15.10.14

FEM modeling of capacitive deionization for complex streams

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International Conference on Numerical and Mathematical Modeling of Flow and Transport in Porous Media

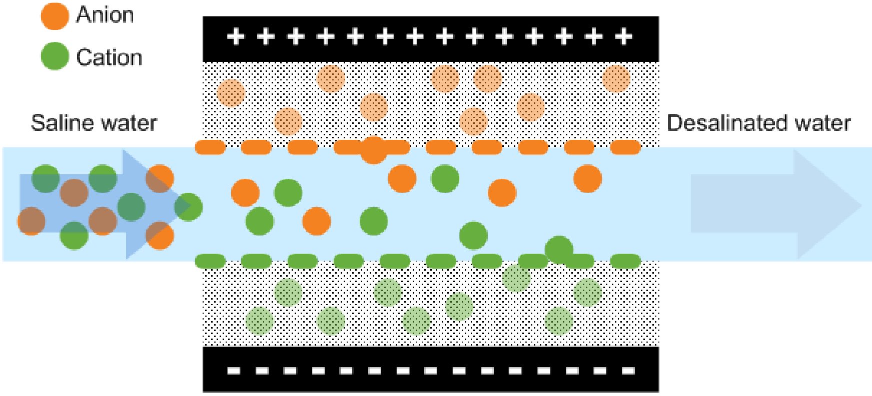
Dubrovnik, Croatia, 29 September - 3 October, 2014

UNIVERSITEIT GENT

FACULTY OF **BIOSCIENCE ENGINEERING**

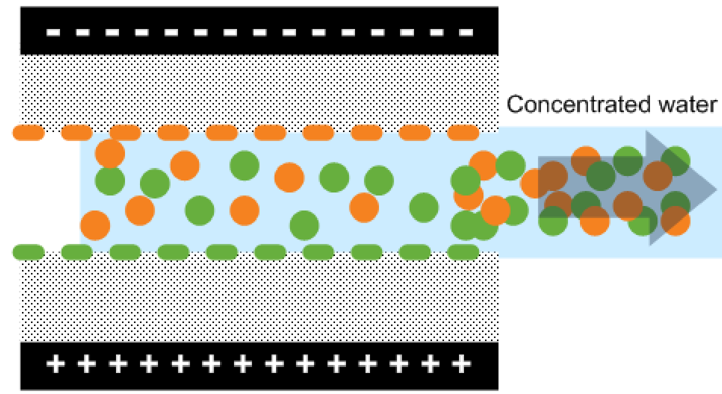
Outline

Purification



Electro-sorption of counter ions on porous electrodes

Regeneration



Voltage reversal for desorption of ions from electrodes

Advantages

Low energy usage

High recovery

No regeneration chemicals

Reversible (long lifetime)/ Low fouling

Disadvantages

Only for low salt concentration streams?

CAPEX (20-30% > RO)

Scaling, oxidation of electrode surface

Current sweet spot

- Low TDS applications
- Complex streams

Established models

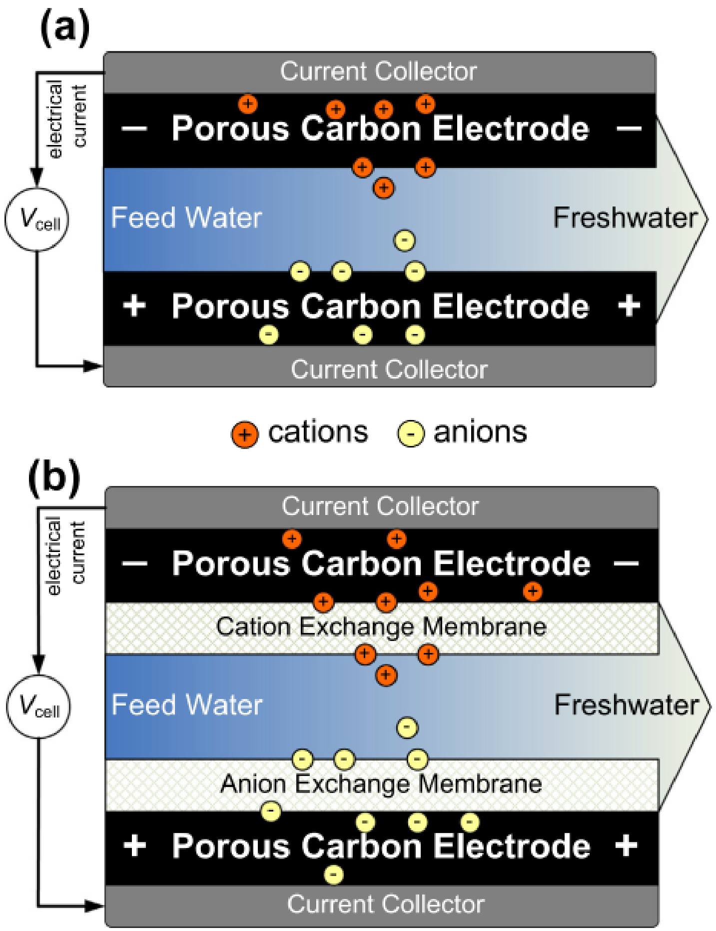
- Low concentrations, equilibrium
- Mostly binary electrolytes

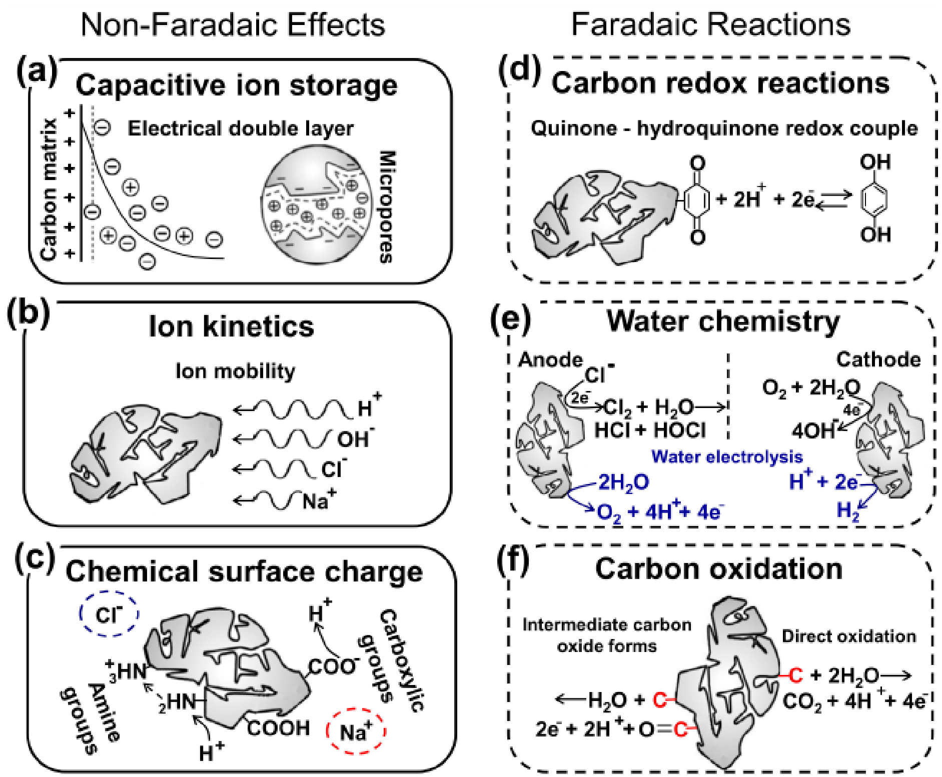
Optimization challenges

- Improving desal rate
- Selective removal of components from complex streams

Modeling challenges

- Dynamic models
- Multi-ionic models





Porada et al.
Prog Mater Sci 2013;58

FEM model → **Operational & design optimization**

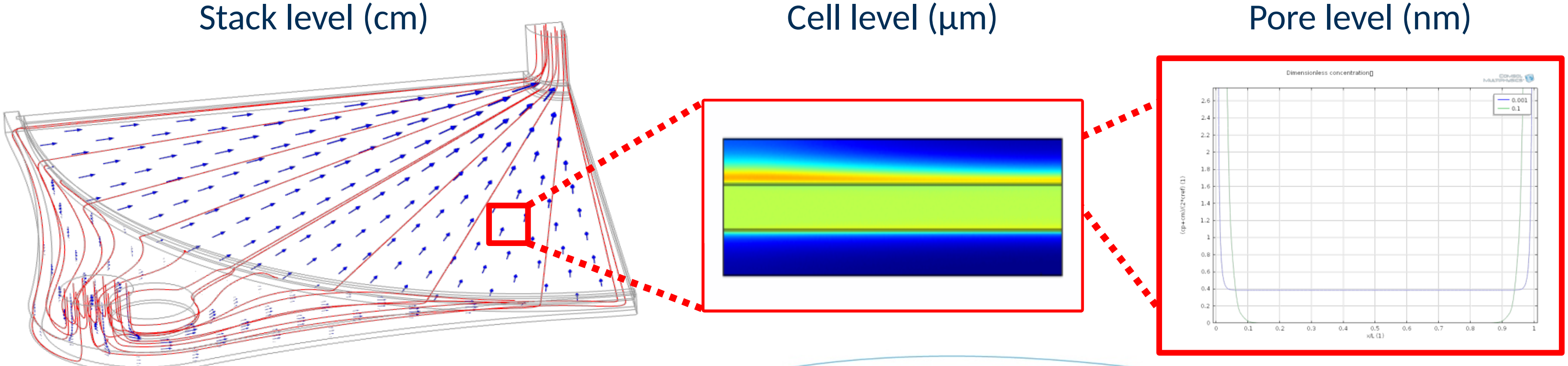
FEM model:

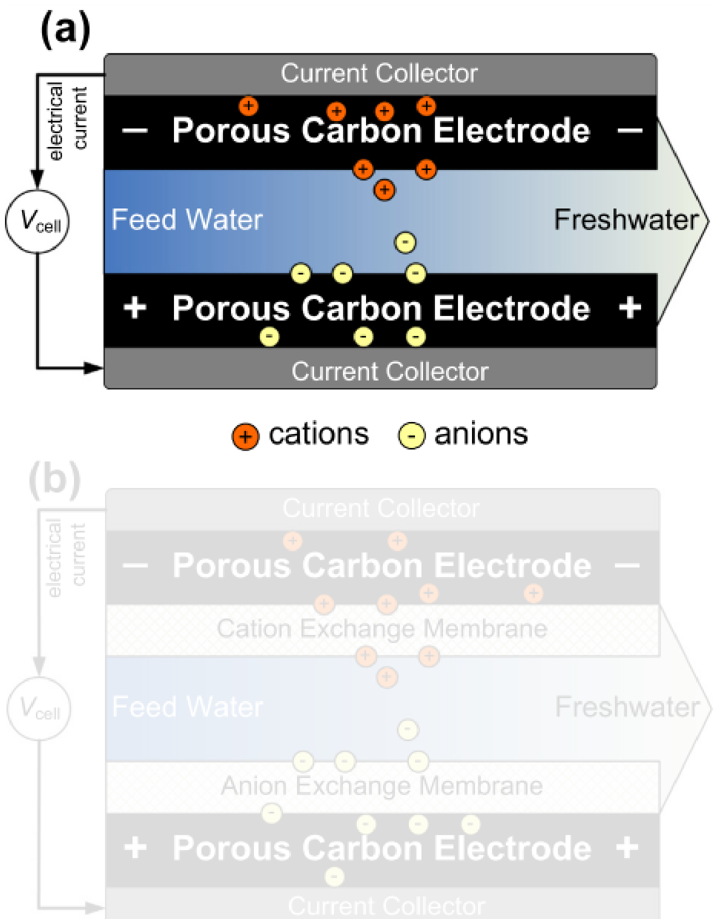
- momentum and mass transport in spacer channel
- mass transport through membrane
- mass transport in porous medium
  - ion storage in EDL
- chemical equilibria
- faradaic reactions

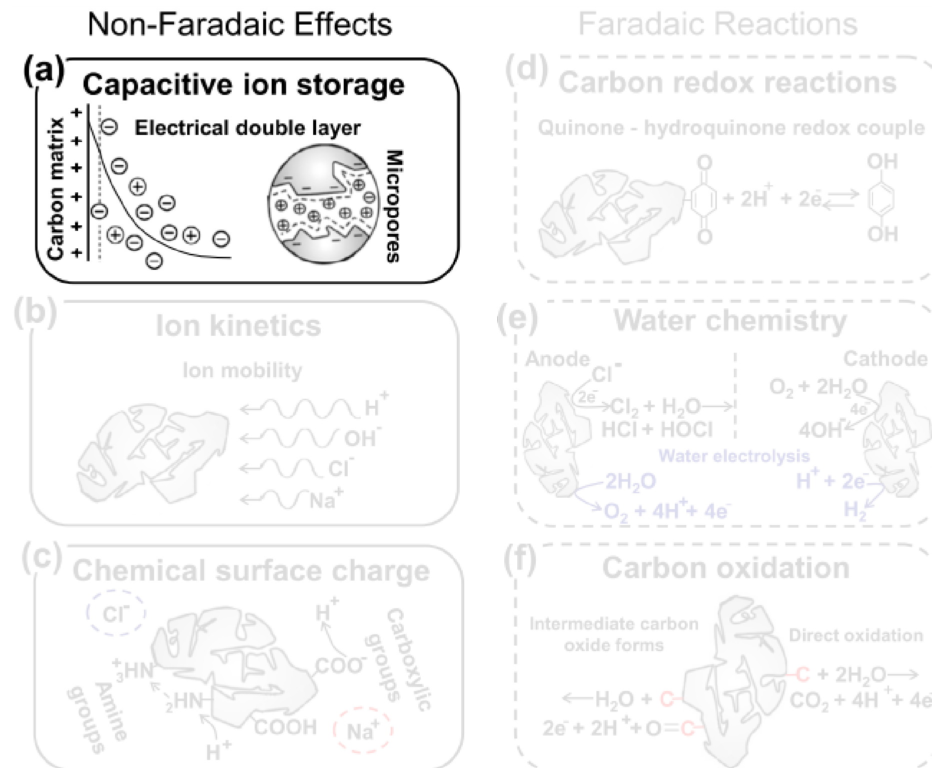
Operational & design optimization:

- operational modes
- operational parameters
- electrode and membrane materials
- stack and cell geometries

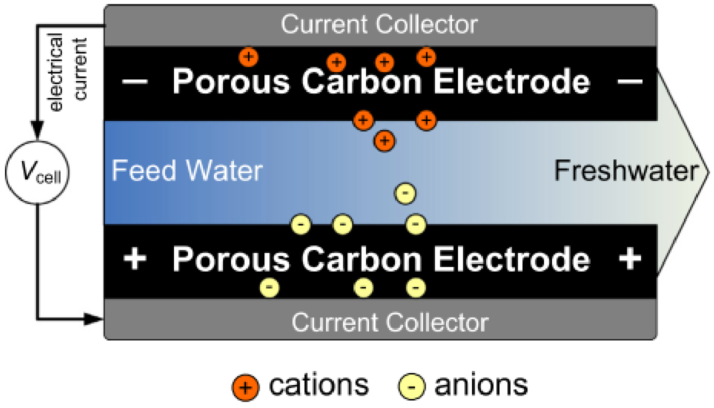
Stack level (cm) | Cell level (µm) | Pore level (nm)

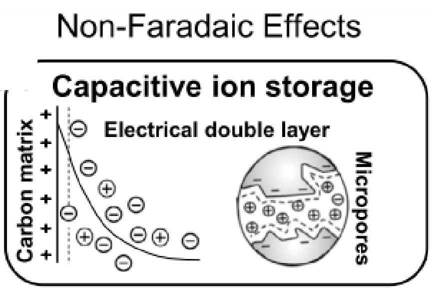






Porada et al.
Prog Mater Sci 2013;58





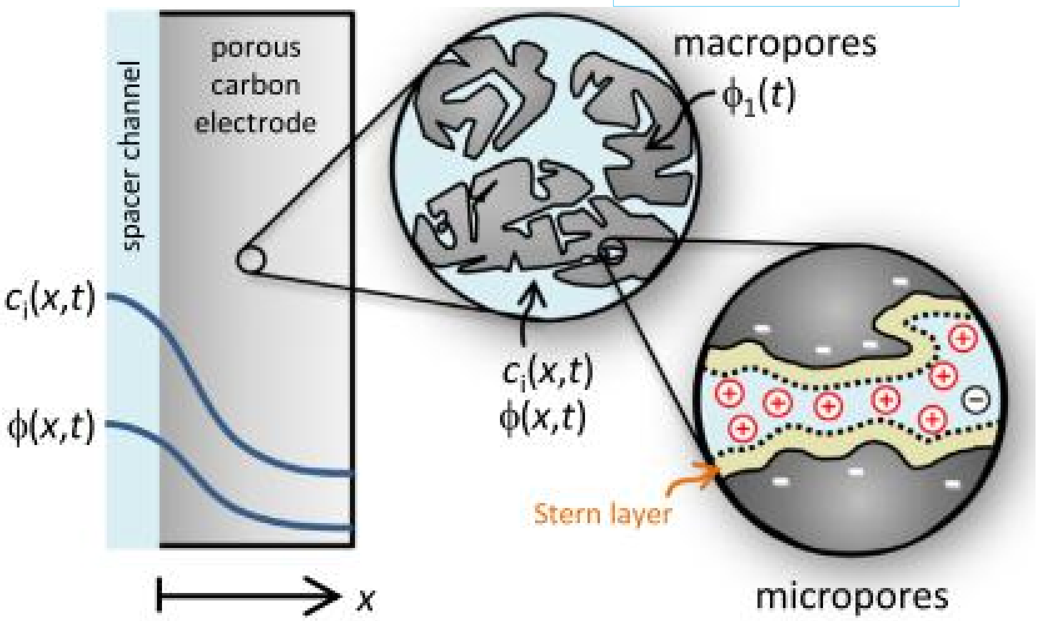
- Momentum transport in spacer channel
- Mass transport (diffusion and electro-migration) in
  - Spacer channel
  - Charged porous medium

Porada et al.
Prog Mater Sci 2013;58

- **Multi-scale**
  - Activated carbon powder electrodes

'Macro' scale

Interparticle scale



Intraparticle scale

Porada et al.
Prog Mater Sci 2013;58

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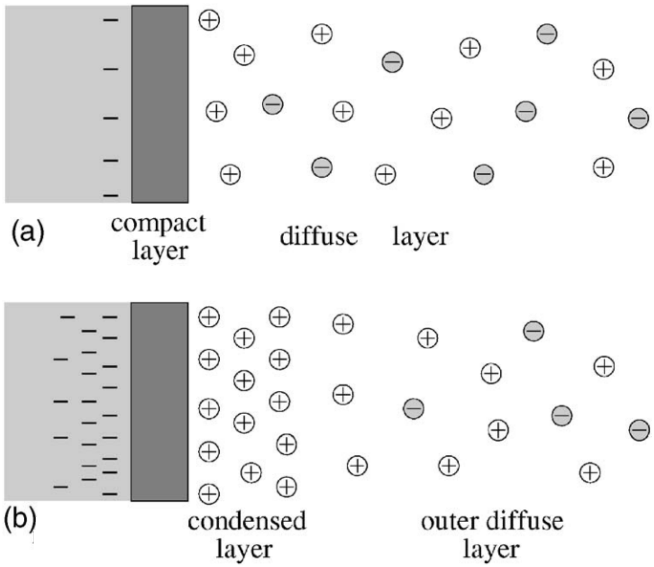
Non-linearity

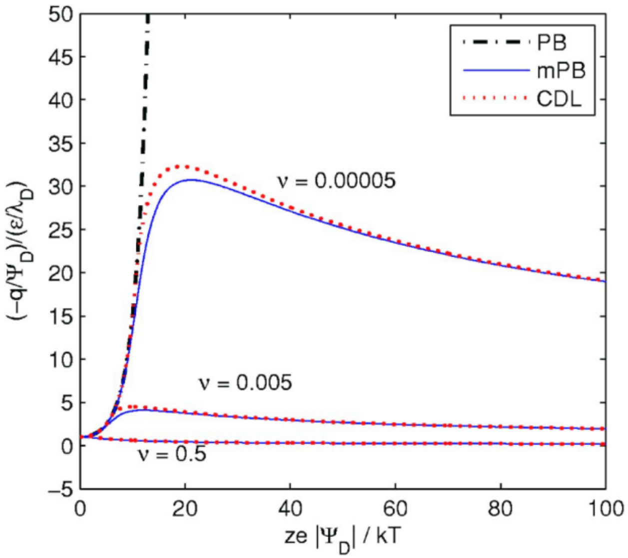
- Electric double layer capacitance (steric effects):

$$\Psi_D \ll \Psi_T \doteq \frac{k_B T}{z e}$$ Linear regime

$$\Psi_T \lesssim \Psi_D \ll \Psi_{smax} \doteq \frac{k_B T}{z e} \ln\left(\frac{c_{smax}}{c_\infty}\right)$$ Weakly non-linear regime

$$\Psi_{smax} \lesssim \Psi_D$$ Highly non-linear regime

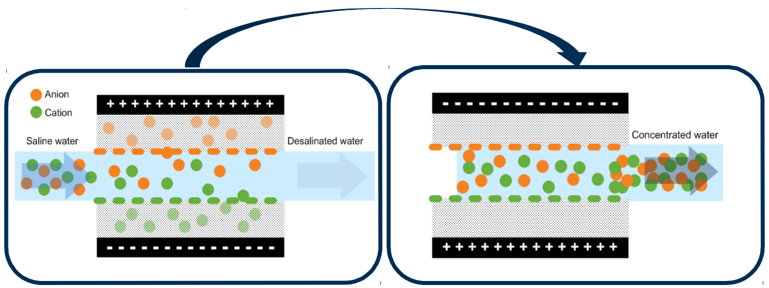


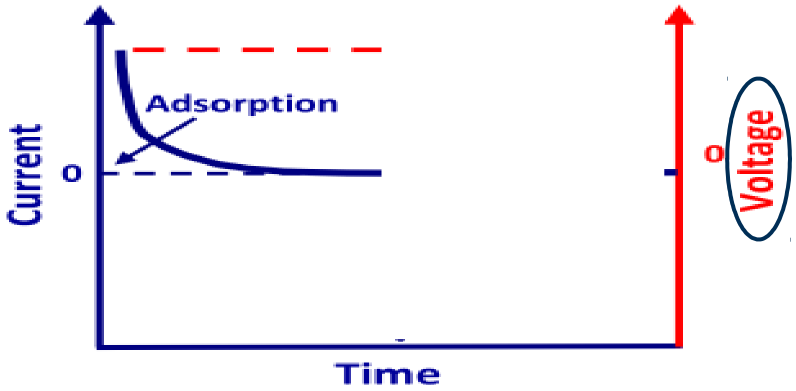


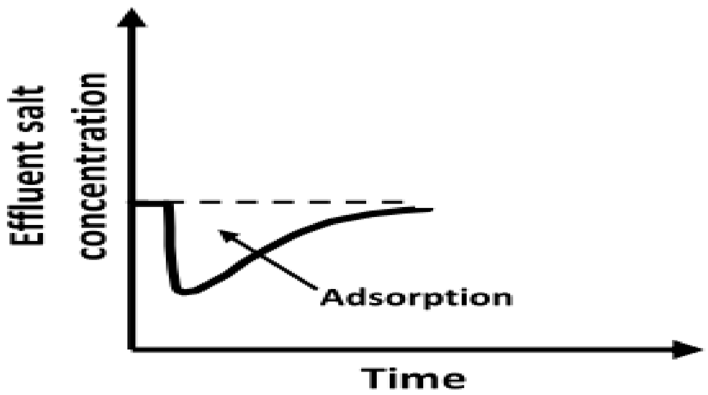
Capacitance of diffuse layer vs Ψ_D

Kilic et al.
Phys Rev E 2007;75

» Time-dependent







Desalination **capacity** (equilibrium)

Desalination **rate** (dynamic)

~~multiscale~~

Electrode-electrolyte interface level models

- *Yang et al*: 1-D Poisson Boltzmann eq. with cut-off pore width

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} = \frac{2zeN_0}{\epsilon}\sinh\left(\frac{ze\Psi}{k_BT}\right)$$

Yang et al.
Langmuir 2001;17(6)

- *Jeon & Cheon*: 2-D Poisson-Nernst-Planck eq. with Stern layer

$$-\nabla\cdot(\varepsilon\,\nabla\Psi) = \mathscr{F}\,(c_+ - c_-) = 0$$

$$\frac{\partial c_i}{\partial t} - \nabla\cdot\left(D_i\nabla c_i + b_i\,z_i\,\mathscr{F}\,c_i\nabla\Psi\right) = 0$$

Jeon & Cheon
Des. and water tr. 2013;51

Based on dilute solutions theory.
Not coupled to macroscale mass transport through porous electrode

- **Linear circuit models**

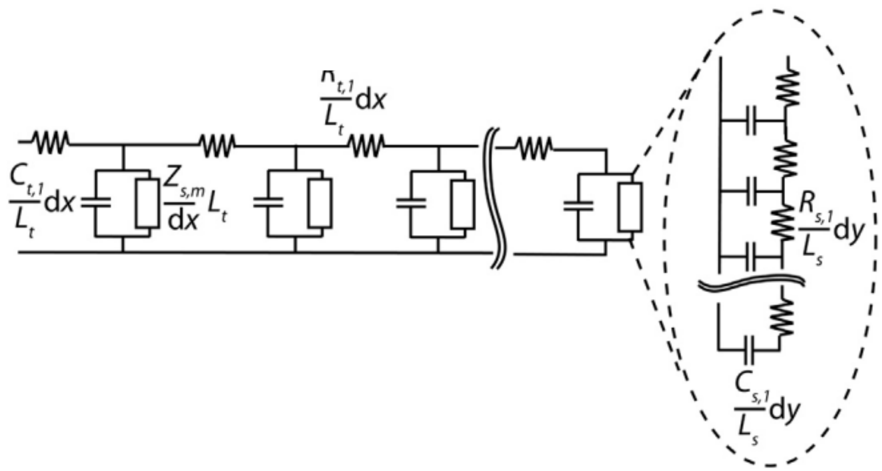
~~Non-linearity~~

  - *Andelman et al*, *Jande & Kim*: Lumped

Andelmann
Sep Pur Tech 2011; 80

Jande & Kim
Sep Pur Tech 2013; 115

  - *Suss et al* :



Interparticle pore

Intraparticle pore

Suss et al.
J Power Sources 2013; 241

Quasi-thermal equilibrium: Equilibration time of double layer is assumed fast compared the time scales of transport in the bulk electrolyte.
Thin double layer limit.
Empirical fitting of 4 parameters: inter- and intraparticle pore resistances and capacitances.

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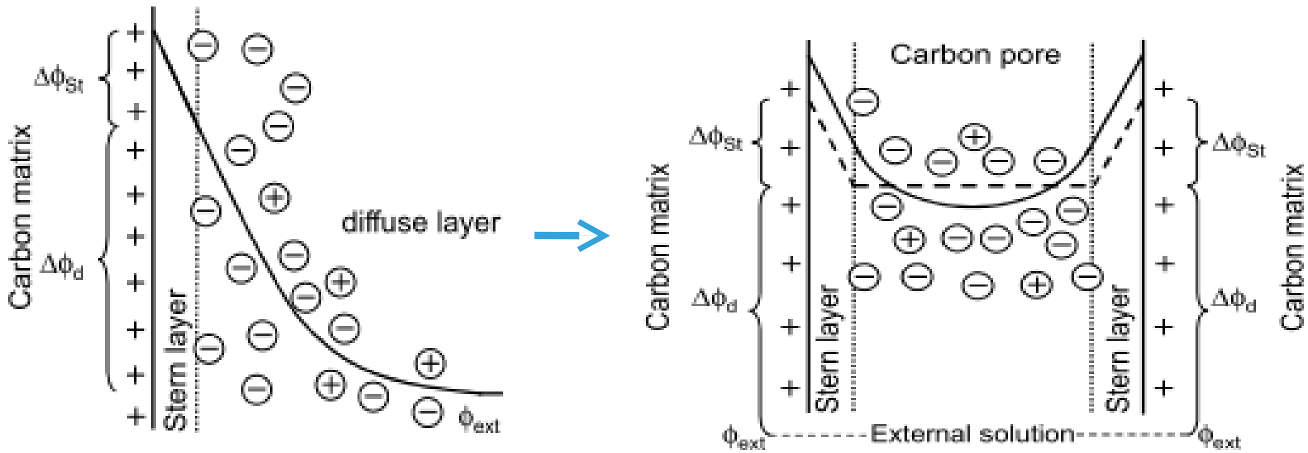
» Highly overlapping double layer model

~~Time-dependance (non-equilibrium)~~

» *Biesheuvel et al*: Modified Donnan model



$$c_{\mathrm{mi,i}} = c_{\mathrm{ma,i}} \exp\left[-z_i(\Psi_{\mathrm{mi}} - \Psi_{\mathrm{ma}}) + \mu_{\mathrm{att,i}}\right]$$

Boltzmann equilibrium between inter- and intraparticle pores

$$\mu_{\mathrm{att,i}} = \frac{z^2 kT \lambda_{\mathrm{B}}}{c_{\mathrm{mi,i}} \lambda_{\mathrm{p}}^4}$$

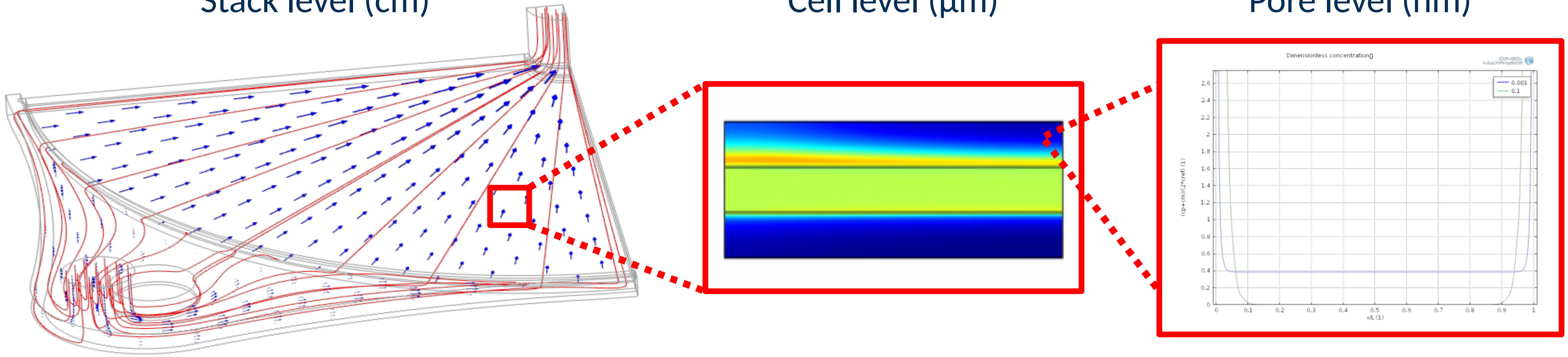
Excess chemical potential

Doesn't account for contributions from non-overlapping EDLs. Equilibrium model.

Biesheuvel et al. J Solid St Electrochem 2014;18:1365–76

- Bimodal pore distribution:
  - Macro-scale mass transport through interparticle pores
    - Electroneutrality in macropores
  - Ion storage in EDL in interparticle and (mainly) in intraparticle pores
    - EDL in quasi-equilibrium with bulk electrolyte
    - Non-overlapping EDLs
- No advective transport in porous electrodes
- One-way coupling between fluid flow and mass transport
- 2D

Stack level (cm) | Cell level (µm) | Pore level (nm)



- Cell level: FEM geometry
- Interparticle: effective medium approximation
- Intraparticle: capacitance source term

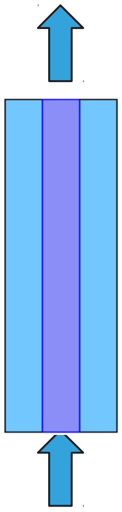
- Dependent variables:

$$\Psi_{ma}$$
$$\Psi_{elc}$$
$$\left.\begin{matrix} c_- \\ c_+ \end{matrix}\right\} \longrightarrow c \qquad \text{(Electroneutrality in interparticle pores)}$$
$$p$$
$$u$$

- Solvent flow
  - Open feed channel
    - Incompressible NS:

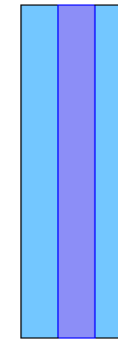
$$\varrho \nabla \cdot u = 0$$

$$\varrho \frac{\partial u}{\partial t} + \varrho (u \cdot \nabla) u = \nabla \cdot \left[-P\,\mathbf{1} + \eta \left(\nabla u + (\nabla u)^T \right) \right]$$



» Mass transport

- Feed channel
  - Nernst-Planck & Einstein: $$\frac{\partial c_i}{\partial t} + u \cdot \nabla c_i - \nabla \cdot (D_i \nabla c_i + b_i \, z_i \, \mathscr{F} \, c_i \nabla \Psi) = 0$$
  - Poisson: Electroneutrality: $$-\nabla \cdot (\varepsilon \, \nabla \Psi) = \mathscr{F} \, (c_+ - c_-) = 0$$
  - Inward flux: Danckwert BC $$N = c_i \cdot u$$



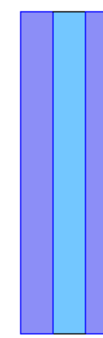
- Porous electrodes
  - Simple mass transport model: Bruggeman equations

$$\epsilon_{ma} \frac{\partial c_i}{\partial t} - \nabla \cdot (D_{i,eff} \nabla c_i + b_{i,\text{eff}} \, z_i \, \mathscr{F} \, c_i \nabla \Psi_{ma}) = 0$$

$$D_{i,\text{eff}} = \epsilon_{ma}^{1.5} D_i \qquad b_{i,\text{eff}} = \frac{D_{i,\text{eff}}}{\Re T}$$

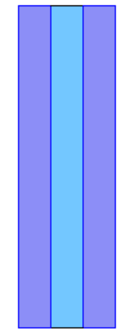
  - Bimodal pore hierarchy: electroneutrality in interparticle pores

$$-\nabla \cdot (\varepsilon \, \nabla \Psi_{ma}) = \mathscr{F} \, (c_+ - c_-) = 0$$

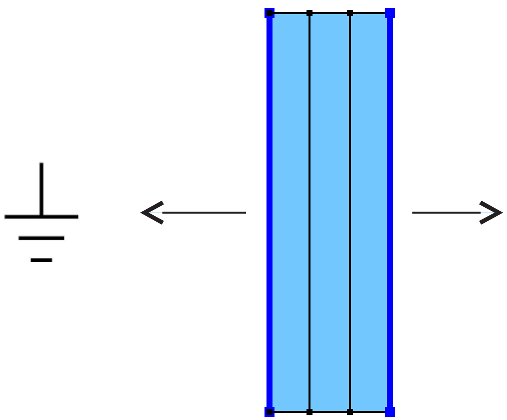


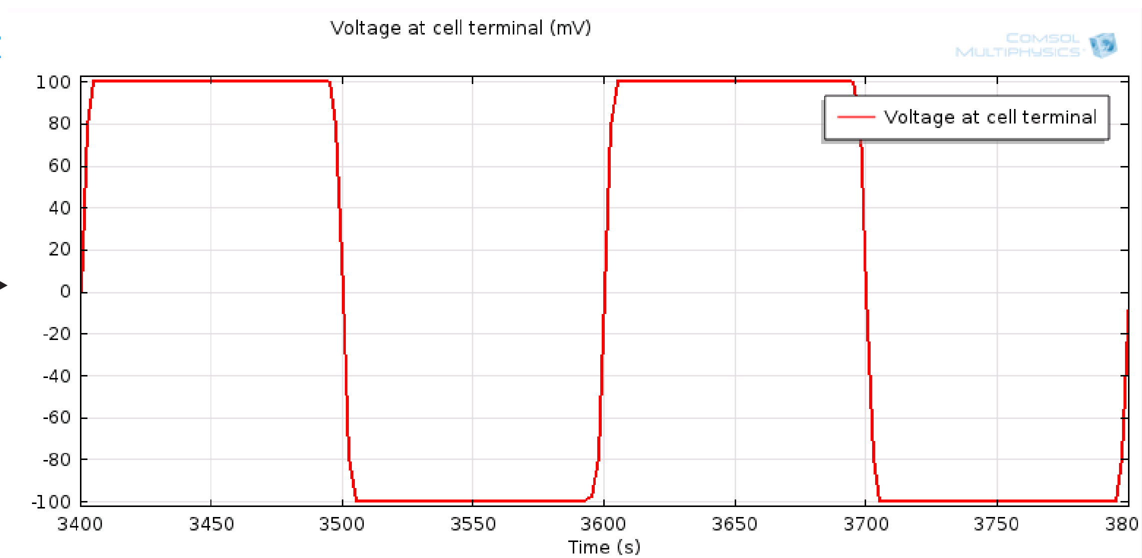
- Electron transport
  - Current conduction through porous electrode

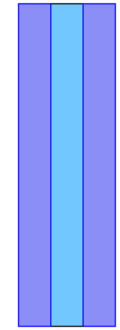
$$i_{\mathrm{elc}} = -\sigma_{\mathrm{elc,eff}} \nabla \Psi_{\mathrm{elc}} \qquad \sigma_{\mathrm{elc,eff}} = \epsilon_{\mathrm{elc}}^{1.5} \sigma_{\mathrm{elc}}$$



  - BC: ti[illegible]ent







- Current source term:

$$\nabla \cdot i_{\mathrm{elc}} = -i_{\mathrm{dl}} \qquad i_{\mathrm{dl}} = \left(\frac{\partial \Psi_{\mathrm{elc}}}{\partial t} - \frac{\partial \Psi_{\mathrm{ma}}}{\partial t} \right) a \, C_{\mathrm{dl}}$$

a → surface area

  - C_{dl}: Electrical double layer differential capacitance:

$$C_{\mathrm{dl}} = \frac{\varepsilon}{\lambda_D} \cosh \left(\frac{ze \left(\Psi_{\mathrm{ely}} - \Psi_{\mathrm{elc}} \right)}{2kT} \right)$$

Poisson-Boltzmann

- Thin double layer approximation: quasi-thermal equilibrium.

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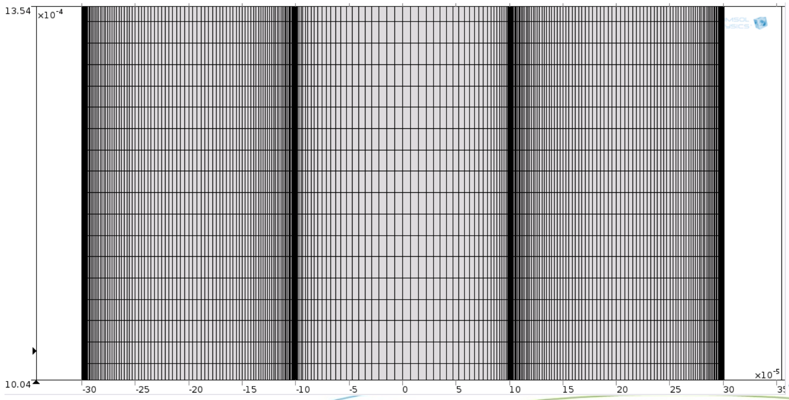
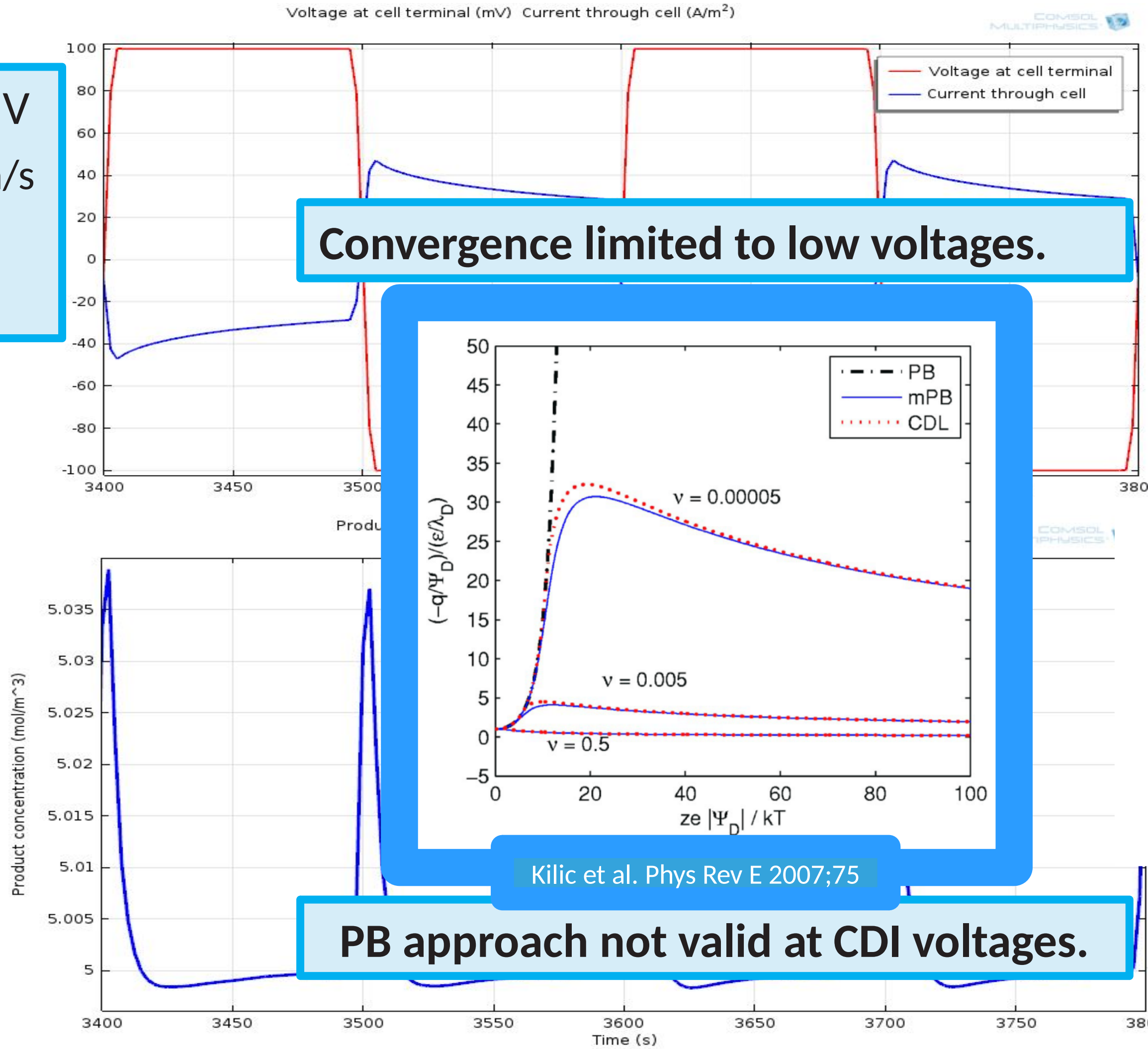
- Solved using COMSOL Multiphysics 4.4
- Solver: MUMPS
- Time-stepping method: BDF (max order 2)
- Mesh:
  - quadrilateral
  - refined near spacer-electrode interface and electrode-current collector interface



Constant voltage, reverse voltage desorption, PB

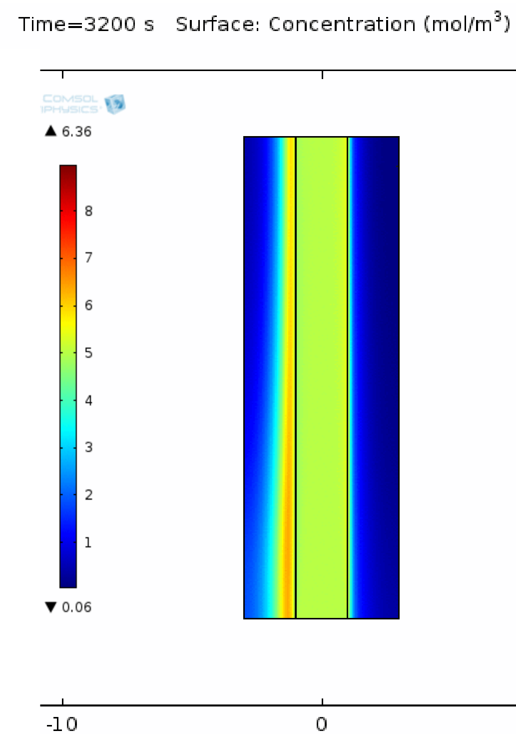
V_{max} = 0.1 V
v_{avg} = 1 cm/s
c = 5 mM
ε_{ma} = 0.5

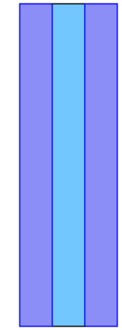


Convergence limited to low voltages.

Kilic et al. Phys Rev E 2007;75

PB approach not valid at CDI voltages.





» Current source term:

$$\nabla \cdot i_{\mathrm{elc}} = -i_{\mathrm{dl}} \qquad i_{\mathrm{dl}} = \left(\frac{\partial \Psi_{\mathrm{elc}}}{\partial t} - \frac{\partial \Psi_{\mathrm{ma}}}{\partial t}\right) a\, C_{\mathrm{dl}}$$

a → surface area

» C_{dl}: Electrical double layer differential capacitance:

$$C_{\mathrm{dl}} = \frac{\varepsilon}{\lambda_D} \cosh\left(\frac{ze\left(\Psi_{\mathrm{ma}} - \Psi_{\mathrm{elc}}\right)}{2kT}\right)$$

Poisson-Boltzmann

$$C_{dl} = \frac{\varepsilon \left|\sinh\left(\frac{ze[\Psi_{ma}-\Psi_{elc}]}{kT}\right)\right|}{\lambda_D \left[1 + 2\nu \sinh^2\left(\frac{ze[\Psi_{ma}-\Psi_{elc}]}{2kT}\right)\right] \sqrt{\frac{2}{\nu} \ln\left[1 + 2\nu \sinh^2\left(\frac{ze[\Psi_{ma}-\Psi_{elc}]}{2kT}\right)\right]}}$$

Modified Poisson-Boltzmann

$$\nu = 2\, l^3\, c_i$$

l : Effective ion size

» Thin double layer approximation: quasi-thermal equilibrium.

Kilic et al.
Phys Rev E 2007;75

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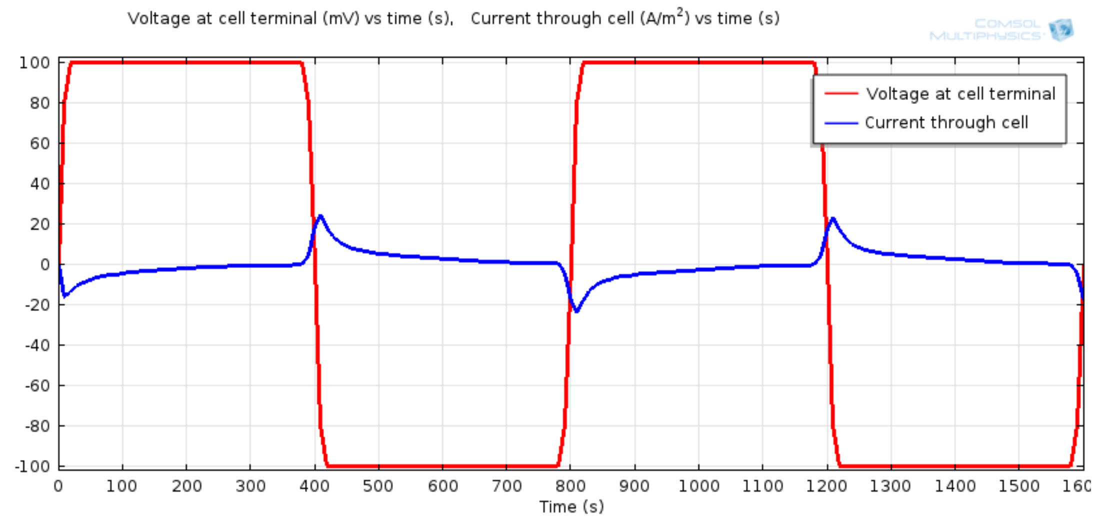
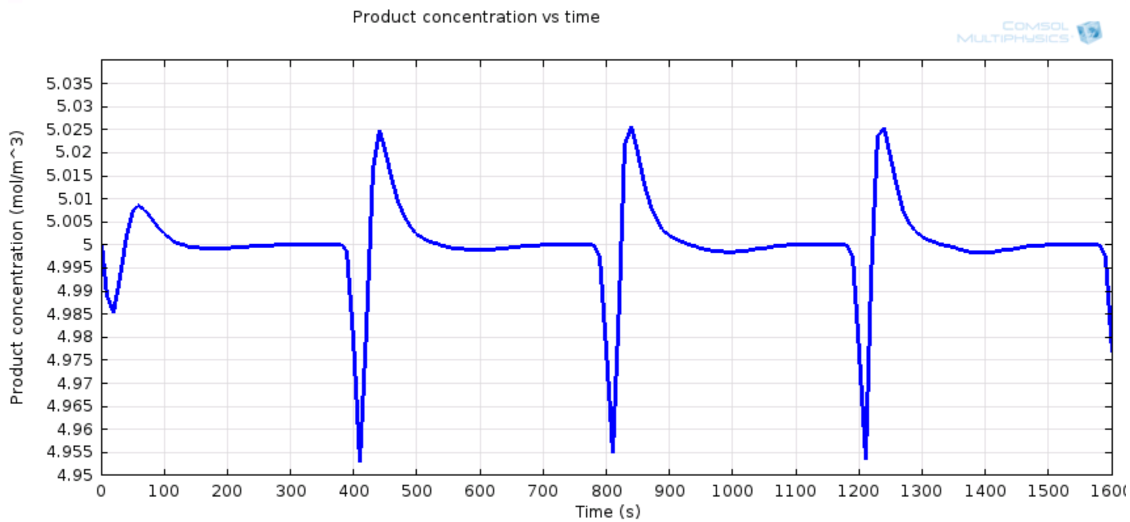
Constant voltage, reverse voltage desorption, MPB

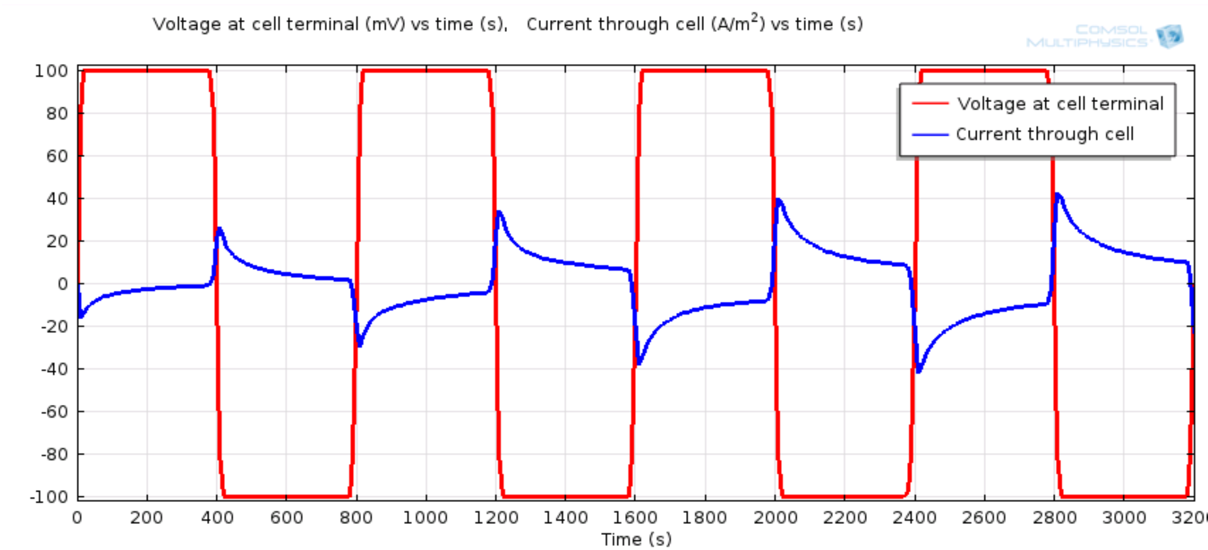
V_{max} = 0.1 V
v_{avg} = 1 cm/s
c = 5 mM
l = 4.5 nm
ε_{ma} = 0.5

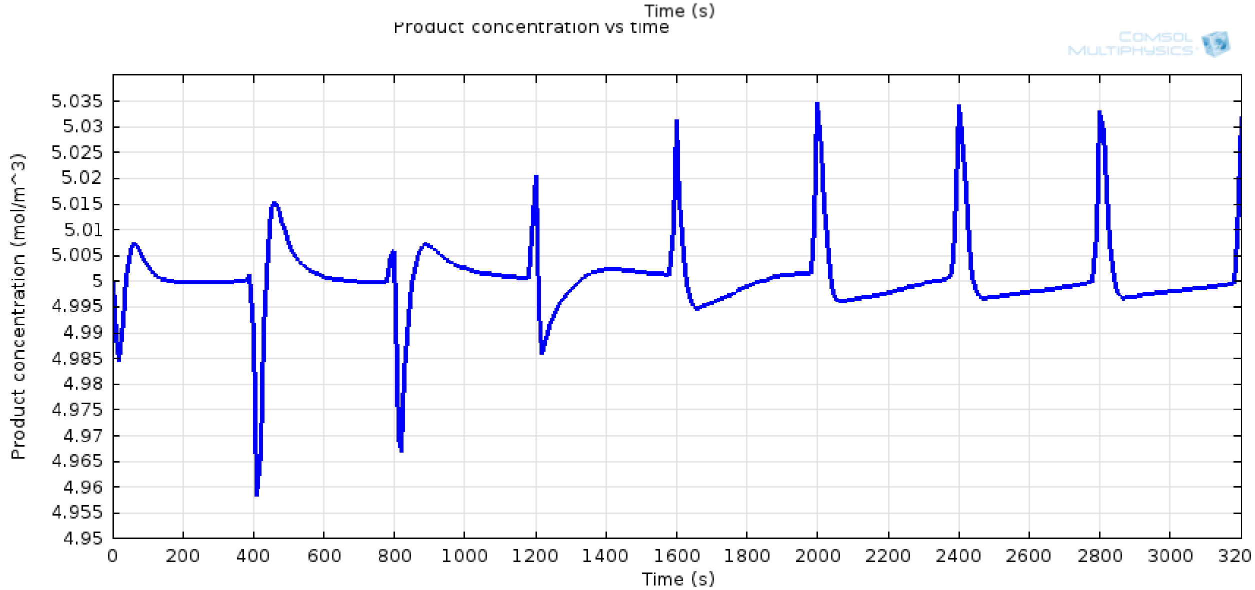




Constant voltage, reverse voltage desorption, MPB

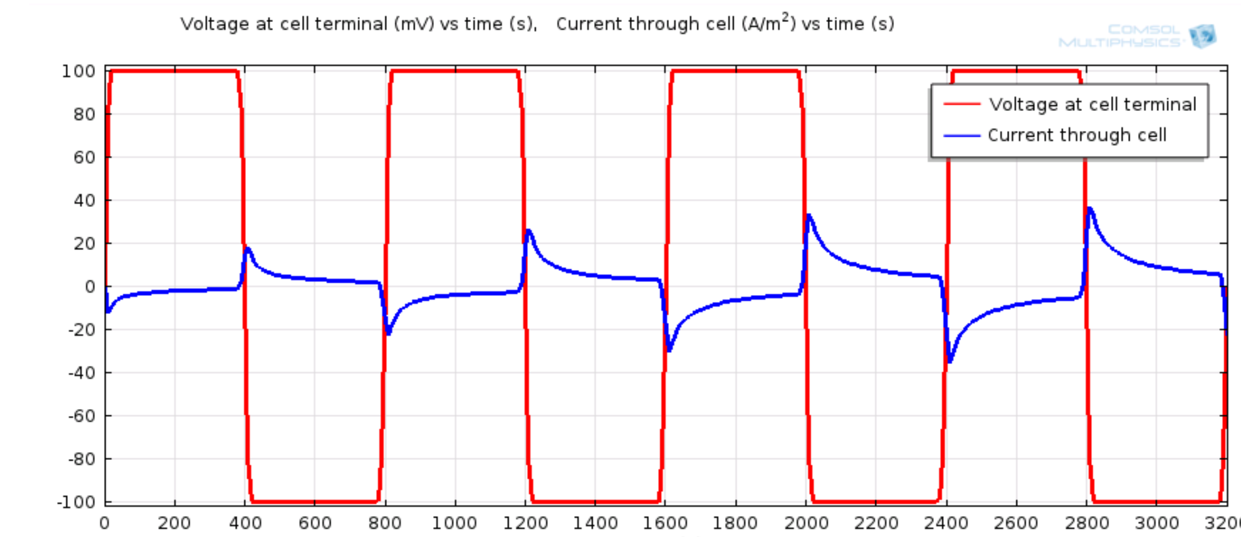
V_{max} = 0.1 V
v_{avg} = 1 cm/s
c = 5 mM
l = 0.45 nm
ε_{ma} = 0.5

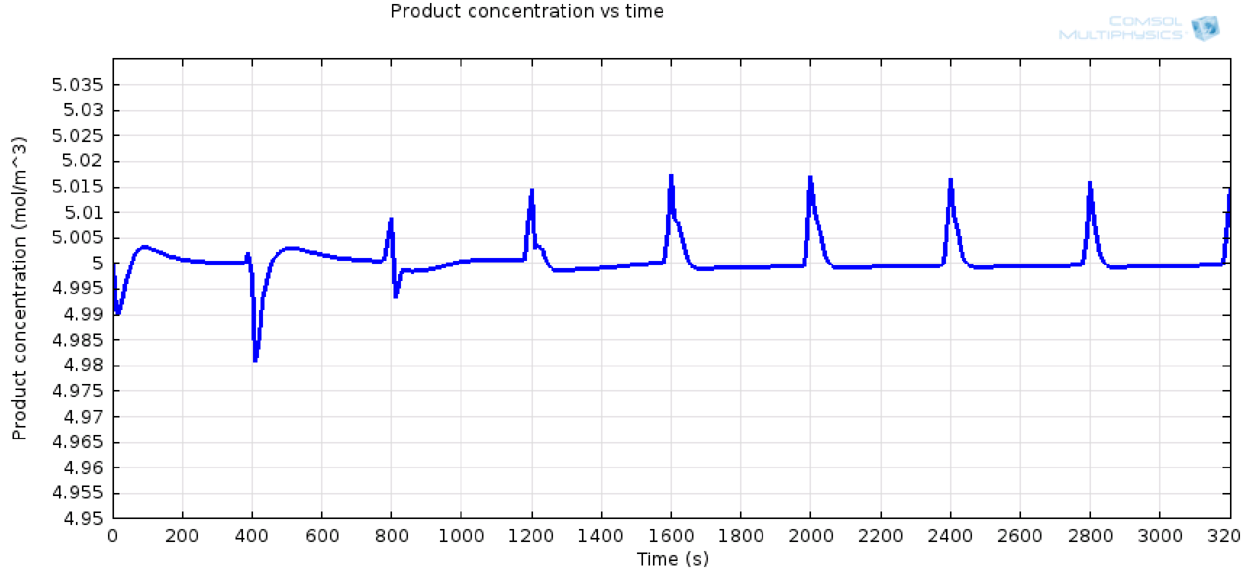




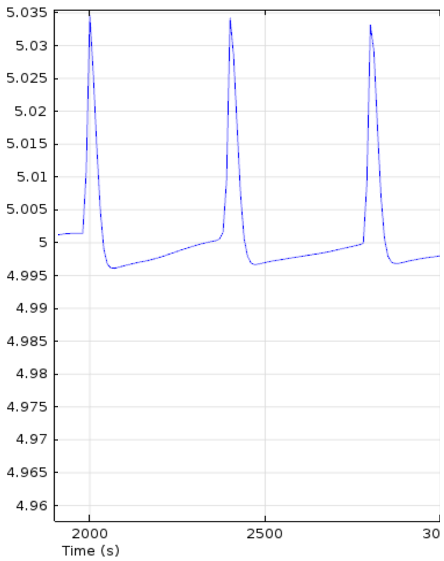
Constant voltage, reverse voltage desorption, MPB

$V_{max} = 0.1$ V
$v_{avg} = 1$ cm/s
c = 5 mM
l = 0.45 nm
$\varepsilon_{ma} = 0.25$

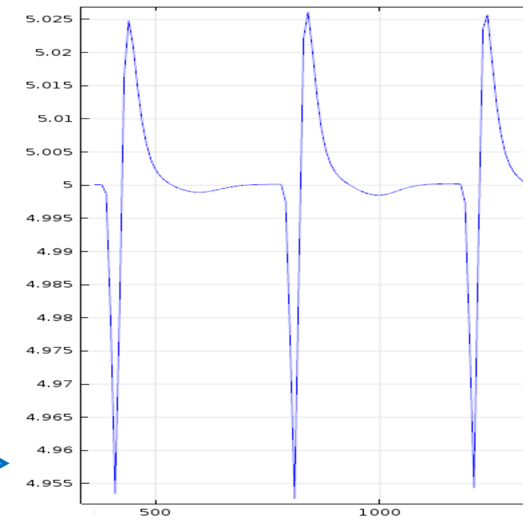




Constant voltage, reverse voltage desorption, MPB



- Speed up mass transport — ε_{ma}
- Increase sterical hindrance effects — I
- Increase driving force — V_{cell}
- Increase concentration — c



At CDI conditions, hypothesis:
Mismatch in time scales of relaxation of C-element (too slow) and macroscale mass transport. Macrotransport too fast close to voltage switching points (strong driving force).
Quasi thermal equilibrium description of C unsatisfactory.

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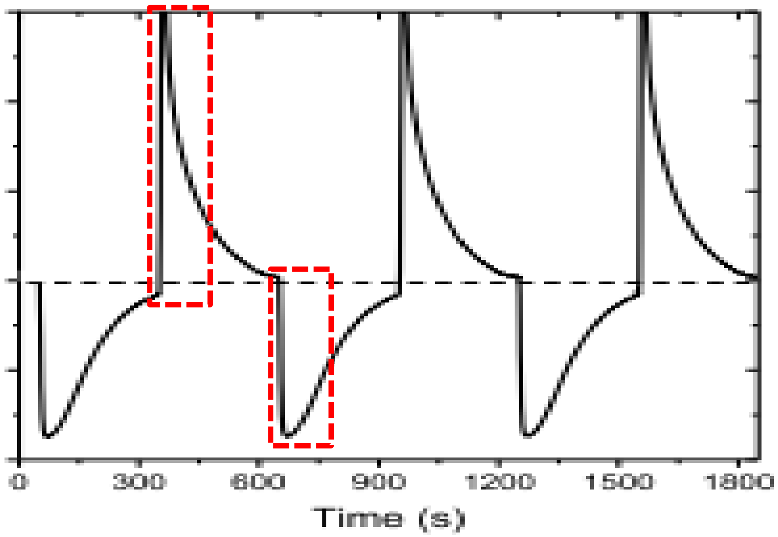
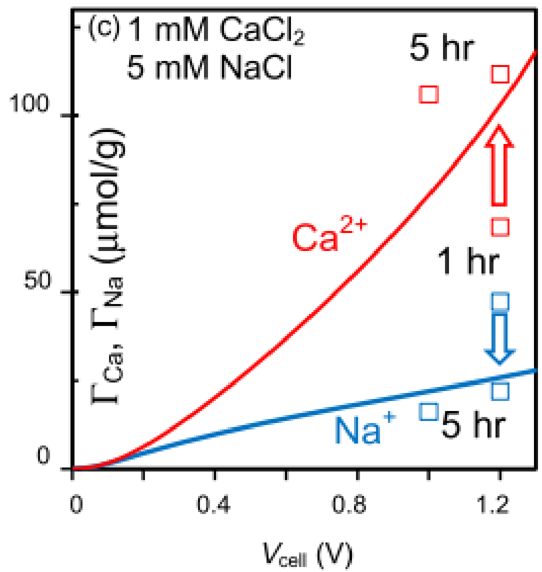
Warning: strong transients



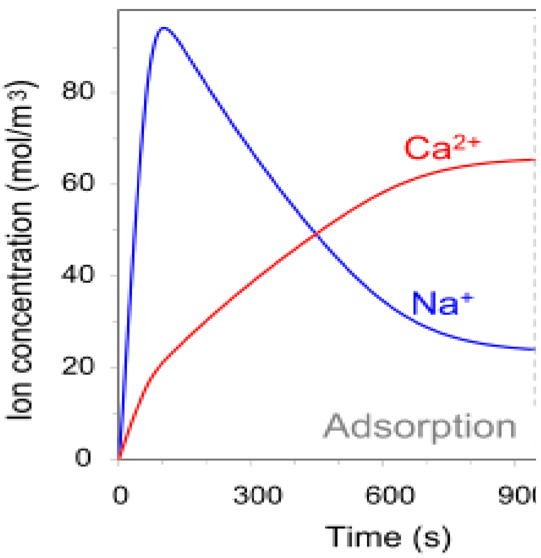
- CDI Optimization potential:
  - Narrowing and deepening the peak (faster desalination rate): material optimization
  - Switching voltages at the optimal moment: operational optimization
  - Importance for selective removal from complex streams

Time-dependent ion selectivity for capacitive deionization of complex streams

Cation storage vs cell voltage



Cation storage vs time

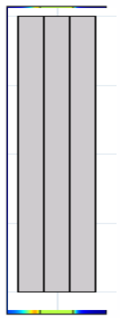


- Equilibrium modified Donnan model not useful (extremely long equilibration).
- Non-equilibrium effects stronger for complex streams.

Zhao et al.
J Colloid & Interf. Sc. 2012;384

Upcoming

- Multiscale model, non-equilibrium description of EDL



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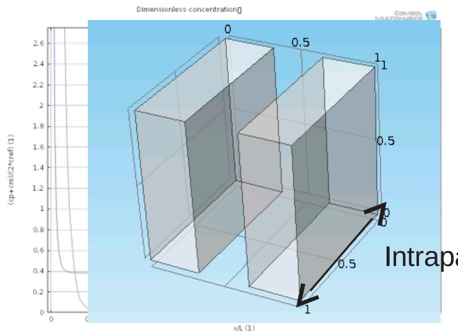

(macro) interparticle

(micro) intraparticle

- Solve (M)PNP equations at microscale level
- Boundary coupling between macro-scale and micro-scale:
  - Boltzmann equilibrium:
  - Non-equilibrium: overpotential formulation

$$c_{\mathrm{mi,i}} = c_{\mathrm{ma,i}} \exp\left[-z_i(\Psi_{\mathrm{mi}} - \Psi_{\mathrm{ma}})\right]$$

Thank you for your attention

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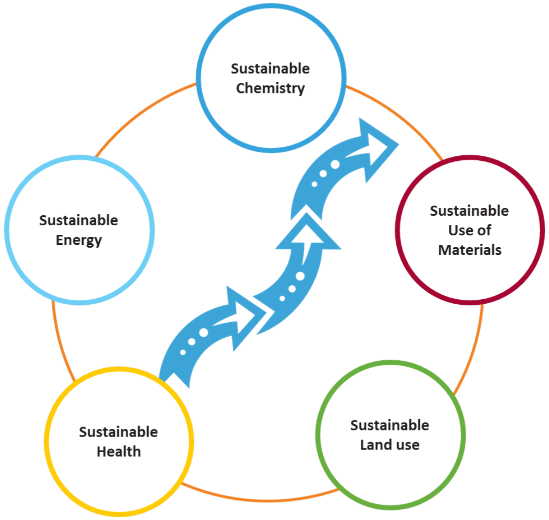

Thanks to:

Bruno Bastos Sales
Joost Helsen
Arne Verliefde