Nanotechnology in Biological Engineering II

THE EFFECT OF ELECTRICAL DOUBLE LAYER ON THE ELECTROCHEMICAL PROCESSES OF NANOMETER INTERDIGITATED ELECTRODES

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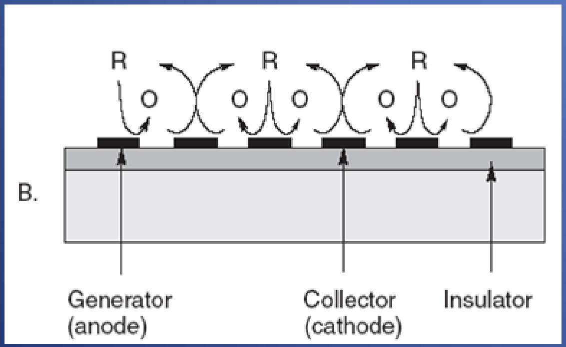
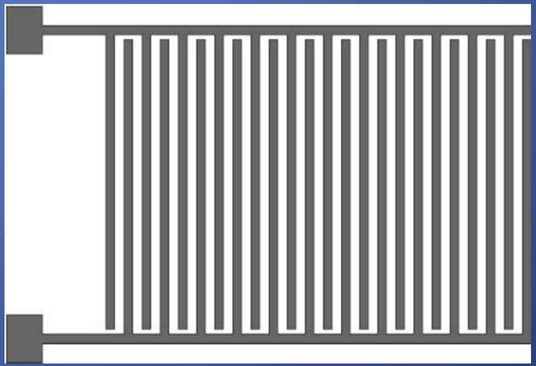
Motivation

- Electrochemical sensor plays an important role in clinical diagnosis:
  Features: High Sensitivity, Real-time detection, Simple operation
- Micro/nano interdigitated electrodes (Micro/Nano IDEs) based electrochemical biosensors are getting more and more popular:
  Features: small dimension, low sample volume, low cost
  Application: Glucose sensor, immune sensor, gas sensor





Motivation

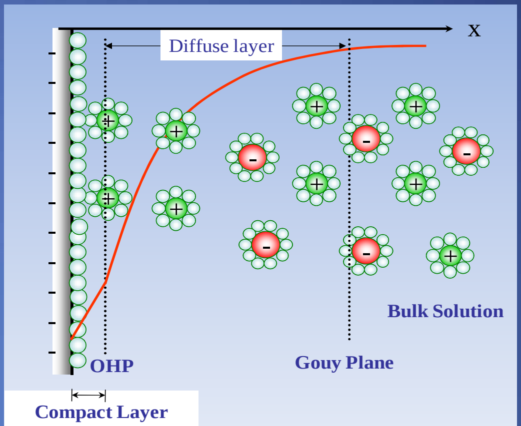
- Problem:

  For sensing purpose, IDEs measure faradic current

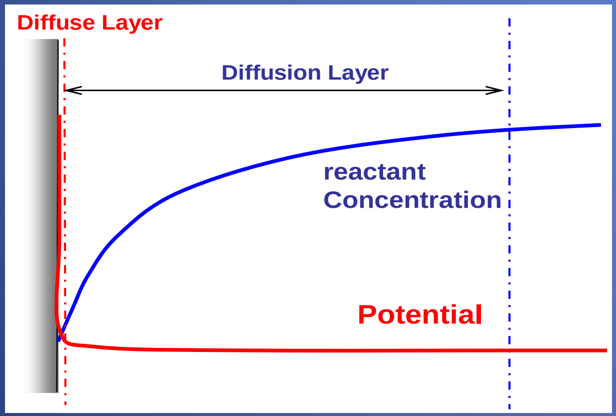
  When the electrodes get to nanometer scale, the faradic response at electrode may be affected by electrical double layer (EDL).

EDL Effect on Single Electrodes

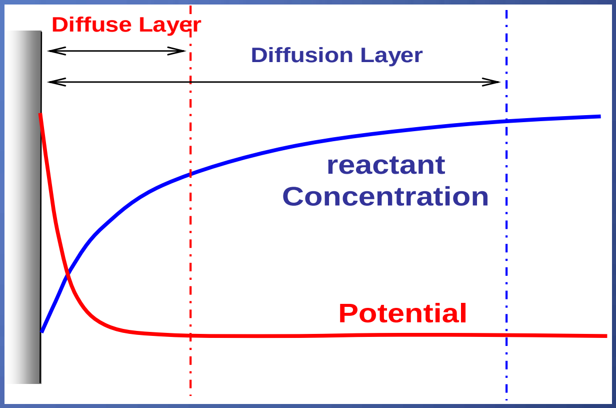
EDL formation: A charged electrode can attract oppositely charged species in the solution and forms EDL (compact layer and diffuse layer)



EDL effect

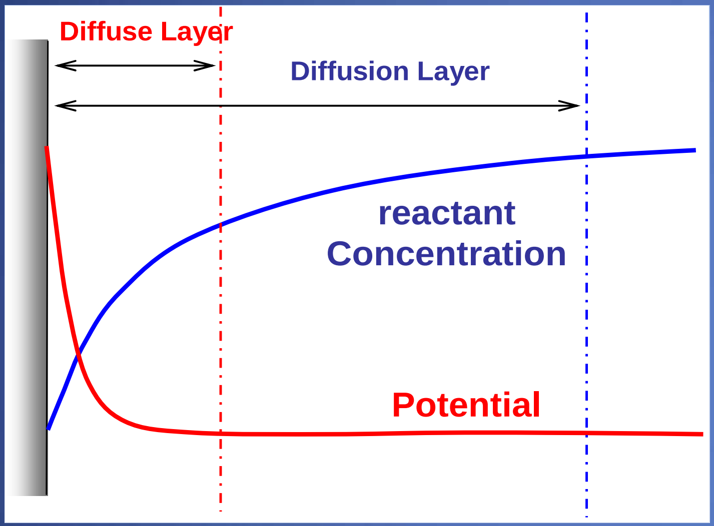


Micro electrodes: diffusion only

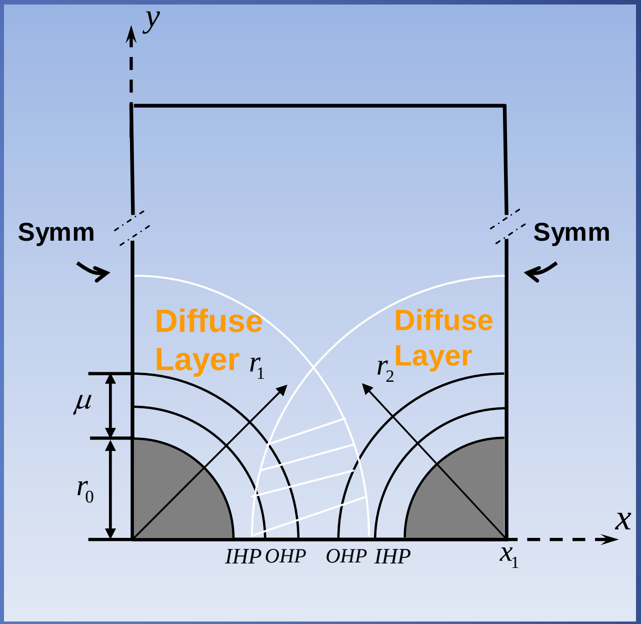


Nano electrodes: diffusion and electromigration

EDL Effect on Nano-IDEs



Diffuse layer and diffusion layer overlap



Diffuse layers overlap at two electrodes of nano-IDEs

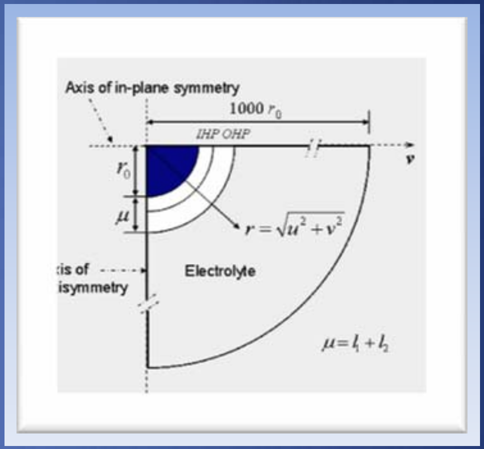
For a widespread application of nano-IDEs, it is imperative to elucidate the effect of the EDL on the faradic reactions of nano-IDEs. But this problem is too complicated to be solved by analytical means.

Objective

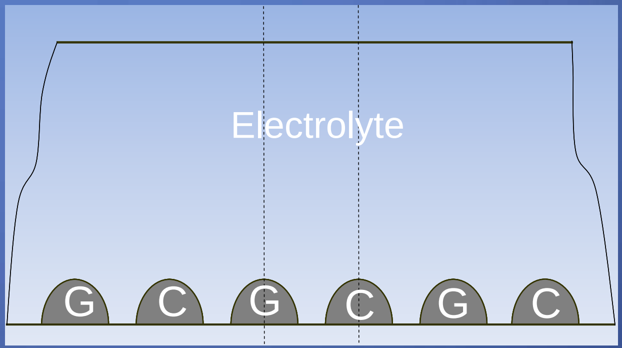
- To investigate the EDL effect on the faradic reaction of nano-IDEs by a fully numerical method developed using COMSOL Multiphysics

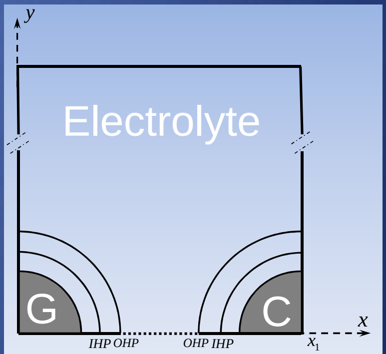
Model Development

- Previously our group developed a fully numerical method by COMSOL Multiphysics using Nernst-Plank-Poisson equation to simulate EDL affected faradic reaction at single nanometer electrodes.*



- In this study we expand previous method to further address the issue at nano-IDEs.





r =1nm

*Yang, X.; Zhang, G. *Nanotechnology* 2007, 18, 335201-335209

Model Development

Initial Concentrations

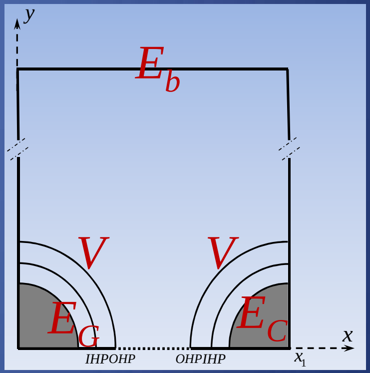
$$O^{z} + e^{-} \underset{b}{\overset{f}{\longleftrightarrow}} R^{z-1}$$

- Oxidized species (OS) and Counter ion : 5mM
- Reduced species: 0mM
- Supporting electrolyte (SE):

SE is excess ➡ C_{SE} = 500mM

Boundary Conditions

- Potential at electrode and bulk solution
  - E_G = 0.3V to -0.4V at 20mV/s;
  - E_C = 0.3V
  - E_b = 0V



- Current Flux

Butler-Volmer Equation

$$J_f = -J_b = k_0 \cdot \exp[-\alpha F(E - V - E^{0'})/RT] \cdot c_O - k_0 \cdot \exp[(1-\alpha)F(E - V - E^{0'})/RT] \cdot c_R$$

V: potential at OHP, i.e. the Position of Electron Transfer

Model Development

--- Governing Equations

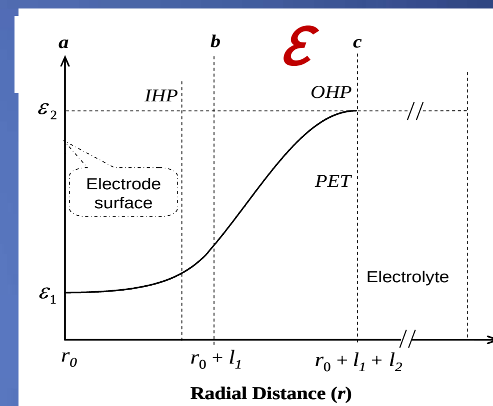
- Potential distribution
  - Poisson equation

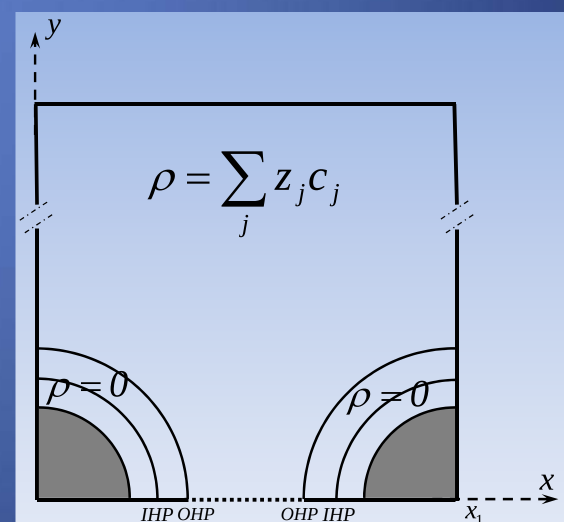
$$\nabla(\varepsilon\varepsilon_0 \nabla V) = -\rho$$
$$\varepsilon_1 = 6$$
$$\varepsilon_2 = 78$$

Assume: perfectly smooth electrode surface; no specific adsorption

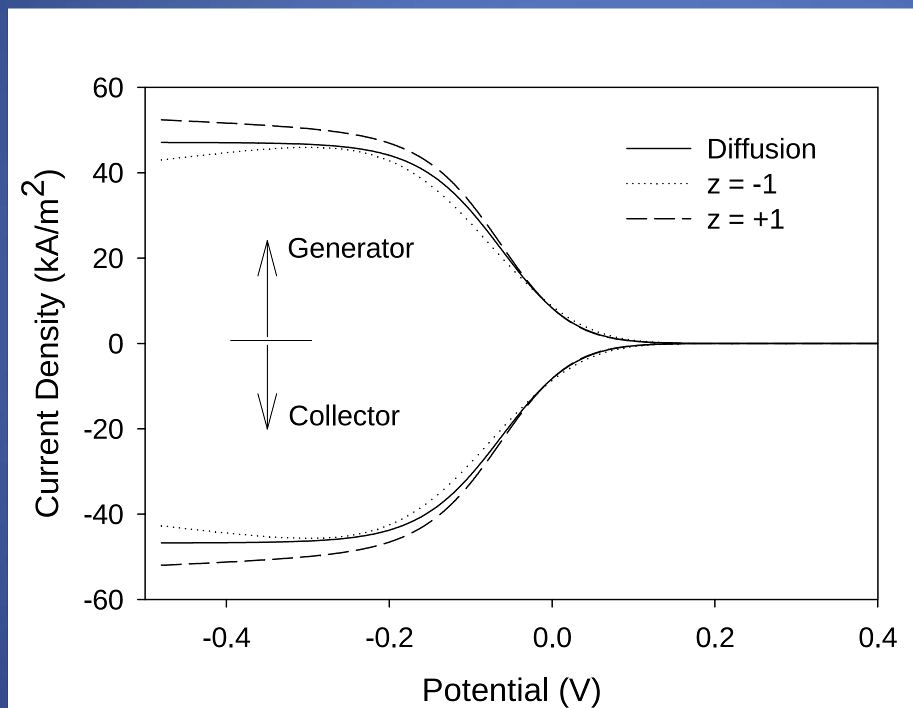
- Mass transport
  - Nernst-Plank equation

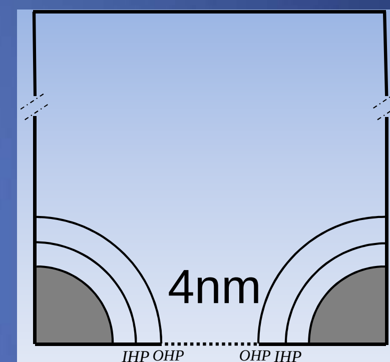
$$\frac{\partial c_j}{\partial t} = \nabla\left(D_j \nabla c_j + \frac{z_j F}{RT} D_j c_j \nabla V\right)$$





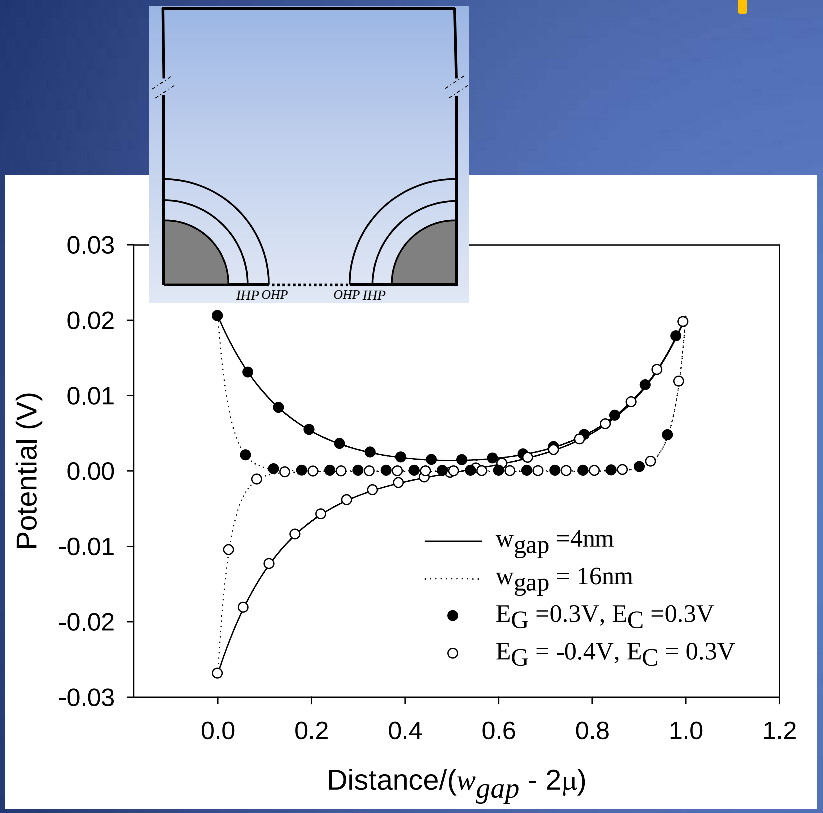
EDL Effect and the Charge Valences of Redox Species

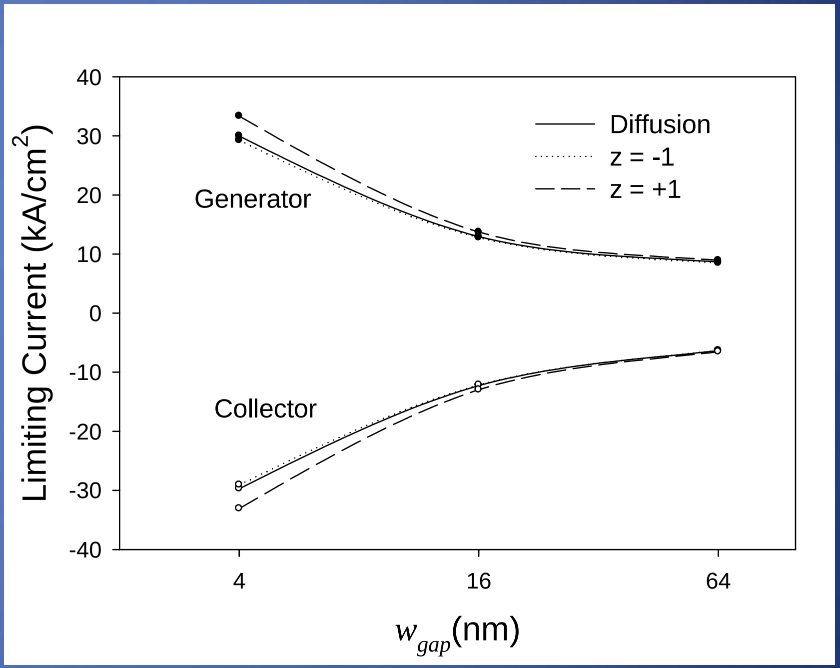




EDL affected voltammetric curve deviated from diffusion controlled case, when inter-electrode spacing w_{gap} = 4nm

EDL Effect with Changing Gap Spacing



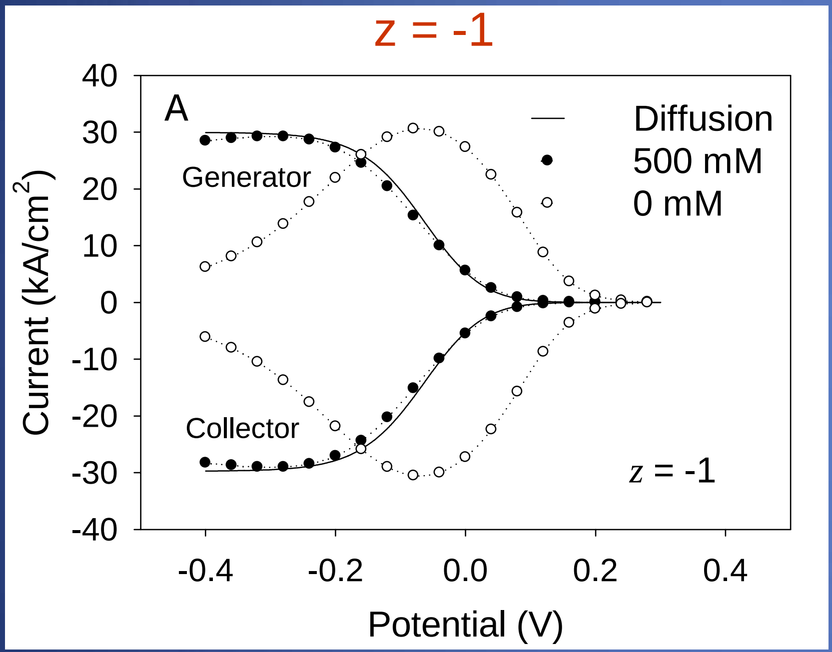


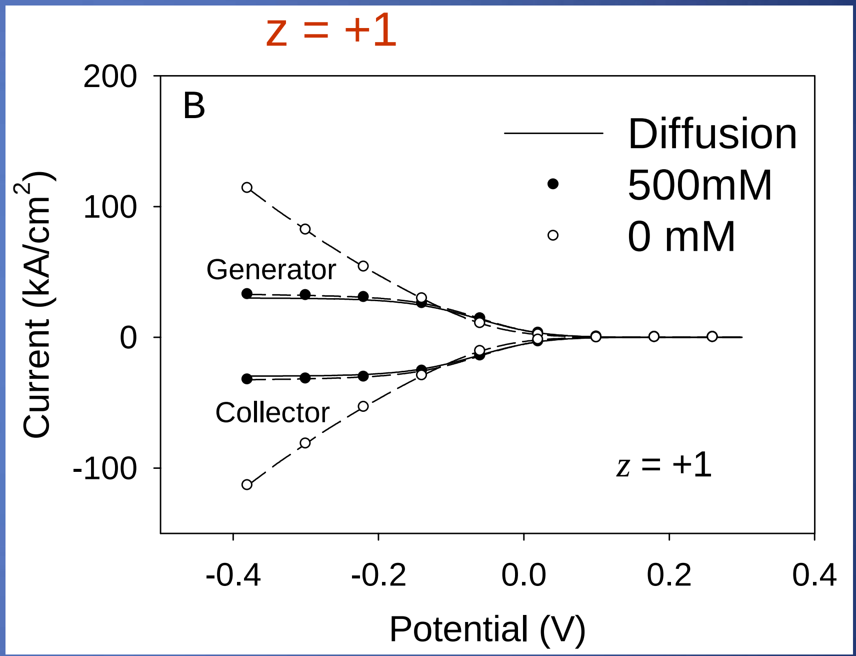
Potential Distribution at w_{gap} = 4nm & 16nm

limiting current and w_{gap}

More diffuse layer overlap have more EDL effect!

EDL Effect and Supporting Electrolyte





The voltammetric curve deviate significantly from diffusion controlled case when supporting electrolyte is absent in the solution.

Conclusion

- The effect of EDL on the voltammetric performance of nano IDEs is dependent on
  - The charge valence of redox species
  - The gap spacing between electrodes
  - The concentration of supporting electrolyte

- This work demonstrates that a complete computer-modeling approach is well suited for elucidating the electrochemical processes of electrodes with complex geometries when <u>faradic reactions and the EDL effect are of concerns</u>.

Acknowledgement

National Science Foundation

The Faculty of Engineering at The University of Georgia.

My advisor Dr. Guigen Zhang

All my group members

Thank you!