

# Capacitive reverse electrodialysis cells for osmotic energy harvesting: Toward real brines and power enhancement

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# OUTLINE

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1

## **Introduction**

Osmotic energy and its harvesting technologies

2

## **Boosting strategy**

Towards power density amelioration

3

## **Divalent ion mixing impact**

Towards real brine application

4

## **pH gradient cell**

Towards pH based osmotic energy harvesting

5

## **Conclusion and Perspectives**



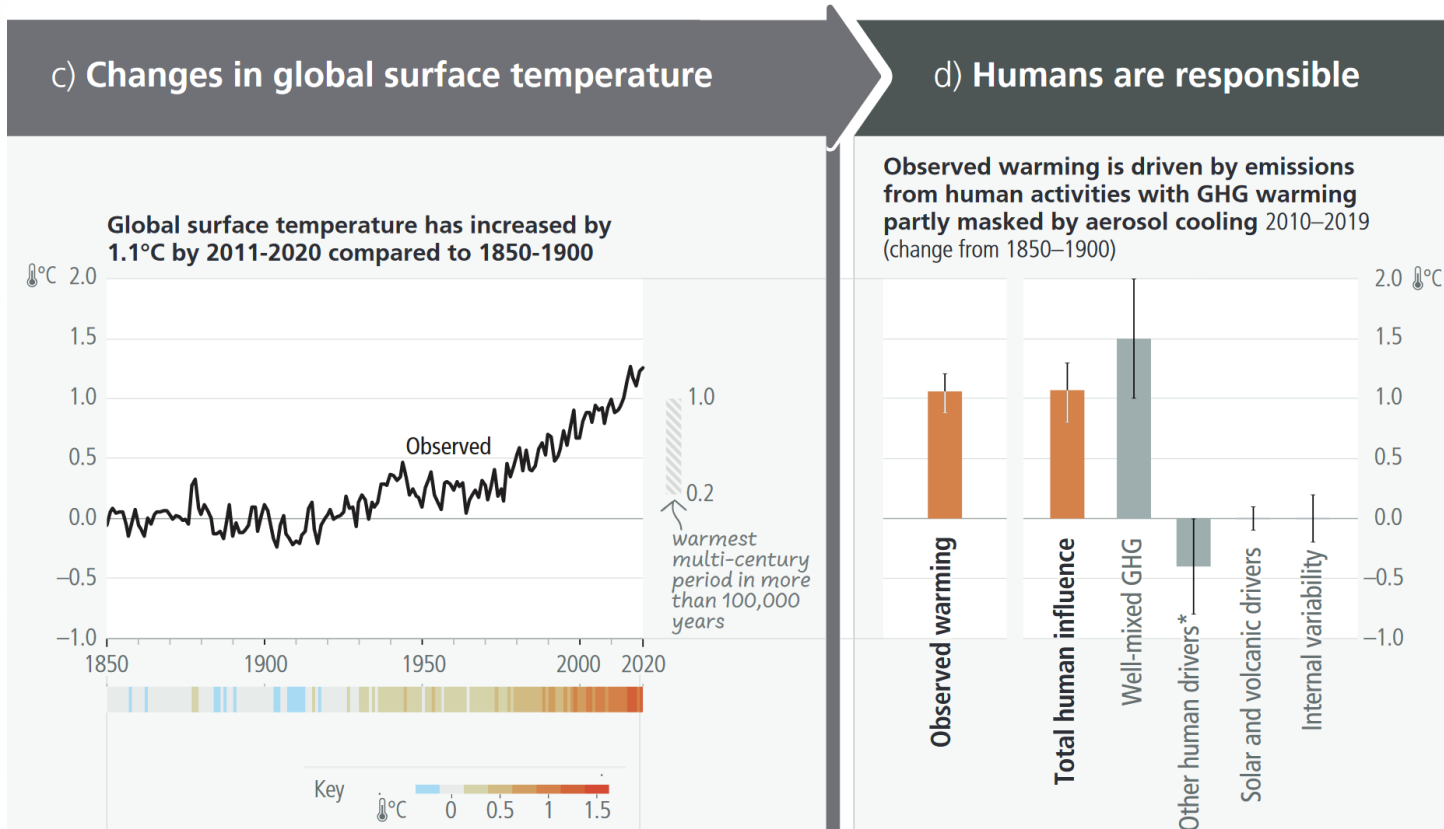
# 01 Introduction

Brief introduction of osmotic energy and its harvesting technologies

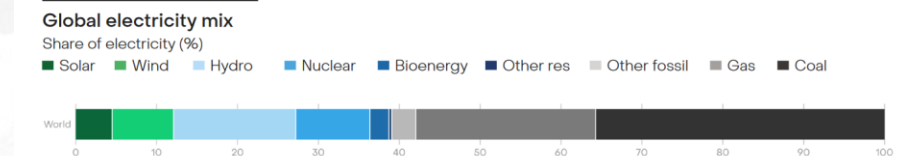
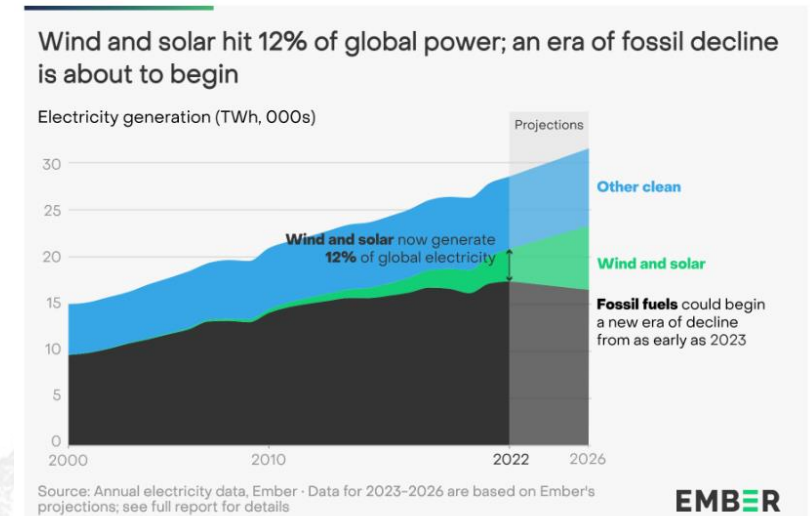
# 01.1 Global warming and energy crisis



## Human activities are responsible for global warming



## Energy transition



Sources: IPCC 2023 report

Ember Global Electricity Review 2023

# 01.1 Osmotic energy harvesting



Image Credit: Peter Bocklandt/Shutterstock.com

## Osmotic Energy

The Gibbs free energy of mixing released by combining two solutions of different salinities.

## Enormous potential

- **Considering all the sites**  
Estimation of 2.4 Terawatts
- **Considering easily accessible sites**  
Estimation of 0.1 Terawatts ~ 3% World electricity power

## Blue Energy harvesting technologies



**PRO**

Pressure Retarded Osmosis



**RED**

Reverse Electrodialysis

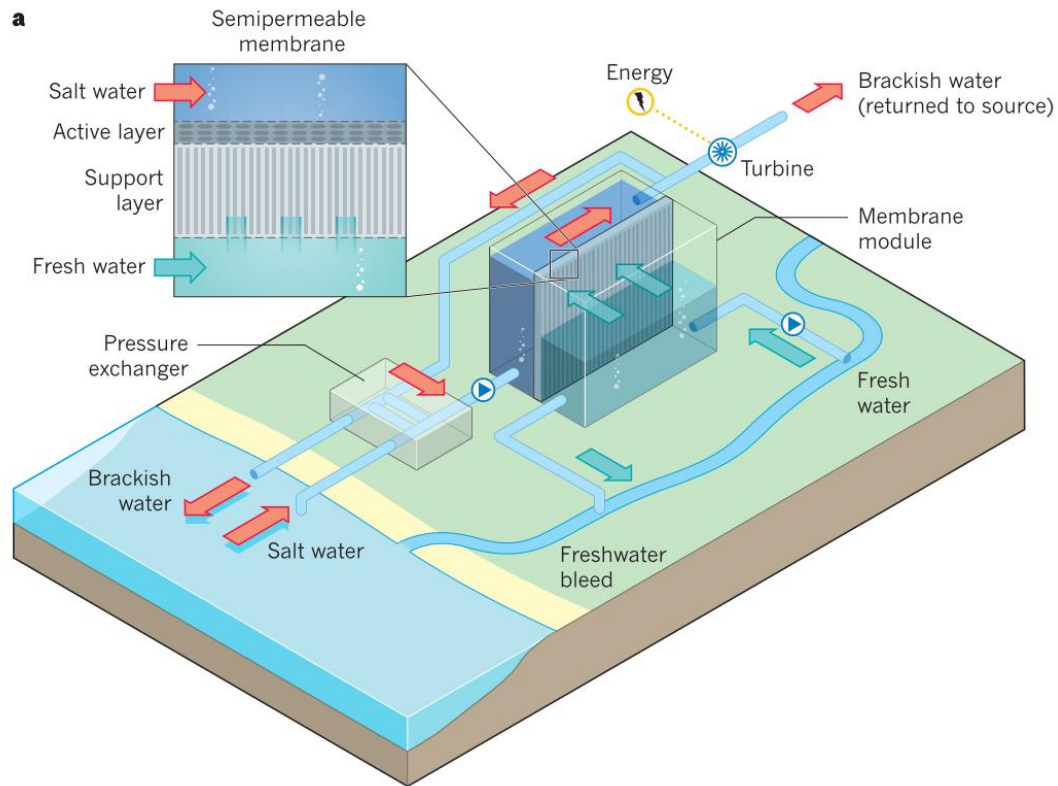


**Capmix**

Capmixing

*Sources: Wu et al. Lab on a Chip 2023  
Wu et al. Nano Energy 2023*

# 01.1 Osmotic energy harvesting



**Figure 1** Energy harvesting procedure via PRO technologies

*Sources: Logan, B. E. and M. Elimelech. Nature 2012*

## PRO Pressure retarded osmosis

### Semipermeable membrane:

Free passage of water molecules  
Block of passage of ions

### Pressurization in salt water chamber:

Water flux from fresh water chamber to seawater chamber

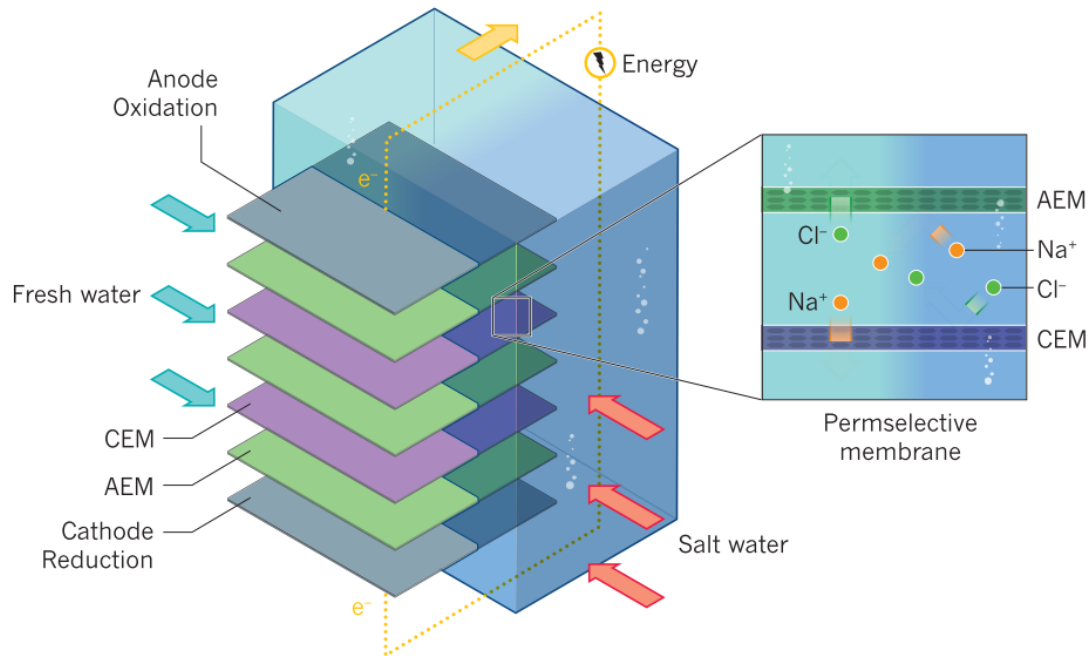
### Energy conversion by turbines:

Depressurization process by accessory installations (turbines)  
Energy conversion from hydrostatic potential to electricity

### State-of-art performance:

$9 \text{ W.m}^{-2} < 25 \text{ W.m}^{-2}$  (Commercialization threshold)  
High cost of accessory systems (turbines, pumps, and etc.) 6

# 01.1 Osmotic energy harvesting



## RED Reverse Electrodialysis

### Ion-exchange membrane:

Free passage of counter-ions  
Block of passage of co-ions and water molecules

### Directional ion flux through membranes:

Directional ion flux under osmotic effects through membranes  
Ion flux from saltwater chamber to freshwater chamber  
Stacks of CEM and AEM enable the voltage addition

### Energy conversion by redox reactions:

Conversion of ionic flux towards electric flux by redox reactions  
Energy conversion from osmotic potential to electricity

**Figure 2** Working principle of energy harvesting by RED

*Sources: Logan, B. E. and M. Elimelech. Nature 2012*

### State-of-art performance:

Pilot-scale RED plant  $0.5 \text{ W}\cdot\text{m}^{-2}$

Toxic electrolytes and overpotential problems

# 01.1 Osmotic energy harvesting



## Capmix Capmixing

CDLE (capacitive energy extraction based on double layer expansion)

### 4-step process using capacitive electrodes:

Step1 Seawater compartment + electrode charging

Step2 Conversion into freshwater + EDL expansion

Step3 Freshwater compartment + electrode discharging

Step4 Conversion into seawater + EDL compression

### Capacitive currents:

Conversion of ionic flux towards electronic flux by capacitive electrodes

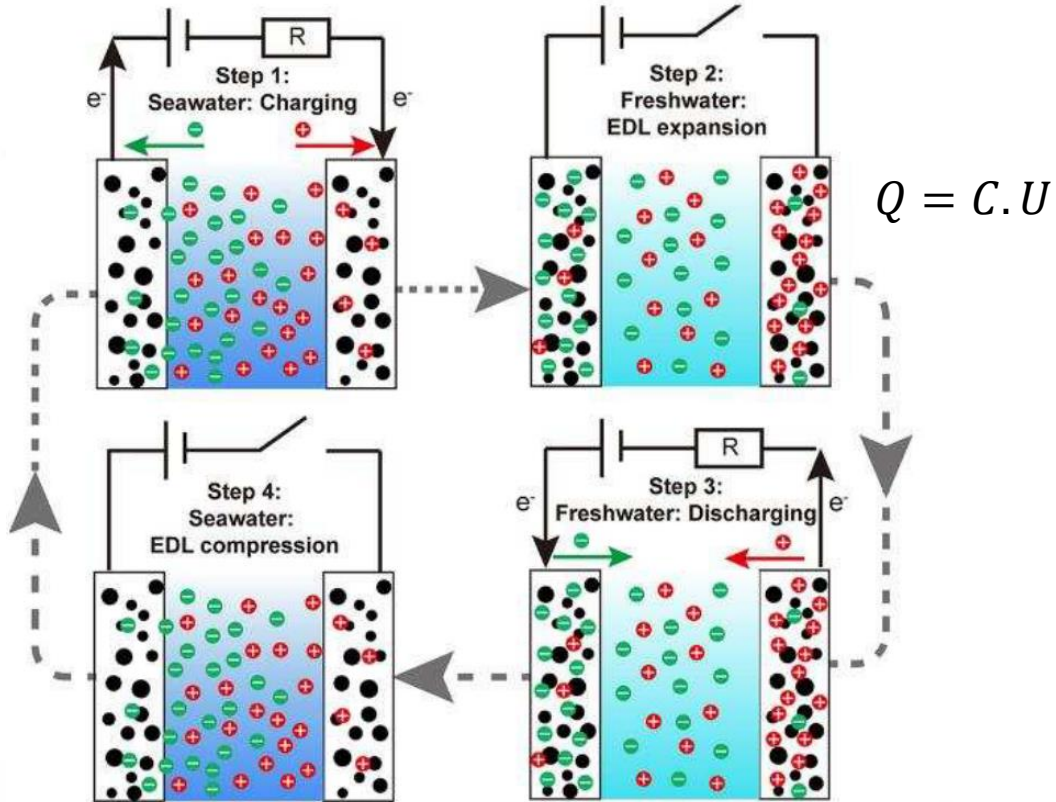
### Advantages:

Suppression of redox reaction related problems

Low cost of carbon based capacitive electrodes

### State-of-art performance:

Power density  $\sim 0.1 \text{ W.m}^{-2}$



**Figure 3** The 4-step energy harvesting via CDLE

*Sources: Zou et al. Energy Reports 2022*



# 01.2 Capacitive RED (CRED)



## Comparison

	<b>PRO</b> Pressure Retarded Osmosis Highest power density High cost of accessory systems
	<b>RED</b> Reverse Electrodialysis High power density Redox reaction related problems (toxic electrolytes; overpotential problems; environmental impact)
	<b>Capmix</b> Capmixing Low cost; No redox reactions Low power density

## Combining RED system with capacitive electrodes:

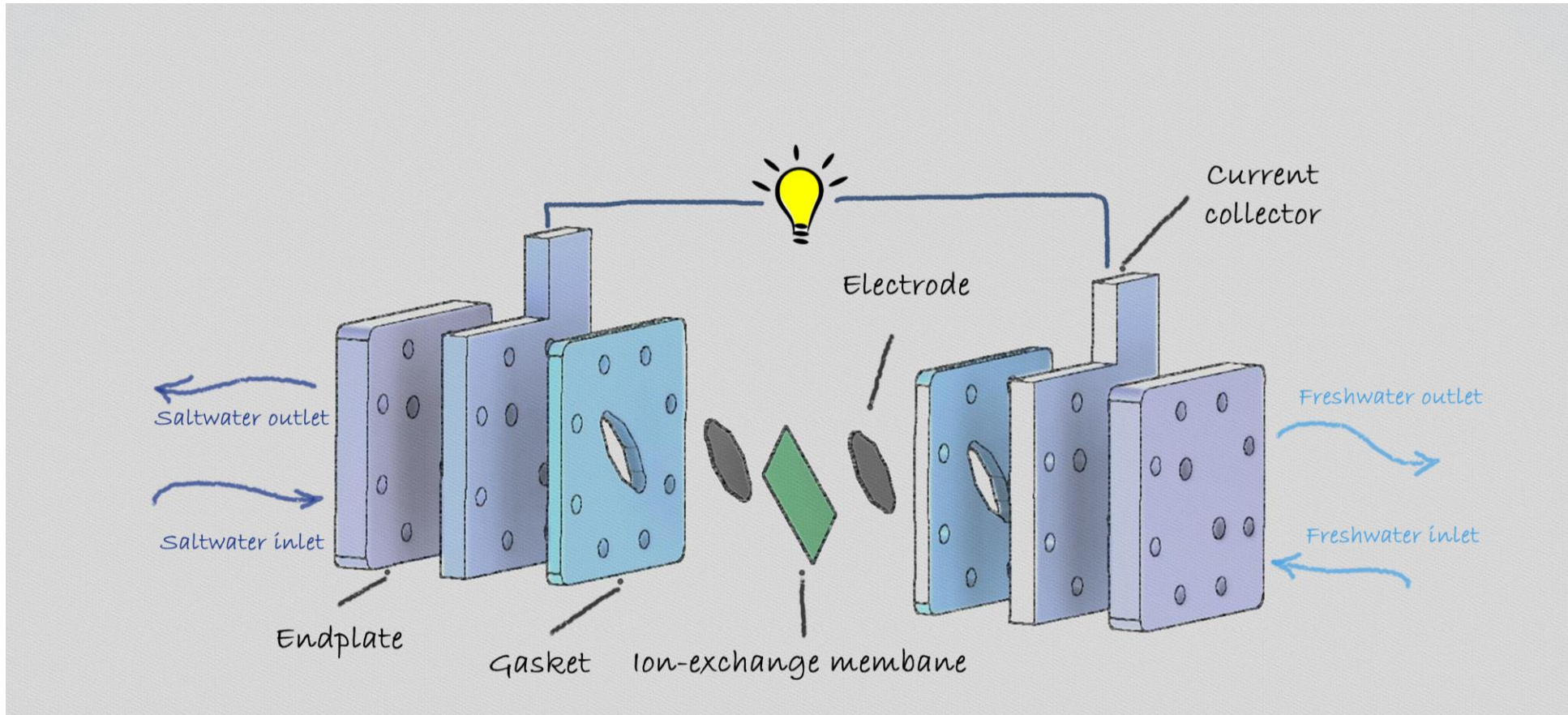
Wonderful combination at the crossroad of RED and Capmixing :  
previous thesis work of Dr. Brahmi Youcef



## Capacitive RED cell

- ✓ **Ion-exchange membranes ('RED')**  
Directional ionic flux creation under osmotic effect  
Possibility of using stacks
- ✓ **Capacitive electrodes ('Capmixing')**  
Capacitive electrodes charging by ion adsorption  
Avoidance of hazardous redox reactions

# 01.2 Capacitive RED (CRED)

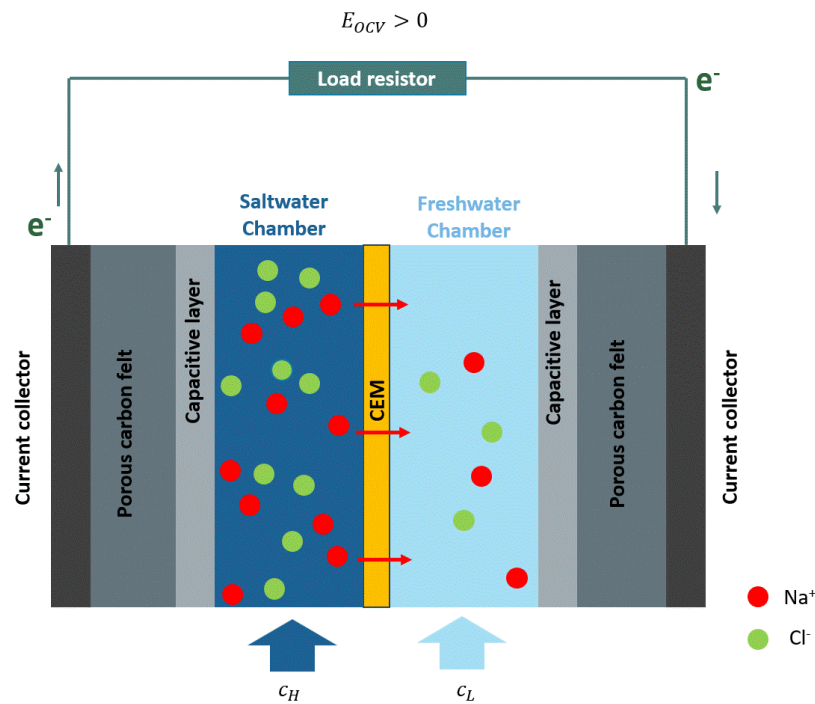


**Figure 4** The design of the CRED assembly

# 01.2 Capacitive RED (CRED)



## Working principle



### Ion-exchange membrane CEM:

Free passage of cations ( $Na^+$ )

Block of passage of anions ( $Cl^-$ ) and water molecules

### Directional ionic flux:

Directional ionic flux under osmotic effects through membranes

Ion flux from saltwater chamber to freshwater chamber

### OCV further enhanced by capacitive electrodes:

$$E_{ocv} = E_{mem} + E_{elec}$$

### Capacitive electrodes:

Conversion of ionic flux towards electronic flux by ion adsorption

A blocking type electrode without redox reactions

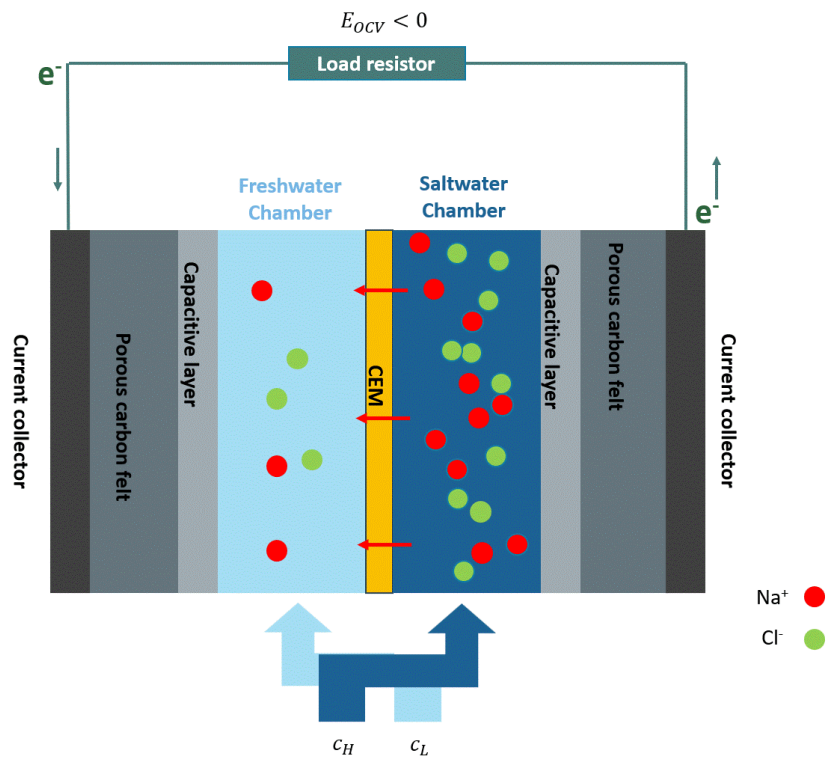
**Figure 5** The working principle of the CRED system

Image Credit: Youcef Brahmi, Thesis 2021

# 01.2 Capacitive RED (CRED)



## Working principle



### Capacitive current decay:

Ionic flux will be slowed down and eventually reaches a saturation regime  
Blocking electrodes requires concentration reversal to deblock this state

### Chamber switch to deblock saturation regime:

Necessity of water chamber switch to deblock the saturation  
Creation of alternating periodic capacitive currents

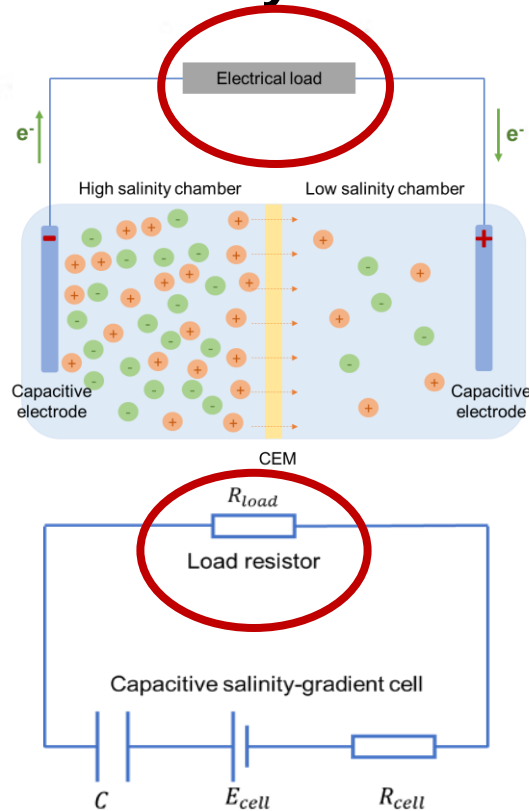
**Figure 5** The working principle of CRED system

*Image Credit: Youcef Brahmi, Thesis 2021*

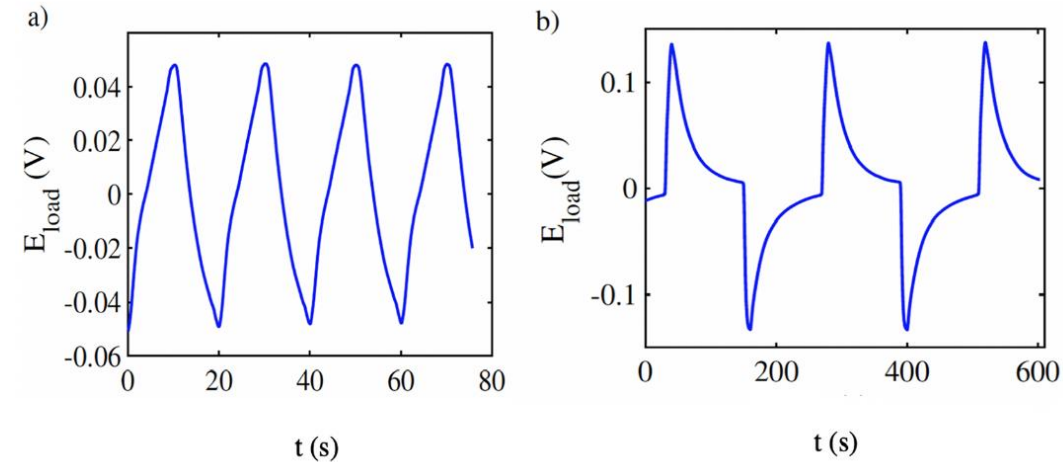
# 01.2 Capacitive RED (CRED)



## Power density measurement



## Cell-Resistor circuit



**Figure 7** Resistor voltage measurement curves as a function of time for different resistance.

$$P_{nb} = \frac{1}{S \cdot T} \int_0^T \frac{E_R(t)^2}{R_{load}} dt$$

**Figure 6** Direct connection of the resistor to the CRED system for power density measurement

# Summary



**CRED cell**

- 01 CRED:  
Reverse electrodialysis + Capacitive electrodes
- 02 Alternating periodic output (switching)
- 03 Direct connection to resistor for power density measurement
- 04 Power density amelioration ?
- 05 Lack of study in real world solutions ?
- 06 Generalization in other forms of osmotic energy ?

# 01.3 Thesis objective



## Objective:

Investigate the fundamental mechanism of the CRED system, aiming to enhance its energy performance and broaden its range of applications.

Towards  
Power density  
amelioration

Towards  
Real brines

Towards  
pH gradient based  
osmotic energy  
harvesting



# 02

## Boosting strategy

Towards higher energy performance  
of CRED system.



# 02.1 Preamble



$E_{ocv} \uparrow$

Membrane selectivity  
 Optimized electrode  
 Salinity gradient  
 ...

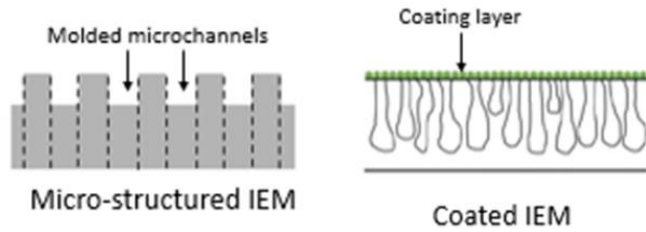
$$P_{max} = \frac{E_{ocv}^2}{4R_{cell}}$$

$R_{cell} \downarrow$

Freshwater chamber  
 Membrane resistance  
 Polarization effect  
 ...

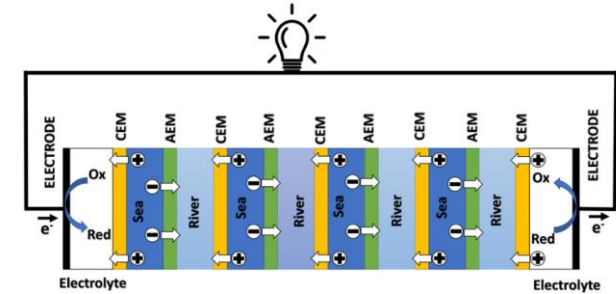
## Membrane Design

*Abidin et al. Desalination 2022*



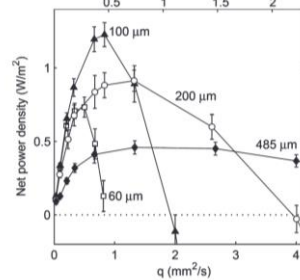
## RED stacking

*Wu et al. Lab on a Chip 2023*



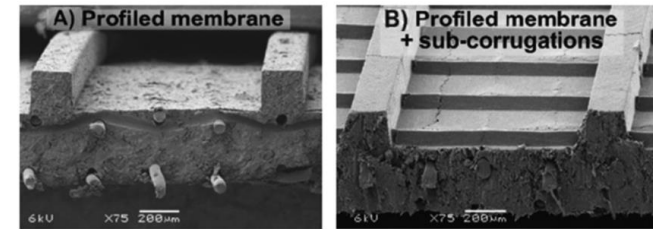
## Inter-distance optimization

*Vermaas et al. Environmental Science & Technology 2011*



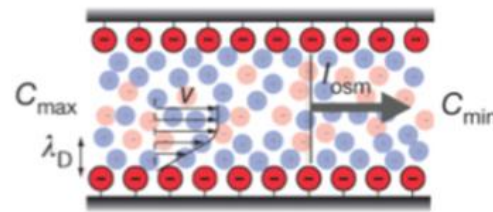
## Local mixing

*Vermaas et al. Journal of Membrane Science 2011*



## Nanopore RED

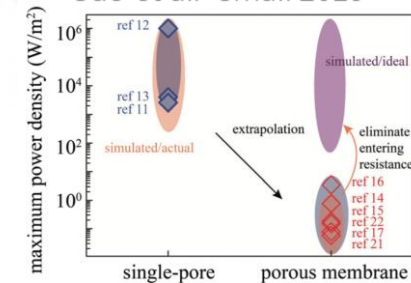
*Siria et al. Nature 2013*



Diffusio-osmotic streaming current

## Scale up difficulty

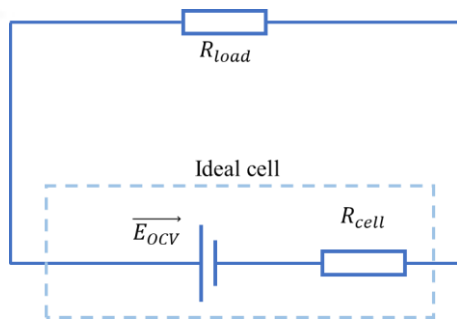
*Gao et al. Small 2019*



# 02.1 Preamble

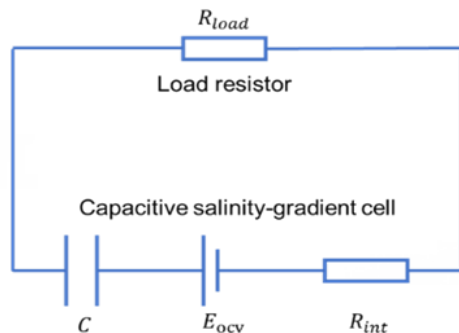


## Ideal cell equivalent circuit



$$P_{max} = \frac{E_{ocv}^2}{4R_{cell}}$$

## CRED cell equivalent circuit



$$P_{capa} \sim 60\% P_{max}$$

## Objective:

- Power density enhancement of capacitive cells
- Optimization of the collection of an ionic current and its transformation into an electric current using a capacitive electrode.

**Boosting  
Principle**

# 02.2 Boosting strategy - Principles



## Boosting system:

An alternating voltage power supply synchronized to the switching period of the salinity-gradient cell.

## Net power density calculation:

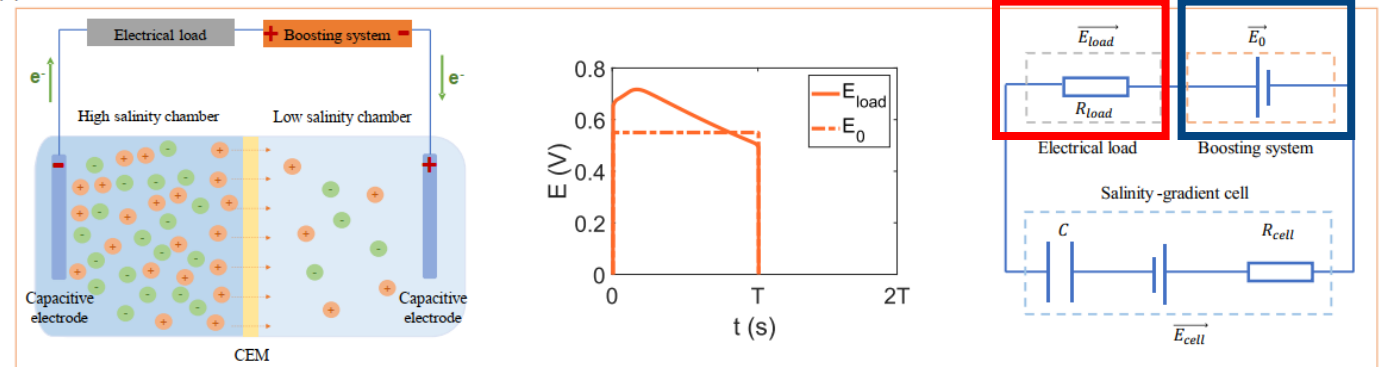
$$P_{b-gross} = \frac{1}{S \cdot T} \int_0^T \frac{E_R(t)^2}{R} dt$$

$$P_{b-boost} = \frac{1}{S \cdot T} \int_0^T E_0(t) \cdot I(t) dt$$

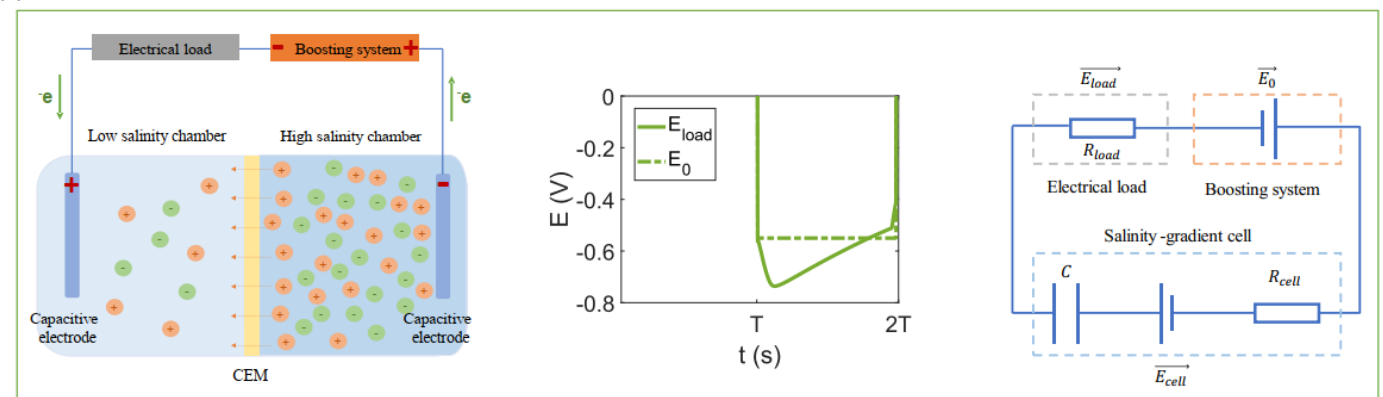
$$P_{b-net} = P_{b-gross} - P_{b-boost}$$

## Cell-Booster-Resistor circuit

(a) Phase 1:  $0 < t < T$



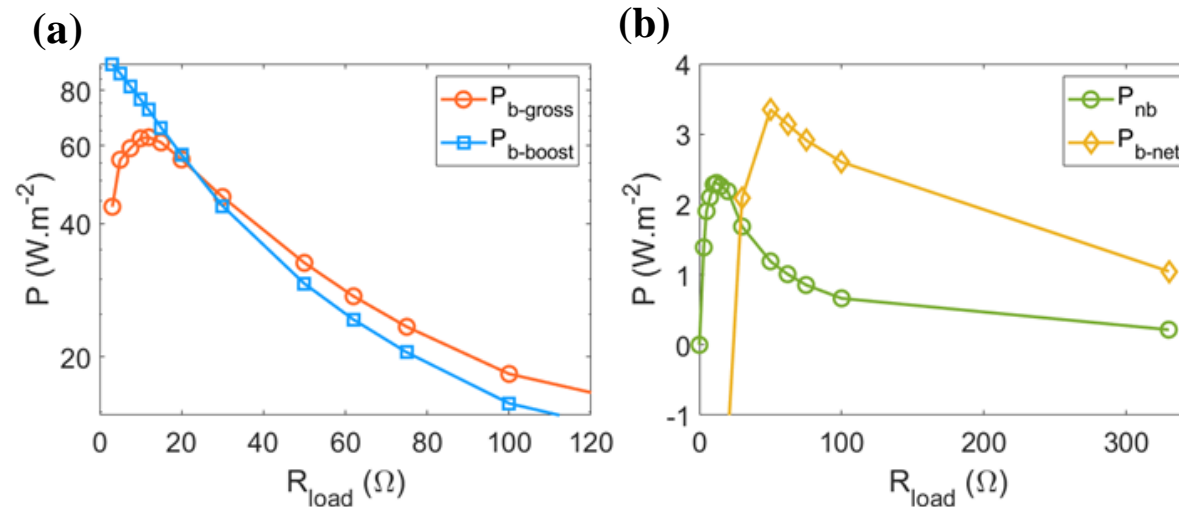
(b) Phase 2:  $T < t < 2T$



# 02.2 Boosting strategy - Principles



$$P_{b-net} = P_{b-gross} - P_{b-boost}$$



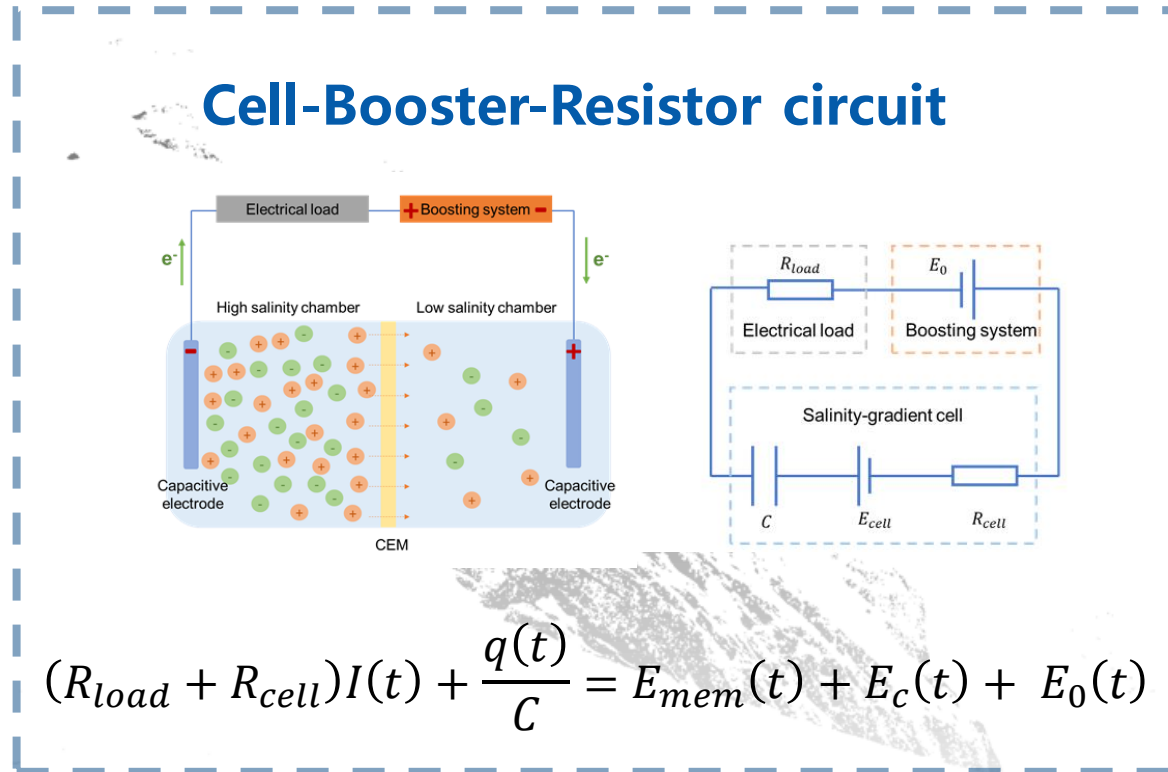
**Figure 8** Salinity gradient of 0.17 mol.L<sup>-1</sup> and 5.17 mol.L<sup>-1</sup>, flow rate of 10 mL/min, switching period of 45s, cation exchange membrane of Nafion 117 and boosting voltage of 0.8V. The chronovoltammetric measurement of  $E_{load}$  illustrated in (a) is for load resistance of 50 Ω.

$P_{nb}$ Non-boosting Power density	$P_{b-net}$ Boosting power density	Gain
3.29 W.m <sup>-2</sup>	5.26 W.m <sup>-2</sup>	59.8%

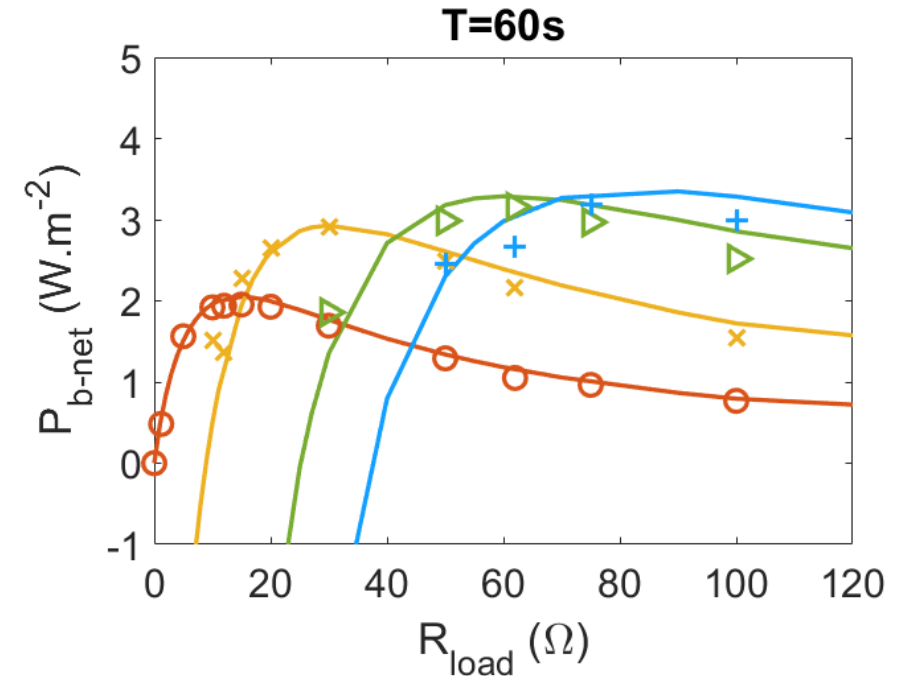
# 02.3 Boosting strategy - Models



## Theoretical models by equivalent R-C circuits

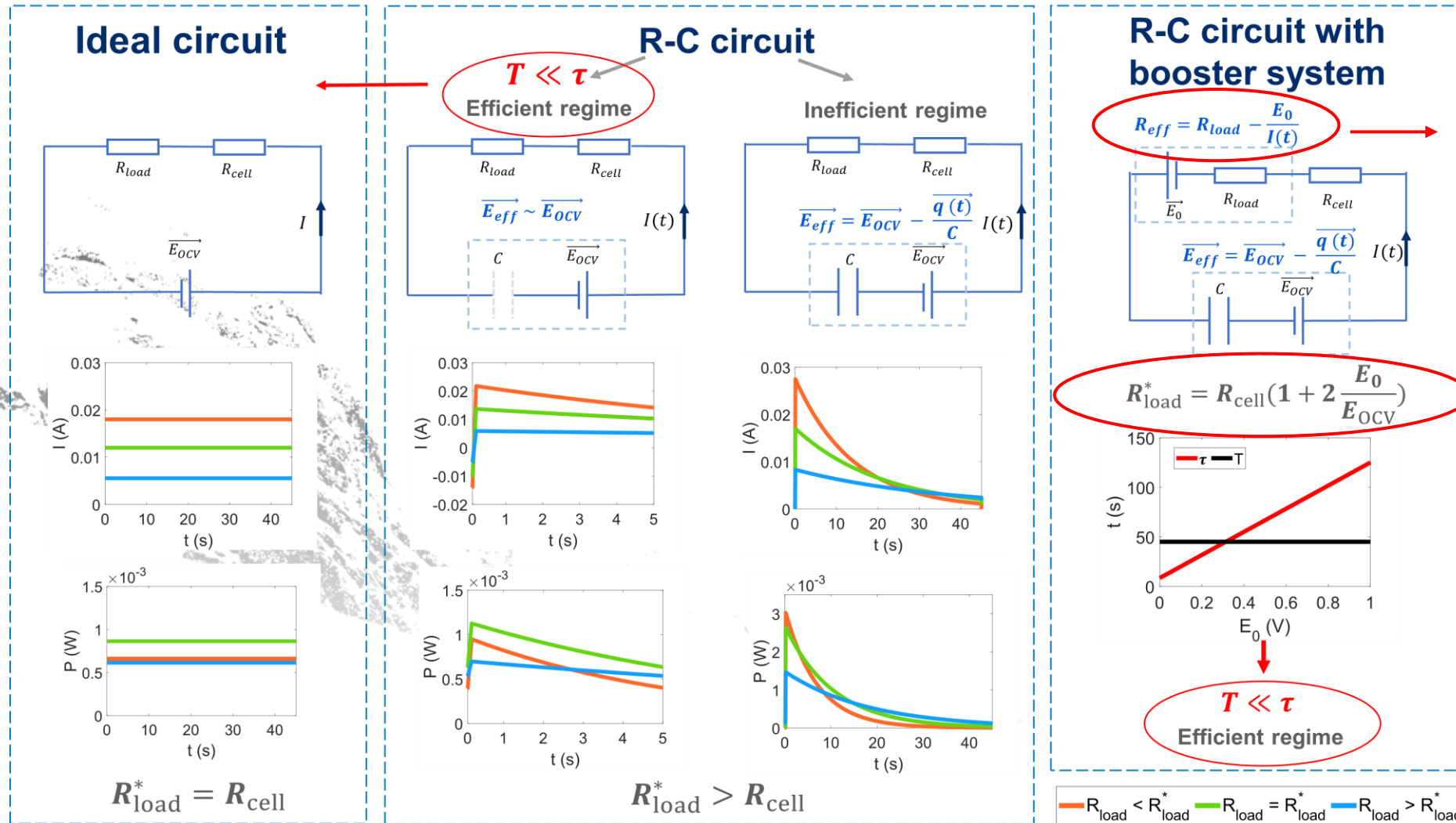


$$P_{th} = \frac{1}{S \cdot T} \int_0^T I(t)^2 R dt$$



**Figure 9** Comparison between theoretical model prediction and experimental data of the cell-resistor circuit and cell-booster-resistor circuit. Salinity gradient of  $0.17 \text{ mol.L}^{-1}$  and  $5.17 \text{ mol.L}^{-1}$ , flow rate of  $10 \text{ mL/min}$ , switching period of  $60\text{s}$ , cation exchange membrane of Nafion 117, and various boosting voltages.

# 02.4 Boosting strategy - Mechanism



# 02 Summary

## Boosting principle

01 Boosting system: electrical signal in phase with switching period

02 Maximum net power density of  $5.2 \text{ W/m}^2$  reaching over 90% of  $P_{max}$

03 Agreement between experimental data and theoretical model

04 Underlying mechanism



# 03

# Divalent ion mixing impact

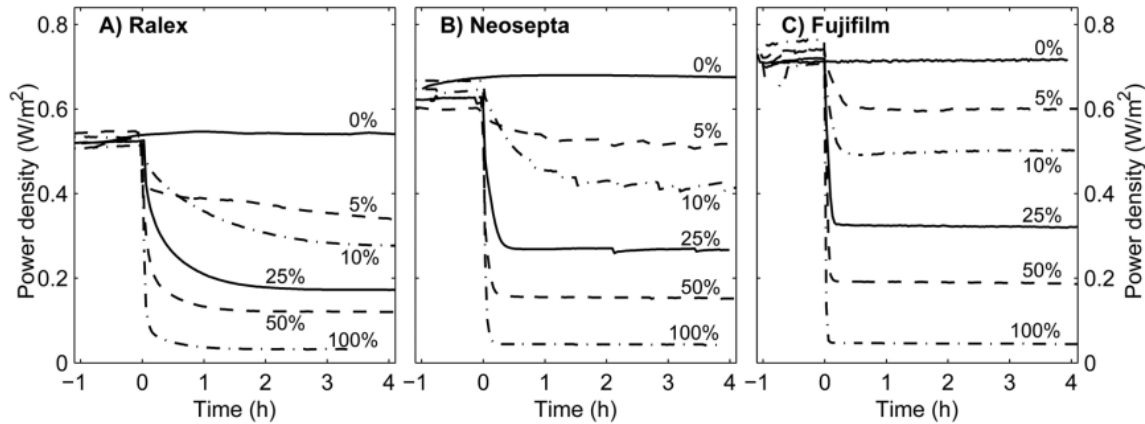
Towards real brines in industrial applications



# 03.1 Preamble

## Towards complex solutions:

Mixing complex multi-valance ions inside the solutions injected in **RED systems**



## Detrimental power density loss due to complex ion mixing

Reported both at lab and industrial scale

RED: 75% power density drop (50% of divalent ions)

**Sources:** Vermaas et al. *Energy & Environmental Science* 2014  
 Veerman et al. *Environmental Science & Technology* 2010  
 Moreno et al. *Journal of Membrane Science* 2018  
 Tedesco et al. *Journal of Membrane Science* 2015

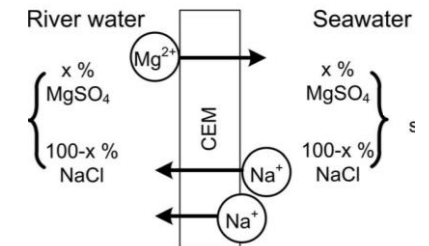
## Uphill effect:

- Ion valence difference results in differed membrane voltage

$$E_m = \frac{\alpha RT}{z_i F} \log \frac{a_{i,1}}{a_{i,2}}$$

$$E_{m,monovalent} = 2E_{m,divalent}$$

- Emergence of a reversed transportation of multivalent ions against the concentration gradient



## Membrane poisoning:

- Trapping of multivalent ions in the membrane
- It results in membrane selectivity decrease and electrical resistance increase.

# 02.1 Preamble



## Current studies on CRED:

- System establishment and working principle
- Power density enhancement and mechanism
- **All studies are conducted using artificial NaCl solutions**

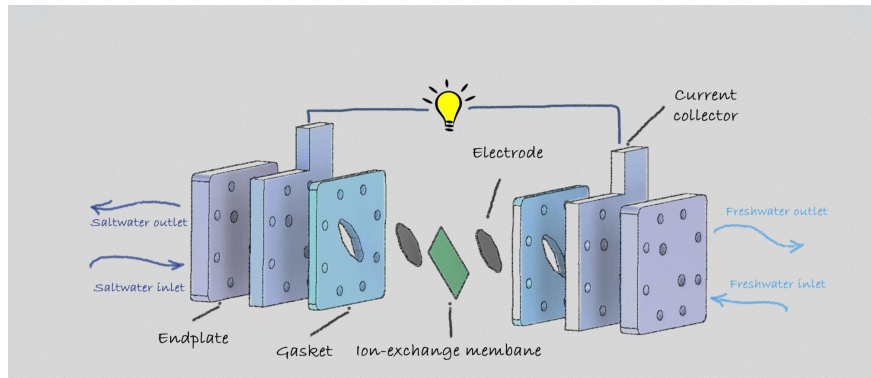
### Objective

- Systematic study of CRED system performance under divalent ion mixing solutions
  - Underlying mechanism analysis
- Economic analysis of CRED system towards industrial applications

# 03.2 Materials and methods



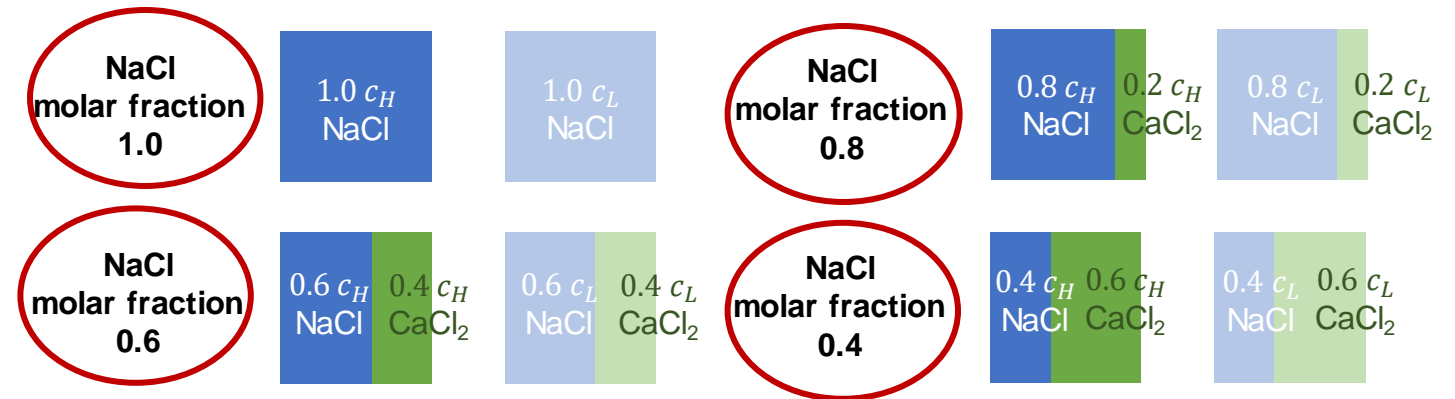
## CRED Cell



*Sources: Y. Brahmi and A. Colin. Energy Conversion and Management 2022*

## Complex ion mixing solutions

Mixture of monovalent ions (NaCl) with divalent ions (CaCl<sub>2</sub> or MgCl<sub>2</sub>)



$$c_H = 0.171 \text{ mol. L}^{-1} \text{ or } 0.513 \text{ mol. L}^{-1} \text{ or } 1.711 \text{ mol. L}^{-1}$$

$$c_L = 0.017 \text{ mol. L}^{-1}$$

**Salinity ratio**  
**Ra = 100 or 30 or 10**

## Electrochemical Characterizations

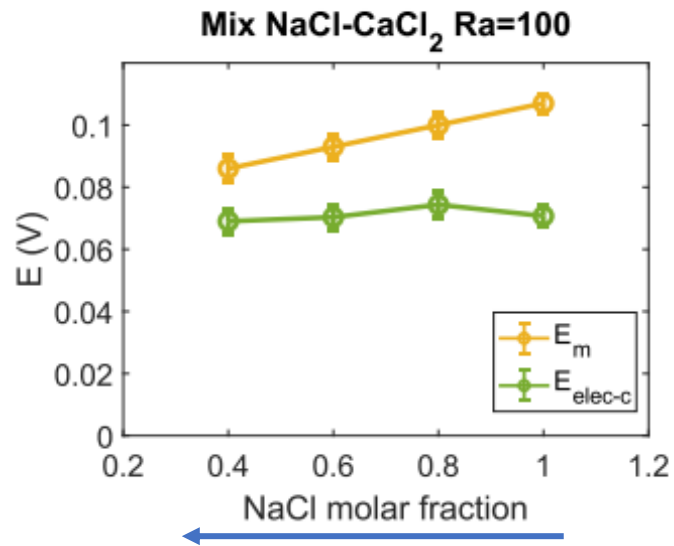
Cell voltage  
 $E_m$   
 $E_{elec}$

Power density

# 03.3 Experimental results

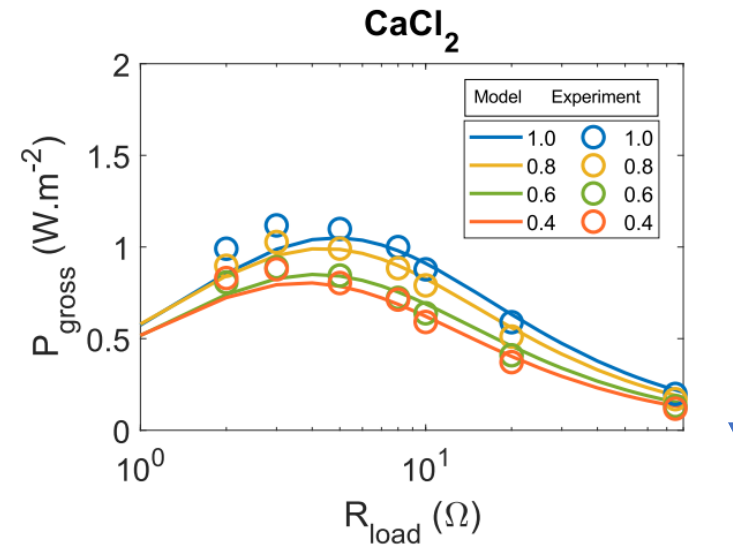


## Cell voltage drop



$E_m$  is severely influenced  
 $E_{elec}$  remains stable

## Power density drop



Smaller power density drop in CRED!

CRED: 34% power density drop

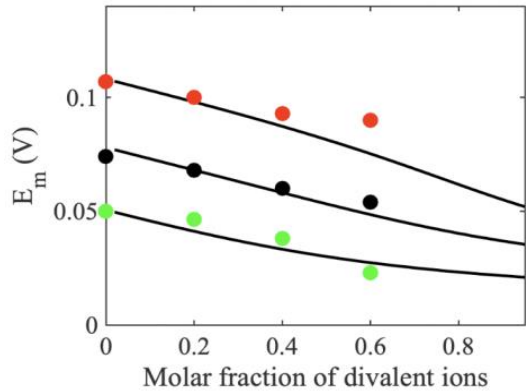
RED: 62% power density drop

# 03.4 Mechanism



## Uphill Effect

Theory V.S. Experiment



The uphill effect is enough to explain the voltage drop in CRED system

## Membrane poisoning

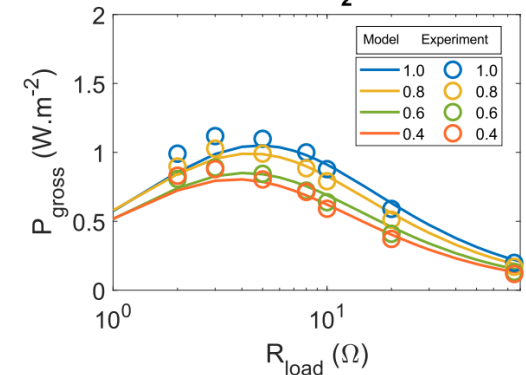
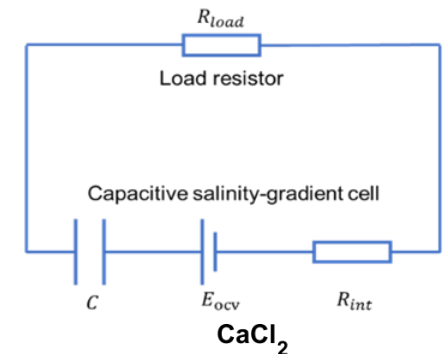
Trapping of multivalent ions in membrane

~~Selectivity drop~~

~~Additional voltage drop~~

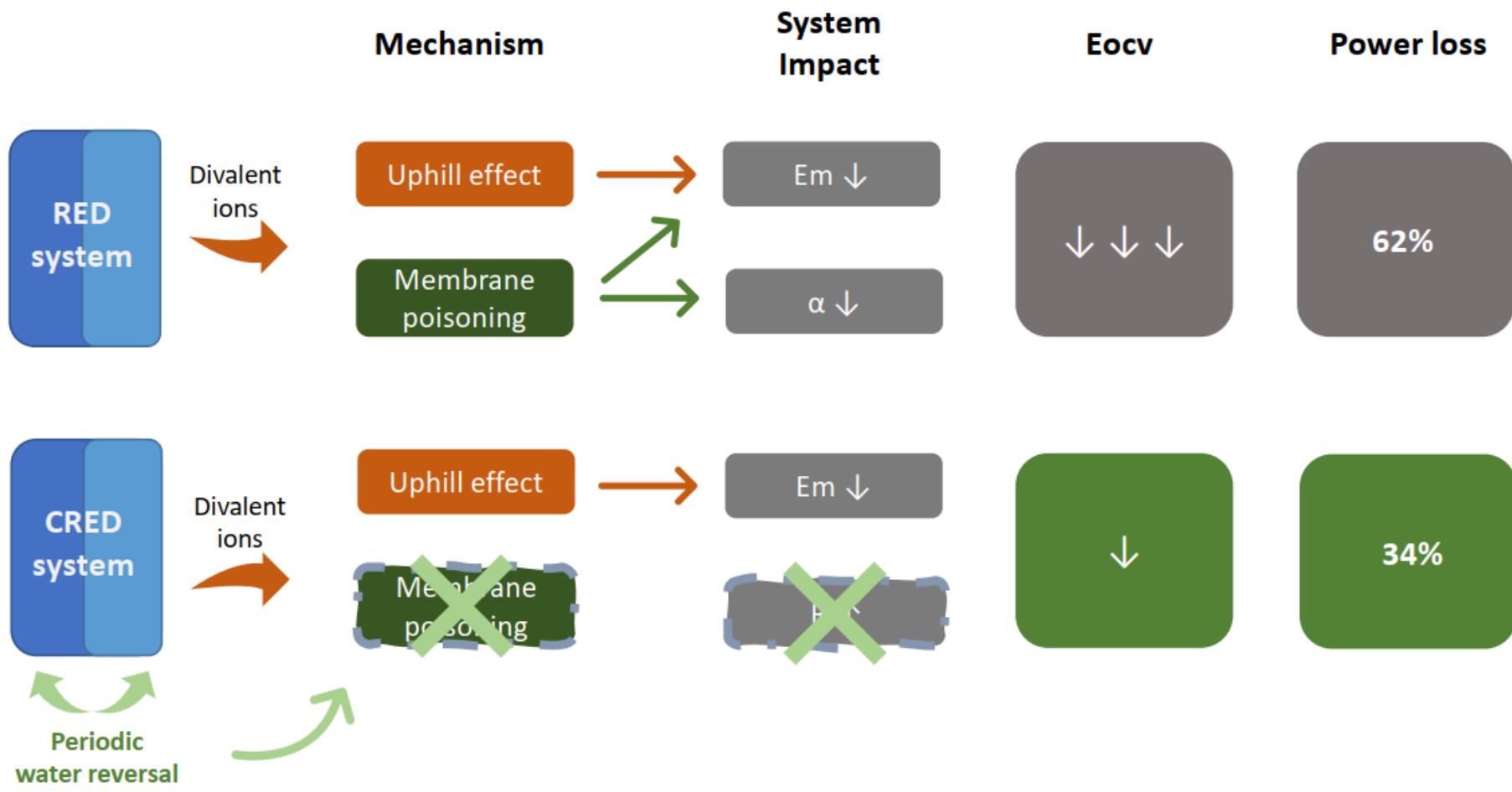
Suppression of Membrane poisoning by flow reversal in CRED system

## Hidden mechanism?



Voltage drop is sufficient to explain the power density drop

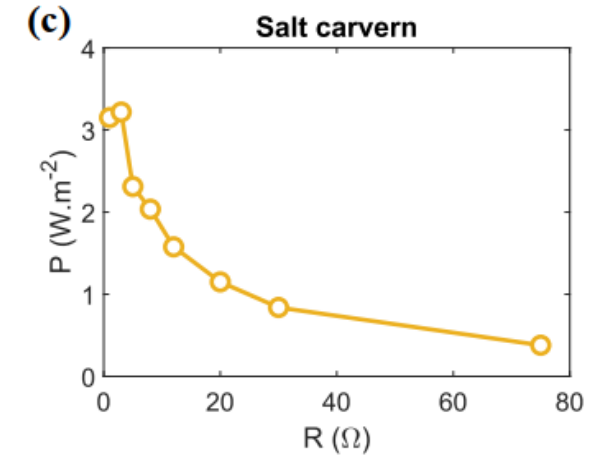
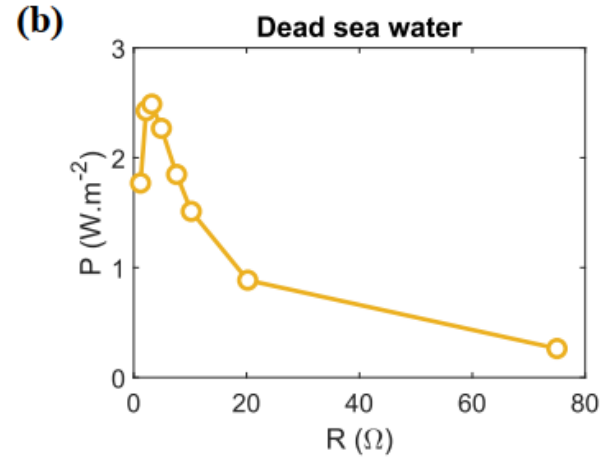
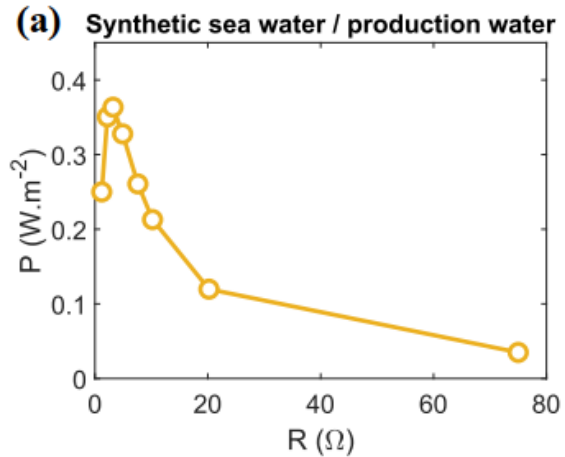
# 03.4 Mechanism



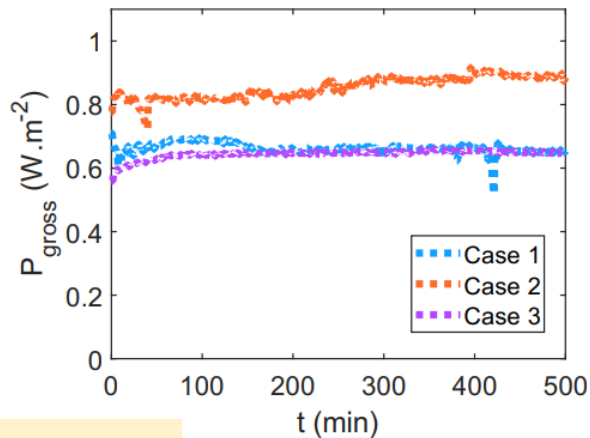
# 03.5 Towards Real solutions



Real solution measurements



Long operation measurements



Case 1: Artificial NaCl (80%) - CaCl<sub>2</sub>(20%) mixed solution; Nafion 117

Case 2: Production water; Nafion 117

Case 3: Artificial NaCl (40%) - CaCl<sub>2</sub> (60%) mixed solution; Fumasep FS720

The power density variation after 8h of operation is **within 6%**.

# 03.6 Economic analysis



## Analysis hypothesis:

- RED membrane surface of 100 000 m<sup>2</sup>
- Membrane lifetime is 7 years
- Production runs 8000 hours per year
- Annual exploitation cost estimated as 9% of the construction cost

## A scenario:

- Great salt lake with treated wastewater
- Supplementary valves for water reversal
- Suppression of filtration cost
- CRED system with a power of 3.2 W.m<sup>-2</sup>
- Membrane price at 60 euros per m<sup>2</sup>

Current sPEEK membrane cost

## B scenario:

- Membrane price at 15 euros per m<sup>2</sup>

Future sPEEK membrane cost estimation

## Post scenario:

- River water-Sea water mixing case.
- RED system with a power of 2 W.m<sup>-2</sup>
- Membrane price at 2 euros per m<sup>2</sup>

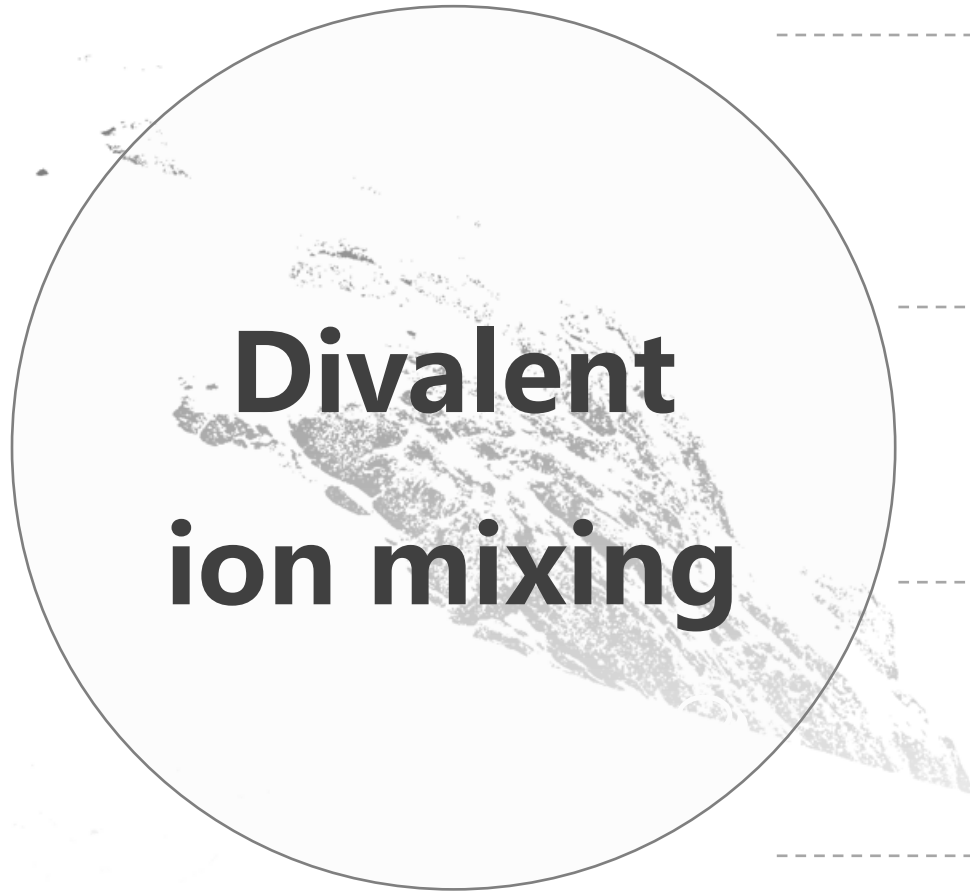
Sources: Post et al. Journal of Membrane Science 2009

	Post scenario	A scenario	B scenario
Membrane cost (€)	254 000	6 000 000	1 500 000
Piping, fittings and pumps (€)	406 400	406 400	406 400
Valves (€)	0	150000	150000
Filtration (€)	469 900	0	0
Total (€)	1 130 300	6 556 400	2 056 400
Annual Costs (9%) (€)	101 727	590 076	185 076
Total (€)	1 232 027	7 146 476	2 241 476
Net Power (kW)	200	320	320
MWh cost (€)	111	399	125

Solar Energy: 40 euros per MWh  
Wind off shore: 120 euros per MWh



# 03 Summary



01 Divalent ion mixing results in cell voltage and power density drop in CRED system.

02 Uphill effect is responsible for the drop.

03 Membrane poisoning is suppressed by water chamber reversal in CRED system

04 It is worthy of further developing CRED system according to economic analysis



# 04

# pH gradient cell

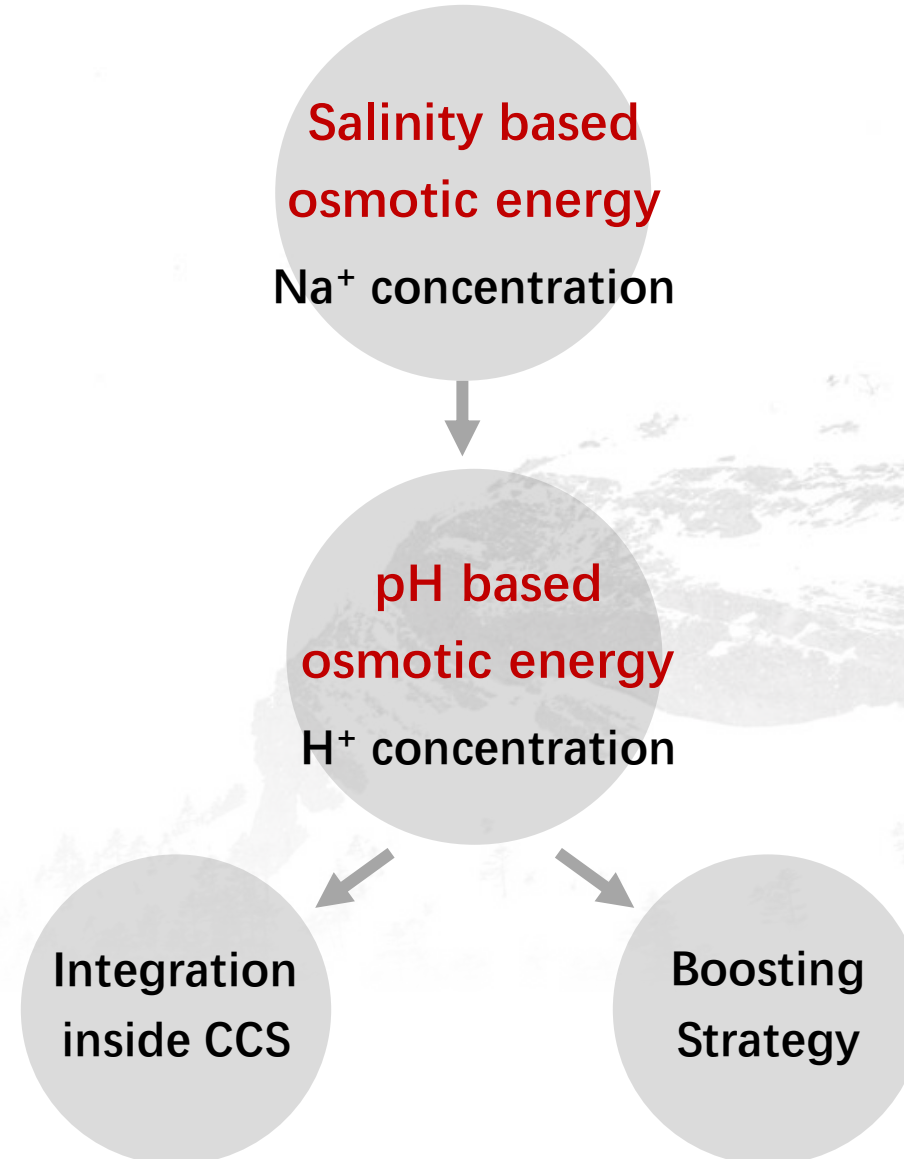
Towards pH gradient based osmotic energy harvesting

# 04.1 Preamble



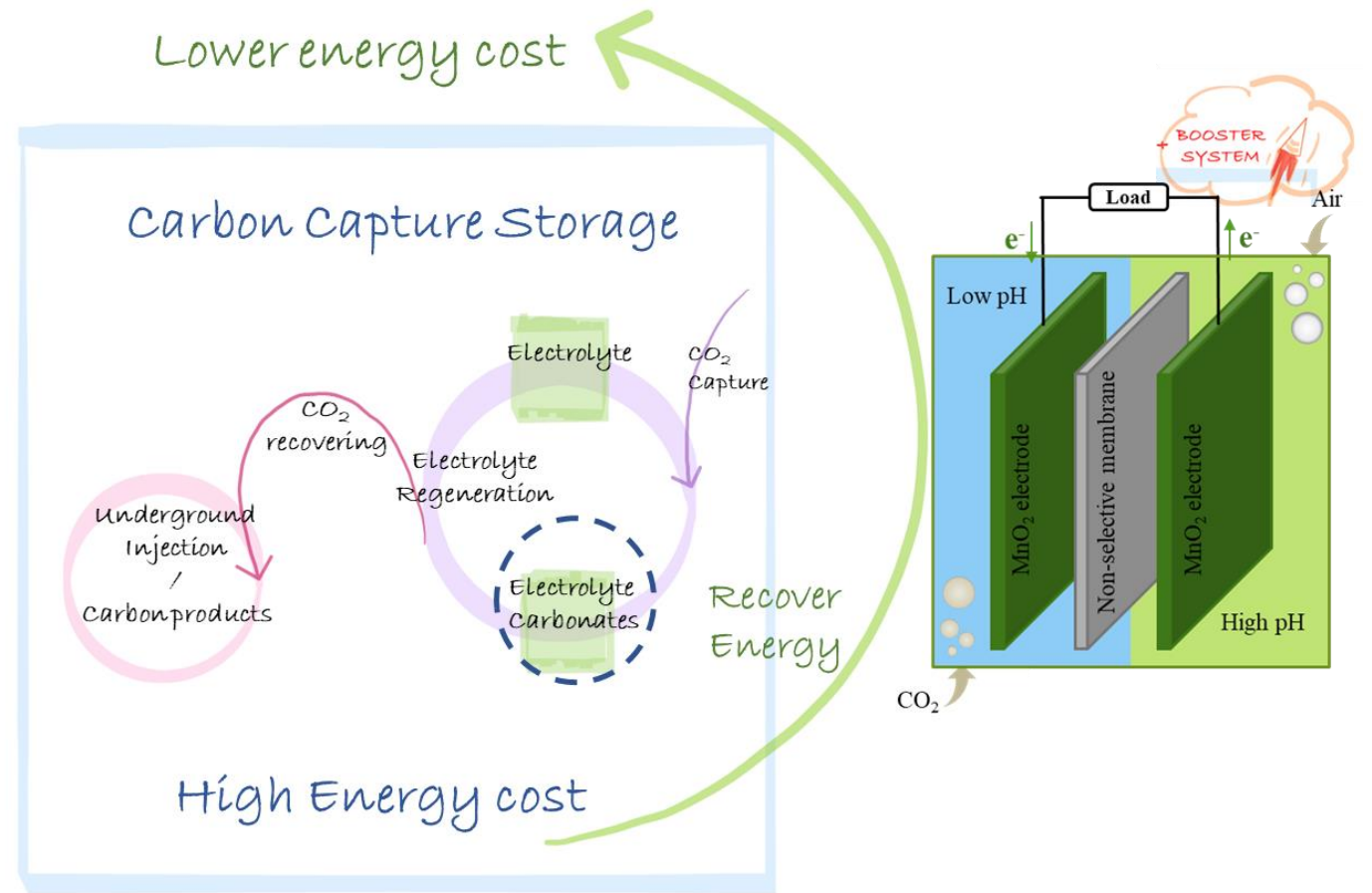
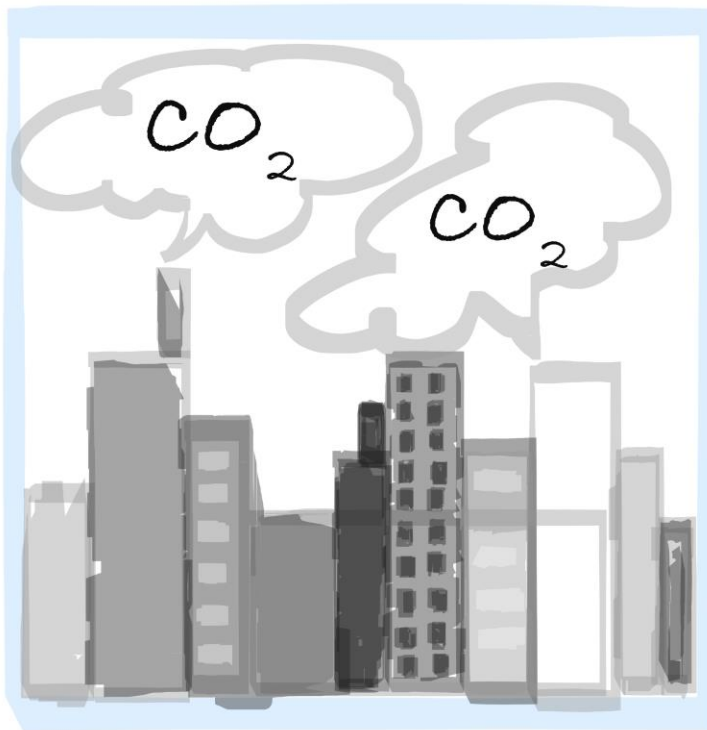
## Objective:

- Generalization towards pH gradient based osmotic energy harvesting system
- Integration inside the carbon capturing & storage (CCS) process
- Energy performance increase by boosting strategy



# 04.2 Osmotic energy source in CCS

## CO<sub>2</sub> Capture & Storage (CCS)



**Sources:** Alaba et al. *International Journal of Precision Engineering and Manufacturing-Green Technology* 2021  
Garcia et al. *Journal of Environmental Chemical Engineering* 2022  
Hamelers et al. *Environmental Science & Technology Letters* 2014

# 04.2 Osmotic energy source in CCS

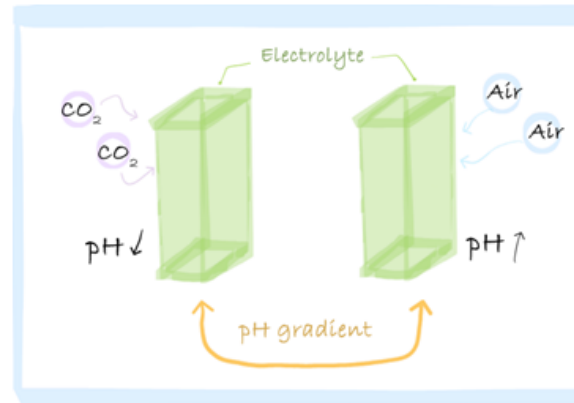
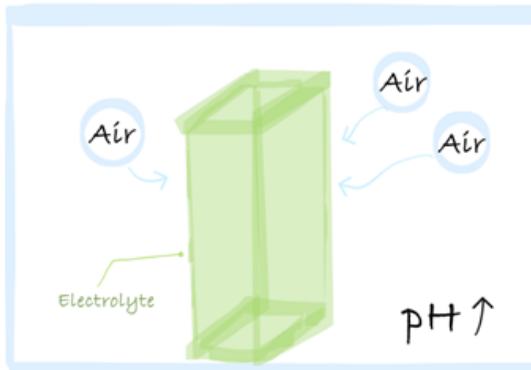
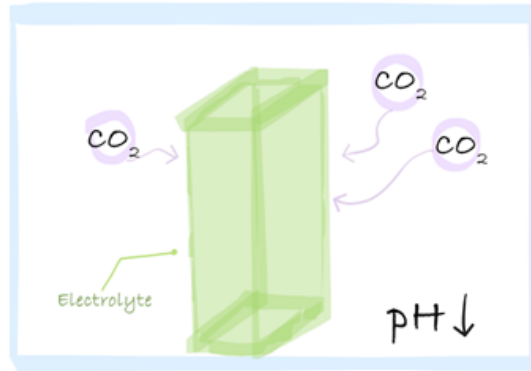
**CO<sub>2</sub> Capture**



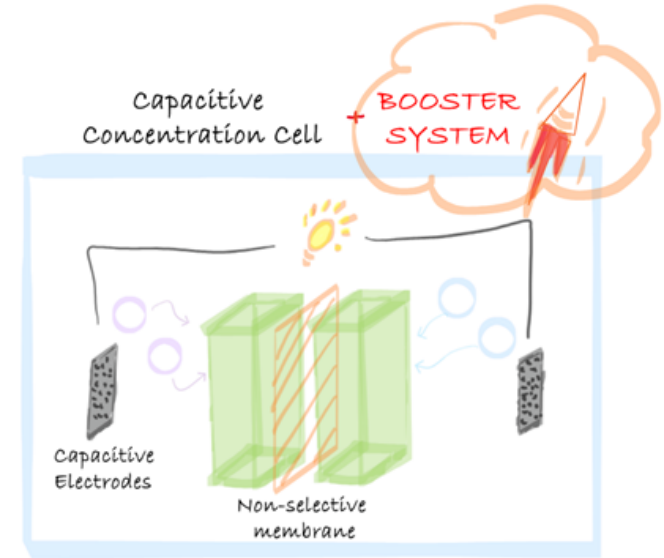
**Energy source**



**Electricity**

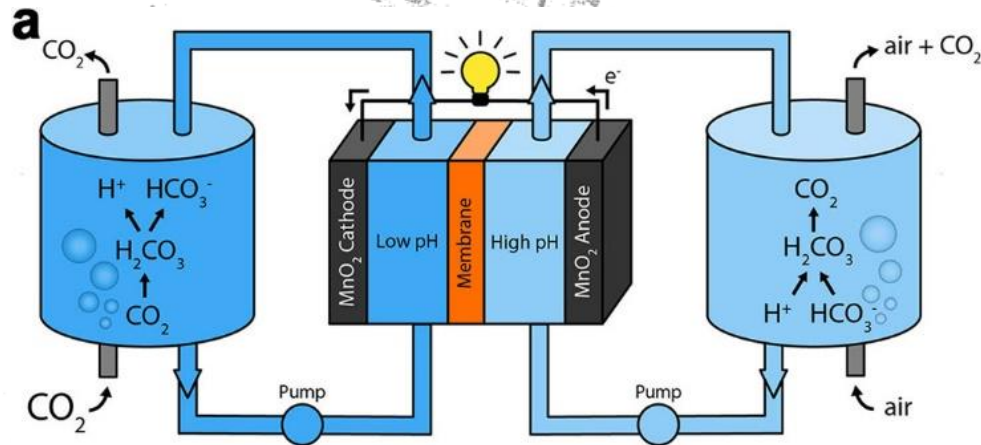
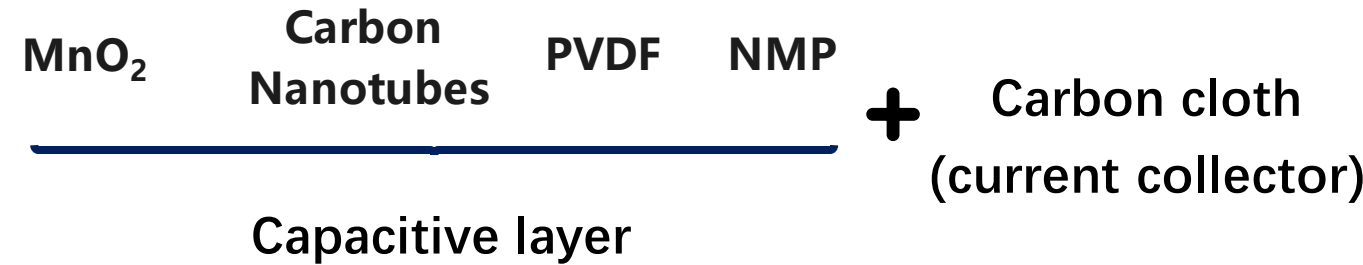
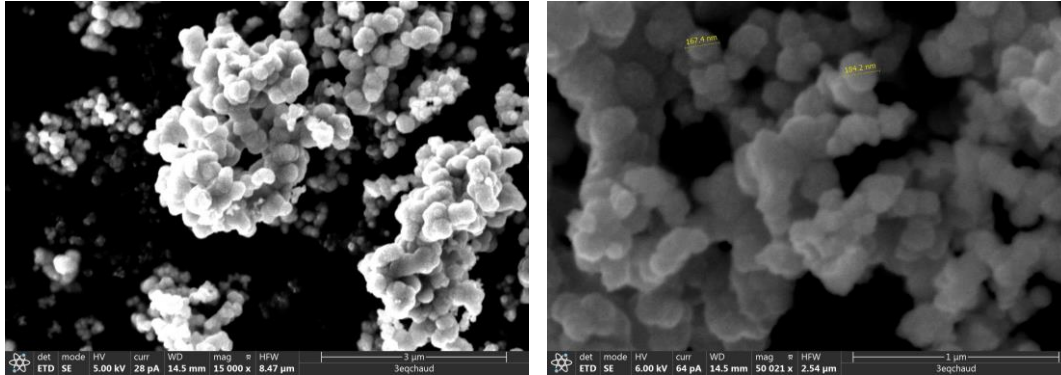


ENERGY SOURCE



ELECTRICITY PRODUCTION

# 04.3 pH gradient cell for energy harvesting



## Osmotic energy source:

CO<sub>2</sub> gas capturing in carbonate solutions

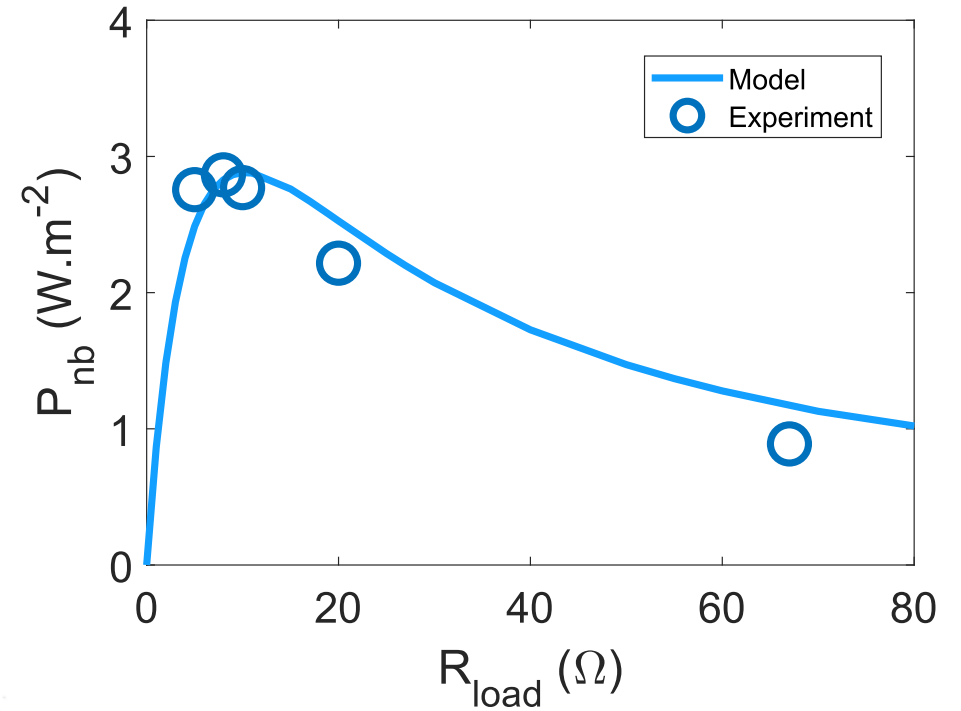
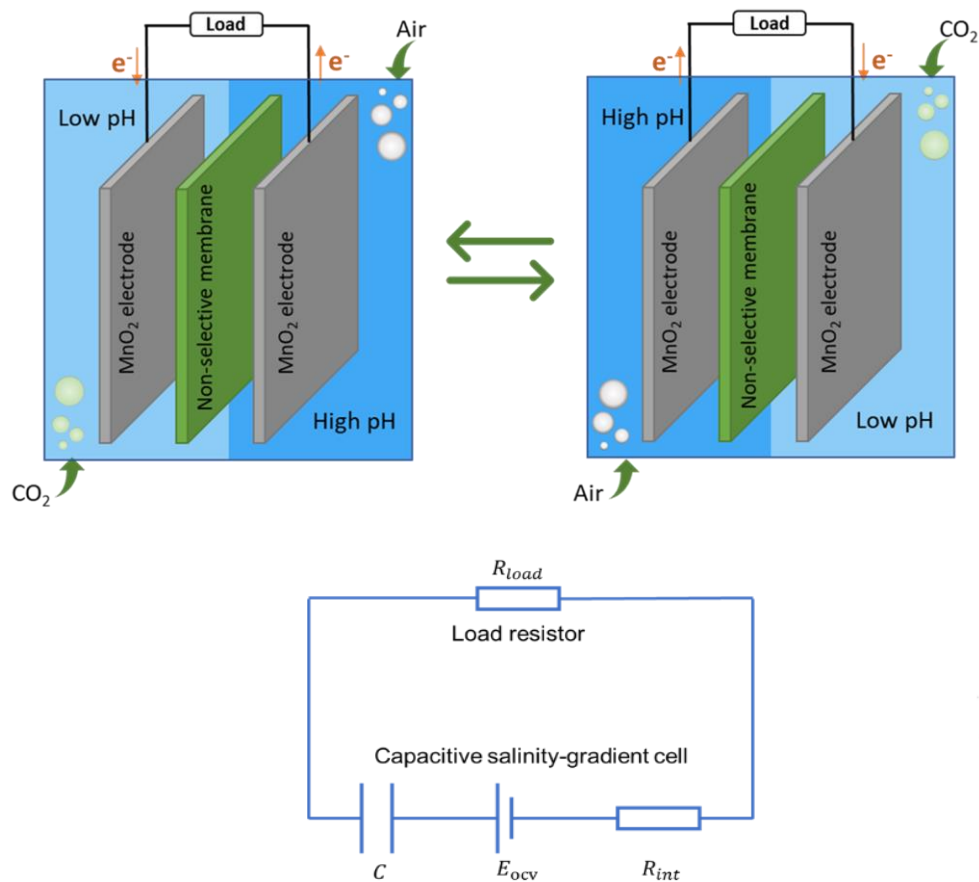
NaHCO<sub>3</sub> (1 M, pH = 7.8) vs. Na<sub>2</sub>CO<sub>3</sub> (0.5 M, pH = 11.7)

## pH gradient based system:

Non-selective membrane is used to prevent direct solution mixing  
 MnO<sub>2</sub> electrodes present prior selectivity for protons H<sup>+</sup>

**Figure 10** pH gradient based energy harvesting system.

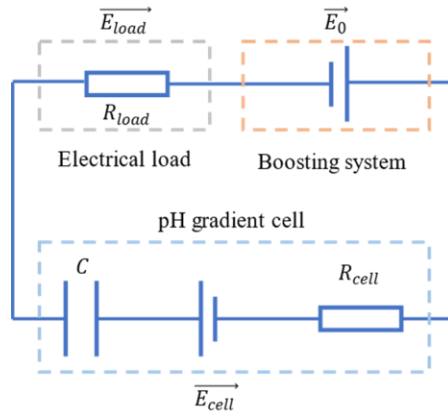
# 04.4 Energy performance



**Figure 11** pH gradient based energy harvesting system coupled with a booster system.

**Energy performance  
matched with capacitive  
equivalent circuit**

# 04.4 Energy performance under boosting strategy

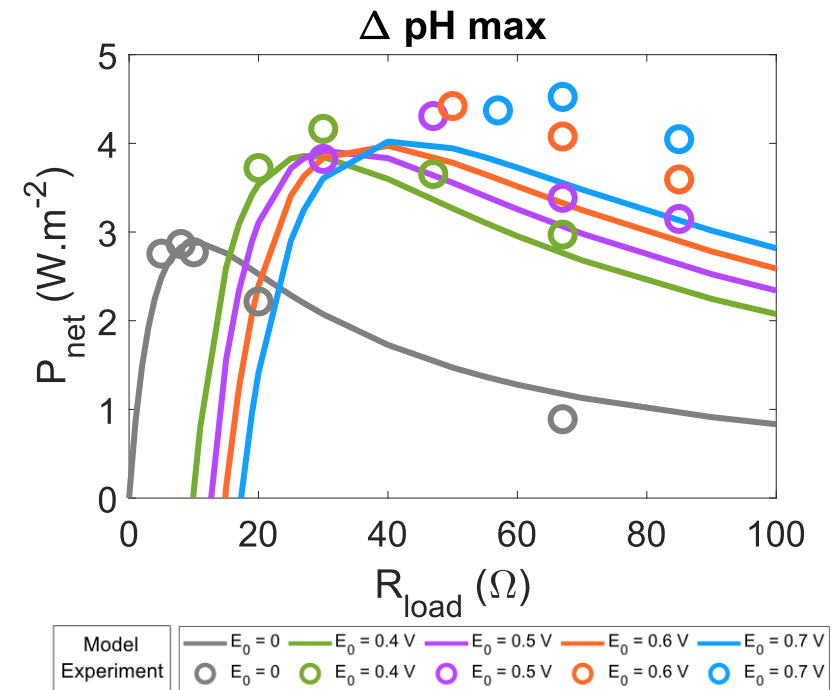


Net power density calculation:

$$P_{b-gross} = \frac{1}{S \cdot T} \int_0^T \frac{E_R(t)^2}{R} dt$$

$$P_{b-boost} = \frac{1}{S \cdot T} \int_0^T E_0(t) \cdot I(t) dt$$

$$P_{b-net} = P_{b-gross} - P_{b-boost}$$



Boosting principle works!

MAX: 4.52 \$W \cdot m^{-2}\$

But BAD prediction of equivalent circuit



# 04.5 Mechanism discussion

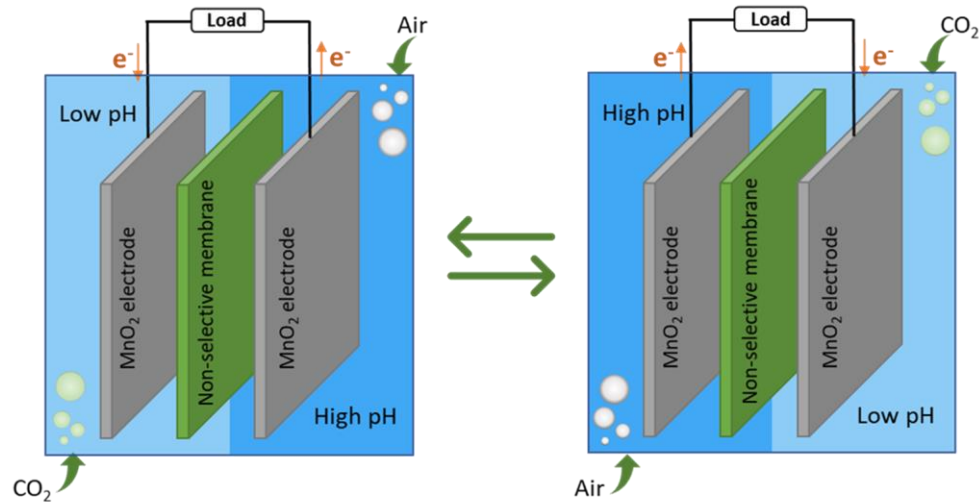


Figure 12 pH gradient based energy harvesting system.

## Faradaic or Capacitive?

*Sources:* Toupin et al. *Chemistry of Materials* 2004  
 Augustyn et al. *Energy & Environmental Science* 2014  
 Lee and Goodenough *Journal of Solid State Chemistry* 1999

*Sources:* Wu et al. *In Preparation*

### Is this a redox reaction governed faradaic process?

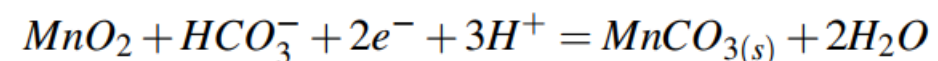
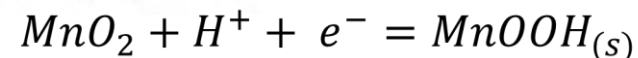
- Electrode related electrical potential well described by Nernst Equation
- **However, the system shows capacitive behavior**

### Is this an ion-adsorption governed capacitive process?

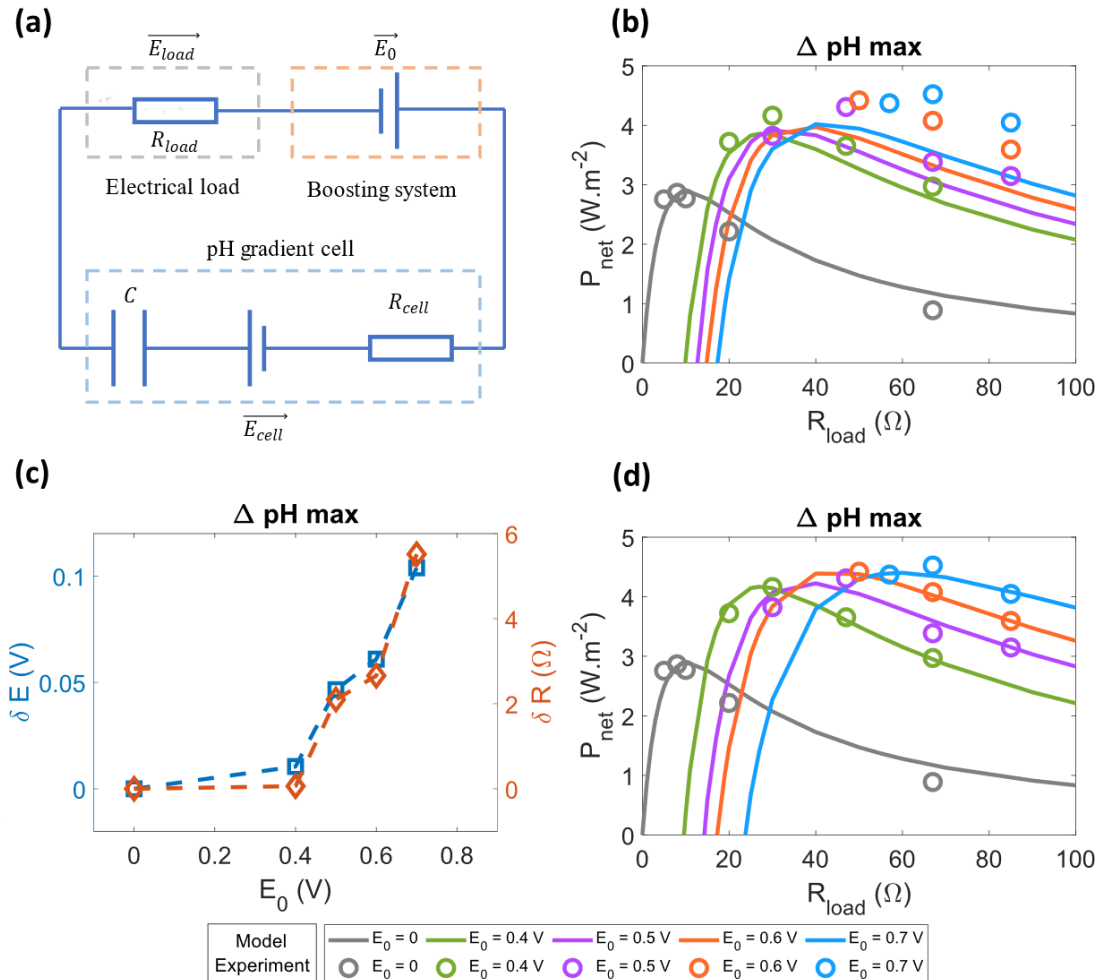
- Established capacitive equivalent circuit
- Capacitive behavior verified by impedance characterization
- Well prediction of energy performance by RC circuit
- **However, the system presents a reversed electrical voltage**

### Faradaic process with capacitive behavior:

- Unique behavior occurred in some materials: **Surface faradaic reactions**
- Redox reactions occurred mainly at the electrode surface
- It presents certain capacitive behavior



# 04.5 Mechanism discussion



## Unexpected boosting result:

- Redox reaction leads to chemical composition variation
- Boosting amplifies such phenomenon
- Material composition variation leads to parameter variations in equivalent circuits
- Cell voltage  $E_{OCV}$  and cell inner resistance  $R_{cell}$

## Fitting correction:

- Use of two fitting parameters:  $\delta E$  and  $\delta R$
- $$E_{OCV-eff} = E_{OCV} + \delta E$$
- $$R_{cell-eff} = R_{cell} + \delta R$$
- Well accordance by adjusted capacitive equivalent circuit
  - This occurred due to the material composition variation inside  $MnO_2$  electrodes

*Sources: Ferrell and Vosburgh Journal of The Electrochemical Society 1951  
Johnson and Vosburgh Journal of The Electrochemical Society 1953  
Conway Electrochimica Acta 1993*

# 04 Summary



**pH-gradient  
cell system**

01 pH gradient based osmotic energy harvesting in CCS cycle

02 pH gradient cell composed of  $\text{MnO}_2$  electrodes and non-selective membrane

03 Faradaic process with capacitive behavior

04 Max net power density of  $4.5 \text{ W/m}^2$  under boosting strategy related to the chemical composition variation in electrodes



# 05

# Conclusion & Perspectives

Some future work to be further developed

# 05.1 Conclusion



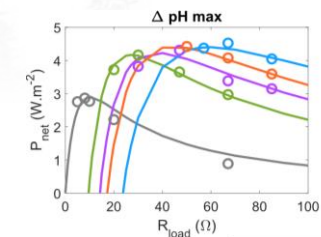
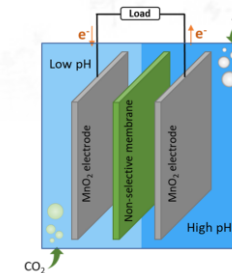
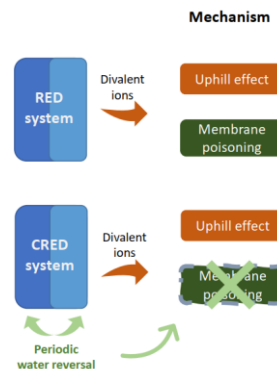
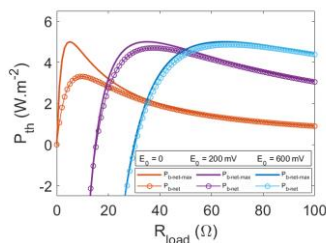
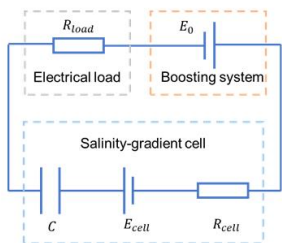
## Thesis Objective:

Investigate the fundamental mechanism of the CRED system, aiming to enhance its energy performance and broaden its range of applications.

Towards  
Power density  
amelioration

Towards  
Real brines

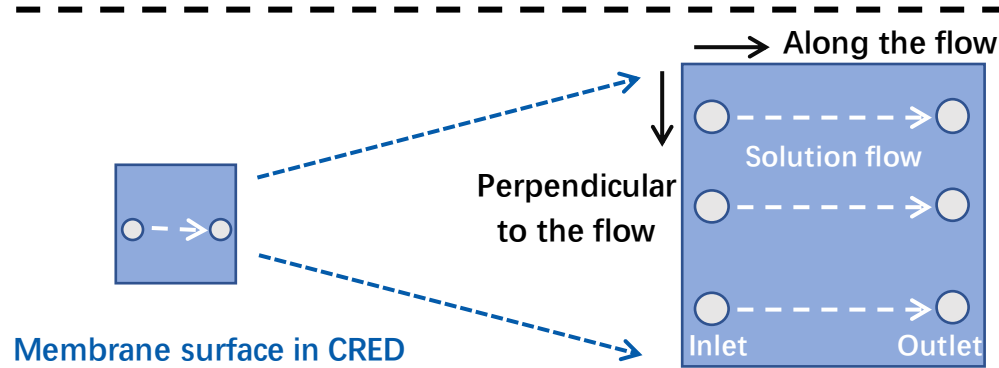
Towards  
pH gradient based  
osmotic energy  
harvesting



# 05.2 CRED system scale up



## Surface area increase



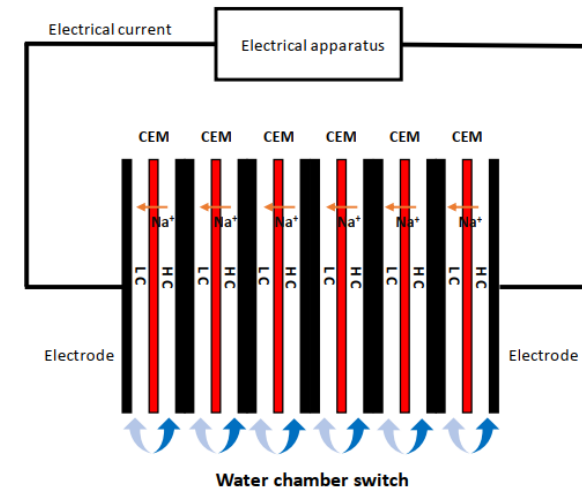
### Along the flow:

- Increase of filling time for the entire system
- Impact on cell voltage and inner resistance due to the inhomogeneous ion concentration profile
- More efforts to fight against viscous dissipation

### Perpendicular to the flow:

- Limited width related to lineic resistance of current collectors
- Structural design of co-flow or counter-flow

## Stacking CRED in series



$$E_{OCV} = N \cdot E_m + N \cdot E_{elec}$$

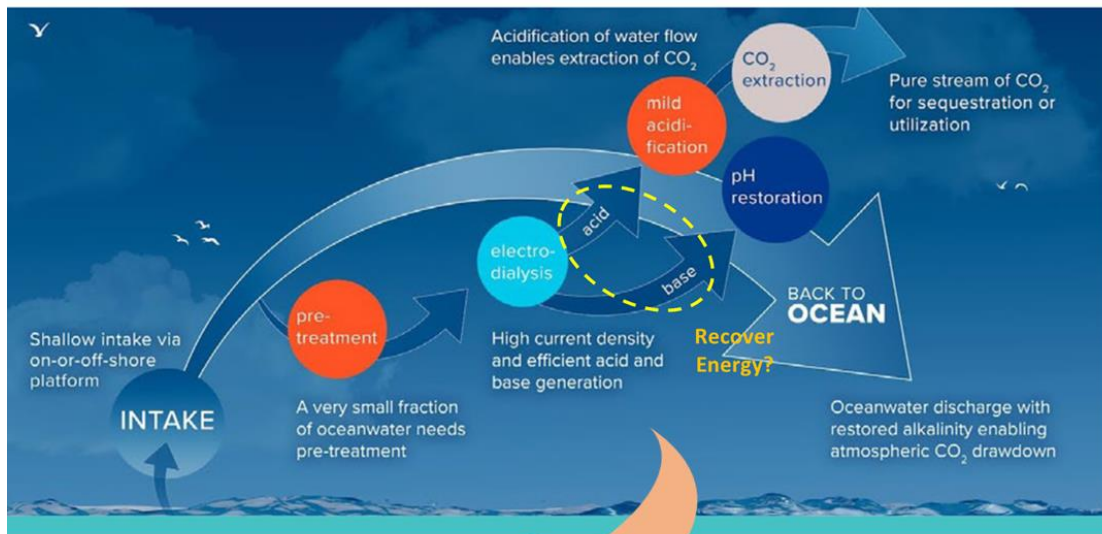
### Stacking CRED units:

- Each unit comprises 1 CEM membrane with 2 capacitive electrodes
- Lower system cost compared with RED system stacking

# 05.3 pH gradient cell in DOC

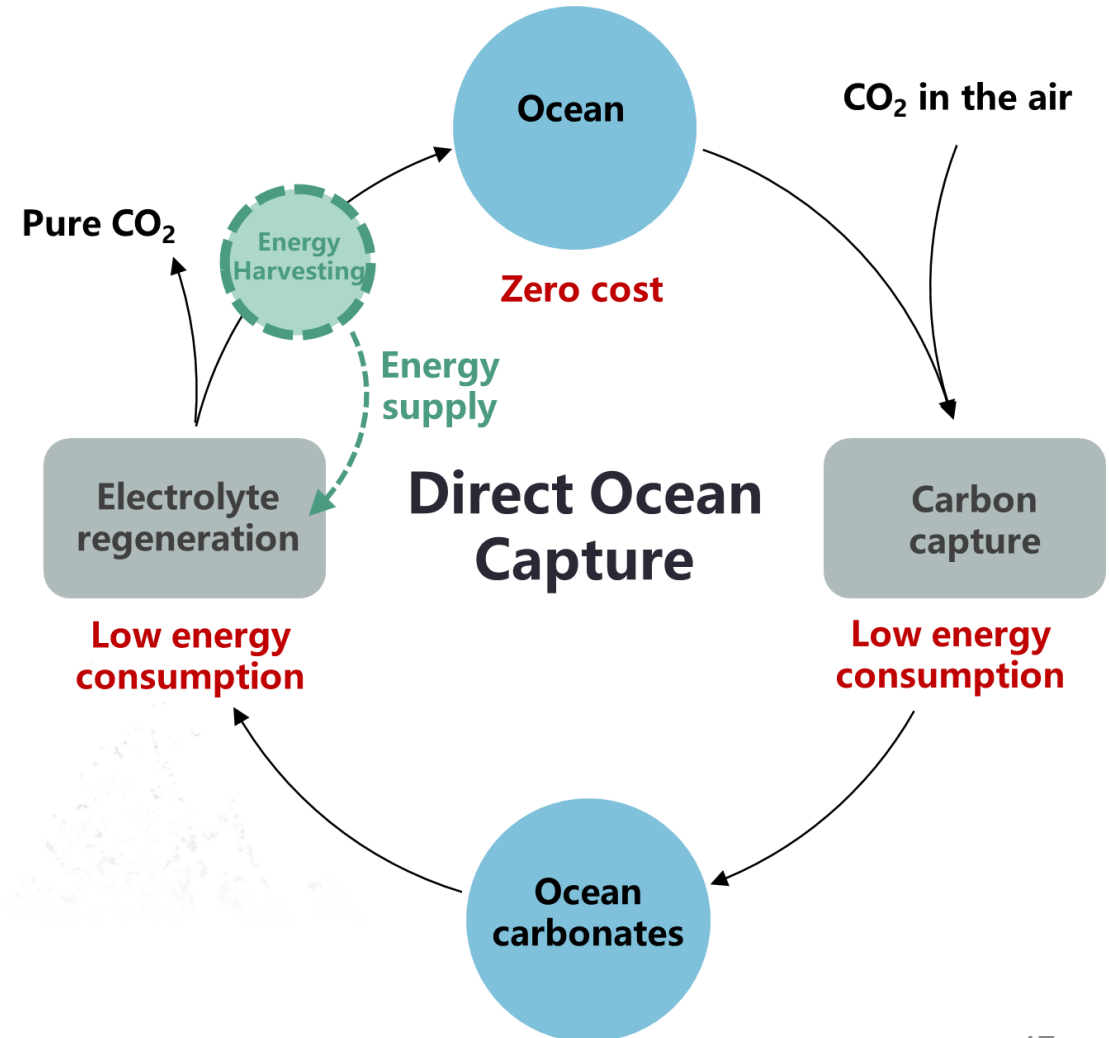
## Direct Ocean Capture (DOC):

Direct removal of Carbon dioxide from oceanwater is a method of capturing dispersed CO<sub>2</sub>.



pH gradient energy harvesting system

Image Credit: Captura



# Acknowledgments

## Jury members:

Pr. Marie-Caroline Jullien  
Pr. Cyril Picard

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Pr. Véronique Balland

Pr. Mikhael Bechelany  
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Hélène Dodier

## IPGG team:

Dr. Bertrand Cinquin  
Dr. Audric Jan

## Thanks for your attention! Any questions?

