Electrokinetic Response of a Floating Bipolar Electrode in a Nanofluidic Channel

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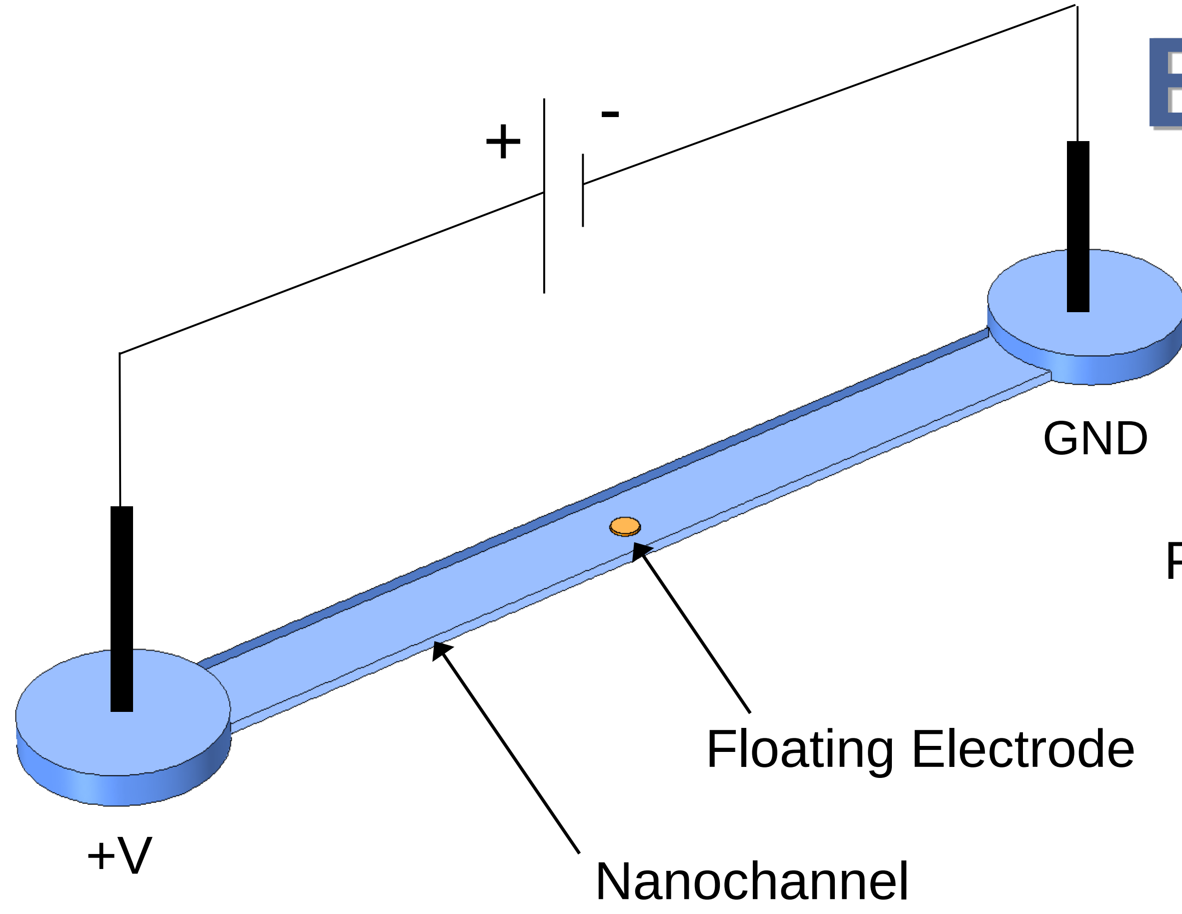
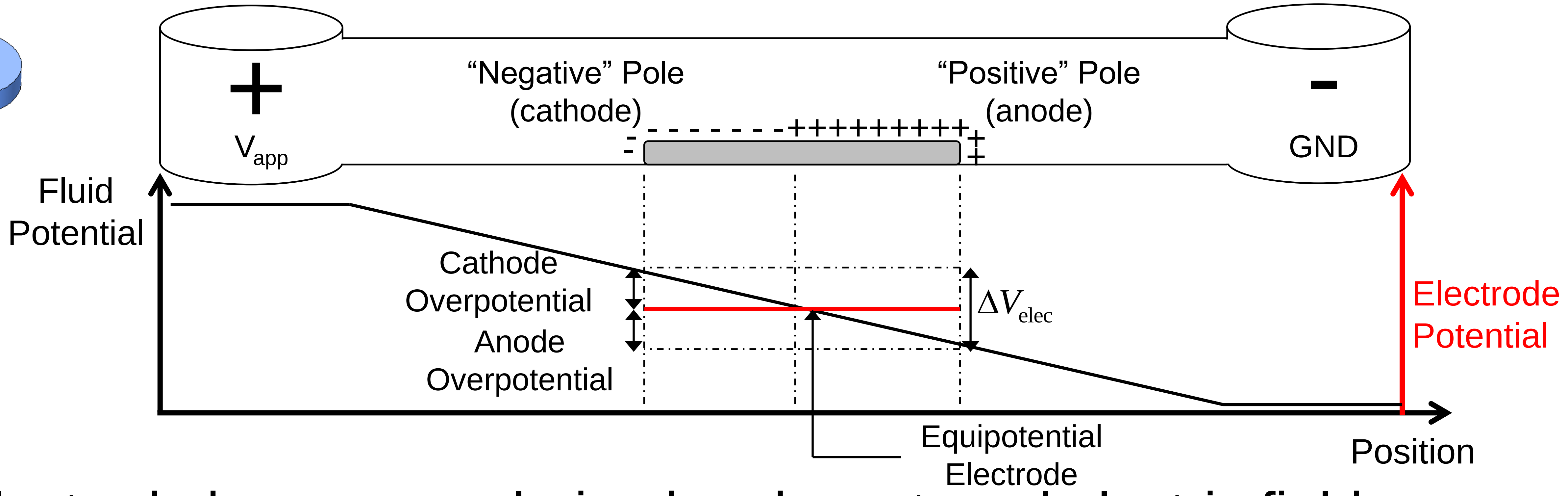
UC SANTA BARBARA mechanical engineering

ICB Institute for Collaborative Biotechnologies

nanolab Pioneers in Fluidic MEMS

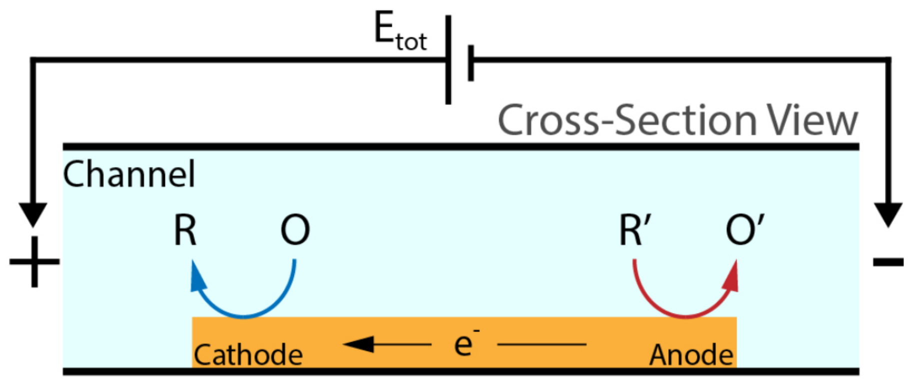
Background: Bipolar Electrodes (BPEs)





- Electrically isolated electrode becomes polarized under external electric field
  - Negative charge accumulates at left side of electrode (cathode), attracting cations
  - Positive charge accumulates at right side of electrode (anode), attracting anions
  - Electrostatic potential floats to uniform value which ensures zero *net* charge on surface
  - If ΔV_{elec} is sufficiently large, Faradic reactions occur at surface and current passes through electrode

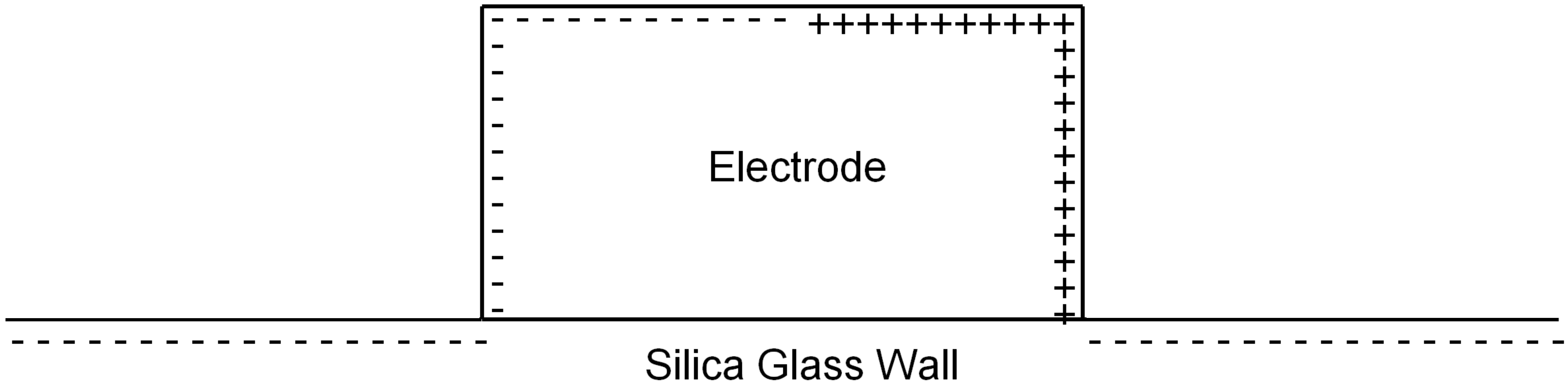
Electrolysis of Water:



Cathodic Reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anodic Reaction: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Electric Double Layers Form at Channel Walls & Electrode



⊕ Wall counter-ions: H^+, Na^+

⊖ Wall co-ions: $H_2PO_4^{\ -}$, $HPO_4^{\ 2-}$, OH^-

- Electrode surface charge comes from polarization under externally applied field

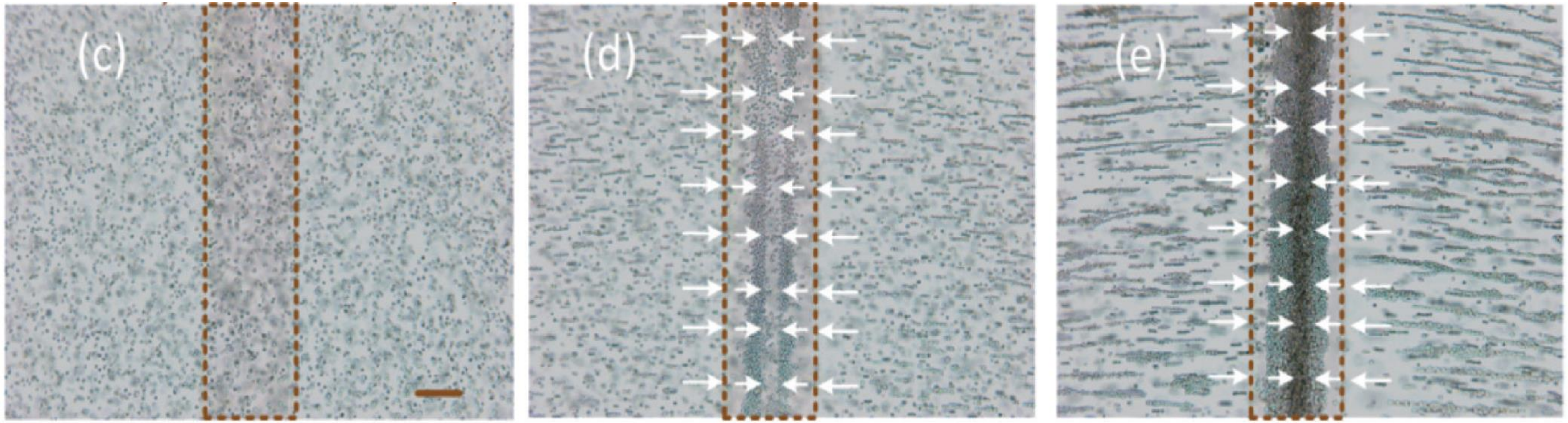
- Glass surface charge comes from protonation/deprotonation surface reactions:

$$\mathrm{SiOH} \rightleftharpoons \mathrm{SiO}^- + \mathrm{H}^+$$

Leads to acquired surface charge σ_0

Why use Bipolar Electrodes?

- Particle Trapping
  - Uses induced charge EOF and DEP
- Analyte Focusing/Separation
  - Leverages electric field gradients produced by nonuniform ion distributions
- Electrocatalysis
  - Driving redox reactions at BPE poles
- Surface patterning/Detection
  - Patterning surfaces with chemical gradients



Ren *et al*, Lab Chip, 2015, 15, 2181

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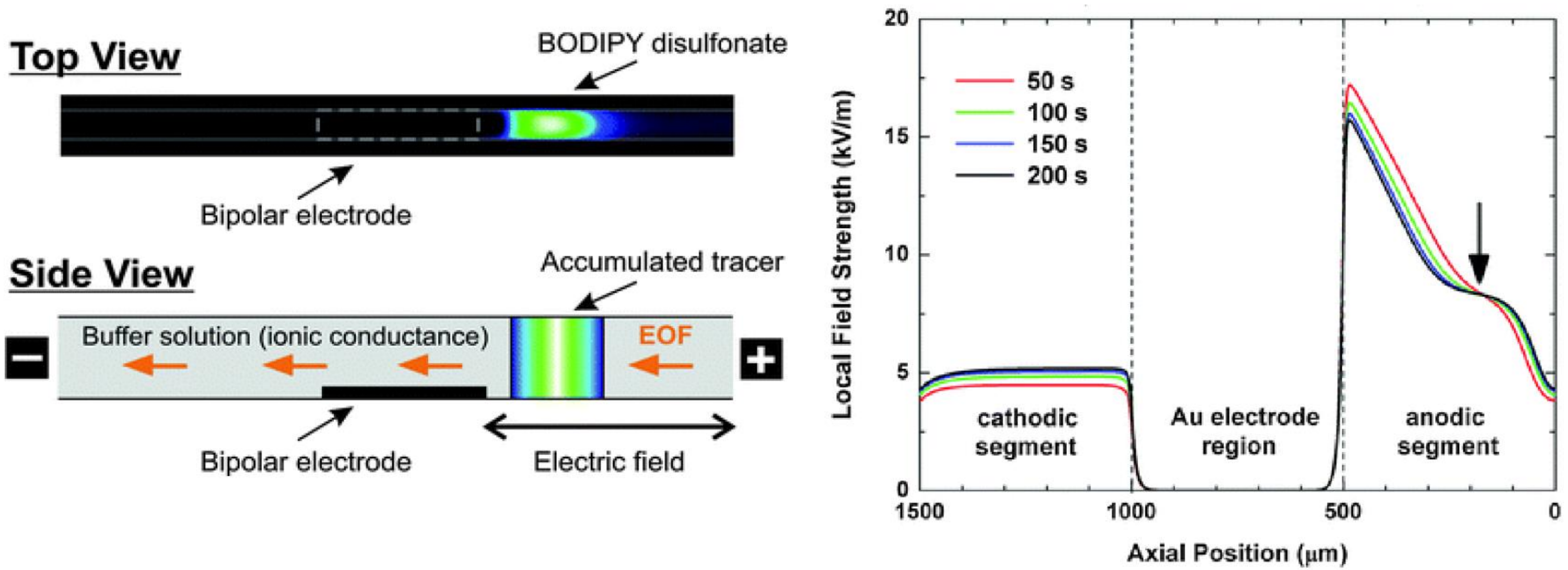

Hlushkou *et al*, *Lab Chip 2009, 9,1903*

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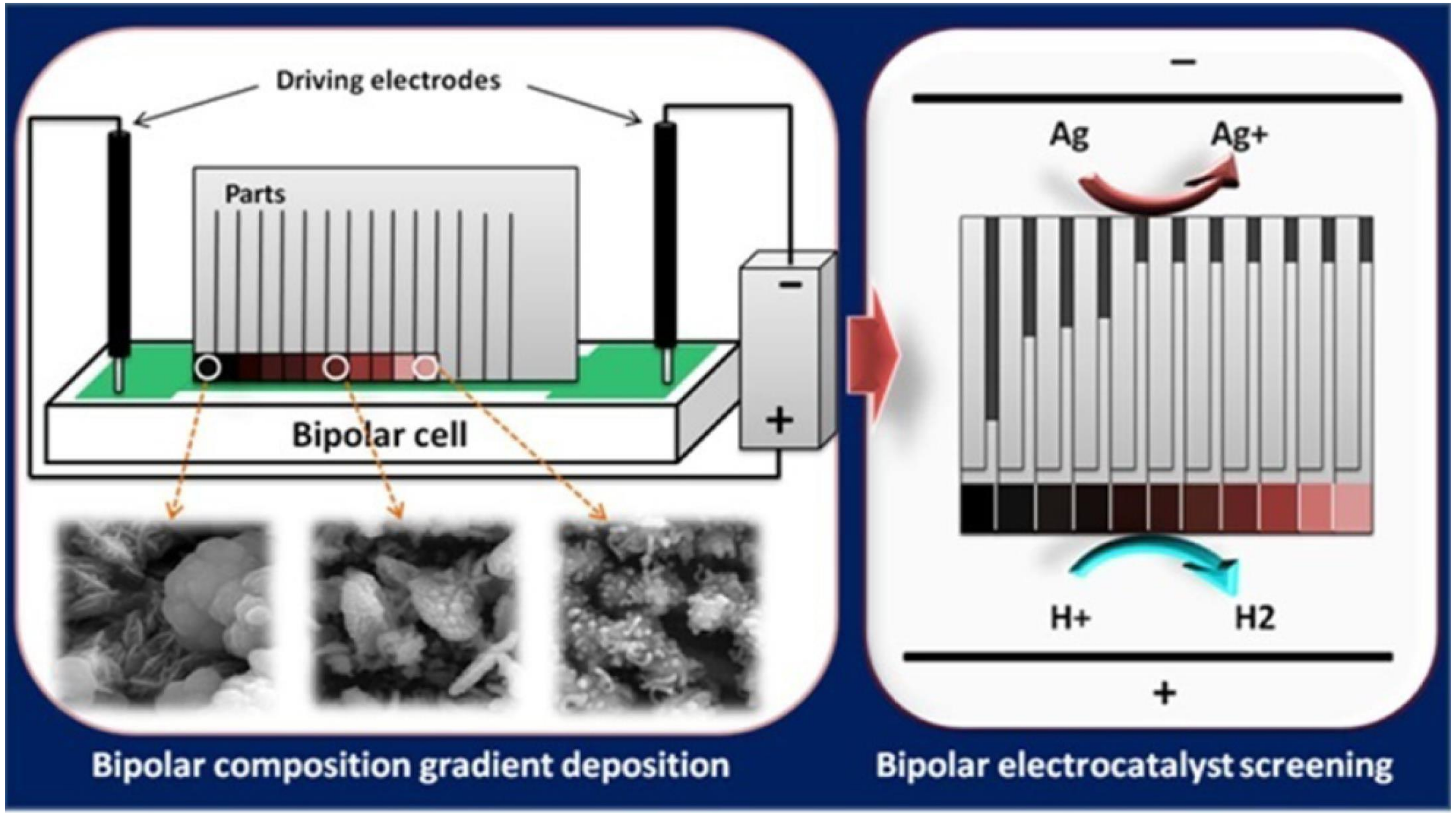

Termebaf *et* al, Langmuir 2015, 31, 13238

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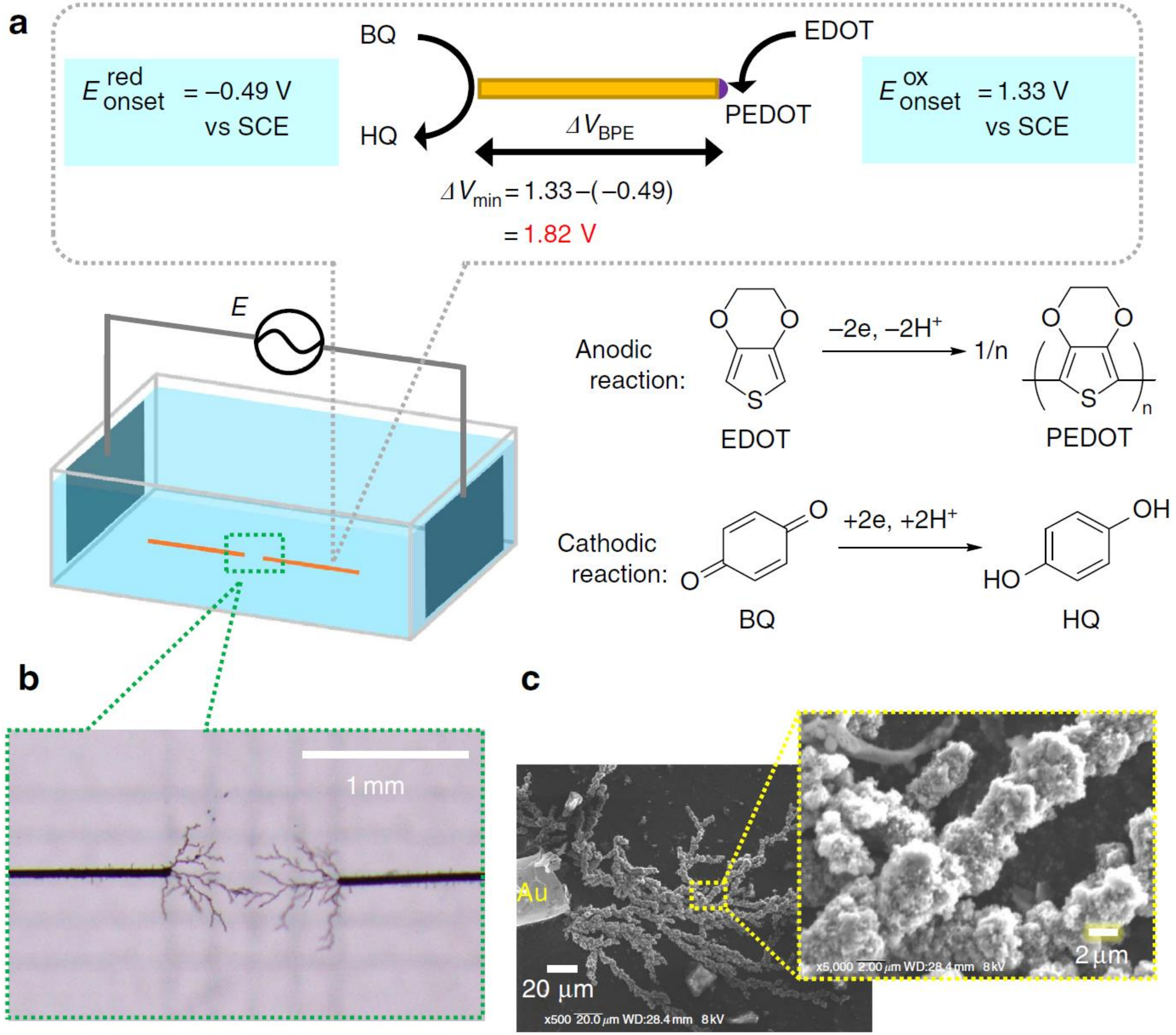
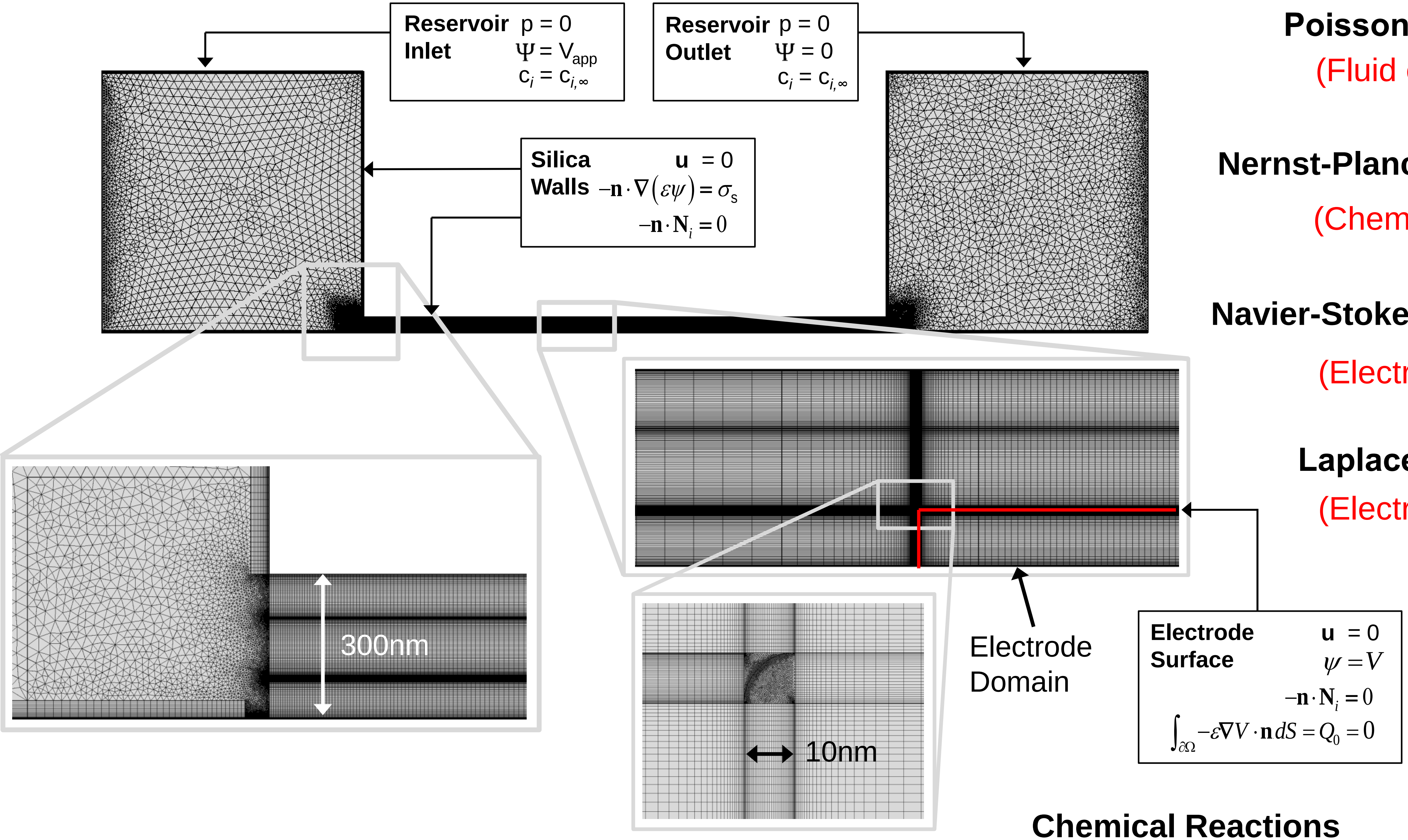
- Surface patterning/Detection
  - Patterning surfaces with chemical gradients, electropolymerization



Koizumi *et al*, Nature Comms 2016, 7, 10404

2D COMSOL Multiphysics Model: Overview



Poisson's Equation: $-\varepsilon_0\varepsilon_f\nabla^2\psi = \sum_i^n F z_i c_i$

(Fluid electrostatic potential)

Nernst-Planck Equation: $\frac{\partial c_i}{\partial t} = -\nabla\cdot\left(\mathbf{u}c_i - D_i\nabla c_i - D_i\frac{e_0 z_i}{k_B T}c_i\nabla\psi\right) + r_i$

(Chemical species conservation)

Navier-Stokes Equations: $\rho_f\left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u}\cdot\nabla\mathbf{u}\right) = \mu\nabla^2\mathbf{u} - \nabla P + \sum_i^n F z_i c_i \mathbf{E};$

(Electroosmotic fluid flow) $\nabla\cdot\mathbf{u} = 0$

Laplace's Equation: $\nabla^2 V = 0$

(Electrode electrostatic potential)

Species Reaction Source Terms	
$H_2PO_4^-$	$-R_{H_2PO_4^-}$
HPO_4^{2-}	$R_{H_2PO_4^-}$
H^+	$R_{H_2PO_4^-} + R_{H_2O}$
OH^-	R_{H_2O}
Na^+	0

$$R_{H_2PO_4^-} = k_{H_2PO_4}\left(K_a - \frac{c_{HPO_4^{2-}}c_{H^+}}{c_{H_2PO_4}}\right)$$

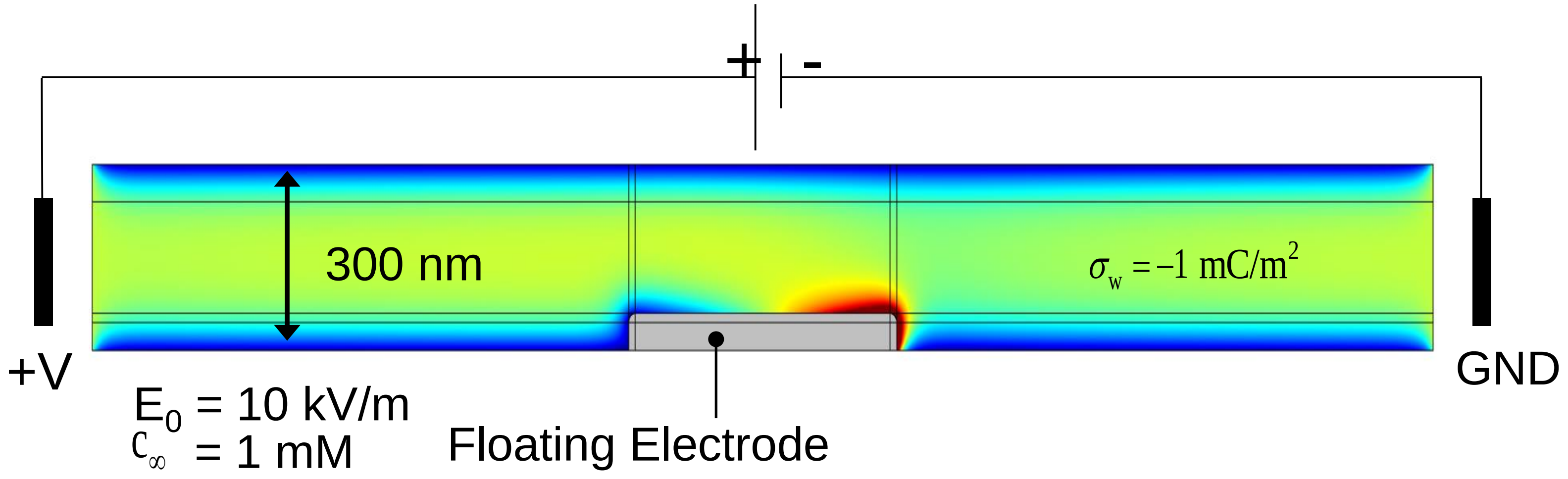
$$R_{H_2O} = k_{H_2O}\left(K_{H_2O} - \frac{c_{HPO_4^{2-}}c_{H^+}}{c_{H_2PO_4}}\right)$$

Chemical Reactions

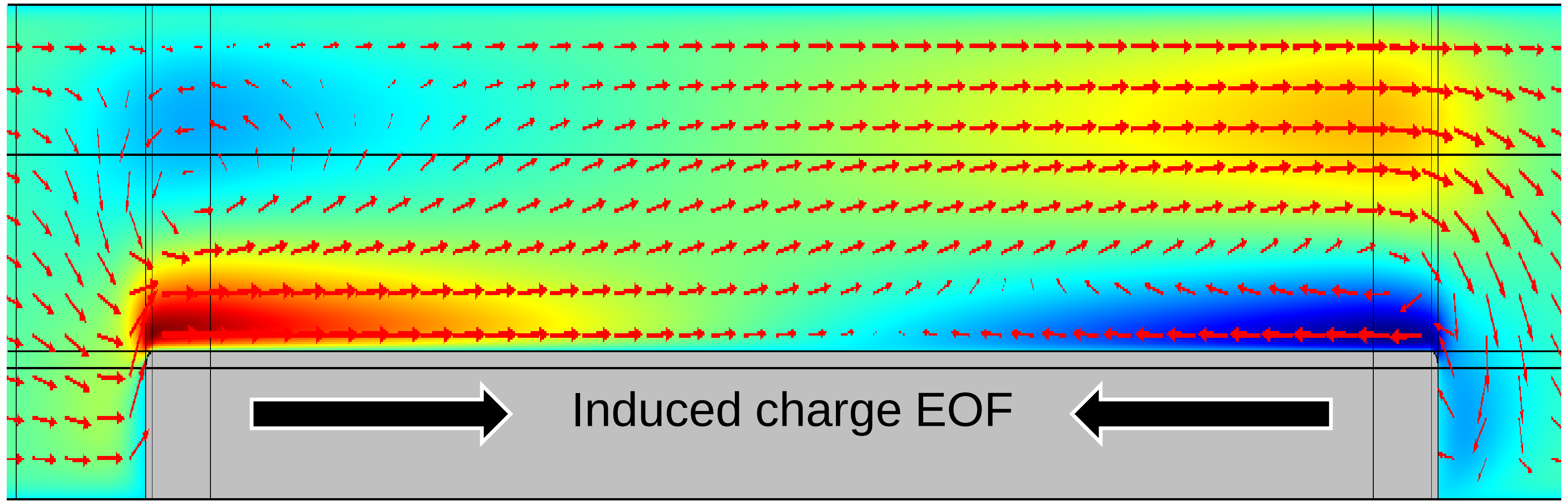
$$H_2PO_4^- \longleftrightarrow HPO_4^{2-} + H^+$$
$$H_2O \longleftrightarrow H^+ + OH^-$$

- Approximately 238,000 mesh elements in model
- Simulated BGE is buffered phosphate solution (pH ~ 7)
- Simulated tracer is fluorescein

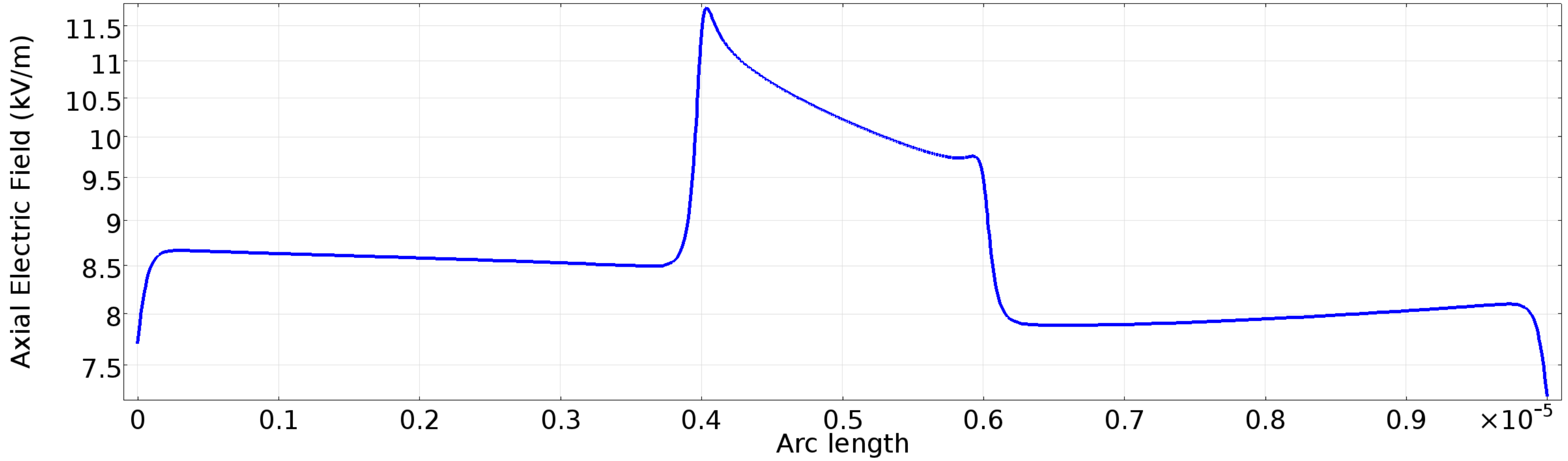
Axial BGE, Velocity, & E Field



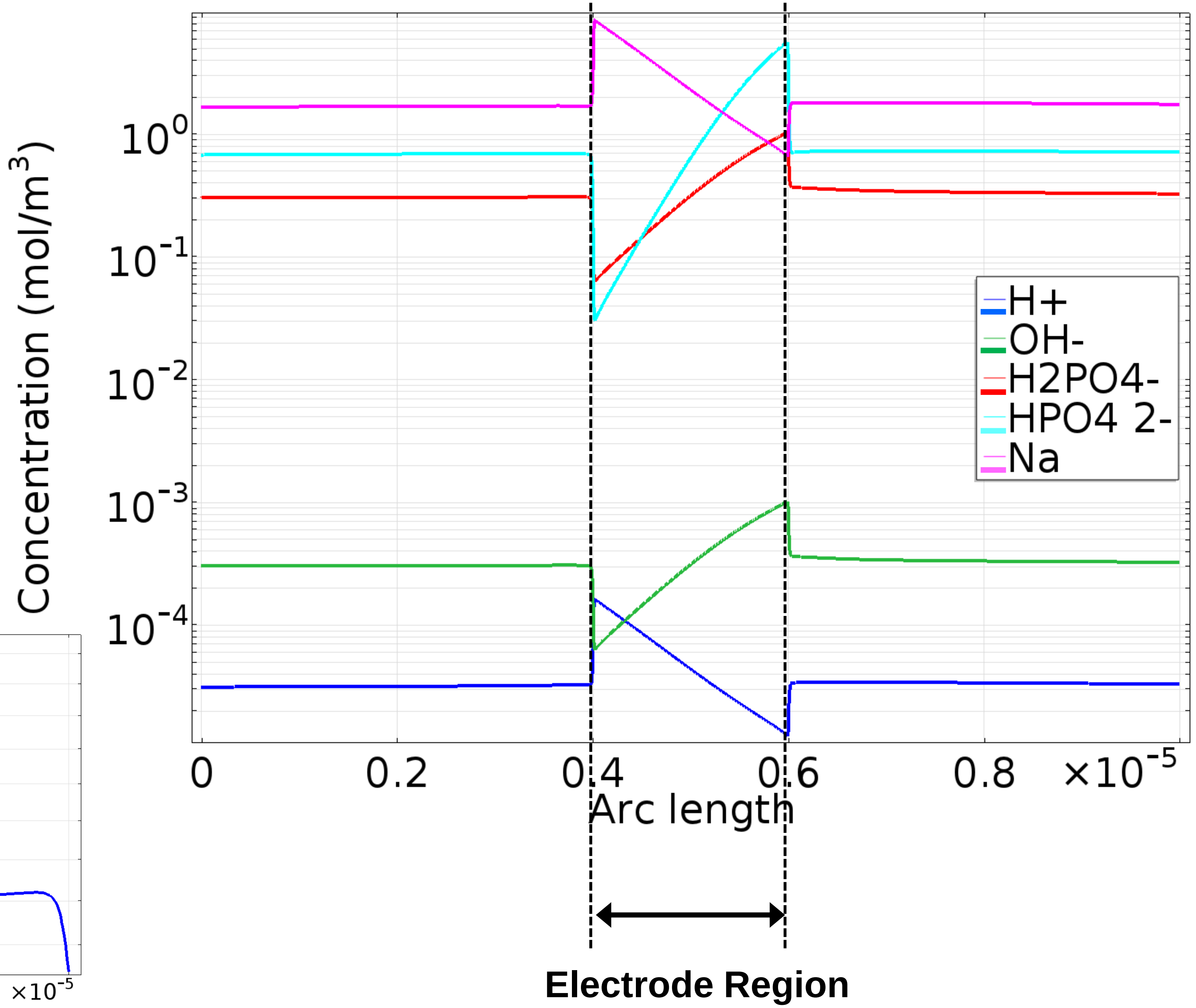
2D Velocity Profile Near Electrode



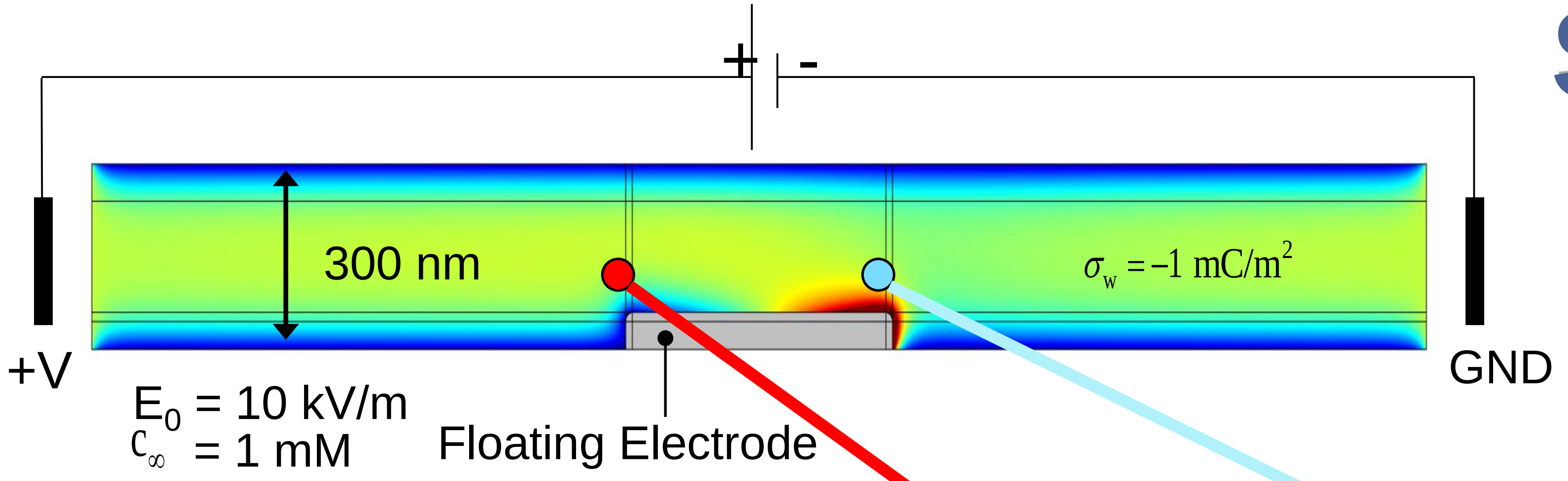
Axial Electric Field Profile



Phosphate Buffer Component Concentrations



Surface Charge and Potential: Temporal Response After Turning Voltage Off



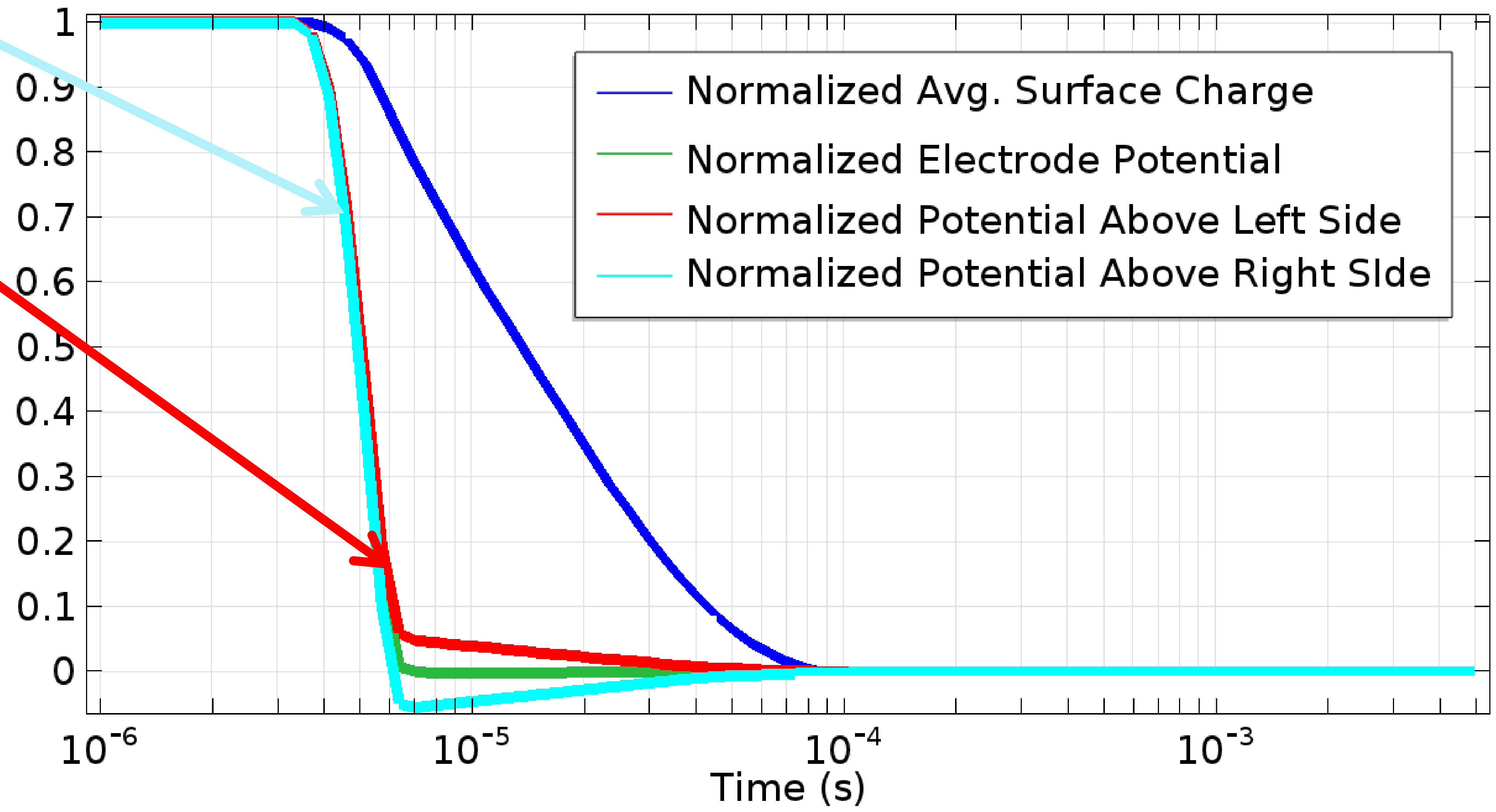
Surface charge depends on potential *difference* in fluid near electrode

- Electrode potential changes with same response as applied field, as does fluid directly in contact w/ electrode

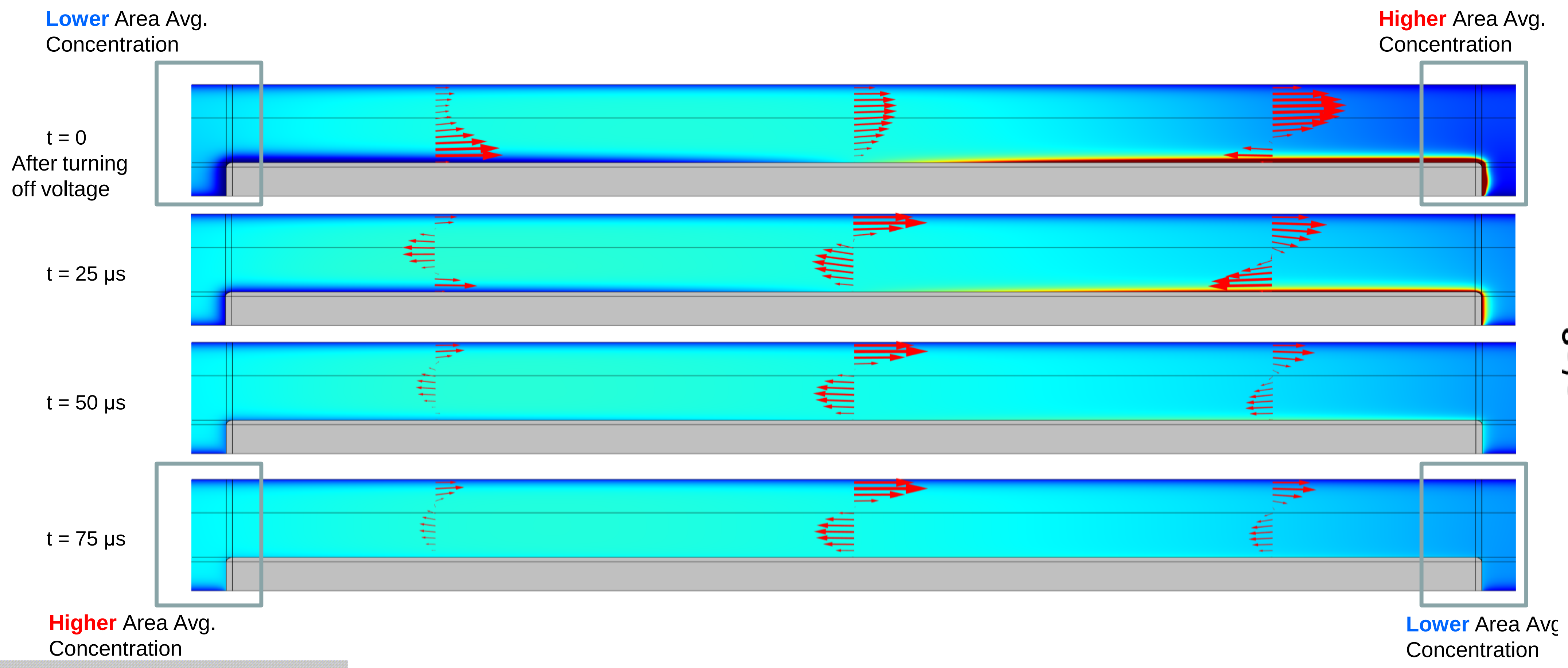
- Ion distribution and EDL potential responds more slowly than electrode potential due to ion accumulation/depletion

- Remaining anionic species accumulated at anode result in local negative potential, cationic species at cathode result in local positive potential

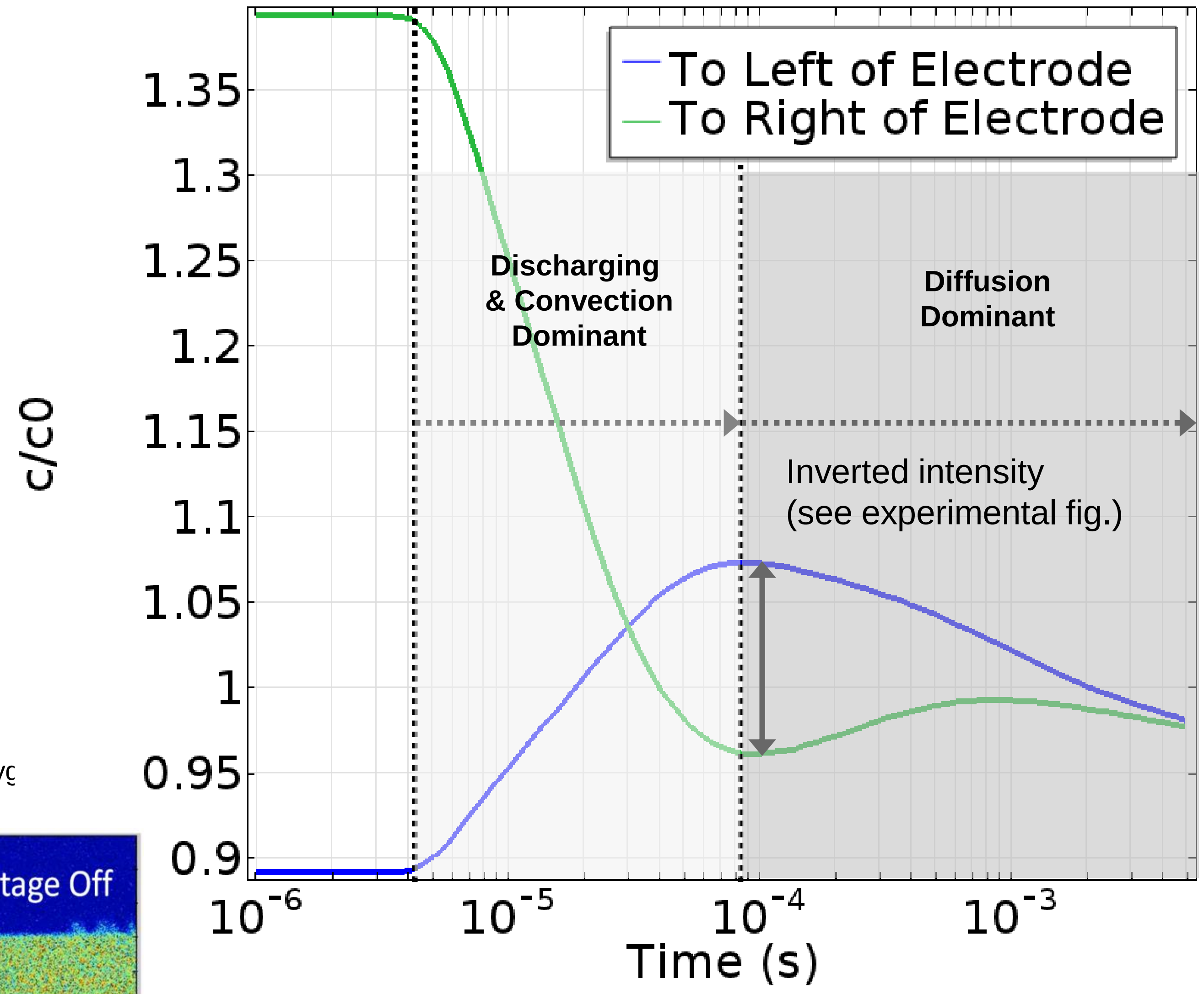
- Potential difference near electrode poles creates electric field which temporarily focuses tracer species at left side of electrode

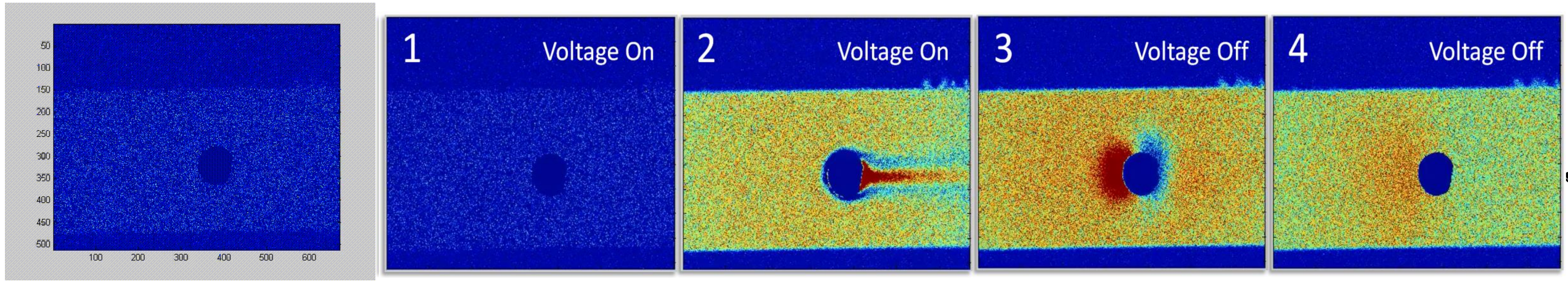


Tracer Ion Temporal Response: Focusing

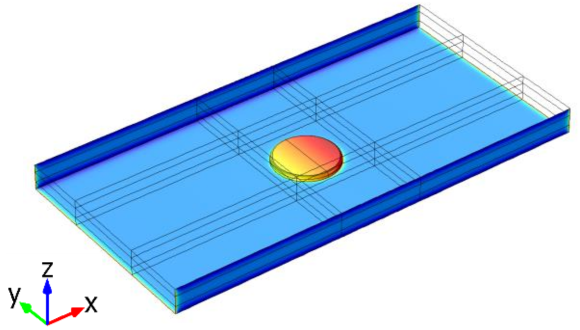


Area Averaged Tracer Species Concentration Over Time

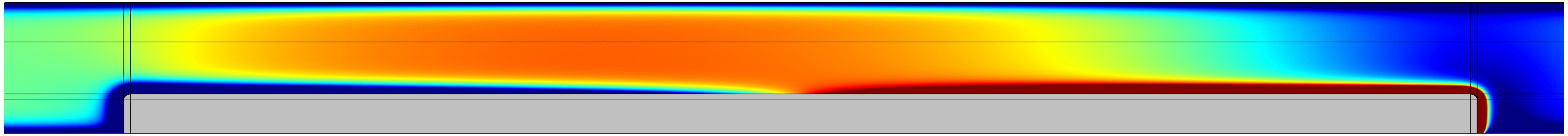




NOTE: Experimental intensity scales include some saturation in regions of high tracer concentration



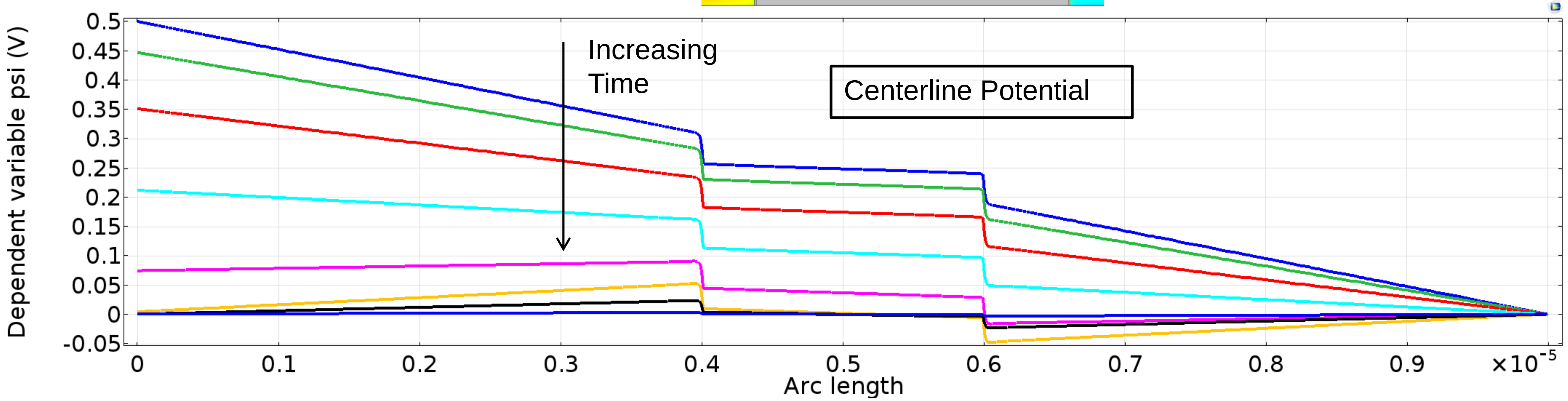
Simulated Tracer Species Concentration over Time



Axial Potential & Electric Field Response

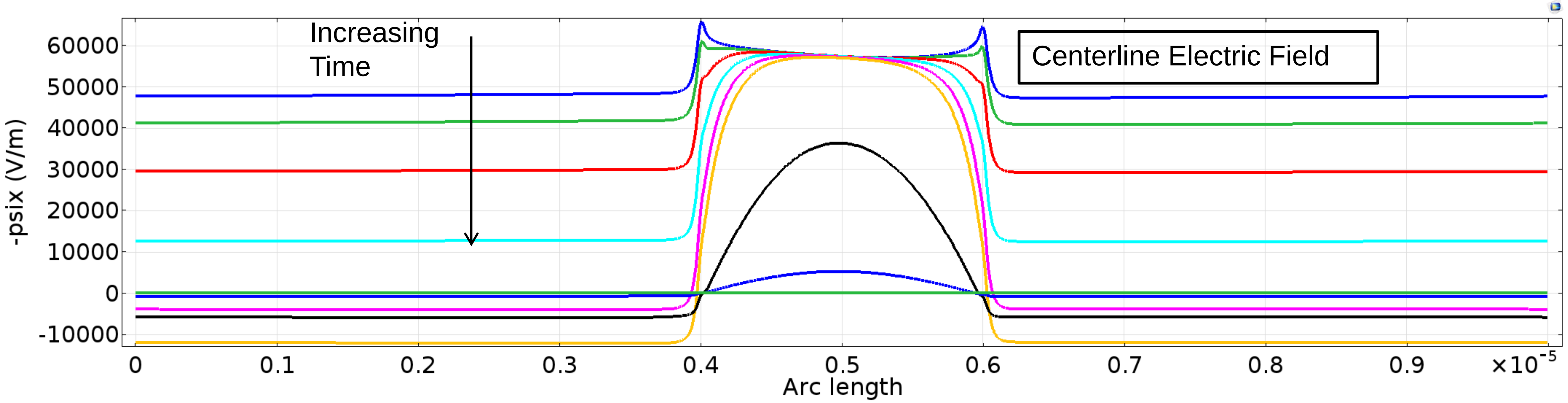
E_0 = 50 kV/m

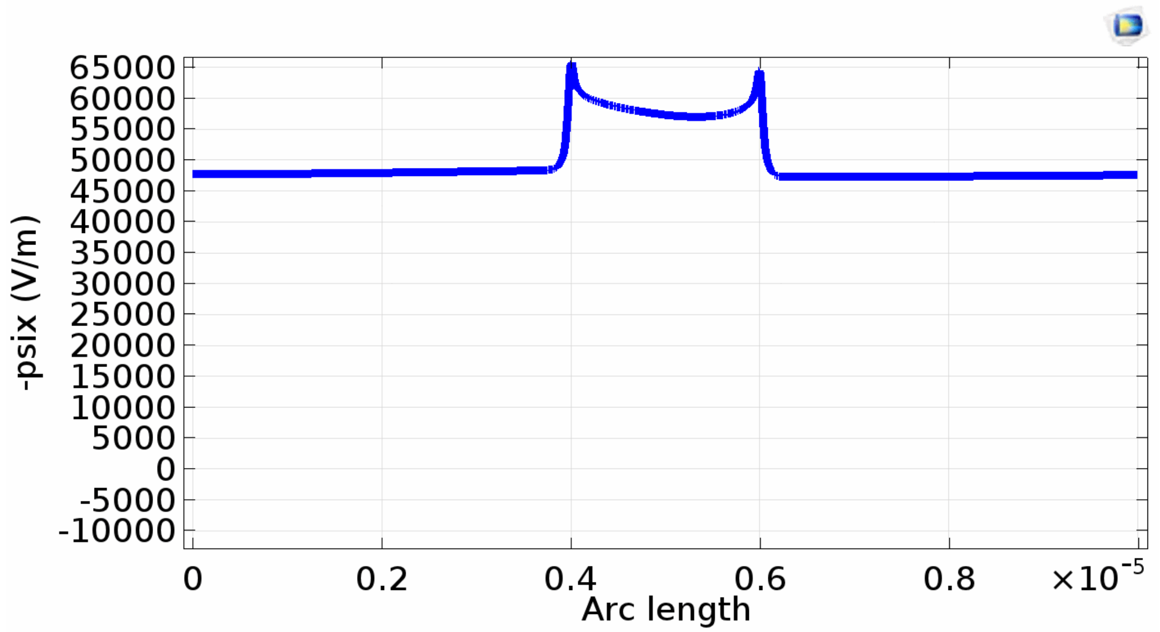
Profiles taken along channel centerline

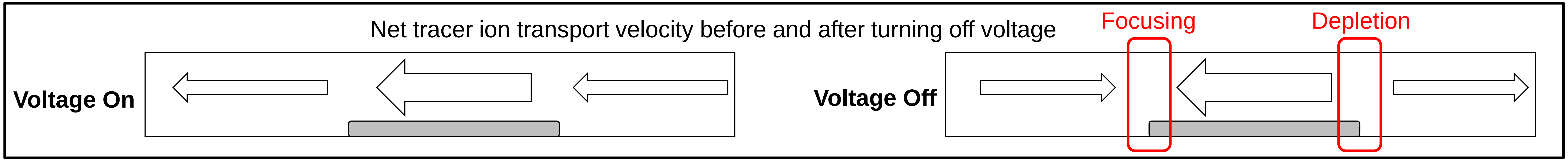


Electric field to left and right of electrode temporarily flip after turning Voltage off (E field points to left)

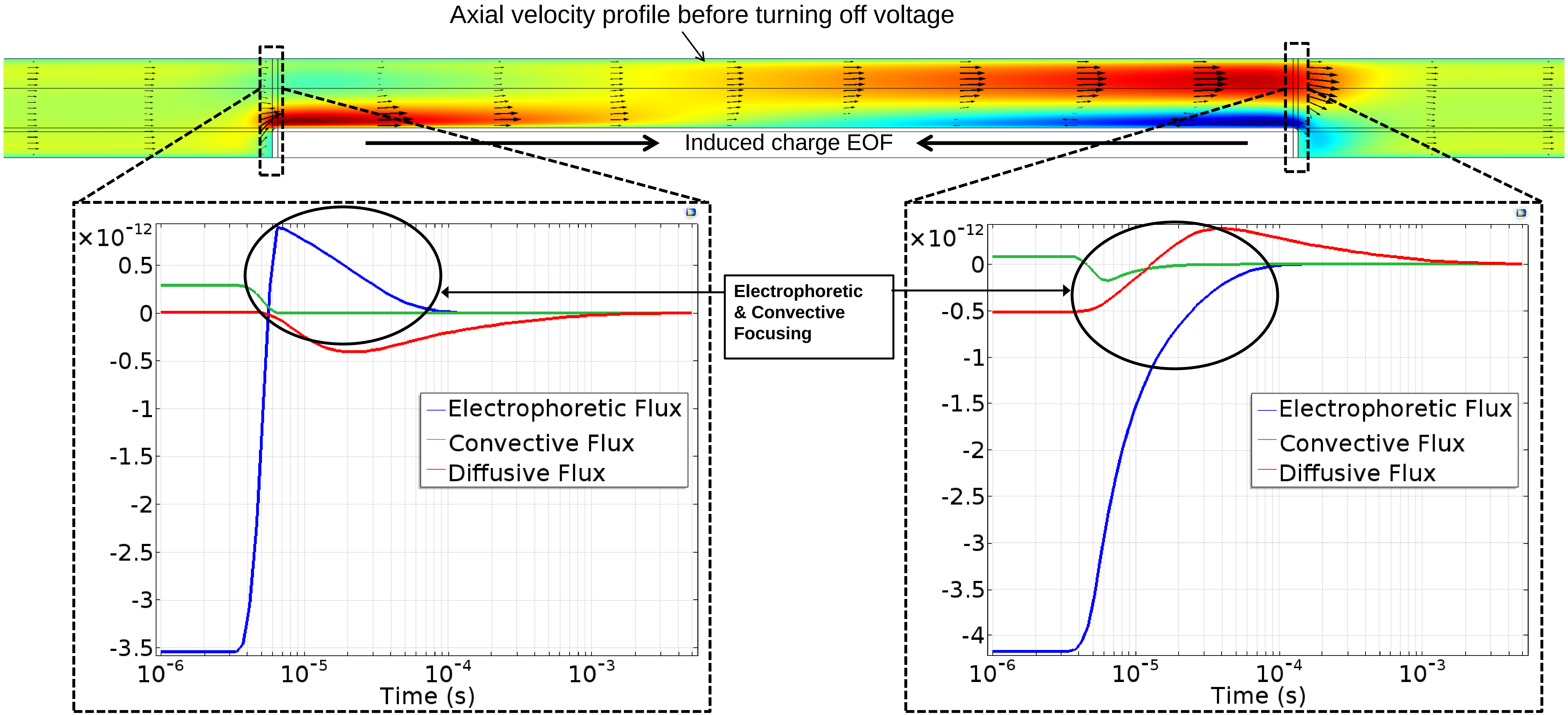
-Creates electrophoretic focusing near left edge and depletion near right edge for negative tracer species







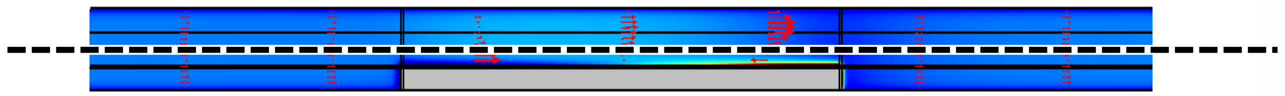
Induced Charge EOF & Temporal Flux Evolution



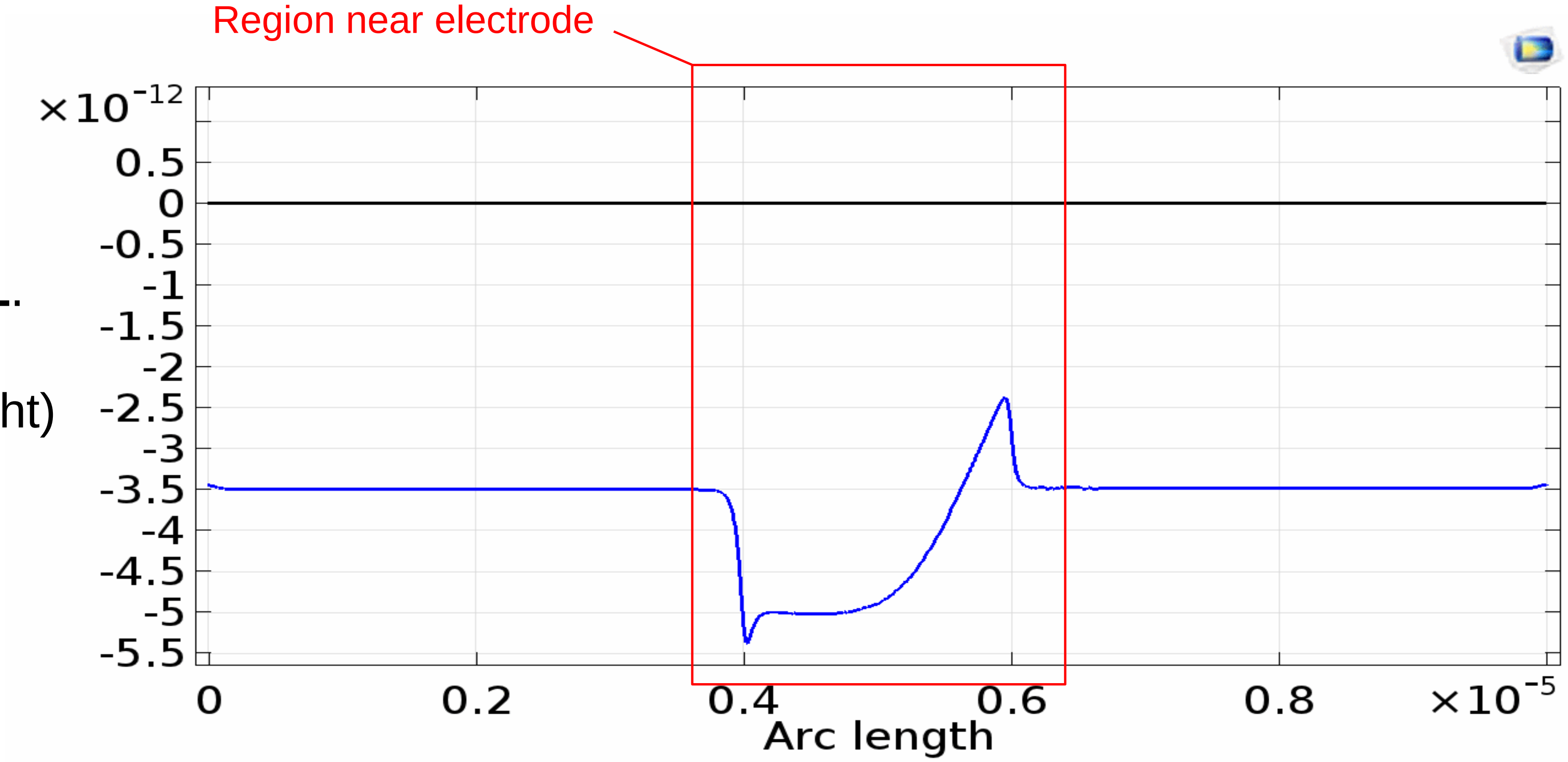
Area-averaged fluxes to left and right of electrode

Net Flux & Temporal Concentration Rate of Change

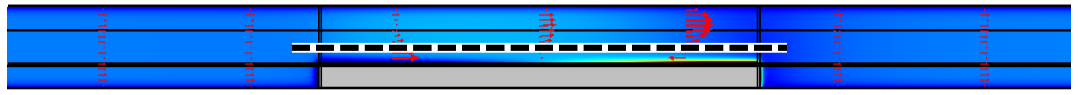
Total flux along channel center



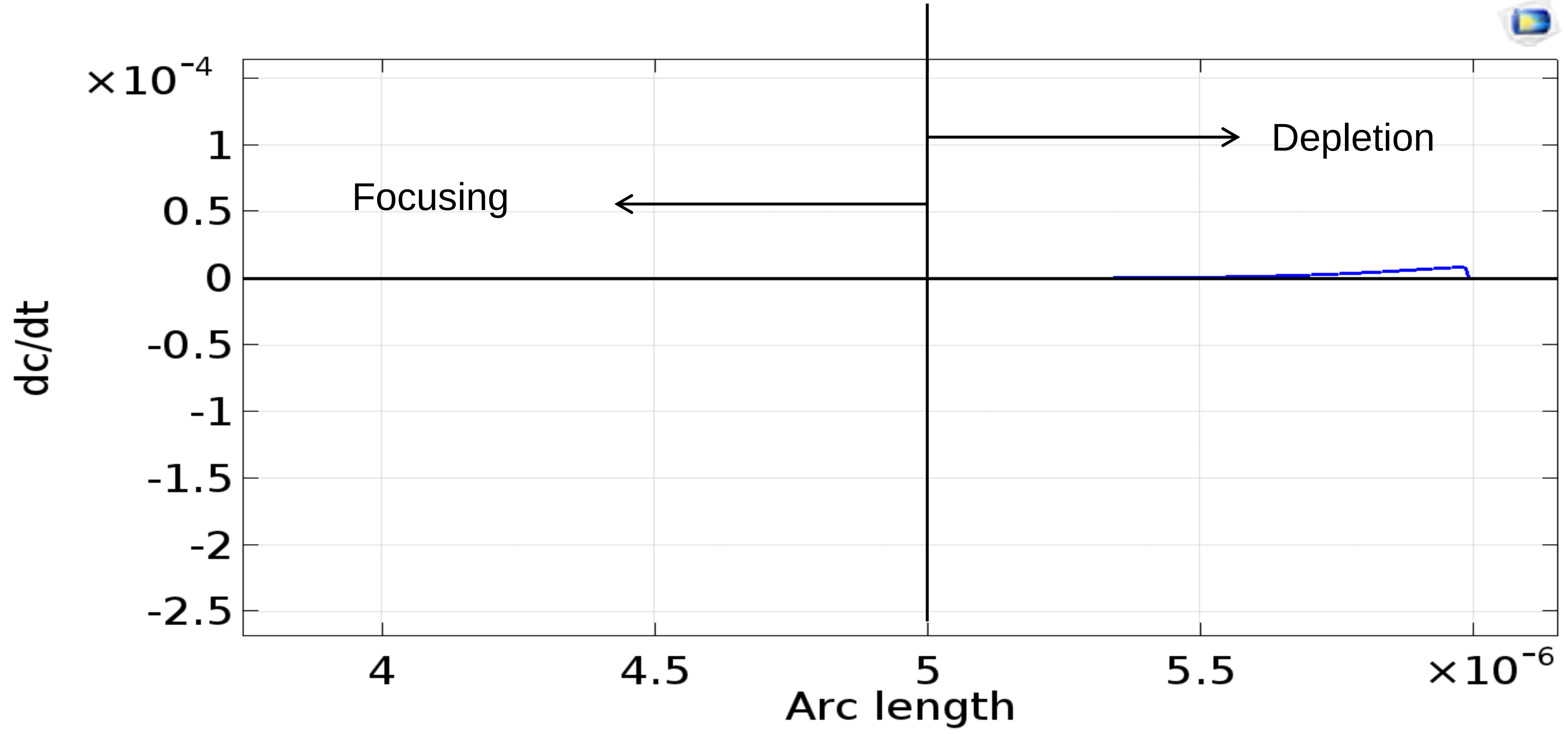
- Flux to left & right of electrode is positive (to the right)
- Flux above electrode is negative (to the left)



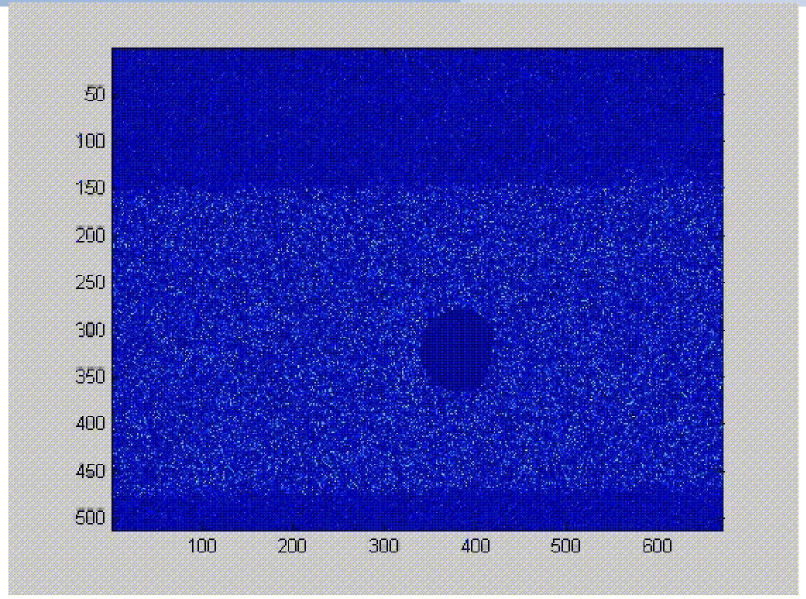
Concentration time rate of change along channel center, near electrode



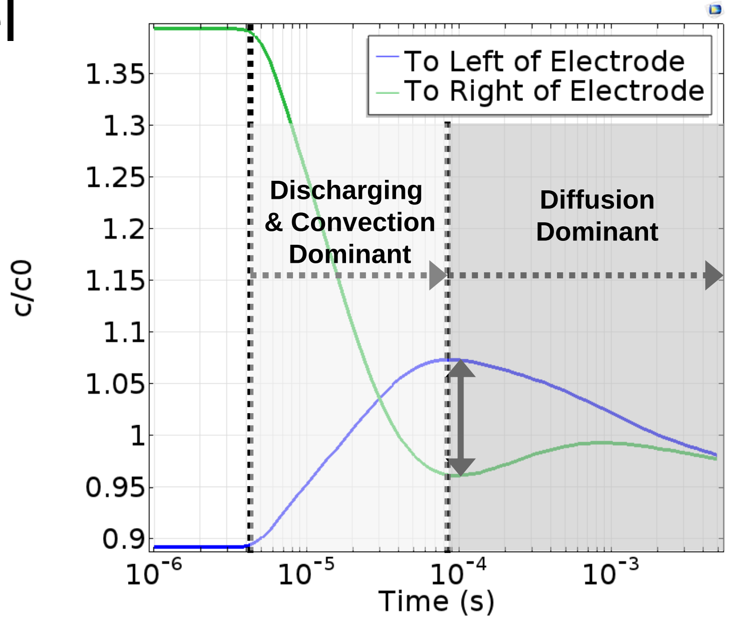
- Concentration above left side of electrode increases over time (focusing)
- Concentration above right side of electrode increases over time (depletion)



Summary:

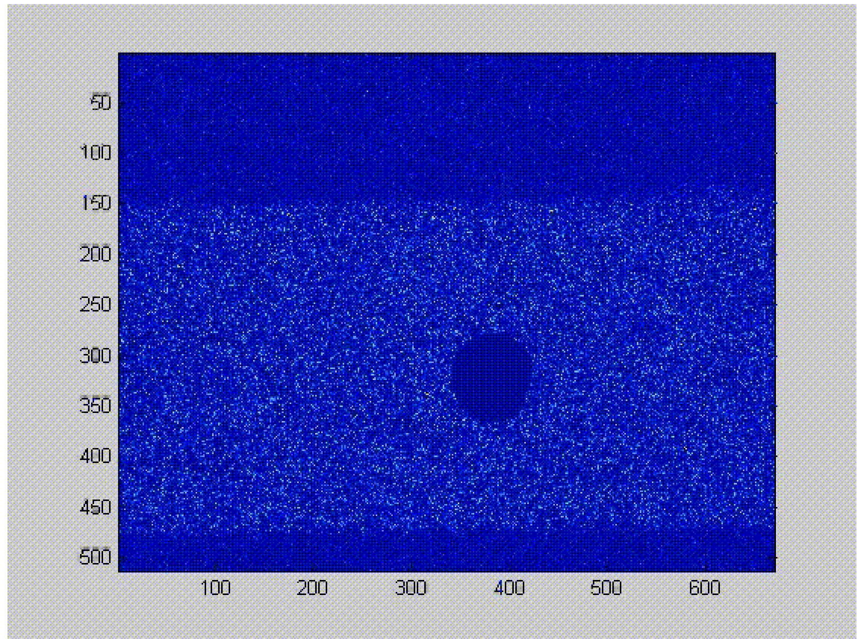


- Floating electrode becomes polarized under external field
  - Left side (cathode) is negatively charged, right side (anode) is positively charged
- Transient response of electrode leads to temporary analyte focusing
  - EDL responds more slowly than electrode, leading to E field reversal in parts of channel
- Simulation results match general trend observed experimentally
  - Tracer molecules shift from anode towards cathode before diffusing away



Future Directions:

- Include Faradaic reactions from electrolysis of water molecules
  - Current passes through electrode due to electron transfer driven by interfacial potential difference between fluid & electrode
- Match faradaic reaction experiments to simulation results



Thank you for your time!

Questions?