Greenhouse Gases Mitigation CO_2 Capture and Utilization

Topic No: 7

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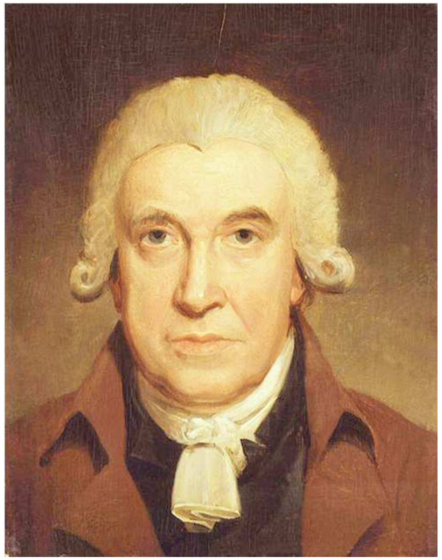
The beginnings of motorized road transport

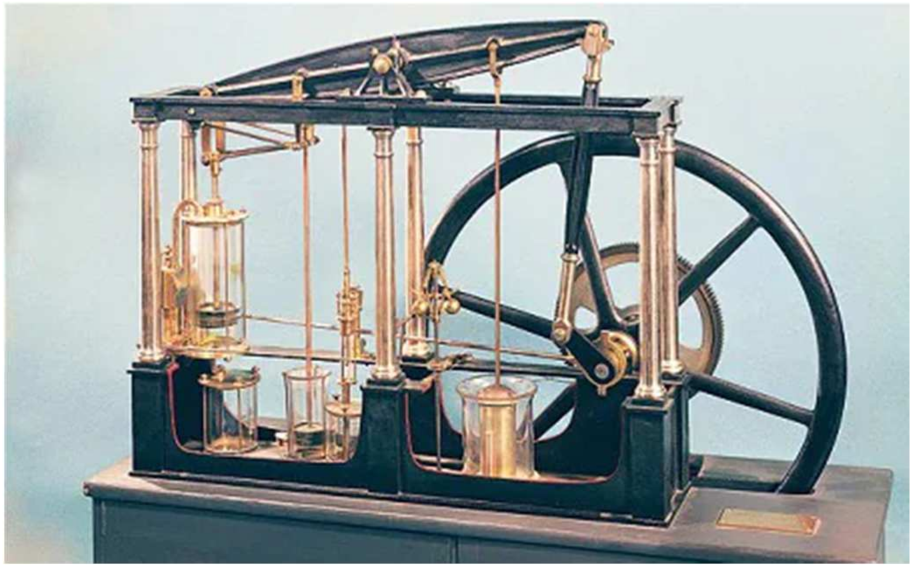
- Nicolas Joseph Cugnot: Le fardier à vapeur (1770)
  - Weight 2.5 t, the payload 4 t, max. speed 9 kmh^{-1}
  - Saturated steam drive, boiler not equipped with superheater
  - Intended for military purposes ….. but the tricycle evaluated as unstable by the army

The beginnings of motorized road transport

- The following 100 years (1780 - 1880) very slow development
  - Basically just improving the steam engine
  - James Watt (1736 – 1819):

1763	–	improvements of the Newcomen‘s steam Engine started
1769	–	patented separate steam condenser = increased machine efficiency
by 1800	–	only ca. 500 engines produced (textiles, metallurgy, mills)
1800	–	patent expiration ⇒ then new manufacturers





The beginnings of motorized road transport

- The following 100 years (1780 - 1880) very slow development
  - ► Slow increase of the steam Engine efficiency from 5 to ca. 12 %
  - ► Steam cars expensive and not very practical (scared horses, unsafe riding)
  - ► Restrictions, e.g. 1865 “Red flag act” speed limit: 4mph in the country 2mph in towns + vehicle had to be preceded by a person carrying a red flag

Trevithick: “The puffing devil” (1801)

Baffrey: steam car (1886)

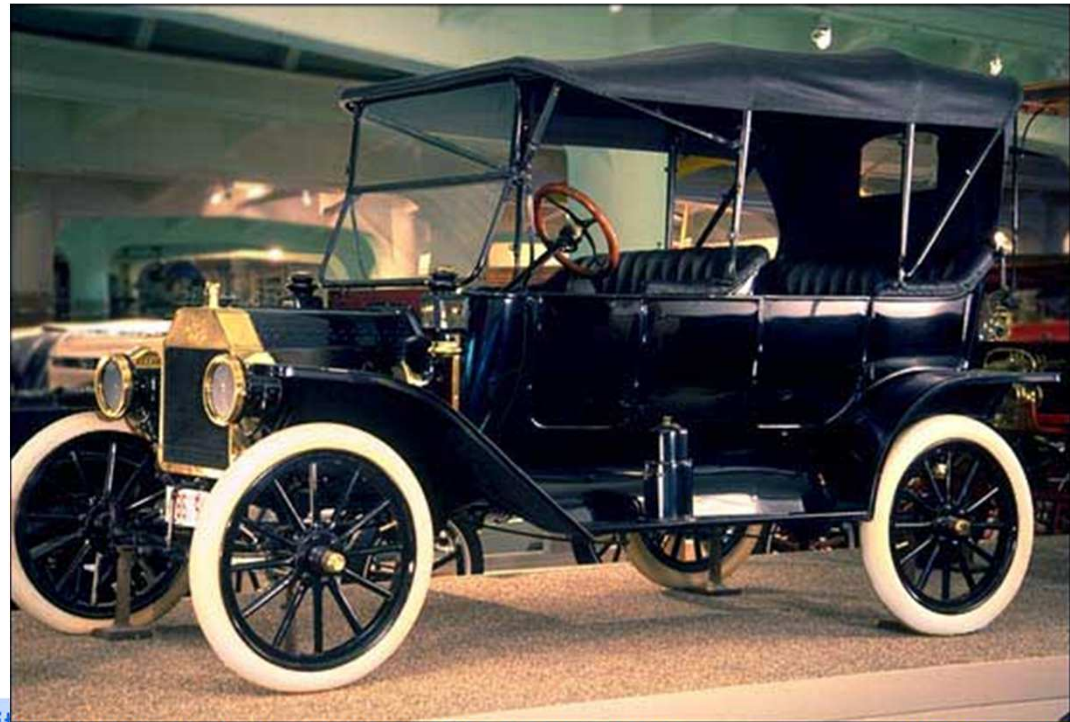
The beginnings of motorized road transport

- Technological breakthrough
  - 1877 – Nicolaus Otto patented the gasoline 4-stroke engine
  - 1886 – Karl Benz: German patent No. 37435a: gasoline tricycle
    power: 0,66 kW at 400 rpm; cylinder vol. 954 cm^3
    Operational speed 11 km h^{-1}; max. speed 16 km h^{-1}

Nicolaus Otto

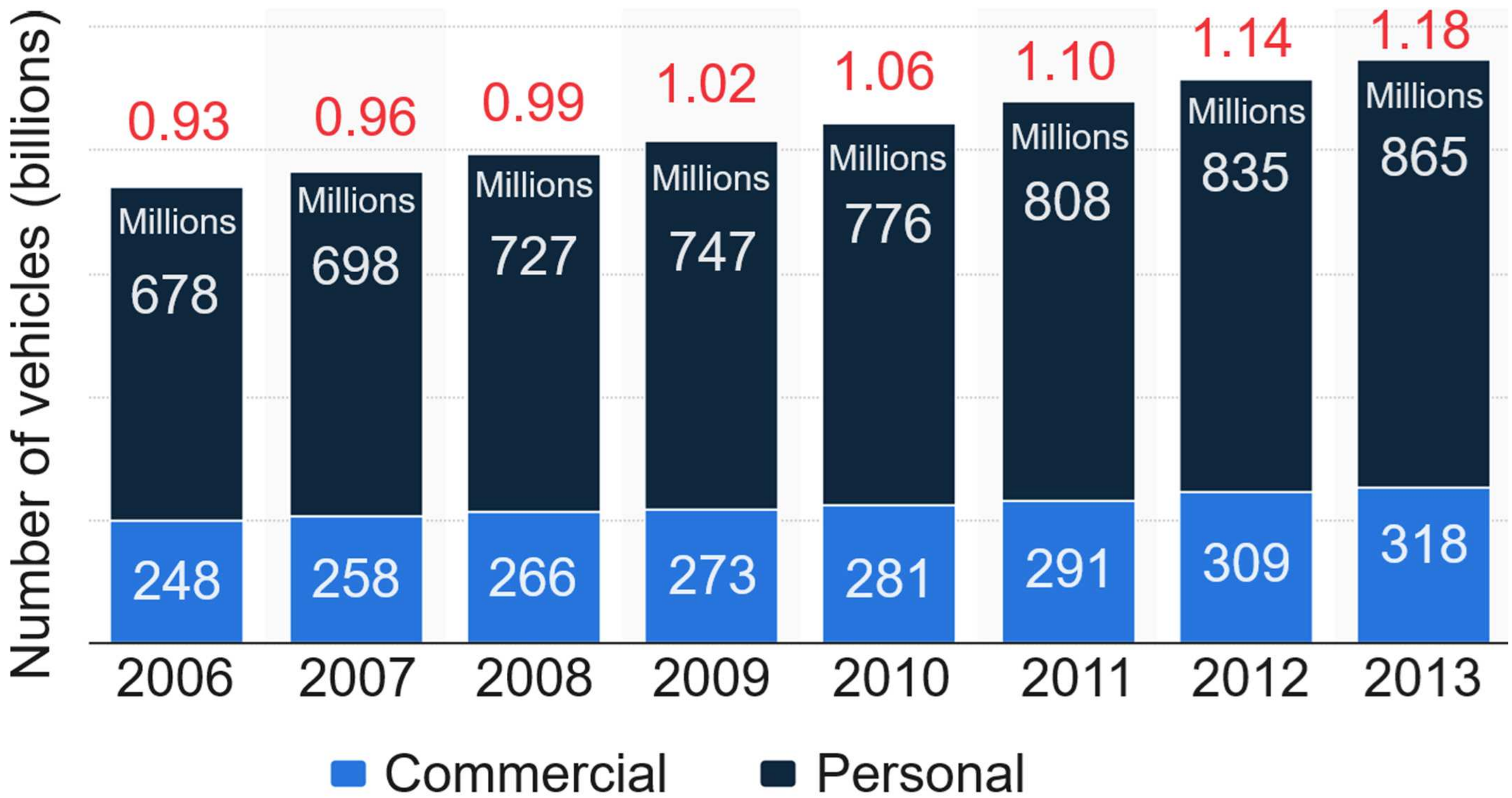
Karl Benz

- Pioneer of world motorization - Henry Ford
  - First production Model T car built in September 27, 1908 at the Piquette Plant in Detroit - start of mass production of vehicles
  - From 1914 the annual production of Model T reached 300,000 cars.



Development of automobile transport

- Continuous increase after WWII
  - ► Actual number (2016): 1.32 10^9 (personal cars + truck + buses)



Currently available energy sources

- Spark ignition engines
  - Gasoline (95, 98, or 100 octane) + up to 5% ethanol (annual sum min. 4.1%)
  - Ethanol-rich fuel E85 with ethanol content 70 – 85% according to the season
  - Compressed Natural Gas (CNG)
  - Liquefied Petroleum Gas (LPG): winter 40% butane / summer 60% butane
- Compression ignition engines
  - Diesel fuel containing up to 7% FAME
  - Mixed diesel fuel containing up to 31% FAME
- Hybrid vehicles
  - MHEV – Mild Hybrid Electric Vehicle
  - HEV – "classic" Hybrid Electric Vehicle
  - PHEV – Plug-in Hybrid Electric Vehicle

  } combustion engine + el. motor
- Electric vehicles
  - BEV – Battery Electric Vehicle
  - FCBEV – Fuel Cell Battery Electric Vehicle

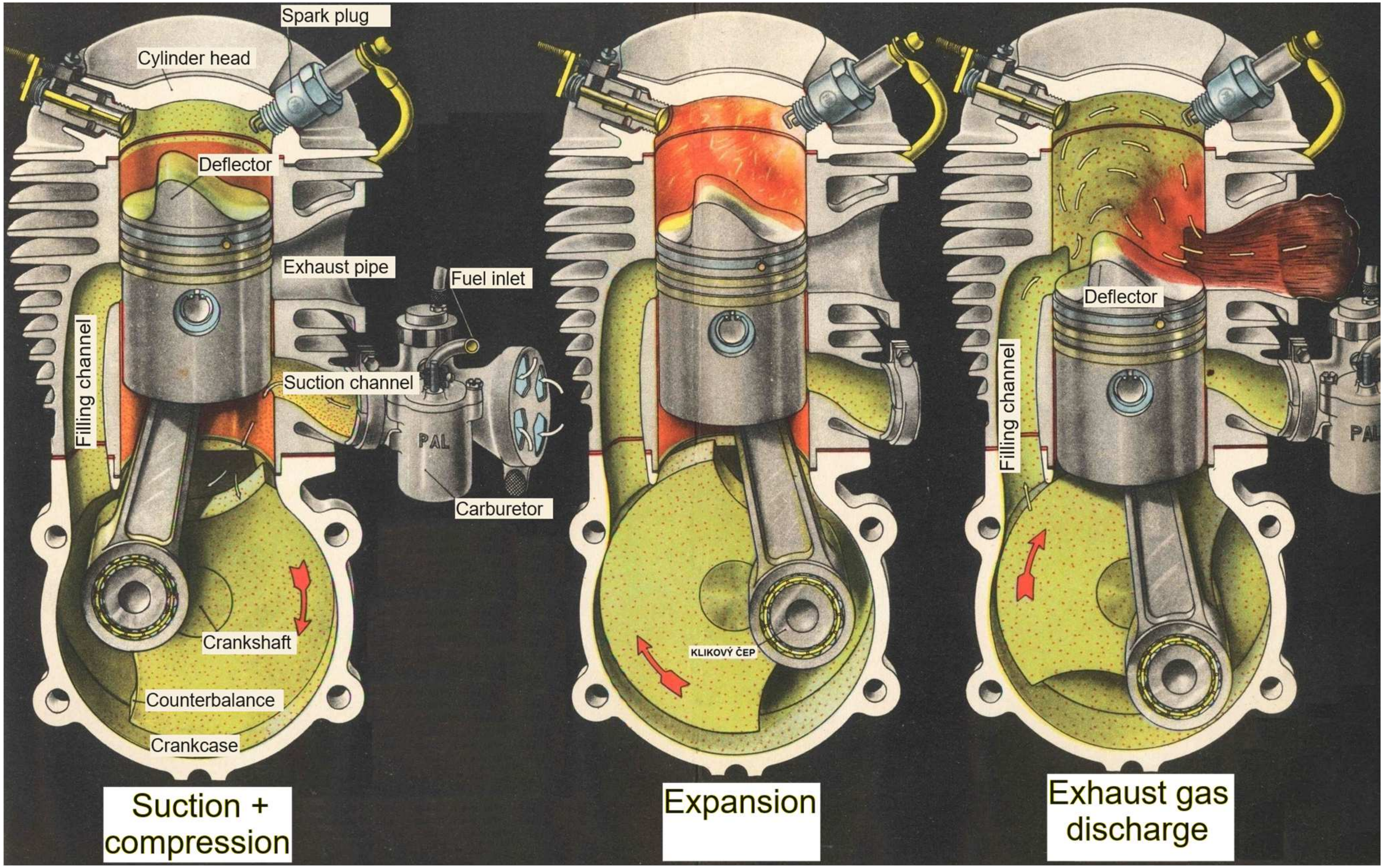
Differences between hybrid technologies

- MHEV – Mild Hybrid Electric Vehicle
  - the main propulsion unit = an internal combustion engine
  - the auxiliary system consists of a starter-generator with a battery
  - the starter-generator most often connected to the engine by a pulley (starter + energy recovery when braking – subsequently used for acceleration)
  - the electric motor power = ca. 12 kW (at 45 V) - not intended to drive
  - sometimes the el. motor drives the air blower and assists the turbocharger
- HEV – "classic" Hybrid electric vehicle
  - electrical assistance during start-up and acceleration + shorter electric drive
  - It does not allow charging from the wall plug.
  - more solutions: possible starting with the combustion Engine, or only electric
- PHEV – Plug-in Hybrid Electric Vehicle
  - two full-fledged motors; purely electric driving in the order of tens of km
  - battery charged externally (like BEV)
  - driving with a dead battery not recommended ⇒ battery only a ballast load

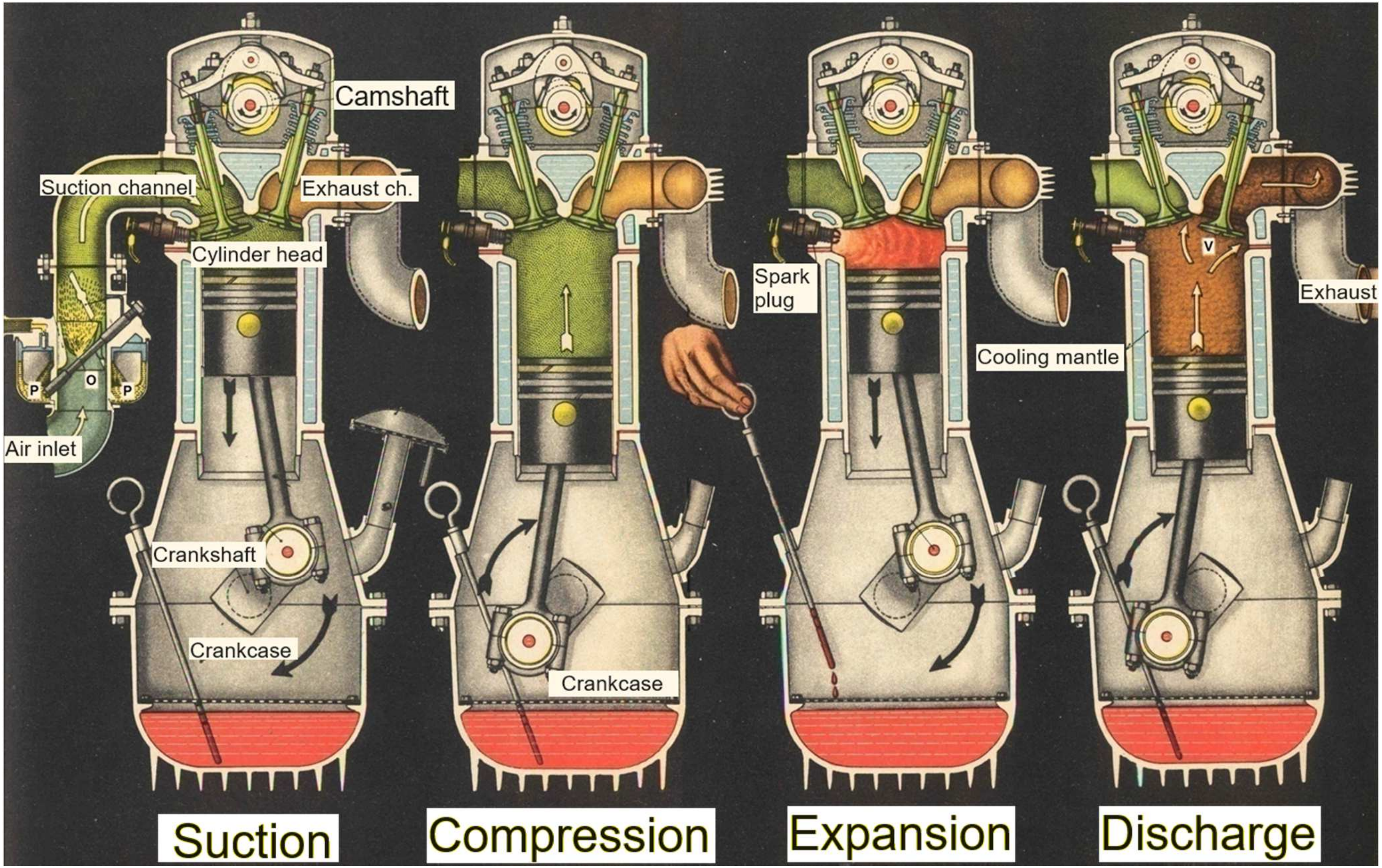
Principle of spark ignition engines

- A mixture of air and gasoline aerosol prepared and subsequently ignited by an electric spark
  - The oldest system with a **carburettor**: the aerosol created by passing air through a nozzle
  - A more modern system with **indirect injection**: gasoline injected outside the cylinder space into the intake air
  - The latest **direct injection system**: gasoline injected directly into the cylinder at the beginning of the compression phase
- Air/fuel ratio
  - Older engines with carburetor used sub stoichiometric air content
  - Modern engines use the excess air coefficient $\lambda = 1 \pm 0.1$
- Working cycle
  - Majority of modern cars uses the Otto 4-stroke cycle
  - Old cars (before 1990) also used Otto 2-stroke cycle
  - Especially for hybrid cars the Atkinson cycle is preferred (higher efficiency, but lower power)

2-stroke spark ign. engines (chainsaws etc.)



4-stroke spark ign. engines (cars)



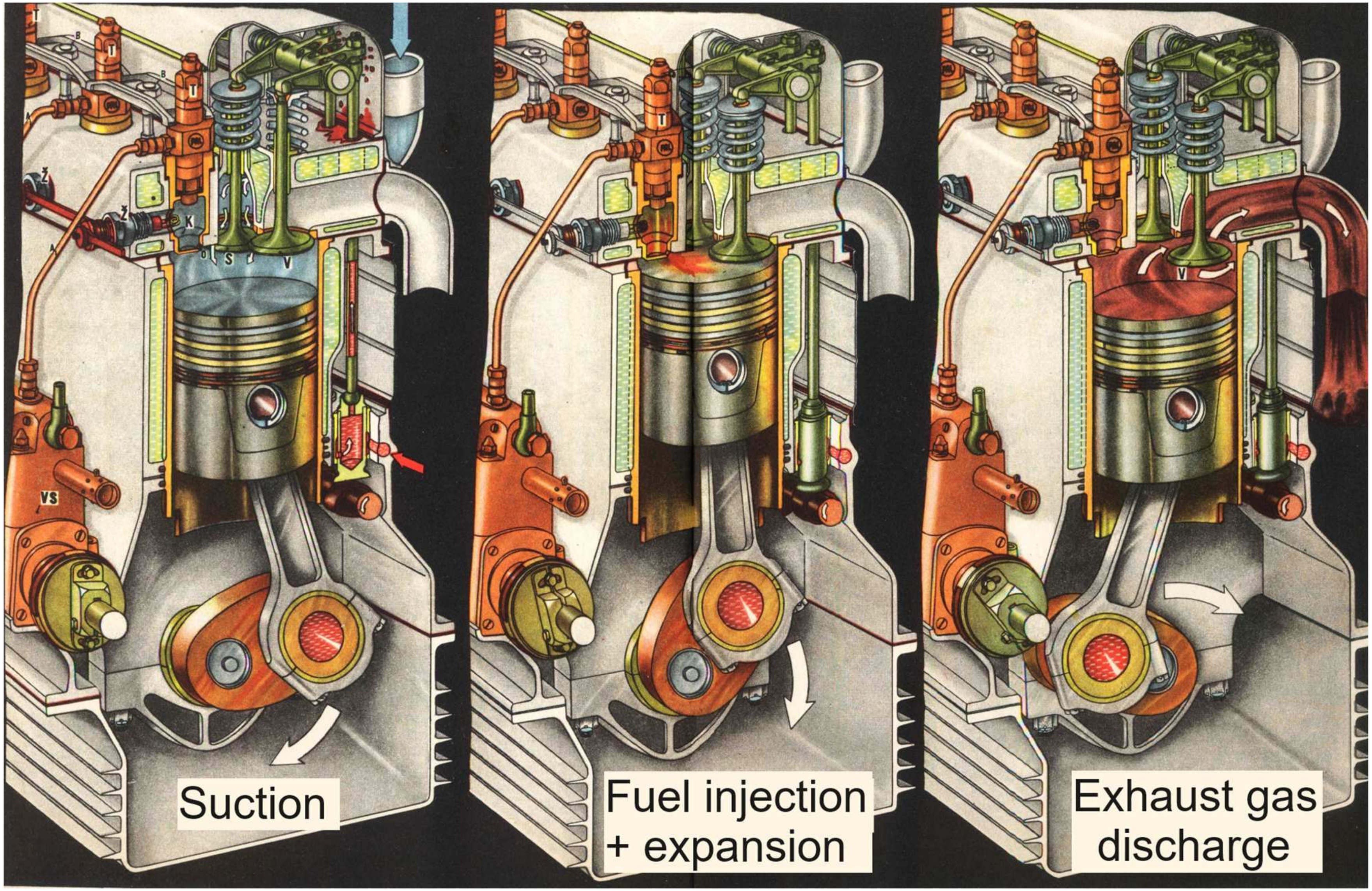
Principle of compression ignition engines

- In the first stage, only air is introduced into the cylinder
- After its adiabatic compression, fuel is injected into the cylinder by a high-pressure pump
  - Temperature of compressed air 700 – 900 °C
  - Temperature must be higher than flammability limit of the fuel (diesel fuel typically 320 – 380 °C)
- Air/fuel ratio
  - Excess air coefficient λ = 1.3 – 1.4 (naturally aspirated engines)
  - Excess air coefficient λ = 1.6 – 2.0 (engines with turbochargers)

  Note: Naturally aspirated engines offer generally low performance

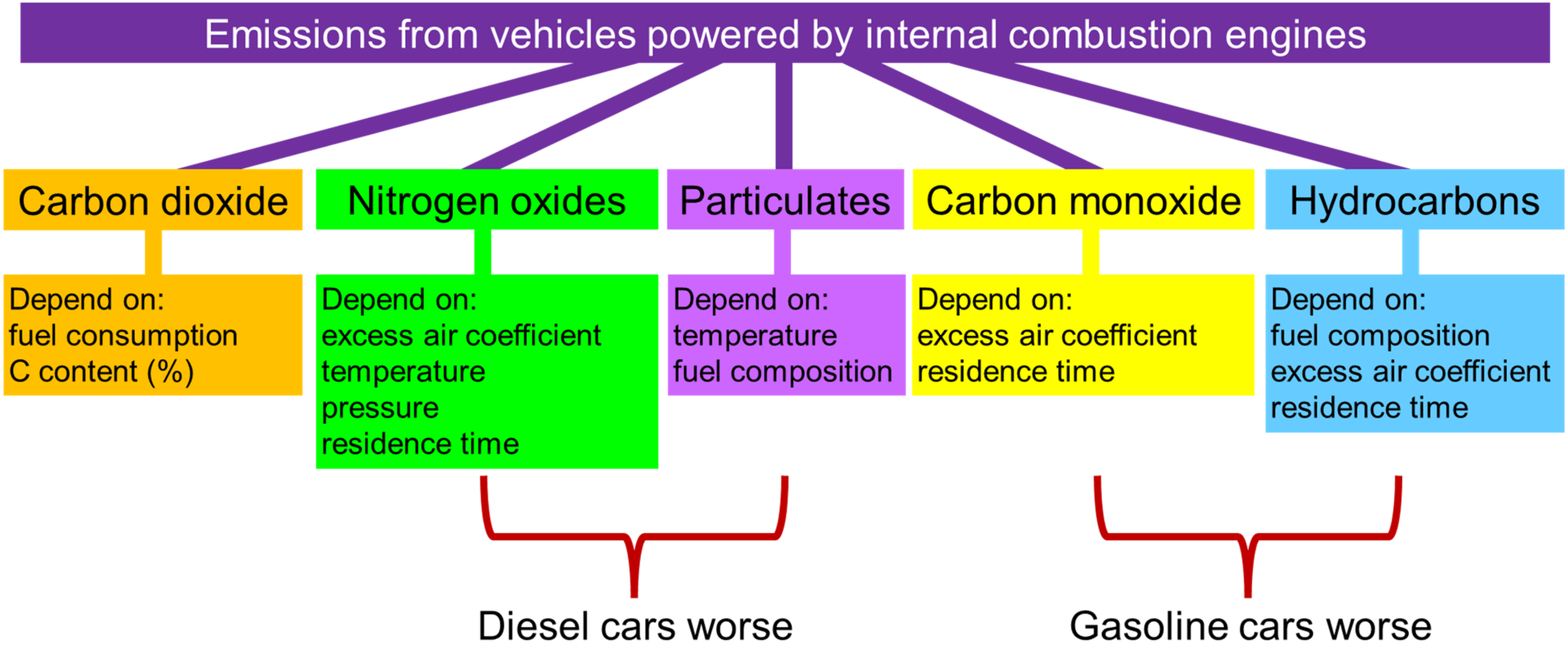
Turbocharger uses residual pressure of exhaust gas to compress the air:

4-stroke compression ign. engines (cars)



Emissions from internal combustion engines

- 5 different groups of emissions
  - CO_2 – cannot be (effectively) captured from exhaust gases
  - NO_x, PM, CO, C_xH_y – there are efficient methods for their removal



Main methods of reducing emissions

- Carbon dioxide
  - product of complete combustion of hydrocarbon-based fuels.
- Carbon content in liquid and gaseous fuels

	Diesel	Gasoline	LPG	CNG	Ethanol	FAME
C content (wt. %)	86,0	85,5	84,0	74,3	52,2	77,0

- Pathways leading to a decrease in emissions
  - to replace high-carbon fuel with low-carbon fuel
  - to decrease total fuel consumption

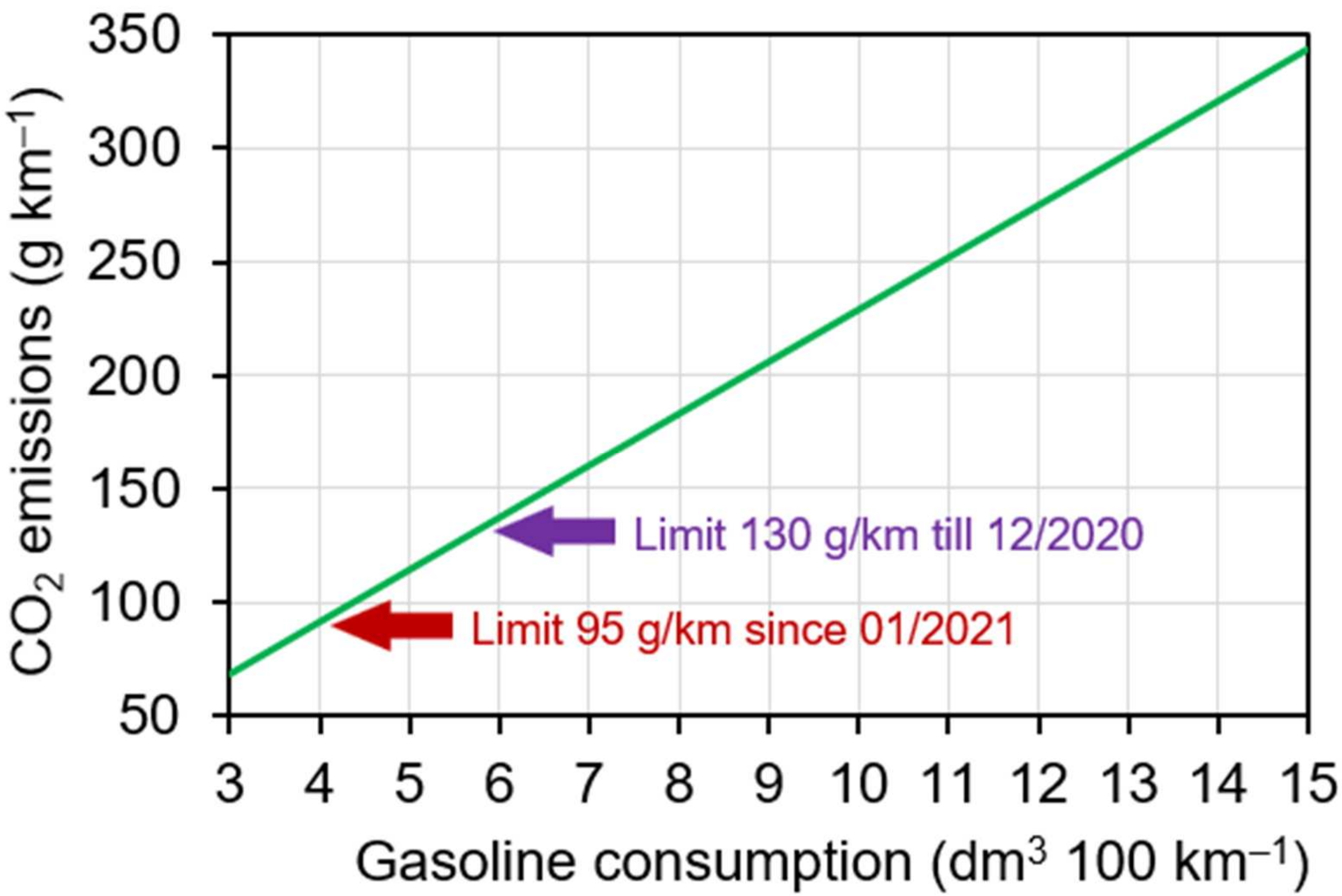
by increasing efficiency (technical limits)

Efficiency $\eta_{\text{Otto cycle}}$ = 25 – 38%

Efficiency $\eta_{\text{Diesel cycle}}$ = 30 – 42%

by hybrid technology implementation

- Carbon dioxide – emissions depend on fuel consumption
  - ► Example for the spark ignition engine combusting 95 octane gasoline:

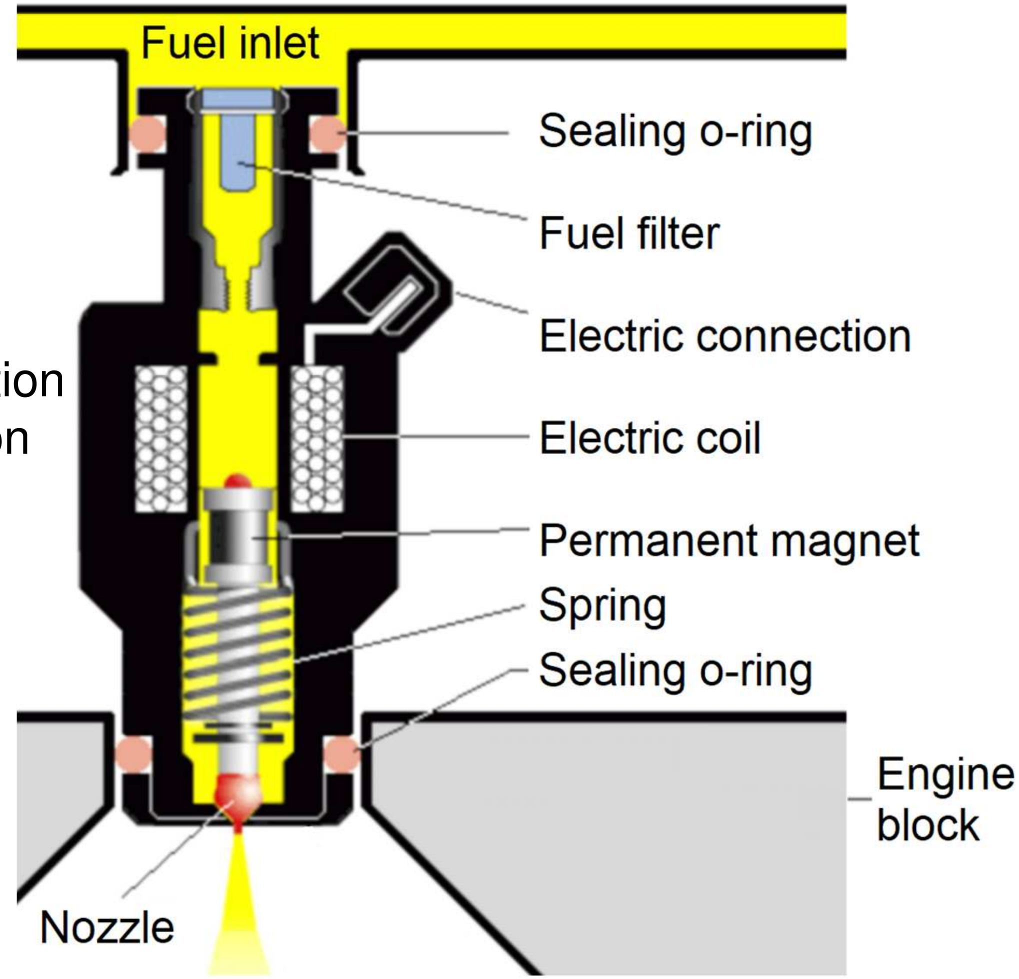


Main methods of reducing emissions

- Primary methods to suppress NO_x, CO, PM and C_xH_y emissions
  - Improvement of fuel mixture preparation (indirect vs. direct injection, “pumpe düse vs. common rail etc.)
  - Improved ignition (longer electrode distance + longer spark time)
  - Exhaust gas recirculation (NO_x suppression)
  - Reduction of tolerances in the combustion part of the engine
  - Lambda combustion control $\Rightarrow$ continuous control of the fuel/air ratio
  - Controlling the movement of the mixture in the cylinder
  - Switching off some cylinders when the engine runs at lower performance
  - Variable Valve Timing …..the Start/Stop system etc.
- Secondary methods
  - Implementation of catalysts (destruction of CO, C_xH_y and NO_x)
  - Implementation of filters (separation of PM)

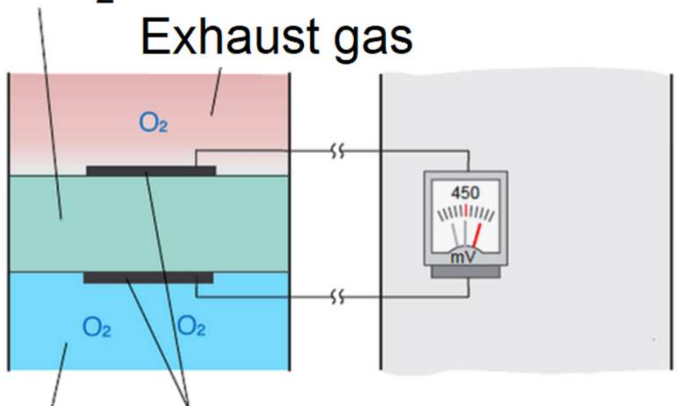
Spark ignition engines: precise fuel dosing

- Gasoline injection (widespread in half of 1980s)
  - replacement of the old carburettor system
  - Unlike the older carburettor, it enables λ-regulation.
  - λ-regulation = precise control of the air/fuel ratio
  - λ-regulation – essential condition for the 3-way catalyst operation



Spark ignition engines: λ-regulation

- The probe detects O_2 in the exhaust gas, the ECU then controls the fuel/air ratio.
- The signal from the common probes is the voltage between the electrodes.
- The signal changes in steps:
  - λ > 1 generates 0.1 – 0.2 V oxygen rich mixture prolong injection
  - λ = 1 generates 0.45 V stoichiometric combustion injection OK
  - λ < 1 generates 0.7 – 1.0 V fuel rich mixture shorten injection



- Three-way catalyst: common destruction of C_xH_y, CO and NO_x
  - As a rule, a ceramic carrier coated by active component (Pt + Pd + Rh)
  - All placed in a metal, internally sprung case
  - Carrier = magnesium-aluminum-silicate ceramic block with an Al_2O_3 surface layer
  - Operating temperature

min.	300°C
optimal	400 – 800 °C
risky	< 1,000 °C
destructive	> 1000 °C

Compression ignit. engines: complex system

- The system consists of separated catalysts and particle filter
- More complicated solutions for emissions – due to $\lambda > 1$ (always);
- Compared to gasoline engines, NO_x must be reduced using SCR and solid particles must be separated by filtration in a DPF filter;
- SCR principle: reduction by injection of urea solution
  - so-called AUS 32 = 32.5% urea in water with a crystallization point of -11 °C
- Urea solution supplied under the trade name AdBlue
  - AdBlue injected before the exhaust gas catalyst (mixing with flue gas followed by decomposition into $NH_3 + CO_2$)

Compression ignit. engines: complex system

- The system consists of separated catalysts and particle filter

EGR – Exhaust Gas Recirculation

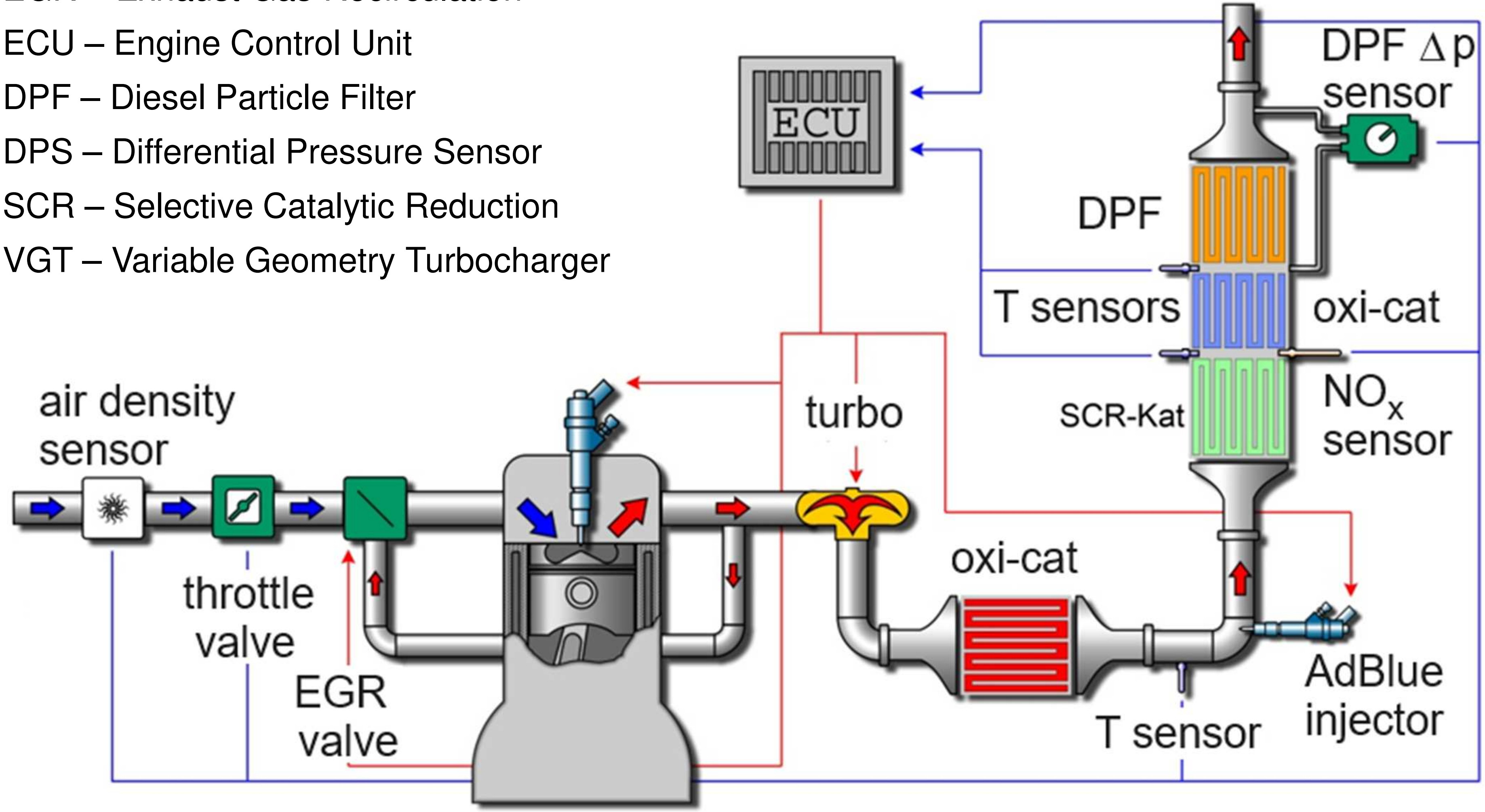
ECU – Engine Control Unit

DPF – Diesel Particle Filter

DPS – Differential Pressure Sensor

SCR – Selective Catalytic Reduction

VGT – Variable Geometry Turbocharger



Compression ignit. engines: DPF

- DPF separates mainly soot with automatic regeneration each 300-500 km
- Regeneration by heating to approx. 600°C with subsequent burning of soot
- Heating by fuel injection into the cylinders with the exhaust valves open

Regen. conditions:

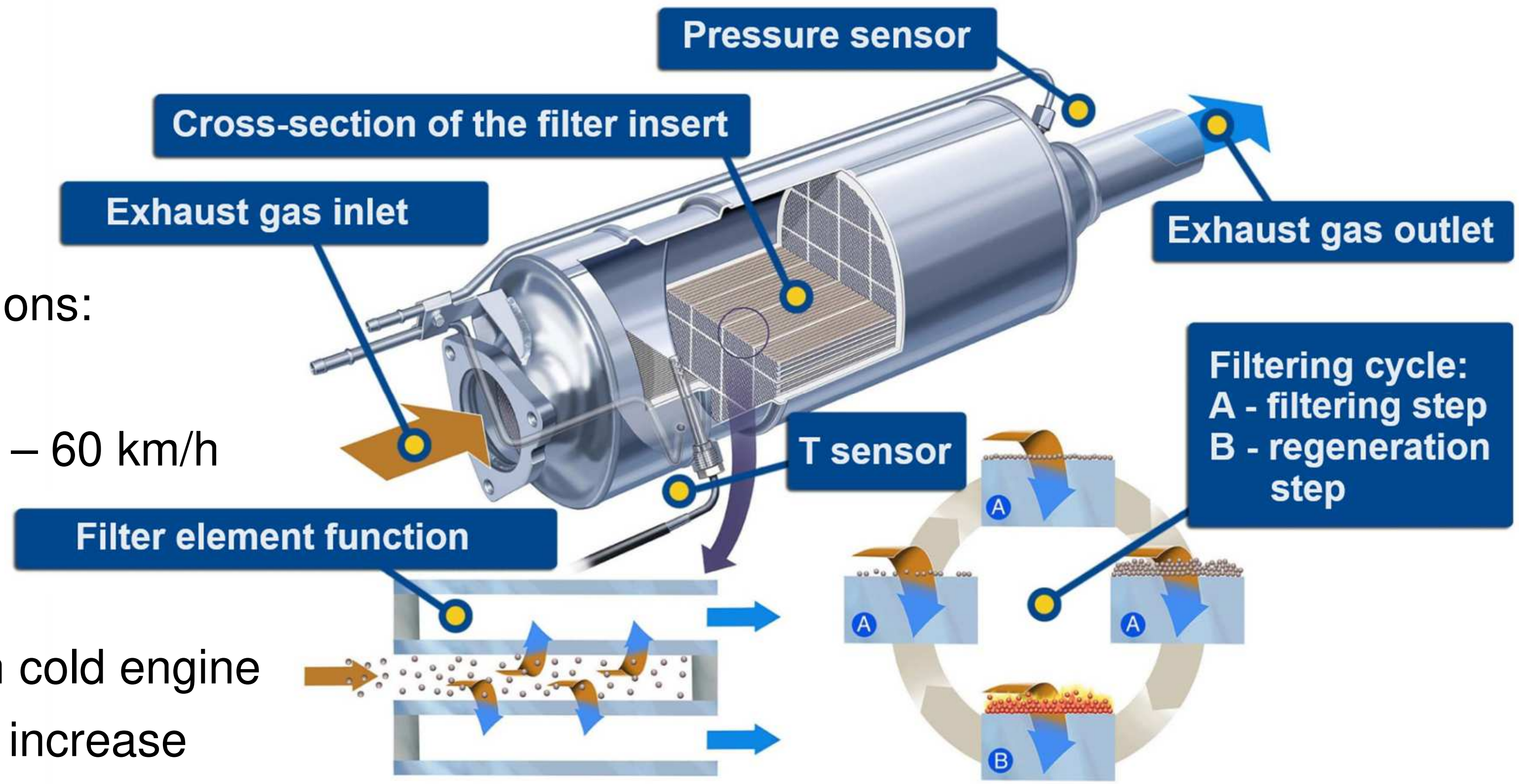
hot engine

speed min. 55 – 60 km/h

Problem:

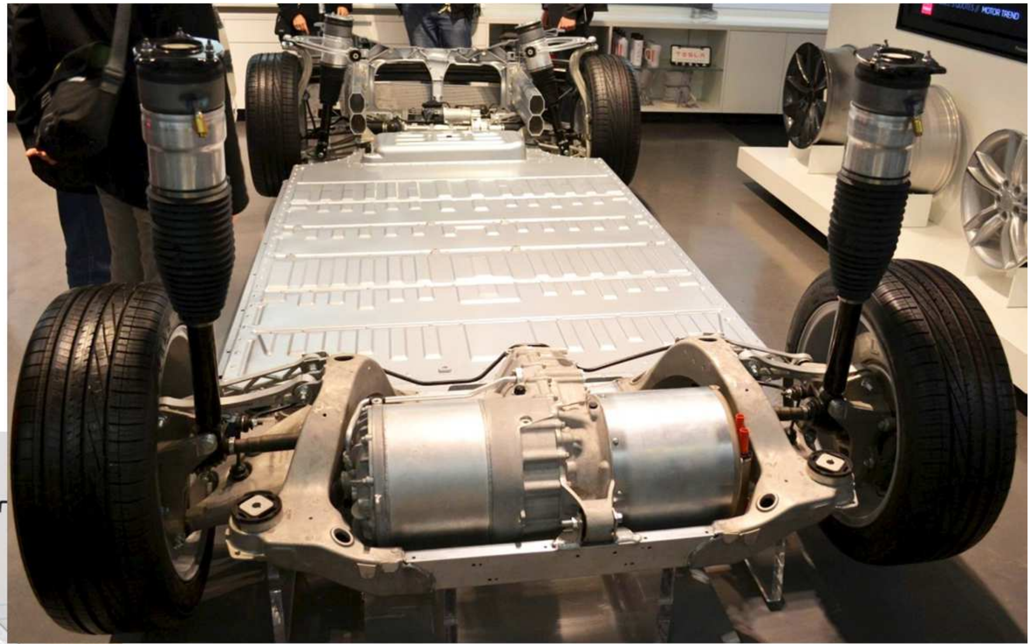
short trips with cold engine

permanent Δp increase



BEV: the main approaches

- Two solutions are currently available
  - System with direct wheel drive
    (without classic gearbox)
    often a chassis on a frame
    (skateboard-like construction)



  - Similar to a classic car
    self-supporting body
    engine with automatic transmission

- Metallic lithium $^{7}_{3}Li$
  - Lithium is a low-density alkali metal with a melting point of only 180.54 °C.
  - It is a highly reactive element that oxidizes even in air. It is stored safely in kerosene.
- Natural occurrence
  - A relatively rare element, contained in rocks especially based on aluminosilicates, but in ores usually less than wt. 5%

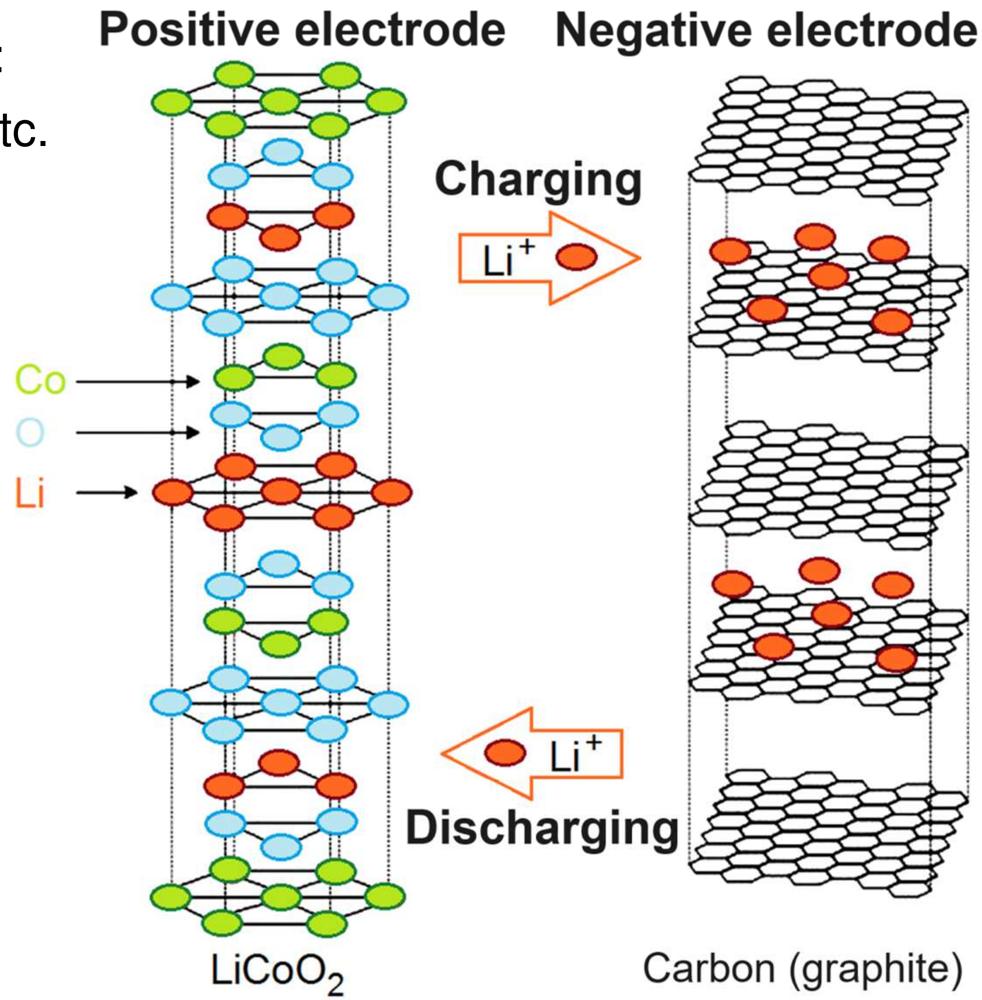
Lithium ore Lepidolite

Metallic Lithium

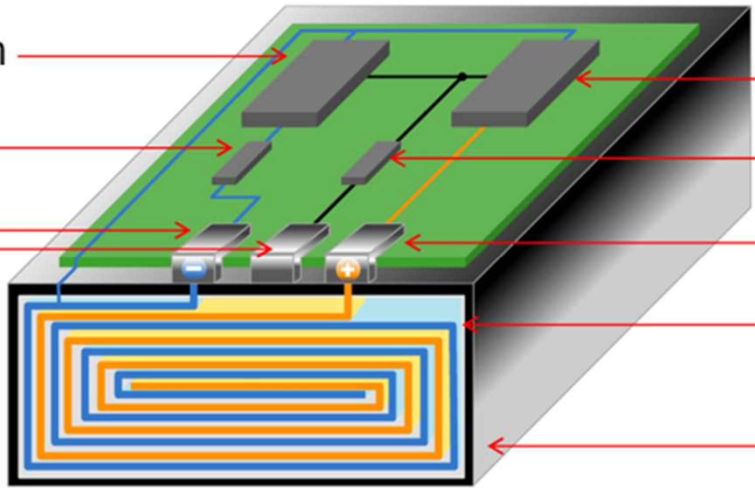
Caustic Flammable

BEV: lithium-ion battery

- Principle of the function
  - Lithium ions transport
  - Cathode on the basis of the oxides: $LiCoO_2$, $Li_xMn_2O_4$, $LiNiO_2$, LiV_2O_5 etc.
  - Anode: graphite
  - Electrolyte: liquid, gel or polymer
    the most widely used: liquid lithium-hexafluorophosphate in solvents (ethylene carbonate + dimethyl carbonate etc.)



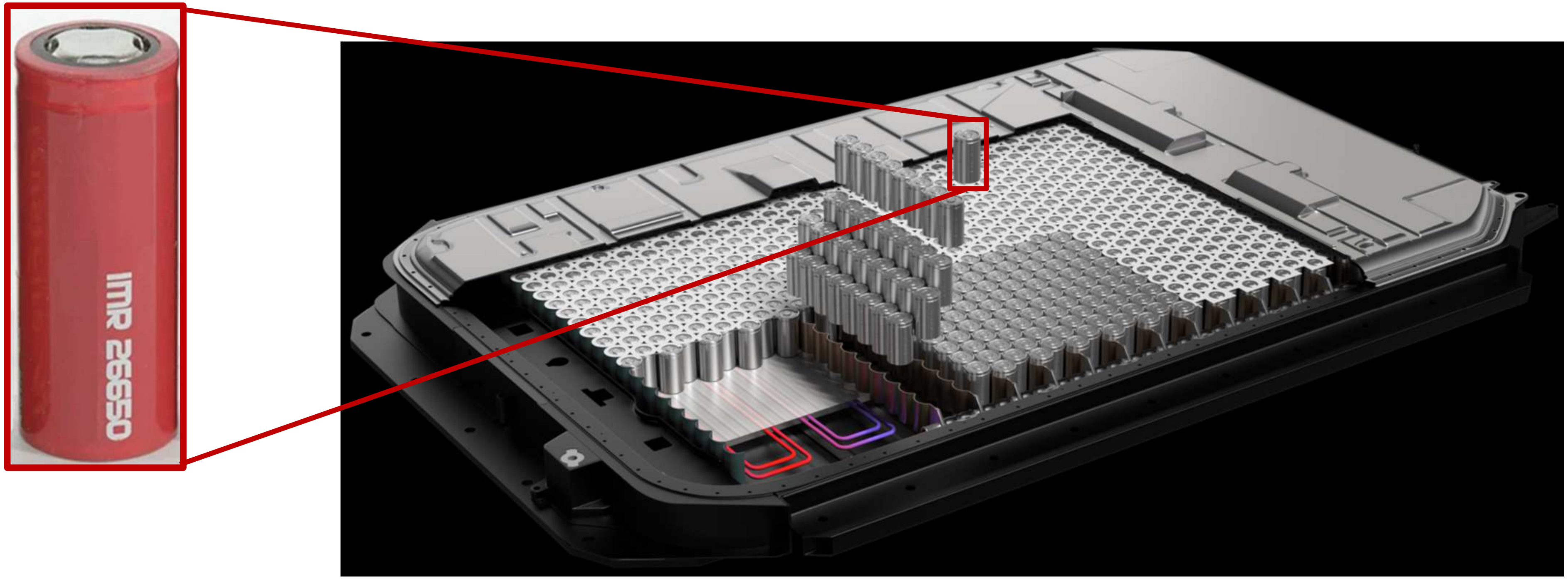
- Construction solution with liquid electrolyte
  - Nominal voltage of one cell = 3.6 V
  - Multiples are achieved by serial sorting, i.e.: 7.2; 10.8; 14.4 V ...etc.
  - The capacity is then increased by parallel switching



- Evolution of Li-ion batteries
  - Initial design - early 20th century proposed by Gilbert Newton Lewis
  - The first practically usable battery – 1970s: Li-TiS_2 developed by Michael Stanley Wittingham
    - Problem: unacceptable titanium sulfide cost
  - Much cheaper LiC_6 introduced by Bell's laboratories AT&T
  - First commercially successful type $LiCoO_2$ introduced by Sony in 1991
  - Today the most produced types:
    - type 18650, 18×65 mm (e.g. for Tesla S)
    - type 20700, 20×70 mm
    - type 26650, 26×65 mm
  - Cathodes vary by applications
    - Li-$NiCoAlO_2$
    - $Li_4Ti_5O_{12}$ etc.

BEV: lithium-ion battery

- Cells assembled into battery packs (1 car needs thousands cells)
  - nominal voltage of one cell = 3.6 V
  - capacity increased by connecting cells in parallel
  - voltage increased by connecting the cells in series
  - battery packs also contain: protective casing, insulation against water, charging/discharging electronics, cooling system



BEV: further development is still needed

- The main problems of BEV that still need development:

1. ► Low energy density of batteries
2. ► Flammability of electrolyte and anode of Li-ion batteries
3. ► Cell degradation causing a drop in capacity (limited lifespan of batteries)
4. ► Dependence of battery capacity on temperature
5. ► Slow charging + unusable 100% capacity
6. ► The need for noble metals (especially for cathodes)
7. ► Lack of **stable** energy supplies from emission-free sources

BEV: energy density of the batteries

1 ■ Energy density

$$ED_V = ED_w \times \rho = \frac{E \times \rho}{m} \xrightarrow{therefore} [ED_V] = [W\ s\ m^{-3}]$$

$$P = \frac{F \times d}{t} = \frac{E}{t} \xrightarrow{therefore} [J] = [W\ s]$$

- Definition: Energy density = the amount of energy stored in a given system per unit volume or unit weight
- Units: 1 watt-second per cubic meter [Ws m^{-3}]
  1 watt-second per kilogram [Ws kg^{-1}]

E	…. energy [Joule], [J]
P	…. power [Watt], [W]
F	…. force [Newton], [N]
d	…. distance [meter], [m]
t	…. time [second], [s]
ED_V	…. volume energy density [watt-second per cubic meter], [Ws m^{-3}]
Ed_W	…. weight energy density [watt-second per kilogram], [Ws kg^{-1}]
ρ	…. (material) density [kilogram per cubic meter], [kg m^{-3}]
m	…. weight [kilogram], [kg]

1

Energy density

- Fuels: the energy density value given by the heat of combustion of the fuel
- Batteries: the energy density given by the amount of charge transferred between cathode and anode

	Max. energy density		Material density	Max. engine/motor efficiency
	($Wh\ kg^{-1}$)	($Wh\ dm^{-3}$)	($kg\ dm^{-3}$)	(%)
Diesel	11,836	9,942	0.84	42%
Gasoline (95 oct.)	12,108	8,839	0.73	38%
Li-ion battery	200	530	2.65	82%
$LiFePO_4$ battery	165	335	2.03	82%

Problem: Actual generation of Li-ion batteries have the energy density too low!

Theoretical maximum of the Li-ion cell is 1.700 $Wh\ h^{-1}$. …. but it is not reached anyway.

BEV: energy density of the batteries

1

- Energy density – example of comparison (including the engine efficiency)
  - Let's have 4 cars with the same power.
  - The car with a diesel engine has a fuel tank of 50 liters.
  - What is the gasoline and Li-ion battery equivalent for the engine to do the same work (incl. low efficiency of fossil fuel cars)?

	Fuel/battery volume	Fuel/battery weight	Effective energy used	Total energy in the fuel/battery
	(dm^3)	(kg)	(kWh)	(kWh)
Diesel	50	42	209	497
Gasoline (95 oct.)	62	45	the same	550
Li-ion battery	481	1,274	the same	255
$LiFePO_4$ battery	761	1,545	the same	255

BEV: energy density of the batteries

1

- Energy density – example of comparison (including the engine efficiency)
  - Let's have the VW ID.5 car with the usable battery capacity of 77.0 kWh (model year 2023).
  - How much fossil fuel (including low efficiency of fossil fuel cars) does this capacity correspond to?

77.0 kWh stored in:		
	Fuel/battery	
	Volume (dm^3)	Weight (kg)
Li-ion battery	145	385
$LiFePO_4$ battery	230	467
Diesel	15	13
Gasoline (95 oct.)	19	14

BEV: flammability of lithium-ion batteries

2

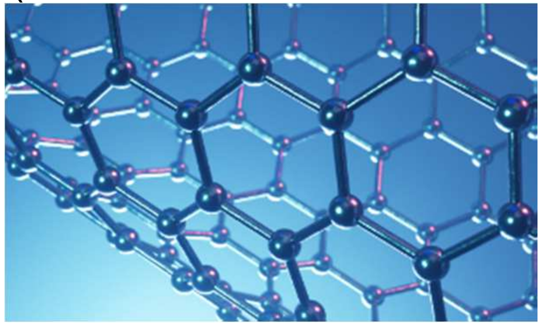
- Li-ion battery fire can occur:
  - due to an internal short circuit (separator damage)
  - as a result of a car accident
  - due to overheating (failure of temperature management, especially during charging)
- The only effective solution:
  - development of batteries without flammable media
  - persisting problem: safe substitutes for liquid organic electrolyte have worse lithium ion transfer ⇒ slower charging, lower capacity
  - many researches in progress, e.g.:

    Solvent-Anchored non-Flammable Electrolyte (SLAC/Stanford University)

    Graphene-based lithium-ion batteries

    (Nanotech Energy)

    …… etc.



BEV: flammability of lithium-ion batteries

2

- Example: Steps of Li-ion battery fire due to overheating:

► Exothermic decomposition of electrolyte interphase	85 °C
► Formation of a secondary film and its subsequent decomposition	110 °C
► Evaporation of electrolyte	140 °C
► Separator melting (between electrodes and electrolyte)	130 – 190 °C
► Short-circuiting of the circuit and spontaneous heating	
► Ignition of electrolyte vapors with oxygen released from the positive electrode after leaving Li	225 °C
► Graphite electrode ignition	330 °C
► Melting of the aluminum collector	660 °C
Explosion	

BEV: Li-ion cell degradation

3

- Cell degradation causing a drop in capacity occurs:
  - ► spontaneously as a result of chemical processes in the cells
  - ► with an increasing number of charge/discharge cycles

    lifespan ca. 2,000 cycles for Li-ion and >2,000 cycles for $LiFePO_4$
  - ► with increasing use of maximum charging speed ("turbocharging")
  - ► by exposing the battery to high temperatures
  - ► by storing the vehicle for a long time:

    with other than 40-60% charge level

    storing at 100% charge or discharged accelerates the degradation

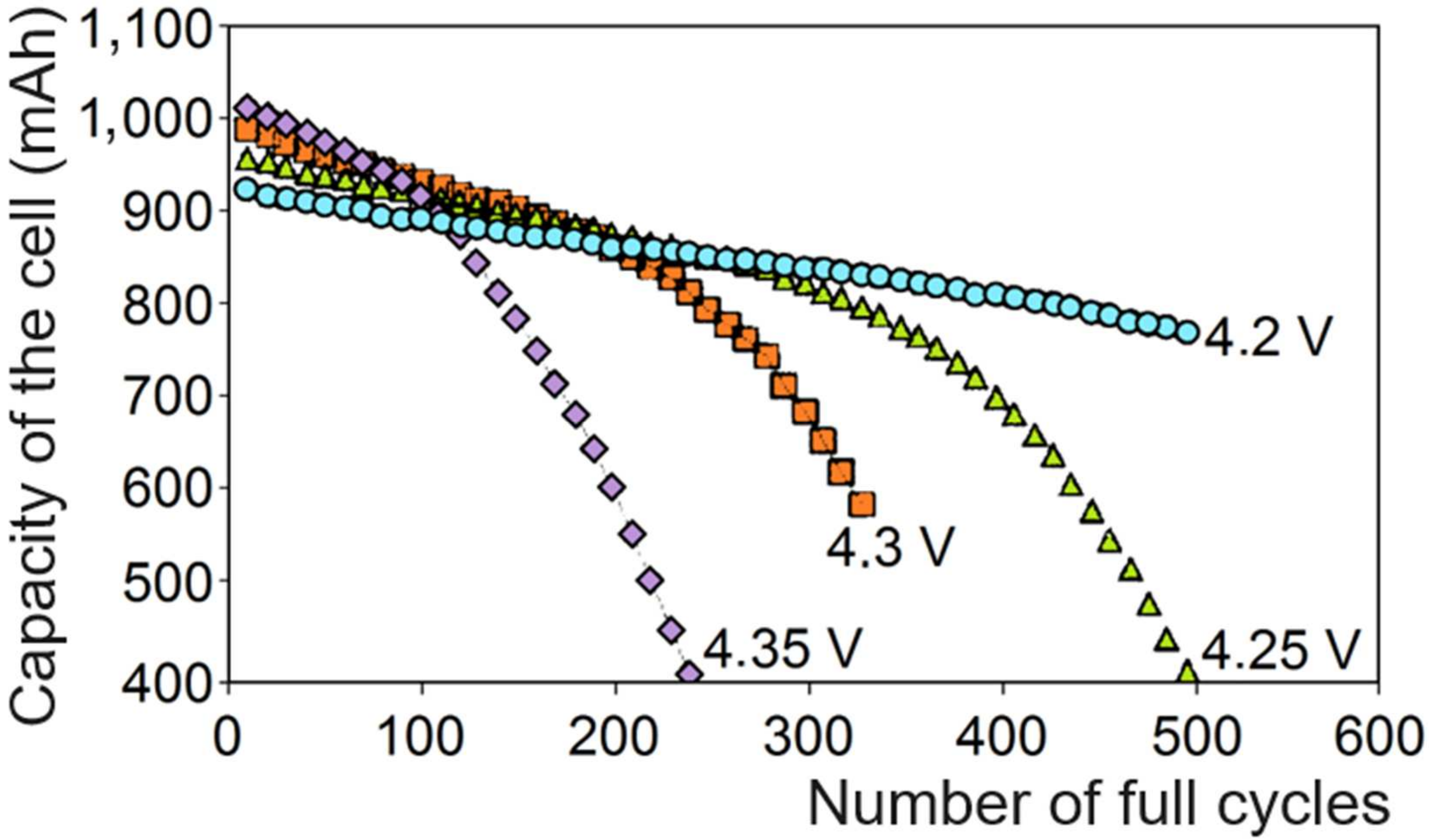
- The definitive death of the cell occurs:
  - ► due to a deep discharge below the 2.8 V limit

    (e.g. when the vehicle is parked for a long time)
  - ► when the battery overheats above the technical limit

BEV: Li-ion cell degradation

3

- Charging with a higher voltage slightly increases the initial capacity, but leads to rapid degradation: limited by the car's power management
  - ► dangerous charging eliminated by the car power management
  - ► Using fast chargers with a higher current load also has a negative effect



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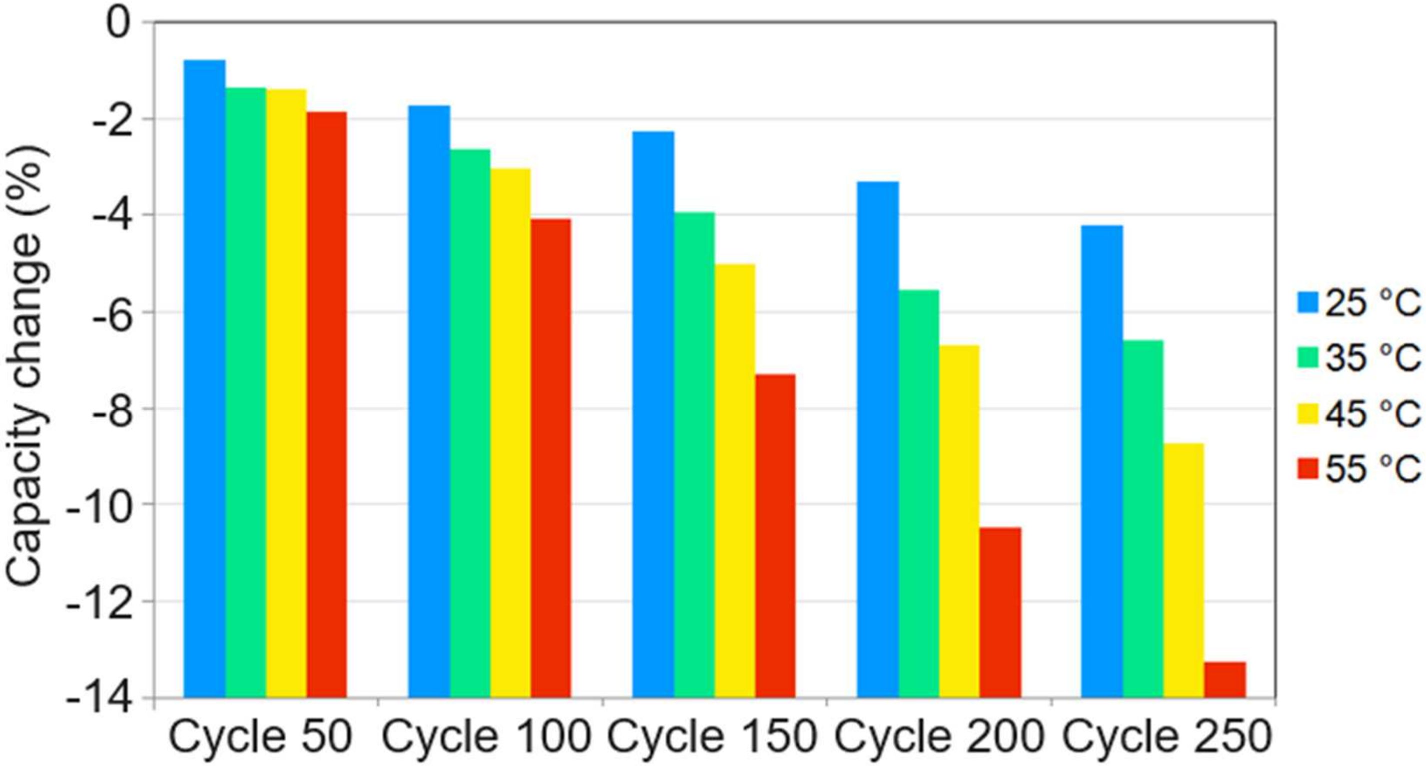
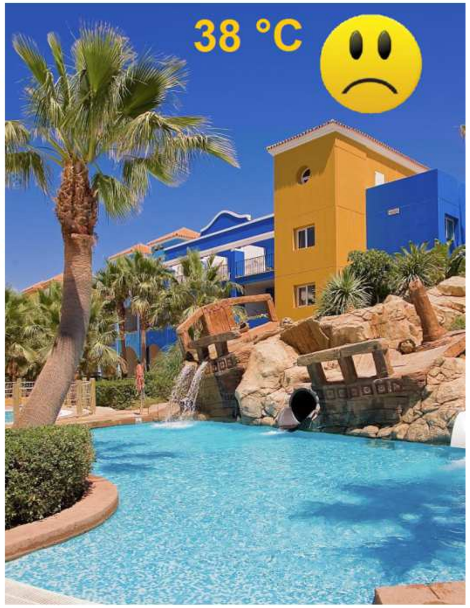
- Low temperature → temporary capacity reduction
  - ► Example: The capacity is 100% at +27°C , but only 50% at -18°C.

- Too high temperature → lifespan shortening (permanent capacity drop)





BEV: Slow charging

- Slow charging compared to fossil fuels vehicles
  - Charging time depends on battery capacity, voltage and current.
  - Problem: The maximum current is limited by the material and cross-section of the conductor (cable).
  - Standard electric cars use **400 V** architecture.
  - Only premium models (Porsche Taycan) allow charging at **800 V**.
  - Battery charging runs with **direct current (DC)**. When **alternating current (AC)** is used a rectifier is activated (it slows charging down)
  - Charging current for DC and single-phase AC

$$I[A] = \frac{P[W]}{U[V]}$$

  - Charging current for 3-phase AC (where Q is so called reactive power)

$$I = \frac{\sqrt{P^2 + Q^2}}{\sqrt{3} \times U}$$

BEV: Slow charging

5

- Slow charging compared to fossil fuels vehicles
  - ► overview of charging systems in Europe

Charger type	AC			DC		
	Charging power	Voltage	Current	Charging power	Voltage	Current
Wall plug (1-phase)	2,3 kW	230 V	10 A	Not available		
Wall plug (1-phase)	3,6 kW	230 V	16 A			
Wallbox (3-phase)	7,2 kW	400 V	10 A			
Wallbox (3-phase)	11,0 kW	400 V	16 A			
Wallbox (3-phase)	22,0 kW	400 V	32 A			
Public charger	22,0 kW	400 V	32 A	22,0 kW	400 V	55 A
Public charger	43,0 kW	400 V	62 A	43,0 kW	400 V	108 A
Public charger	Not available			50,0 kW	400 V	125 A
Public charger				120,0 kW	400 V	300 A
Public charger				150,0 kW	400 V	375 A
Public charger				350,0 kW	800 V	438 A

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BEV: Slow charging

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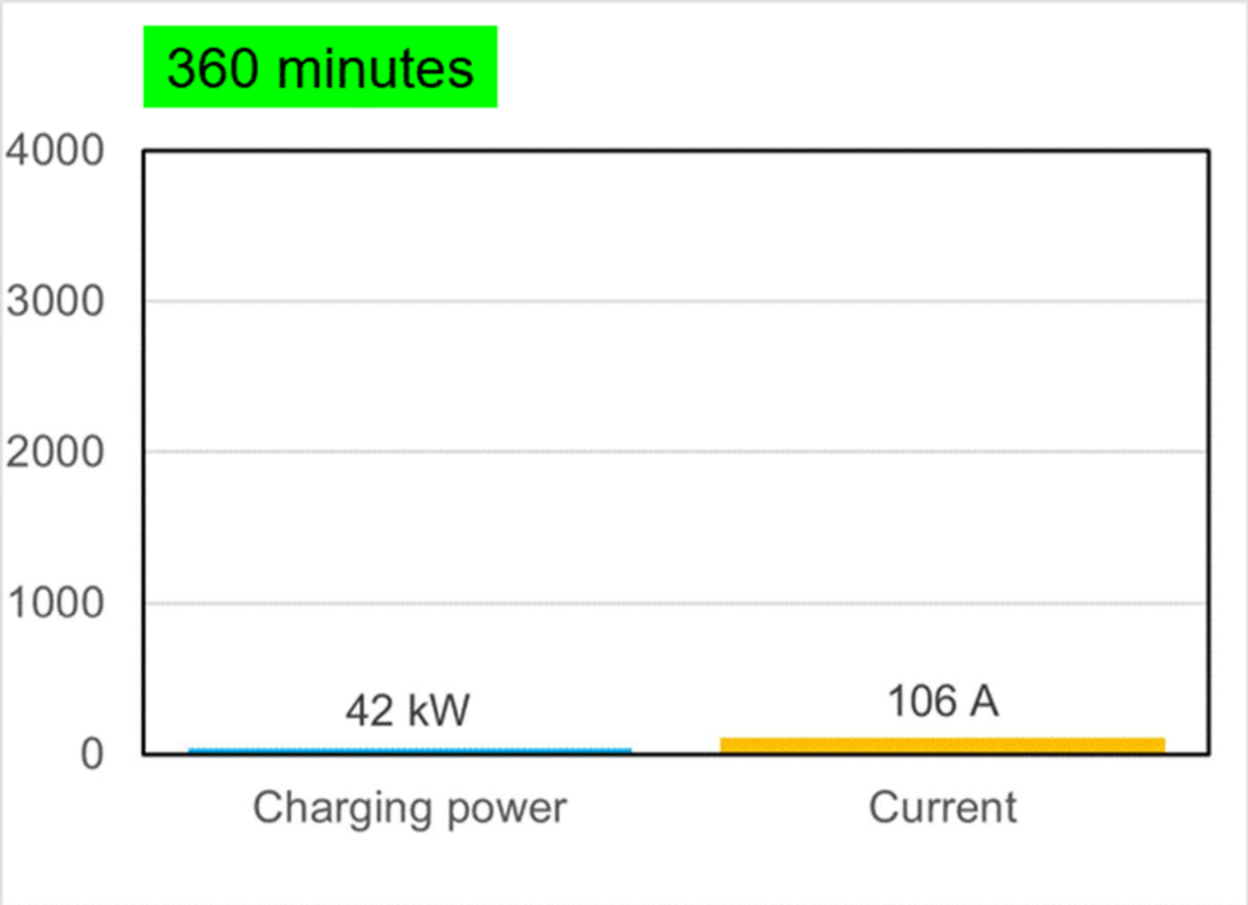
- Example: refueling a 50-liter tank takes 10 minutes, incl. payment
  - ► How would an electric car have to be charged to achieve the same time?
  - ► Conditions: DC charger / 400 V car architecture

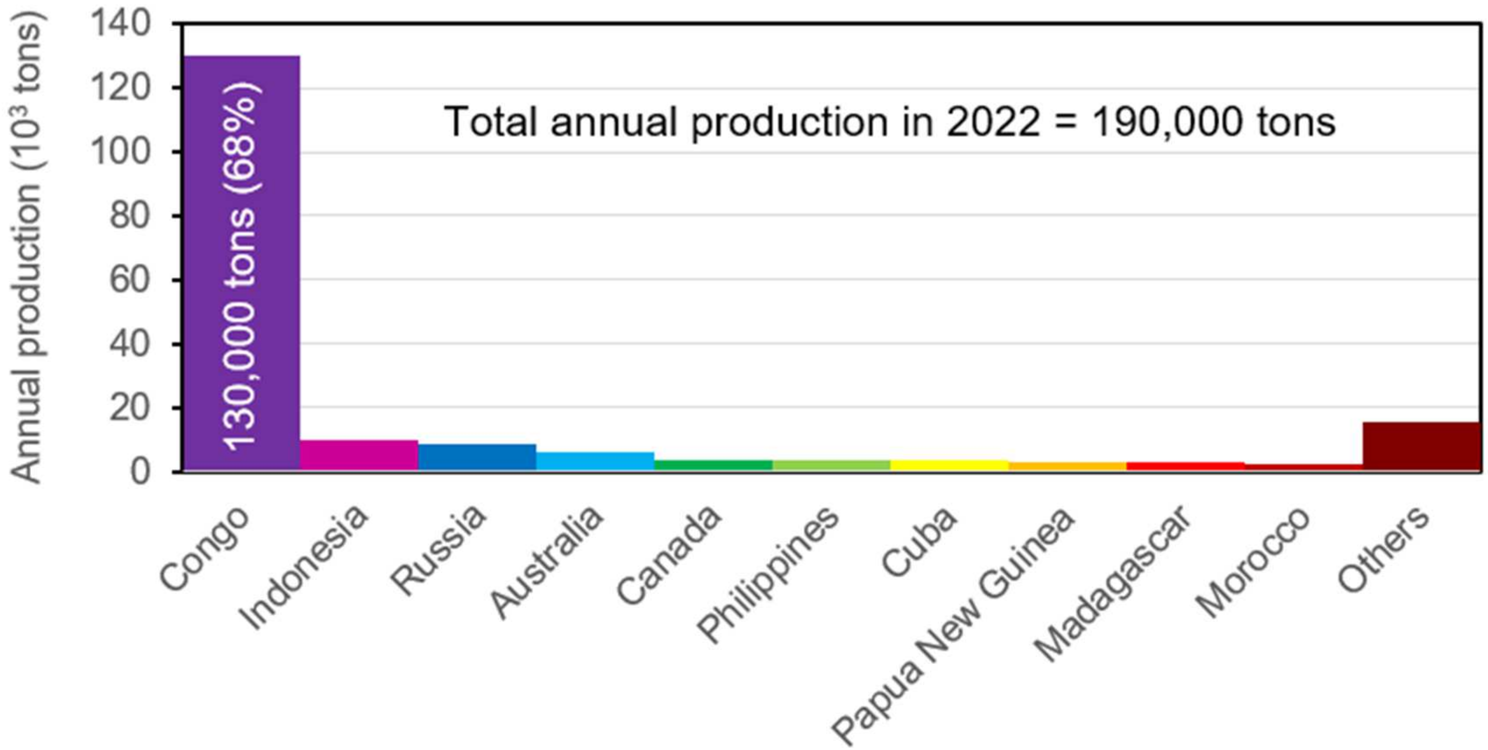


BEV: The need for noble metals (espec. Co)

6

- In addition to Li, other metals such as: Ni, **Co**, Ti, V or Mn necessary
- Co metallurgy: Pressure Acid Leaching ⇒ **environmentally harmful**

Step 1: Cobalt ore leached with a mixture of mineral acids at 4.5 MPa and 255°C
Step 2: Metals precipitated from the solution using H_2S
Step 3: Sulfides converted to sulfates by O_2 under under increased p
Step 4: $CoSO_4$ separated from the solution using liquid extraction.



BEV: The need for noble metals (espec. Co)

- In the Democratic Republic of the Congo, there are about 2/3 of the mineable cobalt reserves.
- Mining: mainly manual (high share of child labor)
- Environmental protection: poor

Mutanda Mine

Unicef data 2021: global share of child labor 160 million children

BEV: Electricity supply

- Stable energy supplies from emission-free sources
  - Solar + wind energy: fluctuating electricity production
  - Combustion proc.: pre-, post- and oxy-combustion CO_2 capture needed
  - Nuclear energy: necessary to solve the management of used fuel
    - permanent storage
    - recycling
    - closed fuel cycle
  - Necessary development and construction of energy storage facilities
    - batteries
    - gravity storage (mechanical)
    - pumped water power plants
    - chemical storage (reversible reactions)

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