Multiscale Modeling of Bipolar Electrochemistry

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Introduction: Bipolar electrodes (BPE) are an important tool not only in micro-electrochemistry. A continuous multiscale model is developed in three steps, incorporating surface redox reactions and microscopic double layer structure present at the idealized solution/BPE interface.

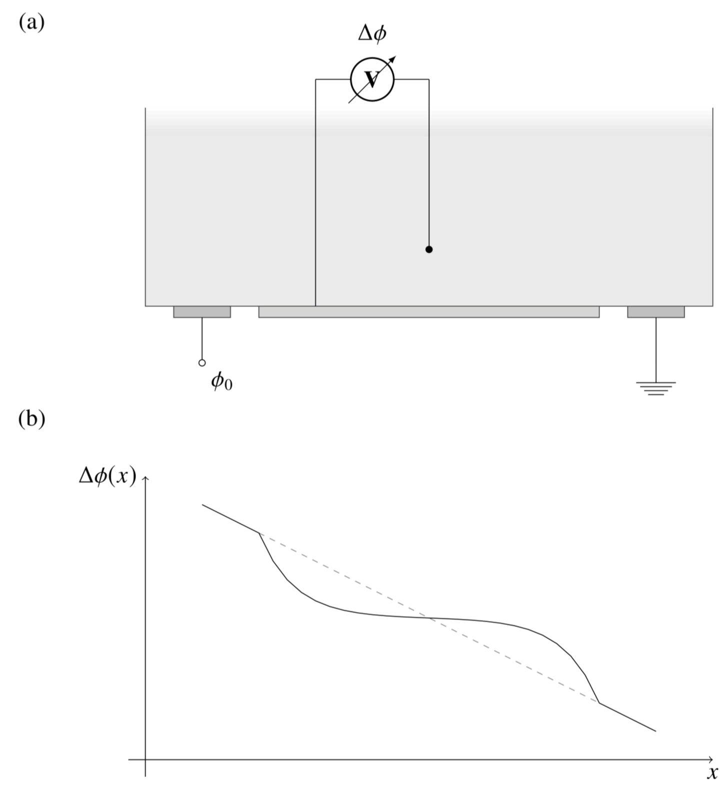


Fig. 1 Electrochemical cell with BPE (a) conceptual potential distribution (b)

Method: Solving slightly varying Poisson-Nernst-Planck equation systems, the BPE's environment is represented by

1. macroscopic 2d model with electroneutrality assumption:

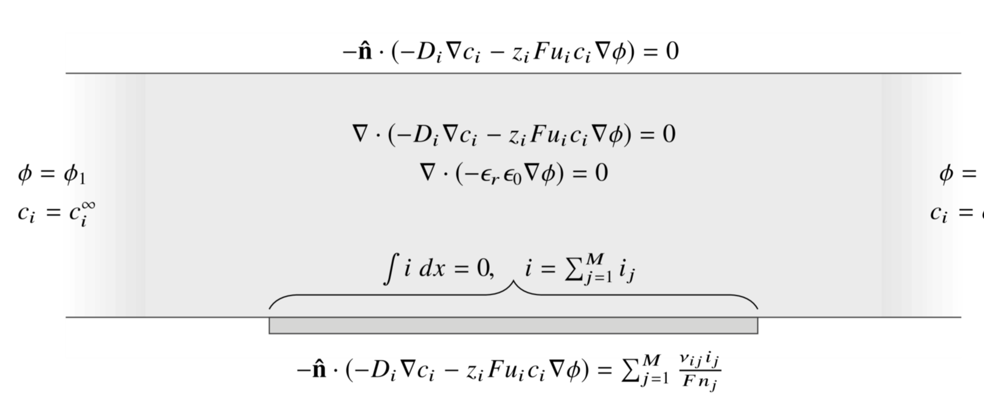


Fig. 2 Electroneutral Nernst-Planck model

Electroneutral model of BPE in microchannel, realized with the Electrochemistry Module's Tertiary Current Distribution interface. BPE potential and surface species flux determined by zero net faradaic current constraint. One solute species dependent by:

$$c_N = -\frac{1}{z_N} \cdot \sum_{i=1}^{N-1} z_i c_i$$

2. microscopic 1d model of double layer region:

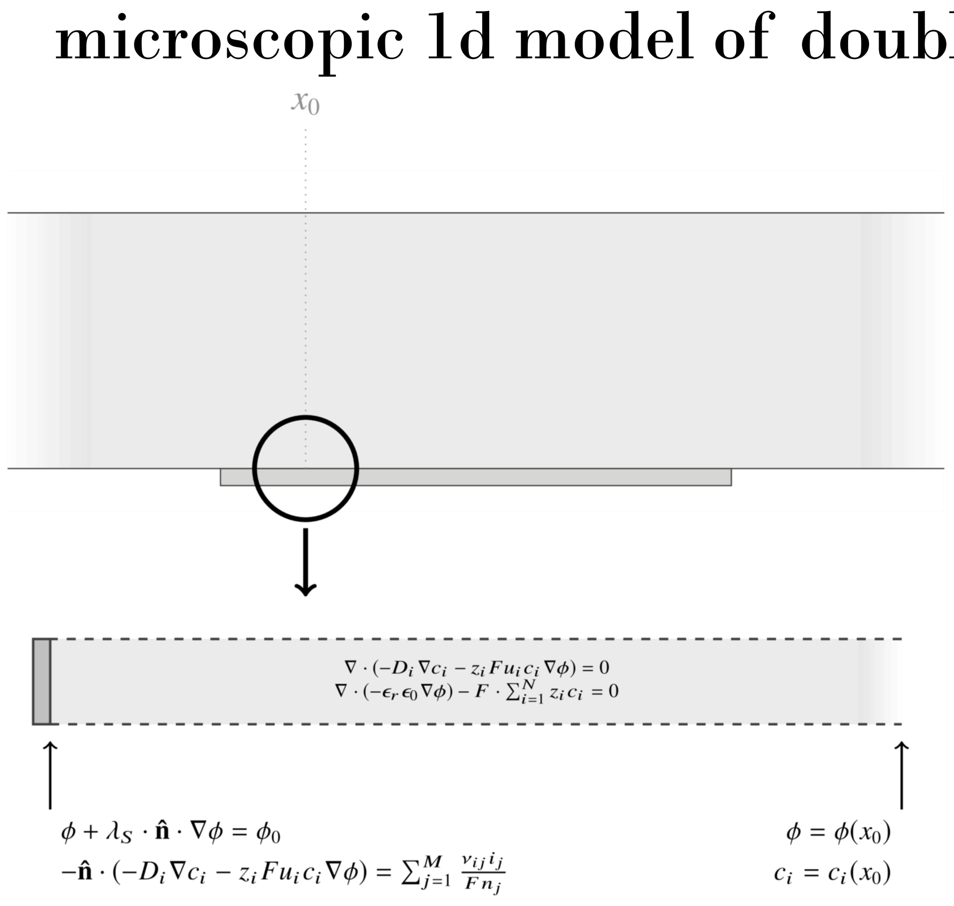
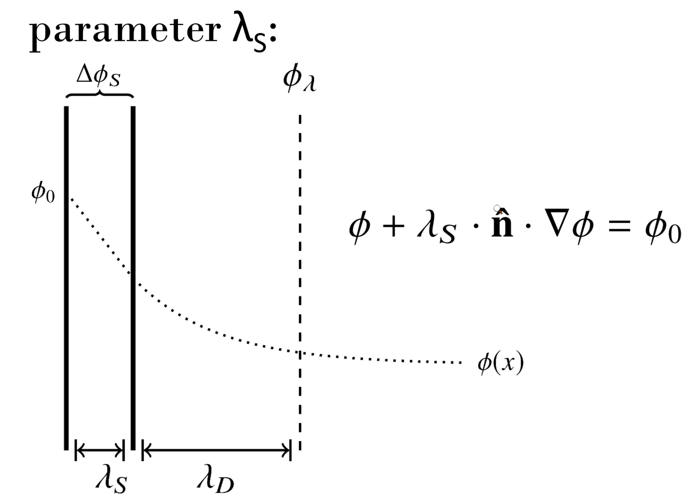


Fig. 3 1d PNP model of double layer

Fully coupled PNP model of interfacial region at Debye length λ_D scale. Neumann and Dirichlet boundary conditions determined by macroscopic 2d model. Robin boundary conditions for potential after [1] represent Stern layer by parameter λ_S:



3. multiscale 2d model of interface and environment:

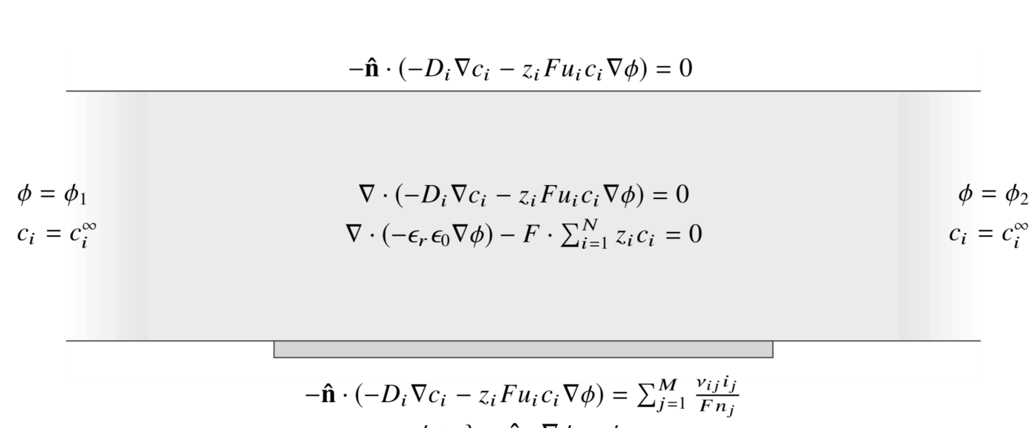


Fig. 4 2d PNP model

Fully coupled PNP model realized with the Chemical Reaction Engineering module's Transport of Diluted Species and the AC/DC Module's Electrostatics interfaces. Species flux boundary conditions and initial configuration from previous models.

BPE interface reactive species flux relates to faradaic current, which may be modeled via appropriate Tafel or Butler-Volmer terms, or by empiric reaction kinetics data.

Results: Displayed are results of a fictive system based upon [2] and [3] at cell potential 0.56 V. H_3O^+ and OH^- participate in electrolysis at BPE surface, described by cathodic and anodic current term:

$$i_c = -i_0^c \cdot e^{-r_c \cdot f \cdot (\phi_{\mathrm{BPE}} - \phi - E_0^c)} \qquad i_a = i_0^a \cdot e^{r_a \cdot f \cdot (\phi_{\mathrm{BPE}} - \phi - E_0^a)} \qquad f = \frac{F}{RT}$$

anodic oxidation of water $O_2 + 4\,H_3O^+ + 4\,e^- \longleftarrow 6\,H_2O$			cathodic reduction of water $2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$		
$\frac{E_0}{\mathrm{V}}$	r	$\frac{i_0}{\mu\mathrm{Am}^{-2}}$	$\frac{E_0}{\mathrm{V}}$	r	$\frac{i_0}{\mu\mathrm{Am}^{-2}}$
0.68	0.552	$30.5 \cdot 10^9$	−0.55	0.531	$13.6 \cdot 10^9$

Electrolyte characteristics					
species	H_3O^+	OH^-	DS^-	Na^+	ClO_4^-
$D \cdot 10^9/\mathrm{m\,s^{-1}}$ *	9.311	5.273	0.639	1.334	1.792
z	1	−1	−1	1	−1
$c/\mathrm{mol\,m^{-3}}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1.5 \cdot 10^{-1}$	$1.015 \cdot 10^1$	$1 \cdot 10^1$

Electrochemical cell parameters		
$W/\mu\mathrm{m}$	1.1	cell width
$W_{\mathrm{bpe}}/\mu\mathrm{m}$	1	BPE width
$H/\mu\mathrm{m}$	0.2	cell height
ϵ_r	78.36	relative permittivity
T/K	298.15	temperature
λ_S/m	$0.1\lambda_D$	Stern layer width

Tab. 1 Parameters

2d Electroneutrality model, at horizontal cross sections:

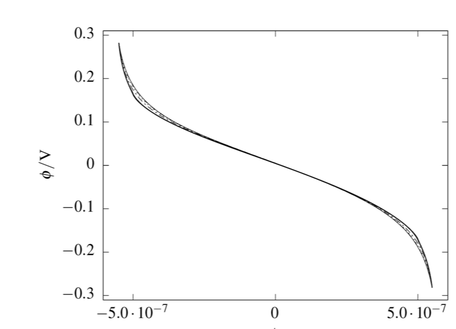


Fig. 5 Potential, at center of domain

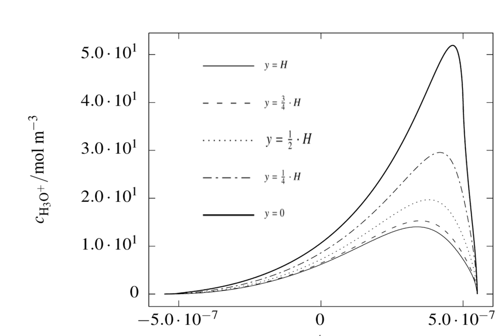


Fig. 6 H_3O^+ Concentration

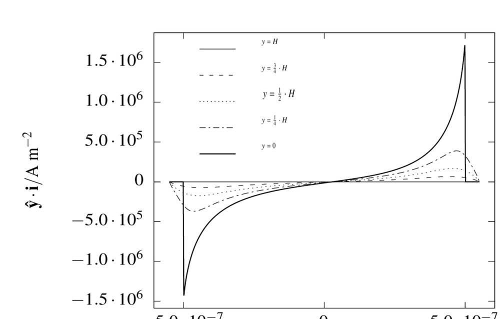


Fig. 7 Vertical Current Flux Density

1d PNP model, surface sweep:

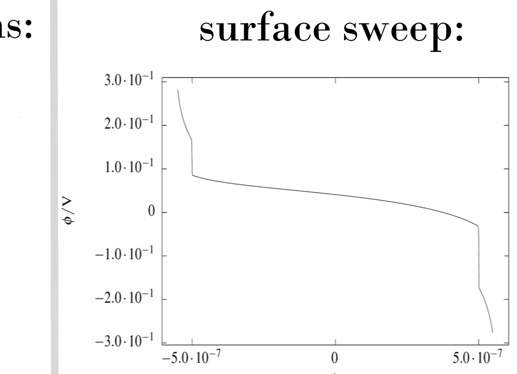


Fig. 8 Potential, at surface

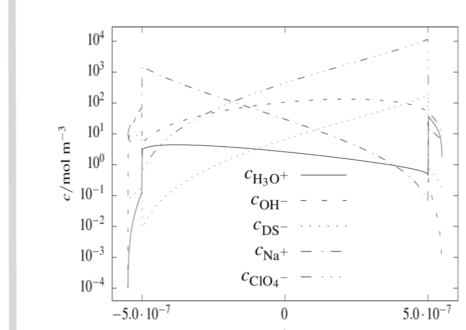


Fig. 9 Concentrations, half-logarithmic

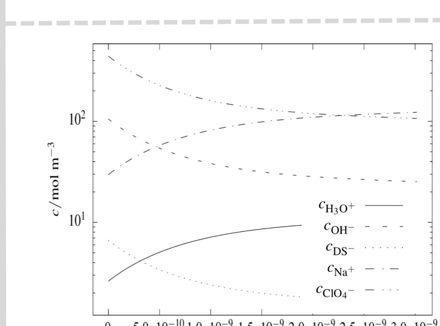


Fig. 10 Concentrations, half-logarithmic, at central vertical cross section

2d PNP model, at horizontal cross sections:

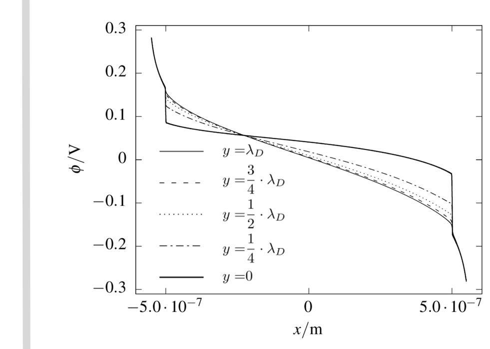


Fig. 11 Potential, at first Debye length above surface

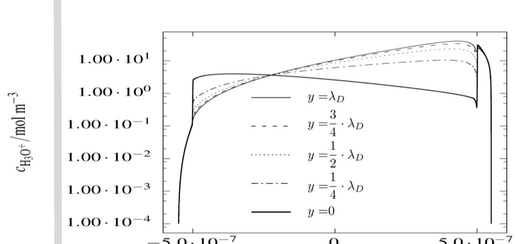


Fig. 12 H_3O^+ Concentration, half-logarithmic, at first Debye length above surface

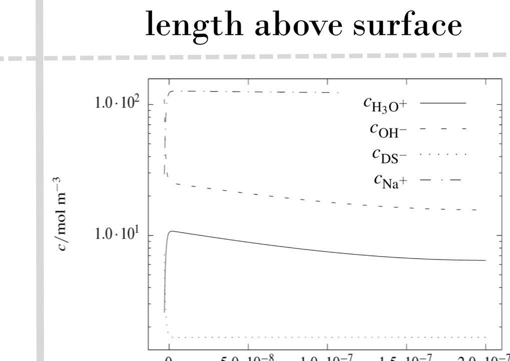


Fig. 13 Concentrations, half-logarithmic, at central vertical cross section

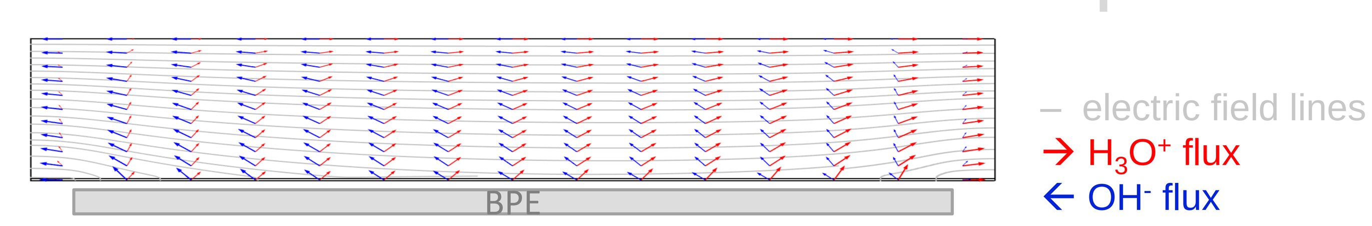


Fig. 14 Species flux and electric field for 2d PNP model

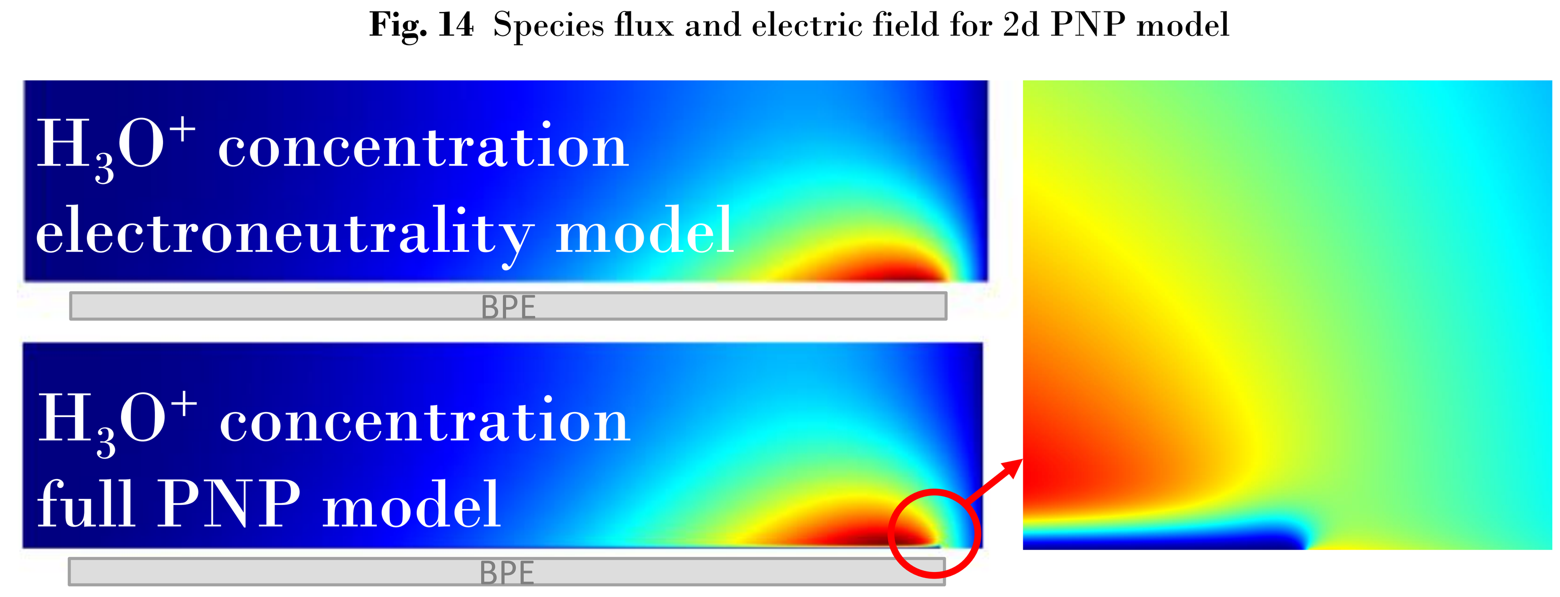


Fig. 15 Qualitative comparison of 2d models' concentration results

Conclusion: In bulk, electroneutral and full PNP model behave equivalently. Nevertheless, PNP resolves details at the transition from bulk to interface scale seamlessly, which neither electroneutral nor 1d double layer model are able to produce.

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