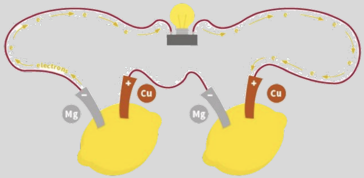
Battery Basics



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Nomenclature

The term "battery" is colloquially used to refer to an electrochemical energy source. A battery normally includes multiple elements:

- Cell: the smallest individual electrochemical unit; it delivers a voltage that depends on the cell chemistry.
- Module: a collection of cells installed in parallel or in series to achieve some design specifications in terms of voltage and current capacity.
- Pack: a collection of modules (and, possibly, sensors, protection systems, and battery management system).

Primary and secondary cells:

- A primary cell cannot be recharged
- A secondary cell is rechargeable

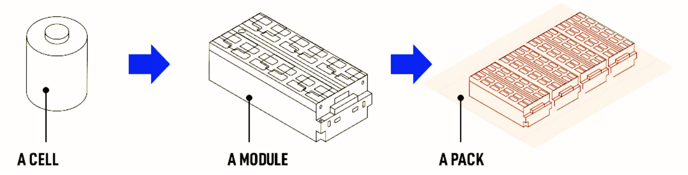
A (secondary) cell implements a chemical reaction that is capable of storing electricity into a chemical form and producing electricity from it when needed at a later stage.

Cell and battery packaging

Cylindrical

Pouch

Prismatic



Some examples of cell electrochemistries – Primary cells

- Alkaline

- Silver-Oxide (normally in a “button” format)
- Zinc-air

Some examples of cell electrochemistries – Secondary cells

- NiCd (nichel cadmium)
- Lead acid
- NiMH (nichel-metal hydride)
- NiZn (nichel zinc)
- Lithium ion. Many variants: LiPo (lithium-ion polymer), $LiFePO_4$ (lithium iron phosphate), NMC (nickel manganese cobalt), etc.

Different electrochemistries imply not only different performance or attributes but also different system requirements (e.g., sensor, software, battery management systems, thermal management, etc).

Cell (and battery) attributes

- Cell nominal voltage: it depends on the implemented electrochemistry. Eg, lead-acid cells deliver around 2 V, lithium-based electrochemistry over 3 V.

- Cell nominal capacity (Ah, Ampere-hour): it denotes the quantity of charge that the battery is rated to hold. Eg, a 1 Ah battery can deliver 1 Ah before being totally discharged.

- C rate: it is is a relative measure of the cell current. It is defined as:

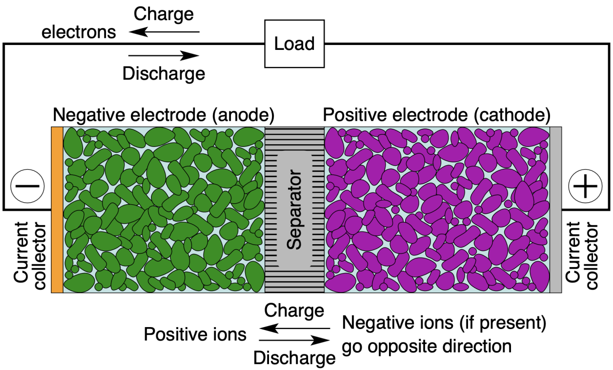
$$\text{C rate current} = \frac{\text{Cell current (A)}}{\text{Cell capacity (Ah)}}$$

  Example: the discharging current of a 20 Ah cell that discharges at a rate of "2C" is 40 A; assuming it is fully charged, it will be totally discharged in 30 minutes.

Cell (and battery) attributes – cont'd

- Connection of cells in series increases the voltage (as per Kirchhoff voltage law).
- Connection of cells in parallel extends the capacity.
- Connections in series and parallel are indicated with the nomenclature "sXpY", where X is the number of cells in series and Y is the number of parallel branches.
- Connection can be implemented within an unit (as in 12 V car batteries) or externally (as in the EPFL's battery system we've visited).
- The energy storage capacity in Wh is given by the cell nominal voltage times the cell capacity.
- The cell power in Wh is the cell current times the nominal voltage.
- Under the same current-to-power parallel, the notion of C-rate can be seen as the ratio between the power and energy capacity.

Cell components



4 components: electrodes (1-negative and 2-positive), 3-separator, and 4-electrolyte

Cell components (cont'd)

1- Positive electrode:

- During discharge, accepts electrons from circuit, is reduced ([1]).
- During charge, gives up electrons to external circuit, is oxidized.

2- Negative electrode:

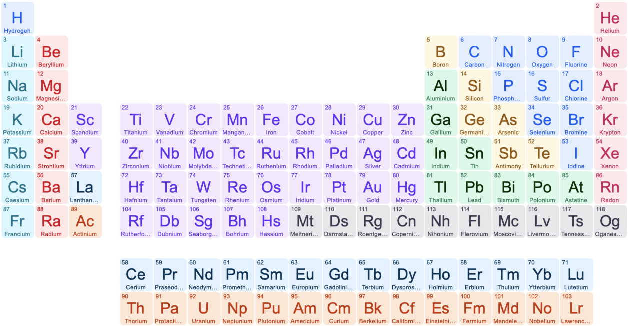
- During discharge, gives up electrons to external circuit, is oxidized.
- During charge, accepts electrons from external circuit, is reduced.

3- Electrolyte: a solvent which allows the transit of positive ions and electronic insolator to avoid self discharge.

4- Separator: it maintains the electrodes apart, avoiding short circuits and self discharge.

[1] **OIL RIG**: Oxidation Is Loss, Reduction Is Gain (of electrons).

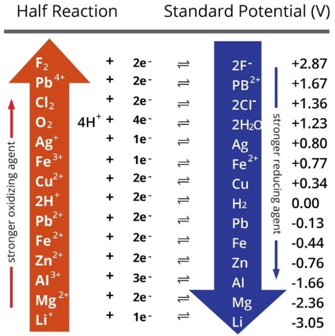
Oxidation and Reduction



$\longleftarrow$ **Reducing elements** **Oxidizing elements** $\longrightarrow$

- Each table's period corresponds to a different electron shell.
- From left to right, elements progressively fulfil their outer shell with 1 one more electron, until completion (noble gases, inert).
- Elements with incomplete shells are "reactive", tending to form covalent bonds with other elements, or create ions.

Which material for battery cells? Electrochemical series



The standard electrode potential (E^o) is the measure of an electrode's potential (ie, voltage difference) with respect to a standard hydrogen electrode. It allows us to determine the relative strengths of oxidizing and reducing agents.

An electrochemical series lists the electrode potentials of different elements.

By selecting elements on the table's top and bottom as positive and negative electrodes, one could create a battery cell with a voltage given by the difference of the two standard potentials.

In the table above, combining fluorine and lithium would achieve 5.92 V. Although higher voltage is desiderable (why?), electrolytes decompose at high voltages due to electrolysis. Eg, acquous-based electrolytes have a voltage limit of around 2 V.

Intuition behind the charging/discharging process

- By composing one electrode with an oxidizing compound and another with a reducing compound within a ionic conducting electrolytes, a voltage is formed across the electrodes.
- The separator among the electrodes and the electronic insulating electrolytes prevent the reaction to happen.
- Once an external load is connected, electron flows and generating electricity; the reaction finally happens.
- Energy is released (or restored, when charging) by the atoms involved in the reaction, that change their energy level by releasing and gaining electrons.

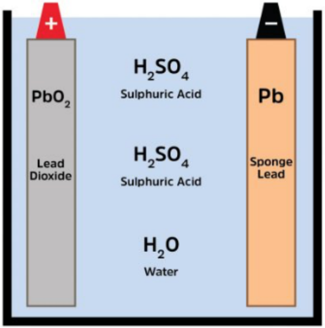
Examples of electrochemistries: lead acid and lithium ions

Lead-acid battery

- Tolerant to abuse, tried & tested widely, and low cost.
- To-go technology for Starting, Lighting and Ignition (SIL) of conventional vehicles, auxiliary supply in trains, Uninterruptible Power Supply (UPS), sometimes grid applications ...
- Bulky, heavy, and small life cycle.
- Lead is toxic and improper disposal can be hazardous to the environment.

Lead-acid battery – Components

- Negative plate: Lead (Pb).
- Positive plate: Lead dioxide (PbO_2).
- Electrolyte: Aqueous sulphuric acid (H_2SO_4) and water (H_2O).
- Cell voltage: 2 V
- Larger voltage achieved by adjacent cells in series.



Lead-acid battery – Reaction

Redox (reduction-oxidation) reaction. Discharging reaction:

Negative pole

$$Pb + HSO_4{}^- \longrightarrow PbSO_4 + H^+ + 2\,e^-$$

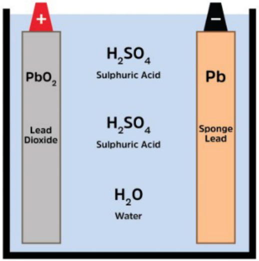
Positive pole

$$PbO_2 + HSO_4 + 3\,H^+ + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O$$

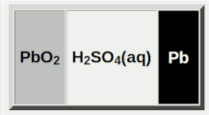
Total reaction

$$Pb + PbO_2 + 2\,H_2SO_4 \longrightarrow 2\,PbSO_4 + 2\,H_2O$$

Inert lead sulfate ($PbSO_4$) forms on both electrodes.

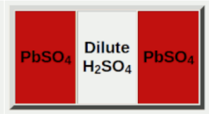


Lead-acid battery – Fully charged and discharged states



Fully charged

Overcharging might cause water evaporation in the electrolyte; non-sealed lead-acid batteries can be refilled.



Fully discharged

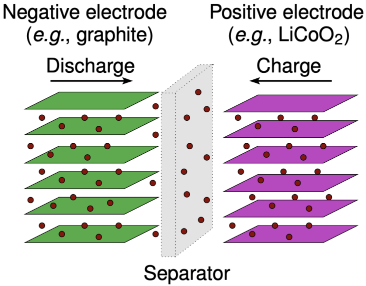
Not harmful per se. However, incomplete recharging might lead to loss of performance due to permanent formation of lead sulfate (sulfation).

Lead-acid battery – Final remarks

- Extremely aggressive reaction that brings to the formation of new compounds ($\rightarrow$ different principle that lithium-ion cells, which are based on the notion of intercalation of lithium-ions into a predefined crystal lattice).
- Degradation occurs due to the loss of active material (Pb).
- Irregular growth of newly formed compounds can lead to "dendrites", which are metallic formation on the electrolytes.
- Accumulated lost material and dendrites can lead to battery failure if they short circuit the electrodes.

Lithium-ion battery

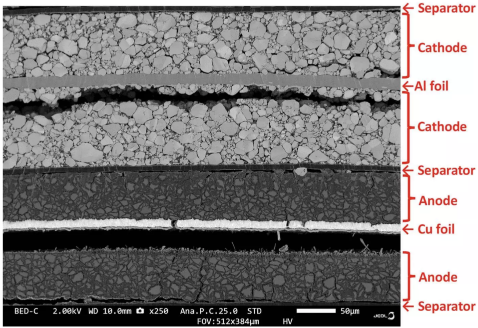
Lithium-ion cell: intercalation [ECE4710]



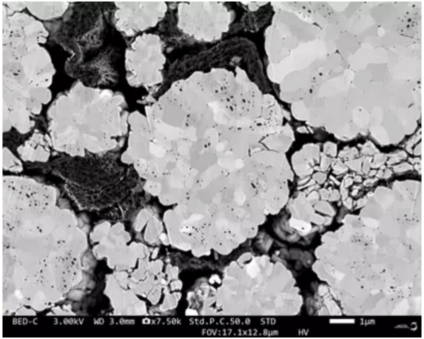
- Lithium-ions do not rely on a redox reaction but on a process called "intercalation".
- In the intercalation process, positively charged lithium-ions (Li^+) are exchanged between two "porous" electrodes, which host them in crystalline lattice.
- Electrodes have two properties: i) open crystal structure capable of hosting lithium atoms in vacant spaces; ii) capability of accepting electrons so that they can recombine with the lithium-ions.
- In the electrodes, electrons recombine with Li^+ to form lithium.

Lithium battery's inside

Battery electrodes are not a continuum material but are composed of millions of small particles. The larger the surface of these particles, the more surface is available for ions/electrons to leave and enter, and the smaller the resistance.



Scanning Electron Microscope image of Cross sectioned battery layers, JEOL USA Blog.



Detail of one electrode.

Lithium-ion cell: intercalation [..], cont'd

During **discharge**, Li-ions are dissociated from the negative electrode, migrate across the electrolyte, and are inserted into the crystal structure of the positive electrode. At the same time, compensating electrons traverse the external circuit and are accepted by the positive electrode to balance the reaction.

Within the electrode, Li atom's electron is loosely shared with neighboring atoms. Li is not tightly bonded in one place and is actually quite free to move around.

Lithium enters the surface of the electrode particles, but diffuses inward to equalize the concentration of lithium in the electrode.

It is helpful to visualize lithium (ions) in the electrodes as water would diffuse in a sponge.

Intercalation mechanism is much less aggressive than reactions happening in other batteries; contributing to

Lithium-ion cell: examples of materials

- Negative electrode: most common is Graphite (C_6), Lithium-Titanate-Oxide (LTO).
- Positive electrode: Lithium-Cobalt-Oxide (LCO), Nickel-Manganese-Cobalt (NMC), Lithium-iron-phosphate (LFP).
- Electrolyte: organic solvent + lithium salt. Do not take part in the reaction. Different electrolytes have different properties in terms of degradation and conductivity.
- Separator: permeable membrane with holes sufficiently large for letting Li-ions pass through, but small enough to separate electrodes compounds effectively. It is also an electronic insulator.

On lithium availability: according to the back-of-the-envelope calculations proposed in [ECE4710], lithium demand for satisfying global demand of electric cars is approx. 10'000 tons vs. available supply of 200 billion tons.

Additional resources

- [ECE4710] Chapter 1 of Course ECE4710/5710 by Gregory Plett at University of Colorado, Colorado Springs (which inspired part of the material shown in this class).
- More on electrochemical series.

Coulombic charge model

Coulombic model of the state of charge (or Coulombic counter)

For lithium-ion electrochemistries, the state of charge (SOC) can be modelled 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 (≥ 0.99) and can be omitted.

Self-assessment of understanding

- What's the role of the electrolyte in a battery cell?
- On what depends the (nominal) voltage of a battery cell?
- Where are reducing elements in the periodic table?
- What is OIL RIG?
- Provide an elementary explain of the intercalation principle.
- What's the difference (in terms of input required for the computation) between the Coulombic model of the state of charge and the model seen in the first week of course?