Tehnološke osnove iskorištavanja obnovljivih izvora energije

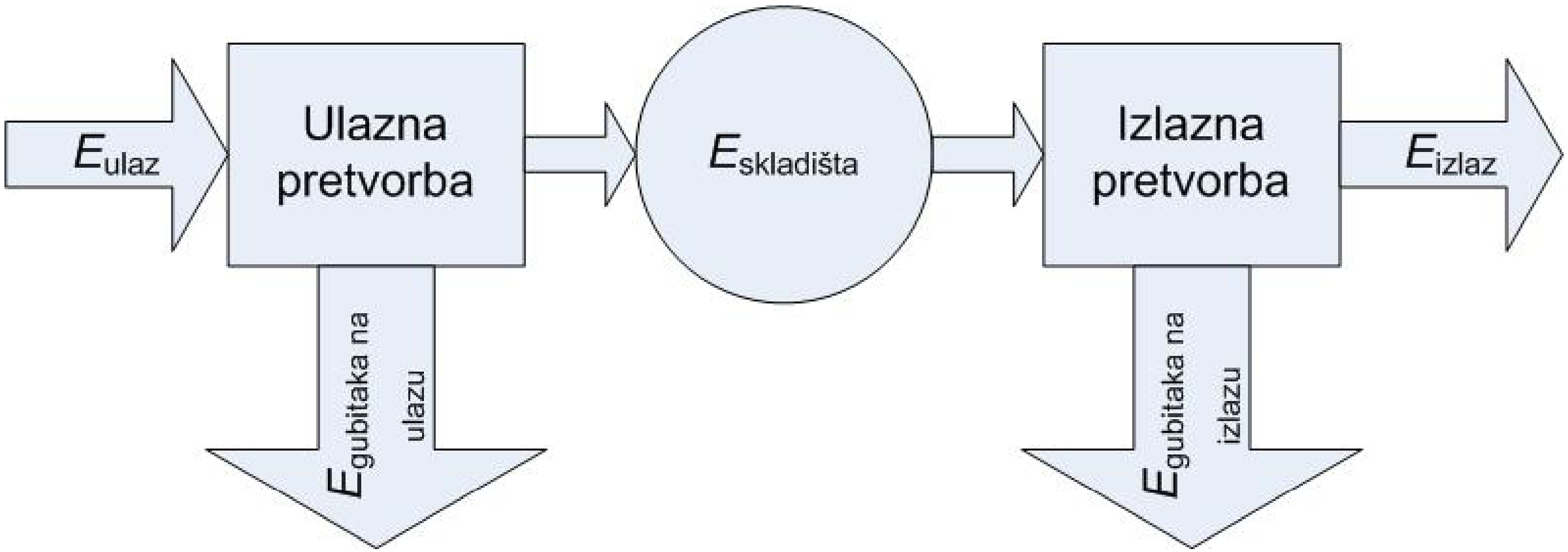
5. Spremanje energije

Spremanje energije

- Što je to?
  - Transformacija energije iz prijelaznog (procesnog) oblika u oblik pogodan za pohranu (unutrašnja energija) uz mogućnost ponovne transformacije u prijelazni oblik.
- Zašto?
  - Usklađivanje proizvodnje i potražnje
  - Rezerva s ciljem sprečavanja "zamračenja"
  - Omogućavanje jače integracije OIE
  - Osiguranje kvalitete napajanja

Opći kriteriji

1. Efikasnost ciklusa



$$\eta = \frac{E_{izlaz}}{E_{ulaz}} = 1 - \frac{E_{gubitaka}}{E_{ulaz}} \qquad \eta = \frac{E_{izlaz}}{E_{ulaz}} = \frac{E_{skladišta}}{E_{ulaz}} \cdot \frac{E_{izlaz}}{E_{skladišta}} = \eta_{ulaz} \cdot \eta_{izlaz}$$

Opći kriteriji

2. Gustoća energije – masena i volumna: $e_m = \frac{E_\mathrm{s}}{m}\ [\mathrm{J/kg}];\ e_V = \frac{E_\mathrm{s}}{V}\ [\mathrm{J/m^3}]$

3. Gustoća izlazne snage – masena i volumna: $P_m = \frac{P_\mathrm{izlaz}}{m}\ [\mathrm{W/kg}];\ P_V = \frac{P_\mathrm{izlaz}}{V}\ [\mathrm{W/m^3}]$

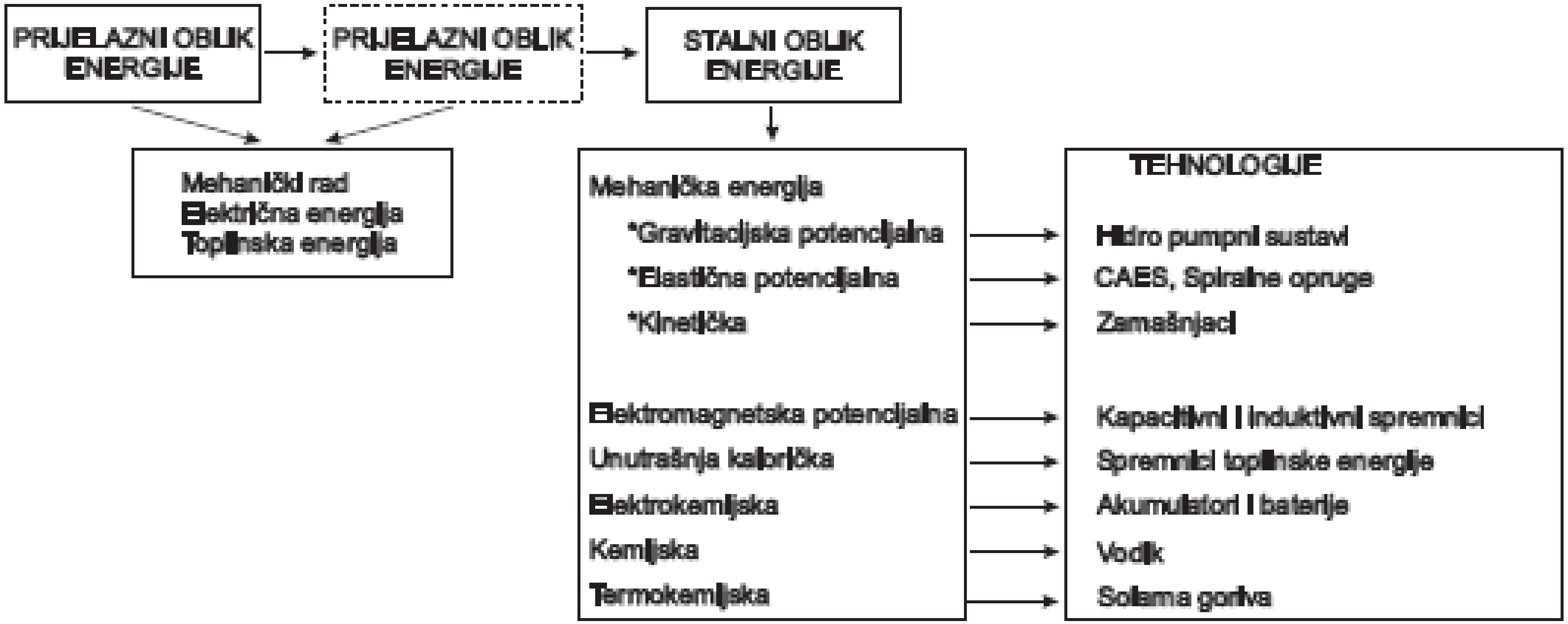
4. Trajanje ciklusa skladištenja: punjenje (τ_c); skladištenje (τ_s); pražnjenje (τ_d)

5. Brzina punjenja i pražnjenja: $P_\mathrm{c} = \frac{\mathrm{d}E_\mathrm{s}}{\mathrm{d}t}\ [\mathrm{W}];\ P_\mathrm{d} = \frac{\mathrm{d}E_\mathrm{s}}{\mathrm{d}t}\ [\mathrm{W}]$

Opći kriteriji

6. Kriterij trajnosti – životni vijek obično izražen preko broja ciklusa punjenje - pražnjenje
7. Kriterij ekonomičnosti – teško za procijeniti; MJ/US$ ili kWh/US$
8. Kapacitet (ukupna količina spremljene energije) [kWh, MWh]
9. Snaga [kW, MW]
10. Dubina pražnjenja (DOD)
11. Vrijeme odziva [ms - min]
12. Kompatibilnost s postojećom infrastrukturom, lakoća implementacije i transporta
13. Autonomnost
14. Pouzdanost
15. Utjecaj na okoliš

Energetska kategorizacija



Slika 10.2: Energetska kategorizacija spremnika energije

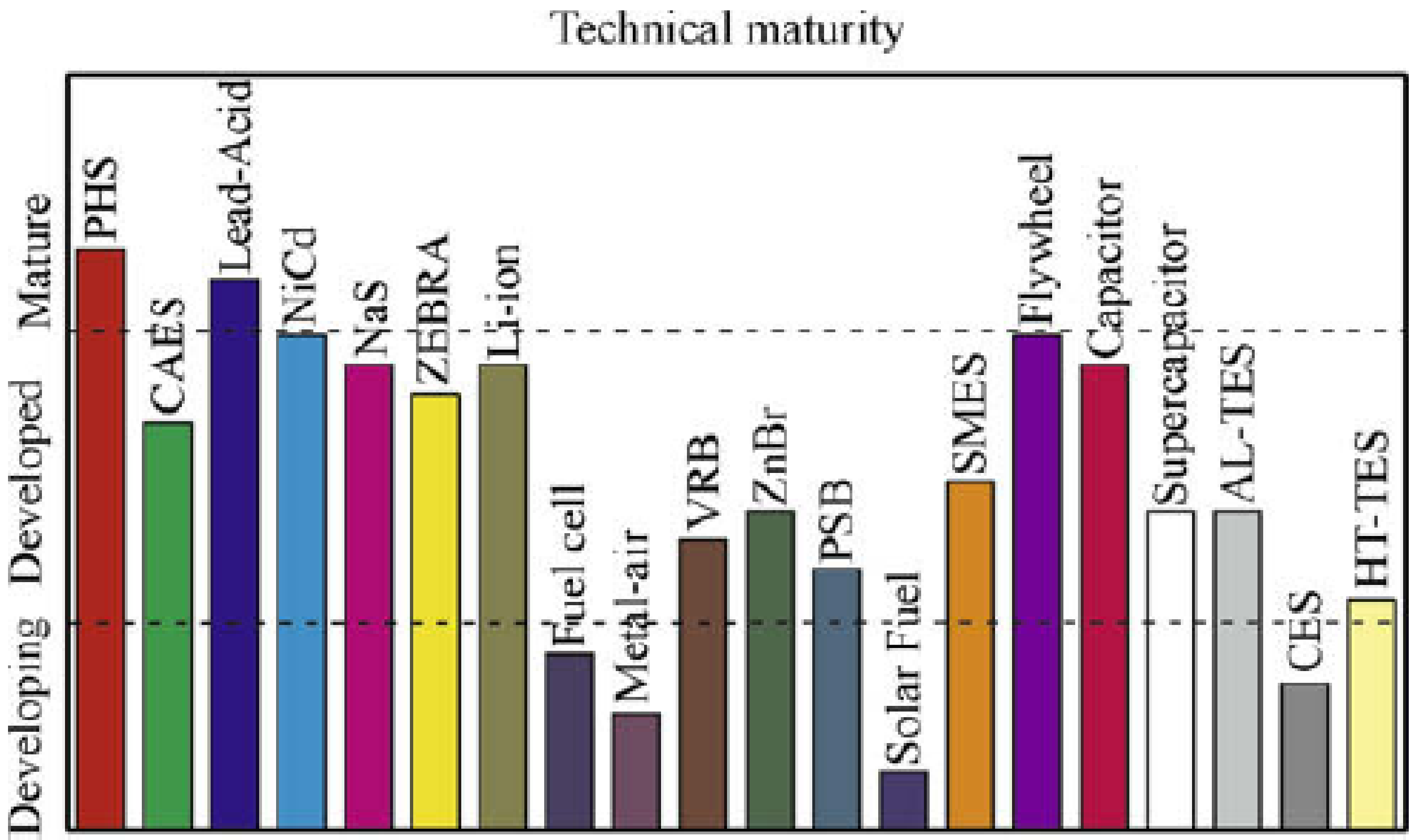
Status tehnologija spremanja sa stajališta EES

- Komercijalna: 5 jedinica, 10 godina iskustva po jedinici, jasne financije – povrat uloženog
- Pred-komercijalna: jedno ili više komercijalno postrojenje, nema dovoljno godina rada za jasna iskustva i financije
- Demonstracijska: postoji iskustvo rada
- Razvojna: laboratorijsko, sub-skalirano postrojenje

Status tehnologija u SAD (2007)

Komercijalna	Pred-komer.	Demonstrac.	Razvojna
Hidro-pumpna	CAES	Zn-Br	Li-ion – EES
Zamašnjaci – kvaliteta napajanja na strani potrošača	Olovni akumulator	Zamašnjaci– EES	SMES – EES
	Ni-Cd	V redox	Kondenzatori
	Na-S	Kondenzatori	Napredne baterije
	Zamašnjaci – mali		
	Mikro SMES – mali		

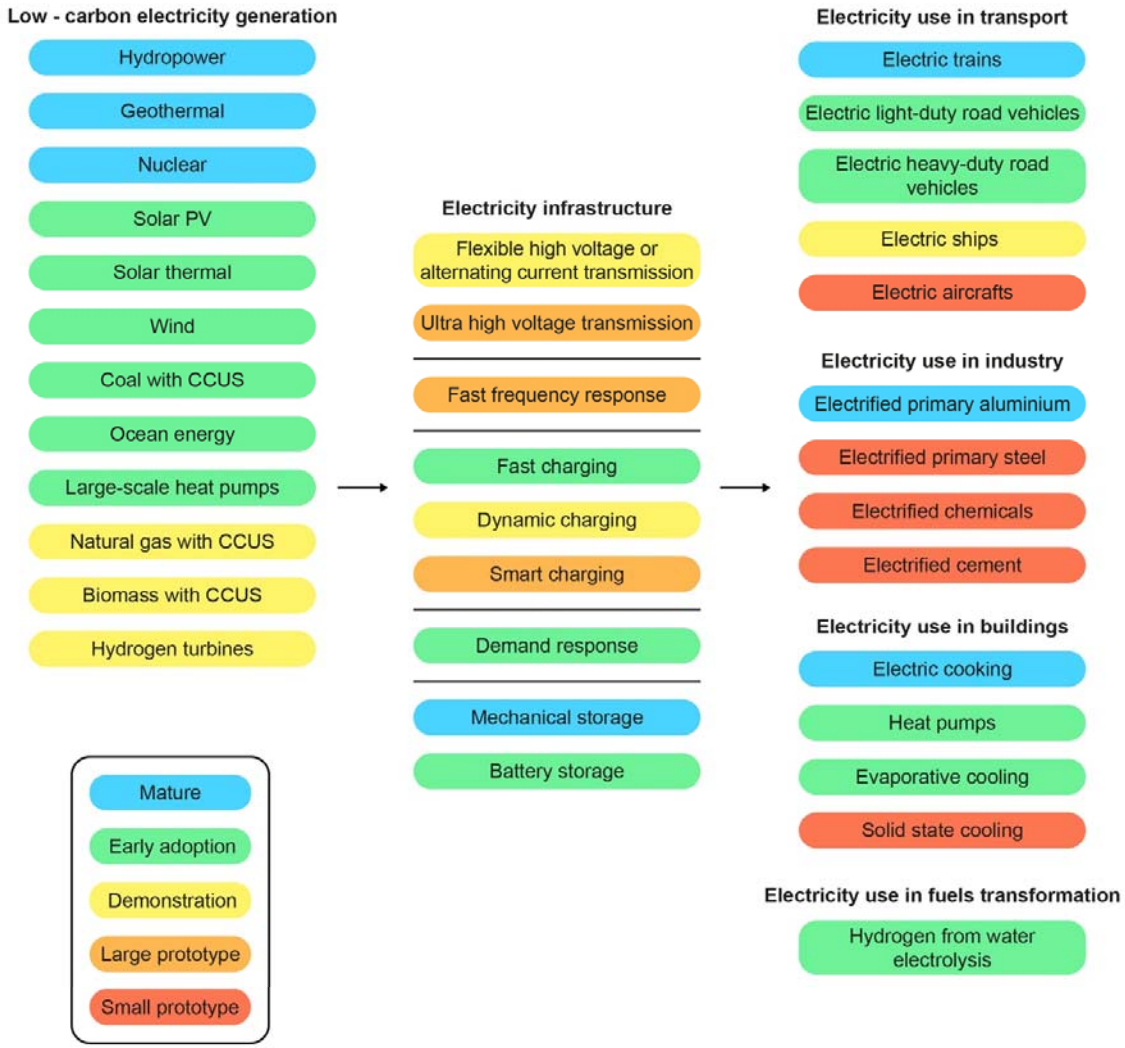
Podjela prema stupnju tehnološke zrelosti – 2015.



Technology Readiness Level (TRL) – International Energy Agency, 2020

Category	TRL	Level	Description	
CONCEPT	1	**Initial idea**	Basic principles have been defined	Beyond the SDS
	2	**Application formulated**	Concept and application of solution have been formulated	
	3	**Concept needs validation**	Solution needs to be prototyped and applied	
SMALL PROTOTYPE	4	**Early prototype**	Prototype proven in test conditions	
LARGE PROTOTYPE	5	**Large prototype**	Components proven in conditions to be deployed	Scope of the SDS
	6	**Full prototype at scale**	Prototype proven at scale in conditions to be deployed	
DEMONSTRATION	7	**Pre-commercial demonstration**	Solution working in expected conditions	
	8	**First of a kind commercial**	Commercial demonstration, full scale deployment in final form	
EARLY ADOPTION	9	**Commercial operation in relevant environment**	Solution is commercially available, needs evolutionary improvement to stay competitive	
	10	**Integration needed at scale**	Solution is commercial and competitive but needs further integration efforts	
MATURE	11	**Proof of stability reached**	Predictable growth	

Technology readiness level of technologies along the low-carbon electricity value chain



TRL	Description of rating	Example technologies*
1	Initial idea: basic principles have been defined	Li-Air electric vehicle batteries (TRL 1-2)
2	Application formulation: concept and application of solution have been formulated	Multivalent ions electric vehicle batteries
3	Concept needs validation: solution needs to be prototyped and applied	Chemical reaction thermochemical heat storage
4	Early prototype: prototype proven in test conditions	Active latent heat storage Li-S electric vehicle batteries
5	Large prototype: components proven in conditions to be deployed	Solid state + Li-metal electric vehicle batteries
6	Full prototype at scale: prototype proven at scale in conditions to be developed	Building integrated phase change materials
7	Pre-commercial demonstration: prototype working in expected conditions	High-temperature-latent heat storage (TRL 5-7)
8	First of a kind commercial: commercial demonstration, full-scale deployment in final conditions	**Compressed air energy storage (CAES)**
9	Commercial operation in relevant environment: solution is commercially available, needs evolutionary improvements to stay competitive	**Flywheel** **Lithium-ion batteries (Li-ion batteries)** **Redox flow batteries**
10	Integration needed at scale: solution is commercial and competitive but needs further integration efforts	Salt cavern storage
11	Proof of stability reached: predictable growth.	**Pumped hydro storage (PHS)**

Kategorizacija prema primjeni

- Mala snaga u izoliranim područjima – prvenstveno za mjernu i sigurnosnu opremu
- Srednja snaga u izoliranim područjima – individualni električni sustavi (domaćinstva), sela i manji gradovi
- Pokrivanje peakova
- Veliki upravljanje

•Kinetička energija (zamašnjaci)

•Kemijska energija

•Komprimirani zrak

•Gorivne ćelije (vodik)

•Superkondenzatori, supravodiči

•Gravitacijska potencijalna energija

•Termička energija

•Kemijska energija (akumulatori i baterije)

•Komprimirani zrak

Grid-side roles of ESS.

Application	Time scales	Example of EES
Energy arbitrage, load leveling	Hours to days	PHS, NaS, CAES, VRB
Frequency regulation	Seconds to minutes	Li-ion, NaS, FES, VRB
Inertia emulation, oscillation damping, voltage support LVRT	<1 s	LA, NAS, FES, VRB
Primary reserves	10 min	PHS, FES, BES
Secondary reserves	Minutes to hours	PHS
Efficiency use of transmission network	Minutes to hours	Li-ion
Emergency power supply, black start	Minutes to hours	LA

Tehničke karakteristike – 1. dio

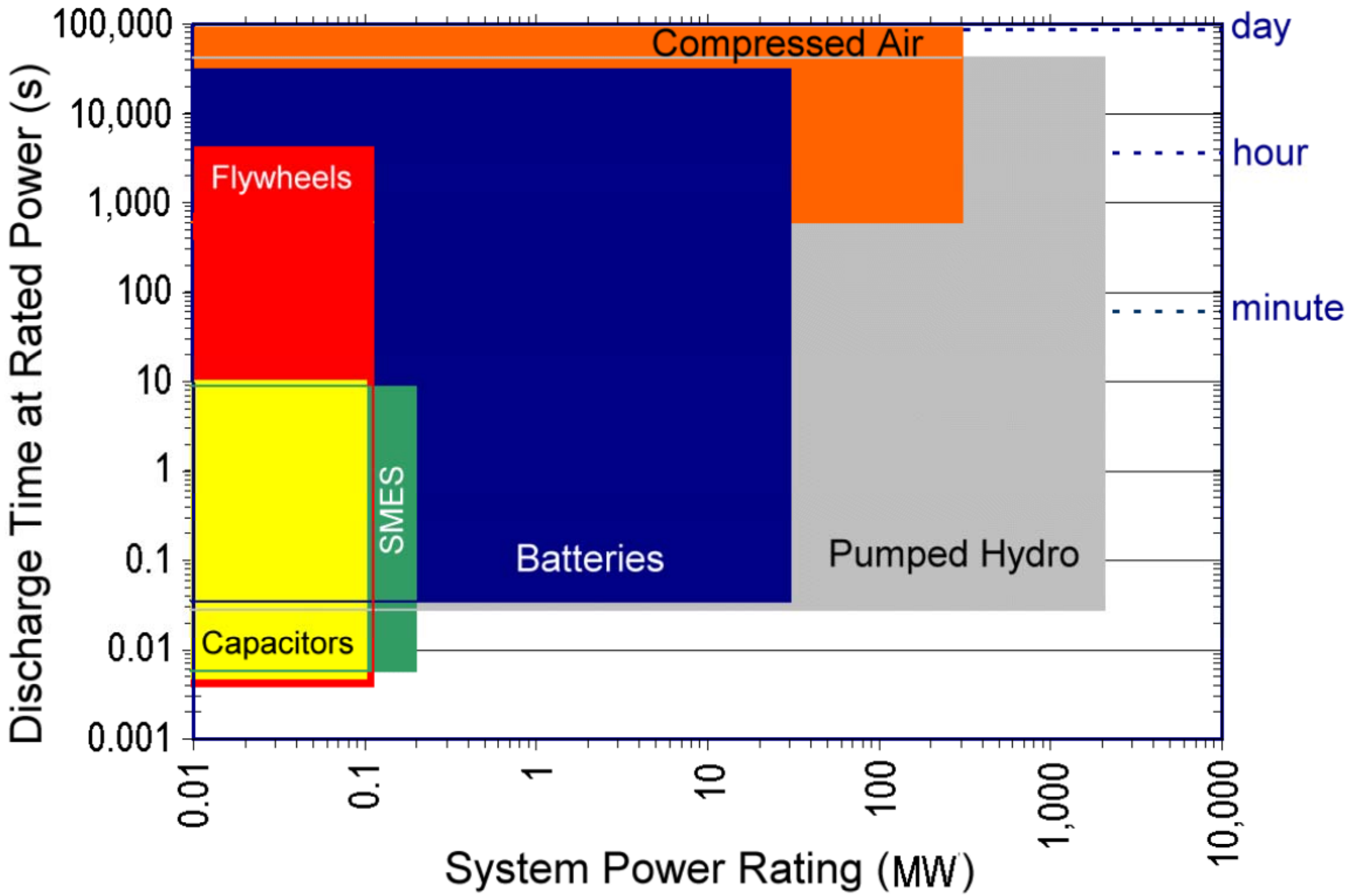
Tehnologija	Nominalna snaga [MW]	Vrijeme pražnjenja	Gustoća snage [W/l]	Gustoća energije [Wh/l]
PHS	100-5000	1-24 h+	0,1-0,2	0,2-2
CAES	5-300	1-24 h+	0,2-0,6	2-6
Zamašnjaci	0-0,25	s-h	5000	20-80
Akumulatori	0-20	s-h	90-700	50-80
Ni-Cd	0-40	s-h	75-700	15-80
Li-ion	0-0,1	min-h	1.300-10.000	200-400
Na-S	0,05-8	s-h	120-160	15-300
VRB	0,03-3	s-10 h	0,5-2	20-70
Zn-Br	0,05-2	s-10 h	1-25	65
Gorive ćelije	0-50	s-24 h+	0,2-20	600
Kondenzatori	0-0,3	ms-1 h	40.000-120.000	10-20
SMES	0,1-10	ms-8 s	2.600	6

Tablica 10.2: Tehničke karakteristike spremnika energije - 1. dio[?]

Tehničke karakteristike – 2.dio

Tehnologija	Vrijeme odziva	Efikasnost [%]	Samopražnjenje po danu [%]	Životni vijek [godine]-[ciklusi]
PHS	min	70-80	Vrlo malo	> 50 - > 15.000
CAES	min	41-75	Malo	> 25 - > 10.000
Zamašnjaci	< s	80-90	100	(15-20)-(104-107)
Akumulatori	< s	75-90	0,1-0,3	(3-15)-(250-1.500)
Ni-Cd	< s	60-80	0,2-0,6	(5-20)-(1.500-3.000)
Li-ion	< s	65-75	0,1-0,3	(5-100)-(600-1.200)
Na-S	< s	70-85	-20	(10-15)-(2.500-4.500)
VRB	s	60-75	Malo	(5-20)-(> 10.000)
Zn-Br	s	65-75	Malo	(5-10)-(1.000-3.650)
Gorive ćelije	s-min	34-44	0	(10-30)-(103-104)
Kondenzatori	< s	85-98	20-40	(4-12)-(104-105)
SMES	< s	75-80	10-15	-

Tablica 10.3: Tehničke karakteristike spremnika energije - 2. dio[?]



Compressed Air
Flywheels
Batteries
Pumped Hydro
SMES
Capacitors
day
hour
minute
Discharge Time at Rated Power (s)
100,000
10,000
1,000
100
10
1
0.1
0.01
0.001
0.01
0.1
1
10
100
1,000
10,000
System Power Rating (MW)

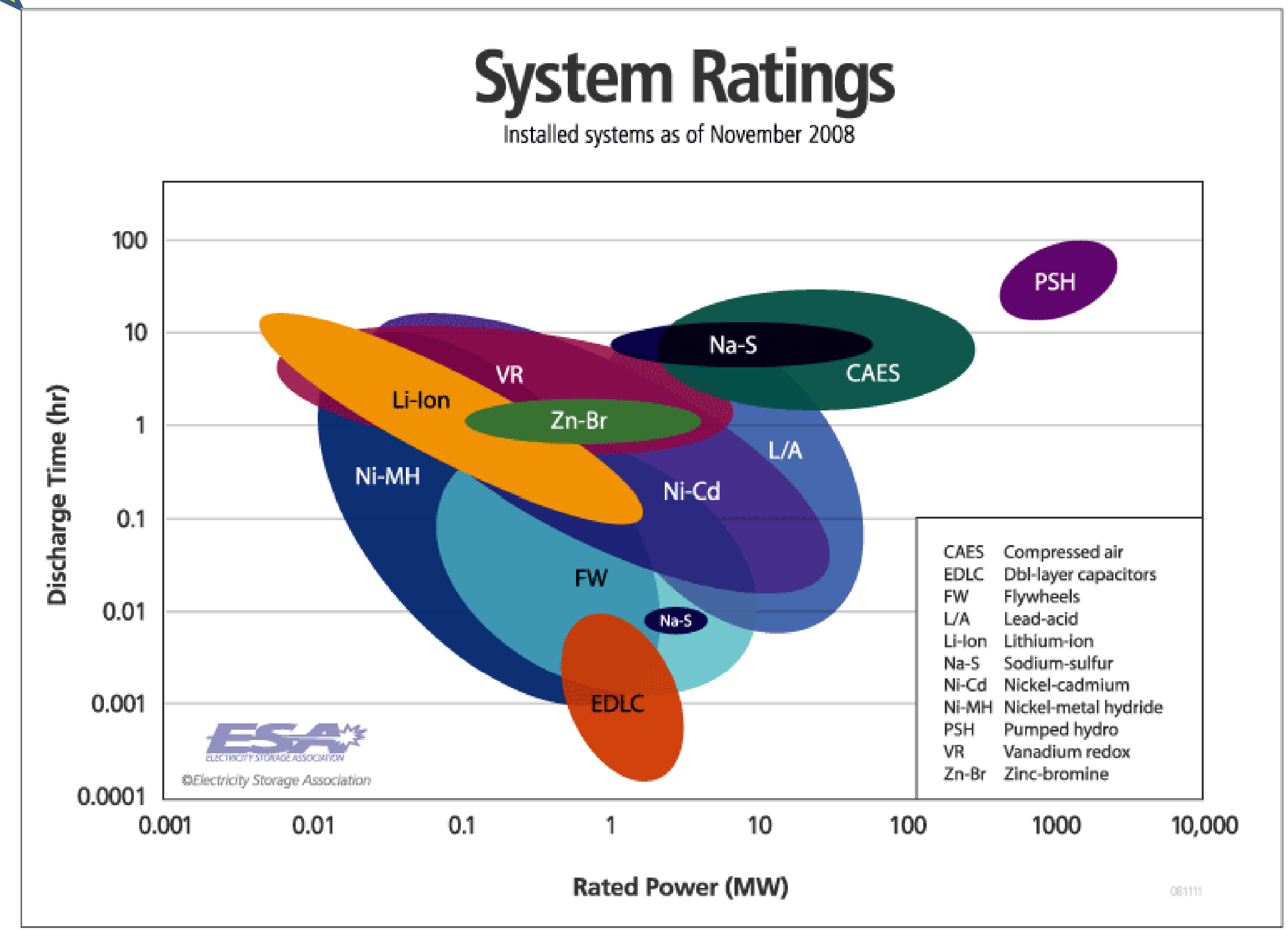

System Ratings
Installed systems as of November 2008
Discharge Time (hr)
100
10
1
0.1
0.01
0.001
0.0001
0.001
0.01
0.1
1
10
100
1000
10,000
Rated Power (MW)
PSH
Na-S
CAES
VR
Li-Ion
Zn-Br
L/A
Ni-MH
Ni-Cd
FW
Na-S
EDLC
CAES Compressed air
EDLC Dbl-layer capacitors
FW Flywheels
L/A Lead-acid
Li-Ion Lithium-ion
Na-S Sodium-sulfur
Ni-Cd Nickel-cadmium
Ni-MH Nickel-metal hydride
PSH Pumped hydro
VR Vanadium redox
Zn-Br Zinc-bromine
ESA
©Electricity Storage Association

Table C1
Total capital cost (TCC) of grid-scale EES systems based on the review of the sources listed in Table 2.

EES technology	Configuration	Total capital cost[a] (TCC), per unit of power rating €/kW			Total capital cost[a] (TCC), per unit of storage capacity[b] €/kWh		
		Min	Average	Max	Min	Average	Max
PHS	Conventional	1030	1406	1675	96	137	181
CAES	Aboveground	774	893	914	48	92	106
	Underground	1286	1315	1388	210	263	278
Flywheel	High-speed	590	867	1446	1850	4791	25049
Lead–acid	Advanced	1388	2140	3254	346	437	721
NaS	–	1863	2254	2361	328	343	398
Ni–Cd	–	2279	3376	4182	596	699	808
ZEBRA	–	874	1160	1786	973	1095	1211
Li-ion	–	2109	2512	2746	459	546	560
VRFB	–	1277	1360	1649	257	307	433
Zn–Br	–	1099	1132	1358	170	220	281
PSB	–	927	1093	1308	1071	1147	1153
Fe–Cr	–	1376	1400	1425	527	569	611
Zn–air	–	1313	1364	1415	262	271	417
Supercapacitors	Double-layer	214	229	247	691	765	856
EES technology	Configuration	Total capital cost[a] (TCC), per unit of power rating €/kW			Total capital cost[a] (TCC), per unit of storage capacity[b] €/kWh		
		Min	Average	Max	Min	Average	Max
SMES	–	212	218	568	5310	6090	6870
Hydrogen	Fuel cell[c] (FC)	2395	3243	4674	399	540	779
	Gas turbine[d] (GT)	1360	1570	2743	227	262	457

[a] It should be noted that the capital costs are calculated based on typical discharge time (storage size) for each technology, which is not necessarily the same among different EES systems (for typical discharge time, see the corresponding table for each technology in Appendix A). Minimum and maximum values are the bands of interquartile range (middle-fifty likelihood) and the average value is the median of whole sample, excluding outliers. It should be noted that the costs of grid interconnections and infrastructure requirements are not included in this estimation.
[b] For the batteries, the storage capacity is equivalent to the rated DoD.
[c] Electrolysis and fuel cell with steel tank storage system.
[d] Electrolysis and small-to medium scale gas turbine with underground storage.

Table 1
Best performance and typical figures of main energy storage systems.

Technology	Top power [MW]	Top energy [MW h]	Energy density [W h/kg]	Discharge time	Response time	Round-trip efficiency	Cycle life $\times 10^3$	Capital cost [k$/kW]	Capital cost [$/kW h]	Capital cost [$/MW h/cycles]
PHES	3000	10^4	0.3	10^1 h	min	70–85%	20	0.4–5.6	10–350	0.5–3
CAES:										
Underground	300	10^3	10–30	10^0–10^1 h	min	60–	30	1.7	130–550	4–18
Aboveground	50	10^2	–	10^1 h	min	75%	> 10	2.2	430	43
TES	20	10^1	70	h	min	–	10	–	5,000	500
FES:										
Commercial	20	5	11–30	min	ms	85%	10^1–10^2	2.3	2,400	25–200
Lab	400	1	1.6	s	ms	–	–	–	–	–
SMES:										
Under development	100	10^1–10^3	–	min	ms	90–95%	10	2	> 10,000	1000
Lab	400	10	1.2	s	ms	–	–	–	–	–
EDLC	100	10^{-2}	10–30	s	ms	95%	500	–	4,600	10
ECES:										
Advanced lead-acid	10–40	10^0–10^1	25–50	10^0 h	ms	75–85%	3	4.6	130	150
Sodium-sulfur	34	10^1	150–120	10^0 h	s	85–90%	4.3–6	3.5	550	90–130
Sodium-nickel-chlorine[a]	1	6	95–120	10^0 h	s	85%	3–4	3.5	650	150–200
Lithium-ion	16	20	100–200	10^0 h	ms	95%	4–8	3–4	600	150–200
Electrolyzer/fuel cells	1	> 10	800–1300	> 10^0 h	ms	35–45%	50	17	> 10,000	200
Redox flow battery	2–100	6–120	10–50	10^0–10^1 h	ms	85%	> > 13	3.2	900	< < 70

Gravitacijska potencijalna: Sustavi mehaničkog podizanja tijela

- Gravitacijska potencijalna energija tijela na visini *h* iznad površine Zemlje
- Promjena potencijalne energije zbog radijalnog pomicanja tijela u iznosu Δh
- Praktična primjena – utegom pogonjeni zidni satovi
- Mala gustoća energije (100 kg na 10 m iznosi 9810 J odnosno 2,725 Wh) zahtijeva veliku masu ili veliki radijalni pomak
- Svemirski lift? – pohrana energije, sredstvo za "lansiranje" solarnih panela

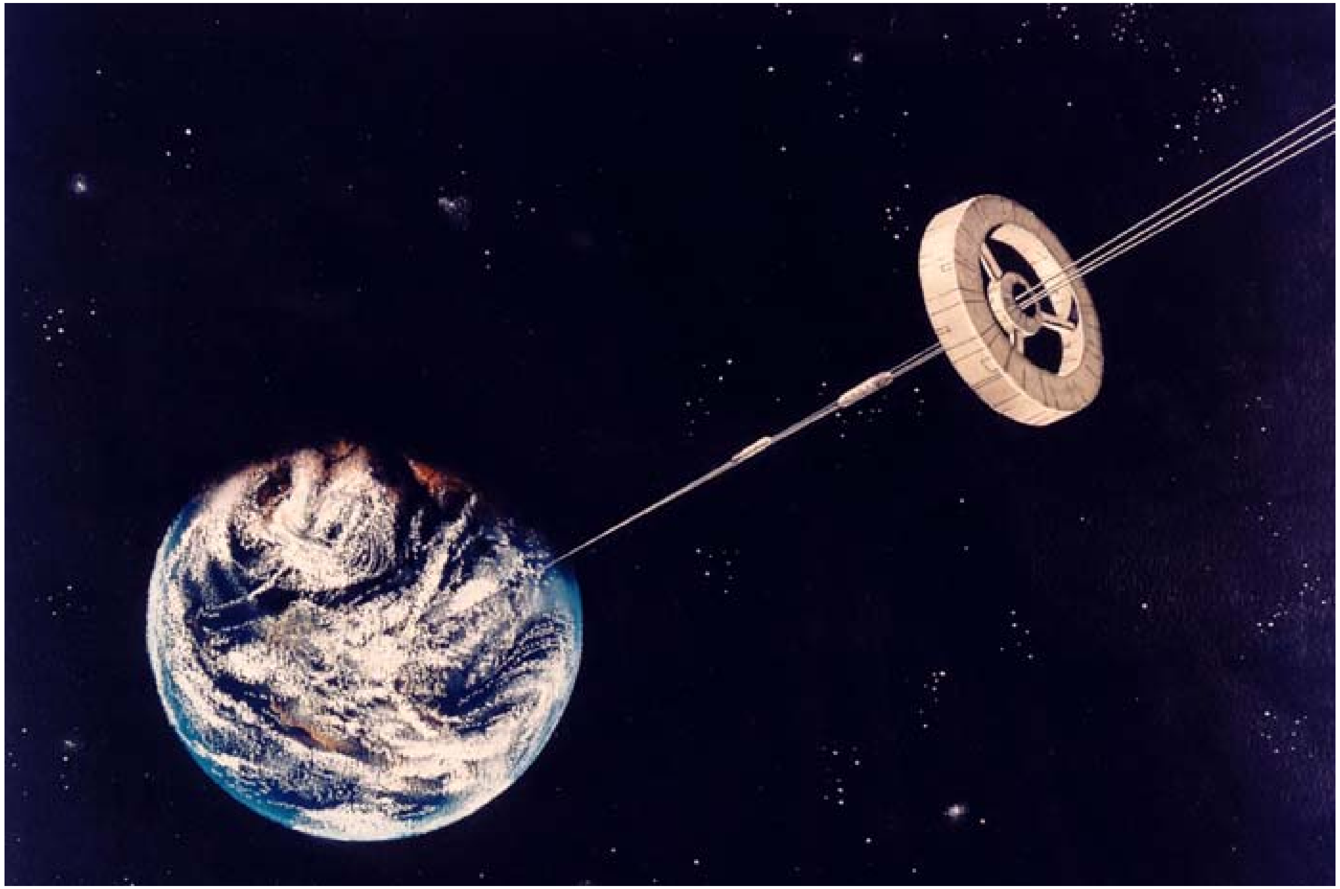
$$E_{\text{pot}} = \frac{-G \cdot M \cdot m}{R+h},$$

$$R = 6378\ \text{km}$$

$$\Delta E_{\text{pot}} = -G \cdot M \cdot m \cdot \left(\frac{1}{R+h+\Delta h} - \frac{1}{R+h} \right)$$

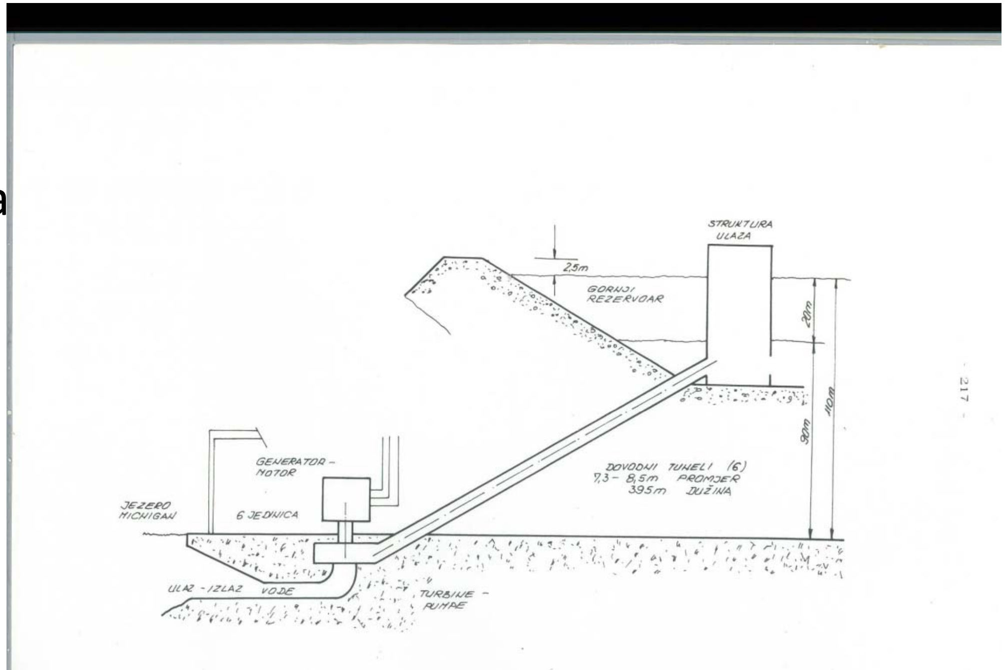
$$\text{uz } h << R \text{ i } (h+\Delta h) << R$$

$$\Delta E_{\text{pot}} = gm\Delta h$$



Gravitacijska potencijalna: Hidro-pumpna pohrana energije (PHS)

- Mehanička energija – gravitacijska potencijalna energija
- Jedini značajni sustav za spremanje energije – gravitacijska potencijalna energija vode,
- 2009. godine u svijetu 300 elektrana (95 GW); EU 2007. 38 GW (4,9%)
- Rotirajuća rezerva, vršna opterećenja, regulacija frekvencije i kontrola napona
- Dva rezervoara – gornji i donji,



Slika A - 1

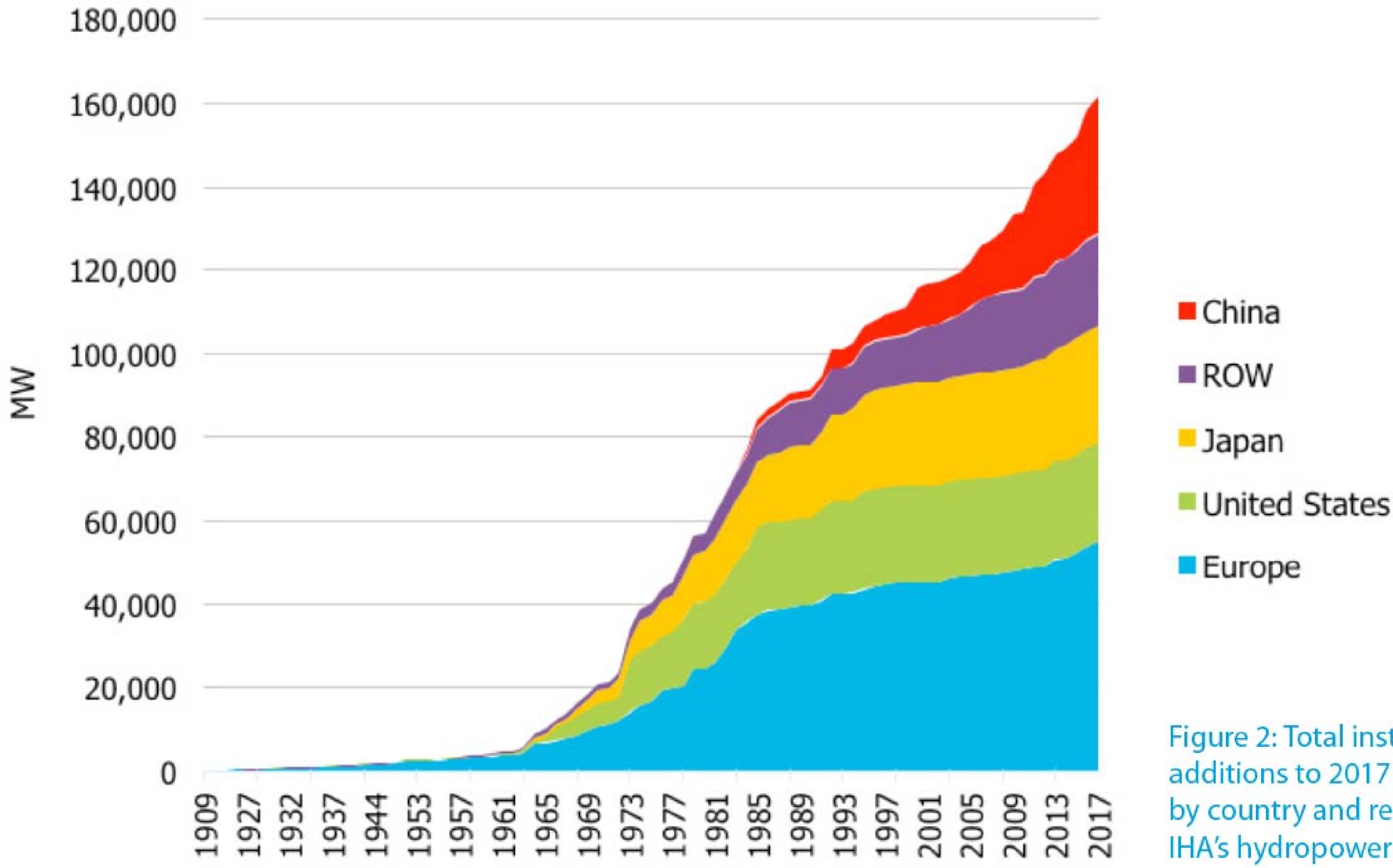
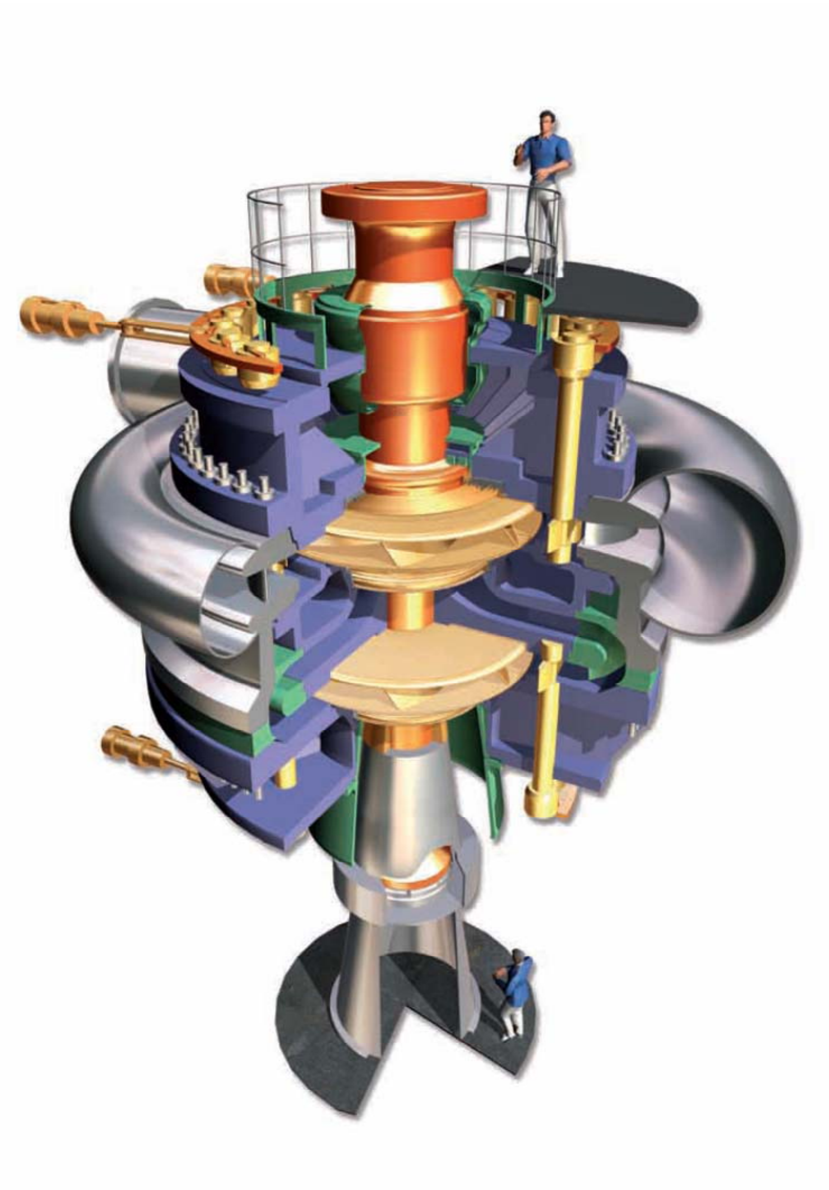


Figure 2: Total installed capacity additions to 2017 broken down by country and region. Source: IHA's hydropower database.

- Najstarija – Zurich, Švicarska, 1882.
- U početku relativno skupe zbog dvoosovinskog principa rada (pumpa i motor + generator i turbina)
- Od sredine 20 st. Tandemski sustav – motor-generator na vrhu osovine, ispod pumpa, a na dnu turbina – u početku turbina propelernog tipa (Kaplan), a sada uglavnom Francis
- Francis može raditi u oba režima – 1956.godina
- U Japanu razvijen dizajn varijabilne brzine – 1990
- U početku "off-peak base loading" za velike termo ili nuklearne elektrane, a sada i za kontrolu frekvencije i u generatorskom i u pumpnom režimu rada

- Izvedba ovisi o Δh:
  - Mali padovi – Kaplan/Nagler turbina u tandemskom sustavu s pumpom
  - Srednji padovi do 600 (700) m – jednostupanjska Francis turbina
  - Veliki padovi (1000-1500 m) – višestupanjska Francis turbina ili tandemski sustav Pelton turbine i zasebne pumpe (višestupanjske)
- Gubici u spojnim cjevovodima, gubici zbog isparavanja



- Čista pumpna stanica - pr. Taum Sauk (SAD)
  - 1963.-1999. 175 MW; 1999.-2005. 225 MW; 2005.-puknuće;

    21.4.2010. - na mreži
  - 5.366.000 m^3; 2.100 m dužina tunela; Δh=244 m; 3,56 GWh (15 h)
- Istraživanja mogućnosti uporabe podzemnog donjeg rezervoara

- Kombinirani pumpni sustav – koristi pumpanu i prirodno prolazeću vodu – pr. RHE Velebit
- Gornji rezervoar Štikada nalazi se u Gračačkom polju; vodni tokovi Opsenice, Ričice, Otuče i potoka Krivka
- Donji rezervoar Razovac; Zrmanja
- Turbinska snaga 276 MW (Δh=519 m), pumpna 240 MW (Δh=559 m)

Analysis of financial mechanisms in support to new pumped hydropower storage projects in croatia
Krajačić et al., Applied Energy 101 (2013) 161-171

- PHS je najraširenija tehnologija spremanje energije u EES,
- Najpraktičnije na velikim snagama, uz vrijeme rada od nekoliko sati do nekoliko dana i efikasnost od 70-85%,
- Dugačko vrijeme konstrukcije i veliki investicijski troškovi 500-3600 EUR/kW,
- Transformacija postojećih HE,
- U RH:
  - RHE-Velebit (276/240 [G/P] MW)
  - CHE-Fužine (4/4,8 MW)
  - CHE-Lepenica (1,4/1,25 MW)
  - CS- Buško Blato (10,5/10,2 MW) (BiH ali upravlja HEP)

- Potencijal u RH za PHS:
  - Kontinentalni – postojeće instalacije HE
  - Otočni – veći otoci (Krk) u kombinaciji s sustavom navodnjavanja i opskrbe vodom; sa solarnim PV sustavima
- Prijedlog: uvođenje poticaja za proizvodnju el.eneg. u PHS ako se na pumpanje troši el.energ. proizvedena u vjetroagregatima (ili PV) – garancija podrijetla (Guaranty of Origin) – plaća se proizvedena energija, a ne ona utrošena na pumpanje
- Procijenjeni interval poticaja: 42-265 EUR/MWh (0,315-1,988 kn/kWh)??
- Vrijeme amortizacija nejasno??

Kinetička energija: zamašnjaci

- Kutna brzina ograničena materijalom
- K_m je faktor oblika ovisan o geometriji, primjerice za puni tanki disk je oko 0,6, a za radijalnu šipku oko 0,33

$$E = \frac{1}{2} I\omega^2; I = \int \rho(\vec{x}) r^2 \mathrm{d}\vec{x}$$

$$\text{za uniformni disk } I = \frac{mr^2}{2}$$

$$\frac{E}{m} = w_m = \frac{\sigma_{\max}}{\rho} K_m$$

Materijal	Maksimalno naprezanje (10^6 Nm^{-2})	Naprezanje kod dizajna (10^6 Nm^{-2})
Drvo	125	30
Legura Al	500	
Čelik	2700	900
Karbonska vlakna	1500	750
Kevlar vlakna	1800	1000

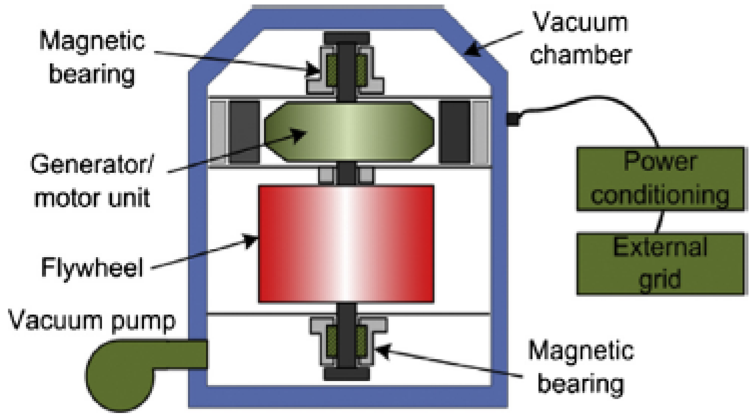
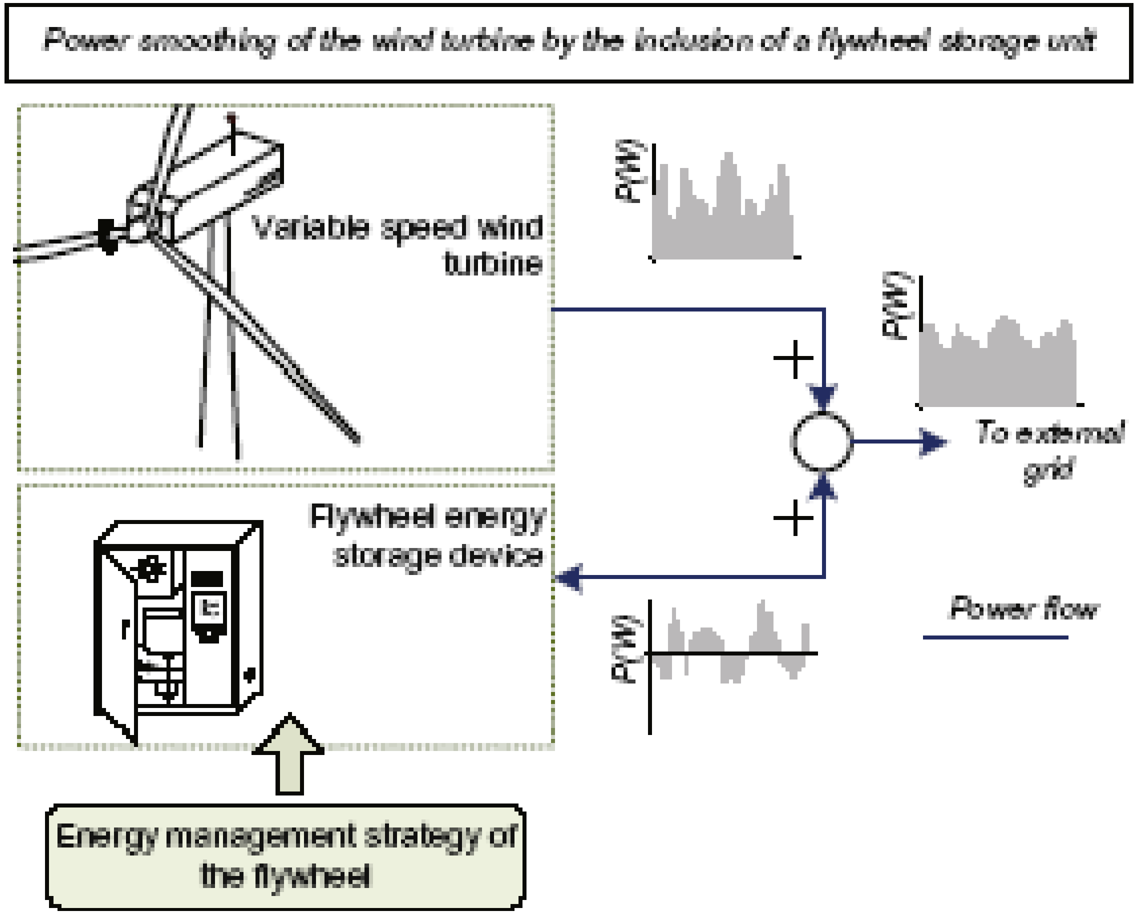


Fig. 6. System description of a flywheel energy storage facility.

Selected flywheel energy storage facilities [18,55,57–60].

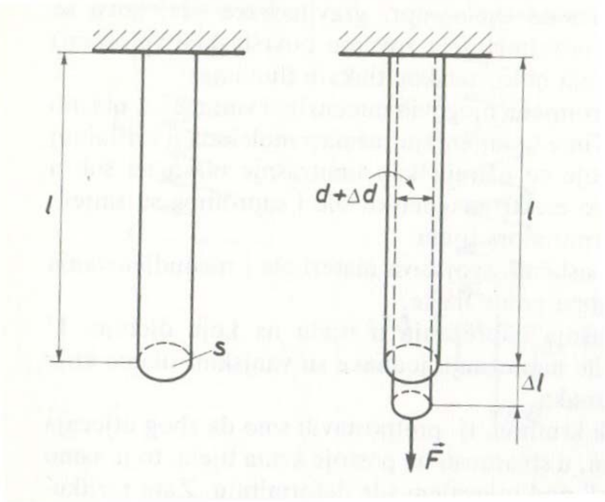
Firms/Institutes	Characteristics	Application area
Active Power Company	Clean Source series 100–2000 kW	Backup power supply, UPS systems
Beacon Power Company	100/150 kW a unit, 20 MW/5 MW h plant	Freq. regulation, power quality, voltage support
Boeing Phantom Works	100 kW/5 kW h, HT magnetic bearings	Power quality and peak shaving
Japan Atomic Energy Center	235 MVA, steel flywheel	High power supply to Nuclear fusion furnace
Piller power systems Ltd.	3600–1500 rpm, 2.4 MW for 8 s	Ride-through power and sources of backup power
NASA Glenn research center	2×10^4–6×10^4 rpm, 3.6 MW h	Supply on aerospace aviation & other transports

Energy management of flywheel-based energy storage device for wind power smoothing
Diaz Gonzales et al., applied energy 110 (2013) 207–219



Elastična: Krute opruge i guma

- Deformacijom tijela u području elastičnosti
- Napetost (naprezanje): $\sigma = F/S$
- Relativna deformacija: $\varepsilon = \Delta x/x$
- U granici proporcionalnosti vrijedi Hookeov zakon:



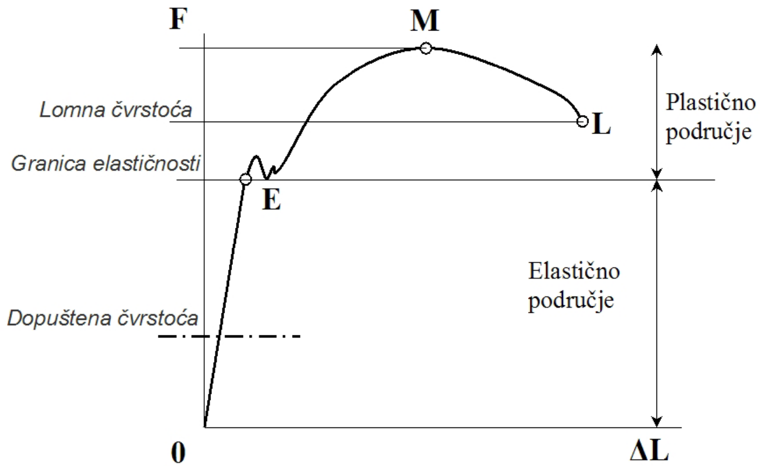
$$\sigma = \frac{F}{S} = E \cdot \frac{\Delta l}{l}$$

$$\frac{\Delta d}{d} = -\mu \cdot \frac{\sigma}{E}$$

$$W = \int_0^{\Delta l} F(x)dx = \frac{1}{2}k(\Delta l)^2$$

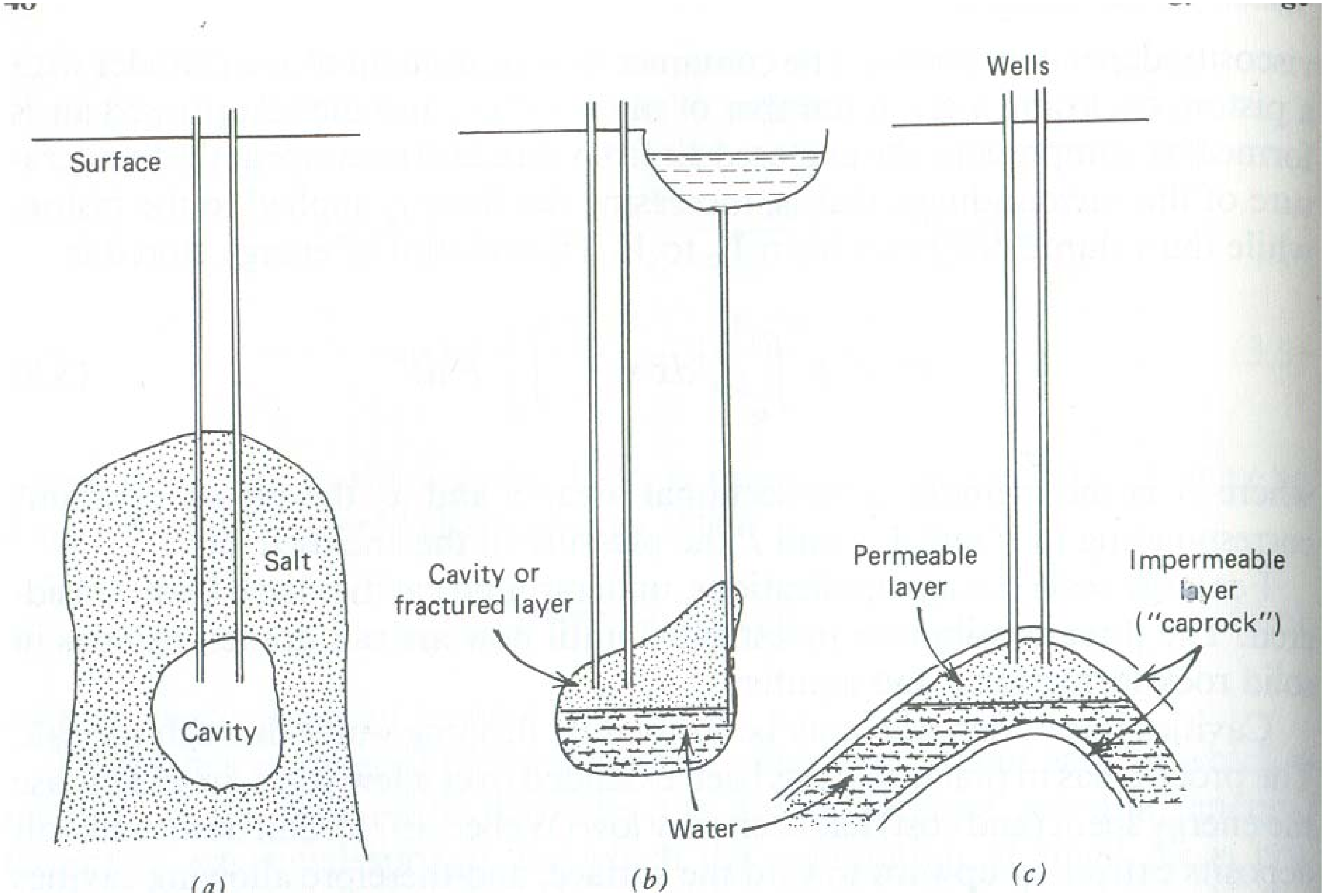
$$\frac{W}{V} = \frac{\sigma^2}{2E}$$

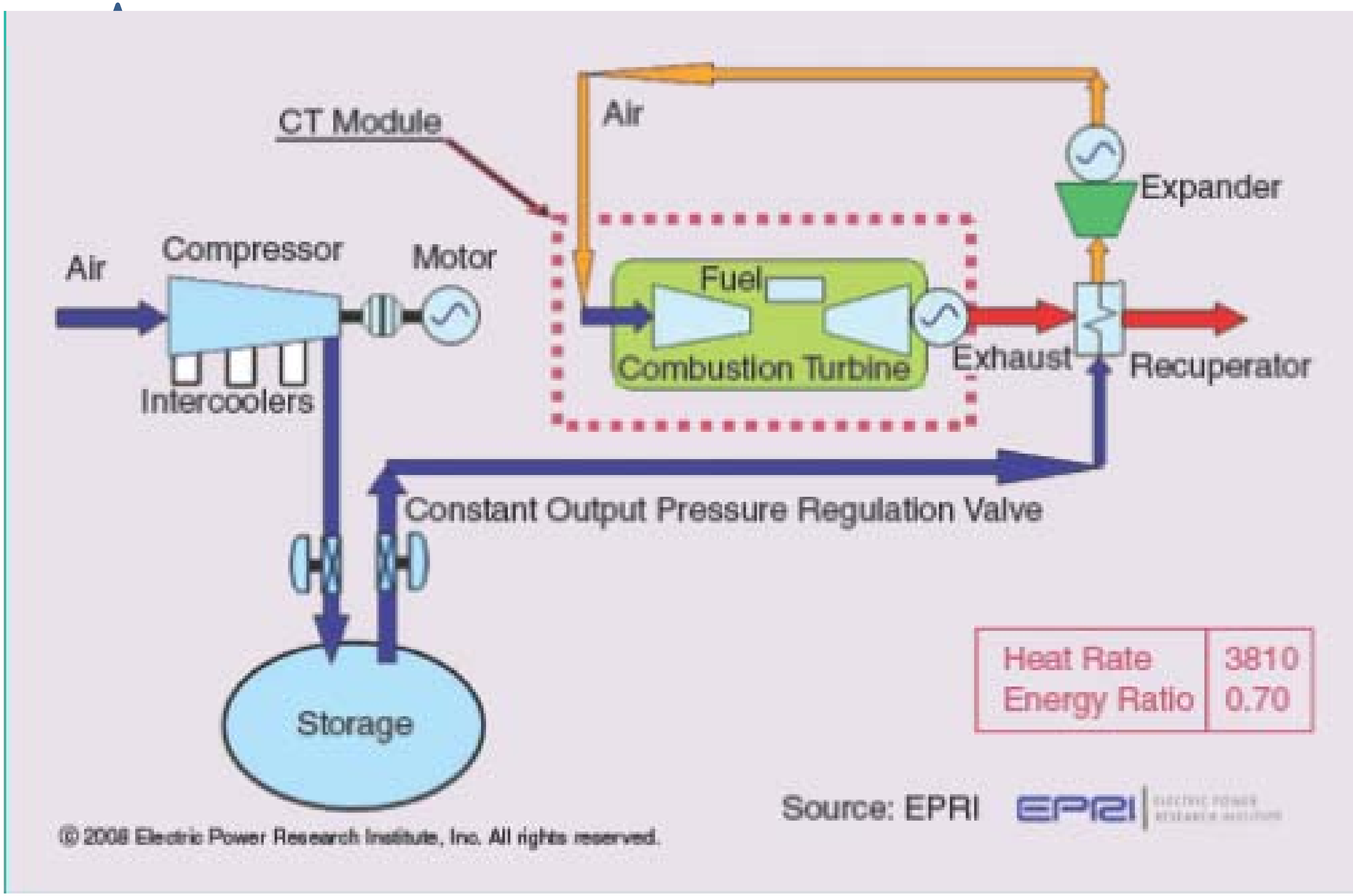
400 J/m³ za čeličnu oprugu



Komprimirani zrak (CAES) – mehanička energija-elastična energija-unutrašnja kalorička energija

- Plinska turbina koja koristi 40%-60% manje plina od klasične plinske elektrane
- Plinovi su stlačiviji od čvrstih tijela i tekućina
- Podzemne šupljine:
  - U naslagama soli (Huntorf $3{,}1 \cdot 10^5$ m^3 i McIntosh $5{,}6 \cdot 10^5$ m^3)
  - U stijenama
  - U vodonosnicima
- Karakteristike šupljine poznate tek na završetku instalacije i ovise o temperaturi i tlaku instalacije – potencijalni problem
  - Problem temperature - adijabatska ili izotermalna kompresija (nepraktična)
  - Problem tlaka – izobarna kompresija uz varijabilni volumen – varijabilni volumen spremnika ili povezivanje s vanjskim rezervoarom (pumpna pohrana)


Wells
Surface
Salt
Cavity
Cavity or
fractured layer
Water
Permeable
layer
Impermeable
layer
("caprock")
(a)
(b)
(c)


CT Module
Air
Expander
Air
Compressor
Motor
Fuel
Combustion Turbine
Exhaust
Recuperator
Intercoolers
Constant Output Pressure Regulation Valve
Heat Rate 3810
Energy Ratio 0.70
Storage
Source: EPRI
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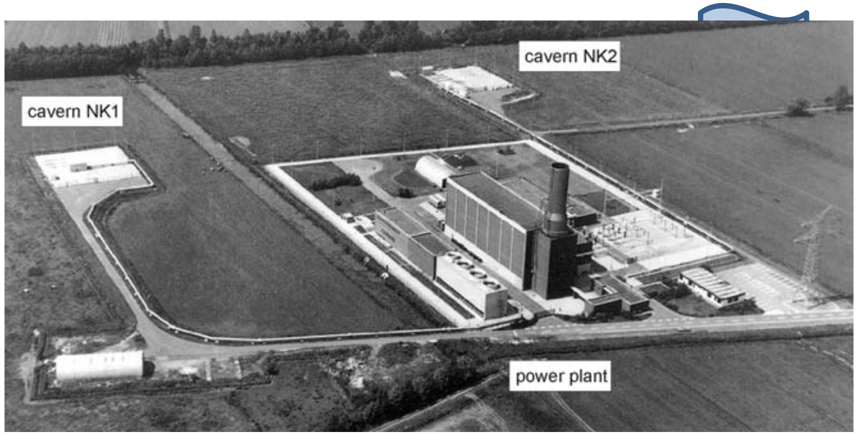
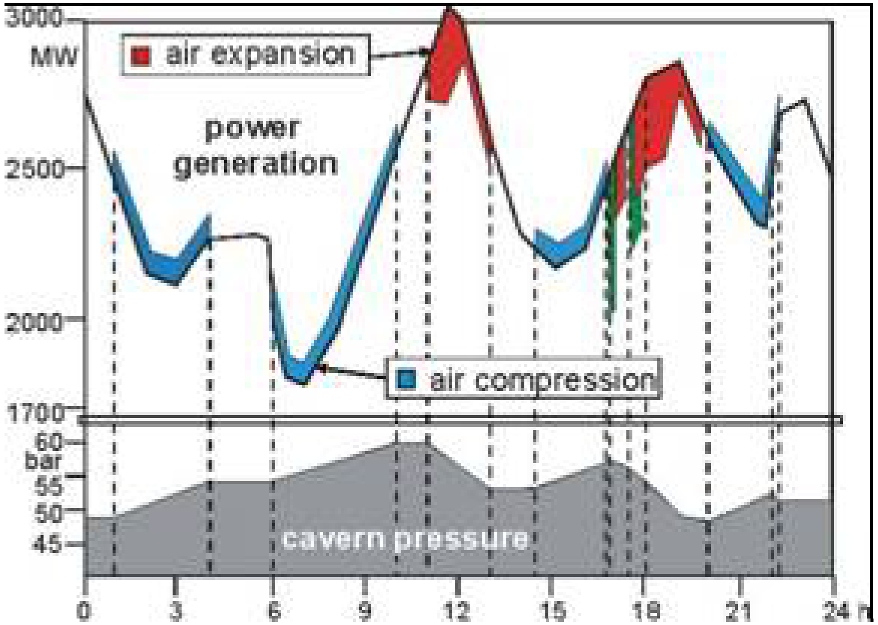
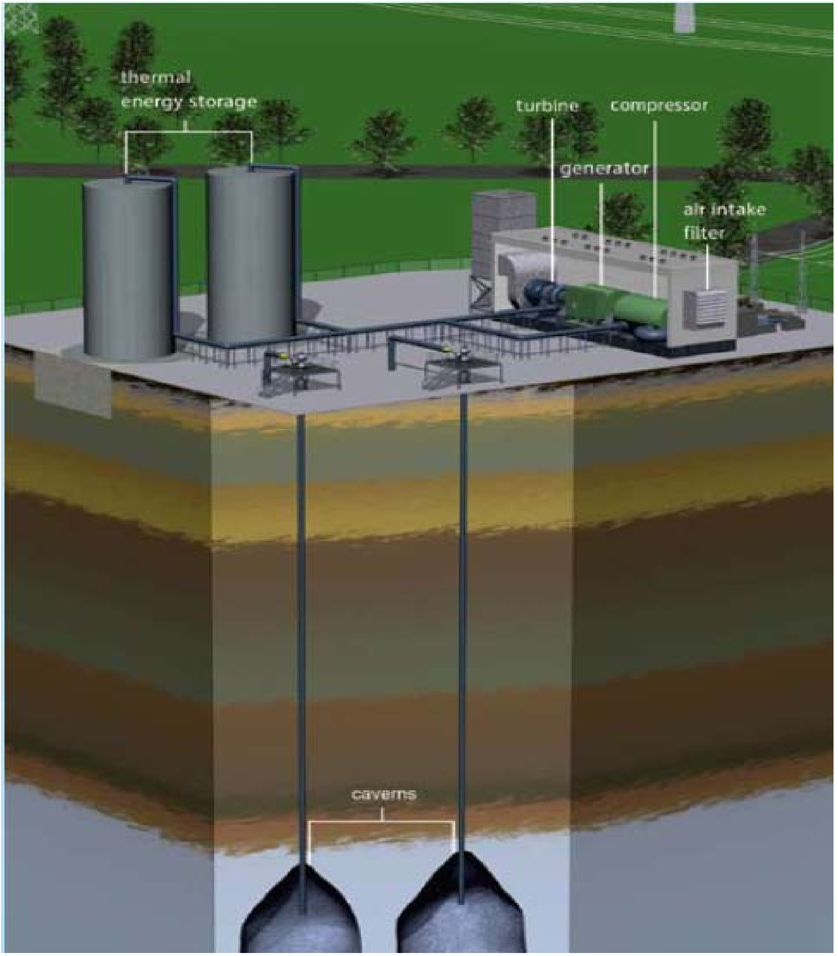
Huntorf CAES (Njemačka)

Turbinska snaga	290 MW (max 3 h)
Snaga kompresora	60 MW (max 12 h)
Protok u turbinskom režimu	417 kg/s
Protok u kompresorskom režimu	108 kg/s
Volumen spremnika	140 000 + 170 000
Vrh spremnika	650 m
Dno spremnika	800 m
Max. promjer	60 m
Udaljenost bušotina	220 m
Min. tlak	1 bar
Min.operativni tlak*	20 bar
Min. operativni tlak	43 bar
Max. tlak	70 bar





“ADELE” - ADIABATIC COMPRESSED-AIR ENERGY STORAGE WITH BETTER EFFICIENCY



Spremnici elektrokemijske energije – baterije i akumulatori

- Elektrokemijski energetski izvor je uređaj u kojem se kemijska energija direktno pretvara u električnu energiju
- Galvani, Volta (“piles a tasses”)

- “Baterija ili akumulator je svaki izvor električne energije proizvedene izravnim pretvaranjem kemijske energije koji se sastoji od jedne ili više primarnih baterijskih ćelija/članaka (koje se ne mogu puniti) ili jedne ili više sekundarnih baterijskih ćelija/članaka (koje se mogu puniti).” (**PRAVILNIK O GOSPODARENJU OTPADNIM BATERIJAMA I AKUMULATORIMA – prosinac 2006.**)
- Gorivne ćelije, primarne baterije (nepunjive) i sekundarne baterije (punjive)
- Sve se sastoje od pozitivne elektrode (anode), negativne elektrode (katode) i elektrolita
- Kruto/tekuće/kruto; tekuće/kruto/tekuće; kruto/kruto/kruto
- Kod gorivnih ćelija se aktivna kemijska komponenta (gorivo) dobavlja van sustava elektroda – vodik, metanol,...
- Sa stajališta EES-a izuzetno je važna i AC/DC, odnosno DC/AC konverzija

Baterijski sustavi – princip rada

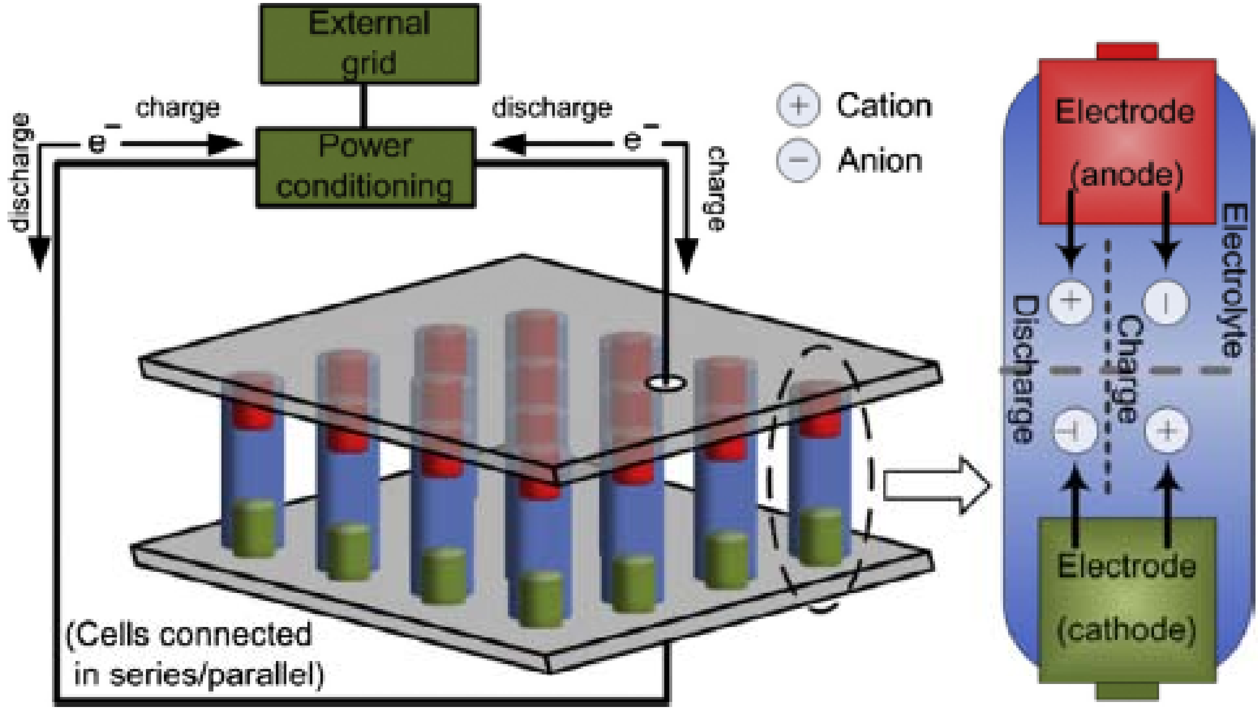
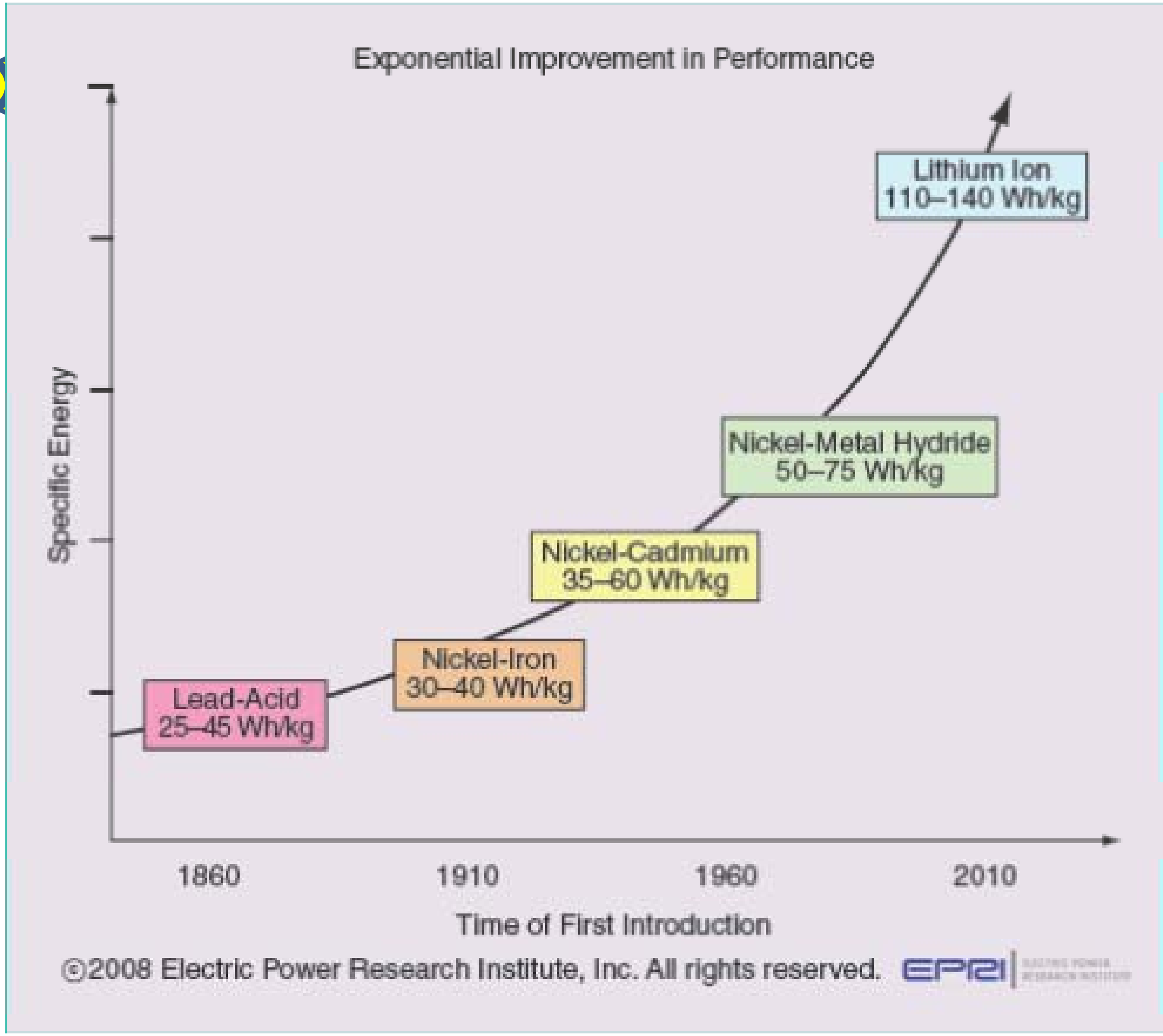


Fig. 7. Schematic diagram of a battery energy storage system operation.

Baterijski sustavi – kemijske reakcije

Chemical reactions and single unit voltages of main batteries available to EES [4,13,67,68].

Battery type	Chemical reactions at anodes and cathodes	Unit voltage
Lead–acid	$Pb + SO_4^{2-} \Longleftrightarrow PbSO_4 + 2e^-$ $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \Longleftrightarrow PbSO_4 + 2H_2O$	2.0 V
Lithium-ion	$C + nLi^+ + ne^- \Longleftrightarrow Li_nC$ $LiXXO_2 \Longleftrightarrow Li_{1-n}XXO_2 + nLi^+ + ne^-$	3.7 V
Sodium–sulfur	$2Na \Longleftrightarrow 2Na^+ + 2e^-$ $\chi S + 2e^- \Longleftrightarrow \chi S^{2-}$	~2.08 V
Nickel–cadmium	$Cd + 2OH^- \Longleftrightarrow Cd(OH)_2 + 2e^-$ $2NiOOH + 2H_2O + 2e^- \Longleftrightarrow 2Ni(OH)_2 + 2OH^-$	1.0– 1.3 V
Nickel–metal hydride	$H_2O + e^- \Longleftrightarrow 1/2H_2 + OH^-$ $Ni(OH)_2 + OH^- \Longleftrightarrow NiOOH + H_2O + e^-$	1.0– 1.3 V
Sodium nickel chloride	$2Na \Longleftrightarrow 2Na^+ + 2e^-$ $NiCl_2 + 2e^- \Longleftrightarrow Ni + 2Cl^-$	~2.58 V


Exponential Improvement in Performance
Specific Energy
Lithium Ion
110–140 Wh/kg
Nickel-Metal Hydride
50–75 Wh/kg
Nickel-Cadmium
35–60 Wh/kg
Nickel-Iron
30–40 Wh/kg
Lead-Acid
25–45 Wh/kg
1860
1910
1960
2010
Time of First Introduction
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EPRI

Olovni akumulator

- Najstarija i najzrelija baterijska tehnologija s najnižom cijenom
- Primjer mrežne aplikacije – 40 MWh u Kaliforniji od 1988. – loša strana je ekonomičnost zbog ciklusnih karakteristika
- Dobra tehnologija za “low-duty cycles” – “black start”
- Napredni dizajn – dodavanje ugljika negativnoj elektrodi – do 2000 ciklusa

Selected lead–acid battery energy storage facilities [4,13,67,75,76].

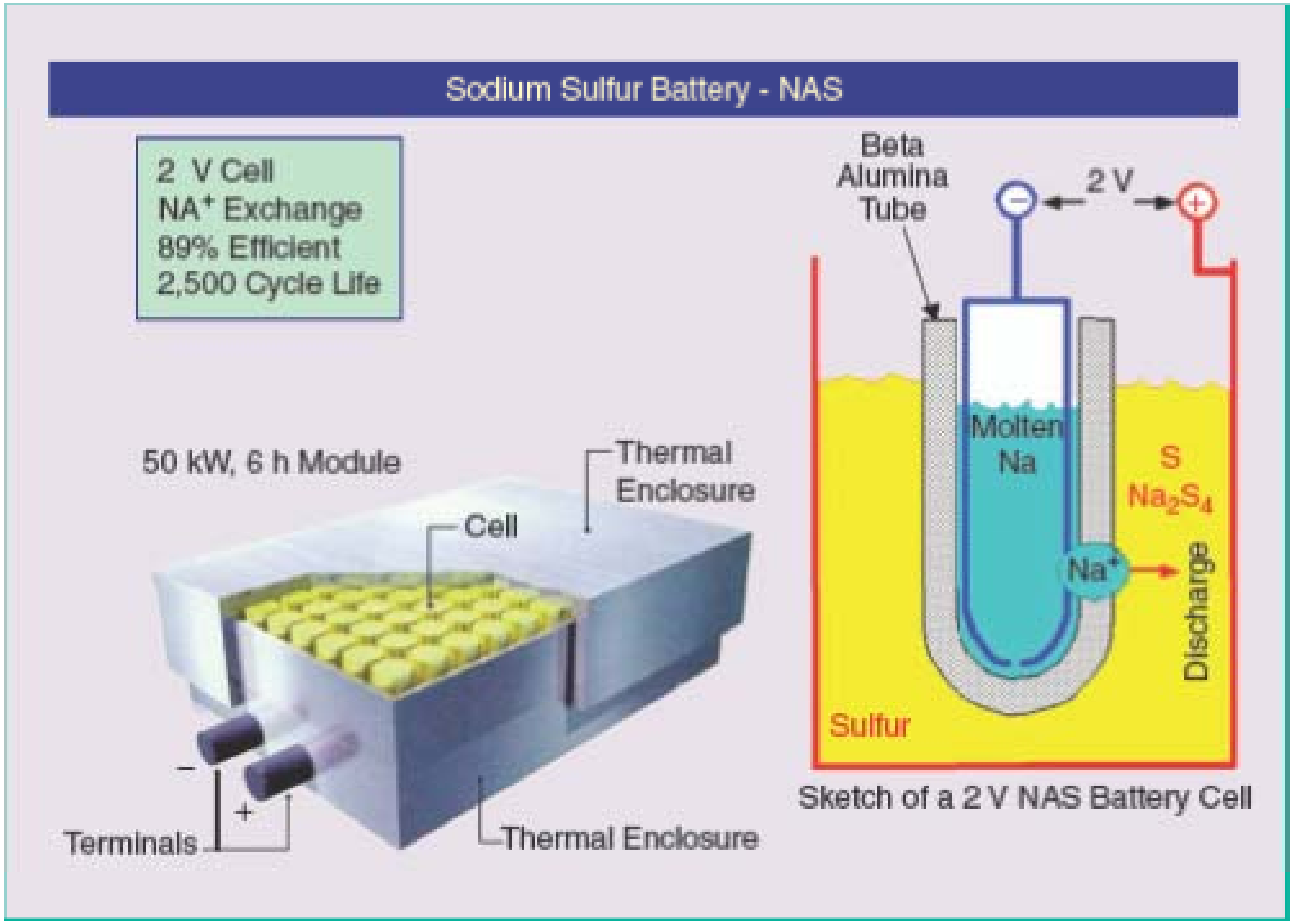
Name/locations	Characteristics	Application area
BEWAG, Berlin	8.5 MW/8.5 MW h	Spinning reserve, frequency control
Chino, California	10 MW/40 MW h	Spinning reserve, load leveling
PREPA, Puerto Rico	20MW/14 MW h	Spinning reserve, frequency control
Metlakatla, Alaska	1 MW/1.4 MW h	Enhancing stabilization of island grid
Kahuku Wind Farm, Hawaii	15 MW/ 3.75 MW h	Power management, load firming, grid integration
Notrees EES project, U.S.	36 MW/24 MW h	Solving intermittency issues of wind energy

NaS baterije

- Visokotemperaturni baterijski sustav koji se sastoji od tekućih elektroda (S-pozitivna i Na-negativna) odvojene keramičkim elektrolitom
- Kroz elektrolit prolaze pozitivni ioni Na i sa S formiraju natrijpolisulfide
- Za vrijeme pražnjenja Na+ ioni idu kroz elektrolit a elektroni idu kroz vanjski krug
- 300°C-350°C, 6 h dnevno, 89% efikasnosti
- U Japanu 190 sustava ukupno 270 MW, 6 h
- Druga visokotemp. je bazirana na kemiji NiNaCl (Zebra baterija)

Selected sodium-sulfur battery energy storage facilities [77,81-83].

Name/locations	Rated power/capacity	Application area
Kawasaki EES test facility, Japan	0.05 MW	The 1st large-scale, proof principle, operated in 1992
Long Island Bus's BES System, New York, US	1 MW/7 MW h	Refueling the fixed route vehicles
Rokkasho Wind Farm ES project, Japan	34 MW/244.8 MW h	Wind power fluctuation mitigation
Saint Andre, La reunion, France	1 MW	Wind power on an island
Graciosa Island, Younicos, Germany	3 MW/18 MW h	Wind & solar power EES for islands, commissioning 2013
Abu Dhabi Island, UAE	40 MW	Load levelling


Sodium Sulfur Battery - NAS
2 V Cell
NA+ Exchange
89% Efficient
2,500 Cycle Life
50 kW, 6 h Module
Thermal Enclosure
Cell
Terminals
Thermal Enclosure
Beta Alumina Tube
2 V
Molten Na
S
Na2S4
Na+
Discharge
Sulfur
Sketch of a 2 V NAS Battery Cell

34 MW, 245 MWh, za vjetrofarmu od 51 MW, 100% u “on-peak” periodu

Litij ionske baterije

- Na tržištu baterije s najvećom gustoćom energije
- Konvencionalni dizajn: anoda je ugljik, katoda je litij metalni oksid ($LiCoO_2$ ili $LiMO_2$), a elektrolit je Li sol u organskom topivu ($LiClO_4$)
- Prednosti: brzina odziva, gustoća energije i snage, ciklusna efikasnost (97%)
- Nedostaci: utjecaj DoD na životni vijek, traži PC!

Area	Technology	Target application	Date	Benefit
Cathode	Manganese spinel (LMO)	Hybrid electric vehicle, cell phone, laptop	1996	durability, cost
	Lithium iron phosphate	Segway Personal Transporter, power tools, aviation products, automotive hybrid systems, PHEV conversions	1996	moderate density (2 A·h outputs 70 amperes) operating temperature >
	Lithium nickel manganese cobalt (NMC)		2008	density, output, safety
	LMO/NMC			power, safety (although limited durability)
	Lithium iron fluorophosphate		2007	durability, cost (replace Li with Na or Na/Li)
	Lithium air	automotive	2009	density, safety[71]
	5% Vanadium-doped Lithium iron phosphate olivine		2008	output

Anode	Lithium-titanate battery (LT)	automotive (Phoenix Motorcars), electrical grid bus	2008	output, charging time, durability (20 years, 9,000 cycles), safety, operating temperature (-50–70 °C)
	Lithium vanadium oxide	automotive	2007	density (745Wh/l)[78]
	Cobalt-oxide nanowires from genetically modified virus		2006	density, thickness[79]
	3D Porous Particles Composed of Curved 2D Nano-Sized Layers	high energy batteries for electronics and electrical vehicles	2011	specific capacity > 2000 mA·h/g, high efficiency, rapid low-cost synthesis [81]
	Iron-phosphate nanowires from genetically modified virus		2009	density, thickness[82][83][84]

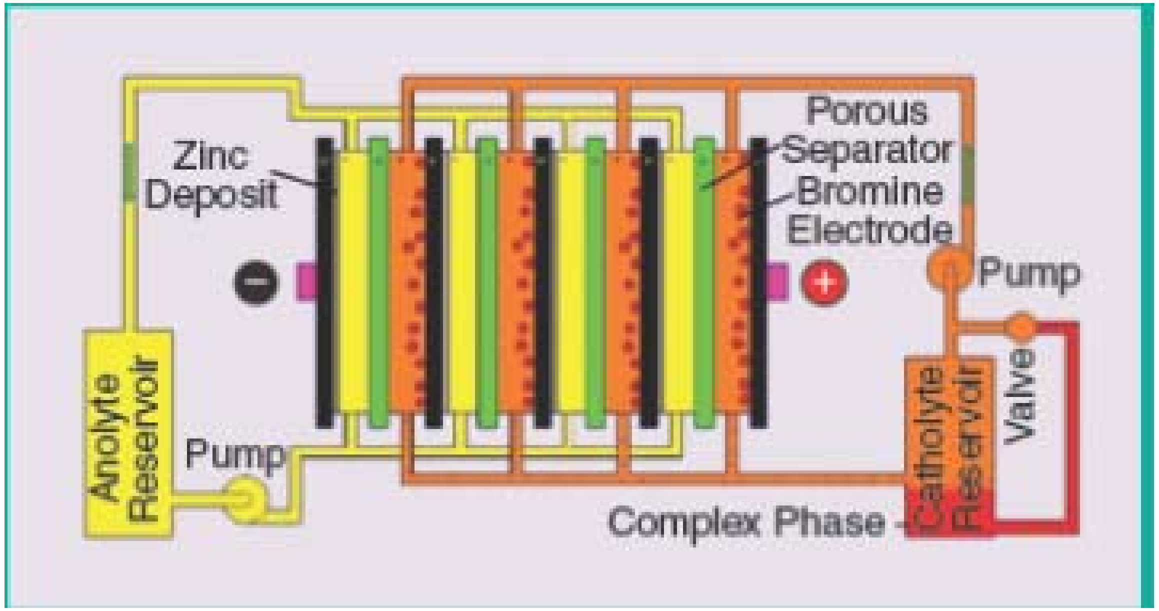
	Silicon/titanium dioxide composite nanowires from genetically modified tobacco virus	explosive detection sensors, biomimetic structures, water-repellent surfaces, micro/nano scale heat pipes	2010	density, low charge time[85]
	Porous silicon/carbon nanocomposite spheres	portable electronics, electrical vehicles, electrical grid	2010	high stability, high capacity, low charge time[86]
	nano-sized wires on stainless steel	wireless sensors networks,	2007	density[8788] (shift from anode- to cathode-limited), durability issue remains (wire cracking)
	Metal hydrides		2008	density (1480 mA·h/g)[89]
	Silicon Nanotubes (or Silicon Nanospheres) Confined within Rigid Carbon Outer Shells	stable high energy batteries for cell phones, laptops, netbooks, radios, sensors and EV	2010	specific capacity 2400 mA·h/g, ultra-high Coulombic Efficiency and outstanding SEI stability [91]
	Silicon nano-powder in a conductive polymer binder	Automotive and Electronics	2011	high capacity anodes (1400 mA·h/g) with good cycling characteristics

- Dva nova dizajna bazirana na litij-ionskoj tehnologiji za mrežnu aplikaciju:
  - Litij-titan dizajn – mangan u katodi i titan u anodi
  - Litij željezni fosfat dizajn – katoda je željezni fosfat

figure 10. A 1,000 kWh lithium-ion battery system applied in a utility frequency regulation application (photo courtesy of ZBB Energy Corporation).

“Flow Battery”

- Punjiva gorivna ćelija u kojoj elektrolit koji sadrži elektroaktivne tvari teče kroz elektrokemijsku (reaktorsku) ćeliju i pretvara kemijsku energiju u električnu energiju
- Primjer – Zn-Br: vodena otopina soli cinkovog bromida pohranjena je u dva rezervoara, za vrijeme punjenja pumpa pumpa elektrolit kroz reaktorsku ćeliju i metalni Zn se taloži na negativnoj površini a bromid se pretvara u bromin na pozitivnoj površini elektrode reaktorske ćelijei tada se pohranjuje u obliku uljne otopine u drugi rezervoar
- Prednost je modularnost sustava, te mala težina (plastični rezervoari i cijevi), nema samopražnjenja


Zinc
Deposit
Porous
Separator
Bromine
Electrode
Pump
Valve
Anolyte
Reservoir
Pump
Catholyte
Reservoir
Complex Phase

Couple	Max. cell voltage (V)	Average electrode power density (W/m^2)	Average fluid energy density (W·h/kg)
Iron-tin	0.62	<200	
Iron-titanium	0.43	<200	
Iron-chrome	1.07	<200	
Vanadium-vanadium (sulphate)	1.4	~800	25
Vanadium-vanadium (bromide)			50
Sodium/bromine polysulfide	1.54	~800	
Zinc-bromine	1.85	~1,000	75
Lead-acid (methanesulfonate)	1.82	~1,000	
Zinc-cerium (methanesulfonate)	2.43	<1,200–2,500	

Redox Flow batteries for the storage of renewable energy: A review
Alotto et al. Renewable and Sustainable Energy Reviews 29 (2014) 325–335

- ZA
  - Odvojena pohrana od konverzije
  - Membrana
  - Nema samopražnjenja
  - Moguće duboko pražnjenje
  - Lakša manipulacija reaktantima nego kod gor.ćel.
  - Lagana kontrola temperature
  - Široki raspon primjene
- PROTIV
  - Mala gustoća snage i energije
  - Gubici zbog strujashunta i protoka fluida

Elektomagnetska pohrana energije

- Kapacitivni spremnik (relativno niska gustoća energije, ali velika gustoća snage – bljeskalice),
- Induktivni spremnik; supravodljivi materijali - [SMES]()

$$D = \varepsilon_0 \varepsilon_r E \quad \left[\mathrm{C/m^2}\right]$$

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \quad [\mathrm{F}]$$

$$w = \frac{1}{2} \varepsilon_0 \varepsilon_r E^2 \quad \left[\mathrm{J/m^3}\right]$$

$$W = \frac{1}{2} C V_0^2 \quad [\mathrm{J}]$$

$$w = \frac{1}{2} \frac{B^2}{\mu} = \frac{1}{2} \mu \mathrm{H}^2$$

$$\mu = \mu_0 \mu_r$$

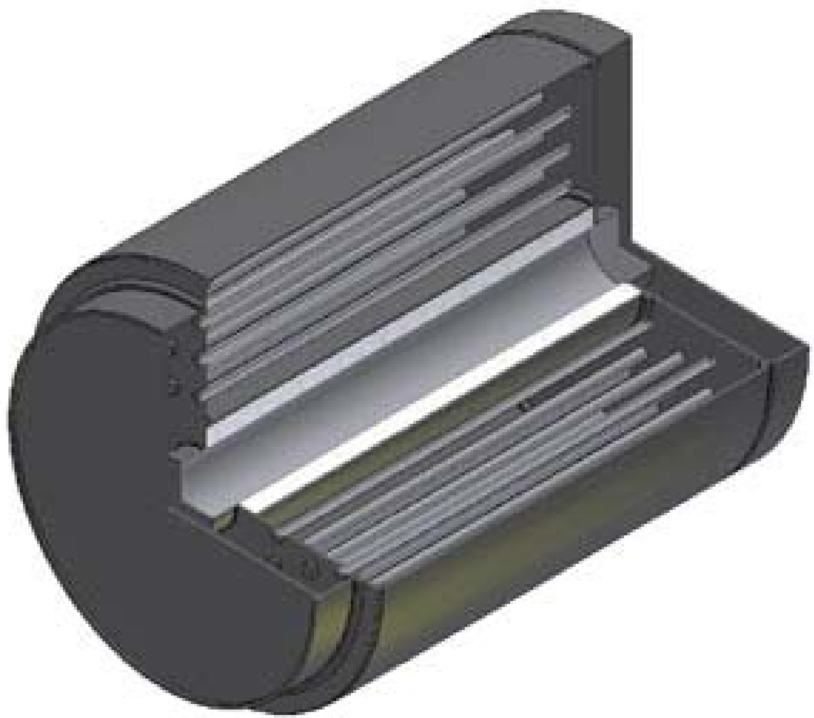
$$E = \frac{L I^2}{2}$$

Pohrana toplinske energije

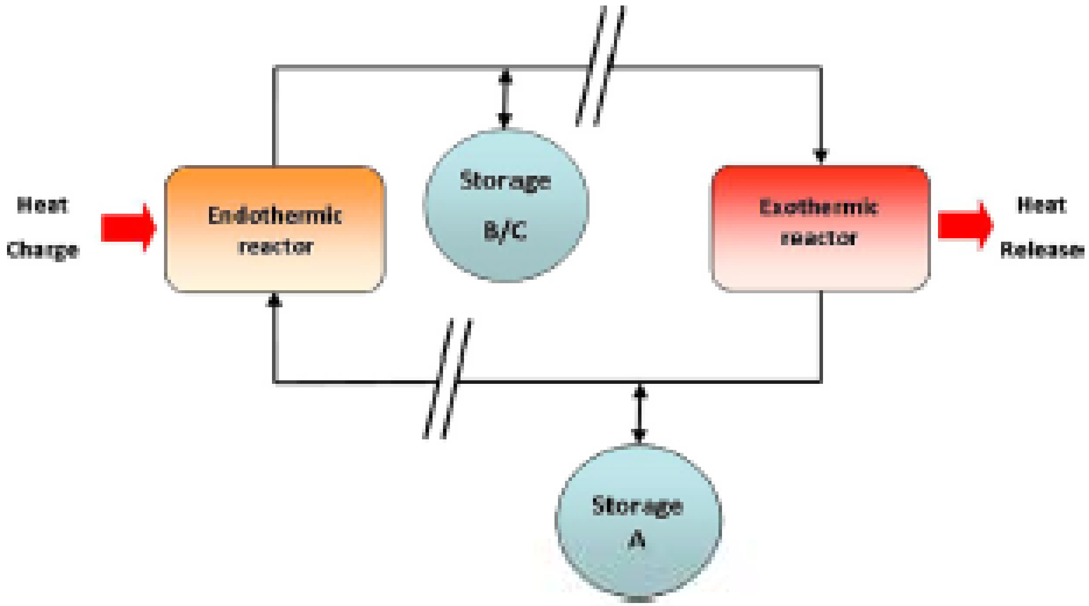
"A review on high temperature thermochemical heat energy storage", Pardo et al., Renewable and sustainable energy reviews, 32 (2014) 591-610

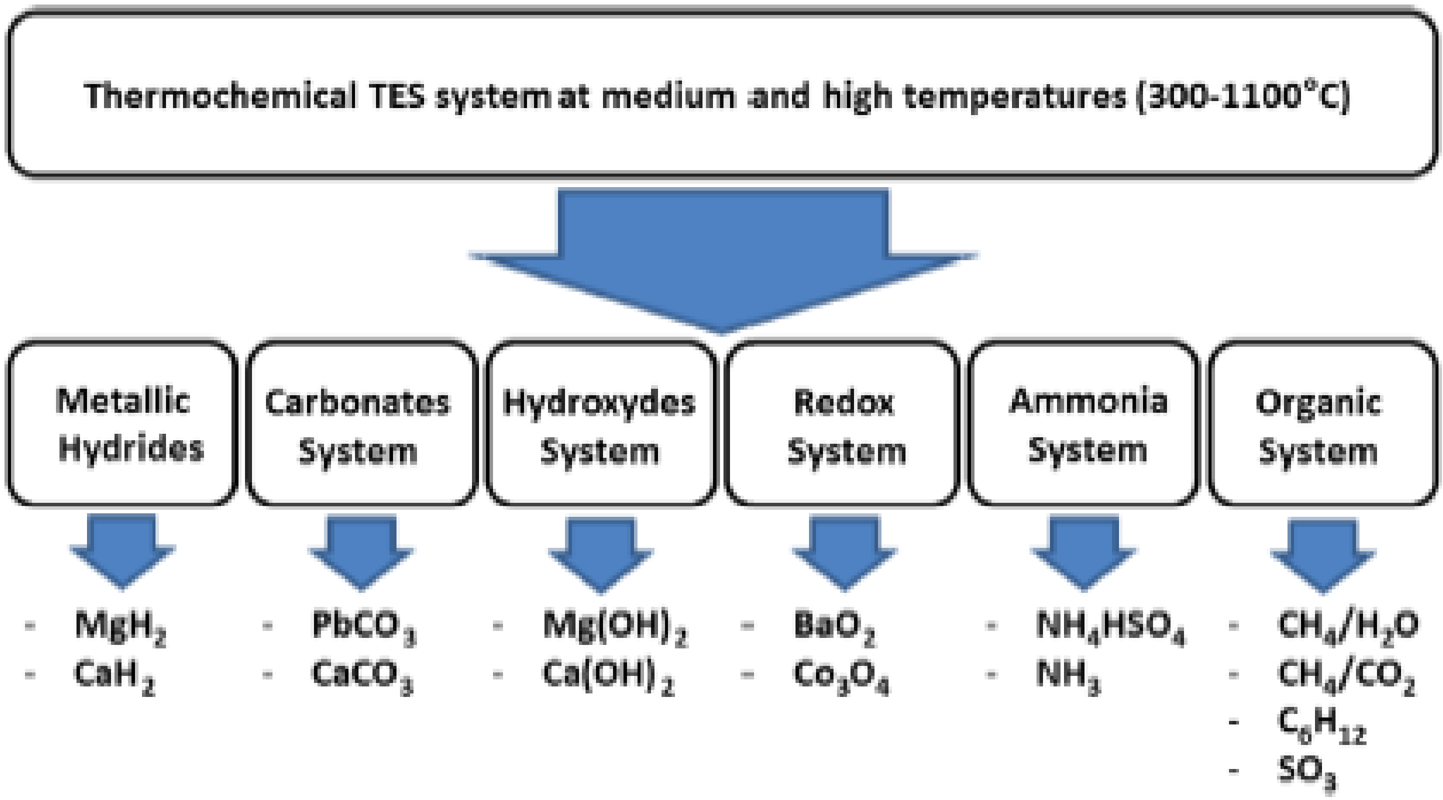
- Koncept toplinskog kapaciteta (promjena temperature medija za pohranu; senzibilna toplina)
  - Zrela tehnologija (Španjolska PS10, PS20, Andasol 1 i 2; SAD Solar One)

- Koncept fazne tranzicije (latentna toplina; *T* = konst)
  - Infinia is developing a thermal energy storage (TES) system that uses Phase Change Material (PCM) as the thermal storage media and employs the high temperature heat pipes to transfer heat from receiver to PCM and PCM to Stirling engine

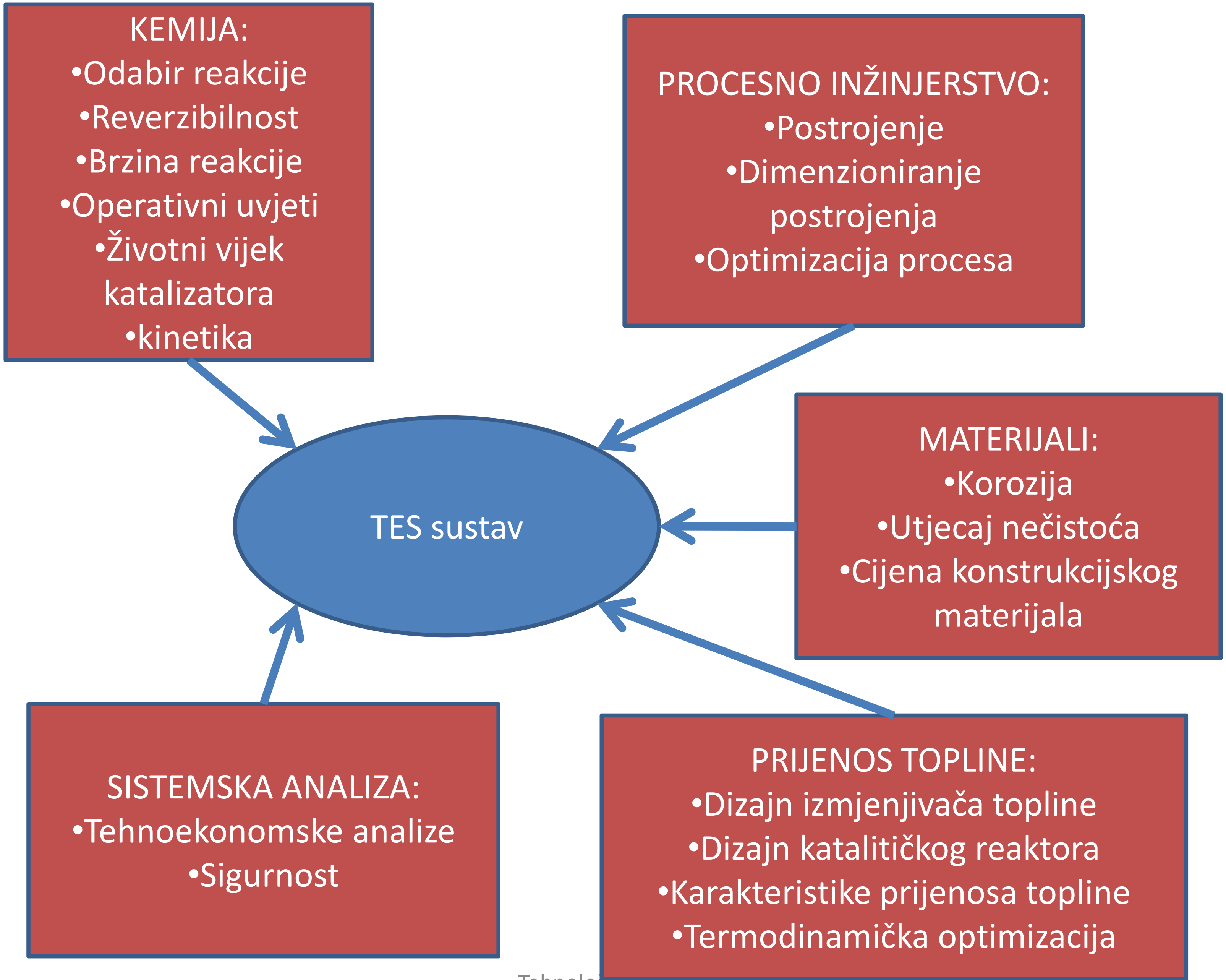


- Koncept kemijskih reakcija
($Q+CH_4+H_2O \leftrightarrow CO+3H_2$; $\Delta H=206$ kJ/mol)
  - Toplina se pohranjuje endoretmnom a oslobađa egzotermnom reakcijom
  - Vrijeme pohrane i mogućnosti transporta su teoretski neograničene
  - Nisko (273-573 K) i <u>visoko (573-1273 K)</u> temperaturni sustavi




Thermochemical TES system at medium and high temperatures (300-1100°C)
Metallic Hydrides
Carbonates System
Hydroxydes System
Redox System
Ammonia System
Organic System
- MgH_2
- CaH_2
- $PbCO_3$
- $CaCO_3$
- $Mg(OH)_2$
- $Ca(OH)_2$
- BaO_2
- Co_3O_4
- NH_4HSO_4
- NH_3
- CH_4/H_2O
- CH_4/CO_2
- C_6H_{12}
- SO_3

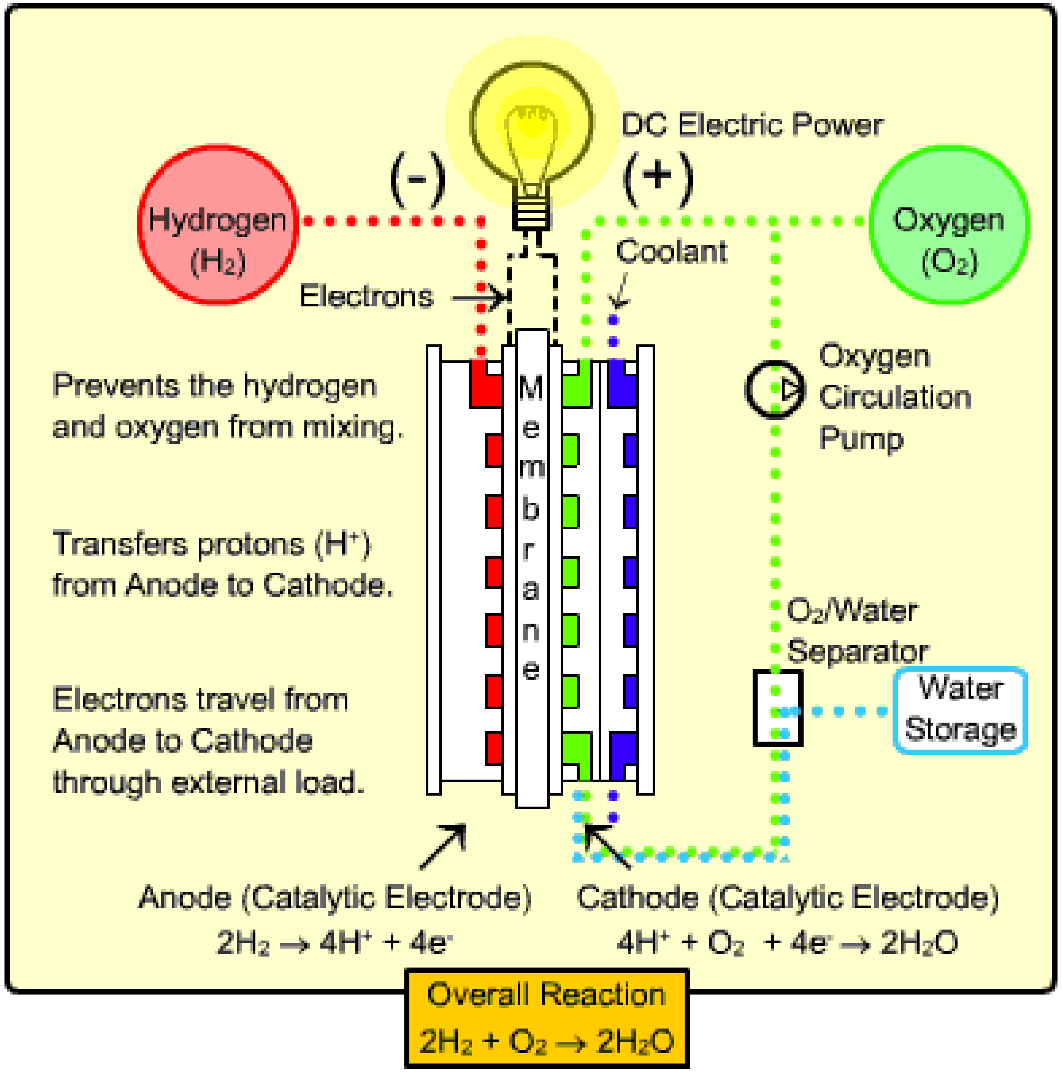
	Senzibilna	Latentna	Termokemijska
Volumna gustoća energije	Mala – 50 kWh/m^3	Srednja – 100 kWh/m^3	Velika – 500 kWh/m^3
Masena gustoća energije	Mala: 0,02-0,03 kWh/kg	Srednja: 0,05-0,1 kWh/kg	Velika: 0,5-1 kWh/kg
Temperatura pohrane	Identična temp. punjenja	Identična temp. punjenja	Ambijentalna temp.
Vrijeme pohrane	Ograničeno (temp. gubici)	Ograničeno (temp. gubici)	Neograničena
Transport	Male udaljenosti	Male udaljenosti	Neograničeno
Zrelost	Industrijski nivo	Pilotska postrojenja	Laboratorijski nivo
Tehnologija	Jednostavna	Srednja	Kompleksna


KEMIJA:
•Odabir reakcije
•Reverzibilnost
•Brzina reakcije
•Operativni uvjeti
•Životni vijek katalizatora
•kinetika
PROCESNO INŽINJERSTVO:
•Postrojenje
•Dimenzioniranje postrojenja
•Optimizacija procesa
TES sustav
MATERIJALI:
•Korozija
•Utjecaj nečistoća
•Cijena konstrukcijskog materijala
SISTEMSKA ANALIZA:
•Tehnoekonomske analize
•Sigurnost
PRIJENOS TOPLINE:
•Dizajn izmjenjivača topline
•Dizajn katalitičkog reaktora
•Karakteristike prijenosa topline
•Termodinamička optimizacija

Zanimljivosti

- Vodikova ekonomija-gorivne ćelije: efikasnost elektrolize 70%; efikasnost gorivnih ćelija 50% → efikasnost tehnologije 35%

Kako radi gorivna ćelija s PEM membranom



Comparison of Fuel Cell Technologies

DOE Hydrogen Program

Fuel Cell Type	Common Electrolyte	Operating Temperature	System Output	Electrical Efficiency	Combined Heat and Power (CHP) Efficiency	Applications	Advantages
Polymer Electrolyte Membrane (PEM)*	Solid organic polymer poly-perfluorosulfonic acid	50 - 100°C 122 - 212°F	<1kW – 250kW	53-58% (transportation) 25-35% (stationary)	70-90% (low-grade waste heat)	• Backup power • Portable power • Small distributed generation • Transportation • Specialty vehicles	• Solid electrolyte reduces corrosion & electrolyte management problems • Low temperature • Quick start-up
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 - 100°C 194 - 212°F	10kW – 100kW	60%	>80% (low-grade waste heat)	• Military • Space	• Cathode reaction faster in alkaline electrolyte, leads to higher performance • Can use a variety of catalysts
Phosphoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	150 - 200°C 302 - 392°F	50kW – 1MW (250kW module typical)	>40%	>85%	• Distributed generation	• Higher overall efficiency with CHP • Increased tolerance to impurities in hydrogen
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600 - 700°C 1112 - 1292°F	<1kW – 1MW (250kW module typical)	45-47%	>80%	• Electric utility • Large distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP
Solid Oxide (SOFC)	Yttria stabilized zirconia	600 - 1000°C 1202 - 1832°F	<1kW – 3MW	35-43%	<90%	• Auxiliary power • Electric utility • Large distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte reduces electrolyte management problems • Suitable for CHP • Hybrid/GT cycle

**Direct Methanol Fuel Cells (DMFC) are a subset of PEM typically used for small portable power applications with a size range of about a subwatt to 100W and operating at 60 - 90°C.*

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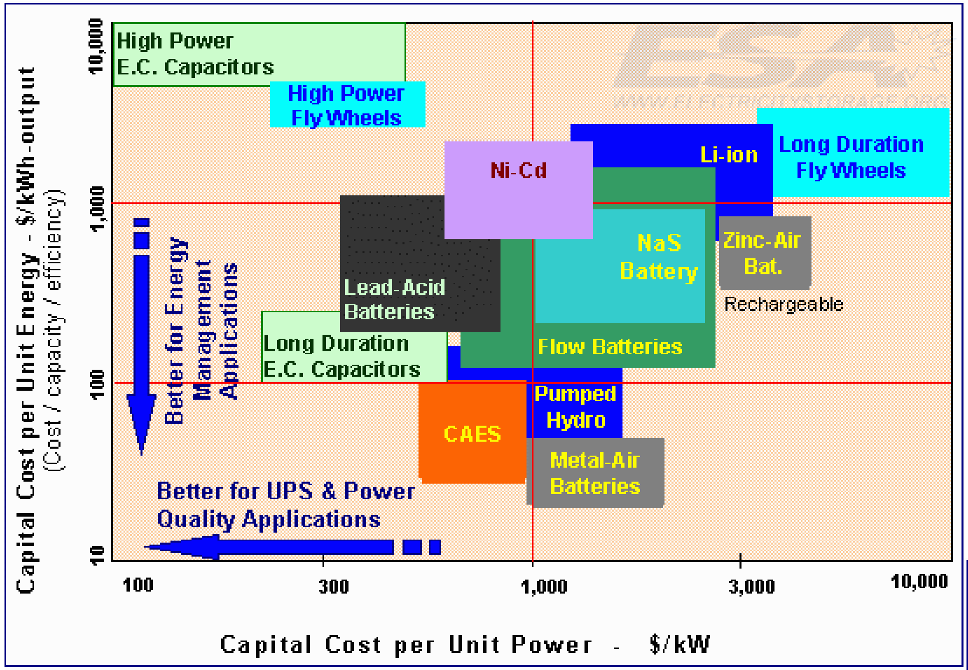
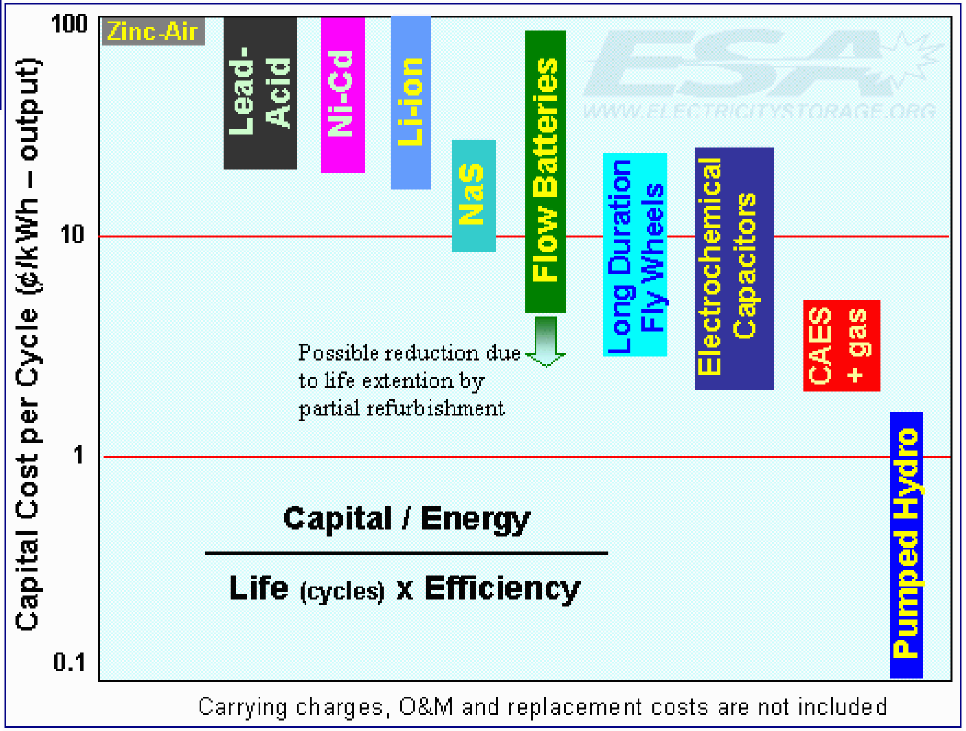
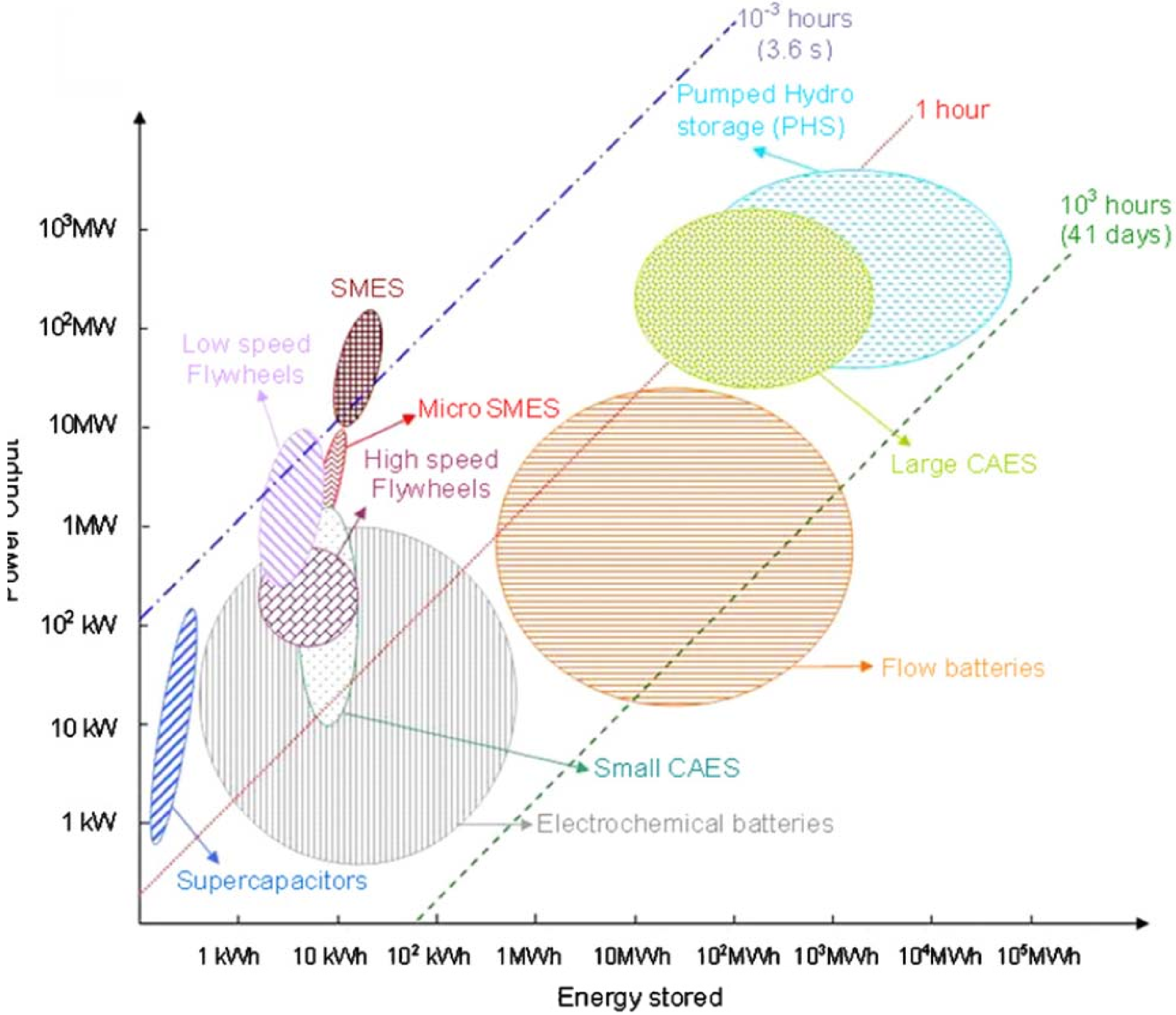
U.S. DEPARTMENT OF ENERGY

U.S. Department of Energy Hydrogen Program
www.hydrogen.energy.gov

Storage Technologies	Main Advantages (relative)	Disadvantages (Relative)	Power Application	Energy Application
Pumped Storage	High Capacity, Low Cost	Special Site Requirement		●
CAES	High Capacity, Low Cost	Special Site Requirement, Need Gas Fuel		●
Flow Batteries: PSB VRB ZnBr	High Capacity, Independent Power and Energy Ratings	Low Energy Density	◐	●
Metal-Air	Very High Energy Density	Electric Charging is Difficult		●
NaS	High Power & Energy Densities, High Efficiency	Production Cost, Safety Concerns (addressed in design)	●	●
Li-ion	High Power & Energy Densities, High Efficiency	High Production Cost, Requires Special Charging Circuit	●	○
Ni-Cd	High Power & Energy Densities, Efficiency		●	◐
Other Advanced Batteries	High Power & Energy Densities, High Efficiency	High Production Cost	●	○
Lead-Acid	Low Capital Cost	Limited Cycle Life when Deeply Discharged	●	○
Flywheels	High Power	Low Energy density	●	○
SMES, DSMES	High Power	Low Energy Density, High Production Cost	●	
E.C. Capacitors	Long Cycle Life, High Efficiency	Low Energy Density	●	◐


High Power
E.C. Capacitors
High Power
Fly Wheels
Ni-Cd
Li-ion
Long Duration
Fly Wheels
NaS
Battery
Zinc-Air
Bat.
Rechargeable
Lead-Acid
Batteries
Long Duration
E.C. Capacitors
Flow Batteries
Pumped
Hydro
CAES
Metal-Air
Batteries
Better for Energy
Management
Applications
Better for UPS & Power
Quality Applications
Capital Cost per Unit Energy - $/kWh-output
(Cost / capacity / efficiency)
10,000
1,000
100
10
100
300
1,000
3,000
10,000
Capital Cost per Unit Power - $/kW


Zinc-Air
Lead-Acid
Ni-Cd
Li-ion
NaS
Flow Batteries
Long Duration
Fly Wheels
Electrochemical
Capacitors
CAES
+ gas
Pumped Hydro
Possible reduction due
to life extention by
partial refurbishment
Capital / Energy
Life (cycles) x Efficiency
Capital Cost per Cycle (¢/kWh – output)
100
10
1
0.1
Carrying charges, O&M and replacement costs are not included



10^{-3} hours
(3.6 s)
Pumped Hydro
storage (PHS)
1 hour
10^3 hours
(41 days)
SMES
Low speed
Flywheels
Micro SMES
High speed
Flywheels
Large CAES
Flow batteries
Small CAES
Electrochemical batteries
Supercapacitors
10^3MW
10^2MW
10MW
1MW
10^2 kW
10 kW
1 kW
1 kWh
10 kWh
10^2 kWh
1MWh
10MWh
10^2MWh
10^3MWh
10^4MWh
10^5MWh
Energy stored

Application	**Matching Electricity Supply to Load Demand**	**Providing Backup Power to Prevent Outages**	**Enabling Renewable Technologies**	**Power Quality**
Discharged Power	< 1MW to 100's of MW	1 – 200 MW	20kW to 10 MW	1 kW to 20MW
Response Time	< 10min	< 10ms (prompt) < 10 min (conventional)	< 1sec	< 20ms
Energy Stored	1 MWh to 1000 MWh	1 MWh to 1000 MWh	10 kWh to 200 MWh	50 to 500 kWh
Need for high efficiency	High	Medium	High	Low
Need long cycle or calendar life	High	High	High	Medium

Storage Technology	Pumped Hydropower	Compressed Air Storage	Batteries	Flywheels	SMES	Capacitors
Energy Storage Capacity	< 24,000 MWh	400 - 7200 MWh	<200 MWh	< 100 kWh	0.6 kWh	0.3 kWh
Duration of Discharge at maximum power level	~ 12 hours	4 – 24 hours	1 – 8 hours	Minutes to 1 hour	10 s	10 s
Power Level	< 2000MW	100-300 MW	< 30 MW	< 100 kW (each)	200 kW	100 kW
Response Time	30 ms	3 -15 min (large scale)	30 ms	5 ms	5 ms	5 ms
Cycle Efficiency	0.87	0.8	0.70 - 0.85	0.93	0.95 [1]	0.95 [1]
Lifetime	40 yrs	30 yrs	2-10 yrs	20 yrs	40 yrs	40 yrs