Lecture #2

Fundamentals of processes occurring in the electrode/solution interface. A charge transfer

Goal

This lecture focuses on the fundamental physical and chemical processes that occur at the electrode/solution interface, where charge transfer takes place. The aim is to provide a detailed understanding of the structure of the electrical double layer, mechanisms of electron and ion transport, and factors affecting the kinetics of interfacial reactions.

Two types of processes occur at electrodes.

Nonfaradaic processes

Processes such as adsorption and desorption can occur, and the structure of the electrode-solution interface can change with changing potential or solution composition. These processes are called ***nonfaradaic processes***. Although charge does not cross the interface, external currents can flow (at least transiently) when the potential, electrode area, or solution composition changes. The effects of the nonfaradaic processes must be taken into account in using electrochemical data to obtain information about the charge transfer and associated reactions.

Since charge cannot cross the ideal polarizable electrode interface when the potential across it is changed, the behaviour 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. When a potential is applied across a capacitor, charge will accumulate on its metal plates until q satisfies following equation:

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

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).

During this charging process, a current (called the ***charging current***) will flow. The charge on the capacitor consists of an excess of electrons on one plate and a deficiency of electrons on the other.

The electrode-solution interface has been shown experimentally to behave like a capacitor, and a model of the interfacial region somewhat resembling a capacitor can be given. At a given potential, there will exist a charge on the metal electrode, q_M, and a charge in the solution, q_s (Figure 1).

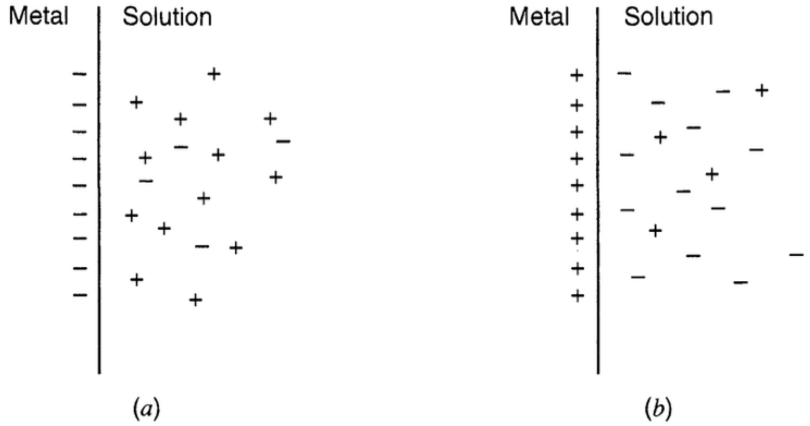

Figure 1. The metal-solution interface as a capacitor with a charge on the metal, q_M, (a) negative and (b) positive [1].

Whether the charge on the metal is negative or positive with respect to the solution depends on the potential across the interface and the composition of the solution. At all times, however, $q_M = -q_s$. The whole array of charged species and oriented dipoles existing at the metal-solution interface is called ***the electrical double layer***. At a given potential, the electrode-solution interface is characterized by a double-layer capacitance, C_{dl}, typically in the range of 10 to 40 $\mu F/cm^2$. However, unlike real capacitors, whose capacitances are independent of the voltage across them, C_{dl} is often a function of potential.

Faradaic processes

Kind of processes in which charges (e.g., electrons) are transferred across the metal-solution interface are called electrochemical reactions. Electron transfer causes oxidation or reduction to occur. Since such reactions are governed by Faraday's law (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called ***faradaic processes***. Electrodes at which faradaic processes occur are sometimes called charge-transfer electrodes.

To understand the difference between a chemical reduction (***homogeneous charge transfer***) and an electrochemical reduction (***heterogeneous charge transfer***), consider the example of the reduction of ferrocenium $[Fe(Cp)_2]^+$ (Cp = cyclopentadienyl), abbreviated as Fc^+, to ferrocene $[Fe(Cp)_2]$, abbreviated as Fc:

Through a chemical reducing agent: $Fc^+ + [Co(Cp^*)_2] \rightleftharpoons Fc + [Co(Cp^*)_2]^+$

At an electrode: $Fc^+ + e^- \rightleftharpoons Fc$

The transfer of an electron between the two molecules in solution is thermodynamically favourable (Figure 2 A), and the difference in energy levels is the driving force for the reaction.

In an electrochemical reduction, Fc+ is reduced via heterogeneous electron transfer from an electrode; but what is the driving force for this process? An electrode is an electrical conductor, typically platinum, gold, mercury, or glassy carbon. Through use of an external power source (such as a potentiostat), voltage can be applied to the electrode to modulate the energy of the electrons in the electrode. When the electrons in the electrode are at a higher energy than the LUMO of Fc^+, an electron from the electrode is transferred to Fc^+ (Figure 2 B). The driving force for this electrochemical reaction is again the energy difference between that of the electrode and the LUMO of Fc^+.

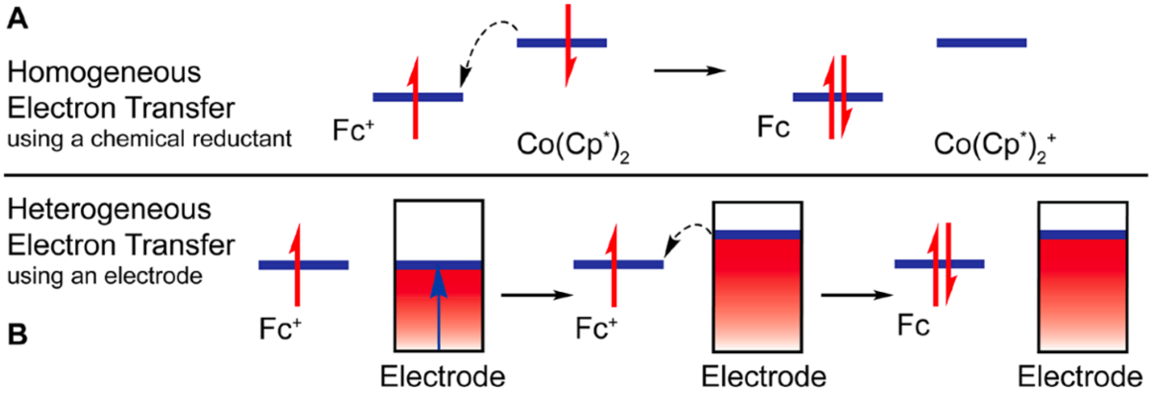

Figure 2. (A) Homogeneous and (B) heterogeneous reduction of Fc^+ to Fc. The energy of the electrons in the electrode is controlled by the potentiostat; their energy can be increased until electron transfer becomes favourable [2].

Both faradaic and nonfaradaic processes occur when electrode reactions take place. Although the faradaic processes are usually of primary interest in the investigation of an electrode reaction (except in studies of the nature of the electrode-solution interface itself), the effects of the nonfaradaic processes must be considered in using electrochemical data to obtain information about the charge transfer and associated reactions according to **double layer structure and properties** (Figure 3).

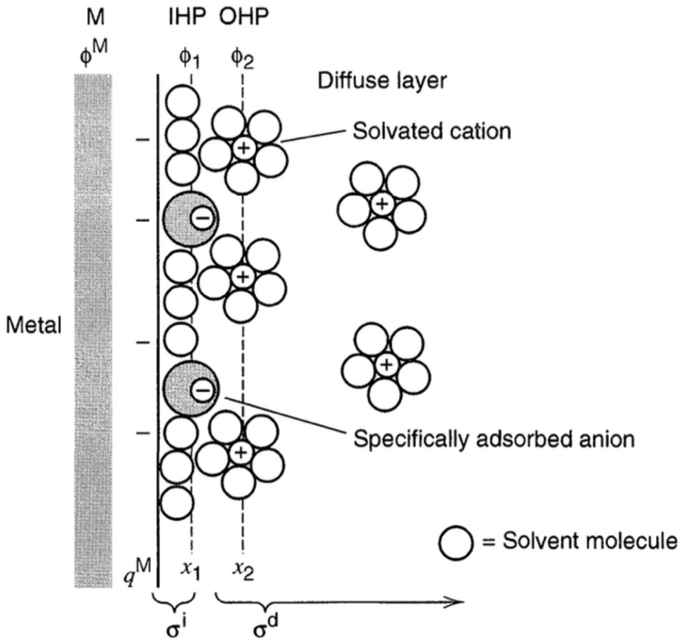

Figure 3. Proposed model of the double-layer region under conditions where anions are specifically adsorbed, OHP are inner and outer Helmholtz planes, respectively.

Learning Outcomes

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

1. *Explain the concept of the electrode/solution interface and the structure of the electrical double layer (related to LO 1.1).*
2. *Describe mechanisms of charge transfer and identify factors influencing electron exchange between electrode and solution (related to LO 1.1 and 1.2).*
3. *Apply fundamental electrochemical equations (e.g., Butler–Volmer equation) to analyze charge transfer kinetics (related to LO 1.2).*

Questions and Self-study Assignments

1. *Describe the differences between the Helmholtz, Gouy–Chapman, and Stern models of the electrical double layer.*
2. *Derive the Butler–Volmer equation and explain each term's physical meaning.*
3. *Discuss how temperature and electrode material influence charge transfer kinetics.*
4. *Solve a numerical example involving calculation of exchange current density for a given system.*

5. *Prepare a short report comparing experimental techniques used to study charge transfer processes (e.g., impedance spectroscopy, cyclic voltammetry).*

References

1. Bard, Allen J., Larry R. Faulkner, and Henry S. White. *Electrochemical methods: fundamentals and applications*. John Wiley & Sons, 2022.
2. Elgrishi, Noémie, et al. "A practical beginner’s guide to cyclic voltammetry." *Journal of chemical education* 95.2 (2018): 197-206.