Shock Electrochemistry in Porous Media

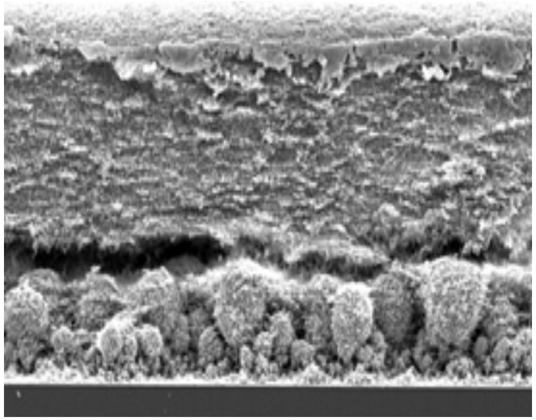
Martin Z. Bazant

Chemical Engineering & Mathematics, MIT

GCEP Chair, Visiting Professor, Stanford (2015-16)

Students:
Sven Schlumpberger, Nancy Lu
(Vicki Dydek)

Postdocs:
Jihyung Han, Peng Bai
(Ali Mani, Daosheng Deng, Matt Suss)



Classical Models of Transport in Porous Media: *Linear Response*

Darcy's law
Ohm's law
Fick's law

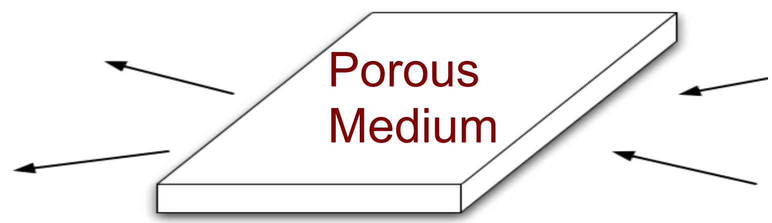
Electro-osmosis Diffusio-osmosis

Diffusion current

$$\text{Fluxes} \quad \begin{pmatrix} Q \\ I \\ F \end{pmatrix} = \begin{pmatrix} K_H & K_{EO} & K_{DO} \\ K_{EO} & K_E & K_{DC} \\ K_{DO} & K_{DC} & K_D \end{pmatrix} \begin{pmatrix} \Delta P \\ \Delta V \\ \Delta C \end{pmatrix} \quad \text{Forces}$$

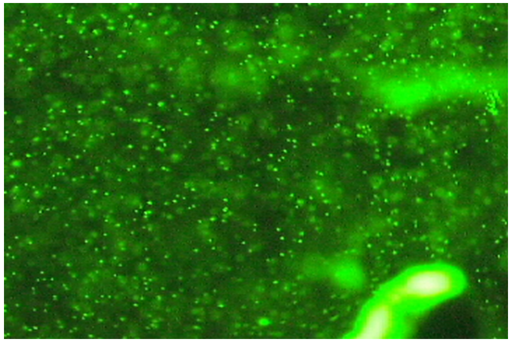
Streaming current

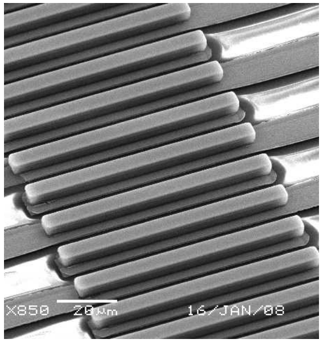
Osmotic flux Electrodiffusion

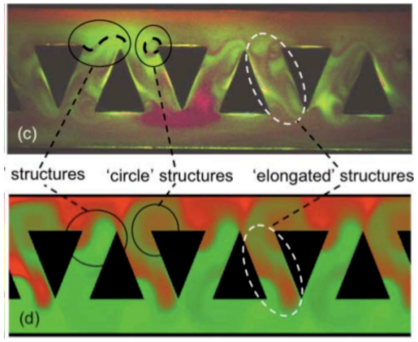


Nonlinear Electrokinetic Phenomena, *K(F)*

1. Surface charge q(V), "induced charge electro-osmosis"

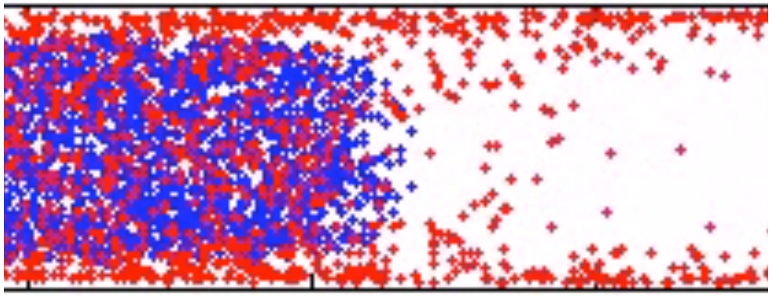


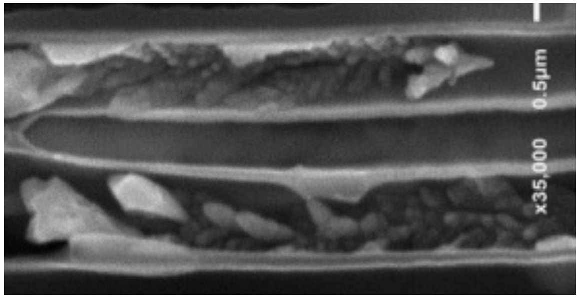




Review: Bazant & Squires, Current Opinion Colloid Interface Science (2010). Microfluidic applications.

2. Salt concentration c(V), "shock electrochemistry"

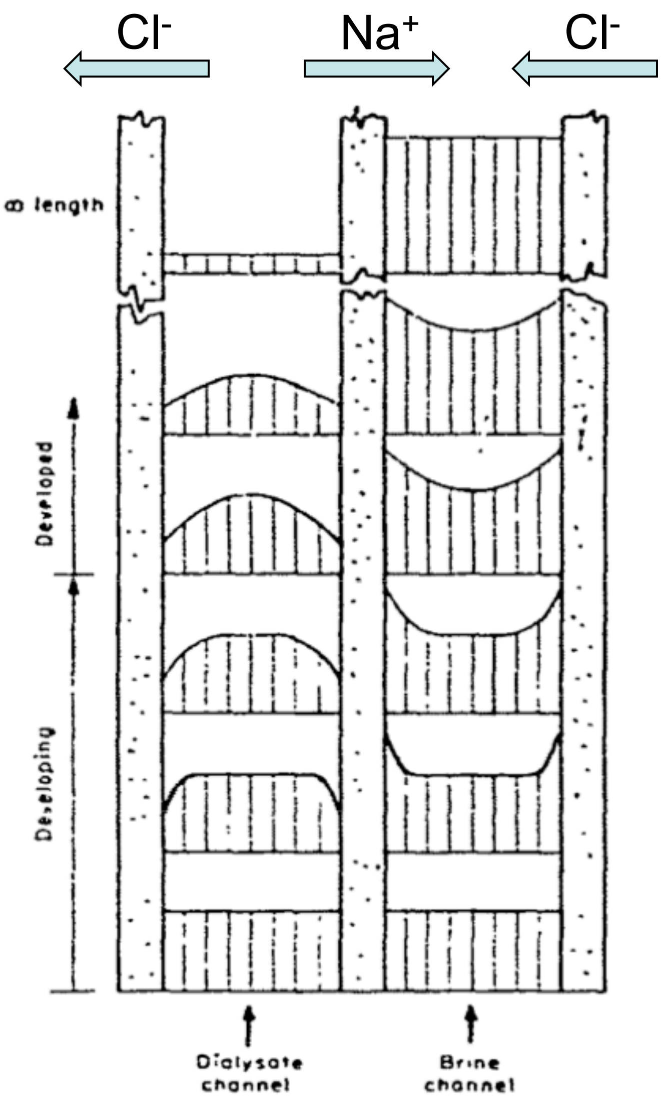




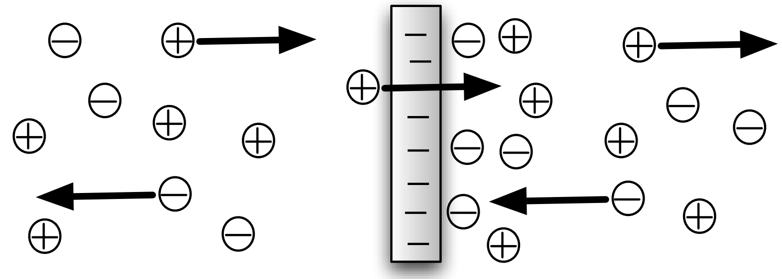
Deionization shock wave in a nanochannel
Mani & Bazant, Phys. Rev. E (2011)

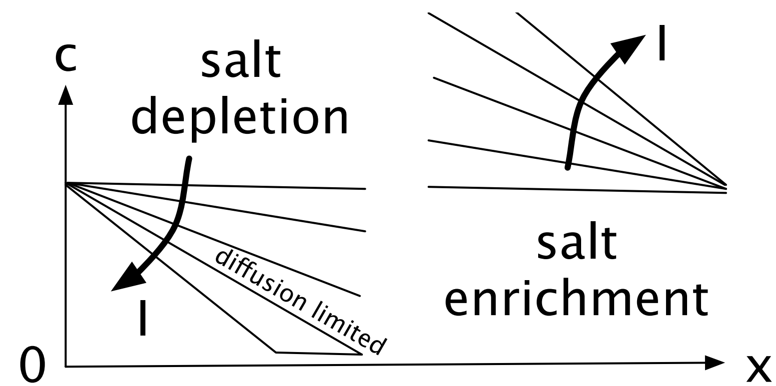
Shock electrodeposition of copper in AAO nanopores
Han, Khoo, Bai & Bazant, Sci. Rep. (2014)

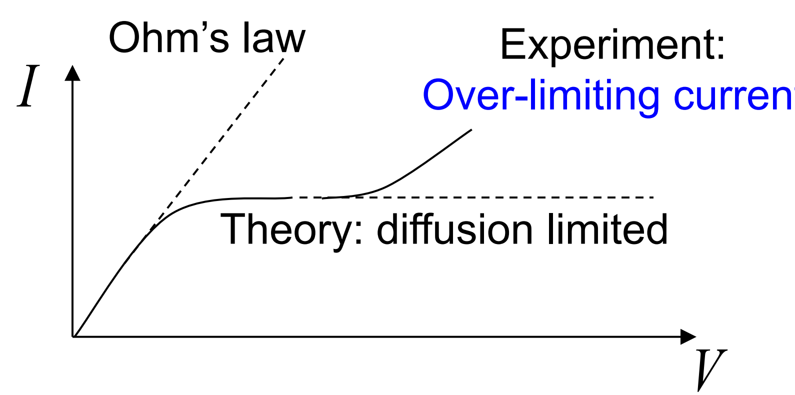
Motivation: Electrodialysis



Sonin & Probstein (1968)







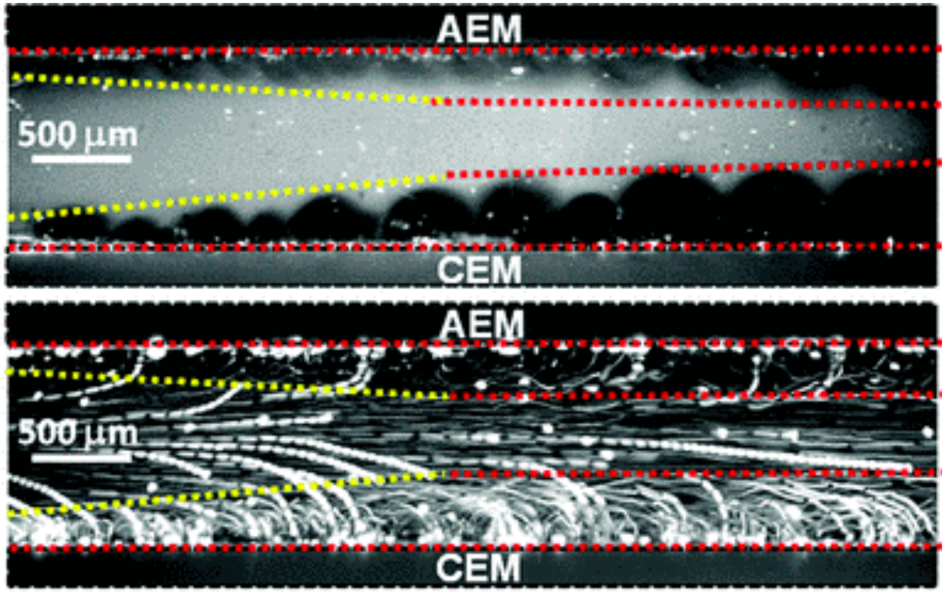
Over-limiting Current in Bulk Electrolytes

1. Electro-osmotic Instability

Idea: I. Rubinstein et al. (1988)

Theory: I. Rubinstein, B. Zaltzman (2000)

Experiment: S. Rubinstein et al. (2008)
G. Yossifon, H.-C. Chang (2008)



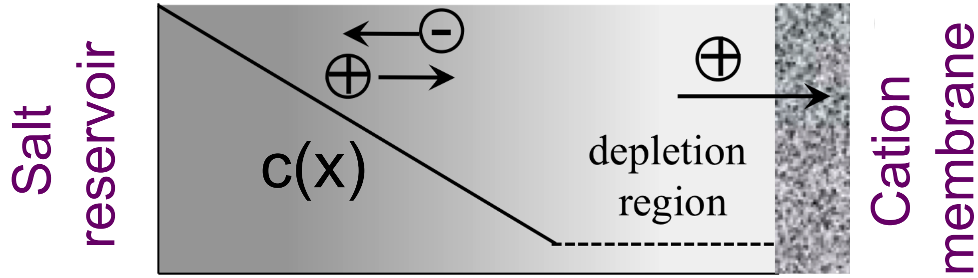
Kwak, Pham, Lim, Han, PRL (2013)

2. Current-Induced Membrane Discharge

M. Andersen, H. Bruus, A. Mani, M. Soestbergen, PM Bieshevuel, MZB, Phys. Rev. Lett. (2012)

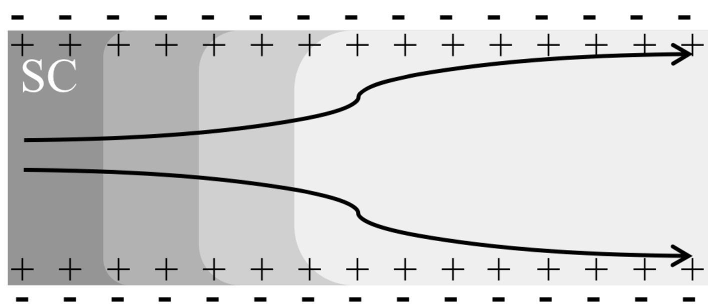
$$\mathrm{H_2O} \leftrightarrow \mathrm{H^+} + \mathrm{OH^-} \qquad XH^+_{surf} \leftrightarrow X_{surf} + \mathrm{H^+}$$

Over-limiting Current in a Microchannel

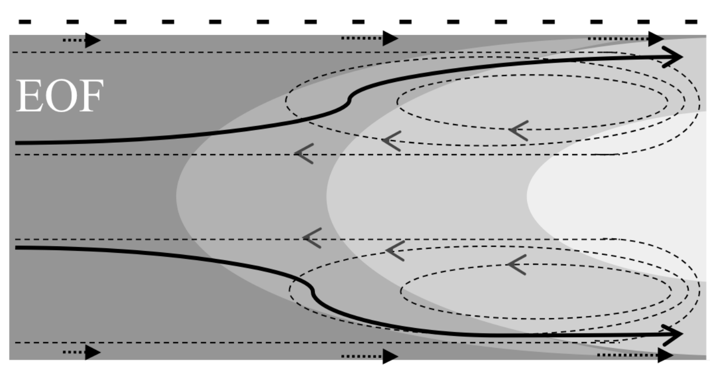


negatively charged microchannel

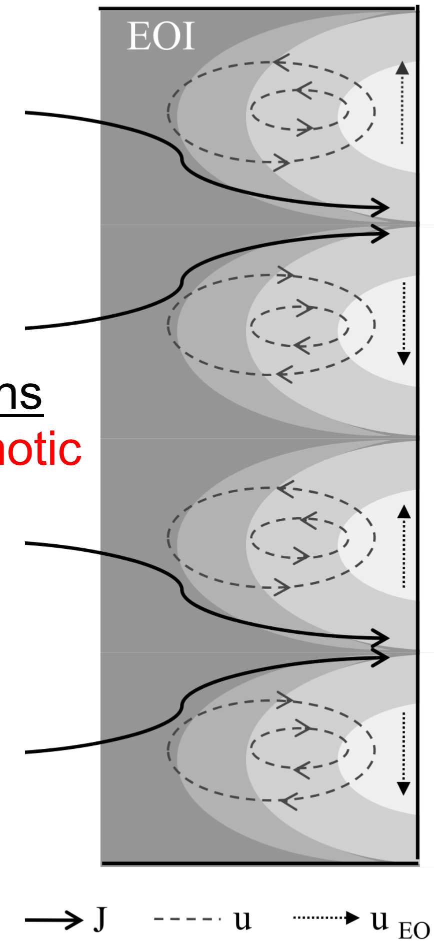
<u>< 5 micron</u>
Surface Conduction
(electro-migration)



<u>1-500 microns</u>
Electro-osmotic Flow
(surface convection)

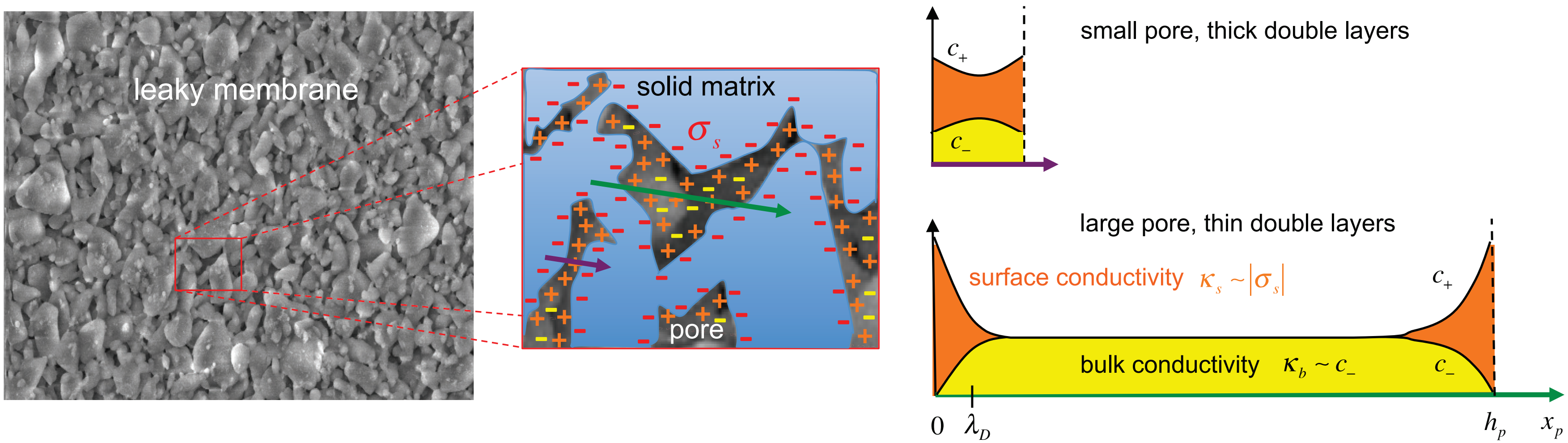


<u>> 100 microns</u>
Electro-Osmotic Instability
(flow on the membrane)

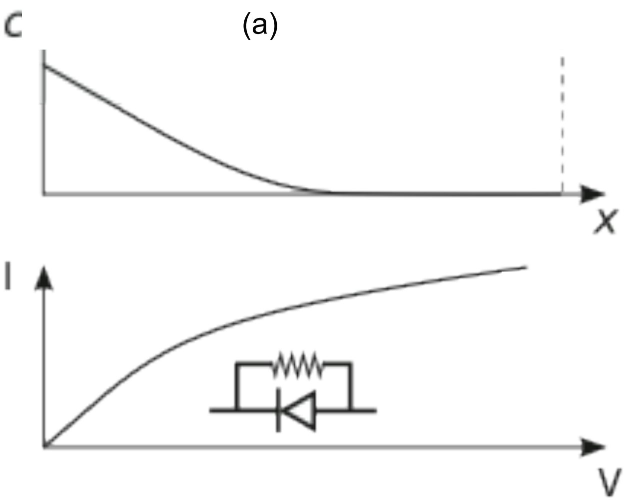


E. V. Dydek, B. Zaltzman, I. Rubinstein, D. Deng, A. Mani, MZB, Phys Rev Lett (2011)
A. Yaroshchuk, E. Zholkovsky, S. Pogodin, V. Baulin, Langmuir (2011)

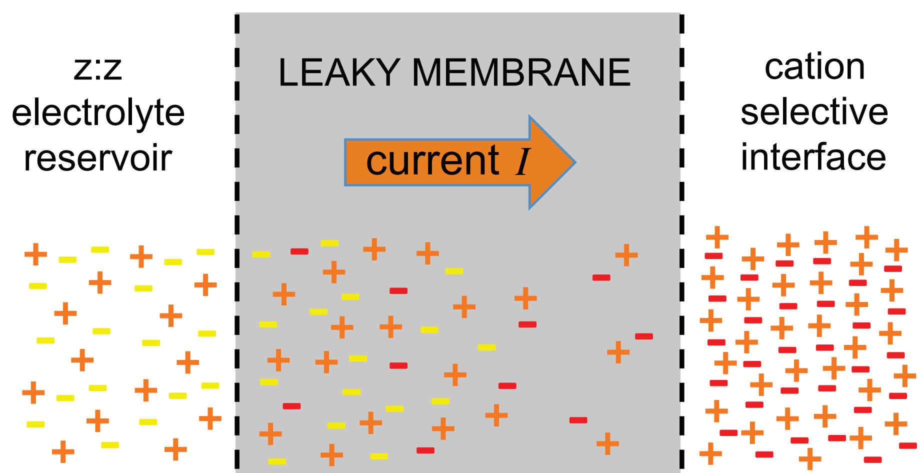
Over-limiting Current in Porous Media



(a) (b) (c)

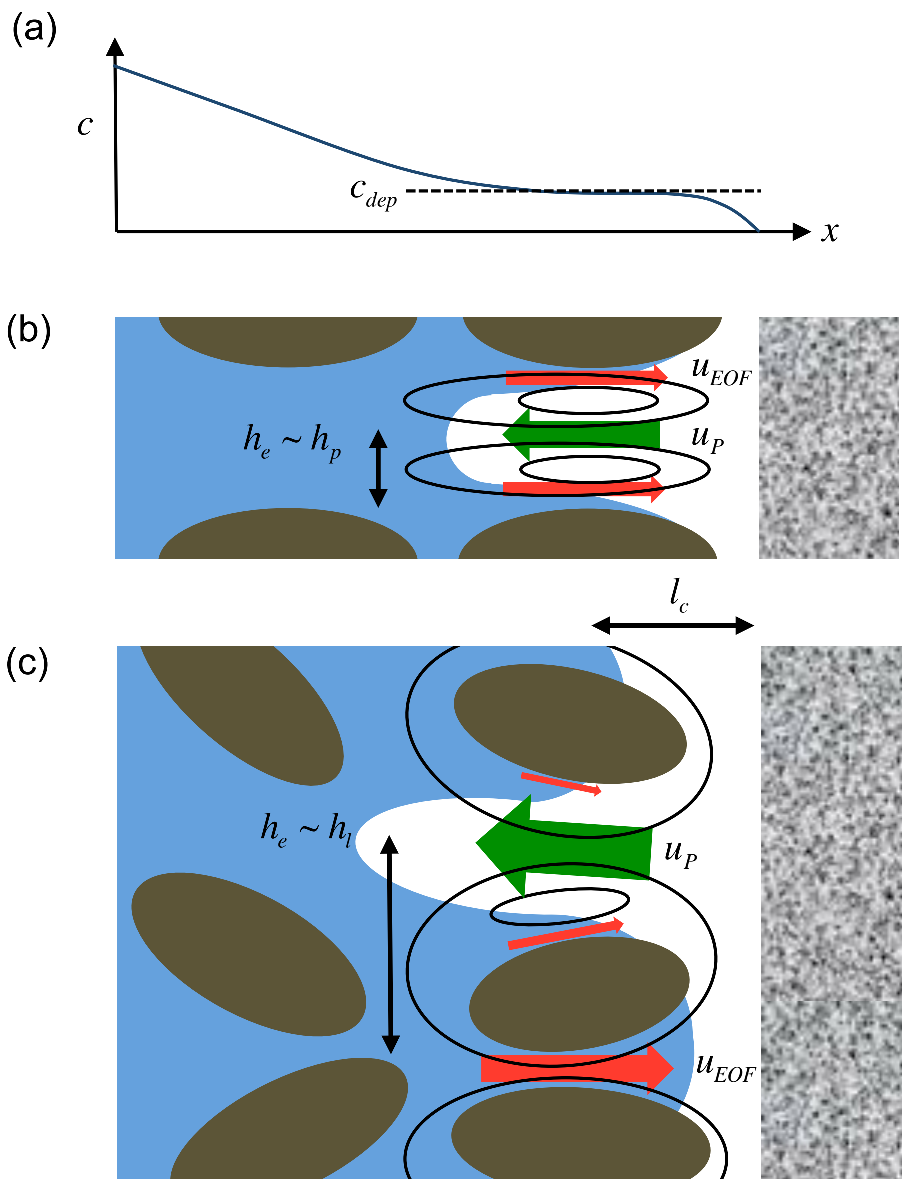


$$I = I_{\lim}\left(1 - e^{-\tilde{V}}\right) - \sigma_{OLC}\tilde{V}$$



A. Mani & MZB, Phys Rev E (2011); E. V. Dydek et al, AIChE J (2013)

Mechanisms for Over-limiting Conductance



1. Surface conduction

$$\sigma_{SC} \approx \frac{zeDq_s}{k_B T L h_p}$$

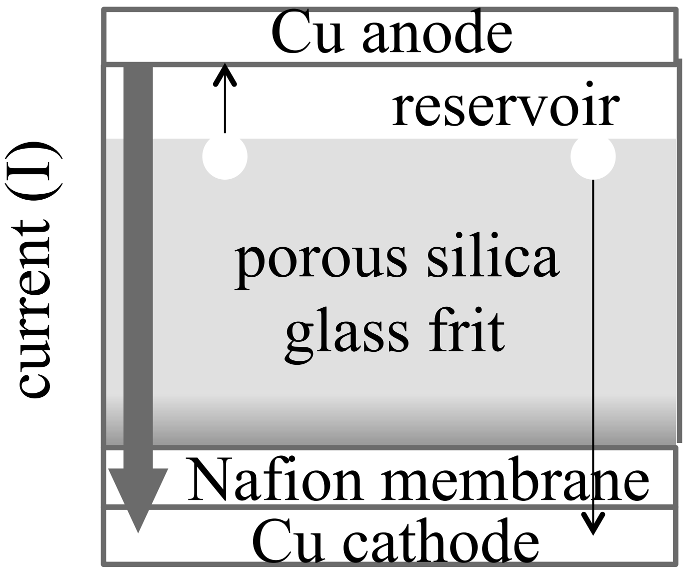
2. Surface convection

(electro-osmotic flow)

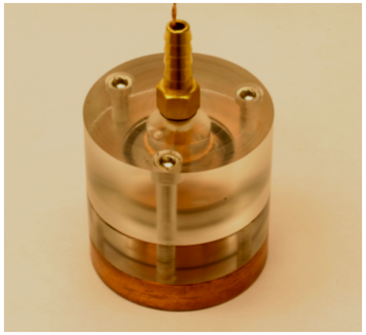
$$\sigma_{EOF} \approx \frac{(ze)^{6/5} \left(2h_e\right)^{4/5} \varepsilon^{1/5} D^{3/5} q_s^{\;2/5} c_0^{\;4/5}}{L^{9/5} (\eta k_B T)^{2/5}}$$

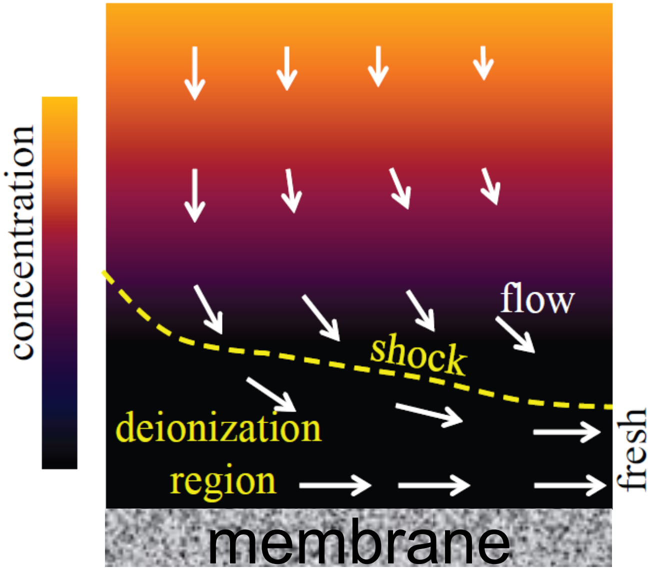
First Experimental Evidence

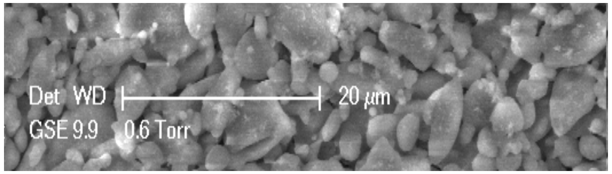
Deng, Han, Dydek, Schlumpberger, Mani, MZB, *Langmuir* (2013)



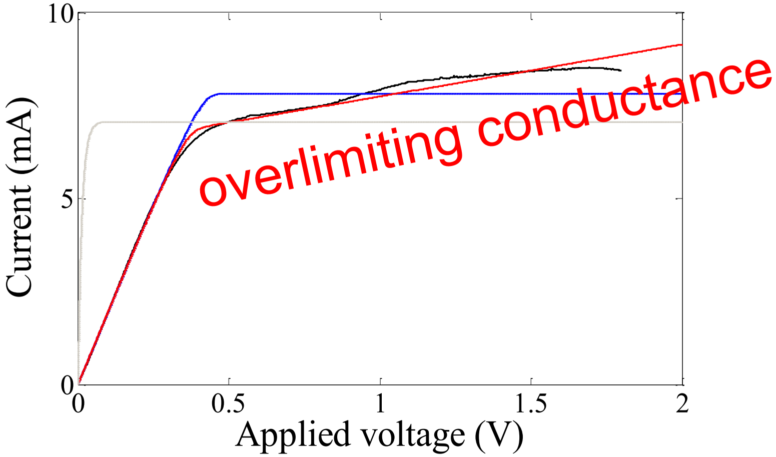
Validate with known chemistry:
$Cu|CuSO_4|Cu$
$SiOH \rightarrow SiO^- + H^+$



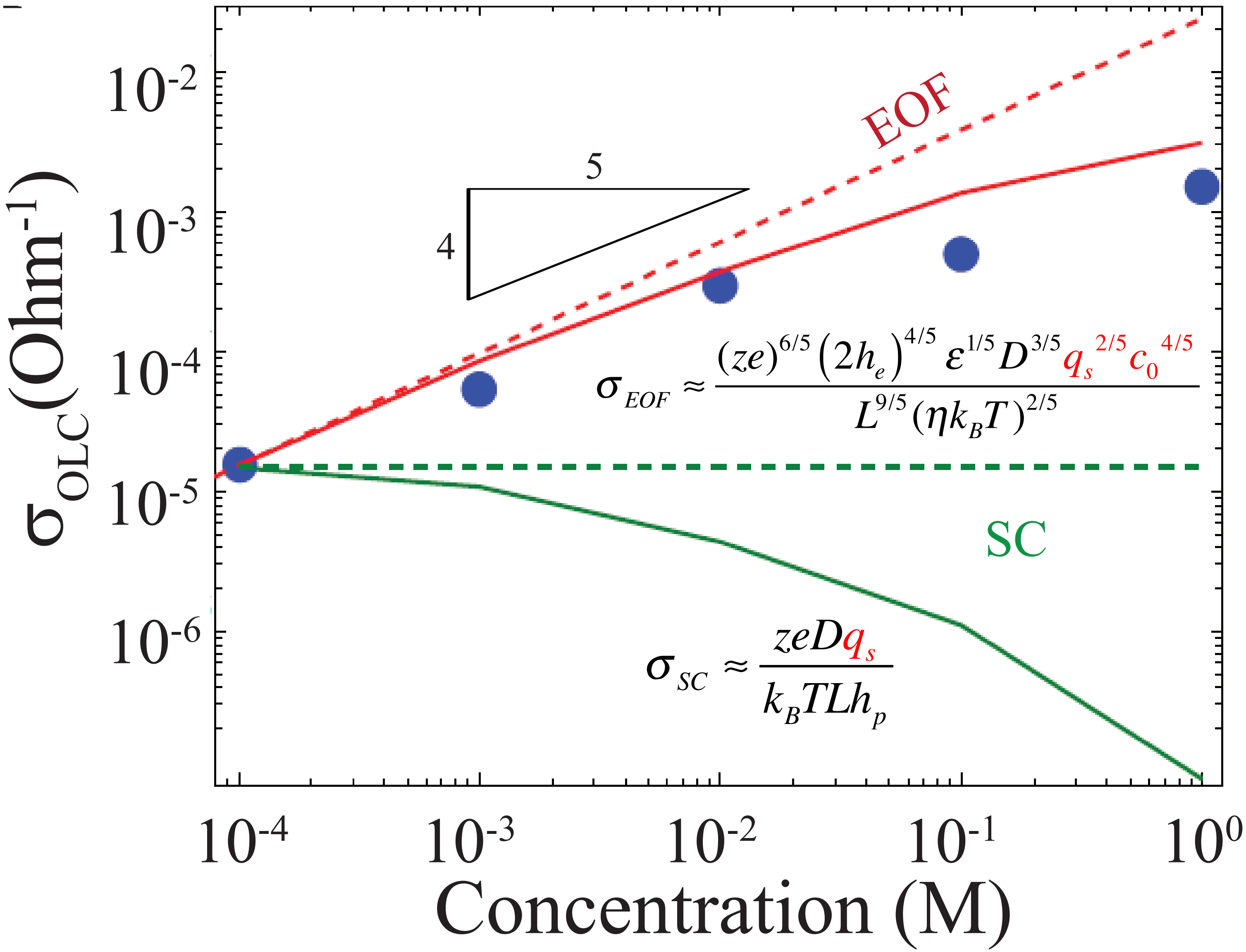




$$I = I_{\lim}\left(1 - e^{-\tilde{V}}\right) - \sigma_{OLC}\tilde{V}$$



Over-limiting Current by Electro-osmotic Flow



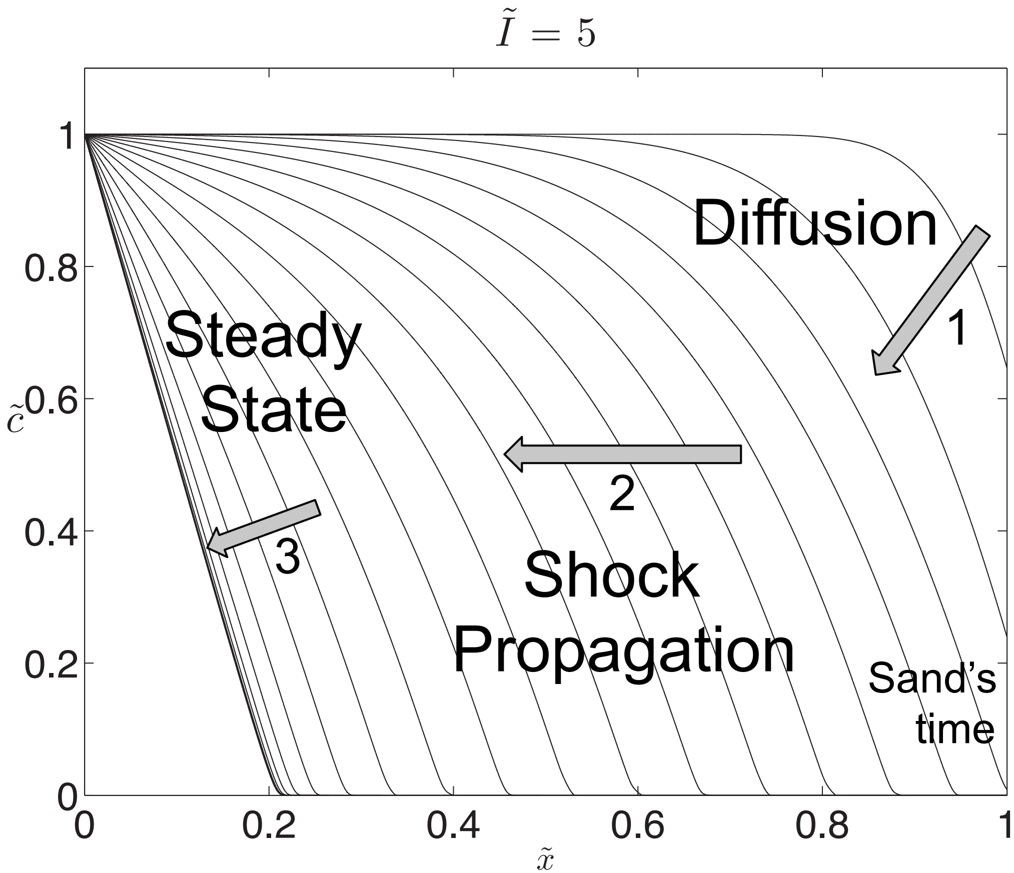
Charge regulation

$SiO^- + H^+ \rightarrow SiOH$

Behrens & Grier (2001)

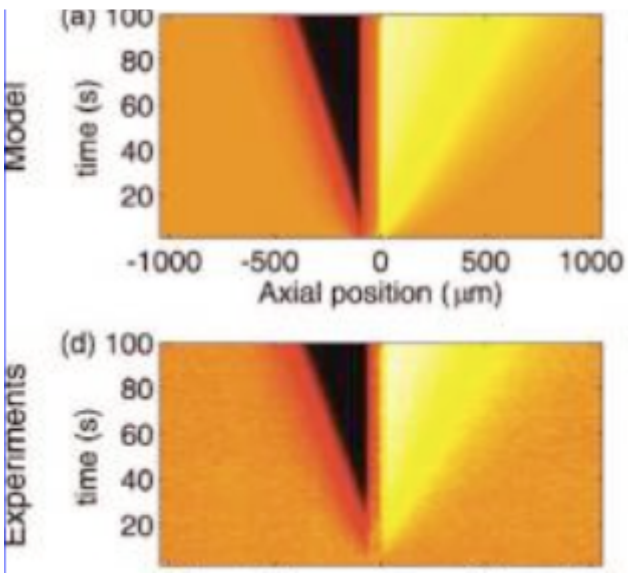
Transients at Constant Over-limiting Current:

Deionization Shock Waves



Theory for porous media, steady over-limiting current in a finite system
A. Mani & MZB, Phys Rev E (2011); E. V. Dydek & MZB AIChE J (2013)

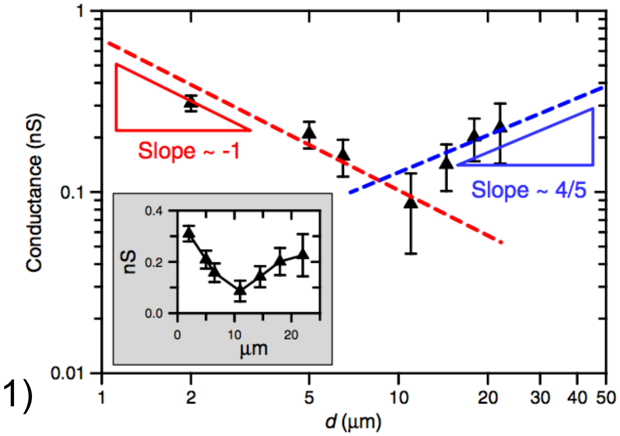
Discovery in Microfluidics:
A. Mani, T. Zangle, J. Santiago,
Langmuir (2009)



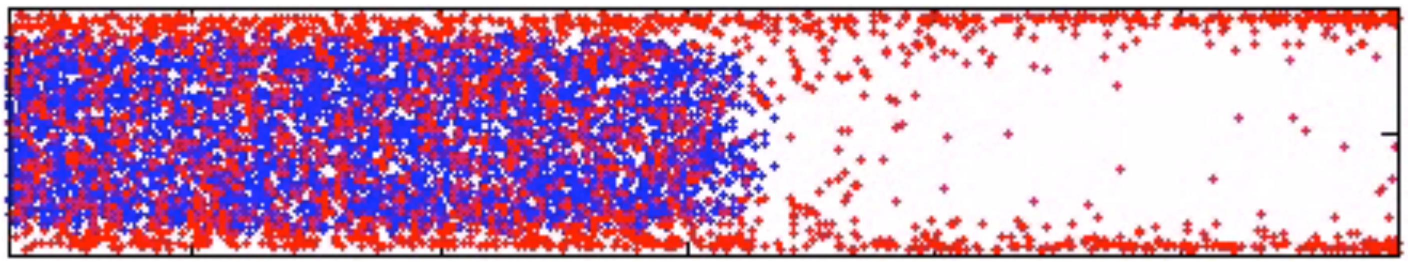
micro | nano | micro
channel junction

Two Shock Mechanisms

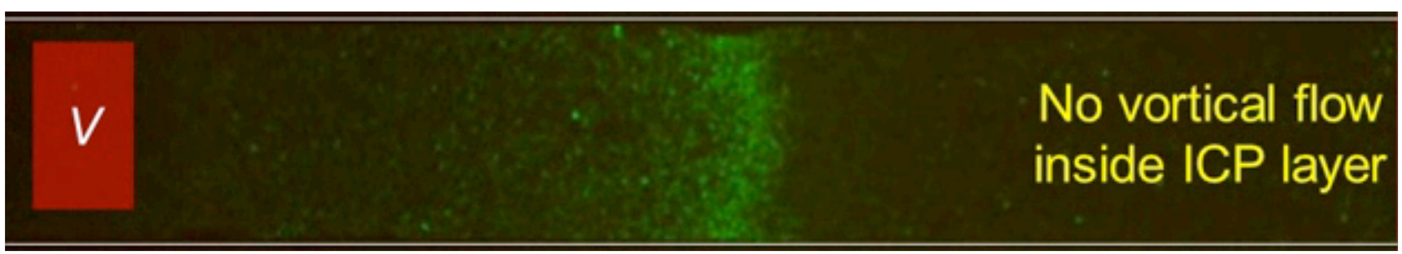
S. Nam, I. Ho, J. Heo, MZB, S. Kim, PRL (2015).



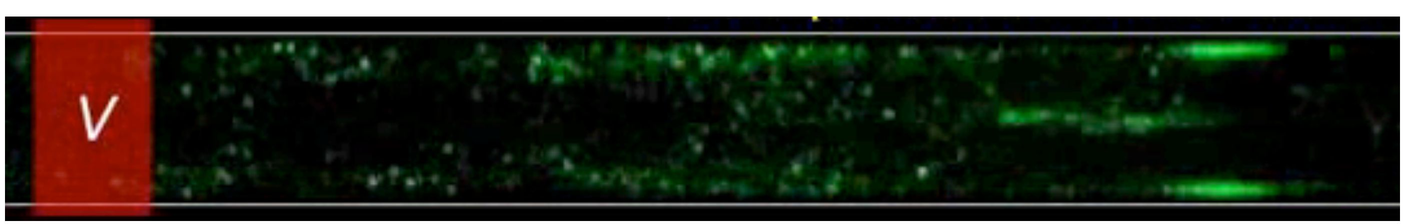
THEORY: SURFACE CONDUCTION (d=2nm)   Mani & MZB (2011)



EXPERIMENT: SURFACE CONDUCTION (d=2um)



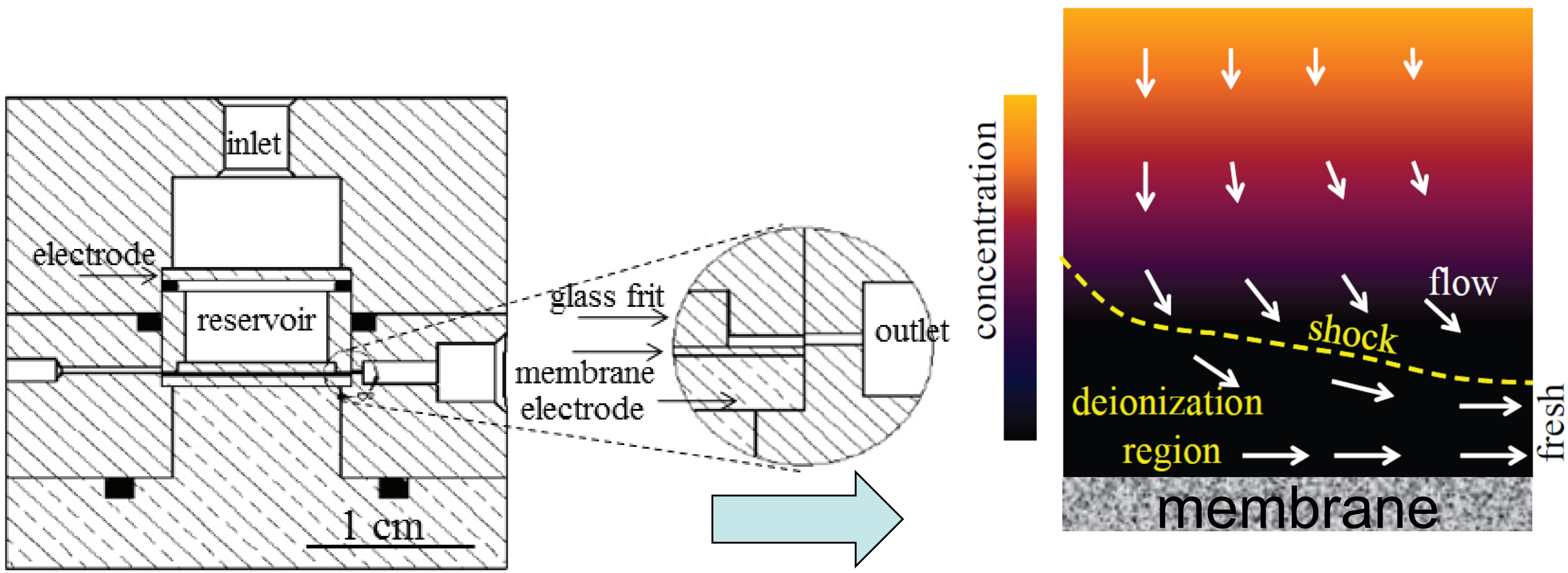
EXPERIMENT: ELECTRO-OSMOTIC FLOW (d=6.5um)



Deionization Shocks in Porous Media:

Experimental Proof and Application to Water Purification

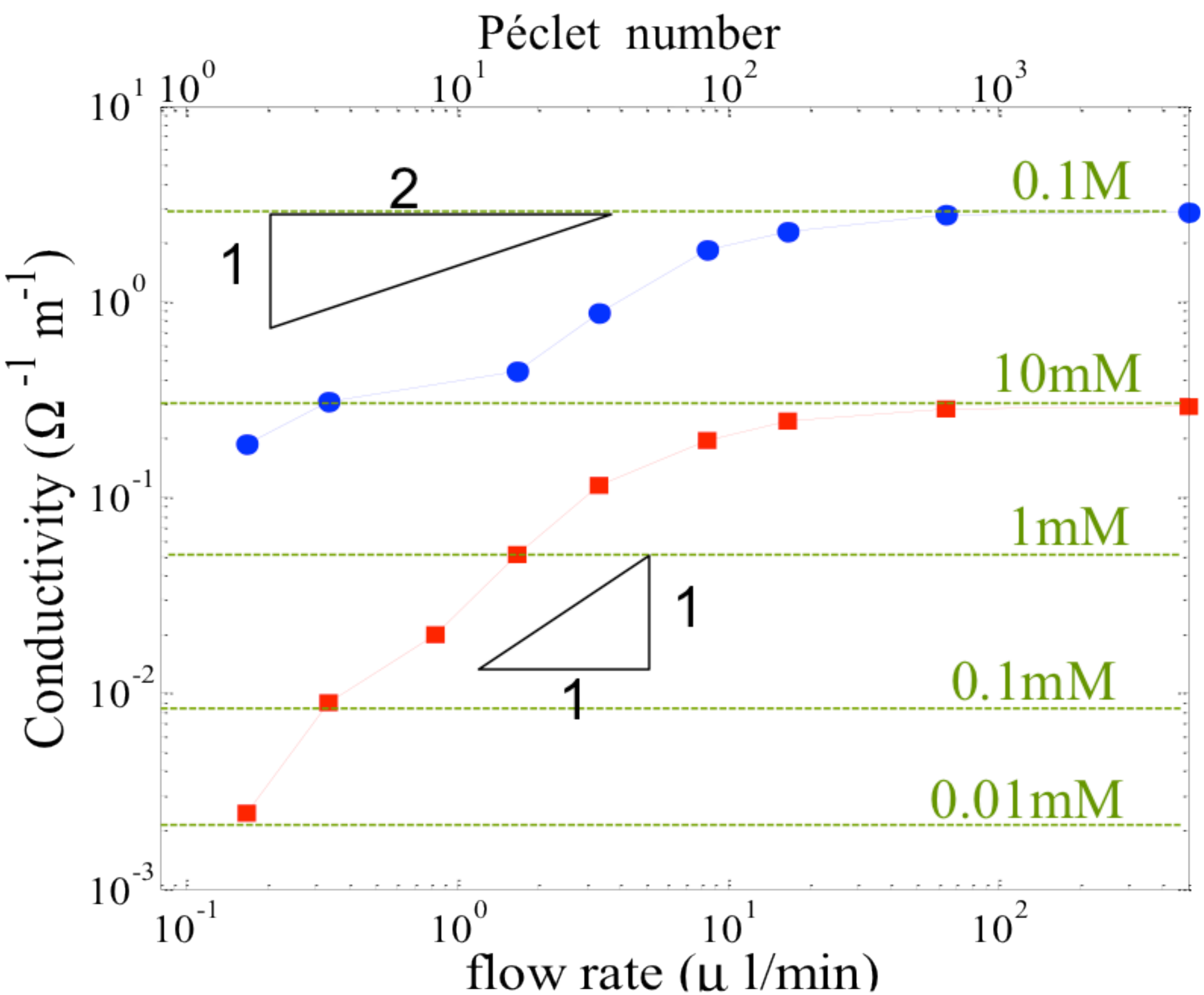
Deng, Han, Dydek, Schlumpberger, Mani, MZB, *Langmuir* (2013)



Shock Electro-deionization of $CuSO_4$

Step 1:
Desalination
0.1 M in
5 mM out

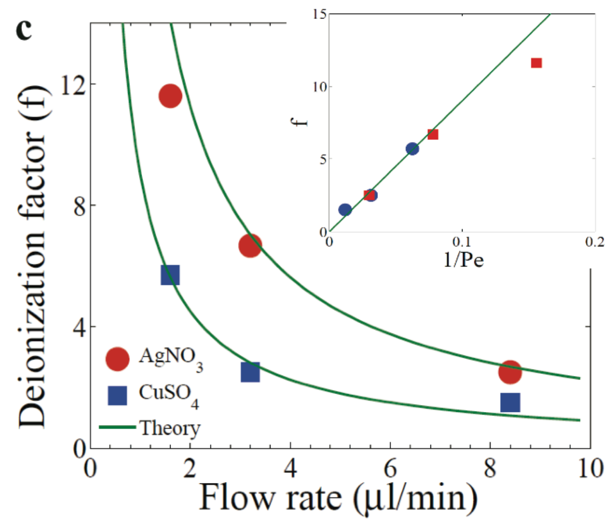
Step 2:
Deionization
10 mM in
10 μM out



Multifunctionality of Shock ED

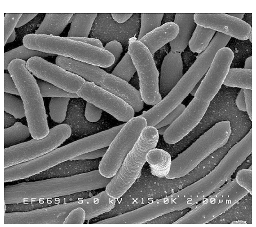
Separations

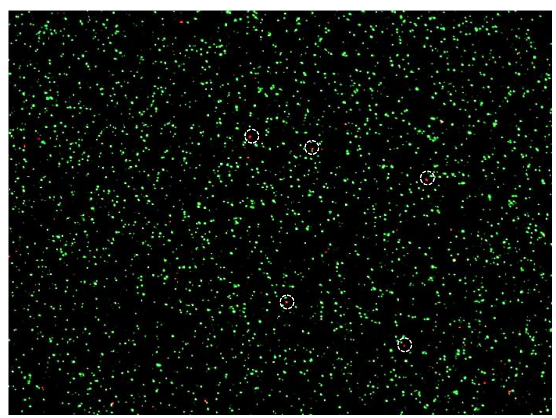
Ionic: Toxic multivalent ions
Molecular: Fluorescein dye
Colloidal: nanoparticles

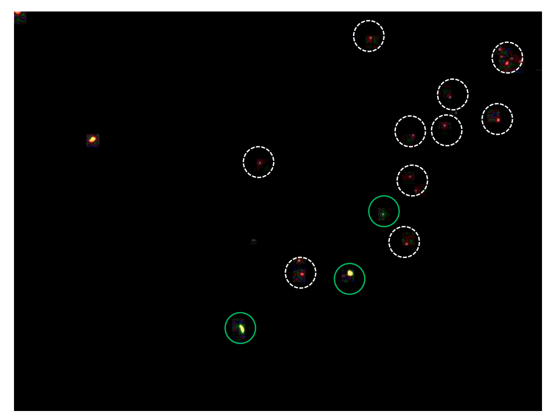


Disinfection

E Coli







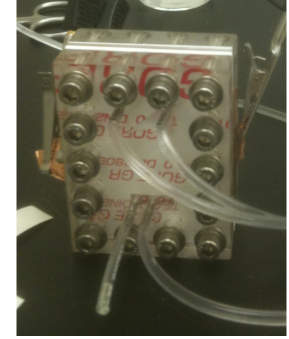
Extraction rate: 0.2ul/min;
Applied voltage: 1.5V.

Inlet (10X)

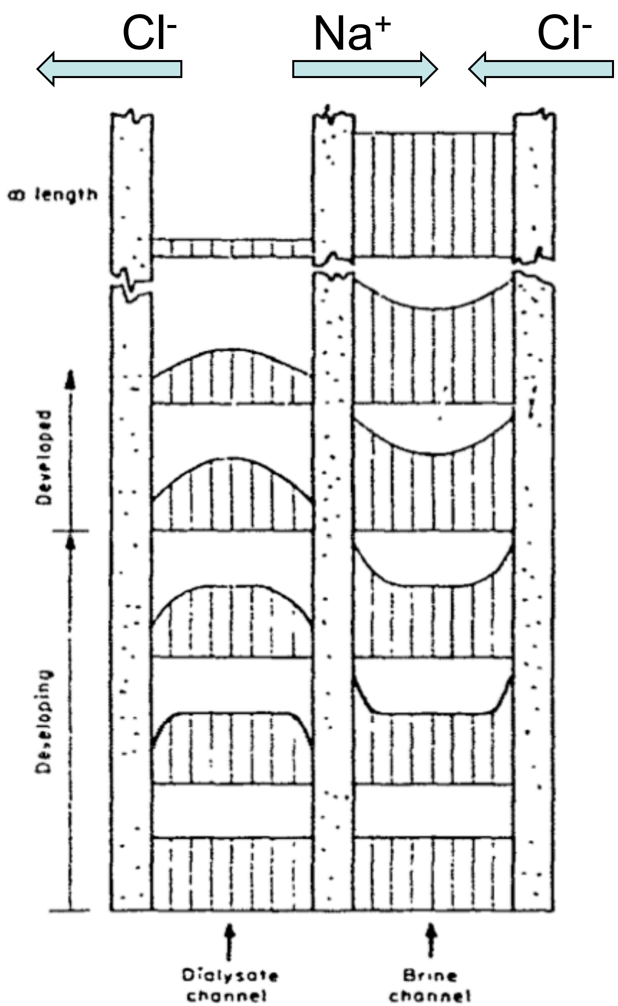
Outlet (4X)

Green: live cells
Red : dead cells

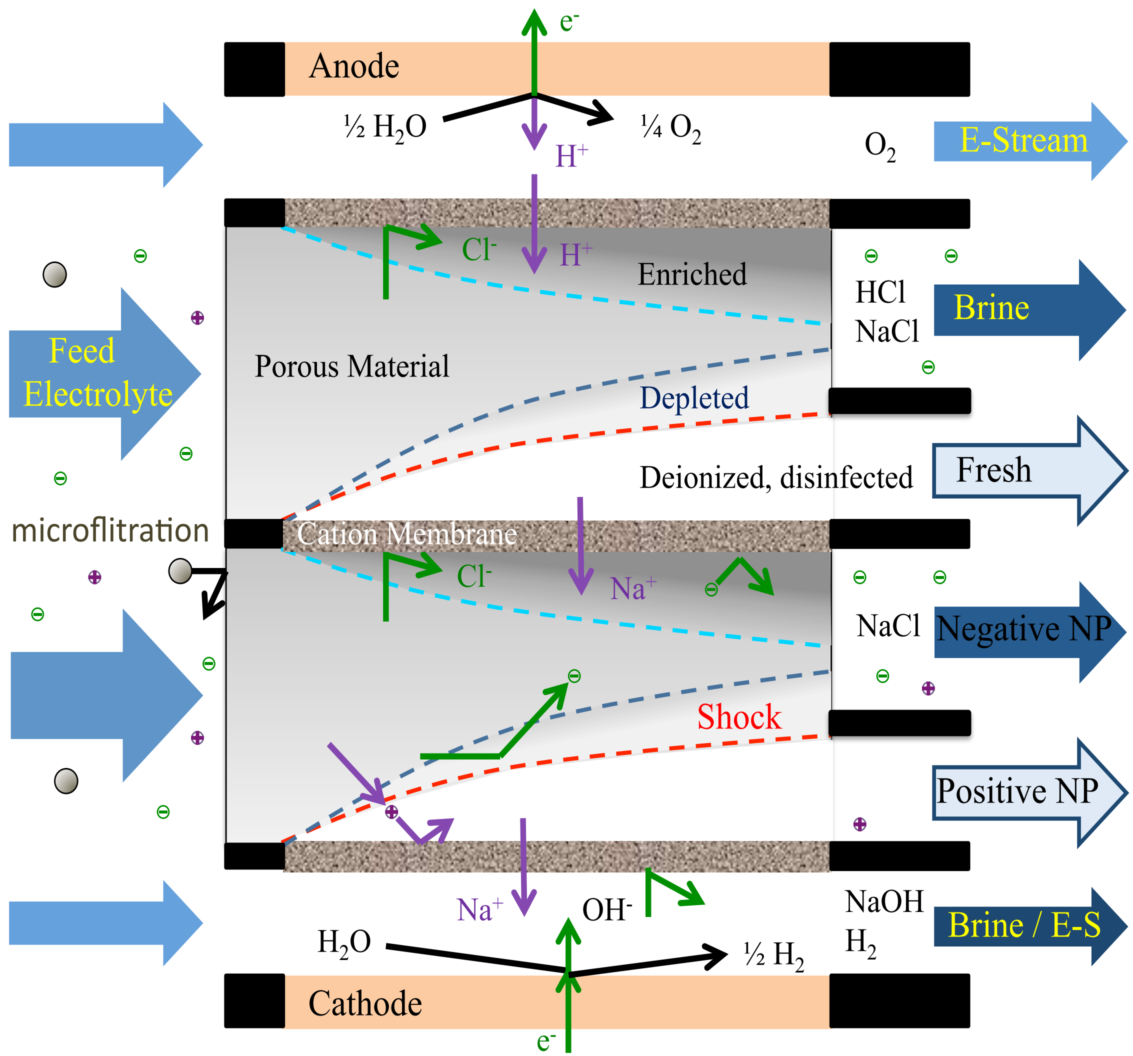
New Science → Engineering



Electrodialysis



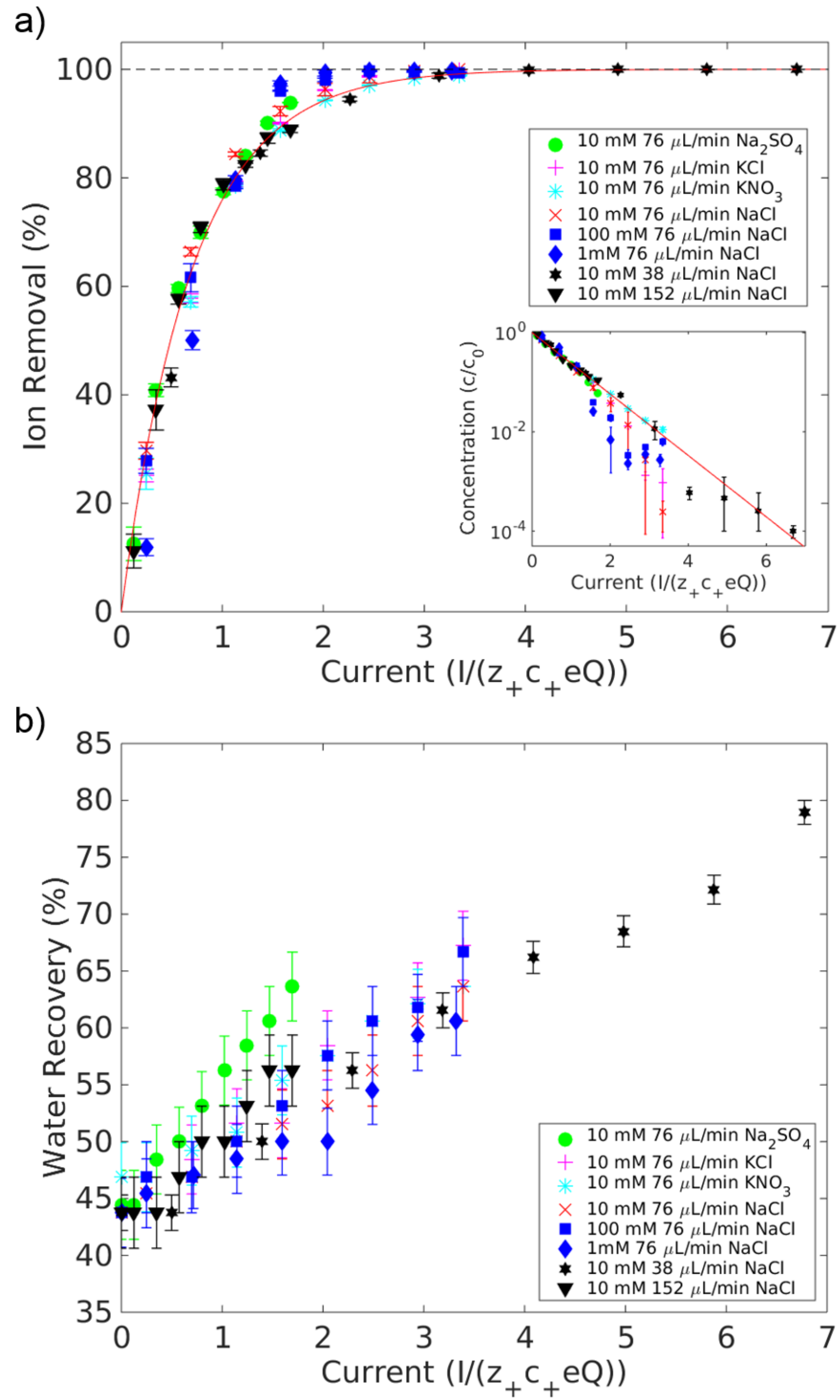
Shock Electrodialysis



First Scalable Shock ED System

S. Schlumberger, N. Lu, M. Suss, MZB, submitted (2015)

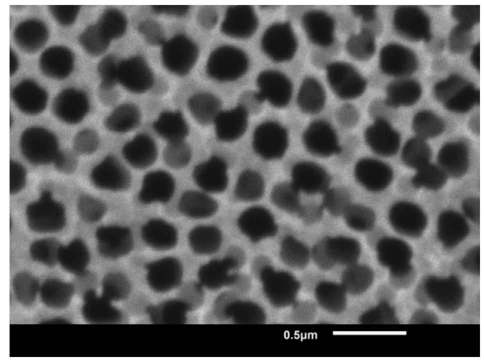
- Up to 99.9% salt removal
- Any electrolyte (NaCl)
- Unexpected result: Enhanced water recovery from electro-osmotic flow

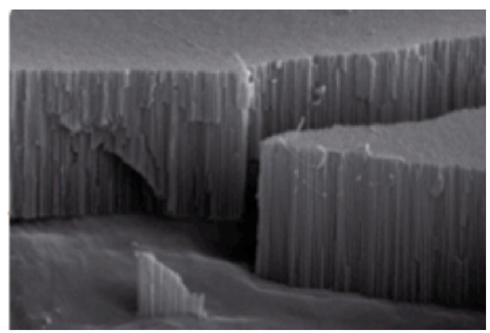


Shock Electrodeposition

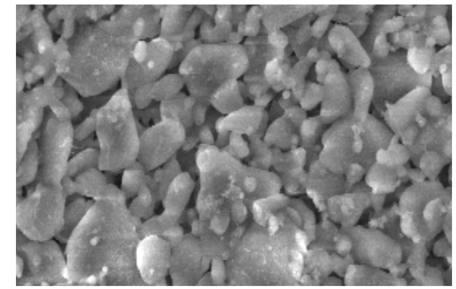
Metal electrodeposition in charged porous media

anodic aluminum oxide (AAO)

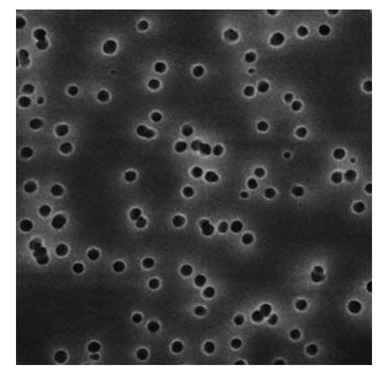




silica glass frit

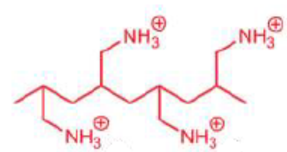


polycarbonate membrane

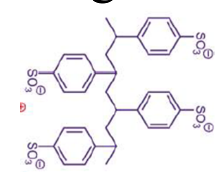


Layer-by-layer charged polymer coatings

PAH (+)

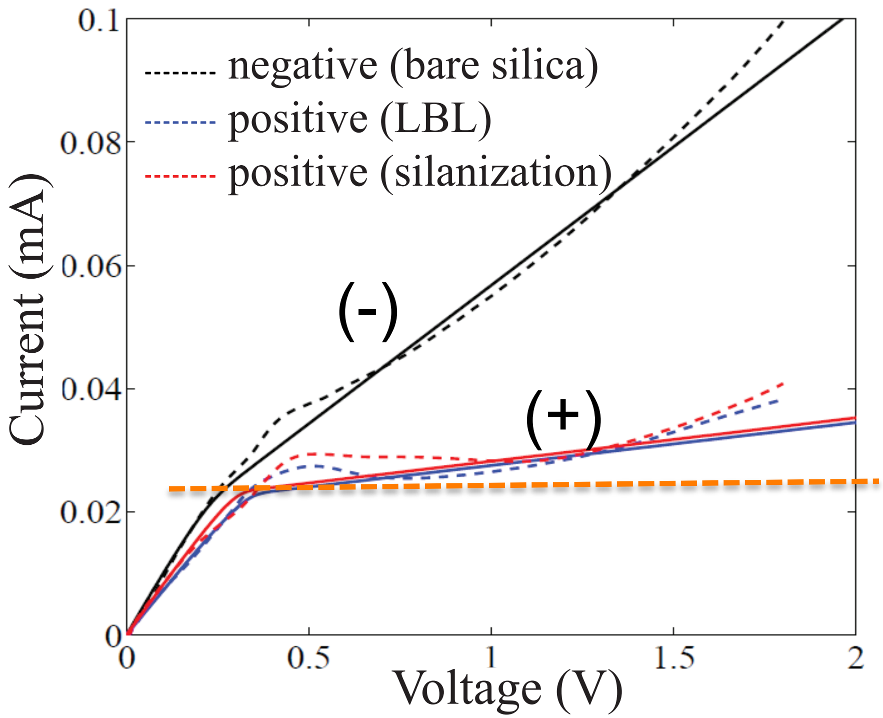


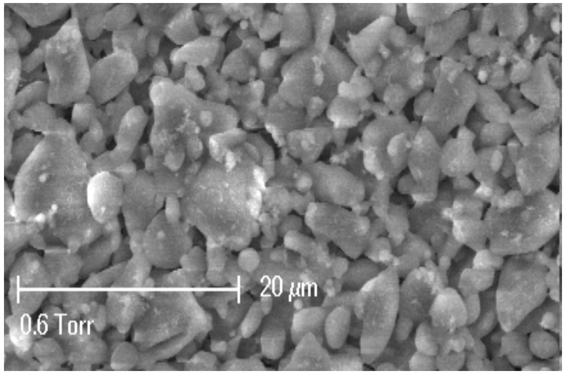
PSS (-)



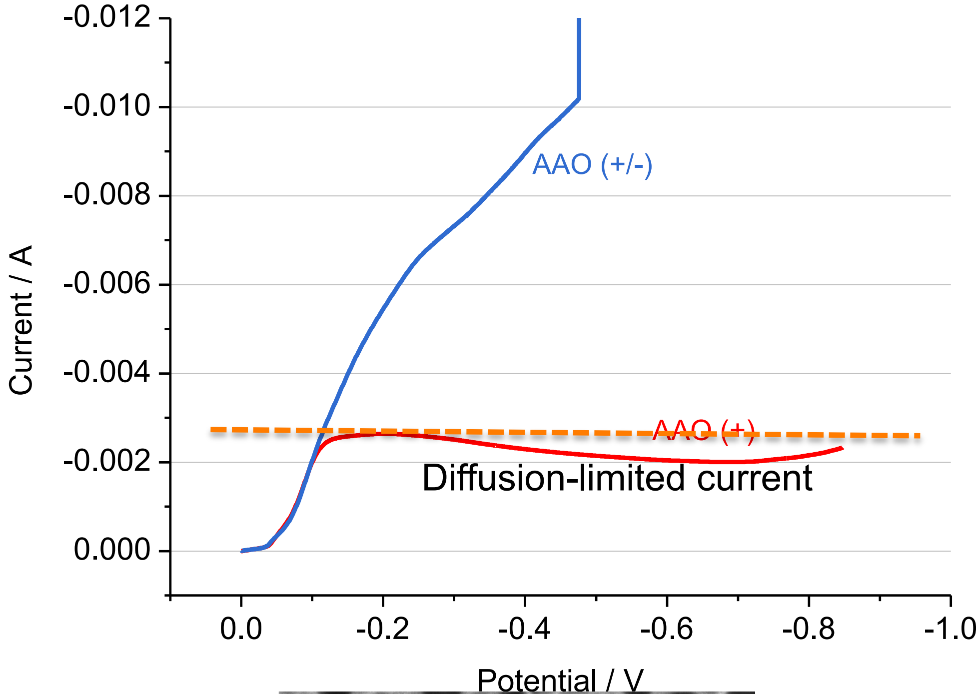
Two Mechanisms for Over-limiting Current

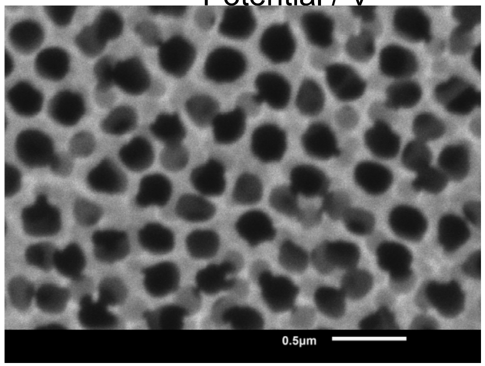
Large, random pores: Electro-osmotic flow





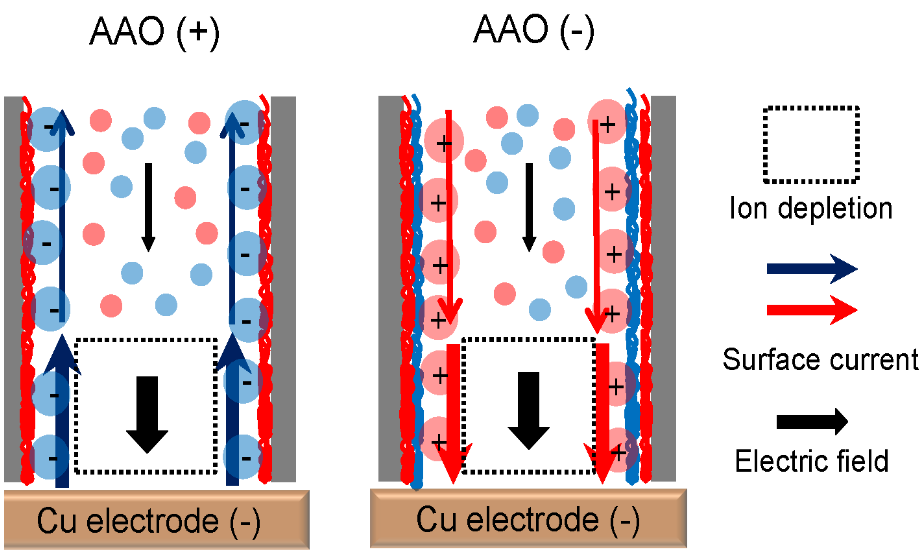
Small, ordered pores: Surface conduction

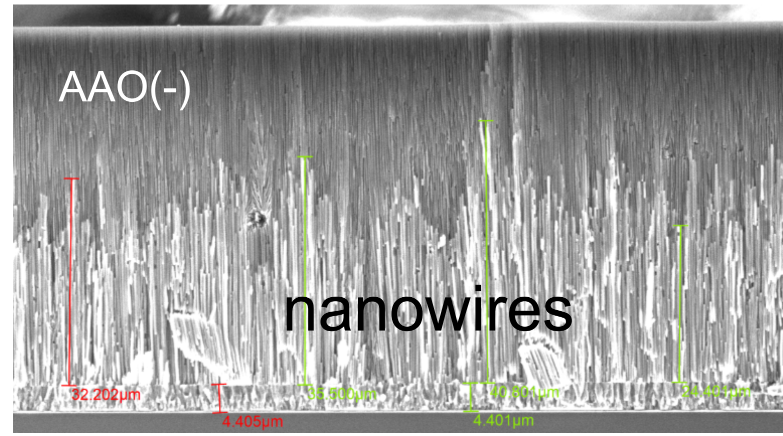


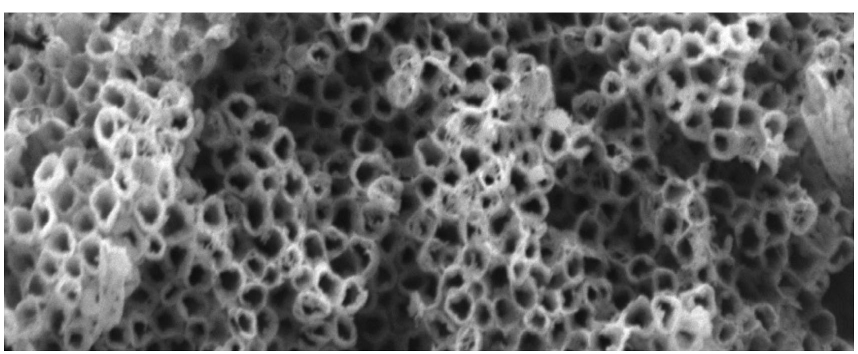


Shock Electrodeposition in Nanochannels

Ji-Hyung Han, Edwin Khoo, Peng Bai, MZB, *Scientific Reports* (2014)



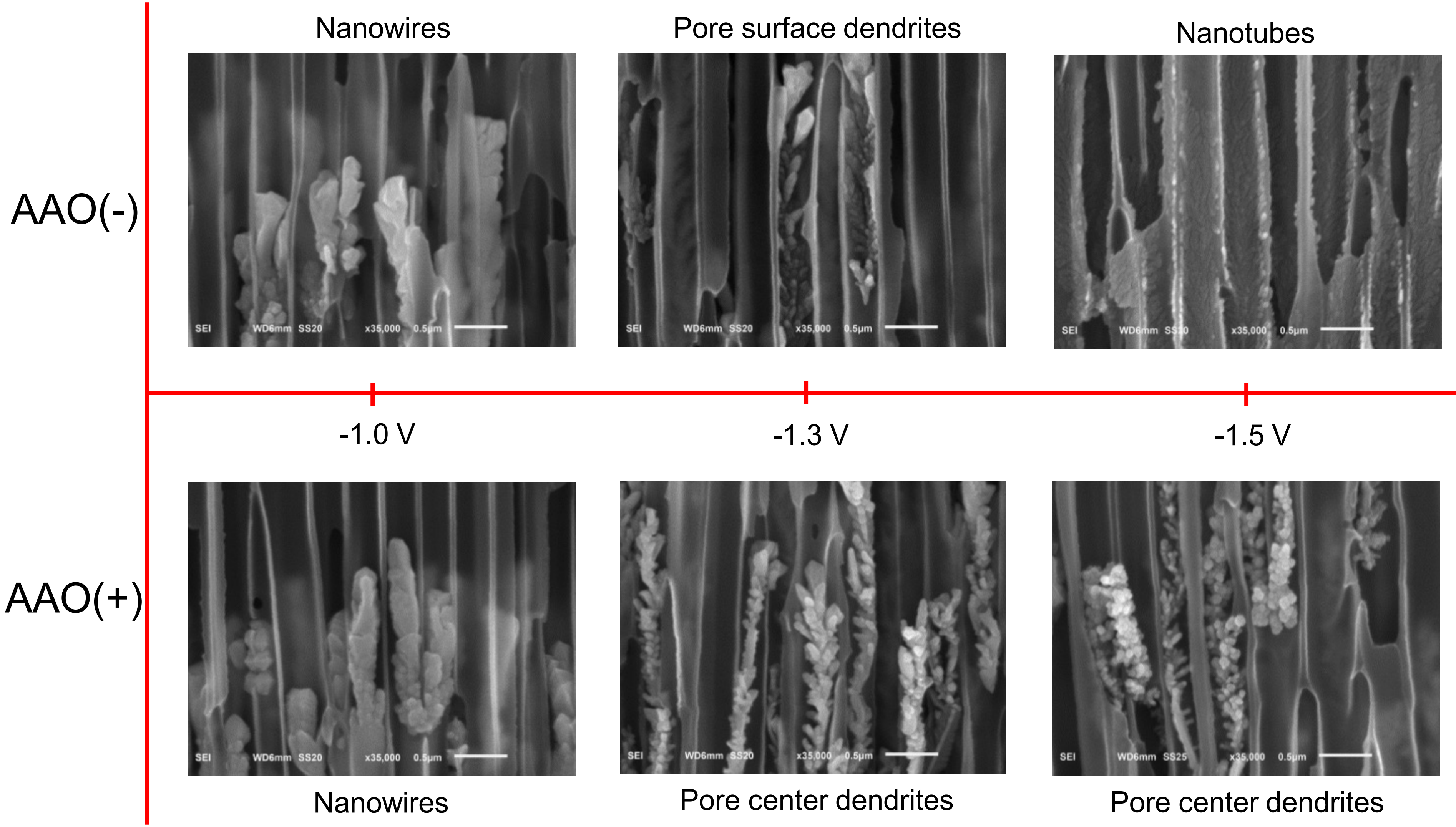




Proof of surface conduction: Nanotubes

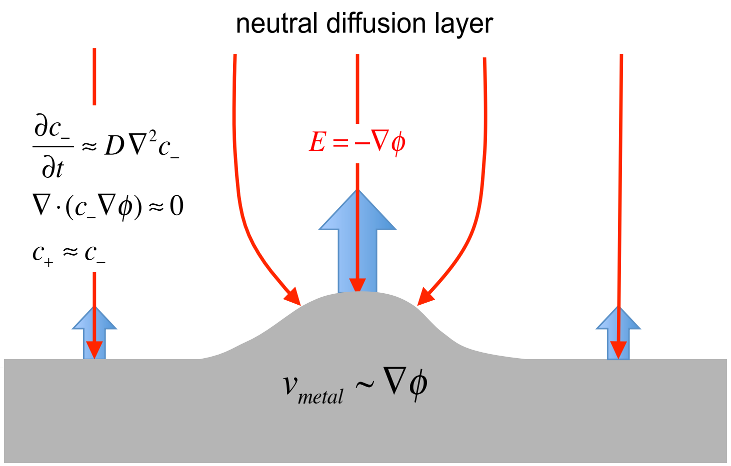
“passively save” high-rate battery separators

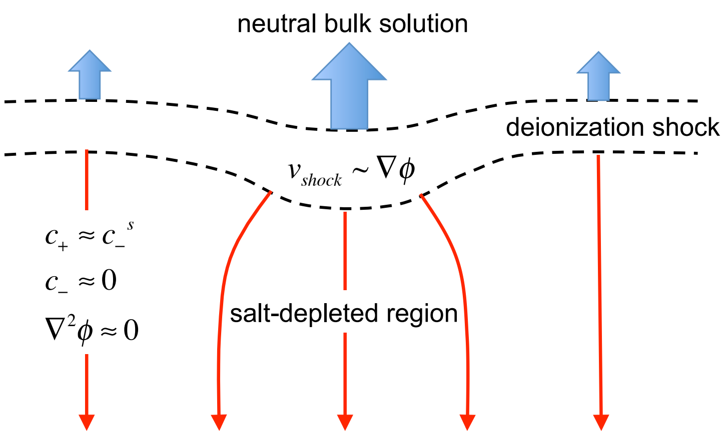
Morphology Control by Surface Conduction



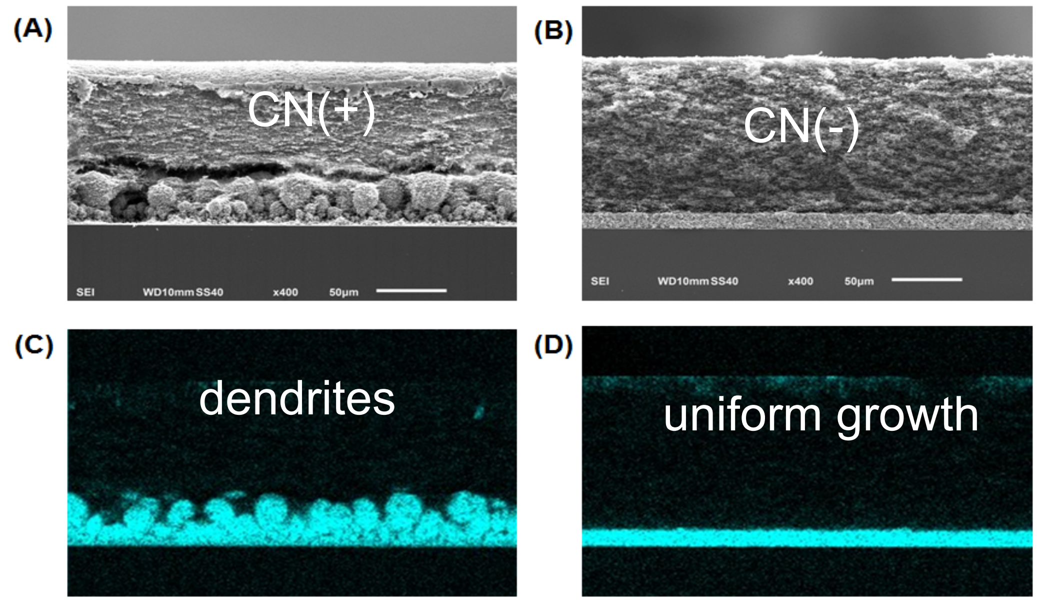
Dendrite Suppression by Shocks

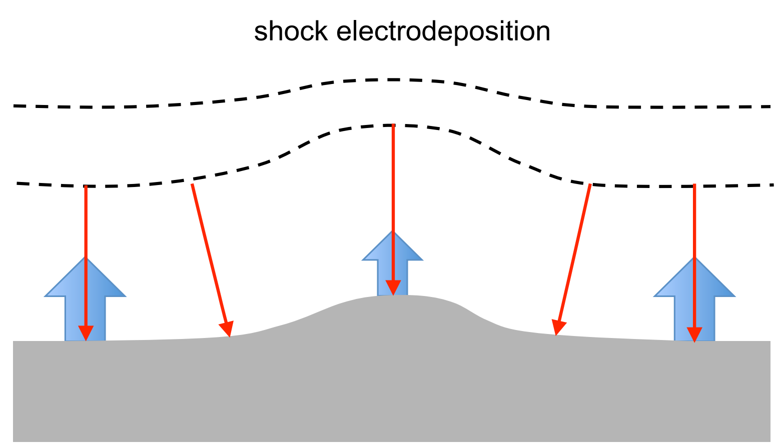
Ji-Hyung Han & MZB, in preparation





Polyelectrolyte coated cellulose nitride membranes



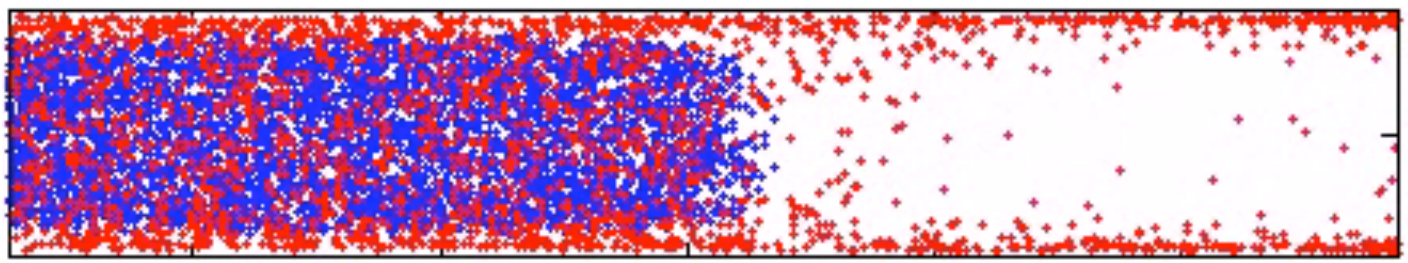


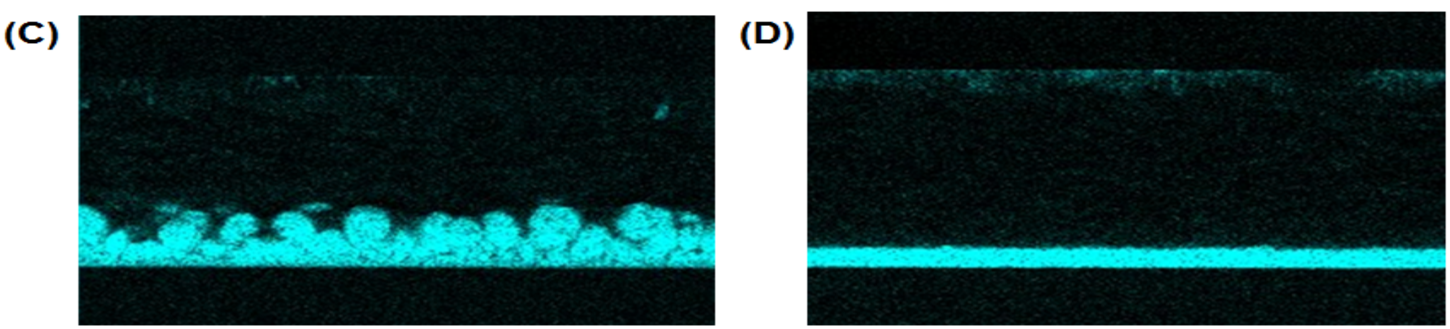
Application: Metal Batteries

May explain expts of L. Archer (2013-14)

Conclusion: Shock Electrochemistry

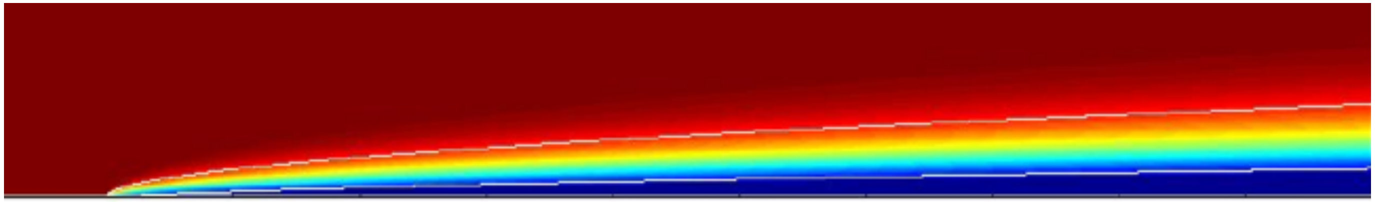
- ~~Electroneutrality.~~ Double layers are important.
- Exceed diffusion-limited current in porous media
- Applications: separations, batteries, nanotechnology

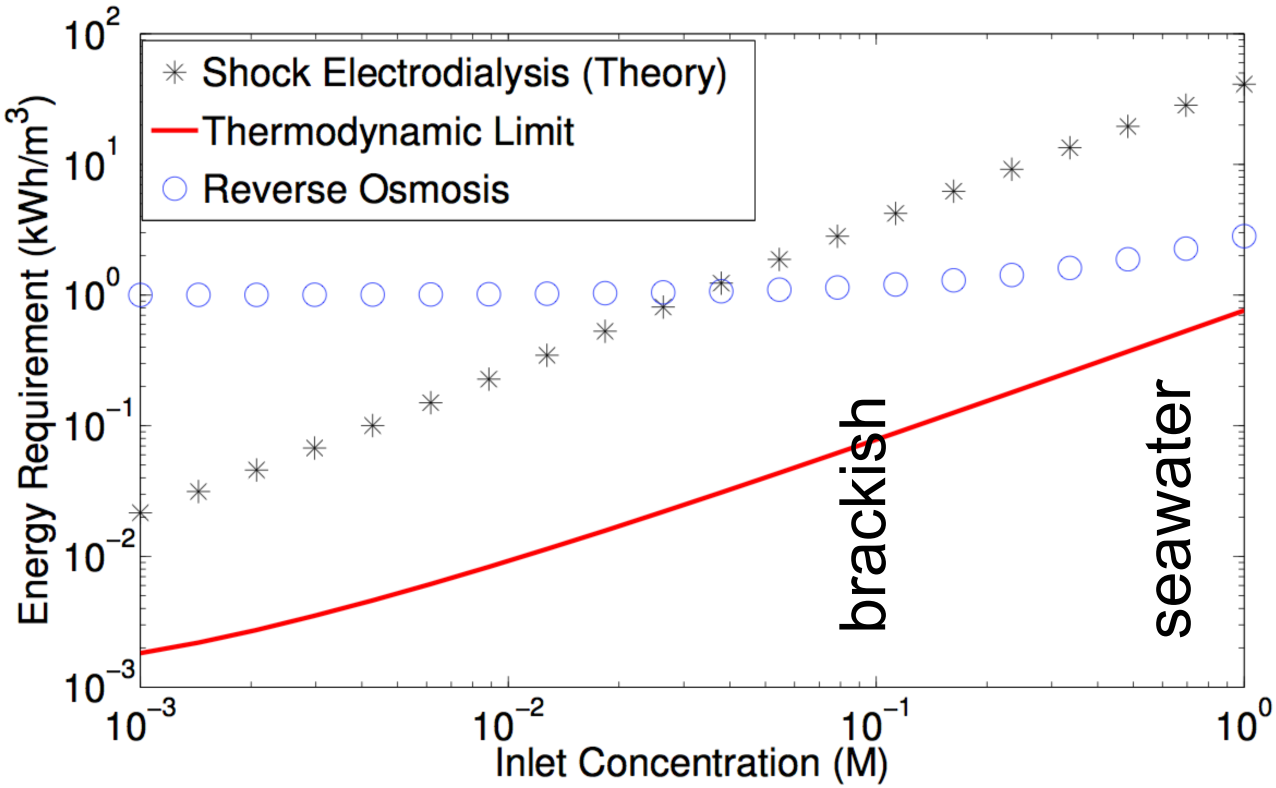


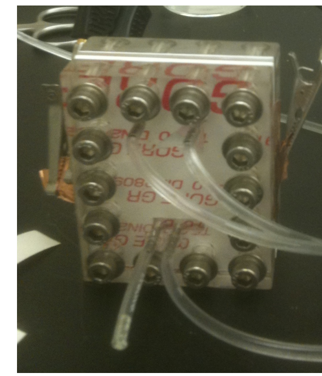


BACKUP SLIDES

Toward Cross-flow Scalable Shock ED





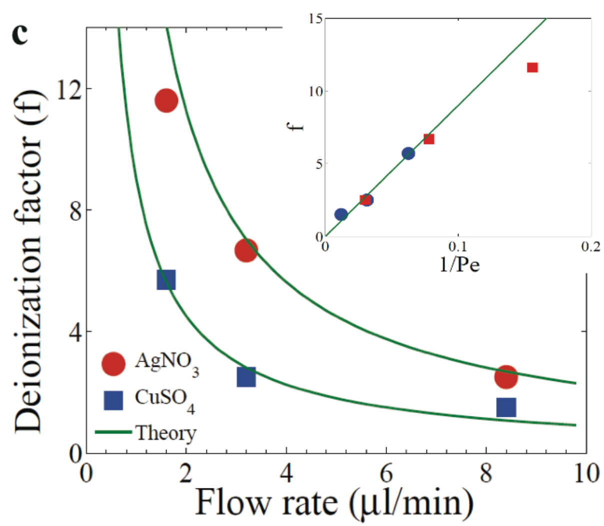


Energy cost to reduce salt by 80%

Multifunctionality of Shock ED

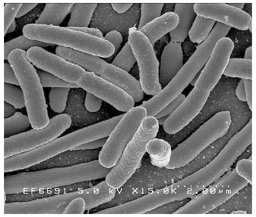
Separations

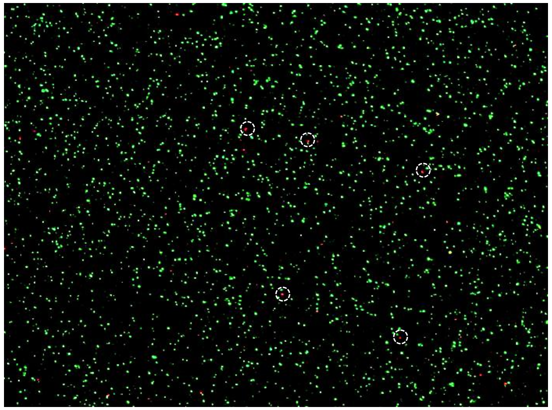
Ionic: Toxic multivalent ions
Molecular: Fluorescein dye
Colloidal: nanoparticles

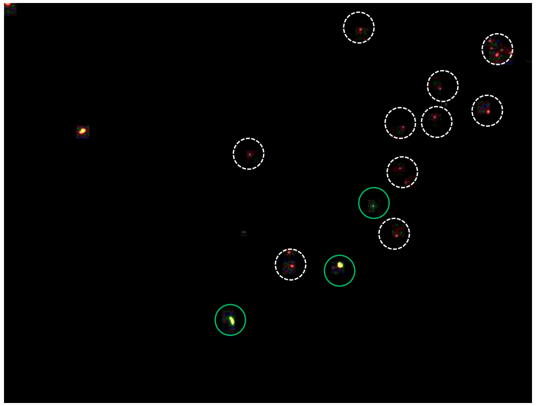


Disinfection

E Coli







Extraction rate: 0.2ul/min;
Applied voltage: 1.5V.

Inlet (10X)

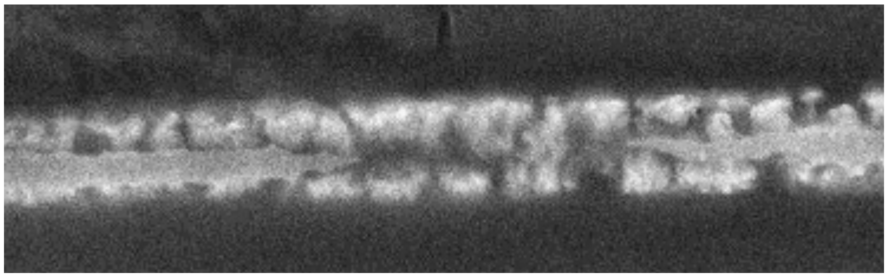
Outlet (4X)

Green: live cells
Red : dead cells

Applications

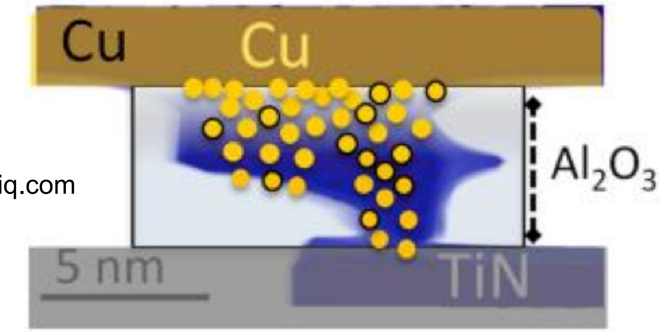
Integrated circuits (IBM)

wikipedia



10-100nm Cu interconnects – supress dendrites

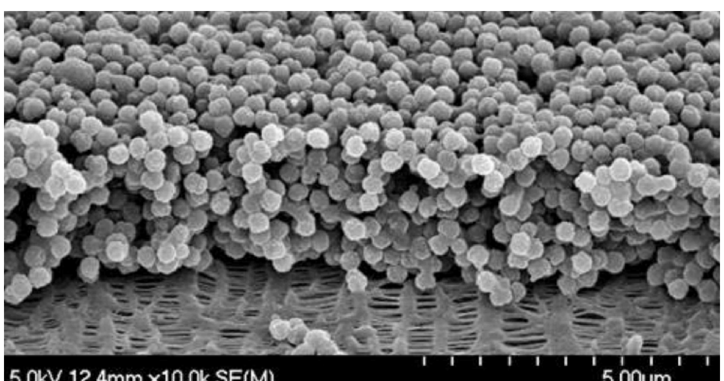
electroiq.com



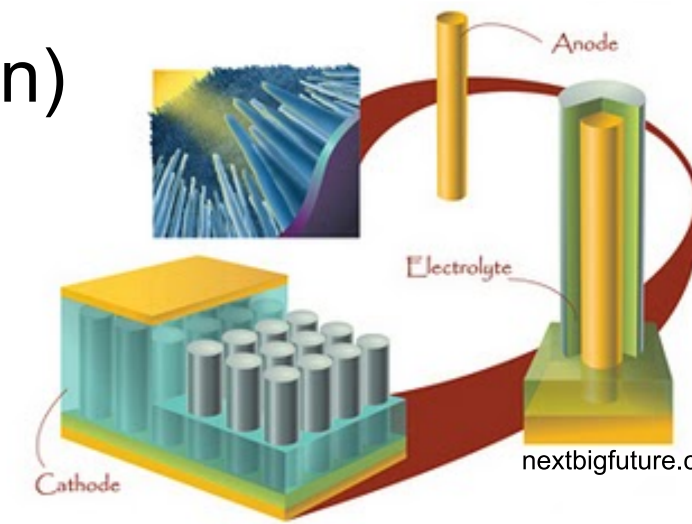
CB-RAM – control dendrites

Battery separators (Saint Gobain)

Kaneda, ECS abstracts 2012



Alumina powders – suppress dendrites

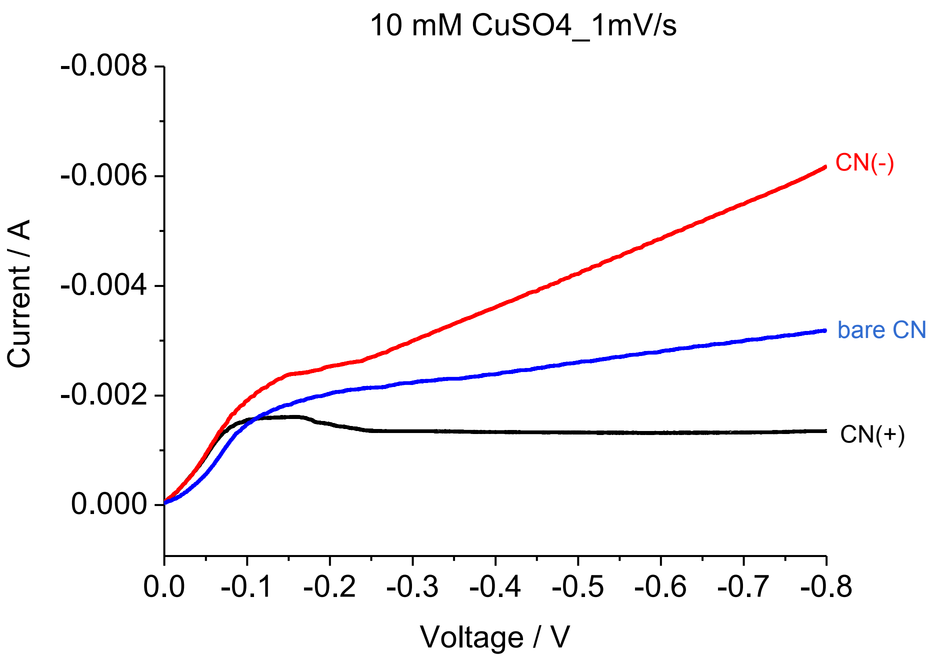


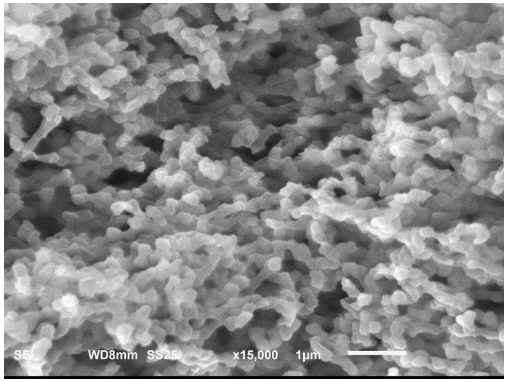
nextbigfuture.com

3D Battery fabrication– control dendrites

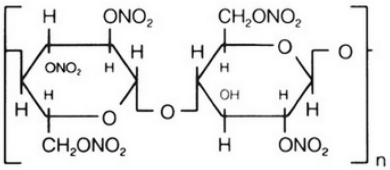
Shock Electrodeposition in Random Nanopores

Ji-Hyung Han

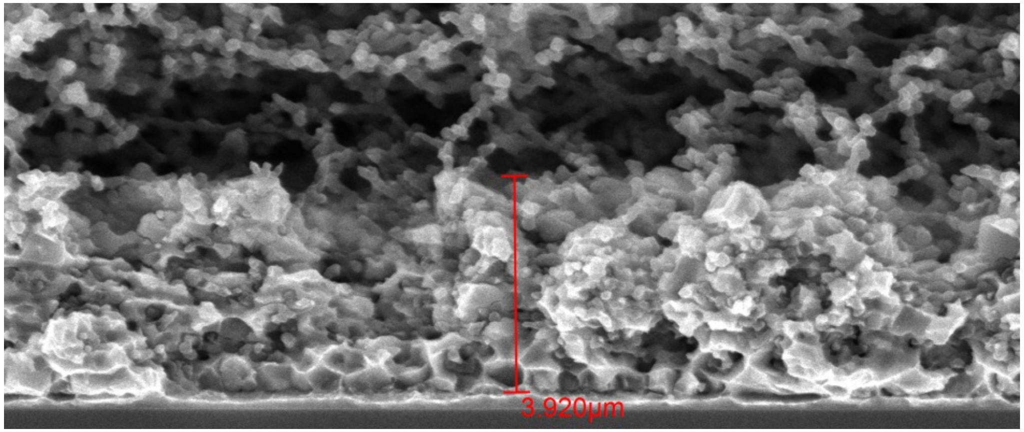




Cellulose nitrate (CN) membrane



Intrinsic surface charge is negative



CN(-) Very uniform growth

CN(+) No metal penetration

Next: Li-ion battery separators