Vehicle Propulsion Systems
Lecture 6
Modeling and Usage of Batteries

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Outline

When I say batteries: What do you think of?

- Consumer products, replaceable.
  $Zn\,Mn\,O_2$ with NH_4Cl electrolyte (Brunstensbatteri)
  → Alkaline Battery $Zn\,Mn\,O_2$ with KOH electrolyte.
  AA, AAA, Button cells (CR=Lithium $LiMnO_2$ 3.7V), (SR=Silver Oxide 1.55V), (LR=Alkaline 1.5 V)
- Consumer products, rechargeable.
  AA, AAA, Formfactors, NiCd (1.25V), NMH (1.2V), LiIon (4V) (1991).
- Lead Acid Batteries.
  Automotive Starter Batteries, UPS.
- Packs of cells.
  Lantern Cell (4.5 V=3x1.5V), Tesla model 3 pack

Batteries can contain poisonous metals, remember to recycle all your electronic devices properly!

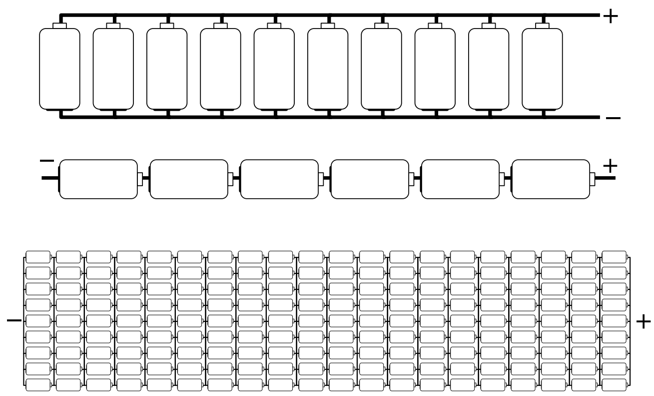
Basic Battery Definitions

Definition of a Battery

A container consisting of one or more cells, in which chemical energy is converted into electricity and used as a source of power. History is associated with Volta's stack of Zinc and Copper disks separated by paper soaked in salt water.

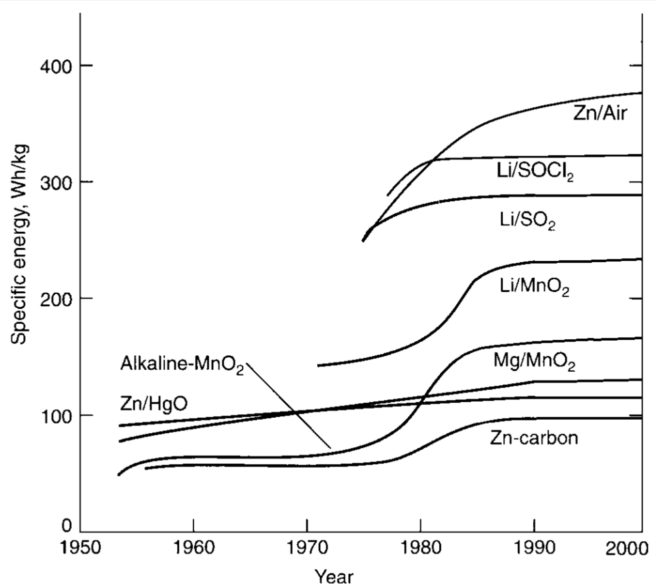
Benjamin Franklin suggested, in 1748, the term battery for this invention, in the sense of a collection of things used together, like a battery of artillery.

- **Cell** - A single Unit
- **Block** - A number of cells in Parallel
- **String** - A number of cells in Series
- **Pack** - A collection of cells connected in series and/or parallel
- **Battery** - A unit with a collection of cells ready for operation, Pack+BMS Battery Management System

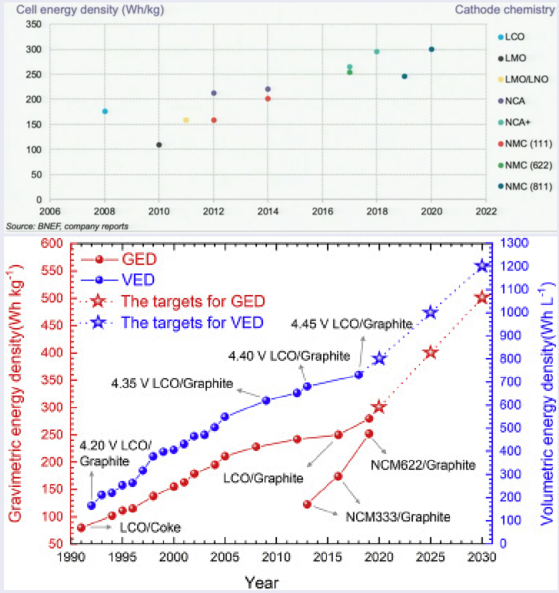


More Battery Definitions

Primary Batteries – Use & Discard



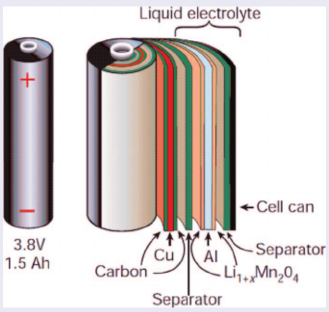
Secondary Batteries – Rechargeable

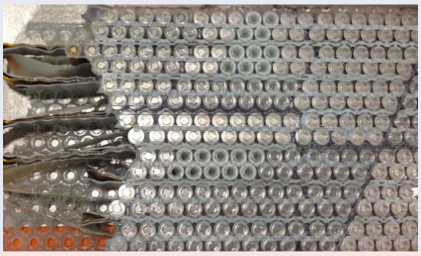


From Handbook of Batteries, Linden ed. (2008)

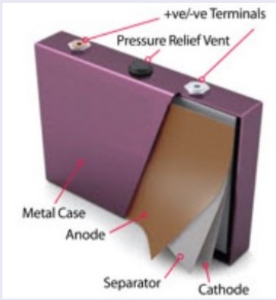
Cell Form Factors

Cylindric Cell

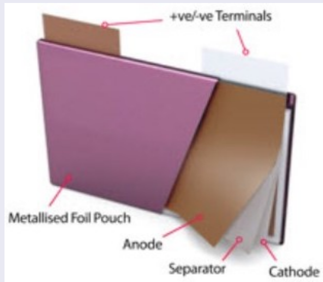




Prismatic Cell



Pouch Cell



The Pouch Cell is sometimes called Lithium Polymer Battery.

Electro-Chemistry Background – Repetition

Electrolyte A substance that produces an electrically conducting solution when dissolved in a polar solvent, an example is table salt in water. The dissolved electrolyte separates into cations (+) and anions (-), which spreads uniformly in the solvent. Electrically, the solution is neutral.

Oxidizing reaction Is when a molecule loses an electron or increases its oxidation state of an atom or ion.

Reducing reaction Is when a molecule gains an electron or decreases its oxidation state of an atom or ion.

Redox reaction The global reaction where there are transfer of electrons between molecules.

Anode The electrode (in batteries) is where the oxidation reaction occurs. Electrons flow out.

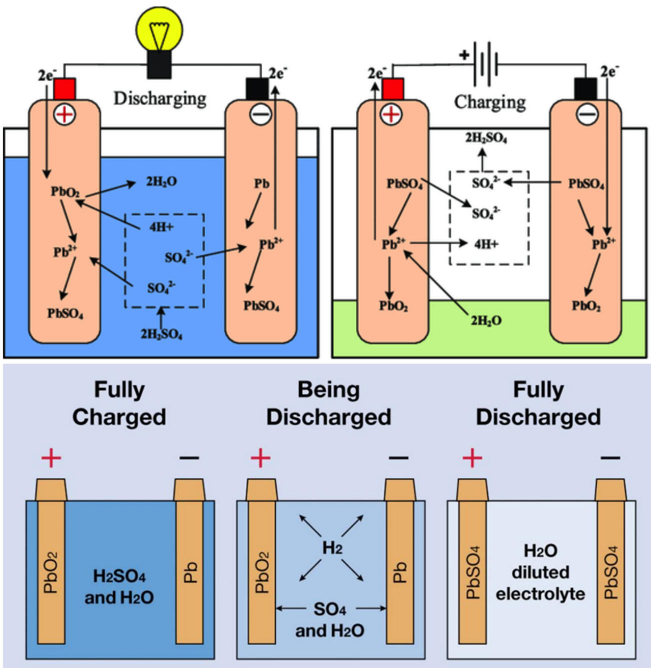
Cathode The electrode (in batteries) is where the reduction reaction occurs. Electrons flow in.

Note that anode is - and cathode is + during discharge of a battery (normal usage). But when charging the battery they switch roles, so anode is + and cathode is -. In most texts this distinction is not made, instead the anode is always considered to be the - pole and the cathode the + pole.

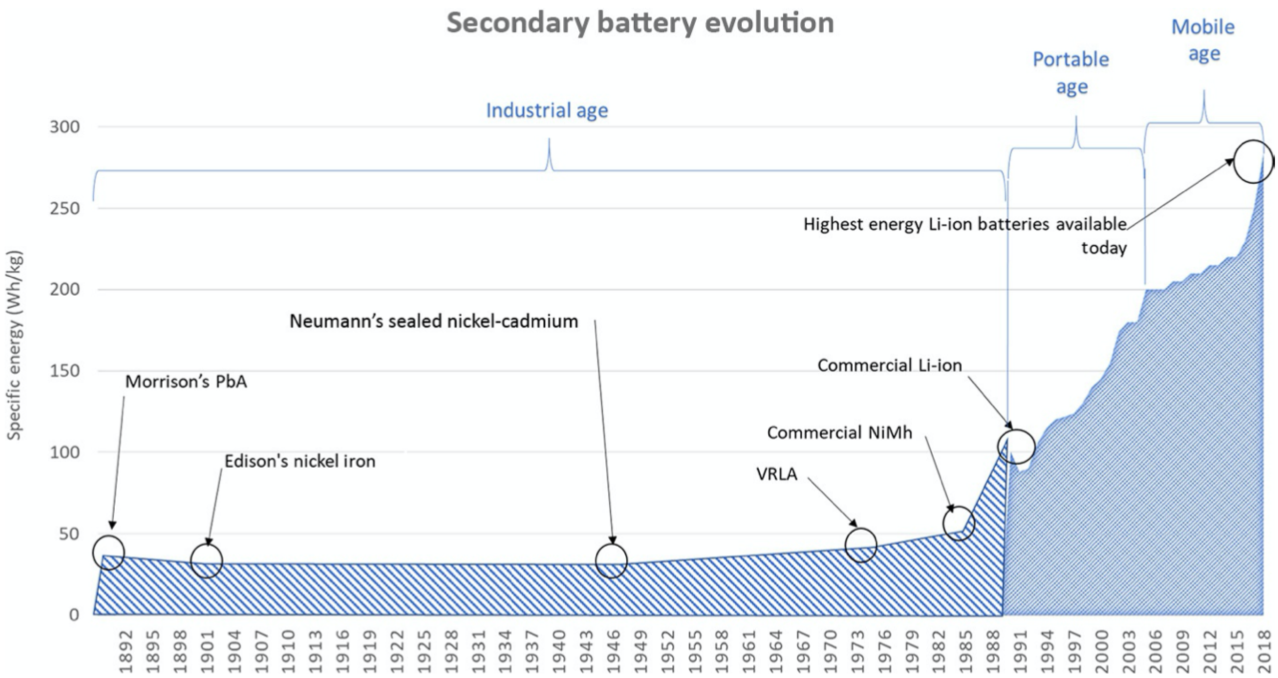
Turn our Attention to Secondary Batteries – Lead Acid as Initial Example

Elements in a secondary battery

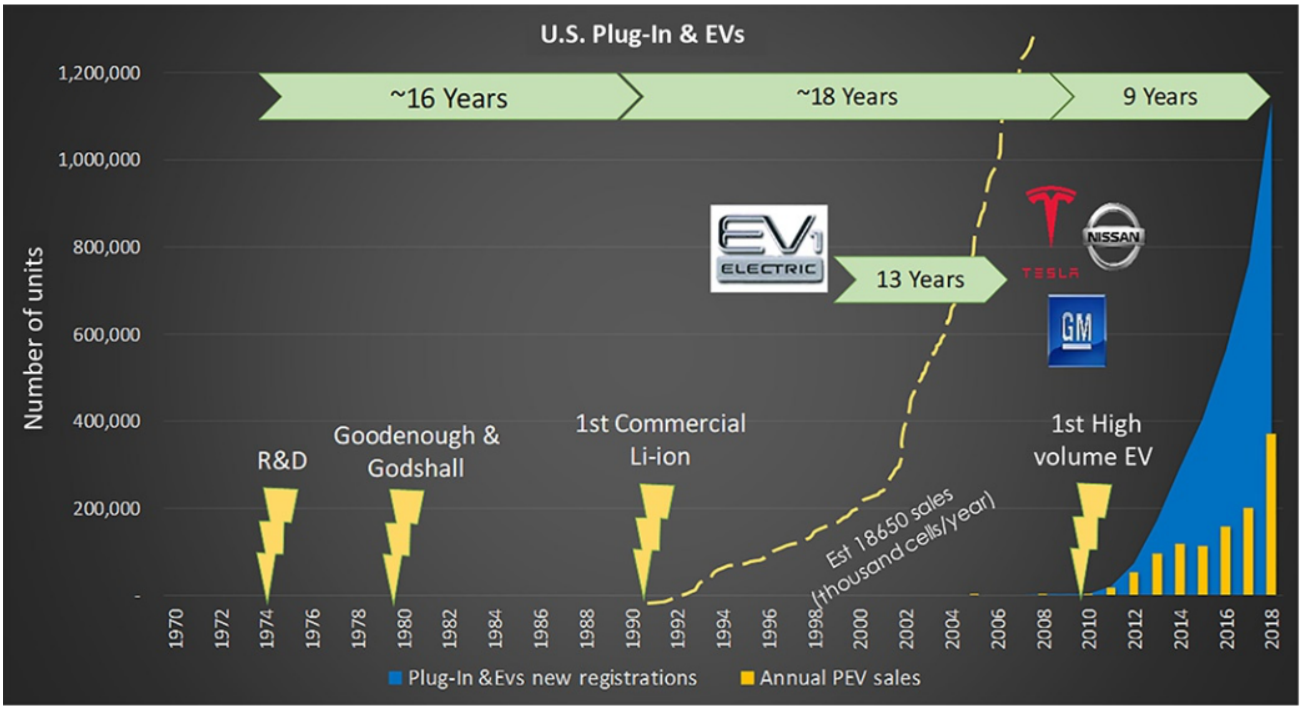
- Electrodes:
  –Positive and
  –Negative
- Active Materials:
  –Positive and
  –Negative
- Cathode and Anode
- Cations and Anions
- Electrolyte
- Ion conducting separator



Historical evolution of Secondary Batteries



Historical Evolution of Lithium Ion Batteries

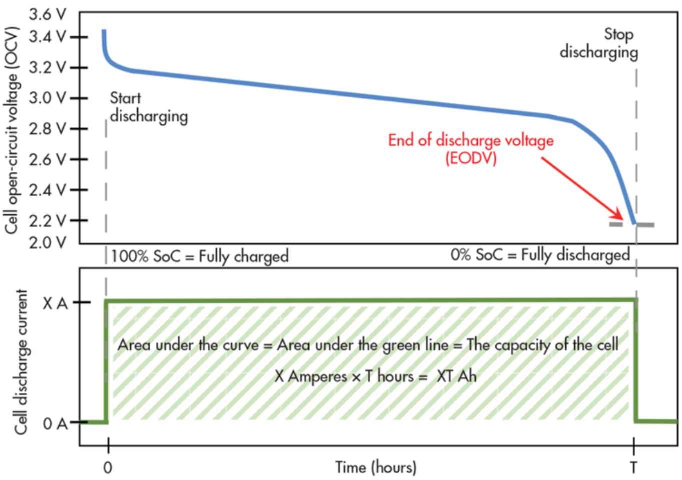


Some definitions that are important

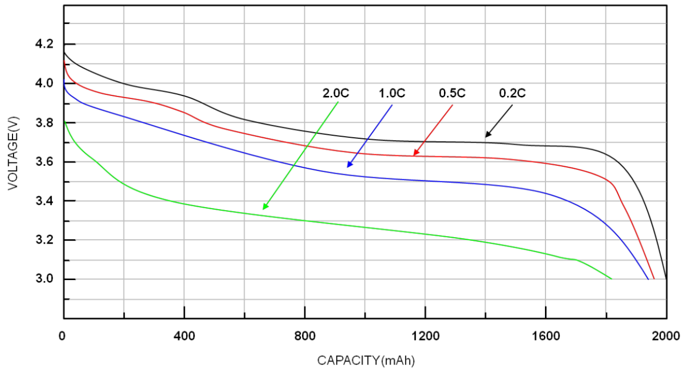
- State of Charge (SOC) [%]
- Open Cirquit Voltage (OCV) [V]
- Internal resistance (IR) [mOhm]
- Depth of Discharge (DoD) [%]
- Cut-off voltage [V] (max & min for safe op.)
- C-rate how fast the battery is charged
  - 1C battery is fully charged in 1h
  - 2C battery is fully charged in 0.5h
  - 0.5C battery is fully charged in 2h
- Cycle 1 full discharge and full charge

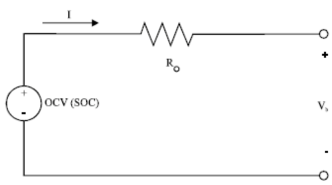
Some definitions that are important

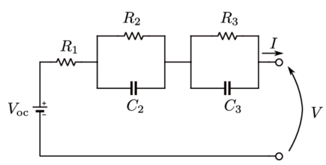
Capacity



Capacity vs C-Rate







State of Health (SOH)

- SOH is a figure of merit that reflects the general condition of a battery and its ability to deliver the specified performance compared with a fresh battery.
- It takes into account factors such as charge acceptance, internal resistance, capacity, voltage and self-discharge.
- It is a measure of the long term capability of the battery and gives an indication of the performance that can be expected from the battery.
- It indicates how much of the lifetime of the battery that has been consumed, and how much that remains.
- In an application the SOH is estimated by the battery management system (BMS).

Outline

Nickel-Metal Hydride – NiMH

Cathode reaction

The reaction at the cathode reduces nickel oxyhodroxide to nickel hydroxide

$$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$$

The energy release gives the voltage $E_0 = 0.52$ V

Anode reaction

The reaction at the anode oxidizes metal hydride (MH) to the metal alloy (M).

$$MH + OH^- \rightarrow M + H_2O + e^-$$

The energy release gives the voltage $E_0 = 0.83$ V

The global redox reaction for the NiMH battery is

$$MH + NiOOH \underset{chg}{\overset{dischg}{\rightleftharpoons}} M + Ni(OH)_2 \qquad E_0 = 1.35\,\text{V}$$

The Hydroxyl Ion and Water pass through the electrolyte while the electron released at the anode goes through the electric circuit to the cathode.

Nickel-Metal Hydride – NiMH

Active Materials

- The active cathode material is Nickel Oxyhydroxide (NiOOH).
- While the active anode metal in NiMH-batteries is not a single metal, but an engineered alloy that contains a mixture of many metals.
- There are three basic types of alloys, that in their turn have internal variations.
  - AB_5 (LaCePrNdNiCoMnAl)
    - $La_{5.7}Ce_{8.0}Pr_{0.8}Nd_{2.3}Ni_{59.2}Co_{12.2}Mn_{6.8}Al_{5.2}$
    - $La_{10.5}Ce_{4.3}Pr_{0.5}Nd_{1.3}Ni_{60.1}Co_{12.7}Mn_{5.9}Al_{4.7}$
  - A_2B_7 (LaCePrNdMgNiCoMnAlZr)
    - $La_{4.8}Ce_{0.4}Pr_{9.1}Nd_{5.4}Mg_{1.7}Ni_{68.8}Co_{3.0}Mn_{0.2}Al_{5.5}Zr_{0.2}$
    - $Nd_{18.7}Mg_{2.5}Ni_{74.7}Co_{0.1}Al_{3.6}Zr_{0.2}$
  - AB_2 (VTiZrNiCrCoMnAlSn)
    - $V_{18}Ti_{15}Zr_{18}Ni_{29}Cr_5Co_7Mn_8$
    - $V_5Ti_9Zr_{26.7}Ni_{38}Cr_5Mn_{16}Sn_{0.3}$
    - $V_5Ti_9Zr_{26.2}Ni_{38}Cr_{3.5}Co_{1.5}Mn_{15.6}Al_{0.4}Sn_{0.8}$

Nickel-Metal Hydride – NiMH

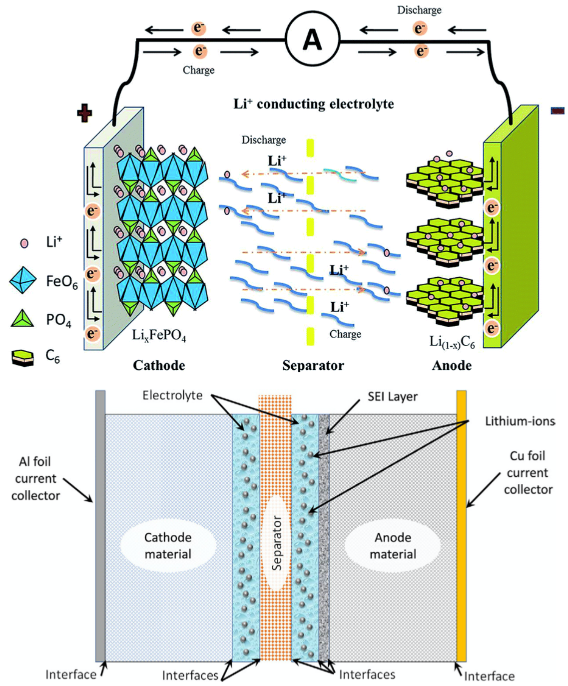
Inactive Materials

- The electrolyte in NiMH batteries of all types is routinely a mixture of about 30% potassium hydroxide (KOH) in water, providing high conductivity over a wide temperature range.
- It is most common for the electrolyte to have a lithium hydroxide additive at a concentration of about 17 g/L to promote improved charging efficiency at the nickel hydroxide electrode. This suppresses the oxygen evolution, which is the competing reaction to charge acceptance.
- It is also possible to substitute a portion of the KOH with NaOH. Where NaOH promotes high-temperature charging-efficiency, although this electrolyte can decrease cycle life through increased corrosion of the active MH materials.
- The electrolyte in the nickel-metal hydride batteries used in the Toyota Prius Hybrid, use a mixture of potassium hydroxide (KOH) and sodium hydroxide (NaOH).
- The separator is termed "permanently wettable polypropylene". This separator is a composite of polypropylene and polyethylene where the base composite fibers require special surface treatments to make them wettable to the electrolyte.

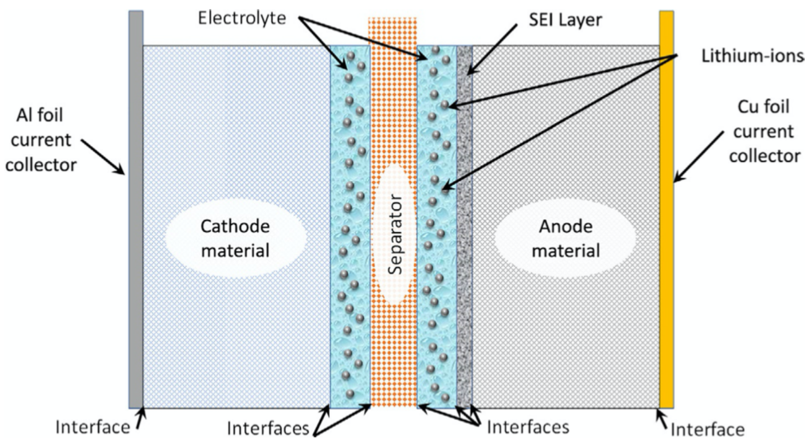
Outline

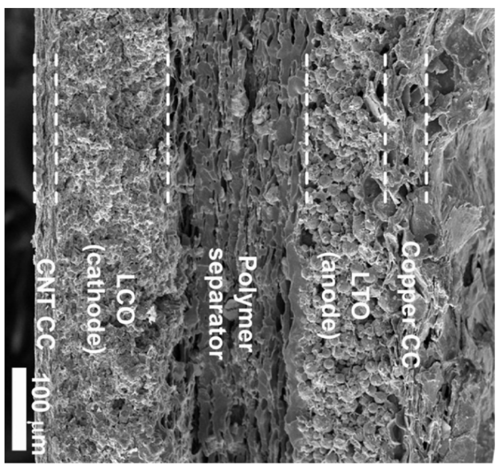
Lithium Ion Batteries – Components and Operating principles

- Anode and Cathode
  Store Lithium inside their structures
- Current Collectors
  Copper @ Anode,
  Aluminum @ Cathode
- Bonding interface materials
  e^{-} conducting glue (Carbonite)
- Electrolyte – Transports Li^{+}
- Separator
  Keeps cathode and anode isolated
  Porous, electrolyte and ion transport
- SEI – Solid Electrolyte Interphase



Lithium Ion Batteries – Components and Operating principles





Chemical Reactions

Cathode reaction (+)

The reaction at the cathode reduces the Lithium Ion to Lithium when it enters the Metal oxide

$$Li_{1-x}MO_2 + xLi^+ + xe^- \rightarrow LiMO_2$$

M is a place holder for various Cathode transition metals. $E_0 \approx 4$ V

Anode reaction(-)

The reaction at the anode oxidizes the Lithium to Lithium Ion when it leaves the Carbon Structure.

$$Li_yC \rightarrow C + y\,Li^+ + y\,e^-$$

The reaction consumes energy reducing the voltage $E_0 \approx -0.2$ V

The global redox reaction for the Lithium Ion battery is

$$x/y\,Li_yC + Li_{1-x}MO_2 \underset{chg}{\overset{dischg}{\rightleftharpoons}} x/y\,C + LiMO_2 \qquad E_0 \approx= 3.7\,\text{V}$$

Lithium Ion Batteries

Key Processes in a Cell – Buzz words

- Intercalation
- SEI - Solid-Electrolyte Interphase
- Dendrite growth
- Swelling during charging

Lithium Ion Batteries

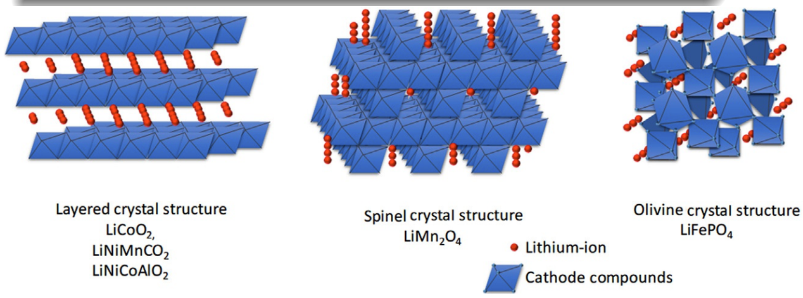
There are different options for materials in Lithium Ion Batteries. They are most often referred to using their Cathode material.

Cathode materials

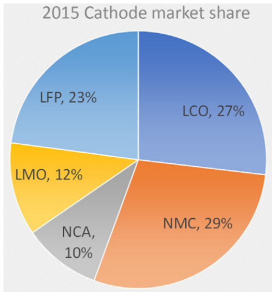
lithium iron phosphate (LFP), nickel cobalt manganese (NCM=NMC), lithium cobalt oxide (LCO), lithium manganese oxide (LMO), nickel cobalt aluminum (NCA), and lithium manganese phosphate (LMP)

Anode materials

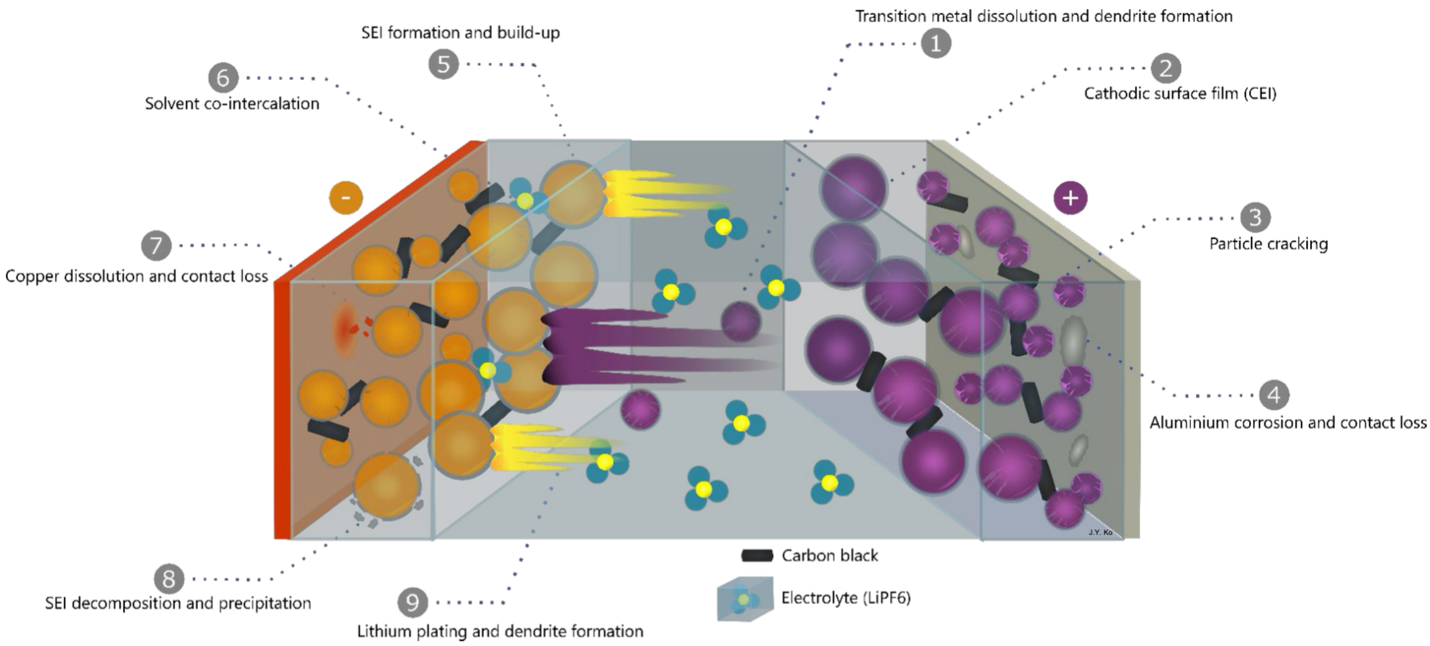
C - Graphite
$Li_4Ti_5O_{12}$ - Lithium Titanate
Si - Silicon



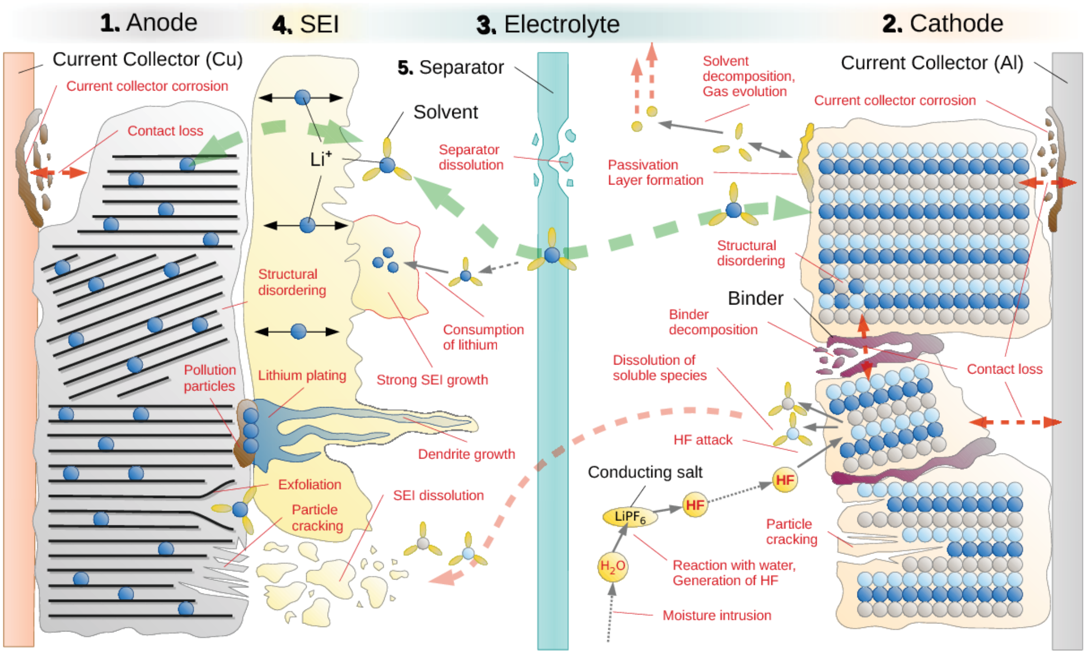
Cathode Market share - 2015



Lithium Ion Batteries – Aging Mechanisms 1 (2)

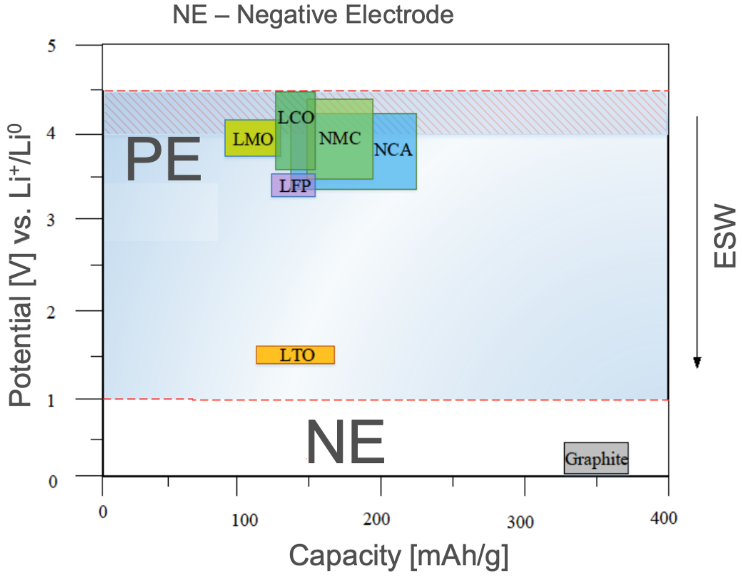


Lithium Ion Batteries – Aging Mechanisms 2 (2)



Lithium Ion Batteries – Cell Voltage and Capacity Comparison

ESW – Electrolyte Stability Window
PE – Positive Electrode
NE – Negative Electrode



Battery Properties vary with Materials

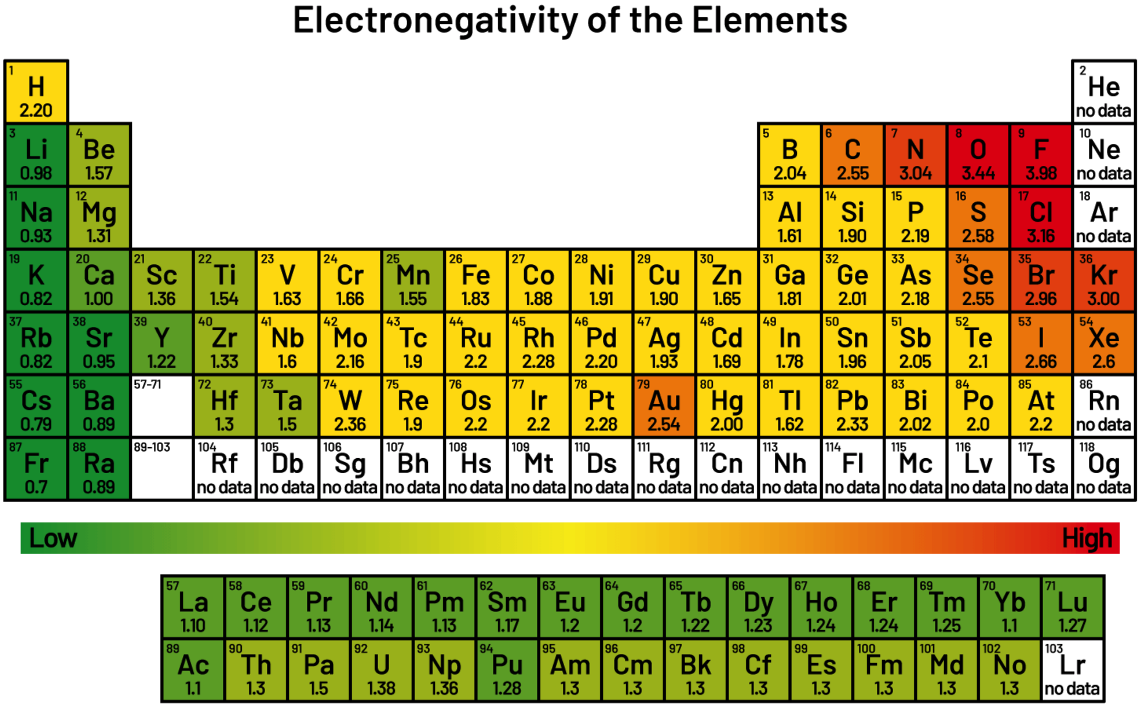
Most variations are in cathode material

LTO and Graphite are most common where the latter gives higher voltage.

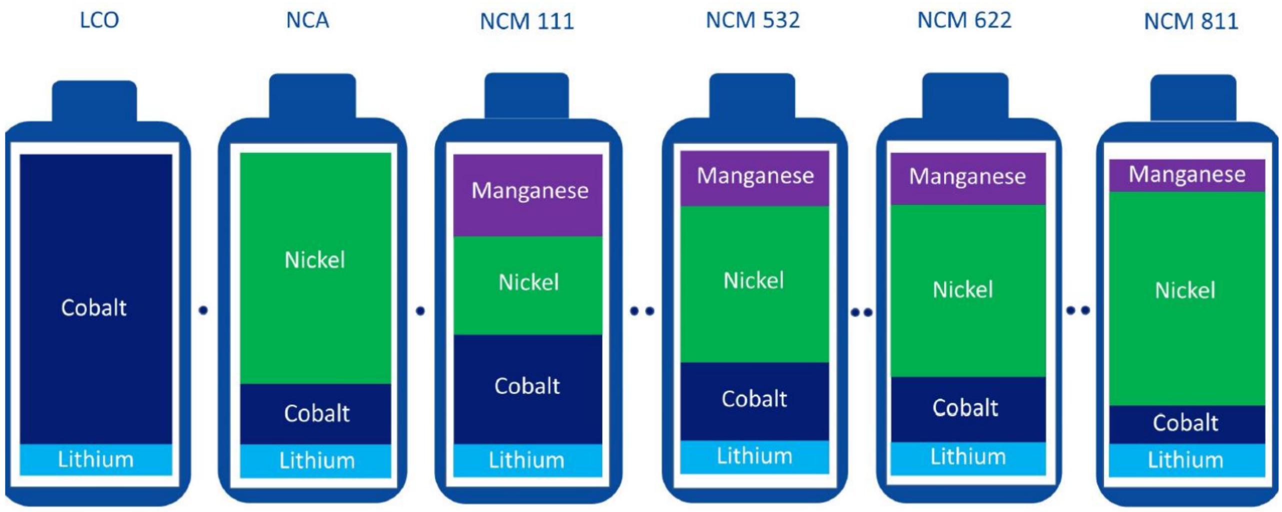
Outside the stability window the Electrolyte will start to oxidize and can become unstable with a high electric field.

Why is Lithium Attractive?

Periodic table, lightweight and electronegativity.



Future evolution of Li-Ion Batteries



Future evolution of Li-Ion Batteries

Cell generation	Cell chemistry specifications	
Generation V	- Li/O_2 (Lithium-air)	>2050??
Generation IV	- All solid-state with metallic lithium anode - Conversion materials (primarily Li-S)	~2025 - 2050
Generation IIIb	- Cathode: HE-NMC, HVS (high voltage spinel) - Anode: Si / carbon	~2020 - 2025
Generation IIIa	- Cathode: NMC 622 to NMC 811 - Anode: carbon (graphite) + 5-10% Si component	~2020 - 2025
Generation IIb	- Cathode: NMC 532 to NMC 622 - Anode: carbon (graphite)	Current
Generation IIa	- Cathode: NMC 111 - Anode: carbon (graphite)	Current
Generation I	- Cathode: LCO, LFP, NCA - Anode: carbon (graphite)	Current

Outline

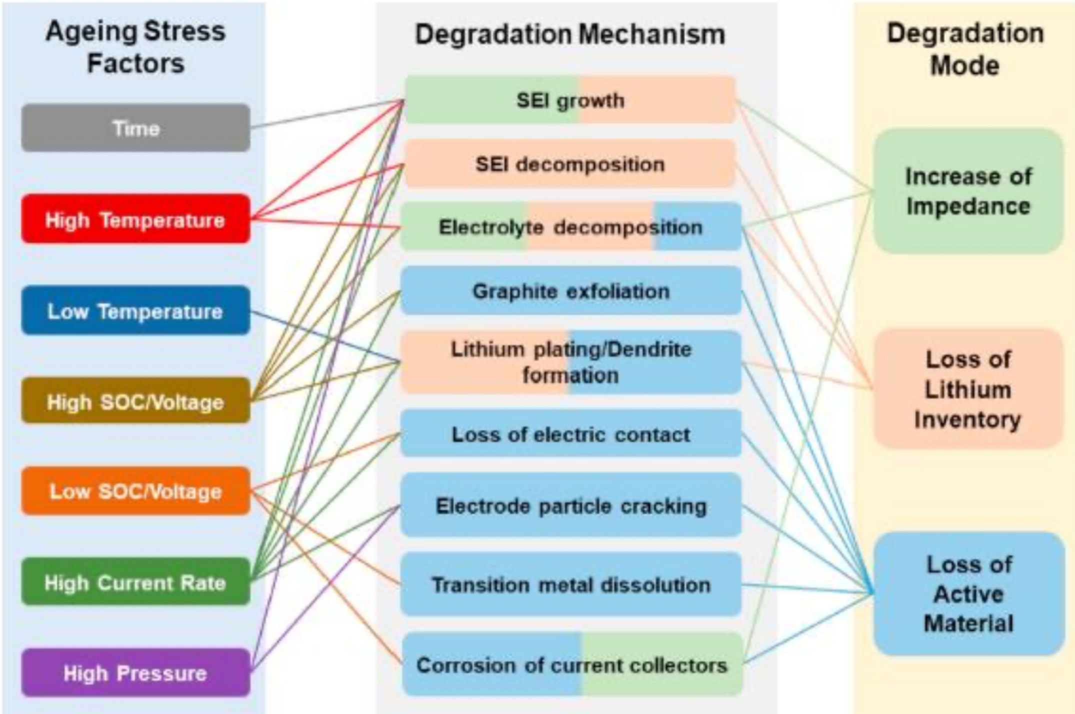
Tesla Shanghai Fire

YouTube on the title...

Secondary Batteries

- What kills a battery?
- Control and monitoring of batteries
- What do we need to monitor?
- How can this be understood?

Lithium Ion Batteries – Aging Mechanisms 3 (3)



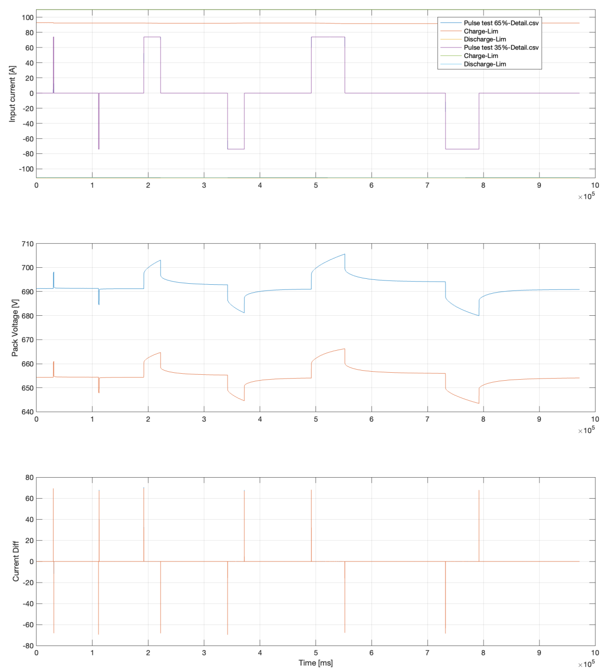
Li-Ion Battery Characteristics & Charging

- Charging Characteristics, Charging Efficiency
- Discharge Characteristics
- Internal Resistance
- Self-Discharge & Storage
- Cycle Life & Factors Affecting Cycle Life
- Effect of Temperature on Voltage, capacity, IR. Self-discharge. life
- State of Health

Outline

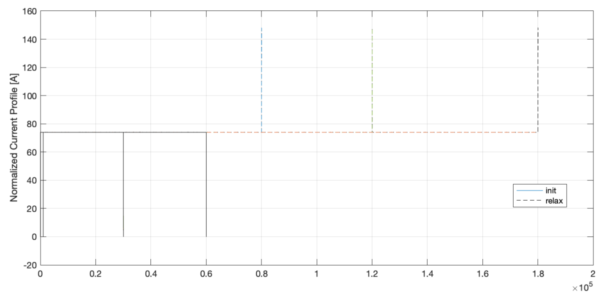
Measurements - Step Responses on a Battery Pack

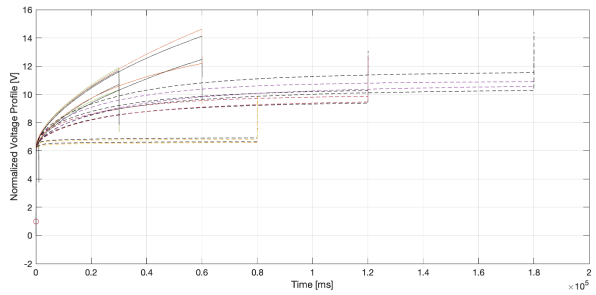
- Experiment: step in Current.
- Dynamic voltage response
- Not a pure resistance and integrator.
- Dynamic elements
- Time constants



Measurements - Step Responses

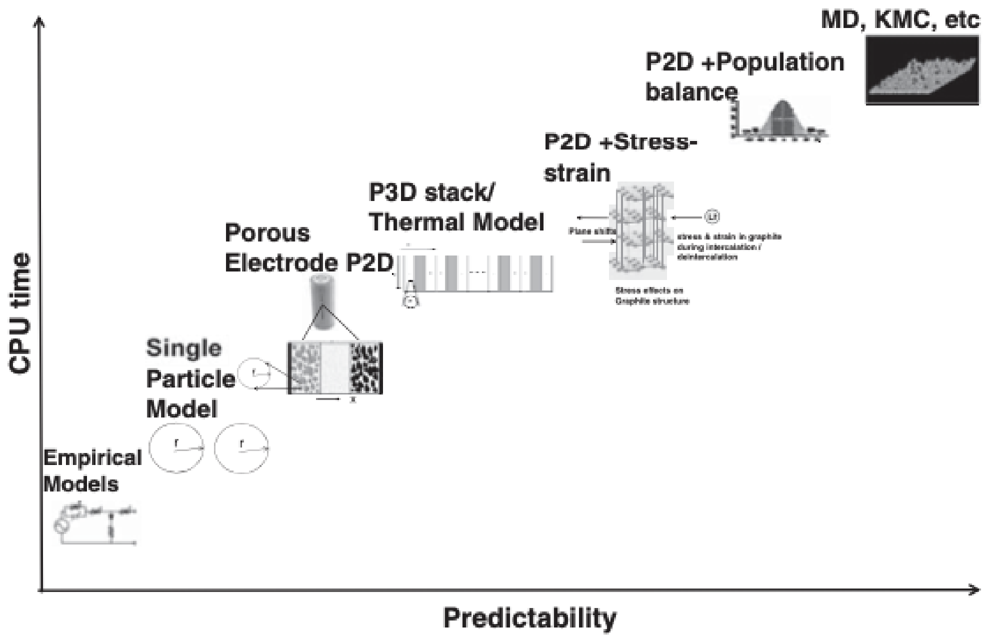
- Steps synchronized
- Steps enlarged



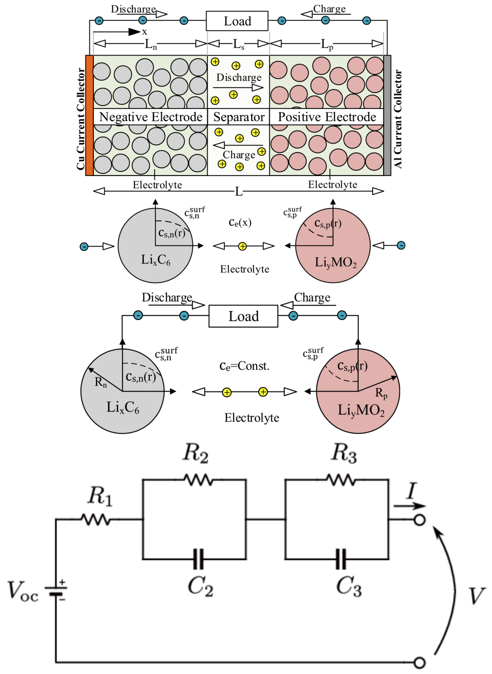


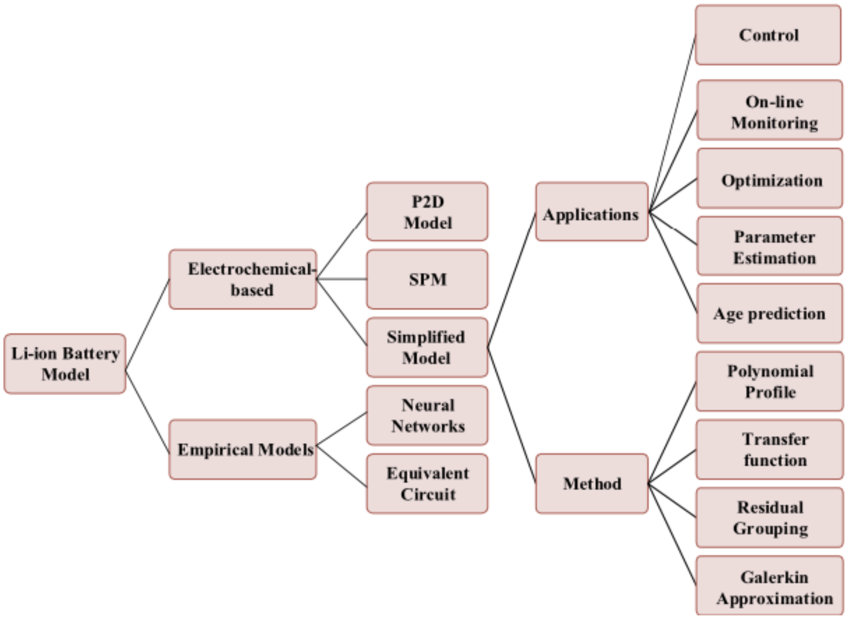
Battery Cell Modeling

- Empirical Models ⟶ Physical Models



Another Classification that Stays Close to Control and Monitoring

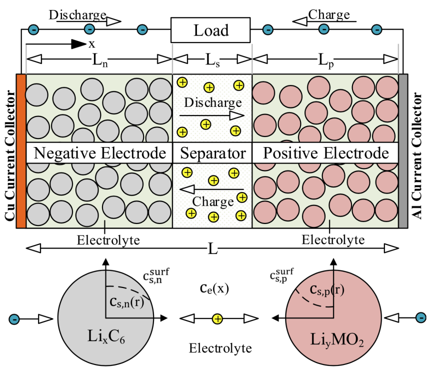




A Dive into the P2D (Doyle-Fuller-Newmann) Model

Describes the spatial state and evolution of:

- solid[2] electrolyte concentrations,
- Ion flows, and
- Potential.



$$\frac{\partial c_{s,k}(x,r,t)}{\partial t} = \frac{D_{s,k}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_{s,k}(x,r,t)}{\partial r}\right)$$

$$\varepsilon_k \frac{\partial c_{e,k}(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D_{eff,k}\frac{\partial c_{e,k}(x,t)}{\partial x}\right) + a_k(1-t_+)J_k(x,t)$$

$$\sigma_{eff,k}\frac{\partial^2 \Phi_{s,k}(x,t)}{\partial x^2} = a_k F J_k(x,t)$$

$$-\sigma_{eff,k}\frac{\partial\Phi_{s,k}(x,t)}{\partial x} - \kappa_{eff,k}\frac{\partial \Phi_{e,k}(x,t)}{\partial x} + \frac{2\kappa_{eff,k}RT}{F}(1-t_+)\frac{\partial \ln c_{e,k}}{\partial x} = I$$

$$J_k(x,t) = K_k(c^{max}_{s,k} - c^{surf}_{s,k})^{0.5}(c^{surf}_{s,k})^{0.5}c^{0.5}_{e,k}\left[\exp\left(\frac{0.5F\mu_{s,k}(x,t)}{RT}\right) - xp\left(-\frac{0.5F\mu_{s,k}(x,t)}{RT}\right)\right]$$

$$\mu_{s,k}(x,t) = \Phi_{s,k}(x,t) - \Phi_{e,k}(x,t) - U_k;\quad V_{cell}(t) = \Phi_{s,k}(0,t) - \Phi_{s,k}(L,t)$$

$$\varepsilon_k \frac{\partial c_{e,k}(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D_{eff,k}\frac{\partial c_{e,k}(x,t)}{\partial x}\right)$$

$$-\kappa_{eff,k}\frac{\partial\Phi_{e,k}(x,t)}{\partial x} + \frac{2\kappa_{eff,k}RT}{F}(1-t_+)\frac{\partial\ln c_{e,k}}{\partial x} = I$$

Examples of model packages with P2D and SPM model.

PyBAMM – Open Source models in Python.
COMSOL Multiphysics –