Electric Energy Storage Systems

Lecture Notes Summer 2024

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Notes and Comments

Ideas, suggestions and hints (in particular to any found errors) are welcome. Please address them to:

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Electric Energy Storage Systems

Chapter 1: Introduction: Energy Carriers and Electric Power Generation

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Electric Energy Storage Systems

Power Generation

Energy Storage ?

Consumption

Wind Power

Solar Power

Electric Energy Storage Systems are necessary to:

- Manage variations in generation and consumption of power
- Supply mobile devices and electrified transport systems with energy

Industry

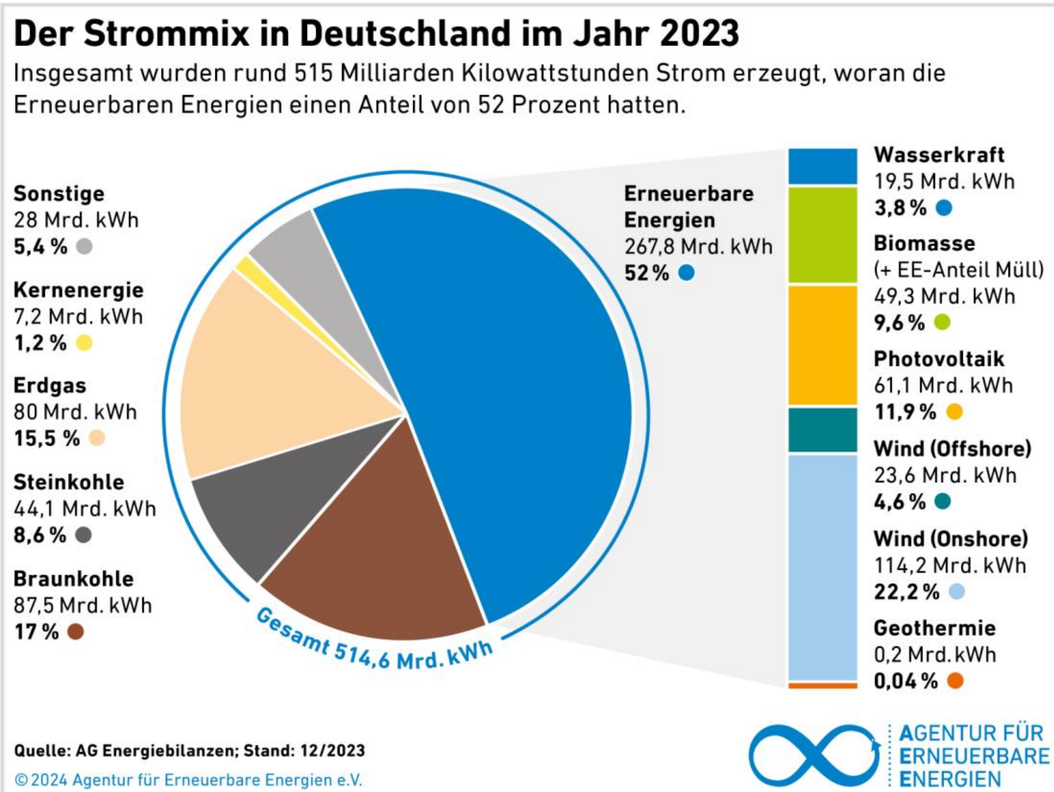
E- Mobility

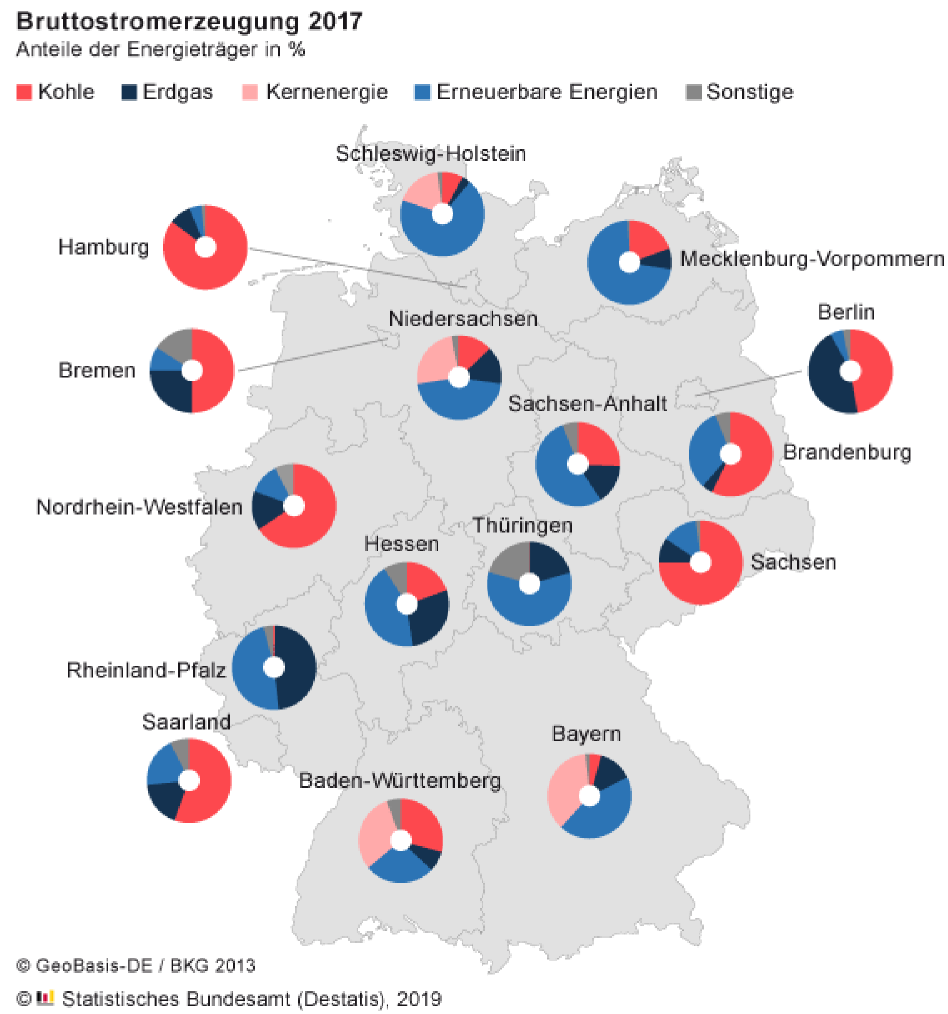
Electrical Energy Storage Technologies

Energy storaging

- **mechanical**
  - kinetic
    - Flywheel
  - potential
    - Pump storage
    - Compressed air
- **electrical**
  - E-field
    - Double layer capacitors (DLC, SuperCap)
  - B-field
    - Superconducting magnetic energy storages (SMES)
- **chemical**
  - Electrodes
    - Batteries
    - Fuel
      - Electrolyser & Fuel cell
  - Electrolyte
    - Redox flow
- **thermal**
  - Heat storage & steam turbine / generator

Electric Power Generation in Germany





Electric Power Demand in Germany(2023): 514 TWh
More than 50% supplied by renewables!

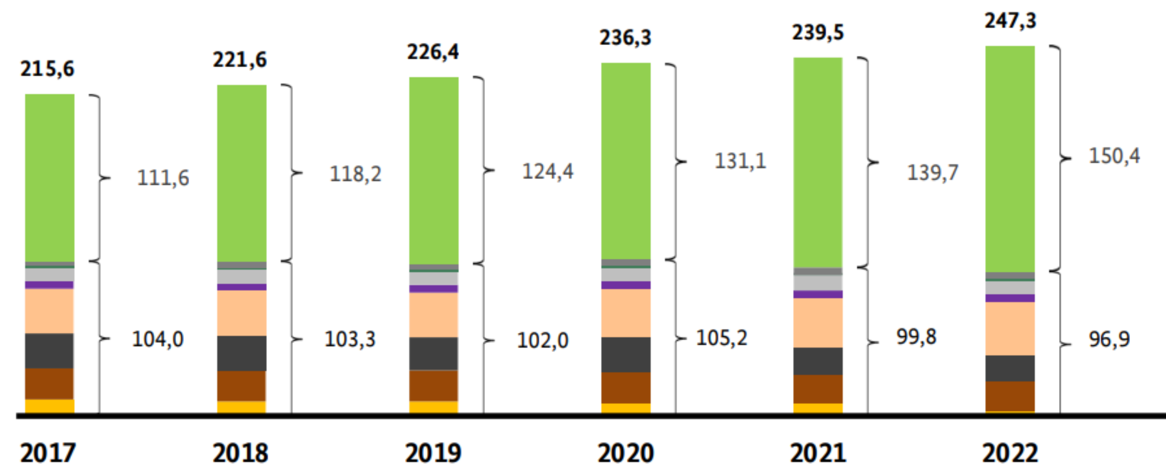
Electric Energy Storage Systems

Power demand in Germany:
514 TWh per year

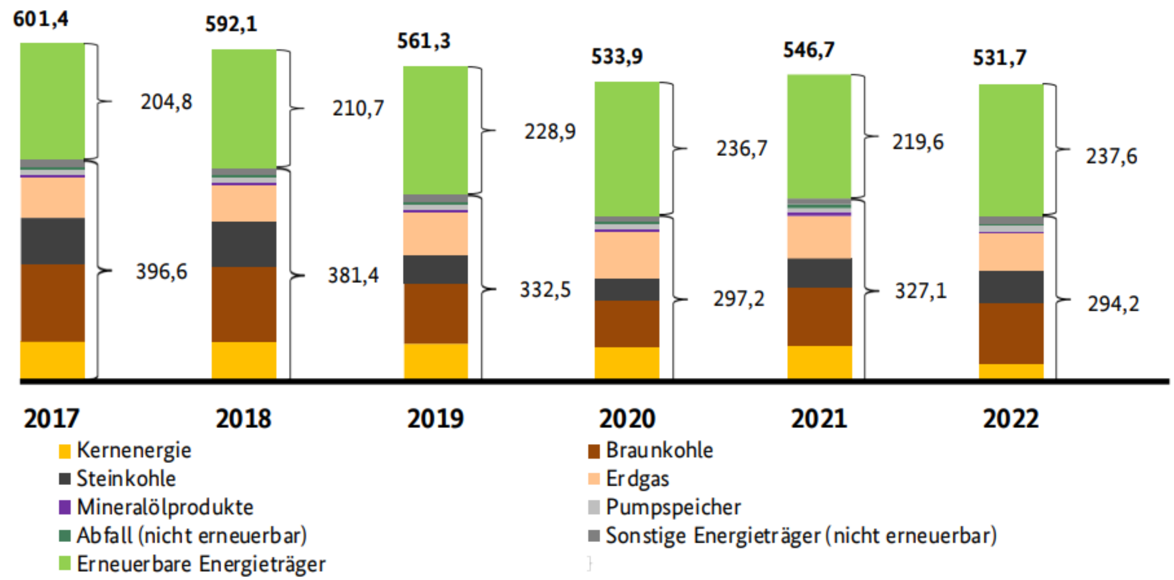
Theoretic average power demand: 58 GW

Installed power generation in 2023: 247,3 GW

Strom: Entwicklung der installierten elektrischen Erzeugungsleistung
in GW



Strom: Entwicklung der Nettostromerzeugung
in TWh



Energy content of different substances, gravimetric and volumetric

$$1MJ = 1MWs$$

$$1MJ = \frac{1MWh}{3600}$$

substance	MJ/kg	kWh/kg	MJ/dm³	kWh/dm³
brown / soft coal	8-11	2,3-3,1		
stone / hard coal	27-32	7,5-8,9		
diesel	43	11,9	36	10
gas / petrol	40	11,1	32	8,9
methane	50	13,9	0,0317	0,008
H2 @700bar	120	33,3	5,6	1,6
H2@LOHC	13,2	3,7	10,4	2,9
fission of U235	79.390.000	22.052.777 (22 GWh/kg)		

Gas-/Diesel Power Generators

- Emergency power supply in Hospitals and Industry
- Grid supply on ships
- On construction sites, when no grid is available
- Camping /leisure time
- All conventional cars and trucks

Consumption depends on operation point:
Diesel: app. 0,3-0,36 l/kWh
Petrol: app. 0,5 l/kWh

Zipper
Power Generator
with Inverter 2 kVA

APT Power 275 kVA diesel generator

Conventional Power Plant
Brown /Soft Coal

Power Plant Schwarze Pumpe

- Combustible consumption 36.000 t/day
- Efficiency app. 40%
- App. 12 Mio t CO_2 per year
- Steam output with 547°C ; 268 bar
- Generator with 27 kV and 1000 MVA

- Schwarze Pumpe 2 times 310-800MW installed

Power Plant Neurath

- Year of construction: 1973 / 1976 / 2012
- Power: 3 times 300 MW / 2 times 600 MW / 2 time 1GW
- Electric efficiency app. 34 % / 36 % / 43 %
- Largest soft coal power plant in Germany

- Neurath 3 times 300 MW; 2 times 600MW ; 2 time 1 GW

Conventional Power Plant
Stone / Hard Coal

Power Plant Datteln 4

- Start of construction 2007
- Start of operation 2020
- Power: 1 Block with 1,1 GW
- Electric efficiency 45%
- District heat power: 380 MW
- Efficiency including district heat app. 60%

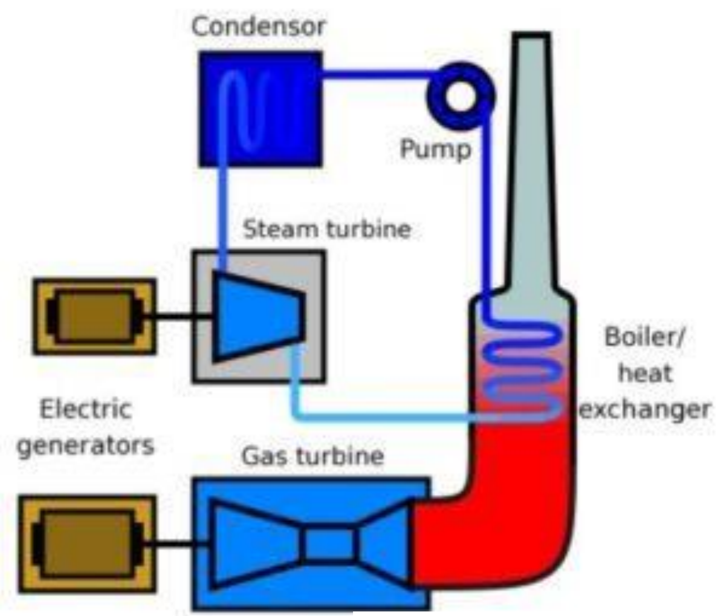
- Datteln 4

Power Plant Westfalen

- Start of operation 2014
- Power: 1 Block with 765 MW
- Electric Efficiency 45-46%

Conventional Power Plant
Natural Gas

- Power generation app. 2/3 gas turbine; 1/3 steam turbine
- Electric Efficiency app. 60 %
- Efficiency including district heat up to 85 %



Quelle: leomaschinen.de

Power Plant Emsland

- Start of Operation 2009
- Power 876 MW
- Electric Efficiency 59,2%

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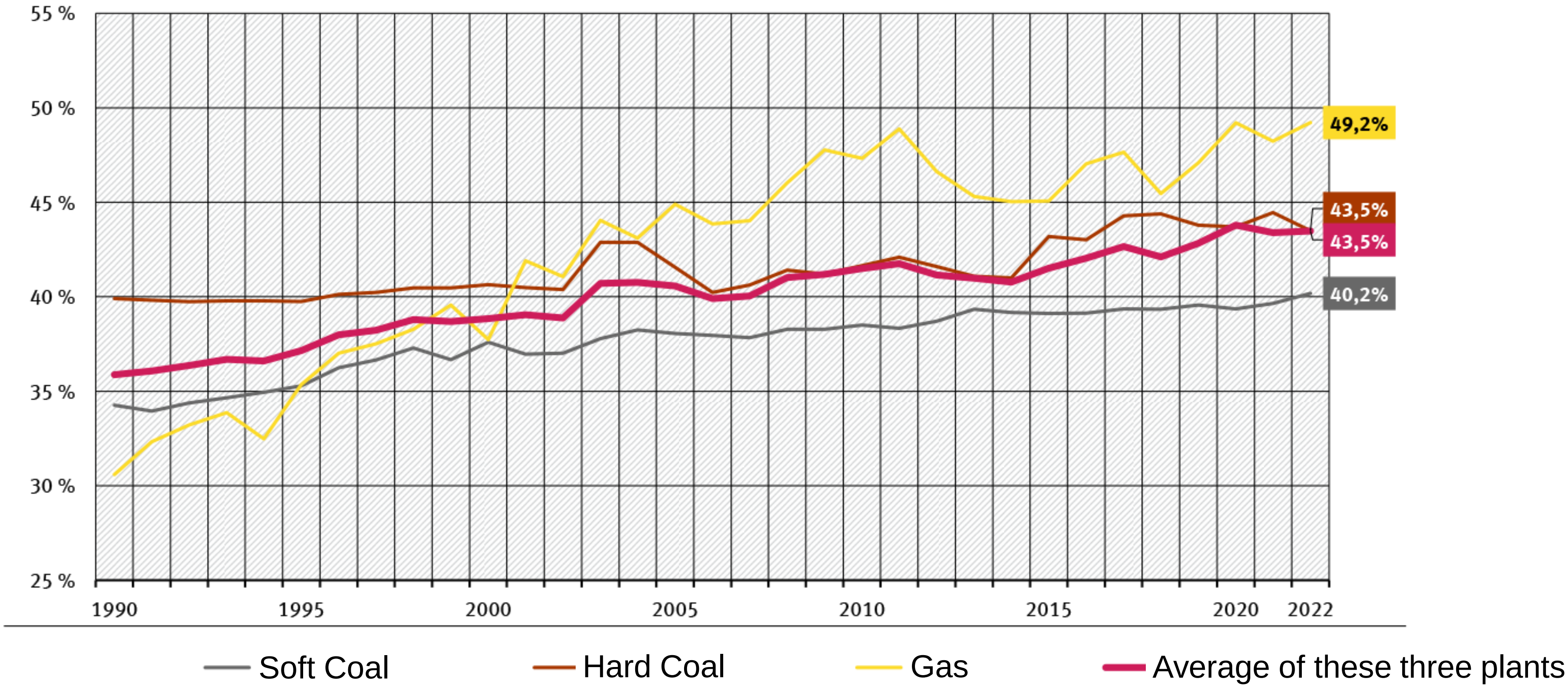
Electric Energy Storage Systems

Development of the average electric efficiency[1] of fossil power plants in Germany

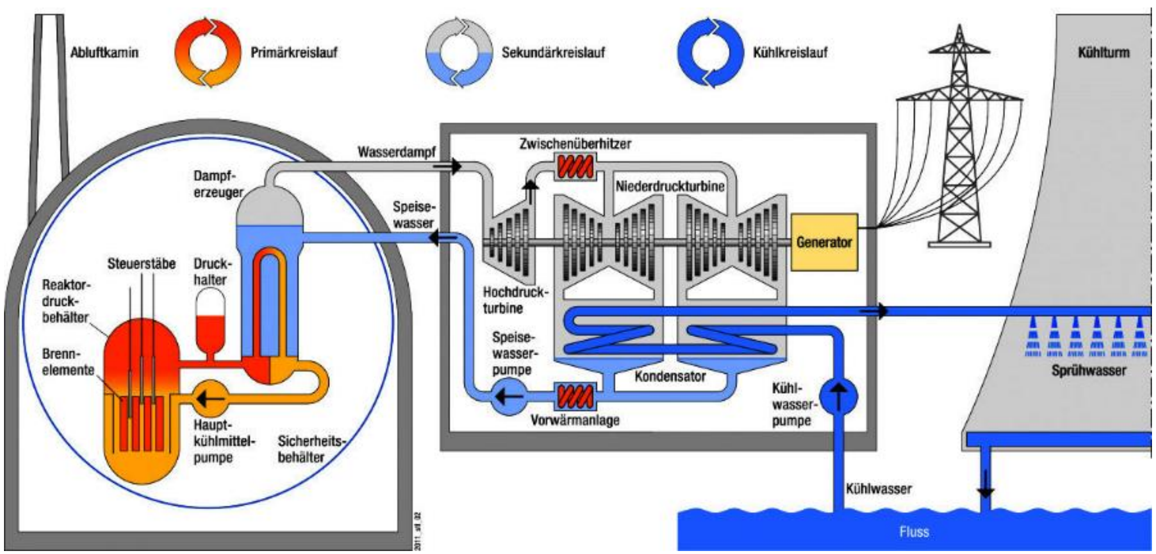


Quelle: Umweltbundesamt, eigene Berechnungen auf Basis AG Energiebilanzen: "Auswertungstabellen" (Stand 09/2023), Tabelle "Stromerzeugung nach Energieträgern" (Stand 09/2023)

Nuclear Power Plant

- First comercial operated plant 1956 in Calder Hall (England) with 55 MW
- First Plant in Germany since Feb. 1962

- In 2024 there are world wide 435 plants in operation
- Shut down of all German Nuclear Power Plants in April 2023
- Electric Efficiency app. 33-35 %



- Grafenrheinfeld
- Power 1275 MW
- Start of operation 9. December 1981
- Shut down 27. June 2015

Quelle: Nuklearsicherheit.de

Photovoltaik Power Plant

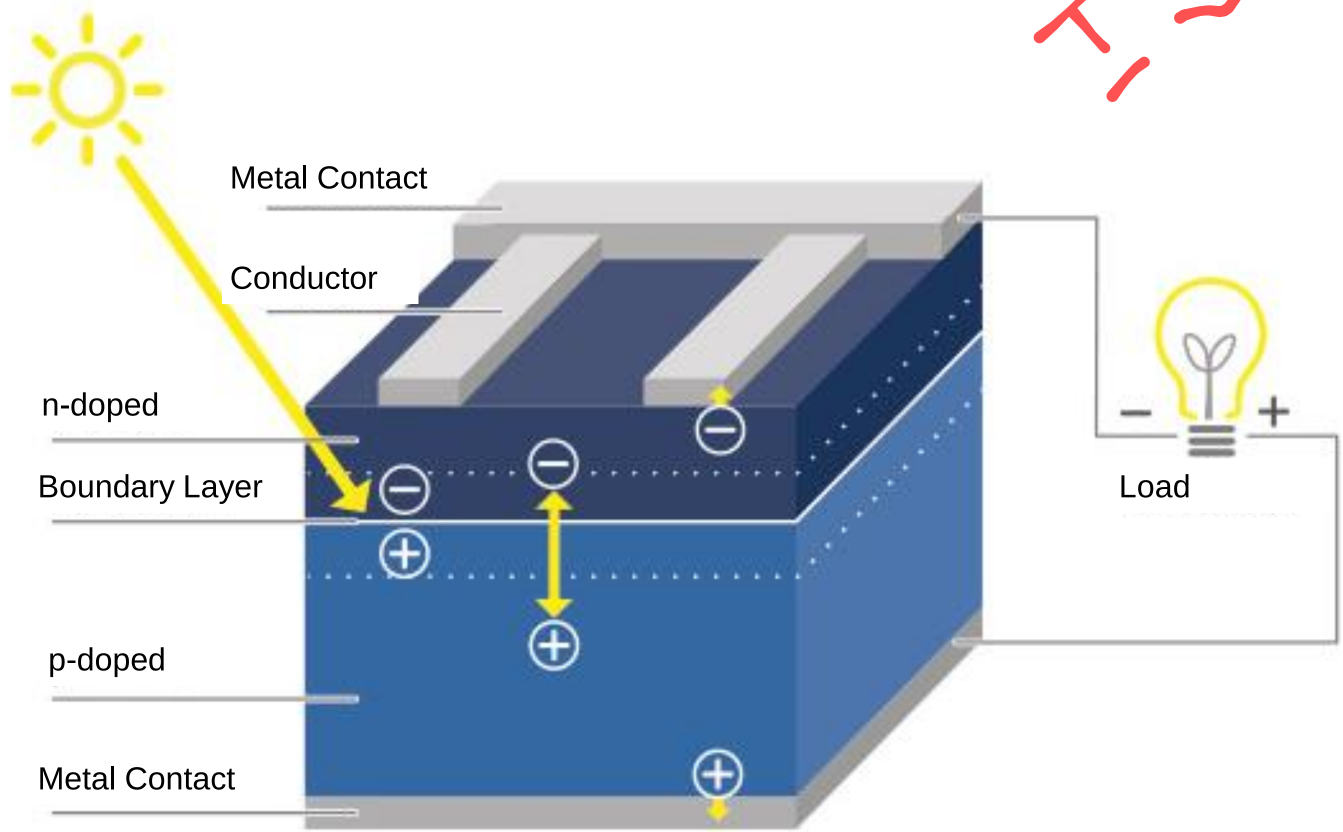
- Solar park Templin-Groß Dölln 2012
- 128 MW installed power
- 1,5 Mio Thin fil solar cells on an area of 214 ha
- Construction costs app. 205 Mio€
- Power generation 115-120 GWh per year

Solar Thermal Power Plant

(Foto: Torresol)

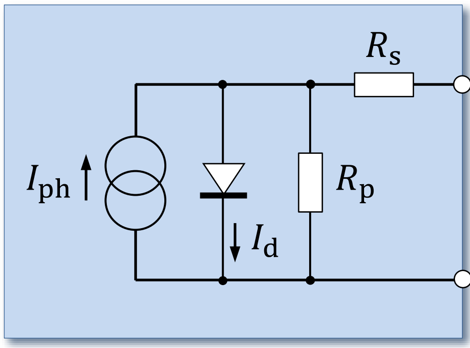
- Solar power plant GEMASOLAR 2010 in Spain
- 19,9 MW installed power (2.500 mirrors each110m²)
- Salt (8500t) is heated up to 560 °C and is powering via a heat exchanger a steam turbine
- Power plant generates electricity up to 15 h without sunlight
- Power generation 110 GWh per year
- Construction costs app. 180 Mio€

Photovoltaik – Funktion of a Solar Cell



(Quelle:Solaranlage.de | emedien.design.hs-anhalt.de)

Photovoltaic - electrical characteristics of a solar cell



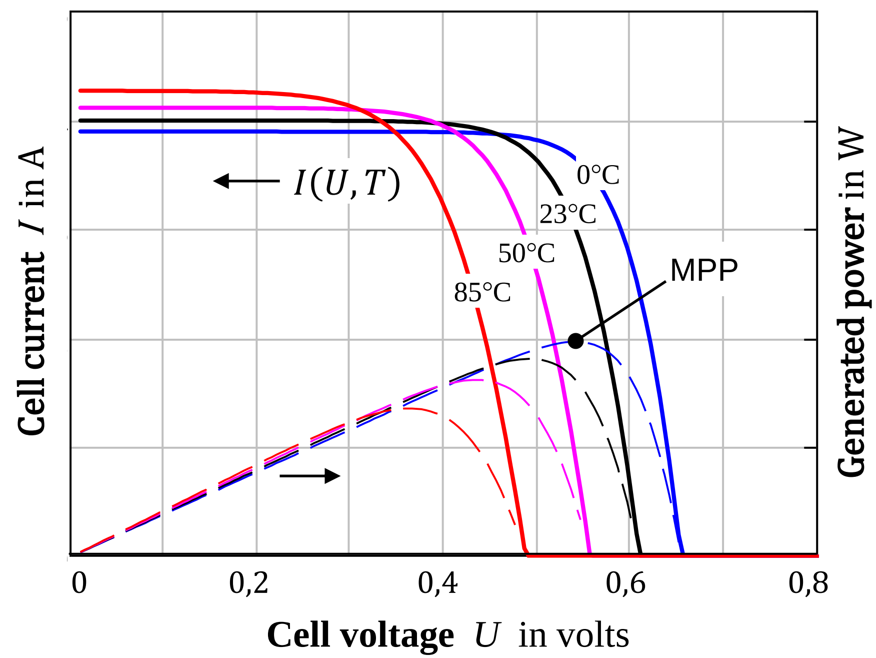
Solar cell characteristic

$$I(U,T,S) = I_{ph}(T,S) - I_s\left(e^{\frac{U+R_S(T)\,I}{n\,U_T(T)}} - 1\right) - \frac{(U+R_S(T)\,I)}{R_p}$$

and if R_s and R_p are negligible:

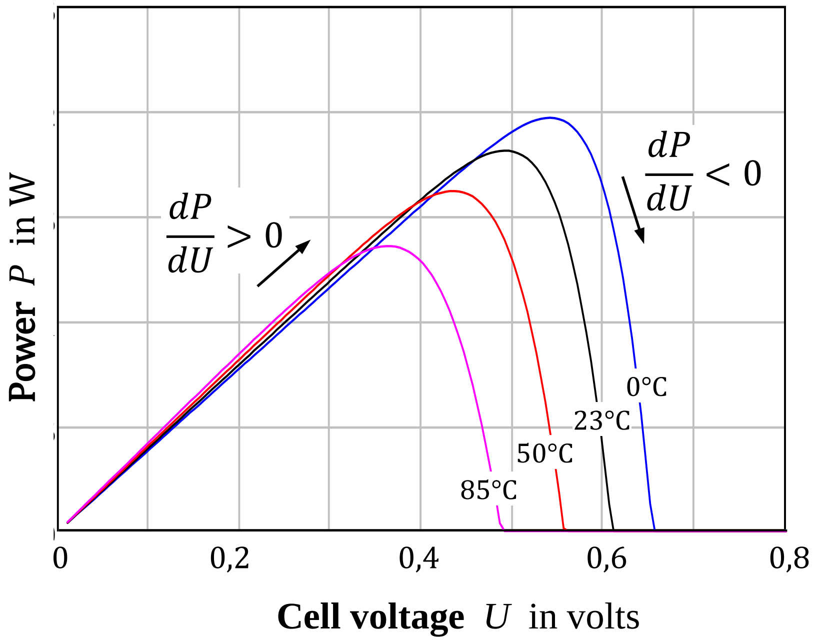
$$I(U,T,S) = I_{ph}(T,S) - I_s\left(e^{\frac{U}{n\,U_T(T)}} - 1\right)$$

S : Solar irradiance in W/cm^2
I_{ph} : Photocurrent
R_s : Series resistance



- Changing from a consumer to a generator arrow system tilts the 4th quadrant of the diode characteristic to the 1st quadrant of the PV cell characteristic.
- The hotter the PV cell, the lower the output power at a given irradiance

Maximum Power Point Tracking (MPPT)



MPP search methods

- Imposing a small disturbance and observing the change in power »perturb and observe«
- Observation of the change in conductance when the operating point changes (»Incremental conductance«). From

$$\frac{dP}{dU} = \frac{d(UI)}{dU} = I\frac{\partial U}{\partial U} + U\frac{\partial I}{\partial U} = I + U\frac{\partial I}{\partial U}$$ it follows

left of the maximum $\frac{dP}{dU} = I + U\frac{\partial I}{\partial U} > 0 \qquad \frac{dI}{dU} > \frac{-I}{U}$

and right of the maximum: $\frac{dI}{dU} < \frac{-I}{U}$

- To impose small changes in the operating point, the current/ voltage ripple caused by a connected switchmode converter or inverter can also be used.
- The MPP search for partially shaded solar modules poses a particular challenge, since the power curve can then have several local maxima.

Wind Power

Electric Power of Wind Turbine

- $P_{el} = \eta \cdot \frac{1}{2} \cdot \rho \cdot A \cdot v^3$

Mit:

P: Electric Power Watt
η: Efficiency (app. 50%)
ρ: Density of the Air
A: Rotor Area in m²
v: Velocity of Air in m/s

	1980	1990	1995	2000	2005	2008	2011	2013	2017	2017	2019[a]
Nominal Power in kW	30	250	600	1 500	3 000	6 000	7 500	7 800	7 850	7 850	11 000
Diameter of Rotor in m	15	30	46	70	90	126	126	113	180	180	193
Hub Height in m	30	50	78	100	105	135	160	149	177	177	100
Power Gen. per Year in MWh	35	95	1 250	3 500	6 900	20 000	28 500	28 900	31 400	31 400	44 000

Quelle: Landesanstalt für Umwelt Baden-Würtenberg

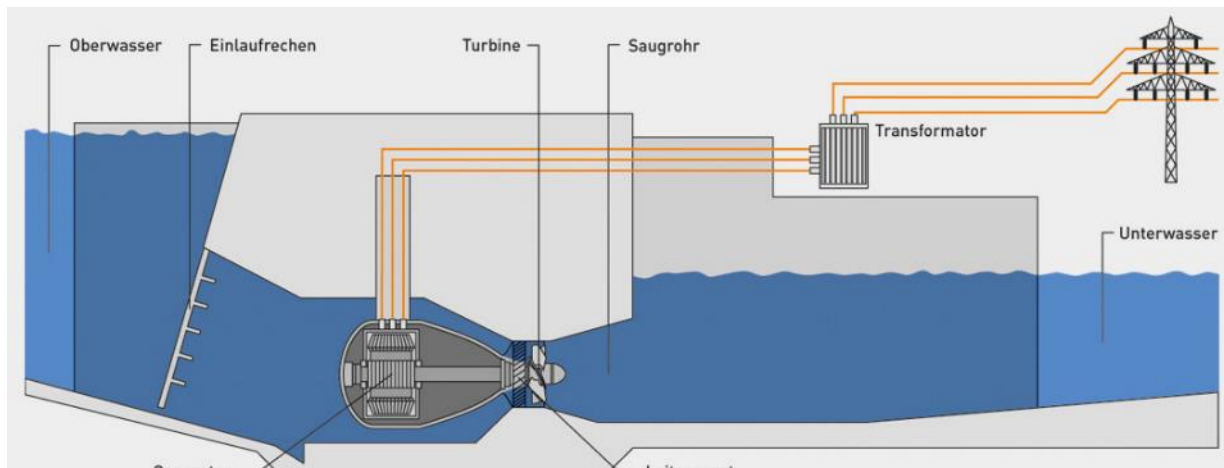
Hydropower Plant

Electric Power Generation of Hydropower Plant

- $P_{el} = \eta \cdot Q \cdot h \cdot g \cdot \rho$

Mit:

P: Electric Power in Watt
η: Efficiency (app. 50%)
Q: Water Flow Rate in m^3/s
h: Height of Water Drop in m
ρ: Density of Water in kg/m^3
g: Acceleration of Gravity in m/s^2

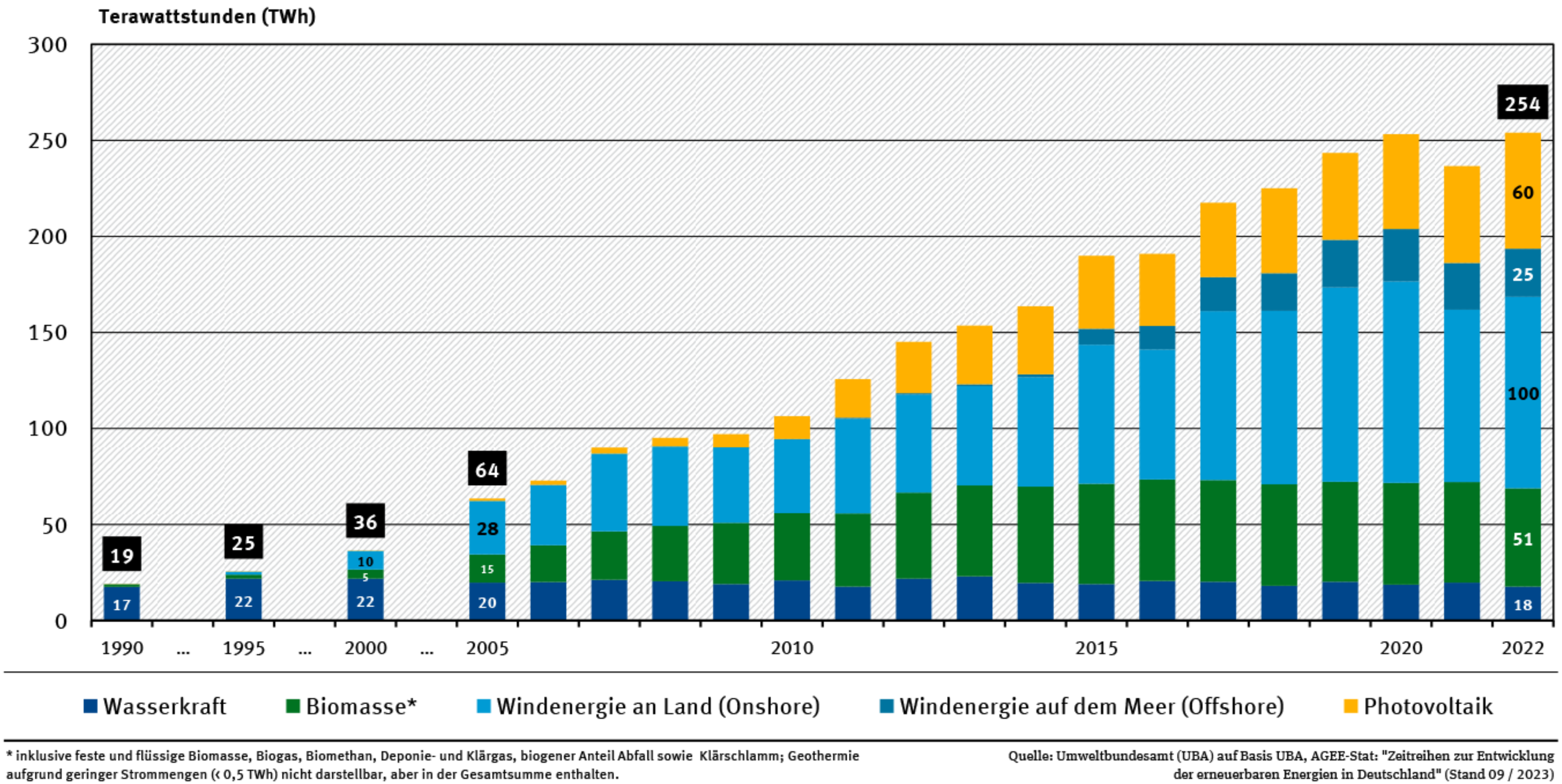


Quelle: www.EnBW.de

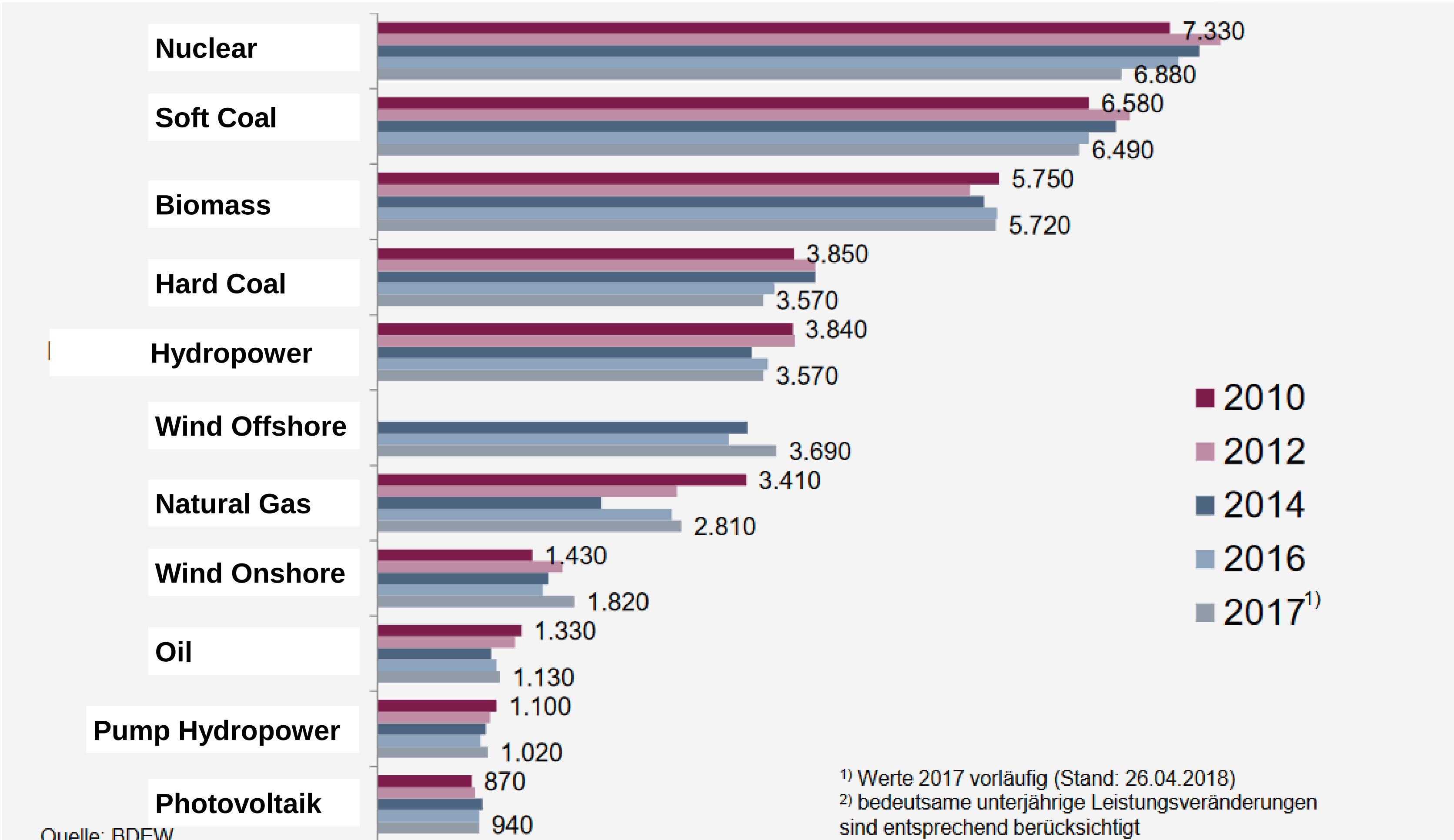
Different Hydropower Plants:
- Stream Hydropower
- Storage Hydropower

- Installed Power in Germany up to146 MW

Development of the Electricity Generation of Renewables

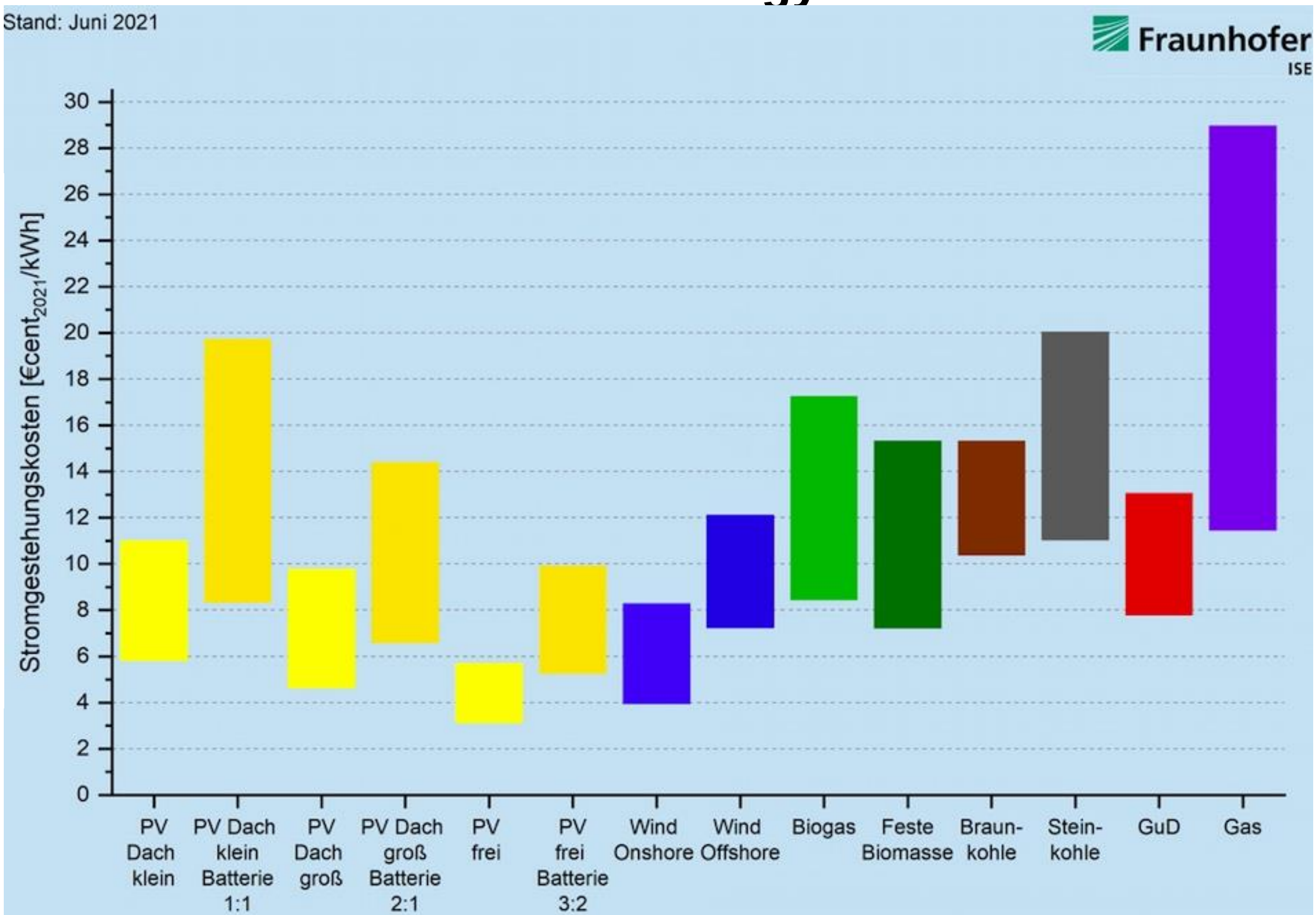


Full load hour of electric power generation per year



Generation Cost of Different Electric Energy Sources

Costs of Power Generation



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Electric Energy Storage Systems

Distribution of Electric Energy by Different Grids

- Very High Voltage Grid
  37.000 km (220 kV and 380 kV)
- High Voltage Grid
  81.000 km (110 kV)
- Medium Voltage Grid
  479.000 km (10kV … 30 kV)
- Low Voltage Grid
  1.123.000 km (400 V, 690 V)

Quelle: www.dena.de

Quelle: Alexrk2 - CC BY-Sa 3.0 / © OpenStreetMap - CC-BY-SA-2.0

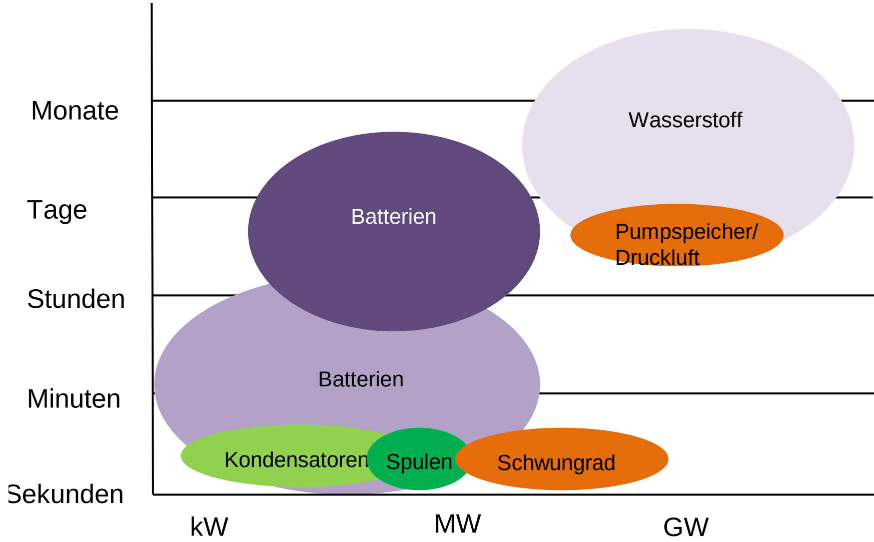
Necessity of Stationary Energy Storage Systems

Due to the increasing supply of the energy grid by fluctuating power of renewable energy sources it can come to a shortage of power delivered to the grid.

Possible actions to handle these challenge:

- Hold peak load power plants ready (e.g. Gas-Steam-Power Plants)
  - Only a few operation hours per year, poor profitableness
  - Air pollution during energy generation
  - At surplus supply of renewables wind and solar power plants must be shut down.

- Setup of Energy Storage Systems
  - Short time storage systems supply peak power in the range of seconds to several minutes
    e.g. Super Capacitors, batteries, Fly Wheels, supra conducting inductors
  - Long time storage systems deliver power of over days up to month e.g. pump-/air pressure storage, Hydrogen,
    Redox-Flow-Batteries, High Energy Batteries



Necessity of Mobile Energy Storage Systems

More and more applications need a mobile energy supply

Starter Batterie
Lead Acid 12 V ca. 60-100 Wh

Battery powered lawn mower
LiIo-Battery 36 V ca. 70-150 Wh

Smartphone
LiIo-Battery 3,7 V ca. 10-15 Wh

E-Forklift
Lead Acid 80 V ca. 4-6 kWh

Electric Car
LiIo-Battery 400 V
ca. 40-100 kWh

Electric Energy Storage Systems

Chapter 1:
Exercise

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Wind Farm:

For a wind farm with 10 wind turbines, a turbine should be selected that can generate 1 MW at wind speeds of 20 m/s.

1. What is the needed diameter of the rotor for a 1 MW wind turbine?

2. How much electricity will the wind farm generate at 20m/s wind in one day?

3.How much electric energy can the wind farm generate max. per year at 20 m/s wind?

4. What will be the average power generation per year for on shore and off shore installation?

5. What is the difference in costs for on and off shore installations per kwh?

Hydro Plant:

A stream hydropower plant should be designed to generate 500 kW. The river has a flow rate of 80000 m^3/h

1. What is the needed height of water drop?

2. What will be the average power generation per year?

3. What are the advantages and disadvantages of a stream hydro power plant?

Conventional Power Plant:

A conventional brown coal power plant with two blocks of 500 kW each. The efficiency is 40%.

1. How much brown coal is needed per day?

2. How can the overall efficiency of a conventional power plant be improved.

3. What kinds of conventional power plants have the highest efficiency?
   How is thise achieved?

Electric Energy Storage Systems

Chapter 2: Basics on electrochemical energy storage systems and Lead Acid Batteries

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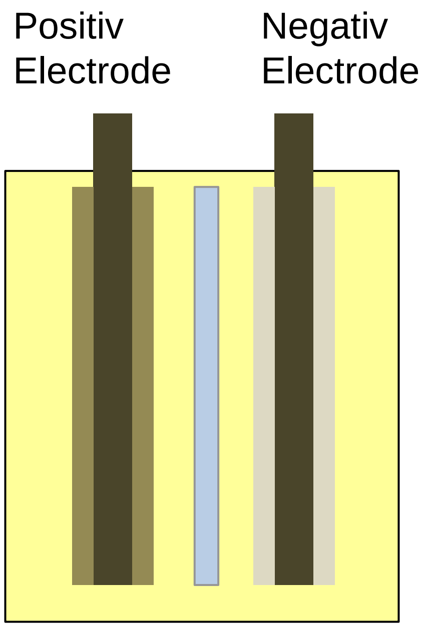
Basics on electrochemical energy storage systems



Basics of electro-chemical energy storage

Historic Development

1780 Luigi Galvani observed contraction of frog muscle by electricity
1800 Allessandro Volta discovers the continuous flow of current between two metal plates (zinc/silver; zinc/copper) immersed in electrolyte (first primary batteries)

1802 first rechargeable battery (first secondary battery) from Johann Wilhelm Ritter

1833 Faraday's Law of Equivalent of Amount of Substance and Amount of Charge

1854 first lead acid battery from Sinsteden

1859 lead acid battery from Plantè

1899 Waldemar Jungner developed the Nikel-Cadmium (NiCd) battery

1990 first marketable nickel-metal hydride (NiMH) rechargeable batteries

1991 first market-ready lithium-ion (LiIo) batteries

Basics of electro-chemical energy storage

The electric charge: $Q = \int_0^t i \, dt$

Imp

For constant current we get: $Q = I \cdot t$

The electrical charge related to the elementary charge of an electron:

$$1\ As = 1C = 6.241 \cdot 10^{18}\ |e|$$

The molar mass corresponds exactly to the mass of N_A molecules:

$$N_A = 6.022 \cdot 10^{23}\ \frac{1}{mol}$$

Equivalence between electric charge and chemical mass:

$$Q = n \cdot z \cdot F$$

With z: amount of substance in mol; n: number of exchanged electrons; F: Faraday constant

Faraday constant F: $F = N_A \cdot e = 96487 \frac{As}{mol}$

Basics of electro-chemical energy storage

Thermodynamics of batteries:

Enthalpy H: Energy stored in a chemical compound
Free Enthalpy G: Amount of energy that can be converted into electrical energy

Reaction enthalpy ΔH : Energy given off or absorbed
Free enthalpy of reaction ΔG : Energy that is converted electrically

Reaction entropy ΔS : Describes the deviation between ΔH and ΔG
The energy difference is proportional to the temperature T,
For the reversible heat effect, $T \cdot \Delta S$ is used

The following relationship applies: $\boxed{\Delta G = \Delta H - T \cdot \Delta S}$

At a constant ambient temperature, a battery has a theoretical efficiency of 100%

The reversible heat effect is: $\boxed{T \cdot \Delta S = \Delta H - \Delta G}$

Basics of electro-chemical energy storage

The equilibrium voltage U_0 of electrochemical systems is calculated as follows:

$$U_0 = -\frac{\Delta G}{n \cdot F}$$

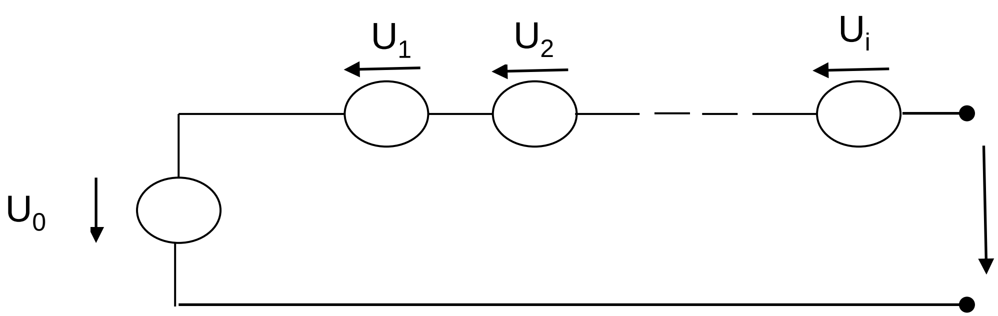
The theoretical (maximum) specific energy:

$$E_{TH} = -\frac{\Delta G}{M}$$

The terminal voltage U of the battery:

$$U = U_0 + \sum_i U_i$$

ΔG : Free enthalpy of reaction
F: Faraday's constant
n: number of exchanged electrons;
M: molar mass of all reactants



equivalent circuit for the terminal voltage U

Influence on the terminal voltage has:

- Self-discharge through secondary reactions
- Ohmic overvoltages
- Penetration overvoltage
- Diffusion overvoltage

Influence on the terminal voltage

Open circuit voltage
The open-circuit voltage, which is measured on the battery cell, is lower than the equilibrium voltage because the cell is loaded by side reactions/self-discharge

Ohmic overvoltage Caused by:
- resistance of the electrical dischargers
- resistance of the electrolyte (strongly dependent on temperature, aging)
- Resistance of the active material (depending on state of charge, aging)

Breakdown overvoltage
The transition from electrical to ionic conduction is referred to as charge transfer,
To activate it, energy in the form of voltage must be applied.

Double layer capacity
A double-layer capacitance forms at the electrode/electrolyte transition.

Diffusion overvoltage
Diffusion of ions in the electrolyte due to the difference in concentration

Basics of electro-chemical energy storage

Electro-Chemical Potential

The electro-chemical potentials related to the hydrogen reference electrode are used to select the positive and negative electrodes.

Element im Redox-Paar, dessen Oxidationsstufe sich ändert	oxidierte Form	+ z e− ⇌	reduzierte Form	Standard-potential E°
Fluor (F)	F2	+ 2 e− ⇌	2 F−	+2,87 V
Schwefel (S)	S2O82−	+ 2 e− ⇌	2 SO_4^{2-}	+2,00 V
Sauerstoff (O)	H2O2 + 2 H3O+	+ 2 e− ⇌	4 H2O	+1,78 V
Chlor (Cl)	Cl2	+ 2 e− ⇌	2 Cl−	+1,36 V
Sauerstoff (O)	O2 + 4 H+	+ 4 e− ⇌	2 H2O	+1,23 V
Nickel (Ni)	NiO2 + 2 H2O	+ 2 e− ⇌	Ni (OH)2 + 2 OH−	+0,98 V
Silicium (Si)	SiO2 + 4 H+	+ 4 e− ⇌	Si + 2 H2O	+0,857 V
Quecksilber (Hg)	Hg2+	+ 2 e− ⇌	Hg	+0,85 V
Silber (Ag)	Ag+	+ e− ⇌	Ag	+0,80 V
Kupfer (Cu)	Cu+	+ e− ⇌	Cu	+0,52 V
Sauerstoff (O)	O2 + 2 H2O	+ 4 e− ⇌	4 OH−	+0,40 V
Eisen (Fe)	[Fe (CN)6]3−	+ e− ⇌	$[Fe (CN)6]_4^-$	+0,36 V
Kupfer (Cu)	Cu2+	+ 2 e− ⇌	Cu	+0,35 V
Wasserstoff (H)	2 H+	+ 2 e− ⇌	H2	0 V
Eisen (Fe)	Fe2+	+ 2 e− ⇌	Fe	−0,41 V
Schwefel (S)	S	+ 2 e− ⇌	S2−	−0,48 V
Mangan (Mn)	Mn2+	+ 2 e− ⇌	Mn	−1,18 V
Aluminium (Al)	Al3+	+ 3 e− ⇌	Al	−1,66 V
Magnesium (Mg)	Mg2+	+ 2 e− ⇌	Mg	−2,362 V
Natrium (Na)	Na+	+ e− ⇌	Na	−2,71 V
Lithium (Li)	Li+	+ e− ⇌	Li	−3,04 V

What is a C Rate?

Charging/discharging currents respectively power values are always to be seen in relation to the capacity or the energy content of a battery!

$$\text{C Rate} = \frac{\text{Current}}{\text{Rated capacity [Ah]}} = \frac{\text{Power}}{\text{Nominal energy content [Wh]}} \qquad [\text{C Rate}] = \text{h}^{-1}$$

Example

Discharging a
100 kWh Battery with a power of 250 kW
(⇨ C Rate = 2,5 h^{-1})

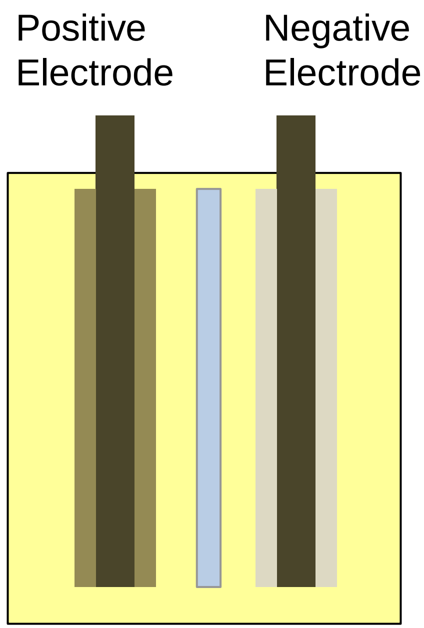
means far less stress on the cells than discharging a
5 kWh Battery with a power of 50 kW
(⇨ C Rate = 10 h^{-1})

For modern Li-Ion cells, guideline values when discharging are

C Rate [h^{-1}]	
< 1	uncritical load
1 - 3	incipient impact on lifetime
3 - 10	Cell technology must be specified for this stress, significant impact on lifetime
> 10	Only possible with certain cell technologies (LFP, LTO), thermal management and temperature monitoring are mandatory

The critical C rates during charging are generally significantly lower than when discharging, especially at low temperatures!

Lead-Acid Batteries



Lead-Acid Batteries

History:
1854 Functional principle discovered by W. J. Sinstreden
1859 Gastron Planté's first functional accumulator
1932 first gel-like electrolyte by Artur Rudolf

Advantages:
- Cell voltage of approx. 2 V
- Good low temperature behavior
- Long service life possible (especially in trickle charge mode (important for UPS))
- High recycling rate (approx. 99%) - Low price per kWh

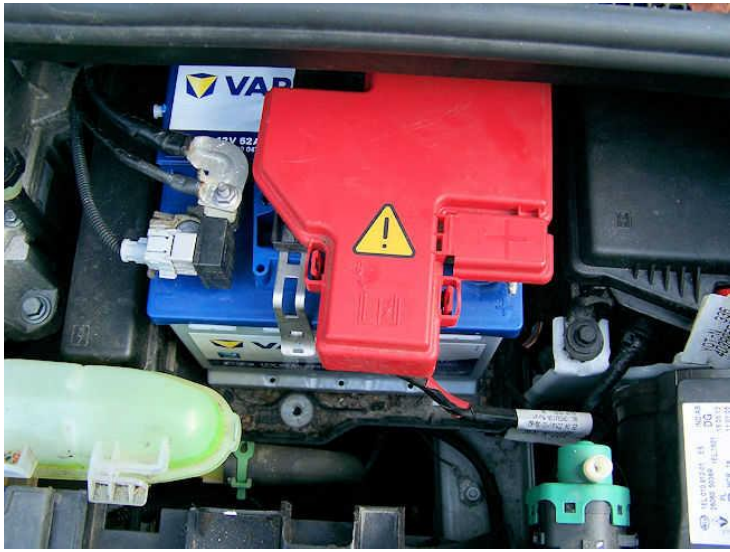
Disadvantages:
- High weight due to low specific energy of approx. 35-40 kW/kg
- Short service life with cyclic loading
- Relatively high self-discharge, therefore only a few months storable
- Ventilation of open cells necessary when charging (oxygen and hydrogen can develop)

Lead-Acid Batteries

Application:

Starter battery for vehicles with combustion engines (approx. 55% of the PB battery market)

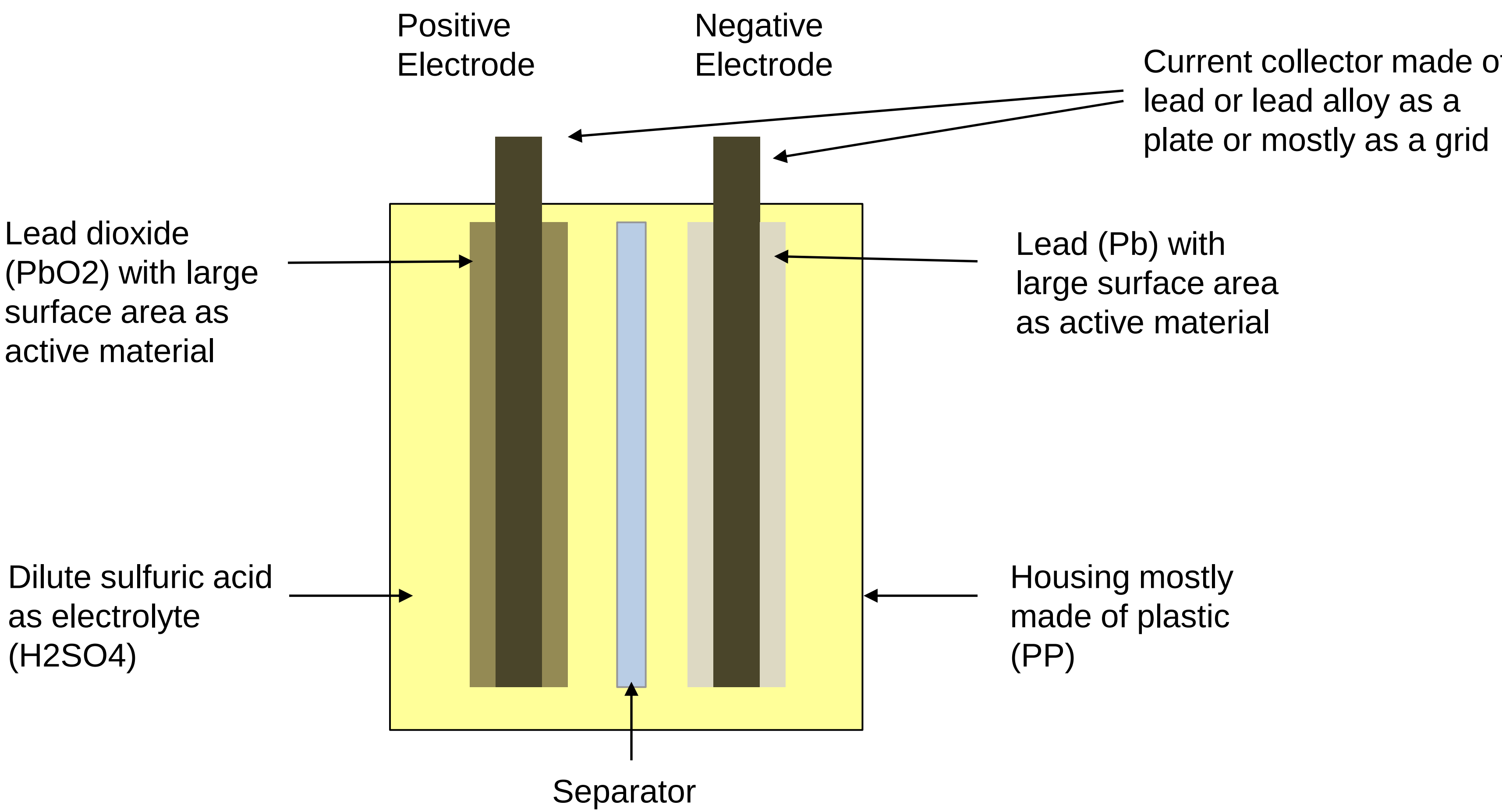
Storage battery for uninterruptible power supply (UPS)



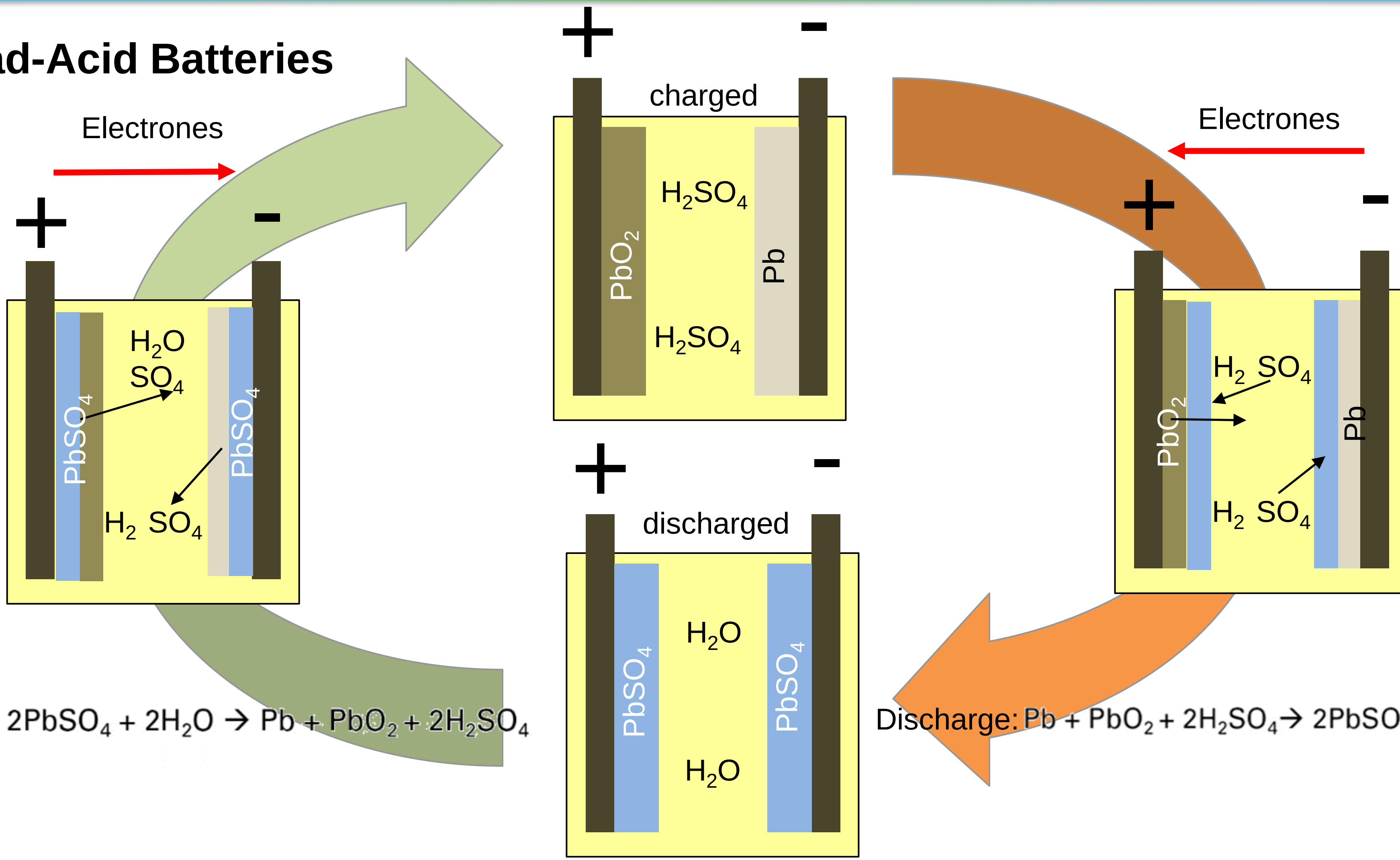
Forklift

Lead-Acid Batteries

Setup:



Lead-Acid Batteries



Charge: $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

Discharge: $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

The mode of operation of the lead-acid battery can be illustrated using the chemical processes that take place during charging and discharging or when current is drawn.

The following chemical processes take place during discharge:
Negative pole:

$$Pb + 2H^{+} + SO_4^{\,2-} \longrightarrow PbSO_4 + 2e^{-} + 2H^{+}$$

Potential: -0,36 V

Positive pole:

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

Potential: +1,68 V

When loading, the processes take place in the opposite direction, it is a question of forced disproportionation.

The overall reaction when discharging and charging:

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

Spannung: 2,04 V

The reversible heat of reaction is approx. 3.3% of the converted energy and leads to heating when discharging and cooling when charging

Side reactions in the lead-acid battery

Self-discharge:

$$2\ PbO_2 + 2\ H_2SO_4 \longrightarrow 2\ PbSO_4 + 2\ H_2O + O_2$$

Lead(IV) oxide is unstable in sulfuric acid solution.

Electrolysis of water

The aqueous electrolyte and a cell voltage of approx. 2 V produce oxygen and hydrogen (from 1,229 V) through electrolysis.

Positive electrode: $2\ H_2O \longrightarrow O_2 + 4\ H^+ + 4\ e^-$

Negative electrode: $4\ H^+ + 4\ e^- \longrightarrow 2\ H_2$

Overall reaction $2\ H_2O \longrightarrow 2\ H_2 + O_2$

High hydrogen and oxygen overvoltages counteract this.
It leads to loss of electrolyte (water has to be refilled)

Secondary reactions in the lead-acid battery - grid corrosion

Positive Electrode: (Potential Dependent Response)

$$Pb + 2\,H_2O \longrightarrow PbO_2 + 4\,H^+ + 4\,e^-$$

$$Pb + 2\,H_2SO_2 \longrightarrow PbSO_4 + 2\,H^+ + 2\,e^-$$

Negative Electrode:

$$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$$

The grid of the positive electrode is slowly decomposed, the internal resistance increases.

Lead-acid batteries - "Grid" current collector (1/3)

Requirements:

- Small ohmic resistance
- Good contact with the active material
- Good mechanical stability
- Good electrochemical stability

Used material:

Pure lead

- Low mechanical stability + High corrosion resistance at the pos. electrode
- After a few deep cycles, contact with active material deteriorates
- Use only in winding cells

Lead-acid batteries - "Grid" current collector (2/3)

Alloy used:

Lead Antimony:

+ improved mechanical stability
+ positive influence on the cycle life
- Reduction of H2 overvoltage on neg. electrode
- increased water consumption
- Cannot be used in sealed batteries

Lead-Calcium-Tin-(Silver)

+ Small amounts (approx. 0.05%) of calcium accelerate hardening when pouring
+ Addition of approx. 1.2% tin increases the cycle life
+ Addition of very small amounts (approx. 0.003%) of silver increases the service life
+ Good contact between grid and active material
+ Low self-discharge

This alloy is used in most sealed batteries

Imp

Lead-Acid Batteries - "Grid" current collector (3/3)

Mechanical construction:

Expanded Metal
+ Very cheap to produce
- Low mechanical stability
- High electric resistance

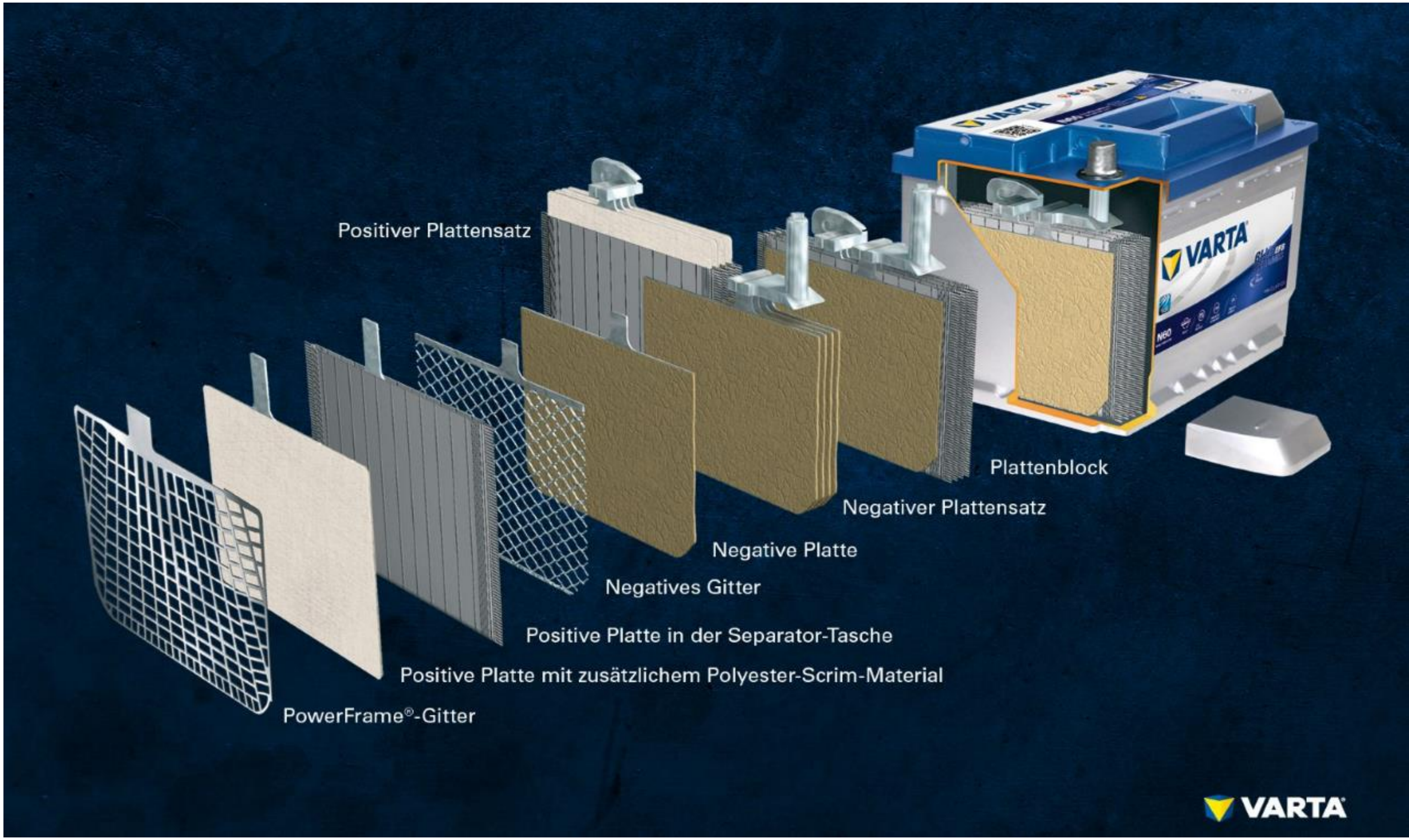
Quelle: microcharge.de

Casted Grid
+ High mechanical stability
+ low electric resistance caused by
+ design of the grid can be optimized

Quelle: Moll Batterien

Lead-Acid Batteries

Construction of a lead-acid Batterie using a Varta batterie for example



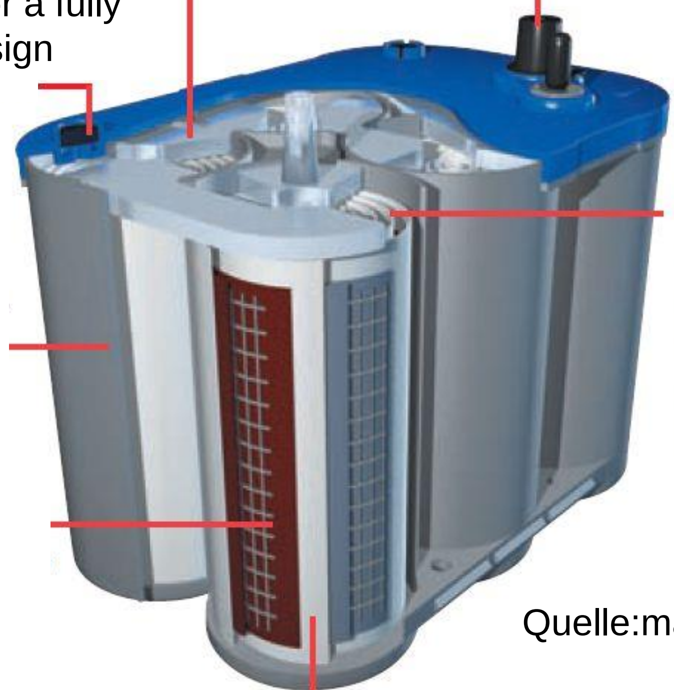
Lead-Acid Batteries

Construction example
Showing cylindrical
windes cells

Solid cast connections

Corrosion resisting
connectors

Safety valve for a fully
sealed cell design



Spiracell Technology
for higher vibration
ruggedness and
longer operation life

Robust
Polypropylene housing

Plates with grid of
pure lead

Quelle:maurelma.ch

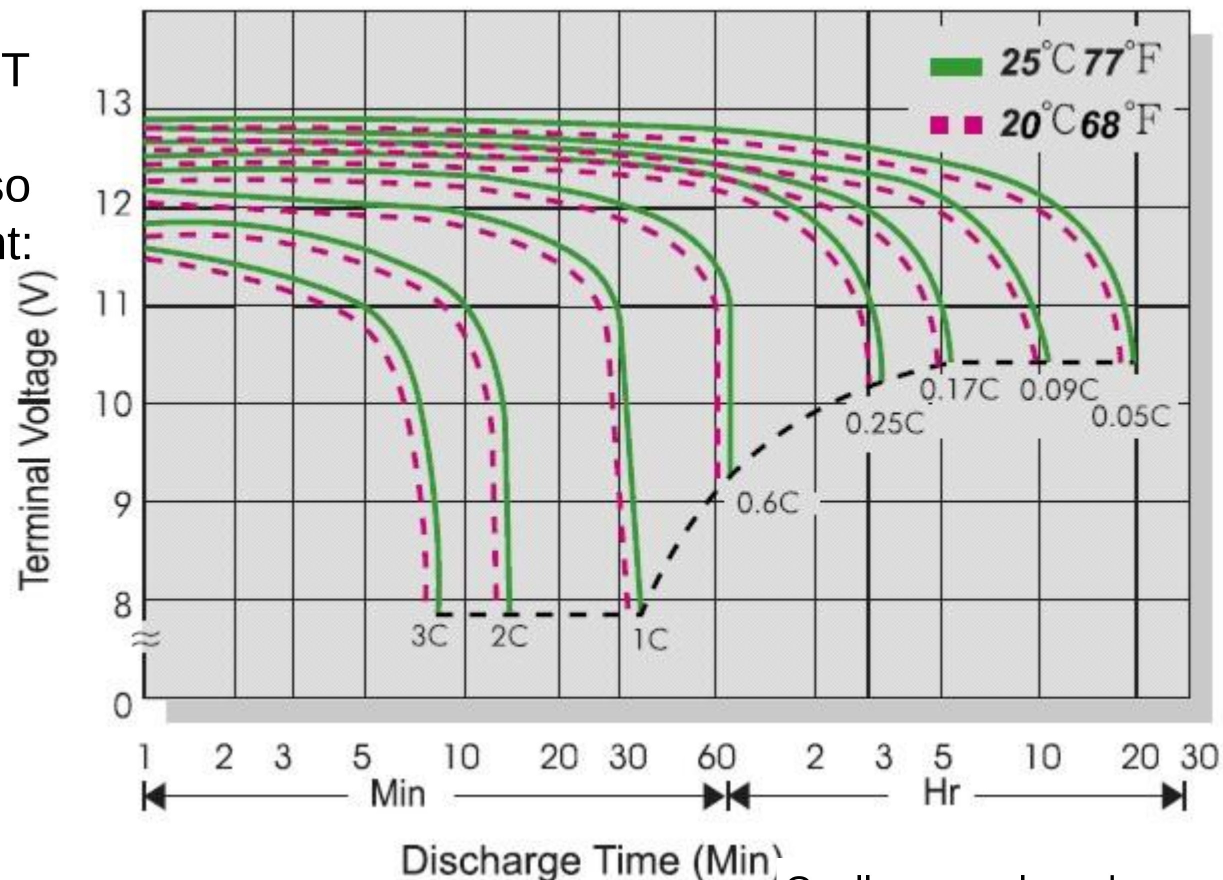
Electrolyte completely bound in the permeable glass fleece separator

Lead-Acid Batteries - Discharge Behavior

Depending on:
Discharge rate in C temperature T

The end-of-discharge voltage also depends on the discharge current:

discharge current	appr. voltage
0,01 C	1,90 V
0,1 C	1,75 V
0,6 C	1,50 V
1 C	1,40 V
10 C	1,30 V



Quelle: maurelma.ch

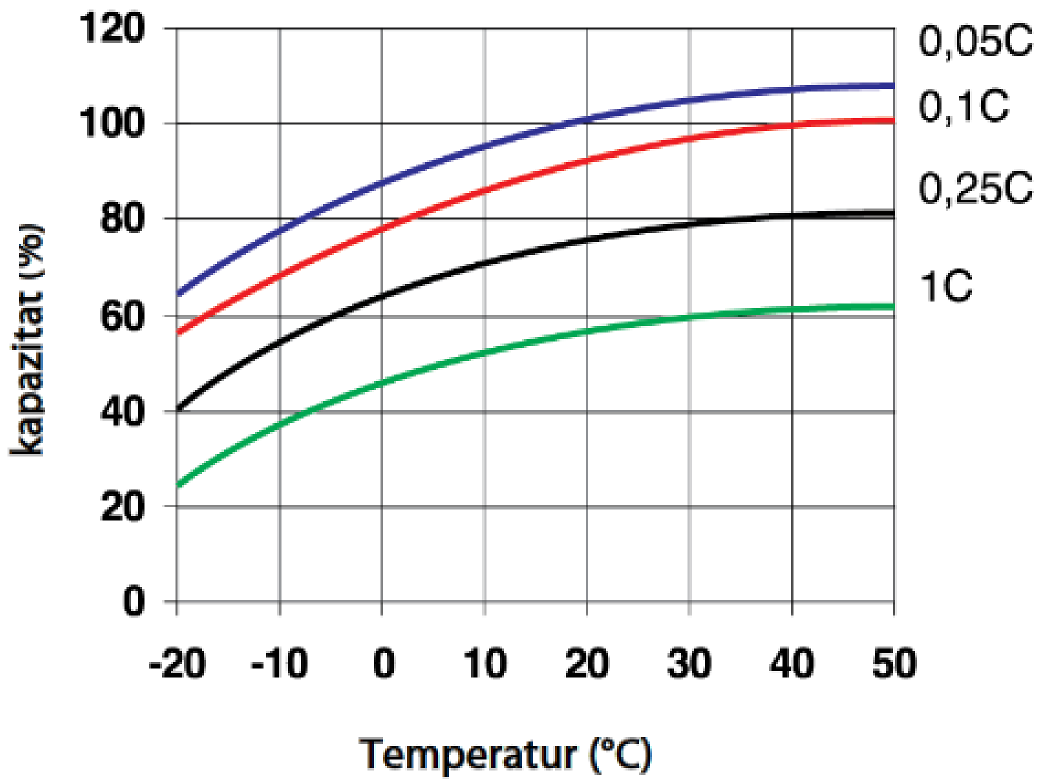
Imp

Quelle: enersys-hawker

Lead-Acid Batteries - Discharge Behavior

Useable capacity depends on:

Discharge rate in C
Temperature



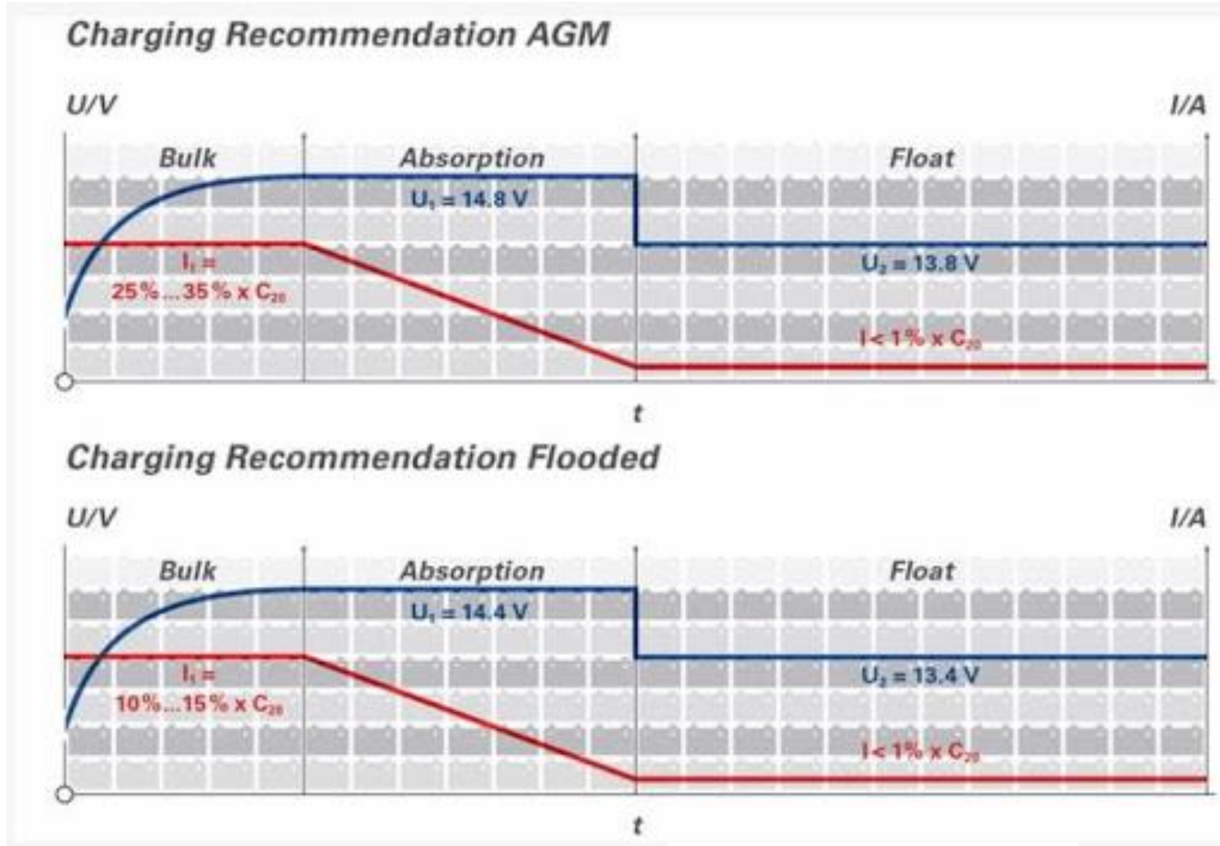
Influence of temperature on capacity

Quelle: victronenergie

Lead-Acid Batteries - Charging Behavior

Lead-acid batteries are charged with constant current/constant voltage (CI/CV).

The charging current and the end-of-charge voltage (trickle charge voltage) depend on the battery technology



Quelle: Varta

Lead-Acid Batteries - Charging Efficiency

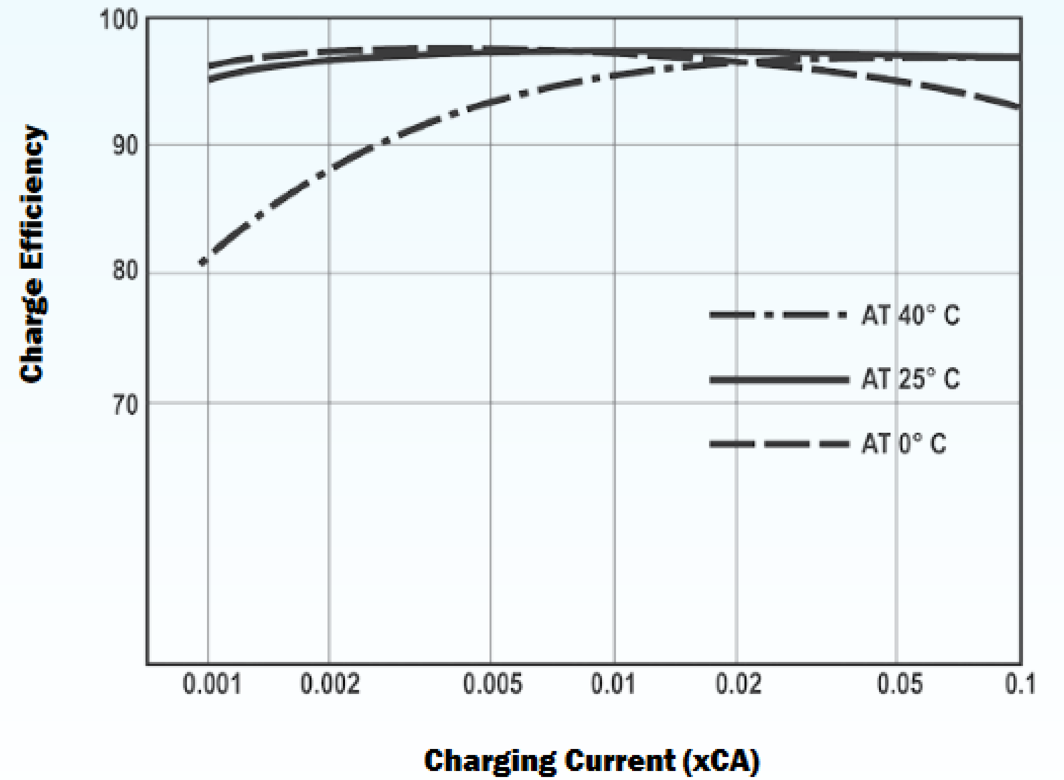
Depends on:

Discharge rate in C
Temperature T

At 25 °C it is over 96%

At high temperatures (40°C) self-discharge increases, which leads to lower charging efficiencies at low charging currents.

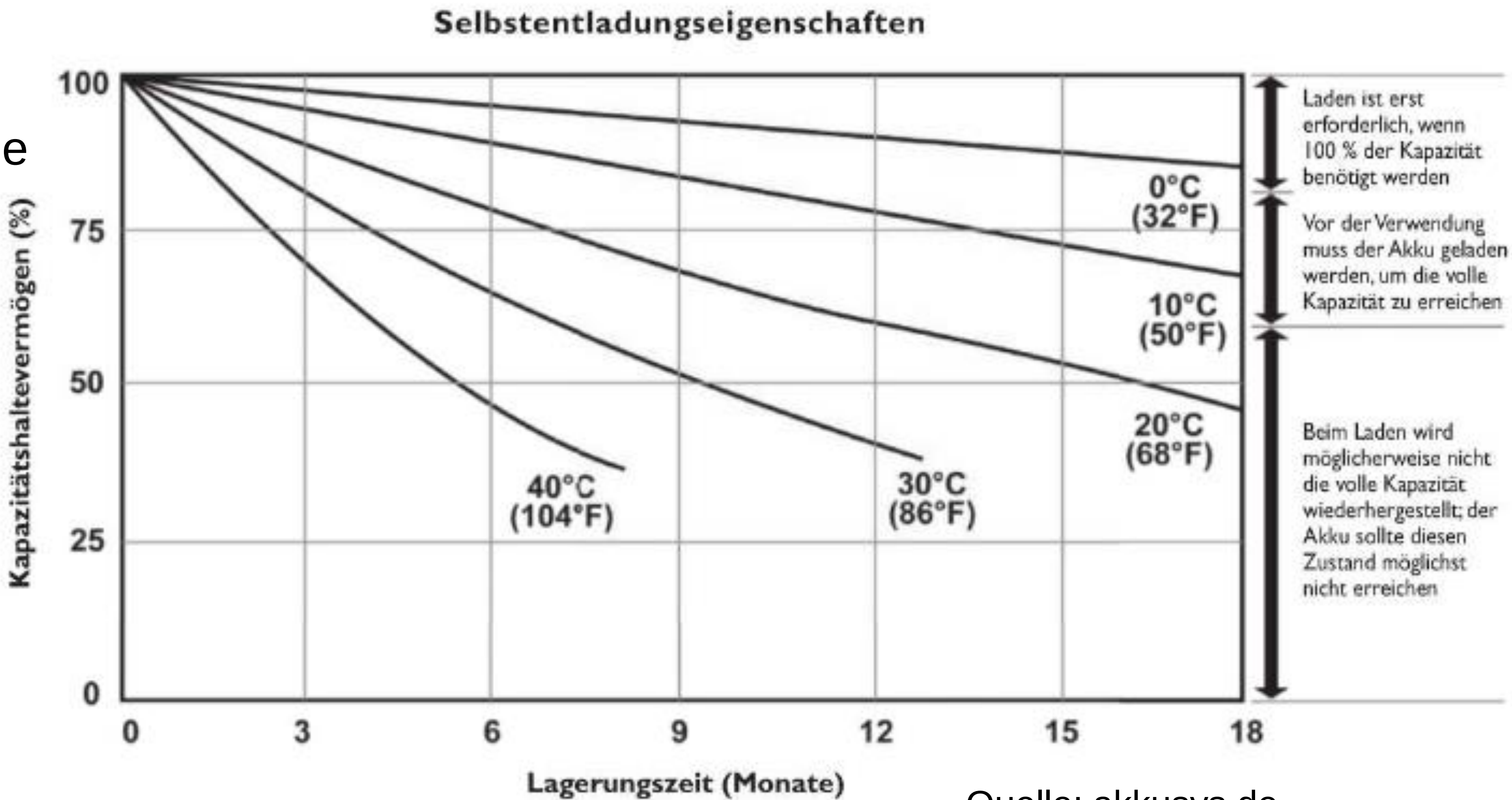
At low temperatures (0°C) the internal resistance increases



Quelle: power-sonic

Lead-Acid Batteries – Self Discharge and Storage

At room temperature (20 °C)
Lead-acid batteries have a self-discharge of approx.
3% per month



Quelle: akkusys.de

Lead-Acid Batteries – Aging (1/2)

Mechanism	Cause	Result
Corrosion of the positive conductor	- High temperature - High charging voltage - Low acid density or acid stratification - Bad alloy	- conductor breaks - rising ohmic contact
Softening of the active mass	- Mechanical stresses during cycling - High current densities when discharging - High charging voltages (gassing) - deep discharge (polarity reversal)	- Loss of active mass (sludge formation) - loss of capacity - short circuit
Sulfation of the plates (pos. and neg.)	- deep discharge - Long storage time - No full charge (charging voltage too low) - acid stratification	- loss of capacity - increase in internal resistance - reduction in acid density

Lead-Acid Batteries – Aging (2/2)

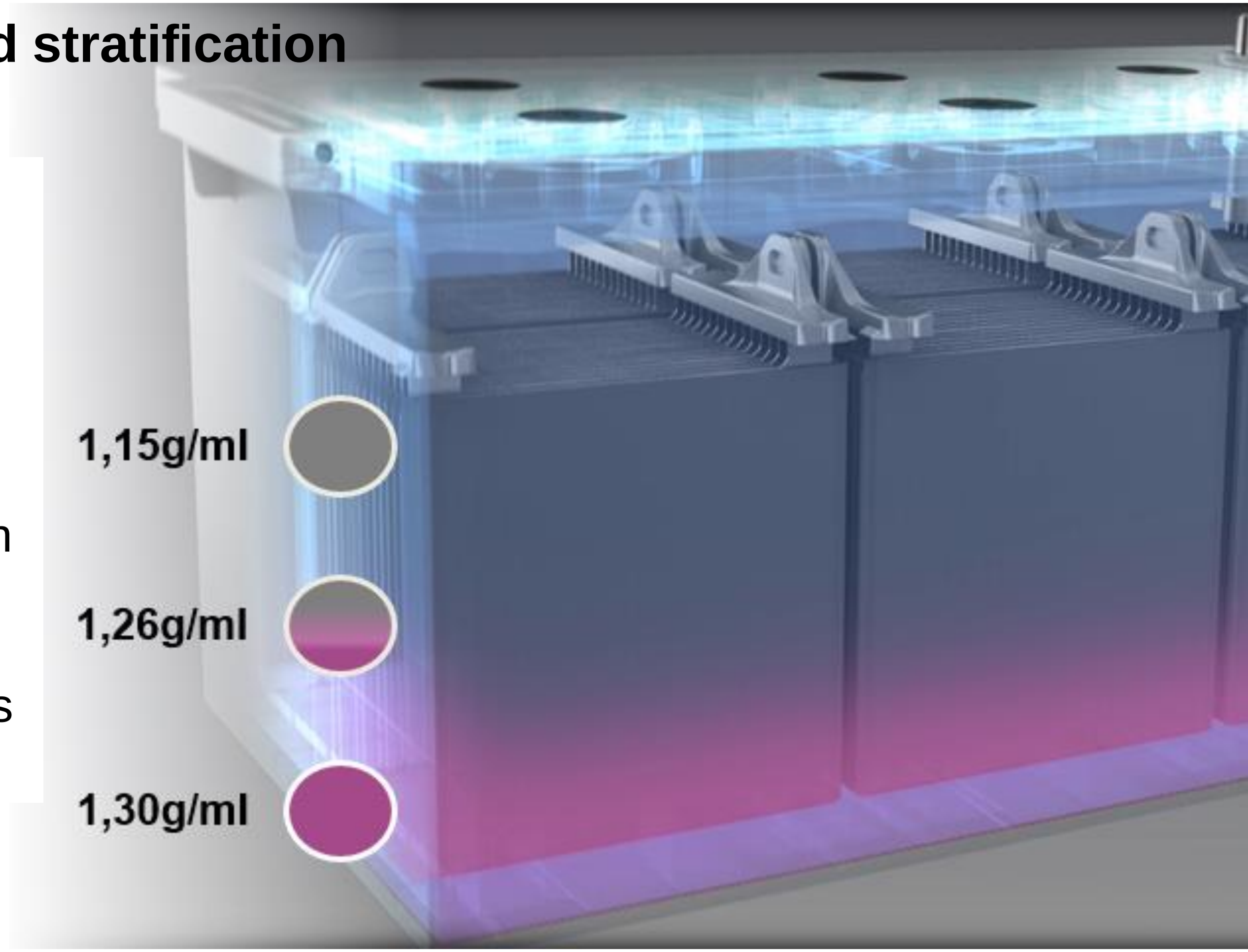
Mechanism	Cause	Result
Leading of the negative active mass	- High load throughput - High temperatures - Gases - Cell reversal	- reduction in capacity
Drid growth through corrosion	- High temperature - High charging voltage - Low acid density or acid stratification - Bad alloy	- short circuit
Dendrite growth	- High current densities when discharging - Acid stratification - Deep discharge (polarity reversal)	- short circuit - sludge formation
Destruction of the separator	- Grid growth - Dendrite growth - Oxidation of the separator	- short circuit

Lead-Acid Batteries with acid stratification

Concentrated sulfuric acid produced during charging is heavier than diluted sulfuric acid and sinks due to gravity.

This effect only occurs in vented and sealed lead-acid batteries with fleece technology.

Almost no acid stratification occurs with gel-bound electrolytes.



Quelle: Varta

Lead-Acid Batteries - Safety

Sulfuric acid can cause severe burns and is hazardous to water

Lead is a heavy metal and must not be disposed of with household waste

Hydrogen can be produced when charging lead-acid batteries
The hydrogen concentration must be kept below 4% by ventilating the installation site

According to standard EN50272, the following applies to the calculation of ventilation:

$$Q = v * q * s * n * IG * CN$$

With:

- v: dilution factor = 96%air / 4%H2 = 24
- q: amount of hydrogen produced = 0.42l/Ah
- s: safety factor = 5
- n: number of cells
- IG: gassing current in mA per Ah capacity (according to EN20272)
- CN: nominal capacity in Ah

Gassing Current IG in mA/A		
loading procedure	vented lead-acid batteries	Sealed lead acid batteries
trickle charge	5	1
Charge	20	8

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Fraunhofer IISB

Lead-Acid Batteries – Optimal Operation

- Always fully charge lead-acid batteries and store them at low temperatures.
- If the storage temperature is below 25°C, recharge every 6 months, if the temperature is above 25°C, recharge every 3 months. If possible, do not store above 35°C.
- The lower the battery temperature, the longer the lifespan. At sub-zero temperatures (below -5°C) there is a risk of freezing.
- Lead-acid batteries should only be discharged as deeply as necessary.
- Recharge the battery as soon as possible after discharging
- Adapt the end-of-charge voltage to the operating mode and the battery type.

Lead-Acid Batteries

Datasheet (1/4)

ENGLISH

Datasheet: 537-7305

RS Pro Rechargeable 12V Lead Acid Battery, 12 Ah

From RS Pro, this is a highly efficient, all purpose, sealed rechargeable lead acid battery. This battery is valve regulated and utilises recombination technology to ensure that it remains maintenance free. The battery casing is constructed from ABS resin, which offers high impact strength, good resistance to chemicals and excellent temperature performance.

Storage:
This lead acid battery can be stored at +25 °C for more than 6 months with a self-discharge ratio of 3 %. It has an excellent standby life of five years. This lead acid battery features a high quality AGM separator which extends the cycle life and prevents micro short circuits.

Features:
- Valve regulated
- Suitable for float or standby use
- Low gas emission
- The resin case features fire resistance to UL94-HB
- Silver coated fast-on F1 terminals improve conductivity

Benefits:
- Maintenance free
- Leak proof
- Excellent recovery from deep discharge
- Five years standby life
- Road transport suitable as per UN2800
- Air transport suitable to Special Provision A67, IATA and ICAO
- Can be used in several orientations, but must not be used inverted

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Lead-Acid Batteries

Datasheet (2/4)

RS PRO

ENGLISH

Applications:

This lead acid battery is an all purpose power solution. Suitable applications include:

- Emergency backup power supplies
- Electric Power Systems (EPS)
- Uninterruptible Power Supplies (UPS)
- DC power supplies
- Communication power supplies
- Emergency lighting
- Railway and aircraft signalling
- Alarms and security systems
- Automated control systems

Specification

Cells Per Unit	6
Voltage Per Unit	12
Capacity	12.0Ah@20hr-rate to 1.80V per cell @25°C
Weight	Approx 3.50 kg
Max. Discharge Current	180 A(5 sec)
Internal Resistance	Approx 14mΩ
Operating Temp.Range	Discharge : -15~50°C (5~122°F) Charge : 0~40°C (32~104°F) Storage : -15~40°C (5~104°F)
Nominal Operating Temp. Range	25±3°C (77±5°F)
Float charging Voltage	13.5 to 13.8 VDC/unit Average at 25°C
Recommended Maximum Charging Current Limit	3.6A
Equalization and Cycle Service	14.4 to 15.0 VDC/unit Average at 25°C
Self Discharge	The batteries can be stored for more than 6 months at 25°C. Self-discharge ratio less than 3% per month at 25°C. Please charge batteries before using.
Terminal	T1
Container Material	A.B.S. (UL94-HB) , Flammability resistance of UL94-V0 can be available upon request.

Electric Energy Storage Systems

Lead-Acid Batteries

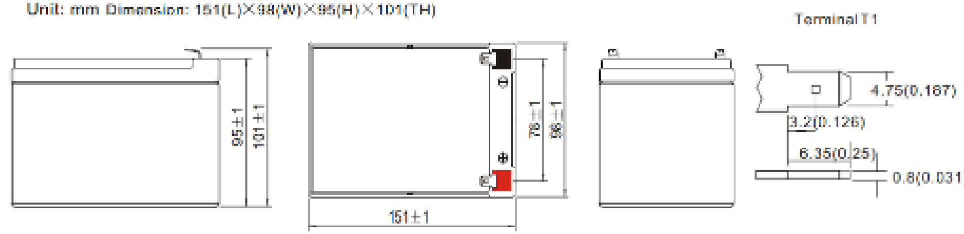
Datasheet (3/4)

RS PRO

ENGLISH

Dimensions:

Unit: mm Dimension: 151(L)×98(W)×95(H)×101(TH)



Discharge characteristics:

Constant Current Discharge Characteristics : A (25°C) **Amps**

F.V/Time	5min	10min	15min	20min	30min	45min	1h	2h	3h	4h	5h	6h	8h	10h	20h
1.85V/cell	22.9	17.5	14.5	12.6	9.72	7.16	6.03	3.57	2.79	2.27	1.85	1.61	1.30	1.08	0.594
1.80V/cell	30.7	22.4	17.6	14.9	11.5	8.33	6.76	3.93	3.00	2.42	1.99	1.72	1.37	1.12	0.600
1.75V/cell	34.6	24.6	19.2	16.0	11.9	8.64	7.07	4.04	3.06	2.48	2.04	1.77	1.40	1.15	0.606
1.70V/cell	38.1	26.9	20.5	16.8	12.4	8.99	7.29	4.14	3.15	2.54	2.09	1.81	1.42	1.17	0.617
1.65V/cell	42.0	29.0	21.8	17.8	13.1	9.21	7.46	4.23	3.28	2.63	2.15	1.85	1.44	1.19	0.625
1.60V/cell	46.3	31.5	23.3	19.0	13.8	9.60	7.54	4.38	3.38	2.71	2.22	1.89	1.45	1.21	0.629

Constant Power Discharge Characteristics : W (25°C) **Watts**

F.V/Time	5min	10min	15min	20min	30min	45min	1h	2h	3h	4h	5h	6h	8h	10h	20h
1.85V/cell	41.8	32.4	27.1	23.7	18.6	13.8	11.6	6.93	5.44	4.44	3.63	3.16	2.56	2.14	1.18
1.80V/cell	55.5	40.9	32.3	27.6	21.6	15.9	13.0	7.51	5.82	4.71	3.88	3.37	2.71	2.21	1.19
1.75V/cell	61.2	44.3	34.9	29.4	22.2	16.3	13.5	7.76	5.91	4.80	3.97	3.46	2.75	2.26	1.20
1.70V/cell	65.6	47.1	36.7	30.7	22.9	16.9	13.9	7.94	6.06	4.92	4.06	3.52	2.78	2.31	1.22
1.65V/cell	71.3	50.4	38.7	32.3	24.0	17.2	14.1	8.01	6.29	5.07	4.16	3.59	2.82	2.35	1.23
1.60V/cell	76.8	53.5	40.8	34.1	25.2	17.8	14.2	8.31	6.45	5.21	4.28	3.65	2.84	2.37	1.24

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Lead-Acid Batteries

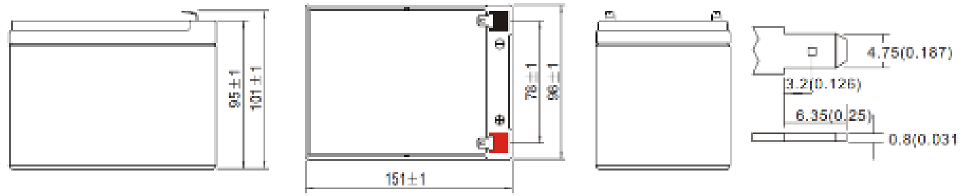
Datasheet (4/4)

RS PRO

ENGLISH

Dimensions:

Unit: mm Dimension: 151(L)×98(W)×95(H)×101(TH)



Discharge characteristics:

Constant Current Discharge Characteristics : A (25°C) — Amps

F.V/Time	5min	10min	15min	20min	30min	45min	1h	2h	3h	4h	5h	6h	8h	10h	20h
1.85V/cell	22.9	17.5	14.5	12.6	9.72	7.16	6.03	3.57	2.79	2.27	1.85	1.61	1.30	1.08	0.594
1.80V/cell	30.7	22.4	17.6	14.9	11.5	8.33	6.76	3.90	3.00	2.42	1.99	1.72	1.37	1.12	0.600
1.75V/cell	34.6	24.6	19.2	16.0	11.9	8.64	7.07	4.04	3.06	2.48	2.04	1.77	1.40	1.15	0.606
1.70V/cell	38.1	26.9	20.5	16.8	12.4	8.99	7.29	4.14	3.15	2.54	2.09	1.81	1.42	1.17	0.617
1.65V/cell	42.0	29.0	21.8	17.8	13.1	9.21	7.46	4.20	3.20	2.63	2.15	1.85	1.44	1.19	0.625
1.60V/cell	46.3	31.5	23.3	19.0	13.8	9.60	7.54	4.38	3.38	2.71	2.22	1.89	1.45	1.21	0.629

Constant Power Discharge Characteristics : W (25°C) — Watts

F.V/Time	5min	10min	15min	20min	30min	45min	1h	2h	3h	4h	5h	6h	8h	10h	20h
1.85V/cell	41.8	32.4	27.1	23.7	18.6	13.8	11.6	6.93	5.44	4.44	3.63	3.16	2.56	2.14	1.18
1.80V/cell	55.5	40.9	32.3	27.6	21.5	15.9	13.0	7.51	5.82	4.71	3.88	3.37	2.71	2.21	1.19
1.75V/cell	61.2	44.3	34.9	29.4	22.2	16.3	13.5	7.76	5.91	4.80	3.97	3.46	2.75	2.26	1.20
1.70V/cell	65.6	47.1	36.7	30.7	22.9	16.9	13.9	7.94	6.06	4.92	4.06	3.52	2.78	2.31	1.22
1.65V/cell	71.3	50.4	38.7	32.3	24.0	17.2	14.1	8.01	6.29	5.07	4.16	3.59	2.82	2.35	1.23
1.60V/cell	76.8	53.5	40.8	34.1	25.2	17.8	14.2	8.31	6.45	5.21	4.28	3.65	2.84	2.37	1.24

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Electric Energy Storage Systems

Chapter 2:
Exercise

Summer 2024

Friedrich-Alexander-Universität Erlangen-Nürnberg

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1. Basics on electro-chemical energy sorage systems

A. How much charge and how much energy did the battery absorb?

B. What is the minimum amount of lead needed for a 100 Ah lead 2V battery?
Lead (207.2 g/mol)
Faraday's constant has a value of 96487 As/mol.

2. Design of a lead acid emergency power supply

For emergency lighting, a 12V lead-acid battery system with a usable capacity of 12 Ah at -20°C is to be set up based on the cells from the data on next page. How much nominal capacity must be installed? How many lead-acid batteries must be used?

ENGLISH

Datasheet: 537-7305
RS Pro Rechargeable 12V Lead Acid Battery, 12 Ah

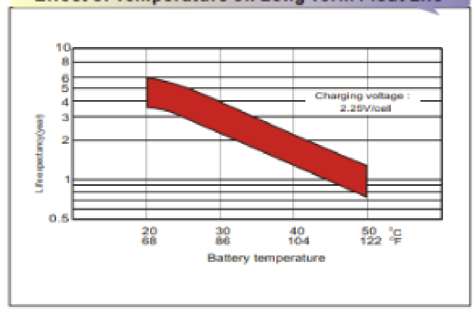
From RS Pro, this is a highly efficient, all purpose, sealed rechargeable lead acid battery. This battery is valve regulated and utilises recombination technology to ensure that it remains maintenance free. The battery casing is constructed from ABS resin, which offers high impact strength, good resistance to chemicals and excellent temperature performance.

Storage:
This lead acid battery can be stored at +25 °C for more than 6 months with a self-discharge ratio of 3 %. It has an excellent standby life of five years. This lead acid battery features a high quality AGM separator which extends the cycle life and prevents micro short circuits.

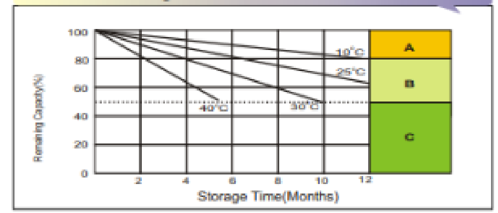
Features:
- Valve regulated
- Suitable for float or standby use
- Low gas emission
- The resin case features fire resistance to UL94-HB
- Silver coated fast-on F1 terminals improve conductivity

Benefits:
- Maintenance free
- Leak proof
- Excellent recovery from deep discharge
- Five years standby life
- Road transport suitable as per UN2800
- Air transport suitable to Special Provision A67, IATA and ICAO
- Can be used in several orientations, but must not be used inverted

Effect of Temperature on Long Term Float Life



Self Discharge Characteristics

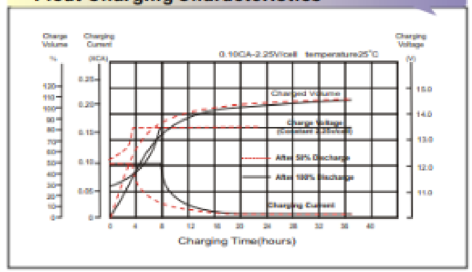


A: No supplementary charge required
(Carry out supplementary charge before use if 100% capacity is required.)

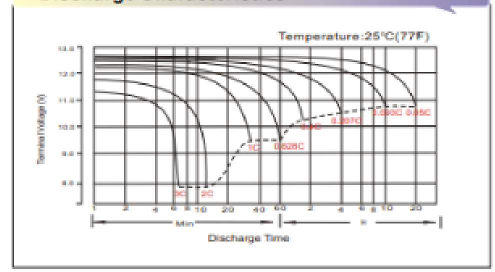
B: Supplementary charge required before use.Optional charging way as below:
1.Charged for above 3 days at limited current 0.25CA and constant volatge 2.25V/cell.
2.Charged for above 20hours at limited current 0.25CA and constant volatge 2.45V/cell.
3.Charged for 8~10hours at limited current 0.05CA .

C: Avoid this storage period unless regular Top charge.
Supplementary charge may often fail to recover the full capacity

Float Charging Characteristics



Discharge Characteristics



Available Capacity Subject to Temperature

Battery Type		-20℃	-10℃	0℃	5℃	10℃	20℃	25℃	30℃	40℃	45℃
AGM Battery	6V&12V	46%	66%	76%	83%	90%	98%	100%	103%	107%	109%

Discharge Current VS. Discharge Voltage

Final Discharge Voltage V/cell	1.80V	1.75V	1.60V
Discharge Current (A)	(A) ≤0.2C	0.2C< (A) <1.0C	(A) ≥1.0C

Charge the batteries at least once every six months, if they are stored at 25°C.

Charging Method:

Constant Voltage	-0.2Cx2h+2.4~2.45V/Cellx24h,Max. Current 0.3CA
Constant Current	0.1C until the voltage reaching 14.4V,then 0.1Cx4h

Maintenance & Cautions

Float Service:
◆It is recommended to check battery/Float voltage each month.
Equalisation charge:
◆Equalisation charging is recommended once every 3 to 6 months using.
◆Discharge 100% rated capacity.
◆Charge 2.35v/cell constant voltage, maximum 0.3CA 24hrs.
Cyclic Service:
◆Temperature compensation for varying temperatures:
-Charge voltage -3mV/Cell/degC from 25degC norm.
◆The service life of your battery will be affected by:
-The number of discharge cycles, depth of discharge, ambient
temperature and charging voltage.

1 year warranty would start from when we have delivered it to the customer.

Electric Energy Storage Systems

Chapter 3: Alkaline Battery Systems – NiCd, NiMh, Na-$NiCl_2$

Summer 2024

Friedrich-Alexander-Universität Erlangen-Nürnberg

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Alkaline Batteries (Nickel Cadmium (NiCd), Nickel Metal Hydride (NiMH))

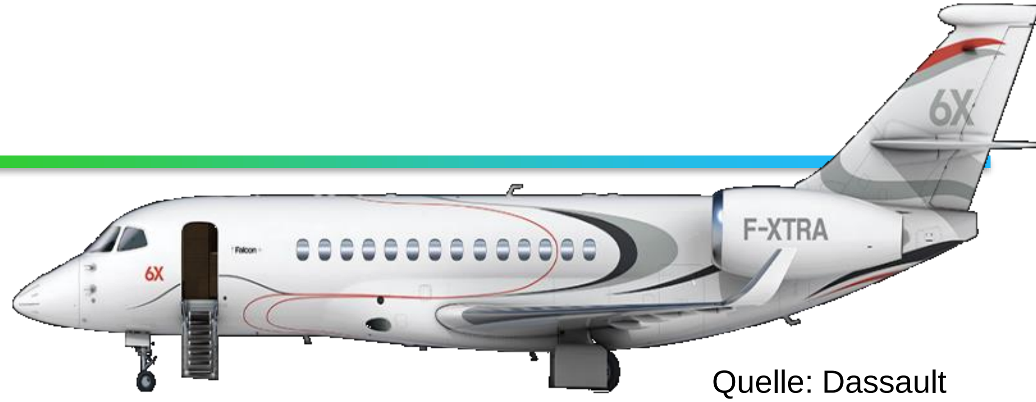
History: (NiCd)
1899 first nickel-cadmium battery developed by Waldemar Junger in Sweden
1910 the industrial production of closed cells began in Sweden
1952 Introduction of gas-tight (sealed) cells by Varta
Advantages:
- Good cycle stability
- Very good low temperature behavior

Disadvantages:
- Contain toxic cadmium

History: (NiMH)
1962-1982 The foundations were laid by S. R. Ovshinsky and brought to market
Advantages:
- High specific energy density of 45-80Wh/kg
- Contains no heavy metals

Disadvantages:
- Slightly poorer low-temperature properties than NiCd
- More sensitive to overcharge and over-discharge

Alkaline Batteries (NiCd, NiMH)



Quelle: Dassault

Application:

- Starter battery for aircraft
- Starter battery for diesel locomotives, especially in cold regions
- Emergency power supply
- Power supply with high cyclic load
- Early e-vehicles or hybrid vehicles

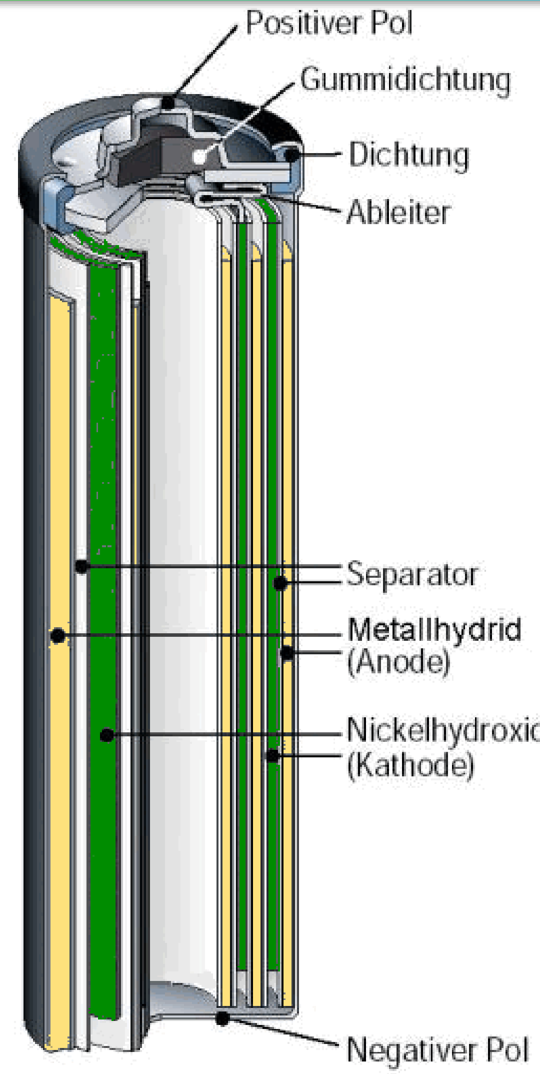
Quelle: bahnbilder.de

Quelle: Toyota

Alkaline Batteries (NiCd, NiMH)

Designs:

Quelle: batterie-info.de



Alkaline Batteries (NiCd, NiMH) – Positive Electrode

The positive electrode active material is nickel hydroxide (NiOOH)
Positive electrode:

$$NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$$

The theoretical capacity is 289 mAh/g.
Of this, practically 80% can be used.

The reaction takes place at the active material/electrolyte interface. The H+ must therefore diffuse through the poorly conductive active material.

By coating the nickel hydroxide (NiOOH) with cobalt hydroxide (CoOOH),
The conductivity can be improved and the internal resistance of the cells can be reduced.

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Alkaline Batteries – Negative Electrode NiCd Batterie

The active material of the negative electrode consists of cadmium when charged and is converted into cadmium hydroxide when discharged

Negative Electrode:

$$Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2\ e^-$$

This reaction does not take place directly, but via a liquid phase:

$$Cd + 3OH^- \longrightarrow [Cd(OH)_3]^- + 2\ e^-$$

$$[Cd(OH)_3]^- \longrightarrow Cd(OH)_2 + OH^-$$

The theoretical capacity is 477 mAh/g Cd active material.
About 50% of this can be used in practice.

Alkaline Batteries – Main reactions of the NiCd battery

Discharging

During discharge, the metallic cadmium gives off two electrons. The nickel oxyhydroxide absorbs a proton, consuming water from the electrolyte (21% potassium hydroxide solution).

Positive Electrode (Cathodic Reduction):

$$2NiO(OH) + H_2O + 2e^- \longrightarrow 2Ni(OH)_2 + 2OH^- \qquad (+0{,}49\ V)$$

Negative Electrode (Anodic Oxidation):

$$Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^- \qquad (-0{,}81\ V)$$

Overall Reaction

$$2NiOOH + 2H_2O + Cd \longrightarrow 2Ni(OH)_2 + Cd(OH)_2 \qquad (1{,}30\ V)$$

The battery has an equilibrium voltage of 1.30V.
The theoretical specific energy is approx. 215 Wh/kg.
In practice, approx. 60 Wh/kg are achieved.
The reversible heat of reaction is 10.6% and causes cooling when charging.

Alkaline Batteries – Side reactions of the NiCd battery
Charging

When charging, a distinction must be made between open and gas-tight cells:

In the case of open cells, at the end of the charge due to overcharging, electrolysis of water occurs, with 0.34 g/Ah being decomposed.
Attention must be paid to ventilation (compare lead-acid batteries).

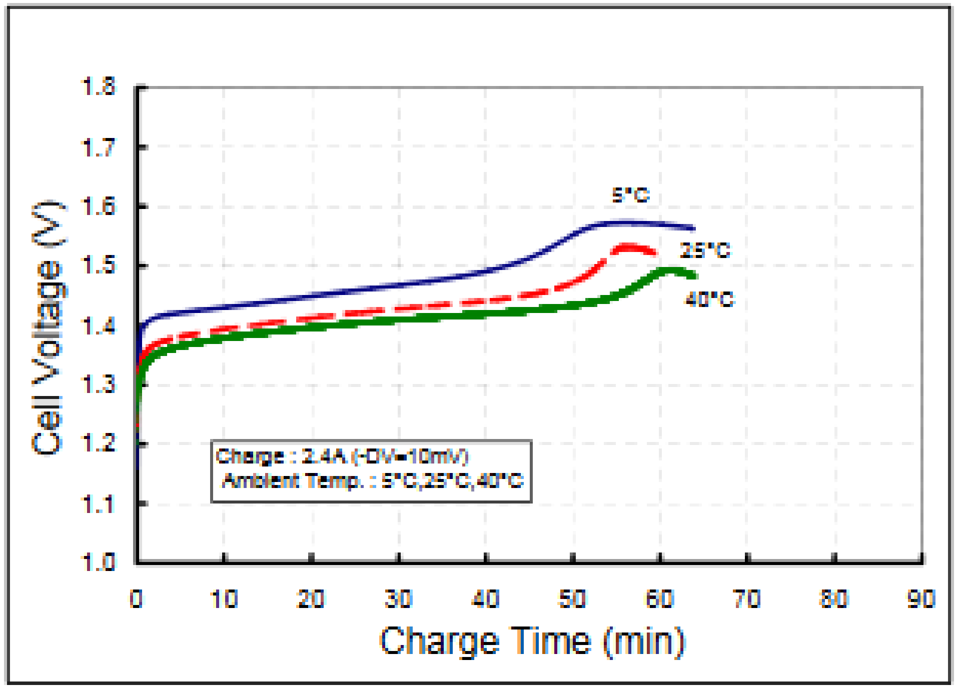
In sealed batteries, the negative cadmium electrode has a greater capacity than the positive nickel electrode, which when overcharged causes:

1. The evolution of oxygen at the positive Ni electrode begins before the evolution of hydrogen at the Cd electrode.
2. Oxygen dissolved in the electrolyte is reduced at the Cd electrode
3. Hydrogen is only produced at the Cd electrode from a charge level of 90%, which is not reached due to the larger dimensioning of the Cd electrode.

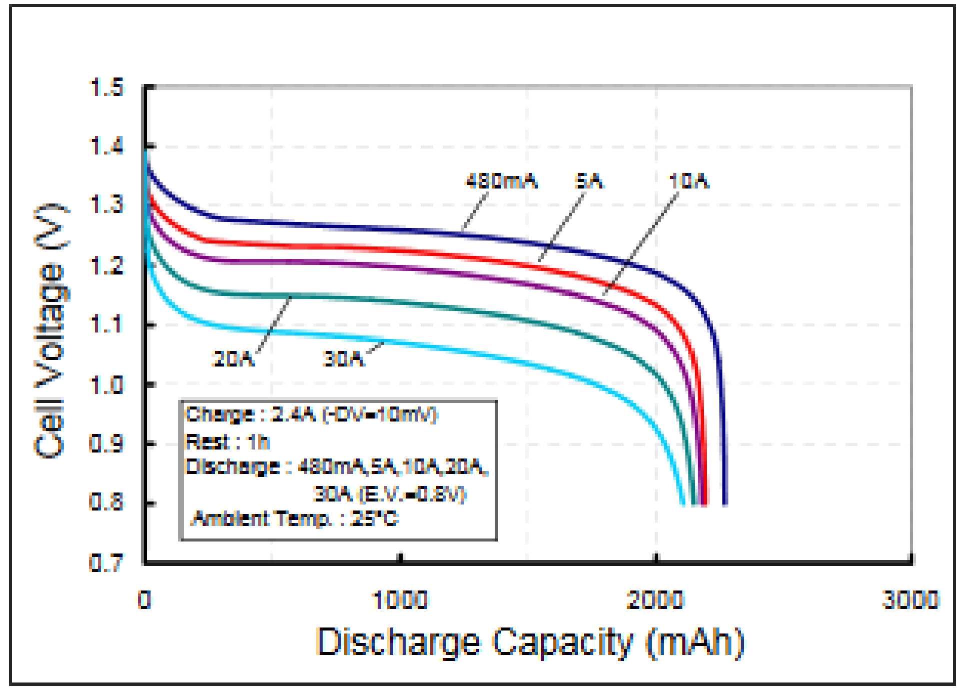
Temp

Alkaline Batteries – Charging / Discharging behavior of NiCd Batterie

Charging



Discharging



Quelle:Panasonic

Charging Behavior

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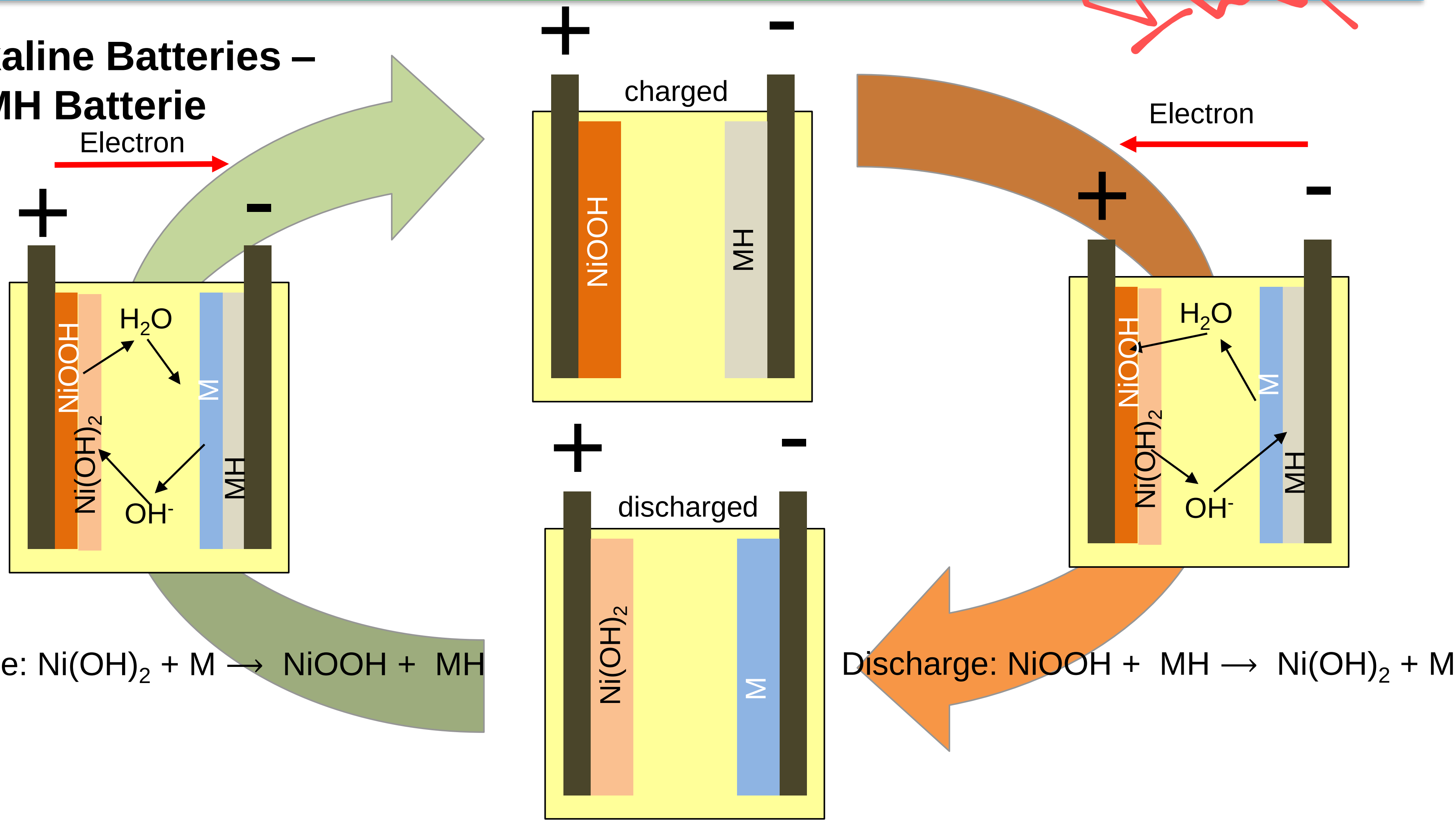
Alkaline Batteries – NiMH Batterie



Charge: $Ni(OH)_2 + M \longrightarrow NiOOH + MH$

Discharge: $NiOOH + MH \longrightarrow Ni(OH)_2 + M$

Alkaline Batteries – Main reactions of the NiMH battery Discharging

The NIMH accumulator has a hydrogen storage electrode M (LaNi5 or NiTi2), which releases hydrogen when discharging and absorbs it again when charging.
The electrolyte consists of 30% potassium hydroxide.

Positive Electrode (Cathodic Reduction):

$$NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^- \qquad (+\,0{,}49\ V)$$

Negative Electrode (Anodic Oxidation):

$$1/6\ LaNi_5H_6 + OH^- \longrightarrow H_2O + 1/6\ LaNi_5 + e^- \qquad (-\,0{,}83\ V)$$

Overall Reaction:

$$NiOOH + 1/6\ LaNi_5H_6 \longrightarrow Ni(OH)_2 + 1/6\ LaNi_5 \qquad (1{,}32\ V)$$

The battery has an equilibrium voltage of 1.32V.
The theoretical specific energy is approx. 216 Wh/kg.
In practice, approx. 80 Wh/kg are achieved.
The reversible heat of reaction is 15.4% and causes cooling when charging.

Alkaline Batteries – Side reactions of the NiCd / NiMH battery
Decomposition of the electrolyte at the end of the charge by electrolysis

Positive Electrode:

$$4OH^- \longrightarrow O_2 + 2\,H_2O + 4\,e^-$$

Negative Electrode:

$$4\,H_2O + 4\,e^- \longrightarrow 2\,H_2 + 4\,OH^-$$

Overall Reaktion:

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

0.336 g of water are decomposed per ampere-hour of overcharging and 0.44 l of hydrogen and 0.22 l of oxygen are produced

Sealed NiMH batteries therefore have to be refilled with electrolyte (water) regularly. The batteries must be ventilated.

Alkaline Batteries – Gas-tight NiCd and NiMH accumulators

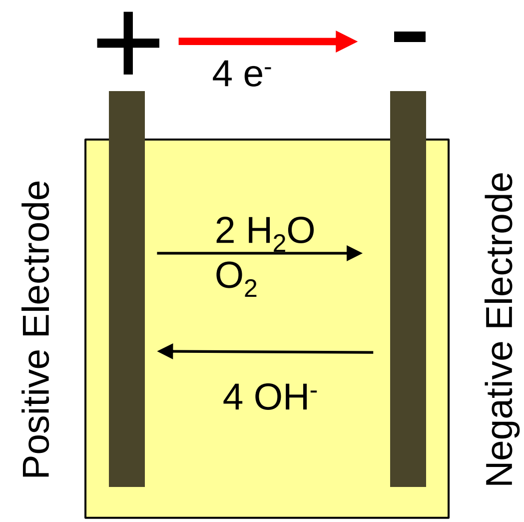
The decomposition of the electrolyte can be prevented by the following measures:

By oversizing the negative electrode, overcharging is avoided there and the formation of hydrogen is prevented.

Oxygen at the pos. Electrode arises with high reaction speed are reduced.

$$O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$$

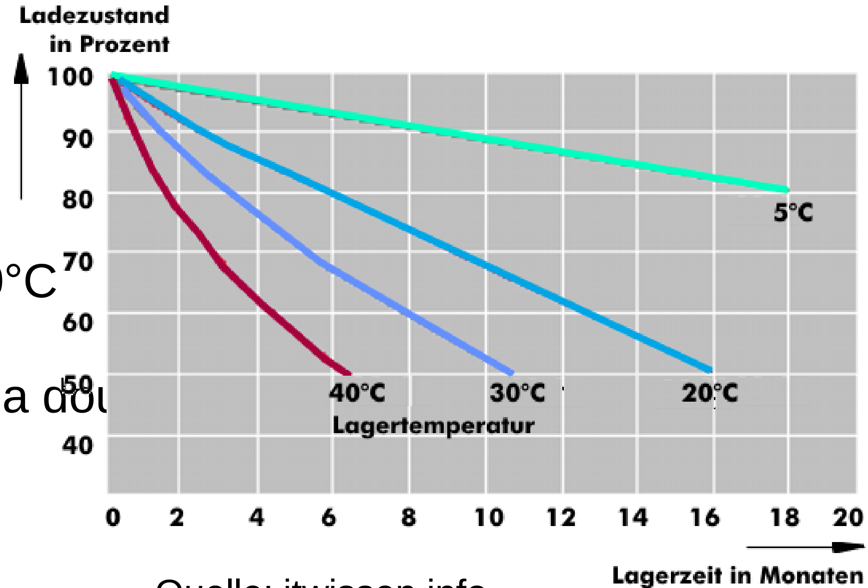
To do this, gas channels must be present in the separator and the cell must be sealed gas-tight



Alkaline Batteries – Self Discharge

NiCd up to 15% per month at 20°C
NiMH up to25% per month at 20°C
NiMH LDS (Low Discharge) appr. 5% per month at20°C

Increasing the storage temperature by 10°C leads to a dou



Quelle: itwissen.info

Cause:
Decomposition of higher-grade nickel hydroxide

Oxygen is split off at the pos. nickel electrode, which is reduced at the neg. electrode (depending on the state of charge).

Shuttle Process

Impurities in the electrolyte lead to processes in which an element at the pos. Electrode is oxidized, migrates to the negative electrode and is reduced

Alkaline Batteries – Shuttle Process NiCd

Self-discharge due to the nitride shuttle process in NiCd batteries

Positive Electrode:

$$NH_3 + 6\ NiOOH + H_2O + OH^- \longrightarrow 6\ Ni(OH)_2 + NO_2^-$$

$$NO_2^- + 2\ NiOOH + H_2O \longrightarrow 2\ Ni(OH)_2 + NO_3^-$$

Negative Electrode:

$$NO_3^- + H_2O + Cd \longrightarrow NO_2^- + Cd(OH)_2$$

$$NO_2^- + 5\ H_2O + 3\ Cd \longrightarrow NH_3 + 3\ Cd(OH)_2 + OH^-$$

Alkaline Batteries – Shuttle Process NiMH

Self-discharge due to the nitride shuttle process in NiMH batteries

Positive Electrode:

$$NH_3 + 6\ NiOOH + H_2O + OH^- \longrightarrow 6\ Ni(OH)_2 + NO_2^-$$

$$NO_2^- + 2\ NiOOH + H_2O \longrightarrow 2\ Ni(OH)_2 + NO_3^-$$

Negative Electrode:

$$NO_3^- + 2\ MH \longrightarrow NO_2^- + 2\ H_2O$$

$$NO_2^- + 6\ MH \longrightarrow NH_3 + 6\ M + OH^- + 2\ H_2O$$

Corrosion of the MH electrode also causes manganese ions to get into the electrolyte, which form an MN(II)/Mn(III) shuttle process.
This effect can be reduced by further developing the separators.

Imp?

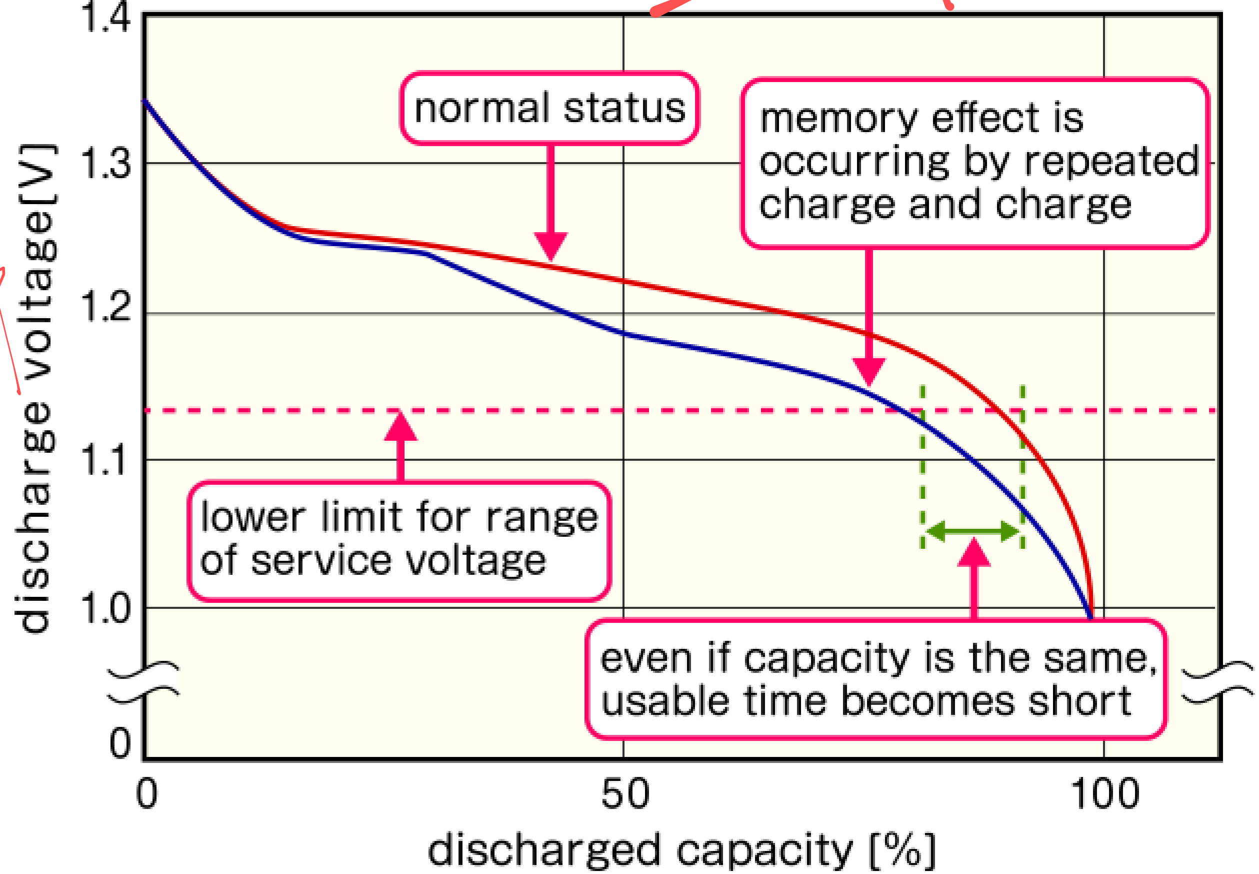
Alkaline Batteries – Ageing (1/2)

Reversible Effects

Memory Effect: Imp
With NiCd cells leads long (many hours) overcharging with low current to form Ni5Cd21 at the Cd electrode, voltage level approx. 120 mV

With NiCd and NiMH cells, partial cycling leads to a voltage step of around 50 mV

The effect can be "reset" by fully charging/discharging



Quelle: matsusada.com

Alkaline Batteries – Ageing (2/2)

Imp

Irreversible Effects

Aging of the Ni electrode:

Volume increase of approx. 40-50%, increase in internal resistance, loss of active material due to mechanical stress and thus capacity. Destruction of the cobalt conductor structure in the case of deep discharge below 1 V in NiMH cells

Aging of the metal hydride (MH) electrode:

Corrosion of the MH electrode and loss of water

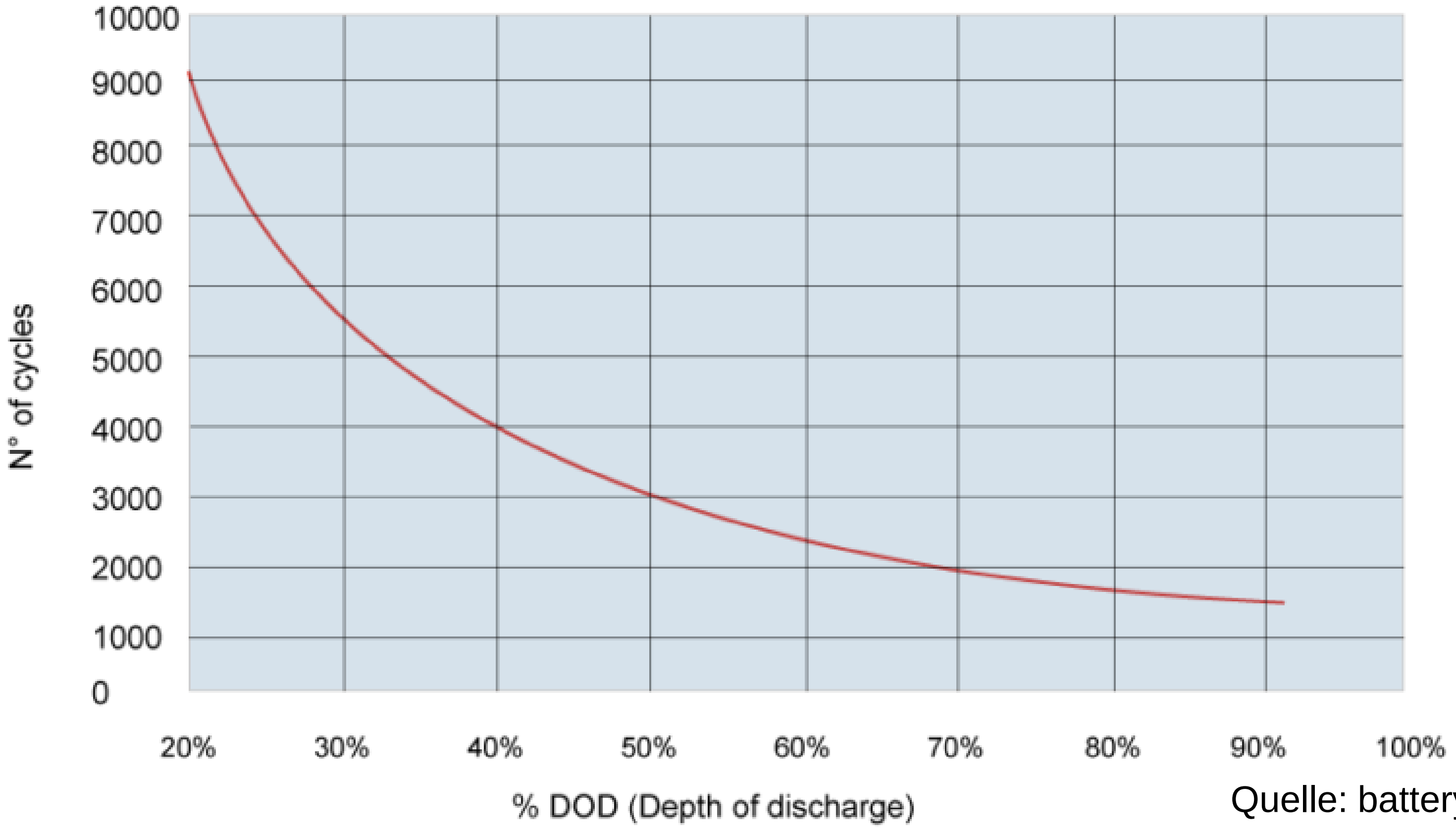
$$(1+x)\ MH + x\ H_2O \longrightarrow M(OH)_x + x\ MH$$

Metal hydroxide forms a protective layer and prevents further corrosion

MH changes its volume by about 15-20% on charging/discharging with hydrogen
Mechanical stress leads to cracks in the material

Alkaline Batteries – Ageing by charging Cycles (E.g. NiCD)

The smaller the cycle depth, the lower the mechanical stresses.



Quelle: batterysupplies.be

Alkaline Batteries - Safety

- NiCd and NiMH are very safe cell systems
- Active material and electrolyte are non-flammable.
- In the event of mechanical damage, caustic potash can escape.

- Hydrogen can escape from NiMH cells (approx. 0.5 l / 1 Ah at normal pressure), e.g. if the cell is mechanically damaged when charged
- In the discharged state, the hydrogen is bound in the Ni(OH)2 electrode and does not escape

- Strong heating (up to approx. 150°C) of the cells when overcharging
- E.g. by failure of the shutdown during fast charging (Delta U shutdown)

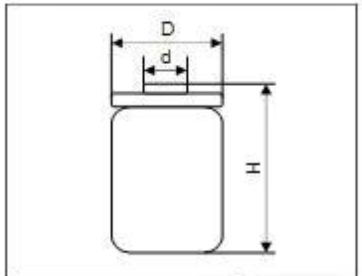
- High currents and cell heating in the event of cell short circuits

Alkaline Batteries – Optimum operation of NiCd and NiMH cells

- Cells can be stored at any (10-100%) state of charge
- The storage temperature should be below 20°C.
- After a long period (<6 months) of storage, a few full cycles with a low charging current (0.1 C for 14 hours) and a medium discharging current (approx. 0.5 C) are necessary
- Greater overcharging must be prevented by charging electronics or a time limit.
- Limit discharge of NiCd to 0.8V/cell and NiMH to 1V/cell.
- In order to avoid the so-called "memory" effect, the cells should be completely discharged and charged from time to time.

NiCd Batterie Datasheet 1/2

Panasonic



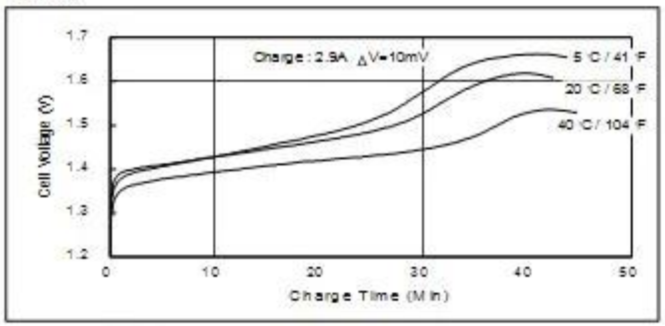
Dimensions of Bare Cell	H	$42.0^{\pm0.4}$	mm
		$1.654^{\pm0.016}$	Inch
	D	$22.0^{\pm0.3}$	mm
		$0.866^{\pm0.012}$	inch
	d	10.0	mm
		0.394	inch

Cell Type NC-1900SCR
Specifications

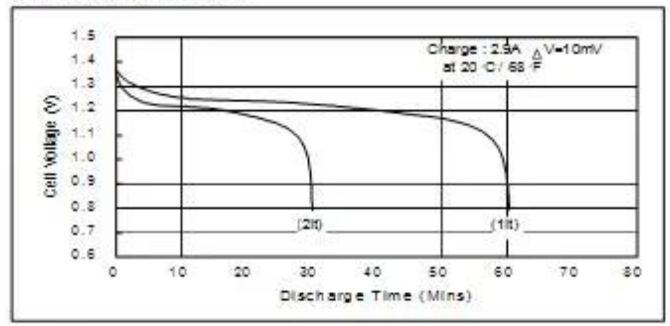
Nominal Capacity			1900mAh
Nominal Voltage			1.2V
Charging Current		Standard	190mA
		Fast	2900mA
Charging Time		Standard	14 to 16Hrs.
		Fast	about 1Hr
Ambient Temperature	Charge	Standard	0 °C to +45 °C [+32 °F to 113 °F]
		Fast	5 °C to +40 °C [+41 °F to 104 °F]
	Discharge		-20 °C to +60 °C [-4 °F to 140 °F]
	Storage		-30 °C to +50 °C [-22 °F to 122 °F]
Internal Impedance (Av.) (at 50% discharge)			4.5mΩ (at 1000Hz)
Weight (with tube)			Approx. 52g / 1.84oz
Dimensions(D) × (H) (with tube)			$22.9^{\,0}_{-1.0}$ × $42.9^{\,0}_{-1.2}$ mm
			$0.90^{\,0}_{-0.04}$ × $1.69^{\,0}_{-0.05}$ inch

Typical Characteristics

Charge



Discharge (at high rate)



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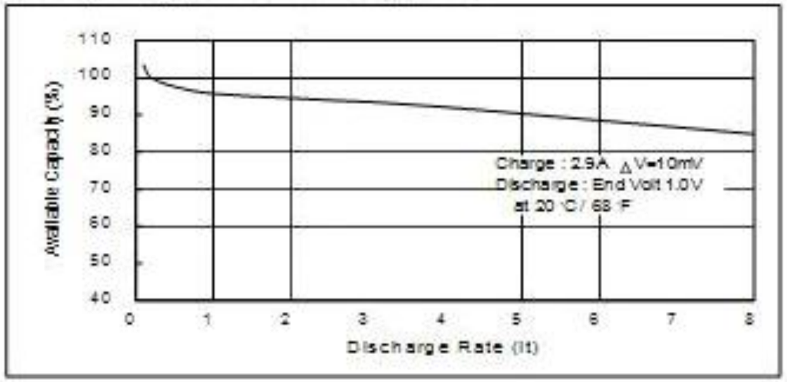
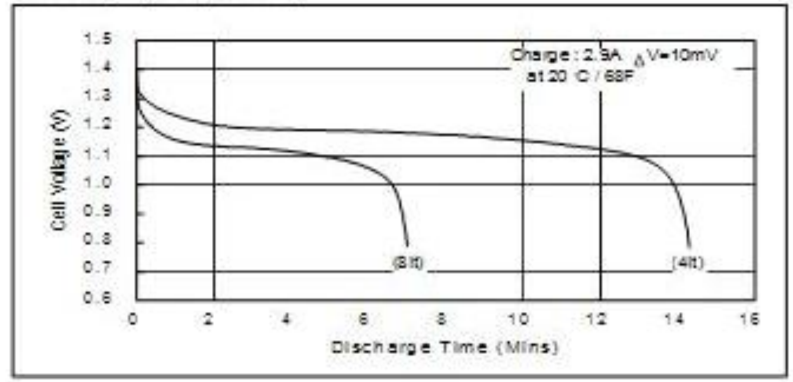
NiCd Batterie Datasheet 2/2

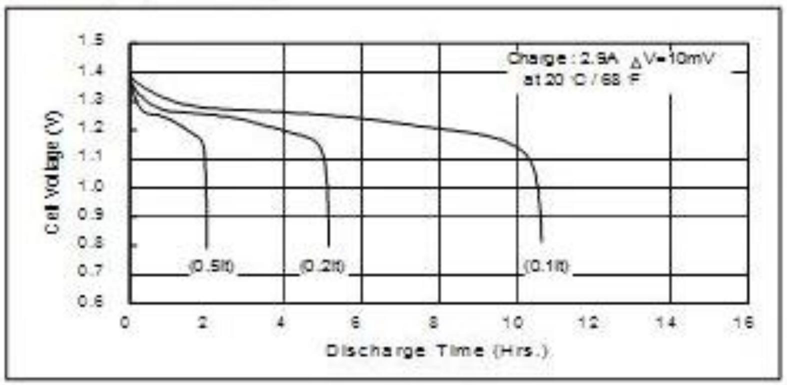
Cell Capacity (at various discharge rate)



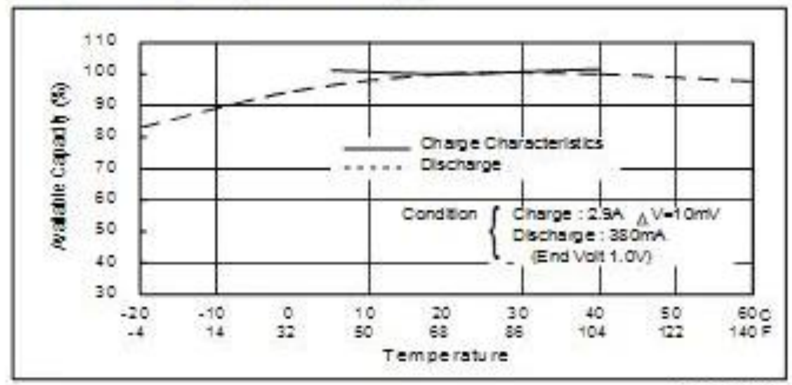
Discharge (at highe rate)



Discharge (at low rate)



Temperature (Charge & Discharge)



CD120229-01

Alkaline Batteries :

High temperature sodium batteries:

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Sodium-Nickel-Chloride Battery ($Na\text{-}NiCl_2$-Battery)
also known as a ZEBRA battery (Zero Emission Battery Research Activities).

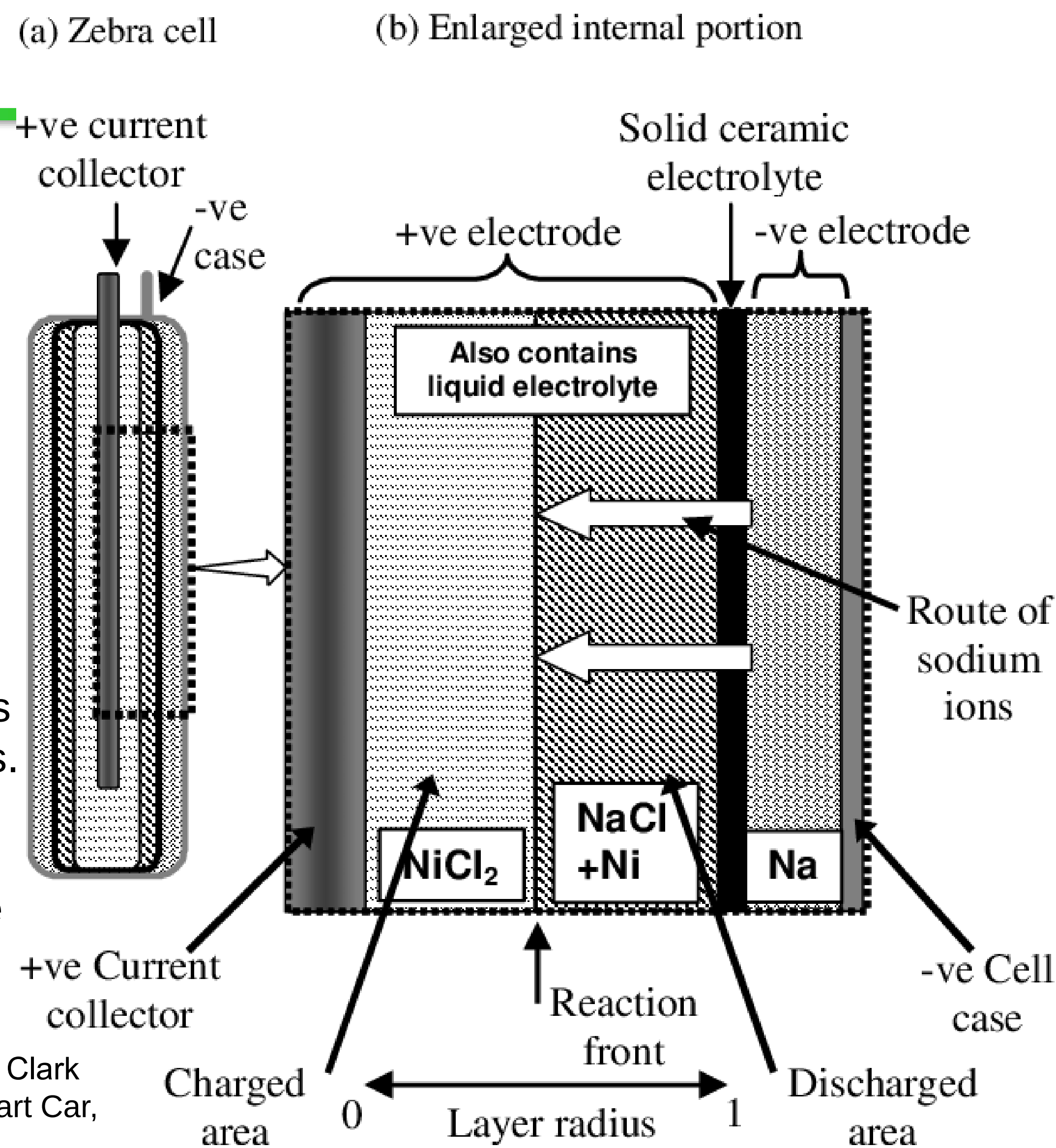
Alkaline Batteries: Sodium-Nickel-Chloride Battery ($Na-NiCl_2$-Battery)

The cathode is made of nickel and sodium chloride (NaCl),

The anode mostly made of sodium.

Ceramic β-aluminum oxide is used as separator and electrolyte, which allows sodium ions to pass between the anode and cathode but no electrons.

The operating temperature is between 270 and 350 °C so that the electrodes are in a liquid state (melted) and the separator achieves high conductivity for sodium ions.



Quelle: T. M. O'Sullivan, C. M. Bingham and R. E. Clark Zebra Battery Technologies for the All Electric Smart Car, SPEEDAM2006

Imp

Alkaline Batteries: Sodium-Nickel-Chloride Battery ($Na\text{-}NiCl_2$-Battery)

Data:

Cell voltage: 2.58 V (fully charged state)
End-of-discharge voltage 1.5 V
Gravimetric energy density: 100 to 120 Wh/kg (theoretically 790 Wh/kg)
Volumetric energy density: about 165 Wh/L
Energy efficiency: 85 to 95 percent (including energy for operation)

Advantages:

Long service life (more than 15 years) and cycle stability (4,500 cycles)
Overcharge and over-discharge tolerance, readily available and inexpensive materials

Disadvantages

The battery must be kept at approx. 300°C for operation.
If the battery is not needed for a longer period of time, the heating can be switched off. Electrodes can become stuck. The state of charge is retained and there are no losses due to self-discharge. The battery can be heated up to operating temperature again at any time and used again. However, the battery takes about 10 to 12 hours to heat up to operating temperature.

Alkaline Batteries – Main Reactions of Sodium-Nickel-Chloride Battery

Discharge

The Na-NiCl2 accumulator has a neg. electrode made of liquid sodium and a pos. Solid NiCl2 electrode. The metal chloride electrode is immersed in molten sodium tetrachloroaluminate (NaAlCl4).

Positive Electrode (Kathodic Reduction):

$$NiCl_2 + Na^+ + 2\,e^- \longrightarrow Ni + 2NaCl$$

Negative Electrode (Anodic Oxidation):

$$2\,Na \longrightarrow 2\,Na^+ + 2\,e^-$$

Full Reaction:

$$NiCl_2 + 2\,Na^+ \longrightarrow Ni + 2\,NaCl$$

Die BatterieThe battery has an equilibrium voltage of 2.58V.

weist eine Gleichgewichtsspannung von 2,58 V auf.

Alkaline Batteries - Sodium-Nickel-Chloride Battery

Example:

Type		Z5-278-ML-64	Z5-557-ML-32
Capacity	Ah	64	32
Rated Energy	kWh	17.8	17.8
Open Circuit Voltage 0-15% DOD	V	278.6	557
Max. discharge current	A	224	112
Cell Type/N° of cells		ML3 / 216	
Weight with BMI	kg	195	
Specific energy without BMI	Wh/kg	94	
Energy density without BMI	Wh/l	148	
Specific power	W/kg	169	
Power density	W/l	265	
Peak power 80% DOD, 2/3 OCV, 30s, 335°C	kW	32	
Ambient temperature	°C	-40 to +50	
Thermal loss at 270°C internal temperature	W	< 110	

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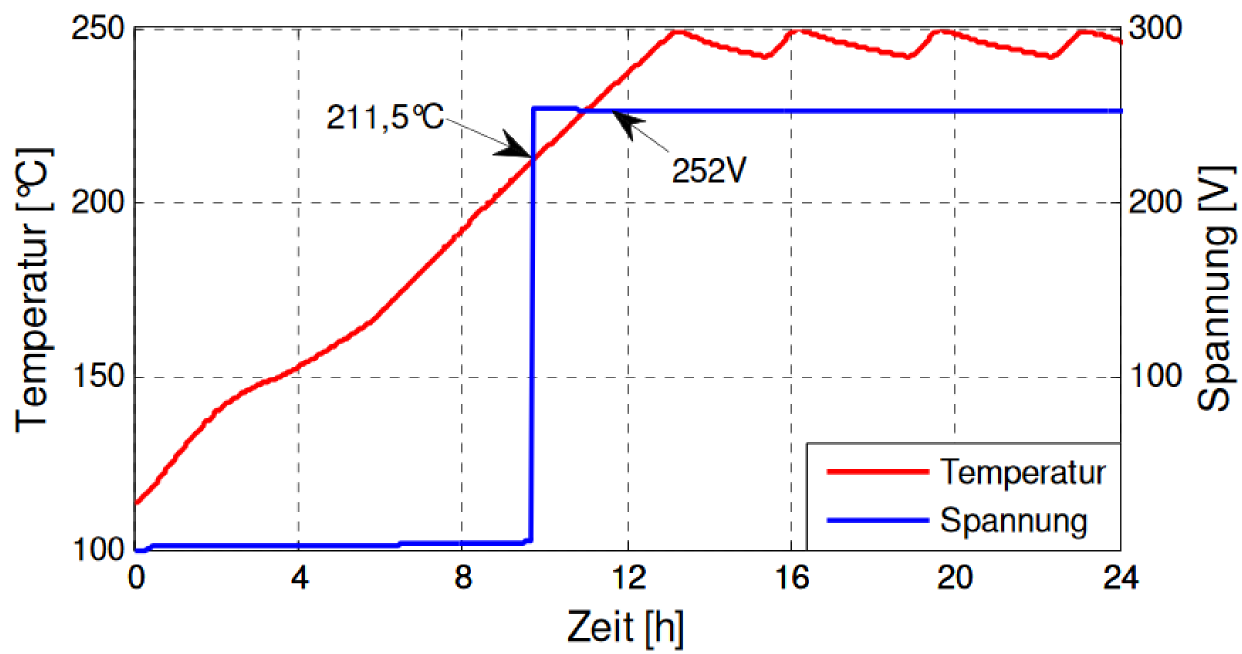
Alkaline Batteries - Sodium-Nickel-Chloride Battery

Heating up a ZEBRA battery type Z5-278 ML-64

Heat output approx. 300 W

In the solid state, there is no voltage, heating power must be supplied externally.

With 2-point controller, the Temperature maintained between 240 and 250°C.



Quelle: Projektbericht Regenerative Modellregion Harz, Elektro-KFZ als Speicher, K. Lipiec

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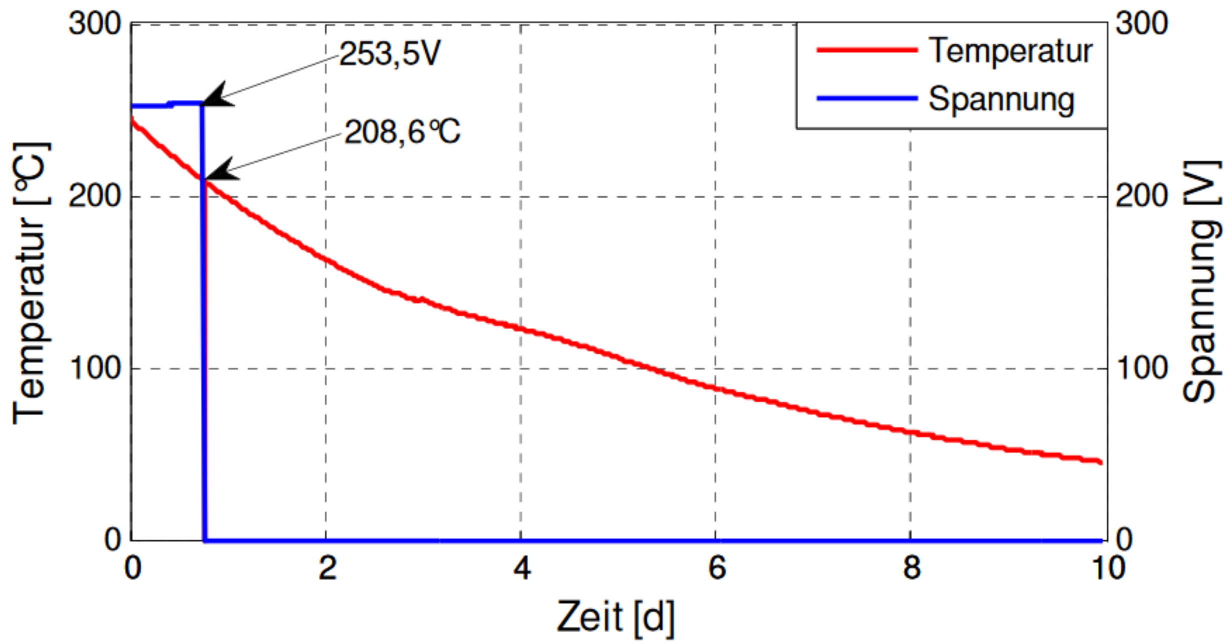
Alkaline Batteries - Sodium-Nickel-Chloride Battery

Cooling down of a ZEBRA battery type Z5-278 ML-64 at an ambient temperature of approx. 20 °C

Cooling time to solidify 8 hours and 30 minutes

In the solid state there is no voltage



Quelle: Projektbericht Regenerative Modellregion Harz, Elektro-KFZ als Speicher, K. Lipiec

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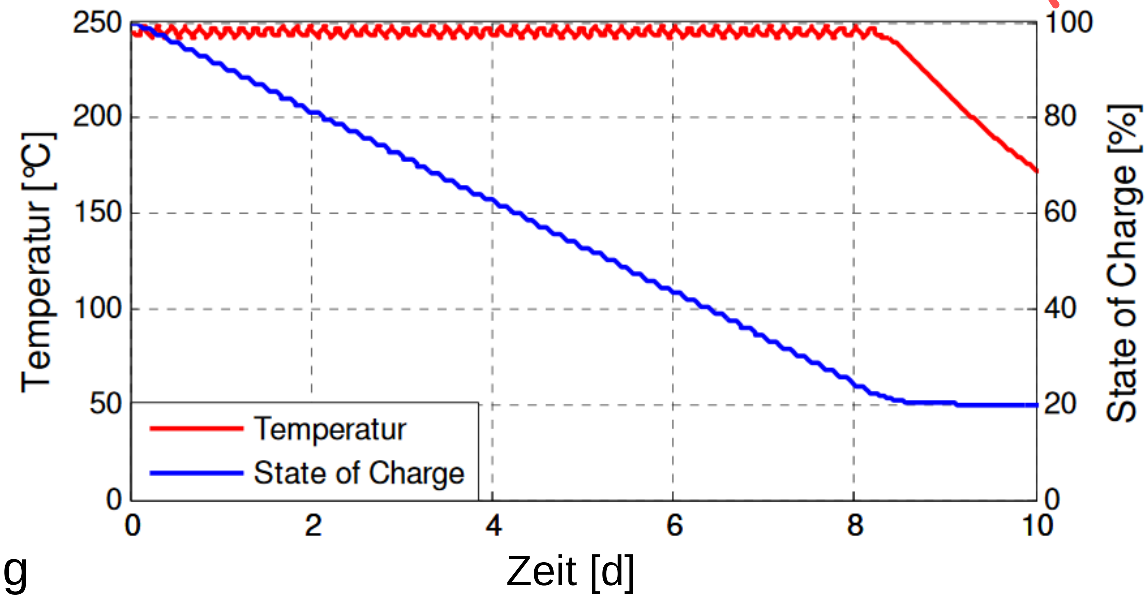
Alkaline Batteries - Sodium-Nickel-Chloride Battery

"Stand By" of a ZEBRA battery type Z5-278 ML-64 at approx. 20 °C ambient temperature

The energy stored in the battery of 17.8 kWh is used to maintain the temperature.

After 8 days and 12 hours, 80% of the capacity is used and the heating up is switched off.



Quelle: Projektbericht Regenerative Modellregion Harz, Elektro-KFZ als Speicher, K. Lipiec

Alkaline Batteries - Sodium-Nickel-Chloride Battery

- Theoretical efficiency close to 100% as there are no side reactions.
- Because of heat loss real. approx. 75-90% depending on the application
- Short-term storage with daily charging and discharging operation if possible
- Long service life of 2500 to 5000 charging cycles

Electric Energy Storage Systems

Chapter 3:
Exercise

Summer 2024

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1. NiCd Battery System

A. Describe the chemical reactions when charging a NiCd battery.

B. A battery system for an aircraft supply uses 22 NiCd cells in series acording to the datasheet on the next page

B1. What is the energy content of the battery system?

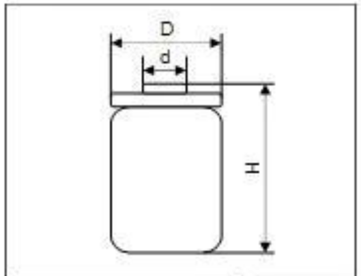
B2. What is the maximum possible short-circuit current?

B3. During operation the battery system has to deliver 1kW of power. What is the battery system voltage at this operation point?

NiCd Batterie Datasheet 1/2

Panasonic

Cell Type NC-1900SCR Specifications

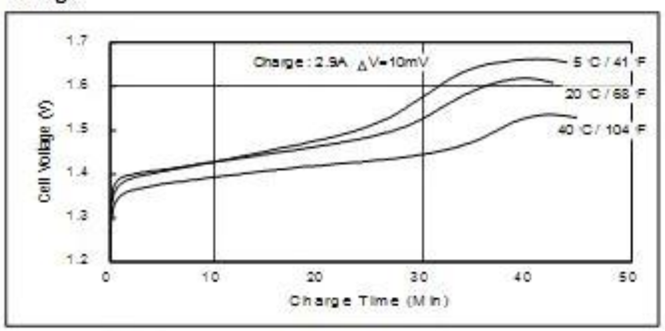


Dimensions of Bare Cell	H	$42.0^{\pm0.4}$	mm
		$1.654^{\pm0.016}$	Inch
	D	$22.0^{\pm0.3}$	mm
		$0.866^{\pm0.012}$	inch
	d	10.0	mm
		0.394	inch

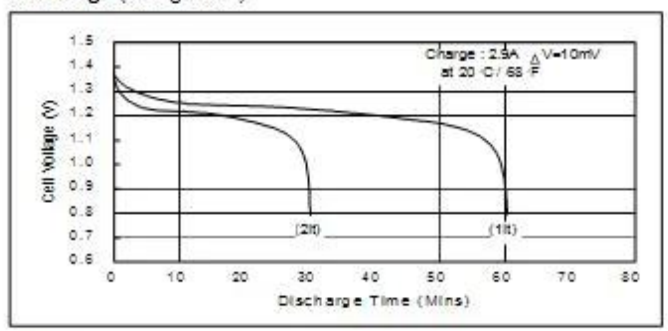
Nominal Capacity			1900mAh
Nominal Voltage			1.2V
Charging Current		Standard	190mA
		Fast	2900mA
Charging Time		Standard	14 to 16Hrs.
		Fast	about 1Hr
Ambient Temperature	Charge	Standard	0 ℃ to +45 ℃ [+32 ℉ to 113 ℉]
		Fast	5 ℃ to +40 ℃ [+41 ℉ to 104 ℉]
	Discharge		-20 ℃ to +60 ℃ [-4 ℉ to 140 ℉]
	Storage		-30 ℃ to +50 ℃ [-22 ℉ to 122 ℉]
Internal Impedance (Av.) (at 50% discharge)			4.5mΩ (at 1000Hz)
Weight (with tube)			Approx. 52g / 1.84oz
Dimensions(D) × (H) (with tube)			$22.9^{\,0}_{-1.0}$ × $42.9^{\,0}_{-1.2}$ mm
			$0.90^{\,0}_{-.004}$ × $1.69^{\,0}_{-.005}$ inch

Typical Characteristics

Charge



Discharge (at high rate)



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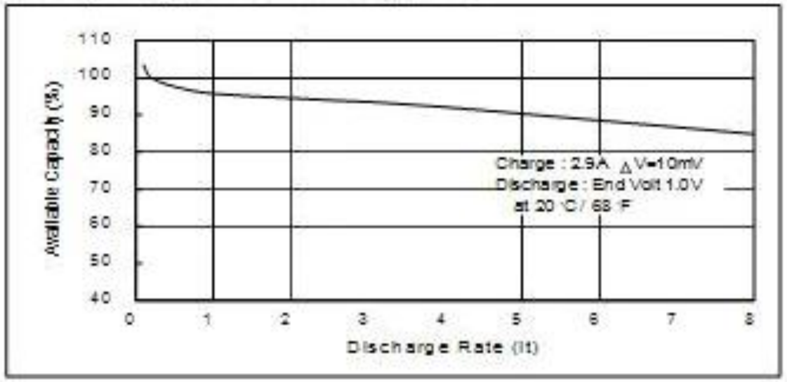
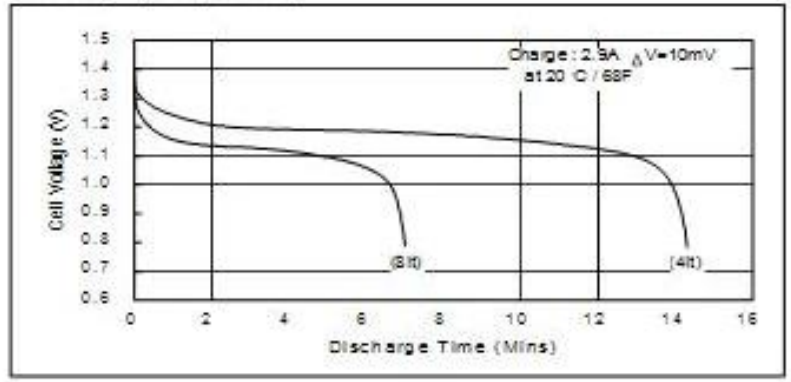
NiCd Batterie
Datasheet 2/2

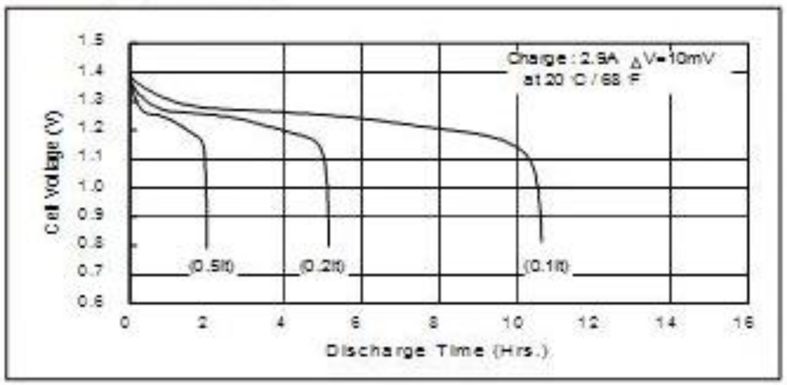
Cell Capacity (at various discharge rate)



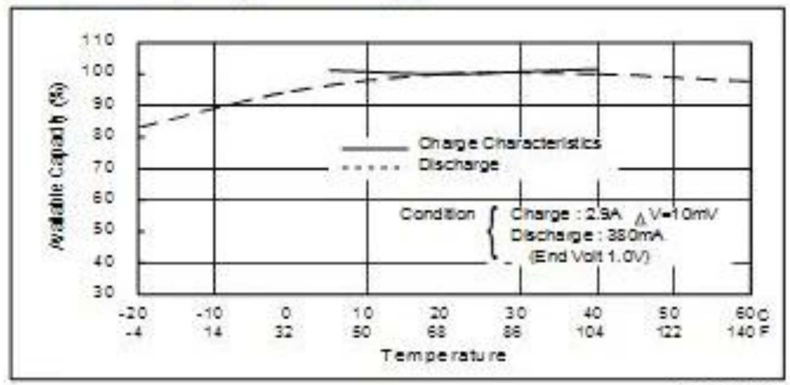
Discharge (at highe rate)



Discharge (at low rate)



Temperature (Charge & Discharge)



CD120229-01

2. NiCd Batteries in Vehicles

The battery storage of one of the first mass-produced e-cars, the AX Electrique, consists of 100 series-connected NiCd batteries, each with a capacity of 100 Ah

a) What is the cell voltage of a NiCd cell?

b) What is the energy content of the vehicle battery?

c) The vehicle battery is charged at 20 A for 4 hours. How much energy was stored in the battery system (assuming 100% charge efficiency)?

d) What is the minimum amount of cadmium required in the vehicle's NiCd battery storage system?
Cadmium (112.4 g/mol) can donate two electrons and becomes divalent Cd^{2+}
The Faraday constant has a value of 96487 As/mol.

Electric Energy Storage Systems

Chapter 4: Lithium-Ion Batteries

Summer 2024

Friedrich-Alexander-Universität Erlangen-Nürnberg

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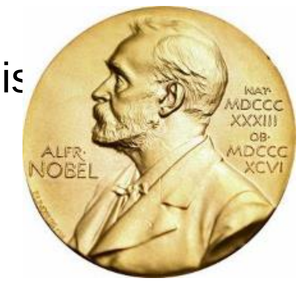
Lithium Ion Batteries

History:
A variety of active materials have been characterized since the 1960s
Since 1970 Li primary cells with lithium anode and manganese dioxide (MnO_2) cathode with 3 V (3.2V)
In the 1970's, S. Whittingham found titanium disulfide that intercalate lithium ions as cathode material
In 1980, John B. Goodenough developed the first rechargeable $LiCoO_2$ battery
In 1985, Akira Yoshino succeeded in commercializing it at A&T Battery in Japan
In 2019, Whittingham, Goodenough and Yoshino received the Nobel Prize in Chemis



Advantage:
- Lithium is the lightest solid element (atomic number 3, 7g/mol, 530g/dm³)
- High cell voltage 3 to 4 V
- High energy density

Disadvantage:
- Lithium reacts very strongly with water, releasing hydrogen
- Lithium-ion batteries can ignite if overcharged or mechanically damaged
- Cell monitoring (Battery Management System, BMS) required

Lithium Ion Batteries (LiIo)

Applications:

- (Starter) battery for aircraft
- Storage battery for electric vehicles
- Cordless tools
- Mobile communication electronics

Quelle:Airliners.de

Quelle:Porsche

Quelle:Makita

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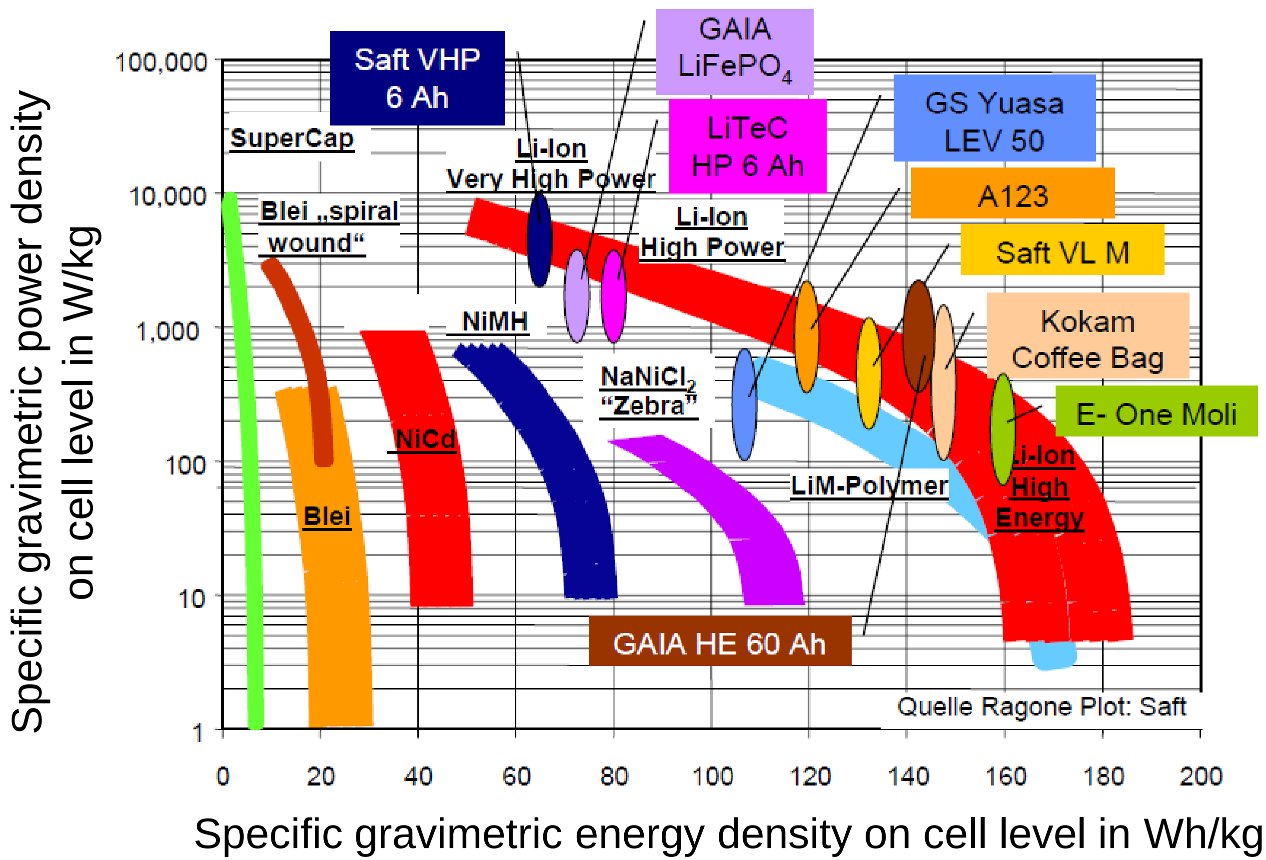
A Comparison of Electrical Storage Technologies



Picture: Dr. Dick, RWTH Aachen, ISEA

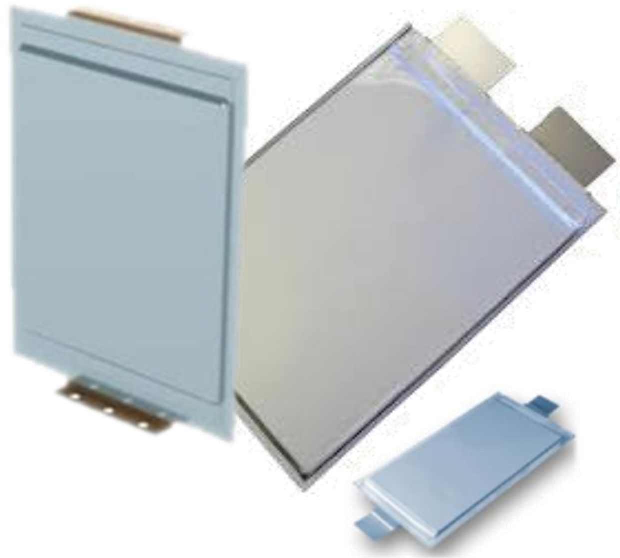
Li-Ion Battery Single Cell Designs

button cell

0,01…0,2 Ah

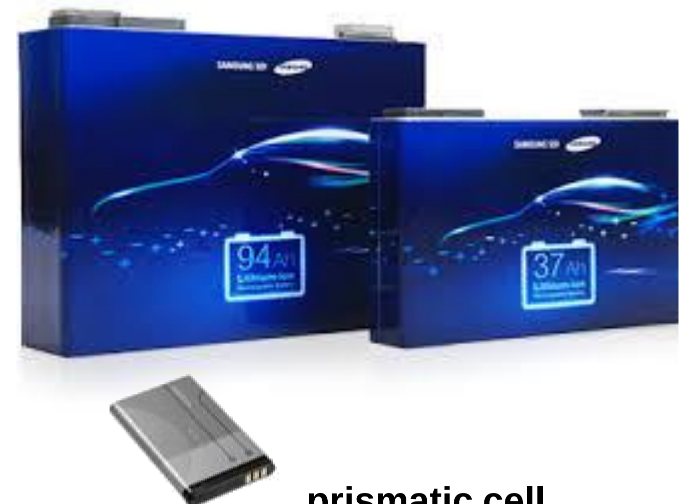
cylindrical cell

2…40 Ah



coffee bag (pouch) cell

2...200 Ah



prismatic cell

0,5…200 Ah

- Long experience with high volume production
- Mechanically robust
- Reliable sealing

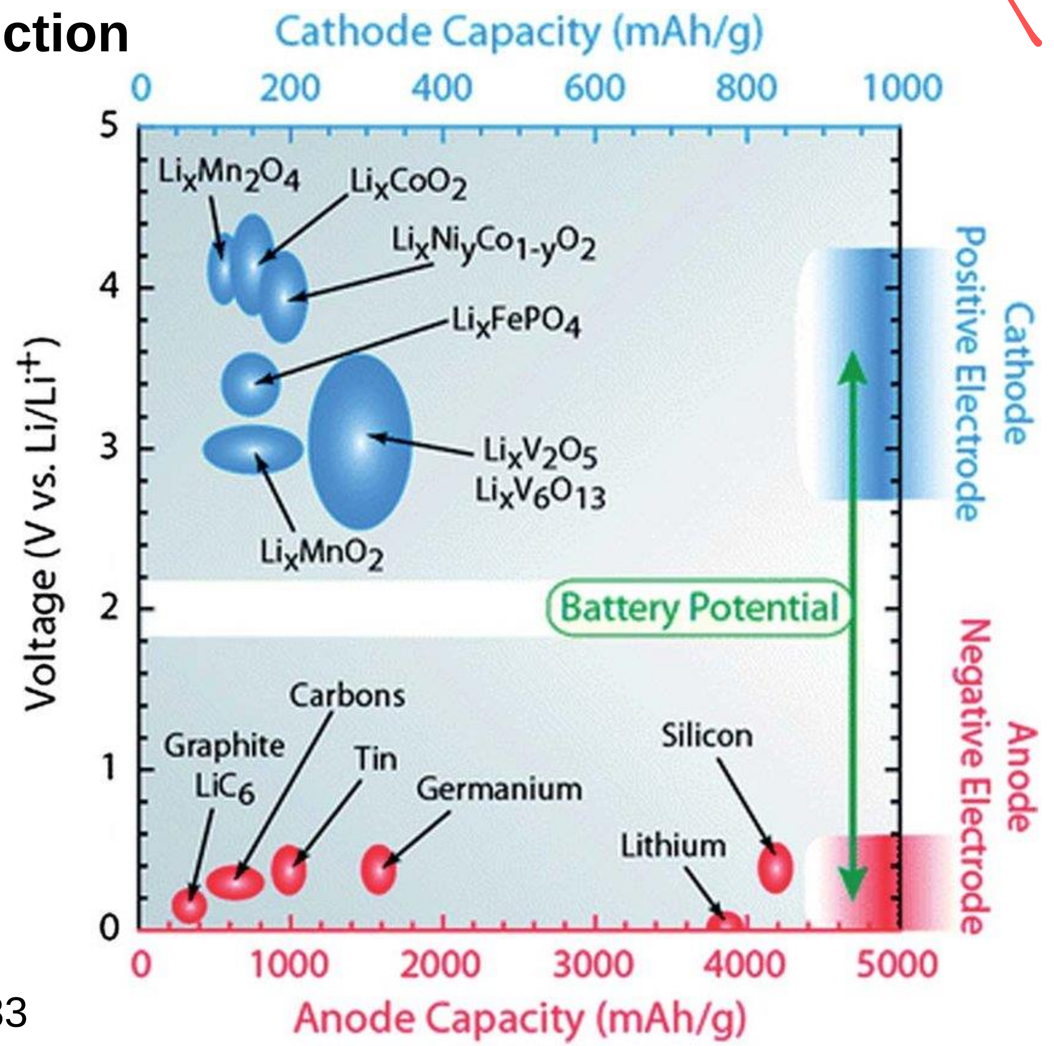
- High energy density due to minimal dead volume in the cell stack
- Easier cooling, more homogeneous temperature distribution

Inf.

Lithium-Ion Accumulator Construction

Electrode Material

- The battery properties can be defined by using different anode and cathode materials
- cell voltage
- Capacity
- Ampacity
- fast charge capability
- security



J. Mater. Chem. A,2014, 2,9433

Li-Ion Battery Technologies

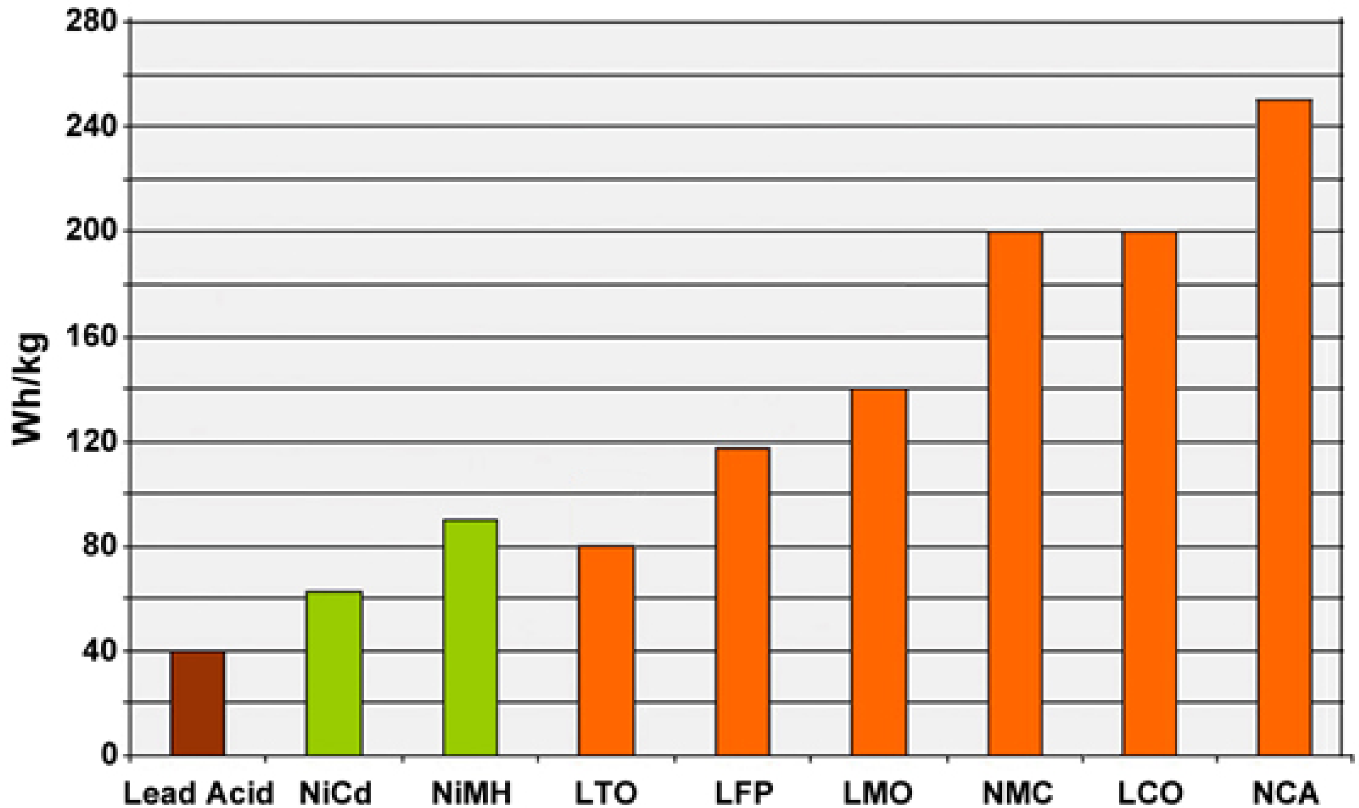
The option of combining different **anode materials**, **cathode materials**, **electrolytes** and **separator** technologies opens up a huge field of cell technologies with a wide variety of properties (in terms of energy density, safety, cycle stability, temperature range, etc.):

Cathode	Anode	Nominal voltage [V]	Energy density [Wh/kg]	Properties	Producer
LCO	Graphite	3,7	110 - 190	A compromise between energy density, cycle stability and safety. High content of the critical raw material cobalt	Sony
NMC	Graphite	3,6	120 - 200	Similar to LCO, but lower costs and less critical raw materials	Panasonic, Li-Tec, Kokam,..
NCA	Graphite	3,6	160 - 230	High energy density, but more safety critical	Saft, Samsung
LFP	Graphite	3,3	90 - 140	High safety, good cycle stability, high power density (high charging/discharging currents), but lower energy density	Sony, A123, ..
LMO	Graphite	3,7	100 - 120	Lower energy density and cost, good safety	LG Chem., ..
NMC/LCO/ LMO/LFP	LTO	2,3	70 - 90	Very high cycle stability, high safety, wide temperature range, safe against deep discharge - but a comparably low energy density	Toshiba, Altair-Nano, Leclanché
:	:			:	

LCO: $LiCoO_2$ (Lithium Cobalt Dioxide)
NMC: $LiNi_{0,33}Mn_{0,33}Co_{0,33}O_2$ (Lithium Nickel Manganese Cobalt Dioxide)
NCA: $LiNi_{0,8}Co_{0,15}Al_{0,05}O_2$ (Lithium Nickel Cobalt Aluminum Dioxide)

LMO: $LiMn_2O_4$ (Lithium manganese spinel)
LFP: $LiFePO_4$ (Lithium iron phosphate)
LTO: $Li_4Ti_5O_{12}$ (Lithium titanate)

Lithium-Ion Batteries: Comparison of Energy DEnsity



Quelle: batteryuniversity.com

Li-Ion Batteries – Construction

Electrolyt

The lithium-ion electrolyte consists of different anhydrous organic solvents with added conductive salts.

Lösemittel	Schmelzpunkt	Siedepunkt	Flammpunkt	Formel
EC: Ethylene Carbonate	36 °C	243 °C	150 °C	$(CH_2O)_2CO$
PC: Propylene Carbonate	-49 °C	242 °C	135 °C	$CH_3C_2H_3O_2CO$
DMC: Dimethyl Carbonate	3 °C	90 °C	18 °C	$OC(OCH_3)_2$
DEC: Diethyl Carbonate	- 43 °C	127 °C	33 °C	$OC(OCH_2CH_3)_2$
EMC: Ethylmethyl Carbonate	- 14 °C	107 °C	25°C	$OC(OCH_3)(OCCH_3)$

A blend used is: 63% DMC, 27% EC and 10% PC

Li-Ion Batteries – Construction

Conductive Salts

Lithium conductive salts are added to the electrolyte to increase conductivity and to provide the lithium ions.

Conductive Salts
Lithiumhexafluorophosphate ($LiPF_6$)
Lithiumtetrafluoroborate ($LiBF_4$)
Lithiumhexaarsenphospahte ($LiAsF_6$)
Lithiumperchlorat ($LiClO_4$)
Lithiumbisoxalatoborate (LiBOB)

Today lithium hexafluorophosphate (LiPF6) is mainly used with a concentration of approx. 1.0-1.2 mol/l.
This results in a conductivity of approx. 10mS/cm at 20°C

Li-Ion Batteries – Construction

Electrolyte

In addition to the liquid electrolytes mentioned, "solid" electrolytes are often used

- Gel-Electrolyte (are used in Lithium-Polymer Cells)
  - Polymerization of the electrolyte by adding approx. 5% PMMA (Polymethylmethacrylat) or PAN (Polyacrylnitril)
- Polymer Electrolyte
  - Plastic PEO (polyethylene oxide) is added to lithium salt. In order to maintain good conductivity, the battery must be operated at 60-80°C
- Solid Electrolyte
  - Ceramic materials to conduct the lithium ions

Li-Ion Batteries – Main Reactions of Lithium-Kobaltoxid

Discharge

The system made of graphite anode and lithium cobalt oxide is shown here as an example.

Positive Electrode: Intercalation (electrochemical reduction)

$$Li_{1-y}CoO_2 + yLi^+ + y\,e^- \longrightarrow Li_1CoO_2 \qquad 3{,}90\ \text{V (vs. Li)}$$

Negative Electrode: Deintercalation (electrochemical oxidation)

$$Li_1C_6 \longrightarrow Li_{1-x}C_6 + xLi^+ + x\,e^- \qquad 0{,}15\ \text{V (vs. Li)}$$

Cell Reaction:

$$\tfrac{1}{2}\,Li_1C_6 + Li_{0,5}CoO_2 \longrightarrow 3C + Li_1CoO_2 \qquad 3{,}75\ \text{V (vs. Li)}$$

The cathode material lithium cobalt oxide must not be completely delithiated,
y is a maximum of 0.5. Graphite can be fully delithiated, $0<X\leq 1$
The battery has an equilibrium voltage of 3.75V.

Li-Ion Akkumulatoren – Main Reactions Lithium Iron Phosphate

Discharge

The system made of graphite anode and lithium iron phosphate is shown here as example.

Positive Electrode: Intercalation (electrochemical reduction)

$$Li^+ + e^- + FePO_4 \longrightarrow LiFePO_4 \qquad 3{,}45\ V\ (vs.\ Li)$$

Negative Electrode: Deintercalation (electrochemical oxidation)

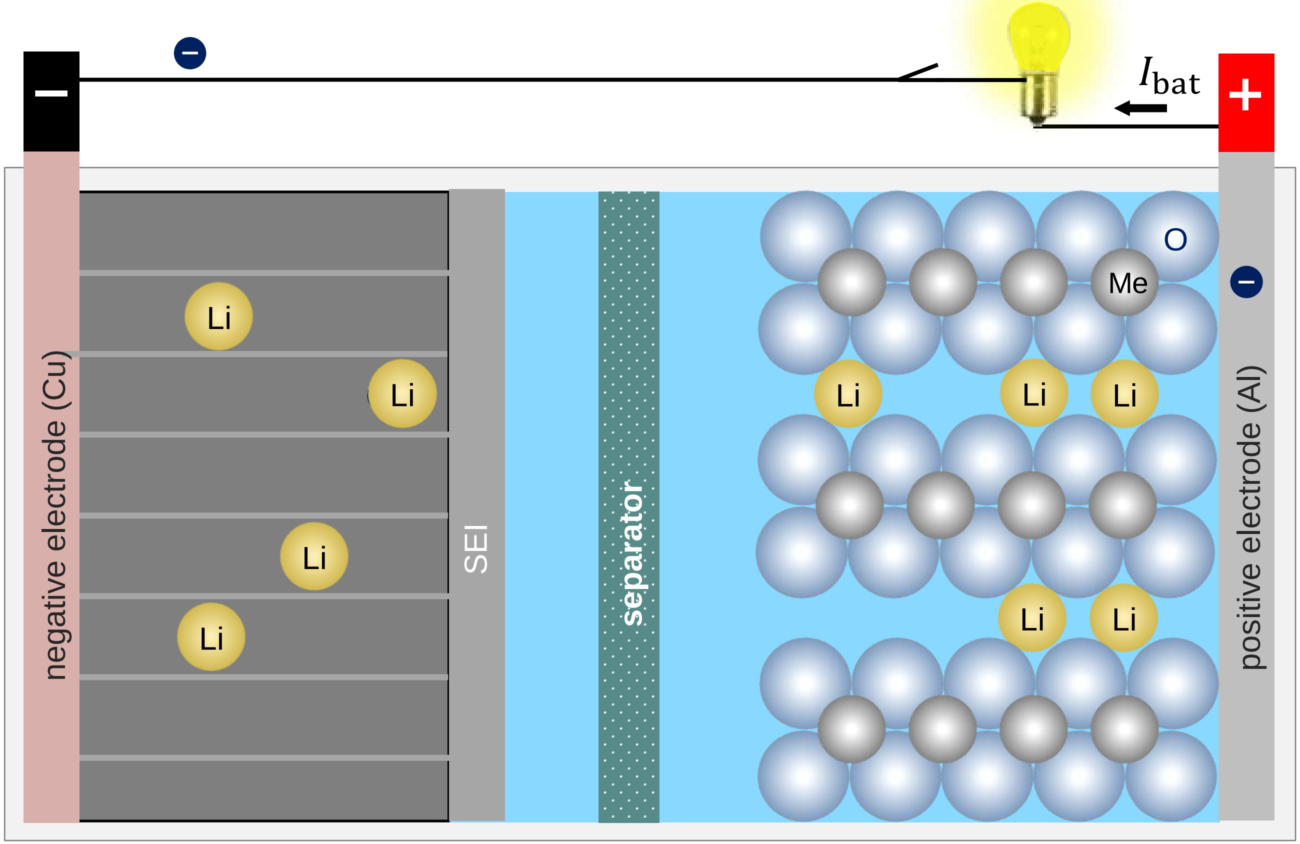
$$Li_1C_6 \longrightarrow Li_{1-x}C_6 + xLi^+ + x\ e^- \qquad 0{,}15\ V\ (vs.\ Li)$$

Cell Reaction :

$$Li_1C_6 + FePO_4 \longrightarrow 6\ C + LiFePO_4 \qquad 3{,}30\ V\ (vs.\ Li)$$

The battery has an equilibrium voltage of 3.30V.
Due to the low volume change of the $LiFePO_4$ of only 6.8%, very good cycle stability.
$LiFePO_4$ is chemically stable, thermally stable (up to 300°C without decomposition) and robust against overcharging and deep discharging

Li-Ion Battery ▪ Discharging



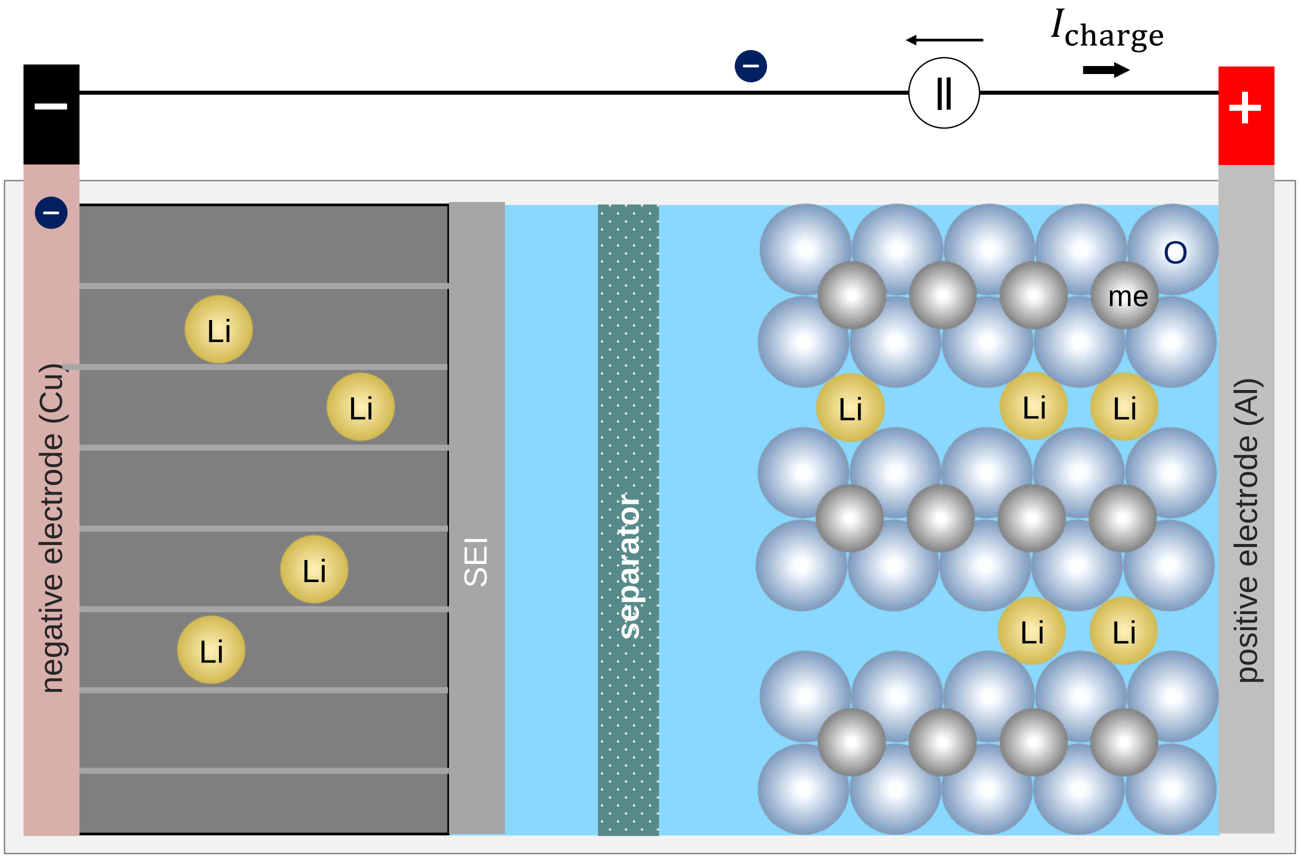
Anode
Graphite, $Li_4Ti_5O_{12}$, Si

Electrolyte
$LiPF_6$, …

Cathode
$LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$

Lithium is intercalated in the electrodes and is exchanged as Li-ion between the positive and negative electrode materials during charging/discharging.

Li-Ion Battery ▪ Charging



Anode
Graphite, $Li_4Ti_5O_{12}$, Si

Electrolyte
$LiPF_6$, …

Cathode
$LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$

Lithium is intercalated in the electrodes and is exchanged as Li-ion between the positive and negative electrode materials during charging/discharging.

Lithium-Ion Batteries

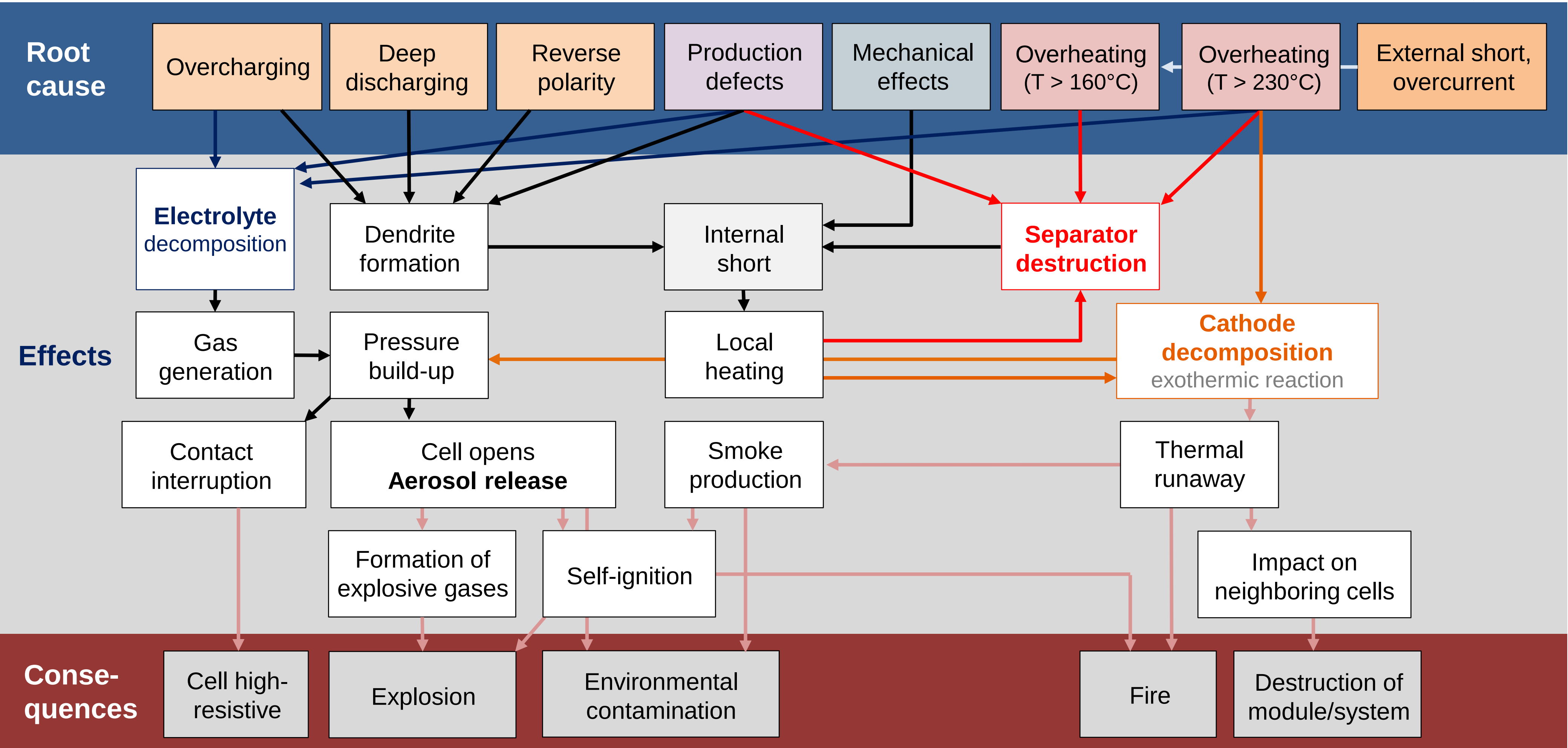
Chemistry	Energy Dens.	Power Dens.	Low-T	Safety	Stability	Costs per Ah
LCO						
NCA						
NMC						
LMO						
LFP						

A "safe" cell chemistry and a safe cell design alone are not a guarantee for the highest level of safety, even at the system level!



Imp

Potential Hazards with Li-Ion Batteries



Representation based on Prof. Dr. J. Tübke, Fraunhofer ICT

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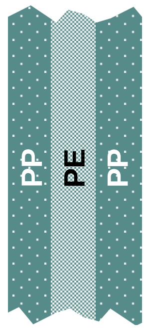
Safety Measures at Cell Level

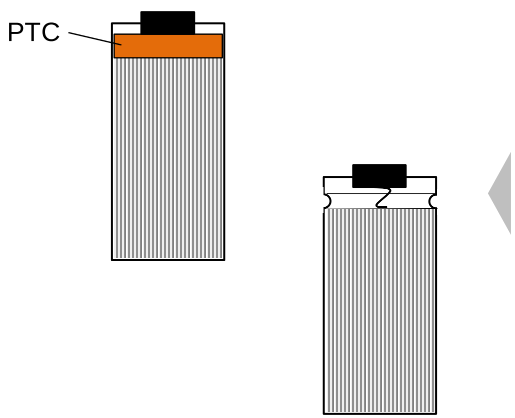


Shut down separator

- Micropores close under the influence of temperature and interrupt the ion transport (i.e. the electric current flow)
- Often implemented as a three-layer film made of polypropylene (PP) and polyethylene (PE): PE melts a bit earlier (130°C) and closes the pores

Separator with a microporous ceramic coating

- SEPARION®: Al_2O_3 powder on carrier fleece; mechanically stable up to 240°C



PTC

- A thermistor (PTC) increases its resistance at a certain threshold temperature, reducing the current and thus the risk of a "thermal runaway"

Current Interrupt Device (CID)

- An increase in pressure leads to a defined deformation of the cell housing and thus to the tearing off of the internal contact (⇨ current interruption)
- Also as a classic internal melting “fuse”

Electrolyte additives

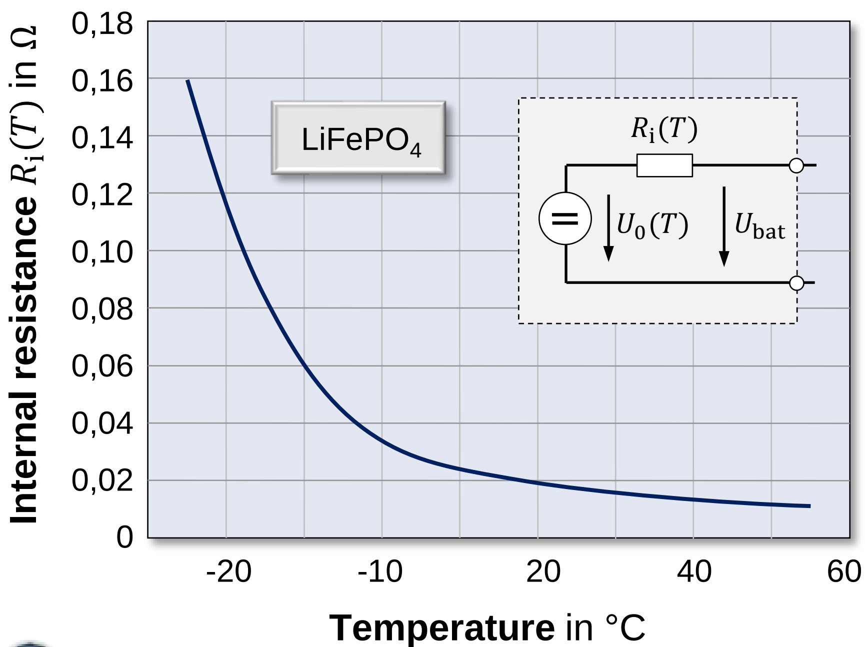
- Flame retardant additives

Safer electrode materials

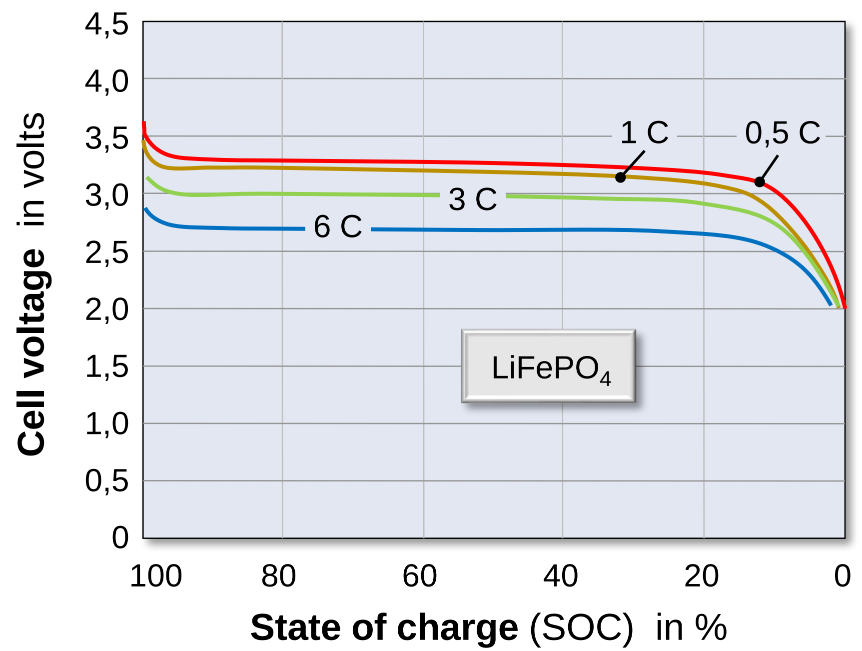
- Use of less critical electrode materials such as lithium iron phosphate

Li-Ion Batteries

Temperature dependence of the internal resistance



Current dependence of the discharge curve



Internal resistance as a function of temperature, measured on a 2.3 Ah cell from A123-Systems (@3,2V)

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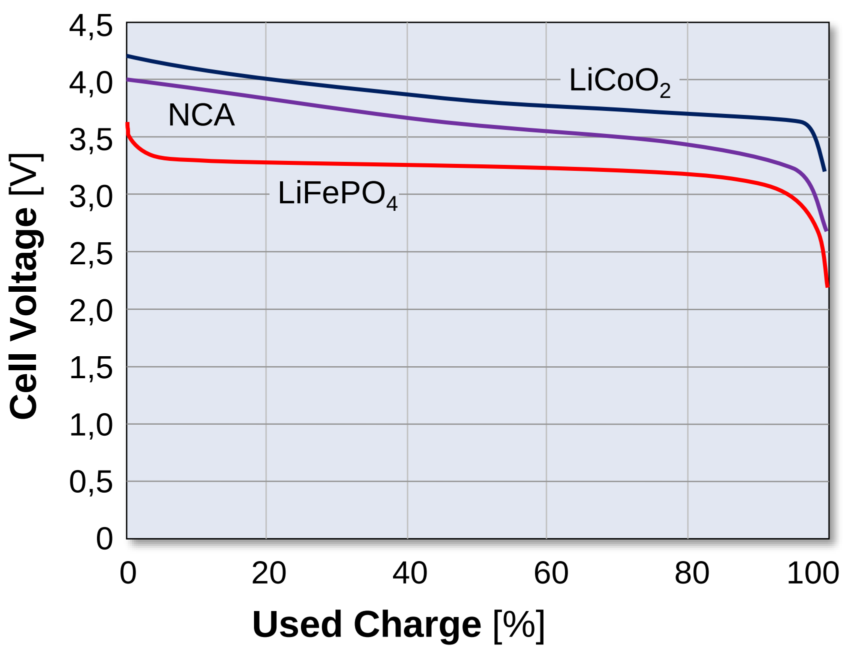
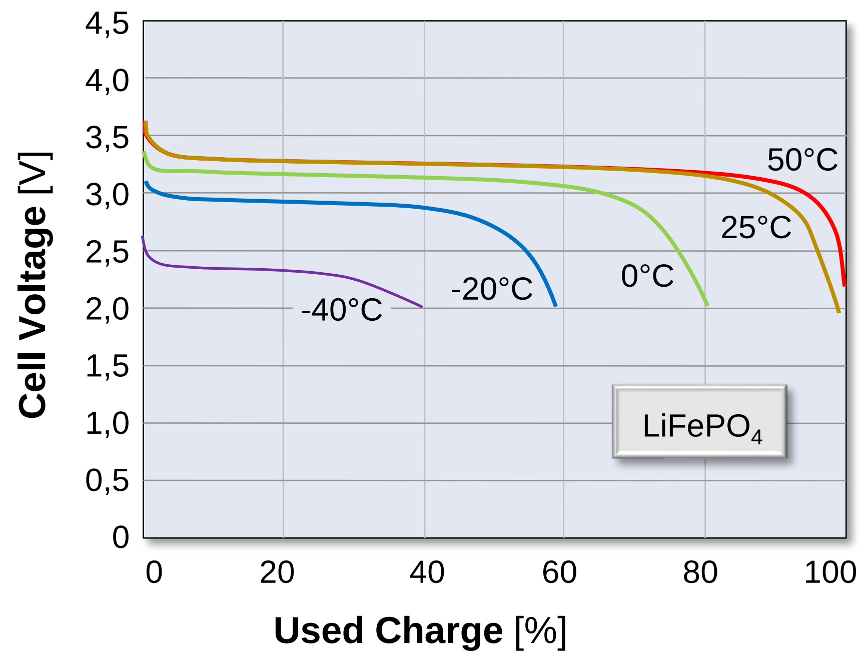
Li-Ion Batteries

Discharge behavior of different LiIO cell technologies



- A flat voltage curve offers application advantages, but makes it almost impossible to determine the state of charge by measuring the cell voltage alone!

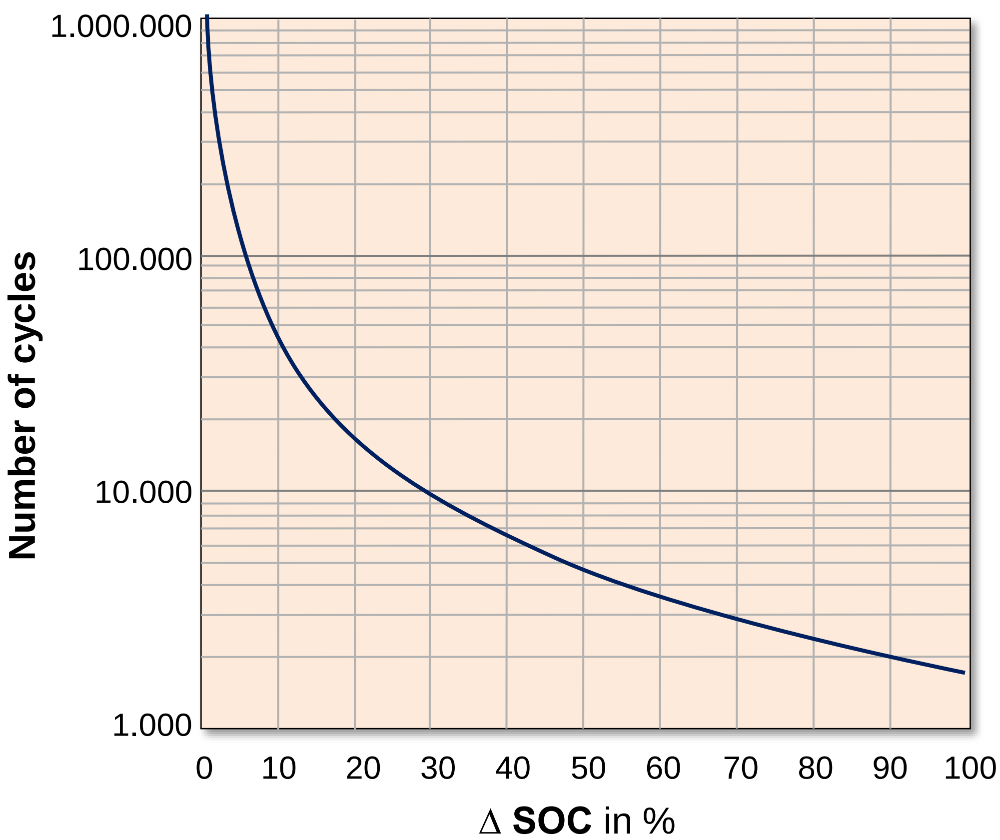
Temperaturabhängigkeit der Entladekurve (LFP)



- At low temperatures, the amount of energy that can be extracted decreases drastically

Typische Verläufe, hinzu kommt eine starke Abhängigkeit vom Entladestrom (C-Rate)

Cycle Life



A high application specific number of cycles requires a drastic reduction of the charge/discharge depth!

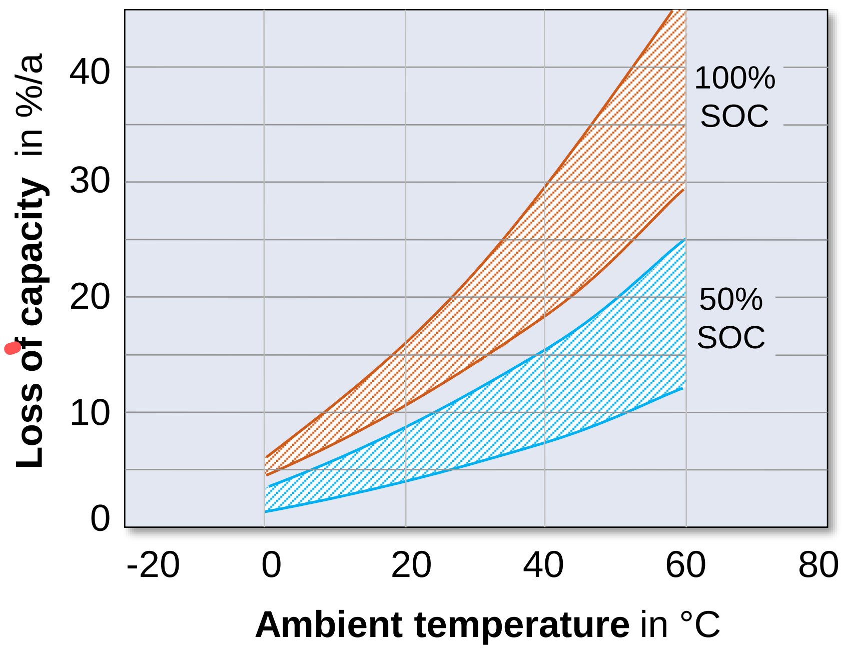
For a given energy exchange, the percentage change in the state of charge (∆ SOC) decreases as the energy content of the battery increases

Typical curve of modern Li-Ion technologies (except lithium titanate) @ battery temperature of about 25°C

Imp

Calendar Lifetime

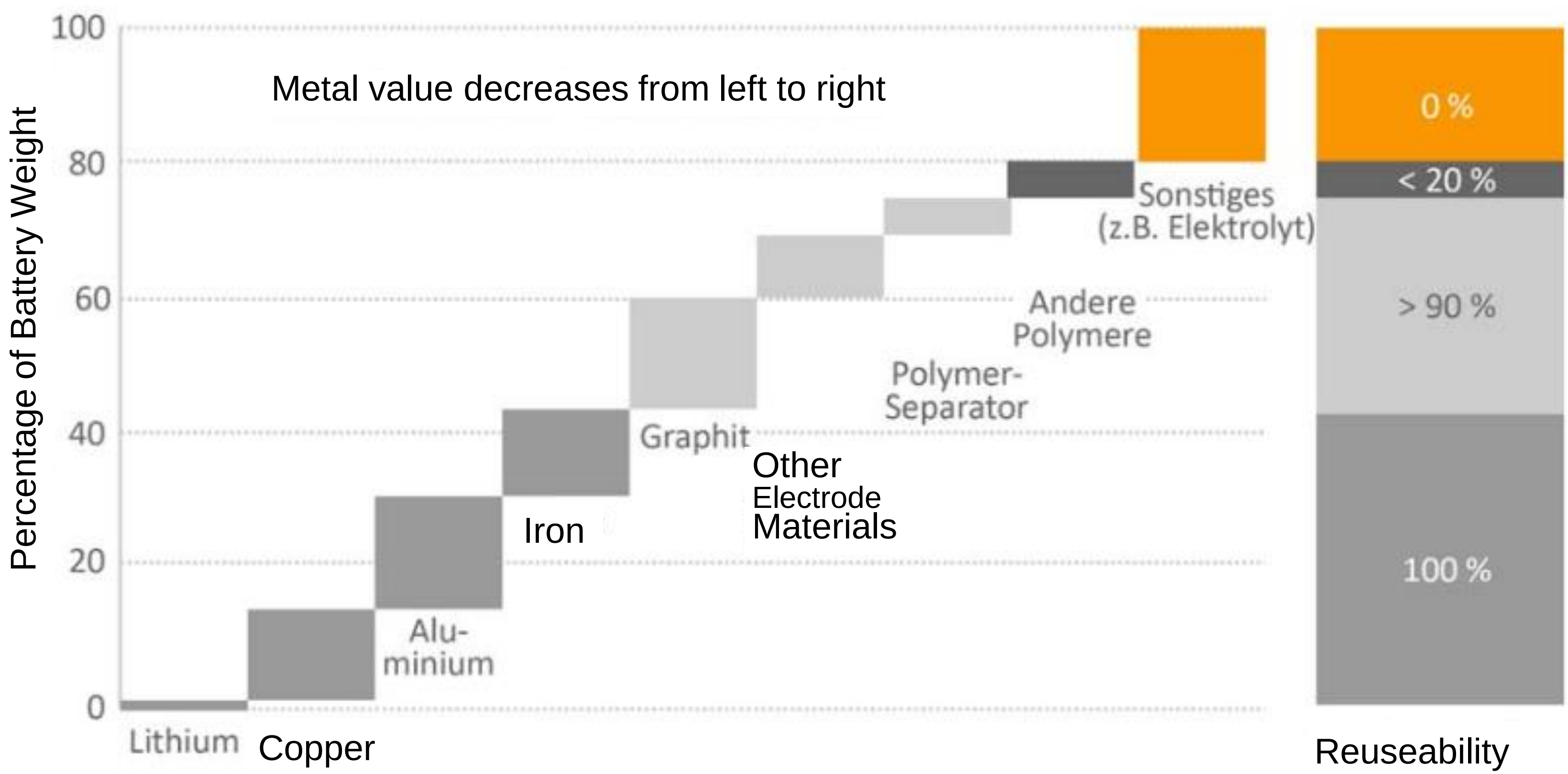
Even without cyclic loading Li-Ion batteries show a permanent loss of capacity depending on the ambient temperature and the state of charge during storage!



- Aging increases dramatically with the "storage temperature" and the state of charge
- The aging behavior is also dependent on the specific cell technology
  - Do not store Li-Ion batteries in warm environment or fully charged ($SOC_{storage\_optimum}$ = 30…50%)
  - A reduction in the state of charge during longer periods of non-use (e.g. vehicle idle times) increases battery life

Data source: Bulletin SEV/AES 3/2009; Prof. Sauer/RWTH

Lithium-Ion Batteries - Recycling shown with $LiFePO_4$



Quelle Kleine-Möllhoff, P.; Benad, H. et al. (2012): Die Batterie als Schlüsseltechnologie für die Elektromobilität der Zukunft, Hochschule Reutlingen

Lithium-Ion Batteries – Optimized Operation

- Cells should be operated at medium (30-70%) state of charge
- The storage temperature should be below 20°C
- Avoid full cycles if possible
- Strong warming of the cells during operation above 40°C is critical
- Deep discharge of the cells below 2.5 V should be avoided
- The charging voltage must be precisely regulated to approx. 20mV
- Each cell must be monitored for its min. and max. voltage during charging and operation

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Electric Energy Storage Systems

Chapter 4:
Exercise

Summer 2024

Friedrich-Alexander-Universität Erlangen-Nürnberg

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1. LiIo Battery System

A. Why can LiIo cells cover such a wide range in terms of power density and energy density?

B. What other materials could be used for the anode besides graphite?

C. What cell chemistry would you suggest for EV applications and aircraft applications? Reason.

D. What are the potential hazards of LiIo batteries and possible safety measures at cell level?

E. LiIo batteries are used in most mobile applications today
Explain the advantages of LiIo batteries over supercapacitors, lead, NiCd and NiMH batteries using a Ragone diagram. Draw the Ragone plot and fill in the different storage systems accordingly.

F. Sketch the discharge curves of LiFePo cells depending on the temperature at -40°C, 0°C and 25°C.

Electric Energy Storage Systems

Chapter 5: Lithium-Ion Batteries
Battery Management and Battery Systems

Summer 2024

Friedrich-Alexander-Universität Erlangen-Nürnberg

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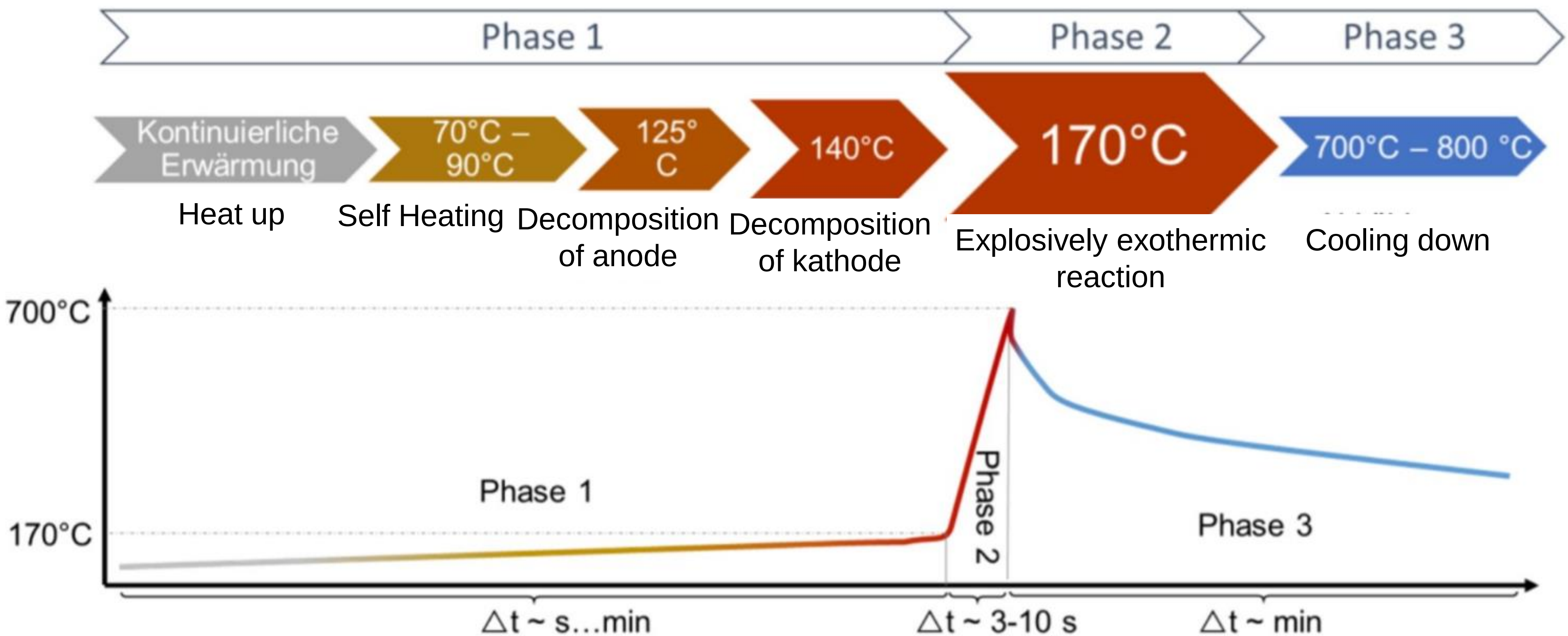
Lithium-Ion Batteries – Cell Monitoring Tasks

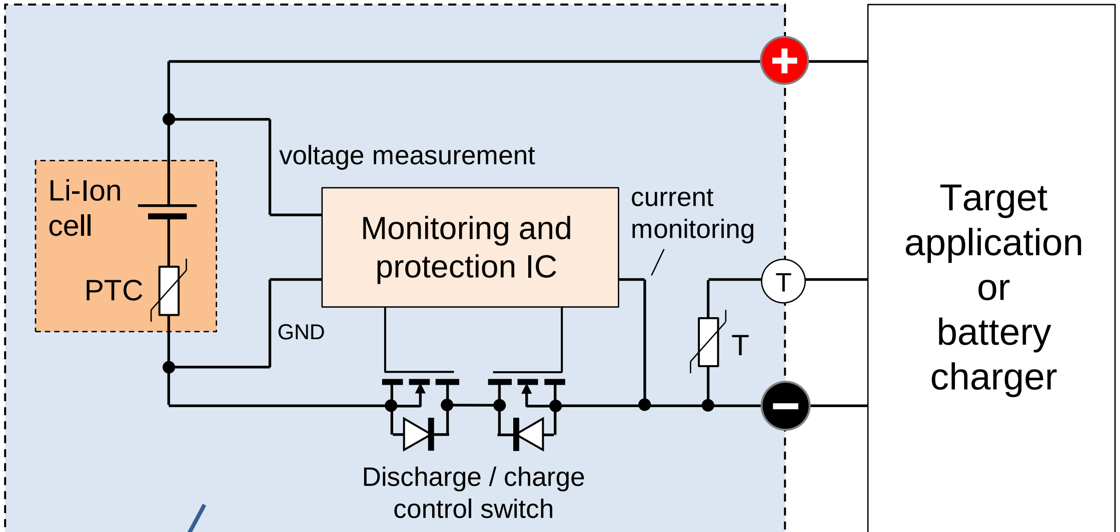
- Avoiding overcharging and deep discharging
- Avoidance of too high temperatures
- Determining the state of charge (SOC)
- Specification of charging/discharging currents or power (State of Power, SOP)
- Determination of the battery status or aging (State of Health, SOH)
- Balancing the cells by adjusting the state of charge

Lithium-Ion Batteries – Overcharging can lead to Thermal Runaway



Quelle: Rössel Messtechnik

Single Cell Monitoring and Protection

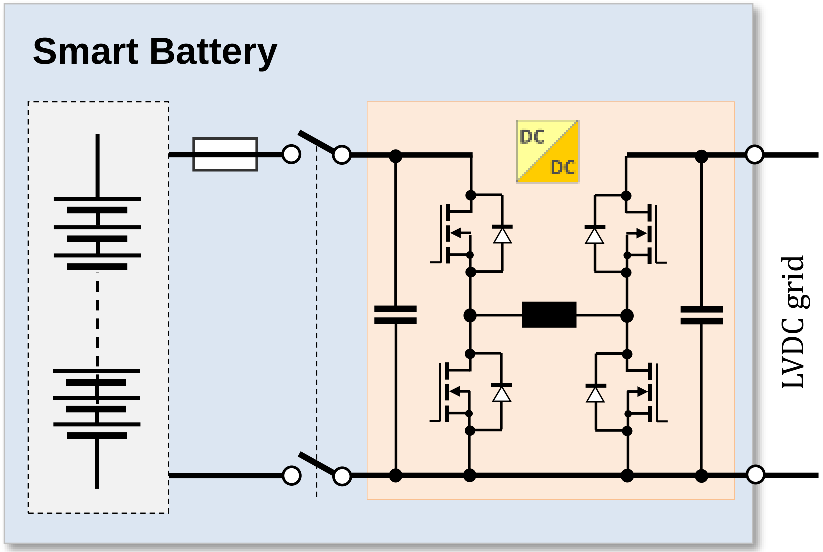


Protection against mishandling

- due to overcharging,
- deep discharging,
- polarity reversal,
- external short circuit,
- overheating as a result of overloading

Electronics cannot make a bad cell safer, but prevent good quality cells from being damaged by the user!

Smart Battery ■ the way to safe, modular and universal battery systems



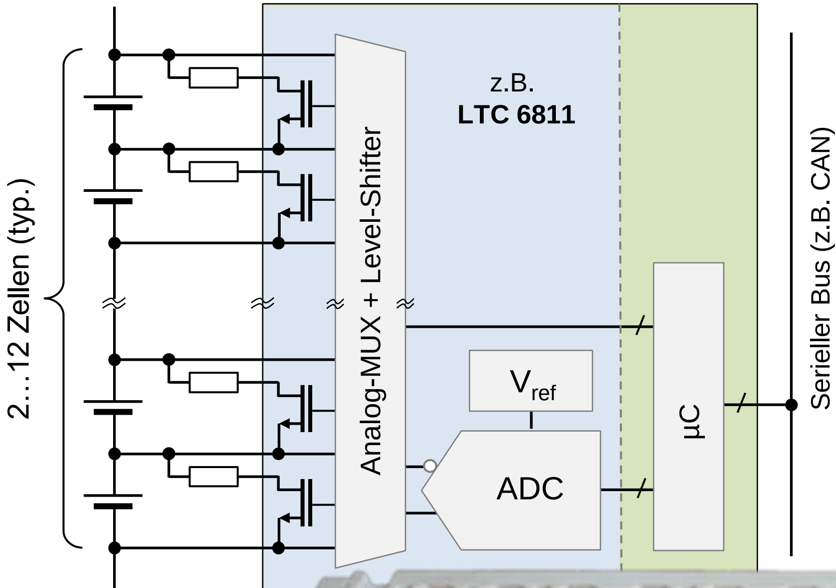
Smart Battery

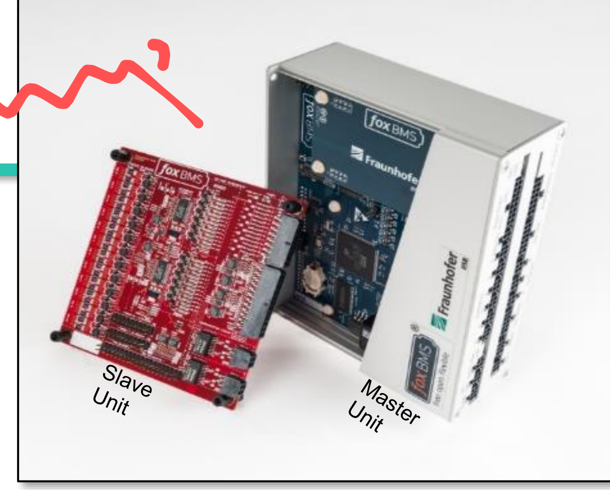
- Output voltage independent of battery voltage or state of charge
- Inherent inrush current limiting and precharge functionality
- Current and energy limitation in the event of a fault in the application
- Precise charge/discharge management
- Overcharge and deep discharge protection

An integration of the **power electronics into the battery system** is a prerequisite for maximum safety, modularity and functional flexibility.

vgl. Patent: WO 03/015237 A1

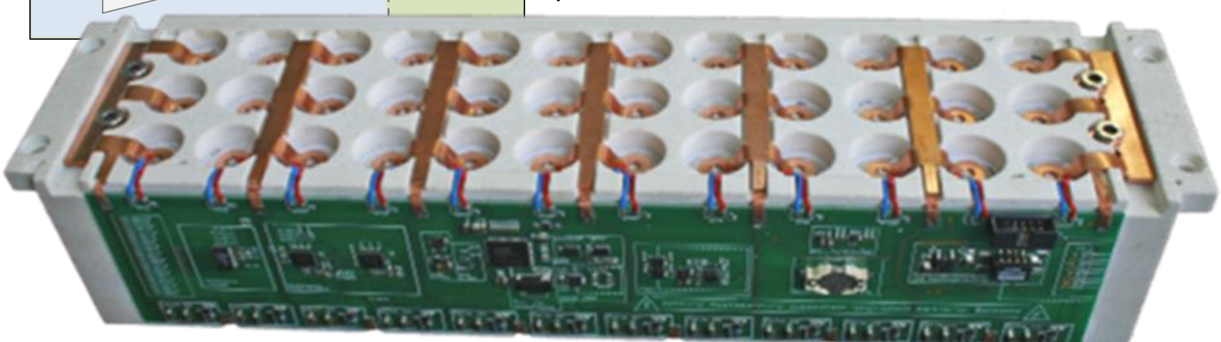
Li-Ion cells in series require individual cell monitoring and charge balancing





Cell electronics for battery modules

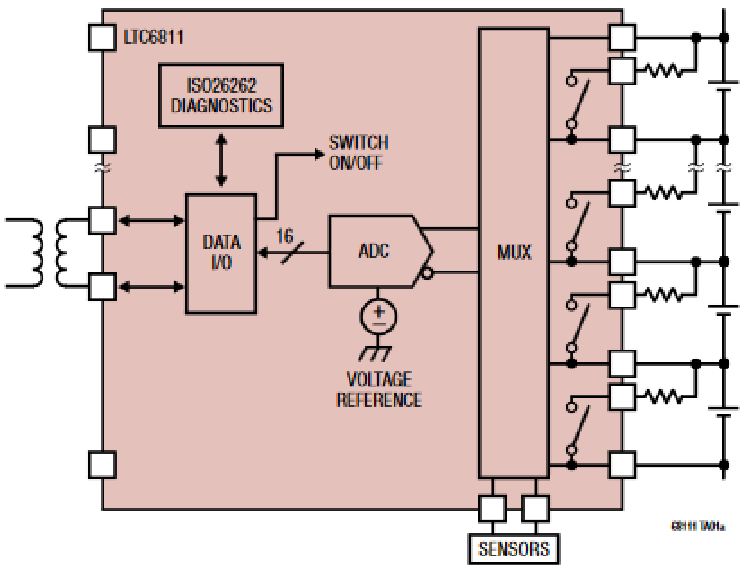
- Individual cell voltage measurement
- Individual cell temperature measurement (optional)
- Cell individual passive charge equalization
- Communication between different modules and with a central battery management system (BMS) via serial data bus

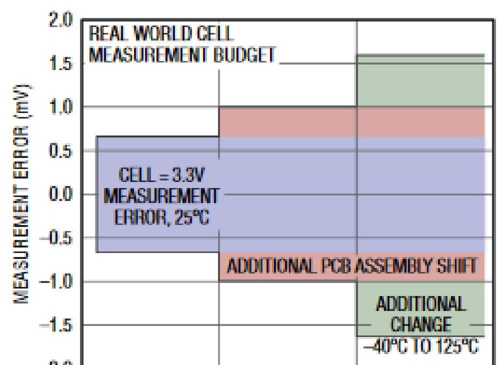


foxBMS®
free.open.flexible

Cell Measurement and Equilization

Example LTC 6811





FEATURES

- Pin-Compatible Upgrade from the LTC6804
- Measures Up to 12 Battery Cells in Series
- 1.2mV Maximum Total Measurement Error
- Stackable Architecture for High Voltage Systems
- Built-in isoSPI™ Interface
  - 1Mb Isolated Serial Communications
  - Uses a Single Twisted Pair, up to 100 Meters
  - Low EMI Susceptibility and Emissions
- 290µs to Measure All Cells in a System
- Synchronized Voltage and Current Measurement
- 16-Bit ADC with Programmable Noise Filter
- Engineered for ISO 26262-Compliant Systems
- Passive Cell Balancing with Programmable Timer
- 5 General Purpose Digital I/O or Analog Inputs
  - Temperature or other Sensor Inputs
  - Configurable as an I^2C or SPI master
- 4µA Sleep Mode Supply Current
- 48-Lead SSOP Package
- AEC-Q100 Qualified for Automotive Applications

APPLICATIONS

- Electric and Hybrid Electric Vehicles
- Backup Battery Systems
- Grid Energy Storage
- High Power Portable Equipment

Cell Measurement and Equilization

Beispiel TLE9012

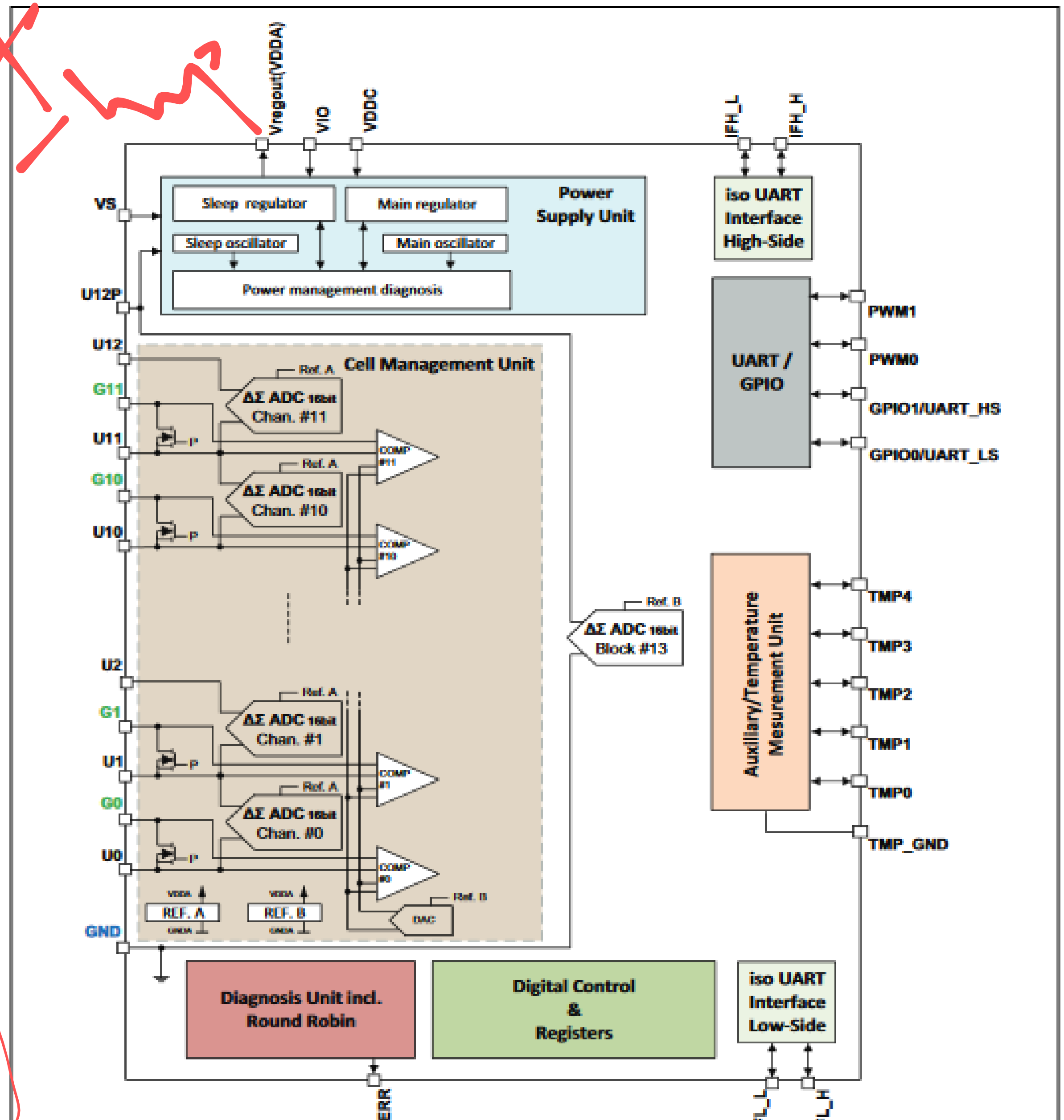
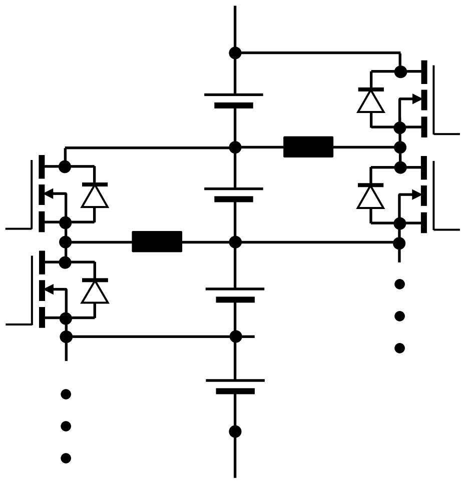


Figure 1 TLE9012AQU block diagram

Working

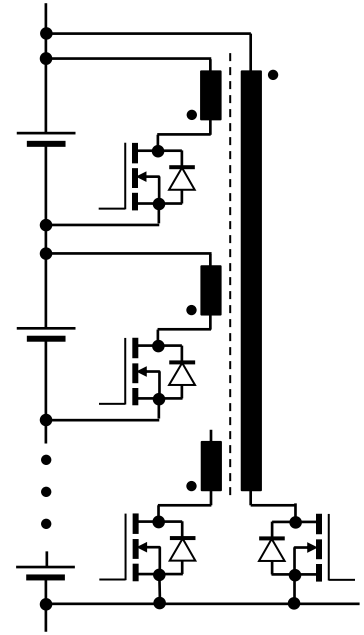
Active Charge Equalization ▪ two of numerous circuit examples

Buck/boost converter principle



- Very high recharging currents possible
- Suitable for cell “preheating” at low temperatures using circulating currents
- Charge can only be "moved further" from cell to cell
- Significant effort

Flyback converter principle



- High recharging currents possible
- Random charge redistribution
- Expensive transformer required
- Significant effort

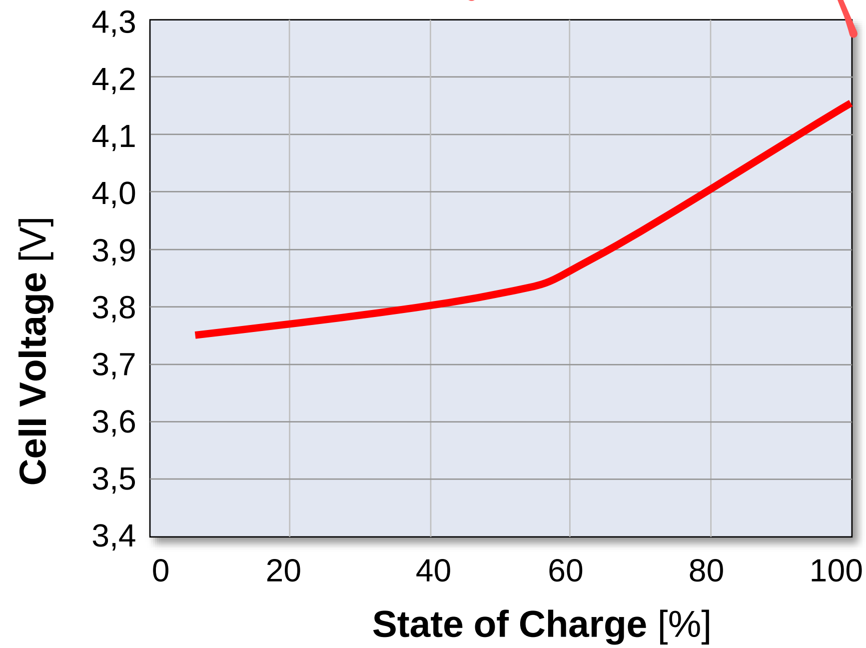
Lithium-Ion Batteries - Determination of the state of charge (SOC)

Definition „State of Charge“ SOC in percent: SOC = $\frac{C_N - Qb}{C_N}$

with C_N: nominal capacity; Q_b: balanced charge

Measurement of resting voltage

- The open-circuit voltage changes over the state of charge by approx. 500 mV
- The open circuit voltage is almost independent of previous history (charging / discharging)
- Overvoltages subside quickly (<1h)
- Method does not work with lithium iron phosphate as it has a very flat voltage characteristic
- Precise cell voltage measurement required (5...20mV)

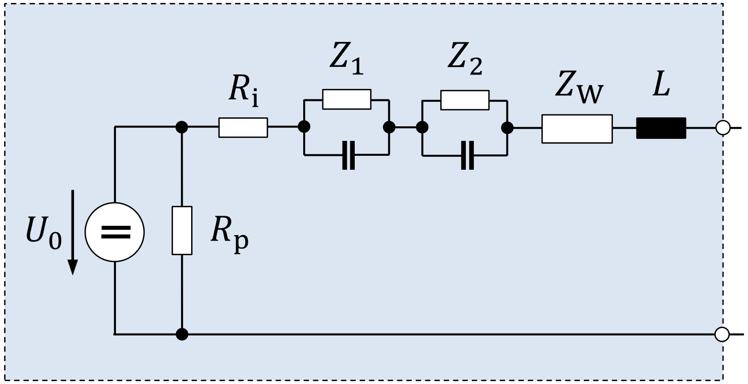


Charge Balance

- Measurement and integration of charge/discharge current
- Depending on the application, high-resolution current measurement is necessary
- Inaccurate with longer measurement times due to integration of current measurement errors

$$SOC = SOC_0 + \frac{1}{C_N}\int_{t_0}^{t} I_{batt}\,dt$$

Electrical Equivalent Circuit of a Li-Ion cell



U_0 : open circuit voltage (= f(SOC, T, ..))

R_p : self-discharge

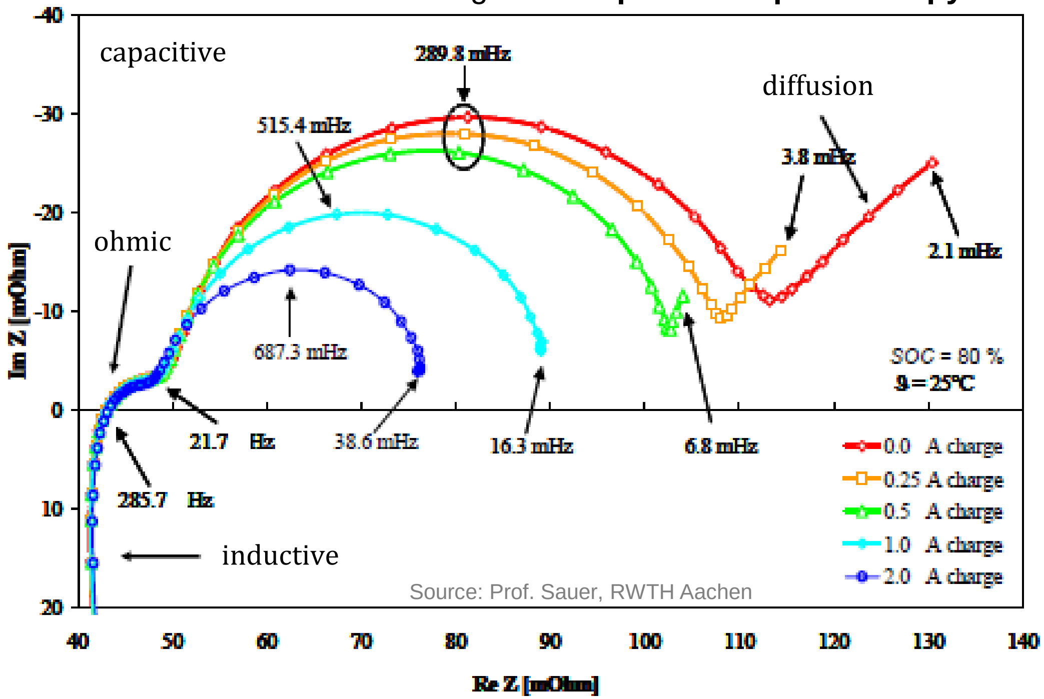
Z_1 : SEI layer

Z_2 : charge transfer and double layer capacitance

L : series inductance (cell bus bars, …)

Z_W : Warburg impedance (diffusion model)

Parameter extraction e.g. from **impedance spectroscopy**



- Almost all elements of the equivalent circuit are functions of the state of charge (SoC), temperature, state of health (SoH), etc.!
- Within the switching frequency range of power electronics, a single Li-Ion cell or a battery module can be described to a very good approximation as a voltage source with an internal ohmic resistance (R_i) and a series inductance (supply leads).
- The capacitive branch is only relevant for very low-frequency events (e.g. load steps)

Lithium-Ion Batteries – Batteriesystem

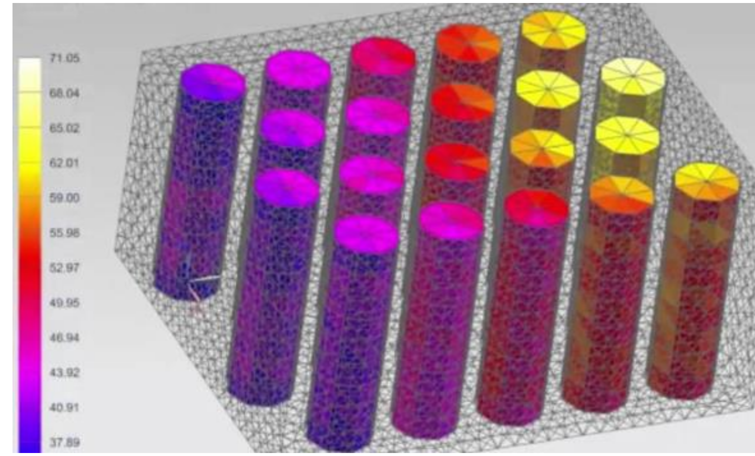
- interconnection of the cells
- thermal management
- Mechanical protection of the cells
- Integration of cells, monitoring, cooling and power electronic converters

Cooling Concepts for LiIo Batterie System

Direct Cooling

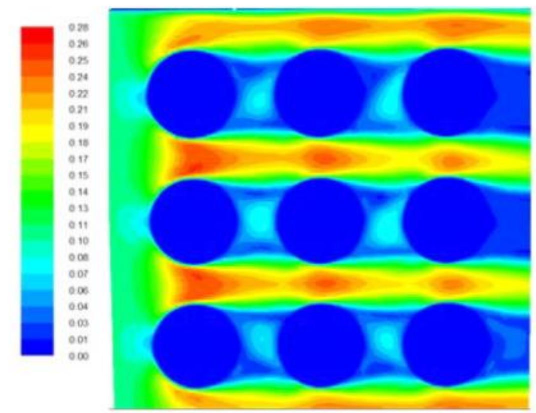
Forced Air Cooling

- Depending on environmental conditions, dust and moisture can get into the battery system
- Difficult to achieve temperature homogeneity across different cells
- Ideal for round cells and low to medium cooling requirements



Direct Liquid Cooling

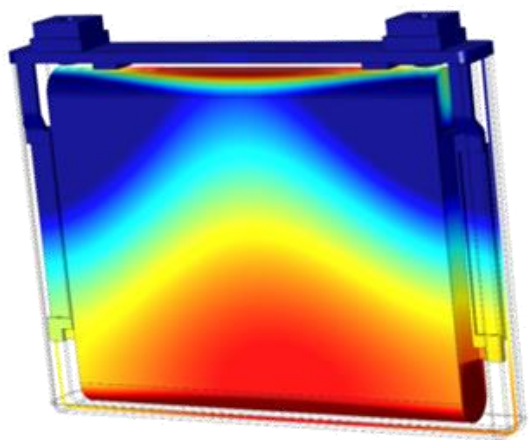
- Higher cooling capacity and temperature homogeneity than with air cooling
- Non-conductive cooling media must be used (dielectric liquids, oil)
- Sealing is a major challenge



Cooling Concepts for LiIo Batterie System with Cold Plate

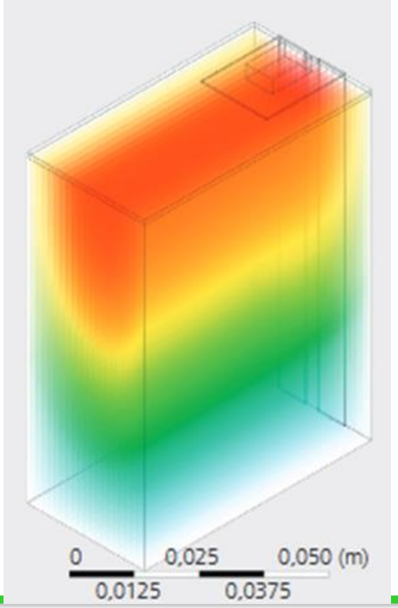
Cooling of Connectors

- The highest losses are in the area of the power connections
- Cooling plate must be installed with electrical insulation



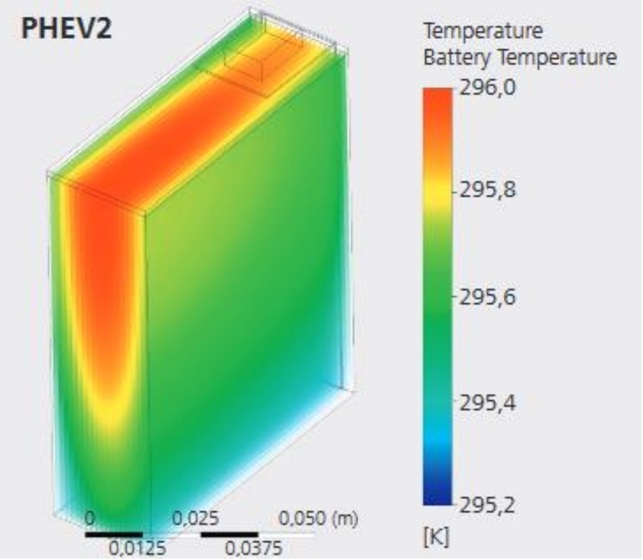
Bottom Cell Cooling

- Cooling of the cell bottom by mounting on a cooling plate
- only low power dissipation can be dissipated



Bottom and Side Cooling

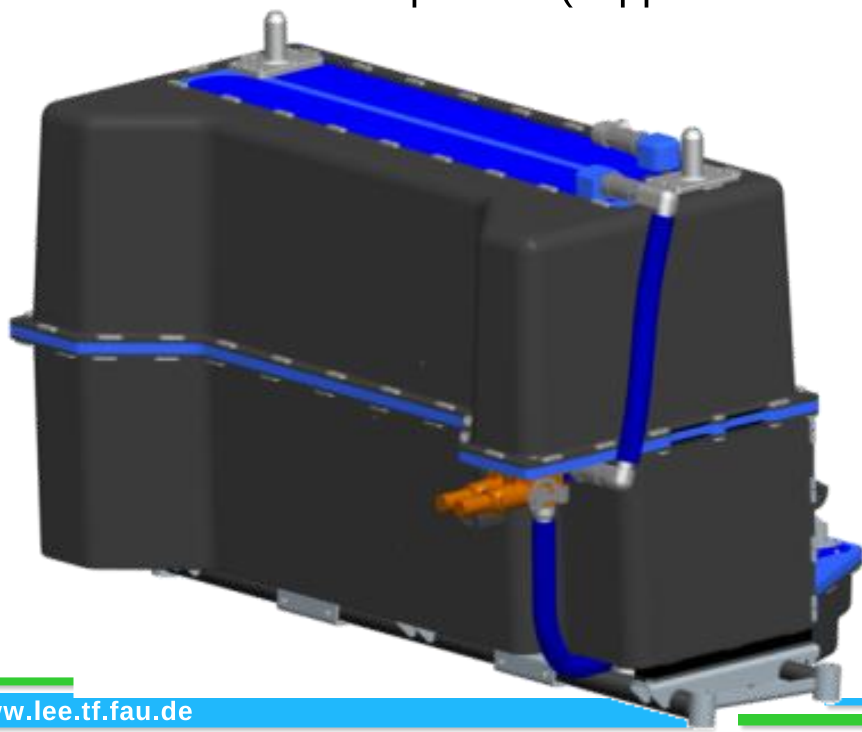
- Cooling of the cell bottom by mounting on a cooling plate and the sides by cooling plates
- Large-area thermal connection possible



 Quelle: Dissertation Wei Zhou (2016), Aachener Beiträge des ISEA, Band 81.

Smart Battery Systems

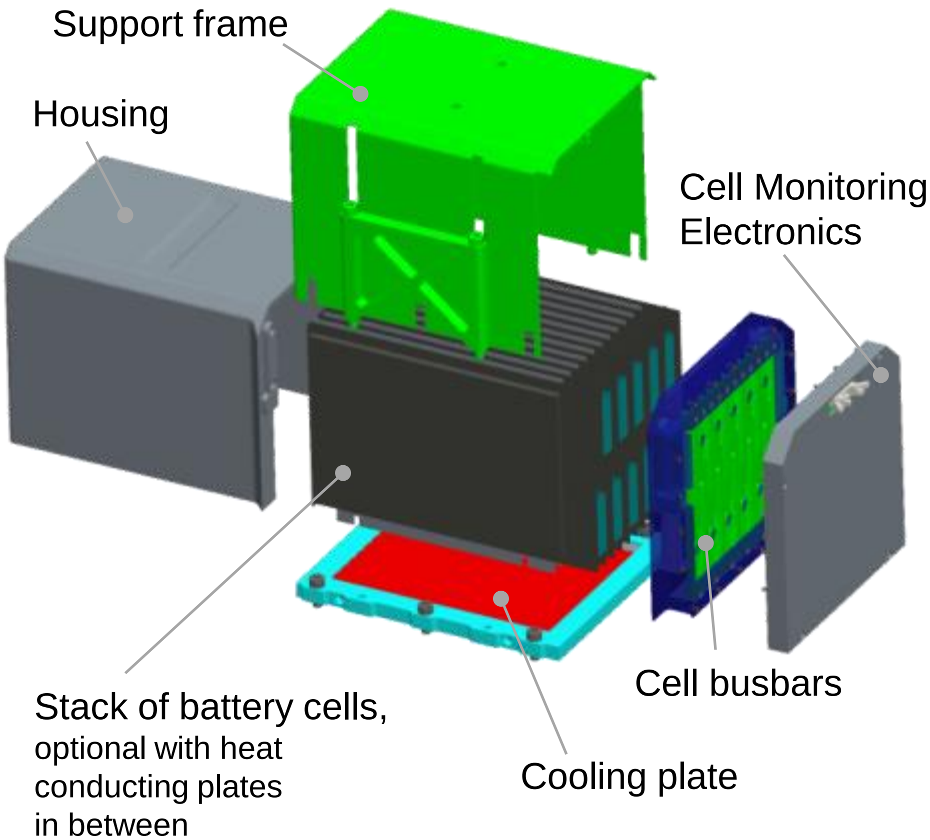
- Placement in the crash-protected vehicle area
- Easy installation/removal (in/out of vehicle)
- Integrated, hermetically separated water cooling
- Voltage converter, charger(s), safety technology integrated
- Can be connected in parallel (supports distributed battery systems)



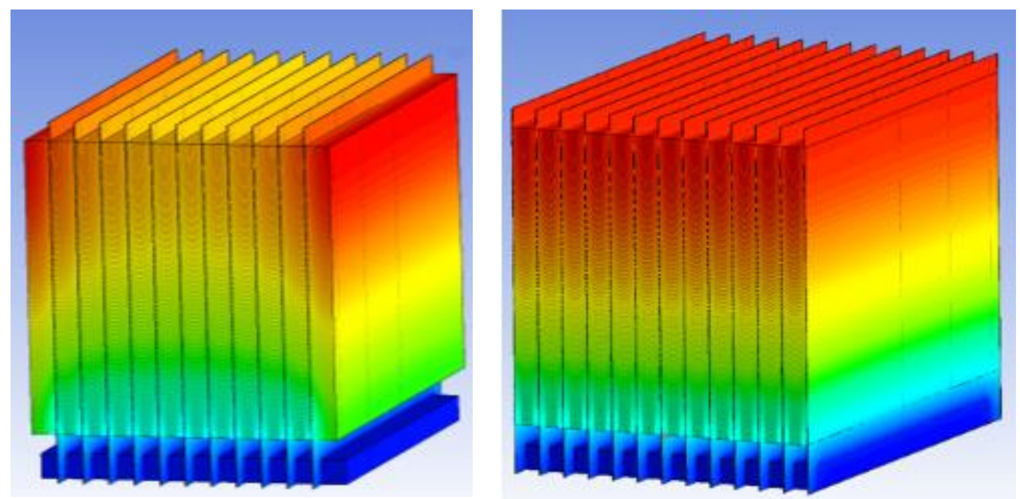
Batteriemodul

- Cells: Kokam (NMC), 12 in Serie
- Volume: 11,7 dm³
- Weight: 16 kg
- Energy: 1,8 kWh

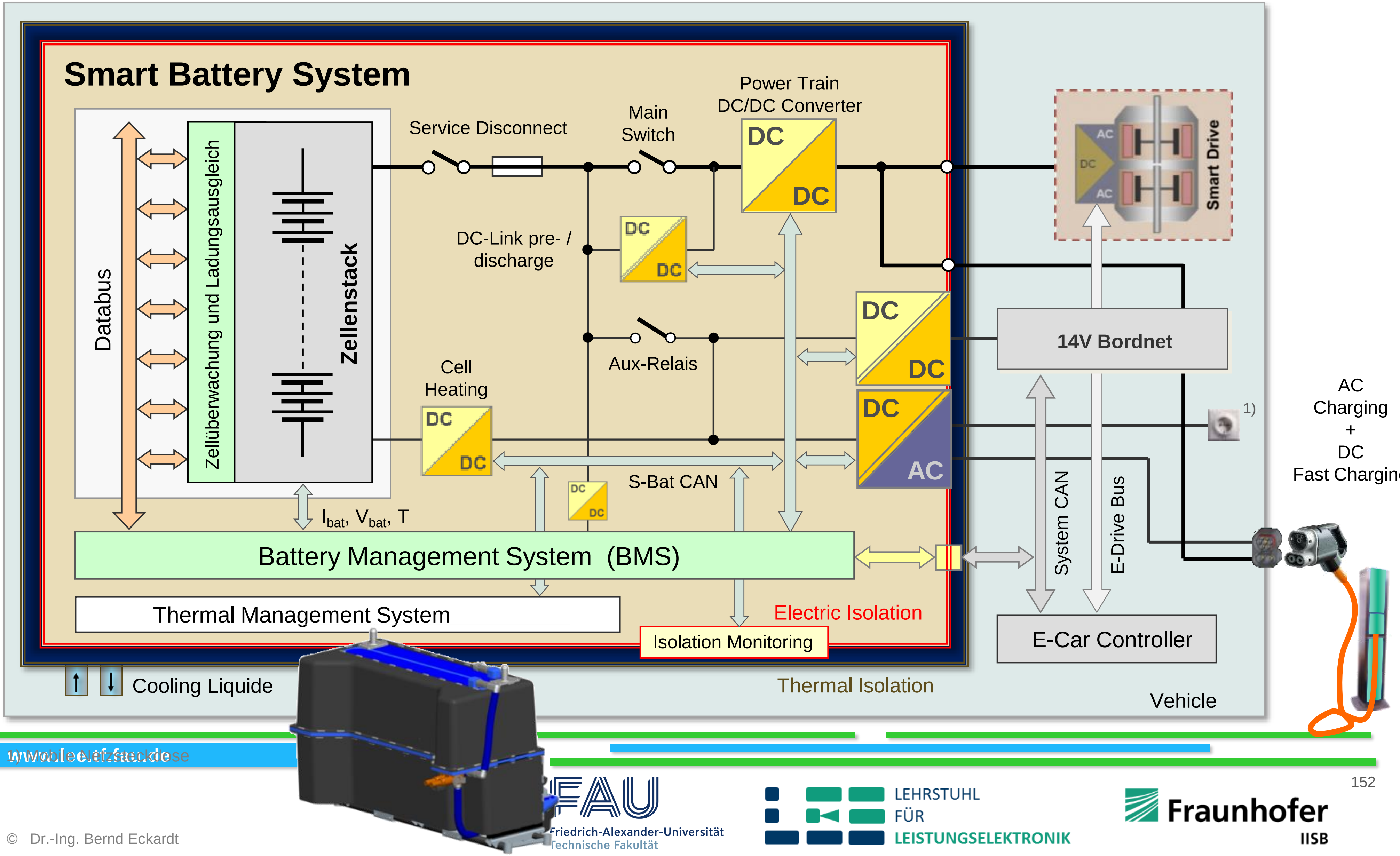
Design of a Battery Module - an example



- A temperature distribution that is as homogeneous as possible within a battery module is essential for an even aging of the cells!
- In the end, the weakest cell in a battery module determines the lifespan of the entire battery!



Electric Energy Storage Systems



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Fraunhofer IISB

Smart Battery Concept – IISB Design 2010

Modular Cell Stack
including cell monitoring and balancing

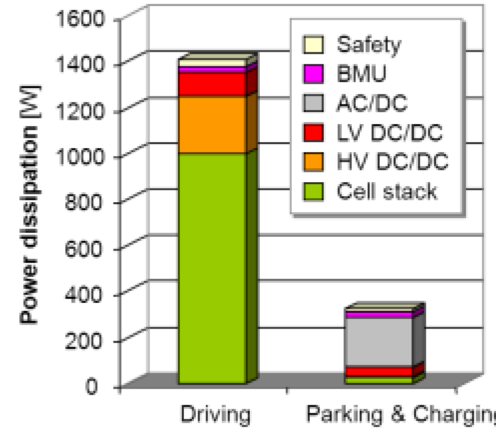
- $LiFePO_4$ Cells (lair cooled)
- Nominal Voltage: 320 V
- Energy: 2,4 kWh

Bidirectional DC/DC-Converter
(50 kW, air coolled)

Multifunctional Grid Interface
(feed back and off-grid capability)

Bordnet DC/DC-Converter
(14 V, 2 kW)

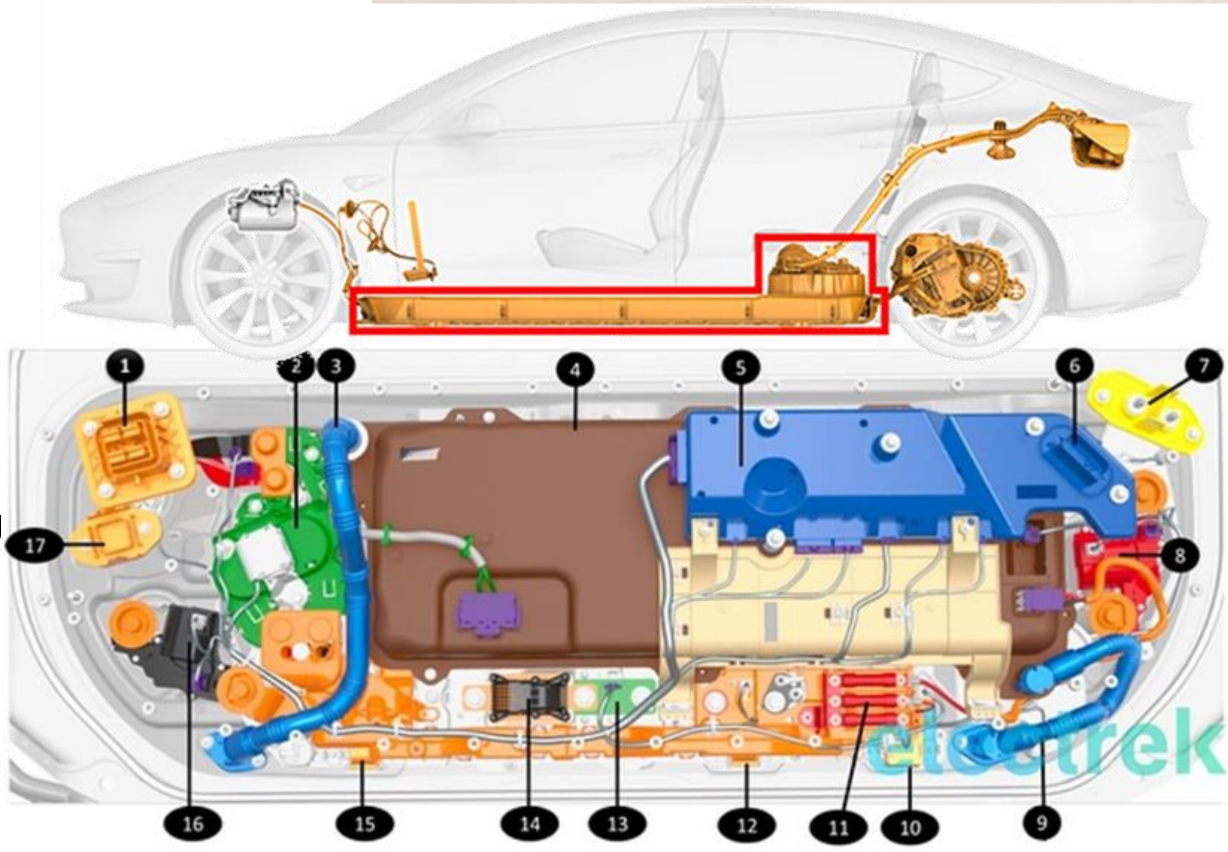
BMs
(Battery Management System)



Highly Efficent Power Electronic
⇨ No problem for the thermal management of the battery system

Smart Battery – Example Vehicle Tesla Model 3

- With the Model 3, Telsa integrates the charger and the 12 V voltage converter directly into the battery system



1. Charging connection
2. Fast charging contactor
3. Coolant connection PCS
4. PCS - Power Conversion System
5. HVC - High Voltage Controller
6. Signal plug for HVC
7. 12V output PCS
8. HV+ disconnect switch
9. Coolant connection PCS
10. HV connection for Hrizer and air conditioning compressor

11 Fuses

12. HV connector for rear drive unit
13. HV pyro fuse
15. HV connector for front drive unit
16. HV disconnect switch
17. Connector for 3 phase AC charging

Quelle:elektrek.co

Stationary Lilo Storage Systems

World Largest Battery System in the year 2020:
LS Power's 250 MW / 1,5 GWh in San Diego, California,

Largest Lilo Battery System in Germany:
48 MW / 50 MWh in Jardelund, near to Flensburg,

Fraunhofer IISB 3x 20kWh 100kW 550V NMC/LT(
Cells with 14x 15s2p

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Fraunhofer IISB

Lithium-Ion Batteries - Systems and Cell Monitoring

- Cell monitoring can significantly increase the safety of LiIo batteries
- It is possible to determine the state of charge (SOC) and the aging (SOH)
- Different self-discharge of the cell can be compensated (active/passive)
- In the battery system, an even cell temperature must be ensured through adapted thermal management.
- Integration of power electronics in/to the battery system reduces weight and costs

Electric Energy Storage Systems

Chapter 5:
Exercise

Summer 2024

Friedrich-Alexander-Universität Erlangen-Nürnberg

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1. LiIo Battery System

A. Draw a sketch of the protective circuitry of a LiIo cell to prevent overcharging, deep discharging, and short circuits.

B. What are the options for active charge equalization in LiIo battery systems? Draw sketches of two possible circuits.

C. A Battery system of 200 cells with each nominal voltage of 3.7 V, internal resistance of 1 mOhm and a capacity of 100 Ah is given.

C.1 How much energy can be stored ?

C.2 Loaded with 200 A. How much power losses are generated in the battery system?

C.3 How much Power is delivered to the application at 200 A discharge current?

Electric Energy Storage Systems

Chapter 6:
Hydrogen Technology and Fuel Cells

Summer 2024

Friedrich-Alexander-Universität Erlangen-Nürnberg

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Hydrogen Technology and Fuel Cells

History:

Already in 1800 W. Cruickshank, W. Nicholson and A. Carlisle discovered the electrolysis of water into hydrogen and oxygen

In 1838 C. F. Schönbein described the first experiment with a "gas battery". This created a voltage on platinum electrodes in sulfuric acid, one of which came into contact with oxygen and the other with hydrogen.

First applications of fuel cells from around 1960 in the Gemini (1965/1966) space program

Advantages:

- Energy converter (fuel cell) and storage (tank) can be designed separately
- Water as a product of the reaction in the fuel cell
- No polluting emissions (with hydrogen fuel cells)

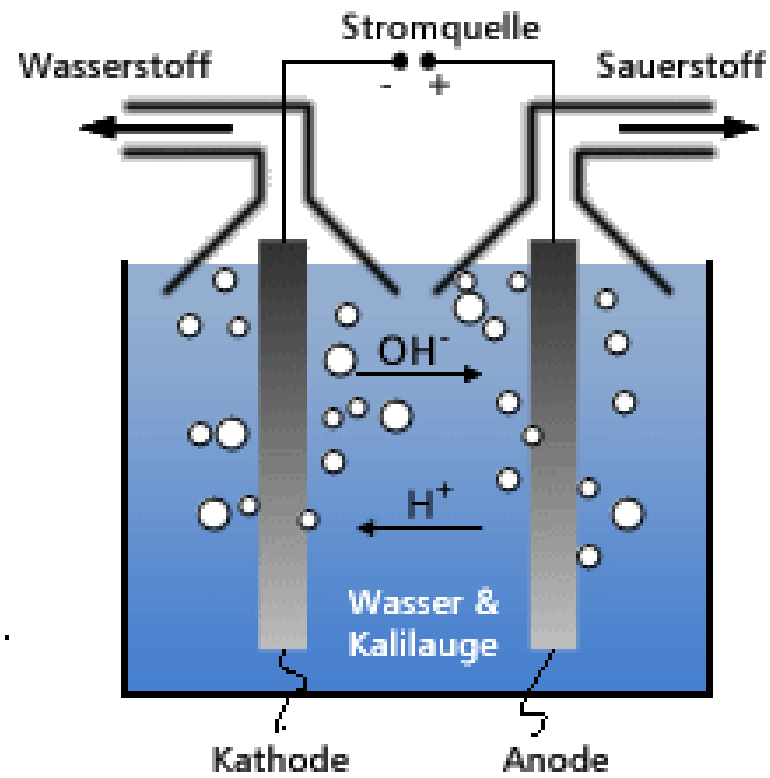
Disadvantages:

- Hydrogen requires complex storage/tanks
- Many ancillary units (air compressors, control valves, humidifiers) are necessary for operation
- So far relatively high costs, therefore only competitive in niche applications

Production of hydrogen from electrical energy

Electrolysis of water to form hydrogen and oxygen in an electrolytic cell The positive and negative poles of the electrolytic cell are reversed compared to batteries

Platinum or platinum alloy is used for the electrodes.



Quelle: Planet GBR

Positive Electrode(anode):

$4OH^- \longrightarrow O_2 + 2\ H_2O + 4\ e^-$ (+0,401V)

Negative Elekcrode (Kathode):

$4\ H_2O + 4\ e^- \longrightarrow 2\ H_2 + 4\ OH^-$ (-0,828V)

Full Reaction:

$2\ H_2O \longrightarrow 2\ H_2 + O_2$ (-1,229V)

The theoretical cell voltage $E_{kathode} - E_{anode}$= -1,229V, is negative.
Hydrogen H_2 and oxygen O_2 are produced in a ratio of 2:1
Electrolysis efficiency is 70-80%
9 kg of water must be decomposed for 1 kg of hydrogen.

Production of Hydrogen

Today, hydrogen is mainly obtained from natural gas (48%), from refinery and chemical waste gases (30%) and coal (18%). Only 4% is produced electrolytically.

Natural gas steam reforming:

Two-stage process, first catalytic steam reforming on Ni catalyst at 700-850°C, 25-30 bar and subsequent water gas shift reaction on Fe3O3/Cr2O3 catalyst at 350-550°C:

steam reforming

$CH_4 + H_2O \longrightarrow CO + 3H_2$ (endotherm: +206 kJ/mol)

$CH_4 + 2\,H_2O \longrightarrow CO_2 + 4H_2$ (endotherm: +165 kJ/mol)

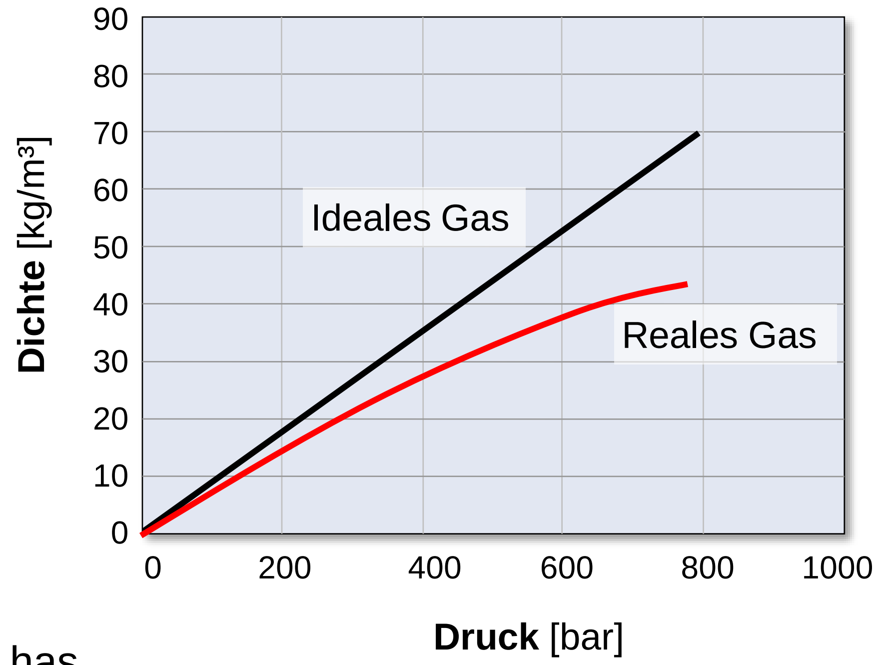
Water Gas Shift Reaction

$H_2O + CO \longrightarrow CO_2 + H_2$ (exotherm: -90 kJ/mol)

Coal Gasification:

At approx. 1000°C, pulverized coal is supplied with water vapor and small amounts of O2. The oxidation produces CO and a water-gas shift reaction takes place (see above).

Storage of Hydrogen



Pressure Storage :

At 350 bar 23kg/m³ and at 700 bar 39 kg/m³

Approx. 12% of the energy content is required to compress hydrogen to 700 bar. At 700 bar 1.3 kWh/dm³.

Liquid Storage :

By cooling and compressing, the hydrogen can be stored in liquid form at -252.8°C (20.4 K) in cryogenic storage. It has a density of 71 kg/m³

About 30-40% of the energy content is required to liquefy hydrogen.

Liquid hydrogen has an energy density of 2.36 kWh/dm³.

Storage of Hydrogen

Druckgasspeicherung in Druckbehältern:

Typ 1: Cylindrical steel cylinders up to 200 bar

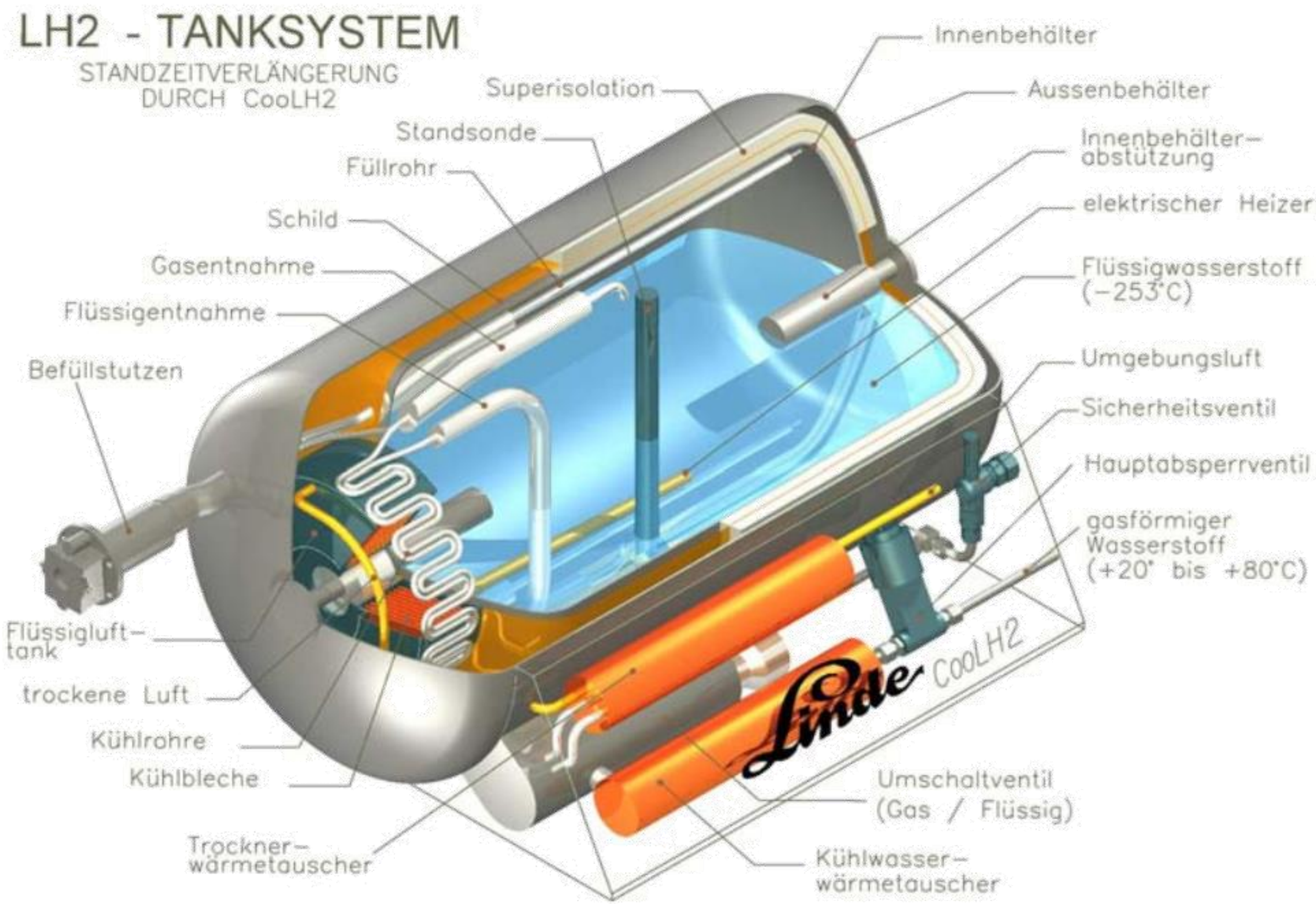
Type 2: Steel cylinders with an additional bandage, including glass or carbon fibers around the cylindrical part, up to 1000 bar, mainly for stationary applications

Type 3: Consists of a liner (aluminium) and a carbon fiber cover, pressure range 350 or 700 bar, mainly mobile applications

Type 3 pressure tank with aluminum liner (1) inside and CFRP coating (2)

Type 4: Like type 3, but with plastic liner (polyamide or polyethylene), lighter than type 3

Storage of Hydrogen



Storage of Hydrogen

Metal Hydride Storage:

Hydride storage is considered a long-term alternative to storage tanks.

For example, magnesium hydride can theoretically be reduced to 7.66% at high temperatures (experimentally up to 7%).

H2 loaded (about 800l per kg).The hydrogen is released at 280-300°C.

Loading takes place at 500° and 200 bar or catalytically at 65°C/ 80 bar (catalyst e.g. TiCl4)

Liquid Organic Hydrogen Carrier (LOHC):

Benzene-like binding systems (aromatic) can absorb hydrogen reversibly (approx. 2.9kWh/dm³).

In the research stage are:

	Melting Point	Boilling	Capacity	Hydrogenation Heat	Density
N-Ethylcarbazol	+68°C	+270°C	5,8 % H2	55 kJ/mol	1,04 g/cm³
Dibenzyltoluol	-39 °C	+ 390°C	6,2 % H2	71 kJ/mol	1,06 g/cm³

Storage of Hydrogen

In organic compounds:

Methan CH_4 can be obtained from H_2 at 300-600°C:

$$3H_2 + CO \longrightarrow CH_4 + H_2O \quad \text{(exotherm: -206 kJ/mol)}$$

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O \quad \text{(exotherm: -165 kJ/mol)}$$

Undesired side reaction

$$H_2O + CO \longrightarrow CO_2 + H_2$$

The synthesis gas obtained consists of 98,5 % CH_4, 0,5% CO_2 and 1% H_2

Synthetic Fuel can be synthetisized of H_2 by Fischer-Tropsch-procedere.

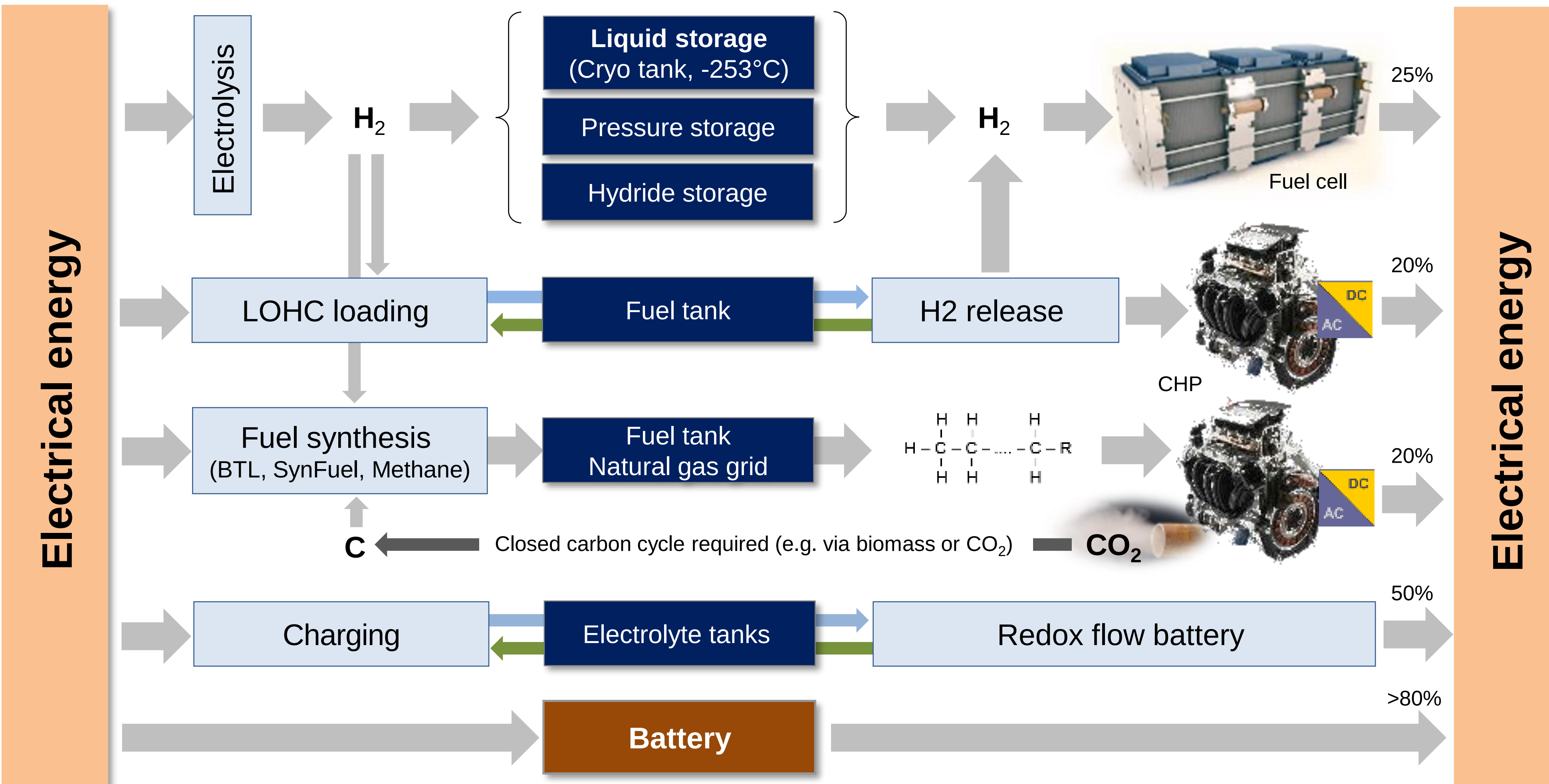
$$(2n+1)H_2 + CO \longrightarrow H[CH_2]_nH + nH_2O \quad \text{(exotherm: -165 kJ/mol)}$$

Undesired side reaction

$$H_2O + CO \longrightarrow CO_2 + H_2$$

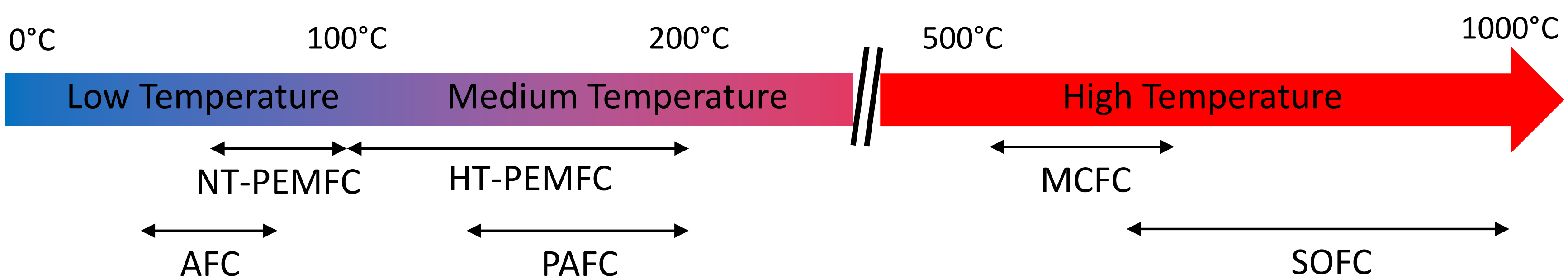
At temperatures of 300-350°C and 10-40 bar, mostly gasoline is produced (C5-C11)

Electro-chemical Energy Storage Technologies

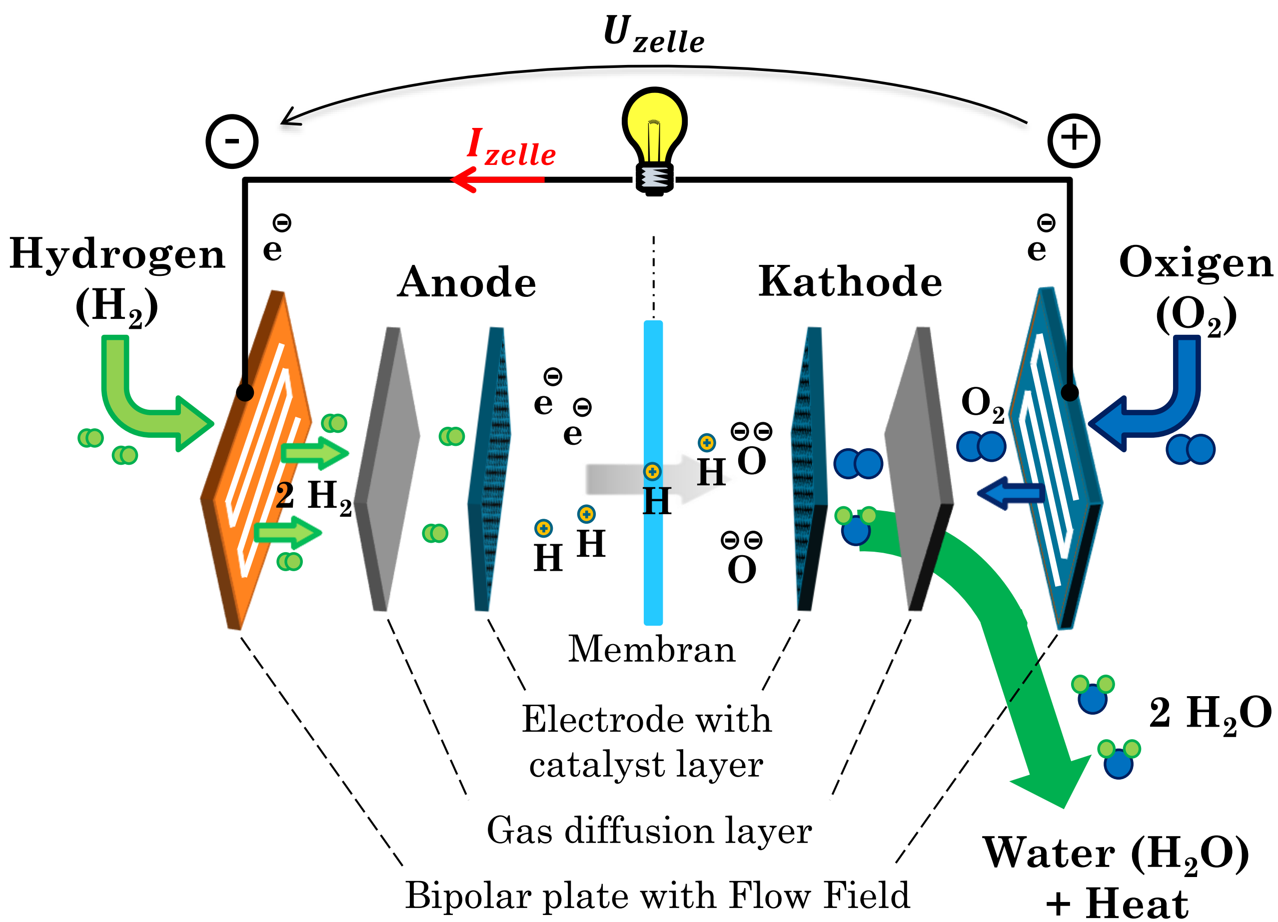


Fuel Cell TEchnologies

Fuel Cell Type	Electrolyte	Fuel	el. Efficiency
Alkaline (AFC)	KOH	H_2	45–60 %
Polymer Electrolyte (PEMFC)	Polymer-Membran	H_2	35-60 %
Direct Methanol (DMFC)	Polymer-Membran	CH_3OH	40 %
Phosphoric Acid (PAFC)	H_3PO_4	H_2	38 %
Melted Carbonat (MCFC)	Alkaline-Carbonat-Melt	H_2, CH_4	48 %
Solid Oxid (SOFC)	Oxid Ceramic Electrolyte	H_2, CH_4	47 %



Design and Function of a PEM Fuel Cell



Anode (Oxidation)

$$2\,H_2 \rightarrow 4\,H^+ + 4\,e^-$$

Kathode (Reduction)

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$$

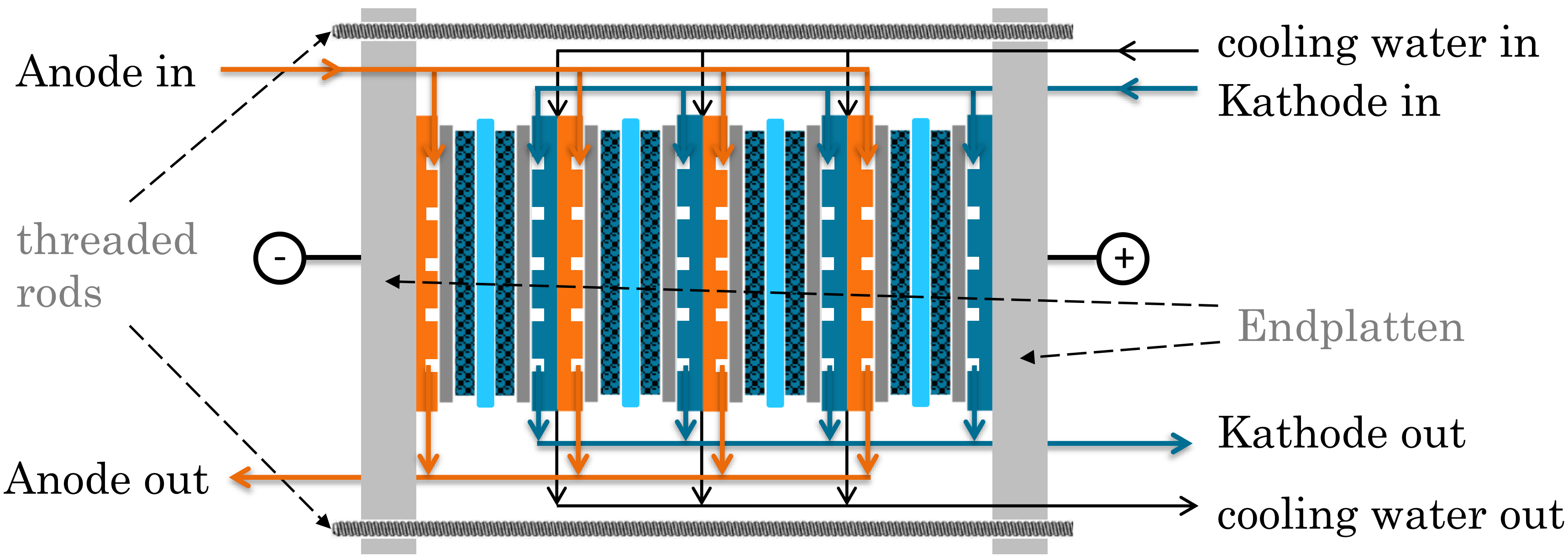
Complete Reaction

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

$$U_{ideal} = 1{,}23V$$

$$U_{real} \approx 0{,}6V$$

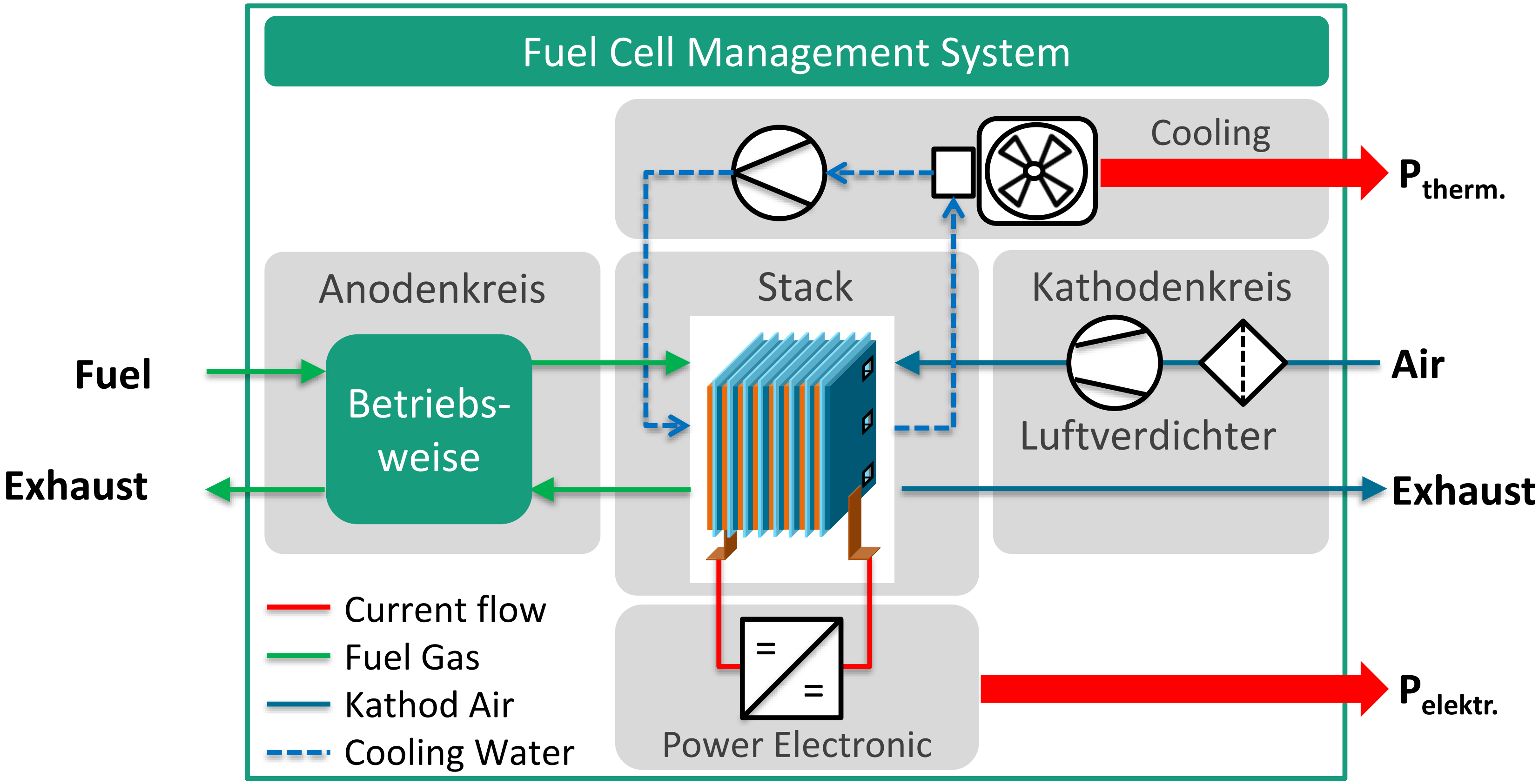
Aufbau und Funktionsweise einer PEM Brennstoffzelle



Electric → Series Connection

Media Supply (Anode, Kathode) → Parallel Connection

Design and Function of a PEM Fuel Cell System



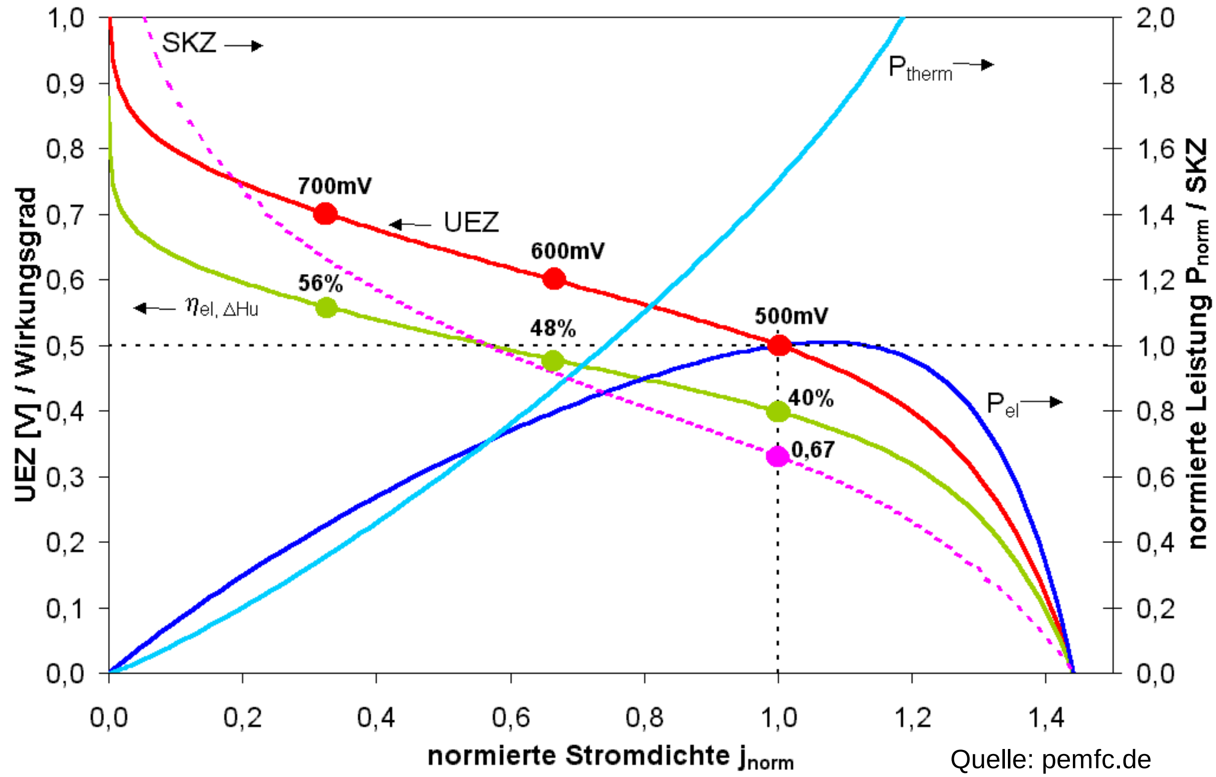
Inj

PEM-Fuel CEll - Electric Characteristic

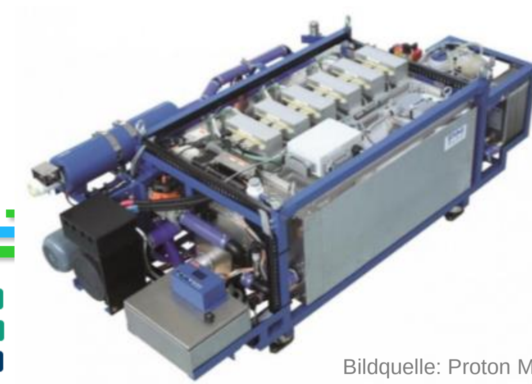
Current-Voltage-Characteristic

- Red: voltage curve
- Dark blue: electrical power
- Light blue: thermal performance
- Green: electrical efficiency
- Magenta: Power metric

- The very "soft" characteristic generally requires a DC/DC converter for coupling to DC voltage networks
- The DC/DC converter allows the operating point of the FC to be optimized between high efficiency and maximum power output (MPP) regardless of the DC mains voltage

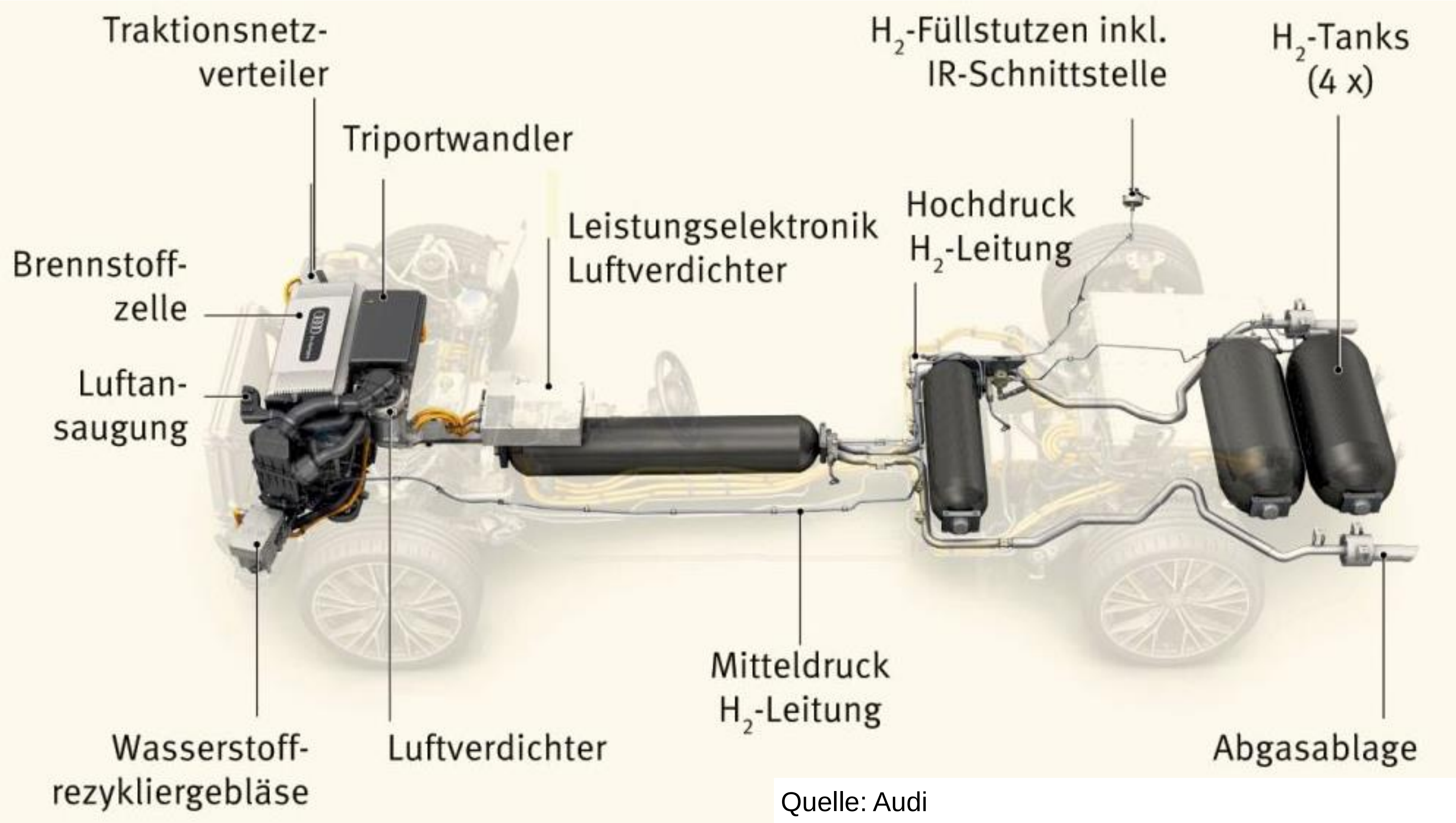


Quelle: pemfc.de



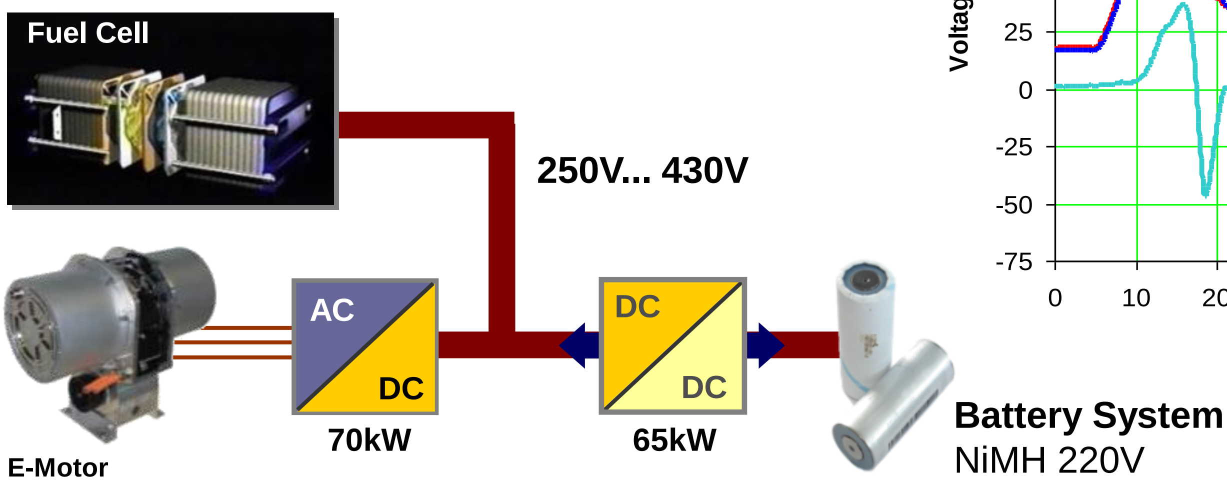
Bildquelle: Proton Motor Fuel Cell GmbH

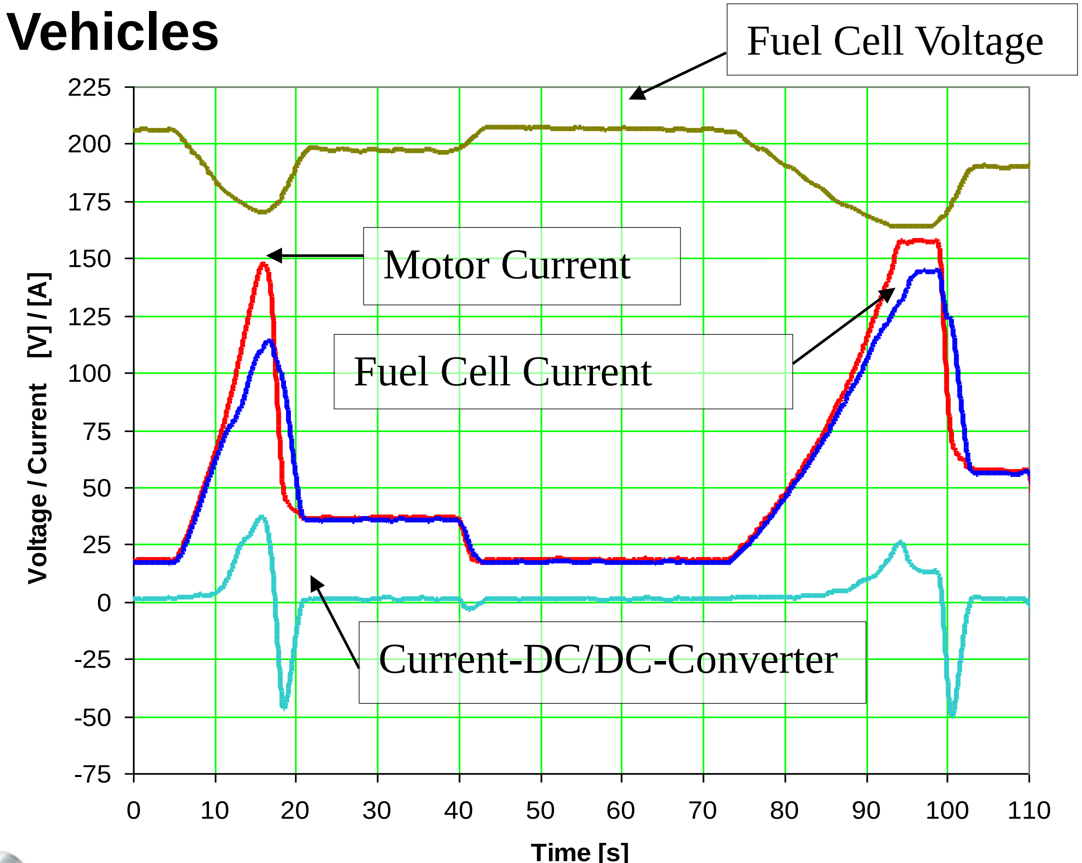
Application of Fuel Cell Systems in Vehicles



Quelle: Audi

Application of Fuel Cell Systems in Vehicles





Application of Fuel Cell Systems in Commercial Vehicles

- Fast refueling possible
- Range of up to 1000 km with pressure accumulators (700 bar)
- For the necessary power of 200-400 kW, 2 to 3 fuel cell systems are operated in parallel.
- Braking energy can be recuperated through hybridization with batteries/capacitors

Quelle: Mahle

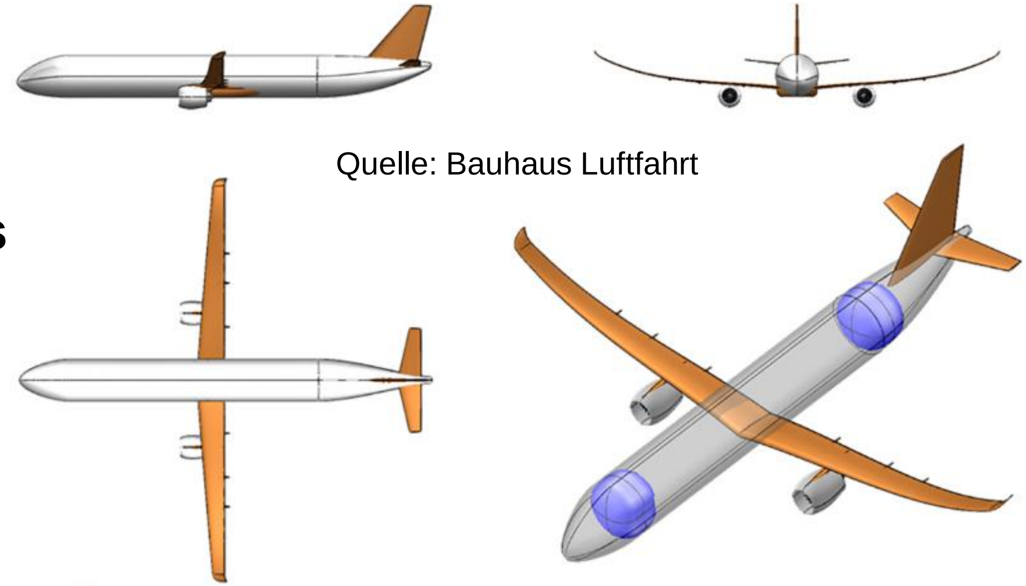
Application of Fuel Cell Systems in Trains

- Routes without overhead lines can be electrified
- Range of up to 1000 km with pressure accumulators (500 bar)

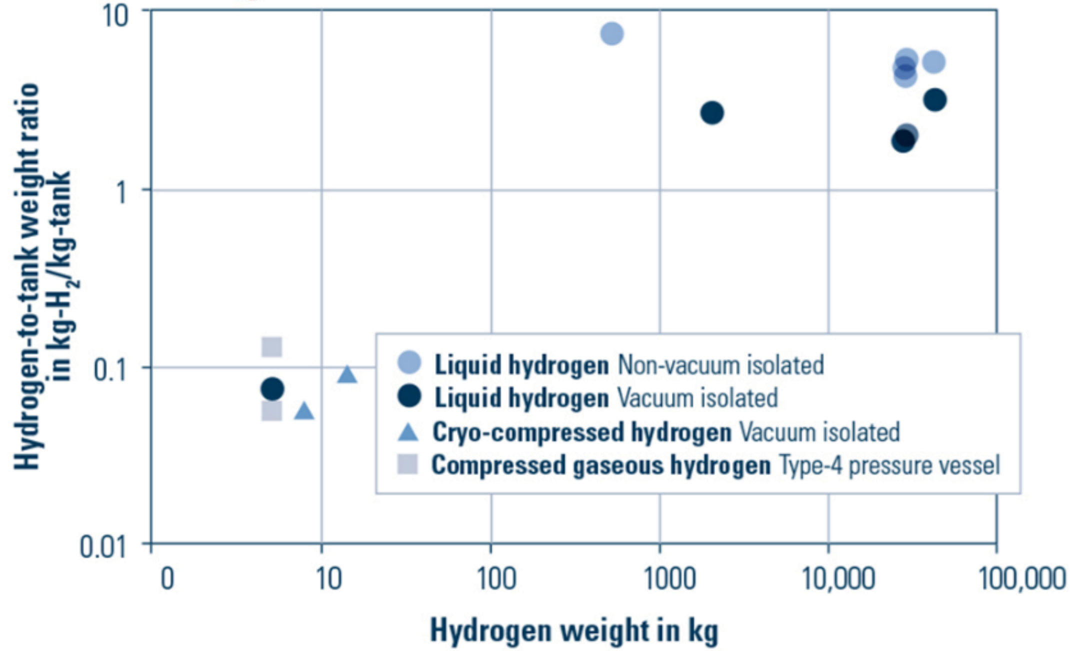
- Use of liquid hydrogen (LOHC) under development

Application of Hydrogen in Aircrafts

- Liquid storage of hydrogen is ideal for use in aircraft.
- Liquid hydrogen has a gravimetric energy density 2.3 times greater than kerosene Reduces take-off weight
- However, more volume and completely new tank concepts are required. Fuselage tank with a lot of volume and a small surface

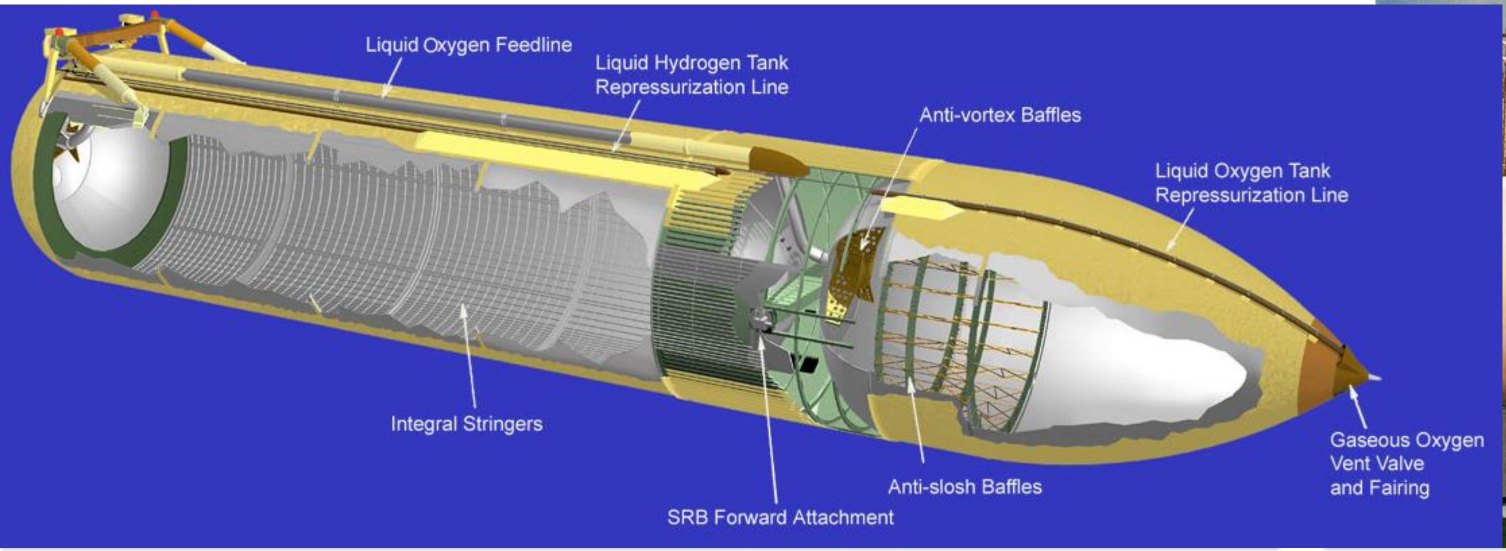


Quelle: Bauhaus Luftfahrt

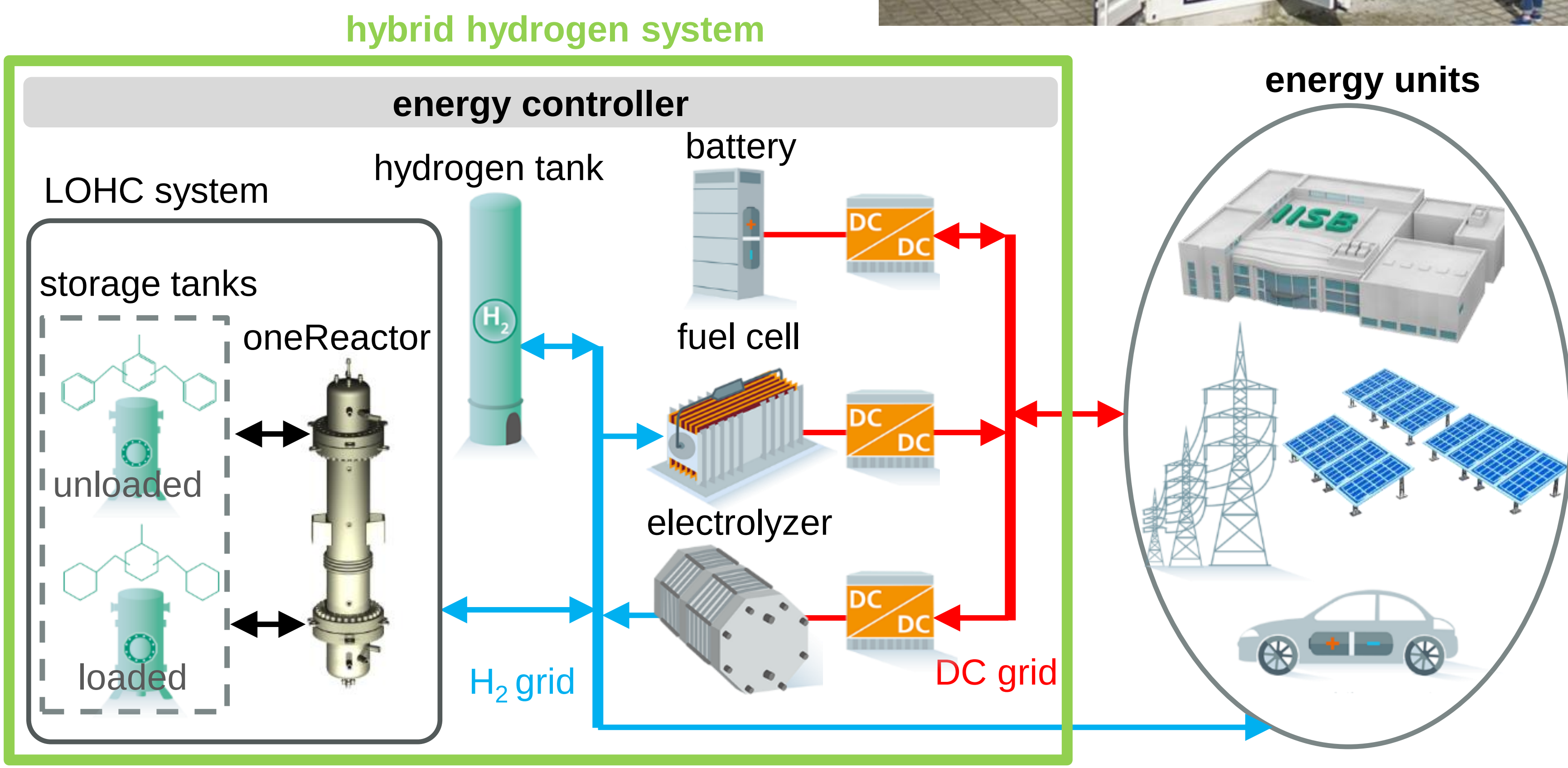


Application of Hydrogen in Space

- The Space Shuttle used liquid hydrogen and oxygen for the main engines.
- The tank contained 553358 dm³ / 629 t oxygen and 1497440 dm³ / 106 t hydrogen
- In orbit, the shuttle is powered by two 7 kW / 12 kW fuel cells

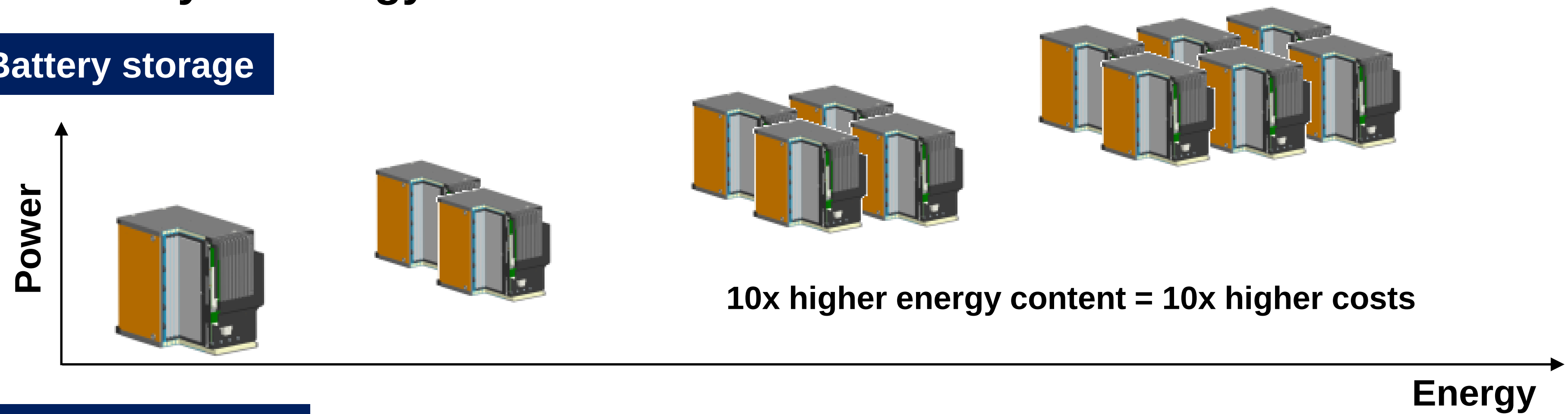


Structure and functionality of a LOHC storage system



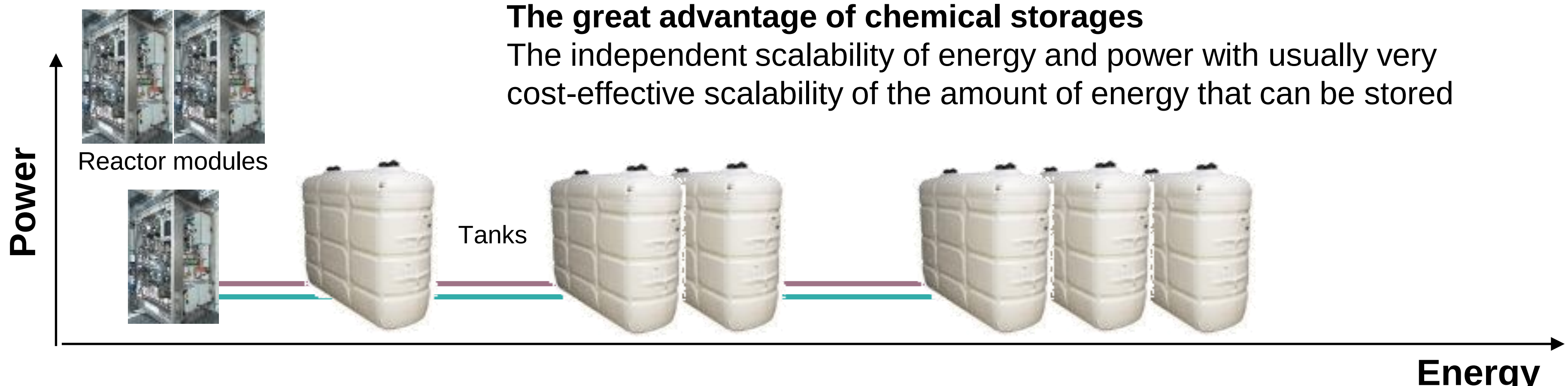
Scalability of Energy and Power

Battery storage



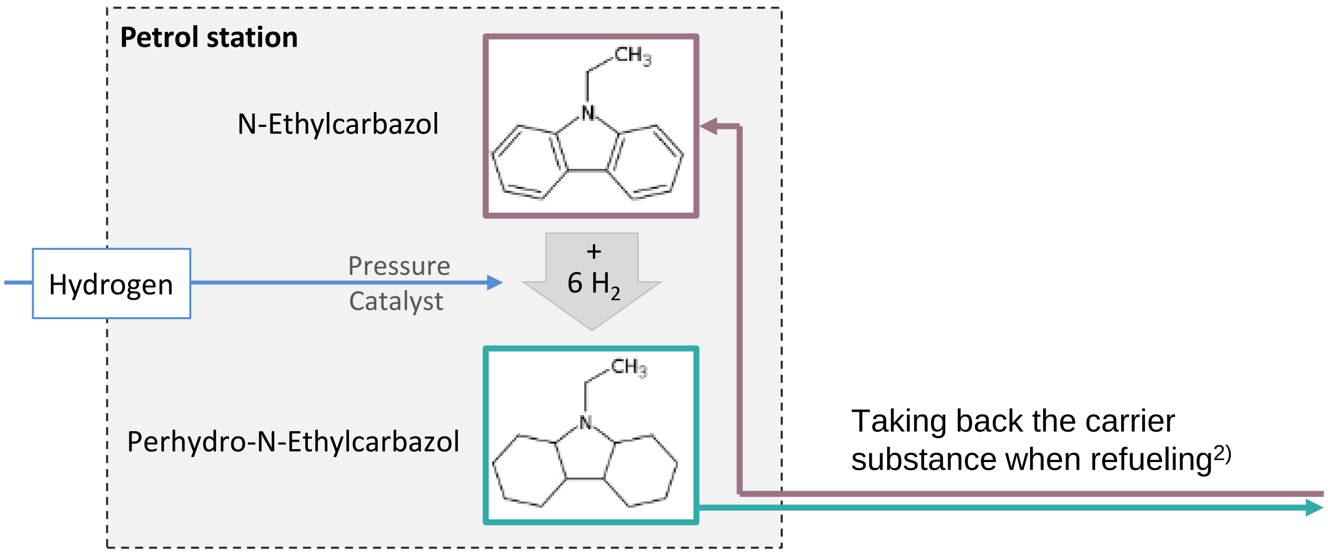
Chemical storage

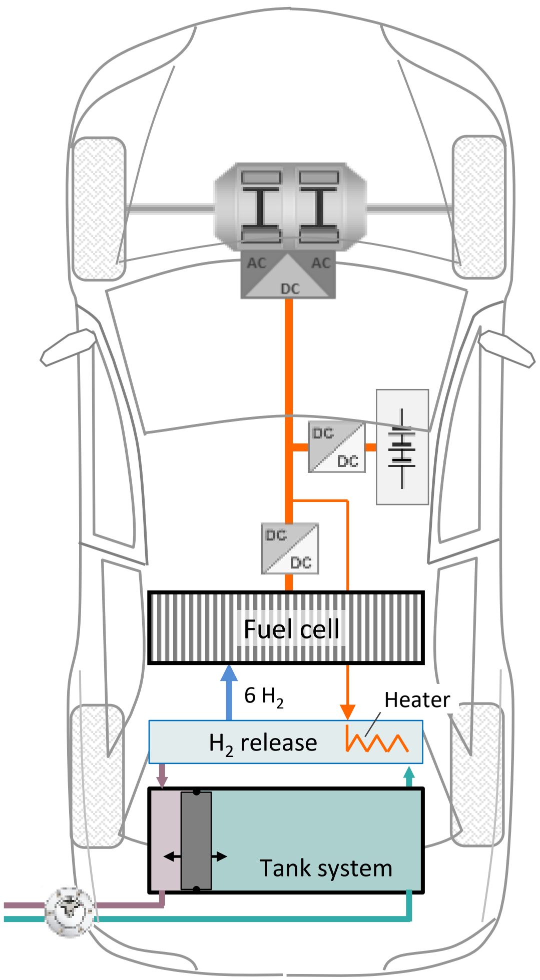
The great advantage of chemical storages
The independent scalability of energy and power with usually very cost-effective scalability of the amount of energy that can be stored



LOHC (Liquid Organic Hydrogen Carrier)

- Organic hydrocarbons that can be loaded with hydrogen relatively easily in terms of process technology and can release this H2 again by returning it to the starting carrier substance
- Typically, hydrogen with an energy content of about 2 kWh can be stored in one liter of these substances[1)]





1) corresponding to about one sixth of the energy content of diesel 2) avoids an open carbon cycle (via e.g. biomass)

Hydrogen propulsion of ships

- The use of LOHC is recommended because of the high volumetric energy density.

- Liquid can also be used to trim the ship

Quelle: dmt-plus.de

Hydrogen and Fuel Cells

- Hydrogen is an energy carrier with a very high gravimetric (33.33 kWh/kg) and a very low volumetric energy density (0.003 kWh/dm³)
- Hydrogen can be obtained from fossil fuels (natural gas, coal) but also from renewable electricity (electrolysis).
- Methane and liquid fuels can be synthesized from hydrogen
- Hydrogen can be converted into electricity in a fuel cell without emissions, the electricity-electricity efficiency is 25-30%
- Fuel cells with hydrogen enable emission-free mobility, especially for commercial vehicles, ships and airplanes

Electric Energy Storage Systems

Chapter 6:
Exercise

Summer 2024

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1. Hydrogen and Fuel Cells

A. How can hydrogen be produced?
Name three possibilities.

B. Sketch the schematic structure of a fuel cell and name the ancillary units required for operation.

C. Sketch the performance characteristics of a fuel cell. Output voltage and efficiency over normalized current.

D. A fuel cell is to be set up for a train drive, which supplies approx. 400V under full load.
How many cells need to be connected in series? What is the open circuit voltage?
What is the performance of the fuel cell if it can supply 500A as the maximum rated current?

Electric Energy Storage Systems

Chapter 7: Redox-Flow Storage Systems und Fly Wheels

Summer 2024

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Redox-Flow bzw. Flow Battery Storage Systems

History:
1884 Charles Renard invented the first zinc-chlorine flow battery
1949 Patent for storing energy in redox pairs by W. Kangro (TU Braunschweig) and
1954 Vanadium flow battery patented for the first time, flow battery type most commonly used today
2014 Presentation of the first flow battery with organic solutions (Havard University)

Advantages:
- Energy converter (flow cell) and storage (tank) can be designed separately
- Good safety (non-flammable)
- Good recyclability, easy recovery of the active ingredients

Disadvantages:
- Energy density is low (lower than that of a lead-acid battery), so it only makes sense in stationary use
- Vanadium is mostly used - the heavy metal with high price fluctuations, it is also considered a critical raw material and toxic.

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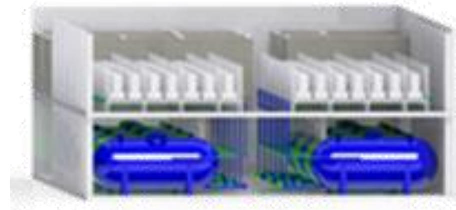
Redox-Flow bzw. Flow Battery Storage Systems

Applications:

- Stationary grid-connected storage
  - Grid stabilization
  - Peak load reduction
- Island grids
  - E.g. mobile phone systems
- Emergency power supply
- Storage of renewable energy to increase self-consumption
  - Quarter storage
  - Home storage
  - Industrial plants

Quelle: Fraunhofer ICT



Quelle: Sumitomo

Quelle: bahnbilder.de

Imp

Redox-Flow bzw. Flow Battery Storage Systems

Various redox couples can be used for flow batteries:
Electrode potential of redox couples versus normal hydrogen electrode

Zn/Zn^{2+}	Cr^{2+}/Cr^{3+}	V^{2+}/V^{3+}	H_2/H^+	Fe^{2+}/Fe^{3+}	V^{5+}/V^{4+}	Br^-/Br^{3-}	H_2O/O_2	Ce^{3+}/Ce^{4+}
- 0,76 V	- 0,42 V	- 0,26 V	0 V	+ 0,77 V	+ 1,00 V	+ 1,09 V	+ 1,23 V	+ 1,44 V

Iron-Chromium: $Fe^{3+} + Cr^{2+} \longrightarrow Fe^{2+} + Cr^{3+}$ (1,18V)

Was researched by NASA in 1970/80, but has a very low energy and power density

Zinc-Cerium: $Zn + 2Ce^{4+} \longrightarrow Zn^{2+} + 2Ce^{3+}$ (2,20V)

Characterized by high voltage and cycle stability, separator and electrolyte are very expensive

Zinc-Chlorine: $Zn + Cl_2 \longrightarrow ZnCl_2$ (2,12V)

Complex system with toxic and corrosive chlorine, zinc dentrides are formed

Vanadium-Vanadium: Currently the most used system

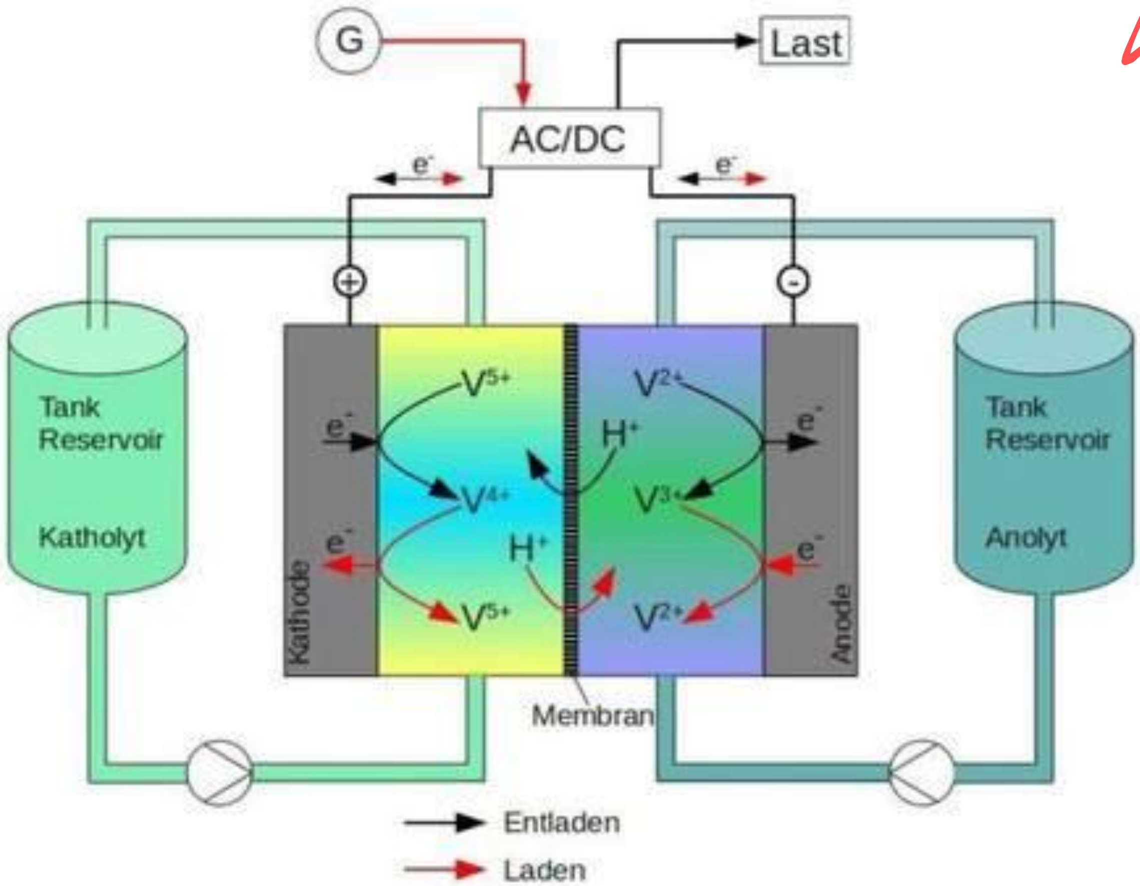
Vanadium Flow Battery

The vanadium flow battery consists of an anode compartment (anolyte) and a cathode compartment (catholyte), which are separated by an ion exchange membrane. The 2 molar solution of vanadium salts in sulfuric acid is pumped into separate circuits. The discharging processes:

Negative Electrode: (Anodic Oxidation)	$V^{2+} \longrightarrow V^{3+} + e^-$	(-0,26 V)
Positive Electrode: (Kathodic Reduction)	$VO_2^+ + 2H^+ + e^- \longrightarrow VO^{2+} + H_2O$	(+1,00 V)
Full Reaction:	$V^{2+} + VO_2^+ + 2H^+ \longrightarrow V^{3+} + VO^{2+} + H_2O$	(+1,26 V)

Energy density: appr. 25-30 Wh/kg, Operating temperature 10-40°C

Vanadium Flow Battery



Quelle:TU Clausthal

Quelle:Wikipedia.org

Aqueous solutions of vanadium salts in different oxidation states:

$[V(H_2O)_6]^{2+}$ (violett)
$[V(H_2O)_6]^{3+}$ (green)
$[VO(H_2O)_5]^{2+}$ (blue)
$[VO_2(H_2O)_4]^{+}$ (yellow)

Vanadium Flow Battery – Performance

Efficiency:

- At current densities of 100mA/cm², 80-90% charge-discharge efficiency is achieved.
- Additional losses of approx. 5% are caused by the pumps.

Life time:

- Very high (over 200,000) charge/discharge cycles are achieved.
- The calendar lifespan is also in the range of 15 to 20 years

Challenges:

- Uneven flow rate of the electrolyte at the electrodes leads to unequal current densities and a voltage drop.
- tightness of the system
- Series connection of many cells difficult / not possible due to leakage currents

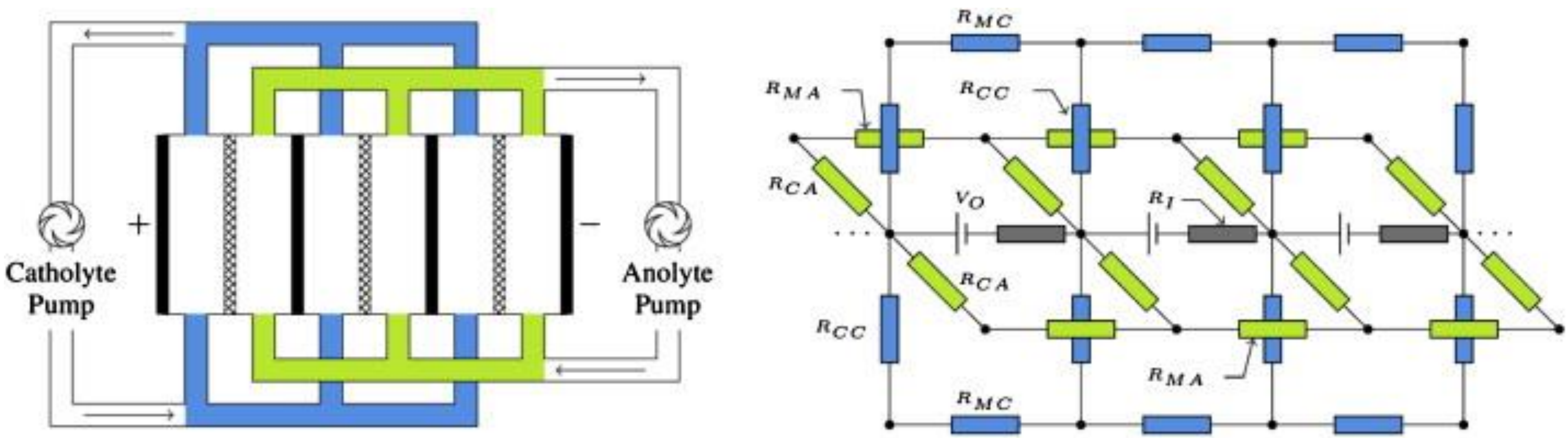
Vanadium Flow Battery – Performance

Challenges: Leakage Currents

Leakage currents through the electrolyte with several flow batteries connected in series

Longer electrolytic tubes with a smaller cross-section,

connect only a small number of cells in series



Quelle: Kim S., E.C. Thomsen, G. Xia, Z. Nie, J. Bao, K.P. Recknagle, and W. Wang, et al. 2013. "1 kW / 1kWh Advanced Vanadium Redox Flow Battery Utilizing Mixed Acid Electrolytes." Journal of Power Sources 237.

Vanadium Flow Battery – Design

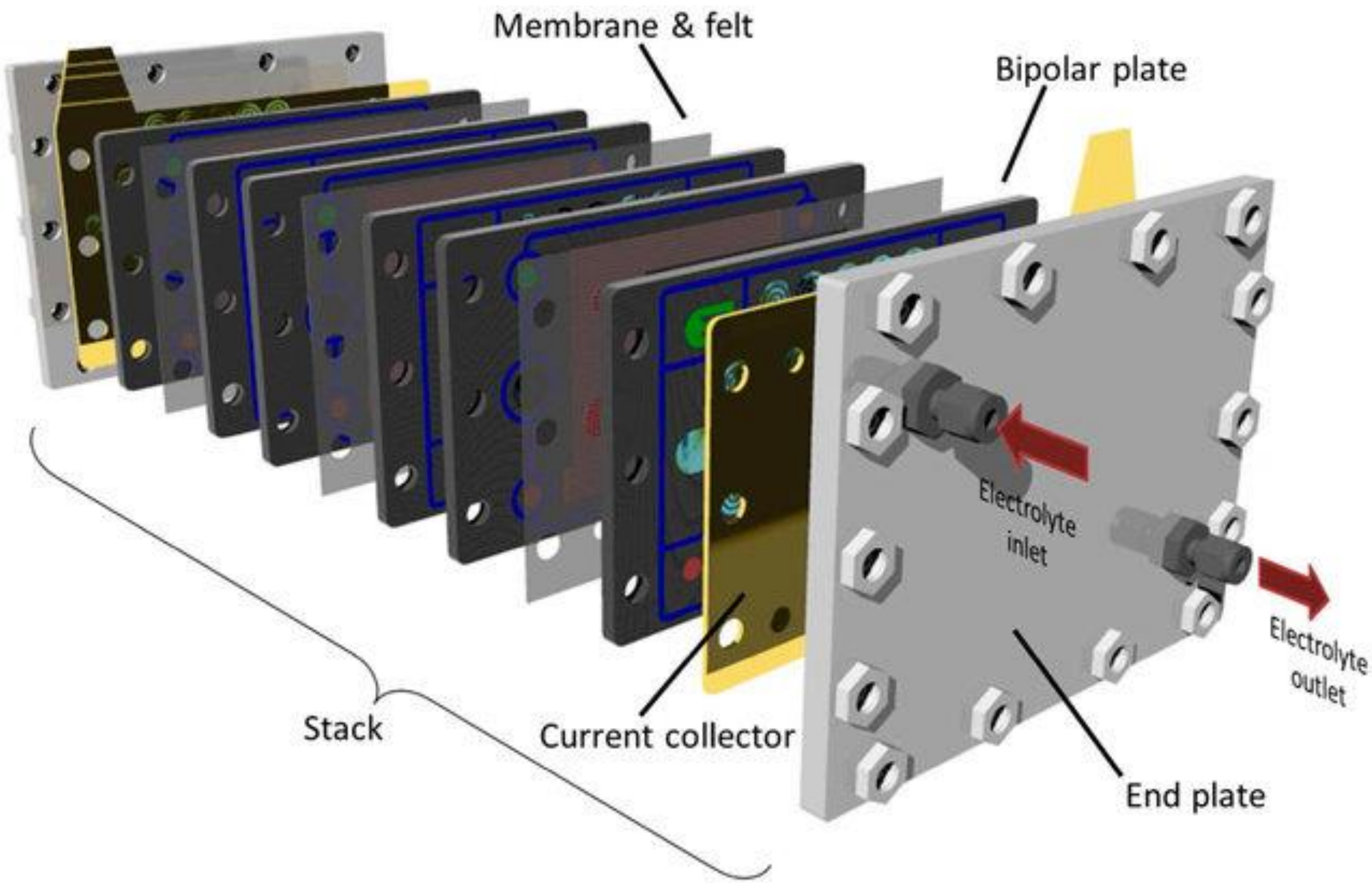
Imp

Electrode materials:
Graphite and carbon felt are used as electrode material, since pentavalent vanadium has a corrosive effect on metals.

Electrolyte:
2.5 molar sulfuric acid with 2 mol/L vanadium sulfate is used as the electrolyte.
The solubility of vanadium V(II), V(III) and V(IV) increases with increasing temperature and in dilute sulfuric acid. At V(V) the solubility decreases. V(II) and V(III) fail at temperatures below 10°C, V(V) fails at temperatures above 40°C.
Therefore only a dilute solution is possible, which reduces the energy content.

Separator:
Uneven flow rate of the electrolyte at the electrodes leads to unequal current densities and a voltage drop

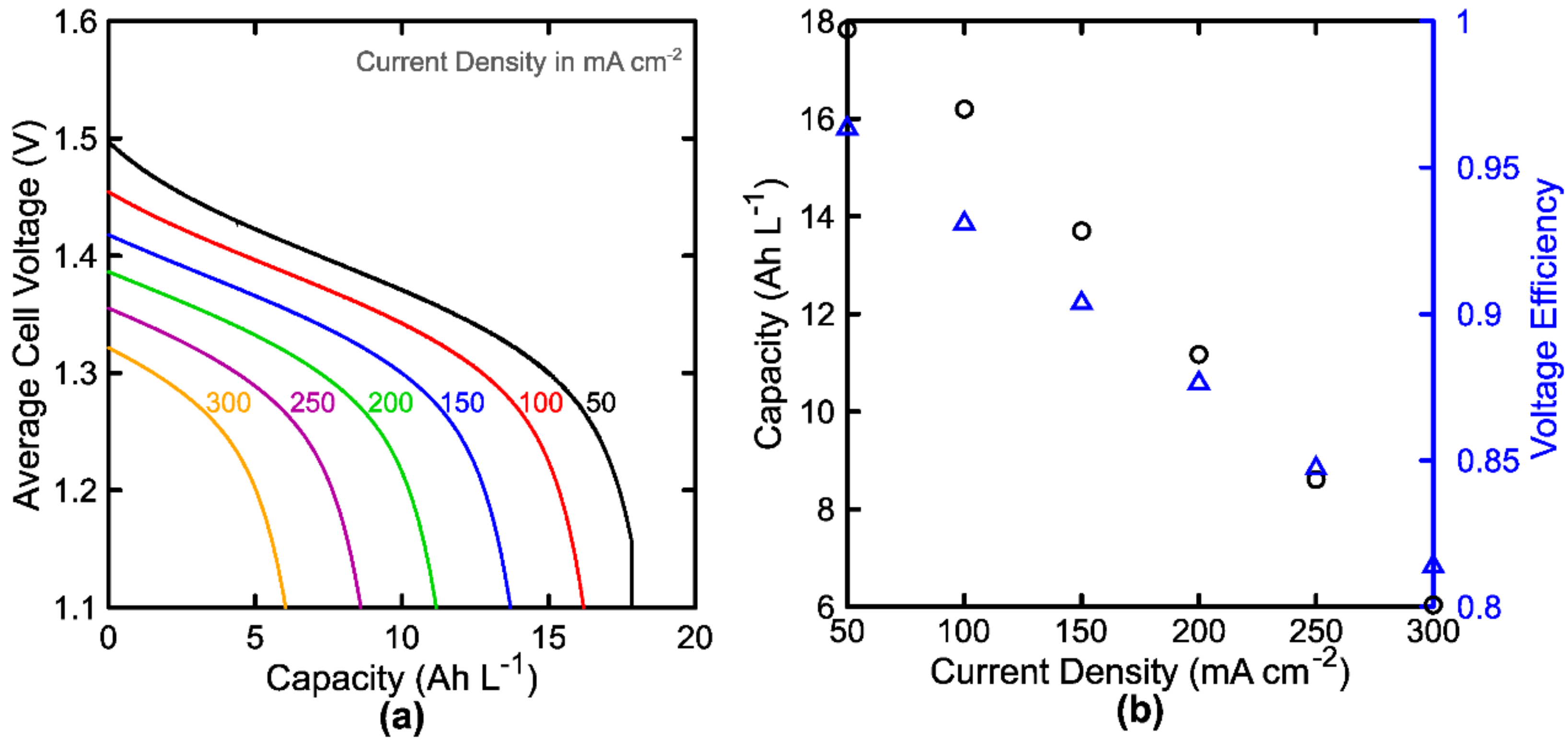
Vanadium Flow Battery – Design



Quelle: Rhodri Jervis, et al., Design of a miniature flow cell for in situ x-ray imaging of redox flow batteries, October 2016, Journal of Physics D Applied Physics 49

Vanadium Flow Battery – Performance

Battery stack with 35 cells connected in series

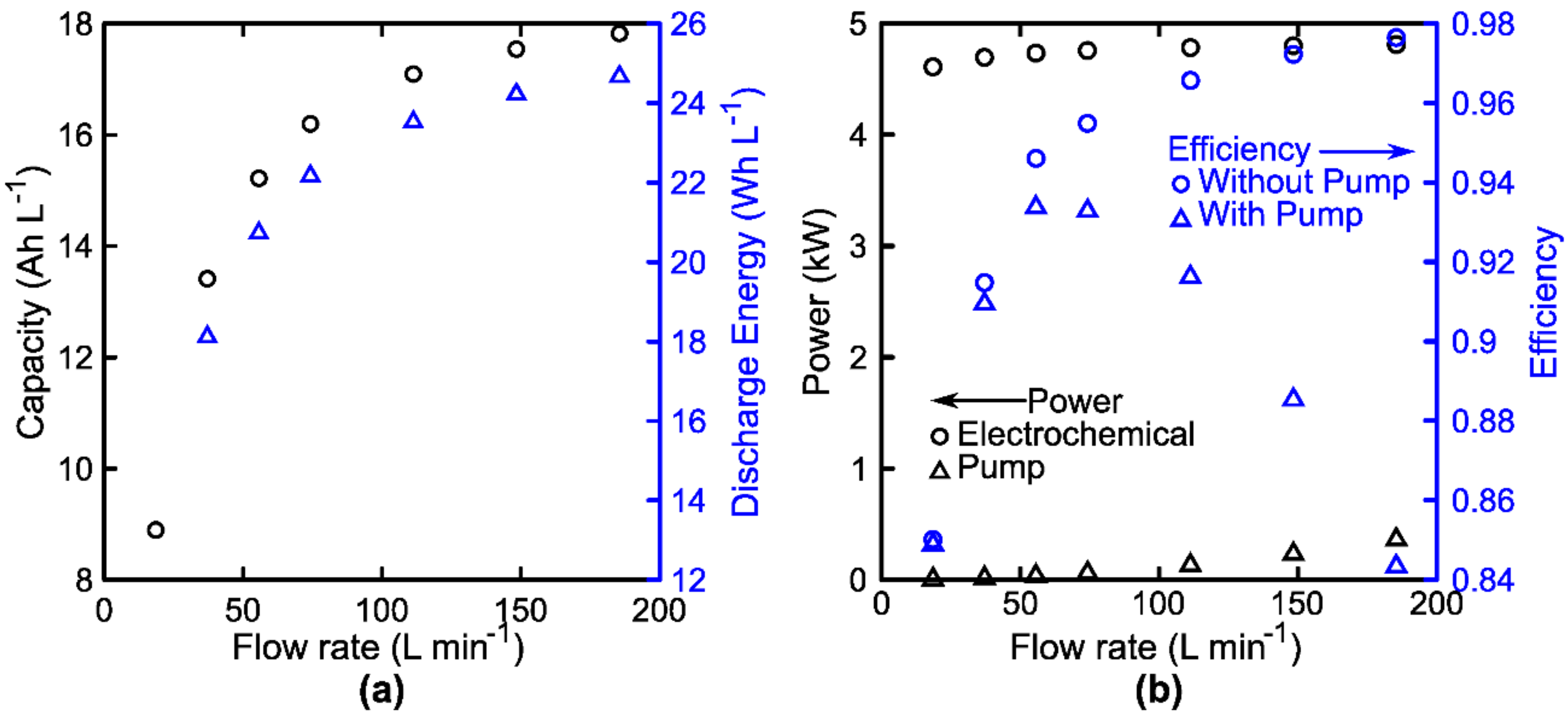


Messurement at 74.2 L min^{-1}. (**a**) Discharge Curve (**b**) Useable Capacity(○, black, left) and Voltage Efficienzy (△, blue, right)

Quelle: J. L. Barton, F. R. Brushett, A One-Dimensional Stack Model for Redox Flow Battery Analysis and Operation, 2019

Vanadium Flussbatterie – Betriebsverhalten

Batteriestack mit 35 in Serie verschalteten Zellen



Messung des Einflusses des Elektrolytdurchsatzes (**a**) auf die entnehmbare Kapazität bzw. Energie (**b**) auf die Leistung und den Wirkungsgrad

Quelle: J. L. Barton, F. R. Brushett, A One-Dimensional Stack Model for Redox Flow Battery Analysis and Operation, 2019

Vanadium Flussbatterie – Application

- **2 MW / 20 MWh Storage at the Fraunhofer ICT**
- **600,000 liters of storage installed**
- **2 MW wind turbine (82 m rotor, 100 m mast)**
- **Solar system with 500 kW**

Quelle: Fraunhofer ICT

Vanadium Flussbatterie – Application

- **Power: 1 MW AC**
- **Capacity: 5 MWh**
- **AC-AC Efficiency: >70%**
- **Cycle Lifetime: >300.000**
- **Calendary Lifetime: 20 Jahre**

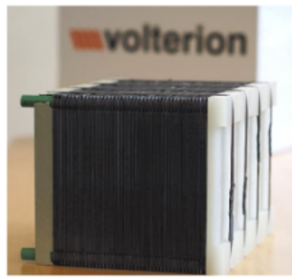
Electric Energy Storage Systems

Vanadium Flussbatterie – Application Example Home Storage

volterion

Product sheet

Flow-Battery Stack VFBS 40



		VFBS 40
Electrical data		
Power	[kW]	2.5
Nominal current	[A]	50
Voltage	[V]	(0) 40 - 62
Number of cells		40
Electric connection		2 x M6 pinhole, 35 mm²
Hydraulic data		
Flow rate	[l/min]	3 - 15
Max pressure	[bar]	1
Nominal pressure	[bar]	0.5
Pipe connection	[mm]	4 x 16
General		
Weight	[kg]	9.9
Size	[mm]	310 x 225 x 280
Chemical		
Membrane		Anion exchange
Electrolyte		All vanadium

volterion powerRFB

TECHNICAL SPECIFICATIONS

ELECTRICAL	
VOLTAGE (nominal)	48 V_{DC} (40–64V)
POWER (constant)	2.5 | 5 | 10 kW
POWER (peak)	3.75 | 7.5 | 15 kW
CAPACITY	13 kWh_{nom}
CYCLES (typical)	20 000+
DISCHARGE DEPTH	100%
SELF DISCHARGE RATE (electrolyte)	1 % per year
ELECTROLYTE	all-vanadium (1.6 mol/l)
HOUSING	
DIMENSIONS	L 120 cm x W 80 cm x H 195 cm
TOTAL WEIGHT (incl. electrolyte)	1500 kg
TANK VOLUME (electrolyte)	660 l
MATERIAL	stainless steel
IP-CLASS	IP56
GENERAL	
STACK TECHNOLOGY	volterion compact sealless stack
BATTERY MANAGEMENT	volterion battery control
ACCESS & MONITORING	ethernet-IP based cloud services modbus TCP | webserver
CONNECTIONS (DC)	3 x 350 A
AUXILIARY SUPPLY	110–230 V_{AC} | 50 / 60 Hz
CERTIFICATION	CE-certified
ENVIRONMENTAL	
AMBIENT TEMPERATURE	0–40 °C
HUMIDITY (non condensing)	max. 95 %
SAFETY	non-flammable | non-explosive
RECYCLABILITY	100% recyclable (active materials)
OPTIONAL	
BALANCING UNIT (integrated)	automated electrolyte reconditioning
BALANCING UNIT (external)	reconditioning of several powerRFBs
VISUALIZATION	display 7 "
COOLING	external water/glycol cooling (high-cycle / high ambient temperatures)

Redox-Flow bzw. Flow Battery Storage Systems

- Very large storage capacities can be realized
- Very long service life of 15-20 years and 200,000 to 300,000 cycles
- Safe operation as there is no risk of fire or explosion
- But use of heavy metal (mostly vanadium)
- Low volumetric and gravimetric storage capacity (approx. 25-30 Wh/kg)
- Relatively complex system, maintenance necessary

Flywheel Storage

History:

The principle was already used 6000 BC. in China for spindles for the production of threads and since approx. 4000 BC. on potter's wheels.
1687 Newton's first law: "A body remains in its state of rest or uniform motion in a straight line as long as the sum of all forces acting on it is zero"
Since 1800, during the first industrial revolution, steam engines have been used.
1946 first applications for electrical energy storage

Advantages:
- Very simple construction
- Easy to scale
- High peak performance possible

Disadvantages:
- Energy density is low
- Storage loses energy due to friction losses
- Danger of bursting flywheels

Flywheel Storage

Applications:

- Stationary application to compensate for fluctuations in load or power generation
- Storage of braking energy in vehicles

Quelle: bahnbilder.de

Flywheel Storage

A mass m rotating at speed n has stored the following energy:

Angular Velocity: $\omega = 2\pi \cdot n$ (n Rotations per s)

Moment of Inertia: $J_m = \int_m r^2 \, dm$ (r Radius in m)

For a cylinder/disk applies: $J_{Zylinder} = \frac{1}{2} \cdot m \cdot r^2$

Stored kinetic energy: $E_{kin} = \frac{1}{2} \cdot Jm \cdot \omega^2$

Advantages :

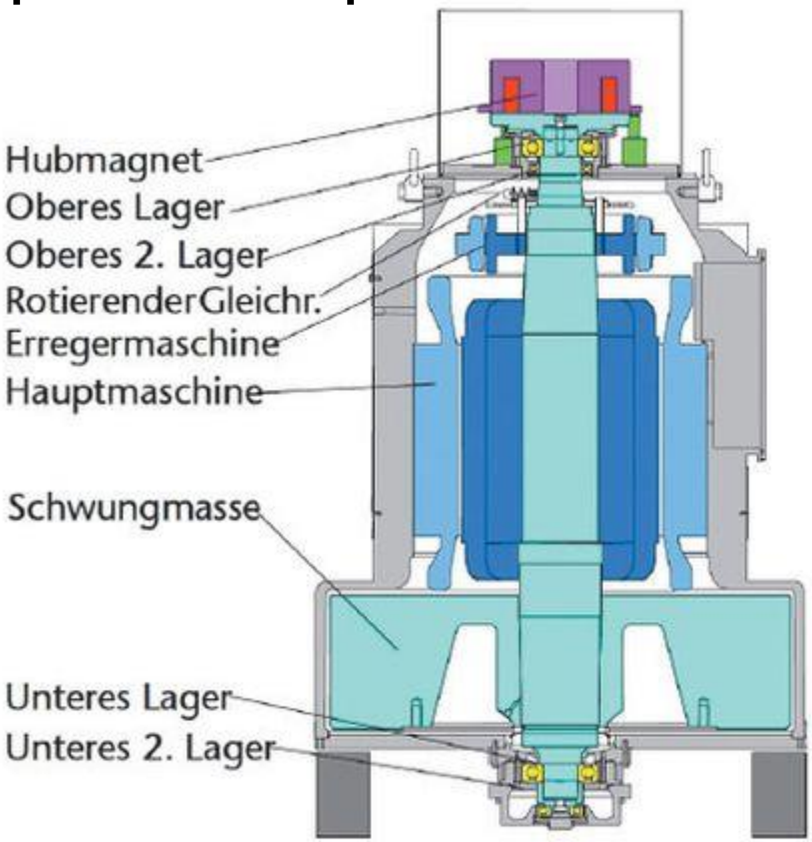
- Number of cycles: >1,000,000
- Efficiency: 80-90% (depending on storage time)
- Losses/self-discharge: 1-10%/h

Disadvantages :

- Risk of the flywheel bursting
- Gyro effect in mobile applications

Flywheel Storage

Application example:



Technische Daten:

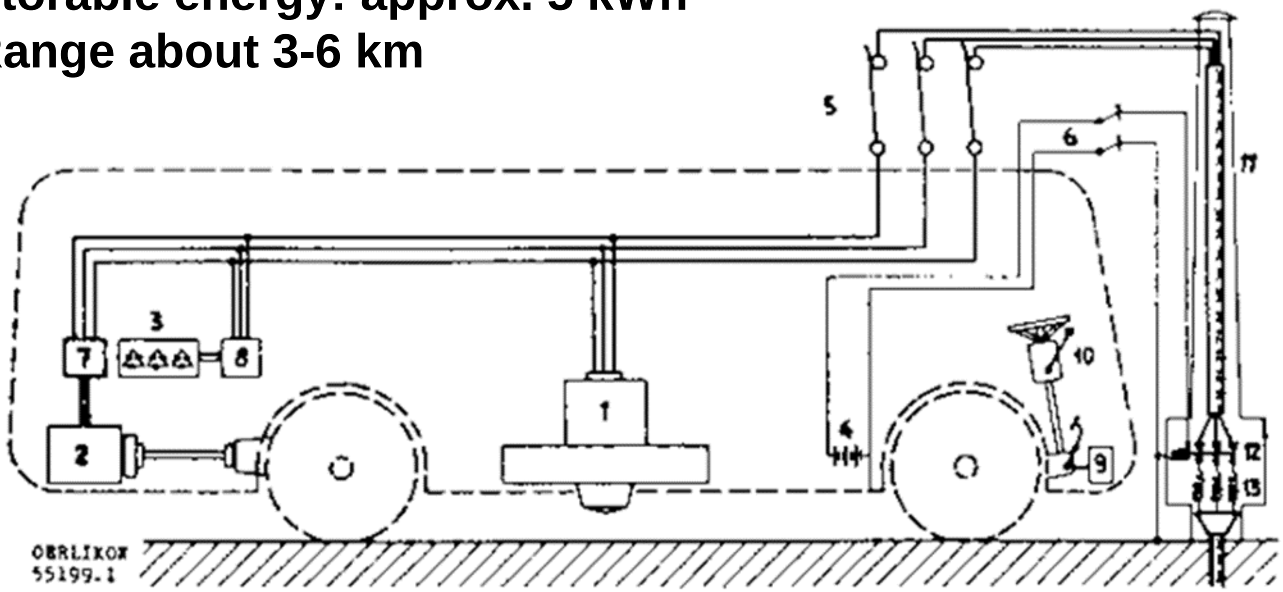
Energieinhalt	16,5 MWs
Leistung	1.650 kW
Drehzahl	1.800 Upm bis 3.300 Upm
Gesamtgewicht	6.000 kg
Rotorgewicht	2.900 kg
Leerlaufverluste	10 kW

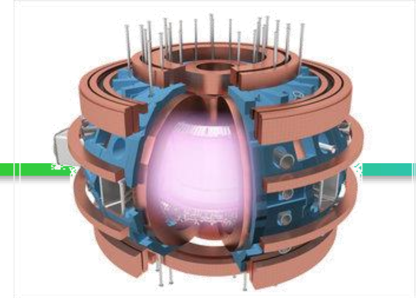
Besonderheiten:
- Heliumfüllung
- Magnetische Entlastung
- Redundante Lager

Quelle: Piller Germany GmbH & Co. KG/ Verlag Bau + Technik

Flywheel Storage

Application example: Gyrobus
Introduced by Oerlikon in 1946
Data:
Flywheel with 1.5t mass
Speed: 3000 rpm
Storable energy: approx. 5 kWh
Range about 3-6 km

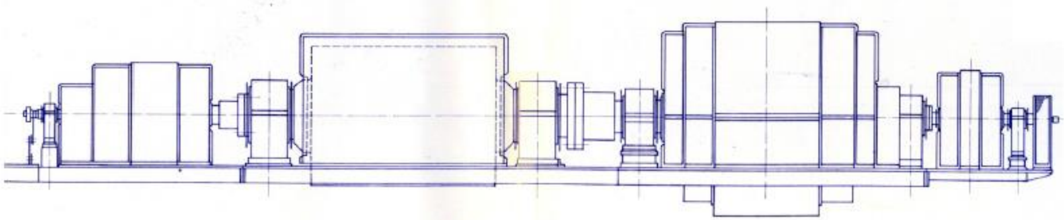




Flywheel Storage

Application example: Energy storage for Asdex Upgrade fusion reactor test facility in Garching of the Max-Plank Institute

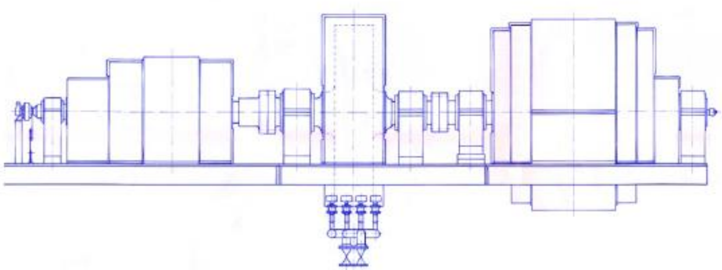
EZ 2



EZ 2:
1514 MJ 1,59 kV
167 MVA 60,6 kA
cos φ 0,93

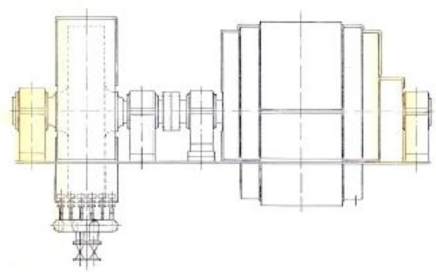
EZ 2

EZ 3



EZ 3: 540 MJ 144 MVA 10,5 kV
cos φ 0,93 7,92 kA

EZ 4



EZ 4: 726 MJ 260 MVA 10,5 kV
cos φ 0,49 14,3 kA

EZ 3

EZ 4

M. Rott, F. Stobbe, IPP

Flywheel Storage

- Very high peak performance can be achieved
- Extremely long service life and number of cycles (>1,000,000) possible
- Due to losses, only short-term energy storage possible (minutes to hours)
- There is a critical risk of the flywheel bursting or bearing damage
- Mostly used stationary

Electric Energy Storage Systems

Chapter 7:
Exercise

Summer 2024

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Redox Flow Battery and Fly Wheel

Redox flow battery

A.1. Write down the reaction equations for discharging a vanadium flow battery.

A.2. How many liters of electrolyte do you need to store 63kWh of energy?

A.3. Calculate the gravimetric energy density related only to the electrolyte, assuming that 1 liter of electrolyte weighs 1 kg.

Fly Wheel storage

B.1 In which applications are flywheel mass storage systems used and what risk do these storage systems entail?

B.2 A flywheel accumulator with a diameter of 1m and a maximum speed of 10000 rpm and a mass of 1000kg is to be used. How much energy can be stored?

Electric Energy Storage Systems

Chapter 8: Super- / Double Layer Capacitors, Supra Conducting Inductors

Summer 2024

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Double Layer Capacitors

History:
1775 Alessandro Volta built a plate capacitor using rubber containing sulfur as the dielectric
1957 H. I. Becker patents the first double-layer capacitor made from black tar in sulfuric acid
1972 B. E. Hart and R. M: Peekema applied for a patent at IBM for a double-layer capacitor made from activated carbon and a spacer filled with caustic potash or sulfuric acid
1999 Maxwell patented a 2300F/2.3V capacitor

Advantages:
- Can be charged and discharged very quickly with very high performance; high power density
- Moderate self-discharge of around 15% per month
- Very high number of cycles

Disadvantages:
- Only low voltages can be realized (2.5 V to 3 V)
- Low energy content compared to batteries

Double Layer Capacitors

Applications:

- Stationary grid-connected storage
  - Grid stabilization
  - Peak load reduction

- Energy storage in electronic devices
  - Memory / Real Time Clock

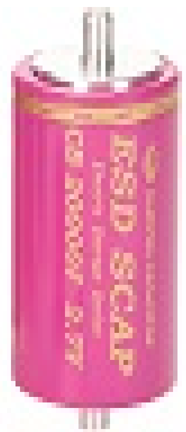
- Recovery of braking energy
  - buses / trains
  - elevators
  - industrial plants

Quelle: Freqcon

Quelle: Skeleton Technologies GmbH

Quelle: bahnbilder.de

Double Layer Capacitors – Designs



PCB mounting
SMD and THD double layer capacitors for mounting on printed circuit boards
e.g. as a memory backup in electronic devices

Screw terminals
Double-layer capacitors with screw terminals for high currents for constructing modules

Module
Modules for energy storage and high charge/discharge currents

Quelle:PK-komponents.de

Ideal Capacitor

Capacitors store energy in the electric field between two electrodes that are insulated from each other by a dielectric.

The capacity is calculated to: $C = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{A}{d}$

With: A area of the electrode, d spacing of the electrodes, ε_0 electric field constant ($8{,}8542.10^{-12}$F/m), ε_r dielectric constant

The energy stored is: $E = \frac{1}{2} \cdot C \cdot U^2$

With: C capacity, U voltage

The performance: $P(t) = (U(t) - I \cdot R_i) \cdot I$

With: I Discharge current, R_i Internal resistance of capacitor

Die Maximale Leistung: $P_{max}(t) = \frac{U(t)^2}{4Ri}$

Dimensioning of the capacitor to absorb/deliver E_{dim}:

$$E_{dim} \geq \frac{1}{2} C \cdot (U_{voll}^2 - U_{leer}^2)$$

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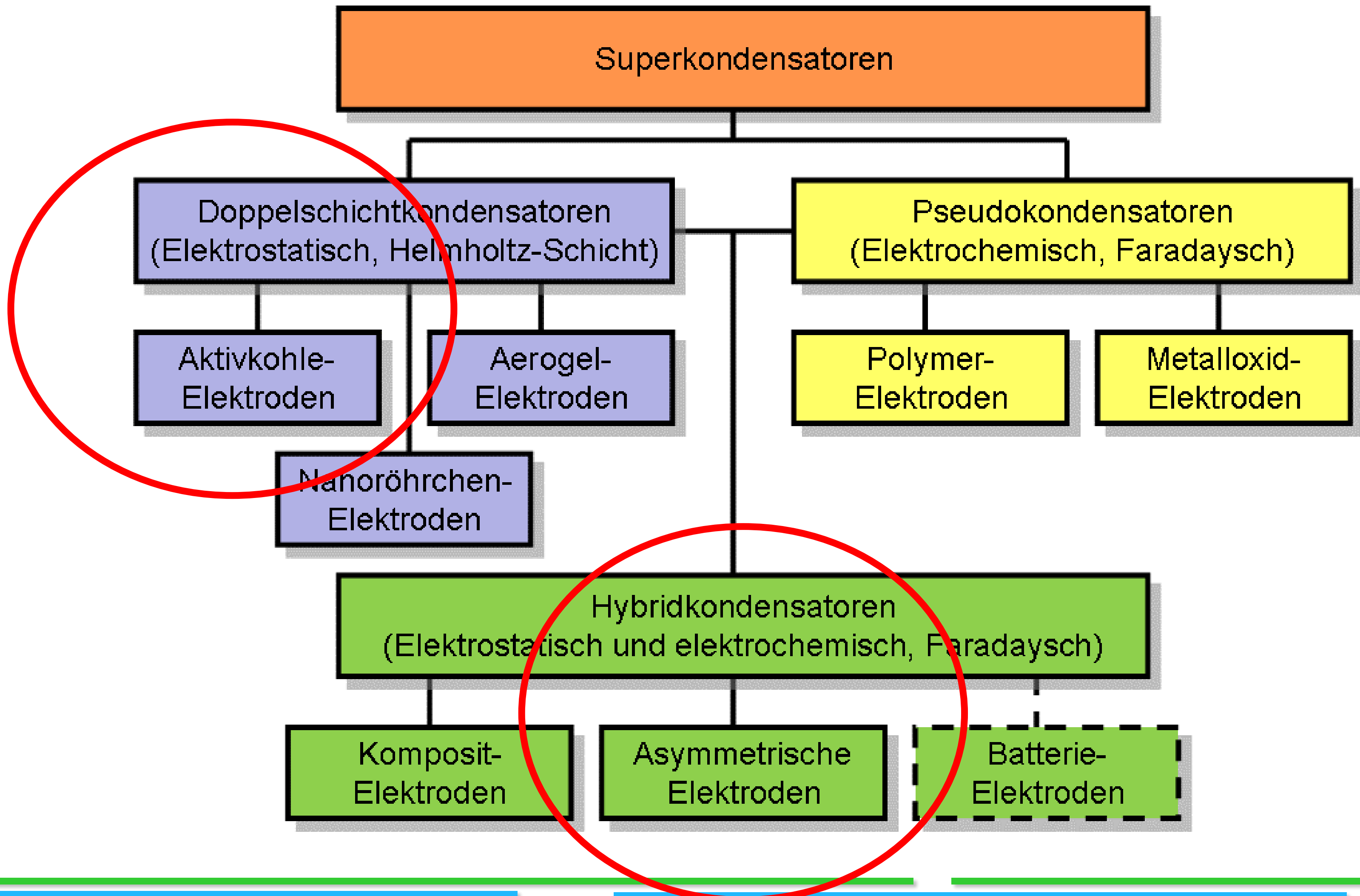
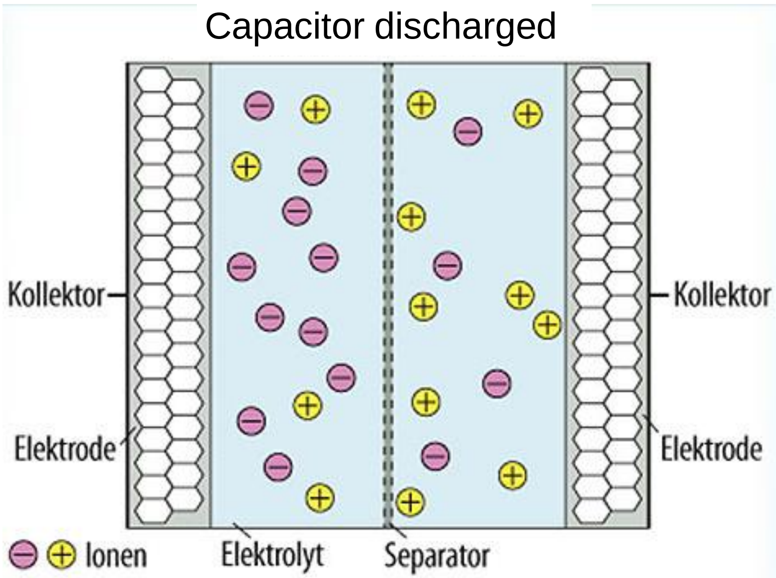
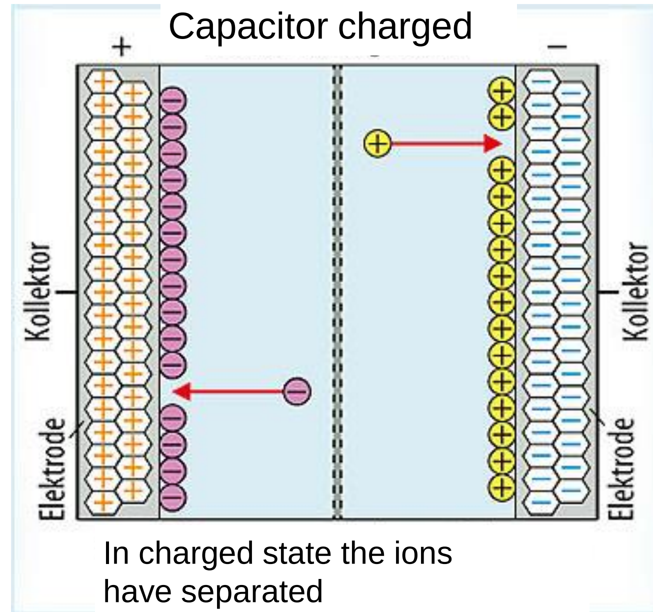

Superkondensatoren
Doppelschichtkondensatoren
(Elektrostatisch, Helmholtz-Schicht)
Pseudokondensatoren
(Elektrochemisch, Faradaysch)
Aktivkohle-
Elektroden
Aerogel-
Elektroden
Nanoröhrchen-
Elektroden
Polymer-
Elektroden
Metalloxid-
Elektroden
Hybridkondensatoren
(Elektrostatisch und elektrochemisch, Faradaysch)
Komposit-
Elektroden
Asymmetrische
Elektroden
Batterie-
Elektroden

Double Layer Capacitors – Design and Function



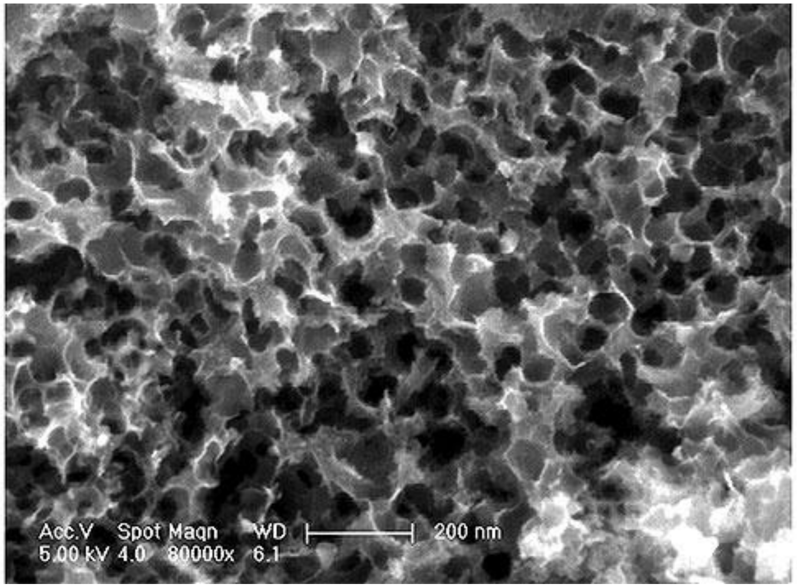


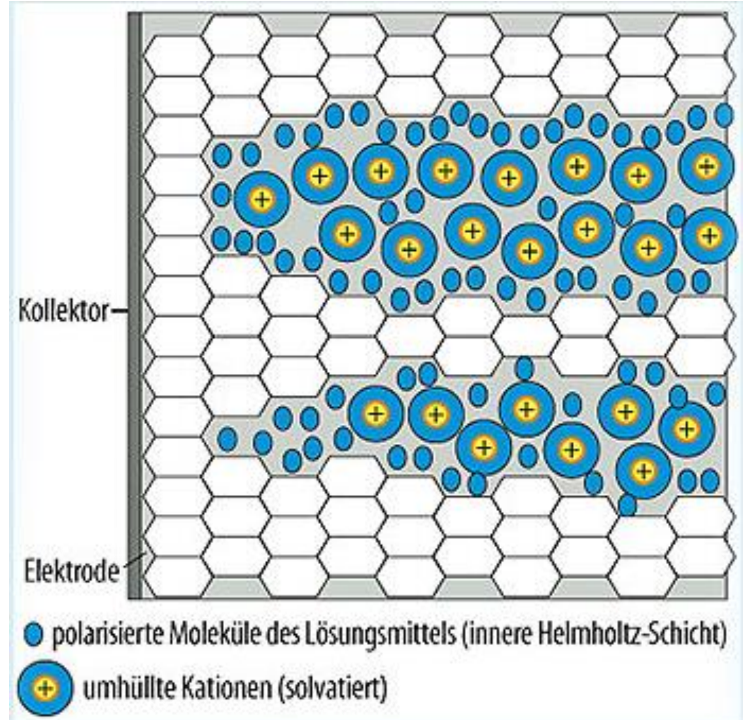
Schematic of an uncharged double layer capacitor (EDLC).

Quelle: Jianghai

Schematic representation of the charged double layer capacitor (EDLC). The ions accumulate at the phase boundaries between the solid electrode and the liquid electrolyte and form the so-called double layer.

Double Layer Capacitors – Design and Function



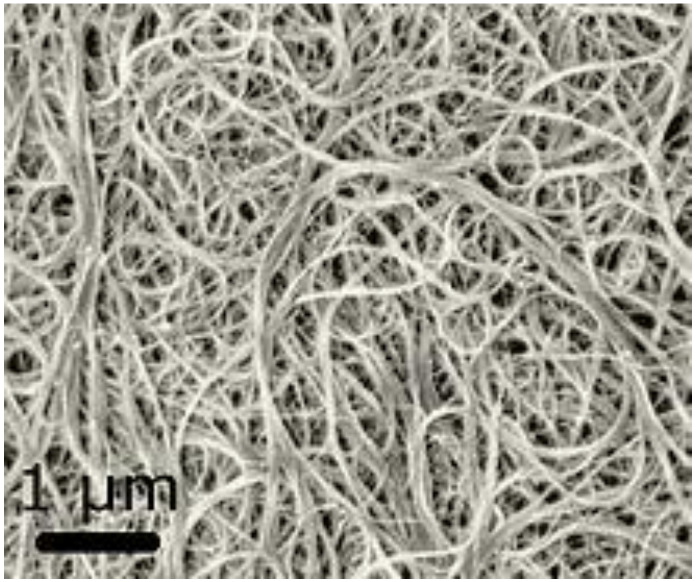


Electron micrograph: pore structure of the activated carbon, which leads to a very large surface. (approx. 300 to 1000m²/g)

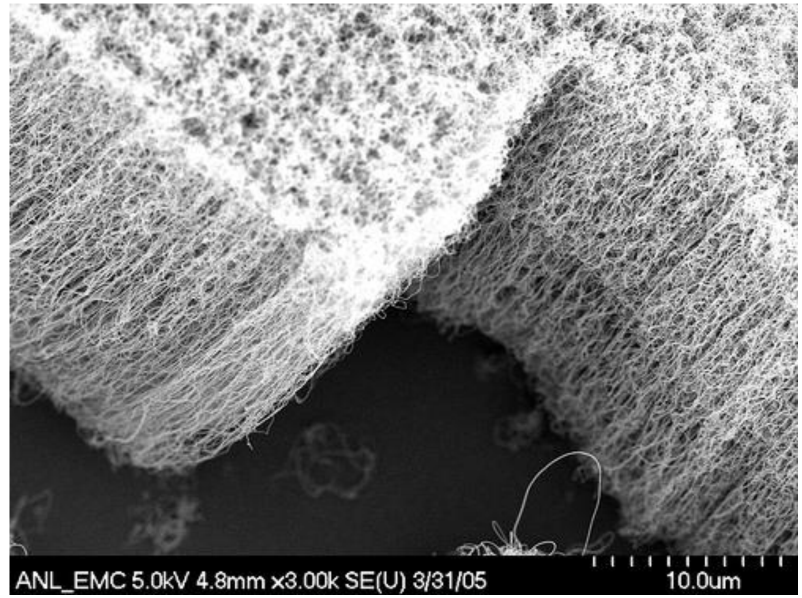
Quelle: Jianghai

Activated carbon forms pores of different sizes. Small pores do not offer as much surface area as large pores, and ions can penetrate small pores only slowly.

Double Layer Capacitors – Design and Function



Electron micrograph: carbon nanofibers with a fiber bundle structure, surface area around 1500 m²/g

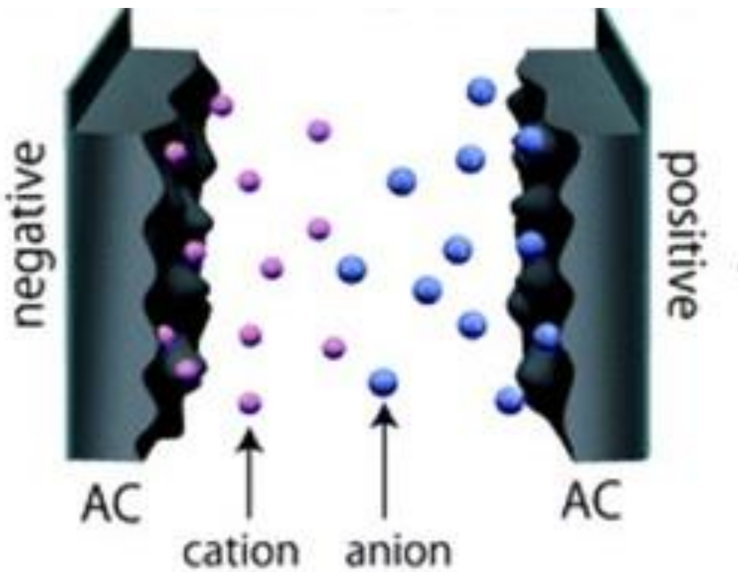


Electron micrograph: upright grown carbon nanotubes, surface area about 2200 m²/g

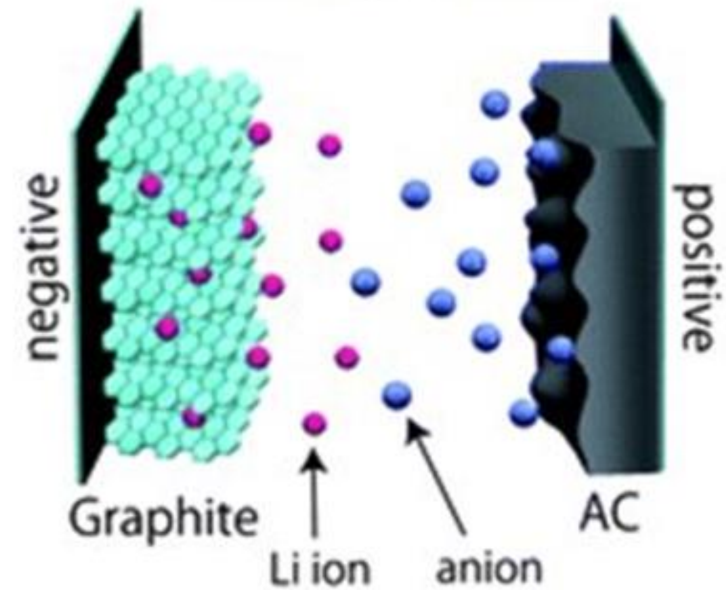
Quelle: decademic.com

Further Development of the Double-layer Capacitor: Lithium Ion Capacitor

EDLC
Electric Double Layer Capacitor



LIC
Lithium Ion Capacitor



	EDLC	LIC
Voltage:	**2,3 to 2,7 V**	**3,8 to 4,2 V**
Energy:	**5 to 20 Wh/kg**	**30 to 50 Wh/kg**

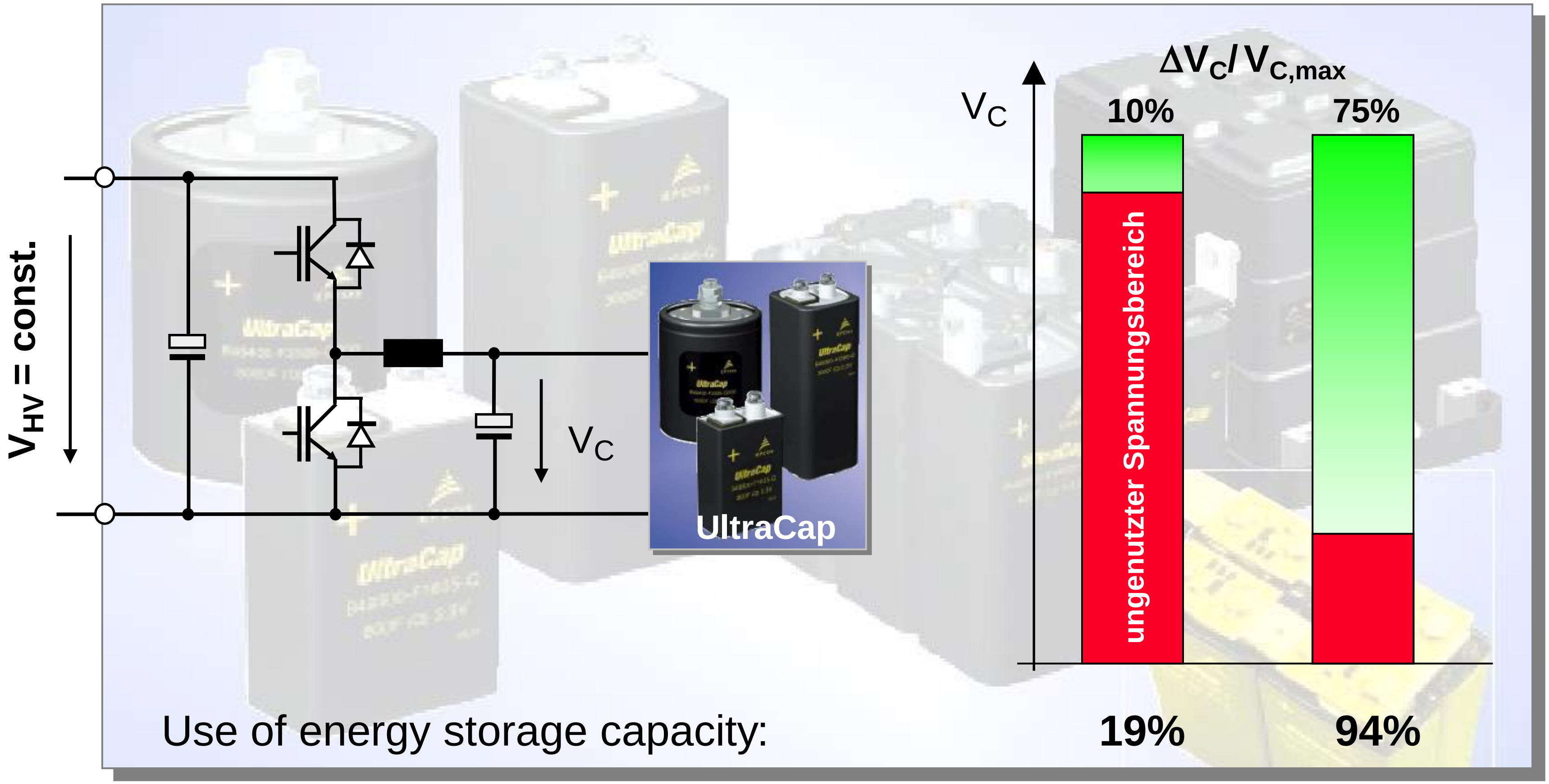
Quelle: Vanchiappan Aravindan, et. al., Insertion-Type Electrodes for Nonaqueous Li-Ion Capacitors, 2016

Comparison:
Double Layer Capacitor – Lithium-Ion Capacitor – LiIo-Battery

Parameter	Doppelschichtkondensator (EDLC)	Lithium-Ionen-Kondensator (LiC)	Lithium-Ionen-Akkuzelle (LiB)
Anode	Aktivkohle	Aktivkohle	$LiCoO_2$ / $LiMnO_4$
Kathode	Aktivkohle	Graphit, dotiert mit Li-Ionen	Graphit
Elektrolyt	Organisches Lösungsmittel	Organisches Lösungsmittel	Organisches Lösungsmittel
Temperaturbereich [°C]	–40 bis 85	–25 bis 70	–25 bis 45
Max. Betriebsspannung [V]	2,3 bis 2,7	3,8 bis 4,2	3,7 bis 4,2
Max. Laderate [C]	ca. 1.000	ca. 100	0,5 bis 1 (normal)
Baugröße/Gewicht	gering	gering	groß
Lade-/Entlade-Zyklen	>500.000	500.000	1000 bis 1500
Selbstentladung	>70 % nach 2000 h	<5 % nach 2500 h	<5 % nach 2500 h
Sicherheit	sehr sicher	sehr sicher	je nach Aufbau und Material „Gefahren minimiert"
Energiedichte	5 bis 7 Wh/kg	30 bis 50 Wh/kg	ca. 250 Wh/kg

Double Layer Capacitors - Applications

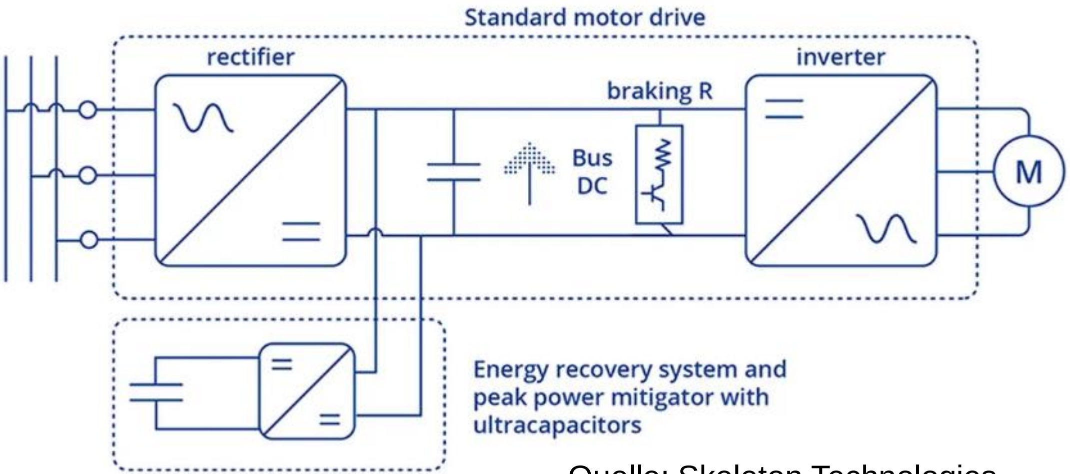
DC-DC converters are required for an efficient use of the capacitors

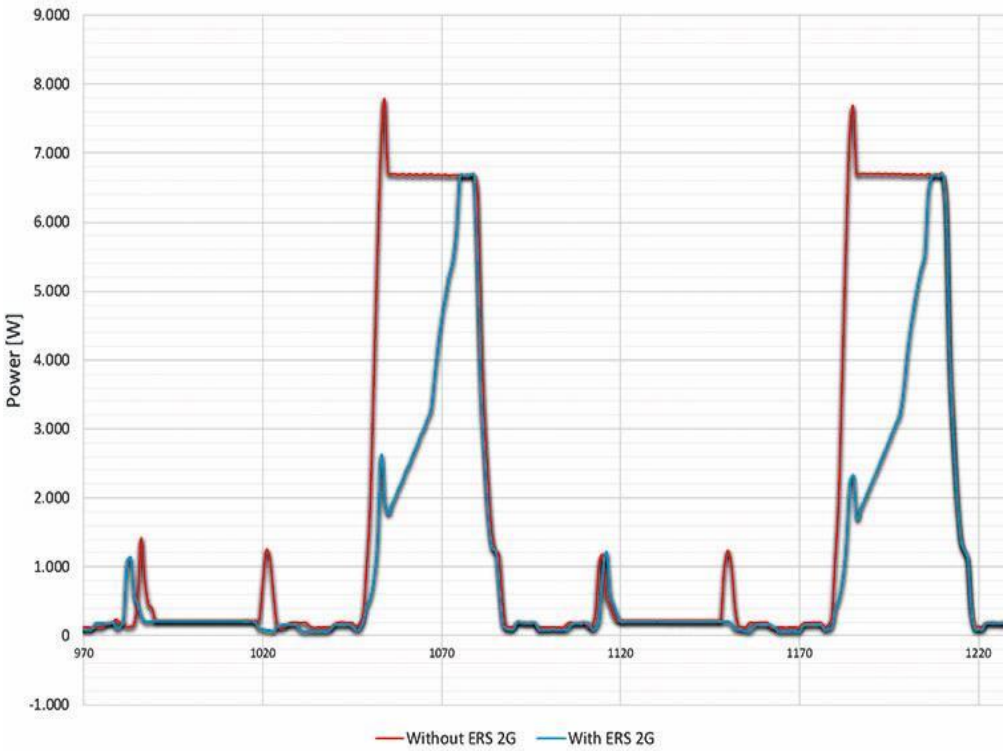


Double Layer Capacitors - Applications

Reducing the energy demand of elevators

- **Recuperation of potential and kinetic energy**
- **capping of power peaks**
- **Reduction of energy demand by 20 to 40%**

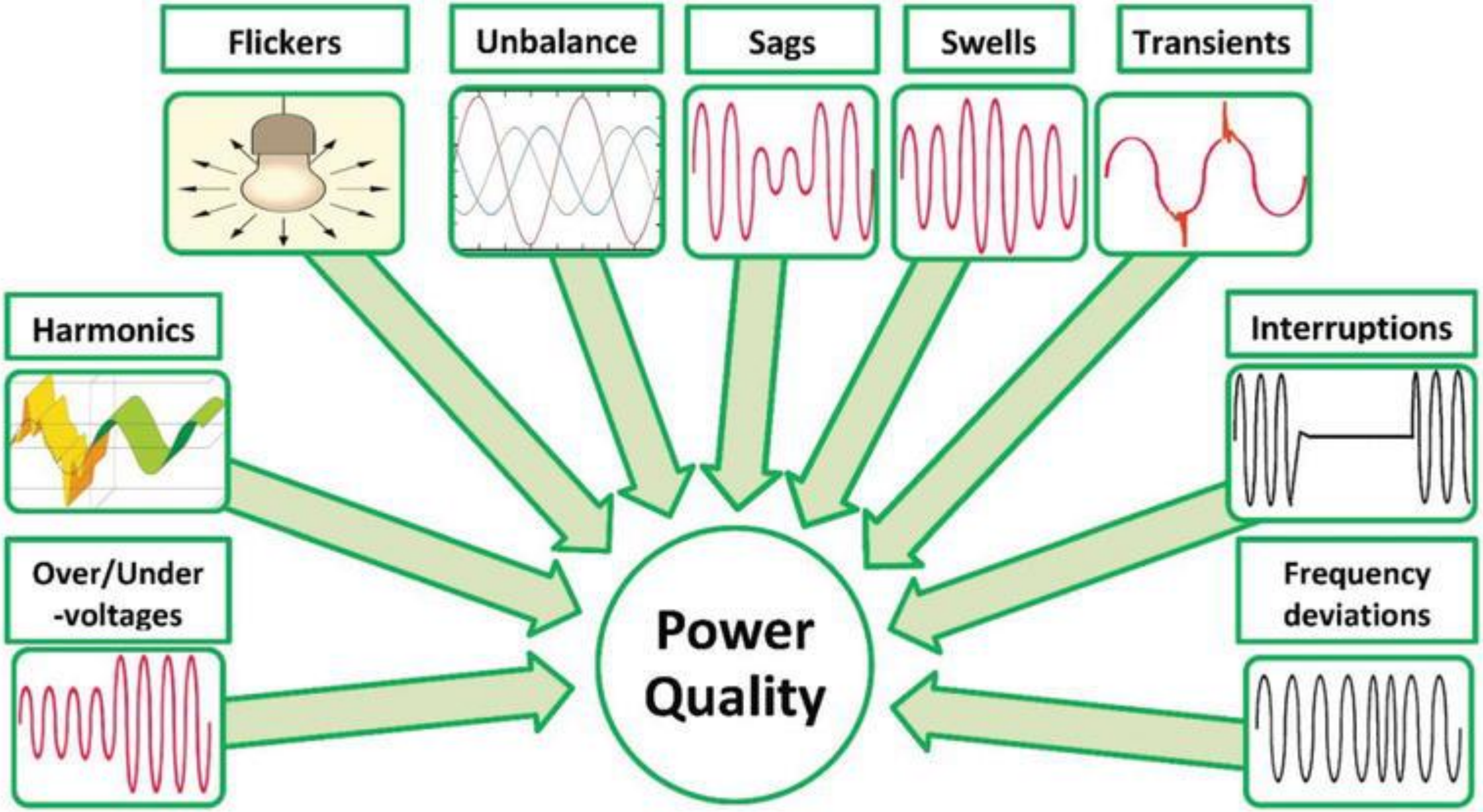




Quelle: Skeleton Technologies

Double Layer Capacitors - Applications

Improving the Power Quality of the Grid



Quelle: A.F. Zobaa, et. al., Power System Harmonics Analysis, Effects, and Mitigation Solutions for Power Quality Improvement, 2018

Double Layer Capacitors - Applications

In Mannheim, Heidelberg and Ludwigshafen, more than 100 trams are running with a double-layer capacitor KERS system: According to an analysis by the Rhein-Neckar transport association, individual trams should save up to 20,000 euros in electricity costs per year.
(Foto: Skeleton Technologies GmbH)

2.7V 3400F ULTRACAPACITOR CELL

FEATURES AND BENEFITS

- DuraBlue® Shock and Vibration Technology
- Up to 1,000,000 duty cycles or 10 year DC life*
- High power and energy
- Up to 17.8 kW/kg of Specific Power[1]
- Up to 7.1 Wh of Stored Energy[1]
- Laser-weldable or threaded terminals

TYPICAL APPLICATIONS

- High shock and vibration environments
- Hybrid vehicles
- Rail
- Heavy industrial equipment

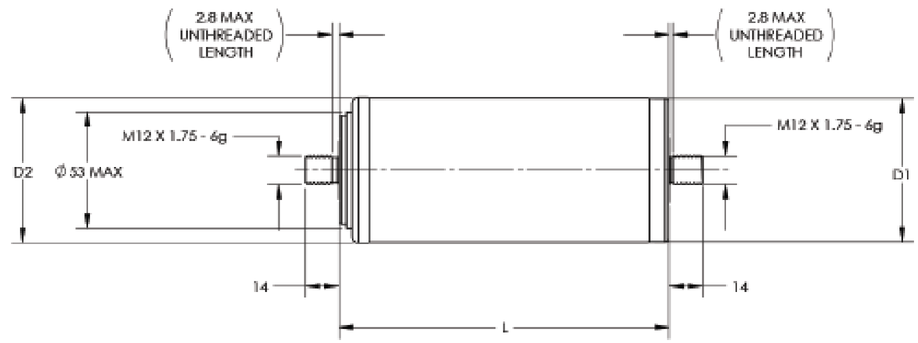
PRODUCT SPECIFICATIONS

ELECTRICAL	BCAP3400
Rated Voltage	2.70 V
Rated Capacitance, initial[2]	3,400 F
Typical Capacitance, initial[2]	3,615 F
Maximum ESR_{DC}, initial[2], rated value, 100 msec	0.23 mΩ
Maximum ESR_{DC}, initial[2], rated value, 5 sec	0.28 mΩ
Typical ESR_{DC}, initial (100 msecs)[1,2]	0.20 mΩ
Typical ESR_{DC}, initial[1,2], 5 sec	0.22 mΩ
POWER & ENERGY	
Minimum Usable Specific Power, P_d[3]	7.4 kW/kg
Typical Usable Specific Power, P_d[1,3]	8.5 kW/kg
Minimum Impedance Match Specific Power, P_{max}[4]	15.5 kW/kg
Typical Impedance Match Specific Power, P_{max}[1,4]	17.8 kW/kg
Minimum Specific Energy, E_{max}[5]	6.7 Wh/kg
Typical Specific Energy, E_{max}[1,5]	7.1 Wh/kg
Minimum Stored Energy, E_{stored}[6,12]	3.44 Wh
Typical Stored Energy, E_{stored}[1,6,12]	3.66 Wh
SHOCK & VIBRATION	
Vibration Specification	ISO 16750-3, Table 12
Shock Specification	IEC 60068-2-27
SAFETY	
Short Circuit Current, typical (Current possible with short circuit from rated voltage. Do not use as an operating current.)	12,000 A
Certifications	UL810a, RoHS, REACH
THERMAL	
Thermal Resistance (R_{ca}, Case to Ambient), typical	3.2°C/W
Thermal Capacitance (C_{th}), typical	640 J/°C
Maximum Continuous Current (ΔT = 15°C)[7]	130 A_{RMS}
Maximum Continuous Current (ΔT = 40°C)[7]	210 A_{RMS}

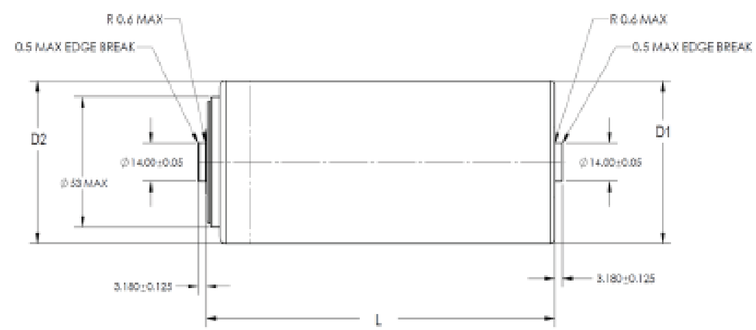
TYPICAL CHARACTERISTICS

TEMPERATURE	BCAP3400
Operating temperature range (Cell case temperature)	
Minimum	-40°C
Maximum	65°C
ELECTRICAL	
Absolute Maximum Voltage[8]	2.85 V
Absolute Maximum Current	2,600 A
Leakage Current at 25°C, maximum[9]	10 mA
LIFE*	
DC Life at High Temperature[2,10] (held continuously at Rated Voltage & Maximum Operating Temperature)	1,500 hours
Capacitance Change (% decrease from rated value)	20%
ESR Change (% increase from rated value)	100%
Projected DC Life at 25°C[2,10] (held continuously at Rated Voltage)	10 years
Capacitance Change (% decrease from rated value	20%
ESR Change (% increase from rated value)	100%
Projected Cycle Life at 25°C[2,9,11]	1,000,000 cycles
Capacitance Change (% decrease from rated value)	20%
ESR Change (% increase from rated value)	100%
Shelf Life (Stored uncharged at 25±10°C)	4 years
PHYSICAL	
Mass, typical	513 g
Terminals	Weldable/Threaded

BCAP3400 P270 K04



BCAP3400 P270 K05



Part Description	Dimensions (mm)			Package Quantity
	L (±0.3mm)	D1 (±0.2mm)	D2 (±0.7mm)	
BCAP3400 P270 K04/05	138	60.4	60.7	15

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Double Layer Capacitors

- Very high peak performance can be achieved
- High number of cycles (>5000,000) possible
- Low energy density (3 to 7 kW/kg)
- High efficiency
- Ideal for frequent charging/discharging with recurring recuperation processes

Supra Conducting Inductors

History:
Superconductivity was discovered by H. Kamerlingh in 1911: mercury has almost no electrical resistance below minus 269 °C. For this he received the Nobel Prize in 1913.

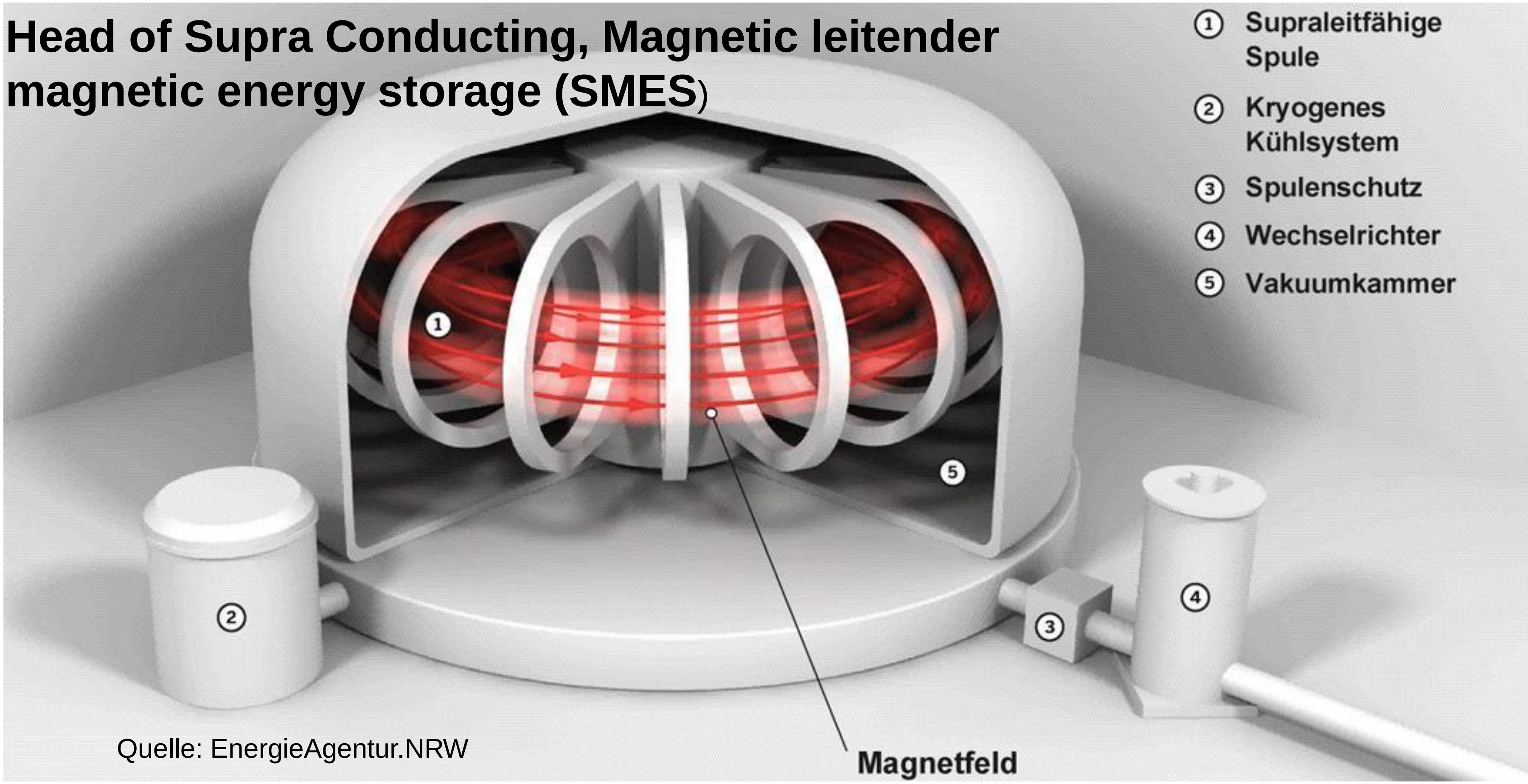
In 1986, however, G. Bednorz and A. Müller found a compound of lanthanum, strontium, copper and oxygen that became superconducting at minus 227 degrees Celsius. For this they received the Nobel Prize in 1987.

The first energy storage device in Europe was developed by the research center in Karlsruhe and installed in a sawmill in the Albtal at the end of the 1990s. It had a storage capacity of 55.6 Wh and an output of 80 kW and compensated for network feedback caused by consumers.

Advantage:
- Unlimited number of cycles (related to the coil)

Disadvantage:
- Cooling to minus 227 °C necessary
- Very low energy content compared to batteries

Head of Supra Conducting, Magnetic leitender magnetic energy storage (SMES)



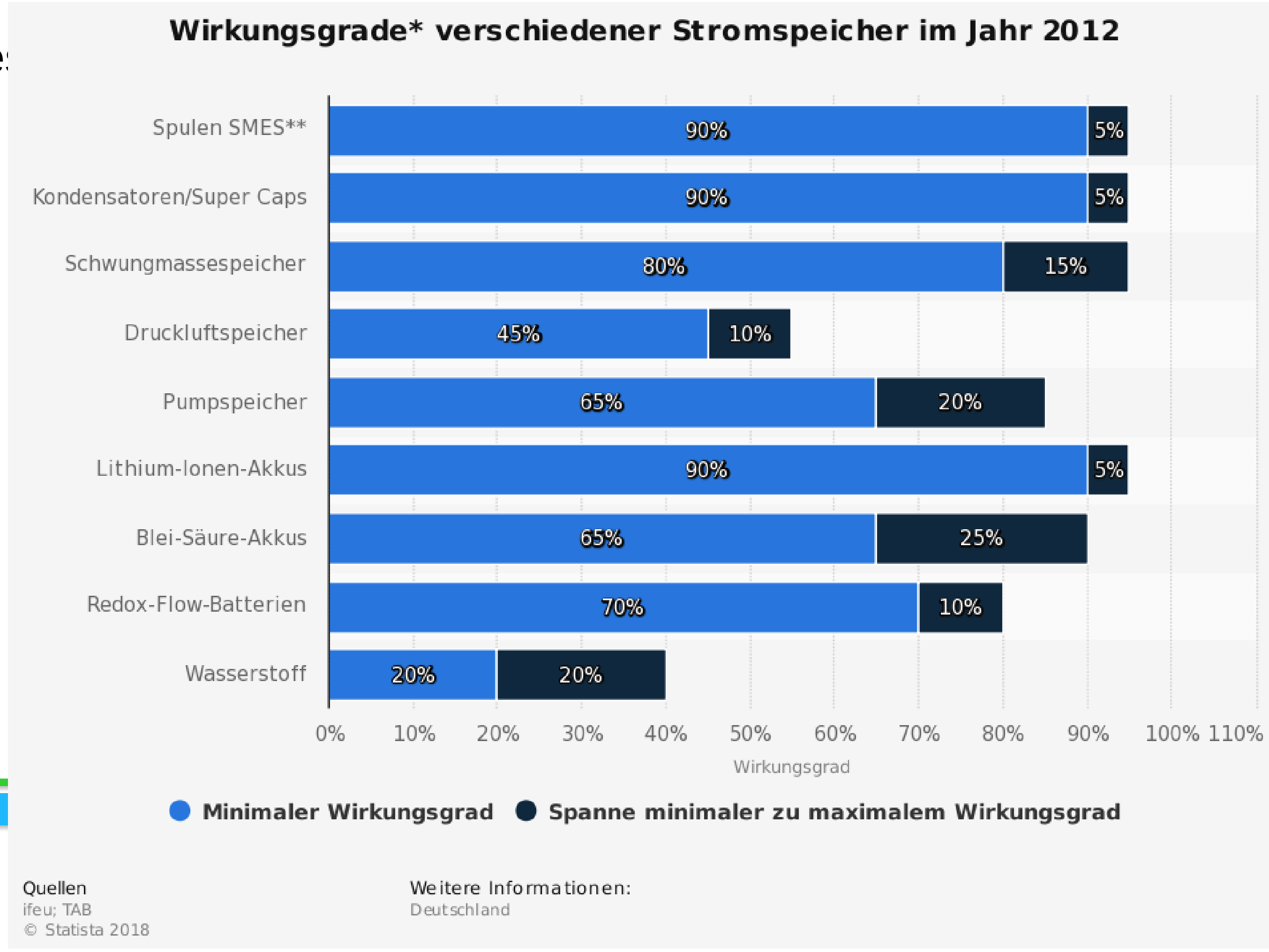
Quelle: EnergieAgentur.NRW

The energy stored is: E= $\frac{1}{2} \cdot L \cdot I^2$

With: L Indcktivity, I Current

Superconducting coils as energy storage

- High peak performance can be achieved
- Unlimited number of cycles
- High efficiency
- Very complex cooling
- Expensive



* Efficiency = ratio of absorbed to emitted energy.
** SMES = Superconducting Magnetic Energy Storage.

Electric Energy Storage Systems

Chapter 8:
Exercise

Summer 2024

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Double Layer Capacitors and Superconducting Coils

A.1 Explain the basic structure and function of the double layer capacitor.

A.2 What is the energy content of a double layer capacitor with a capacity of 2.3 V and 50 F?

A.3 A double-layer capacitor is constructed with 5 grams of activated carbon per electrode with a surface area of 500 m²/g. The dielectric constant εr = 5 and the distance between the charge carriers is 0.5 *10-9m. What is the capacitance of the capacitor?

A.4 Why is a DC/DC converter usually required when using double layer capacitors?

Superconducting Coils

B.1 What is the stored energy in a superconducting coil with 500 mH at a current flow of 5000 A?

Electric Energy Storage Systems

Chapter 9: Pump Storage, Thermal Storage

Summer 2024

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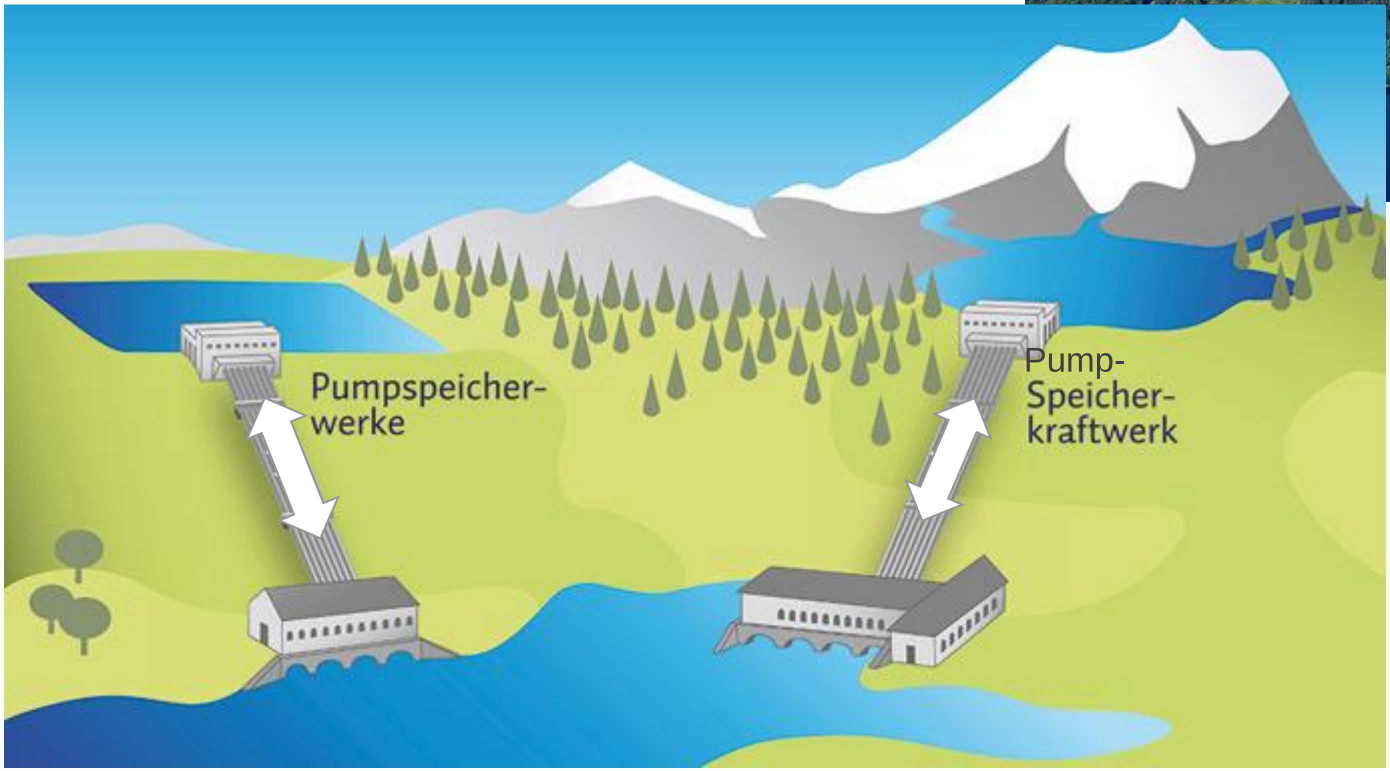
Pumped Storage Power Plants

History:
Already in the 18th century pumped storage facilities operated by windmills were used
From 1920 the first pumped storage power plants for storing and generating electricity
In Germany, the development was primarily driven by A. Koepchen, after whom the PSW Koepchenwerk of RWE AG was named in 1930.
Due to the increasing proportion of regenerative energy, the need for storage also increases, e.g.
Currently, however, the operation in Germany is almost not cost-covering due to the network fee.

Advantage:
- Large amounts of energy can be stored
- Established technology and good efficiency
- provision of peak load

Disadvantage:
- Large landscape interventions necessary
- Opportunities depend heavily on the topography

Pumped Storage Power Plants
- Realization

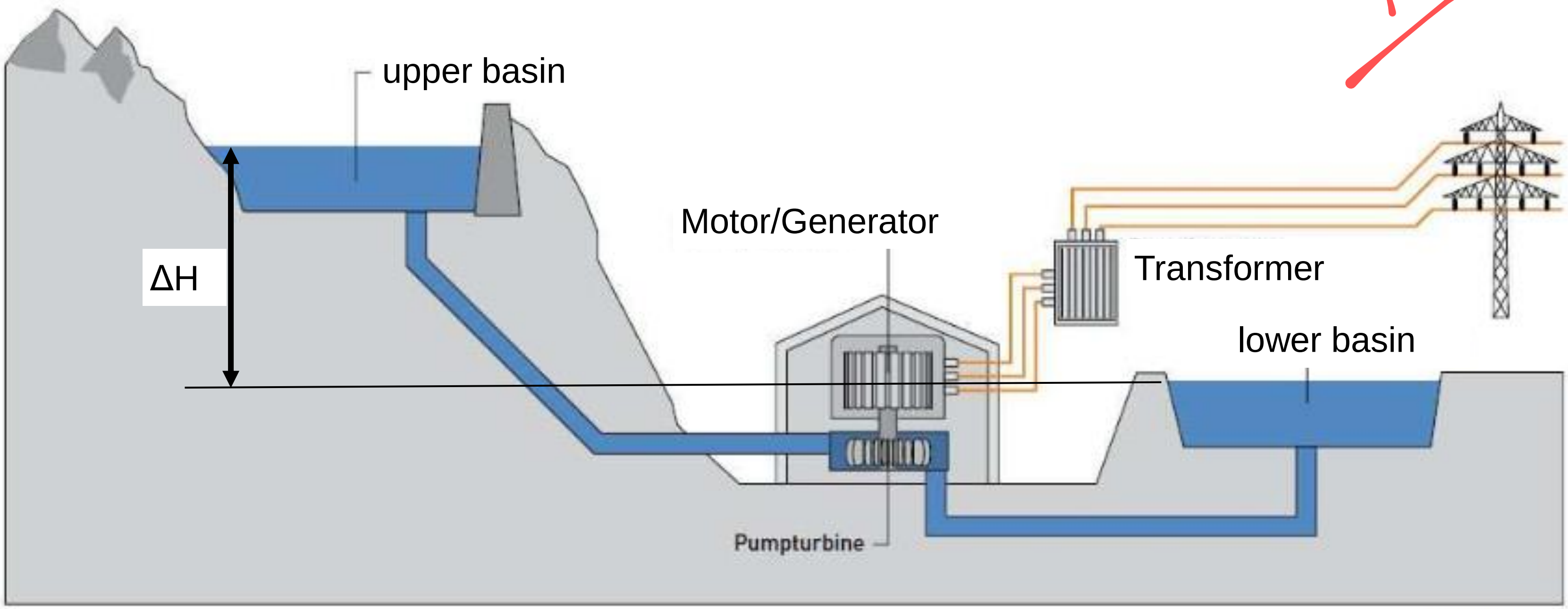


Pure pump storage

Pump storage with natural inflow

Imp

Pumped Storage Power Plants - Realization



For the useable stored energy (E in J) applies:

$$E = \eta_T \cdot \rho_{Water} \cdot VWater \cdot g \cdot \Delta H$$

η_T:	Efficiency [%]
ρ_{Water}:	Density of Water [kg/m³]
V_{Water}:	Useabel water volume of upper basin [m³]
g:	Gravity konst. [m/s²]
ΔH:	Usable height [m]

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Pumped Storage Power Plants - Efficiency

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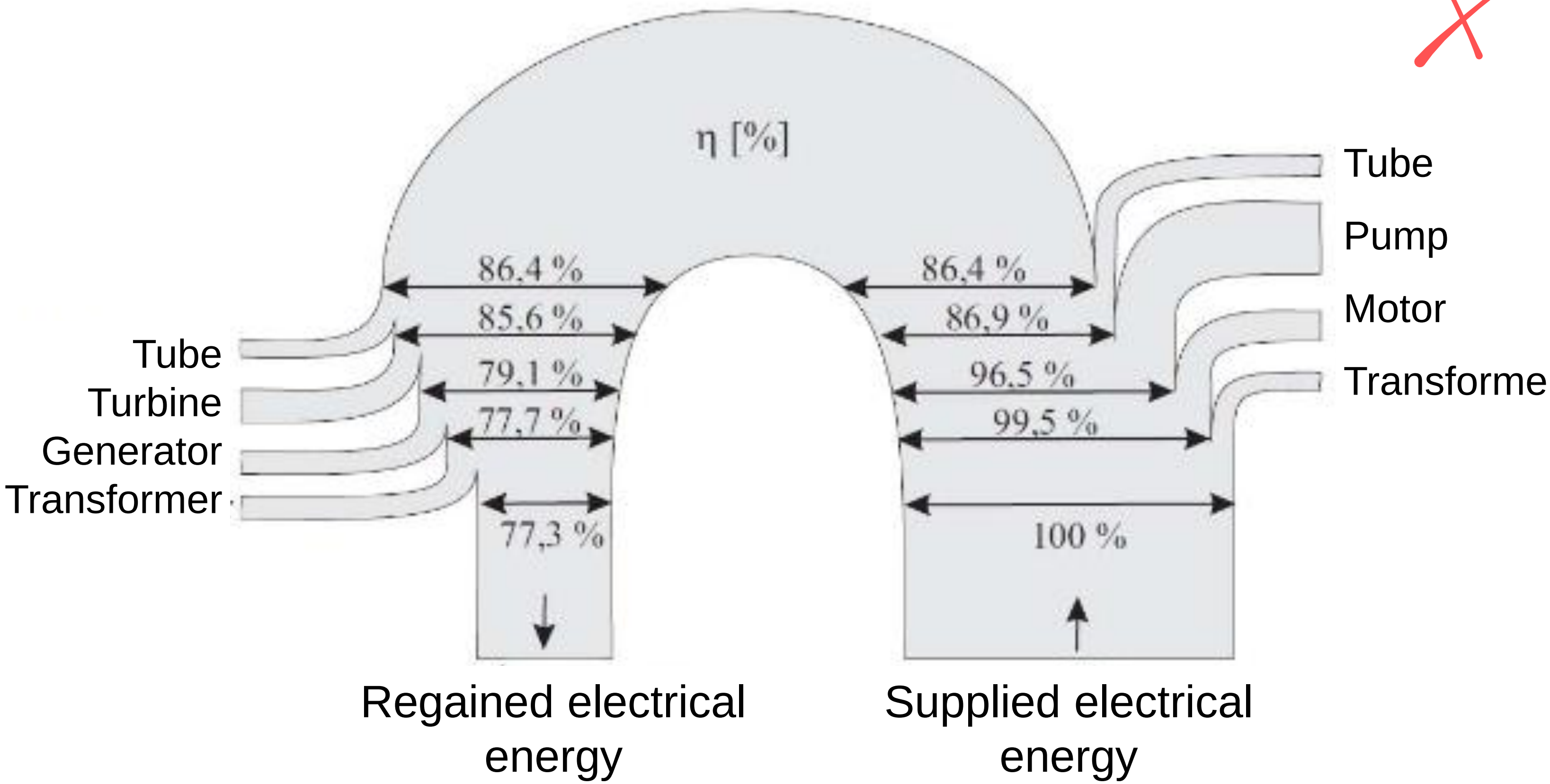


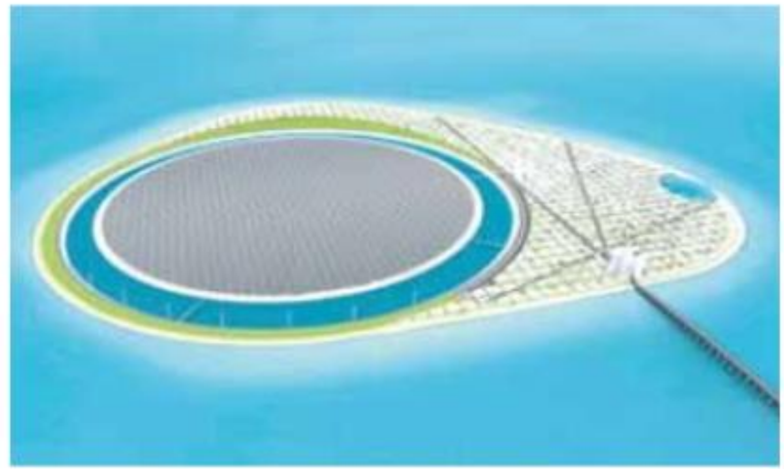
Quelle: [Giesecke & Mosonyi, 2009b] IEK-STE 2012

Pumped Storage Power Plants – New Concepts

Concept for Off Shore Pump Storage

Green Power Island in Florida

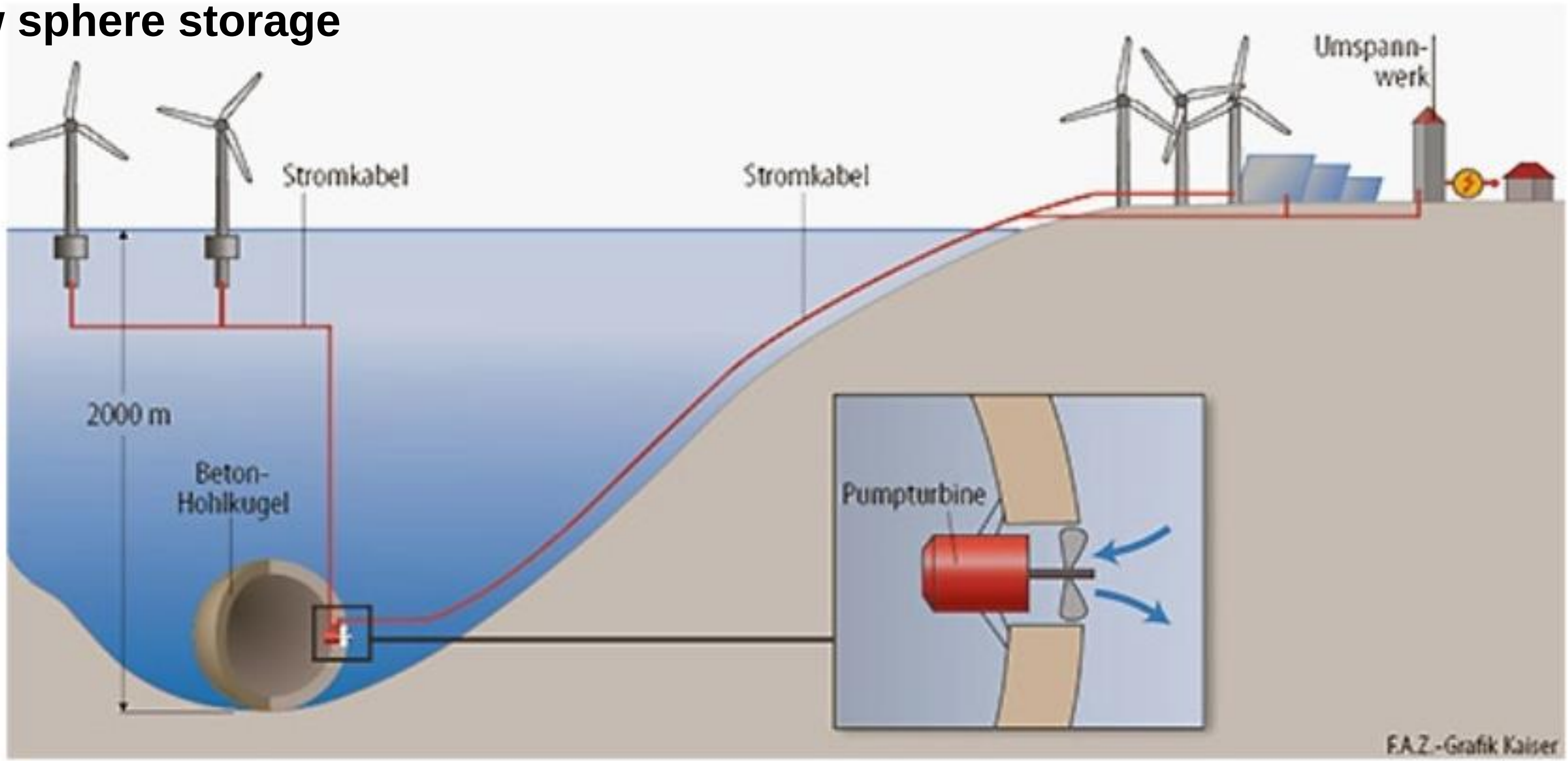
Energy Island in Bahrain



Quelle: [Gottlieb, 2012] IEK-STE 2012

Pumped Storage Power Plants – New Concepts

hollow sphere storage



Quelle: [Küffner, 2011] IEK-STE 2012

Pumped Storage Power Plants

- Large energies can be stored
- Long service life and high number of cycles possible
- Good efficiency of approx. 75 to 80%
- Large area requirement and strong intervention in the landscape
- Storable energy is highly dependent on topography.

Imp

Thermal Energy Storage

History:
Ever since the use of fire, stones have been used as thermal storage.
In the 1970s, night storage heaters were introduced for "electrical" energy storage, so that the excess night-time electricity from the nuclear power plants could be used (stored).
Since 2000, research into the use of high-temperature heat storage systems for storing electricity has been intensified

Advantages:
- Storage can very easily be combined with conventional power generation (e.g. from natural gas).
- If waste heat is also used, efficiencies of up to 90% can be achieved

Disadvantage:
- Electrical efficiency usually only approx.35-40%

Thermal Energy Storage – Realisierung

Thermal Storage
For service water (left 5L boiler) and heating (right 1000 L)

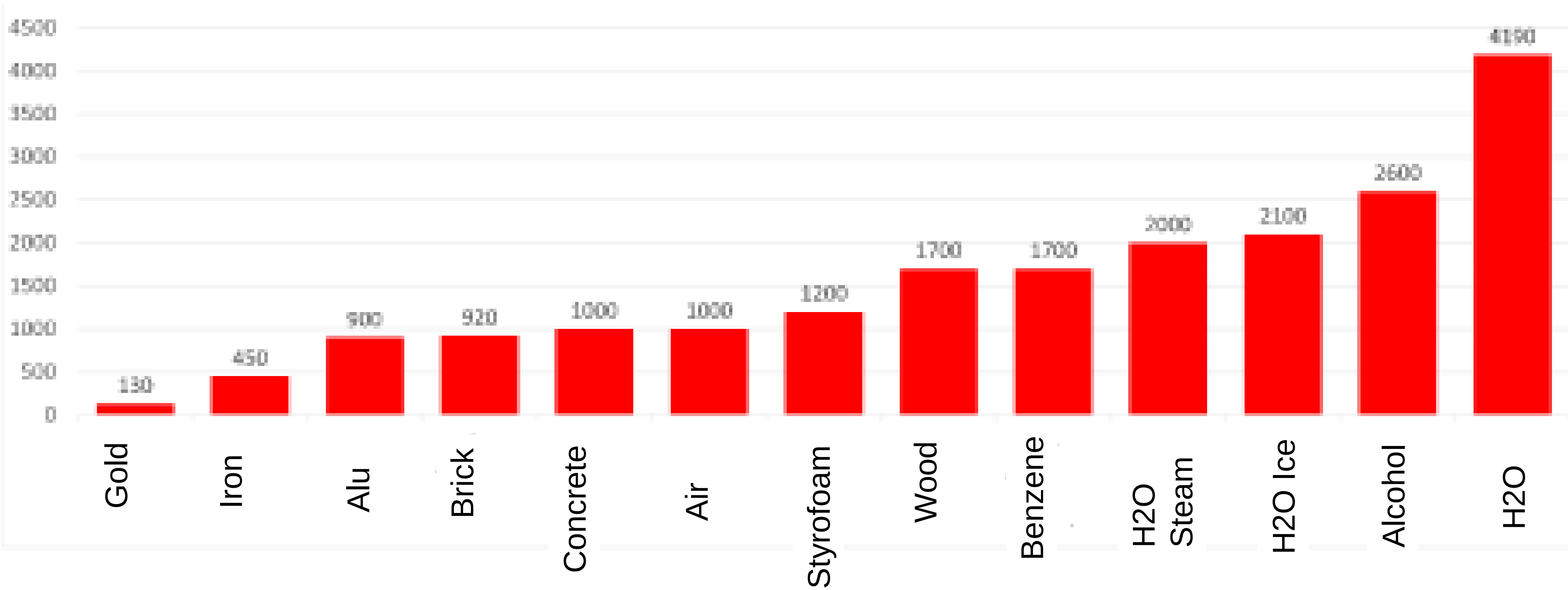
Quelle: Siemens Gamesa

Thermal Electric Energy Storage for 150 MWh
Test facility with volcanic stone storage that went into operation in 2019

Thermal Energy Storage – Specific Heat Capacity

The specific heat capacity is the measure of the energy required to heat 1kg of a substance by 1K or 1∘C.

$$c_{heat} = \frac{\Delta E}{m \cdot \Delta T}$$



Thermal Storage

	Einheit	Feststoff-speicher	Flüssig-speicher	Latent-wärme-speicher	Thermo-chemische Speicher
Spez. Energiespeicherdichte (abhg. vom Anwenderprozess)	kWh/m^3	70-150	70-200	~100	150-500
Spez. Leistungsdichte	kW/m^3	20-400	Keine Limi-tierung	15-80	-
Typ. realisierbare Speichergröße	MWh	1-1.000	500-5.000	0,1-500	-
Speicherwirkungsgrad	%	98	98	98	60-95
Verluste (% der Kapazität pro Tag)	%/d	2-4	2-4	2-4	0
Speicherdauer		Stunden bis Tage	Stunden bis Tage	Stunden bis Tage	Stunden bis Monate
Reaktionszeit		Minuten	Minuten	Minuten	Minuten

Thermal storage –
Realization of solid storage
Storage of heat in stones

- High temperature capability of 850 to 1200°C
- High heat capacity
- Simple construction and installation of the electric heating elements
- High compressive strength (important for stacking)
- Good flow with low pressure loss

Pile of volcanic stone

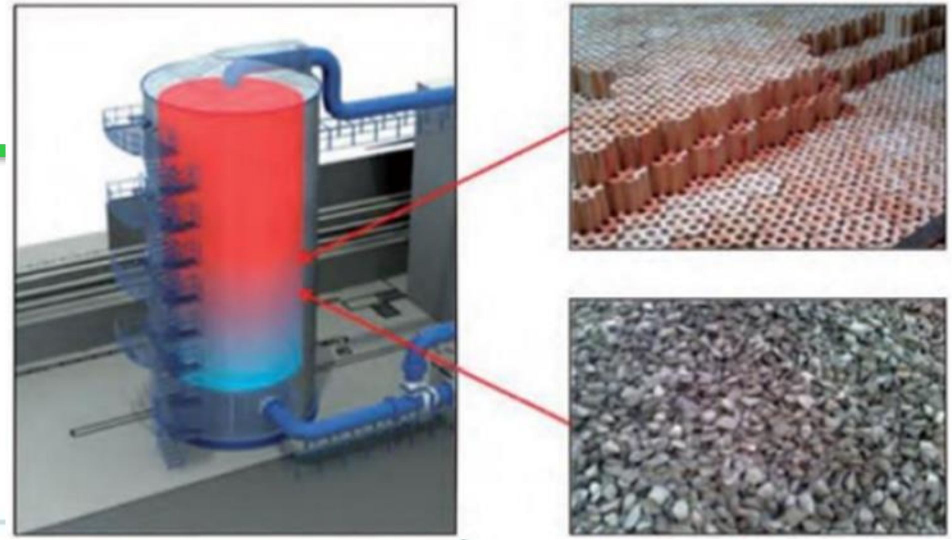
Quelle: Sven Rieken

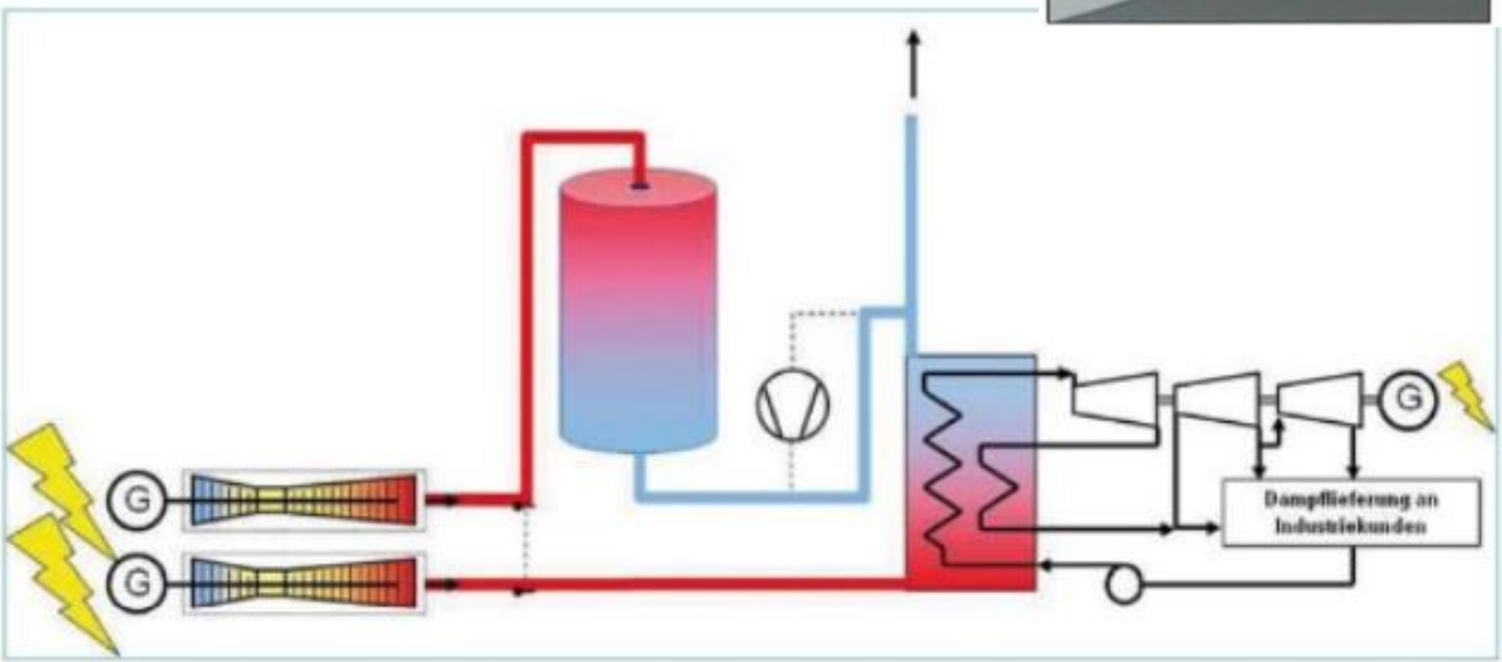
Stacked shaped stones

www.weiku.com (Refractory fireclay checker Brick)

Thermal Storage

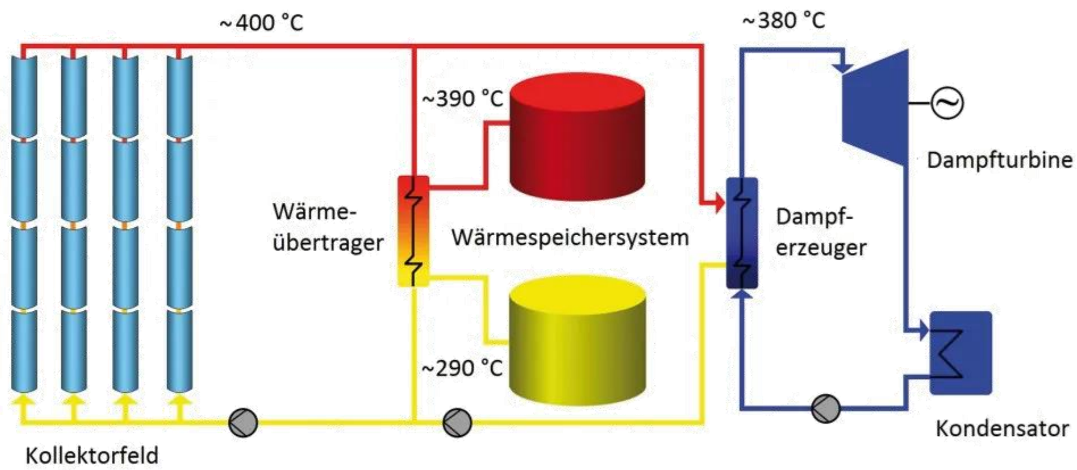
Integration into conventional gas power plants possible

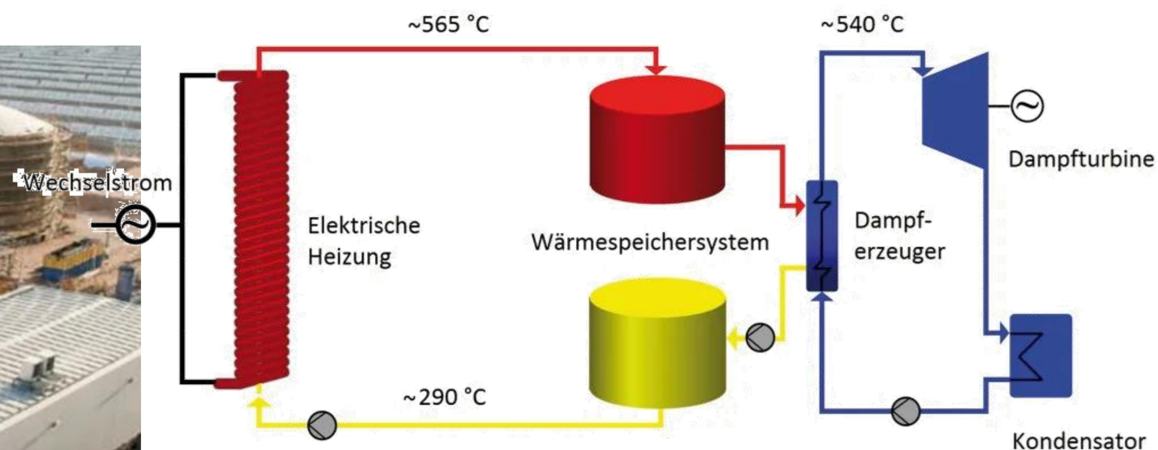




Thermal Storage

- **Combination with solar thermal**
- **Generation and storage significantly increase profitability**
- **Pure storage efficiency only 35-40%**

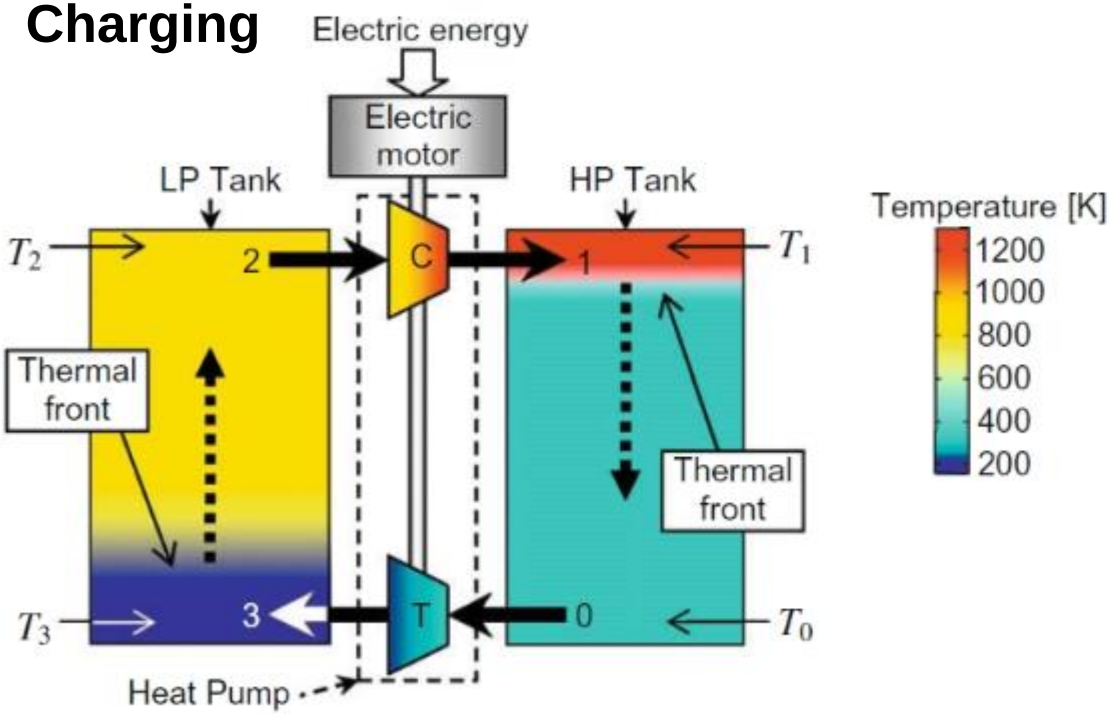


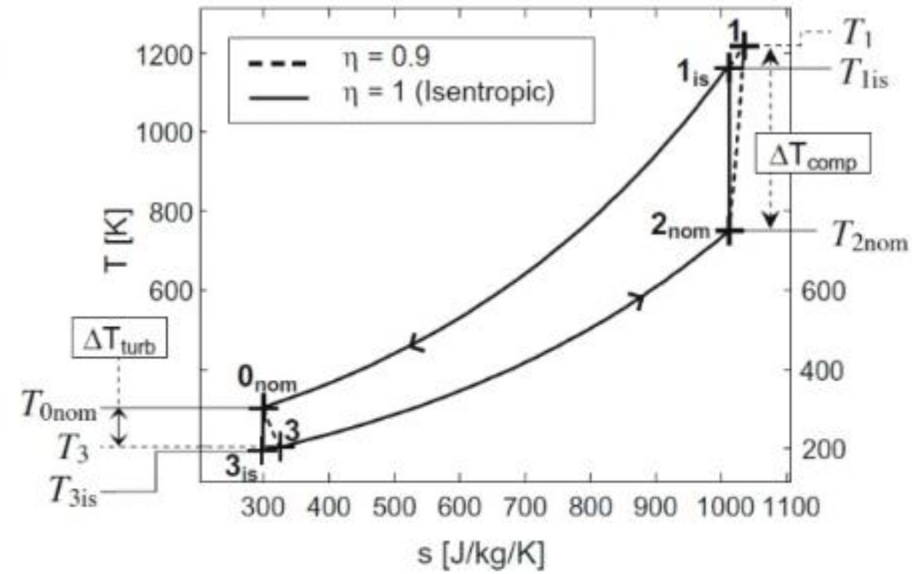


Quelle:www.ingenieur.de/wp-content/uploads/2020/01/EF-BA9553-Dittmann_B2.jpg

Thermal Storage – Thermopotential Storage

Charging

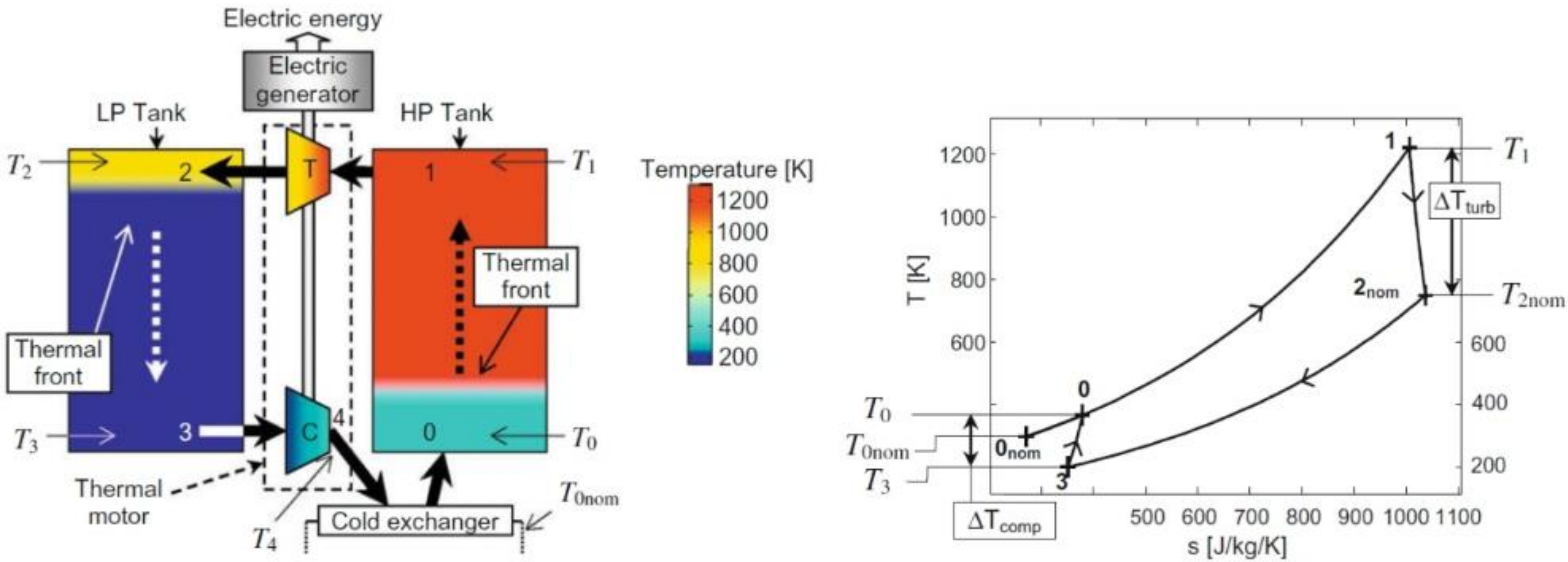




- Thermal potential storage is still under development, so far only test systems are in operation
- Theoretical efficiency of up to 85% possible, 60 to 75% can be achieved in operation

Quelle: [Desrues et al., 2010] IEK-STE 2012

Thermal Storage – Thermopotential Storage Discharging



Quelle: [Desrues et al., 2010] IEK-STE 2012

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Thermal Storage

- Can be combined very well with conventional gas or thermal solar power plants
- Electrical efficiency of classic thermal storage only 35-40%
- In combination with heat utilization, an efficiency of 90% is possible
- New thermopotential storage systems enable efficiencies of 60 to 75%. So far, however, only test systems have been in operation

Elektrische Energiespeichersysteme

Chapter 9:
Excercise

Summer 2024

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Thermal storage

A.1 A hot water tank has a volume of 1.0 m^3. How much energy can be stored in this when the water temperature is increased from 20°C to 95°C.

A.2 The energy from the storage tank is to be used to heat a room from 5m to 5m and 2m in height at an outside temperature of 10 to 20 degrees. Thermal losses of 15 $J/(s*m^2)$ must be covered. How long can the room be heated with the stored energy of the hot water tank?

Pump storage

B.1 A pumped storage power plant is to be built to store 100 GWh of wind energy. A height difference of 100 m is feasible.

What is the minimum size of the upper reservoir?

What is the efficiency of a pump turbine?

How much energy can be fed back into the grid as electricity?

Electric Energy Storage Systems

Chapter 10:
Design of storage systems

Summer 2024

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IISB

1. Design of electro-chemical energy storage

1. A 12 V lead battery is charged with 1000 mA for 12 hours.
How much charge and how much energy did the battery absorb?

2. What is the minimum amount of cadmium needed for a 100 Ah NiCd battery?
Cadmium (112.4 g/mol) can donate two electrons and becomes divalent Cd2+
Faraday's constant has a value of 96487 As/mol.

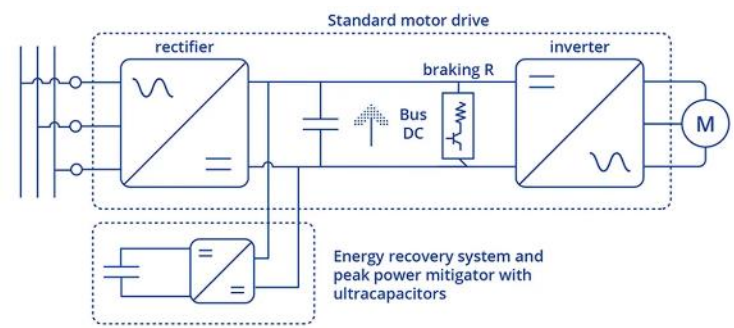
2. Energy storage in elevators:

The elevator of a high-rise building has a travel height of 100m. The cabin has a mass of 1000 kg and a maximum payload of 1600 kg.
The propulsion system is to be equipped with an energy recovery system.
It is coupled to the elevator drive via a DC-DC converter.
The voltage of the capacitor can be between 540V and 200V.
The internal resistance is negligible.

1. What is the maximum potential energy of the elevator?

2. How large must the capacitor be designed

3. How many capacitors must be installed if Maxwell 2.7V 3400µF
used.



Quelle: Skeleton Technologies

3. Battery electric vehicle:

The battery system of an electric vehicle consists of 100 LiFePO cells connected in series, each with a capacity of 50 Ah, a nominal voltage of 3.2 V each and an internal resistance of 3.2 mOhm each.

1. What is the energy content of the battery system?

2. What is the maximum possible short-circuit current?

3. The battery system is fully charged with 10 A in 5 hours (cell voltage V0 constant 3.2V). What is the charging power on the mains side (socket) if the charger has an efficiency of 90%?

4. When driving on the motorway, the battery is discharged with a power of 50 kW. What is the discharge current

4. Fuel cell electric vehicle :

The fuel cell in this vehicle delivers an output voltage of 430 V when idling and 250 V at an output current of 400 A. In simplified terms, it can be assumed that the internal resistance is constant.

1. What is the maximum power of the fuel cell?

2. What is the internal resistance?

3. When driving on the Autobahn, an output of 50 kW from the fuel cell is required.
   a) What is the voltage at this operating point?
   b) What is the power loss in the fuel cell?

5. Energy storage system for a tram:

Design an energy storage system for a tram with a top speed of 60 km/h and a mass of 34 t that can absorb all of the braking energy.

1. What is the kinetic energy of the tram?

2. A flywheel mass accumulator with a diameter of 1m and a maximum speed of 30000 rpm is to be used. How much mass does the flywheel have to have?

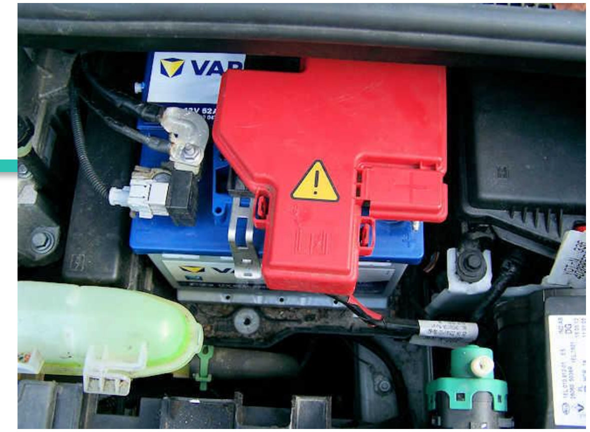
3. How heavy will an energy storage device with supercapacitors that are 2.7V at 3400F and 0.5 kg?

6. Energy storage system for wind farm:

For a wind farm with 10 wind turbines, each with a rotor diameter of 100 m, a pumped storage facility is to be installed that can store the maximum possible electricity generation for a day at wind speeds of 20 m/s.

1. What is the output of a wind turbine at a wind speed of 20m/s?

2. What is the minimum storage volume for a height difference of 100m?



7. Lead acid battery:

Lead-acid batteries are still used in many applications today.

1. Sketch the structure of a lead-acid battery. What material is used on the electrodes and what is used as the electrolyte.

2. Which electrochemical processes take place during discharging (please state chemical reaction)

3. What is the cell voltage of a lead-acid battery

4. How is the current collector implemented in real lead-acid batteries? What are pros cons.

8. Alkaline batteries

1. Sketch the 1C fast charging process for a NiCd battery?

2. What influence does the discharge rate have on the capacity of a NiCd battery?

3. What is special about a sodium nickel chloride battery?

Electric Energy Storage Systems

Apendix: Literature

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Literature for the lecture

Studying the following accompanying literature is not necessary for the examination.

[1] Andreas Jossen, Wolfgang Weydanz: *Moderne Akkumulatoren richtig einsetzen*, 2. Auflage, Cuvillier Verlag, 2019, ISBN 978-3-7369-9945-9

[2] Peter Kurzweil, Otto K. Dietlmeier: *Elektrochemische Energiespeicher*, 2. Auflage, Springer Vieweg 2018, ISBN 978-3-658-21828-7

[3] Peter Kurzweil: Brennstoffzellentechnik *der Kraftfahrzeugelektronik*, 3. Auflage, Springer Vieweg 2016, ISBN 978-3-658-14934-5

[4] Eckbert Hering, Rolf Martin, Martin Stohrer: *Physik für Ingenieure*, 6. Auflage, Springer 1997, ISBN 3-540-6244-2

[5] Martin März, Richard Öchsner: *Innovative Technologien für intelligente dezentrale Energiesysteme*, Fraunhofer Verlag, 2019, ISBN 978-3-8396-1486-0