Hydrogen and Electrical Energy Storage

26 March 2013

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Radiation, Radionuclides and Reactors

Delft University of Technology

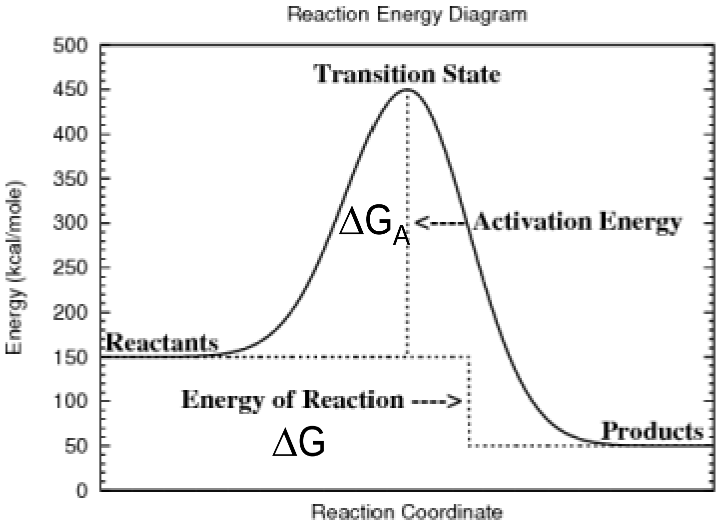
Program Batteries

Lecture 1: Feb 27	History, Applications, basic Electrochemistry and thermodynamics of batteries: Redox reactions, Gibbs free energy, chemical potential, Nernst.	
Lecture 2: March 6	Solid state electrode reaction mechanisms, phase diagrams, phase rule, Gibbs Free energy, voltage profiles, capacities and energy densities. Li-ion batteries	
Lecture 3: March 13	Continue topics Lecture 2. Electrolyte stability: Pourbaix diagram, band structure solids, Cycle life.	
Lecture 4: March 20	Kinetics, Buttler-Volmer, diffusion, solid state diffusion Discussion on Science paper 6 seconds discharge.	
Lecture 5: March 27	Super capacitors	
	Future large energy density systems:	Li-air Li-sulfur
	Batteries for large scale applications:	Lead-acid Li-ion Flow-cells Sodium aqueous batteries
	Costs and Performance comparison batteries/systems	

Recap last week...

Kinetic electrochemistry, charge transfer

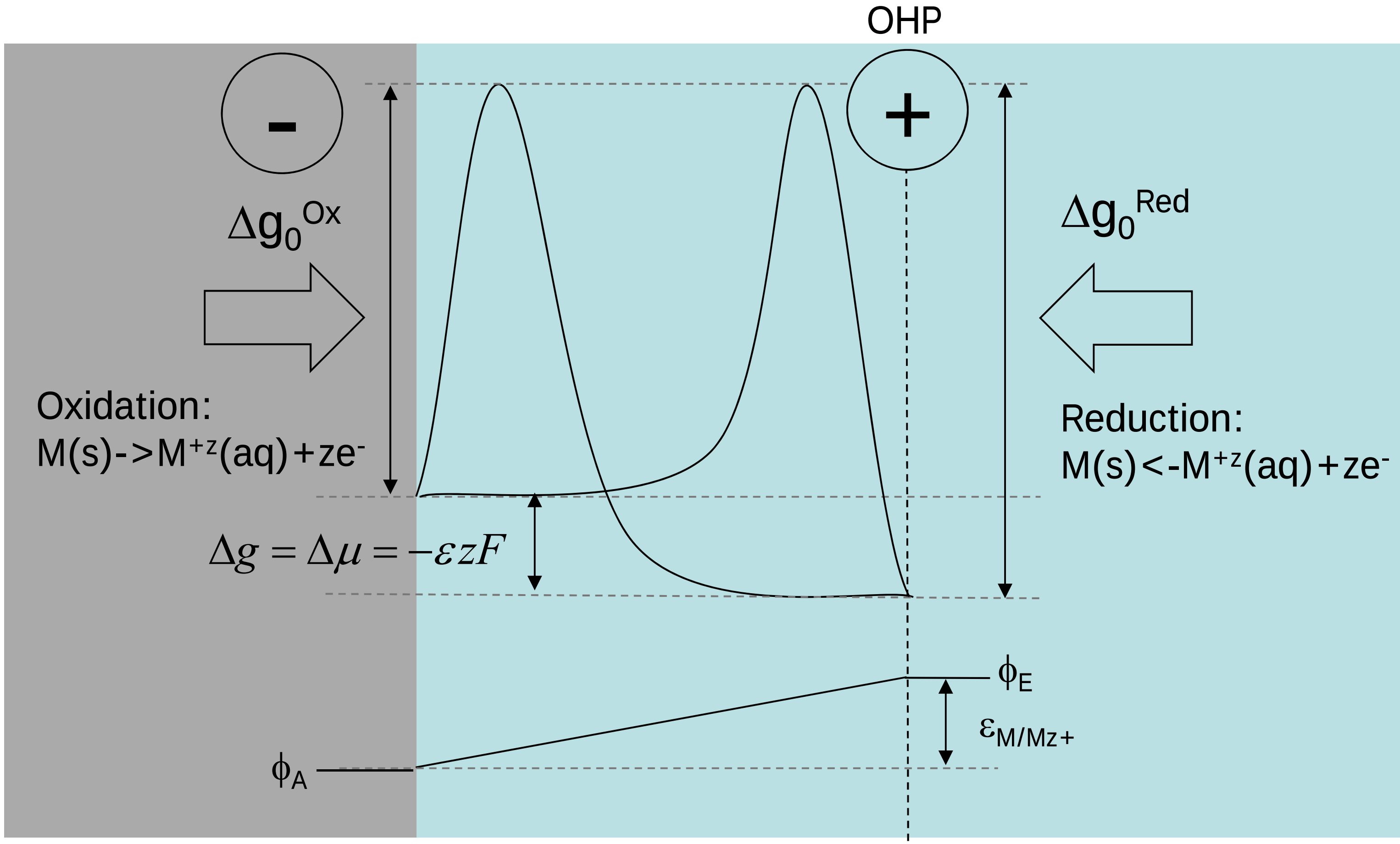
Although during discharge the charge transfer process is spontaneous, it does need to overcome a barrier (step 1 and 2).



Relationship of the current density [A/cm^2] with the activation barrier ΔG_A, Arrhenius law:

$$i = zFcke^{-\frac{\Delta G_A}{RT}}$$

c: concentration [mol/cm^3], F: Faradays constant [C/mol] and k: rate constant [cm/s]



OHP

-

+

Δg_0^{Ox}

Δg_0^{Red}

Oxidation:
$M(s) \rightarrow M^{+z}(aq) + ze^-$

Reduction:
$M(s) \leftarrow M^{+z}(aq) + ze^-$

$\Delta g = \Delta\mu = -\varepsilon zF$

ϕ_E

$\varepsilon_{M/Mz+}$

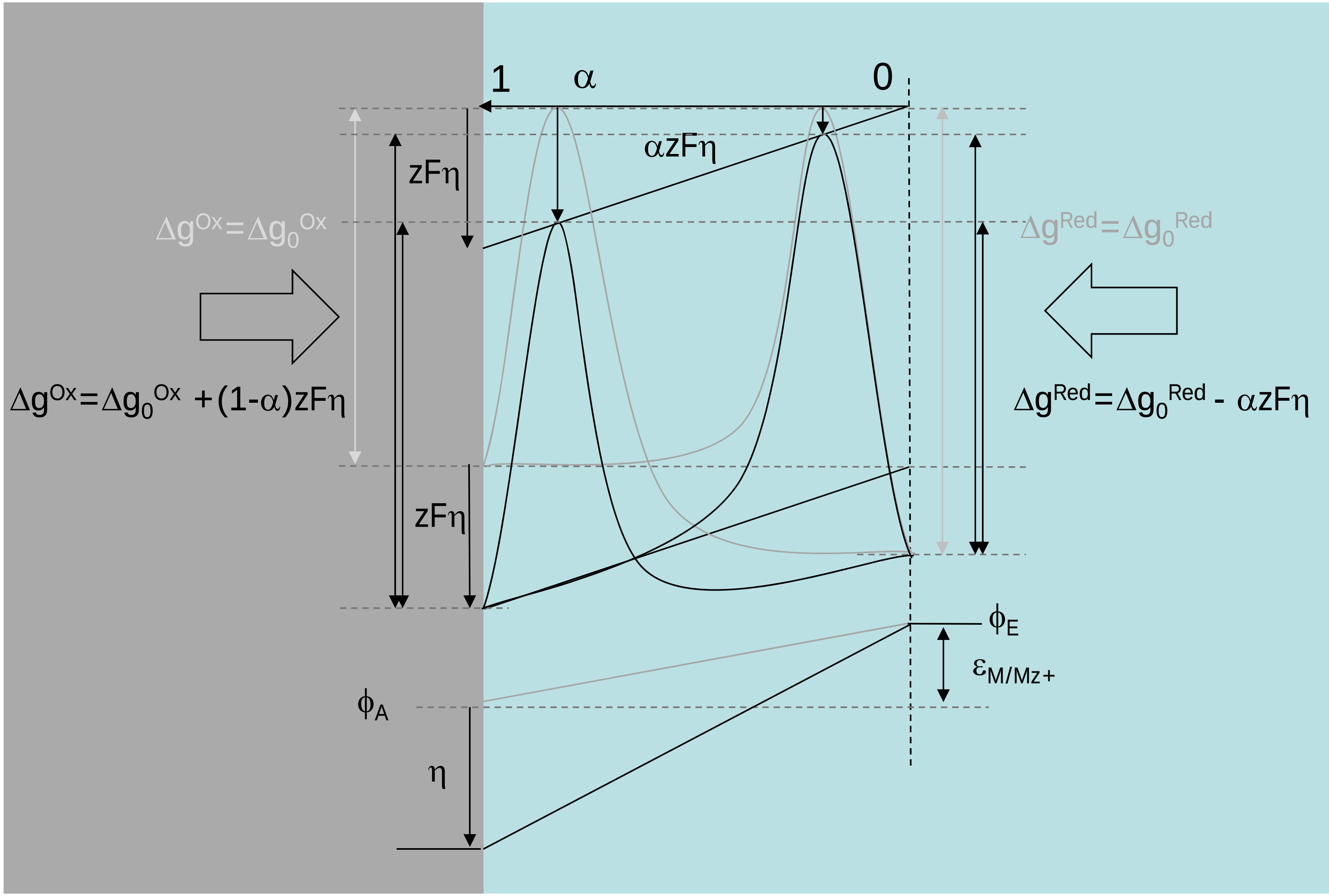
ϕ_A

$$i_0 = i_A = zFc_R k_A e^{-\frac{\Delta g_0^{Ox}}{RT}}$$

$$i_0 = i_C = zFc_O k_C e^{-\frac{\Delta g_0^{Red}}{RT}}$$

Dynamic equilibrium:

Zero netto current: $i_{netto} = i_A - i_C = 0$
definition exchange current density
(equilibrium current): $i_0 = i_A = i_C$



1
α
0
$\alpha zF\eta$
$zF\eta$
$\Delta g^{Ox}=\Delta g_0^{Ox}$
$\Delta g^{Red}=\Delta g_0^{Red}$
$\Delta g^{Ox}=\Delta g_0^{Ox}+(1-\alpha)zF\eta$
$\Delta g^{Red}=\Delta g_0^{Red}-\alpha zF\eta$
$zF\eta$
ϕ_E
$\varepsilon_{M/Mz+}$
ϕ_A
η

Kinetic electrochemistry, charge transfer

So for the netto current density (difference anodic and cathodic current at one electrode):

$$i_{netto} = i(\eta) = i_A - i_C = i_0\left(e^{\frac{(1-\alpha)zF\eta}{RT}} - e^{-\frac{\alpha zF\eta}{RT}}\right)$$

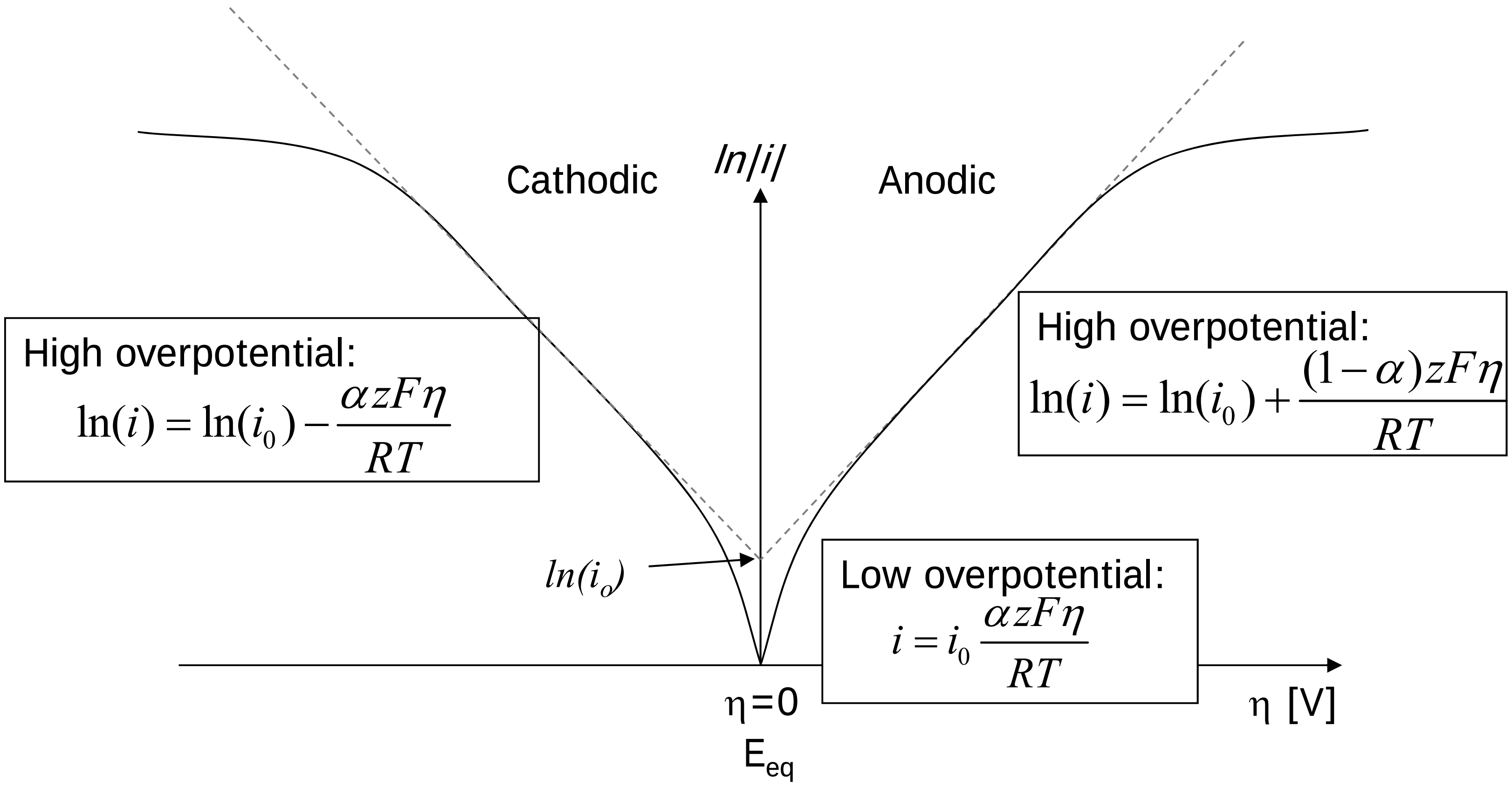
Butler-Volmer equation

This is the fundamental equation of electrode kinetics, relates the **current density** with the exchange current density, the **overpotential** η and the transfer coefficient.

Remember, we only considered the charge transfer at the electrode-electrolyte interface (η_2)

Kinetic electrochemistry, charge transfer

Tafel Plots: Determine the exchange current density i_0 and the transfer coefficient α



High overpotential:

$$\ln(i) = \ln(i_0) - \frac{\alpha z F \eta}{RT}$$

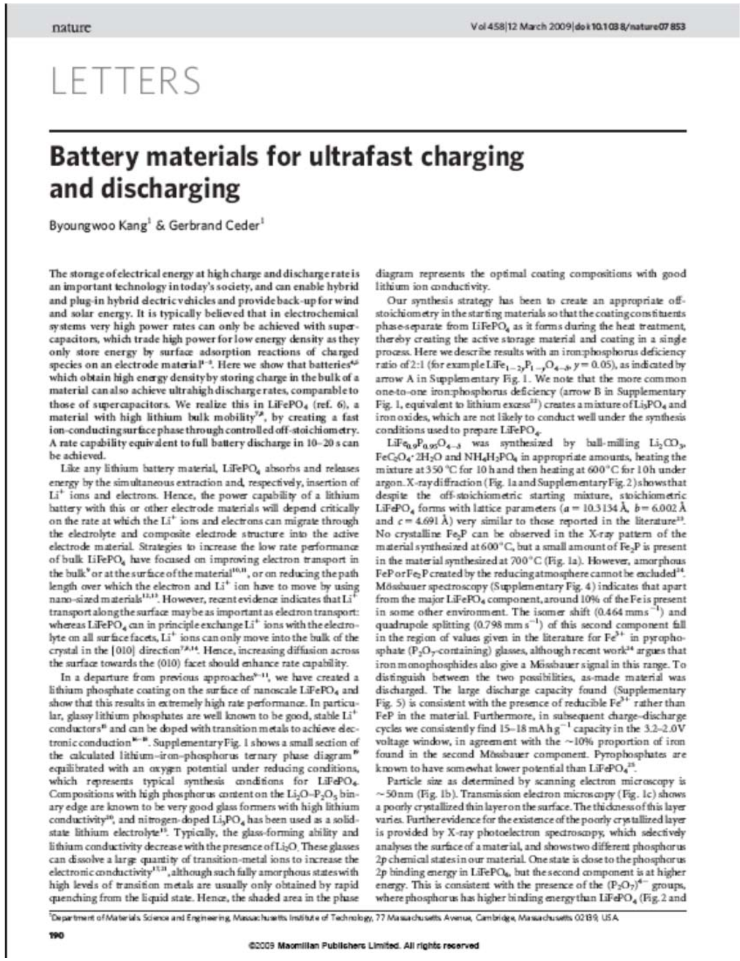
High overpotential:

$$\ln(i) = \ln(i_0) + \frac{(1-\alpha) z F \eta}{RT}$$

Low overpotential:

$$i = i_0 \frac{\alpha z F \eta}{RT}$$

Discussion Nature paper



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LETTERS

Battery materials for ultrafast charging and discharging

Byoungwoo Kang[1] & Gerbrand Ceder[1]

The storage of electrical energy at high charge and discharge rate is an important technology in today's society, and can enable hybrid and plug-in hybrid electric vehicles and provide back-up for wind and solar energy. It is typically believed that in electrochemical systems very high power rates can only be achieved with supercapacitors, which trade high power for low energy density as they only store energy by surface adsorption reactions of charged species on an electrode material[1–3]. Here we show that batteries[4,5] which obtain high energy density by storing charge in the bulk of a material can also achieve ultrahigh discharge rates, comparable to those of supercapacitors. We realize this in $LiFePO_4$ (ref. 6), a material with high lithium bulk mobility[7,8], by creating a fast ion-conducting surface phase through controlled off-stoichiometry. A rate capability equivalent to full battery discharge in 10–20 s can be achieved.

Like any lithium battery material, $LiFePO_4$ absorbs and releases energy by the simultaneous extraction and, respectively, insertion of Li^+ ions and electrons. Hence, the power capability of a lithium battery with this or other electrode materials will depend critically on the rate at which the Li^+ ions and electrons can migrate through the electrolyte and composite electrode structure into the active electrode material. Strategies to increase the low rate performance of bulk $LiFePO_4$ have focused on improving electron transport in the bulk[9] or at the surface of the material[10,11], or on reducing the path length over which the electron and Li^+ ion have to move by using nano-sized materials[12,13]. However, recent evidence indicates that Li^+ transport along the surface may be as important as electron transport: whereas $LiFePO_4$ can in principle exchange Li^+ ions with the electrolyte on all surface facets, Li^+ ions can only move into the bulk of the crystal in the [010] direction[7,8,14]. Hence, increasing diffusion across the surface towards the (010) facet should enhance rate capability.

In a departure from previous approaches[9–11], we have created a lithium phosphate coating on the surface of nanoscale $LiFePO_4$ and show that this results in extremely high rate performance. In particular, glassy lithium phosphates are well known to be good, stable Li^+ conductors[15] and can be doped with transition metals to achieve electronic conduction[16–18]. Supplementary Fig. 1 shows a small section of the calculated lithium–iron–phosphorus ternary phase diagram[19] equilibrated with an oxygen potential under reducing conditions, which represents typical synthesis conditions for $LiFePO_4$. Compositions with high phosphorus content on the Li_2O–P_2O_5 binary edge are known to be very good glass formers with high lithium conductivity[20], and nitrogen-doped Li_3PO_4 has been used as a solid-state lithium electrolyte[21]. Typically, the glass-forming ability and lithium conductivity decrease with the presence of Li_2O. These glasses can dissolve a large quantity of transition-metal ions to increase the electronic conductivity[17,21], although such fully amorphous states with high levels of transition metals are usually only obtained by rapid quenching from the liquid state. Hence, the shaded area in the phase diagram represents the optimal coating compositions with good lithium ion conductivity.

Our synthesis strategy has been to create an appropriate off-stoichiometry in the starting materials so that the coating constituents phase-separate from $LiFePO_4$ as it forms during the heat treatment, thereby creating the active storage material and coating in a single process. Here we describe results with an iron:phosphorus deficiency ratio of 2:1 (for example $LiFe_{1-2y}P_{1-y}O_{4-\delta}$, $y = 0.05$), as indicated by arrow A in Supplementary Fig. 1. We note that the more common one-to-one iron:phosphorus deficiency (arrow B in Supplementary Fig. 1, equivalent to lithium excess[22]) creates a mixture of Li_3PO_4 and iron oxides, which are not likely to conduct well under the synthesis conditions used to prepare $LiFePO_4$.

$LiFe_{0.9}P_{0.95}O_{4-\delta}$ was synthesized by ball-milling Li_2CO_3, $FeC_2O_4 \cdot 2H_2O$ and $NH_4H_2PO_4$ in appropriate amounts, heating the mixture at 350 °C for 10 h and then heating at 600 °C for 10 h under argon. X-ray diffraction (Fig. 1a and Supplementary Fig. 2) shows that despite the off-stoichiometric starting mixture, stoichiometric $LiFePO_4$ forms with lattice parameters ($a = 10.3134$ Å, $b = 6.002$ Å and $c = 4.691$ Å) very similar to those reported in the literature[23]. No crystalline Fe_2P can be observed in the X-ray pattern of the material synthesized at 600 °C, but a small amount of Fe_2P is present in the material synthesized at 700 °C (Fig. 1a). However, amorphous FeP or Fe_2P created by the reducing atmosphere cannot be excluded[24]. Mössbauer spectroscopy (Supplementary Fig. 4) indicates that apart from the major $LiFePO_4$ component, around 10% of the Fe is present in some other environment. The isomer shift ($0.464\ \mathrm{mm\,s^{-1}}$) and quadrupole splitting ($0.798\ \mathrm{mm\,s^{-1}}$) of this second component fall in the region of values given in the literature for Fe^{3+} in pyrophosphate (P_2O_7-containing) glasses, although recent work[24] argues that iron monophosphides also give a Mössbauer signal in this range. To distinguish between the two possibilities, as-made material was discharged. The large discharge capacity found (Supplementary Fig. 5) is consistent with the presence of reducible Fe^{3+} rather than FeP in the material. Furthermore, in subsequent charge–discharge cycles we consistently find $15\text{–}18\ \mathrm{mA\,h\,g^{-1}}$ capacity in the 3.2–2.0 V voltage window, in agreement with the ~10% proportion of iron found in the second Mössbauer component. Pyrophosphates are known to have somewhat lower potential than $LiFePO_4$[25].

Particle size as determined by scanning electron microscopy is ~50 nm (Fig. 1b). Transmission electron microscopy (Fig. 1c) shows a poorly crystallized thin layer on the surface. The thickness of this layer varies. Further evidence for the existence of the poorly crystallized layer is provided by X-ray photoelectron spectroscopy, which selectively analyses the surface of a material, and shows two different phosphorus 2p chemical states in our material. One state is close to the phosphorus 2p binding energy in $LiFePO_4$, but the second component is at higher energy. This is consistent with the presence of the $(P_2O_7)^{4-}$ groups, where phosphorus has higher binding energy than $LiFePO_4$ (Fig. 2 and

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Question 5

How will the electrode loading (mg/cm^2) will affect the charging time?

a) No effect

b) Increase charging time

c) Decrease charging time

d) no clue

Question 5

NC rate: 1/N hours total (dis)charge

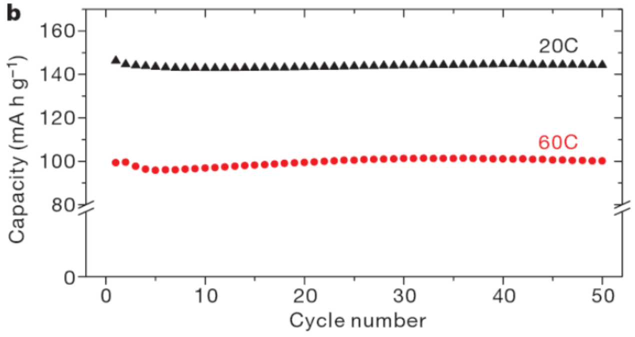
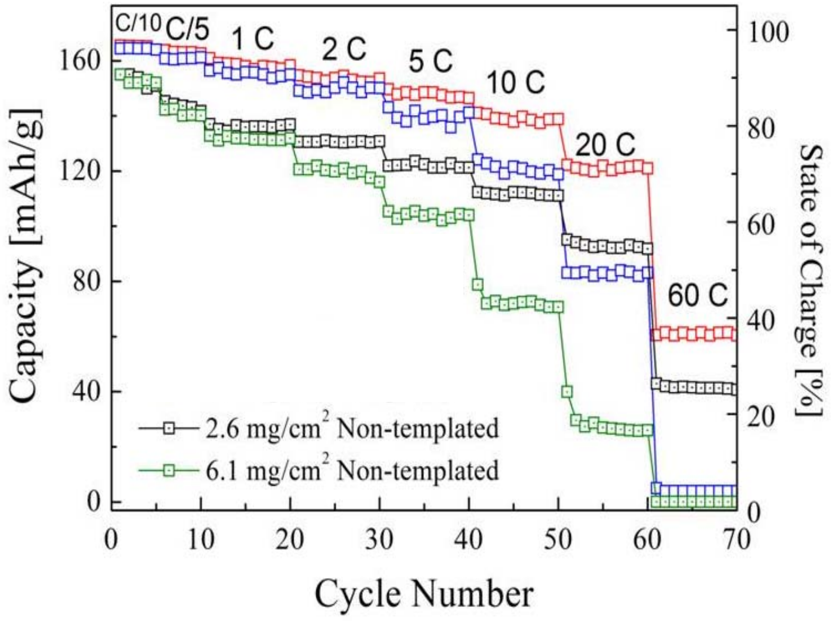


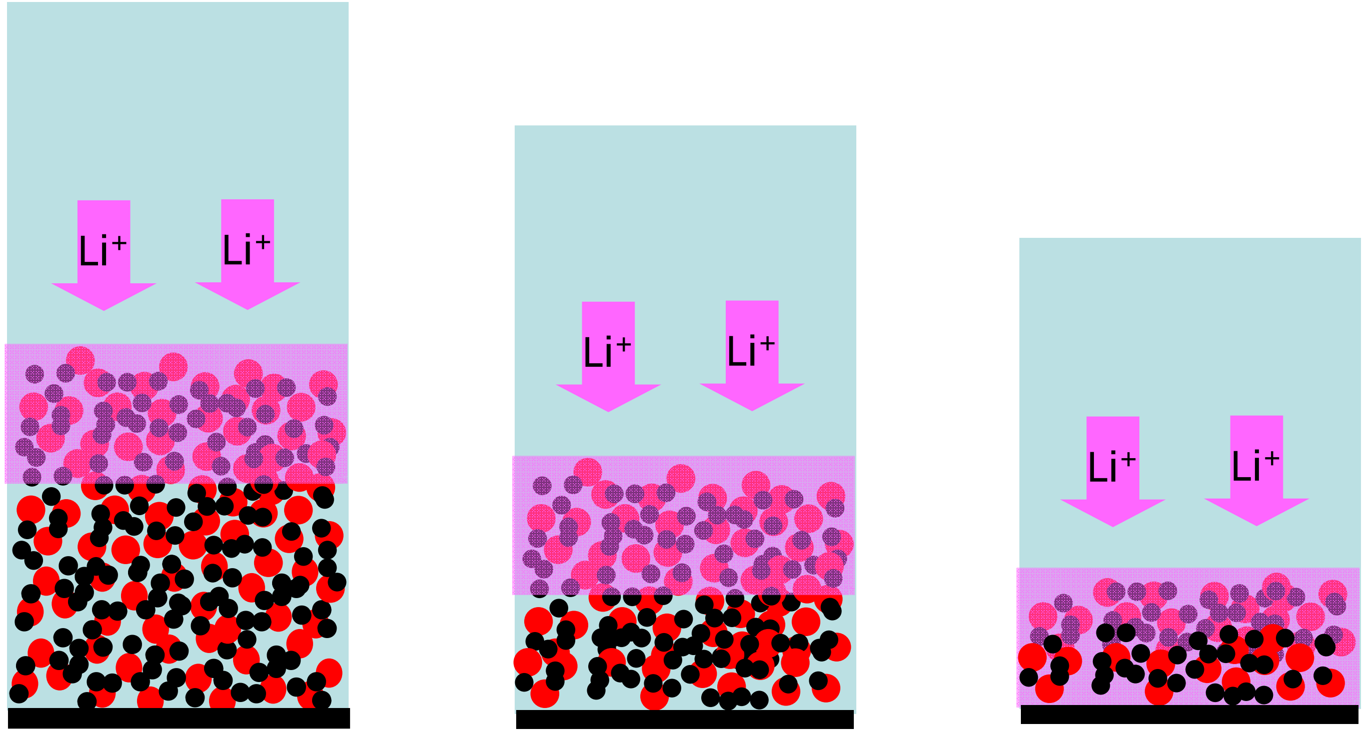
Figure 3 | Discharge rate capability and capacity retention for $LiFe_{0.9}P_{0.95}O_{4-\delta}$ synthesized at 600 °C. a, Discharge rate capability after charging at C/5 and holding at 4.3 V until the current reaches C/60. C/*n* denotes the rate at which a full charge or discharge takes *n* hours. The loading density of the electrode is 3.86 mg cm^{-2}. At 2C, the capacity is close to the theoretical value. **b**, Capacity retentions when performing full charge–discharge cycles at constant 20C and 60C current rates for 50 cycles. The loading density of the electrode is 3.60 mg cm^{-2} for the 20C rate and 2.71 mg cm^{-2} for the 60C rate. The voltage window is approximately 2.5–4.3 V. The electrode formulation is active material (80 wt%), carbon (15 wt%) and binder (5 wt%).



Question 5

Diffusion distance: $d \approx \sqrt{\pi D t}$

Diffusion time: $t \approx \dfrac{d^2}{\pi D}$



Question 6

Assume the charging time increases with increasing electrode loading (mg/cm^2) (equivalent with increasing electrode thickness). Which charge transport step do you conclude could to be rate limiting:

a) Electronic conduction through the electrode

b) Li-ion conduction through the electrolyte

c) Li-ion conduction over the surface of the electrode

d) Li-ion conduction through the electrode

e) Both a) and d)

f) No clue

Question 6

Resistance that scales with the electrode thickness:

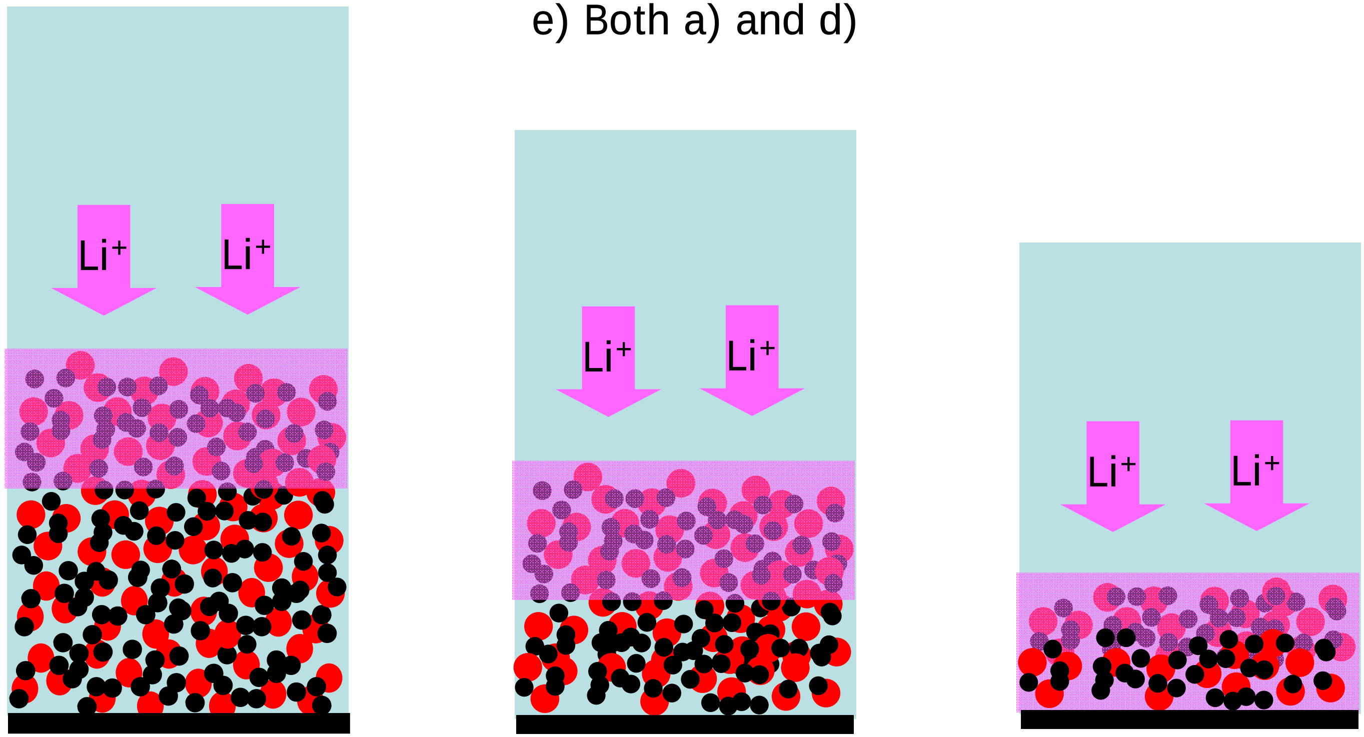
a) Electronic conduction through the electrode

b) Li-ion conduction through the electrolyte

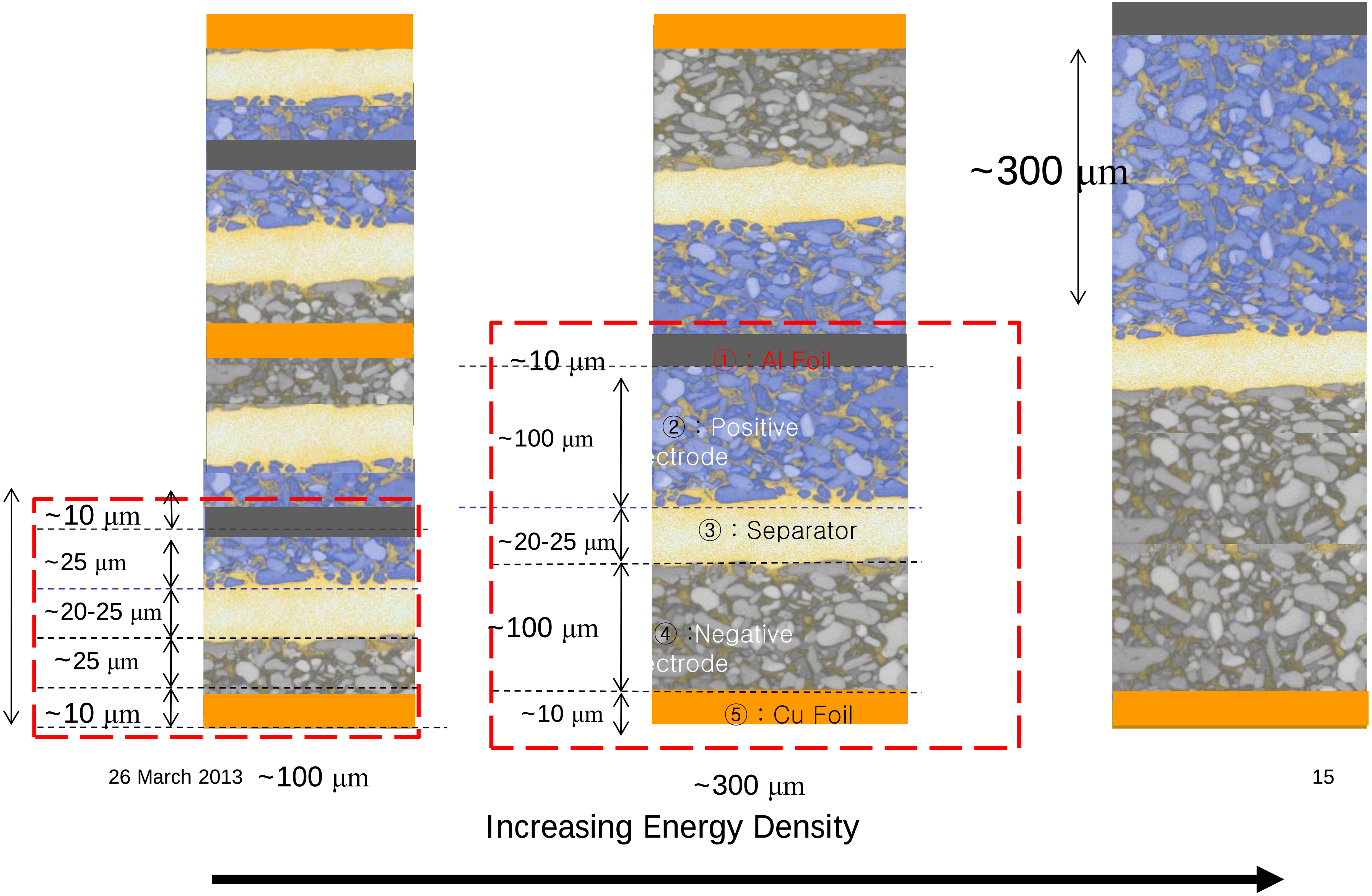
c) Li-ion conduction over the surface of the electrode

d) Li-ion conduction through the electrode

e) Both a) and d)

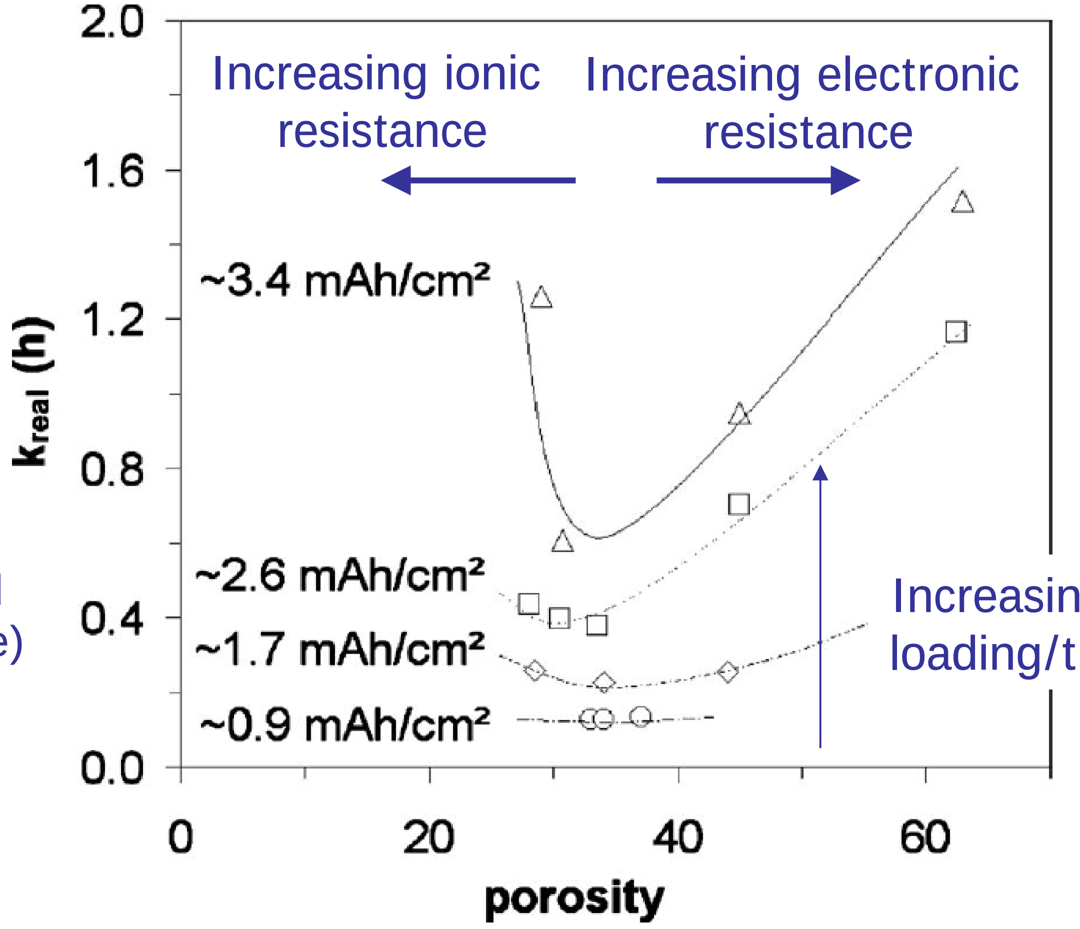


Energy density: amount of active material



Increasing Energy Density

Ionic versus electronic conduction of the electrode



Increasing ionic resistance

Increasing electronic resistance

Increasing electrode loading/thickness

Time constant related to the (discharge time)

Question 7

By adding relatively more carbon black faster charging may be the result of:

a) Better electronic conduction in the electrode

b) better Li-ion conduction through the electrode

c) Less storage material ($LiFePO_4$) in the electrode

d) Both a) and c)

e) No clue

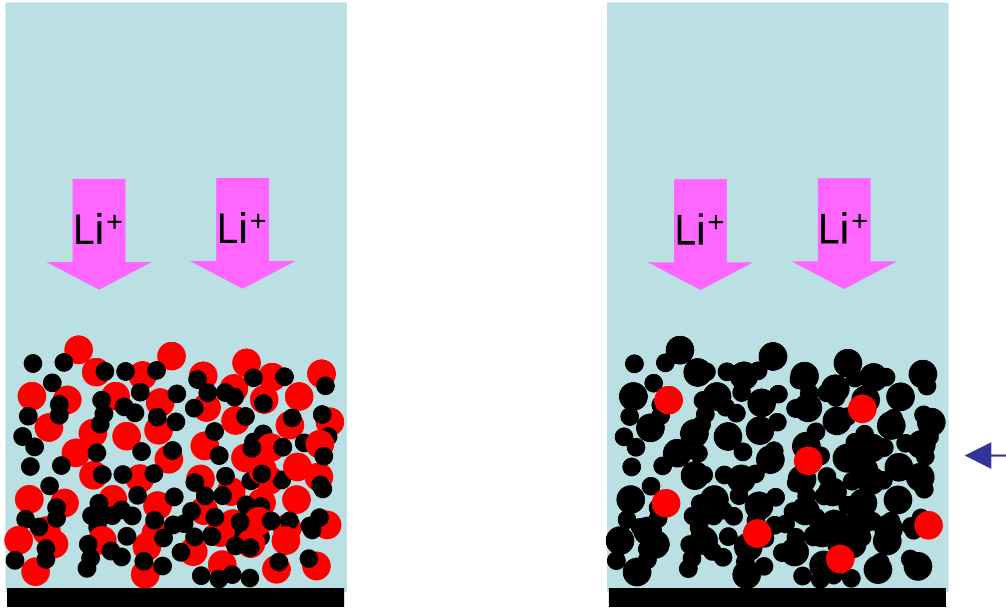
Question 7

Yes: Better electronic conduction in the electrode => a)

But also Less storage material ($LiFePO_4$) in the electrode

Results in less Li-ion flux required through the electrode => c)

So answer d) both a) and c)

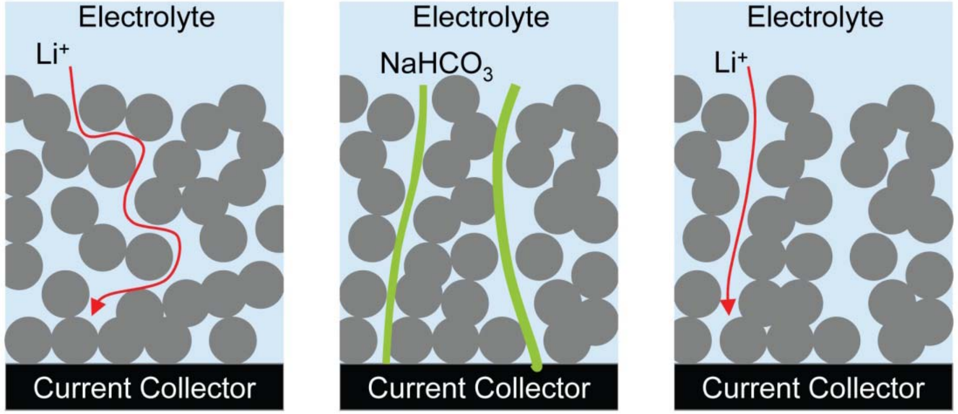


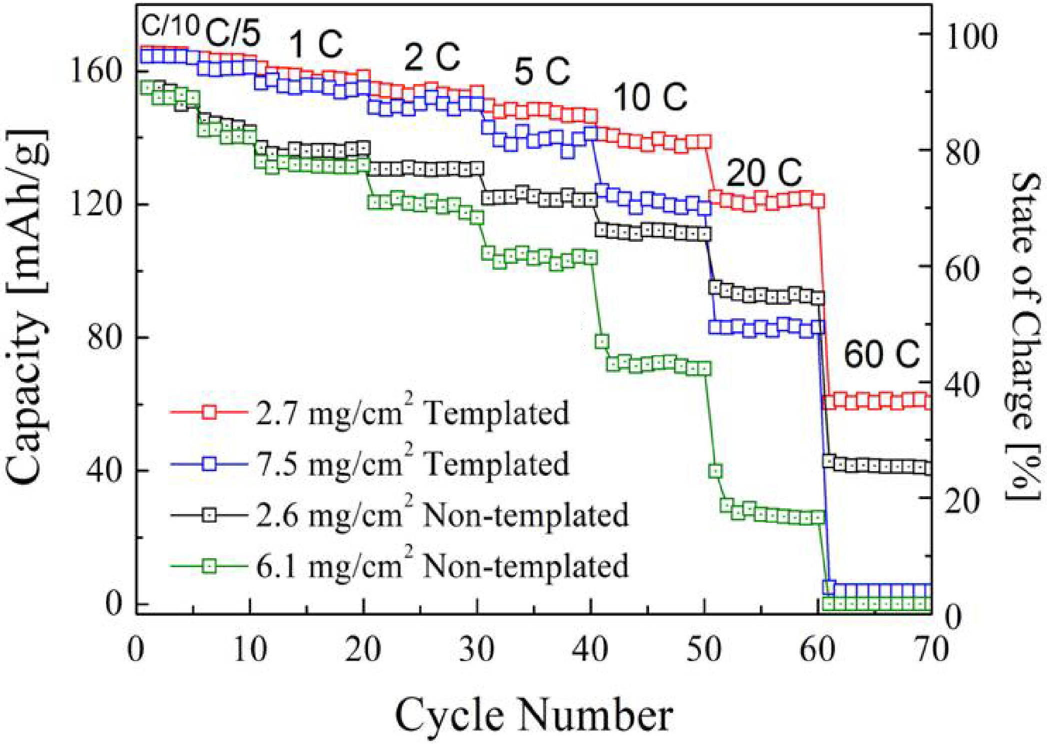
Note:
Low energy density!

Conclusions

High power density	↔	**High energy density**
Thin electrodes		Thick electrodes
Porous electrodes		Dense electrodes
Nano structured electrodes		Large particles
(low packing density)		(large packing density)
“Diluted” electrodes		Concentrated electrodes
(carbon addition)		(pure storage material)

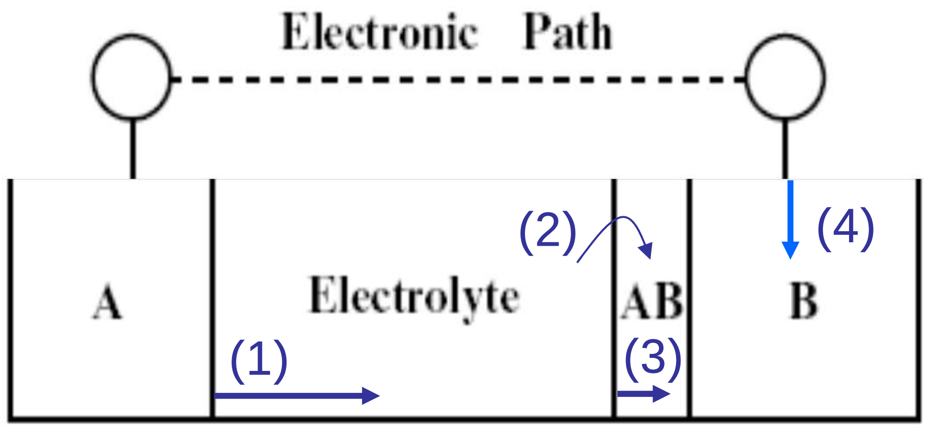
Improving the electrode morphology





Summarize charge transport

(1a) Ionic transport through electrolyte:	No problem
(1b) Ionic transport through the electrolyte in the electrode	In practice rate limiting Requires smart electrode design
(2) Charge transfer from electrolyte to the electrode:	Usually not rate limiting in Li-ion batteries, it usually is in other types of batteries.
(3) Ionic transport through the electrodes:	Often rate limiting, not for small particles!
(4) Electronic transport through the electrodes:	Often rate limiting, can be solved with carbon



$$\eta_{Total} = \eta_1 + \eta_2 + \eta_3 + \eta_4$$

$$r_{i,Total} = r_1 + r_2 + r_3 + r_4$$

Program Batteries

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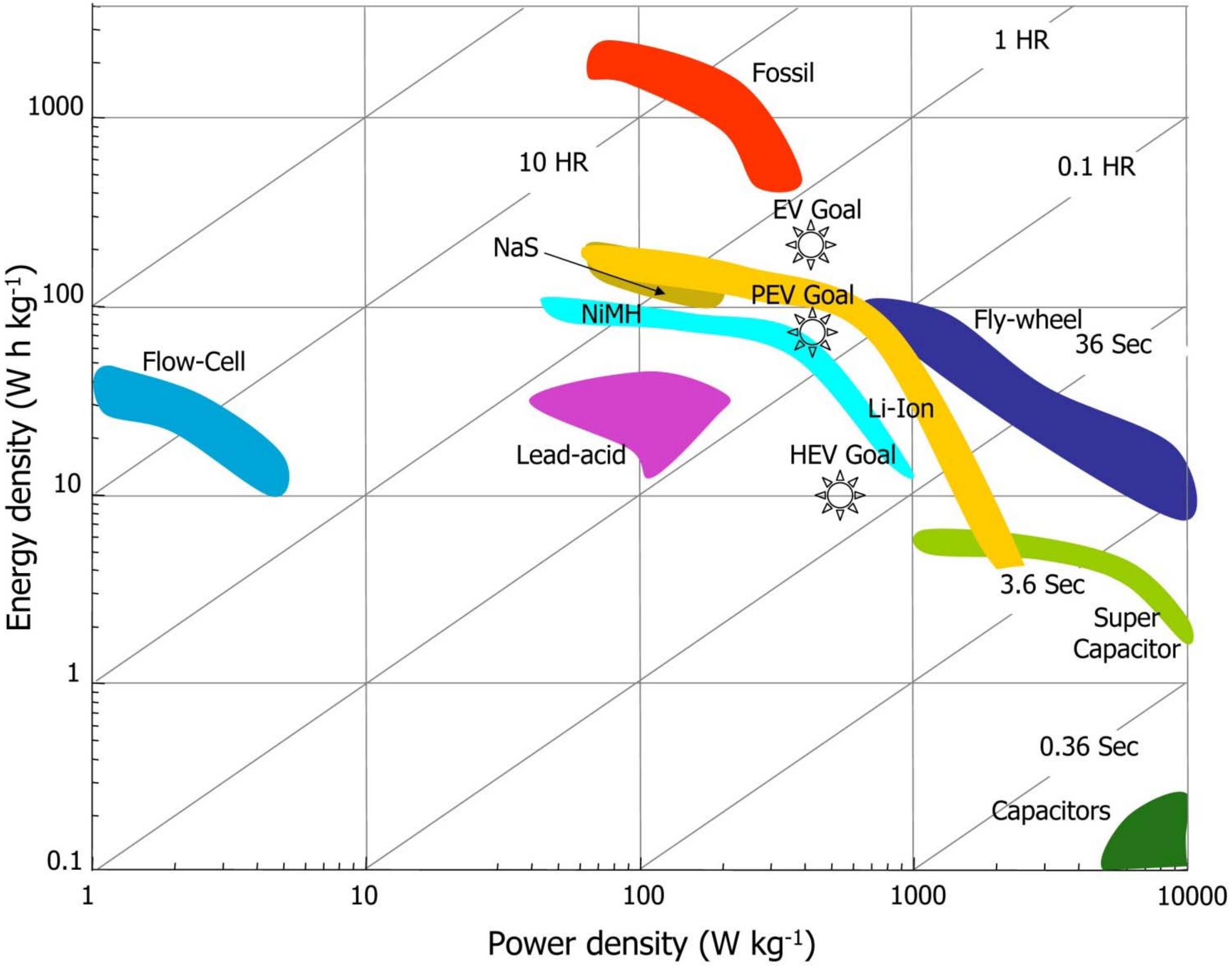
Supercapacitors

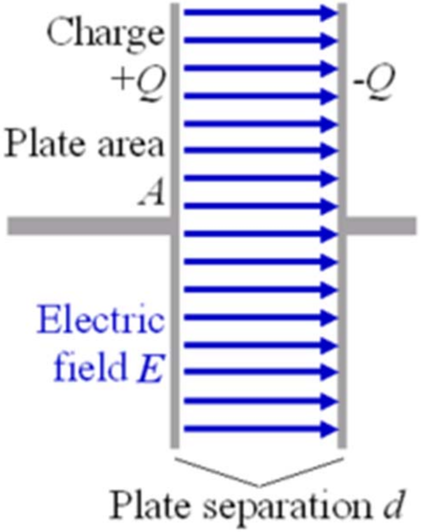
Ragone Plot Energy vs Power density



Capacitors

Capacitance *(F):* $C = \dfrac{Q}{V}$

Q charge *(Coulomb), V* potential difference between plates *(V)*



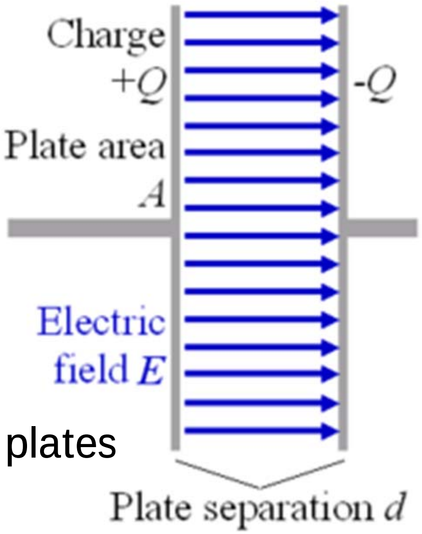
Flat plate capacitor: $C = \dfrac{\varepsilon A}{d}$

ε*:* permittivity *(C²/Jm), A:* plate area, *d:* distance between the plates
Permittivity: ability transmit an electric field

Stored energy *(J):* $E_{Stored} = \dfrac{1}{2} C V^2 = \dfrac{1}{2} Q V = \dfrac{\varepsilon A V^2}{2d}$

Power *(W):* $P = \dfrac{V^2}{4R}$

Solid Capacitors



$$E_{Stored} = \frac{1}{2}CV^2 = \frac{1}{2}QV = \frac{\varepsilon A V^2}{2d}$$

Flat plate capacitor:

ε*:* permittivity *(C^2/Jm), A:* plate area*, d:* distance between the plates
Permittivity: ability transmit an electric field

Increase energy density by thin dielectric with high permittivity and high breakdown voltage

Conventional capacitors (conducting plate/vacuum): 360 J/kg (0.1 Wh/kg)

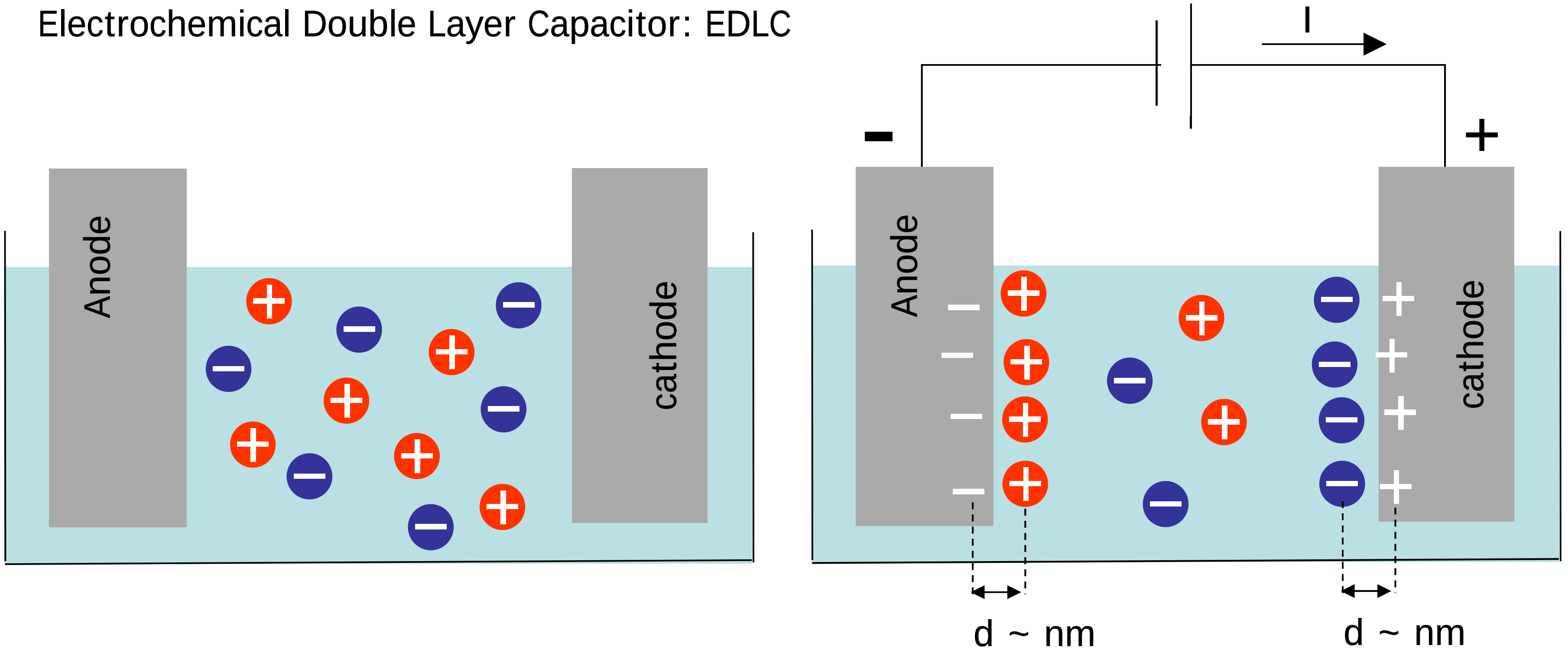
New materials (high permitivity/high voltage breakdown): 2.5 kJ/kg (0.7 Wh/kg)

Permitivities:		
	Vaccuum:	1
	Water:	80
	Titanium oxide:	90
	Barium titanate:	1250

Super Capacitors or EDLC

Assume an electrolyte with + and – ions and
an electrode that does not react with the ions.

Electrochemical double layer is created
Electrochemical Double Layer Capacitor: EDLC

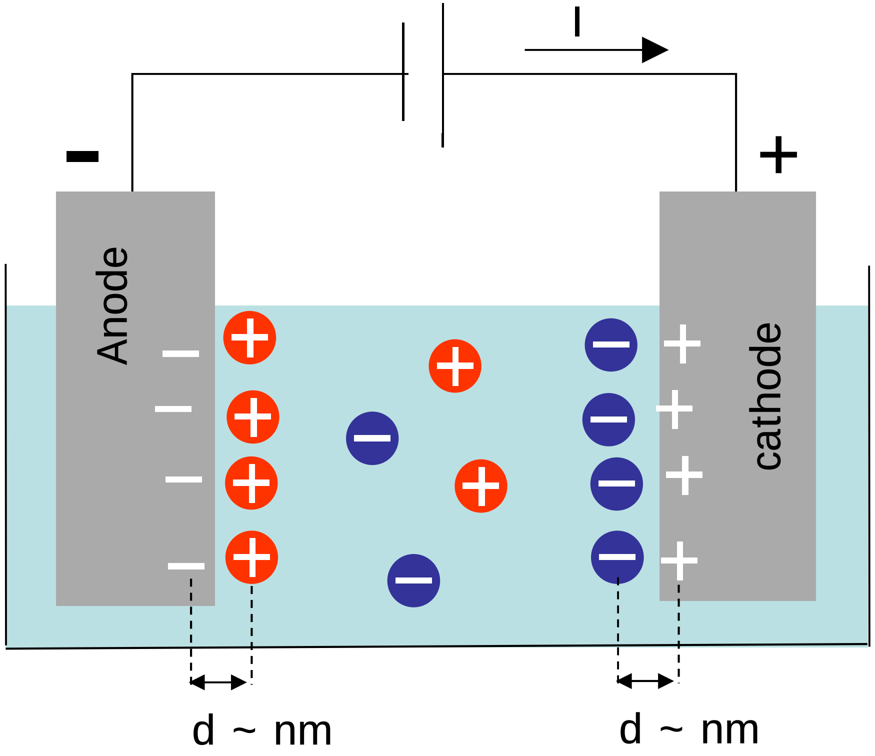


Question Super Capacitors

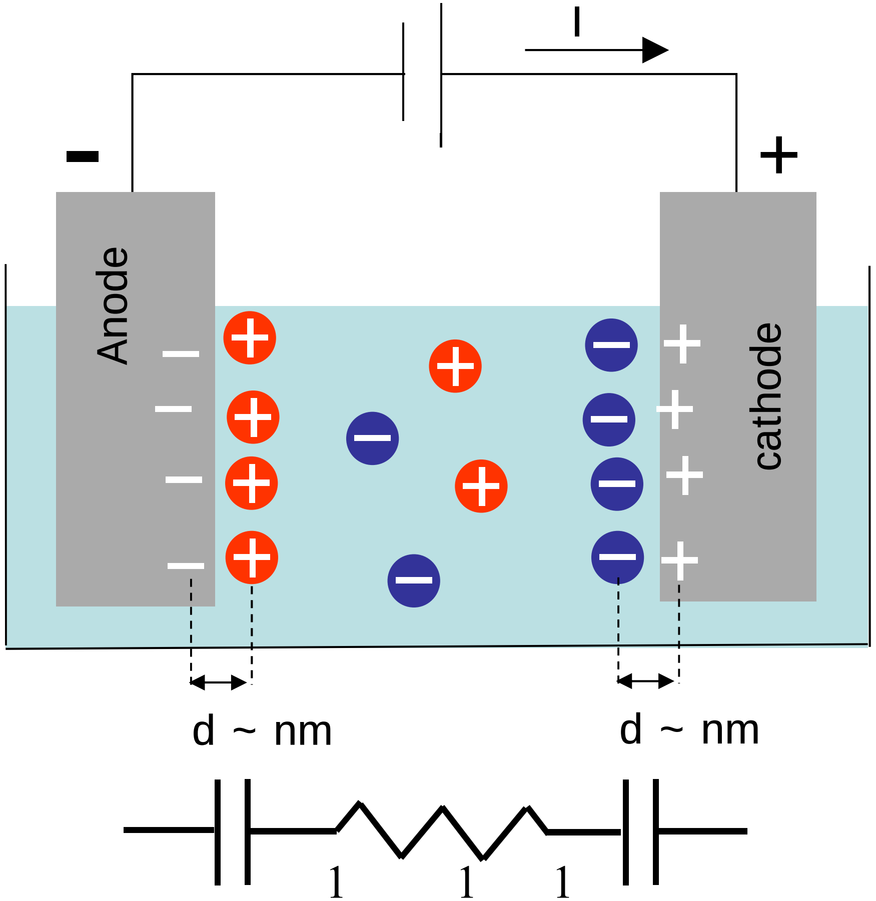
What makes the energy density of super capacitors high?

a) Large V and ε
b) Large A and small d
c) Large V and A
d) Large ε and small d

$$E_{Stored} = \frac{1}{2}CV^2 = \frac{1}{2}QV = \frac{\varepsilon A V^2}{2d}$$



Super Capacitors or EDLC



$$\frac{1}{C_{EDLC}} = \frac{1}{C_1} + \frac{1}{C_2}$$

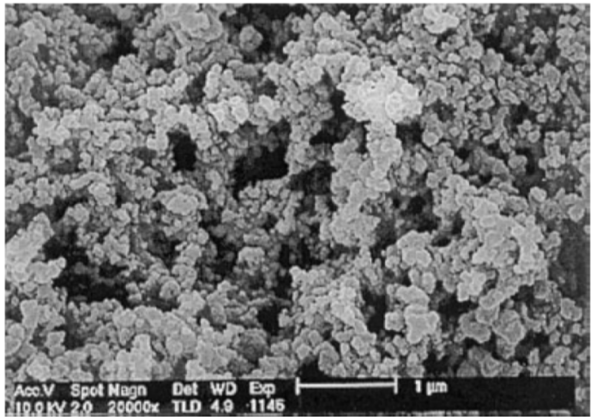
$$C = \frac{Q}{V} = \frac{\varepsilon A}{d}$$

$$E_{Stored} = \frac{1}{2} C V^2 = \frac{1}{2} Q V = \frac{\varepsilon A V^2}{2d}$$

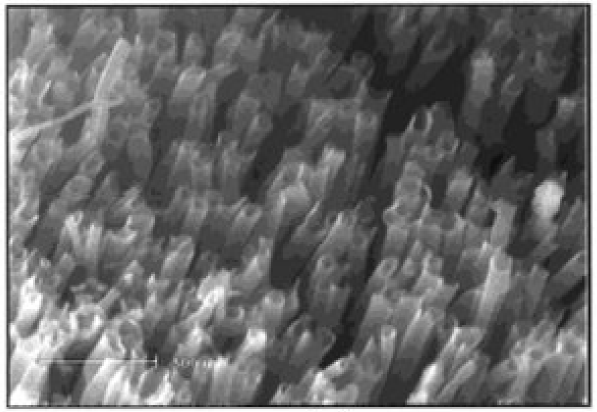
Capacitors: V and ε large, d large

SuperCap: V and ε small, d small and A large
(answer b)

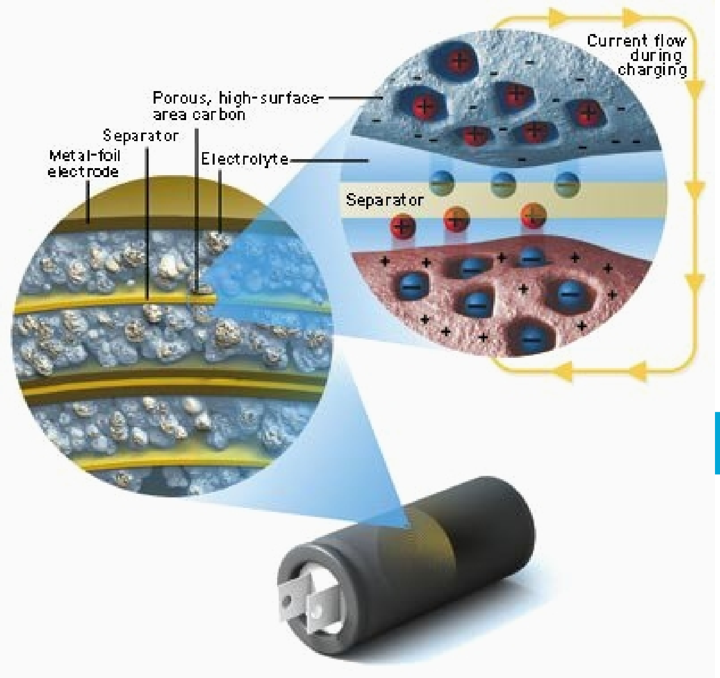
Super Capacitors or EDLC



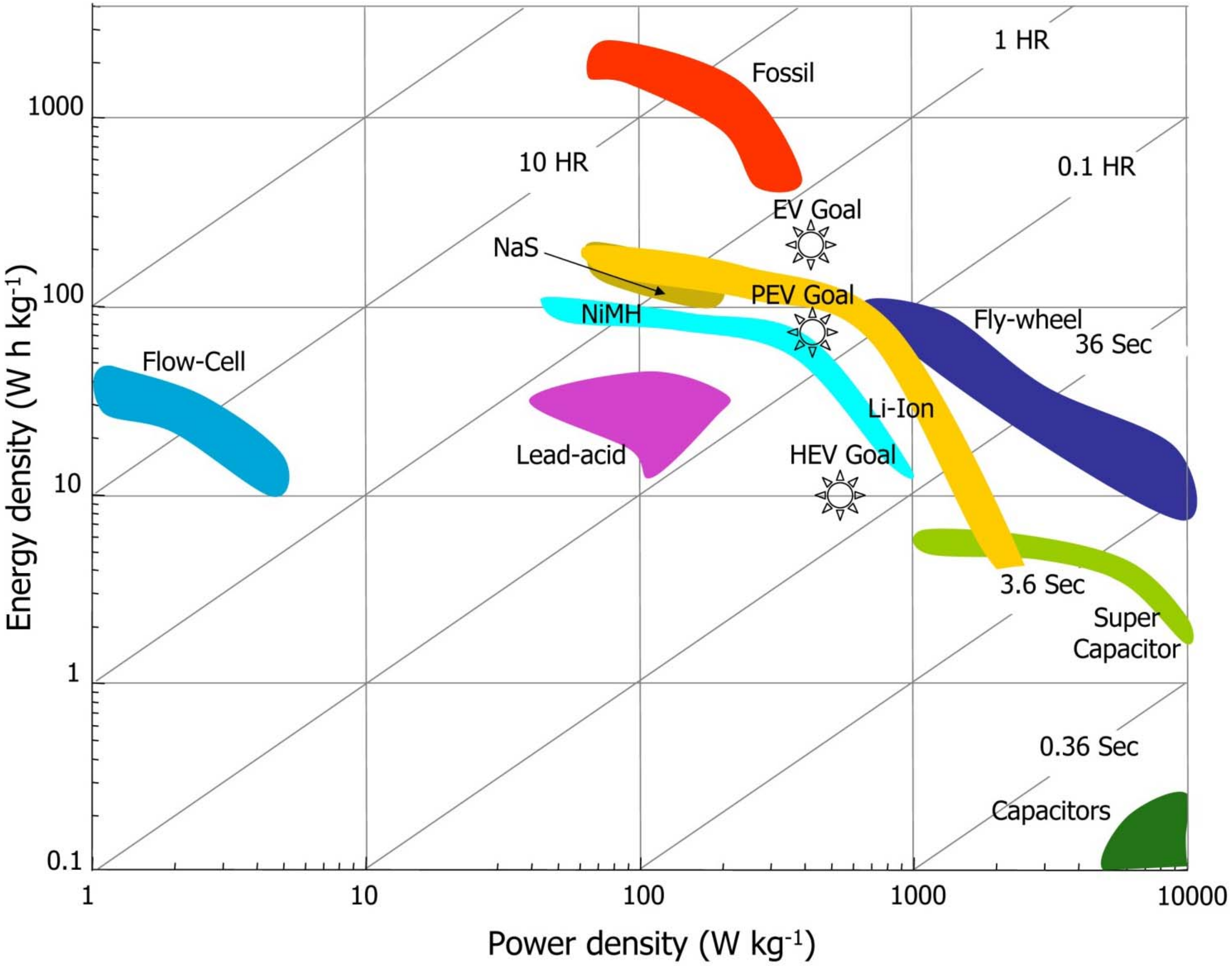
Nano porous carbon electrode, A = 1500 m^2/g



Hollow carbon nano tubes, A ~ 2200 m^2/g

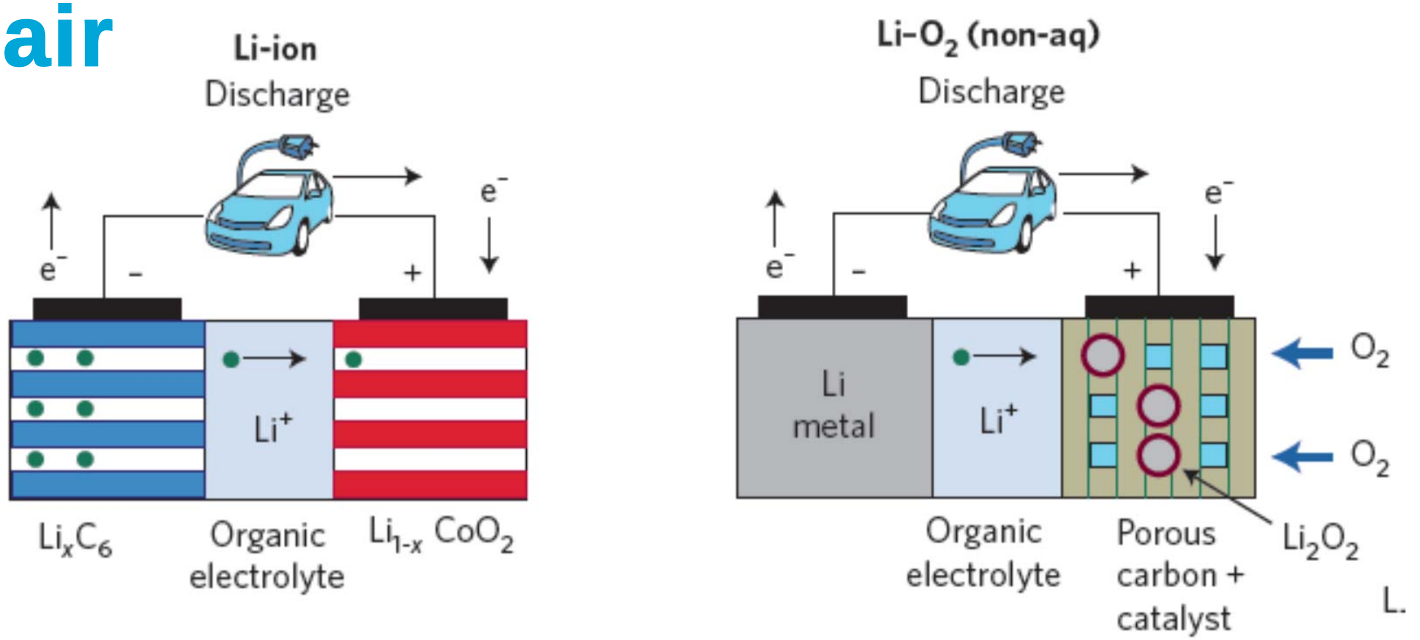


Ragone Plot Energy vs Power density



Future High energy density systems: Li-air and Li-sulfur

Li-air

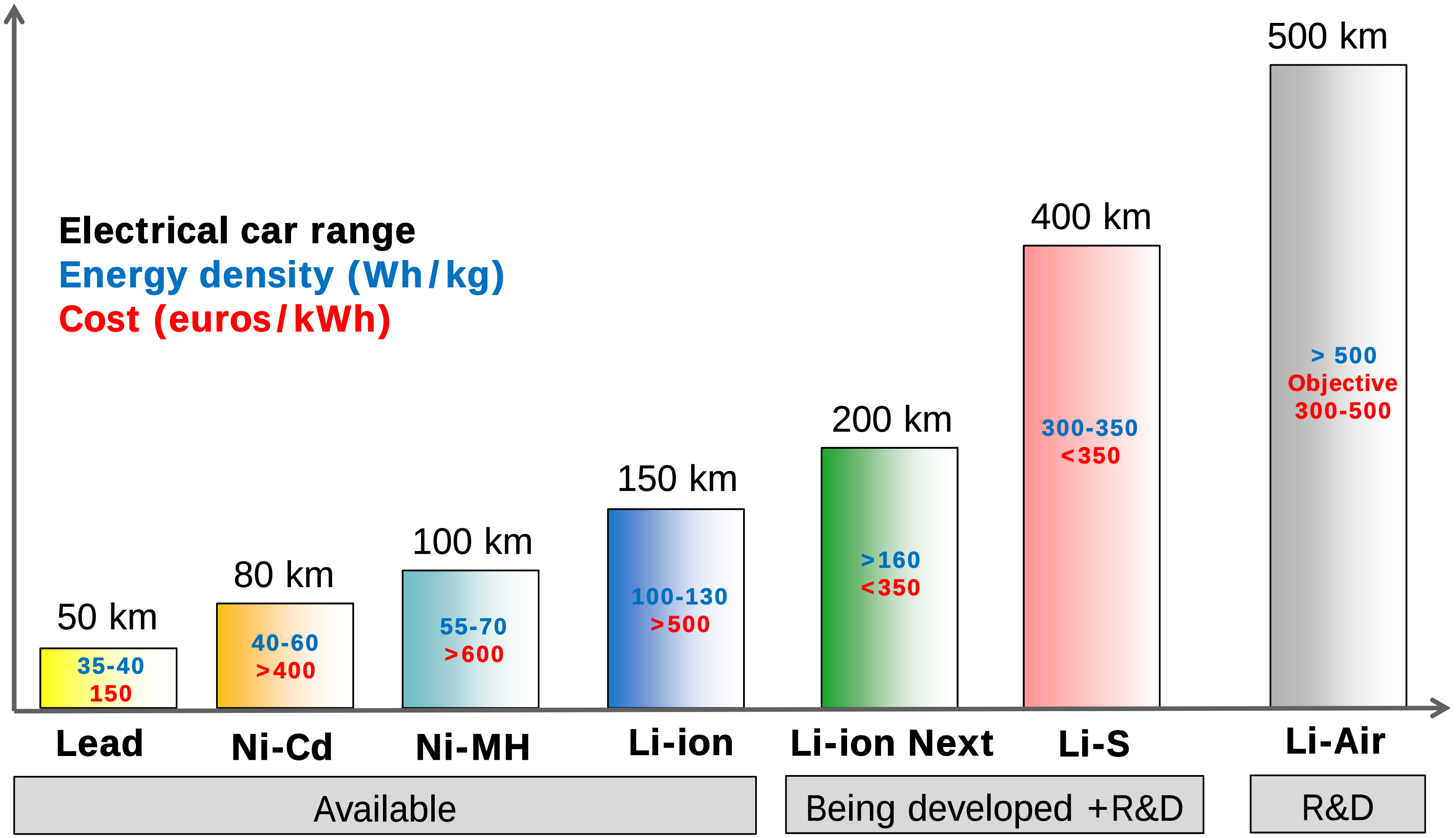


$½\ C_6Li + Li_{0.5}CoO_2 \leftrightarrow 3C + LiCoO_2$

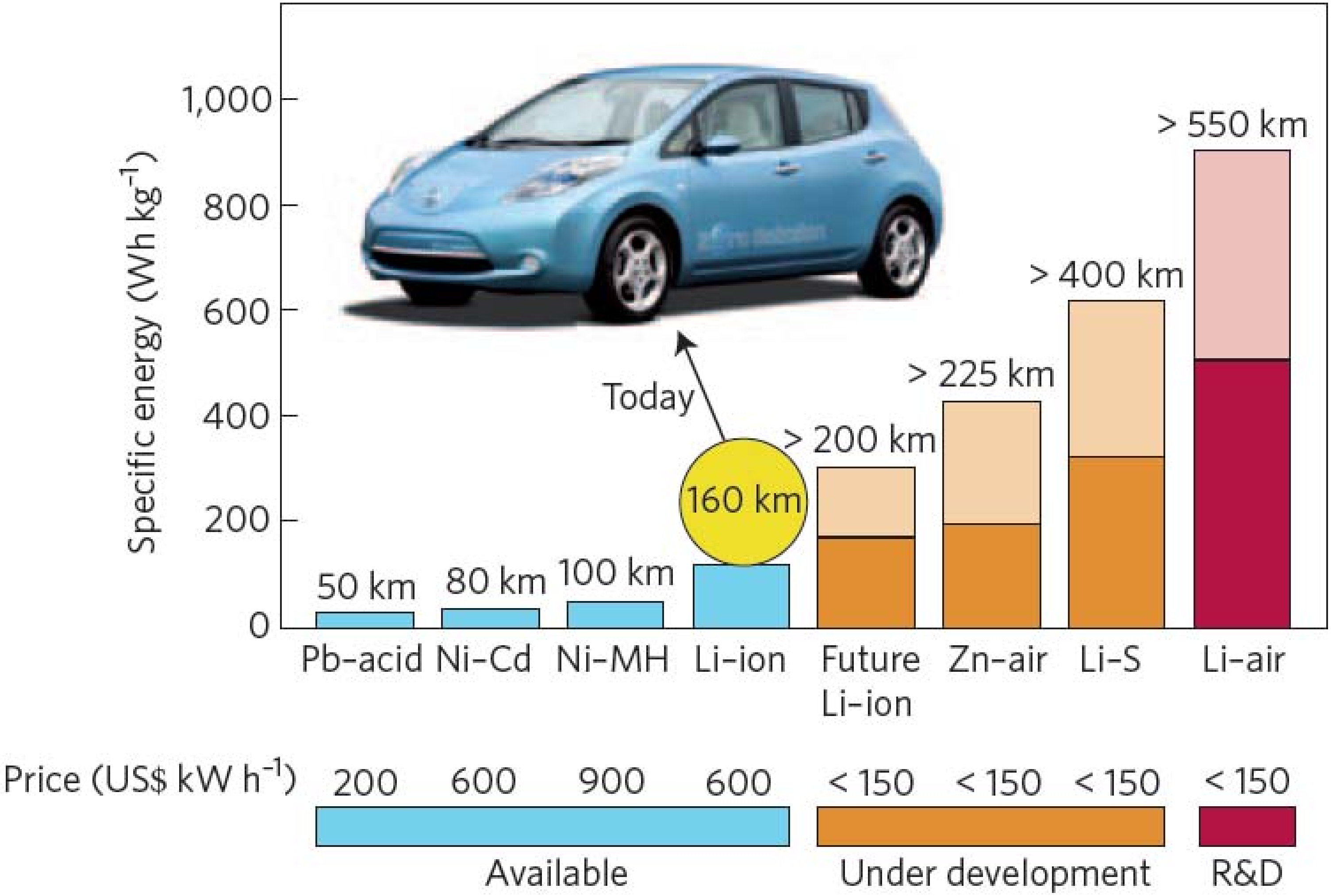
$2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$

Note: $2Li + Li_2O_2 \rightarrow 2Li_2O$
even higher capacity but appears not to occur, and if it occurs it seems to be irreversible

Li-air and Li-sulfur



Li-air and Li-sulfur



Question Li-air

Given the molecular mass of Li_2O_2 = 46 g/mol, and Faraday's constant = 96500 C/mol, what is the capacity of the Li_2O_2 electrode?

a) ~2100 C/g
b) ~4200 C/g
c) ~ 1050 C/g
d) ~ no clue

Capacity Li_2O_2:

M=2x7+2x16=46 g/mol
F=96500 C/mol
Cap=2F/M=4200 C/g

Question Li-air

Given the capacity of Li_2O_2 = 4200 C/g as positive electrode, and Li-metal as negative electrode giving a voltage of ~ 3 V, what would be the theoretical energy density of this battery? (1 Ah = 3600 C)?

a) ~ 1000 Wh/kg
b) ~ 7 Wh/g
c) ~ 3.5 Wh/g
d) ~ no clue

Capacity Li_2O_2: M=2x7+2x16=46 g/mol
F=96500 C/mol
Cap=2F/M=4200 C/g = 1.17 Ah/g

Energy density Li-metal/Li_2O_2: $E_{dens} = E_{cell} x Cap$ = 3.505 Wh/g

Question Li-air

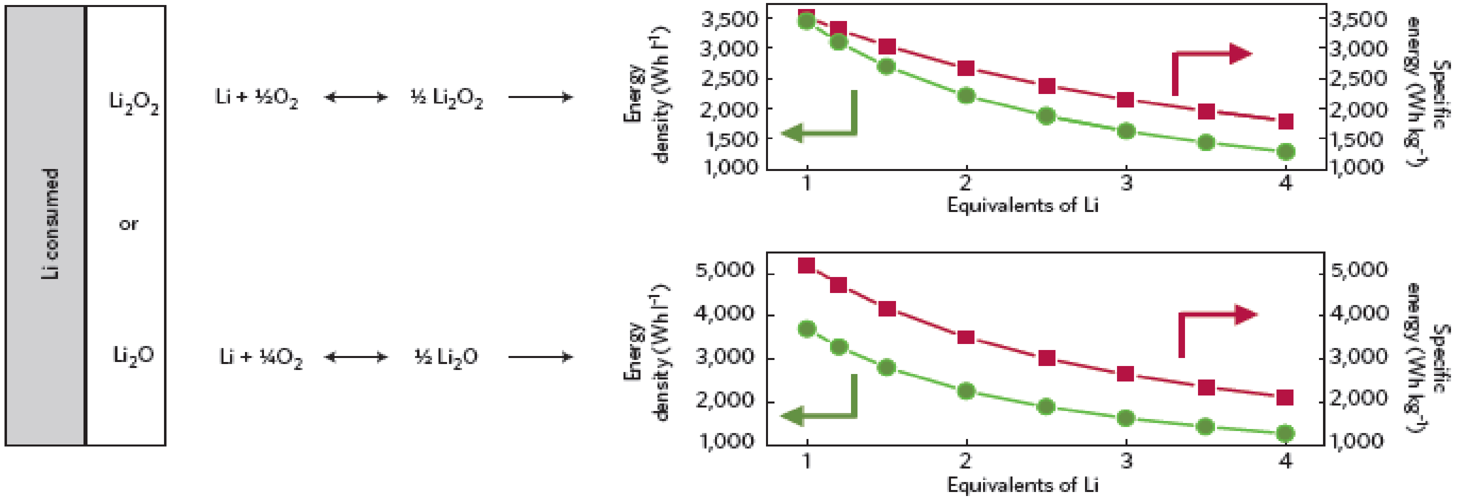
What makes the practical energy density lower?

a) Loss of Li-ions in side reactions (need of larger Li-metal electrode)
b) Li_2O_2 requires porous carbon
c) Weight of electrolyte and packing
d) a)-c)
e) ~ no clue

Energy density due to oversized Li-electrode

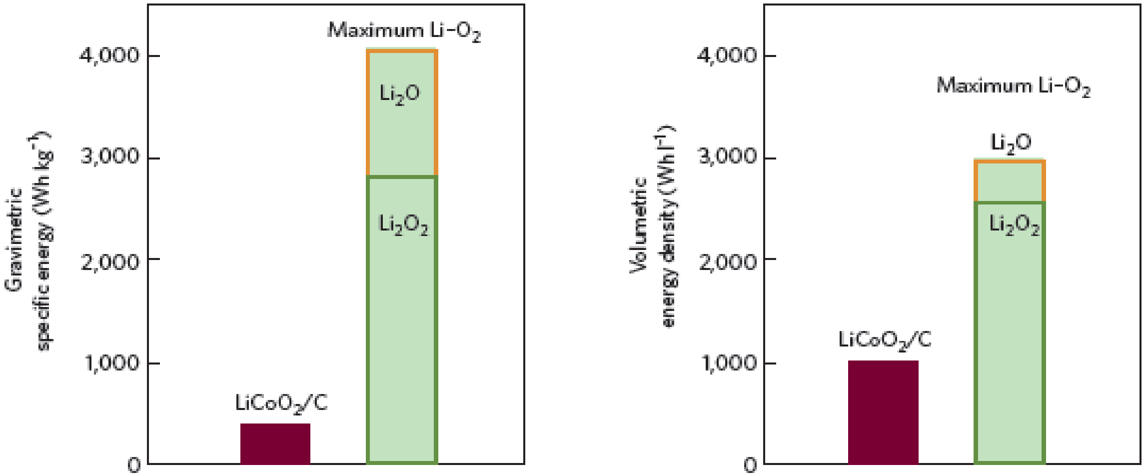
Reasons for additional Li metal (oversized Li-electrode):

a) Li-metal operates at 0V vs Li/Li^+ below the electrolyte stability window -> Li-ions react with electrolyte -> SEI formation
b) O_2^- radical reacts with electrolytes (all electrolytes up to date) and Li-salts (it has a very high nucleophilic strength creating new bonds by donating electrons)



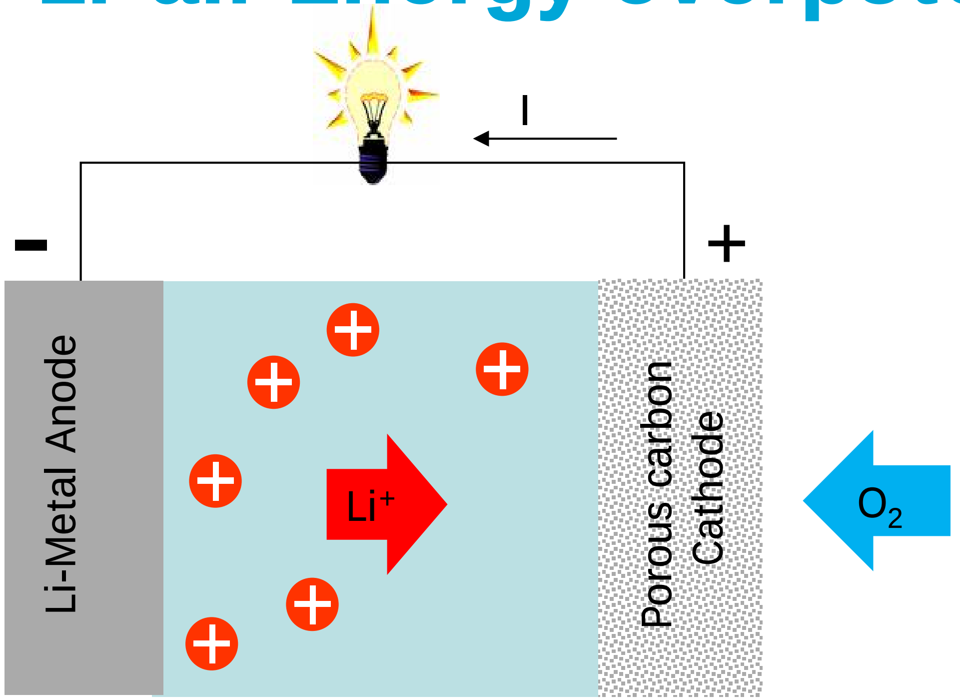
Theoretical Energy density Li-metal/Li_2O_2: $E_{dens} = E_{cell} x Cap = 3.505$ Wh/g

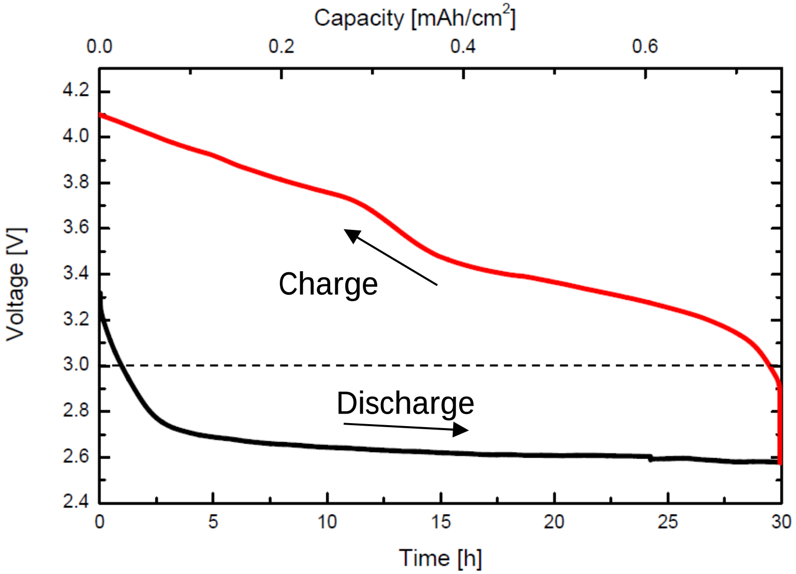
Energy density due to porous carbon membrane



Theoretical Energy density Li-metal/Li_2O_2: $E_{dens} = E_{cell} x Cap = 3.505$ Wh/g

Li-air Energy overpotential

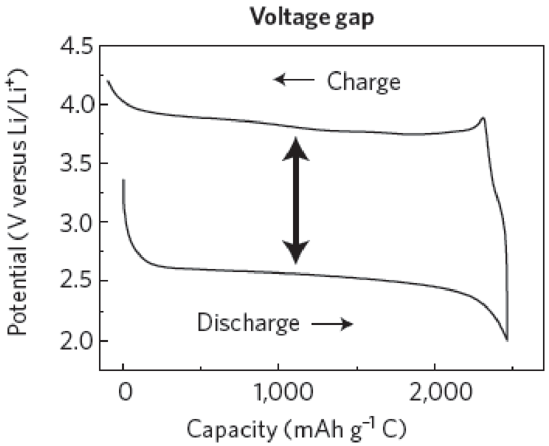




Discharge:	Anode/Oxidation	$Li \rightarrow Li^+ + e^-$
	Cathode/Reduction	$2Li^+ + 2e^- + O_2 \rightarrow ½Li_2O_2$
	Total	$2Li + O_2 \rightarrow ½Li_2O_2$

Theoretical average voltage ~ 3V

Origin of polarization



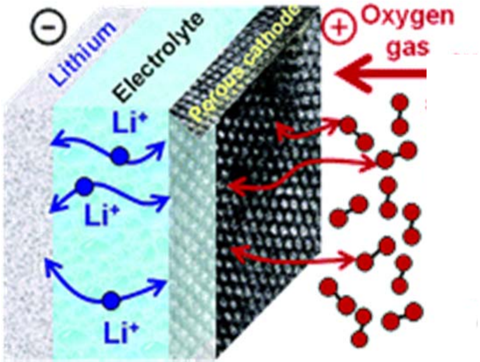
Internal Resistance:

(a) Large polarization due to blocking of the O_2 by formation of Li_2O_2 and poor electronic/ionic conductivity Li_2O_2
(b) Over potential for the oxidation of $Li_2O_2 \rightarrow 2Li^+ + e^- + O_2$

Thermodynamic:

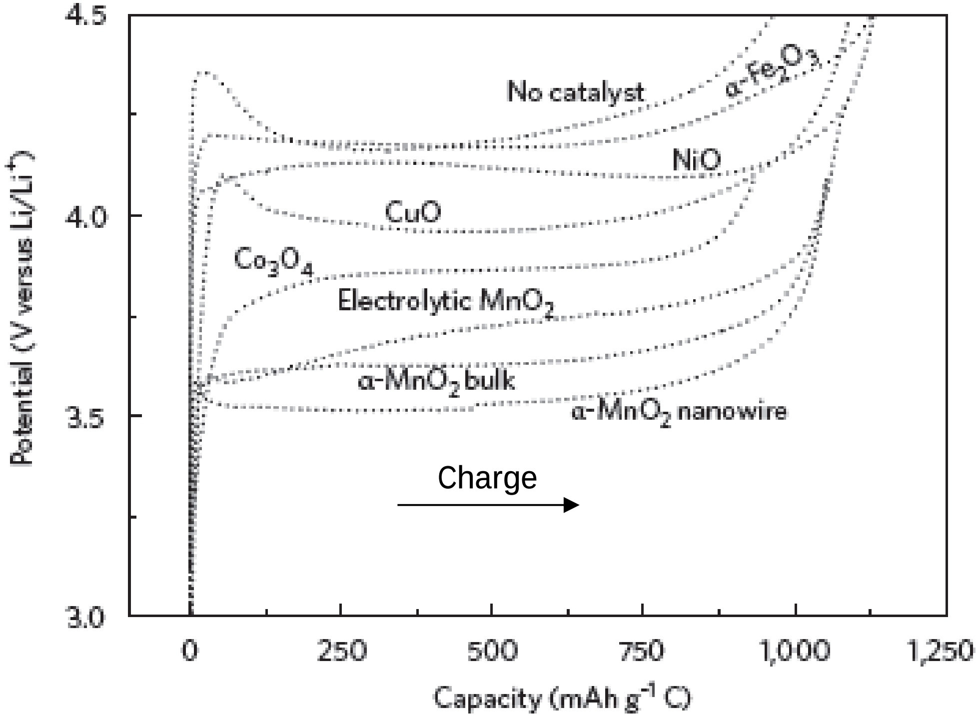
(c) Difference in reaction path formation and deformation Li_2O_2

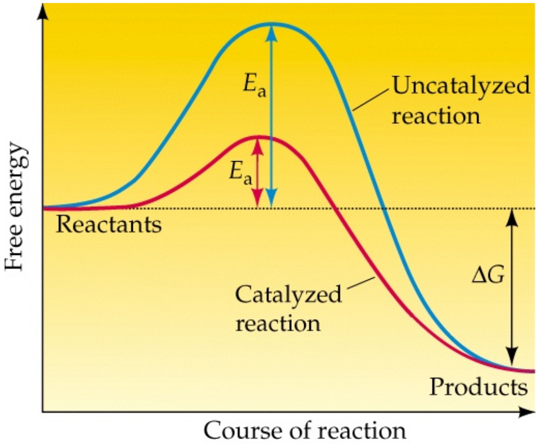
(a)



Origin of polarization

(b) Over potential for the oxidation of Li_2O_2 -> $2Li^+ + e^- + O_2$





Origin of polarization

(c) Difference in reaction path formation and deformation Li_2O_2

Discharge: $Li^+ + e^- + O_2 \rightarrow Li_2O_2$

Reality (concencus)

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

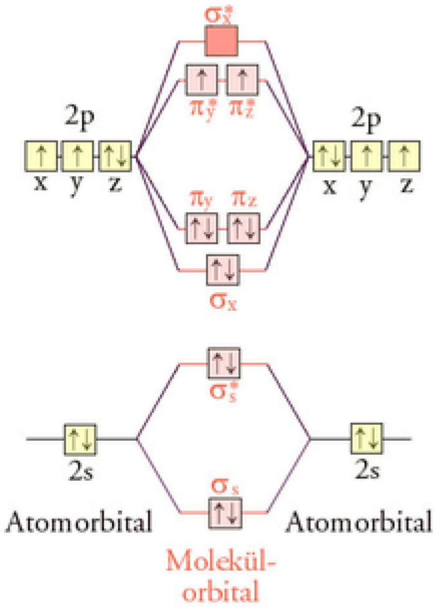
$O_2^- + Li^+ \rightarrow LiO_2$

$2LiO_2 \rightarrow Li_2O_2 + O_2$

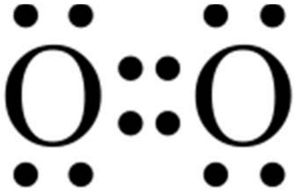
Charge: $Li_2O_2 \rightarrow Li^+ + e^- + O_2$

Difference in reaction path between discharge and charge -> difference in change in Free energy (loss of Free energy during discharge)

Does not violate reversiblity of this reactions, but oxidation of Li_2O_2 is just much easier than reduction of O_2


σ*x
π*y π*z
2p
x y z
2p
x y z
πy πz
σx
σ*s
2s
2s
σs
Atomorbital
Atomorbital
Molekül-
orbital

1



2

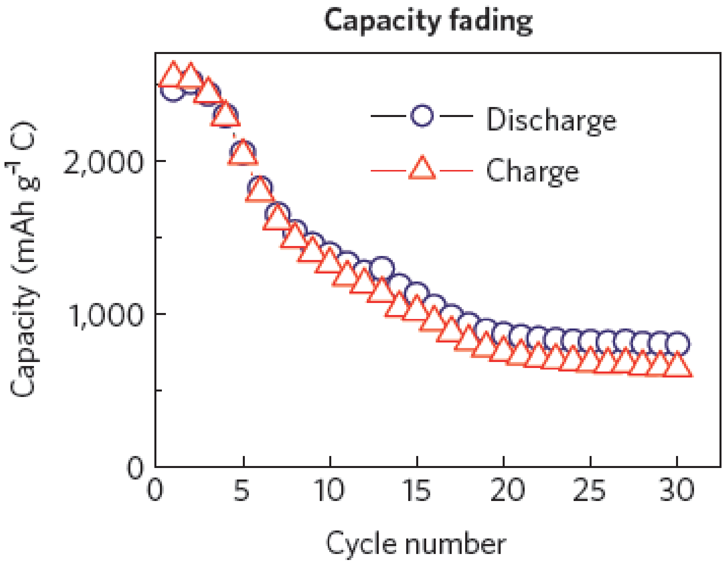
4

5

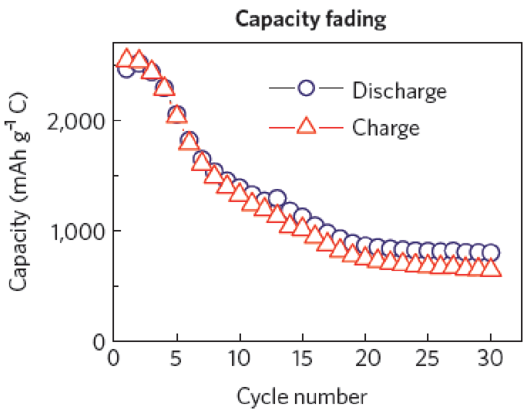
Li-air Cycle life

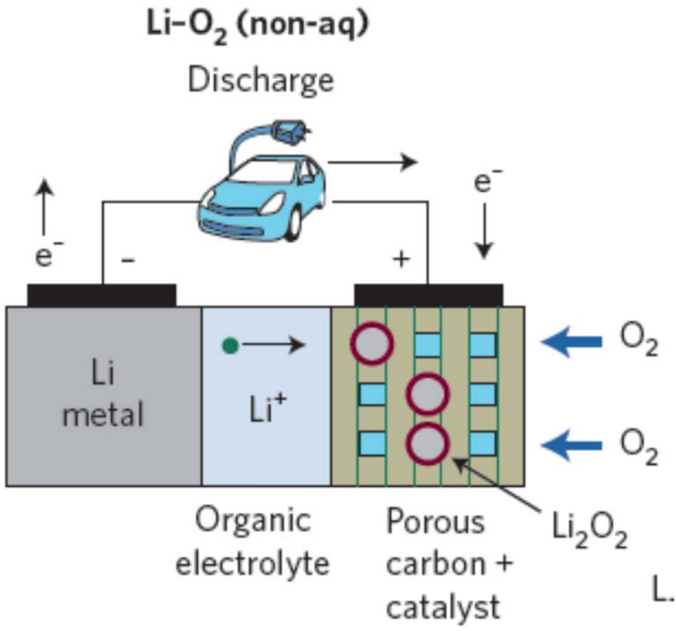
Reasons for reduced cycle life

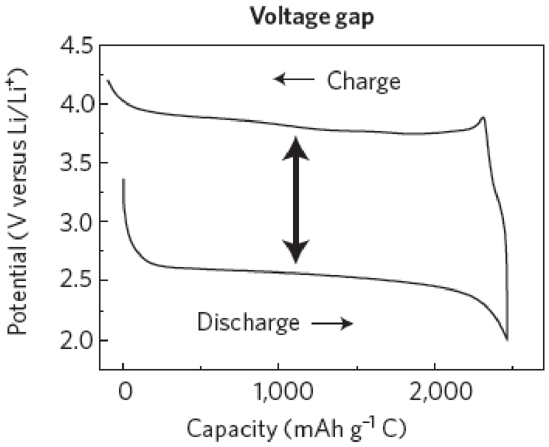
a) Minor effect: Li-metal operates at 0V vs Li/Li$^+$ below the electrolyte stability window -> Li-ions react with electrolyte -> SEI formation
b) Major effect: O_2^- radical reacts with electrolytes (all electrolytes up to date) and Li-salts (it has a very high nucleophilic strength creating new bonds by donating electrons)

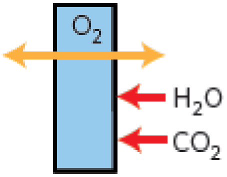


Li-air Challenges







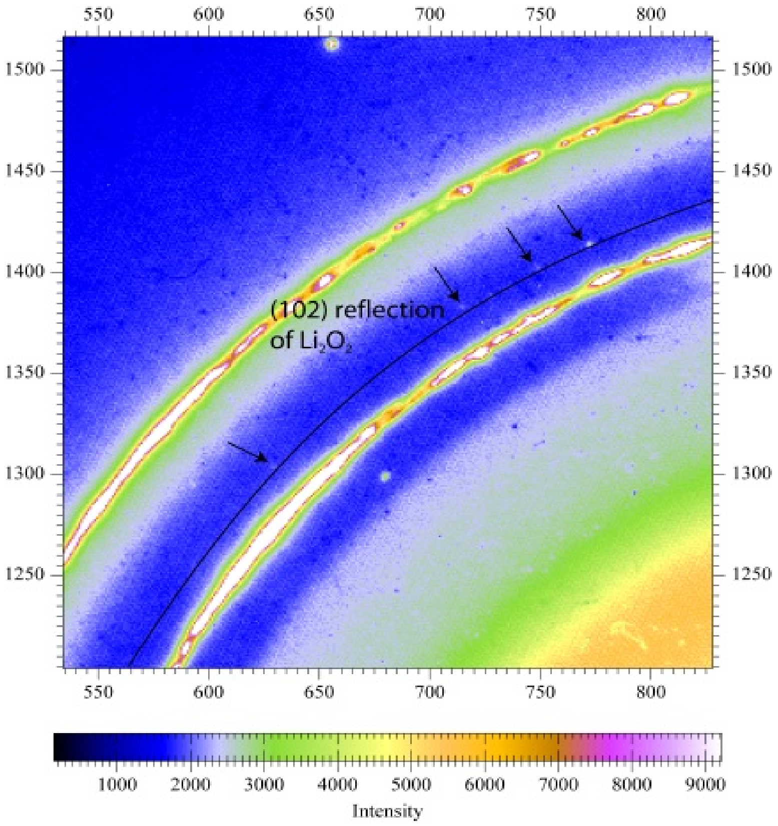


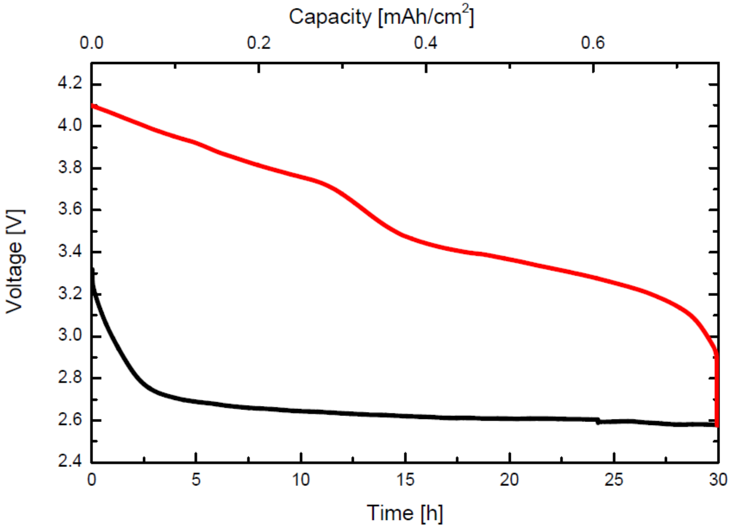
Anode (Li metal)
(1) Dendrite formation
(2) Formation of stable electrolyte interface
(3) Protection against O_2

Organic Electrolyte
Stability electrolyte on reduction
Stability versus O_2^- radical
O_2 solubility and diffusivity

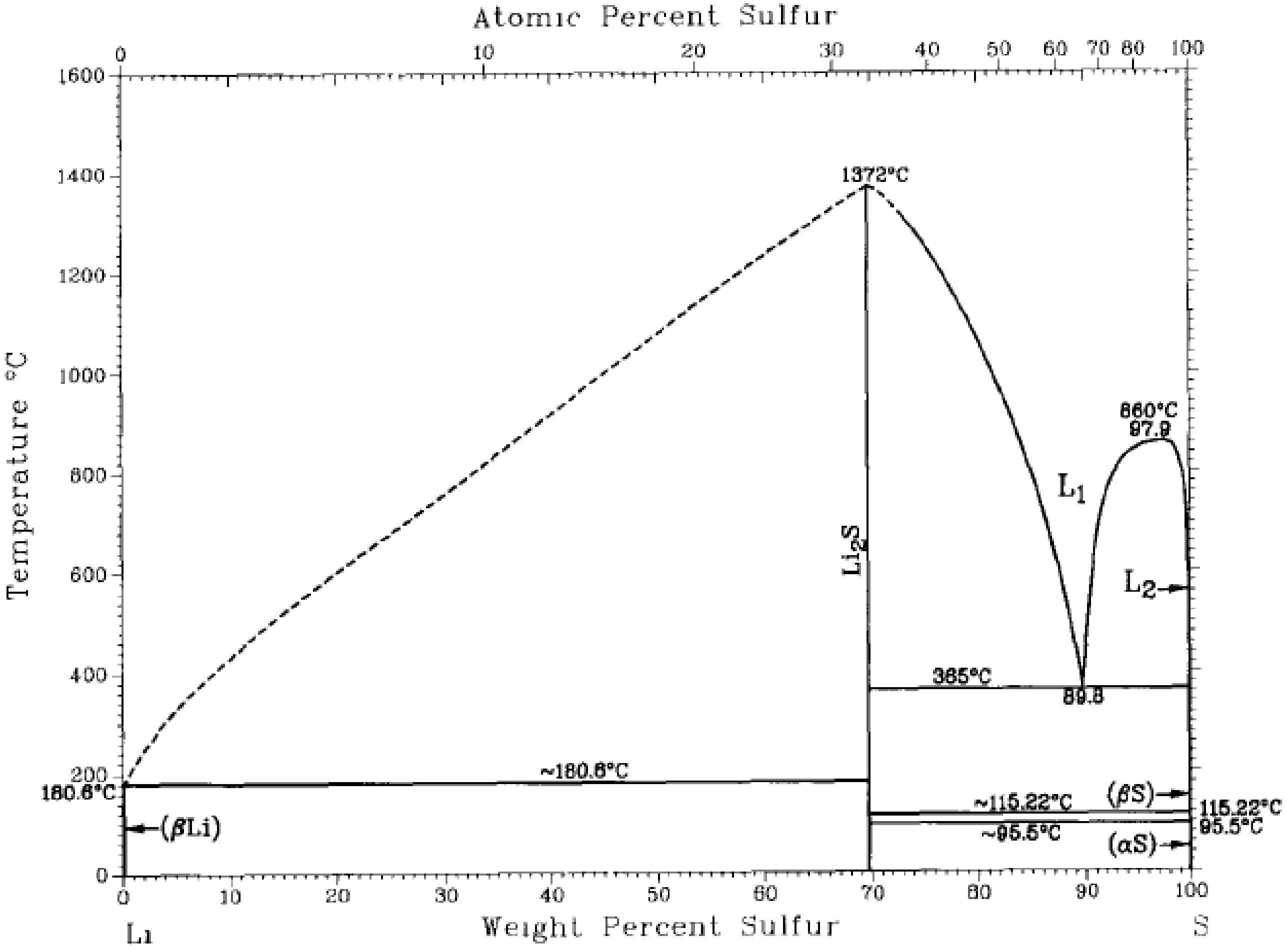
Cathode
Block CO_2 and H_2O and allow O_2
Catalyze right reaction
Porous carbon structure

Current research at TUDelft





Lithium-Sulfur batteries



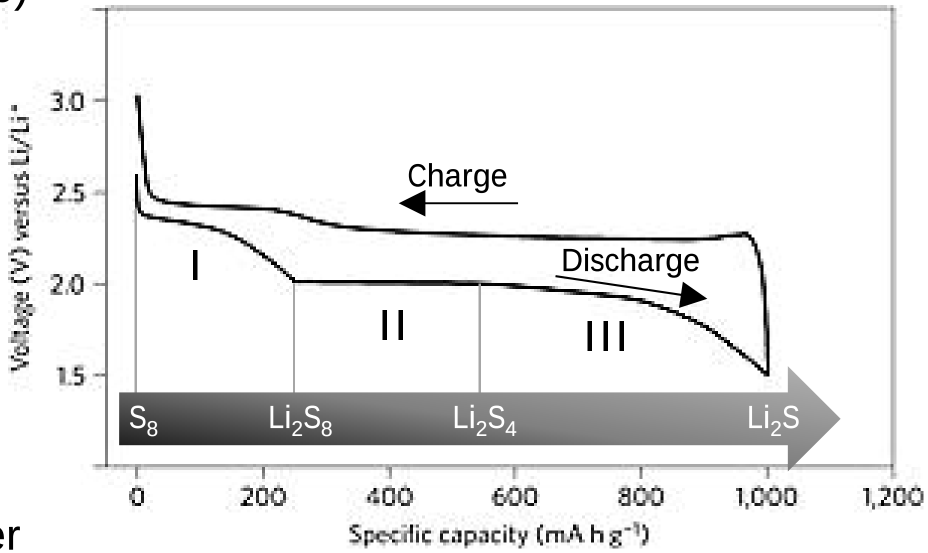
Lithium-Sulfur batteries

$16Li^+ + e^- + S_8 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} 8Li_2S$ (Positive Electrode)

$Li \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} Li^+ + e^-$ (Negative Electrode)

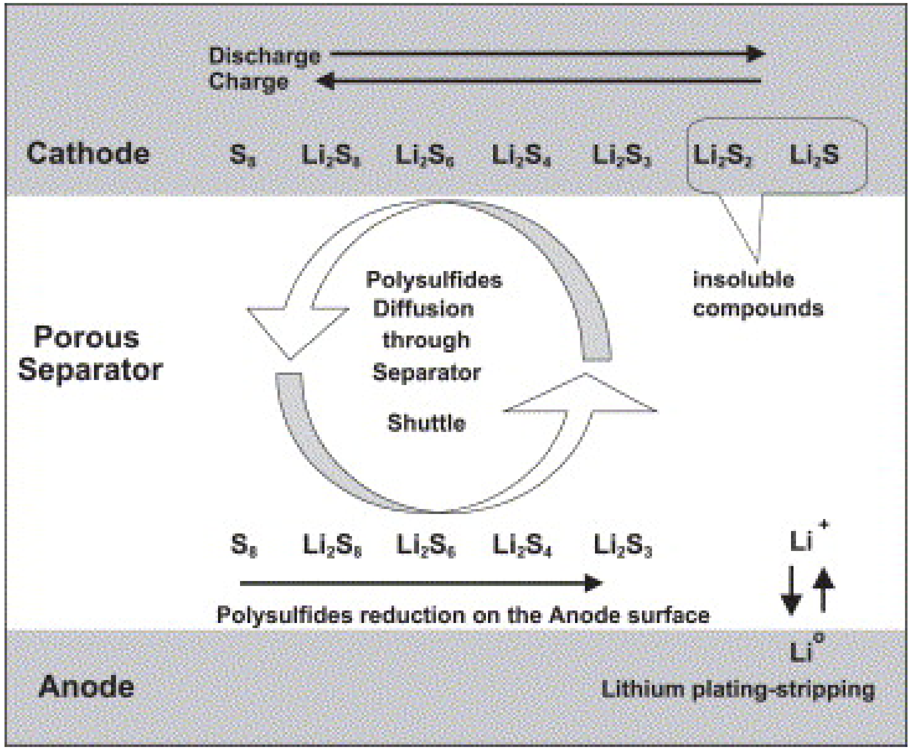
Properties:

- Sulfur is cheap and abundant
- Relatively low voltage 2.15 V versus Li/Li^+
- High theoretical capacity 1675 mAh/g
- Sulfur very poor electronic conductor (high over potentials)
- Polysulfides (intermediate products) dissolve in the electrolyte (capacity loss) and may migrate to the negative electrode forming solid precipitates (Li_2S_2 or/and Li_2S)



I: Conversion of solid sulfhur to soluble polysulfides
II: Conversion of polysulfides to solid Li_2S_2
III: Conversion of solid Li_2S_2 to solid Li_2S

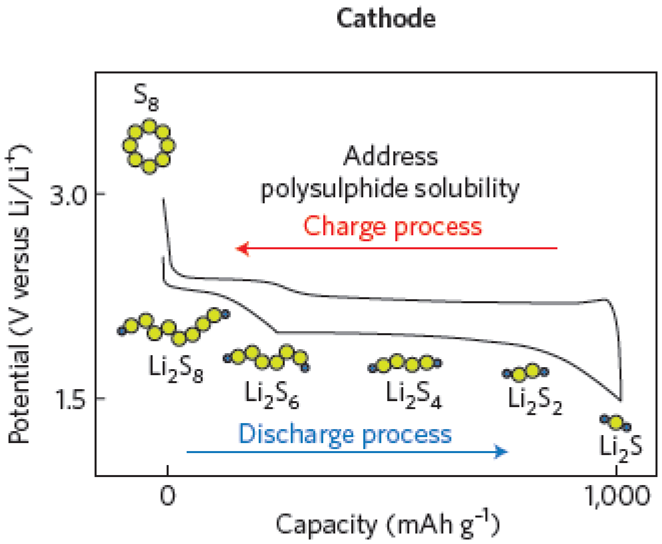
Lithium-Sulfur batteries

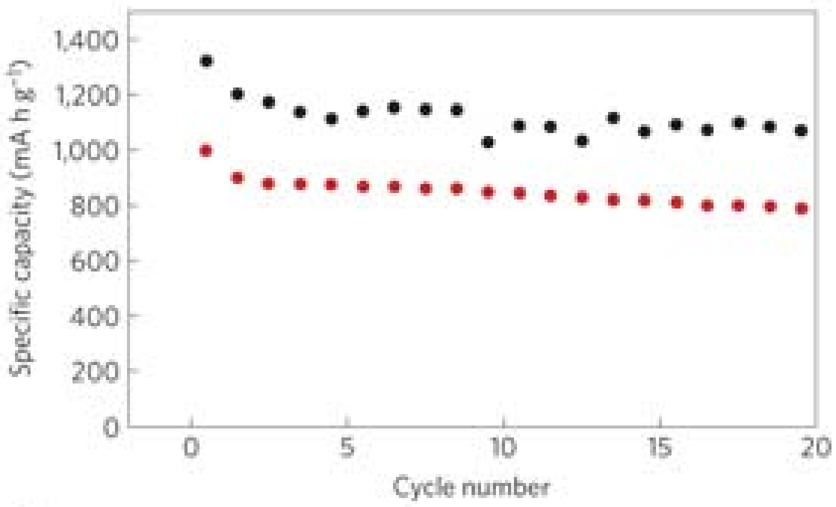


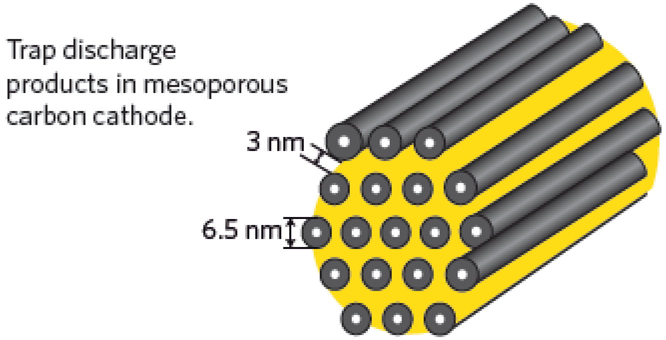
Lithium-Sulfur batteries research

Recent strategy: nano-structured carbon-sulfur structures

- Nano-structured carbon matrix provides good electronic contact to the insulating Sulfur
- Diffusion of large soluble polysulfides away from the electrode is difficult.







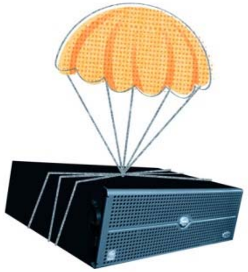
Prof. Nazar and coworkers, Waterloo University

Batteries for Large scale applications

Lead Acid, why (not)?

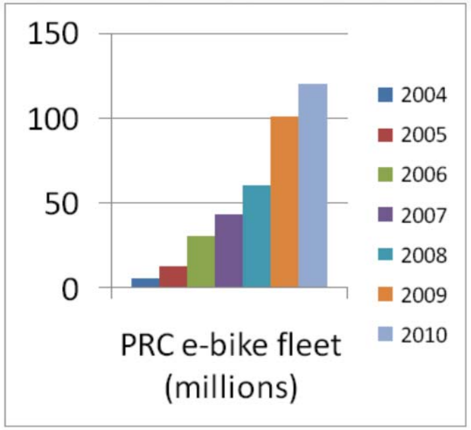
Applications

Automobile starting engine



Back Up Telephone/Computer systems

Pb-acid powered e-bikes China



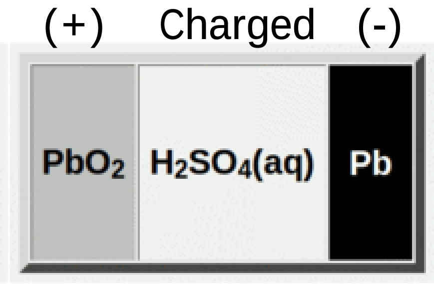
Typical PRC e-bike – average cost $800 each

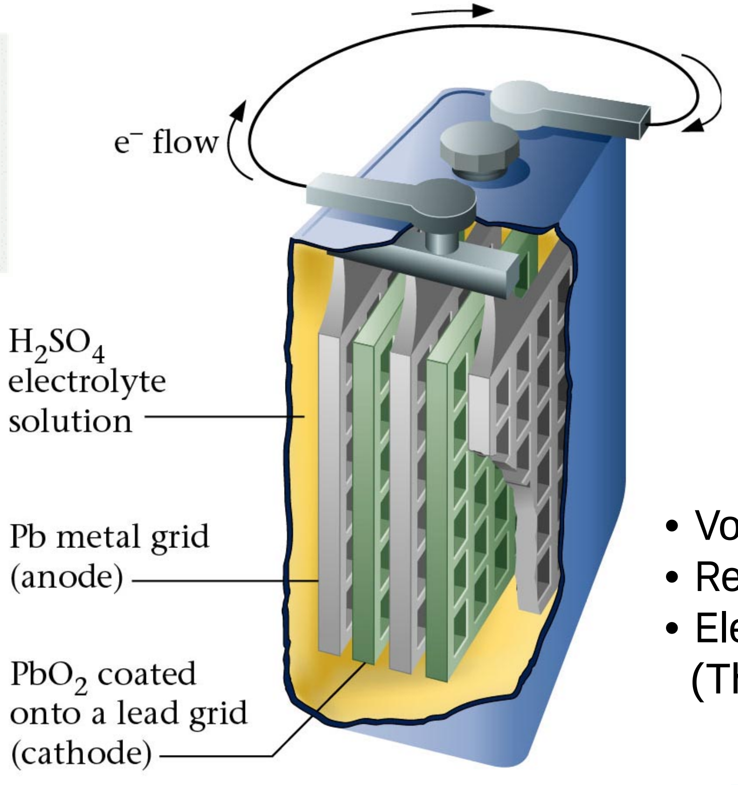
Chino South California 1997
40 MWh, 10 MW

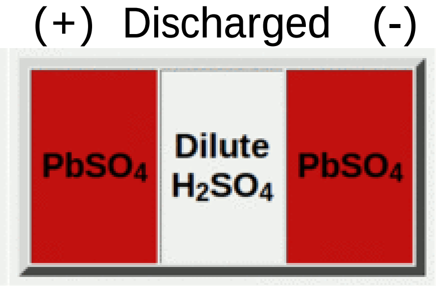
Lead-Acid

$$(-)\quad Pb(s) + HSO_4^-(aq) \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} PbSO_4(s) + H^+(aq) + 2e^-$$

$$(+)\quad PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} PbSO_4(s) + 2H_2O\ (aq)$$



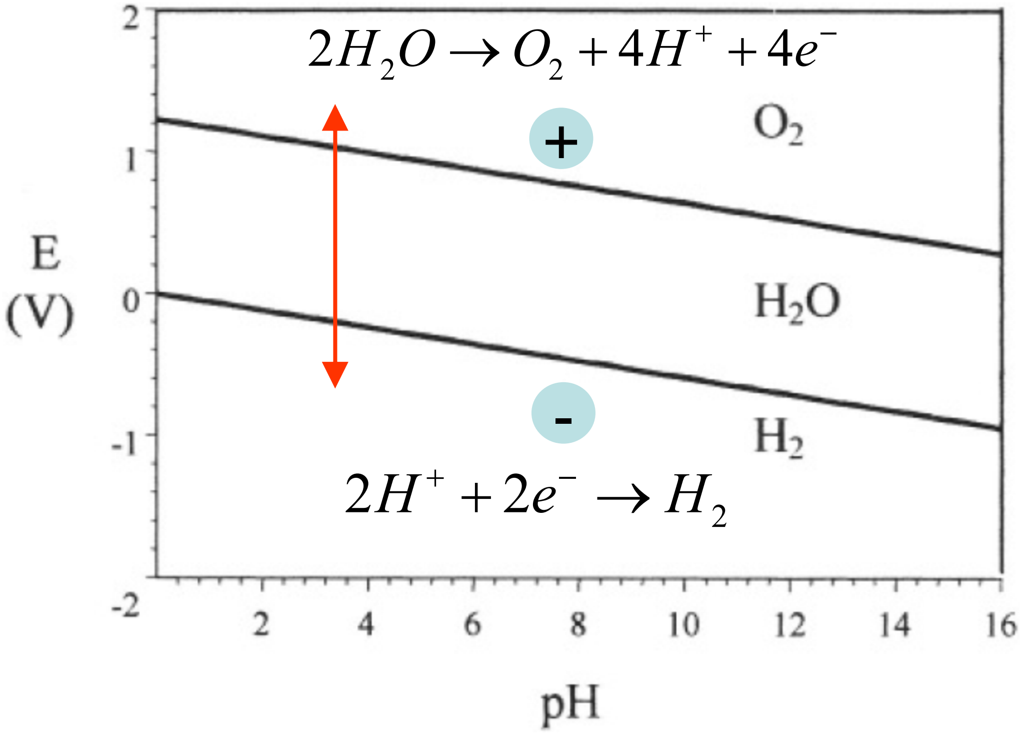




- Voltage: ~2.1 V
- Reconstitution formation reaction
- Electrolyte participates in reaction (The electrodes dissolve)

Decomposition of water

Pourbaix Diagram

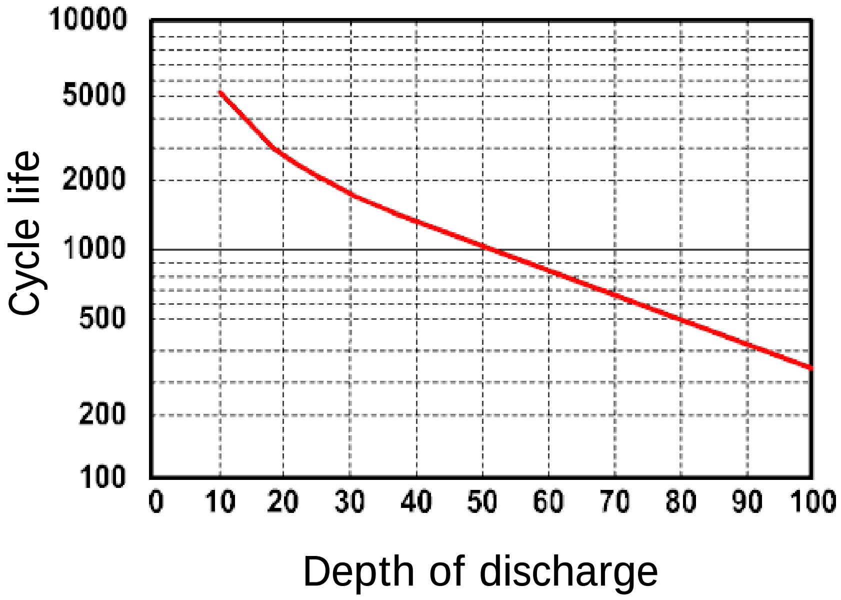


With 2.1 V and an aqueous electrolyte it is an intrinsically unstable system.

The kinetics of electrolysis at the surface of lead are sluggish (Pb is a poor catalyst) -> 2.1 V is stable

Fast charging *(E_{App}>2.1 V)* leads to electrolysis (gassing)

Cycle life



Reconstitution formation reaction (structure of electrode changes completely when (dis)charged)

Consequence is that it varies strongly with the DOD (best stay charged)

Electrode sulfating: $PbSO_4$ is formed upon discharge in a amorphous state, a reaction that is easily reversed. In time amorphous-> crystalline, which is more stable, more difficult to charge.

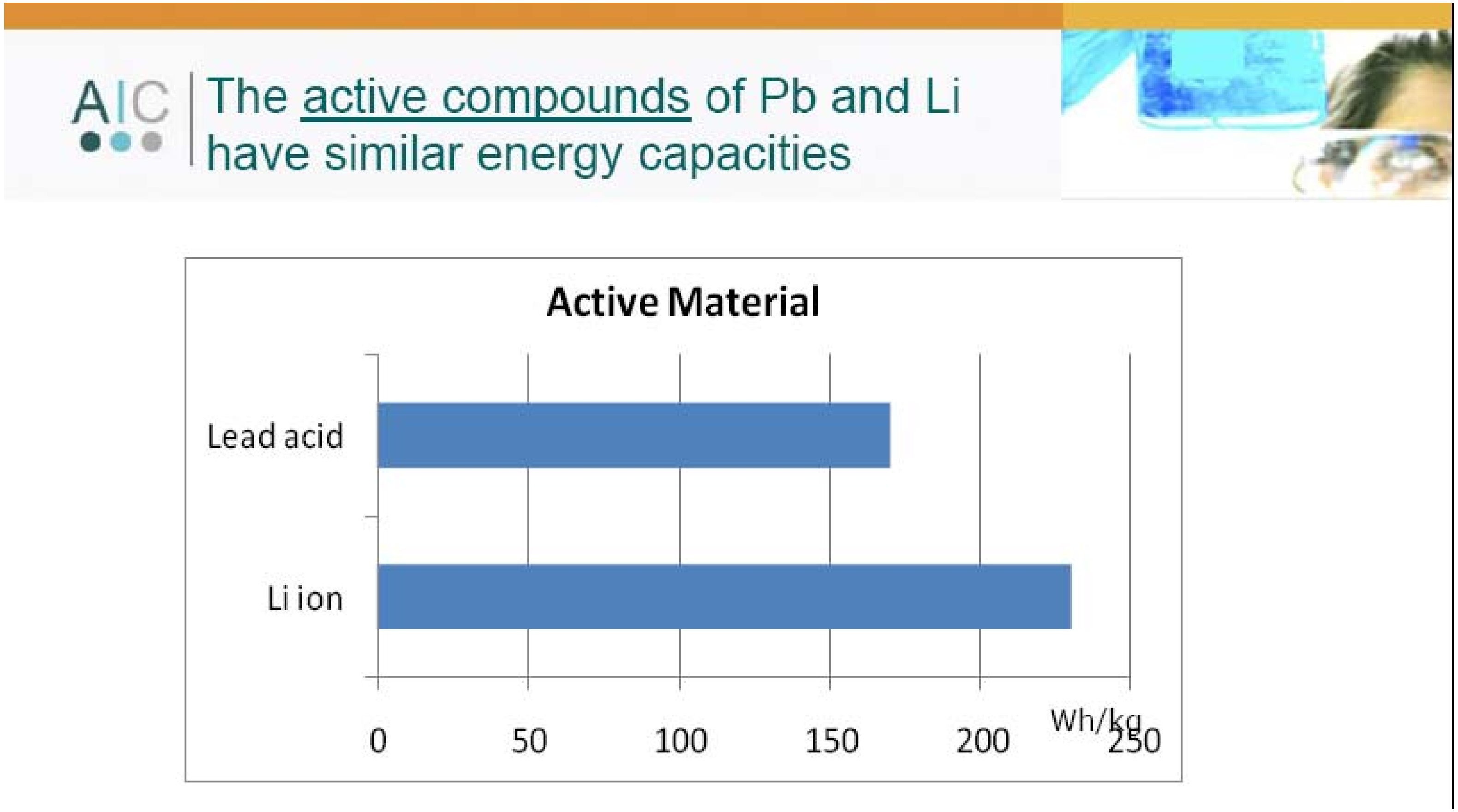
Recycling

Europe and USA > 97%

Africa ~ 120% (?)

100% recycling -> No pollution issue

Playing with numbers



AIC | The active compounds of Pb and Li have similar energy capacities

Playing with numbers

$$(-)\ Pb(s) + HSO_4^-(aq) \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} PbSO_4(s) + H^+(aq) + 2e^- \quad \text{at } 2.1\ V$$

$$(-)\ LiC_6 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} C_6 + Li^+ + e^- \quad \text{at } 3.6\ V \text{ (depends on + electrode)}$$

Energy density, capacity times voltage:

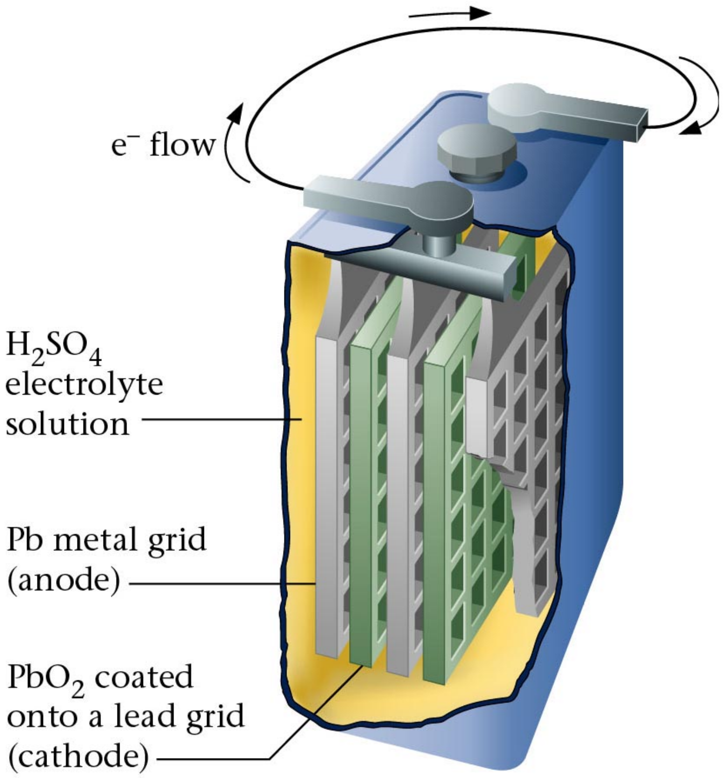
$$EnergyDensity[J/g] = \frac{xzF\varepsilon_{Cell}}{M}$$

x: Fractional occupancy host materials Li_xM
F: Faraday's constant [C/mol]
z: number of electrons involved in the reaction ε_{Cell}*: cell potential [V]*
M: mass of the electrodes [g/mol]

Pb	*M=207.2, z=2* →	*Energy density = 1950 J/g = 540 Wh/kg*
$Pb + HSO_4$	*M=304.2 z=2* →	*Energy density = 1332 J/g = 370 Wh/kg*
Li	*M=6.9, z=1* →	*Energy density = 50000 J/g = 1400.0 Wh/kg*
LiC_6	*M=78.9, z=1* →	*Energy density = 4400 J/g = 1220 Wh/kg*

With respect to energy density, be critical!

Lead-Acid Overview



Energy Density:	30-50 Wh/kg, 60-75 Wh/l
Power Density:	75-250 W/kg
Price per kWh:	200-600 Eur
Price per kW:	300-750 Eur
Self discharge:	5-10%/month
Cycle life:	500-800
Efficiency:	70-80%

Advantages:	Cheap High power Good efficiency Well established recycling
Disadvantages:	Poor cycle life Shorter life time upon deep discharge Large self discharge Relatively low energy density Lead is toxic

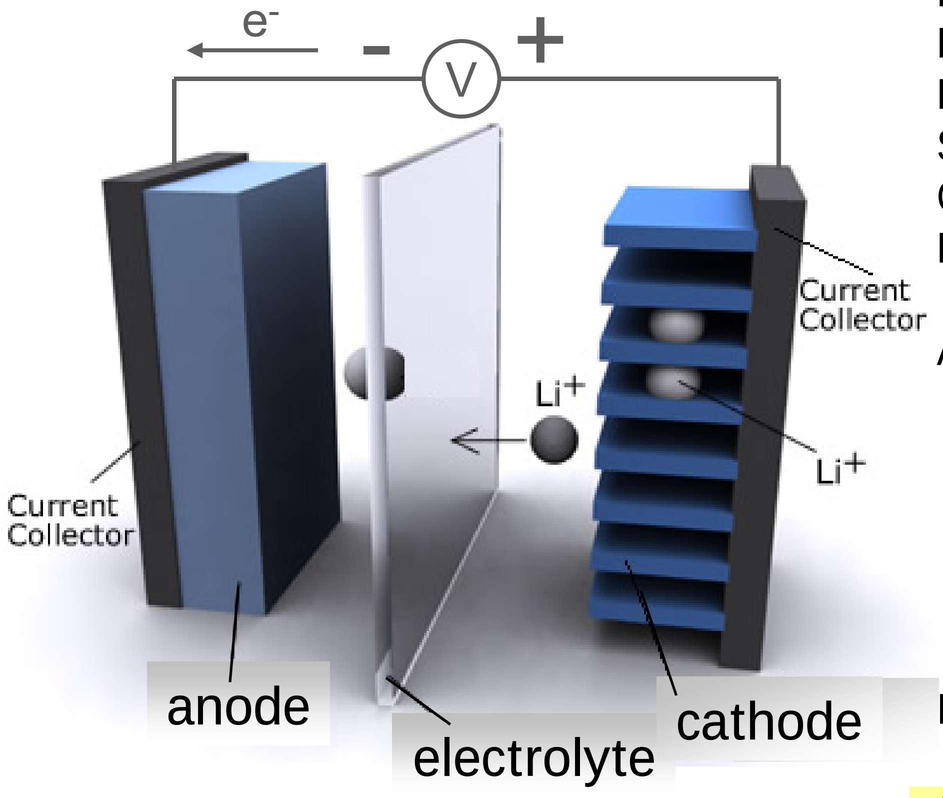
Status: Commercially available. Standard technology for grid stabilization and support

Conclusions

Why?	High power Cheap Well recycled
Why not?	Low energy density Poor cycle life Deep discharge leads to very short cycle life
Mobile applications:	(+) e-bikes, starting engines, cheap and sufficient energy density (costs per cycle?) (-) EV, energy density is not sufficient
Static applications:	(+) Backup, as long as no deep discharge (-) Grid stabilization and load leveling, cycle life and deep discharge issues

Lithium Ion

Lithium-ion



Energy Density: 100-200 Wh/kg, 200-350 Wh/l
Power Density: 150-330 W/kg
Price per kWh: 400-1800 Eur
Price per kW: 150-3000 Eur
Self discharge: 1-3%/month
Cycle life: 1000-10000
Efficiency: 90-98%

Advantages:

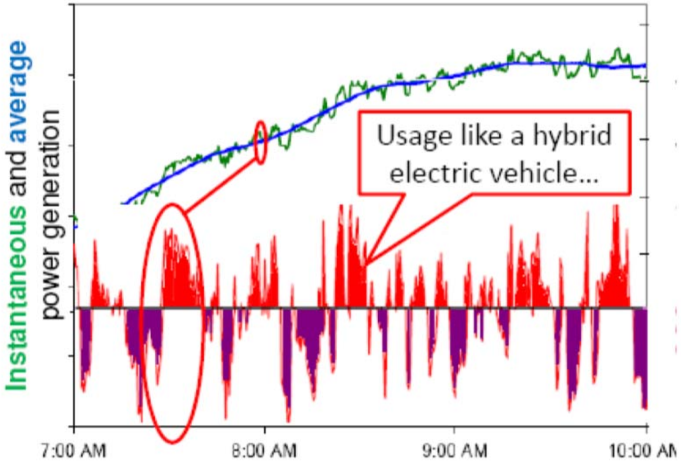
- High energy/power density
- High efficiency
- No deep discharge problems
- Low self discharge
- Long cycle life
- Room for improvement

Disadvantages:

- Expensive

Status: Pilot projects and first commercial projects (A123) up to 12 MW

Toepassing Li-ion (A123, $LiFePO_4$)



Atacama desert north Chili (2009):

12 MW (3MWh) battery for efficiency (>10% increase)

Milli second responds time

Full (dis)charge 15 minutes

500 MW Powerplant

Toepassing Li-ion (A123, $LiFePO_4$)

Being realized:

36 MW grid energy commercially installed

DOE Smart Grid Demo for Wind Integration

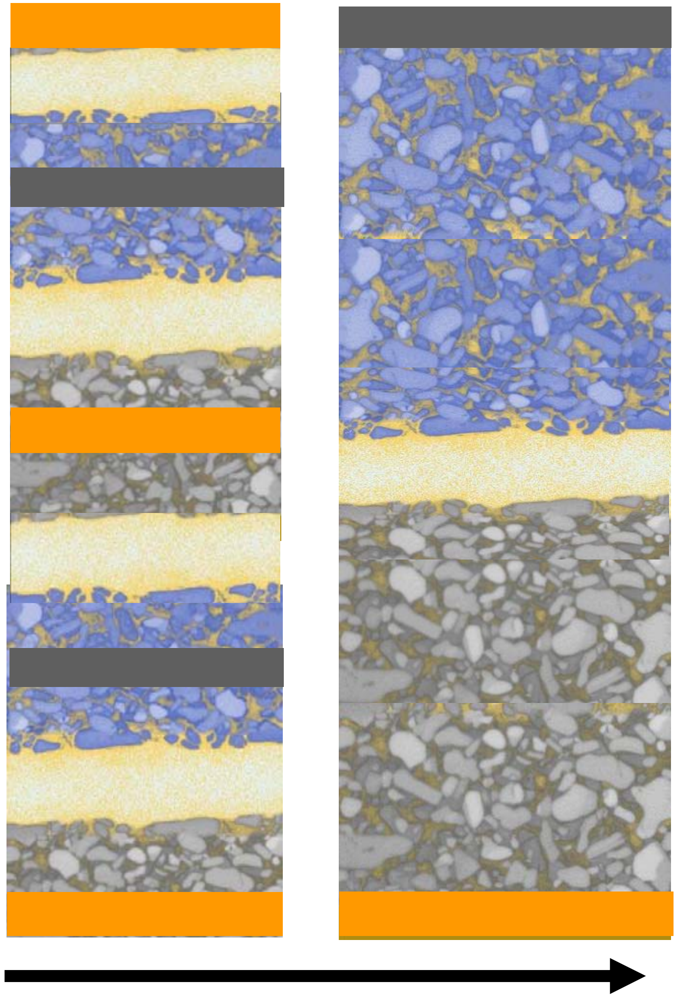
2012 South California,

32 MWh, 8 MW

Load leveling, grid stabilization

Flow Cells

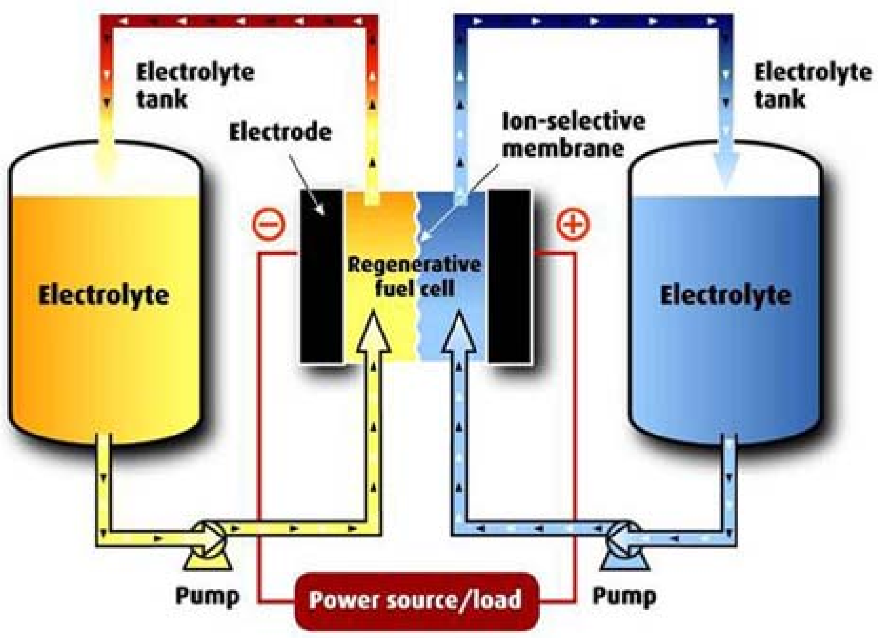
Flow cells



Increasing Energy Density

What if we could refresh the discharged electrodes?

Redox Flow Cells

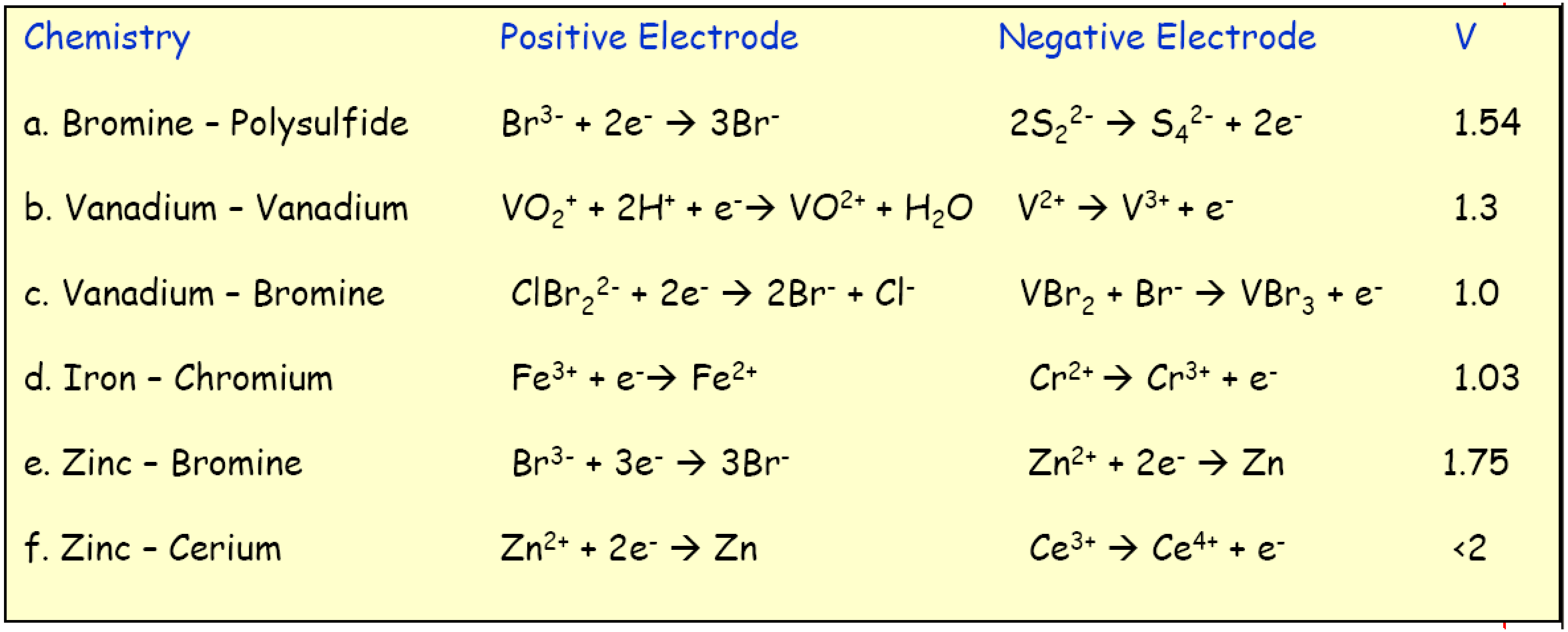


$$(+)\ VO_2^+ + H^+ + e^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} VO^{2+} + H_2O$$

$$(-)\ V^{2+} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} V^{3+} + e^-$$

- Voltage: 1.3 V
- Mild acidic aqueous solution
- Two electrolytes with electroactive species (The electrodes are liquid)
- Membrane to prevent self discharge and to transport ionic charge

Known electrolyte couples for Redox Flow Cells

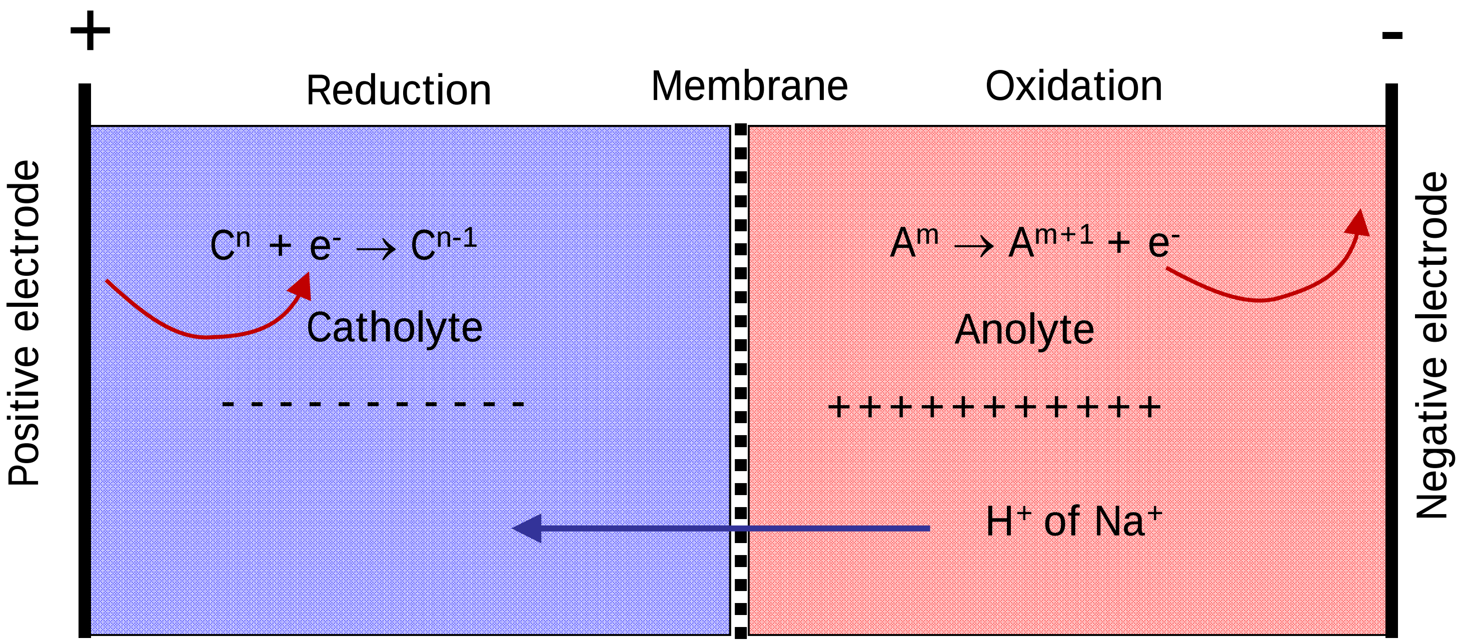


Chemistry	Positive Electrode	Negative Electrode	V
a. Bromine - Polysulfide	$Br^{3-} + 2e^{-} \rightarrow 3Br^{-}$	$2S_2^{2-} \rightarrow S_4^{2-} + 2e^{-}$	1.54
b. Vanadium - Vanadium	$VO_2^{+} + 2H^{+} + e^{-} \rightarrow VO^{2+} + H_2O$	$V^{2+} \rightarrow V^{3+} + e^{-}$	1.3
c. Vanadium - Bromine	$ClBr_2^{2-} + 2e^{-} \rightarrow 2Br^{-} + Cl^{-}$	$VBr_2 + Br^{-} \rightarrow VBr_3 + e^{-}$	1.0
d. Iron - Chromium	$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	$Cr^{2+} \rightarrow Cr^{3+} + e^{-}$	1.03
e. Zinc - Bromine	$Br^{3-} + 3e^{-} \rightarrow 3Br^{-}$	$Zn^{2+} + 2e^{-} \rightarrow Zn$	1.75
f. Zinc - Cerium	$Zn^{2+} + 2e^{-} \rightarrow Zn$	$Ce^{3+} \rightarrow Ce^{4+} + e^{-}$	<2

+
Reduction

-
Oxidation

Role of the membrane



(1) Provides the ionic charge transport, keeping the electrolytes neutrally charged

(2) Separates C and A preventing direct reaction of the electrolytes:

$$C^n + A^m \rightarrow C^{n-1} + A^{m+1}$$

(useless self discharge of the electrolytes)

Redox-Flow

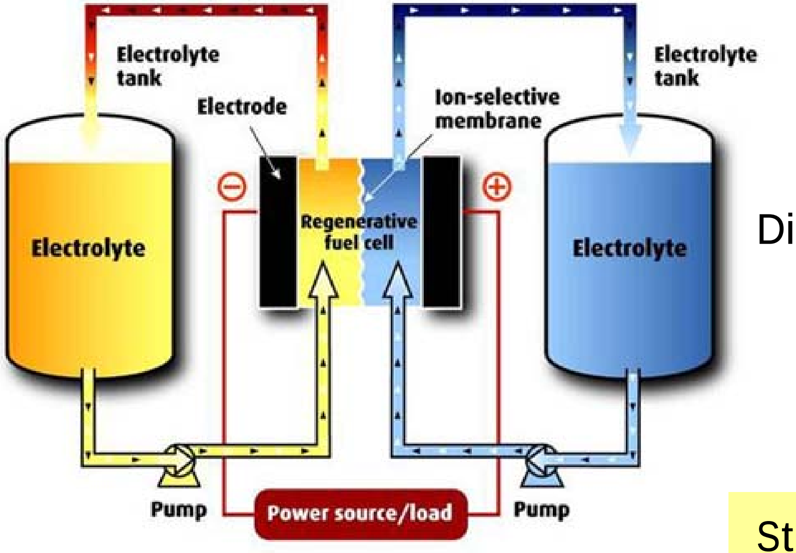
Energy Density: 10-40 Wh/kg, 15-25 Wh/l
Power Density: 1-5 W/kg
Price per kWh: 150-1000 Eur
Price per kW: 600-2500 Eur
Cycle life: 2000-15000
Efficiency: 65-80%
Self Discharge: Small

Advantages:

- Cheap (large applications)
- long lifetime
- can be instantaneously recharged (just refresh the electrolytes)
- flexible design for power or energy

Disadvantages:

- Efficiency depends on the membrane
- Only large systems (many MWh)
- Requires tubes, sensors, pumps (corrosion problems)
- Low energy density (~ 25-35 Wh/kg)



Status: Several demonstration projects and commercial projects are realized (mostly < MW)

Current research Redox Flow Cells

Electrolytes
- Better reversibility, lower overpotentials
- Higher voltage
- Higher concentrations electroactive species in electrolyte
- Higher energy density
- Cheaper and less poisonous materials

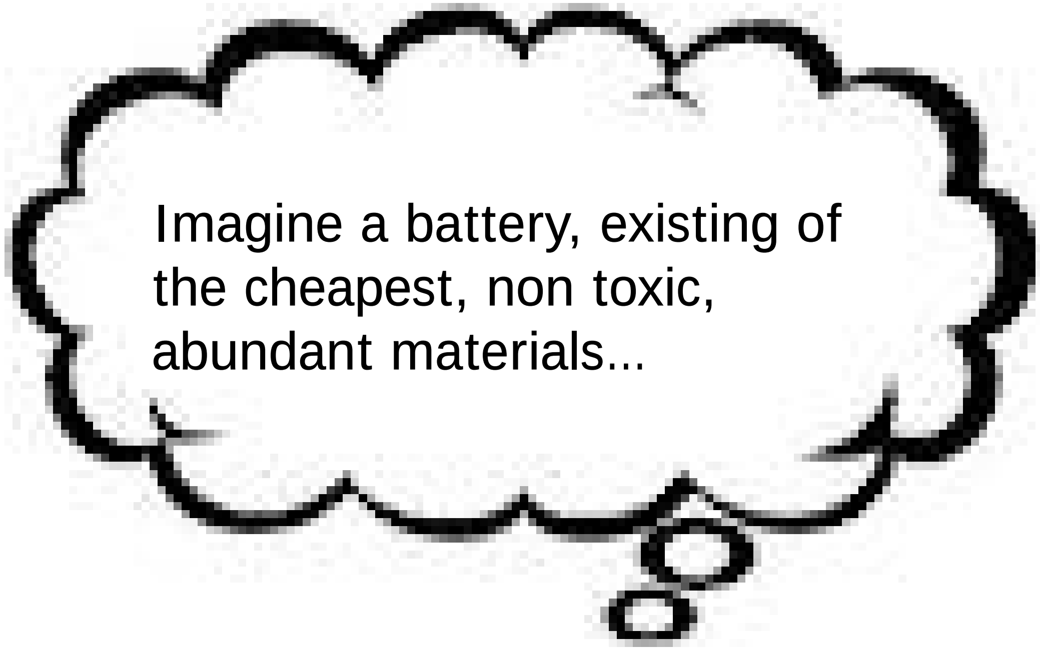
Membrane
- Improve selectivity with fast ionic transport.
- Longer lifetime

Electrodes
- Cheaper materials (like carbon and carbon composites
- Improved electrode design for better charge transfer -> higher power

Application: Stationary high energy/power

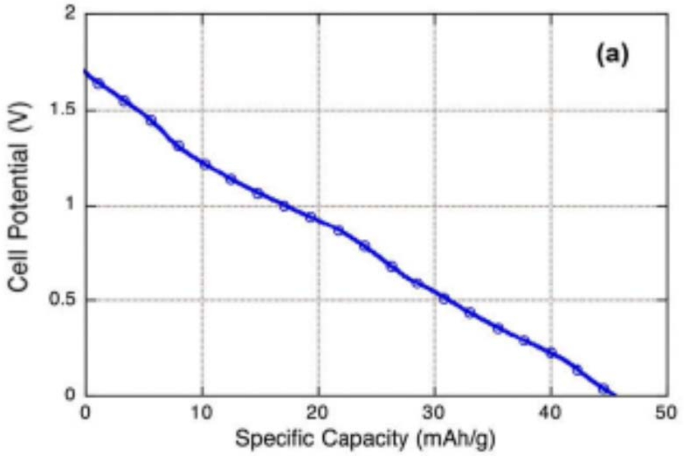
4 MW, 1.5 h,
Vanadium system
Japan

Sodium Aqueous batteries

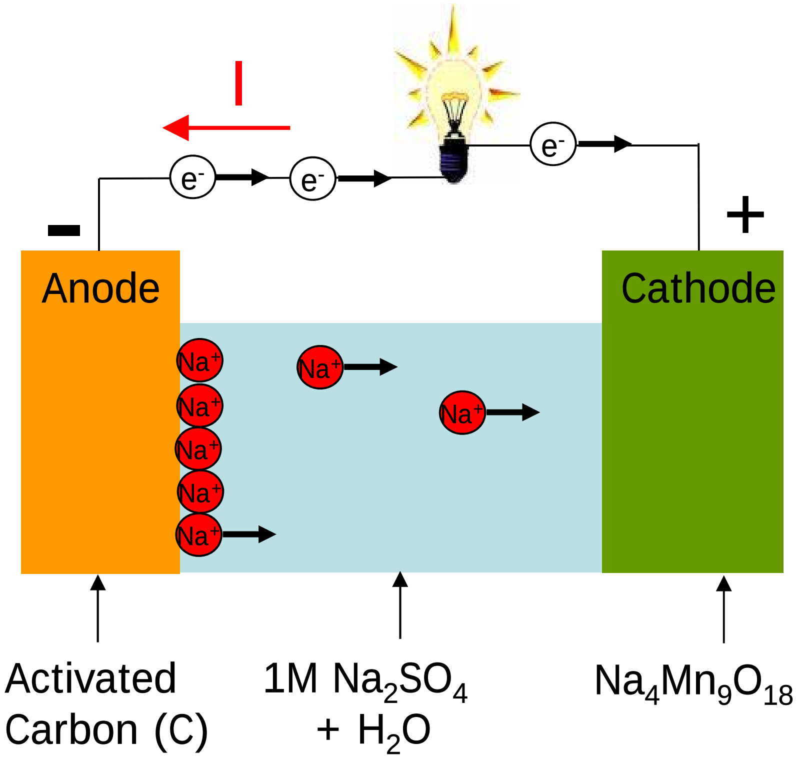


Imagine a battery, existing of the cheapest, non toxic, abundant materials...

Na-water



Whitacre et al Electro. Comm. 2010



Activated Carbon (C)

1M Na_2SO_4 + H_2O

$Na_4Mn_9O_{18}$

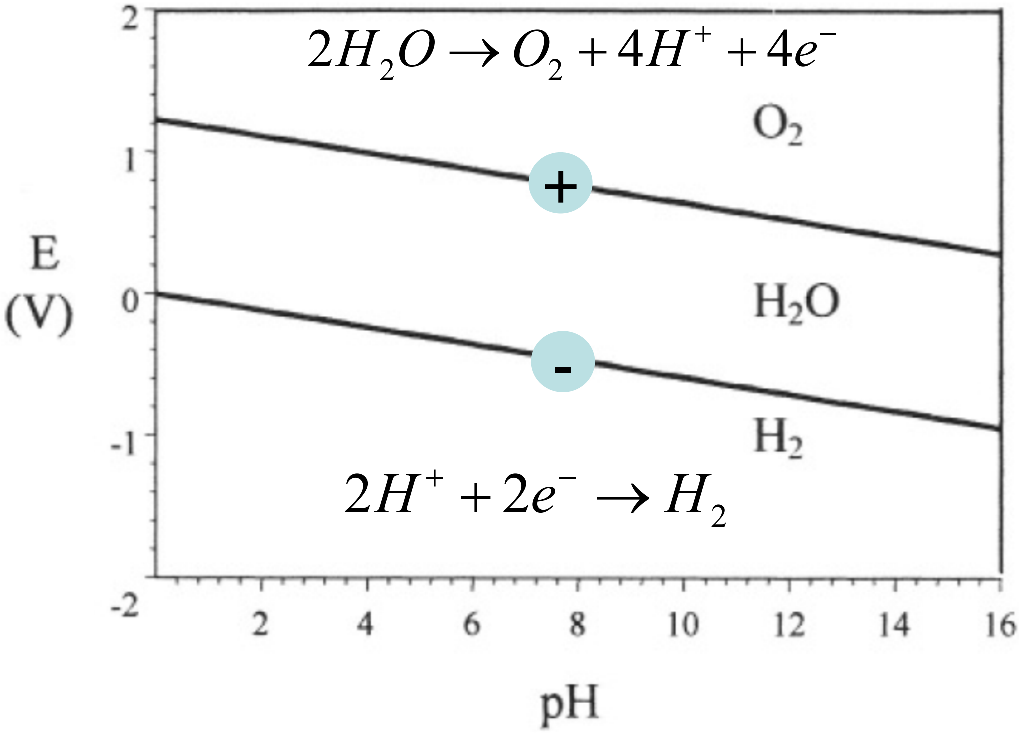
$$(+)\ Na_2Mn_9O_{18} + 2Na^+ + 2e^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} Na_4Mn_9O_{18}$$

$$(-)\ NaC_y \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} C_y + 2Na^+ + 2e^-$$

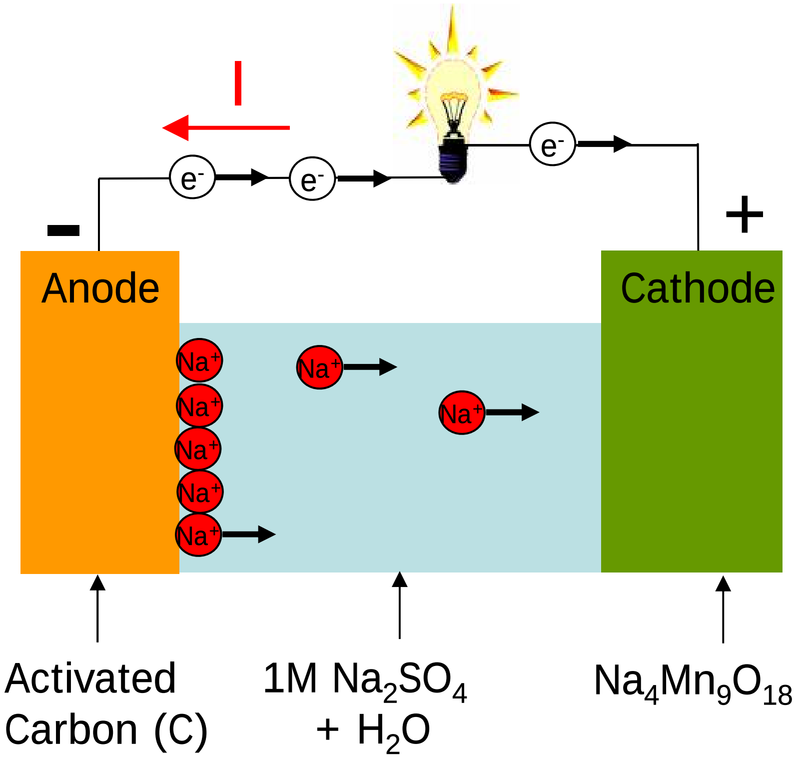
- Average voltage: ~0.8 V
- Aqueous electrolyte
- Abundant and non toxic materials
- Equivalent Li-ion insertion reaction

Decomposition of water

Pourbaix Diagram



Na-water



Energy Density: 15-30 Wh/kg, 30 Wh/l
Power Density: 10-30 W/kg
Price per kWh: target < 200 Eur
Price per kW: target < 200 Eur
Cycle life: target >> 5000 (proven 5000)
Efficiency: > 90%
Self Discharge: nihil

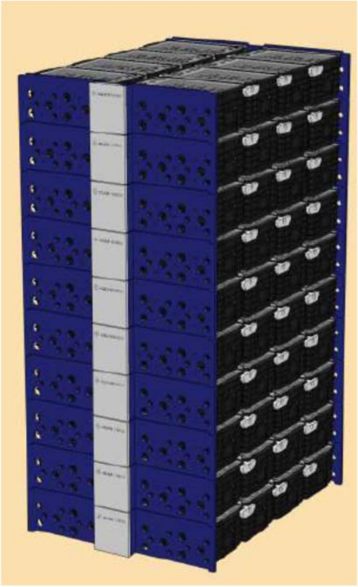
Advantages:
- Very Cheap
- excellent efficiency
- long cycle life
- high currents
- Environmentally benign materials
- 100% recyclable

Disadvantages:
- Low energy/power density
- Decreasing voltage

Status: Testing, production start 2011/2012

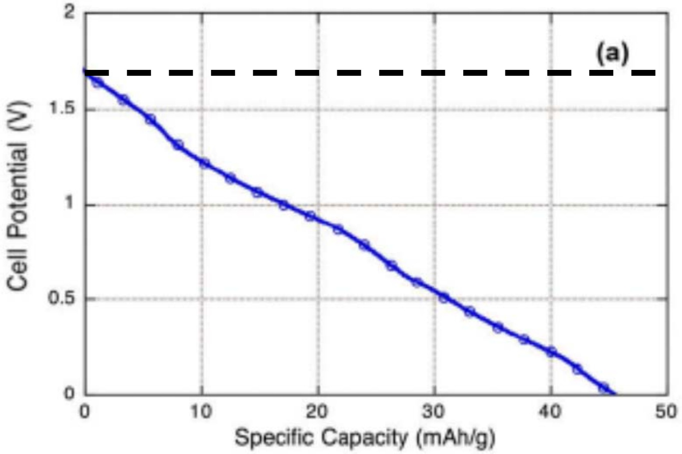
Na-water

2011 Aguion Na-aqueous battery



AQUION ENERGY

Double the energy density



Challenges:

- Other anode:
  Activated carbon is relatively expensive
  Activated carbon functions as a supercap -> voltage variation
- Na-ion storage material research is undeveloped compared to Li-ion field

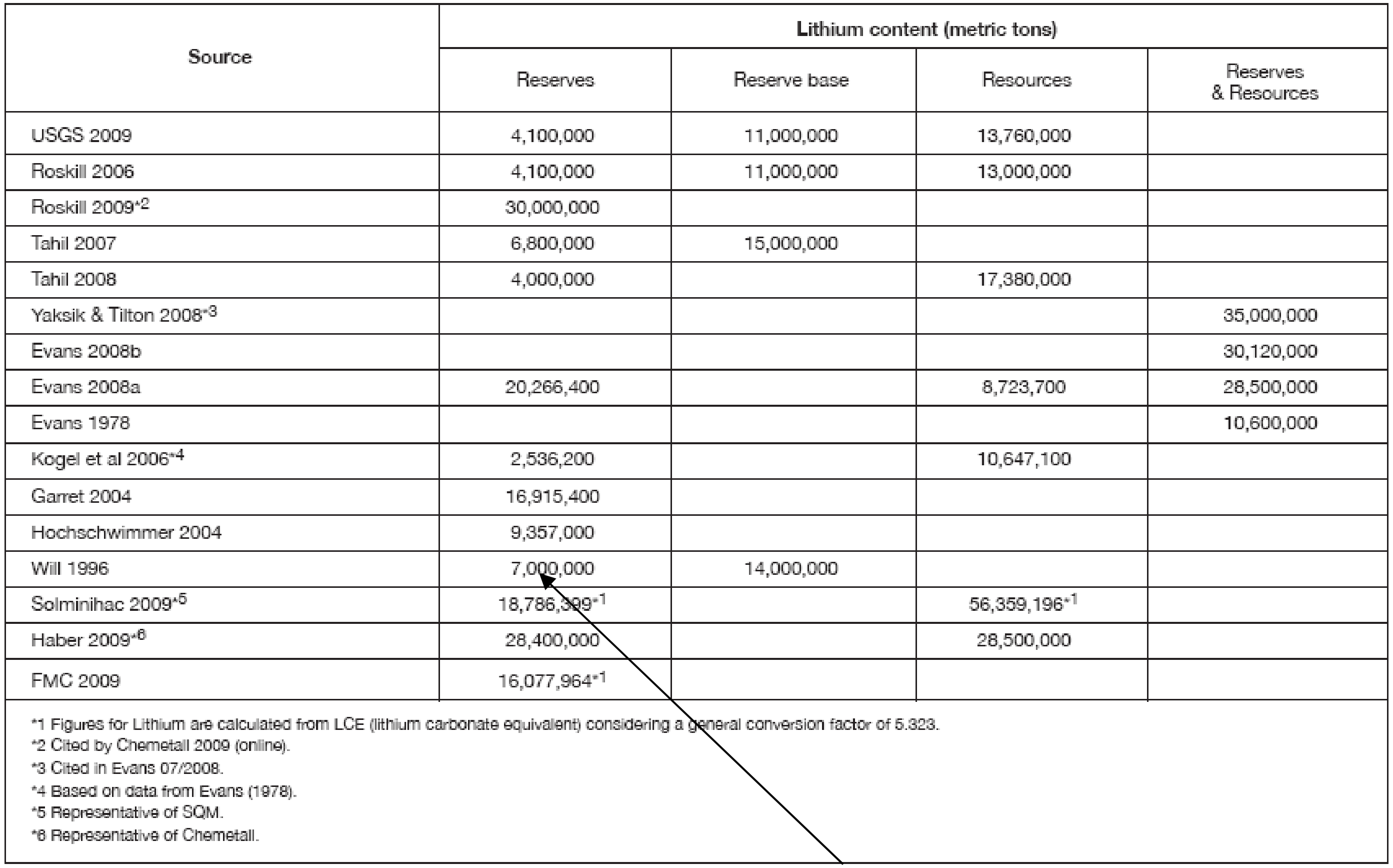
Material Abundance

But what about Li abundance?

Uyuni Bolivia

But what about Li abundance?

TABLE I: Worldwide lithium reserves, reserve base and resources of different publications.



Source	Lithium content (metric tons)			
	Reserves	Reserve base	Resources	Reserves & Resources
USGS 2009	4,100,000	11,000,000	13,760,000	
Roskill 2006	4,100,000	11,000,000	13,000,000	
Roskill 2009*2	30,000,000			
Tahil 2007	6,800,000	15,000,000		
Tahil 2008	4,000,000		17,380,000	
Yaksik & Tilton 2008*3				35,000,000
Evans 2008b				30,120,000
Evans 2008a	20,266,400		8,723,700	28,500,000
Evans 1978				10,600,000
Kogel et al 2006*4	2,536,200		10,647,100	
Garret 2004	16,915,400			
Hochschwimmer 2004	9,357,000			
Will 1996	7,000,000	14,000,000		
Solminihac 2009*5	18,786,399*1		56,359,196*1	
Haber 2009*6	28,400,000		28,500,000	
FMC 2009	16,077,964*1			

*1 Figures for Lithium are calculated from LCE (lithium carbonate equivalent) considering a general conversion factor of 5.323.
*2 Cited by Chemetall 2009 (online).
*3 Cited in Evans 07/2008.
*4 Based on data from Evans (1978).
*5 Representative of SQM.
*6 Representative of Chemetall.

Li-ion battery equivalent of 3 x Current world amount of cars

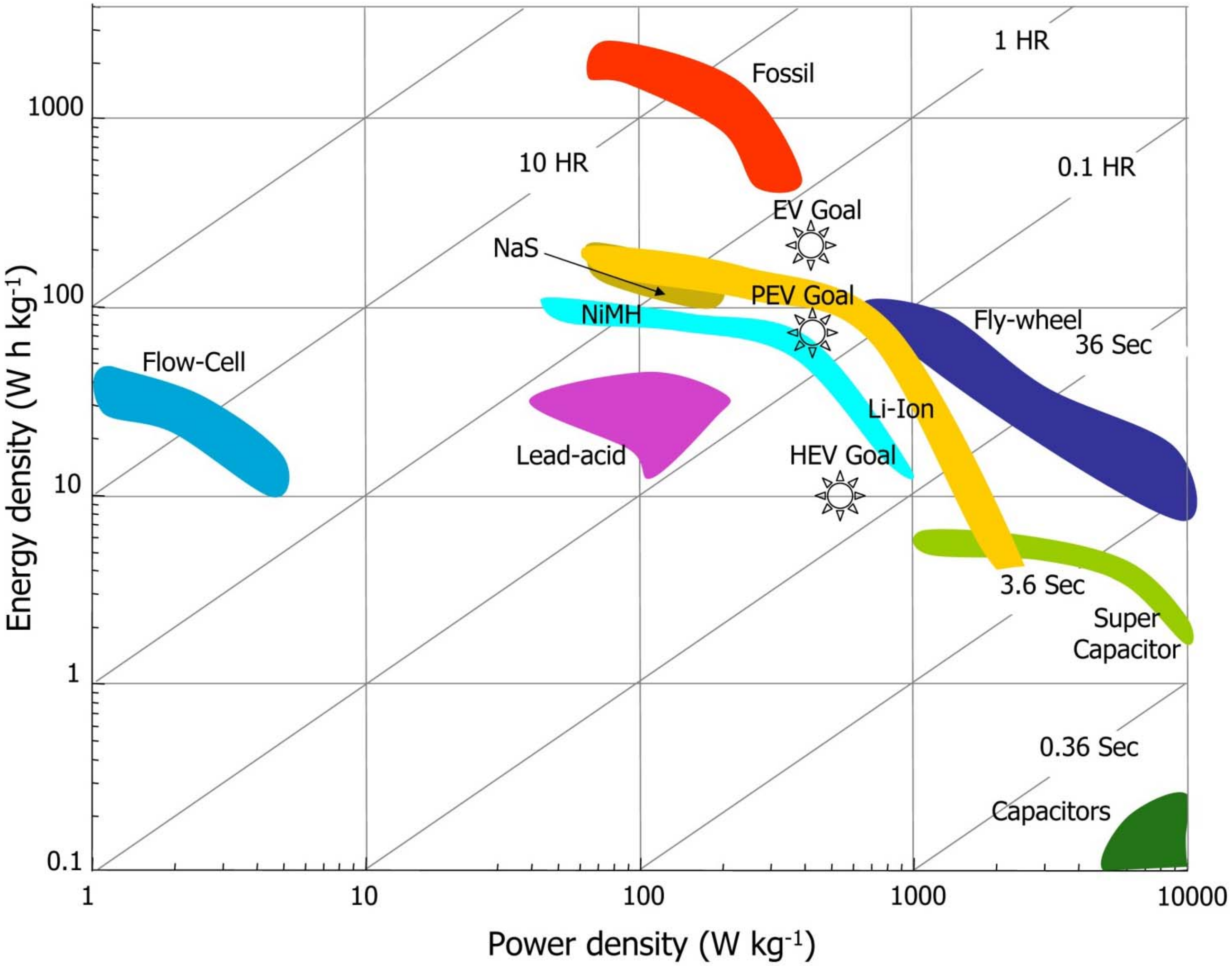
Reserves: Economically recoverable part of a mineral resource demonstrated by at least a preliminary feasibility study. (easy bit)

Reserve base: Part of the resource that meets specified minimum criteria of current mining and production practices. (harder but possible)

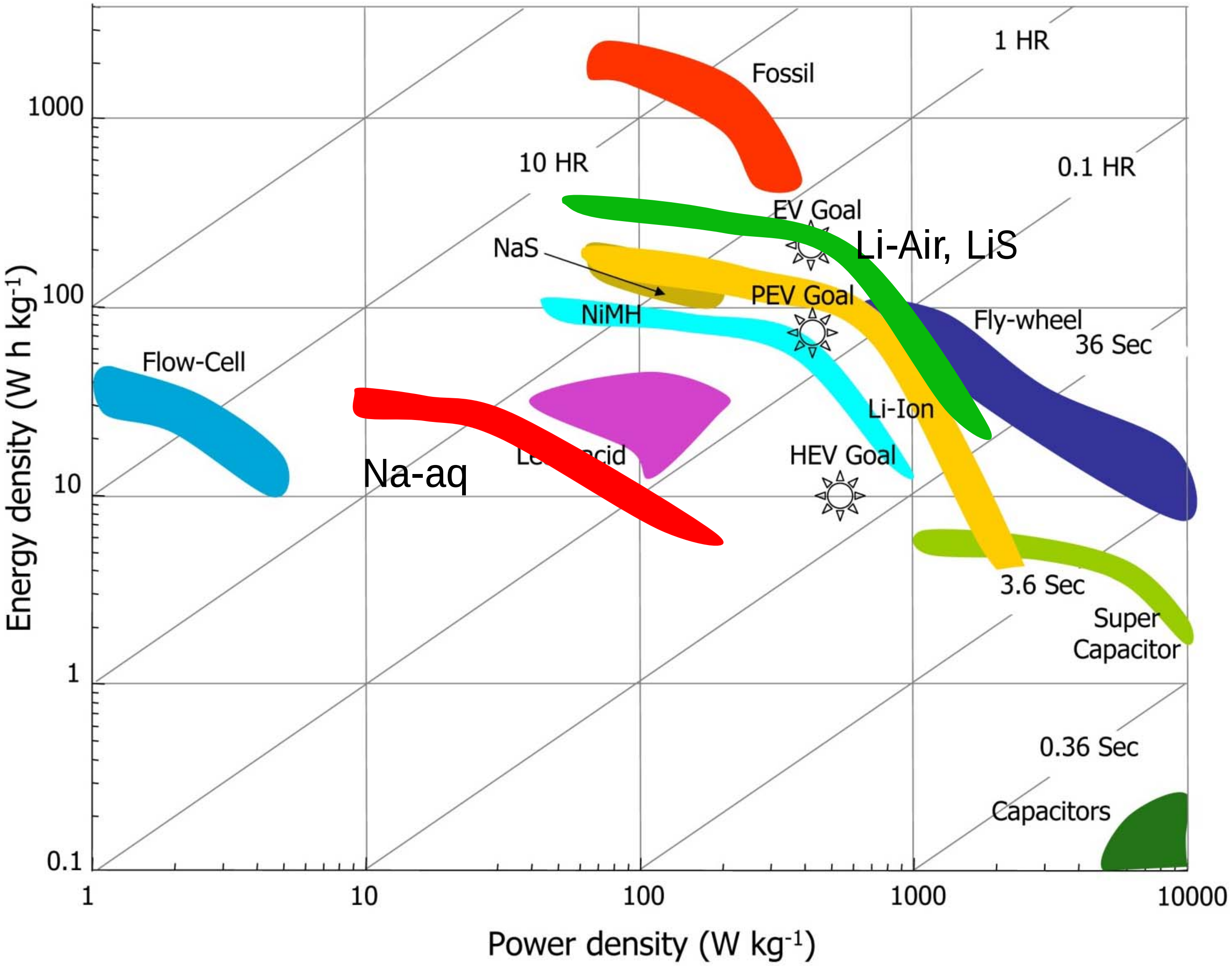
Resources: Concentration of naturally occurring material that can be potentially feasible. (even harder, but possible)

Cost and performance comparison battery systems

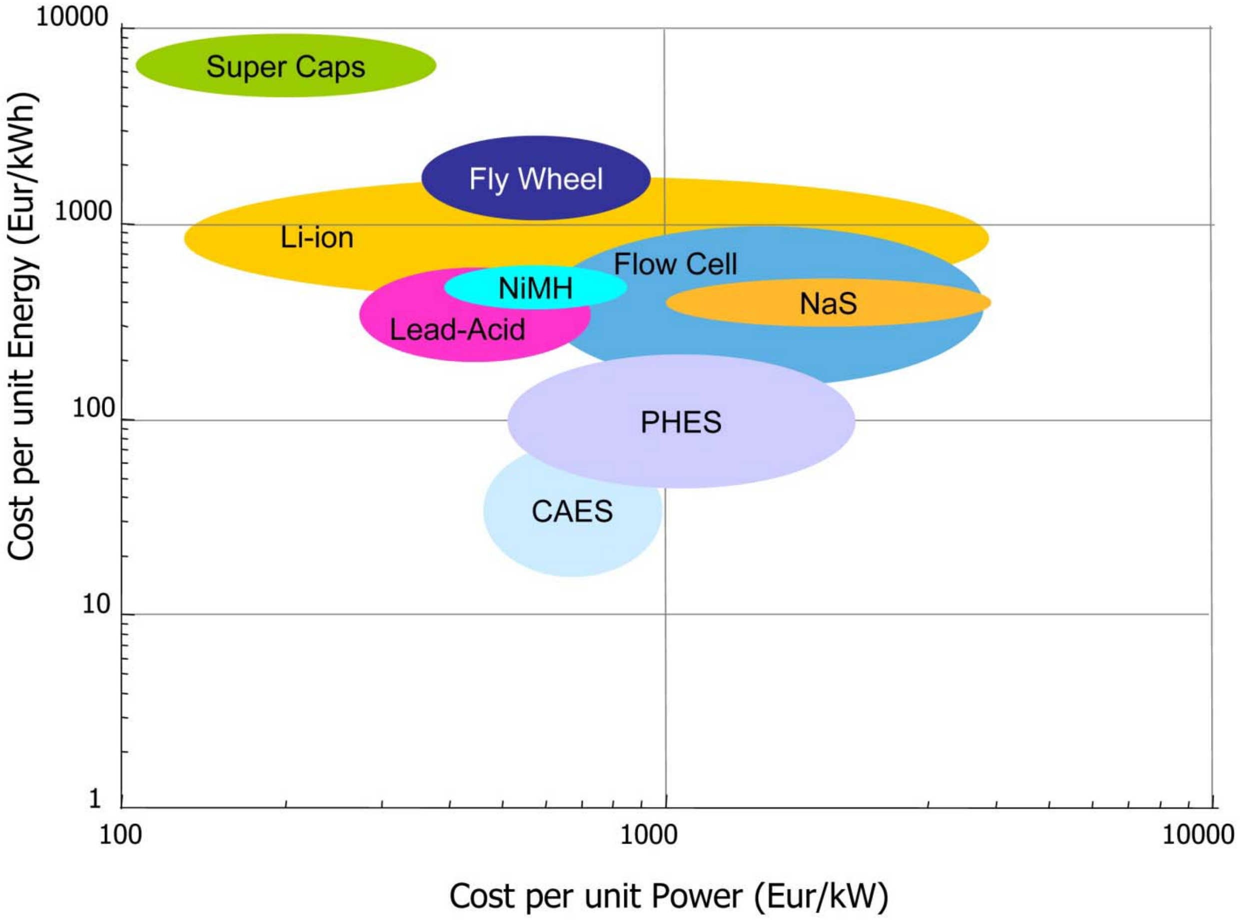
Ragone Plot Energy vs Power density



Ragone Plot Energy vs Power density



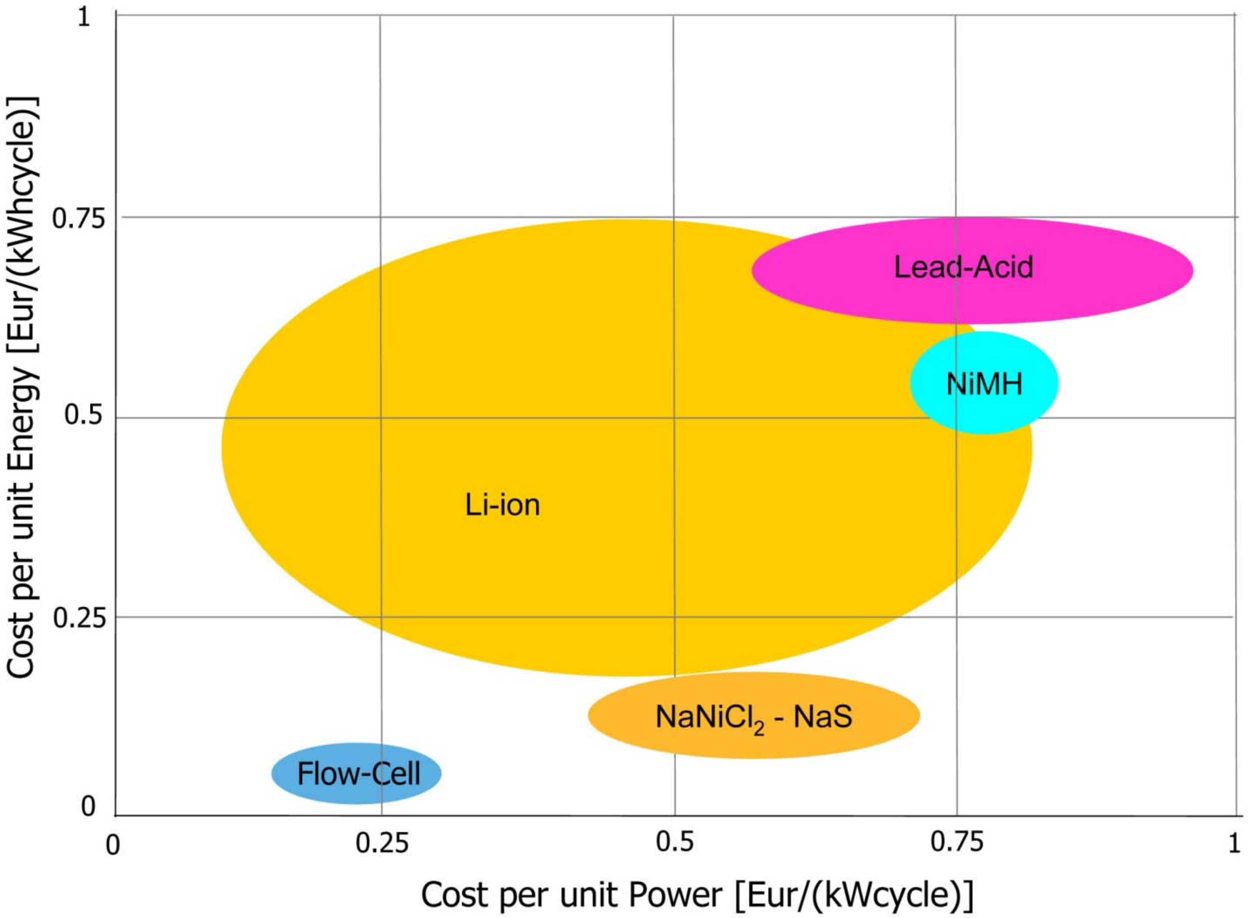
Price per kWh



PHES: Pumped hydro energy storage

CAES: Compressed air energy storage

Price per kWh and per cycle



Conclusions batteries for static energy storage

Advantages	**Disadvantages**
Efficiency	
Can be applied in any situation	Costs
Large energy and power density	Cycle Life
New technologies	New technologies

Flow-Cell: Large scale storage 1-50 MW, timescale days (Backup, Enabling PV/Wind)

NaS: Intermediate scale storage 0.1-30 MW, timescale hours/days (Backup, Grid stabilization, enabling PV/Wind)

Li-ion: Intermediate scale storage 0.1-20 MW, timescale ms to days (Grid stabilization and efficiency)

Lead-acid: Intermediate scale storage 0.1-20 MW, timescale ms to days (backup)

Na-Water: A promise for 0.1-50 MW Storage, seconds to days

Large potential to improve costs and performance (Li-ion, Flow Cell, Na-Water), requires large research efforts.

Conclusions energy storage for mobile transport

Advantages	**Disadvantages**
Efficiency	Costs
Large energy and power density	Cycle Life
New technologies	New technologies

Pb-acid, Flow-Cell, NaS, Na-Water:	Energy density is intrinsically to low
Li-ion:	Current state range ~150 km but there is room for improvement to ~350 km (increase amount of active material in battery)
Li-S:	Large promise Range >350 km, much research required
Li-Air:	In theory Range ~ 500km, but we are in the beginning of exploring

Li based technologies will always remain expensive, large amount of energy requires expensive safety measures.

The End

Program Batteries

Lecture 1: Feb 27	History, Applications, basic Electrochemistry and thermodynamics of batteries: Redox reactions, Gibbs free energy, chemical potential, Nernst.	
Lecture 2: March 6	Solid state electrode reaction mechanisms, phase diagrams, phase rule, Gibbs Free energy, voltage profiles, capacities and energy densities. Li-ion batteries	
Lecture 3: March 13	Continue topics Lecture 2. Electrolyte stability: Pourbaix diagram, band structure solids, Cycle life.	
Lecture 4: March 20	Kinetics, Buttler-Volmer, diffusion, solid state diffusion Discussion on Science paper 6 seconds discharge.	
Lecture 5: March 27	Super capacitors	
	Future large energy density systems:	Li-air Li-sulfur
	Batteries for large scale applications:	Lead-acid Li-ion Flow-cells Sodium aqueous batteries
	Costs and Performance comparison batteries/systems	

Program Batteries

Lecture 1: April 25	History, Applications, basic Electrochemistry and thermodynamics of batteries: Redox reactions, Gibbs free energy, chemical potential, Nernst.
Lecture 2: May 2	Solid state electrode reaction mechanisms, phase diagrams, phase rule, Gibbs Free energy, voltage profiles, capacities and energy densities. Li-ion batteries
Lecture 3: May 9	Continue topics Lecture 2. Cycle life: Electrolyte stability: Pourbaix diagram, band structure solids.
Lecture 4: May 16	Kinetics, Buttler-Volmer, diffusion, solid state diffusion Discussion on Science paper 6 seconds discharge.
Lecture 5: May 23	Super capacitors Future systems: Li-air, Li-sulfur Lead-acid Flow-cells Sodium aqueous batteries Material Abundance Costs and Performance comparison batteries/systems

Learning goals Batteries

Learning Goals

At the end of the 5 battery lectures you should be able to:
Knowledge:
List the major types of Li batteries and their characteristics
Reproduce the major challenges in batteries
Understand:
Explain how a battery works and the functioning of each component
List and explain the different reaction types in batteries
Explain the different charge transfer processes in batteries
Explain the working of super capacitors
List and explain the different mechanisms that limit the cycle life of batteries.
Apply:
Apply Nernst Law describing redox reactions
Apply the Tafel equation describing the charge transfer between electrode and electrolyte
Calculate energy densities and power densities from observed properties
Derive from a phase diagram the different phases that will occur upon lithiation.
Apply the Gibbs Phase rule to predict constant of variable output voltage
Derive the voltage curve from the shape of the Gibbs Free energy
Analyse:
Predict the basic redox reaction of two electrodes given the formation energy or the standard potentials
Compare different battery systems and differentiate.
Synthesize:
Discuss scientific results observed battery performance and to relate this to material properties.