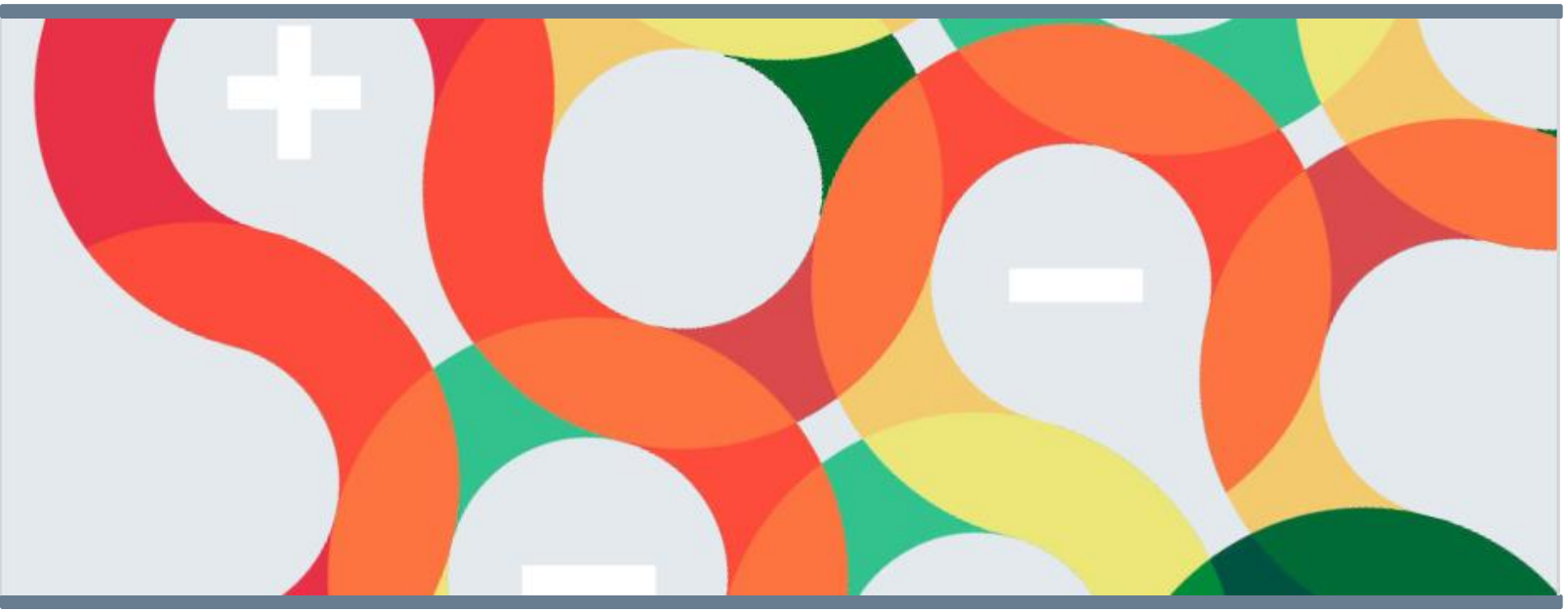
Elektrotechnik und
Informationstechnologie

Berner Fachhochschule
Haute école spécialisée bernoise
Bern University of Applied Sciences



Battery Technology
EPFL – Electrochemistry for materials technology

2024-10-07 Intro

Prof. Dr. Priscilla Caliandro

- BFH-Zentrum Energiespeicherung

Organization

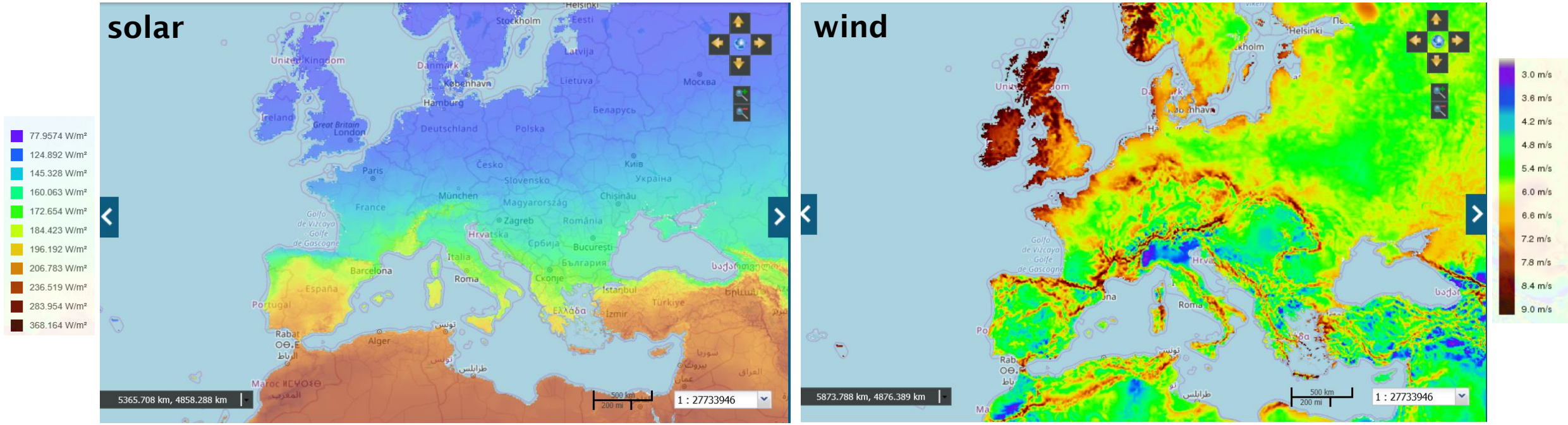
Program - Lecture 07/10

1. Problem statement
2. Motivation
3. Battery history and electrochemistry basics
4. Battery materials
5. Fundamental and working principle of Li-ion batteries
6. Battery definition
7. Battery performance

Problem Statment

Why do we need Energy storage?

Resources are unevenly spread over regions

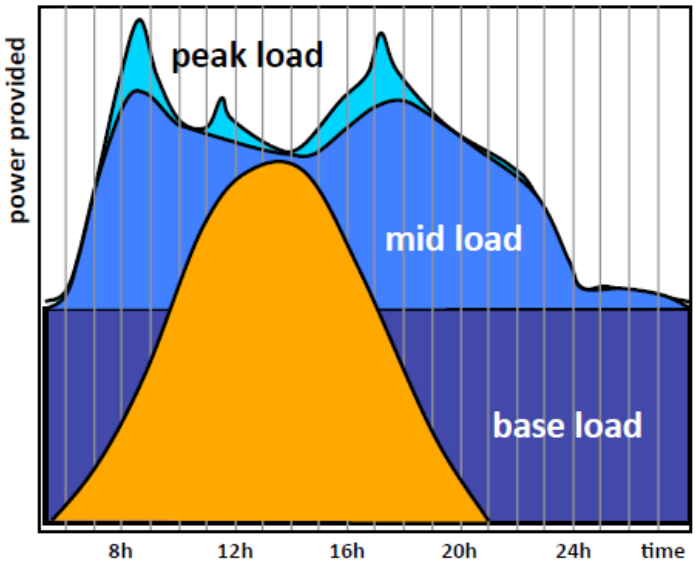


IRENA, VAISAL, global solar and wind maps https://irena.masdar.ac.ae/gallery/#map/543

and…

Why do we need Energy storage?

…they vary along the day



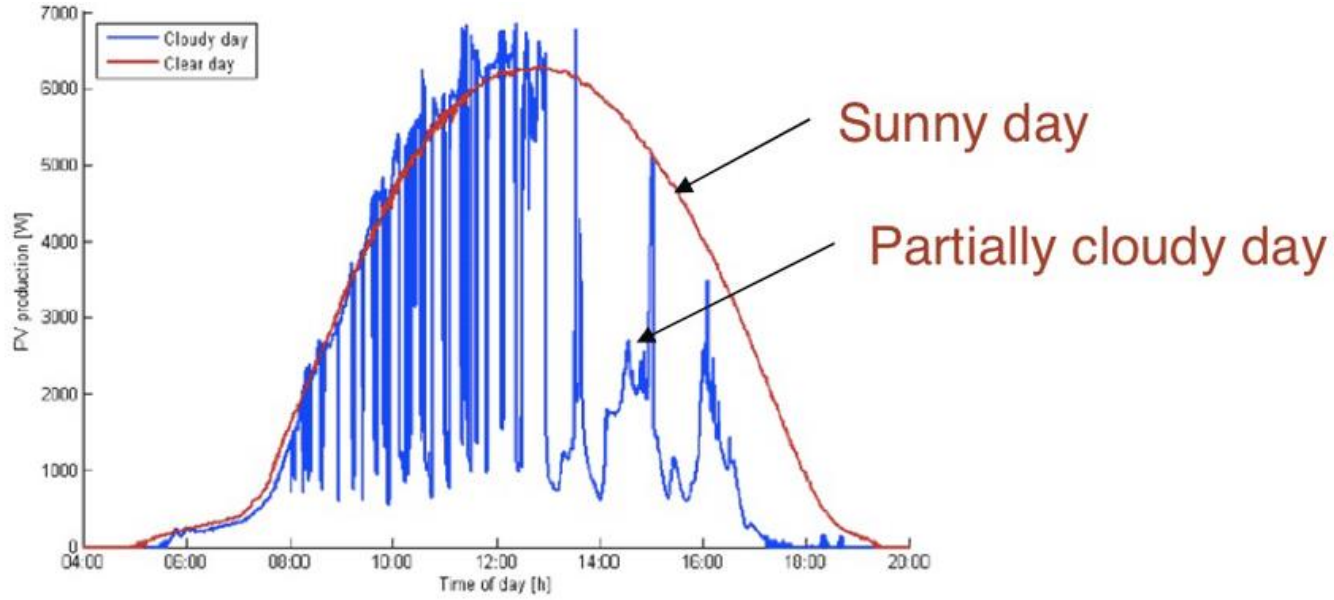
Problem 1:
Base load cannot be provided by renewables

Problem 2:
Peak load partially required when no renewables are generated

Need for energy storage to bring periods between when/where energy is **available** & when/where it is in **demand**

Why do we need Energy storage?

…they vary along the day



Problem 1:
Base load cannot be provided by renewables

Problem 2:
Peak load partially required when no renewables are generated

Need for energy storage to bring periods between when/where energy is **available** & when/where it is in **demand**

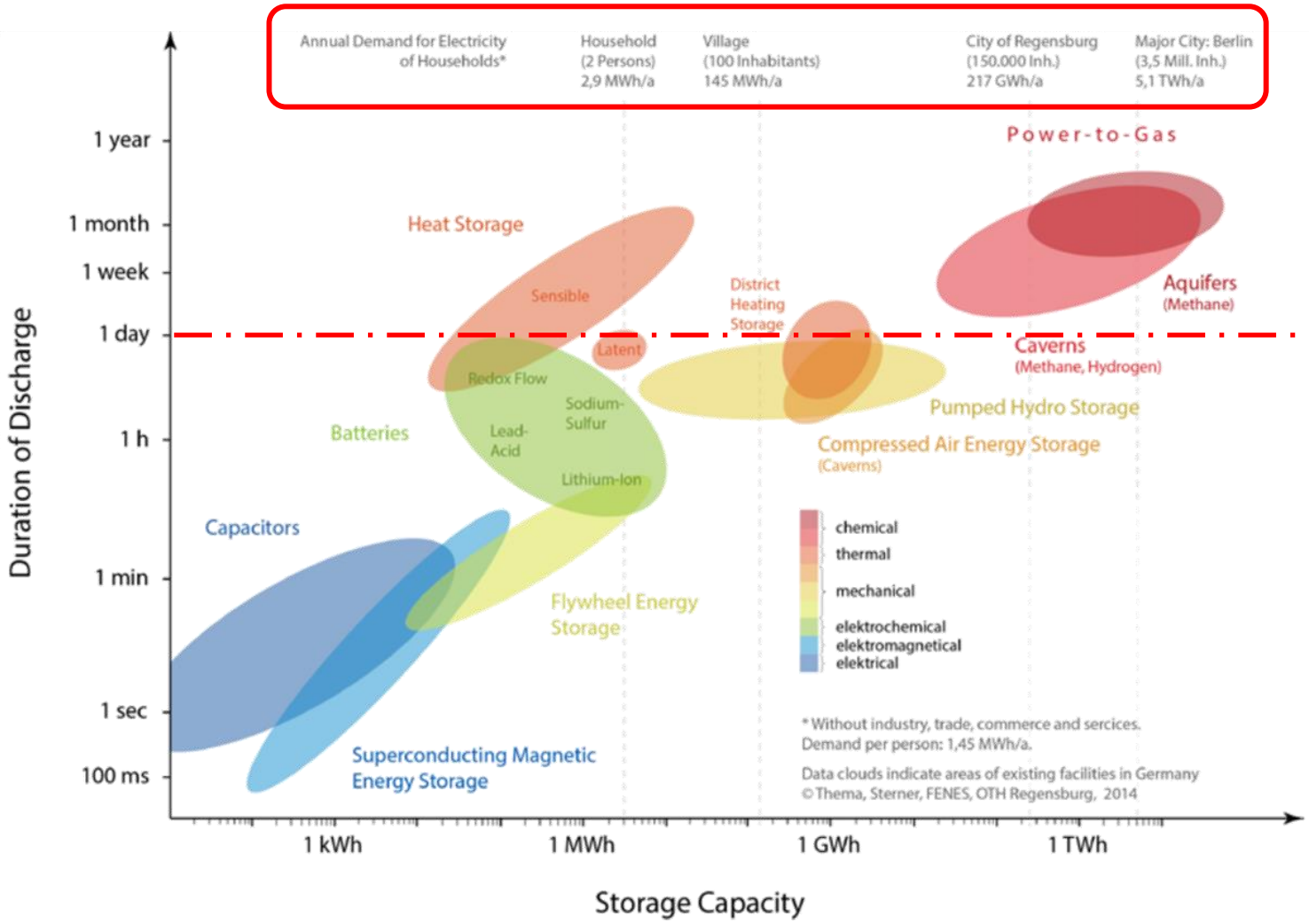
Why do we need Energy storage?

Energy storage can have different aims:

- Compensate **geographical distances** between supply and demand
- Compensate **time differences** between production and demand, fluctuations:
  - Bridging **seasonal differences** and imbalances
  - Leveling daily load cycles, '**peak shaving**'

- Improving stability, power quality, and reliability of supply

Comparison of Energy Storage technologies

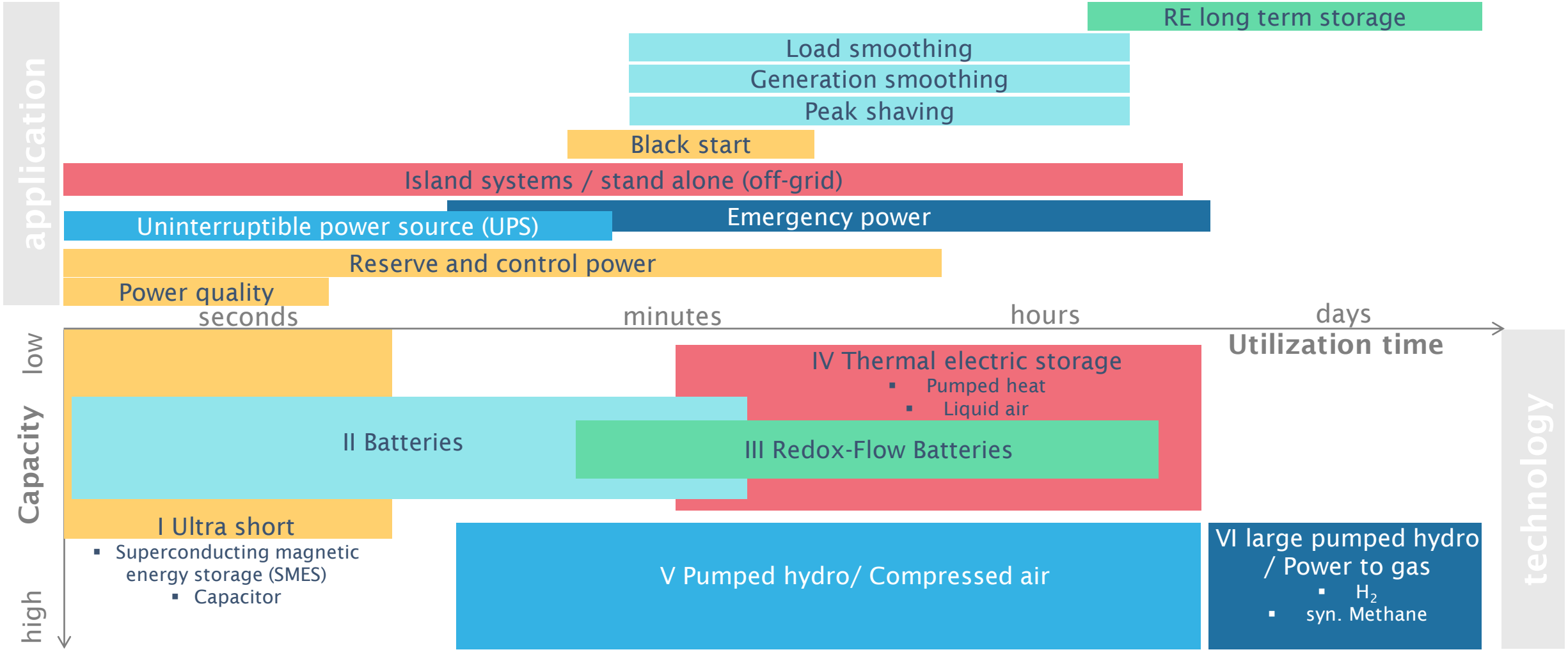


Observations:

- Reference energy needs as term of comparison
- Facilities comparison
- Different technologies for different applications
- Most technologies in the short-term storage range (t < 24h)
- Only chemical-energy storage systems using Power-to-Gas technologies reach the same scale and range as fossil fuel

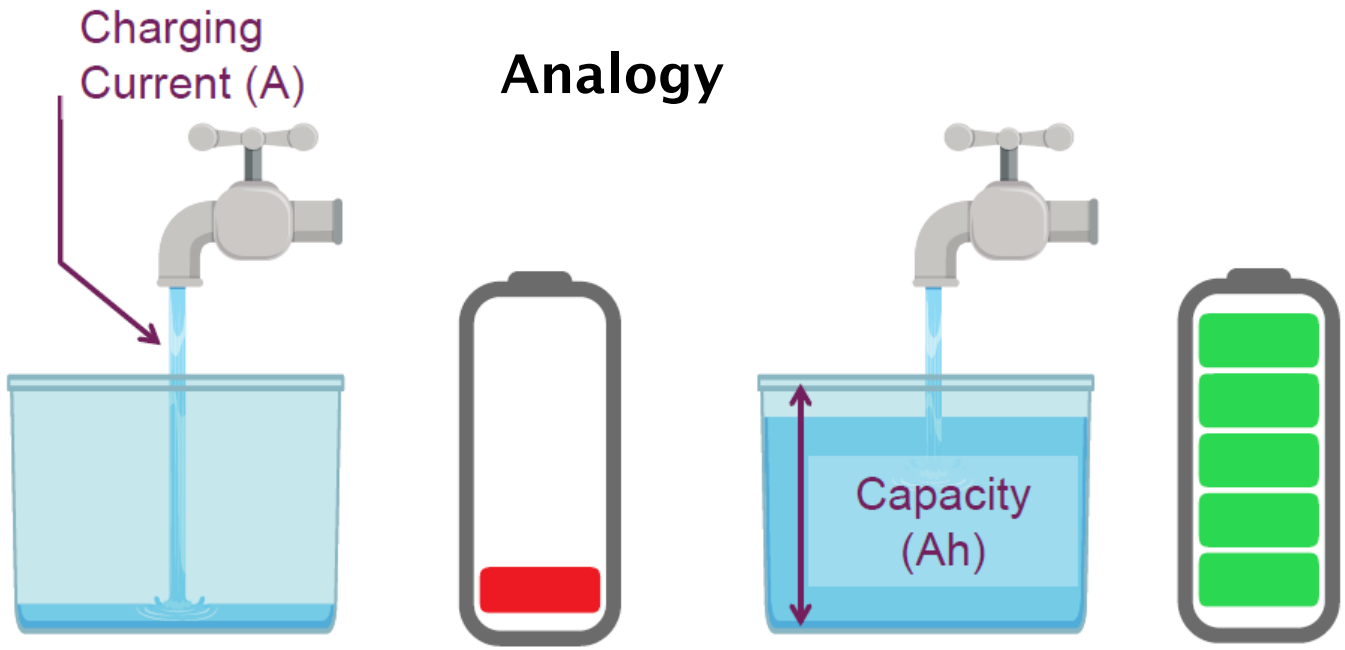
Source: Energy storage as strategic reserve and synergies in existing infrastructures – a systematic view Prof. Dr.-Ing. Michael Sterner et al.

Classification of Energy storage technologies



Source: Institute of Energy and Climate Research, Systems Analysis and Technology Evaluation (IEK-STE)

Energy Storage – Terminology



- Current (Amps): Rate of electron flow (water flow)
- Capacity (Amp -hours): Amount of electrons a battery can store (container size)
- Voltage (Volts): How much work can be done by each electron (like water pressure)
- Energy (Watt -hours): Total ability to do work –Capacity x Voltage

Electrochemical storage

Power density:
How quickly can that energy be delivered?

Supercapacitors:
specific energy 10^{-2}-10^{-1} Wh/kg
specific power 10^{1}-10^{4} W/kg
time scale 10^{-1}-10^{-5} h

- High power output
- Limited storage capacity

Batteries:
specific energy 10^{0}-10^{3} Wh/kg
specific power 10^{1}-10^{4} W/kg
time scale 10^{0}-10^{-1} h

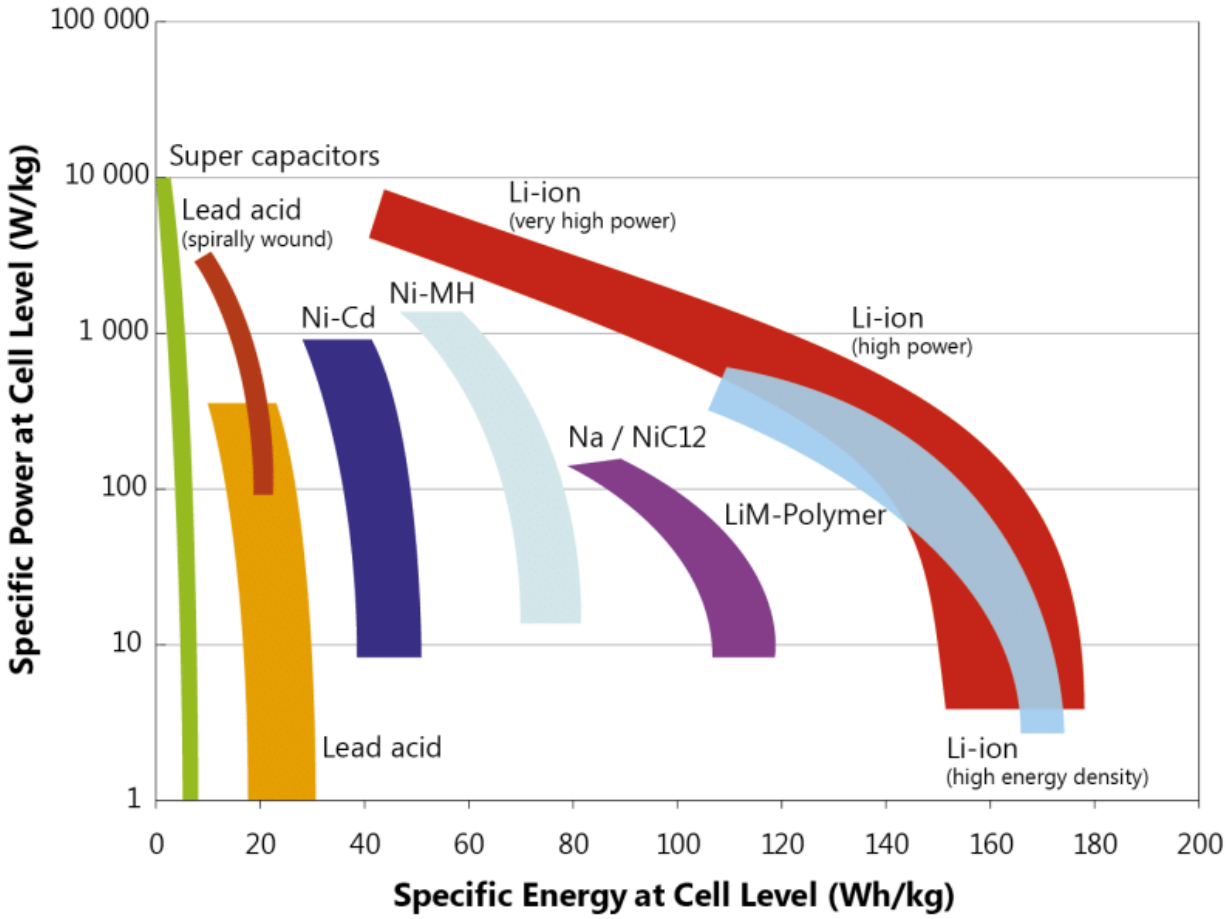
Fuel cells:
specific energy 10^{2}-10^{3} Wh/kg
specific power 10^{0}-10^{1} W/kg
time scale 10^{1}-10^{2} h

- low power output
- High storage capacity

Source: Rüdiger-A. Eichel, introduction to battery technology JESS 2014.

Energy density:
How much energy is available?

Batteries can be optimised for energy and power



Ragone diagram of the most common accumulators with distinction between high energy and high-power cells. Power values refer to the cell level

Electrochemical storage

- Batteries are Electrochemical energy storage devices
- Electrochemical devices can **convert electrical energy into chemical energy** and vice versa
- Since the conversion from chemical energy into electric energy is direct, the **conversion efficiency is high** (for batteries above 90%)

  (Internal Combustion engine efficiency: ~30-40%)

  (Fuel Cells: ~40-60%)

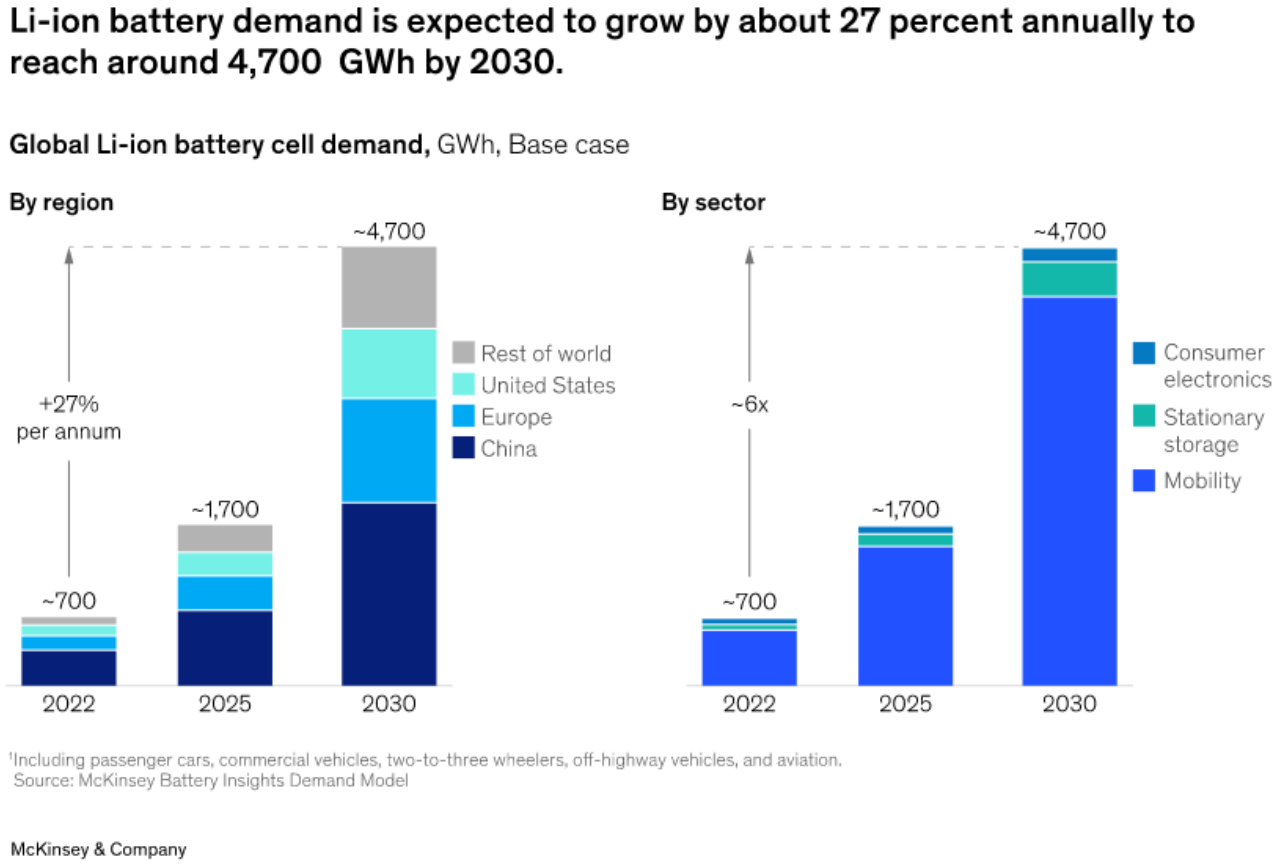
Motivation

Contex

Source: https://news.inventuspower.com/blog/li-ion-battery-regulations

Battery capacity needed in 2030

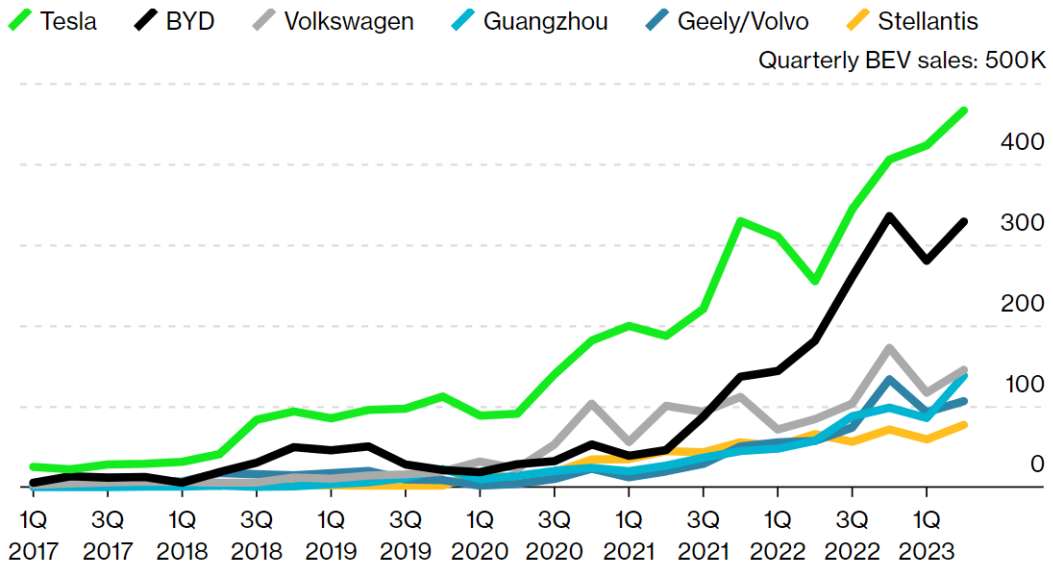
- **4’700 GWh a year** globally **by 2030**
- In 2030, 40 % of demand for lithium-ion batteries is expected to come from China
- Approximately **90 %** of the demand will come from **mobility** applications most importantly, electric vehicles (EVs)
- Over 26 million electric cars were on the road in 2022. (IEA 2023)



Source: https://www.mckinsey.com/industries/automotive-and-assembly/our-insights/battery-2030-resilient-sustainable-and-circular. McKinsey January 2023

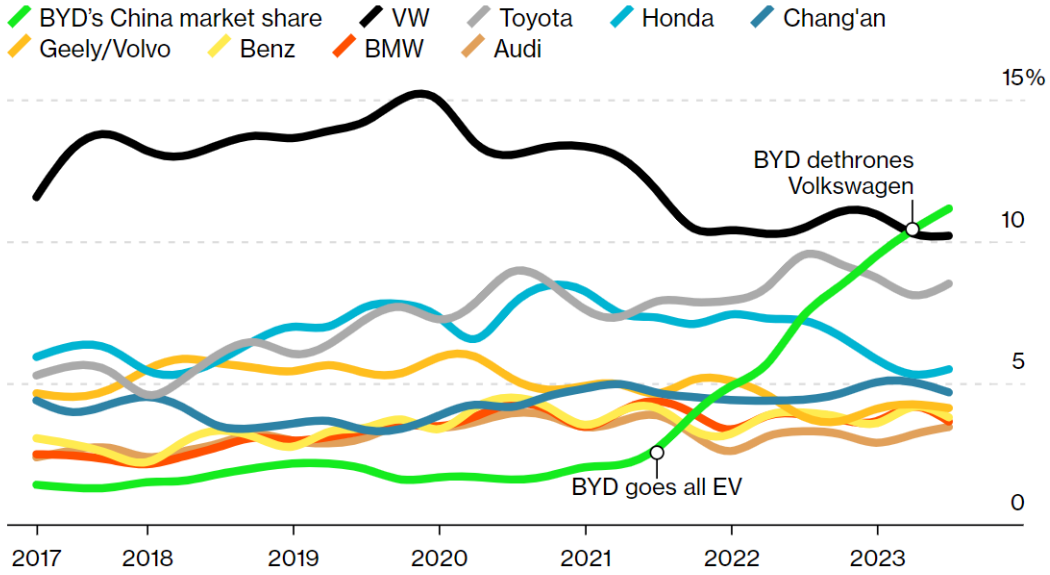
Electrification of Light Duty Vehicles (LDV)

- Old-school car manufacturers are losing the global **EV race.**
- **Volkswagen** is a distant third behind the new giants of the industry



Source: BloombergNEF

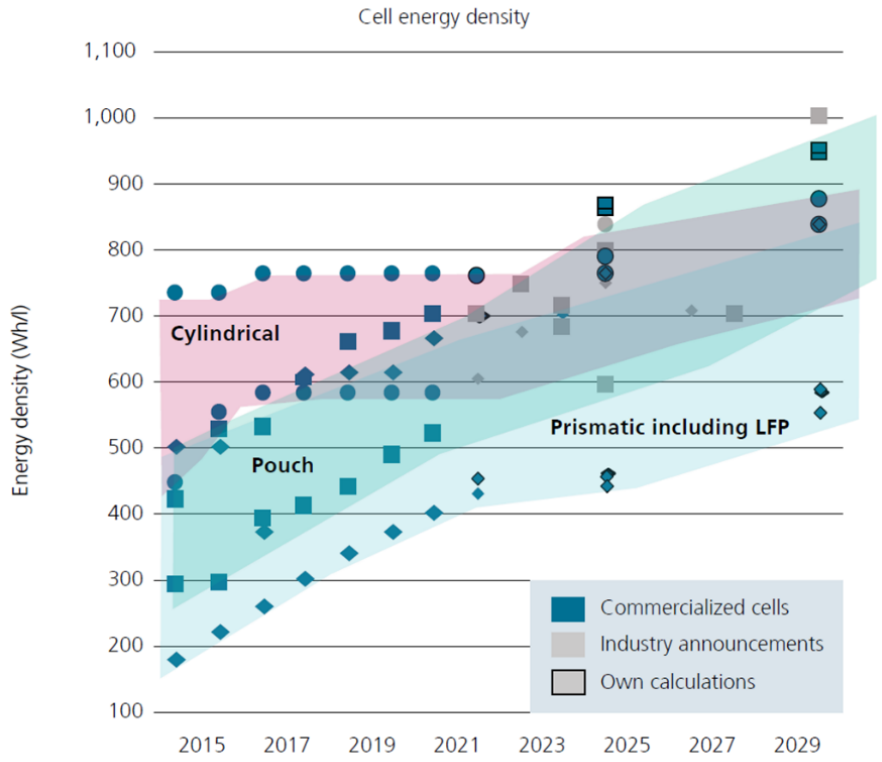
- Welcome to the future - China Edition BYD became the **best-selling car brand in China** by winning the EV market



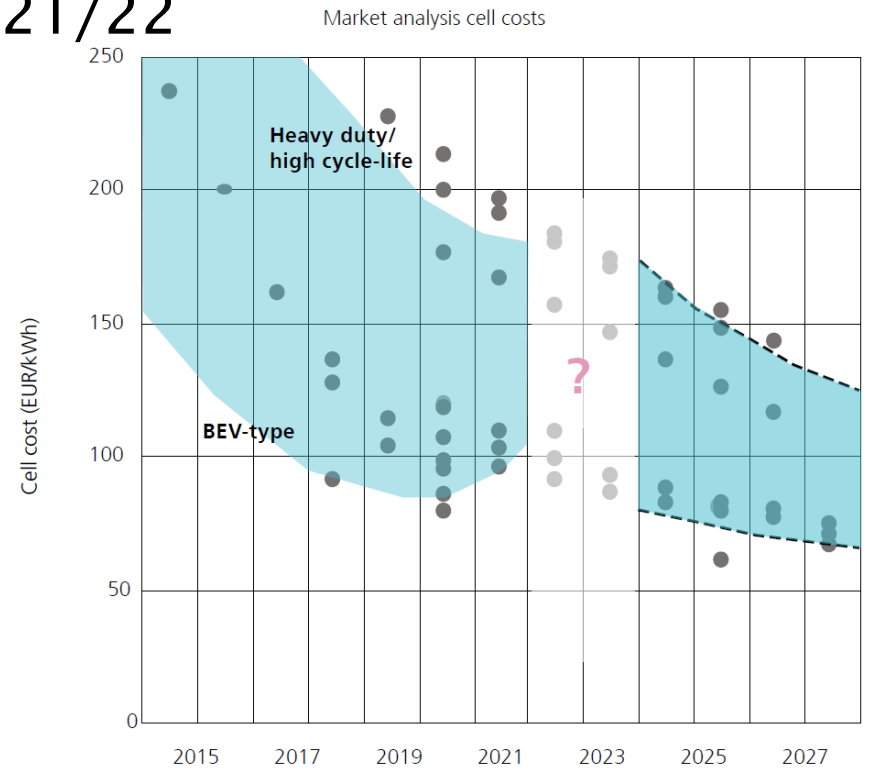
Source: China Automotive Technology and Research Center, Bloomberg Green

LIB Energy density increases, price falls

- Density development for LIBs: Industry announcements and development activities



- Analysis of the LIB cell cost forecasts of various analysts and the impact of the increase in raw material costs in 2021/22



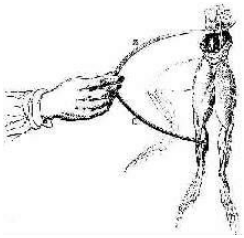
Quelle: Alternative Battery Technologies Roadmap 2030+; Fraunhofer ISI, Sept. 2023

Battery history and electrochemistry basics

Milestones in battery development

L.Galvani

1790

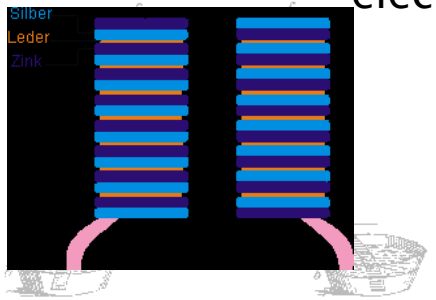


First electrochemical findings through **animal experiment**

A.Volta

1800

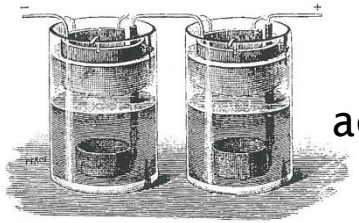
Bipolar battery



J.W.Ritter

1802

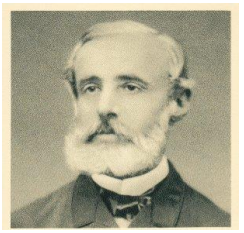
Rechargeable battery with copper electrodes



J.F. Daniell

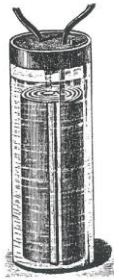
1836

"Commercial" primary battery for telegraphs



G.Planthé

1859

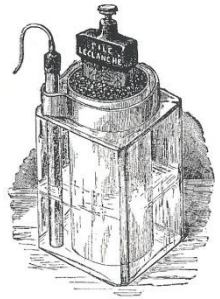


"Usable" accumulator

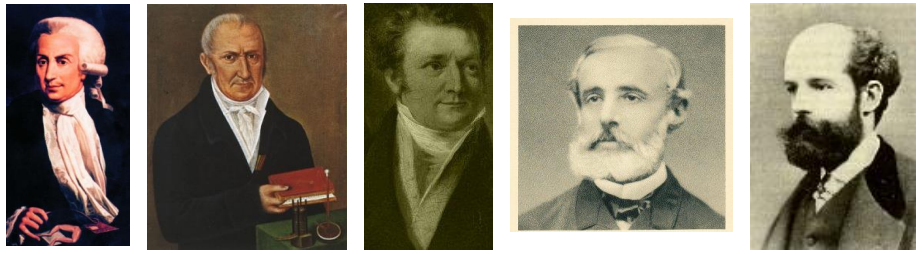
G.Leclanché

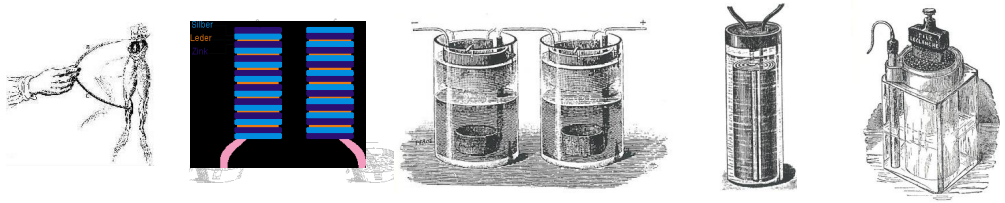
1860

Development of a "dry battery"



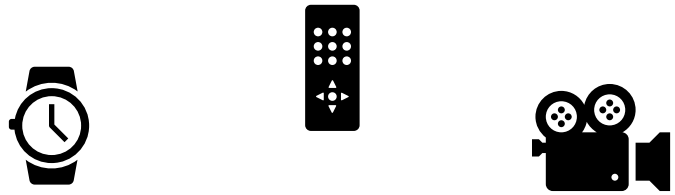
Milestones in battery development





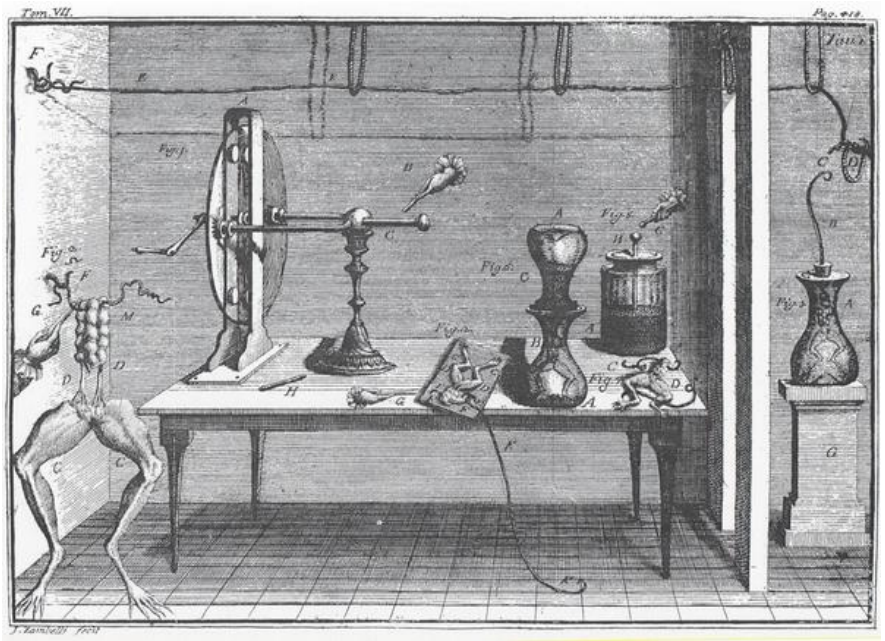
Overview:

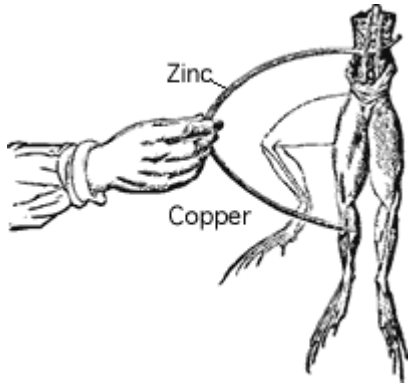
- First battery application **telegraph** (1836), until invention of **dynamo** 1869 for producing current
- 1970: first **rechargeable battery**
- Li-ion battery is a game changer for rechargeable batteries – New application



Luigi Galvani's error

Galvani carried out experiments with an **electrostatic machine and frogs' legs**. He hung prepared frog legs with a **brass hook on a metal railing on his balcony**. Whenever a frog leg touched the railing (wind), it started to twitch. He attributed this to a so-called "**animal electricity**"..



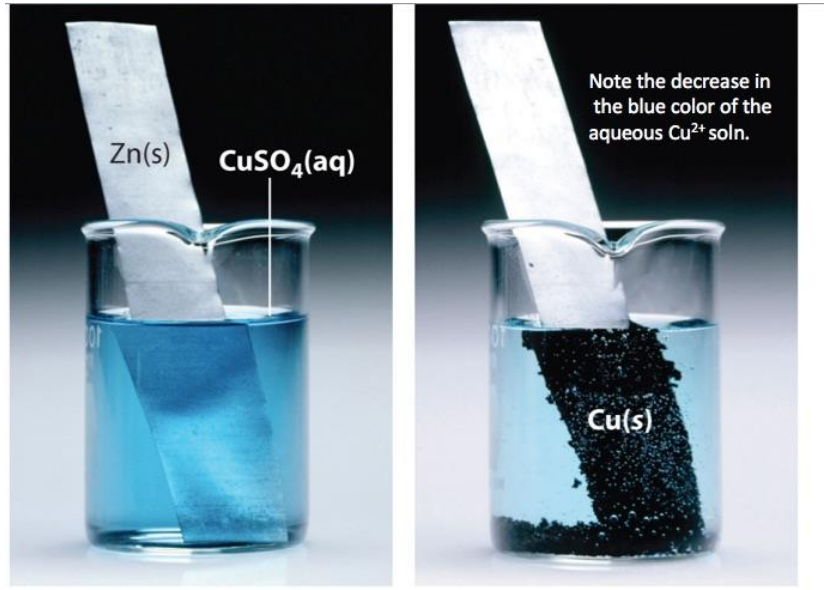


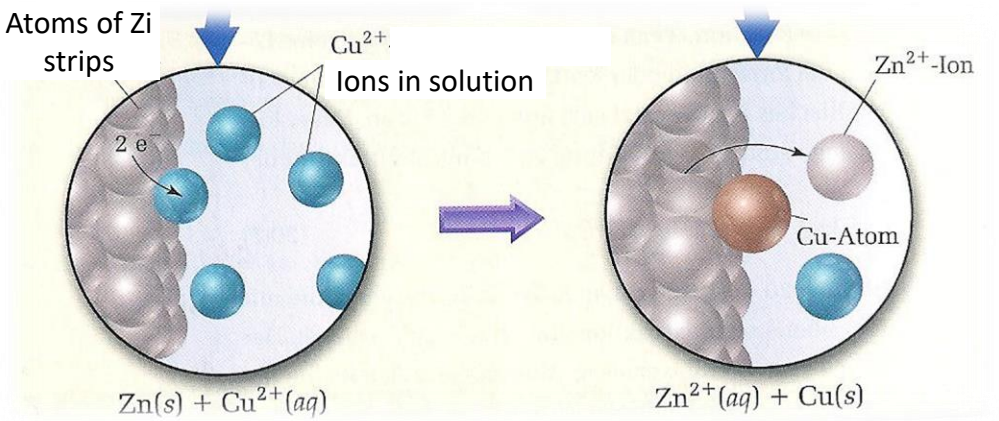
Volta realized a few years later that the frog's legs were only the **electrolyte**, which forms a so-called **galvanic element** with a **brass electrode and an iron electrode**.

Galvanic element - Redox Reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

- In a spontaneous redox reaction, **electrons are transferred**, and **energy is released**.
- using the example of **zinc** and **copper**
- Such a spontaneous reaction is obtained by placing a **strip of zinc** in a **solution containing Cu2+ ions**. The bluish particles of the Cu2+(aq) ions fades and metallic copper settles as dark material on the zinc strip and beaker bottom.



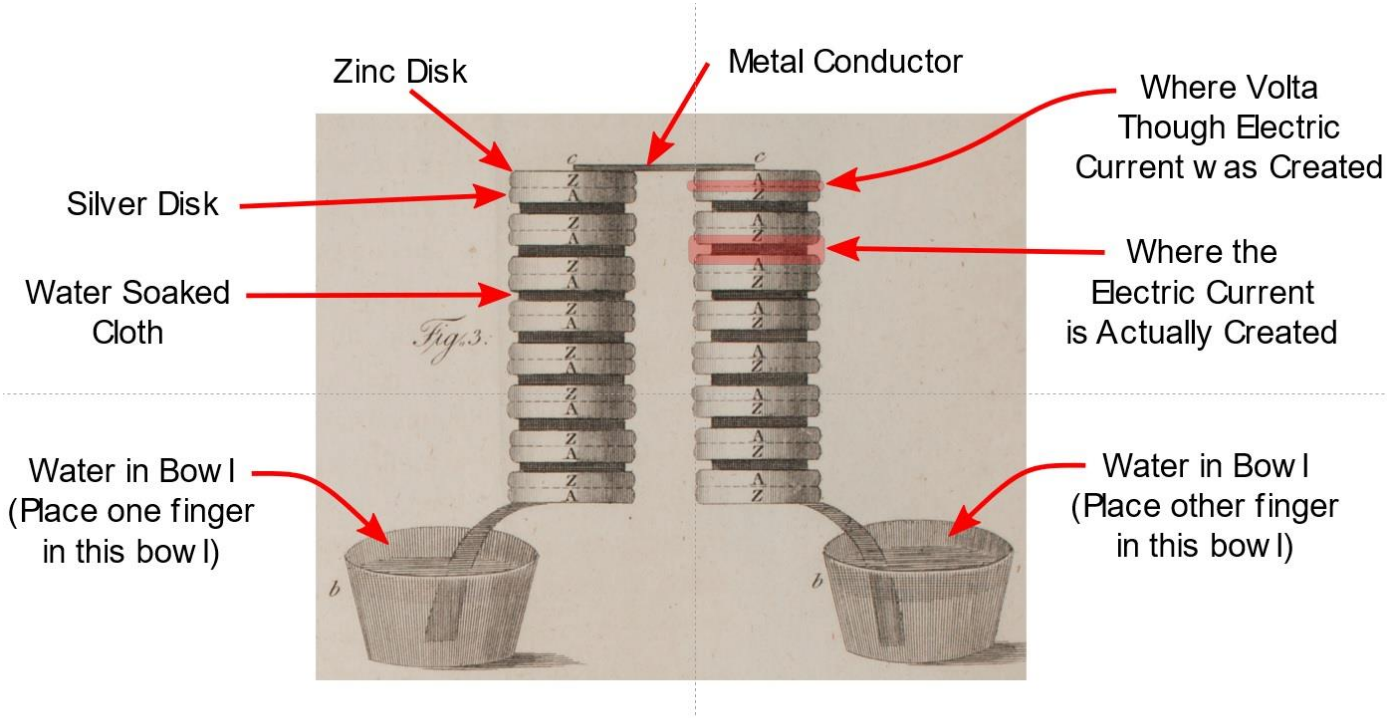


- **Galvanic cells** use this **spontaneous redox reaction**, whereby there must be **no direct contact** between the elemental zinc and the copper ions. The reduction and the oxidation **take place locally separated in so-called half cells**.
- **Electrons** can only move via an **external path**.

Oxidation is the *loss* of electrons or an *increase* in the oxidation state of an atom (Anode)
Reduction is the *gain* of electrons or a *decrease* in the oxidation state of an atom (Cathode)

Alessandro Volta and the voltaic pile

- Volta stacked **several pairs of alternating** copper (or silver) and zinc discs (electrodes) separated by cloth or cardboard soaked in brine (electrolyte) to increase the electrolyte conductivity. When **the top and bottom plates were connected by a wire**, an electric current flowed through the voltaic pile and the connecting wire.

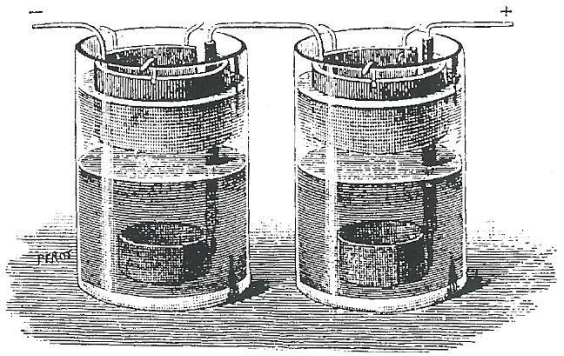


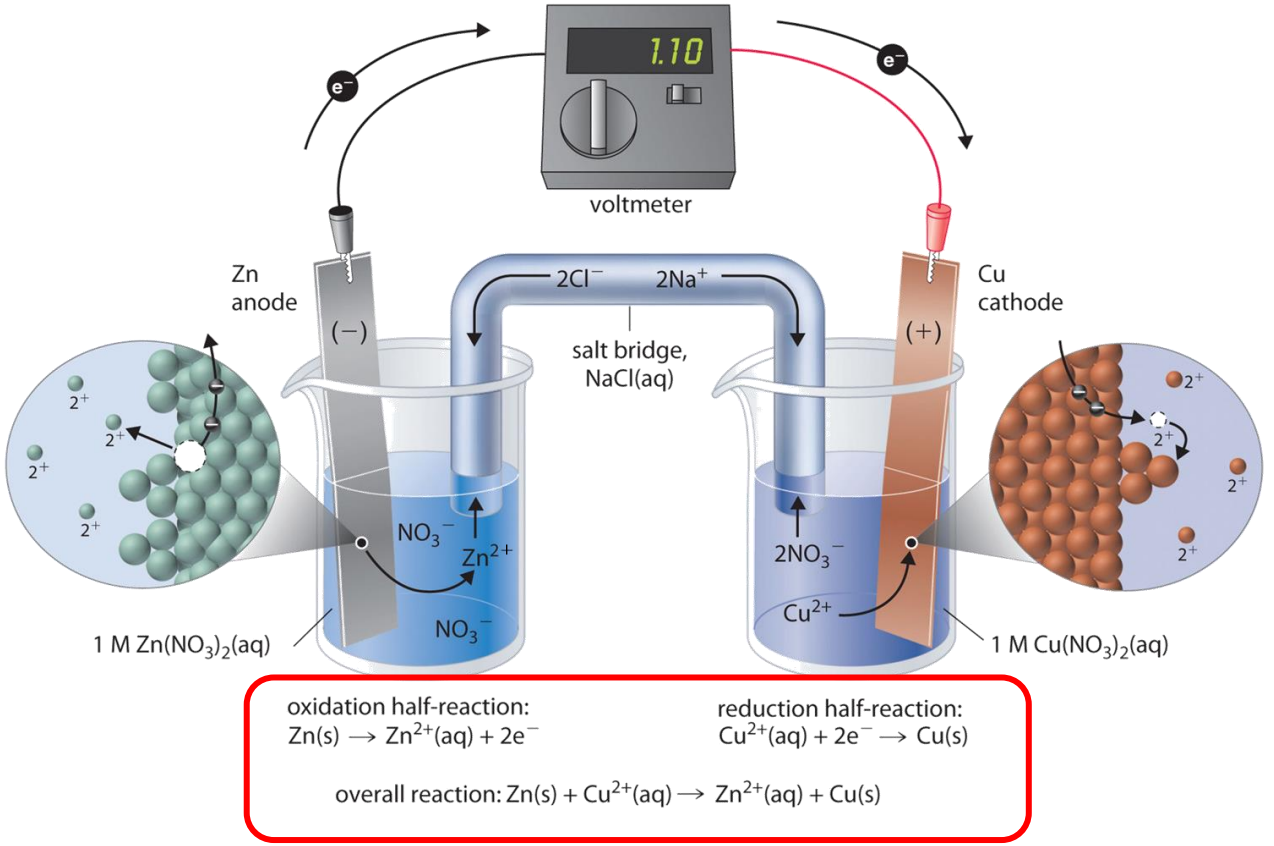
Daniell cell by John Frederic Daniell

It became the main source of power for electric telegraphs!

If the two half cells are connected via an electrolyte bridge, the ions (cations, anions) can migrate and **balance the charges in the two half cells**. Electrolytes consist either of:

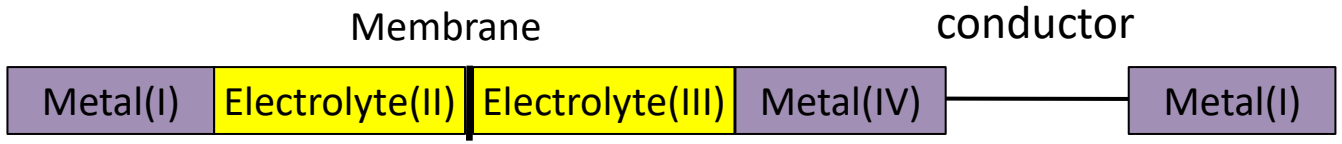
- acids (H2SO4)
- bases (NaOH, KOH)
- or salts (NaCl, nitrates)





Basic structure of a galvanic cell

A prerequisite for the generation of electrical energy from chemical energy is **charge separation**. This means that the chemical reaction must be separated into an **anodic and a cathodic electrode reaction** . The two electrodes must be separated/connected by an **ion conductor**. The electrons are exchanged via an external circuit. **The structure of the so-called galvanic cell**:



e.g.: $Zn \rightarrow 2e^- + Zn^{2+} \rightarrow ZnSO_4$ $Na^+NO_3^-$ $CuSO_4 \rightarrow Cu^{2+} + 2e^- \rightarrow Cu$

At the **anode** the reducing agent Zn is oxidised

At the **cathode** the oxidant $CuSO_4$ is reduced

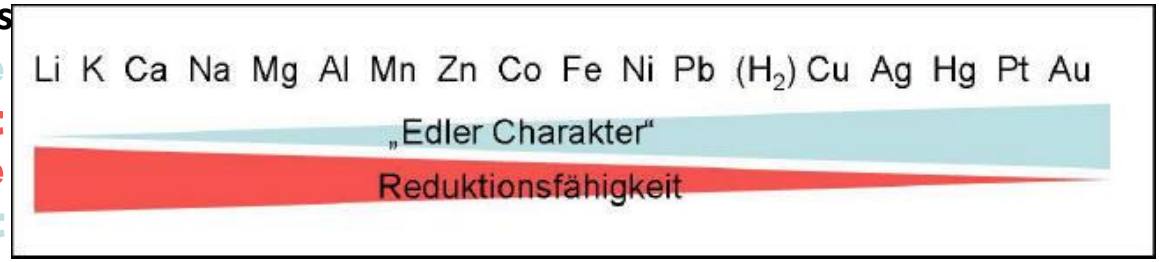
Alkaline metals

The easiest to oxidize

The strongest reducing agent

The most difficult to reduce

The weakest oxidant



Precious metals

The most difficult to oxidize

The weakest reducing agent

The easiest to reduce

The strongest oxidizer

Precious metals tend to accept electrons and are thus **reduced**

Alkaline metals tend to give up electrons and are therefore easily **oxidized**.

The Relationship of Cell Potential & Gibbs Free Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the **amount of energy available** to do electrical work, depends on both the **cell potential and the total number of electrons** that are **transferred** during a **reaction**.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process.

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

$\Delta G^0 = Gibbs\ Free\ Energy$
$\Delta H^0 = Standard\ Enthalpy\ Change$
$\Delta S^0 = Standard\ Entropy\ Change$
$T = Temperature$

Relationship with electrical potential

$\Delta G = -nFE$ *or in* ***standard condition*** $\Delta G^0 = -nFE^0$

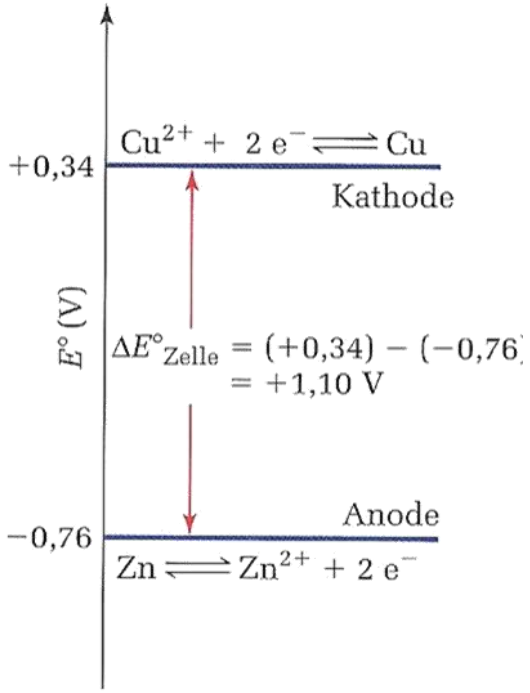
$\Delta G^0 = Gibbs\ Free\ Energy$
$n = no\ of\ moles\ of\ electrons\ transferred$
$F = Faraday's\ constant$
$E^0 = EM\mathrm{F} = \mathrm{Electromotive\ Force}$

The emf E of the source is defined as the work dW done per charge dq: E = dW/dq

Standard electrode potential

It is the measure of the individual potential of a reversible electrode at **standard state with ions at an effective concentration of 1mol dm^{-3} at the pressure of 1 atm and 25 ° C.**

$\Delta G = -nFE$ *or in* ***standard condition*** $\Delta G^0 = -nFE^0$



Strong oxidizing agent

Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$
+1.51	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$
+1.36	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
+1.23	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
+1.06	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$
+0.96	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$
+0.54	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$
+0.40	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
0 [defined]	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$
−0.83	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Strong reducing agent

The EMF under non-standard conditions: The Nernst equation

- The EMF depends on the **temperature** and the **concentration** of the reaction mixture

$$\Delta E = \Delta E^0 - \frac{RT}{nF}\ln Q \qquad \Delta E = \Delta E^0 - \frac{0.0592}{n}\log Q \quad at \quad T = 298K$$

ΔE^0 is the equilibrium potential, Q is called "reaction coefficient“ (ratio of concentration)

$$\Delta E = E^0 - \frac{0.0592}{n}\log\frac{[Ox]}{[Red]}$$

- In the case of the zinc/copper redox reaction, the following relationships are obtained:

$$\Delta E = 1.10V - \frac{0.0592V}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

- For concentration 5.0 M for [Cu2+] and 0.05 M for [Zn2+] and n=2 (2 electrons) the equation is:

$$\Delta E = 1.10V - \frac{0.0592V}{2}\log\left(\frac{0.050}{5.0}\right) = 1.10V - \frac{0.0592V}{2}\cdot(-2.00) = 1.16V$$

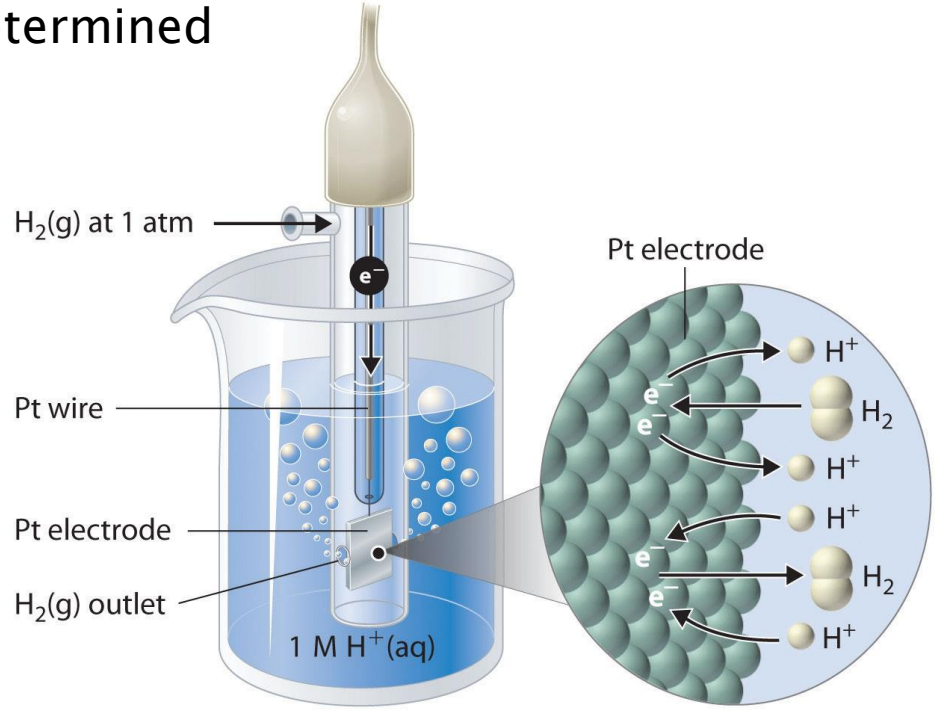
At this concentration, a **high initial EMF is achieved**, and this occurs at **OPEN CIRCUIT**. Through the operation (discharge) of the cell, **the voltage then decreases** further and further.

The standard hydrogen electrode (SHE)

The standard hydrogen electrode (SHE) serves as a reference electrode.

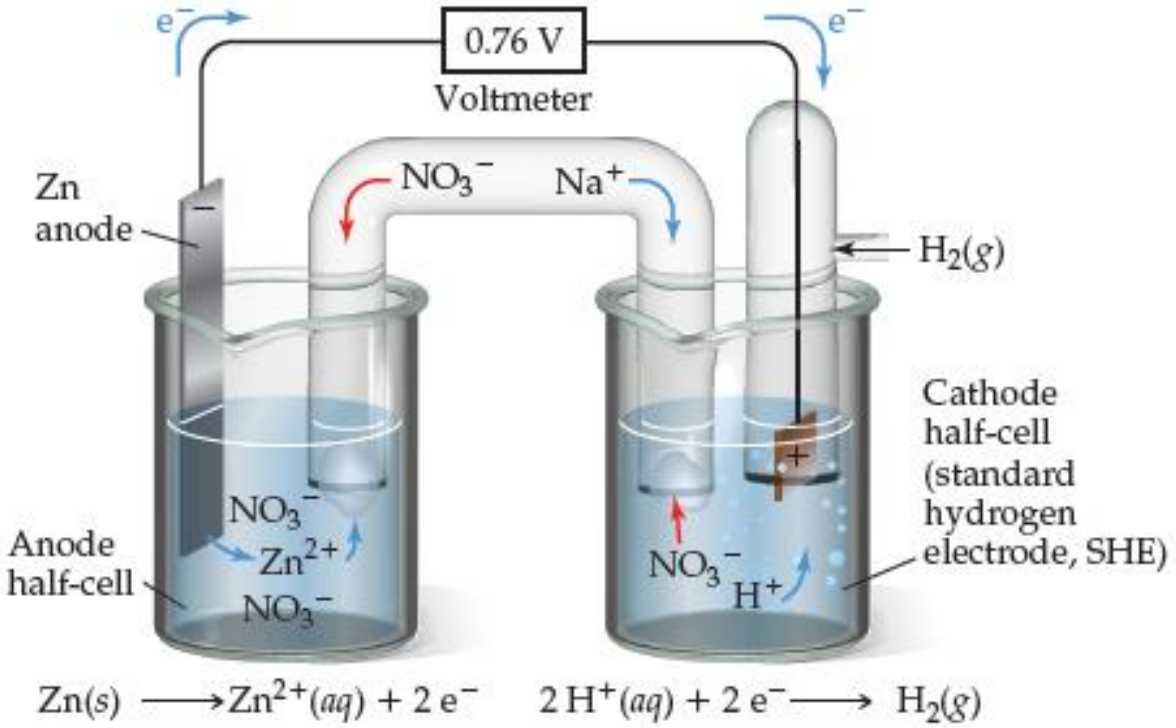
A SHE consists of an electrode with finely divided platinum, which is in contact with H_2 at 1 atm, and a solution with the H^+ ion concentration of 1M (mol/l).

Combining the Zn^{2+}/Zn^{-} half-cell with the SHE, the normal potential of this half-reaction can be determined



half-reaction at Pt surface:

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$



Energy and Power content

C: Capacity = Current content

The **specific energy content** is determined by the electrode material used. The specific capacity can be derived from the **specific material data** and the F = Faraday constant = 96485 $Asmol^{-1}$ (As = ampere-second)

storage capacity (Wh)	free energy of reaction ($\Delta G = -n\ F\ E$)
specific energy (Wh/kg)	$n\ F\ E\ /\ \Sigma\ R_{wt}$
specific power (W/kg)	$V\ I\ /\ \Sigma\ R_{wt}$

$R_{wt} = molecular\ weight$

Tabulated values

Computed values

The theoretical capacity C indicates how much charge a cell can hold.

Active Material	Molecular weight (g/mol)	Nbr of exchanged electrons	Specific Capacity (mAh/g)	Standard Electrode potential against SHE (V)	Specific Energy (Wh/g)
Li	6.94	1		-3.05	
Na	22.99	1		-2.71	
Mg	24.31	2		-2.38	
Zn	65.38	2		-0.76	
Cd	112.41	2		-0.40	
Pb	207.20	2		-0.13	
Cu	63.55	2		0.34	

The data refer to the charged **active material**. Any active **electrolyte masses**, e.g. H_2SO_4 in the lead battery or H_2O in the Ni-Cd battery, and all inactive masses are **not included**.

Battery Materials

Why Lithium?

Strong oxidizing agent

Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$
+1.51	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$
+1.36	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
+1.23	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
+1.06	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$
+0.96	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$
+0.54	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$
+0.40	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
0 [defined]	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$
−0.83	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

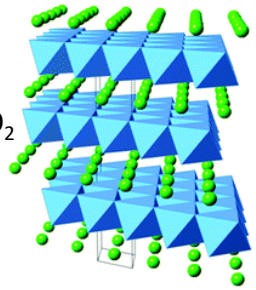
Strong reducing agent

Lithium-ion batteries

- Lithium-Nickel-Manganese-Cobalt (NMC) – positive electrode
- Lithium-Nickel-Cobalt-Aluminum (NCA) – positive electrode
- Lithium Iron Phosphate (LFP) – positive electrode
- Lithium Titanate (LTO) – negative electrode

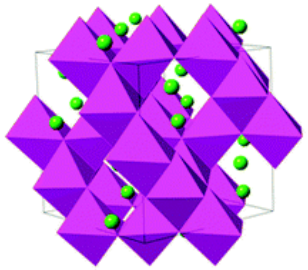
Electrodes materials of conventional Li ion battery

MeOx: Layered structure



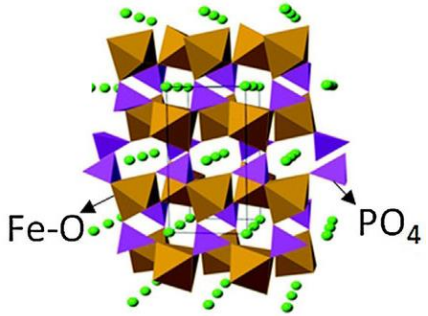
$LiCoO_2$
$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
$LiNiO_2$

MeOx: Spinel structure

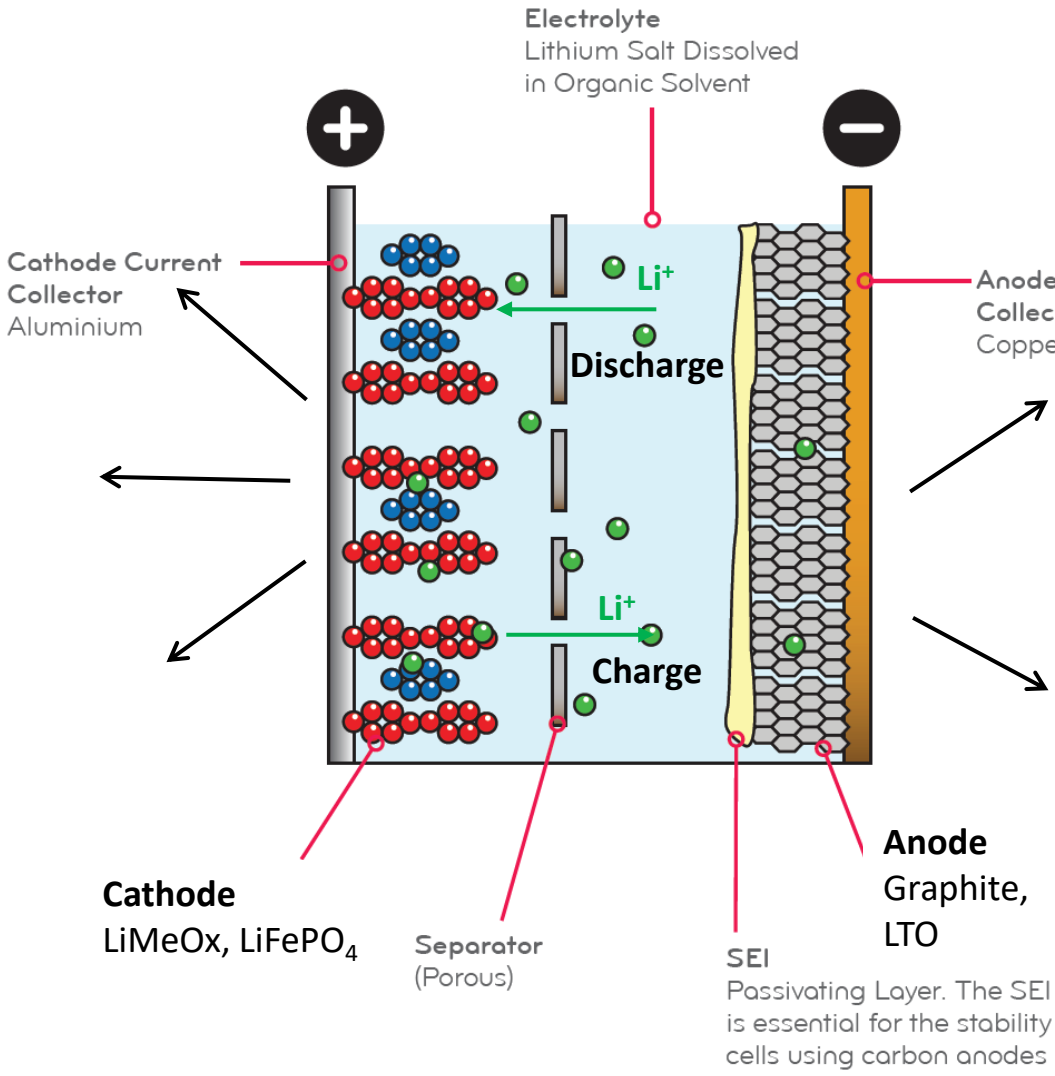


$LiMn_2O_4$

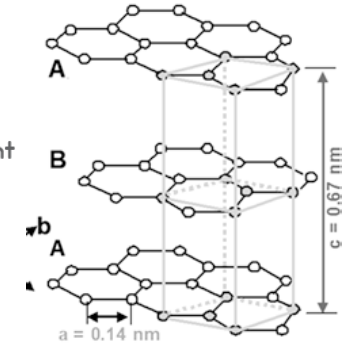
$FePO_4$: Olivine structure



$LiFePO_4$

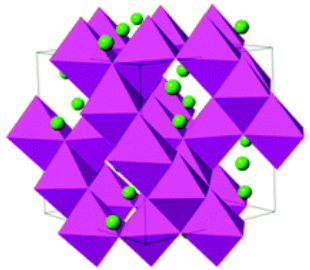


Graphite or C: Layered structure



C

Lithium titanate LTO: Spinel structure

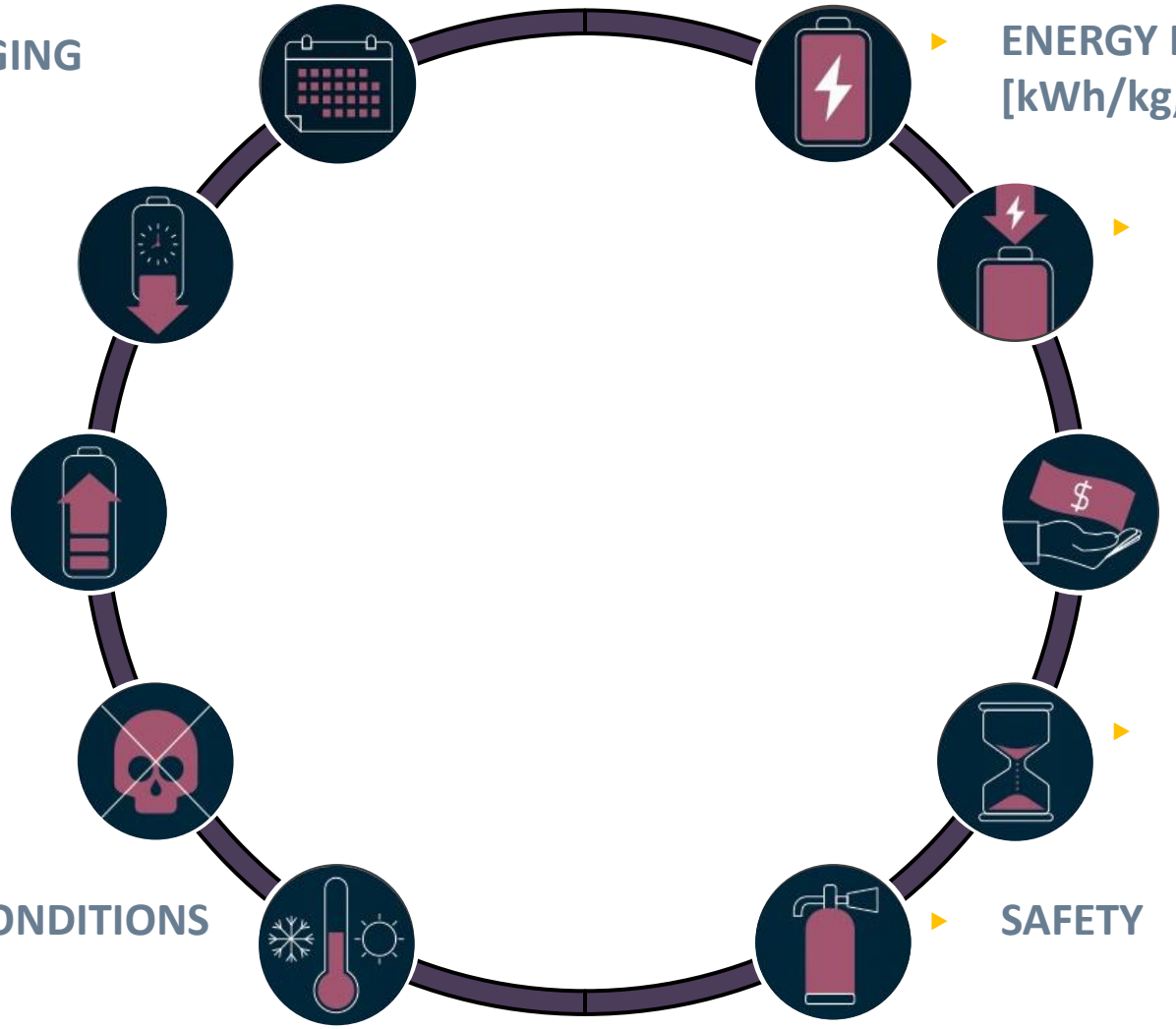


$Li_4Ti_5O_{12}$

Source: Nitta et al., Materials Today, „Li-ion battery materials: present and future", 2014

Important battery assessment criteria

- CALENDARIC AGING
- ENERGY DENSITY [kWh/kg, kWh/m³]
- SELF-DISCHARGE
- POWER DENSITY [kW/kg, kW/m³]
- FAST CHARGE/DISCHARGE [C-Rate]
- COST [CHF/kWh, CHF/kW]
- TOXICITY, RECYCLABILITY
- LIFETIME [Full Cycles]
- OPERATING CONDITIONS [T_{min}, T_{max}]
- SAFETY



Source: https://www.visualcapitalist.com/evolution-of-battery-technology/

Overview of electrode materials

Positive Electrode materials

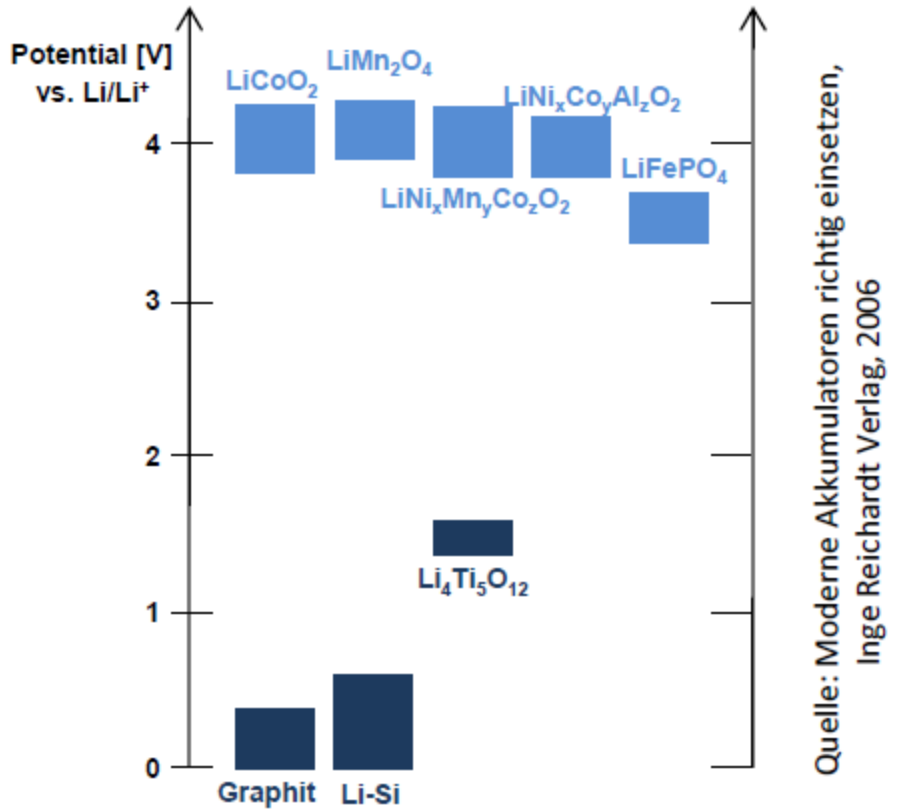
Metal -oxide

$LiCoO_2$	«LCO»
$LiNi_xMn_yCo_{1-x-y}O_2$	«NMC»
$LiNi_aCo_bAl_{1-a-b}O_2$	«NCA»
$LiNiO_2$	«LNO»
$LiMn_2O_4$	«LMO»

Phosphate

$LiFePO_4$	«LFP»

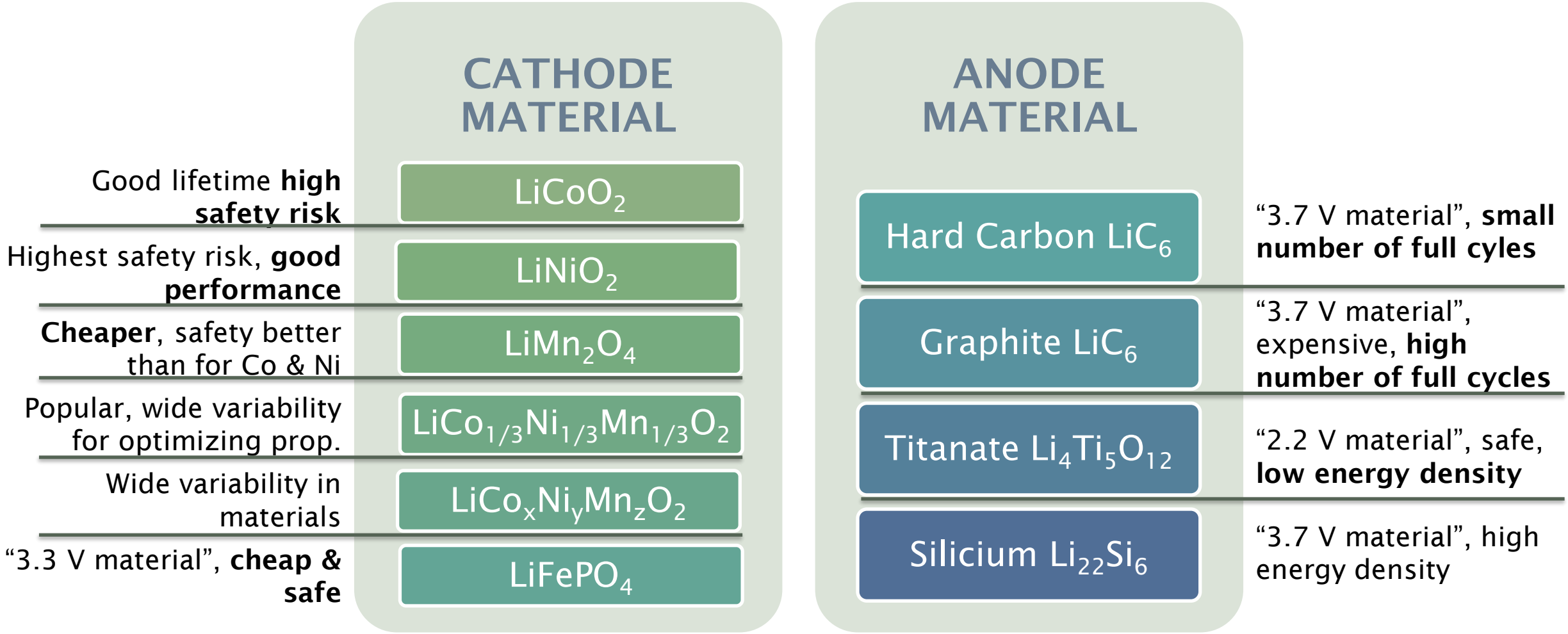
x mostly 0.33; y mostly 0.33 (Less Co in the Future, but more Ni)
a mostly 0.80; b mostly 0.15;



Negative Electrodes materials

C	«Graphite»*
$Li_4Ti_5O_{12}$	«LTO»

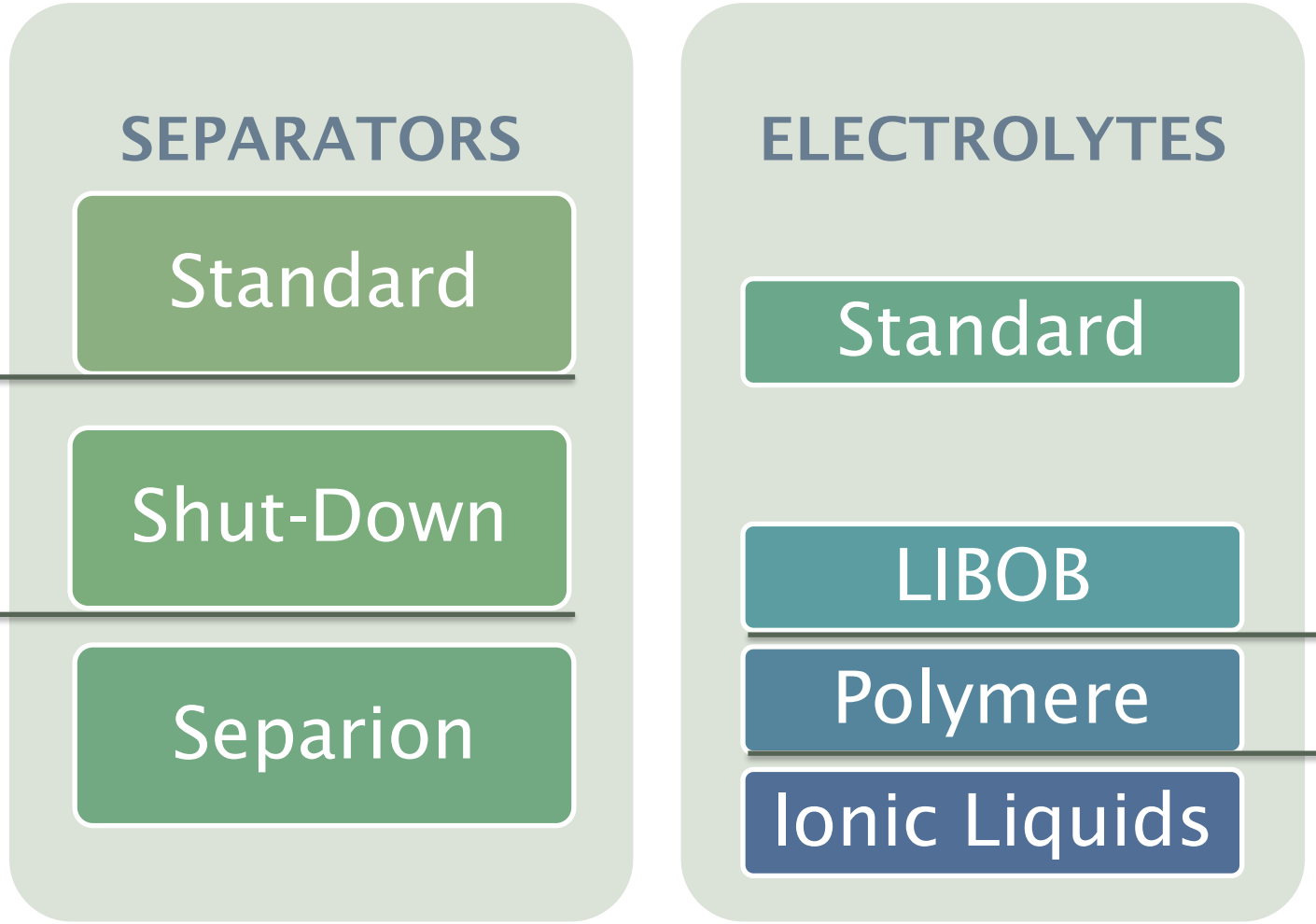
Electrodes materials of conventional Li ion battery



Adapted from Dirk Uwe Sauer - Summer School on Fuel Cells, Battery, and Hydrogen Technology Greece, 19.09.2013

Electrodes materials of conventional Li ion battery

Electrolyte and binding materials are central component regarding low-temperature and lifetime performance.



Generally: expensive subcomponent in Li-Ion cells

Multilayered separator with melting layer (**high resistance when overheating**)

Ceramic separator **avoids short-circuits when overheated**

Electrolytes: EC, PC, DMC, DEC, EMC
Conducting Salt: $LiPF_6$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$
Additive

Higher safety

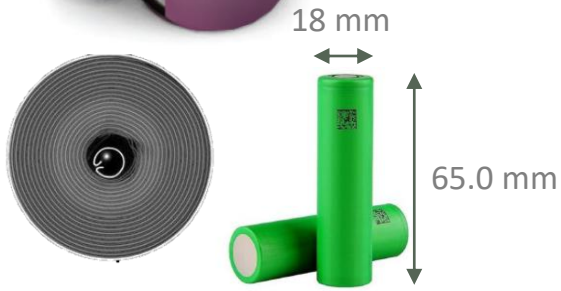
Safe, low conductance at room temperature

Possible electrolyte for 5-volt cells

Adapted from Dirk Uwe Sauer - Summer School on Fuel Cells, Battery, and Hydrogen Technology Greece, 19.09.2013

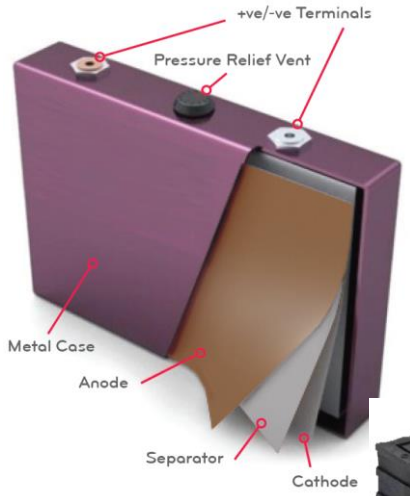
Different cell formats

Cylindrical



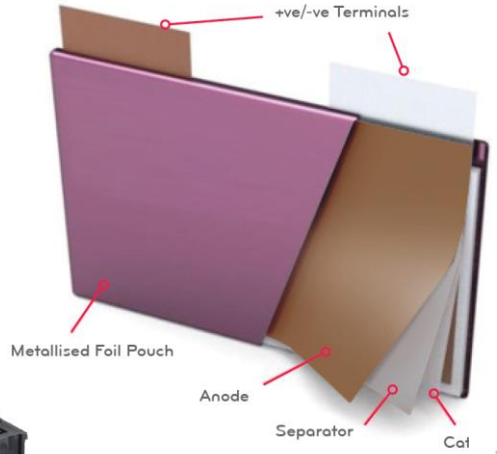
- A lot of experience in cell design
- High life-time
- Complex Cooling
- Supplier e.g. Saft, Sanyo, LG

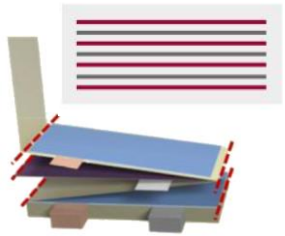
Prismatic



- Easy stacking in battery packs
- Combines characteristics of the other cell designs
- Supplier e.g. Sanyo, Lishen

Pouch

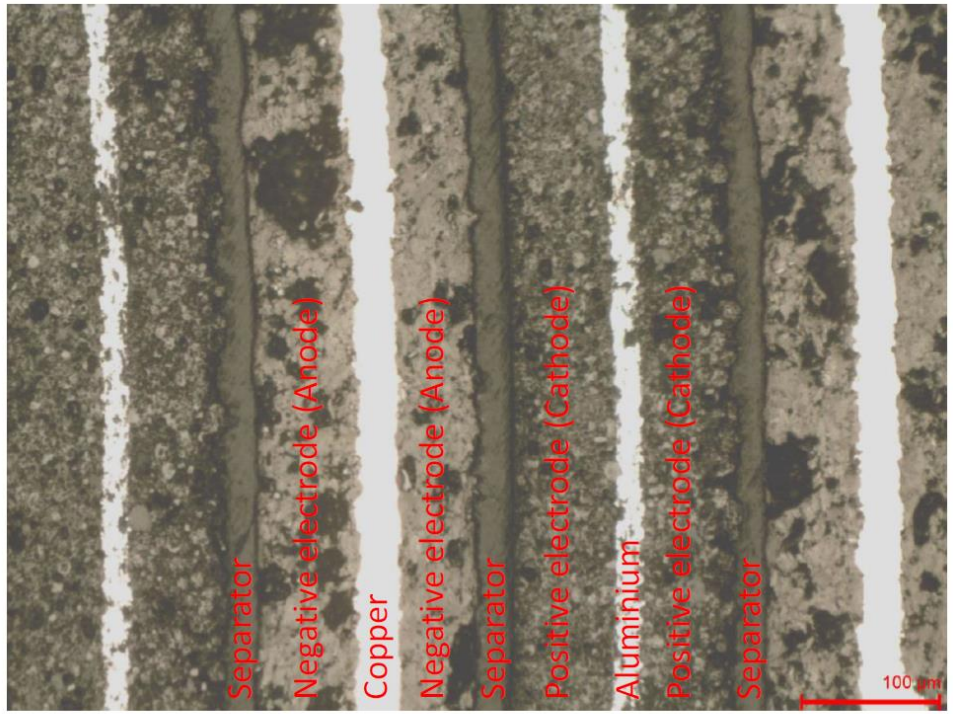




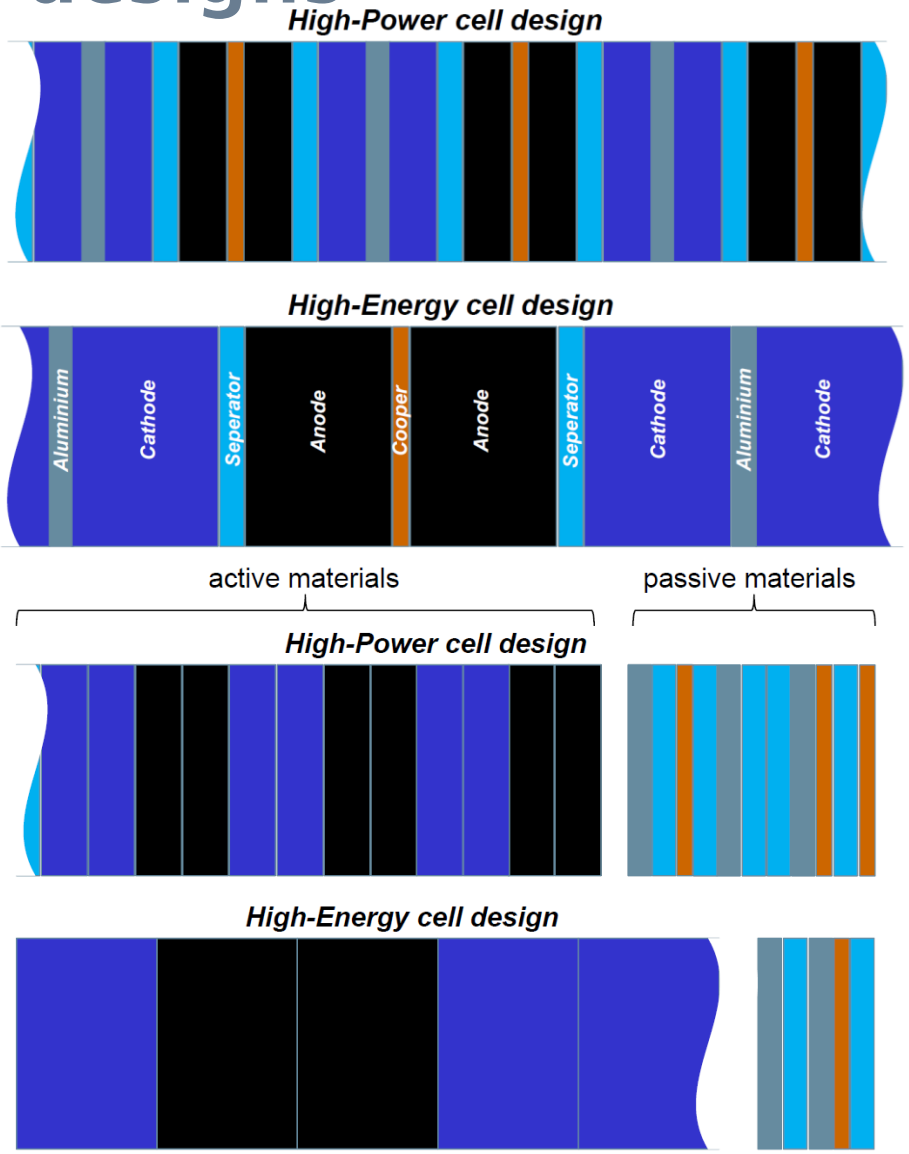
- Good cooling character
- High energy density
- Main question: Tightness of the film
- Supplier e.g. Kokam, Leclanche

Quelle: Johnson Matthey Battery Systems, 2012, „Our Guide to Batteries“

High-Power and High-Energy cell designs

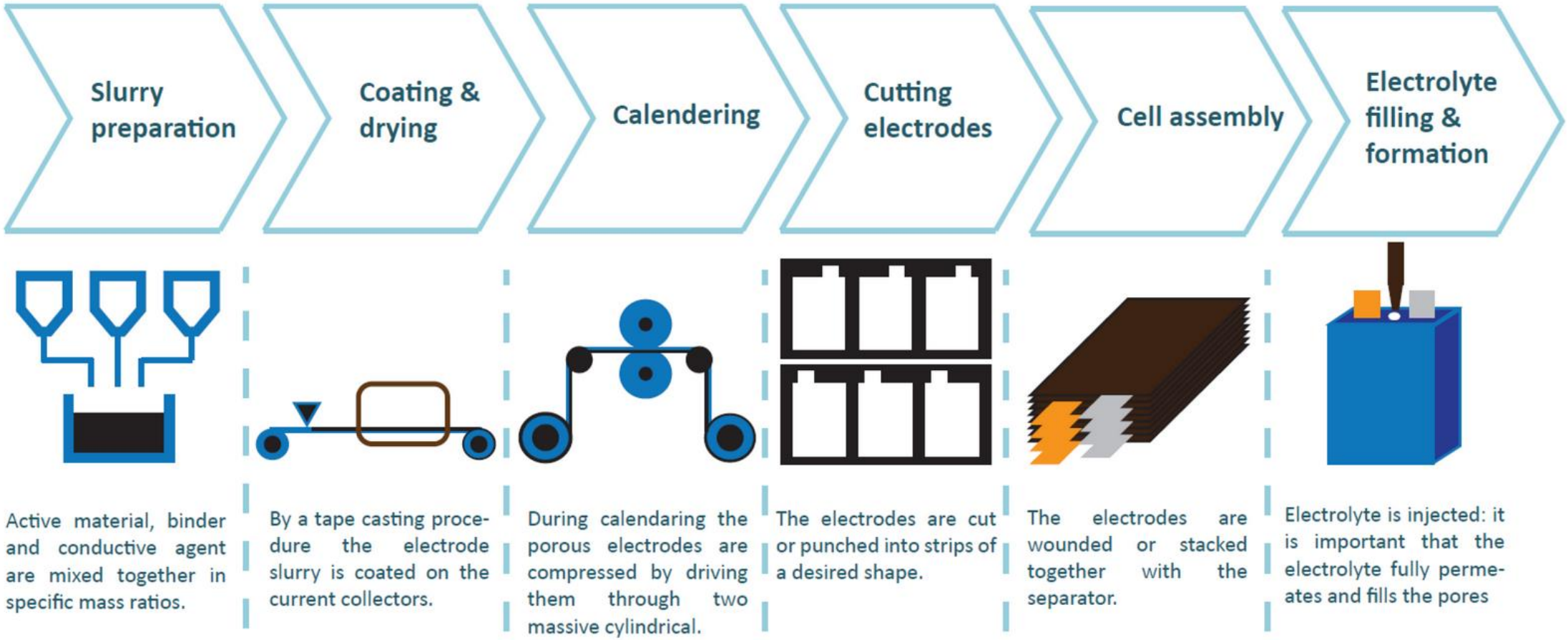


View of the jelly roll design



Adapted from Dirk Uwe Sauer - Summer School on Fuel Cells, Battery, and Hydrogen Technology Greece, 19.09.2013

Manufacturing steps of lithium-ion batteries

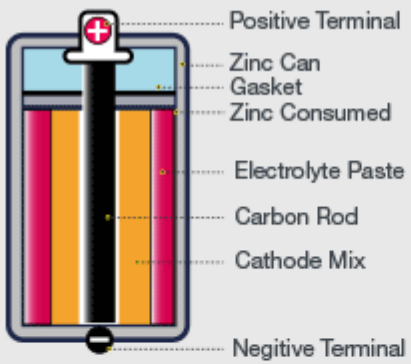


Cell manufacturing processes is the greatest source of variation in energy consumption

Smekens, Jelle & Gopalakrishnan, Rahul & Van den Steen, Nils & Omar, Noshin & Hegazy, Omar & Hubin, Annick & Van Mierlo, Joeri. (2016). Influence of Electrode Density on the Performance of Li-Ion Batteries: Experimental and Simulation Results. Energies. 9. 104. 10.3390/en9020104.

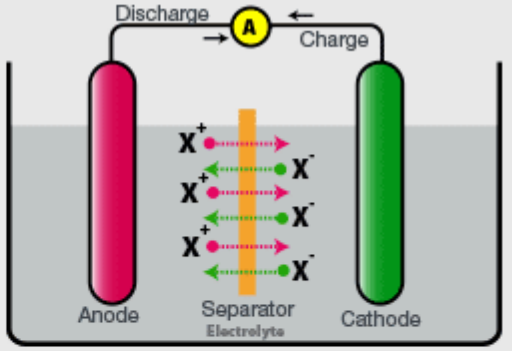
Fundamental and working principle of Li-ion batteries

Primary vs secondary batterie cells



PRIMARY CELL

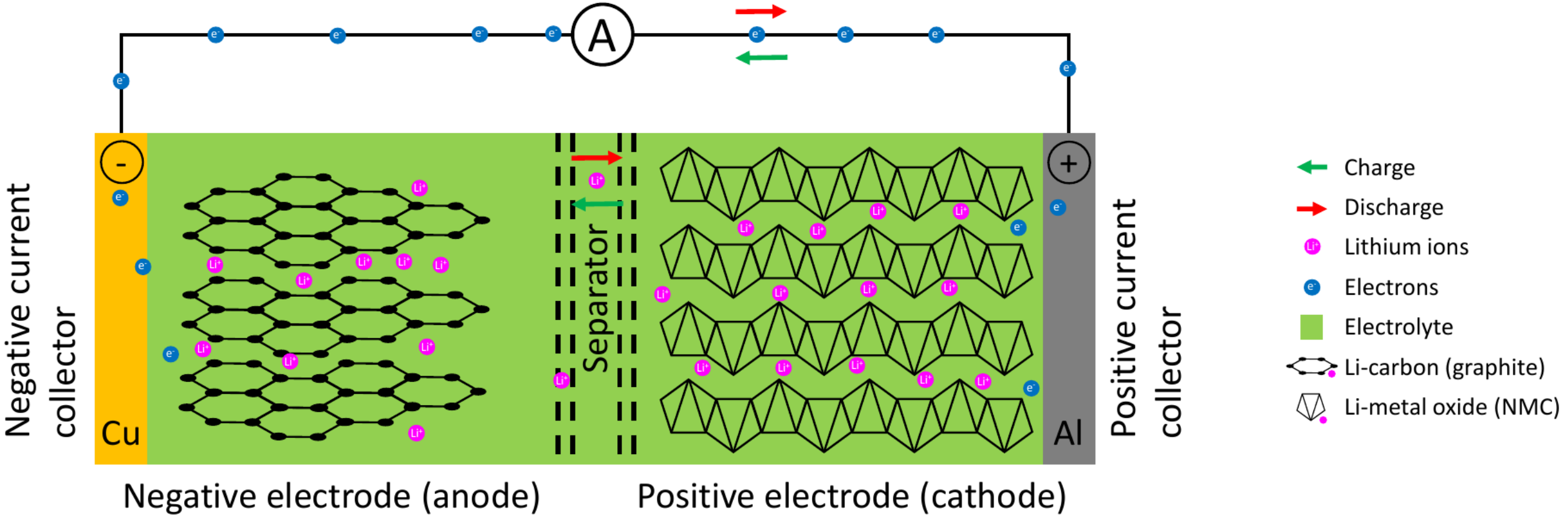
A PRIMARY CELL IS A BATTERY THAT IS DESIGNED TO BE USED ONCE AND DISCARDED



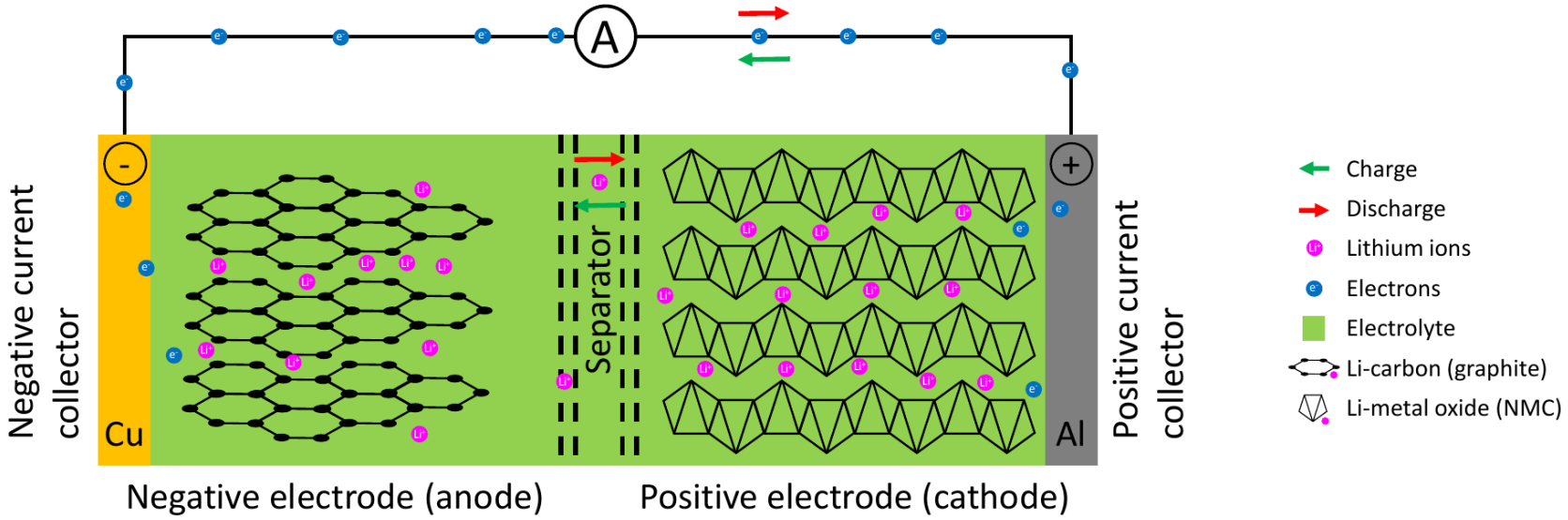
SECONDARY CELL

A SECONDARY CELL IS A TYPE OF BATTERY WHICH CAN BE CHARGED AND DISCHARGED MANY TIMES

Lithium-Ion Batteries



Lithium-Ion Batteries



A= ammeter (device to measure electric current)

- The **collector** is a conductive material that **collects the current** generated by the electrochemical reactions occurring at the electrodes
- **Collectors** are responsible for **conducting the electrical current** from the electrodes to the **external circuit**
- **Electrodes** are conductive materials that facilitate the **electrochemical reactions** within the cell
- **Electrodes** are composed of active materials that undergo **oxidation and reduction** reactions during charge and discharge cycles
- **Separator** made of a porous material that allows for the passage of ions while preventing direct contact between the electrodes

Lithium-Ion Batteries

Discharge example:

Positive electrode: $Li_{1-x}MO_2 + xe^- + xLi^+ \rightarrow LiMO_2$

Negative electrode: $Li_xC_n \rightarrow C_n + xLi^+ + xe^-$

Overall Reaction: $Li_{1-x}MO_2 + Li_xC_n \longleftrightarrow LiMO_2 + C_n$

Material (Kathode)	Mittlere Spannung (V)	Energiedichte (Wh/kg)
$LiCoO_2$	3,7	110–190
$LiMnO_2$	4,0	110–120
$LiFePO_4$	3,3	95–140
$Li2FePO_4F$	3,6	70–105
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	3,7	95–130
$Li_4Ti_5O_{12}$	2,3	70–80

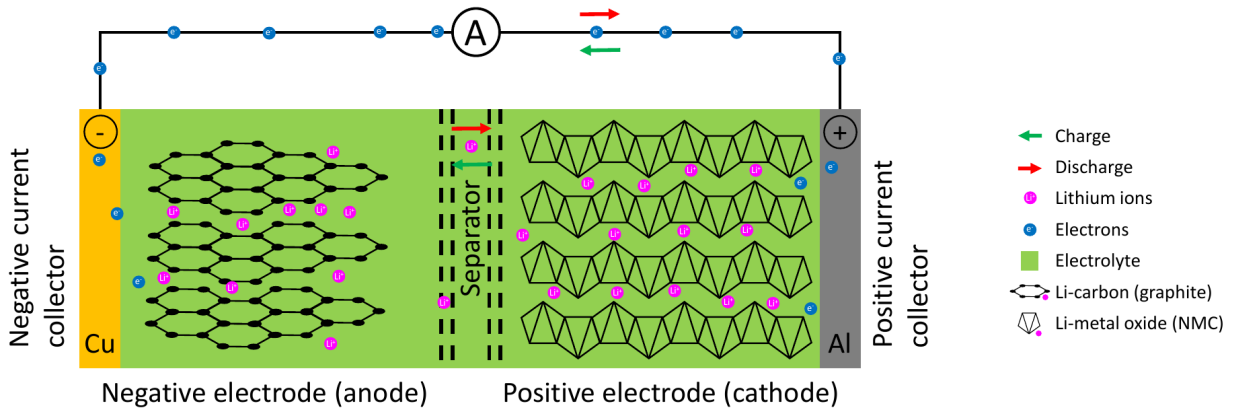
- **Positive electrode active materials (cathode):** Co, Ni, Mn, LiFe-PO4.

- **Negative electrode (anode)**: intercalation of lithium ions between graphite planes, nanocrystalline or amorphous silicon or lithium titanate oxide (Li4Ti5O12)

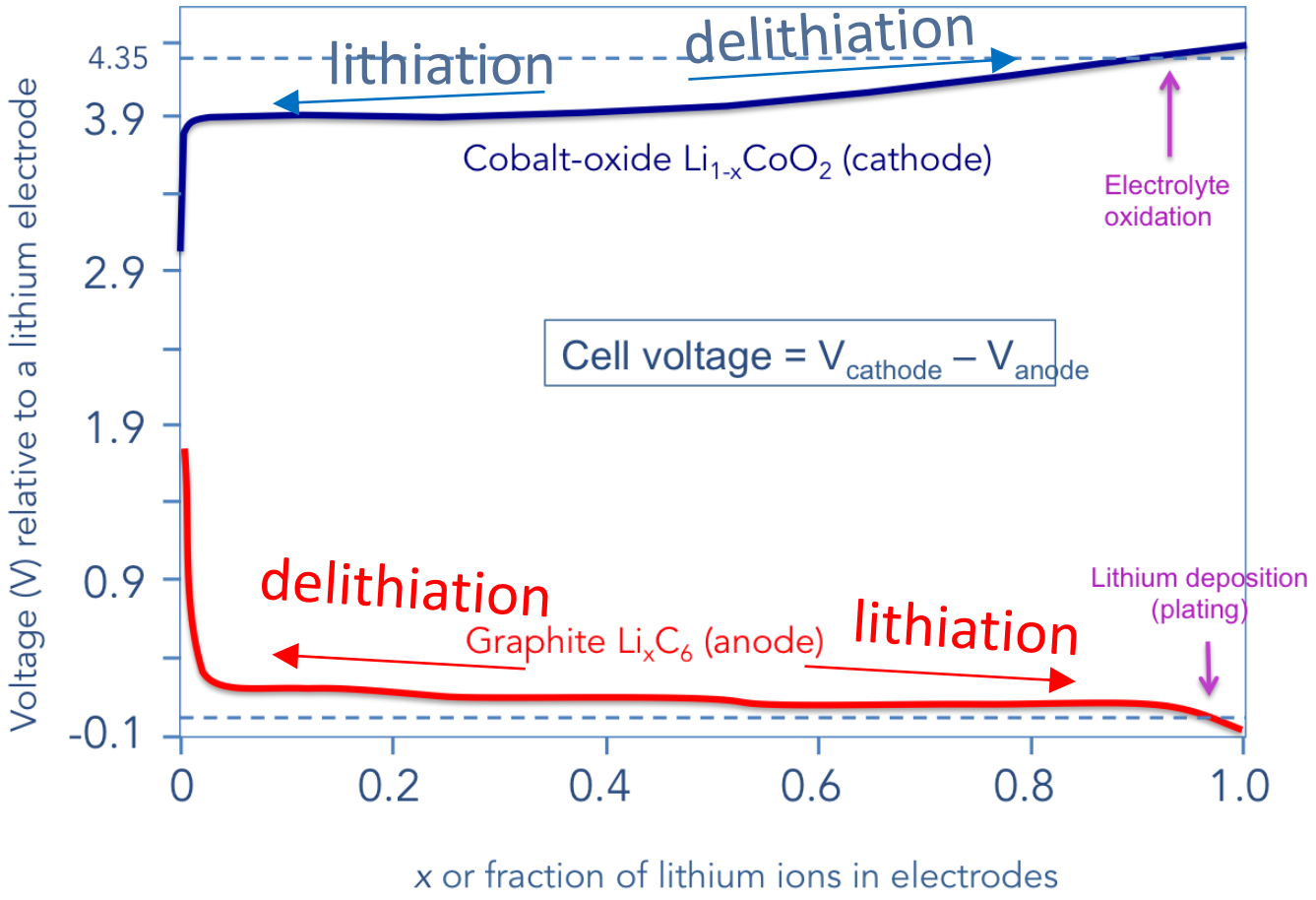
- **Electrolytes:**

Solutions of high purity, anhydrous, organic solvents in which conducting salts (LiClO4, LiAsF6, LiBF4, LiPF6, LiCF3SO3) are dissolved in porous separator.

System of polymer (polyethylene oxide (PEO), ...) and a salt and a solvent.



What is the voltage of a cell composed of?

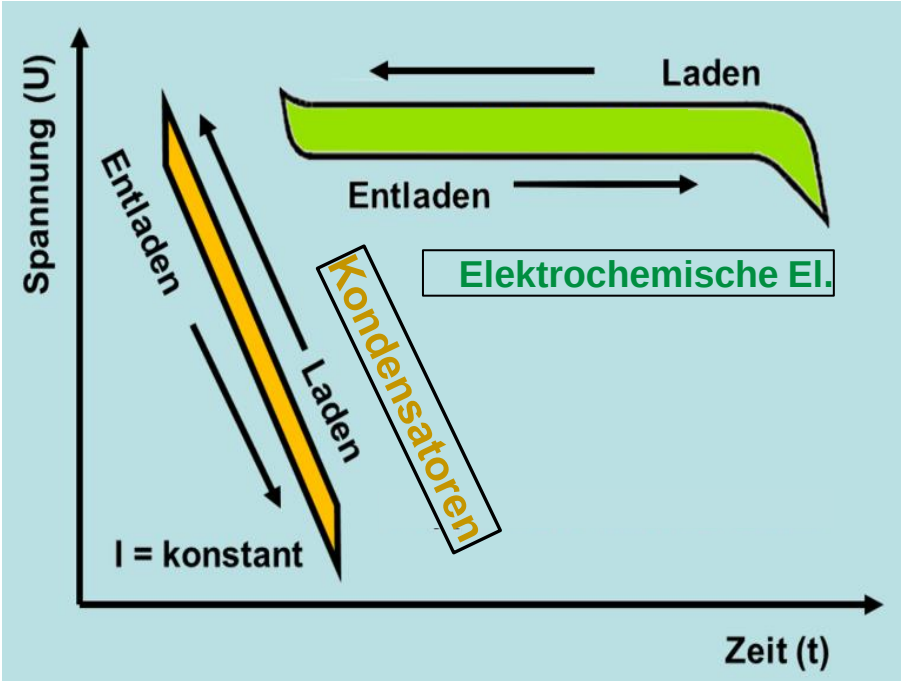


Source: https://qnovo.com/category/chemistry/page/5/

- The voltage of a cell is the difference in potential between the two electrodes at any given state of charge.

Characteristic curves

- The **voltage curve for capacitors and batteries** is normally shown as a function of the state of charge.
- The areas between the charge and discharge curves show that the **internal losses.** In electrical and electrochemical storage systems these are normally **extremely low**.
- In **capacitors**, the **voltage decreases linearly** at a constant discharge current.
- In **batteries** the extracted charge is supplied via the electrodes by an **electrochemical reaction**. The voltage do **not follow a linear decreasing trend**.



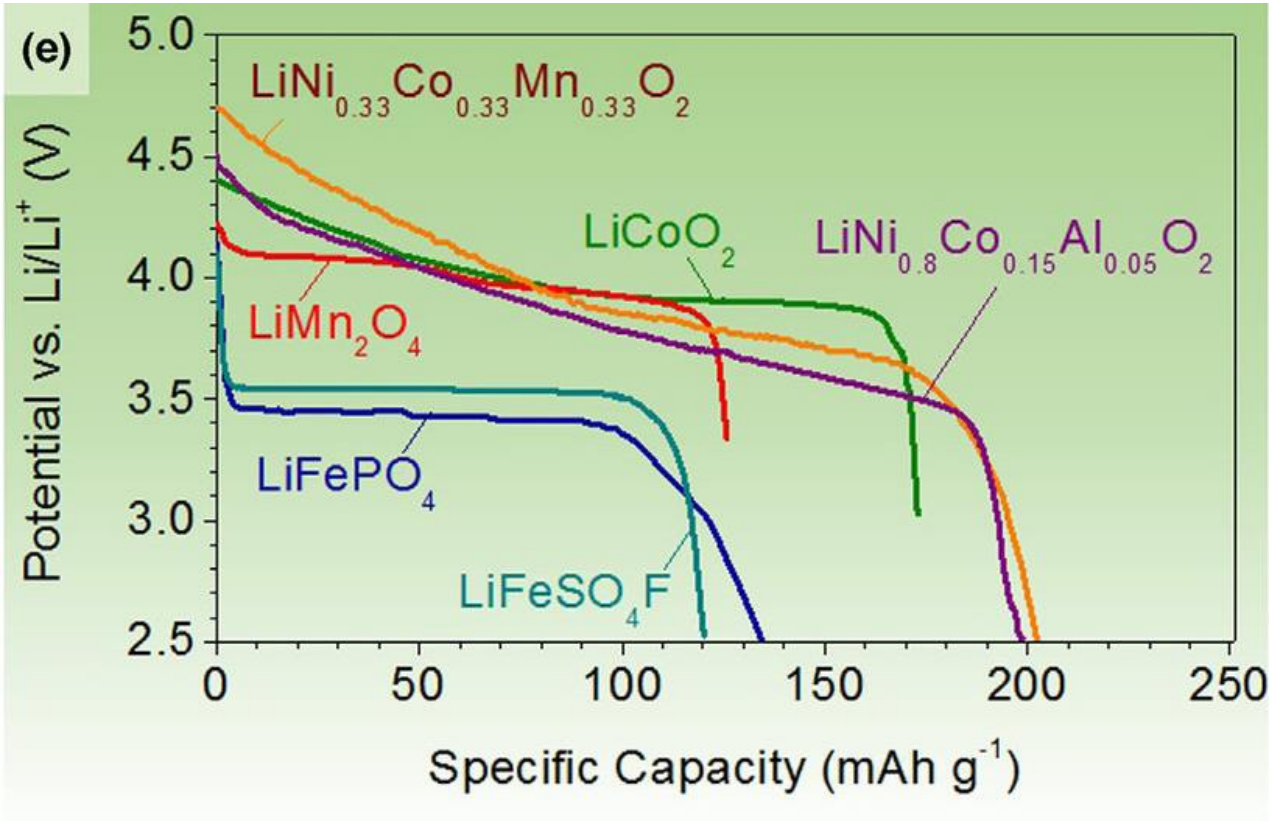
Charge and discharge characteristics are strongly **influenced by chemistry environmental conditions** (temperature and currents).

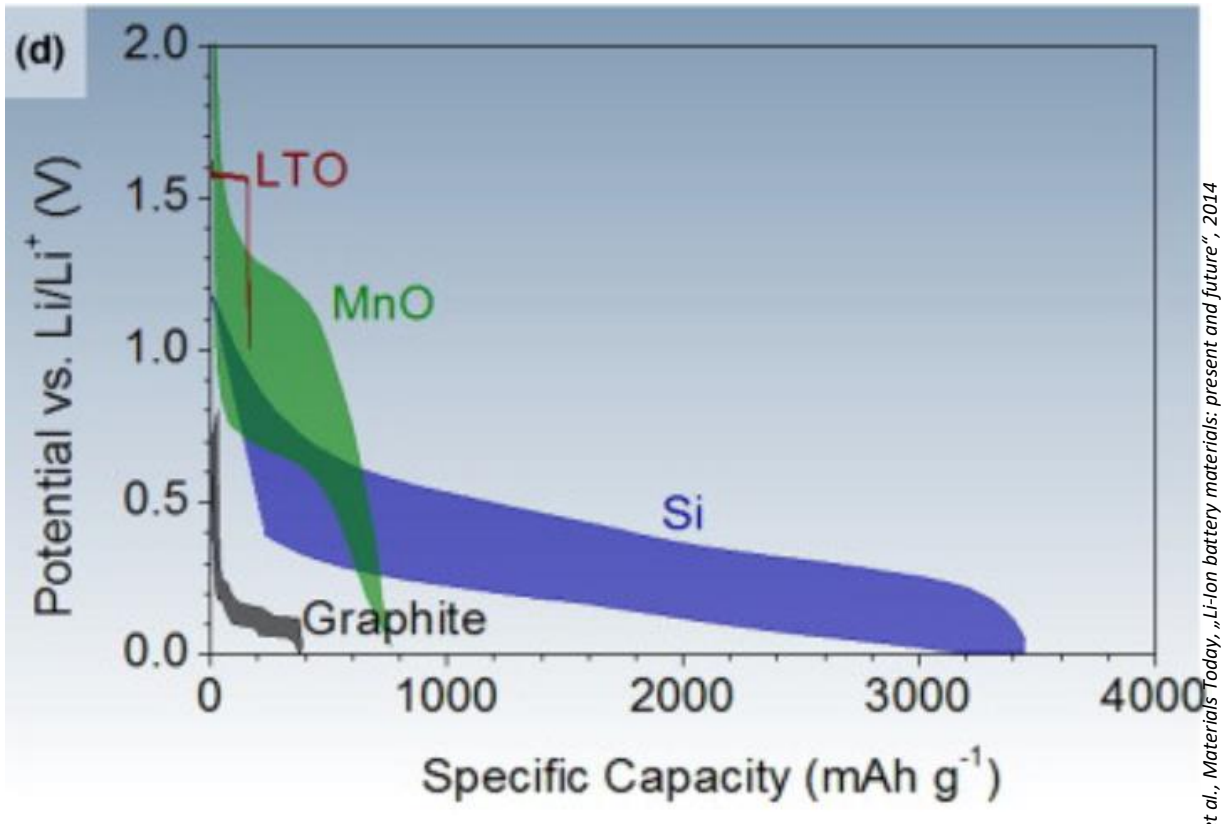
The **discharge characteristic is lower at low temperatures and high currents**.

Charge-/discharge graphs

Positive electrode materials

Negative electrode materials



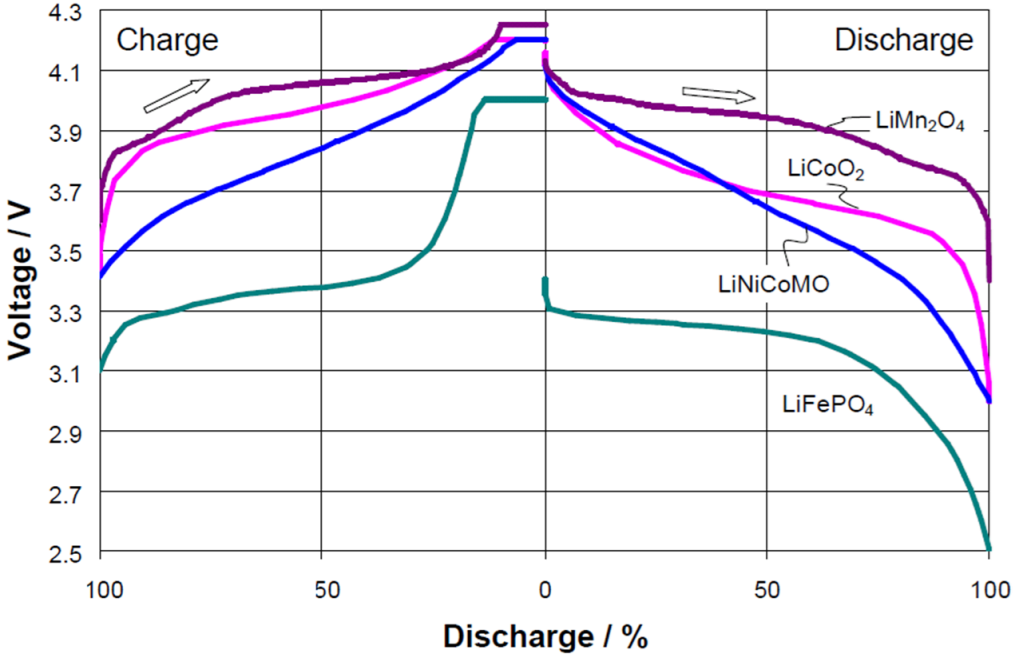


Source: Nitta et al., Materials Today, „Li-ion battery materials: present and future", 2014

- Each electrode material has its own characteristic charging/discharge behavior
- **$LiFePO_4$ and lithium titanium oxide ($Li_4Ti_5O_{12}$, LTO) have a flat (plateau) voltage curve**
- Charge and discharge parameters must be adjusted in appropriate monitoring

Properties of lithium-ion cells

- **High energy densities** achievable due to the **low weight of the electrode materials** and **the high electrochemical potential of lithium**.
- **Low internal resistance and thus high cycle efficiency**
- Overcharging, deep discharging and overheating can trigger irreversible processes.
- At low temperatures, performance drops sharply.
- The level of **charge and discharge currents** (20C / C10) and the **operating temperature** have a decisive **influence** on **voltage, capacity and service life**.



The properties can be influenced by **combining different electrode materials** (designer electrodes).

- Cells with cobalt or manganese cathodes have **energy densities** up to 200 Wh/kg.
- Titanate cells reach about 10'000 **cycles**
- Iron phosphate cells are very **safe** because the thermal runaway does not occur.

Exercise

Considering the following Overall reaction

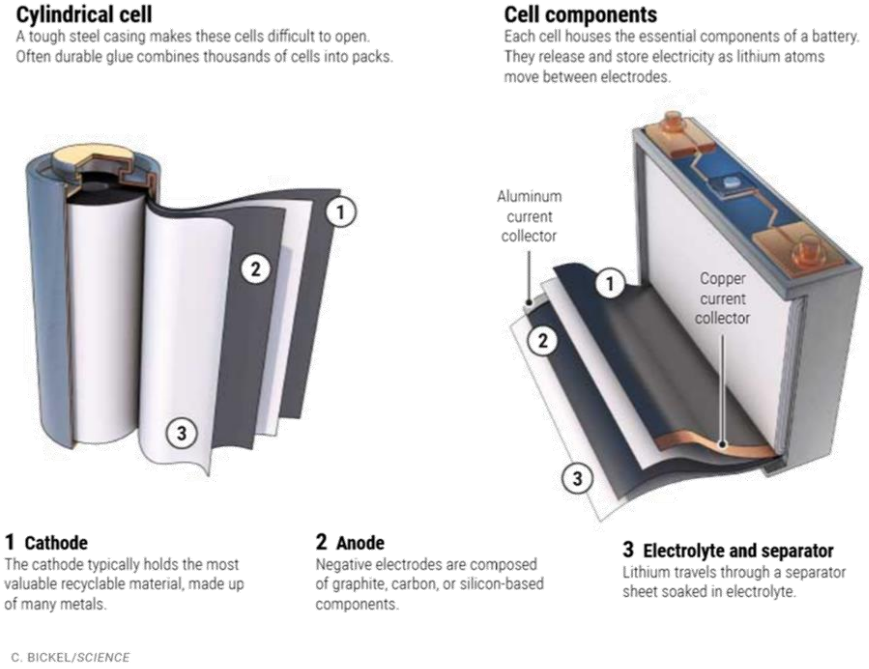
$$Li_{0.4}CoO_2 + 0.6LiC_6 \Leftrightarrow LiCoO_2 + 0.6C_6$$

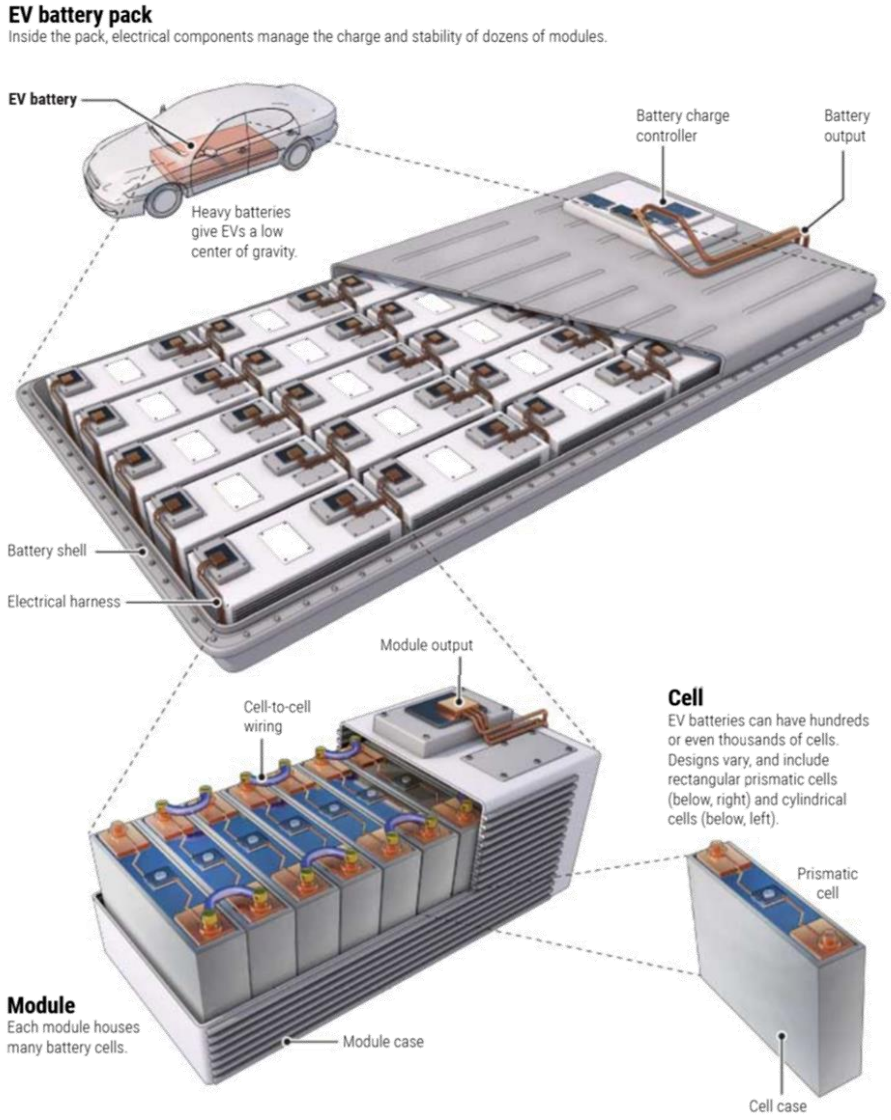
1. Write the corresponding anodic and cathodic reactions during charge
2. Which are the oxidizing and reducing agents?
3. What is the Gibbs free energy of the overall cell reaction?
4. What is the theoretical gravimetric energy density?
5. How big is the theoretical gravimetric energy density with respect to the available energy density reported for the same material (graph on slide 45)?

Battery Definitions

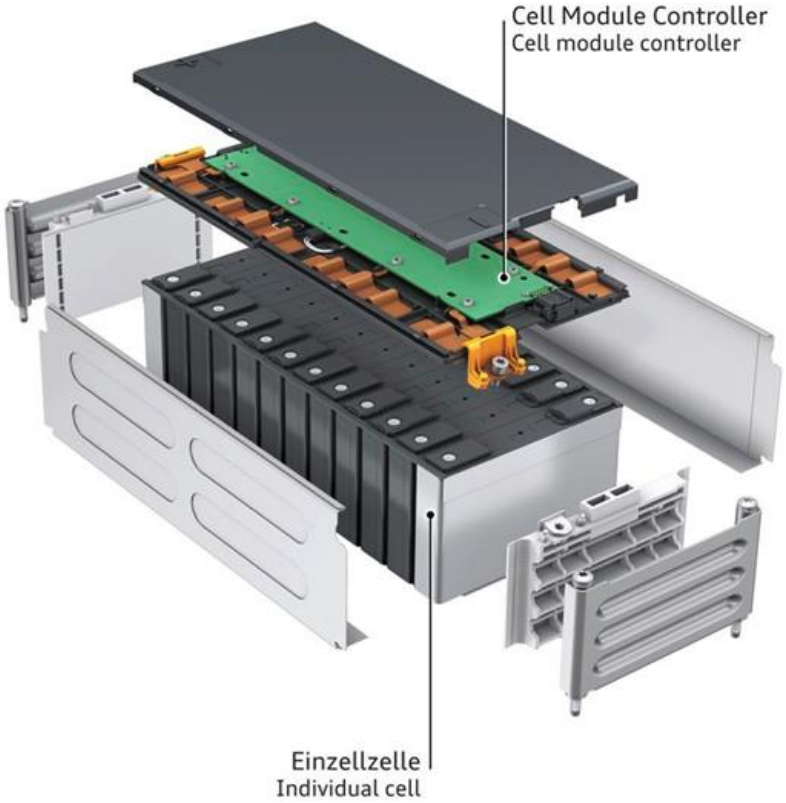
EV Battery Pack

- **Cells** are the smallest individual electrochemical unit and deliver a voltage that depends on the cell chemistry.
- **Batteries modules** and **packs** are made up from groups of cells connected in series and parallel



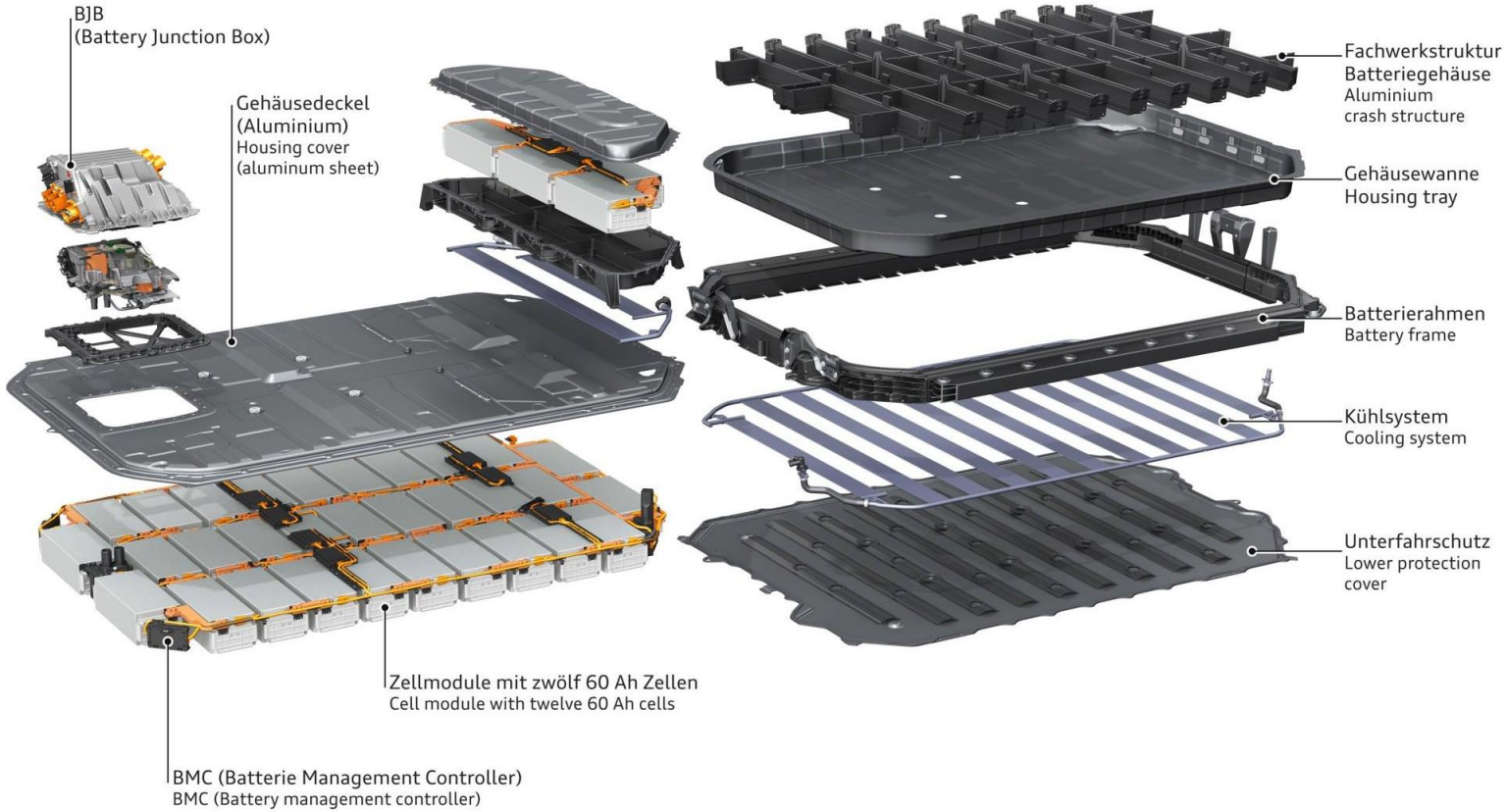


Battery module



40 – 60 V

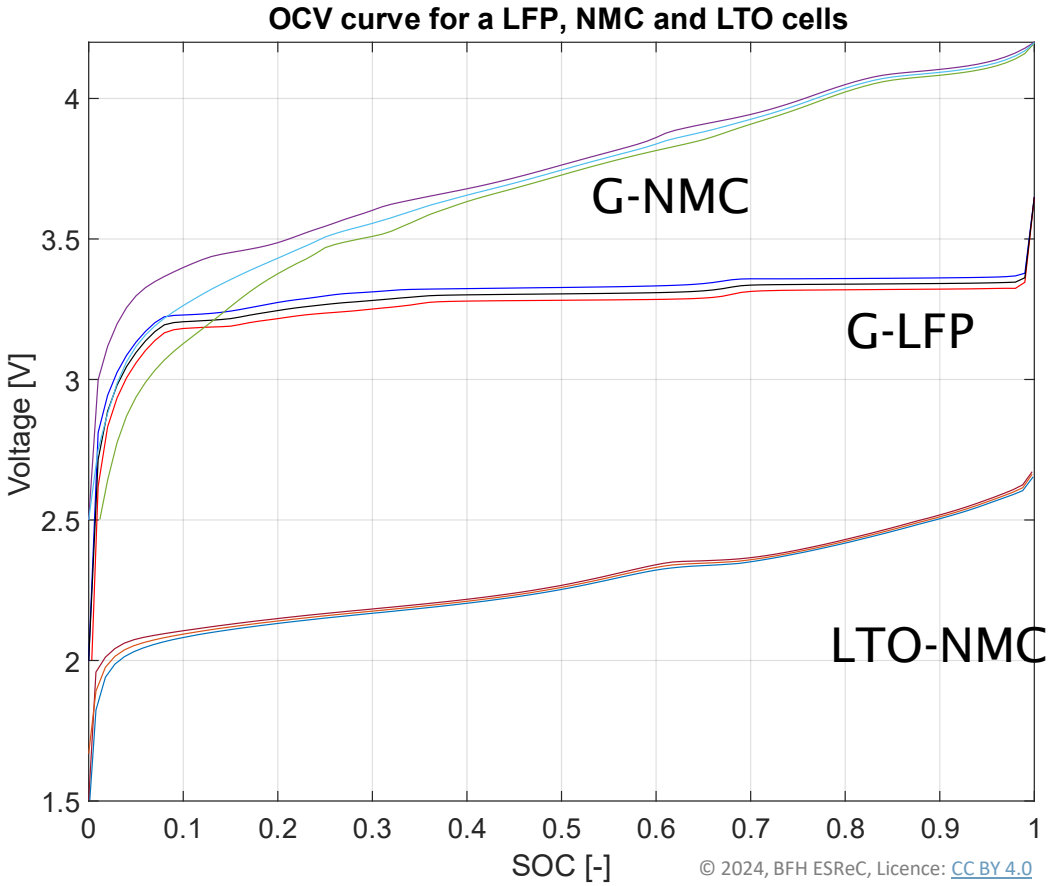
Battery pack

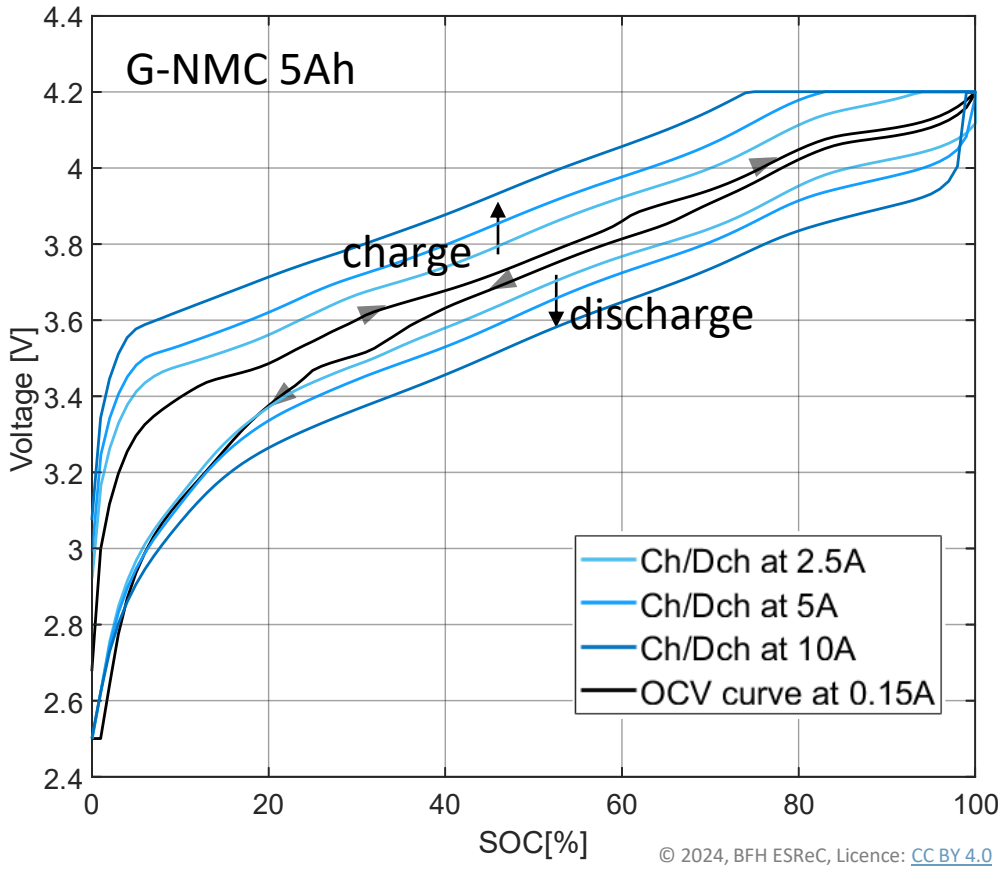


300 – 800 V

Quelle: Audi

Li-ion Battery Voltage



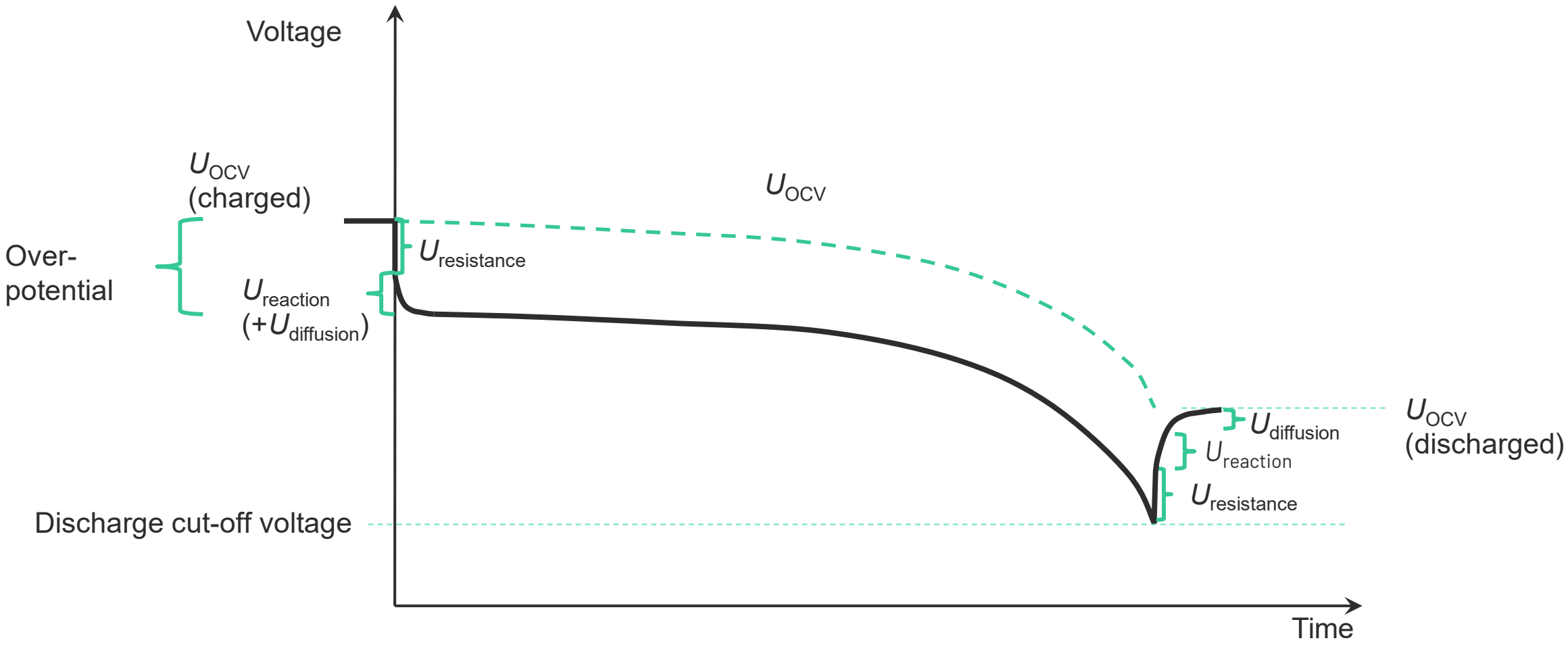


- The voltage of a cell is the difference in potential between the two electrodes
- It depends on Li particle average concentration in the two electrodes, the materials used as electrodes and temperature
- If the cell is under current the voltage deviates from the OCV because of losses

Stored energy and open circuit voltage

- The multiplication of open circuit voltage by capacity defines the maximal removable energy from the battery.
- The capacity has a linear relationship with the available amount of electrode materials.
- The voltage of the battery during discharge is always lower than the open circuit voltage at every state of discharge.
- The voltage of the battery during charging is always higher than the open circuit voltage at every state of discharge.
- Deviations from the open circuit voltage are losses.

Voltage of a battery during discharge

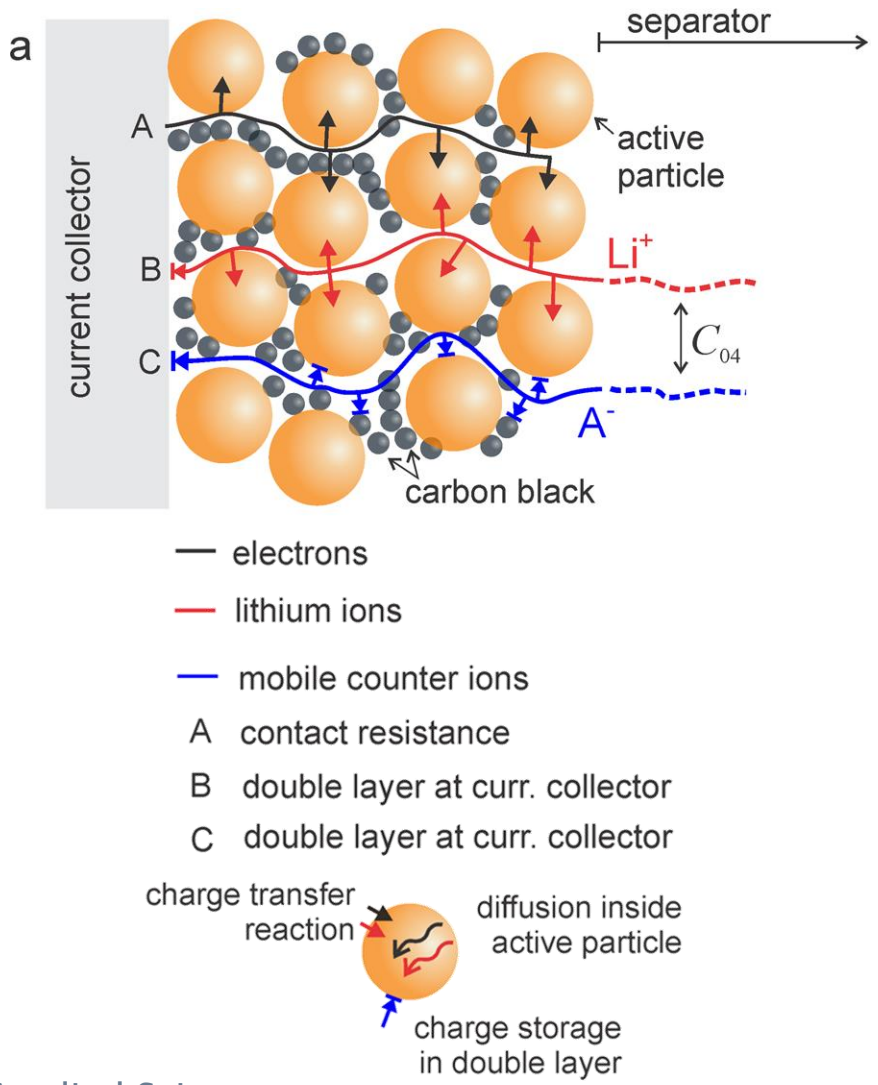


Voltage of a battery during charging and discharge

Ucharge/discharge = Uequilibrium + Uresistance + Ureaction + Udiffusion

- $U_{equilibrium}$ (OCV) depends on electrode materials, electrolyte concentration and temperature
- $U_{resistance}$ ohmic drops in poles, current collectors, grid and electrolyte.
- $U_{reaction}$ voltage drops caused by electrochemical and chemical reaction at inner surfaces (Butler-Volmer equation).
- $U_{diffusion}$ voltage drops through a deficit or surplus of reactants at the reaction locations.

$U_{resistance}$, $U_{reaction}$, $U_{diffusion}$ will be normally considered as positive during charging and negative during discharge.



https://www.nature.com/articles/s41467-021-26894-5

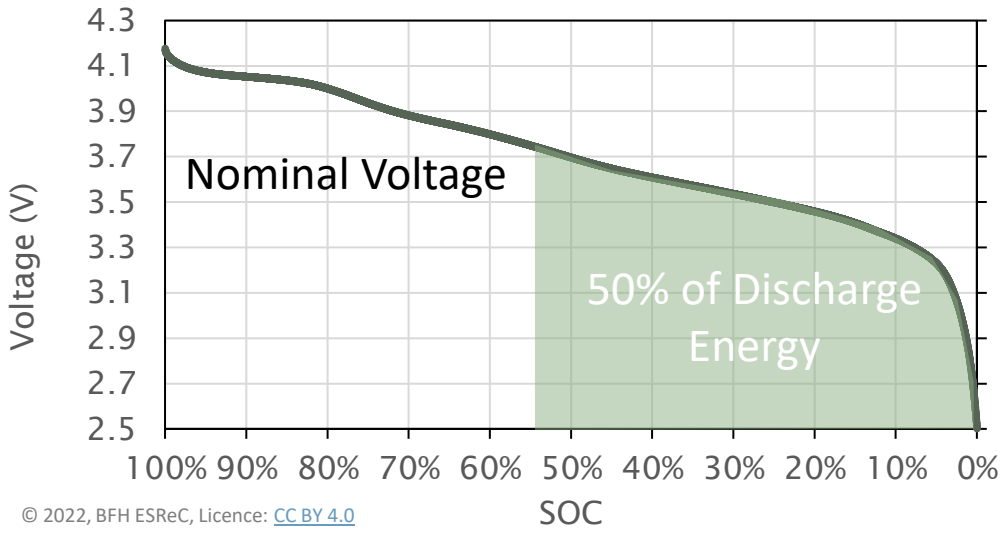
Cell Datasheet

Item	Condition / Note	Specification
2.1 Energy	Std. charge / discharge	Nominal 18.20Wh Minimum 17.60Wh
2.2 Nominal Voltage	Average	3.63V
2.3 Nominal Shipping SOC		30%
2.4 Standard Charge (Refer to 4.2.1)	Constant current Constant voltage End current(Cut off)	0.3C (1,455mA) 4.2V 50mA
2.5 Max. Charge Voltage		4.20 ± 0.05V
2.6 Max. Charge Current	0 ~ 25℃	0.3C (1,455mA)
	25 ~ 50℃	0.7C (3,395mA)
2.7 Standard Discharge (Refer to 4.2.2)	Constant current End voltage(Cut off)	0.2C (970mA) 2.50V
2.8 Max. Pulse Discharge Power	Pulse Power(10sec), 25 ºC ± 2 ºC	≤ 80W (SOC 80%)
2.9 Max. Discharge Current	-30 ~ -20℃	0.2C(970mA)
	-20 ~ 5℃	0.3C(1,455mA)
	5 ~ 45℃	1.5C(7,275mA)
	45 ~ 60℃	1.5C(7,275mA)

https://www.dnkpower.com/wp-content/uploads/2019/02/LG-INR21700-M50-Datasheet.pdf

Cell Datasheet

- **Cell (nominal) voltage** depends on the combination of active chemicals used in the cell.
- **Cell (nominal) capacity** specifies the quantity of charge, in ampere hours (Ah), that the battery is rated to hold.



$Q = \int_{\Delta t} I \, dt$ or Q = I x t

[Ah] = [A] x [h]

Basic concepts of Li-ion Battery

- The **C rate** is a relative measure of cell current. It is the constant current charge or discharge rate that the cell can sustain for one hour.
  - A 20Ah cell should be able to deliver 20A (“1C”) for 1 h
    or 2 A (“C/10”) for about 10 h

C-Rate = I / Q
[h-1] = [A]/[Ah]

- The total **energy** storage capacity of a cell is roughly its nominal voltage multiplied by its nominal capacity (Wh).

$$E = \int_{\Delta t} U_{battery} * I \, dt$$

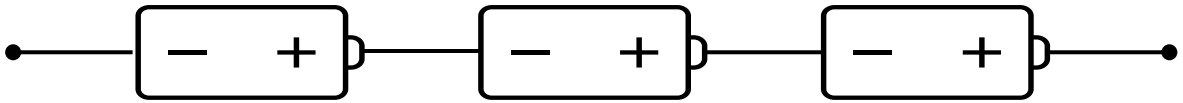
E = U x I x t
[Wh] = [V] x [A] x [h]

- The energy release rate is the cell’s instantaneous **power** (W).

P = U x I
[W] = [V] x [A]

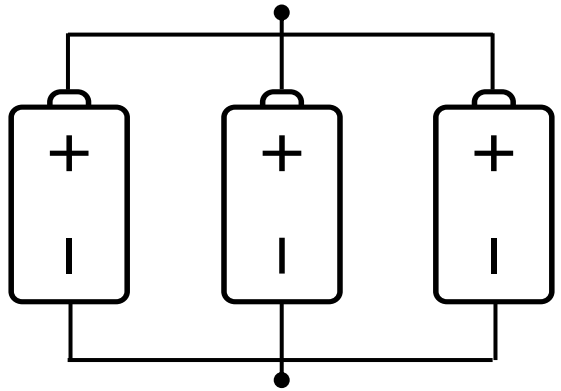
Basic concepts of Li-ion Battery

- Cells connected in series:



  - increases voltage proportional to the number of cells
  - capacity remains unchanged
  - Energy capacity and power increase proportional to the number of cells.

- Cells connected in parallel:
  - voltage remains unchanged
  - increase capacity proportional to the number of cells
  - And energy capacity and power increase proportional to the number of cells.



Recap

- Battery cell: The smallest component of a battery pack or system. A cell may have ca. 2.5 – 4.2 V.

Voltage: 3.5V
Capacity: 3.0 Ah
} Energy: 10.5 Wh

Voltage: 2.3V
Capacity: 20 Ah
} Energy: 46 Wh

- Battery pack: cells connected in series and/or parallel

Parallel connection

Voltage:
Capacity:
} Energy:

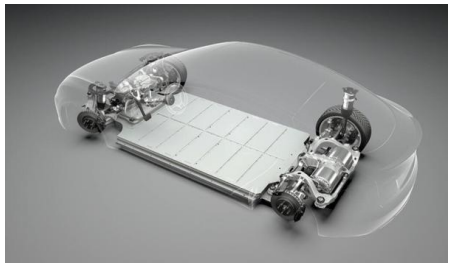
Voltage:
Capacity:

Series connection

} Energy:

- Battery (Battery system): battery packs connected incl. batterie management system.

Voltage: 360 V
Capacity: 60 Ah
} Energy: 21.6 kWh



Voltage: 350 V
Capacity: 230 Ah

→ Energy: 80.5 kWh

Efficiency

- Capacity efficiency or Charge factor

$$L = Q_{discharge} / Q_{charge}$$

- Energy efficiency:

$$\eta = E_{discharge} / E_{charge}$$

Influence factors: current density, charge characteristics, temperature

Typical data for the energy effectiveness are:

- Lead-acid batteries: 80 - 90 %
- Lithium-ion batteries: 90 - 95 % (ηAh ~ 100%)
- NiMH: 75 - 85 %

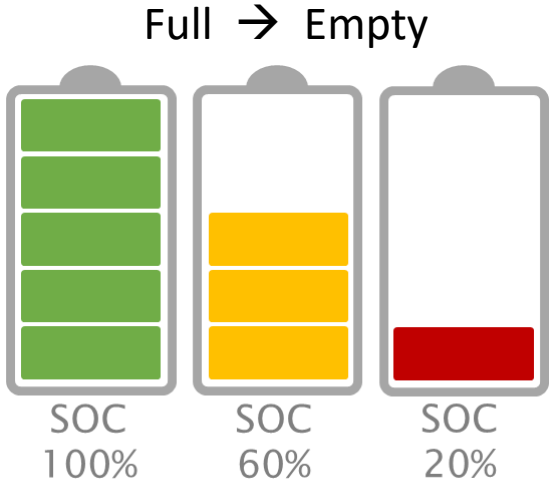
Increased current, lower temperature or aged batteries will lead to higher voltage deviation from the open circuit voltage → decreasing energy effectiveness

Battery State of Functions - SOC

- The **State of Charge (SoC)** is a percentage value that expresses the remaining charge Q of a battery
- SoC is something like a dashboard fuel gauge that reports a value from “Empty” (0%) to “Full” (100%) → no sensor is available to directly measure SoC.

- Charging state (SOC -> State Of Charge) describes the charging rate of the active materials and will be determined through the Ah-balance.

- The integral of the current flowing in the main reaction represents which proportion of the active material is charged and which one is discharged.
- DOD -> Depth Of Discharge: DOD = 100% - SOC
- SOC = 100 % → DOD = 0 %
- SOC = 0 % → DOD = 100

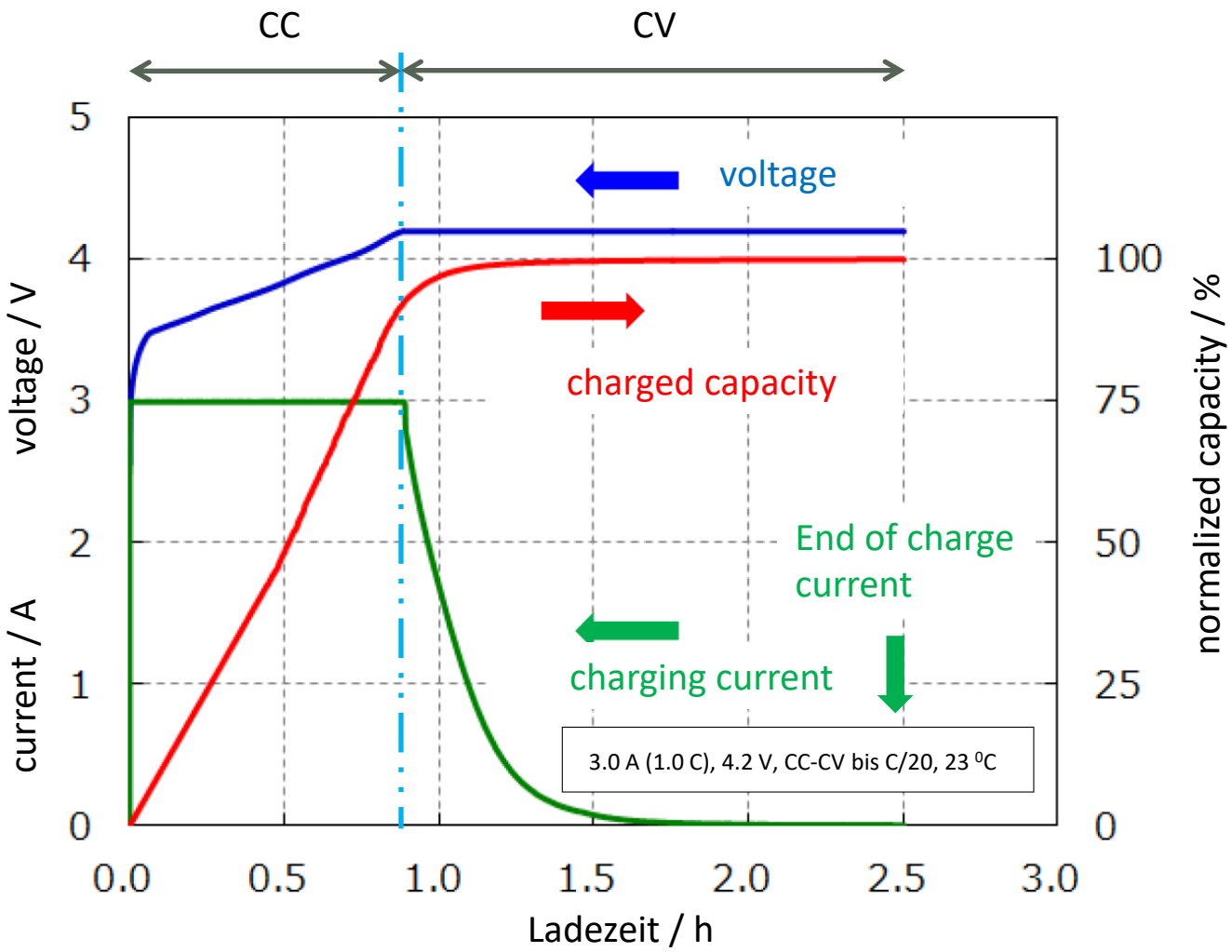


$$SoC = Q_{actual} / Q_{full}$$

$$SOC(t) = SOC(t = 0) + \frac{1}{C_{nom\,(t=0)}} * \int_{t=0}^{t} I\,dt$$

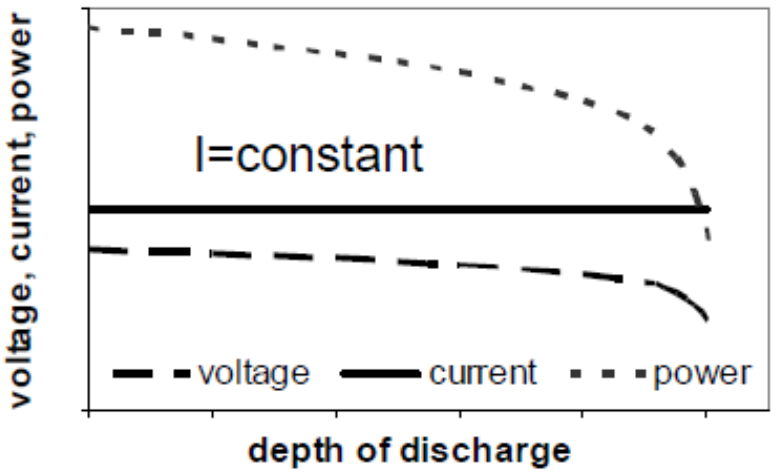
Charging Lithium-Ion Batteries

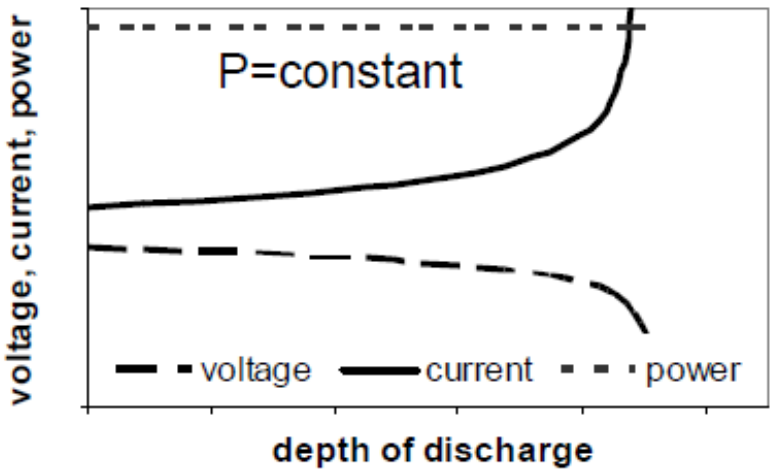
- Lithium-ion batteries are charged with a constant current (CC or constant current) up to the final charging voltage.
- Once the end-of-charge voltage has been reached, charging continues at a constant voltage (CV).
- Charging stops when the end-of-charge current is reached → generally C/10 to C/20 or 0.10 C to 0.05 C.

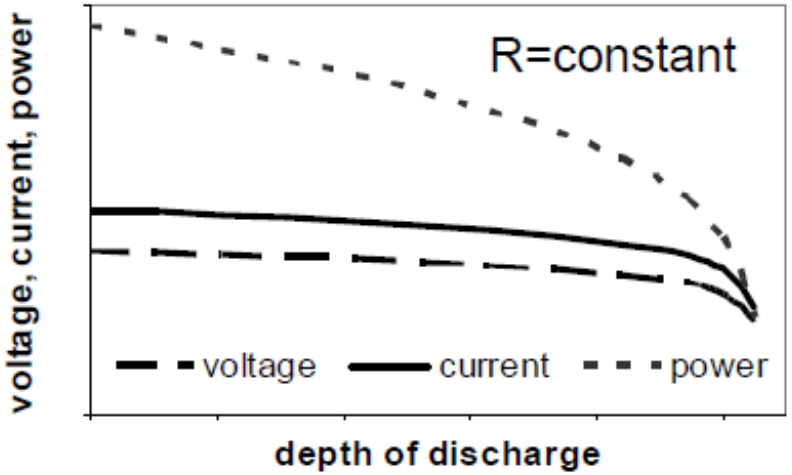


Discharging Lithium-Ion Batteries

- Lithium-ion batteries can be discharge in three different ways:
  - Constant current
  - Constant resistance
  - Constant power







Basic concepts of Li-ion Battery - Exercise

Consider a battery pack made the cell you are using in the laboratory part:

- Cell voltage
- Nominal voltage
- Cell capacity

1. Compute Battery capacity and voltage for a configuration made by 8 cell in series and 4 in parallel 8s4p
2. What is the nominal battery energy?
3. If the maximum continuous discharge current is 3C, which is the corresponding Current?
4. What is the corresponding power at this C-rate?
5. Which efficiency are you expecting to have?

C-Rate = I / Q
[h-1] = [A]/[Ah]

$$E = \int_{\Delta t} U_{battery} * I \, dt$$

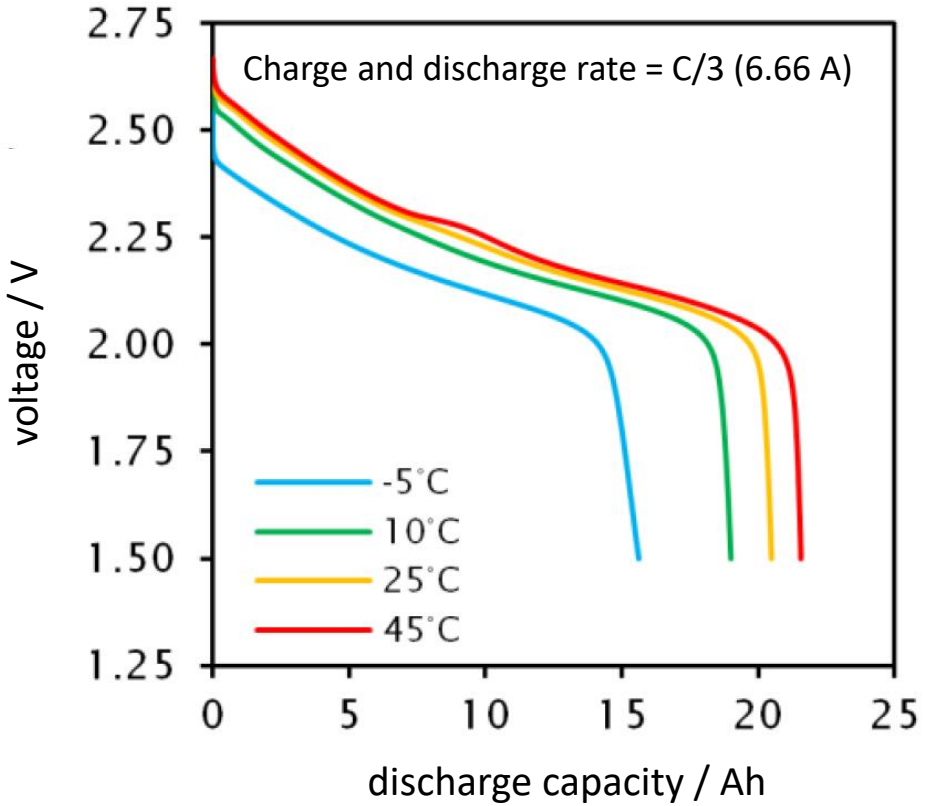
E = U x I x t
[Wh] = [V] x [A] x [h]

P = U x I
[W] = [V] x [A]

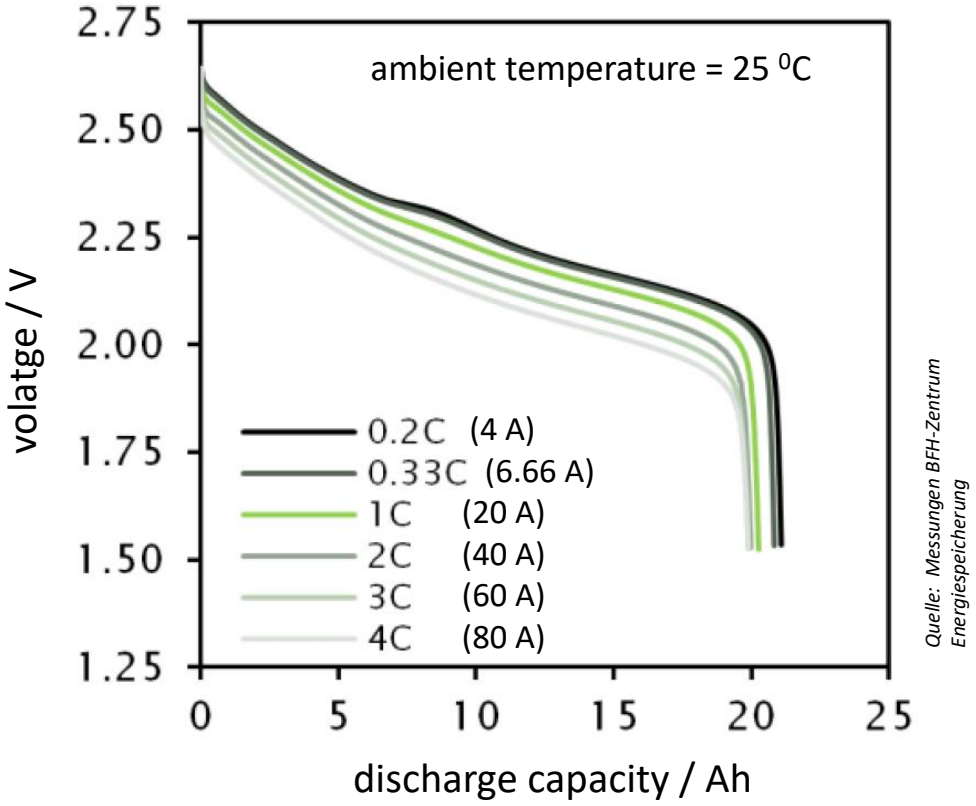
Battery Performance

Capacity depends on load and temperature

Influence of ambient temperature



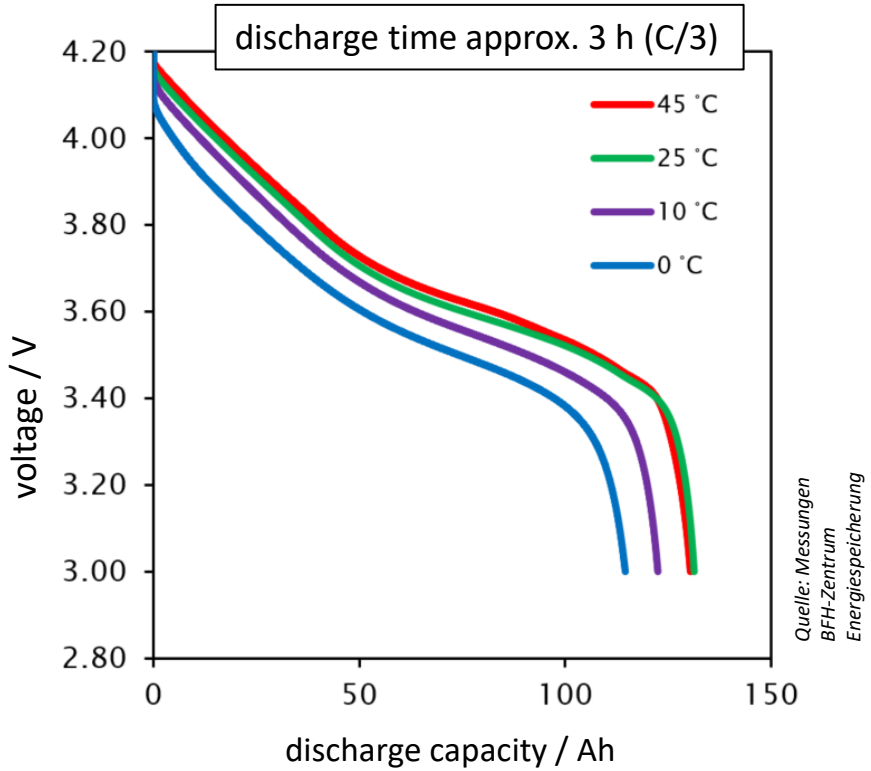
Influence of the discharge rate



Quelle: Messungen BFH-Zentrum Energiespeicherung

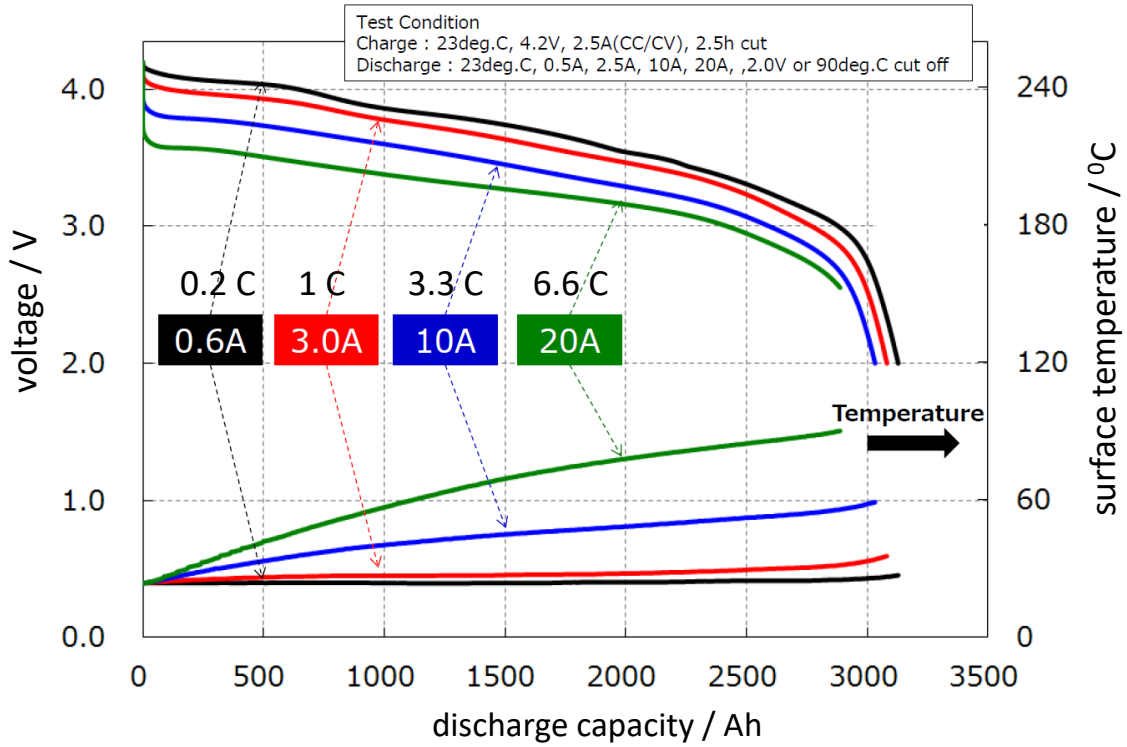
Capacity depends on load and temperature

Influence of ambient temperature



Quelle: Messungen BFH-Zentrum Energiespeicherung

Influence of the discharge rate



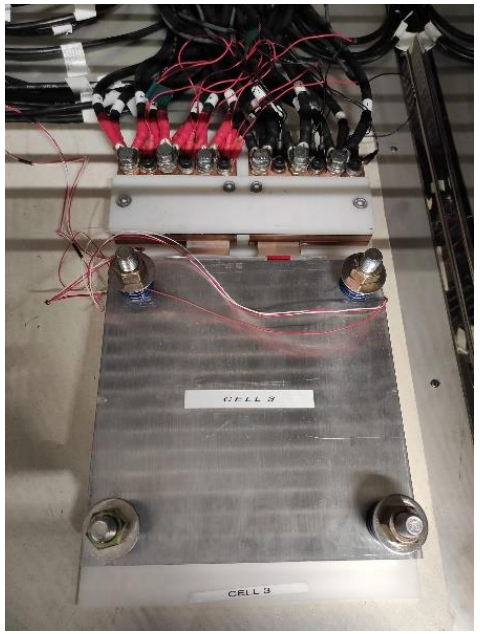
Quelle: Datenblätter Sony 18650-Zelle

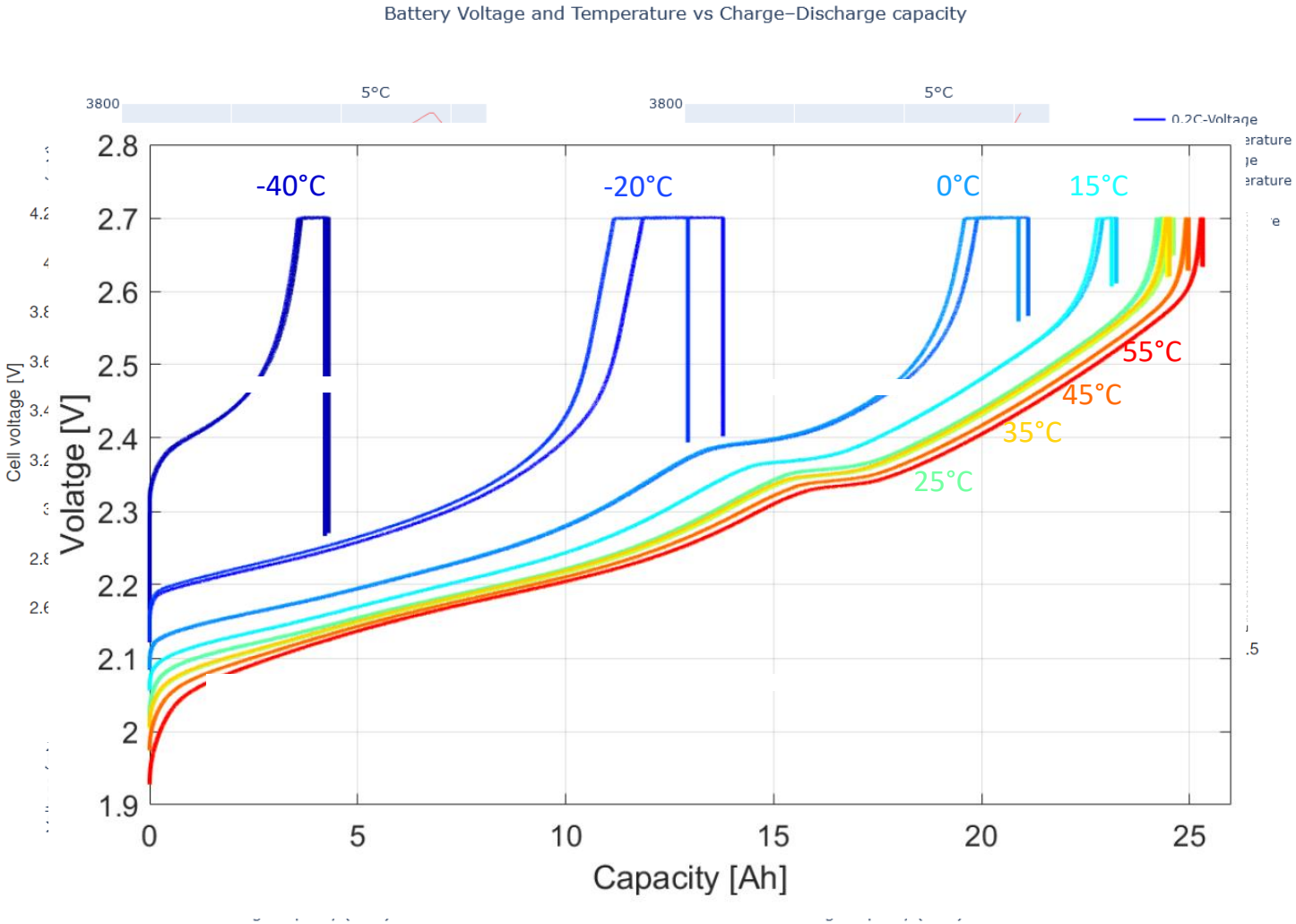
Battery Testing-Performances @ different operating conditions

Verification of Battery Datasheet

Full Capacity variation

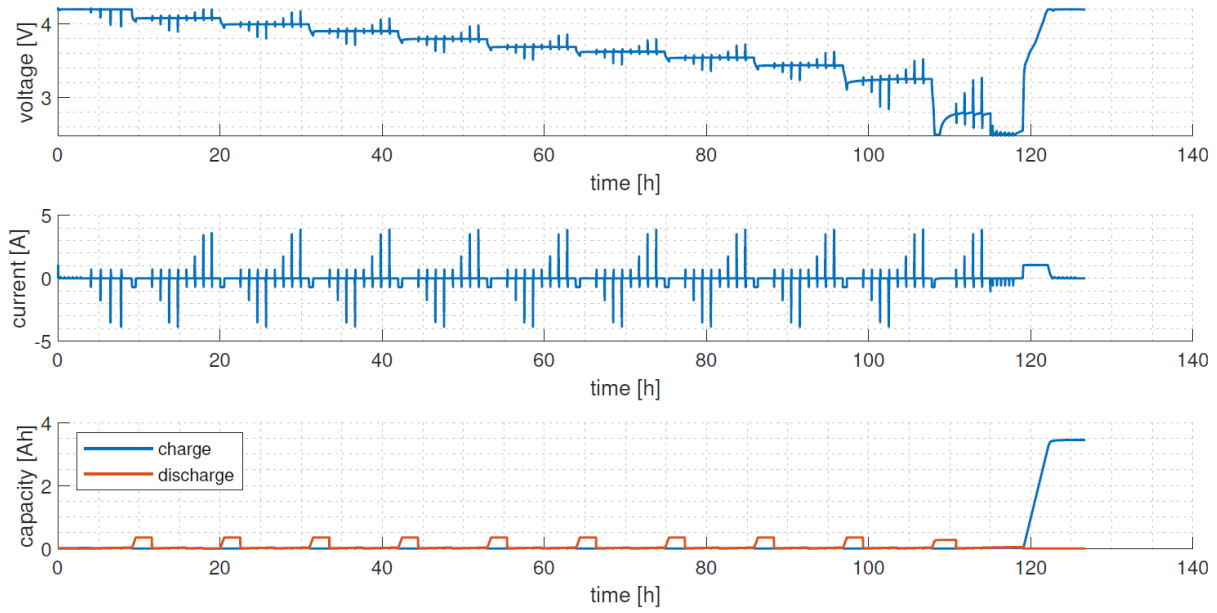
- @different temperatures
- @different Crates

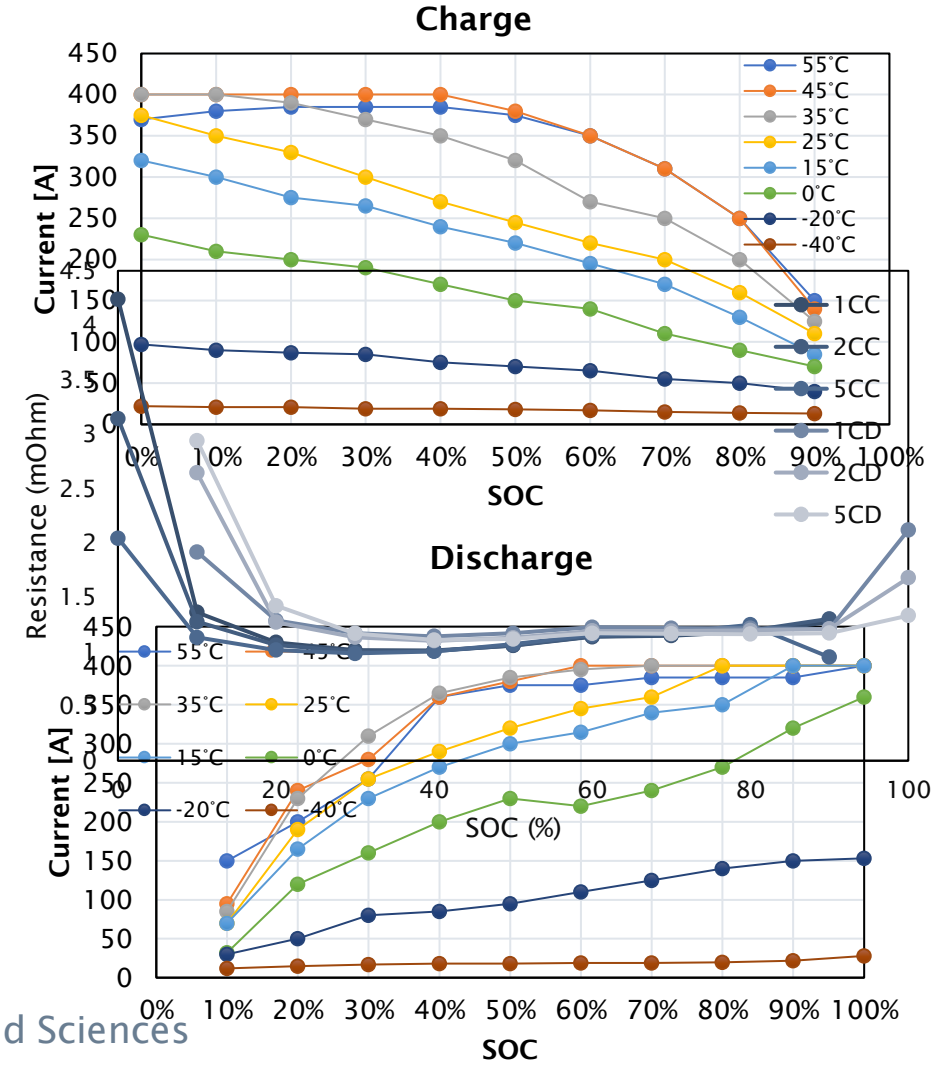




Battery Power – Internal resistance Maps

- Pulse tests at different SOC (10% resolution) with different currents (from 1 to 20C) for different duration (1 to 30s)
- Power capabilities (during acceleration/deceleration) or internal resistance behvaiour at different SOCs





Exercise

Exercise

Looking at the following datasheet try to answer the following questions:

- a) What is the nominal voltage?
- b) How is the nominal voltage defined and why do we need it for sizing?
- c) What is the capacity (Ah) of the battery cells?
- d) There are two ways of computing the battery capacity based on the available data on the datasheet. Could you indicate another way with respect the one you used in point c?
- e) According to you, why on the datasheet the producer indicates two energy values? Nominal and Minimum?
- f) What energy will you achieve if you connect 7 cells in parallel and 13 cells in series (7p13s)?
- g) What power can be achieved by running the battery module defined in point f with 2Crate?
- h) Considering the value of pulse power in 4.2.8 at which current you can run the battery cell to achieve the peak power of 80W? Is it possible to use this current in continuous mode?
- i) Why does the capacity of the cell decrease with decreasing temperature?