Novel concept to extract salinity energy using capacitive layers

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Outline

- **Background on the blue energy:**
  Context & extraction approaches.
- **Aim of my thesis:**
  Increasing the Power density.
- **Materials & Methods:**
  The cell and the electrochemical analysis.
- **Results & Discussions:**
  The characterization and Modeling
  The energy production and Modeling.
- **Conclusion & Outlooks:**
  The importance of the capacitive layers.

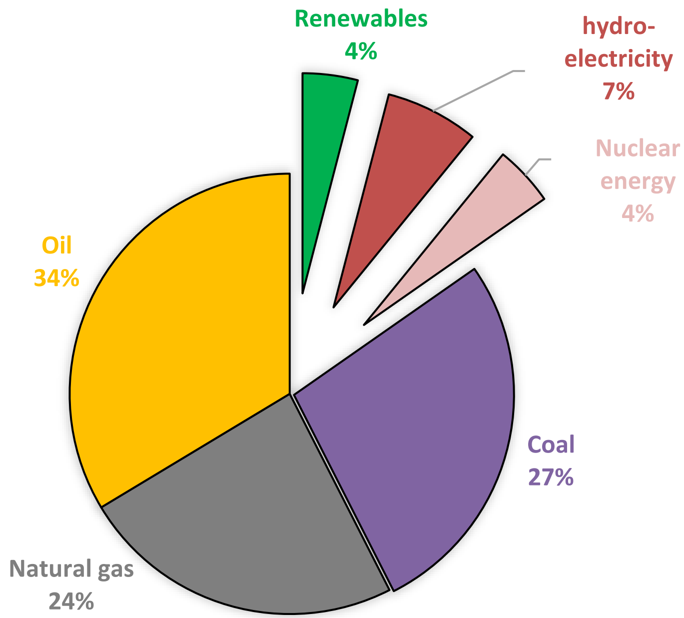
Background
on the blue energy

BACKGROUND

Energy context

Solar Credit: google

Hydro Credit: google



WORD ENERGY CONSUMPTION

BP 2018

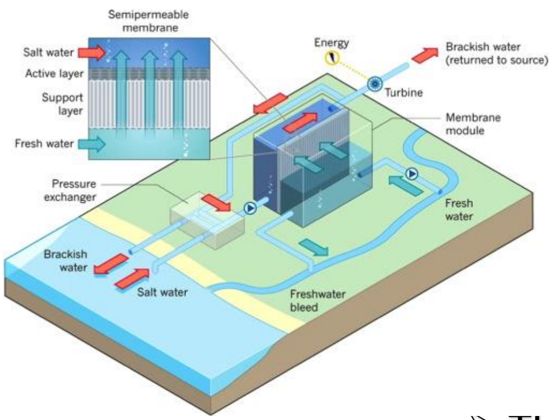
Wind Credit: google

Nuclear Credit: google

BACKGROUND

Blue Energy

A.Siria et al. (Nat Rev Chem 2017)



$$\Delta G_{mix} = G_{mix} - (G_L + G_H)$$

Credit: google

Amazon river

- The total dissipated Power ≈ 2.4 TW (J N Weinstein et al. science 1976)

Pressure retarded osmosis

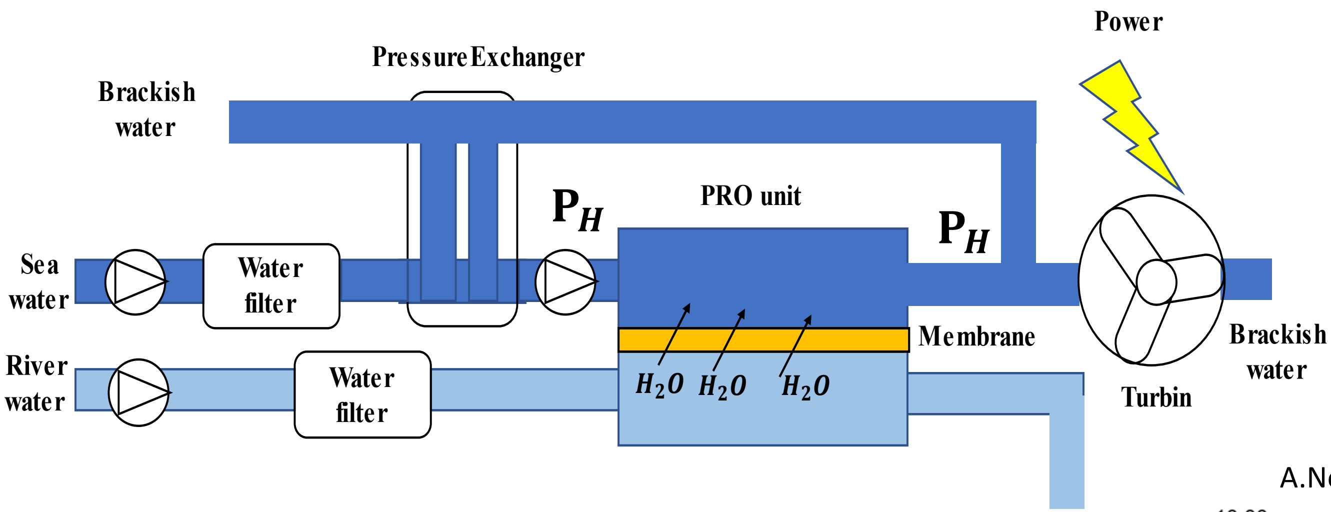
Reverse electrodyalisis

Accmixing

Diffusio osmosis

BACKGRAOUND

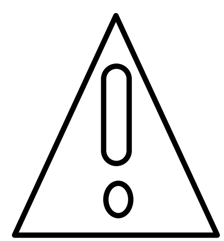
Pressure retarted osmosis



Van't Hoff

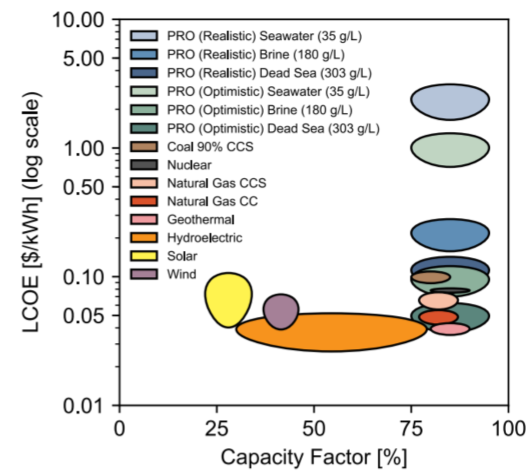
$$\Delta\pi = i(C_H - C_L)RT$$

$$P_{gross} = (\Delta V + V_H)\Delta P \quad \text{with } \Delta P = P_H$$

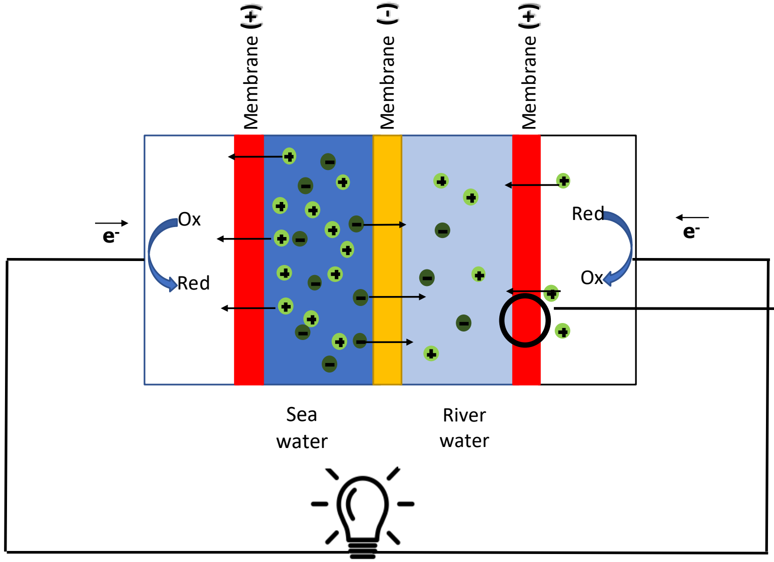


Cost

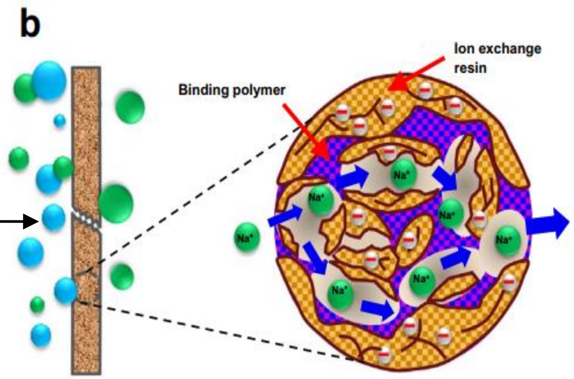
A.Newby et al. (acsestengg 2021)



Reverse Electrodialysis



Y. Mei et al (J. desal. 2017)



Donnan Potential

$$E_{emf} = \frac{\alpha RT}{zF} log(\frac{a_H}{a_L})$$

$$P = \frac{E_{emf}^2 \, R_{Load}}{(R_{Cell} + R_{Load})^2}$$

$$P = \frac{E_{emf}^2}{4R_{Cell}}$$

Internal resistance

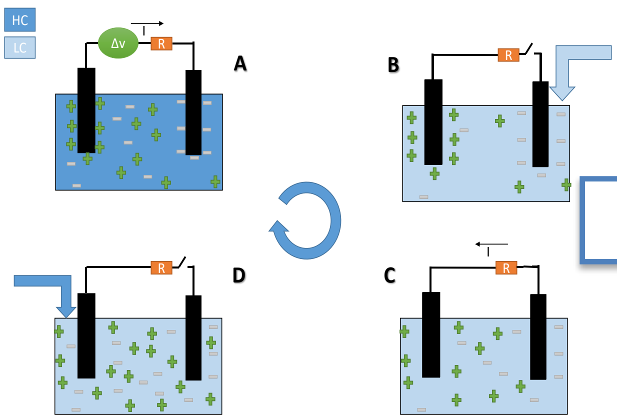
$$R_{Cell} = R_{ohm} + R_{\Delta C} + R_{BL}$$

$$R_{Ohm} = R_{C_H} + R_{C_L} + R_{MEM}$$

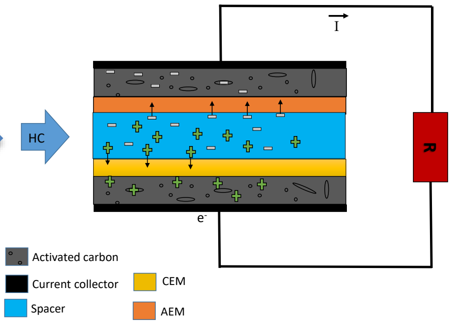
Accumulating mixing

$$
\begin{cases}
P_{gross} = \oint E(q)\,dq \\
C_L < C_H \qquad E = \dfrac{q}{C}
\end{cases}
$$

CAPMIXING

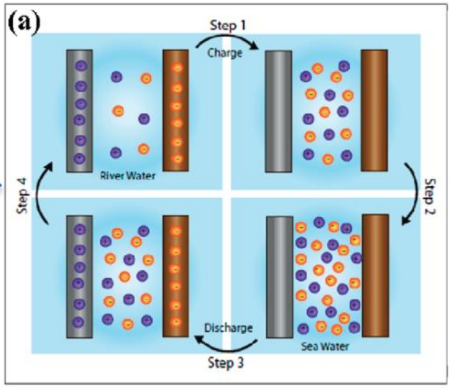


CAPACIVITE DONNAN POTENTIAL



BATTERY ENTROPY MIXING

La Mantia et al. (NanoLett 2011)



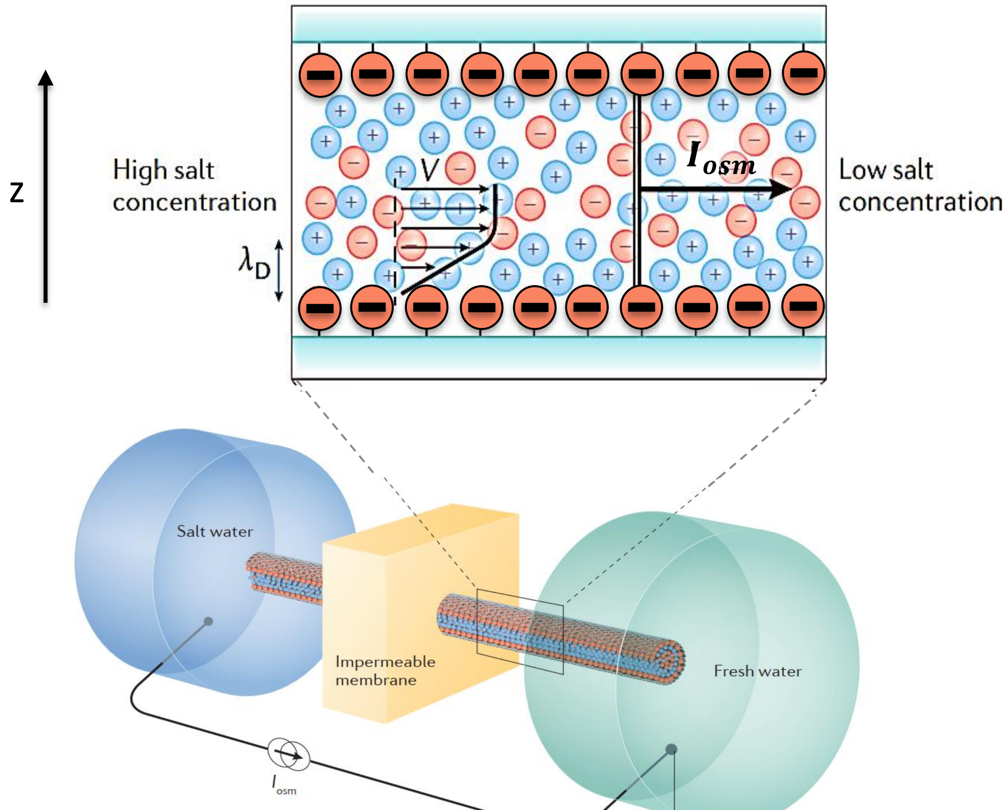
- *External charge*
- *capacitive electrodes*

- *Donnan charge*
- *capacitive electrodes*

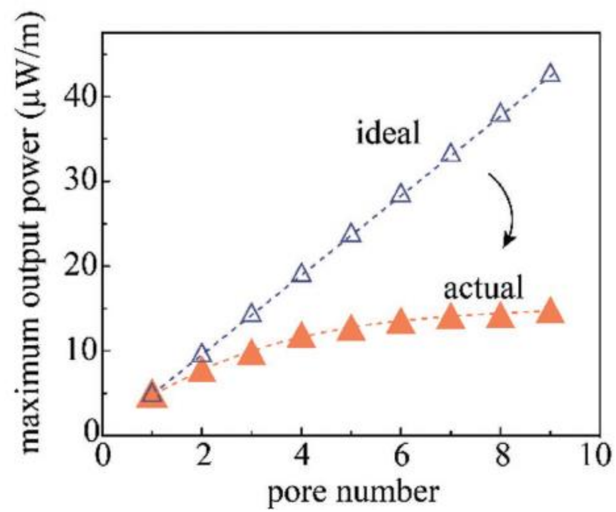
- *Pseudo capacitive electrodes*

Diffusio Osmosis

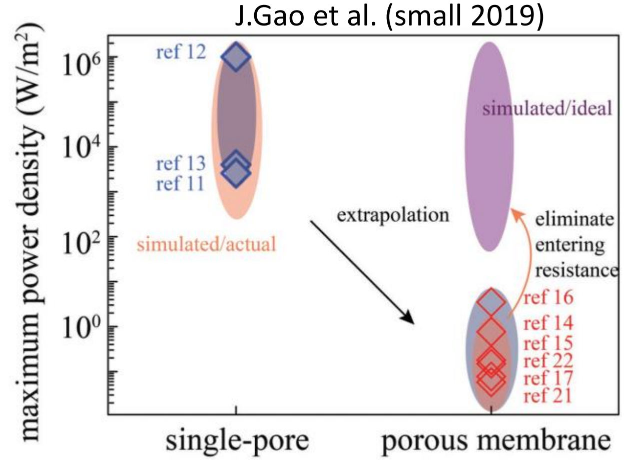
A.Siria et al. (Nature 2013)



J.Gao et al. (small 2019)



J.Gao et al. (small 2019)



$$P = \frac{I_{DO}^2 R_{Cell}}{4}$$

$$I_{DO} = 2\pi r \sigma V_{DO}$$

Aim of my thesis

How to extract more energy ?

$$P_{max} = \frac{{E_{emf}}^2 \nearrow}{4R_{Cell} \searrow}$$

Centimeter-scale membrane

No chemicals (low cost/safe)

No external Charge

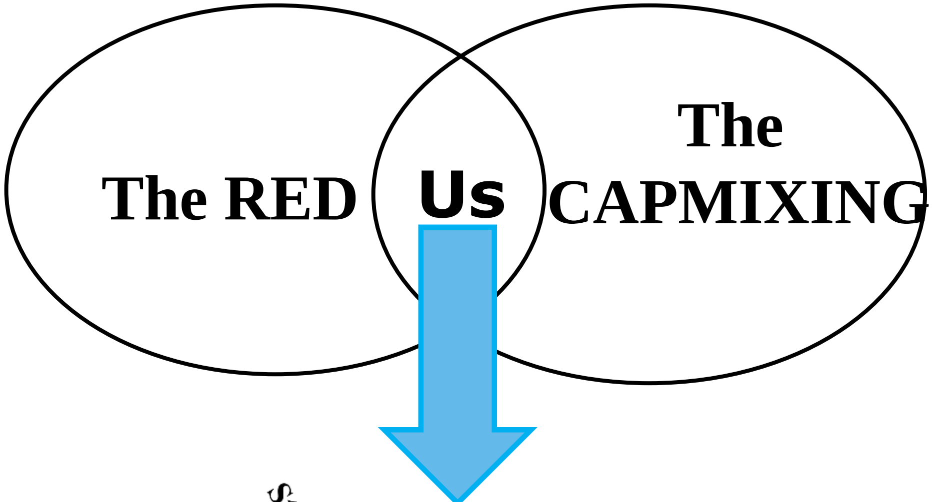
✖ *Diffusio osmosis*

✖ *RED*

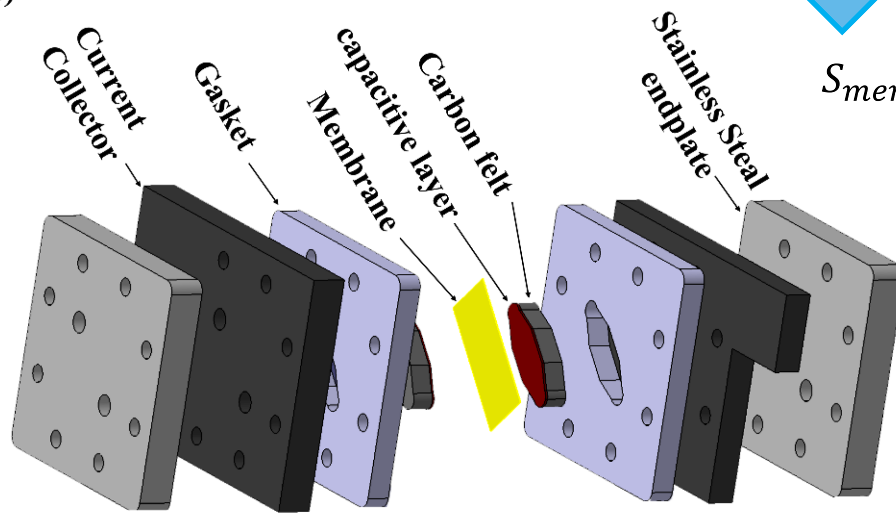
✖ *Capmixing*

Materials & methods

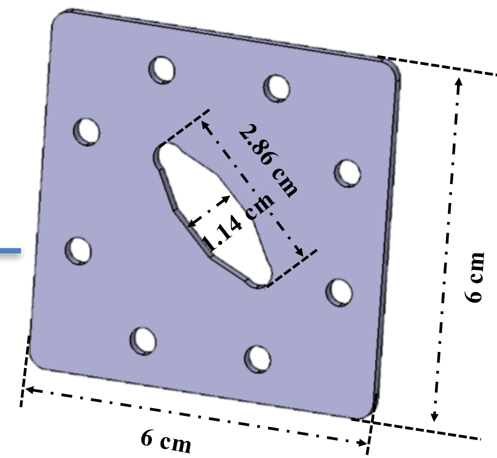
The Cell

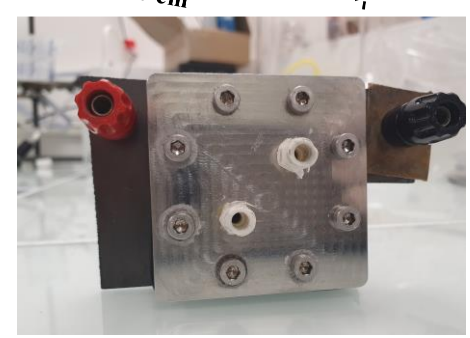


a)



$$S_{membrane}(Nafion\ 211) = 2{,}24\ cm^2$$

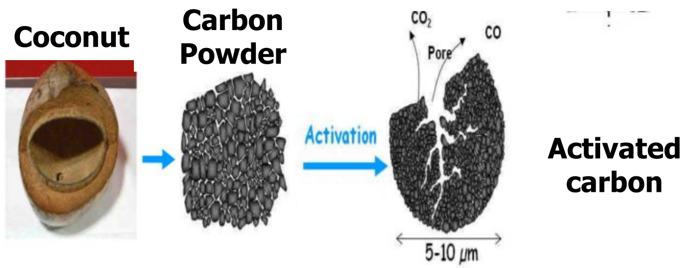




Capacitive layers

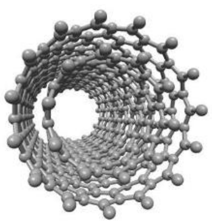
AC

Adapted from P.SIMON (2014)

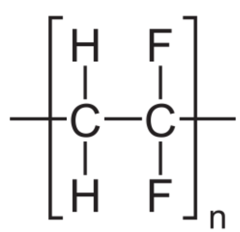


~ 1700 m²/g

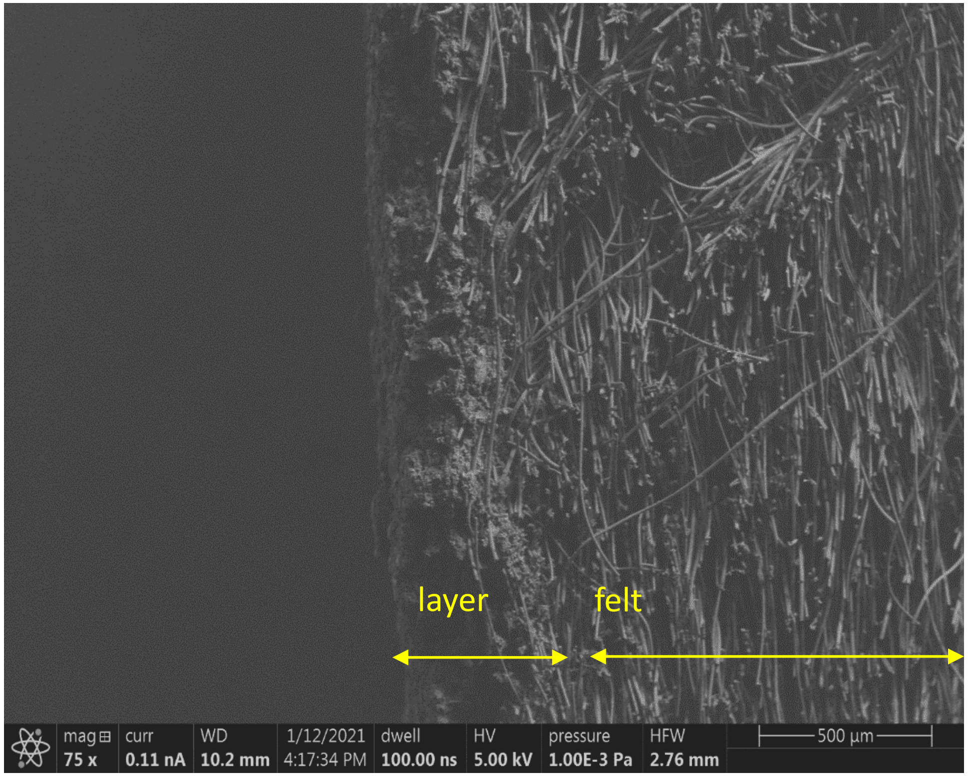
MWCNT



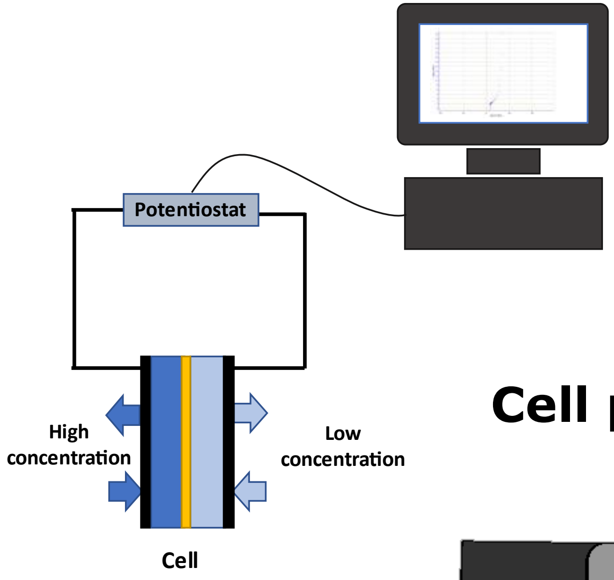
PVDF



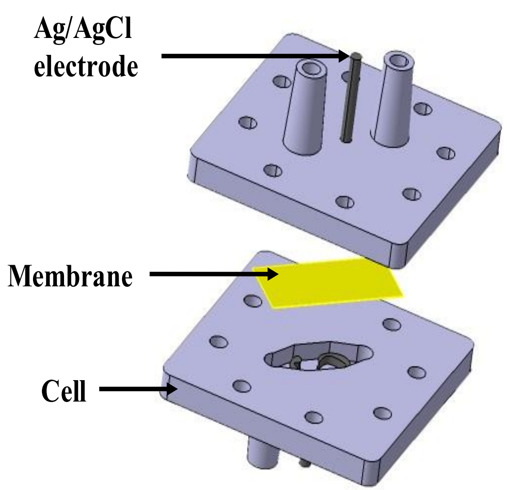
Credit : google



The Cell Potential

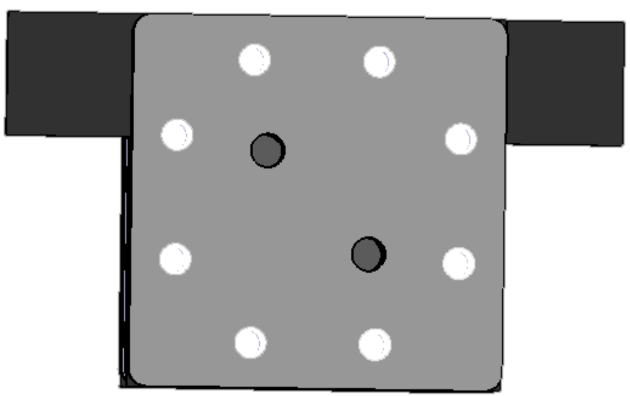


Membrane potential



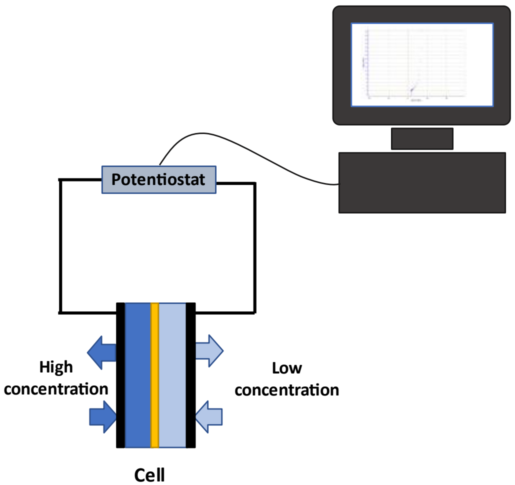
$$E_m = E_{ddp2} - E_{Ag/AgCL}$$

Cell potential



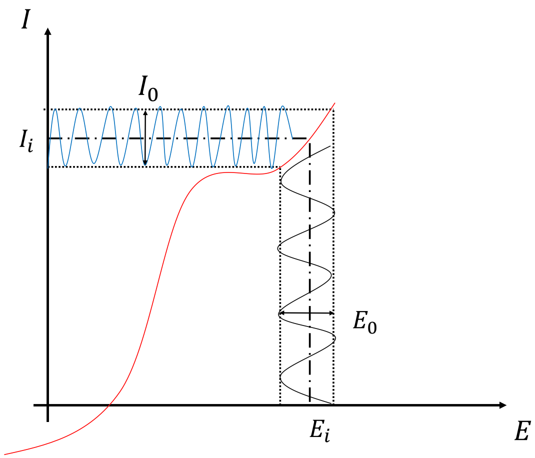
$$E_{ddp1} = 2\ E_{OCV}$$

The EIS



Hardware

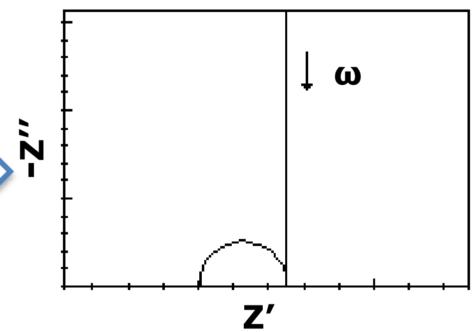
$$E = E_0 sin(\omega t)$$



Software

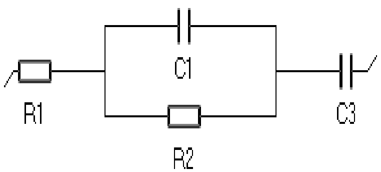
$$Z(\omega) = \frac{E_0 sin(\omega t)}{I_0 sin(\omega t + \varphi)}$$

$$Z(\omega) = Z'(\omega) + j\, Z"(\omega)$$



Nyquist diagram

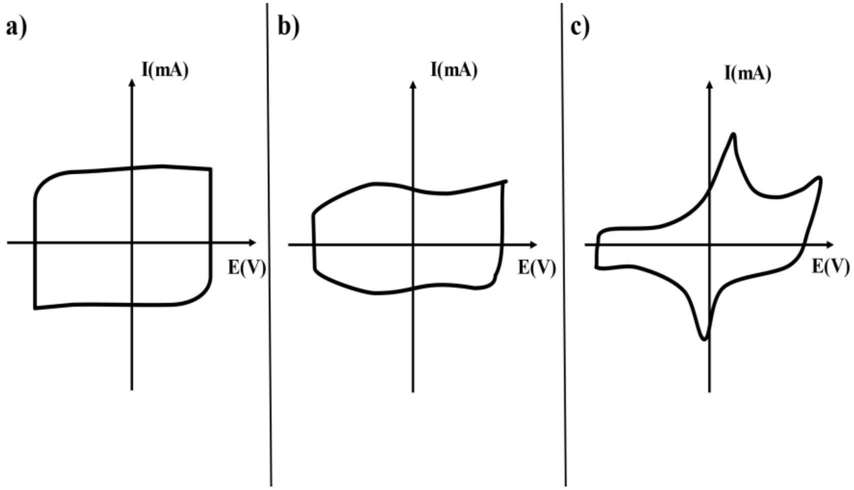
Electrochemical



Equivalent circuit

Direct current

Cyclic voltammetry

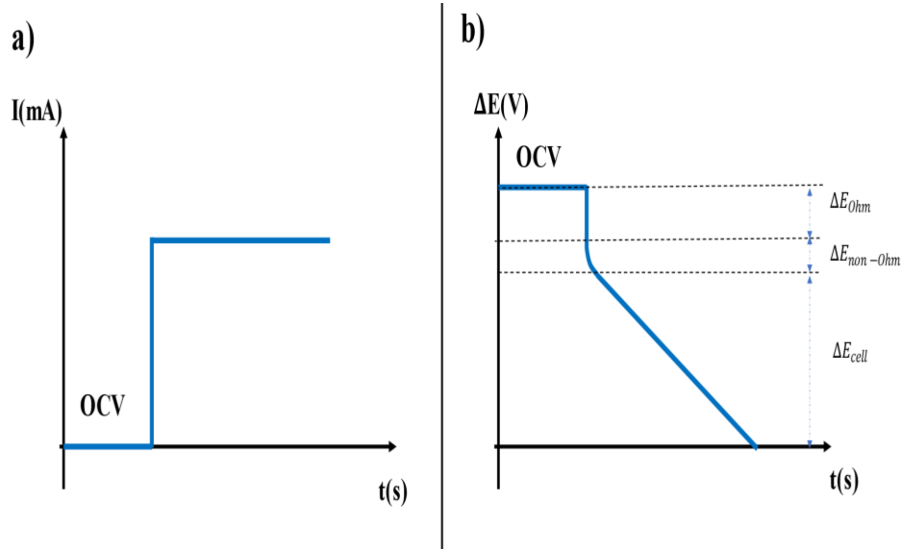


- The nature of the Electrodes

$$C = \frac{I}{v} = \frac{I}{\Delta E} dt$$

$$\mathrm{C} = \frac{Q}{\Delta E}$$

chronopotentiometry



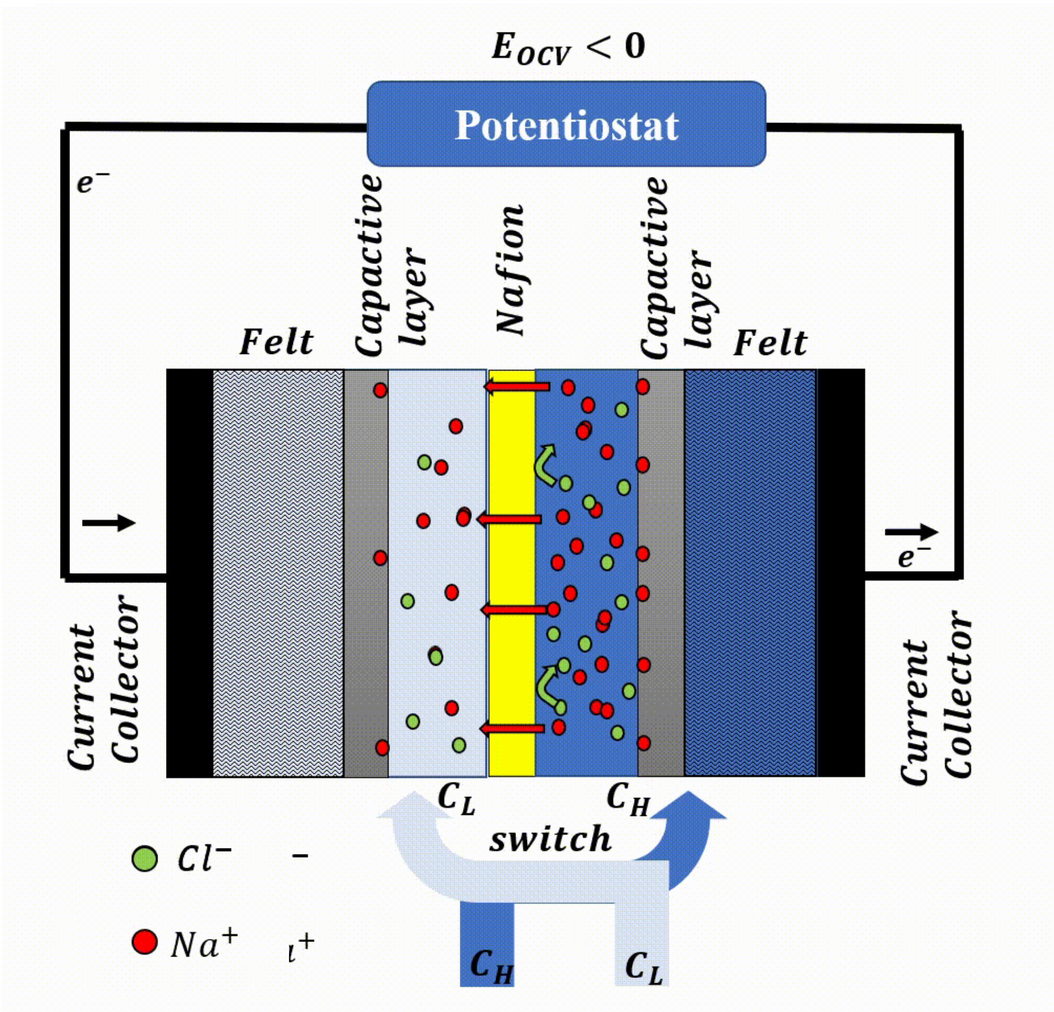
$$C = \frac{I \Delta t}{\Delta E_{cell}}$$

$$\Delta E = I.\mathrm{R}$$

Results & Discussion

CHARACTERIZATION OF THE CELL

Voltage measurement



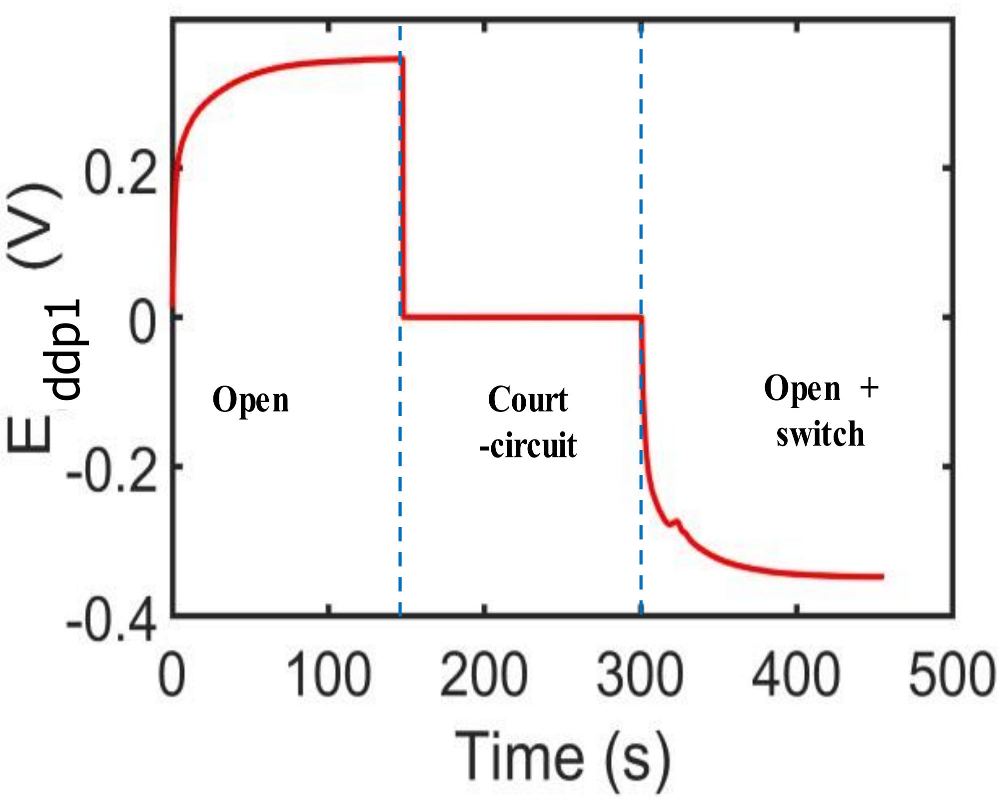
EDL formation (Capacitor) ($t(\infty)$)

Electrons stop moving

No current

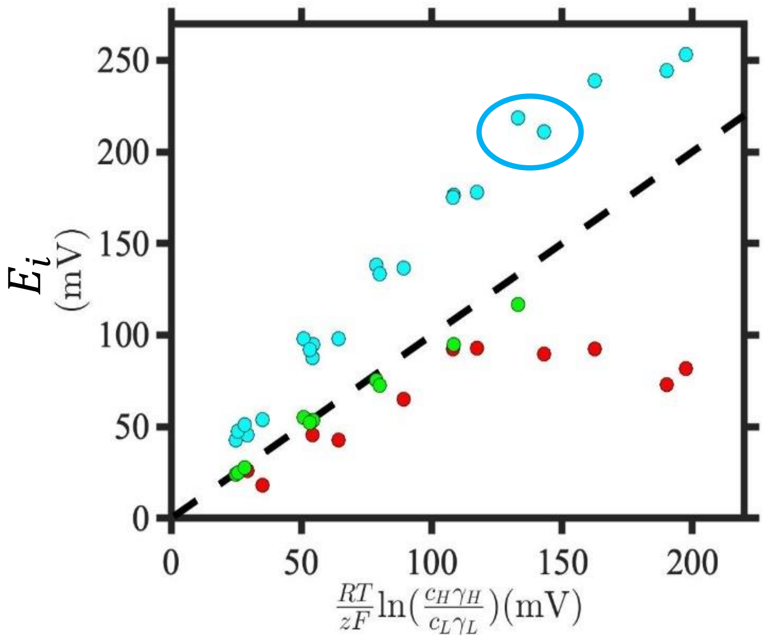
Open circuit Voltage

100 g/L Vs 1 g/L



$$E_{ddp1} = 2\,E_{OCV}$$

Concentration effect



- E_m for $C_H < 0.5$ Mol.L^{-1}
- E_m for $C_H > 0.5$ Mol.L^{-1}
- E_{OCV}

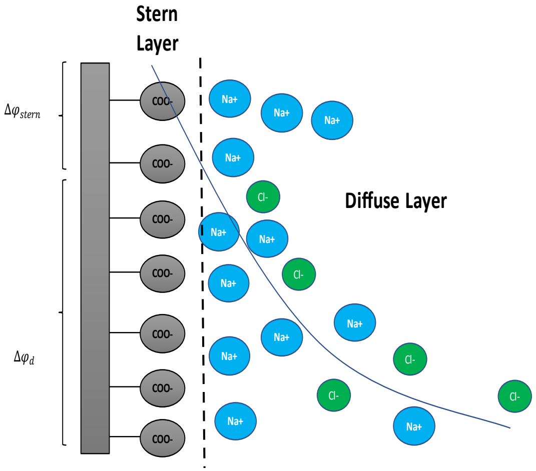
$$- \frac{RT}{zF}\ln\left(\frac{a_H}{a_L}\right)$$

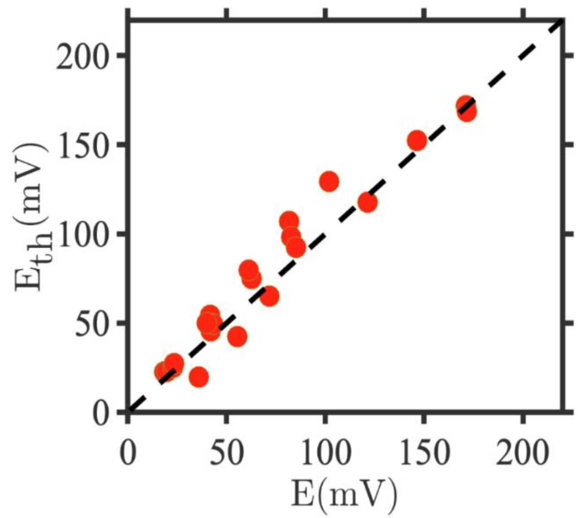
$$E_m = \mathrm{E_{ddp2}} - \mathrm{E_{Ag/AgCL}}$$
$$with\ \ E_{Ag/AgCl} = -\frac{RT}{F}\ln\left(\frac{a_{Cl_L^-}}{a_{Cl_H^-}}\right)$$

$$\frac{1}{2}\mathrm{E_{ddp1}} = E_{OCV} = \mathrm{E_C} + \mathrm{E_m}$$
$$with\ \ E_m = \alpha\frac{RT}{zF}\ln\left(\frac{a_L}{a_H}\right)$$

- At high concentration α starts to vanish.
- The open circuit potential is doubled.
- E_C is stable even at high concentrations

The Potential modeling





$\sigma_{St} = -0.12\ C/m^2$

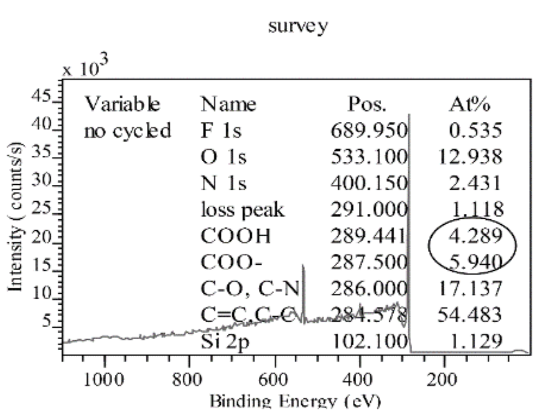
$$E_{ocv} = E_m + \Delta\varphi_{C_H} - \Delta\varphi_{C_L}$$

Gouy Chapman Stern

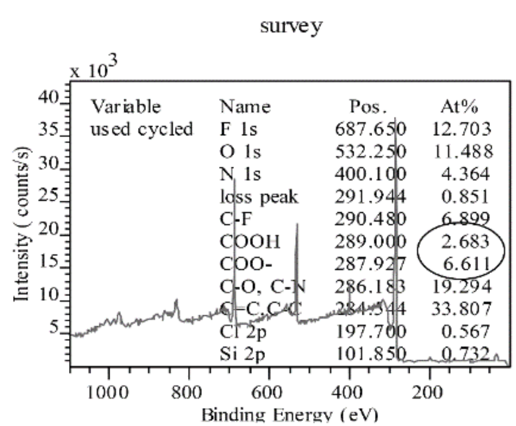
$$\Delta\varphi_i = \frac{\sigma_{St}}{C_{st}} + \varphi_d - \varphi_i$$

➢ $\boldsymbol{COO^-}$ attracts the $\boldsymbol{Na^+}$ Ions creating Nernst behavior.

a) Before

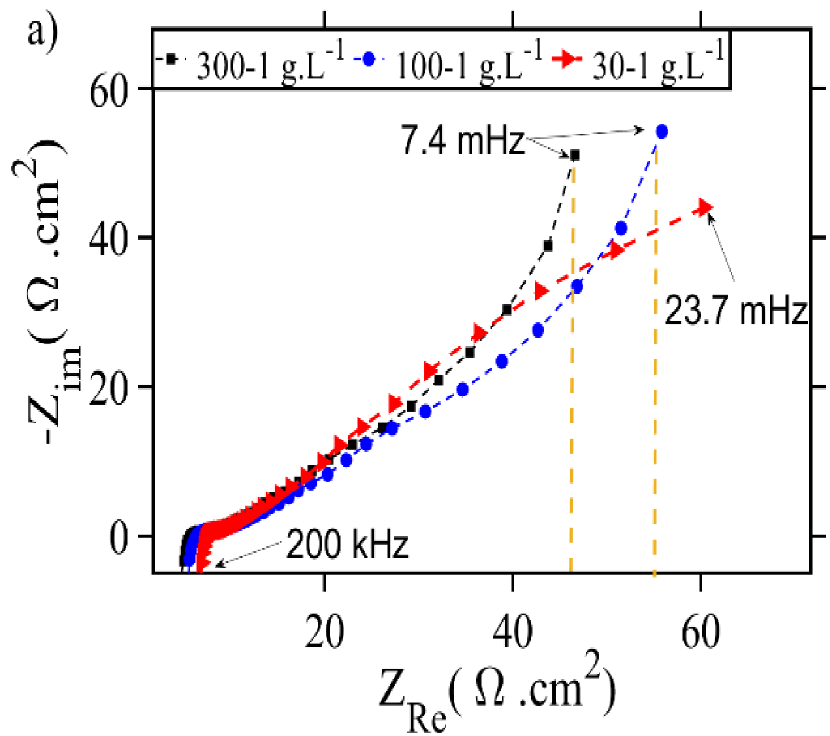


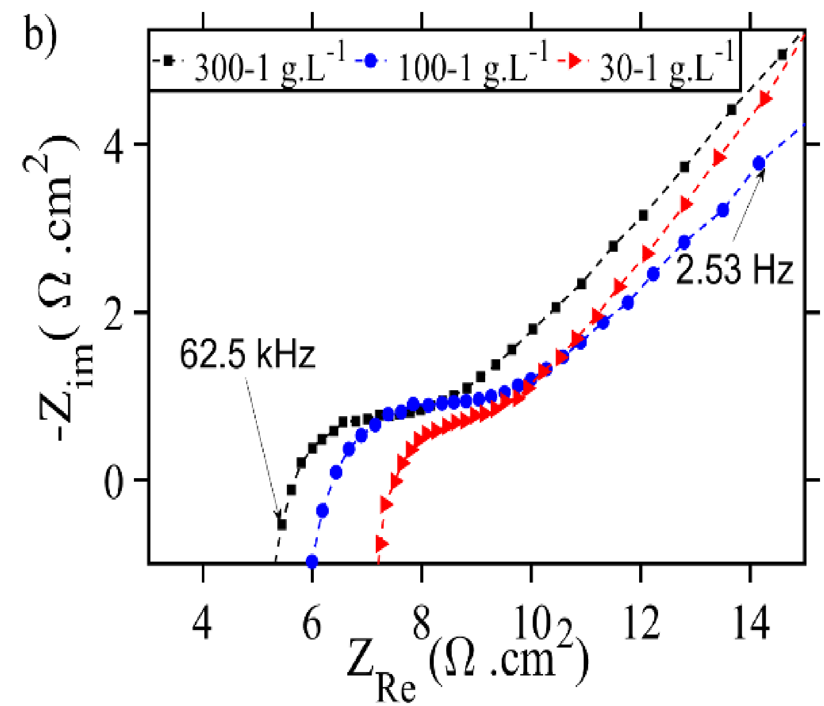
b) After



$$\boldsymbol{E_{ocv} - E_m = \frac{RT}{z\,F}\ln\left(\frac{C_{C_H}}{C_{C_L}}\right)}$$

The EIS





Midrange & low frequencies

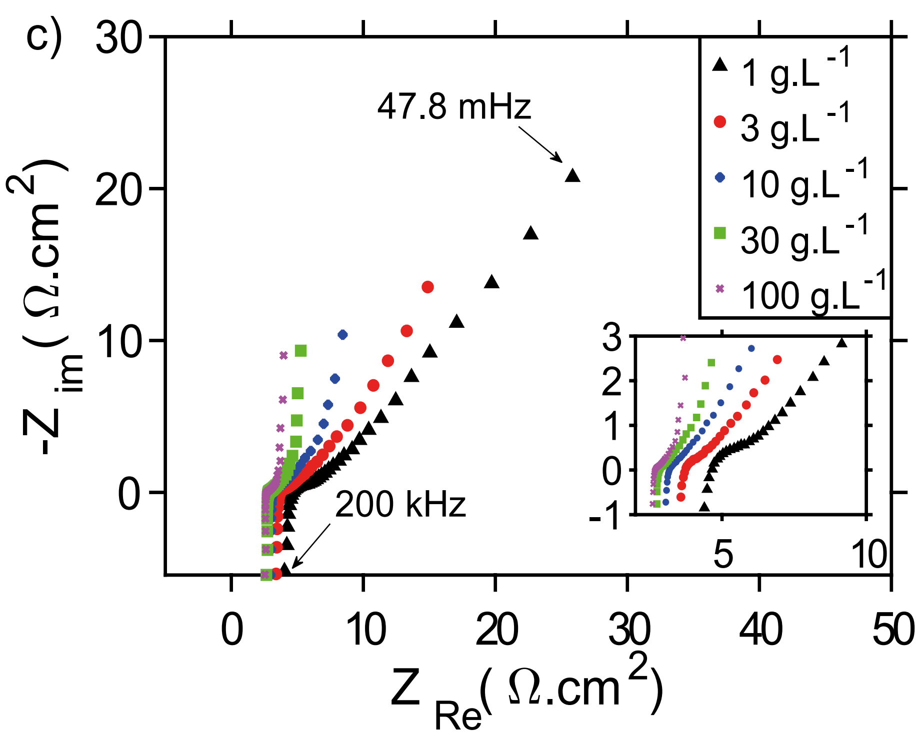
- Ion transport from the bulk electrolyte to the porous electrode
- A dominant capacitive behavior.

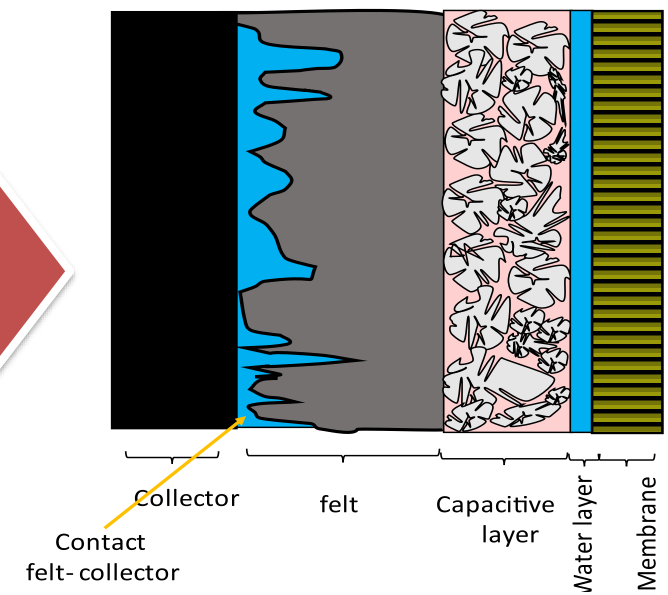
High frequencies

- The equivalent series resistance (ESR).
- Charge transfer resistance.

The impedance modeling

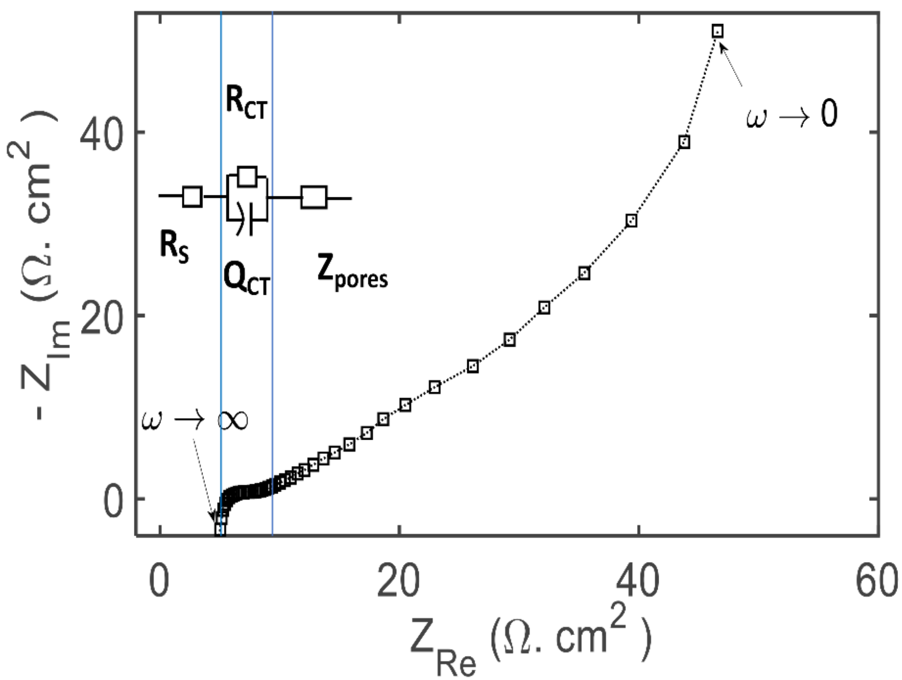
$C_H = 300\ g/L\ \ vs$



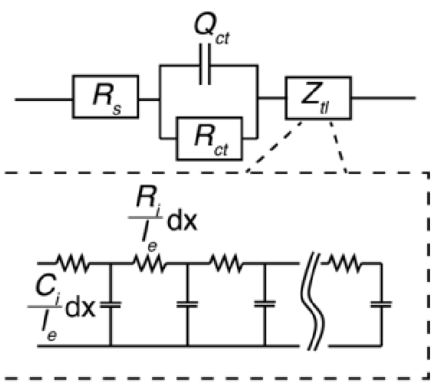


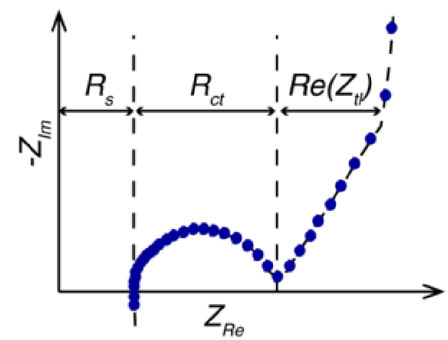
The impedance modeling

100 g/L Vs 1 g/L



A. Kuo *(Environ. Sci.: Water Res. Technol.*, 2020)
Yatian Qu , *(Environ. Sci. Technol. , 2015)*





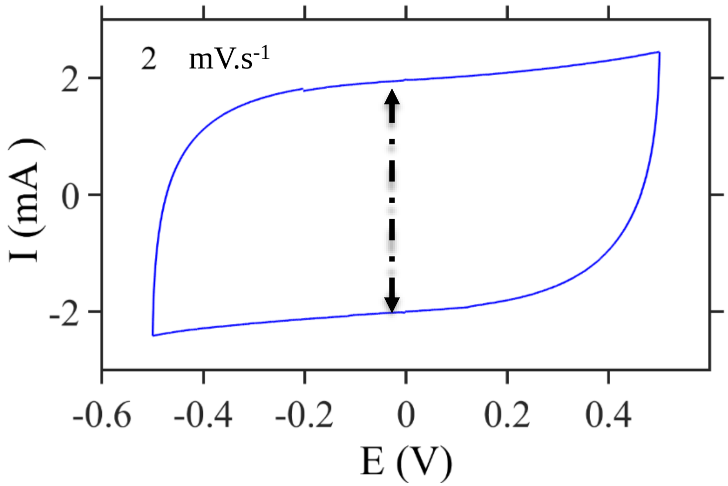
$$Z_{Re}^{\omega\to\infty} = R_s = R_{felt} + R_{collector} + R_{membrane} + R_{ls}$$

$$Z_{Re}^{\omega\to 0} = R_s + R_{CT} + \frac{R_{Pores}}{3}$$

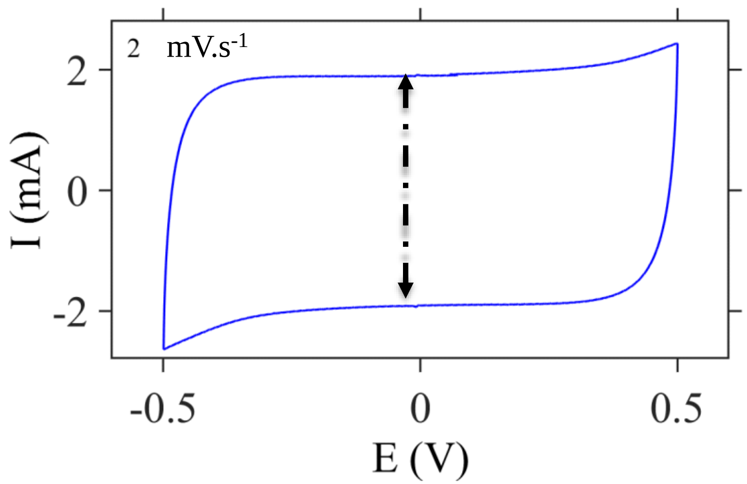
$$Z_{im}^{\omega\to 0} = \frac{1}{C\omega}$$

Cyclic voltametry

100 g/L Vs 1 g/L



300 g/L Vs 1 g/L



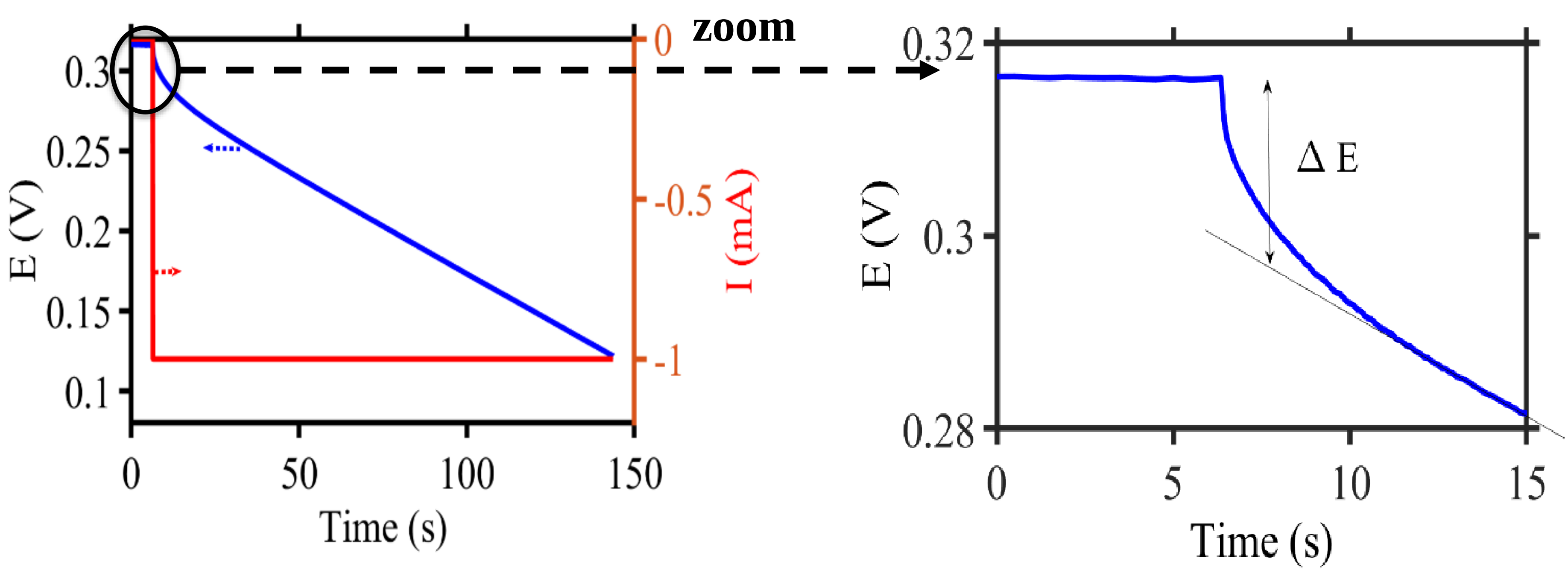
C = 0,87 F

C = 0,95 F

- *Capacitive behavior*
- $C\ (F) \propto c_i(mol.L^{-1})$

Chronopotentiometry

100 g/L Vs 1 g/L



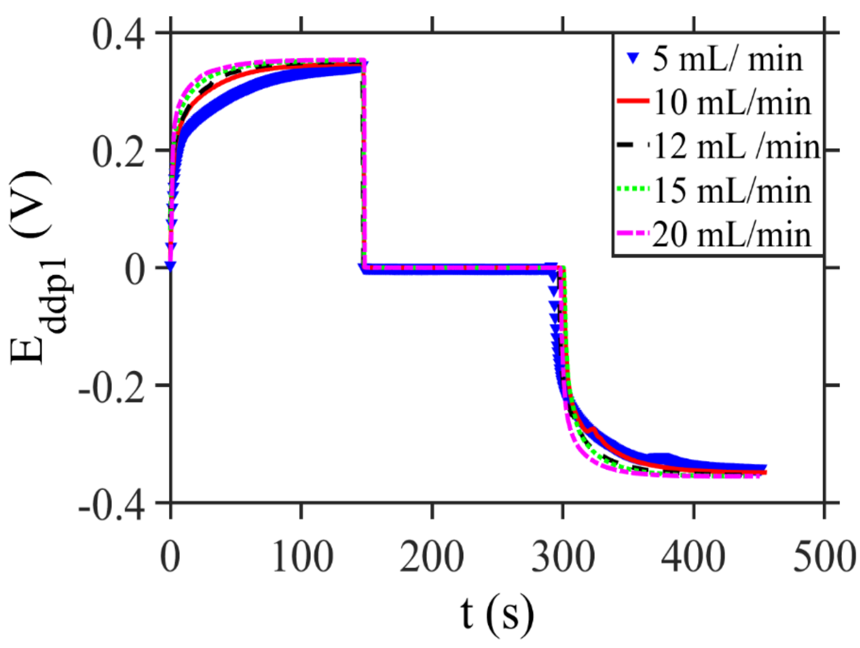
- *Capacitive behavior*
- $R \approx Z_{re}^{\omega \to 0}$
- $C \approx Z_{im}^{\omega \to 0}$

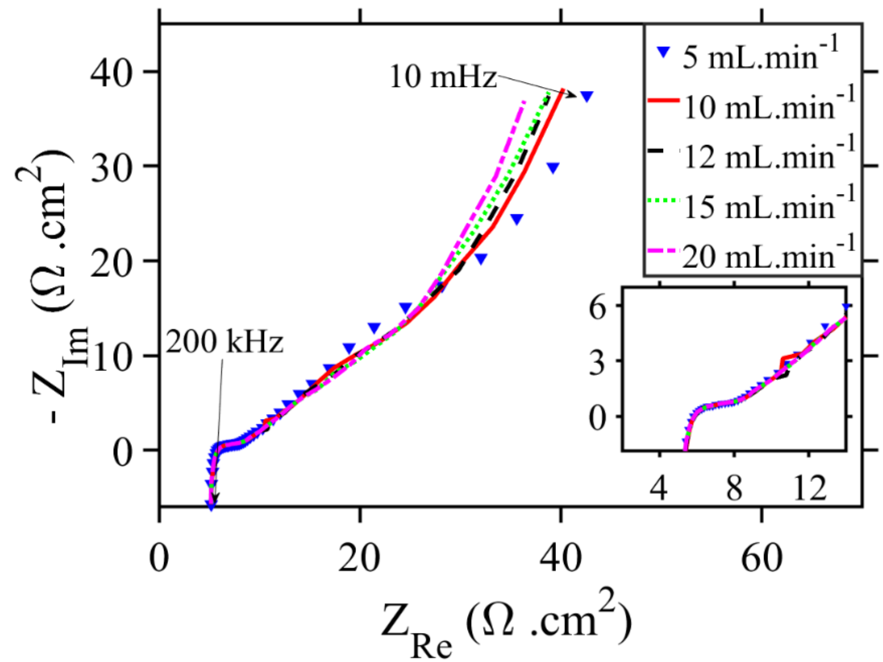
$$C = \frac{I\Delta t}{\Delta E} = 0{,}84\ F$$

$$R = \frac{\Delta E}{I} = 24\ \Omega$$

The flow rate

100 g/L Vs 1 g/L

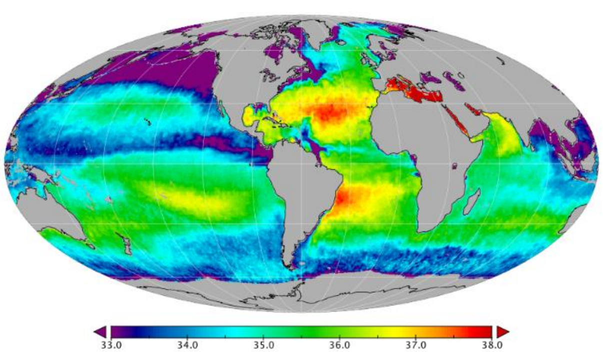




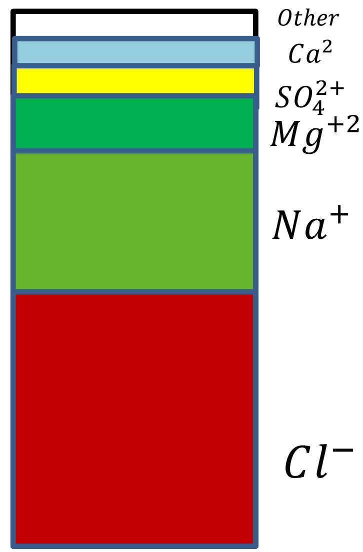
- ➢ Time to reach the $E_{OCV}(\infty)$ depends on the flow rate
- ➢ The ions transport inside the pores is modified.

Solutions effect

W. Wurtsbaugh et al. (ngeo 2017)

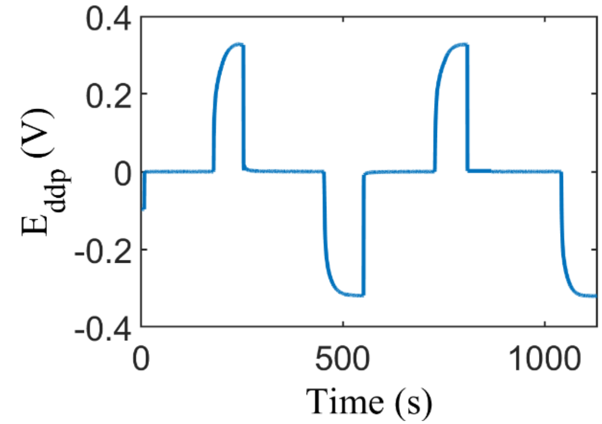


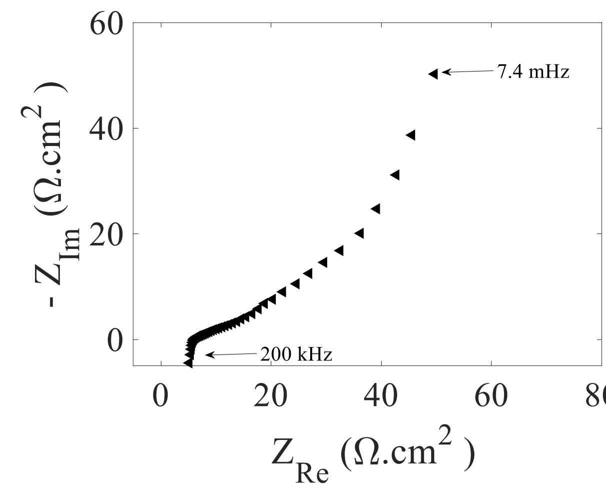
salinity.oceansciences.org



Artifcial sea water
100g/L
ASTM D1141-98

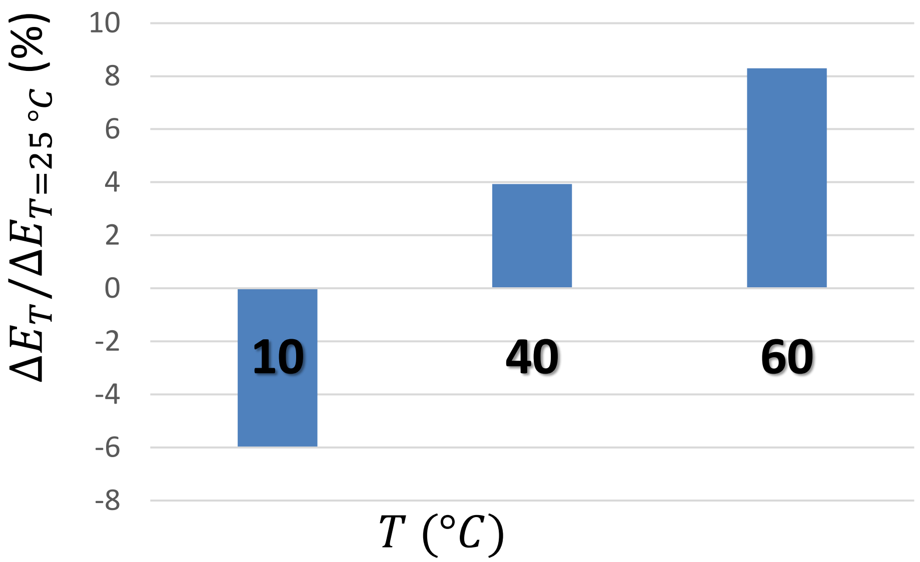
$C_H/C_L = 100$

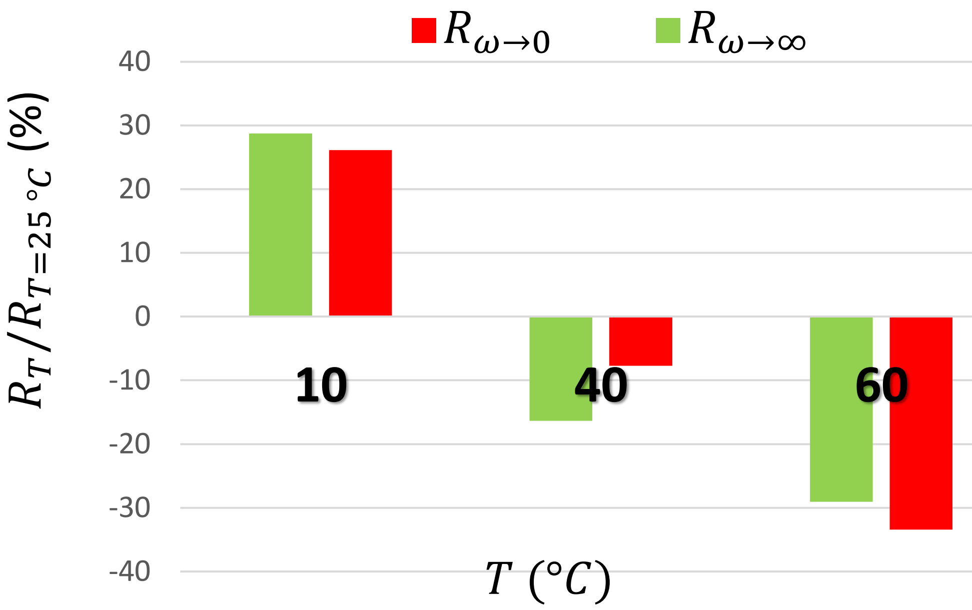




Temperature

100 g/L Vs 1 g/L



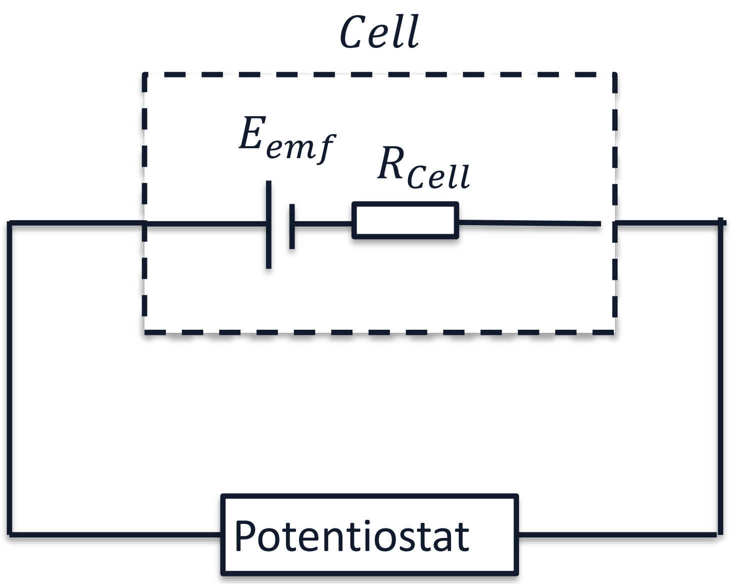


- ↗ Ions transport inside the pores
- ↗ Ions mobility
- ↗ Conductivity

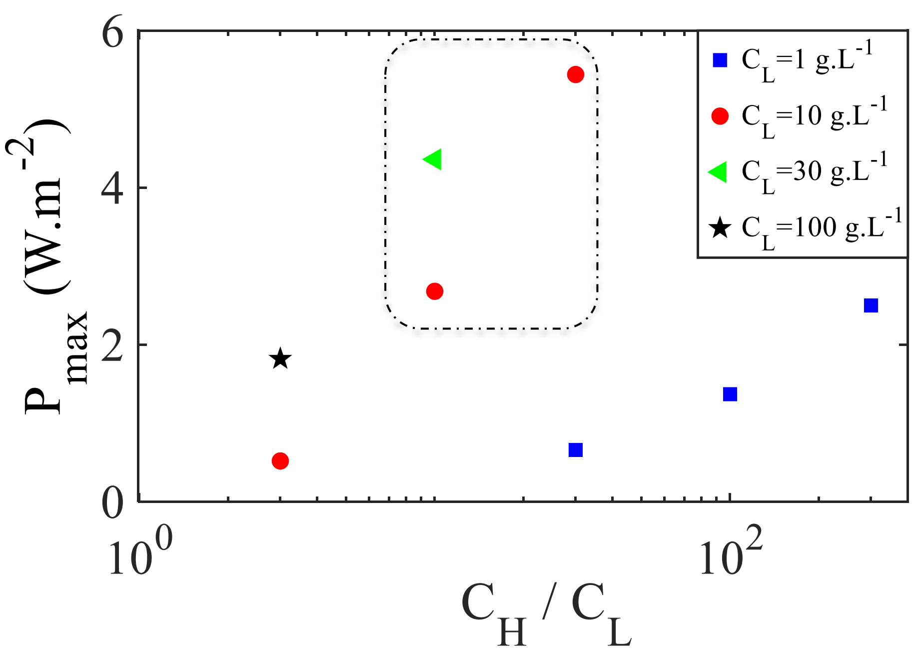
The Power density

The Calculated Power density

Simplified circuit

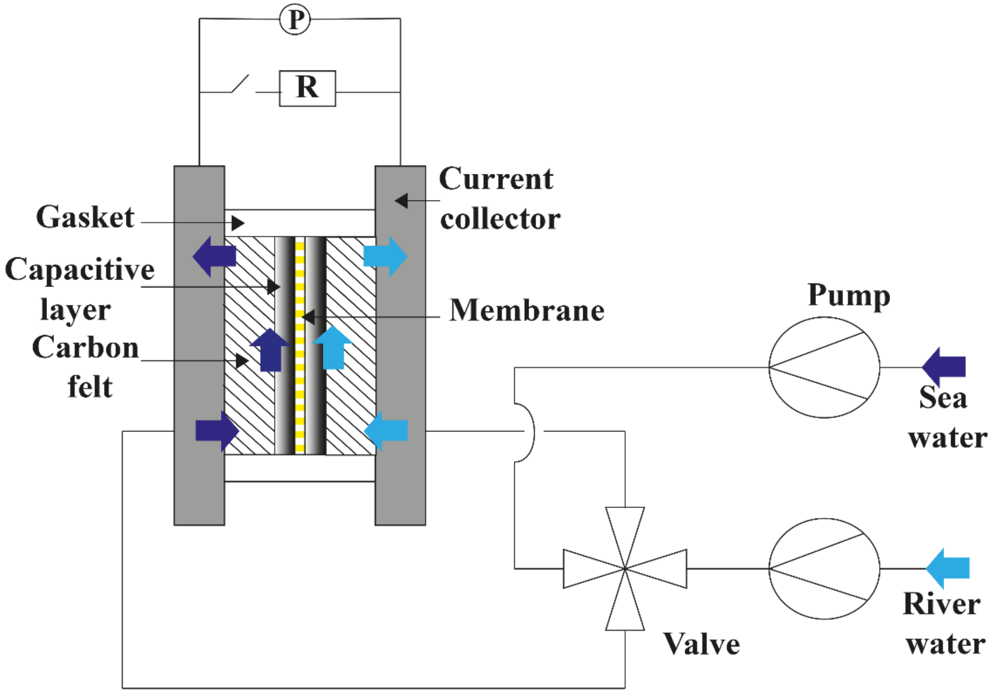


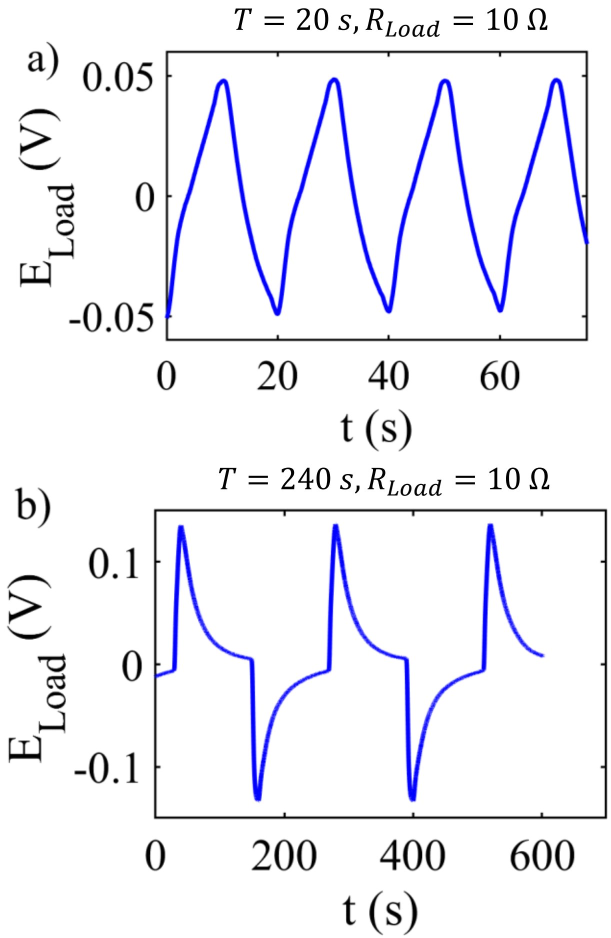
$$P_{max} = \frac{{E_{emf}}^2}{4R_{Cell}}$$



- ↗ P_{max} for hypersaline solutions

The efficient Power density

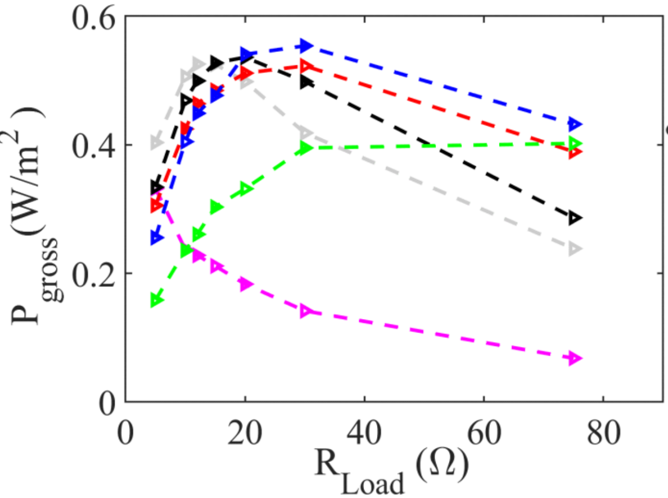




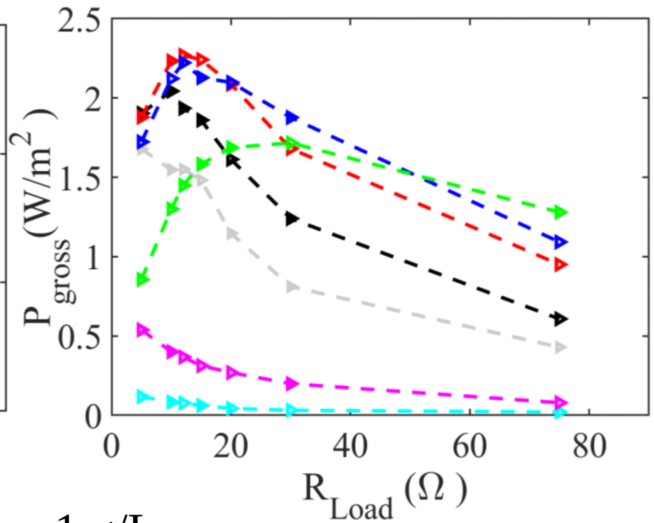
S=2,24 cm² | C_H=100 g/L|C_L=1 g/L

The efficient Power density

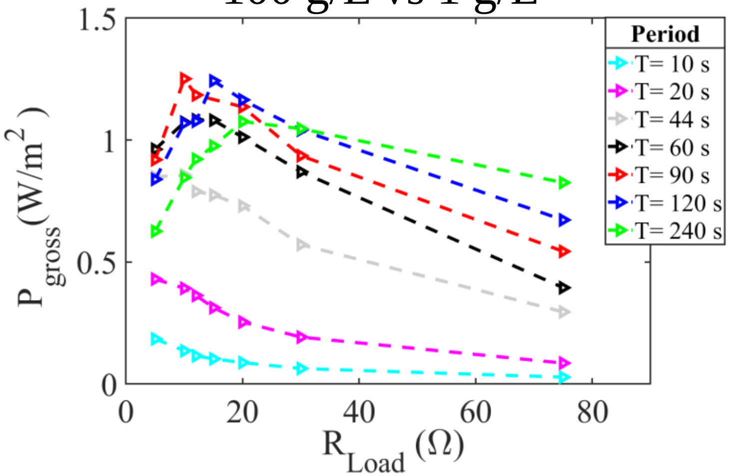
30 g/L vs 1 g/L



300 g/L vs 1 g/L



100 g/L vs 1 g/L



$$P = \frac{1}{A.T}\int_0^T \frac{E_{Load}^2(t)}{R_{Load}(t)}dt$$

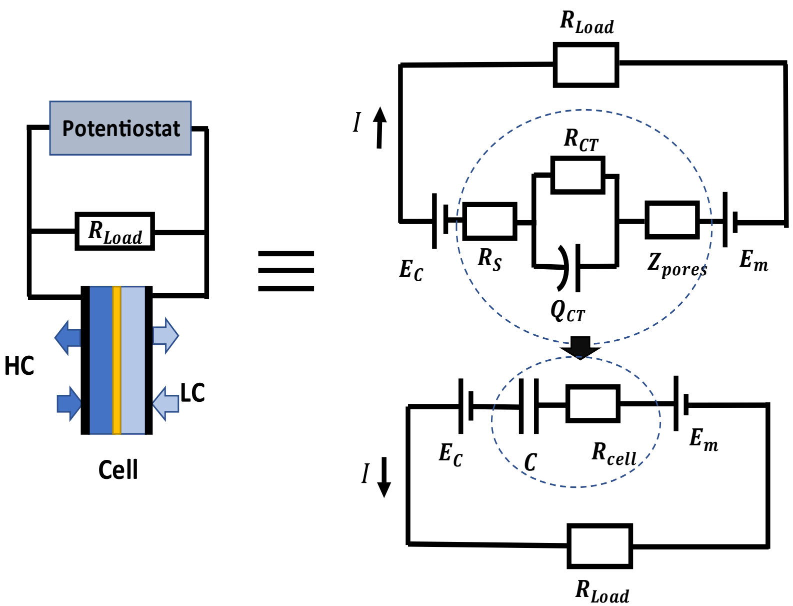
E_c & E_m

R_{Cell}

- *The concentrations*
- *Ions transport's inside the pores*
- *Time constant*
- *Ions generation*

Power Modeling

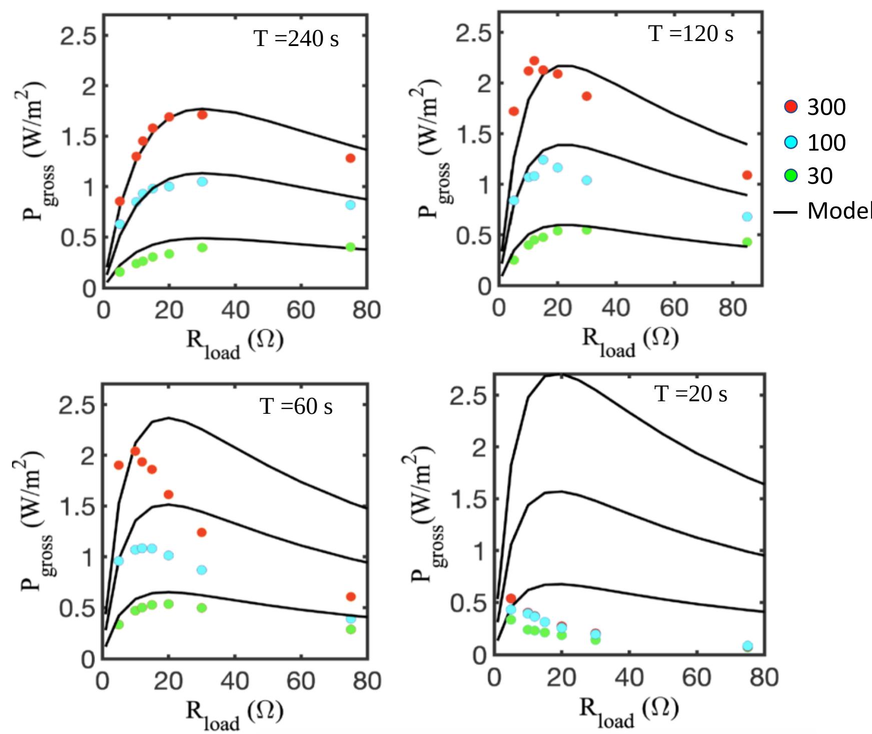
Equivalent Model



$$E_{OCV} = (R_{Load} + R_{Cell})I(t) + \frac{q(t)}{C}$$

$$\frac{dq(t)}{dt} = I(t)$$

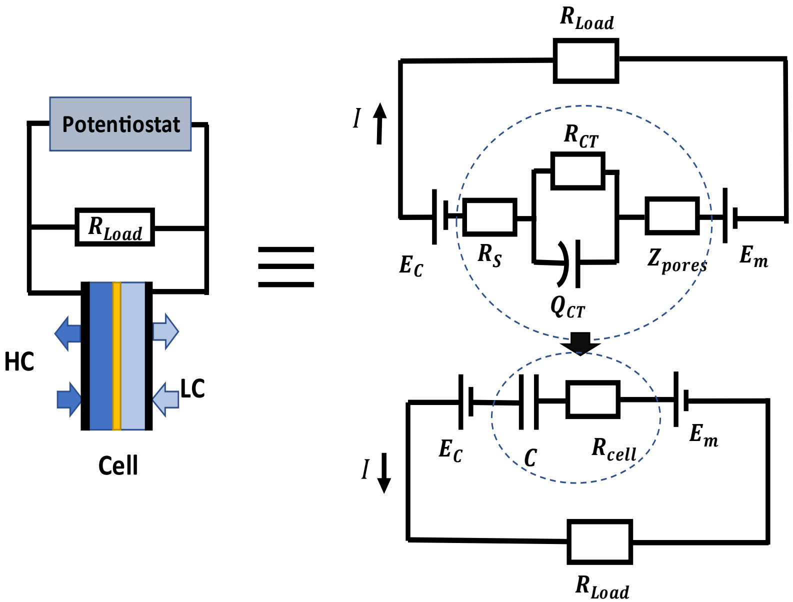
Power modeling



- ➢ A good match at long periods
- ➢ Time to fill & develop the potential is estimated **X**

Power Modeling

Equivalent Model

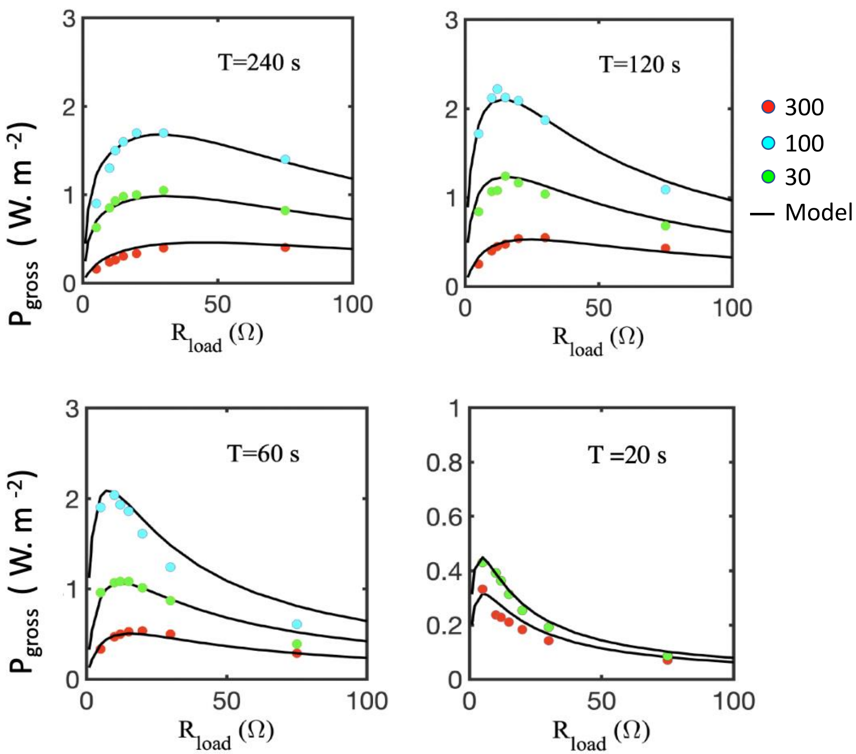


$$E_{OCV}(t) = \left(R_{load} + R_{Cell}(t)\right)I(t) + \frac{q(t)}{C}$$

$$E_{OCV}(t) = \frac{E_{OCV}(\infty)}{2} + \frac{E_{OCV}(\infty)}{2} * (1 - e^{-t/\tau})$$

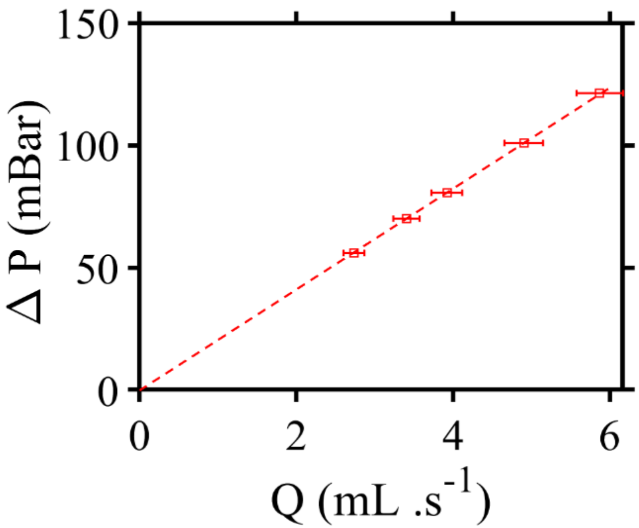
$$R_{Cell}(t) = R_{Cell}(\infty) * (1 - B\, e^{-t/\tau})$$

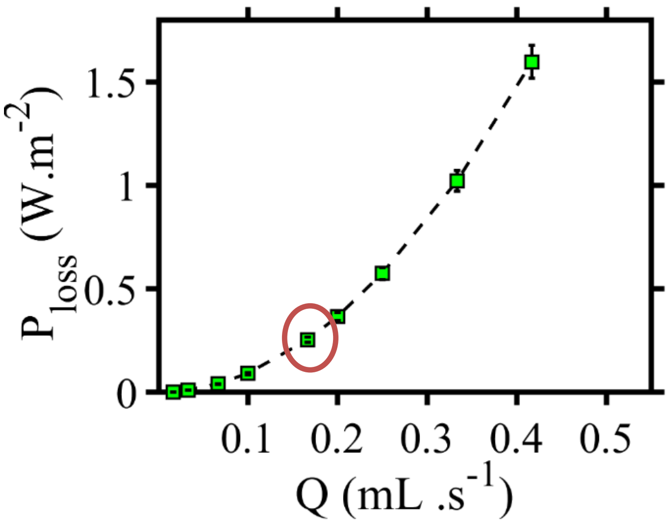
Power modeling



- ➢ A perfect match with R(t)
- ➢ B is equal to 0.9 and τ =30 s for all the experiments.

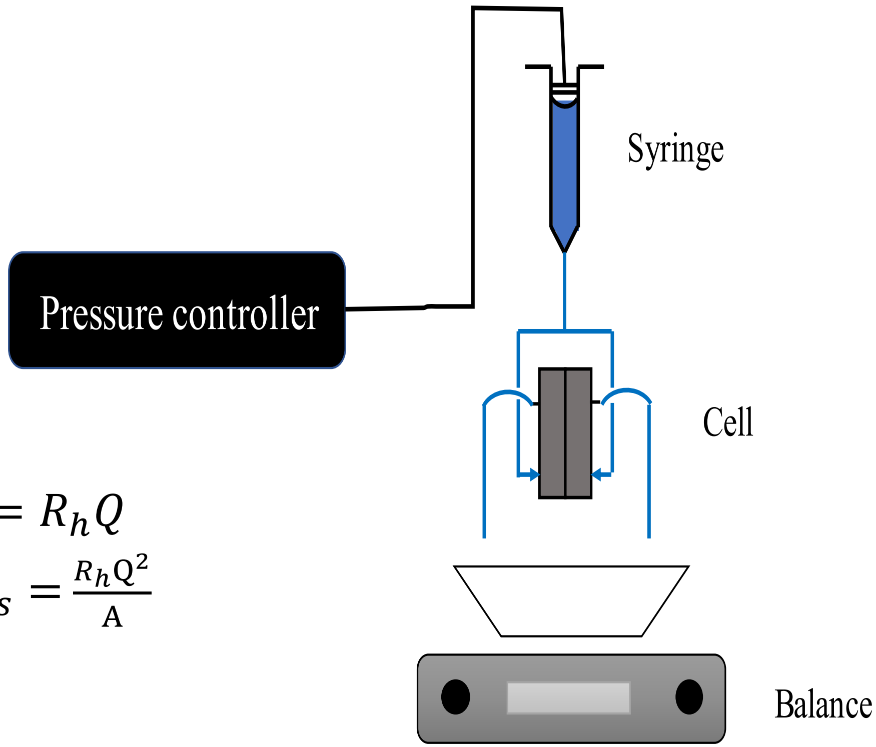
Power loss





$$\Delta P = R_h Q$$

$$P_{loss} = \frac{R_h Q^2}{A}$$



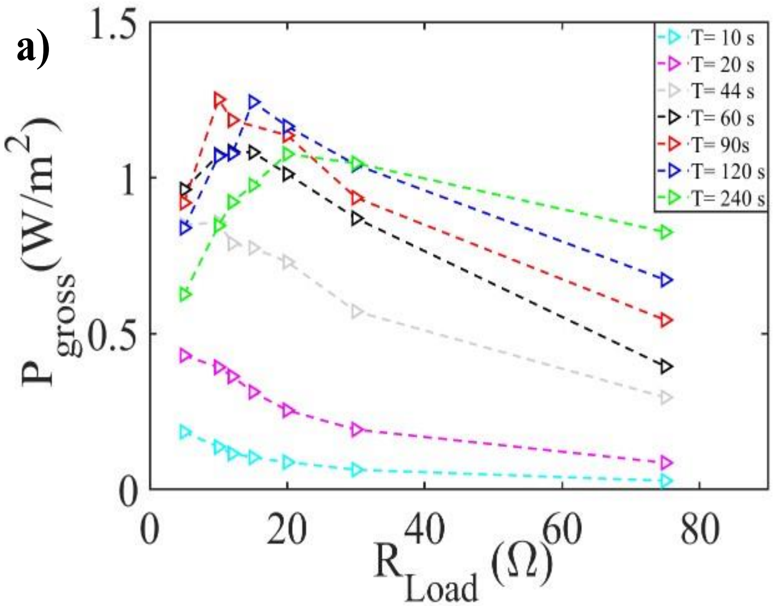
$for\ Q = 10\ mL\ /min$

$P_{loss} = 0{,}23\ W/m^2$

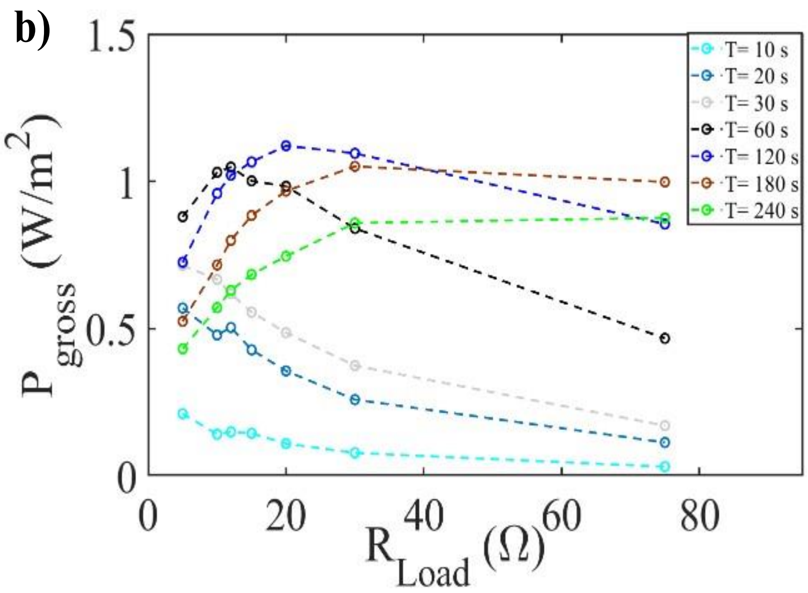
The felt thickness

S=2,24 cm² | C_H=100 g/L|C_L=1 g/L

6 mm



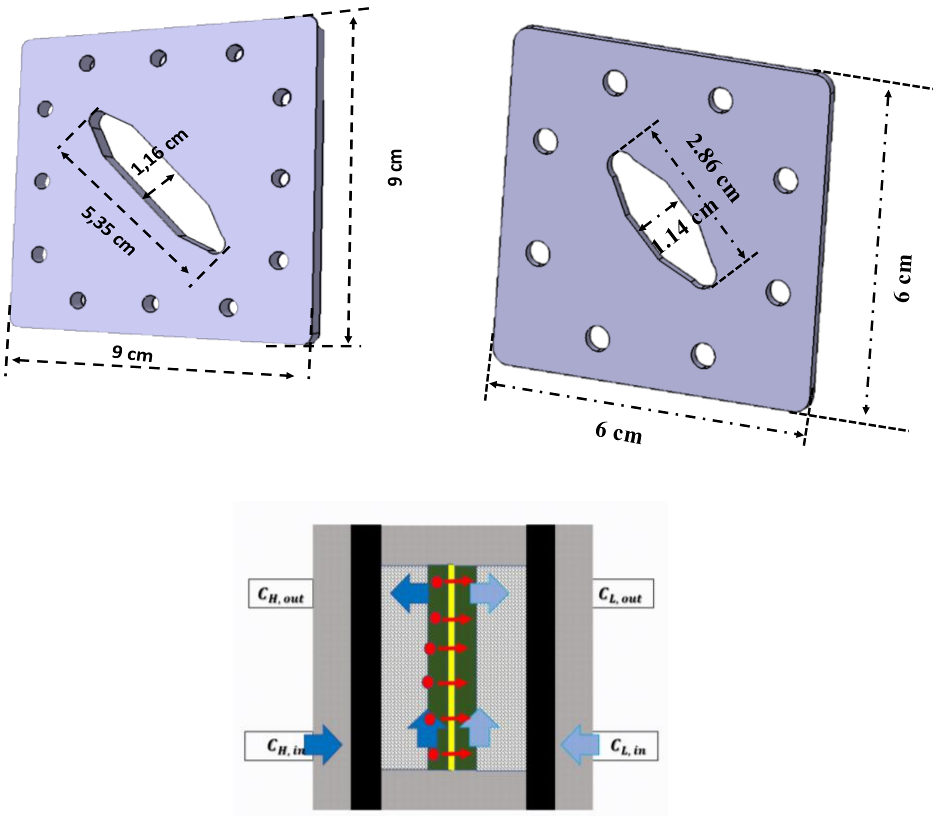
2 mm



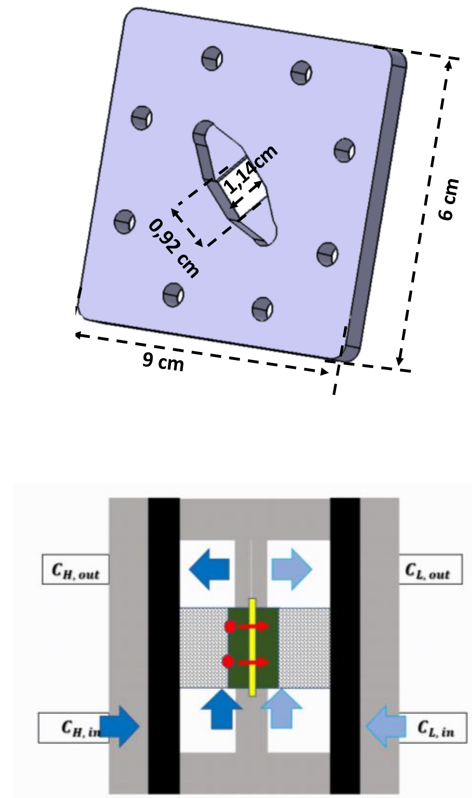
- The gross power density is barely affected
- The Power loss is 3 times bigger in thinner felt

Membrane length (surface)

C_H=100 g/L|C_L=1 g/L



Cross flow

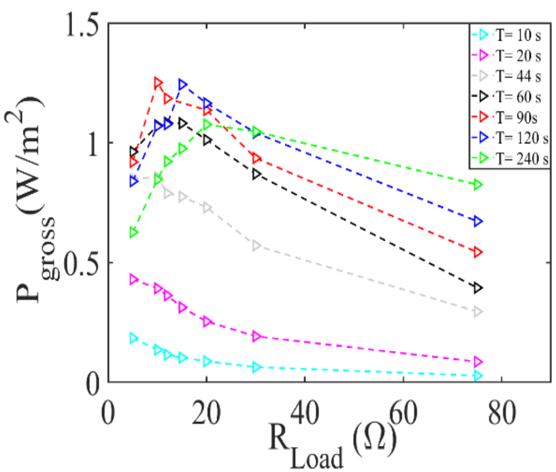


Co-flow

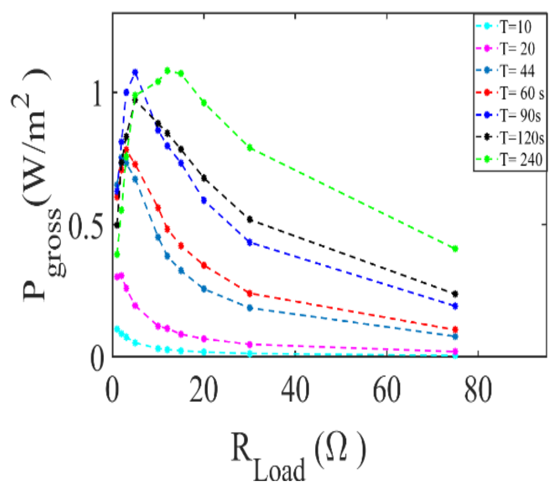
Membrane length (surface)

C_H=100 g/L|C_L=1 g/L

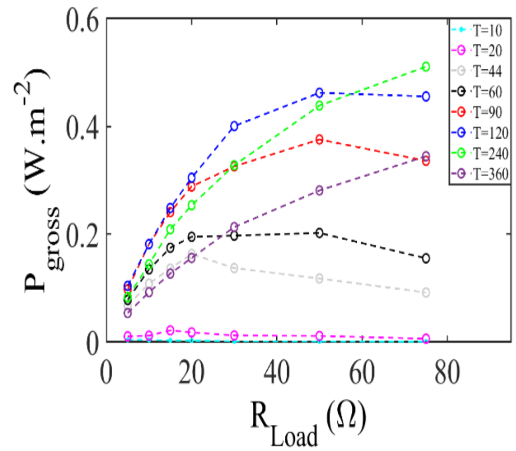
S = 5,25 cm²



S = 2,24 cm²



S = 1,07 cm²

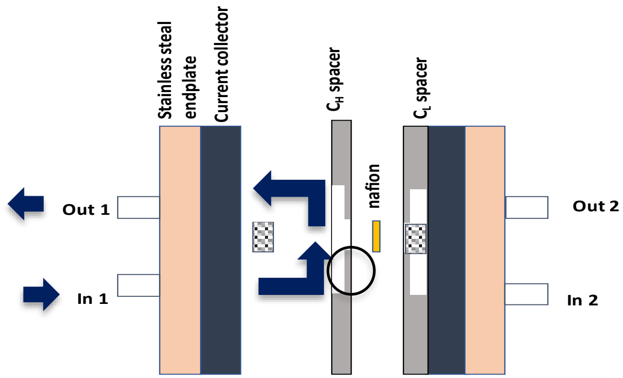


- The time to fill the cell depends on the membrane length
- The power density is barly changed for the crossflow
- The **CP** is more important in co-flow

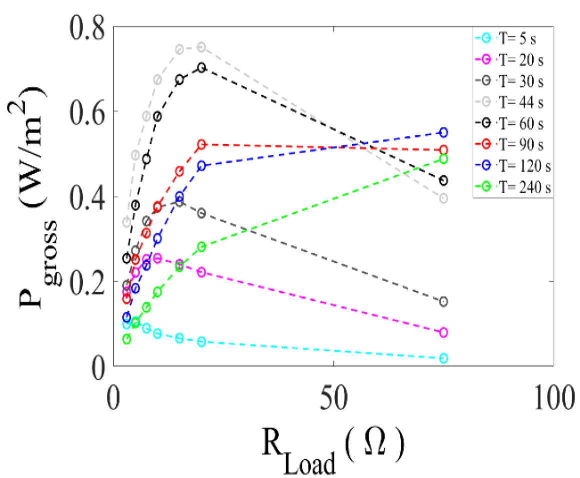
RESULTS & DISCUSSION

The flow rate

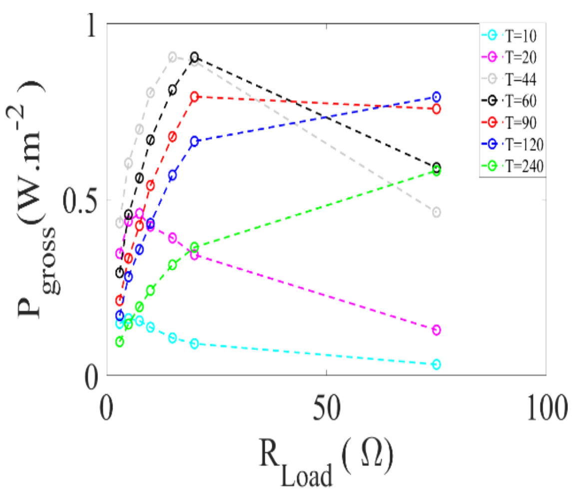
S=1,07 cm²
C_H=300 g/L
C_L=10 g/L



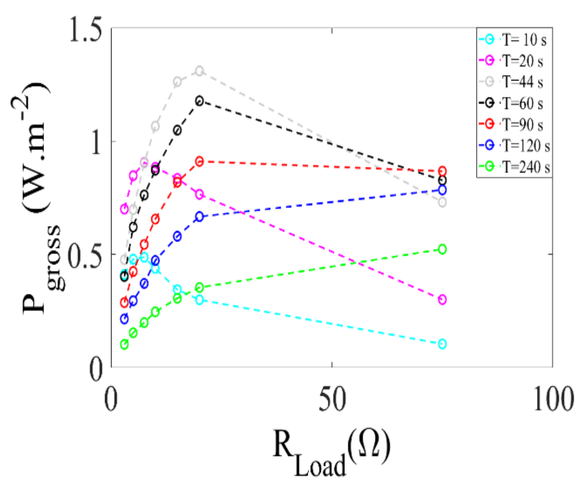
D=10 mL/min



D=20 mL/min



D=30 mL/min

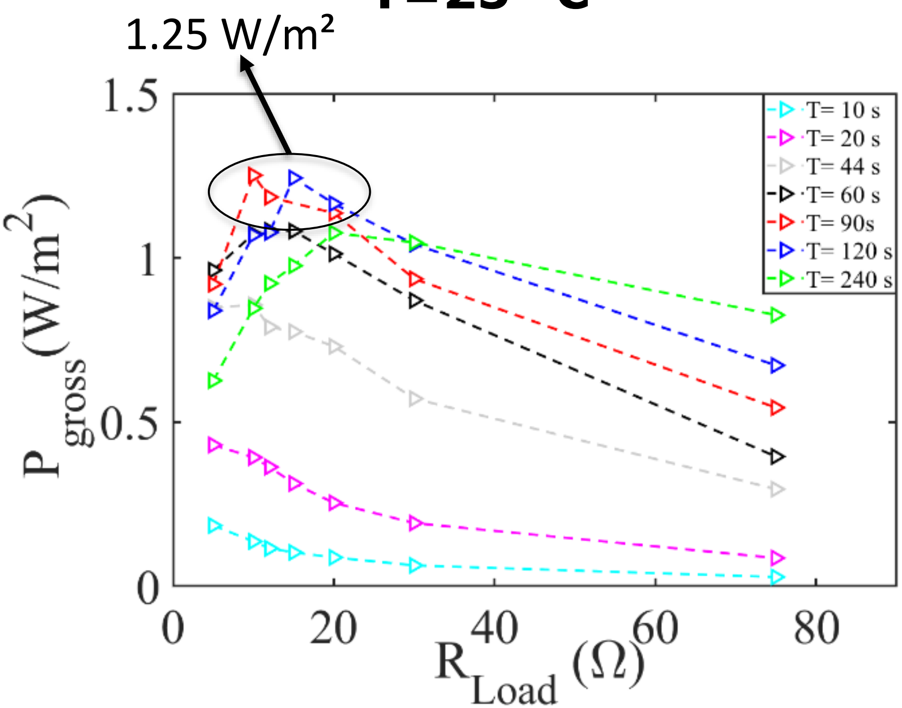


↗ ***Flow rate*** ⇨ $\begin{cases} \textbf{Ion transport} \nearrow \\ R_{\Delta C}\ \textbf{(Polarization)} \searrow \end{cases}$ ⇨ P_{gross} ↗

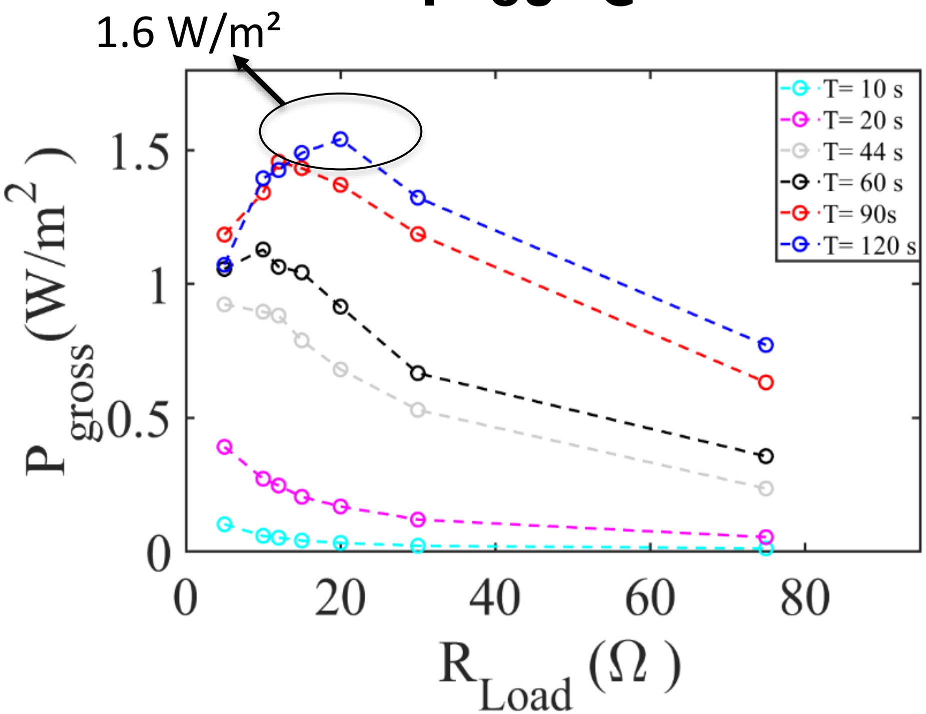
Temperature

S=2,24 cm² | C_H=100 g/L|C_L=1 g/L

T=25 °C



T=60 °C



$$T \nearrow \quad \Rightarrow \quad \begin{cases} E_m \nearrow \\ R_{Cell} \searrow \end{cases} \quad \Rightarrow \quad P_{gross} \nearrow$$

Conclusion & Outlooks

General conclusion

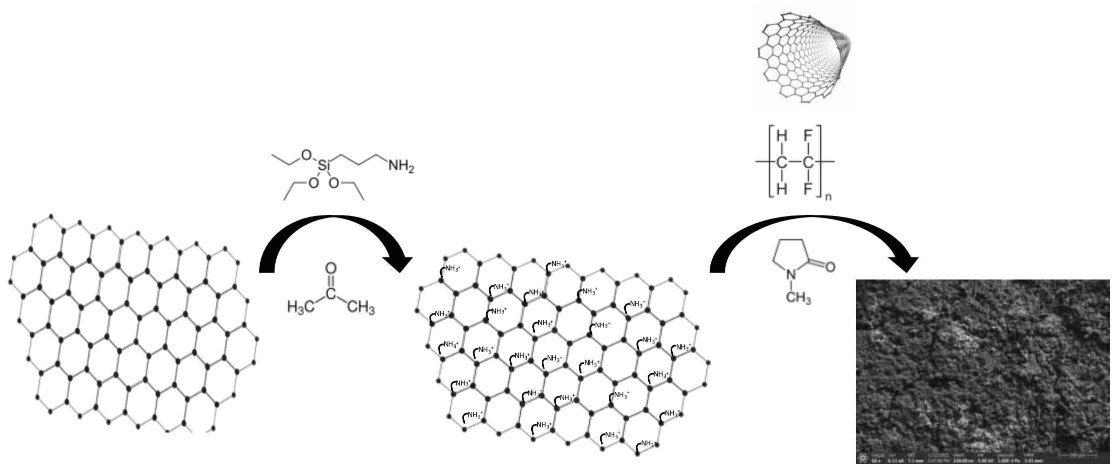
- **Attaching tailored capacitive layers with charged surface to the IEM membranes double the potential.**
- **The capacitive layers can be used in hypersaline solutions.**
- **The transport inside the pores controls the impedance.**

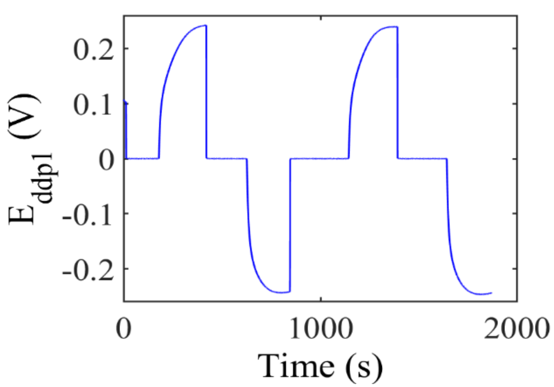
General conclusion

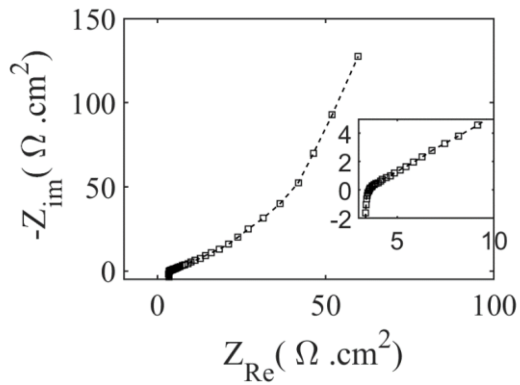
- **A tradeoff between R_h , R_{Cell} and C must be carefully optimized to maximize power generation.**
- **The CP is inherent of all membrane separation processes and can be reduced by using the appropriate flow.**
- **A Net power density of 2 W/m² is achieved using a 300 gradient.**

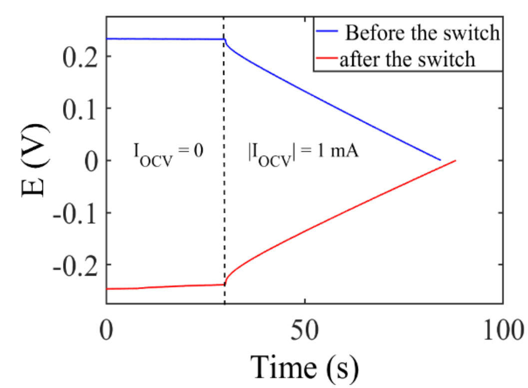
Outlooks

COULD WE INVERSE THE CAPACTIVE LAYERS CHARGE ?







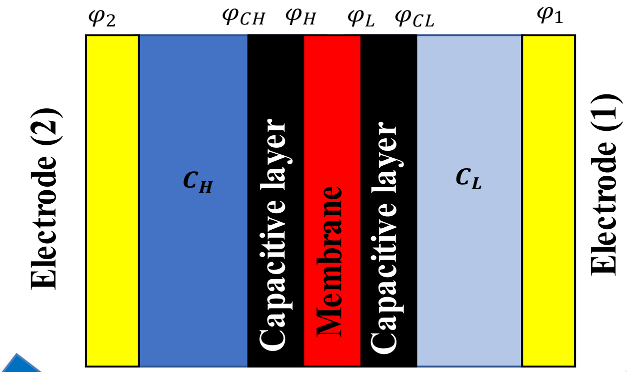


S=2,24 cm² Membrane FAS 30

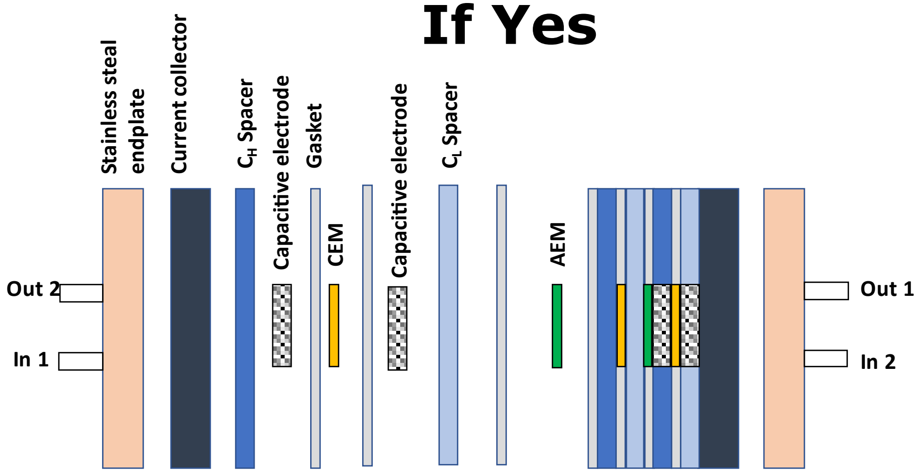
C_H=100 g/L vs C_L=1 g/L

Outlooks

Could we add capacitive layers inside the cell between EIMs?

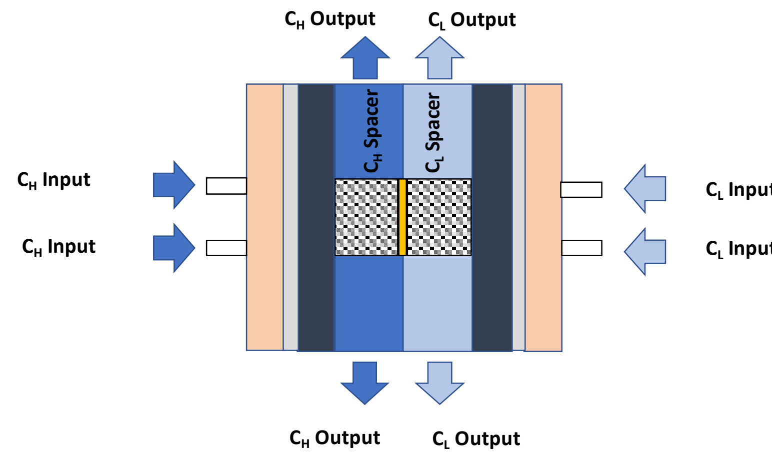


If Yes



RED stack

If No



Design

Thank you for your attention !