

# Batteries

## Renewable Energy Conversion Systems Course

Lecture 2

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# Electrical Energy Storage – Lecture II

## Outline

- Introduction to electrochemistry
- Working scheme of a battery
- Elements of battery theory
  - Equilibrium
  - Non-equilibrium

# Introduction to Electrochemistry

## Battery

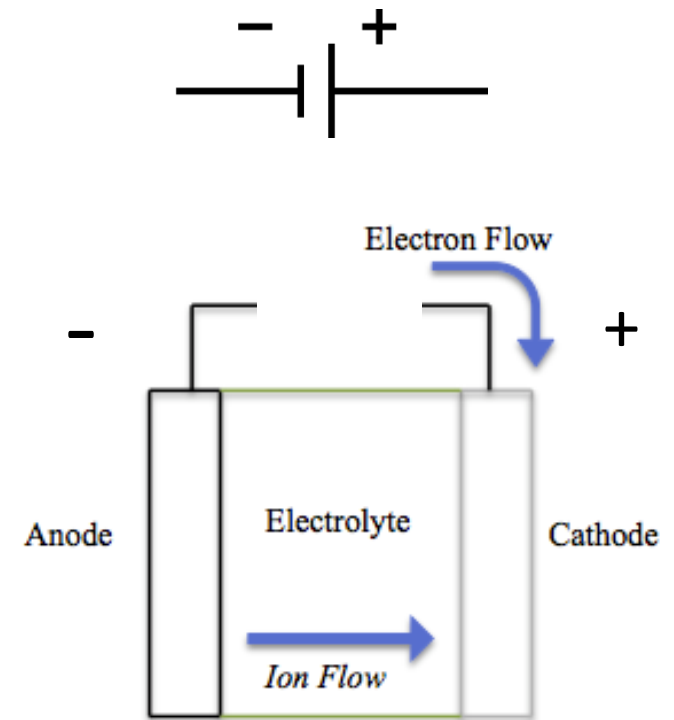
*Ideally → Circuit element*

Device able to absorb and emit current holding a constant voltage

*Realistically → Electrochemical Cell*

Device connecting two electrodes with different equilibrium potentials through one or more electrolyte paths

With the result of electronic current flowing in an external circuit and ionic current flowing through the electrolyte(s).





# Introduction to Electrochemistry

## Electrochemistry

This subject deals with the molecular bonds deep into materials. Exhaustive treatment would require strong physics and chemistry background, so we just give here what is needed to understand the working principle and some elements of the operating behavior of batteries.

### **Definitions**

- *Electrolyte* → Ionic solution (Aqueous, Organic, molten salt, ceramic)
- *Electrode* → Metallic or conductive material in contact with an electrolyte
- *Redox Reaction* → Chemical Reaction Involving exchange of electrons between species
- *Electrochemical reaction* → Chemical reaction involving the exchange of electrodes with an electrode surface. **All electrochemical reactions are redox reactions.**
- *Equilibrium potential* → Voltage level at which an electrode naturally sets by interacting with an electrolyte. It is linearly correlated with the level of chemical energy of the ions present in the electrolyte (Gibbs free energy → electrochemical potential)



# Introduction to Electrochemistry

## Chemical Reactions

- *Homogeneous Reaction* → Chemical reaction occurring in a single phase, e.g. gaseous, liquid, or solid (gas combustion, acid-base reactions). These reactions take place in the bulk of a substance (3D).
- *Heterogeneous Reaction* → Chemical reaction in which the reactants are components of two or more phases, e.g. solid and gas, solid and liquid, two immiscible liquids, or in which one or more reactants undergo chemical change at an interface, e.g., on the surface of a solid electrode. These reactions take place at the interface between two substances (2D).

**Electrochemical reactions are heterogeneous redox reactions.**

They can be of two types: *reduction reactions* or *oxidation reactions*

Reduction reactions always involve an *oxidated* chemical specie that reacting with one or more electrons produce a *reduced* chemical specie:  $Ox + n e^- \rightarrow Red$

Oxidation reactions are the inverse of reduction ones, i.e. reacting in the opposite direction (toward oxidated species)



# Introduction to Electrochemistry

## Types of Electrochemical Reactions

### *...of our interest*

- Liquid - Liquid → All reactants are miscible in a liquid solvent



- Liquid - Gas → Some reactants are miscible in a liquid solvent, while others are gases



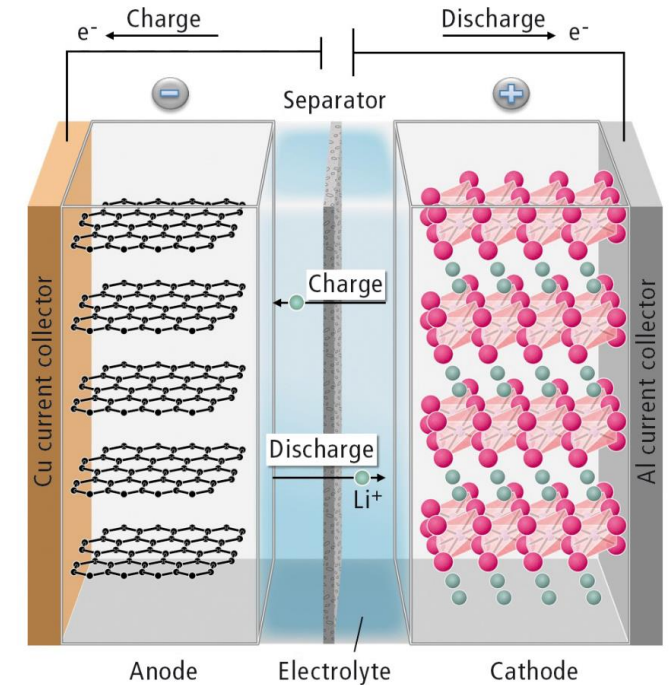
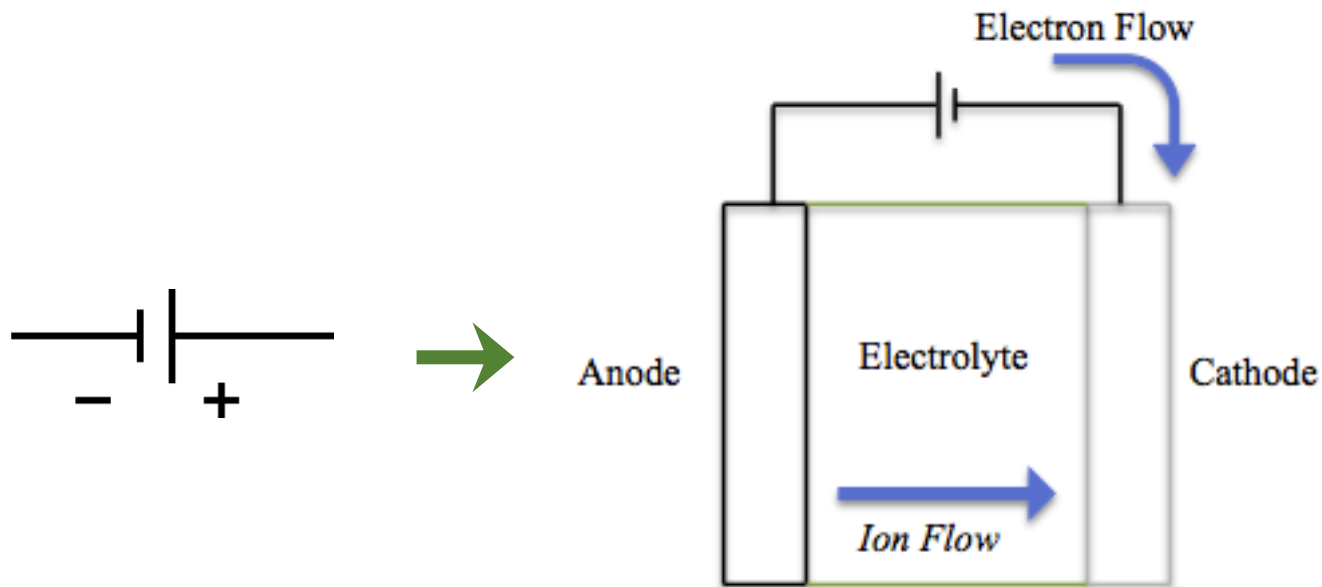
- Liquid - Solid → Some reactants are miscible in a liquid solvent, while others are solid or “intercalated” in a solid



Here liquid generally refers to the electrolyte, which can be water based, but also organic solvents, molten salts, viscous polymeric media, etc.

# Working Scheme of a Battery

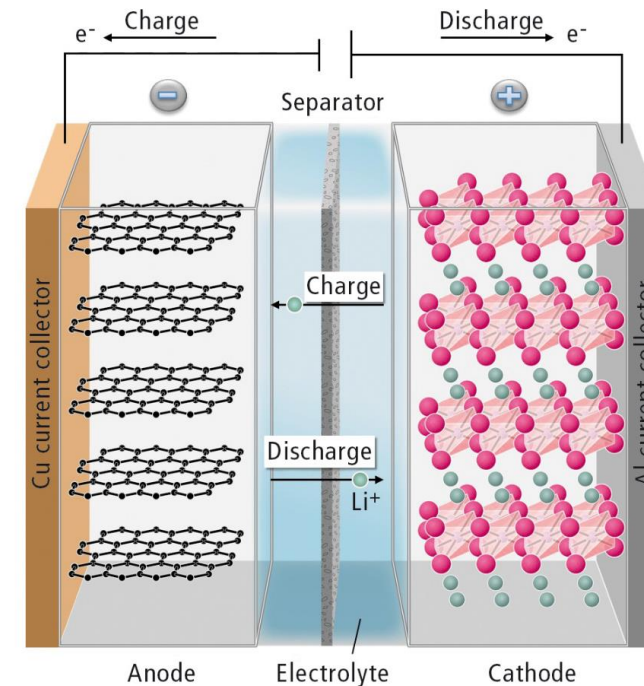
## Working Scheme of a Battery



# Working Scheme of a Battery

## Li-ion battery

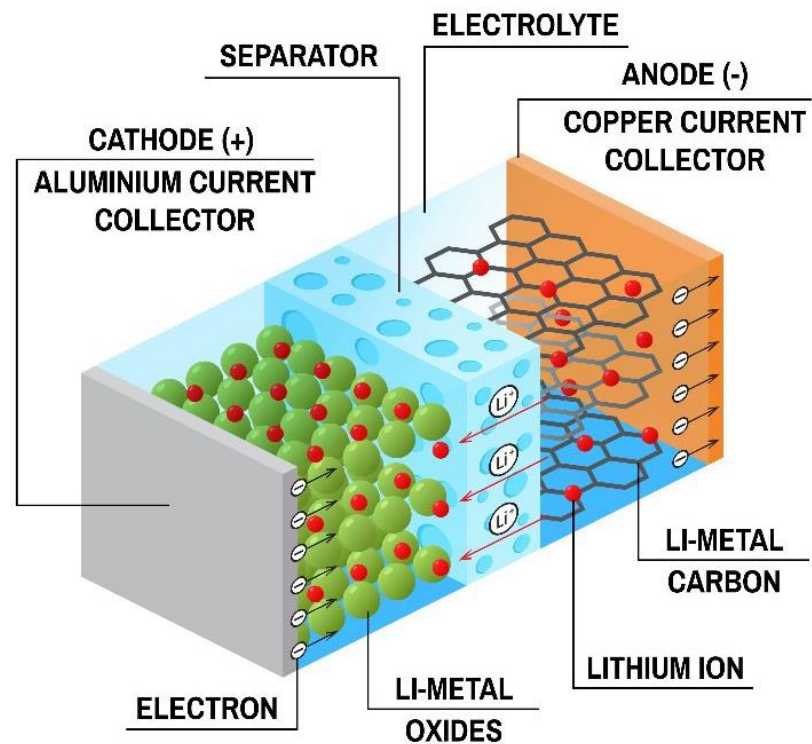
- **Electrodes:** The positively and negatively charged ends of a cell. Attached to the current collectors
- **Anode:** The negative electrode
- **Cathode:** The positive electrode
- **Electrolyte:** A liquid or gel that conducts ionic current
- **Current collectors:** Conductive foils at each electrode of the battery that are connected to the terminals of the cell. The cell terminals transmit the electric current from the battery to the external circuit
- **Separator:** A porous polymeric film that separates the electrodes while enabling the exchange of lithium ions from one side to the other



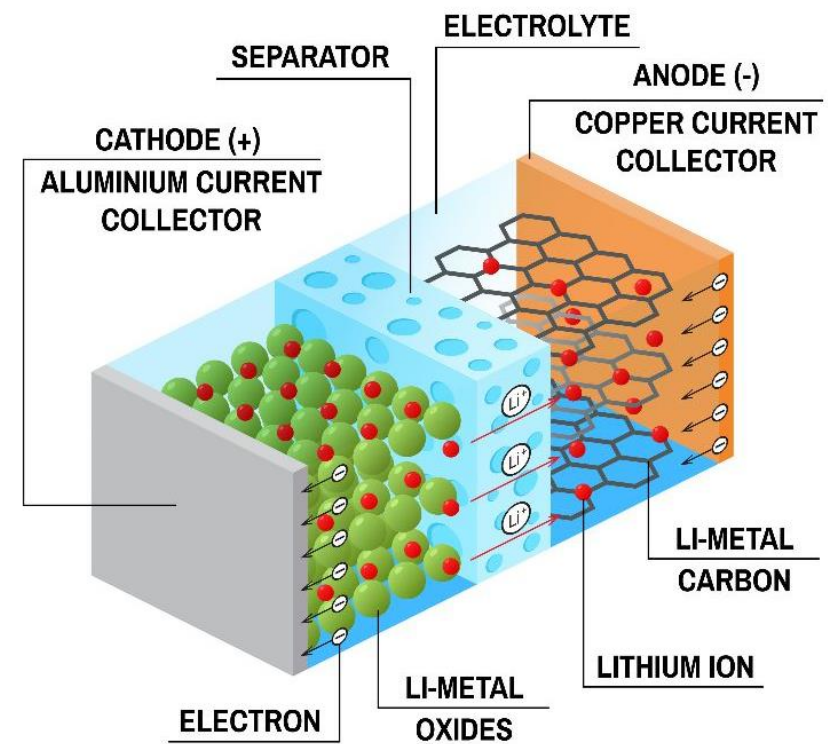


# Working Scheme of a Battery

## DISCHARGE



## CHARGE



# Elements of Battery Theory

## Theory - Equilibrium

- Cathodic and Anodic Potential and Cell potential*

$$E_c = - \frac{\Delta G_{\text{cat.reac.}}}{n F}, \quad E_a = - \frac{\Delta G_{\text{ano.reac.}}}{n F}, \quad E_{\text{cell}} = E_c - E_a$$

Where  $\Delta G$  is the Gibbs free energy associated to the reaction with respect to a reference reaction (Hydrogen reduction reaction),  $n$  is the number of exchanged electrons and  $F$  is the Faraday constant.

$$F = N_A e = 96485 \text{ C/mol}$$

- Standard Reduction Potentials*

Standard reduction potentials are defined as the potential of a reaction where the availability to reaction of all active species are equal to 1, with respect to the hydrogen electrode. They are used as a reference to calculate cell potentials

$$E_c^0 = - \frac{\Delta G_{\text{cat.reac.}}^0}{n F}, \quad E_a^0 = - \frac{\Delta G_{\text{ano.reac.}}^0}{n F}, \quad E_{\text{cell}}^0 = E_c^0 - E_a^0$$

# Elements of Battery Theory

## Theory - Equilibrium

- *Nernst Equation*

Correlates the concentrations of active species to the electrode equilibrium potential, using the reference potential.

Given a reduction reaction in the form  $Ox + n e^- \leftrightarrow Red$ , the electrode equilibrium potential is

$$E_i^{eq} = E_i^0 - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox}}$$

where  $a_{Red}$  and  $a_{Ox}$  are the activities of the active species (the ones contributing to the reaction), i.e. the availability of the specific molecule to be involved in the electrochemical reaction.

Activities are functions of the concentrations of active species and can be approximated with them at very low concentrations.

$$a_{Red} = \gamma_{Red} c_{Red}$$

$$a_{Ox} = \gamma_{Ox} c_{Ox}$$

$$\text{when } c \rightarrow 0, \gamma \rightarrow 1$$

# Elements of Battery Theory

## Theory - Equilibrium

- The Cell Equilibrium Potential is the difference between the equilibrium potential of the cathodic reaction and of the anodic reaction

$$E_{cell}^{eq} = E_c^{eq} - E_a^{eq}$$

- The potentials  $E_c^e$  and  $E_a^e$  can be determined, assuming a reversible ideal (diluted) system from the Nernst equation using species concentrations

$$E_i^e = E_i^0 + \frac{RT}{nF} \ln \left( \frac{c_{ox}}{c_{red}} \right)$$

- Using concentrations in the Nernst equation is an approximation, strictly valid at low concentrations only, since activities would be required. Batteries typically use high concentrations of active species to increase the energy and power density. This approximation is anyway good to understand the general behavior of a battery

# Elements of Battery Theory

## Theory – Equilibrium

- *Faraday's Law* → The number of molecules produced or consumed in an electrochemical process is proportional to the amount of electricity (charge,  $Q$ ) that passes through the electrochemical system

$$N = \frac{Q}{zF}$$

where  $N$  is the number of moles,  $z$  is the number of charges, and  $F$  is Faraday's constant.

$$F = N_A e = 96485 \text{ C/mol}$$

- The *State of Charge*  $SoC = \frac{Q_{charged}}{Q_{total}}$  is therefore a measurement of the “accumulation” of active species, i.e., of their concentrations.
- Deriving Faraday's law over time, the current  $I = dQ/dt$  is a direct measure of the reaction rate

$$\frac{dN}{dt} = \frac{I}{zF}$$



# Elements of Battery Theory

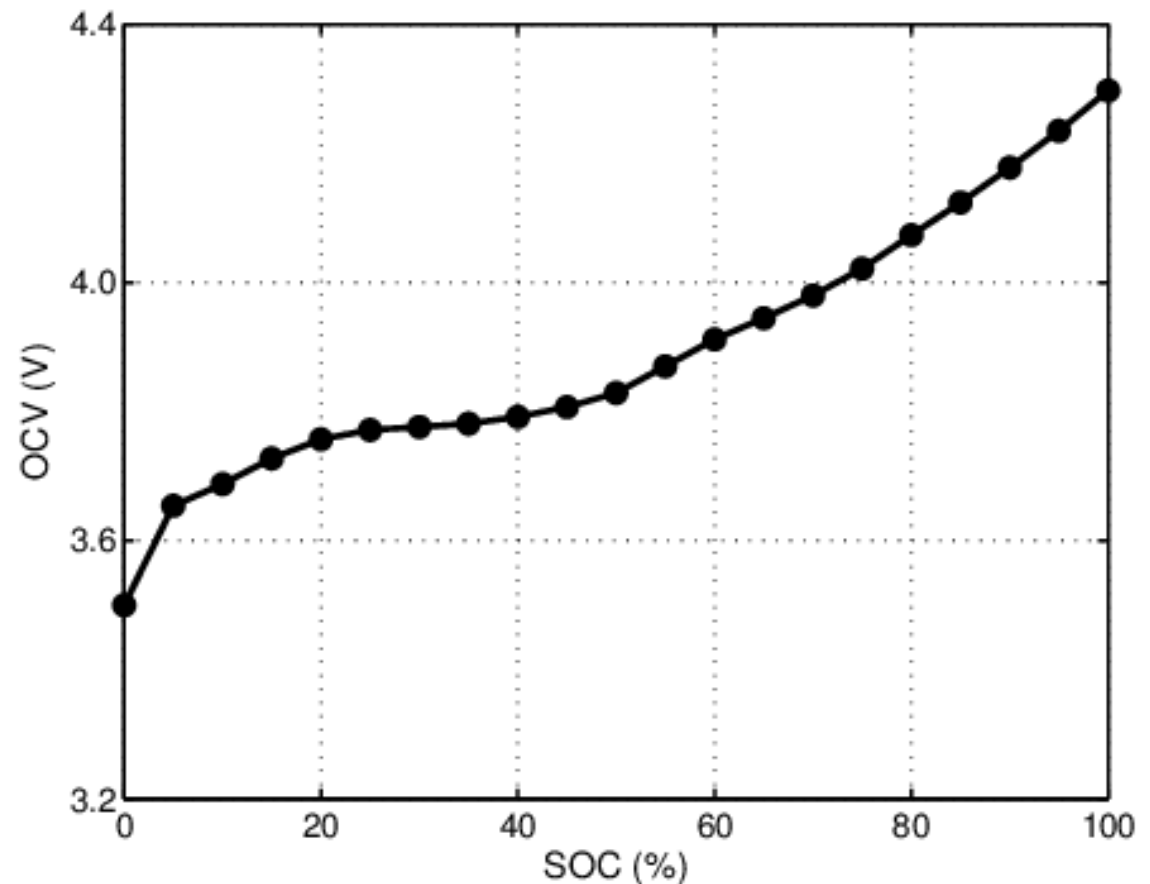
- *Open Circuit Voltage (OCV)*

OCV is the voltage that is naturally set in a battery when the external circuit is open.

It equals the equilibrium voltage of the cell

$$E_{cell}^{eq} = E_c^{eq} - E_a^{eq}$$

Following from Nernst equation, OCV is a function of the concentrations of the active species, therefore a function of the State of Charge SoC



# Elements of Battery Theory

## Theory - Dynamics

- In dynamic conditions, the cell voltage  $E_{cell}$  deviates from the equilibrium potential due to the presence of losses such as overvoltage at each electrode and ohmic losses in the various components of the cell. Cell potential can be then calculated as

$$E_{cell} = E_{cell}^e - \sum |\eta| - \sum |I|R$$

- $\sum |I|R$  takes into account the electron and ionic resistance of all the components of an electrochemical cell (electrodes, electrolytes, separator, etc.)

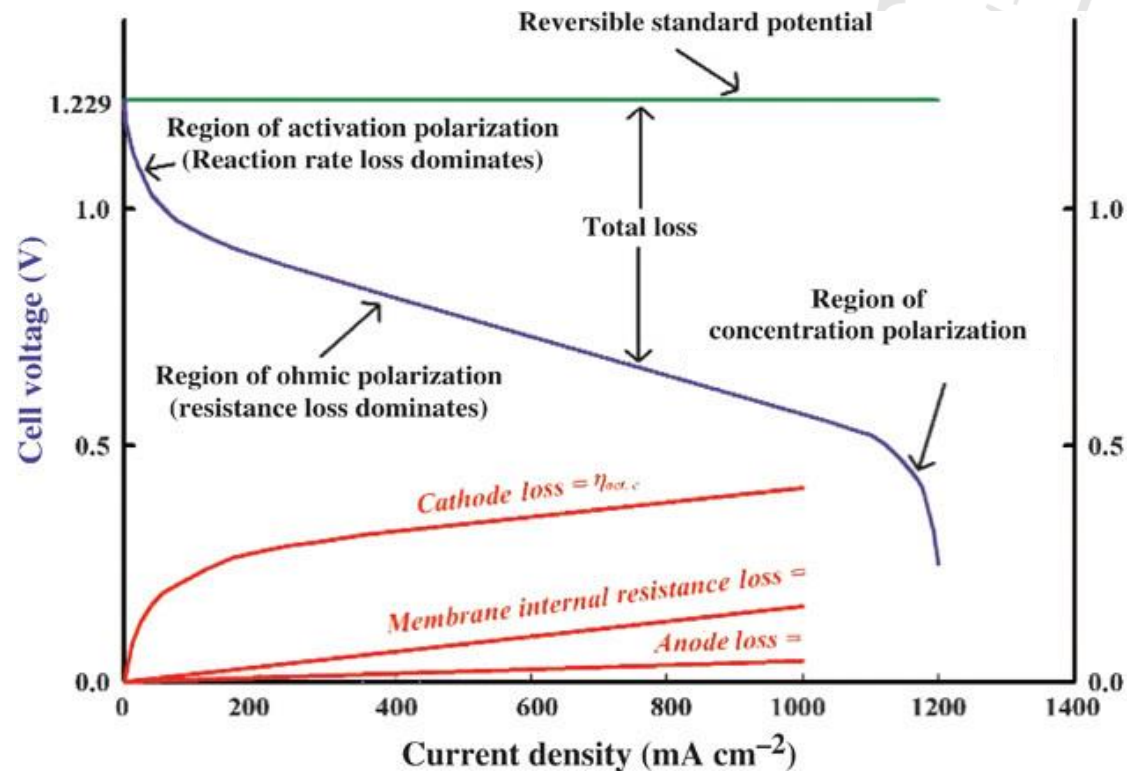
# Elements of Battery Theory

## Theory - Dynamics

- $\sum |\eta|$  includes activation and mass transport overvoltages (or concentration polarization) for cathodic and anodic reactions
$$\sum |\eta| = |\eta_{act}^c| + |\eta_{act}^a| + |\eta_{conc}^c| + |\eta_{conc}^a|$$
- The activation overvoltage  $|\eta_{act}^c| + |\eta_{act}^a|$  is an additional voltage difference potential (in addition to the equilibrium potential) that must be provided in order for the reactions to take place. This overpotential can be minimized by employing catalysts or high temperatures.
- The concentration overvoltage  $|\eta_{conc}^c| + |\eta_{conc}^a|$  is a change in the electrode voltage due to the fact that local concentrations of active species are different from concentrations in the bulk. This overpotential can be reduced by using electrodes with high surface area and operating with sufficient mass transport on the electrode (to avoid starving)
- All overpotentials are current dependent  $\rightarrow \eta = \eta(I)$

# Elements of Battery Theory

## Theory - Dynamics



$$E_i^e = E_i^0 + \frac{RT}{nF} \ln \left( \frac{c_{ox}}{c_{red}} \right)$$

$$E_{cell} = E_{cell}^e - \sum |\eta| - \sum |I|R$$

$$\sum |\eta| = |\eta_{act}^c| + |\eta_{act}^a| + |\eta_{conc}^c| + |\eta_{conc}^a|$$



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End of the Lesson

