

Electroanalytical Sensors

6.1 INTRODUCTION

A large part of analytical instrumentation systems uses sensors that can detect electrochemical actions in the analysis media. The detection is, however, neither a simple phenomenon nor a direct transduction. The basic approach is to use a pair of electrodes in the analysis medium that sense the actions and reactions in the medium in the form of current, voltage, or power. The electrodes themselves are specially developed devices, and in operation, they may have to produce electrical energy or consume it from an external source in the process of transduction. These are often termed as electrochemical cells—galvanic or electrolytic. Once the function of an electrochemical cell is understood, its variation in design can be taken up along with the ‘sensing ranges’.

6.2 THE ELECTROCHEMICAL CELL

The electrochemical cell consists of two electrodes or may be just two conductors, immersed in suitable electrolyte solutions. The cell functions if these electrodes are connected externally by metal conductors and internally, the electrolyte solutions are in contact so that ion movement can take place between them. The electrodes are commonly known as anode and cathode where oxidation and reduction respectively, take place. Oxidation and reduction are ‘interfacing mechanisms’ where the ionic conduction of the solution is coupled to the electronic conduction of the electrode (metal) and thus, an electrical circuit is completed in a cell.

Each cell consists of two half-cells where each half-cell is said to be consisting of its electrode and electrolyte solution. If the electrolytes of the two half-cells are different in composition, they are not allowed to mix as this would decrease cell efficiency because of deposition, recombination, and so on. Instead, a liquid junction is created by special arrangement and as a consequence, a junction potential arises at this interface. The electrolytes in the anode and cathode compartments are often separated by a ‘salt bridge’ that is created when chemical reaction takes place in the cell. It has a variety of forms. A third solution (saturated) of a specific salt is often interposed for bridging purpose.

A typical representation of an electrochemical cell follows certain conventions adopted by the chemists. One such cell is shown in Fig. 6.1. The left part contains the anode and the information regarding the solution in its contact. Vertical line represents phase boundary. The cathode and its associated solution as well as its states are on the right. Any salt bridge is indicated by a discontinuous line.

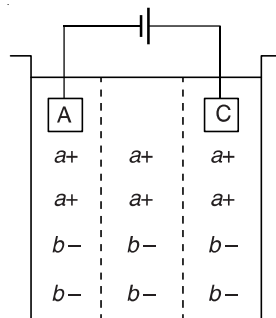


Fig. 6.1 An electrochemical cell.

The reactions in a cell occur in two phases: (i) the electronic ones at the metal electrode interfaces and (ii) ionic ones at the electrolyte level.

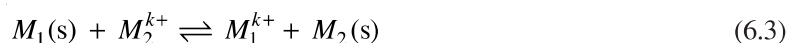
At the cathode, the reaction is



and at the anode



Therefore, the net cell reaction is



At the electrolytes, ionic movement takes place. The ions, however, have different mobility. The speed of an ion depends on its relative concentration as also on its inherent mobility. For example, in HCl, H^+ and Cl^- are produced but a proton (H^+) being five times more mobile than Cl^- ion current is largely contributed, in fact, 5/6th of it, by H^+ and only 1/6th by Cl^- . In Fig. 6.1, if a^+ is H^+ and b^- is Cl^- , after current flow, ion distribution will be different in the three compartments. The direct current flowing in a closed-circuited cell follows the Ohm's law except when polarization occurs. The electrolyte resistance is employed for the purpose.

For the dc current to flow with a dc potential applied between the electrodes, oxidation and reduction at the anode and cathode occur. Such a process is sometimes called *faradaic process*. If, an ac potential is applied, with cyclic change of positive and negative values at the same electrode, situation takes a new dimension. With sudden application of potential to the metallic electrode in an electrolyte, the electrode surface acquires an excess or deficiency of negative charge and the layer of electrolyte solution adjacent to the electrode acquires an opposing charge because of ionic mobility and a so called *electrical double layer* at the electrode solution interface develops. This double layer consists of an inner compact layer in which the potential decreases linearly with separation from the electrode and a relatively diffuse layer in which the potential decreases exponentially. When an ac potential is applied, the process is reversed every half cycle and then either positive or negative ions are attached to the electrode surface. Electrical energy is thus, consumed and converted to heat because of this ionic movement. Each electrode

surface thus, behaves as a capacitor plate with the current increasing with surface area (capacitance) and frequency. This process is a nonfaradaic process.

Electrochemical cells can be reversible or nonreversible. A cell, a galvanic cell for example, formed with electrodes and an appropriate electrolyte solution develops certain amount of potential, say, E volts. If from an external source a potential greater than E volts is applied between the electrodes with the negative of the source connected to the anode, a reversal in electron flow direction is observed. This may cause a reversal of the electrochemical reaction and in such a case, the cell is said to be ‘chemically reversible’. If the current reversal causes a different set of reactions, the cell is said to be ‘chemically irreversible’.

6.3 THE CELL POTENTIAL

The potential of an electrochemical cell depends on the electrode potentials which are the characteristic of the half-cells with the concerned electrodes and the effect of concentration of reactants and their products in the solution. This effect of concentration is often termed as ‘activity’.

From thermodynamical considerations, the maximum work obtainable from the cell at a constant temperature and pressure called the *free energy* or *Gibbs free energy* ΔG for a cell reaction, is given by

$$\Delta G = RT \ln B - RT \ln A \quad (6.4)$$

where

$R = 8.316 \text{ Jmol}^{-1}\text{deg}^{-1}$, is the gas constant,

T is the temperature (in K), and

A is the equilibrium constant for the reaction given by

$$A = \frac{[a^+][b^-]}{[ab]} \quad (6.5)$$

where a stands for acid, b for base, and the $[ab]$ for activity.

The term B in Eq. (6.4) is similarly defined as

$$B = \frac{[a^+]_x[b^-]_x}{[ab]_x} \quad (6.6)$$

where the subscript x denotes instantaneous concentrations. In fact, Eq. (6.4) states that the amount of free energy is dependent on how far away is the system from equilibrium state. The cell potential E_c is related to the free energy as

$$\Delta G = -nFE_c \quad (6.7)$$

where n is the number of equivalents of electricity, that is, ‘moles’ of electrons associated with the oxidation–reduction process and F is Faraday which is 96487 coulomb/chemical equivalent.

Combining Eqs. (6.4), (6.5), (6.6), and (6.7), we derive

$$E_c = E_c^0 - \left(\frac{RT}{nF} \right) \ln \frac{[a^+]_x[b^-]_x}{[ab]_x} \quad (6.8)$$

where

$$E_c^0 = \left(\frac{RT}{nF} \right) \ln \frac{[a^+][b^-]}{[ab]} \quad (6.9)$$

which is a constant called the ‘standard potential of the cell’ that is, the potential of the cell when the reactants and products are at unit activity and pressure. In fact, the superscript 0 is used to denote standard in thermodynamical studies. Equation (6.9) is the Nernst equation and is widely used in analysis.

The activity α_m of a species is related to its molar concentration $[M]$ by the equation

$$\alpha_m = f_m[M] \quad (6.10)$$

where f_m is called the ‘activity coefficient’ which, in effect, implies the activity of $[M]$ and it varies with the ionic strength of the solution.

Electrode potentials basically go in to form the cell potential as the cell itself is made up of two half-cells. Thus, one can write

$$E_c = E_{\text{cath}} - E_{\text{an}} \quad (6.11)$$

where E_{cath} and E_{an} are electrode potentials for the corresponding half-cell reactions.

Nernst equation Eq. (6.8), is a very common equation for many transducers that use electrodes and a reaction medium which may be liquid or gaseous in states and the equation then is

$$E = E^0 - \frac{0.0591}{n} \ln \frac{[a_1][a_2] \cdots}{[b_1][b_2] \cdots} \quad (6.12)$$

where $RT/(nF)$ for half-cell at 298 K is given as $0.02568/n$ volts, and $[a_i]$ and $[b_j]$ represent partial pressures in atmospheres of reacting species when a_i, b_j are gases, and represent concentration in moles per litre when they are solutes with activity α_r . The half reaction for Eq. (6.12) is given as

$$\alpha_1 a_1 + \alpha_2 a_2 + \cdots + ne = \beta_1 b_1 + \beta_2 b_2 + \cdots \quad (6.13)$$

Here, a_i and b_j represent the ‘chemical formulae’ for reactants while α_i and β_j represent the number of moles or partial pressures and e , as usual, the electron.

6.4 STANDARD HYDROGEN ELECTRODE (SHE)

Since the absolute potential of a half-cell is not measurable and it is the potential difference that is measured, a second half-cell has to be formed. If this second half-cell can be made as a ‘common reference electrode’, this measured value would be available as a relative one but with respect to a standard reference. Such a standard reference is the *standard hydrogen electrode* (SHE) whose cell potential has been standardized by assignment. However, SHE is not easily reproducible and instead conveniently produced secondary standard electrodes or reference electrodes are used and the measured potentials using these references are easily converted to hydrogen reference standards.

As SHE is considered as the ‘primary’ standard, it is described here in some details. Its standard half reaction potential at 25°C, E^0 , has been assigned a value exactly 0 (zero) volts by international agreement, assuming that the activity of H^+ and fugacity (partial pressure) of $H_2(g)$