

Introduction

Reverse electro dialysis (RED) generates electric power by direct conversion of the chemical potential difference of two saline solutions (salinity gradient power). A RED stack is fed by the two solutions in alternated channels, separated by anion and cation exchange membranes. An electric potential difference, due to the chemical potential difference, is established over each membrane, along with an "oriented" flux of cations and anions from each concentrate channel towards the two adjoining dilute ones. Ionic flux is converted into electric current by means of reversible redox reactions at the electrodic compartments (Figure 1).

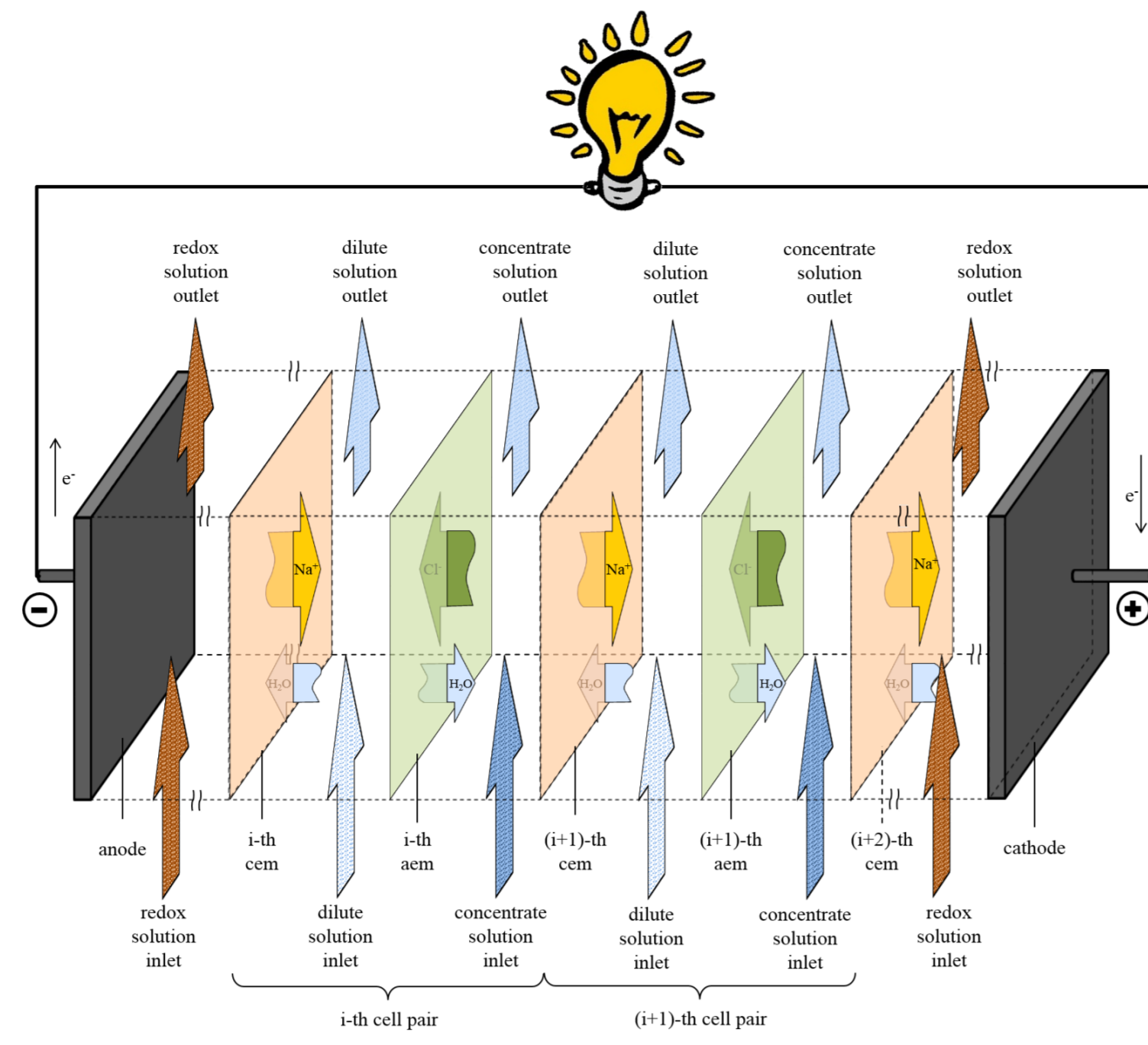
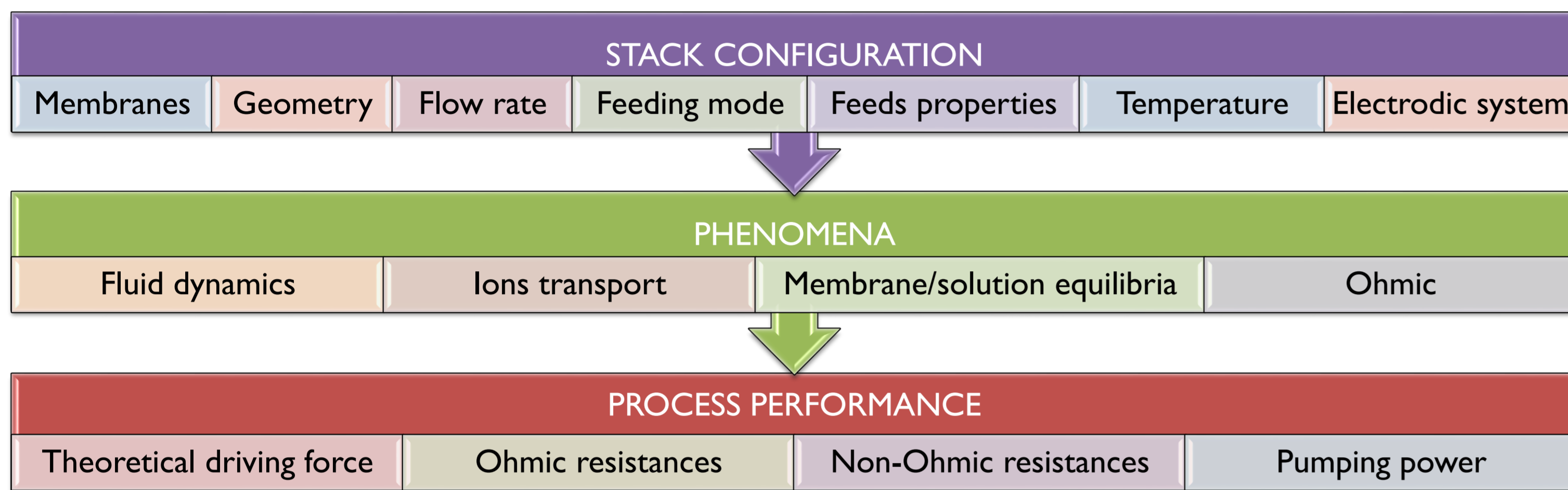


Figure 1. Reverse electro dialysis stack.

Various factors, identifying the stack configuration, affect in a complex way a number of phenomena that interact at various scales and affect the power output and the energy efficiency.



Aim of the work

Developing a multi-physics modelling tool for the Reverse ElectroDialysis process, being able to describe the main phenomena involved and evaluate the process performance.

Modelling

Computational domain

The model was developed in COMSOL Multiphysics®. A single 2D cell pair is simulated as periodic unit of the stack (Figure 2). The discretisation was done by multi-block quadrilateral grids with finer discretisation near the walls. A preliminary grid dependence analysis was performed and a 12,200 nodes-per-cell grid was adopted in the end, corresponding to 37 and 24 divisions for channels and membranes thickness, respectively.

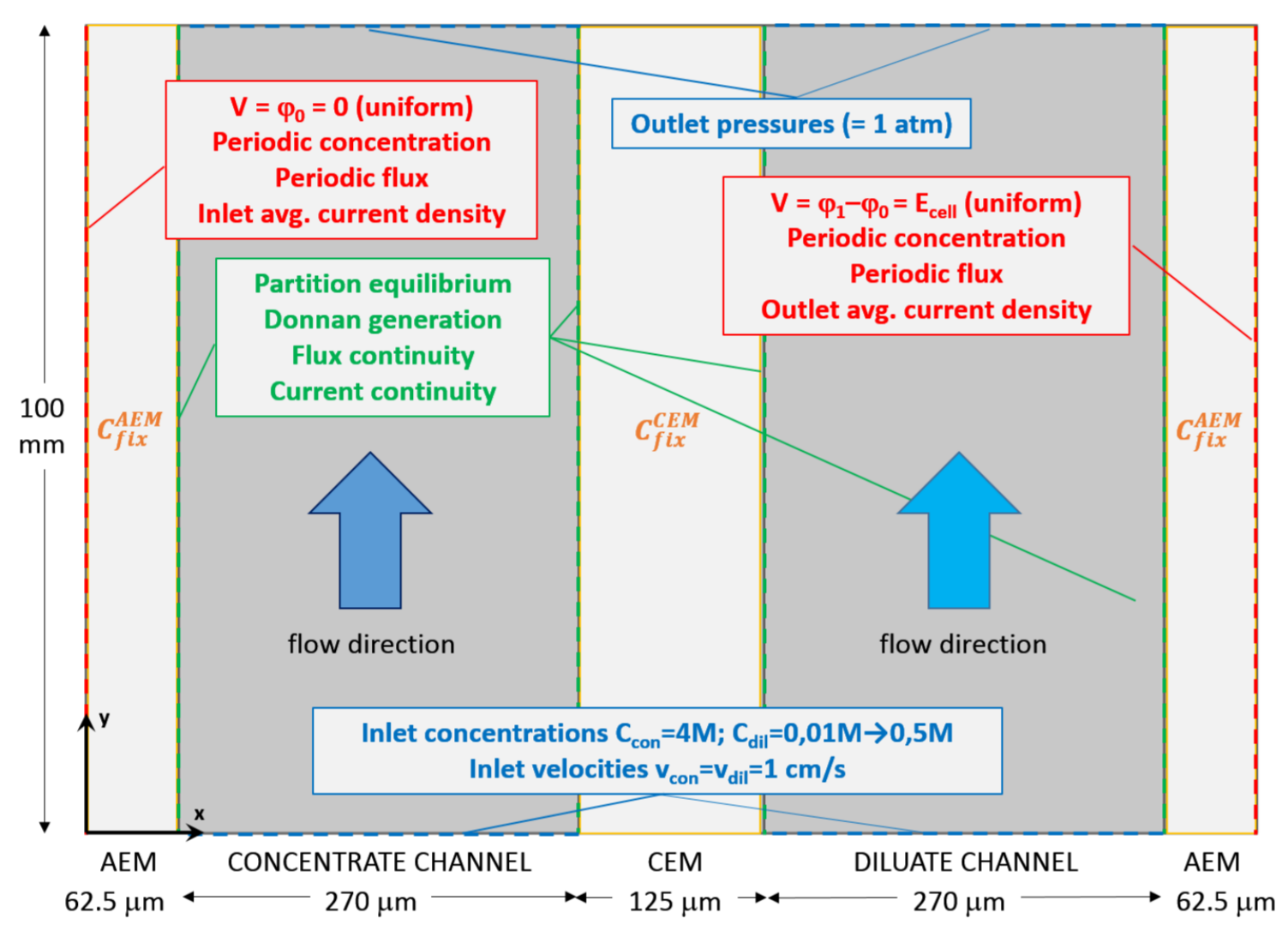


Figure 2. Schematics of a cell pair domain, equations at the interfaces & boundary conditions.

Equations system

Mass balance	$\vec{\nabla} \cdot \vec{N}_i = 0$
Current balance	$\vec{\nabla} \cdot \vec{j} = 0$
Electroneutrality	$\sum_i z_i C_i = 0$
Mass flux (Nernst-Planck eq.)	$\vec{N}_i = -D_i \vec{\nabla} C_i - z_i u_{m,i} F C_i \vec{\nabla} \phi + \vec{v} C_i$
Electric current	$\vec{j} = F \sum_i z_i (-D_i \vec{\nabla} C_i - z_i u_{m,i} F C_i \vec{\nabla} \phi)$
Continuity*	$\rho \vec{\nabla} \cdot \vec{v} = 0$
Momentum*	$\rho (\vec{v} \cdot \vec{\nabla}) \vec{v} = \vec{\nabla} \cdot [-p + \mu (\vec{\nabla} \vec{v} + (\vec{\nabla} \vec{v})^T)]$

* solved in the fluid domains only

The system is completed by the algebraic equations for the cell pair potential, the average current density module, the stack potential and the power density (Figure 3):

Cell pair potential	$E_{cp} = \phi_1 - \phi_0$	with $\phi_0 \neq f(y) \neq \phi_1$
Avg. current density	$\bar{j}_{cell} = (NE_{cp}) / [A(R_{blank} + R_{ext})]$	
Stack potential	$E_{stack} = NE_{cp} - A \bar{j}_{cell} R_{blank}$	
Power density	$P_d = E_{stack} \bar{j}_{cell} / N$	

Boundary conditions

The boundary conditions are reported in Figure 2. Periodic conditions for concentrations and fluxes were imposed at the terminal boundaries, while continuity of mass fluxes and electric current was imposed at each solution-membrane interface. Finally, the average computed current density was imposed at the terminal boundaries, assuming constant potential along them (this is supported by many other multi-cells simulations).

Donnan potential generation

The voltage generation at the membrane-solution interfaces was calculated by the Donnan exclusion theory (assuming unitary activity coefficients):

$$\phi_{Don} = \phi_m - \phi_s \cong \frac{RT}{z_i F} \ln \frac{C_i^s}{C_i^m}$$

Interface sorption equilibrium

Partition coefficients were adopted to relate the membrane-side co-ions concentration to the solution-side one:

$$\frac{C_{coi}^m}{C_{coi}^s} = K_{eq} = \frac{1}{2} \sqrt{C_{fix}^2 + 4C_{coi} C_{cou} - C_{fix}}$$

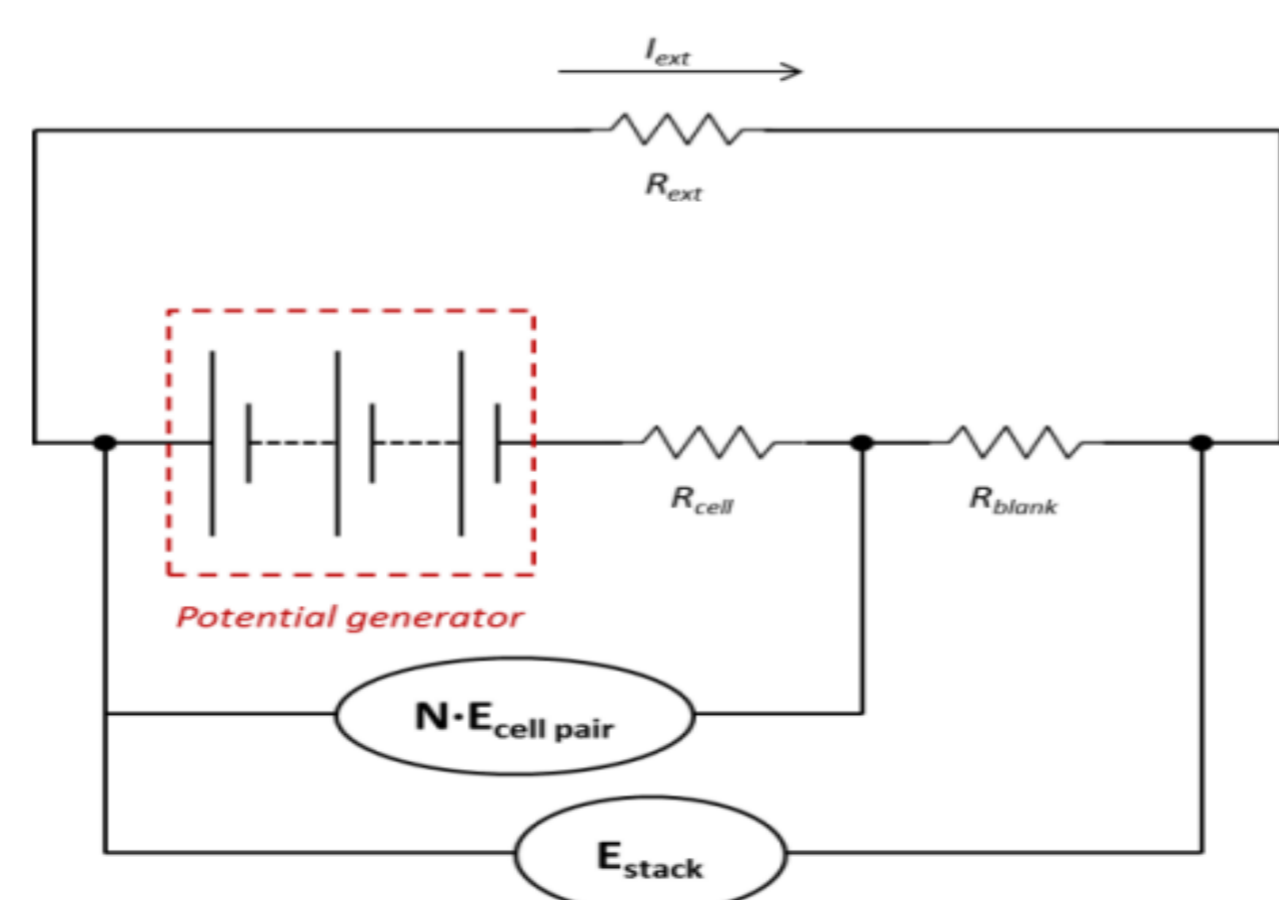
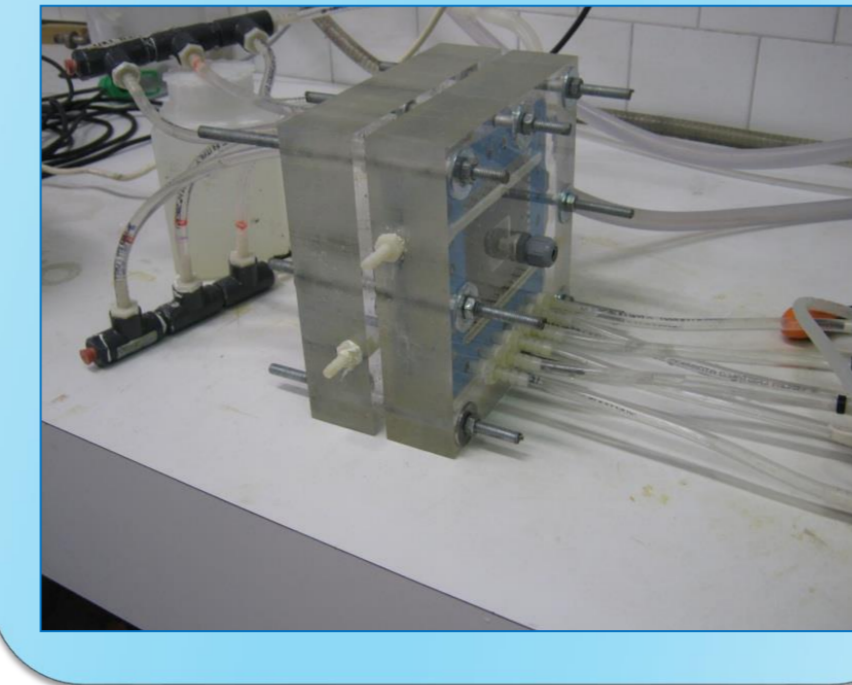


Figure 3. Equivalent electric circuit.

Model calibration and validation

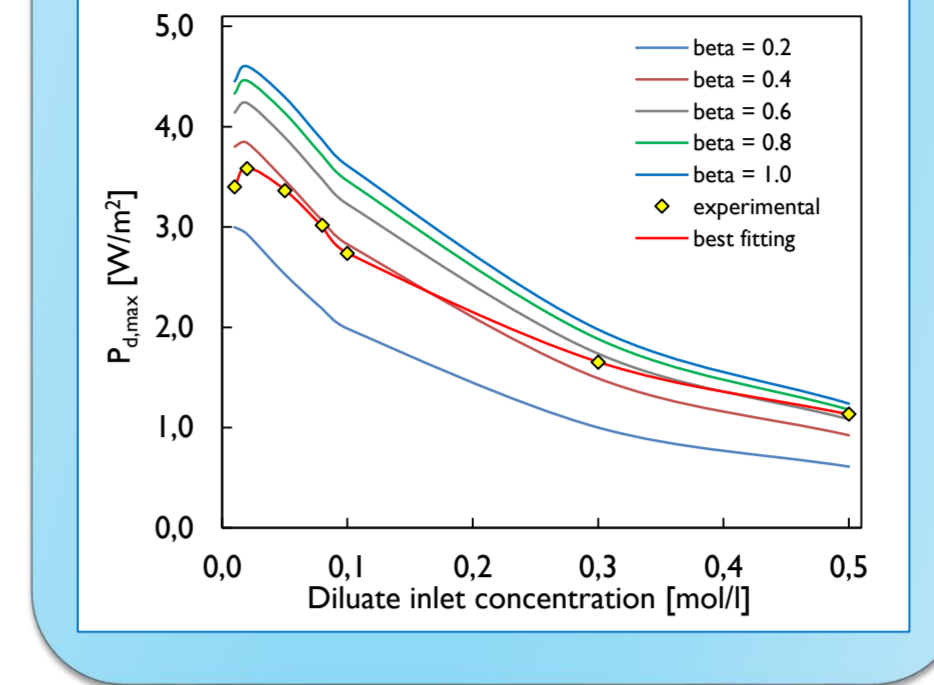
Experimental data measurement:

- Lab stack 10x10 cm²
- Fujifilm membranes
- Pure NaCl solutions

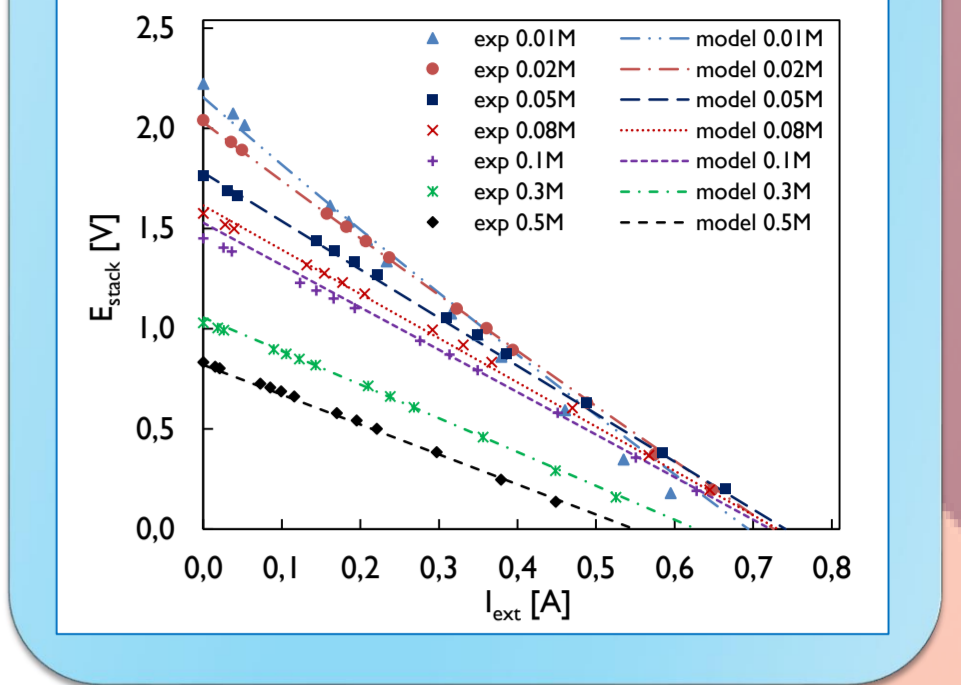


Tuning of two parameters characterizing membranes:

- Ions diffusion coefficient, D_i
- Ions mass mobility, $u_{m,i}$ (...by a β factor)



Validation exploring a wide range of dilute inlet concentrations and plotting electrical variables (e.g. V-I and P_d-I diagrams)



Assumptions and constant parameters

- Pure NaCl solutions
- Linear velocity = 1 cm/s
- Temperature = 20 °C
- Concentrate concentration = 4 M
- $C_{fix,aem} = 1.28 \text{ meq/g}_{dry}$; $C_{fix,cem} = 1.45 \text{ meq/g}_{dry}$
- Number of cell pairs = 10
- Blank resistance = 0.94 Ω

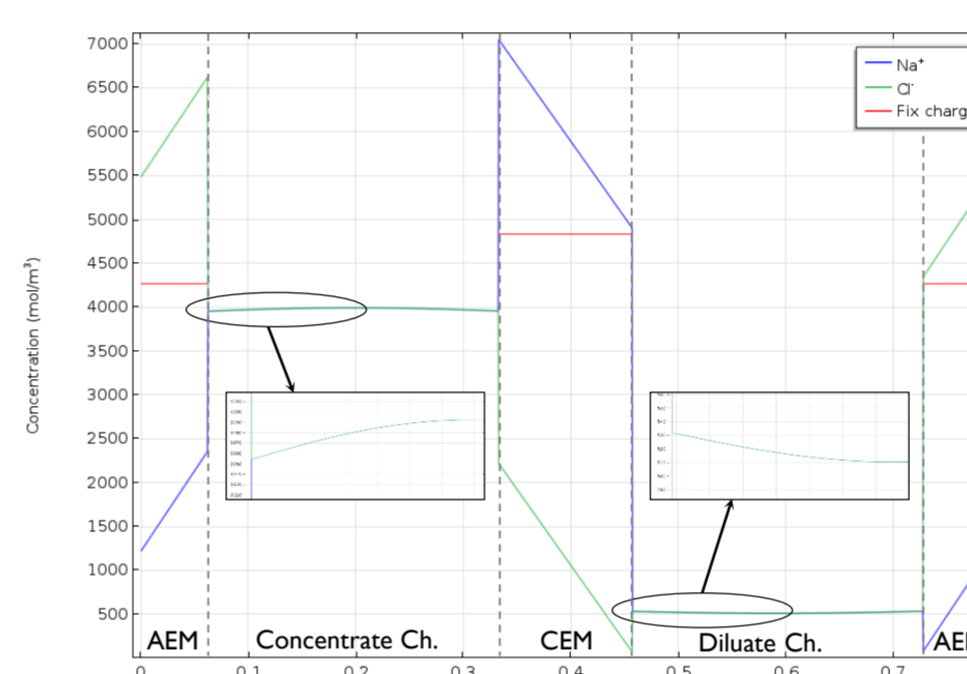
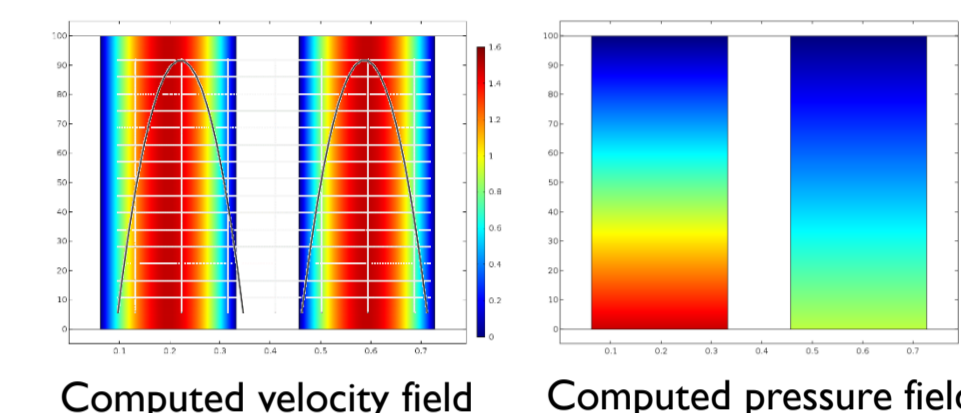
Cases investigated

- Dilute concentration: 0.5 M – 0.01 M
- Channel filling (Figure 4):
 - Empty channels
 - Insulating squared cross-section filaments spacers
 - Insulating round cross-section filaments spacers
 - Profiled membranes

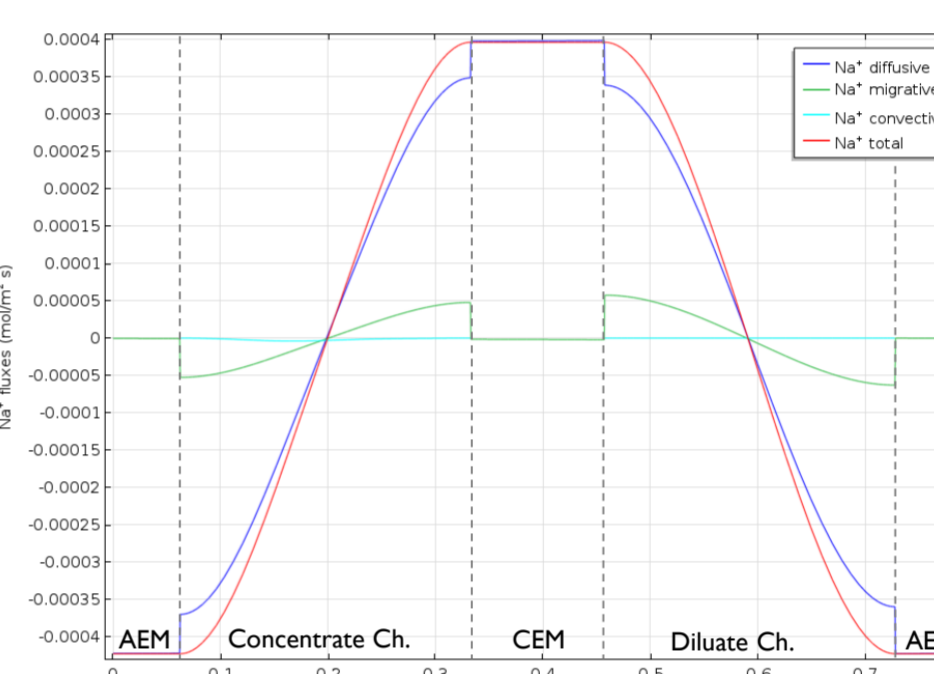
Results and discussion

Phenomenological description of the RED process

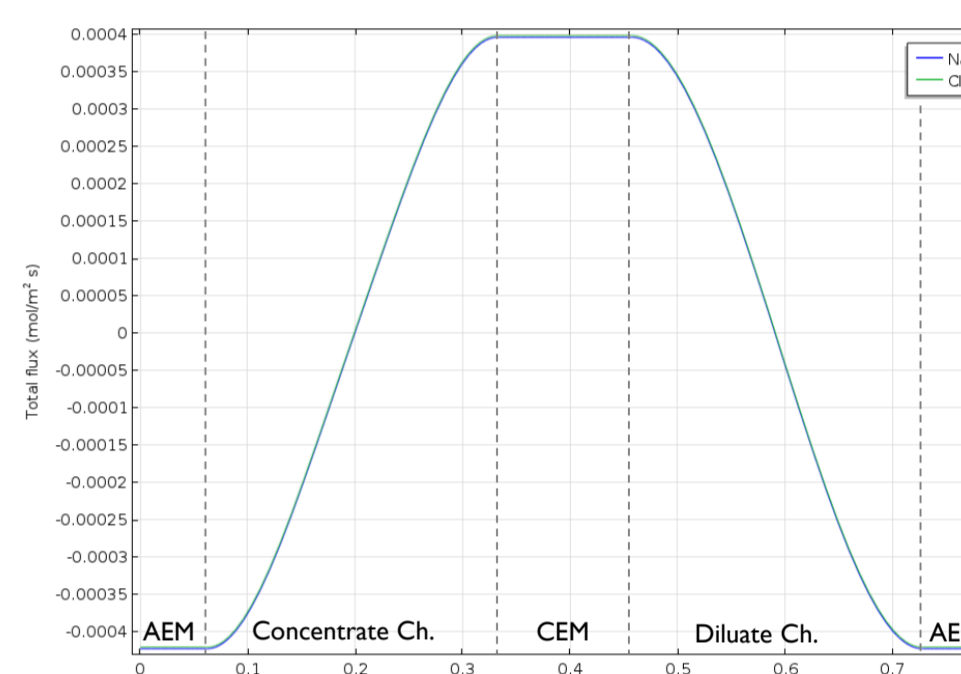
The governing phenomena were accurately predicted, as confirmed by the fields of the main computed quantities. Some examples (computed with the single-cell approach) are reported here, related to the case of a 10-cells empty-channels stack, fed with 4M–0.5M NaCl solutions.



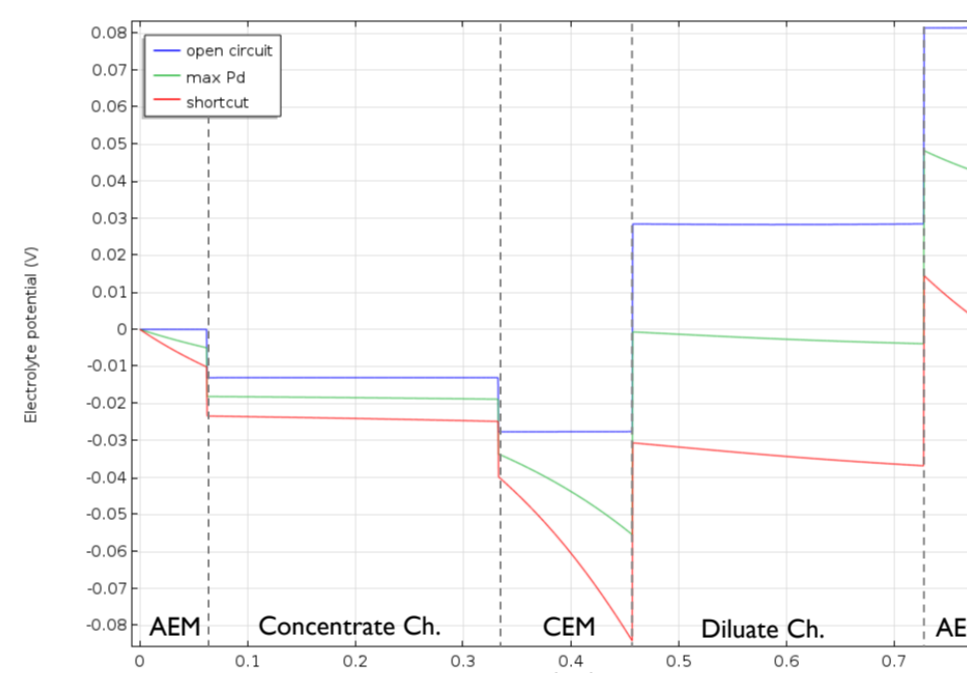
Concentration profiles, with polarisation phenomena in open circuit (O.C.) conditions



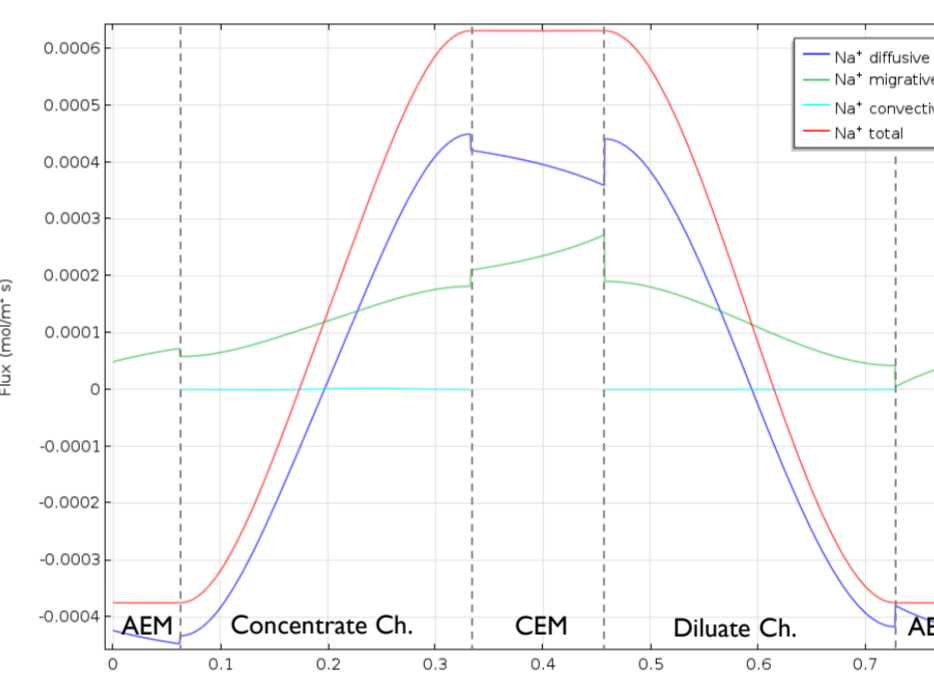
Computed Na⁺ fluxes (diffusive, migrative, convective and total) in O.C. conditions



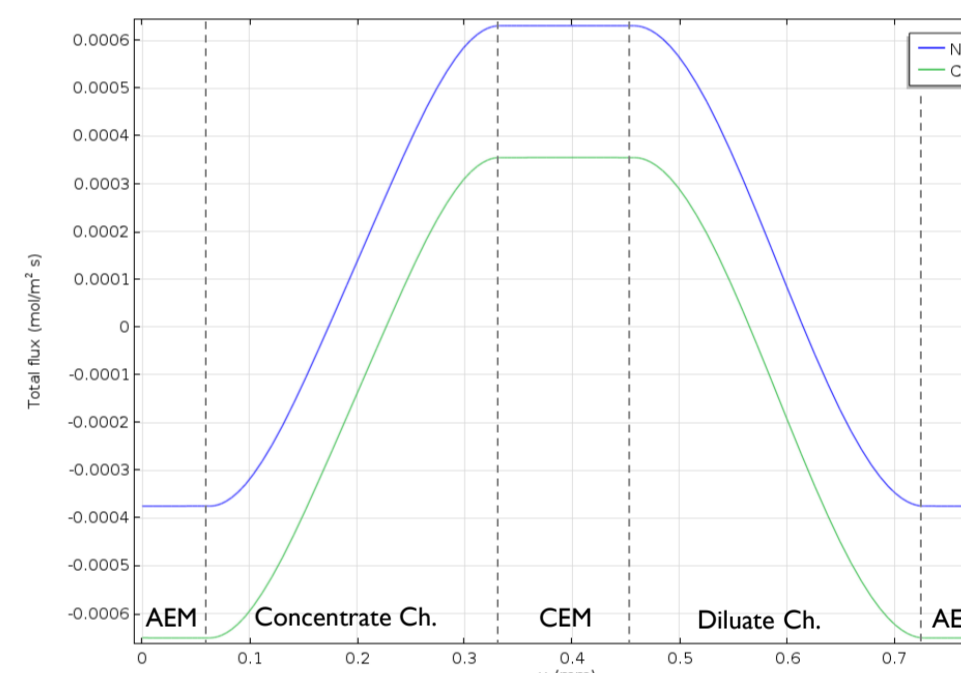
Computed Na⁺ and Cl⁻ total fluxes in condition of maximum power density.



Computed potential profiles in condition of open circuit, maximum Pd and shortcircuit (blank resistance neglected).



Computed Na⁺ fluxes (diffusive, migrative, convective and total) in condition of maximum power density.

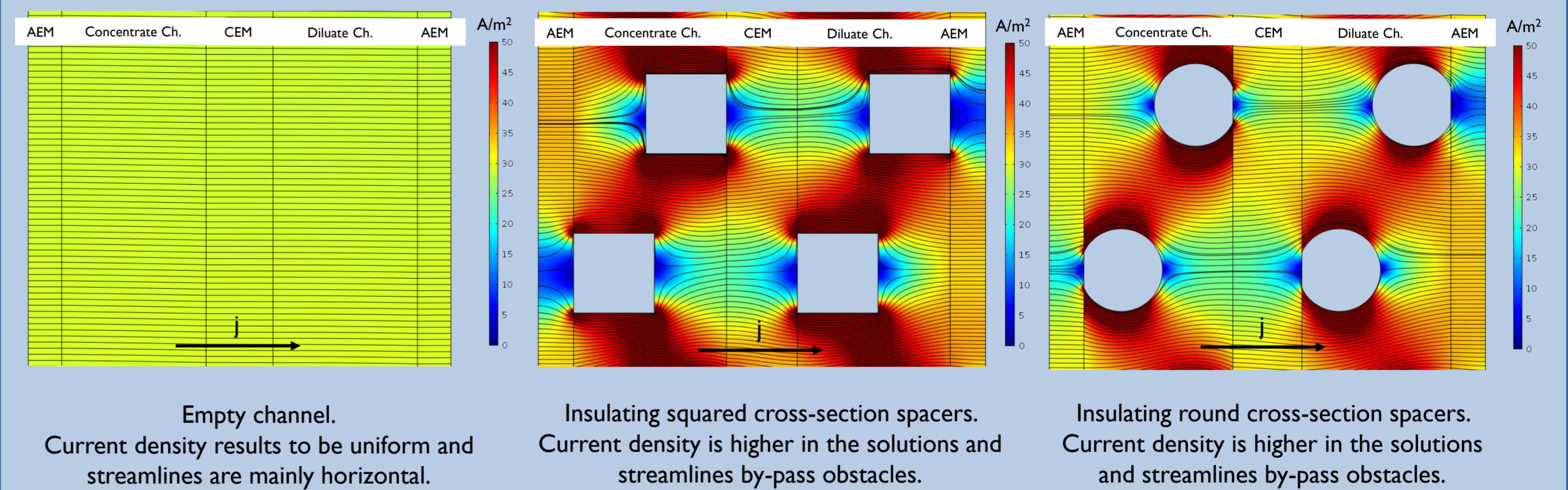


Computed Na⁺ and Cl⁻ total fluxes in condition of maximum power density.

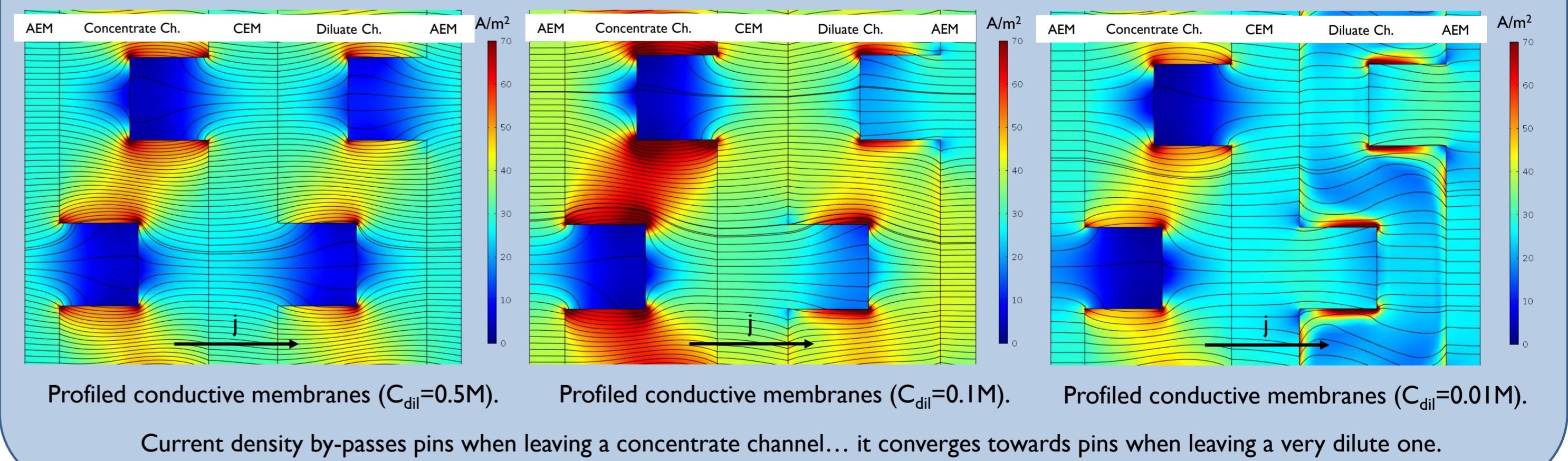
Effect of spacers and dilute concentration

RED stacks equipped either with standard non-conductive spacers or with profiled membranes are compared. In this part of the study, the channel length was reduced to 1.2 mm and the number of grid nodes increased to about 30,000 per cell. This allowed to efficiently compare the four scenarios.

Current density surface plots and streamlines (0.5M-4M, max Pd conditions)



What happens when changing dilute concentration in profiled membranes?



Conclusions and future remarks

A multi-physics model for the RED process was developed as a powerful tool for the thorough characterisation of the complex process phenomenology and for the prediction of the stack performance. The behaviour of different spacers and profiled membranes was analysed and compared, highlighting advantages and limitations of each case.

Future developments: (i) 3D simulations for accurate predictions with complex spacers/channels geometry; (ii) structural mechanics analysis to simulate membranes bending and channel geometry deformation; (iii) implementation of an all-embracing model for the process design and optimisation.