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Investigation of transport phenomena in nanochannels and its applications in energy conversion using COMSOL Multiphysics

Speaker: Chih-Chang Chang (張志彰)
Researcher
Green Energy and Environment Research Laboratories

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COMSOL CONFERENCE
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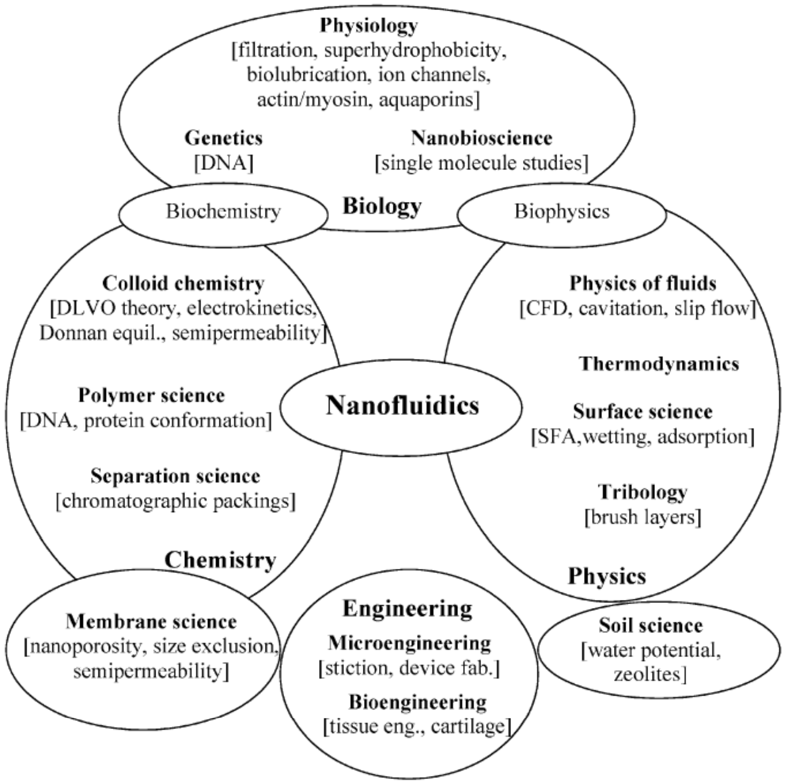
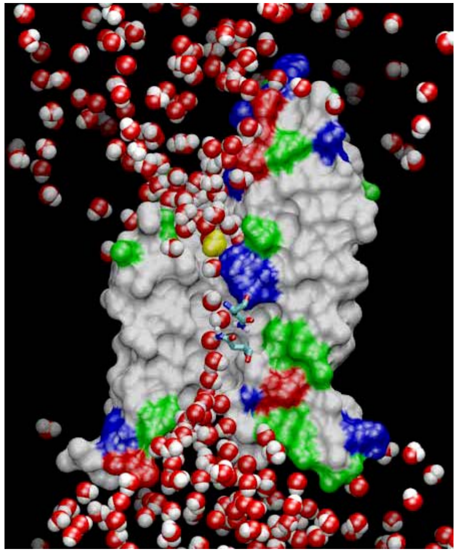
Outline

- Nanaofluidics: fluid/ion transport
- Electrokinetics: electrical double layer
- Modeling using COMSOL Multiphysics
- Physical problems
- Conclusions

What is "Nanofluidics" ?

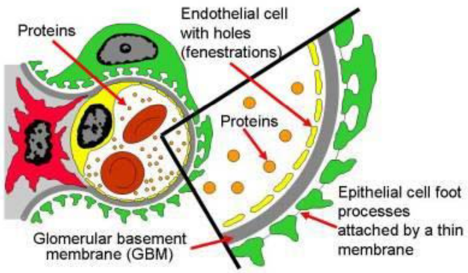


Aquaporins (AQP)



- Slippage
- Electrostatic gate

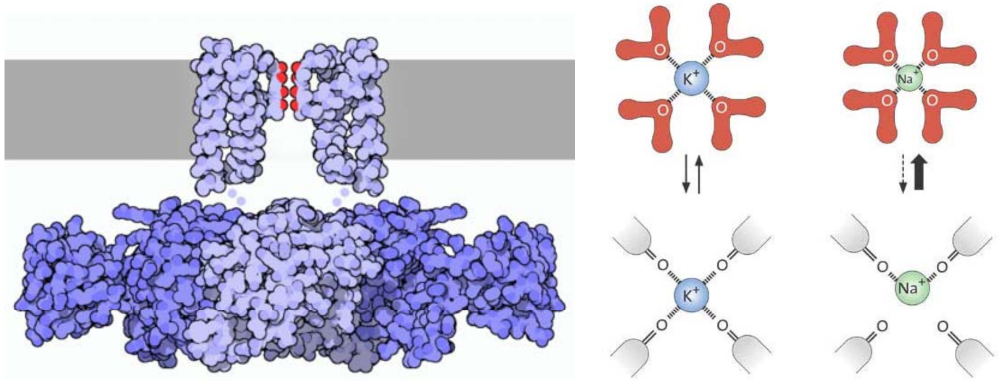
Kidney



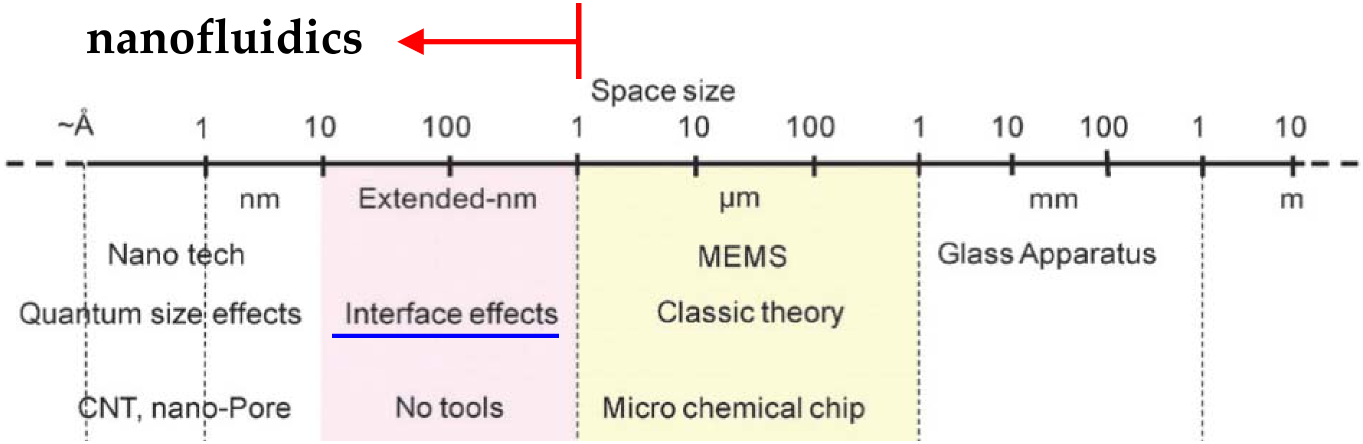
Electrostatic repulsion of proteins

Glomerular proteinuria

Potassium channel



Engineered Nanofluidics



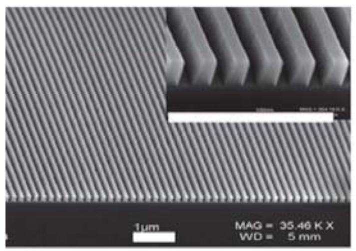
Tsukahara *et al.*, *Chem. Soc. Rev.* **39,** 1000 (2010).

New nanofluidics (engineered nanofluidics):

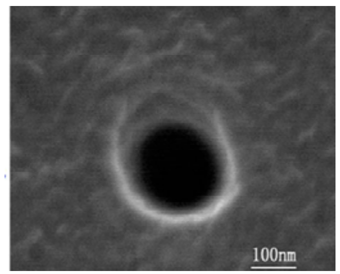
1. **Well-designed and controlled nanochannels** are ideal physical modeling systems to study fluidics in a precise manner.

2. Learning **new science** using **controlled regular nanospaces**.

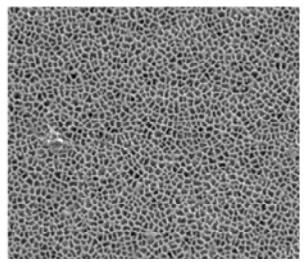
Silica



PET



AAO



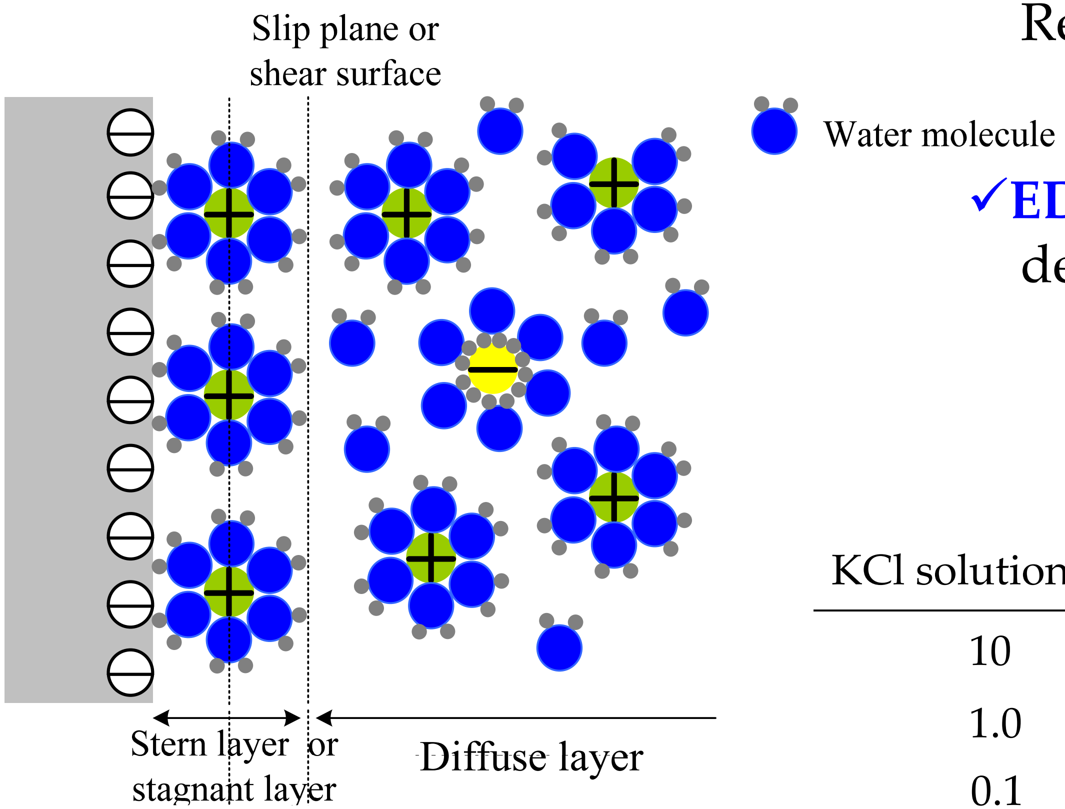
Electrokinetics

✓**Electrokinetics** refers to transport phenomena related to the **non-electroneutral EDL**, which is created to neutralize the **surface charges** produced on surface.

✓**Surface charges** are produced by the dissociation of surface functional groups:

Reactions: $AH \leftrightarrow A^- + H^+$

$AH_2^+ \leftrightarrow AH + H^+$



✓**EDL thickness** (i.e., Debye length) is dependent on salt concentration c_0 :

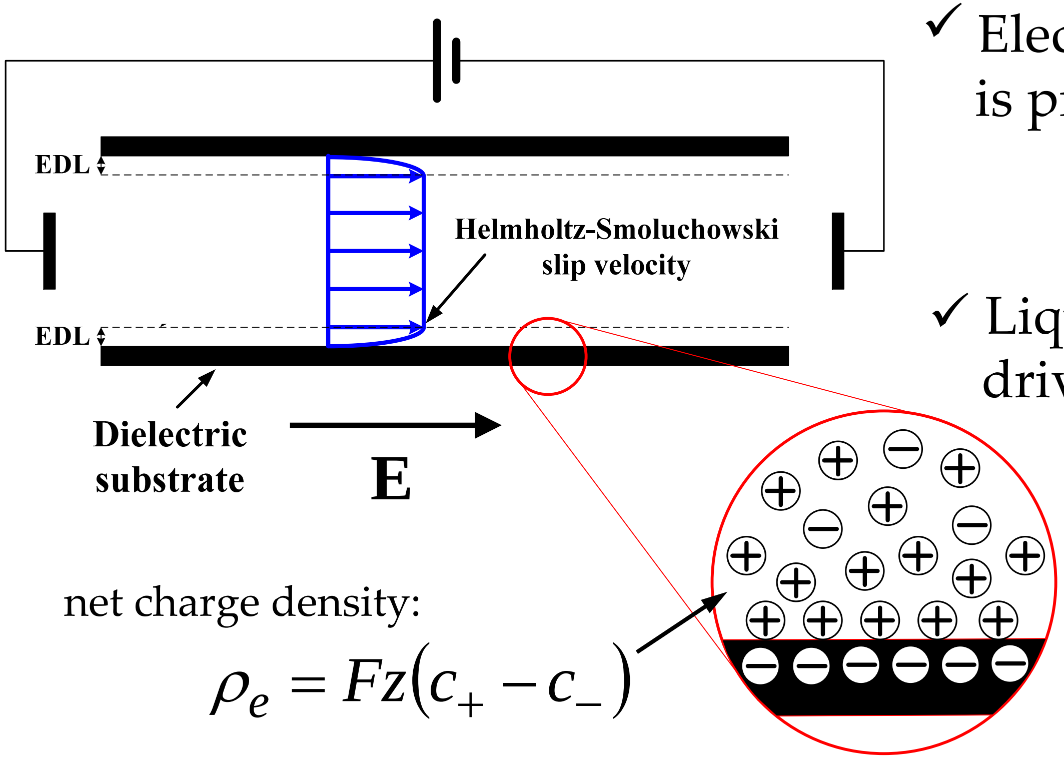
$$\lambda_D = \sqrt{\frac{\varepsilon_f \varepsilon_0 RT}{2z^2F^2c_0}} \propto \frac{1}{\sqrt{c_0}}$$

KCl solution (mM)	λ_D (nm)
10	3
1.0	10
0.1	30

DI water: 300nm

Electro-osmosis

Electro-osmosis refers to the movement of liquid relative to a stationary charged surface under an external electric field.



net charge density:

$$\rho_e = Fz(c_+ - c_-)$$

- ✓ Electrical body force (Coulomb force) is produced within EDL:

$$\mathbf{F}_e = \rho_e \mathbf{E}$$

- ✓ Liquid motion outside of EDL is driven by viscous diffusion

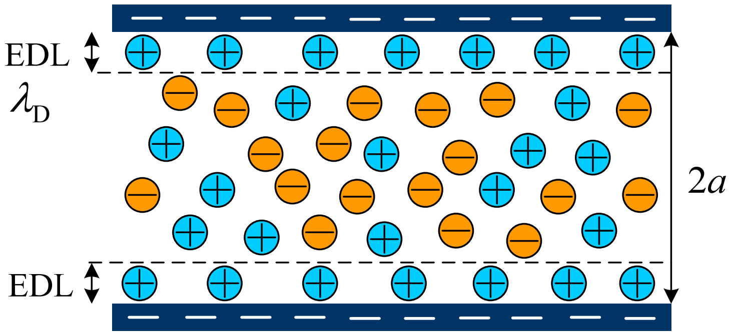
- ✓ Plug-like flow

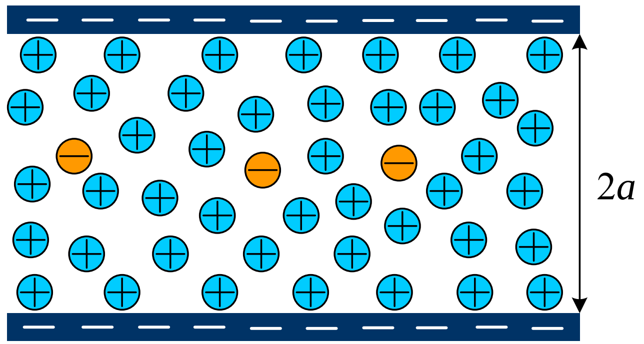
Electro-osmotic flow (EOF) in a thin EDL microchannel

Nanochannel: ion selectivity

Microscale: $a > 1\,\mu m >> \lambda_D$

Nanoscale: $a < 1\,\mu m \sim \lambda_D$

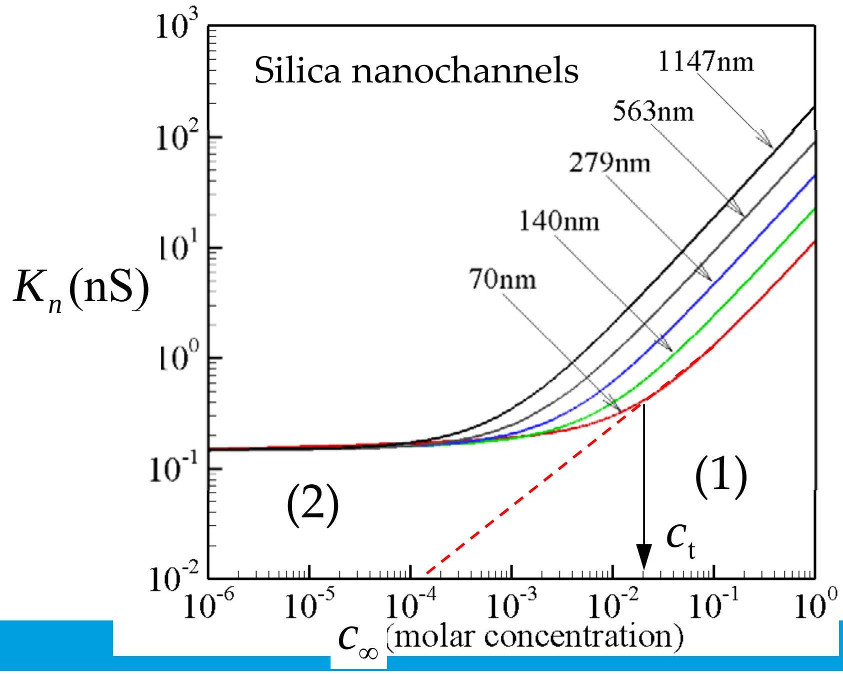




$$K_n = \frac{2wh}{l} c_\infty (\Lambda_+ + \Lambda_-) + \frac{2w}{l} \frac{|\sigma|}{zF} \Lambda_+$$

(1) bulk conductance

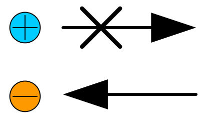
(2) Surface conductance

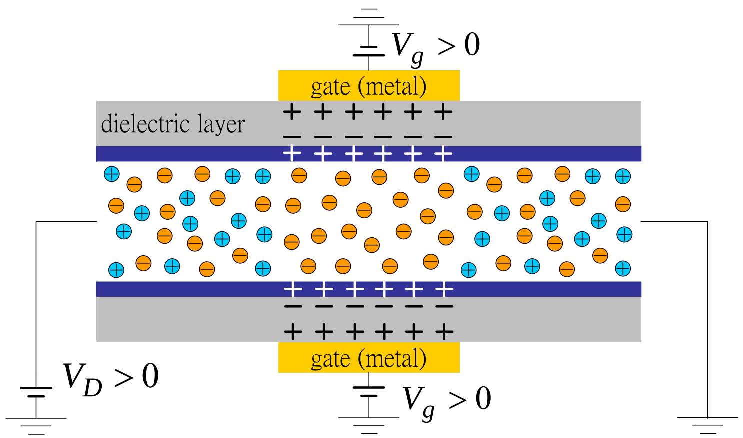


- ion-transport/ion-current control
- electrical sensing
- separators: energy conversion

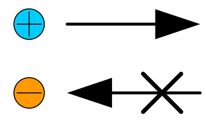
Nanofluidic transistor

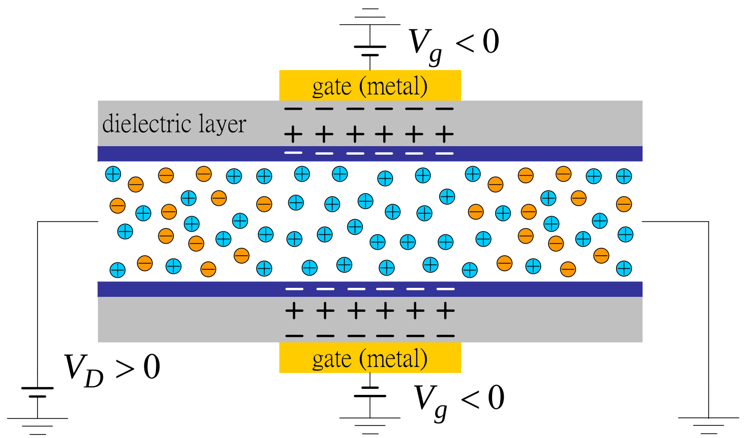
$\Delta V_g = V_g - V_D/2 > 0$



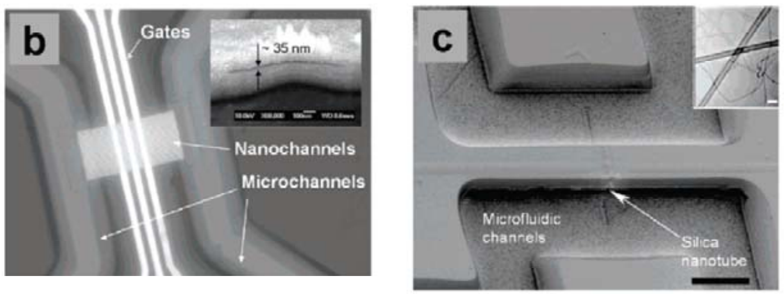


$\Delta V_g < 0$





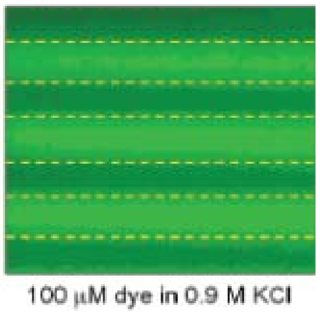
Its function looks like a metal-oxide-semiconductor field-effect transistor (MOSFET).



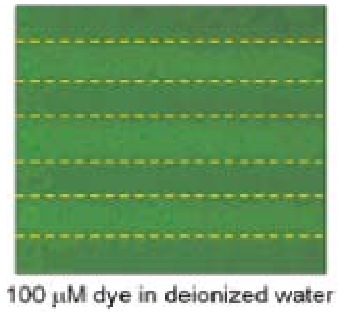
R. Karnik *et al.*, ***Nano Lett.* 5**, 943 (2005)

Negatively charged dye: exclusion effect

Thin EDL



Thick EDL



Mathematical Model (cont.)

Flow field: incompressible Navier-Stokes equation (continuum theory)

$$\mathbf{u}\cdot\nabla\mathbf{u} = -\nabla p + \mu\nabla^2\mathbf{u} + \mathbf{F}_e$$

$$\nabla\cdot\mathbf{u} = 0$$

where $\mathbf{F}_e = -\rho_e \nabla\phi$

Poisson-Nernst-Planck model

Electric field: Poisson equation (electrostatics)

$$\nabla^2\phi = -\frac{\rho_e}{\varepsilon_f \varepsilon_0}$$

where $\rho_e = F\sum_i z_i C_i$

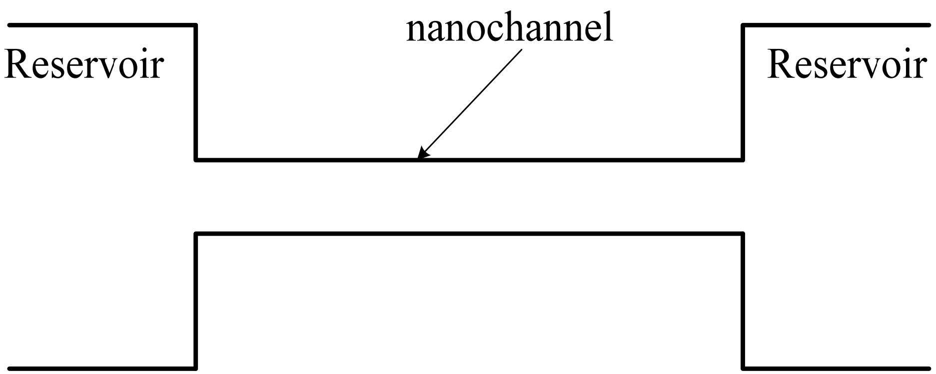
Ionic concentration field:

$$\mathbf{j}_i = -v_i z_i F c_i \nabla\phi - D_i \nabla c_i + c_i \mathbf{u}$$ **: Nernst-Planck equation**

$$\nabla\cdot\mathbf{j}_i = 0$$ **: Species transport equation**

Mathematical Model

Geometry:



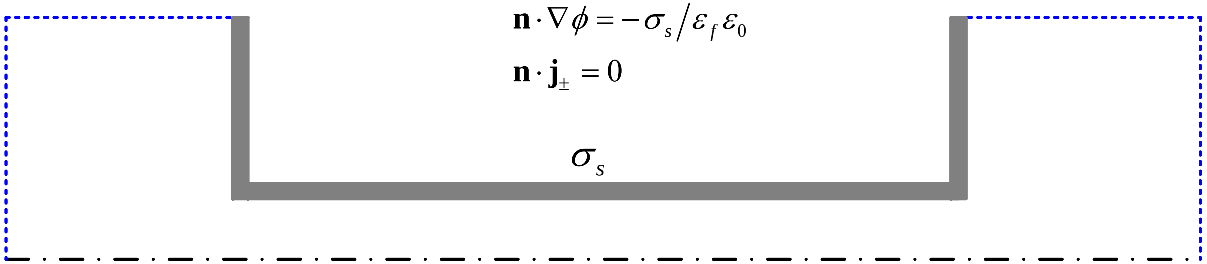
Boundary condition:

$\mathbf{n}\cdot\nabla\mathbf{u}=0$
$\mathbf{n}\cdot\nabla\phi=0$
$\mathbf{n}\cdot\nabla c_{\pm}=0$

$\mathbf{u}=0$
$\mathbf{n}\cdot\nabla\phi=-\sigma_s/\varepsilon_f\varepsilon_0$
$\mathbf{n}\cdot\mathbf{j}_{\pm}=0$

$\mathbf{n}\cdot\nabla\mathbf{u}=0$
$\mathbf{n}\cdot\nabla\phi=0$
$\mathbf{n}\cdot\nabla c_{\pm}=0$

$p=p_L$
$\phi=\phi_L$ or $\mathbf{n}\cdot\nabla\phi=0$
$c_{\pm}=c_0$

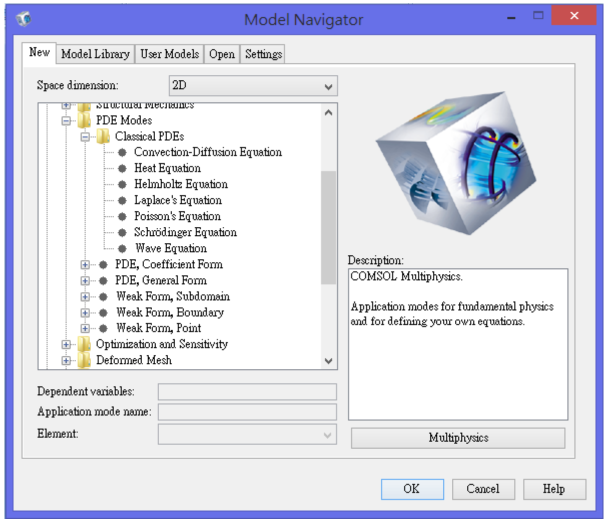


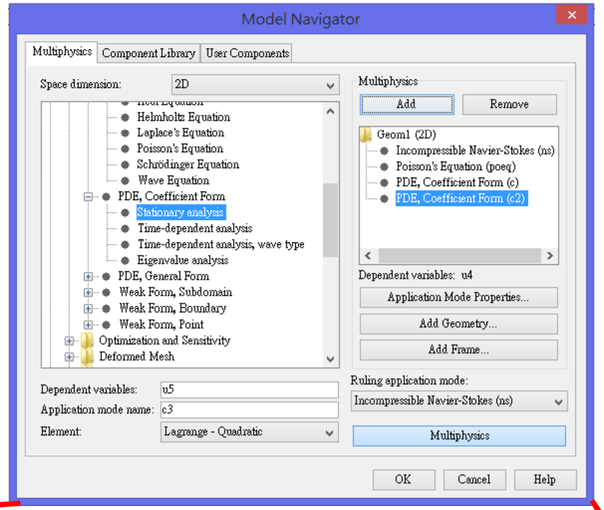
$p=p_R$
$\phi=\phi_R$
$c_{\pm}=c_0$

Symmetric boundary condition

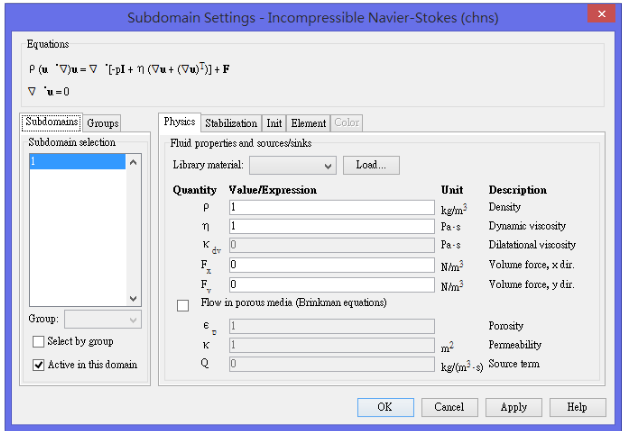
$\mathbf{n}\cdot\nabla\mathbf{u}=0$
$\mathbf{n}\cdot\nabla\phi=0$
$\mathbf{n}\cdot\nabla c_{\pm}=0$

COMSOL Modeling using PDE Mode

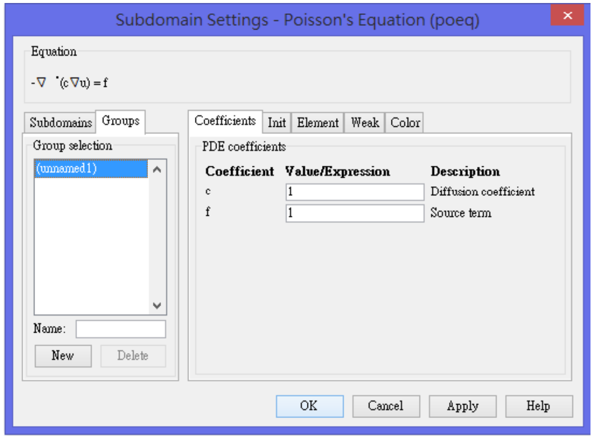




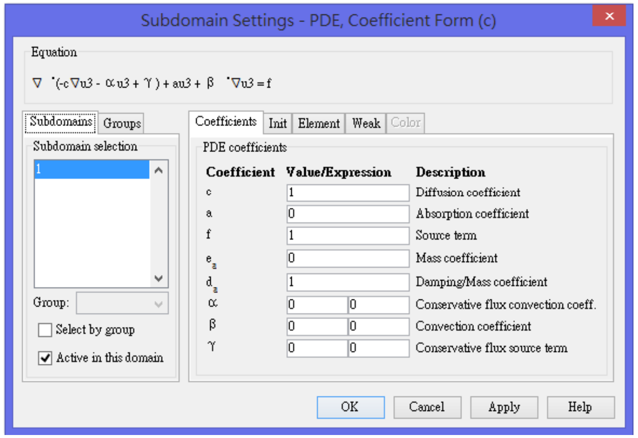
Navier-Stokes eq.



Poisson eq.



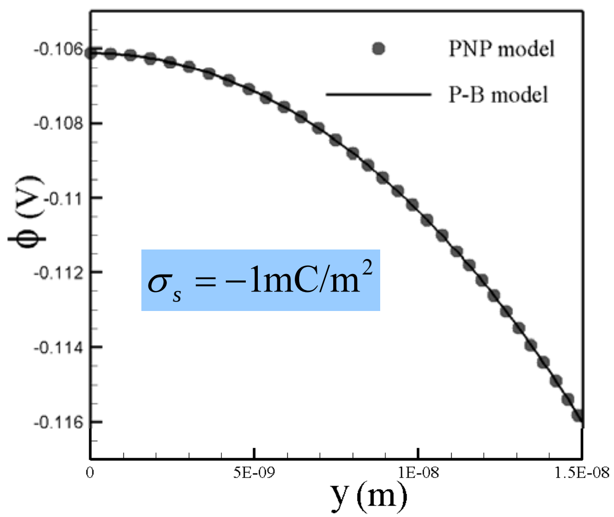
Nernst-Planck eq.

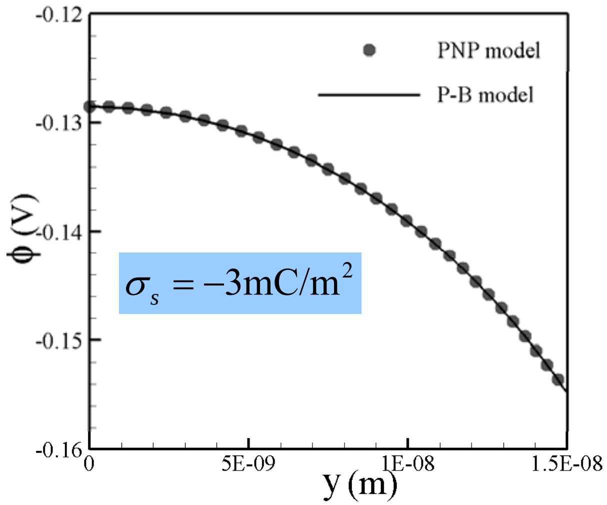


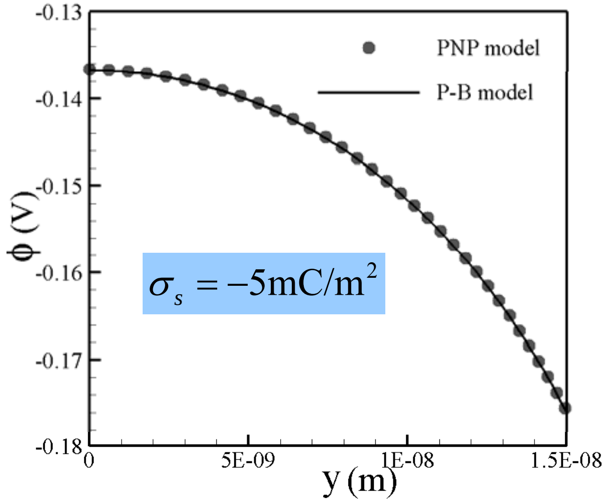
Validation with PB model

MESH: 28000-32000 quadrilateral elements

Results: compared with analytical solution of PB model

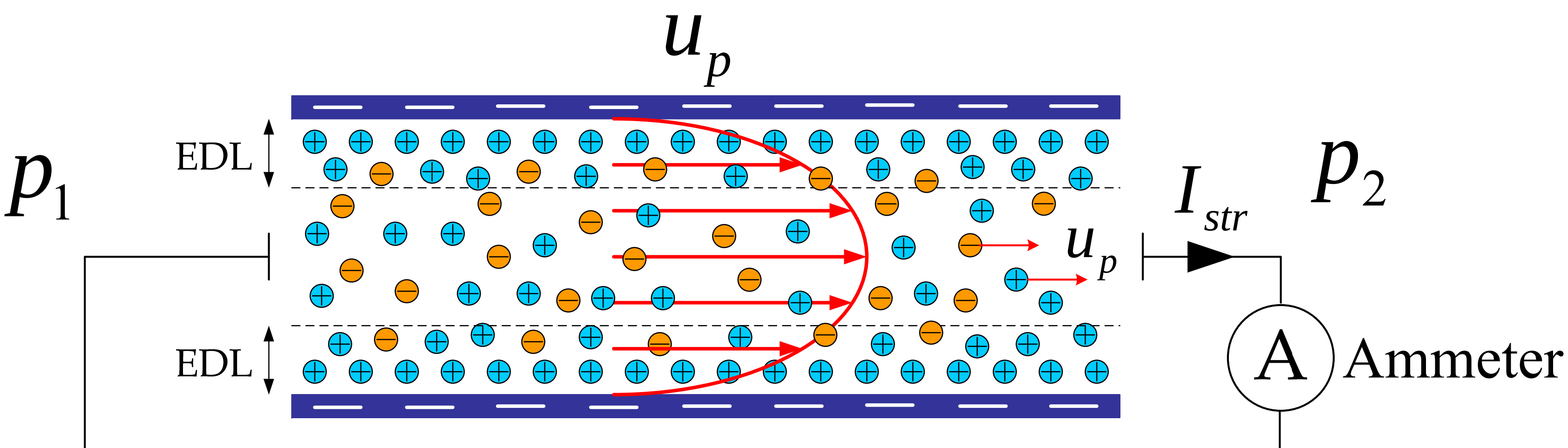






Streaming current

Under a hydrostatic pressure (Δp), the pressure-driven liquid flow carries the charges within EDL towards the downstream end and results in an electrical convection current, namely the ***streaming current***.

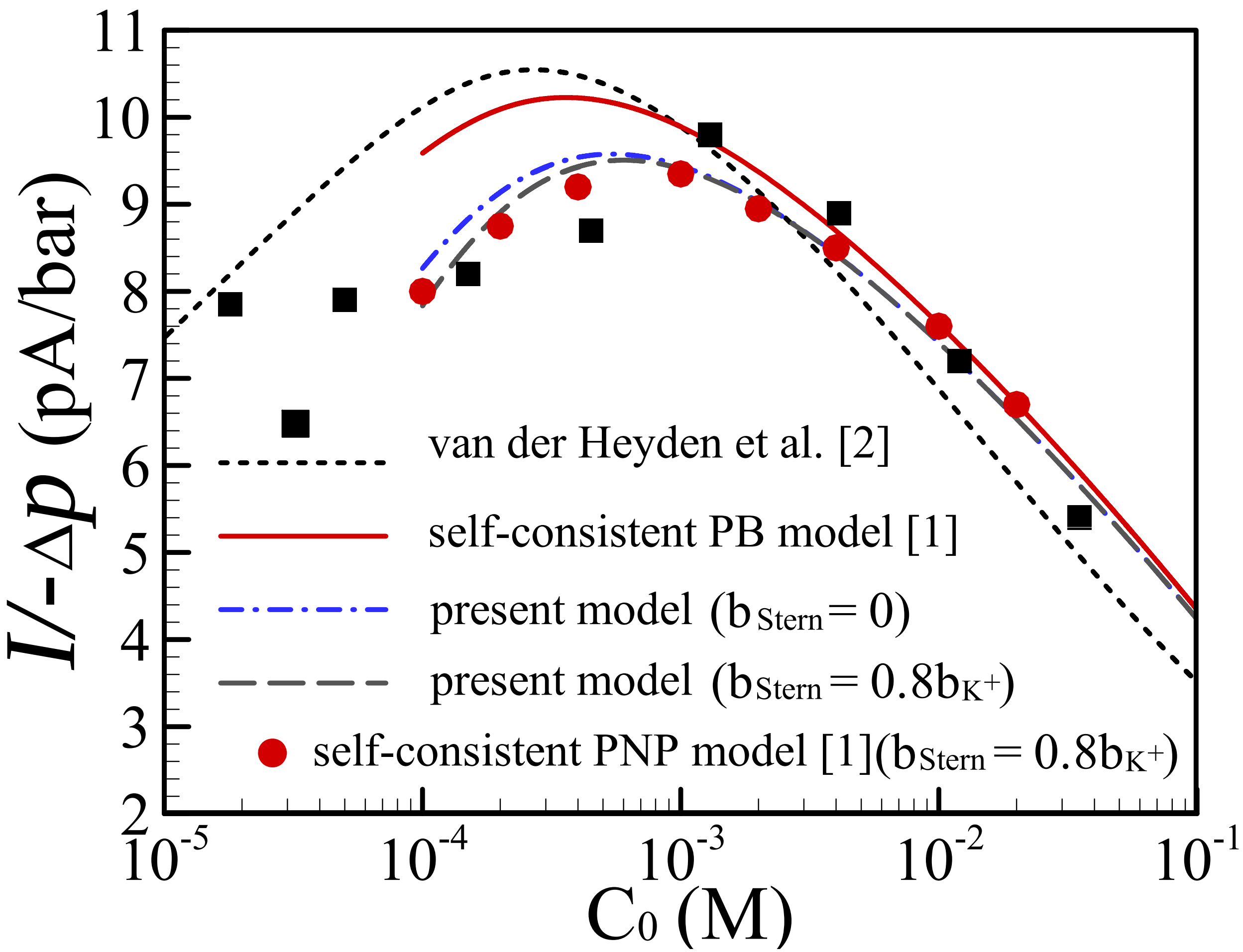


$$\Delta p = p_2 - p_1$$

Streaming current: $I_{str} = S_{str}\left(-\Delta p\right) = \int_A \rho_e u_p dA$

Streaming current in silica nanochannels

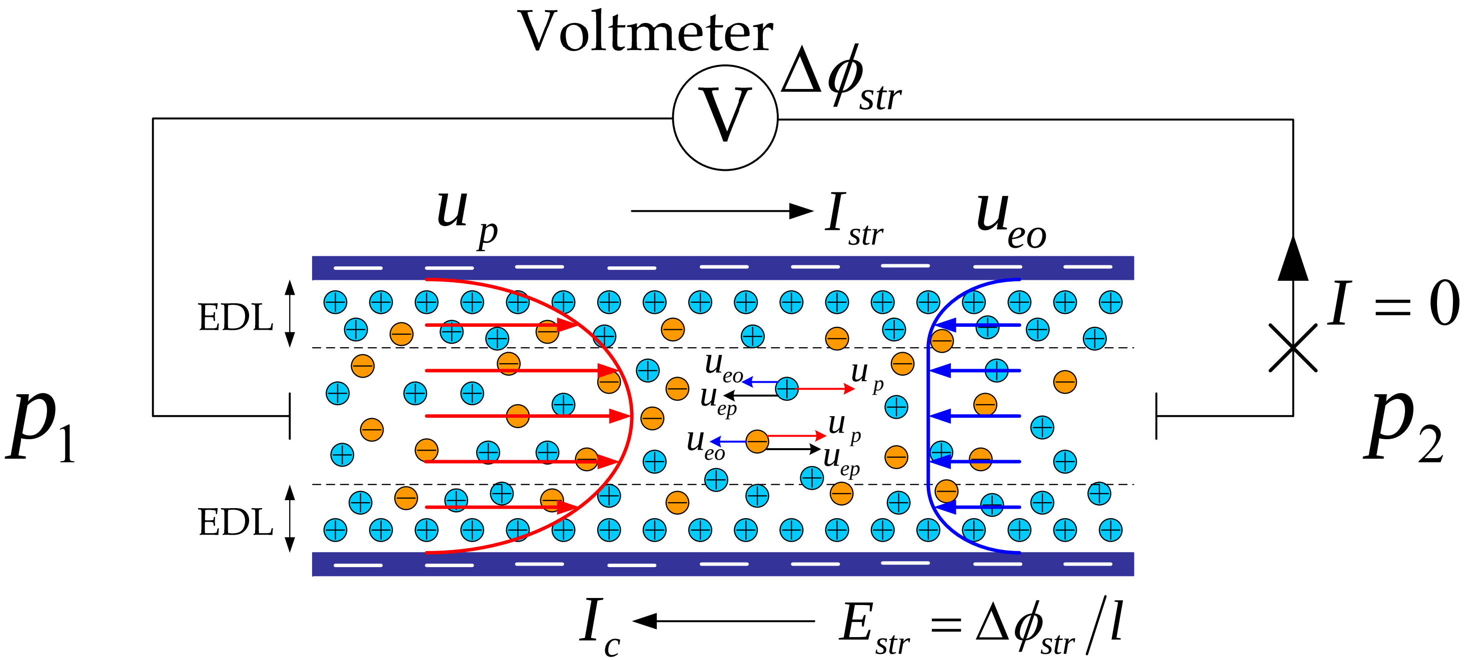
140 nm silica nanochannel



<u>C.-C. Chang</u> and R.-J. Yang, ***J. Colloid Interface Sci.*** **339**, 517 (2009).

Streaming potential

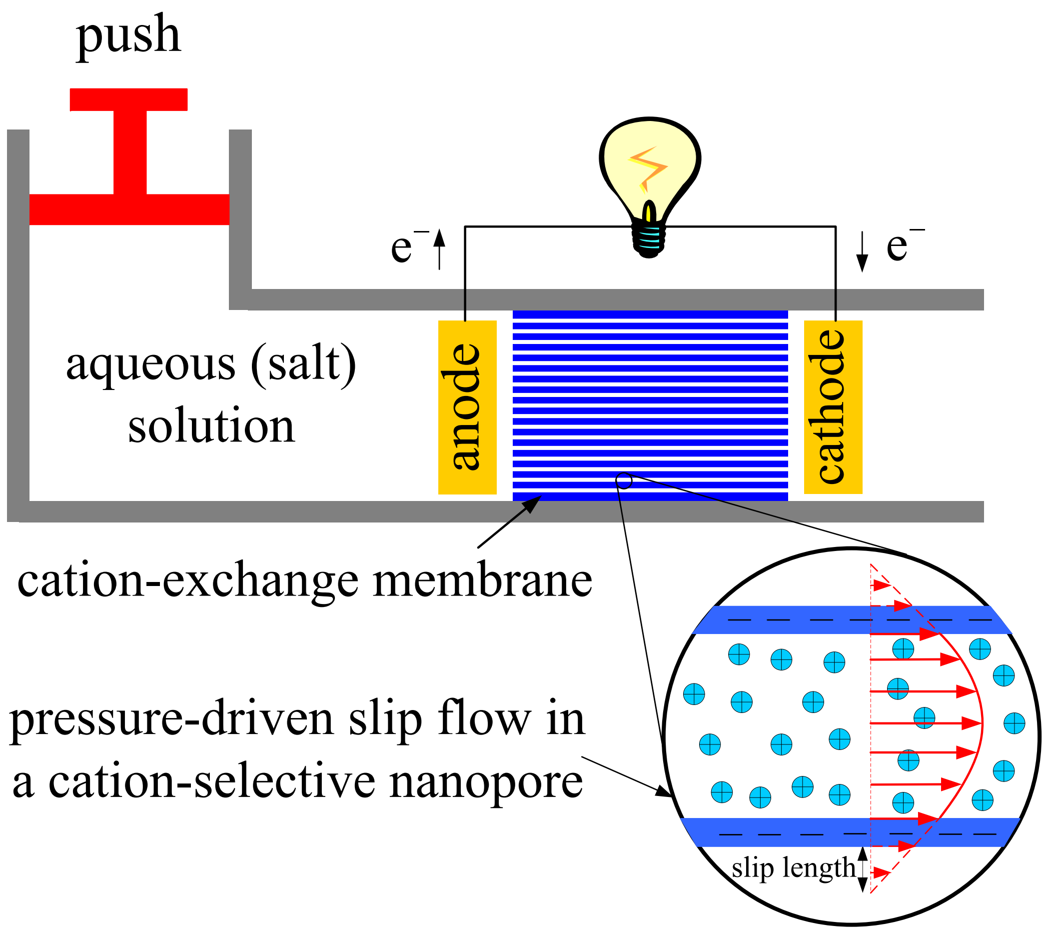
At open-circuit condition (i.e., zero-current condition), the charges accumulate at the downstream end and then an electrical potential difference called the ***streaming potential*** (i.e., open-circuit voltage, OCV) is produced.



Streaming potential: $$I = I_{str} + I_c = 0 \Rightarrow \Delta\phi_{str} = \frac{S_{str}(-\Delta p)}{K_c}$$

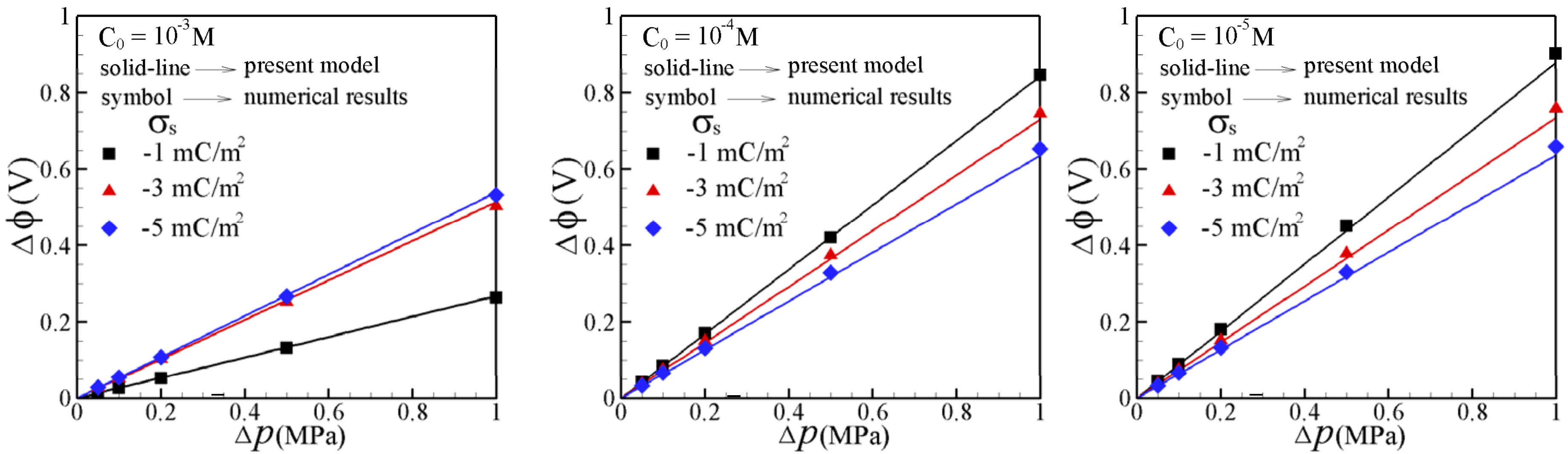
Electrokinetic energy conversion

Electro-kinetic battery refers to the external electronic load driven by the electric power from streaming current/potential.

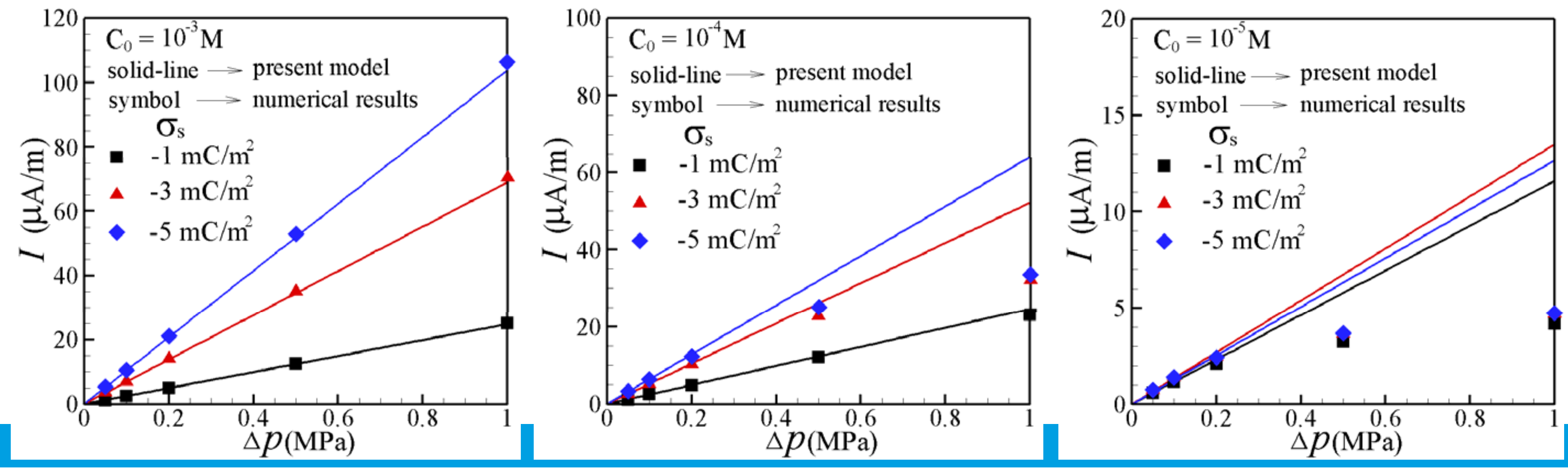


Open circuit voltage verus Short-circuit current

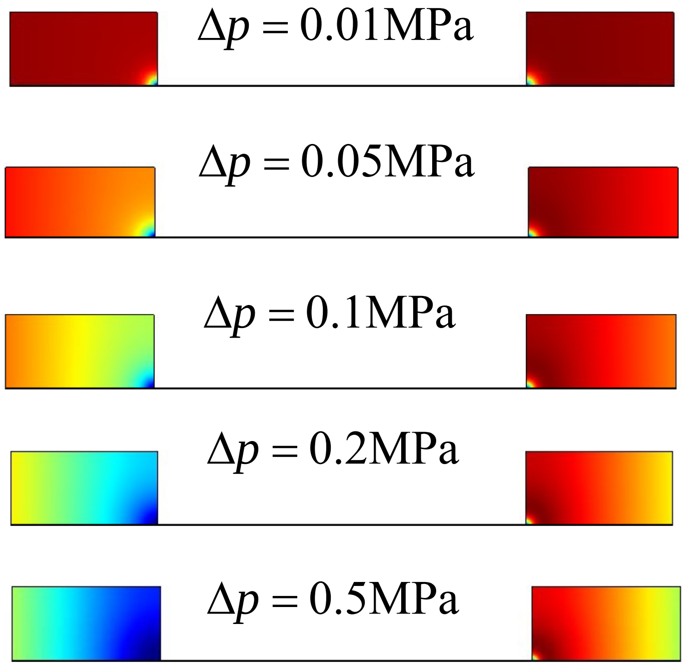
Open-circuit voltage

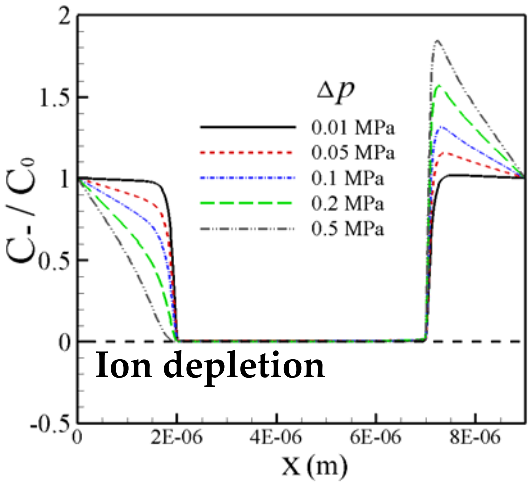


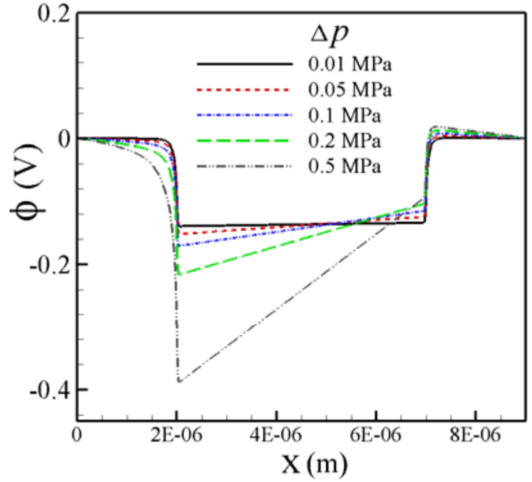
Short-circuit current



Short-circuit condition: Concentration polarization







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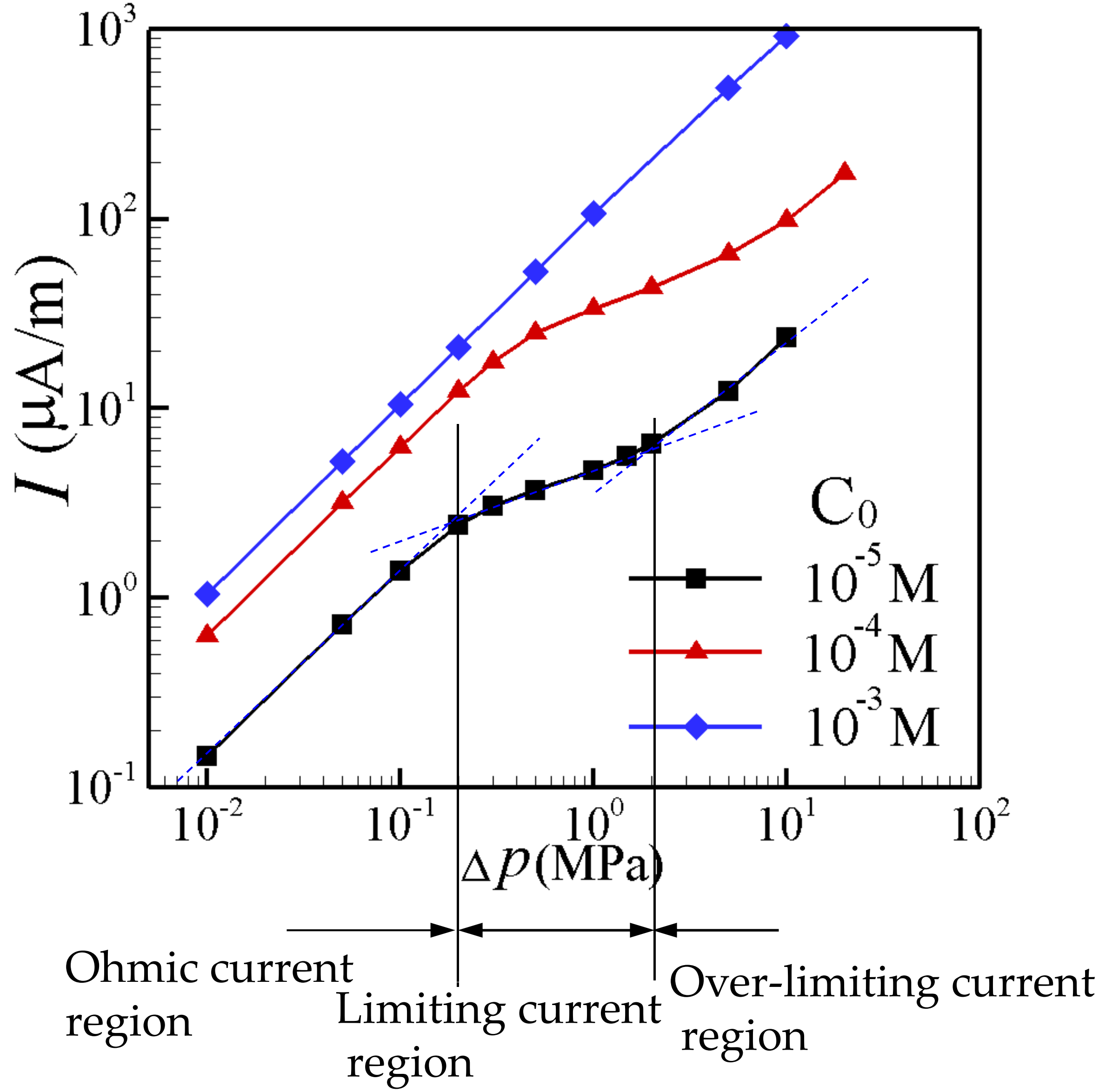
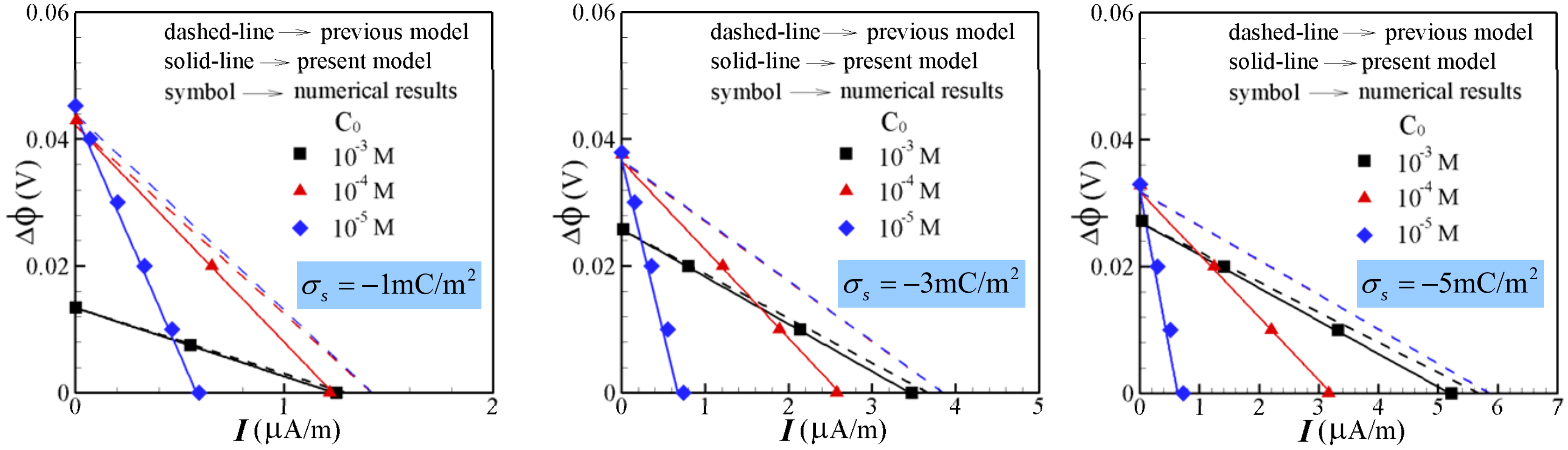
Numerical results: I-P curve

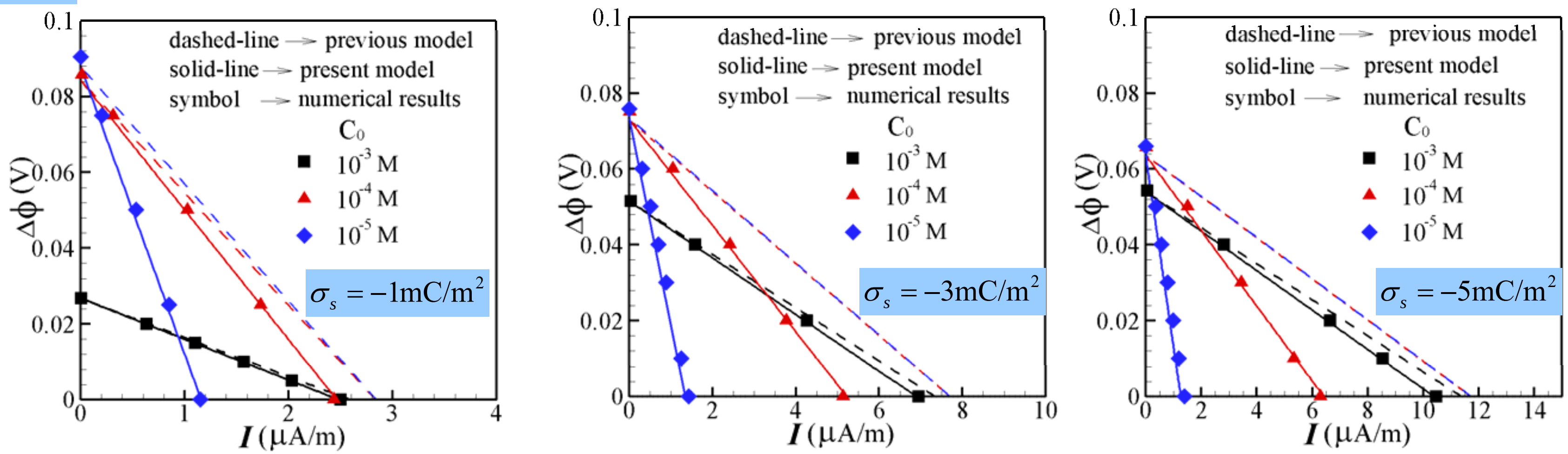


Numerical results: I-V curve

$\Delta p = 0.05\text{MPa}$

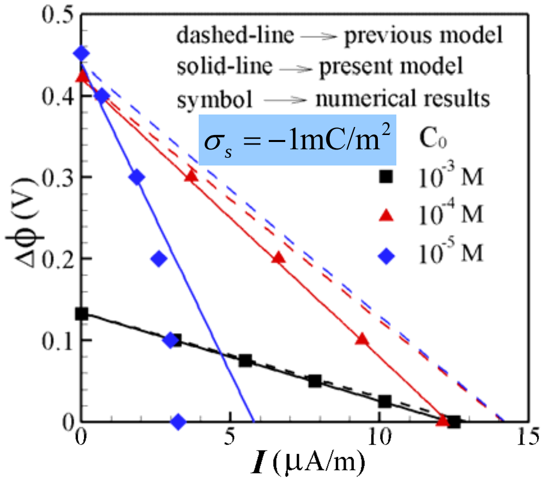


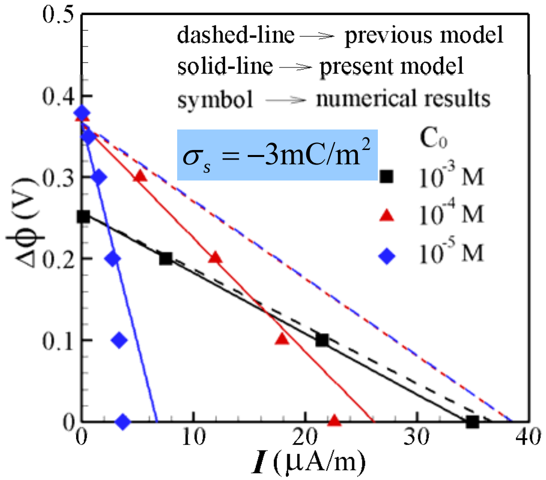
$\Delta p = 0.1\text{MPa}$

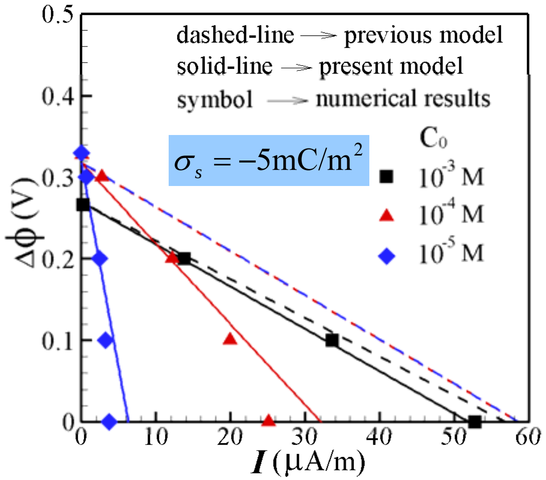


Numerical results: I-V curve

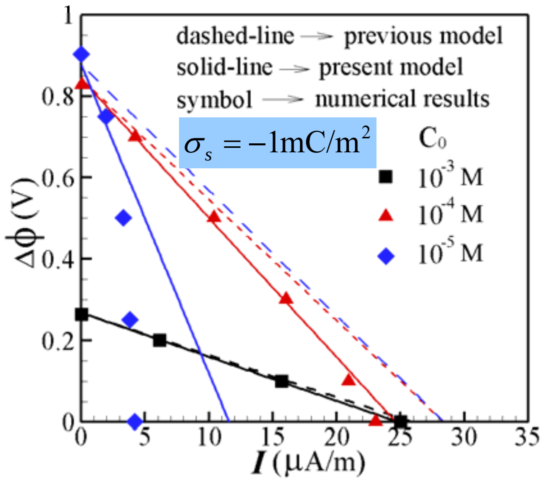
$\Delta p = 0.5\text{MPa}$

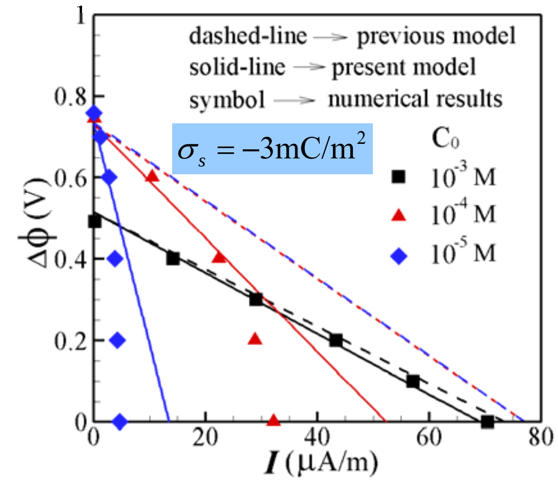


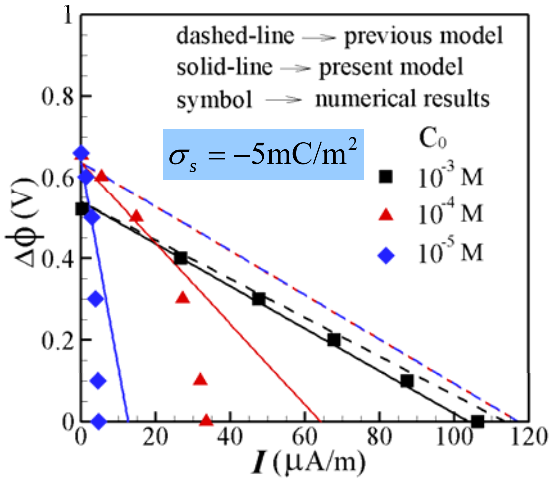




$\Delta p = 1.0\text{MPa}$

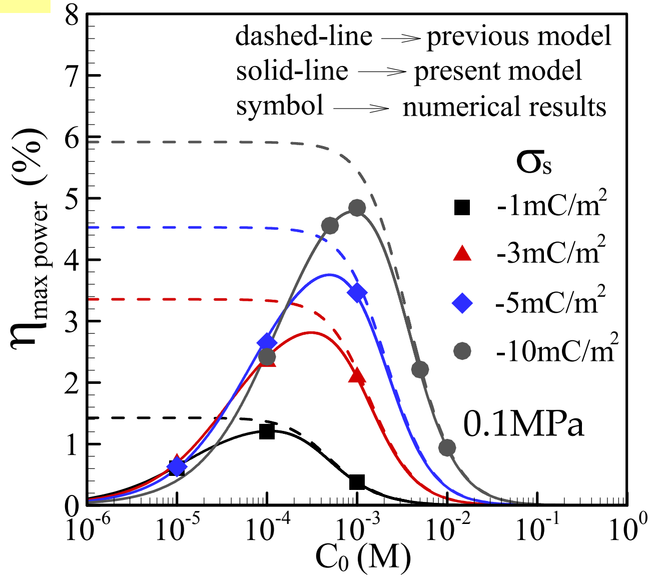




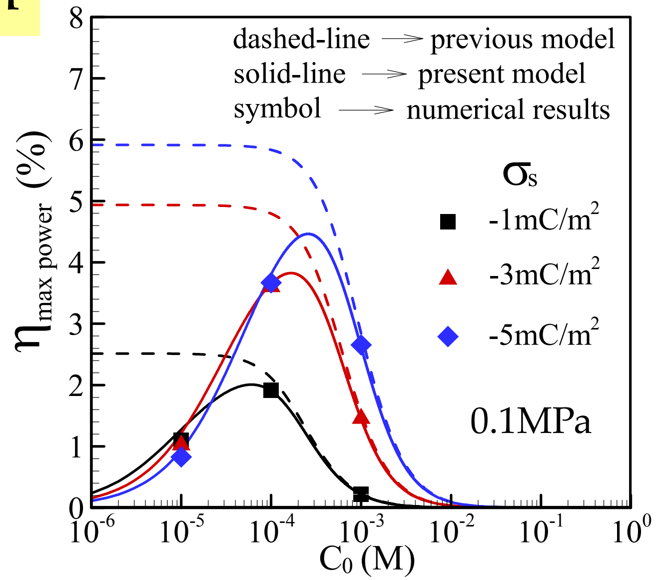


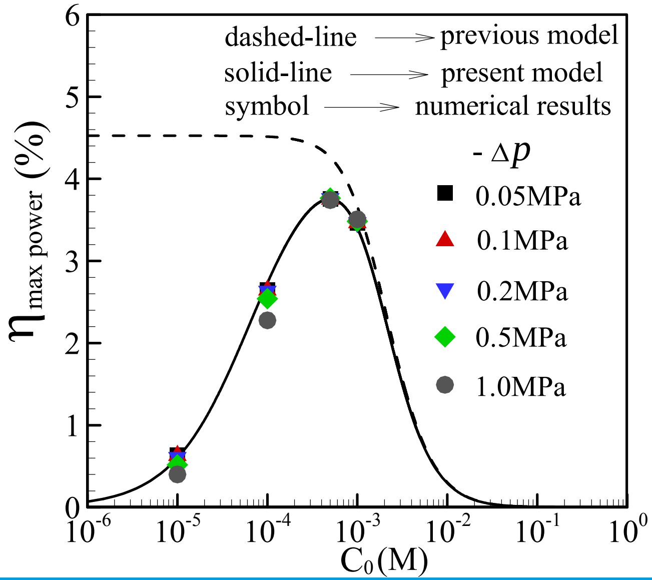
Conversion efficiency

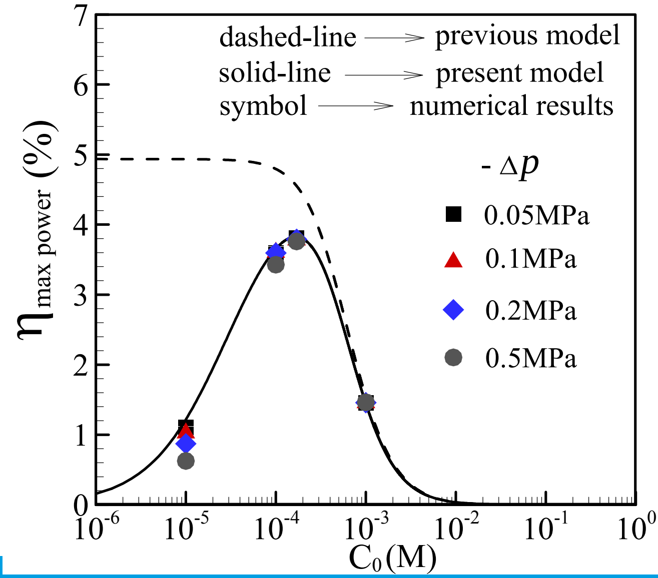
30 nm



60 nm





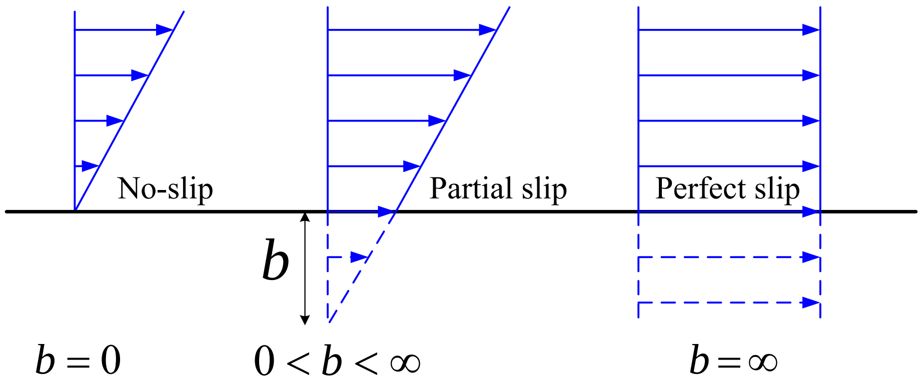


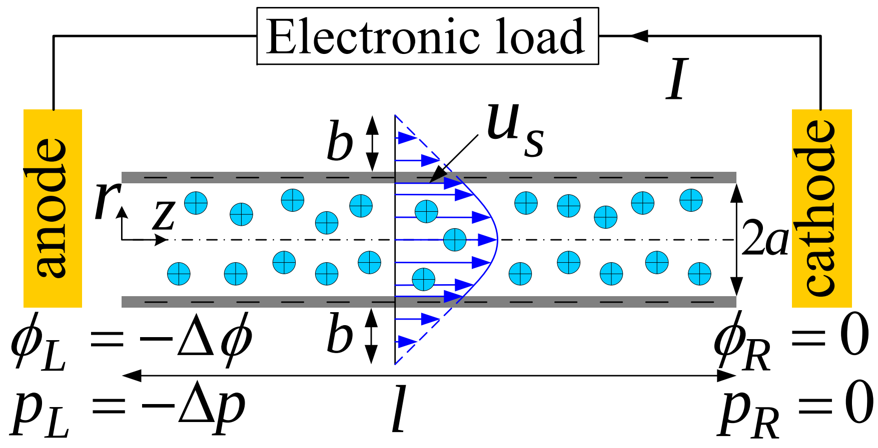
Conversion efficiency-slippage

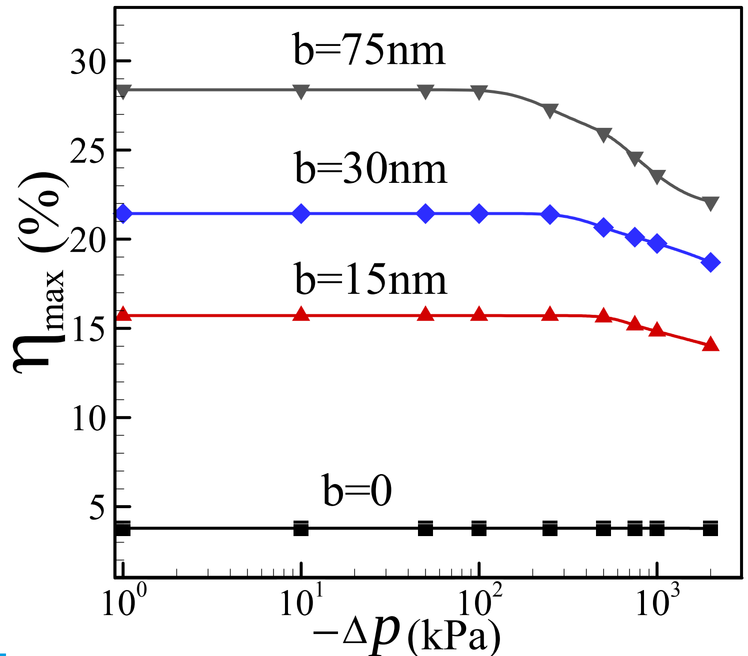
- **Navier slip velocity:**

$$u_s = b\frac{\partial u}{\partial y}$$

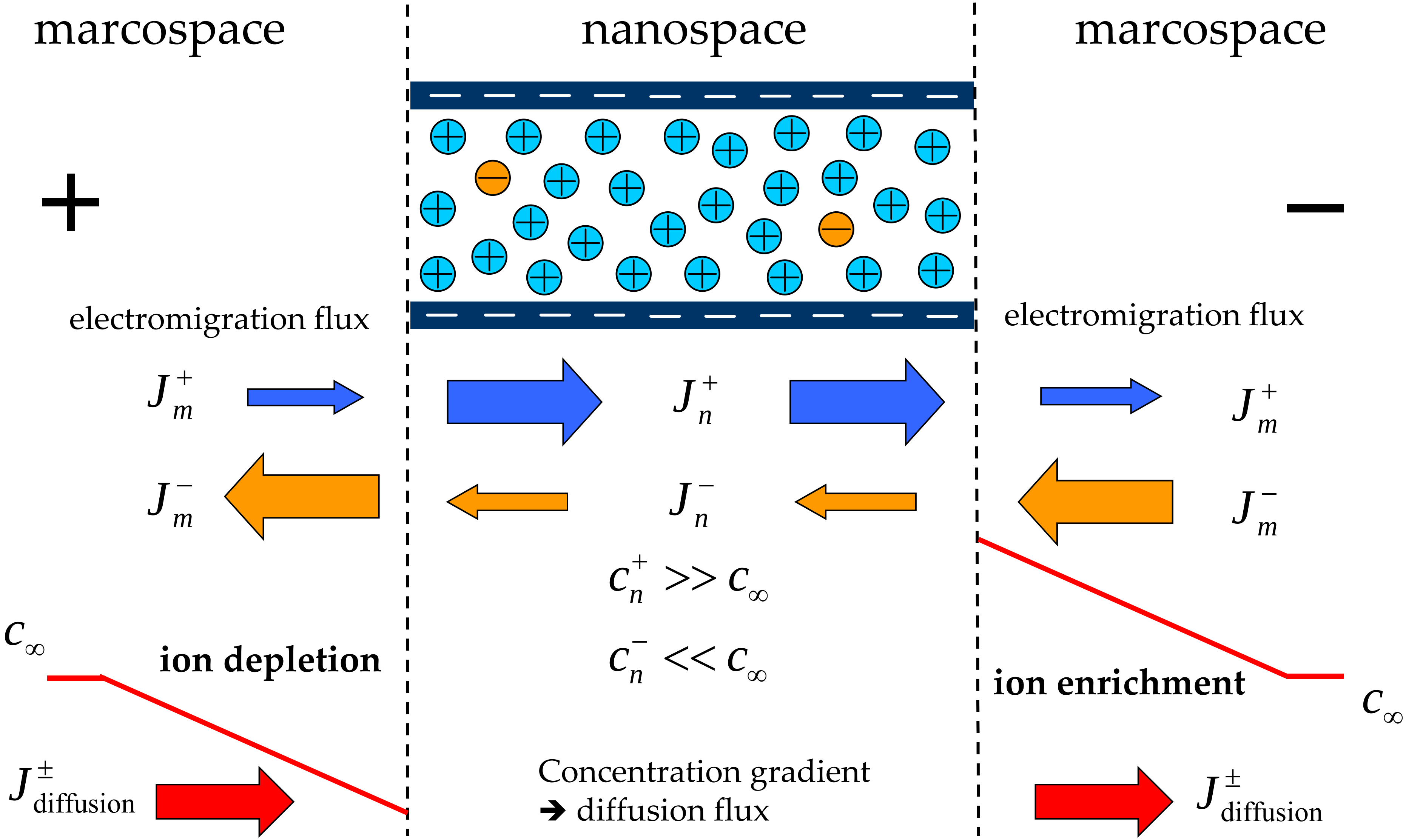
where b is the slip length







Ion concentration polarization (ICP) - nonequilibrium phenomenon at interface



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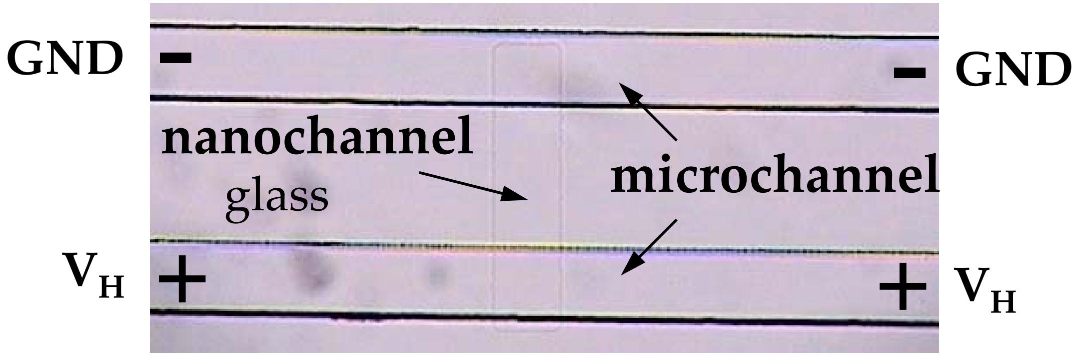
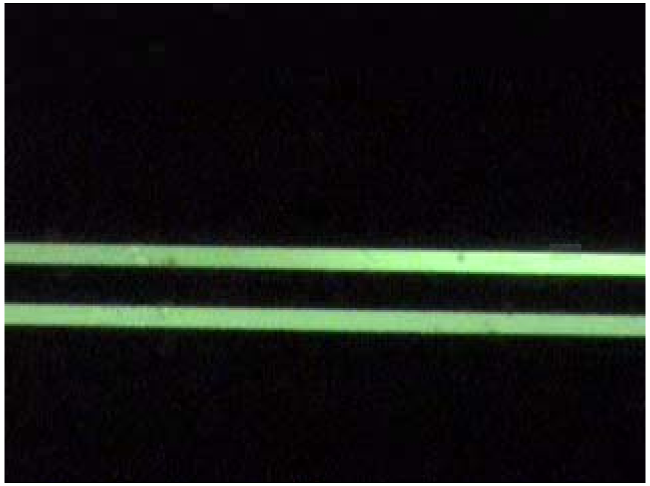
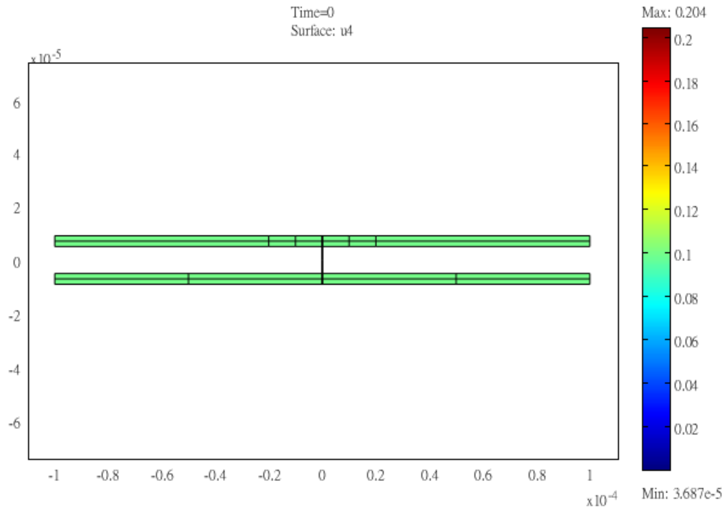
Ion depletion and enrichment

~ 60 nm nanochannel

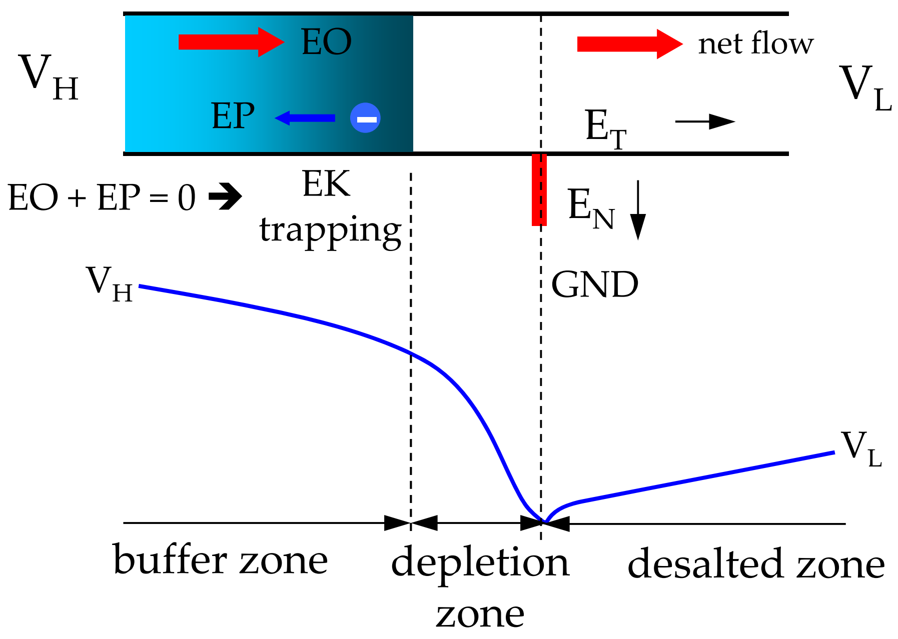


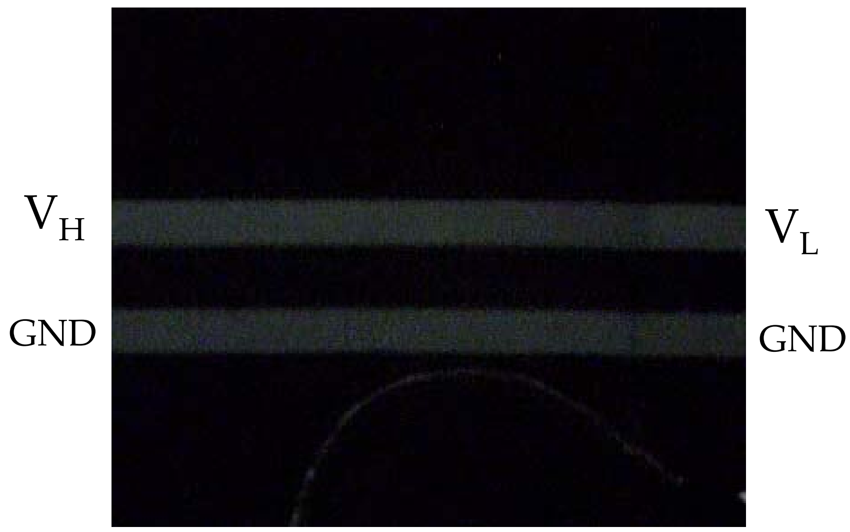


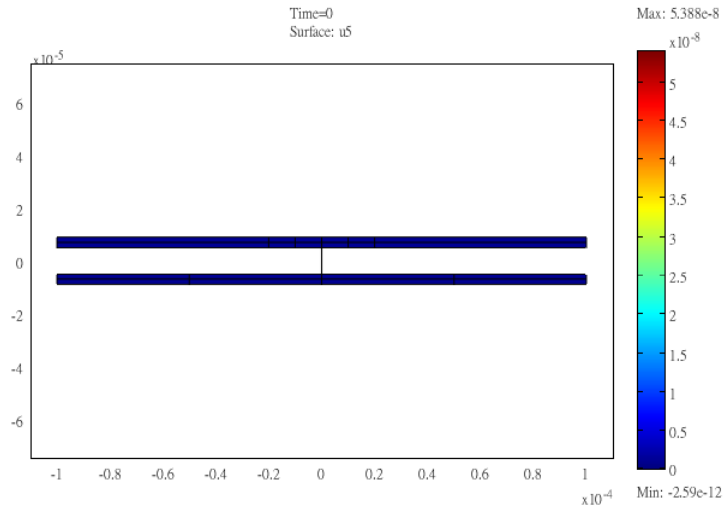


Simulation using COMSOL

Nanofluidic sample preconcentration/ desalination



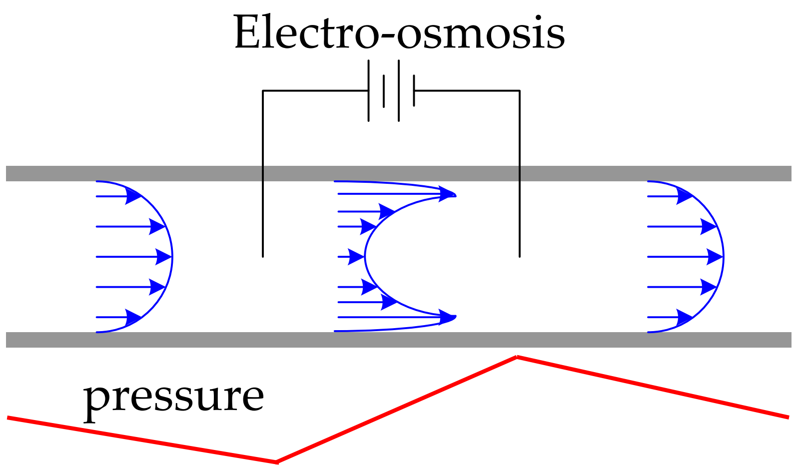


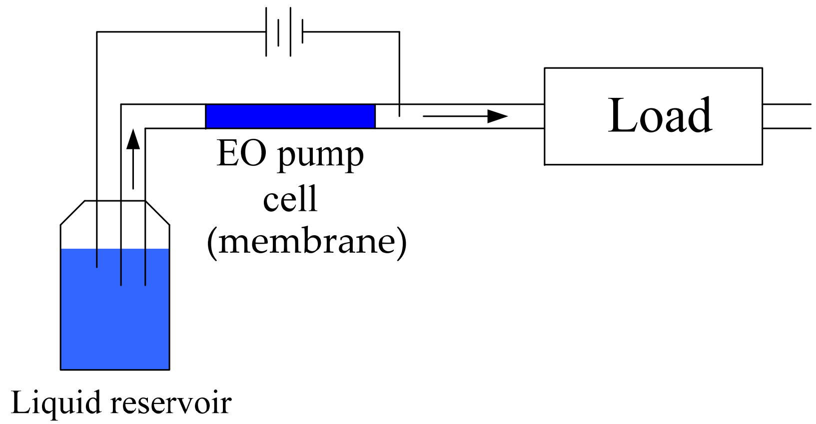


Simulation using COMSOL

Applications:
1. bio-sample preconcentration
2. species separation
3. sea water desalination

Electroosmotic pump using a conical-nanopore membrane (cont.)

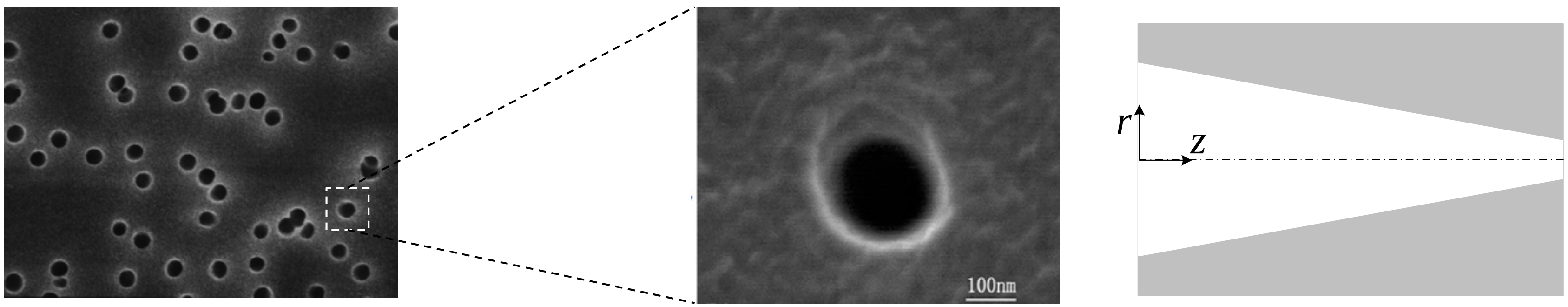




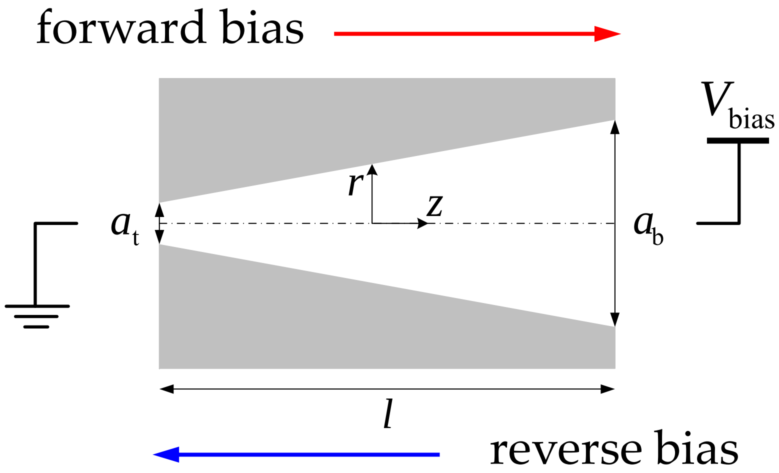
Electric power ➔ hydraulic power

Track-etched PET membrane

A single conical-shaped nanopore

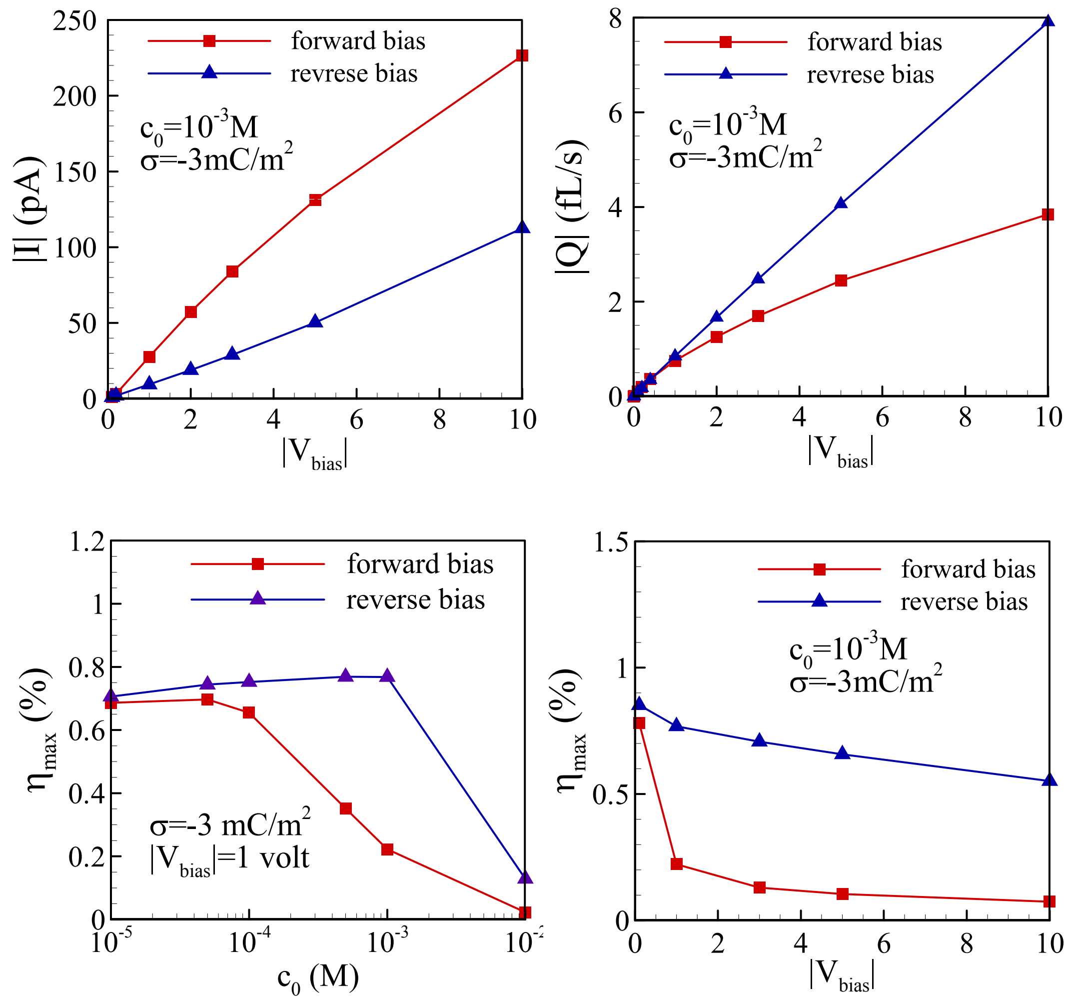


Electro-osmotic pump using a conical-nanopore membrane



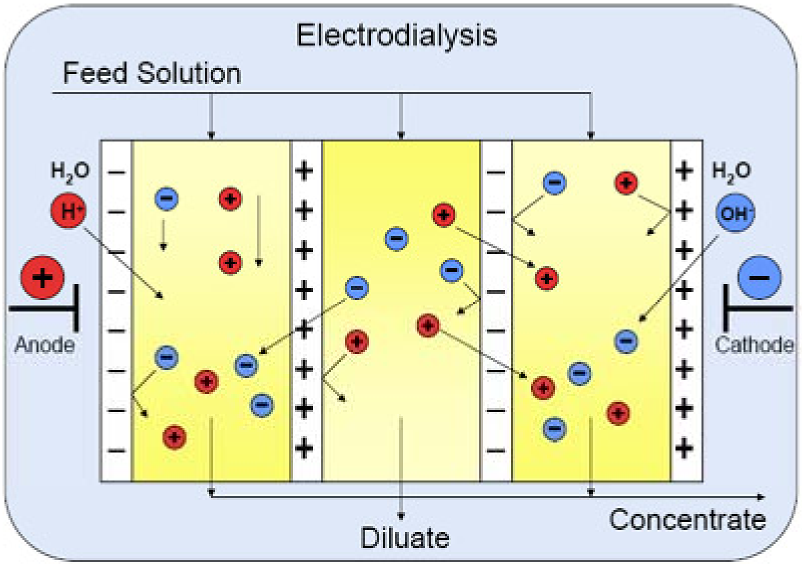
- **Forward bias:** ion-enrichment
  - ➔ resistance is decreased.
  - ➔ decreased electric field.
  - ➔ lower pumping efficiency.
- **Reverse bias:** ion-depletion
  - ➔ resistance is increased.
  - ➔ increased electric field.
  - ➔ amplified EK flow.
  - ➔ better pumping efficiency.

Current rectification | **Flow rectification**



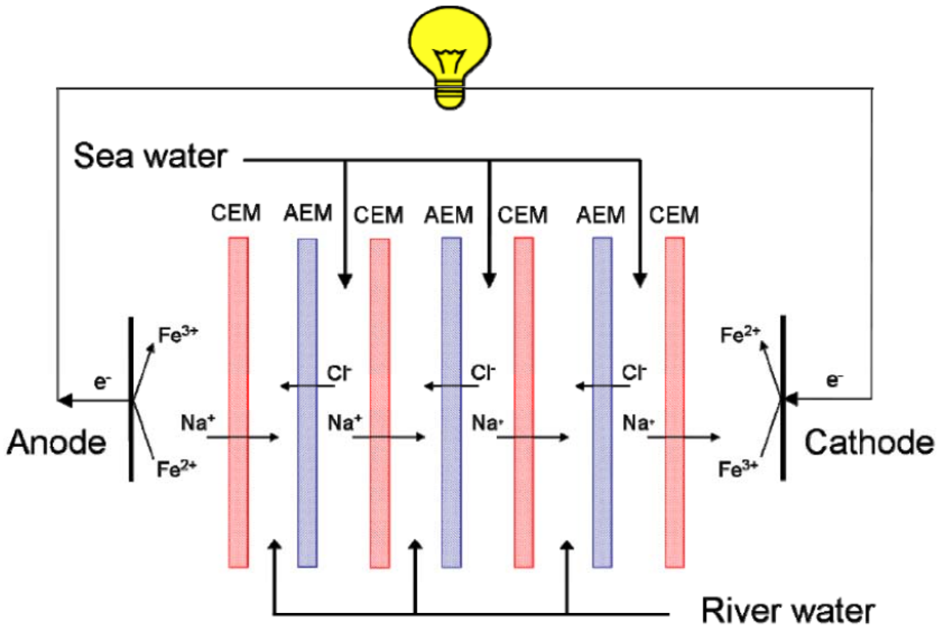
Reverse electro-dialysis (RED)

Electrodialysis



Electricity ➔
Gibbs free energy of mixing

RED

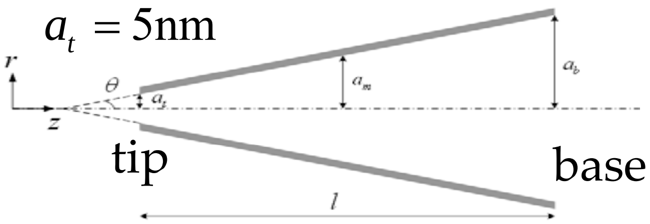


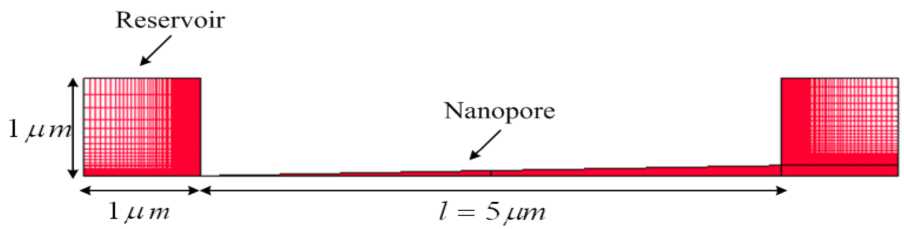
Gibbs free energy of mixing
➔ Electricity

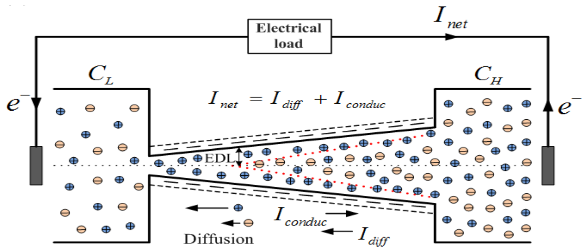
Diffusion current/potential

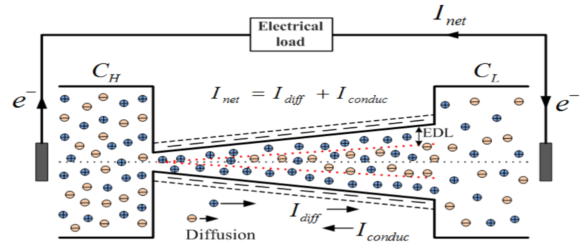
RED in a conical-shaped nanopore

$a_t = 5\text{nm}$

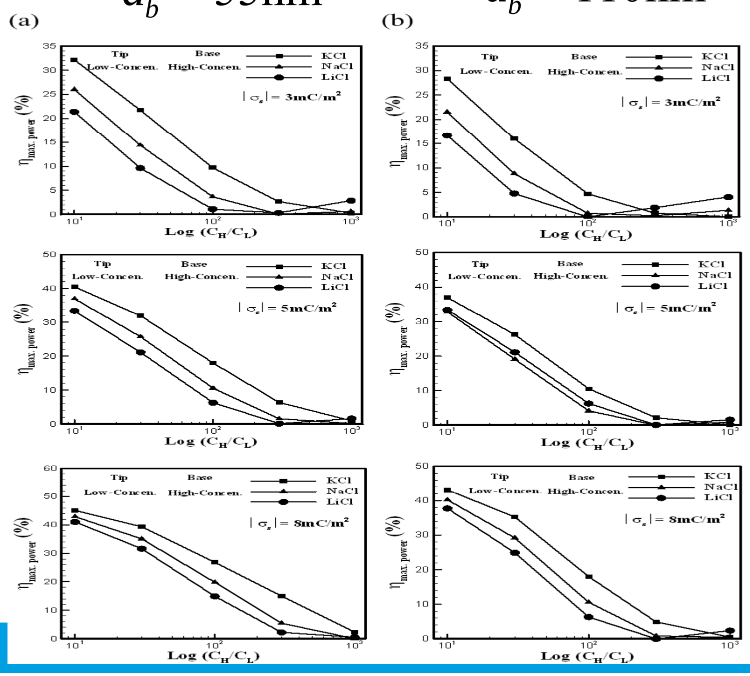




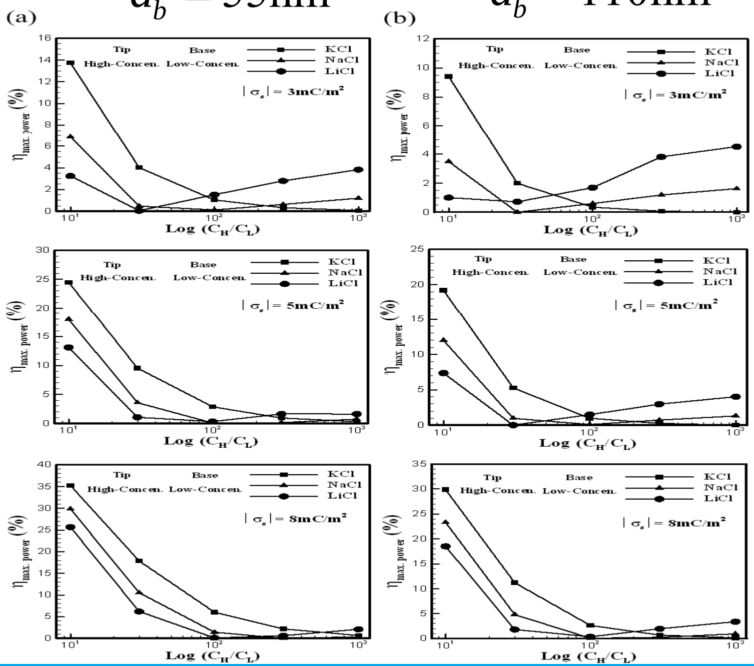




$a_b = 55\text{nm}$ $a_b = 110\text{nm}$



$a_b = 55\text{nm}$ $a_b = 110\text{nm}$



Conclusions

COMSOL Multiphysics

- ☐ User friendly
- ☐ Flexibility: PDE mode
- ☐ A quick simulation tool for continuum nanofluidics and multiphysics
- ☐ A very good tool for researchers and graduated students to speed up their research works.