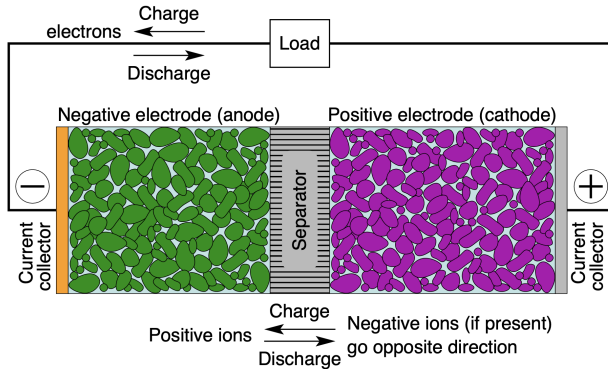


Some General Concepts of Battery Electrochemistry and Their Relation to Equivalent Circuit Models

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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 insulator to avoid self discharge.

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

Oxidation and Reduction

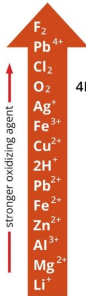
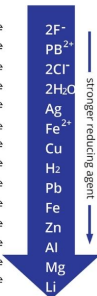
1 H Hydrogen																	2 He Helium						
3 Li Lithium	4 Be Beryllium																	5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium																	13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton						
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon						
55 Cs Caesium	56 Ba Barium	57 La Lanthanum	58 Hf Hafnium	59 Ta Tantalum	60 W Tungsten	61 Re Rhenium	62 Os Osmium	63 Ir Iridium	64 Pt Platinum	65 Au Gold	66 Hg Mercury	67 Tl Thallium	68 Pb Lead	69 Bi Bismuth	70 Po Polonium	71 At Astatine	72 Rn Radon						
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson						
58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium										
90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium										

← 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)
 $\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$	+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
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	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
	

The standard electrode potential (E°) 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 desirable (why?), electrolytes decompose at high voltages due to electrolysis. Eg, aqueous-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:

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

where

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

Examples of electrochemistries: lead acid and lithium ions

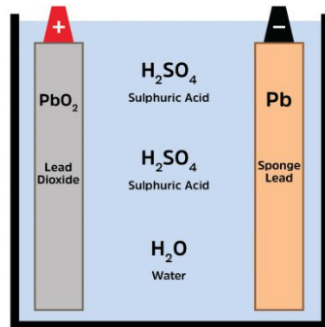
Lead-acid battery

- Tolerant to abuse, tried & tested widely, and low cost.
- To-go technology for Starting, Lighting and Ignition (SLI) 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

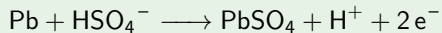
- Negative plate: Lead (Pb).
- Positive plate: Lead dioxide (PbO_2).
- Electrolyte: Aqueous sulphuric acid (H_2SO_4) and water (H_2O).
- Cell voltage: 2 V
- Larger voltage achieved by adjacent cells in series.



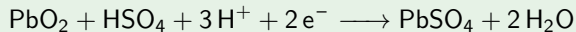
Lead-acid battery – Reaction

Redox (reduction-oxidation) reaction. Discharging reaction:

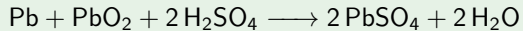
Negative pole



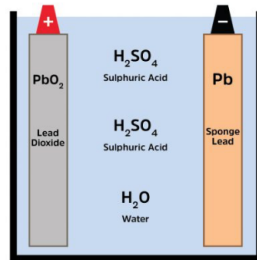
Positive pole



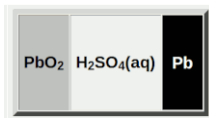
Total reaction



Inert lead sulfate (PbSO_4) forms on both electrodes.

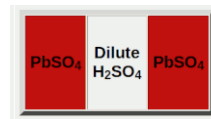


Lead-acid battery – Fully charged and discharged states



Fully charged

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



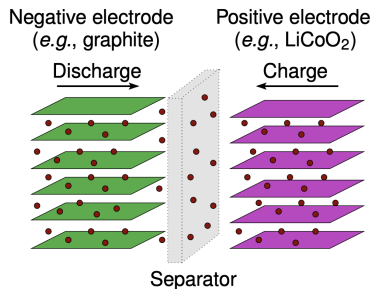
Fully discharged

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 (→ different principle than 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 formations on the electrolytes.
- Accumulated lost material and dendrites can lead to battery failure if they short circuit the electrodes.

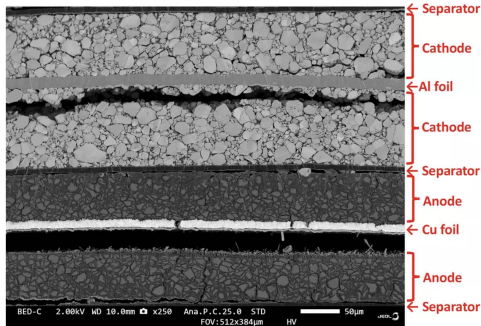
Lithium-ion cell: intercalation [ECE4710]



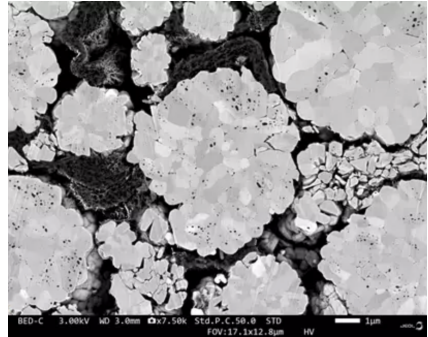
- Lithium-ions do not rely on a redox reaction but on a process called “intercalation”.
- In the intercalation process, positively charged lithium-ions (Li^+) are exchanged between two “porous” electrodes, which host them in crystalline lattice.
- Electrodes have two properties: i) open crystal structure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

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

where the terms e_{act} , e_{ohm} , e_{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 $\Rightarrow \eta_{\text{conc}}$.
- Long (rest): diffusion (mass transport due to different concentration of ions within the electrodes) smooths gradients; voltage relaxes back towards Nerst (non-equilibrium 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 Nernst 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.