**Batteries**
**ACME Faculty, EHVE course**
**B.Sc. Studies, III year, V semester**
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## Lead-acid batteries

## Rechargeable batteries types

Among the most popular rechargeable batteries technologies are:

- Lead-acid (Pb-acid)
- Nickel-Cadmium (Ni-Cd)
- Nickel-Metal Hydride (Nickel-Hydride) (NiMH)
- Lithium-ion (Li-ion)



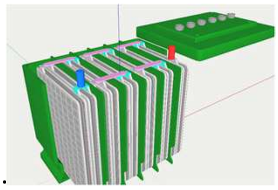
## Lead-acid batteries

Invented by Gaston Plante, French physicist, in 1859. Until the beginning of XX century there was no other industrial solution that allowed for the galvanic cell to be of the multiple use.



## Lead-acid batteries

$Pb|H_2SO_{4(aq)}|PbO_2,Pb$



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Reactions at the electrodes:

$$Pb \rightleftharpoons Pb^{2+} + 2e^-$$

$$PbO_2 + 4H_3O^+ + 2e^- \rightleftharpoons Pb^{2+} + 6H_2O$$

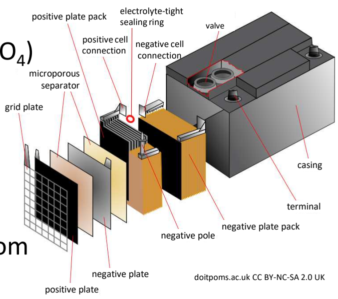
Total reaction:

$$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O$$



## Lead-acid batteries: structure

- lead oxide plate ($PbO_2$, not $PbO$ or $Pb_3O_4$)
- separator
- electrolyte ($H_2SO_{4(aq)}$)
- lead plate

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Both plates are made from active material in form of paste with additives pressed onto the metal lead grid (usually lead-antimony alloy) and then dried



## Lead-acid batteries

Due to their design, traditional lead-acid batteries require maintenance on the regular basis.

During operation, water amount inside decreases (vaporizes, undergoes electrolysis to hydrogen) just as sulfuric acid is consumed in reactions (only in those irreversible, but these are always taking place at least as side-reactions). Sulfates particles from plates/grids are settling after time. That is why batteries require water addition and/or exchange of sulfuric acid. Battery works properly only in the narrow acid concentration range (usually provided as a density, as it is directly related to concentration in case of sulfuric acid). Due to the design with valves on top as well as liquid content, battery should not be kept upside down or even tilted.

## Lead-acid batteries: variants

Maintenance-free batteries types (also nothing happens to them when tilted/rotated upside down):

- **MF** – Maintenance-Free;
- **VRLA** (SLA) – Valve-Regulated Lead-Acid (Sealed Lead-Acid) – with one-way safety valves;
- **AGM** – Absorbed Glass Mat (separator is made of glass fibers);
- **GEL** – with gel electrolyte.

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## Lead-acid batteries: variants

Maintenance-free batteries:

- **MF** – has large extent of electrolyte - does not need refill. However, it has smaller energy density;
- **VRLA** – properly sealed and with decreased working potential, so it does not allow water electrolysis; additionally, lead-calcium alloy is used (instead of typical lead-antimony), so hydrogen evolution overpotential is increased (and thus, less possible);
- **AGM** – similar to VRLA; also: uses glass fiber separator (instead of typical PE), however it is more expensive than typical ones (but it makes hydrogen evolution and vaporization harder);
- **GEL** – uses gel electrolyte (hinders vaporization).

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## Lead-acid batteries: modifications

- There are multiple variants of battery resulting from electrolyte, separator, grid and general design modifications.
- Electrodes modifications:
  - porosity modifiers (enhancing soakability, reaction surface -> current density, decreasing passivation effect);
  - reactions overpotential decreasing additives;
  - changing of paste structure and/or additives changing activation energy of lead oxide reaction with sulfate; additives promoting proper structure of oxide forming on the electrode (the most important issue is capacity fade due to the non-active particles/crystallites formation).

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## Lead-acid batteries: pros and cons

**Pros:**

- slow self-discharge;
- cheap;
- tolerates partial charging and discharging;
- tolerates impulse discharge (short, high rate/C) (that is why they are great for engine ignition).

**Cons:**

- 200-300 cycles only; VRLA/AGM can do more, but 800 max;
- contains very toxic lead and sulfuric acid;
- poorly works after deep discharge (can't work below 2.1 V);
- low energy density – 30 Wh/kg (results from lead and its compounds high density and low voltage of a single cell).

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## Lead-acid batteries: operating conditions

- Optimal operation temperature 20-25°C, storage or operation at temperature higher by 8-10°C halves cell's life (by each 8-10°C);
- Cycling in 2.1 V(or even 2.2 V)-2.4 V range. Do not discharge below 2.1 V as it can damage the cell. Charging above 2.4 V accelerates hydrogen evolution;
- Charging and discharging in C/10 to C/20 range, however it withstands impulses to ca. 5C (ignition requires 100-200 A and batteries have 30-60Ah);
- Need to be stored in charged state.

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## Lead-acid batteries: operating conditions

Charging/discharging state can be measured through a electrolyte density (apart from the voltage of course). Electrolyte participates in electrode reactions that change its concentration and its density (change of concentration of heavy sulfuric acid to in light water). Charged battery contains $40\%_{weight}$ sulfuric acid which is ca. 1.3 g/cm$^3$. Discharged battery contains $15\%_{weight}$ sulfuric acid which is ca. 1.1 g/cm$^3$.

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## Lead-acid batteries: operating conditions

Due to the ease and absolute nature of density measurement there are tabulated values (density-concentration) and dedicated devices for sulfuric acid density measurement for measuring its concentration. That combined with the initial value (of charged battery) yields the charged state.

This method works only for traditional design, where actually is water solution of sulfuric acid inside and there is physical access to it (so it is useless with „maintenance”-free”, gel and AGM).

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## Lead-acid batteries: operating conditions

Typical reasons for flaws leading to permanent damage or at least big capacity fade:

- sulfation of electrode and/or sulfate particles disconnection with electrodes and settling;
- self-discharge (microcells, spontaneous reactions);
- short circuits resulting from dendrites growth;
- electrolyte separation – by density/concentration (different reactions and rates depending on the altitude inside);
- electrodes cracking;
- grid corrosion;
- too big amount of gas inside (plates cracking due to the pressure, bubbles formation leading to microcracks, *etc.*);

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## Lead-acid batteries: applications

- Energy source for ignition in internal combustion engines (as well as for car internal devices);
- Traction battery for forklifts, small vehicles like electric wheelchairs, golf carts, e-bikes, e-scooters, *etc*.
- UPS, emergency power supplies in buildings, for critical infrastructure (power grid, telecommunications, hospitals);
- Stabilizing systems for power grid (frequency regulation, voltage support, peak shaving, *etc*.).

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