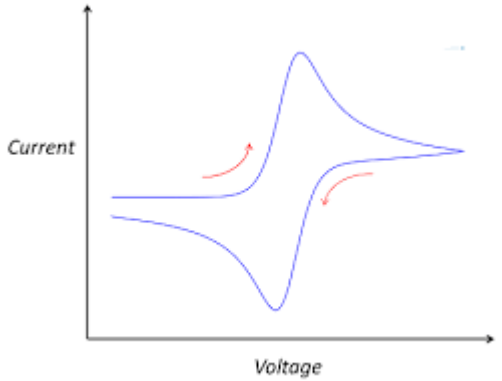
Fundamentals of Electrochemistry



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References

1. **Electrochemical Methods–Fundamental and Applications, A. J. Bard and L. R. Faulkner, Wiley, 1980**

2. **Modern Electrochemistry, Bockris, John O'M., Reddy, Amulya K.N., Gamboa-Aldeco, Maria E.**
3. **Electrode Kinetics — Principles and Methodology, C. H. Bamford, R. G. Compton (Eds.)**

4. **Recent research articles and reviews**

Outline

1. Introduction to Electrochemistry

How it works

2. Concept of electrochemical double layers

why are we so much interested in?

3. Instrumentation

Working principles

Three electrodes set-up

4. Sample preparation

Roles of electrolyte (electronically-conducting phase)

***D*ata collection**

5. Heterogeneous electron transfer and concept of capacitive and faradic current

6. Measurements and analyses of various voltammograms

Organic, metal-complexes (ferrocene), electrochemical grafting (diazonium salts)

Process and factors influencing transport of charge across the interfaces

Pros and cons of voltammogram techniques

Some Fundamentals of Electrochemistry

What is electrochemistry?

Chemical reactions are triggered by applied voltage or vice versa (a battery or fuel cell). These chemical reactions involve electron(s) transferred to and from the working electrode. Electron flow requires electrolyte (solid, liquid) electronically-conducting phase.

What is an electrode?

An electrode a conductor of electric charges. It originated from two Greek words: elektron, meaning amber, and hodos, a way. The term was coined by William Whewell upon a request of Michael Faraday.

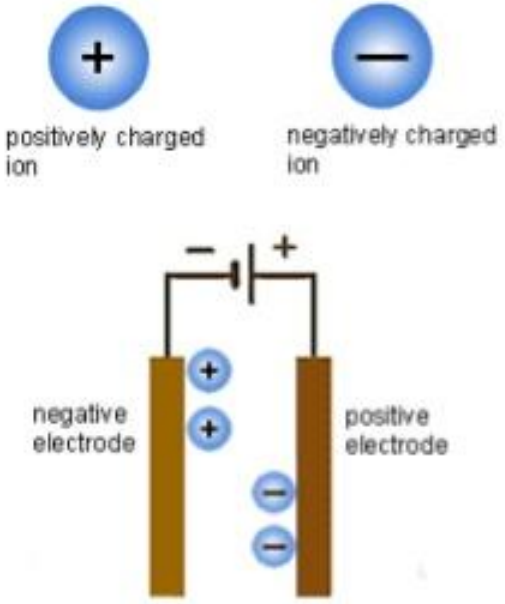
It can either be Anode or Cathode. At the anode, electrons leave the cell and oxidation takes place, while at cathode electrons enter the cell and reduction happens. (Remember RED-CAT & An-OX)

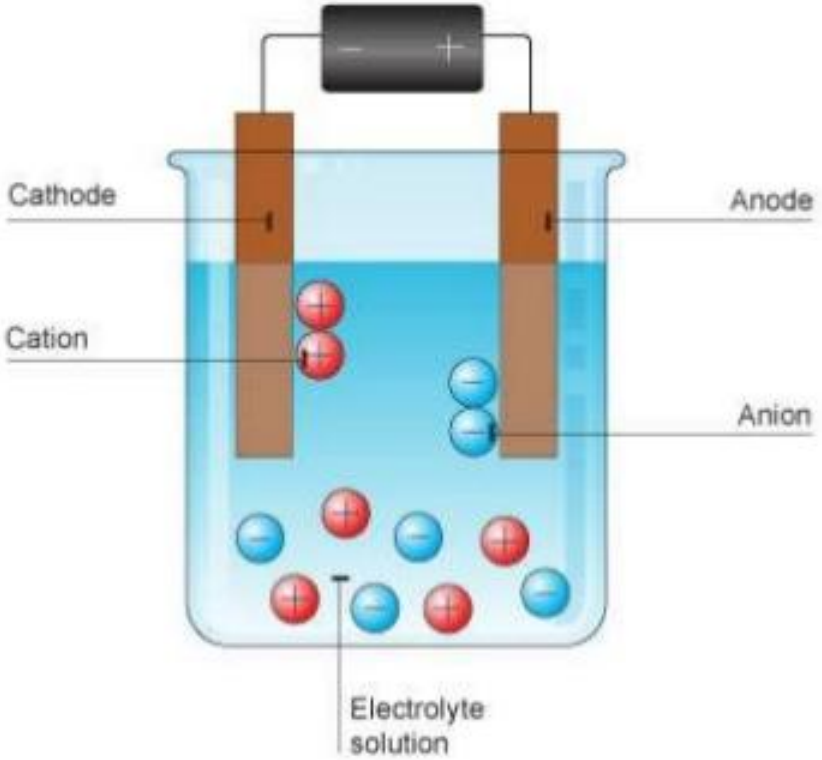
When an electrode plays dual functions, both cathode and anode are referred to as bipolar electrode.

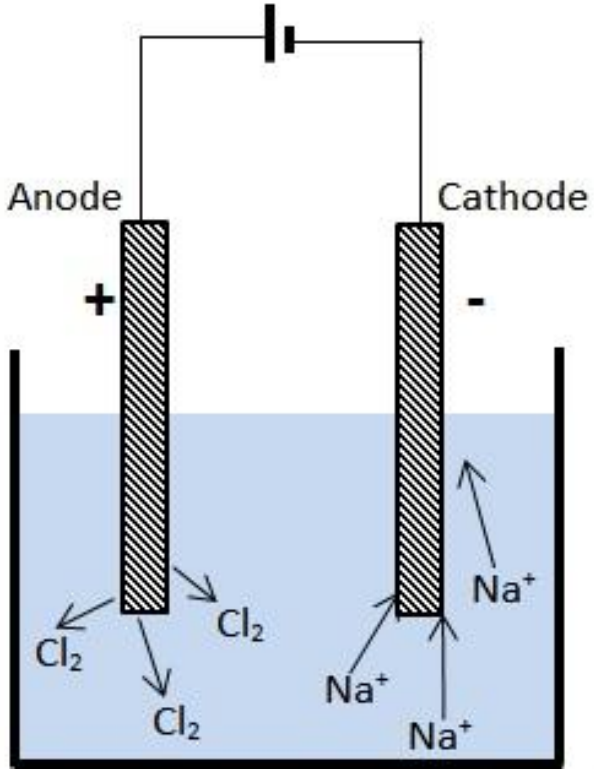
Representation of Anode & Cathode in a Cell

In an electrolytic cell, the negatively charged electrode is the cathode, since a positively charged ion gains electrons from the cathode, and hence reduction occurs.

Don't **PANIC** - **P**ositive is **A**node, **N**egative **I**s **C**athode.



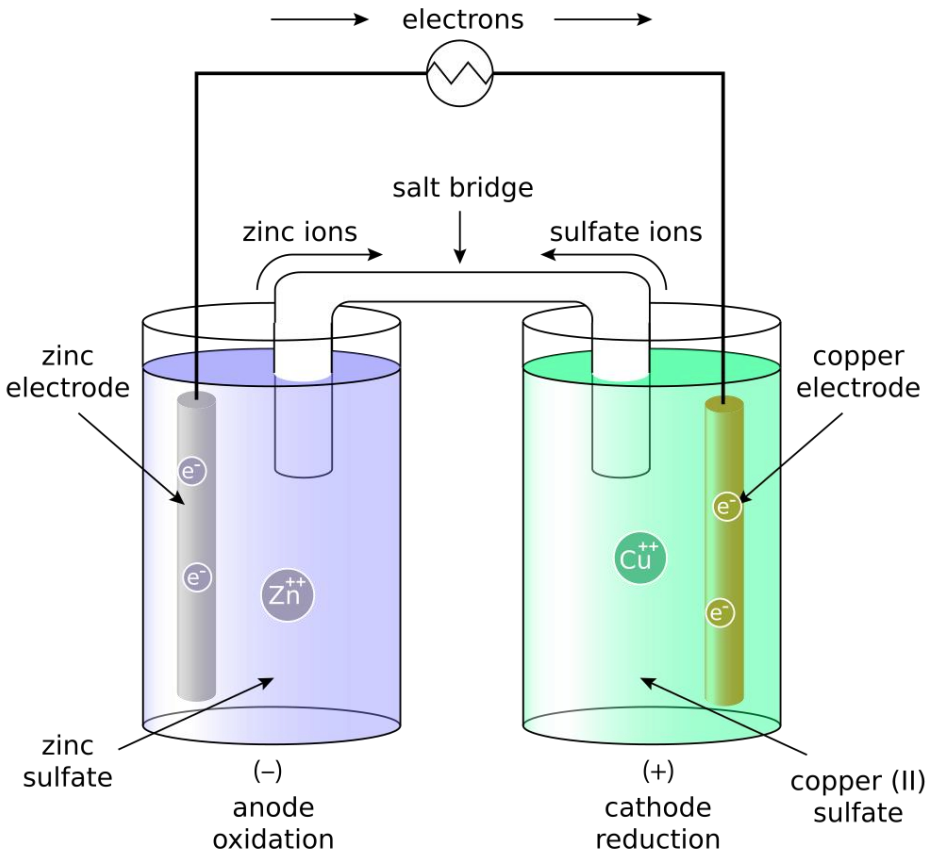




Daniel Cell

A Daniell cell is the best example of a galvanic cell, which converts chemical energy into electrical energy.

Zinc ions get oxidized, and the copper ions get reduced, with the electrons flowing from the zinc to the copper through the external wire, generating electricity



$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \; ; \; E^o = +0.34 \text{ V}$$

$$Zn^{2+} + 2e^- \rightleftharpoons Zn \; ; \; E^o = -0.76 \text{ V}$$

$$\log_e K = \frac{\nu_e F E^\circ_{\text{cell}}}{RT}$$

where

F is the Faraday constant,

R is the gas constant, and

T is the absolute temperature in Kelvins.

For the Daniell cell, $K \approx 1.5 \times 10^{37}$

More about Electrochemistry

How do chemical reactions differ from electrochemical reactions?

A chemical reaction occurs between molecules via electron transfer that does not require electrical potential, but electrochemical reaction does need such potential.

Why do we need to apply a potential for a chemical reaction to happen?

A chemical reactions (changes) is governed by certain potential difference. Thus, we need to apply the same energy.

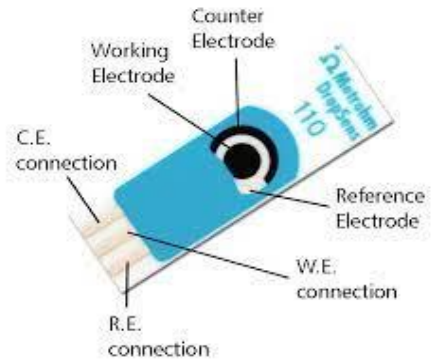
Why do we need to study electrochemistry?

Electrochemical study deals with electrical and chemical effects simultaneously. This study is used to explain many phenomena such as electrochemical charge transfer (Faradaic), capacitor, electrophoresis, corrosion, devices such as electrochromic displays, electro analytical sensors, batteries, and fuel cells, and technologies like electroplating of metals and the large-scale production of aluminum and chlorine.

Spectroelectrochemical techniques further encompass spectroscopic analysis upon chemical changes caused by electrical means.

Examples of Various Electrodes

Typical electrode materials include solid metals (e.g., Pt, Au), liquid metals (Hg, amalgams), carbon (graphite), and semiconductors (indium-tin oxide, doped Si), and many more



Electrochemical Cells and Reactions

Electrode/electrolyte interface: **It's different chemical phases, for example, between an electronic conductor (an electrode) and an ionic conductor (an electrolyte). At the interfaces, an electric potential is applied and current passes. Charge is transported through the electrode by the movement of electrons or holes.**