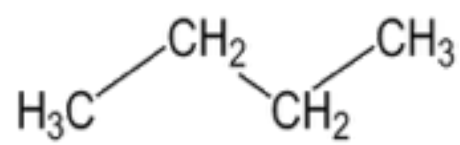

$$+ \; n\, O_2 = m\, CO_2 + p\, H_2O$$

$$+ \; \mathbf{Q}$$

тепло

↓

свет

?

Электрохимические накопители энергии

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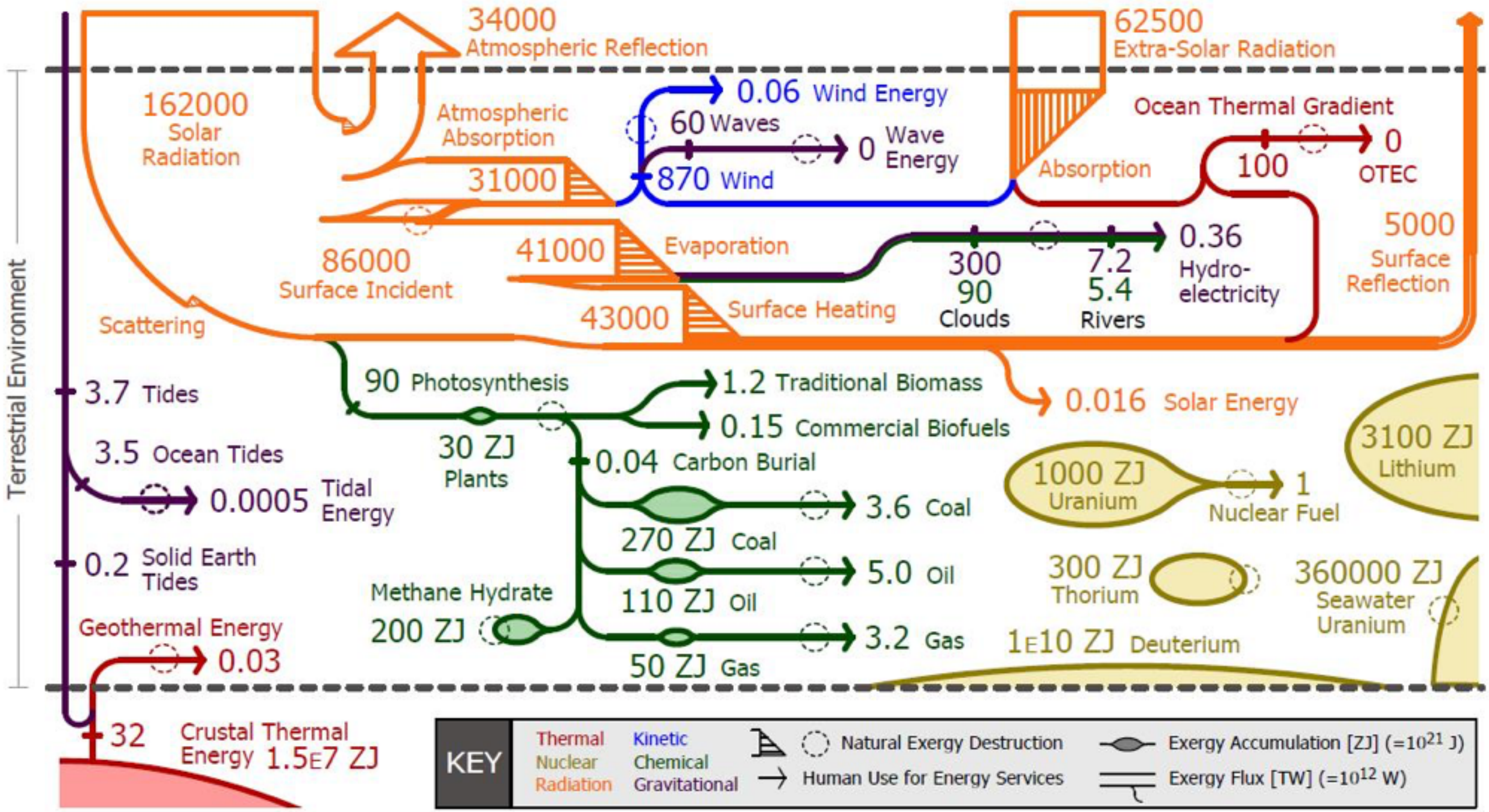
Химический факультет
Московский государственный университет имени М.В.Ломоносова

16 июля 2017
Сочи



Источник: Global Climate and Energy Project, http://gcep.stanford.edu

Зачем вообще нужны накопители энергии?

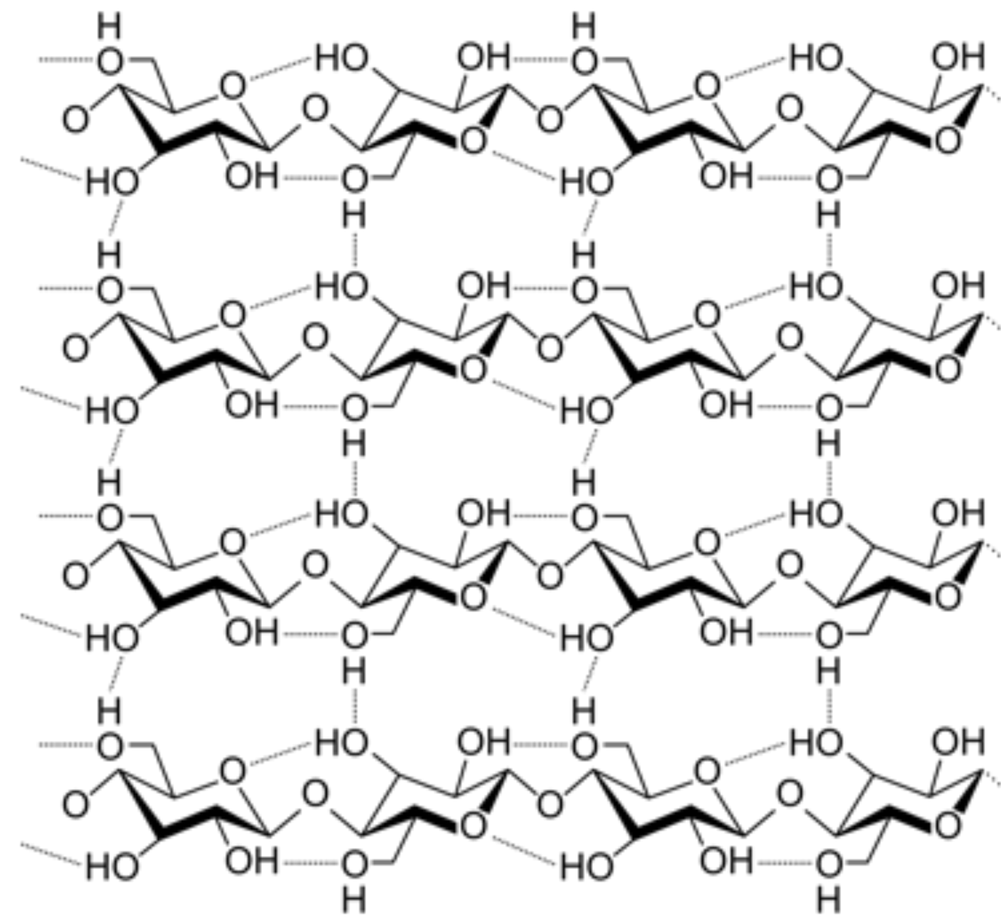
Транспортировка энергии

- портативные устройства
- транспорт

Баланс выработки/потребления

- при неравномерной выработке – например, альтернативные источники энергии
- при неравномерном потреблении – например, атомные электростанции

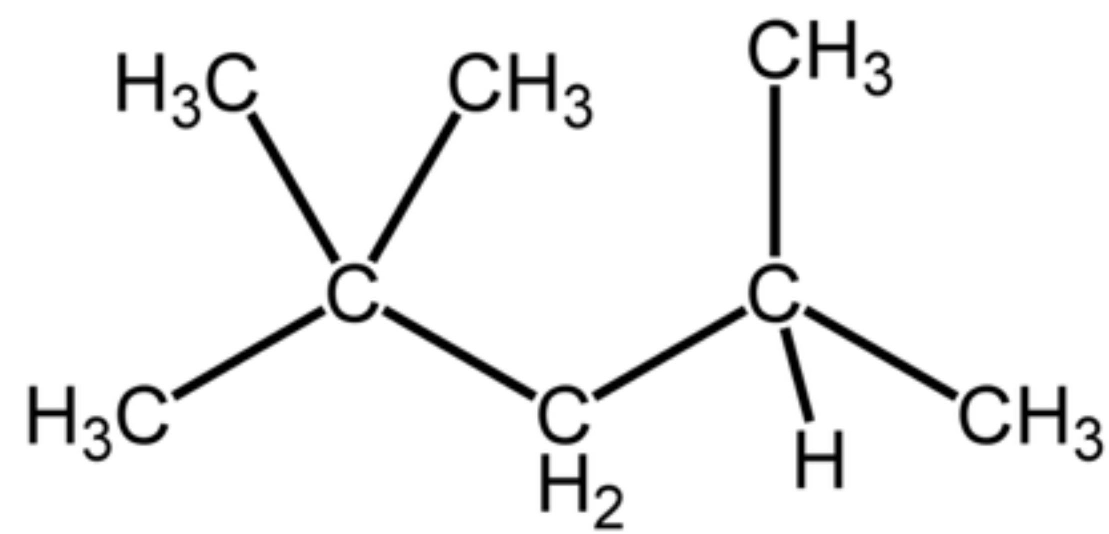
Накопители энергии



$+ \; n \, O_2 = m \, CO_2 + p \, H_2O + \mathbf{Q}$

3.5 кВт·ч / кг

Накопители энергии



$+\ n\ O_2 = m\ CO_2 + p\ H_2O +$ **Q**

10 – 12 кВт·ч / кг

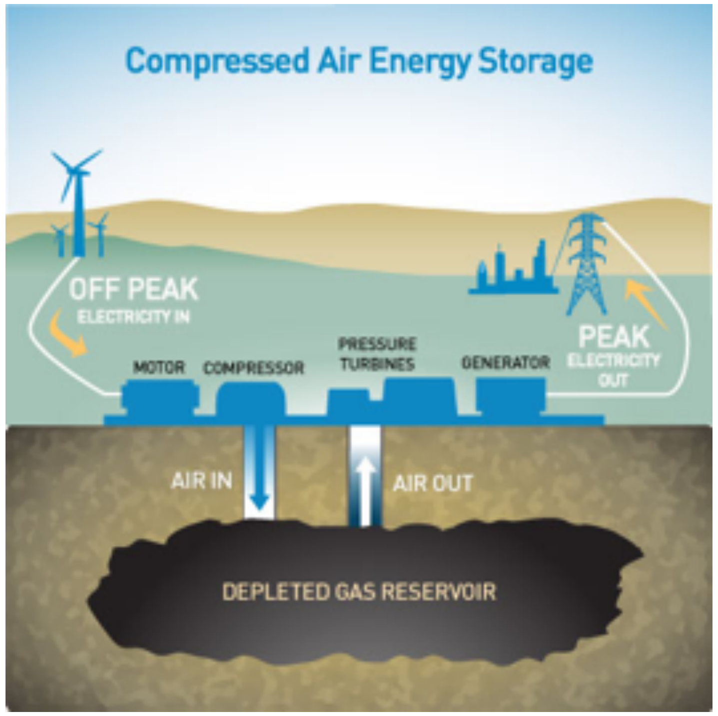
Накопите ли?

~ 10 – 100 лет

~ 10 – 100 млн. лет

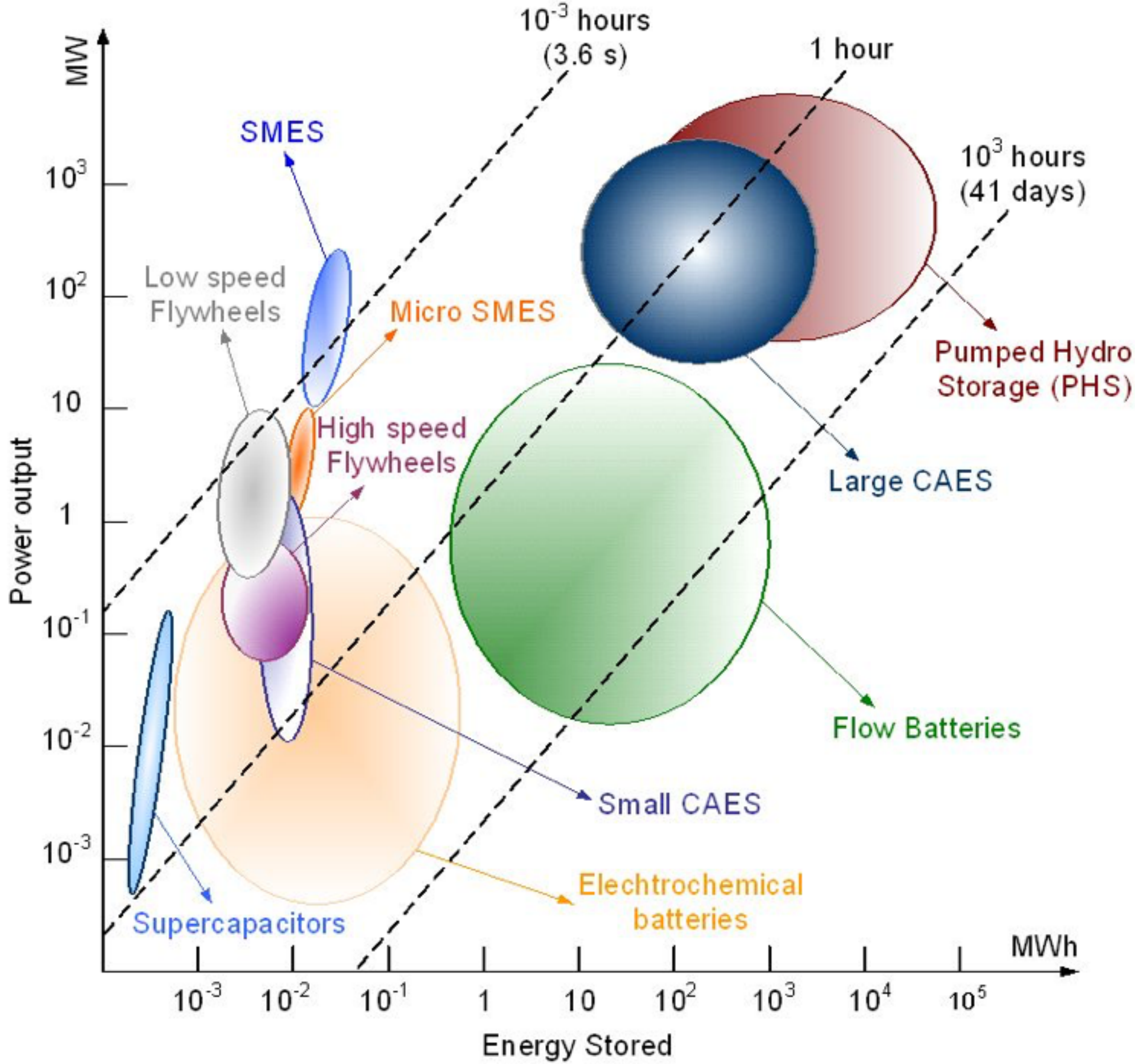
“Нехимические” накопители энергии

Гидроаккумуляторы

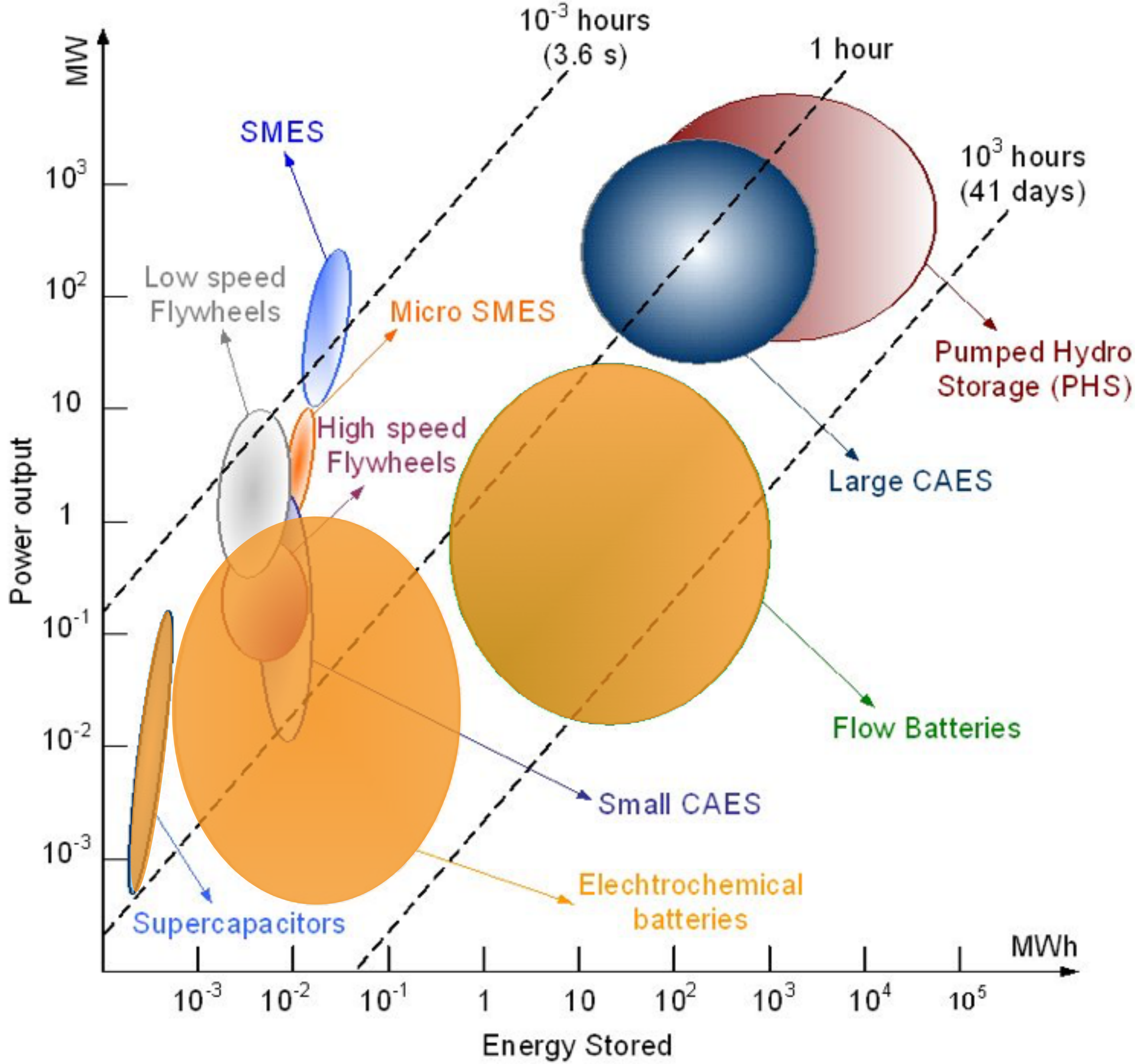


Хранилища сжатого воздуха

Маховики



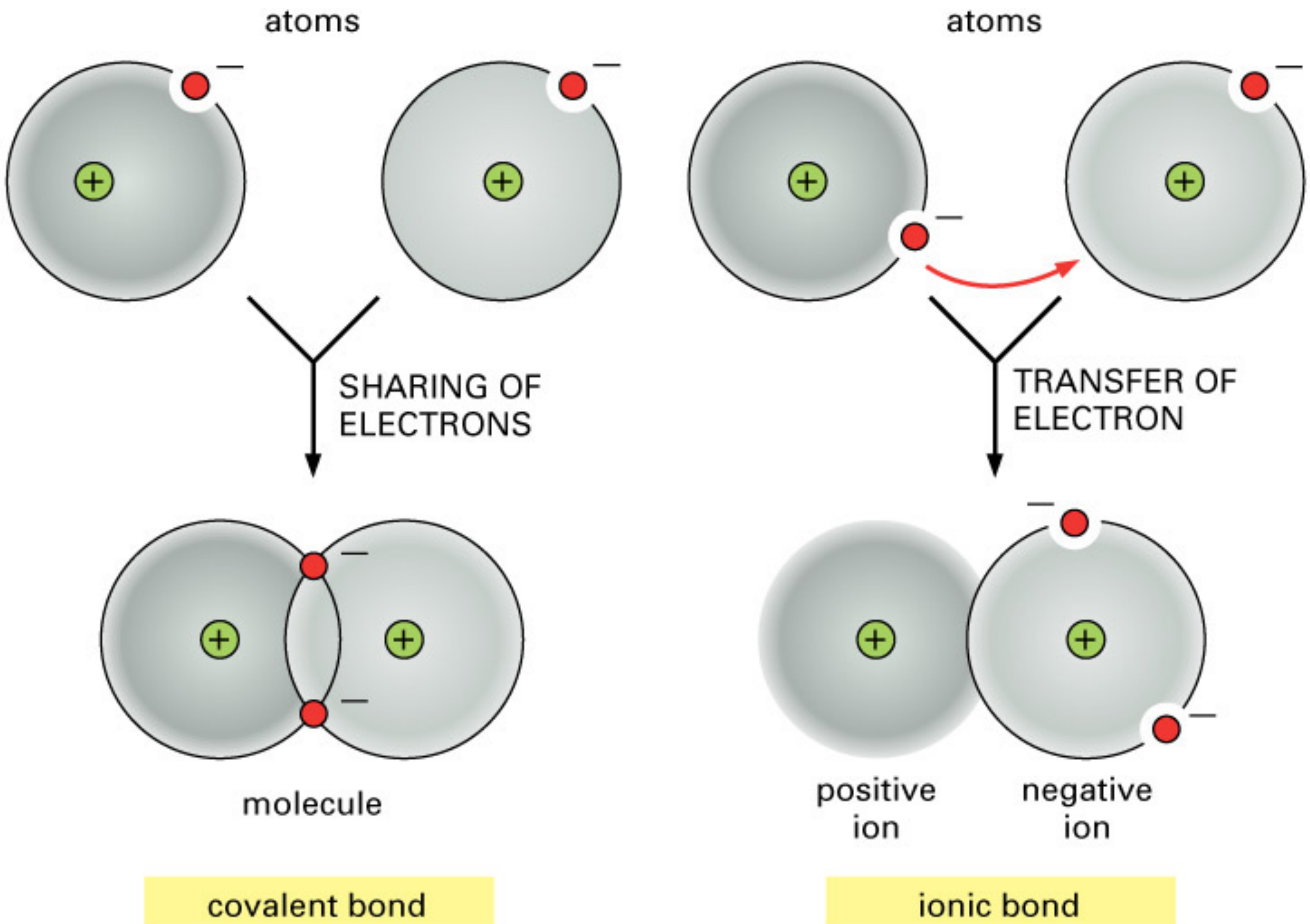
Energy Storage - Technologies and Applications, ed. by A.Zobaa, 2013



Energy Storage - Technologies and Applications, ed. by A.Zobaa, 2013

План

- Что такое электрохимические накопители? Их основные характеристики
- От свинцово-кислотных к литий-ионным аккумуляторам
- Новые поколения металл-ионных аккумуляторов
- Пост-литий-ионные технологии: литий-сера и литий-воздух
- Проточные батареи (redox flow batteries)
- Суперконденсаторы

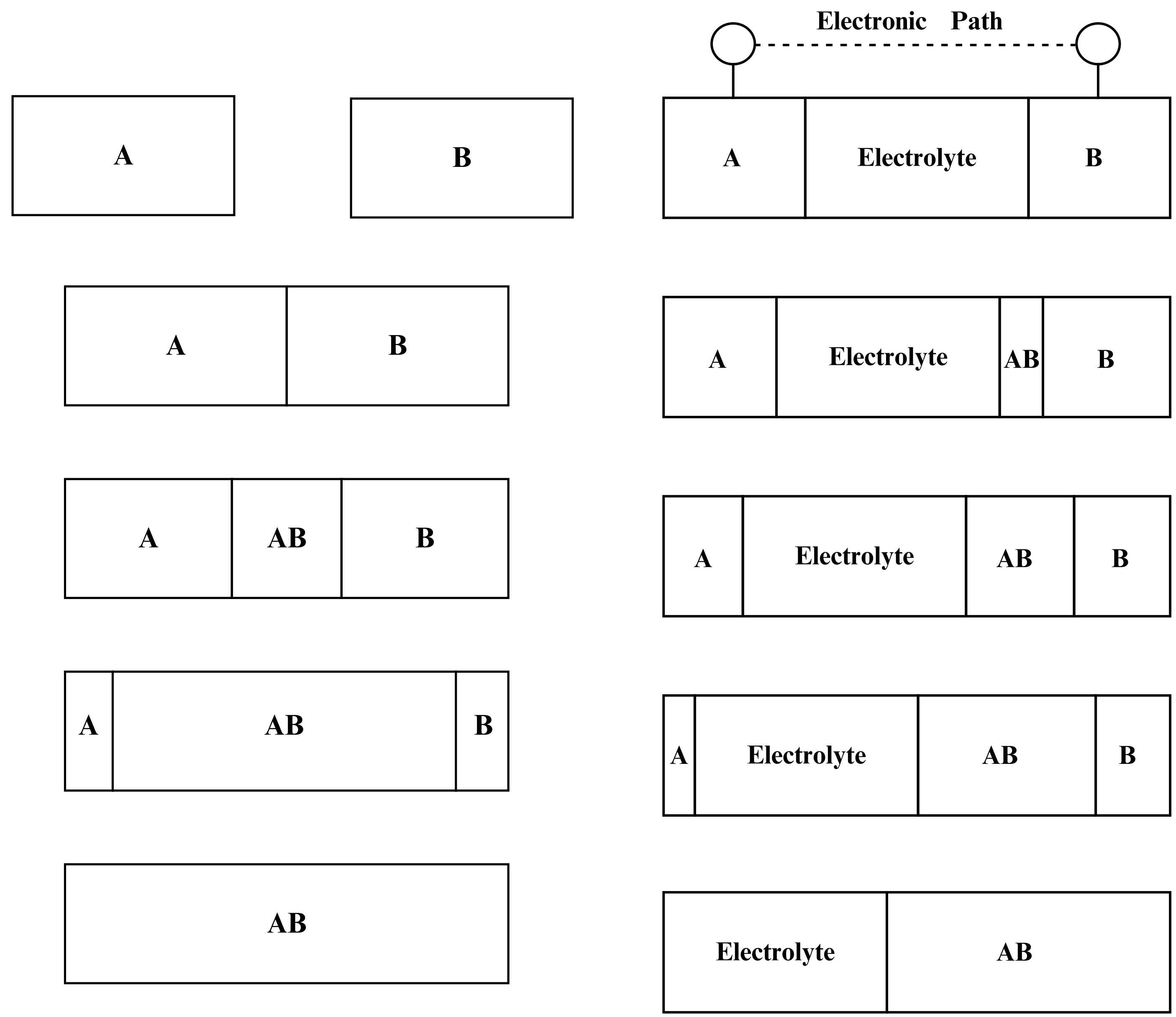

atoms
SHARING OF ELECTRONS
molecule
covalent bond
atoms
TRANSFER OF ELECTRON
positive ion
negative ion
ionic bond

A + B = AB

$$\Delta G_r^\circ = \sum \Delta G_f^\circ(products) - \sum \Delta G_f^\circ(reactants)$$

0.05 %

1%



3%

15%

Advanced batteries, ed. by R.Huggins, 2009

$$\Delta G_r^\circ = -zFE$$

Химические источники тока

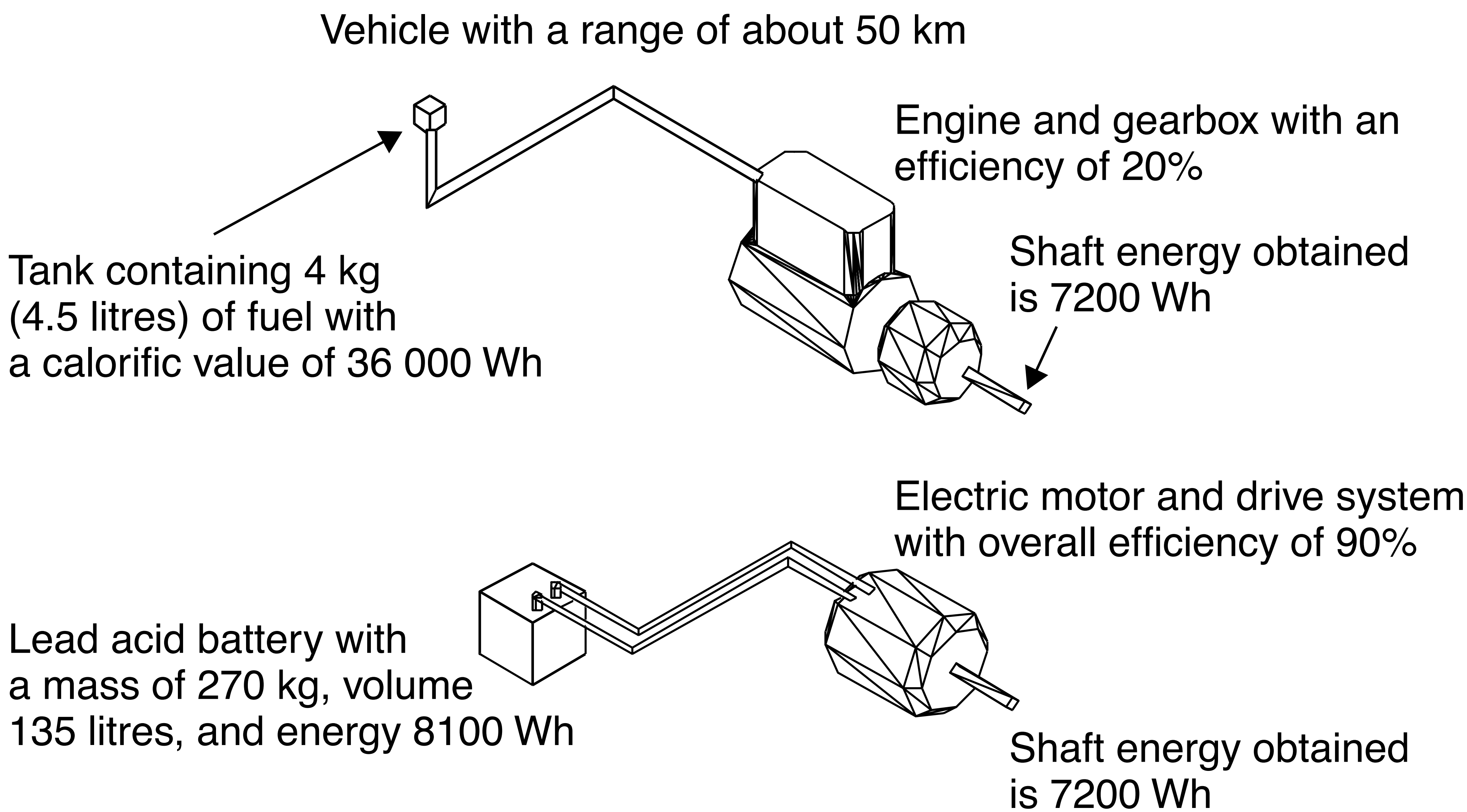
“накопители”

- **Батарейки**
  - первичные (гальванические элементы)
  - вторичные (аккумуляторы)
  - проточные батареи
- **Суперконденсаторы**

“преобразователи”

- топливные элементы

Энергоэффективность электрических систем



Electric Vehicle Technology Explained by J.Larminie and J.Lowry, John Willey&Sons, 2010

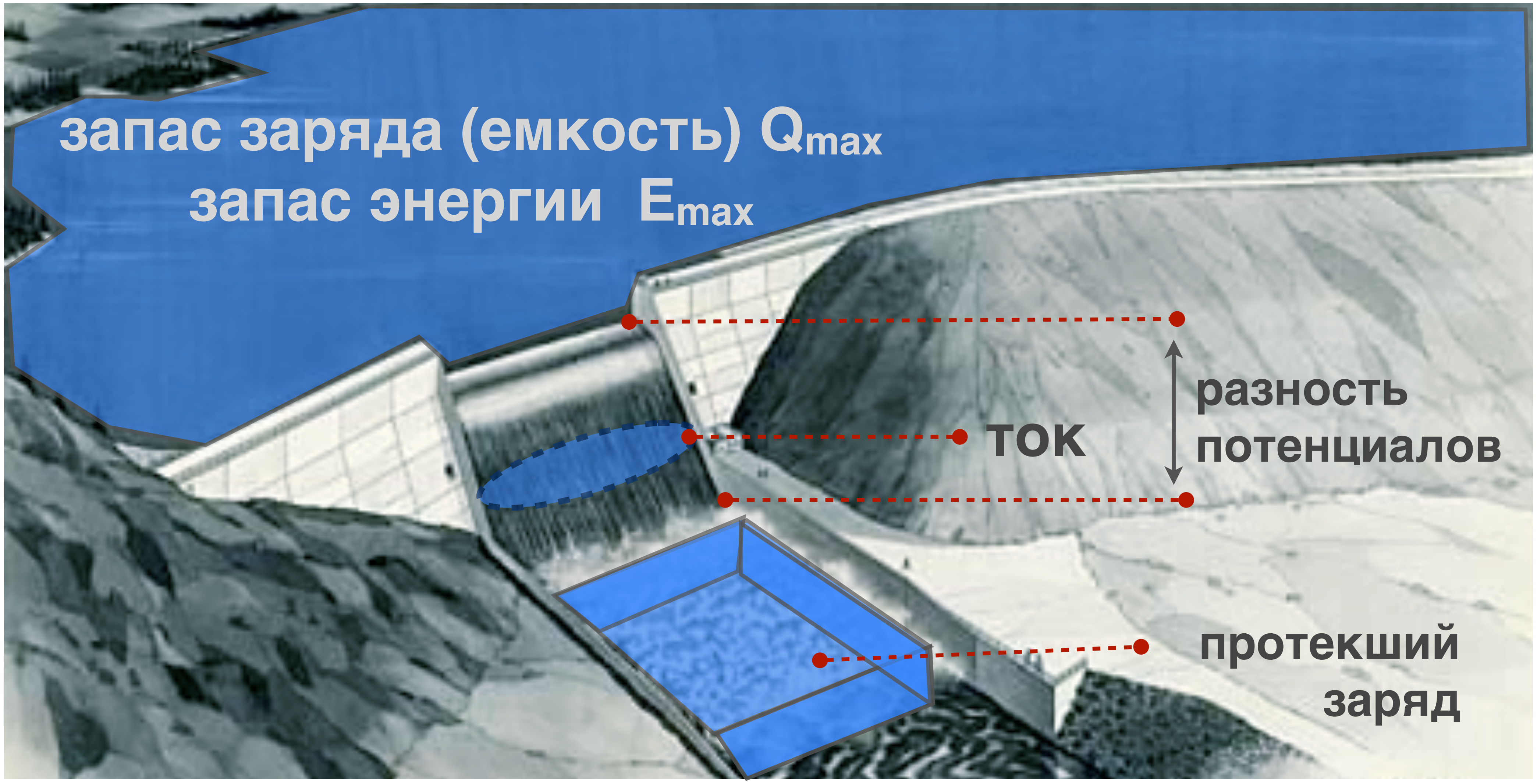
La Jamais Contente

1899 год, Франция

- 2 электромотора (общая мощность 50 кВт)
- 200 Pb-PbO_2 ячеек
- Масса 1450 кг
- Масса аккумулятора > 700 кг
- Максимальная скорость 106 км/ч

Напряжение U [В]
Заряд Q [Кл] = $I \cdot t$
Отдаваемый ток I [А] / Мощность P [Вт]

Работа A [Дж] = $P \cdot t = U \cdot I \cdot t = Q \cdot U$



Свинцово-кислотный аккумулятор

$PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

$Pb - 2e^- + HSO_4^- \rightarrow PbSO_4 + H^+$

$$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$

1 моль 239 г **1 моль 207 г** **2 моль 196 г**

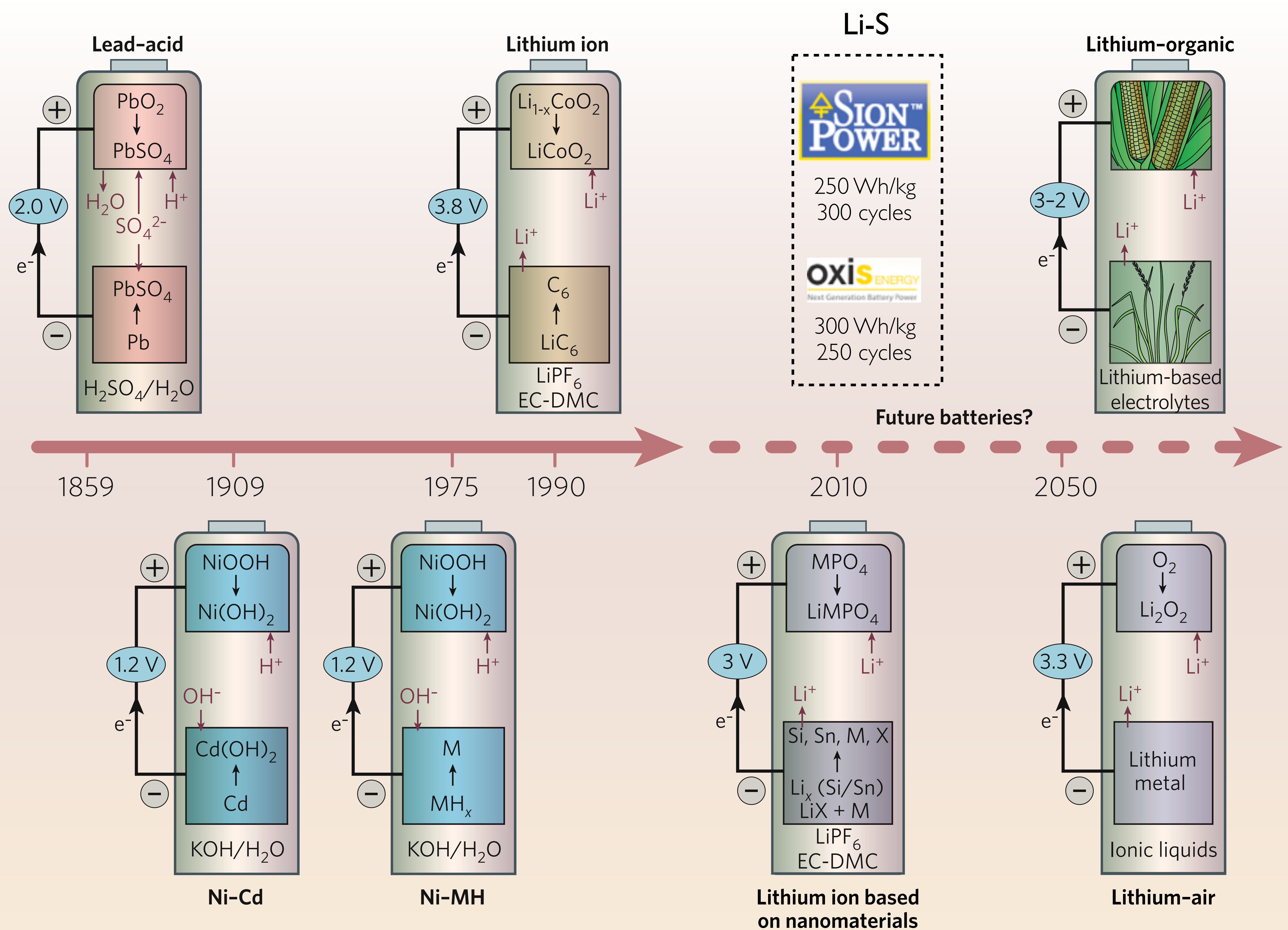
642 г

2 моль e^-
$2 \cdot N_A \cdot e$ =
= 193 кКл (кА·с) =
= 53.6 А·ч

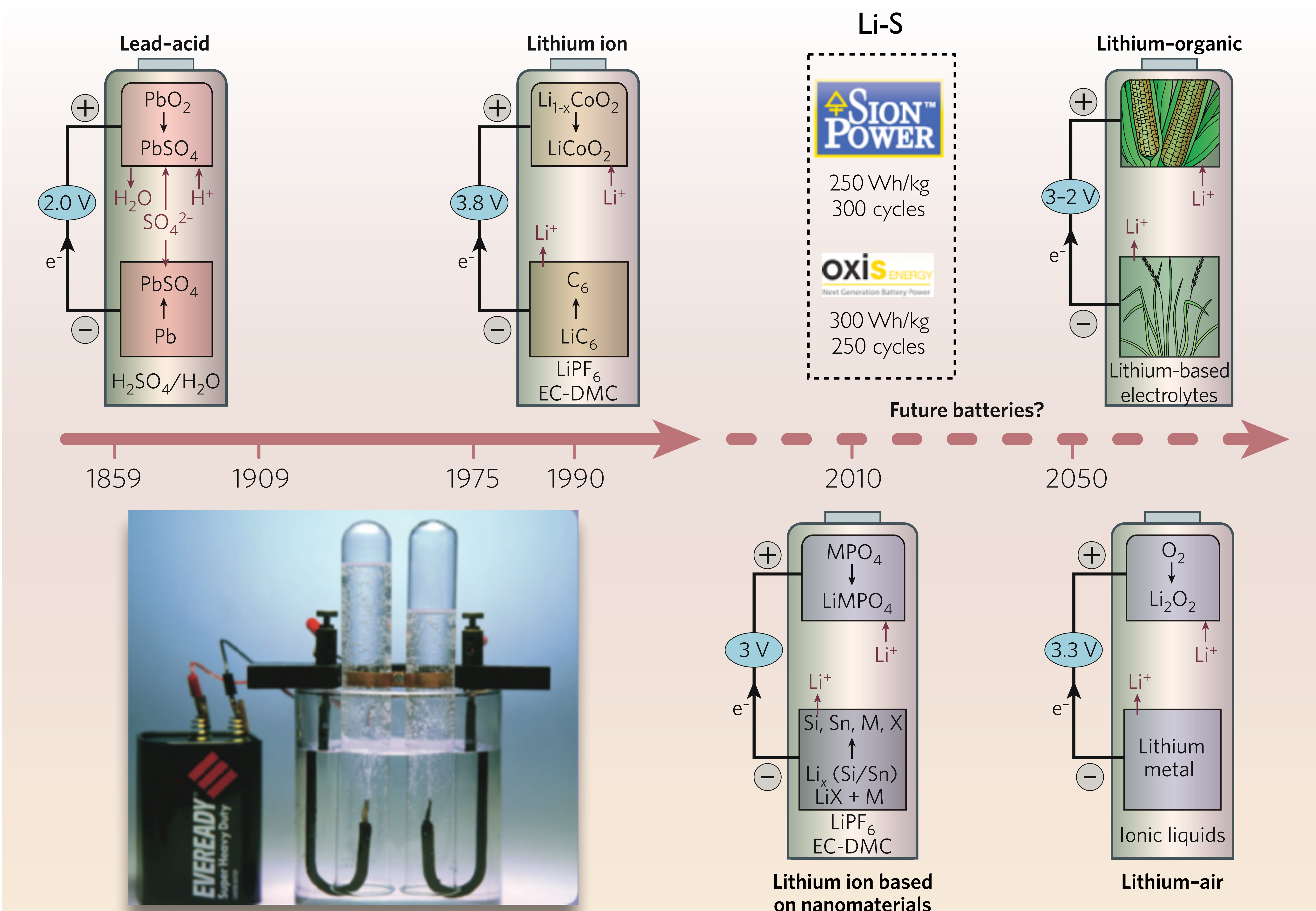
30 – 40 Вт ч/кг

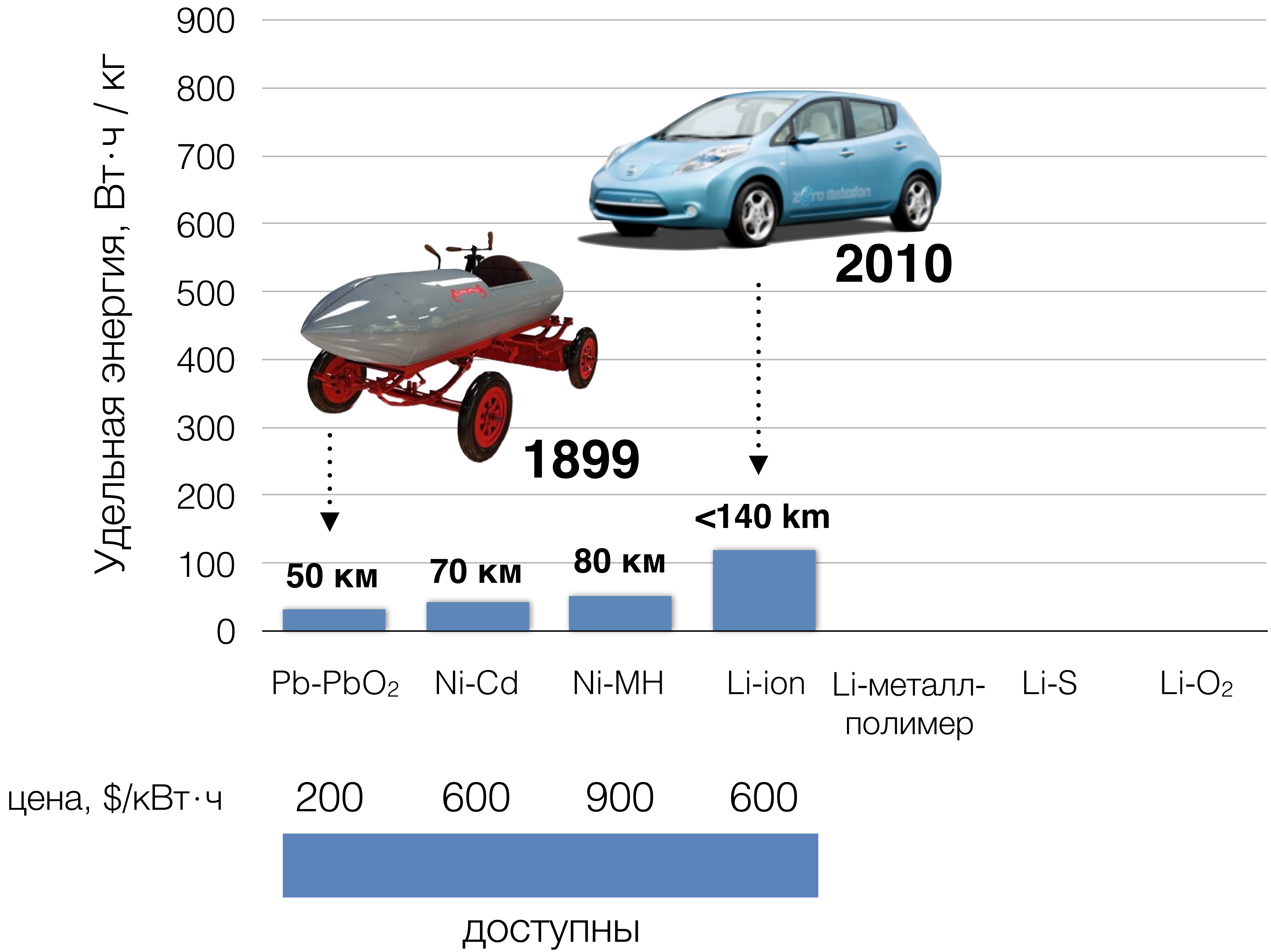
≈ 170 Вт·ч / кг

Свинцово-кислотный аккумулятор изнутри

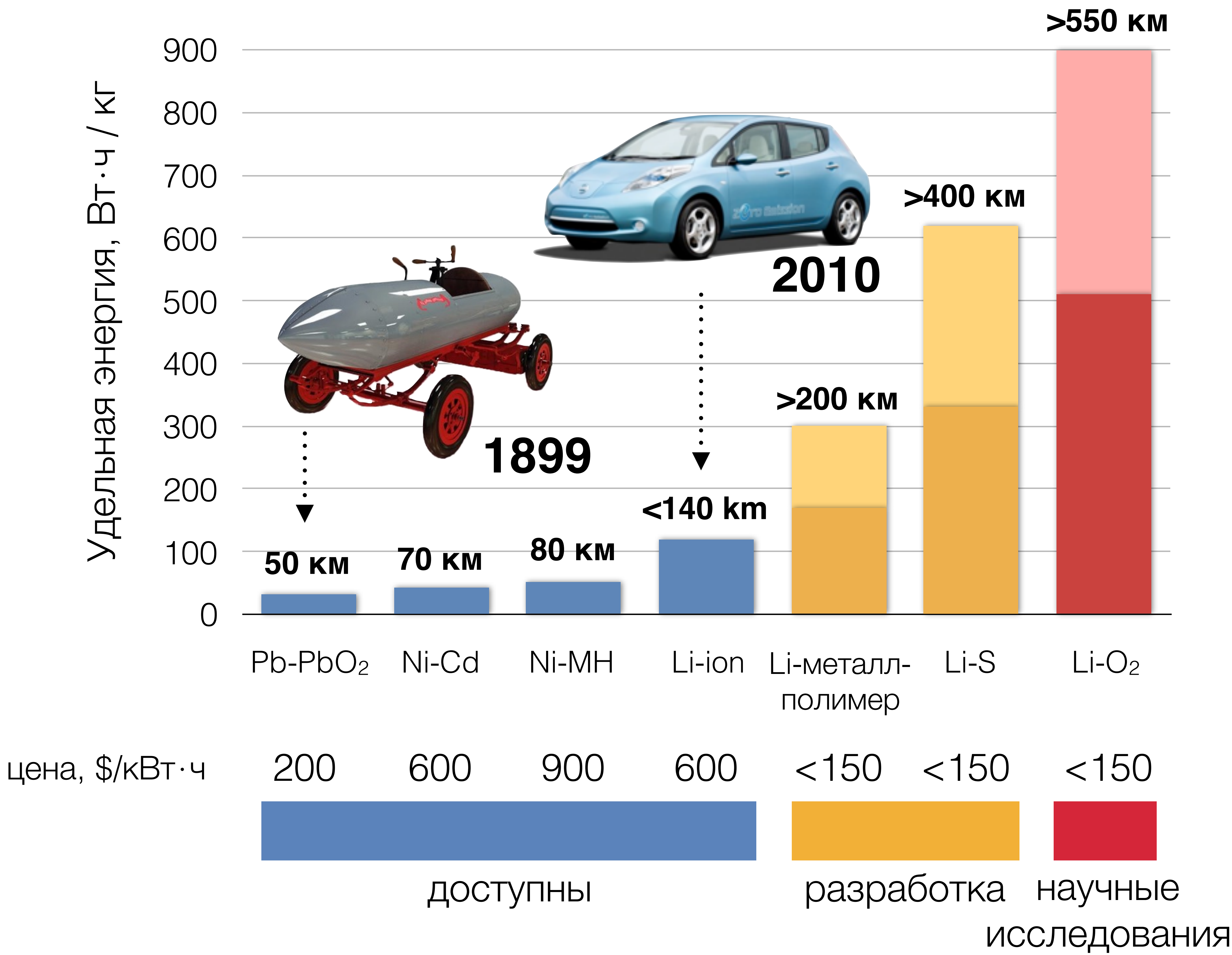


Lead-acid
PbO_2
$PbSO_4$
H_2O
H^+
SO_4^{2-}
2.0 V
e⁻
$PbSO_4$
Pb
H_2SO_4/H_2O
Lithium ion
$Li_{1-x}CoO_2$
$LiCoO_2$
Li^+
3.8 V
C_6
LiC_6
$LiPF_6$
EC-DMC
Li-S
SION POWER
250 Wh/kg
300 cycles
OXIS ENERGY
Next Generation Battery Power
300 Wh/kg
250 cycles
Lithium-organic
3-2 V
Lithium-based electrolytes
Future batteries?
1859
1909
1975
1990
2010
2050
NiOOH
$Ni(OH)_2$
H^+
1.2 V
OH^-
$Cd(OH)_2$
Cd
KOH/H_2O
Ni-Cd
NiOOH
$Ni(OH)_2$
1.2 V
M
MH_x
KOH/H_2O
Ni-MH
MPO_4
$LiMPO_4$
3 V
Si, Sn, M, X
Li_x (Si/Sn)
LiX + M
$LiPF_6$
EC-DMC
Lithium ion based on nanomaterials
O_2
Li_2O_2
3.3 V
Lithium metal
Ionic liquids
Lithium-air


Lead-acid
PbO2
PbSO4
H2O
H+
SO4 2-
PbSO4
Pb
H2SO4/H2O
2.0 V
e-
Lithium ion
Li1-xCoO2
LiCoO2
Li+
Li+
C6
LiC6
LiPF6
EC-DMC
3.8 V
e-
Li-S
SION POWER
250 Wh/kg
300 cycles
oxis ENERGY
300 Wh/kg
250 cycles
Lithium-organic
3-2 V
Li+
Li+
e-
Lithium-based electrolytes
Future batteries?
1859
1909
1975
1990
2010
2050
EVEREADY
MPO4
LiMPO4
3 V
Li+
Li+
e-
Si, Sn, M, X
Lix (Si/Sn)
LiX + M
LiPF6
EC-DMC
Lithium ion based on nanomaterials
O2
Li2O2
3.3 V
Li+
Li+
e-
Lithium metal
Ionic liquids
Lithium-air



* данные из P.G.Bruce et al. Li-O_2 and Li-S batteries with high energy storage // *Nature Materials* **11** 19-29 (2012)



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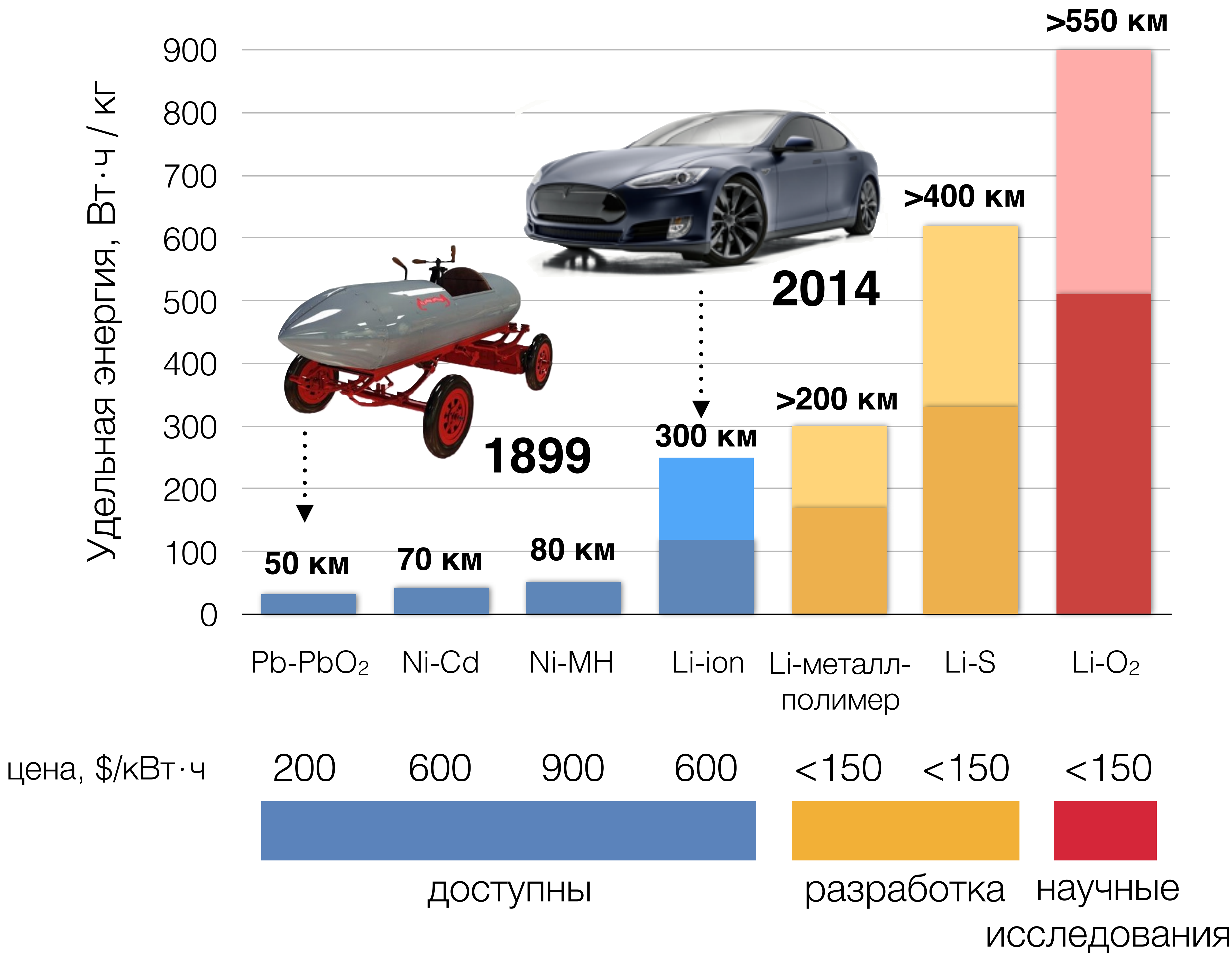


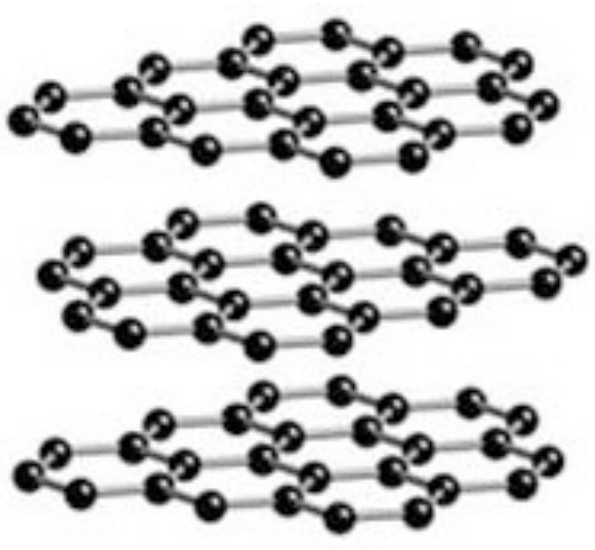
* данные из P.G.Bruce et al. Li-O_2 and Li-S batteries with high energy storage // *Nature Materials* **11** 19-29 (2012)

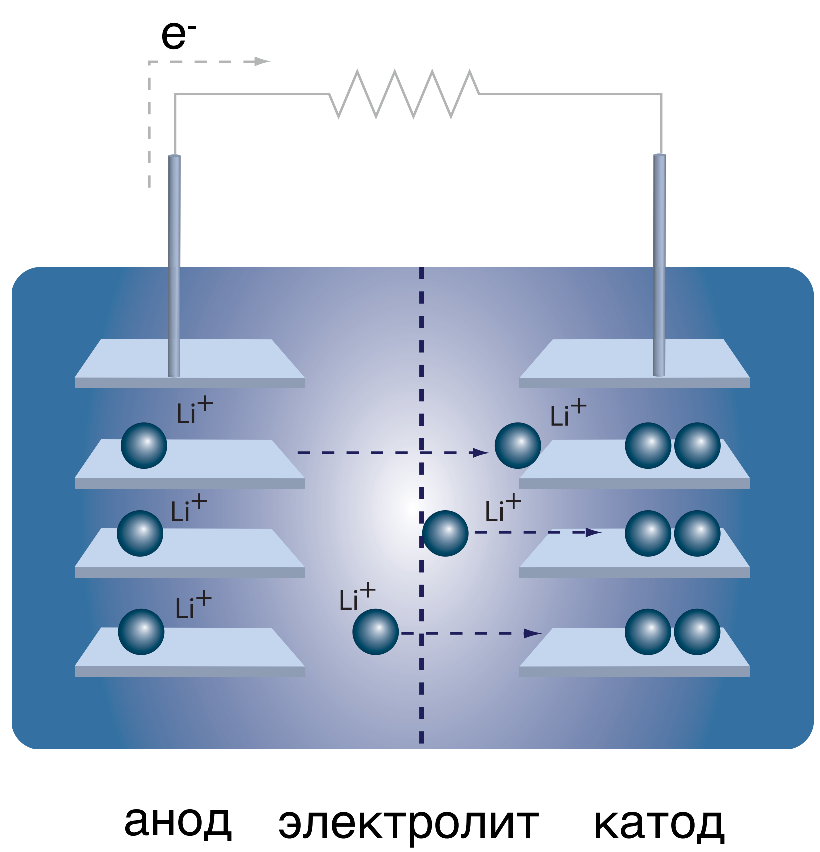
Tesla Model S

- Электромотор 310 кВт
- Литий-ионный аккумулятор 85 кВт·ч
- Общая масса 2100 кг
- Масса 550 кг

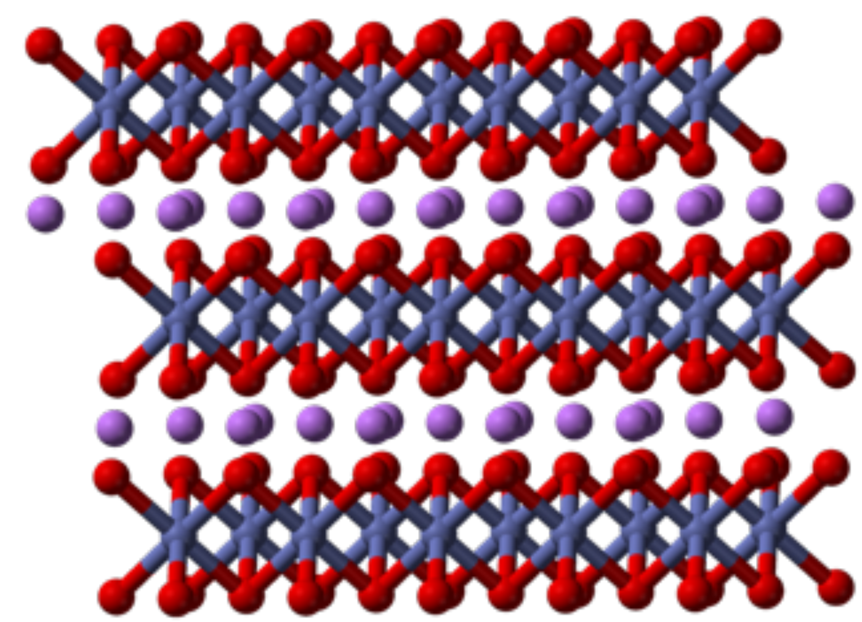
Литий-ионный аккумулятор

графит





$LiCoO_2$

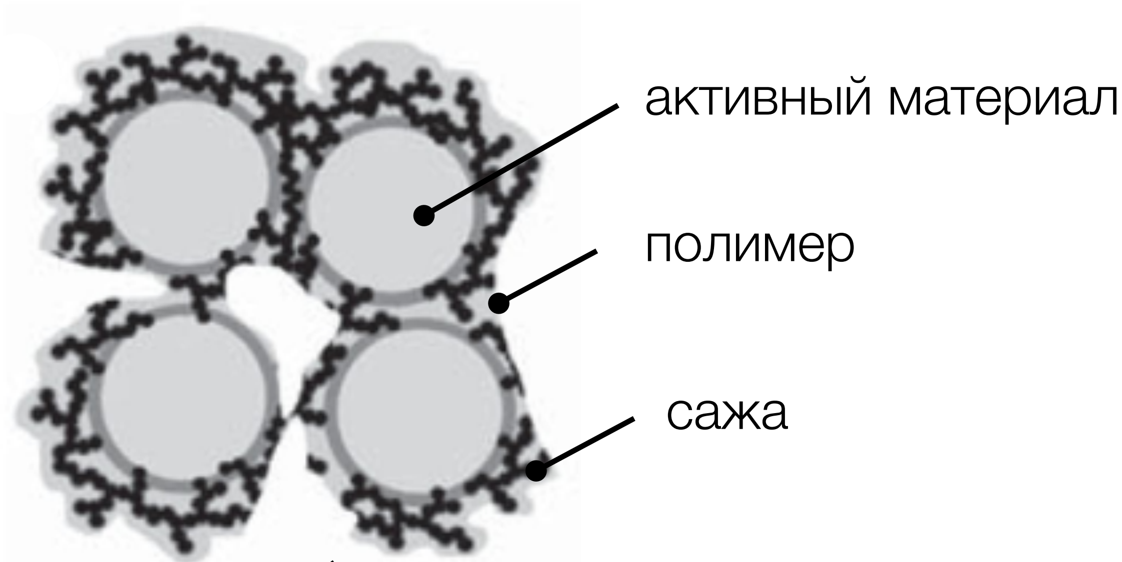


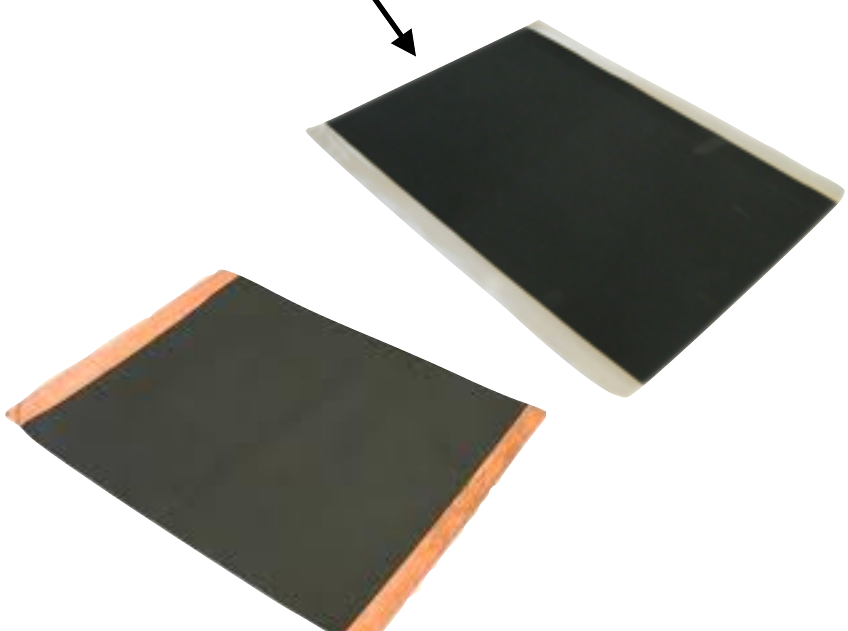
$C_6 + xLi^+ \leftrightharpoons Li_xC_6 + e^-$

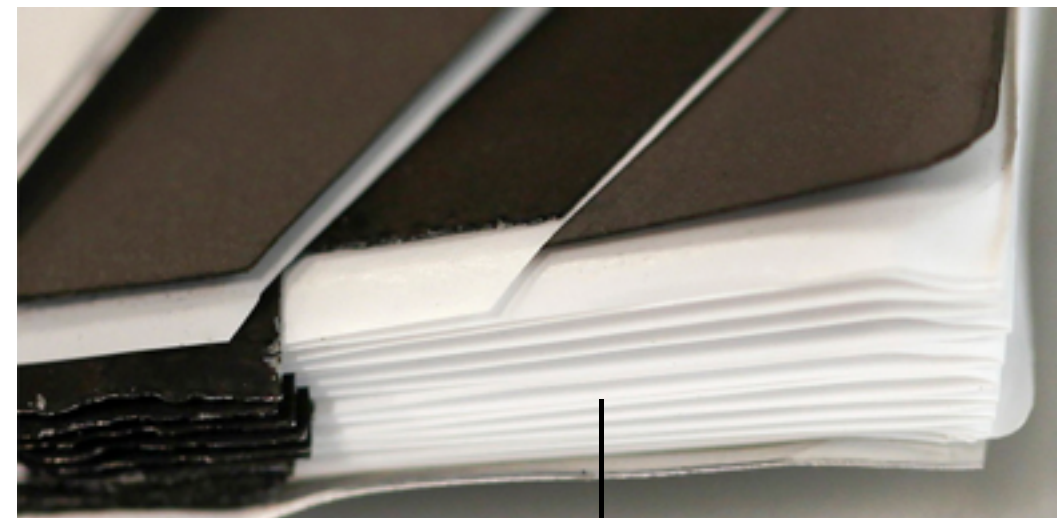
$LiCoO_2 \leftrightharpoons Li_{1-x}CoO_2 + xLi^+ + xe^-$

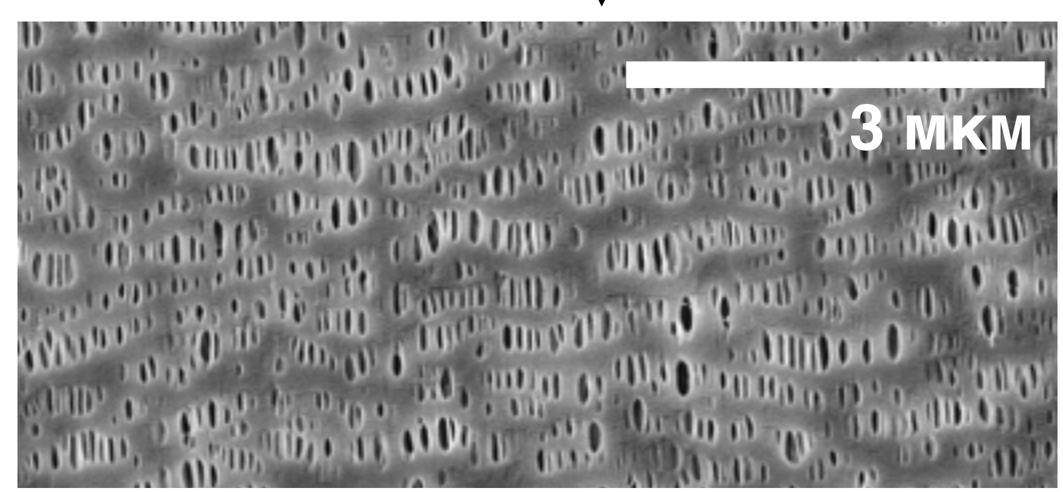
$\approx$ **600 · *x* Вт · ч / кг**$_{\text{теор.}}$

Литий-ионный аккумулятор в реальности

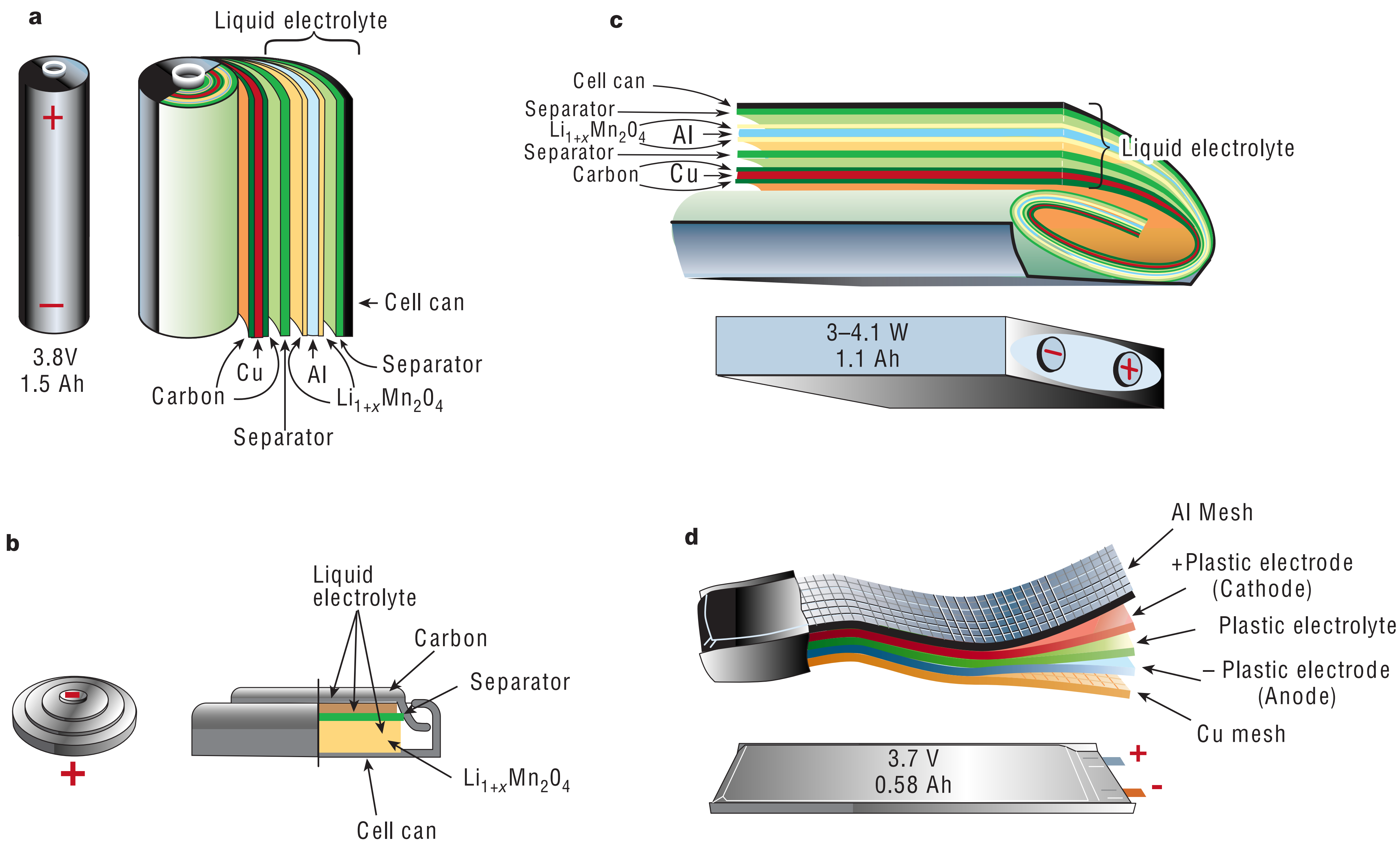




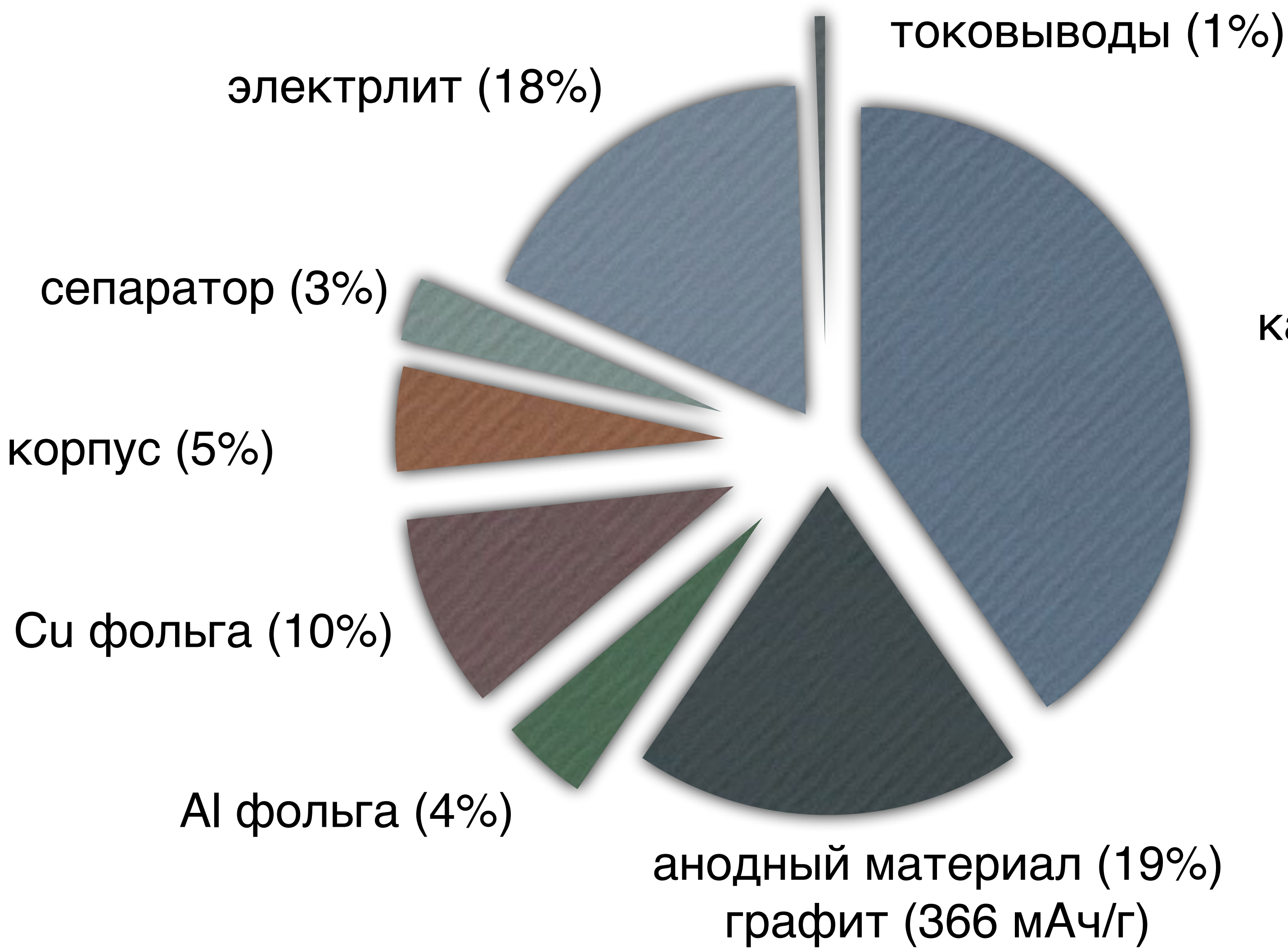




Литий-ионный аккумулятор в реальности



Литий-ионный аккумулятор в реальности

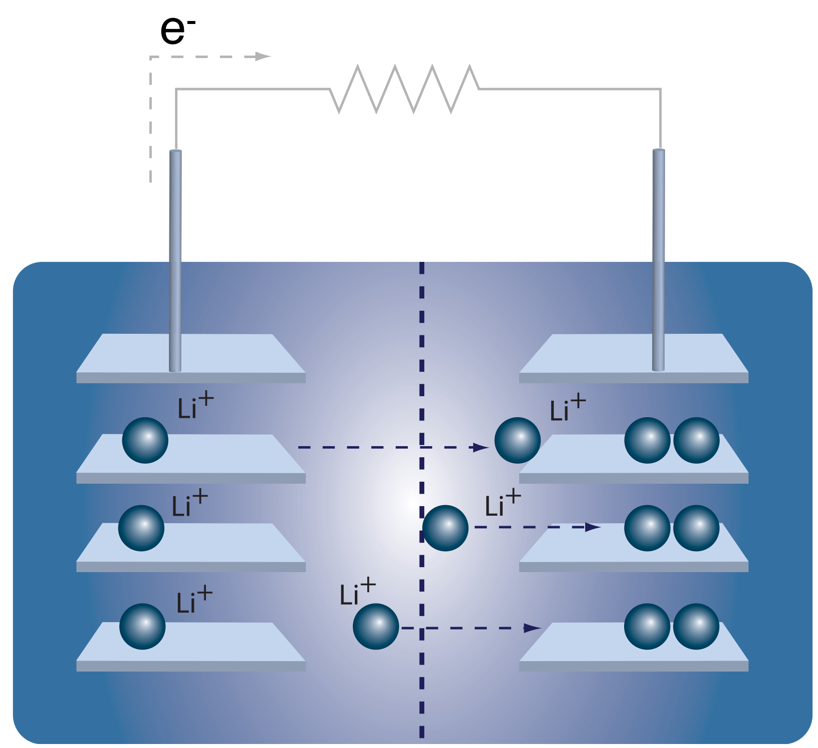


220 - 240 Вт·ч/кг

графит
(0.3 Ач на 1 г LiC_6)

выше емкость
нано-Si
(2.0 Ач на 1 г $Li_{4.4}Si$)

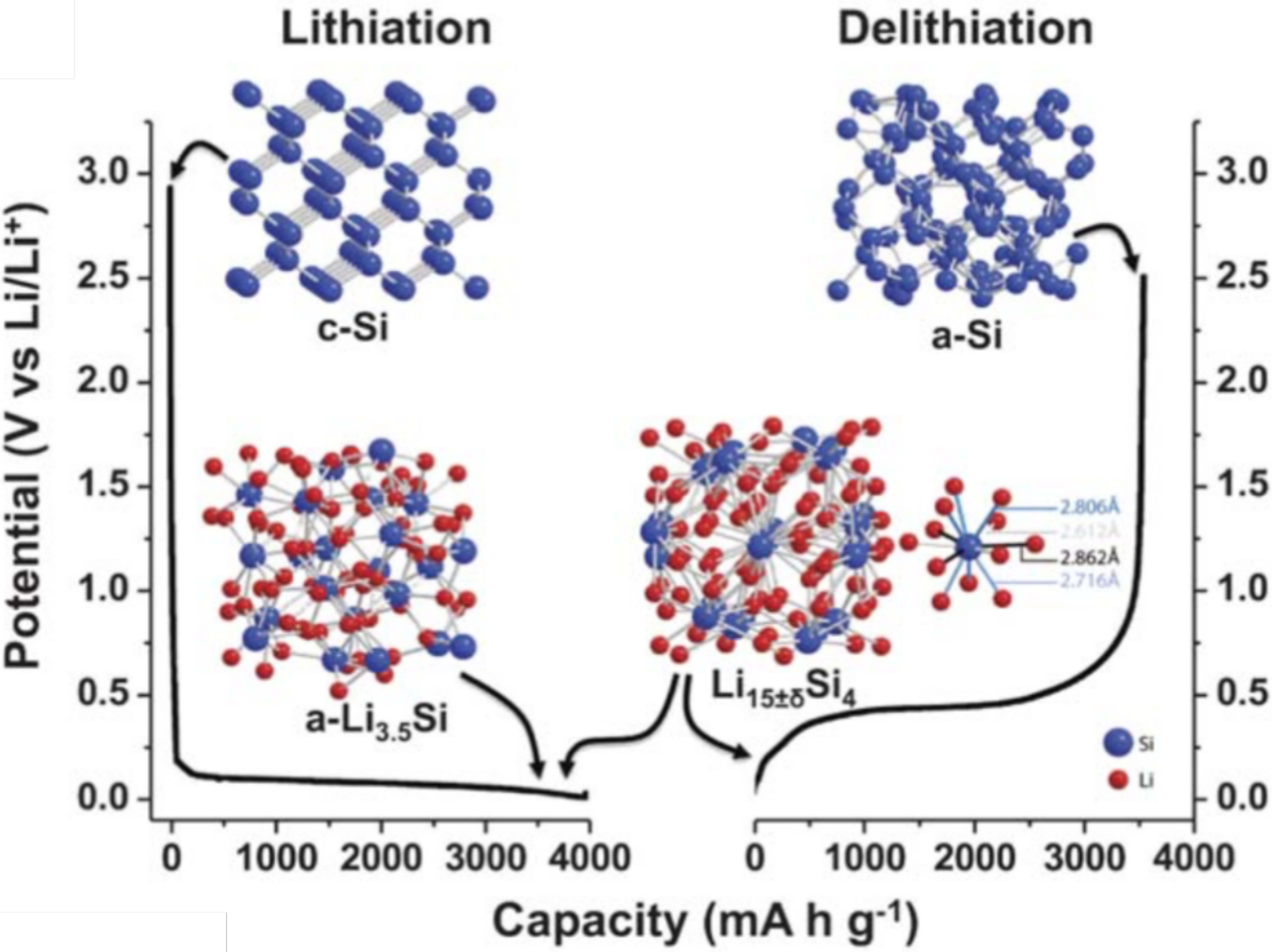
литий-ионный аккумулятор



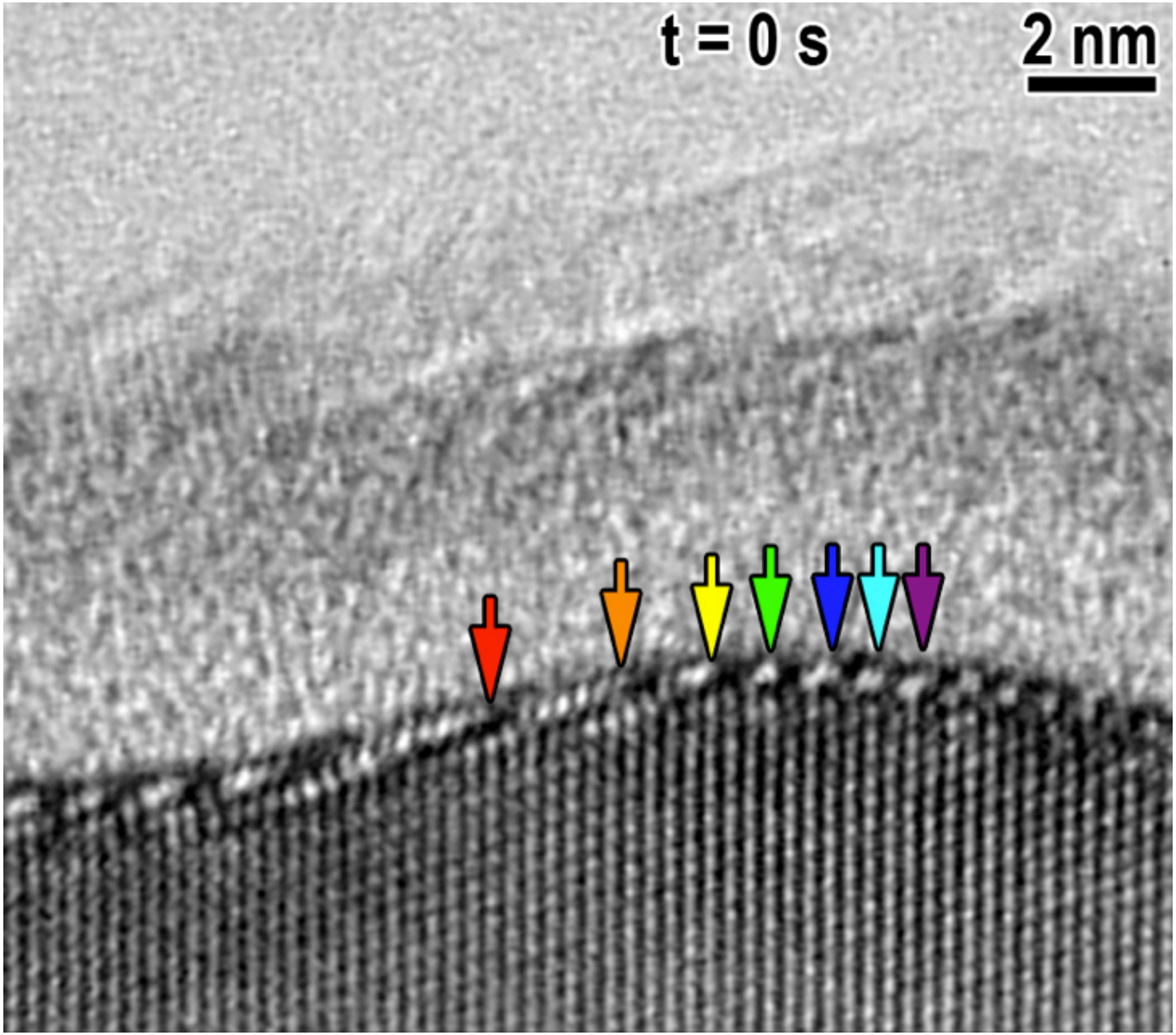
$LiCoO_2$ или **$LiFePO_4$**
(< 0.2 Ач/г)

выше напряжение:
например,
Li_2CoPO_4F (>5 В)

выше емкость:
например, **NMC**, **V_2O_5**
(0.3 – 0.4 Ач/г)

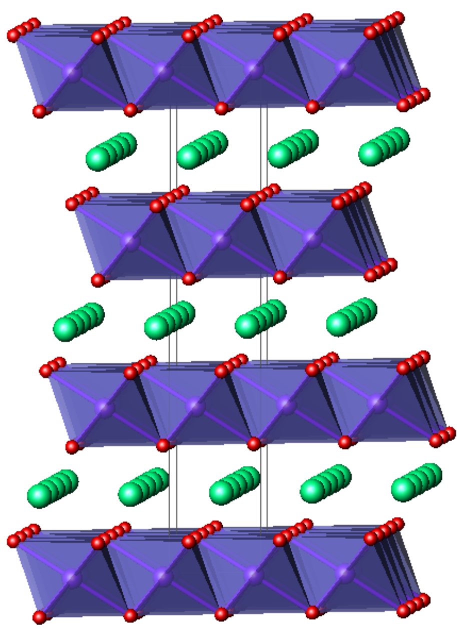
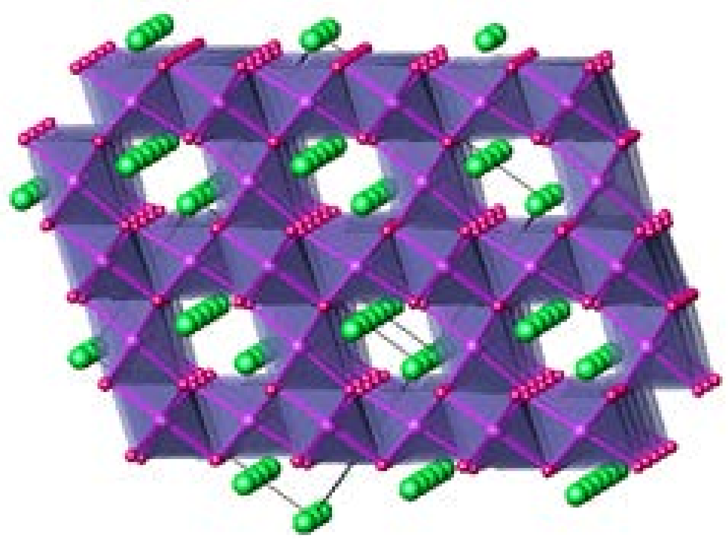
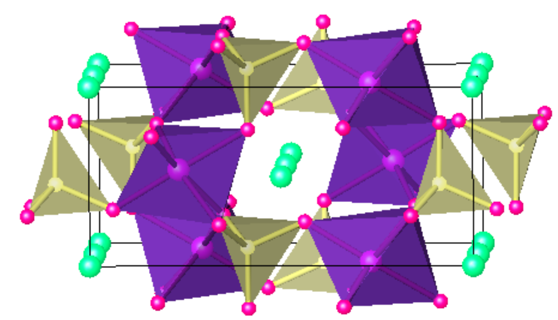


J. Mater. Chem. A, 2013, 1, 9566–9586



Nature Nanotechnology 7, 749–756 (2012)

Материалы положительных электродов

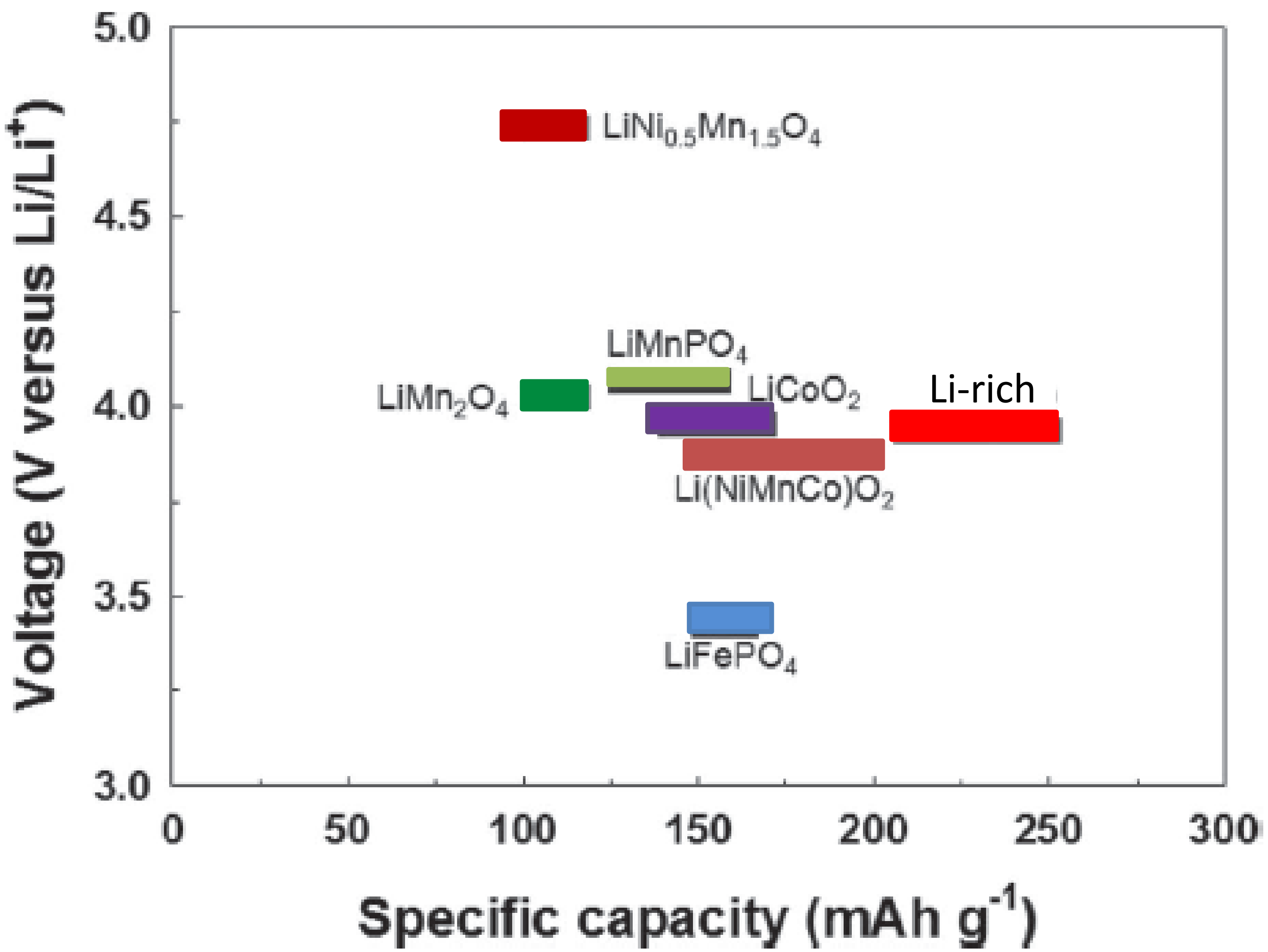
$LiCoO_2$	$LiMn_2O_4$	$LiFePO_4$
		

кубическая плотнейшая упаковка

гексагональная плотнейшая упаковка

	$LiCoO_2$	$LiMn_2O_4$	$LiFePO_4$
$C_т$	278 мА·ч/г	148 мА·ч/г	177 мА·ч/г
σ	10^{-3} С/см	10^{-5} С/см	10^{-9} С/см
k_D	10^{-9} см^2/с	10^{-10} см^2/с	10^{-15} см^2/с

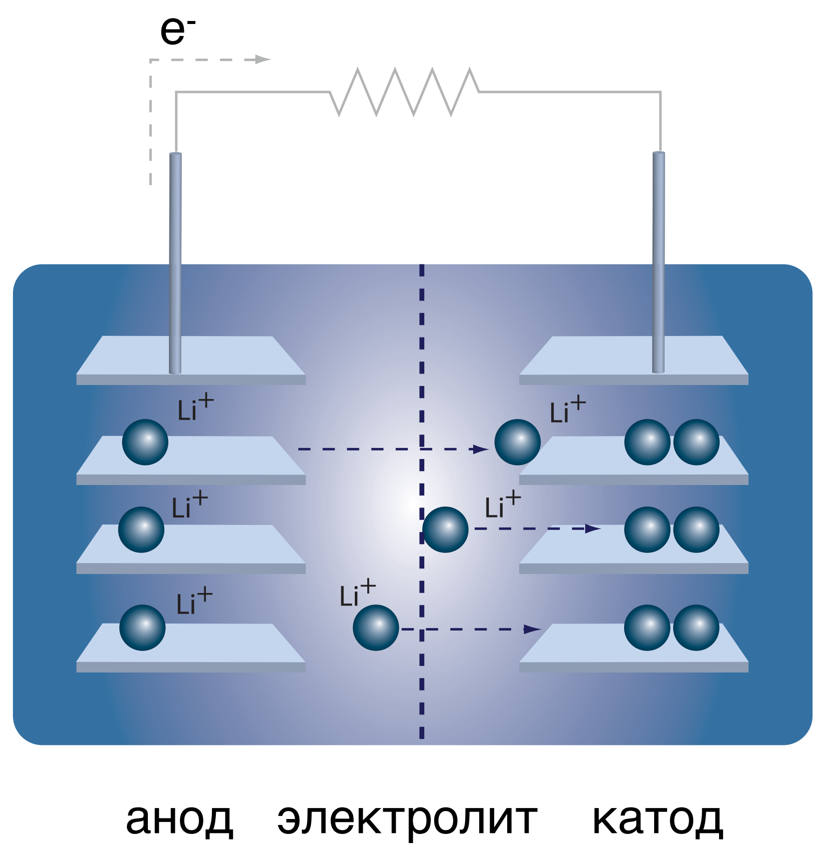
Материалы положительных электродов



литий-ионный аккумулятор

графит
(0.3 Ач на 1 г LiC_6)

выше емкость
нано-Si
(2.0 Ач на 1 г $Li_{4.4}Si$)



$LiCoO_2$ или **$LiFePO_4$**
(< 0.2 Ач/г)

выше напряжение:
например,
Li_2CoPO_4F (>5 В)

выше емкость:
например, **NMC**, **V_2O_5**
(0.3 – 0.4 Ач/г)

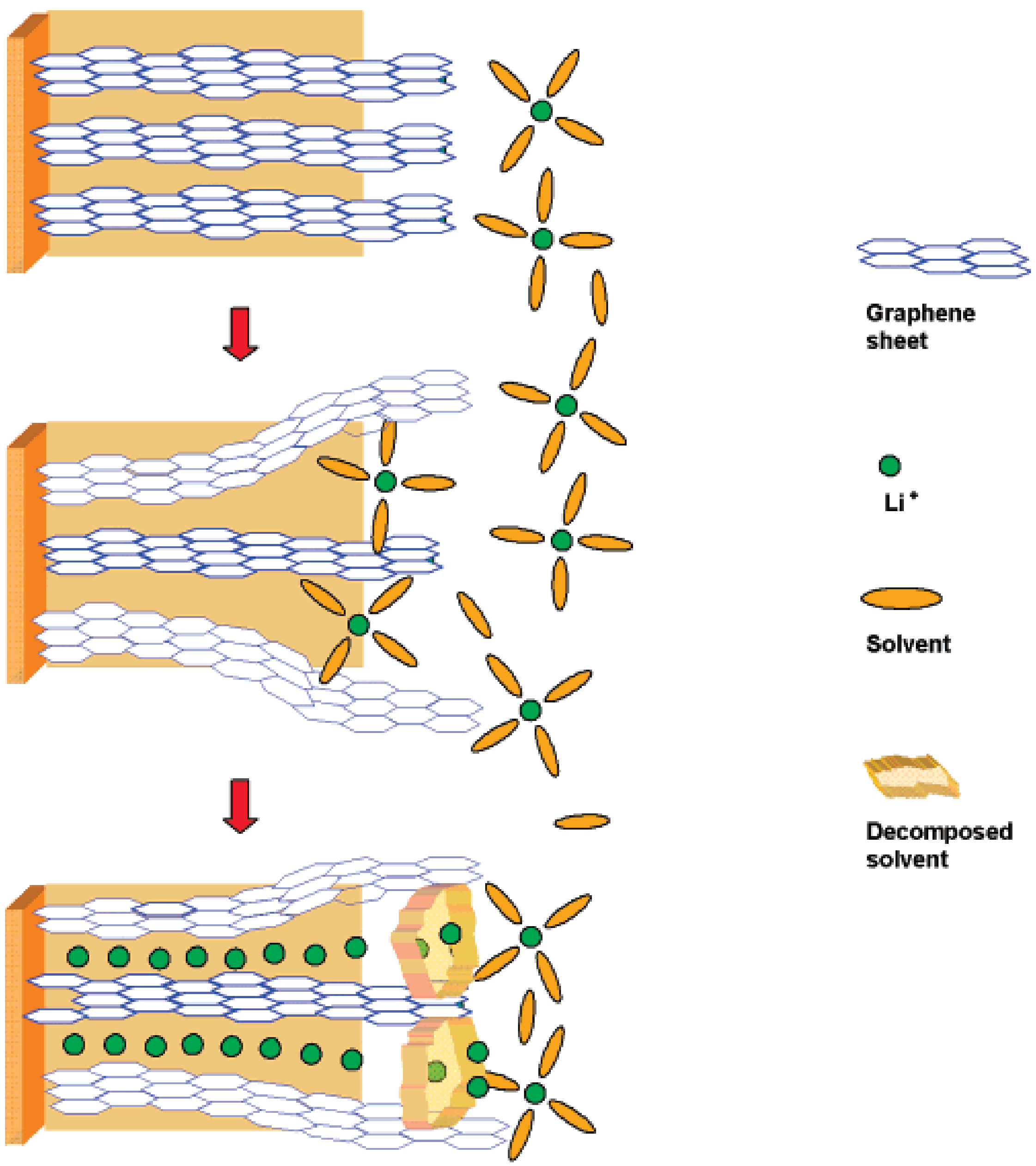
пост-литий-ионные технологии…

металлический Li
(3.8 Ач на 1 г Li)

сера
как оксилитель
(до 600 Вт ч/кг ?)

oxygen
как окислитель
(до 1000 Вт ч/кг ?)

LiC_6
200 мАч/г



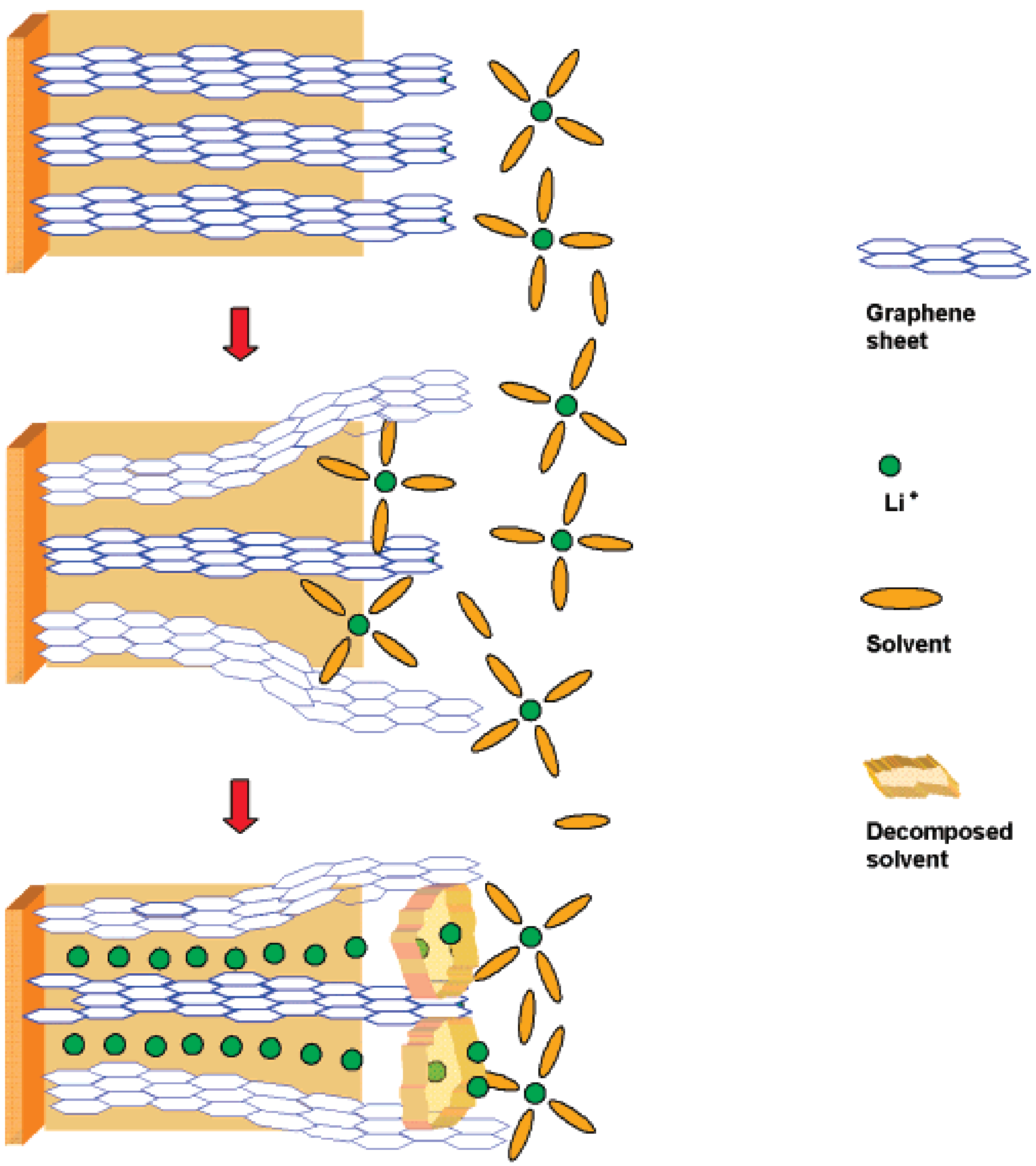
Li
3830 мАч/г

$Li \rightarrow Li^{+} + e^{-}$

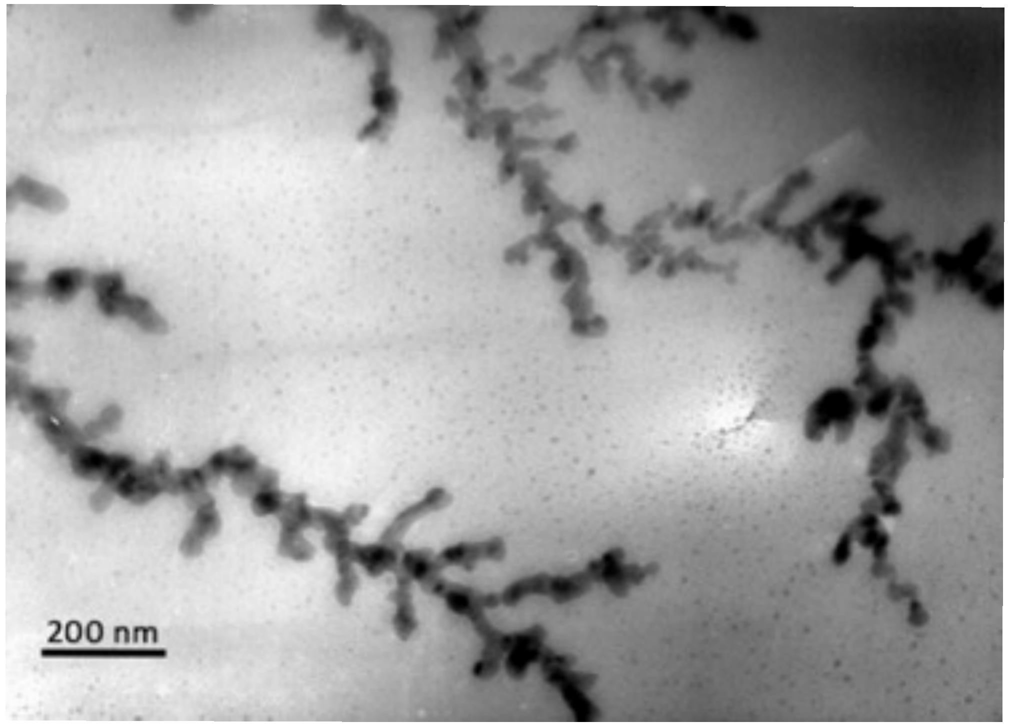
$\mathbf{E^0 = -3.05\ V}$ **отн. СВЭ**

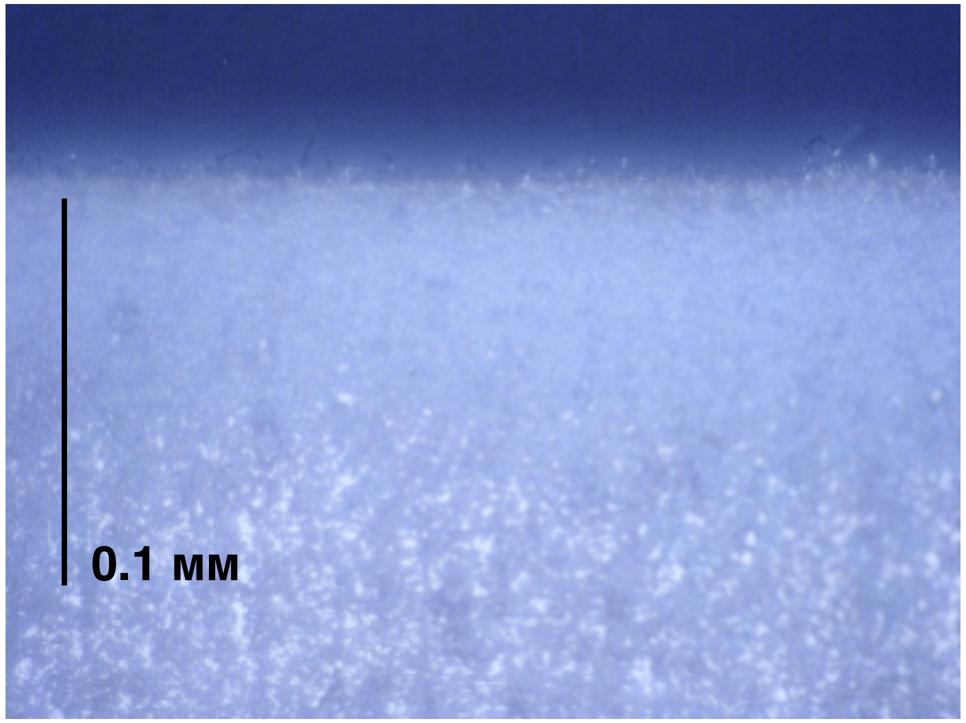
$\mathbf{Q_{spec}} = N_A \cdot e\ /\ M =$
3 830 мАч/г

LiC_6
200 мАч/г

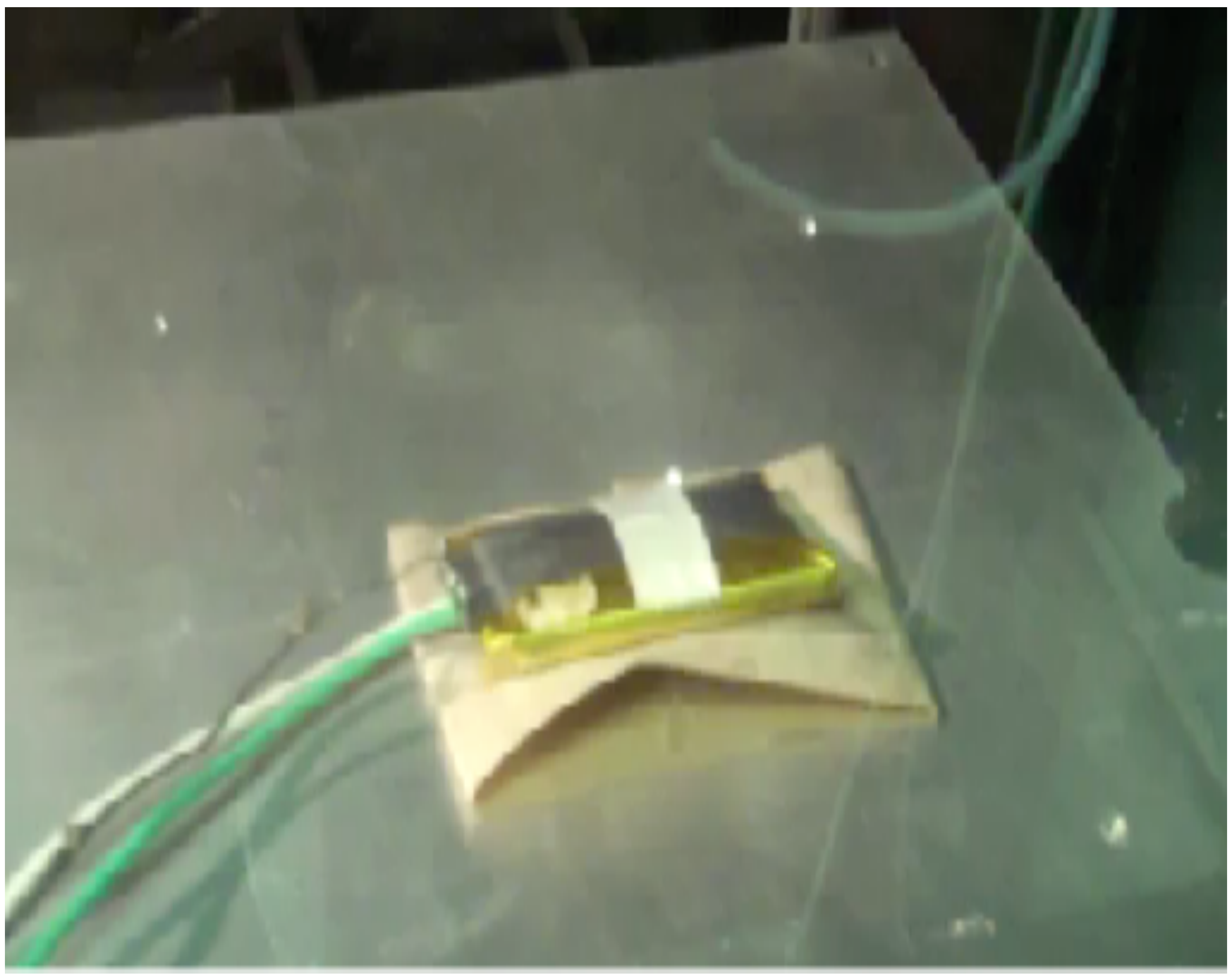


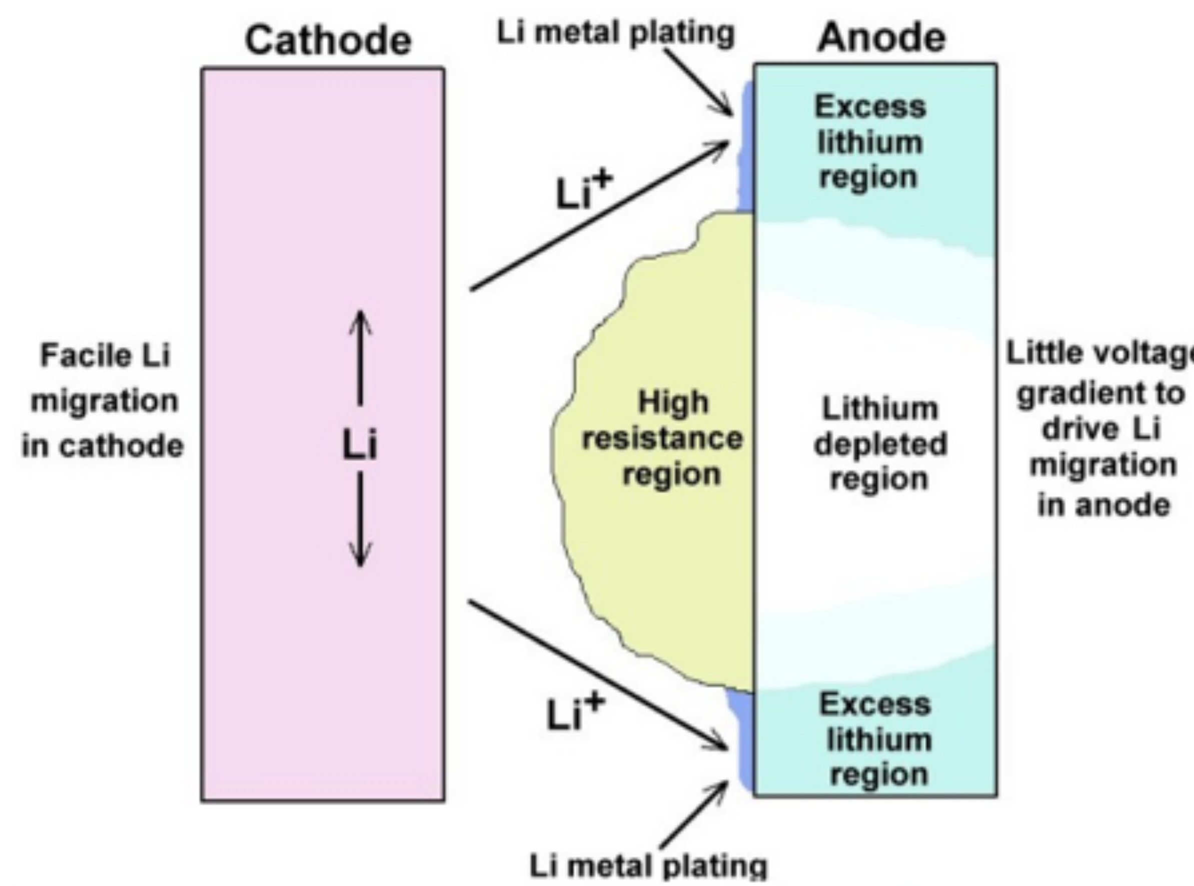
Li
3830 мАч/г



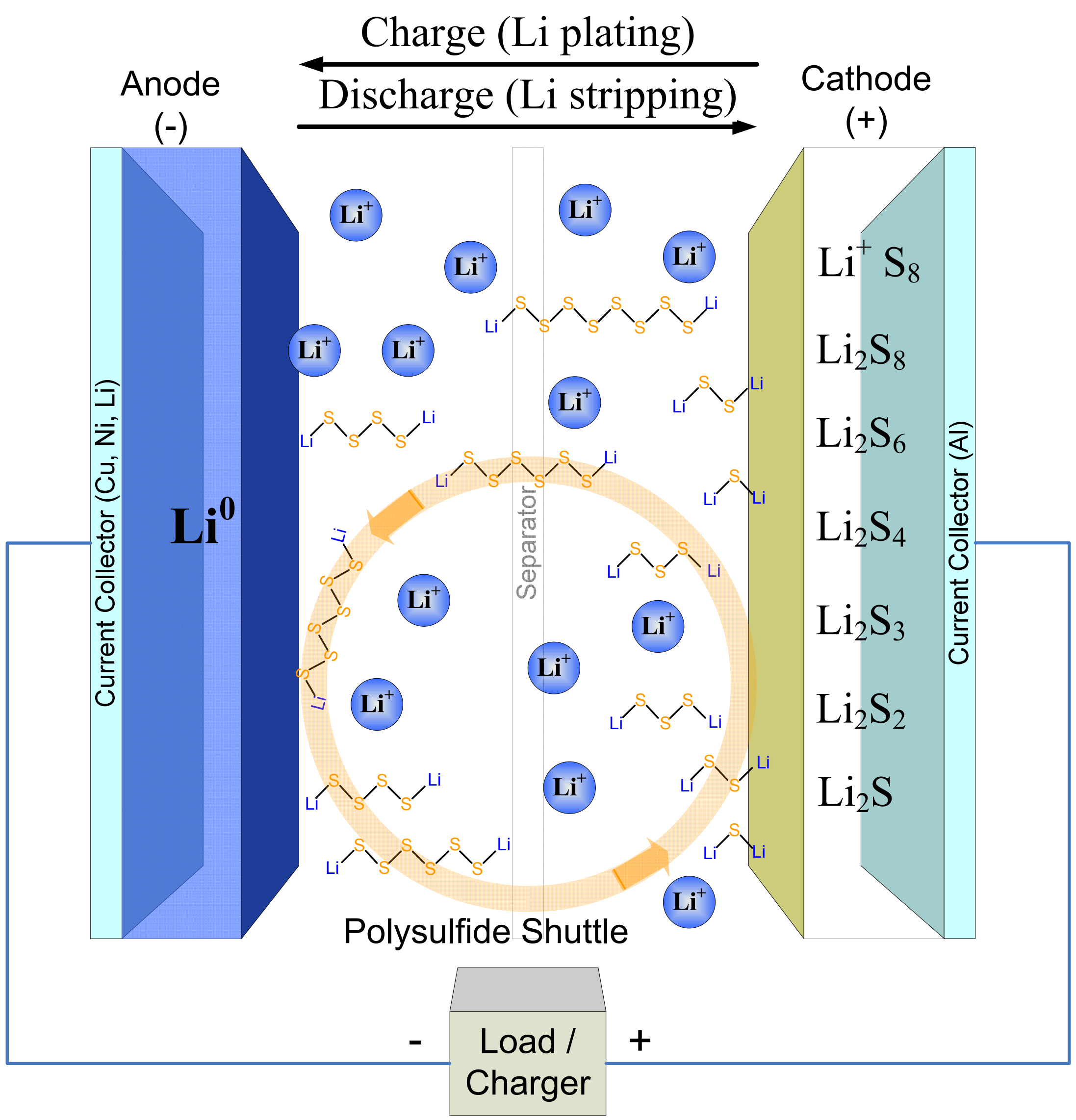


“Дендриты” могут вырасти и в литий-ионном аккумуляторе





Li – S аккумулятор



Отрицательный электрод:

$Li \rightleftarrows Li^{+} + e^{-}$

Положительный электрод:

$S + 2e^{-} + 2Li^{+} \rightleftarrows Li_2S$

Общая реакция:

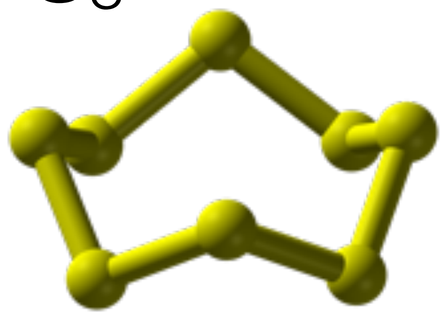
$2Li + S \rightleftarrows Li_2S$

Теоретическая удельная энергия (на массу активных компонентов):

$E_{уд} = 2F \cdot U / M(Li_2S) =$

$= 2 \cdot 96500 \cdot 2.1 / 46$ Дж/г = **2450 Вт · ч / кг (2800 Вт · ч/л)**

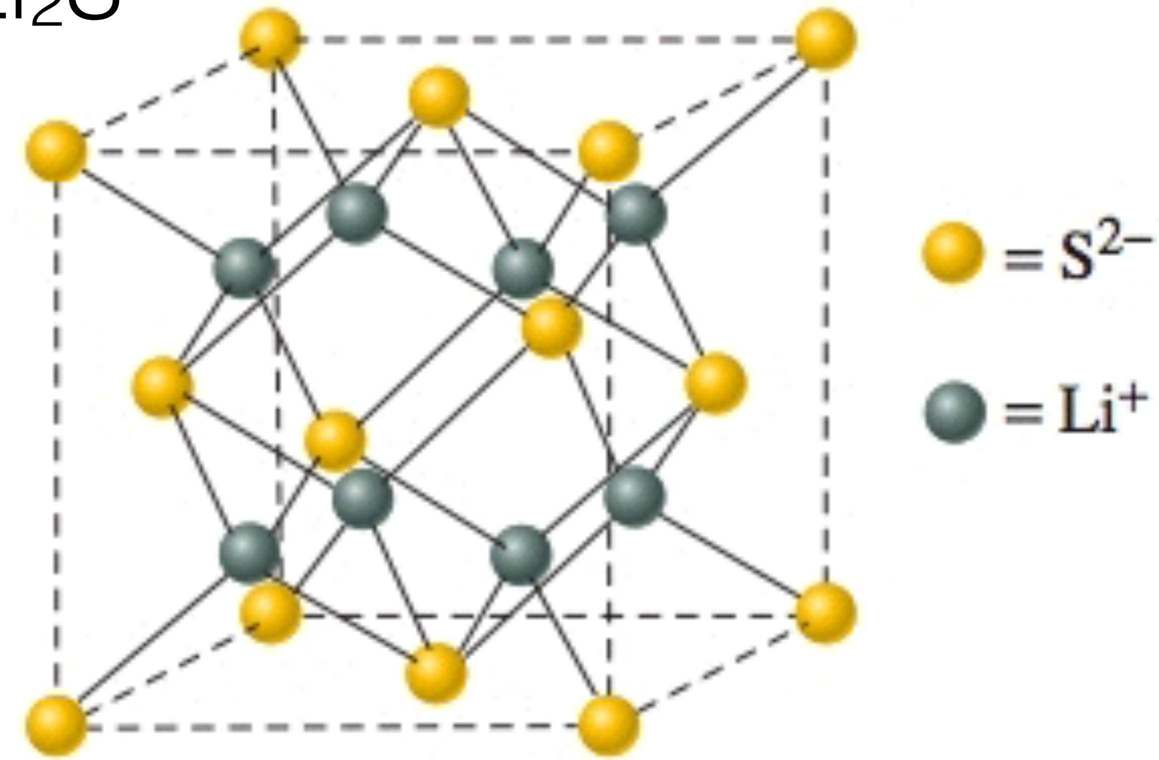
S_8

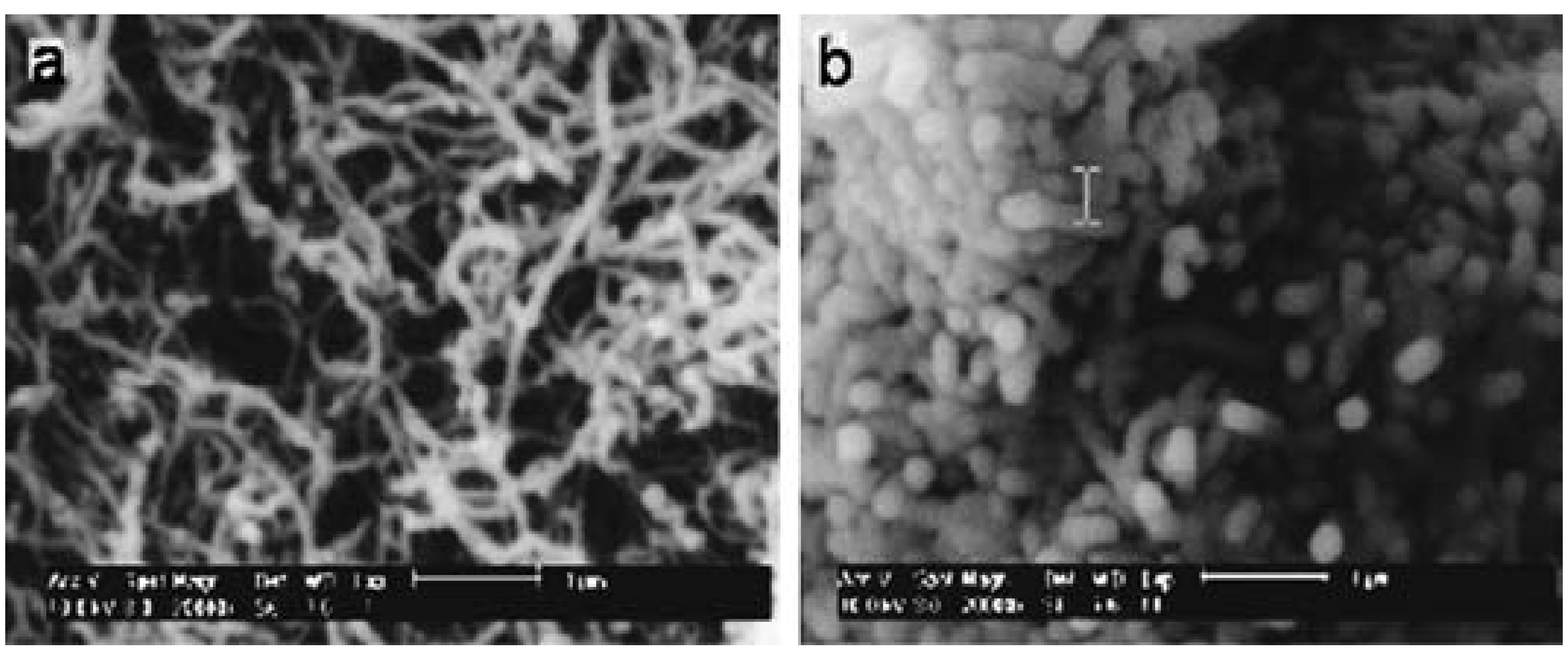


5×10^{-30} S/cm

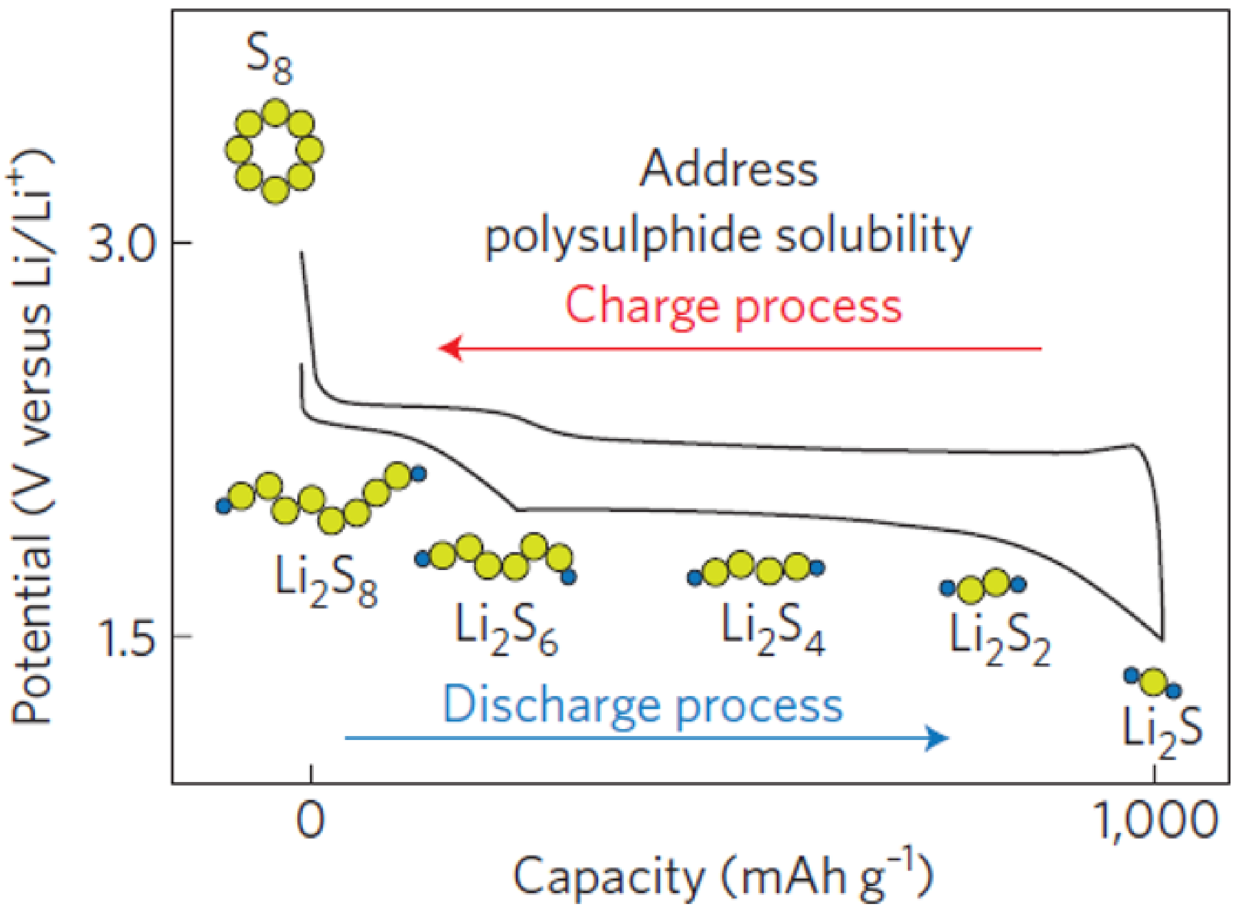
80% vol. change

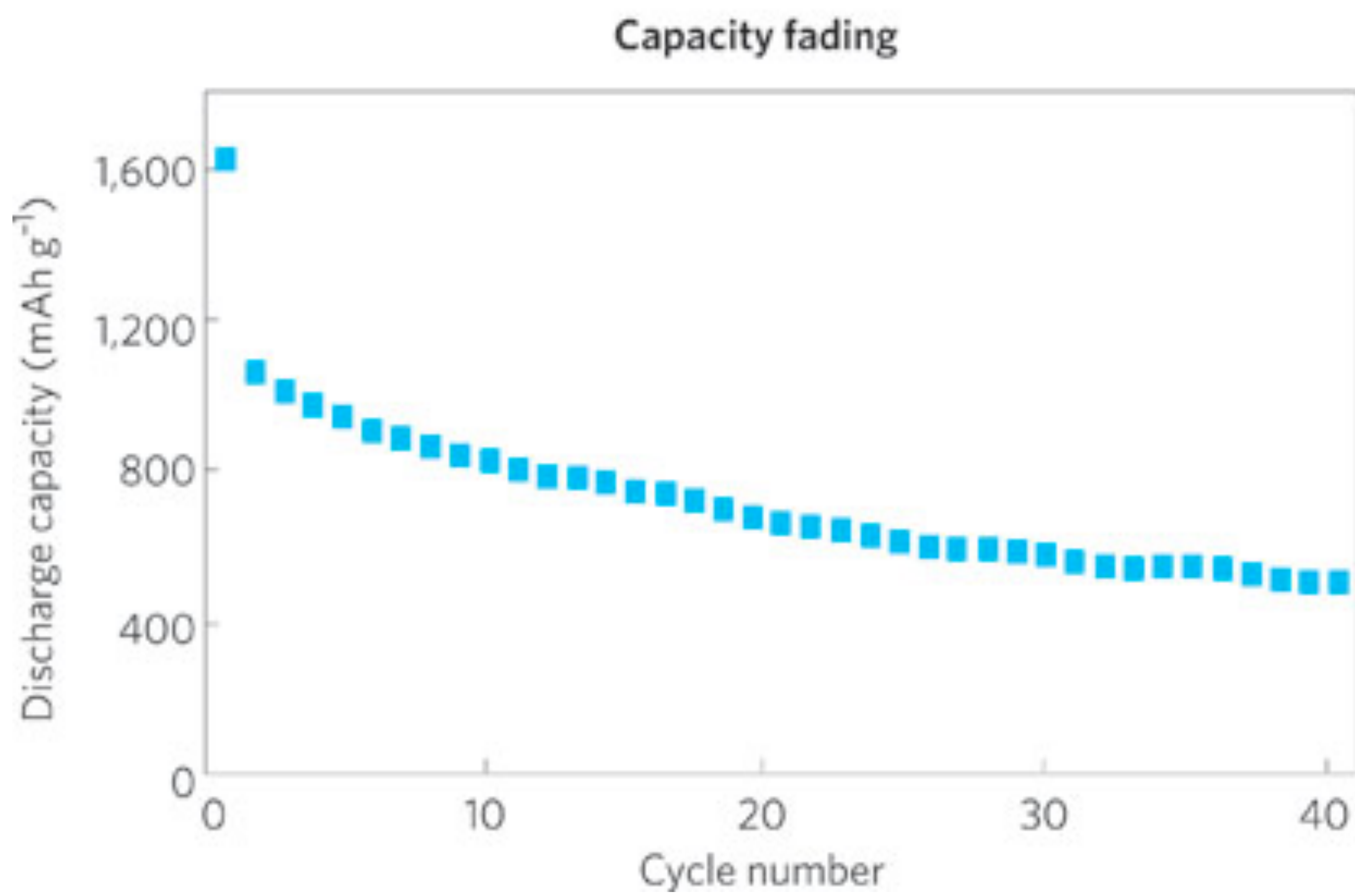
Li_2S





Electrochim. Acta, 2006, 51, 1330





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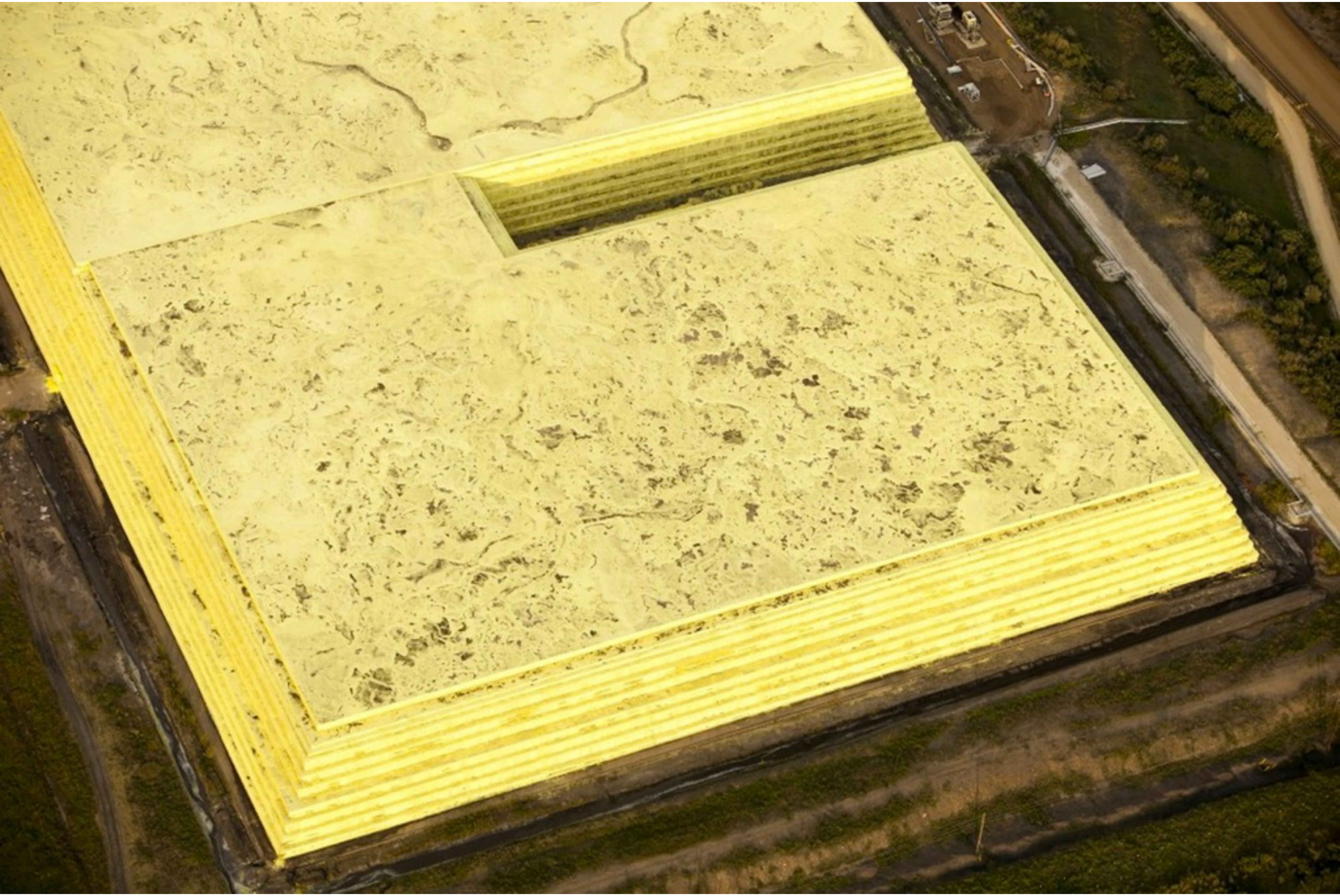


Литий как топливо

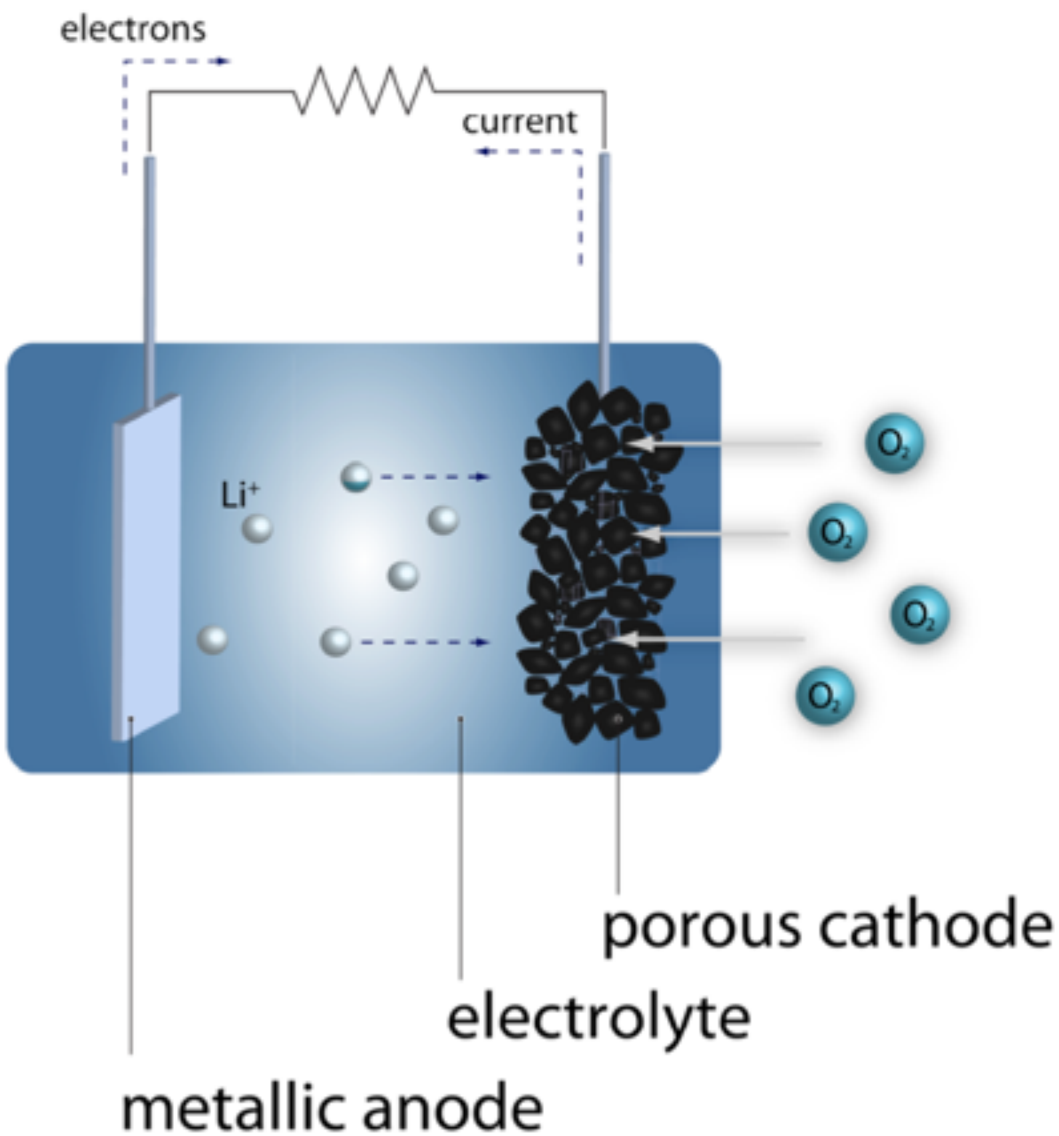
Сжатый водород (горение)	40 кВт ч/кг
Бензин (горение)	10 - 12 кВт ч/кг
Цинк (цинк-воздушная батарея, водная)	1.4 кВт ч/кг
Литий (литий-воздушная батарея, неводная)	11.6 кВт ч/кг

$Li \rightarrow Li^{+} + e^{-}$

$\mathbf{E^{0} = -3.05}$ **В отн. СВЭ**

$\mathbf{Q_{spec}} = N_A \cdot e / M =$ **3 830 мАч/г**

Литий-воздушный аккумулятор



теоретическое напряжение **2.96 В**

общая реакция
$2Li + O_2 \rightleftarrows Li_2O_2$

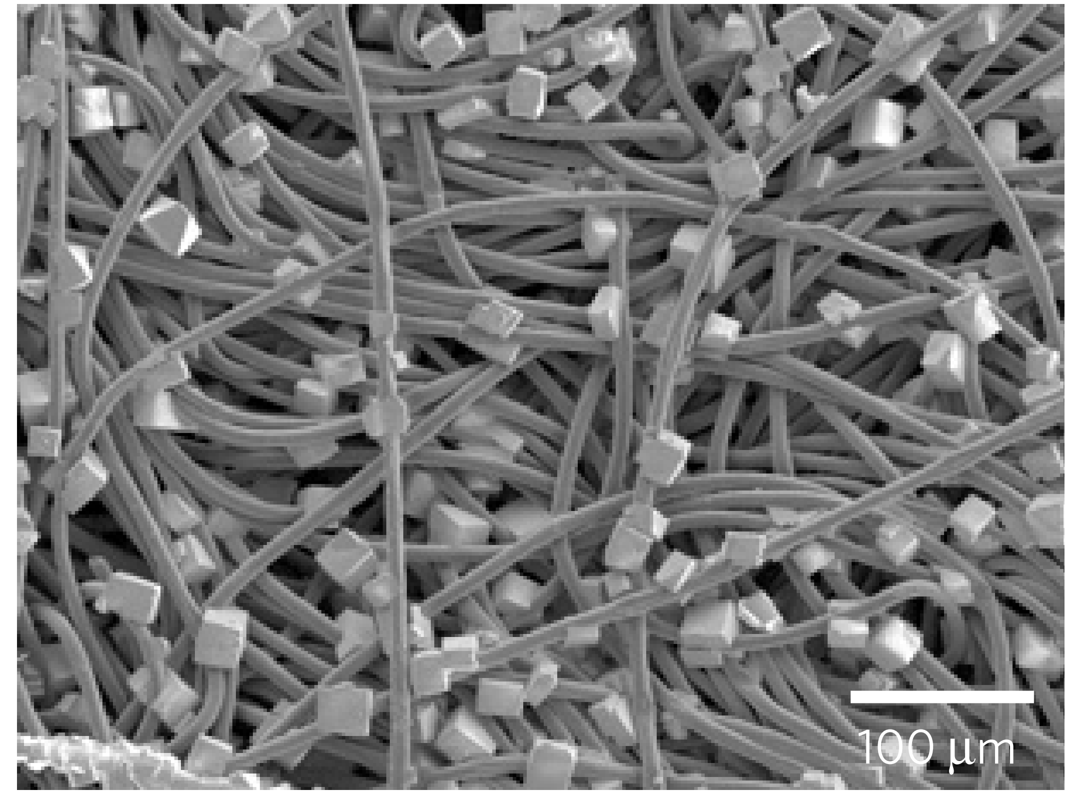
отрицательный электрод
$Li \rightleftarrows Li^+ + e^-$

положительный электрод
$O_2 + 2Li^+ + 2e^- \rightleftarrows Li_2O_2$

Требования к положит. электроду
- транспорт O_2 и Li^+
- электронная проводимость
- малый вес
- **химическая стабильность**

при использовании углеродных электродов
теор. удельная энергия до **900 Вт ч/кг** (200 Вт ч/кг для Li-ion)

$$Na^+ + e^- + O_2 \rightarrow NaO_2$$



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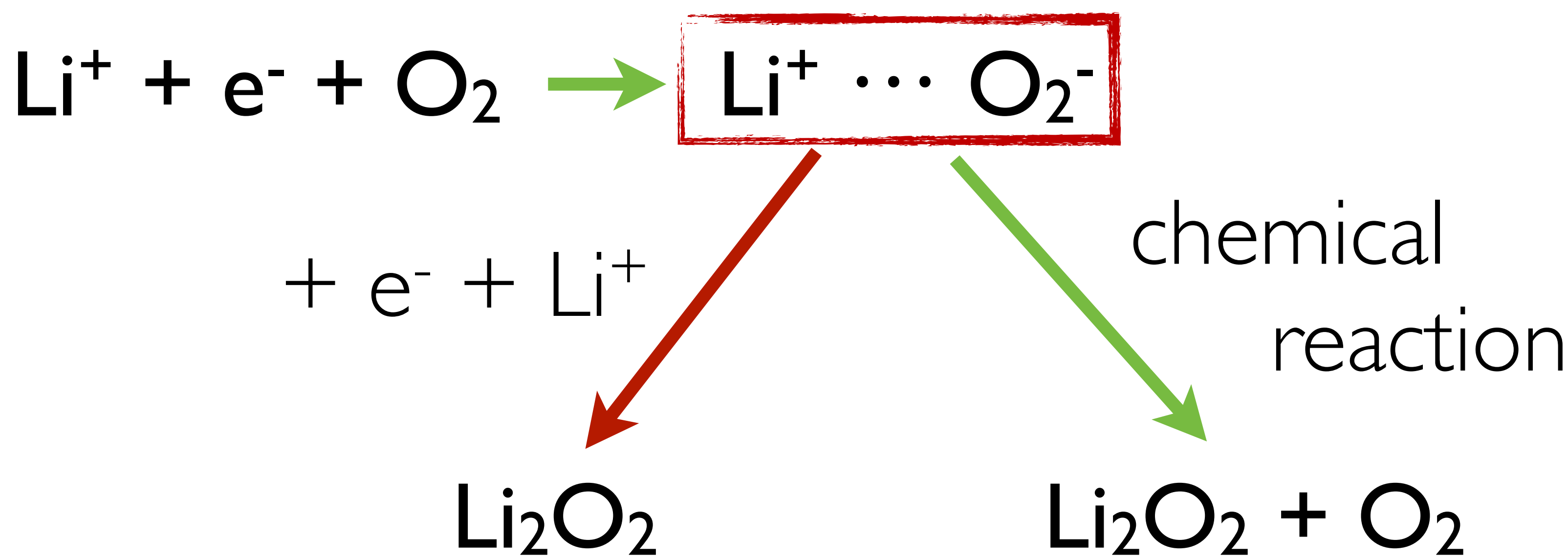

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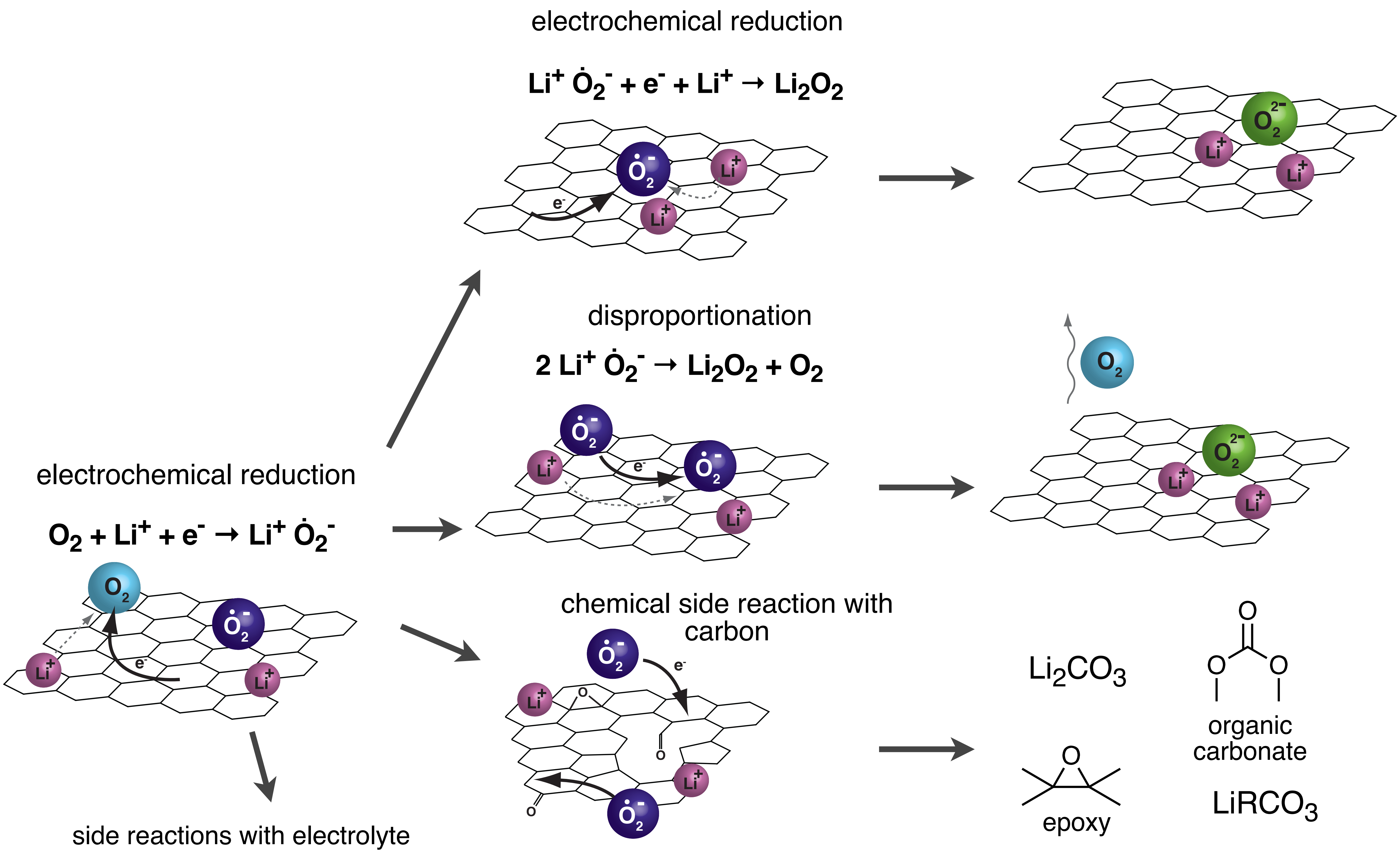

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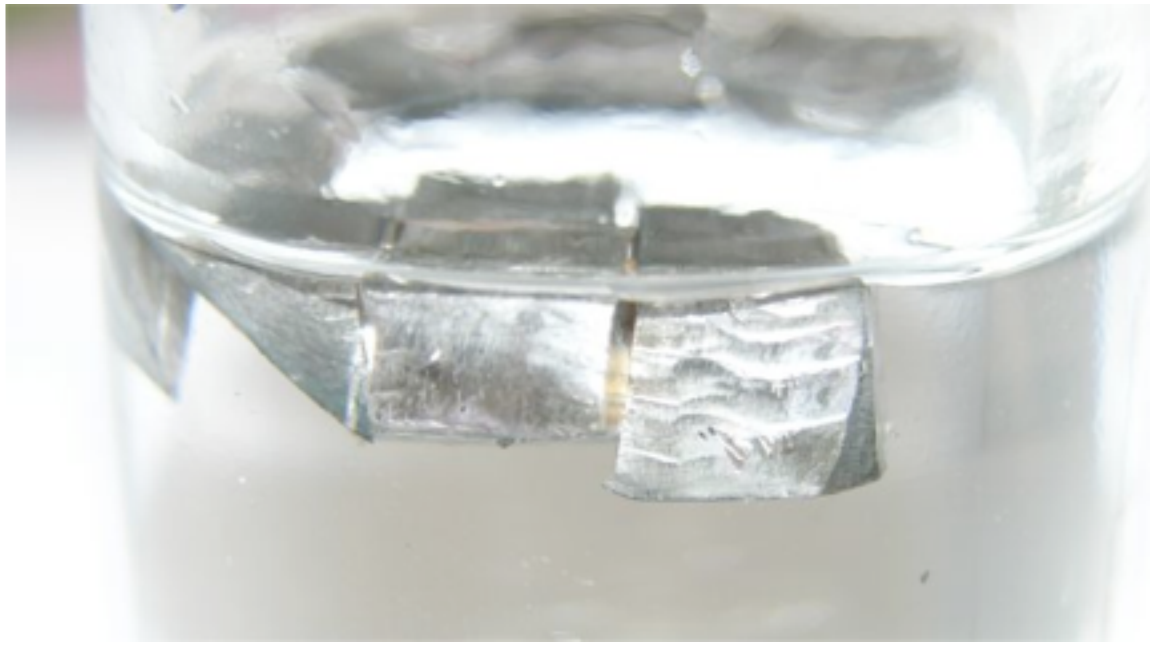

3.5 кВт·ч / кг

Is lithium the new gold?

Jean-Marie Tarascon ponders on the value of lithium, an element known for about 200 years, whose importance is now fast increasing in view of the promises it holds for energy storage and electric cars.

Although it has been known for almost two centuries, lithium is suddenly making the news: it is the primary ingredient of the lithium-ion batteries set to power the next generation of electric vehicles and, as such, could become as precious as gold in this century[1]. It is also non-uniformly spread within the Earth's crust, sparking rumours that Andean South American countries could soon be the 'new Middle-East'. Together, these factors set the scene for controversial debates about the available reserves[2–4] and the anticipated demands[1]: if all cars are to become electric within 50 years, fears of a crunch in lithium resources — and thus a staggering price increase such as that faced today with fossil fuels — are permeating.

With its atomic number of 3, lithium is located in the top left corner of the periodic table. It was Johann August Arfvedson, one of Jöns Jakob Berzelius's students, who first detected its presence in 1817 while analysing the mineral petalite ($LiAlSi_4O_{10}$), itself discovered in 1800. Berzelius called this new element *lithos* (Greek word for stone).

Lithium, whose silvery-white colour tarnishes on oxidation when exposed to air, is the most electropositive metal (−3.04 V versus a standard hydrogen electode), the lightest (M = 6.94 g mol^{-1}) and the least dense (ρ = 0.53 g cm^{-3}) solid element at room temperature, and is also highly flammable. Owing to this high reactivity, lithium is present only in compounds in nature — either in brines or hard rock minerals — and must be stored under anhydrous atmospheres, in mineral oil or sealed evacuated ampoules.

Their particular physical, chemical and electrochemical properties make lithium and its compounds attractive to many fields. Apart from the recent advent of lithium-based batteries, lithium niobate ($LiNbO_3$) is an important material in nonlinear optics. Engineers use lithium in high-temperature lubricants, to strengthen alloys, and for heat-transfer applications. It is also widespread in the fine chemical industry, as organo-lithium reagents are extremely powerful bases and nucleophiles used to synthesize many chemicals. Its effect on the nervous system has also made lithium attractive as a mood-stabilizing drug, and in nuclear research tritium (^3H) is obtained by irradiating ^6Li. Annual demand has therefore grown by 7–10%, currently reaching about 160,000 tons of lithium carbonate (Li_2CO_3) per year — about 20–25% of which is for the battery sector.

Energy storage, which should help mitigate the issues of pollution, global warming and fossil-fuel shortage, is becoming more important than ever, and Li-ion batteries are now the technology of choice to develop renewable energy technology and electric vehicles. They typically consist of a Li-containing positive electrode and a Li-free negative electrode, separated by a Li-based electrolyte. From simple calculations, assuming a one-molar Li-based electrolyte and a 3.6 V $LiMPO_4$ electrode (where M is Fe or Mn), the demand is estimated to be about 0.8 kg Li_2CO_3 per kWh — and this number is not expected to decrease with recently developed batteries such as lithium–air or lithium–sulfur, which need an excess of lithium at the negative electrode to function properly. The fact that tritium might also be used with deuterium for nuclear fusion could increase demands.

Extracting lithium from hard rocks is laborious and expensive, however, and most of that produced (roughly 83%) at present comes from brine lakes and salt pans: salty water is first pumped out of the lake into a series of shallow ponds, then concentrated using solar energy into a lithium chloride brine, which is subsequently treated with soda to precipitate Li_2CO_3. Considerable amounts of lithium are present in sea water, but its recovery is trickier, and highly expensive.

It is extremely difficult to estimate the world's lithium reserves[1–3] — a debate typically fed by investors and venture capitalists. The present production of Li_2CO_3 is about half what would be needed to convert the 50 million cars[4] produced every year into 'plug-in hybrid electric vehicles' (with an electric motor powered by a 7 kWh Li-ion battery and a combustion engine). The demand becomes astronomic if we consider full electric vehicles — which require an on-board battery of 40 kWh. These numbers bring fears of a potential Li shortage in a few decades, painting a dim picture.

This alarming global situation will hopefully drive researchers to investigate new battery technologies[5] and loosen our dependence on lithium. Fortunately, the situation improves if one also considers recycling — the low melting point (180 °C) of lithium metal and the very low water solubility of its fluoride, carbonate and phosphate salts make its recovery quite easy. Combining further brine exploitation with an efficient recycling process should be enough to match the demands of a 'propulsion revolution' that would solely rely on Li-ion cells, lessening geopolitical risks. ❐

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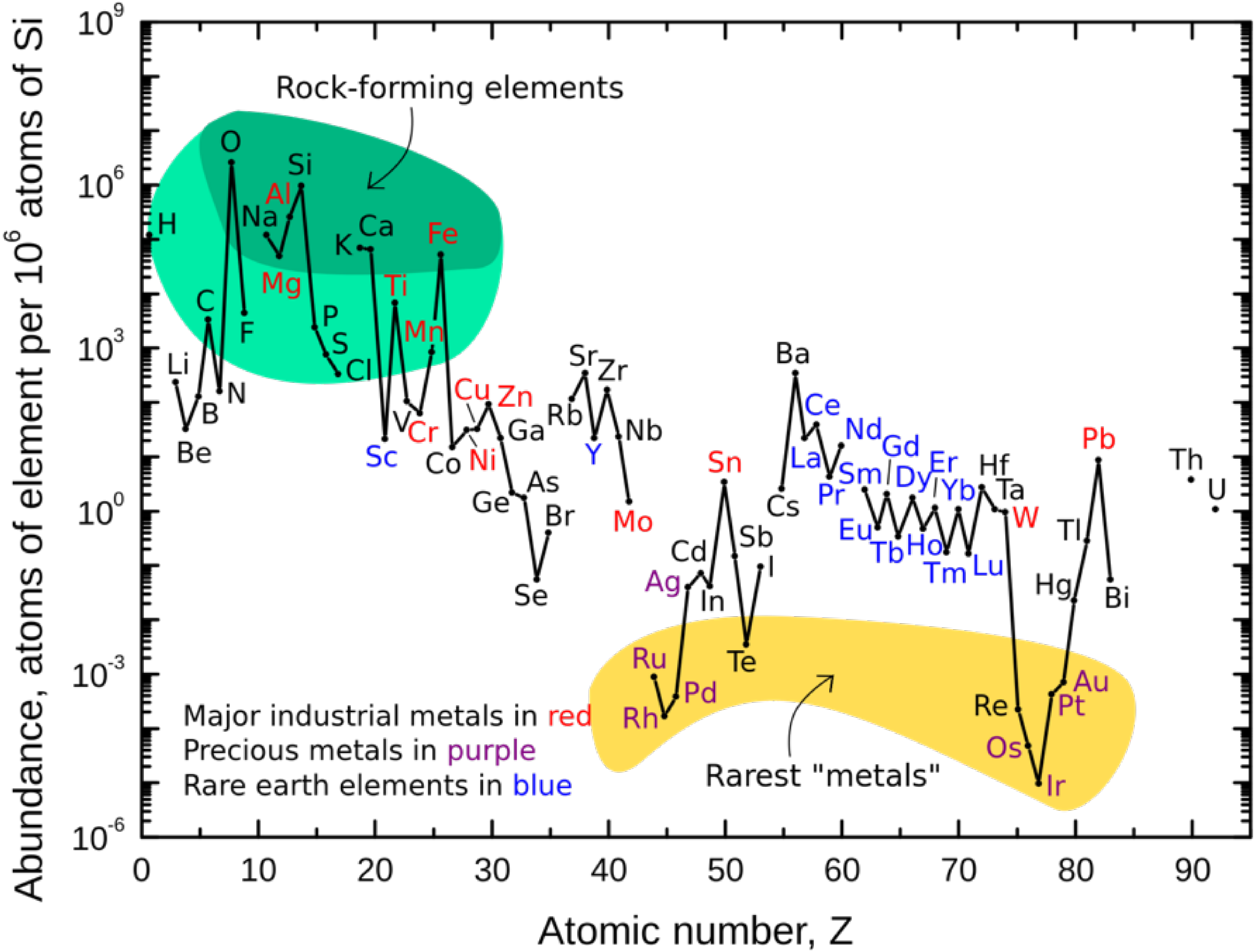
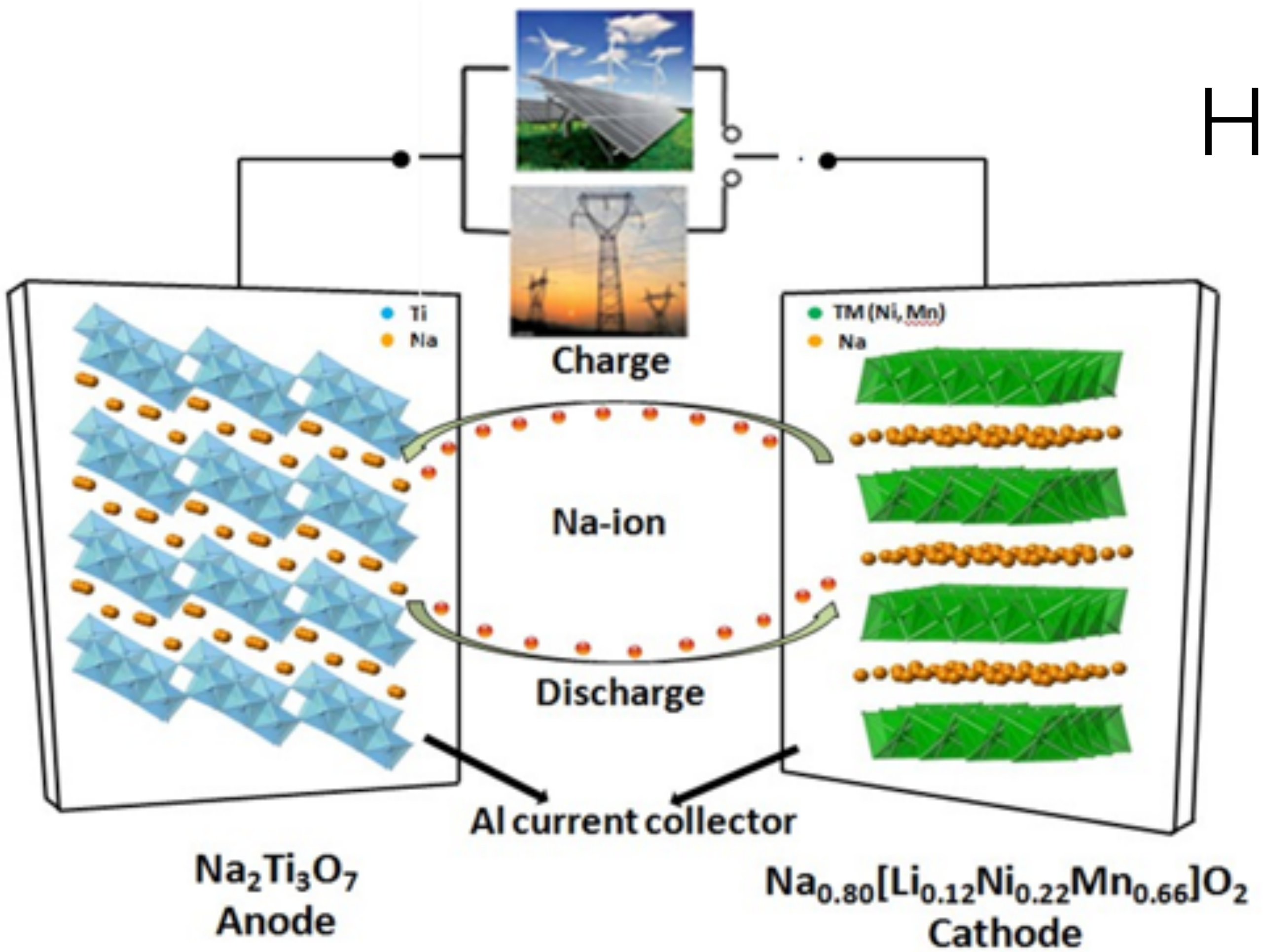


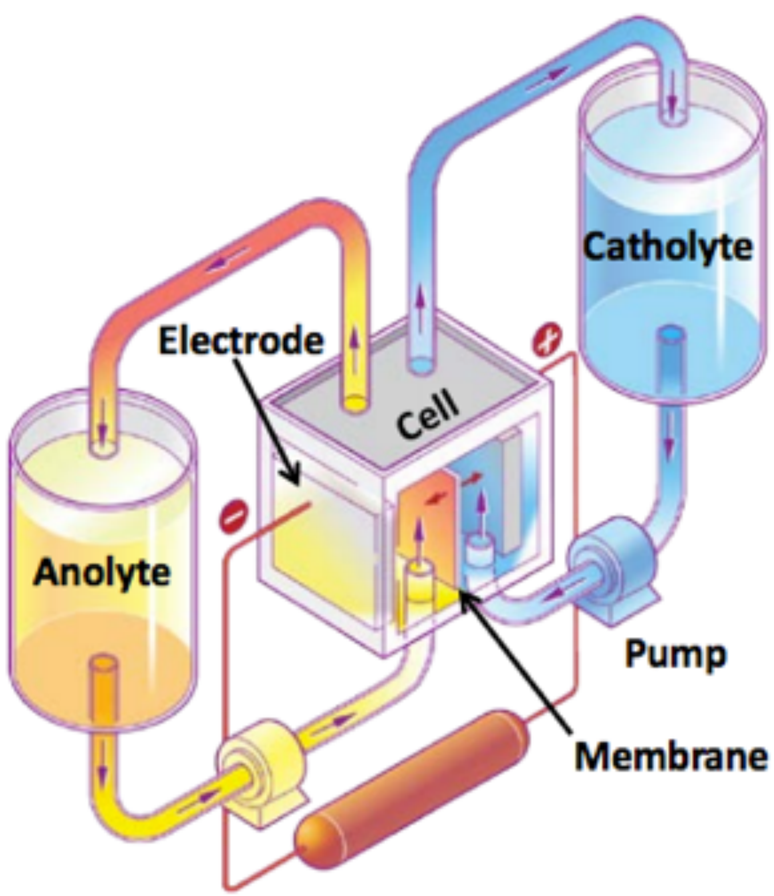
Rock-forming elements
Rarest "metals"
Major industrial metals in red
Precious metals in purple
Rare earth elements in blue
Abundance, atoms of element per 10^6 atoms of Si
Atomic number, Z
10^9
10^6
10^3
10^0
10^{-3}
10^{-6}
0
10
20
30
40
50
60
70
80
90
H
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

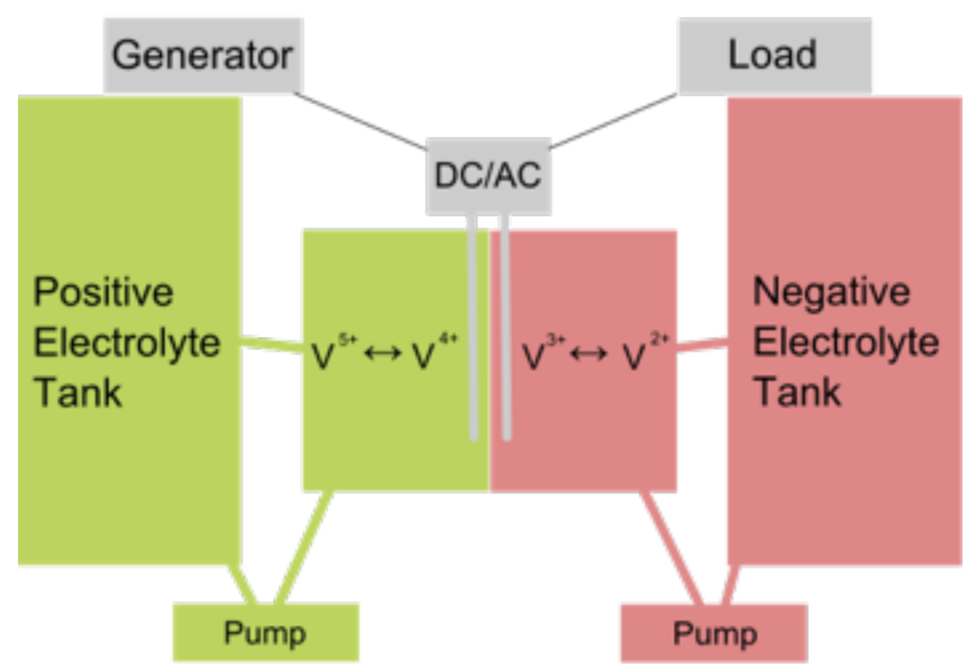
Натрий-ионные аккумуляторы – уже реальность



90 Вт ч / кг

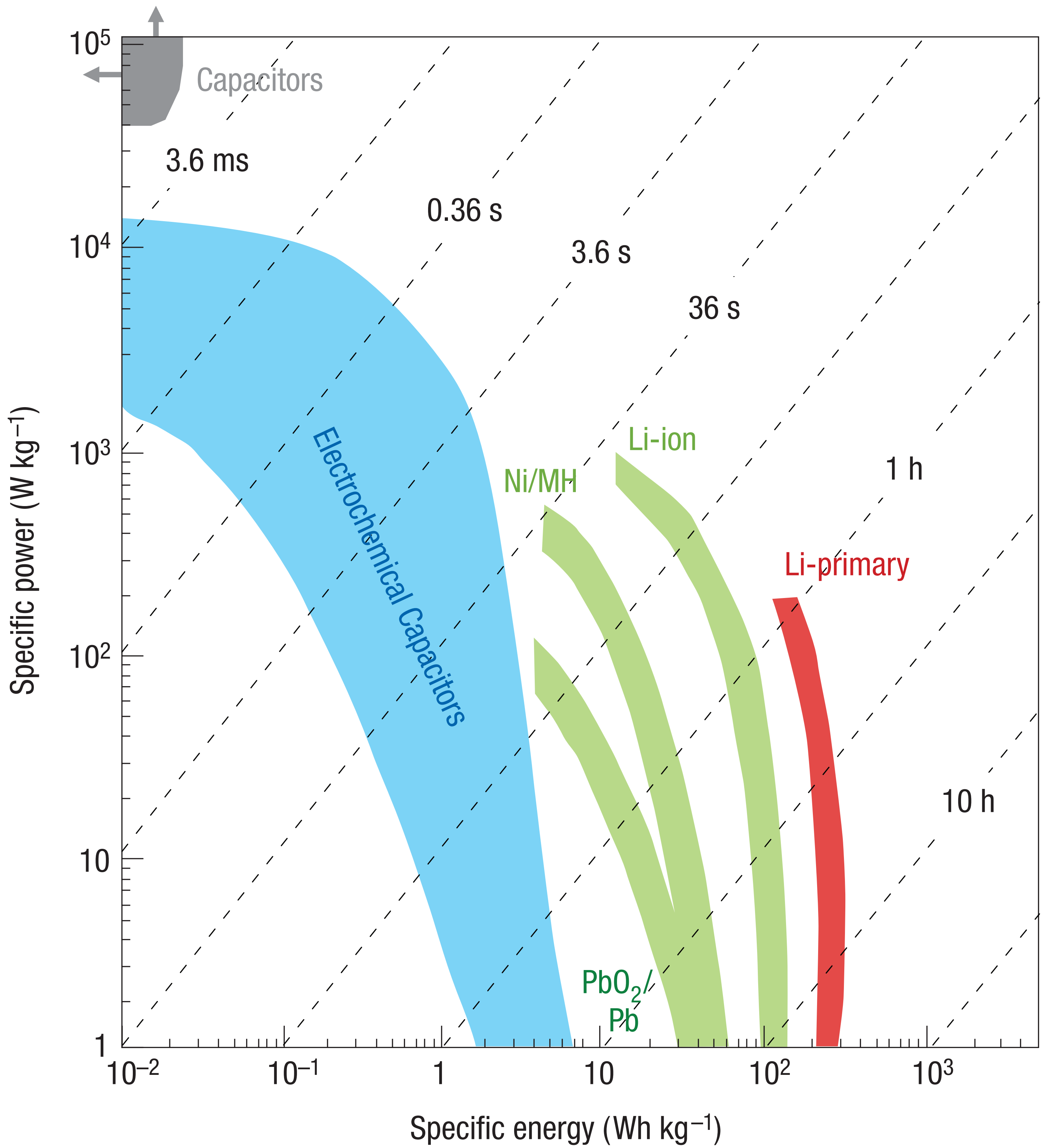
Проточные батареи





$$VO_2^+ + 2H^+ + e^- \leftrightharpoons VO^{2+} + H_2O$$

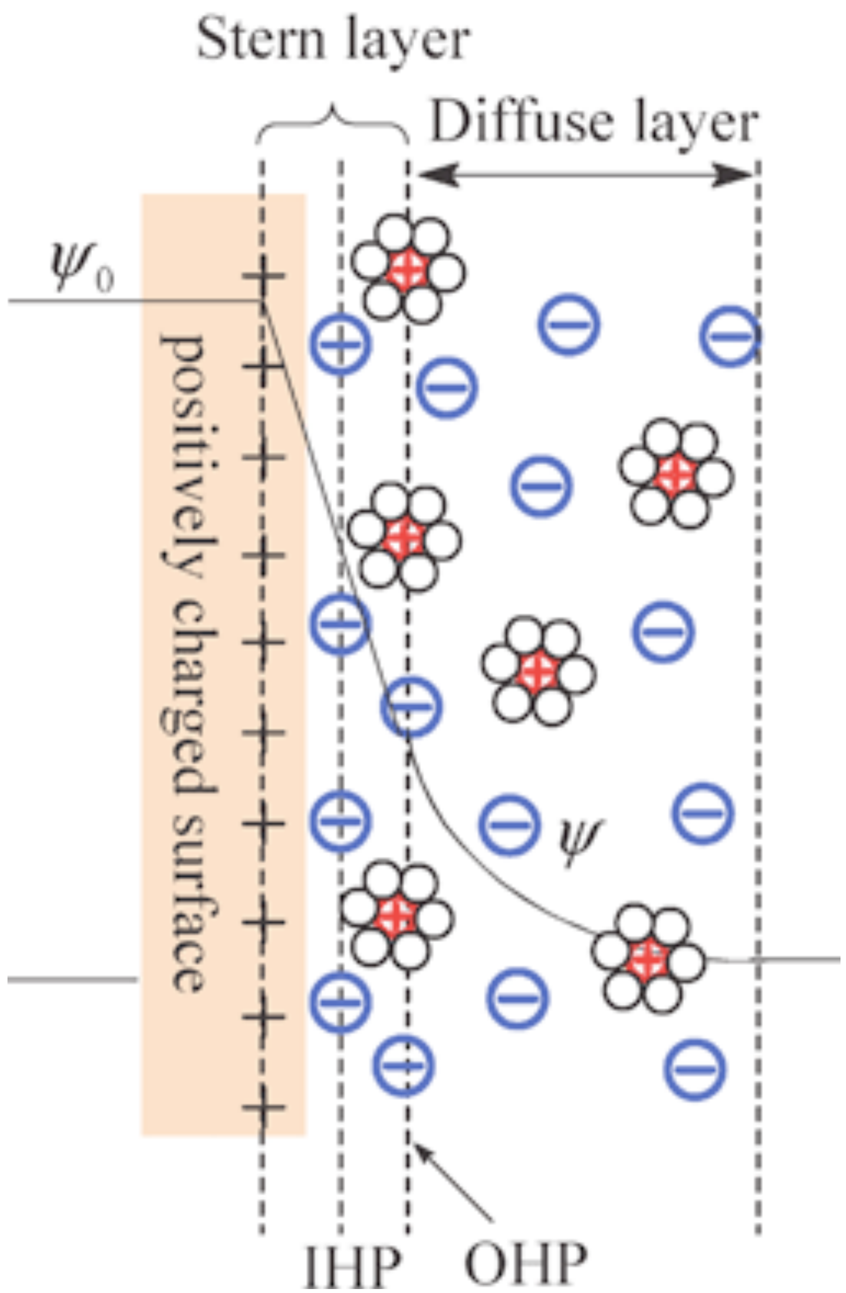
$$V^{2+} \leftrightharpoons V^{3+} + e^-$$

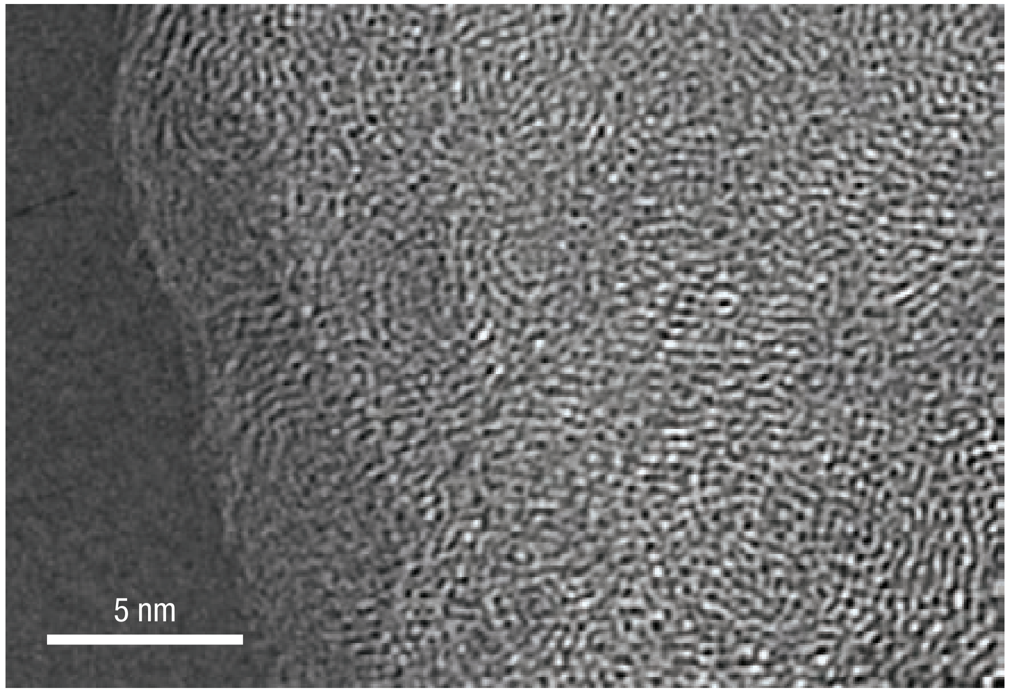


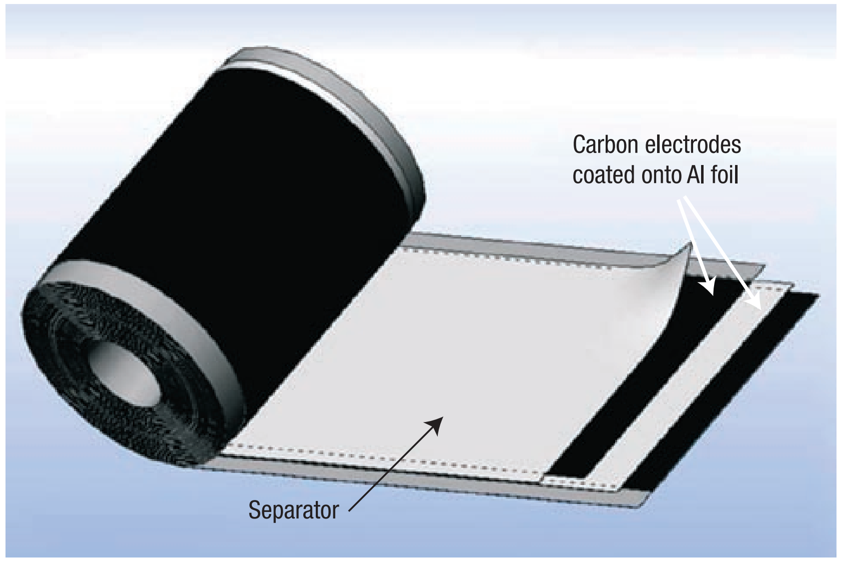
Capacitors
3.6 ms
0.36 s
3.6 s
36 s
1 h
10 h
Electrochemical Capacitors
Li-ion
Ni/MH
Li-primary
PbO2/
Pb
10^5
10^4
10^3
10^2
10
1
10^−2
10^−1
1
10
10^2
10^3
Specific power (W kg^−1)
Specific energy (Wh kg^−1)

Суперконденсаторы

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d}$$







Спасибо за внимание!

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