Some General Concepts of Battery Electrochemistry and Their Relation to Equivalent Circuit Models

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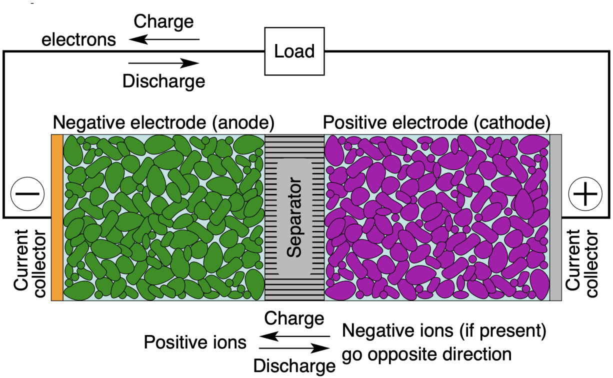
Battery cell components



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

Battery cell components (cont'd)

1- Positive electrode:

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

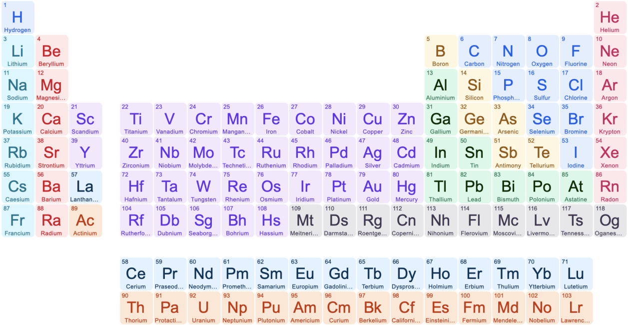
2- Negative electrode:

- 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.

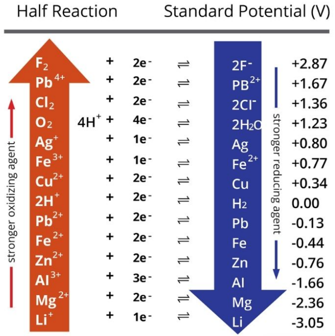
Oxidation and Reduction



⟵ **Reducing elements** **Oxidizing elements** ⟶

- 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



Half Reaction	Standard Potential (V)
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Pb^{4+} + 2e^- \rightleftharpoons PB^{2+}$	+1.67
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05

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.

Nerst equation under non-standard equation (and cell equilibrium)

Assuming a resting cell and with no current (equilibrium), Nerst equation can be used to compute the voltage under non-standard cell conditions:

$$E = E^\circ - \frac{RT}{zF} \ln \left(\frac{a(Red)}{a(Ox)} \right)$$

where

- R is the ideal gas constant
- T is the temperature in kelvins
- F is the Faraday's constant
- n the number of electrons exhanged in the reactions
- $a(\cdot)$ is the so-called activity of the compounds, which reflects the concentration of the reactants
- $E^0 = E^0_{cathode} - E^0_{anode}$ is cell voltage in standard conditions (tabulated and known, so called standard series)

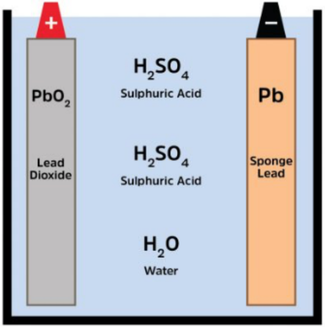
Examples of electrochemistries: lead acid and lithium ions

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

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

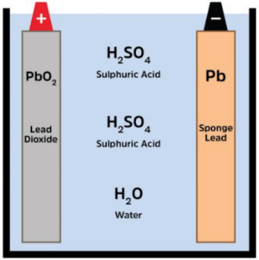
Positive pole

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

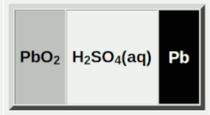
Total reaction

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

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

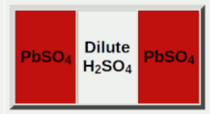


Lead-acid battery – Fully charged and discharged states



Fully charged

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



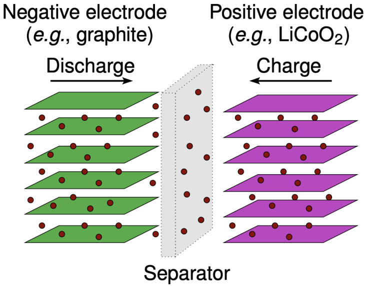
Fully discharged

Overdischarge might not be 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.

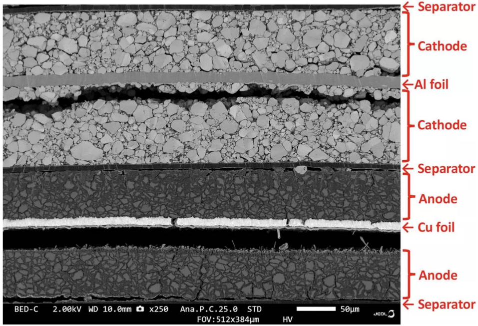
Lithium-ion cell: intercalation [ECE4710]



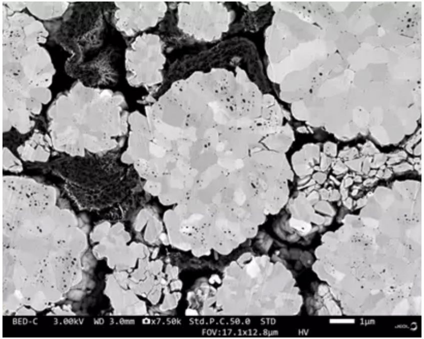
- Lithium-ions do not rely on a redox reaction but on a process called "intercalation".
- In the intercalation process, positively charged lithium-ions (Li^+) are exchanged between two "porous" electrodes, which host them in crystalline lattice.
- Electrodes have two properties: i) open crystal structure 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.

Inside a lithium-ion battery's

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 less ageing.

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.

Explaining battery voltage

Voltage during the non-equilibrium conditions

Nerst potential is valid at equilibrium (cell is resting, and current is zero).

During non-equilibrium, the cell voltage is

$$V_{cell} = E - e_{\mathrm{act}} - e_{\mathrm{ohm}} - e_{\mathrm{conc}}$$

where the terms $e_{\mathrm{act}}, e_{\mathrm{ohm}}, e_{\mathrm{conc}}$ reflects ‘voltage disturbances’ that occur due to kinetics, transport of ions, and ohmic losses.
During non-equilibrium, the cell voltage thus drifts away from the Nerst voltage.

Voltage during the non-equilibrium conditions (cont'd)

- Activation: reflects the extra work needed to make the reaction to happen.
- Ohmic: ionic/electronic resistance in electrolyte, electrodes, collectors, contacts.
- Concentration: concentration gradients near the interface because ions are produced at a faster rate at which they are transported between the cell electrodes (mass transport limits).

Intuition behind voltage dynamics

- Short (ms–s): electrons readjusts within the electrodes, and chemical kinetic of the reaction office (simply put: a chemical reactions might take time of apply).

- Intermediate (s–min): ion transport limitations create interfacial depletion/accumulation $\Rightarrow \eta_{\mathrm{conc}}$.

- Long (rest): diffusion (mass transport due to different concentration of ions within the electrodes) smooths gradients; voltage relaxes back towards Nerst (non-equilibirum potential).

Final notes

- Main reactions are in condensed phases (no gas), so pressure does not enter Q or E_{eq} in normal operation.
- Transient voltage differences largely reflect activation, ohmic, and concentration rather than a change in Nernst potential.
- Long-term voltage variations depend on SOC variations and affects modified Nerst potential (different concentration)xs

→ Equivalent circuit models allow us to represent all these electrochemical effects, without explicitly modeling the underlying physical or chemical processes. They reproduce the observed behavior (voltage response, dynamics, impedance) rather than the mechanistic details.

In this sense, they are a grey-box modeling approach, capturing the effect rather than the cause — a concept you may already know from other courses.