Energy Storage

2nd lecture: Electrochemical Storage - Batteries

Electrochemical Storage

Chemical Energy Storage:

Electricity → some storage material → electricity

The storage material can be a fuel.

Electrochemical Storage: the "→" parts are electrochemical reactions AND the storage material is not a fuel (In this way, Hydrogen-based energy storage is not electrochemical, but chemical, because the storage material is a fuel).

Battery Types

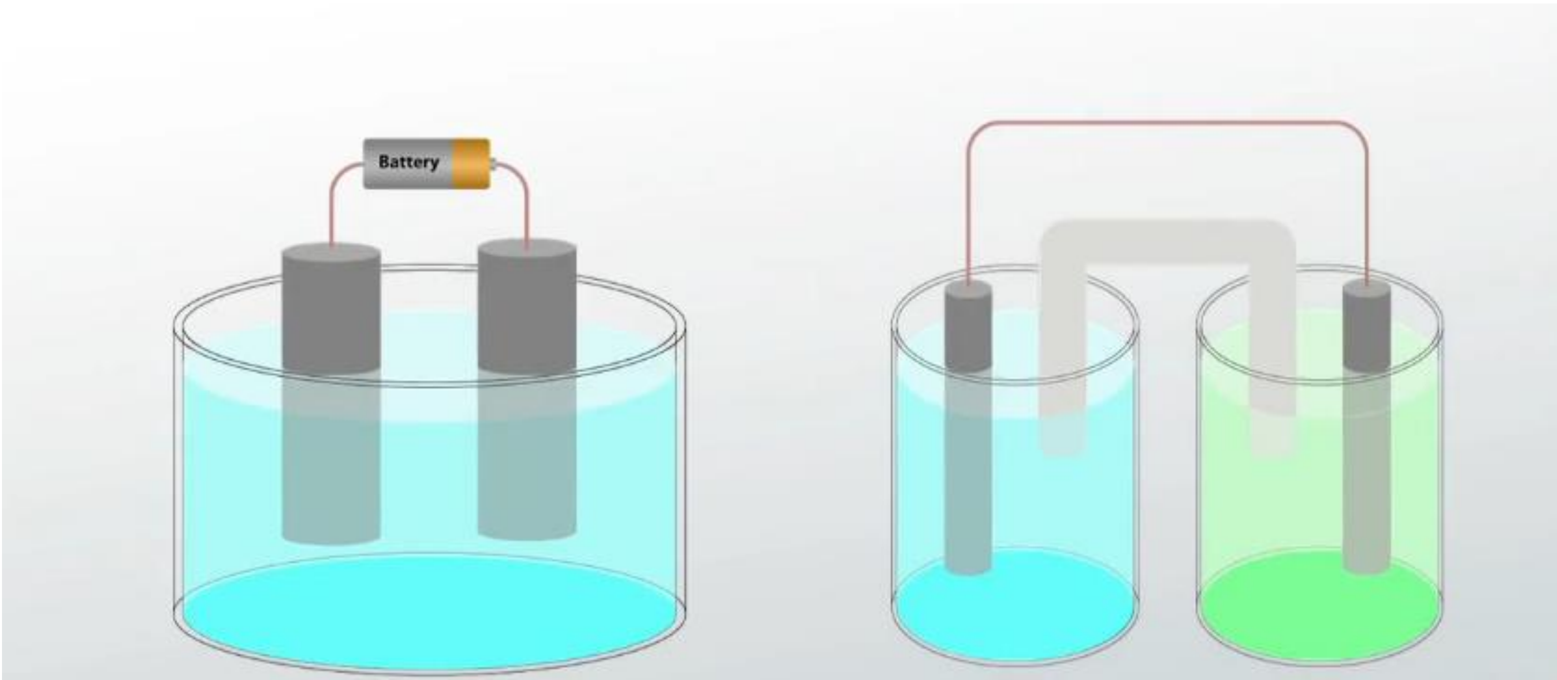
- Chargeable/reusable …. These are the real storing devices
- Non-reusable batteries, not real storage devices, can be used only once.

In English, both groups are batteries; in some languages, they have different names.

Battery Types

- Acidic lead batteries
- Nickel batteries
  - Nickel-Cadmium
  - Nickel-Metal Hydrid
- High temperature / molten electrode batteries
  - Sodium-Sulphur (NaS)
  - Sodium-Nickel Chloride (ZEBRA)
- Lithium-ion
- Flow/Redox

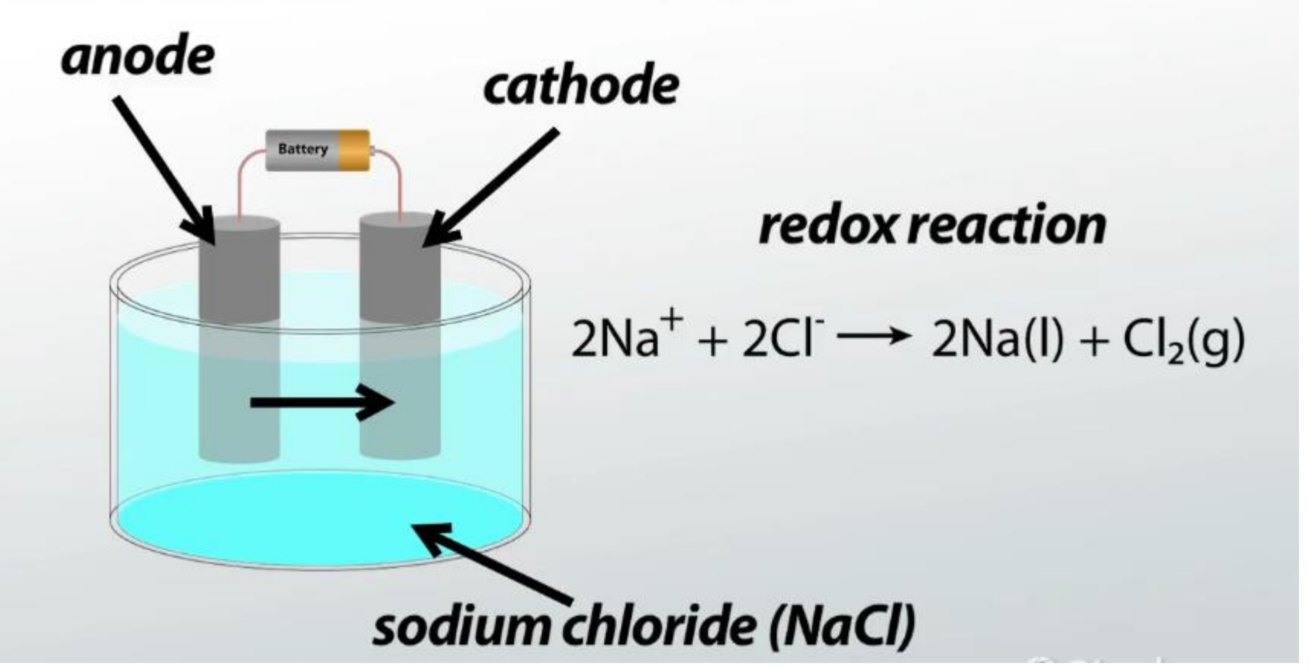
Elektrochemical cells



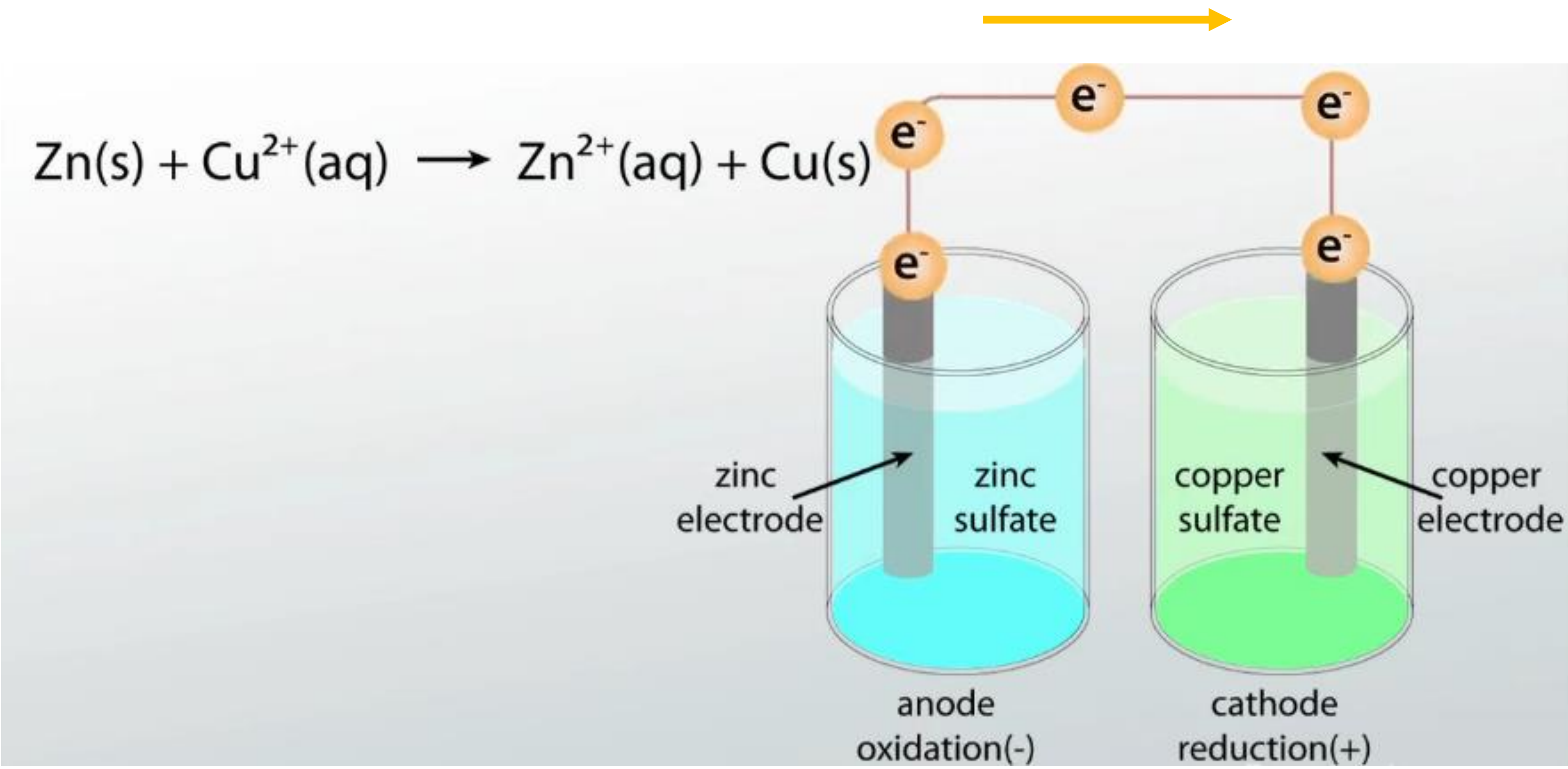
Electrolitic ……………………..Galvanic
For charge………………………for discharge

Képek:study.com

Electrolitic

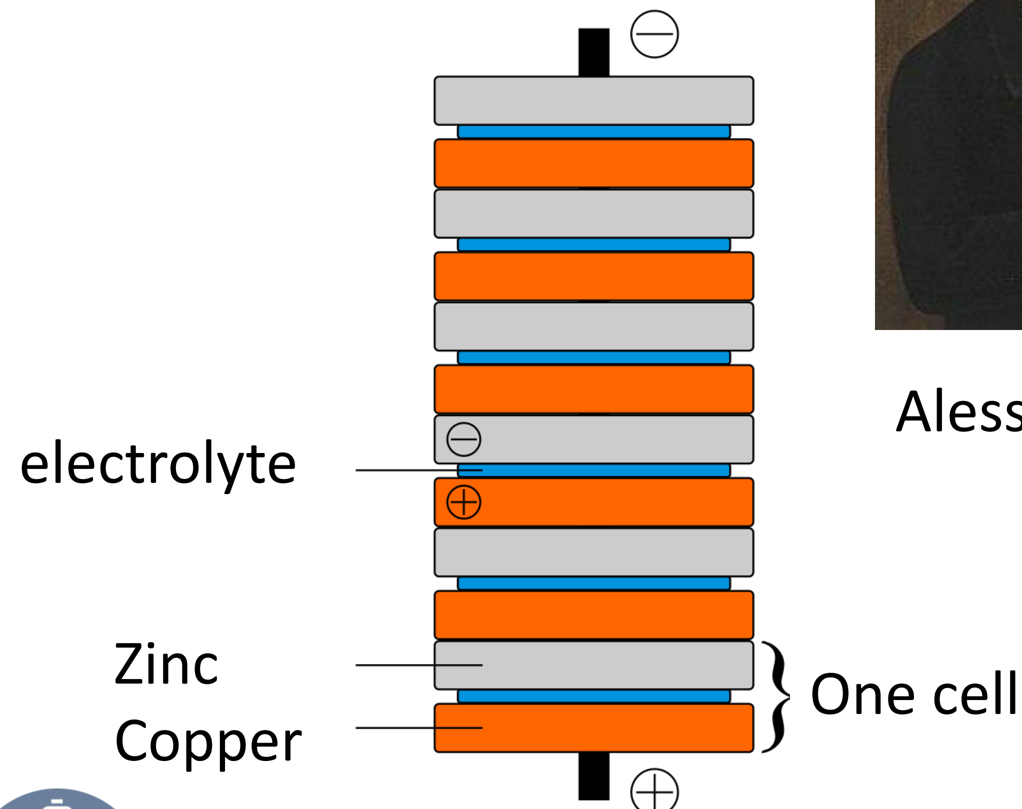


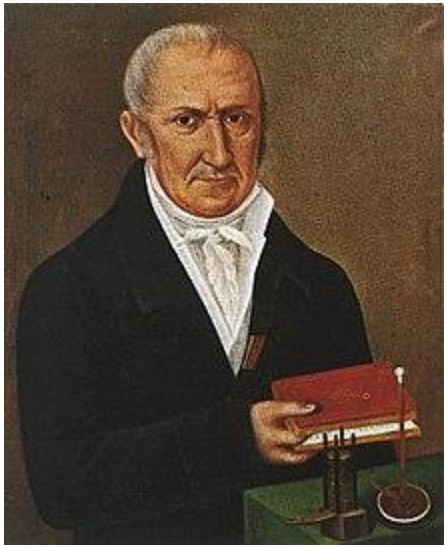
Galvanic



$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$
e⁻
zinc electrode
zinc sulfate
copper sulfate
copper electrode
anode oxidation(-)
cathode reduction(+)

Simple battery





Alessandro Volta

Luigi Galvani

Simple battery

olta

Luigi Galvani

Batteries

- Storage capacity is usually given is storable charges (Ah; Amper*hours), instead of energy (kJ, kWh), except for BIIIIIG batteries. It is not a fix value, depends on the load on the battery.
- For comparison, specific stored energy or specific power (kWh/kg, kW/kg) are given.

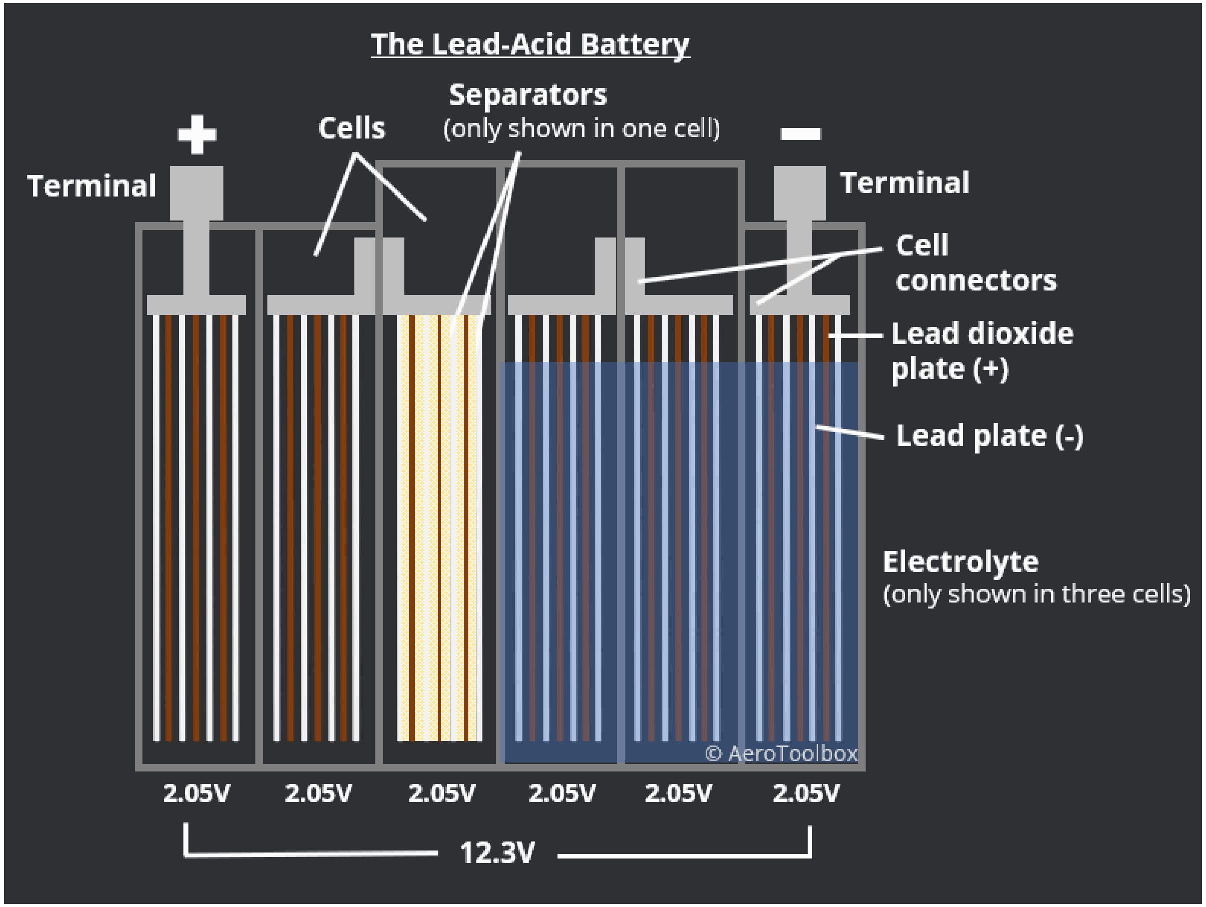
Single-use batteries

- Carbon/Zinc, most traditional, electrolyte is ammonium-chloride. Best in price! Nominal voltage/cell: 1,5 V.
- Mangane-dioxid/zinc with gel-like potassium-hydroxide electrolyte (alkali, not acidic!). More power than for Carbon-Zinc, but higher cost! 1,5 V/cell.
- Zinc/air with water as electrolyte. Zn+oxygen from air + water to ($Zn(OH)_2$). Mostly used as button-sized battery (35-600 mAh) , 1,4 V.
- Lithium-metal battery (mostly lithium/ mangane dioxide); with lithium salt electrolyte in some organic solvent. Powerfull, long-life, high price, 3V. A version ($Li\text{-}FeS_2$) can have 2.5 longer lifetime, 1.5 V.
- Lithium-thionil-chloride ($SOCl_2$ – $LiAlCl_4$ -$NbCl_4$), 3,5 V. For application which requires very low (mA or below) current; lifetime can be even 40 years.

And now, the real (rechargeable) batteries….

Acidic Lead battery

Has been in market for more than 150 years, known as traditional car-battery.



Inexpensive, can be charged/discharged several times!

Acidic Lead battery

Problems – parasitic reactions, causes losses and/or permanent damages

- Gas production (hydrogen, oxygen), causes loss of water
- Corrosion: lead and its oxide can react with the electrolyte even in unloaded state
- Growth of Lead-oxide layer – can separate the electrode and electrolyte
- Dissipative heat (general problems for all batteries)
- Cannot be discharged in 100%

Nickel-based batteries

- Nickel-cadmium
- Nickel-metal hydrides

- Alkalic electrolytes
- Cell voltage is smaller, than for acidic ones
- Better chemical stability, they can be charged/discharged several times
- Can be used in low temperature

Nickel-cadmium batteries

Problems

- For long use, unwanted chemical reactions cause contamination/recrystallization of electrodes.
- Can be charged/discharged easily, but simple measurement of voltage is not enough to monitor these processes.
- Not very sensitive for overcharging.
- Can be charged in any condition, not only in fully uncharged state.

Nickel-cadmium batteries

This type cannot be sold for the public since 2016 (USA, EU), except for medical purpose. In the EU, producers has to collect and recycle these batteries.

Nickel-hydrid batteries

Cadmium is replaced with some other metal.

Negative: $Me(H)+OH^{-} \leftrightarrow Me+H_2O+e^{-}$

Positive: $2NiO(OH)+2H_2O+2e^{-} \leftrightarrow 2Ni(OH)_2+2OH^{-}$

Hydrogen forms on the negative side, but not as gas. Atoms can diffund to the metal. Therefore the metal has to be some compound, good for interstitial hydrogen storage, like AB5 (from nickel, cobalt. Mangane, aluminum, lantana, prazeidymium, neodymium) or AB2 ötvözetek (zirconium, vanadium, mangane. titane).

Example (AB5) $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35}$

One A (Li) and 5 others)!

Nickel-hydrid batteries

- Forlonger life, voltage has to be kept in the 0,85 V (fully discharged) and -1,42 V (fully charged) condition.
- Life-time (in cycle number) is smaller than for the one with cadmium.

Comparison

	Lead acid	Ni-Cadmium	Ni-hydrid
Work range	20-45 ^{0}C **	-50-70 ^{0}C-ig	-30-75^{0}C
Max. voltage.***	0,84-2,1 V****	1,2 V	1,2 V
Max. cycle number	20-1000*	2000	180-2000
capacity	Size-dependent	size-dependent (600 mAh, AA)	size-dependent (2500 mAh, AA)
Specific energy	25-40 Wh/kg	40-60 Wh/kg	60-120 Wh/kg
Specific power	180 W/kg	150 W/kg	250-1000 W/kg
Self-discharge on room temperature	3-20%/month	10-20%/month	20% (first day), later 10%/month
Storage efficiency	50-95%	70-90 %	66-92%
lifetime	5 year (33^{0}C); 10 year (25^{0}C)	Longer than lead-acid	<5 year

*depends on the level of discharge ** optimal value *** for a cell
****depends on the concentration

Lithium-ion batteries

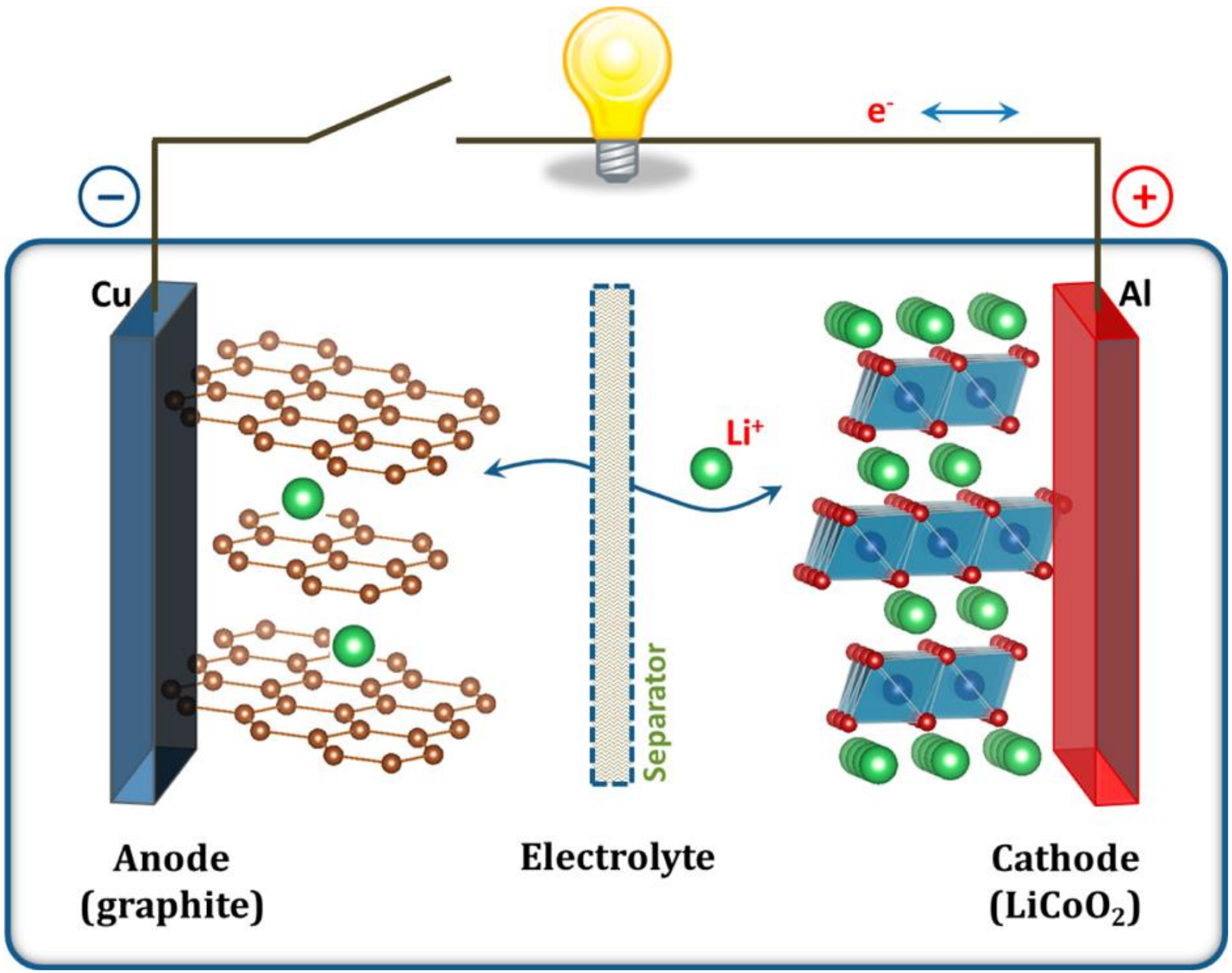
Collective name for all batteries, containing Lithium electrode. Li(metal) are for single use, Li-ion and Li-polymer are for rechargeable application.

Names: lithium-ion, Li-ion or LIB (B, as battery)

Electrodes: metal ot metal-oxide doped with Li on one side (like Cobalt-Oxide+Li), Graphite on the other side.

Electrilyte: usually liquid, an organic solution of a Li-salt, like $LiPF_6$, $LiBF_4$ or $LiClO_4$ in ethylene-carbonate, dimethyl-carbonate or diethyl carbonate solutions. Solid (ceramic) electrolytes are also exist.

Lithium-ion batteries



Types

Code	cathode	Anode	Cell-voltage (V)	Energy density (Wh/kg)
LCO	$LiCoO_2$; layered oxyde	Graphite	3,7–3,9	140
LNO	$LiNiO_2$; layered oxyde	Graphite	3,6	150
NCA	$LiNi_{0,8}Co_{0,15}Al_{0,05}O_2$; layered oxyde	Graphite	3,65	130
NMC	$LiNi_xMn_yCo_{1-x-y}O_2$; layered oxyde	Graphite	3,8–4,0	170
LMO	$LiMn_2O_4$; spinell	Graphite	4,0	120
LNM	$LiNi_{0,5}Mn_3O_4$; spinell	Graphite	4,8	140
LFP	$LiFePO_4$; olivin	$Li_4Ti_5O_{12}$	2,3–2,5	100

	NMC	LMO	NCA	LFP	LTO
Advantage	•Generally good •High power and capacity •Thermally stable •Can work on high voltage	•Low price (mangane is cheap) •Thermally stable •High power	•High power and capacity •Can endure several cycles •Long life (in time)	•Thermally stable •Can endure several cycles •High power •Low price	•Thermally stable •Can endure several cycles •Fast discharge •Chemical stability
Disadvantage	•Legal problem in several countries (patent-related)	•Very low cycle numbes •Low capacity	•Bad thermical stability in fully charged states •Storage capacity is bad in the 40–70 °C range	•Low energy density	•High price (titane) •Low cell-voltage •Low energy density

Overcharge

Copper dissolution

High temperature – thermal degradation

Flammable gases

Size

- From very small, like AAA with capacity below 1 Ah.
- 55 mm diameter, 220 mm long rods, 40 Ah capacity.
- Same with a prism (220 mm*210 mm*11 mm)

Lifetime

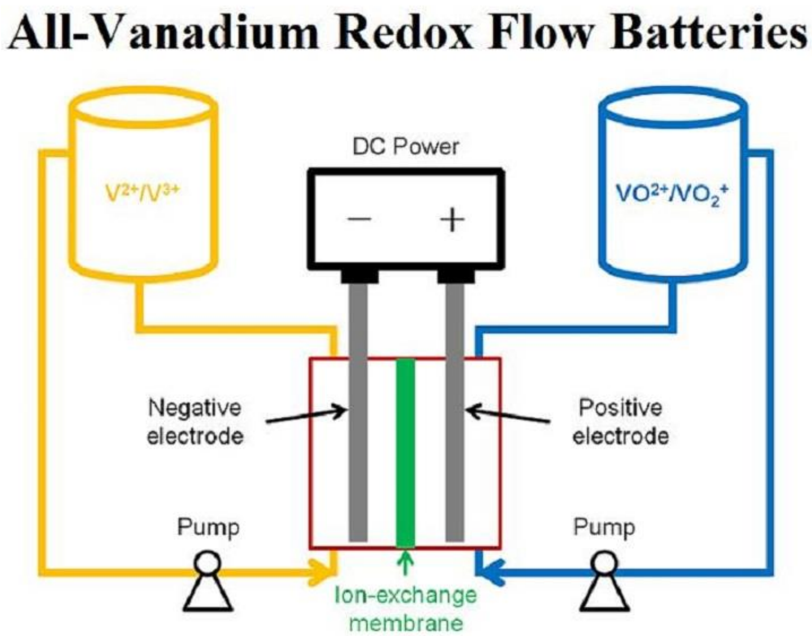
Defined as the time or cycle number, where the storage capacity drops to the 80% of the initial value $\rightarrow$ SECOND LIFE BATTERIES

Biggest problem

Limited source of Li!!!!

Redox flow batteries

Redox flow batteries



Vanadium Redox Flow Battery (VRB)

10 kW; 30 kWh

Two eletrolytes are separated by a membrane (like 2 M sulphuric acid, 1,5 M vanadium sulphate); electrodes are similar in both side (like graphite). Cell voltage: 1.4 V

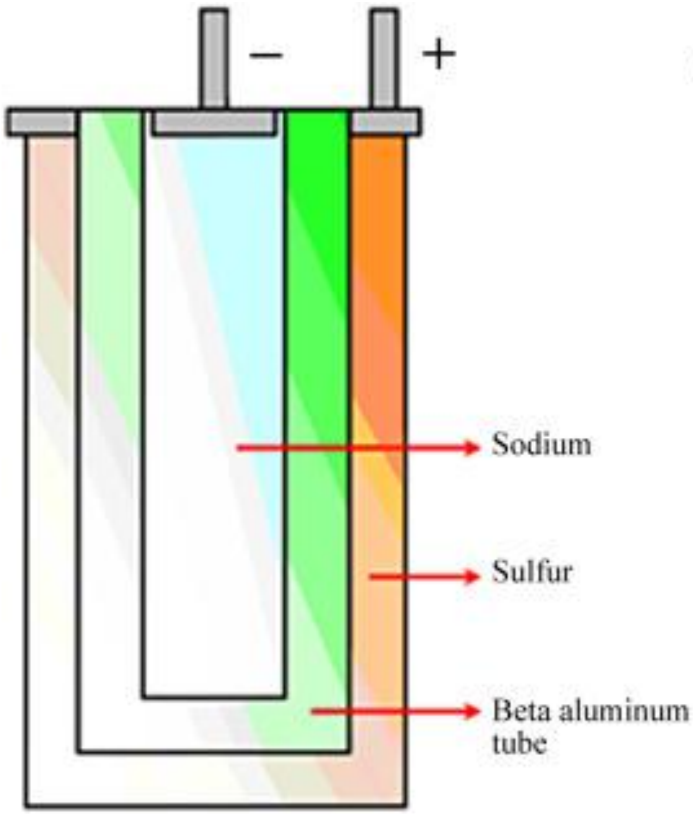
Problems

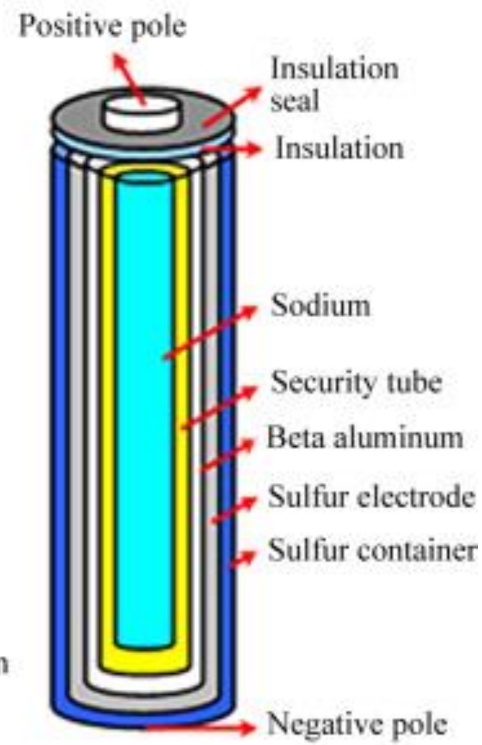
- It is like a small chemical factory!
- Vanadium-mining???? What????

Advantages

- Lifetime 20-40 year or 13,000-100,000 deep cycle without membrane replacement.
- From standby mode it can be ready in 0.001-0.02 s.
- Total discharge time is 4-5 h. Direction (charge/discharge) can b switched at any time.
- Can be fully discharged.
- Minimal self-discharge, in unconnected state it can store energy for decades.
- Can be left in fully discharged state for years.
- Easy to install, no emission, no fire or explosion, fully recyclable.

Sodium-Sulphur battery



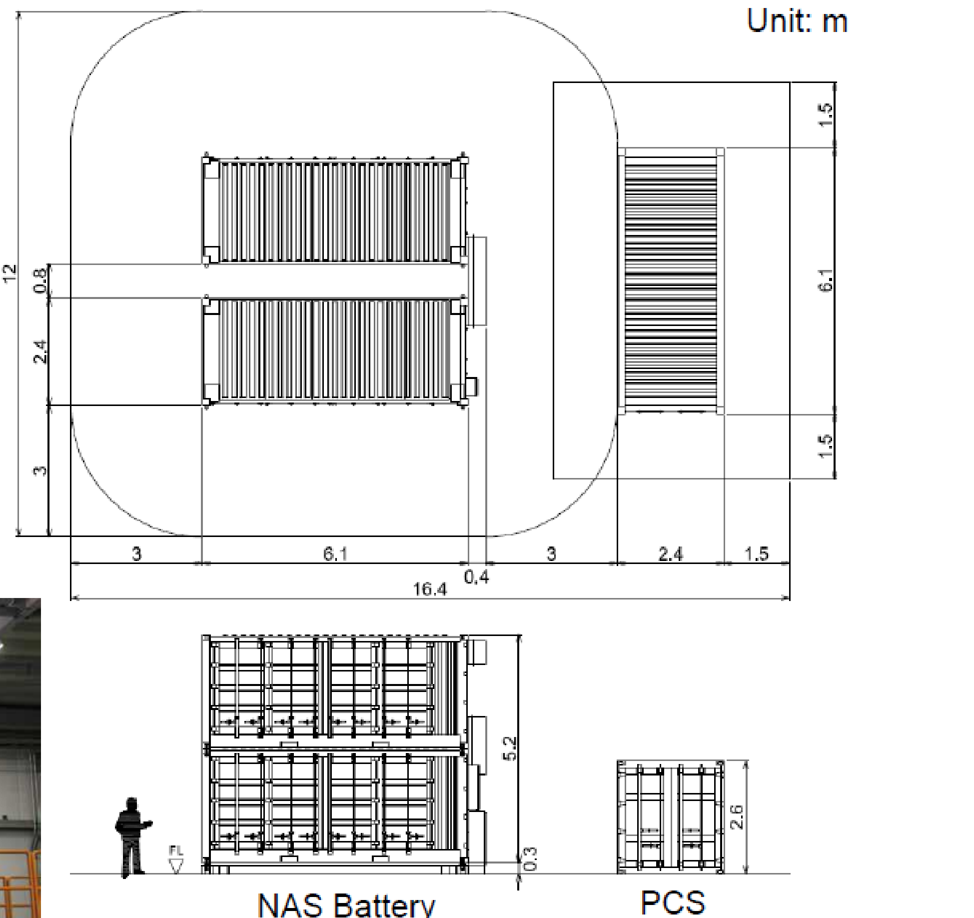


- Molten electrodes, solid electrolyte.
- Needs ≥300 °C, during charge/discharge it is provided by dissipation. 32 kW heating needed!
- Commercial version: rod, diam. 90 mm, length 520 mm, 1,2 kWh nominal capacity (per rod). 2 V nominal voltage (per rod).

Real ones

1,2 MWh, 200 kW or 100 kW charge/discharge , i.e. 6/12 hours.

Example of 800kW NAS Battery layout



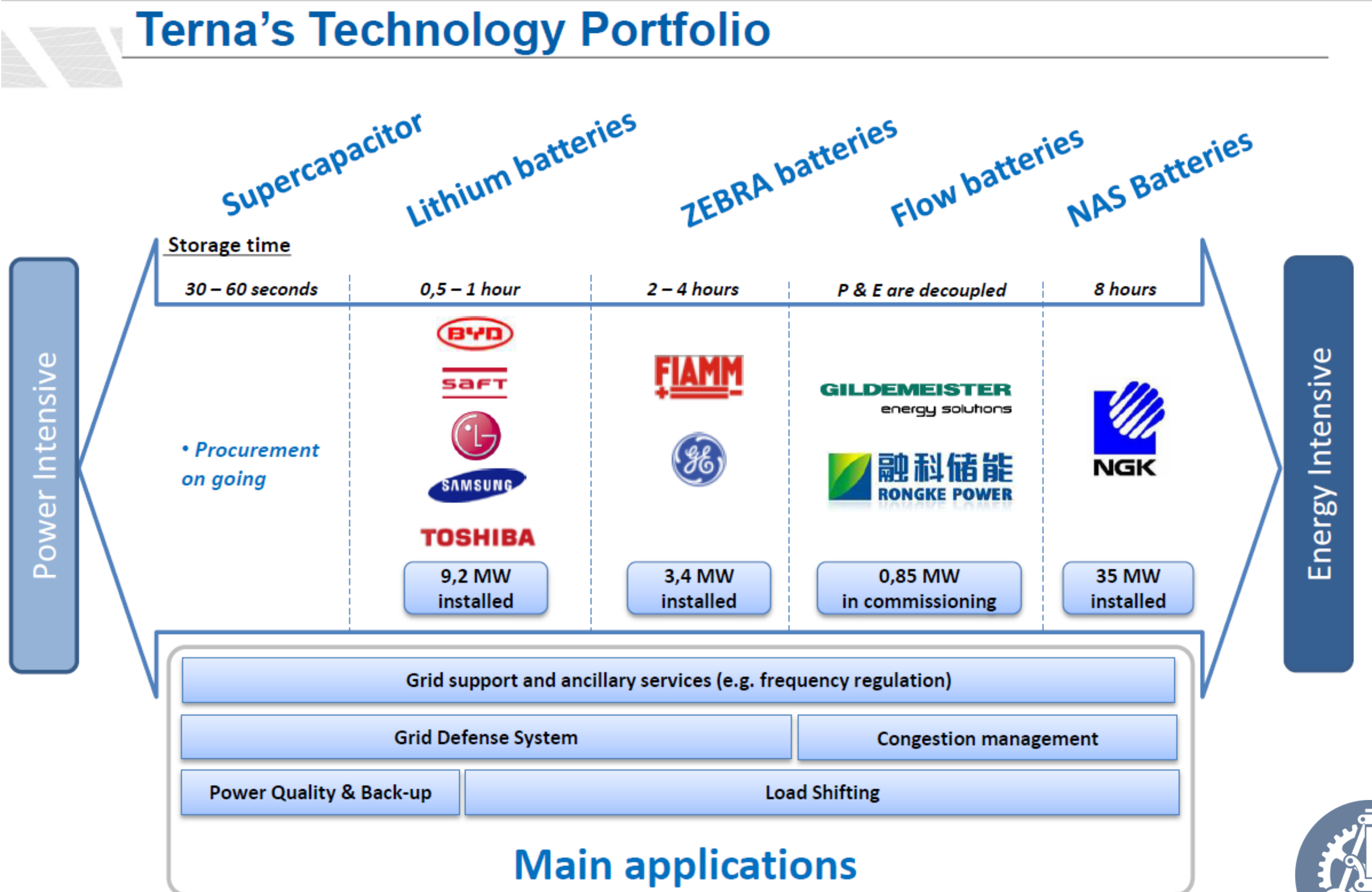
NaS (TERNA)

Data sheet

Battery Technology	NAS (Sodium/Sulfur)
Rated Power	12 MW
Gross Energy Capacity (discharged)	90 MWh
Net Energy Capacity (discharged)	80 MWh
Net Round-trip AC efficiency (*)	75%
Storage time (from 0% to 100%SOC to rated power)	10 h
Response time	12 MW/sec
Operating battery temperature	305-350 °C

* *Round-trip AC: related to a complete daily reference cycle*

TERNA project (Italy)



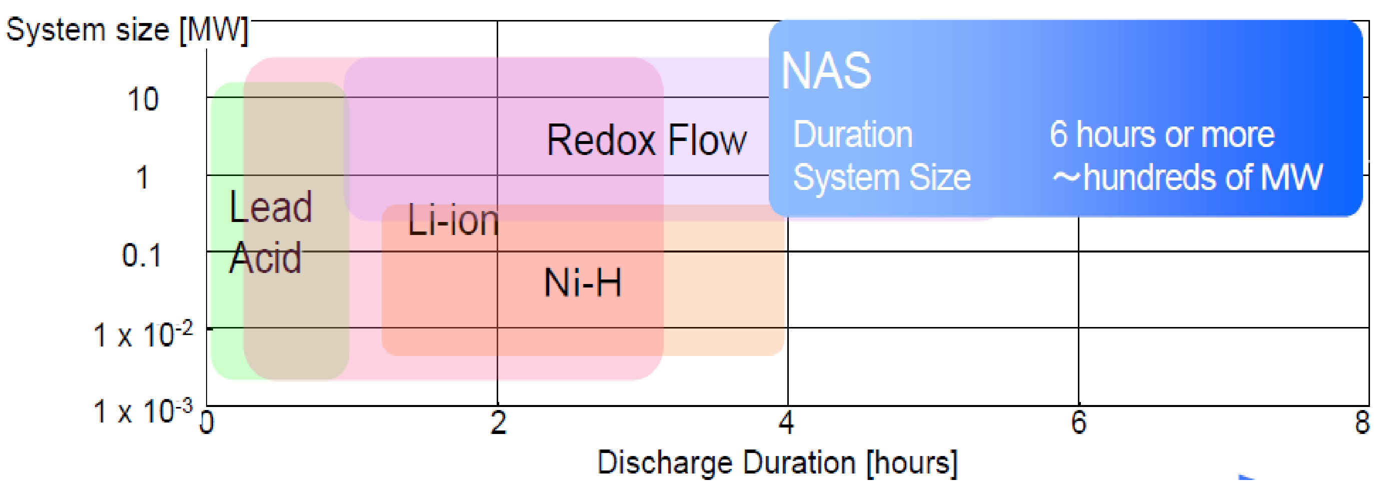
Comparison

	Li-ion	Redox flow	NaS
Work range	0-45 ^{0}C*	10-40 ^{0}C (definitely not above 60 ^{0}C)	300-350 ^{0}C***
Max. voltage.***	2,5 -4,35 V/cella	1,15-1,55 V/cell	2 V/cell
Max. cycle number	400-1200	12000-14000	2500-4500 (usually one cycle/day)
capacity	-	-	-
Specific energy	100-300 Wh/kg	10-20 Wh/kg	100-200 Wh/kg
Specific power	250-350 W/kg	1-10 W/kg	1-50 W/kg
Self-discharge on room temperature	0,35% - 2,5% per month (depends on charge level)	1-2 day; „infinite”**	Caused by heat loss, 0-20%/day
Storage efficiency	80-95%	75-80 %	70-90%
lifetime	2-5 year	20-30 year	10-25 year

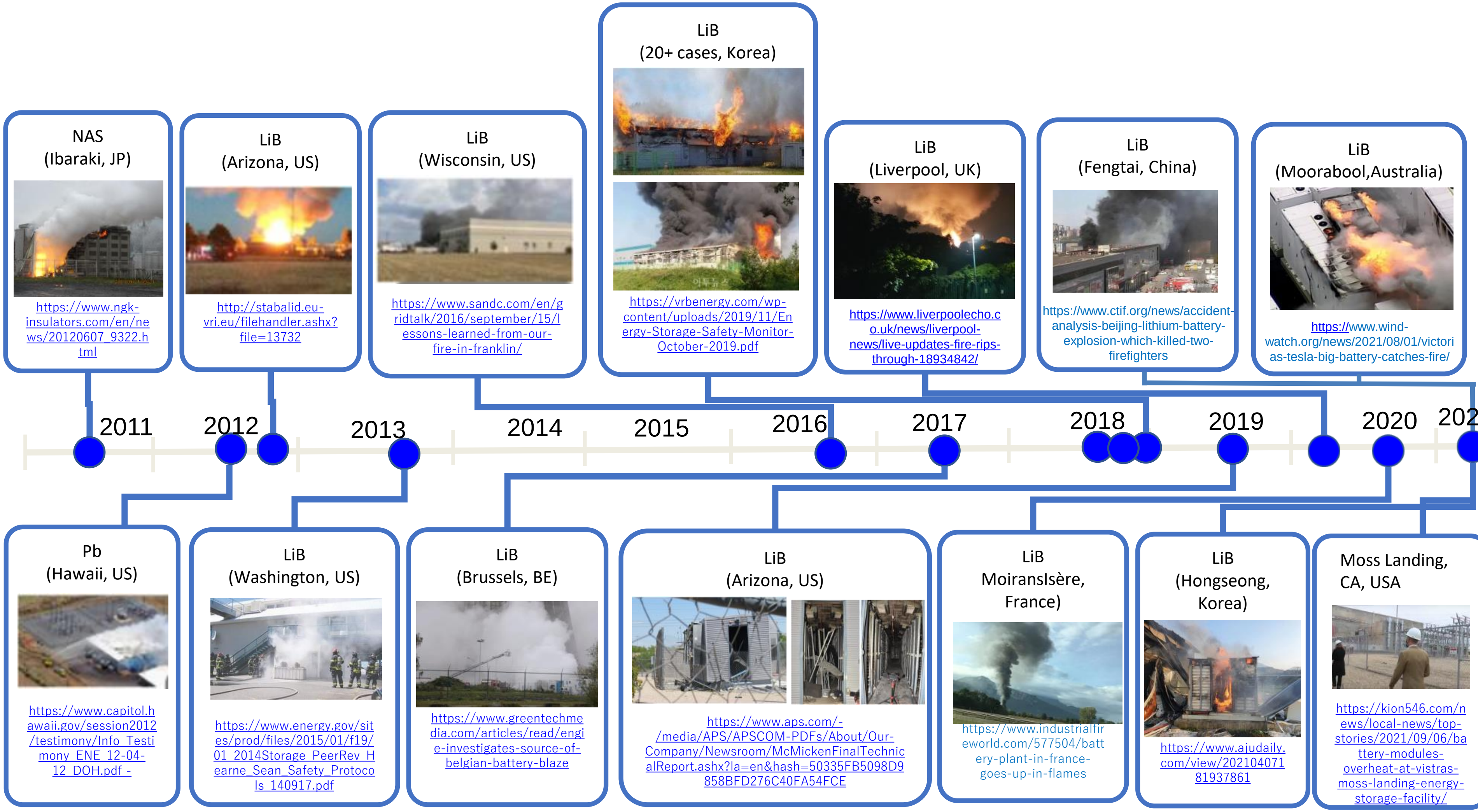
* works, but cannot be charged; ** no pump, no self-discharge, but response time will be very slow *** internal temperature (external is not specified)

Application

		Lead-acid	Li-ion	Redox flow	NaS
Size		medium	medium	Small or big	big
compactness		big	medium	big	small
lifetime		long	medium	long	long
price	Ár/kW	high	Alacsony	High	medium
	Ár/kWh	medium	high	high	low



Grid scale battery fires since 2011



Summary

Needs inverter for most application (true for all batteries).

Usually big self-discharge (loss of stored energy in unloaded condition), therefore they are not good for long storage (like seasonal one) (except redox-flow, but the availability of vanadium is low).

Special batteries for special need!

Speciális feladatra speciális akkumulátor

Thanks for your attention