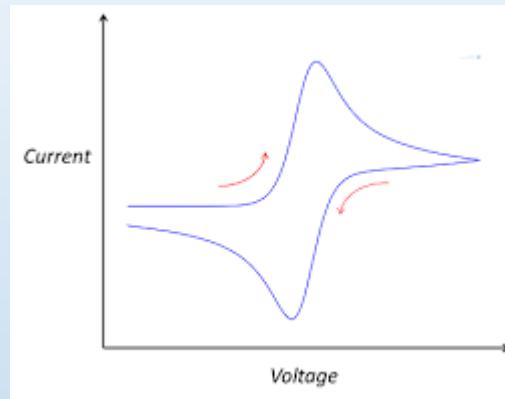


Fundamentals of Electrochemistry



Course: CSO 203

Instructor: Dr. Prakash Chandra Mondal

Department of Chemistry, IIT Kanpur

For any queries, please email at pcmondal@iitk.ac.in

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)

Data 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.

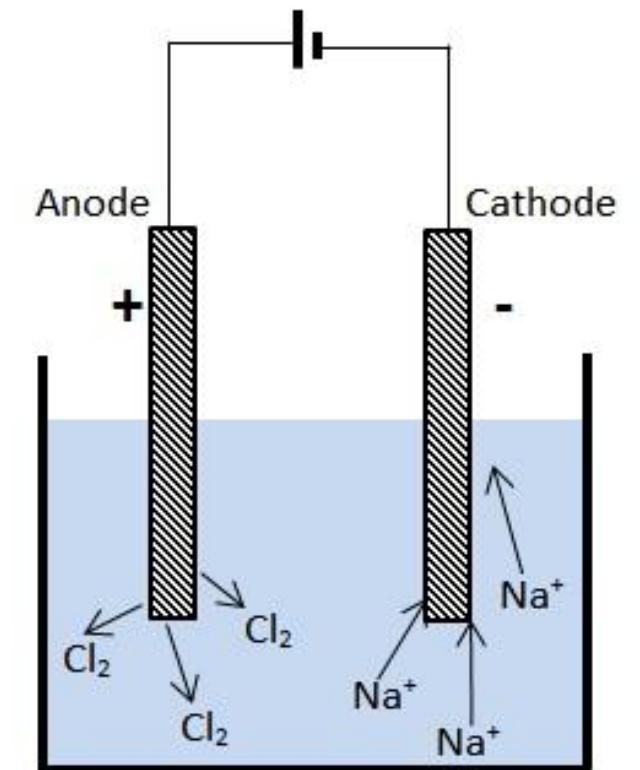
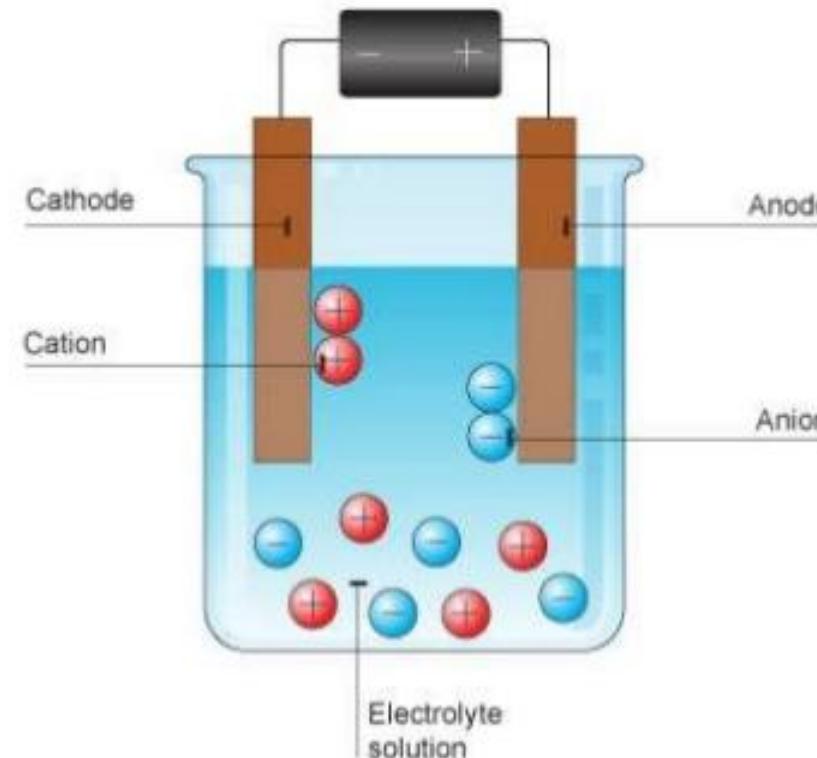
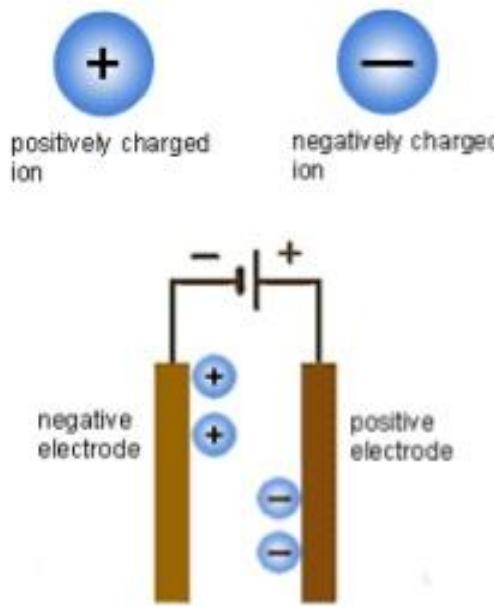
It can either be Anode or Cathode. At the anode, electrons leave the cell and oxidation takes place, while at cathode electrons enter the cell and reduction happens. (Remember RED-CAT & An-OX)

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.

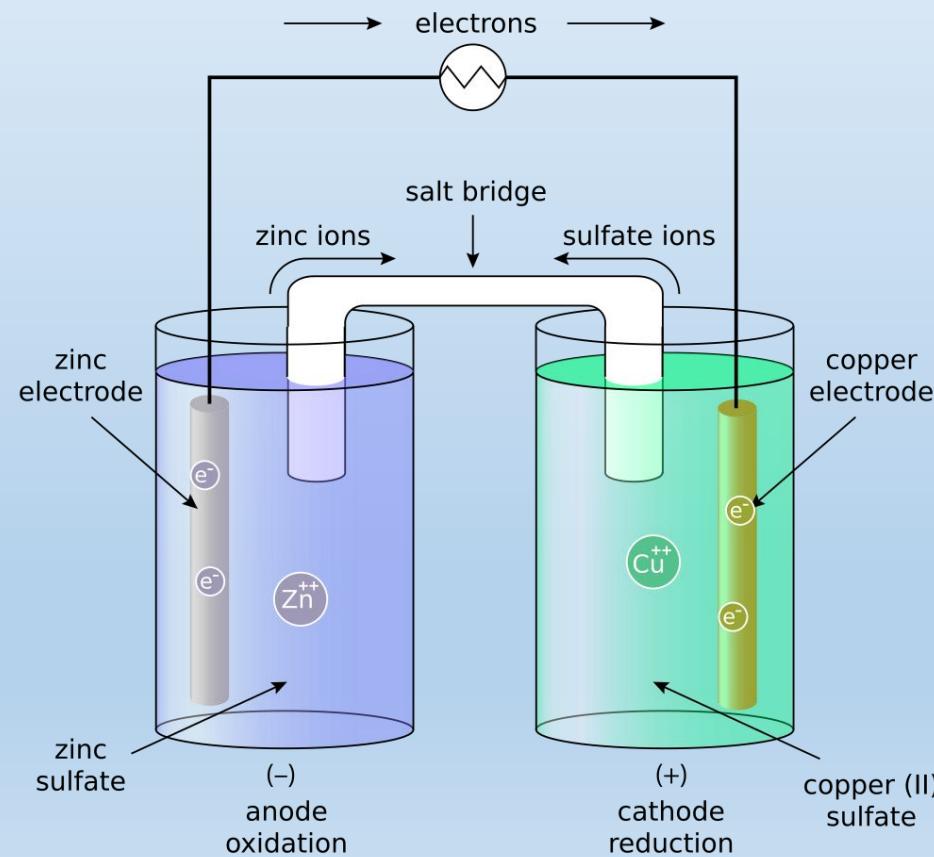
**Don't PANIC - Positive is
Anode, Negative Is Cathode.**



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



$$\log_e K = - \frac{\nu_e F E_{\text{cell}}^\circ}{R T}$$

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.

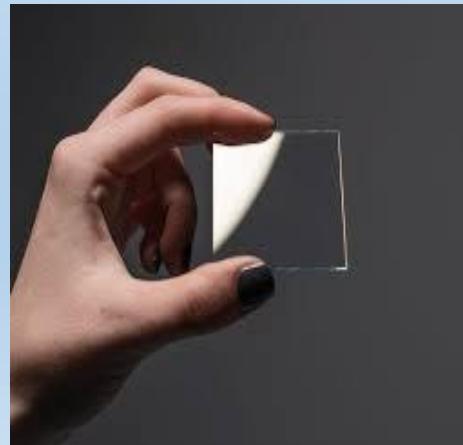
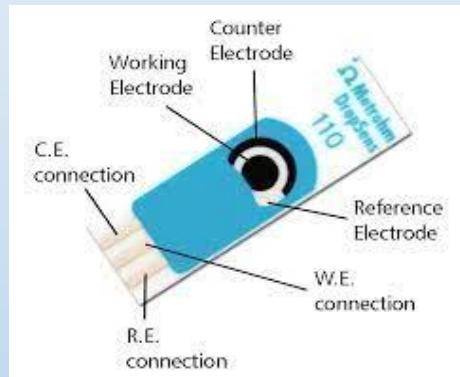
Why do we need to study electrochemistry?

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.

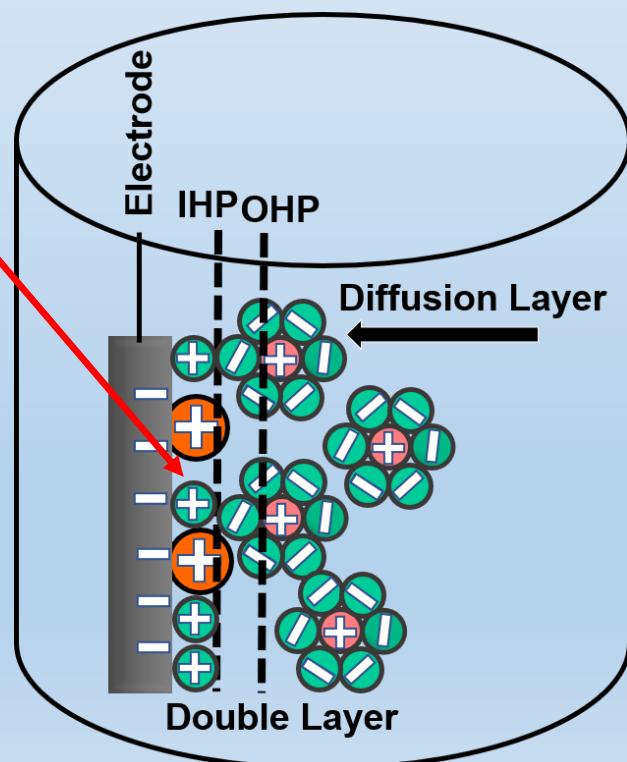
Examples of Various Electrodes

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

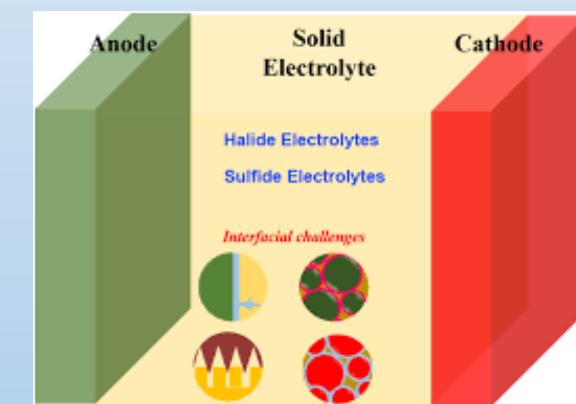
Electrode/electrolyte interface: It's different chemical phases, for example, between an electronic conductor (an electrode) and an ionic conductor (an electrolyte). At the interfaces, an electric potential is applied and current passes. Charge is transported through the electrode by the movement of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



Electrolyte phase

In the electrolyte phase, charge is carried by the movement of ions. The most common electrolytes used are liquid solutions containing ionic species, such as, H^+ , Na^+ , Cl^- , in either water or a nonaqueous solvent.

For the electrochemical experiments, electrolyte must be of sufficiently low resistance i.e., good conductive.



Electrochemical Cells and Reactions

Electric potential: a difference in electric potential can be measured between the electrodes in an electrochemical cell

What is 1 volt?: A difference in electric potential in Volt (V) is measured between the electrodes in an electrochemical cell. 1 volt is defined as the work done (Joule) to bring unit charge (1 Coulomb) from point A to point B, **1 V = Joule/Coulomb**

According to Ohm's law (**V = IR**), it can also be defined as electro motive force (EMF) that required to pass 1 ampere of current through an electrical conductor possesses 1 Ohm of resistance.

Transition in electric potential: Transition in electric potential happens during crossing of electrons from one (semi)conducting phase to another but only at the interface. The sharpness of the transition implies that a very high electric field exists at the interface, and one can expect it to exert max. effects by charge carriers (electrons or holes) in the interfacial region.

Also, the magnitude of the potential difference at an interface affects the relative energies of the charge carriers in the two phases.

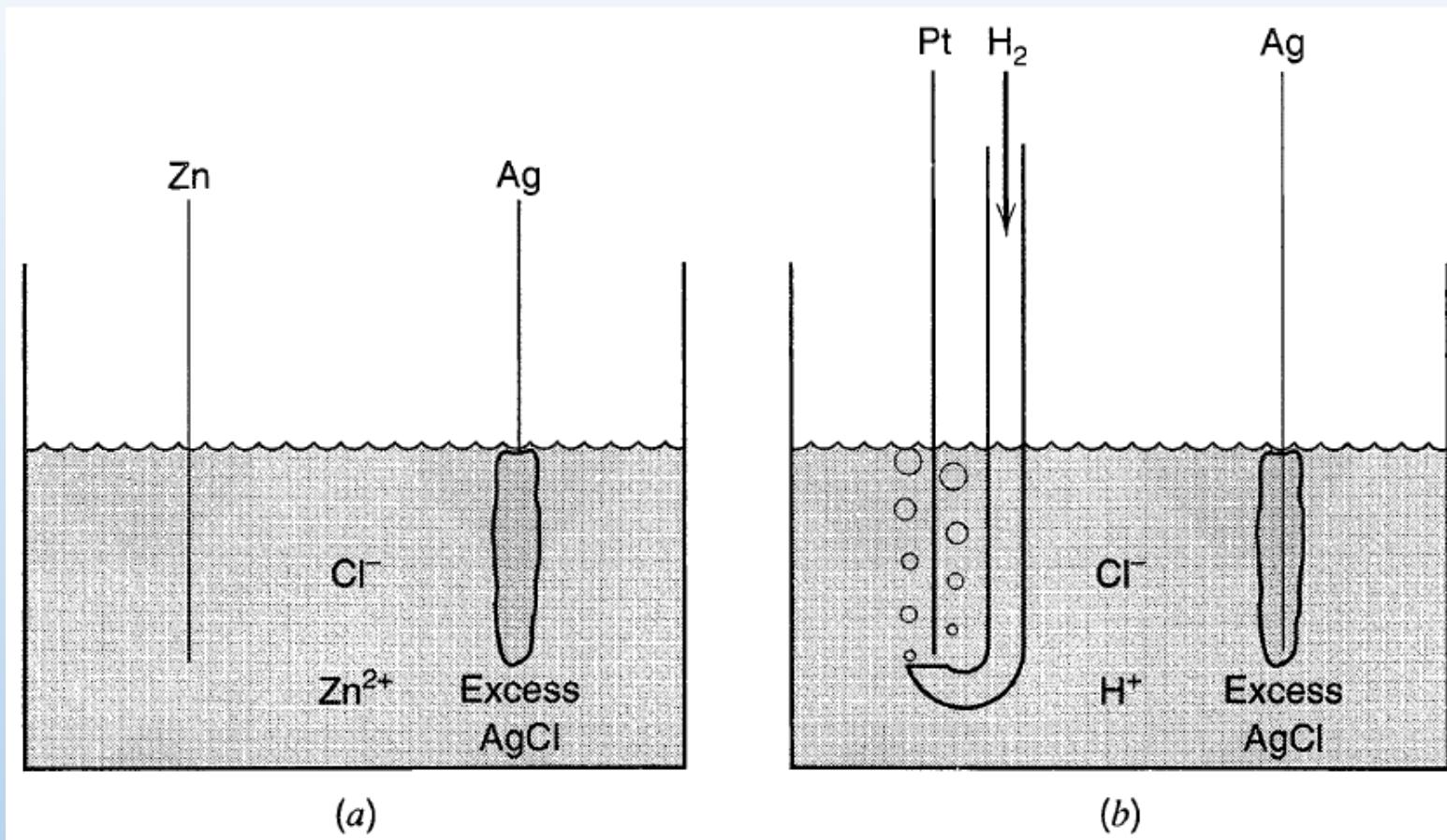
Short-hand notation for electrochemical cells

Zn/Zn²⁺, Cl⁻/AgCl/Ag: a slash represents a phase boundary, and a comma separates two components in the same phase. A double slash, not yet used here, represents a phase boundary whose potential is considered as a negligible component of the overall cell potential

Pt/H₂/H⁺, Cl⁻/AgCl/Ag: When a gaseous phase is involved, it is written adjacent to the electrode.

Half-reactions: Chemical reactions occurring in a cell can be considered as it is made up of two independent half-reactions, which describe overall chemical changes at the two electrodes. Remember that each half-cell reaction must be considered near the electrodes only but not far. The reaction occurs due to the interfacial potential difference at the corresponding electrode.

Typical Electrochemical Cells Consisting of Two Electrodes



If we want to make those redox reactions to happen only at one electrode surface, and the electrode at which it occurs is called the *working* (or indicator) electrode (WE). In this case, potential of WE is standardized by another electrode (called a *reference electrode/RE*) made up of phases having essentially constant composition.

Some Reference electrodes used in Electrochemistry

The internationally accepted primary reference is the *standard hydrogen electrode* (SHE), or *normal hydrogen electrode* (NHE), which has all components at unit activity: Pt/H₂(a = 1)/H⁺(a = 1, aqueous)

Potentials are often measured and quoted with respect to reference electrodes other than the NHE.

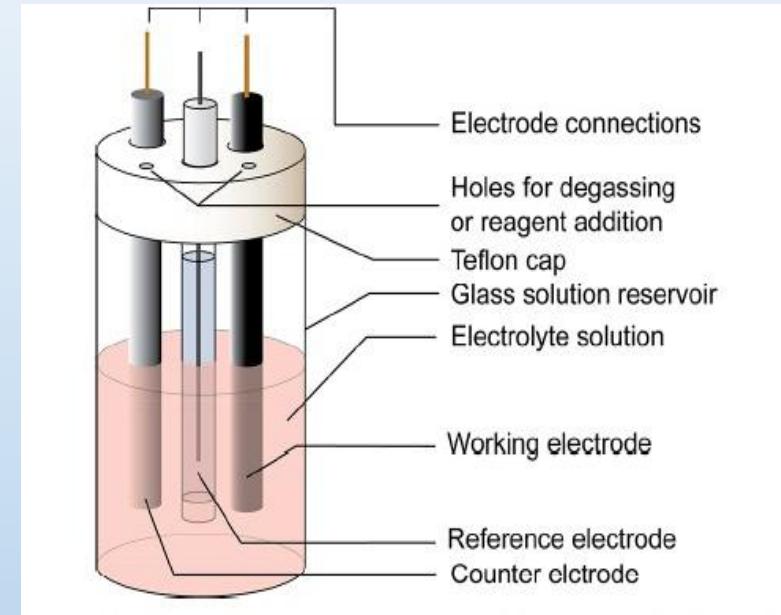
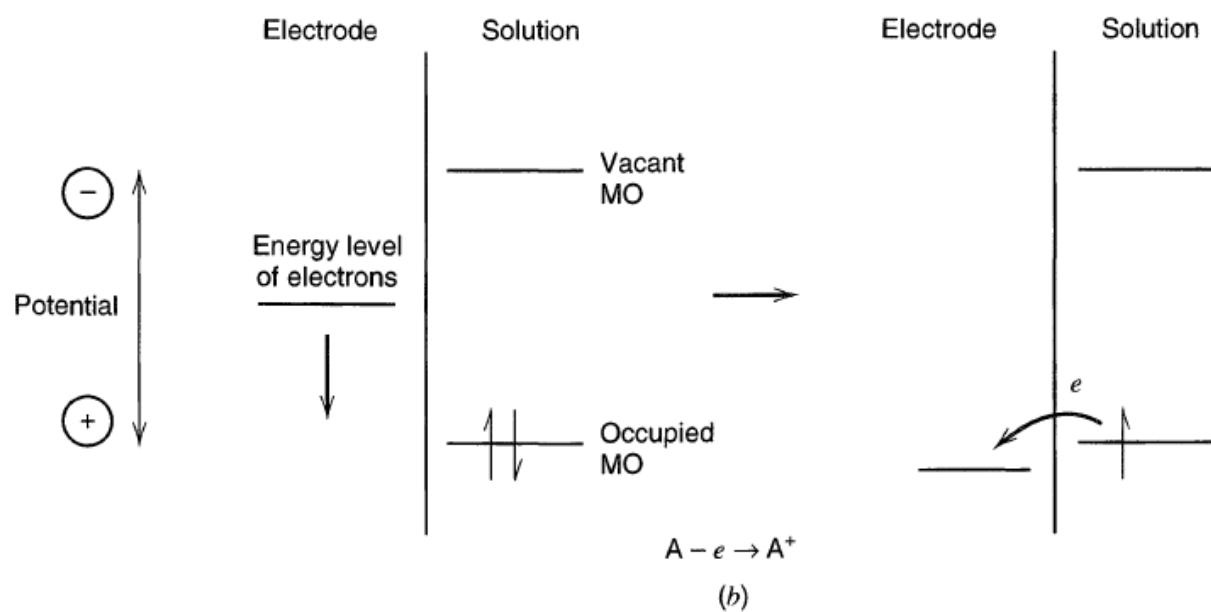
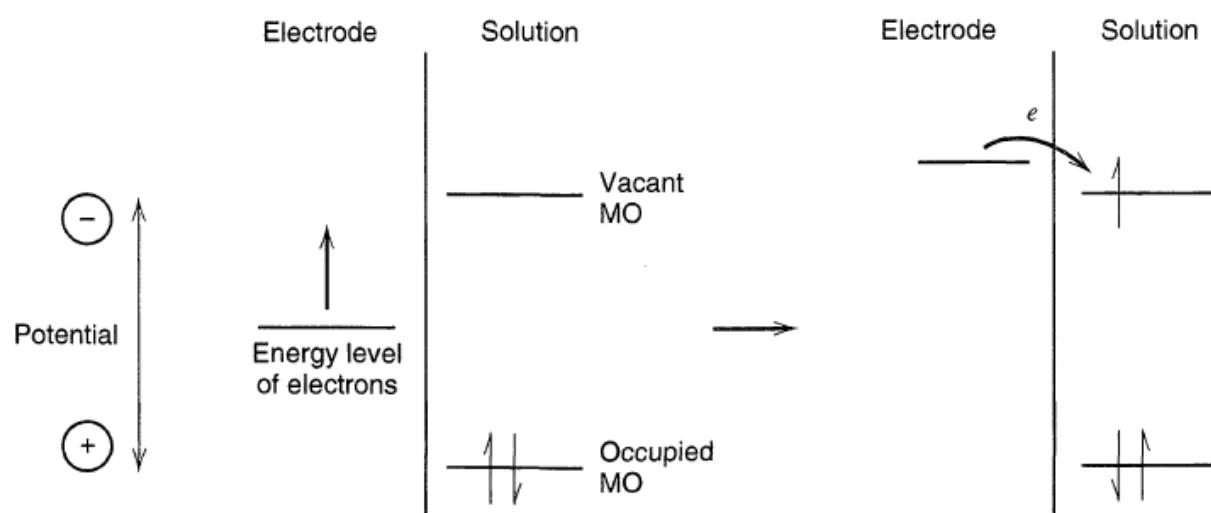
A common reference is the *saturated calomel electrode* (SCE), which is Hg/Hg₂Cl₂/KCl (saturated KCl in water)

Its potential is +0.242 V vs. NHE.

Another is the *silver-silver chloride electrode*, Ag/AgCl/KCl (saturated KCl in water) having a potential of +0.197 V vs. NHE.

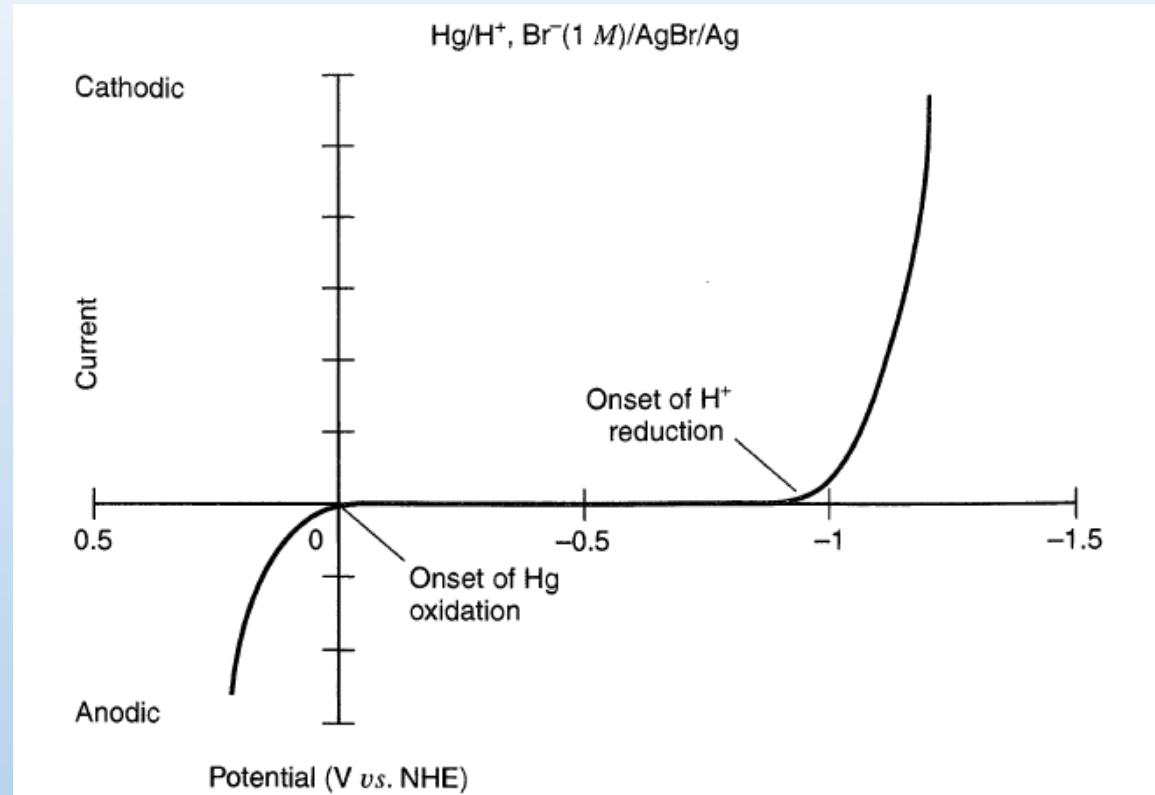
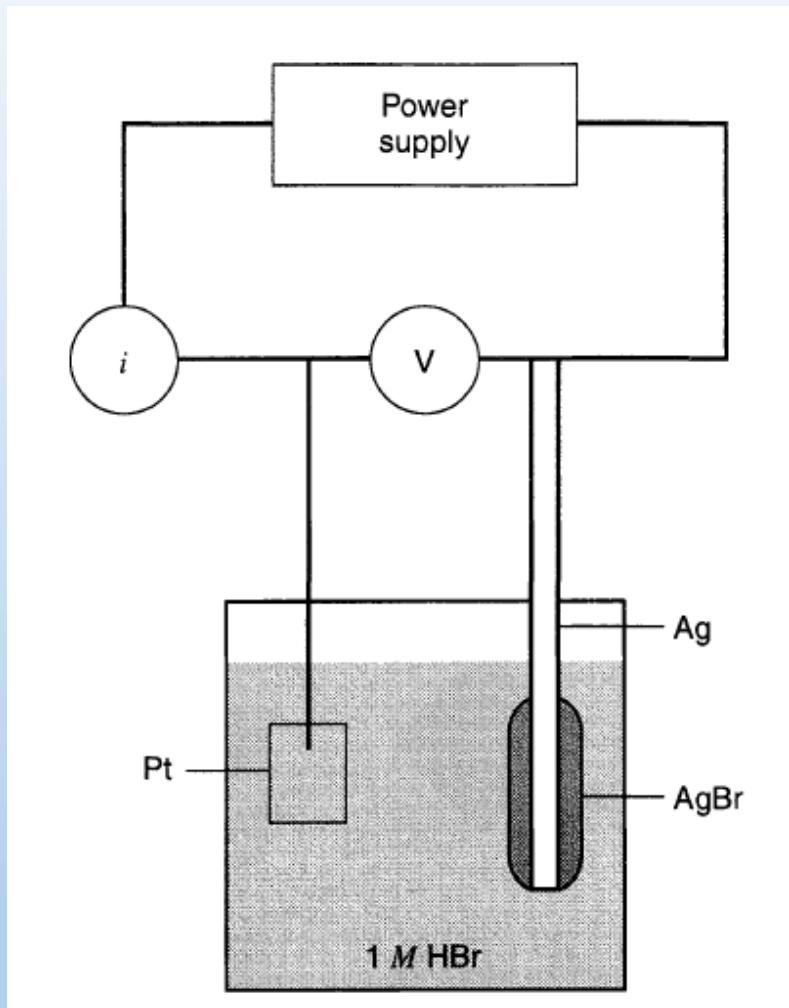
Since the **reference electrode** has a constant makeup, its potential is fixed. So, any changes in the cell happened, ascribable to the working electrode. If we want to control the potential of the working electrode with respect to the reference, and that potential must be experienced by the **working electrode**

Mechanism of reduction and oxidation at Working electrode



**Reduction and oxidation (redox) process happens at the Working electrode interfaces.
The WE is called bipolar electrode.**

Instrumentation (potentiostat) and Current-Potential Curves



Concept of the Electrical Double Layer

Brief Description of Electrochemical Double layer

Electrified interface

Theories of double layer formation

Contribution of E_{dl} to electrochemical charge transfer process

PIONEERS OF ELECTROCHEMISTRY

- Humphry Davy: British Chemist (1778-1829)



Worked on production of electricity in an electrolytic cell resulted from chemical reactions between electrolyte and metal

- Michael Faraday: British Chemist (1791-1867)



Electrical force exerted on molecules to cause them dissociate.
Amount of materials decomposition related directly to the amount of electricity passing through the solution

- Hermann Von Helmholtz: German Physicist (1821-1894)



Made significant contribution in fluid dynamics, including Helmholtz's theorems

Formation of Electrical Double Layer

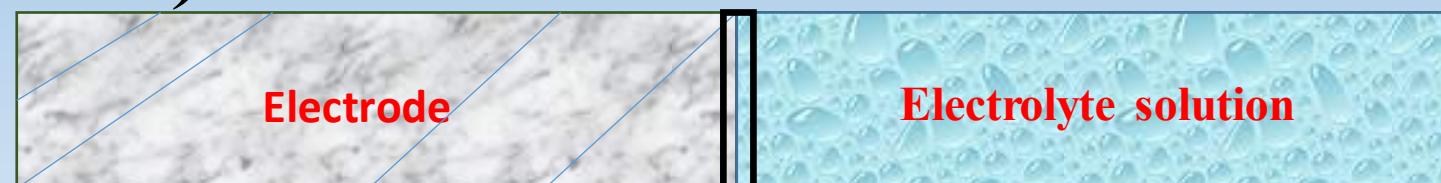
When an electrode (macroscopic object) is brought in contact with liquid ionic conductor (electrolyte), interactions of ions assist to develop interfacial region at the electrode surface, which is termed as electrical double layer

The first layer, the surface charge (either positive or negative). The second layer is composed of ions attracted to the surface charge via the Coulomb force, electrically screening the first layer.

Closely contact of two phases. Two layers of opposite polarity formed at the interface between electrode and electrolyte.

Difference of electric potential accompanied by charge separation.

Interface region has different scenario (electronic property, structure, electric field compared to the bulk)



Important aspects of electrical double layer

Generation of induced charge depending on direction of electric field

Separation of charge across the electrode–electrolyte interface

Interface region as a whole electrically neutral

Arrangement of charges and oriented dipoles constitute the interface architecture

