Ústav fyzikální chemie J. Heyrovského
Akademie věd České republiky

Využití lithia v pokročilých technologiích ukládání energie

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J. Heyrovský 1959

(Elektrochemická) akumulace (elektrické) energie:

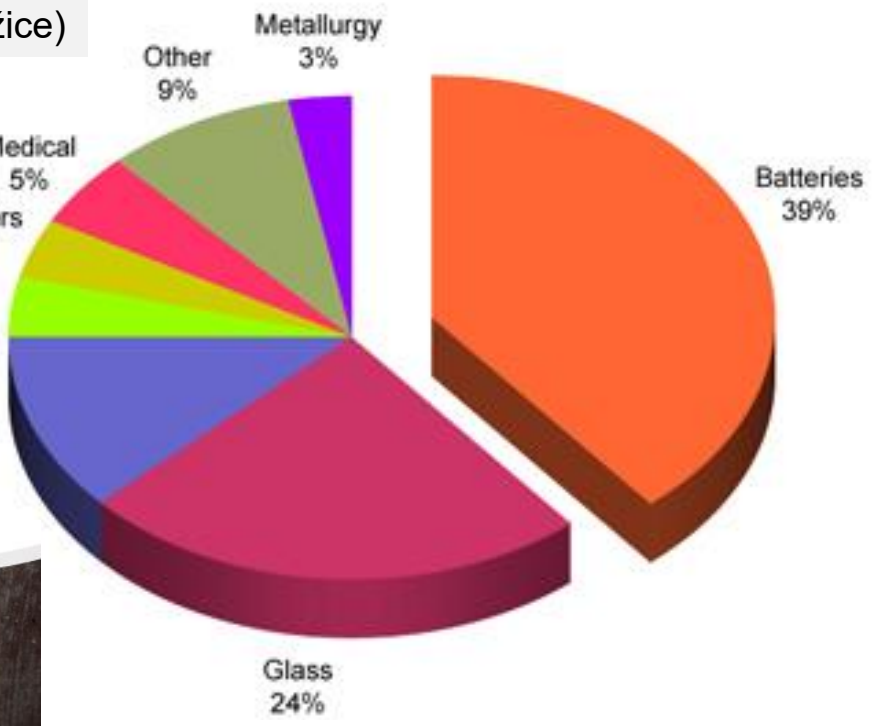
baterie, superkondenzátory, palivové články

Proč Li-baterie?....: Využití lithia (2015)

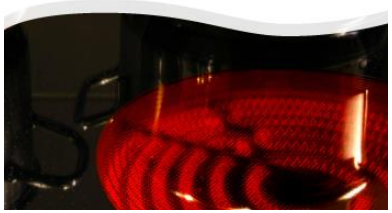
LiOH (ponorky, družice)

antidepresiva

LiBr (místo freonu)



ztužování maziv
Li-stearát



sklo, keramika
Li_2CO_3

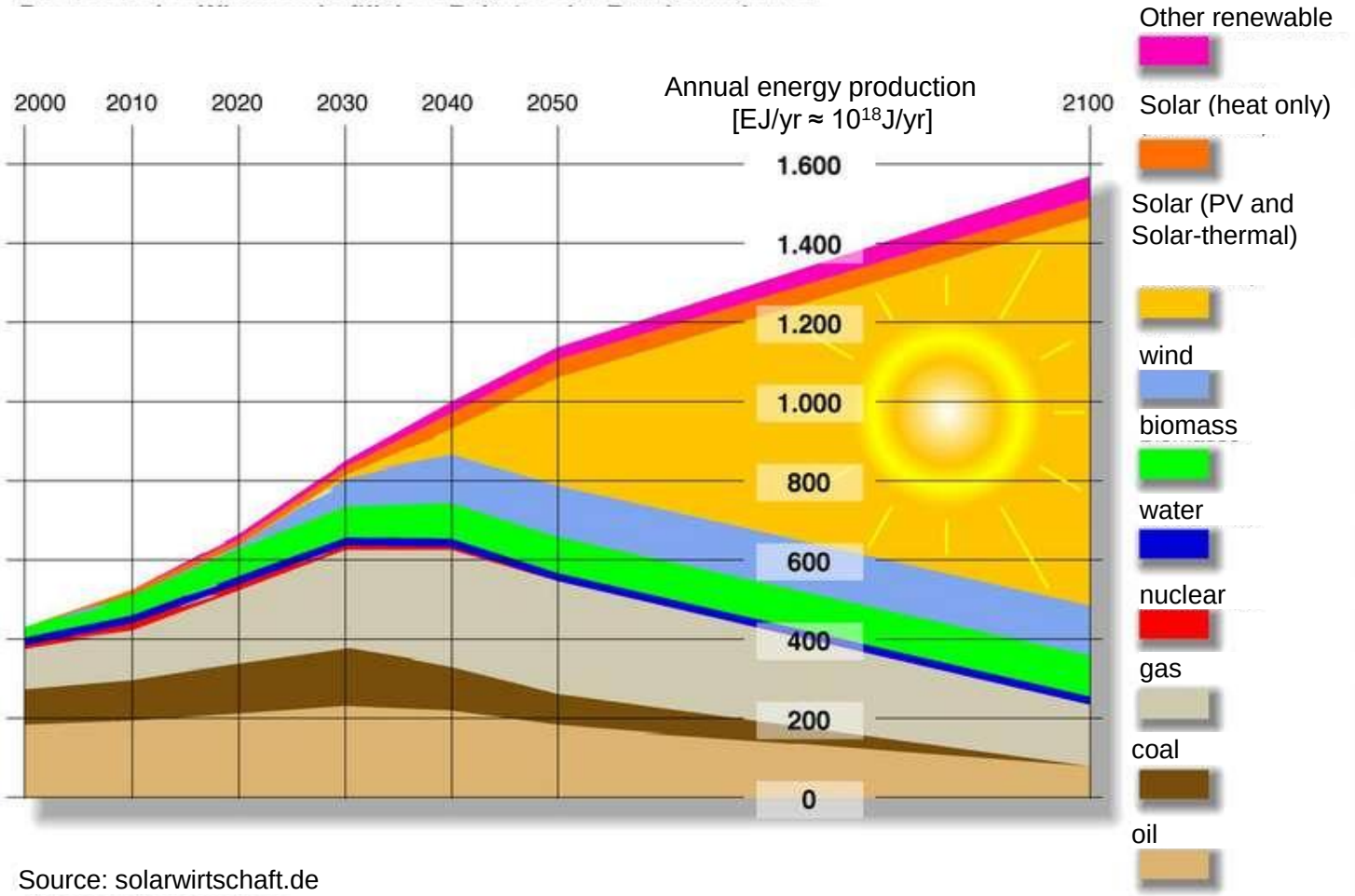
Zdroj: Global Lithium LLC 2016

Humanity's top ten problems for next 50 years

1. Energy
2. Water
3. Food
4. Environment
5. Poverty
6. Terrorism & War
7. Disease
8. Education
9. Democracy
10. Population

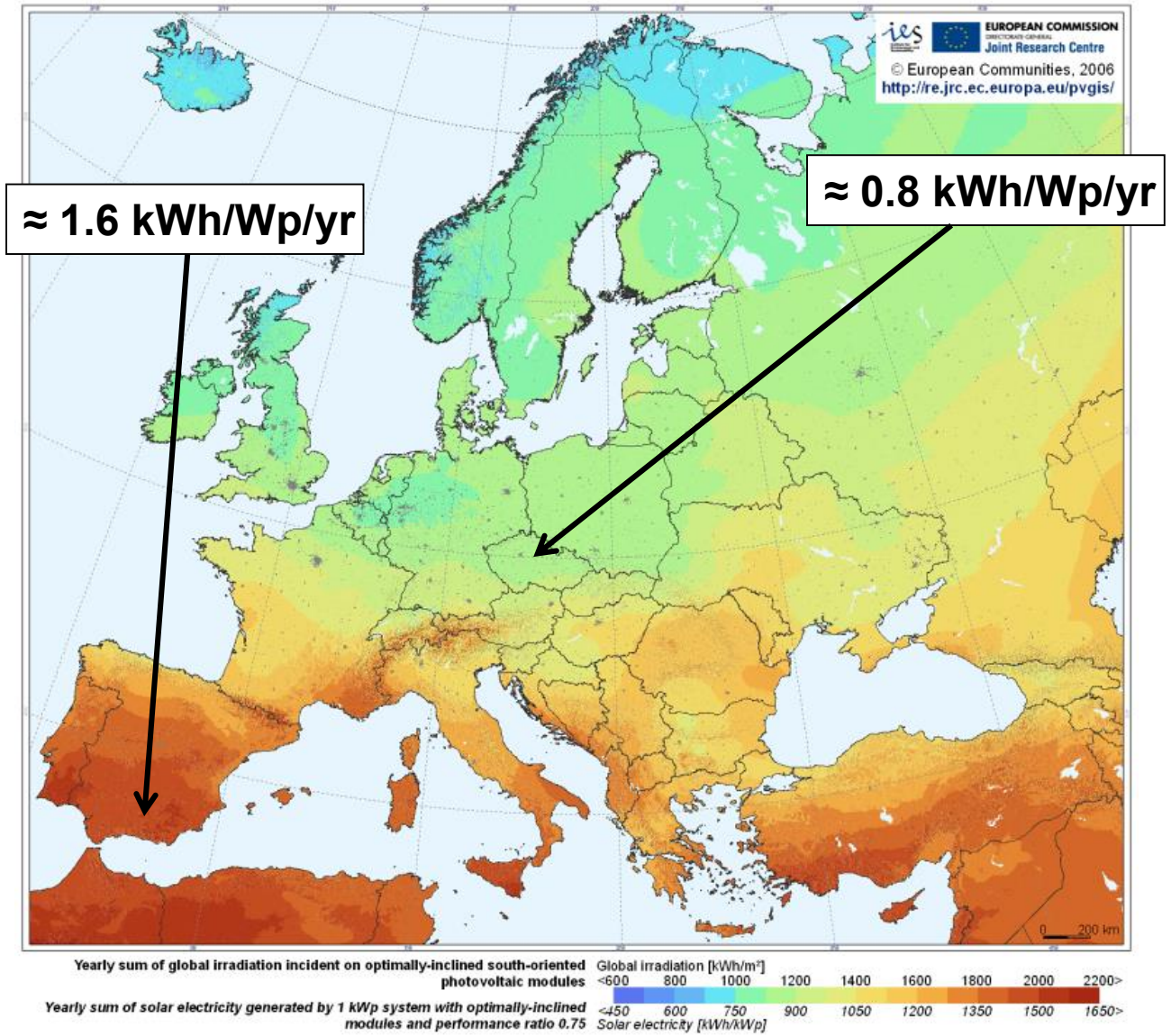
(Source: WTO)

Světové zdroje energie do r. 2100



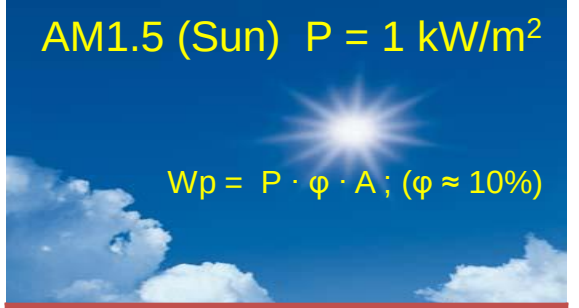
Source: solarwirtschaft.de

Photovoltaic Solar Electricity Potential in European Countries



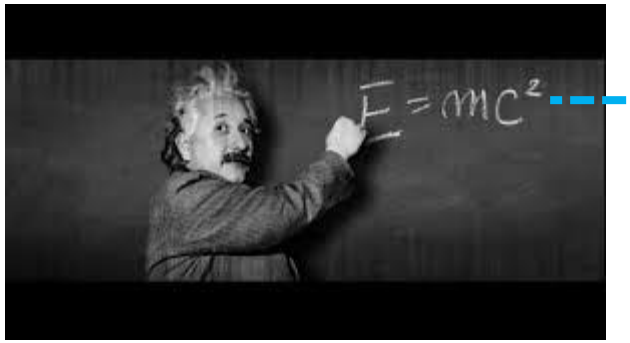
Prům spotřeba (CZ): 1400 kWh/capita/rok≈ 1750 Wp (pouze domácnosti)
Zdroj/Spotřeba se nekryjí (časově, geograficky). Fluktuace! →"Solární baterie"

Source: ***Photovoltaic energy barometer*** **2016 - EurObserv'ER1**



No.	Country	Wp/capita (2015)
1	Germany	489.8
2	Italy	311.3
3	Belgium	286.7
4	Greece	241.7
5	Luxembourg	222.0
6	Czech Republic	197.7
7	Malta	170.5
8	Bulgaria	141.7
9	Denmark	94.8
10	Unied Kingdom	137.7
11	Slovenia	124.8
12	Slovakia	109.8
13	Austria	108.9
14	Spain	106.0
15	France	99.1
16	Netherlands	83.1
17	Cyprus	82.0
18	Romania	66.7
19	Portugal	44.3
20	Lithiuania	25.0
21	Sweeden	13.3
22	Croatia	10.6
23	Estonia	3.1
24	Finland	2.7
25	Poland	2.3
26	Latvia	0.8
27	Ireland	0.5

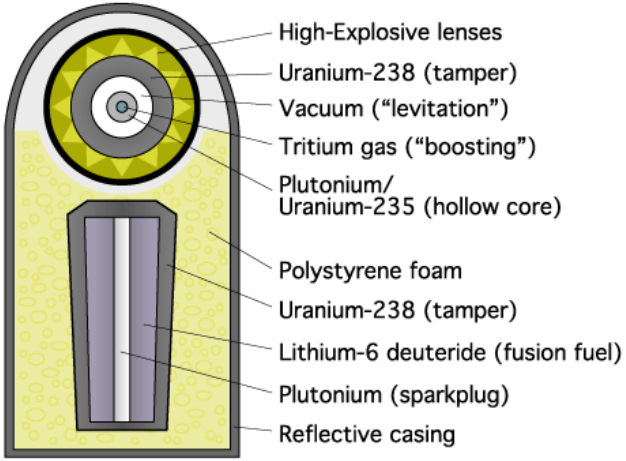
Kolik energie lze uložit v 1 kg hmoty..?



25 TWh/kg **(T ≈ 10^{12})**

H/He jaderná fúze (slunce)...0.2 TWh/kg
($D^2 + T^3 = He^4 + n + 17.6$ MeV
($Li^{6,7} + n \rightarrow T^3 + He^4$)

^{235}U (jaderné štěpení)…….25 GWh/kg **(G ≈ 10^9)**



Světová spotřeba ……. ≈20 PWh/yr **(P ≈ 10^{15})**

(≈ 10^6 kg ^{235}U/yr)
(≈ 10^6 toe/yr; toe = *ton of oil equivalent*)

1 toe= 11.63 MWh = 1.42857143 tce

Energetická kapacita materiálů

Nosič energie	kWh/kg	kWh/L
Vodík (kap. 23 K)	33	2.4
Vodík (plyn 20 MPa)	33	0.5
Benzín	13	9
Pb-baterie	0.03	0.09
Li-baterie	0.2	0.5
Superkondenzátor	0.005	0.01

Gaston Planté (1834-1889)

Objevitel olověného akumulátoru (1859)

***Gastornis*:**
(pták, paleoncen)

12V, 40 Ah autobaterie:

40 Ah @ C/24 rychlost nabíjení

BATERIE (sekundární; akumulátory)

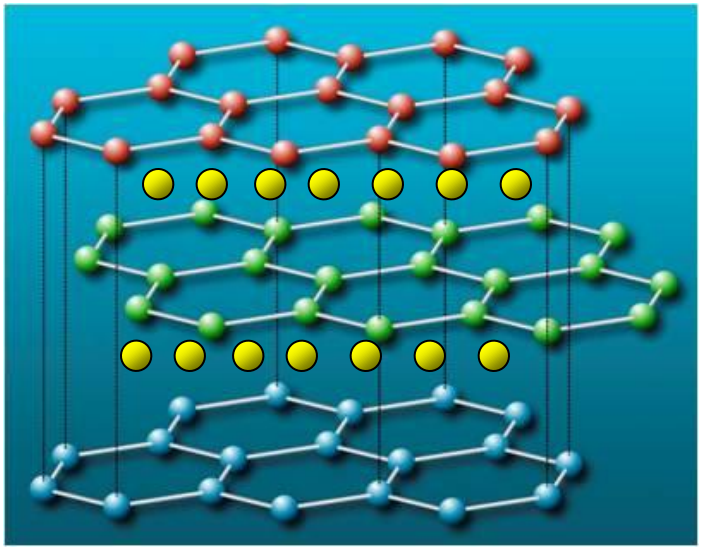
	Napětí	Hustota energie (Wh/kg)	(Wh/l)
Vodný elektrolyt			
Olověný akum.	2.0	30	100
Ni-Cd	1.2	35	100
Ni-MH	1.2	75	300
Nevodný elektrolyt			
Lithium-Ion	3.7	150	400
Lithium-Polymer	3.7	150	400

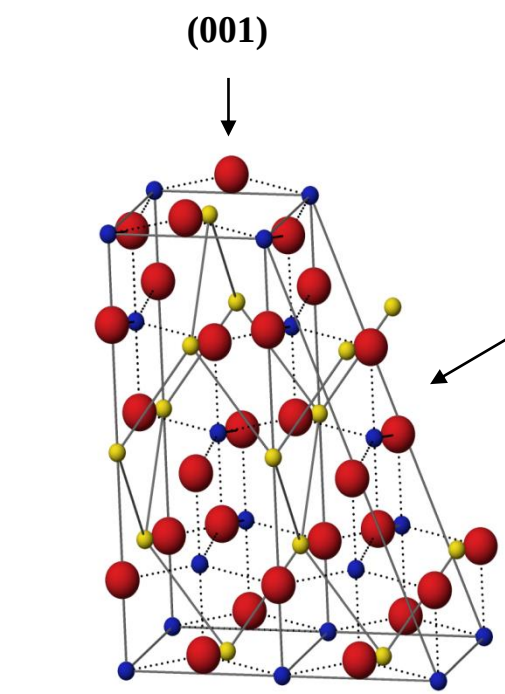
● Li^+

Grafit interkalace:

$C + 1/6\ (e^- + Li^+) \rightarrow 1/6\ LiC_6$

E_{form} ≈ 0.2 V vs. Li/Li^+
Q_{spec} = 1340 C/g = 372 mAh/g





TiO_2 (anatas) inserce:

$TiO_2 + 1/2\ (e^- + Li^+) \rightarrow Li_{0.5}TiO_2$

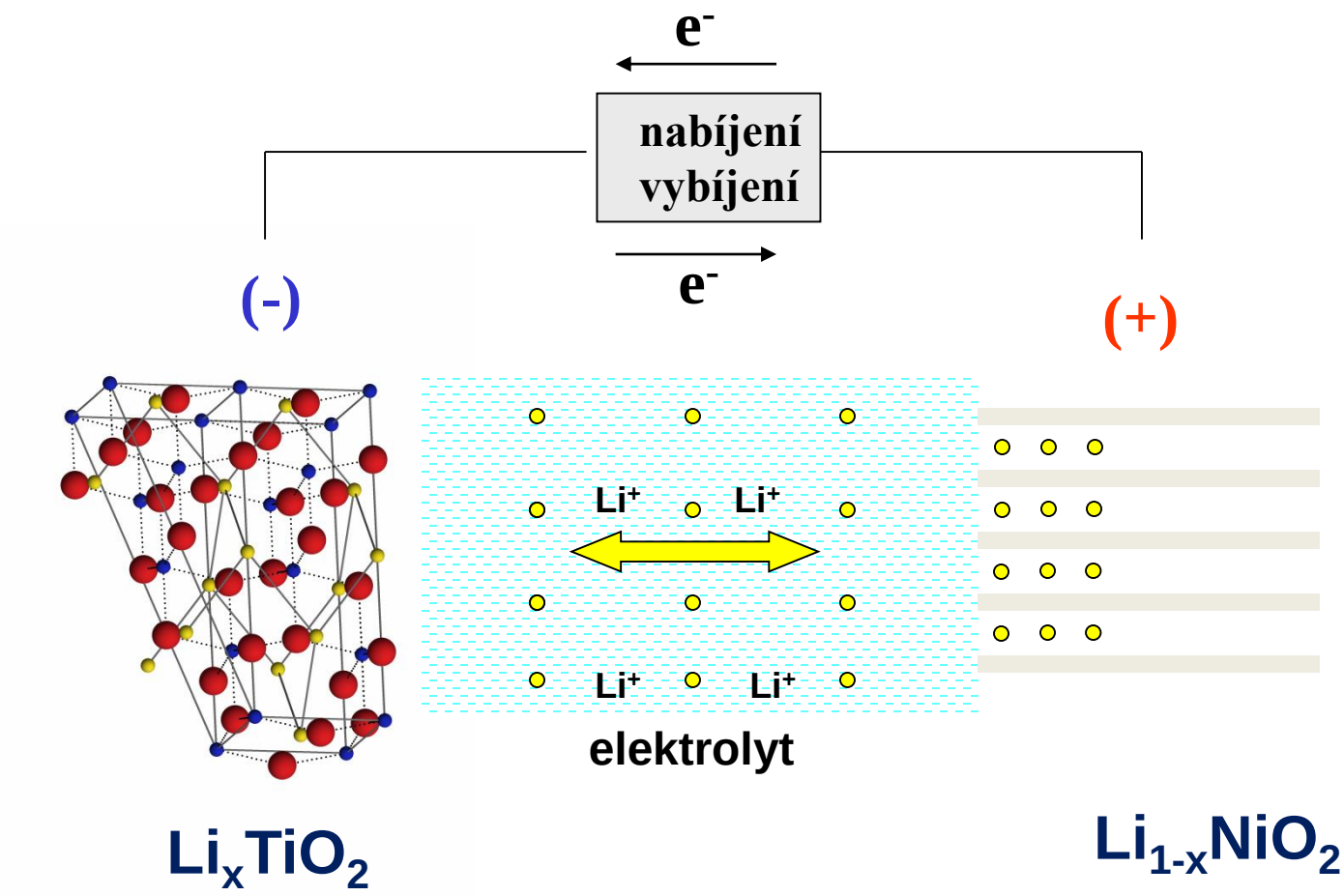
E_{form} ≈ 1.85 V vs. Li/Li^+
Q_{spec} = 168 mAh/g

IUPAC definice:

"Intercalation" = non covalent inclusion into laminar hosts
G. P. Moss, P. A. S. Smith, D. Tavernier, *Pure Appl. Chem.* 1995, *67,* 1307-1375

Lat.: *mensis intercalarius* (Julianská/Gregoriánská reforma kalendáře, 46 BC)

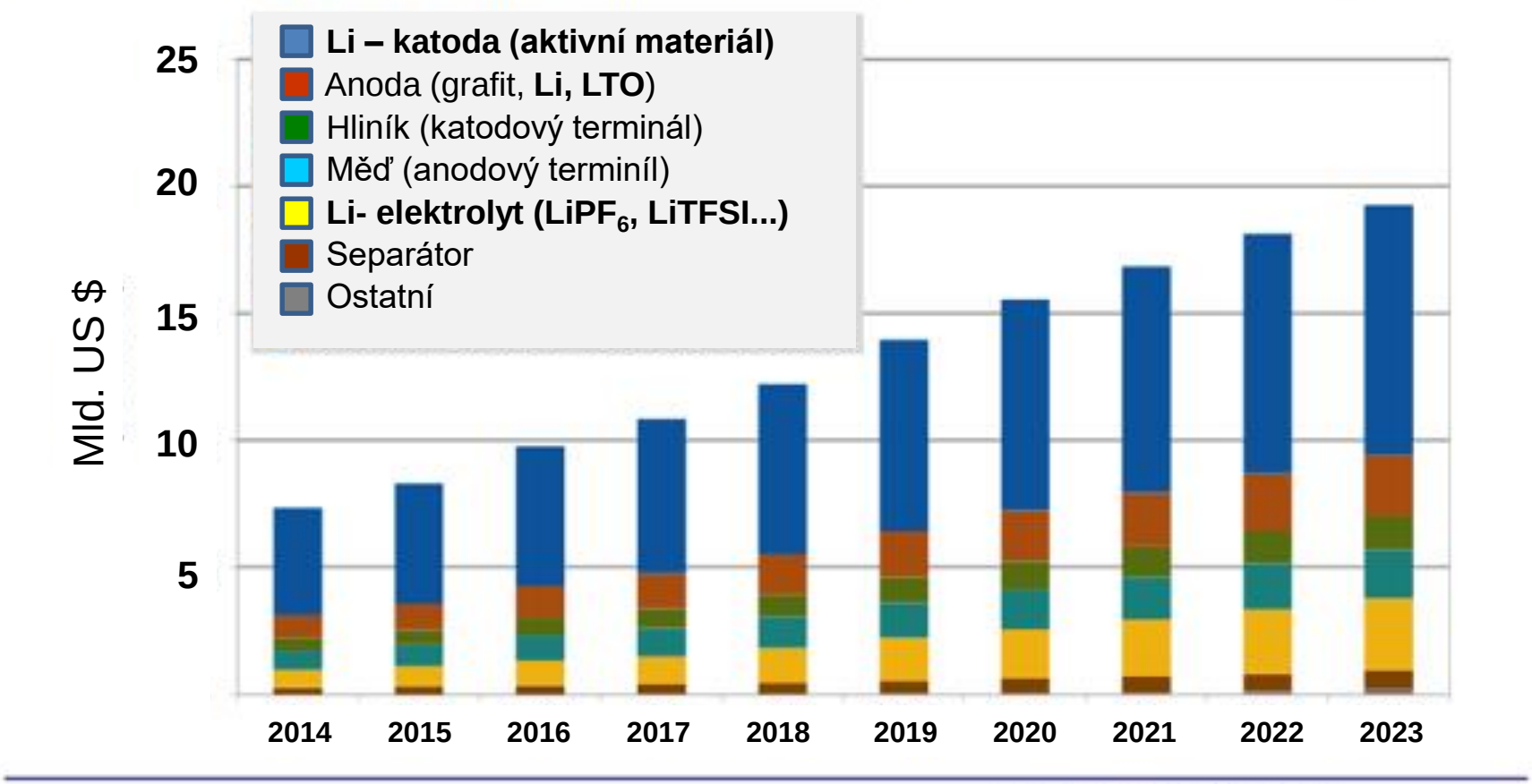
Baterie Li-ion: SONY 1991 (první komerční)



[grafit, Li, $Li_4Ti_5O_{12}$...]

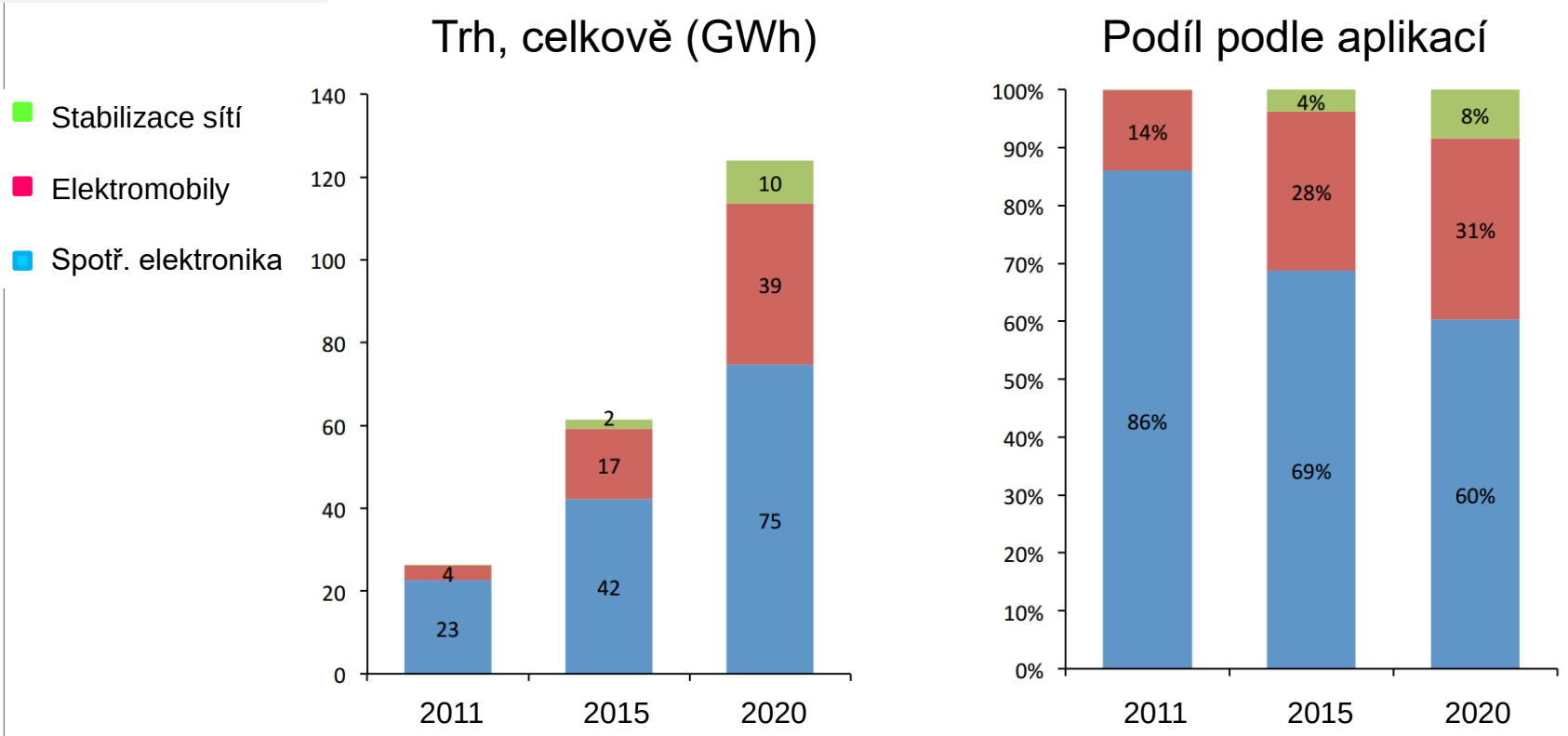
[$LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, ...]

Světový trh komponent pro Li-baterie (2014-2023)



Zdroj: Navigat research

Trh Li-baterií podle aplikací: střednědobý trend

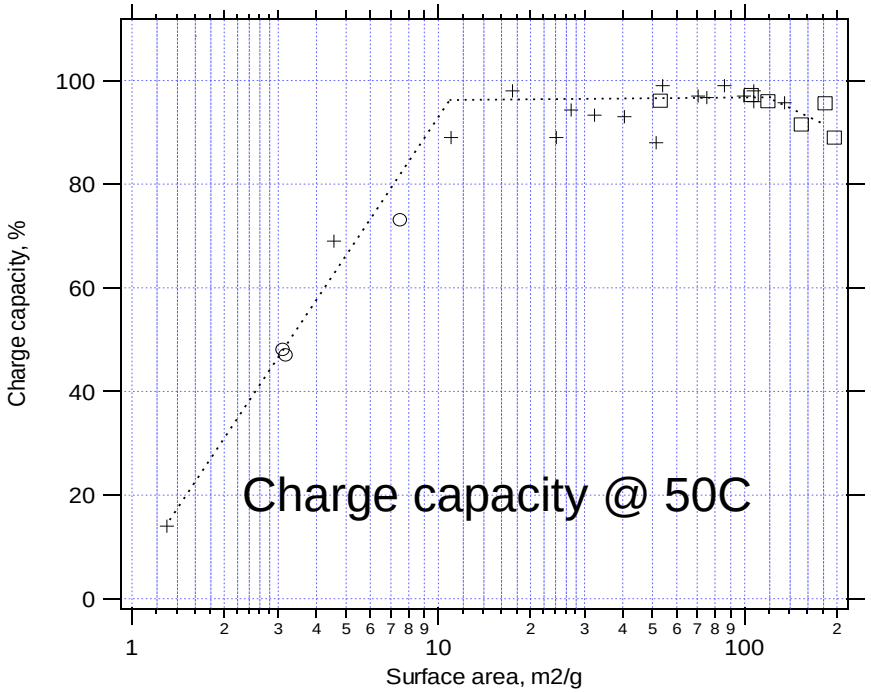


1) Spotřební elektronika trhu dominuje a pozice se uchová i ve střednědobém výhledu
1) Nejrychlejší nárůst trhu baterií pro stabilizaci sítí, avšak celkově minoritní segment
2) Nárůst trhu baterií pro elektromobily, v dynamice i objemu

Zdroj: CEMAC: *Clean Energy Manufacturing Center*

1) Nanotechnologie & Li-ion bat.

LTO: $Li_4Ti_5O_{12}$



Altairnano
innovation at work

HIGH ENERGY 3D ACCUMULATOR
HE3DA
Bringing future closer

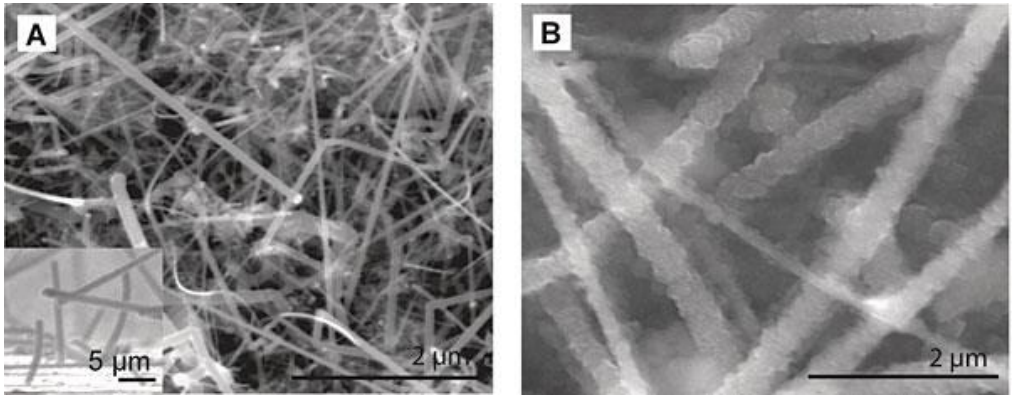
Spitler, Procházka, Kavan et al.: US 7,547,490 (2009)

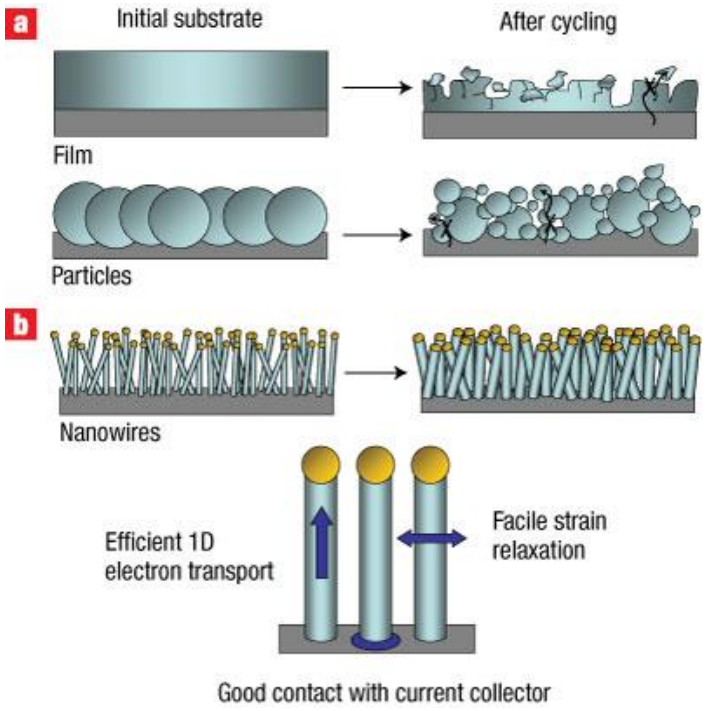
Kavan, Procházka et al.: *J.Electrochem.Soc.* 150, A1000 (2003)

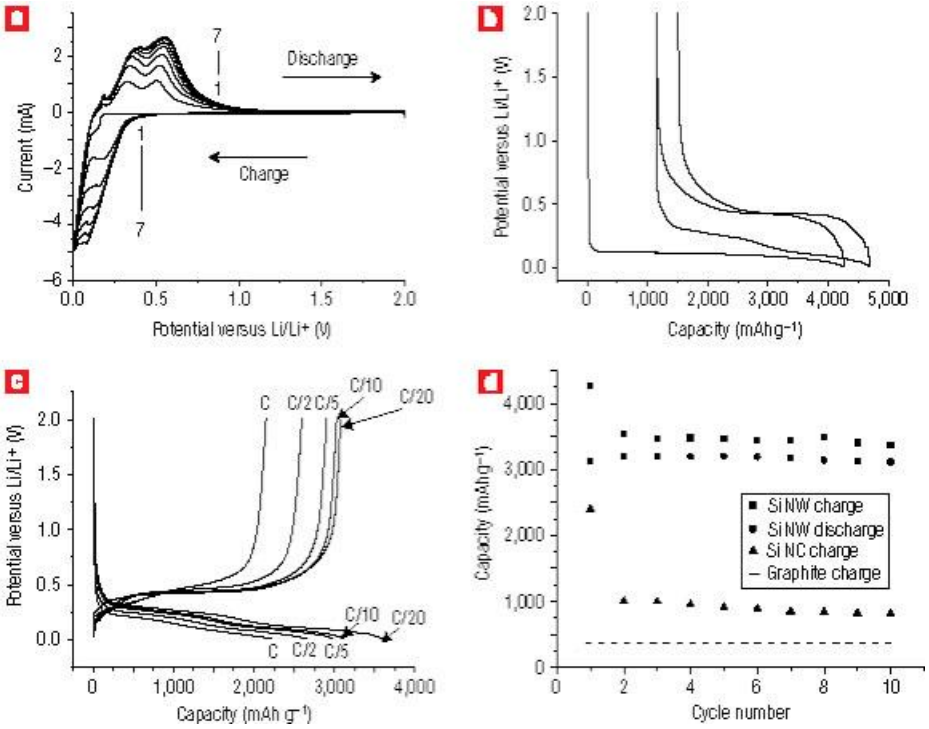
2) Nanotechnologie & Li-ion bat.

Si-nanodráty: anoda pro Li-ion
>3000 mAh/g (srov. grafit 372 mAh/g)

***Nature Nanotechnology,* 3, 31, 2008**

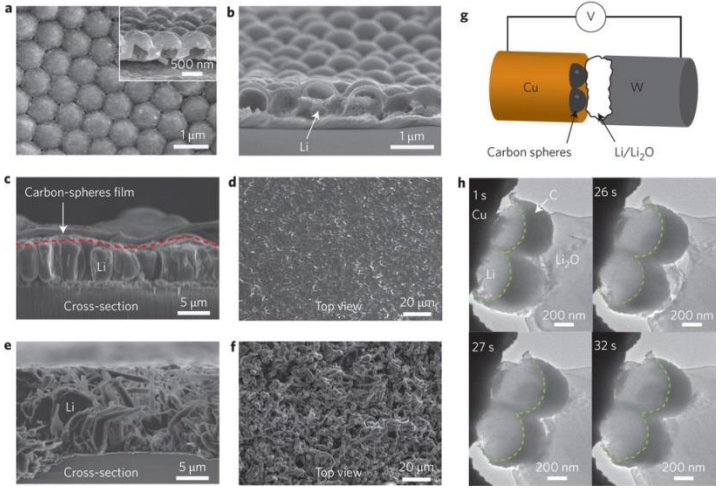


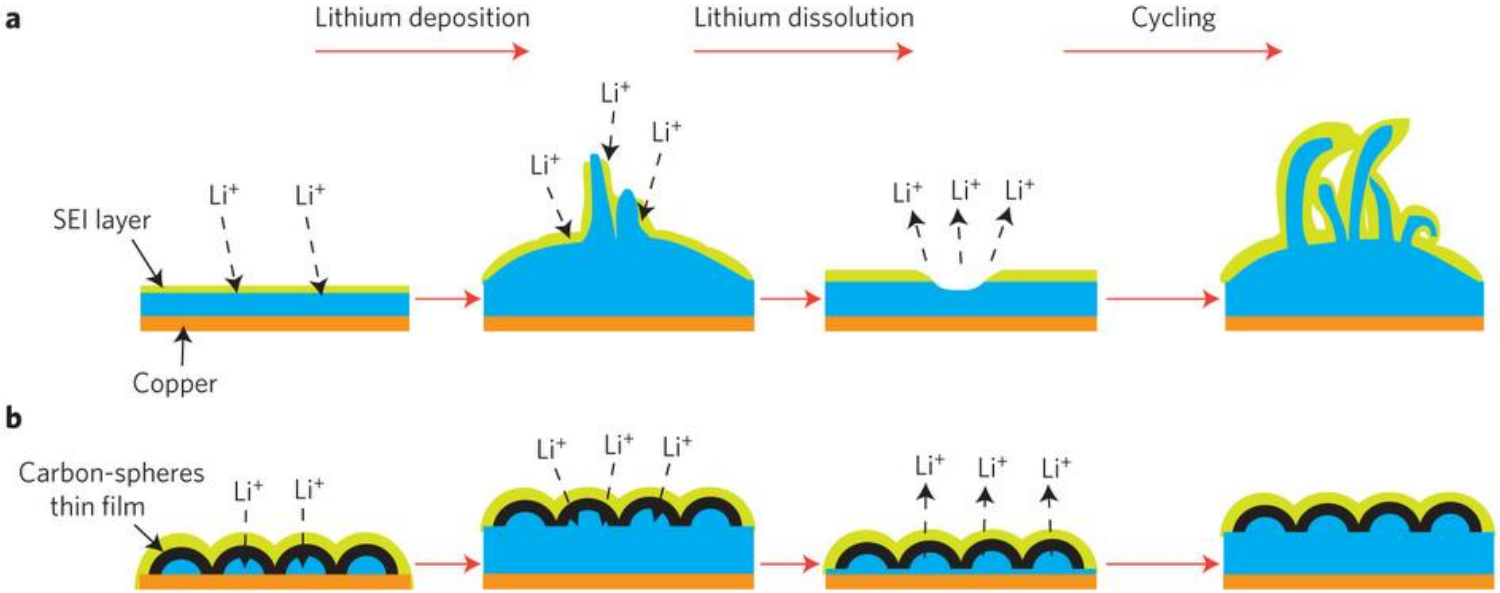




3) Nanotechnologie & Li-ion bat.

Anoda z čistého Li (3850 mAh/g)





Další antikorozní vrstvy : grafen, BN…

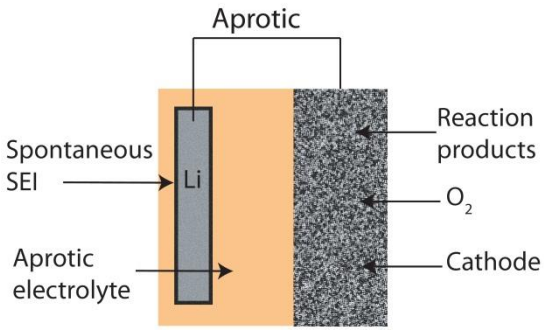
Zdroj: *Nature Nanotech*. 9, 618, 2014

Baterie Li-vzduch

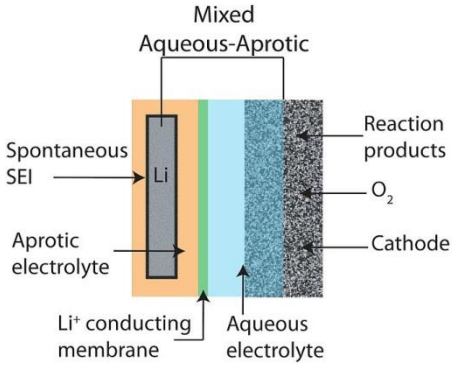
Anoda: $Li \leftrightarrow Li^+ + e^-$ ….. [3850 mAh/g]

Katoda: $½O_2 + 2e^- \leftrightarrow O^{2-}$ ….. [$LiOH$; Li_2O, Li_2O_2,Li_2O_2 ….]

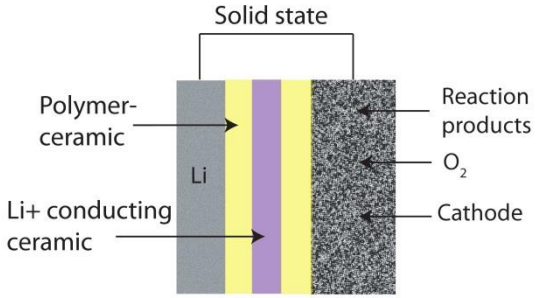
Nevodný elektrolyt



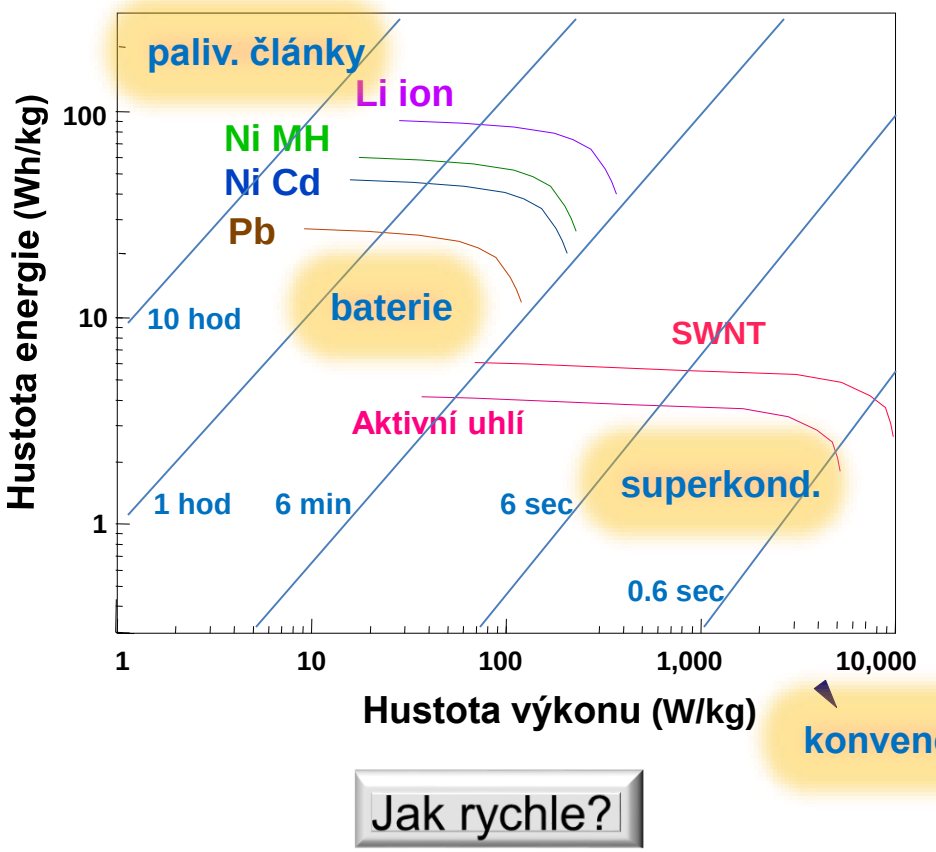
Smíšený (kapalný) elektrolyt



Pevný elektrolyt



David V. Ragone
rektor CWR Uni, 1988

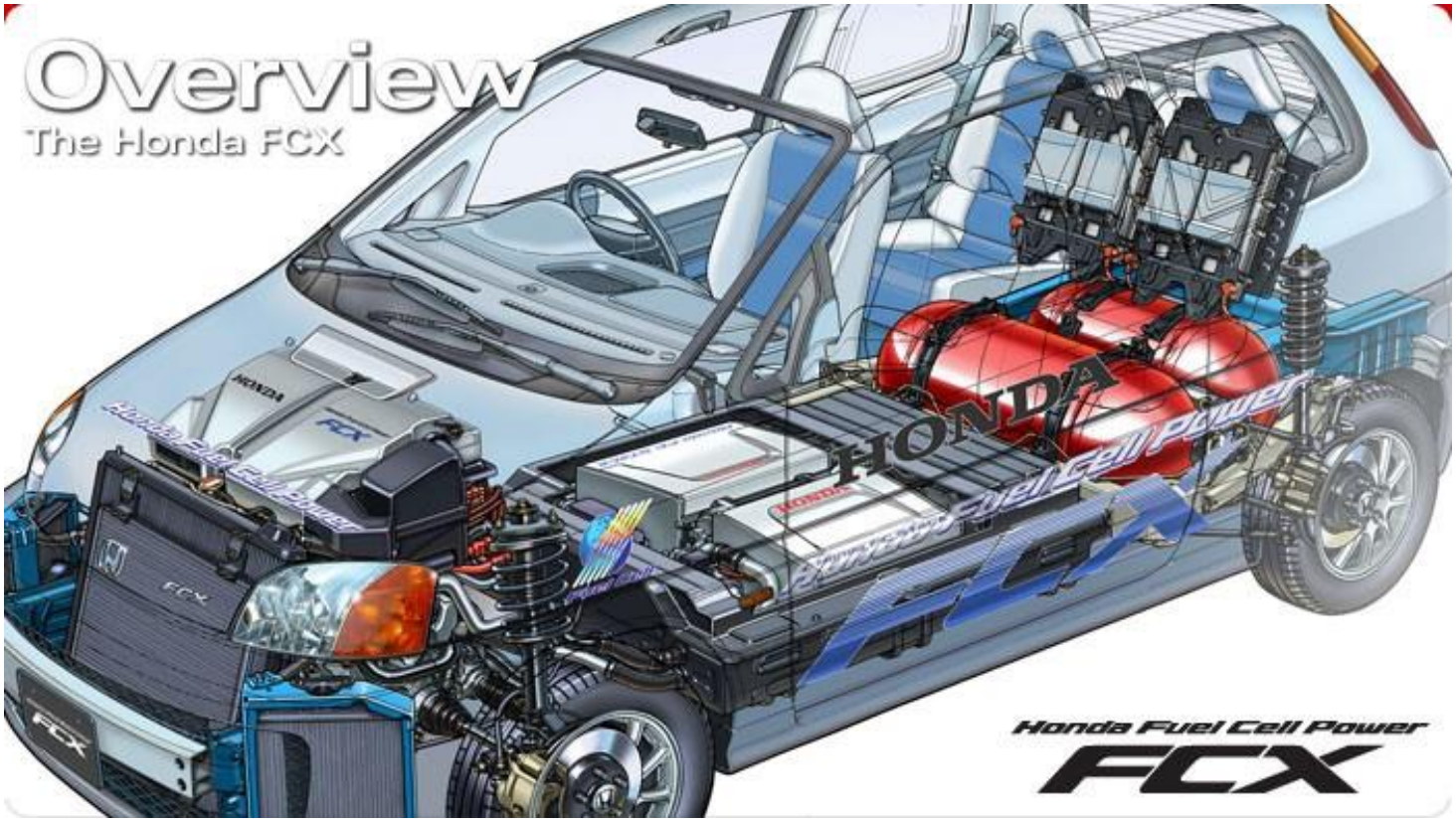


Hustota energie: U.I.t/m

Hustota výkonu: U.I/m

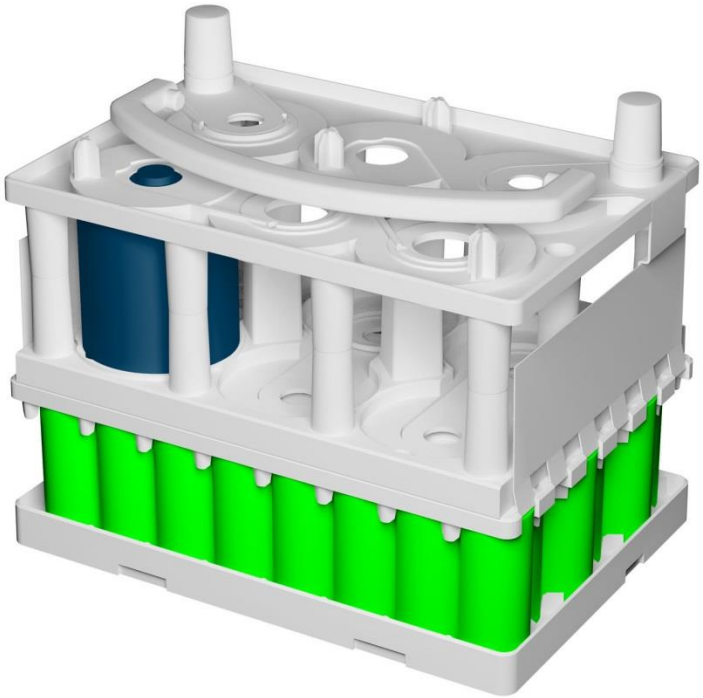
Užitečné schema pro libovolné zařízení:
Vertikální osa: Kolik energie lze uložit
Horizontální osa: Jak rychle lze uloženou energii uvolnit

Honda elektromobil: paliv. článek + superkondenzátor



Energie je krátkodobě ukládána v superkondenzátoru
Během brždění: nabíjení
Akcelerace: vybíjení

1) CZ firmy na trhu Li-baterií

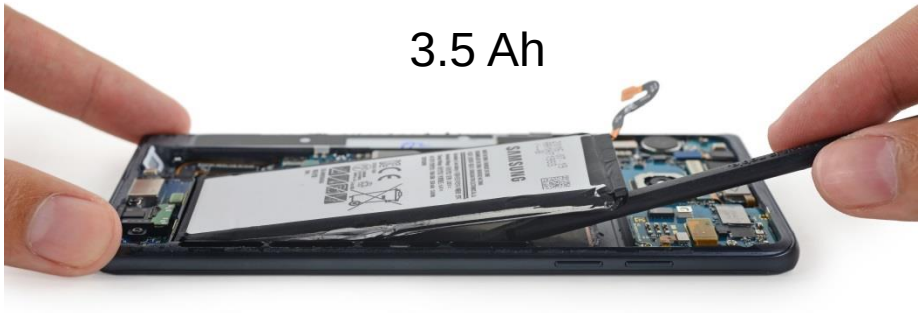


supercapacitor

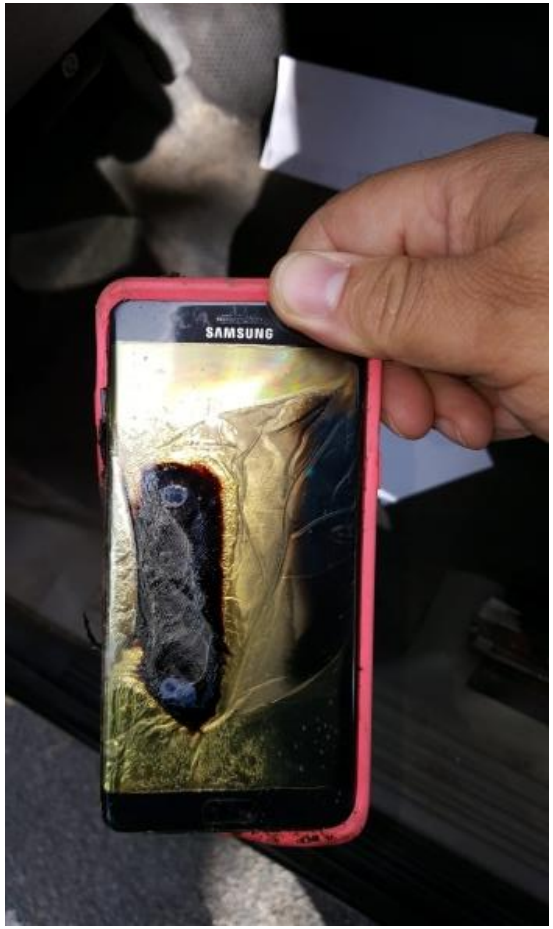
Li-ion battery ($LiFePO_4$)

Zdroj: http://www.olife-energy.com/

Bezpečnost Li-ion baterií



Sony batterie: Dell-notebook



Samsung Galaxy Note 7

2) CZ firmy na trhu Li-baterií

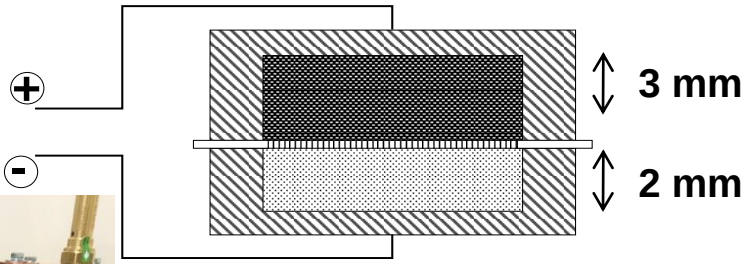
HIGH ENERGY 3D ACCUMULATOR

HE3DA

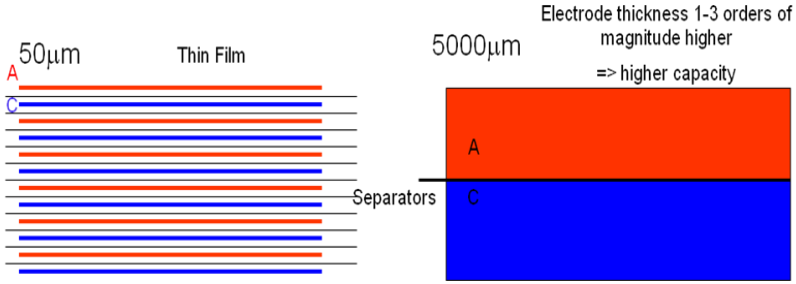
Bringing future closer

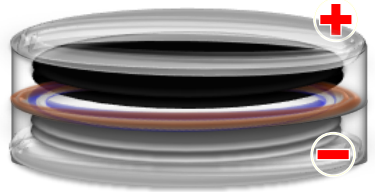
1 kWh; 12 V 90 Ah, HE3DA battery

LCMS ($LiCo_{0.1}Mn_{1.9}O_4$)
4.1 V; 90 Ah/kg



LTO ($Li_4Ti_5O_{12}$)
1.5 V; 170 Ah/kg





Nové výzvy: Na-ion

Katoda: uhlík, grafen

Anoda: Na_2FePO_4F, Li_2FePO_4F, $NaVPO_4F$, LTO…

slitinové anode: Na_3Sb, Na_3Sn and Na_3P…

Na/S baterie, ZEBRA: $Na/NiCl_2$

Zeolite battery research Africa, Pretoria

Další možnosti (teoreticky): Mg^{2+}, Al^{3+}

ALE: Potřebujeme opravdu nahradit Li?

Světové zásoby Li….. **14-40 Mio tun** (bez oceánů)

Zásoby pod Cínovcem.. 1 Mio tuny?

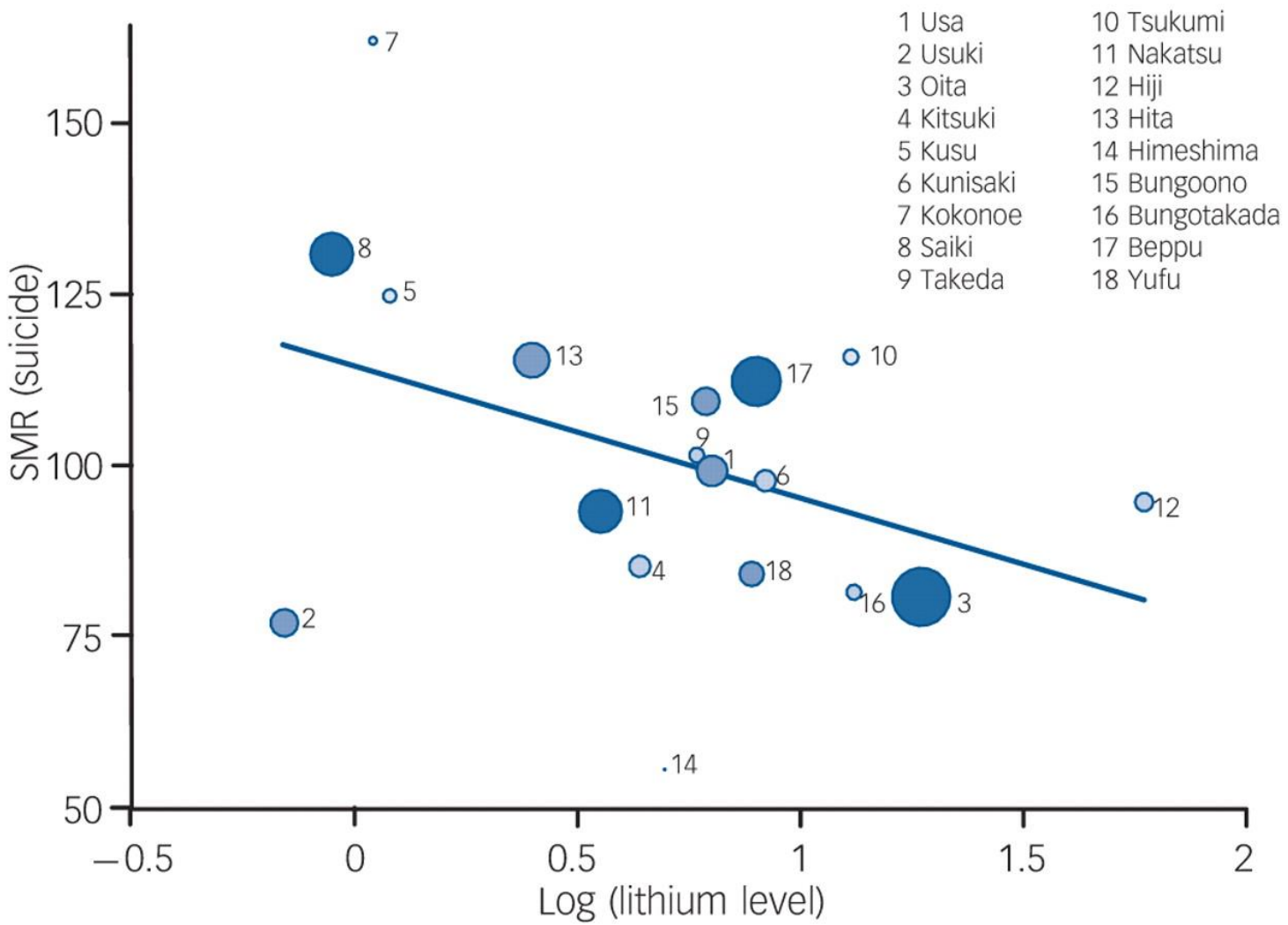
≈ 240 TWh ≈ 1 % světové spotř. elektřiny

Tesla S Model: 85 kWh; 14 kg Li => 3 mld vozů

Nissan Leaf: 24 kWh; 4 kg Li => 10 mld vozů

(celkově na světě ca. 1 mld. automobilů)


Děkuji za pozornost



SMR: standard mortality rate, %
Velikost bodu – velikost populace

The British Journal of Psychiatry 2009, 194 (5) 464-465.

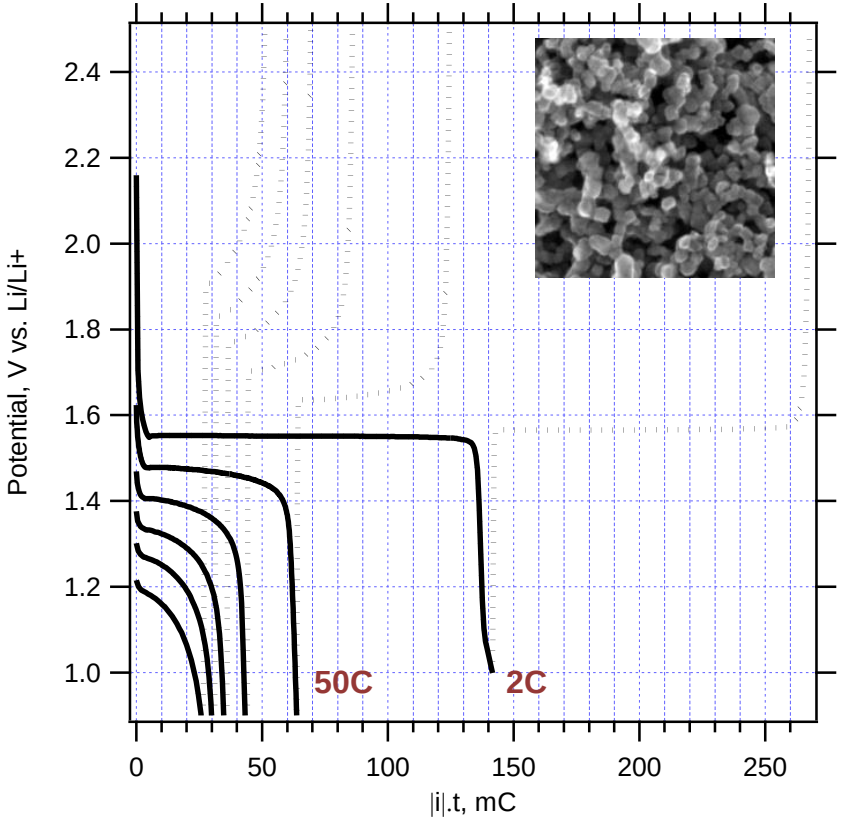
1) Nanotechnologie & Li-ion bat.

$Li_4Ti_5O_{12}$ (spinel): nabíjení/vybíjení

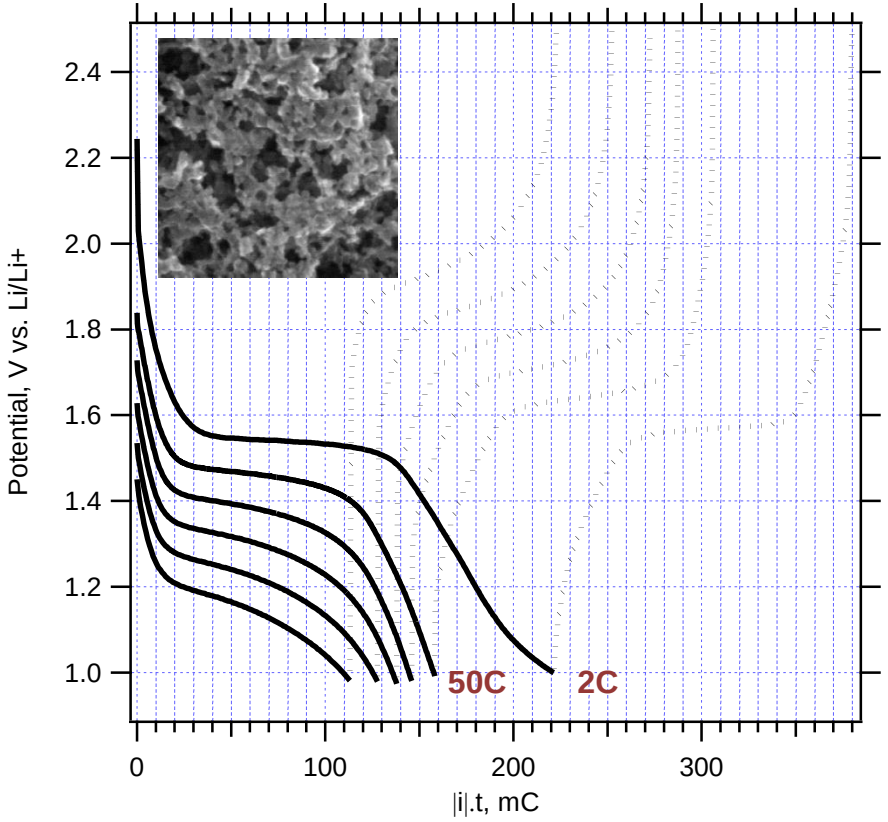
Rychlost (proud):

2C, 50C, 100C, 150C, 200C, 250C

$$Li_4Ti_5O_{12} + (3e^- + 3Li^+) \rightarrow Li_7Ti_5O_{12}$$



- **Komerční materiál (∅ ≈ 1 μm)**



- **nanomateriál (∅ ≈ 10 nm)**