Lecture 1

Introduction to the modelling of electrochemical processes

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].

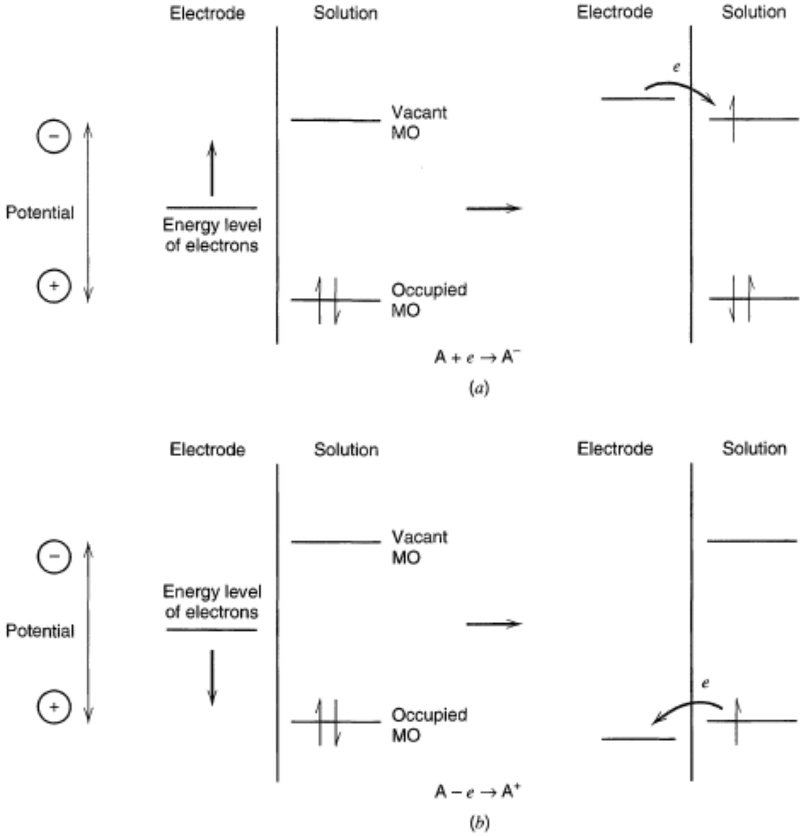

Figure 1. Representation of (a) reduction and (b) oxidation process of a species, A, in solution. The molecular orbitals (MO) of species A shown are the highest occupied MO and the lowest vacant MO. These correspond in an approximate way to the E°s of the A/A^- and A^+/A couples, respectively. The illustrated 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**).

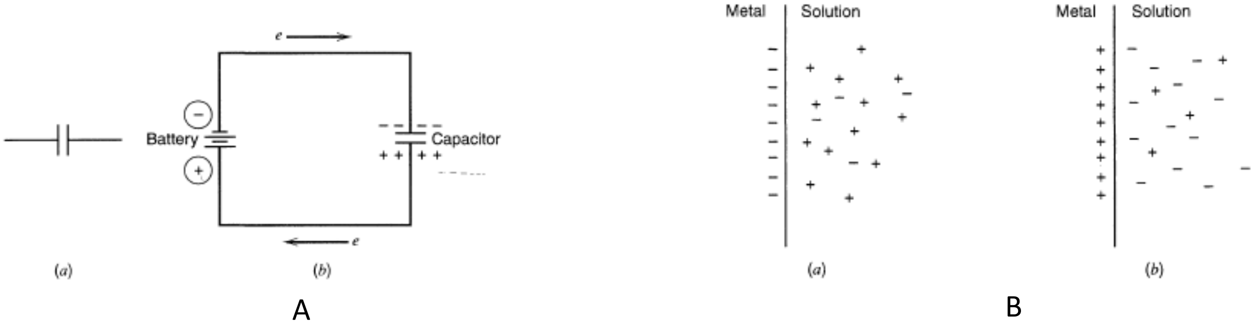

Figure 2. A) (a) A capacitor, (b) Charging a capacitor with a battery. B) The metal-solution interface as a capacitor with a charge on the metal, q^M, (a) negative and (b) positive [1].

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**.

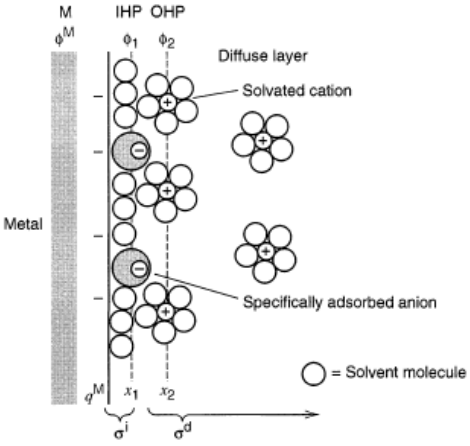

Figure 3. Proposed model of the double-layer region under conditions where anions are specifically adsorbed [1].

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].

Reference

1. Bard A. J. et al. Fundamentals and applications //Electrochemical Methods. – 2001. – Т. 2. – №. 482. – С. 580-632.