

ELECTROCHEMICAL PROCESSES

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Summary

The general principles of electrochemistry and laws of electrolysis are reviewed. The relevant features concerning desalination of seawater are outlined.

1. Introduction

The science of electrochemistry is concerned with the electrical circuits that are associated with chemical changes. Water is a key player in electrochemistry.

- (a) As an electrolyte in an electrochemical cell.
- (b) As reaction product of a fuel cell (a voltaic cell).

- (c) As fuel source in hydrogen - producing separation cell (a driven cell).

In the context of desalination, the relevance of electrochemistry is apparent from the following.

- (a) A major operational problem in desalting processes is the corrosion of metallic components, which essentially takes place by electrochemical mechanisms.
- (b) Electrodialysis, which is basically an electrochemical process, is an important technique for desalting brackish waters.
- (c) Many of the analytical techniques used for characterizing feed and product waters are electrochemical in nature.
- (d) An electrochemical method is utilized to generate the chlorine gas needed to chlorinate water.
- (e) Some of the complex metabolic processes occurring in biological organisms and contributing to biofouling are electrochemical.

1.1. Electrochemical Cell

As shown in Figure 1, a typical electrochemical cell has two different metals, A and C, immersed in aqueous solution and joined externally by a wire. The aqueous solution contains the ions of the two metals A^+ and C^+ , in addition to the ions X^- , H^+ , and OH^- . The flow of electrical current through such a system takes place by the following mechanisms.

- (a) Through the connecting wire by normal “free electron” conduction.
- (b) Through the aqueous solution by movement of charged ions.

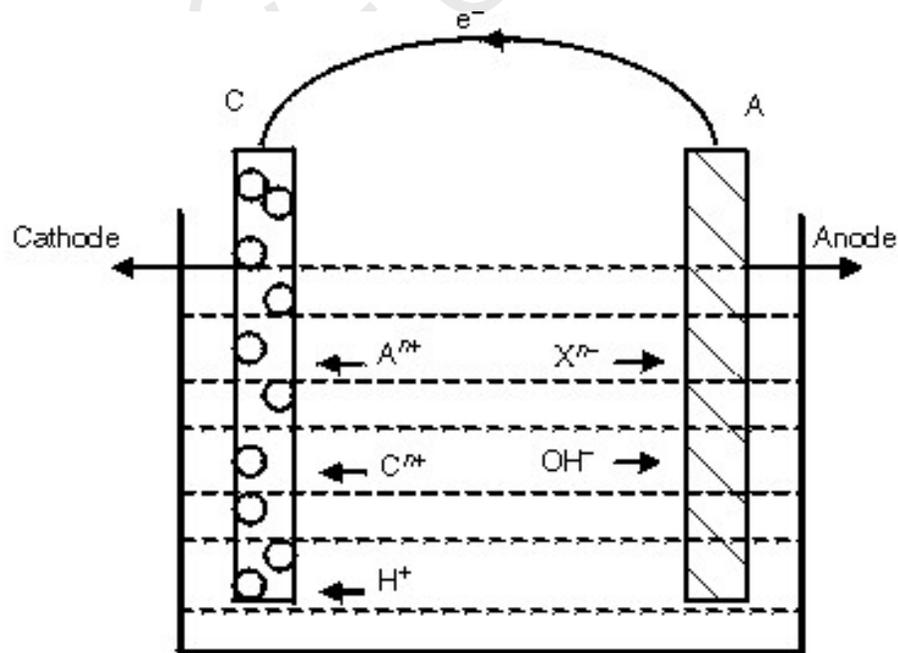


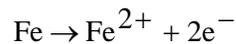
Figure 1. Electrochemical cell with two different metals, A and C.

In the above arrangement, the charge-transfer process involves chemical reactions at the interfaces between the metals and the solution, which occur either spontaneously or due to a supply of electrical energy from an external source. The two interfaces are known as *electrodes* and the transfer of charged particles across an electrode is associated with a potential difference. In the external circuit, the current flows from the electrode known as *anode* towards the electrode called *cathode*.

Finally, an electrochemical cell need not necessarily contain an aqueous solution; any medium such as molten salt, which can conduct electricity, would serve the purpose.

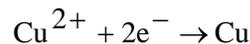
1.2. Electrode Reactions

The electrodes are usually made up of metals and the electrode reactions occurring on their surface involve either the electrode metal itself or the metallic ions dissolved in the aqueous medium. For example, if one of the electrodes comprises a piece of iron, the following electrode reaction could take place:



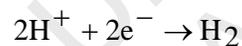
where “e” represents an electron. This type of reaction constitutes a charge-transfer process releasing electrons; therefore, it is known as an *anodic reaction*.

On the other hand, if copper ions are present in the solution (termed as electrolyte), then the following electrode reaction takes place with the deposition of copper on the electrode surface (which may or may not be a piece of copper):

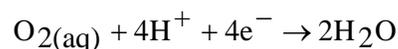
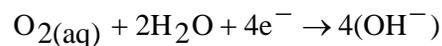


This type of reaction, which consumes electrons, is called a *cathodic reaction*.

The electrode reactions in electrochemical cells often involve non-metallic species such as the following hydrogen evolution reaction:



Oxygen dissolved in water can also take part in the electrode reactions given below:



In the above reactions, the term “aq” emphasizes that the reacting oxygen is dissolved in water. These are important aqueous corrosion reactions which arise during oxygen determination methods using special instruments.

2. Faraday's Laws of Electrolysis

In the electrode reactions, the relationship between the amount of electrical charge transferred and the quantity of substance discharged is given by laws of electrolysis as described by Faraday.

2.1. First Law

The amount of any substance dissolved or deposited at an electrode is directly proportional to the quantity of electricity flowing in the circuit.

2.2. Second Law

The masses of different species dissolved or deposited at electrodes by the same quantity of electricity are in direct proportion to their equivalent weights.

The above laws are quantitatively expressed as follows: the passage of one Faraday of charge, i.e. 96 500 coulombs, across an interface involves the consumption or liberation of $1/n$ moles of substance. Here, n is the number of electrons involved in the reaction and it is often but not always equal to the valency of the species in the electrode reaction. For instance, in the above reaction of dissolution of iron as Fe^+ ions, the passage of 96 500 coulombs would result in the dissolution of $1/2$ mole = $55.85/2 = 27.93$ g of iron, where 55.82 is the atomic weight of iron.

Similarly, passage of the same charge would result in the deposition of $1/2$ mole = $63.54/2 = 31.77$ g of copper, where 63.54 is the atomic weight of copper.

Thus, the above quantities of iron dissolved and copper deposited are in proportion to their respective equivalent weights. For an electric current of I A, i.e. I coulombs s^{-1} , the number of moles of a substance dissolved or deposited would be I/nF , where $F = 96\,500$ coulombs. If the electrode surface area is a cm^2 , then the current density $i = I/a$. Therefore, the deposition or dissolution rate would be i/nF moles $\text{cm}^{-2} \text{s}^{-1}$.

3. Electrode Potential

The potential difference across the interface of an electrode is called the *electrode potential*. It is an important parameter which can be construed as a measure of the thermodynamic tendency for the spontaneity of the electrode reactions.

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