Lecture 3

Electrical double layer (DL). Charge transfer through DL.

Goal of the Lecture

The goal of this lecture is to deepen students' understanding of the physical and mathematical description of charge transfer processes occurring across the electrical double layer and to introduce the modeling of electrochemical kinetics using coupled Poisson–Nernst–Planck (PNP) equations in COMSOL Multiphysics. The lecture integrates theoretical electrochemistry (double layer structure and interfacial kinetics) with computational modeling of charge transfer phenomena at electrode interfaces.

Lecture Objectives

By the end of this lecture, students will be able to:

1. **Explain** the mechanisms of charge separation and transfer within the electrical double layer (EDL).
2. **Formulate** the coupled Poisson–Nernst–Planck (PNP) system for ion transport and electrostatic potential in the diffuse layer.
3. **Apply** appropriate boundary conditions to represent electrode reactions and Stern layer effects.
4. **Simulate** charge transfer through the double layer using COMSOL Multiphysics, analyzing concentration, potential, and charge density distributions.
5. **Interpret** dimensionless parameters (e.g., Debye length ratio, reaction rate constants) that control electrochemical cell performance.

In the very vicinity of an electrode surface (in the range of up to a few nanometers), in the diffuse double layer, the assumption of electroneutrality is not valid due to charge separation. Typically the diffuse double layer may be of interest when modeling very thin layers of electrolyte, for instance in electrochemical capacitors and in atmospheric corrosion problems.

To model the behavior of the diffuse double layer, one needs to solve for the Nernst-Planck equations for all of the ions, in combination with the

Poisson's equation for the potential. The combination of these equations is frequently referred to as the Poisson-Nernst-Planck (PNP) equations.

This example shows how to couple the Nernst-Planck equations, solved using the Transport of Diluted Species interface, to the Poisson's equation, solved using the Electrostatics interface.

A problem that arises when modeling the PNP equations is that of how to handle the boundary condition for the potential equation. In this example an assumption of a Stern layer with a constant capacity is used to derive surface charge boundary conditions for Poisson's equation.

The model reproduces the results of Bazant and Chu [1, 2].

The model geometry is in 1D (a single interval between 0 and L) and consists of one single domain, representing the electrolyte phase, including the diffuse double layer [3].

Boundary conditions

The boundaries reside in the reaction plane of the electrodes on each side. The same electrode reaction, in which the positive ion, Me^+, participates, takes place on both electrodes.

$$Me^+ + \bar{e} = Me_s$$

The reaction rate *r* (mol/(m^2·s)) is

$$r = K_a C_{Me} \exp\left(\frac{\alpha_a F \phi_\Delta}{RT}\right) - K_c C_{Me^+} \exp\left(\frac{-\alpha_c F \phi_\Delta}{RT}\right)$$

where K_a and K_c (m/s) are the anodic and cathodic rate constants, C_{Me} the metal species activity (mol/m^3, constant) and α_a and α_c the anodic and cathodic transfer coefficients. ϕ_Δ (V) is the difference in potential between the metal phase, ϕ_M (V), and the reaction plane:

$$\phi_\Delta = \phi_M - \phi$$

The electrode reaction renders an inward flux for the positive ion according to

$$-\boldsymbol{nN}_+ = r$$

on both boundaries. For the negative ion, a zero flux condition is used

$$-\boldsymbol{nN}_- = 0$$

Assuming the reaction plane to be placed at the boundary between the inner and diffuse double layer, and with the assumption of a Stern compact layer of a constant thickness, λ_S (m), one can derive the following Robin type of boundary condition for the potential:

$$\phi + \lambda_S(n \cdot \nabla\phi) = \phi_M$$

This condition reduces to a Dirichlet voltage condition for λ_S = 0, that is, in the absence of a Stern layer. For the case of a non-zero stern layer thickness, the condition can be reformulated as a surface charge condition

$$n \cdot (-\varepsilon\nabla\phi) = -\frac{\varepsilon\phi_\Delta}{\lambda_S}$$

Domain Equations

The concentrations, ci (mol/m^3, i=+,-), of two ions of opposite charge (+1/-1) are solved for in the electrolyte phase. The fluxes (N_i,mol/(m^2·s)) of these are described by the Nernst-Planck equation

$$\boldsymbol{N_i} = -D_i\nabla C_i - u_{m,i}z_iFc_i\nabla\phi$$

with D_i (m^2/s) being the diffusion coefficient, $u_{m,i}$ (s·mol/kg) the mobility, *F* (C/mol) Faraday's constant, and ϕ (V) the potential.

Assuming no heterogenous reactions in the electrolyte, the governing equations for the two species become:

$$\nabla\boldsymbol{N_i} = 0$$

For the potential, Poisson's equation states

$$\nabla(-\varepsilon\nabla\phi) = \rho$$

where ε is the permittivity (F/m) and *ρ* the charge density (C/m^3), depending on the ion concentrations according to:

$$\rho = F(c_+ - c_-)$$

Cell potential equation

The problem formulated above can now be solved for given voltages of ϕ_M in the metal electrode phase for each side. Typically one grounds one electrode and specifies the cell voltage as *V* so that

$$\phi_M|_{x=0} = 0$$

$$\phi_M|_{x=L} = V$$

However, to solve for a given cell current density, i_{cell} (A/m^2), with V not known a priori, an additional global equation, solving for V, is used, fulfilling the condition:

$$i_{cell} = Fr|_{x=L}$$

Global concentration constrain for the negative ion

When solving this system for a stationary solution, the negative ion concentration needs an additional "boot-strap" to render a stable, unique, solution. This is done by adding the following global constraint to the equation system:

$$c_0 L = \int_0^L c_- dx$$

where $c_0$is the initial ion concentration (mol/m^3), equal for both ions.

The constraint assures that the total number of negative ions is preserved during the iterative solver process. For time-dependent simulations the constraint can be omitted.

Dimensionless numbers and parameter values

A number of dimensionless numbers can be derived that govern the behavior of the cell. The problem is solved using a parametric study for a dimensionless parameter ε_D = (0.001, 0.01, 0.1), defined as

$$\varepsilon_D = \lambda_D / L$$

$$\lambda_D = \sqrt{\frac{\varepsilon RT}{2F^2 c_0}}$$

where λ_D is the Debye length.

The current of the cell is defined via the dimensionless number j =0.9,

$$j = i_{cell} / i_D$$

$$i_D = 4FD_+ c_0 / L$$

where i_D is the Nernstian limiting current density.

The cathodic reaction rate constant is defined using the dimensionless number k_c = 10,

$$k_c = \frac{K_c L}{4D_+}$$

The rate of the anodic reaction term is governed by the dimensionless number k_r = 10,

$$k_r = \frac{K_r L c_M}{4D_+ c_0}$$

and the Stern layer thickness is set using the dimensionless number δ =0.1,

$$\delta = \frac{\lambda_S}{\lambda_D}$$

The dimensionless variables used in the results:

$$\tilde{x} = \frac{x}{L}$$

$$\tilde{c} = \frac{(c_+ + c_-)}{2c_0}$$

$$\tilde{\rho} = \frac{(c_+ - c_-)}{2c_0}$$

$$\tilde{\phi} = \frac{F\phi}{RT}$$

Results and discussion

Figure 1 shows the dimensionless concentration, $\tilde{c}$. The concentration gradients are steepest close to the electrodes

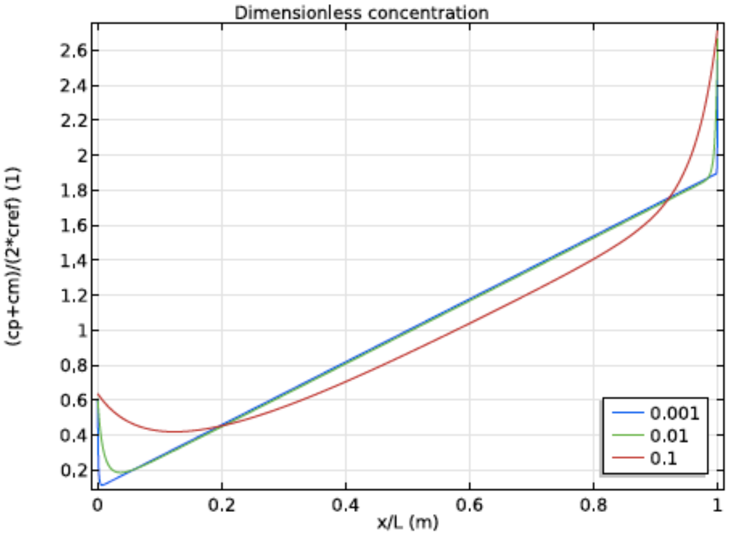

Figure 1. Dimensionless concentration profile.

Figure 2 shows the dimensionless charge density profile. Charge separation occurs close to the electrodes. For higher values of ε_D, the region of charge separation, the diffuse double layer, stretches further into the domain. This is expected since higher ε_D values effectively mean a shorter domain length

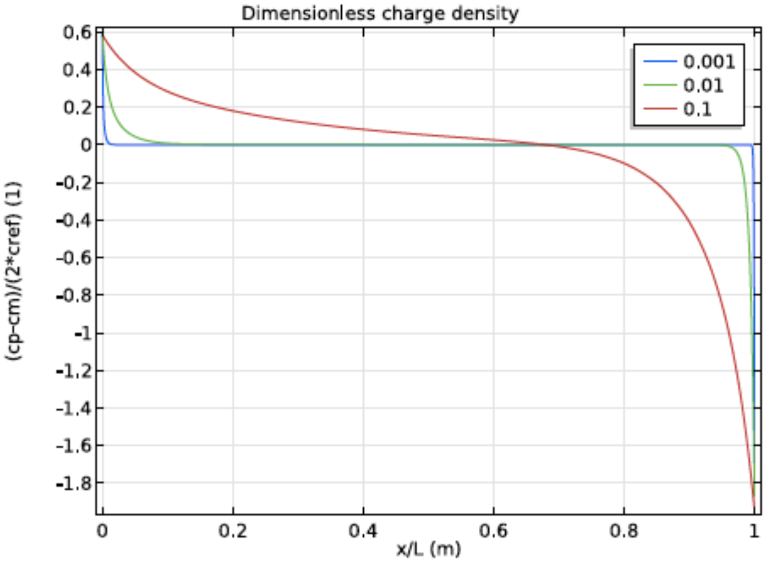

Figure 2. Dimensionless charge density profile.

Figure 3 shows the potential profile. For higher values of ε_D the voltage over the cell decreases. This is an expected result since a shorter domain length shortens the potential losses due to ion transport.

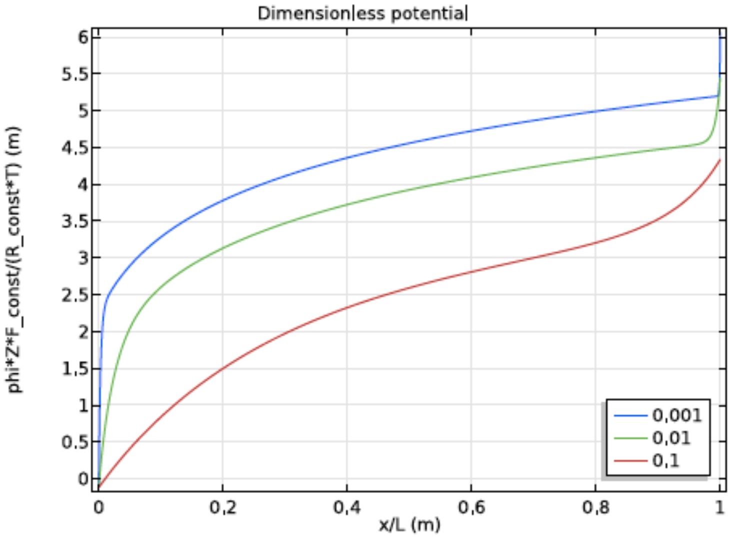

Figure 3. Dimensionless potential profile.

Questions for Self-Examination

1. Why is the assumption of electroneutrality invalid within the diffuse double layer near an electrode surface?
2. What physical processes are described by the Poisson–Nernst–Planck equations in electrochemical systems?
3. Explain the role of the **Stern layer** in defining the potential drop and boundary conditions at the electrode interface.
4. How does the charge transfer reaction affect the flux boundary conditions for ionic species?
5. How do variations in Debye length and electrode potential influence the thickness of the diffuse double layer and charge density profiles?
6. Discuss the physical meaning of the potential and concentration profiles near the electrode as obtained from simulation results.

Self-Study Assignment

Assignment Title: *Modeling Charge Transfer Through the Electrical Double Layer Using Poisson–Nernst–Planck Equations*

Objective:
To model the steady-state charge transfer process through an electrical double layer, using the coupled Poisson–Nernst–Planck (PNP) equations in COMSOL Multiphysics, and to analyze the influence of reaction kinetics and Stern layer effects on potential and charge distributions.

Tasks:
1. **Model setup:**
    - Open the COMSOL example **“Diffuse Double Layer with Charge Transfer”**.
    - Create a **1D geometry** representing the electrolyte between two planar electrodes.
    - Define two ionic species (e.g., cation A^+ and anion B^-) with equal bulk concentrations (e.g., 1 mol/m³).
2. **Physics coupling:**
    - Use **Transport of Diluted Species (tds)** to describe ionic fluxes according to the Nernst–Planck equation.
    - Use **Electrostatics (es)** to solve Poisson’s equation for potential.
    - Couple *tds* and *es* through **space charge density ($\rho = F \Sigma z_i c_i$)**.
3. **Boundary conditions:**
    - At both electrodes: implement charge transfer reaction of the form $A^+ + e^- \rightleftharpoons A$ (solid).
    - Define **anodic** and **cathodic** rate constants (k_a, k_c), **transfer coefficients (α_a, α_c)**, and **Stern layer thickness (δ_S)**.
    - Apply **Robin-type boundary condition** for potential to represent the Stern layer capacitance.
    - Impose **zero flux** for the anion (inert species).
4. **Simulation setup:**
    - Conduct a **parametric sweep** for the dimensionless parameter β = L/λ_D (where L is the domain thickness and λ_D is the Debye length).
    - Record and plot:
        Concentration profiles for cations and anions (c_i vs x).

Charge density distribution (ρ(x)).
Potential profile (ϕ(x)).

- Compare results for β = 0.001, 0.01, 0.1.

5. **Analysis and Report:**
    - Discuss how varying β affects the extent of charge separation and potential drop.
    - Identify which region (Stern layer, diffuse layer, bulk) dominates the total voltage loss.
    - Evaluate the influence of reaction kinetics (rate constants) on current–voltage characteristics.
    - Include a **dimensionless analysis** table summarizing parameters used.

Learning Outcomes (According to Syllabus)

Learning Outcome (LO)	Indicator of Achievement (ID)	Description
LO 1: Explain the principles of modelling electrochemical systems and appraise the use of modelling in electrochemical research.	ID 1.3: Structure and properties of electrical double layer; charge transfer through double layer.	Students will describe the structure and dynamics of the EDL and simulate charge transfer reactions across the double layer using PNP modeling techniques in COMSOL Multiphysics.

References

1. M. Bazant, K. Chu, and B. Bayly. “Current-Voltage Relations for Electrochemical Thin Films,” SIAM Journal of Applied Math, vol. 65, no. 5, pp. 1463–1484, 2005.

2. K. Chu and M. Bazant, “Electrochemical Thin Films at and Above the Classical Limiting Current,” SIAM Journal of Applied Math, vol. 65, no. 5, pp. 1485–1505, 2005.

3. https://www.comsol.com/model/diffuse-double-layer-with-charge-transfer-13525