

Willkommen
Welcome
Bienvenue

Electrochemical energy storage: batteries

Simone Pokrant



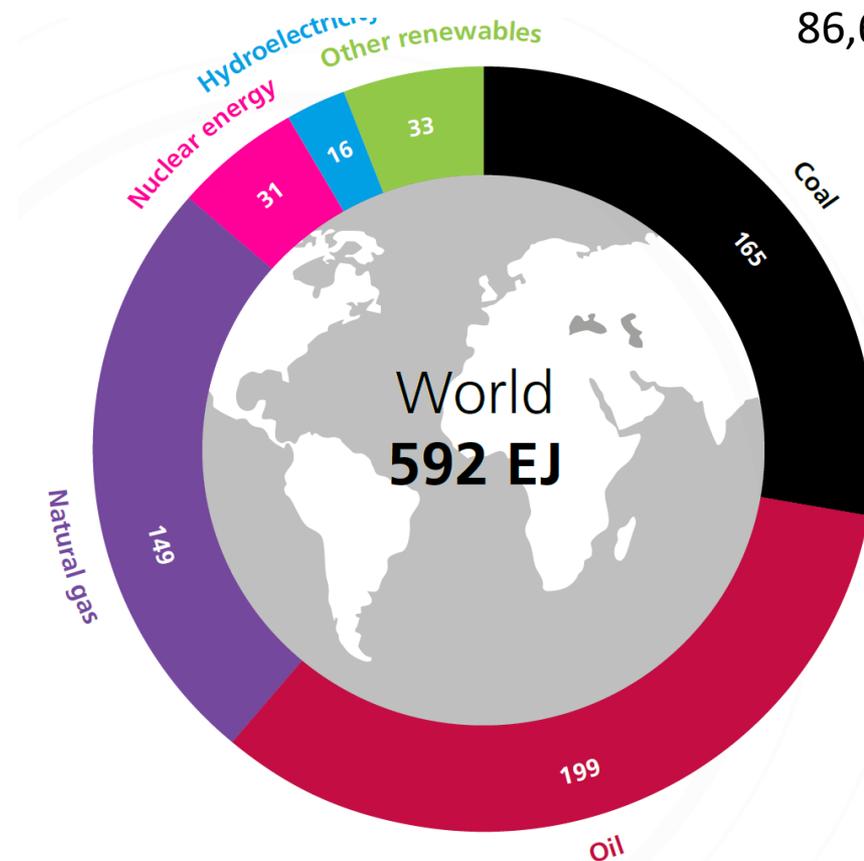
Literature

- Michael Sterner, Ingo Stadler,
Handbook of Energy Storage
Springer 2019
<https://doi.org/10.1007/978-3-662-55504-0>
- O.Rummich, E: *Energiespeicher*. Expert Verlag, 2009
- Huggins, R.A.: *Energy Storage*, Springer, 2010
- Tarascon, J. M. ; Simone, P. *Electrochemical Energy Storage*, Wiley, London, 2015
- Strauss K. *Kraftwerkstechnik*, 7. Auflage
Springer 2016, ISBN 978-3-662-53029-0

Content

- Energy turnaround and the importance of stationary energy storage
- Basics in electrochemistry
- Lead acid batteries for stationary energy storage
- Li ion batteries for stationary energy storage
- Comparison Li-ion battery and lead acid battery

Primary energy consumption 2024



86,6 % Fossile Energies



Exa = 10^{18}

Note: energy sources in the charts are ordered according to their carbon intensity.

<https://www.energyinst.org/statistical-review>

2021: 595,15 EJ (563,26 EJ)

2022: 604,04 EJ (571,04 EJ)

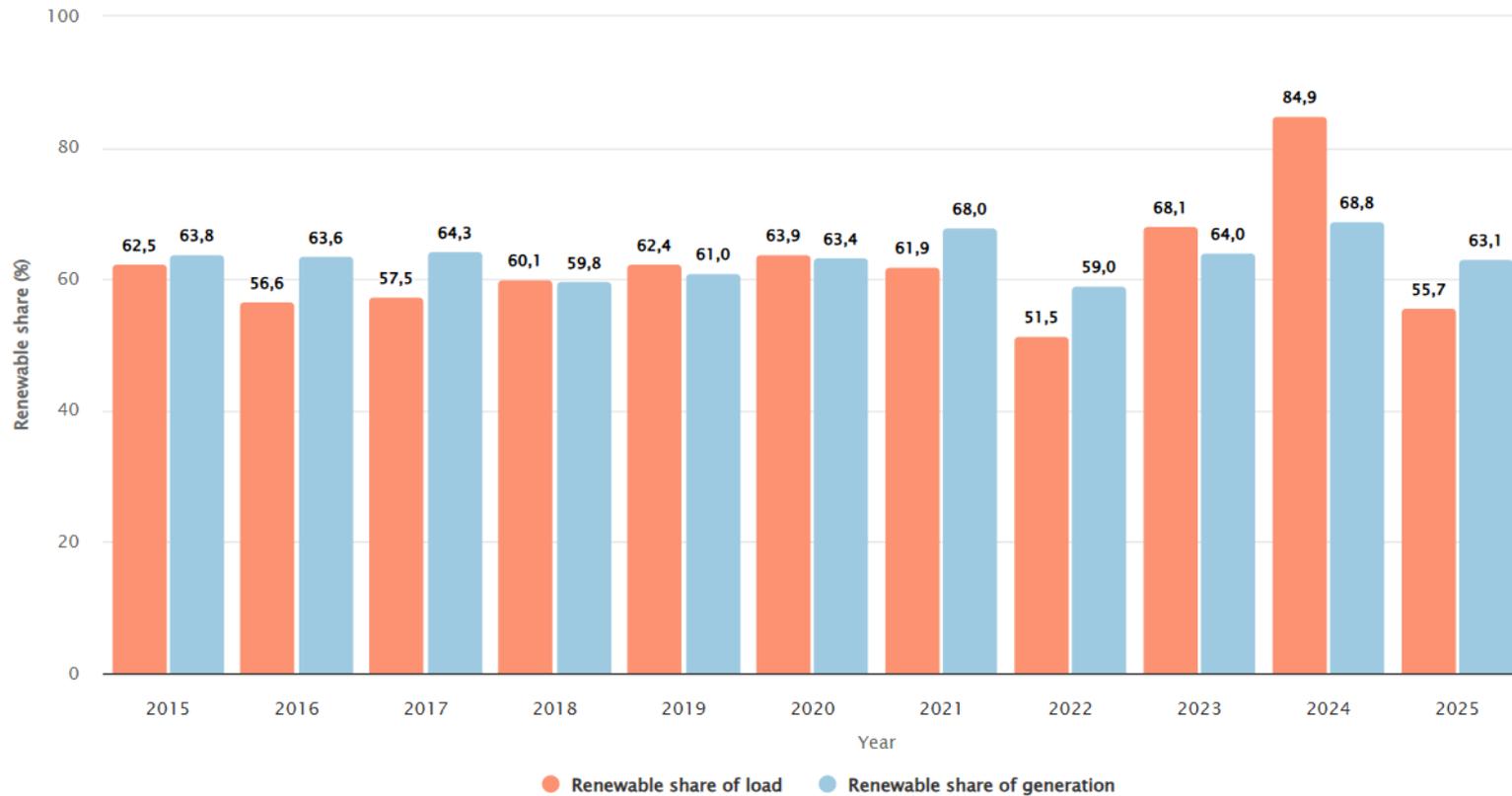
2023: 619,63 EJ (580,28 EJ)

2024: (592,22 EJ)

Energy turn-around Switzerland

Annual renewable share of net electricity generation and load in Switzerland

Energetically corrected values

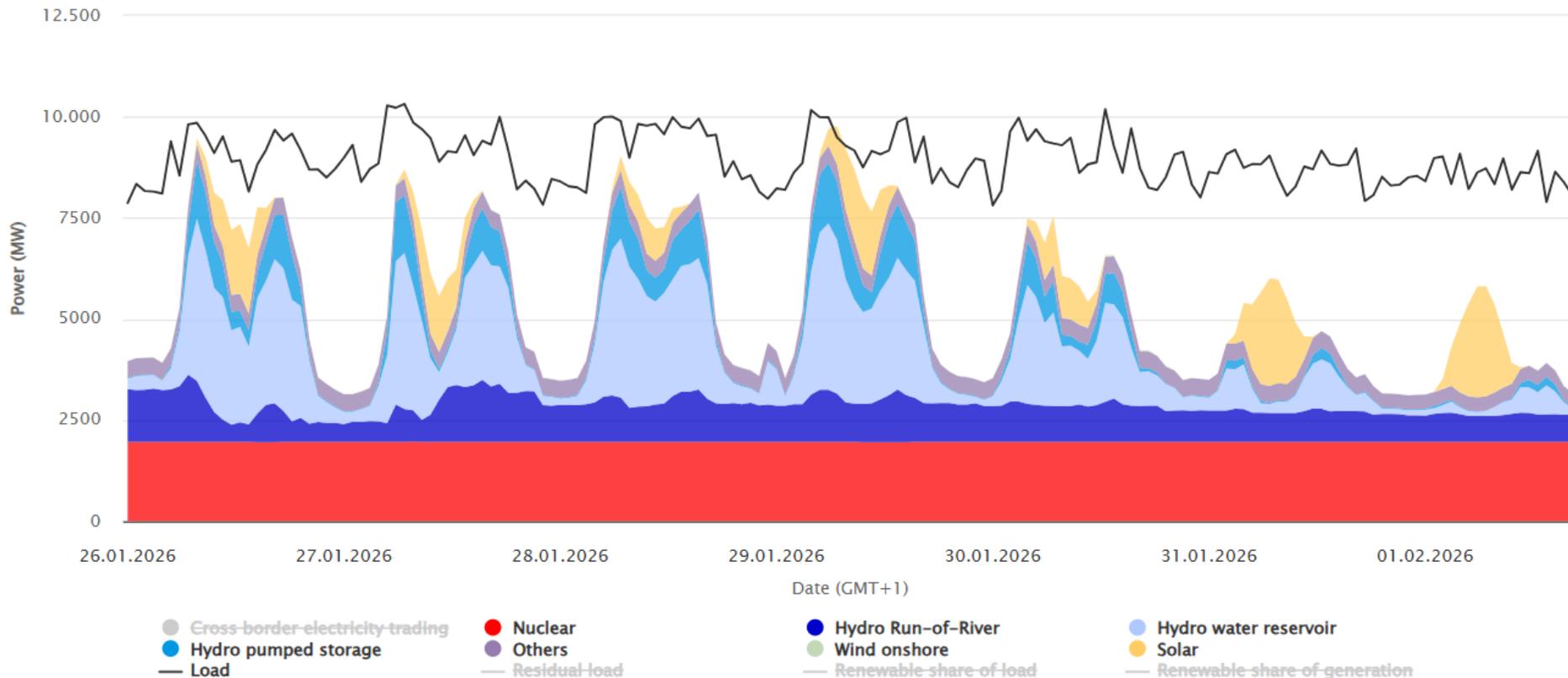


Energy-Charts.info - last update: 11.02.2026, 12:49 MEZ

Electricity generation and demand in week 5 2026

Net electricity generation in Switzerland in week 5 2026

Energetically corrected values

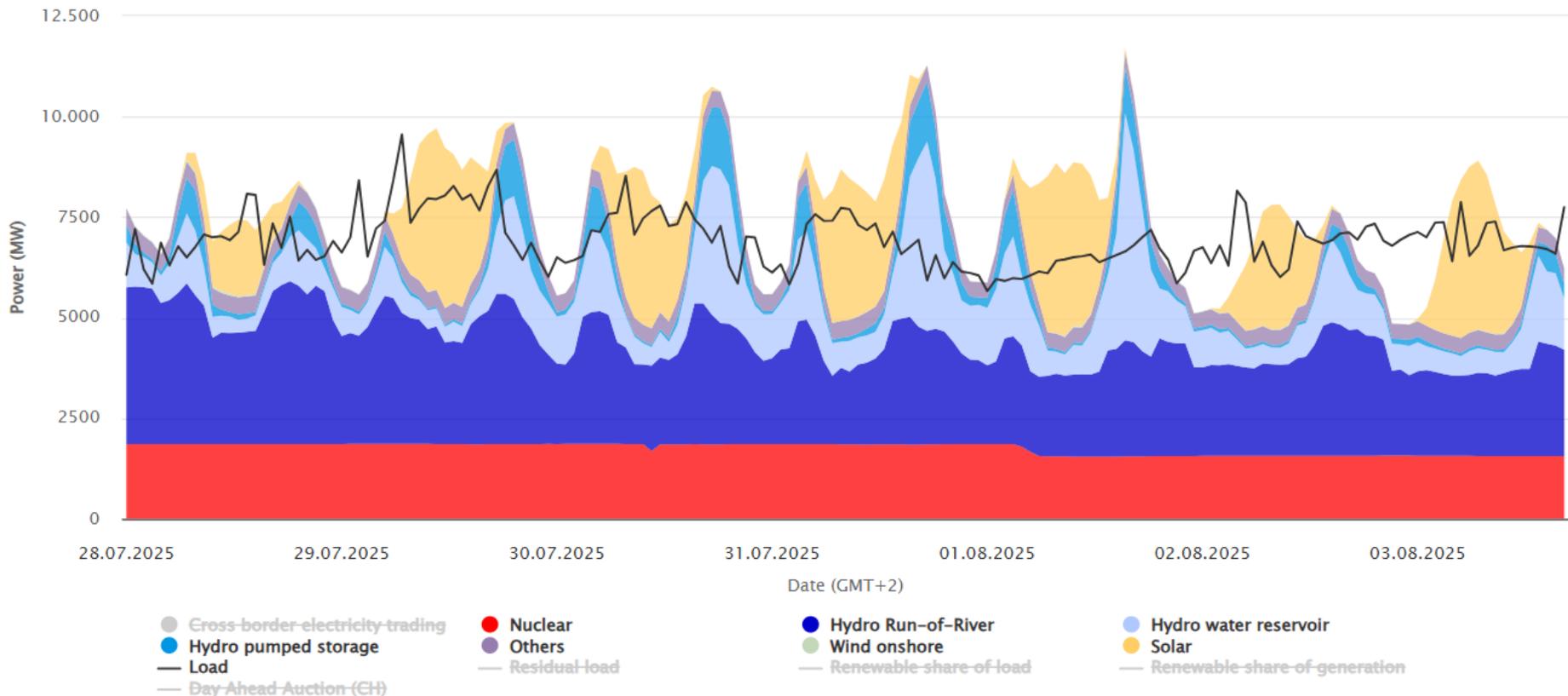


<https://www.energy-charts.info/charts/power/chart.htm?c=CH&year=2026&week=05&l=en&legendItems=1w8w4>

Electricity generation and demand in week 31 2025

Net electricity generation in Switzerland in week 31 2025

Energetically corrected values

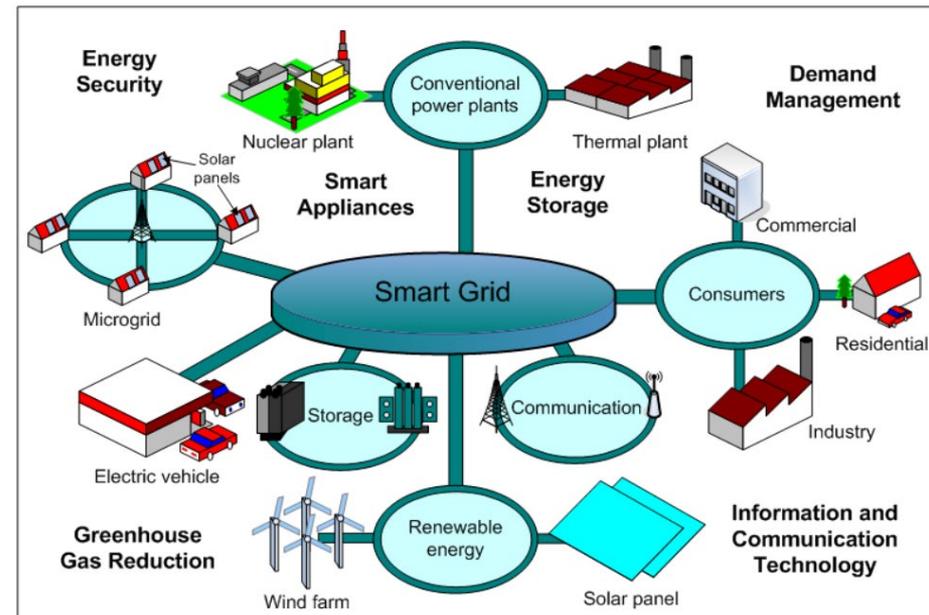
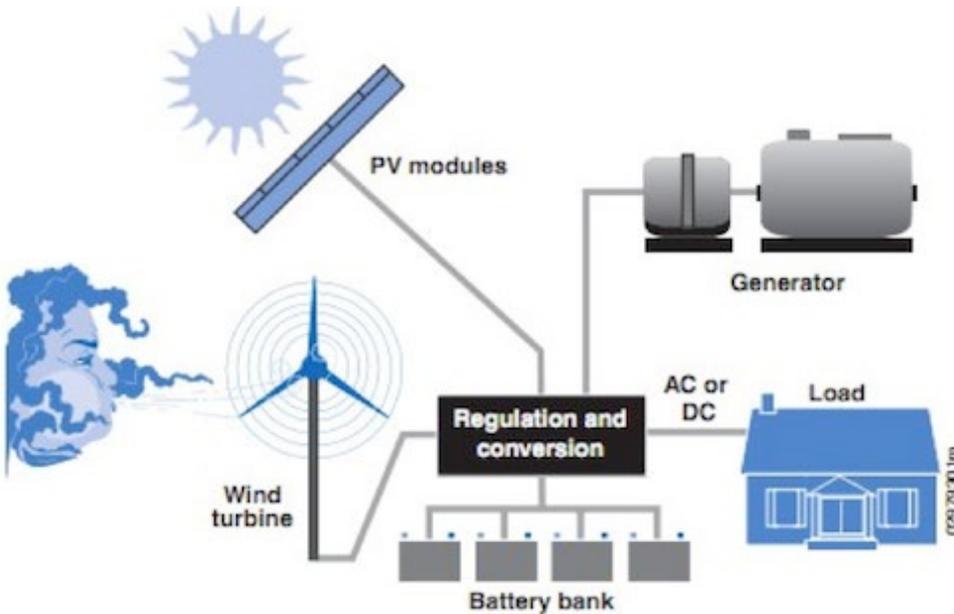


<https://www.energy-charts.info/charts/power/chart.htm?c=CH&year=2026&week=05&l=en&legendItems=1w8w4>

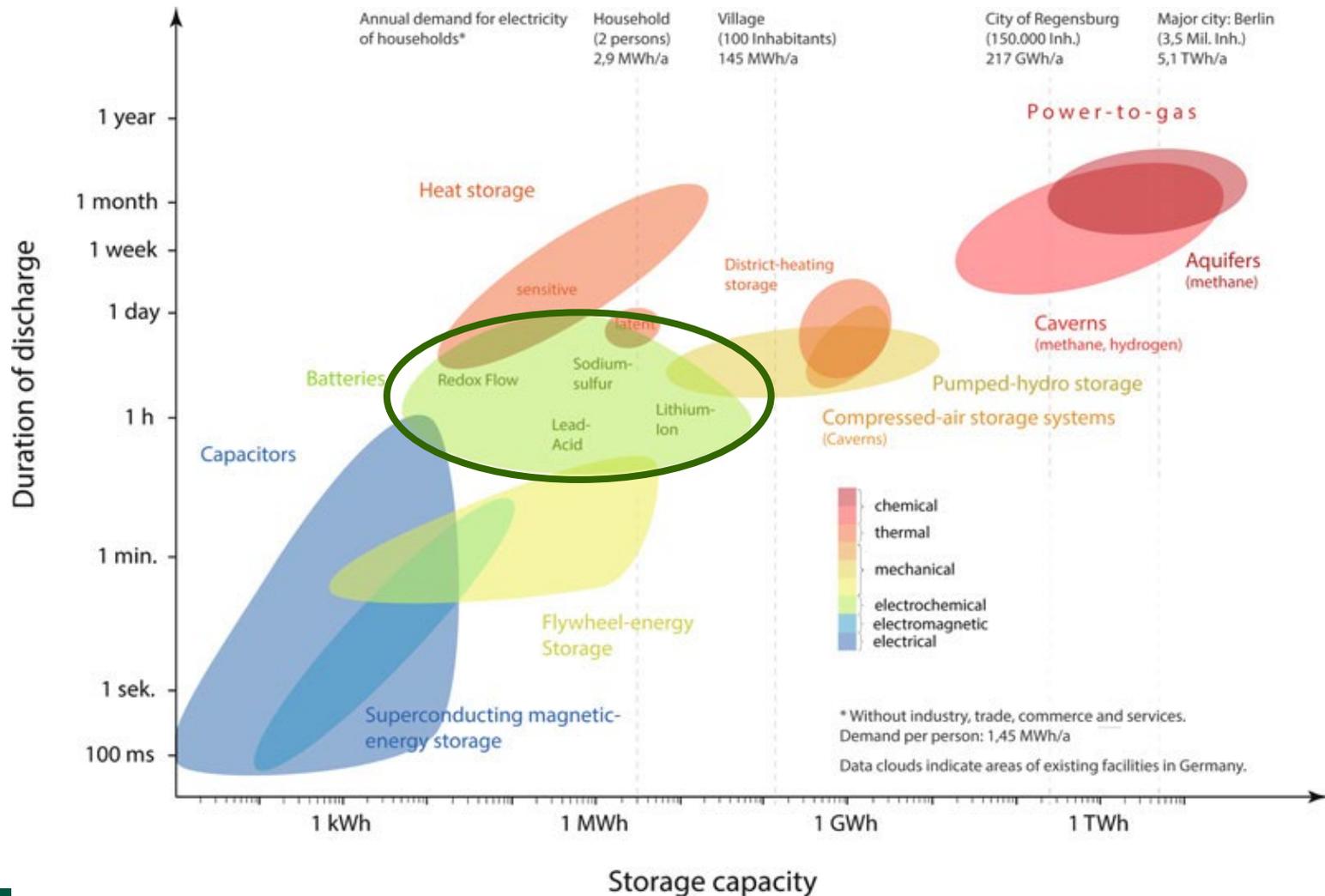
Consequences of increasing renewable energy shares

- Wind, sun and water are neither constant nor demand oriented energy sources
- Alternative energies generate strong fluctuations in the energy production, that are not related to the load
- Necessity for energy storage or distribution

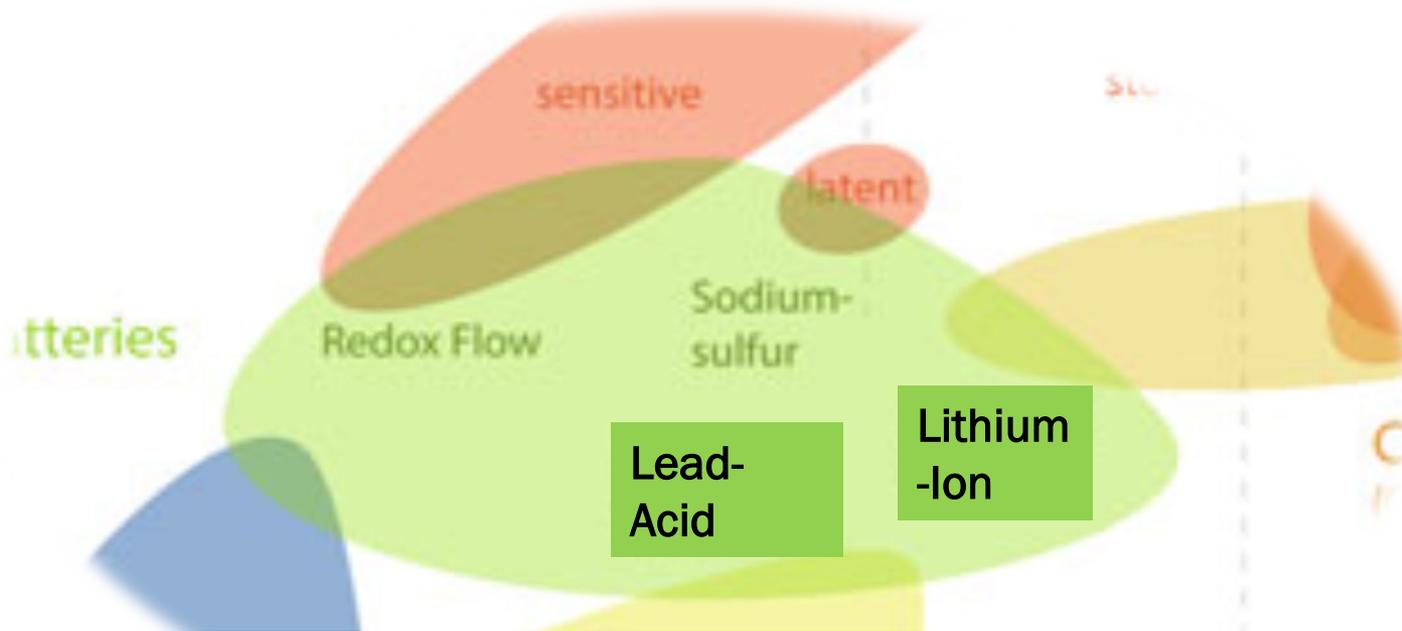
http://ec.europa.eu/research/energy/pdf/smartgrids_en.pdf DOI:[10.1109/ECCE.2011.6063795](https://doi.org/10.1109/ECCE.2011.6063795)



Technical solutions - Energy storage



Technical solutions - Energy storage - Batteries



Technologies	Sub-technologies	Use	Energy installed capacity	Power installed capacity
Electrochemical	Lead acid batteries (Pb-Acid)	FTM/BTM	up to 10MWh	Some MW
	Lithium-ion batteries (Li-ion) –	FTM/BTM	up to 100MWh	Several MW

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Oxidation and Reduction

- Oxidation: Loss of electrons

Example: Rust formation:



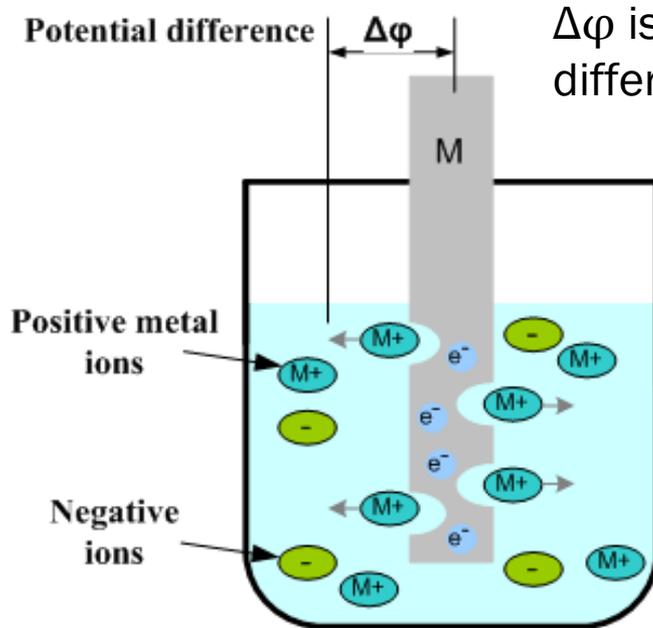
- Reduction: Electron gain

Example: Rust formation:



Electrochemical potential of half cells I

Single electrode cell (half-cell)



$\Delta\phi$ is the Galvani potential (= electrochemical potential difference of a half cell)

- Right after dipping: chemical potential is not in equilibrium.
- M^+ goes into solution or deposits on the electrode
- Charges are built up and a double layer is formed at the electrode/electrolyte interface
- A potential difference $\Delta\phi$ (Galvani potential) is generated at the interface

Electrochemical potential of half cells II

- To calculate $\Delta\varphi$ in equilibrium, the equality of the chemical potentials for the species μ_{M^+} is used. For electrochemical systems the potential needs to be considered as well.

In equilibrium: $\mu_{M^+}(\text{solution}) + zF\varphi_{M^+}(\text{solution}) = \mu_{M^+}(\text{metal}) + zF\varphi_{M^+}(\text{metal})$

μ : chemical potential φ : electrochemical potential F: Faraday constant
 z : charge $\Delta\varphi$: Galvani potential

$$zF\Delta\varphi = zF(\varphi_{M^+}(\text{metal}) - \varphi_{M^+}(\text{solution})) = \mu_{M^+}(\text{solution}) - \mu_{M^+}(\text{metal})$$

With $\mu_{M^+} = \mu_{0M^+} + RT \ln a_{M^+}$ and a_{M^+} : Activity (M^+) $\approx [M^+]$ for small concentrations $[M^+]$

$$\Delta\varphi = \frac{\mu_{M^+}(\text{solution}) - \mu_{M^+}(\text{metal})}{zF} = \frac{\mu_{M^+}^0(\text{solution}) - \mu_{M^+}^0(\text{metal})}{zF} + \frac{RT}{zF} \ln \frac{[M^+(\text{solution})]}{[M^+(\text{metal})]}$$

With $\Delta\varphi_0 = \frac{\mu_{M^+}^0(\text{solution}) - \mu_{M^+}^0(\text{metal})}{zF}$ and $[M^+(\text{metal})] = 1$

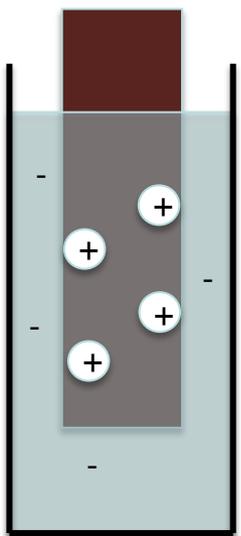
Nernst equation: $\Delta\varphi = \Delta\varphi_0 + \frac{RT}{zF} \ln([M^+(\text{solution})])$

Electrochemical potential of half cells III

$$\mu_{M^+}(\text{solution}) < \mu_{M^+}(\text{metal})$$

- Metal ions are dissolved from the electrode
- Metal is charged negatively
- Solution is charged positively

For example CuSO_4/Cu

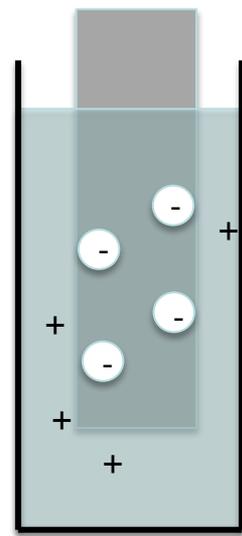


$$\Delta\varphi(\text{I}) = \Delta\varphi_0(\text{I}) + \frac{RT}{zF} \ln([M^+(\text{I})])$$

$$\mu_{M^+}(\text{solution}) > \mu_{M^+}(\text{metal})$$

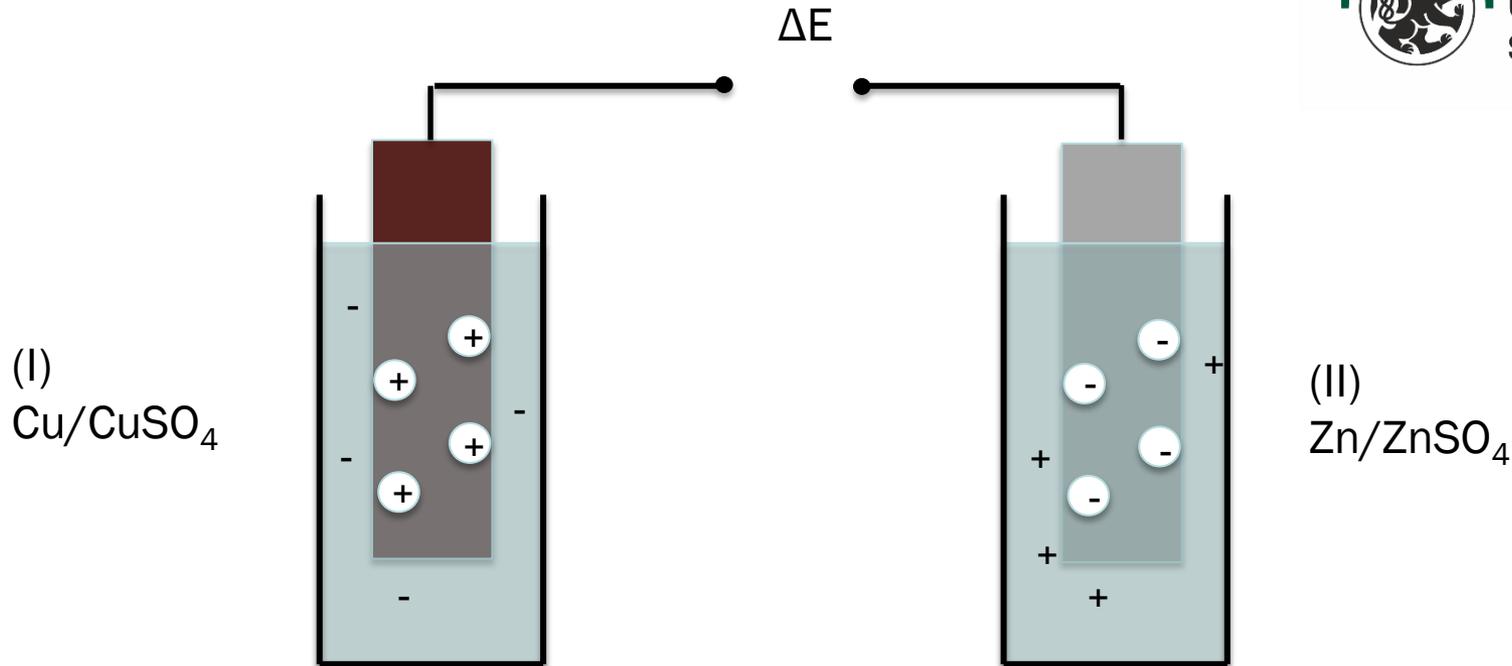
- Metal ions are deposited on the electrode
- Metal is charged positively
- Solution is charged negatively

For example ZnSO_4/Zn



$$\Delta\varphi(\text{II}) = \Delta\varphi_0(\text{II}) + \frac{RT}{zF} \ln([M^+(\text{II})])$$

Galvanic cell



Nernst equation for two metal electrodes (valid only in equilibrium = no current):

$$\Delta E = \Delta\varphi(\text{I}) - \Delta\varphi(\text{II}) = \Delta\varphi_0(\text{I}) - \Delta\varphi_0(\text{II}) + \frac{RT}{zF} \ln \left(\frac{[\text{M}^+(\text{I})]}{[\text{M}^+(\text{II})]} \right)$$

Concentration dependence: There is a potential difference between two metal electrodes of the same kind immersed into different concentrations M⁺

$$\Delta E = \frac{RT}{zF} \ln \left(\frac{c_1(\text{M}^+)}{c_2(\text{M}^+)} \right)$$

Standard electrode potentials

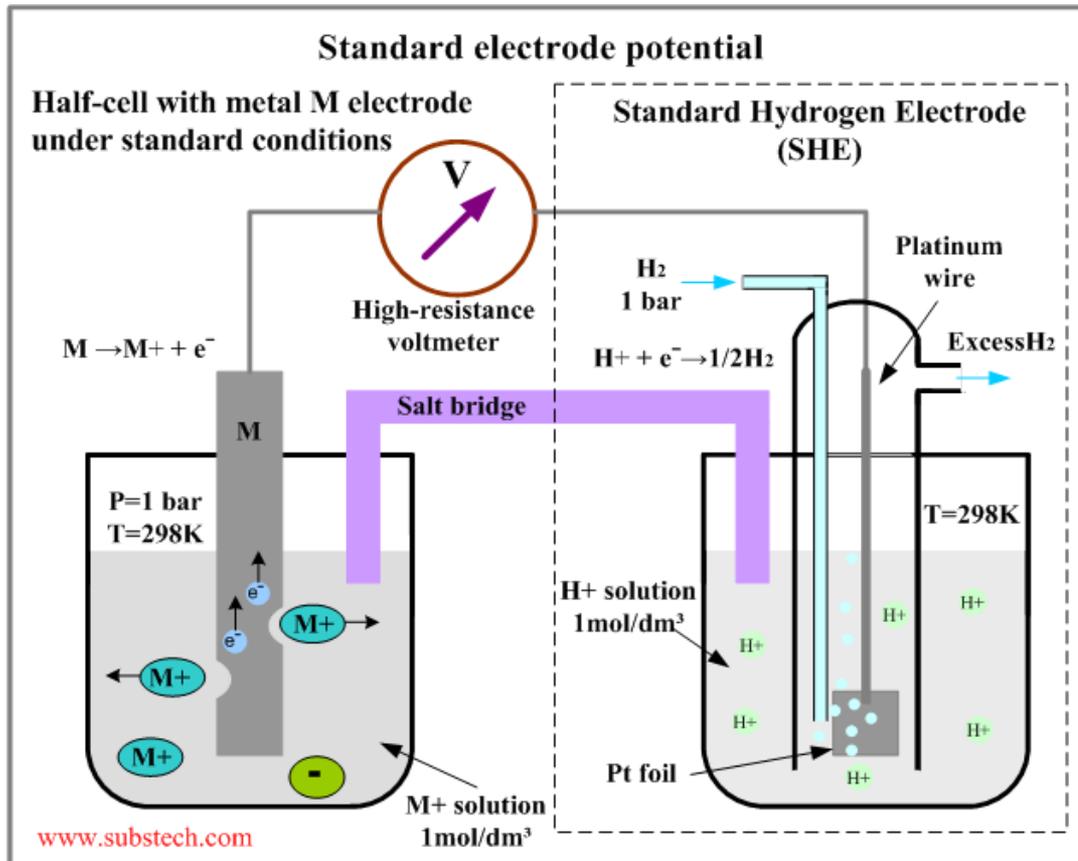
	Reduction Half Reaction	Standard Potential (V) $\Delta\phi_0$
	F₂ + 2e ⁻ ⇌ 2F ⁻	+2.87
	Pb⁴⁺ + 2e ⁻ ⇌ Pb ²⁺	+1.67
	Cl₂ + 2e ⁻ ⇌ 2Cl ⁻	+1.36
	O ₂ + 4H ⁺ + 4e ⁻ ⇌ 2H ₂ O	+1.23
	Ag ⁺ + 1e ⁻ ⇌ Ag	+0.80
	Fe ³⁺ + 1e ⁻ ⇌ Fe ²⁺	+0.77
	Cu ²⁺ + 2e ⁻ ⇌ Cu	+0.34
	2H ⁺ + 2e ⁻ ⇌ H ₂	0.00
	Pb ²⁺ + 2e ⁻ ⇌ Pb	-0.13
	Fe ²⁺ + 2e ⁻ ⇌ Fe	-0.44
	Zn ²⁺ + 2e ⁻ ⇌ Zn	-0.76
	Al ³⁺ + 3e ⁻ ⇌ Al	-1.66
	Mg ²⁺ + 2e ⁻ ⇌ Mg	-2.36
	Li ⁺ + 1e ⁻ ⇌ Li	-3.05




Noble metals:
Positive potentials

Potential scale: 0 level is at
standard hydrogen electrode (SHE)
Energy scale: 0 level is vacuum level

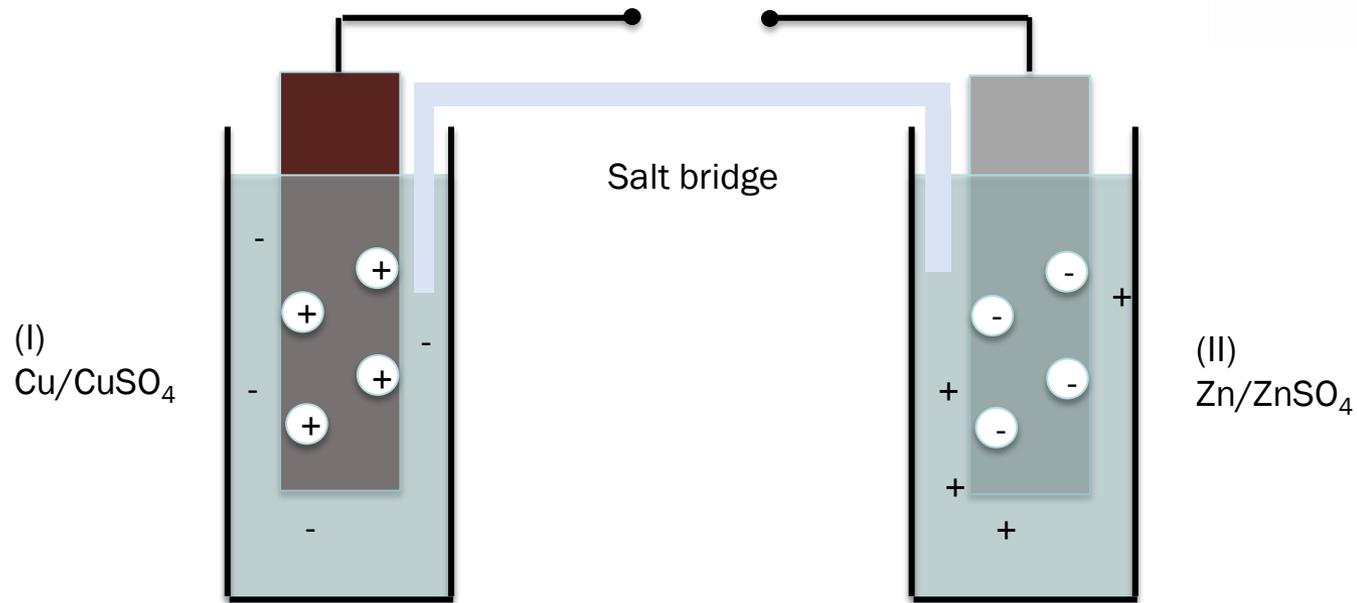
Standard electrode potential (measurement)



Standard electrode potential φ_0 is the individual potential of a reversible electrode at standard state versus the standard hydrogen electrode (SHE):

H₂ electrode:
concentration of 1 mol/L [H⁺]
gases at a pressure of 1 atm at
25 °C.

Galvanic cell



	Anode	Electrolyte	Cathode
el. Conductivity	✓	✗	✓
ion conductivity	can	✓	can

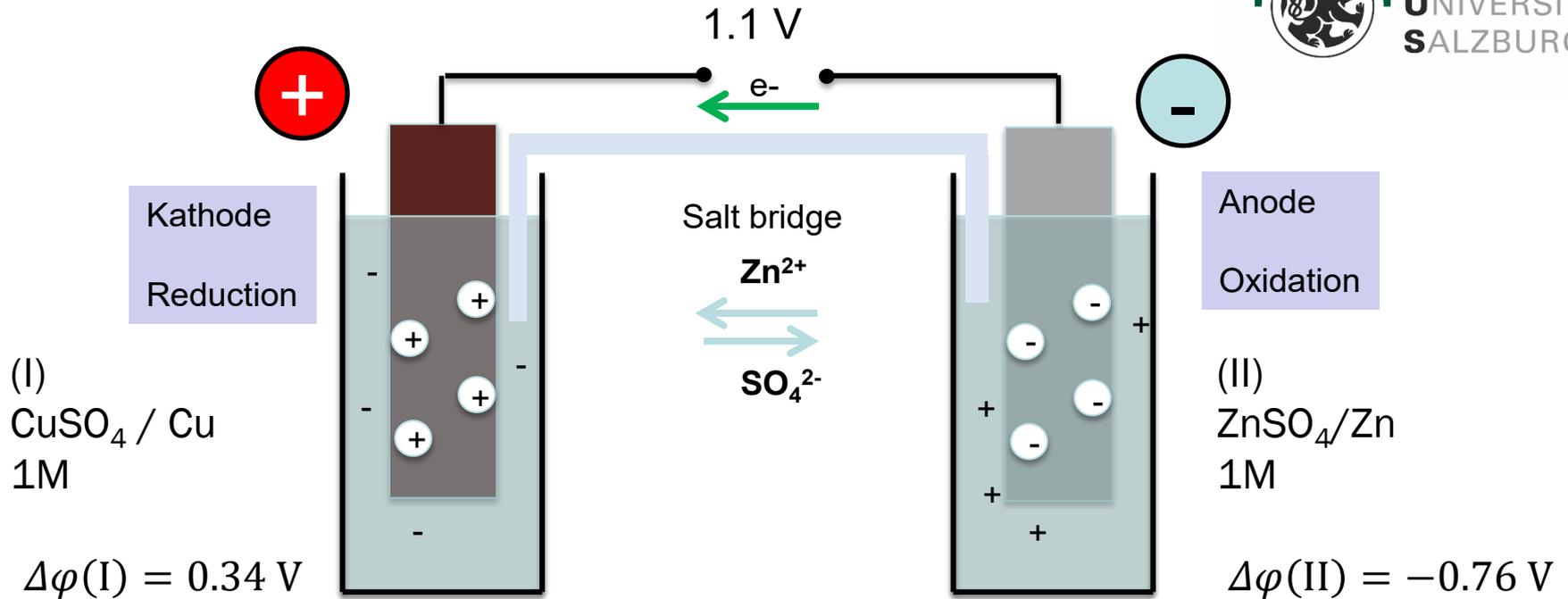
Standard electrode potentials

	Reduction Half Reaction	Standard Potential (V) $\Delta\varphi_0$
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	Pb⁴⁺ + 2e ⁻ ⇌ Pb ²⁺	+1.67
	Cl₂ + 2e ⁻ ⇌ 2Cl ⁻	+1.36
	O ₂ + 4H ⁺ + 4e ⁻ ⇌ 2H ₂ O	+1.23
	Ag ⁺ + 1e ⁻ ⇌ Ag	+0.80
	Fe ³⁺ + 1e ⁻ ⇌ Fe ²⁺	+0.77
	Cu ²⁺ + 2e ⁻ ⇌ Cu	+0.34
	2H ⁺ + 2e ⁻ ⇌ H ₂	0.00
	Pb ²⁺ + 2e ⁻ ⇌ Pb	-0.13
	Fe ²⁺ + 2e ⁻ ⇌ Fe	-0.44
	Zn ²⁺ + 2e ⁻ ⇌ Zn	-0.76
	Al ³⁺ + 3e ⁻ ⇌ Al	-1.66
	Mg ²⁺ + 2e ⁻ ⇌ Mg	-2.36
	Li ⁺ + 1e ⁻ ⇌ Li	-3.05

Noble metals:
Positive potentials

Potential scale: 0 level is at standard hydrogen electrode (SHE)
Energy scale: 0 level is vacuum level

Galvanic cell



Nernst equation for two metal electrodes (valid only in equilibrium = no current):

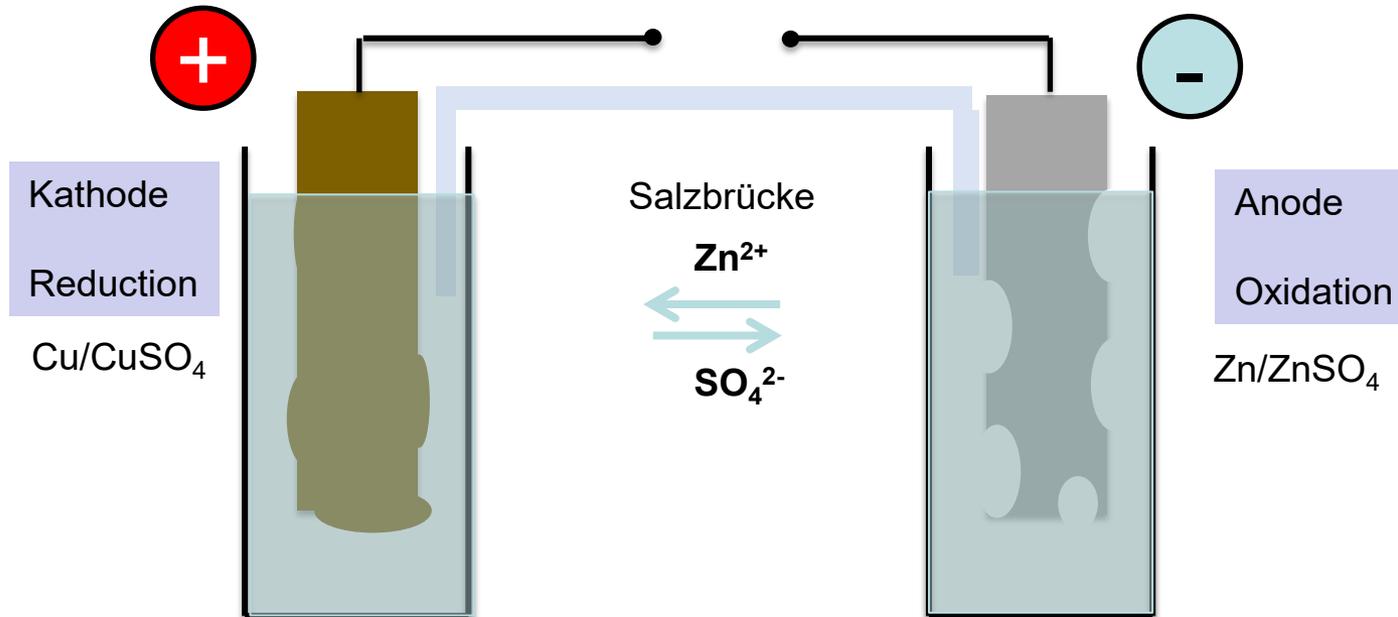
$$\Delta E = \Delta\varphi(I) - \Delta\varphi(II) = \Delta\varphi_0(I) - \Delta\varphi_0(II) + \frac{RT}{zF} \ln \left(\frac{[M^+(I)]}{[M^+(II)]} \right)$$

$$\Delta E = 0.34 V + 0.76 V = 1.1 V$$

Conversion of chemical energy into electrical energy by redox potential differences,

Primary battery:

- Not reversible Galvanic cell: primary battery



Zn corrodes, Cu electrode is built up, not reversible

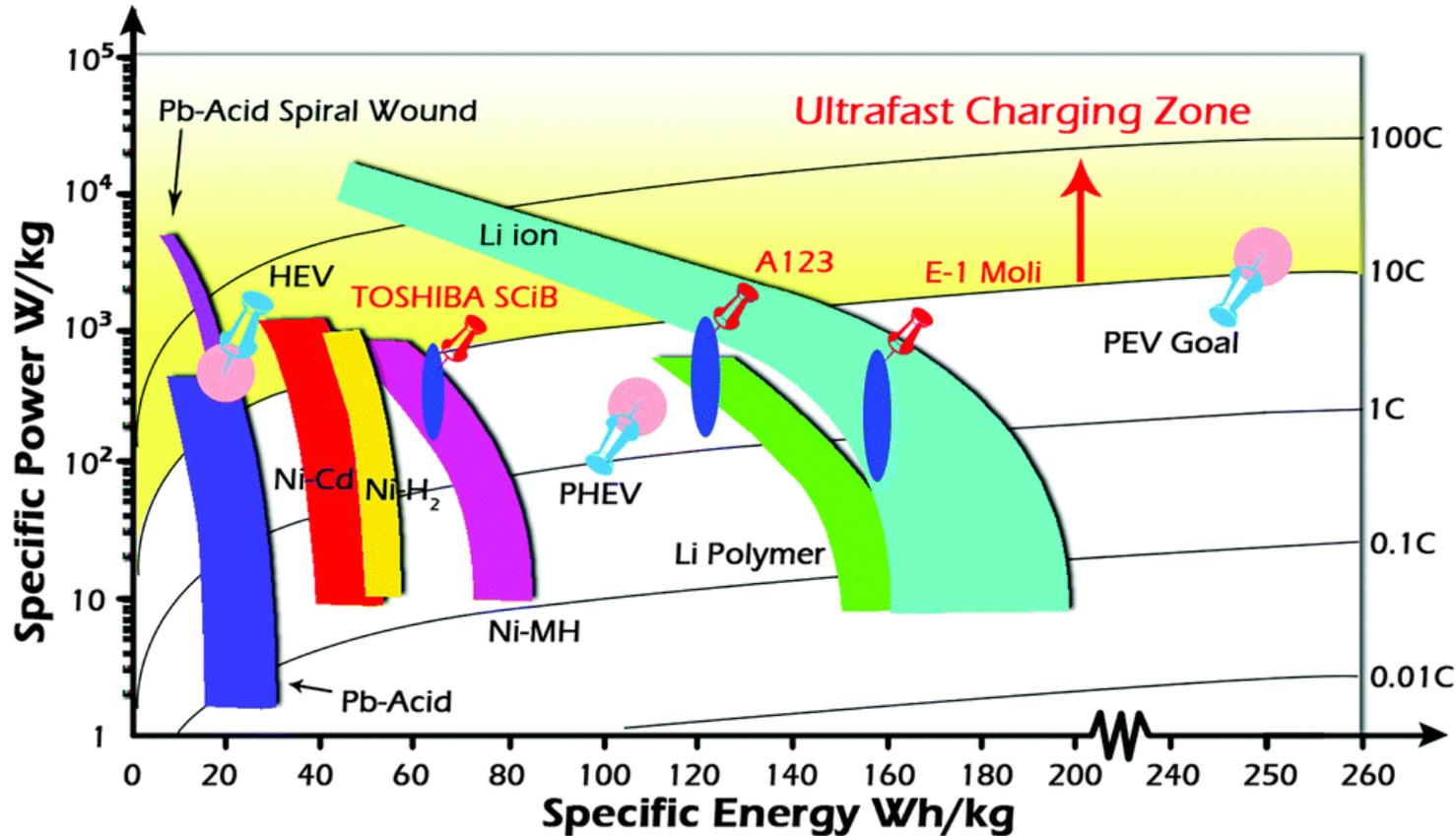
Electrolyte stability window is not at the «right» place: $\text{H}_2\text{O}/\text{H}_2$ is at 0V

Overpotential of Zn: 0.77V, therefore stable in water

Chem Mater Rev **22** (2010) 587, *Chem. Rev.* 104(2004) 4245

Secondary Batteries

To solve energy storage problems, we need rechargeable batteries: Reversible redox reactions, i.e. secondary batteries



<https://doi.org/10.1016/j.rser.2022.112213>

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Market leader in rechargeable batteries: lead acid battery

- invented in 1859 by Planté
- Up to now research is conducted in this field (i.e. improvement of the specific energy density¹)
- Three main applications: (deep cycle, auto SLI, industry)



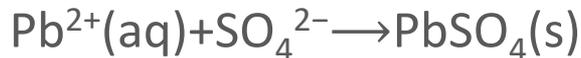
¹Journal of Power Sources 219 (2012) 75-79

Lead acid battery: The concept

Discharge

Negative electrode (Anode):

$$E_0(\text{Pb}) = -0.36\text{V}$$

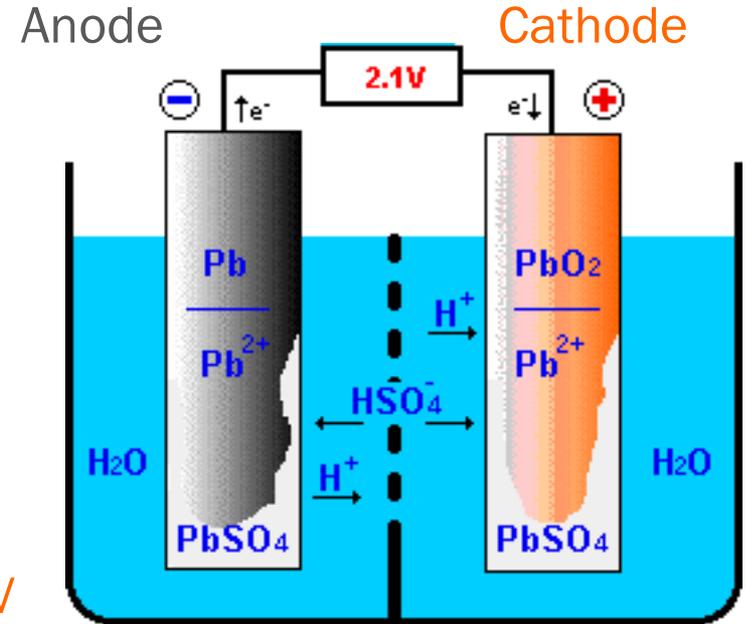


Positive electrode (cathode):

$$E_0(\text{PbO}_2) = +1.68\text{V}$$



Electrolyte: H_2SO_4



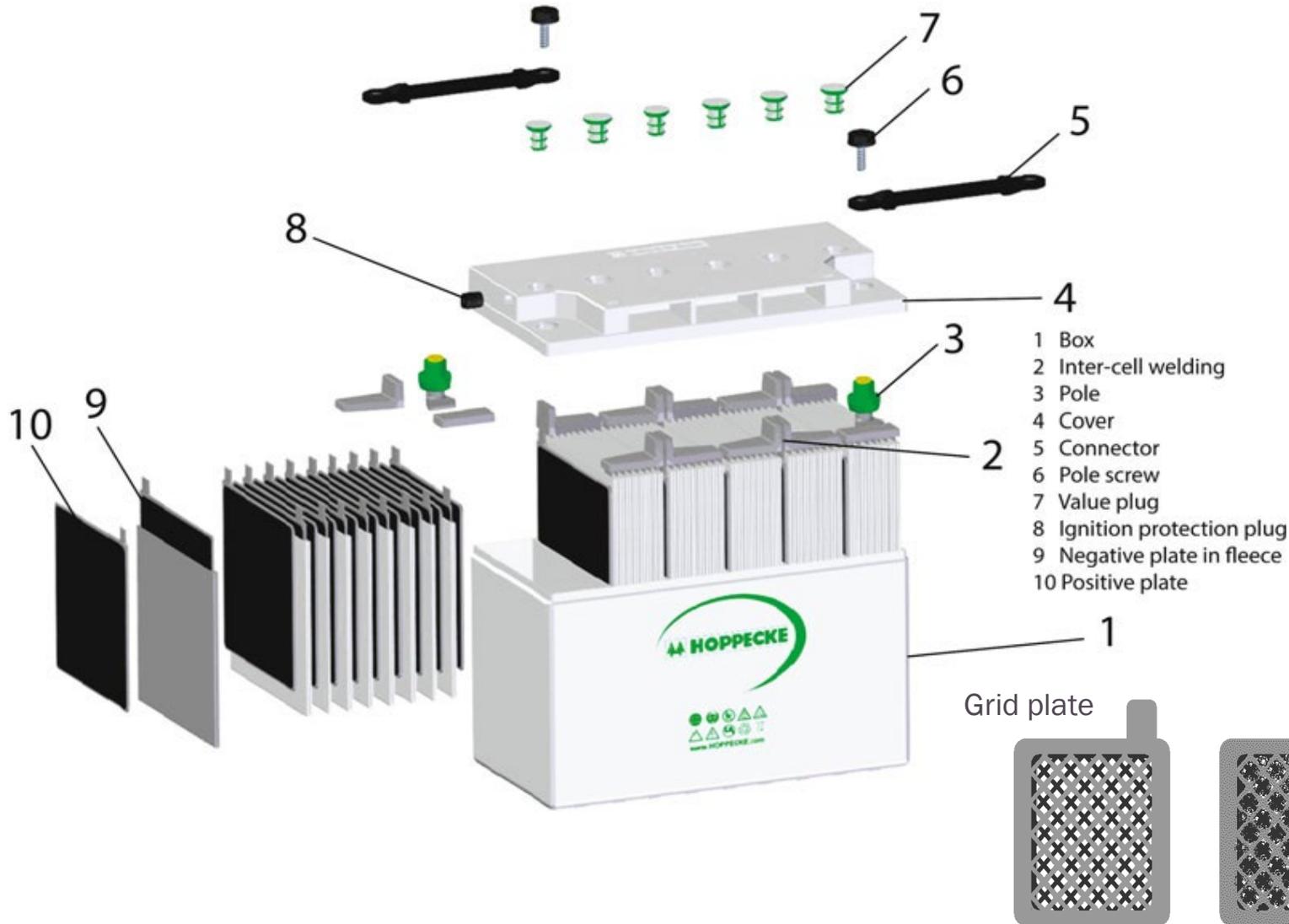
<http://www.erikdeman.de/html/sail080e.htm>

$$E_{0\text{ges}} = 1.68\text{V} - (-0.36\text{V}) = 2.04\text{V}$$

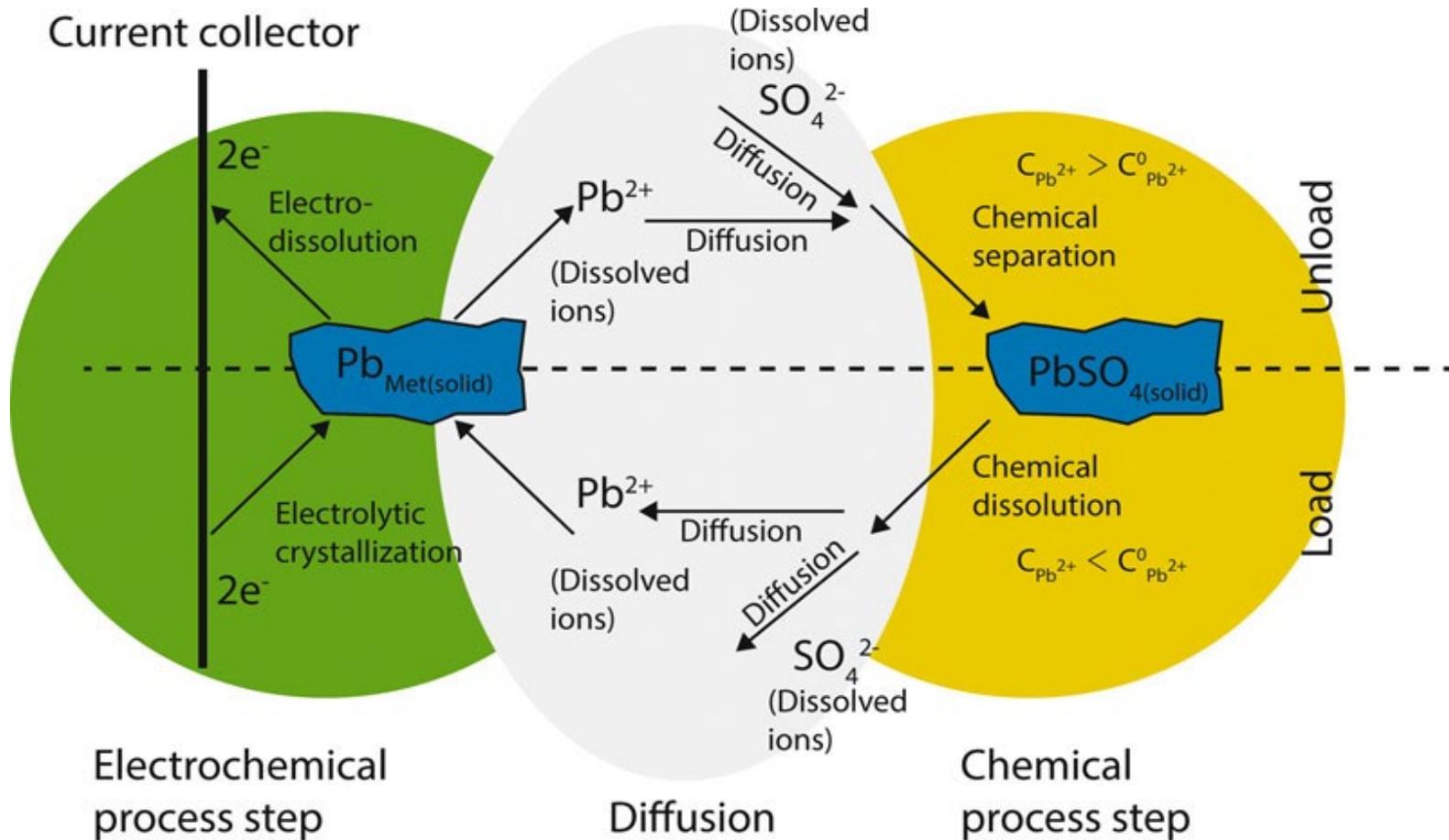
Potential difference: 2.04V

Open circuit voltage: 2.1 - 2.13V

Design of a Lead Acid Battery

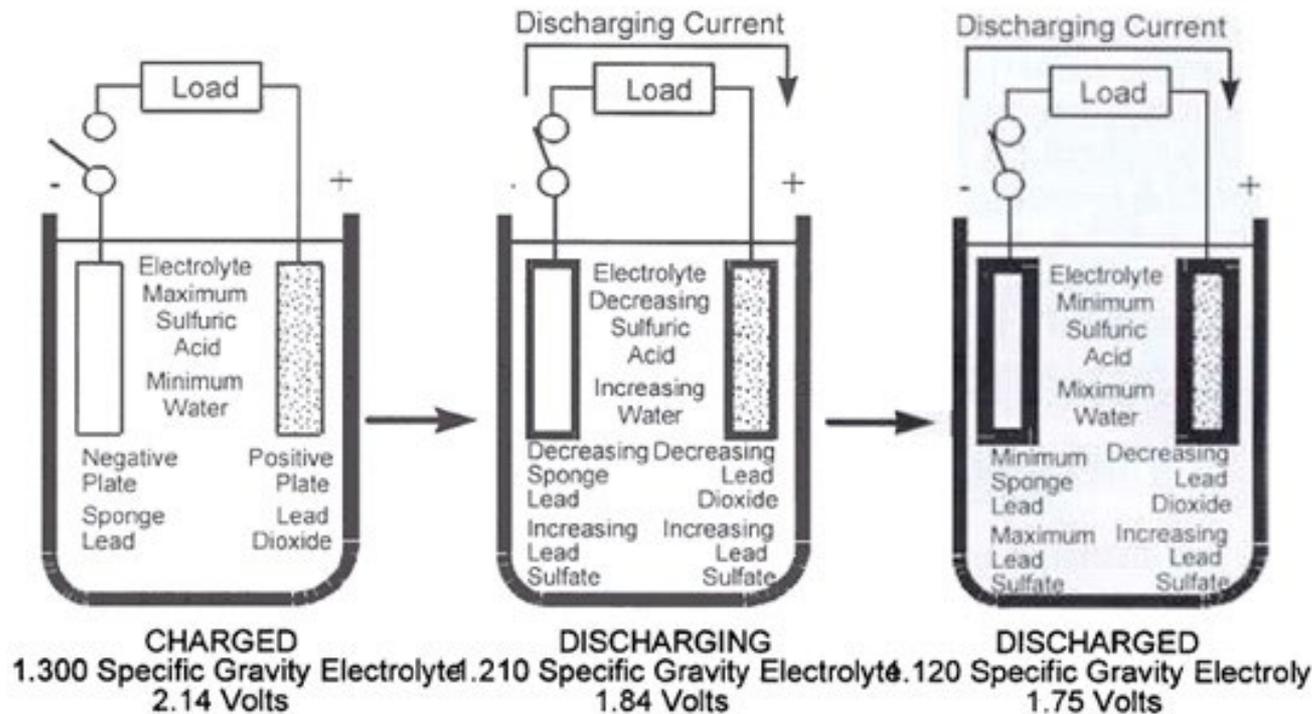


Lead Acid Battery - Mechanism



Electrolyte and charge and discharge state of the lead acid battery

- Electrolyte: aqueous H_2SO_4
- Specific density of the electrolyte is connected to the charge state of the battery



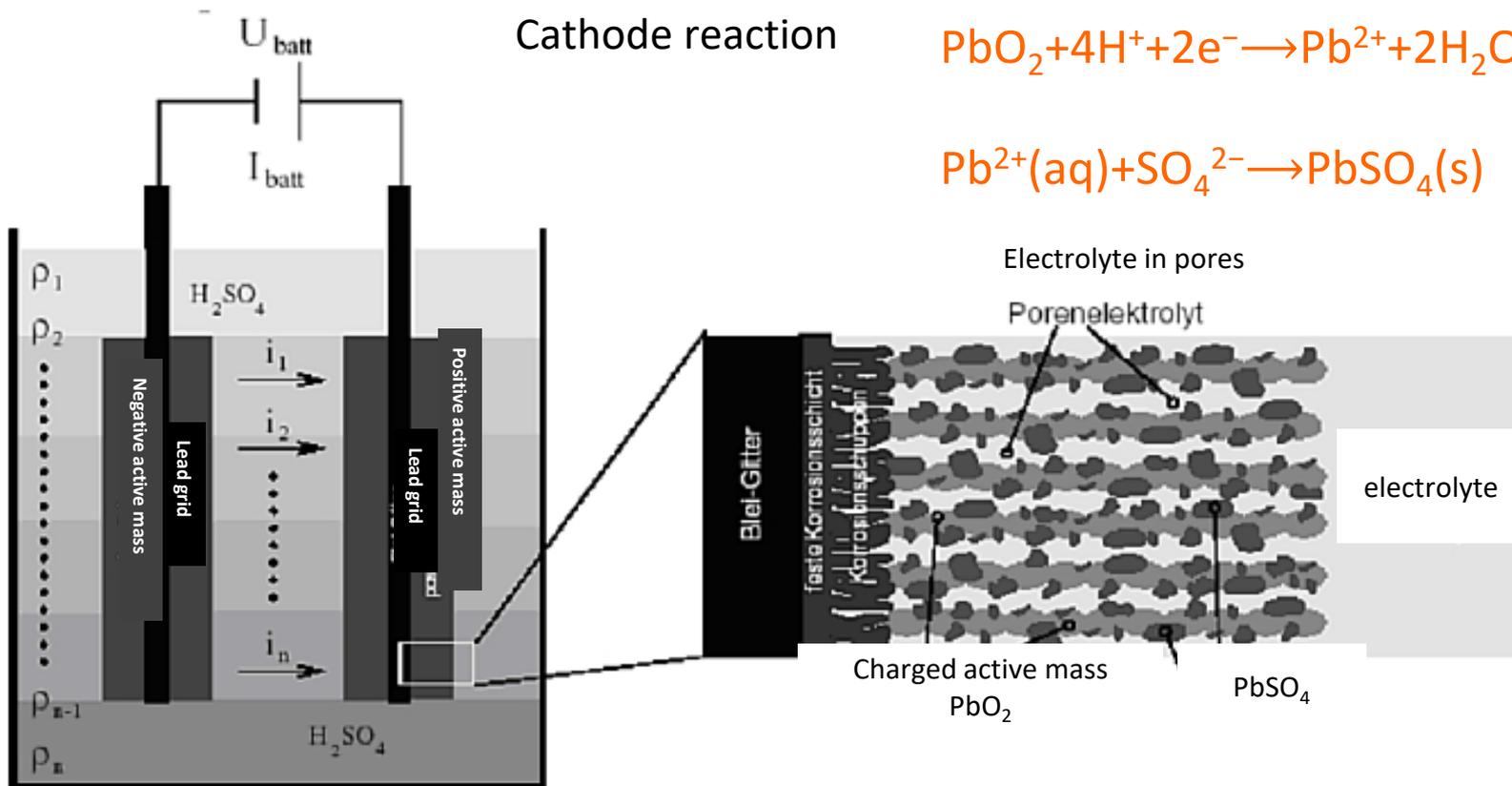
Change of cell voltage during discharge!

Microscopic view of the electrode

Three phase system: Pb or PbO₂, PbSO₄, electrolyte

For reversibility it is important that the PbSO₄ stays close to the electrode

Cathode reaction



Reversible conversion reaction

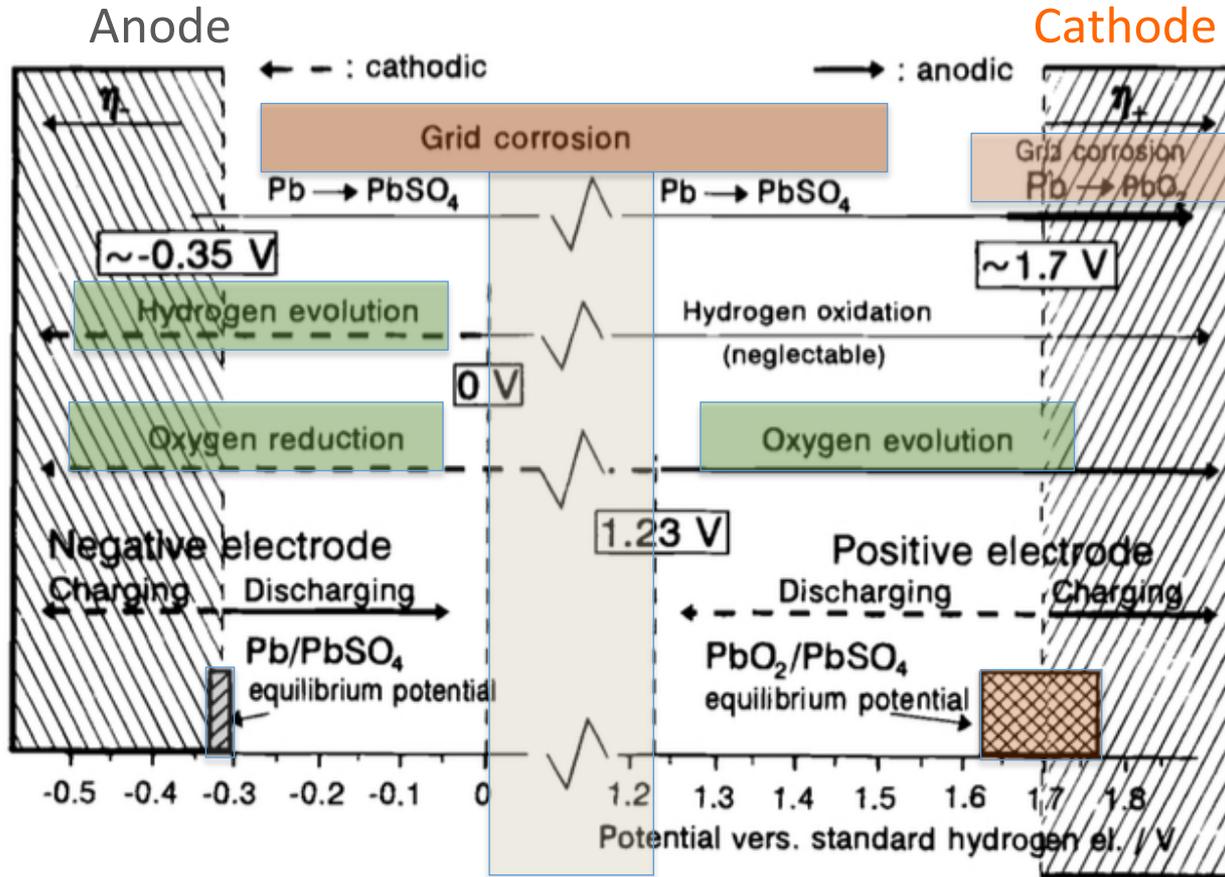
Self-discharge, overpotential, side reactions

$$E_0(\text{Pb}) = -0.36\text{V}$$

$$E_0(\text{PbO}_2) = +1.68\text{V}$$

$$E_0(\text{H}_2) = 0\text{V}$$

$$E_0(\text{O}_2) = 1.23\text{V}$$

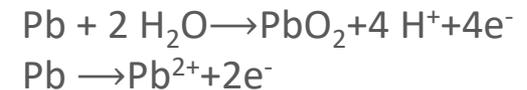


Anodic (electrons generated):

Oxygen evolution:



Grid corrosion:



Cathodic (electrons consumed):

Oxygen reduction/evolution:



Hydrogen evolution:



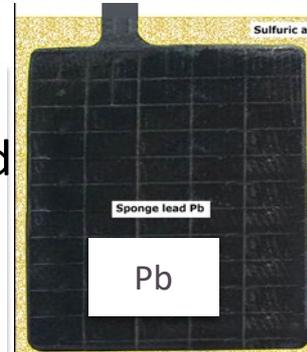
Stability window of the Electrolyte (H_2O)

Side reactions are slow (overpotential)!

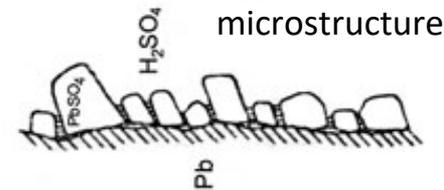
Active Materials and grid plates

Anode (negative pole)

- Pb electrode in charged state
- Additives like BaSO_4 are necessary to obtain small highly distributed PbSO_4 particles (Reversibility)
- Sb (5-12%) und Cd for enhanced hardness
- C for enhanced conductivity
- Sodiumlignosulfates for higher surface areas

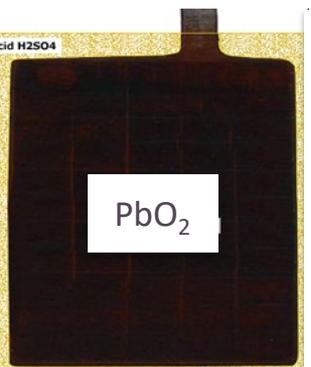


Electrode plate



Cathode (positive pole)

- PbO_2 electrode in charged state
- Will be annealed at 100°C up to 72h for hardening
- Annealing defines porosity (particle sizes 2-4 μm depending on process)



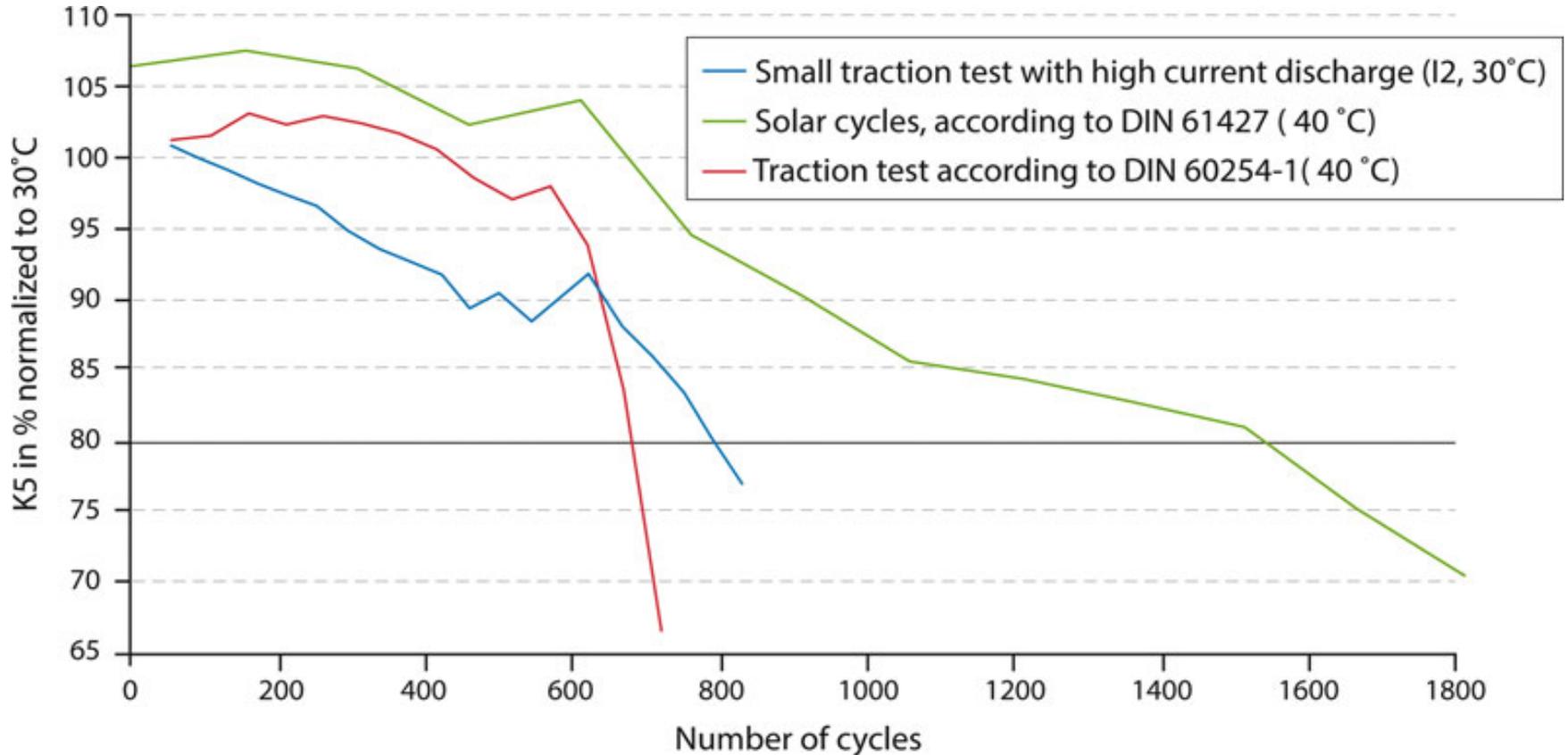
Elektrodenplatte

Lead acid batteries for stationary applications

- Long lifetimes: Need to be kept at constant charge (constant float current)
- Heavy thick plates with high density active pastes (high energy and power density is not so important for stationary applications)
- Active materials are chosen such as to suppress H_2 or O_2 evolution (for example caution by the choice of additives like Sb)
- Space for the growth of the positive electrode plate, since during aging PbO_2 is generated.
- As little service as possible (for example H_2O is added more than necessary)
- valve regulated versus flooded lead acid batteries.

Lead-Acid Battery in Electrochemical Technologies for Energy Storage and Conversion, Volume 1&2
<http://www.batterypoweronline.com/main/wp-content/uploads/2012/07/Lead-acid-white-paper.pdf>

Lead acid batteries – Aging mechanisms



Application examples

- **Eigg, Scotland:** Off grid Insel
<http://www.bbc.com/future/story/20170329-the-extraordinary-electricity-of-the-scottish-island-of-eigg>

Stationary energy storage of wind and solar energy



Not very successful commercially 1986:
Southern California Edison
Chino facility
(10 MW/40 MWh) high
maintenance costs



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Applications for Li-ion batteries

- Portable electronics



- Electrical / hybrid vehicles

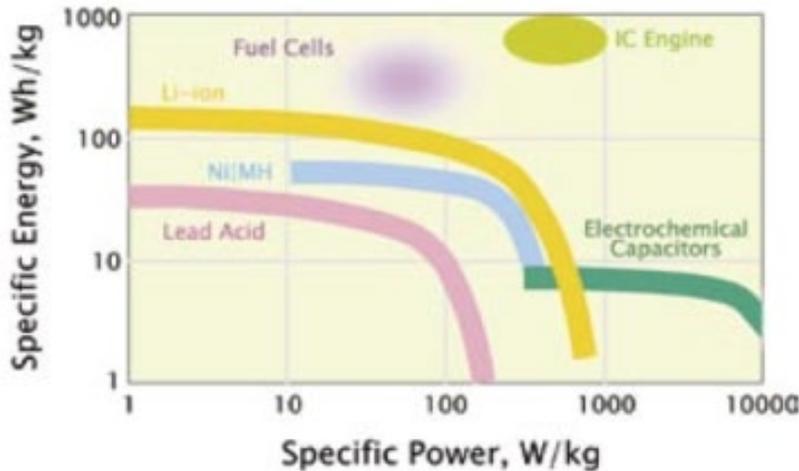


- Energy storage in remote areas / renewables / backup power



Li-ion Battery applications - summary

- Li-ion batteries are mainly used for mobile applications
- Li-ion batteries are in the test phase for stationary applications
- Lead acid batteries are considered to exhibit only a limited development potential, while Li-ion batteries are considered as a solution for the future

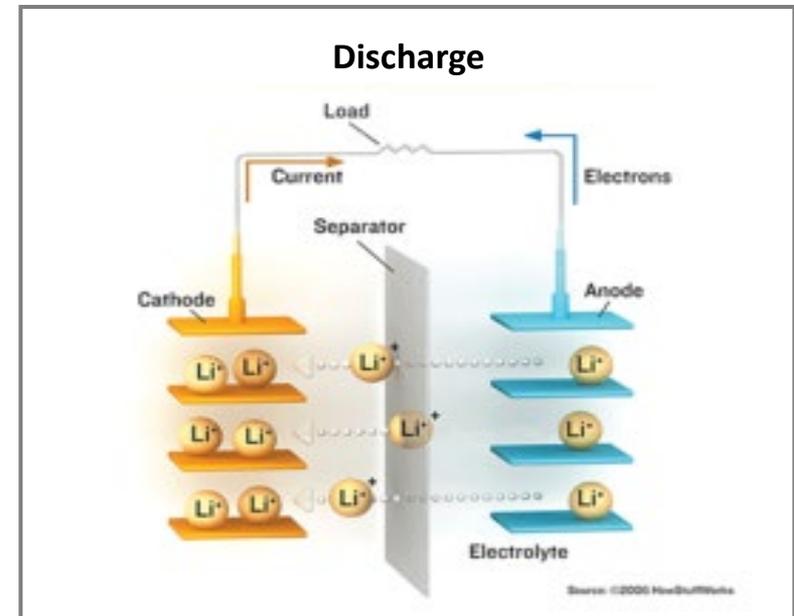
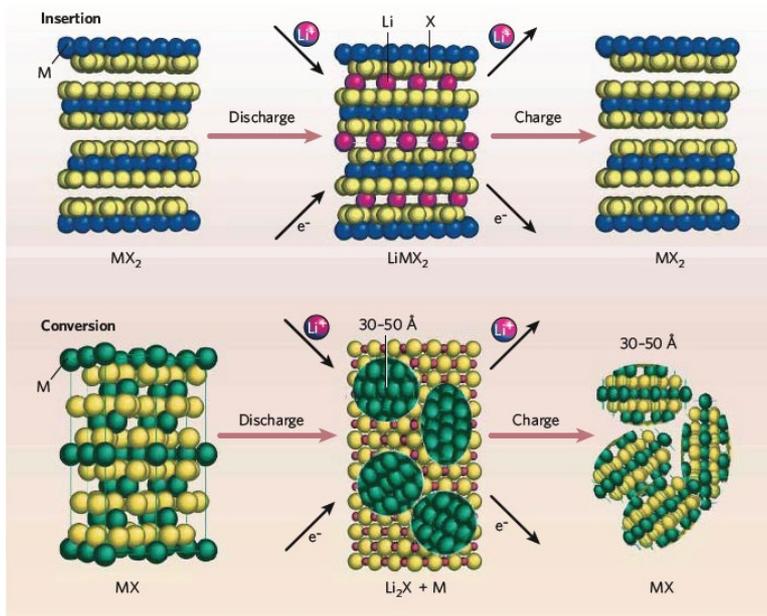


Ragone plot: Specific energy versus specific power

<http://berc.lbl.gov/venkat/Ragone-construction.pps>

Li – ion battery: concept

- In contrast to lead acid batteries (conversion batteries), Li-ion batteries are called intercalation or insertion batteries.
- Large energy density, since large potential difference (>3V)
- Electrolyte consists of (expensive) organic polymers (stability window of the electrolyte)

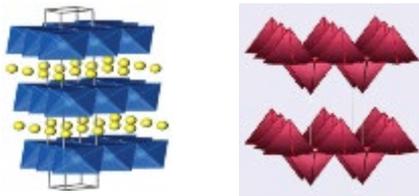
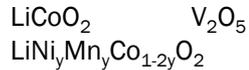


Nature, 451 (2008) 652

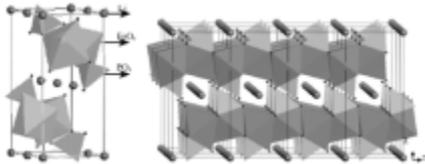
Cathode materials

• Cathode

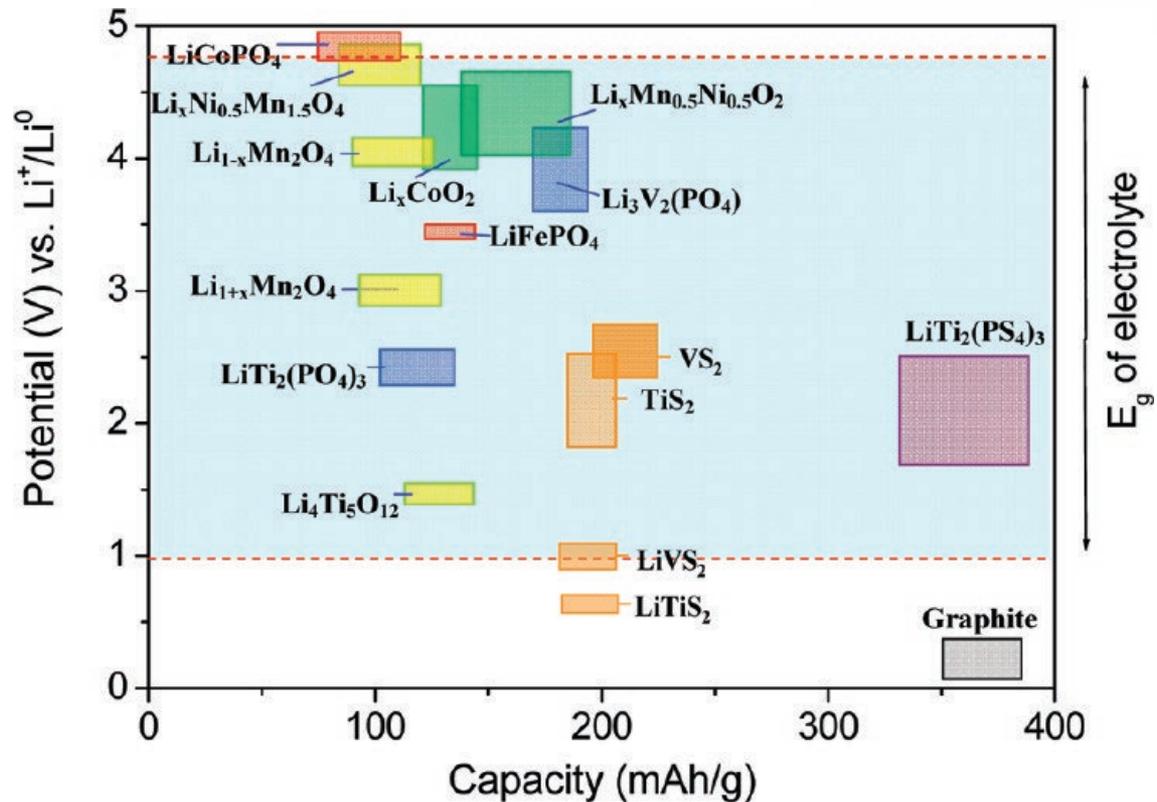
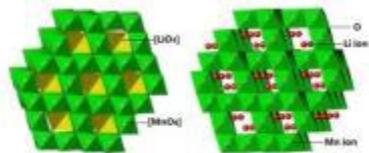
Layered oxides



Olivine



Spinel

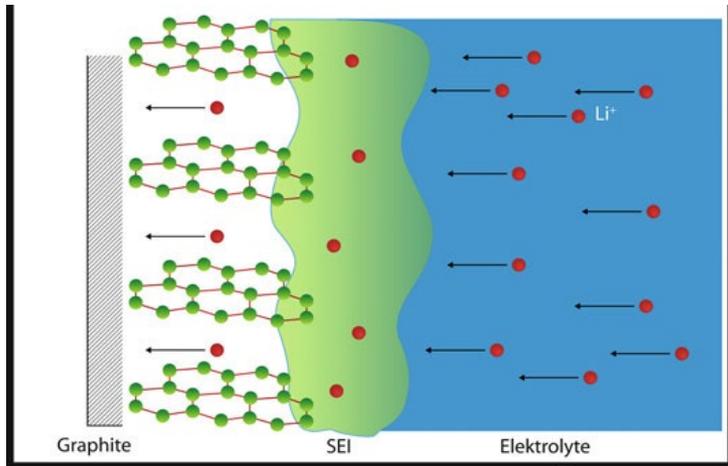


- Many different material systems are possible
- Various potential differences are possible
- Most famous: Li_xCoO₂ with around 4.2 V

J. Goodenough, Chem. Mater. 22 (2010) 587-601

- Anode

Graphite:



Alternatives:

Si, Si/C, and Li_xTiO_y

- Discharge (example Li_xCoO_2)

Cathode:

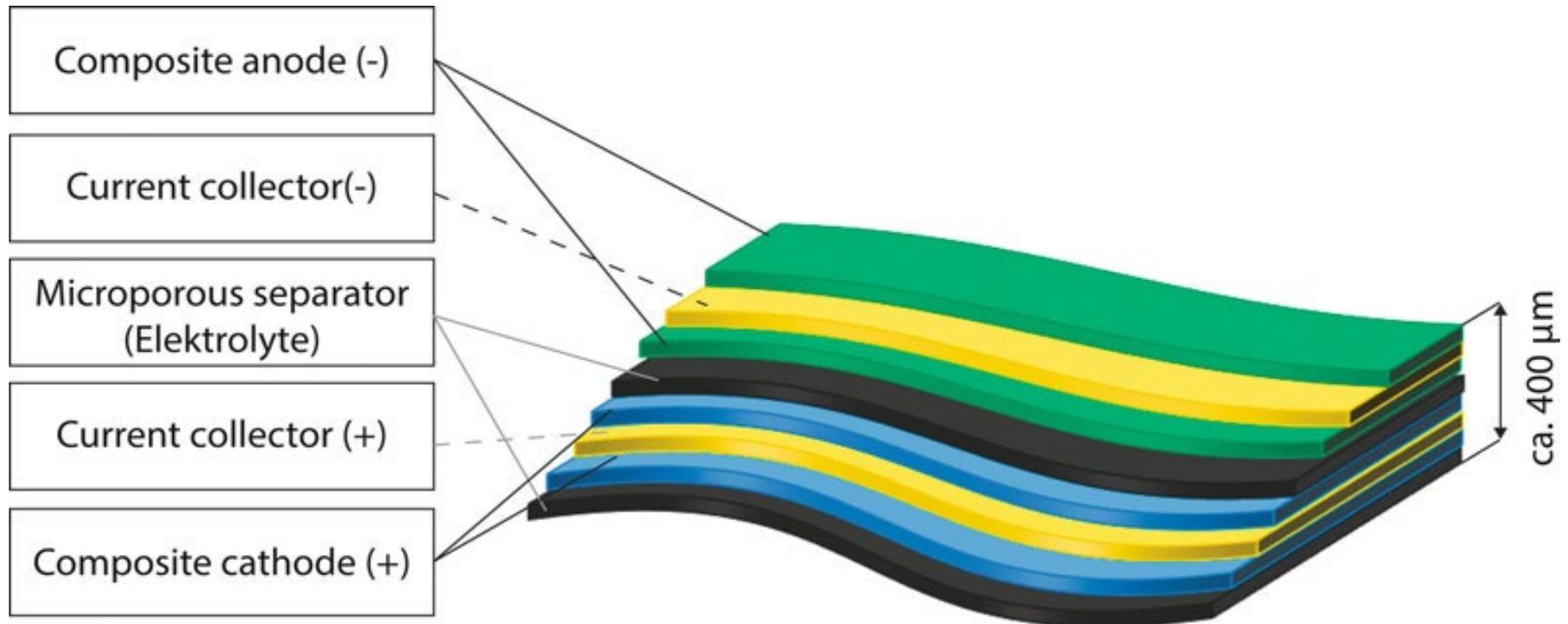


Anode:



Active material	Potential vs. Li/Li^+ [V]	Maximum usable specific capacity [A h/kg]
Li_xCoO_2	3.9	130–150
$\text{LiNi}_{1-a-b}\text{Mn}_a\text{Co}_b\text{O}_2$	~ 3.8	150–190
$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$	3.8	~ 190
LiFePO_4	3.4	150–160
$\text{Li}_x\text{Mn}_2\text{O}_4$	4.1	100–120

Battery pack



- Slurry coating on current collectors (metal foils)
- Assembly of sheets

Electrodes and Packaging

- Electrode

Active material slurry is coted on metal foil



Single layer electrode for a 10Ah cell (dimension 15x15cm)

CCEM Project report, 2014

- Cell

Cathode, anode and electrolyte will be sealed in a package



<http://german.alibaba.com/store/200793064>

- Battery pack



1.2 kWh

20kWh



<http://imgarcade.com/1/lithium-ion-battery-pack-car/>

Electrolyte

Liquid (a separator is needed between cathode and anode):

Important parameters:

- Li^+ ion conductivity

- Electrochemical stability window
- Chemical compatibility

Electrolytes	Example of classical electrolytes	Ionic conductivity ($\times 10^{-3}$ s/cm) at room temp	Electrochemical window (V) vs Li^+/Li^0		Remark
			Reduction	Oxidation	
Liquid organic	1M LiPF_6 in EC:DEC (1:1)	7^3	1.3^7	4.5^6	Flammable
	1M LiPF_6 in EC:DMC (1:1)	10^3	1.3^7	$> 5.0^3$	
Ionic liquids	1M LiTFSI in EMI-TFSI	2.0^{15}	1.0^{15}	5.3^{15}	Non-flammable
	1M LiBF_4 in EMI- BF_4	8.0^{15}	0.9^{16}	5.3^{16}	
Polymer	$\text{LiTFSI-P(EO/MEEGE)}$	0.1^{24}	$< 0.0^{24}$	4.7^{24}	Flammable
	$\text{LiClO}_4\text{-PEO}_8 + 10 \text{ wt } \% \text{ TiO}_2$	0.02^{26}	$< 0.0^{26}$	5.0^{26}	
Inorganic solid	$\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ ($x = 0.75$)	2.2^{28}	$< 0.0^{28}$	$> 5.0^{28}$	Non-flammable
	$0.05\text{Li}_4\text{SiO}_4 + 0.57\text{Li}_2\text{S} + 0.38\text{SiS}_2$	1.0^{30}	$< 0.0^{30}$	$> 8.0^{30}$	
Inorganic liquid	$\text{LiAlCl}_4 + \text{SO}_2$	70^{20}	-	4.4^{20}	Non-flammable
Liquid organic + Polymer	$0.04\text{LiPF}_6 + 0.2\text{EC} + 0.62\text{DMC} + 0.14\text{PAN}$	4.2^{38}	-	4.4^{38}	Flammable

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Safety issue!

Content

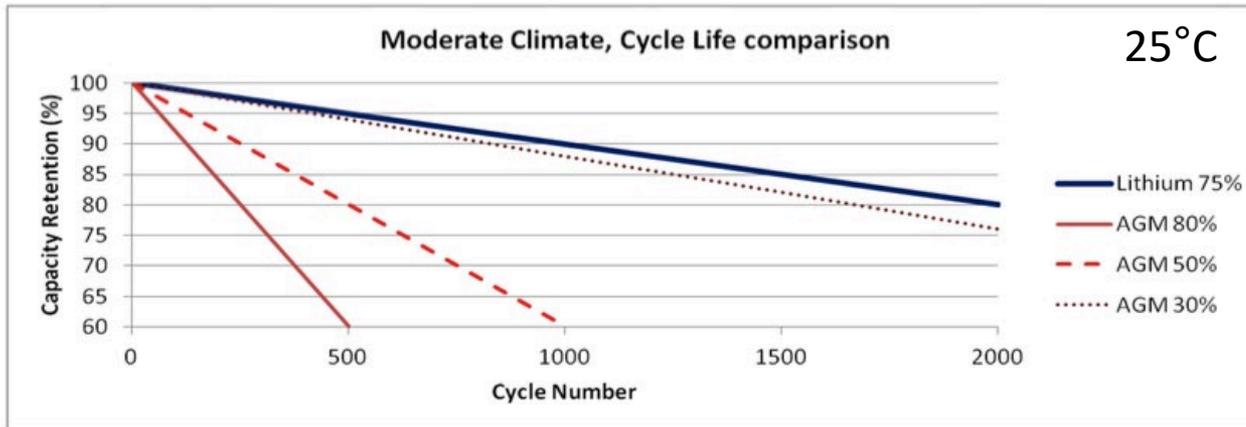
- Energy turnaround and the importance of stationary energy storage
- Basics in electrochemistry
- Lead acid battery for stationary energy storage
- Li-ion batteries for stationary energy storage
- Comparison Li-ion battery and lead acid battery

Comparison lead acid and Li ion batteries –technical specifications

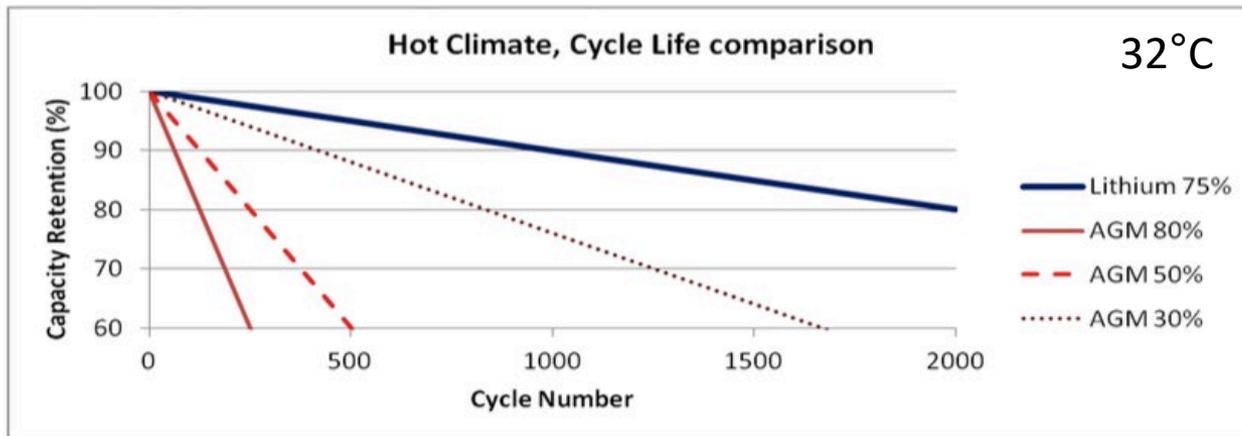
	Flooded lead acid	VRLA lead acid	Lithium-ion (LiNCM)
Energy Density (Wh/L)	80	100	250
Specific Energy (Wh/kg)	30	40	150
Regular Maintenance	Yes	No	No
Initial Cost (\$/kWh)	65	120	600 ¹
Cycle Life	1,200 @ 50%	1,000 @ 50% DoD	1,900 @ 80% DoD
Typical state of charge window	50%	50%	80%
Temperature sensitivity	Degrades significantly above 25°C	Degrades significantly above 25°C	Degrades significantly above 45°C
Efficiency	100% @20-hr rate 80% @4-hr rate 60% @1-hr rate	100% @20-hr rate 80% @4-hr rate 60% @1-hr rate	100% @20-hr rate 99% @4-hr rate 92% @1-hr rate
Voltage increments	2 V	2 V	3.7 V

<http://www.batterypoweronline.com/main/wp-content/uploads/2012/07/Lead-acid-white-paper.pdf>

Climate dependence of the battery performance



AGM, absorbed glassmat Deep cycle lead acid batteries.



Life time of Li ion batteries is much enhanced in warmer climate in contrast to lead acid batteries

<http://www.batterypoweronline.com/main/wp-content/uploads/2012/07/Lead-acid-white-paper.pdf>

Comparison lead acid and Li-ion batteries - general

	Lead acid battery	Li-ion battery	
	CO ₂ footprint	15kg CO ₂ per kWh	70kg CO ₂ per kWh 
	Safety	Water as electrolyte	Organic electrolyte (flameable) 
	Long live in cycles	500 (3 years)	<1000 (<10 years) 
	Recycling	yes	no 
	Investment	100 Eu/kWh	350 Eu/kWh 
	Stationary applications	yes, (i.e. 40 MWh, Chino, CA)	Test runs (i.e. 50MWh)