Lecture 2

Basic concepts of electrochemical processes,

the stages of electrode reaction. Modelling of diffuse double layer

When a polarizable electrode is held at a certain voltage compared to a reference, it will have a corresponding net surface charge density. This charge attracts or repels ions in the neighboring solution, depending on their charge.

At equilibrium, there is a layer of space charge density adjacent to the electrode due to unequal amounts of different types of ions.

The charge in solution is equal and opposite to the charge on the electrode: “double layer” (**Figure 1**).

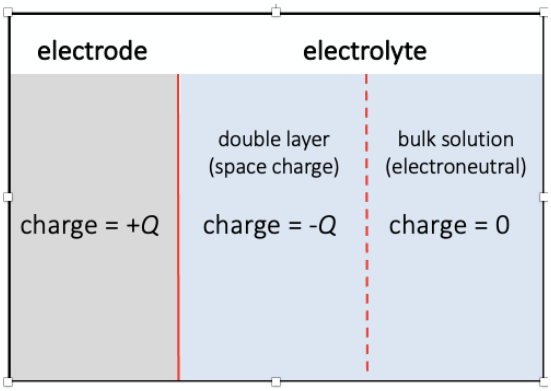


Figure 1. Simplified scheme of the double “layer”.

Electrostatics

The electric field obeys **Gauss’s law**.

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_{\text{soln}} \varepsilon_0}$$

– assume that solvent permittivity is unaffected by ion density (dilute solution).
– assume that only dissolved ions contribute to the space charge density in solution.

$$\rho = F \sum_i z_i c_i$$

E = electric field (V/m); ρ = space charge density (C/m^3); $\varepsilon_{\text{soln}}$ = solvent dielectric constant; ε_0 = vacuum permittivity; F = Faraday constant; z_i = charge number of ion i; c_i = concentration of ion i (mol/m^3).

Mass transport of diluted species

Dilute species (at low concentration) obey the Nernst-Planck equations for mass transport.

- flux includes diffusion and migration terms
- assume no reactions in solution (no source term)

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = 0$$

$$\mathbf{N}_i = -D_i \nabla c_i + z_i c_i u_i \mathbf{E}$$

$$u_i = \frac{F}{RT} D_i$$

$\mathbf{N}_i$ = molar flux of ion *i* (mol/(m^2*s)); D_i = diffusion coefficient of ion *i* (m^2/s); u_i = electrical mobility of ion *i* (m^2/s/V); R = gas constant; T = temperature (K).

Nernst-Planck-Poisson equations

Combine the equations at steady-state.

Nernst-Planck-Poisson (or Poisson-Nernst-Planck) equations describes charge and mass distribution in dilute electrolyte.

- for ***n*** ions, gives (***n+1***) equations in (***n+1***) unknowns:
- ***n*** ion concentrations
- electric potential (***φ***)

$$\nabla \cdot \left(D_i \nabla c_i + z_i \frac{F}{RT} D_i c_i \nabla \phi \right) = 0$$

$$\nabla^2 \phi + \frac{F}{\varepsilon_{\text{soln}} \varepsilon_0} \sum_i z_i c_i = 0$$

Gouy-Chapman theory

- Solve Nernst-Planck-Poisson equations at steady-state to find double layer structure.
- Specify a charge density or fixed potential at the electrode surface.
- Set electroneutral bulk concentrations and zero electrical potential at large distance.

Key prediction of Gouy-Chapman theory:

- Extent of the double layer (region of space charge density) is of the order of the Debye length x_D.

$$x_{\text{D}} = \sqrt{\frac{RT \varepsilon_{\text{soln}} \varepsilon_0}{2F^2 I_{\text{ion}}}}$$

$$I_{\text{ion}} = \frac{1}{2} \sum_i z_i^2 c_{i,\text{bulk}}$$

Stern modification (GCS theory)

Account for potential drop across the region from the metal surface to the centre line of the closest approach of an ion.

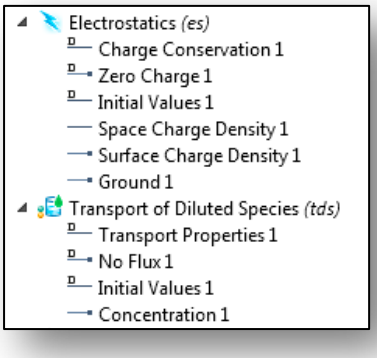
- This line is called the outer Helmholtz plane (OHP).
- Region outside the OHP is the “diffuse double layer” where there is space charge due to ion excess / depletion.
- Region inside the OHP is the “compact double layer” or “Stern layer” where the electric field is near-constant.

Treat the solvent inside the OHP as a classical rectilinear dielectric of fixed length (x_S), usually < 1 nm.

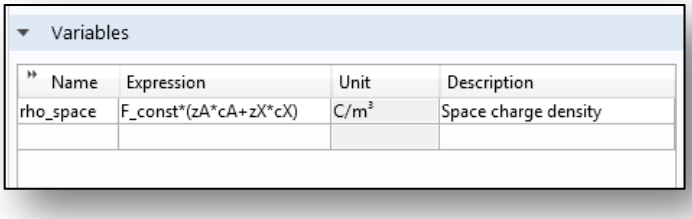
$$\phi_{\mathrm{OHP}} = \phi_{\mathrm{M}} - x_{\mathrm{S}} \frac{\rho_{\mathrm{surf}}}{\varepsilon_{\mathrm{soln}} \varepsilon_0}$$

Setup interfaces and domains in COMSOL Multiphysics

- Couple **Electrostatics** with **Transport of Diluted Species**.
- Solve for as many concentrations as there are ions.



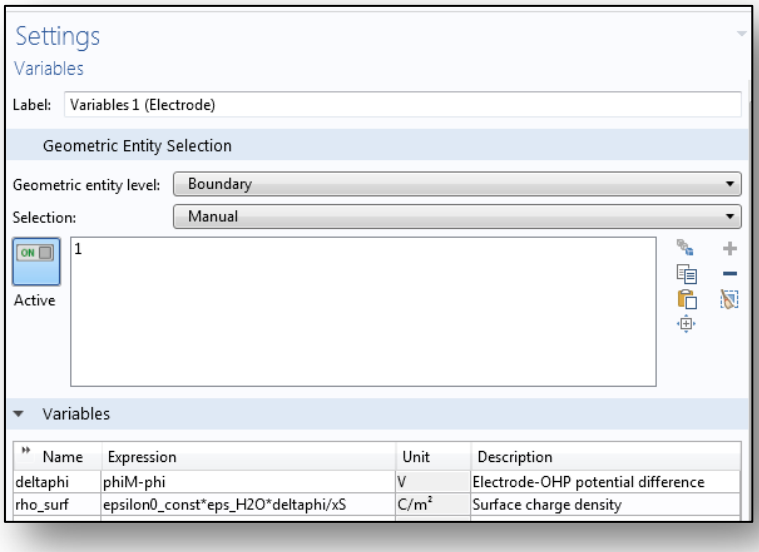
- Add a **Space Charge Density** to electrostatics according to the ion concentrations.



Setup (electrode boundary)

Electrode:

- Set a **Surface Charge Density** in **Electrostatics**.
- The surface charge density is a function of the applied voltage and the local electric potential according to the Stern expression.
- Set **No Flux** of ions (no electrode reaction).



Setup (bulk boundary)

Bulk:

- Set **Ground** in **Electrostatics**.
- Bulk boundary must be several Debye lengths from the surface in order that the electric field tends to zero here.
- Set **Concentration** condition to define bulk ion concentrations.
- Bulk ion concentrations must be defined to give a neutral solution.

cA_bulk	1[mol/m^3]	1 mol/m³	Bulk cation concentration
cX_bulk	cA_bulk	1 mol/m³	Bulk anion concentration

xD	sqrt(epsilon0_const*eps_H2O*V_therm/...	9.6198E-9 m	Debye length
xS	0.5[nm]	5.0000E-10 m	Stern layer thickness
L_cell	xD*10	9.6198E-8 m	Cell length

Results

- Parametric sweep on voltage vs potential of zero charge (PZC) of the working electrode, from ***1*** to ***10 mV***.
- ***Potential*** and ***concentration*** profiles for the double layer.
- Output "*rho_surf*" to find surface charge.

References:

1. https://www.comsol.com/model/diffuse-double-layer-21981
2. Chapter 13: "Double-Layer Structure and Adsorption" in *Electrochemical Methods: Fundamentals and Applications, 2nd ed.*, 2001, Wiley.