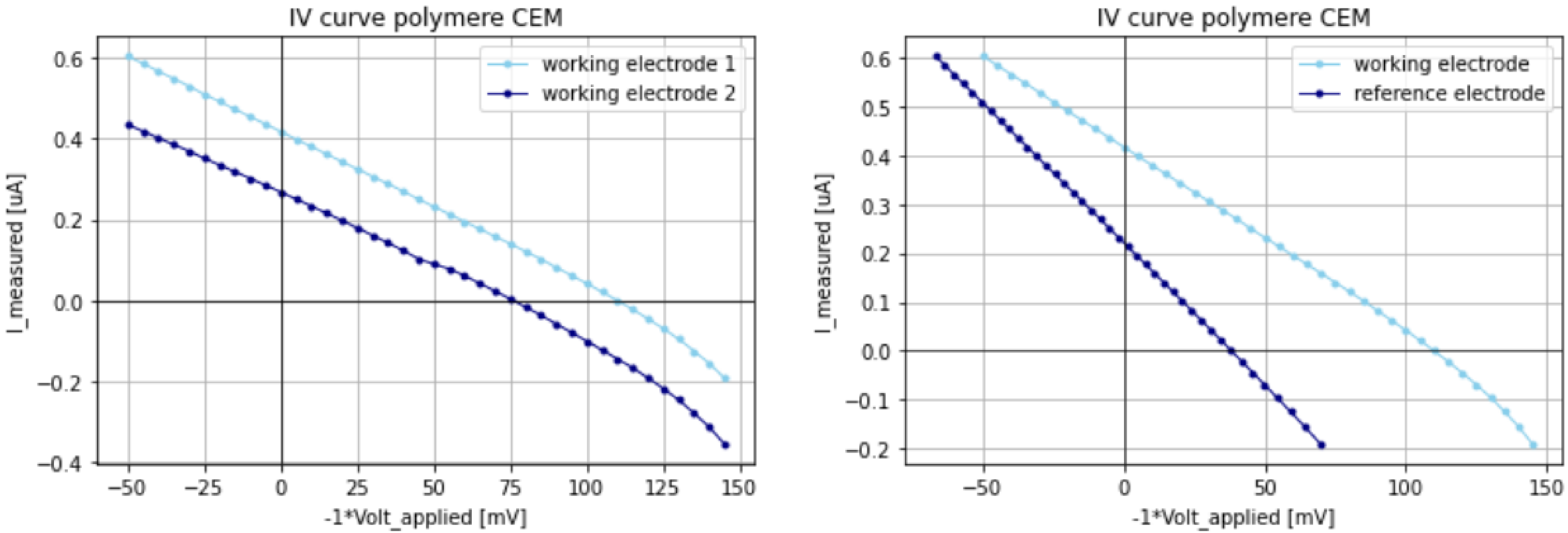
- Nernst modified : 2 ions

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

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

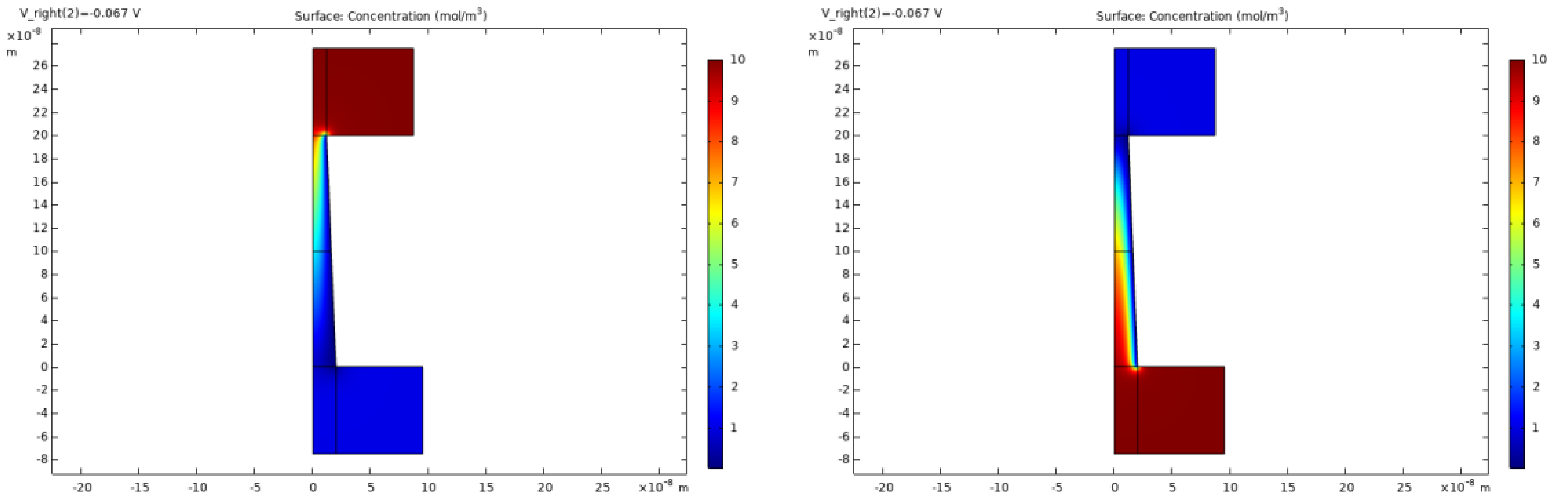
$$E_m = \frac{RT}{F} \ln\left(\frac{\sum_i^n P_{M_i^+}[M_i^+]_{\mathrm{out}} + \sum_j^m P_{A_j^-}[A_j^-]_{\mathrm{in}}}{\sum_i^n P_{M_i^+}[M_i^+]_{\mathrm{in}} + \sum_j^m P_{A_j^-}[A_j^-]_{\mathrm{out}}}\right)$$

Reference electrode



Standard deviation : 1 mV, 15 nA

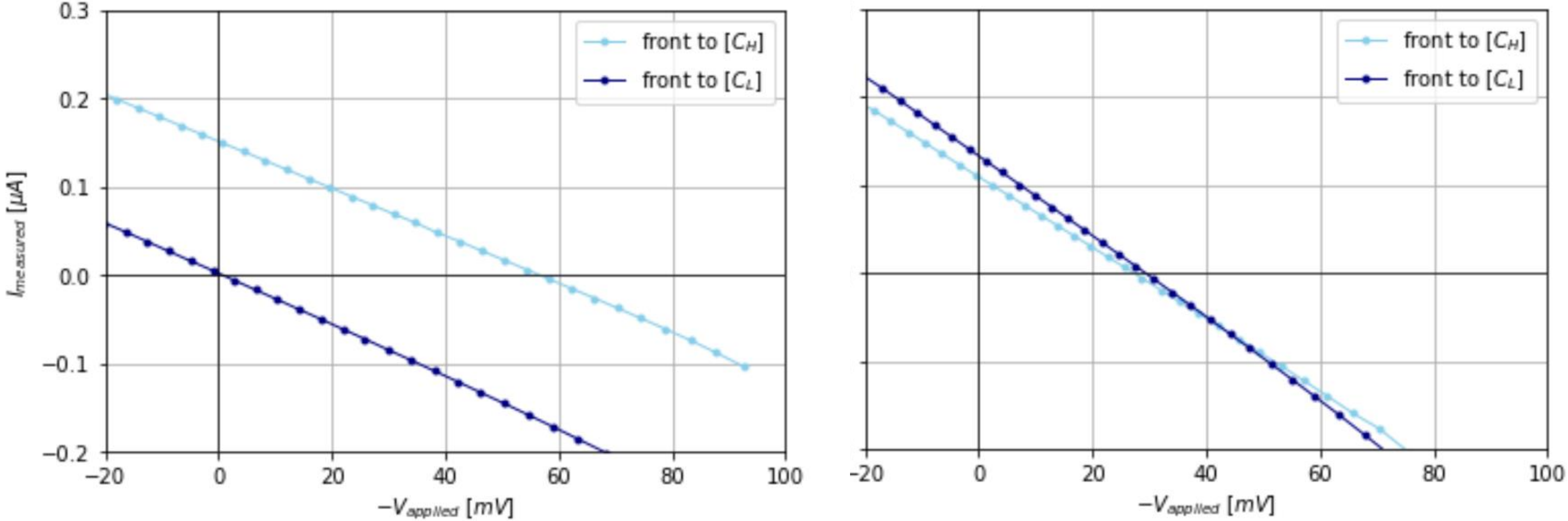
Concentration of anion in mol/m³
Blue = flow mainly due to cation = selectivity



Choice of parameter in single layer

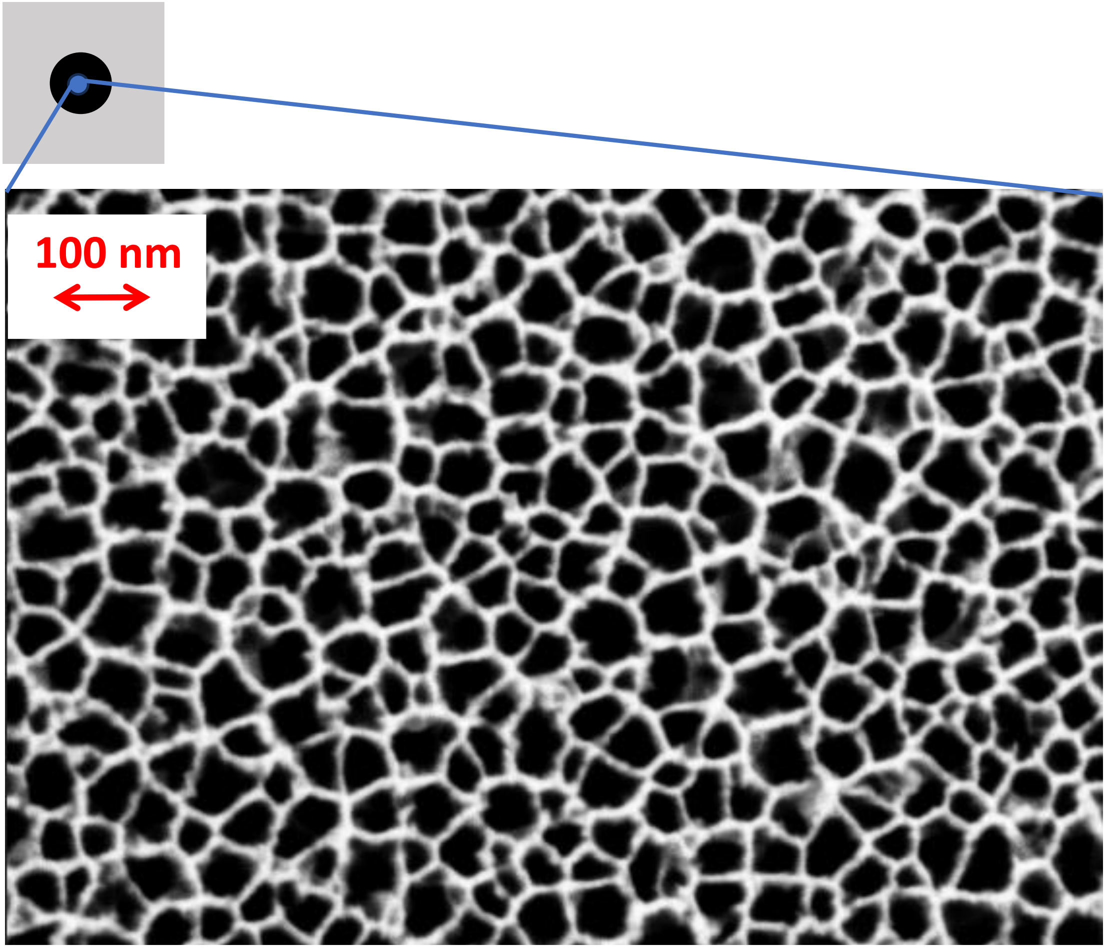
- The minimal current density is set to 20 mA/cm^2 to ensure the proper thickness of the PSi. This density corresponds to a diameter of 15 nm which is sufficient to obtain the EDL overlap as the Debye length is around 10-20 nm.
- The maximal current density is set to 100 mA/cm^2 to avoid detachment problems 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.

Concentration impact

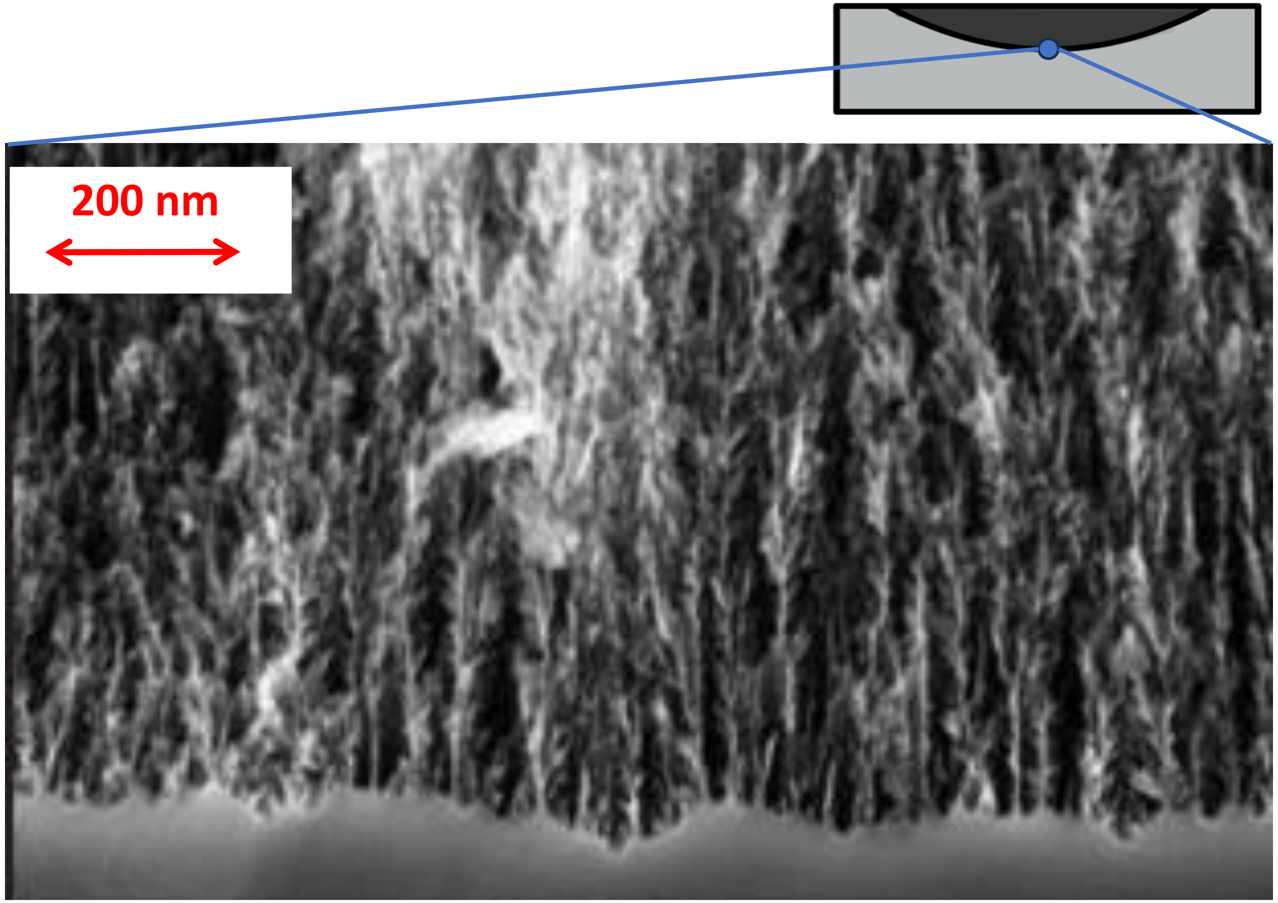


Summary results

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



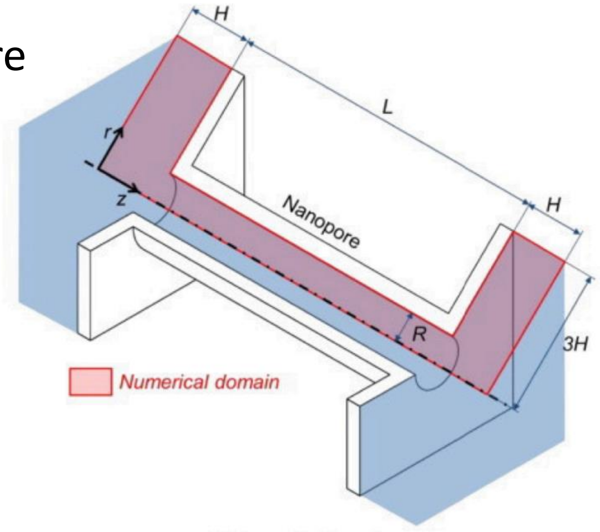
Top view SEM image of PSi



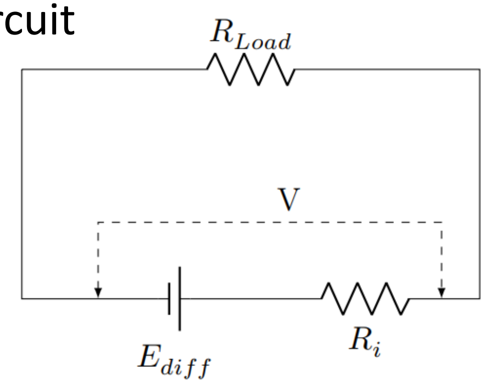
Cross sectional view SEM image of PSi

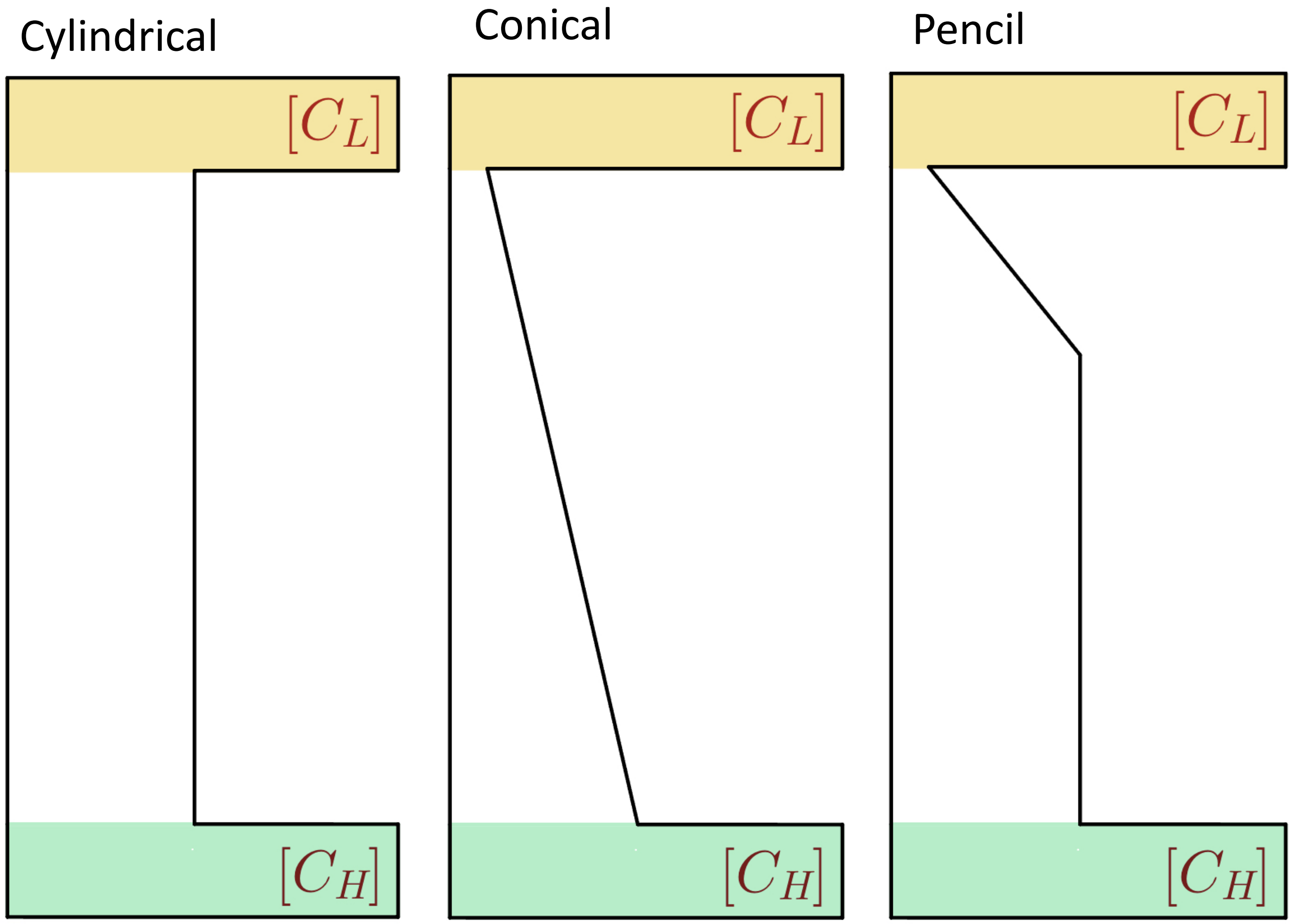
Simulation model

- Domain: 2D half pore



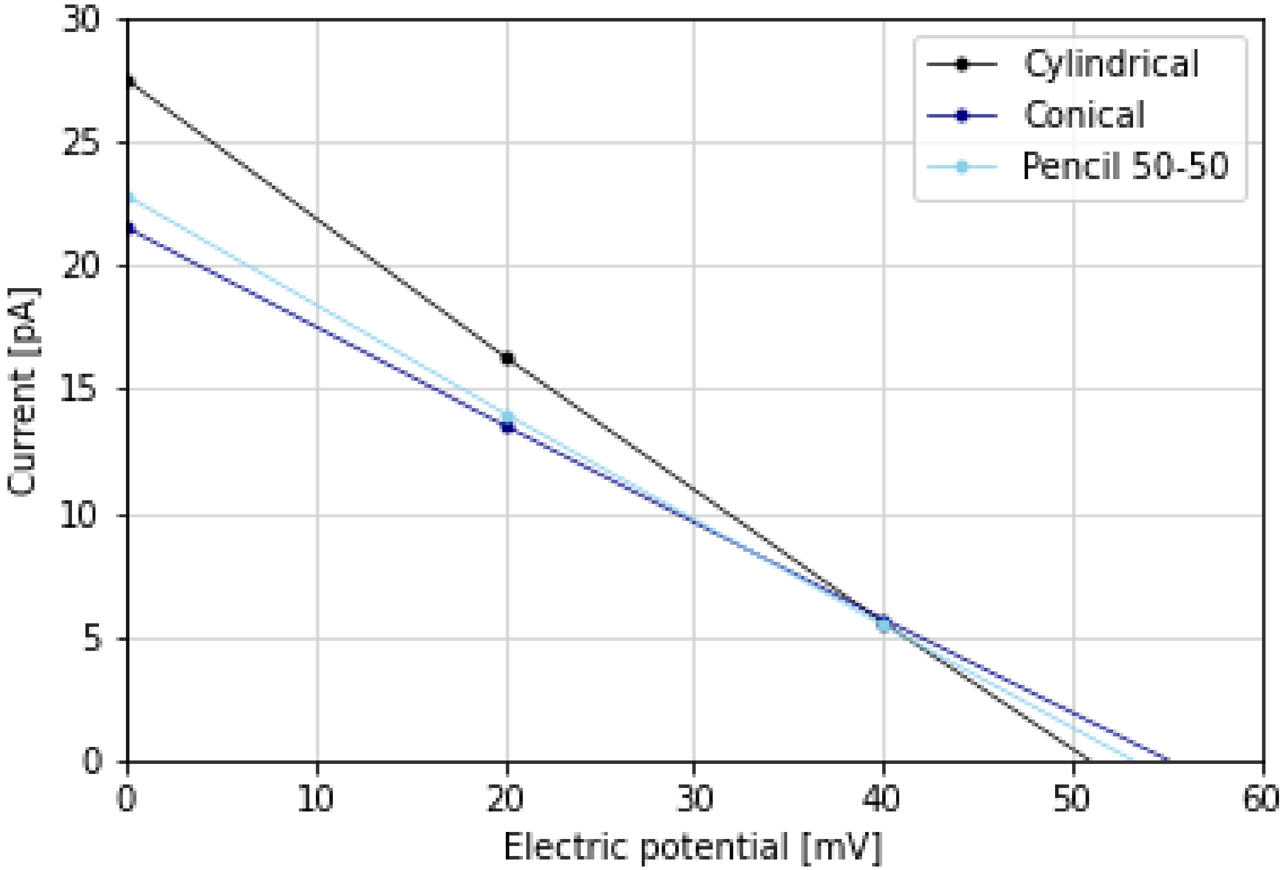
- Equivalent electrical circuit





Topology impact

- ➢ Numerical simualtion IV curves for a single pore in different shapes



[CH]=1 mM and [CL]=0.1 mM

trade-off selectivity-current

➢ **PENCIL SHAPE**