Willkommen
Welcome
Bienvenue

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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

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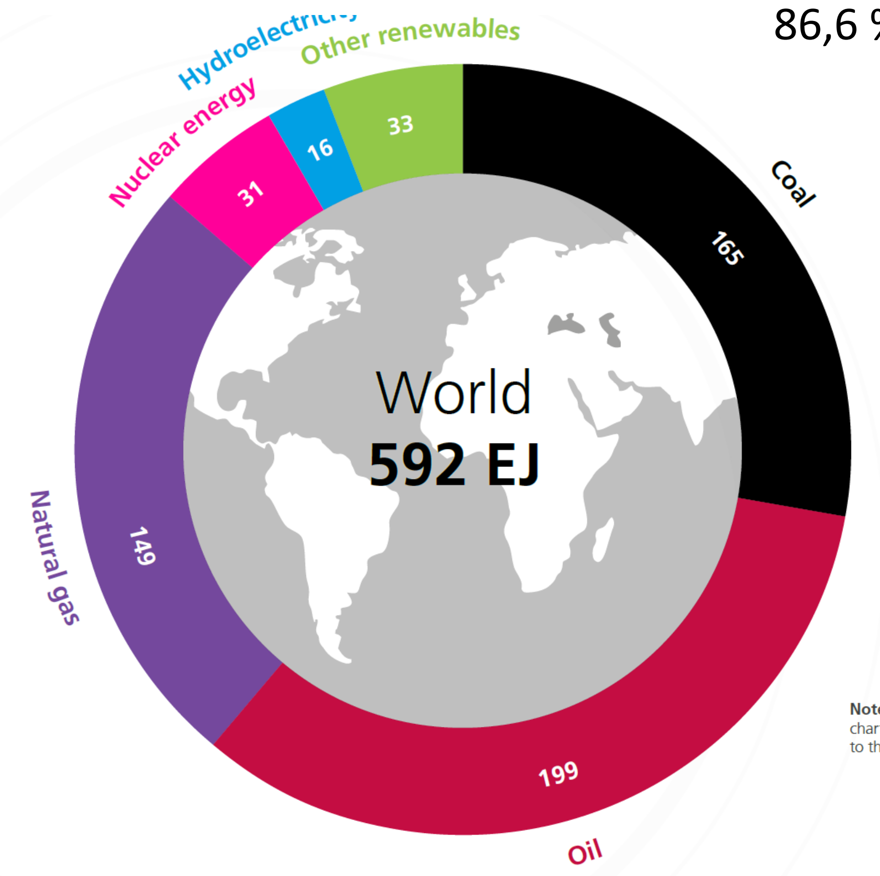
86,6 % Fossile Energies



Exa = 10^{18}

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

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

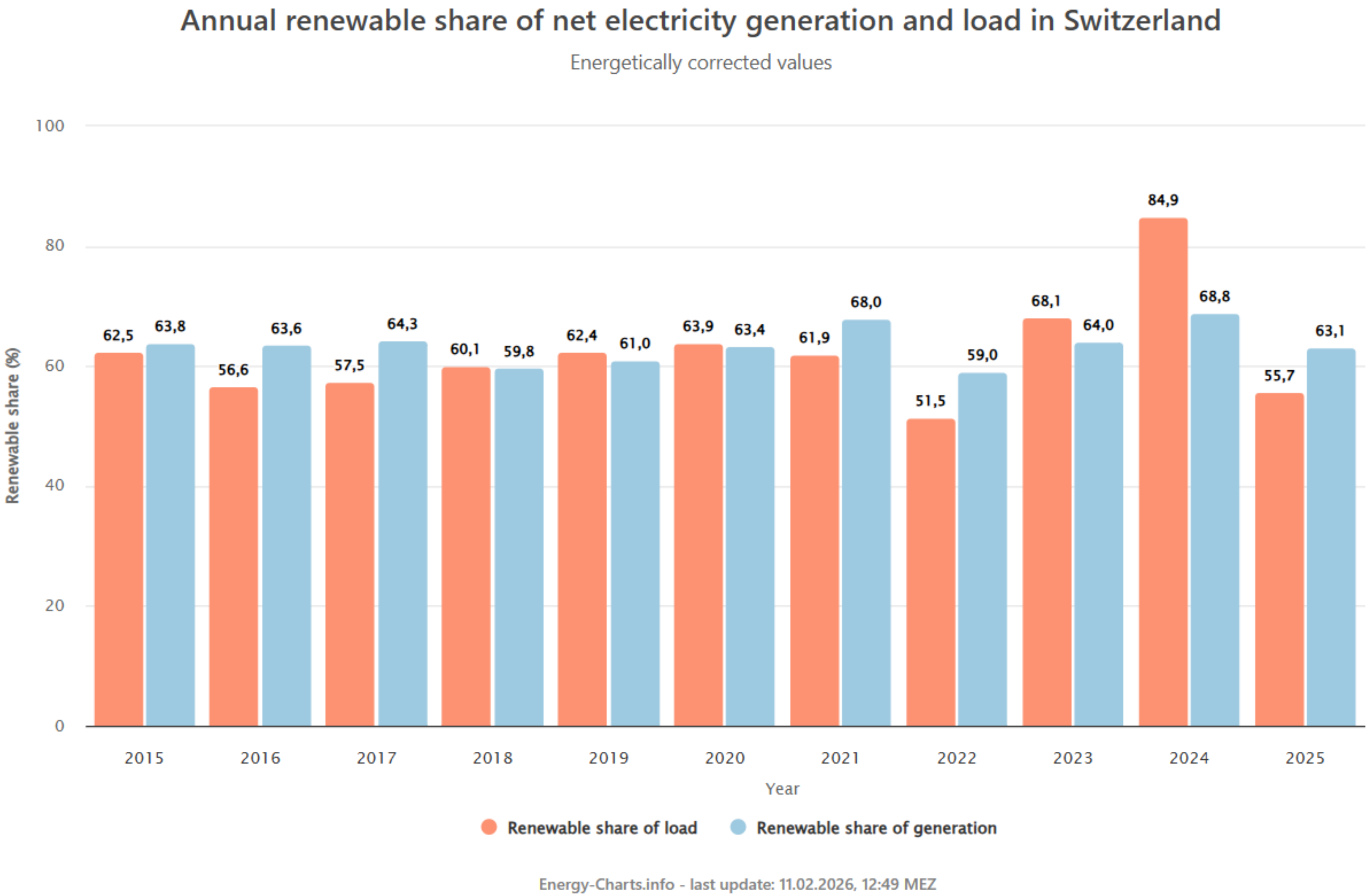
2021: 595,15 EJ (563,26 EJ)

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

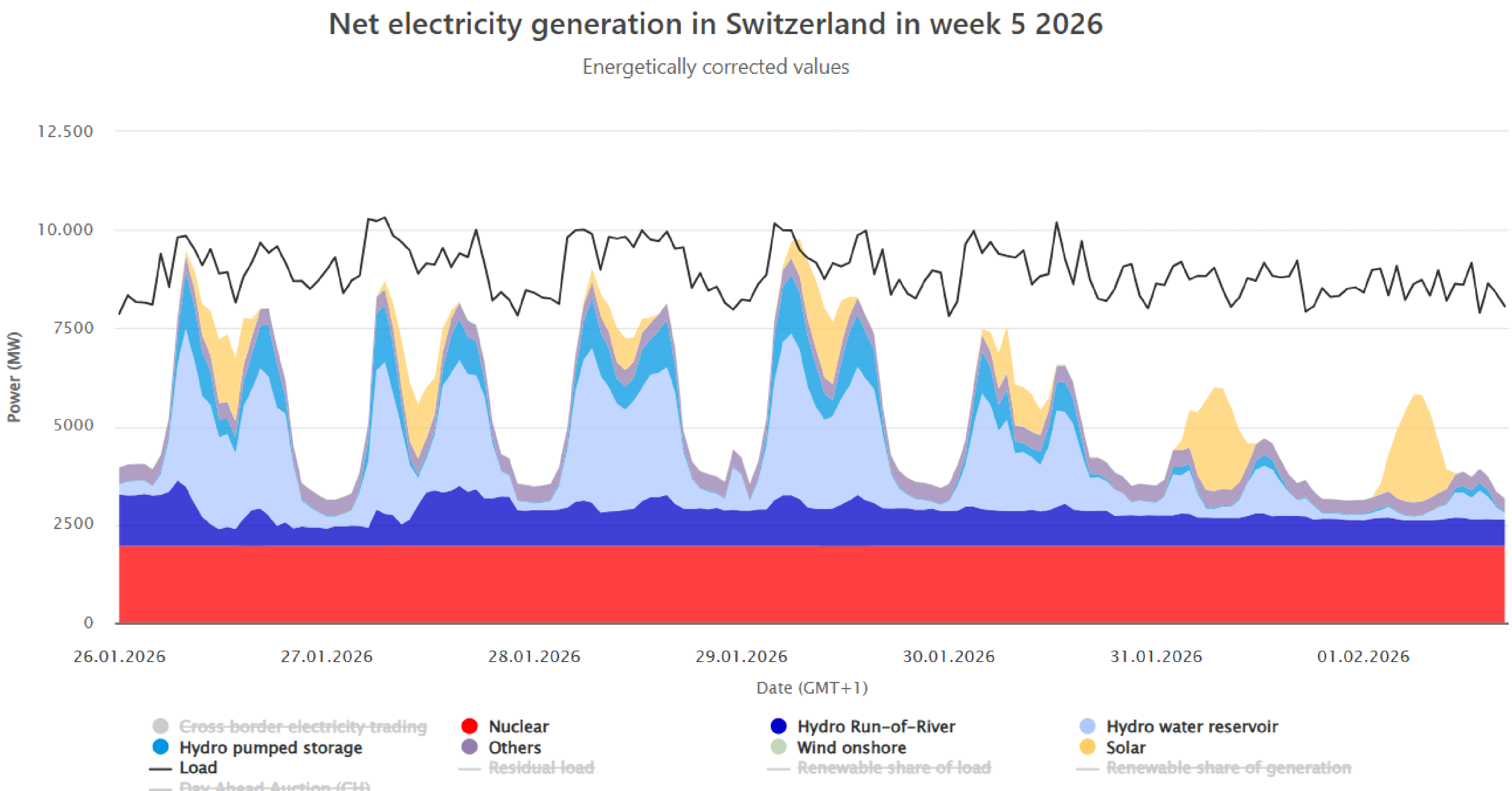
2023: 619, 63 EJ (580,28 EJ)

2024: (592,22 EJ)

Energy turn-around Switzerland

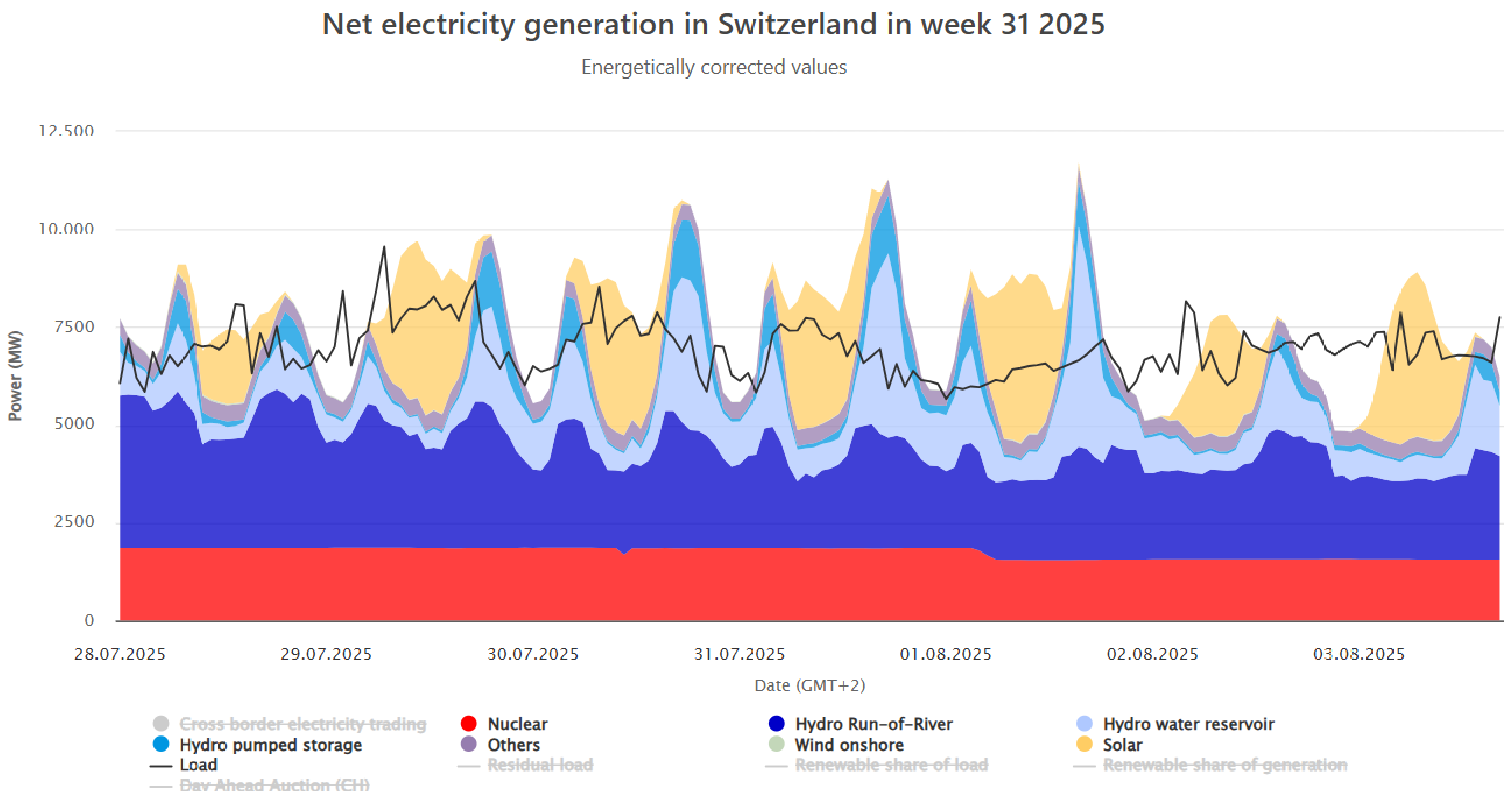


Electricity generation and demand in week 5 2026



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

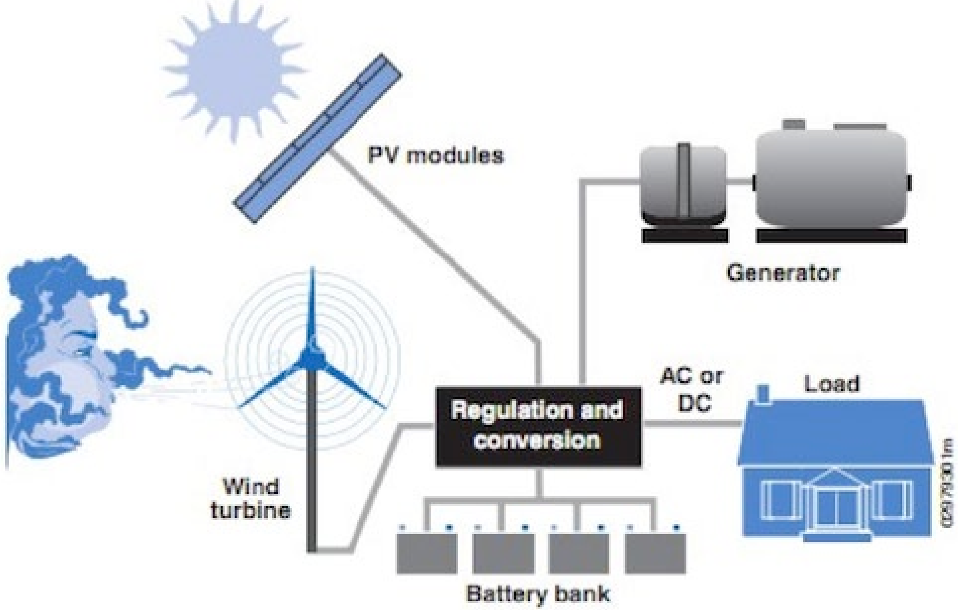


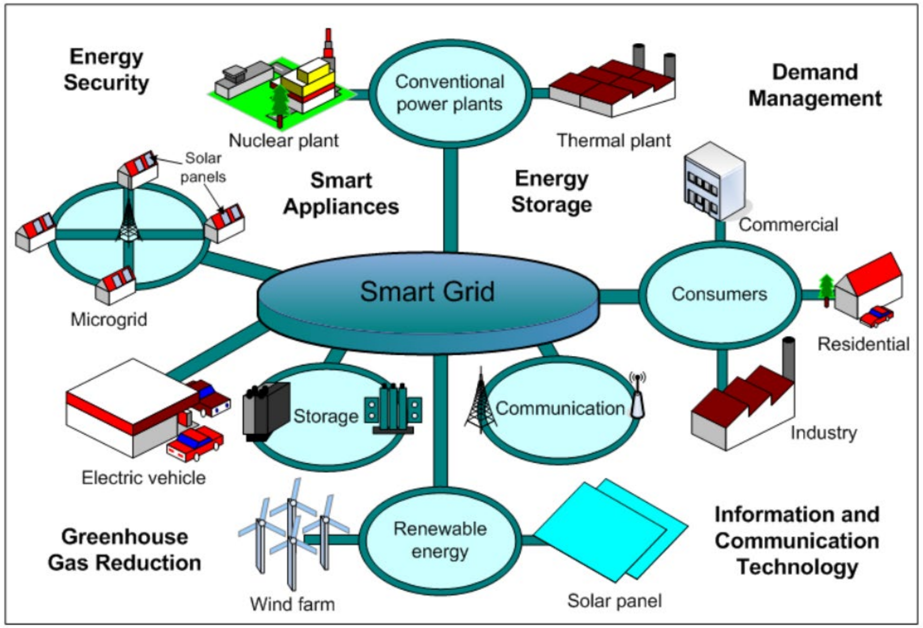
https://www.energy-charts.info/charts/power/chart.htm?c=CH&year=2026&week=05&l=en&legendItems=1w8w4

Consequences of increasing renewable energy shares

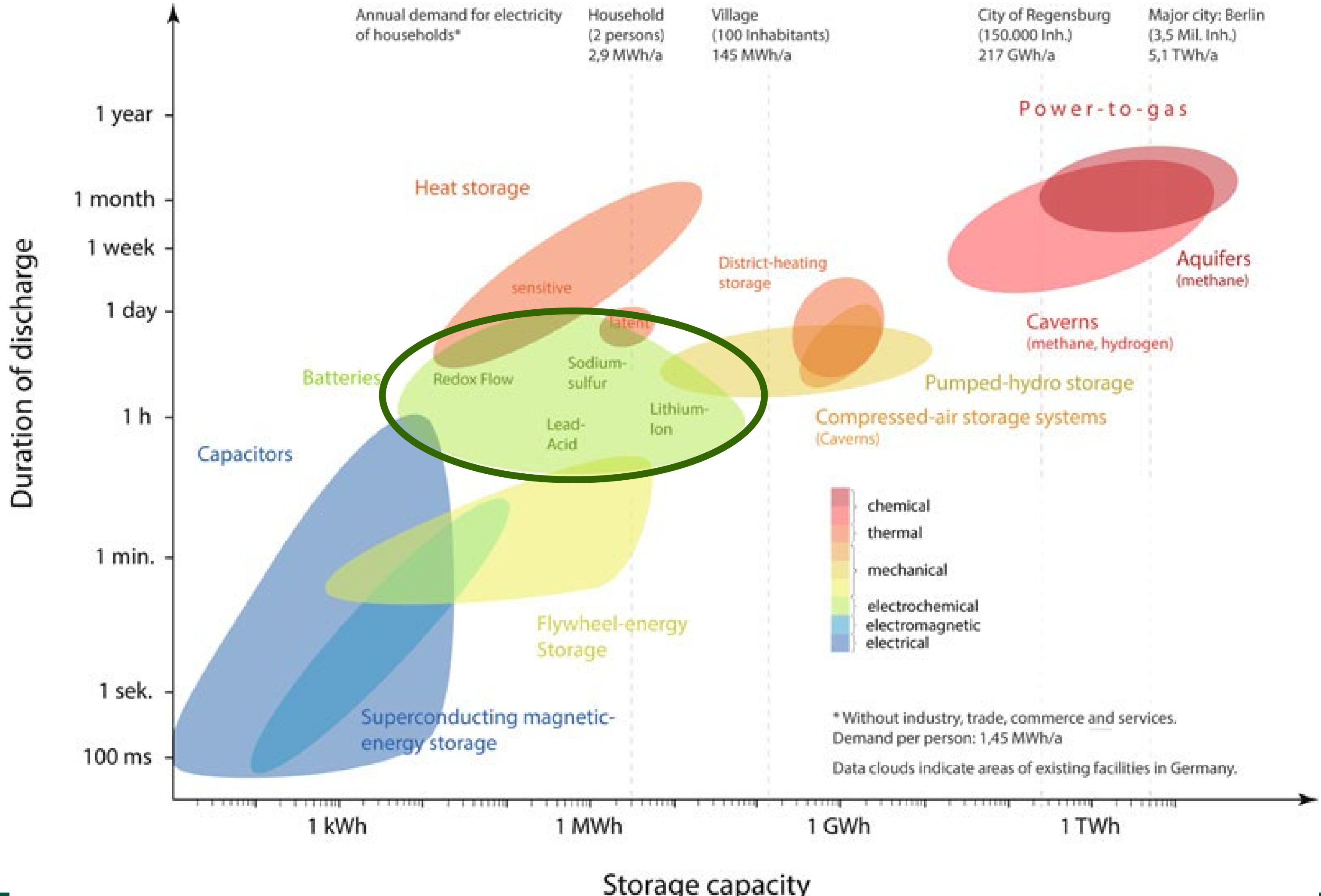
- Wind, sun and water are neither constant nor demand oriented energy sources
- Alternative energies generate strong fluctuations in the energy production, that are not related to the load
- Necessity for energy storage or distribution

http://ec.europa.eu/research/energy/pdf/smartgrids_en.pdf DOI:10.1109/ECCE.2011.6063795



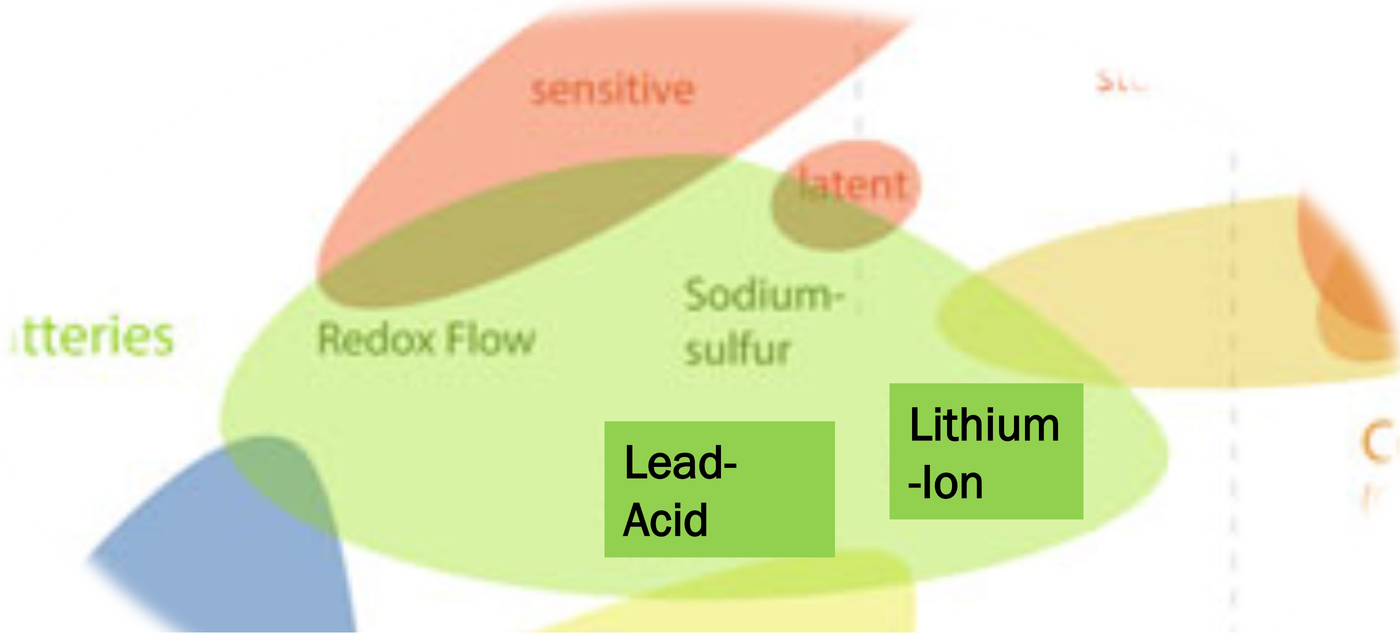


Technical solutions - Energy storage



M. Sterner and I. Stadler, Energiespeicher. 2017, Berlin: Springer, Abb. 12.2

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

M. Sterner and I. Stadler, Energiespeicher. 2017, Berlin: Springer, Abb. 12.2 https://doi.org/10.1016/j.rser.2022.112213

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Oxidation and Reduction

- Oxidation: Loss of electrons

  Example: Rust formation:

  $Fe \longrightarrow Fe^{3+} + 3\ e^-$

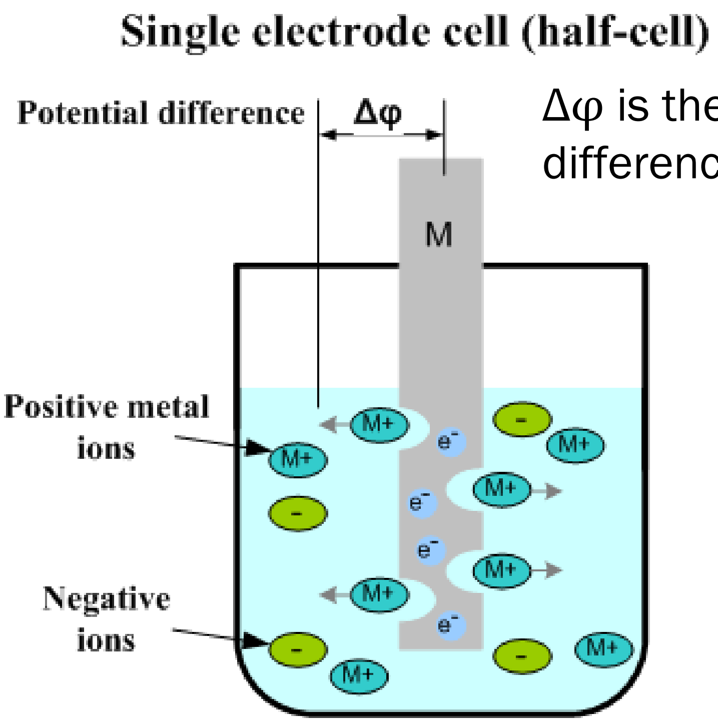
- Reduction: Electron gain

  Example: Rust formation:

  $O_2 + 4\ e^- \longrightarrow 2\ O^{2-}$

www.chem.umass.edu

Electrochemical potential of half cells I



Δφ 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 Δφ (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 Δφ: 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 In a_{M^+} and a_{M^+}: Activity (M^+) ≈ [M^+] for small concentrations [M^+]

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

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

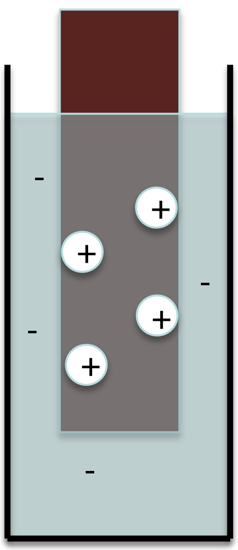
Nernst equation: $\Delta\varphi = \Delta\varphi_0 + \frac{RT}{zF}\ln([M^+(\text{solution})])$

Electrochemical potential of half cells III

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

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

For example $CuSO_4$/Cu

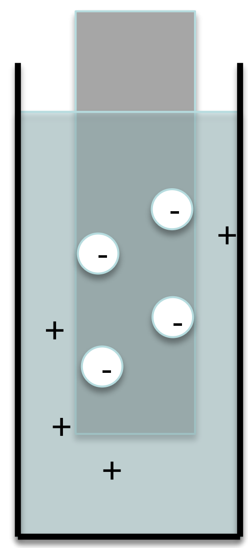


$$\Delta\varphi(\mathrm{I}) = \Delta\varphi_0(\mathrm{I}) + \frac{\mathrm{RT}}{\mathrm{zF}} \ln([\mathrm{M}^+(\mathrm{I})])$$

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

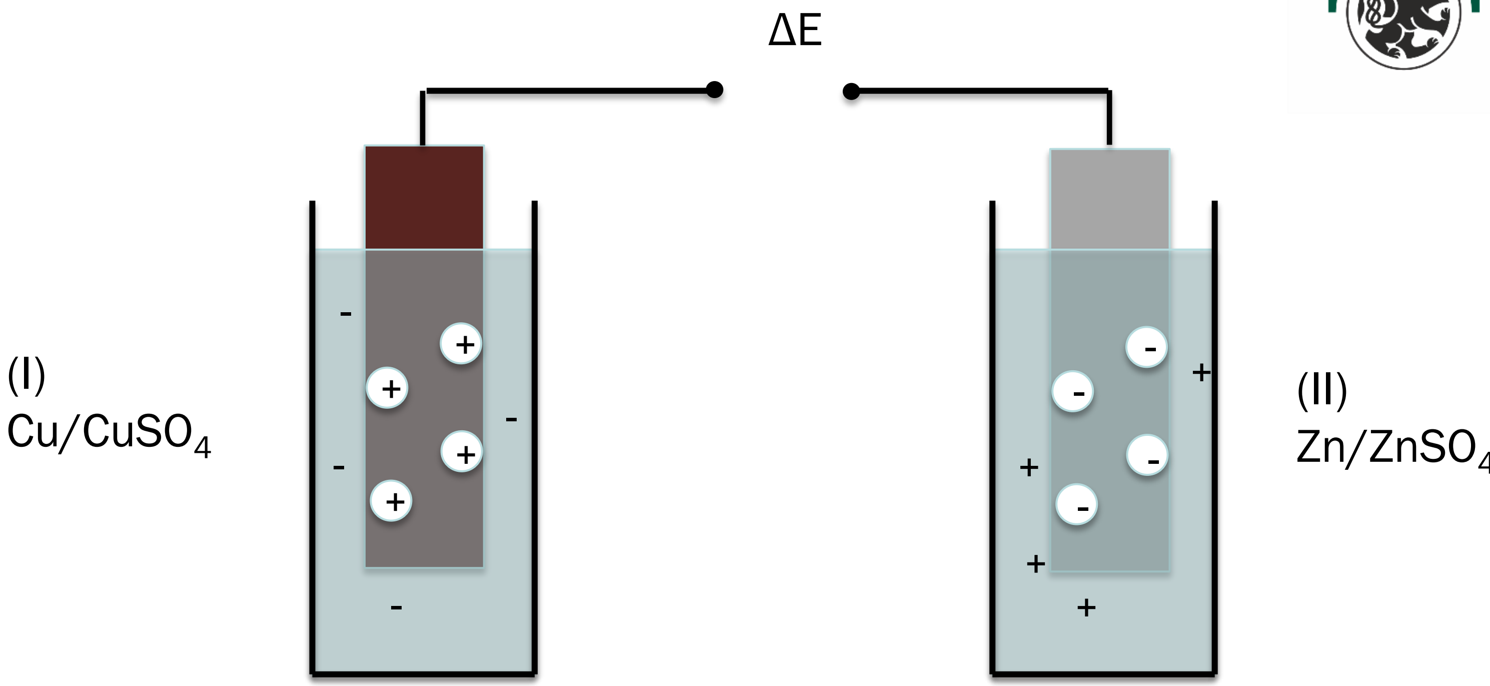
- Metal ions are dissolved from the electrode
- Metal is charged negatively
- Solution is charged positively

For example $ZnSO_4$/Zn



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

Galvanic cell



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

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

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

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

Standard electrode potentials

Reduction Half Reaction	Standard Potential (V) $\Delta\varphi_0$
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.67
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05

stronger oxidizing agent

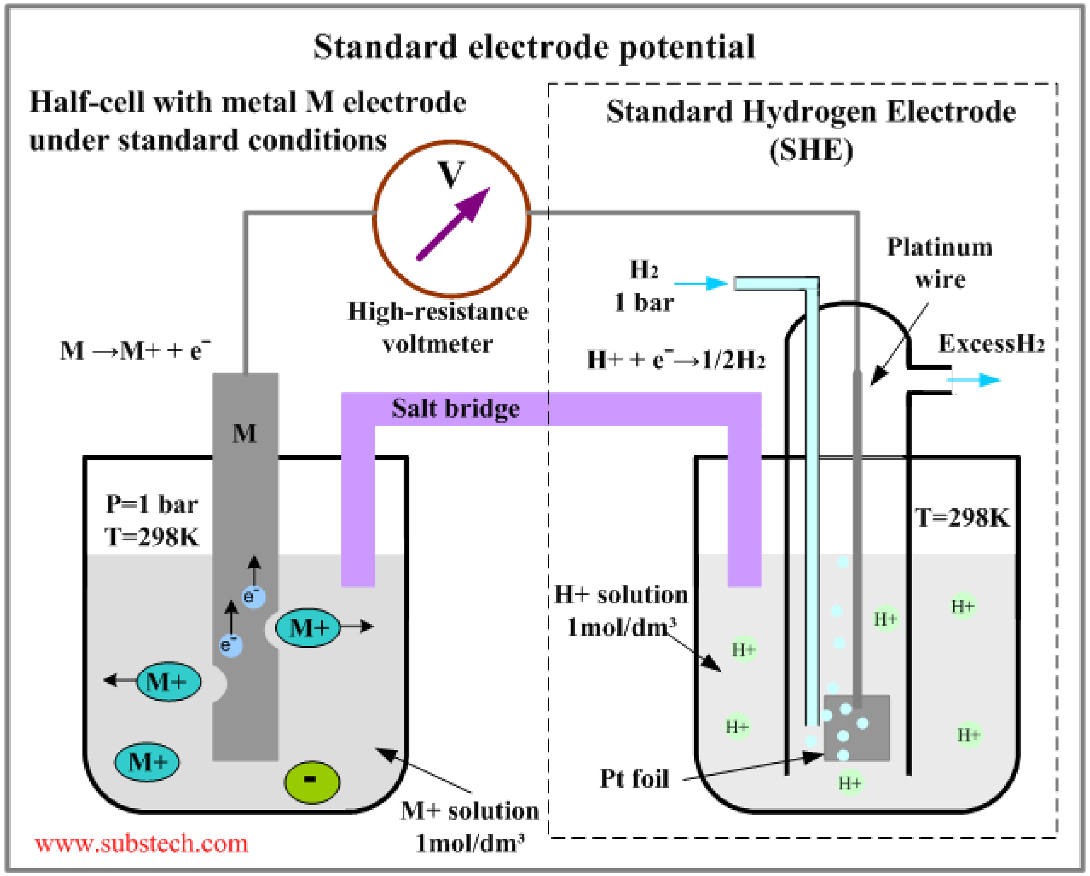
stronger reducing agent

Noble metals:
Positive potentials

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

www.chem.umass.edu

Standard electrode potential (measurement)



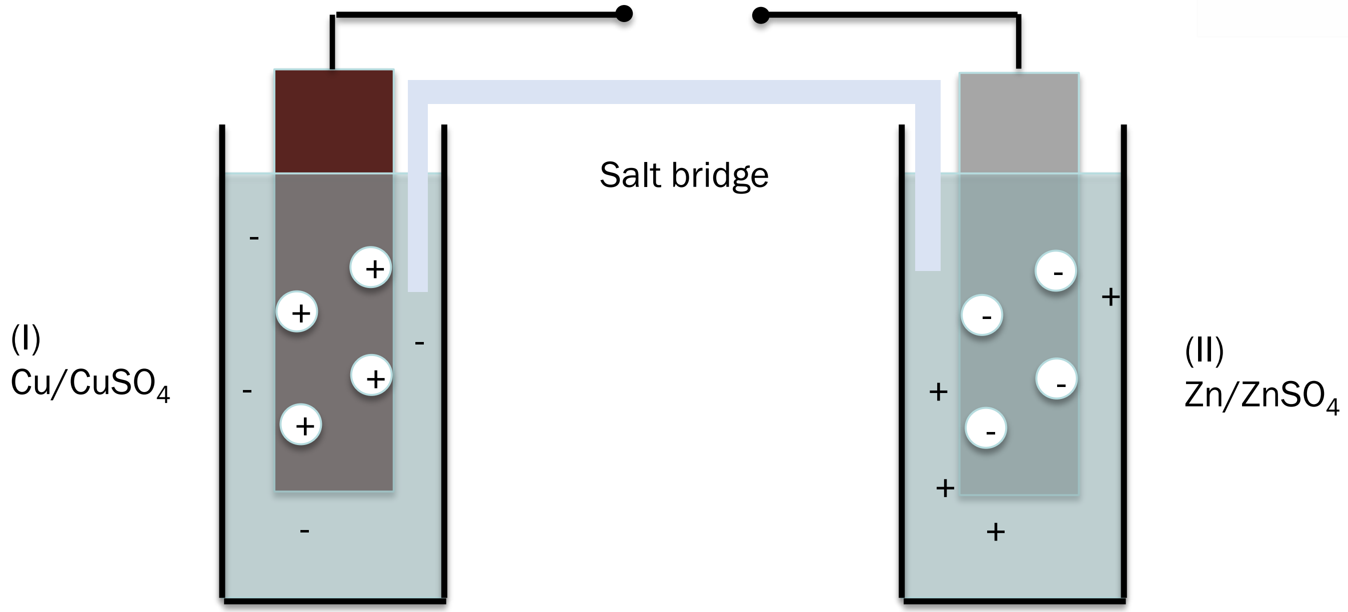
Standard electrode potential

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

H_2 electrode:
concentration of 1 mol/L $[H^+]$
gases at a pressure of 1 atm at 25 °C.

www.substech.com

Galvanic cell



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

Standard electrode potentials

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Reduction Half Reaction				Standard Potential (V) $\Delta\varphi_0$
F_2	+ $2e^-$	⇌	$2F^-$	+2.87
Pb^{4+}	+ $2e^-$	⇌	Pb^{2+}	+1.67
Cl_2	+ $2e^-$	⇌	$2Cl^-$	+1.36
O_2 + $4H^+$	+ 4e-	⇌	$2H_2O$	+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

stronger oxidizing agent

stronger reducing agent

Noble metals:
Positive potentials

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

Electrolyte stability window is not at the «right» place: H_2O/H_2 is at 0 V
Overpotential of Zn: 0.77V, therefore stable in water

www.chem.umass.edu

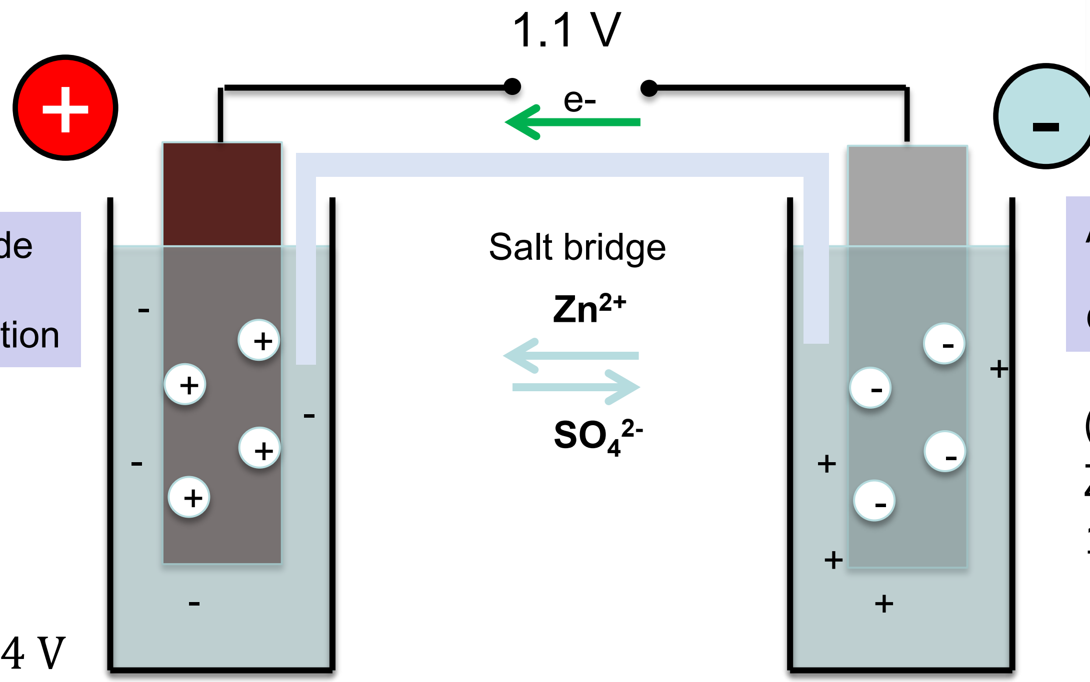
Galvanic cell

Cathode

Reduction

(I)
$CuSO_4$ / Cu
1M

$\Delta\varphi(\mathrm{I}) = 0.34\ \mathrm{V}$



Anode

Oxidation

(II)
$ZnSO_4$/Zn
1M

$\Delta\varphi(\mathrm{II}) = -0.76\ \mathrm{V}$

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

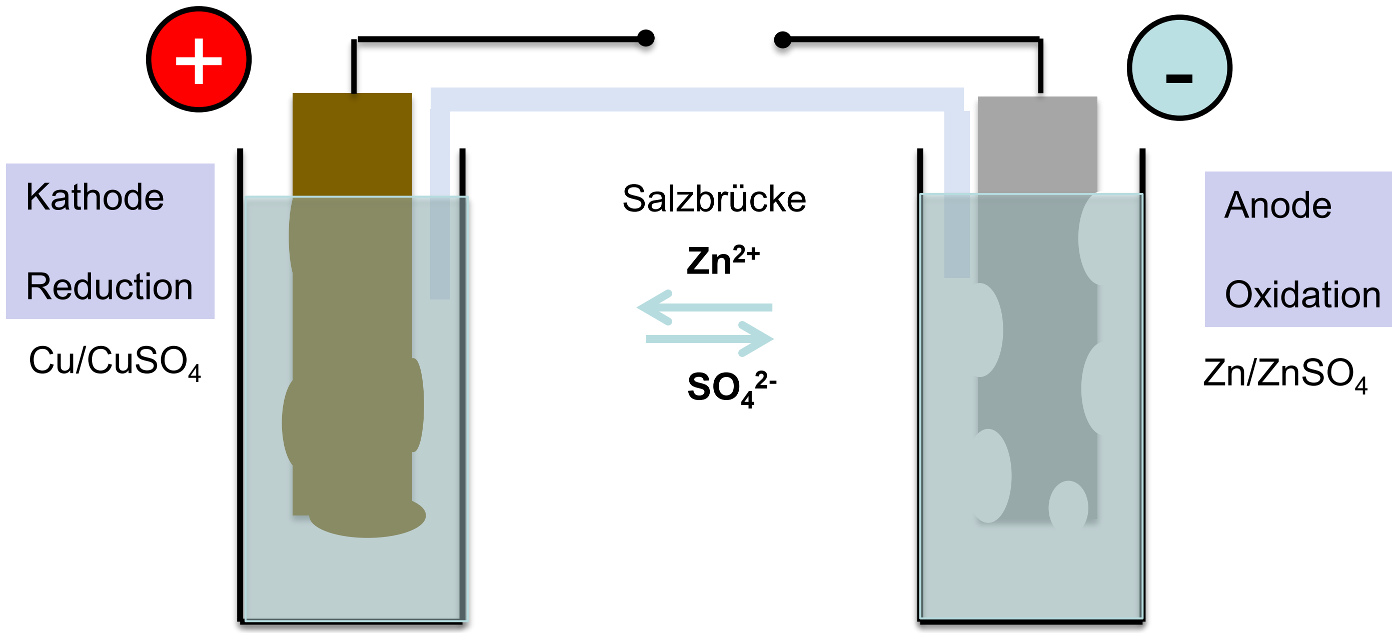
$$\Delta E = \Delta\varphi(\mathrm{I}) - \Delta\varphi(\mathrm{II}) = \Delta\varphi_0(\mathrm{I}) - \Delta\varphi_0(\mathrm{II}) + \frac{\mathrm{RT}}{\mathrm{zF}} \ln\left(\frac{[\mathrm{M}^+(\mathrm{I})]}{[\mathrm{M}^+(\mathrm{II})]}\right)$$

$$\Delta \mathrm{E} = 0.34\ \mathrm{V} + 0.76\ \mathrm{V} = 1.1\ \mathrm{V}$$

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

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

Secondary Batteries

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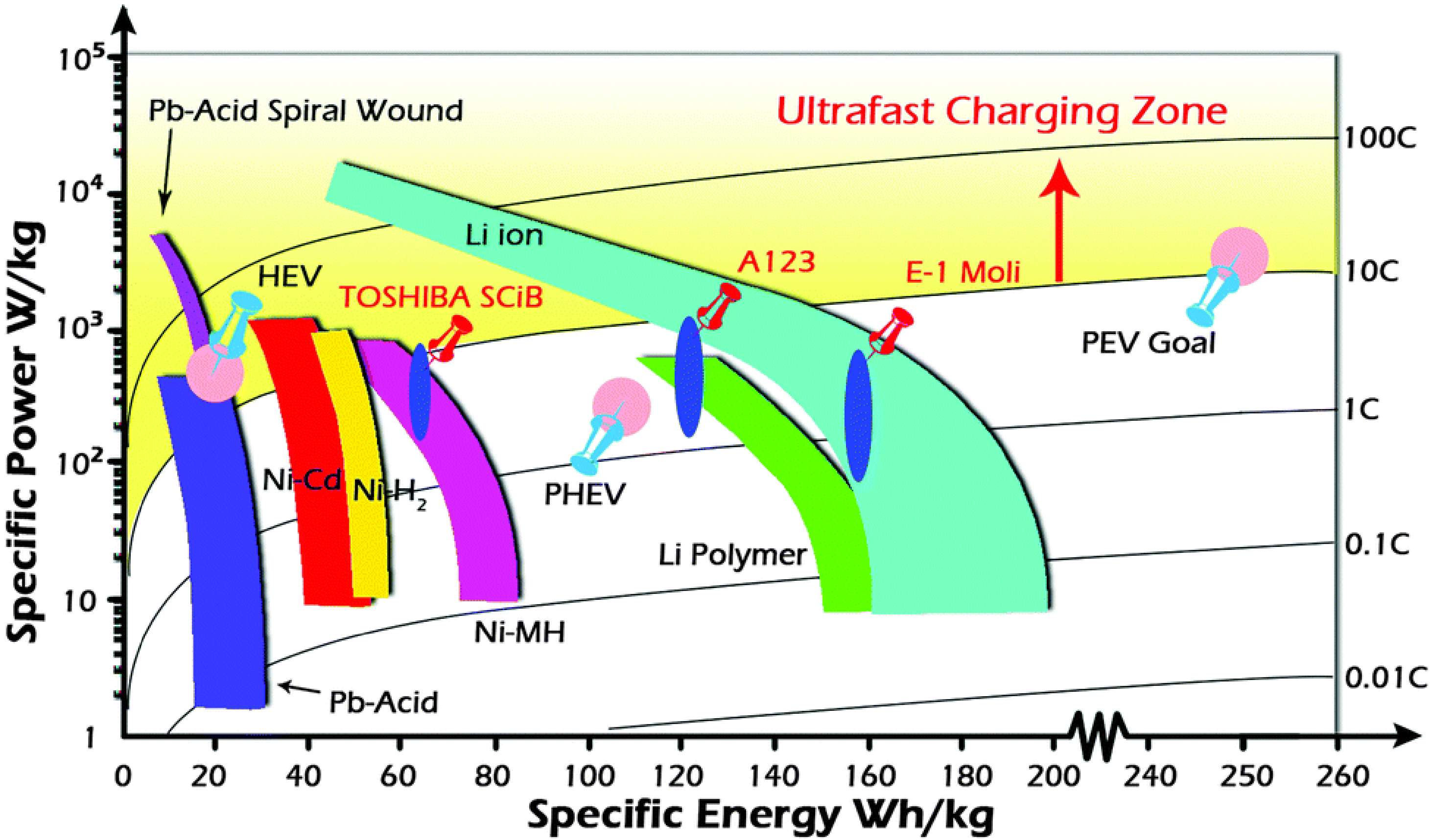
To solve energy storage problems, we need rechargeable batteries: Reversible redox reactions, i.e. secondary batteries



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 density[1])
- Three main applications: (deep cycle, auto SLI, industry)

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

Lead acid battery: The concept

Discharge

Negative electrode (Anode): $E_0(Pb)=-0.36V$

$Pb(s) \longrightarrow Pb^{2+}(aq)+2e^-$

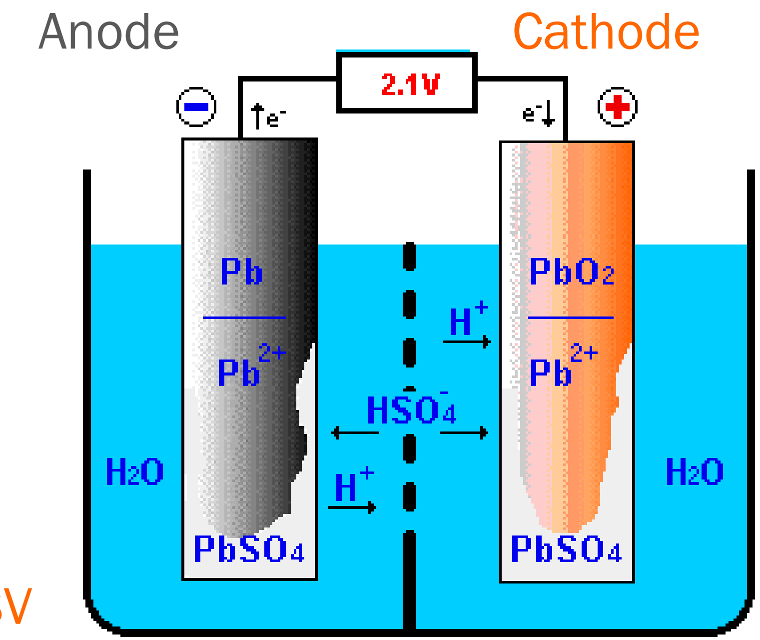
$Pb^{2+}(aq)+SO_4^{2-} \longrightarrow PbSO_4(s)$

Positive electrode (cathode): $E_0(PbO_2)=+1.68V$

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

$Pb^{2+}(aq)+SO_4^{2-} \longrightarrow PbSO_4(s)$

Electrolyte: H_2SO_4



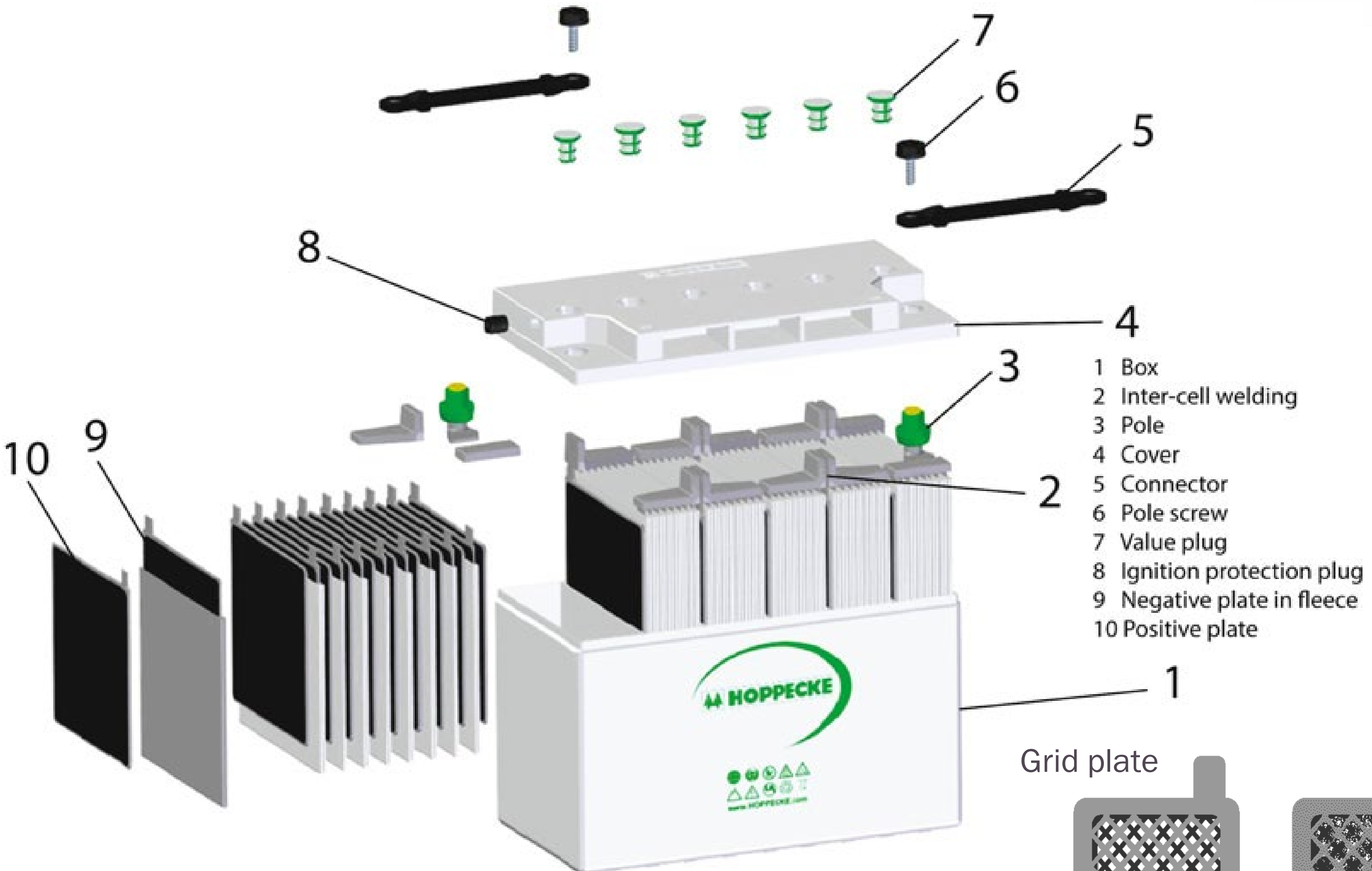
http://www.erikdeman.de/html/sail080e.htm

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

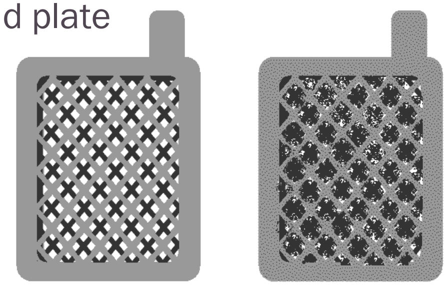
Potential difference: 2.04V

Open circuit voltage: 2.1 -2.13V

Design of a Lead Acid Battery



Grid plate

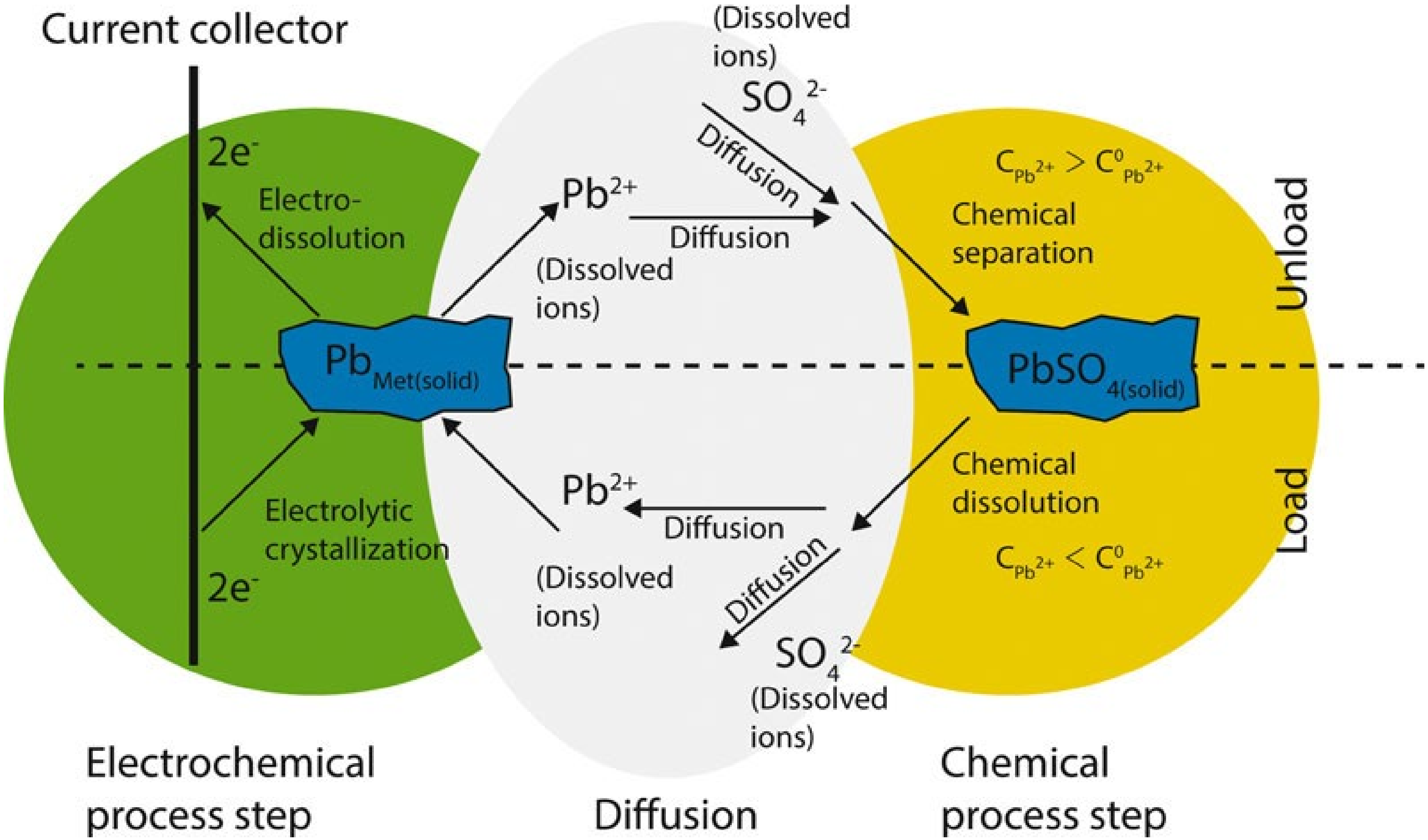


Grid plate with active material

http://www.electrical4u.com/construction-of-lead-acid-battery/

http://www.danielmetzsch.de/Batterie.html

Lead Acid Battery - Mechanism



Electrolyte and charge and discharge state of the lead acid battery

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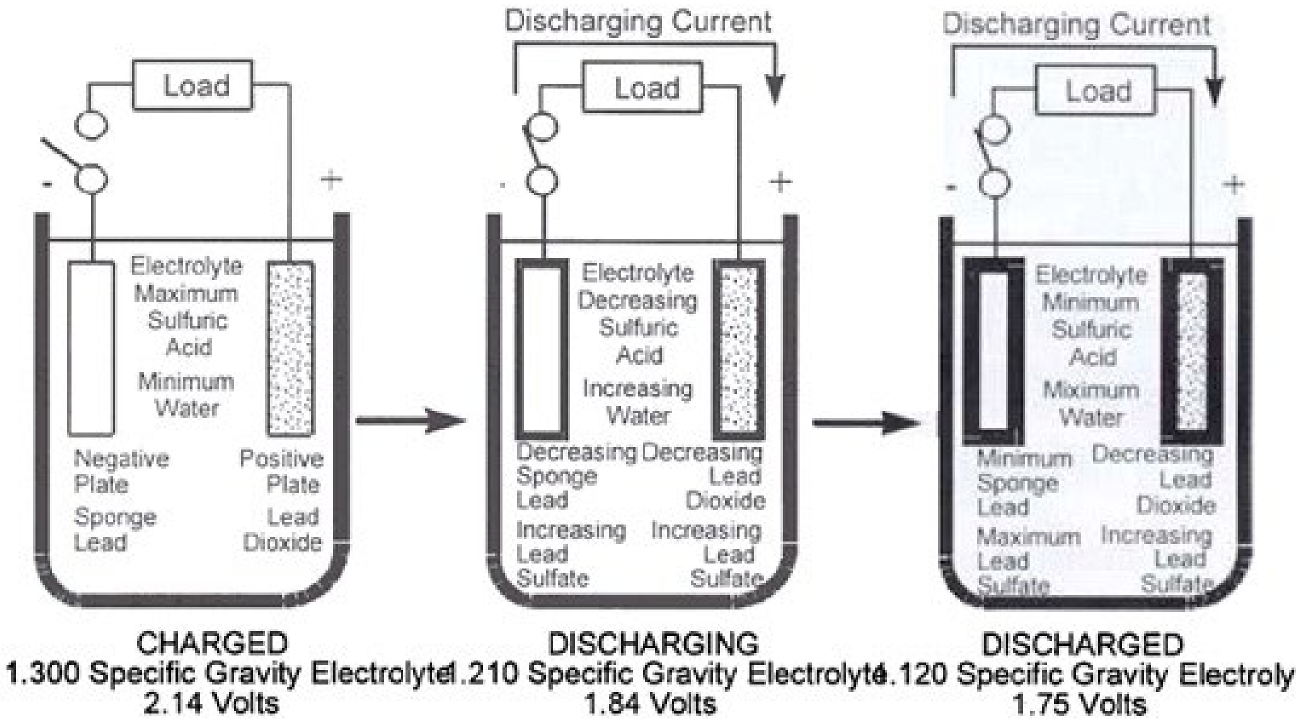
- Electrolyte: aqueous H_2SO_4
- Specific density of the electrolyte is connected to the charge state of the battery



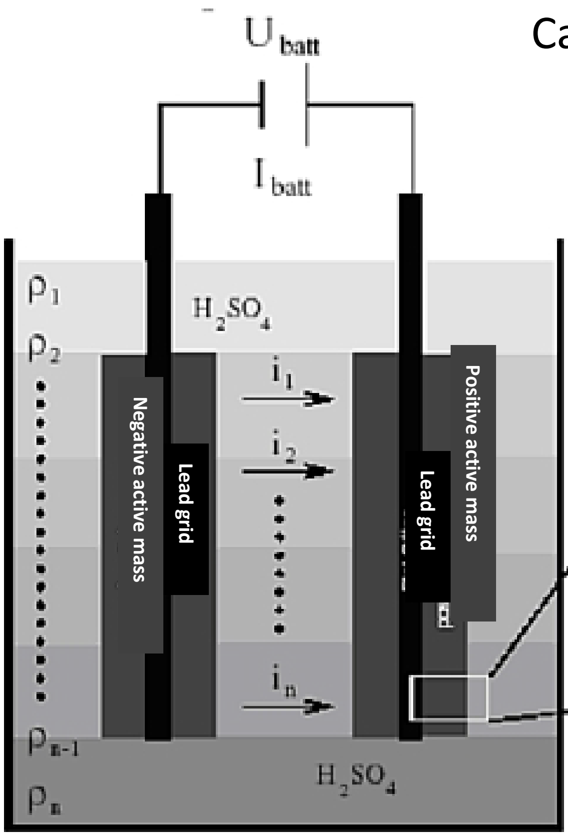
Change of cell voltage during discharge!

http://www.longwaybattery.com/en/displaynews.html?newsID=159060

Microscopic view of the electrode

Three phase system: Pb or PbO_2, $PbSO_4$, electrolyte

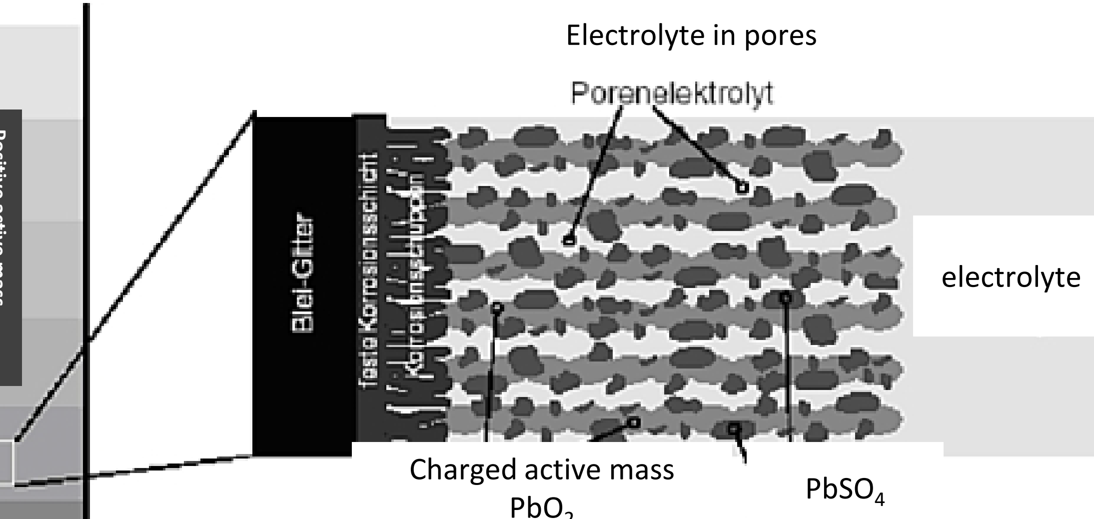
For reversibility it is important that the $PbSO_4$ stays close to the electrode



Cathode reaction

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

$$Pb^{2+}(aq) + SO_4^{2-} \longrightarrow PbSO_4(s)$$



Reversible conversion reaction

Self-discharge, overpotential, side reactions

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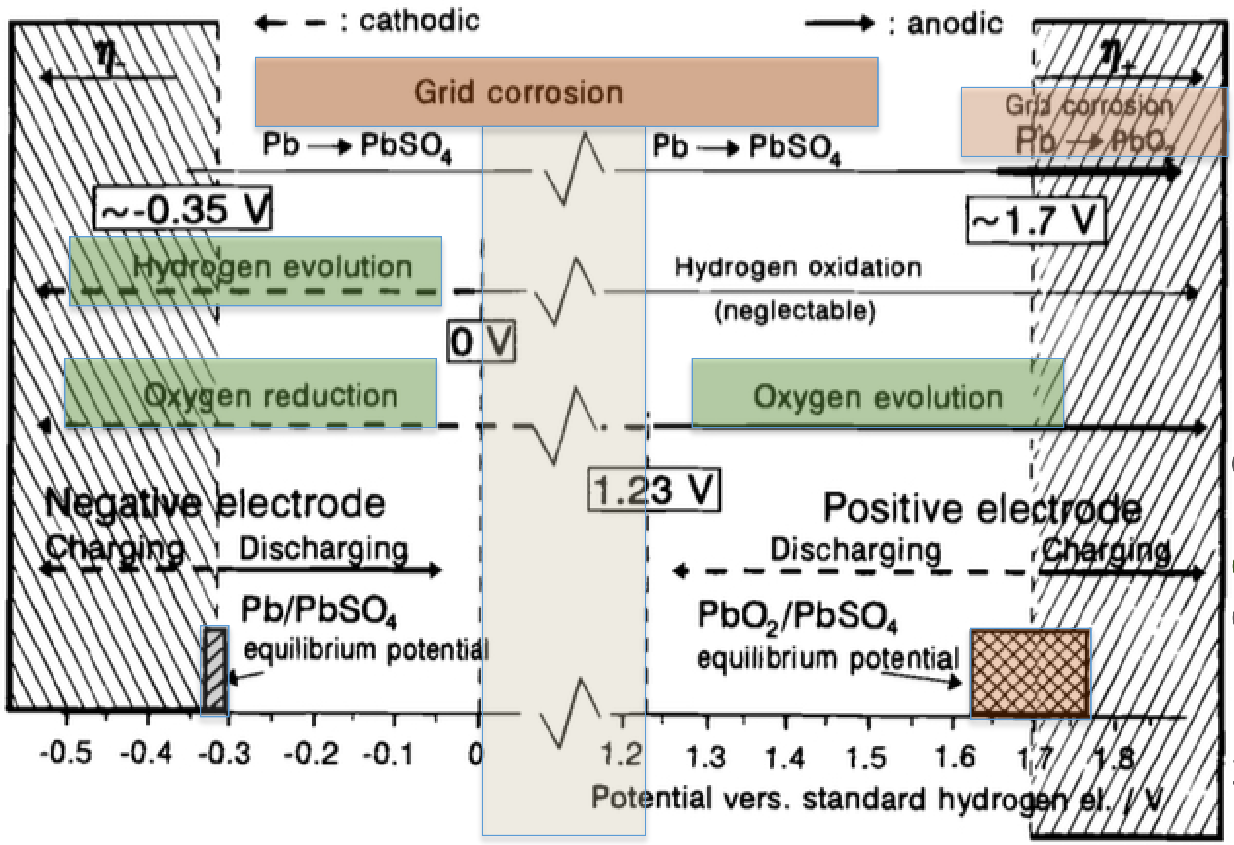
$E_0(Pb)$=-0.36V $E_0(PbO_2)$=+1.68V

$E_0(H_2)$=0V $E_0(O_2)$=1.23V

Anode   Cathode



Anodic (electrons generated):

Oxygen evolution:

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

Grid corrosion:

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

$Pb \longrightarrow Pb^{2+} + 2e^-$

Cathodic (electrons consumed):

Oxygen reduction/evolution:

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

Hydrogen evolution:

$2\ H^+ + 2e^- \longrightarrow H_2$

Stability window of the Electrolyte (H_2O)

Side reactions are slow (overpotential)!

J. Electrochem. Soc. 143 (1996) 790-798

Active Materials and grid plates

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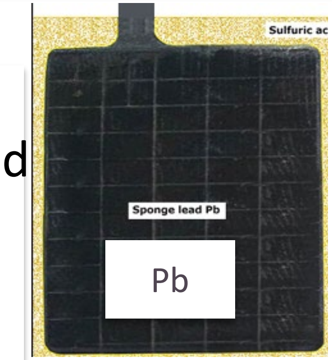
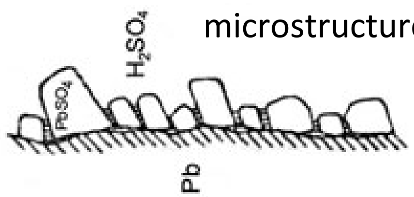
Anode (negative pole)

- 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



Elektrodenplatte

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)

http://www.agcoauto.com/content/news/p2_articleid/136

Lead acid batteries for stationary applications

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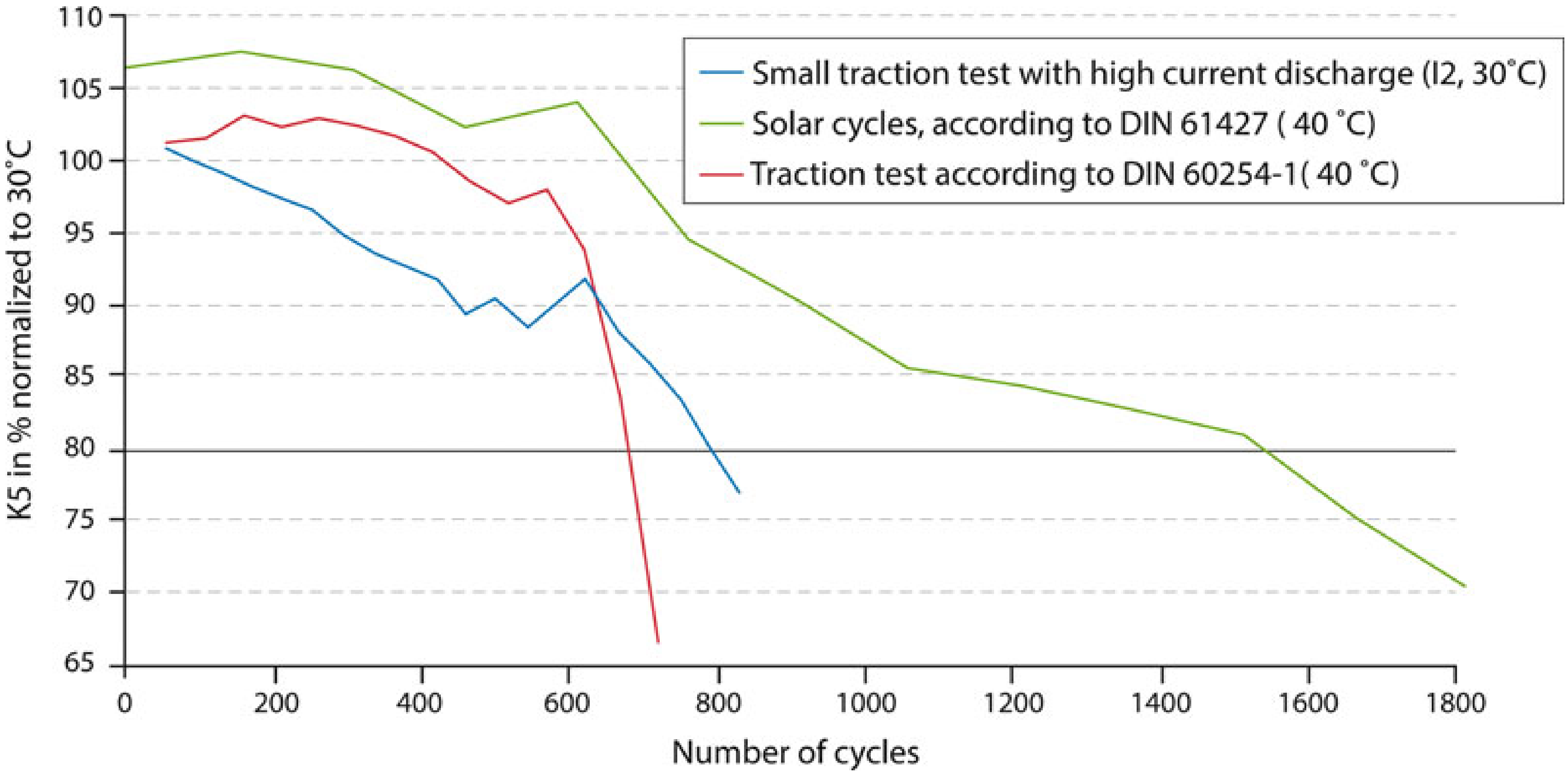
- Long lifetimes: Need to be kept at constant charge (constant float current)
- Heavy thick plates with high density active pastes (high energy and power density is not so important for stationary applications)
- Active materials are chosen such as to suppress H_2 or O_2 evolution (for example caution 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

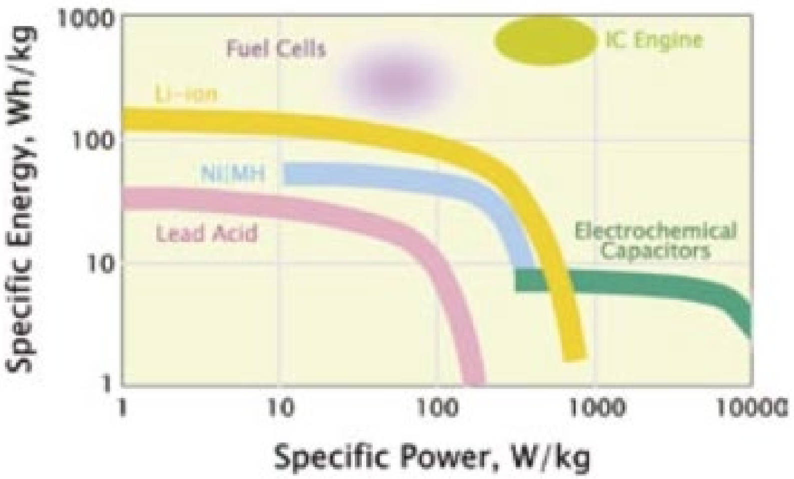


- Energy storage in remote areas / renewables / backup power




Li-ion Battery applications - summary

- Li-ion batteries are mainly used for mobile applictions
- 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

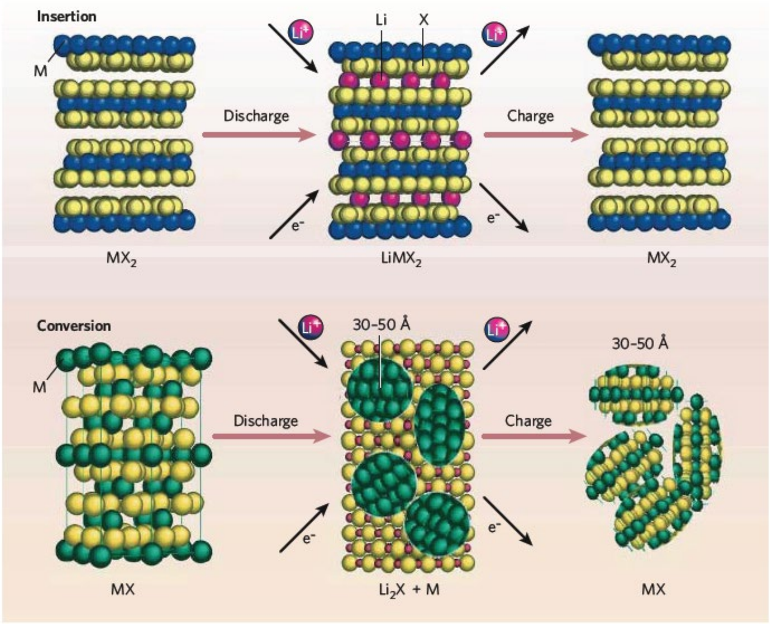


Ragone plot: Specific energy versus specific power

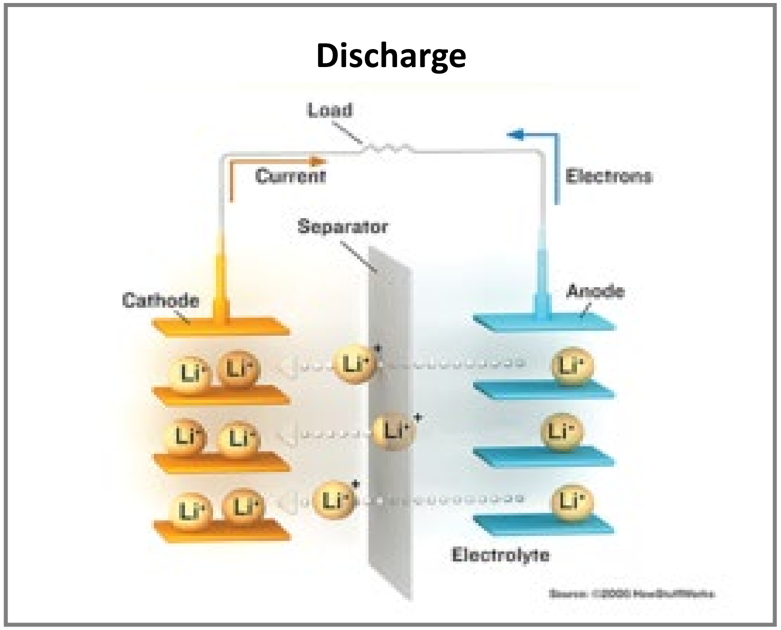
http://berc.lbl.gov/venkat/Ragone-construction.pps

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



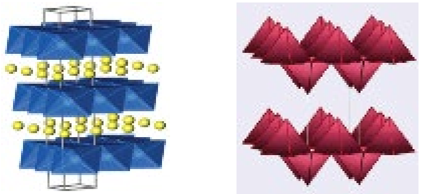
Cathode materials

- Cathode

Layered oxides

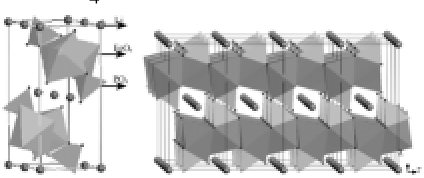
$LiCoO_2$ V_2O_5

$LiNi_yMn_yCo_{1-2y}O_2$



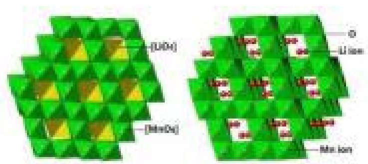
Olivine

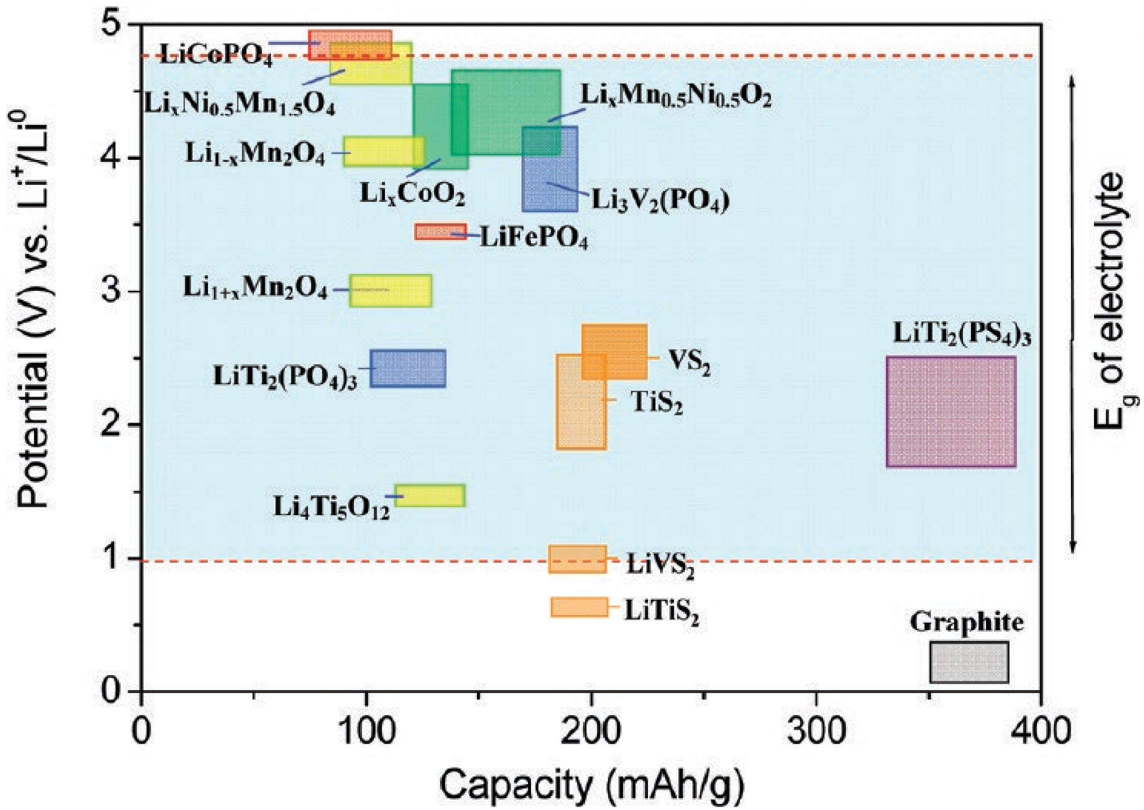
$LiFePO_4$



Spinel

z.B.: $LiMn_2O_4$





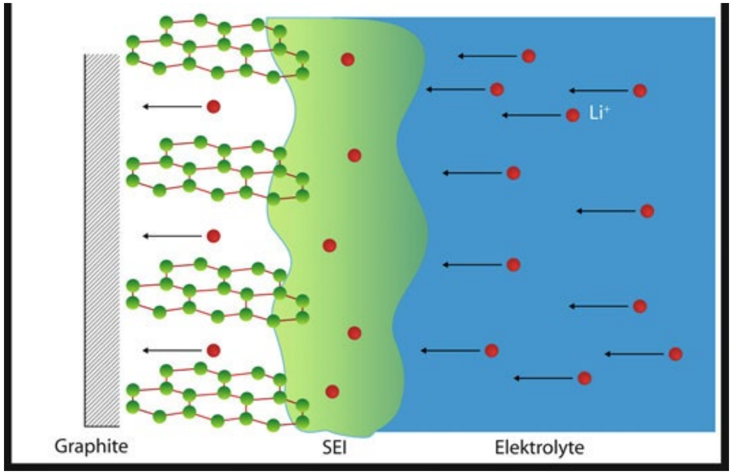
- Many different material systems are possible
- Various potential differences are possible
- Most famous: Li_xCoO_2 with around 4.2 V

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

Anode and global reaction

- Anode

Graphite:



Alternatives:

Si, Si/C, and Li_xTiO_y

- Discharge (example Li_xCoO_2)

Cathode:

$x\,Li^+ + x\,e^- + Li_yCoO_2 \longrightarrow Li_{(x+y)}CoO_2$

Anode:

$Li \longrightarrow Li^+ + e^-$

Active material	Potential vs. Li/Li⁺ [V]	Maximum usable specific capacity [A h/kg]
Li_xCoO_2	3.9	130–150
$LiNi_{1-a-b}Mn_aCo_bO_2$	$\sim$ 3.8	150–190
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	3.8	$\sim$ 190
$LiFePO_4$	3.4	150–160
$Li_xMn_2O_4$	4.1	100–120

Battery pack

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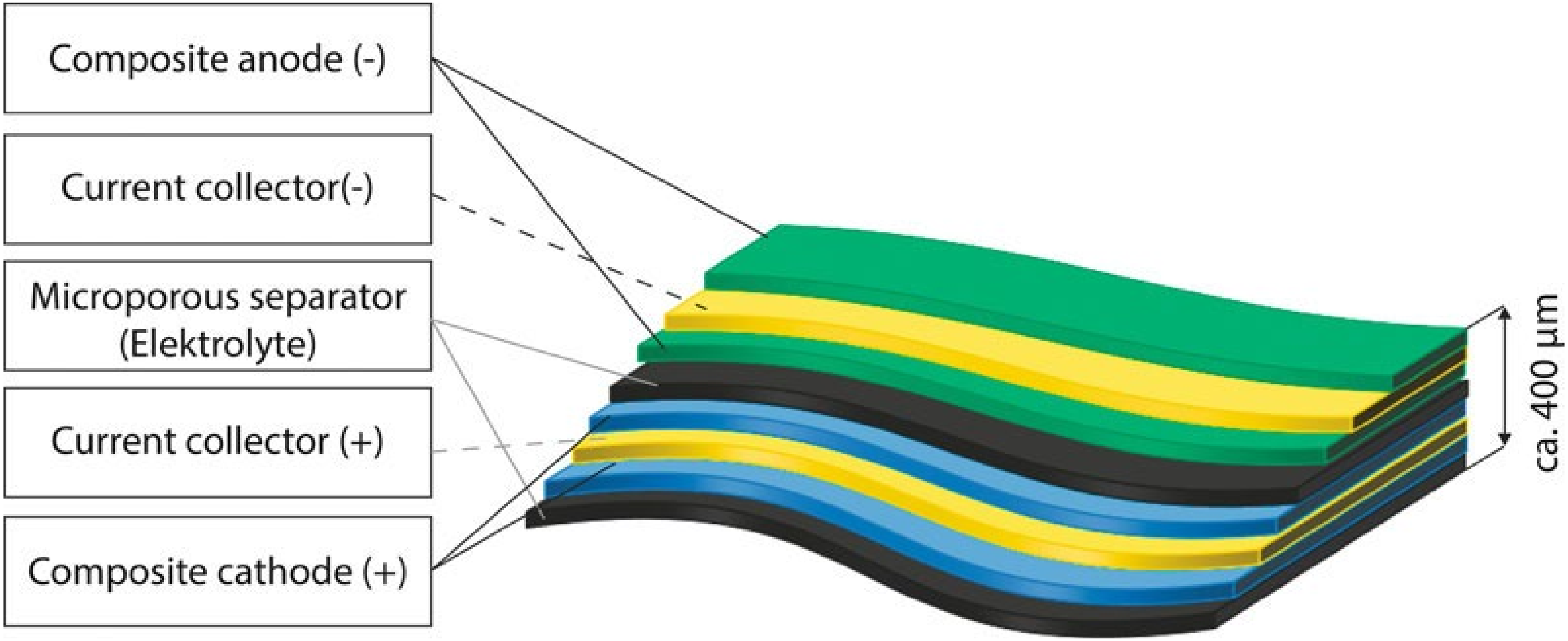

- Slurry coating on current collectors (metal foils)
- Assembly of sheets

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) 1M $LiPF_6$ in EC:DMC (1:1)	7[3] 10[3]	1.3[7] 1.3[7]	4.5[6] > 5.0[3]	Flammable
Ionic liquids	1M LiTFSI in EMI-TFSI 1M $LiBF_4$ in EMI-BF_4	2.0[15] 8.0[15]	1.0[15] 0.9[16]	5.3[15] 5.3[16]	Non-flammable
Polymer	LiTFSI-P(EO/MEEGE) $LiClO_4-PEO_8$ + 10 wt % TiO_2	0.1[24] 0.02[26]	< 0.0[24] < 0.0[26]	4.7[24] 5.0[26]	Flammable
Inorganic solid	$Li_{4-x}Ge_{1-x}P_xS_4$ ($x = 0.75$) $0.05Li_4SiO_4 + 0.57Li_2S + 0.38SiS_2$	2.2[28] 1.0[30]	< 0.0[28] < 0.0[30]	> 5.0[28] > 8.0[30]	Non-flammable
Inorganic liquid	$LiAlCl_4 + SO_2$	70[20]	-	4.4[20]	Non-flammable
Liquid organic + Polymer	$0.04LiPF_6$ + 0.2EC + 0.62DMC + 0.14PAN	4.2[38]	-	4.4[38]	Flammable

Chem. Mater. 22 (2010) 587-601

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

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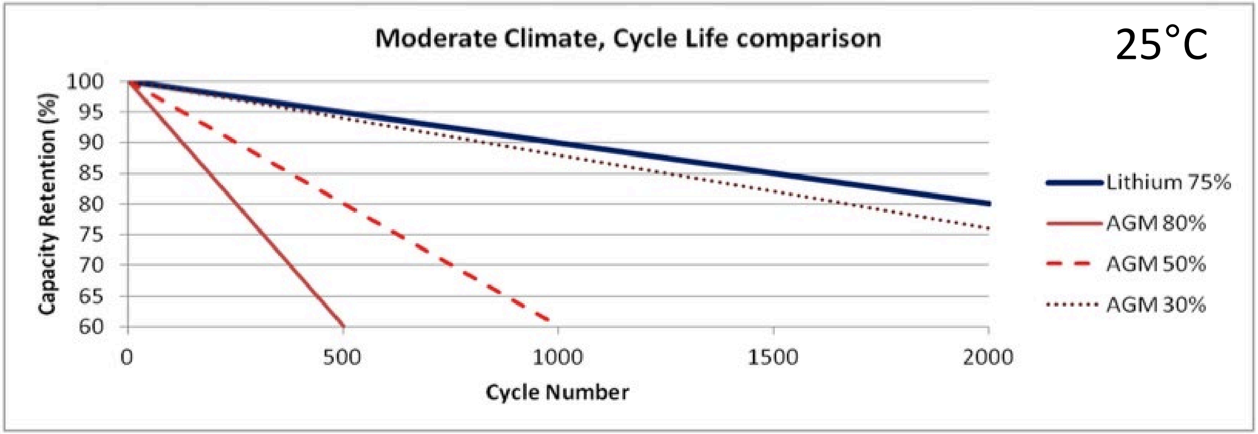
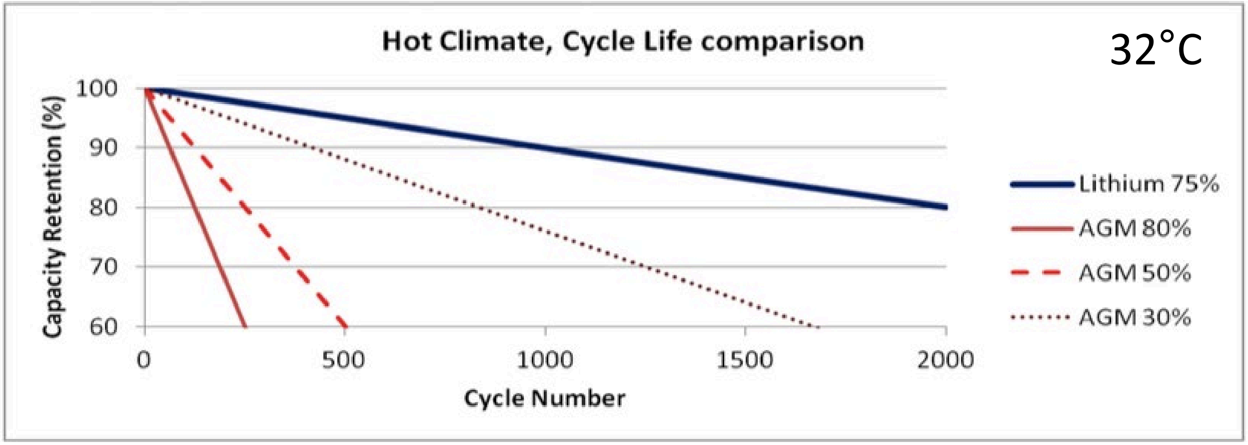
	Flooded lead acid	VRLA lead acid	Lithium-ion (LiNCM)
Energy Density (Wh/L)	80	100	250
Specific Energy (Wh/kg)	30	40	150
Regular Maintenance	Yes	No	No
Initial Cost ($/kWh)	65	120	600[1]
Cycle Life	1,200 @ 50%	1,000 @ 50% DoD	1,900 @ 80% DoD
Typical state of charge window	50%	50%	80%
Temperature sensitivity	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)	