Future in Electrochemical Storage

Anne de Guibert

Energy Storage Global Conference – November 19, 2014 - Paris

Introduction: a set of obviousness

- In our present life, we expect to have energy (electricity) available everywhere at any time
- Storage is necessary when it is not possible to remain plugged to a 100% reliable grid:
  - Electronic mobile devices (off-grid by nature)
  - Green mobility (Evs, HEVs…)
  - Weak grids (remote places, too much intermittent energy)
- Needs are increasing in all three domains plus new ones:
  - "Connected objects", big data centers needing high reliability

Scope of the presentation

- Answer to the need is storage in electrochemically rechargeable batteries in the majority cases:
  - Batteries based on at least six different electrochemistries already in production
  - Plus development of redox flow, at the stage of numerous demonstration projects

- I will start from applications domains already given on the first slide and for each one address the present situation and foreseen evolution in terms of markets and new technologies

Battery technologies

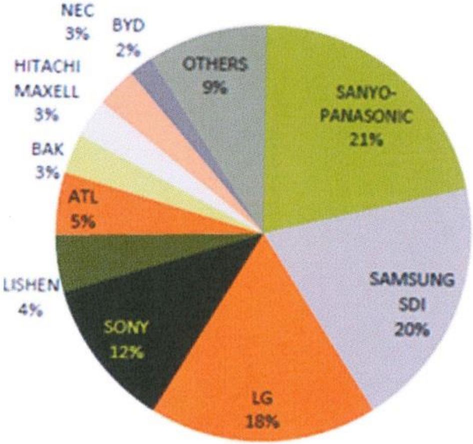
System	Characteristics (cell level)		Applications		
	Energy (Wh/kg	Cycle life (*)	Portable	Green car	Stationary
Lead-acid	25-35	70 (SLI) to 1000 (traction)	No	limited to SLI & micro hybrids	Yes
Ni-Cd	40-50	300-1000	limited	No	Yes
Ni-MH	55-75	300-1000	Yes	HEV	Yes
Li-ion	110-260	300-3000	Yes	HEV, PHEV, EV	Yes
Li metal- poly	130	1000	No	EV	Yes
Na-S	110	> 1000	No	No	Yes
Na-NiCl2	100-110		No	trucks	Yes

(*) number of cycles 80-100% DOD, room temperature or nominal temperature, low power

1. Portable applications

Energy for electronic mobile devices

- ☐ The market is continuously growing at a pace of 5-7 % per year. It is totally dominated by lithium-ion technology.
- ☐ The worldwide production will reach 4.5 billion cells in 2014
- ☐ The supply is 100% from Asia with a domination of Korean and Japanese companies manufacturing home or in China
- ☐ Expected life: 2-3 years



Source: Avicenne

Energy for electronic mobile devices: cells

- A mix of cylindrical cells (18650), prismatic hard case and pouch cells coexist according to application and manufacturer

Sony alloy negative

Ultra fast charge

Pouch cell

Saft range

- Cells are small (<4 Ah for cylindrical, 20 Ah max for flat cells): safety is not an issue as long as cells are manufactured with care

Technology evolution

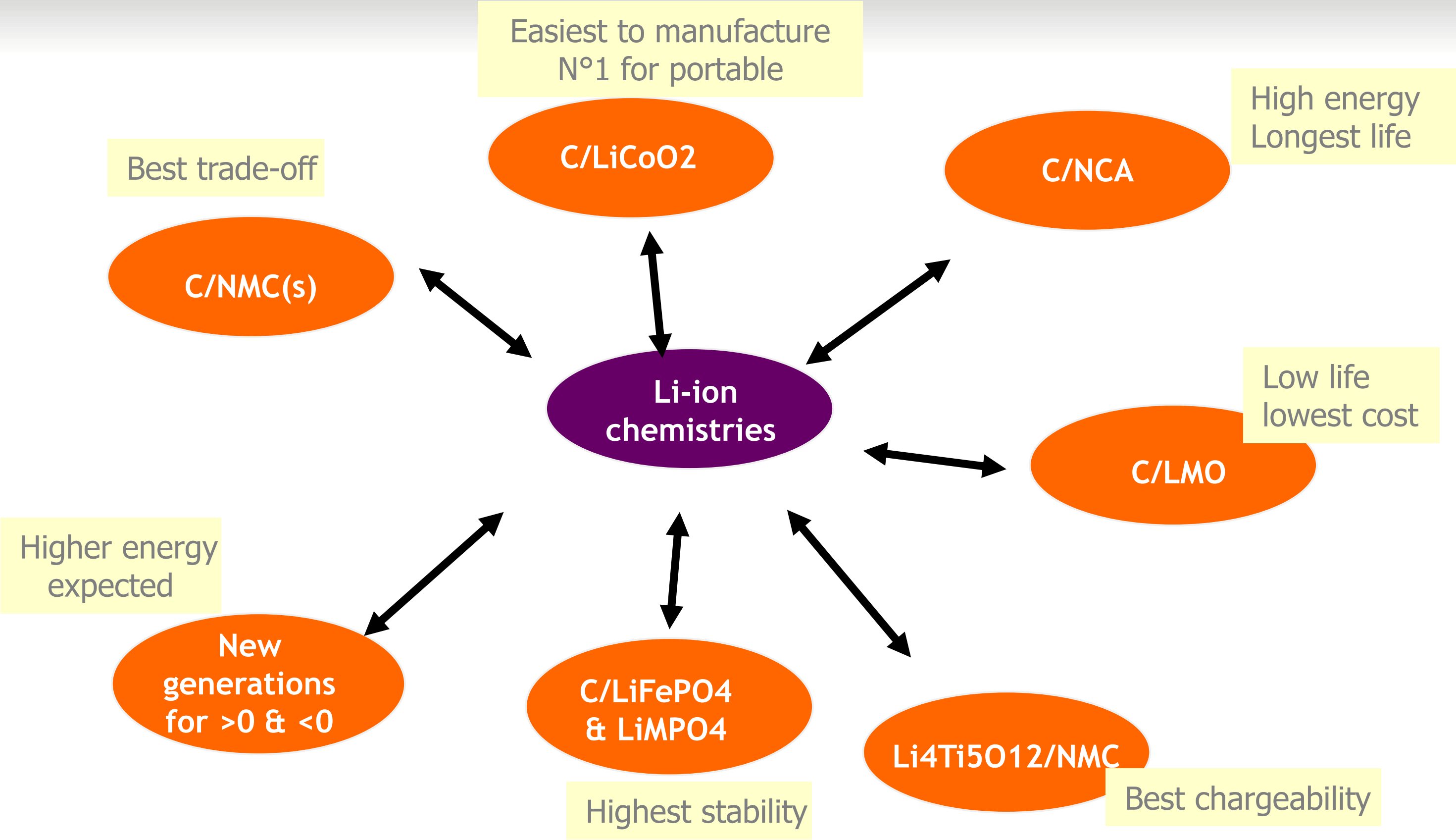
- Global demand: more energy on the same volume. Electrical consumption of each electronic circuit decreases but the number increases faster

- The highest specific energy reached up-to-now: **274 Wh/kg** at the cell level (optimized for low power for computer, proposed by a Japanese company)

- It is the first cell of a new generation: it includes silicon in the negative electrode, announced since 3 years. Modest introduction: 2-3 %

- At least in the next eight years Li-ion should remain THE reference with materials and process continuous evolution

Li-ion subsystems



Li-ion chemistries

C/LiCoO2

Easiest to manufacture
N°1 for portable

C/NCA

High energy
Longest life

C/NMC(s)

Best trade-off

C/LMO

Low life
lowest cost

New generations for >0 & <0

Higher energy
expected

C/LiFePO4 & LiMPO4

Highest stability

Li4Ti5O12/NMC

Best chargeability

New generations for >0 & <0

Challenges to 300 Wh/kg

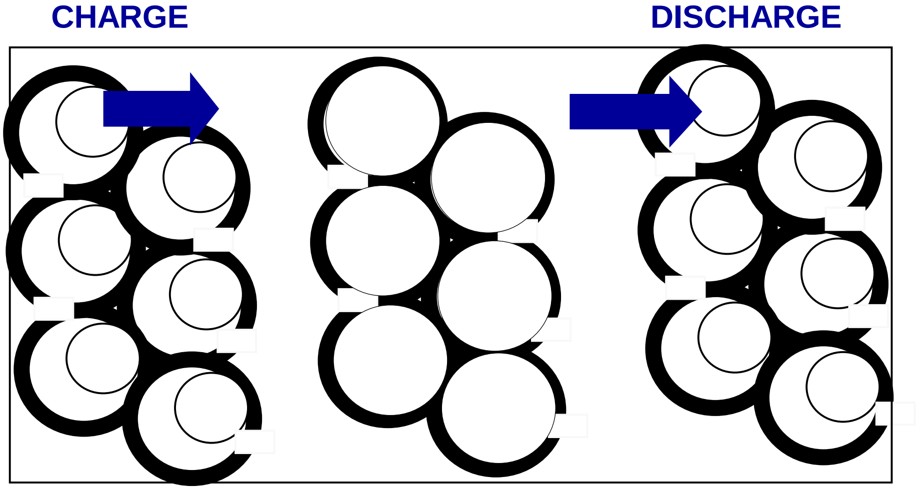
- ☐ Silicon based negative active material (composites, blends, oxides, nanostructures…
  - ☐ 4000 mAh/g possible in theory,
  - ☐ Short life (100 cycles) due to monstrous swelling

- ☐ Other advanced positive active materials with high voltage (> 4 V) and/or high capacity (> 200 mAh/g) such as HE NMC

- ☐ Association Li-ion battery, micro fuel cell as range extender, plus fast charge. Today, not yet out from universities

New negatives: solving the poor cycle life issue

- Si or Sn swell during lithium insertion (charge)
- Consequence is materials desaggregation, conductivity loss, and need to reform passivation layer on the negative at each cycle
- Research programs everywhere in the world propose possible solutions

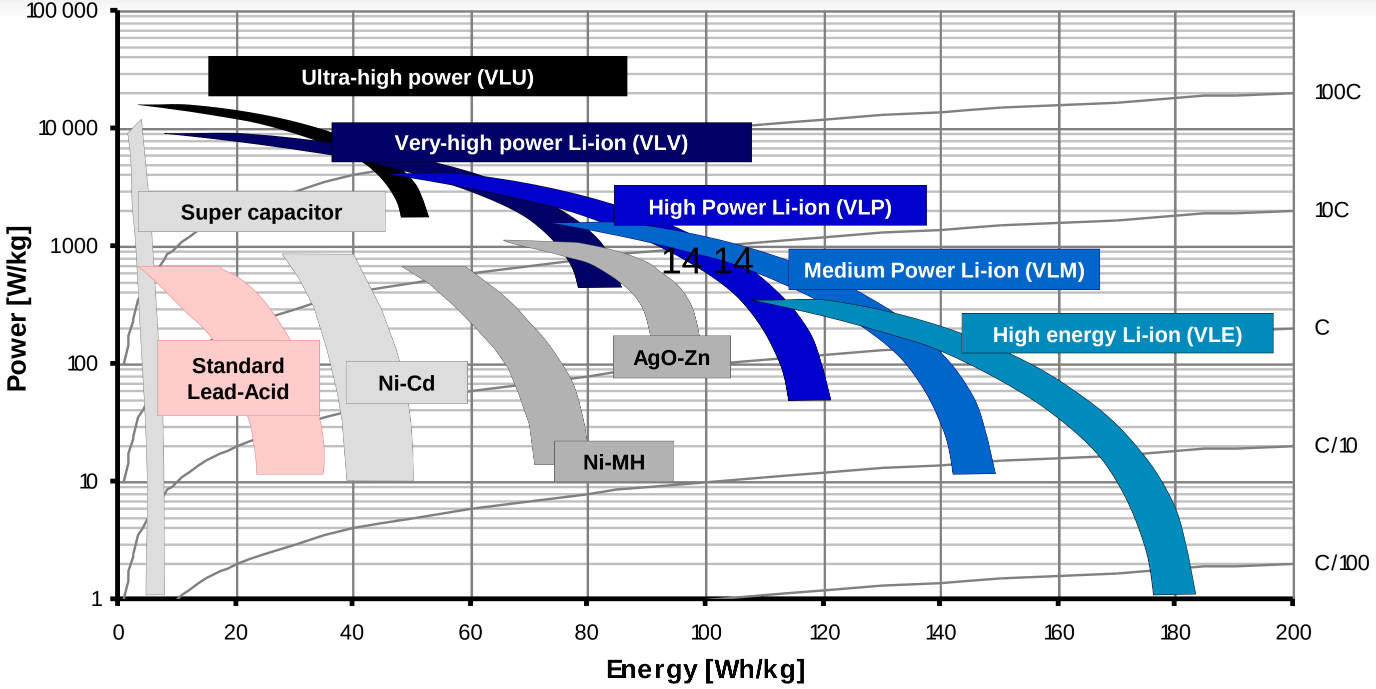


Green mobility

Li-ion: the main solution for vehicles electrification

Type of vehicle	Type of battery	Energy range (kWh)	Car makers
Stop-and-start	Lead-acid w/wo supercapacitor	< 1	All
HEV	NiMH, High power Li-ion	1-2	Toyota (Prius)
PHEV	Mid power Li-ion	4-8	Volvo, BMW, Mercedes, Kia
EV	High energy Li-ion	25-35	Renault/Nissan (Leaf, Zoé), Bolloré, Chevy Volt, Tesla

Lithium-ion from energy to power: from HEV to EV



Ragone diagram

The road to electrification

- Stop-and-start principle:
  - Fuel economy: motor is stopped when the vehicle is idle
  - Small consumption decrease, but envisaged on the majority of new cars because low additional cost

- Lead-acid batteries (alone or in association with supercapacitors) are winning the battle of stop-and-start through substantial remediation to weaknesses of SLI batteries:
  - Improved positive active mass for cycling
  - “Lead-carbon” negative for longer life
  - Sometimes cylindrical cells

- **Small decrease, many cars: economically important for Pb**

- But it is likely that lead-acid will not go beyond: they dislike too much to operate at partial SOC

HEV & PHEV

- The industrial history of HEV began with Toyota Prius and Ni-MH batteries:
  - 17 years ago
  - More than 1.5 million vehicles sold
  - 3 generations of vehicles and batteries
  - Progressive improvement of the ratio power/energy of the battery

Toyota Ni-MH battery Gen2

- A new generation is being introduced by Toyota:
  - Plug-in vehicle with Li-ion battery (4,4 kWh)

Bolloré Blue car: innovation in utilization

1. Innovation in utilization (Autolib, Blue Cub')
2. Utilizes metallic lithium as negative active material

Technical characteristics:
. Energy 30 kWh
. Power 60 kW
. Specific energy 140 Wh/kg
. Autonomy 250 km
. Life: 10 years/ 1200 cycles
. Lithium polymer technology
. $LiFePO_4$ cathode

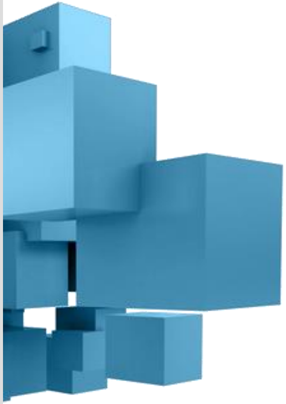
Available with a specific renting system:
. > 3000 cars in operation
. High investment, claim to be at breakeven in 2014

The 2020 generation of car batteries

- Lithium-ion is now the general choice

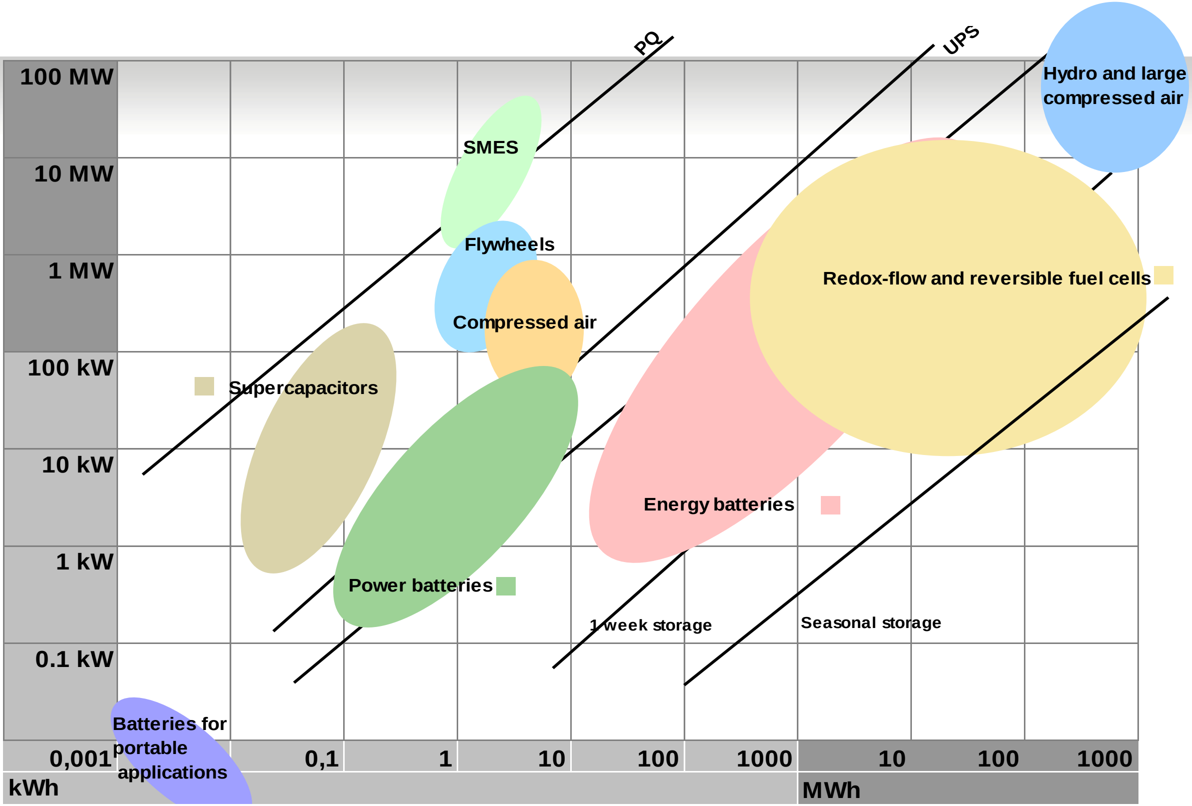
- The sub-system chemistry choice will be different from portable: the rationale is not the same
  - Increase of energy is a demand but cost of ownership is priority n°1
  - Decrease of the cost of positive active material is the most important target for the cell (cobalt is too expensive)
  - BMS and mechanics should simplified while maintaining safety

- Introduction of Fuel Cells vehicles (hydrogen) has been expected for many years and is supposed to come soon (Toyota 2015). At least where an hydrogen grid is available



3. Electrochemical storage for stationary applications

The various storage possibilities: energy and power



EC Document “Energy Storage : A key technology for decentralized power, power quality and clean transport” - 2001

Needs of stationary energy storage

- Stationary energy use in remote places exists already (e.g. outdoor telecom cabinets, oil and gas platforms). It uses lead-acid batteries for 90% and Ni-Cd, Ni-MH or Na-S for the rest

- The game is changing with the introduction of a large amount of intermittent electricity in the grid

- There is not yet a massive demand for storage associated with intermittent energy, but sufficient for testing some applications and preparing the ramp-up
  - Systems for the reliability of electricity supply in sensible plants or services
  - Autonomous storage for weak grids in islands
  - Individual or group of houses storage

- Electrochemical storage is one solution among others

- Low cost and high reliability are the key factors

Technologies for long duration storage

TECHNOLOGY	Hydraulic	CAES (*)	Batteries	Redox flow
Energy density	1 kWh/m^3 for a drop of 360 m	12 kWh/m^3 for a cavern at 100 bars	30 kWh/t (Pb) to 100 kWh/t (Li-ion)	33 kWh/m^3
Possible capacity	1000 to 100 000 MWh	100 to 10 000 MWh	0,1 to 40 MWh	1000 to 100 000 MWh
Possible power	100 to 1000 MW	100 to 1000 MW	0,1 to 10 MW	10 to 100 MW
Electrical efficiency	65 to 80 %	50%	60 to 90 %	70%
Existing installation	100 000 MWh 1000 MW	600 MWh	40 MWh 10 MW	120 MWh 15 MW
Cost (€/kWh, €/kW)	from 70 to 150 from 600 to 1500	50 to 80 400 to 1200	200 (Pb) to 500 (Li-ion)	100 to 300 1000 to 2000
Experience	very good ; more microturbines in the future	several experiments in the world	Pb, NaS, Li-ion	demonstration ; prototypes in operation

(*) CAES : compressed air energy storage

Remark : thermochemical cycles + turbines not included (long term)

Technologies for short duration storage

TECHNOLOGY	**SMES**	**Supercapacitors**	**Batteries**	**Flywheels**	**Compressed air bottles**	**Reversible hydrogen FC**
type of energy	***magnetic***	***electrostatic***	***chemical***	***mechanical***	***compressed air***	***fuel***
Energy density (without annex equipments)	1 to 5 Wh/kg	1 to 5 Wh/kg	20 to 200 Wh/kg	1 to 5 Wh/kg	8 Wh/kg (200 bars)	300 to 600 Wh/kg (200 to 350 bars)
Possible capacity	some kWh	some kWh	some kWh to MWhs	some kWh to 10MWhs	up to ±10 kWh	
Time constant	ss to 1 mn	ss to 5 mn	mn to hours	ss mn to 1 hour	1 hour to few days	1 hour to few days
Cyclability	± 10000 to ± 100000	± 10000 to ± 100000	200 to 1500 full cycles	± 10000 to ± 100000 (mechanical stress)	± 1000 to ± 10000 (mechanical stress)	.-
Electrical efficiency	> 90%	80 to 90%	70 to 90% (techno, rate)	80 to 90%	30 to 50%	30 to 50%
state of charge knowledge	easy (current)	easy (voltage)	not so easy	easy (speed)	easy (pressure)	easy (H_2 filling)
Cost (€/kWh)	very expensive	50 000 (?)	80 (Pb) to 2000 (Li)	150 to 2000 (technology)	?	500 to 1500
Remarks	needs cryogeny for supraconductors				low efficiency	interesting if H_2 network

Li-Ion for standby energy delivery

- Energy systems

- > 600 Wh
- > 1U- 19 ''

- > 300 Wh
- > 1U- 1/2 19 ''

48 V
2 300 Wh
102 Wh/kg
3U- 19 ''

IntensiumFlex

Tension Maximum : 750V DC
Courant Maximum: 300A, 300 sec

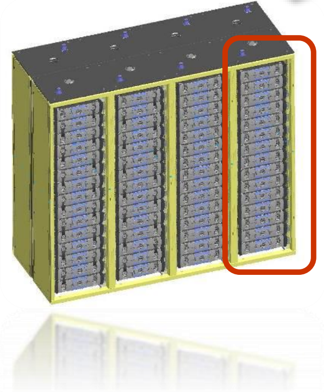
Large energy Li-ion storage batteries

1. Network stabilization with intermittent supply from photovoltaic origin
2. Islands weak networks

accu

module

chassis

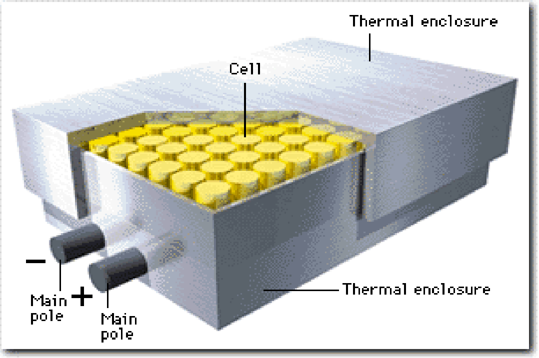


Battery in container

560kWh battery
20 ft container height 3m – width 2.5m
1.1MW (730V-770Ah) ; 14 tons

Storage systems with NaS batteries

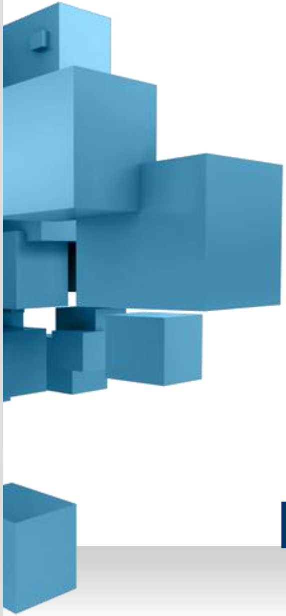
- ☐ Invented in 1965 by Ford for electric vehicles
- ☐ NaS batteries are developed by NGK & Tepco and manufactured by NGK as stationary batteries for load leveling and peak shaving
- ☐ No other industrial manufacturer



Source of photos : NGK website

Conclusions

- From its introduction in 1991, lithium-ion has growing faster than all other batteries:
  - 60 % of Li-ion are presently used in mobile electronic devices
  - Li-ion is also predominant in EV and HEV and PHEV segments
- It will continue to grow fast with electrified vehicles
- Batteries will share storage associated with renewable energy with other technologies
- Inside batteries, Li-ion will take profit of its versatility energy/power and numerous sub-systems.
  - It will have an important role in high power applications
  - while NaS or redox flow will be present in low power applications



Batteries beyond Li-ion

Beyond Lithium-ion

Negative materials
Exchanging more than electron per mole (Mg, Al)

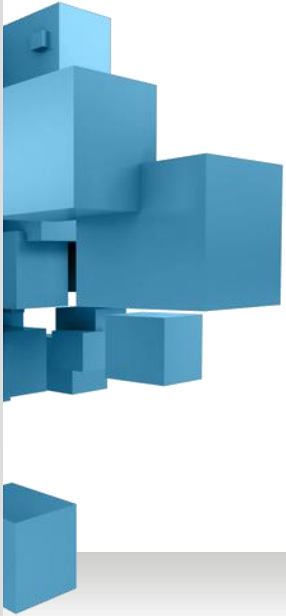
Lithium air 1000 Wh/kg ?

Lithium-sulfur
300 Wh/kg ?

Use of bio materials ?

Low cost sodium-ion batteries ?

Redox flow ?



Merci

Vielen dank

Dekuji

תודה, תודה לך!

Thank you

谢谢

Tack

Sodium-ion

Claimed advantages

- Lower cost of materials (easier process)
- No lithium
- Good for stationary
- Same manufacturing equipment as Li-ion

Known drawbacks

- Lower energy (-300 mV vs Li-ion ; lower specific capacities)
- Power ?
- Could the cost decrease high enough to displace Li-ion?

Our plan:

➡ Join a European consortium to be partner of a proposal

➡ Make real personal tests, discuss with materials suppliers.

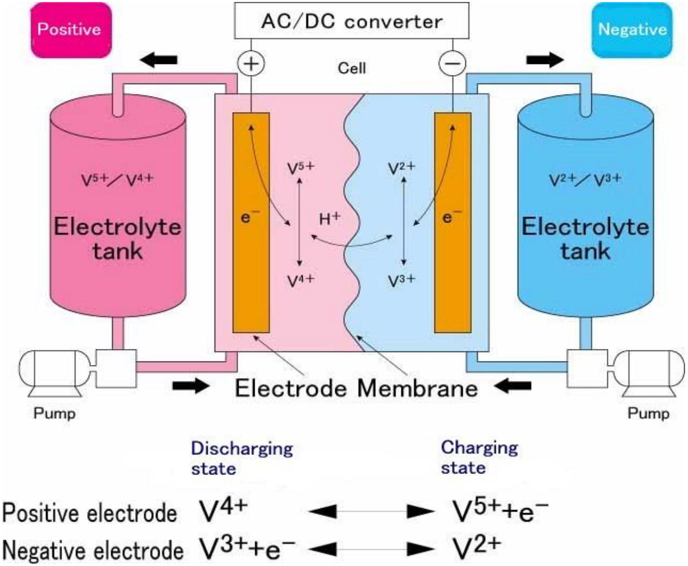
Lithium-sulfur: 300 Wh/kg ?

- Advantages
  - Sulfur is los cost and abundant
  - High capacity (exchange 2 electrons)

- Limitations and problems
  - Voltage lower than 3 V
  - Insulating discharge materials (rapid ageing)
  - High self-discharge of intermediate discharge compounds in organic media
  - Risk H_2S

- Numerous projects running
  - Polyplus + Sion Power, Oxis Energy : industrial projects
  - Nanostructured electrodes sulfur/mesoporous carbon(Univ.München)
  - Task Force of European network Alistore
  - Research step not finished

Redox flow batteries



Positive electrode $V^{4+} \longleftrightarrow V^{5+}+e^-$

Negative electrode $V^{3+}+e^- \longleftrightarrow V^{2+}$

Capacity depends only of the size of the tanks ; power is related to the membrane surface

Redox flow : advantages and drawbacks

- Advantages
  - Global efficiency 70-78%
  - Adapted for large, long storage
  - Reasonable cost

Economical viability not proven with present conditions

- Drawbacks
  - Life lower than expected
  - Efficiency lowered by cross-over
  - More complex maintenance than expected
  - Vanadium system today the best one
  - Limited specific power