



# **EMA4303/5305**

# **Electrochemical Engineering**

# **Lecture 01 Basic Concepts**

**Prof. Zhe Cheng**  
**Mechanical & Materials Engineering**  
**Florida International University**



# Electrochemistry (1)

## □ Definition

“Electrochemistry is the branch of physical chemistry that studies the relationship between **electricity**, as a measurable and quantitative phenomenon, and identifiable **chemical change**, with either electricity considered an outcome of a particular chemical change or vice versa. These reactions involve electric charges moving between **electrodes** and an **electrolyte** (or ionic species in a solution). Thus electrochemistry deals with the interaction between electrical energy and chemical change.” <https://en.wikipedia.org/wiki/Electrochemistry>

“Electrochemistry is the branch of chemistry concerned with the **interrelation of electrical and chemical effects**. A large part of this field deals with the study of chemical changes caused by the passage of an electric current and the production of electrical energy by chemical reaction” Bard & Faulkner (2001).



# Electrochemistry (2)

## History aspect

- Early Cu-Zn battery, by Alessandro Volta in late 1790s

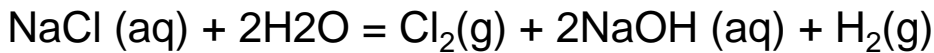
## Major applications

- Energy storage/conversion, e.g., via batteries

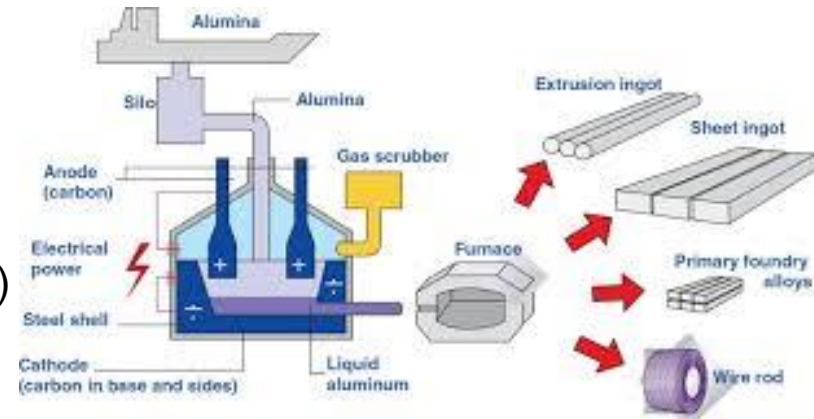


- Electrolysis for production of chemicals/materials

- Chlorine & sodium hydroxide



- Aluminum



[https://www.researchgate.net/figure/262148554\\_fig3\\_Flow-sheet-of-the-aluminum-production-process](https://www.researchgate.net/figure/262148554_fig3_Flow-sheet-of-the-aluminum-production-process)

- Electro-deposition

- Sensors

- Glucose sensor for blood sugar monitoring

- Obtaining basic thermodynamic properties

**Benefits from accurate measurement of electrical signal (current)**





# Electrode

❑ A substance that primarily conducts electrons  $e^-$  (can also be electron holes  $h^+$ ) in an electrochemical system.

- It serves the purpose as the electronic conductor

## ❑ Categories

- Metallic electrode
  - Ni
  - Au
  - Pt
  - Cu
  - ...etc.
- Non-metallic electrode
  - Ceramics:
    - Carbon (as graphite or carbon black)
    - Conducting oxides:  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , etc.
  - Conducting polymers



# Electrolyte

❑ A substance that primarily conducts electrically charged ions (not so much electrons or holes) either by itself or after dissolution in a solvent (e.g., water) and forming charged ions.

- It serves the purpose as the ionic conductor

## ❑ Categories

- Liquid electrolyte solution in a solvent/solvents
  - NaCl in water
- Molten/Liquid electrolyte
  - NaCl
- Solid electrolyte



# Solution

## □ Solution

A uniform, homogeneous mixture of two or more substances (or components)

- Example: HCl solution

## □ Solvent

The continuous (often majority) substance (or component) that forms the medium in a solution

- Example:
  - $H_2O$  in the HCl aqueous solution

## □ Solute

The dissolved substance (or component) in a solution

- Example:
  - HCl in the HCl aqueous solution

<https://en.wikipedia.org/wiki/Solution>

HCl aqueous solution  
2 substances  
Homogeneous



Water-Oil mixture  
2 substances  
NOT homogenous



<http://www.carolina.com/specialty-chemicals-d-1/hydrochloric-acid-in-plastic-coated-safety-bottle-12-1-m-reagent-ac-grade-25-l/867793.pr>

<http://carpinteriavalleyassociation.org/2013/07/oil-and-water-do-not-mix/>

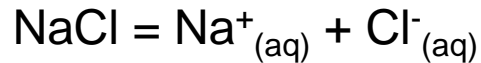


# Liquid Electrolyte Solution

□ **Electrolyte Solution** - the solute, which is polar or ionic, upon dissolution in the liquid solvent (or solvents), dissociate (completely or partially) into positively and negatively **charged ions**

Example:

- NaCl in water:



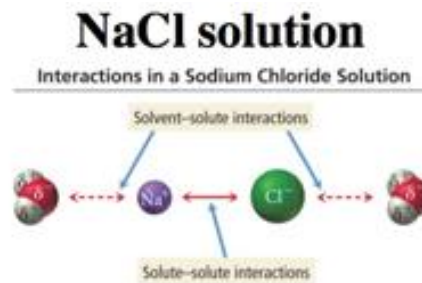
Notes:

- Both + and - ions surrounded by (polar) solvent molecules

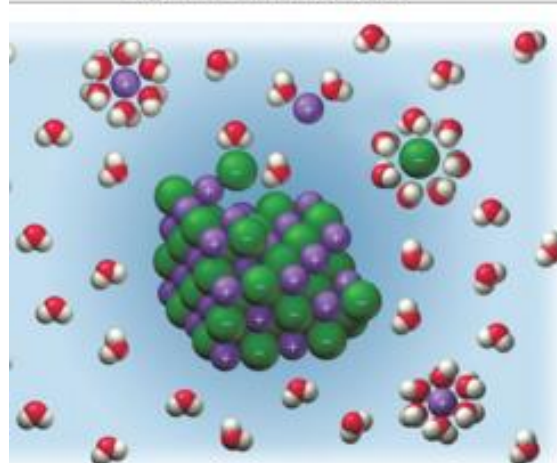
□ **Nonelectrolyte solution** - the solute remains as molecules in solvent

Example:

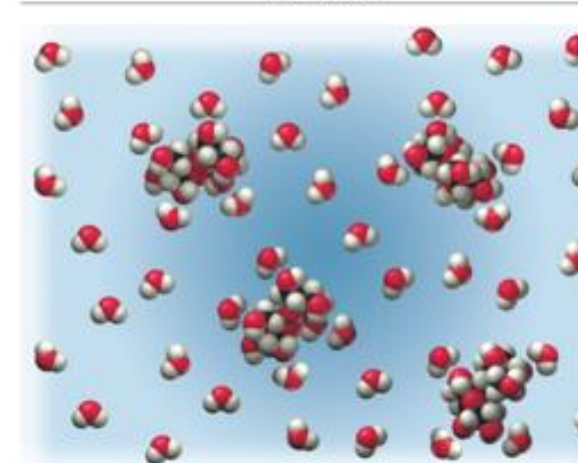
- Sugar in water



Dissolution of an Ionic Compound



Sugar Solution





# Molten Electrolyte (Salt)

❑ The electrolyte, upon heating to above the melting point, dissociates (completely or partially) into positively and negatively **charged ions** without the need for a liquid solvent.

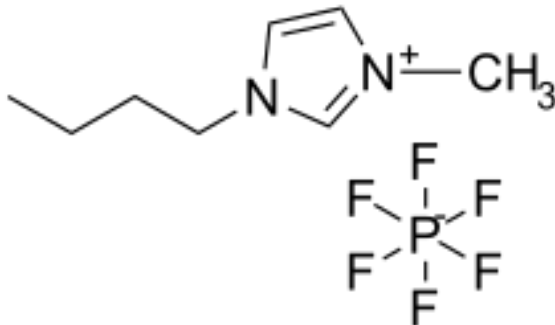
## ❑ Examples:

- Many salts in the molten state



- Ionic liquid (electrolyte with melting point below  $\sim 100^\circ\text{C}$ )

1-butyl-3-methylimidazolium  
hexafluorophosphate ([BMIM]PF<sub>6</sub>)



[https://en.wikipedia.org/wiki/Ionic\\_liquid](https://en.wikipedia.org/wiki/Ionic_liquid)





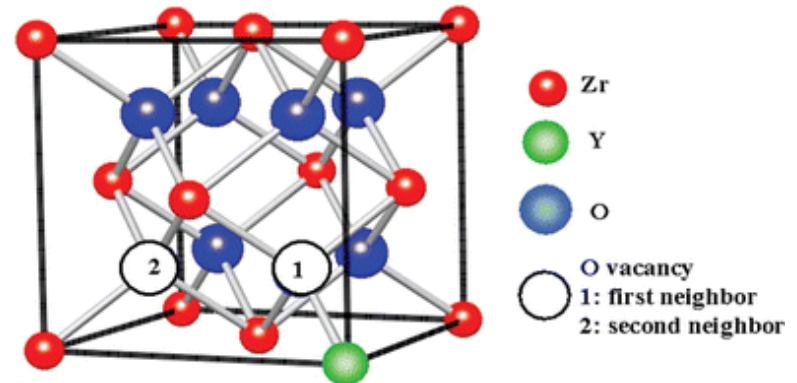
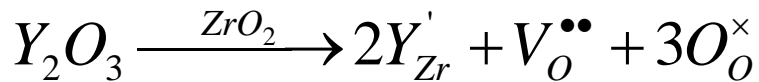
# Solid Electrolyte

❑ A solid phase containing **charged ions** and/or **vacancies**.

❑ **Examples:**

**Yttria-stabilized zirconia (YSZ or  $Y_2O_3$  doped in  $ZrO_2$ )**

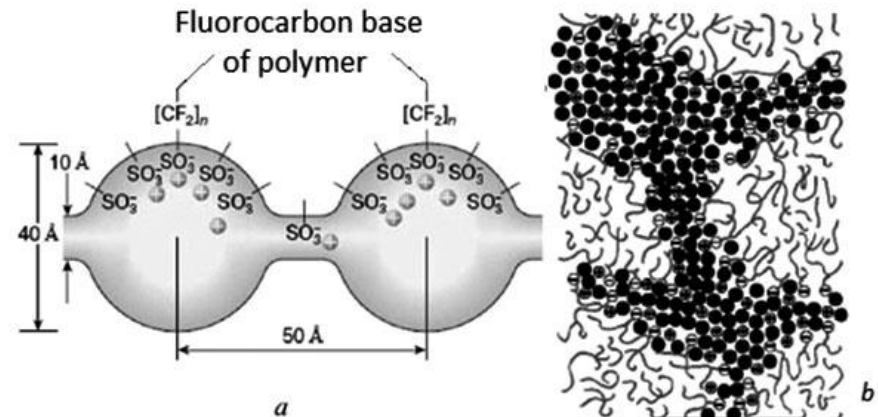
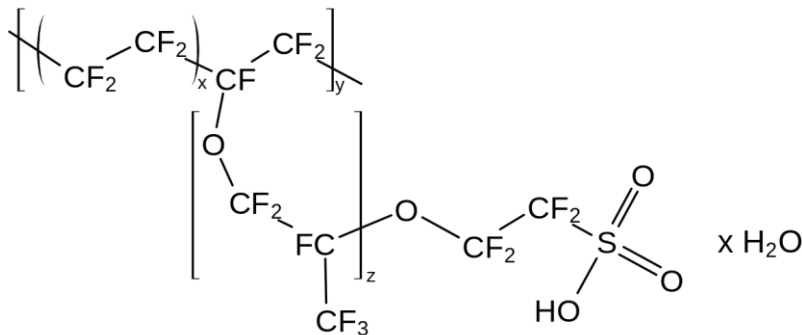
- $Y_2O_3$  uniformly & randomly “dissolved” in  $ZrO_2$
- Charged species (ions) of  $V_O^{\bullet\bullet}$  and  $Y_{Zr}'$



**Nafion®**

- Charged species of  $H^+$  and  $-SO_3^-$  (on backbone)

<http://pubs.rsc.org/en/content/articlelanding/2005/im/b417143h/unauth#!divAbstract>



<https://en.wikipedia.org/wiki/Nafion>

<http://www.orientjchem.org/vol32no5/proton-exchange-membranes-based-on-sulfonated-polymers/>

# Electrochemical Cell/System

□ A basic electrochemical cell or system consists of “**two electrodes** separated by at least **one electrolyte**”

- Example 1

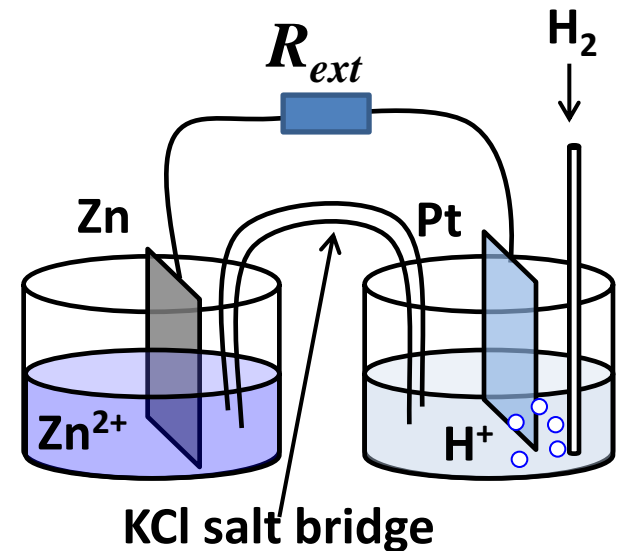
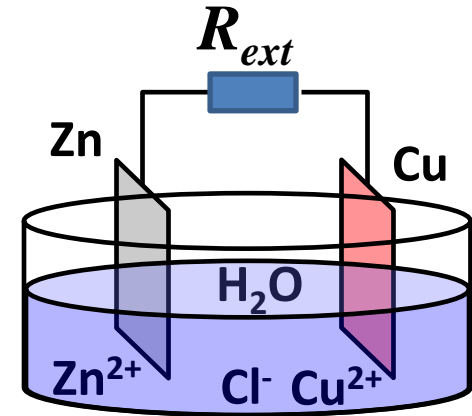
Zn & Cu immersed in a  $ZnCl_2 + CuCl_2$  mixed solution and also connected through an external circuit (can be open)

- Example 2

Zn immersed into  $ZnCl_2$  solution, while Pt immersed into dilute HCl solution with bubbling  $H_2$ , with the two metal connected through an external circuit and the two solutions are connected by a KCl salt bridge.

□ Electrochemical cell potential

Generally, a potential difference could be measured between the two electrodes, which depends on the external circuit resistance.



Bard & Faulkner (2001)



# Half Cell & Overall (Full Cell) Reactions

## ❑ Electrochemical reaction

Once such an electrochemical cell is built (either intentionally or occurs naturally), the (electro-) chemical reaction(s) could happen, in certain way:

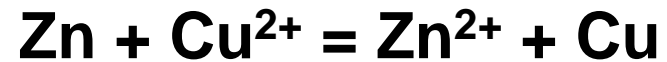
## ❑ Two half (cell) reactions

The overall electrochemical reaction always involve/is made of two half (cell) reactions with each half (cell) reaction at one of the electrode/electrolyte interfaces

### Reduction/cathodic half (cell) reaction:



### Oxidation/anodic half (cell) reaction:



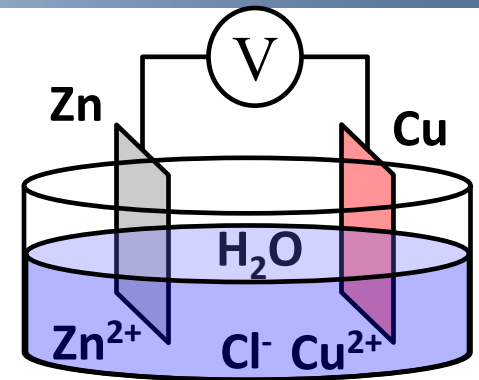
Note: Each reaction (whether full cell or half cell) must satisfy BOTH mass balance & charge balance

## ❑ Overall/full cell reaction

Combination of the reduction (cathodic) and oxidation (anodic) half (cell) reactions  
For the Zn(s)/Zn<sup>2+</sup>, Cu<sup>2+</sup>, Cl<sup>-</sup>/Cu(s) cell, the overall reaction is obtained by addition

## ❑ Difference from general chemical reactions

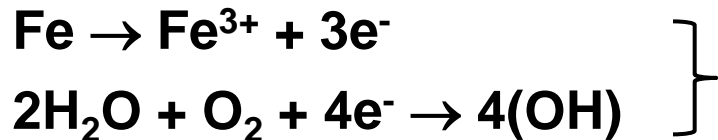
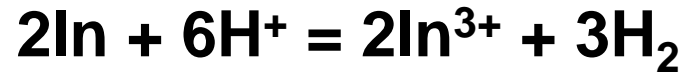
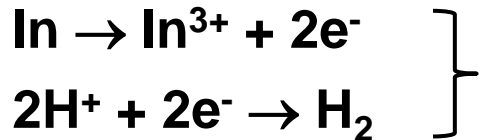
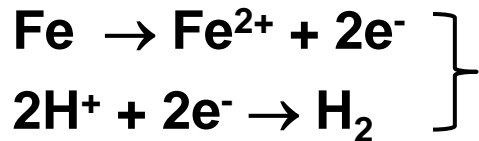
Electrons must go through (at least for a short distance) the external circuit from the species experiencing oxidation to the species experiencing reduction





# Class Exercises

For the given pair of reduction (cathodic) and oxidation (anodic) half (cell) reactions, please write the full (cell) reactions





# Anode & Cathode in an Electrochemical Cell (1)

## □ Cathode

The electrode (electronic conductor) where the reduction or cathodic half (cell) reaction occurs:

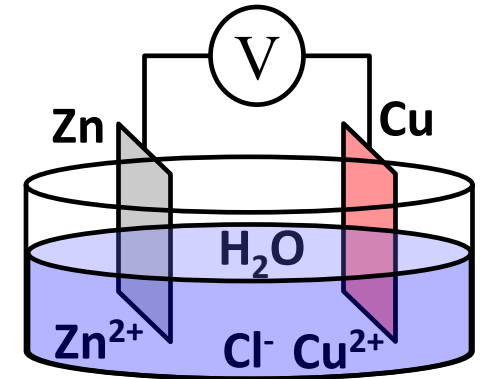
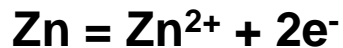
e.g., Cu electrode in this Zn(s)/Zn<sup>2+</sup>, Cu<sup>2+</sup>, Cl<sup>-</sup>/Cu(s) cell



## □ Anode

The electrode (electronic conductor) where the oxidation or anodic half (cell) reaction occurs:

e.g., Zn electrode in this Zn(s)/Zn<sup>2+</sup>, Cu<sup>2+</sup>, Cl<sup>-</sup>/Cu(s) cell

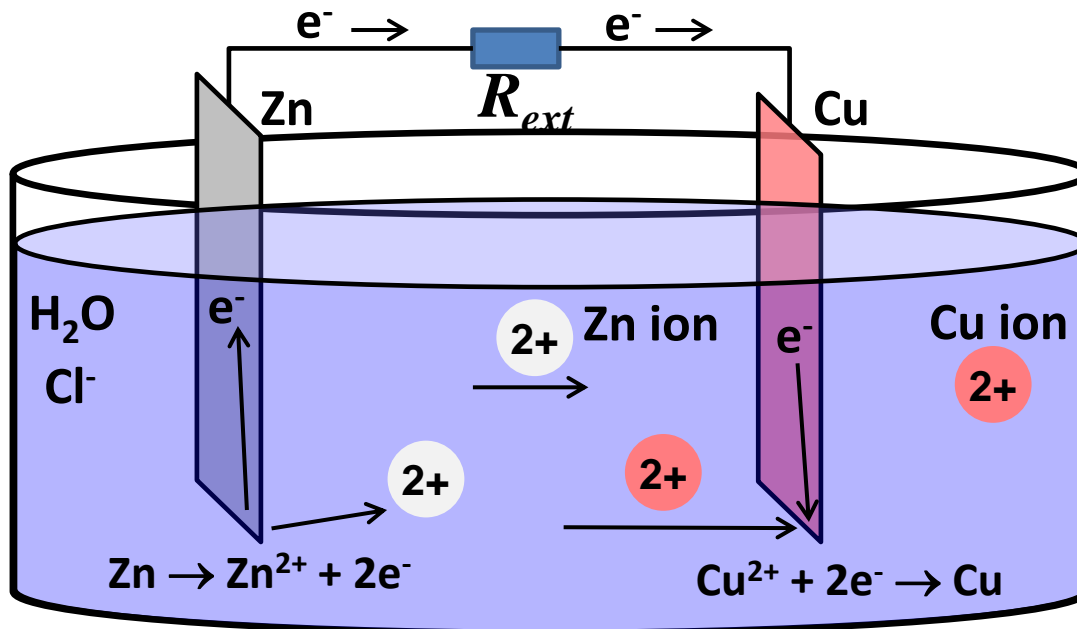




# Reactions at Electrode/Electrolyte Interfaces

## □ Interface & transition from electronic conduction to ionic conduction

- In an electrochemical cell, both the cathode (e.g., Cu) and the anode (e.g., Zn), conduct primarily electrons, while, in between the two electrodes, the electrolyte (e.g.,  $\text{ZnCl}_2\text{-CuCl}_2$  water solution here) primarily conducts charged ions
- For the electrochemical reaction to occur, there must be transitions from electronic conduction to ionic conduction, which occur through the half (cell) reaction(s) across the **electrode (cathode or anode)/electrolyte interface(s)**



Alan C West (2012)

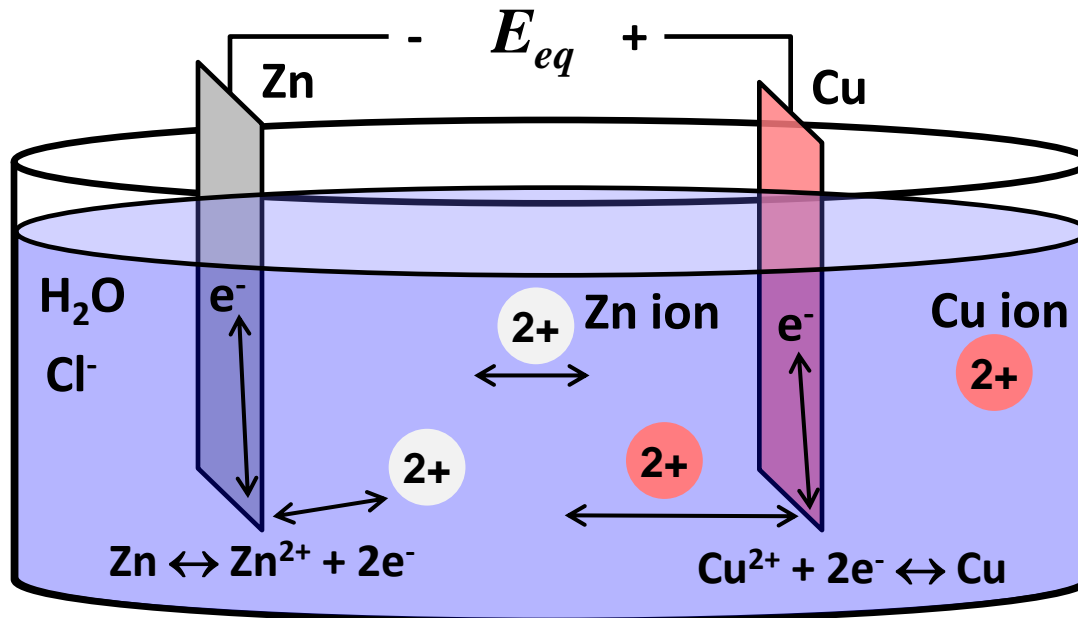


# Equilibrium & Equilibrium Cell Potential

When the external circuit connecting the two electrodes is open (open circuit or when external resistance  $R$  goes to infinity), the resulting external current is zero, assuming

- Reversible reactions at both electrodes
- No internal electronic leakage through the electrolyte,
- Single electrochemical reaction at each electrode

The electrochemical cell/system will reach equilibrium, and a reversible & stable potential between the two electrodes is obtained, called equilibrium potential  $E_{eq}$





# Galvanic Cell

Without applying any external power source, while controlling the external resistance to be finite, the overall electrochemical reaction would proceed in a spontaneous way, with electron flowing out from the anode where oxidation half (cell) reaction occurs through the external circuit to the cathode where the reduction half (cell) reaction occurs. Such a cell is called a **galvanic cell**. In a galvanic cell, the conversion from (stored) chemical energy to electrical work is realized, as encountered in battery or fuel cell discharge.

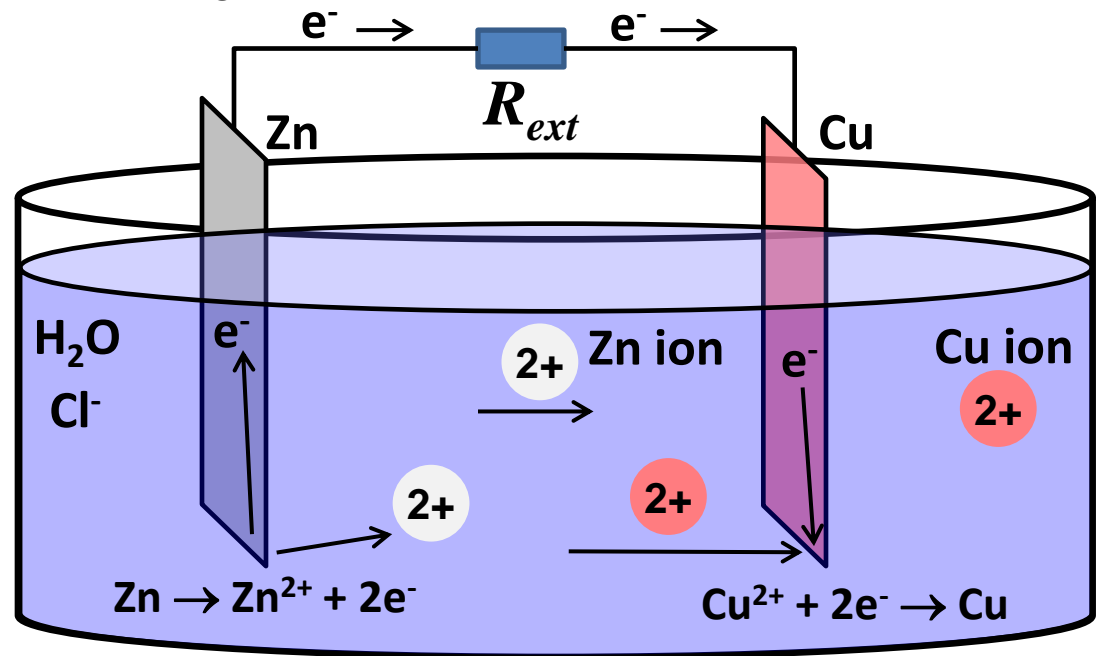
If  $I$  is the net current through the cell, based on Ohm's Law and addition of potential, we have:

$$E_{eq} = I (R_{int} + R_{ext})$$

$R_{int}$  and  $R_{ext}$  are cell internal resistance and external circuit resistance

Cell (external circuit) potential

$$E_{ext} = IR_{ext} = E_{eq} - IR_{int}$$





# Electrolytic Cell

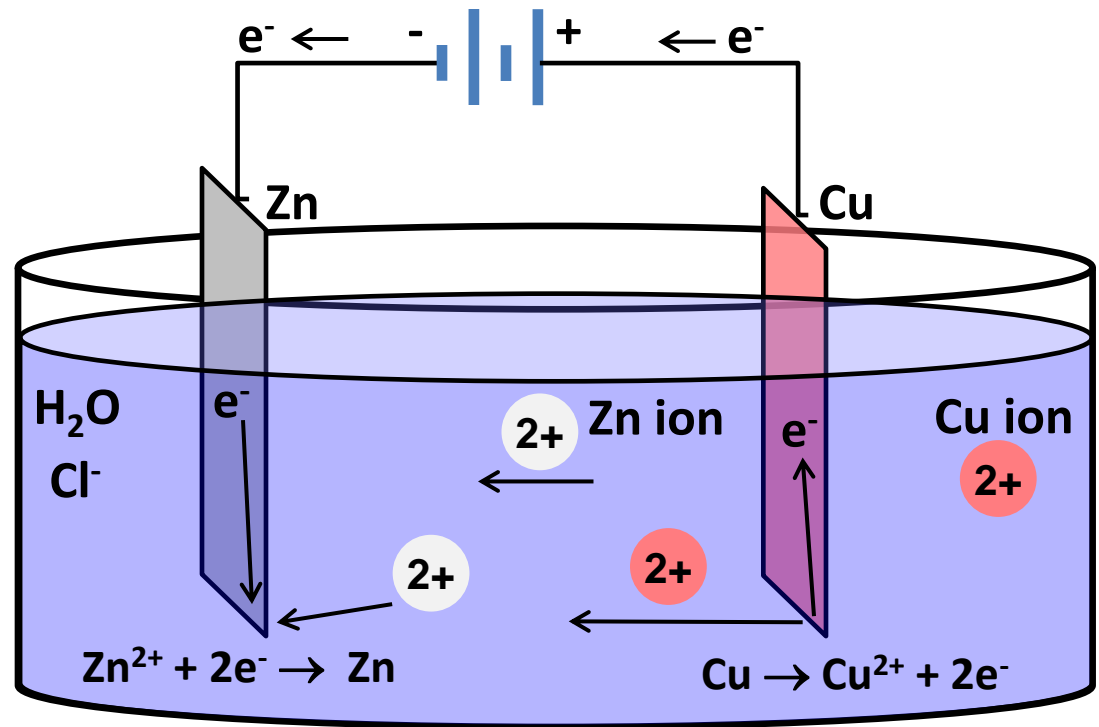
By applying a counter potential larger than  $E_{eq}$ , the cell current will be reversed, and the overall electrochemical reaction would proceed in the reverse direction. Such a cell is called a **electrolytic cell**. The conversion from electrical energy (provided) to chemical energy (stored) is realized, as encountered in rechargeable batteries charging or electrolytic cell chemical production processes.

If  $I$  is the net current through the cell, based on Ohm's Law and assuming zero additional external resistance,

the applied potential  $E_{app}$

$$E_{app} = E_{eq} + IR_{int}$$

$R_{int}$  is cell internal resistance





# Faraday's Law

□ For simple electrochemical cell/system, the amount of charge transferred in the reaction is related to the amount of product generated/reactant consumed:

1 mole of  $e^-$  =  $6.02 \times 10^{23}$  of  $e^-$

1 coulomb of  $e^-$  =  $6.24 \times 10^{18}$  of  $e^-$

Therefore, the conversion factor

Faraday constant  $F = (6.02 \times 10^{23} \text{ mol}^{-1}) / (6.24 \times 10^{18} \text{ C}^{-1}) = \mathbf{96485 \text{ C/mol}}$