MECA0527: ENERGY AND POWER STORAGES: Part I: Batteries

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References

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Outline

- Introduction
- Energy sources characteristics
- Electrochemical batteries
- Ultra capacitors
- Flywheels
- Comparison

Characteristics of Energy Sources

Energy source characteristics

- Energy and coulometric capacity
- Cut-off voltage and usable capacity
- Discharging/charging current
- State-of-charge
- Energy density
- Power density
- Cycle life
- Energy efficiency and coulometric efficiency
- Cost

Energy and coulometric capacities

- Energy capacity EC [J] or [Wh]

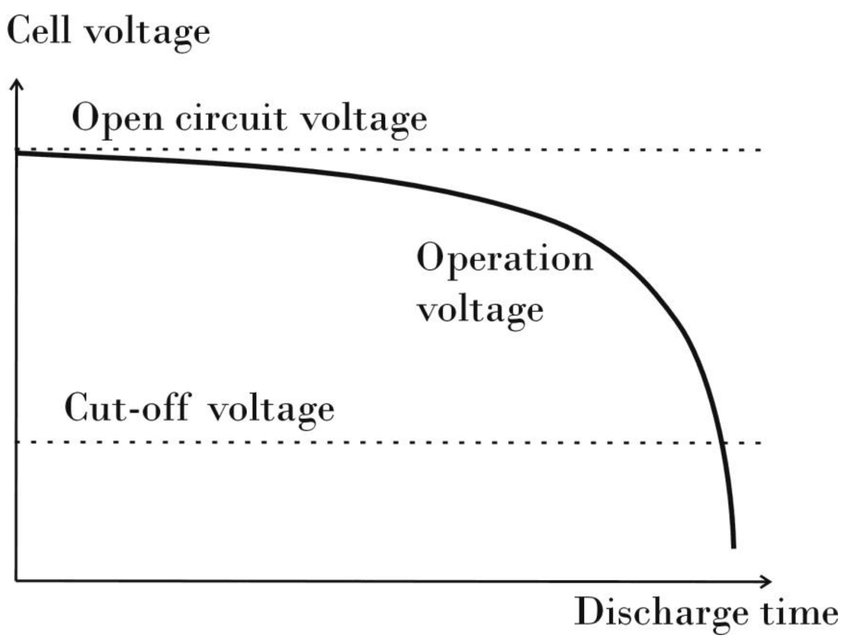
$$\mathrm{EC}(T) = \int_0^T v(\tau)\, i(\tau)\, d\tau$$

  - v(t) and i(t) instantaneous voltage and current
- Coulometric capacity [Ah]

$$\mathrm{CC}(T) = Q(T) = \int_0^T i(\tau)\, d\tau$$

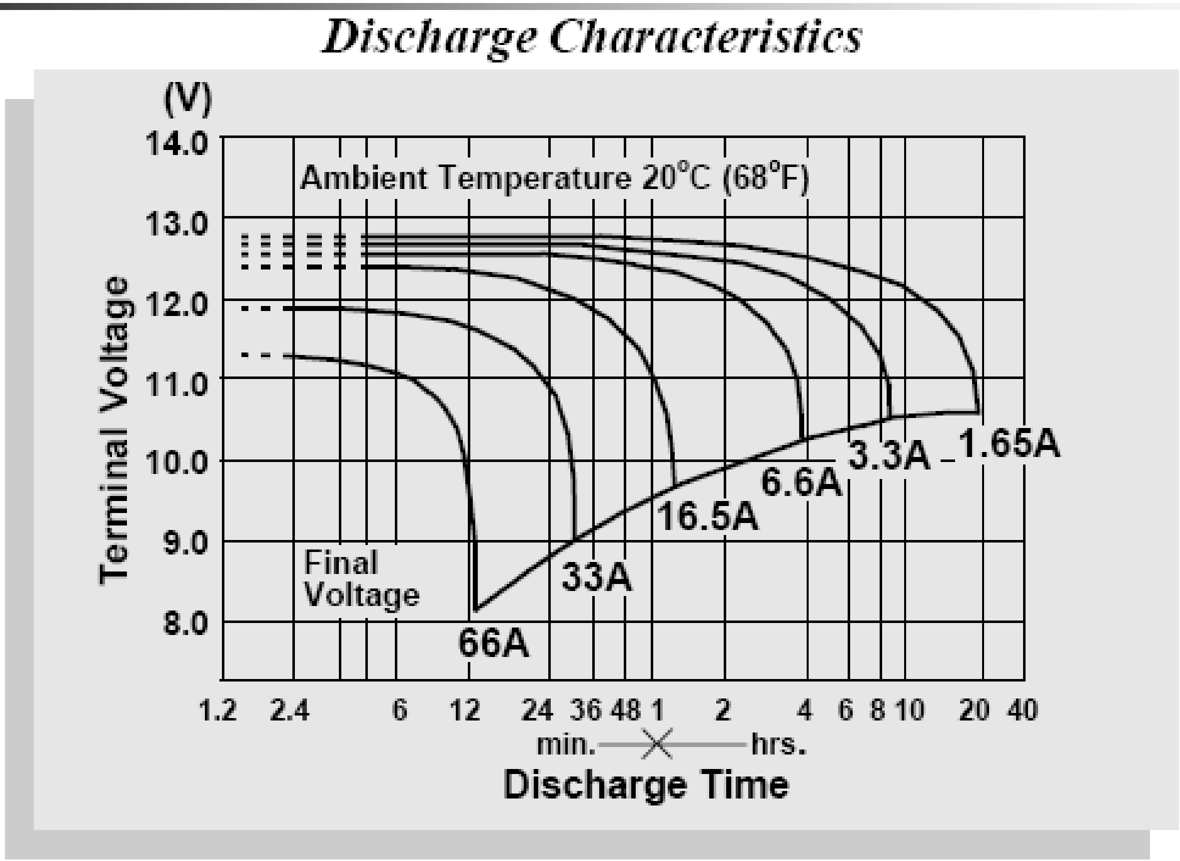
- Mission of EV energy sources: supply electrical energy for propulsion
- For EV, energy capacity is more important and useful than coulometric capacity
- However, the coulometric capacity (or capacity) is widely employed to describe the capacity of batteries

Cut-off voltage and usable capacity



- Energy capacity does not represent well the energy content of electrochemical sources
- Batteries can not be discharged down to zero voltage unless being permanently damaged
- Cut-off voltage: knee of discharging curve at which the battery is considered as fully discharged, so called 100% depth of discharge (DoD)
- Usable energy capacity and usable coulometric capacity before cut-off

Cut-off voltage and usable capacity



Discharge curves for Powersonic VRLA batteries

Discharging/charging current

- The battery capacity is determined with constant current discharge-charge tests
  - In a typical constant current test, the battery is initially fully charged, and the voltage equals the open-circuit voltage V_{0c}.
  - A constant discharge current is applied. After a certain time t_f, called the discharge time, the voltage drops below the cut-off voltage and the battery is empty.

- For batteries, energy capacity and coulometric capacity vary with
  - Their discharging current,
  - The operating temperature,
  - And the ageing.

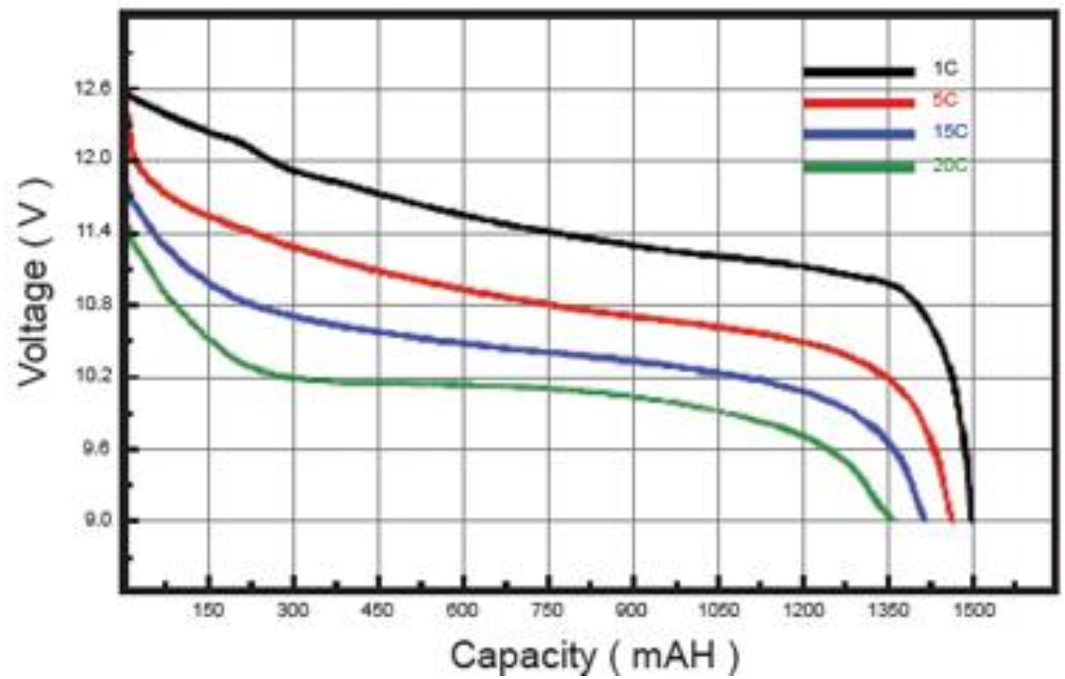
Discharging/charging current

Rate of Discharge :

Rate Discharge Characteristics

Charge:
1A.4.2V(CC-CV).
50mA cut-off. at23±2℃

Discharge:
at each rate.CC.
3.0V cut- off. at23±2℃



Discharge curves for LiPo Ultimate PX-01 batteries

Discharging/charging current

- The C-rate current is defined as the current I_0 that discharges the battery in one hour and which has the same value as the battery capacity Q_0=CC expressed in [Ah].

- Discharge currents are given using a unit-less value called C-rate

$$I = k\, C_n$$

- The C rate is often written as C/k where k is the number of hours needed to discharge the battery with a C-rated current,
  - I=C/k current is a current k times lower than the rated current I_0.
  - Example: C/5 rate for a 5 Ah battery means that kC_n = 1/5*5=1A

Discharging/charging current

- CC (and also the EC) decreases with the increasing C rate

- The discharge time is a function of the discharge current. The phenomenon is often described using the empirical Peukert equation :

$$t_f = \mathrm{K}\, I_2^{-n}$$

'n' is the Peukert exponent which varies between 1 and 1.5 (e.g. in VRLA n~1.35)

$$Q(I) = I_2\, t_f = I_2\, K\, I_2^{-n} = K\, I_2^{1-n}$$

Discharging/charging current

- Peukert equation also expresses the dependency of the battery capacity on the discharge current. If the capacity is Q_2* for a reference current I_2*, the capacity for a discharge current I_2 is

$$\frac{Q_0}{Q_0^*} = \left(\frac{I_2}{I_2^*}\right)^{1-n}$$

- Other more sophisticated models of current dependency can be found in literature:
  - Neural Network-based models
  - Modified Peukert equation for low currents (Kc a constant)

$$\frac{Q_0}{Q_0^*} = \frac{K_c}{1 + (K_c - 1)\left(\frac{I_2}{I_2^*}\right)^{1-n}}$$

State-of-charge

- The residual coulometric capacity is termed as the State-of-Charge (SOC)
- SOC defined as the percentage ratio of the residual coulometric capacity to the usable coulometric capacity

$$q(t) = \mathrm{SOC} = \frac{Q(t)}{Q_0(t)}$$

- SOC is affected by
  - discharging current,
  - operating temperature,
  - and ageing

State-of-charge and energy capacity

- Variation of the state of charge in a time interval dt with discharging current i is approximated using the discharge current by charge balance

$$\frac{d\,\mathrm{SOC}}{dt} = \frac{i}{Q_0(i,t)}$$

where Q(i) is the amp-hour capacity of the battery at current rate i

- Thus the state of charge SOC writes:

$$\mathrm{SOC} = \mathrm{SOC}_0 - \int_0^t \frac{i(t)}{Q_0(i,t)}\,dt$$

State-of-charge and energy capacity

- In case of charge, the state of charge must take into account the fact that a fraction of current I_2 is not transformed into charge due to irreversible & parasitic reactions.

- It is often modeled using the charging or coulometric efficiency

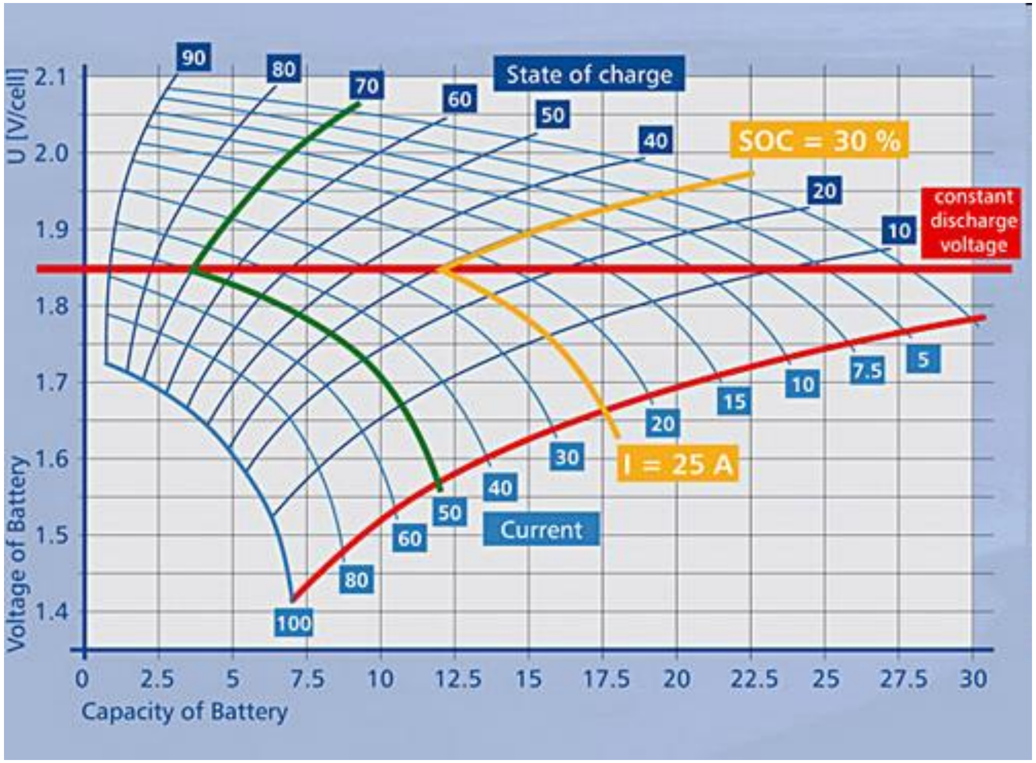
$$\frac{dQ}{dt} = -\eta_c \, I_2(t)$$

- The coulometric counting method is simple but requires frequent recalibration points.

State-of-charge and energy capacity

- The energy capacity can also be related to the current

$$\mathrm{EC} = \int_0^t v(i, \mathrm{SOC})\, i(t)\, dt$$



Energy density

- Energy densities = usable energy density per unit mass or volume of energy storage
  - Gravimetric energy density or specific energy: [Wh/kg]
  - Volumetric energy density [Wh/l]

- Gravimetric energy density
  - The more important because of weight penalty on consumption and driving range
  - Key parameter to assess suitability to EV

Power density

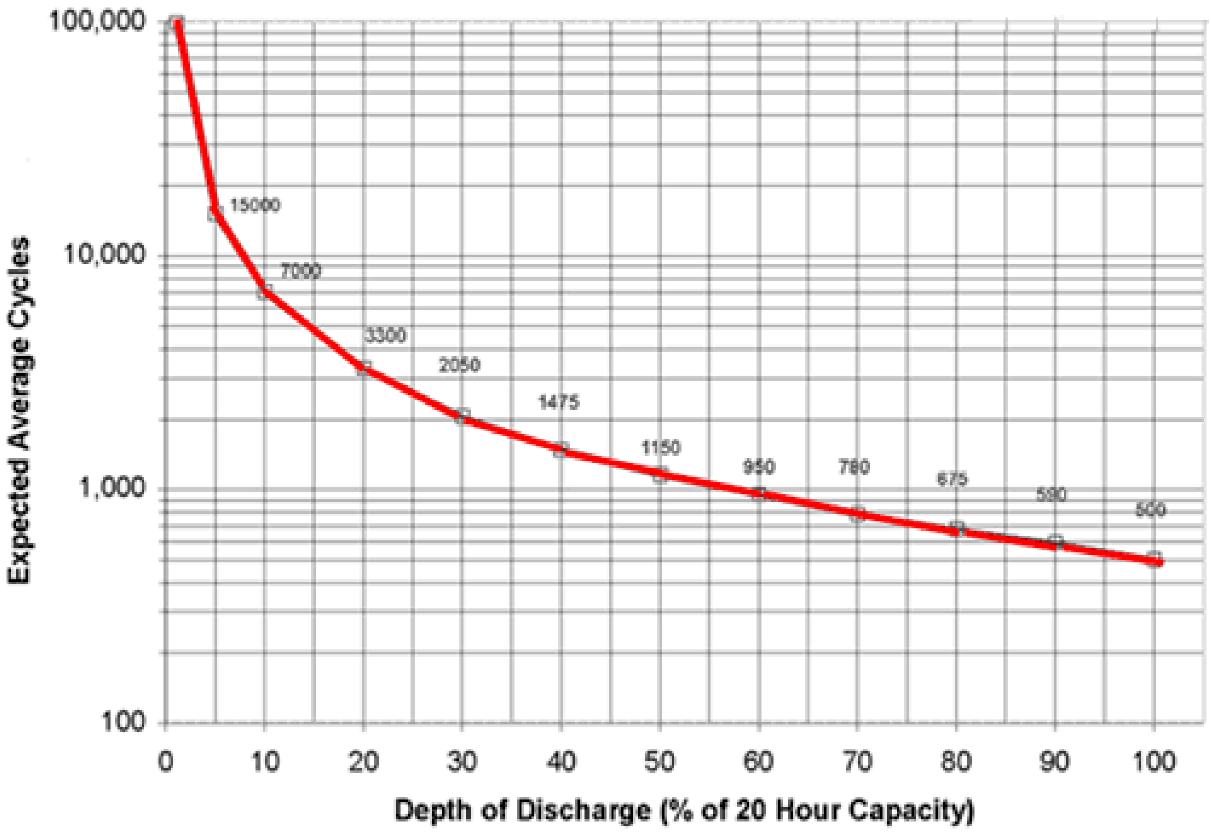
- Power density = deliverable rate of energy per unit of mass or volume
  - Specific power [W/kg]
  - Power density [W/l]
- Specific power is important for EV applications because of acceleration and hill climbing capability
- For batteries, specific power varies with the level of DoD
- Specific power is quoted with the percentage of DoD

Cycle life

- Cycle life: number of deep-discharge cycles before failure
- Key parameter to describe the life of EV sources based on the principle of EV storage
- Cycle life is greatly affected by the DoD characteristics and its is quoted with the percentage of DoD.
  - Example: 400 cycles at 100% DoD or 1000 cycles at 50% DoD
- For energy generation, the life of energy storage systems is defined by the service life in hours or kilohours

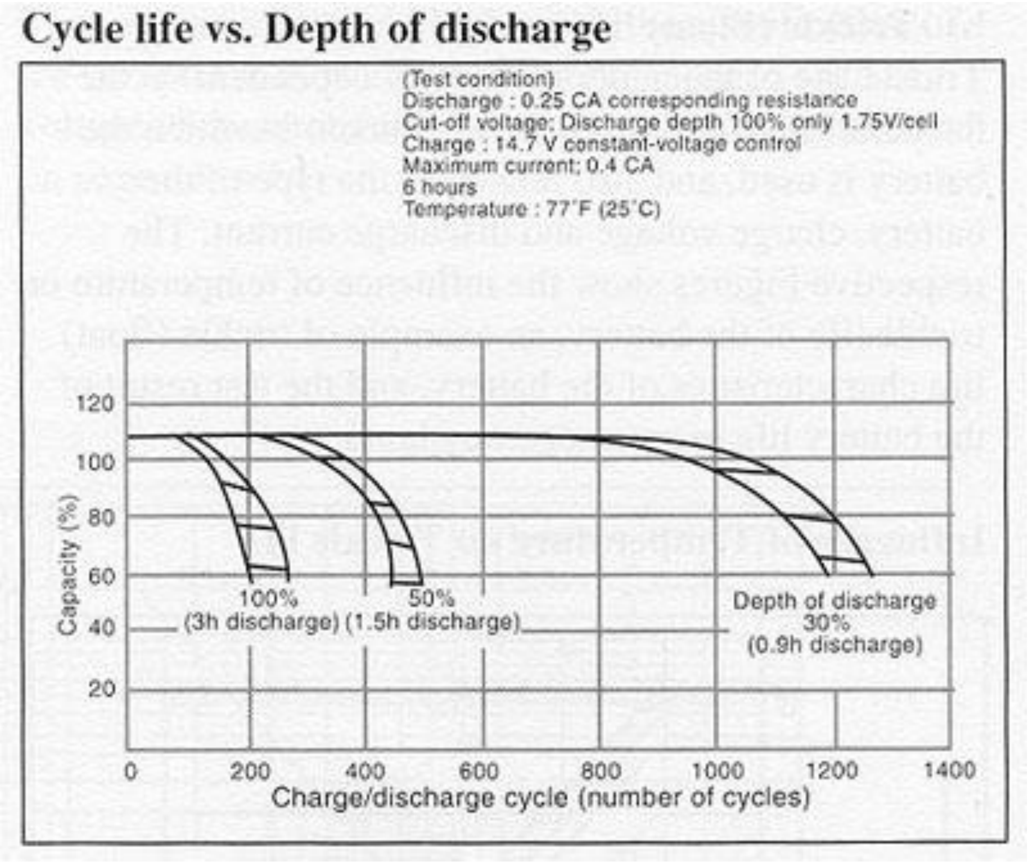
Cycle life

- Influence of DoD on Life time for Lead Acid batteries



Cycle life

- Influence of DoD on Life time for Lead Acid batteries



Energy efficiency

- Energy efficiency is defined as the output energy over the input energy
- For energy storage source, the energy efficiency is simply the ratio of the output electrical energy during discharging over the input electrical energy during charging.
  - Typically for batteries in the range of 60-90%

- Charge efficiency is defined as the ratio of discharged coulometric charge Ah to the charged coulometric capacity Ah.
  - Typically for batteries in the range of 65-90%

- For EV, energy efficiency is more important than charge efficiency

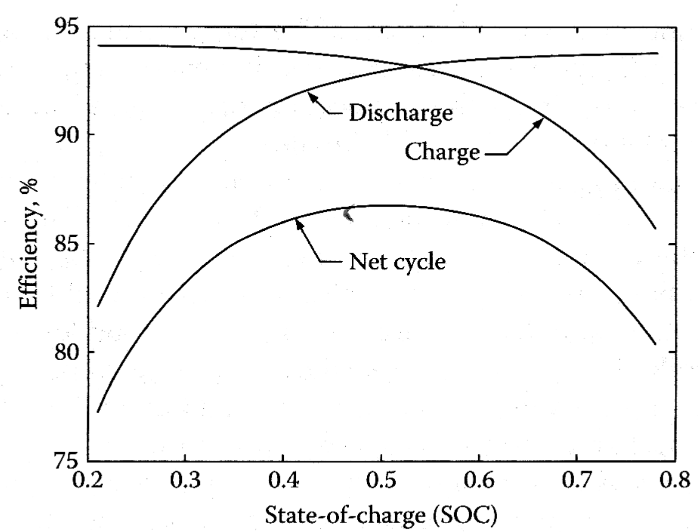
Energy efficiency

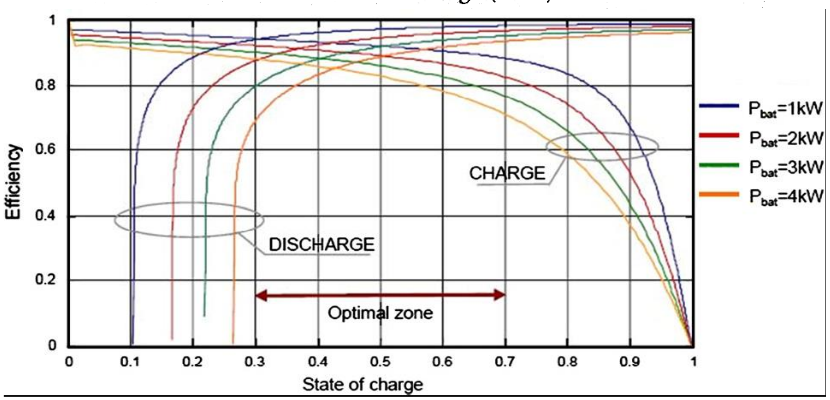
- The energy or power losses of batteries during charging discharging appear in the form of voltage losses. Thus, the efficiency of the battery during charging / discharging can be defined at any operating point as the ratio of the cell voltage V to the thermodynamic voltage V_0.

- During discharging: $$\eta_d = \frac{V}{V_0}$$

- During charging $$\eta_c = \frac{V_0}{V}$$

Energy efficiency





- The terminal voltage is a function of the current, the stored energy and the SOC. The terminal voltage is lower in discharging and higher in charging than the electrical potential produced by chemical reactions.

- The battery has a high discharging efficiency with a high SOC and a high charging efficiency with a low SOC.

- Thus, net cycle efficiency is maximum around the middle range of SOC

Cost

- Cost includes initial (manufacturing) cost + operational (maintenance) cost
  - Manufacturing cost is the most important one
- Cost is a sensitive parameter for EV sources because it is a penalty with respect to other energy sources
- Cost in €/kWh or $/kWh
- Presently cost in the range of 120 to 1200 €/kWh
- Cost is decreasing and tends to the level of 100 €/kWh in 2024.

Cost

Table 6: Energy Storage System Capacity Capital Costs[14] [15] [16] [17] [18] [19] [20] [21] [22]

Technology	Current Cost ($/kWh)	10-yr Projected Cost ($/kWh)
Flooded Lead-acid Batteries	$150	$150
VRLA Batteries	$200	$200
NiCd Batteries	$600	$600
Ni-MH Batteries	$800	$350
Li-ion Batteries	$1,333	$780
Na/S Batteries	$450	$350
Zebra Na/NiCl Batteries	$800 [1]	$150
Vanadium Redox Batteries	20 kWh=$1,800/kWh; 100 kWh =$600/kWh	25 kWh=$1,200/kWh 100 kWh=$500/kWh
Zn/Br Batteries	$500	$250/kWh plus $300/kW [2]
Lead-carbon Asymmetric Capacitors (hybrid)	$500	<$250
Low-speed Flywheels (steel)	$380	$300
High-speed Flywheels (composite)	$1,000	$800
Electrochemical Capacitors [3]	$356/kW	$250/kW

In 2010

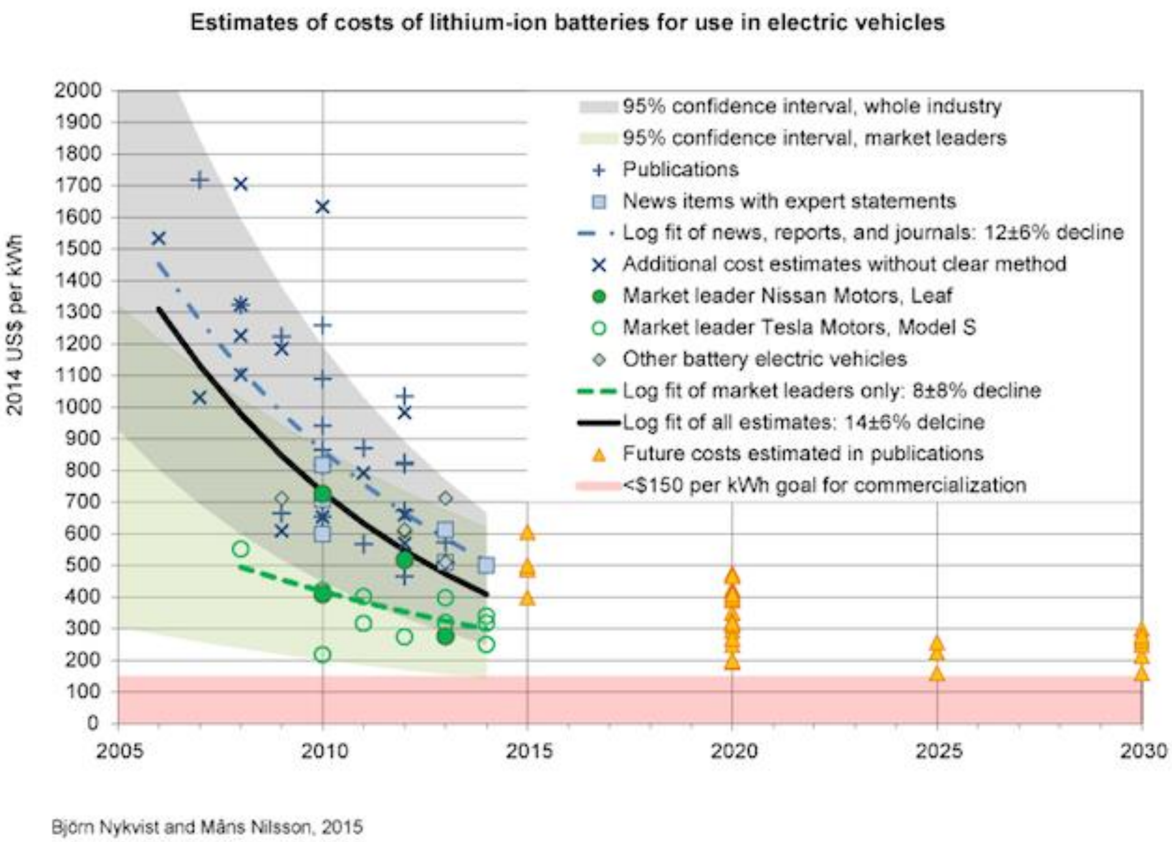
[1] €600/kWh

[2] The battery system includes an integrated PCS; the PCS price will vary with the rated system output.

[3] Electrochemical capacitors are power devices used only for short-duration applications. Consequently, their associated costs are shown in $/kW rather than $/kWh.

- Source: http://www.altenergystocks.com/archives/2010/03/

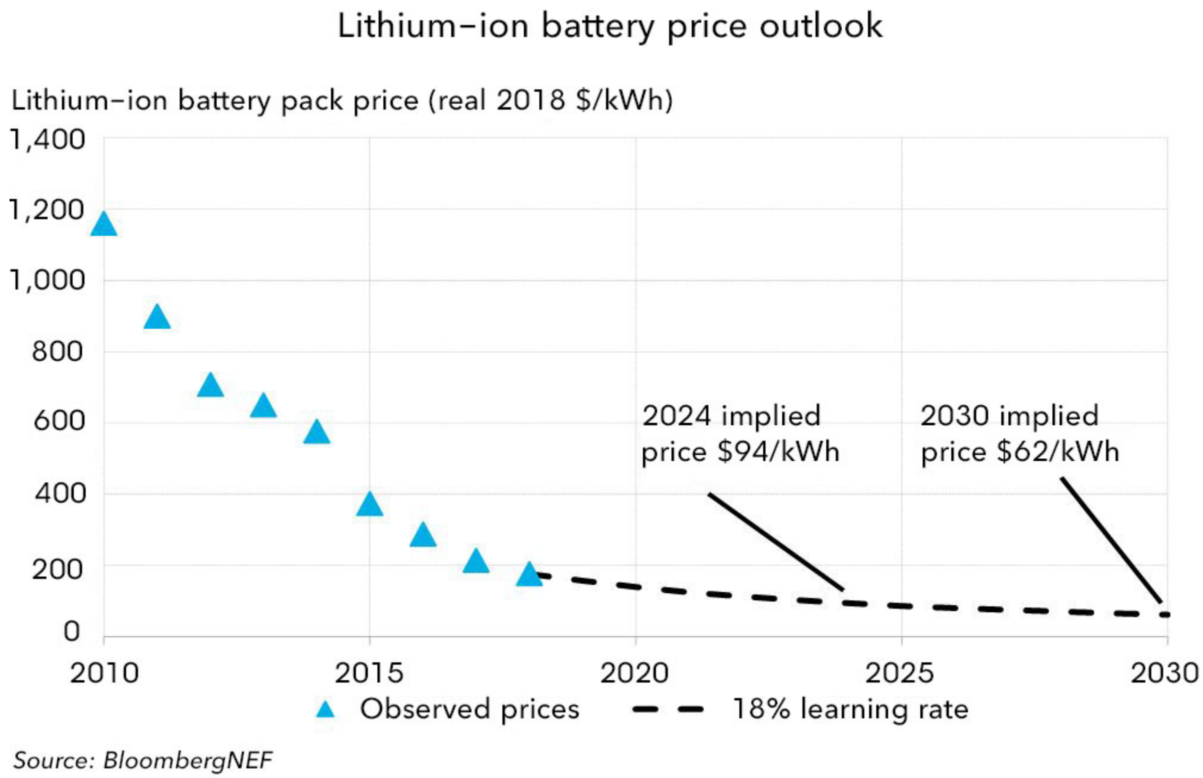
Cost



- Source: **EV Battery Costs Already 'Probably' Cheaper Than 2020 Projections** *https://cleantechnica.com/2015/03/26/ev-battery-costs-already-probably-cheaper-than-2020-projections/*

Cost

- The cost of EV battery cells dropped dramatically in recent years. Total battery **pack price / kWh** is expected to **drop below $100 in next 5 years**



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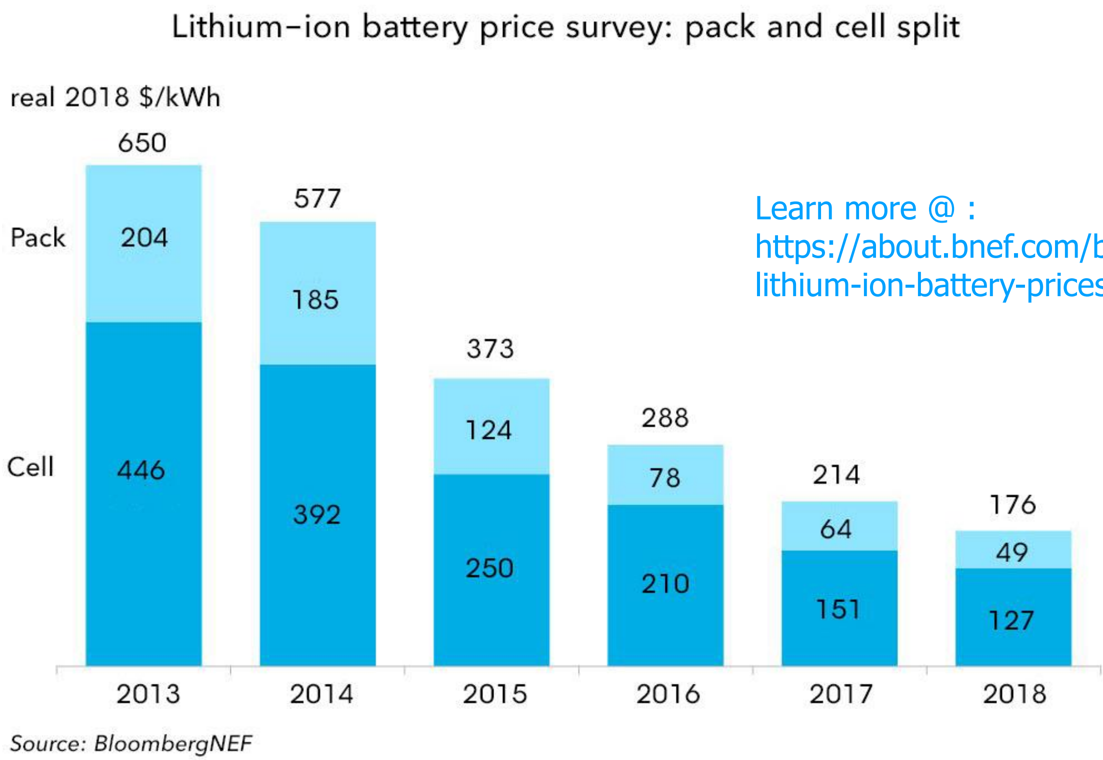


Learn more @ :
https://about.bnef.com/blog/behind-scenes-take-lithium-ion-battery-prices/

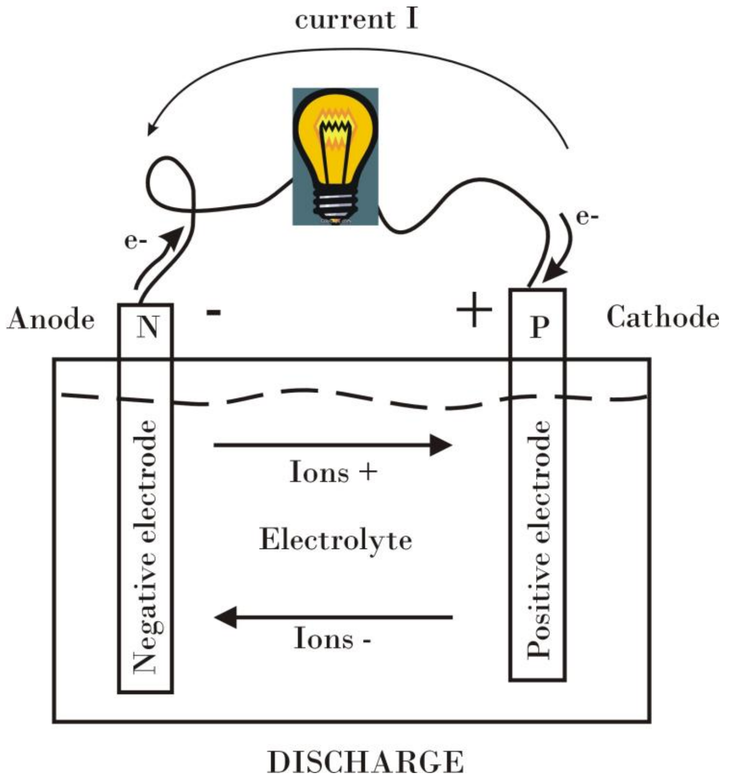
Ideal batteries for EV

- High specific energy ➔ great range and low energy consumption
- High specific power ➔ high performance
- Long life to enable comparable vehicle life
- High efficiency and cost effectiveness to achieve economical operation and maintenance free

Electrochemical batteries

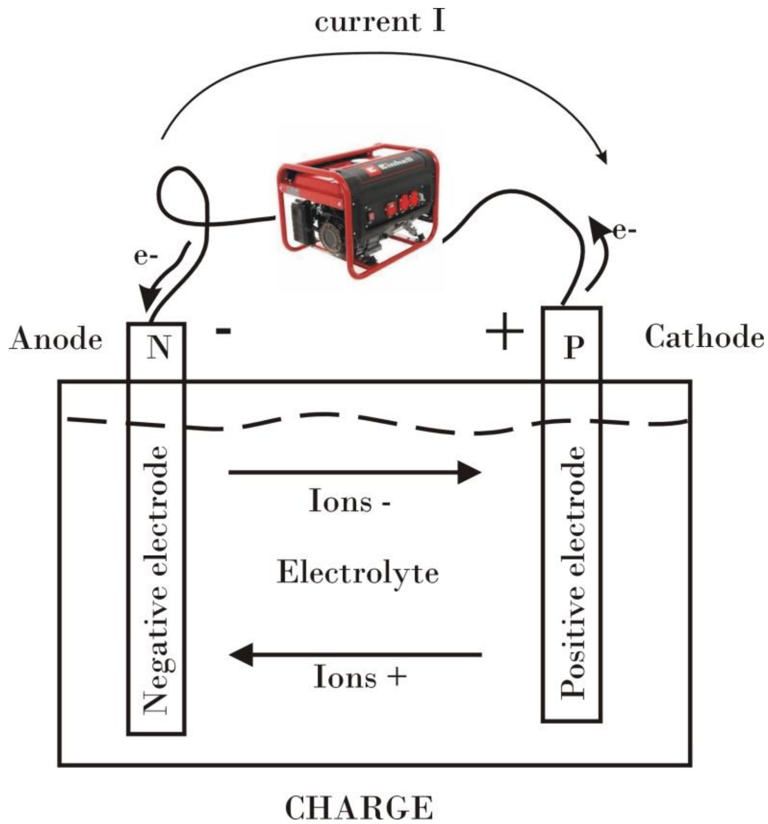
Batteries: principles

- Basic element of each battery is the electrochemical cell
- Cells are connected in series or in parallel to form a battery pack
- Basic principle of batteries
  - Positive and negative electrodes are immersed in an electrolyte
  - Electrochemical Redox reactions happen in both electrodes



Batteries: principles

- During discharge, negative electrodes performs oxidation reaction and electrons are supplied to the positive electrode via the external circuit. Positive electrode performs reduction reaction that absorbs electrons
- During charge, the process is reversed and electrons are injected in negative electrode to perform reduction on negative electrode and oxidation in positive electrodes



Lead-acid batteries

- Invented in 1860, lead acid batteries are a successful product for more than one century
- Low price and mature technology even if new designs are still continuously developed to meet higher performance criteria.

- Battery principle:
  - Negative electrode: metallic lead
  - Positive electrode: lead dioxide
  - Electrolyte: Sulfuric acid
  - Electrochemical reaction:

$$\mathrm{Pb} + \mathrm{PbO_2} + 2\mathrm{H_2SO_4} \leftrightharpoons 2\mathrm{PbSO_4} + 2\mathrm{H_2O}$$

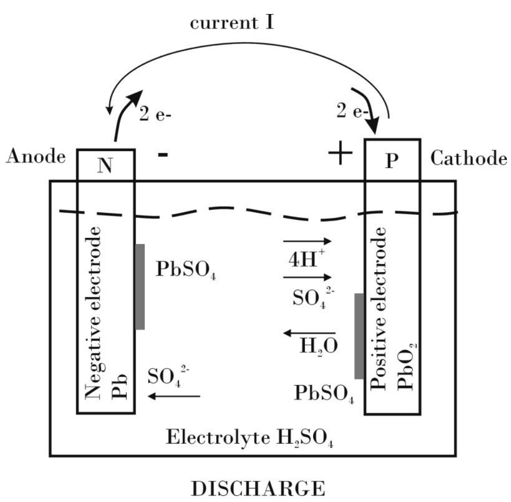
Lead-Acid batteries: electrochemical reactions

- Discharging:
  - Anode (negative electrode): porous lead

$$\mathrm{Pb} + \mathrm{SO}_4^{2-} \rightarrow \mathrm{PbSO}_4 + 2\mathrm{e}^-$$

  - Cathode (positive electrode): porous lead oxide

$$\mathrm{PbO}_2 + 4\mathrm{H}^+ + \mathrm{SO}_4^{2-} + 2\mathrm{e}^- \rightarrow \mathrm{PbSO}_4 + 2\mathrm{H}_2\mathrm{O}$$



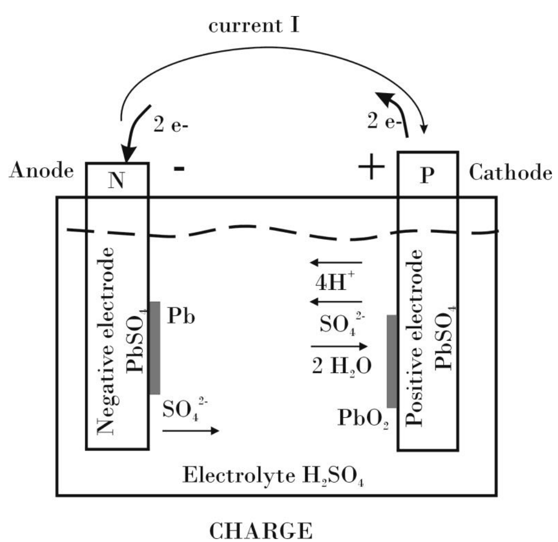
Lead-Acid batteries: electrochemical reactions

- Charging
  - Anode (negative electrode)

$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$$

  - Cathode (positive electrode)

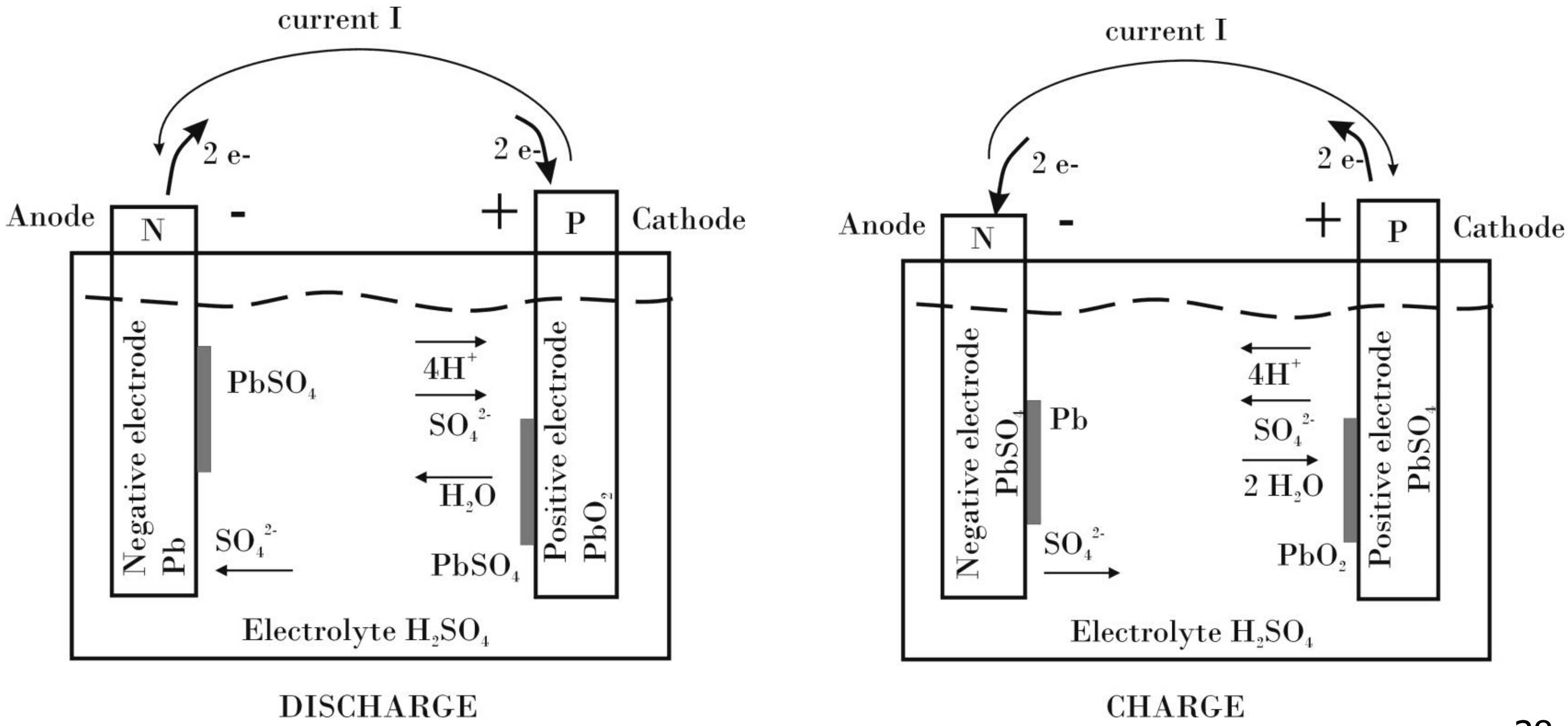
$$PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$$



Lead-Acid batteries: electrochemical reactions

- Overall

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



Lead-Acid batteries: Thermodynamic voltage

- Thermodynamic voltage of the battery cell is related to energy released and the number of electrons transferred in the reaction
- The energy released is given by the change of Gibbs free energy ΔG usually expressed per mole quantity

$$\Delta G = \sum_{\text{Products}} G_i - \sum_{\text{Reactants}} G_j$$

In which G_i and G_j are the free energy of products i and reactant species j.

Lead-Acid batteries: Thermodynamic voltage

- In reversible conditions, all the ΔG is converted in electric energy

$$\Delta G = -n\,\mathcal{F} V_{rev}$$

$\mathcal{F}$=96495 F, the Faraday constant, the number of coulombs per mole and V_{rev} the reversible voltage

- At standard conditions T=25°C, p=1 atm

$$V_{rev}^0 = -\frac{\Delta G^0}{n\,\mathcal{F}}$$

Lead-Acid batteries: Thermodynamic voltage

- The change of free energy and thus cell voltage are function of the activities of the solution species

- The Nernst relationship gives the dependence of ΔG on the reactant activities

$$V_{rev} = V_{rev}^{0} - \frac{RT}{n\mathcal{F}} \ln \left[\frac{\prod \text{Activities of Products}}{\prod \text{Activities of Reactants}} \right]$$

- R universal constant R=8,314 J/mol.K and T absolute temperature

Lead-Acid batteries: Specific energy

- Specific energy is defined as the energy capacity per unity battery weight (Wh/kg)
- The theoretical specific energy is the maximum energy that can be generated by unit total mass of reactants

$$E_{spec}^{th} = -\frac{\Delta G}{3,6\ \sum_i M_i} = \frac{n\,\mathcal{F}\,V_{rev}}{3,6\ \sum_i M_i}\ [\mathrm{Wh/kg}]$$

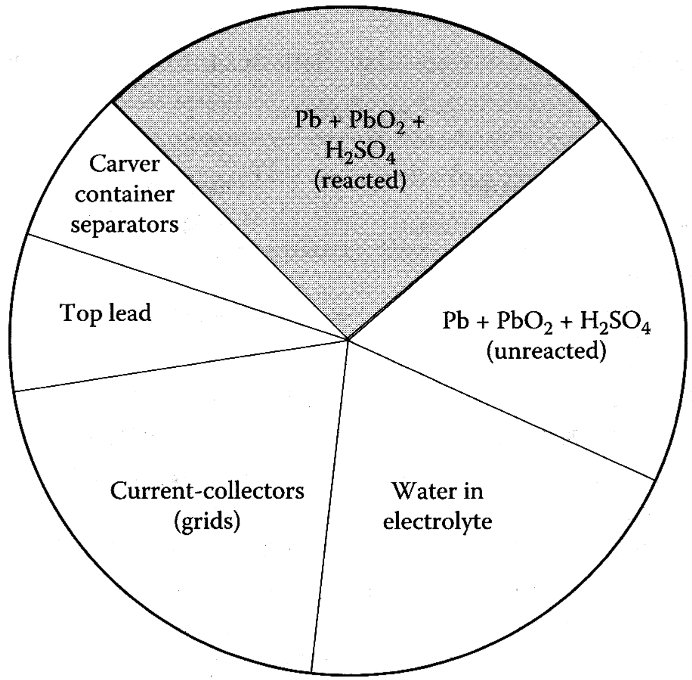
- For lead-acid batteries: V_r=2,03 and ΣM_i=642g

$$E_{spec}^{th} = 170\ [\mathrm{Wh/kg}]$$

- Actual specific energy (with container, etc.):

$$E_{spec}^{real} = 45\ [\mathrm{Wh/kg}]$$

Lead-Acid batteries: Specific energy



Weight distribution of the component of a Lead Acid battery with a specific energy of 45 Wh/kg and C5/5 rate. From Eshani, Gao, Emadi (2010). Fig 12.5

Maximizing specific energy

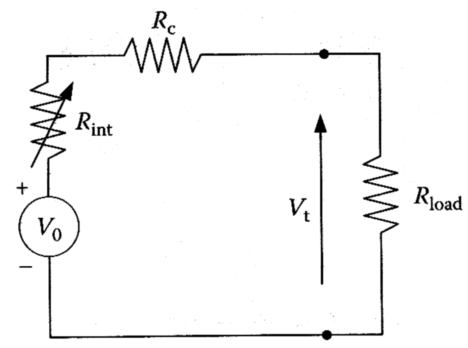
- Best specific energy is obtained with the lightest elements:
  - H, Li, Na… for negative electrode reactants
  - Halogens, O, S… for positive reactants
  - Exclude elements, which are not abundant
- Optimized electrode design for effective utilization of the contained active materials
- Electrolytes of high conductivity compatible with materials in both electrolytes
  - Oxygen and Sulfur are often used as oxides or sulfides.
  - Aqueous electrolytes are advantageous at room temperature but forbid the use of alkali-group metals
  - → other metals with a reasonable electro negativity: Zn, Al, Fe and which are rather abundant while not too expensive

Maximizing specific energy

Cathode (+)	Anode (-)	Cell reaction Discharge → / Charge ←	Specific Energy (Wh/kg)
Acidic Aqueous Solutions			
PbO_2	Pb	$PbO_2 + 2H_2SO_4 + Pb \rightleftharpoons 2PbSO_4 + 2H_2O$	170
Alkaline Aqueous Solutions			
$NiOOH$	Cd	$2NiOOH + 2H_2O + Cd \rightleftharpoons 2Ni(OH)_2 + Cd(OH)_2$	217
$NiOOH$	Fe	$2NiOOH + 2H_2O + Fe \rightleftharpoons 2Ni(OH)_2 + Fe(OH)_2$	267
$NiOOH$	Zn	$2NiOOH + 2H_2O + Zn \rightleftharpoons 2Ni(OH)_2 + Zn(OH)_2$	341
$NiOOH$	H_2	$2NiOOH + H_2 \rightleftharpoons 2Ni(OH)_2$	387
MnO_2	Zn	$2MnO_2 + H_2O + Zn \rightleftharpoons 2MnOOH + ZnO$	317
O_2	Al	$4Al + 6H_2O + 3O_2 \rightleftharpoons 4Al(OH)_3$	2815
O_2	Fe	$2Fe + 2H_2O + O_2 \rightleftharpoons 2Fe(OH)_2$	764
O_2	Zn	$2Zn + 2H_2O + O_2 \rightleftharpoons 2Zn(OH)_2$	888
Flow			
Br_2	Zn	$Zn + Br_2 \rightleftharpoons ZnBr_2$	436
Cl_2	Zn	$Zn + Cl_2 \rightleftharpoons ZnCl_2$	833
Molten salt			
S	Na	$2Na + 3S \rightleftharpoons Na_2S_3$	760
$NiCl_2$	Na	$2Na + NiCl_2 \rightleftharpoons 2NaCa$	790
FeS_2	$LiAl$	$4LiAl + FeS_2 \rightleftharpoons 2Li_2S + 4Al + Fe$	650
Organic Lithium			
$LiCoO_2$	$Li-C$	$Li(y+x)C_6 + Li(1-y-x))CoO_2 \rightleftharpoons Li_yC_6 + Li(1-y)CoO_2$	320

Maximizing specific power

- Specific power is defined as the maximum power per unit battery weight that can be delivered
- Specific power is important for battery weight especially in high-power demand applications such as HEV
- The specific power depends mostly on the battery internal resistance



$$P_{peak} = \frac{V_0^2}{4\left(R_c + R_{int}\right)}$$

- R_{int} represents the voltage drop which is associated with the battery current

Maximizing specific power

- The R_{int} represents the voltage drop which is associated with the battery current
- R_{int} depends on two components:
  - Reaction activity

$$\Delta V_A = a + n \log I$$

  - Electrolyte concentration

$$\Delta V_C = -\frac{R\,T}{n\mathcal{F}} \ln\left(1 - \frac{I}{I_L}\right)$$

I_L = limit current

Lead-Acid batteries: Specific power

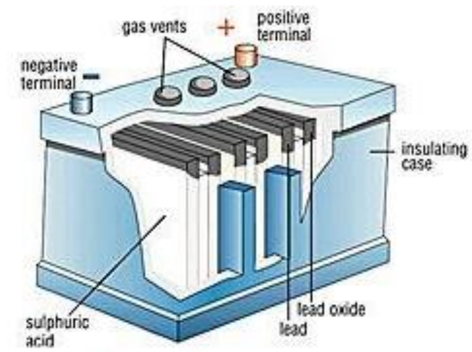
- The voltage drop
  - Increases with increasing discharge current
  - Decreases with the stored energy
- Specific energy is high in advanced batteries, but still it needs to be improved
- Specific energy of 300 Wh/kg is still an optimistic target
- Some new developments with SAFT
  - HEV batteries with 85 Wh/kg and 1350 W/kg
  - EV batteries with 150 Wh/kg and 420 W/Kg

Energy sources categories

- Rechargeable electrochemical batteries
  - Lead Acid (Valve Regulated Lead Acid=VRLA)
  - Nickel based: Ni-Iron, Ni-Cd, Ni-Zn, Ni-MH
  - Metal/air: Zn/air, Al/air, Fe/air
  - Molten salt: Sodium-β: Na/S, $Na/NiCl_2$, FeS_2
  - Ambient temperature lithium: Li-polymer, Li-ions

- Supercapacitors
- Ultrahigh speed flywheels
- Fuel cells

Lead-acid batteries

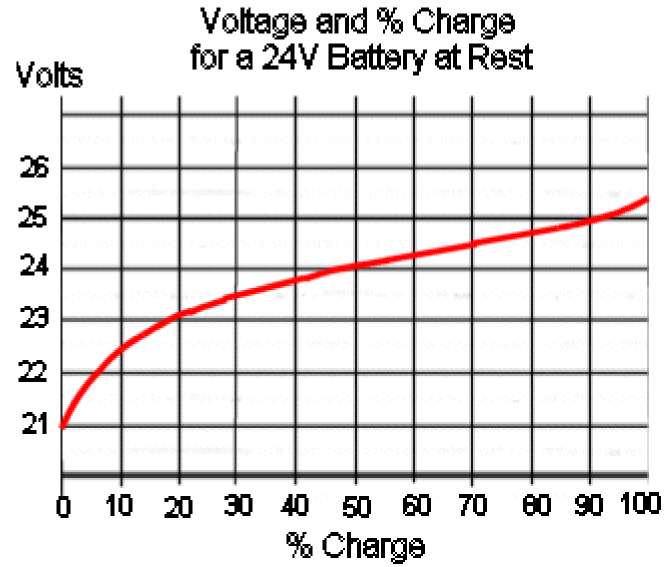


Lead Acid Battery

- Voltages:
  - Nominal cell voltage: 2,03 V (the highest one of all aqueous electrolytes batteries)
  - Cut-off voltage: 1,75 V
  - Voltage depends on sulfuric acid concentration, so that voltage varies with SOC
  - Gassing voltage (decomposition electrolysis of water at 2.4 V)
- Energy/ power density
  - Specific energy density: 35 Wh/kg
  - Energy density 70 Wh/l
  - Specific power density: 200 W/kg
- Energy efficiency: >80%
- Self discharge rate: <1% per 48 hours
- Cycle life: 500-1000 cycles
- Cost: 120-150 $/kWh

Lead-acid batteries

- Drawbacks of Lead-Acid batteries:
  - Use of lead and acid (recyclable, but polluting)
  - Weak energy density
  - Weak charge-discharge efficiency (50%)
  - Voltage depends on sulfuric acid concentration, so that voltage strongly varies with SOC

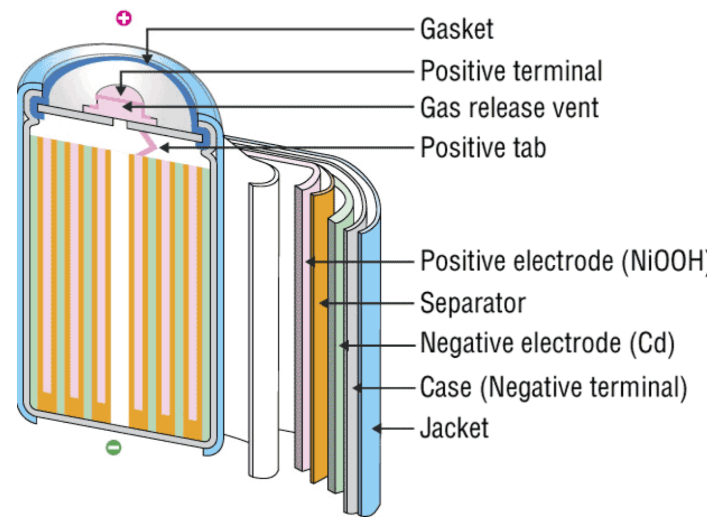


Nickel-based batteries

- Family of different kinds of electrochemical batteries using nickel oxyhydroxide (-OOH)
  - Ni-Fe invented by Edison
  - Ni-Cd is known from 1930ies
  - Ni-MH is used in modern HEV vehicles (1990ies)
  - Ni-Zn is still under development
- Use Nickel oxy hydroxide (NiOOH) as the active material for the positive electrode

Ni-Cd batteries

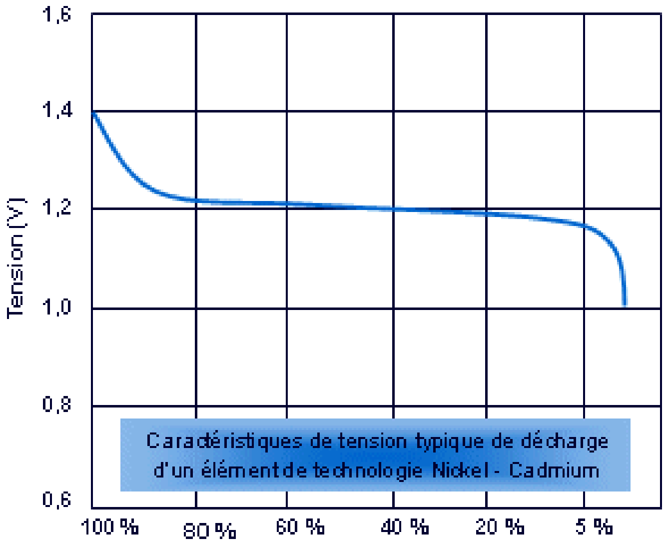
- Developed in the 1930ies, it has been used in heavy industry for 80 years
- Battery principle:
  - Negative electrode: metallic cadmium Cd
  - Positive electrode: nickel oxyhydroxide NiOOH
  - Electrolyte: KOH
  - Electrochemical reaction:



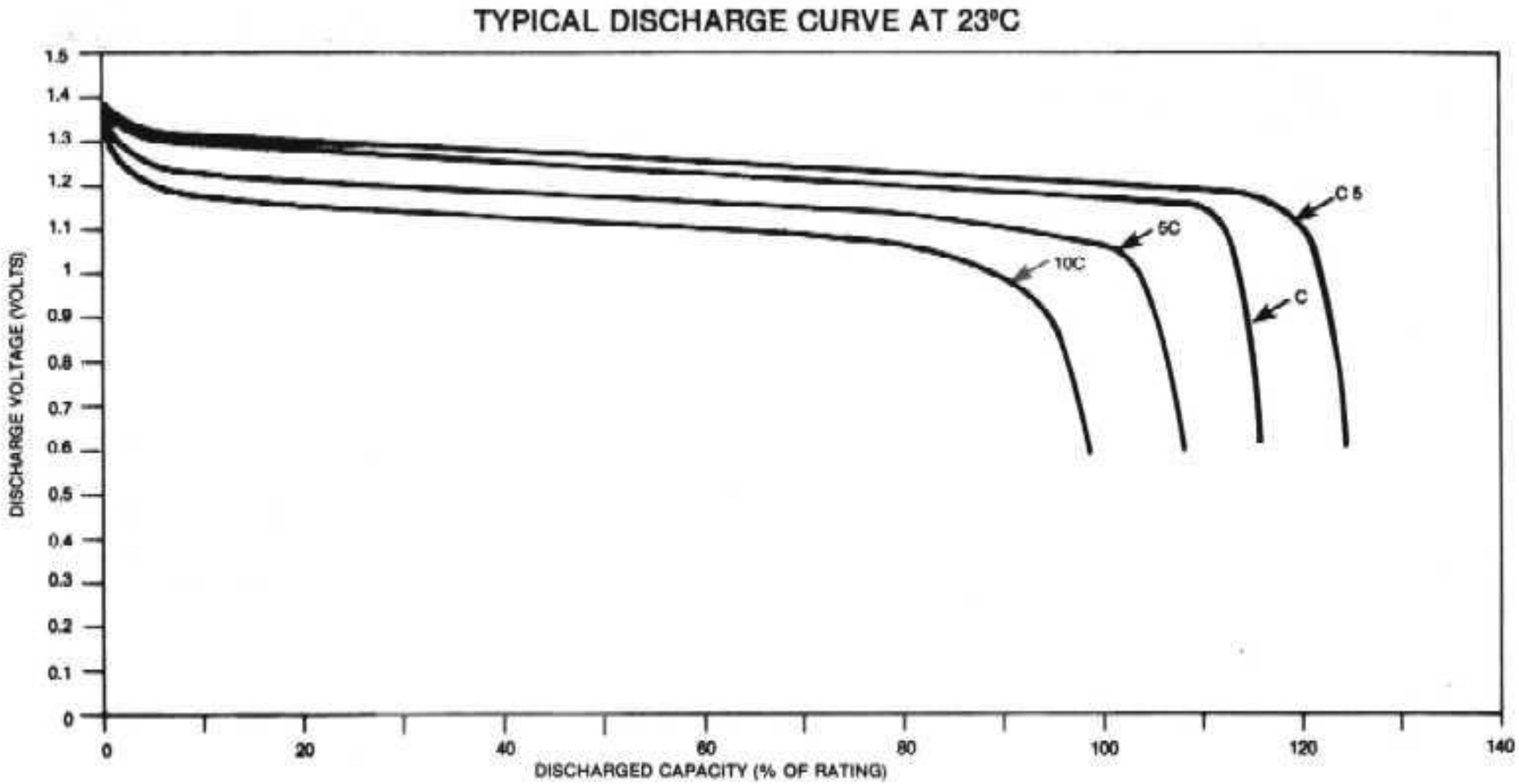
$$\mathrm{Cd} + 2\mathrm{NiOOH} + 2\,\mathrm{H_2O} \leftrightharpoons 2\,\mathrm{Cd(OH)_2} + 2\,\mathrm{Ni(OH)_2}$$

Ni-Cd batteries

- Voltages:
  - Nominal cell voltage: 1,2 V
  - Cut-off voltage: 1,00 V
- Energy/ power density
  - Specific energy density: 56 Wh/kg
  - Energy density 110 Wh/l
  - Specific power density: 80-150 W/kg
- Energy efficiency: 75%
- Self discharge rate: 1% per 48 hours
- Cycle life: ~800 cycles
- Cost: 250-350 $/kWh



Ni-Cd batteries



Discharge curves of Ni-Cd

Ni-Cd batteries

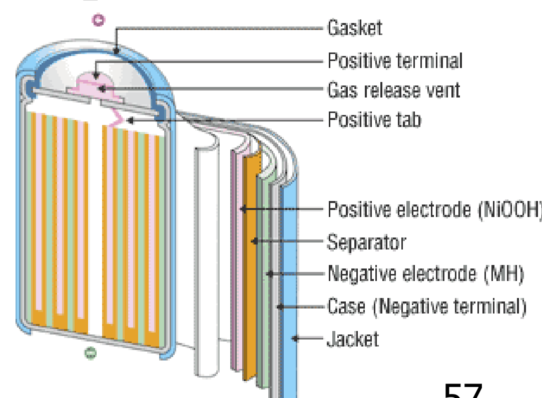
- Advantages:
  - Medium specific energy
  - Medium cycle life
  - Flat curve
  - Good performance in low temperatures
  - Easiness of charge
- Disadvantages
  - Cd is environmentally not friendly and carcinogenicity
  - Memory effect sensitivity
  - Self discharge

Ni-MH batteries

- Developed and marketed in the 1990ies, it is a standard battery used in many modern HEV
- Similar principle to Ni-Cd but it uses hydrogen absorbed in a metal hydride for the active material in negative electrode

- Battery principle:
  - Negative electrode: hydrogen absorbed in metal hydride: MH
  - Positive electrode: nickel oxyhydroxide $Ni(OH)_2$
  - Electrolyte: KOH
  - Electrochemical reaction:

$$\mathrm{MH} + \mathrm{NiOOH} \leftrightharpoons \mathrm{M} + 2\,\mathrm{Ni(OH)}_2$$



Ni-MH batteries

- Key compound is MH, the metal alloy that is able to absorb / desorb hydrogen with a high efficiency and with a high number of cycles.
  - AB_5 rare-earth such us Lanthanum with Ni
  - AB_2: Ti or Zr alloys with Ni
- Voltages:
  - Nominal cell voltage: 1,2 V
- Energy/ power density
  - Specific energy density: 70 - 95 Wh/kg
  - Energy density 150 Wh/l
  - Specific power density: 200 – 300 W/kg
- Energy efficiency: 75% (70→90) Cycle life: 750-1200 cycles
- Self discharge: 6% per 48 hours Cost: 200-350 $/kWh

Ni-MH batteries

- A porous metal absorbs et exudes the hydrogen atoms

Charge

$$MH_2 \rightleftharpoons M + 2H$$

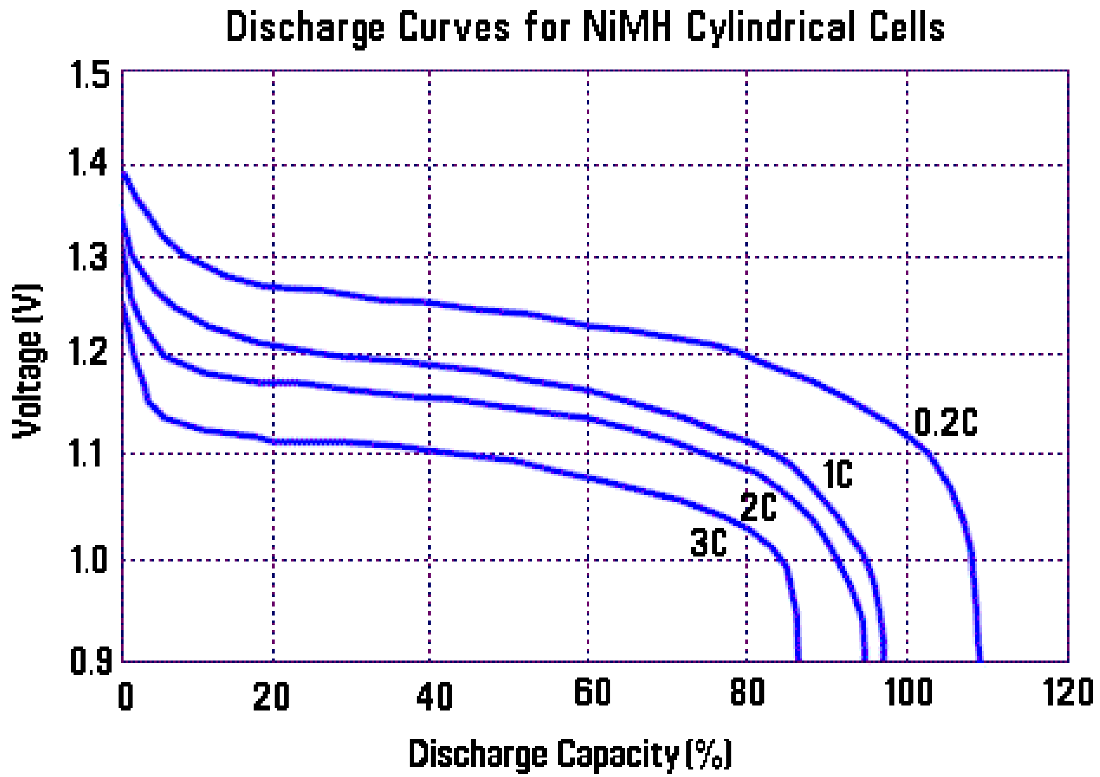
$$2\,H + 2\,OH^- \longrightarrow 2\,H_2O + 2\,e^-$$

$$K^+ + OH^- + H_2O \longrightarrow KOH + H_2O$$

$$2\,NiO(OH) + 2\,H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 + 2OH^-$$

Discharge

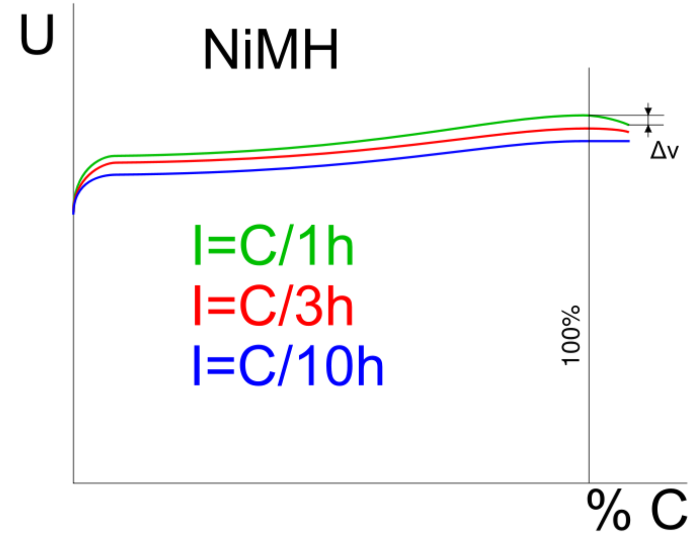
Ni-MH batteries



Discharge curves of Ni-MH

Ni-MH batteries

- Advantages:
  - High specific energy
  - High specific power
  - Flat discharge curve
  - Fast charge
  - Low sensitivity to memory effect
- Disadvantages
  - Do not withstand overcharging
  - Detection of end of charge
  - Little longer life cycle than Ni-Cd



Nickel-Zinc batteries

- Reaction:

$$2\,\mathrm{Ni(OH)_2(s)} \;+\; \mathrm{Zn(OH)_2(s)} \leftrightharpoons 2\,\mathrm{Ni(OH)_3(s)} \;+\; \mathrm{Zn(s)}$$

- ΔV = 1.65 V per element
- Energy density: ~100 Wh/kg
- Self-discharge: 1% /day
- Number of charge-discharge cycles: 400~1000 cycles
- Charge discharge efficiency: 65%
- No heavy metals (Hg, Pb, Cd)
- No metal hydrides difficult to recycle
- Zn degradation (growth of dendrites)
- High self-discharge

Lithium-based batteries

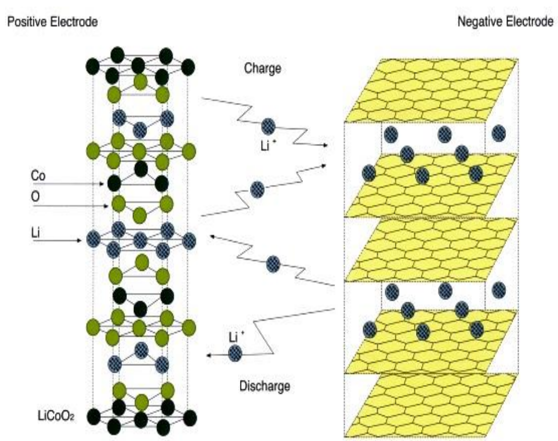
- Lithium is the lightest metallic element which allows for interesting electrochemical properties:
  - High thermodynamic voltage
  - High energy and power density

- Two major technologies of electrochemical batteries using lithium
  - Lithium-polymer
  - Lithium-ions

Li-ions batteries

- First developed in the 1990ies, it has experienced an unprecedented raise and it is now considered as one of the most promising rechargeable battery of the future
- Although still at development stage, it has already gained acceptance in HEV and EV.

Li-ions battery principle



[redacted]

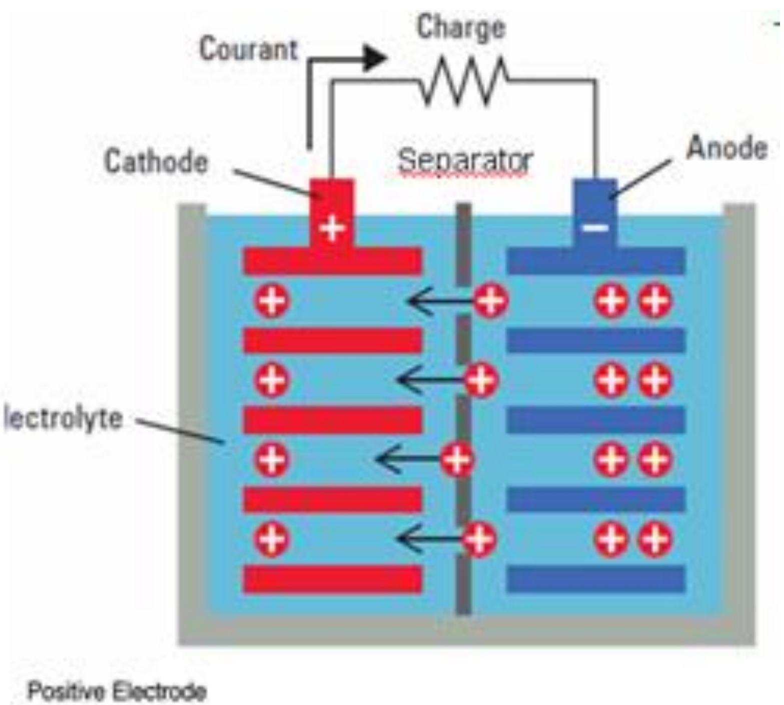
- Negative electrode: lithiated carbon intercalated Li_xC
- Positive electrode: lithiated transition metal intercalation oxide $Li_{1-x}M_yO_z$ (ex $LiCoO_2$)
- Electrolyte: liquid organic solution or a solid polymer

$$\mathrm{Li_xC} + \mathrm{Li_{1-x}M_yO_z} \leftrightharpoons \mathrm{C} + \mathrm{LiM_yO_z}$$

- Electrochemical reaction: for instance with cobalt oxides

$$\mathrm{Li_{(x+y)}C_6} + \mathrm{Li_{(1-x-y)}CoO_2} \leftrightharpoons \mathrm{Li_yC_6} + \mathrm{Li_{(1-y)}CoO_2}$$

Li-ions batteries

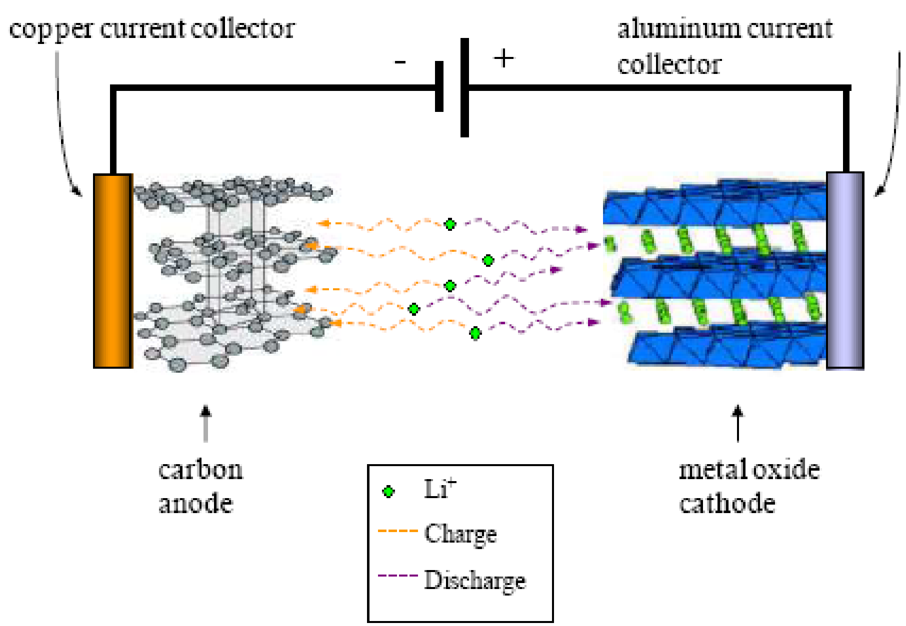


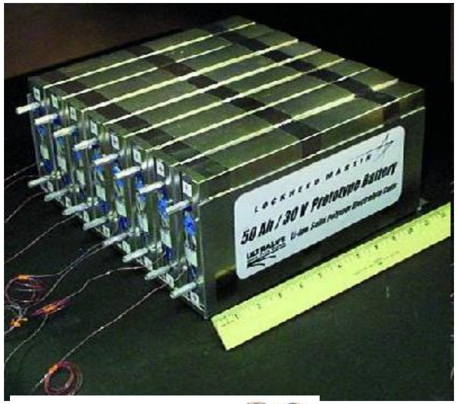
- Reversible exchange of charges (Li+ ions) between two intercalation compounds
- Discharge: Li ions are released from negative electrodes, migrate via the electrolyte and are caught up by the positive electrode.
- Possible positive electrode materials are $Li_{1-x}CoO_2$, $Li_{1-x}NiO_2$, and $Li_{1-x}Mn_2O_4$ that are stable in air, high voltage, reversibility for lithium intercalation reaction.

Li-ions batteries

- Exchange of lithum ions by intercalation between a carbon electrode (anode) and a cathode made of a metal oxyde

$$\mathrm{Li}_{(x+y)}\mathrm{C}_6 + \mathrm{Li}_{(1-x-y)}\mathrm{CoO}_2 \leftrightharpoons \mathrm{Li}_y\mathrm{C}_6 + \mathrm{Li}_{(1-y)}\mathrm{CoO}_2$$

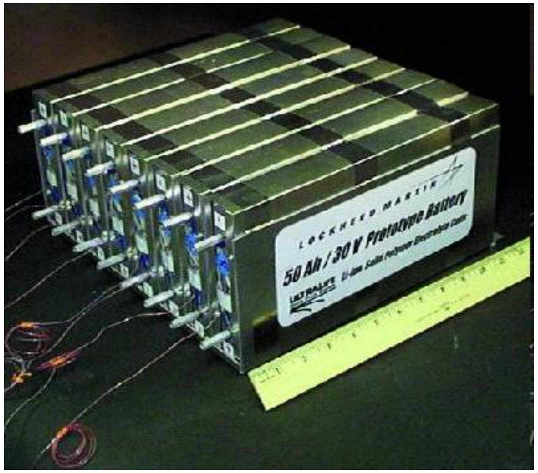




Li-ions batteries

For Li_xC / $Li_{1-x}NiO_2$ battery (C/$LiNiO_2$ or nickel based li-ion battery)

- Voltages:
  - Nominal cell voltage: 4 V
- Energy/ power density
  - Specific energy density: 100-180 Wh/kg
  - Energy density 200 Wh/l
  - Specific power density: 200-300 W/kg
- Energy efficiency: →95%
- Cycle life: > 1000 cycles
- Self discharge rate: 0,7% per 48 hours
- Cost: <200 $/kWh and decreasing
- Higher performance for Li_xC / $Li_{1-x}CoO_2$ but also higher cost due to Cobalt



Li-ions batteries

- Advantages:
  - High specific energy and high specific power
  - No memory effect
  - Low self discharge
  - No major pollutants
- Disadvantages
  - Do not withstand overcharging,
  - May present a dangerous behavior when misusage
  - Short circuit can occur due to metallic Lithium dendritic growth

Li-ions batteries

- Characteristics of Li ions batteries

Cathode materials	$LiCoO_2$	$LiMn_2O_4$	$Li(NiCoMn)O_2$	$LiFePO_4$
Reversible capacity (mAh/g)	140	100	150	145
Working voltage plateau (V)	3.7	3.8	3.6	3.2
Charge termination voltage (V)	4.25	4.35	4.3	4.2
Overcharge tolerance (V)	0.1	0.1	0.2	0.7
R.T. Cycle life (cycles)	400	300	400	1000
55℃ Cycle life (cycles)	300	100	300	800
Heat Flow by DSC (kJ/g)	650	150	600	10
Overcharge without PCB	4.9/3C Explosion	8V/3C Firing	8V/3C Firing	25V/3C Pass
Battery energy density (Wh/kg)	180	100	170	130

Li-ions batteries

Cathode

Material	Average voltage	Specific capacity	Specific energy
$LiCoO_2$	3.7 V	140 mAh/g	0.518 kW.h/kg
$LiMn_2O_4$	4.0 V	100 mAh/g	0.400 kW·h/kg
$LiNiO_2$	? V	? mAh/g	? kW·h/kg
$LiFePO_4$	3.3 V	150 mAh/g	0.495 kW·h/kg
Li_2FePO_4F	3.6 V	115 mAh/g	0.414 kW·h/kg

Anode

Material	Average voltage	Specific capacity	Specific energy
Graphite (LiC_6)	0.1-0.2 V	372 mAh/g	0.0372-0.0744 kW.h/kg
Carbone (LiC_6)	? V	? mAh/g	? kW.h/kg
Titanate ($Li_4Ti_5O_{12}$)	1-2 V	160 mAh/g	0.16-0.32 kW·h/kg
Silicium ($Li_{22}Si_6$)	? V	? mAh/g	? kW·h/kg
Si ($Li_{4.4}Si$)	0.5-1 V	4212 mAh/g	2.106-4.212 kW·h/kg
Ge ($Li_{4.4}Ge$)	0.7-1.2 V	1624 mAh/g	1.137-1.949 kW·h/kg

Li-ions batteries : comparison table

Table 1: Characteristics of lithium-ion batteries using various chemistries

Chemistry Anode/cathode	Cell voltage Max/nom.	Ah/gm Anode/cathode	Energy density Wh/kg	Cycle life (deep)	Thermal stability	
Graphite/ $NiCoMnO_2$	4.2/3.6	.36/.18	100-170	2000-3000	fairly stable	Leaf - V2
Graphite/ Mn spinel	4.0/3.6	.36/.11	100-120	1000	fairly stable	Leaf - V1
Graphite/ $NiCoAlO_2$	4.2/3.6	.36/.18	100-150	2000-3000	least stable	Tesla Model S
Graphite/ iron phosphate	3.65/ 3.25	.36/.16	90-115	>3000	stable	A123
Lithium titanate/ Mn spinel	2.8/2.4	.18/.11	60-75	>5000	most stable	Altairnano

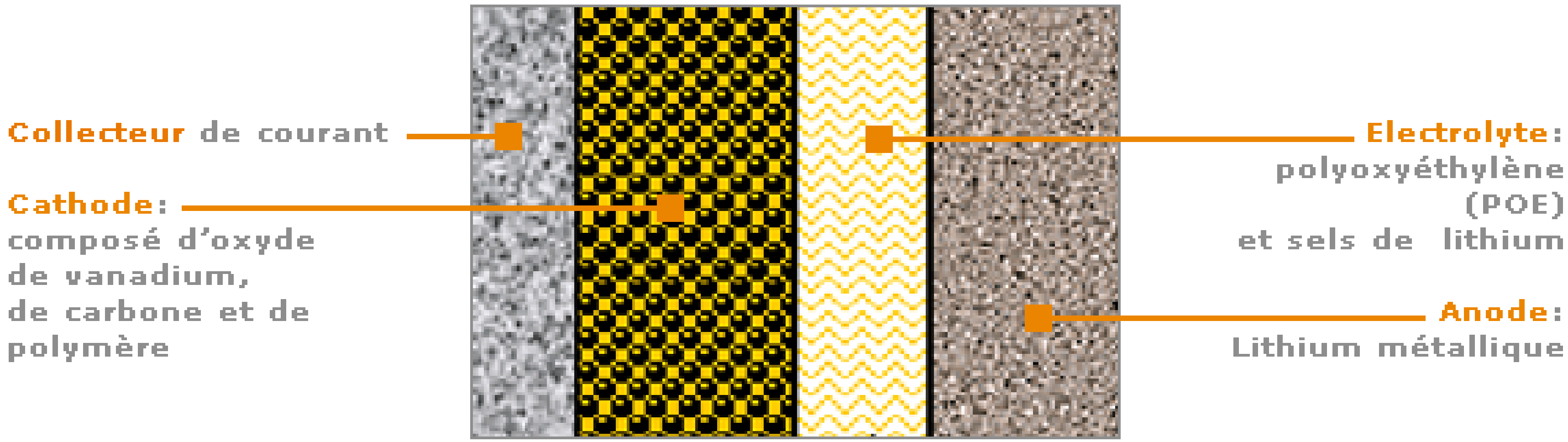
Li-polymer batteries

- Li-ions battery principle:
  - Negative electrode: lithium metal
  - Positive electrode: transition metal intercalation oxide M_yO_z
  - Electrolyte: thin solid polymer electrolyte (SPE)
  - Electrochemical reaction:

$$\mathrm{x\,Li} + \mathrm{M_yO_z} \leftrightharpoons \mathrm{Li_xM_yO_z}$$

- The layered structure of transition metal oxide M_yO_z allows lithium ions to be inserted and removed for charge and discharge
- Discharge: Li ions that are formed at the negative electrodes migrate through the SPE and are inserted into the crystal structure at the positive electrode.

Li-polymer batteries



Li-polymer batteries

- Thin solid polymer electrolyte improves safety and flexibility
- Capability of fabrication in various shapes and sizes and safe designs
- Possible positive electrode material are Vanadium oxides: V_6O_{13}

Battery Li/SPE/V_6O_{13}

- Voltages:
  - Nominal cell voltage: 3 V
- Specific energy density: 155 Wh/kg
- Specific power density: 315 W/kg
- Energy efficiency: 85%
- Self discharge: 0,5% per month

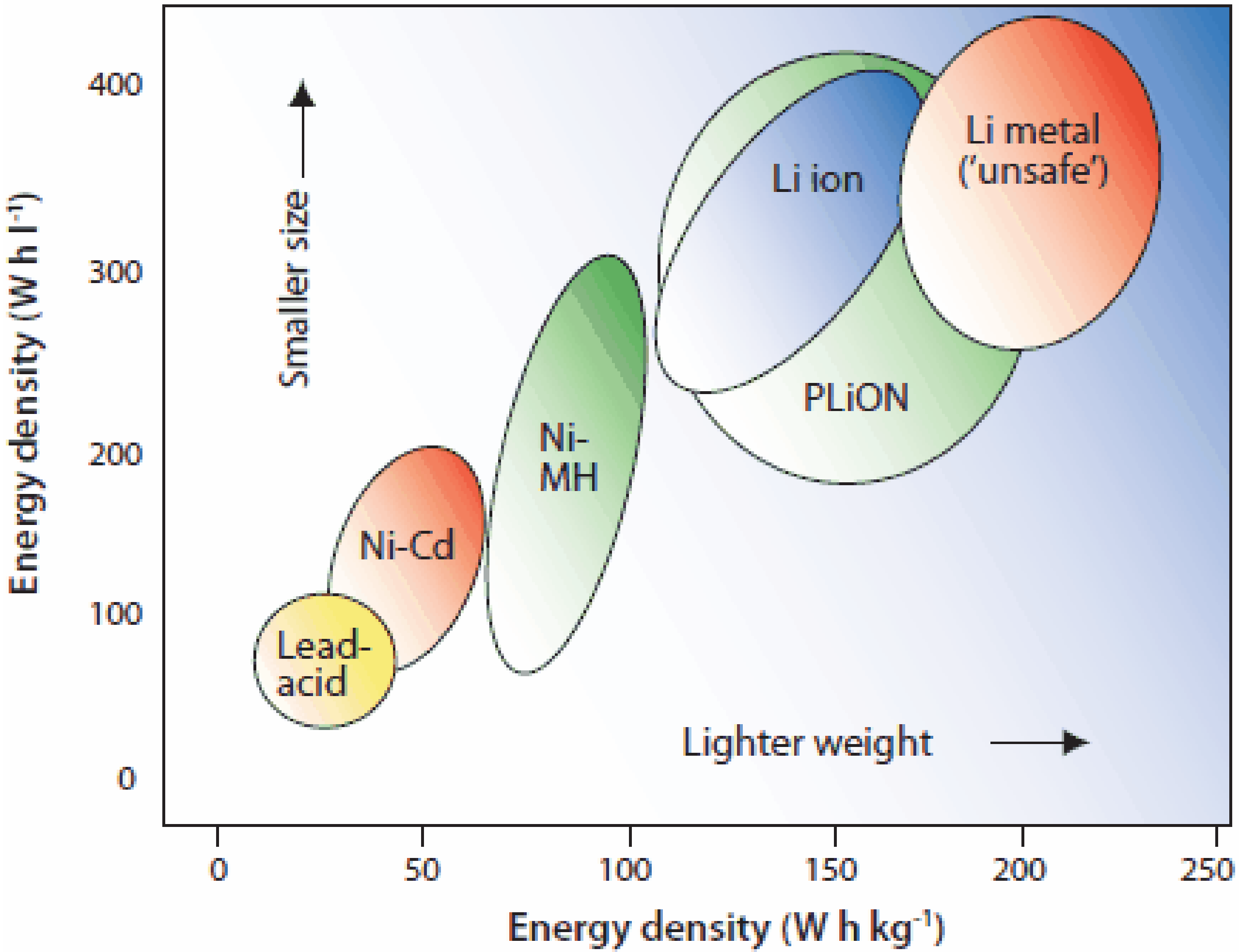
Li-polymer batteries

- Advantages:
  - High specific energy and high specific power
  - No memory effect
  - Low self discharge
  - No major pollutants
  - Various shapes and sizes
- Disadvantages
  - Lower energy density than Li-ions
  - More expensive than Li-ions
  - Specific energy density: 155 Wh/kg
  - Charging must be carefully conducted to avoid inflammation

Lithium batteries: comparaison

	Pb	Ni-Cd	Ni-MH	Li-ion
Energy density [Wh/kg]	30	30-50	70-80	160-200
Cycles [-]	500-1200	2000	500-1000	1200
Charge time [min]	300-600	180-300	180-300	90-120
Self-discharge max. [%/month]	50	10-20	20	5-10
Ch./disch. Yield [%]	50	70-90	66	99.9
Lifetime [years]	4-5	2-3	1-2	2-3

Lithium batteries: comparaison



EV and HEV Applications

NiMH battery Pack of Toyota Prius II

EV and HEV Applications

Honda Insight

Ni-MH Battery Pack of Honda Insight

EV and HEV Applications

Tesla Model S

Li ion Battery Pack of Tesla