Lecture 1

Introduction to the modelling of electrochemical processes

Goal of the Lecture

The goal of this lecture is to introduce students to the fundamental physical and chemical principles underlying electrochemical processes and their representation in computational models. Students will gain an understanding of charge transfer phenomena at the electrode–electrolyte interface and the conceptual basis for translating these phenomena into mathematical and numerical models used in electrochemical simulations.

Lecture Objectives

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

- ***Explain** the physical basis of electrochemical charge transfer between electrode and electrolyte phases.*
- ***Differentiat**e between Faradaic and non-Faradaic (capacitive) processes and their implications for modeling electrochemical systems.*
- ***Describe** the structure and role of the electrical double layer (EDL) in charge separation and interfacial potential distribution.*
- ***Identify** the parameters influencing electrochemical reaction kinetics and current–potential relationships.*
- ***Recognize** how these principles are incorporated into COMSOL Multiphysics electrochemical modeling environments.*

In electrochemical systems, we are concerned with the processes and factors that affect the transport of charge across the interface between chemical phases, for example, between an electronic conductor (an electrode) and an ionic conductor (an electrolyte) [1].

By driving the electrode to more negative potentials (e.g., by connecting a battery or power supply to the cell with its negative side attached to the working electrode), the energy of the electrons is raised. They can reach a level high enough to transfer into vacant electronic states on species in the electrolyte. In that case, a flow of electrons from electrode to solution (**a reduction current**) occurs (**Figure 1a**) [1].

Similarly, the energy of the electrons can be lowered by imposing a more positive potential, and at some point electrons on solutes in the electrolyte will find a more favorable energy on the electrode and will transfer there. Their flow, from solution to electrode, is an **oxidation current** (**Figure 1b**). The critical potentials at which these processes occur are related to the **standard potentials**, E°, for the specific chemical substances in the system [1].

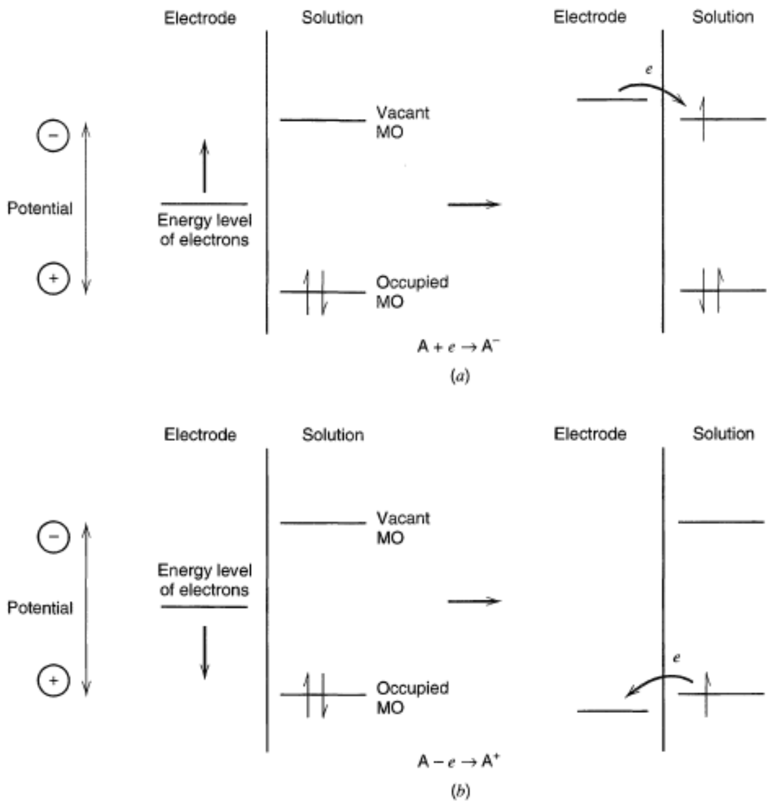

Figure 1. Representation of (a) reduction and (b) oxidation process of a species, A, in solution. The molecular orbitals (MO) of species A shown are the highest occupied MO and the lowest vacant MO. These correspond in an approximate way to the E°s of the A/A^- and A^+/A couples, respectively. The illustrated system could represent an aromatic hydrocarbon (e.g., 9,10-diphenylanthracene) in an aprotic solvent (e.g., acetonitrile) at a platinum electrode [1].

NONFARADAIC processes

An electrode at which no charge transfer can occur across the metal-solution interface, regardless of the potential imposed by an outside source of voltage, is called an ideal polarized (or ideal polarizable) electrode (**IPE**). For example, a mercury electrode in contact with a de-aerated potassium chloride solution approaches the behavior of an IPE over a potential range about 2 V wide [1].

Since charge cannot cross the IPE interface when the potential across it is changed, the behavior of the electrode-solution interface is analogous to that of a capacitor. A capacitor is an electrical circuit element composed of two metal sheets separated by a dielectric material (**Figure 2a**). Its behavior is governed by the equation:

$$\frac{q}{E} = C$$

where q is the charge stored on the capacitor (in coulombs, *C*), E is the potential across the capacitor (in volts, *V*), and C is the capacitance (in farads, *F*).

When a potential is applied across a capacitor, charge will accumulate on its metal plates until q satisfies above given equation. During this charging process, a current (called the **charging current**) will flow [1].

The charge on the capacitor consists of an excess of electrons on one plate and a deficiency of electrons on the other (**Figure 2b**).

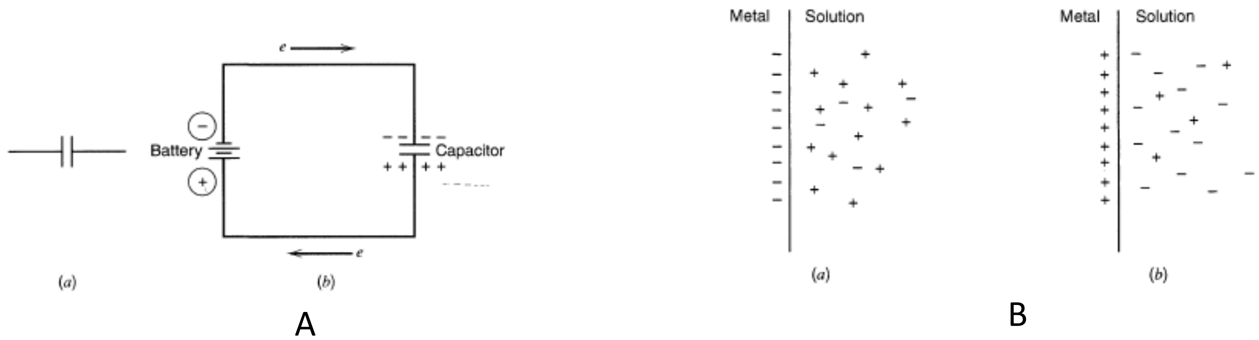

Figure 2. A) (a) A capacitor, (b) Charging a capacitor with a battery. B) The metal-solution interface as a capacitor with a charge on the metal, q^M, (a) negative and (b) positive [1].

Electrical double layer

The solution side of the double layer is thought to be made up of several "layers." That closest to the electrode, the inner layer, contains solvent molecules and sometimes other species (ions or molecules) that are said to be specifically adsorbed (**Figure 3**). This inner layer is also called the compact, *Helmholtz*, or *Stern* layer. The locus of the electrical centers of the specifically adsorbed ions is called the *inner Helmholtz plane* (**IHP**), which is at a distance x_1.

Solvated ions can approach the metal only to a distance x_2; the locus of centers of these nearest solvated ions is called the *outer Helmholtz plane* (**OHP**).

The interaction of the solvated ions with the charged metal involves only long-range electrostatic forces, so that their interaction is essentially independent of the chemical properties of the ions. These ions are said to be nonspecifically adsorbed. Because of thermal agitation in the solution, the nonspecifically adsorbed ions are distributed in a three dimensional region called the ***diffuse layer***, which extends from the OHP into the bulk of the solution. The excess charge density in the diffuse layer is σ^d, hence the total excess charge density on the solution side of the double layer, σ^s, is given by

$$\sigma^s = \sigma^i + \sigma^d = -\sigma^M$$

The thickness of the diffuse layer depends on the total ionic concentration in the solution; for concentrations greater than 10^{-2} M, the thickness is less than ~10 nm [1].

The potential profile across the double-layer region is shown in **Figure 4**.

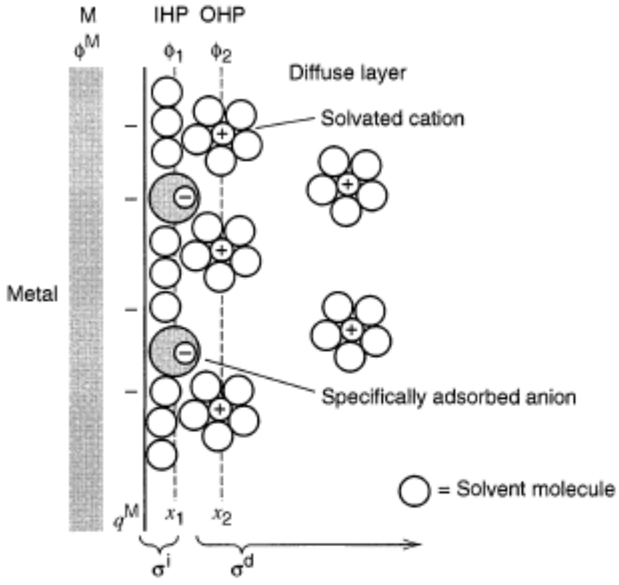

Figure 3. Proposed model of the double-layer region under conditions where anions are specifically adsorbed [1].

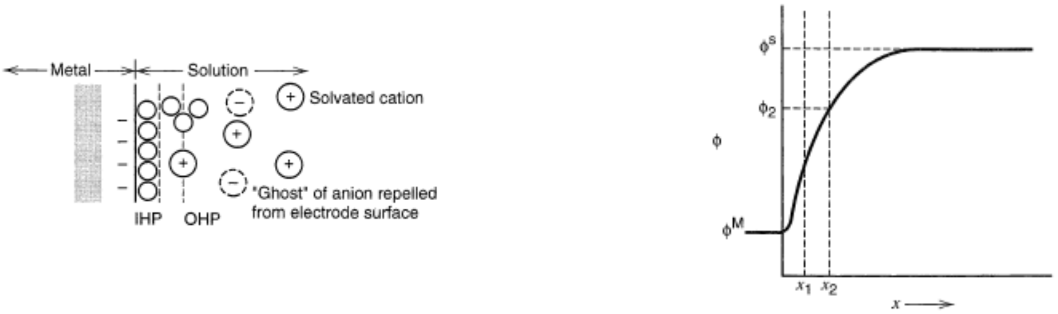

Figure 4. Potential profile across the double-layer region in the absence of specific adsorption of ions. The variable ϕ, called the inner potential [1].

Questions for Self-Examination

1. What distinguishes Faradaic from non-Faradaic processes at the electrode interface?
2. Explain how the potential difference between an electrode and electrolyte affects the direction of charge transfer.

3. Describe the structure and components of the electrical double layer (Helmholtz layer, diffuse layer, IHP, OHP).
4. How does ionic concentration influence the thickness of the diffuse double layer?
5. What physical analogy can be used to model the non-Faradaic behavior of an electrode interface?
6. Which parameters are essential when setting up a basic electrochemical model in COMSOL (e.g., electrode potential, electrolyte conductivity, boundary conditions)?
7. In your own words, define what is meant by “modeling of electrochemical systems.”

Self-Study Assignments

Assignment Title: Introduction to COMSOL Multiphysics and Simulation of an Electrochemical Interface

Objective: Apply fundamental electrochemical concepts to construct a simplified model of an electrochemical cell using COMSOL Multiphysics.

Tasks:

1. Review COMSOL documentation or tutorial: “Primary Current Distribution in an Electrochemical Cell.”
2. Using COMSOL Multiphysics, set up a 2D model representing a metal electrode and electrolyte interface.
- Define appropriate domains for electrode and electrolyte.
- Assign boundary conditions for electric potential (e.g., cathode and anode potentials).
- Use “Secondary Current Distribution” physics interface to simulate potential and current distribution.
3. Generate plots for:
- Equipotential lines in the electrolyte.
- Current density at the electrode surface.
4. Write a short report (1–2 pages) summarizing:
- The assumptions made in the model.
- The relation between potential distribution and electrochemical reaction rate.
- Comparison between Faradaic and non-Faradaic behavior based on your results.

Learning Outcomes

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 1.1: Use electrochemical modelling terminology and concepts.	Students will demonstrate understanding of key electrochemical concepts (electrode potential, current, charge transfer, EDL) and describe how these are represented in electrochemical modeling software such as COMSOL Multiphysics.

Reference

1. Bard A. J. et al. Fundamentals and applications //Electrochemical Methods. – 2001. – T. 2. – №. 482. – C. 580-632.
2. Franco, A. A. et al. Physical Multiscale Modeling and Numerical Simulation of Electrochemical Devices for Energy Conversion and Storage, Springer, 2015.
3. COMSOL Multiphysics Documentation: Electrochemistry Module User’s Guide, COMSOL.