Simulation of Nanopores in Capacitive Energy Extraction based on Double Layer Expansion (CDLE)

Emilio Ruiz-Reina[1], Félix Carrique[2], Ángel Delgado[3], María del Mar Fernández[3]

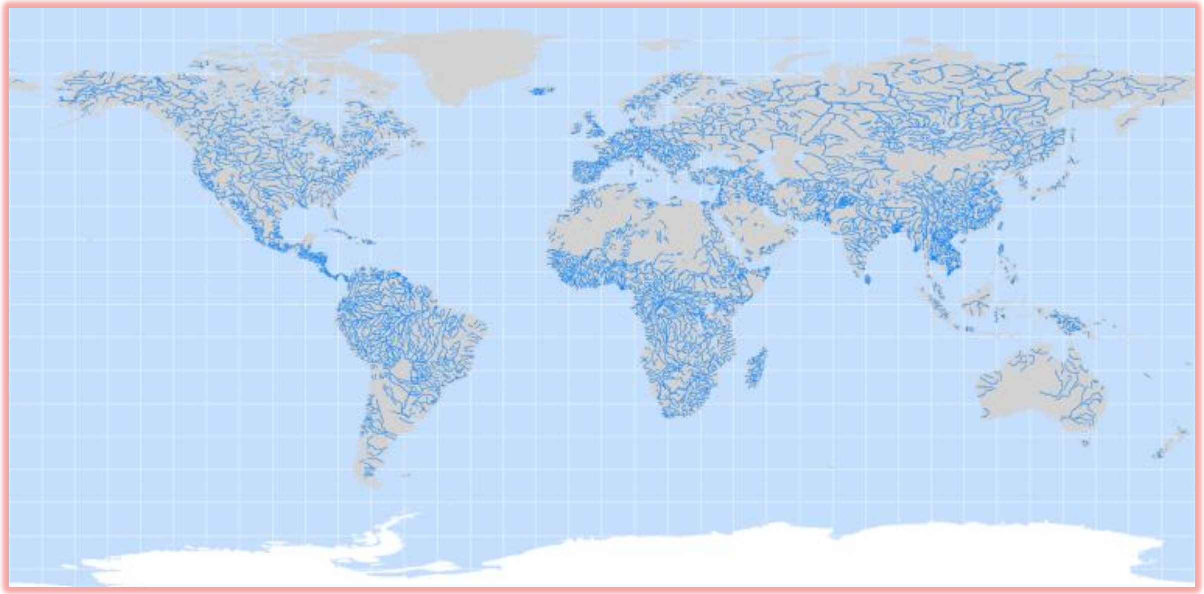
[1]*Department of Applied Physics II, University of Málaga, Spain.*
[2]*Department of Applied Physics I, University of Málaga, Spain.*
[3]*Department of Applied Physics, University of Granada, Spain.*

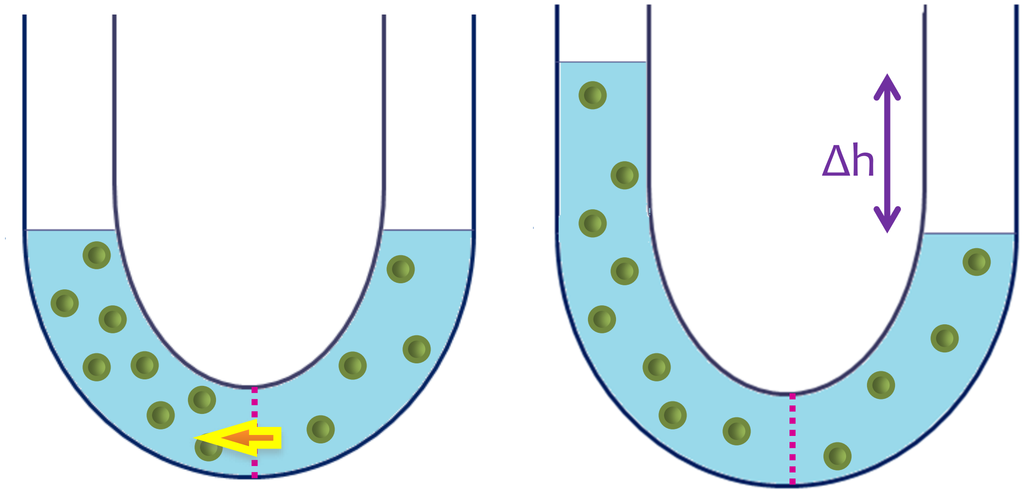
COMSOL CONFERENCE
2015 GRENOBLE

Universidad de Granada

UNIVERSIDAD DE MÁLAGA

What is salinity gradient energy or blue energy ?

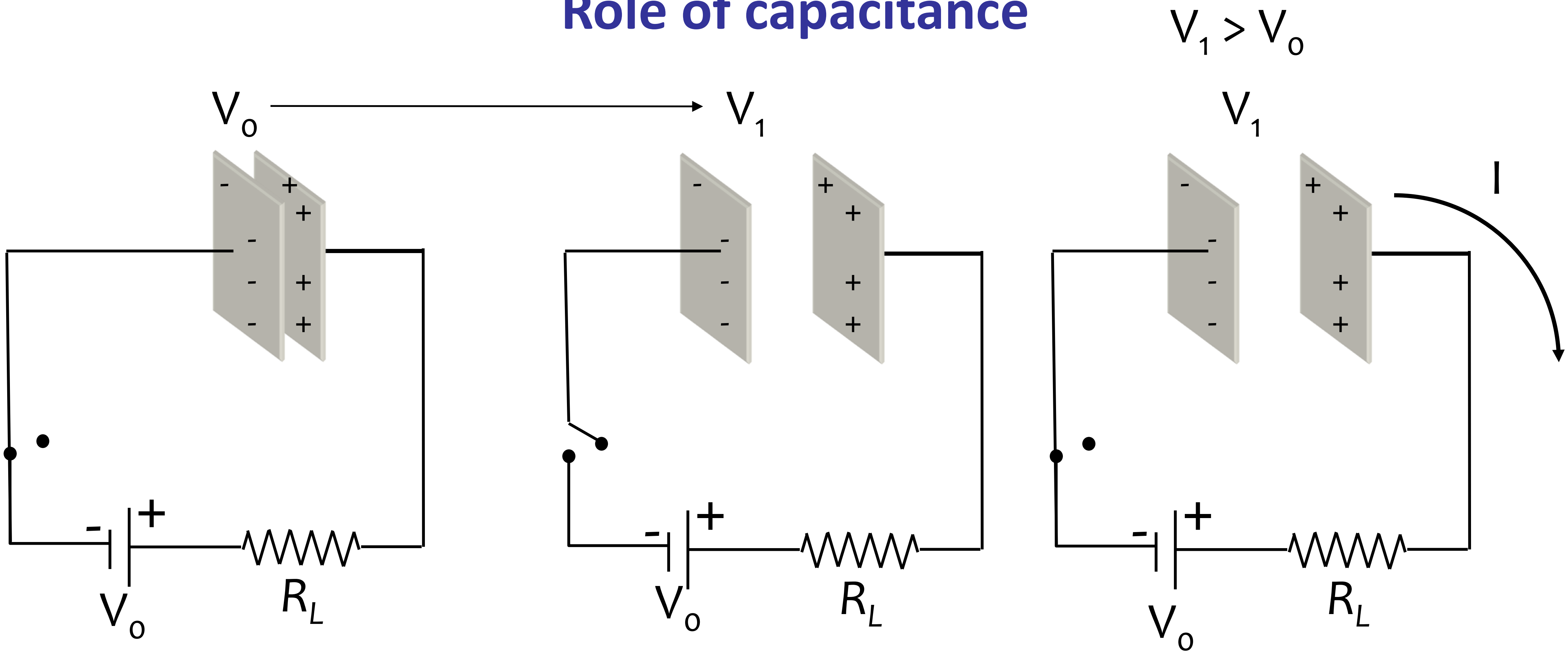




It’s a new renewable energy source that has been proposed, based in the mixing of two solutions with different concentrations, which is available worldwide.

Guadalquivir river estuary (Cádiz, Spain)

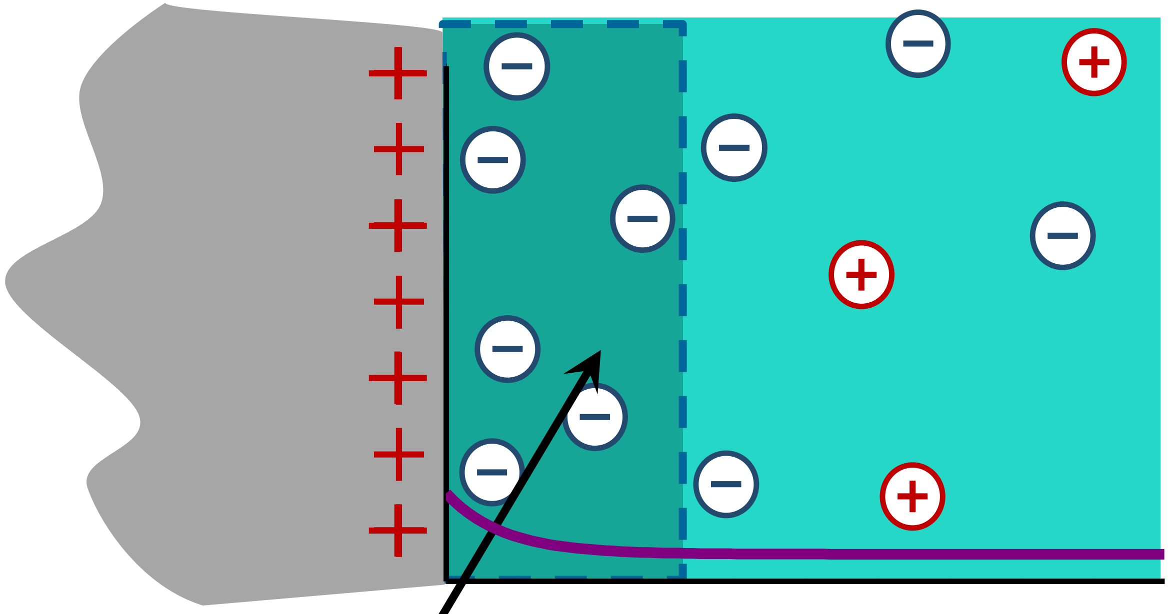
Role of capacitance



$C\downarrow$ (constant Q) $\Rightarrow V\uparrow$

By decreasing the capacitance of a charged capacitor, the stored energy increases.

How do we control capacitance?
The role of charged interfaces: CDLE technique



(Gouy-Chapman model)

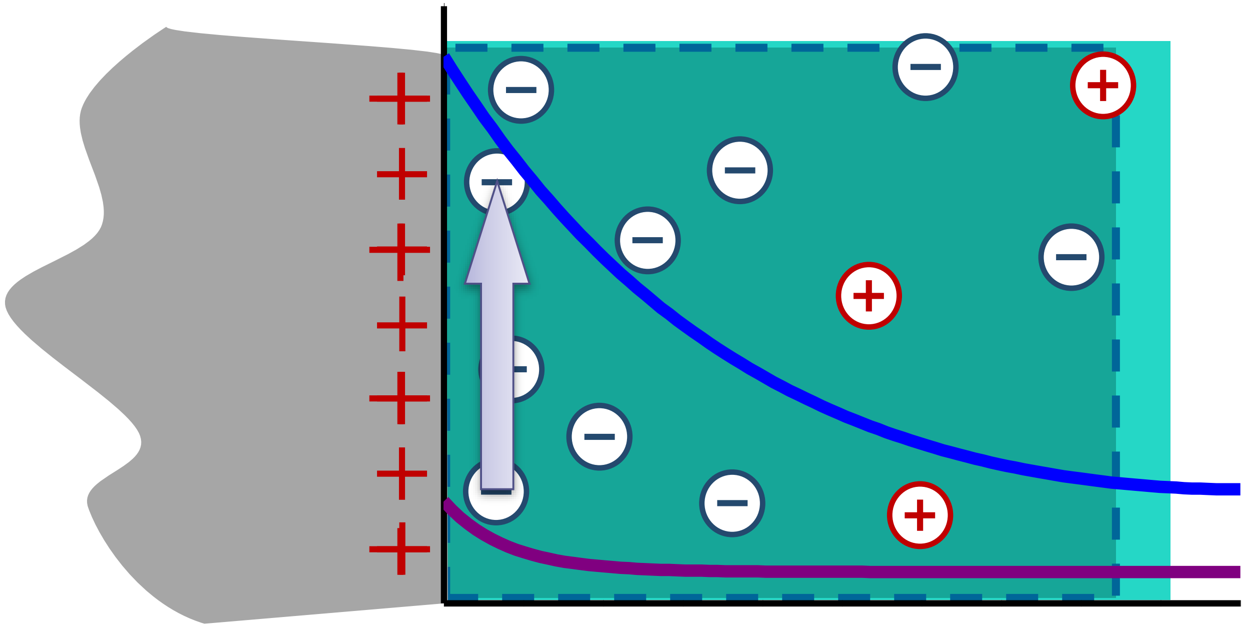
$$\sigma \approx \sqrt{\frac{2z^2e^2}{k_B}} \sqrt{\frac{c\varepsilon_m(T)}{T}} \Psi_d$$

Surface charge density

Surface potential

- Surfaces in contact with a solution can store charge in the EDL.
- The capacitance of the EDL increases with the salinity.

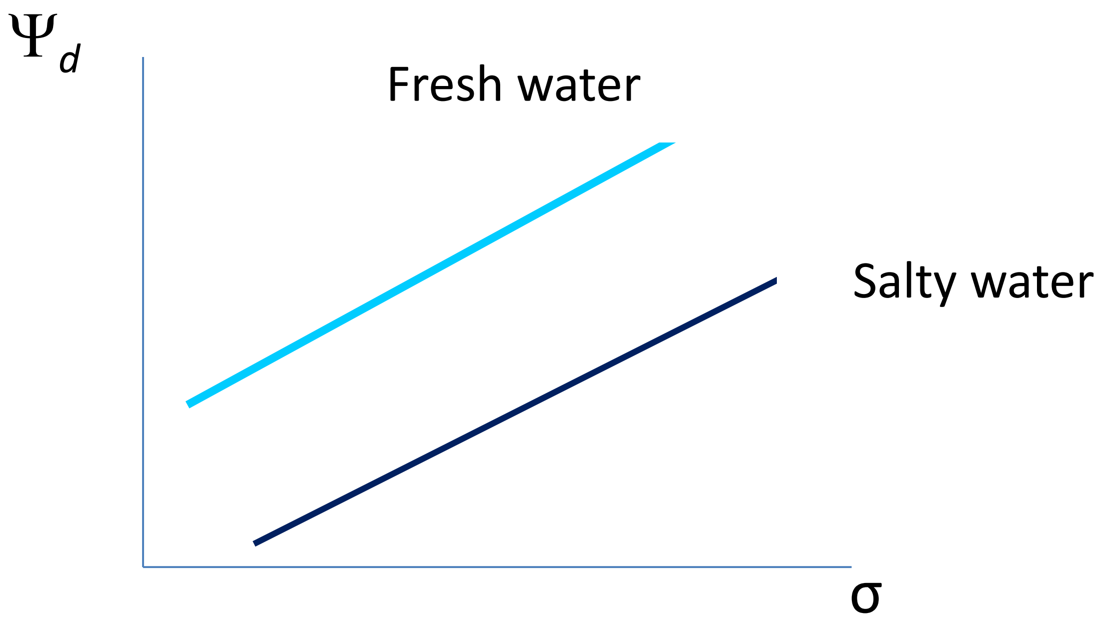
How do we control capacitance?
The role of charged interfaces: CDLE technique



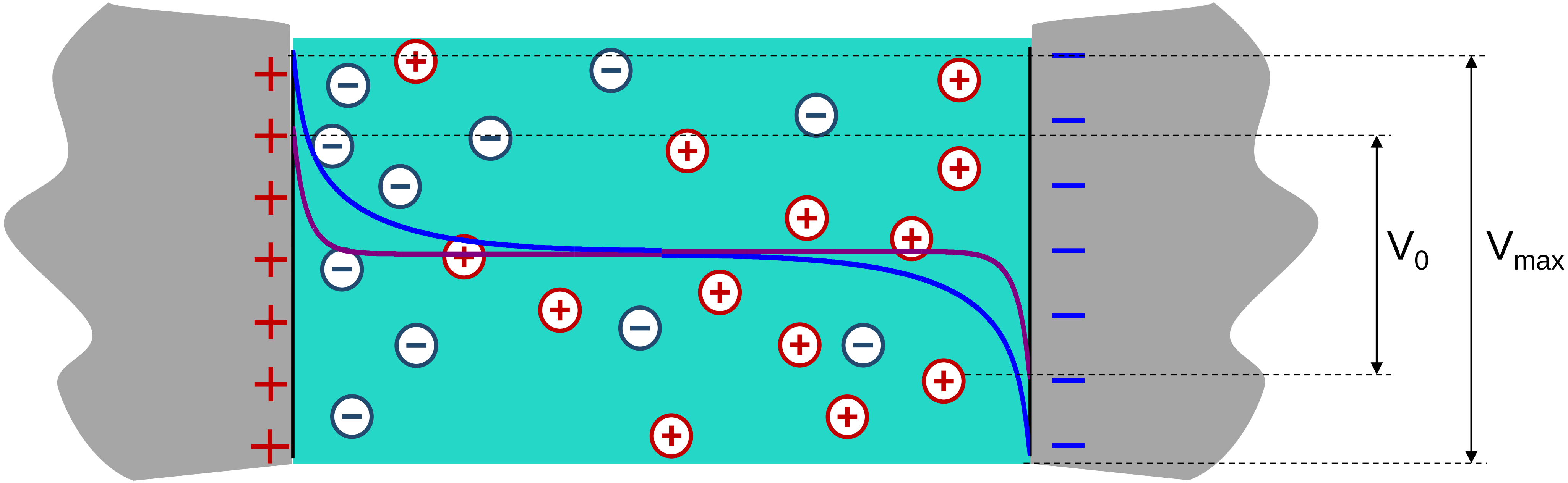
$$\sigma \approx \sqrt{\frac{2z^2e^2}{k_B}}\ \sqrt{\frac{c\varepsilon_m(T)}{T}}\ \Psi_d$$

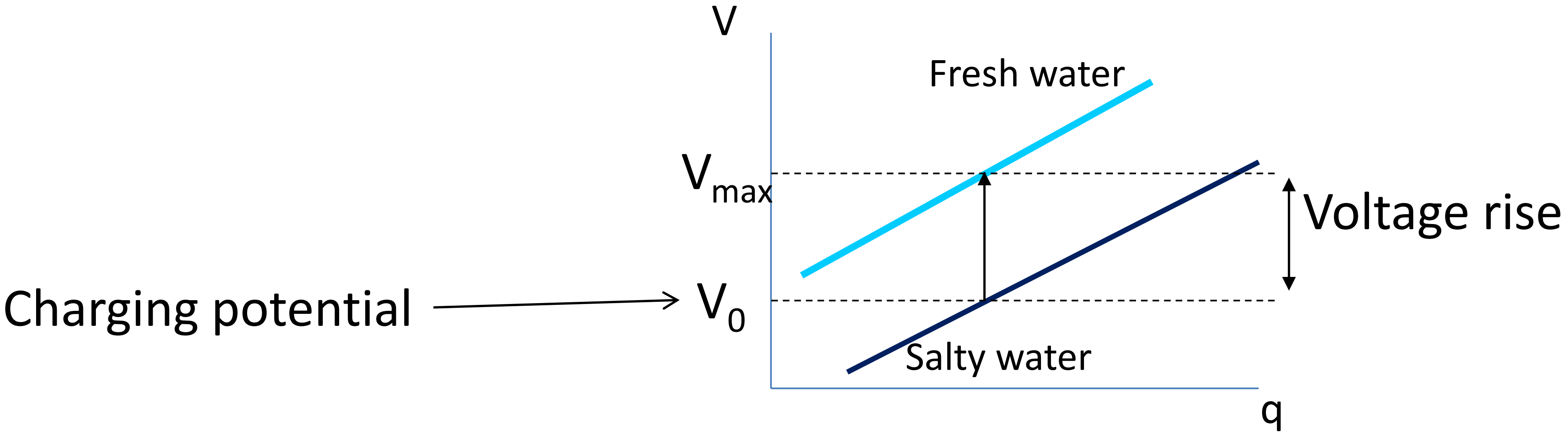
Surface charge density

Surface potential

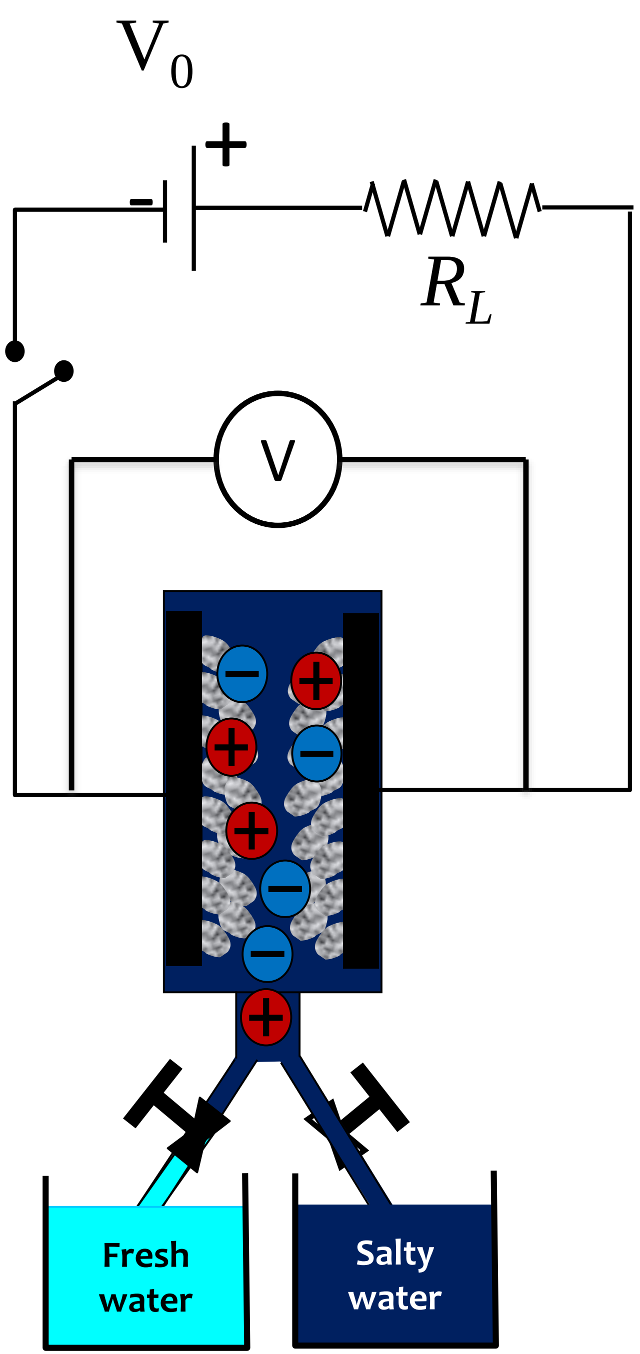


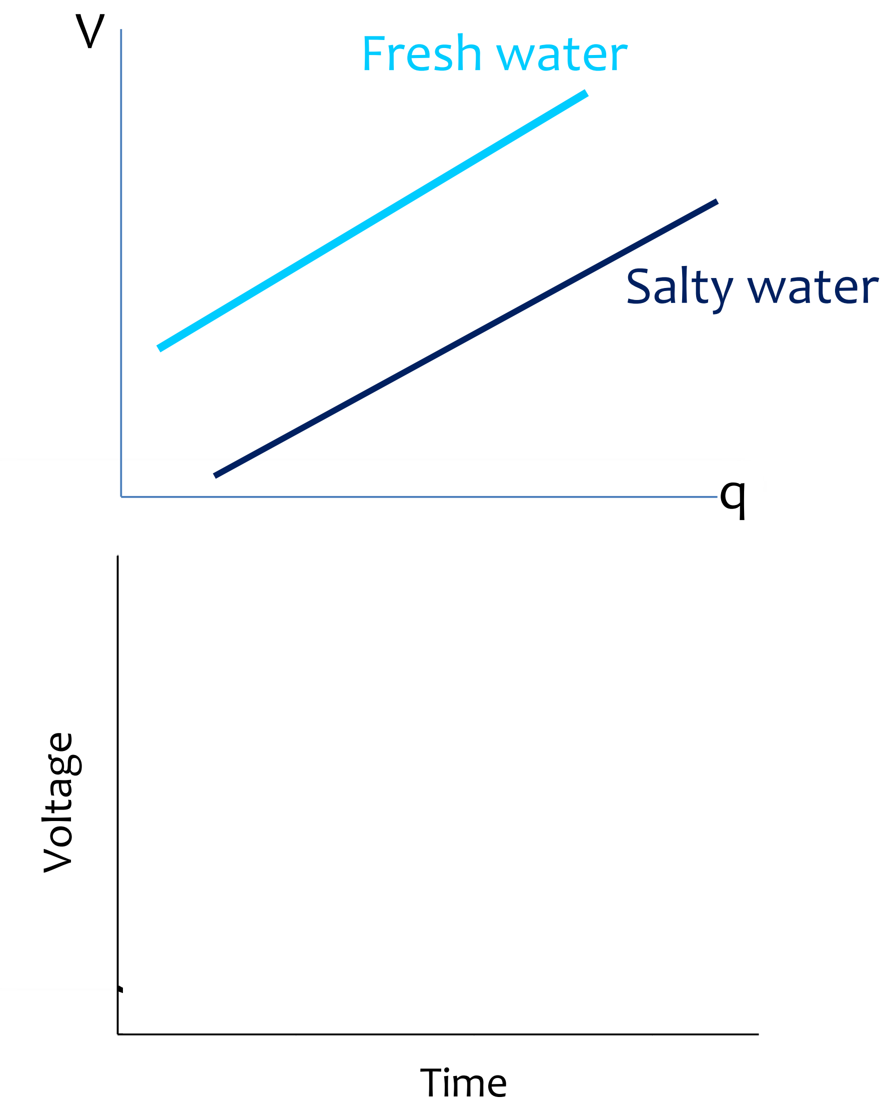
How do we control capacitance?
The role of charged interfaces: CDLE technique



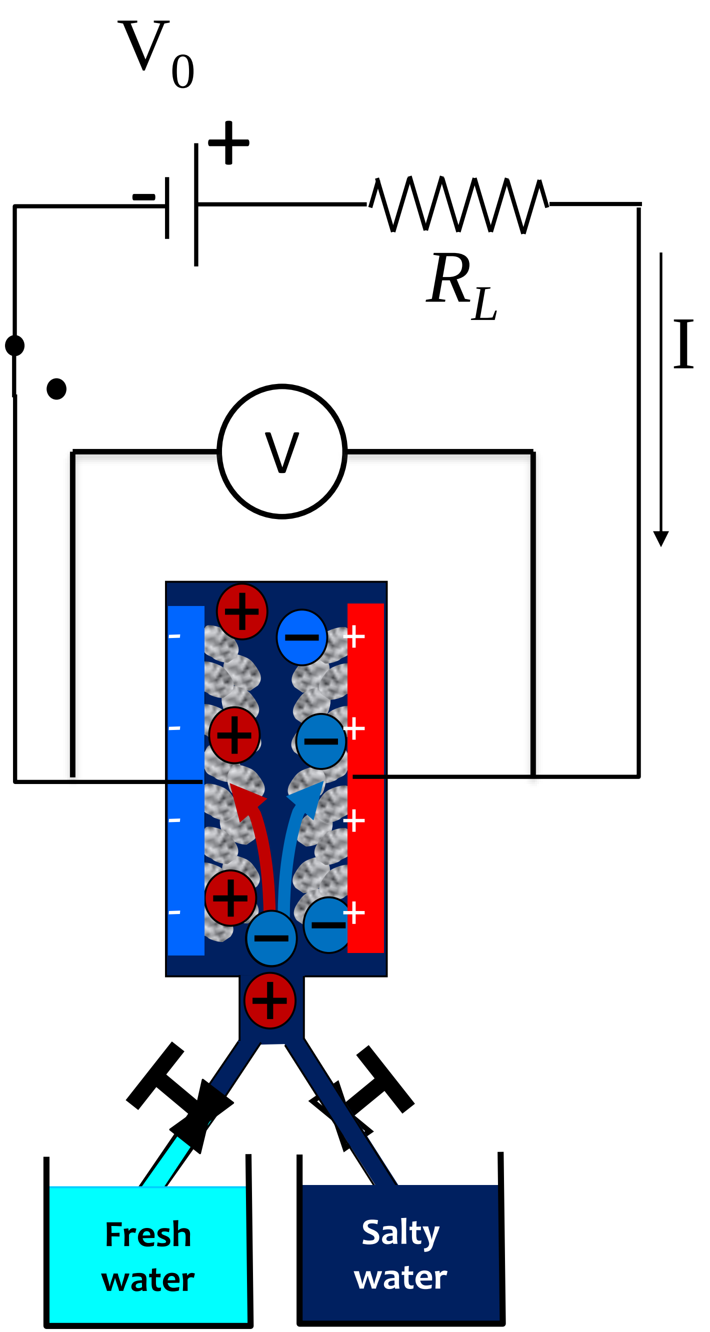


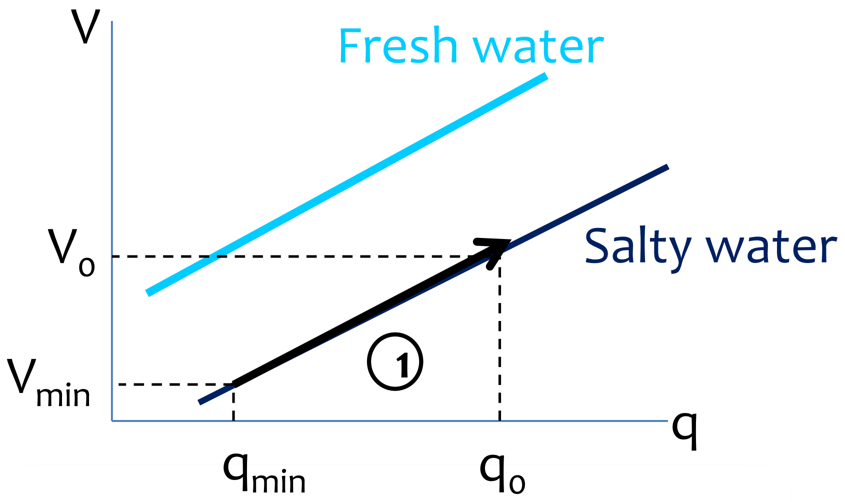
CDLE cycle

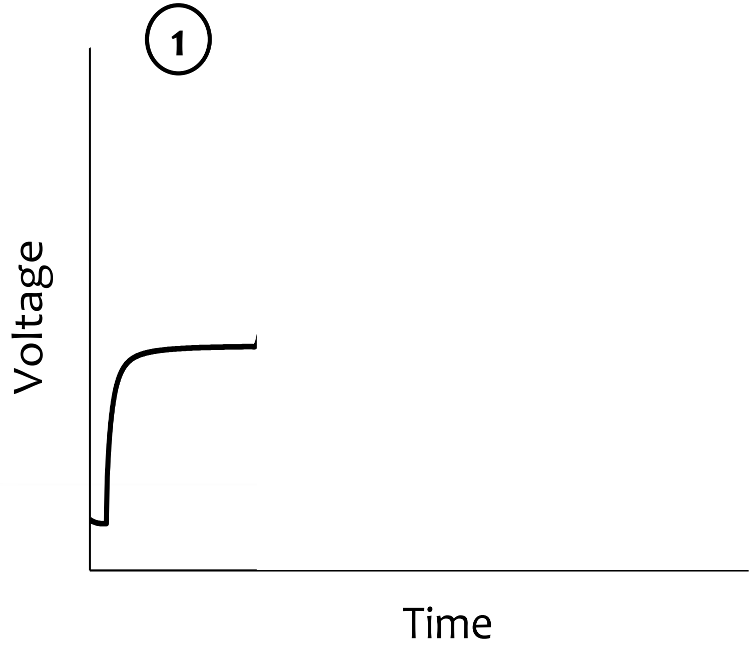

V_0
+
-
R_L
V
Fresh water
Salty water


V
Fresh water
Salty water
q
Voltage
Time

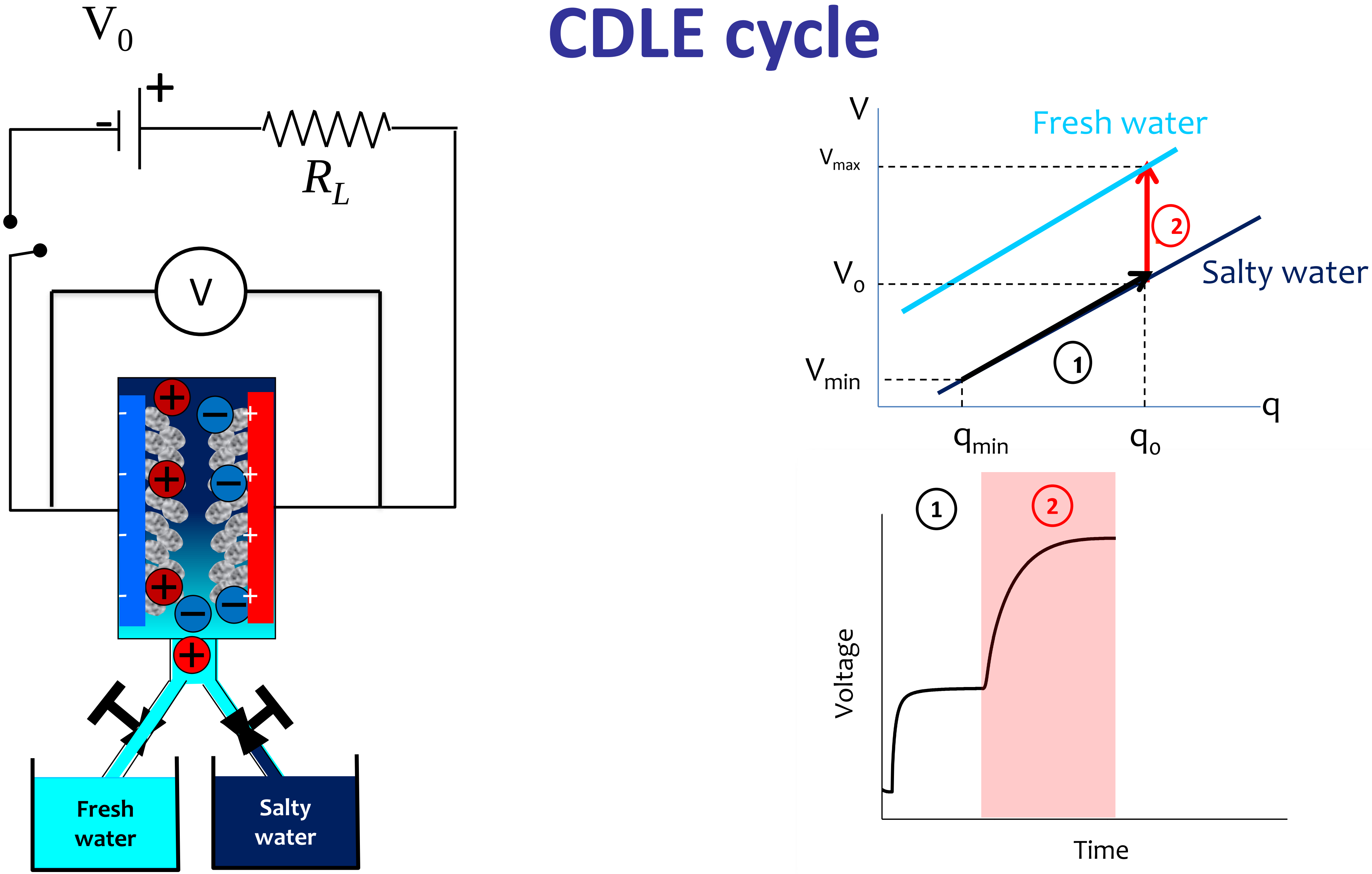
CDLE cycle


V0
+
-
RL
I
V
-
+
Fresh water
Salty water


V
Fresh water
Vo
Salty water
Vmin
1
q
qmin
qo

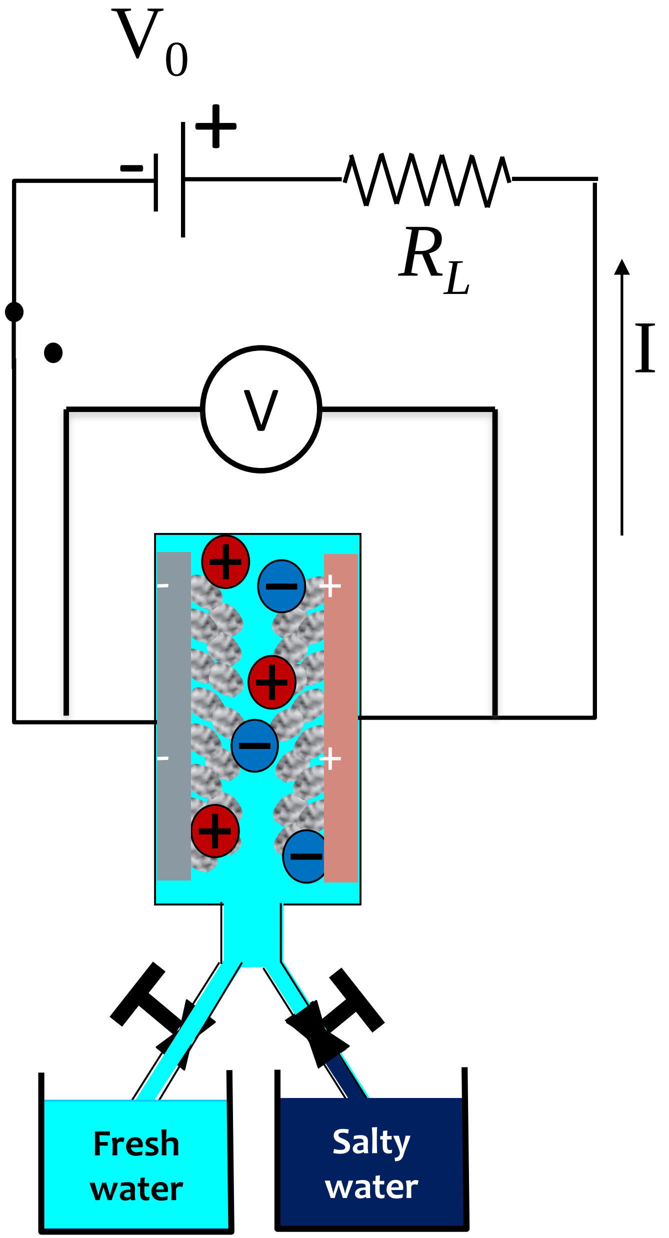

1
Voltage
Time

CDLE cycle

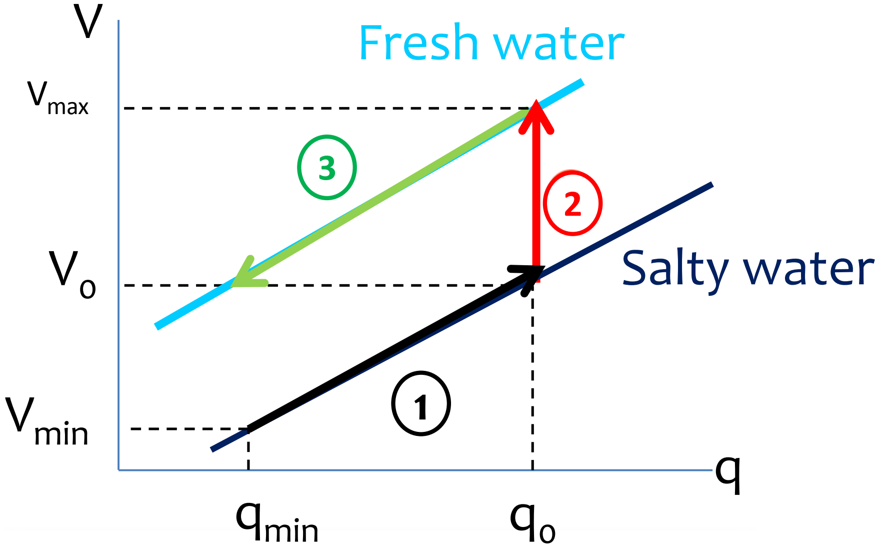


V_0
+
-
R_L
V
-
+
Fresh water
Salty water
V
Fresh water
V_{max}
2
V_o
Salty water
V_{min}
1
q
q_{min}
q_o
1
2
Voltage
Time

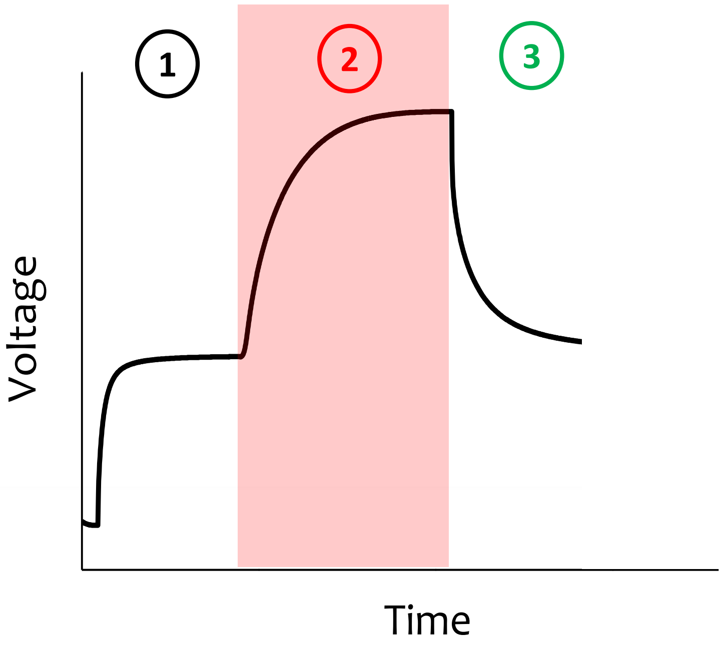
CDLE cycle



V0
+
-
RL
I
V
-
+
Fresh water
Salty water

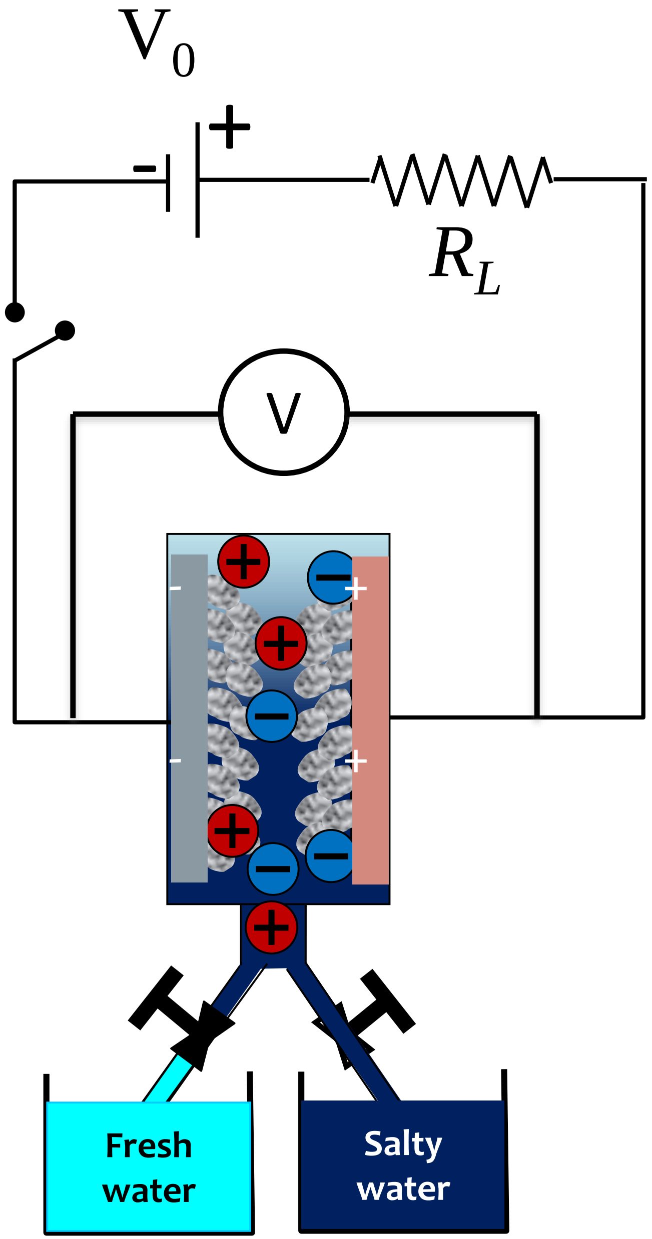


V
Fresh water
Vmax
3
2
Vo
Salty water
Vmin
1
q
qmin
qo

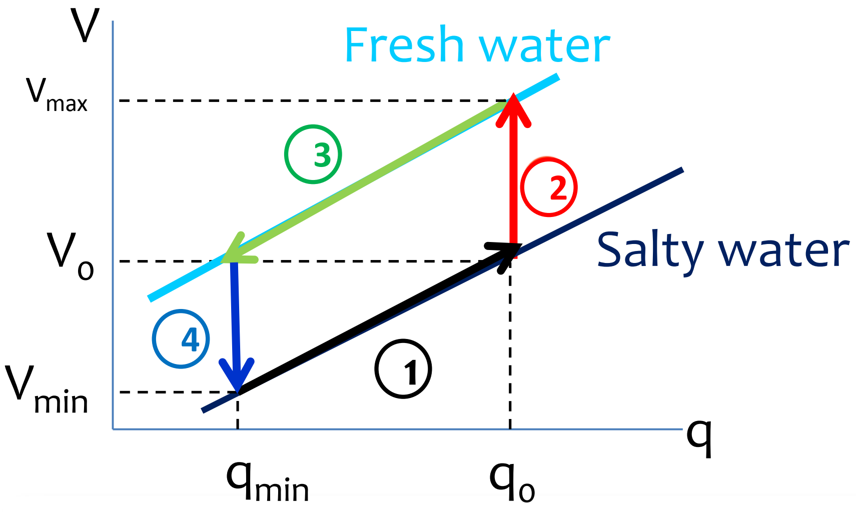


1
2
3
Voltage
Time

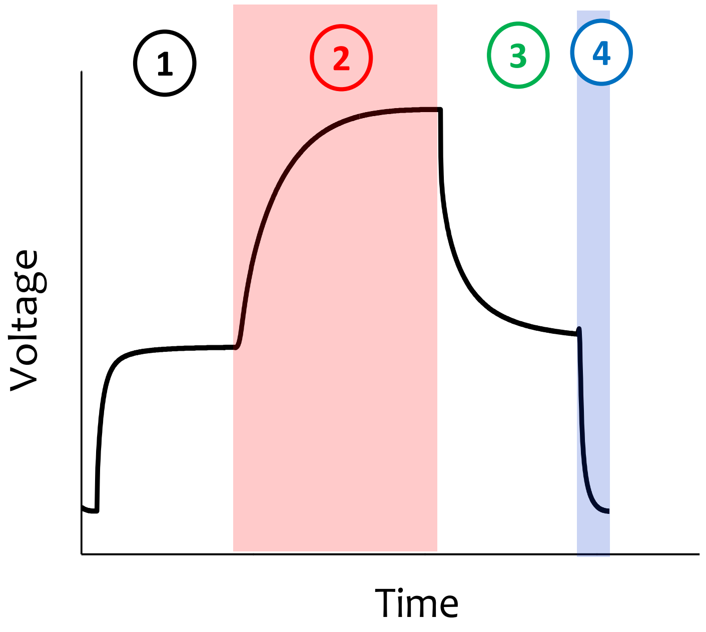
CDLE cycle



V_0
+
-
R_L
V
Fresh water
Salty water

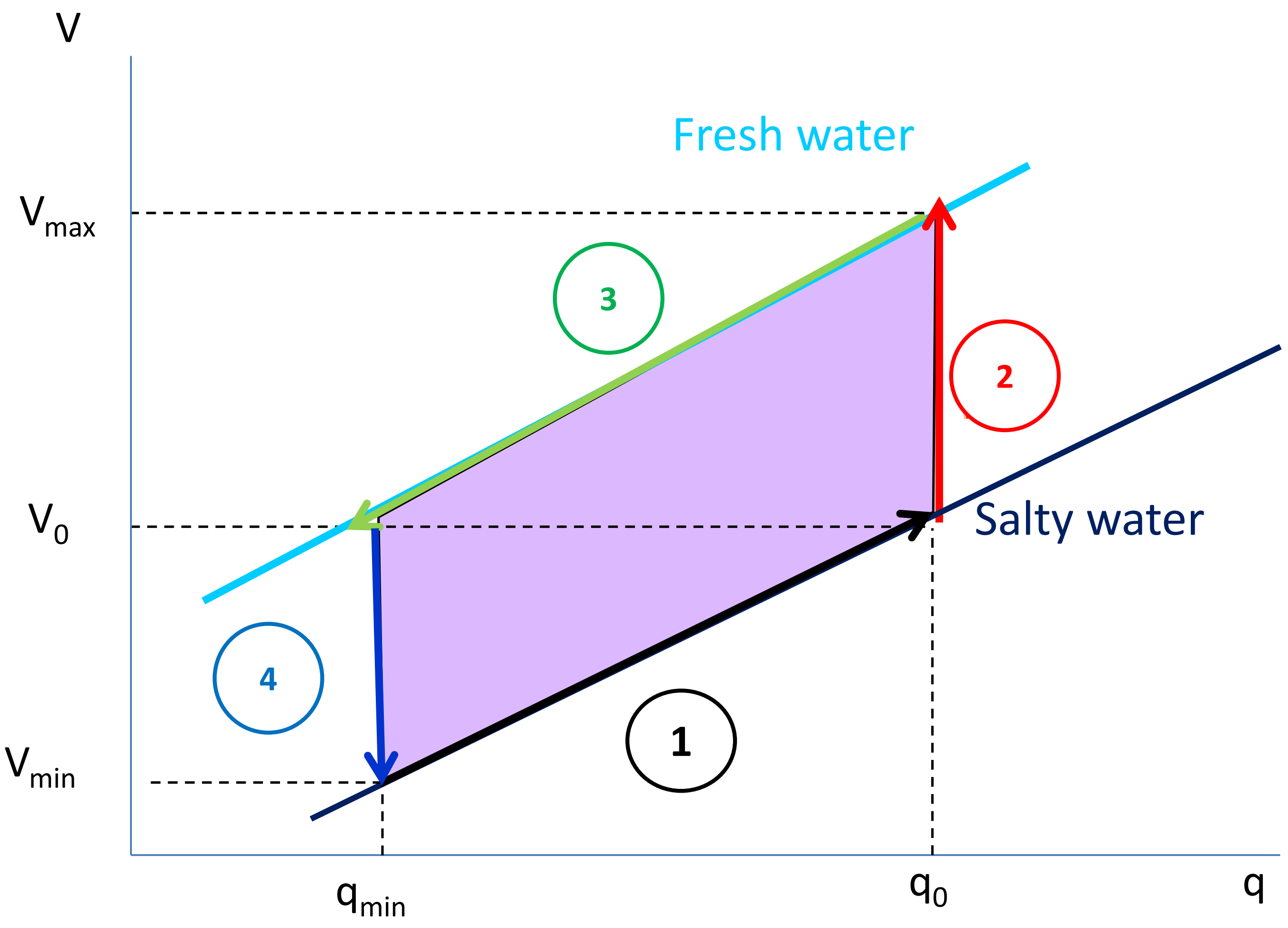


V
Fresh water
V_{max}
3
2
Salty water
V_o
4
1
V_{min}
q
q_{min}
q_o



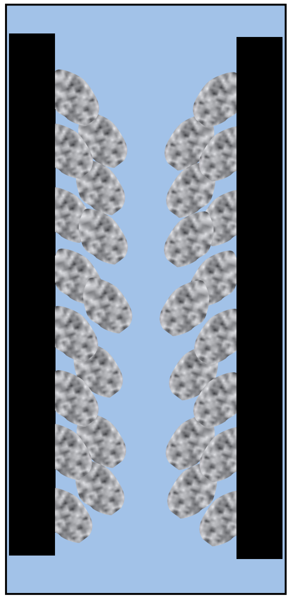
1
2
3
4
Voltage
Time

CDLE cycle

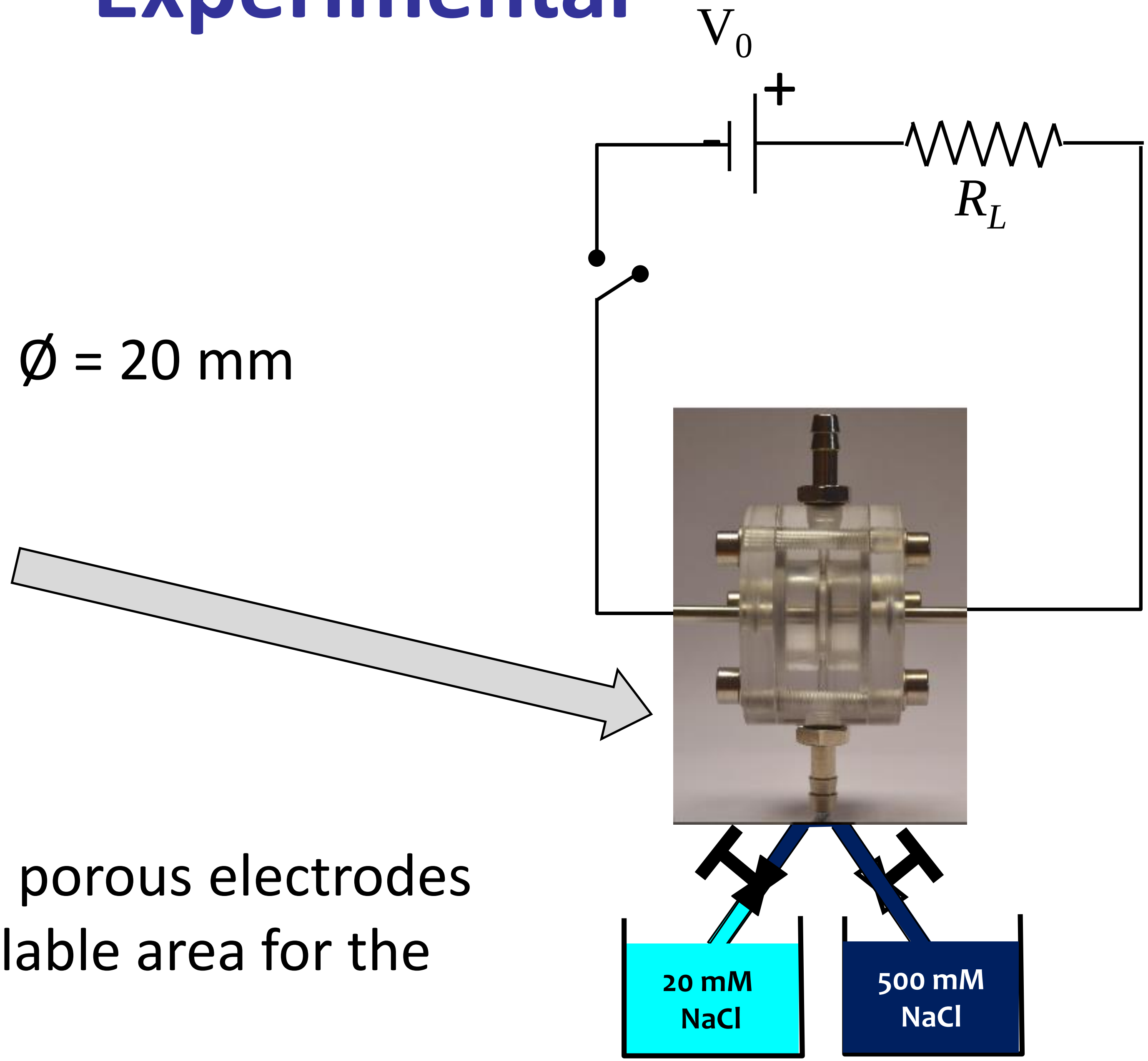


$$W = \int_{q_{min}}^{q_{max}} (V_{fresh} - V_{salty})\,dq$$

Experimental



Ø = 20 mm



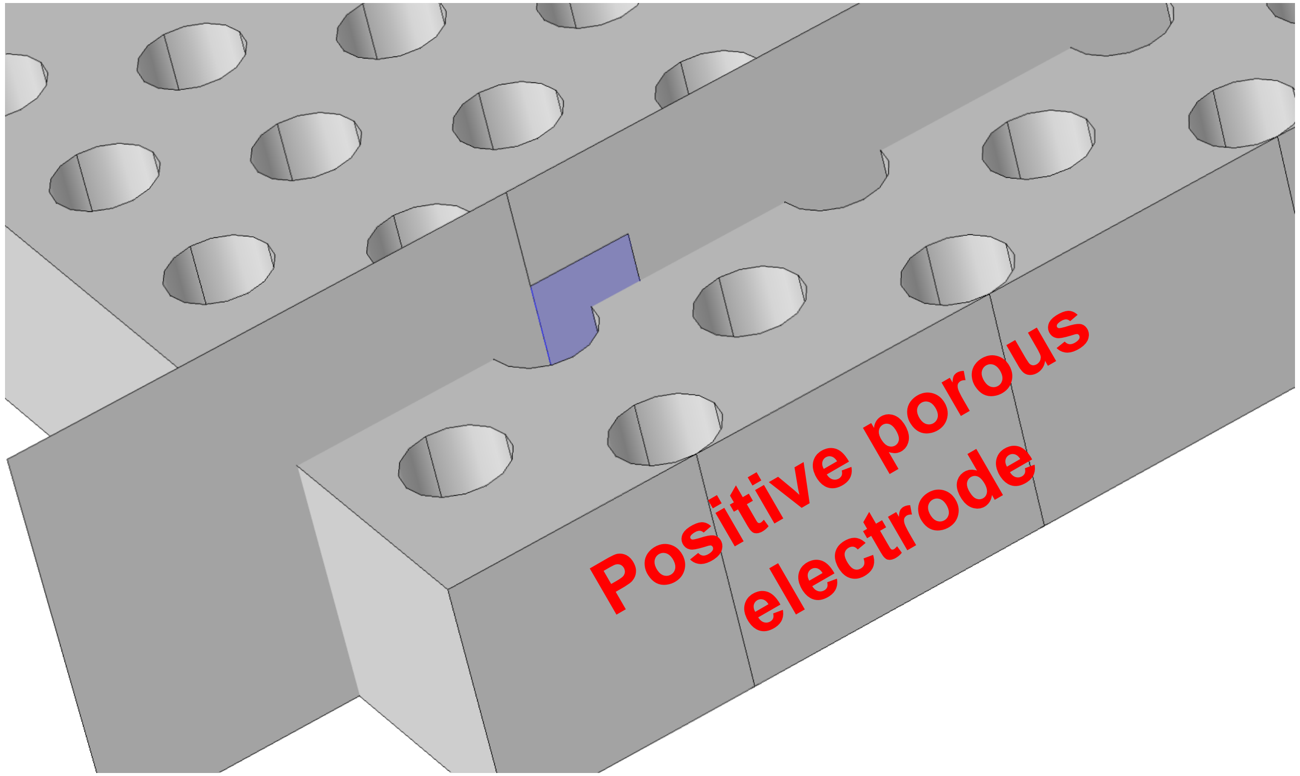
The cell is made with porous electrodes to obtain a huge available area for the formation of the EDL

Numerical simulation of nanopores with COMSOL Multiphysics

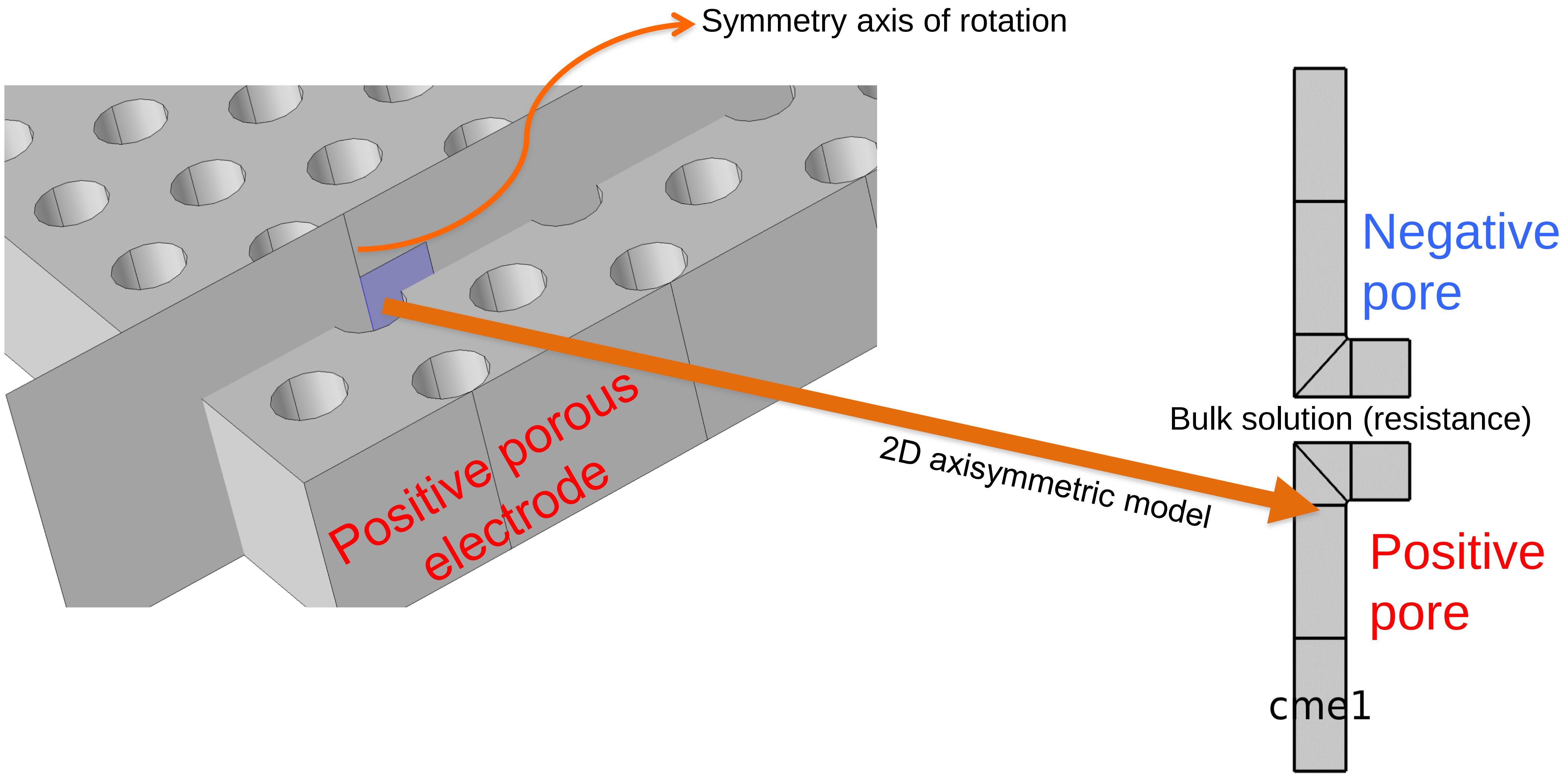
Goal:

Simulate the full CDLE cycle inside the electrode nanopores with COMSOL Multiphysics to:

- estimate the value of the energy/cycle,
- understand the dynamics of the processes involved,
- analyze the role of the different parameters and
- finally optimize the generated power.



Geometry



Symmetry axis of rotation
Positive porous electrode
2D axisymmetric model
Negative pore
Bulk solution (resistance)
Positive pore
cme1

Parameters

Name	Expression	Value	Description
Temp	25[degC]	298.15 K	Temperature
a	10[nm]	1E-8 m	Pore radius
L	100[um]	1E-4 m	Pore length
Sp	20/100	0.2	Ratio pore area/total electrode area
N_poros	(9[mm]/a)^2/Sp	4.05E12	Numbers of pores
R	a/sqrt(Sp)	2.2361E-8 m	Entrance radius
conc	500[mmol/l]	500 mol/m^3	Higher electrolyte concentration (Initial)
conc2	20[mmol/l]	20 mol/m^3	Lower electrolyte concentration
val_Cl	-1	-1	Cl- Valence
D_Cl	76.31[cm^2/(ohm*mol)]*k_B_const*Temp/(N_A_const*e_const^2*abs(val_Cl))	2.032E-9 m^2/s	Cl- Diffusion coefficient
D_Na	50.11[cm^2/(ohm*mol)]*k_B_const*Temp/(N_A_const*e_const^2*abs(val_Na))	1.3344E-9 m^2/s	Na+ Diffusion coefficient
val_Na	1	1	Na+Valence
V_in	300[mV]	0.3 V	Cell potential (connected)
Res_sol	14[ohm]	14 Ω	Ionic solution resistance (bulk)
Res	1[ohm]	1 Ω	Load resistance (charge)
Super_Cap	350[F]	350 F	Supercapacitor capacity

Governing Equations

Poisson’s equations for the electric potential.

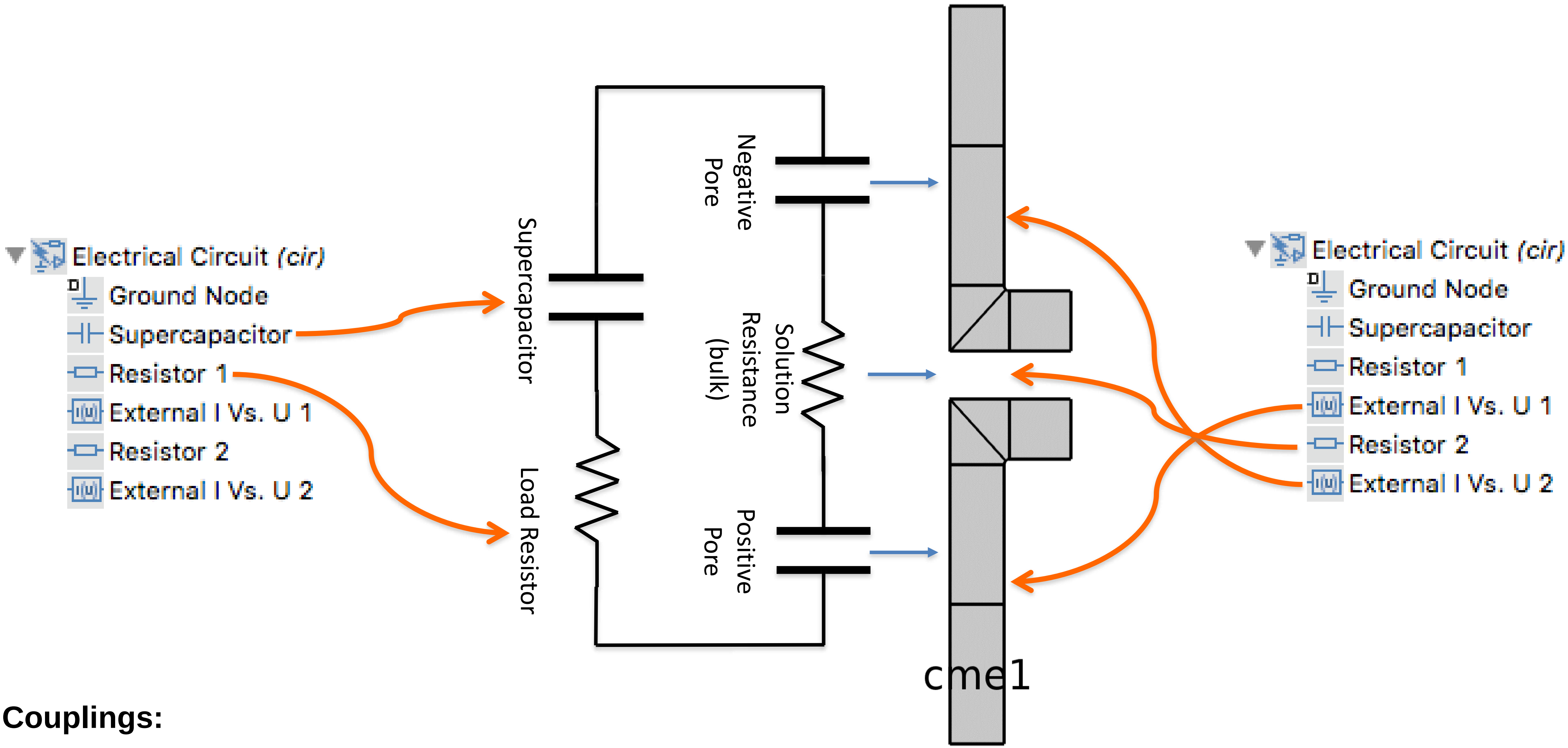
Fick’s second law with diffusion, flow convection and electromigration for the ionic concentrations.

Navier-Stokes equations for incompressible flow with an electric body force.

Kirchhoff’s laws for electrical circuit coupled at the boundaries of the computational domains.

There are several cross-couplings between these equations that have to be implemented in COMSOL Multiphysics.

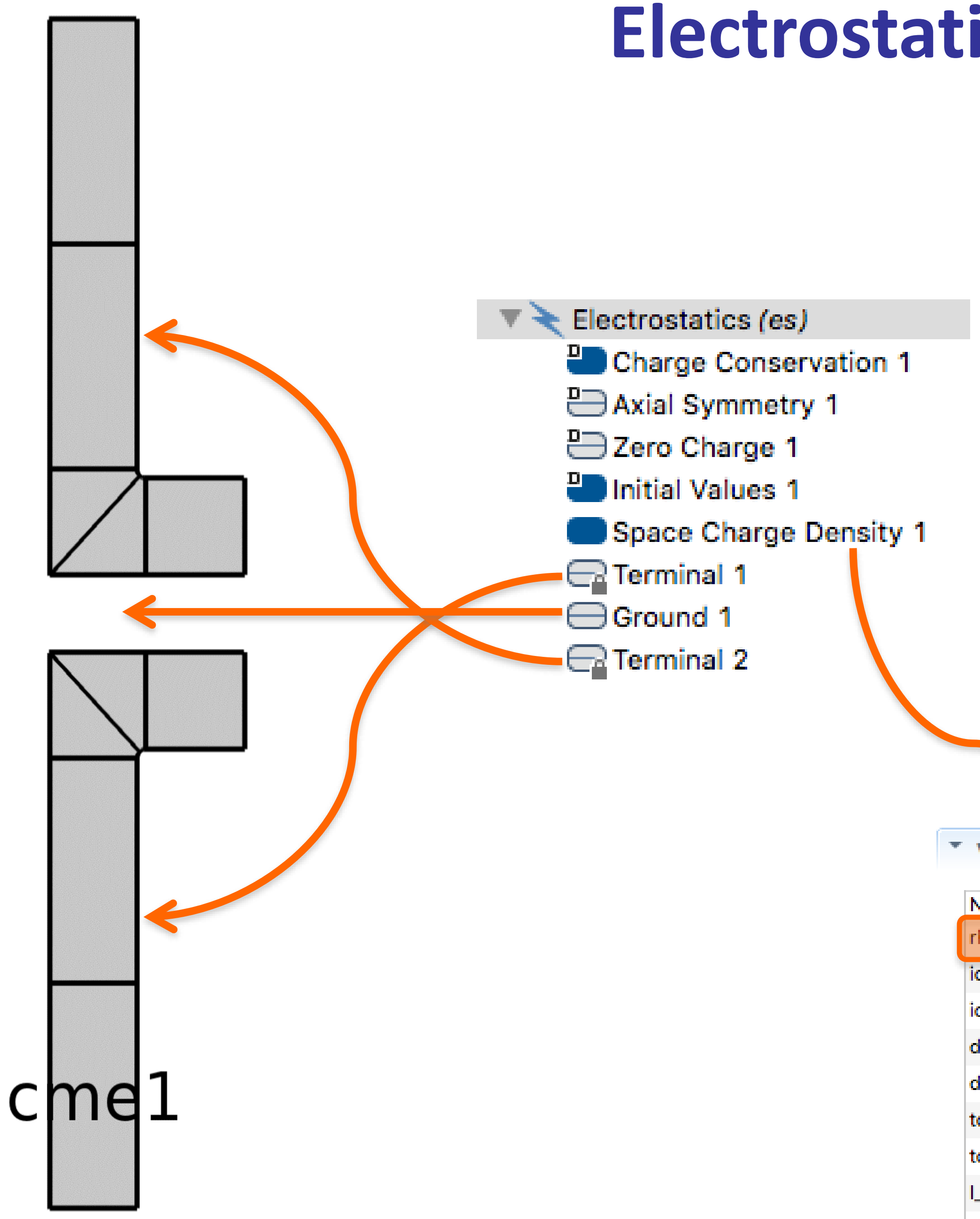
Electrical circuit



Couplings:

- External I Vs. U connected to Terminals in Electrostatic Interface.

Electrostatics



Modify the terminal equation:

- All the N_pores are paralell connected capacitors.

Weak Expressions

Weak expression	Integration frame	Selection
-es.term1.Q0_ode*test(es.term1.V0_ode)		Global
(es.term1.I_cir/N_poros-es.term1.Q0_odet)*test(es.term1.Q0_ode)		Global

Couplings:

- Space Charge Density from Transport of Dilute Species via Variable Definition (rhocharge).
- Terminals connected to Electrical Circuit Interface.

$$\rho_{charge} = (z_{Cl^-}c_{Cl^-} + z_{Na^+}c_{Na^+})eN_A$$

Variables

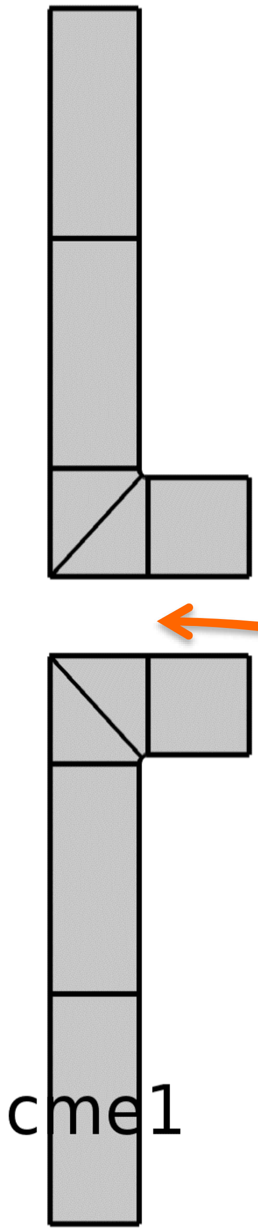
Name	Expression	Unit	Description
rhocharge	(c_Cl*val_Cl+c_Na*val_Na)*e_const*N_A_const	C/m³	Space charge density
ioncurrent_z	(chds.tflux_c_Clz*val_Cl+chds.tflux_c_Naz*val_Na)*e_const*N_A_const	A/m²	Ionic current density z
ioncurrent_r	(chds.tflux_c_Clr*val_Cl+chds.tflux_c_Nar*val_Na)*e_const*N_A_const	A/m²	Ionic current density r
despcurrent_z	epsilon0_const*78.55*d(es.Ez,t)	A/m²	Displacement current density z
despcurrent_r	epsilon0_const*78.55*d(es.Er,t)	A/m²	Displacement current density r
totalcurrent_z	ioncurrent_z+despcurrent_z	A/m²	Total current density z
totalcurrent_r	ioncurrent_r+despcurrent_r	A/m²	Total current density r
I_total_poro_pos	abs(intop1(totalcurrent_z*es.nz+totalcurrent_r*es.nr))	A	Total current positive pore
I_total_poro_neg	abs(intop2(totalcurrent_z*es.nz+totalcurrent_r*es.nr))	A	Total current negative pore

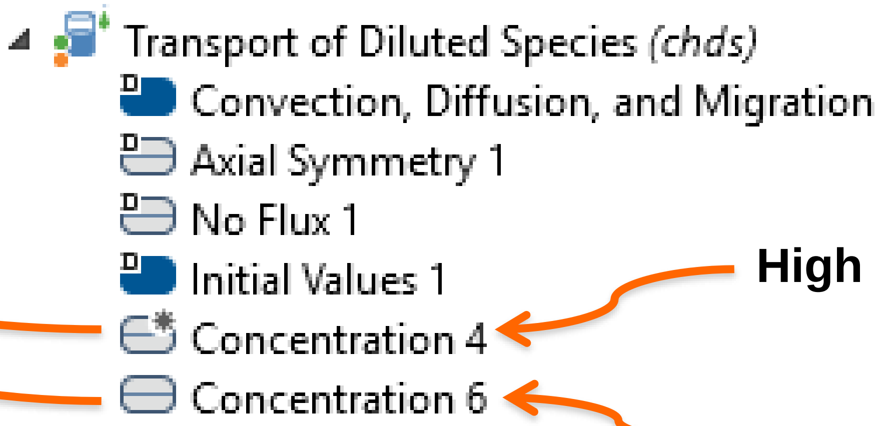
Transport of dilute species

We have two charged ionic species: Na^+ and Cl^-

Couplings:

- Convection from Laminar Flow Interface
- Migration in electric field from Electrostatic Interface



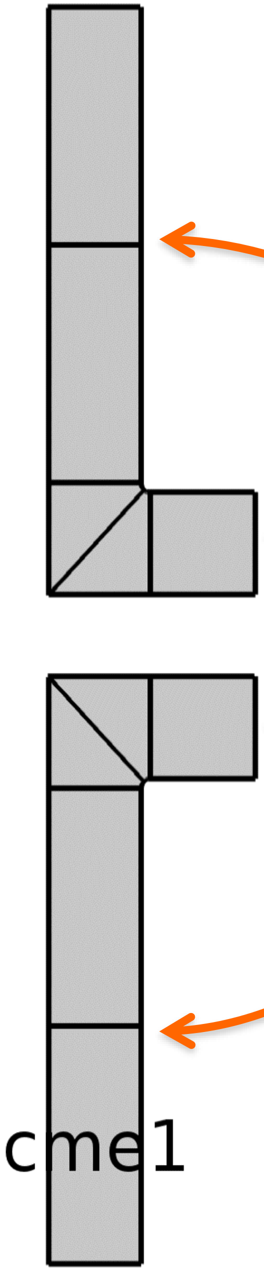


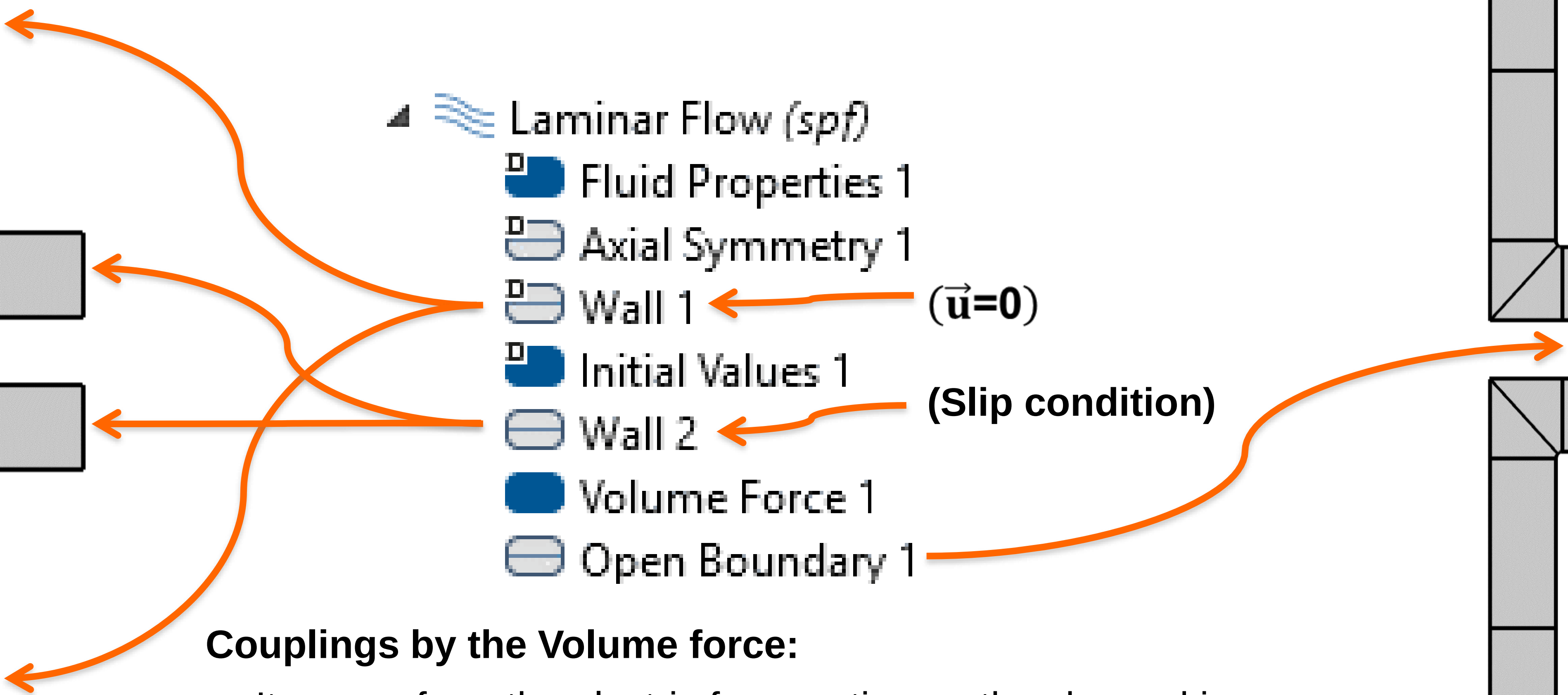
High concentration

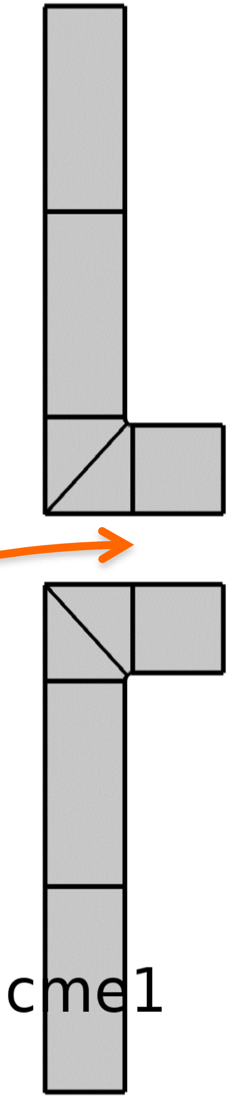
Low concentration

<u>No flux</u> boundary condition except concentration constraint at the bulk boundaries

Navier-Stokes equations





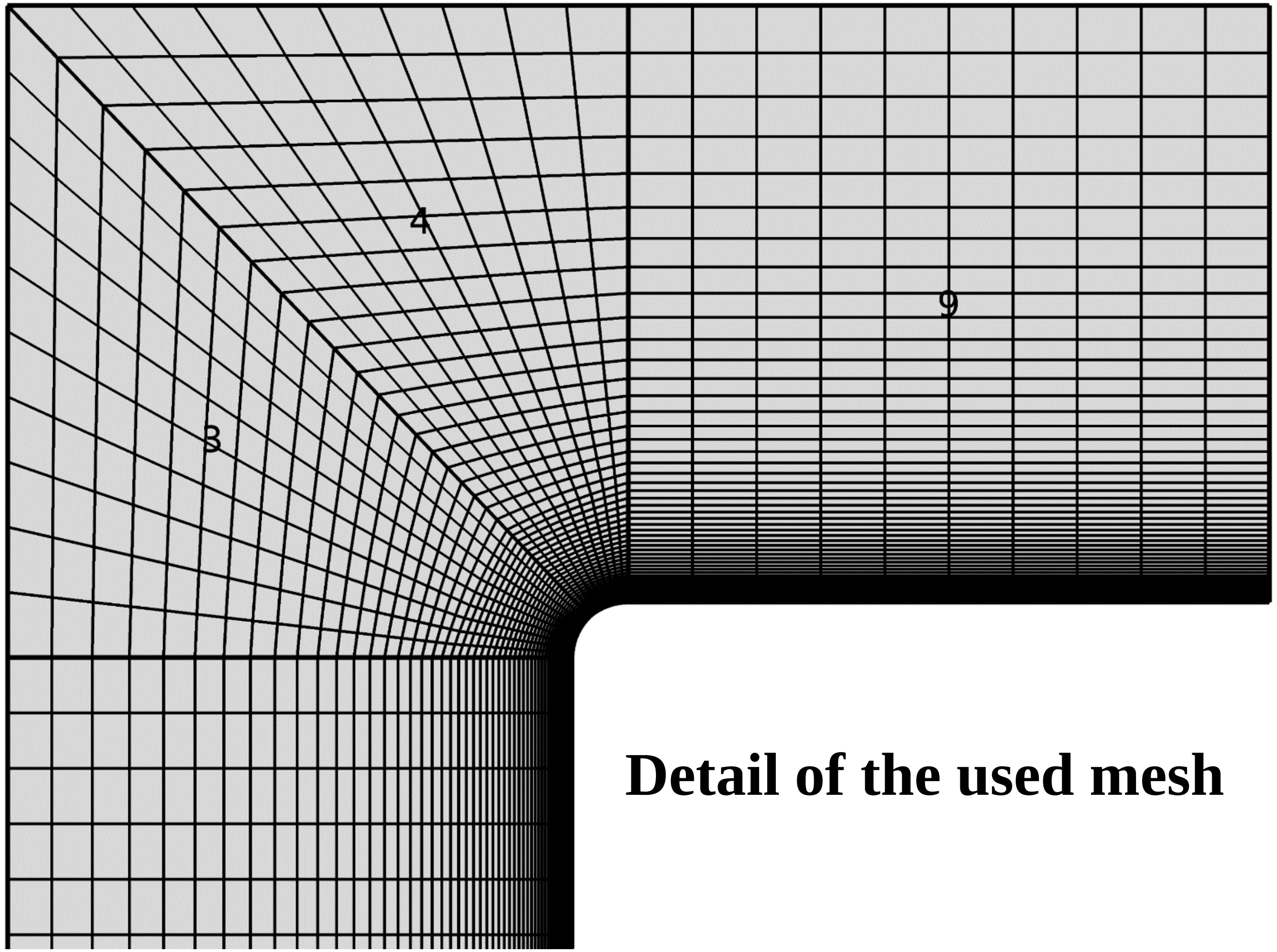


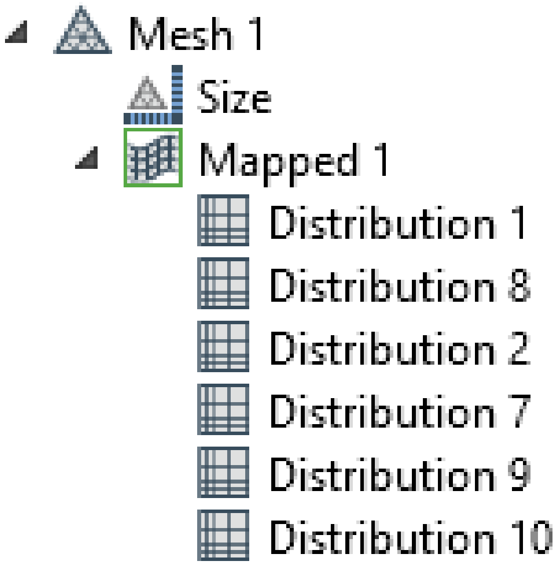
Couplings by the Volume force:

- It comes from the electric force acting on the charged ions that are present in the solution. $\vec{F} = -\rho_{charge}\vec{\nabla}V$
- Couples with the Transport of Dilute Species and the Electrostatics interfaces. $\rho_{charge} = (z_{Cl^-}c_{Cl^-} + z_{Na^+}c_{Na^+})eN_A$

Structured Mesh

Geometric sequence for distributions





Detail of the used mesh

Time dependent studies

- ✓ **First step: Charging of the nanopores at the higher ionic concentration.**

The supercapacitor has an initial charge, we have the highest ionic concentration inside the nanopores and they are connected with the external circuit reaching the initial voltaje difference.

- ✓ **Second step: Changing to the lower ionic concentration.**

We disconnent the circuit, the surface charge of the nanopores remains constant and the bulk concentration changes to the lower value. The electric potential rises and the EDL expands with time.

- **Third step: Discharging the nanopores at the lower ionic concentration.**

We connect again the external circuit, the nanopores and the voltage difference decreases to the initial value.

- **Fourth step: Changing to the higher ionic concentration.**

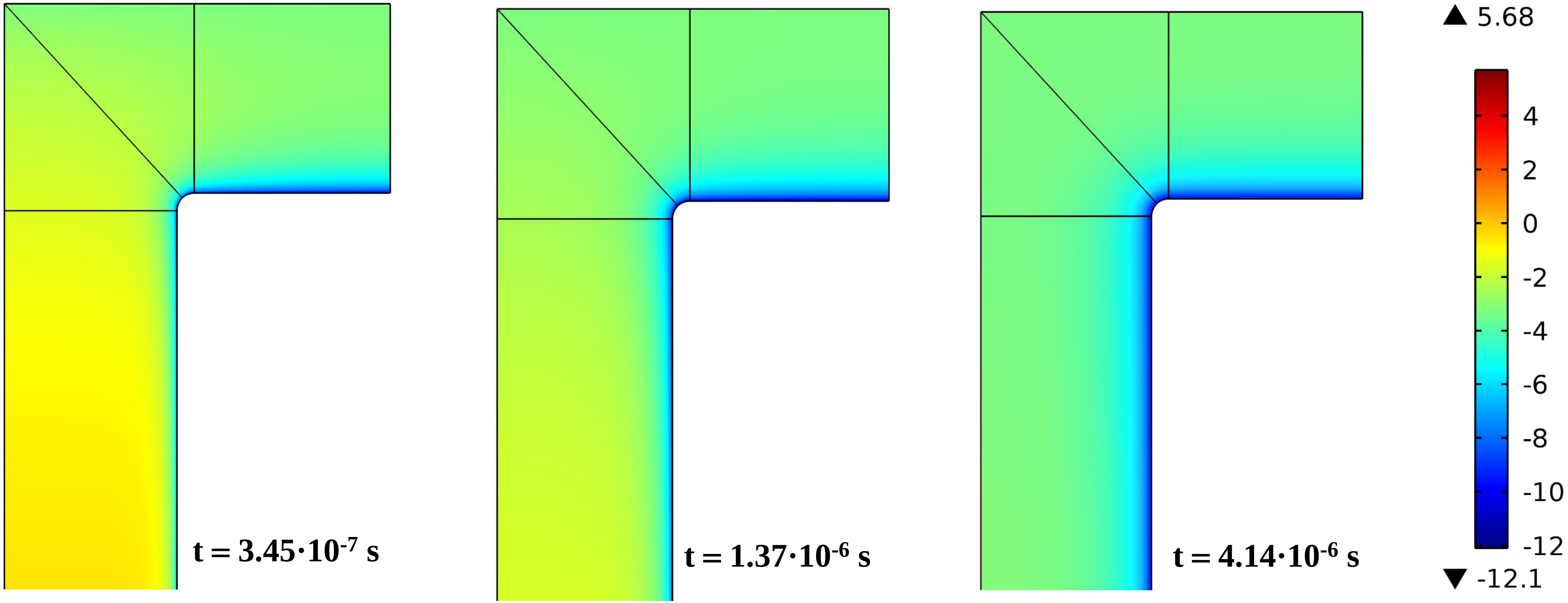
We disconnent the circuit, the surface charge of the nanopores remains constant and the bulk concentration changes to the higher value. The electric potential decreases and the EDL contracts.

➡ **Back to the first step.**

Results

Second step: Changing to the lower ionic concentration.

Time evolution of $\log(c_{Na^+}/c_{high})$ in the positive pore after entrance of low salt solution.

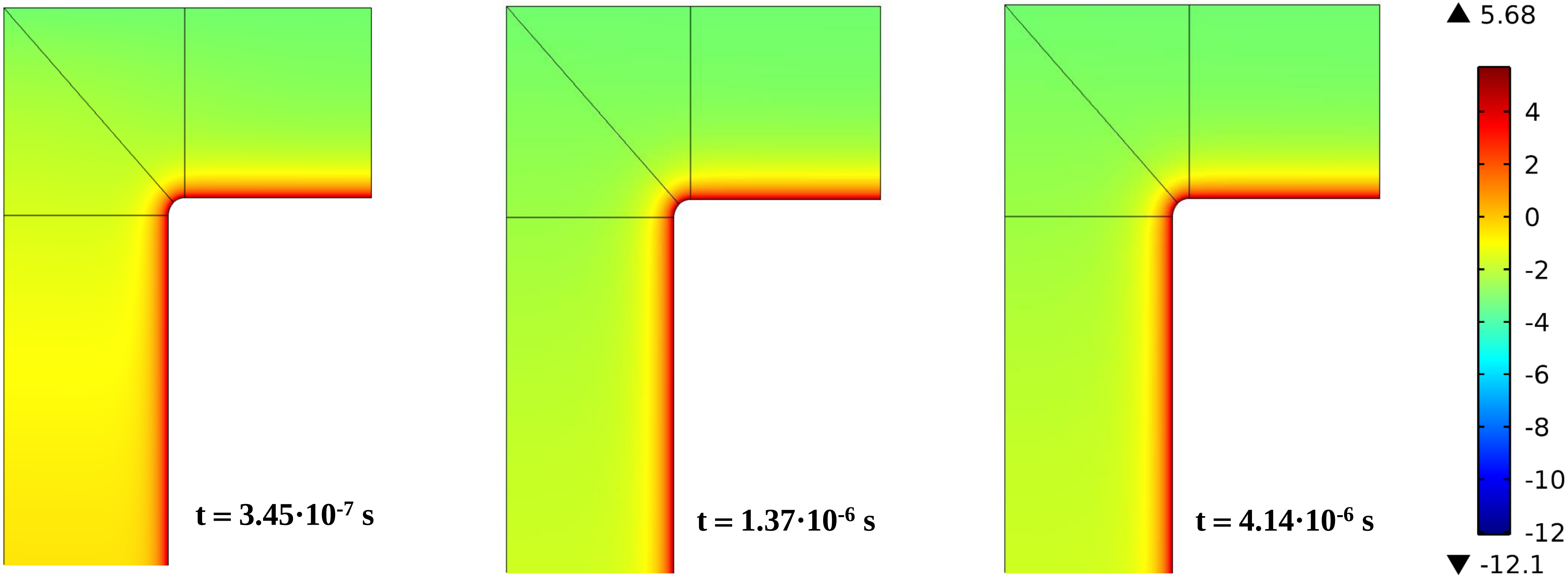


The expansion of the EDL has started in the region close to the mouth of the nanopore and ***it is extending*** towards its interior.

Results

Second step: Changing to the lower ionic concentration.

Time evolution of $\log(c_{Cl^-}/c_{high})$ in the positive pore after entrance of low salt solution.

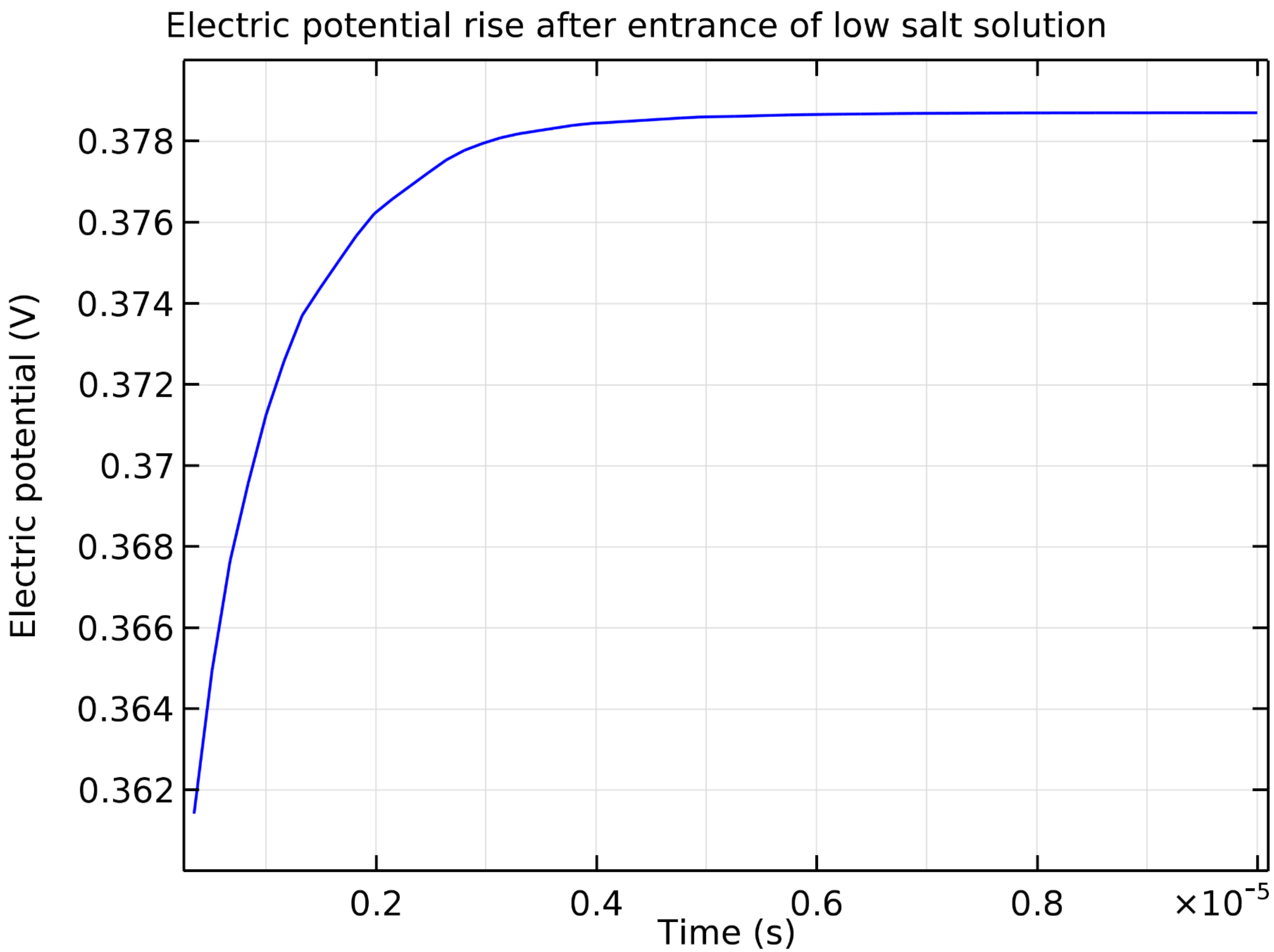


The expansion of the EDL has started in the region close to the mouth of the nanopore and ***it is extending*** towards its interior.

Results

Second step

- There is a rise of approx. 17 mV electric potential in each electrode after entrance of low salt solution.
- This result agrees well with the measured value, which is an increment of 40 mV in the whole experimental cell.



Summary and conclusions

- We have made dynamic simulations of the CDLE steps in the nanopores by using COMSOL Multiphysics. The software is able to solve the complex couplings that exist in the governing equations.
- From these simulations we can obtain important information that is not accessible experimentally, as the time dependence of the ionic distributions, for example.
- The initial numerical results obtained from the simulation of the first and second steps of the CDLE cycle agree well with the experiments.

Next steps

- Finish the complete CDLE cycle and validate the simulations with the experimental results of the energy/cycle extracted.
- Extend the calculations to deeper nanopores --> *Problem*: extremely high aspect ratio between pore radius and pore length. Any tip or trick?
- Recognize the relevant parameters and make an optimization process of the generated power in a cycle.

Some bibliography

① R. E. Pattle, *Nature* **174**, 660 (1954).

② D. Brogioli, *Phys. Rev. Lett*. **103**, 058501 (2009).

③ D. Brogioli *et al.*, *J. Coll. Int. Sci.* **407**, 457 (2013).

④ M.L. Jiménez *et al.*, *J. Coll. Int. Sci.* **402**, 340 (2013).

⑤ G. R. Iglesias *et al. Journal of Power Sources* **261**, 371 (2014).

⑥ M. Bijmans *et al.*, *Energy Procedia* **20**, 108 (2012).

Acknowledgements

❑ Financial supports for this work by MICINN, Spain (projects FIS2010- 18972, FIS2013-47666-C3-1R, 2R, 3R) and Junta de Andalucía, Spain (project P2012-FQM-694), co-financed with FEDER (European Fund for Regional Development) funds by the EU, are gratefully acknowledged.

Thank you very much for your attention!

UNIVERSIDAD DE MÁLAGA