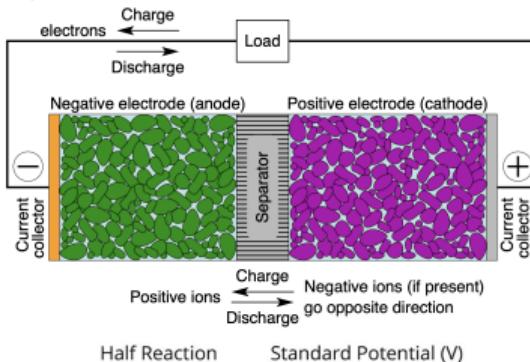


# Battery (equivalent circuit) models

Prof. Dr. Fabrizio Sossan

Slides compiled on: October 31, 2024

# Short recap of last class – Batteries

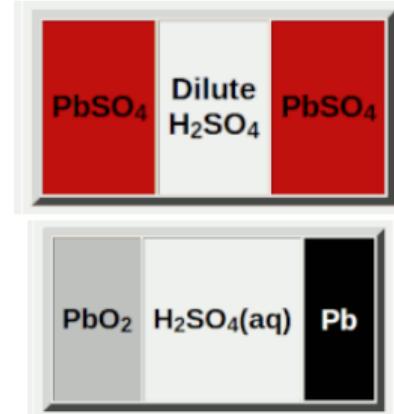
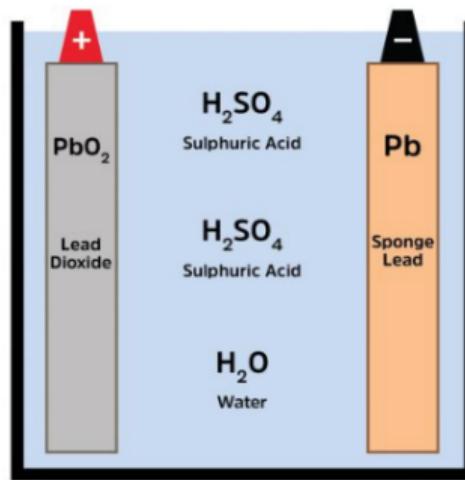


Half Reaction	Standard Potential (V)
$\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$	+2.87
$\text{Pb}^{4+} + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}$	+1.67
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.23
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	+0.80
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	+0.34
$\text{H}_2 + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.00
$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$	-0.13
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-0.44
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76
$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$	-1.66
$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$	-2.36
$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$	-3.05

- Batteries consist of 2 electrodes, a separator to keep them far apart, and an ionic conductor electrolyte.
- Batteries are realized by coupling an oxidizing element with a reducing element.
- Voltage levels are limited by the electrolyte, which decomposes when exposed to a large difference of potential (eg, 2 V for water-based electrolyte, as in lead-acid batteries)
- Higher voltage levels are achieved by combining cells in series

## Short recap of last class – Lead-acid batteries

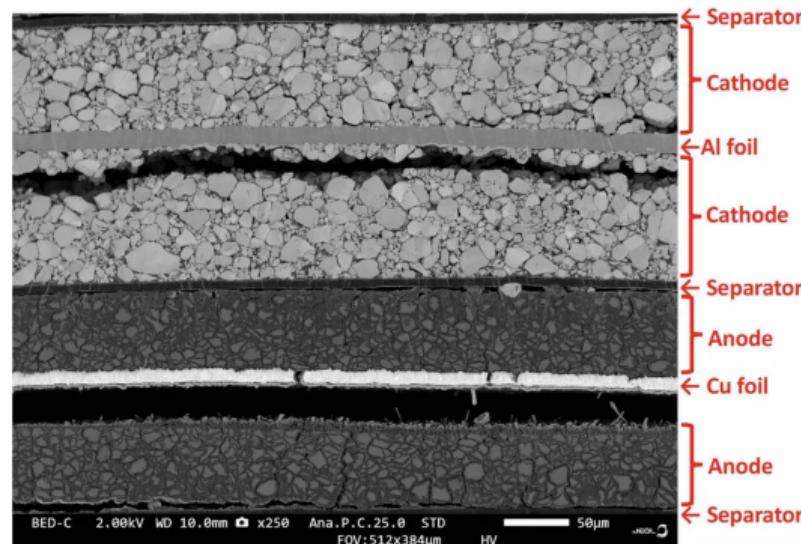
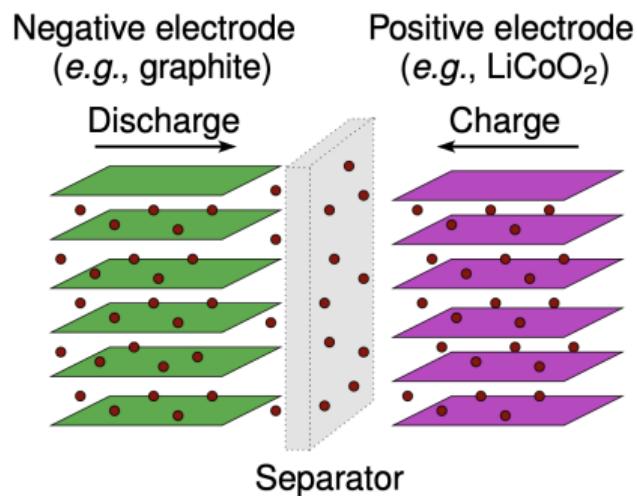
Tested, robust, to go choice in SLI applications and others.



Flip side: heavy (low specific energy density, Wh/kg), bulky (low volumetric energy density, Wh/L), poor life cycle due to extremely aggressive reaction, components are toxic.

## Short recap of last class – Lithium-ions battery

Lithium tends to form positive electrons (to be oxidized, OIL: oxidation is loss of electrons, that means it is a reducing element), losing electrons that can be made available to an external load.



## Short recap of last class – Lithium-ions battery (cont'd)

Discharge and charge reactions are made possible by transferring positive Li-ions between the electrodes. Electrodes host Li-ions in their crystalline structure. This process is known as intercalation and is extremely gentle compared to the redox reaction of lead-acid batteries, allowing for longer life.

Advantages: high-energy density, long cycle life, low self-discharge.

On the flip side:

- Very well capable to undercharge or overcharge, requiring dedicated chargers and specialized circuitry for monitoring.
- When overcharged or undercharged, parasitic reactions develop (some very poorly understood). Parasitic reactions' consequences range from loss of capacity (lithium is transformed into compounds which do not allow the formations of ions) to increase of internal resistance (and why this is bad, it will be evident today).
- Subject to thermal runaway and certainly a fire hazard. If mistreated (mechanical abuse, thermal abuse, electrical abuse), lithium cells can catch fire. Thermal runaway refer to the fact some parasitic reactions are exothermic, and that can lead to fire.

Example that something has happened ...



## Coulombic charge model for a lithium cell

For lithium-ion electrochemistries, the state of charge (SOC) can be approximated as:

$$SOC(t) = SOC(0) + \frac{1}{C_{nom}} \int_0^t i(\tau) d\tau$$

where  $C_{nom}$  is the cell energy capacity in Ah and  $i(t)$  is the charging current over time. The charging efficiency is large ( $\geq 0.99$ ) and can be omitted.

In discrete time:

$$SOC(t+1) = SOC(0) + \frac{\Delta_T}{C_{nom}} \sum_{\tau=0}^t i(\tau)$$

With abuse of notation, now  $t$  denotes the index of the discretized time interval with a step of  $\Delta_T$  in hours.

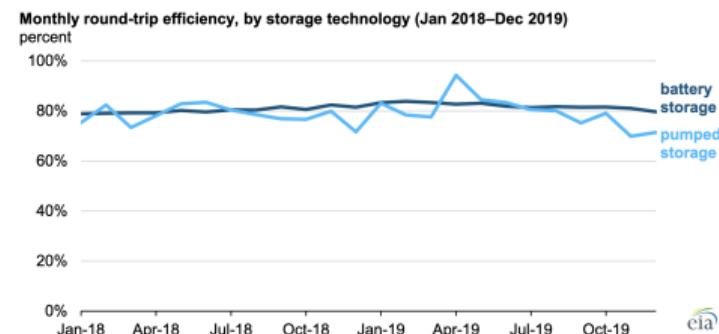
# Pending question from the last class

## Week 1:

$$SOC(t+1) = SOC(0) + \frac{\Delta_T}{E_{nom}} \sum_{\tau=0}^t \left( \eta [P(\tau)]^+ - \frac{1}{\eta} [P(\tau)]^- \right)$$

with  $[x]^+$  and  $[x]^-$  positive and negative part of  $x$ , respectively.

## Week 2:



## Week 8:

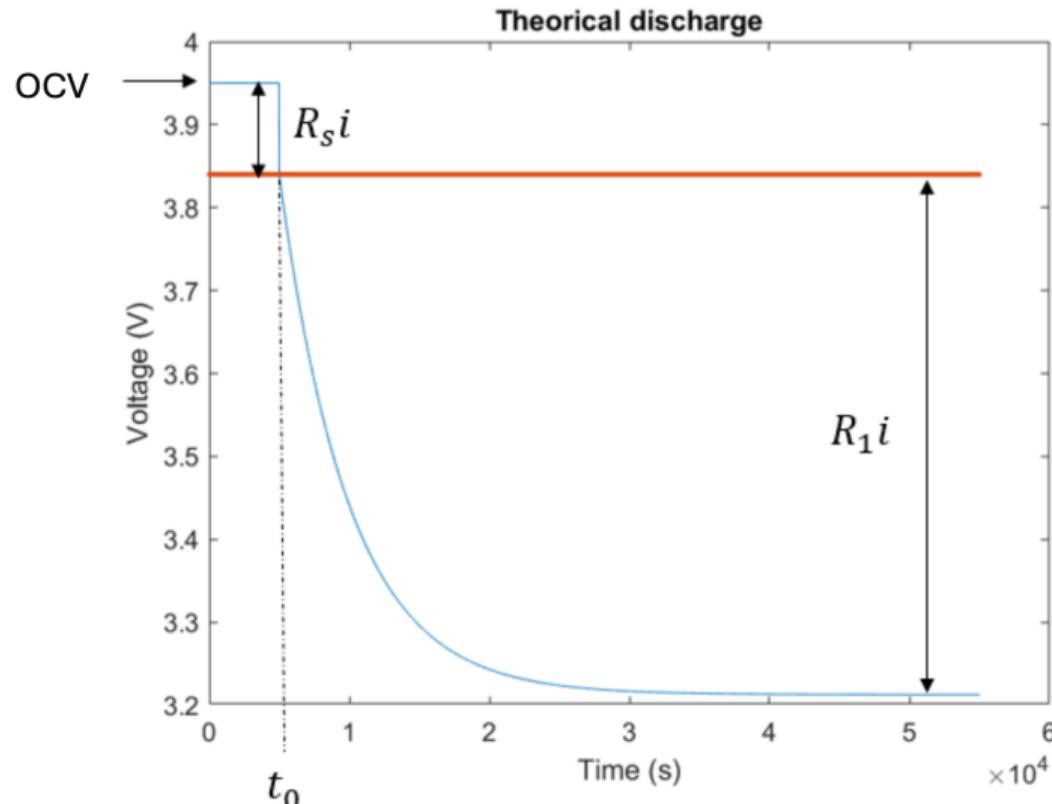
$$SOC(t+1) = SOC(0) + \frac{\Delta_T}{C_{nom}} \sum_{\tau=0}^t i(\tau)$$

Essentially, we are dropping the efficiency (which does not seem to be a good idea, because losses in physical systems are always there)... what's going on here?

## Modelling battery voltage

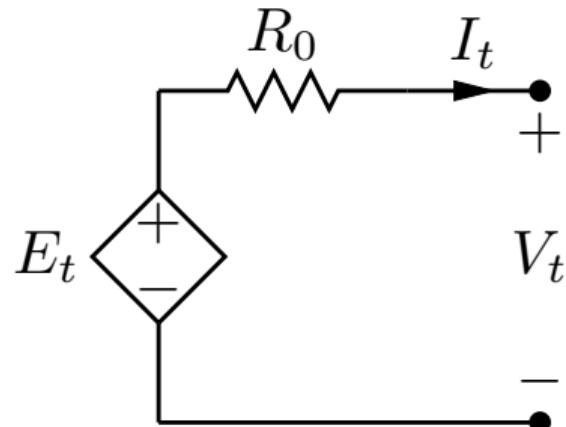
- Battery voltage reflects the concentration of Li-ions in the battery electrodes and electrolytes. As this concentration changes over time (eg, due to charge and discharge), voltage will also change.
- If one could model the interaction of each Li-ions particle within the battery, one could build a very detailed model of the voltage. Complex endeavor due to the many particles and interactions on three-dimensional (3D) surfaces (partial differential equations in time and space).
- Physical modeling of lithium-ion cells has been tackled with approximated models that simplify complex interactions in 3D space on 2D surfaces (pseudo 2D models), and single particle models, that assume that the electrodes (formed by a complex crystal structure) can be approximated as a single element.
- A (computationally tractable) alternative to physical models is Equivalent Circuit Models (ECMs). They (try to) describe the voltage of the battery as a function of the charging/discharging current, without however offering much interpretability of the parameters.
- Under certain assumption, ECM can be also derived from models such as the single-particle model.

# Voltage dynamics as a function of the charging/discharging current



# Equivalent circuit models

## ECM of battery cell: internal resistance



- $E_t$ : cell internal voltage
- $V_t$ : cell terminal voltage
- $I_t$ : cell current
- $R_0$ : cell resistance