# NUMERICAL STUDY OF PORE SHAPE INFLUENCE ON POWER DENSITY IN POROUS SILICON MEMBRANES FOR REVERSE ELECTRODIALYSIS

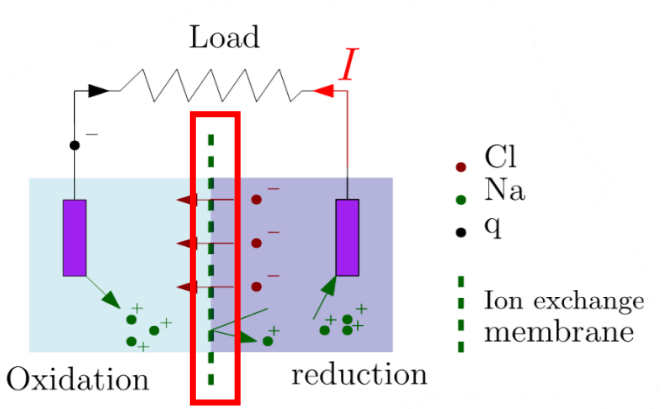
Author: **Romain HANUS*, Laurent A. FRANCIS***

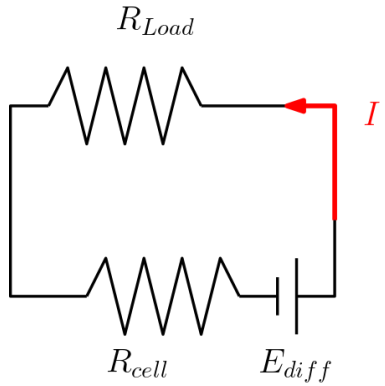
*ICTEAM Institute, UCLouvain, Belgium
romain.hanus@uclouvain.be

**Adelaide, Australia, April 15th to April 19th, 2025**

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

## RED cell




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

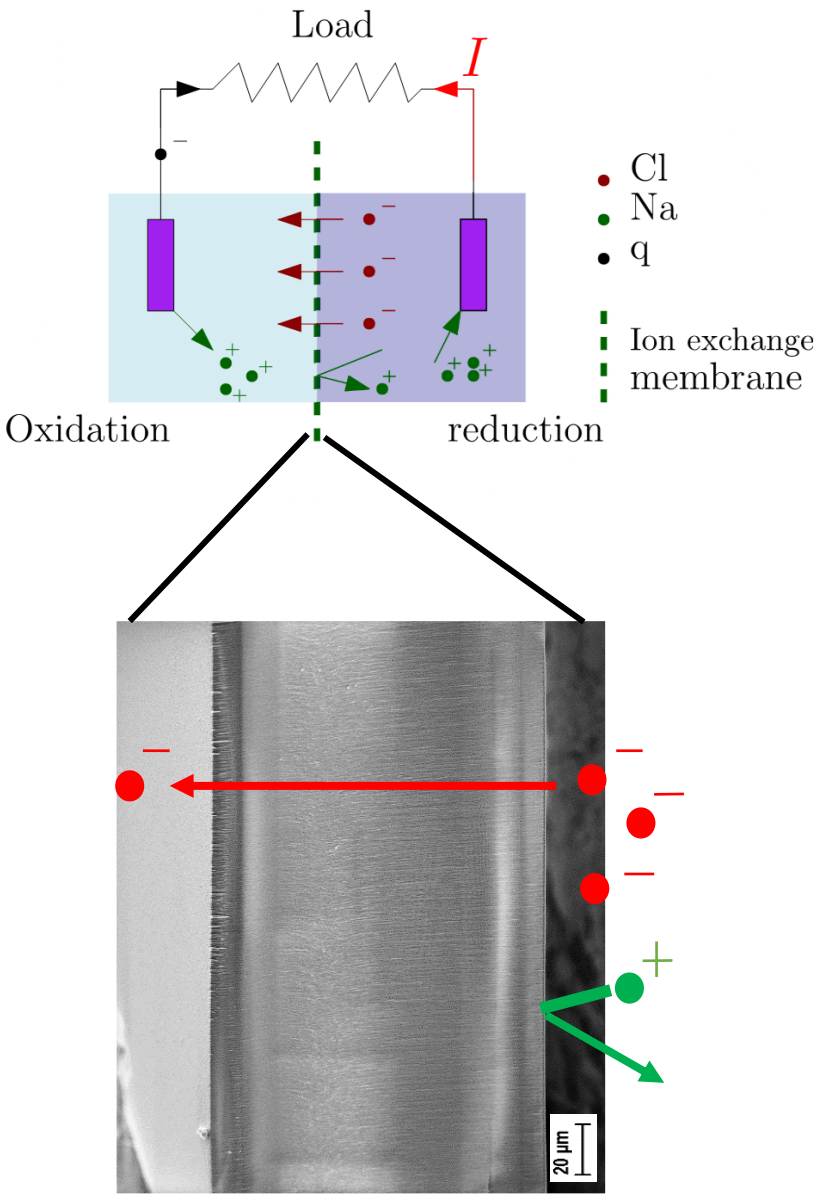
- High ionic selectivity → High $E_{diff}$ (~ tens of mV)
- Low membrane ionic resistance ($R_{cell}$) → High $I_{cell}$

Maximal power:

- $\boldsymbol{P_{max} = \frac{E_{diff}^2}{4R_{cell}}} \sim$ 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

# Porous silicon as ion exchange membrane




PSi membrane - side view

| 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 |

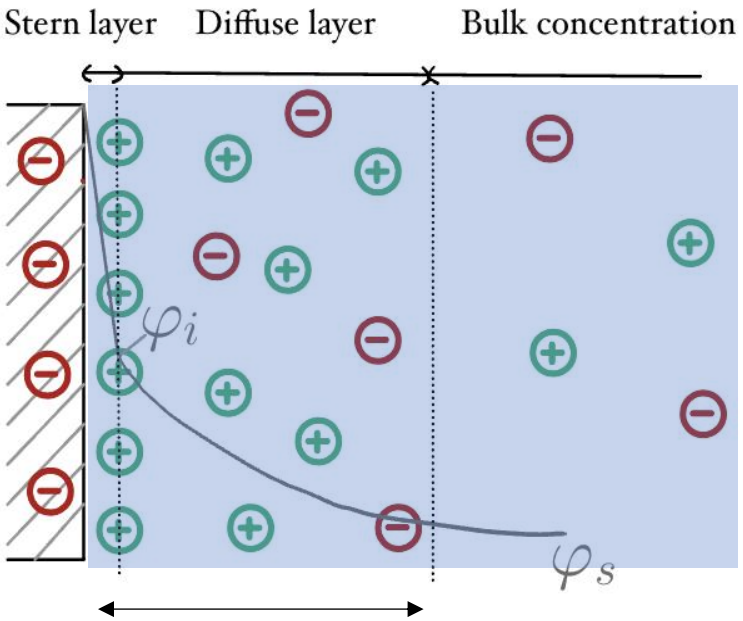
a few $W/m^2$
on full membrane

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

**Motivation : full membrane in Si**

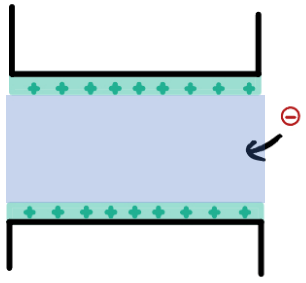
# Selectivity through EDL overlap and Debye length

**Electrical double layer (EDL)**

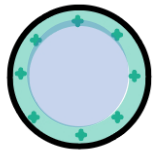



$$\lambda_D \propto \sqrt{\frac{1}{C_i}}$$

**Electrical double layer overlap**



$$\frac{r}{\lambda_D} \gg 1$$

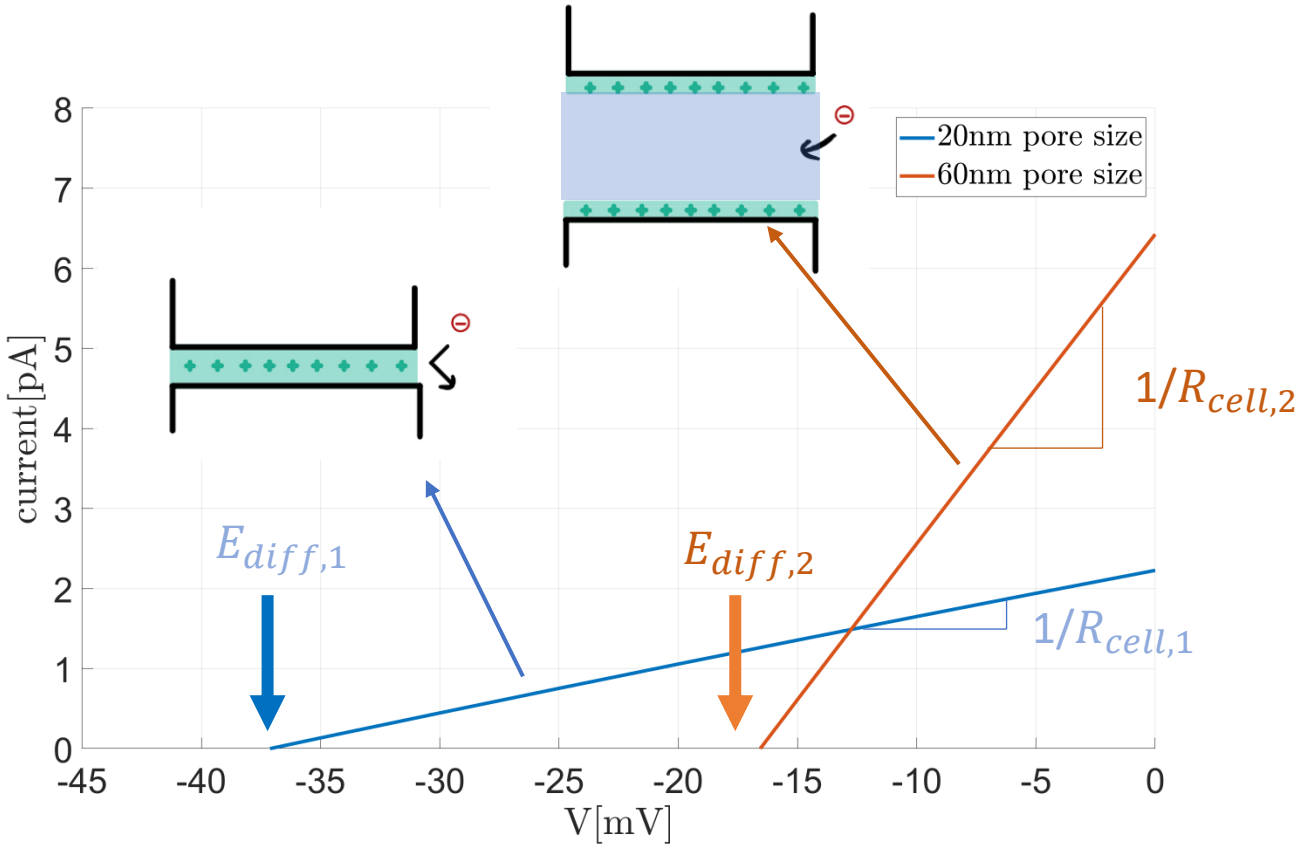


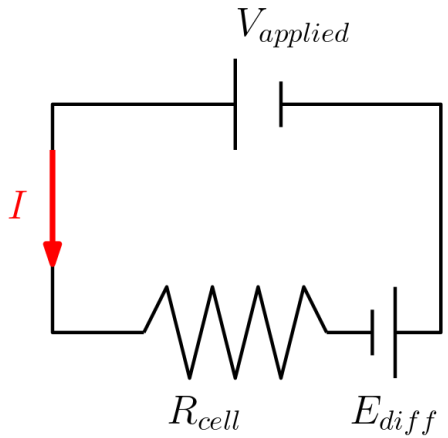
- $C_i$ = 1mM → $\lambda_D$ ~ 10 nm
- $C_i$ = 0.1 mM → $\lambda_D$ ~ 30 nm

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

# Numerical study of selective properties of single nanopore

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

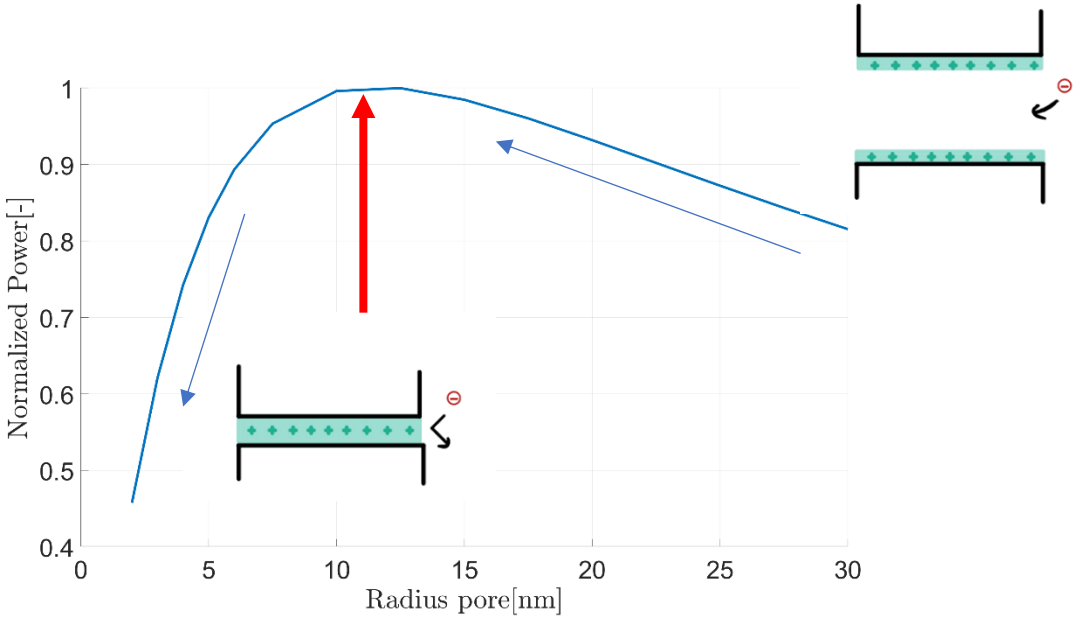


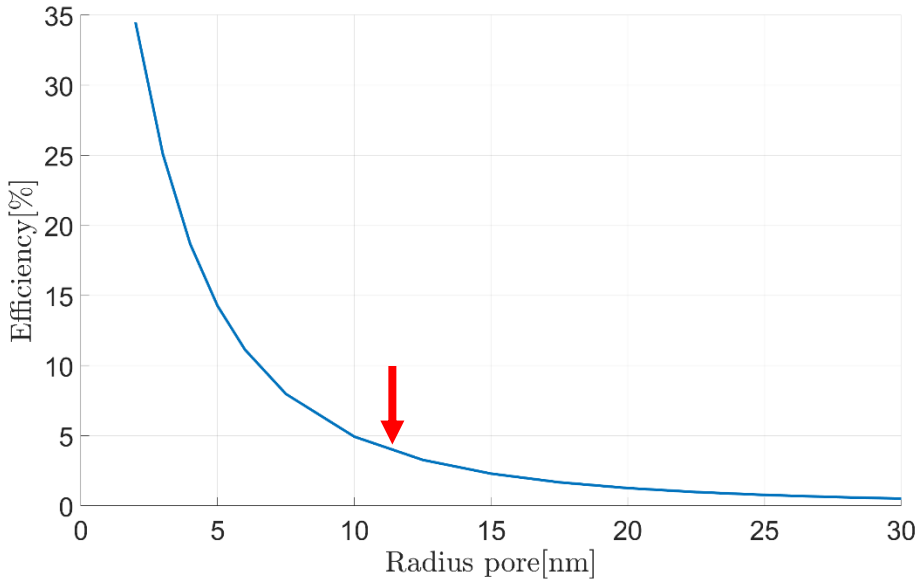

- Smaller pore radius→ higher $E_{diff}$: $E_{diff,1} > E_{diff,2}$
- Larger pore radius→ lower resistance $R_{cell}$: $R_{cell,2} < R_{cell,1}$

**Trade-off between selectivity and resistance !**
**Max power for which one ?**

# Numerical study for the power output: pore radius dependance



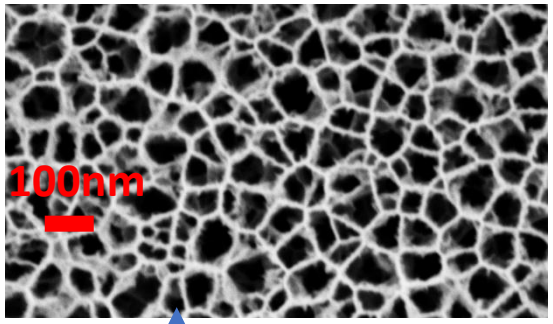

→Maximal power for pore radius ~11[nm]

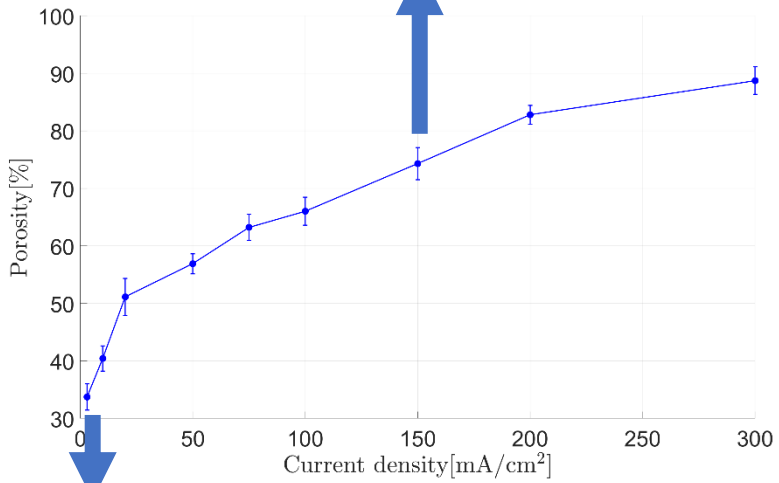


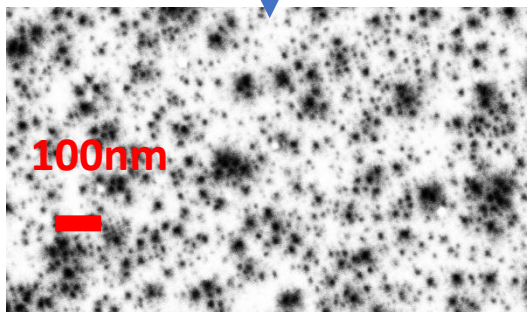

→But this is not the most efficient case

# Considerations for Full scale membrane

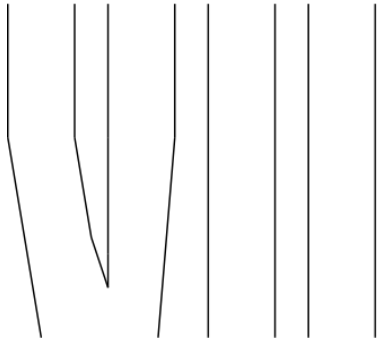
1) Pore size=fct(porosity)



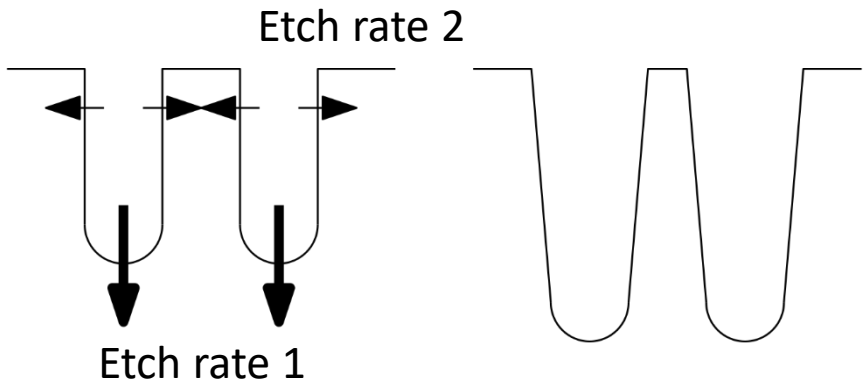



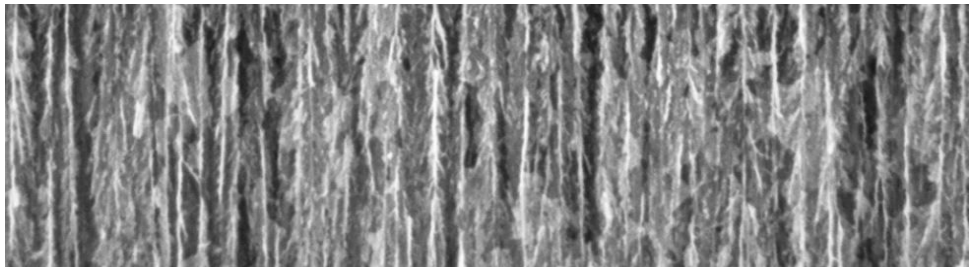

2) Branching



3) Pore shape variation

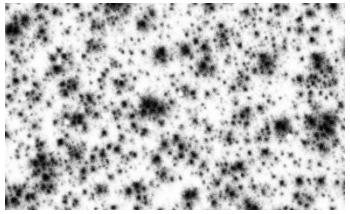


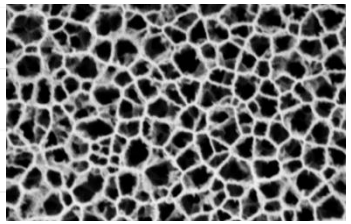

Etch rate 1>> Etch rate 2



# Choosing the optimal pore size: porosity consideration

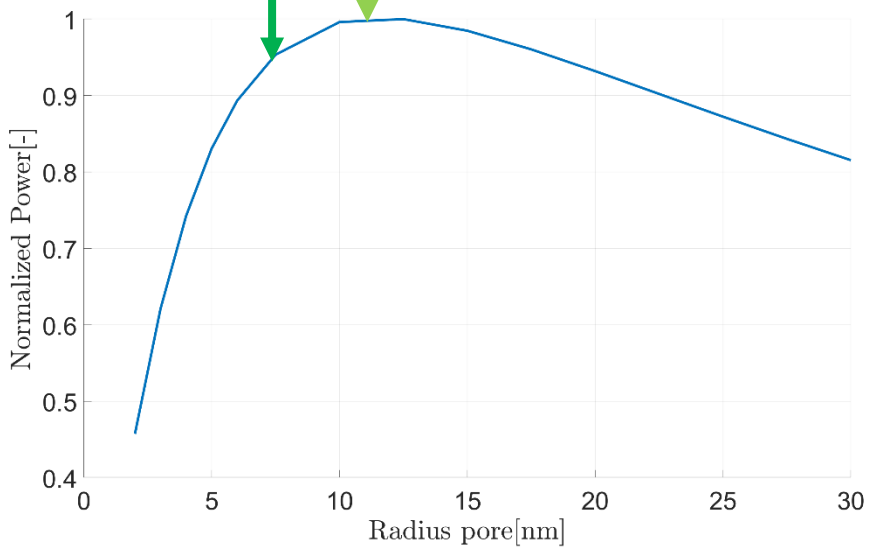
1) Porosity

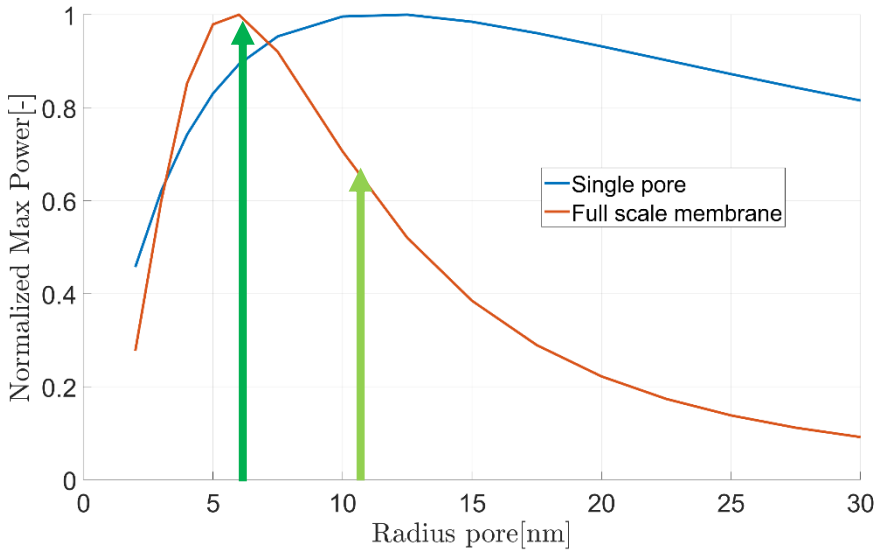






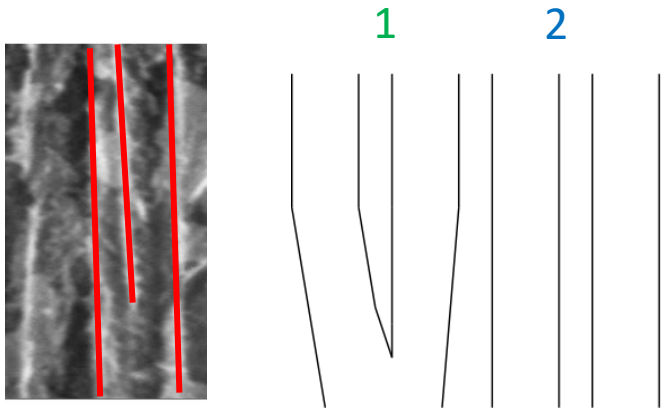


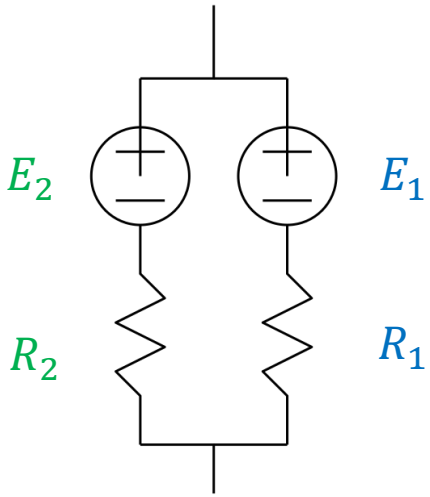




→On a full scale membrane, using 7.5[nm] instead of 11[nm] improves the max power by more than 50%

# Choosing the optimal pore size: branching and pore shape

2) Branching

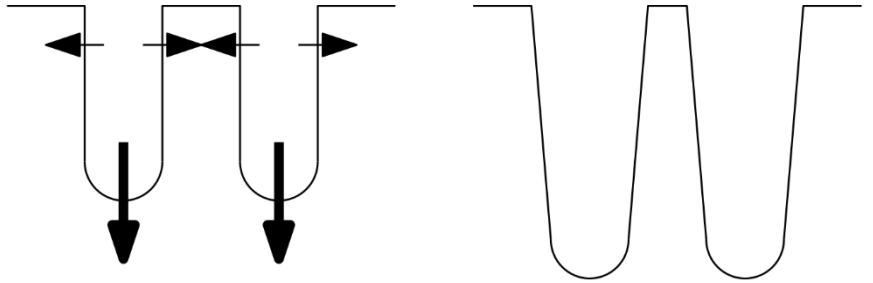


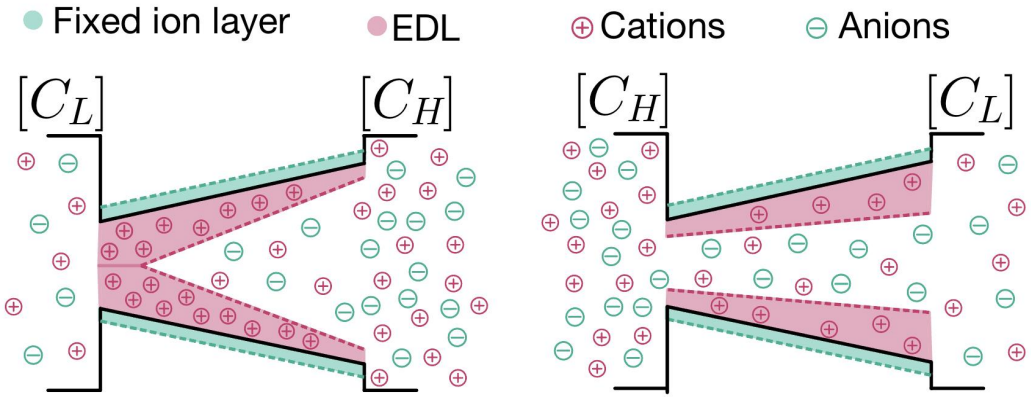




$$E_2 < E_1 \quad R_2 < R_1 \Rightarrow E_{eq} < E_1 \quad R_{eq} < (R_1, R_2)$$

Impact on power ? Depends on porosity chosen

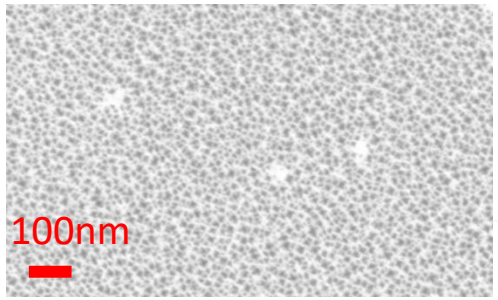
3) Pore shape variation

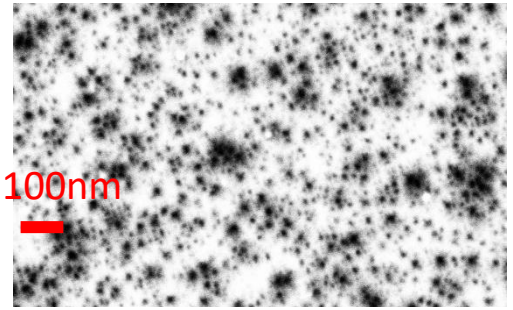




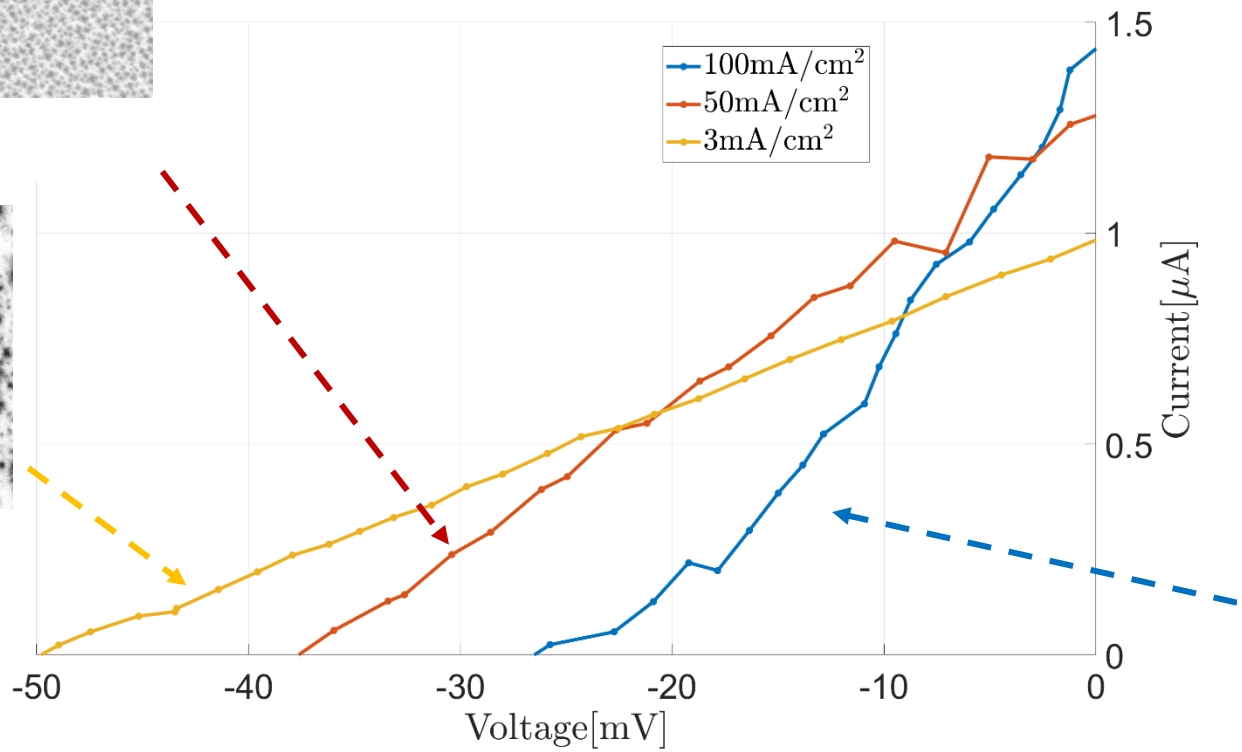

Side effects: asymmetry of selectivity

# Experimental observations of PSi membrane




**Experimental results**




**Parameter:**

Membrane thickness: ~97µm

Membrane area: 0.13cm²

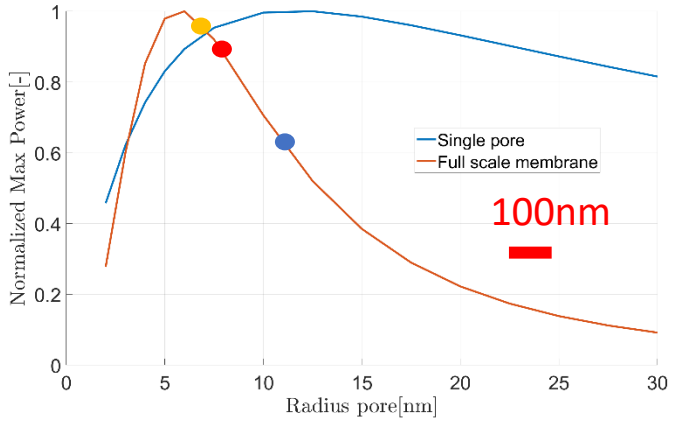
Ionic solutions: $\sigma$[KCl] ~ 170µS/cm

*vs.* $\sigma$ [KCl] ~ 1770 µS/cm

**Results:**

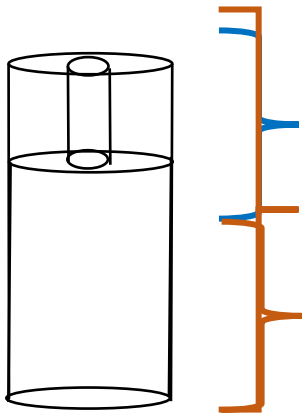
Power:

- 100mA/cm²: 0.65mW/m²
- 50mA/cm²: 0.92mW/m²
- 3mA/cm²: 0.94mW/m²

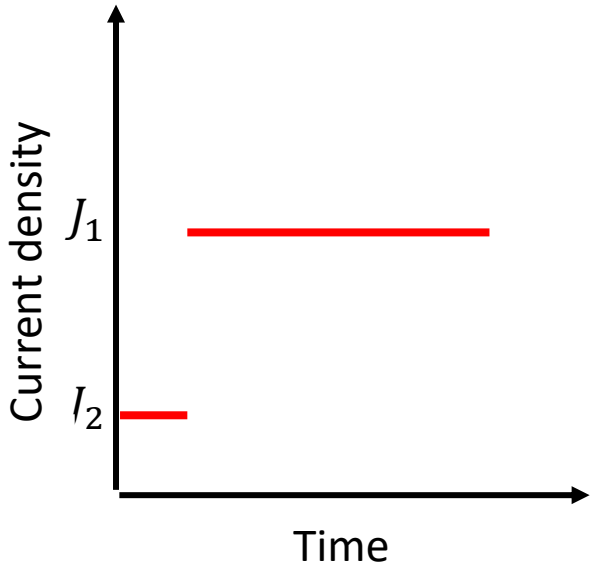


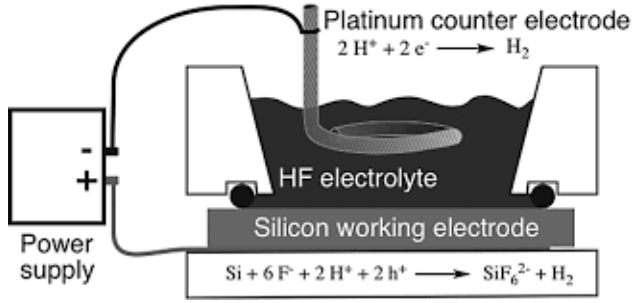

The numerical analysis suggests there is still room for improvement.

# Further improvement for PSi membranes



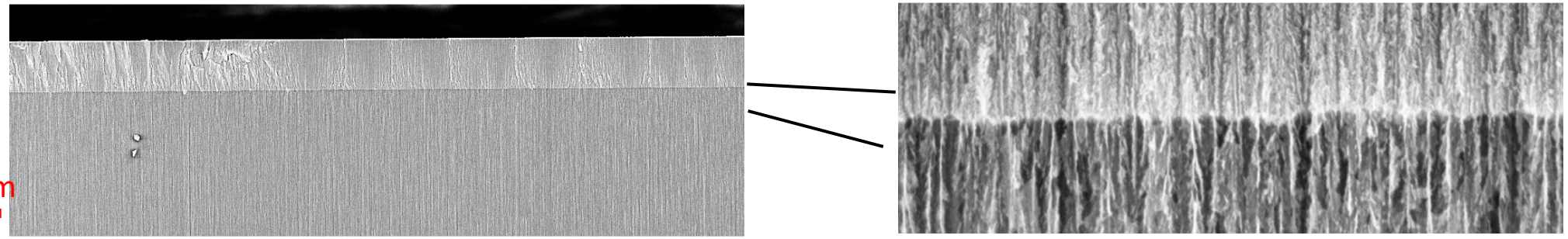
Thin layer of small pore radius=High selectivity layer of large pore radius =Low resistance, Thicker layer of larger pore radius =Low resistance



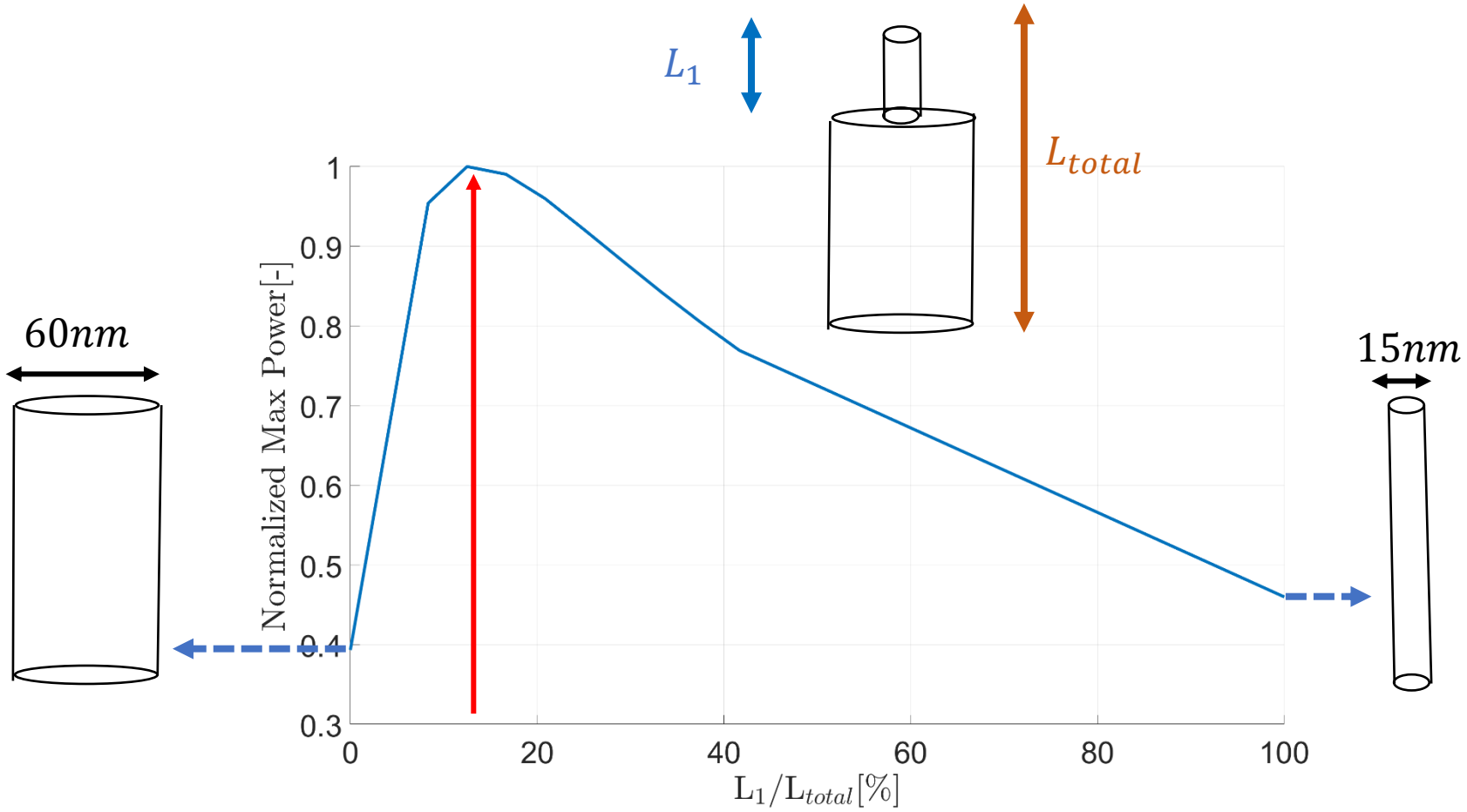




Control of the pore size along the thickness with the applied current density

**Membrane STEP-Side view**

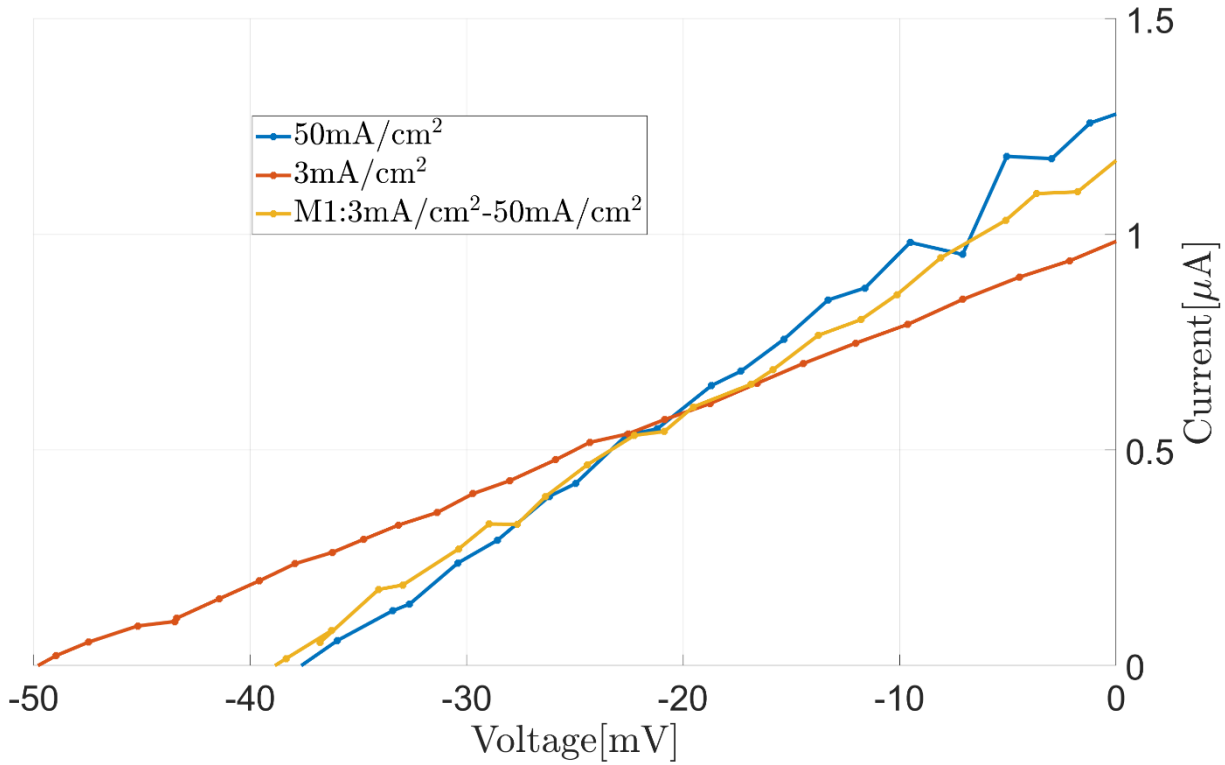


# Finding the best ratio using the numerical model




→ Numerically, adding a thin layer can double the maximal power output. However, this model neglects the pore size/porosity relation

# Experimental observations




**Parameter:**

Membrane thickness: ~97µm

Membrane area: 0.13cm²

Ionic solutions: $\sigma$[KCl] ~ 170µS/cm

*vs.* $\sigma$ [KCl] ~ 1770 µS/cm

M1: $L_1$ =11.71µm→12%

M2: $L_2$=17.6µm→18%

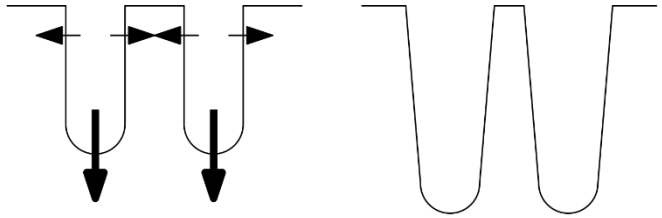
**Results:**

Power:

- 50mA/cm²: 0.92mW/m²
- 3mA/cm²: 0.94mW/m²
- M1: 0.88mW/m²
- M2: 0.84mW/m²

→ Experimentally, no improvement of the maximal power

This might be explained by the lateral etching of the thin porous layer when porosifying the thicker more porous layer, the porosity variation

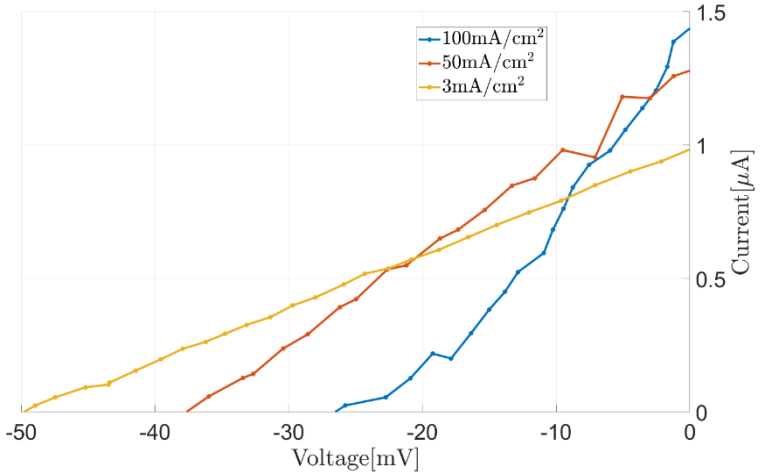


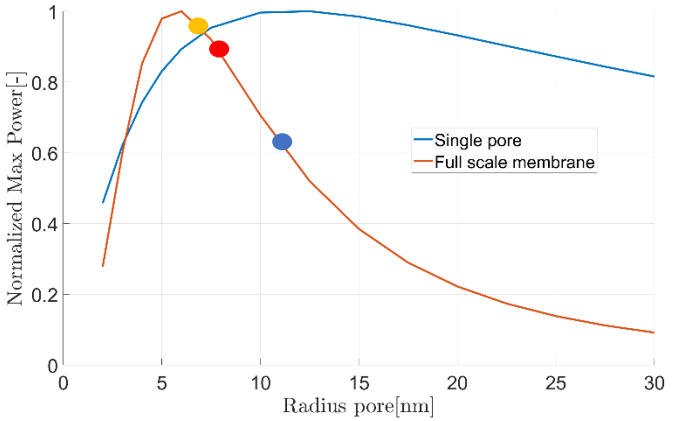
# Conclusion

- **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

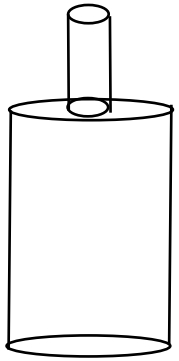
- **Numerical modelling** of the pore can be used to **improve the membrane output power** by considering the structural properties of Psi



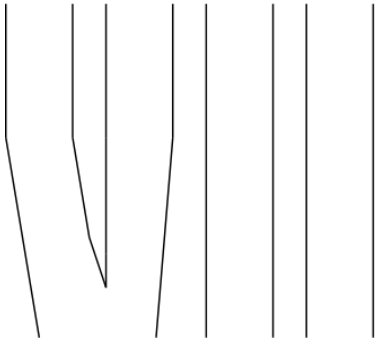



# Future work

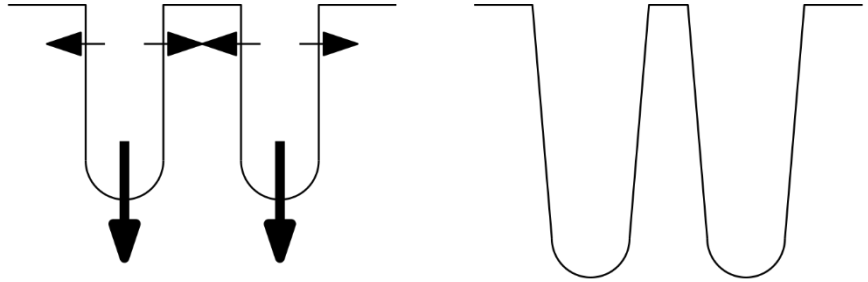
- Further study for the addition of a small selective layer required



- Improvement the model for a full scale membrane
  - Articfact such a lateral ecthing and branching must be better modelled



- Improvement of the fabrication process required
  - Compensation of the lateral etching and other side effect



PSST
POROUS SEMICONDUCTORS SCIENCE & TECHNOLOGY
International Conference

# Thank you for your attention !
# Any questions ?

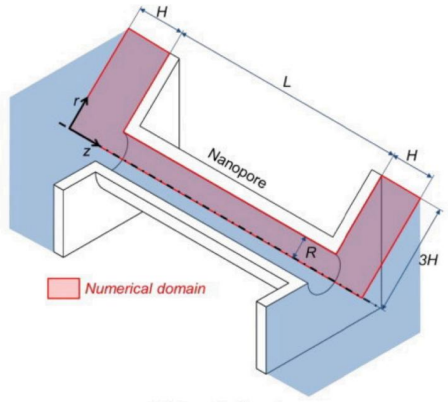
Romain.hanus@uclouvain.be

UCLouvain

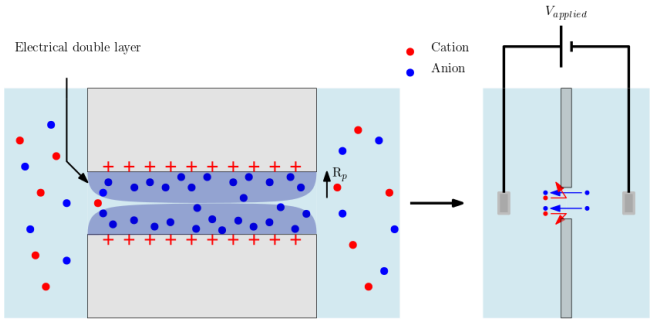
icteam

# Numerical study of selective properties of single nanopore

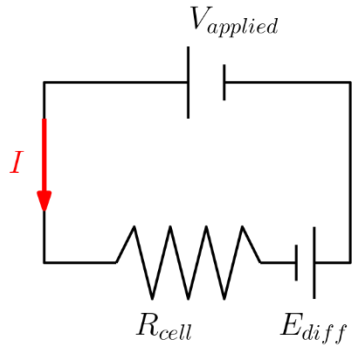
**Numerical domain: 2D axysymmetric half pore**




**Schematic of the model**

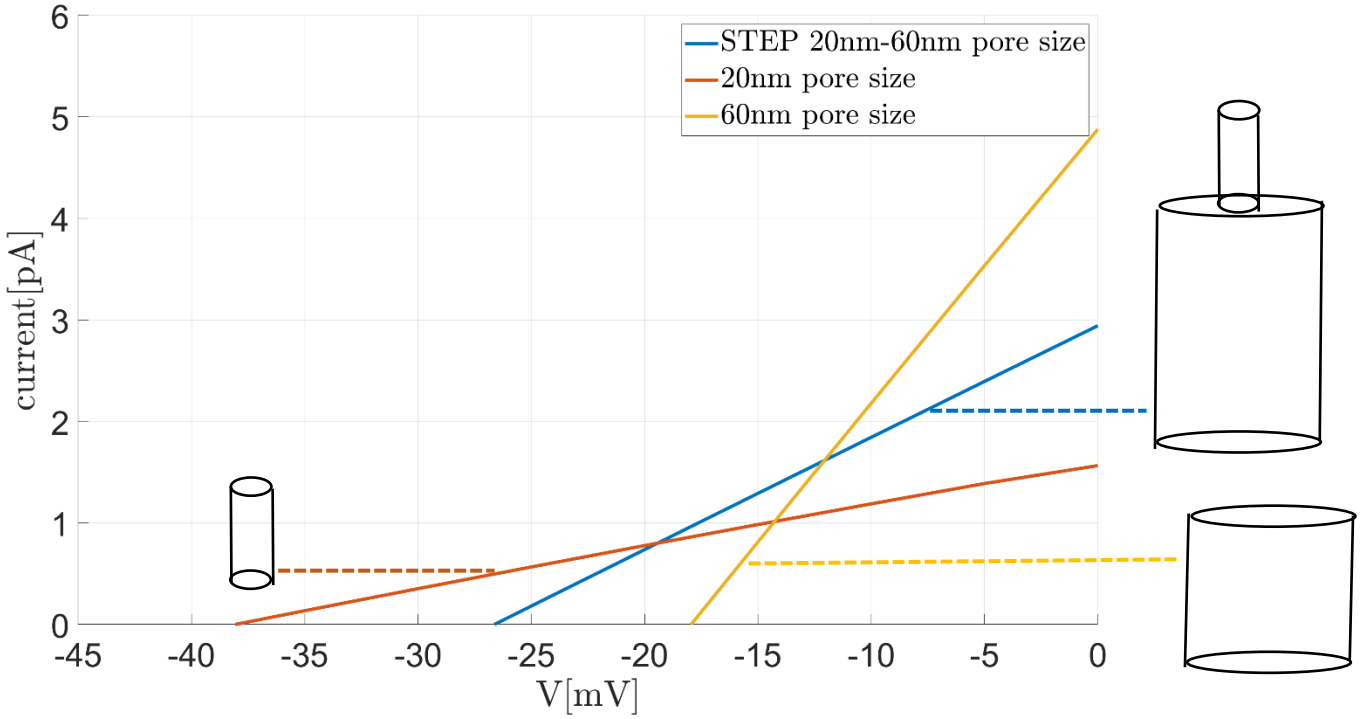



**Electrical equivalent circuit of the models**



# Numerical comparison ‘step’ pores *vs*. conical pores

**Numerical results**




**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:**

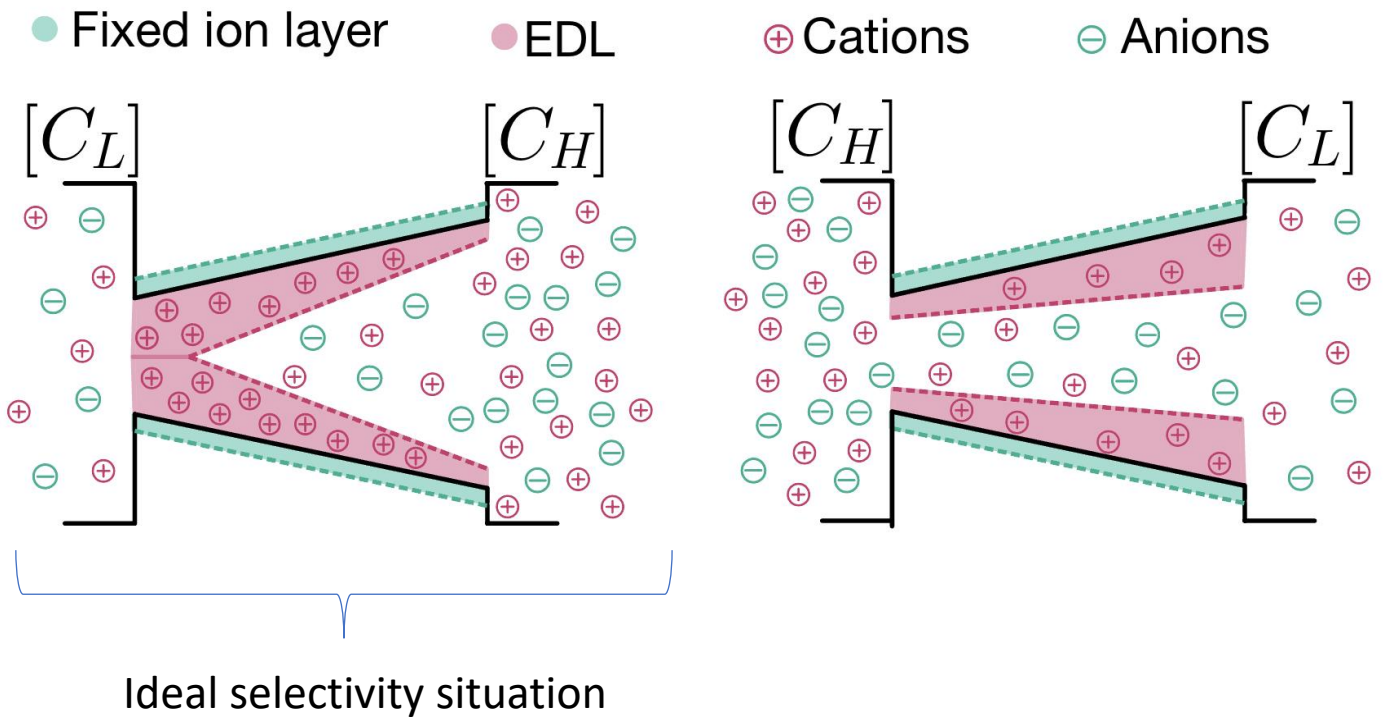
- $E_{diff}$ ’step’ intermediate between $E_{diff}$ 20nm and $E_{diff}$ 50nm
- Similar conclusion for resistance ‘step’

# 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



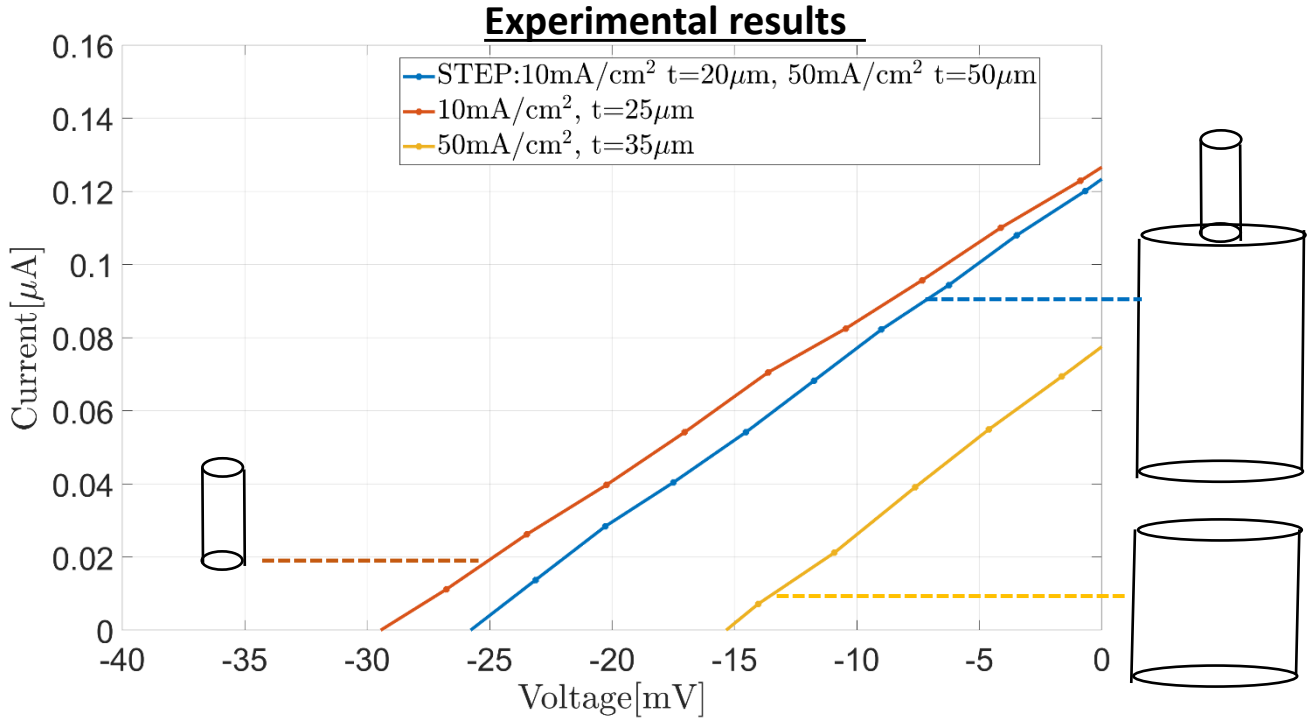

Ideal selectivity situation

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

# What about the power comparison ?

Max power:

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




**Experimental results:**

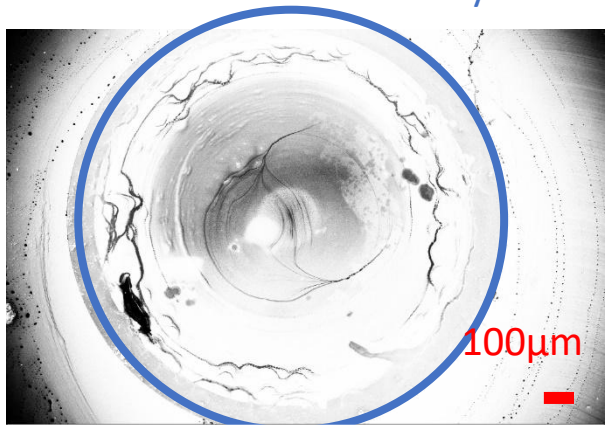
- Maximal power :
  - 60 nm: $P_{max} = 0.29$ nW
  - STEP: $P_{max} = 0.792$ nW
  - 20 nm: $P_{max} = 0.93$ nW
- Maximal power density (3.14 mm² membrane)
  - 60 nm: $P_{max,d} = 0.0922$ mW/m²
  - STEP: $P_{max,d} = 0.252$ mW/m²
  - 20 nm: $P_{max,d} = 0.297$ mW/m²

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**

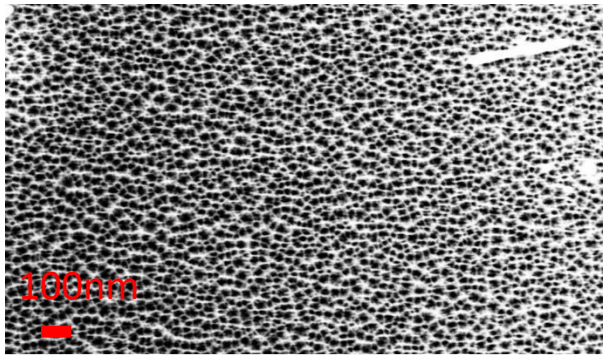
# Few issues…

- 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

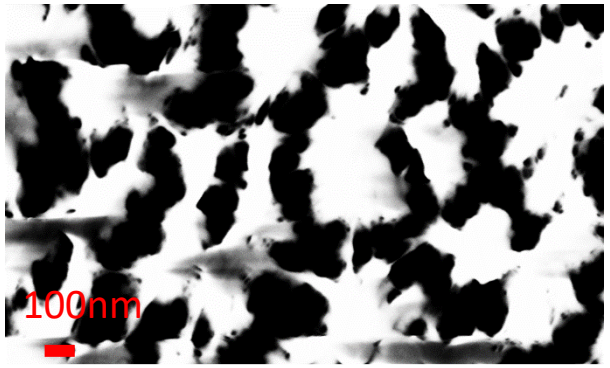
Back side membrane not uniformly released



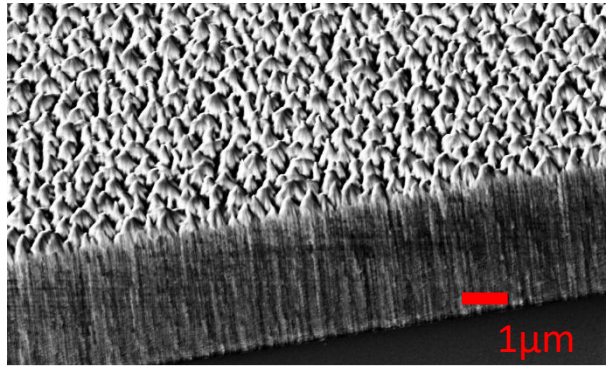

Top view Psi 50mA/cm^2




DRIE



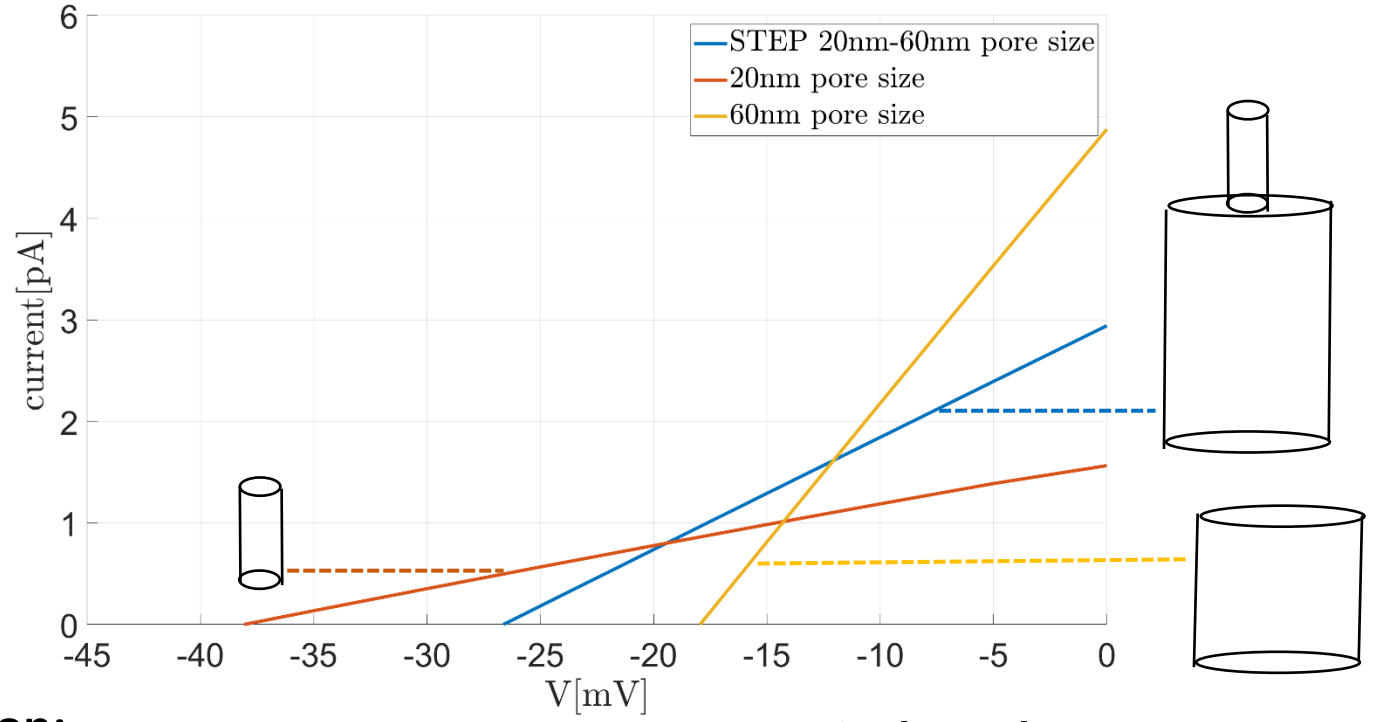

Top view and side Psi 50mA/cm^2 after 3 cycles DRIE




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

# Numerical comparison ‘step’ pores *vs*. conical pores

**Numerical results**

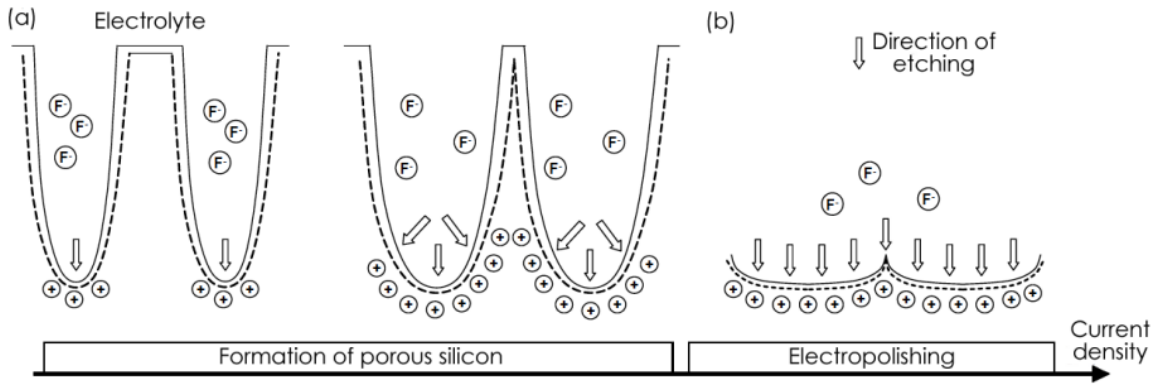


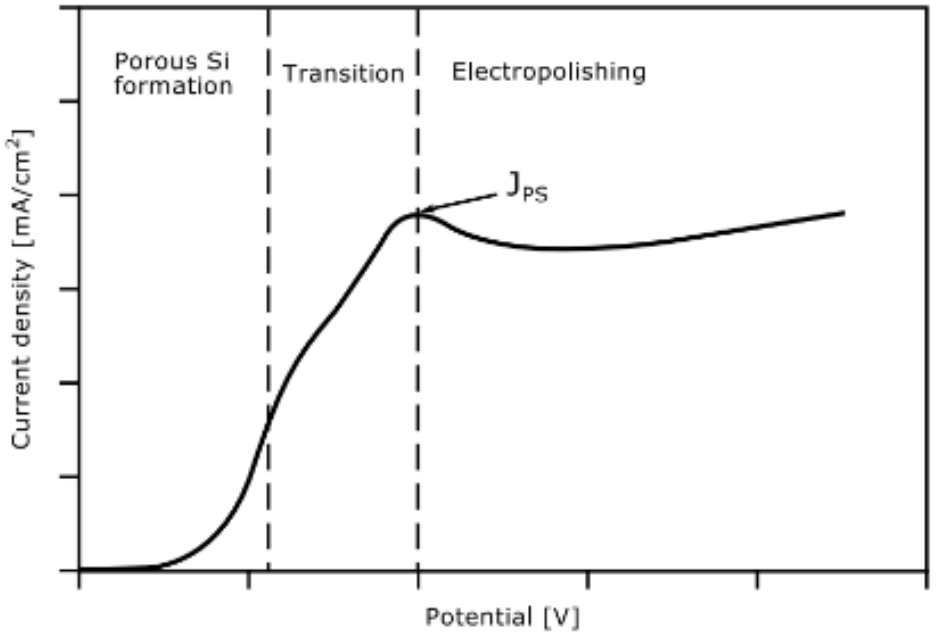

**Numerical I-V test on:**

- 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

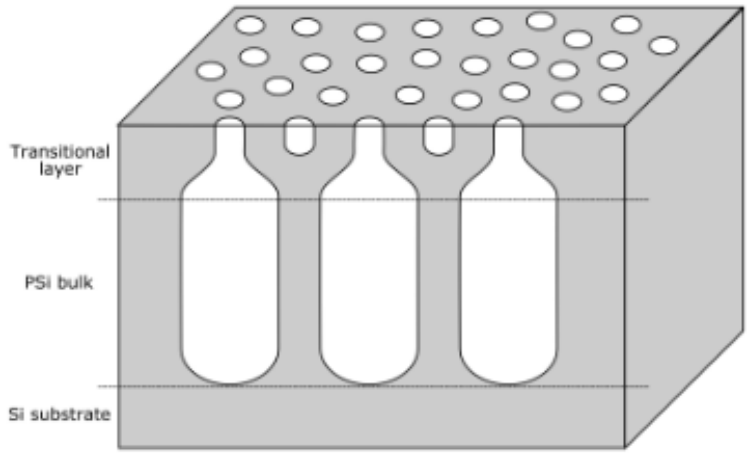
**Numerical results:**

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



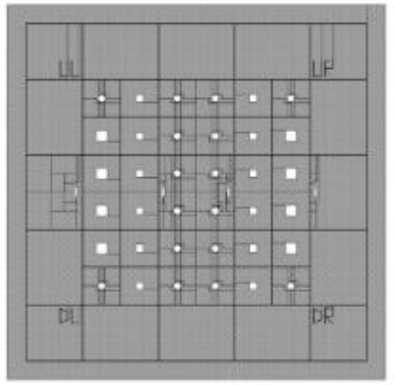



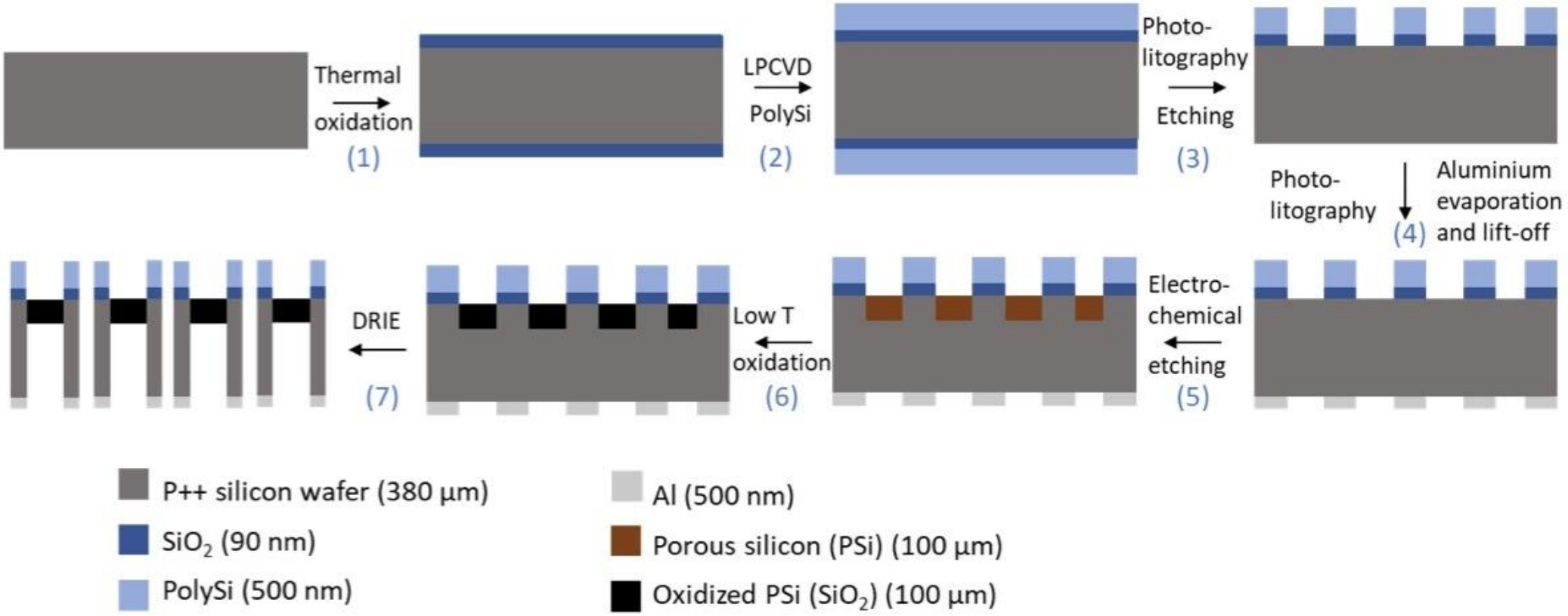

| Increase of | Porosity | Etching rate | Critical current |
|---|---|---|---|
| HF concentration | Decreases | Decreases | Increases |
| Current density | Increases | Increases | - |
| Anodization time | Increases | Almost constant | - |
| Temperature | - | - | Increases |
| Wafer doping (p-type) |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



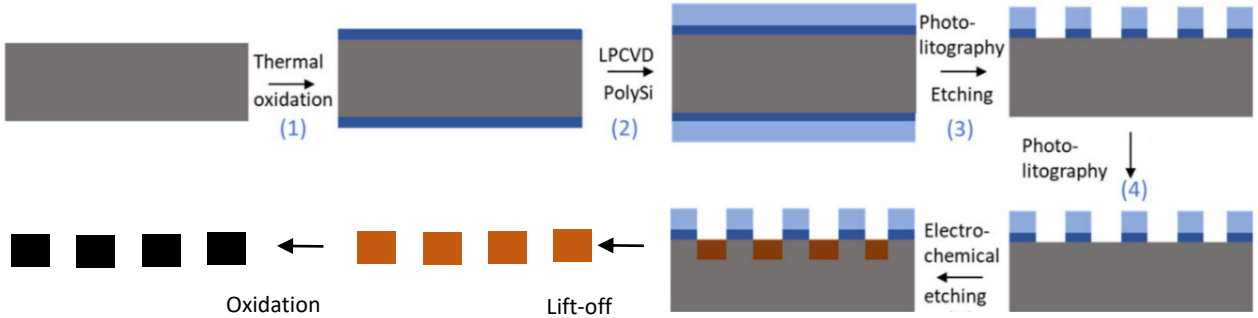

- Substrate: Si p++ boron, 0.8-0.9m Ω.cm
- Current density range: 100mA/cm^2→ 20mA/cm^2

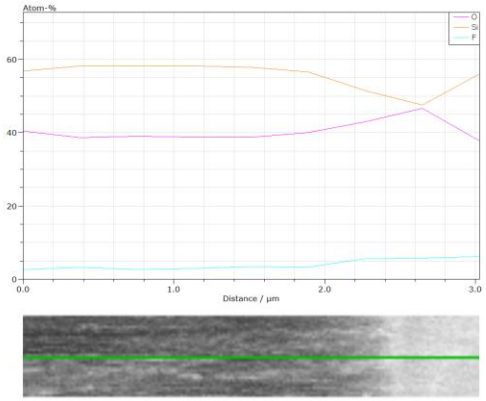
# Additional support : process

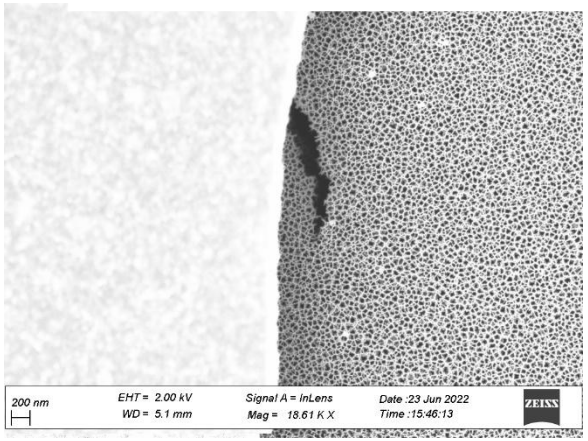


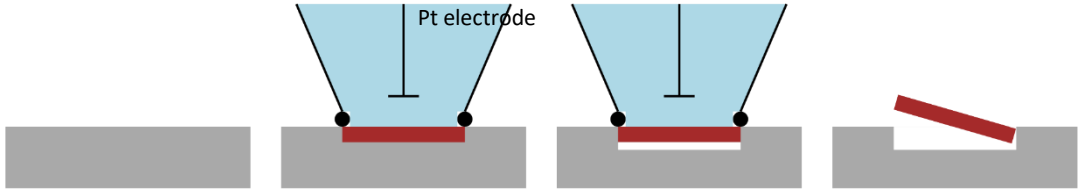



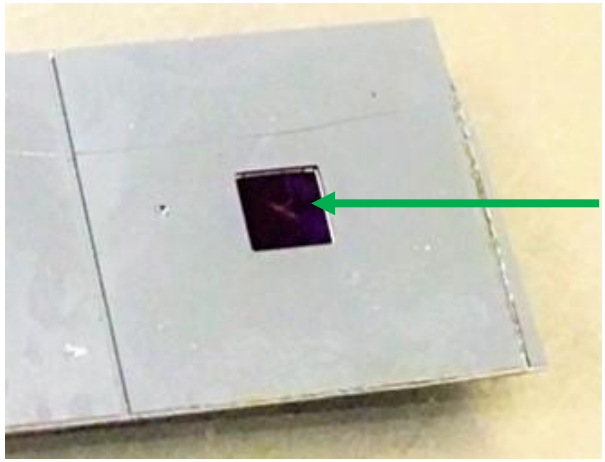
- # PSi-clamped vs free membranes



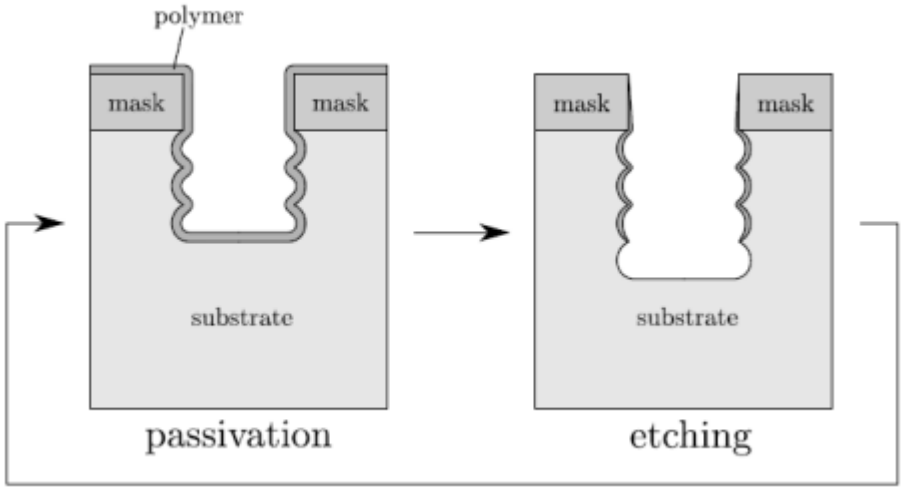



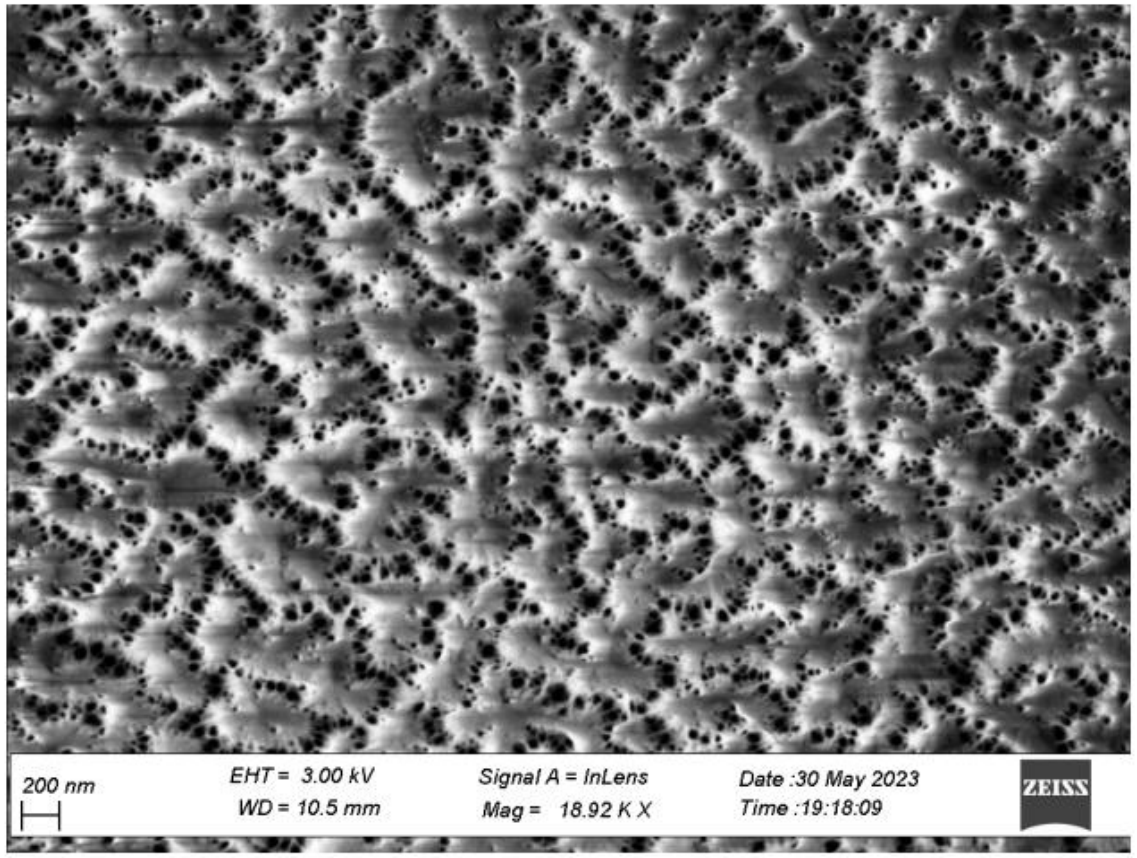
PSi

- Simpler process
- No DRIE required

# 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

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

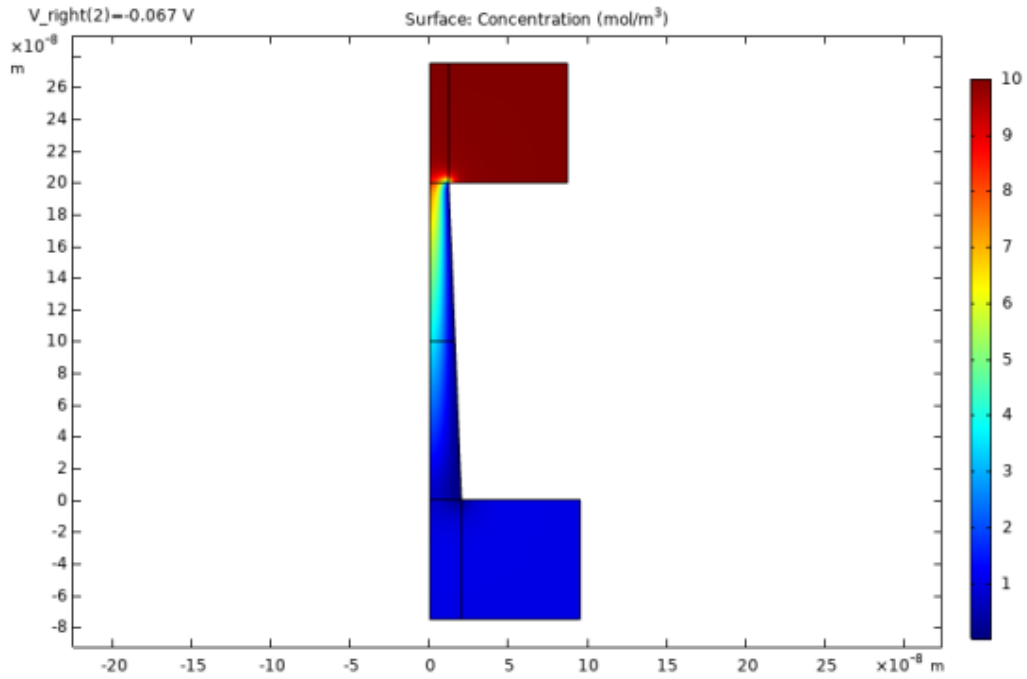
- Nernst modified : 2 ions

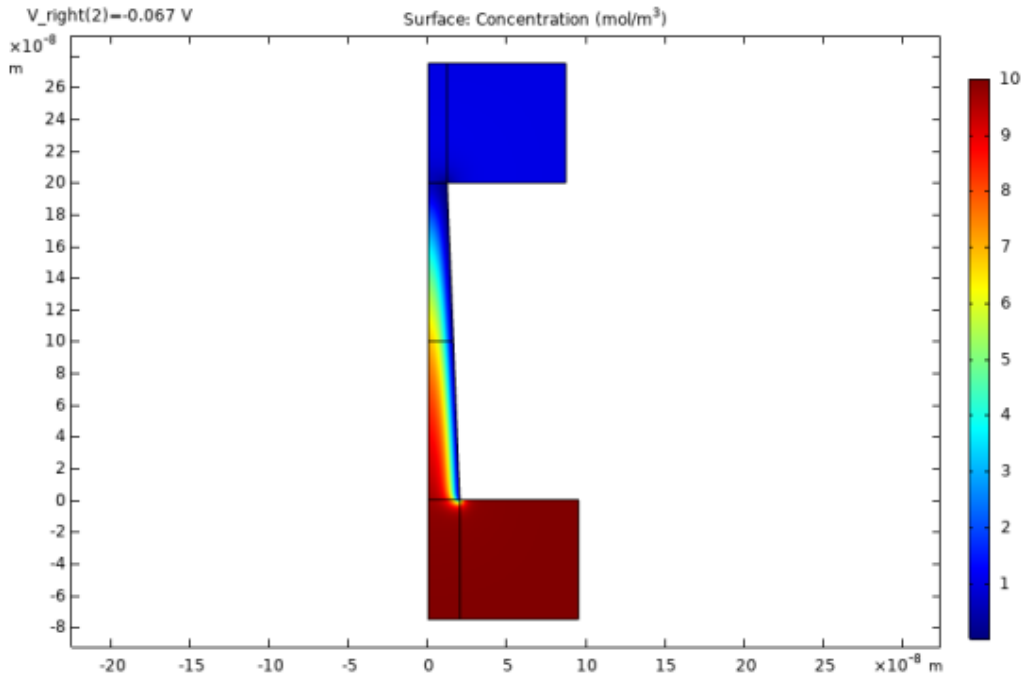
$$E_{redox} = \frac{\mathrm{RT}}{z\mathrm{F}} ln(\frac{\gamma_H C_H}{\gamma_L C_L})\ (1\text{-}2t_+ + \frac{D_{Cl^-} - D_{Na^+}}{D_{Cl^-} + D_{Na^+}})$$

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

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

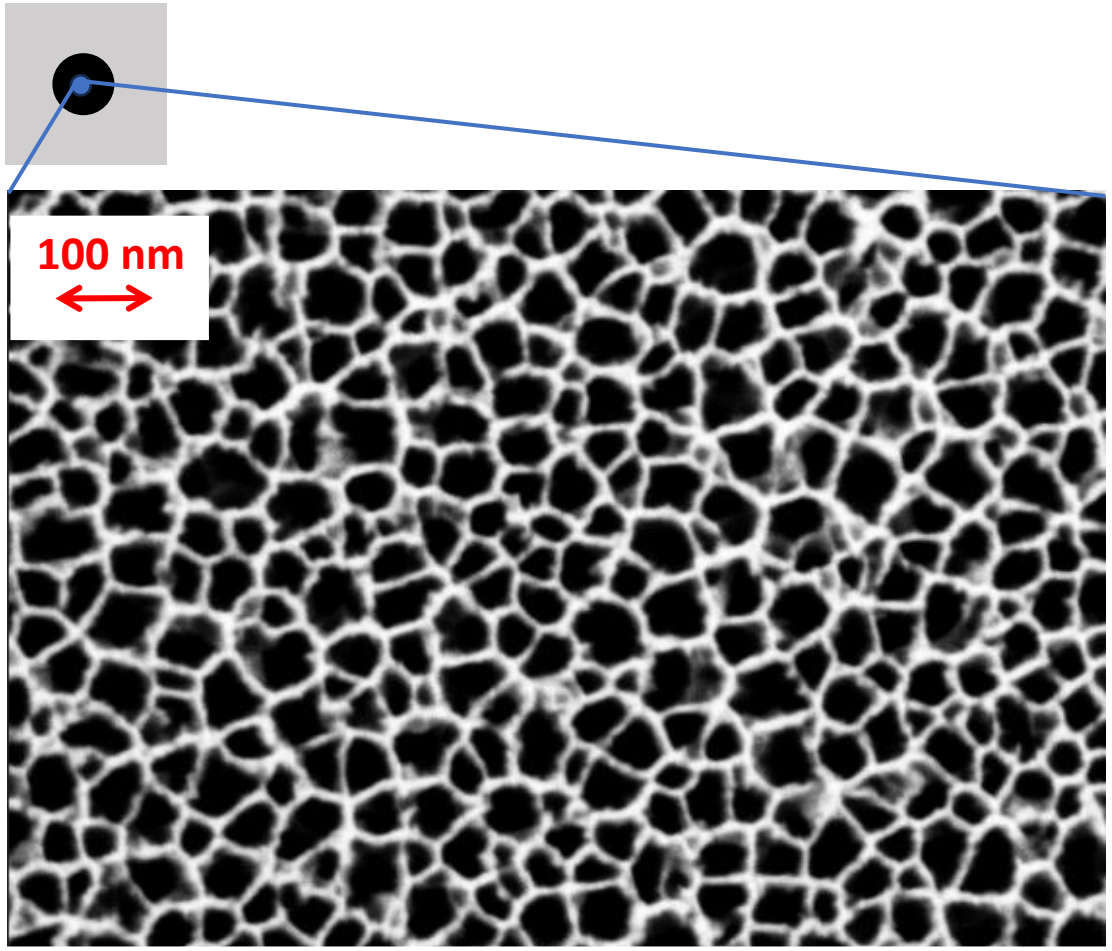
# Concentration of anion in mol/m³
# Blue = flow mainly due to cation = selectivity



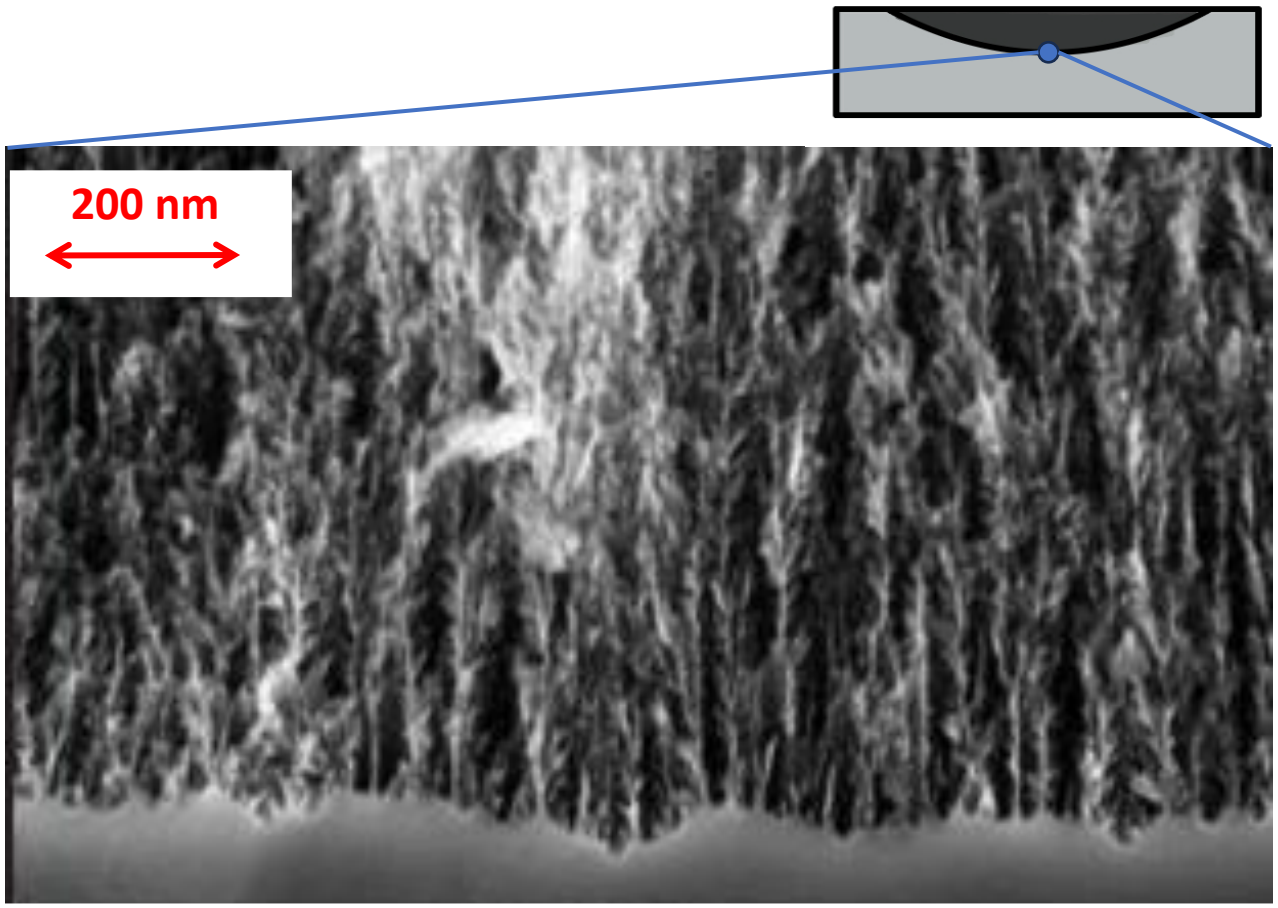



# Choice of parameter in single layer

- 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 $\mu m$. As explained in section 4.1.3, the electrical resistance of the channel is proportional to its length. Additionally, detachment and cracks were more frequently observed for longer pores.



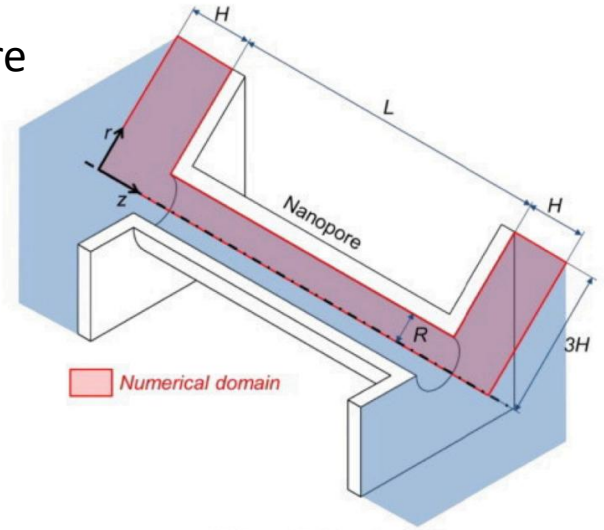

Top view SEM image of PSi



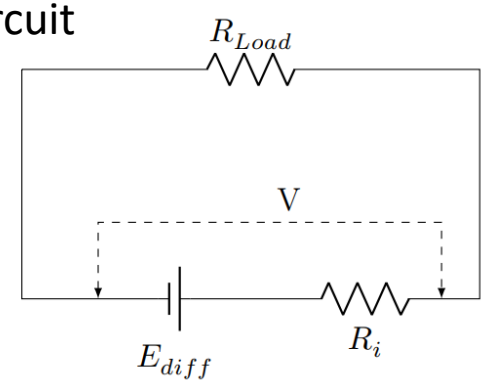

Cross sectional view SEM image of PSi

# Simulation model

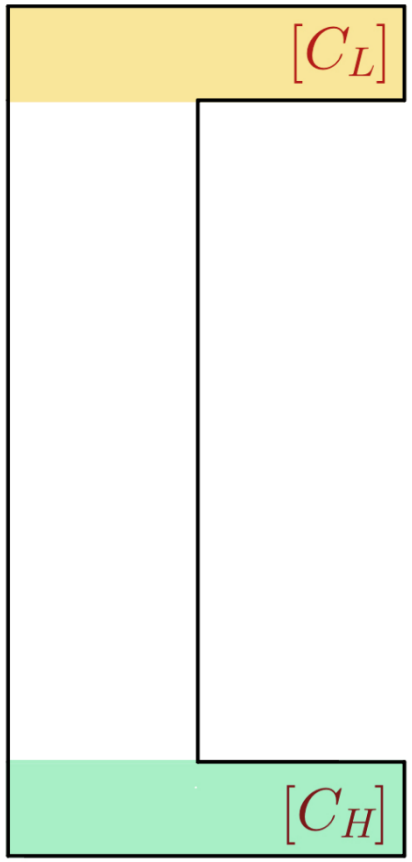
- Domain: 2D half pore



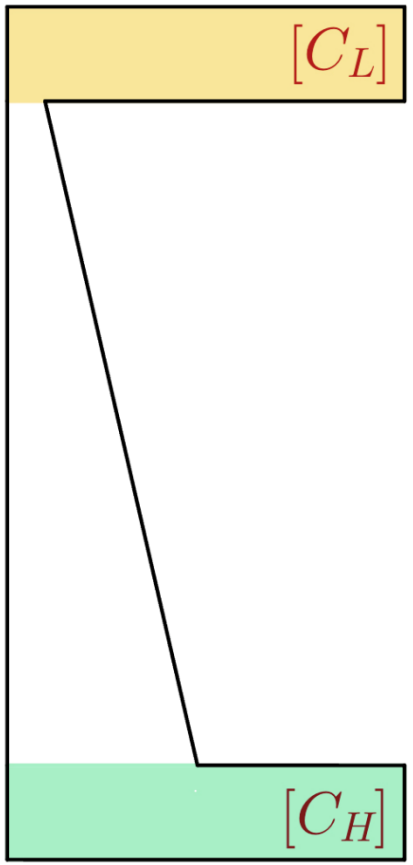

- Equivalent electrical circuit



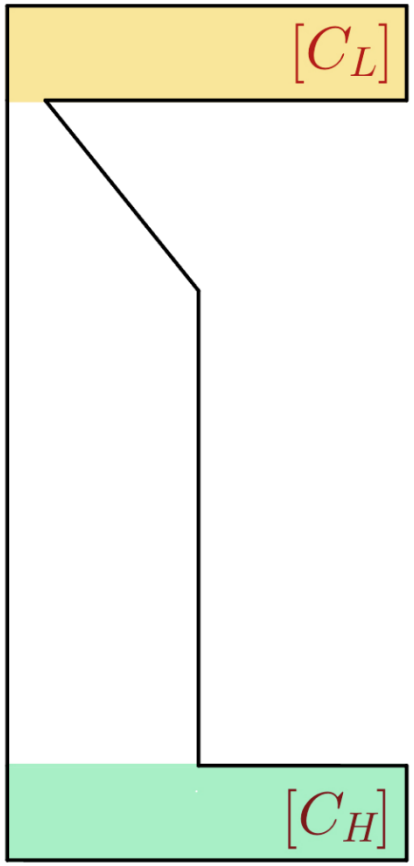

Cylindrical




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