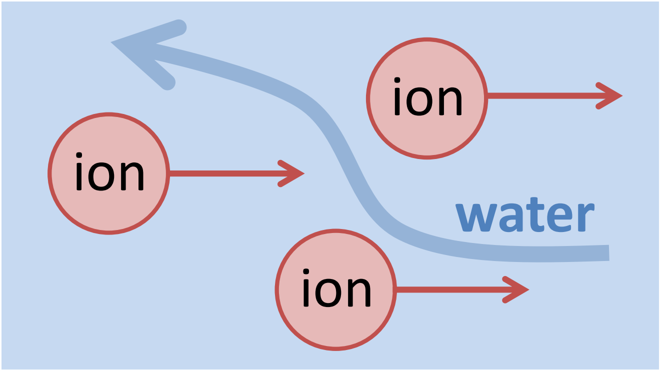
Transport of ions, colloids and water in porous media and membranes

with special attention to

water desalination by capacitive deionization

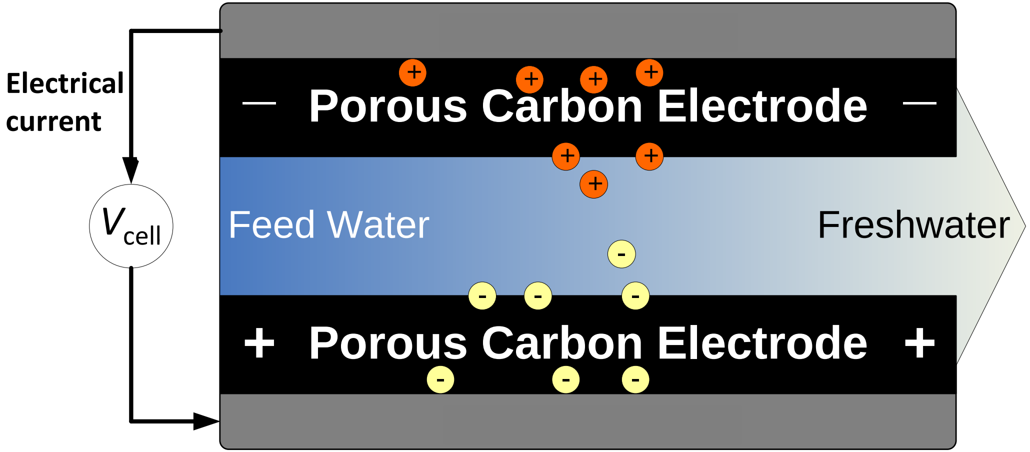


Maarten Biesheuvel

Overview

- Capacitive Deionization (CDI)
- Porous electrode theory
- Modeling ion electrokinetics (combined flow of water, ions, colloids)
- Sedimentation of colloidal particles

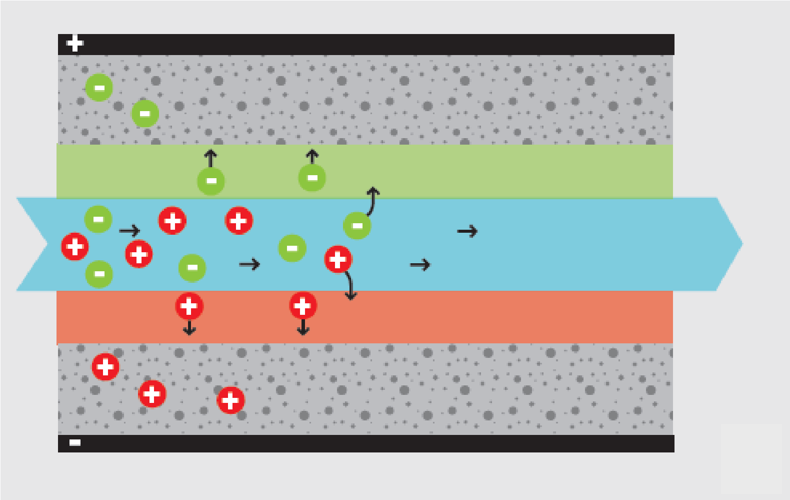
Capacitive Deionization



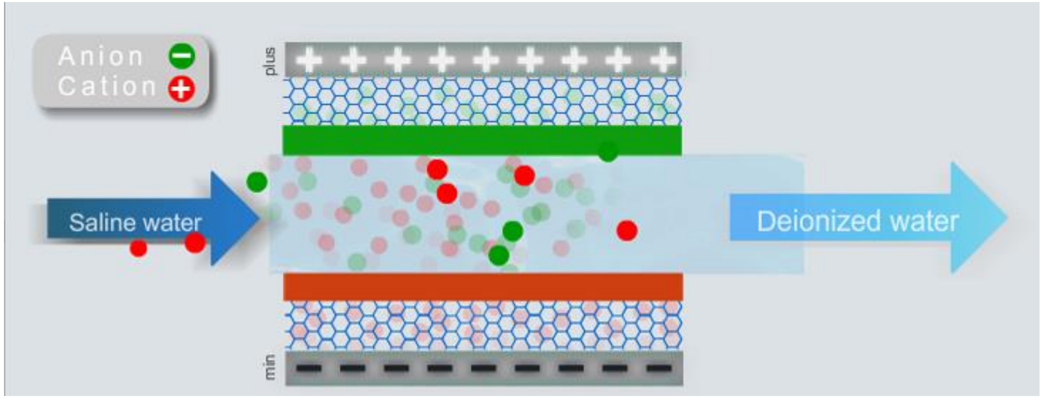
Voltea

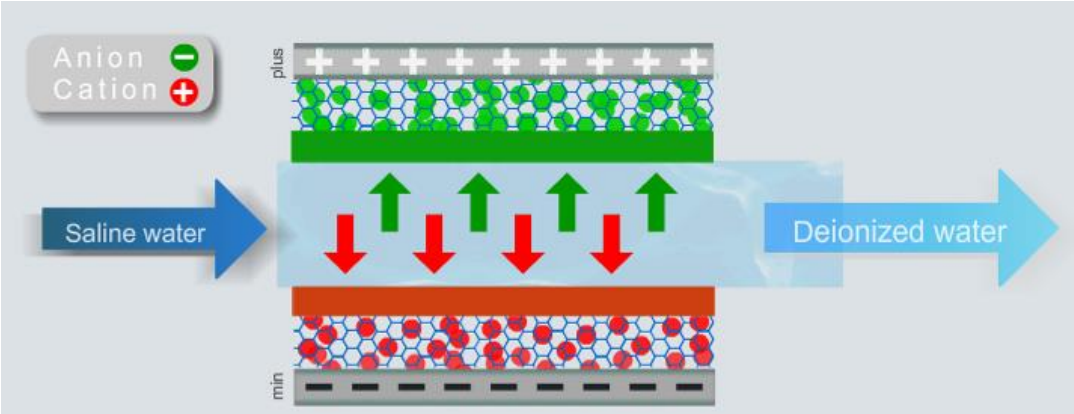
Membrane Capacitive Deionization

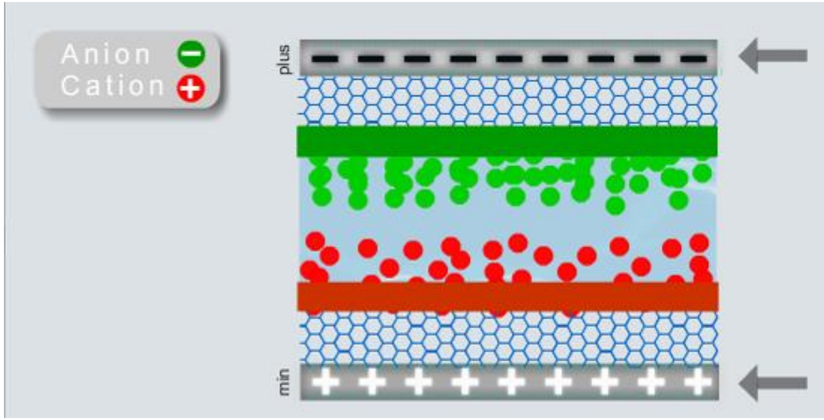
with ion-exchange membranes

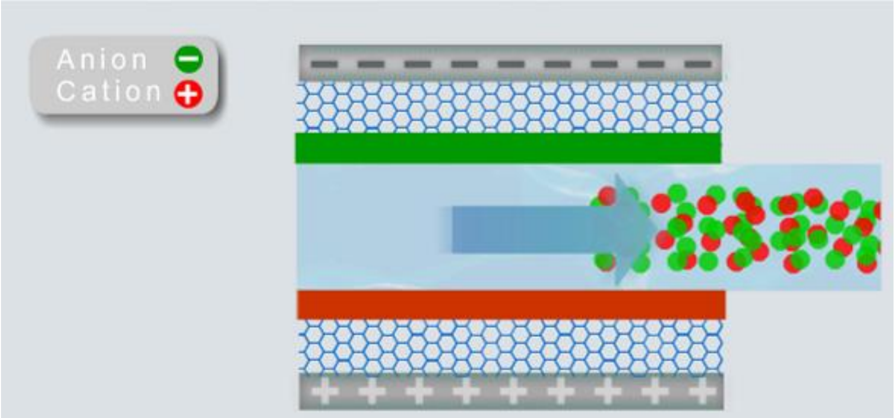


Membrane Capacitive Deionization

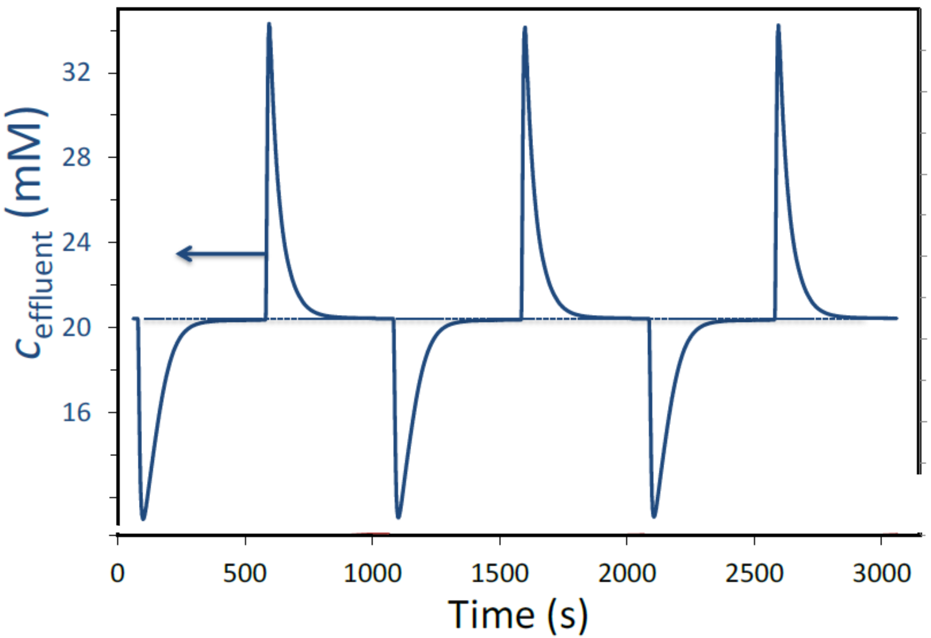





Anion
Cation
plus
min

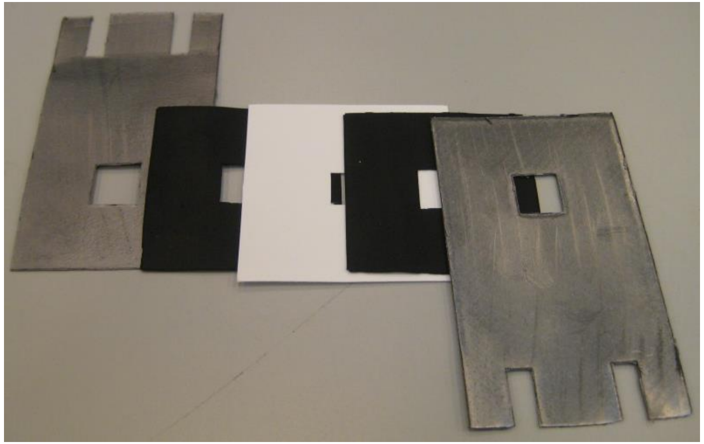

Anion
Cation

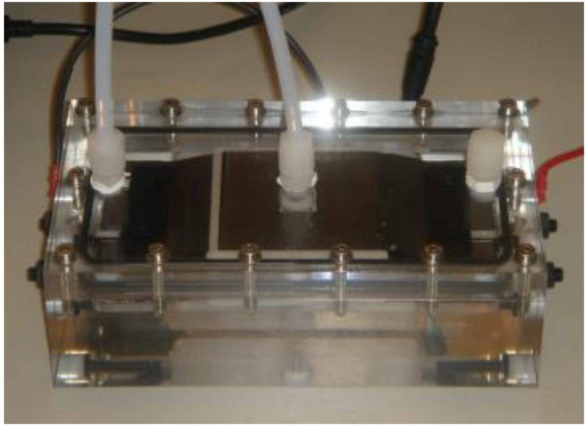
CDI testing



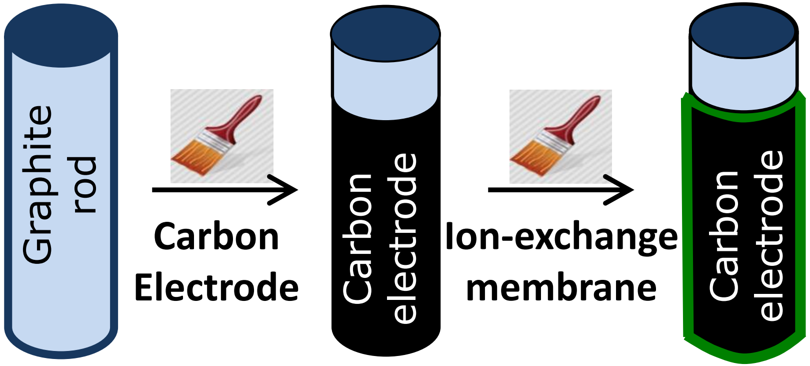
32
28
24
20
16
$c_{effluent}$ (mM)
0
500
1000
1500
2000
2500
3000
Time (s)

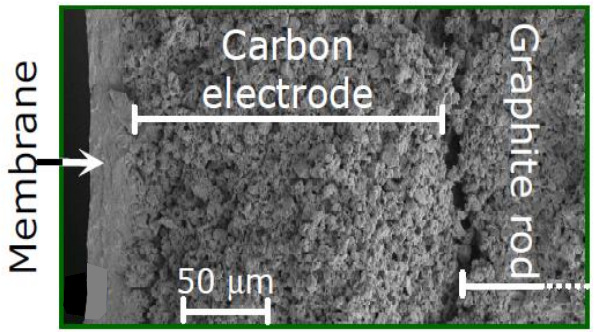
What does CDI look like?

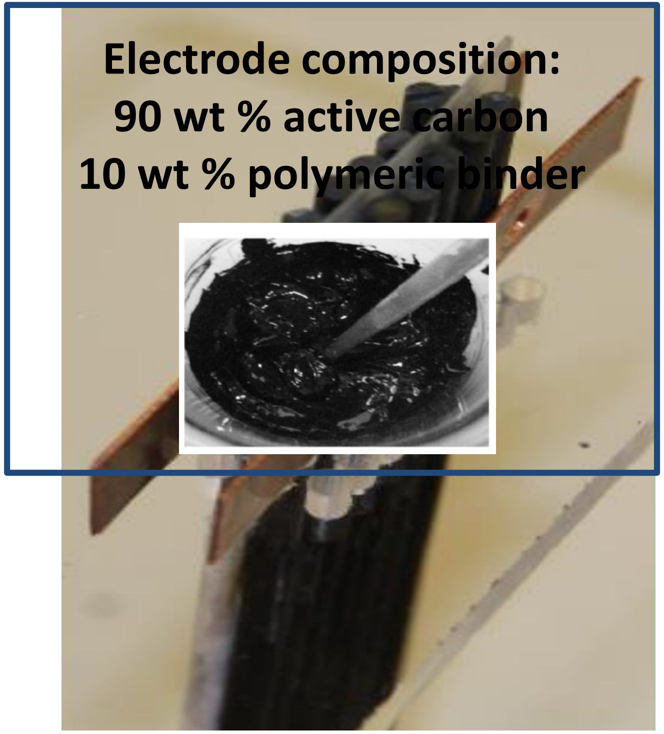


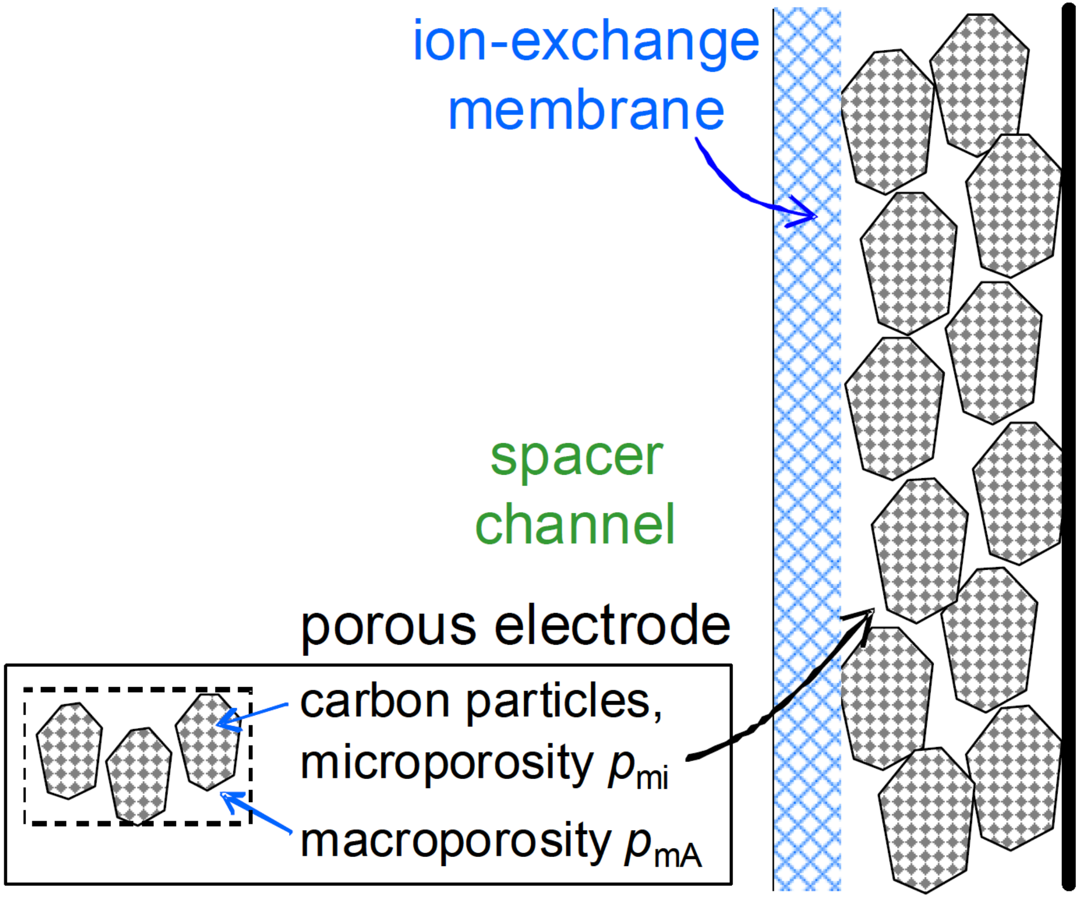


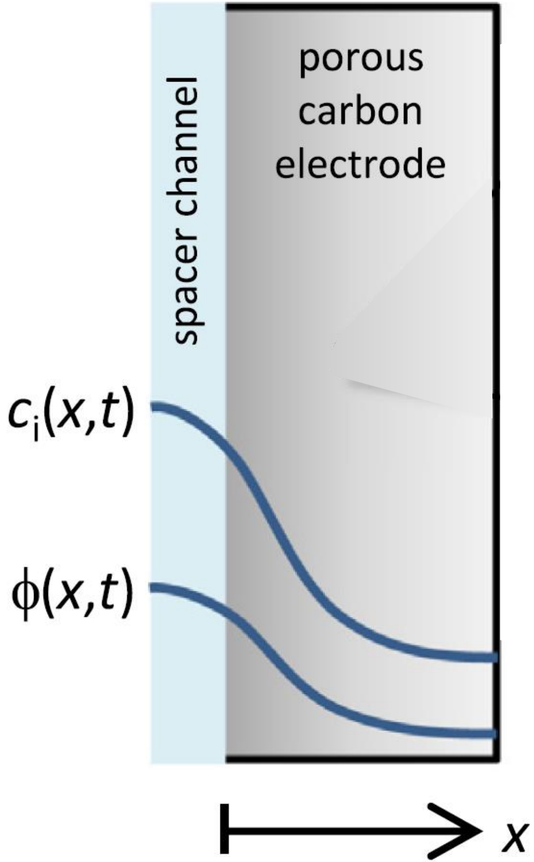
CDI designs using cylinders (wires)



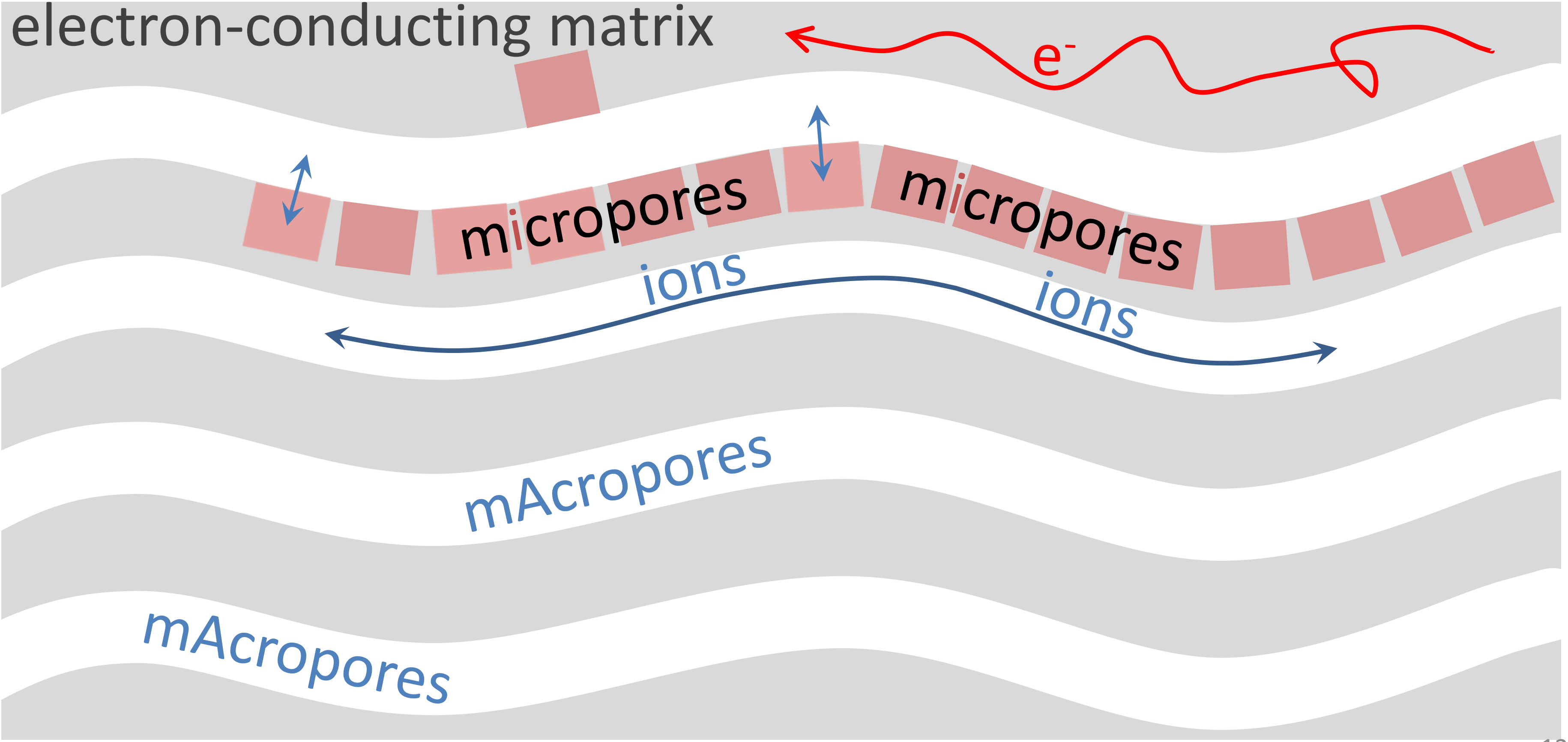





ion-exchange membrane
spacer channel
porous electrode
carbon particles, microporosity p_{mi}
macroporosity p_{mA}


porous
carbon
electrode
spacer channel
$c_i(x,t)$
$\phi(x,t)$
x

Transport in porous electrodes

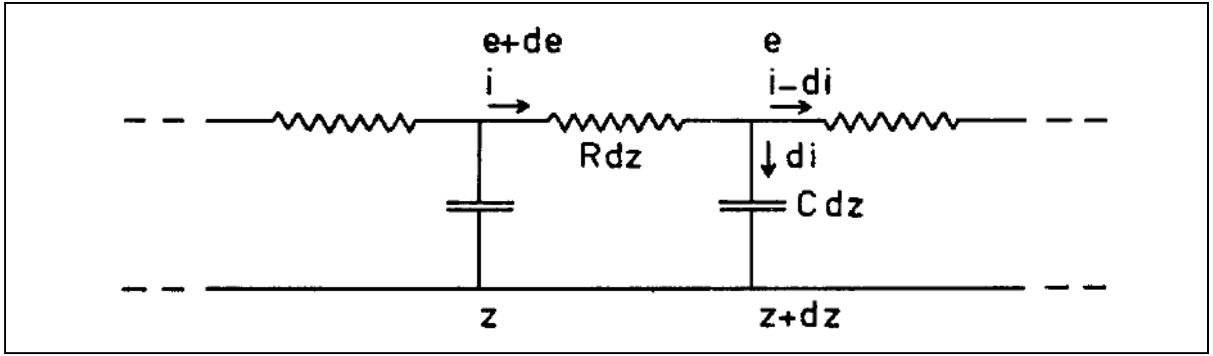


Transport in porous electrodes

Electrochimica Acta, 1963, Vol. 8, pp. 751 to 780.

ON POROUS ELECTRODES IN ELECTROLYTE SOLUTIONS*

R. DE LEVIE§
Electrochemistry Laboratory, University of Amsterdam, Holland



"RC Transmission Line Theory", or "De Levie Theory"

Bob (Robert)
de Levie

ISE, Prague, 2012

RC transmission line theory

$$\frac{\partial^2 \phi_{\text{pore}}}{\partial x^2} - RC\frac{\partial \phi_{\text{pore}}}{\partial t} = 0$$

ϕ_{pore} is potential in aqueous pore
relative to conducting matrix (metal, carbon)

Generalized porous electrode theory

PHYSICAL REVIEW E **81**, 031502 (2010)

Nonlinear dynamics of capacitive charging and desalination by porous electrodes

P. M. Biesheuvel[1,2] and M. Z. Bazant[3]

Prof. Martin Bazant
MIT, USA

Generalized porous electrode theory

PRL **113**, 097701 (2014) PHYSICAL REVIEW LETTERS week ending 29 AUGUST 2014

Enhanced Charging Kinetics of Porous Electrodes: Surface Conduction as a Short-Circuit Mechanism

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(Received 13 April 2014; published 25 August 2014)

From abstract:

morphologies, but only at low applied potentials. Charging dynamics are slowed appreciably at high potentials, yet not as significantly as predicted by the nonlinear transmission line model of Biesheuvel and Bazant. We identify surface conduction as a mechanism which can effectively "short circuit" the high-

relevant for most technologies. A more advanced model, developed by Biesheuvel and Bazant (BB) [15], reveals ion

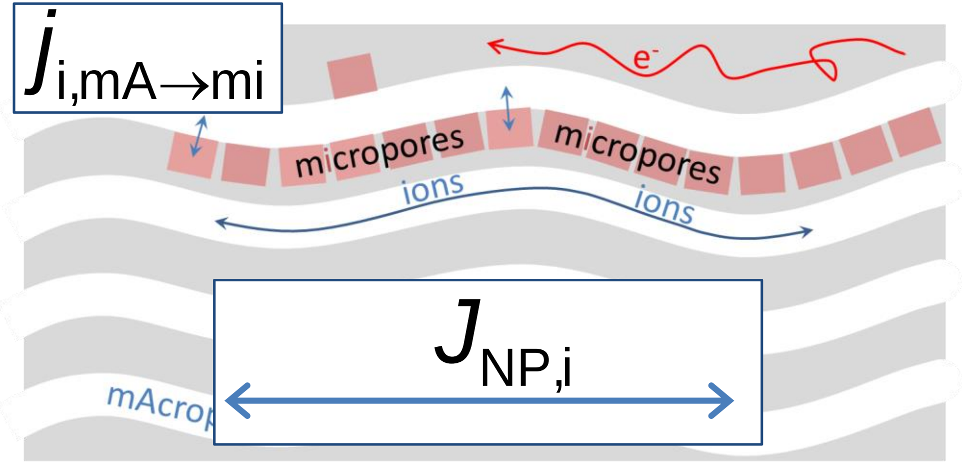
layers under strong potentials in complex geometries. We directly test both linear (TL) and nonlinear (BB) transmission-line models against the full ion transport dynamics.

Todd Squires

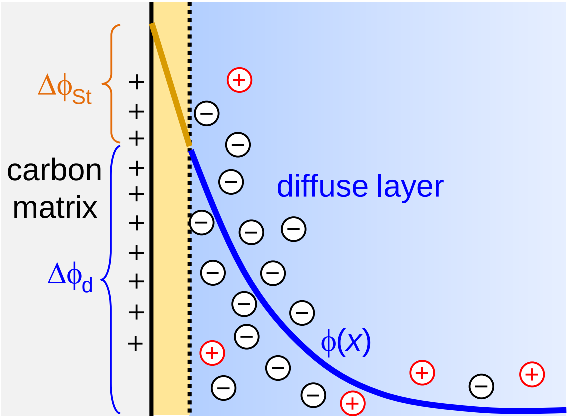
Transport in porous electrodes

Transport equation in mAcropores

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_{NP,i} - j_{i,mA\rightarrow mi}$$



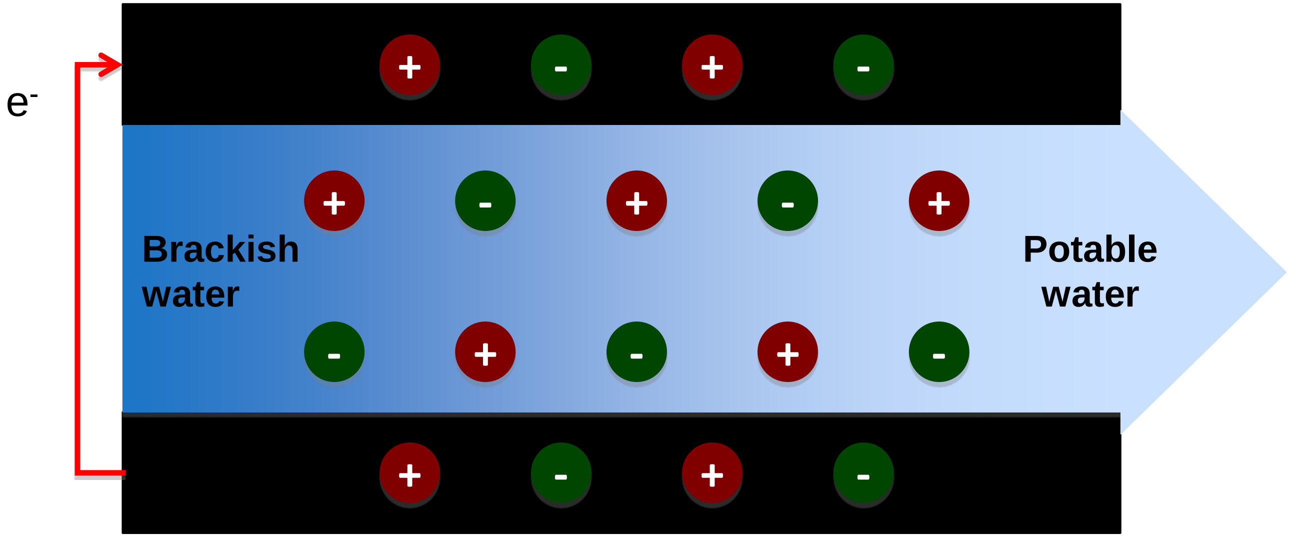
"Electrical double layer" model in micropores



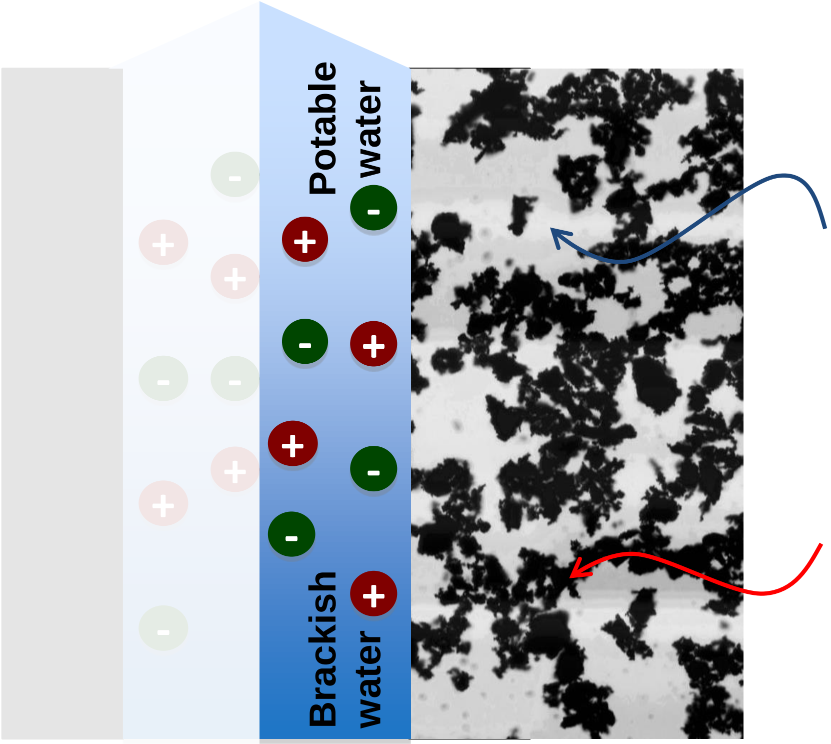
$$\sigma, c_{i,mA} \Leftrightarrow \Delta V, c_{i,mi}$$

$$J_{NP,i} = -D_i\left(\nabla c_i + z_i c_i \nabla \phi\right)$$

Porous electrode transport theory

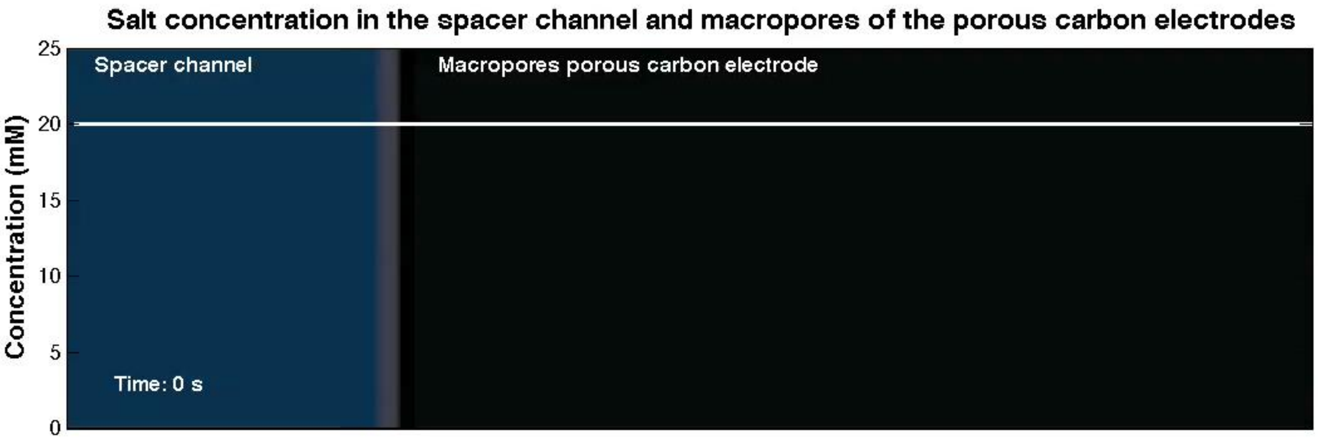


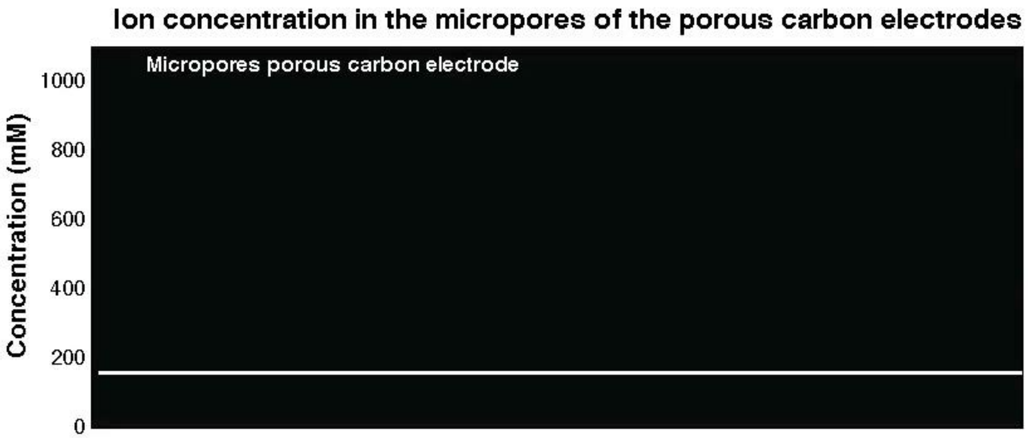
Porous electrode transport theory



Ion transport in the mAcropores

Ion adsorption in the micropores





J.E. Dykstra
P.M. Biesheuvel
A. van der Wal

Including acid/base reactions
In NP-transport modeling in porous media

- Water not just contains a salt like NaCl which can be assumed fully dissociated
- Instead, more realistically there are many ions that can undergo acid/base reactions, such as NH_3, NH_4^+, HCO_3^-
- Of special relevance the reactions with and between H^+ and OH^-
- All these species must be considered !

F.G. Helfferich
(1922-2005)

Helfferich-approach

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_{NP,i}$$

$$J_{NP,i} = -D_i\left(\nabla c_i + z_i c_i \nabla \phi\right)$$

$$R_A = R_B = -R_C$$

$$A + B \Leftrightarrow C$$

$$\cancel{R_A = k_{\rightarrow}[A][B] - k_{\leftarrow}[C]}$$

$$K_i = \frac{[A][B]}{[C]}$$

$$K_i = \frac{\left[CO_3^{2-}\right] \cdot \left[H^+\right]}{\left[HCO_3^-\right]}$$

F.G. Helfferich

Advantages Helfferich-approach

- By addition of balances, for each "group" such as $CO_2/HCO_3^-/CO_3^{2-}$, only one balance per group remains (expressed in one chosen "master species")
- All dummy parameters *R* disappear !
- Very elegant now to include electrochemical reactions at electrodes, or evaporation

F.G. Helfferich

Steady-state diffusion of “acid/base ions”

H_2CO_3

HCO_3^-

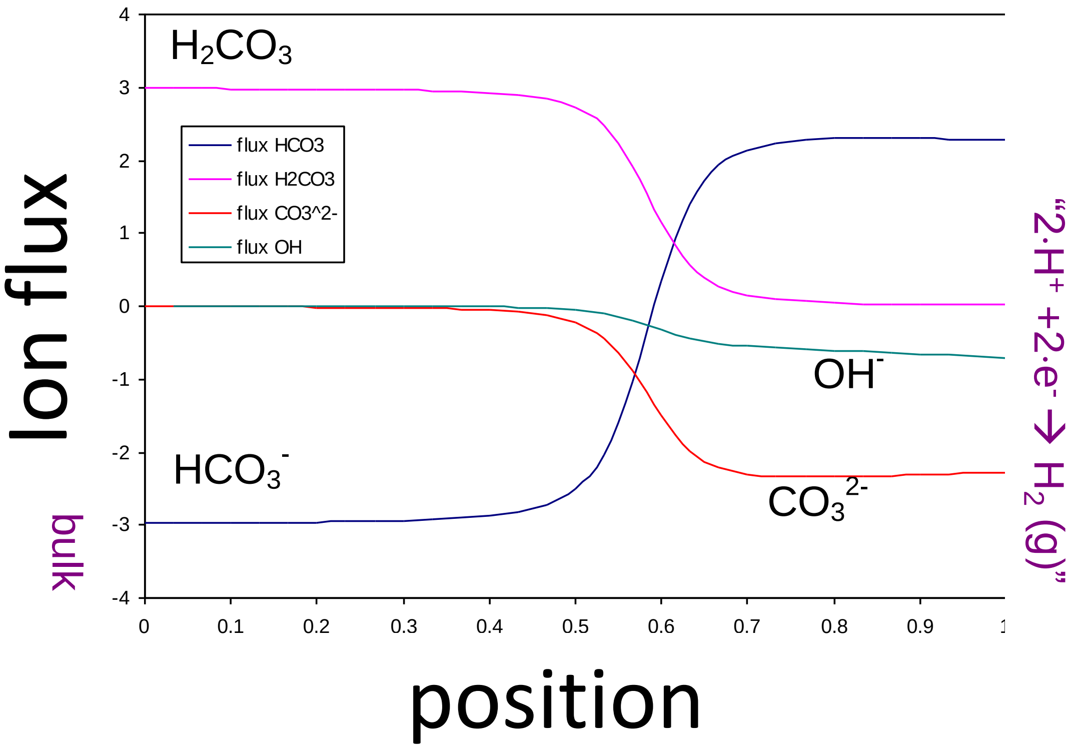
CO_3^{2-}

Na^+

Cl^-

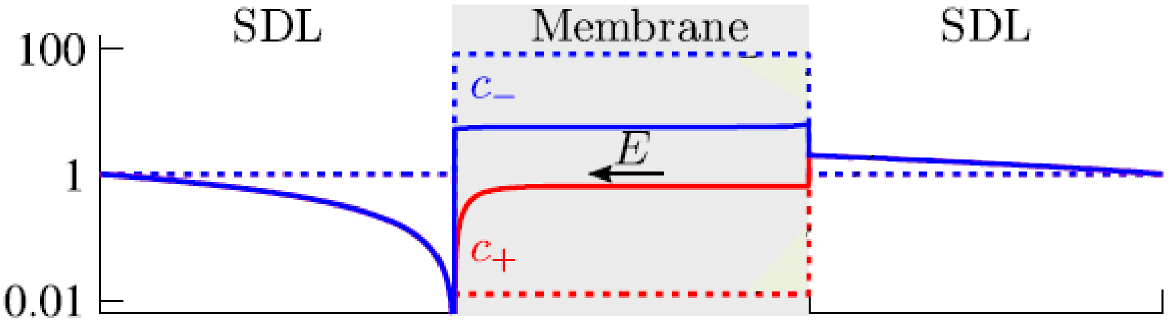
H^+

OH^-



It’s not the proton that flows,
and it is not the source of the formed H_2-gas !!!

Current-induced membrane discharge



water in membrane pores

$$H_2O \overset{K_w}{\leftrightharpoons} OH^- + H^+$$

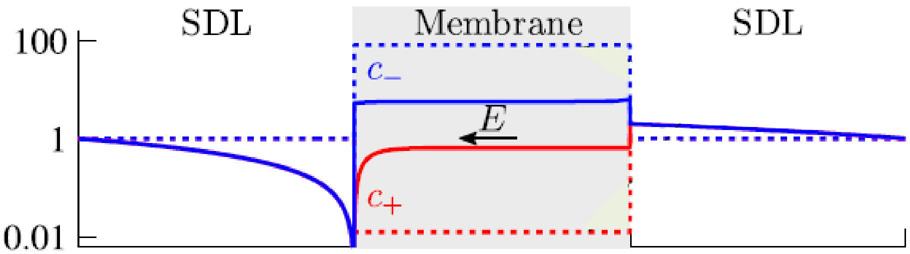
membrane discharge

$$RH^+ \leftrightharpoons R + H^+$$

SDL: stagnant diffusion layer

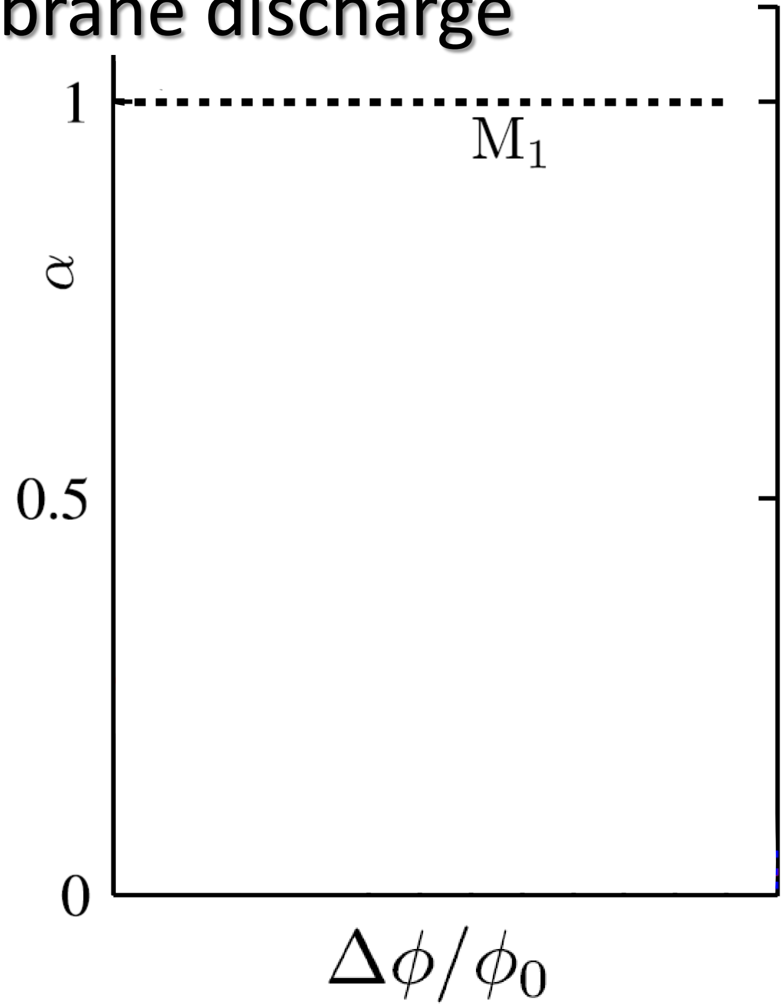
Membrane: water-filled structure with very high concentration of fixed charge, such as RH^+, e.g. 5 M

Current-induced membrane discharge

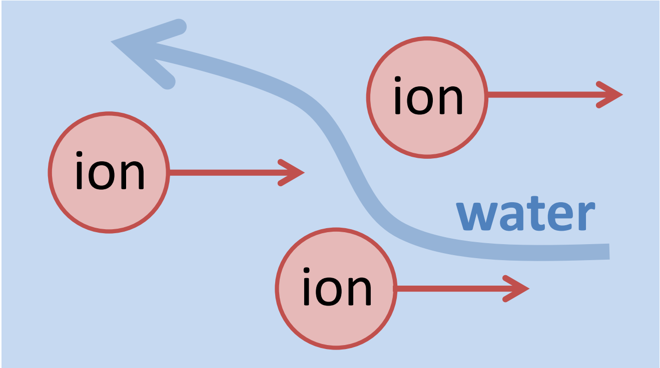


charge parameter

$$\alpha = \frac{[RH^+]}{[RH^+] + [R]}$$

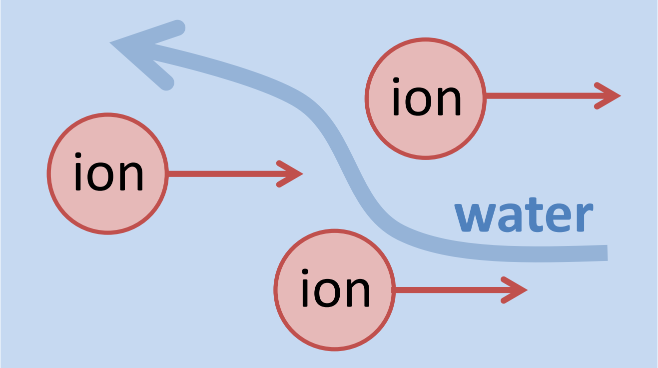


Ion electrokinetics incl. flow of water



- Same approach for ions as for colloids, protein and larger particles
- The ion (with its hydrated water molecules) is a dispersed particle
- Water is the continuum fluidum in between – described very differently from the ions !!
- Extension of <u>two-fluid model</u> to "colloidal regime"

Two-fluid model



Chemical Engineering Science, Vol. 47, No. 8, pp. 1913–1924, 1992.
Printed in Great Britain.

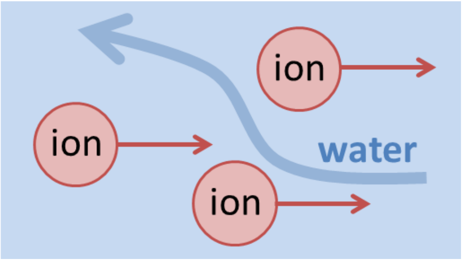
0009–2509/92 $5.00 + 0.00

A NUMERICAL MODEL OF GAS-FLUIDIZED BEDS

(*First received* 19 *September* 1990; *accepted in revised form* 5 *June* 1991)

Abstract—A first-principles model for a gas-fluidized bed based on the so-called "two-fluid model" (TFM) has been developed. In the TFM approach, both phases are considered to be continuous and fully interpenetrating. The equations for mass, momentum and thermal energy conservation, supplemented with

Two-fluid model for colloidal mixtures



$$\mathbf{v}_i - \mathbf{v}_{water} = -D_i \nabla \mu_i$$

$$\mu_i = \underbrace{\ln(c_i) + z_i \phi}$$

$$P^{total} = P^{hydr}$$

Nernst-Plan

“Two fluid Navier-Stokes Equation”

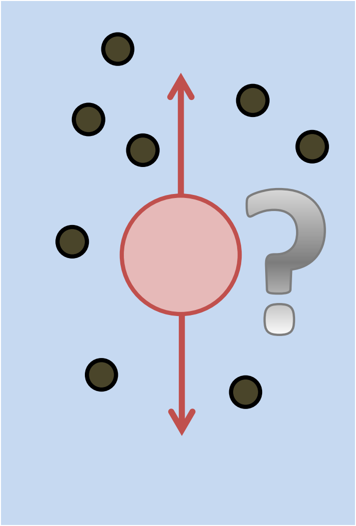
$$\nabla P - \rho_{water}\mathbf{g} - \eta \nabla^2 \mathbf{v}_{water} = \sum_i \frac{c_i}{D_i}\left(\mathbf{v}_i - \mathbf{v}_{water}\right)$$

$$\boxed{\nabla P^{hydr} - \rho_{avg}\mathbf{g} - \eta \nabla^2 \mathbf{v}_{water} = \rho_{elec}\mathbf{E}}$$

Paradox in sedimentation

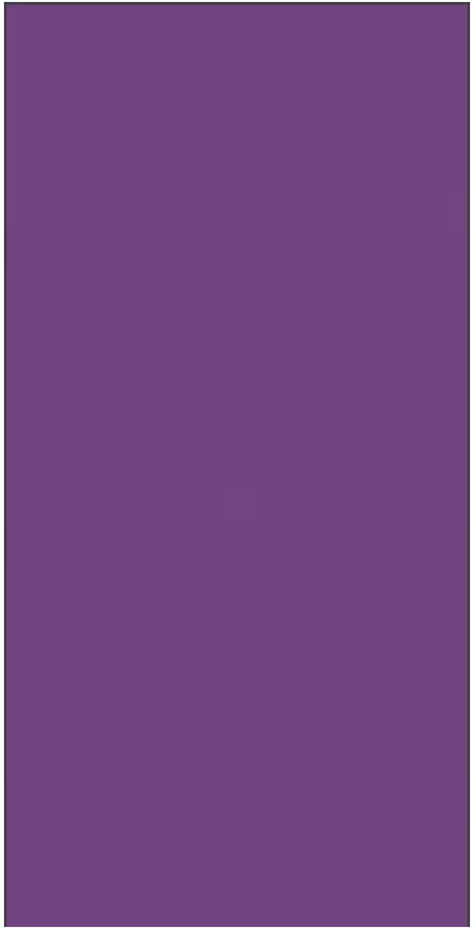
(Theoretical) physicist: at equilibrium, the gravitational force a colloidal particle feels is its mass density minus that of the solvent (the liquid in between)”

(Chemical) engineer: in a mixed system, a particle feels the average, suspension density (*)



(*): and for non-colloidal (larger) particles always

Sedimentation of colloidal particles



Solvent/supernatant

- Three types of colloidal particles (< 1 micron size) with different colors
- All heavier than the solvent
- Purple is mixture
- Not a “solid” sediment that is formed

Thank you for your attention !