IPHE Workshop

Hydrogen – A competitive Energy Storage Medium to enable the large scale integration of renewable energies

Seville, Spain | 15-16 November 2012

Battery Energy Storage technologies for power system

Vincenzo Antonucci

Project leader in Distributed Energy Systems of CNR
Department of Energy and Transportation

The Role of Energy Storage and Benefits

Contingency Service ***Area Control*** ***Black-Start***
Generation - Conventional ***Commodity Storage***
Spinning Reserve - Frequency Regulation

Off-grid applications ***Dispatch***
Generation - Renewable
Energy Balancing ***Smoothing & Ramping***

System Stability
Transmission and Distribution ***Voltage Regulation***
Asset Deferral

Energy Management – Peak Shaving
Energy Service ***Power Quality***
Power Reliability

✓Reduce the need for additional transmission assets

✓Be the preferred supplier of ancillary services

✓Provide better integration of renewables into the system

✓ Support more efficient use of existing assets

✓Improve the reliability of electricity supply

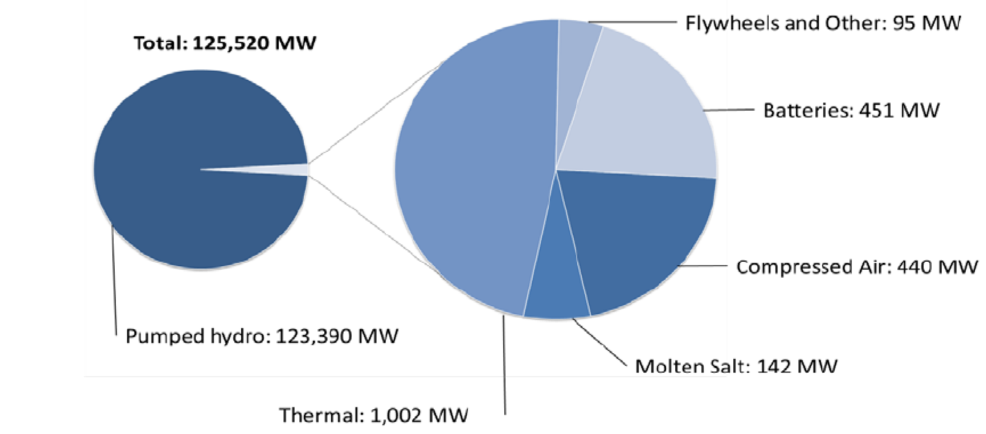
✓Increase the efficiency of existing power plant and transmission facilities

✓Reduce the investment required for new facilities

Market

Estimated Installed Capacity of Energy Storage in Global Grid (2011)

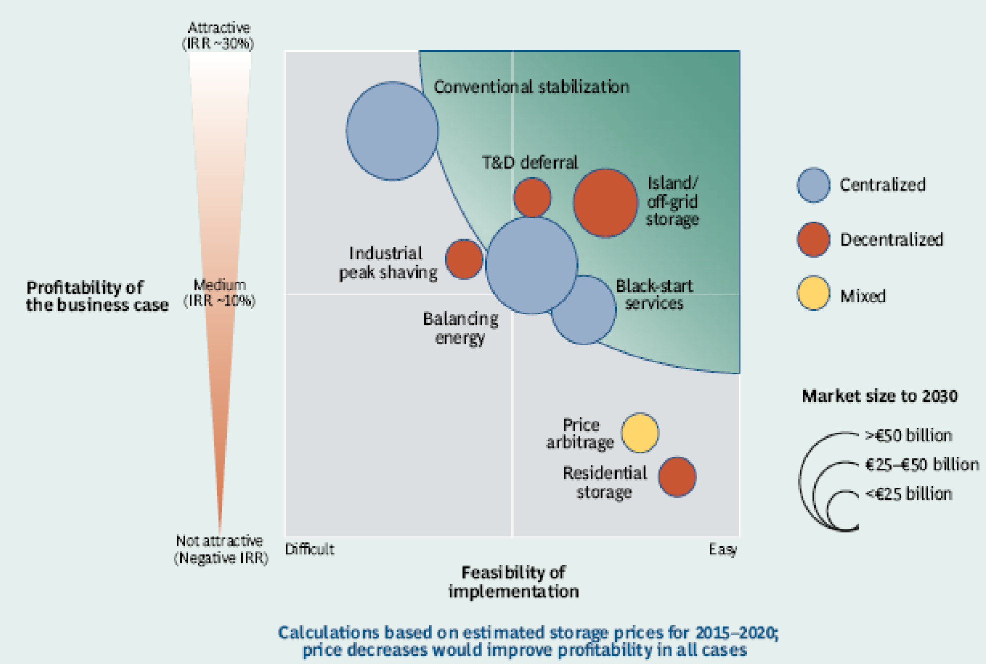
- Excluding pumped hydro, the other technologies cover 2129MW (about 1.7% of the global market)
- Only 451MW for Batteries



Source: StrateGen Consulting 2011.

More attractive business cases in the near future

- Conventional stabilization
- Balancing Energy
- Black start services
- Island / off grid storage



Source: BCG analysis.

Market

Promised technologies per application in the next future

➢ Battery Energy Storage Technologies are expected very attractive starting from 2015

➢ Considering actual development High temperature batteries, Redox Flow Batteries and Lithium-Ion batteries are the most promising

Application	Pumped hydro	CAES	A-CAES[1]	Hydrogen	Sodium-sulfur batteries	Redox-flow batteries (VRBs)	Lithium-ion batteries
Price arbitrage	Needs further cost degression	Needs further cost degression	Needs further cost degression	Needs further cost degression	Needs further cost degression	Needs further cost degression	Needs further cost degression
Balancing energy	Attractive today	Attractive today	Needs further cost degression	Needs further cost degression	Needs further cost degression	Pooling of many dispersed installations needed to achieve minimum power	
Provision of black-start services	Attractive today	Attractive today	Needs further cost degression	Needs further cost degression	Needs further cost degression	Needs further cost degression	NA
Stabilizing conventional generation	Attractive today	Attractive today	Attractive today	Needs further cost degression	Attractive in 2015	NA	NA
Island and off-grid storage	NA	NA	NA	Needs further cost degression	Attractive in 2015	Attractive in 2015	Attractive in 2015
T&D deferral	NA	NA	NA	NA	Attractive in 2015	Attractive today	Attractive in 2015
Industrial peak shaving	NA	NA	NA	NA	NA	NA	Attractive in 2015
Residential storage	NA	NA	NA	NA	NA	NA	Needs further cost degression

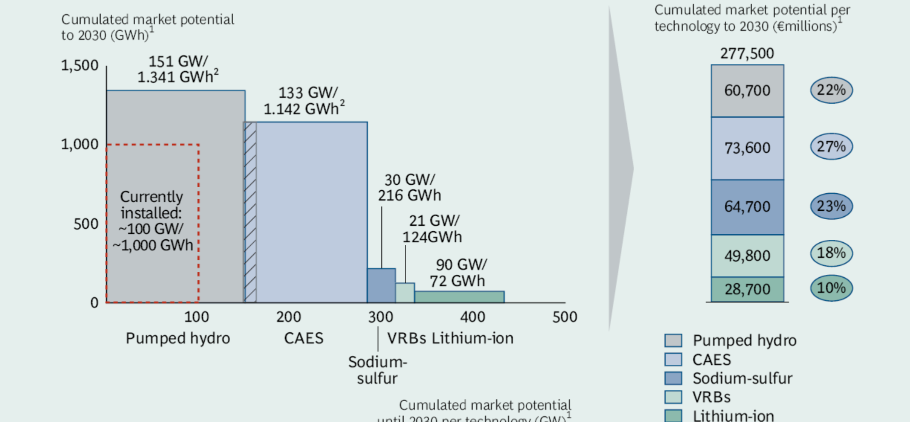
Attractive today[2] — Attractive in 2015 (given expected 2015 costs) — Needs further cost degression and/or subsidies to be viable

Source: BCG analysis.
[1]A-CAES is the second generation of CAES technology. It includes a thermal storage unit to avoid thermal energy losses during compression and decompression, thereby potentially increasing round-trip efficiency to approximately 70 percent. The technology is not yet mature and faces several challenges.
[2]Expected IRR of 7 percent or more.

Market potential of the storage technologies

➢ Batteries will account for half the market in terms of power but significantly less in terms of capacity

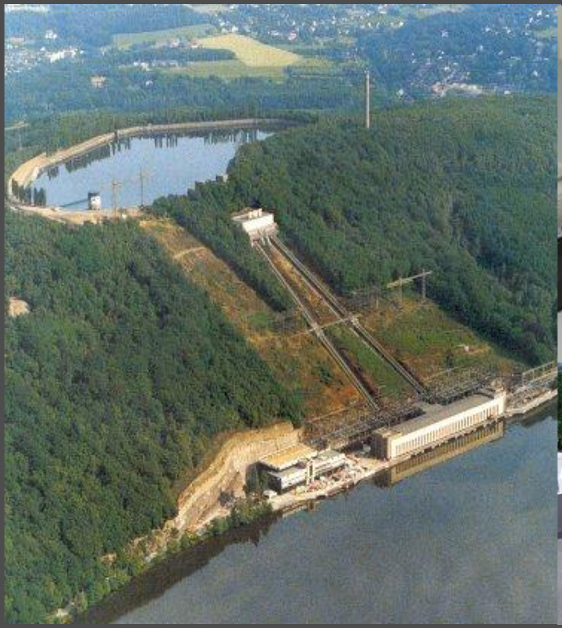
➢ Batteries will represent 50 percent of cumulated market potential to 2030



Source: BCG analysis.
[1]Without price arbitrage, driver trees based on 2030 values, 2015 technology costs.
[2]The future split between pumped hydro and CAES will be driven largely by site restrictions; the gradual replacement of both technologies by hydrogen storage is expected after 2020.

Why batteries?

- *Pumped Hydro needs large scale installation with heavy environment impact*
- *CAES and Flywheel have reduced size respect pumped hydro but not respect batteries. They need complex balance of plant.*



- *Batteries show high efficiency and can be containerized and easy installed in distributed and centralized applications. They need technological development in terms of safety, operating costs and life cycle. Optimum in applications with fast interventions.*

Vincenzo Antonucci

Applications and requirements

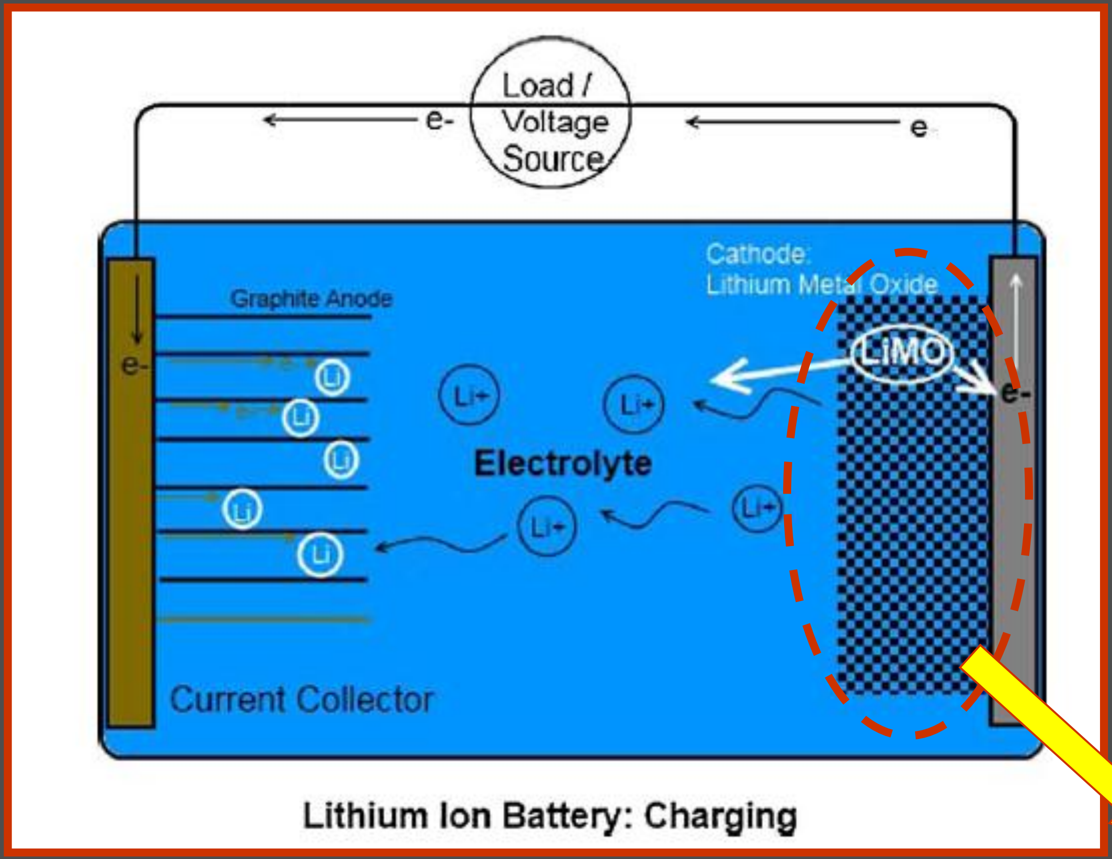
Application	Use/Duty Cycle	Application
Long Duration storage, frequent discharge	1 cycle/day X 250 days/year	Load-Levelling, source-following, arbitrage, Distribution Deferral
Long Duration storage, infrequent discharge	20 times/year	Capacity credit,
Short-duration storage, frequent discharge	4x15 minutes of cycling X 250 days/year=1000 cycles/year	Frequency or area regulation
Short-duration storage, infrequent discharge	20 times/year	Power quality, monetary carry-over

Application	Storage Support Time
Frequency Regulation	1-5 minutes
Spinning Reserve	15-20 minutes
Distribution Upgrade Deferral	1-4 hours
Demand Management	15 minutes – 1 hour
Power Quality	Seconds to 5 minutes

Most promising battery technologies

- ✓ *Lithium based*
- ✓ *Metal – Air*
- ✓ *Redox Flow Batteries*
- ✓ *Sodium based*

Lithium



C. de las Casas, W. Li / Journal of Power Sources 208 (2012) 74–85

Lithium-ion Battery

Cathode: lithium metal oxide

$LiMO_2 \leftrightarrow Li_1{-}xMO_2 + xLi+ + xe^-$

Anode: graphite or lithium titanate

$xLi^+ + xe^- + 6C \leftrightarrow Li_xC_6$

Electrolyte: lithium salt

e.g. $LiPF_6$ in organic solvent

Stable crystal structure required

Lithium

Manufacturers: SAFT, BYD, LiTec, Enersys, Oxi, etc

- High energy and power density
- Low self-discharge rate
- Light weight
- Small size
- Longer life
- Low maintenance
- Quick charging (typically 1-2 hours)
- No memory effect

Sources: Frost & Sullivan

Key End-user Groups

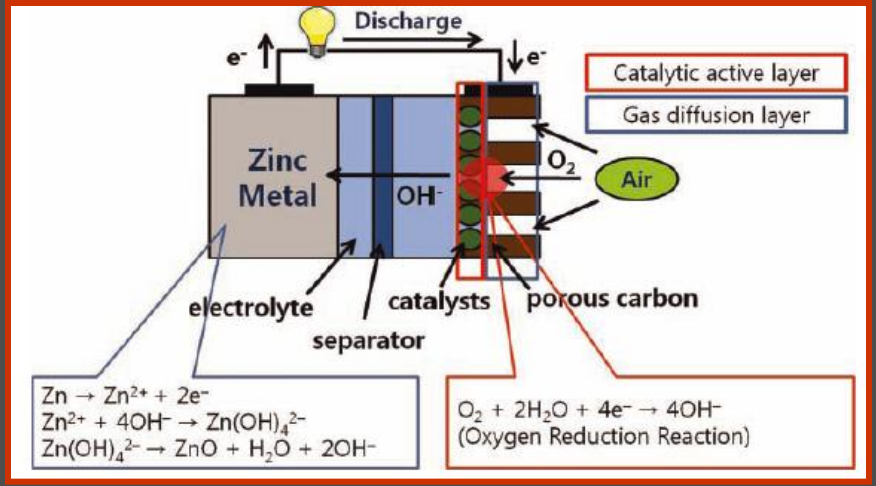
- Military
- Medical
- Data Collection
- Heavy-duty Cordless
- Telecom and Data Communication
- Equipment
- **STATIONARY APPLICATION**

Stationary applications are not as volumetrically and weight constrained as portable/vehicle application:

COST AND SAFETY are needed to satisfy

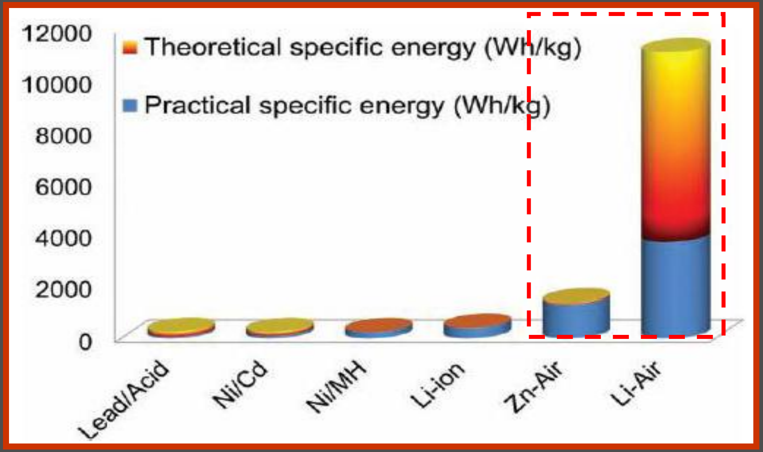
Metal-Air

Metal-air batteries have garnered much attention recently as a possible alternative, due to their extremely high energy density compared to that of other rechargeable batteries as well as the low cost



Sources: *Adv. Energy Mater.* **2011**, *1*, 34–50

Theoretical and practical energy densities of various types of rechargeable battery



Zn-air (theoretical: 1084 Wh/kg)	Li-air (theoretical: 11000 Wh/kg)
Stable towards moisture, can be assembled outside of glovebox.	Not moisture-stable, increasing cost and manufacturing complexity.
Zinc metal and aqueous electrolytes are inexpensive	Lithium and non-aqueous electrolytes are costly
Technology is closer to or already in practical applications.	Still in research phase
Poor reversibility of reactions	Reversible reactions (and improving!)
Low life-cycle: dendride formation	Low life-cycle: dendride formation
Low operating potential	Highest operating potential

Metal-Air

Developers: AER Energy Resources, Aluminum Power, Alupower, Chem Tek, Electric Fuel, Evionyx, Metallic Power, Power Zinc, Zoxy Energy Systems

High energy density and low cost in terms of materials

Main drawback is Low cycle-life

Electrical recharge ability feature of these batteries needs to be developed

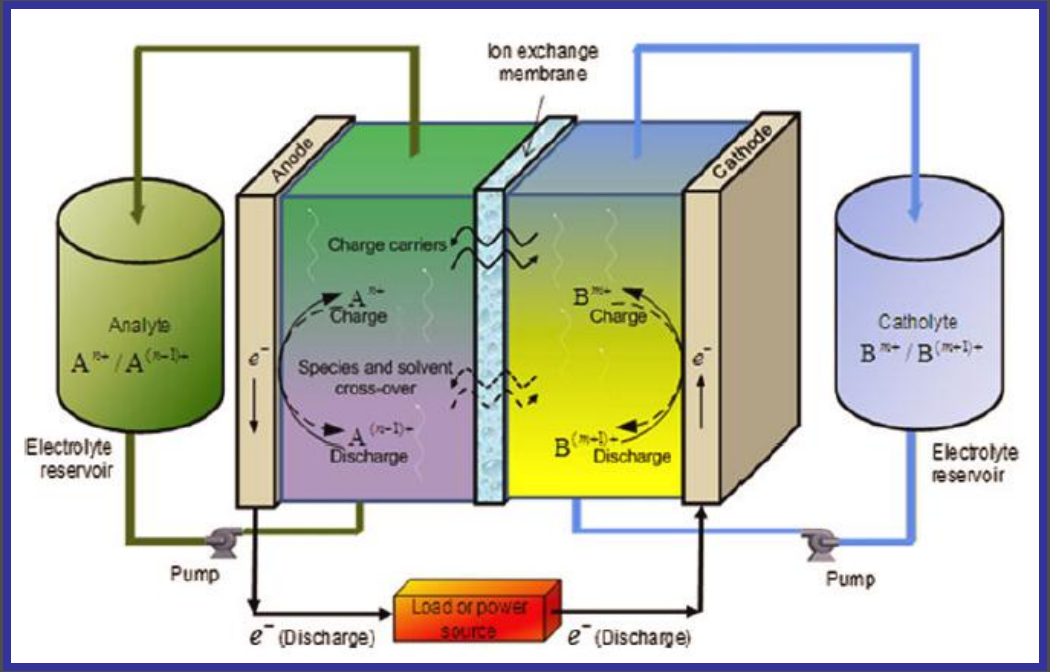
Comparison among several metal-air batteries

	ADVANTAGE	*DISADVANTAGE*
Zn-air	• High theoretical energy density of ~1084Wh/kg • Zinc is a common, cheap, abundant material • Good energy density • Rely in a cheap and available material. • Zinc is stable in aqueous and alkaline electrolytes without significant corrosion. • Potential for low cost: ~ US $250/kWh	• Zinc-air system seemed very promising but despite the efforts made in the past two decades there are still no commercial systems due to low cycle life: ~500 cycles demonstrated until date. • Low cycle life caused by dendrite formation in the zinc electrode. Dendrites can pierce the membrane and even reach the air cathode, forming a dangerous short circuit. • In the most common embodiment employs 2 different electrolytes for the positive and negative electrodes and an expensive ion-exchange membrane is required to separate them.
Lithium-Sulfur	• High theoretical energy density: ~2600Wh kg^{-1} • High energy and power densities 350Wh kg^{-1}, 400 to 2000W kg^{-1} depending application and energy density. • Low cost potential	• Low cycle-life. • Sulfur is a poor conductor • Safety issues related with metallic-lithium • Lower lithium resources compared with other metals • Higher lithium cost
Iron-air	• High theoretical energy density of around 1000Wh kg^{-1} • solution of KOH as the electrolyte: not membrane is required • iron, a common, abundant and cheap material available worldwide • iron does not form dendrites • Safe and non-toxic materials	• Hydrogen evolution in the iron electrode reduces overall efficiency • Reaction rate has been traditionally limited by the air-electrode, reducing power density of the battery. • Cycle life limited traditionally by the degradation of the air electrode. • Slight self-discharge of the battery caused by corrosion of the iron-anode.

Redox Flow Batteries

Manufacturers: Prudent Energy, ZBB, EN Storage

The redox flow cell or battery is an electrochemical system that stores energy in two solutions containing different redox couples (electroactive species)



Source: J Appl Electrochem (2011) 41:1137–1164

Iron/chromium

$Fe^{2+} \rightleftarrows Fe^{3+} + e^-$ E= 0,77V vs RHE

$Cr^{2+} \rightleftarrows Cr^{3+}$ + e- E= - 0,41V vs RHE

Bromine/polysulphide

$3Br^- \rightleftarrows Br_3^- + 2e^-$ E= 1.09V vs RHE

$2S_2^{2-} \rightleftarrows S_4^{2-} + 2e^-$ E= - 265V vs RHE

Zinc/bromine

$3Br^- \rightleftarrows Br^{3-} + 2e^-$ E= 1.09V vs RHE

$Zn \rightleftarrows Zn^{2+} + 2e^-$ E= - 0.76V vs RHE

Zinc/cerium

$Zn \rightleftarrows Zn^{2+} + 2e^-$ E= - 0.76V vs RHE

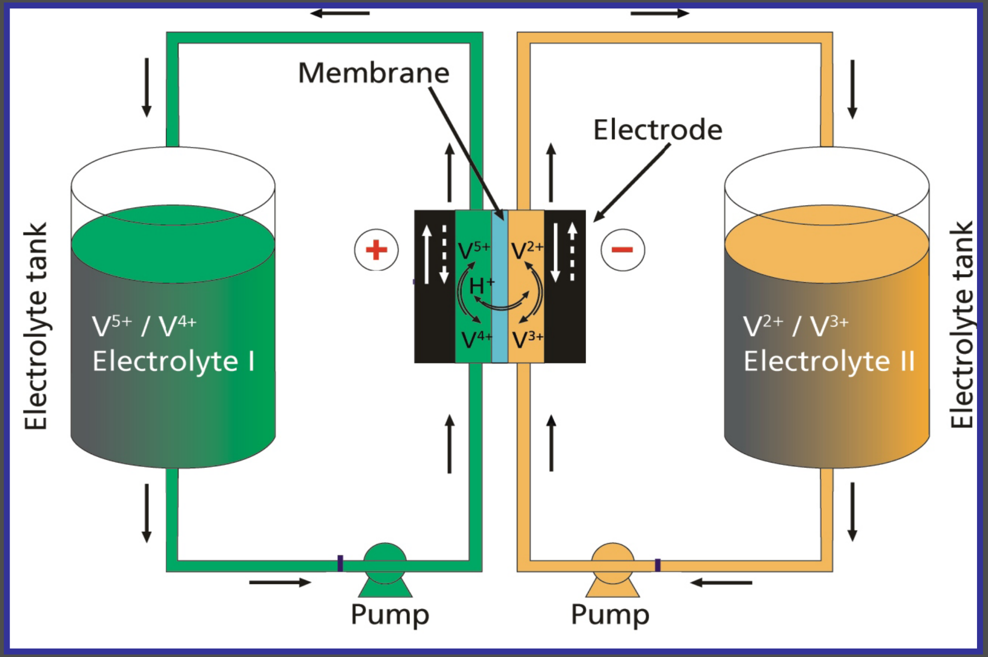
$Ce^{3+} \rightleftarrows Ce^{4+} + e^-$ E= 1.75V vs RHE

Redox Flow Batteries

Vanadium

The all-vanadium battery is the most widely commercialised RFB used for large-scale energy storage

The electrolyte containing the active vanadium redox couples in sulfuric acid solution is circulated in two independent loops through the electrode compartments divided by a microporous separator or an ion conducting membrane



$VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O$ E= +1.00 V

$V^{2+} \leftrightarrow V^{3+} + e^-$ E= -0.26 V

Cell reaction **:** $V^{2+} + VO_2^+ + 2H^+ \leftrightarrow VO^{2+} + V^{3+} + H_2O$ ***E = 1.26 V***

Redox Flow Batteries

Vanadium

Advantages :

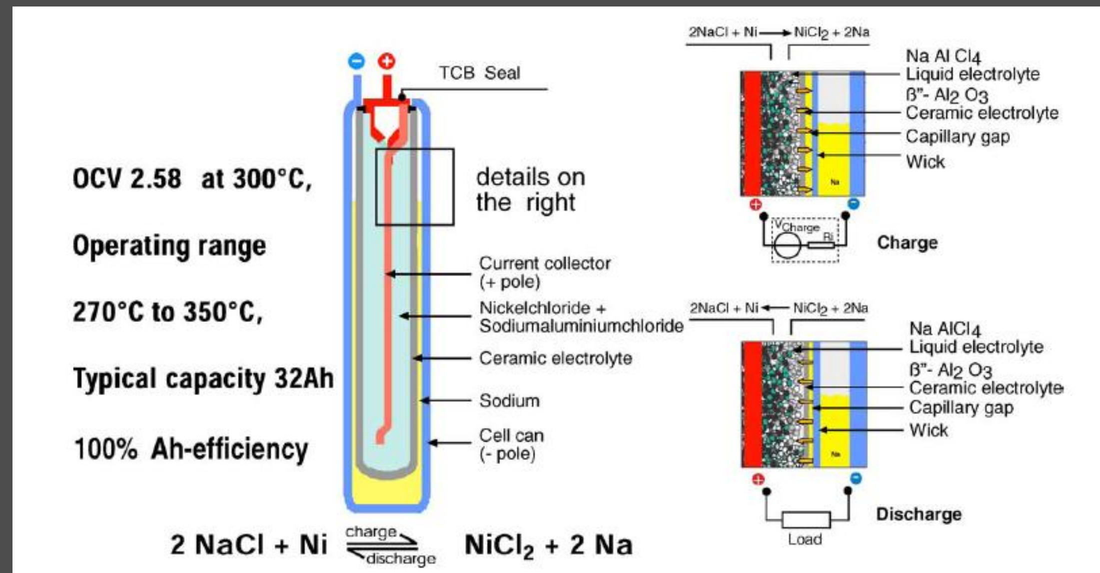
- ✓ Power is determined by the number of cells in the stack and the size of the electrodes while the energy capacity storage is determined by the concentration and volume of the electrolyte
- ✓ High efficiency
- ✓ Long Cycle Lifetime in Deep Charge/Discharge
- ✓ Easy Increase of Capacity
- ✓ Normal Temperature Operation
- ✓ Can be both electrically recharged and mechanically refueled
- ✓ Low cross-contamination of the two half-cell electrolytes

Drawbacks :

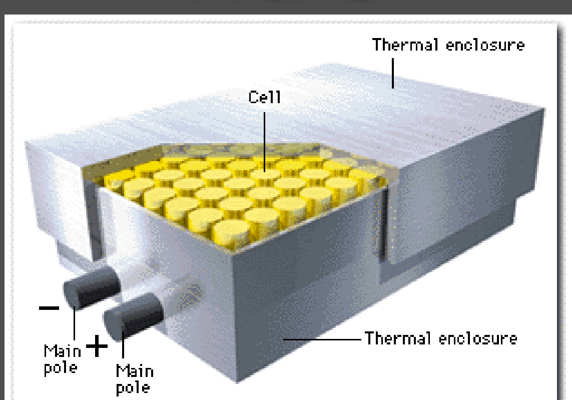
- ➢ Low energy density 20-30 Wh L^{-1}
- ➢ Critical aspect of the technology is concerning with the electrocatalytic activity and the reversibility of the redox reaction at the positive electrode $[VO]^{2+}/[VO_2]^+$
- ➢ Materials costs represent a fundamental driver of applicability of these systems

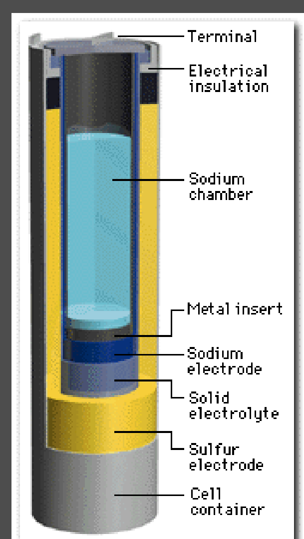
Sodium

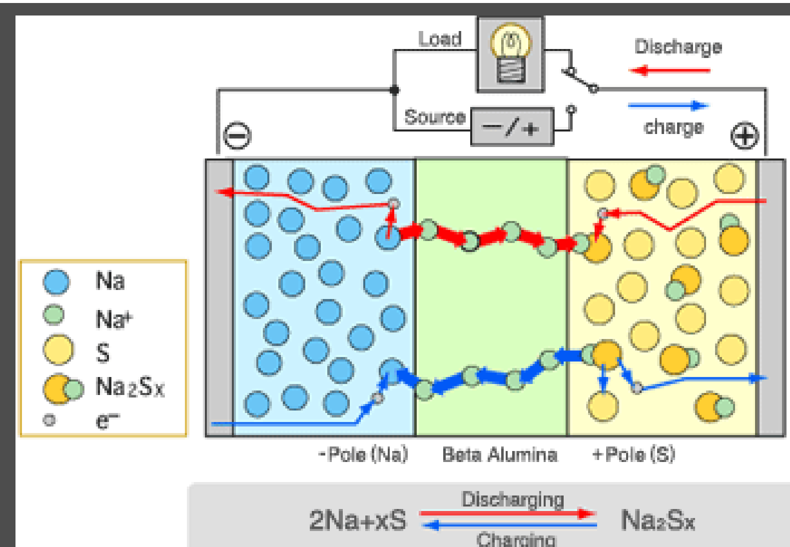
NaNiCl



Na-S







Sodium

Manufacturers: NGK Insulator, FIAMM Sonick, GE

High Temperature Batteries:

~ 270-350 °C

Na-S Battery

NGK Insulator (Japan)

NaNiCL

ZEBRA Battery

FIAMM (Italy), GE (USA)

	ADVANTAGE	*DISADVANTAGE*
NaS	• High energy density (110 Wh/kg) • High eff iciency of charge/discharge (> 90 %) • Long cycle life • no self discharge • Low cost materials • No gas emission • Good Safety	• Current collector corrosion due to the high operation temperatures • Highly corrosive nature of the sodium polysulfides • the system must be protected from moisture • Dendritic-sodium growth
ZEBRA	• High energy density (90 Wh/kg) • Long cycle life • no self discharge	• High costs • Thermal management

Performance and Costs Analysis

Source: Kyle Bradbury

Technology	Li-ion	Na-S	ZEBRA	VRB	Zn-Br
Roundtrip Efficiency [%]	85-98	70-90	85-90	60-85	60-75
Self-discharge [% Energy/day]	0.1-0.3	0.05-20	15	0.2	0.24
Cycle Lifetime [cycles]	1k-10k	2.5k	2.5k	12k-14k	2k
Expected Lifetime [Years]	5-15	5-15	10-14	5-15	5-10
Specific Energy [W/kg]	75-200	150-240	100-120	-	-
Specific Power [W/kg]	150-315	150-230	150-200	16-33	30-60
Energy Density [Wh/L]	200-500	150-250	150-180	-	-

Technology	Li-ion	NaS	ZEBRA	VRB	ZnBr
Power Cost [$/kW]	175-4000	150-3000	150-300	175-1500	175-2500
Energy Cost [$/kWh]	500-2500	250-500	100-200	150-1000	150-1000
BoP Cost [$/kWh]	120-600	120-600	120-600	120-610	120-600
O&M Fixed Cost [$/kW-y]	12-30	23-61	23-61	24-65	15-47

Comparative Analysis

Centralized Storage

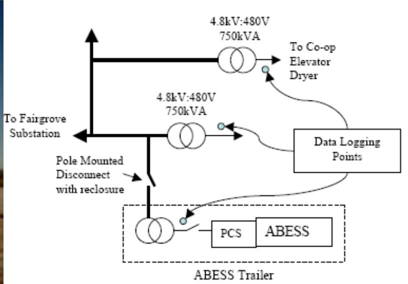
	Energy Density	Temperature/ Safety	Operating Cost	Efficiency	Lifecycle	Capital Cost	Development Stage	Total
Pumped Hydro	○	◕	●	◑	●	◑	Most widely used form of storage	*21*
Flow Batteries	◔	◕	◔	◔	◕	○	Commercialised but only very few projects implemented in Europe	*15*
Lithium-ion	◕	◔	○	◕	◑	◔	Research stage	*16*
CAES	◑	◑	◕	○	◕	◕	Commercialised. 2 plants in operation globally – Germany and US	*19*
Thermal Storage	◔	◔	●	●	◑	◑	Molten salt widely used for CSP plants	*20*
Lead Acid	○	●	◑	◑	○	◔	Widely used	*14*
Sodium Sulfur	●	○	◑	◕	◕	●	165 MW installed capacity in Japan. No projects as yet in Europe	*22*
Sodium Nickel Chloride	◑	◔	◔	◕	◑	◑	Been in existence for over 20 years. FIAMM only company in Europe manufacturing these batteries	*17*

● Very High Attractiveness = 5 ◕ High Attractiveness = 4 ◑ Moderate Attractiveness = 3 ◔ Low Attractiveness = 2 ○ Very Low Attractiveness = 1

Source: Frost & Sullivan

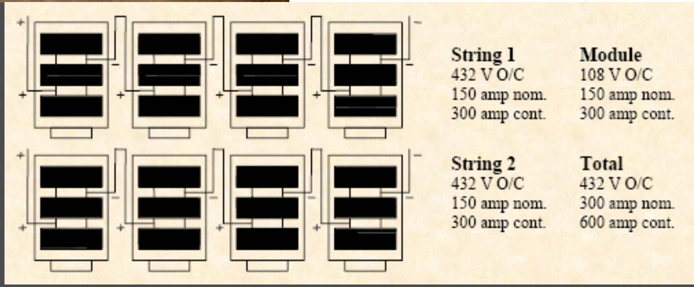
Pilot Plant

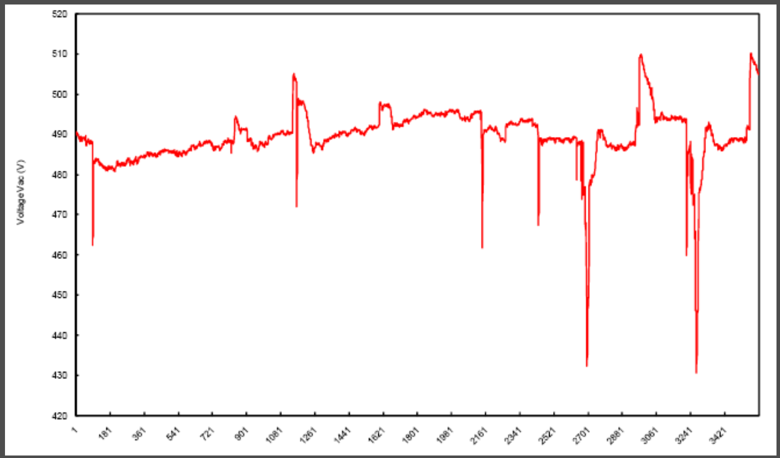
ZBB - Akron Grain Drying Facility
400 kWh Zinc/Bromine Battery Configuration
App: load leveling



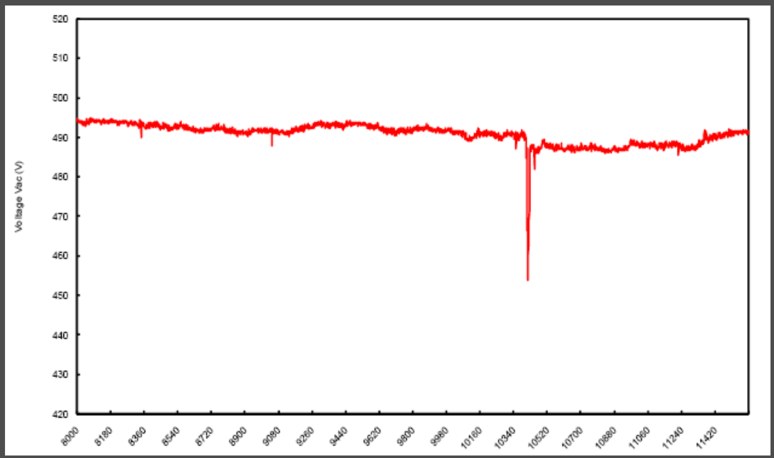
Energy Storage System responded to system needs

- ✓**Grain dryer caused 850 kVA spike**
- ✓**Spike was higher than unit capability**
- ✓**Energy storage system reduced voltage drop**
- ✓**Energy storage system eliminated voltage overshoot when dryer turned off**





Line voltage without compensation

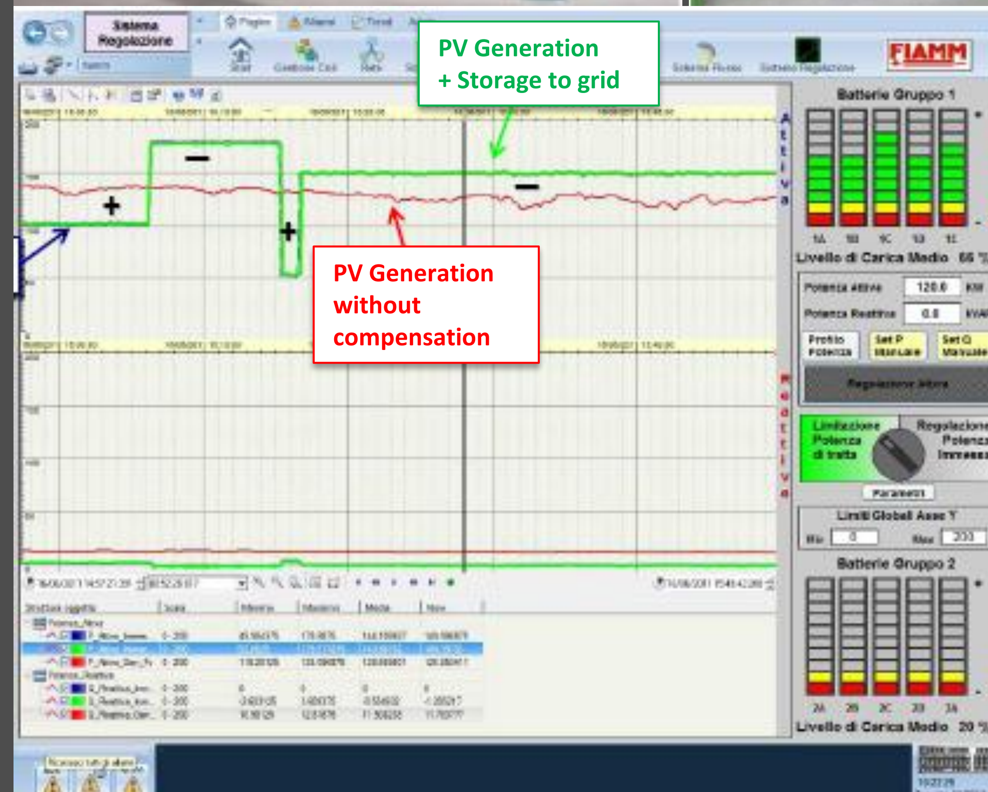


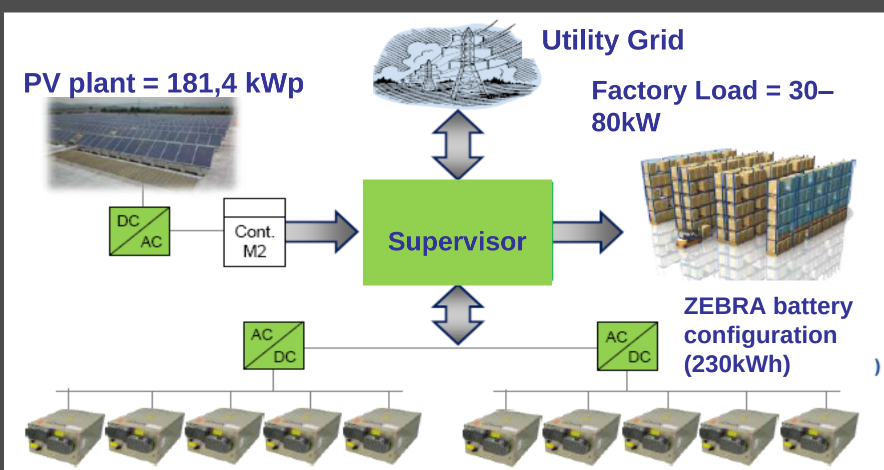
Line voltage with compensation

Pilot Plant

FIAMM Green Energy Island
230 kWh ZEBRA Battery Configuration
App: Generation Management-Load shifting

- ✓ **Power regulation released to grid**
- ✓ **Peak shaving & load shifting**
- ✓ **Tariff optimization (sell & buy)**
- ✓ **Back-up service**





Pilot Plant

NGK Insulator
App: AEP Distribution Substation with Sodium-Sulfur Unit

NGK Insulator
App: Energy balancing- Peak shaving of wind park in Rokkasho
Stored Energy = 34MWh Wind Park = 51MW

Demonstration plants in Japan, USA and Asia.

NAS are produced in fundamental unit of 1 MW (6MWh) for plants typically with a size in the range between 2-10MW.

Industrial plans were stopped due to a big fire occurred on 21 september 2011 in Tsukuba plant of the Mitsubishi Material Corporation in Japan.

Conclusions

- ✓ **Battery Energy Storage Technologies are expected penetrate significantly the global market of energy storage to 2030 (50% of the whole power foreseen)**
- ✓ **The use of batteries in grid applications represent a good choice in terms of cost saving respect building new infrastructures, and in terms of guarantying security and stability to electrical grid**
- ✓**The most promising batteries are Li-Ion, VRB, Sodium-sulfur, ZEBRA and Zinc-bromide**
- ✓ **Several demonstration projects have already shown the capability of batteries to respect requirements and functionality**
- ✓ **Advances have to be done in terms of fast charge, life cycle, security of such technology, and reducing costs**

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Battery Energy Storage technologies for power system

APPENDIX

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Lithium

Lithium-Ion Energy storage: Chemistry

Cathode materials	Energy density / Wh kg^{-1}	Voltage / V
$LiCoO_2$	170-185	3.65
$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$	155-185	3.7
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	145-165	3.65
$LiFePO_4$	100-140	3.2
$LiMn_2O_4$	90-120	3.8

- Low cost materials
- Environmental friendly transition metal ions

Electrode performance depends on the electrode microstructure and morphology. Lithium ions intercalation and deintercalation occur along specific crystallographic planes and directions, so higher crystallinity improves electrode performance.

Lithium

Metal and alloy based anodes

Anode materials	Theoretical capacity / mAh g^{-1}
Graphite	372
$LiTi_5O_{12}$	175
$Li_{22}Sn_5$	994
Li_3Sb	536
Al_4Li_9	2234
$Li_{21}Si_5$	4000

Much higher storage capacity but large volumetric expansion

(Pulverization Process)

Characteristics of Anode Materials

- Large reversible capacity
- Small irreversible capacity
- Desirable charge profile
- Desirable kinetics (rate capability)
- Long cycle and calendar life
- Ease of processing
- Safety
- Compatibility with electrolyte and binder systems
- Low cost

Redox Flow Batteries

Vanadium

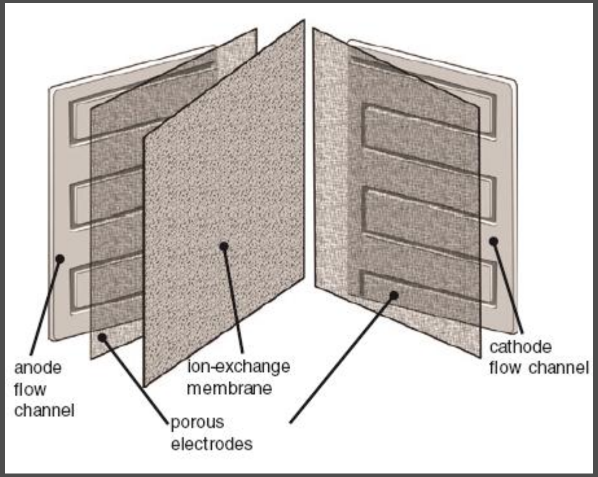
Commercial used materials

- **Electrodes:** High surface area, high reaction rates, low polarization are required to ensure adequate cell performance. e.g. Carbonaceous materials, carbon felt, graphite felt, carbon paper, carbon cloth, graphite powder

- **Cation Exchange Membrane:** good ion conductivity, high ionic, good chemical stability e.g. Nafion 117, Gore, Daramic, Asahi Selemion CMV

- **Electrolyte solution:** proper vanadium concentration 1-3 M $VOSO_4 \cdot nH_2O$ in 1-4 M H_2SO_4

- **Operative temperature:** from room temperature up to 50 °C due to V^{5+} precipitation



Source: J Appl Electrochem (2011) 41:1137–1164