Electrochemistry for Materials Technology

ENERGY APPLICATIONS

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EPFL-Valais GEM (Group of Energy Materials)

BATTERIES : a brief overview

Battery design

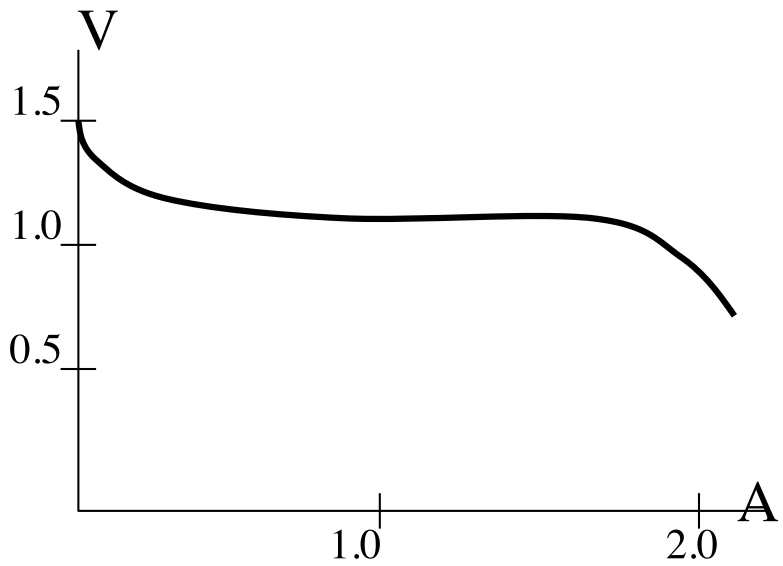
- 2 electrodes = 2 active masses → negative : **Me**, H_2, CH_x ; positive : **MeO_x**, O_2
- 1 electrolyte
- active mass stock; separation foils

1) active mass ≠ electrodes (FC)
   continuous feed in H_2 (CH_x), O_2 (air)
2) active mass = electrodes (battery)
   - reversible reactions : rechargable batteries (accumulators, 2°)
   - irreversible reactions : primary batteries (1°)

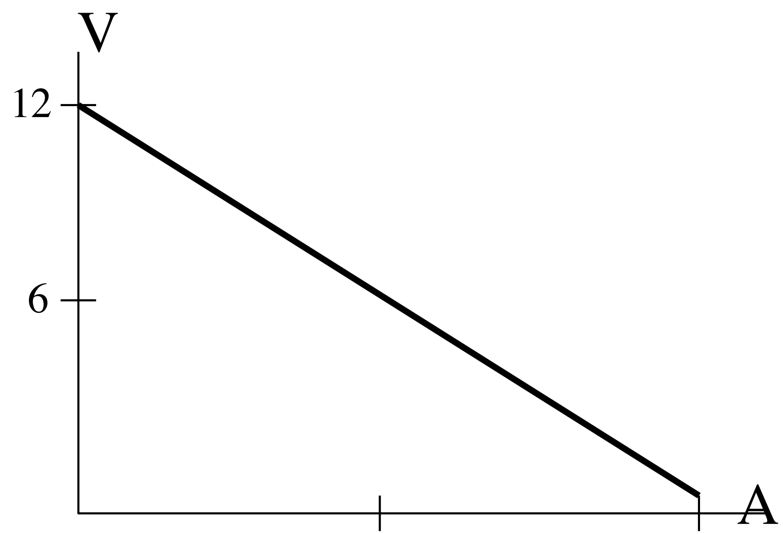
Desired battery properties

- usually: high current i density (>0.5 A/cm^2)
  - but not always! Depends on the application
- low overpotentials η (<0.1V)
- high rest potential E^o (>1 V) (zero current, open circuit)
- very low corrosion (=self-discharge)
- high energy density (J / L, J / kg)
- high power density (W / L, W / kg)
- cheap materials
- non-toxic, recyclable

Discharge behaviour (i-V): examples



- Leclanché cell
  (AA battery)



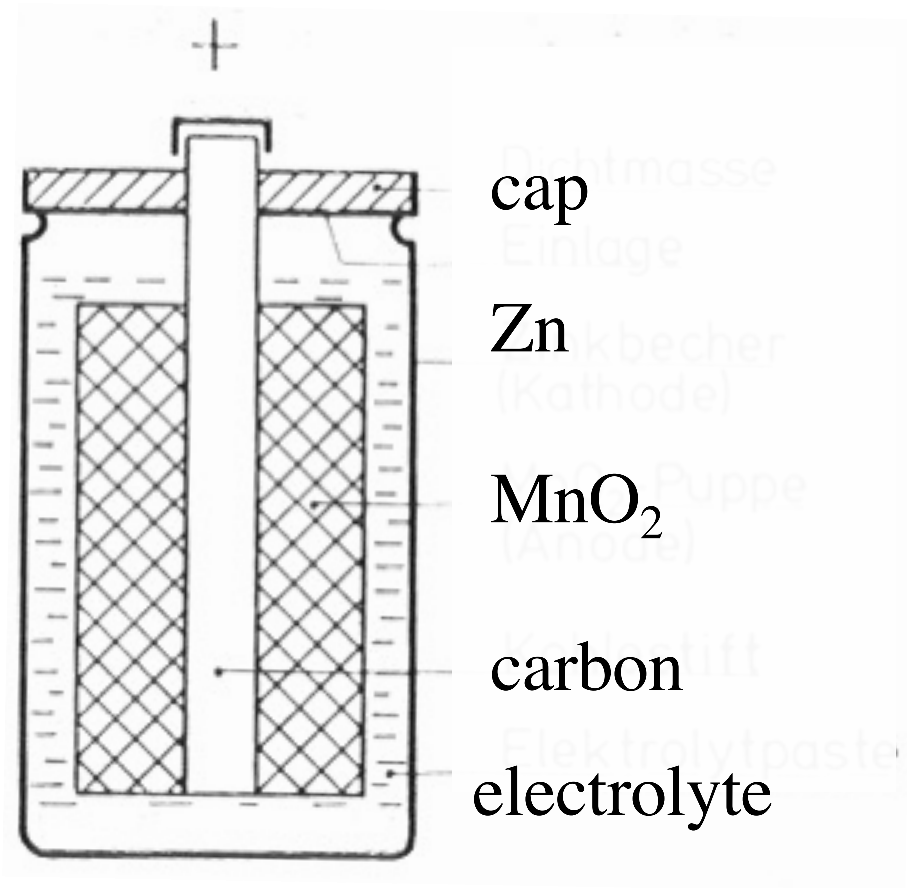
- Pb-acid cell
  (car battery)

Primary battery: Leclanché (alcaline)

$$Anode: \quad \overset{0}{Zn} \Leftrightarrow \quad Zn^{2+} + 2e^- \quad Electrolyte: \quad Zn^{2+} + 2NH_4Cl + 2OH^- \Rightarrow Zn(NH_3)_2Cl_2 + 2H_2O$$

$$Cathode: \quad 2\overset{4+}{Mn}O_2 + 2H_2O + 2e^- \quad \Rightarrow \quad 2\overset{3+}{Mn}O(OH) + 2OH^-$$

$$Total: \quad 2MnO_2 + Zn + 2NH_4Cl \quad \Rightarrow \quad 2MnO(OH) + Zn(NH_3)_2Cl_2$$

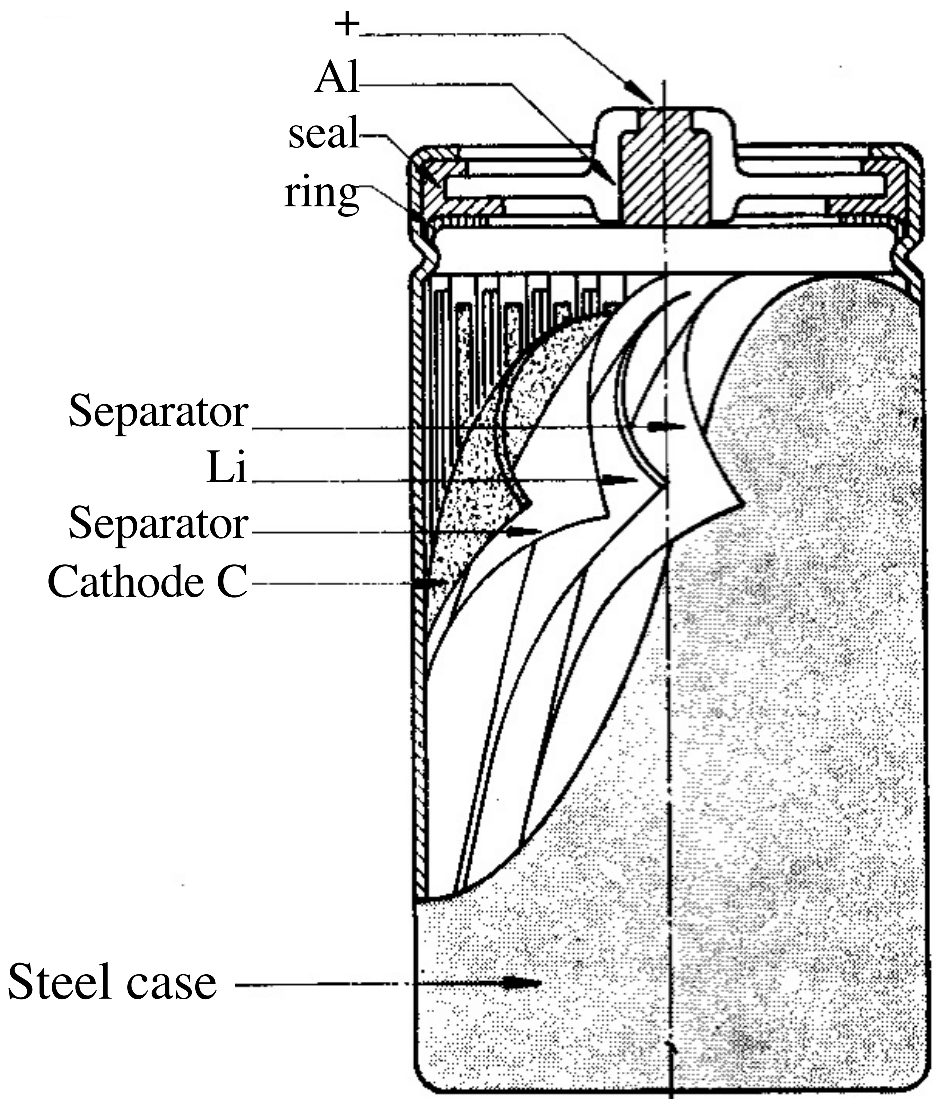


- cathode = carbon rod
  immersed in cathode paste (MnO_2)
  and electrolyte paste
- container = Zn (or Al, Mg) = anode
- 1.5 V "AA" battery = reverse design (Zn inside)

Primary Li batteries

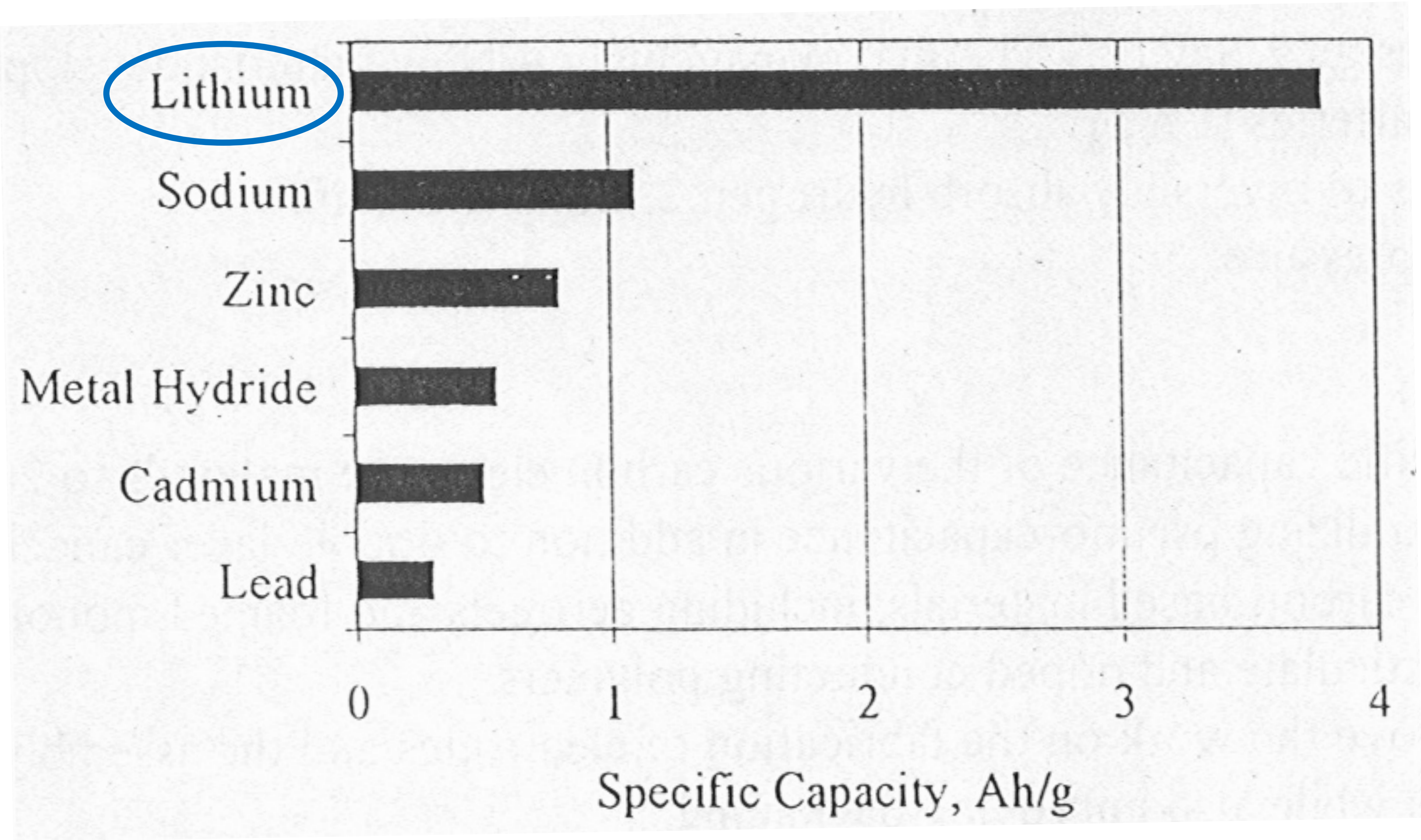
- Li metal as anode
- cathode = $SOCl_2$
- **Li** : - low density (0.53 g/cm^3)
  - most negative potential of all elements (-3 V)
  - high theoretical energy density (300 Wh/kg)
- electrolyte ≠ H_2O !
  - polymer foils, organic solvents
- free of corrosion (life > 10 ans)
- application f.ex. implants (pacemaker,…)

Li/$SOCl_2$ primary battery

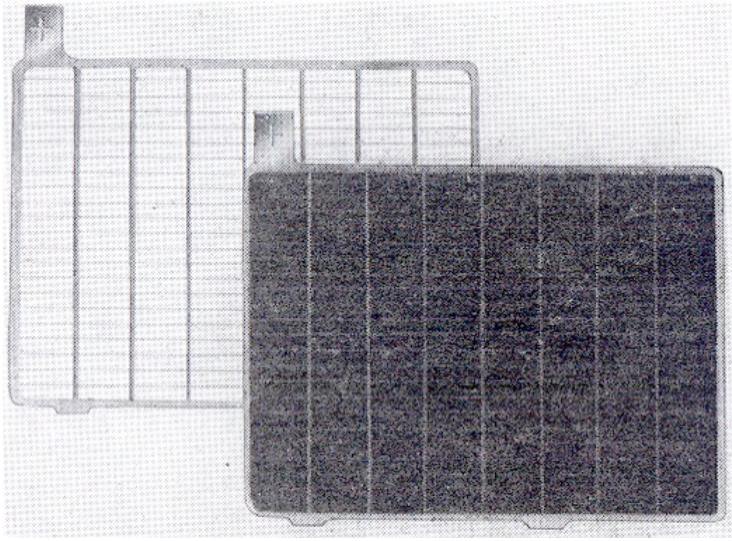


- Li-foil (-);
- separator in polypropylen (PP);
- steel grid (+) enrolled in a steel casing
- electrolyte : LiBr salt, organic solvent, $SOCl_2$ impregnated in PP foil

Storage capacity of battery metals



Pb-acid secondary battery (reversible)



$$PbO_2 + 2H^+ + 2e^- + H_2SO_4 \Rightarrow PbSO_4 + 2H_2O$$

$$Pb + H_2SO_4 \Rightarrow PbSO_4 + 2H^+ + 2e^-$$

- Pb grids filled with a paste of $Pb/PbO/PbSO_4$:
  the active mass is formed during the 1st charging process
- self-discharge : 0.5% / day
- **poor energy** density E_s (40 Wh/kg)
- **high power** density (250 W/kg), 600A @ 6V
- degradation : - Pb corrosion (by acid)
  - sulfatation (loss of $PbSO_4$)
  - cycles (1000)
- but : cheap and very well studied system

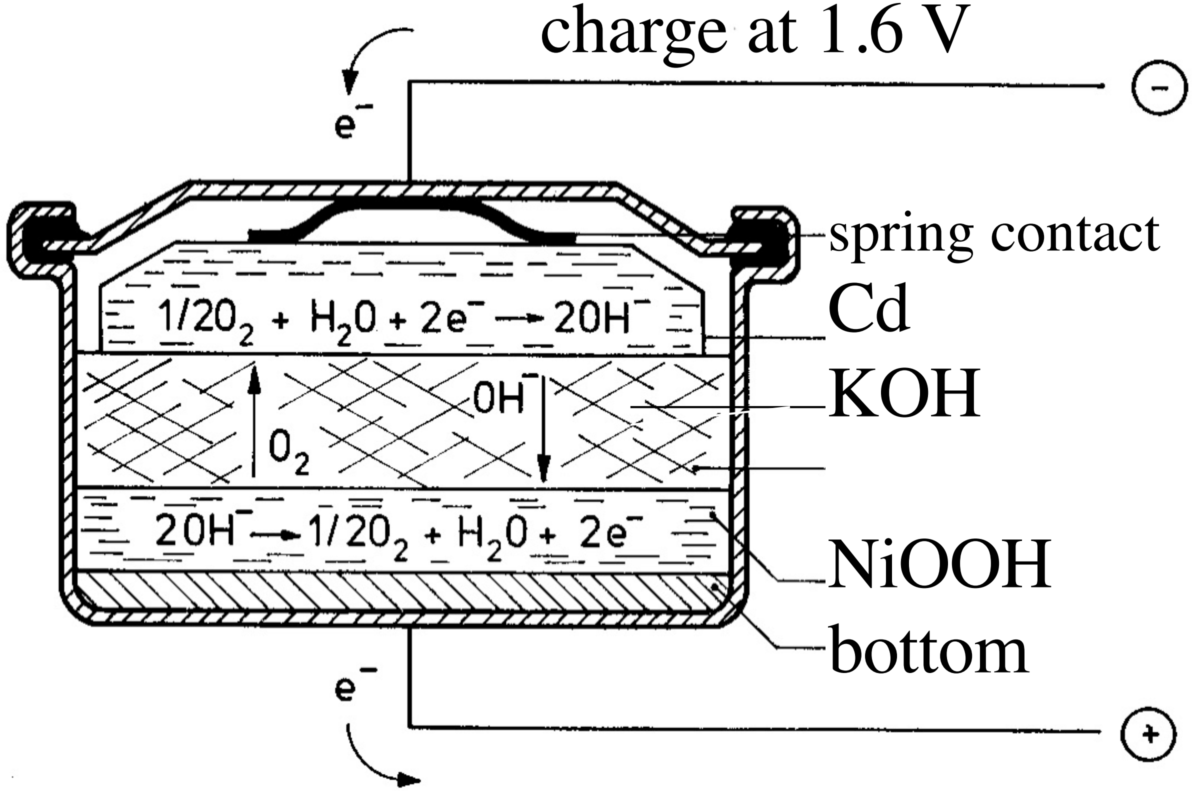
Ni(+)/Cd(-) (secondary battery)

- Button cells (portable electronics)
- Electric vehicles

www.saftbatteries.com

- Cd toxicity : replaced in part by Fe (‘steel accumulator’)
- Ni-Cd now replaced by :
  - Ni-MeH
  - Li ion

Ni-Cd 'button' cell



- gastight
- protection against overcharge (=formation of O_2 -> risk of rupture) : avoided by a internal short-circuit

$$\overset{0}{Cd} + 2OH^- \Leftrightarrow \overset{2+}{Cd}(OH)_2 + 2e^-$$

$$2\overset{3+}{Ni}O(OH) + 2H_2O + 2e^- \Leftrightarrow 2\overset{2+}{Ni}(OH)_2 + 2OH^-$$

‘Soluble’ accumulators

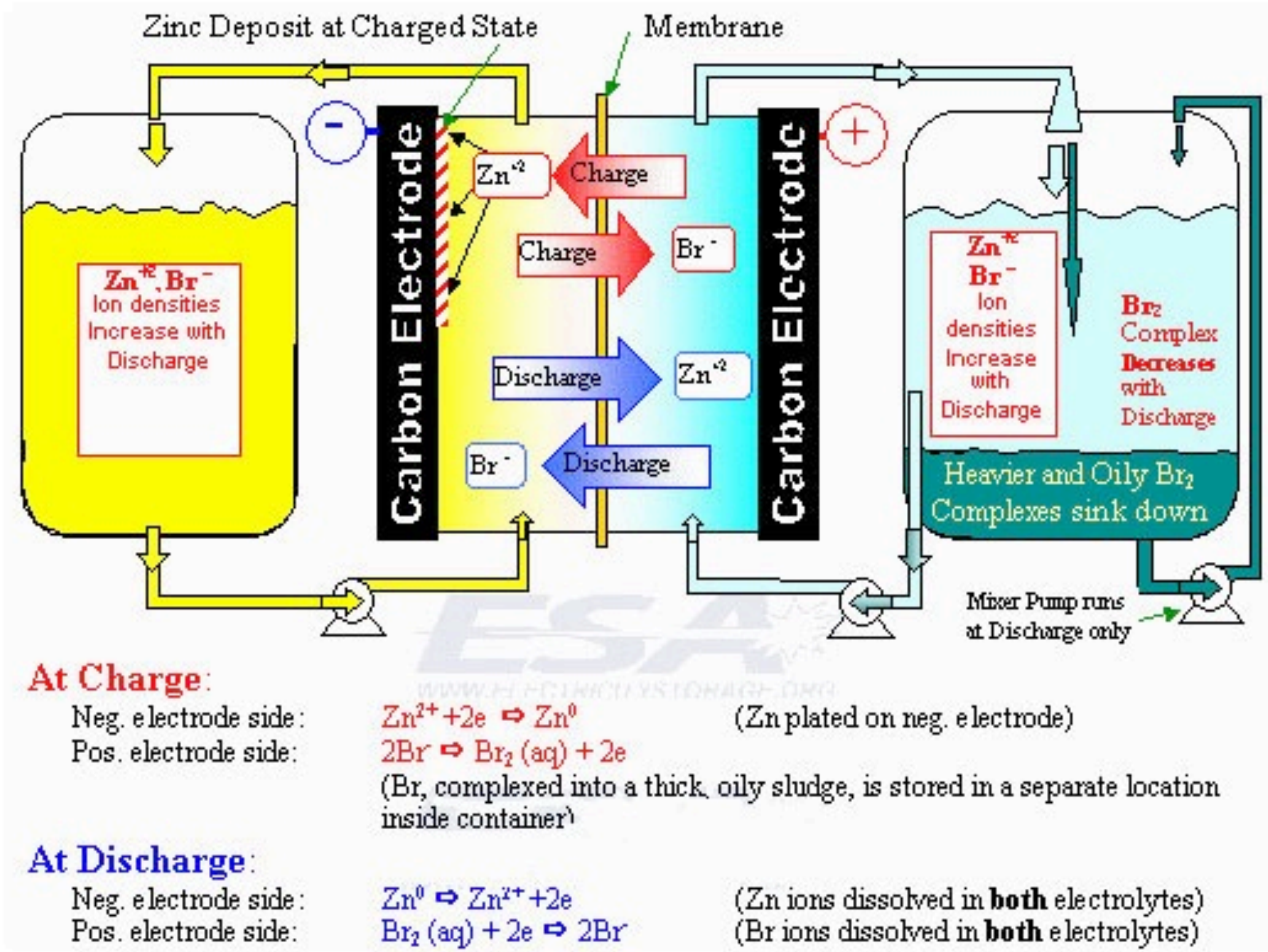
- the active anode mass (**Zn**) is dissolved during discharge (f.ex. solution of $ZnBr_2$)

  = 100% utilisation of the active mass
- system separated in components : Br_2 reservoir, pump to circulate the electrolyte
- high energy density, low cost : -> vehicles
- limited operation regime (T-range, self-discharge)
- also : good potential in electricity storage

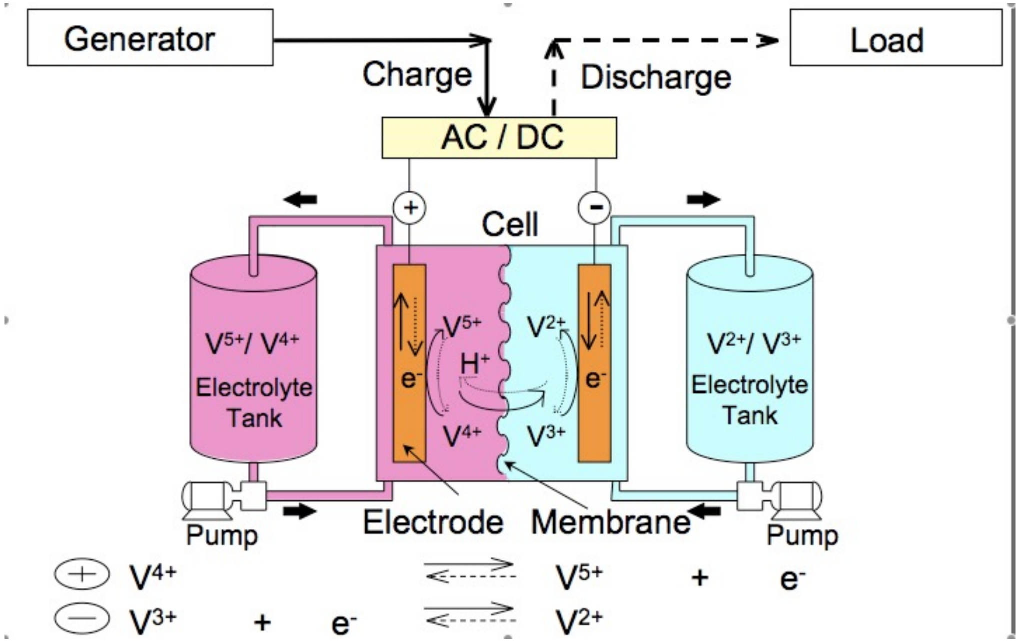
  (“**REDOX FLOW**”)

“REDOX FLOW”

- net efficiency 75%
- since 1970 (Exxon)
- installations of
  1 MW / 4 MWh

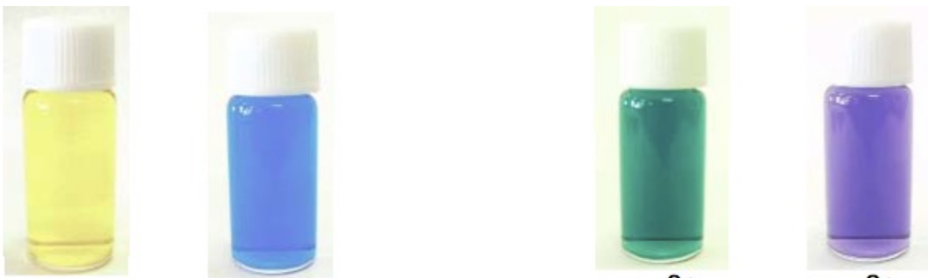


Vanadium redox flow (VRB)

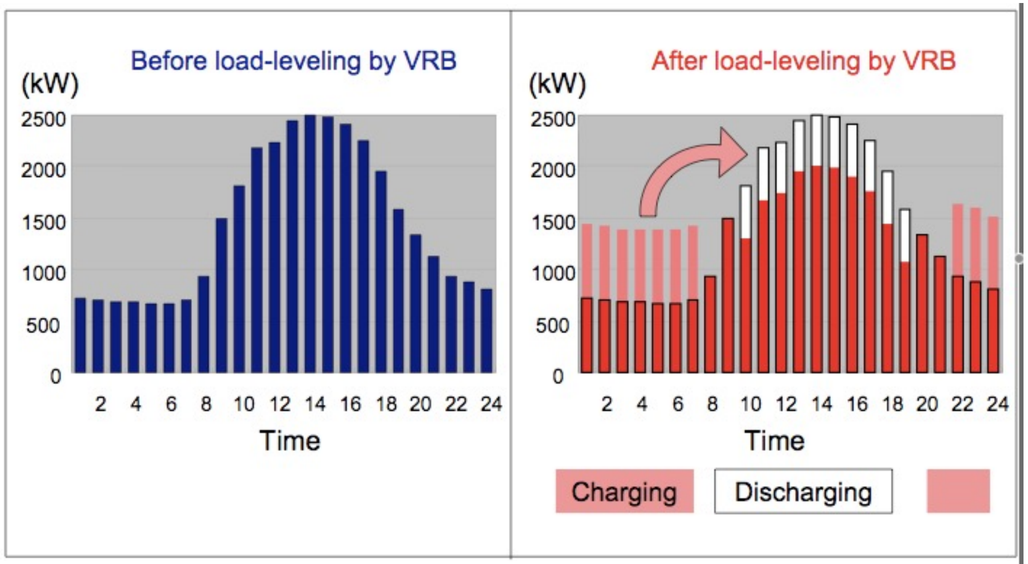


- 10' 000 cycles (>10 yrs); 85% efficiency
- 25 Wh/kg (low); 0.35 ms response time
- for storage ('load-leveling') or peak power ('peak-shaving', f.ex. 3 MW/2s):
  - Hokkaido (Jap,2005) : 30 MW wind farm, for 4 MW/90 min VRB capacity
  - Castle Valley (Utah,2004): 250 kW/8 h VRB to avoid a 5M$ transmission line

500 kW/10h



V^{5+} V^{4+} V^{3+} V^{2+}

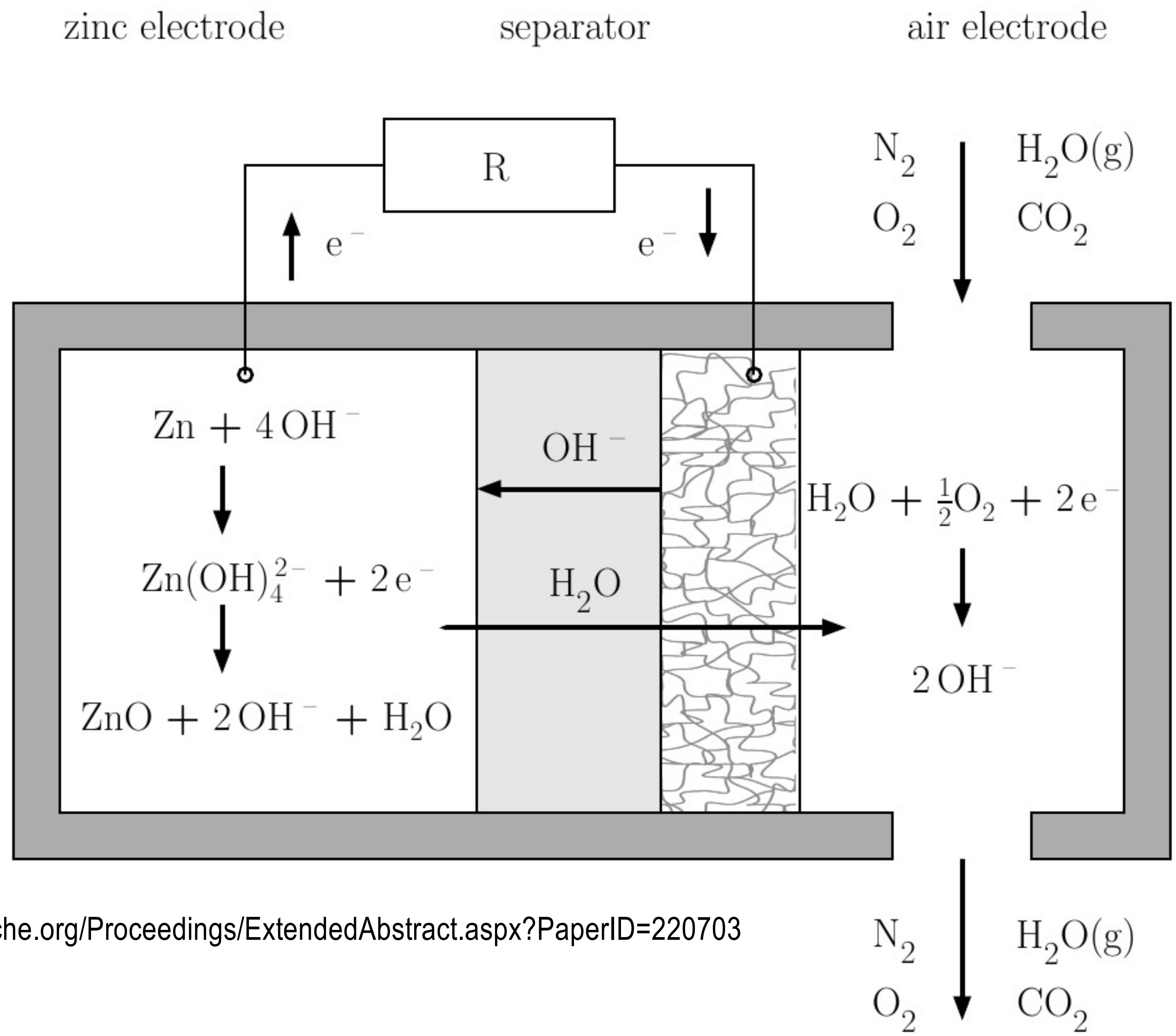


‘Hybrid’ accumulators

- **Zn/air**
  - a battery that “breaths air” (O_2 = active mass) : fuel cell-like O_2 diffusion cathode
  - the anode is a Zn paste made as a rechargable cartridge
  - commercialised

- **Ni/MeH** (metal-hydrides)
  - H_2 stored in special alloys, released by mild heating
  - dominates (with Li-ion batteries) the ‘3C’ electronics market (computers, cameras, cellular phones)
  - high densities in J/kg and W/kg, rapid recharge, 2000 cycles

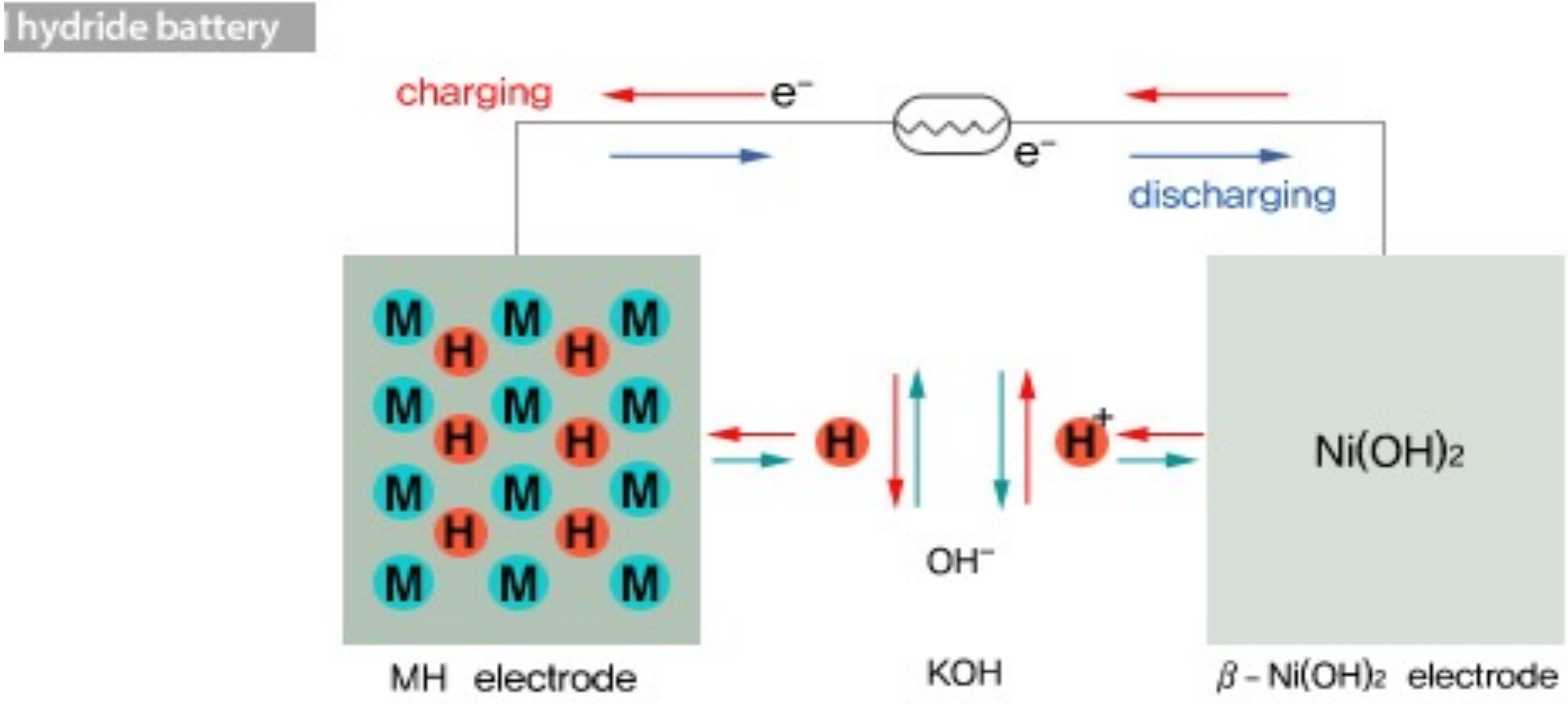
Zn-air battery



http://www3.aiche.org/Proceedings/ExtendedAbstract.aspx?PaperID=220703

Principle of operation : Ni-MeH

http://batteryrocket.com/eng/html/tech.php



(−) $M + H_2O + e^- \longleftrightarrow MH + OH^-$ $E = -0.82V$ (vs.SHE)

(+) $\beta-Ni(OH)_2 + OH^- \longleftrightarrow \beta-NiOOH + H_2O + e^-$ $E = 0.52V$(vs.SHE)

Overall rx. $M + \beta - Ni(OH)_2 \longleftrightarrow MH + \beta - NiOOH$ $E = 1.34V$

Liquid sodium accumulators (high T)

- Na/S
  - ceramic β-Al_2O_3 tube filled with Na_{liq}
  - 350° C
  - $3S + 2Na^+ + 2e^- \rightarrow Na_2S_3$
  - low cost (-> vehicles)
  - problem : maintenance of temperature

- $Na/NiCl_2$
  - more advanced
  - **ZEBRA** battery (EV)
  - 100'000 km, 4 yrs
  - 150 km autonomy
  - commercialised

- 18 kWh
- 280 V
- 195 Wh/kg
- 265 kW peak

http://www.mpoweruk.com/zebra.htm

Secondary Li batteries (rechargeable)

At first:

- Li metal
  - LiAl anode
  - FeS cathode
  - 450° C
  - molten salt electrolyte

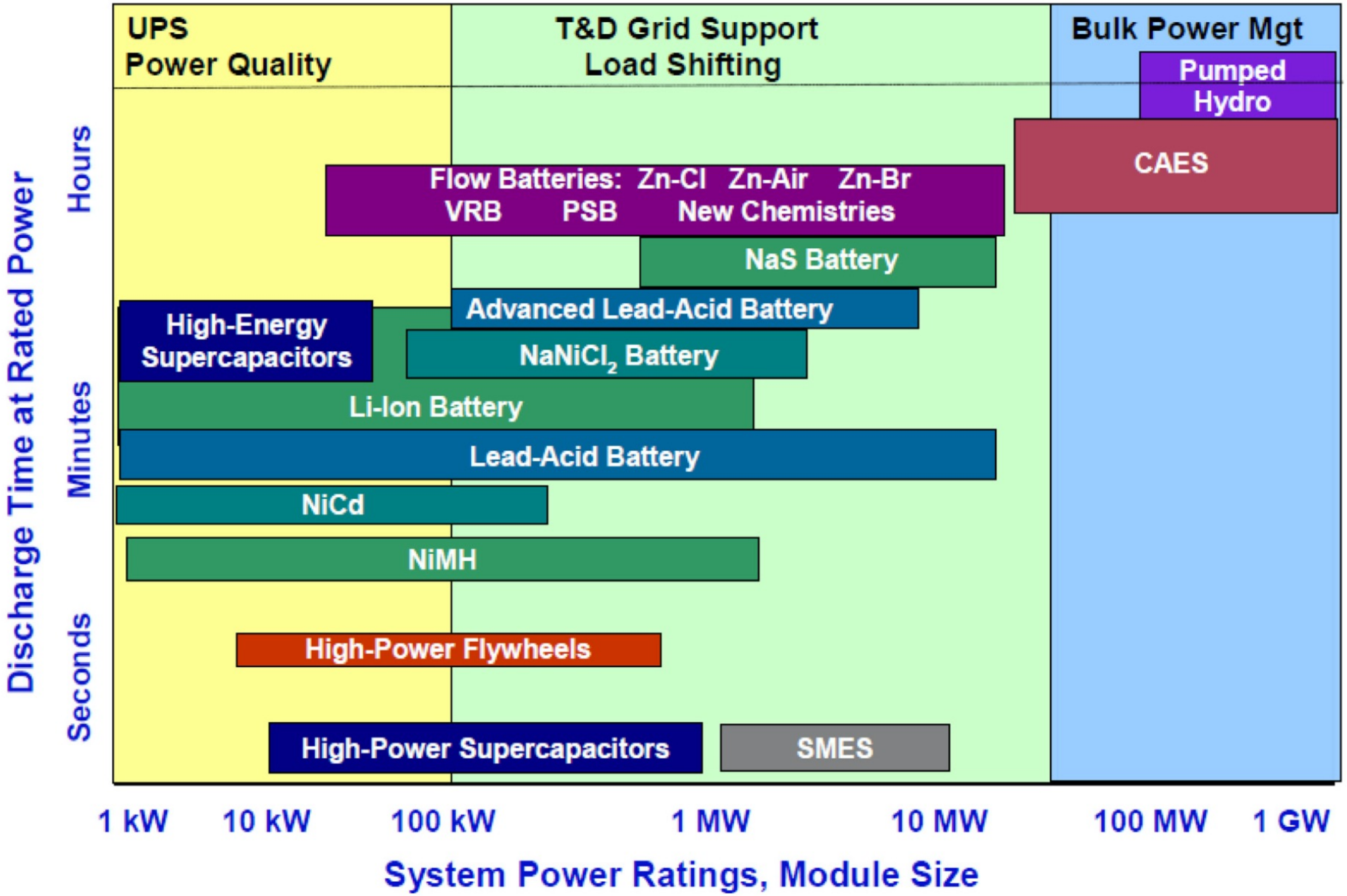
- Probleme of Li metal: passivation

Now :

- **<u>Li ion</u>**
  - Li storage in layered structures :
    - C (LiC_6 anode)
    - oxides, sulphides (cathode)
  - electrolyte :
    - polymer film
    - organic liquid
- Li moves back and forth in-between intercalation electrodes ("rocking chair battery")

Possible technologies for electricity storage

A.Z. AL Shaqsi, K. Sopian and A. Al-Hinai / Energy Reports 6 (2020) 288–306 293



Existing electrical storage capacity

<u>2018</u>: 173 GWe, of which
98% pumped hydro schemes

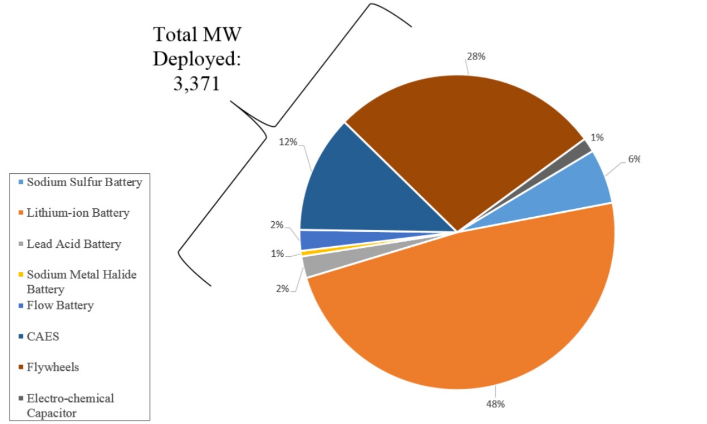
2.0 Worldwide Energy Storage Deployments by Technology

As of 2018, nearly 173 GW of energy storage had been deployed across the world. Table 2.1 outlines the current total installed capacity in megawatts by technology type worldwide up to 2018. Information was gathered from the DOE Storage Database (DOE 2018a) and compiled by technology type. Note that some of the records from the database are unverified and therefore the numbers below should be considered approximate.

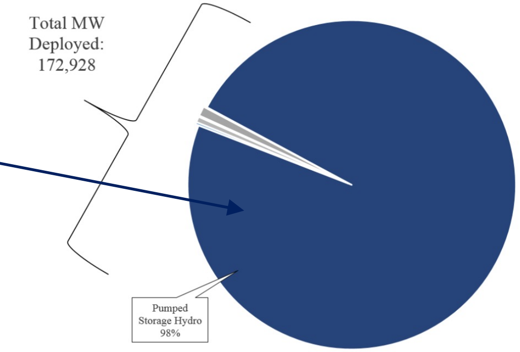
Table 2.1. Worldwide deployment by technology type, 2018.

Technology	MW Deployed
Sodium sulfur	189
Lithium-ion	1,629
Lead acid	75
Sodium metal halide	19
Flow battery	72
PSH	169,557
CAES	407
Flywheels	931
Electrochemical capacitor	49
Total	172,928

Li-ion dominate batteries schemes



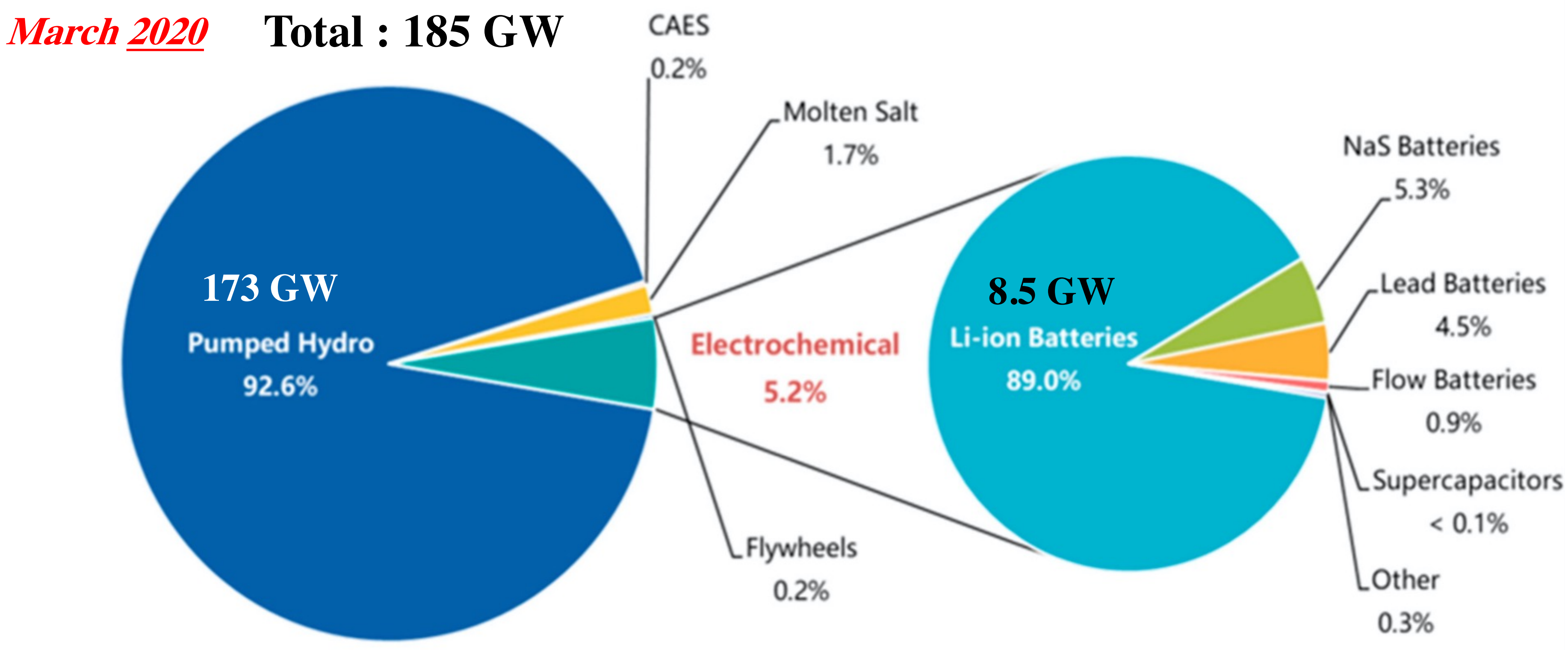
Breakdown of energy storage deployed internationally by technology type and excluding pumped storage hydro.



Proportion of megawatts of internationally deployed pumped storage hydro in comparison to other technologies.

Energy Storage Technology and Cost Characterization Report, July 2019
K Mongird, V Viswanathan, P Balducci, J Alam, PNNL-28866
https://www.energy.gov/eere/water/hydrowires-initiative

Rapid growth in storage capacity (esp. Li-ion)



Sustainability 2020, *12*, 10511; doi:10.3390/su122410511
A Review of Energy Storage Technologies Application Potentials in Renewable Energy Sources Grid Integration
Henok Ayele Behabtu, Maarten Messagie, Thierry Coosemans, Maitane Berecibar, Kinde Anlay Fante, Abraham Alem Kebede, Joeri Van Mierlo

LCOES

PHS / CAES: slow response time (>10 s) and large minimum sizes (>5 MWe) => not suited for primary response and power quality and small-scale consumption.

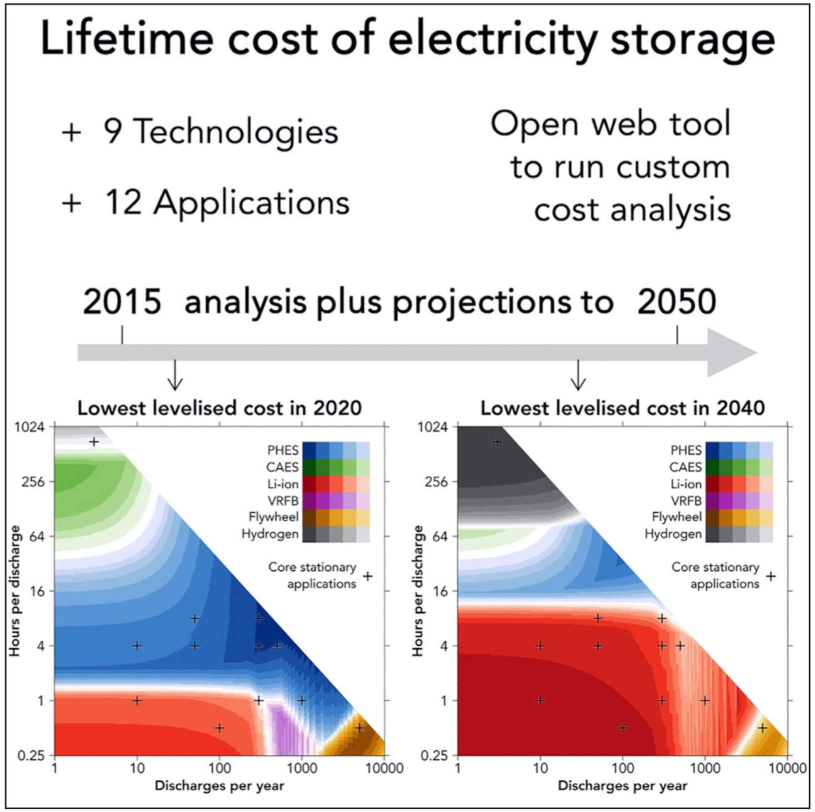
Flywheels and supercapacitors : short discharge (<1 h) => not suited for longer-term power.

Seasonal storage (months, >700h): only met by technologies where energy storage capacity is fully independent of power capacity. (PtG, H_2)

Schmidt et al., Joule 3, 81–100
January 16, 2019 a 2018 Elsevier Inc.
https://doi.org/10.1016/j.joule.2018.12.008

Article

Projecting the Future Levelized Cost of Electricity Storage Technologies



Oliver Schmidt, Sylvain Melchior, Adam Hawkes, Iain Staffell

o.schmidt15@imperial.ac.uk

HIGHLIGHTS

Lifetime cost for 9 storage technologies in 12 applications from 2015 to 2050

Lowest lifetime costs fall by 36% (2030) and 53% (2050) across the 12 applications

Lithium-ion batteries are most competitive in majority of applications from 2030

Pumped hydro, compressed air, and hydrogen are best for long discharge applications

ELECTRIC VEHICLES

- Advantages :
  - **efficiency 75% (200Wh/km battery => 150 Wh/km at wheel)**
    - 3-4 times better than a gasoline car
  - low pollution (local ! not necessarily global !)
  - low noise

- Limitations :
  - range (**low energy** density)
  - acceleration, slopes (**low power** density)
  - recharging
  - battery materials availability

Energy densities

TABLE 3 : ENERGY DENSITIES OF FUELS

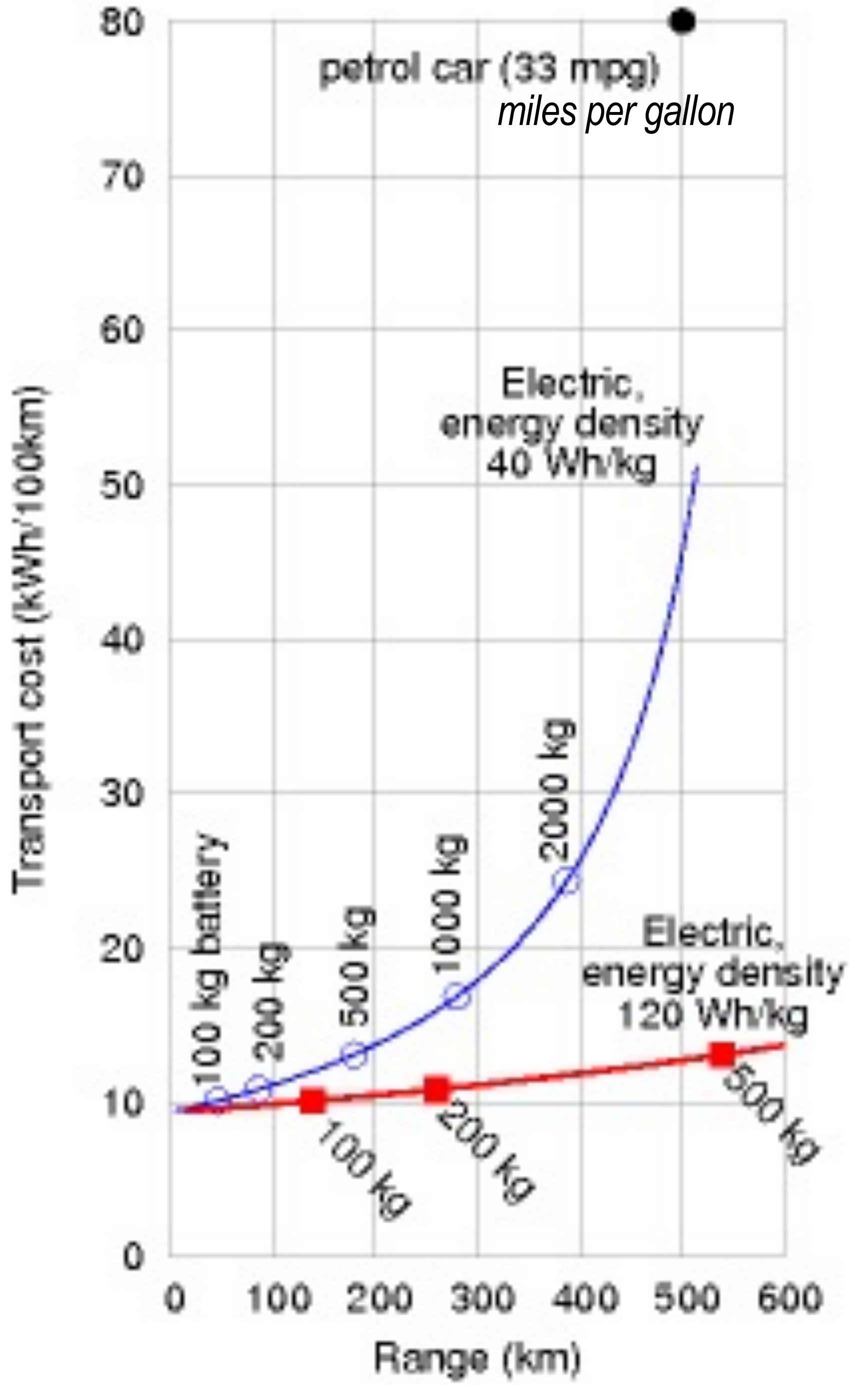
Fuel	MJ / kg	kWh / L
Gasoline	36	10.4
Diesel	35	10.8
MeOH	16.7	5
LPG	21	7.5
CNG	7.7	2
LH_2	22	2.8
CH_2	3.9	0.6
Pb-battery	0.16	0.06
NiMH	0.22	
MgH_2		4.4

Battery cars

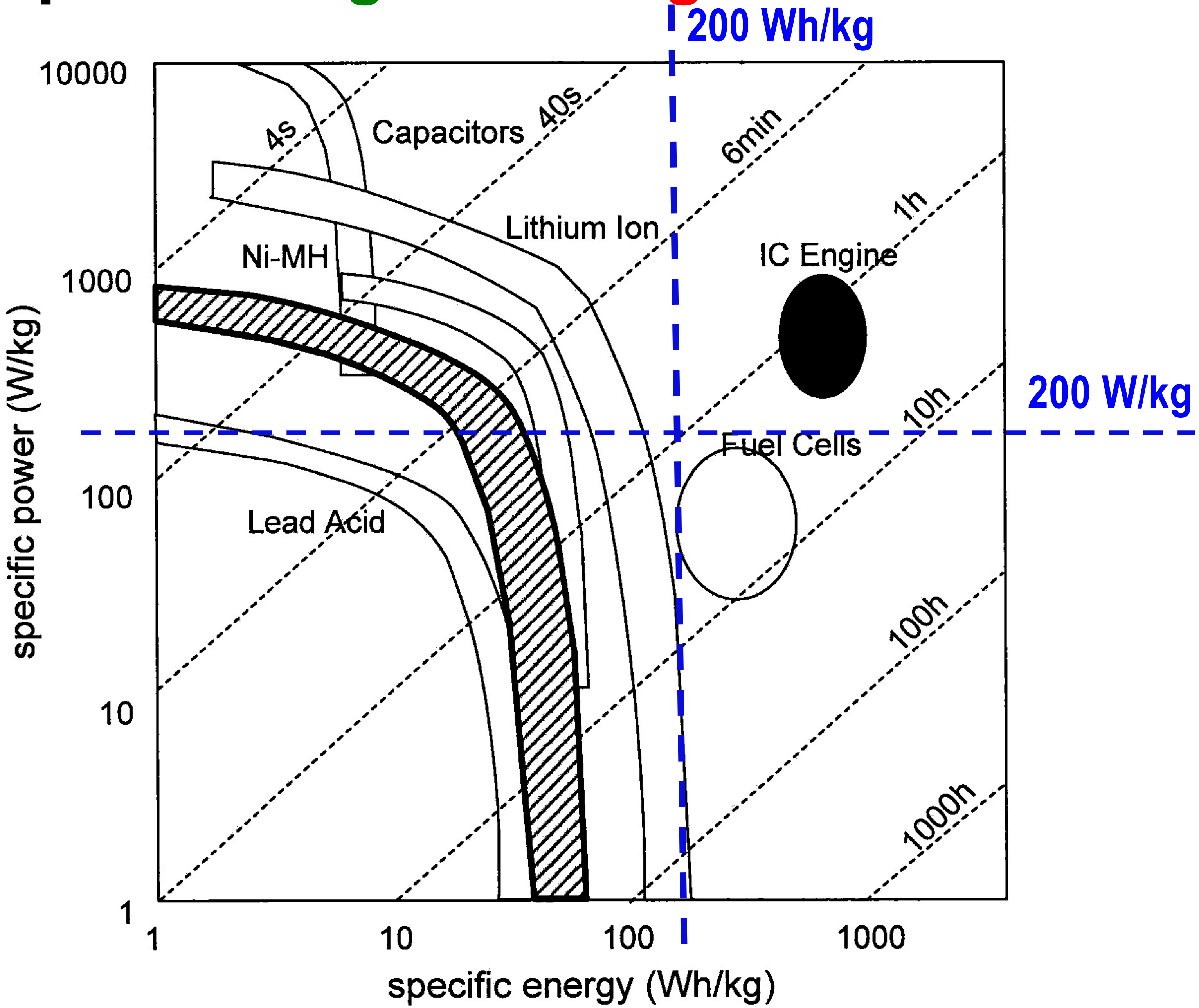
m_{car}=740 kg, without batteries
ε = 0.85 (charging / discharging efficiency)
$c_d A$ = 0.8 m^2 (air resistance cross-section)
c_r = 0.01 (road rolling resistance)
v=15 m/s (50 km/h)
d = 500 m (avg. distance btw start-stop)
(with 50% regenerative braking)

Allow for a 500 kg battery:
difficult with Pb-acid (40 Wh/kg)
→ range < 200 km
possible with Li-ion (120 Wh/kg)
→ range > 500 km

(D McKay, 'Sustainable Energy')

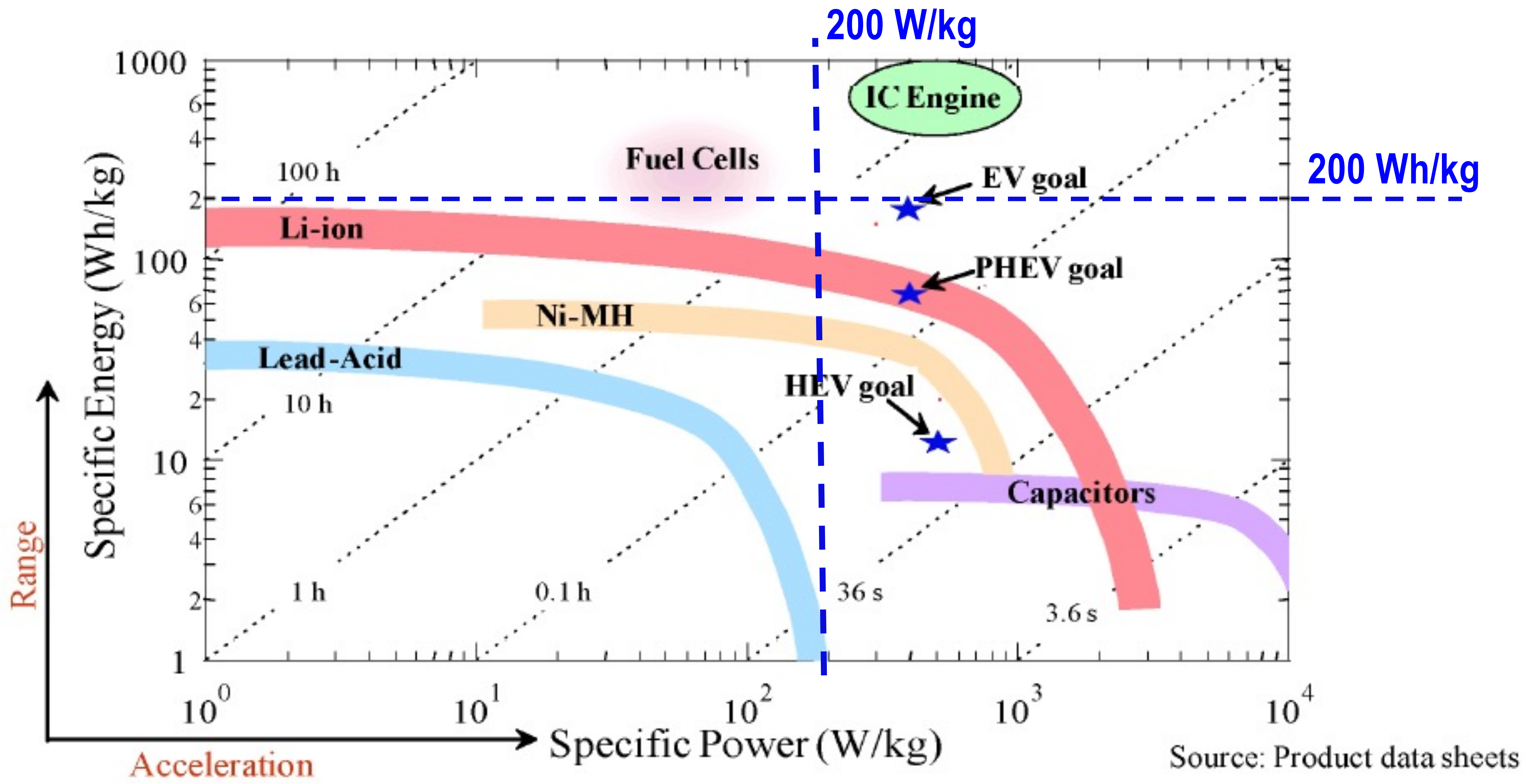


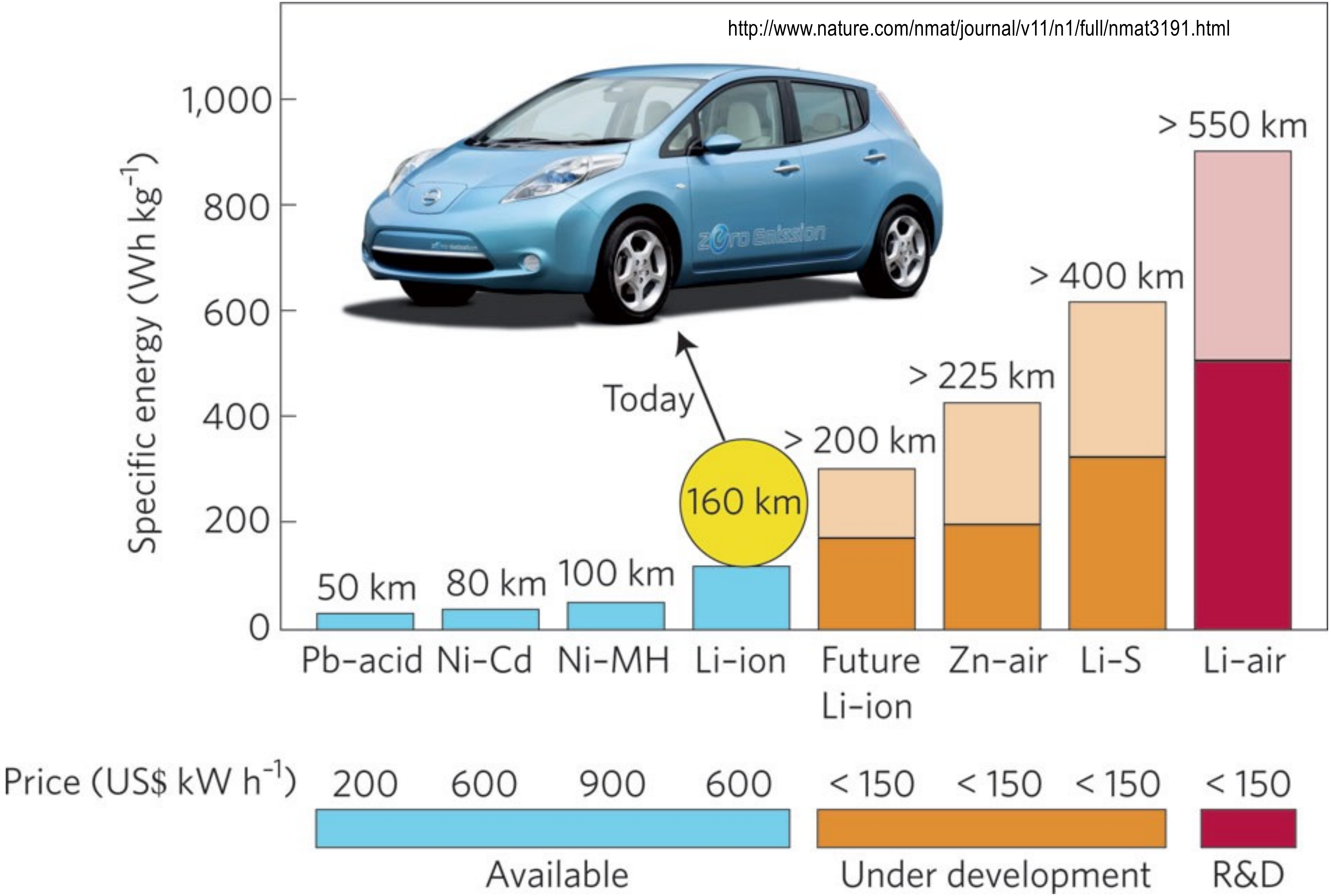
Ragone plot : W/kg vs Wh/kg



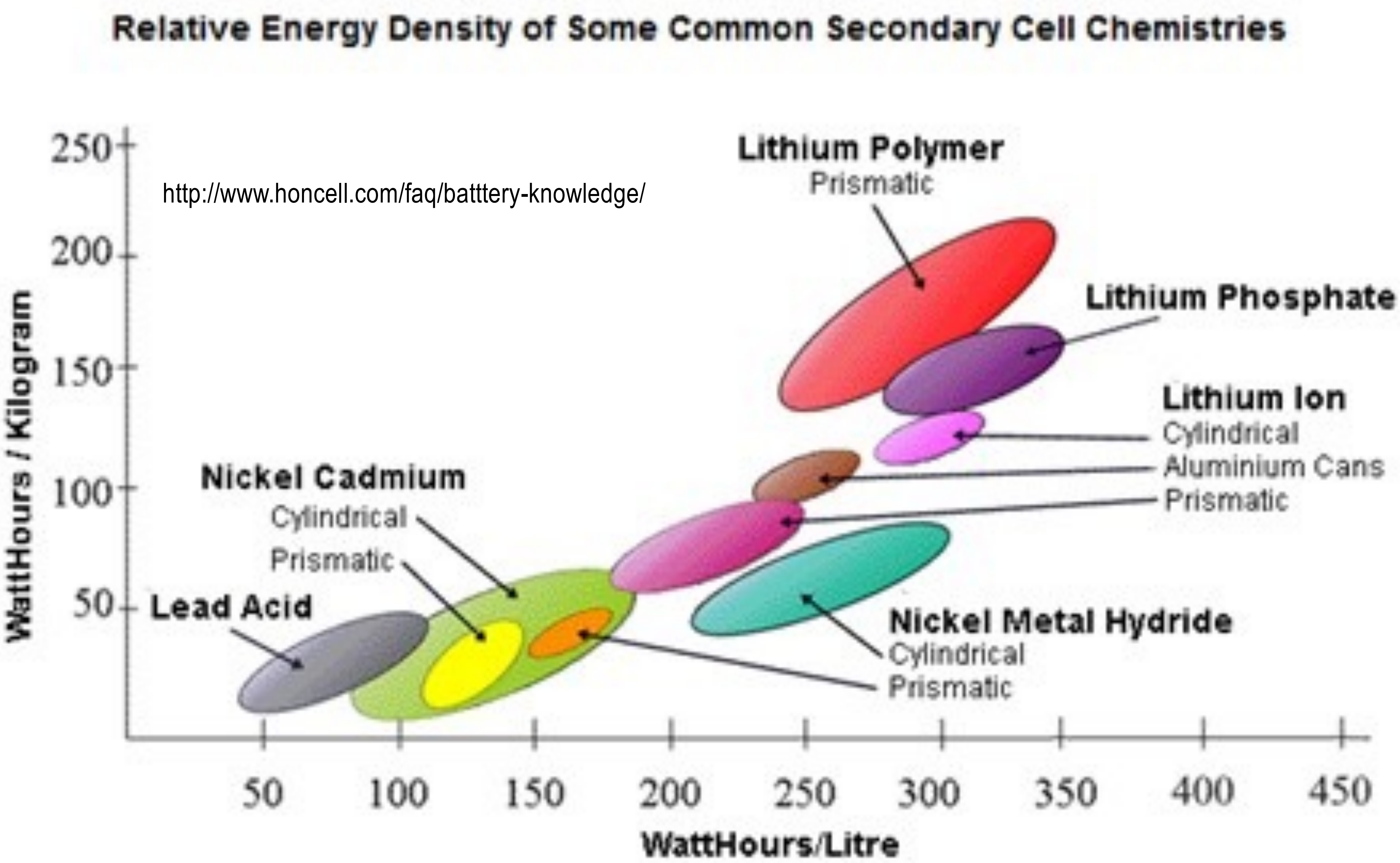
Ragone plot Wh/kg vs W/kh

http://physics.ucsd.edu/do-the-math/2012/08/battery-performance-deficit-disorder/




http://www.nature.com/nmat/journal/v11/n1/full/nmat3191.html
Specific energy (Wh kg^{-1})
1,000
800
600
400
200
0
Today
50 km
80 km
100 km
160 km
> 200 km
> 225 km
> 400 km
> 550 km
Pb–acid
Ni–Cd
Ni–MH
Li–ion
Future Li–ion
Zn–air
Li–S
Li–air
Price (US$ kW h^{-1})
200
600
900
600
< 150
< 150
< 150
< 150
Available
Under development
R&D

Wh/kg and Wh/L (energy per weight, and per volume) of common bateries



Recap on batteries for E-Vehicles

- batteries fulfill conditions for a city car
- to reach the performances of a gasoline car, a huge battery is required, constituting a big part of the weight of the vehicle…
- **electric driving = very efficient** : 0.2 kWh/km

(gasoline : 0.7 kWh/km)

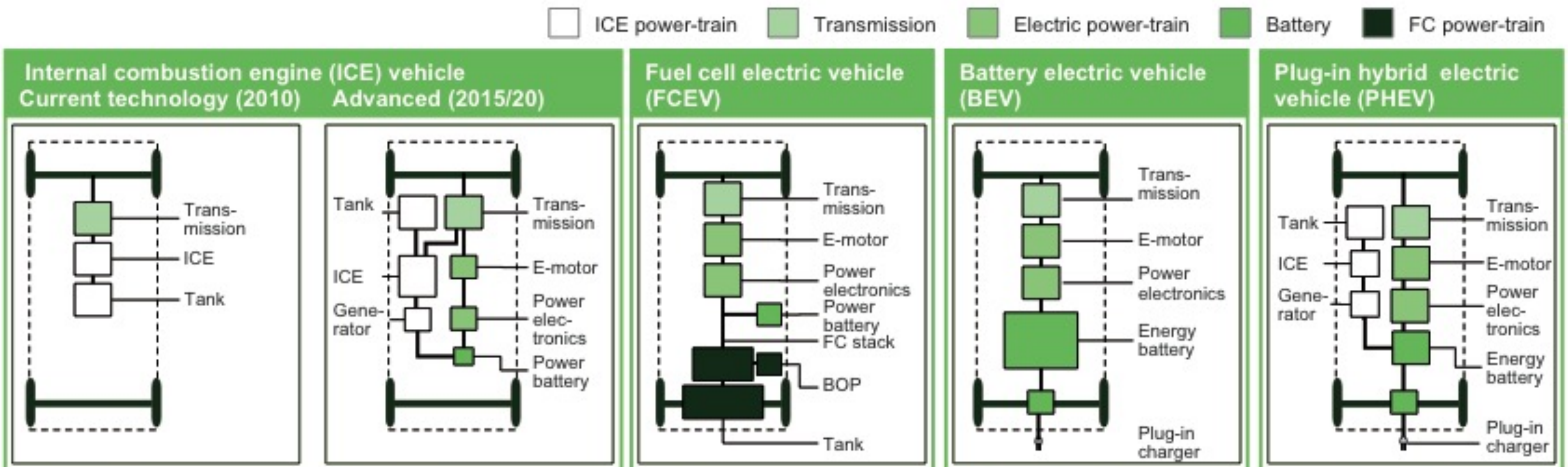
- recharge ?
  - infrastructure
  - installed power

example (CH) : 30 kWh car, recharge time 10 h, charging source of 4 kW, 30% of the vehicle fleet (1.5 mio cars)

→ **requires a charging source of 6 GW !**

Annex – EU study report on transport

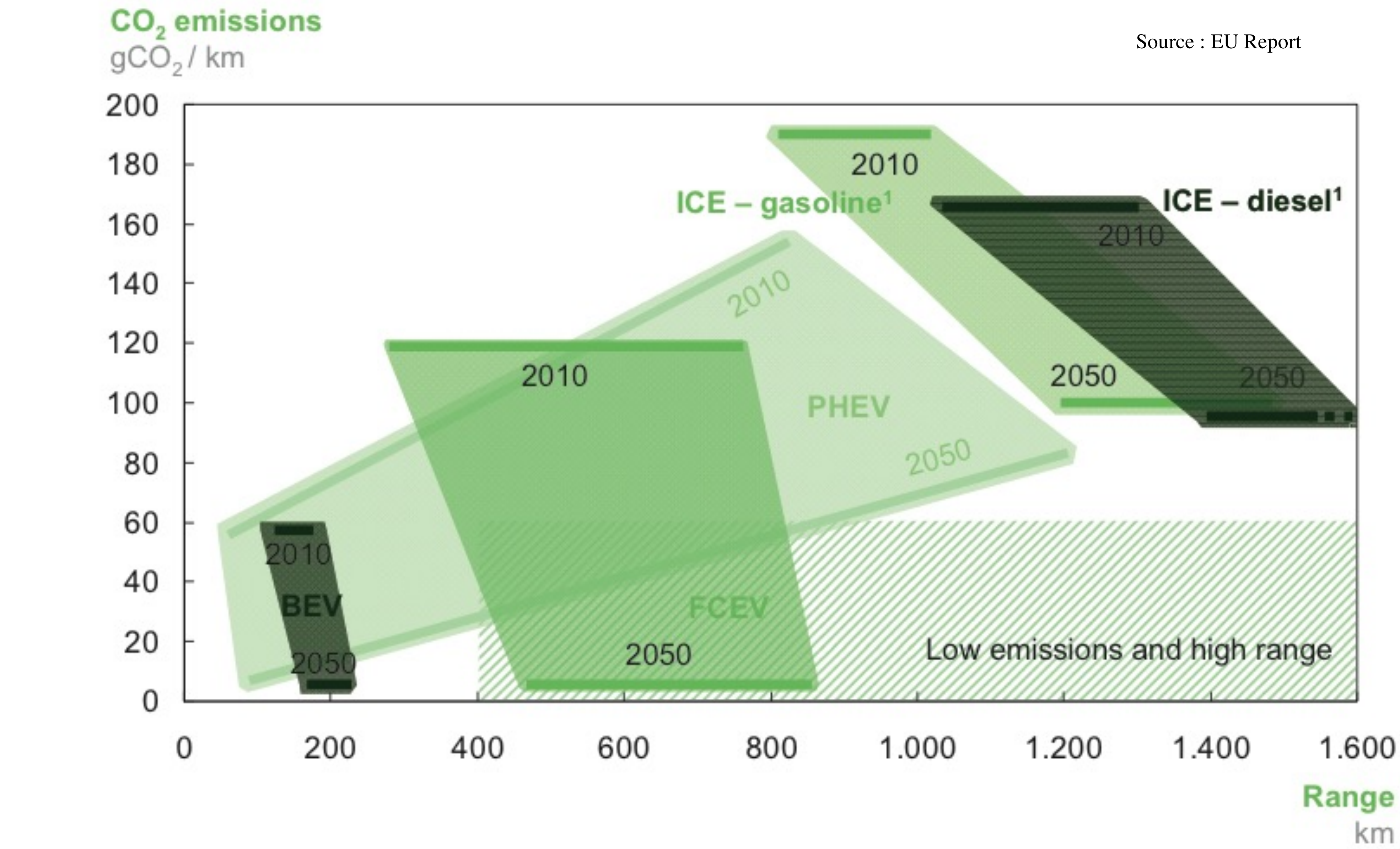
Possible drive trains: ICE, electric, FC and hybrids



Internal combustion engine (ICE) vehicle — Current technology (2010)	Advanced (2015/20)	Fuel cell electric vehicle (FCEV)	Battery electric vehicle (BEV)	Plug-in hybrid electric vehicle (PHEV)
▪ **Conventional** internal combustion engine ▪ **No dependency** on electric infrastructure ▪ **High fuel consumption** and exhaust emissions ▪ **High range**: typically 800-1200 km	▪ **Parallel** hybrid configuration of electric and ICE drive; also known as hybrid electric vehicle (HEV) ▪ **ICE is primary mover** of the vehicle with support from small electric motor ▪ **Small battery** charged by the ICE ▪ Fully electric driving only at **low speed** for **smaller distances** (<5 km) ▪ **Better fuel economy** than conventional ICE	▪ **Series** configuration of fuel cell system and electric drive ▪ **Fuel cell stack** based on PEM technology ▪ Hydrogen tank pressure typically 350 or 700 bar ▪ **Medium range**: typically 400-600 km	▪ **Purely electric** drive ▪ Large battery capacity, Li-ion technology ▪ Only charging of battery **from the grid** while stationary[1] ▪ **Short range**: typically 150-250 km (based on battery weight of 70-180 kg[2])	▪ **Series hybrid** configuration of electric and ICE drive[3] ▪ **Smaller battery capacity** than BEV, (Li-ion) ▪ Vehicle can be **plugged-in** to charge from the grid ▪ **Small ICE**-based generator for larger range ('range extender') ▪ **Short range**: typically 40-60 km) electric driving. (based on battery weight of 20-80 kg[2])

Main study outcome:

Source : EU Report



1 ICE range for 2050 based on fuel economy improvement and assuming tank size stays constant. Assuming 6% CO2 reduction due to biofuels by 2020; 24% by 2050

Annex – Mobility Seminar EPFL Nov 2020

by

Dr Priscilla Caliandro (BFH, Biel, PhD at EPFL-GEM, 2018)

on (Li-) batteries

Vehicle architecture in the different configuration

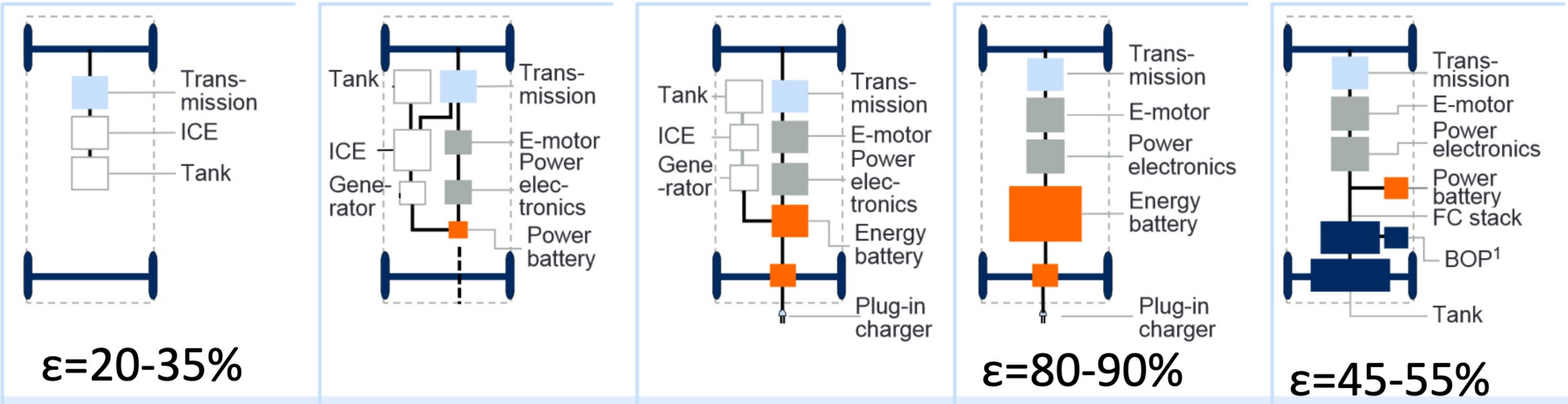
Internal combustion engine, ICE

Hybrid electric vehicles, HEV

Plug-in hybrid electric vehicles, PHEV

Battery electric vehicle, BEV

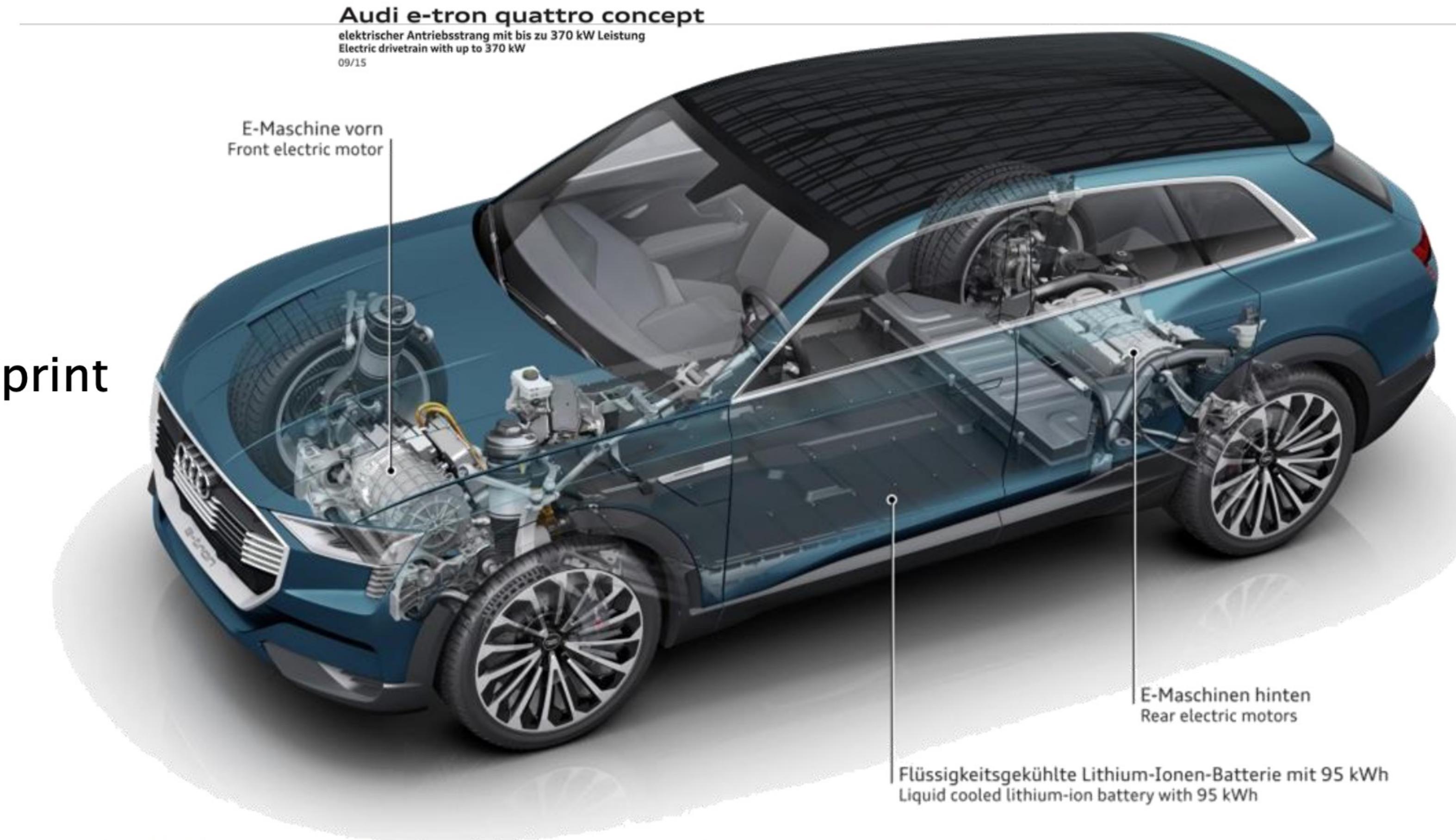
Fuel cell electric vehicle FCEV



Source: Electric vehicles in Europe:gearing up for a new phase? Amsterdam Roundtable Foundation and McKinsey & Company The NetherlandsApril 2014

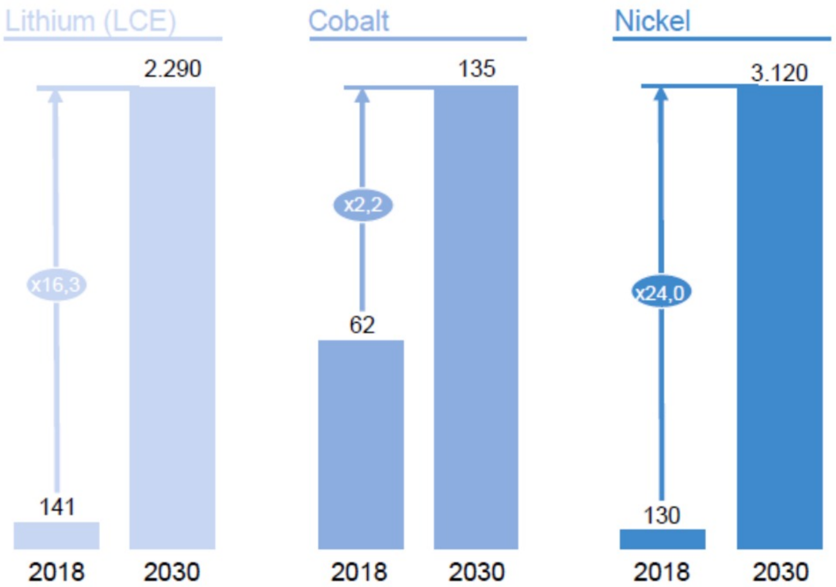
The battery is the defining component of an EV

- Range
- Charging
- Cost
- Power
- Lifetime
- Environmental footprint

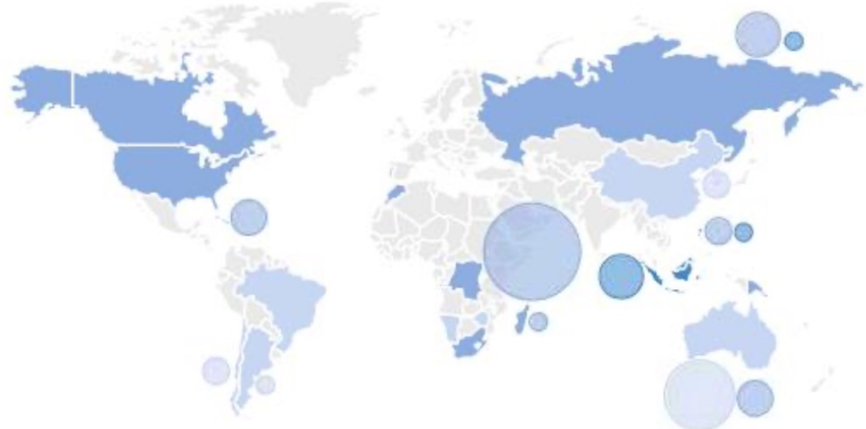


Resources demand

Demand for lithium, cobalt, nickel in 2030
Demand for raw materials in kilotons per year



Quelle: Global Battery Alliance, Sep 19
AVICIENNE Energy, Jan 20
Mining Weekly, Sep 20



- Metal consumption per vehicle battery

	2018		2030
3 Li	35 kg	=	40 kg
27 Co	12 kg	↘	5 kg
28 Ni	25 kg	↗	50 kg

Quelle: Umicore, Sep 2019

Source: Trends im Lithium-Ionen-Batteriemarkt – Klib Frnakfurt 07.10.2020; Dr. Jochen Mähliß, VDE Renewables

Examples of metals need

Metal	kg in one EV	Metal production	No. of cars	Reserves
Li	4 kg (Li-battery)	80’000 t/yr	20 million	11 Mt Li
Co	3 kg (Li-battery)	140’000 t/yr	47 million	13 Mt Co
Nd	1 kg (el.motor)	30’000 t/yr	30 million	18 Mt Nd
Pt	3 g (FC-EV)	200 t/yr	67 million	30’000 t Pt

Car production : 70 million / yr

EV : electric vehicle
FC : fuel cell

What about buses, trucks, bikes, motocycles?

What about the other uses of those metals?

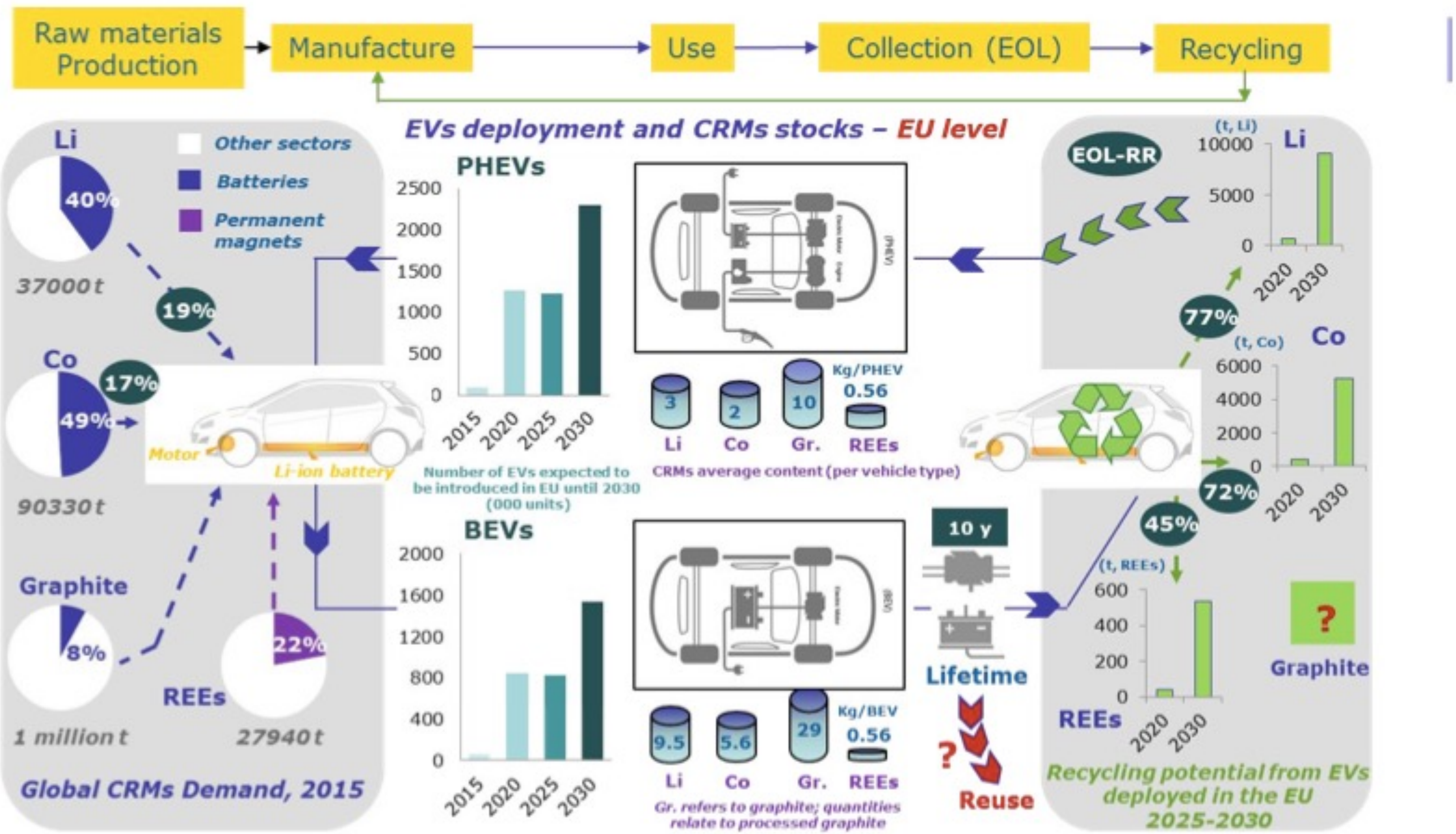
Automotive sector:

- Biggest metal using sector together with ‘Buildings’
- …but much shorter lifetime (15 yrs vs. 50 yrs)
- 70 million cars/yr, and growing
- 20 million/yr light commercial vehicles, 4 million/yr trucks
- Total fleet : 1 billion cars, 400 mio trucks/buses/light commercial vehicles

- for ‘high performance materials’, the steel cannot be recycled
- Recycling can be done for Al, Cu, Pb

Critical materials in EV

Figure 19: CRMs use in the EVs sector (battery electric vehicles (BEVs), plug-in hybrid vehicles, (PHEVs)) and potential flows resulting from recycling of EVs deployed in the EU[158]



[EU Report on Critical Raw Materials and the Circular Economy]

Growth in EV puts pressure on Li, rare earths

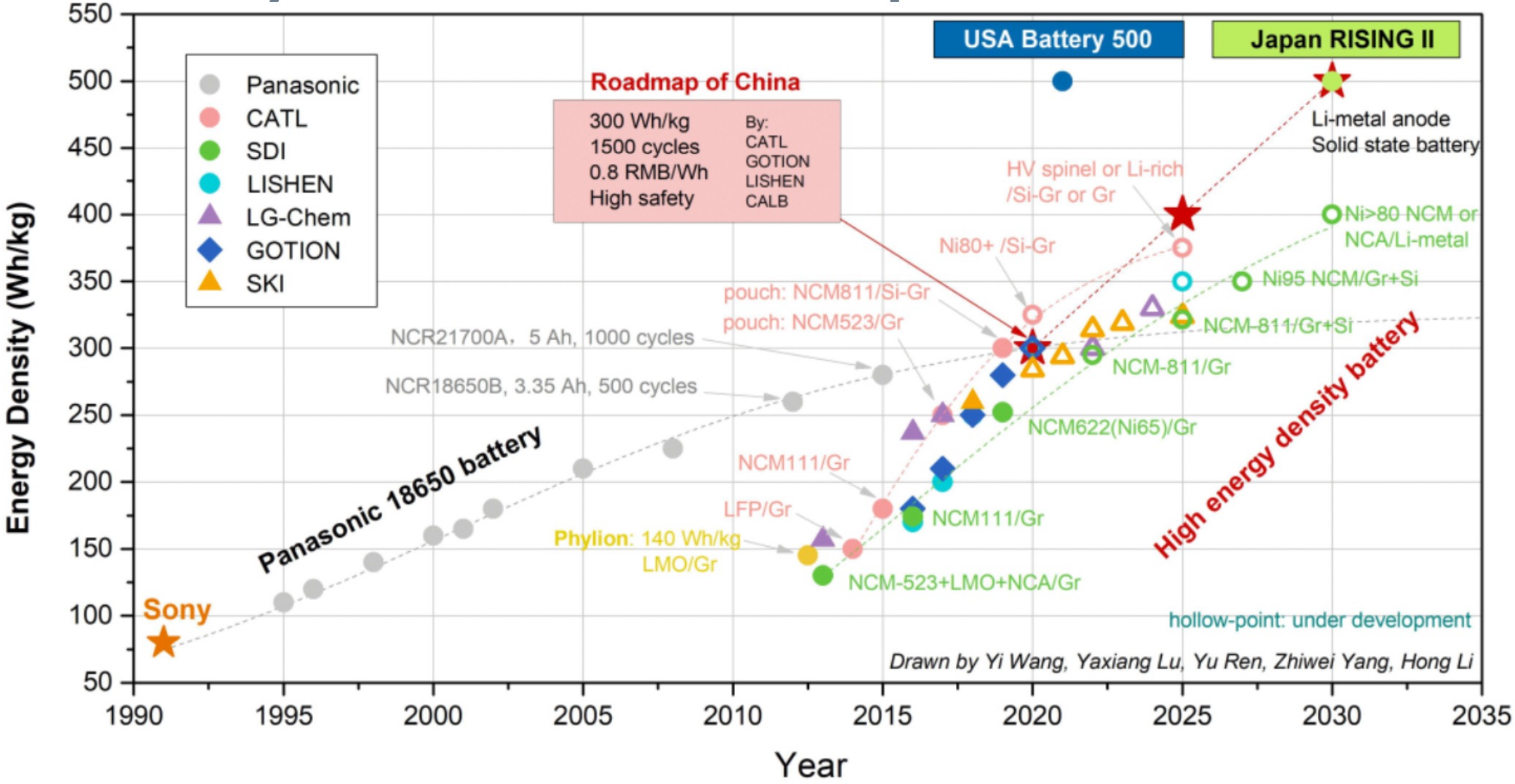
*0.6 kg Li_2CO_3 for 1 kWhe storage

Drive train	kg Li*	kg Ni	kg Mn	kg Nd**
Hybrid EV	2.0	0.4	3.0	1
Plug-in HEV	1.4	2.4	18	
Pure BEV	3.0	5.0	38	
Need 2030	53 kt	88 kt	670 kt	52 kt
Prod. 2019	77 kt	2.7Mt	20Mt	30 kt
% of prod.	70%	3%	3.5%	160%

** Nd is used as permananent magnet in electric motors. Demand is high also in windmills. >90% of RE production is in China.

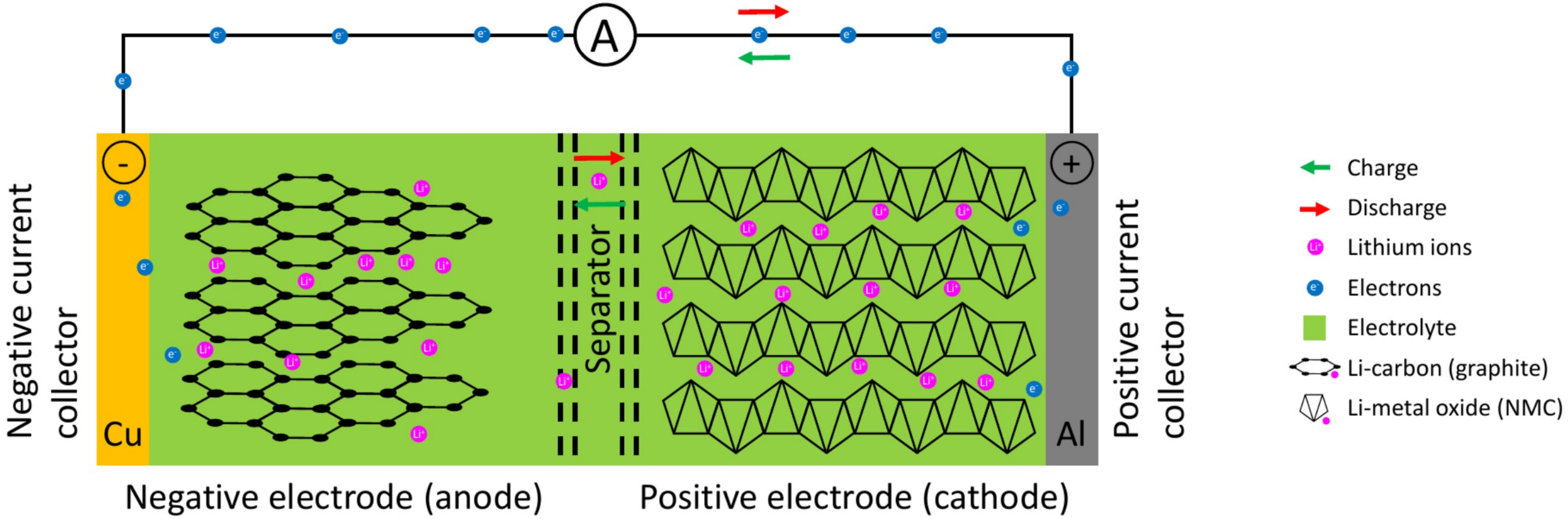
- Li-batteries demand is equally strong in the IT sector.
- Li-batteries require a minimum metal purity.
- Li-reserves are very concentrated (Chile, Bolivia, Argentina)
- NiMnCo-cathodes have alternatives: Li-$FePO_4$, C nanotubes

Li ion battery innovation road map

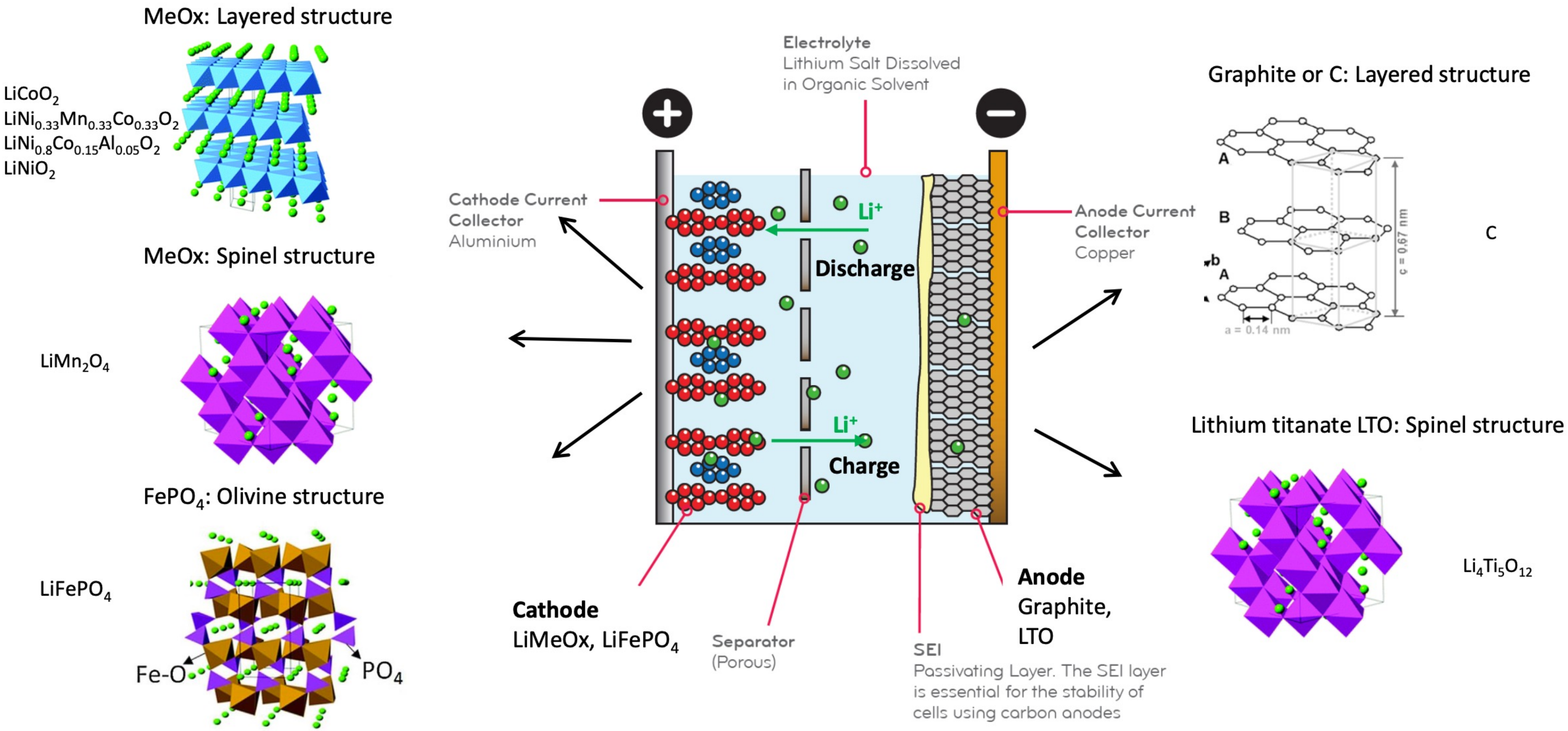


https://battery2030.eu/digitalAssets/816/c_816048-l_1-k_roadmap-27-march.pdf

Lithium-Ion Batteries



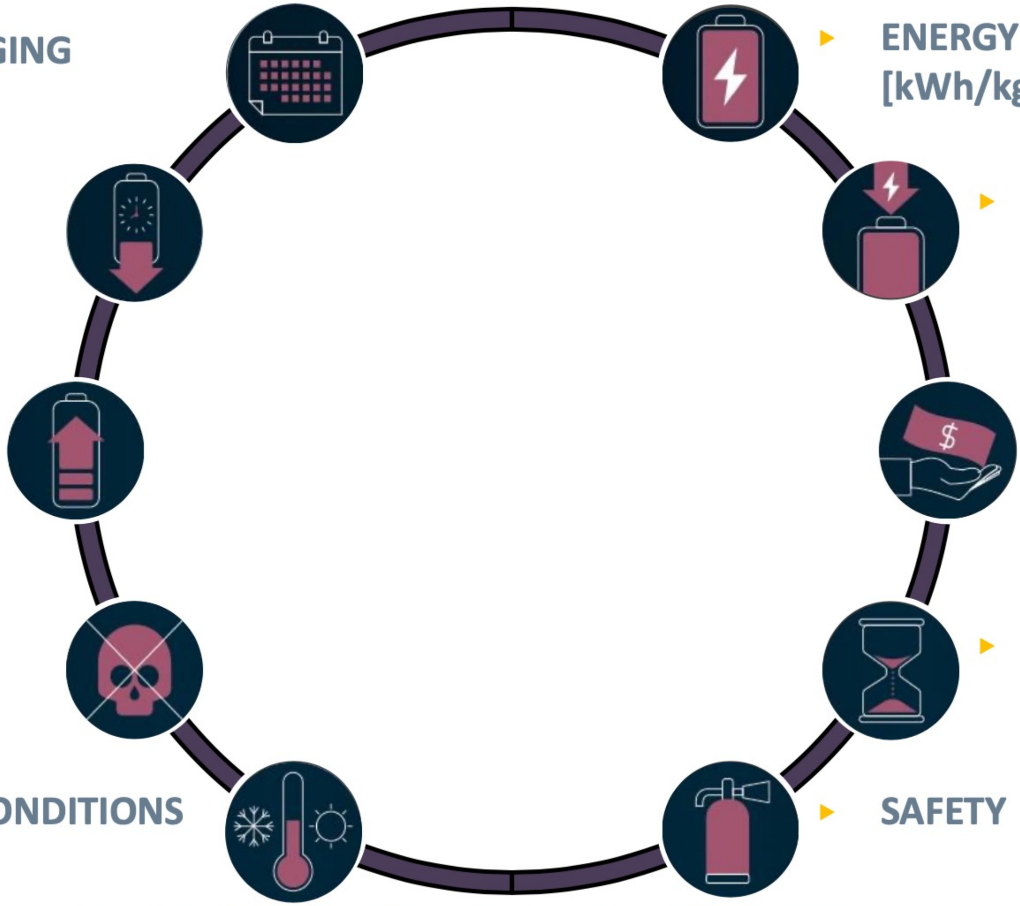
Electrodes materials of conventional Li ion battery



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

Important battery assessment criteria

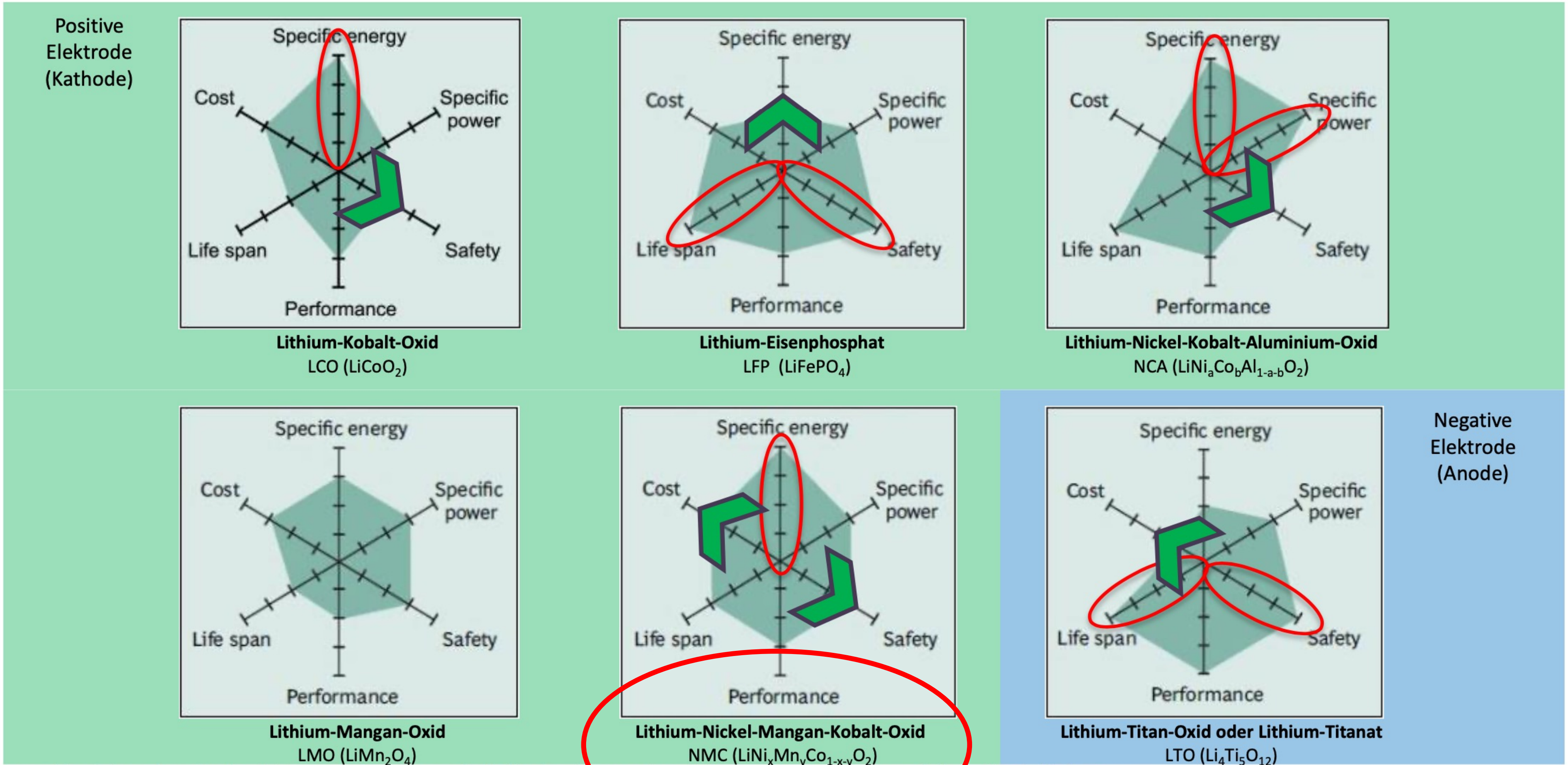
- CALENDARIC AGING
- SELF-DISCHARGE
- FAST CHARGE/DISCHARGE [C-Rate]
- TOXICITY, RECYCLABILITY
- OPERATING CONDITIONS [T_{min}, T_{max}]



- ENERGY DENSITY [kWh/kg, kWh/m³]
- POWER DENSITY [kW/kg, kW/m³]
- COST [CHF/kWh, CHF/kW]
- LIFETIME [Full Cycles]
- SAFETY

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

Versatility of lithium-ion technology



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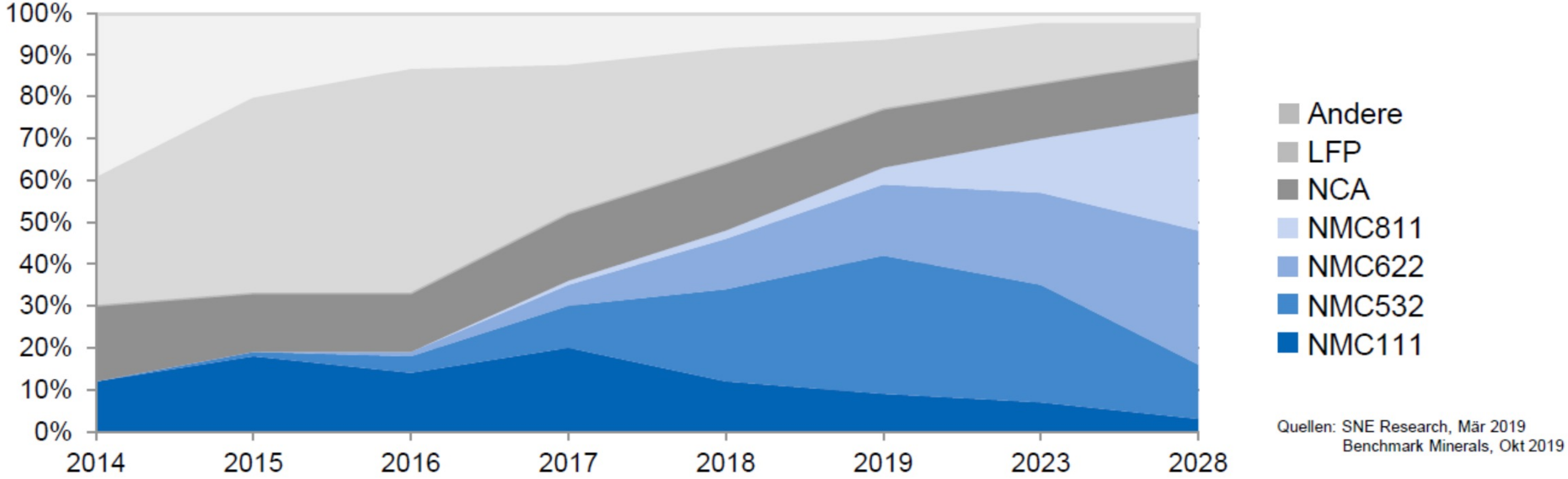
NMC

Source: Battery University & Yu Miao et al. 'Current Li-Ion Battery Technologies in Electric Vehicles and Opportunities for Advancements' Energies 2019, 12(6), 1074; https://doi.org/10.3390/en12061074

Market share of individual lithium-ion technologies

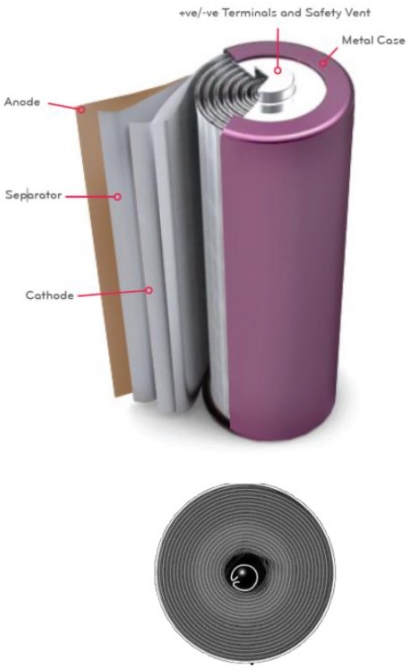


- Lithium-ion technology will continue to accompany us for some time
- Reduction of cobalt in the battery
- Li $N_1M_1C_1$ → Li $N_5M_3C_2$ → Li $N_7M_2C_1$ → Li $N_9M_{0.5}C_{0.5}$ → next ?

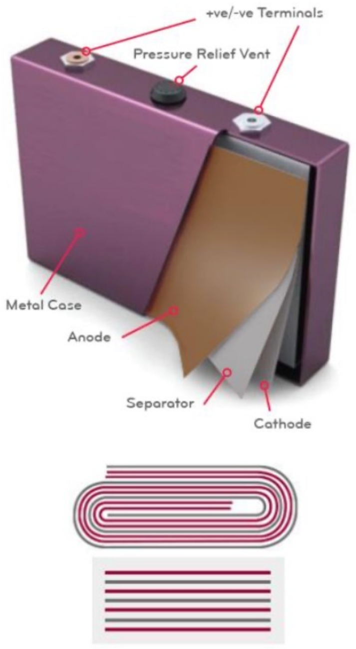
Source: Trends im Lithium-Ionen-Batteriemarkt – Klib Frnakfurt 07.10.2020; Dr. Jochen Mähliß, VDE Renewables

Different cell formats

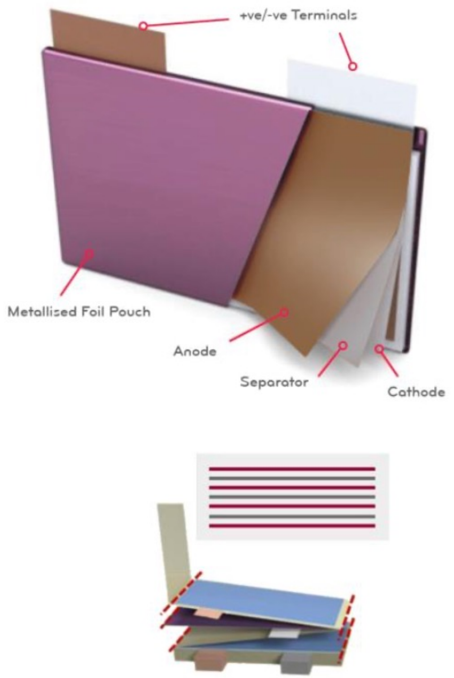
Cylindrical



Prismatic

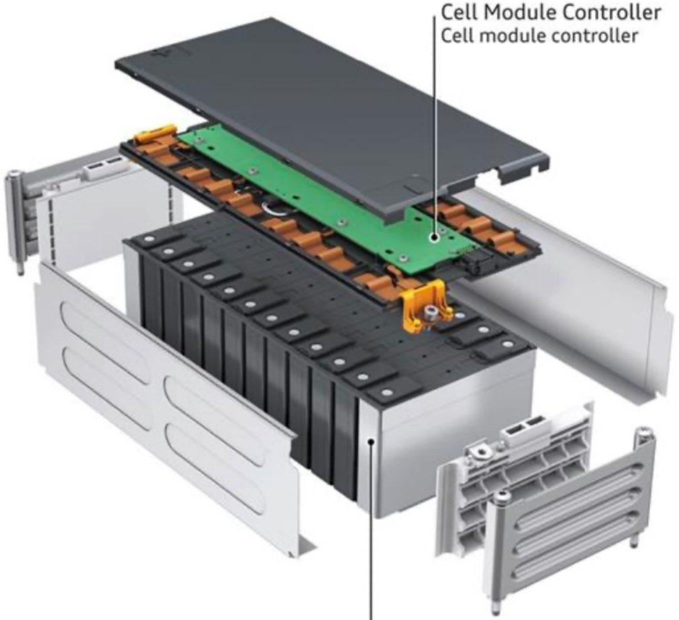


Pouch



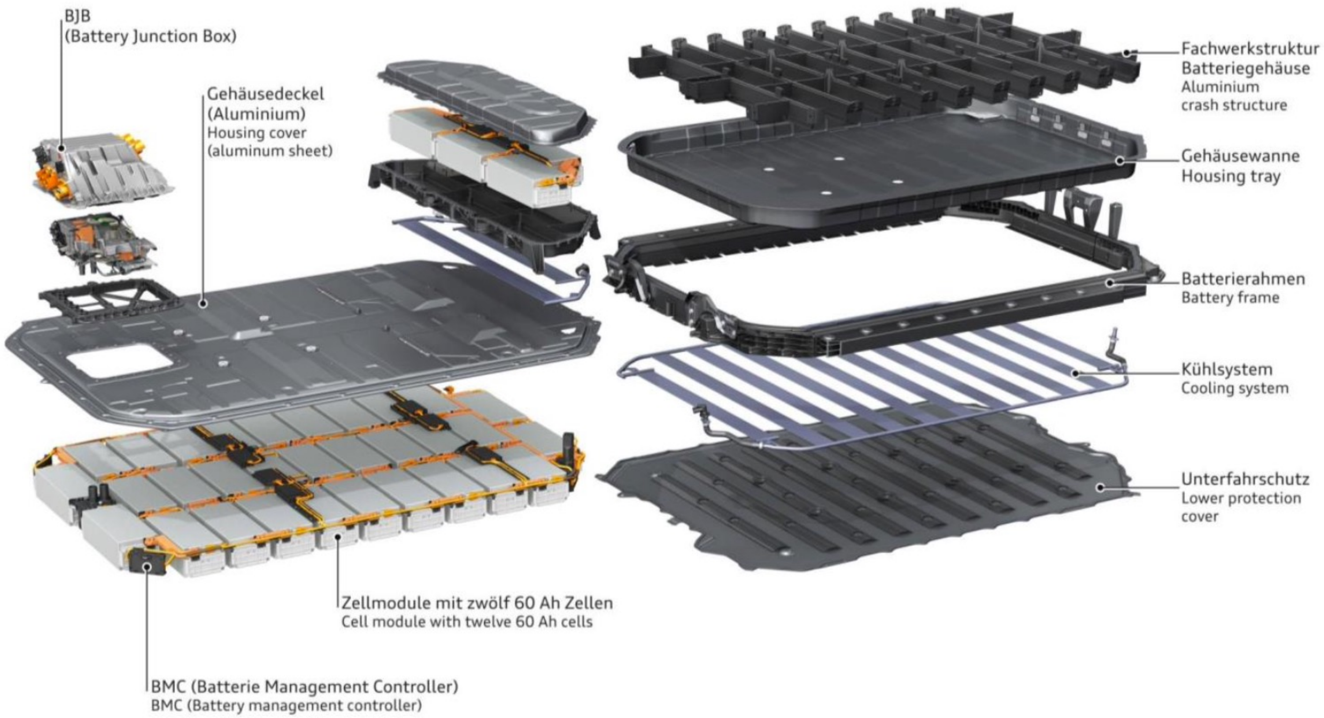
Quelle: *Johnson Matthey Battery Systems, 2012, „Our Guide to Batteries"*

Battery module



40 – 60 V

Battery pack



300 – 800 V

Quelle: Audi

Energy density

$E = U \times Q$

$[Wh] = [V] \times [Ah]$

- 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

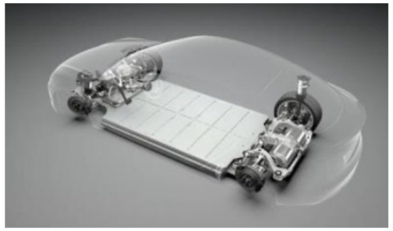
Voltage: 3.5V
Capacity: 4 x 3.0Ah = 12 Ah
} Energy: 42 Wh

Series connection

Voltage: 3.5V x 8 = 28 V
Capacity: 3.0 Ah
} Energy: 94 Wh

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

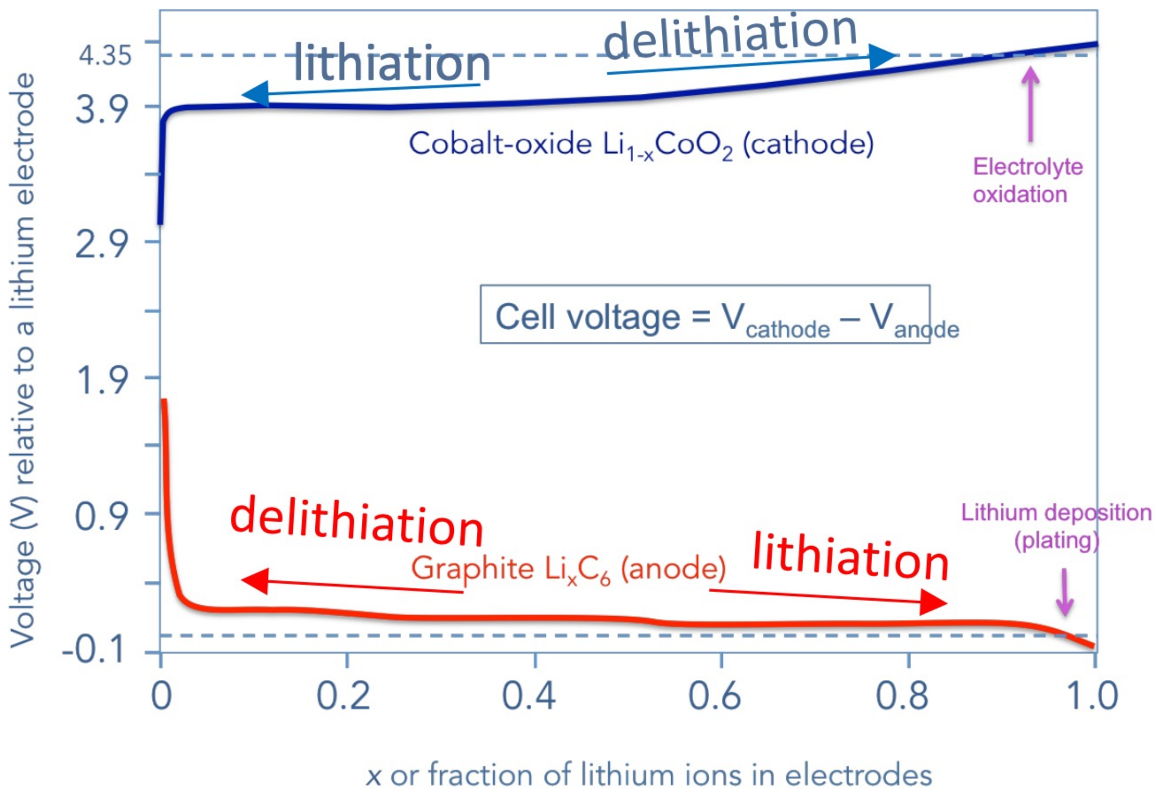
Voltage: 360 V
Capacity: 60 Ah
} Energy: 21.6 kWh



Voltage: 350 V
Capacity: 230 Ah

→ Energy: 80.5 kWh

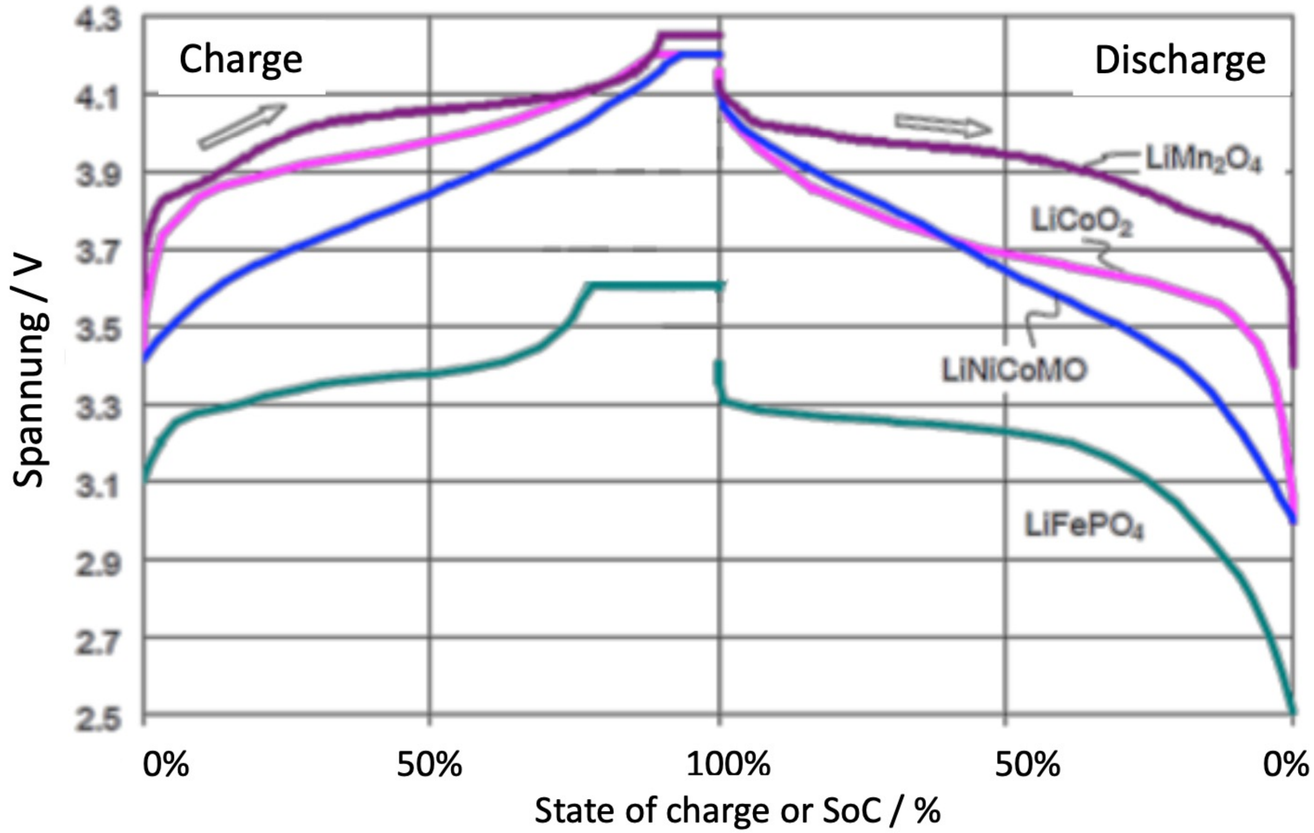
What is the voltage of a cell composed of?



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 charging and discharging curves



Graphite as Anode material

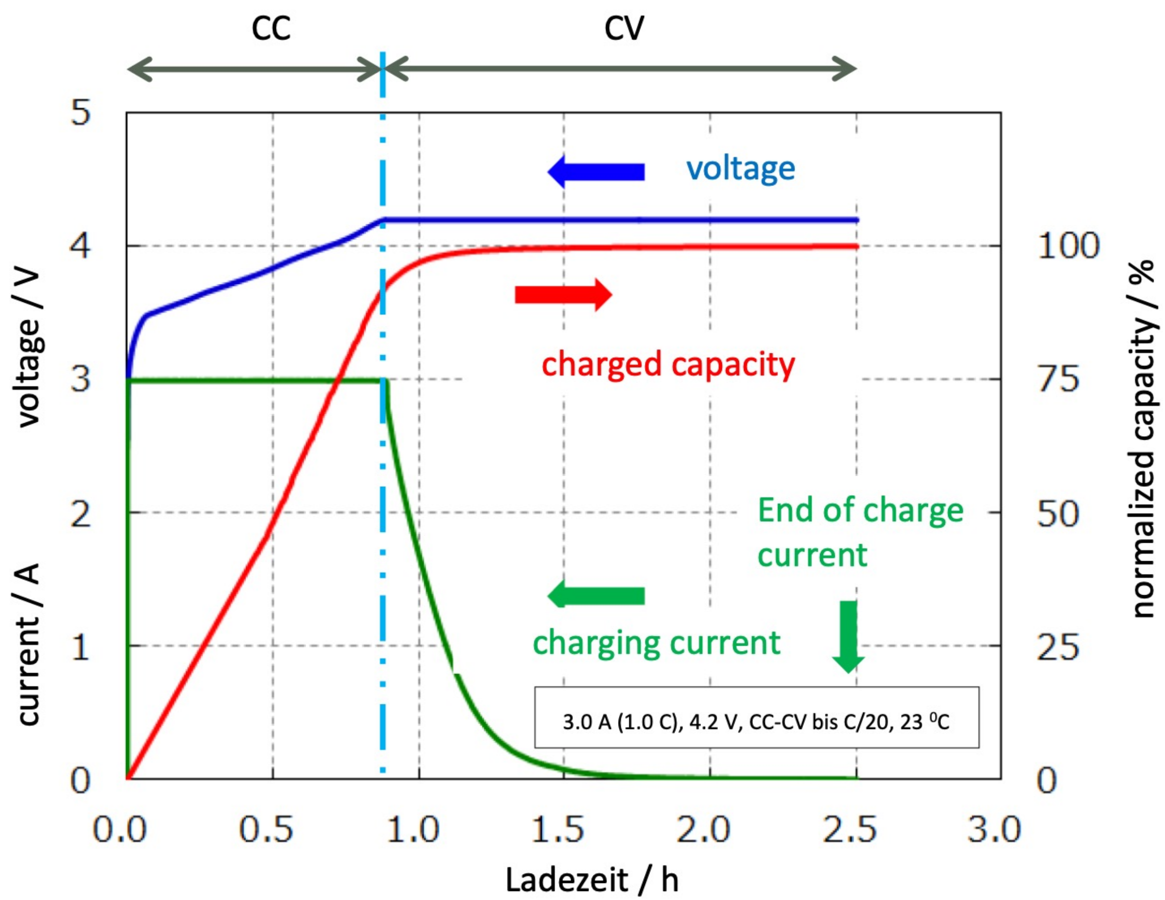
- Each cathode material has its own characteristic charge/discharge curve.
- Charge and discharge parameters must be adapted in suitable monitoring electronics.

Charging Lithium-Ion Batteries

- C-Rate [h-1]: Rate, at which the battery is charged or discharged using a constant current

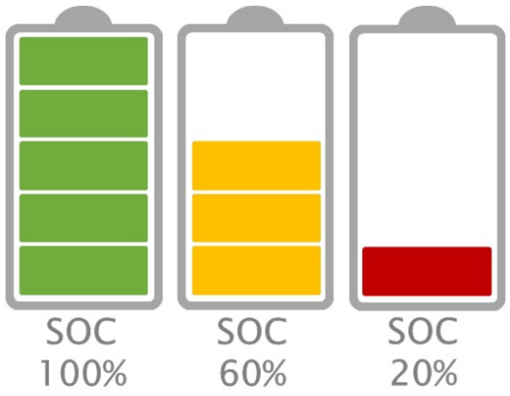
C-Rate = I / Q
[h^{-1}] = [A]/[Ah]

- 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.



SOC & SOH definition

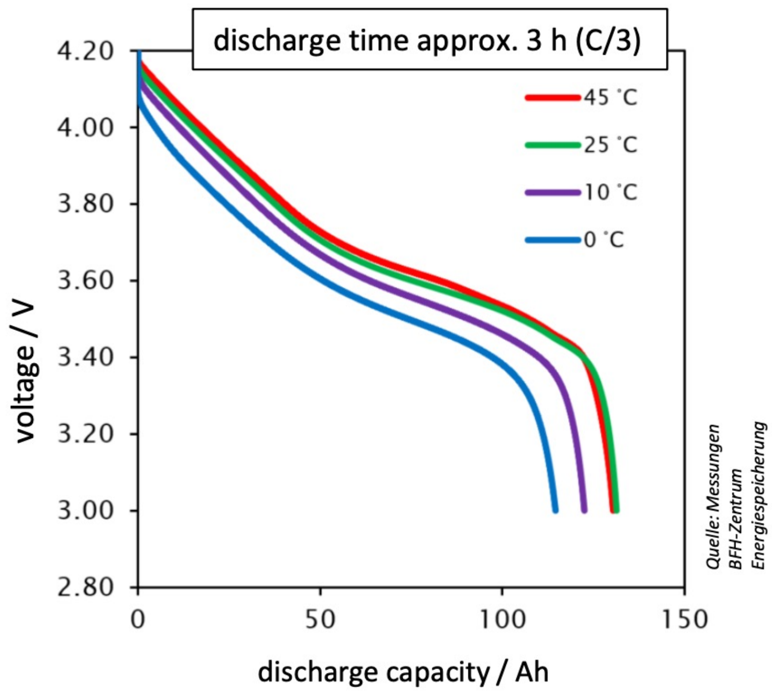
- The SOC is a percentage value that expresses the remaining charge Q of a battery
- SOC is something like a dashboard fuel gauge that reports a value from “Empty” (0%) to “Full” (100%) → no sensor is available to directly measure SOC.



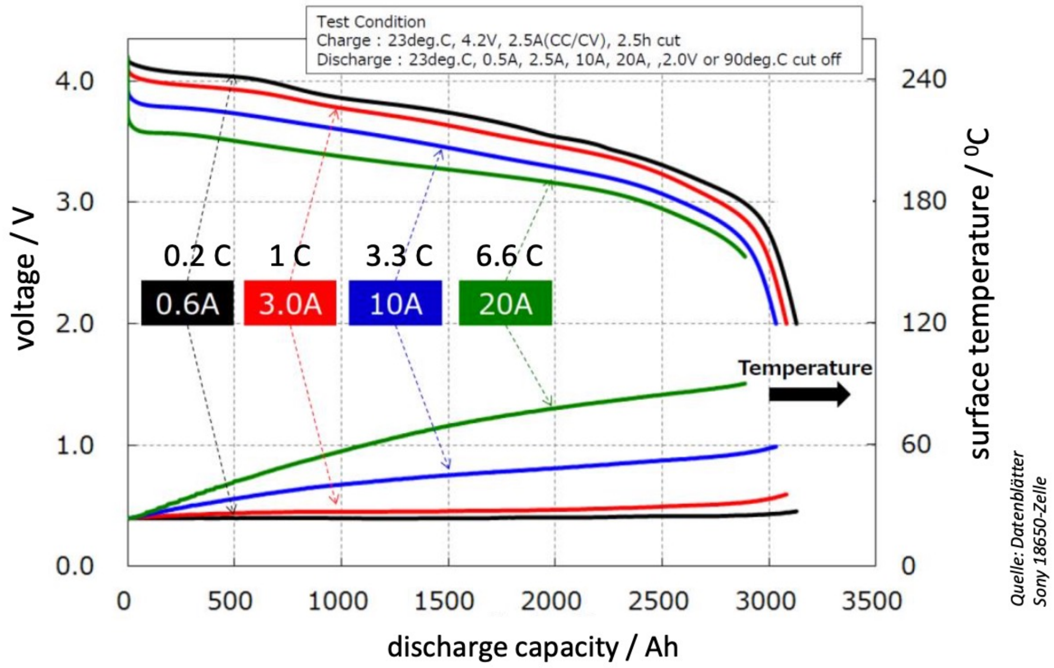
- SOH is defined as the fade of the capacity of the cell or the increase of the internal resistance of the battery

Capacity depends on load and temperature

Influence of ambient temperature

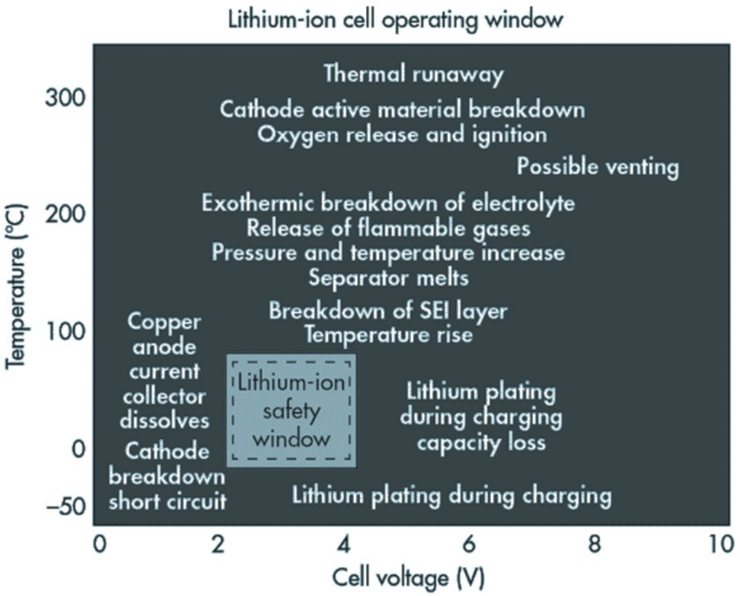


Influence of the discharge rate

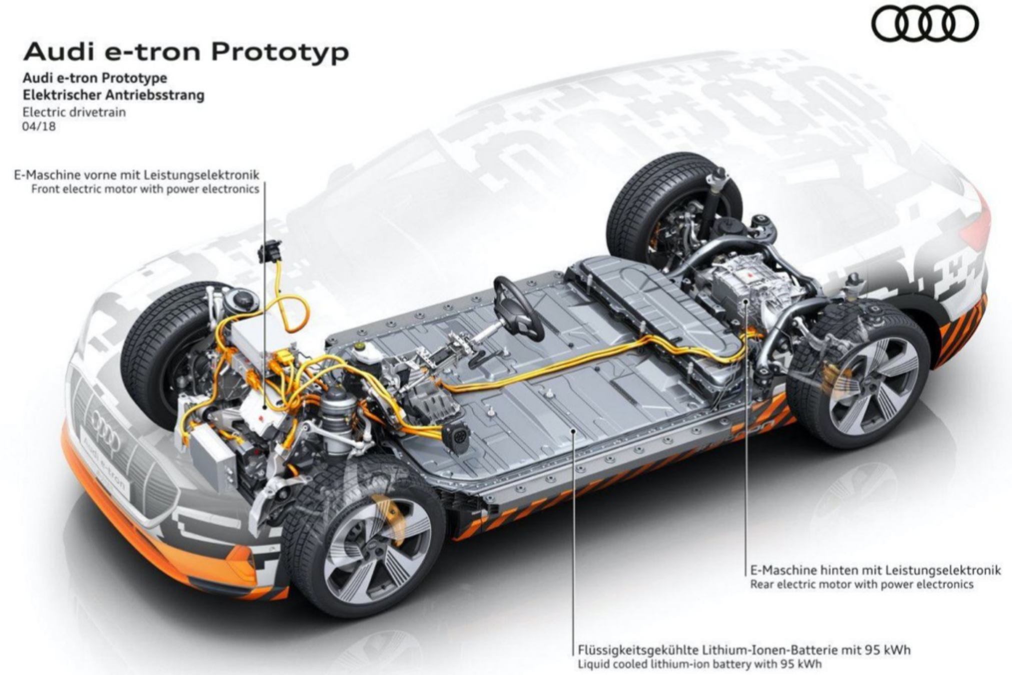


Safety and reliability of battery systems

https://www.mpoweruk.com/lithium_failures.htm

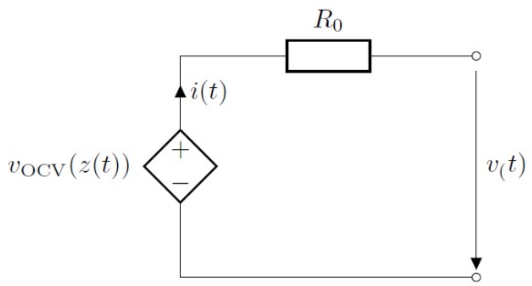


- Lithium-ion (Li-ion) batteries have a limited region of safe operation (light blue area)
- Danger is mitigated by implementing functionally safety concepts and by monitoring battery states

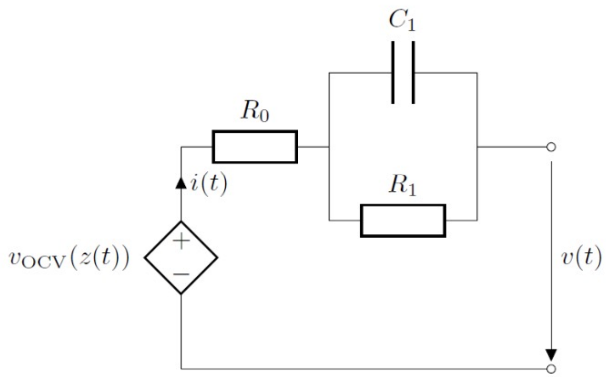


Battery Management System (BMS) enables batteries to provide **safety** while keeping **high performance** and **long lifetime**.

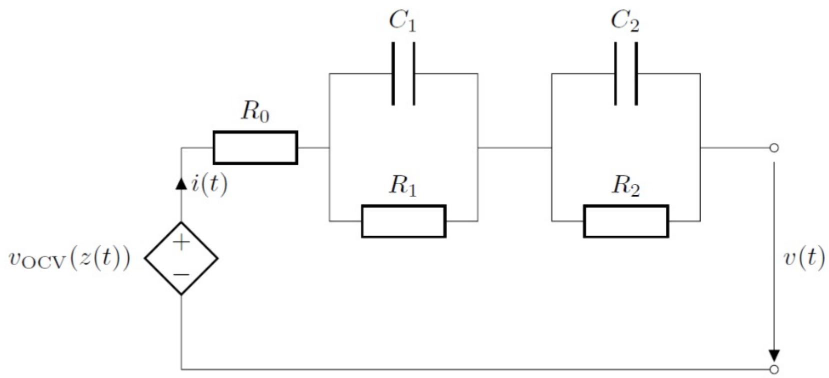
Equivalent Circuit Models (ECMs)



Rint model



Thévenin model



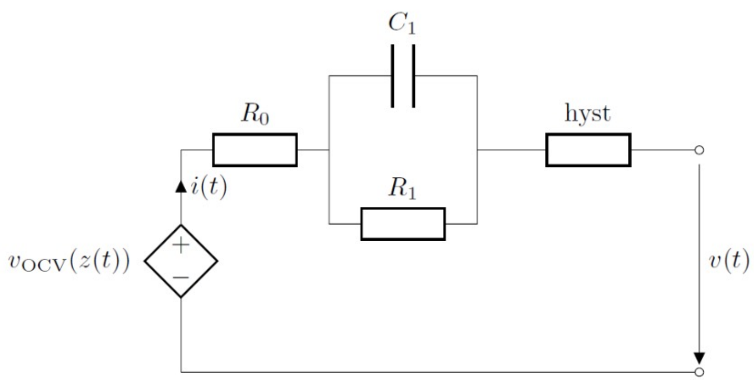
Dual polarization model

Benefits

- easy interpretability
- simple parameter identification
- robustness against high current changes
- Low computing power

Drawbacks

- Lack of representation of electrochemical state like single electrode potentials



Enhanced Self-Correcting (ESC) battery model

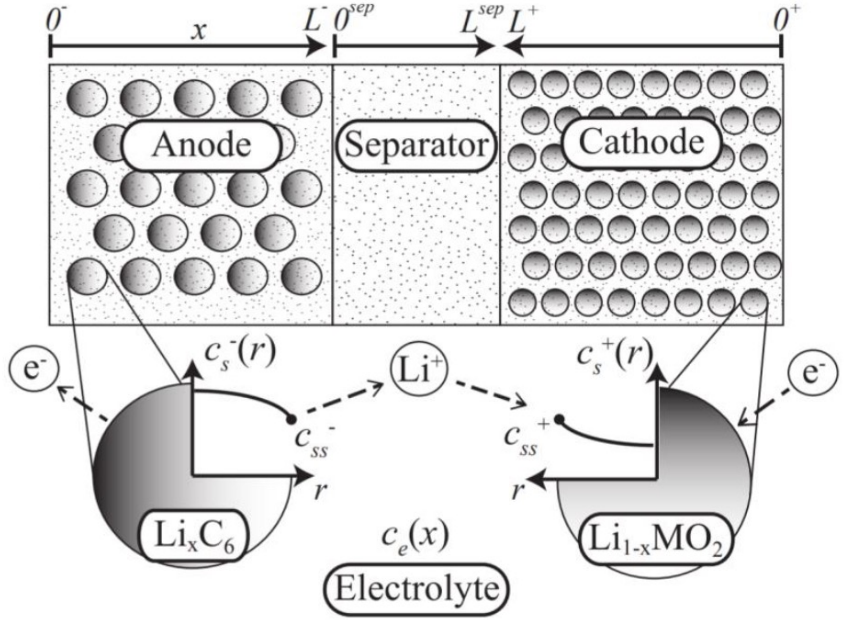
Physics-Based Battery Models (PBMs)

Doyle-Fuller-Newman (DFN) battery model

- Pseudo-2D physics-based battery model
- Based on multiphase porous electrodes and concentrated solution theories
- Governed by a set of coupled nonlinear Partial Differential Equations (PDE):
  - Charge/mass conservation in the homogeneous solid/liquid phase:

    Li concentration in the solid phase $c_s(x,r,t)$/Li concentration in the liquid phase $c_e(x,t)$/Electric potential in the solid phase $\Phi_s(x,t)$/Electric potential in the liquid phase $\Phi_e(x,t)$
  - Electrochemical kinetics described by the Butler-Volmer equation:

    Molar flux density at the solid/liquid interface j(x,t)



Enhanced Physics-Based Model for State Estimation of LIB (BFH, D. Luder 2020)

Experimental Characterization | **Physics-Based Models** | **Implementation**

18650 Li-ion cell

Time-Domain
Frequency-Domain
Optical, SEM and EDX

Sensitivity Analysis
Parameter Identification

Model Validation

Doyle–Fuller–Newman (DFN)
Single Particle Model (SPM)

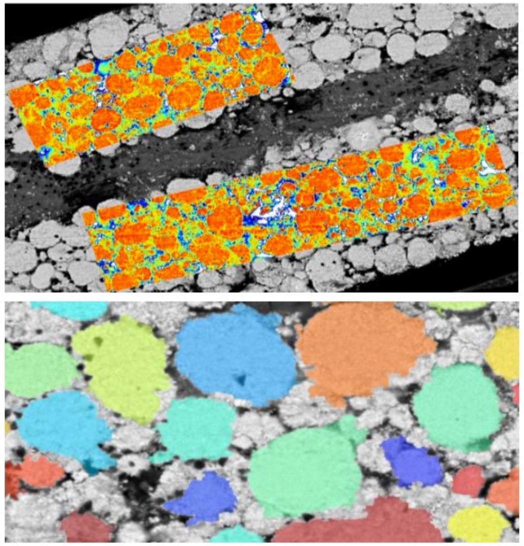
Simplification

Validation

State-Space Representation
Extended Kalman Filter
Simulink Model

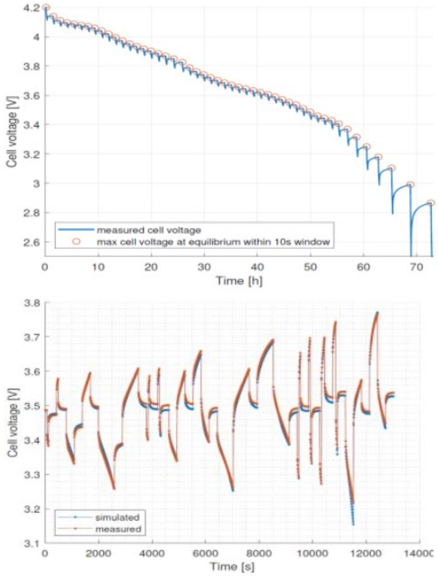
Microstructure

Active Area, Layer Thickness
Porosity, Volume Fraction
Particle Radius



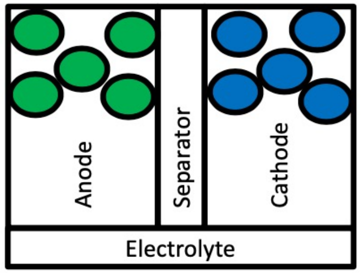
Performance

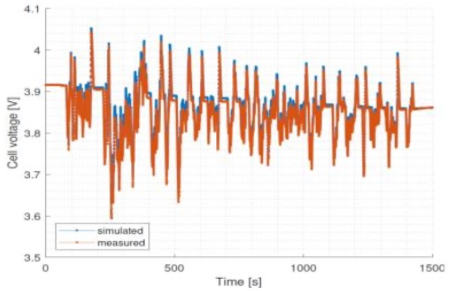
OCV, GITT, CC and CCCV
Pulse, Dynamic, Driving Cycles



Model

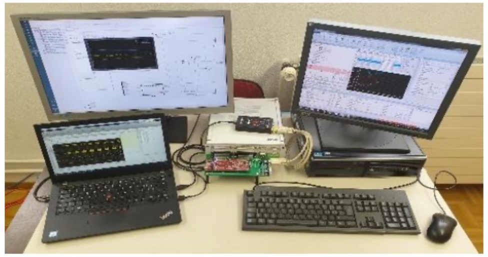
OCP Models
Physics-Based Models

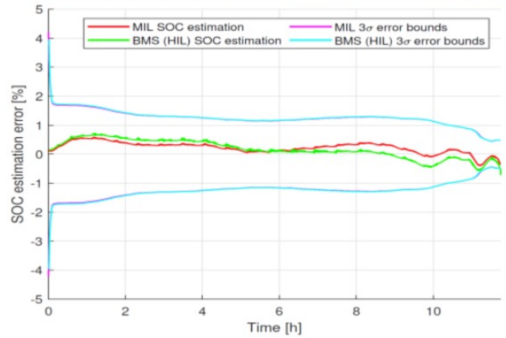




Model-Based Design

C Code Generation
MIL, SIL, PIL, HIL validation





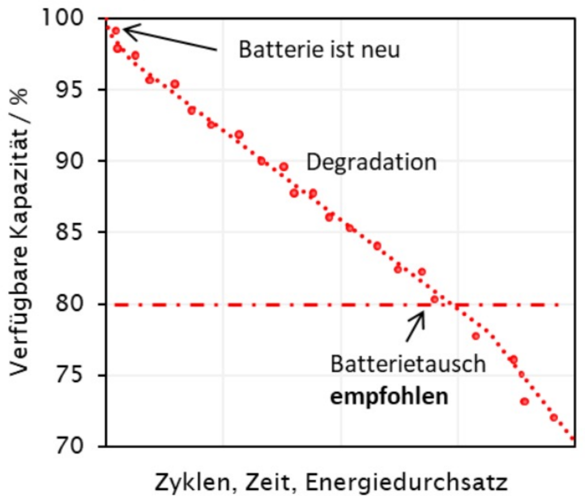
Definition of Lifetime of lithium-ion batteries

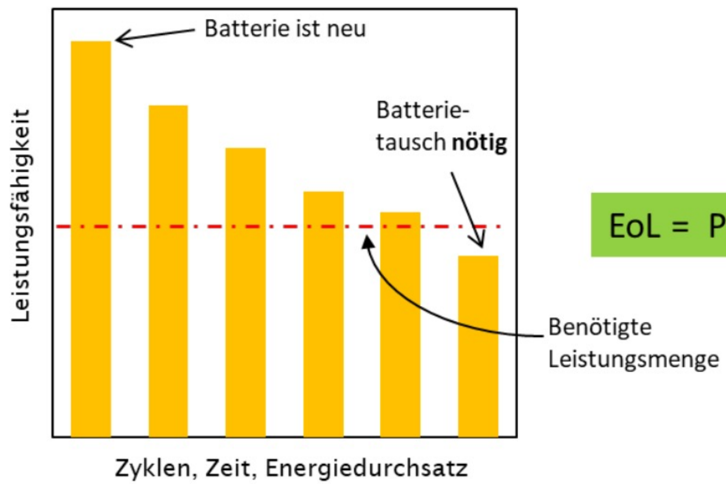
- EoL: End of Life (end of battery life for specific application)

Energy relatd EoL

Power related EoL

$SoH \leq 0.8$
$EoL = Q_{voll} / Q_{voll,neu} \leq 0.8$
$EoL = E_{voll} / E_{voll,neu} \leq 0.8$





$EoL = P_{Last} > P_{Batterie}$

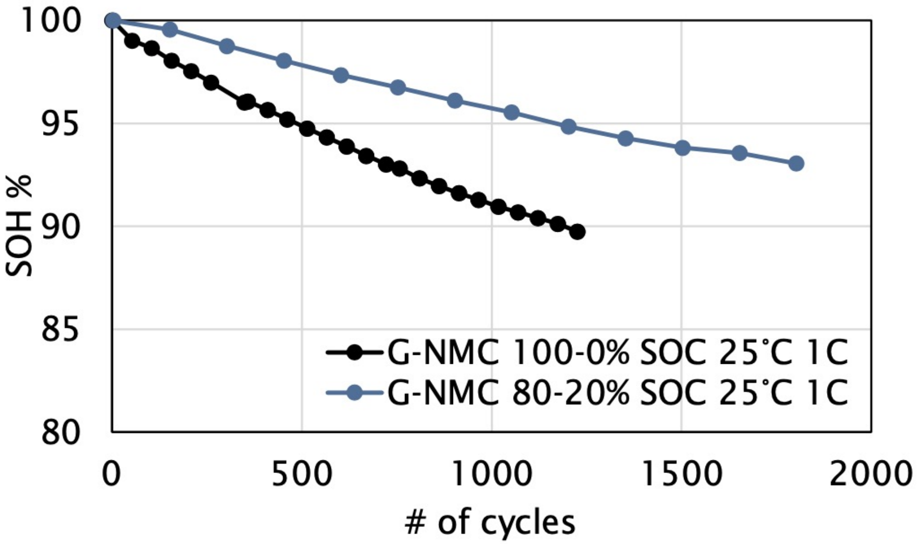
- Range of vehicle
- Running time (e.g. Smartphone)

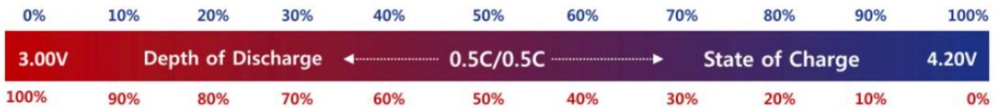
- Power applications (e.g.. Starter-Batteries)
- Higher peak speed (e.g. Formula E, swissloop)

Two types of aging

Cyclic aging

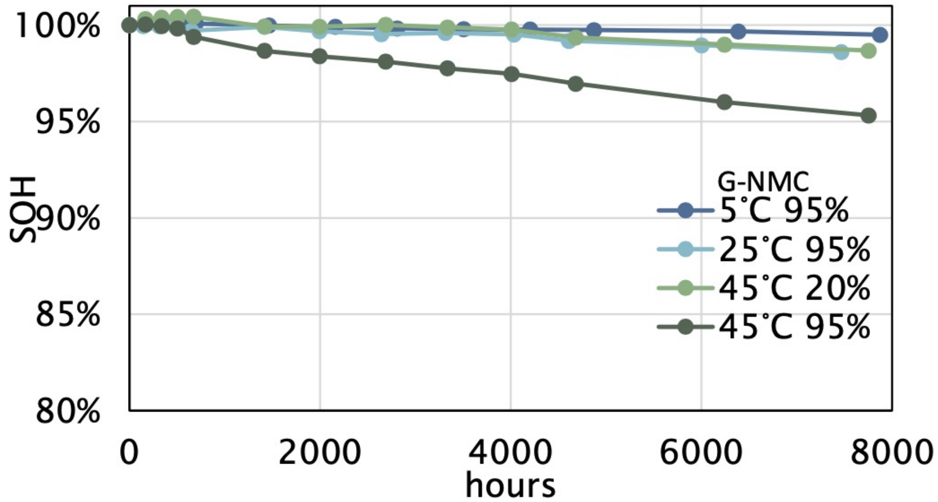
- Decrease in available capacity due to use (charge/discharge)





Calendaric aging

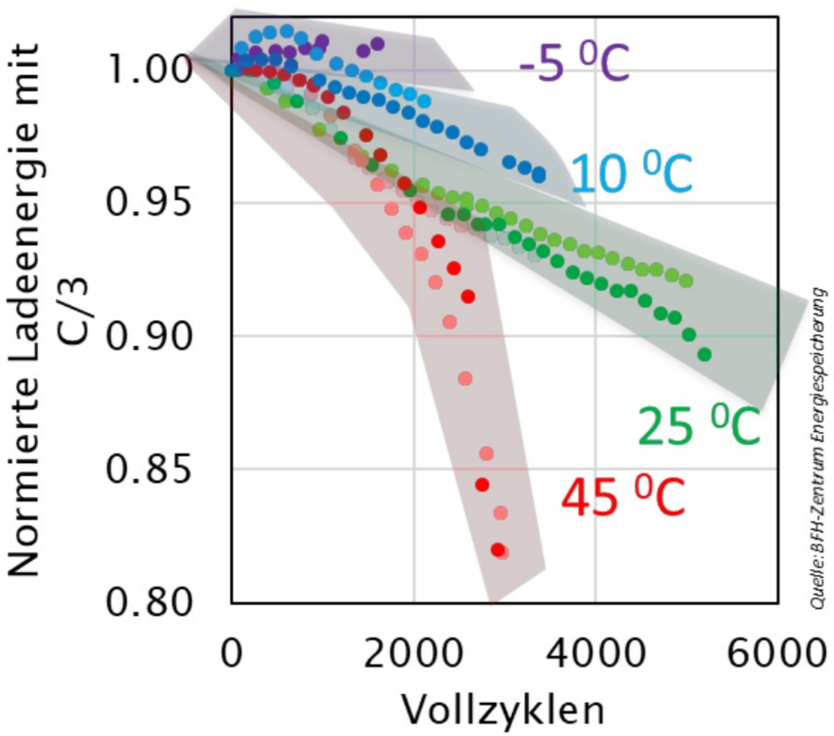
- Regardless of use
- Relevant for storage/non-use

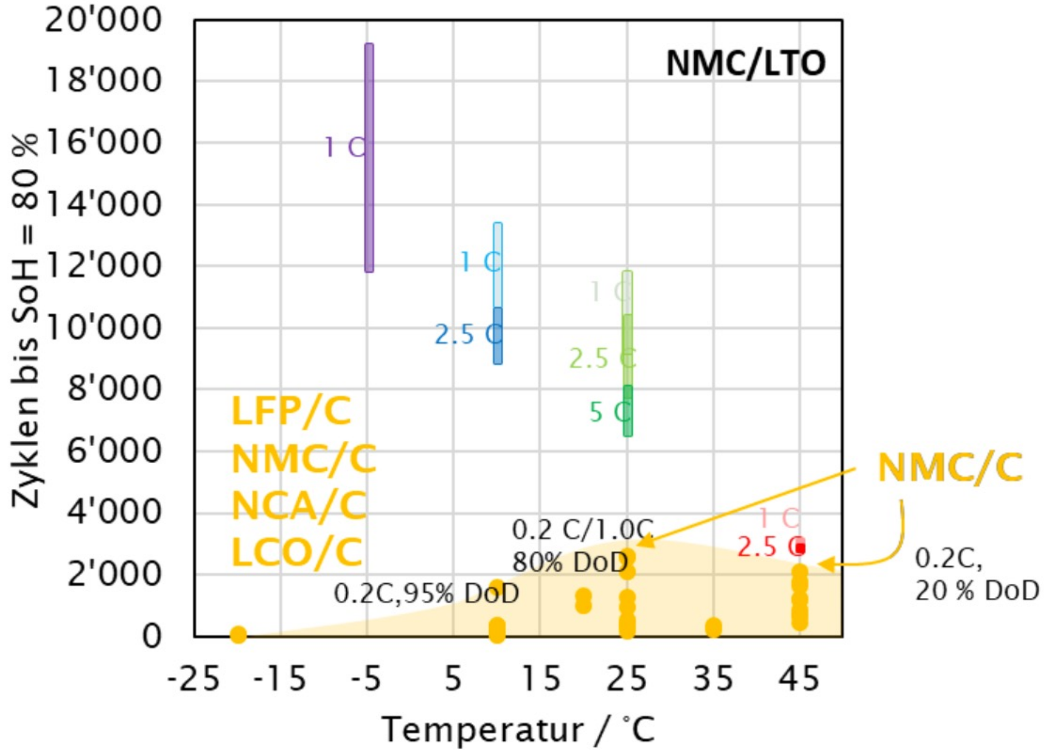


Quelle: Lebensdauertests im Auftrag der Industrie am BFH-Zentrum Energiespeicherung

Impact of temperature and C-Rate on life cycles

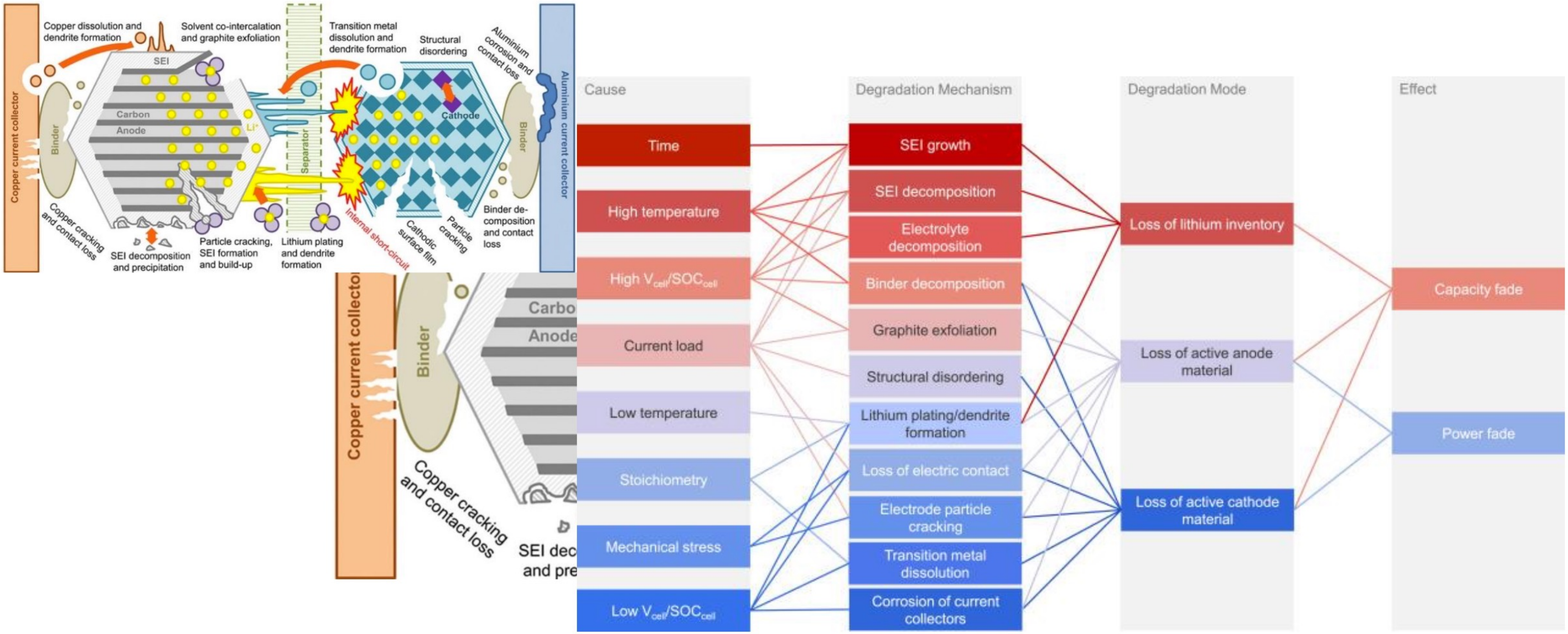
NMC/Titanate vs. NMC/Graphite





- Cycling from 100 – 0 % SoC (charge with CC-CV, discharge with CC), 30min break each halfcycle
- Extrapolation with normalized energy and capacity values

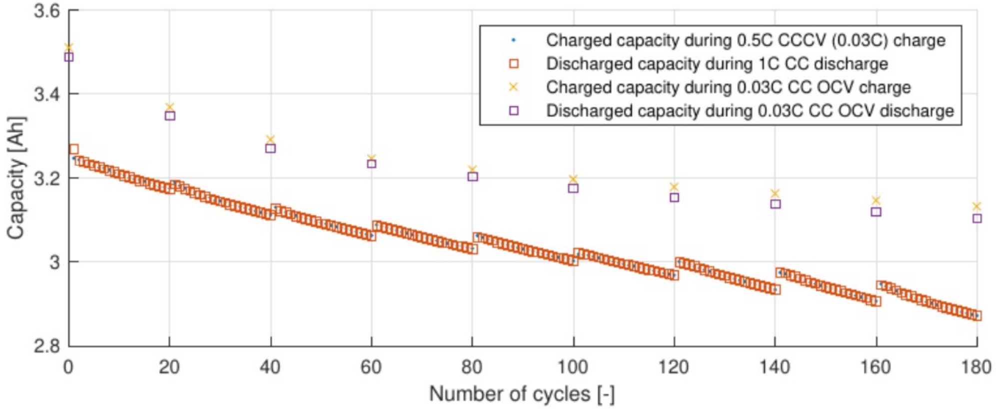
Degradation mechanisms



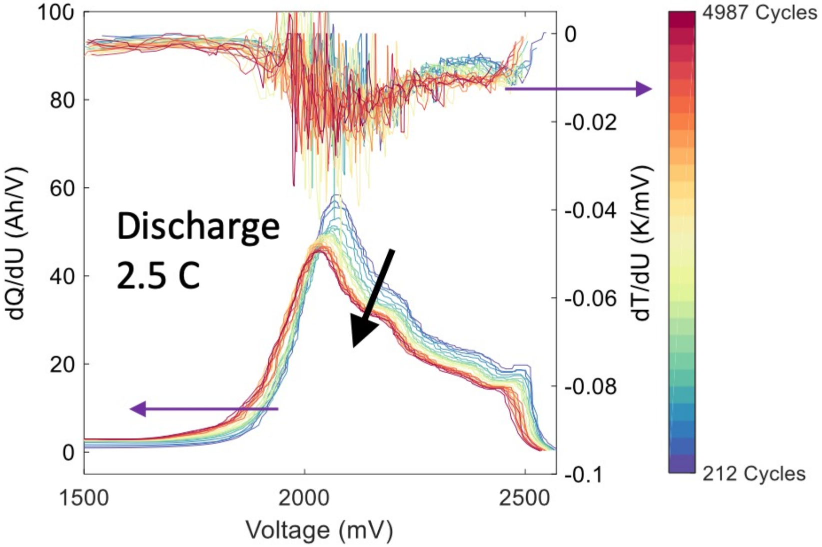
Christoph R. Birkl, Matthew R. Roberts, Euan McTurk, Peter G. Bruce, David A. Howey, Degradation diagnostics for lithium ion cells, Journal of Power Sources, Volume 341, 2017, Pages 373-386, https://doi.org/10.1016/j.jpowsour.2016.12.011.

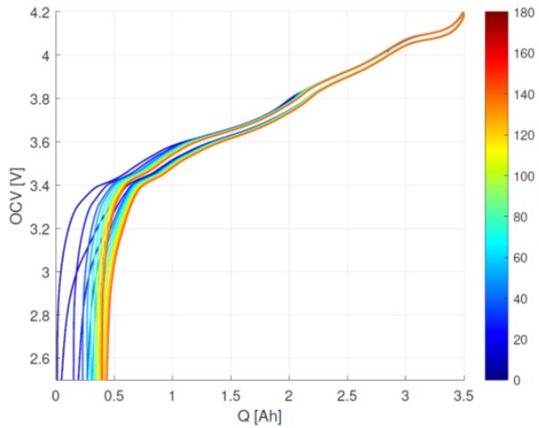
Aging Tests with intermediate Diagnostic Cycles

Change of dQ/dU vs. U towards the left: <u>increase of internal resistance</u>
Change of dQ/dU vs. U downwards: material change during operation

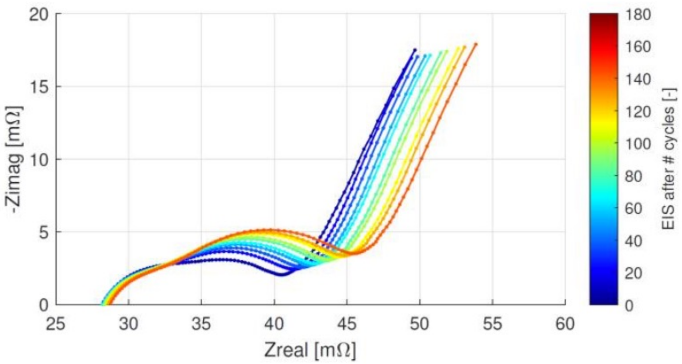


Incremental Capacity Analysis





Intermediate OCV



Intermediate EIS @ 10% SOC

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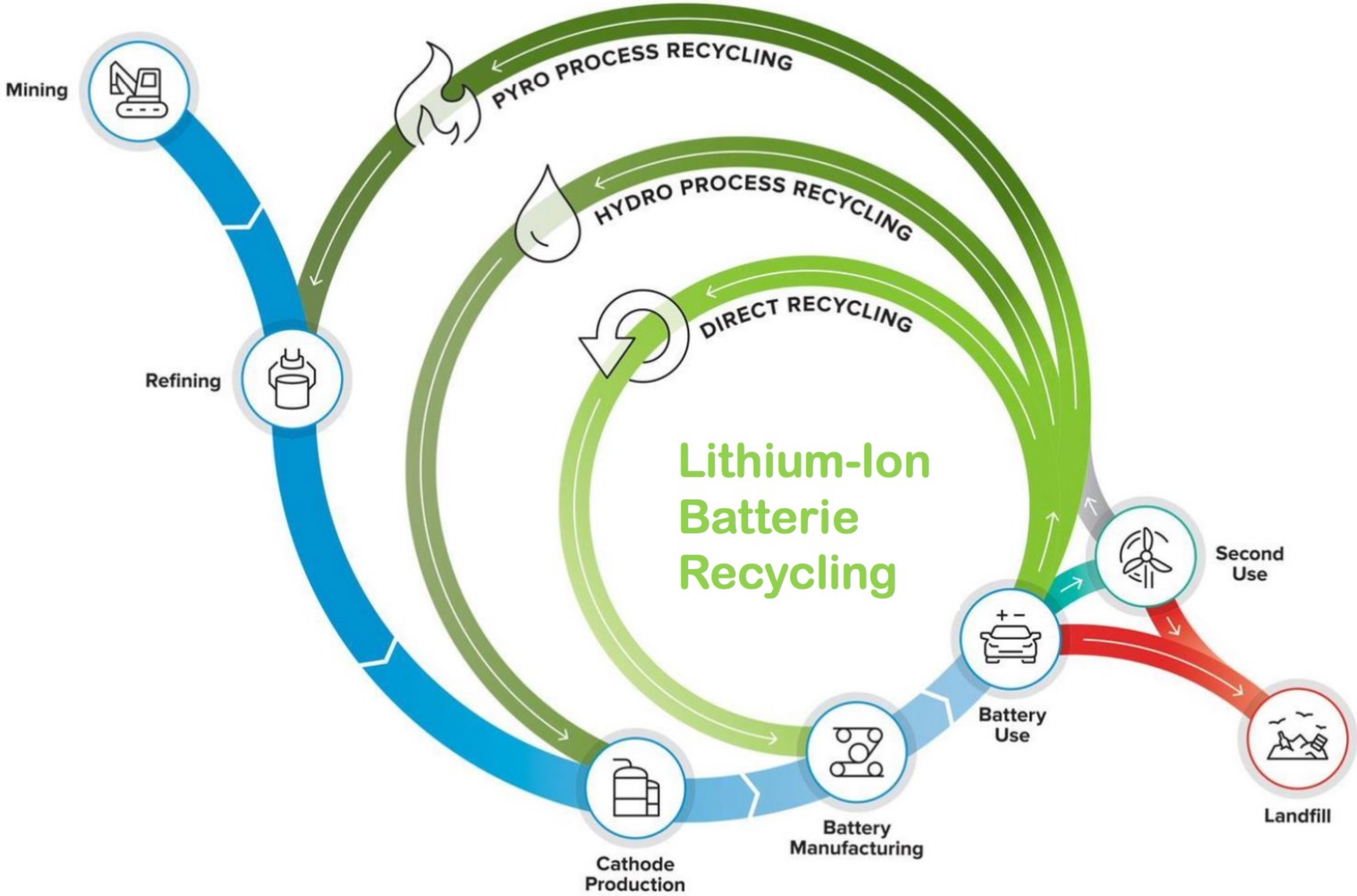
Product cycle of a lithium-ion battery

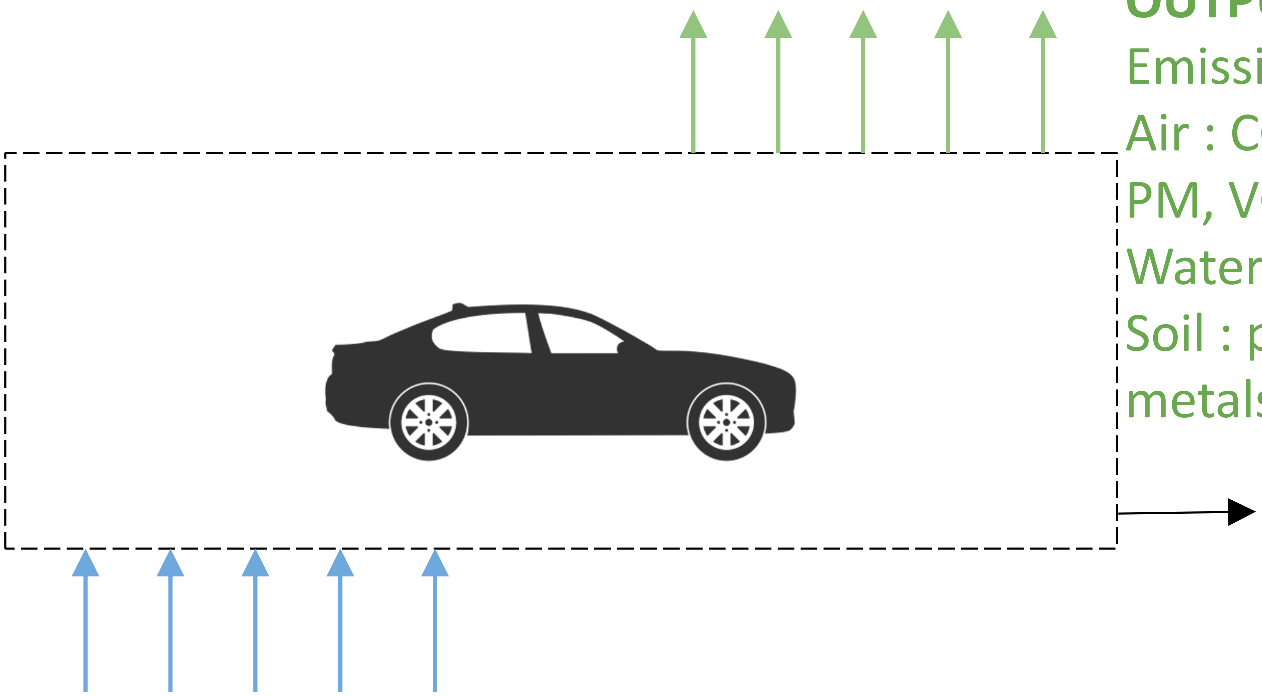
Very high energy and resource consumption calls the ecology of the approach into question



Quelle: https://edu.rsc.org/feature/new-power-old-batteries/4010760.article

Life cycle **inventory** of a car

OUTPUTS
Emissions to
Air : CO_2, SO_2, PM, VOC
Water : PO_4, NO_3
Soil : pesticides, metals

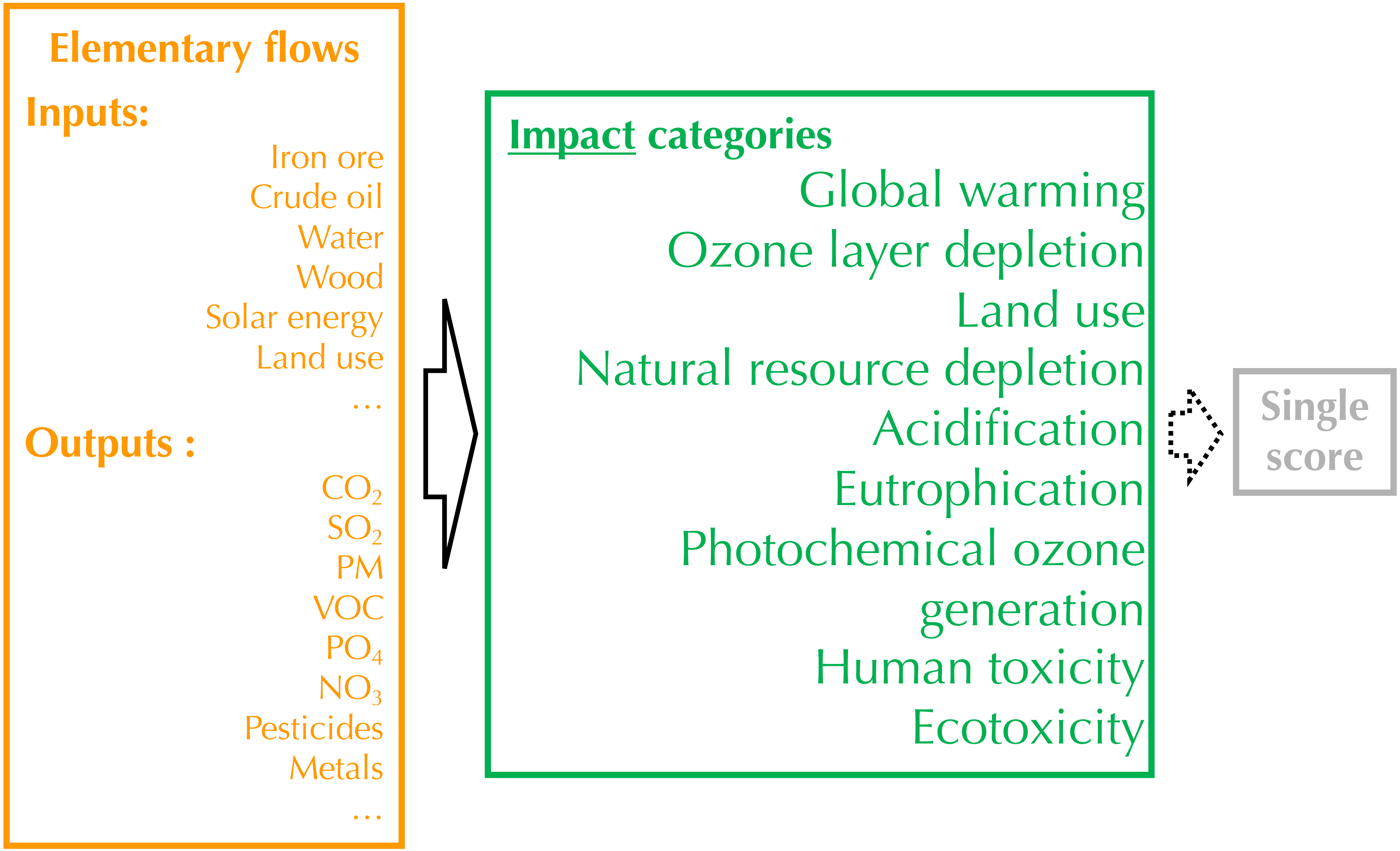


Functional unit

INPUTS
Natural resources
- Iron ore
- Crude oil
- Water
- Wood
- Land use

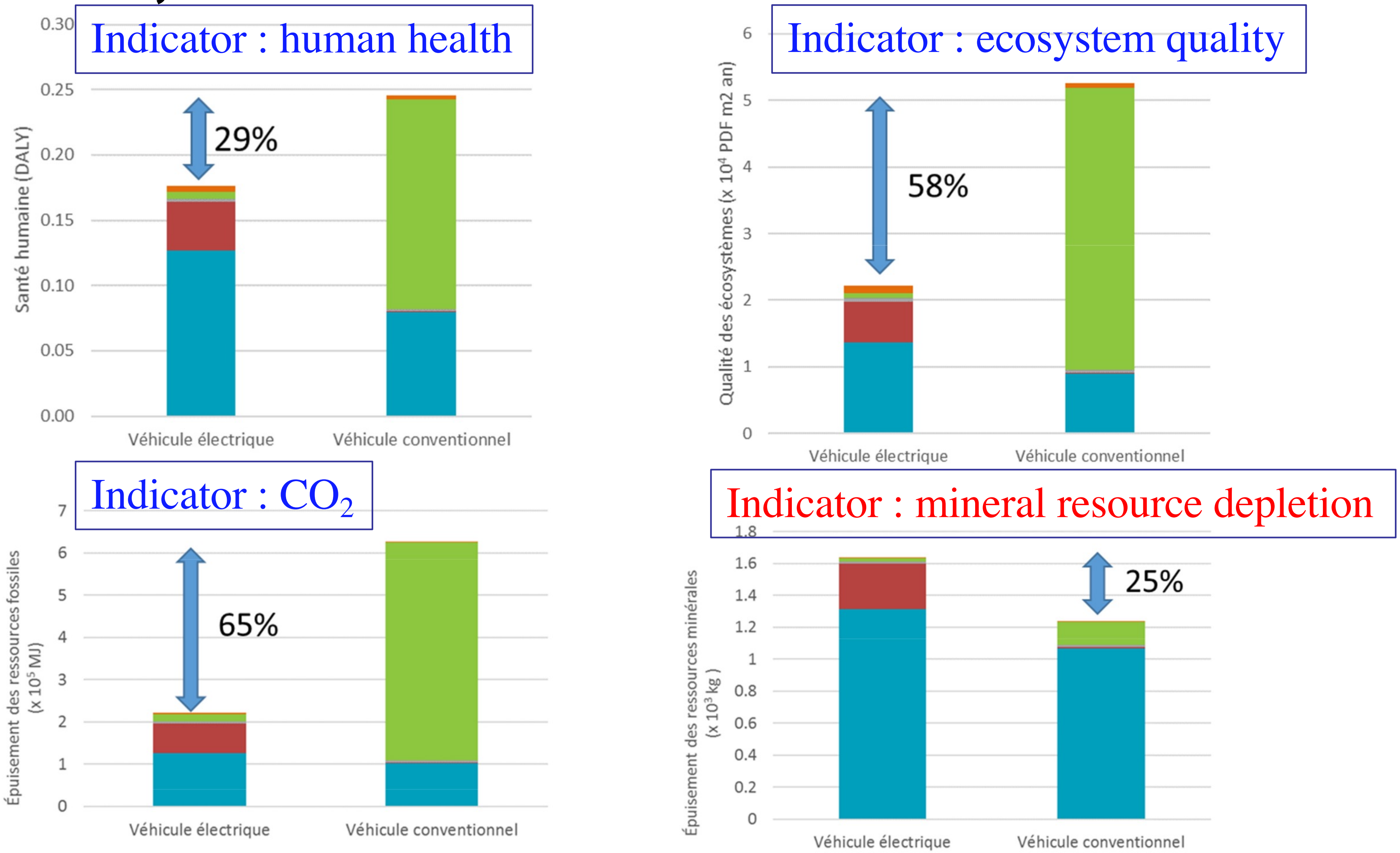
These inputs and outputs can be quantified, compared & aggregated for the entire system

Life cycle impacts



Comparison electric vs. conventional car in Québec, Canada

Functional unit 150,000 km



(CIRAIG, 2016; https://www.hydroquebec.com/data/developpement-durable/pdf/analyse-comparaison-vehicule-electrique-vehicule-conventionnel.pdf

Lithium facts

- 20 ppm avg abundance (rare)
- Exploitable reserves 4.1 Mt (potential: 11 Mt)
- Production now: 82’000 t/yr (~ 50yrs)
- Minerals (Li_2CO_3): 80% salt brines in deserts, 20% in aluminosilicates/clay
- concentrated in few countries: Chile (mainly), CHN, AUS, BRA, CAN. Bolivia has 47% of base reserves, as yet unexploited.
- Extraction from sea-water ($0.17 g/m^3$) is utopic

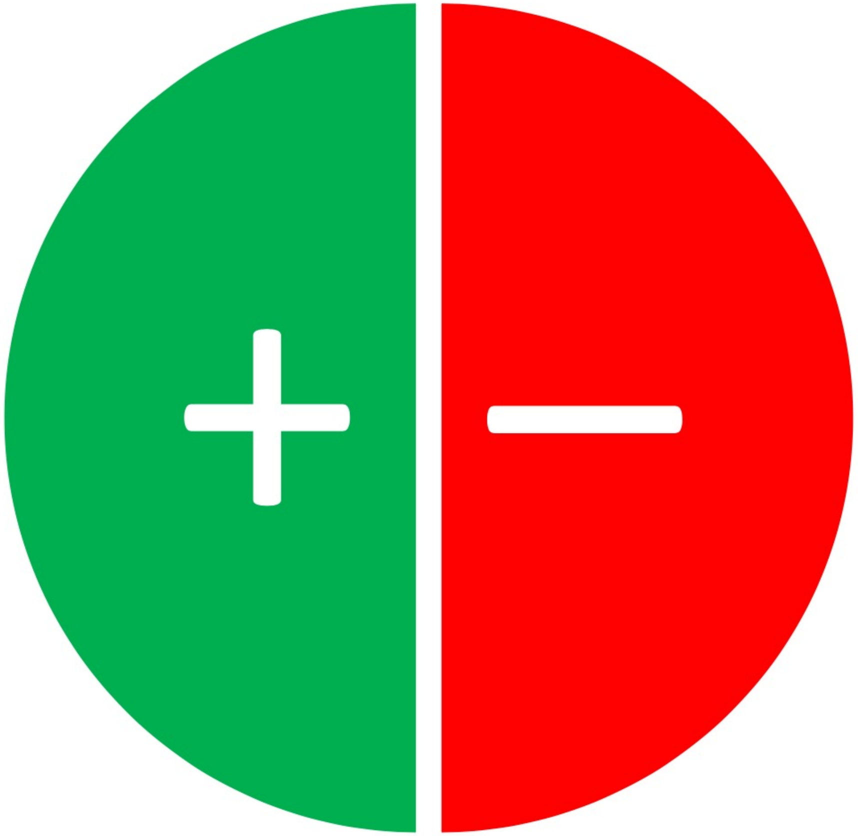
Uses of Li

- Additive to glasses, ceramics
- Lubricants
- Alloys
- Polymers, pharmacy,..
- BATTERIES
  - @4kg/BEV, hence total world production could equip 20 million BEV
  - alternatives: Ni, Zn, Cd, Pb, …; H_2 FCEV

CONCLUSION – SUMMARY

Battery electric mobility

- High system energy efficiency (BEV 75-90%, ICE 25-35%)
- Less harmful to the environment (GHG Well-to-Wheel) https://www.psi.ch/en/media/our-research/make-way-for-electric-cars
- Lifetime https://youtu.be/pOQQTwYkg08
- No local emissions
- Recuperation
- Fewer components
- Less maintenance
- …



- Energy density
- Long distance
- Loading times
- Toxicity
- Recycling
- …

Quelle: https://www.pv-magazine.de/2018/06/29/neuer-energiespeicher-in-amsterdam-eingeweiht/

63