## **Energy Storage: Batteries**

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## **Energy Storage Technologies**

### □ Can be categorized as:

#### Mechanical:

- Flywheel;
- Pumped hydro;
- Compressed air.
- Electrochemical:
  - Batteries.

#### **Electrical:**

- Supercapacitors;
- Magnetic superconductors.

### Chemical:

- Fuel cells.
- Other technologies

### Compressed air energy storage





- Electrochemical devices
- Potential difference between two different metals submerged in an electrolyte solution
- Potential difference enables generation of the electrical energy
- Chemical energy is converted to electrical energy by an electrochemical process – therefore, batteries have efficient energy conversions



- Primary or non-rechargeable cannot be recharged after a single discharge cycle
  - Zinc-carbon
  - Zinc-chloride
  - Alkaline
  - Silver-oxide based
- Secundary or rechargeable capable of performing multiple charging/discharging cycles



#### Reserve batteries

- They need to be activated as one key component is isolated from the rest of the battery
- Therefore, there is no self-discharge and battery can be in stand-by for a long period of time
- Usually the electrolyte is isolated
- Thermal battery not active until heated, which causes solid electrolyte to melt and become conductive for ions
- Reserve batteries are designed to endure long and extreme conditions, which is hard and expensive to achieve with active batteries
- They are used in torpedos, rockets and other weapons where high power must be delivered in short time period, but also, for instance, in airplane life jackets



- Positive electrode:
  - electrode with higher standard electrode potencial
  - reduction or electron acceptance occurs during discharge
  - oxidation or electron release occurs during charge
- □ Negative electrode:
  - electrode with lower standard electrode potencial
  - oxidation or electron release occurs during discharge
  - reduction or electron acceptance occurs during charge
- Electrolyte substance that enables ion flow between the two electrodes
- Separator membrane that is immersed into electrolyte and used to mechanically separate electrodes



- Anode electrode where the oxidation occurs
- Cathode electrode where the reduction occurs
- Non-rechargeable batteries:
  - positive electrode is cathode and negative electrode is anode
- Rechargeable batteries:
  - positive electrode is cathode during discharge and anode during charge
  - negative electrode is anode during discharge and cathode during charge
  - positive electrode and cathode, as well as negative electrode and anode, are not synonyms

### **Batteries - example**

### □ Structure of a lithium-ion battery







- Charging: electrical energy from the grid is stored in the battery in the form of chemical energy
- Disharging: chemical energy from the battery is injected into the grid in the form of electrical energy
- Outer electrical flow: electrons use the outer circuit through the grid, in order to move between the electrodes
- Inner ion flow: ions use the inner flow to move between the electrodes, either through the electrolyte (passive electrolyte) or to be stored from the electrodes to the electrolyte (active electroylte)



- Battery can be made of a single cell or multiple cells
- Battery cell is the smallest separable battery part which constitutes out of active parts (electrodes, electrolyte with separator)
- Cell voltage is determined by the electrochemical characteristics of the material, while capacity is determined by the size of the cell (electrode surface, amount of electrolyte...)
- Connecting multiple cells in series and/or in parallel results in a battery with higher voltage and/or capacity, respectively



- In case of large batteries, several electrically connected cells that are enclosed in a mechanical frame are called battery module
- Mechanical frame of the battery module protects the cells against impacts, heat and vibrations
- Several modules constitute a battery or a battery pack
- Battery pack connects modules electrically and uses battery management system (BMS) to supervise, control and protect them



Battery pack in BMW i3 consists of 96 cells, 12 cells being connected into a module and 8 modules to a pack



## Capacity of a Battery

 $\Box$  The battery capacity in Ah at 25° is given by:

$$C(t) = \frac{kC_n}{1 + \alpha \left(\frac{|I_{bat}(t)|}{I_n}\right)^{\beta}}$$

where  $k, \alpha, \beta$  are model parameters,  $C_n$  is the rated battery capacity,  $I_n$  is the discharge current corresponding to  $C_n$  and  $I_{bat}$  is the current flowing through the battery.

# State of Charge (SoC)

The SoC is an indicator of the electrical charge stored in the battery (0 < SoC < 1, usually expressed in %):

$$SoC(t_i) = SoC(t_0) + \frac{1}{C(t_i)} \int_{t_0}^{t_i} \eta I_{bat}(\tau) d\tau$$

where  $\eta$  is the charging/discharging efficiency and  $I_{bat}$  is the current through the battery. ( $I_{bat}$  positive during charging and negative during discharging).

If  $I_{bat}$  = constant:

$$SoC(t_i) = SoC(t_0) + \frac{\eta \times I_{bat} \times (t_i - t_0)}{C(t_i)}$$

# Depth of discharge (DoD)

The depth of discharge (DoD) is defined as:

 $DoD = \frac{Capac.discharged from full charged battery}{battery nominal capacity}$ 

- The DoD is the complement of SoC: as one increases, the other decreases;
- For example, if a 100 Ah battery is discharged for20 min at a current of 50 A:

$$DoD = 50 \times \frac{20}{60} \times \frac{1}{100} = 16.7 \%$$

Some manufacturers specify maximum DoD for better performance



- **Types of batteries:** 
  - Lead-acid
  - Nickel-cadmium
  - Nickel-metal-hydride
  - Lithium-ion
  - Zinc-air
  - Vanadium redox (flow battery)



- Two lead plates (electrodes) immersed in sulfuric acid (electrolyte)
- At 100% SOC:
  - negative electrode consists of metallic lead (Pb)
  - positive electrode consists of lead dioxide (PbO<sub>2</sub>)
  - electroyte is concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)
- During discharge:
  - both plates gradually transition into lead sulfate (PbSO<sub>4</sub>)
  - sulfuric acid becomes ever sparser and finally transitions to water (0% SOC)



- Two lead plates (electrodes) immersed in sulfuric acid (electrolyte)
- □ At 0% SOC:
  - both plates are lead sulfate (PbSO<sub>4</sub>)
  - electrolyte is water
- During charge:
  - lead sulfate (PbSO<sub>4</sub>) on positive electrode oxidises to lead dioxide (PbO<sub>2</sub>)
  - lead sulfate (PbSO<sub>4</sub>) on negative electrode reduces to metallic lead (Pb)
  - electrolyte becomes concentrated sulfuric acid



- In lead-acid batteries, electrolyte participates in chemical reactions when charging/discharging and its density may be used as a SOC measure
- Admixtures are often added to lead electrodes in order to improve their characteristics, e.g. antimony, calcium, tin and selenium
- One of the basic development directions of lead-acid batteries is adding carbon based materials to the negative electrode in order to reduce sulfation, increase conductivity and charge acceptance

## Sulfation

Sulfation is a build-up of lead sulfate crystals and is a major cause of battery failure in leadacid batteries.





- High reliability
- Low price (low investment cost per power)
- □ High specific power (discharge power)
- Medium life-time duration
- □ No memory effect
- □ Low self-discharge rate
- Perform well at low, even negative temperatures



- □ Low specific energy
- Slow charge, cannot be charged fast
- Must be stored with high SOC, as low SOC leads to sulfation

# Lead-acid batteries – divison

- By type of electrolyte:
  - Flooded non-sealed with liquid electrolyte
  - VRLA (Valve Regulated Lead-Acid) sealed
    - □ AGM (Abosrbent Glass Mat)
    - GEL
- Flooded batteries produce gas if overcharged this gas must be released
- VRLA batteries have a valve which releases gases in the extreme conditions, while during the normal operation gases recombine inside the battery
- VRLA advantages over the flooded batteries
  - Do not require regular addition of water (often advertised as "maintenance free")
  - Cannot spill its electrolyte when inverted

# Lead-acid batteries – divison

- □ AGM batteries have fiberglass linings which absorbs sulfuric acid
- Higher cycle count, as well as higher charge/discharge currents in comparison to flooded batteries
- Less prone to sulfation
- Depth of discharge up to 80%, as opposed to the flodded batteries, which achieve depth of discharge up to 50%
- Higher manufacturing price and somewhat lower specific energy compared to the flooded batteries



# Lead-acid batteries – divison

- GEL contains gelified electrolyte (sulfuric acid is mixed with sillicon dioxide based polymer)
- Better heat transfer compared to the AGM batteries -> longer lifetime
- Slower capacity fade during working life in comparison to the AGM batteries
- Higher manufacturing costs compared to AGM batteries





- Nickel-cadmium batteries (NiCd)
- Nickel-metal-hydride batteries (NiMH)
- Nickel-cadmium batteries ruled the world of portable devices for more than 50 years
- Due to the problems with toxicity they are being replaced by nickel-metal-hydride batteries



#### □ NiCd battery consists of:

- Nickel oxide hydroxide (NiO(OH)) as positive electrode
- Metallic cadmium (Cd) as negative electrode
- Alkaline electrolyte (usually potassium hydroxide, KOH, in distilled water)
- Separator



- During discharge:
  - positive electrode transitions to nickel hydroxide (Ni(OH)<sub>2</sub>)
  - negative electrode transitions to cadmium hydroxide (Cd(OH)<sub>2</sub>)
- During charge, the reverse reactions occur
- Electrolyte does not take part in the reactions, so it cannot be used as a SOC measure like with lead-acid batteries



- High number of cycles
- Fast charging
- Operation at low temperatures
- □ High profitability considering price per cycle
- Low specific energy
- Memory effect
- Toxicity of cadmium
- □ High degree of self-discharge
- Low cell voltage



- Positive electrode is, as in NiCd batteries, nickel oxide hydroxide (NiO(OH))
- Electrolyte is again alkaline (usually potassium hydroxide, KOH)
- Cadmium negative electrode is substituted with the hydrogen-absorbent alloy, metal hydride
- During discharge positive electrode gradually transitions to nickel hydroxide (Ni(OH)<sub>2</sub>), while metallic negative electrode releases ions (OH<sup>-</sup>) and receives hydrogen
- During charging, the reverse reactions take place



- No problems with electrode toxicity
- Higher capacity
- Less prone to memory effect compared to NiCd

#### Downsides:

- Limited working life with deep discharges
- Require complex charging algorithm (sensitive to overcharge)
- Heat up during fast charges and discharges
- Low cell voltage
- High degree of self-discharge
- Very low coulombic efficiency

# Lithium-ion batteries (LIB)

- Named after lithium ions which travel among electrodes during chemical reactions of charging and discharging
- Higher capacity
- Conventional li-ion battery consists of:
  - Negative carbon electrode (e.g. graphite,  $C_6$ )
  - Positive lithium metal oxide electrode (e.g lithium cobalt oxide, LiCoO<sub>2</sub>)
  - Electrolyte is lithium salt in an organic solvent
- Both electrodes allow lithium ions to go in and out of their structures

# LIB charging/discharging

- During discharge, lithium ions (Li<sup>+</sup>) and electrons travel from negative to positive electrode through electrolyte and circuit, respectively
- Discharge is possible until the negative electrode becomes pure graphite (C<sub>6</sub>), i.e. it loses all the lithium, while in the meantime the positive electrode transitions to lithium cobalt oxide (LiCoO<sub>2</sub>)
- During charging, the process is reversed and lithium ions (Li<sup>+</sup>) and electrons travel from positive (LiCoO<sub>2</sub>) to negative electrode (C<sub>6</sub>)
- Process is possible until positive electrode loses all the lithium and becomes cobalt oxide (CoO<sub>2</sub>)





Lithium-ion Rechargeable Battery Discharge Mechanism



#### Lithium-ion Rechargeable Battery Charge Mechanism



- High specific energy
- Good discharge possibilities
- Long working life, no need for maintenance
- Low internal resistance
- □ Good coulombic efficiency
- □ Simple charging algorithm
- Short charging time
- Low self-discharge


- Need for Battery Management System (BMS)
- Degradation at high temperatures and voltages
- Hard or impossible charging at low temperatures



- LIB batteries can be divided by electrode materials
- Positive electrode (underlined are commercially available):
  - Lithium cobalt oxide LiCoO<sub>2</sub> (LCO, ICR)
  - Lithium nickel oxide LiNiO<sub>2</sub> (LNO)
  - Lithium nickel cobalt aluminum oxide LiNi<sub>x</sub>Co<sub>v</sub>Al<sub>z</sub>O<sub>2</sub> (NCA, NCR)
  - Lithium manganese dioxide LiMnO<sub>2</sub> (LMO)
  - Lithium nickel manganese oxide LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> (NMO)
  - Lithium nickel manganese cobalt oxide LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub> (NMC, CGR, INR)
  - Lithium manganese oxide LiMn<sub>2</sub>O<sub>4</sub> (LMO, IMR)
  - Lithium iron phosphate LiFePO<sub>4</sub> (LFP, IFR)



Negative electrode (underlined are commercially available):

- Graphite C<sub>6</sub>
- Hard carbon
- Lithium titanate Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO)
- Silicon/carbon alloy
- Electrolyte lithium salts in organic solvent (this division does not alter features like various electrode materials):
  - Organic solvent is most commonly ethylene carbonate ((CH<sub>2</sub>O)<sub>2</sub>CO), dimethyl carbonate (OC(OCH<sub>3</sub>)<sub>2</sub>) or diethyl carbonate (OC(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>)
  - Lithium salts can be lithium hexafluorophosphate (LiPF<sub>6</sub>), lithium hexafluoroarsenate monohydrate (LiAsF<sub>6</sub>), lithium perchlorate (LiClO<sub>4</sub>), lithium tetrafluorborate (LiBF<sub>4</sub>) or lithium trifluoromethanesulfonate (LiCF<sub>3</sub>SO<sub>3</sub>)



- Immersed in electrolyte is separator, a thin porous plastic sheet, the function of which is electrical separation of the electrodes
- Separator allows lithium ion flow, but prevents electron flow through the electrolyte
- Besides being thin and very porous, separator must be able to soak up in electrolyte
- Separator can be made of polyethylene (PE), polypropylene (PP) or their combination



### LIB can be:

- Conventional Li-ion
- Li-polymer
- Conventional LIB uses separator with bigger pores which is immersed in a liquid electrolyte
- Li-polymer uses gel electrolyte with a micro-porous separator
- □ The amount of electrolyte is about the same
- Upside of Li-polymer batteries is somewhat higher specific energy and fact that cells can be produced thinner than those with conventional separator
- Downside is higher price



### Cylindrical solid frame

#### Prismatic solid frame





### Pouch cell

Cells can be constructed in any shape, but they are most commonly prismatic













#### □ LIB capacity drops with temperature





- ☐ When storing LIB, losses occur for two reasons:
  - Self-discharge of the battery (energy loss)
  - Overall battery capacity reduces as the time passes, the so called "calendar aging"
- LIB should not be stored completely empty, because the battery voltage can drop below the minimum allowed value due to self-discharge
- On the other hand, storing LIB at high SOC values leads to faster calendar aging of the battery
- Optimal SOC for storaging LIB is 30-50%



Battery	Nominal voltage	Efficiency	Specific energy
Lead-acid	2 V	50-85%	35-40 Wh/kg
NiCd	1.2 V	70-90%	40-60 Wh/kg
NiMH	1.2 V	70-90%	60-120 Wh/kg
Li-ion	3.2-3.7 V	80-95%	100-265 Wh/kg
Zinc-air	1.65 V	?	450 Wh/kg
Vanadium	1.4 V	75-80%	100 Wh/kg



Advantages	Limitations
Independent electrical power source	High electrical energy price compared to the electric power system
<ul> <li>Adaptability to the user:</li> <li>Small size and mass</li> <li>Various voltages, sizes and configurations</li> </ul>	Usage of expensive materials
Efficient conversion for various applications	Low energy density
Reliability, safety, no moving parts	Limited standing time



- State of Charge (SoC)
- Depth of Discharge (DoD)
- $\Box \quad SoC + DoD = Capacity$
- Repeated deep discharges have a negative influence on batteries' working life, as they reduce the available capacity more quickly than moderate discharges
- □ The deeper the discharging cycles, the more capacity is lost



- Experiments are conducted by subjecting batteries to charge/discharge cycles with the same DoD
- Process is repeated until the useful battery capacity drops below certain percentage of the initial capacity, usually 80%, which is considered to be battery's end-of-life



## □ This limitation is not correct

$$p_{t,}^{\mathrm{ch}} \leq P^{\mathrm{bat}}, \quad \forall t \in \Omega^{\mathrm{T}}$$







## It is necessary to know how much energy can be charged to a battery in a single time step (1 hour) for every SoC



Energy Storage Course  $\ensuremath{\textcircled{O}}$  Faculty of Electrical Engineering and Computing University of Zagreb

# Battery voltage characteristic





- Losses are caused by the internal resistance of electrodes and electrolyte
- □ Types of efficiencies:
  - Coulombic (Ah)
  - Voltaic (V)
  - Energy (Wh) includes the former two

# Battery Capacity in Ah

- □ Voltage varies considerably through the discharge period ⇒ difficulties to specify amount of energy discharged;
- To avoid ambiguity, battery storage capacity is expressed in Ah, rather than Wh;
  - A 200 Ah batt delivering 20 A would fully deplete in 10 h (C/10 discharging rate);
  - Same batt wouldn't be able to deliver 50 A for a full 4 h (C/4); however, it would deliver 10 A for more than 20 h (C/20).
- Conclusion: amp-hour capacity depends on the rate at which current is withdrawn.
- □ For PV, 20-h discharge rate (C/20) is a standard.

# Coulomb Efficiency x Energy Efficiency

If a batt is charged with a constant current  $I_c$  over a period  $\Delta T_c$  and applied voltage  $V_c$ , energy input is:

$$E_{in} = V_C I_C \Delta T_C$$

If the batt is discharged at current  $I_D$  over a period  $\Delta T_D$ and voltage  $V_D$ :

$$E_{out} = V_D I_D \Delta T_D$$

□ The batt *Energy Efficiency* would be

$$Energy \ efficiency = \frac{E_{out}}{E_{in}} = \frac{V_D I_D \Delta T_D}{V_C I_C \Delta T_C}$$

# Coulomb Efficiency x Energy Efficiency

□ The batt Energy *Efficiency*:

Energy efficiency 
$$= \frac{E_{out}}{E_{in}} = \frac{V_D I_D \Delta T_D}{V_C I_C \Delta T_C}$$

Since *current* (A)  $\times$  *time* (h) = Coulombs of charge:



# **Coulomb Efficiency**

- It is the ratio between coulombs of charge out of the battery to coulombs that went in;
- □ If they don't all come back, where did they go?
  - When battery approaches full charge its cell voltage gets high enough to electrolyze water  $\Rightarrow$  H and  $O_2$  gases are released;
  - Charging electrons are lost with the escaping gases.
- □ While batt SoC is low, above effect doesn't occur and Coulomb efficiency  $\cong$  100%;
- □ Over a full charge cycle,  $90\% \leq Coulomb \ eff. \leq 95\%$
- Coulomb eff. is the most appropriate for batt sizing.

# Battery efficiency: Example

□ A typical 12 V lead-acid batt is charged at 14 V, and its discharged voltage is  $\cong$  12 V. Thus:

$$Voltage \ efficiency = \frac{12 \ V}{14 \ V} = 0.86 = 86 \ \%$$

Assuming a 90% Coulomb efficiency, then

*Energy efficiency* =  $0.86 \times 0.90 = 77\%$ 

which is close to the usual estimate of 75% for leadacid battery energy efficiency.







#### Battery cells contain:

- a molten sodium (Na) negative electrode
- a molten sulfur (S) positive electrode
- a solid ceramic electrolyte Beta-Alumina Solid Electrolyte (BASE) - allows only positively charged sodium-ions to pass through
- Operating temperature:
  - 300-350 °C
- Stationary ES applications
- Lifespan between 10 and 15 years, depending on frequency of use and depth of discharge





- Relatively high energy densities (150–300 Wh/l)
- Almost zero daily self-discharge
- Higher rated capacity than other types of batteries
- Battery type: "Energy" ability of discharging up to 6 hours
- Uses inexpensive, non-toxic materials leading to high recyclability (99%)



□ High annual operating cost (80 \$/kW/year)

# An extra system required to ensure its operating temperature



- □ Stabilizing renewable energy output
- Providing ancillary services
- Peak shaving
- Backup power
- Firming wind capacity



- □ 35 MW NaS battery project
- Applications:
  - Frequency regulation: primary and secondary
  - Voltage support
  - Peak shaving
  - Reducing grid congestion





#### **Energy Intensive**

- Mission : reduce grid congestions
- Total Power: ≈35 MW
- Solution: NaS Sodium Sulfur
- Number of sites: 3
- Investment Size: 160 €mln;

Rated Output	1,200kW and 8,640kWh
Configuration	40 NAS modules, each rated at 30kW and 216kWh.
Dimension	10.2W x 4.4D x 4.8H (m)
Weight	132tonnes

#### Site 1: Ginestra

- Total Capacity: ≈ 12 MW
  - Status: operational
- 🔻 Site 2 Flumeri
  - Total Capacity: ≈ 12 MW
  - Status: operational

#### Site 3 Scampitella

- Total Capacity: ≈ 10.8 MW
- Status: operational



Dimension : m





# VANADIUM REDOX FLOW BATTERIES (VRFB)





## □ The main components:

- A liquid electrolyte
- A carbon felt electrode
- An ion exchange membrane that separates the electrolytes
- A bipolar plate that separates cells
- Electrolyte tanks (2 or 4), pumps, and piping

Catholyte

Pump

Membrane

Electrode

Anolyte

Cell



- □ The redox cell means: reduction—oxidation
- VRFB employs <u>vanadium ions</u> in **four** oxidation states to store chemical potential energy
- Reaction on positive electrode:

$$VO^{2+} + H_2O \xrightarrow{punjenje} VO_2^+ + 2H^+ + e^-$$

Reaction on negative electrode:

$$V^{3+} + e^{-} \xrightarrow{punjenje} V^{2+}$$

□ The operating temperature: 10-40 °C



- Liquid electrolyte of metallic salts is pumped through a core that consists of a positive and negative electrode, separated by a membrane
- The ion exchange that occurs between the cathode and anode generates electricity
- Viable choice for energy applications requires discharge durations greater than 5 hours
- The ability to independently <u>vary energy and</u> <u>power capacity</u>

# Charging/Discharging process




- The energy capacity is a function of the electrolyte volume amount of liquid electrolyte
- □ The power is a function of the surface area of the electrodes
- The voltage is lower
  than other types of
  batteries:

1.15–1.55 V





- Long cycle life 10-15 years with 1000 cycles/year
- Quick response times
- No harmful emissions
- Can operate at much higher current and power densities
- Roundtrip efficiency ranges between 60 and 70 %



- The energy densities vary considerably but are <u>lower</u> compared to portable batteries, such as li-ion batteries
- Cost and construction complexity
- Efficiency losses accrued by auxiliary equipment



- Load shifting (peak shaving)
- Firming capacity
- Transmission and distribution operational support:
  - Frequency regulation
  - Voltage support
  - Spinning reserve
- Power quality and reliability (especially long duration)