UNIVERSITÀ
DEGLI STUDI
DI TRIESTE

Dipartimento di
Ingegneria
e Architettura

BATTERIES

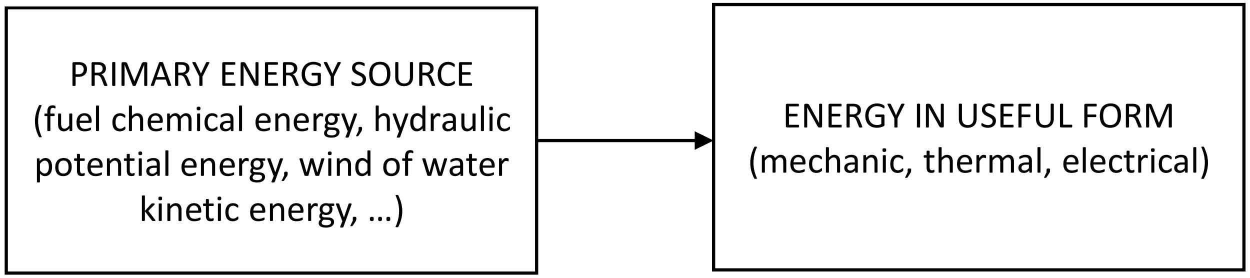
ELECTROCHEMISTRY AND WORKING PRINCIPLES

Prof. Marco Bogar

A.A. 2022-2023

INTRODUCTION

A machine can be described as a device used for converting energy.



PRIMARY ENERGY SOURCE
(fuel chemical energy, hydraulic potential energy, wind of water kinetic energy, …)

ENERGY IN USEFUL FORM
(mechanic, thermal, electrical)

Operating machines	Mechanical energy	→	Other forms of energy
Driving machines	Other forms of energy	→	Mechanical energy
Generating machine	Mechanical energy	→	Electrical energy

INTRODUCTION

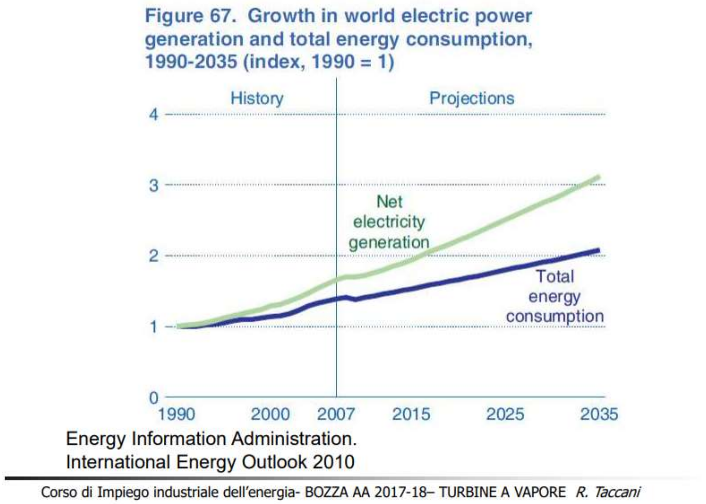
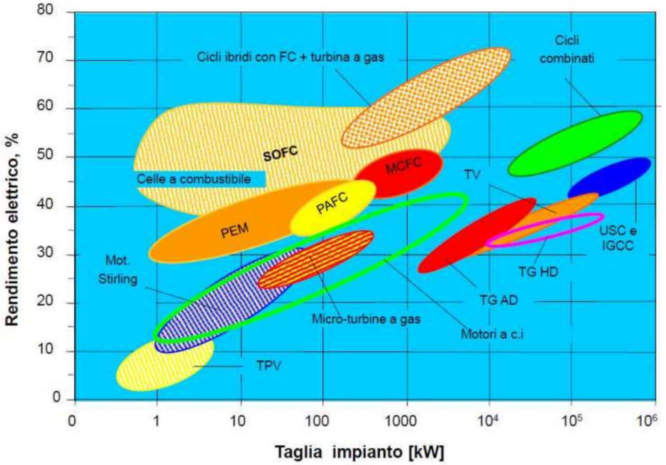
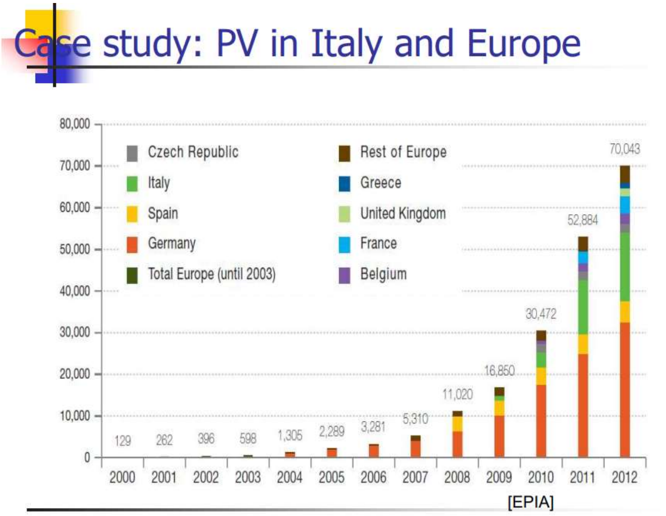


Figure 67. Growth in world electric power generation and total energy consumption, 1990-2035 (index, 1990 = 1)

Energy Information Administration.
International Energy Outlook 2010

Corso di Impiego industriale dell'energia- BOZZA AA 2017-18– TURBINE A VAPORE *R. Taccani*



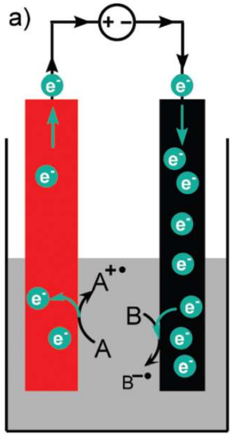


Case study: PV in Italy and Europe

[EPIA]

ELECTROCHEMISTRY AND THE ELECTROCHEMICAL CELL

Electrochemistry is the science dealing with the interconversion of electrical and chemical energies.
In particular, it deals with chemical reactions in which an electron transfer takes place in between two conductive electrodes, divided by an insulating and ionically conductive electrolyte.



Schotten C., Green Chem., 2020,22, 3358-3375

An electrochemical cell is a general device capable of converting chemical energy into electrical one. If current is generated during cell operation, the electrochemical cell is also known as Galvanic electrochemical cell.

In example, the electrochemical cell can be viewed as the fundamental brick constituting batteries.

REDOX (REDUCTION-OXIDATION) REACTIONS

Redox, is a term used to describe a couple of specular electrochemical reactions.

$$aA + bB \rightleftharpoons cC + dD$$

Composed by:

Reduction reaction

the oxidation number of a specimen is reducing (+ e^-)

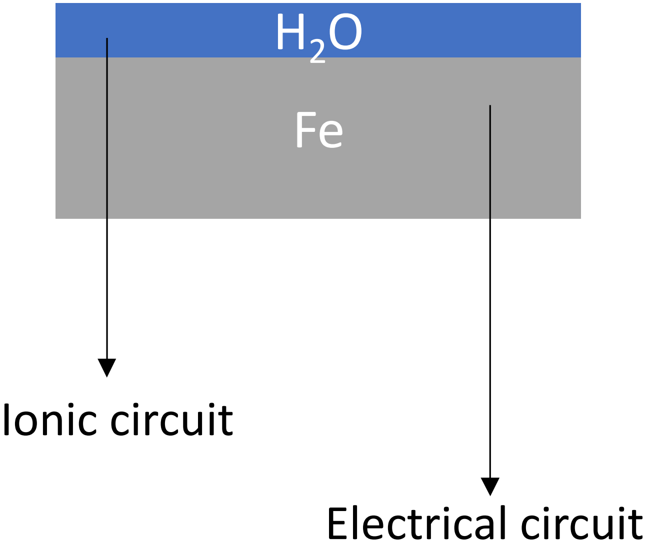
$$M^{n+} + ne^- \rightarrow M$$

Oxidation reaction

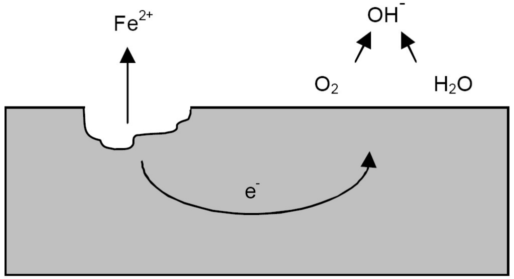
the oxidation number of a specimen is increasing (- e^-)

$$M \rightarrow M^{n+} + ne^-$$

AN EXAMPLE: IRON OXIDATION



1. In the anodic part of the circuit:
$$2Fe \rightarrow 2Fe^{2+} + 4e^{-}$$



https://it.wikipedia.org/wiki/Corrosione#cite_note-CEST-13

2. In the cathodic part of the circuit:
$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

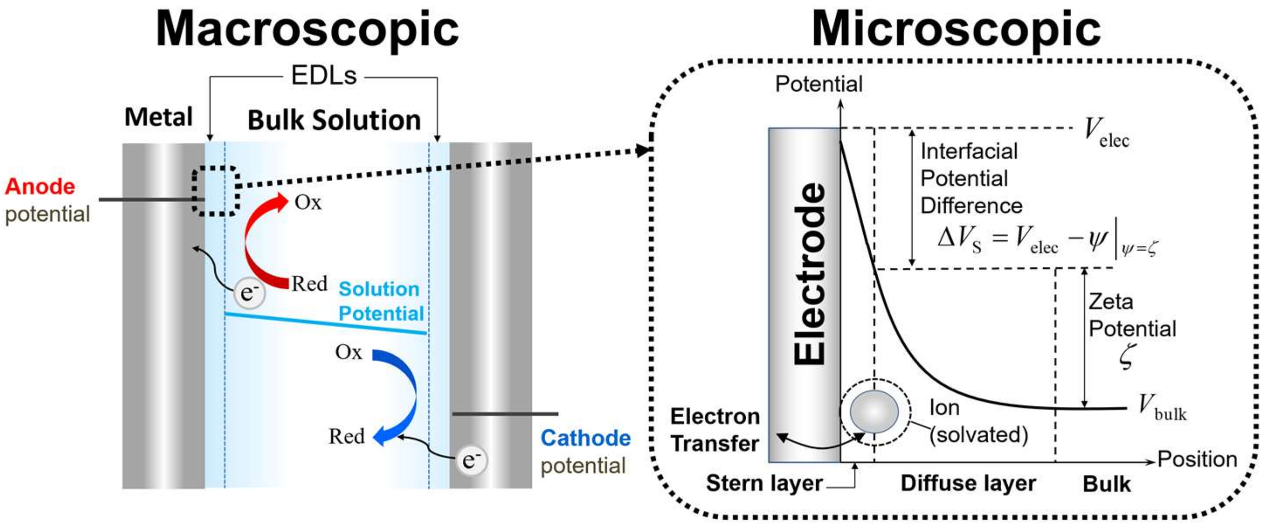
3. In the anodic part of the circuit:
$$2Fe^{2+} + 4OH^{-} \rightarrow 2Fe(OH)_2$$

4. Thus:
$$2Fe(OH)_2 + 1/2O_2 \rightarrow Fe_2O_3 \cdot nH_2O + H_2O$$

PROCESSES AT THE ELECTRODE SURFACE

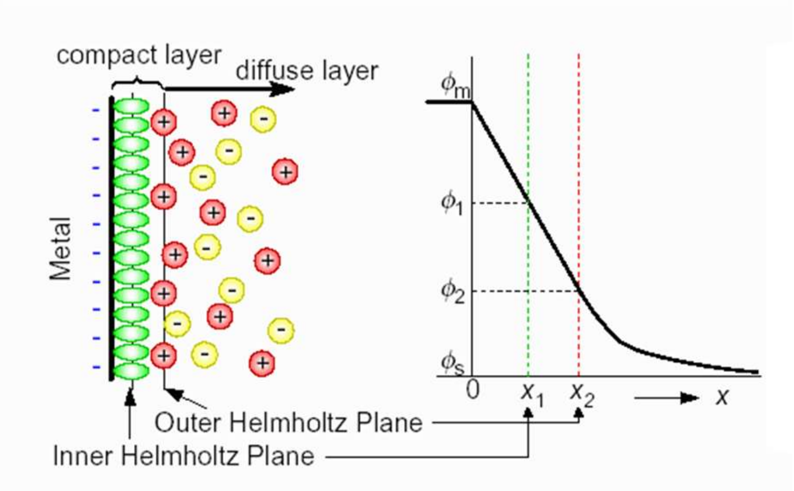
Processes involved in electrochemical reactions:

1. Transport by diffusion or migration of EC active species towards electrode surface
2. The EC active atom/ion has to adsorb a the electrode surface
3. Charge transfer (redox) has to take place
4. The reacted atom/ion has to desorb the electrode surface
5. It migrates back in the electrolyte bulk

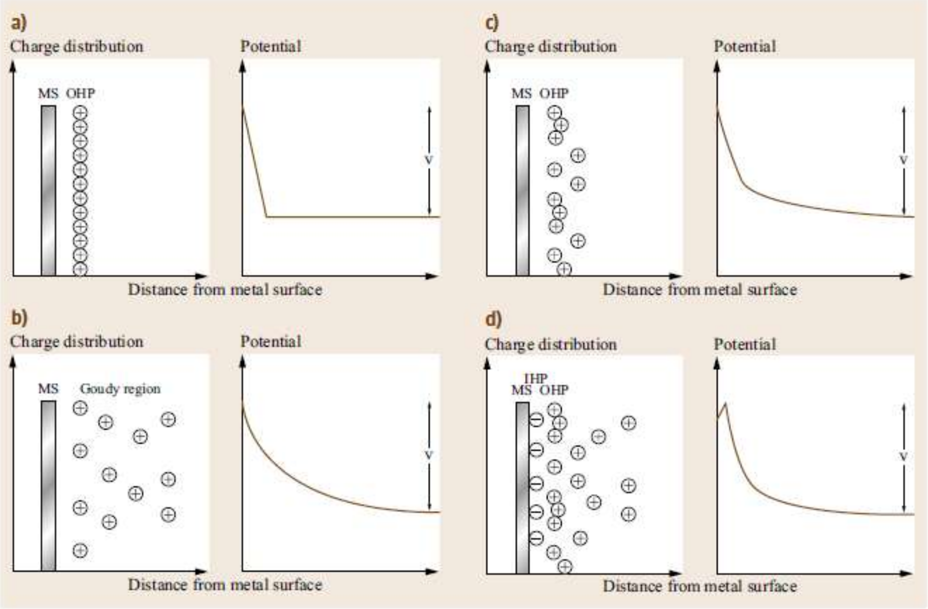


https://nanolab.engineering.ucsb.edu/research/electrochemistry-nanoscale

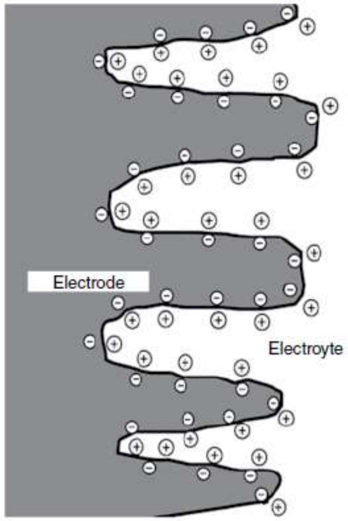
THE CHARGED ELECTRODE INTERFACE AND THE DOUBLE LAYER

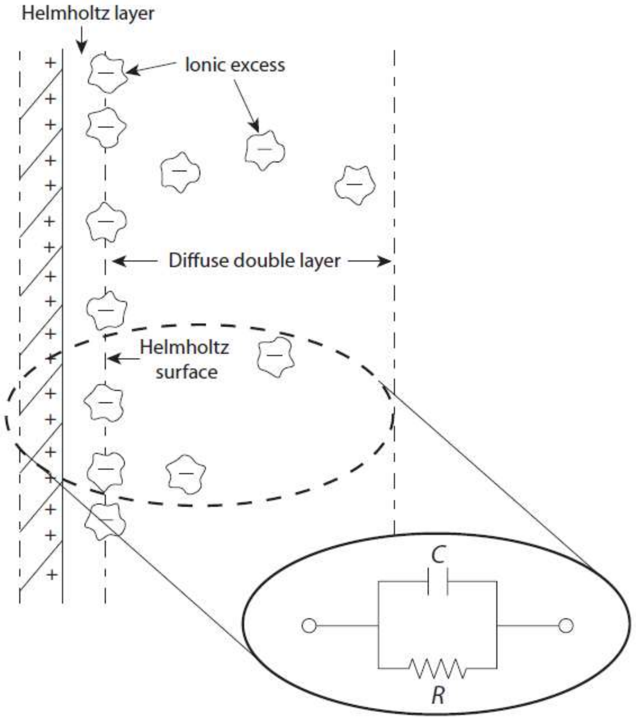


https://web.nmsu.edu/~snsm/classes/chem435/Lab14/double_layer.html



THE CHARGED ELECTRODE INTERFACE AND THE DOUBLE LAYER





AN EXAMPLE: THE Zn-Cu GALVANIC CELL

It is composed by two half-EC-cells:

- Anodic cell, composed by a $Zn(s)$ electrode immersed in $ZnSO_4(aq)$ solution
- Cathodic cell, composed by a $Cu(s)$ electrode immersed in $CuSO_4(aq)$ solution
- A bridge filled with $NaSO_4(aq)$ solution, working as ionic conductor.

At the anode side, Zn is oxidized: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

The electrons migrate from the anode to the cathode where

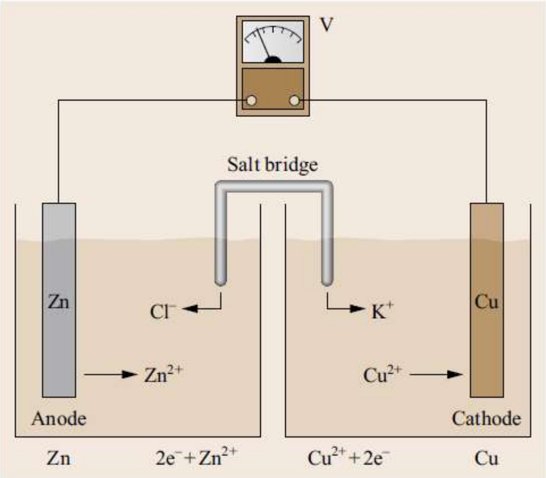
Cu is reduced: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Cu is deposited on the Cu electrode

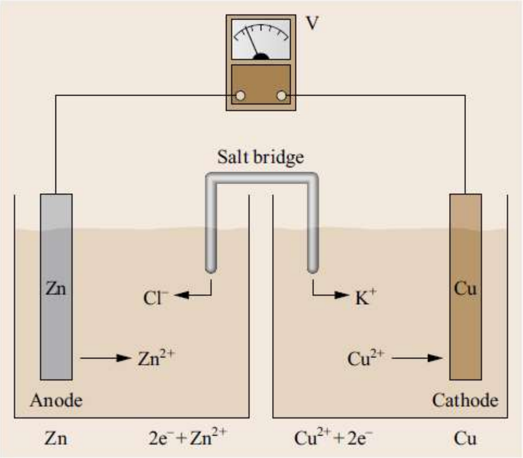
The overall redox reaction is: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

The difference of potential rising from the spontaneous reactions is:

$$E^0 = E^0_{ox} + E^0_{red} = 0.7996 - 0.3419 = 0.4577\ V$$



FROM THE EC CELL TO (Li-ION) BATTERIES



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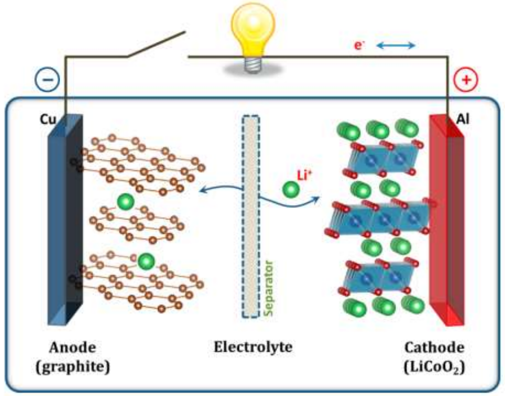
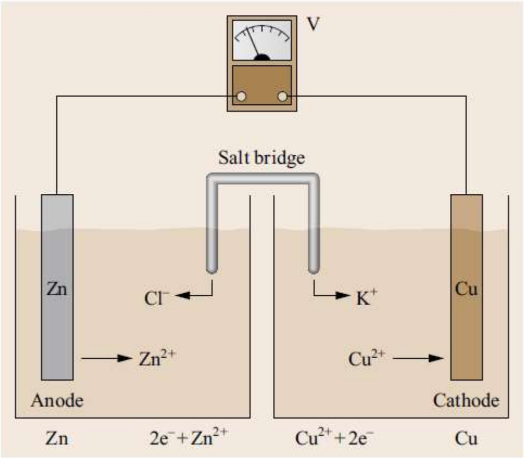


J. B. Goodenough, K.-S. Park, *J. Am. Chem. Soc.* 2013, 135, 4, 1167–1176

A battery is a galvanic cell that converts chemical energy into electrical one. Rechargeable batteries combine the galvanic cell (discharge) with an electrolytic cell (charge).

$$\begin{aligned} &Anode &&LiC_6 \rightarrow C_6 + Li^+ + e^- \\ &Cathode &&CoO_2 + Li^+ + e^- \rightarrow LiCoO_2 \\ &Overall &&LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2 \end{aligned}$$

FROM THE EC CELL TO (PEMFC) FUEL CELLS



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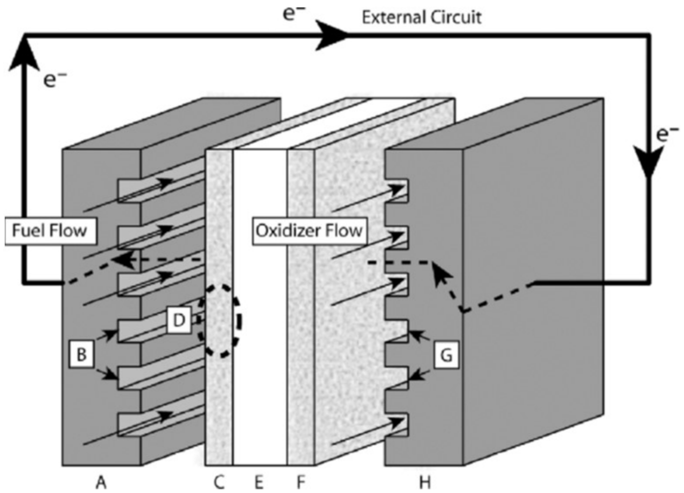
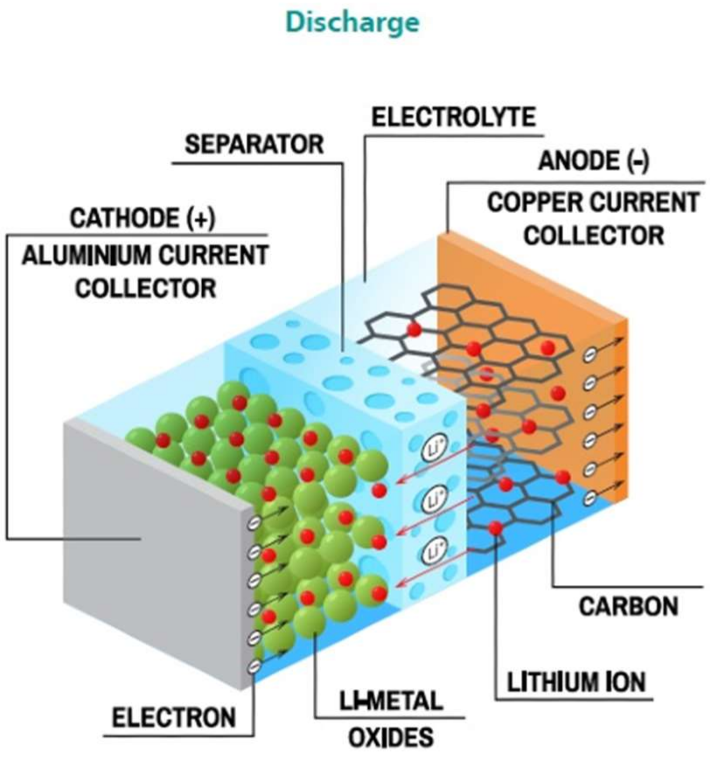


A fuel cell is an electrochemical cell in which fuel and oxidant are continuously fed to the electrodes in order to promote occurrence of redox reactions to generate electric current.

$$\begin{array}{rl} Anode & 2H_2 \rightarrow 4H^+ + 4e^- \\ Cathode & O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \\ Overall & 2H_2 + O_2 \rightarrow 2H_2O \end{array}$$

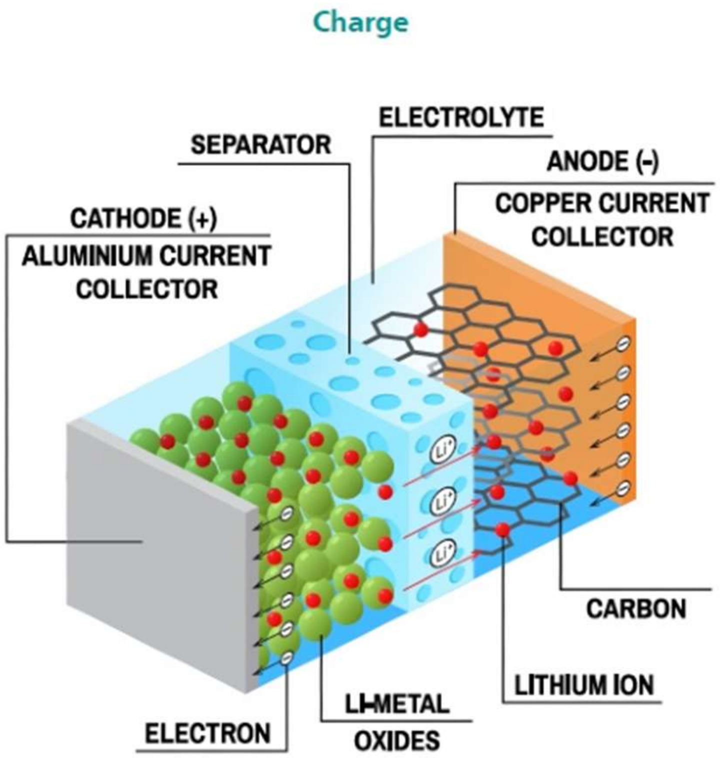
(LI-ION) BATTERIES / WORKING PRINCIPLE



https://www.azom.com/article.aspx?ArticleID=19013

A spontaneous Li-oxidation reaction at the anode produces free Li^+-ions and free electrons. The electrons are conveyed from the copper current collector. By flowing across the electrical circuit they migrate towards the cathode. To maintain system neutrality, Li^+-ions migrate across via the electrolyte and across the separator to the cathode side as well, where they recombine forming Li-metal oxides.

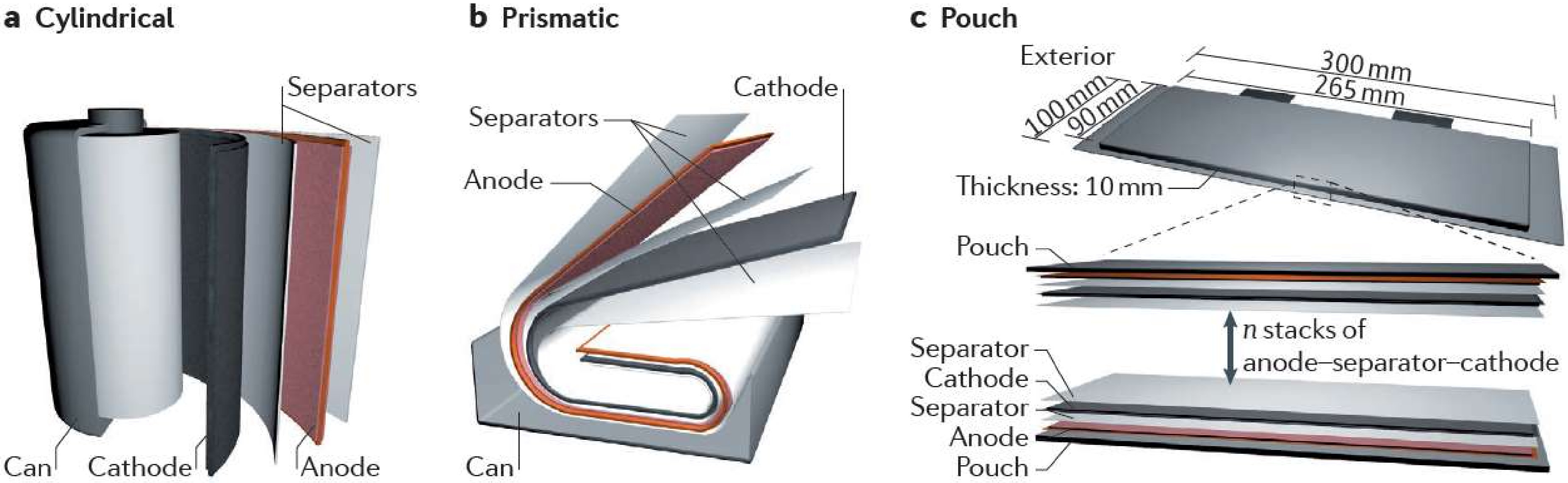
(LI-ION) BATTERIES / WORKING PRINCIPLE



https://www.azom.com/article.aspx?ArticleID=19013

The application of the charging potential oxidizes the Li-metal oxides: Li+ cations and electrons are made migrate back to the anode, where they reduce to their initial chemical state

(LI-ION) BATTERIES / ARRANGEMENT



J. W. Choi, D. Aurbach, Nat Rev Mater 1, 16013 (2016)

BATTERIES / FIGURES OF MERIT / CAPACITY

Capacity

Battery capacity is determined from the amount of materials composing the cell and it defines the total quantity of electric charge involved in the electrochemical reaction. It is measured in terms of Ampere-hour (Ah).

Specific capacity is then defined as the amount of charge which can be stored by the battery system relatively to the mass of material and it is in terms of Ah/kg.

When battery capacity is expressed in function of the volume of the material, Ah/L, it is called as charge density.

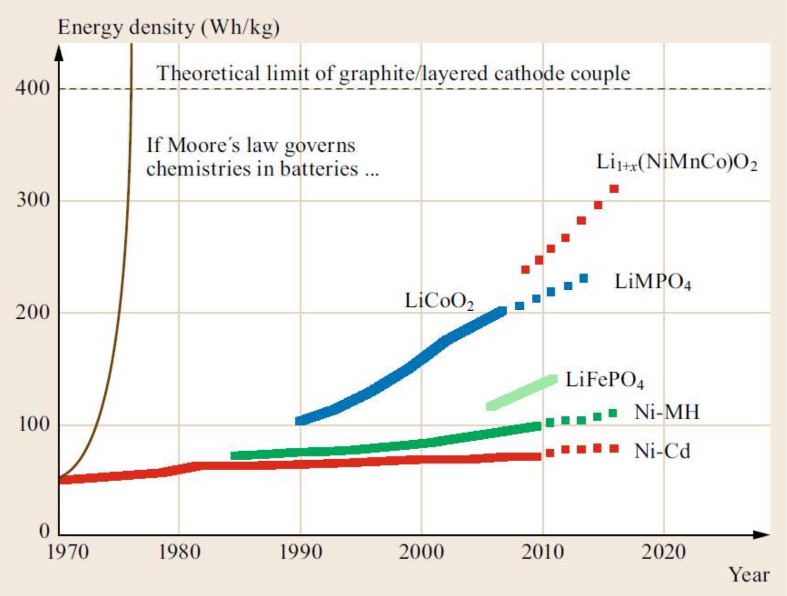
BATTERIES / FIGURES OF MERIT / SPECIFIC ENERGY

Specific energy

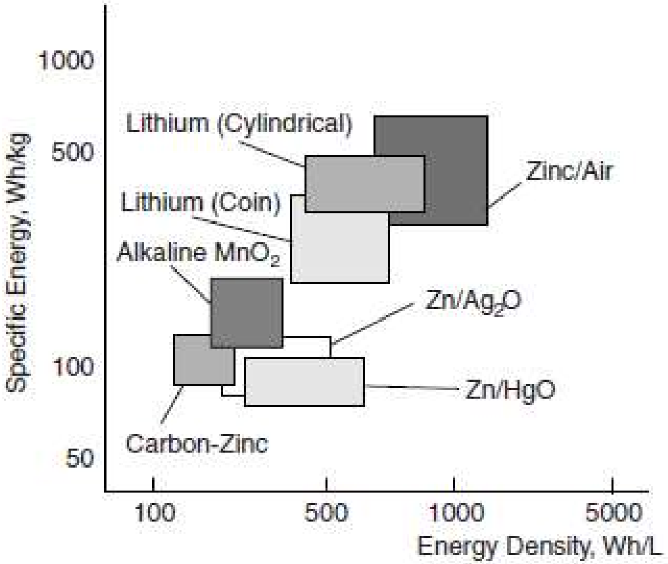
It allows to provide information from the capacity of the system from the energy-point-of-view, by adding also information about the battery voltage. It is expressed in Wh/kg (or J/kg) and it provides a measure of how much energy a battery contains in comparison to its weight.

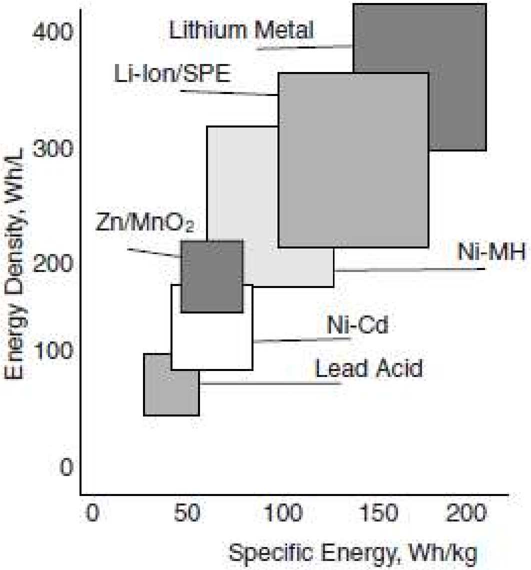
When the battery energy is referred to the battery volume, it is common to describe this quantity as energy density (J/L or Wh/L)

The performative increase of this feature is related to improvements in materials morphology, processes for fabricating electrodes with reduced nonactive materials contents, and packaging methods.



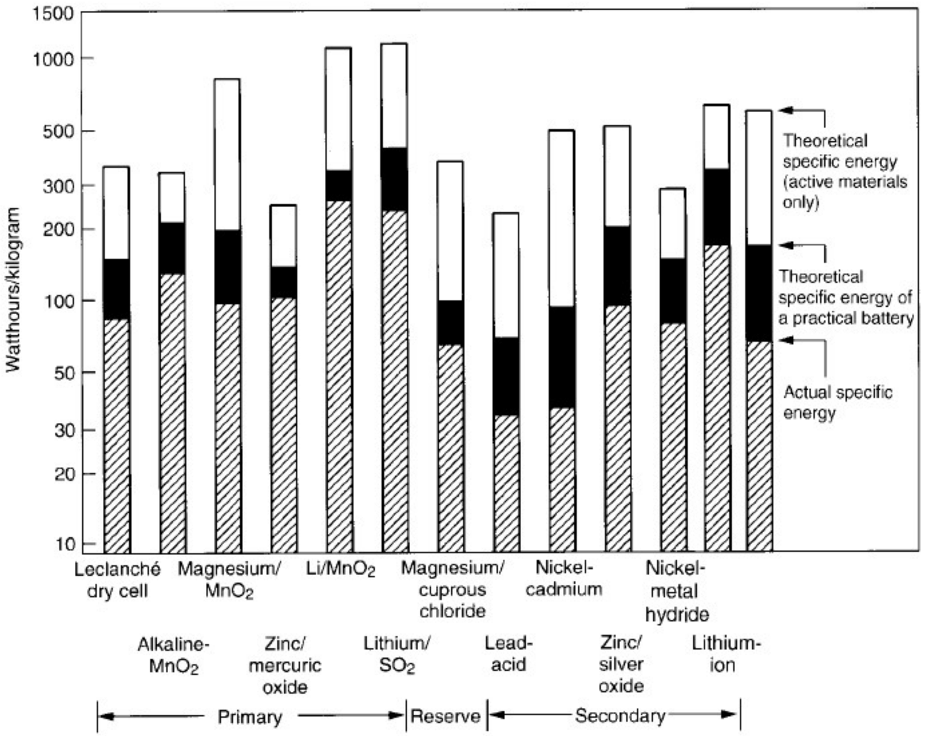
BATTERIES / FIGURES OF MERIT / SPECIFIC ENERGY





The energy storage capability is shown as a field, to illustrate the spread in performance of that battery system under different conditions of use

BATTERIES / FIGURES OF MERIT / SPECIFIC ENERGY



Specific energy can be then further classified into:

- theoretical specific energy: based on the active anode and cathode materials only
- theoretical specific energy of a practical battery: accounting for the electrolyte and non-reactive components (≈ 0.5 * theoretical specific energy)
- actual specific energy of these batteries (measured under optimal conditions, it may only be 50 to 75 percent of that lowered value)

Thus, the actual energy that is available from a battery under practical, but close to optimum, discharge conditions is only about 25 to 35 percent of the theoretical energy of the active materials.

BATTERIES / FIGURES OF MERIT

Specific power

Specific power (W/kg) or Power density (W/L): are related to loading capability. They provide a measurement of the amount of energy that battery is able to provide in comparison to its weight or volume.

Voltage efficiency

Voltage difference when a battery is charging versus discharging.

Coulombic efficiency

Also known as charge/discharge efficiency, is the ratio of the charge extracted from the battery (C_d) over the charge injected to the battery (C_c) over one cycle:

$$\eta = \frac{C_d}{C_c}$$

BATTERIES / FIGURES OF MERIT

Intrinsic Voltage

The intrinsic voltage of battery systems at equilibrium is ruled by the Nernst equation; for the generic electrochemical reaction $aA + bB \rightleftharpoons cC + dD$, the voltage of the system can be expressed as:

$$E = E^0 - \frac{RT}{nF}\ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right) \cong E_{OCV}$$

BATTERIES / VOLTAGES DEFINITION

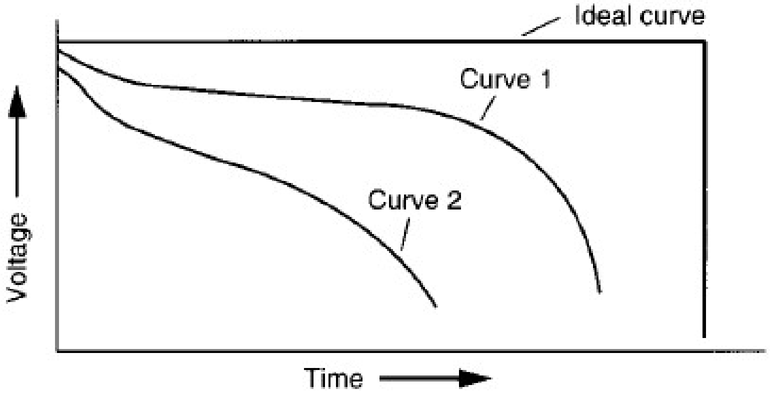
		e.g. Pb-acid battery
1	Theoretical voltage: is a function of the anode and cathode materials, the composition of the electrolyte and the temperature (usually stated at 25°C).	2.1 V
2	Open-circuit voltage: voltage under a no-load condition; it is usually a close approximation of the theoretical voltage.	
4	Nominal voltage: generally accepted as typical of the operating voltage of the battery (e.g., 1.5 V for a Zn-MnO_2 battery).	2.0 V
4	Working voltage: representative of the actual operating voltage of the battery under load (it is lower than the open-circuit voltage).	1.8 ÷ 2.0 V
5	Average voltage: averaged voltage during the discharge.	Load-dependant
6	Midpoint voltage: central voltage during the discharge of the cell or battery.	Load-dependant
7	End or cut-off voltage: it defines the end of the discharge. Usually it is the voltage above which most of the capacity of the cell or battery has been delivered. The end voltage may also be dependent on the application requirements.	1.75 V (low drain) 1.5 V (high load)
8	Charging voltage	2.3 ÷ 2.8 V

BATTERIES / THE POLARIZATION CURVE AND THE DISCHARGE CURVE

Discharge curve $V = f(t)$

Polarization curve $V = f(I)$

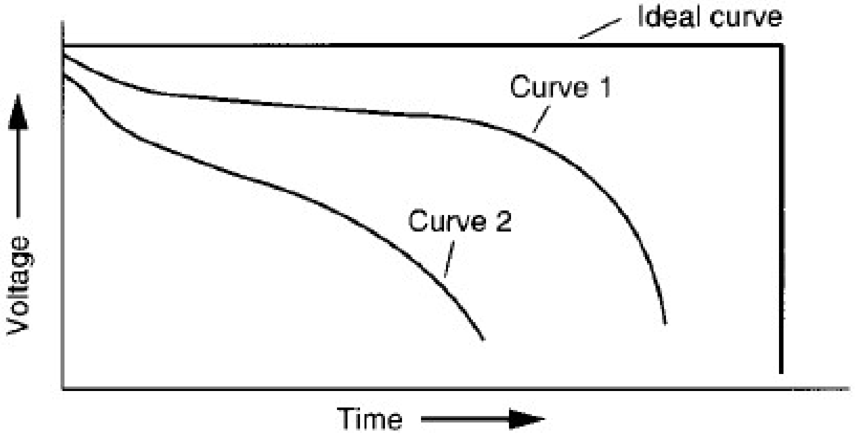
During discharge, the battery voltage level drops below the theoretical value. The discharge curve allows to define the health of the battery and the end (cut-off) voltage.



BATTERIES / THE DISCHARGE CURVE

Worse discharge profiles can be due to:

- Higher R_i (different materials, older component, …)
- Higher C-rate

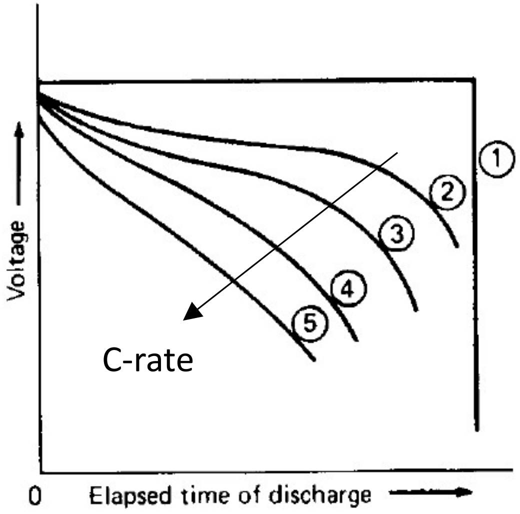


BATTERIES / THE C-RATE

Is a notation for the charge and discharge current used for batteries:

$$I = MC_n$$

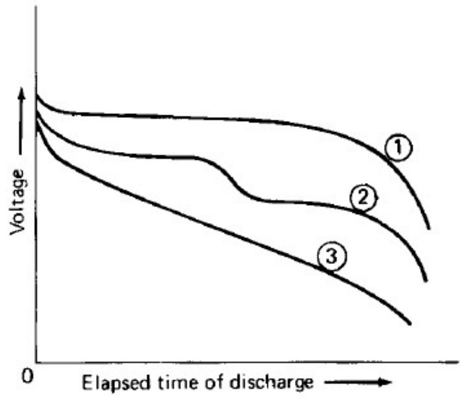
And it is expressed as a multiple of the battery capacity. For example, discharging a 2000mAh battery at 1A is equivalent to state that the discharging current is equal to 0.5C.



BATTERIES / THE POLARIZATION CURVE

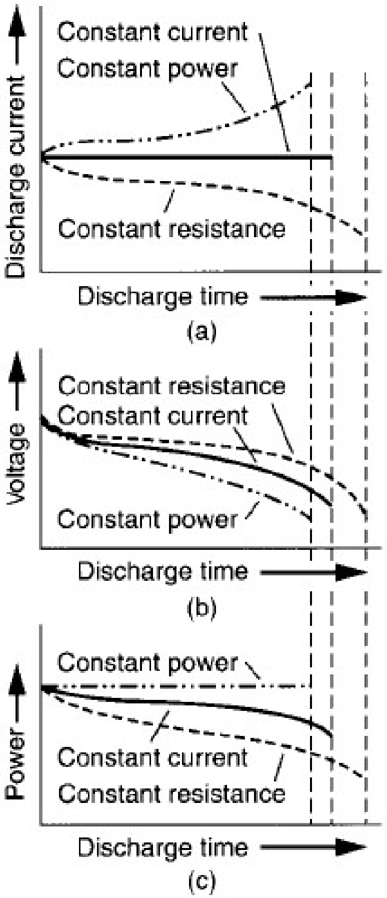
The polarization curve can be also used to identify other features of the battery:

1. Flat discharge: representative of a discharge where the effect of change in reactants and reaction products is minimal until the active materials are nearly exhausted.
2. Representative of two-step discharge indicating a change in the reaction mechanism and potential of the active material(s)
3. The composition of the active materials, reactants, internal resistance, and so on, change during the discharge, affecting the shape of the discharge curve similarly



BATTERIES / CONTINUOUS MODES OF DISCHARGE

1. **Constant Resistance:** The resistance of the load remains constant throughout the discharge (The current decreases during the discharge proportional to the decrease in the battery voltage)
2. **Constant Current:** The current remains constant during the discharge.
3. **Constant Power:** The current increases during the discharge as the battery voltage decreases, thus discharging the battery at constant power level (power current voltage).



$$t_{CP} < t_{CC} < t_{CV}$$

$$\downarrow$$

1. At Constant Power:

$$P = VI \rightarrow I \propto 1/V$$

$$\downarrow$$

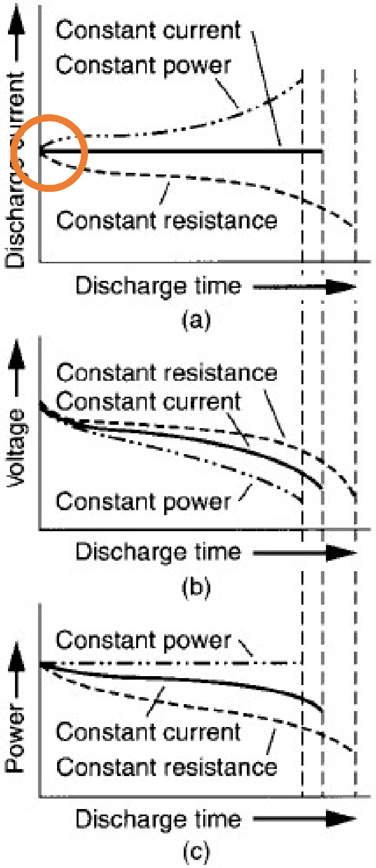
I increases while discharging

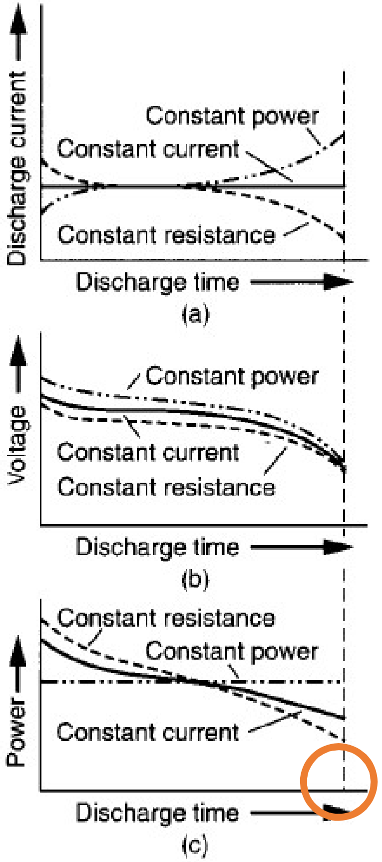
2. At Constant Resistance:

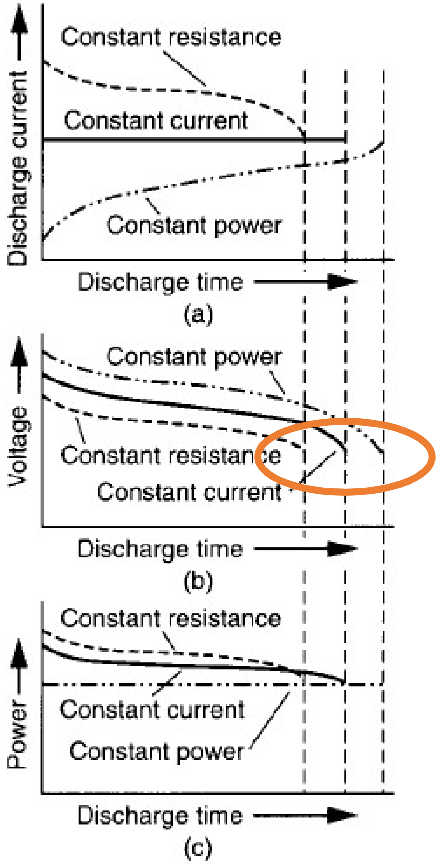
$$V = RI \rightarrow I \propto V$$

I decreases while discharging

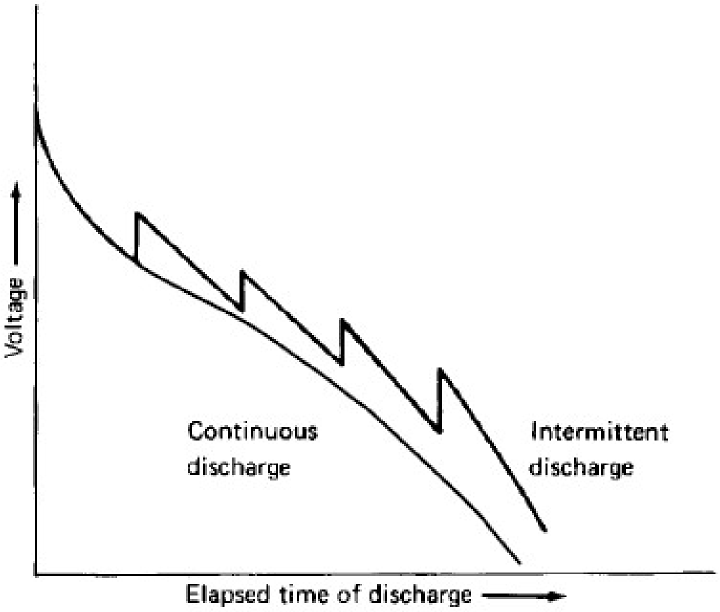
BATTERIES / CONTINUOUS MODES OF DISCHARGE

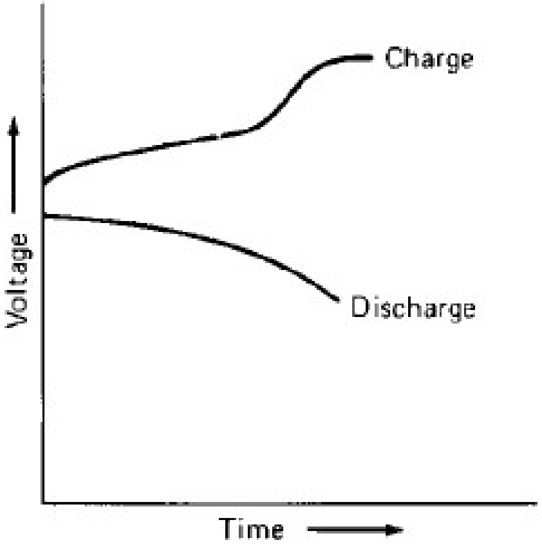






BATTERIES / OTHER MODES OF DISCHARGE, CHARGE / DISCHARGE





BATTERIES / THE POLARIZATION CURVE AND VOLTAGE LOSSES

The polarization curve is useful to highlight voltage losses. In a battery, voltage losses are due to ohmic polarization and polarization losses.

- **Ohmic polarization** is related to battery internal resistance and it is proportional to the current drawn from the system: $R_i I$
- **Polarization losses** can be further classified into *activation polarization* and *concentration polarization*. Activation polarization losses are represented by the formation of an overpotential (η_{ct}) due to the occurrence of the electrochemical reaction at the electrode surface, while concentration polarization losses are represented by the formation of an overpotential (η_c) arising form the concentration of the reactants and products at the electrode surface and in the bulk as a result of mass transfer.

Summarizing:

$$E = E_{OCV} - [(\eta_{ct})_a + (\eta_c)_a] - [(\eta_{ct})_c + (\eta_c)_c] - iR_i = iR$$

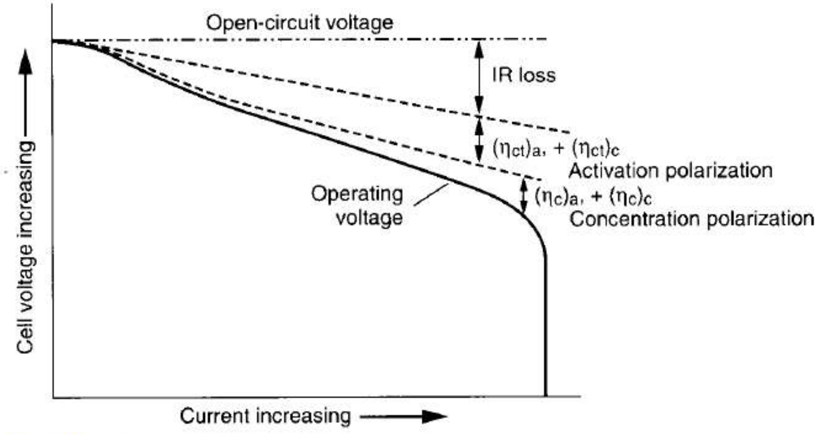
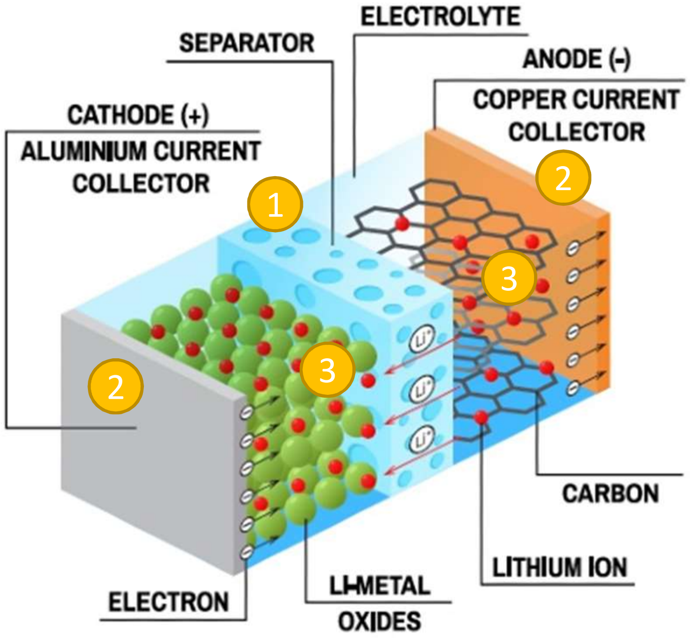


FIGURE 2.1 Cell polarization as a function of operating current.

BATTERIES / INTERNAL RESISTANCE

$$R_i = \underset{①}{R_{electrolyte}} + \underset{②}{R_{electrodes}} + \underset{③}{R_{catalyst-support-charge-transfer}}$$



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