PAUL SCHERRER INSTITUT

Energy Storage in Advanced Batteries

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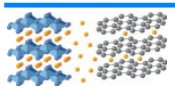
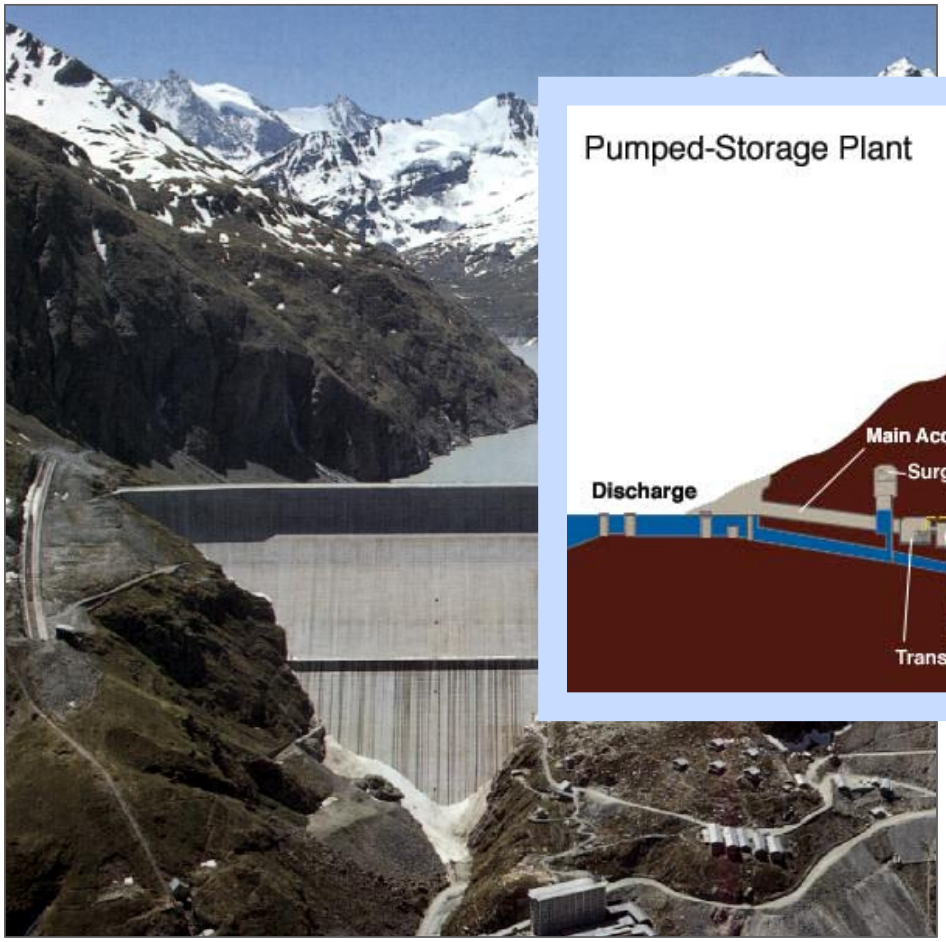
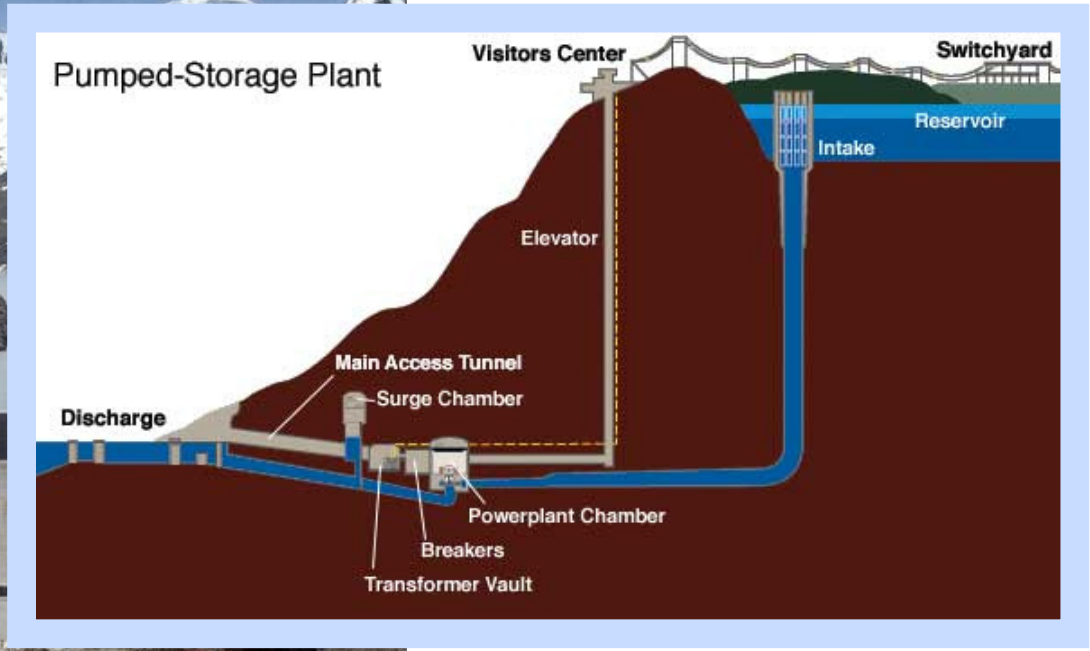


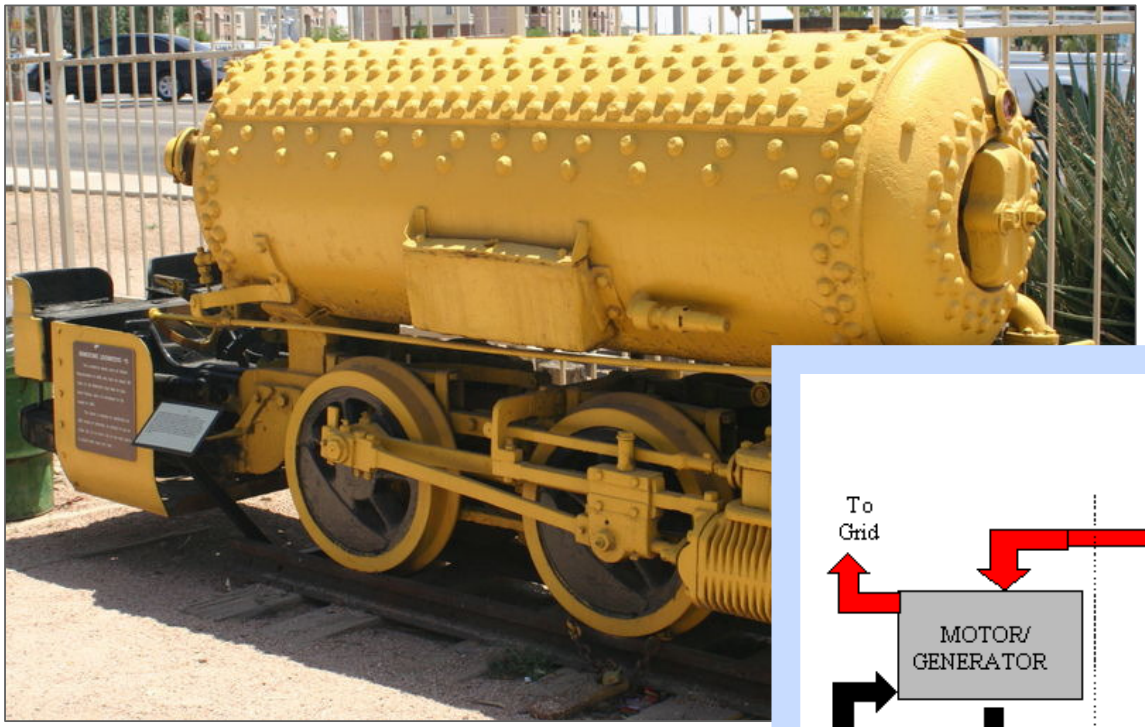
Energy Storage

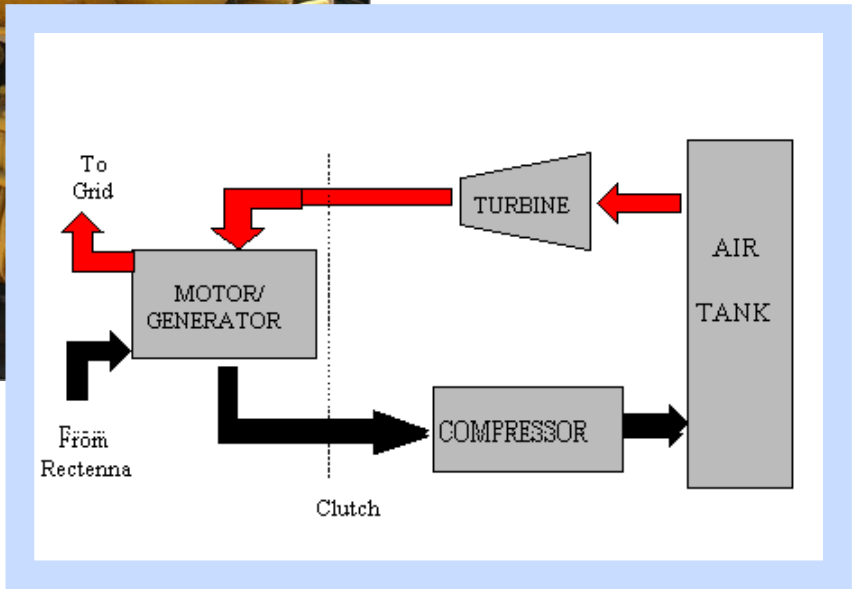
The Swiss Way of Energy Storage





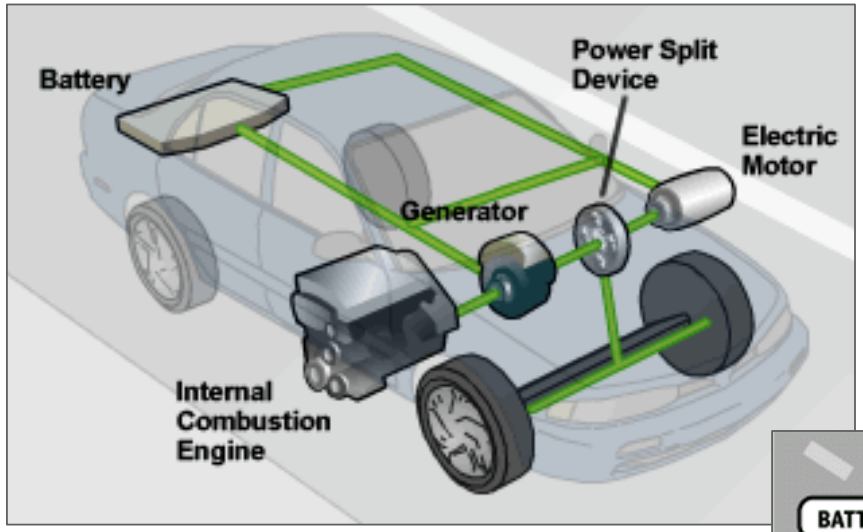
Energy Storage in Transport Sector

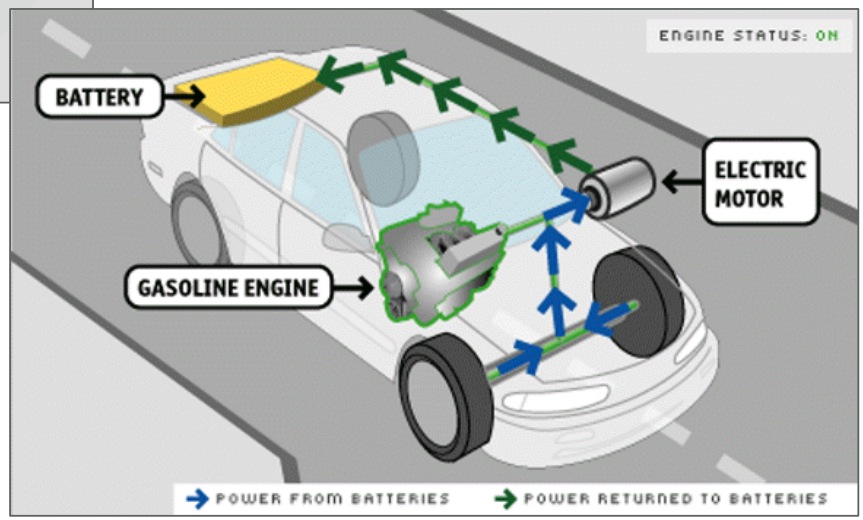




Energy Storage in Transport Sector

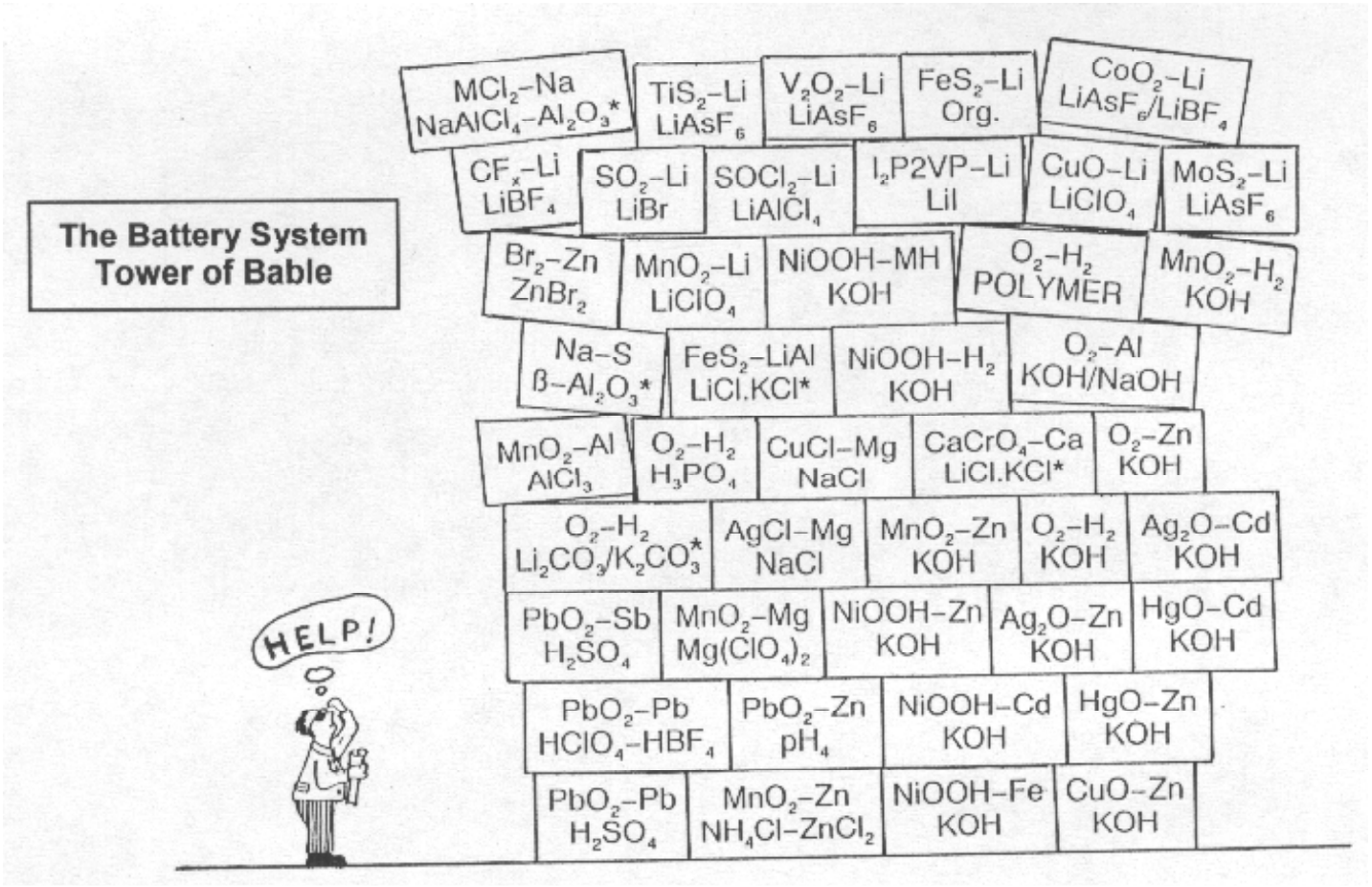
Hybrid Vehicles





Energy Storage in Advanced Batteries

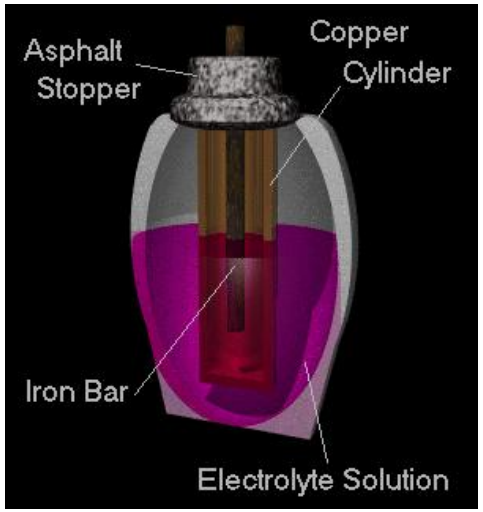
Electrochemical Energy Storage in Batteries

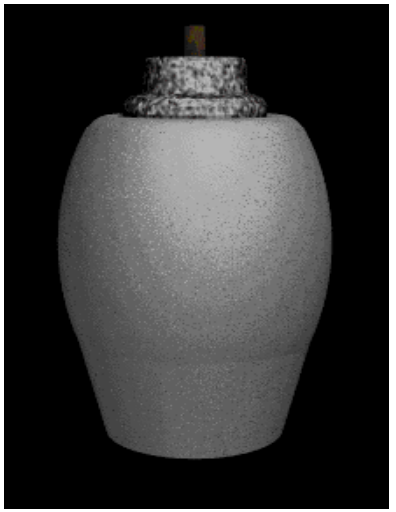


History

- ***about 2000 years ago:***

  first known battery from Khujut Rabuah (near Bagdad), excavated in 1938





A 2 Volt cell using fruit juice as an electrolyte…

History

- ***1834 - 1889:* Raymond Gaston Planté**
  – *"Father" of the lead-acid battery*

Batteries

Primary

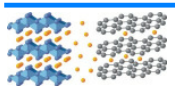
Secondary
(rechargeable)

Changing Requirements

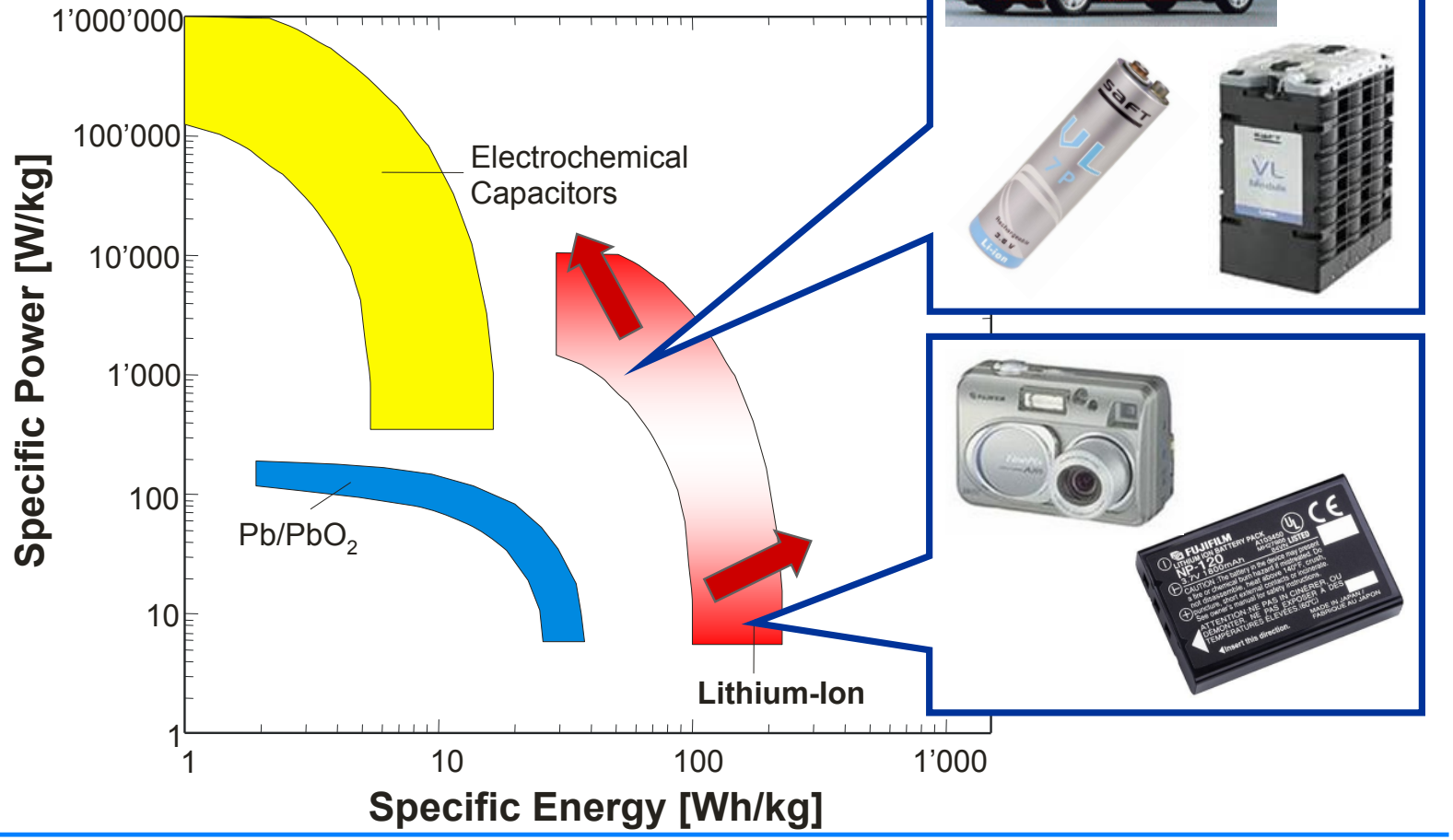
- *Operating temperature:*
  +5 – +40°C
- *Calendar life:*
  3 – 5 years
- *Cycle life:*
  500 – 1000 deep cycles
- *Charge / discharge rate:*
  0.5 – 2 C

- *Operating temperature:*
  -40 – +60°C
- *Calendar life:*
  10 – 15 years
- *Cycle life:*
  3000 – 7000 various cycles
- *Charge / discharge rate:*
  *1 – **10 C***

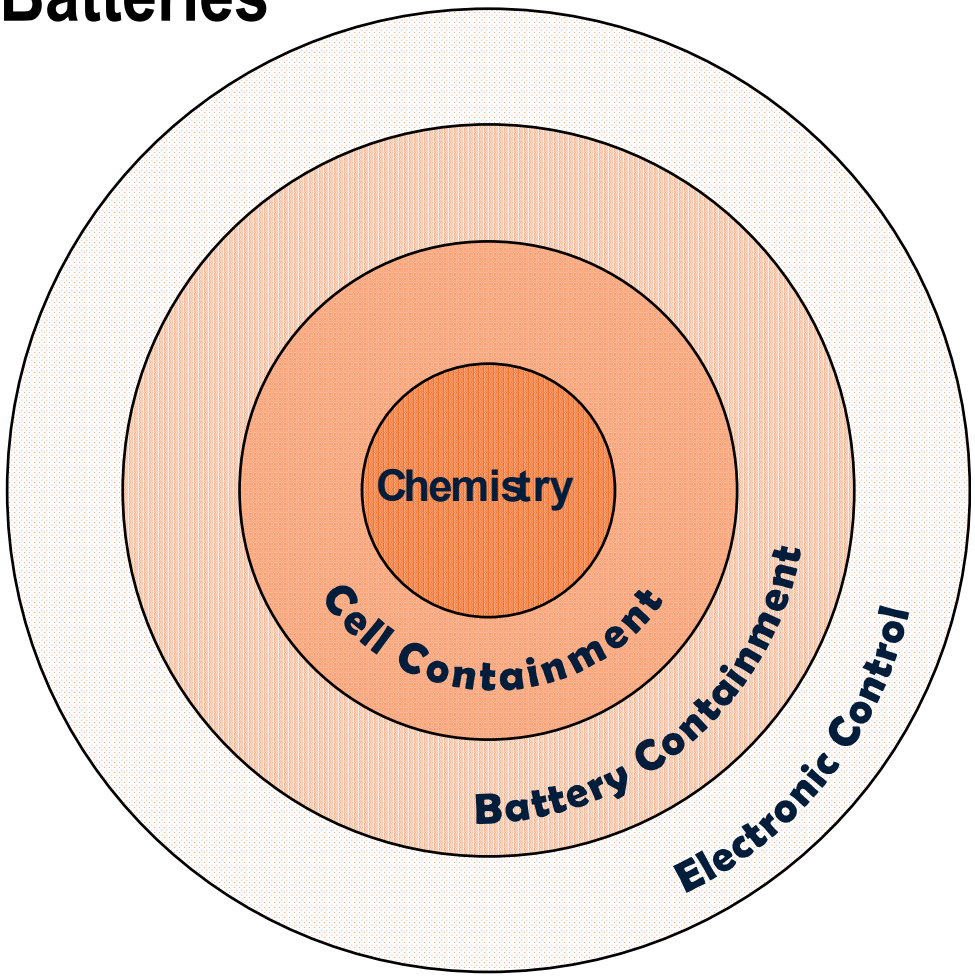
- *Operating temperature:*
  -20 – +50°C
- *Calendar life:*
  15 – 20 years
- *Cycle life:*
  10000 – 15000 shallow cycles
- *Charge / discharge rate:*
  0.1 – 0.5 C



Ragone-Plot


1'000'000
100'000
10'000
1'000
100
10
1
1
10
100
1'000
Specific Power [W/kg]
Specific Energy [Wh/kg]
Electrochemical
Capacitors
Pb/PbO2
Lithium-Ion
saft
VL
FUJIFILM
NP-120

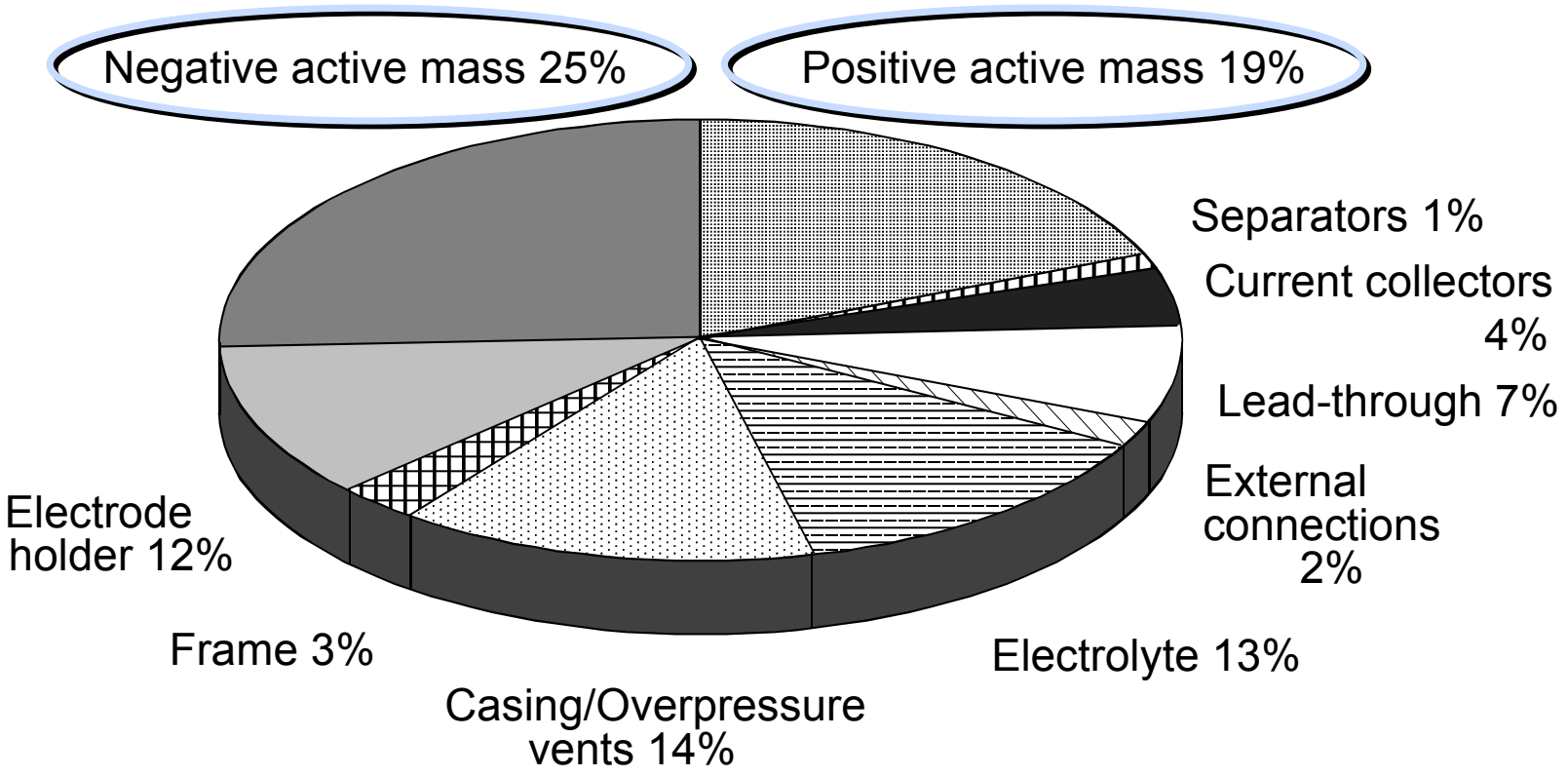
Batteries


Chemistry
Cell Containment
Battery Containment
Electronic Control

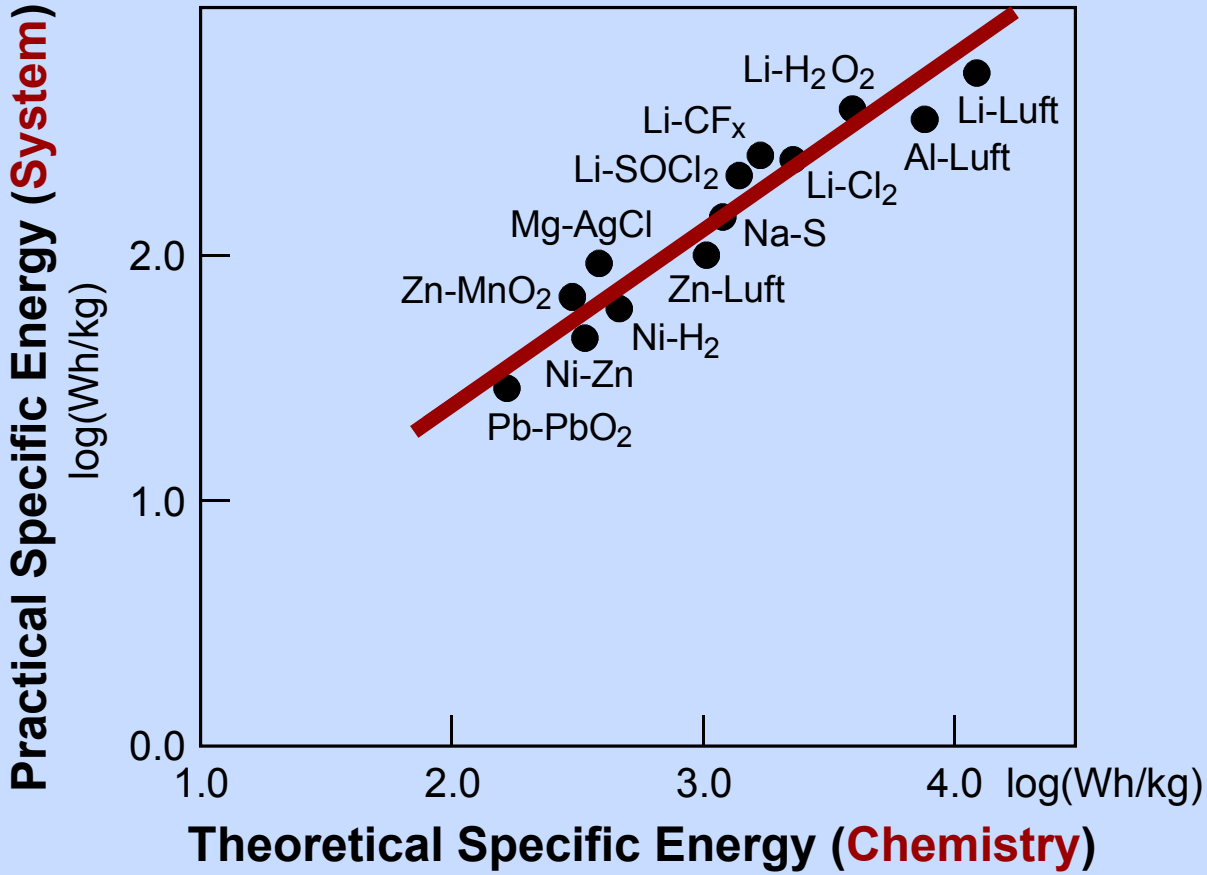

Module
Cell

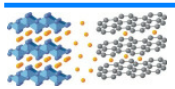
Batteries

Mass distribution of the components of a NiMH battery (24 V, 10 Ah)



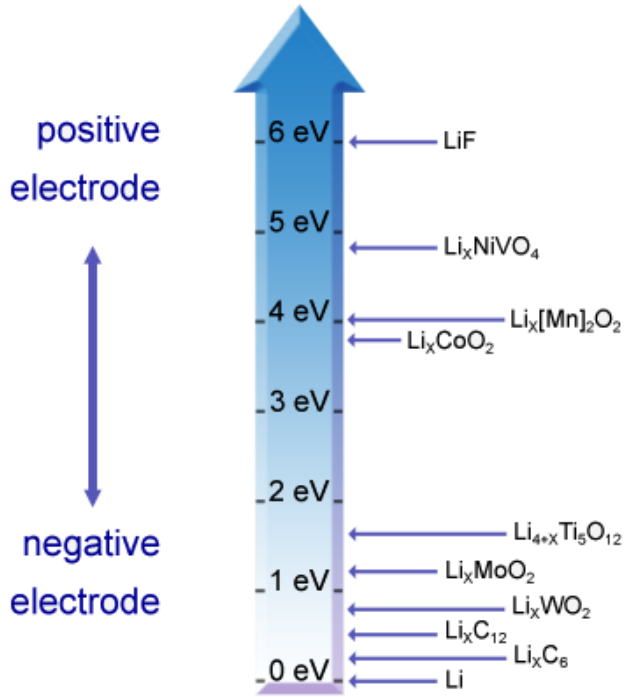
Specific Energy





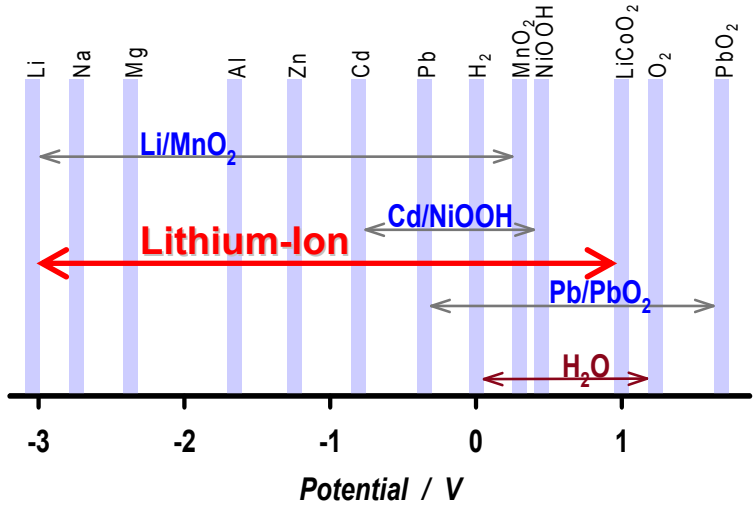
Electrochemistry: Nonaqueous Electrolytes

Potentials of Li-ion battery materials (vs. Li/Li⁺)

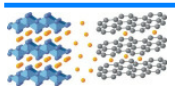


Source: Solid Energy GmbH, www.solid-energy.com

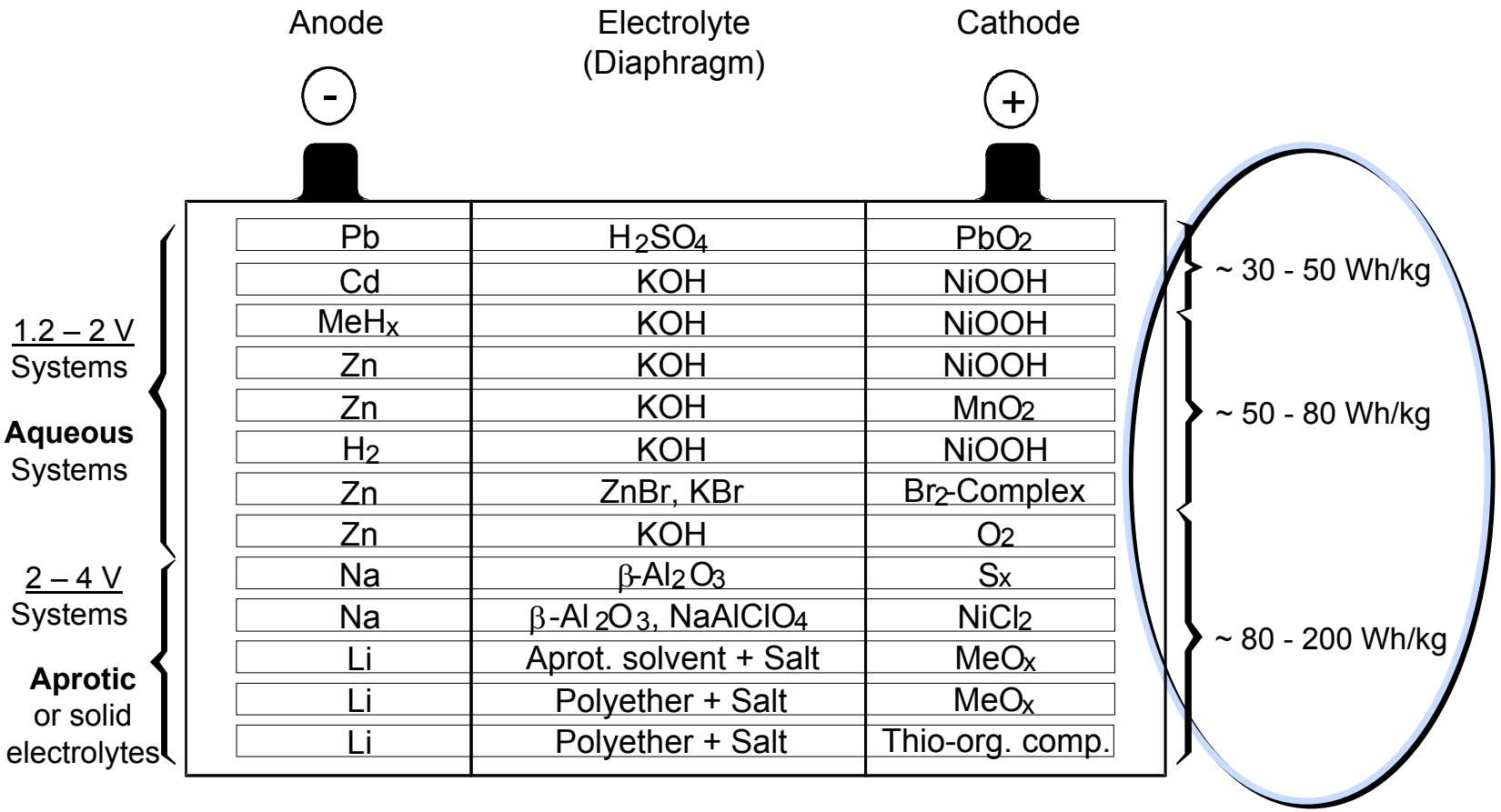
Standard potentials of battery electrodes



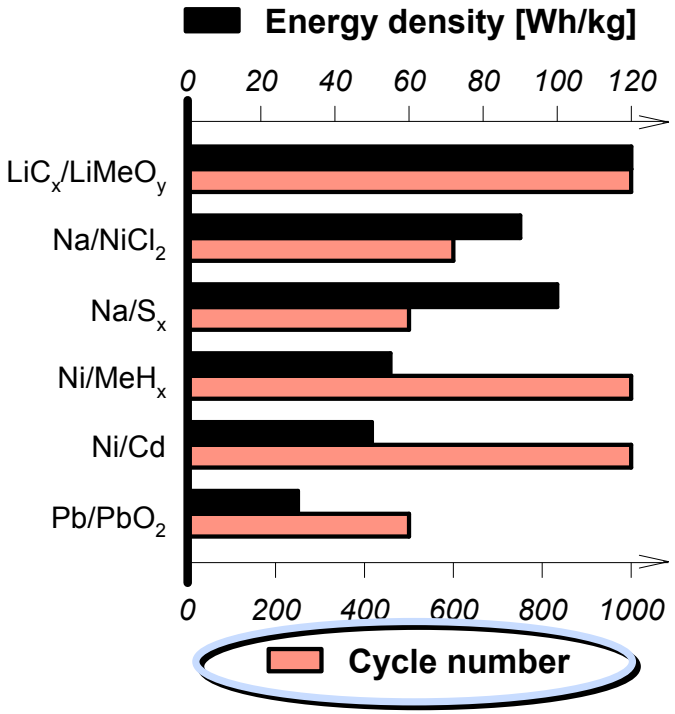
- ***Wide potential window***
- ***Very negative potential at the anode (reductive conditions)***
- ***High potential at the cathode (oxidative conditions)***

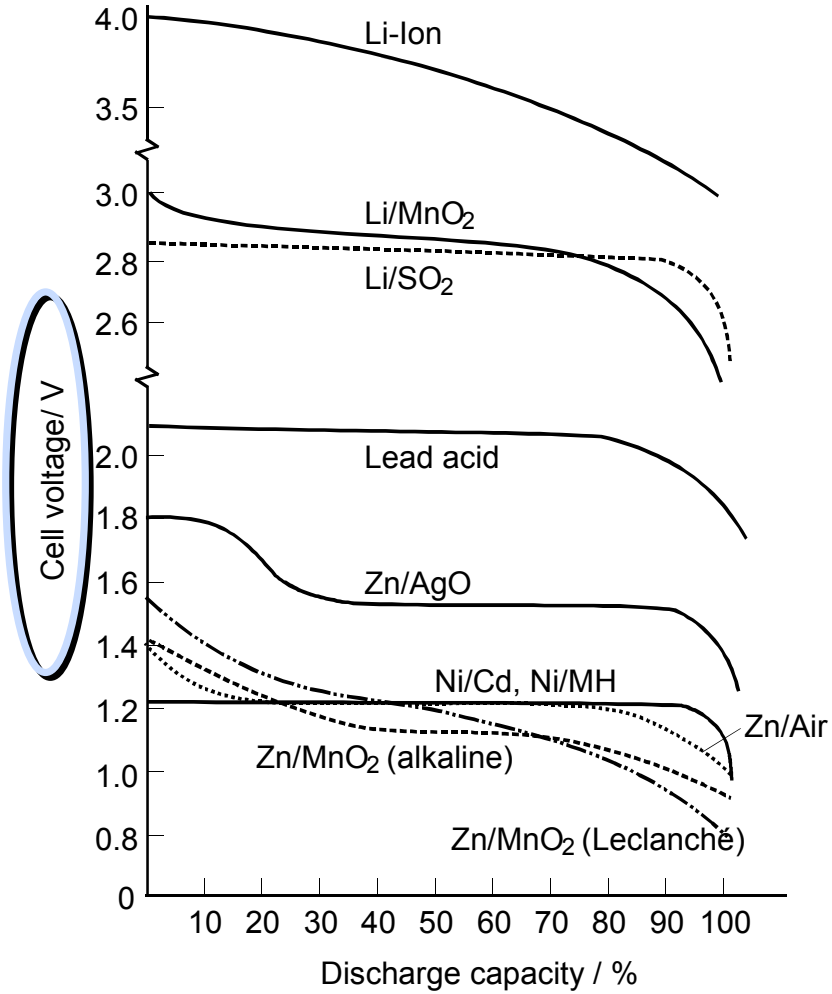


Batteries: Chemistry



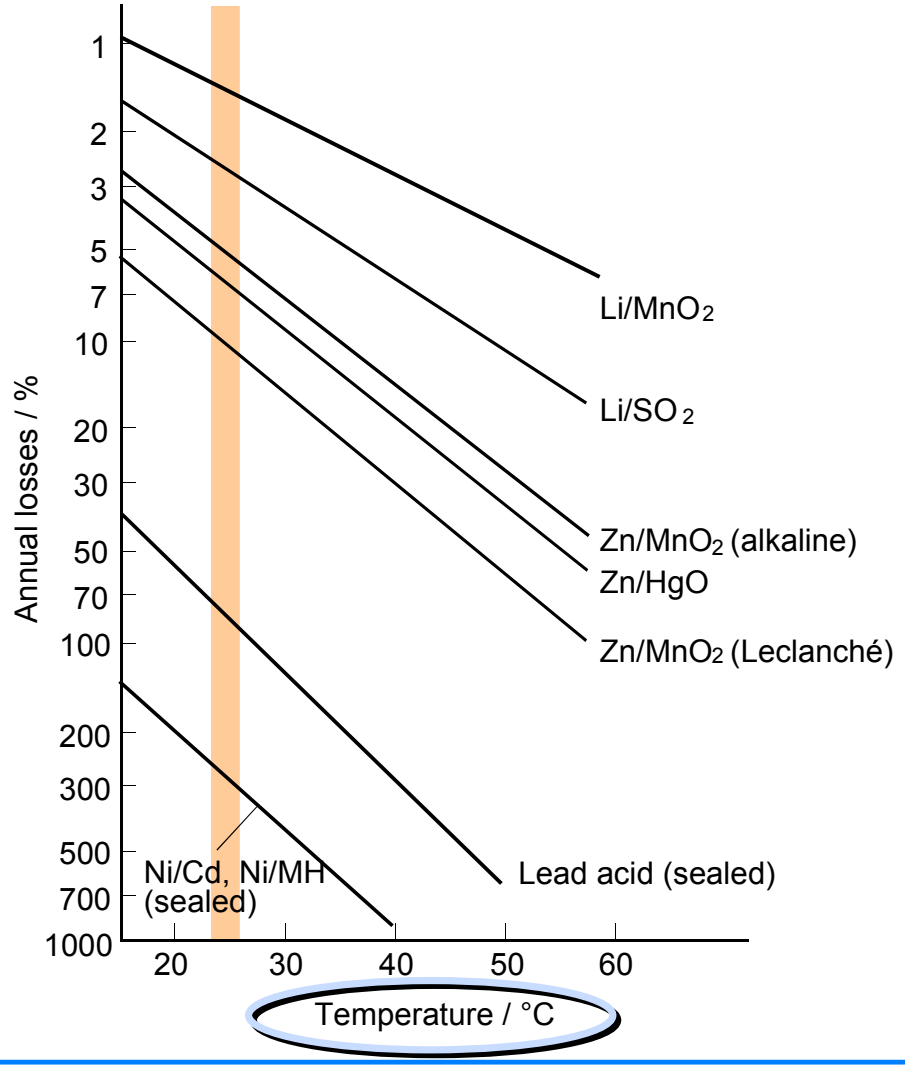
Batteries


Energy density [Wh/kg]
0 20 40 60 80 100 120
LiC$_x$/LiMeO$_y$
Na/NiCl$_2$
Na/S$_x$
Ni/MeH$_x$
Ni/Cd
Pb/PbO$_2$
0 200 400 600 800 1000
Cycle number

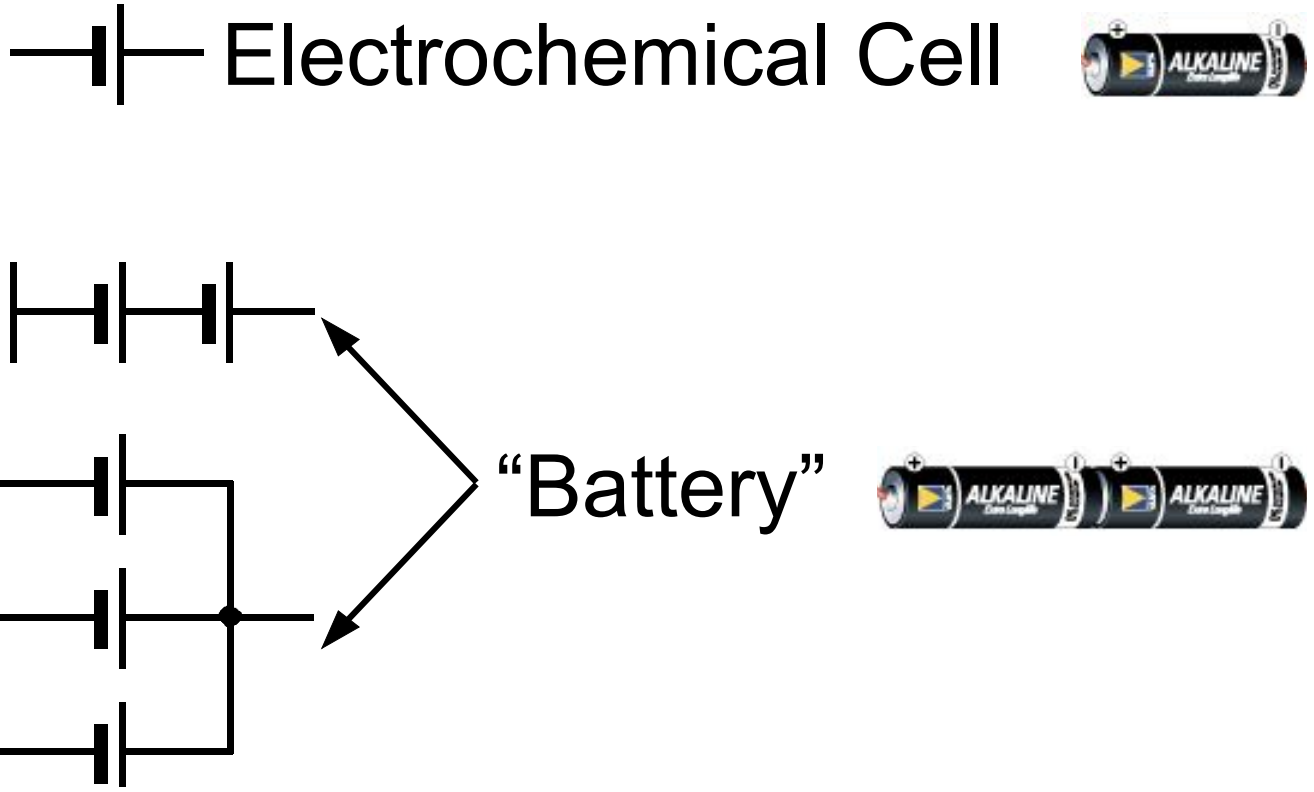

Cell voltage/ V
4.0
3.5
3.0
2.8
2.6
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0
Li-Ion
Li/MnO$_2$
Li/SO$_2$
Lead acid
Zn/AgO
Ni/Cd, Ni/MH
Zn/Air
Zn/MnO$_2$ (alkaline)
Zn/MnO$_2$ (Leclanché)
10 20 30 40 50 60 70 80 90 100
Discharge capacity / %

Batteries

Rate of self-discharge of some primary and secondary cells



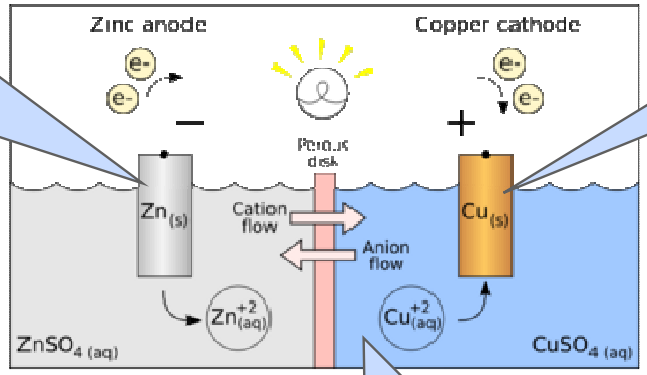
Batteries and Cells



The Electrochemical Cell

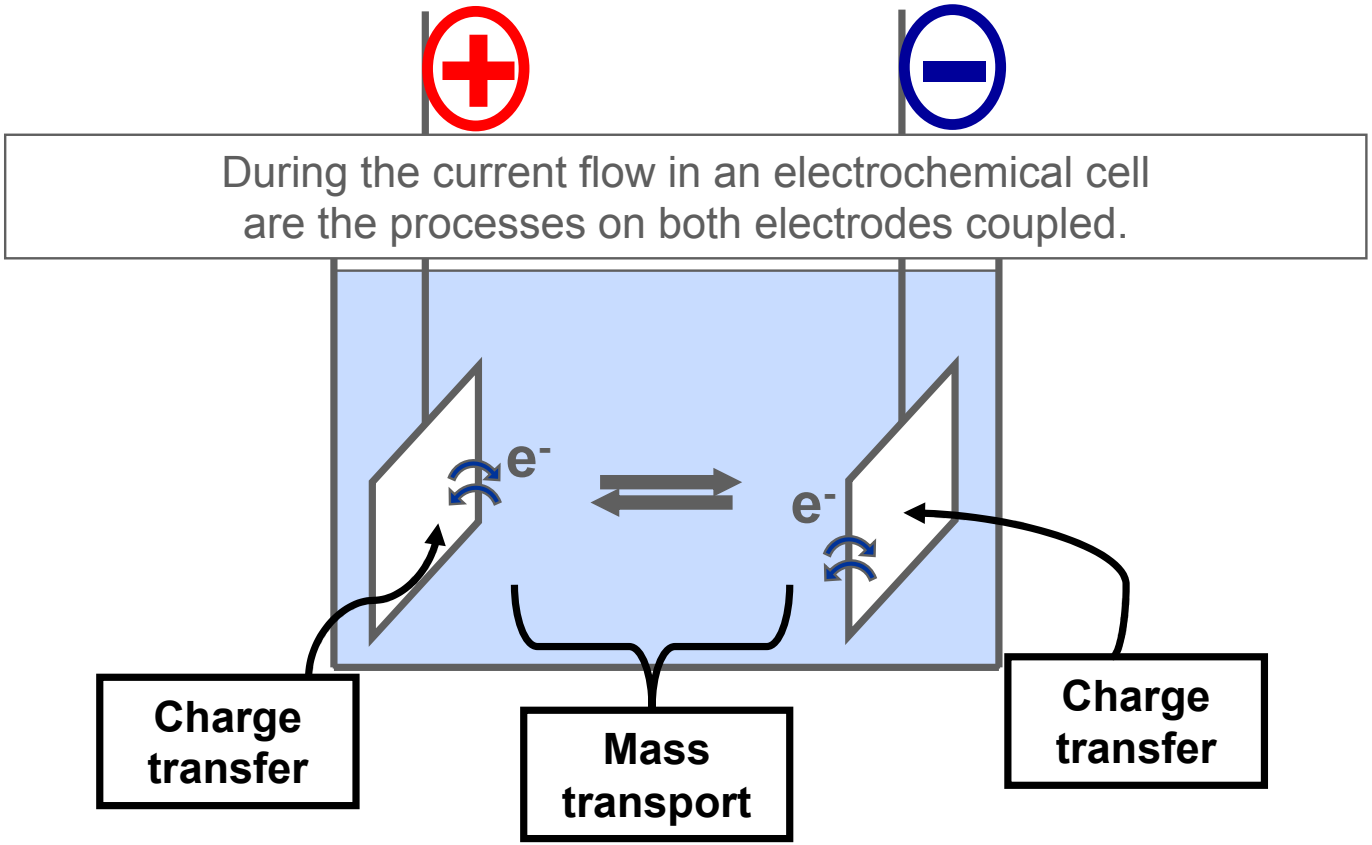
Negative Electrode

Positive Electrode

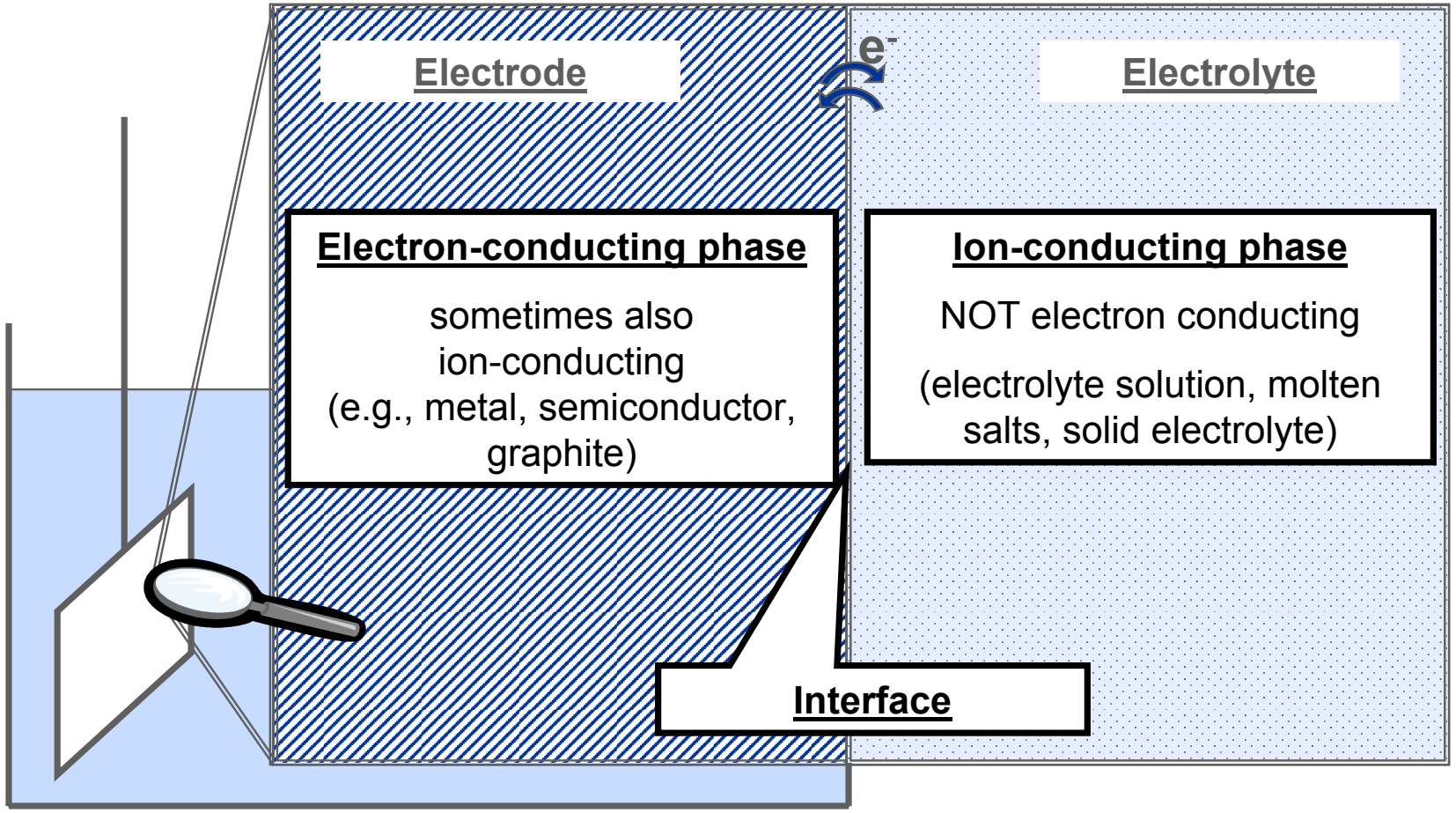


Electrolyte

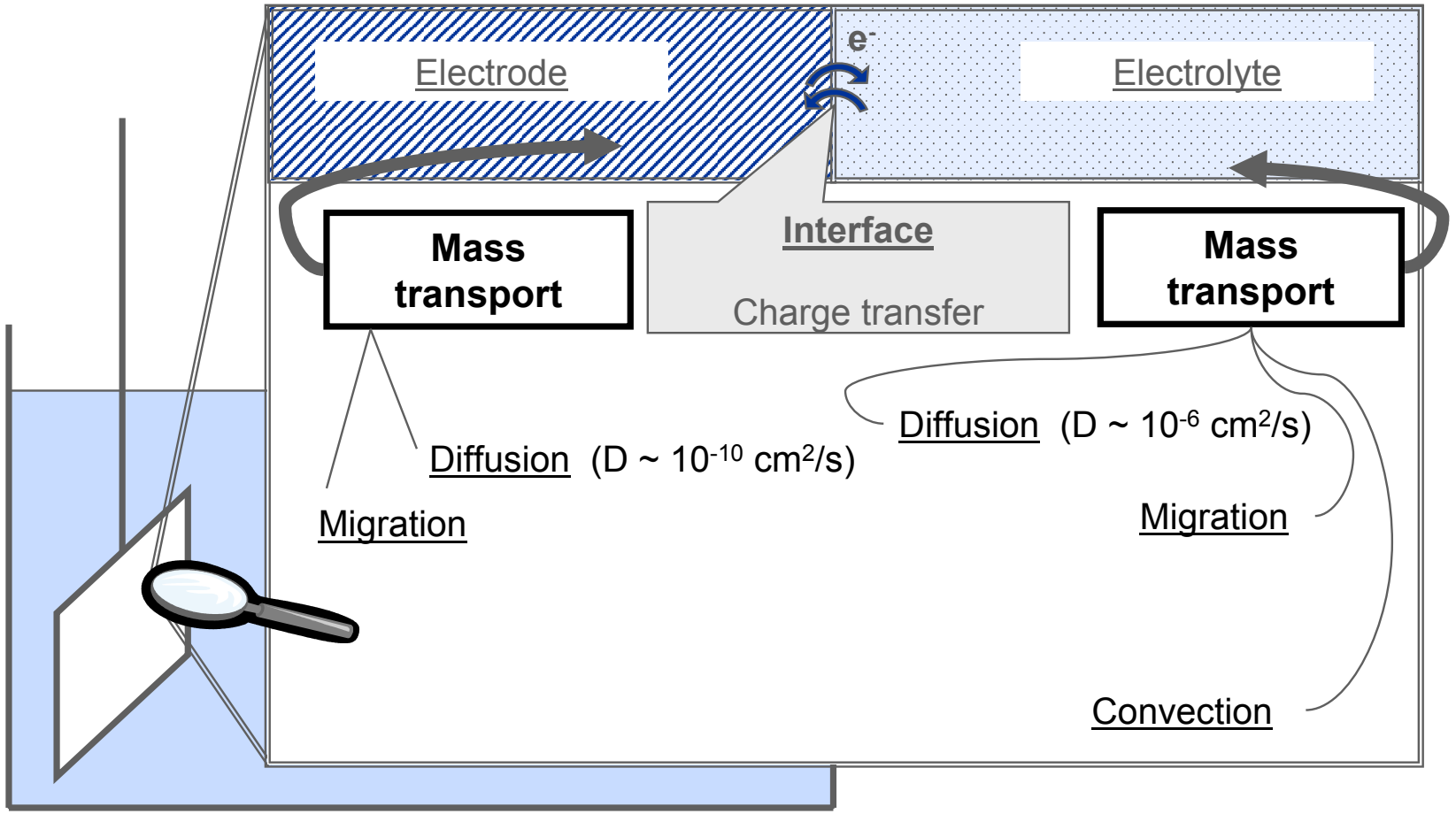
Electrochemical Cells



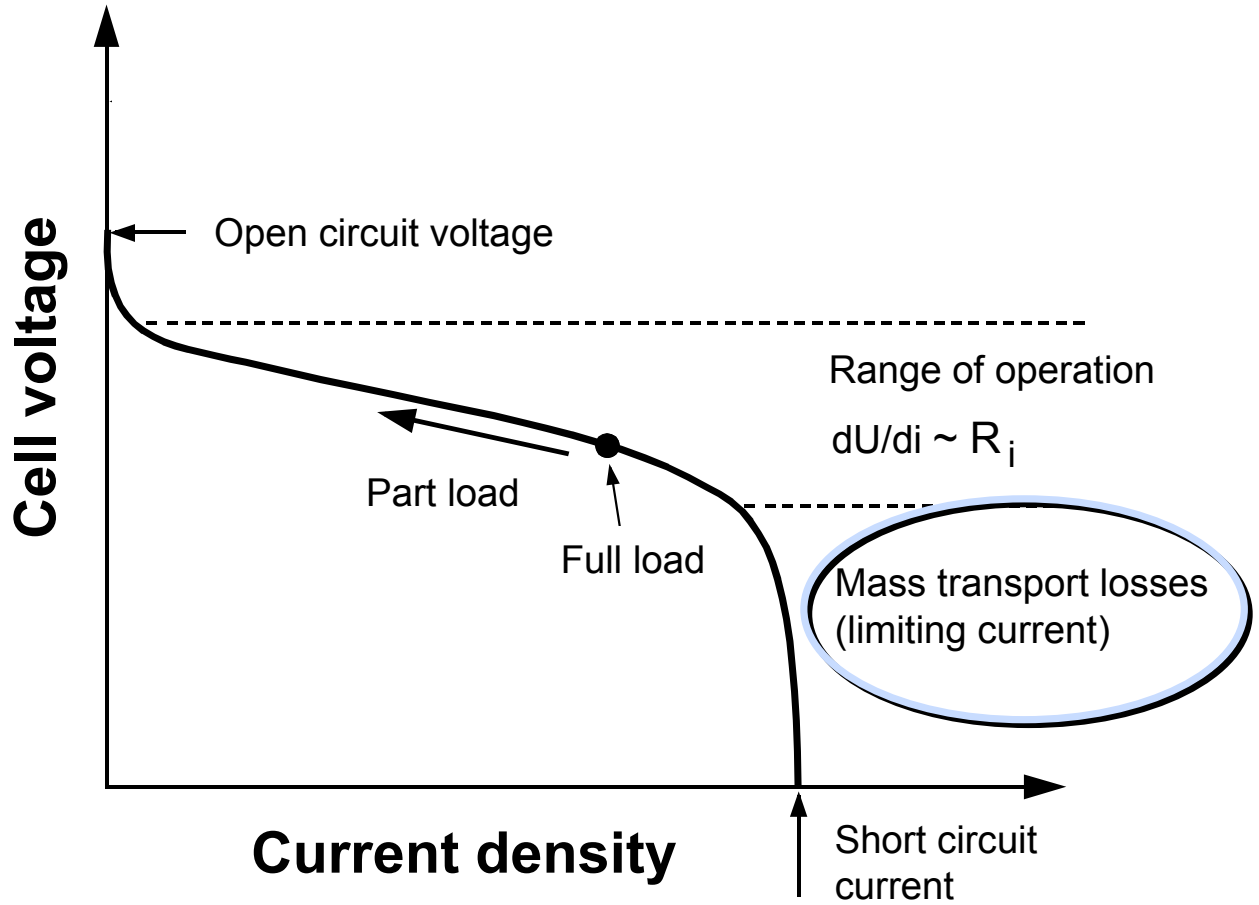
Electrochemical Cells



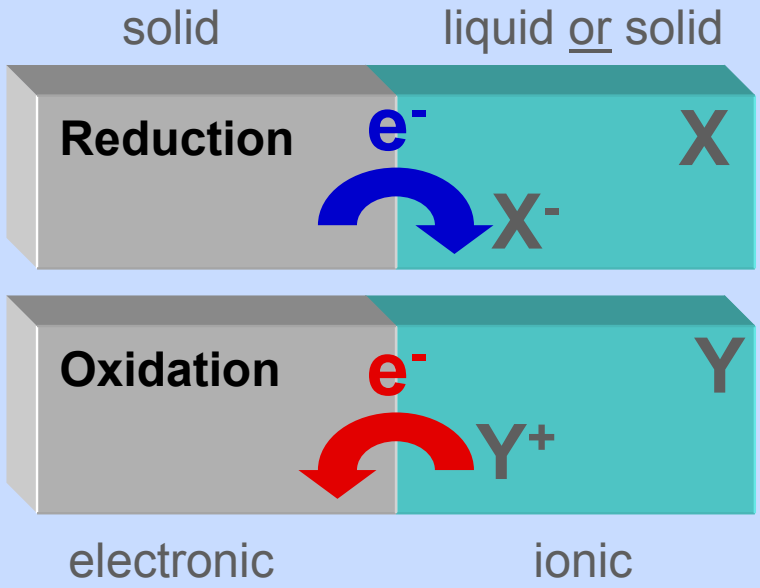
Electrochemical Cells



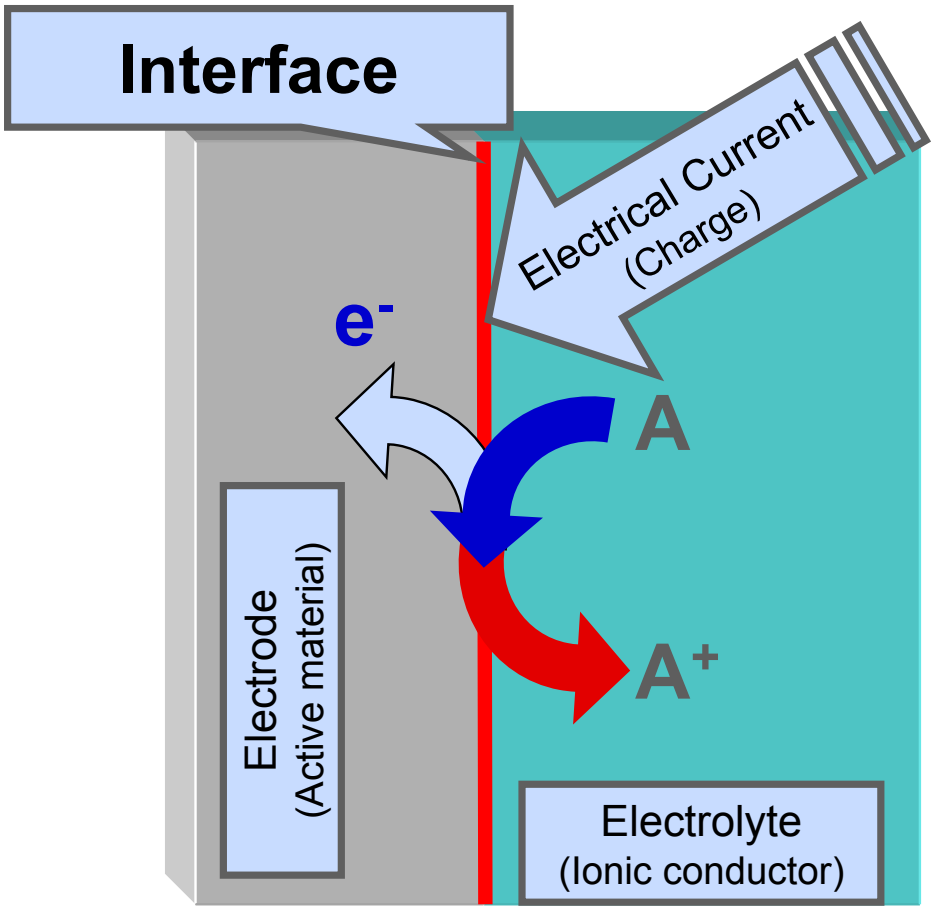
Polarization Curve



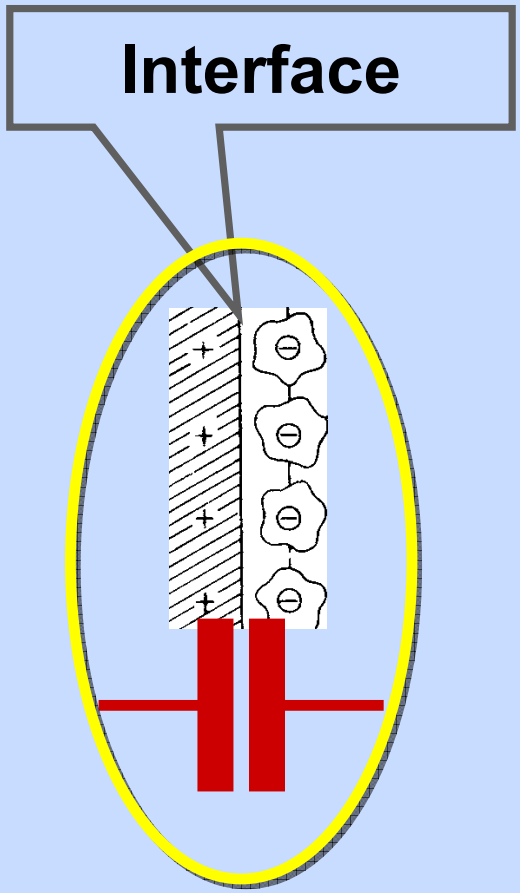
Electrodes


solid
liquid or solid
Reduction
e-
X
X-
Oxidation
e-
Y
Y+
electronic
ionic

Electrode/Electrolyte Interface

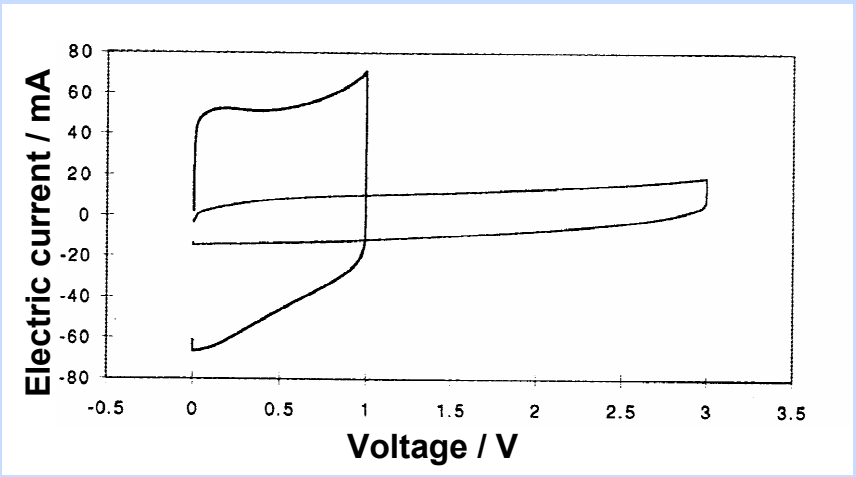


Electrochemical Double Layer

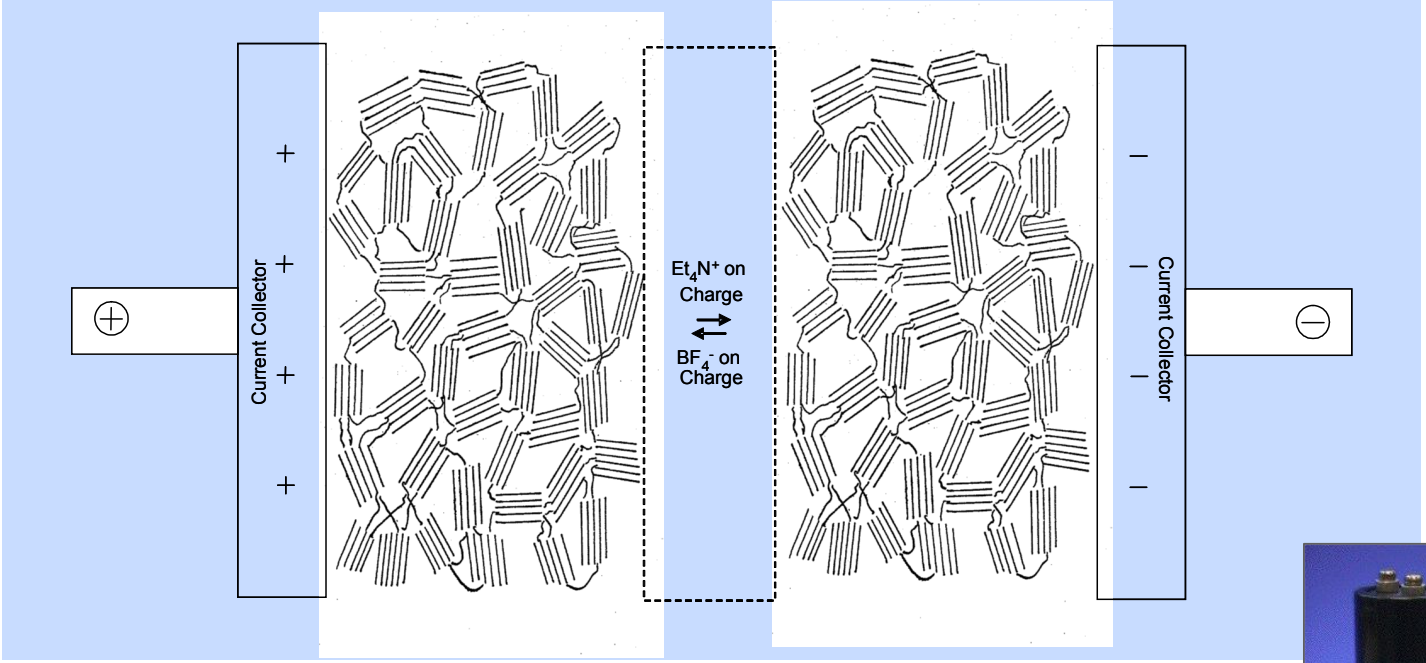


$$i_C = C_d \cdot \frac{d\varphi}{dt}$$

$$\frac{d\varphi}{dt} = \text{konst} \quad \Rightarrow \quad i_C \cong \text{konst}$$



Electrochemical Capacitors

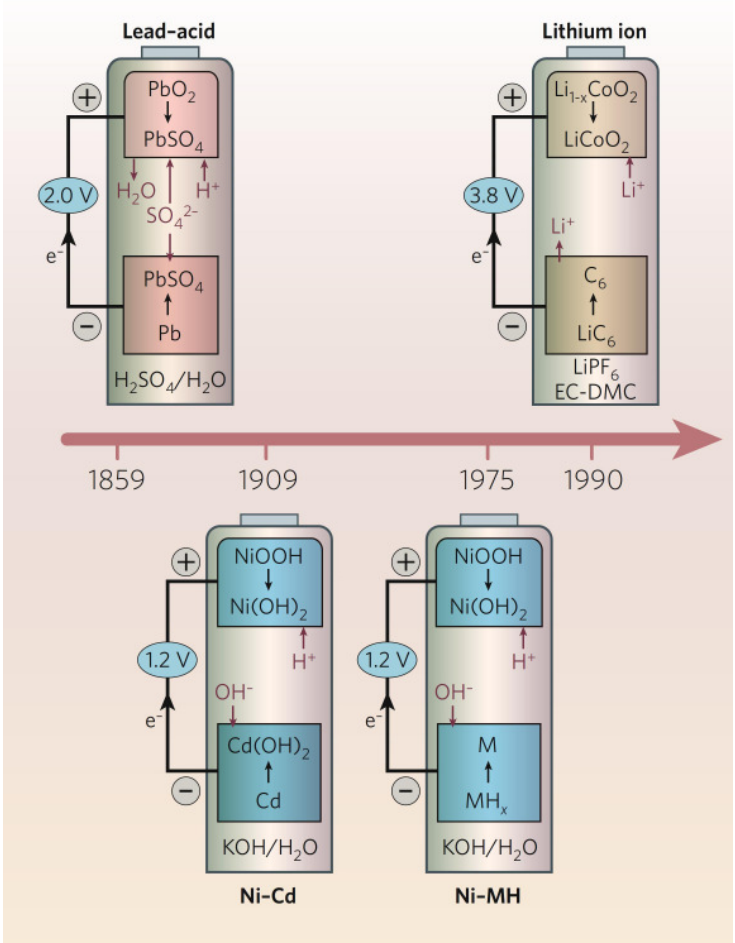


Interface processes are fast...
...but the energy density is low!

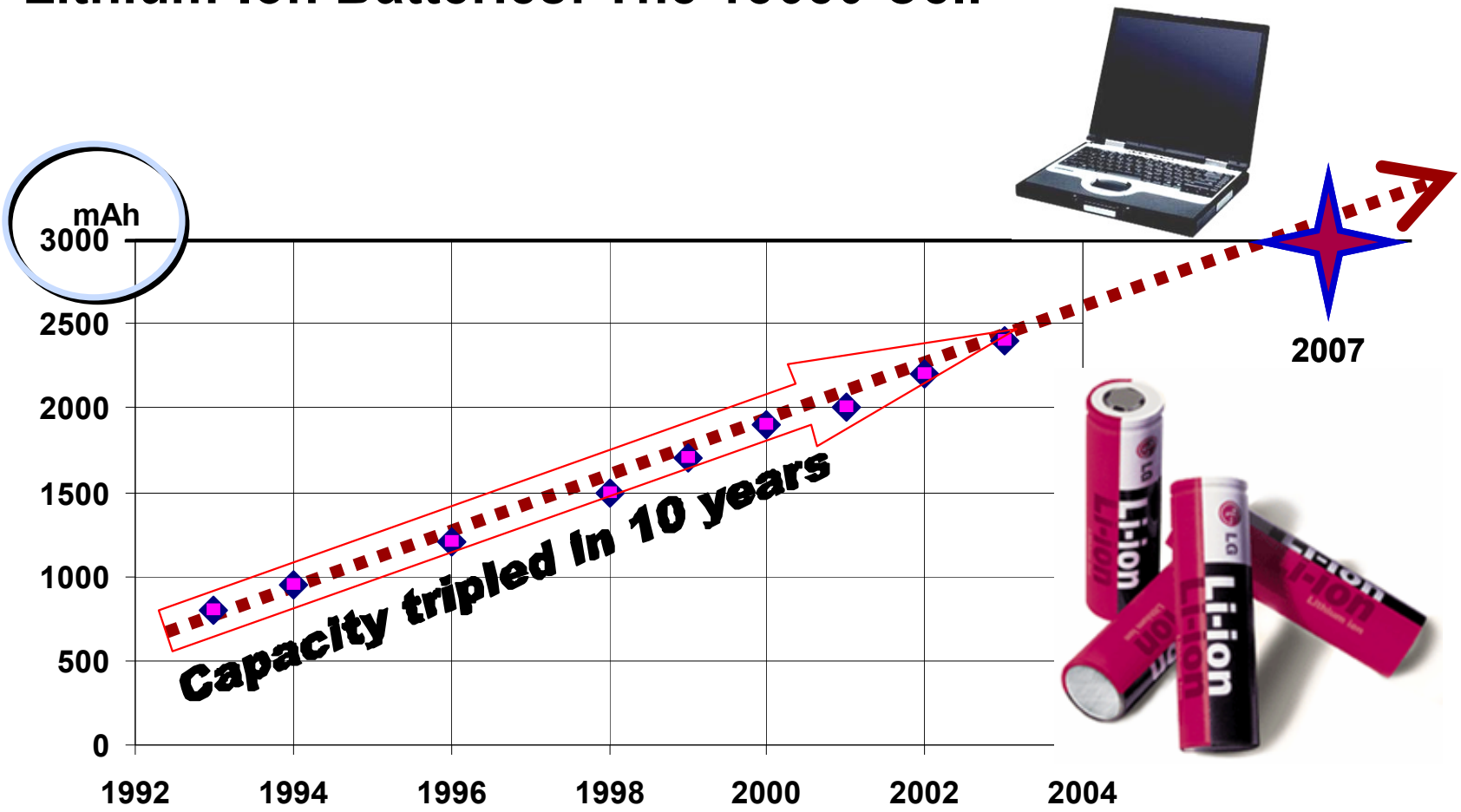
Electrochemical Energy Storage in Batteries

Faraday Law

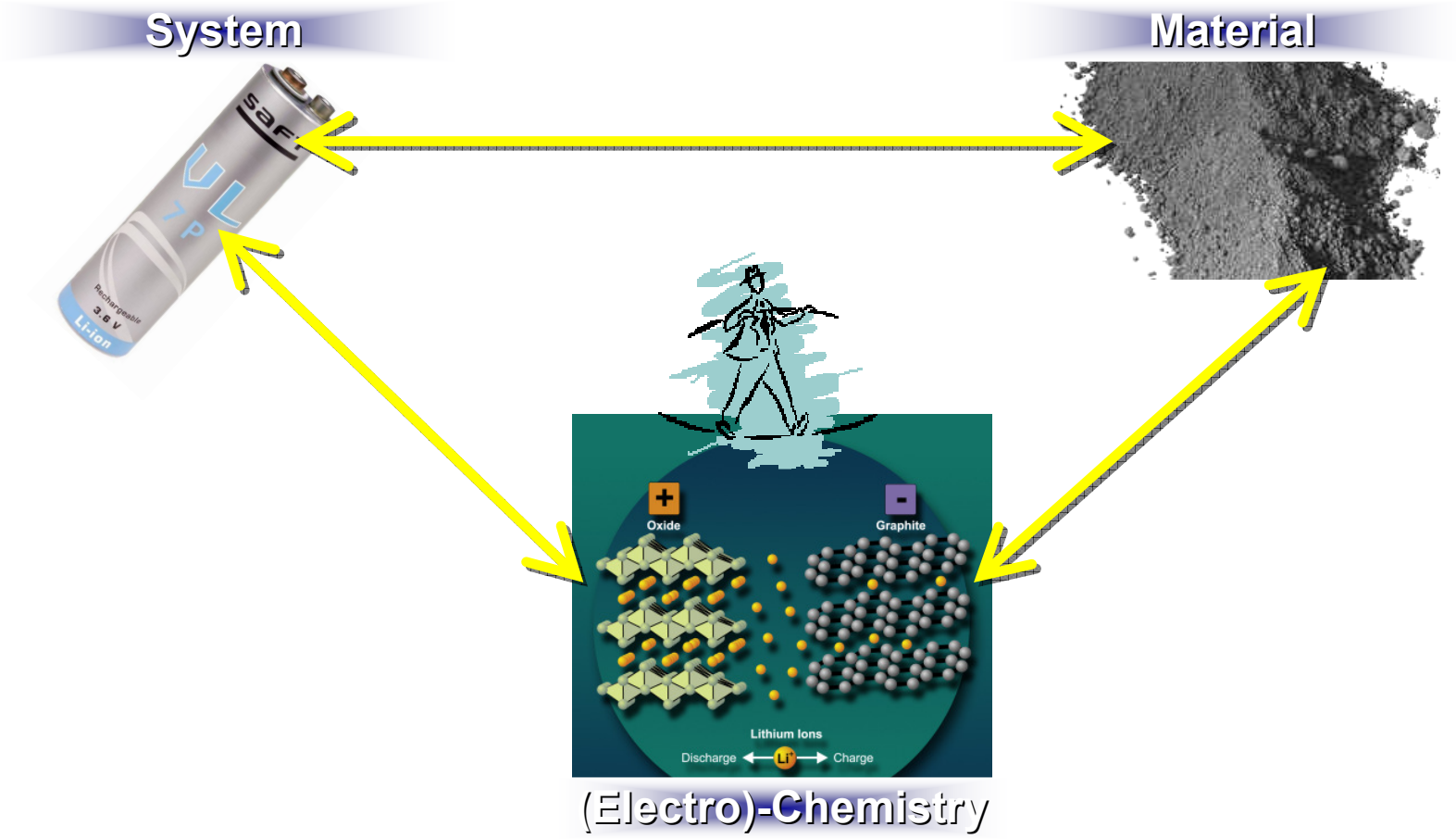
$$Q = zF\frac{m}{M}$$



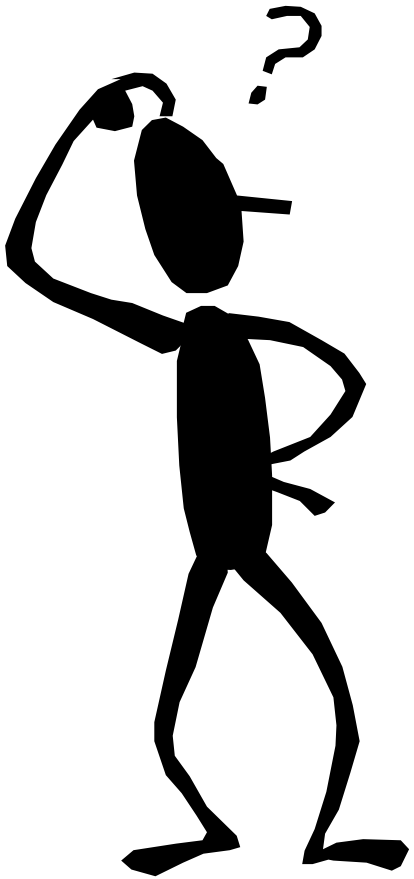
Lithium-Ion Batteries: The 18650 Cell



The Battery Research



The Challenges



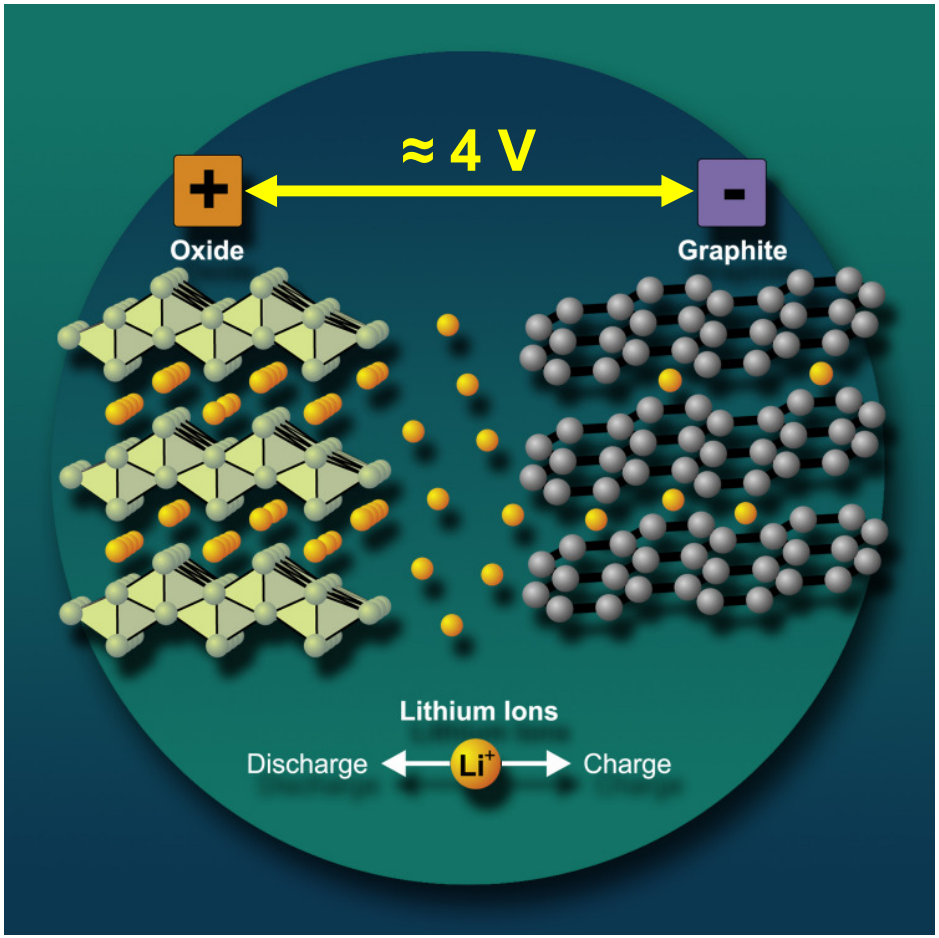
- **Environment:** ~~Hg~~, ~~Cd~~, ... ; recycling
- **Cost:**
  - cheap raw materials
  - cheap technology
- **Safety:**

The Best System So Far: The Lithium-Ion Battery

$LiCoO_2$,
$LiNiO_2$,
mixed

$LiMn_2O_4$

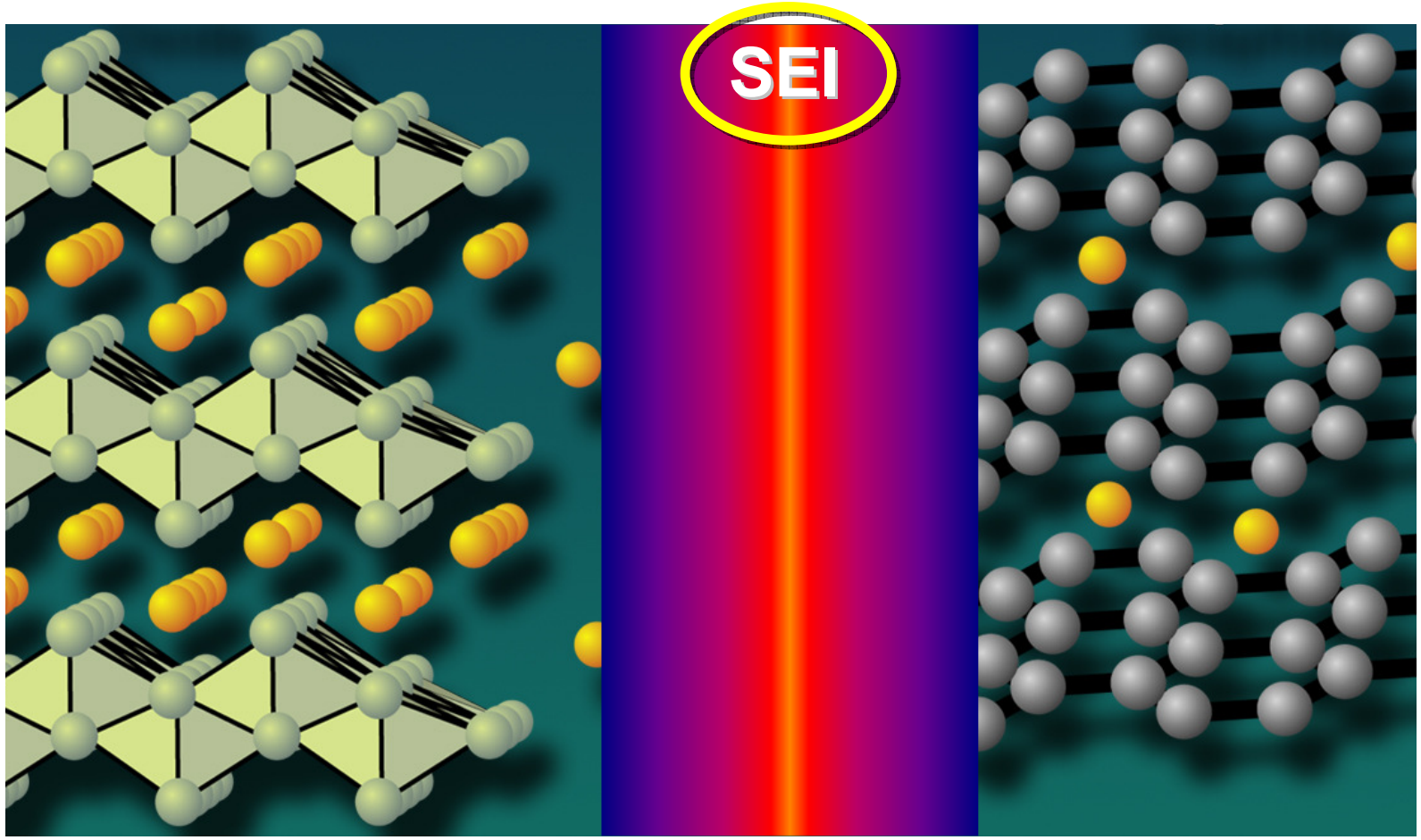
$LiFePO_4$



Graphite

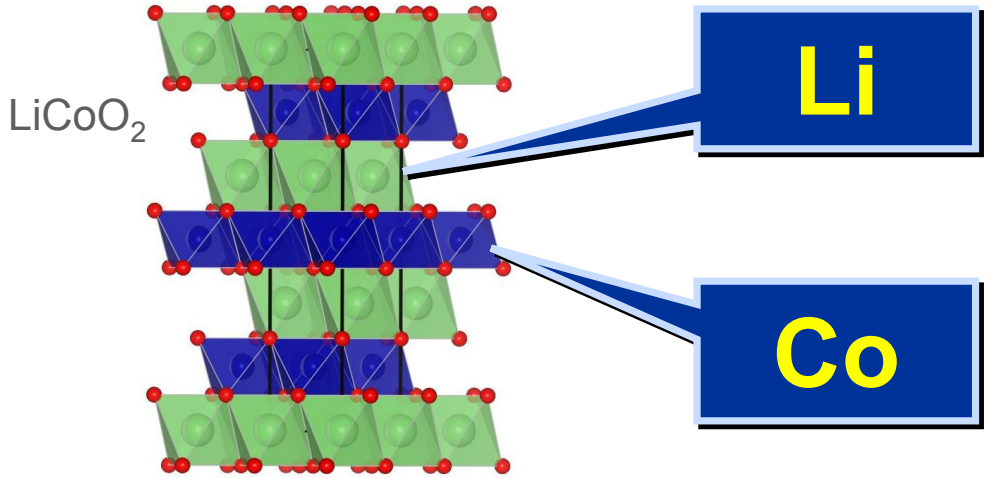
Hard Carbons

Solid Electrolyte Interphase (SEI)



Active Materials

Insertion compound	Density [g/cm^3]	y (utilizable)	Ah/kg (utilizable)	$\bar{E}$ vs. Li_yC_6 [V]	D [cm^2/s]
$Li_{1-y}NiO_2$	4.81	~0.7	160	3.6	$2 \cdot 10^{-7}$
$Li_{1-y}CoO_2$	5.16	~0.5	140	3.7	10^{-11}
$Li_{1-y}Mn_2O_4$	4.28	~1.0	115	3.8	$5 \cdot 10^{-10}$
Li_yC_6	2.2	~1.0	360	0.0	10^{-9}



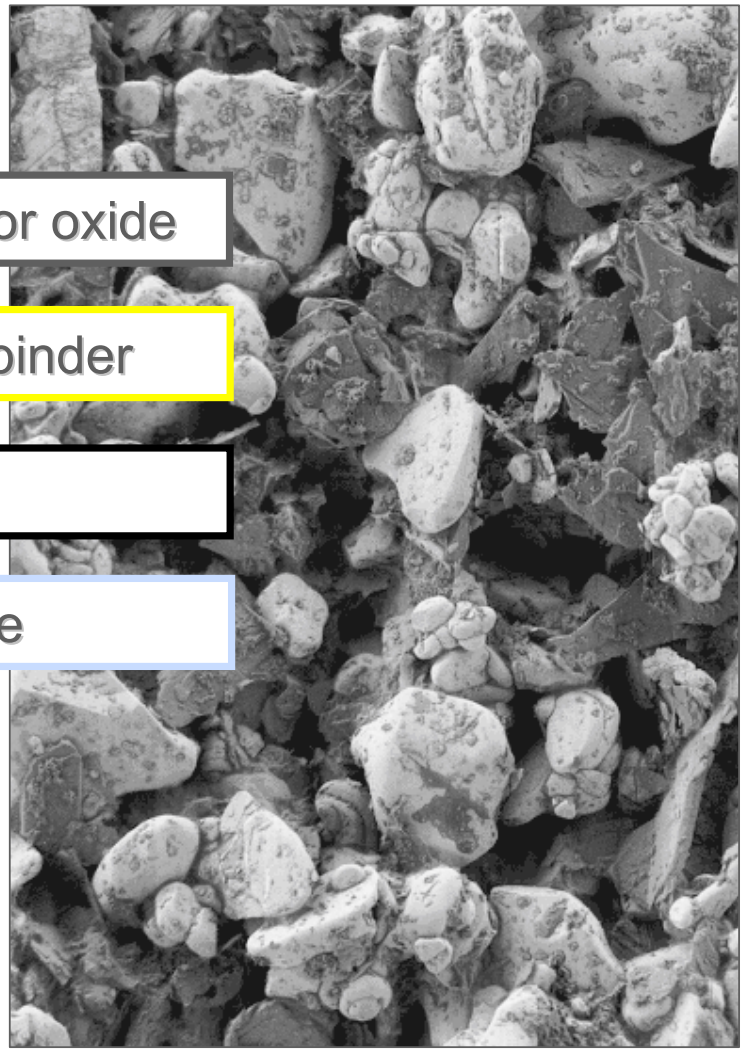
Battery Electrodes

graphite or oxide

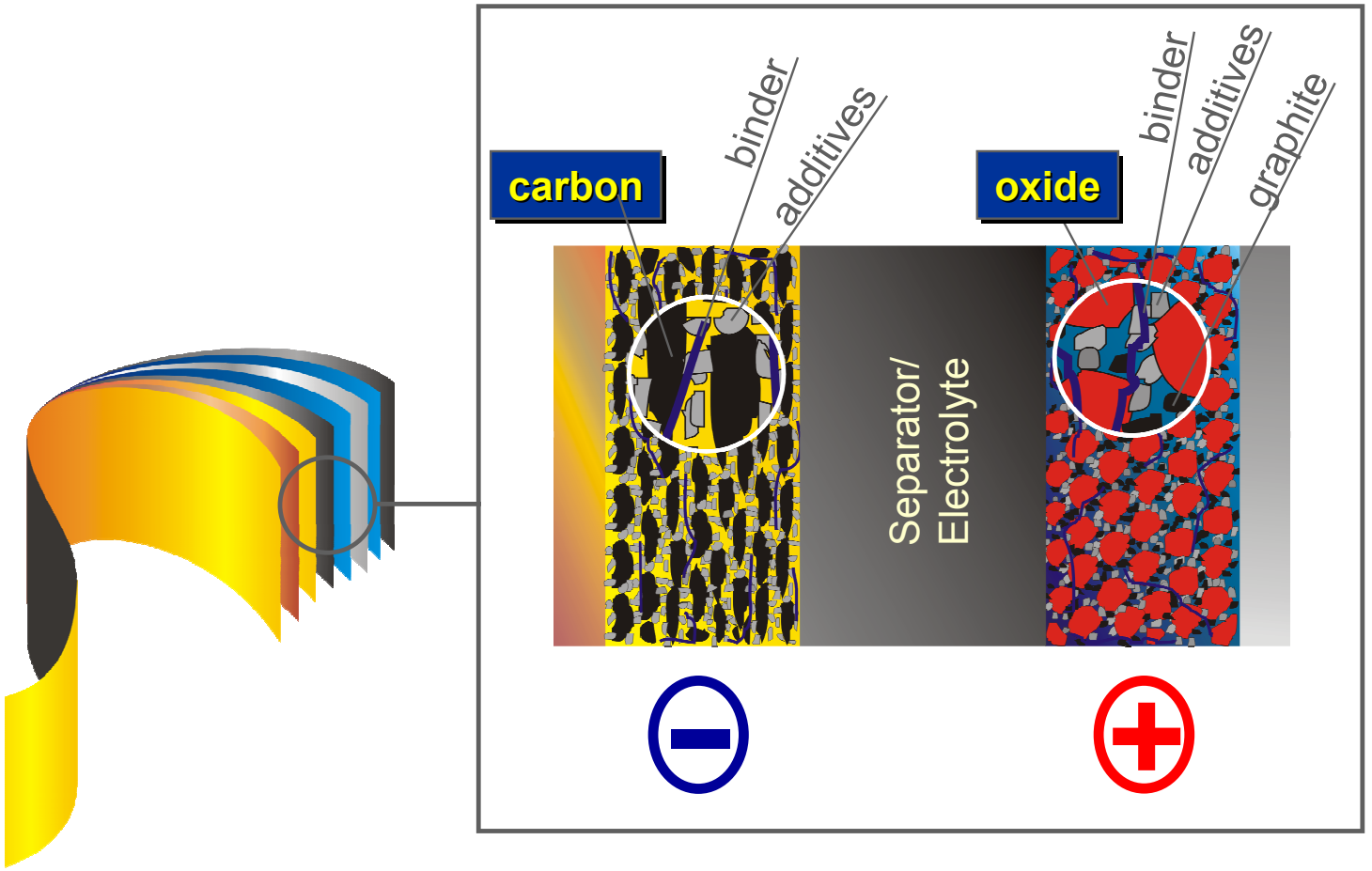
polymer binder

soot

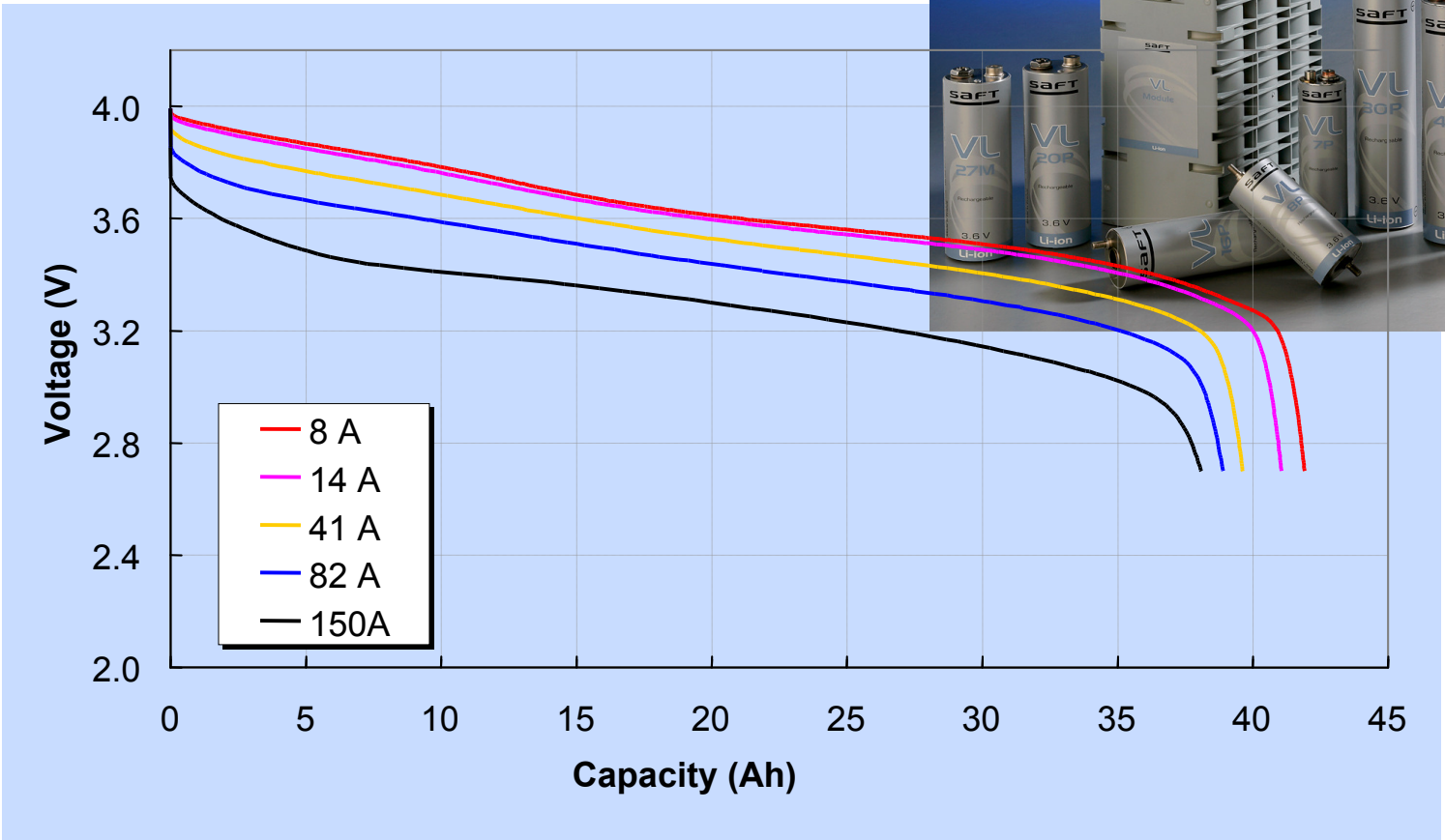
electrolyte



Battery Electrodes



Discharge Curves



VL41M typical discharge at +20°C [M. Broussely, SAFT, 2005]

Aging of Lithium-Ion Batteries

*"Aging of a battery can be defined as the modification of its properties with **time** and **use**."*

Calendar Life

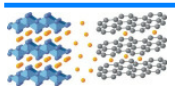
↓

Aging during Storage

Cycle Life

↓

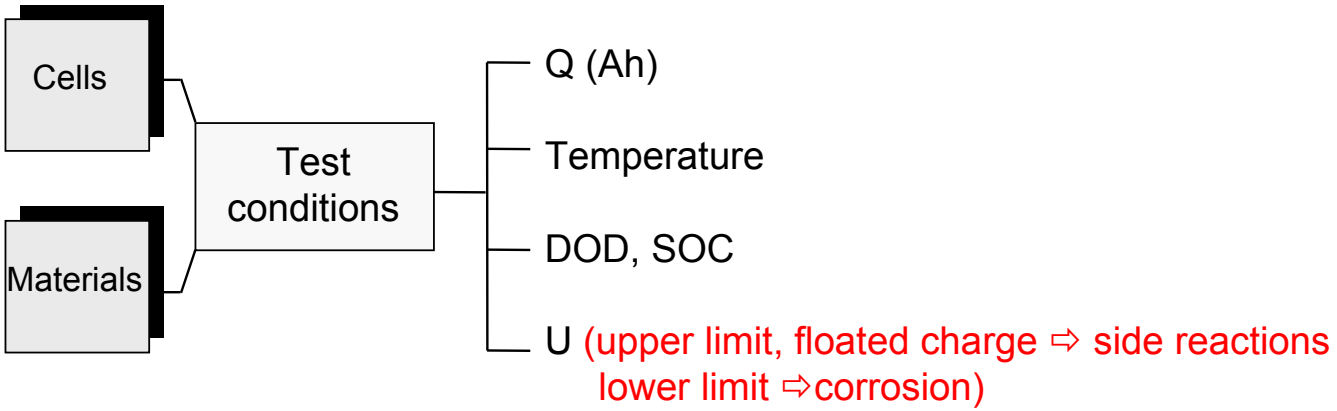
Aging during Use

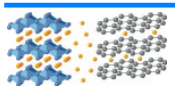


Aging of Lithium-Ion Batteries

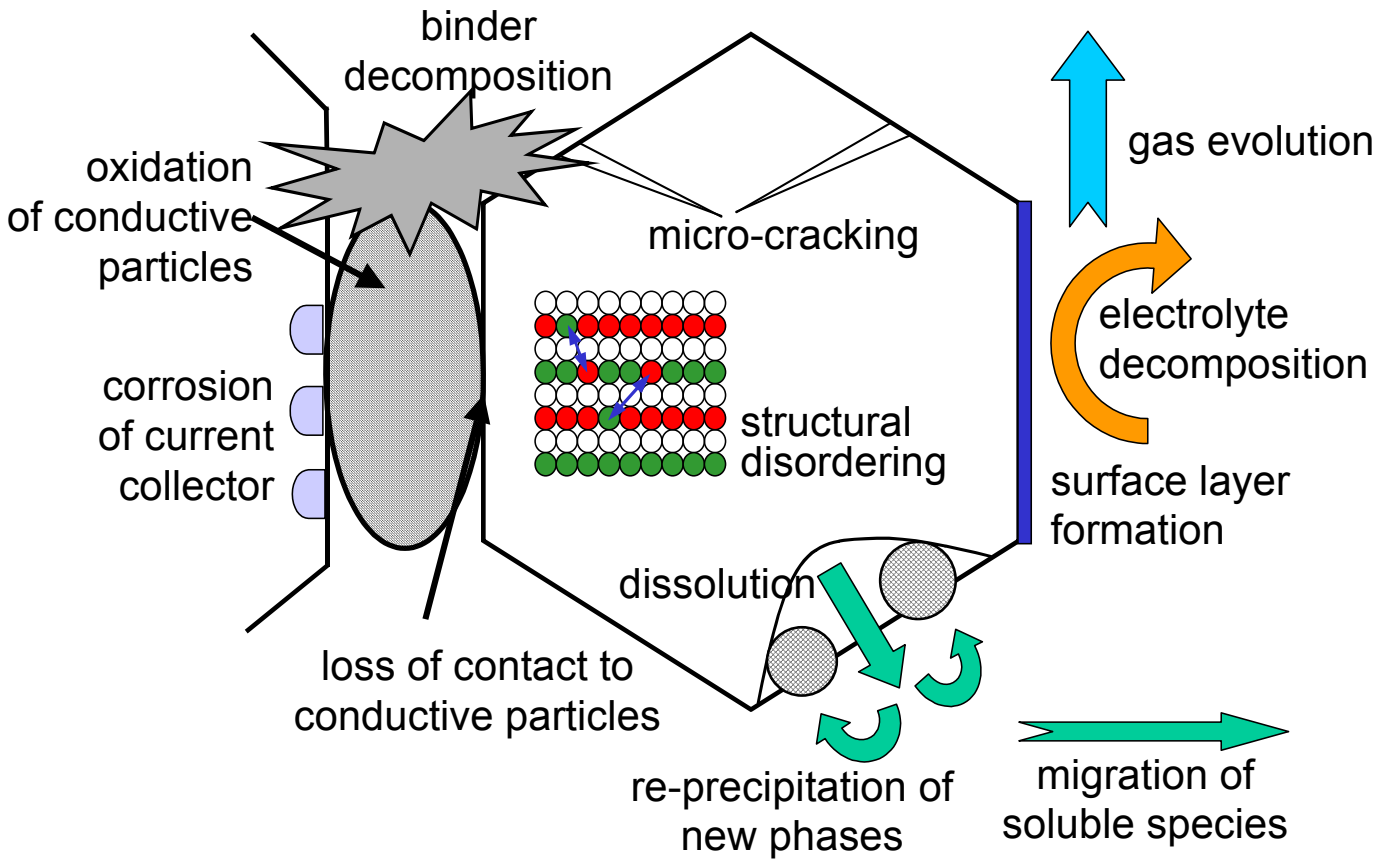
Battery aging will depend on

- ***Conditions of use***
  (number of cycles, DOD, temperature, power, etc.)
- ***Module type and general cell chemistry***
  - ***Lithium-ion: LiC_6//liquid electrolyte//$Li(Ni,Mn,Co)O_2$ [$LiMn_2O_4$]***
  - ***Lithium polymer: Li//dry polymer//vanadium oxide***
  - ***Lithium-ion polymer: LiC_6//polymer + liq.//$LiMn_2O_4$***

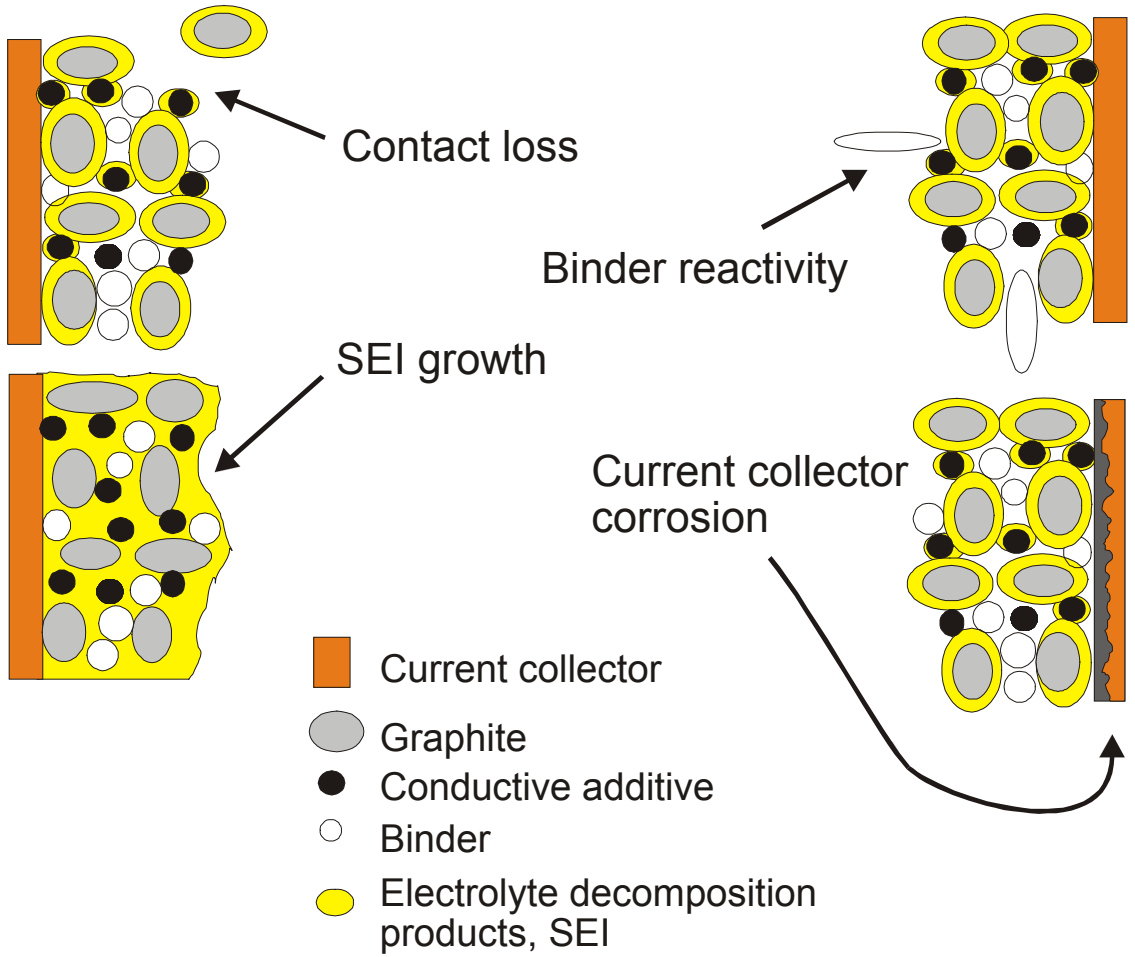




General Degradation Mechanisms of Positive Electrodes

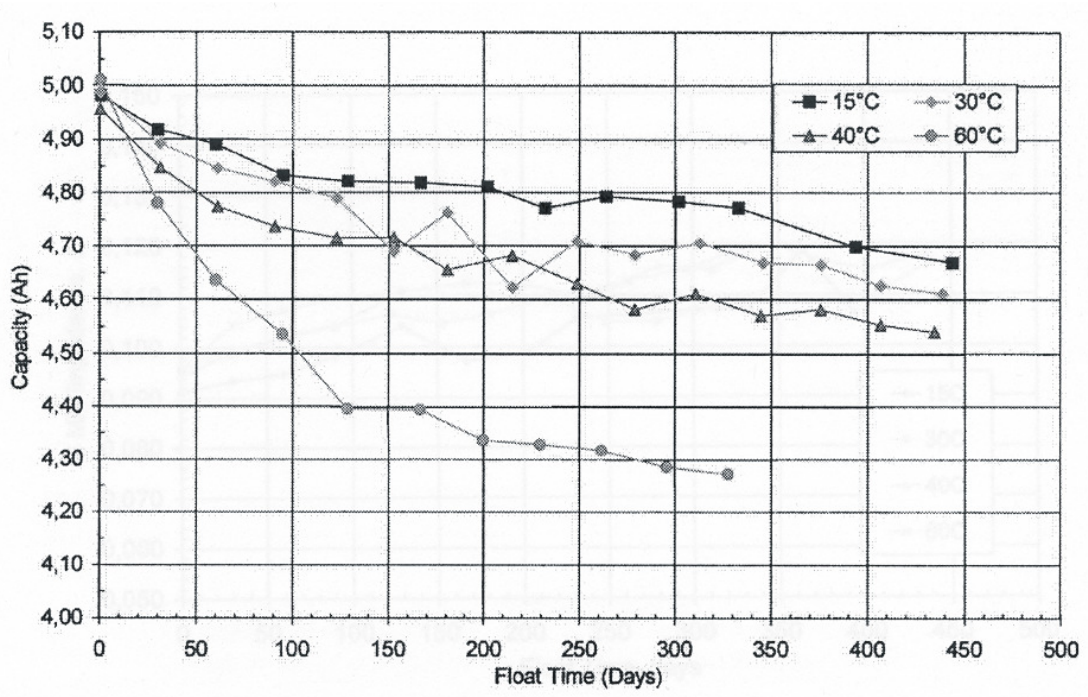


Changes at the Negative Electrode



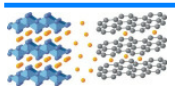
Factors that Influence Aging during Storage

- *High temperature, above 50°C is considered as critical*
- *Self discharge increases with state of charge (SOC)*
- *Both mechanisms are additive*



Recommendations

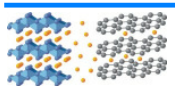
- *Avoid high temperatures, both during storage and operation!*
- *Do not unnecessarily charge the cells/modules!*
- *Avoid full discharge whenever possible!*
- *Store cells at 30-50% charge level!*
- *Store cells at low temperatures!*

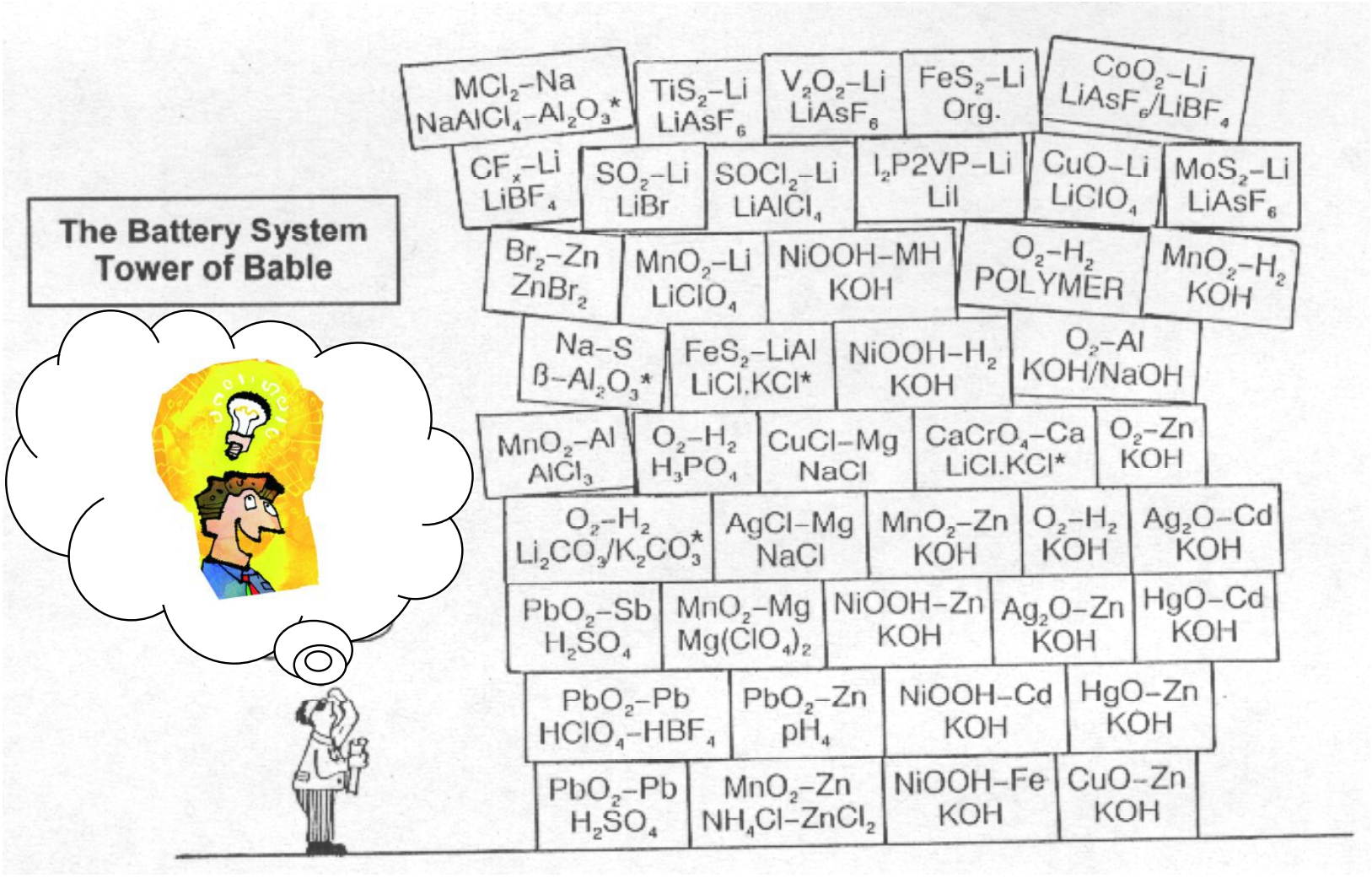


Conclusion: Why Lithium-Ion Batteries?

- *Mobile phones*
- *Notebooks, organizers*
- ***Vehicle applications***
- *Emergency power*

- *Low weight*
- *High energy- and power-density*
- ***Efficiency >90 %***
- *Very low self-discharge rate*
- ***>1000 cycles***




The Battery System
Tower of Bable
MCl2–Na
NaAlCl4–Al2O3*
TiS2–Li
LiAsF6
V2O2–Li
LiAsF6
FeS2–Li
Org.
CoO2–Li
LiAsF6/LiBF4
CFx–Li
LiBF4
SO2–Li
LiBr
SOCl2–Li
LiAlCl4
I2P2VP–Li
LiI
CuO–Li
LiClO4
MoS2–Li
LiAsF6
Br2–Zn
ZnBr2
MnO2–Li
LiClO4
NiOOH–MH
KOH
O2–H2
POLYMER
MnO2–H2
KOH
Na–S
ß–Al2O3*
FeS2–LiAl
LiCl.KCl*
NiOOH–H2
KOH
O2–Al
KOH/NaOH
MnO2–Al
AlCl3
O2–H2
H3PO4
CuCl–Mg
NaCl
CaCrO4–Ca
LiCl.KCl*
O2–Zn
KOH
O2–H2
Li2CO3/K2CO3*
AgCl–Mg
NaCl
MnO2–Zn
KOH
O2–H2
KOH
Ag2O–Cd
KOH
PbO2–Sb
H2SO4
MnO2–Mg
Mg(ClO4)2
NiOOH–Zn
KOH
Ag2O–Zn
KOH
HgO–Cd
KOH
PbO2–Pb
HClO4–HBF4
PbO2–Zn
pH4
NiOOH–Cd
KOH
HgO–Zn
KOH
PbO2–Pb
H2SO4
MnO2–Zn
NH4Cl–ZnCl2
NiOOH–Fe
KOH
CuO–Zn
KOH

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- *my group*

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