UNIVERSITY OF PADOVA
ITALY

DEPARTMENT OF INDUSTRIAL ENGINEERING

Prospettive per l'accumulo energetico strategie e tecnologie

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CICLO SEMINARI LEDS 2015-16

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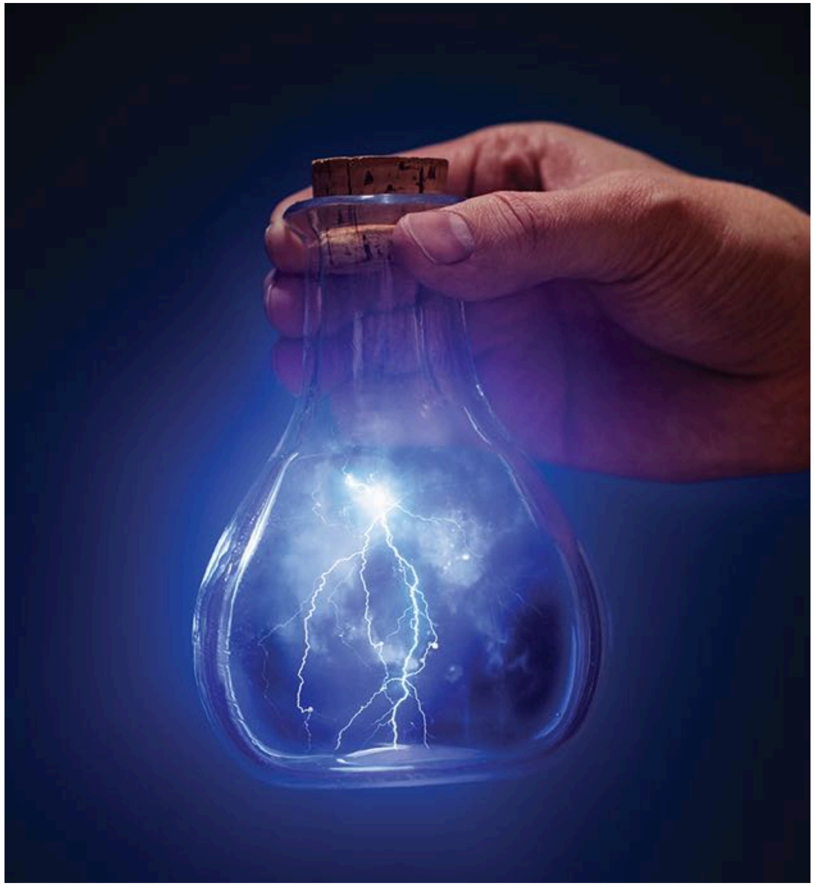
Sectors requiring Energy Storage

- **Labs (Big Science)**
- **Portable personal electronics**
- **Mobility (road and beyond)**
- **Stationary (Grid/Island)**



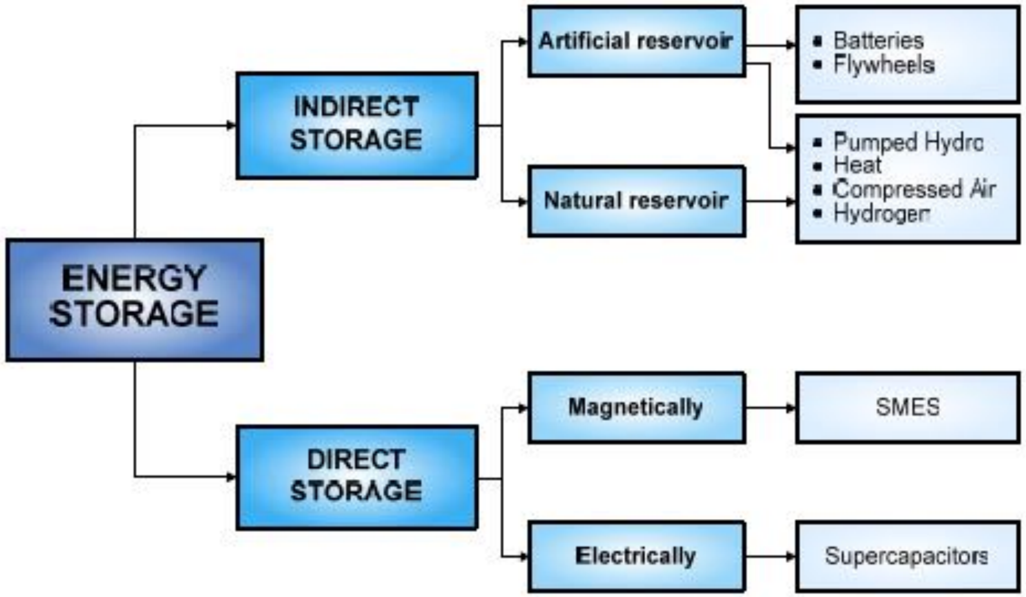
In ordine crescente di:

- **potenza/energia**
- **progressione temporale**

Technologies for Energy Storage

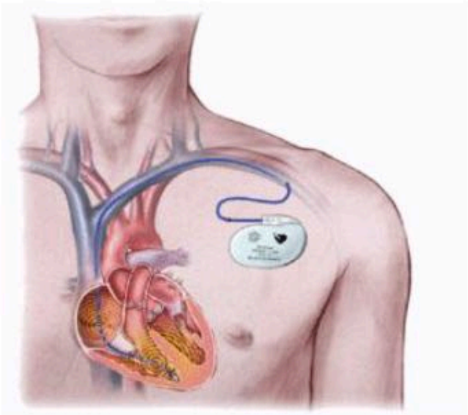
- Magnetic Energy
- Electrical Energy

- Kinetic Energy
- Chemical Energy
- Thermal Energy
- Elastic (Pressure) Energy
- Gravitational Energy
- ...



Energy storage range

Capacitor: Implantable defibrillator



- Voltage: 800 V
- Capacitance: 100 µF

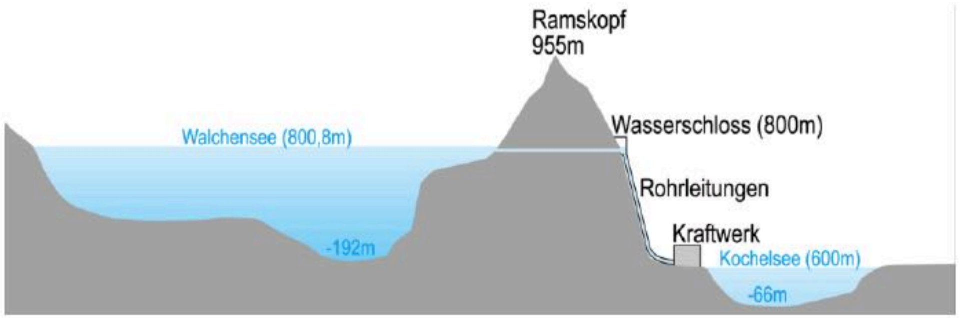
$U = 800\ V,\ C = 10^{-4}\ F$

$E = 1/2 \cdot C \cdot U^2$

⇓

Theoretical energy content:
$E = 8.8 \cdot 10^{-6}$ kWh

Pumped-storage power plant: ‚Walchensee'



- Height difference: 200 m
- Max. lowering of water table: 6 m
- Equivalent in water volume: 10^{11} L

$m = 10^{11}\ kg,\ g = 9{,}81\ m/s^2,\ h = 200\ m$

$E = m \cdot g \cdot h$

⇓

Theoretical energy content:
$E = 60 \cdot 10^{6}$ kWh

➡ Energy and power density determine field of application for different technologies

Sources: H. Haase, Institut für Grundlagen der Elektrotechnik und Messtechnik, Leibniz Universität Hannover, 2007 | E.ON Wasserkraft, 2010

Interessi legati ai programmi energetici governativi/comunitari

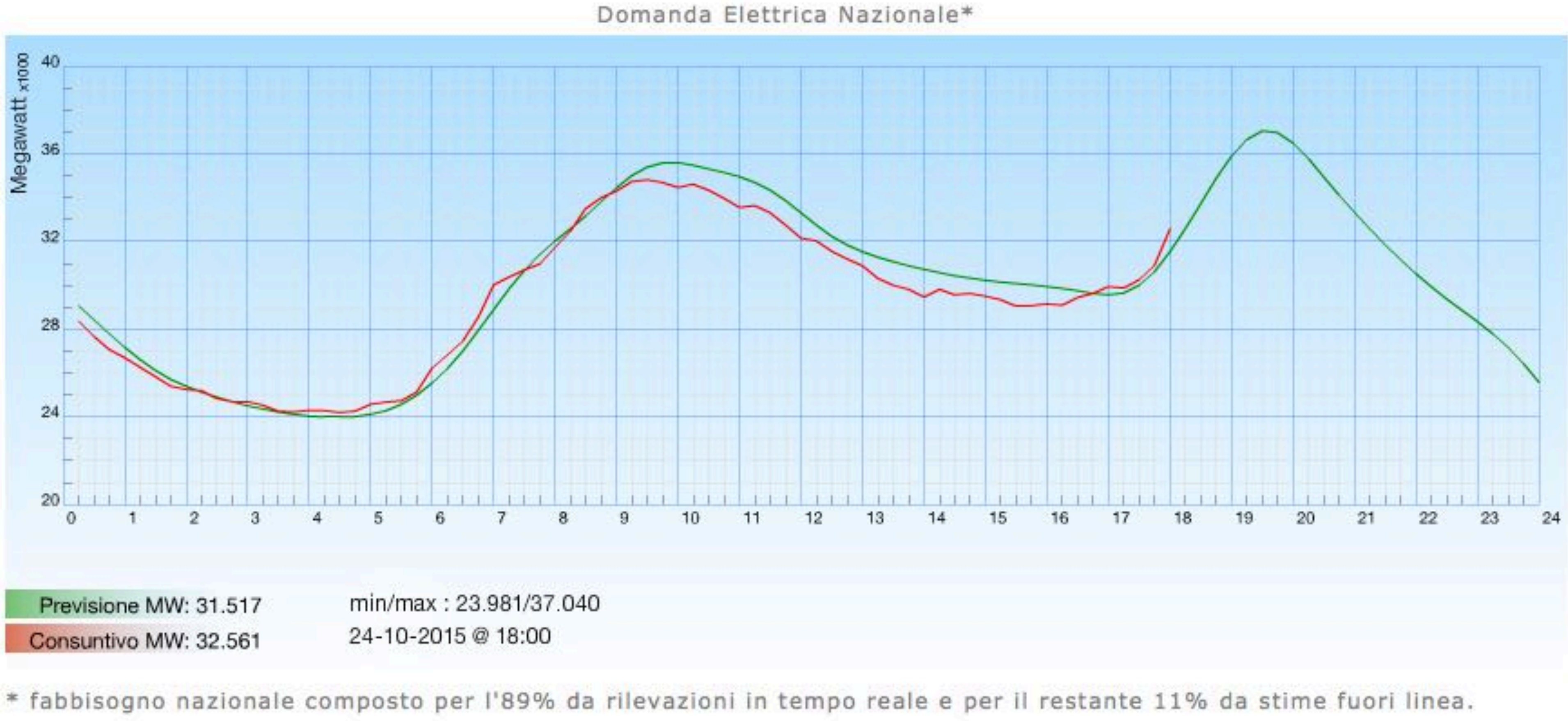
Obiettivi della strategia Europa 2020

1. Occupazione ....
2. R&S ....
3. **Cambiamenti climatici e sostenibilità energetica:**
   - **riduzione di emissioni di gas serra del 20% (o persino del 30%, se le condizioni lo permettono) rispetto al 1990**
   - **20% del fabbisogno di energia ricavato da fonti rinnovabili**
   - **aumento del 20% dell'efficienza energetica**

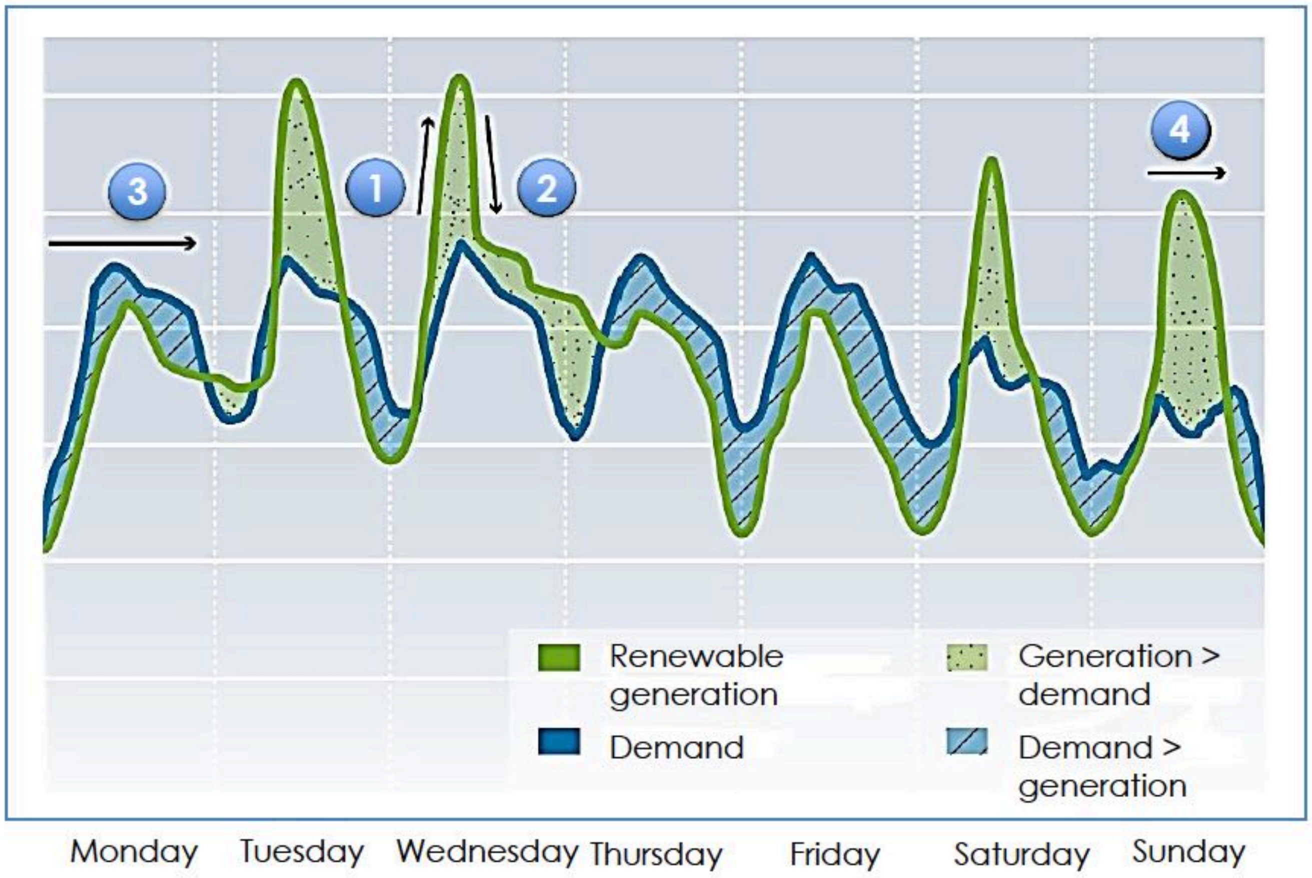
     → **decarbonizzazione**
4. Istruzione
5. Lotta alla povertà e all'emarginazione

Anche negli altri paesi industrializzati

PARADIGMA TRADIZIONALE:
ADEGUAMENTO ISTANTANEO DELLA GENERAZIONE ALLA DOMANDA
TERNA: Diagramma di carico 24/10/15 (MW) - Previsione ed effettivo
http://www.terna.it/default.aspx?tabid=1024



RENEWABLE SOURCES: INTERMITTENT GENERATION AND MISMATCH

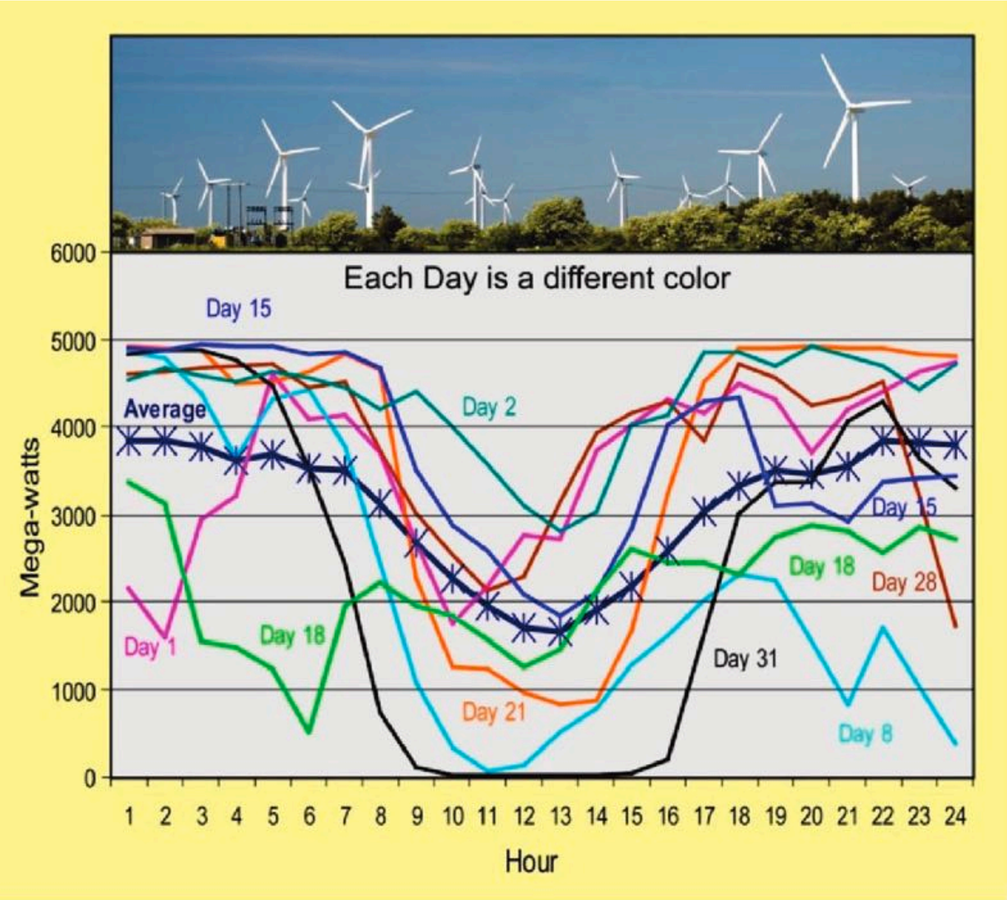


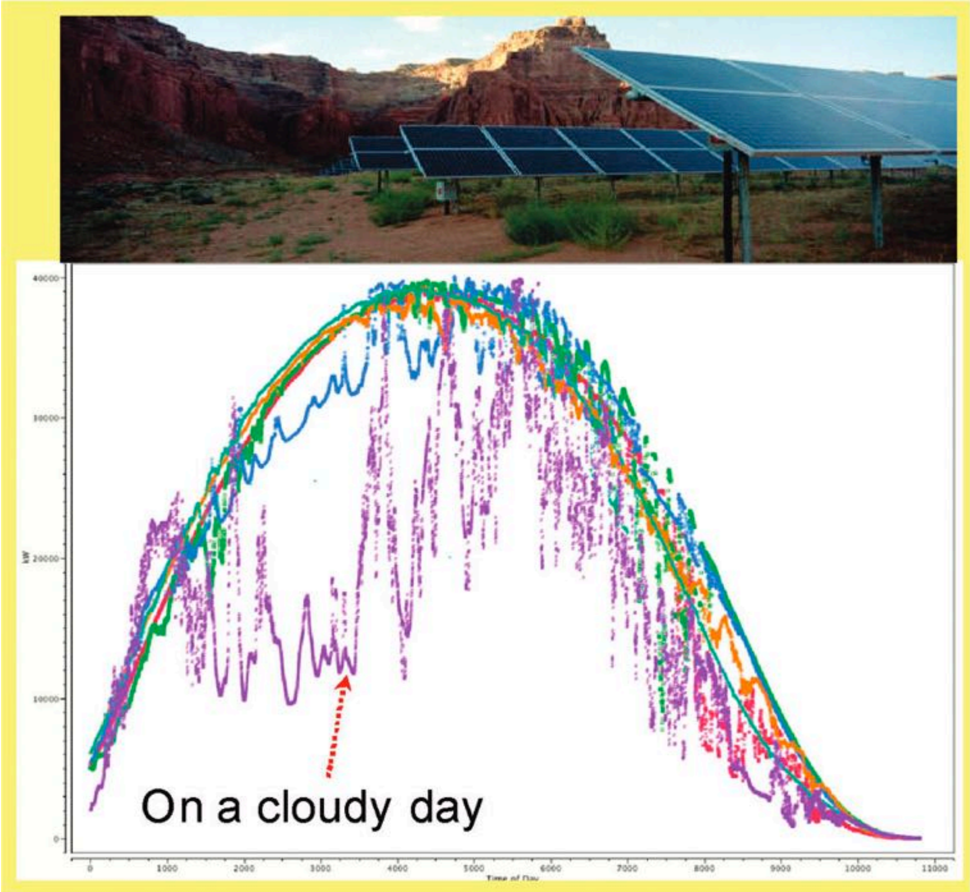
1. Generation from renewable sources is volatile, typical peak shape at noon from PV
2. Rapid decline in renewable generation due to weather conditions
3. Demand > generation: Controllable consumers (heat pumps, BEVs, cold storage houses) reduce load and electricity from energy storage devices is fed into grid
4. Generation > demand: Energy storage devices and controllable consumers take up excess electricity

Fast/slow mismatches

Major side effects of renewable power sources expansion

Intermittency of renewable power sources with slow and fast dynamics





Services differ according to power and intervention times

Power quality = fast storage modes:

- sag compensation (compensazione dei buchi di tensione)
- power smoothing (spianamento della potenza)
- grid stabilization (stabilizzazione di rete)
- frequency regulation (regolazione di frequenza)

- UPS (uninterruptable power supply)

Services differ according to power and duration times

Energy management = slow storage modes:

- load leveling (livellamento del carico)
- load following (inseguimento del carico)
- power balancing (bilanciamento di potenza)
- peak shaving (spianamento dei picchi)
- time shifting (traslazione temporale)
- load factor Improvement (miglioramento del fattore di carico)

- … investment deferral (rinvio di investimento)

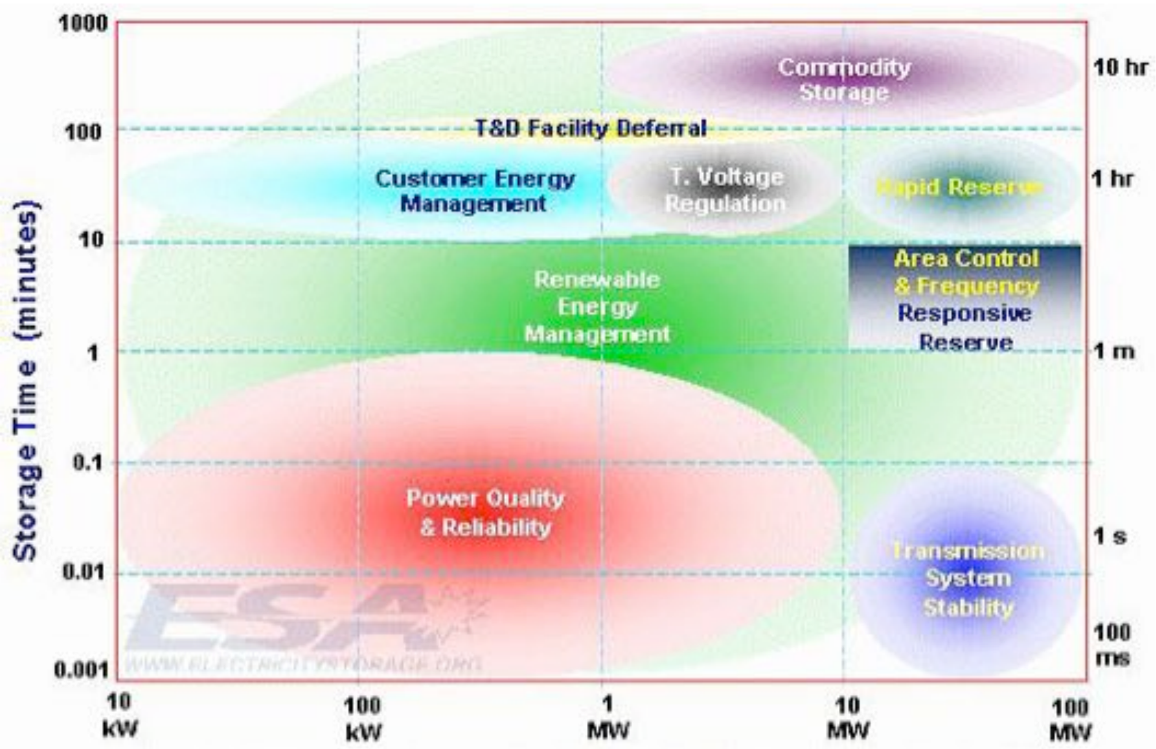
Stationary energy storage services

Power – Time requirements

Output powers: some kW to some GW

Response time: millisecs to minutes

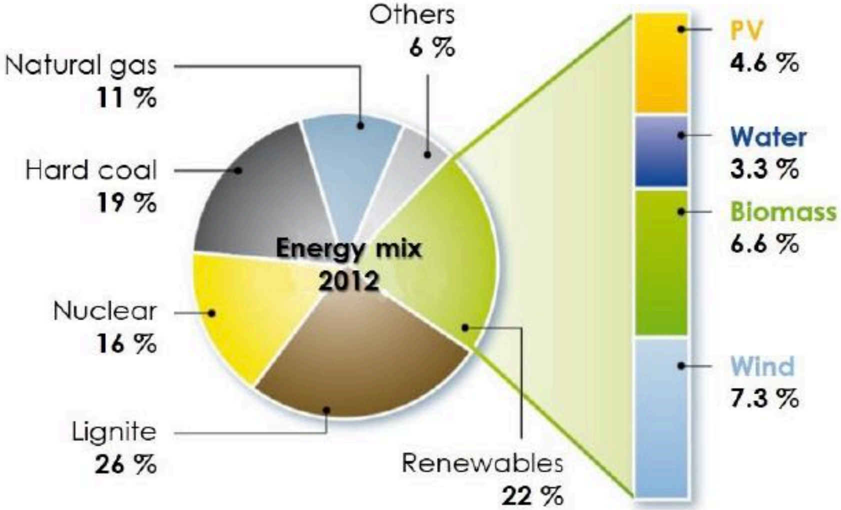
Discharge times: minutes to several hours



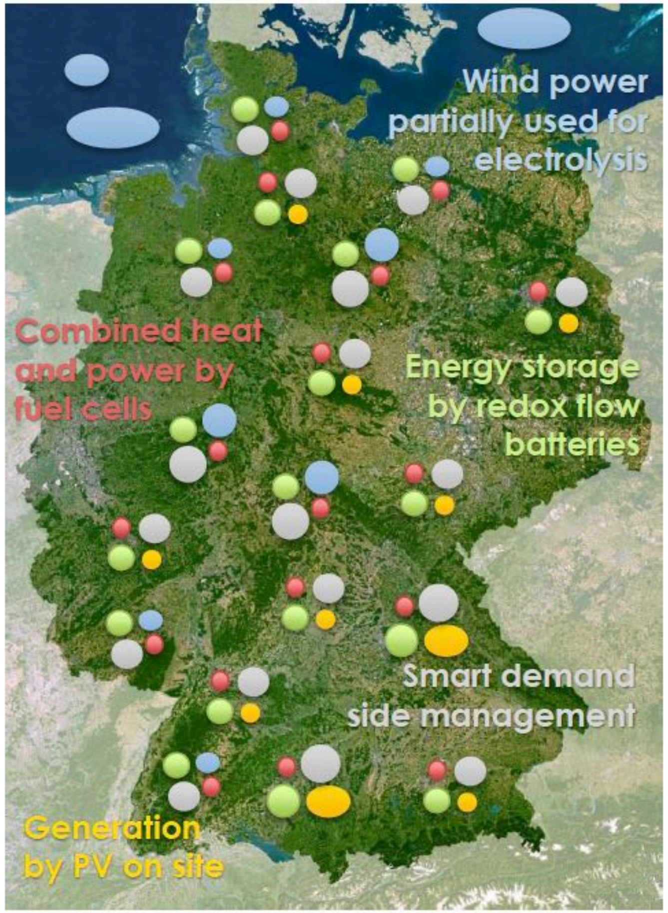
Allocation of energy storage services in the power–discharge duration diagram (source: Electricity Storage Association)

Germany - Evolution to Smart Grids
Technische Universität München

Bottom-Up Approach



2050: 100 %
Energy target 2050:
100% renewable electricity supply

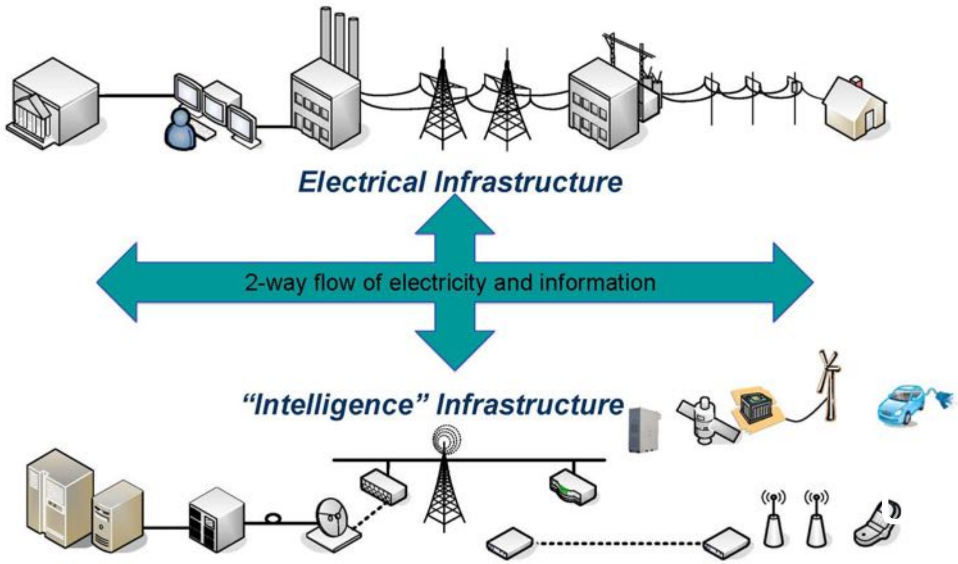


Alternate approach: Decentralization

„Many small producers vs. many consumers"

- Self-sustaining communities / production sites / households / …
- Generation of electricity where it is needed
- Minimized need for energy storage and minimal supplement from the grid

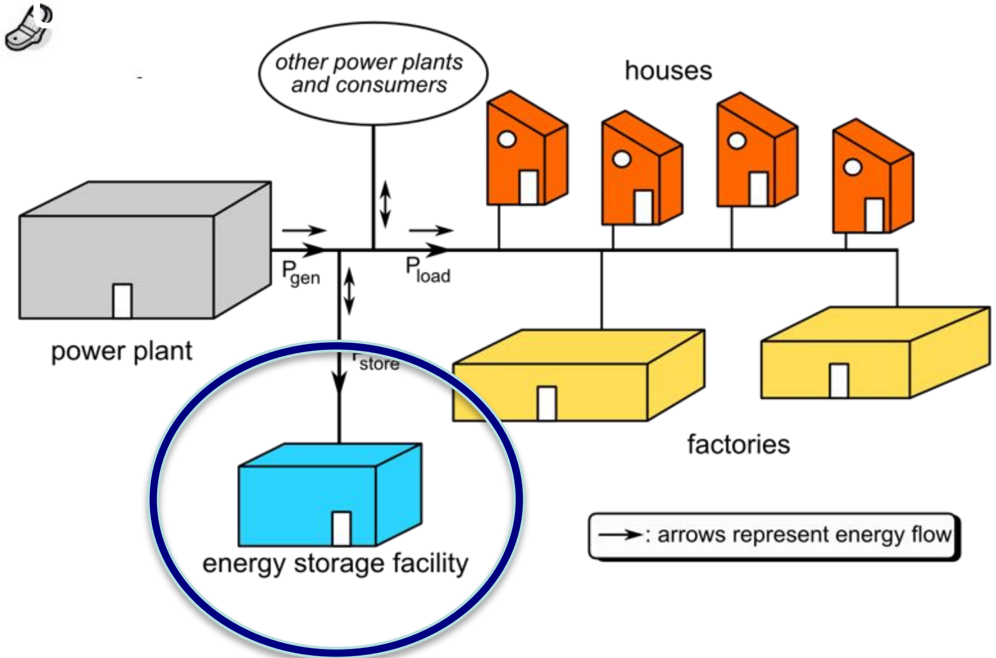
Combination of multiple **small-scale technologies** to design generation, storage and consumption in a **smart** way!



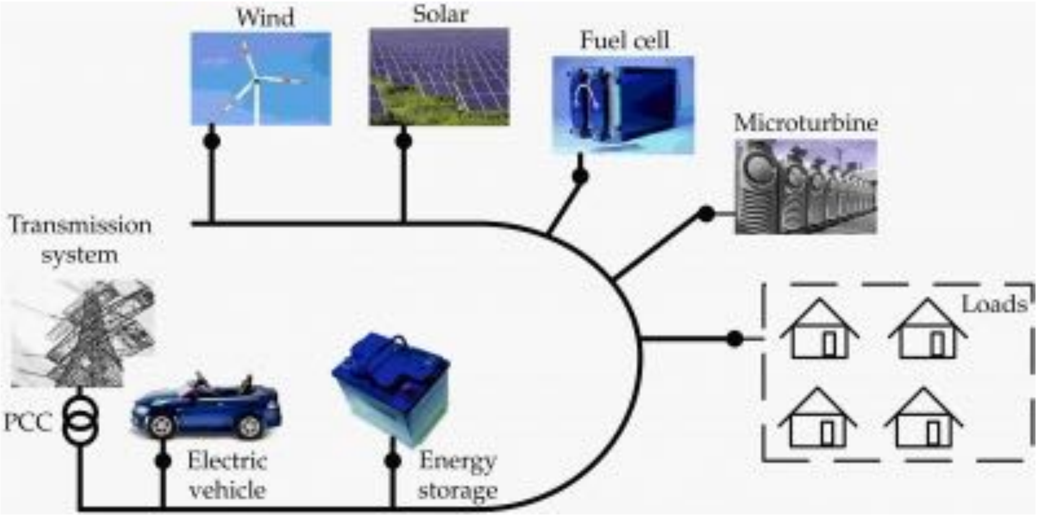
Smart Grid: Two Way Information and Power Flows

Energy Storage: Add a Third Dimension

Breaks the century old constraint to match instantaneous generation to instantaneous demand !!!!



Distributed Energy + Smart Grid + Energy Storage → Microgrid



Generation – Demand – Storage
- *Local energy management*
- *Renewable generation*
- *Co-generation: electricity+heating*
- *Short delivery distance*
- *Reduced dependence on grid*
- *Service profile tailored to customer*
- *"Personalized" energy*

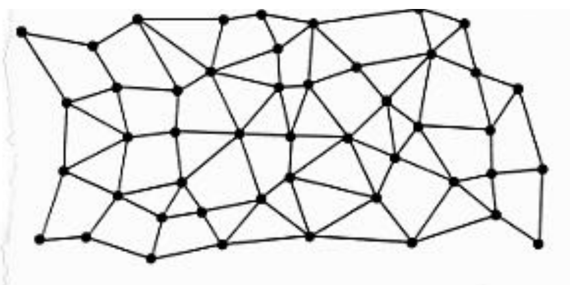
Tailor service for customer
- *Residence*
- *Neighborhood*
- *Office buildings*
- *Shopping center*
- *Factory*
- *Campus*
- *Military base*
- One size does not fit all

A DC Microgrid?

DC components
- *Solar panel*
- *Battery*
- *LED lighting*
- *Electronics*
- *Everything except motors*

Short delivery distance

Simplified, less expensive



A network of interacting microgrids

Energy storage technologies

PHES (Pumped Hydro Energy Storage)

CAES (Compressed Air Energy Storage)

TES (Thermal Energy Storage)

FES (Flywheel Energy Storage)

SMES (Superconducting Magnetic Energy Storage)

SCES (Supercapacitor Energy Storage)

ECES (ElectroChemical Energy Storage)

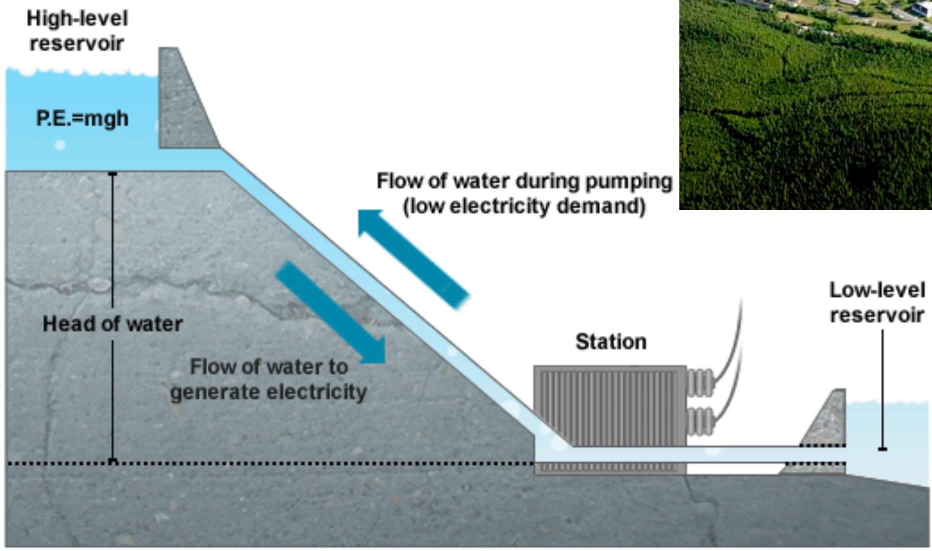
PHES (Pumped Hydro Energy Storage)

Large P/W, P/W unbound, mature, slow, site issues, environmental impacting

127 GW of the total 128 GW worldwide stationary storage capacity

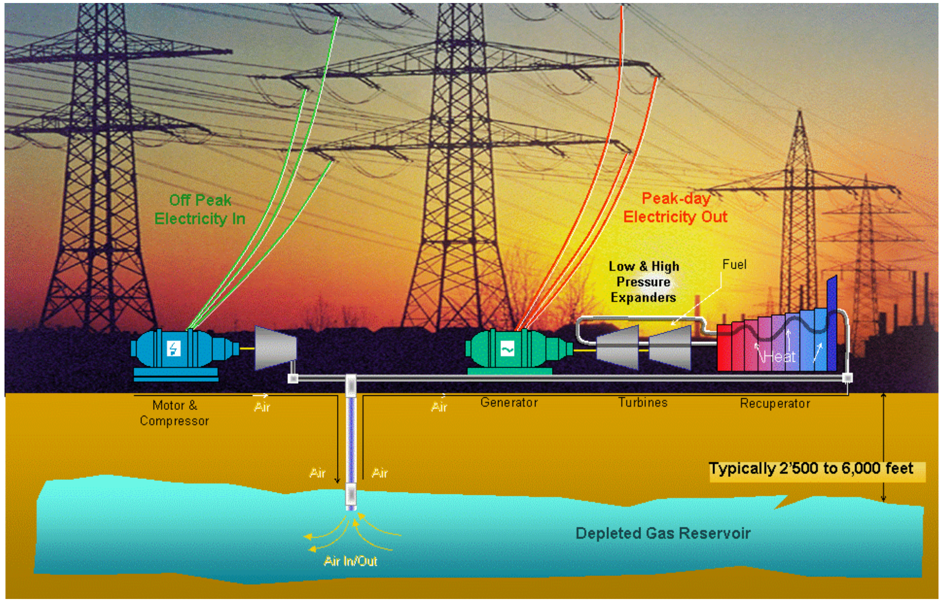
- **Top plants:**
- **Bath County Pumped Storage Station** (US-VA): 3 GW – 10 h = 30 GWh
- **Huizhou Pumped Storage Power Station** (China): 2.45 GW
- **Guangdong Pumped Storage Power Station** (China): 2.4 GW
- …
- **Entracque Power Plant** (Italy): 1.137 GW

- **Typical plants**: > 20 MW – 50 MWh



CAES (Compressed Air Energy Storage)

- **Underground:**
- mature, large P/W, P/W unbound, slow, site issues



- **Huntorf** (Germany, 1978):
  290 MW – 900 MWh (3 h)
  2 caverns ($310 \cdot 10^3$ m^3; –655 –800 m)
  p≤66 bar
- **McIntosh** (US-AL, 1991):
  110 MW – 2800 MWh (25 h)
- 1 cavern ($560 \cdot 10^3$ m^3;–460 m)
  p≤74 bar

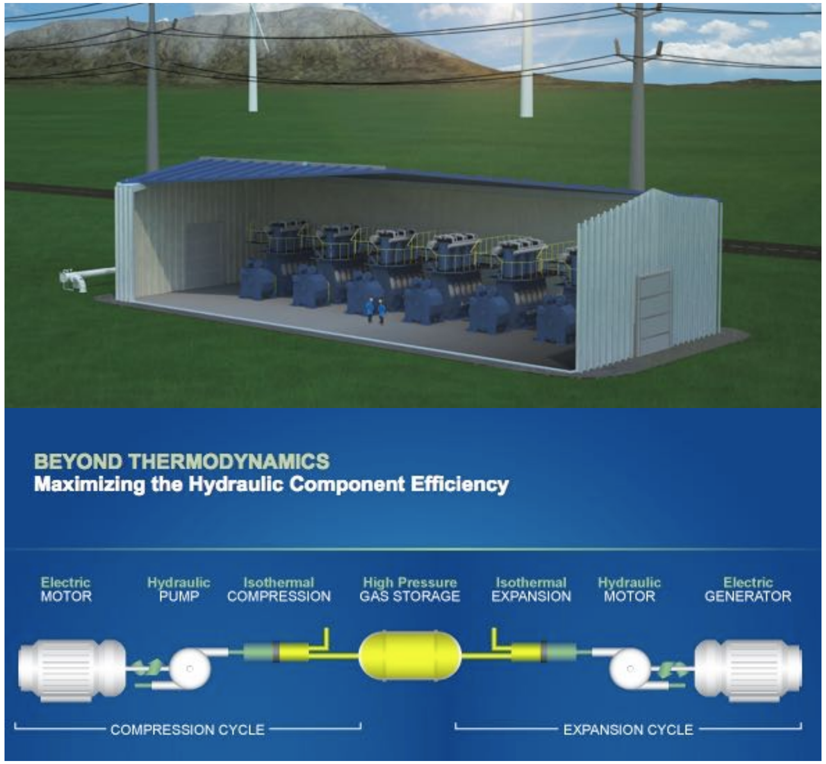
- Under construction:
- **Kern County** (US-CA): 300 MW – 3000 MWh (10 h, $ 2 M)

- In progress:
- Adiabatic (ADELE, Germany, 200 MW, 1000 MWh)

CAES (Compressed Air Energy Storage)

- Aboveground (A-CAES):
- development, slow, costs

- **Queens** NY (US-NY): 9 MW – 40 MWh
- **Seebrook** (US-NH): 1.5 MW – 1.5 MWh
- ....



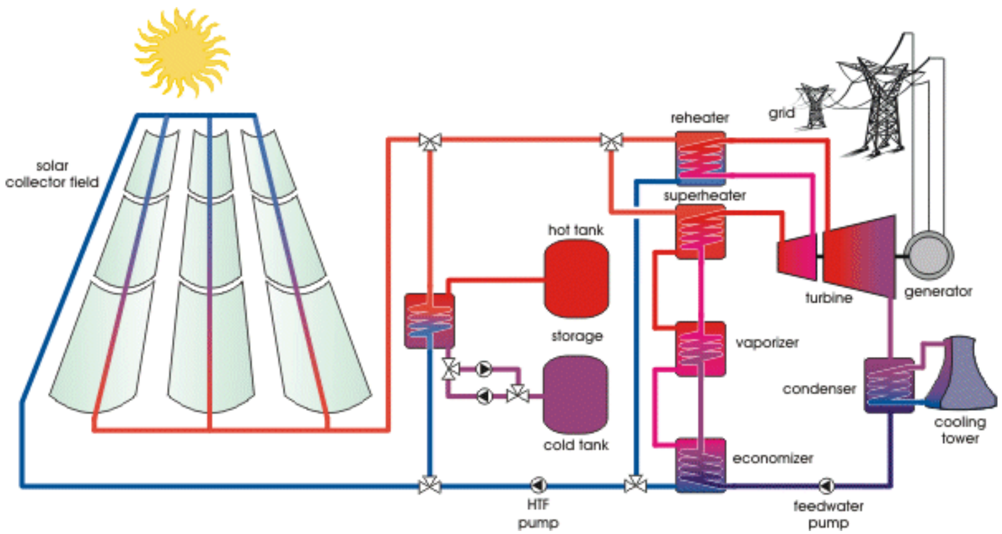
- Underwater (UW-CAES):

TES (Thermal Energy Storage)

- Development/operation, slow, costs, time shifting (i.e. night generation), very limited
- Alta temperatura: sali fusi (calcio, sodio, nitrato di potassio, …)

Impieghi non elettrici:

- Trasferimento del calore ad un serbatoio coibentato per utilizzo differito
- Vettore termico: vapore pressurizzato, ghiaccio, calcestruzzo,



Crescent Dunes Plant (US-NV): 110 MW

FES (Flywheel Energy Storage)

Stazionari
Beacon Power (e altri)

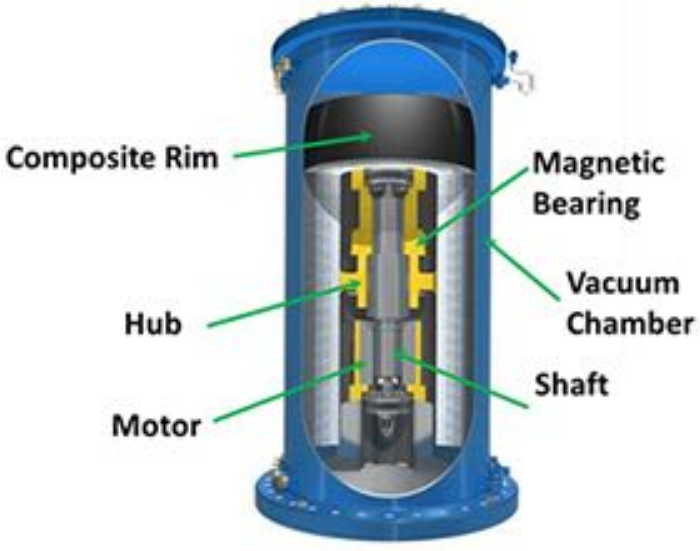
- 40-60 10^3 rpm
- Cuscinetti magnetici
- Trasmissione magnetica
- Camera depressurizzata

•Top plant (**BPFES US-NY**)

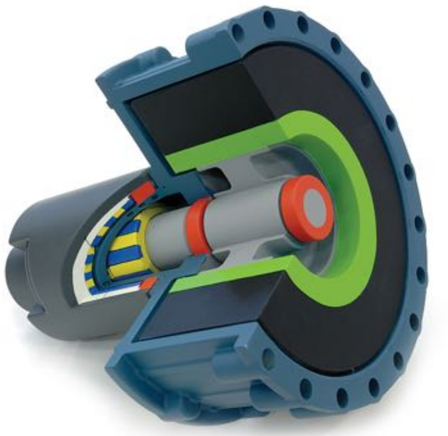
- 20 MW – 5 MWh (15 min) con 10 unità da 2 MW

Mobilità

- per bus: accumulo da frenata rigenerativa
- criticità: effetto giroscopico



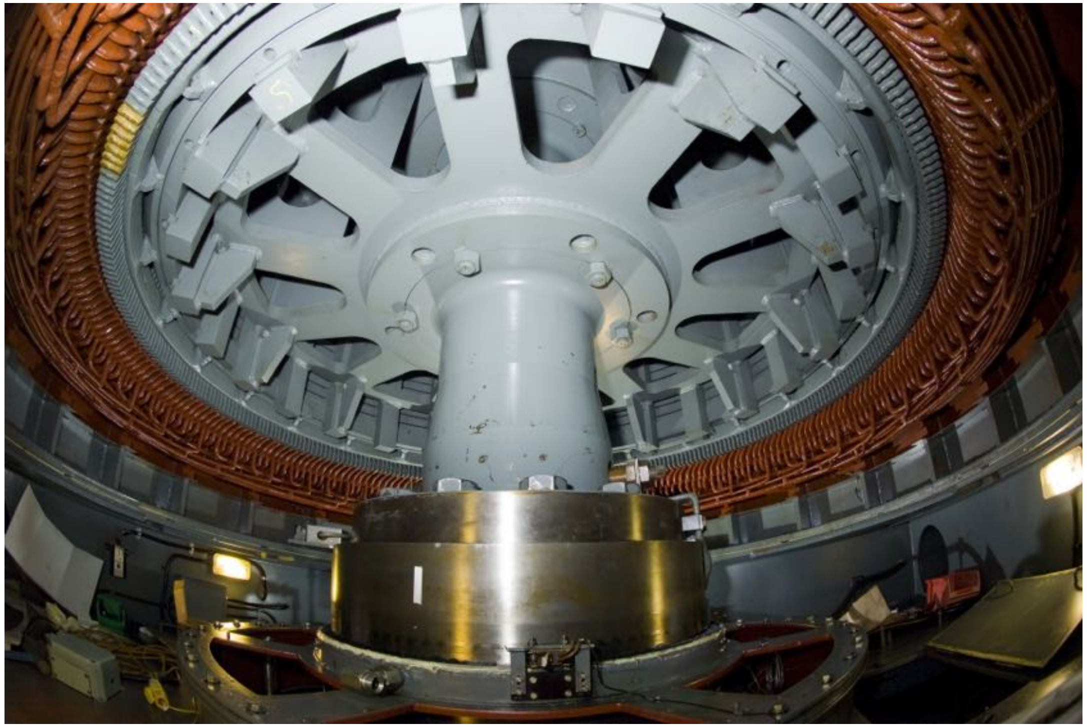
Source: Beacon Power, LLC



FES (Flywheel Energy Storage)

LAB (P/W record)

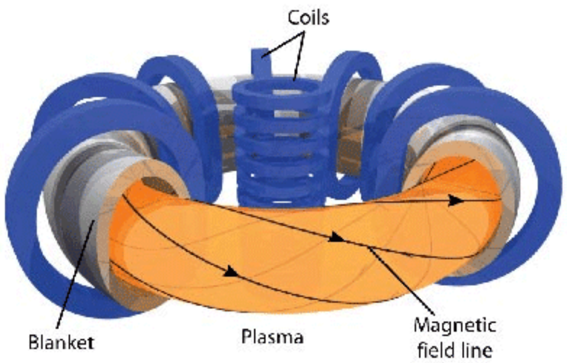
JET Tokamak (EU)
Flywheels
2 x 775 tons, diameter 9 m
225 rpm (380 km/h)
Charge: 2 x 8.8 MW – 1 MWh
Discharge: 2 x 400 MW



Fusion Institute of JAEA (Japan)
2.2 MWh

Lab - Magnetic Energy Storage

RFX - Avvolgimento Magnetizzante (costruzione ABB):
40 bobine con diametro fino a 8 m
200 spire
60 mH



Carica: 1 kV (100 MW) in 3 s
50 kA
15 Wb
75 MJ (20 kWh)

Scarica: 200 kV 10 GW in 30 ms
→corrente di plasma di 2 MA

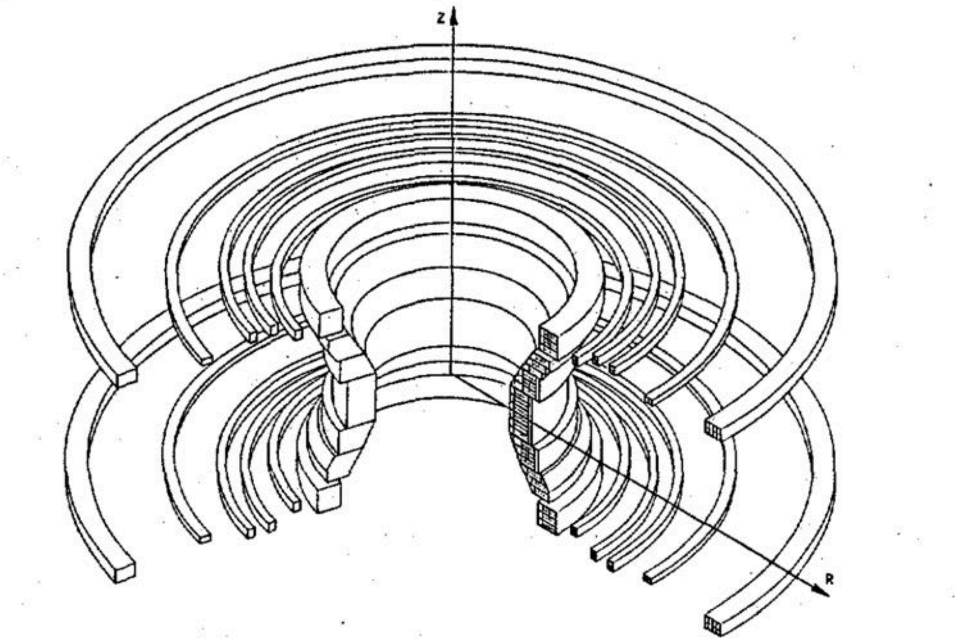
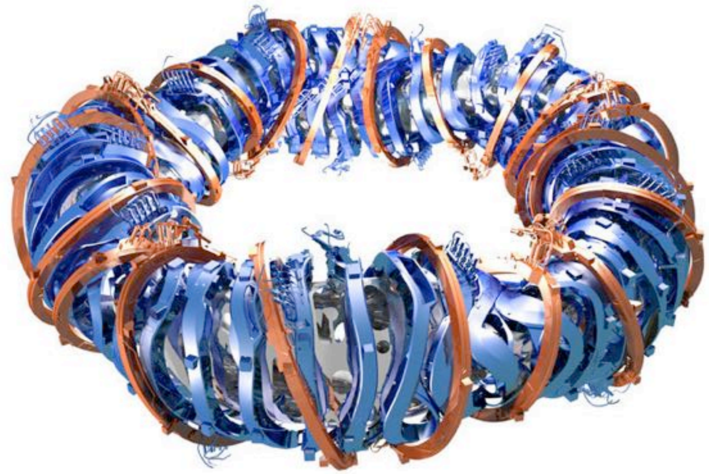


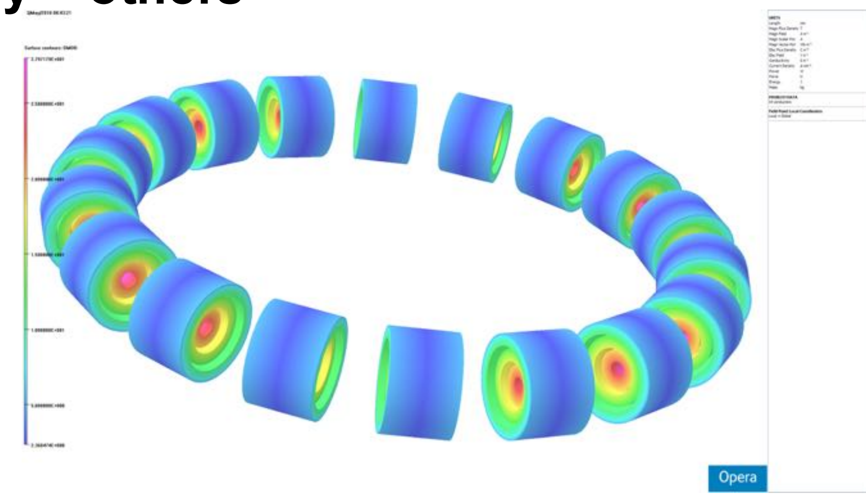
Fig. 1 Pictorial view of a typical magnetizing winding arrangement. The vacuum vessel is placed in a region completely enclosed within the coils.

Superconducting Magnet Energy Storage

•Fusion Experiments
- ITER, Wendelstein 7-X, …



•Storage for renewable energy
- US Department of Energy's (DOE) – ARPA-E
- Brookhaven National Laboratory + others
- 5.2 M$



•Taglie tipiche
- ≤ 20 MWh
- ≤ 40 MW

Banco di condensatori di crossover di Eta Beta II

Banco Poloidale:

3.6 kV

89.5 mF

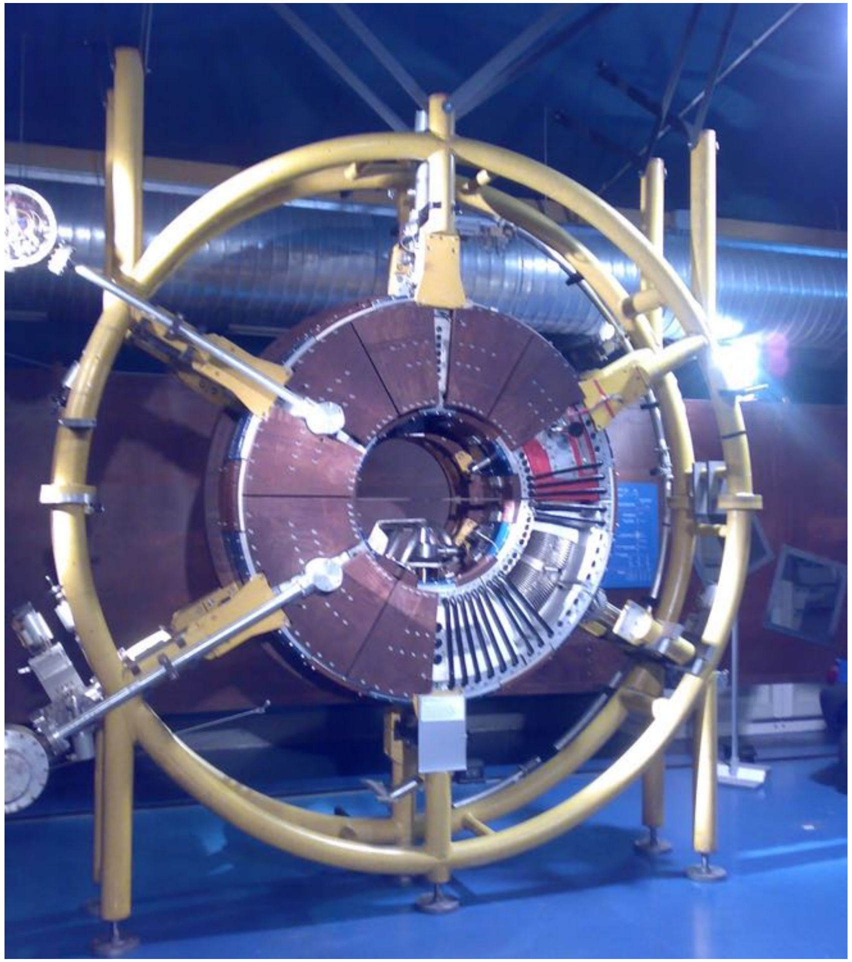
580 kJ

Carica in 10 s

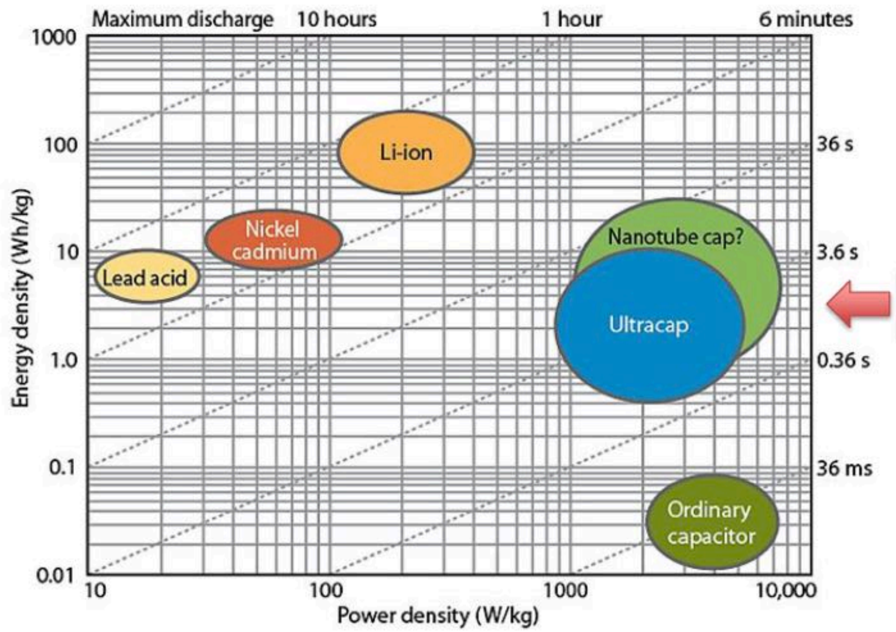
50 kW

Scarica in 100 ms

6 MW



SCES (Supecapactor Electric Energy Storage)



Supercondensatori

Single unità:

- 10^0 V
- 10^3 F
- Carica e scarica molto rapide
- Lunghissima vita (10^6 cicli)
- Assemblabili in banchi s/p

  e.g.: 120 V - 63 F - 126 (105) Wh

Impieghi:

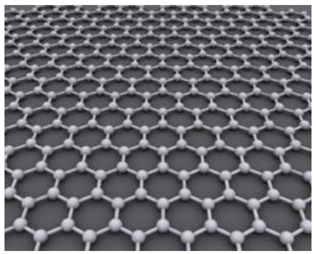
Mobilità

- Capabus (EXPO 2010) → ?
- propulsione ibrida → !

Sviluppi:

Mobilità

- graphene
- ….



Modularità
Flessibilità logistica
Non impattanti
Mobilità

Chiuse

- A bassa temperatura (Pb, Cd, Ni, Li)
- Ad alta temperatura (Na)
  - → P/W vincolate

Aperte

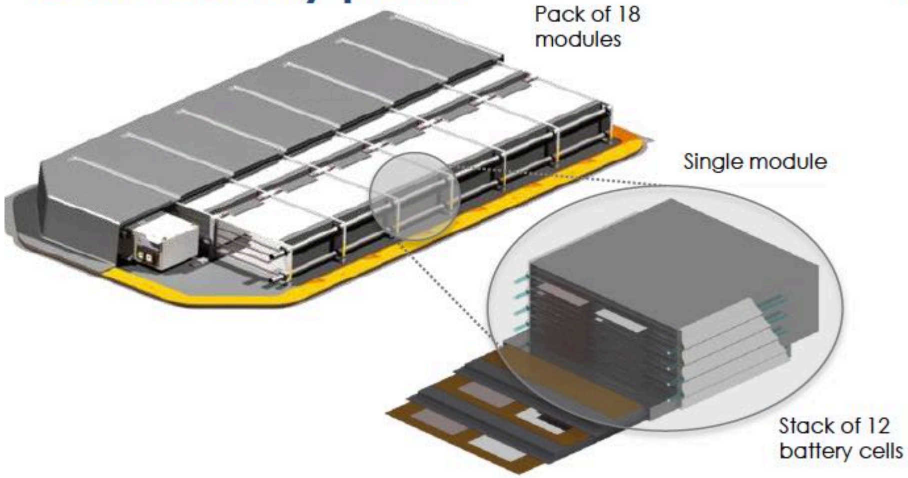
- A flusso (V, Fe-Cr, Br, …)
- Celle a Combustibile (H_2, Metano, Etanolo, Metanolo)
  - → P/W svincolate

Batterie chiuse a bassa temperatura per impieghi mobili e stazionari

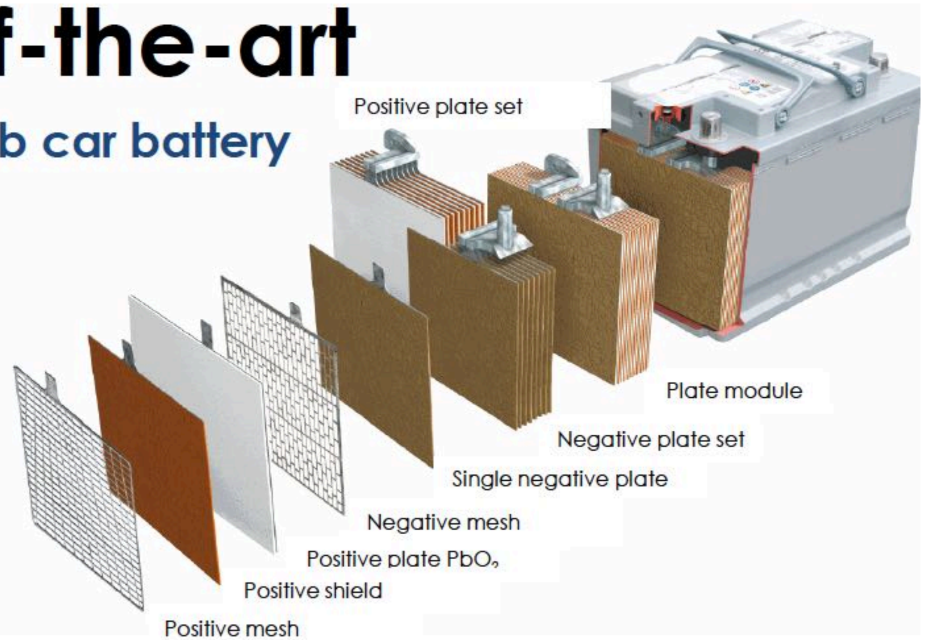
chimica	dati essenz.	portabilità leggera	automotive	impieghi stazionari di potenza
Pb-acido	42 Wh/kg 0.18 kW/kg 800 c 2 V		X	X
Ni-Cd (1980)	60 Wh/kg 0.15 kW/kg 2000 c 1.2 V	X		
Ni-MH (1989)	120 Wh/kg 1 kW/kg 2000 c 1.2 V	X →	X →	X
Li-ion (1991) Li-pol	200 Wh/kg 10 kW/kg >1000 c 3.7 V	X →	X →	X

Batteries – state-of-the-art

Li-ion battery pack



Pb car battery



Battery type	Pb	Ni-Cd	Ni-MeH	Na-S/Na-$NiCl_2$	Li-ion
Energy density vol. [Wh/L]	90	150	200	345/190	300-400
Energy density grav. [Wh/kg]	35	50	70	170/120	200-300
Power density vol. [W/L]	910	2000	3000	270	4200-5500
Power density grav. [W/kg]	430	700	1200	180	3000-3800
Self-discharge	+	+	+	-	++
Fast charging	--	++	+	-	+

Reaction mechanism

$$Li^+ + e^- + 2\,Li_{0.5}CoO_2 \leftrightarrow 2\,LiCoO_2 \quad \text{(cathode)}$$

$$LiC_6 \leftrightarrow Li^+ + e^- + 6\,C \quad \text{(anode)}$$

$$LiC_6 + 2Li_{0.5}CoO_2 \leftrightarrow 2LiCoO_2 + 6C\ ;\ \Delta U_0 \approx 4.1\ V$$

Electrodes

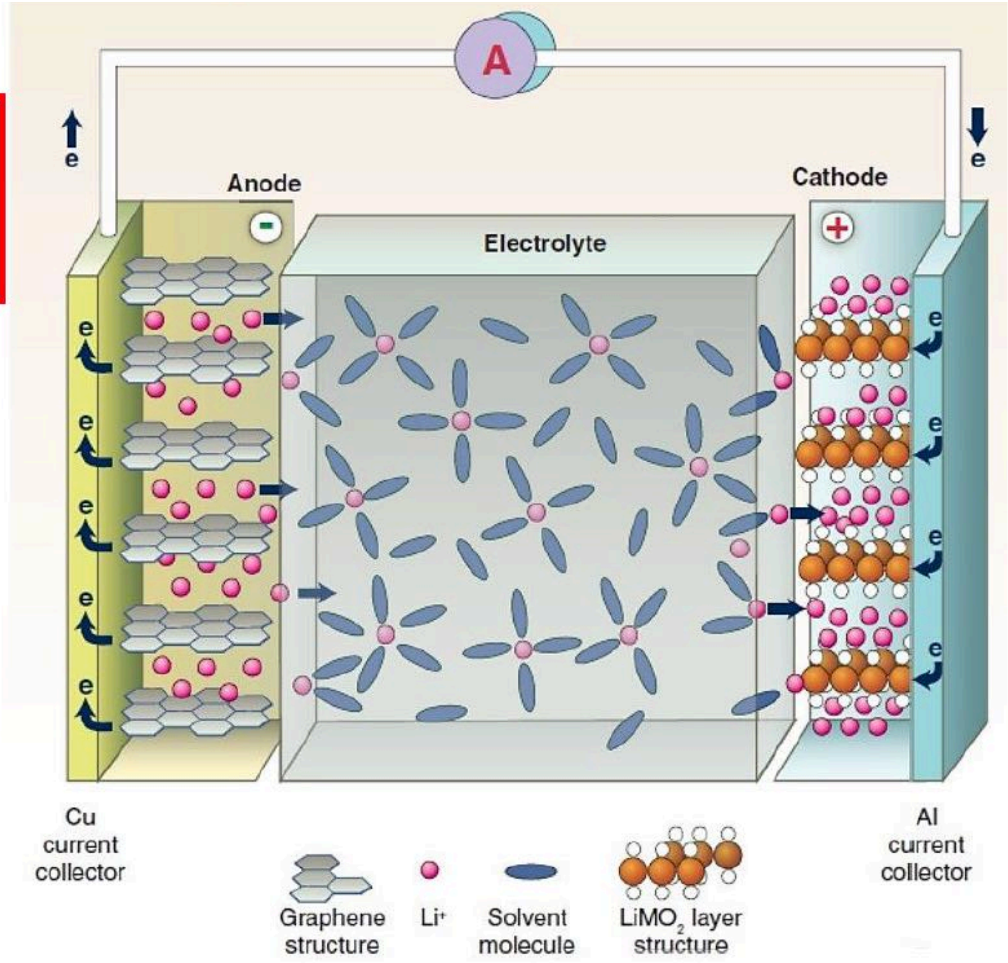
Intercalation / deintercalation of Li^+ ions into host structures

Limit: Energy density

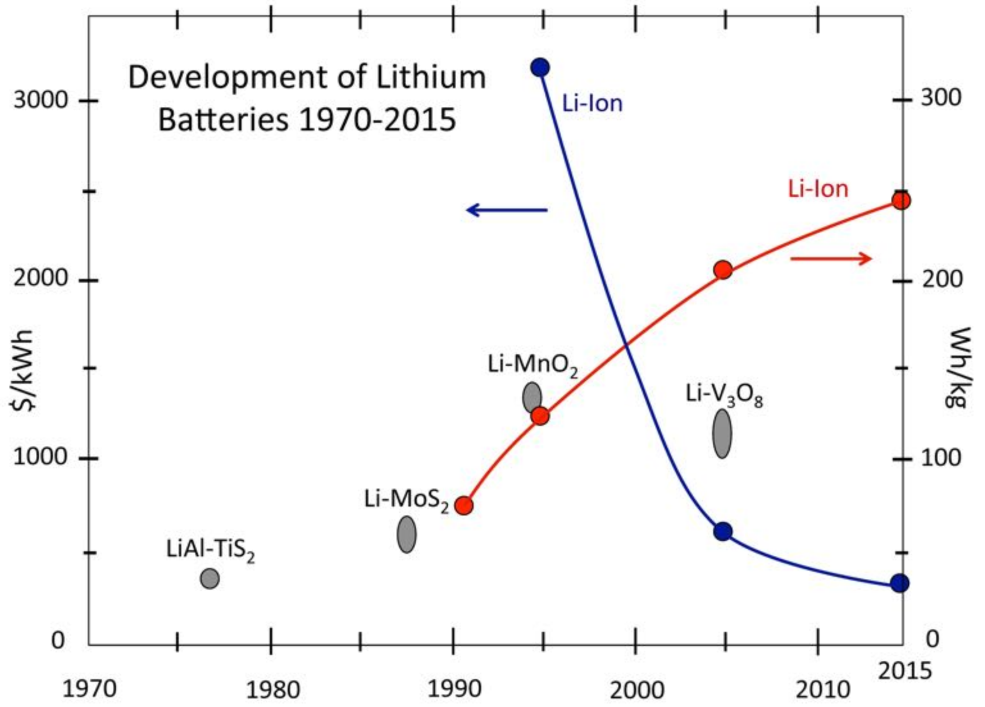
Example: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ / Graphite

Electrodes: 70 % of cell weight
Rest (current collectors, electrolyte): 30 %

- Electrodes : 430 Wh/kg
- Complete cells: 300 Wh/kg
- Total battery pack: **200 Wh/kg**



Lessons from Lithium-ion inform JCESR



Crabtree, Kocs, Trahey, MRS Bulletin, Dec 2015

1971
Conceptualization
Li metal anode
Intercalation cathode

1991
Commercialization
Sony Lithium-ion

Steady but saturating
post-commercialization
discovery and development

20 year incubation period

Simple, elegant concepts, but . . .

Complex interfering side effects
Detrimental side chemical reactions
Incompatible materials

"Murphy's Law" worst case scenario

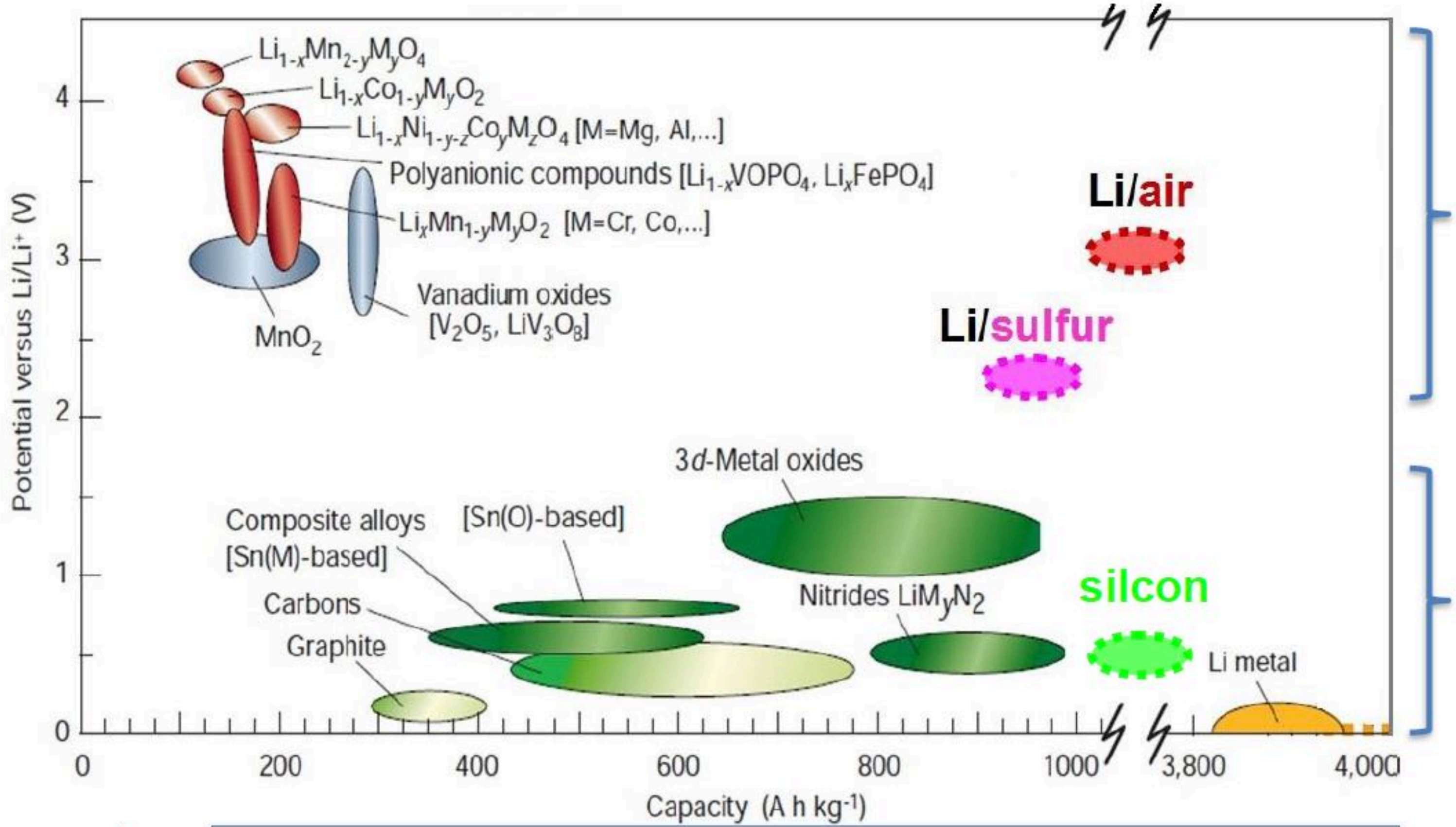
Many (most) ideas do not work
Many strategic pivots

Balance targeted outcomes
with back up alternatives

"Convergent" and "divergent" research

After 40 years, the "holy grail" of
Lithium metal anodes still eludes us

Tante chimiche diverse – metalli diversi accoppiati al litio all'anodo



Compound formation / alloying rather than **intercalation** in host structure

Post Li-ion batteries: Li-air and Li-S batteries with Si or Li anodes

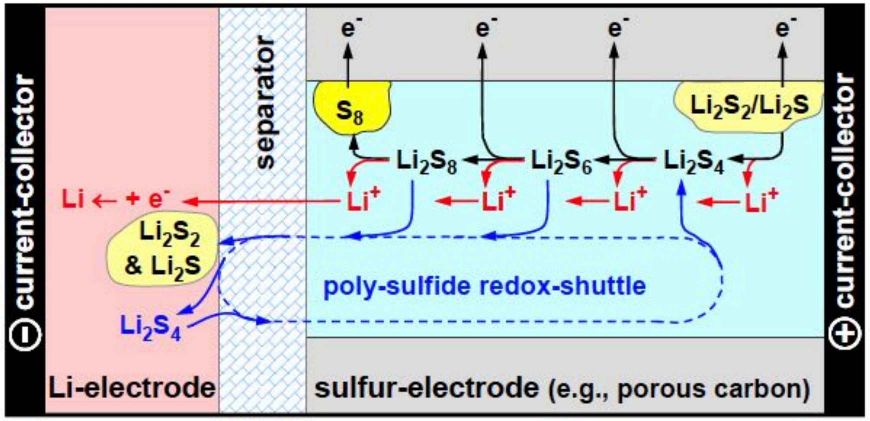
Future Concepts – Li-S Batteries

Concept

$$S + 2\,Li^+ + 2\,e^- \leftrightarrow (Li_2S)_{solid} \quad \text{(cathode)}$$

$$2\,Li \leftrightarrow 2\,Li^+ + 2\,e^- \quad \text{(anode)}$$

$$2\,Li + S \leftrightarrow (Li_2S)_{solid}\ ;\ \Delta U_0 \approx 2.0\ V$$



Challenges and R&D needs

- Polysulfide diffusion to anode ➡ Li^+-conducting diffusion barrier
- Poor C-rate & cathode "clogging" ➡ Cathode design
- Stable anode configuration ➡ Improved Li-metal anode design or alternative

Advantages

- High specific capacity: 630 $Ah/kg_{electrode}$
- High energy density: **950 $Wh/kg_{electrode}$**
- Low cost of sulfur
- Minimal degradation during charge cycling

Gain vs. state-of-the-art batteries: 2-fold

Novel Concept: Magnesium Batteries

Novel Concept – F-ion Batteries

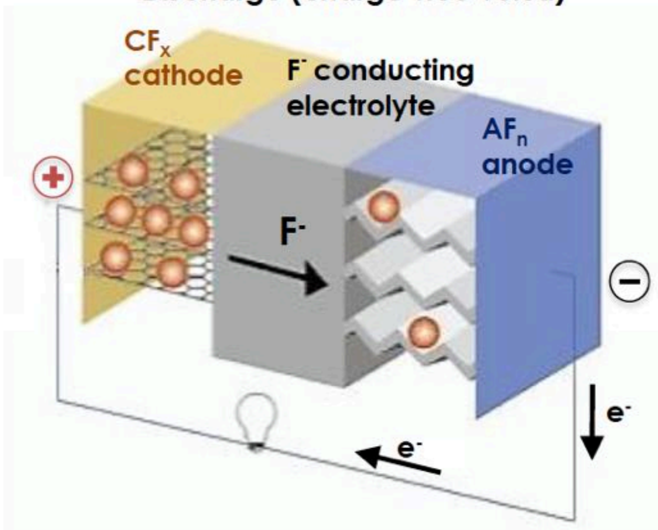
Concept

Reminder: Li-ion reaction

$$LiC_6 + 2Li_{0.5}CoO_2 \leftrightarrow 2LiCoO_2 + 6C \; ; \; \Delta U_0 \approx 4.1 \text{ V}$$

F-ion reaction

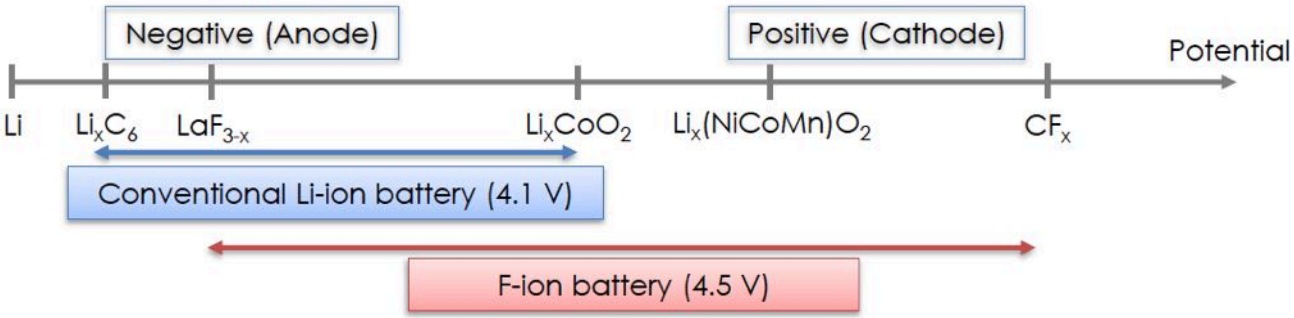
$$LaF_3 + 3CF_y \leftrightarrow LaF_{3(1-x)} + 3CF_{x+y} \; ; \; \Delta U_0 \approx 4.5 \text{ V}$$



Advantages

- High theoretical energy density: **1560 Wh/kg**
- No need for scarce elemental lithium
- **Safer** than Li-ion batteries (no oxygen present)

Choice of redox couple



Redox Flow Battery – Principle

Reaction mechanism

$V^{5+} \rightarrow V^{4+}$: $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$

$U_0 \approx +1.00$ V vs. NHE

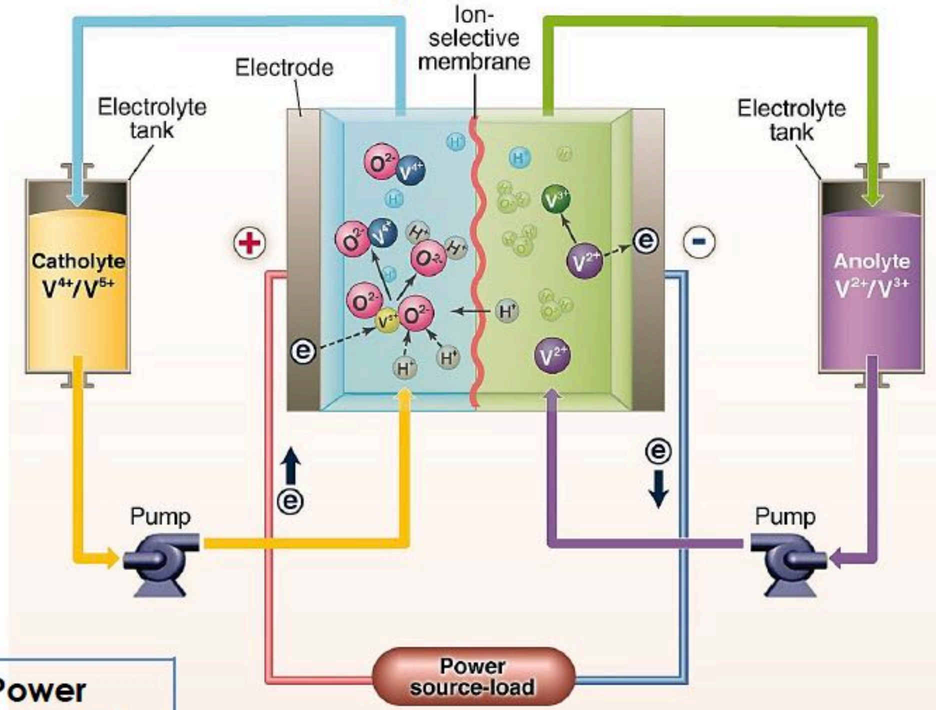
$V^{2+} \rightarrow V^{3+}$: $V^{2+} \rightarrow V^{3+} + e^-$

$U_0 \approx -0.26$ V vs. NHE

Discharge operation (charge operation vice versa)

Advantages of Redox flow batteries

- Energy and power of battery scale independently
- Instantaneously refuelable
- High cycle-lifetime
- Non-hazardous materials



Redox couple	E_{cell} [V]	Overall efficiency [%]	Energy density [Wh/L]	Power density[a] [W/m²]
Iron-Chromium	1.2	95	13-15	200-300
All-Vanadium	1.6	83	25-35	600-700
Vanadium-Bromide	1.4	74	35-70	220-320
Mega-ions	**1.5**	**96[b]**	**250[c]**	**2000**

Low energy and power density!
Compare to Li-ion battery:
300 Wh/L and 4200 W/L

[a] Estimated as measured current density times cell voltage
[b] Coloumb efficiency of half-cell
[c] Estimated value based on solubility of 1 mol/L and 6 electrons per redox molecule

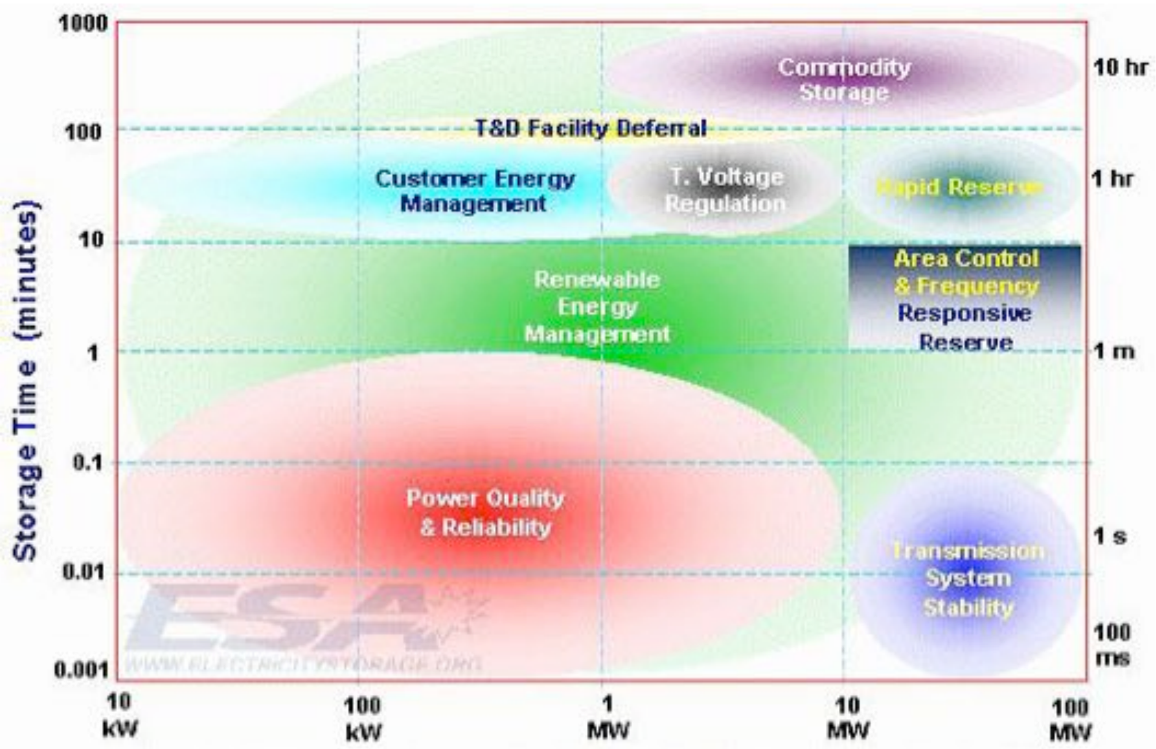
Stationary energy storage services

Power – Time requirements

Output powers: some kW to some GW

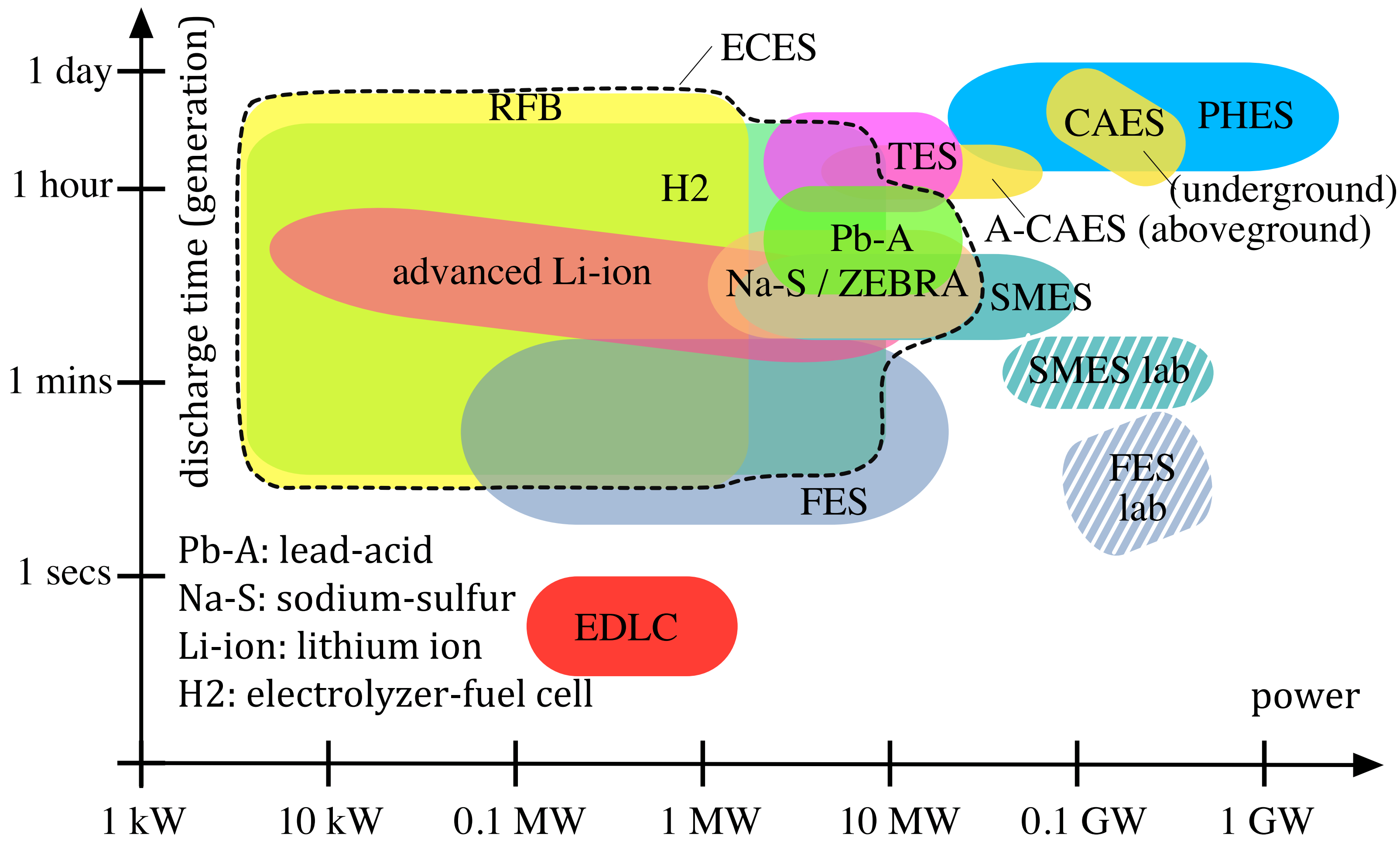
Response time: millisecs to minutes

Discharge times: minutes to several hours



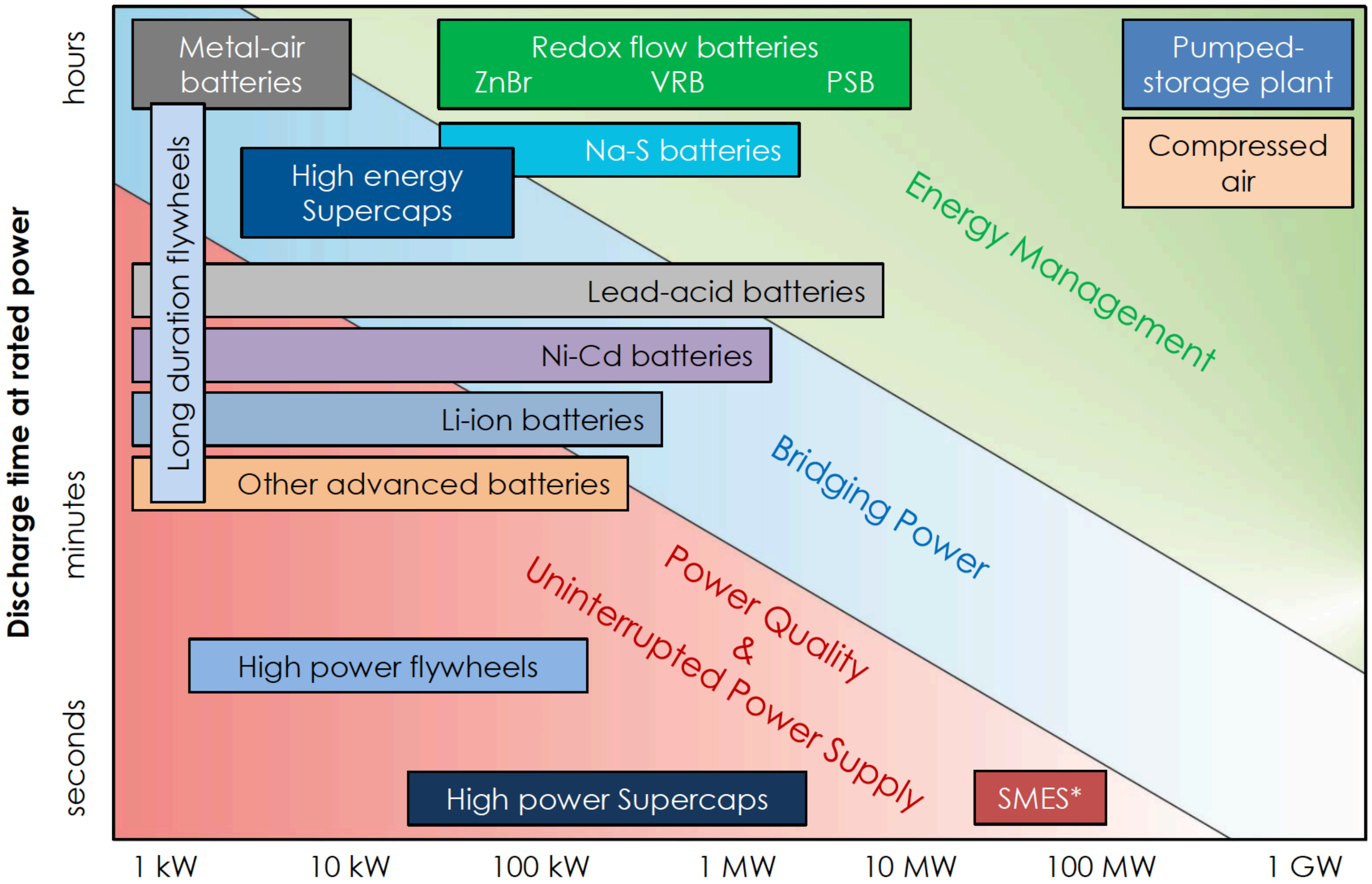
Allocation of energy storage services in the power–discharge duration diagram (source: Electricity Storage Association)

ES technologies allocation



Allocation of ES technologies in the power – discharge duration diagram

ES technologies allocation



Parametri da osservare

P [W] = potenza
W [kWh] = energia **utile**
tr [s] = tempo di risposta
ts [s] = tempo di scarica
tc [s] = tempo di ricarica
p [W/kg] = densità di potenza (impieghi mobili)
η [%] = rendimento sul ciclo scarica/carica
n = numero di cicli
w [kWh/kg] = densità di energia **utile** (impieghi mobili)
cp [€/kW] = costo specifico in potenza
cw [€/kW] = costo specifico in energia utile
cwn [€/kW.n] = costo specifico in energia **gestita**

Modularità
Impatto ambientale
Versatilità logistica

US - Next Generation Energy Storage Needed to Transform Transportation and the Grid

Two biggest energy uses and markets

Transportation 28%

Replace gasoline with electricity

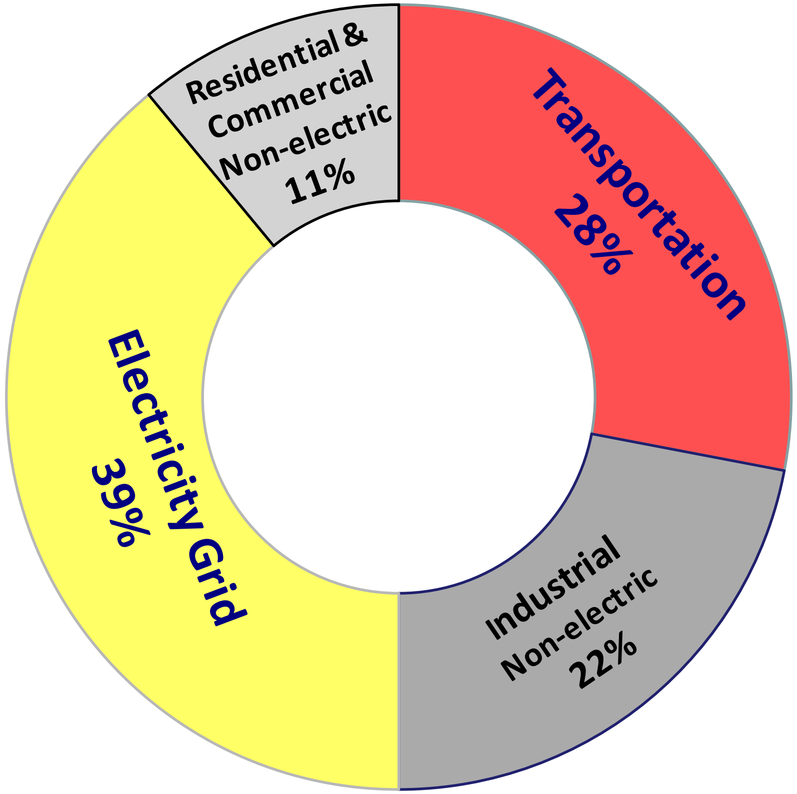
Electricity 39%

Uncouple instantaneous generation from instantaneous demand

Personal electronics < 2%

In energy terms, half the market for cars and the grid is ~10x personal electronics

Energy Demand



2013
EIA Monthly Energy Review Table 2.1 (May 2014)

The bottleneck for both transitions is inexpensive, high performance electrical energy storage

US - Next Generation Energy Storage Needed to Transform Transportation and the Grid

Grid-scale electricity storage?

Enable widespread deployment of wind and solar

Enhance reliability, flexibility, resilience

Uncouple instantaneous generation from instantaneous demand

$20K electric cars?

Displace gasoline cars

Replace foreign oil with domestic electricity

Reduce energy use and carbon emissions

More on JCESR website
www.jcesr.org

Perspective

Vision: Transform transportation and electricity grid with high performance, low cost energy storage

Mission: Deliver electrical energy storage with five times the energy density and one-fifth the cost

→ Beyond lithium ion

Legacies:

A library of the fundamental science of the materials and phenomena of energy storage at atomic and molecular levels

Two prototypes, one for transportation and one for the electricity grid, that, when scaled up to manufacturing, have the potential to meet JCESR's performance and cost goals

A new paradigm for battery R&D that integrates discovery science, battery design, research prototyping and manufacturing collaboration in a single highly interactive organization

- A bold new approach to battery R&D
- Accelerate the pace of discovery and innovation
- Bring the community to the beyond lithium-ion opportunity

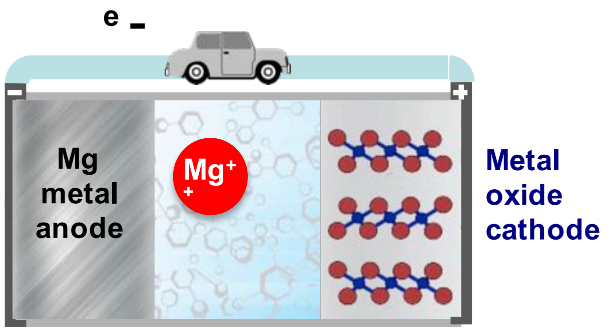
Argonne NATIONAL LABORATORY

UNIVERSITY OF PADOVA
ITALY

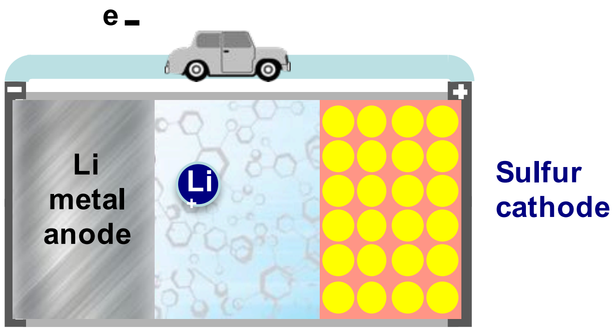
Techno-economic Modeling

Transportation

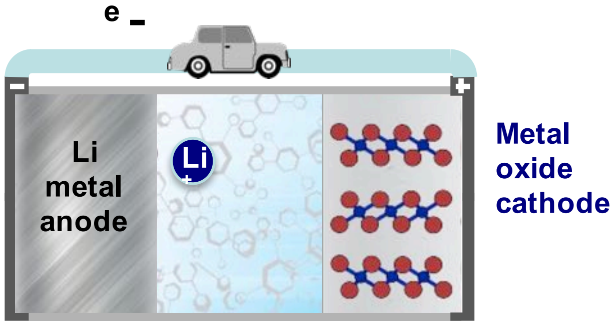
Magnesium/Metal-Oxide

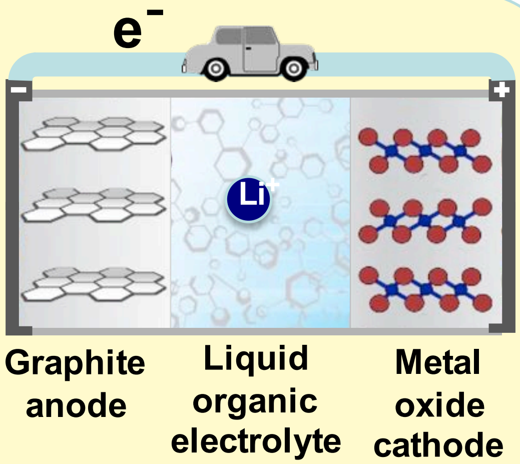


Lithium/Sulfur



Lithium/Metal-Oxide





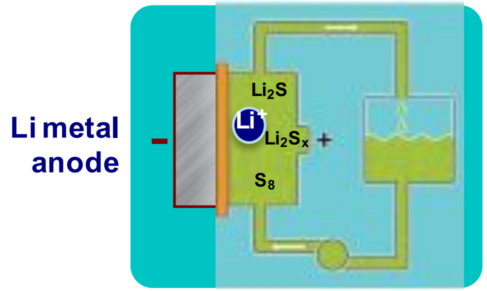
Lithium-ion

System-to-materials performance and cost thresholds

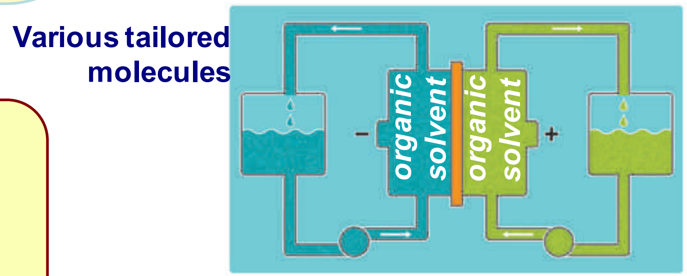
All have challenges that must be overcome to bridge the gap from today to $100/kWh

Grid

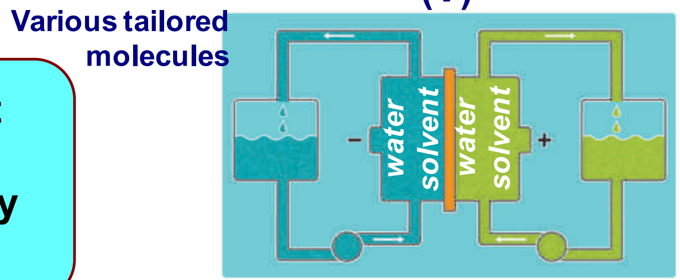
Polysulfide suspension semi-flow



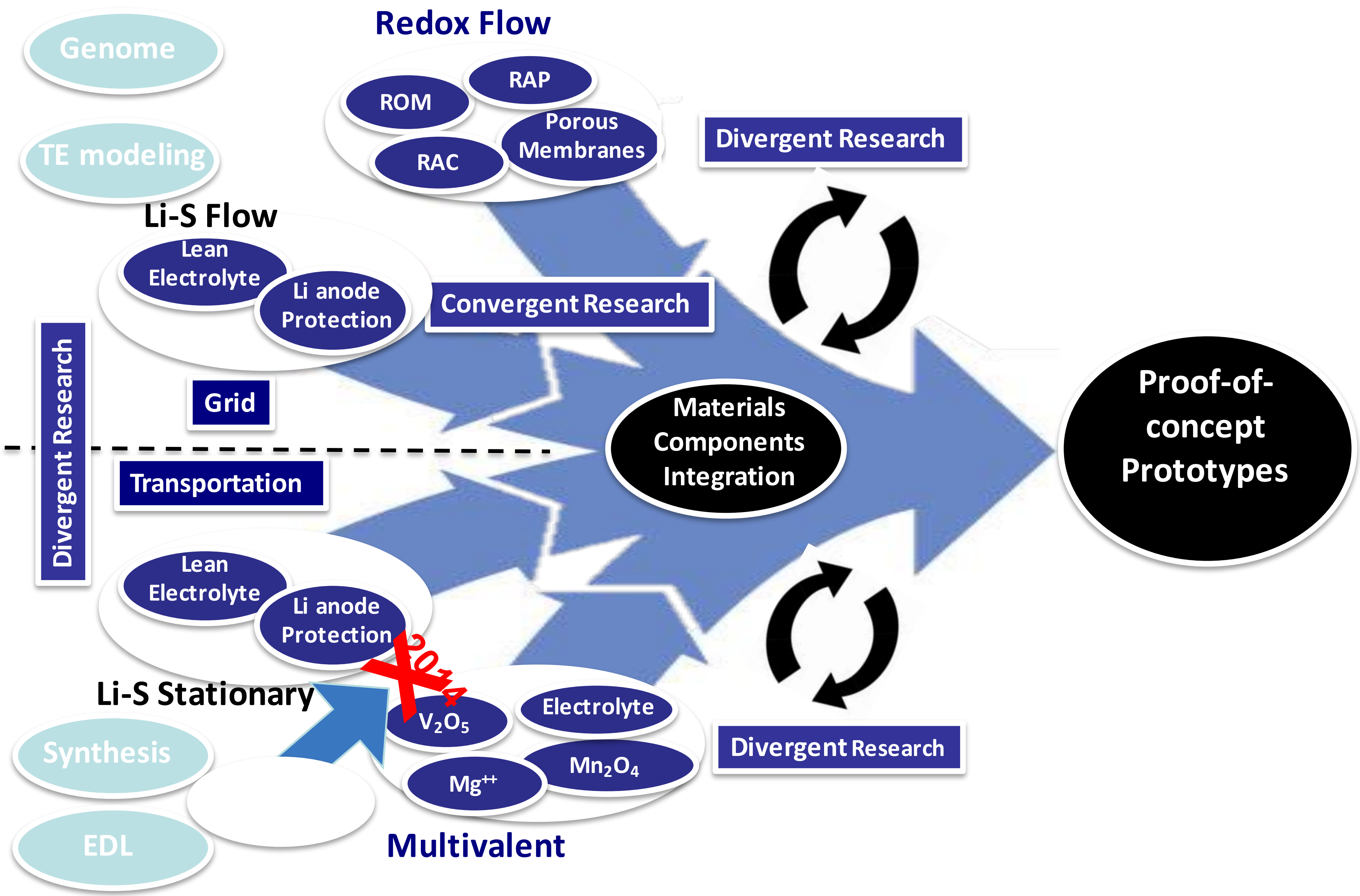
Non-aqueous redox flow (Zn-Br)



Aqueous redox flow (V)



JCESR - Four Convergent Pathways



Electric mobility trends

Previsione forte espansione del mercato:

- EV, HEV, PHEV, BEV, FCEV
- major US-D-J-K (Ford, Chrysler, GM, Mercedes, BMW, Audi, WV, …)

Riduzione dei costi: 1000$/kWh→500$/kWh→100$kWh

Aumento dell'autonomia: (attuale<150-200 km, tranne Tesla)

<65 km/dì: 68% degli autisti

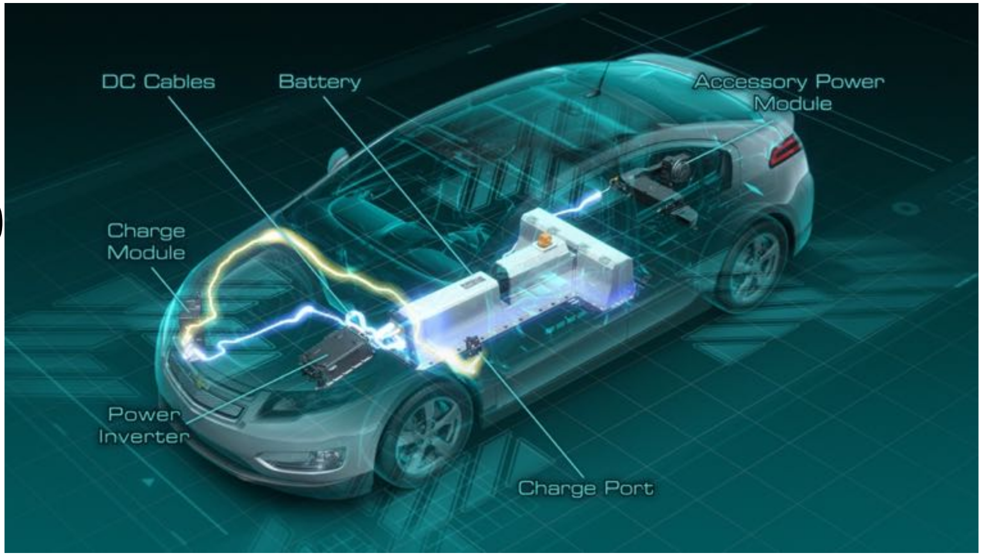
65<X<160 km/dì: 25% degli autisti

>160 km/dì: 7% degli autisti

Aumento dei cicli di vita: → 15.000

Riduzione dei tempi di ricarica:

- (fastcharge, supercharge, …)
- Elevamento della tensione
- 12V→24V→48V→60V→…800V



Electric mobility trends

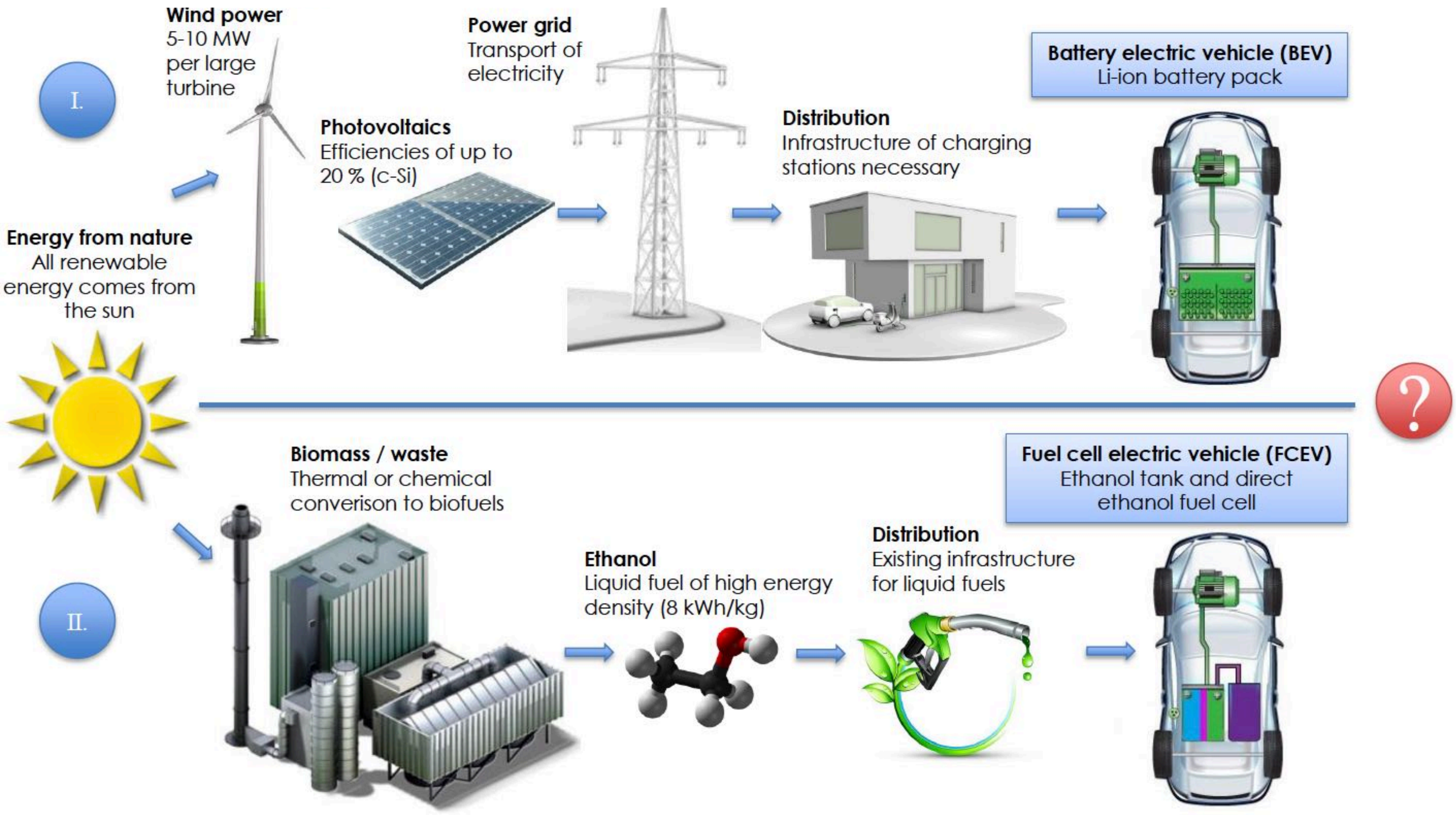
Riutilizzo a fine vita del veicolo:

- Riciclate garantite
- Riciclate
- Declassate e/o smaltite
- Da mobilità a stazionario
- 3 G$ entro 2020

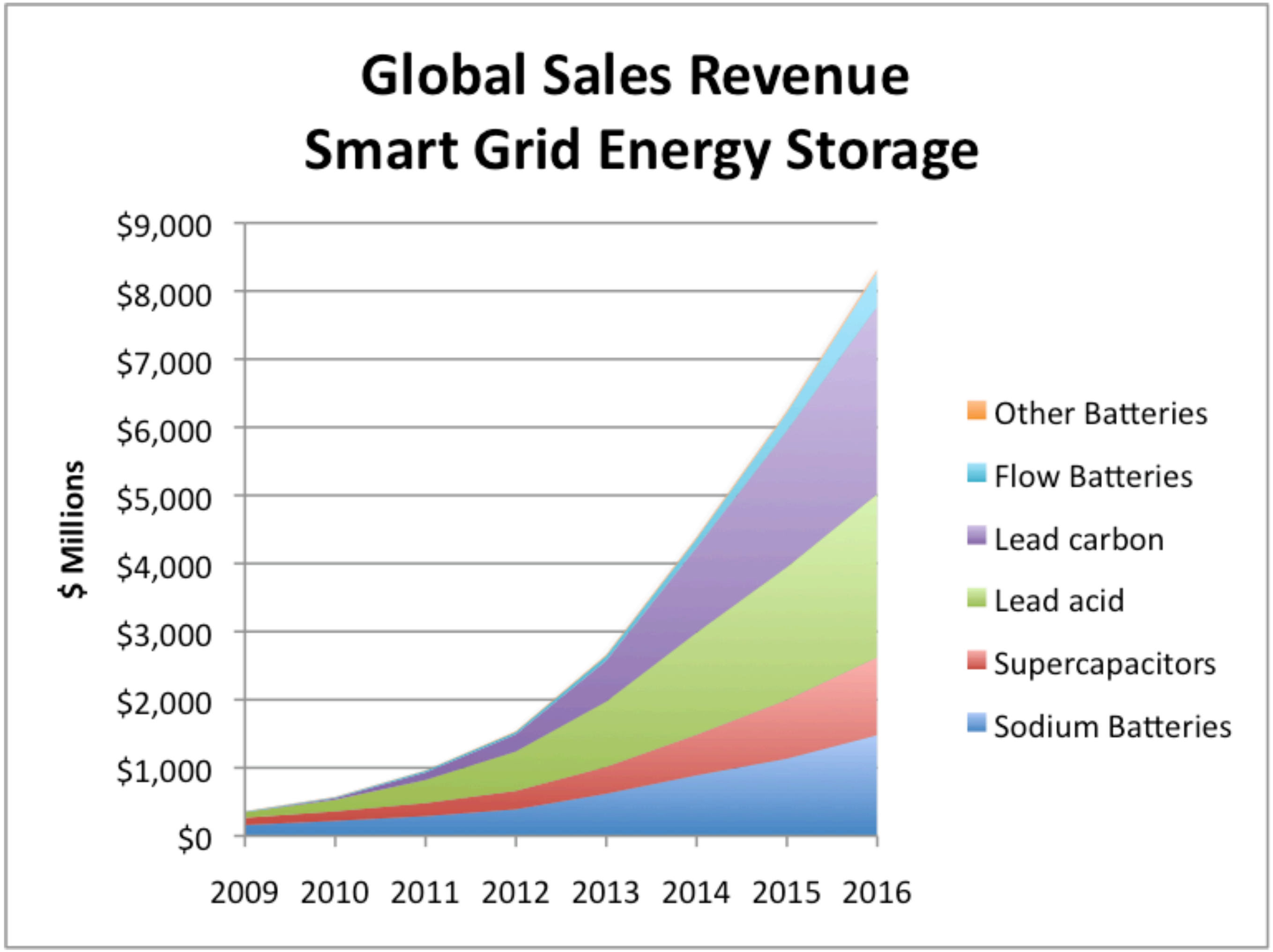
Creatività, multidisciplinarietà e vision:

- Competizioni studentesche
- 3D-printed electric car

Fueling the e-car



Battery sales



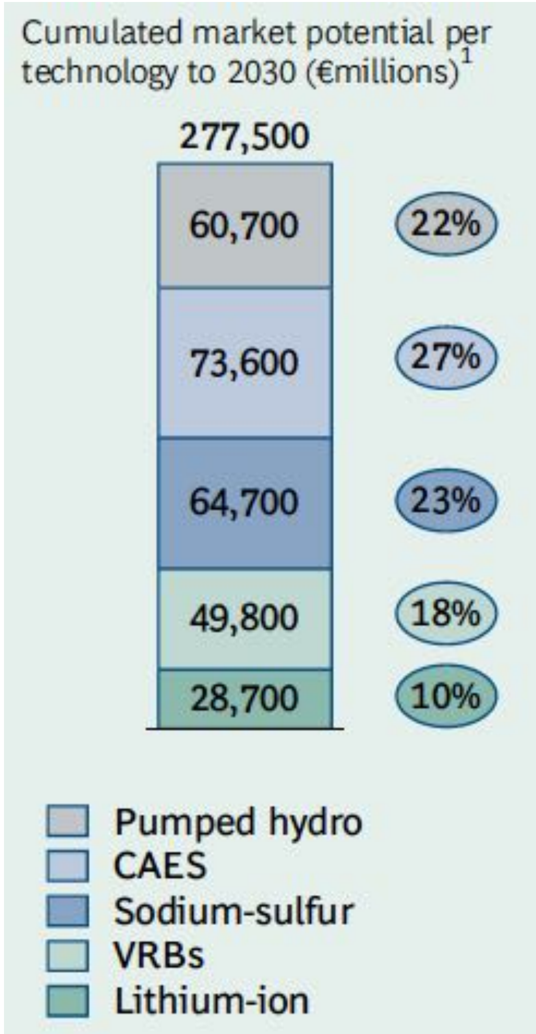
Estimated Market Growth

Economical aspects

Estimated global market growth:

- 330 GW by 2030 (250÷300% of present)
- € 280 billion investments

C. Pieper, H. Rubel, "Revisiting Energy Storage. There is a Business Case," *Boston Consulting Group Report*, February 2011.



Horizon 2020 (FP8) - 2014-2020: 80 G€

- Ricerca di base
- Ricerca tecnologia
- Innovazione

- **24 G€ - Excellence science** – base research: scientific excellence, future and emerging technologies, research mobility, research infrastructures
- **14 G€ - Leadership in enabling and Industrial technologies** – ICT, Nanotech, Adv materials, Adv manufacturing and proc, Biotech, Space.
- **31 G€ - Social challenges** – health, food, **energy (5.9 G€)**, **transport (6.3 G€)**, environment, society, secutity, …

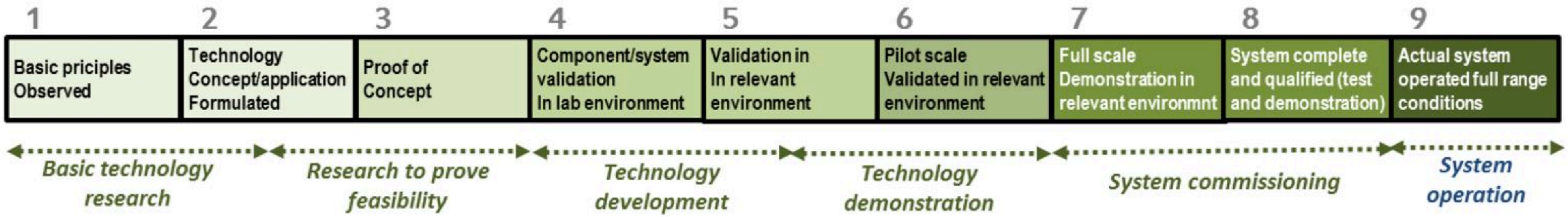
JOINT UNDERTAKINGS - 2014-2020: 17 G€

- Innovative Medicines Initiative (IMI)
- Aeronautics and Air Transport (Clean Sky)
- **Fuel Cells and Hydrogen (FCH) : 1.3 G€**
- Embedded Computing Systems (ARTEMIS)
- Nanoelectronics Technologies 2020 (ENIAC)

- Fusion for energy (897 M€ solo 2014)

TRL – Technology readiness levels

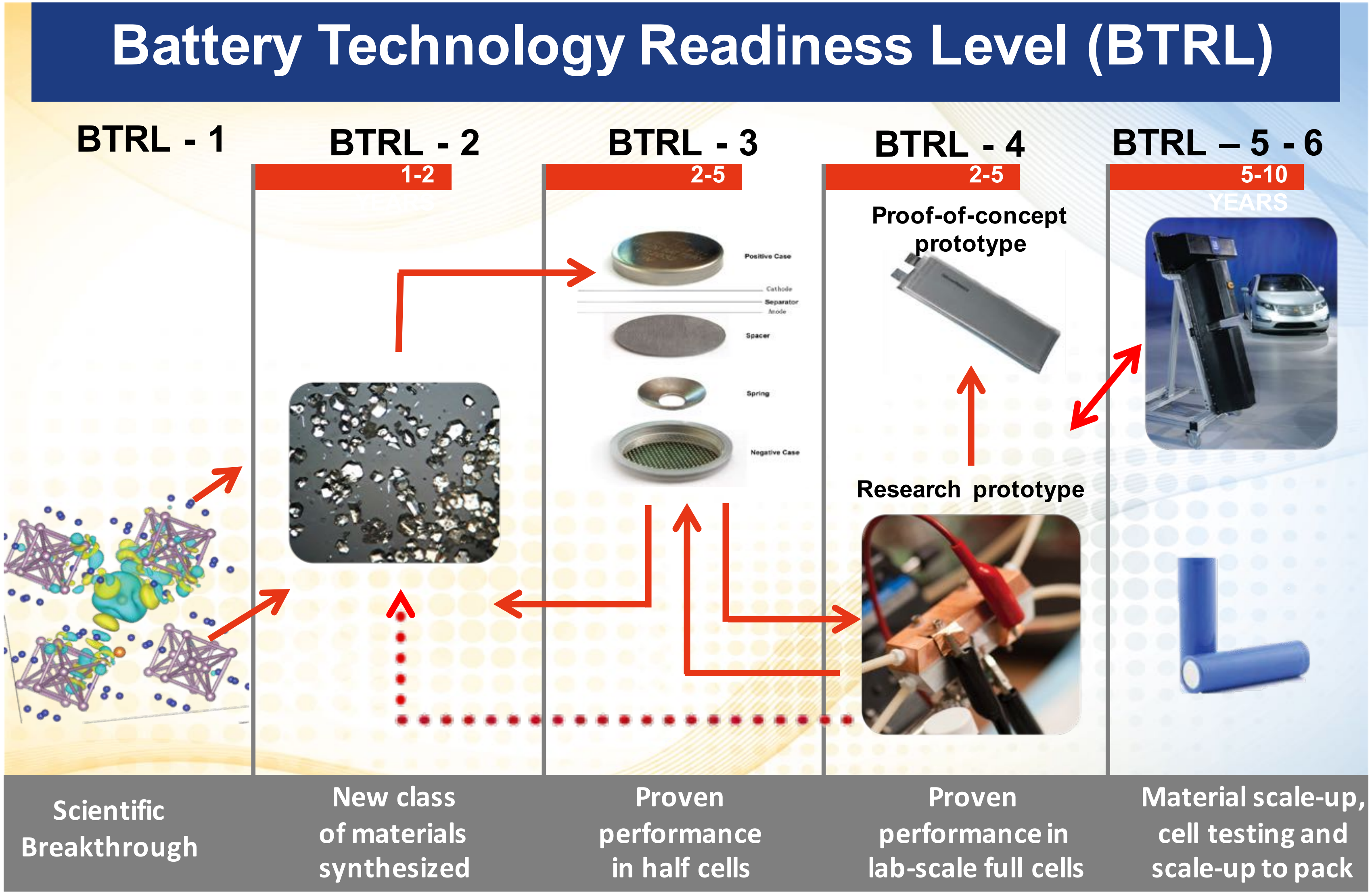
Figure 3: Adaptation of the TRL scale by US-DoE introducing 6 levels of technological development



TRL scale used in EU - Horizon 2020

1	2	3	4	5	6	7	8	9
Basic principles observed	Technology concept formulated	Experimental proof of concept	Technology validation in lab	Tech validation in relevant environment	Demonstration in relevant environment	Demonstration in operational environment	System complete and qualified	Successful mission operations

US - Battery Technology Readiness Level (BTRL)



Developed collaboratively with
JCI, NASA-Glenn, TARDEC

JCESR
"sweet spot"

e a Padova?

Batteria al Magnesio

- Primo brevetto mondiale (1999)
  http://archiviostorico.corriere.it/1999/ottobre/31/Col_magnesio_superbatterie_lunga_vita_co_0_9910311369.shtml
- Batterie Li di terza generazione (S, Ni, graphene, …)

Batterie a flusso di Vanadio

- Primo programma di ricerca italiano (Progetto strategico UNIPD)

Sperimentazione industriale:

- Esperimento MATTM: microgrid multitecnologia Pb-Li-Na-V-H_2 (Marghera)
- Propulsione navale ibrida (imbarcazioni tecniche a Venezia)

Tematiche per tesi di laurea magistrale

- Per chi non ha paura delle sfide

Peter Kreef - affronta le sfide: se vincerai sarai felice, se perderai sarai più saggio

grazie dell'attenzione