Hydrogen and Electrical Energy Storage

12 March 2013

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Radiation, Radionuclides and Reactors

TU Delft

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 systems: Li-air, Li-sulphur Flow-cells Costs and Performance comparison batteries/systems Material Abundance

Practical Issues

Book chapters, scientific literature and sheets will be available on BB

Lecture 1: Electrochemistry 2.3-2.5

Lecture 2: Advanced Batteries: Chapter 1, 2 and 3.1-3.3

Lecture 3: Advanced Batteries Chapter 14.1,14.2,14.B1-4, 16.1-2,16B,
Review Goodenough et al. Chemistry of Materials and lecture sheets

Lecture 4: Electrochemistry 3.1-3.3, Lecture sheets

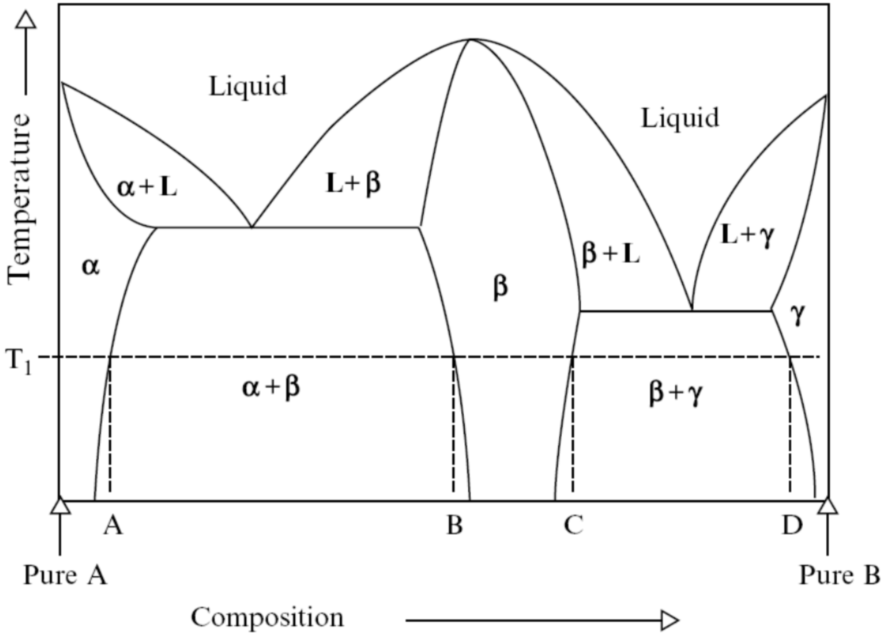
Lecture 5: Lecture sheets, Review Bruce et al. Li-air/Li-sulphur

Home assignment

Consider the following phase diagram for a cathode, and assume that the anode has a constant voltage independent of the composition and that T and p are constant:

a) Apply the Gibbs Phase Rule along T_1 in the regions $\alpha+\beta$ and β, is the potential constant?

b) Sketch the voltage diagram



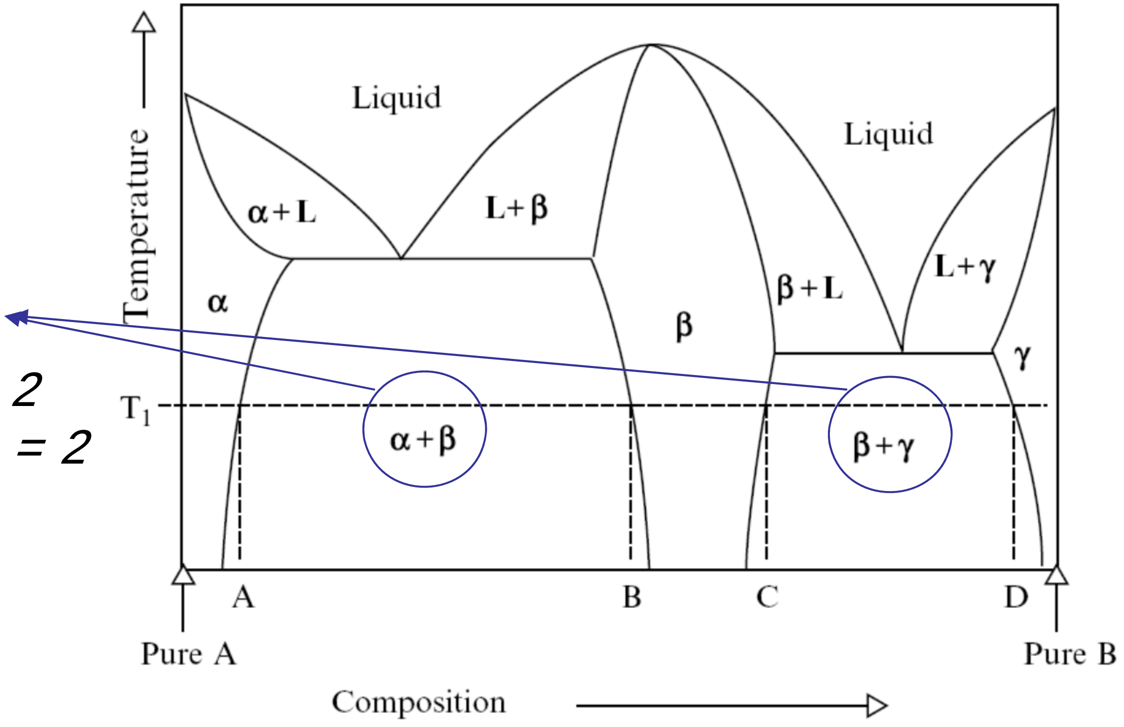
Gibbs Phase Rule

$$F = C - P + 2$$

F:	Number of degrees freedom
C:	Number of components (e.g. elements)
P:	Number of phases present in this system

Number of degrees freedom: Number of intensive thermodynamic parameters (T, p, μ, x) that must be specified to define the system (if true other intensive parameters are constant, if not they vary)

Example: suppose F=1 and T is specified => p, μ and x are fixed
Example: suppose F=3 and p,T is specified => μ will vary (depending on x)



$$F = C - P + 2$$
$$= 2 - 2 + 2 = 2$$

F=2 and p,T is specified => other intensive variables are fixed/constant
μ is constant => voltage is constant.
Note, composition of phases (ratio A/B) at points, A, B, C and D is also constant (also intensive variable)

Question Gibbs Phase Rule 3

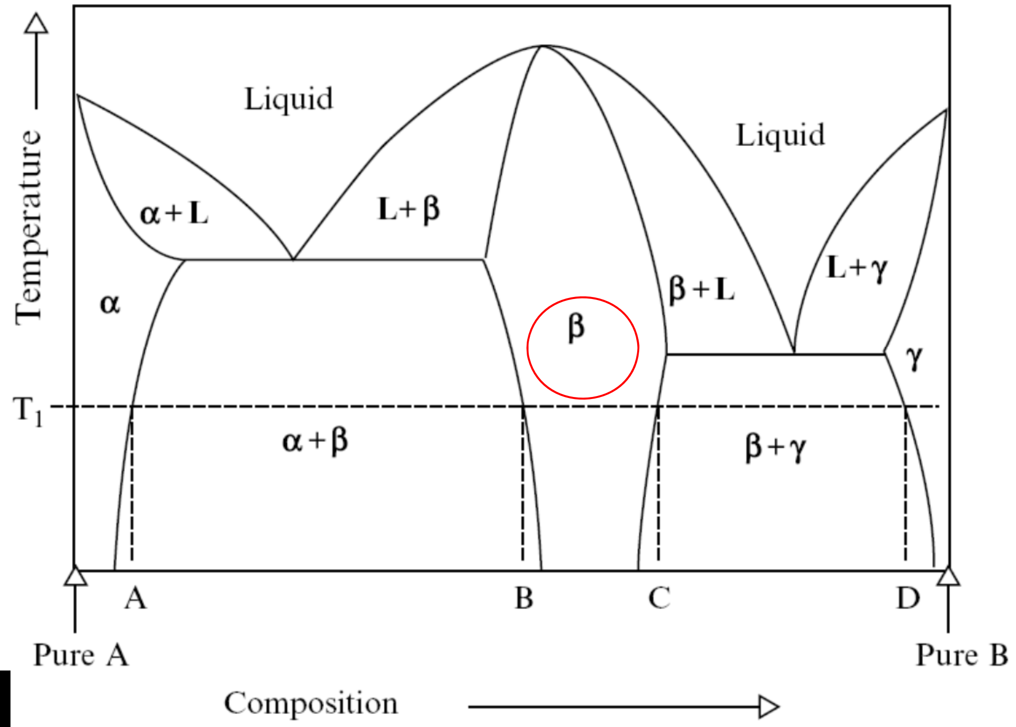
19. What is the number of degrees of Freedom, *F=C-P+2*, in the red circle?

a) 1

b) 2

c) 3

d) no clue



20. What does this mean assuming constant p,T?

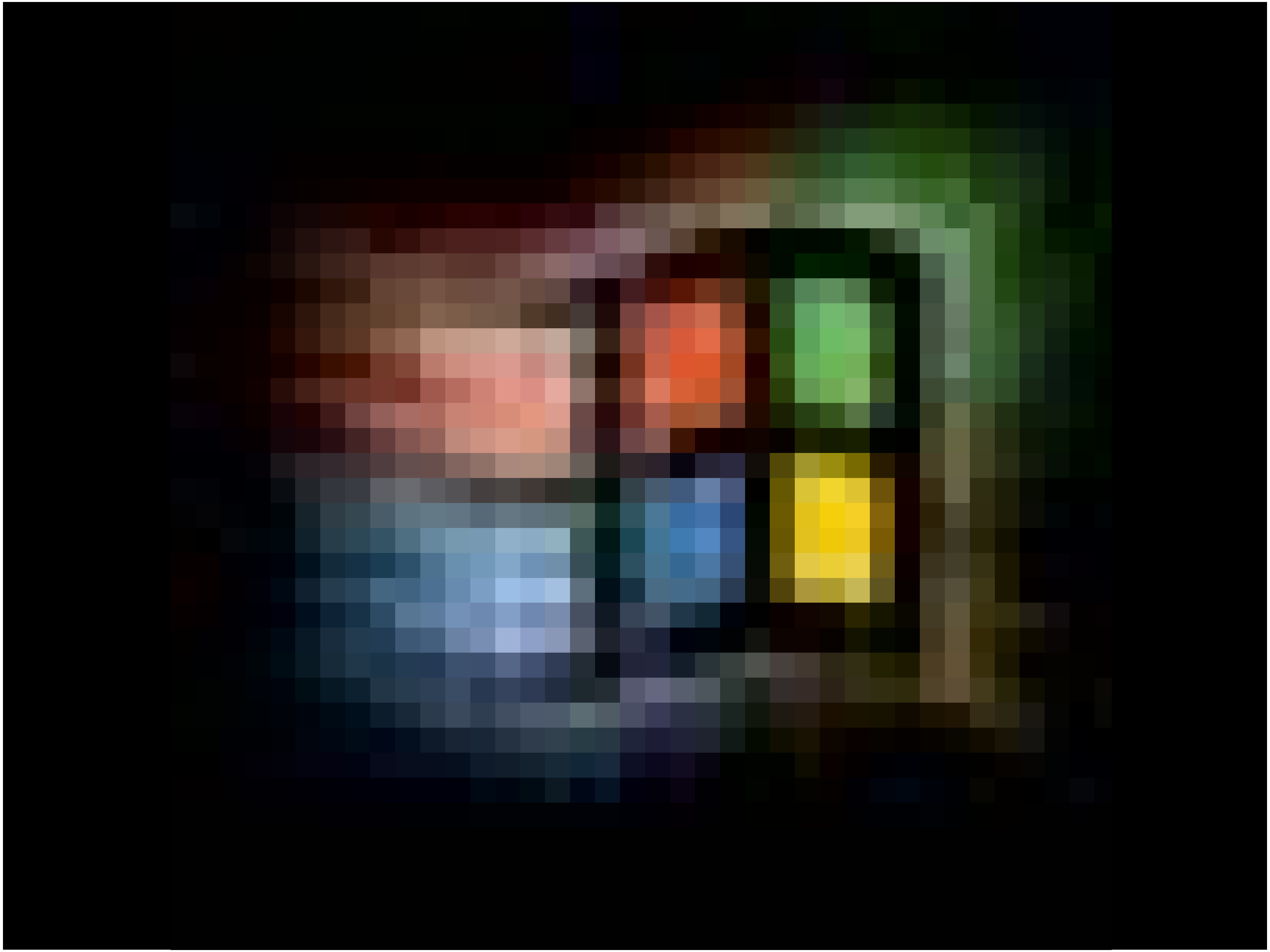
a) constant voltage

b) variable voltage

d) no clue

http://www.edupinion.nl/c548

Result



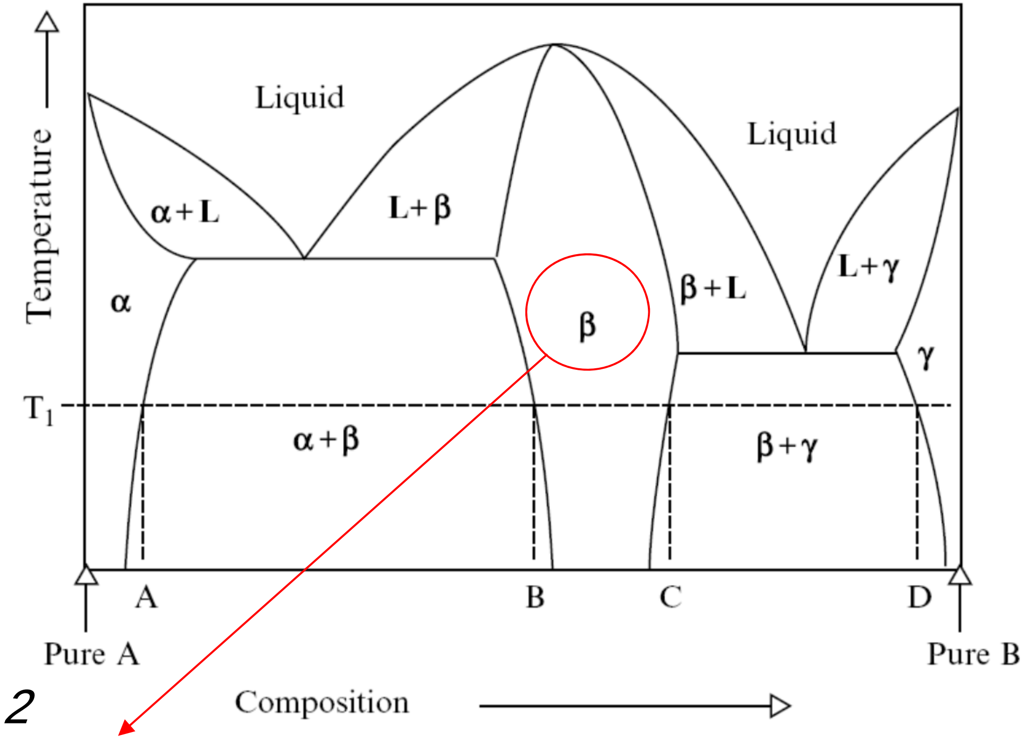
Question Gibbs Phase Rule 3

19. What is the number of degrees of Freedom, F, in the red circle?

a) 1
b) 2
c) 3
d) No clue

20. What does this mean assuming constant p,T?

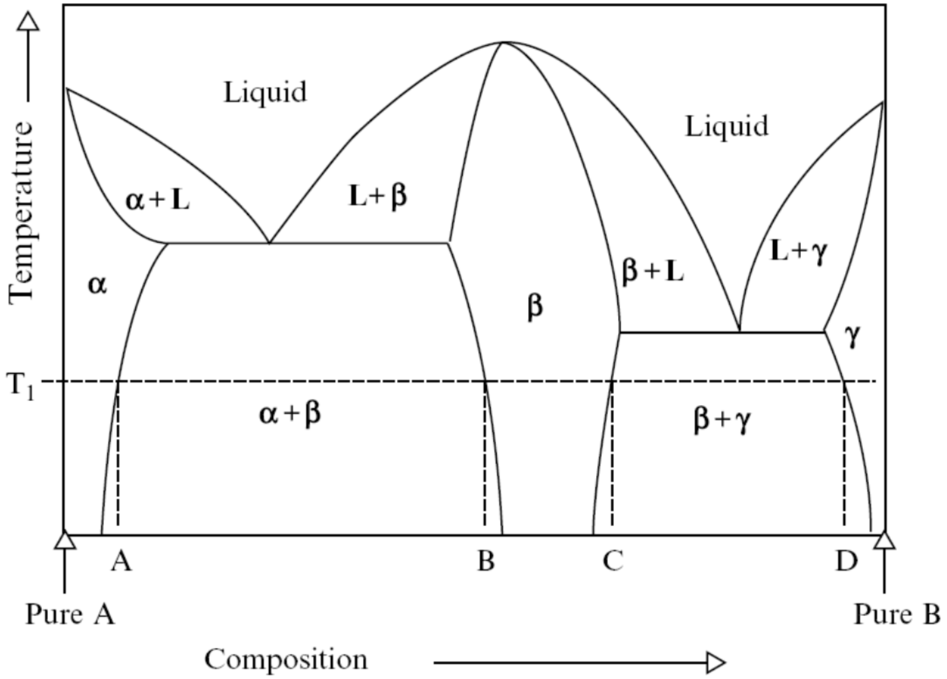
a) Constant voltage
b) variable voltage
c) no clue

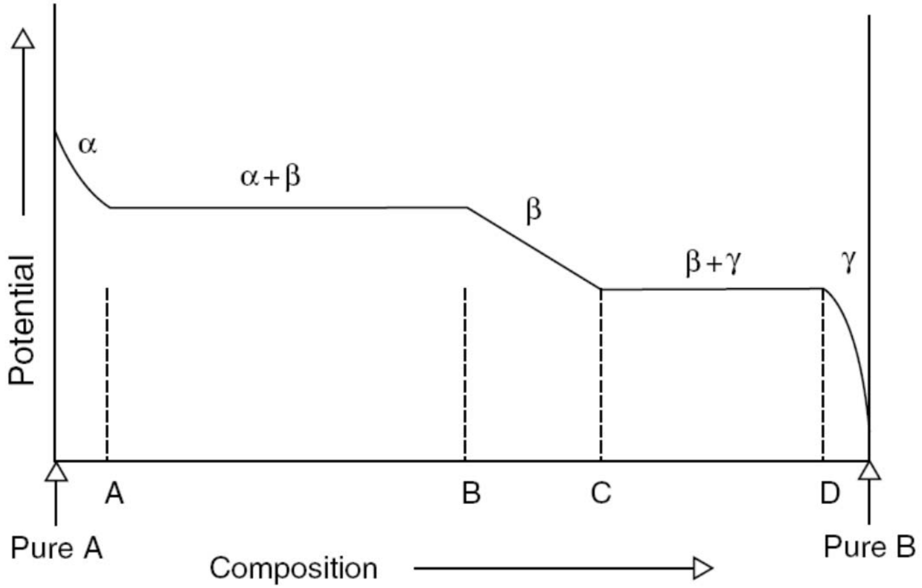


$F = C - P + 2$

$= 2 - 1 + 2 = 3$

E_{cell} = variable (depends on composition)!=> 19c) and 20b)


Temperature
Liquid
α+L
L+β
Liquid
L+γ
α
β+L
β
γ
T_1
α+β
β+γ
A
B
C
D
Pure A
Pure B
Composition


Potential
α
α+β
β
β+γ
γ
A
B
C
D
Pure A
Pure B
Composition

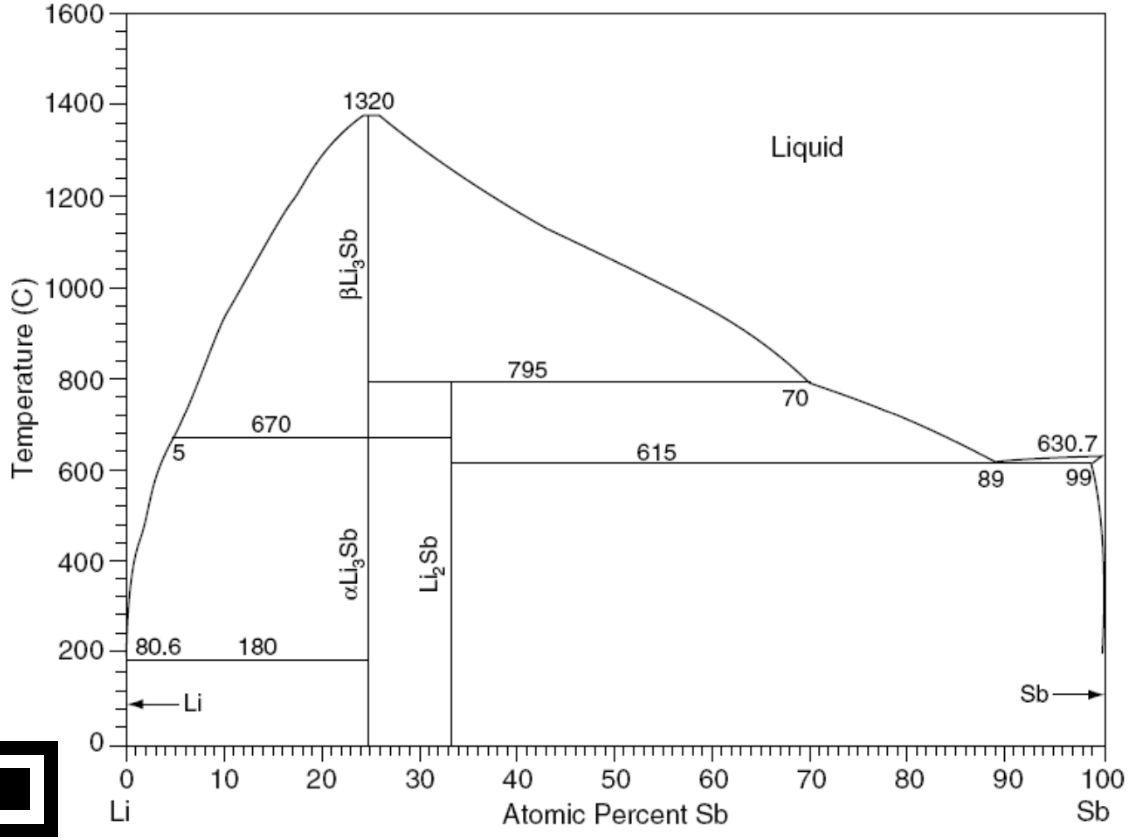
Question Lithium storage in Antimony

21. What kind of reaction is this?

a) Reconstitution-displacement
b) Reconstitution-formation
c) Insertion
d) No clue

22. If the maximum composition is Li_3Sb how many voltage plateau’s do you expect? Assume room temperature

a) 0
b) 1
c) 2
d) No clue



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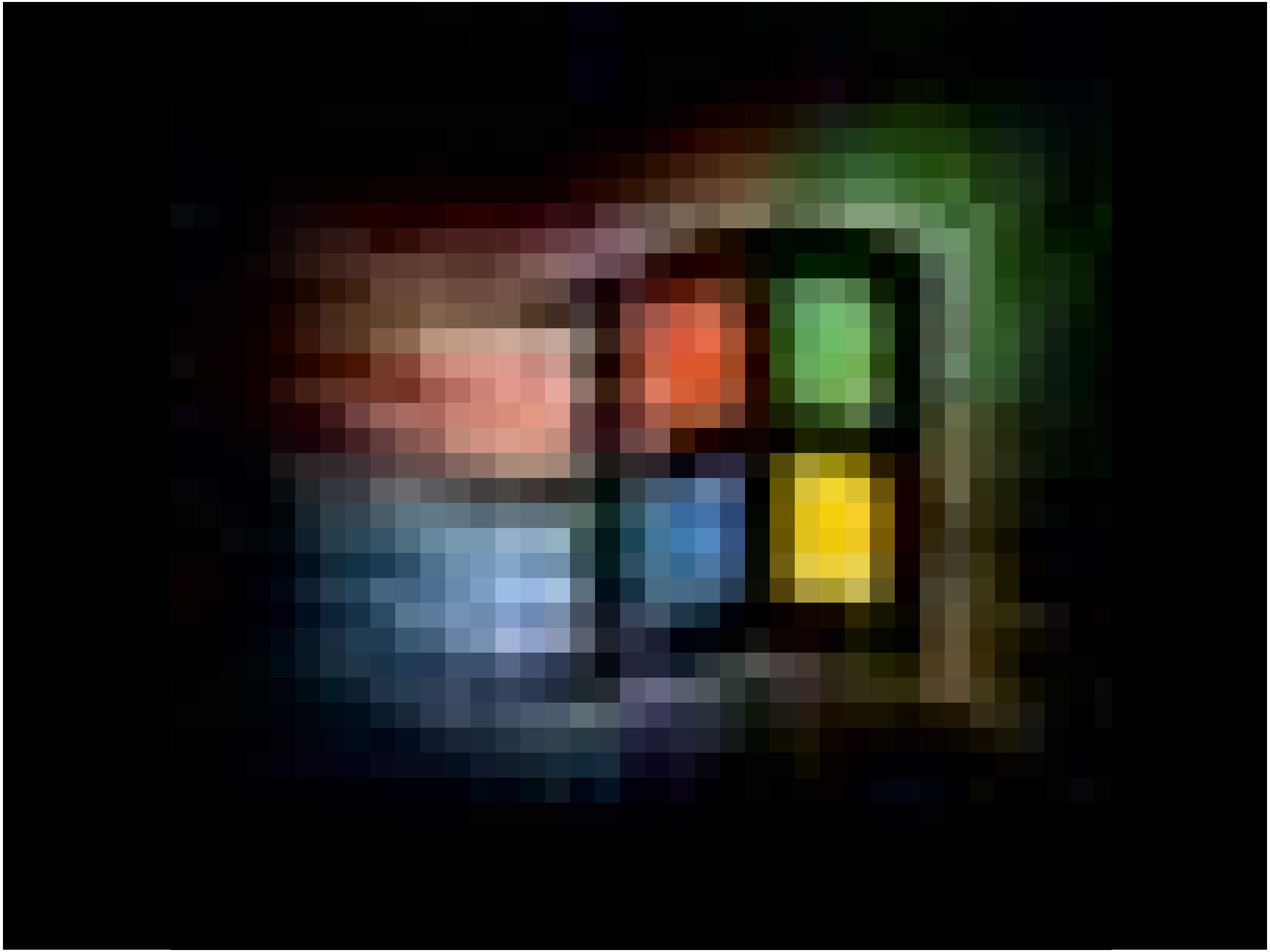
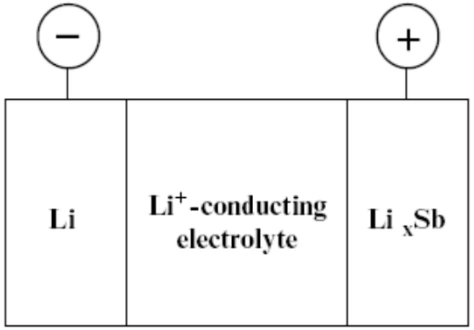
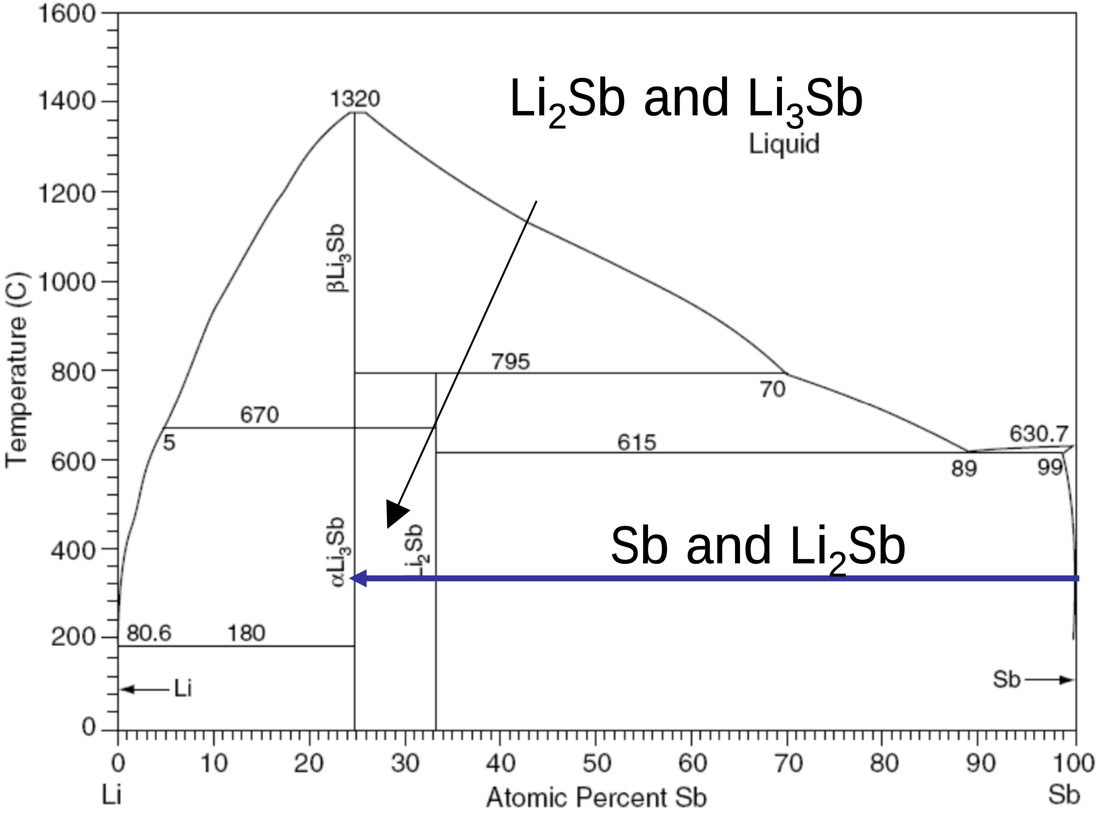


Question Lithium storage in Antimony





Li_2Sb and Li_3Sb

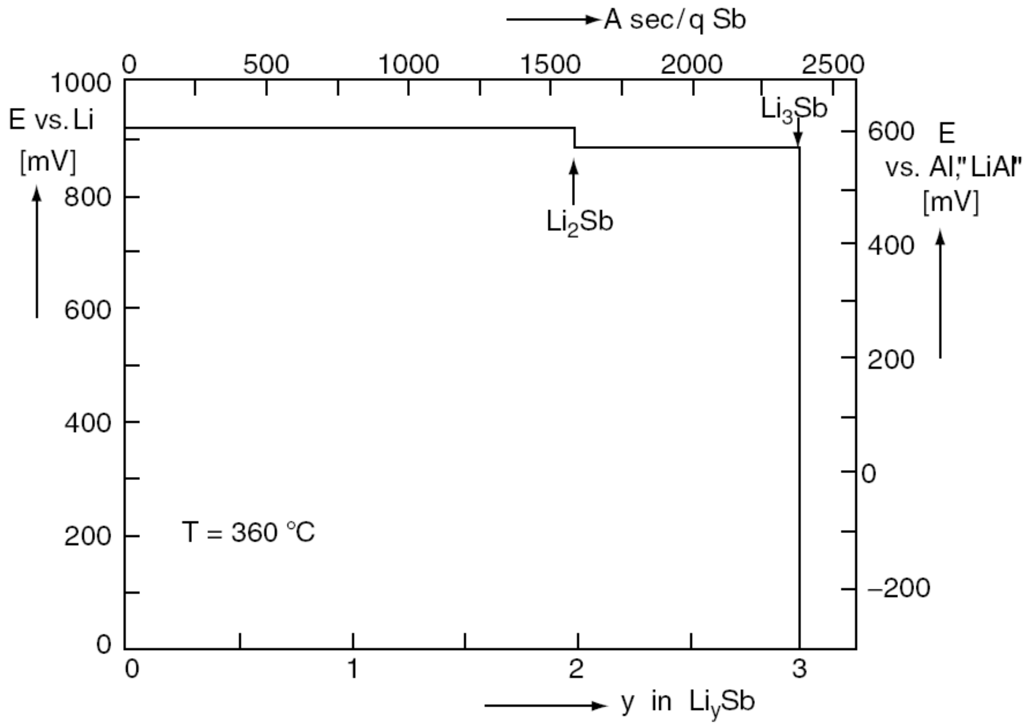
Sb and Li_2Sb

$2Li + Sb = Li_2Sb$
$Li + Li_2Sb = Li_3Sb$

Type: A+B=AB: Reconstitution-formation => 21b)

Question Lithium storage in Antimony

Two two phase regions
=> two voltage plateau's
=> 22c)



$$E^1_{Cell} = -\frac{\Delta G^0_r(Li_2Sb)}{2F} = 0.912 \text{ V versus Li-metal}$$

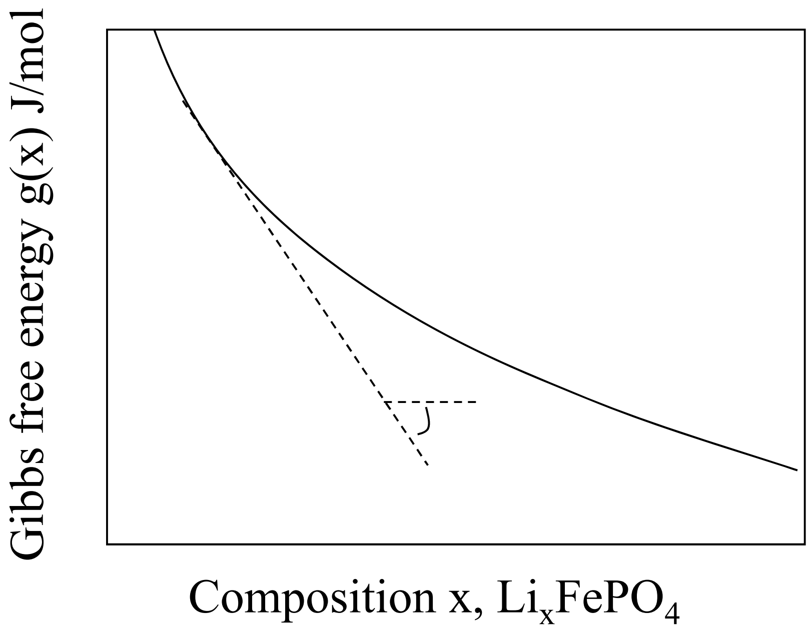
$$E^2_{Cell} = \frac{\Delta G^0_r(Li_3Sb)}{F} - \frac{\Delta G^0_r(Li_2Sb)}{2F} = 0.871 \text{ Vversus Li-metal}$$

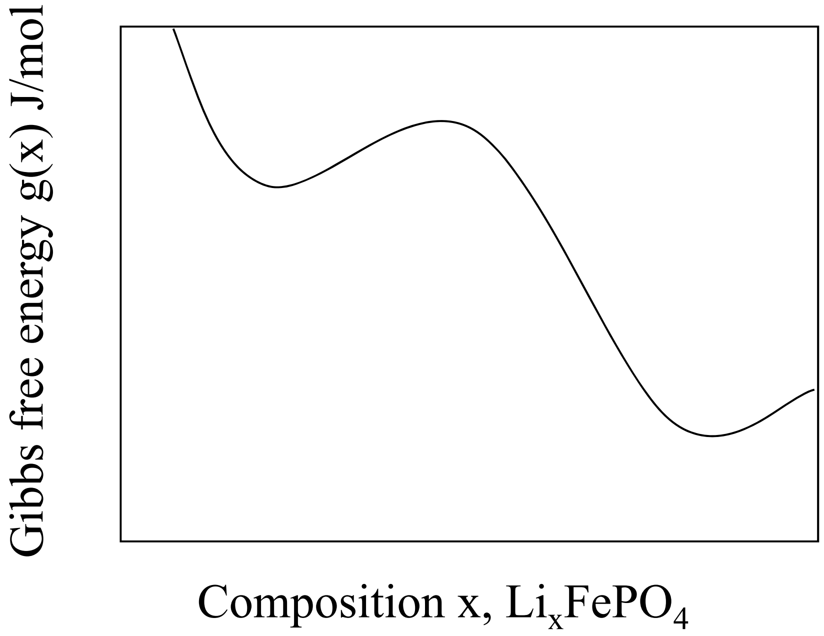
A different view, Voltage profile from the Gibbs Free Energy

Gibbs Free Energy

$$dG = Vdp - SdT + \sum_j \mu_j dn_j \overset{\text{Constant p and T}}{=} \sum_j \mu_j dn_j \Rightarrow \left.\frac{\partial G(x)}{\partial n}\right|_{T,p} = \mu^{Li}_{Electrode}$$

ΔG determines the direction of the reaction (and W_{chem}).
The shape of G(x) how it gets there



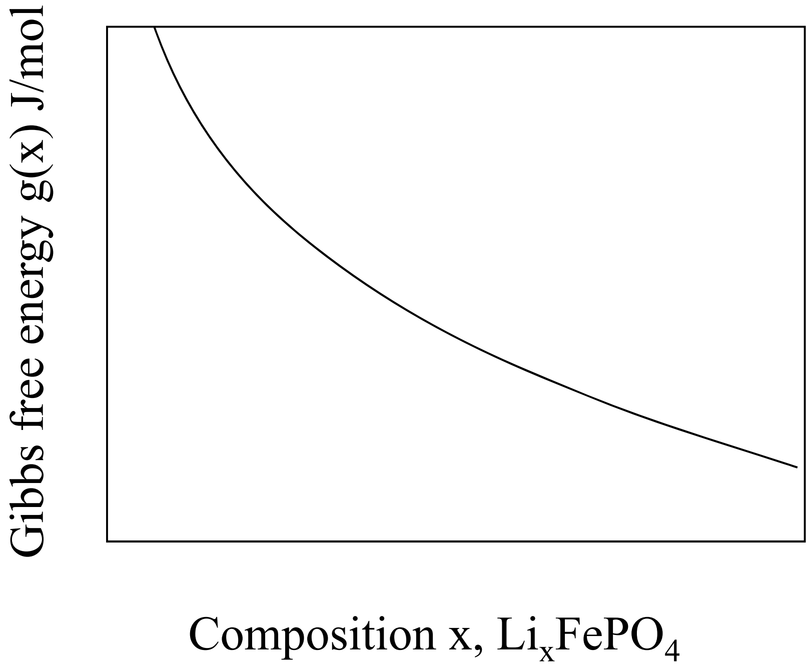


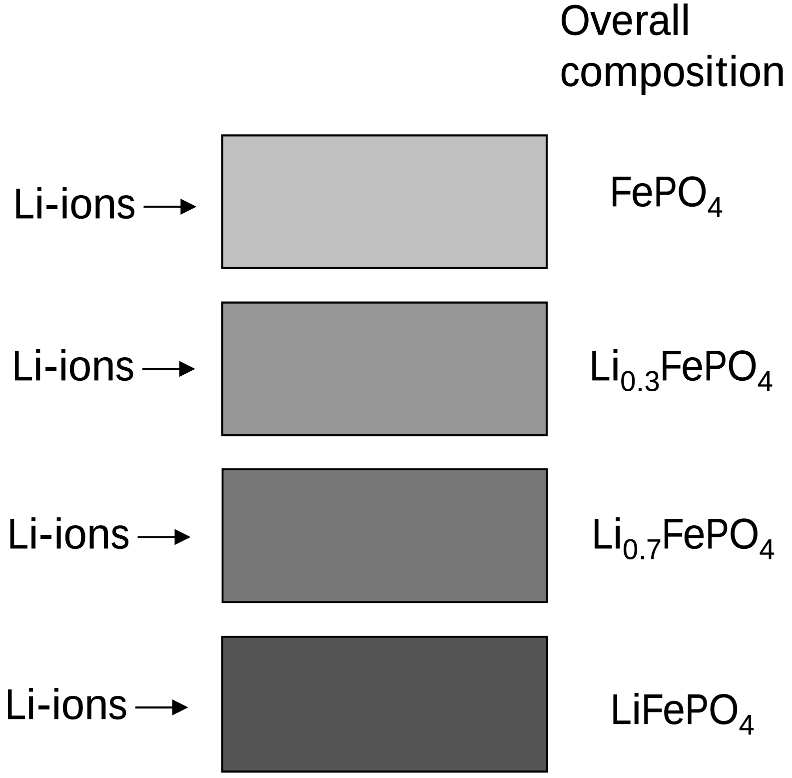
Gibbs Free Energy

LiFePO$_4$ ■

FePO$_4$ □

Gradual compositional change: solid solution





Overall composition

Li-ions → FePO$_4$

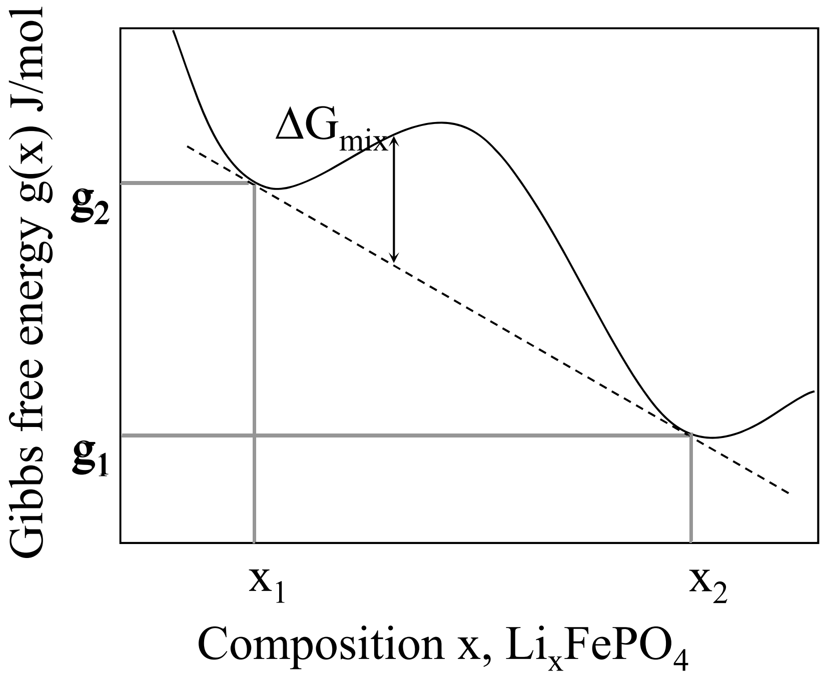
Li-ions → Li$_{0.3}$FePO$_4$

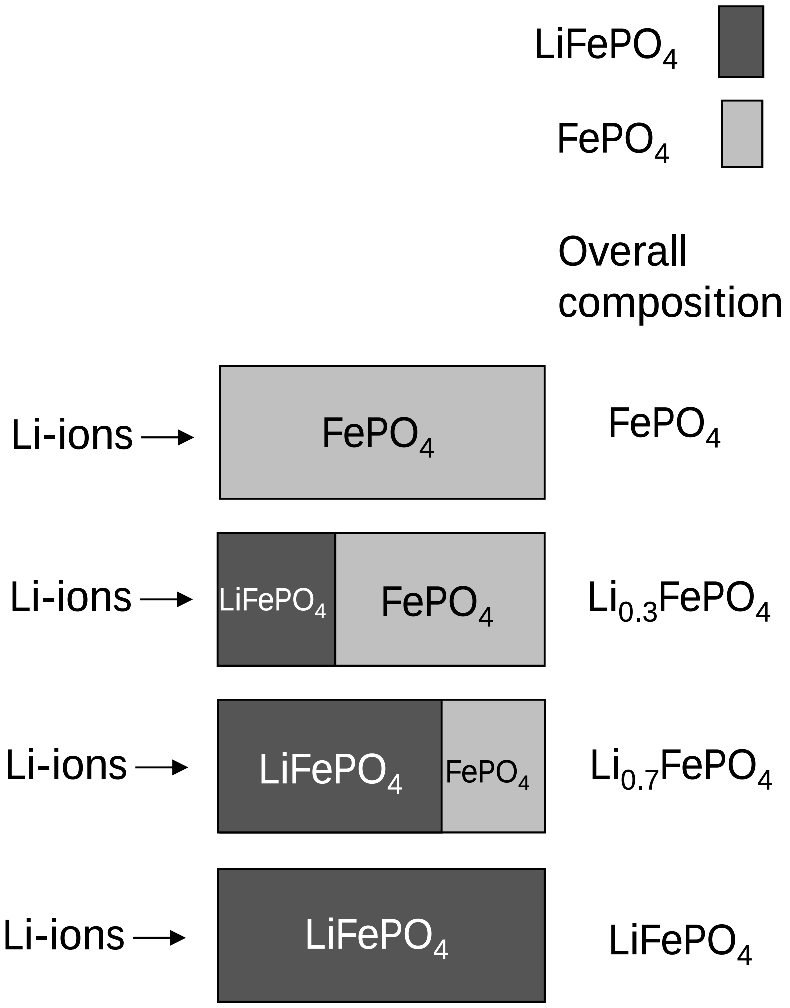
Li-ions → Li$_{0.7}$FePO$_4$

Li-ions → LiFePO$_4$

Gibbs Free Energy

Segregation: Phase transition





$LiFePO_4$ ▆

$FePO_4$ ▢

Overall composition

Li-ions →	$FePO_4$	$FePO_4$
Li-ions →	$LiFePO_4$ | $FePO_4$	$Li_{0.3}FePO_4$
Li-ions →	$LiFePO_4$ | $FePO_4$	$Li_{0.7}FePO_4$
Li-ions →	$LiFePO_4$	$LiFePO_4$

From the Gibbs Free energy to voltage

Discharge of Li-ion battery:

$Li_xC_6 = Li^+ + e^- + C_6$ (Oxidation/Anode)
$FePO_4 + Li^+ + e^- = LiFePO_4$ (Reduction/Cathode)

Overall reaction:

$LiC_6 + FePO_4 = C_6 + LiFePO_4$

$$E_{Cell}dQ = E_{Cell}zFdn = -\sum_{\mathrm{j}} \mu_{\mathrm{j}} dn = \left(\mu^{Li}_{LiFePO_4} - \mu^{Li}_{LiC_6}\right) dn$$

$$\Rightarrow \quad E_{Cell}(x) = -\frac{\mu^{Li}_{LiFePO_4} - \mu^{Li}_{LiC_6}}{F} = -\frac{\mu^{Li}_{Cathode}(x) - \mu^{Li}_{Anode}}{F}$$

Assume $\mu^{Li}_{Anode} = \text{constant}$

From the Gibbs Free energy to voltage

In order to know the Voltage profile $E_{Cell}(x)$ we need $\mu_{Cathode}(x)$, which will depend on the Gibbs free energy $G(x)$ of the cathode.

We know: $\mu^{Li}_{Cathode} = \frac{dG_{Cathode}(x)}{dn}$ where *dn* is the number of moles of Li

It is more convenient to work with the Gibbs free energy per mole host material *g(x).*

Suppose we have *N* mole of Cathode C and *n* moles of interstitial Li ions in the Cathode

such that: $n = xN$, then $g(x) = \frac{G(x)}{N}$

$$\mu^{Li}_{Cathode} = \left.\frac{\partial G(x)}{\partial n}\right|_{T,p,N} = \left.\frac{\partial (Ng(x))}{\partial n}\right|_{T,p,N} = \left.\frac{N\partial g(x)}{N\partial x}\right|_{T,p,N} = \left.\frac{\partial g(x)}{\partial x}\right|_{T,p,N}$$

Slope in g(x) plot!

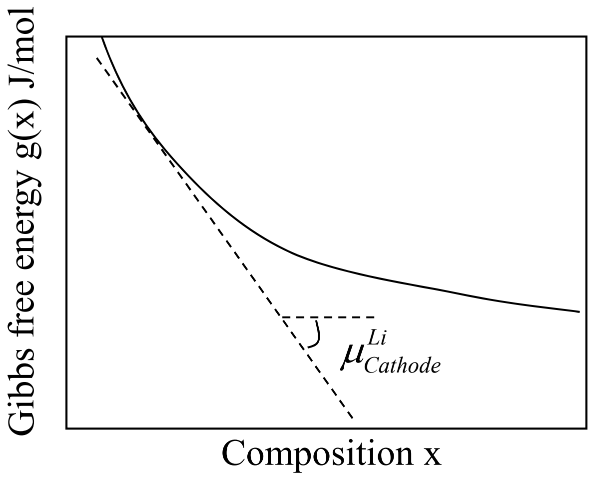
From the Gibbs Free energy to voltage

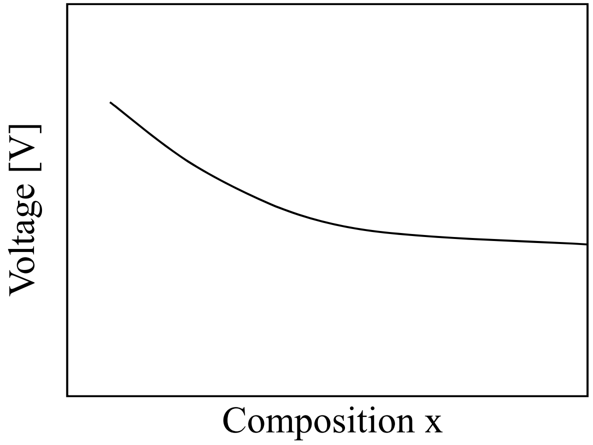
Solid solution

$$\mu^{Li}_{Cathode} = \frac{\partial g(x)}{\partial x}$$

$$E_{Cell}(x) = -\frac{\mu^{Li}_{Cathode}(x) - \mu^{Li}_{Anode}}{zF}$$

Open cell voltage is changing with composition:





From the Gibbs Free energy to voltage

Two phase decomposition

$$g(x)_{\text{common tangent}} = \frac{g_2 - g_1}{x_2 - x_1}x + \frac{g_1 x_2 - g_2 x_1}{x_2 - x_1}$$

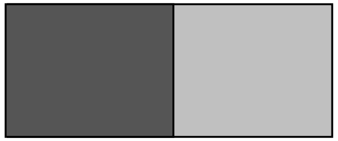
$$\Delta g_{mix} = g(x)_{\text{common-tangent}} - g(x)_{\text{solid-solution}}$$

$$\mu_C = \frac{\partial g}{\partial x} = \frac{g_2 - g_1}{x_2 - x_1} = \text{constant } (\mathrm{x}_1 < \mathrm{x} < \mathrm{x}_2)$$

$$E_{Cell} = -\frac{\mu^{Li}_{Cathode}(x) - \mu^{Li}_{Anode}}{zF} = \text{constant } (\mathrm{x}_1 < \mathrm{x} < \mathrm{x}_2)$$

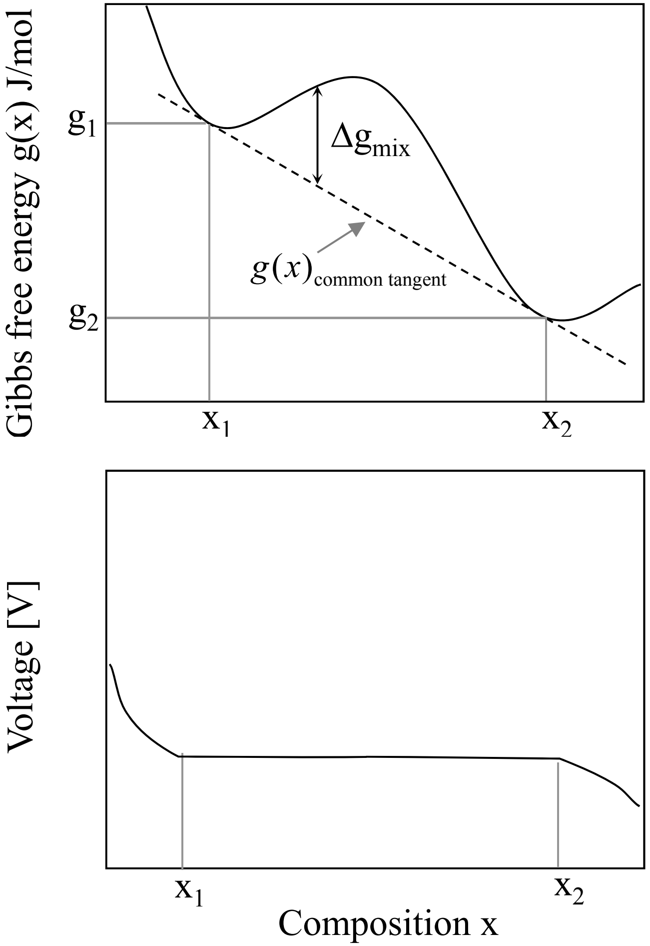
Open cell voltage is constant between x_1 and x_2

Overall
Composition
Li_xFePO_4 $x_1<x<x_2$



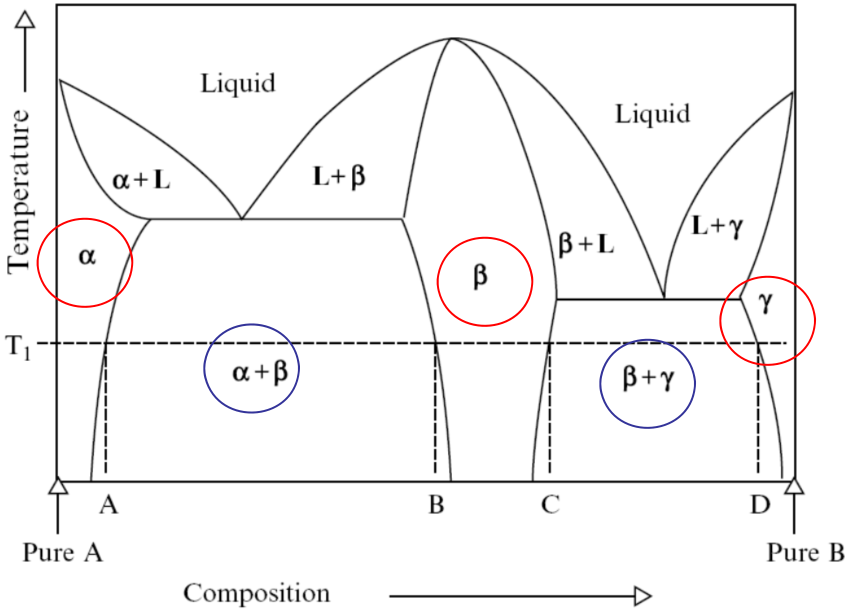
$Li_{x2}FePO_4$ ■

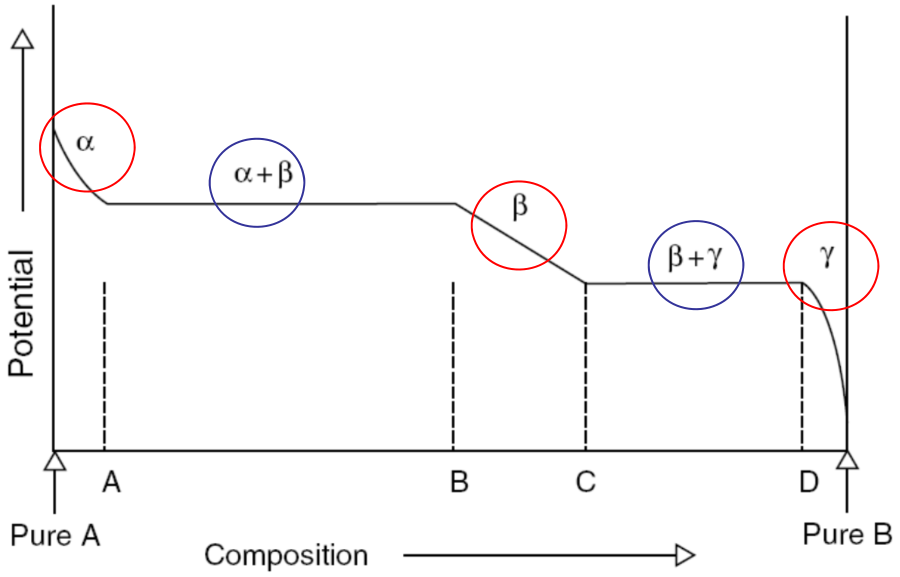
$Li_{x1}FePO_4$ □



From the Gibbs Free energy to voltage

Gibbs phase rule <-> Shape Gibbs Free energy



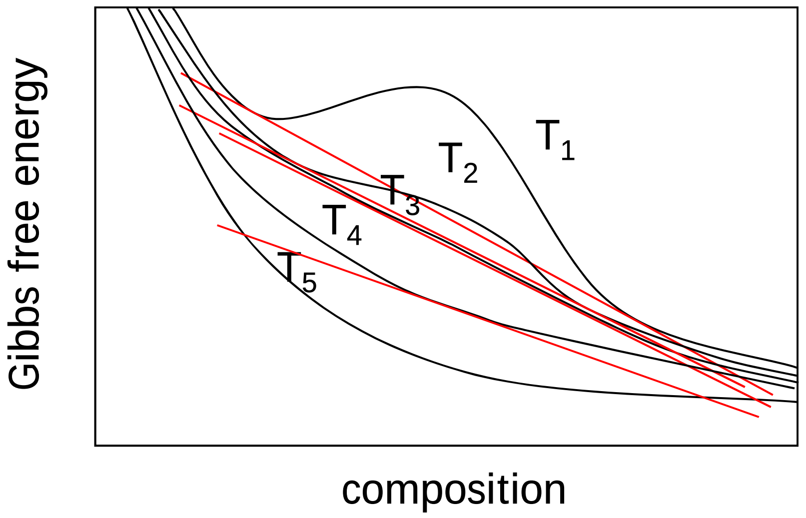


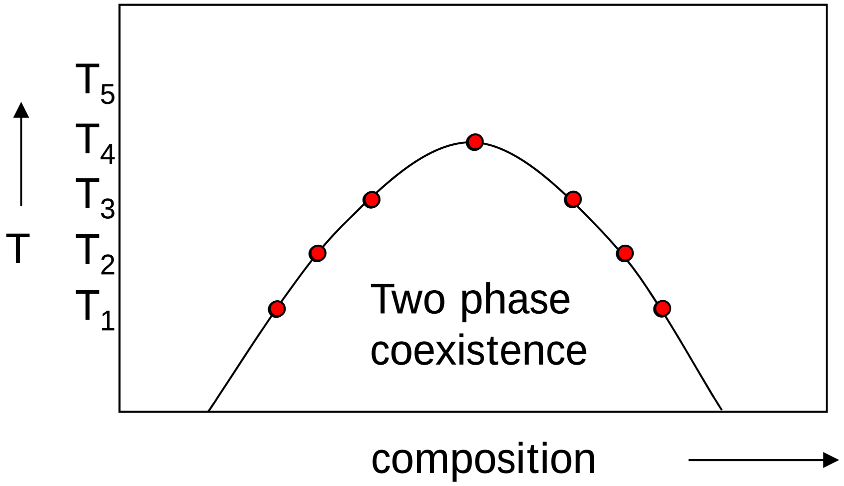
○ Solid solution phase -> Variable composition -> variable potential

○ Phase transition -> constant composition -> constant potential

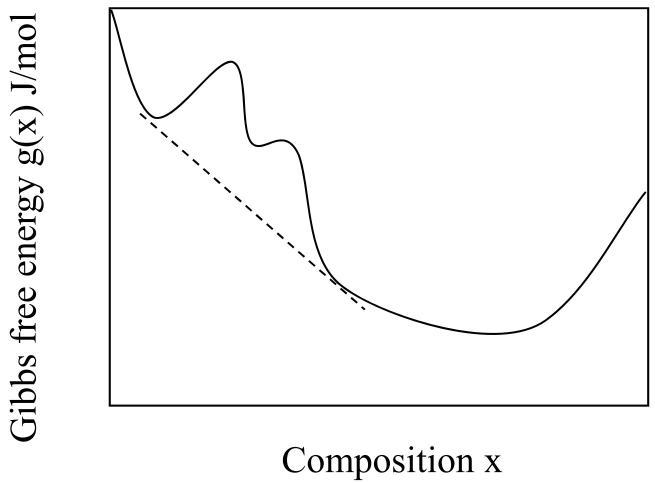
Li-ion batteries, relation Gibbs and phase diagram

Construction
phase diagram:

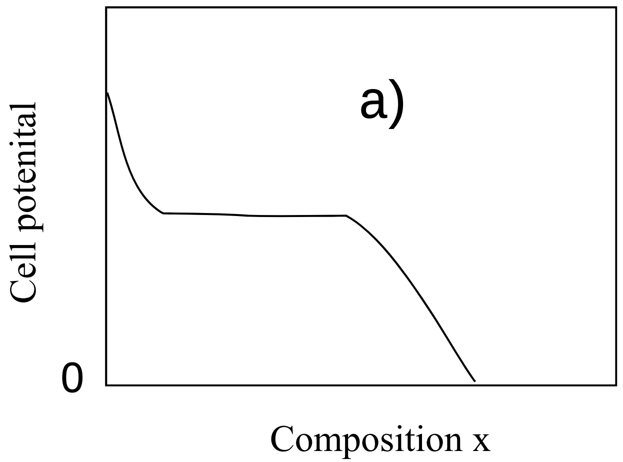


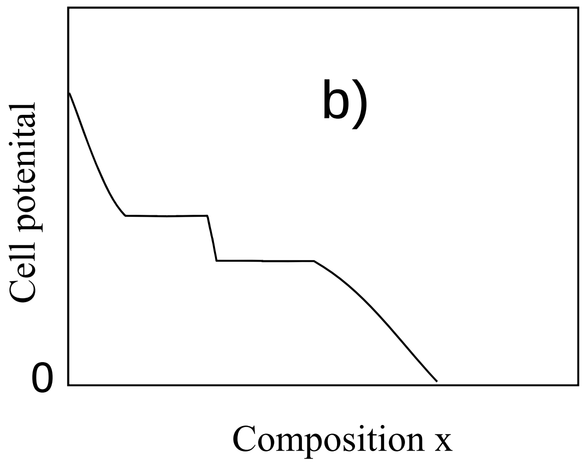


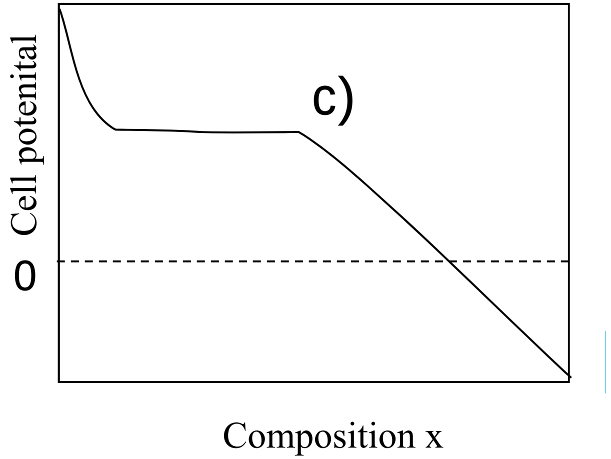
Ouestion Gibbs Free Energy 1



23. Based on the Gibbs Free Energy of the cathode, and assuming Li metal as anode, how does the voltage profile look like?







d) no clue

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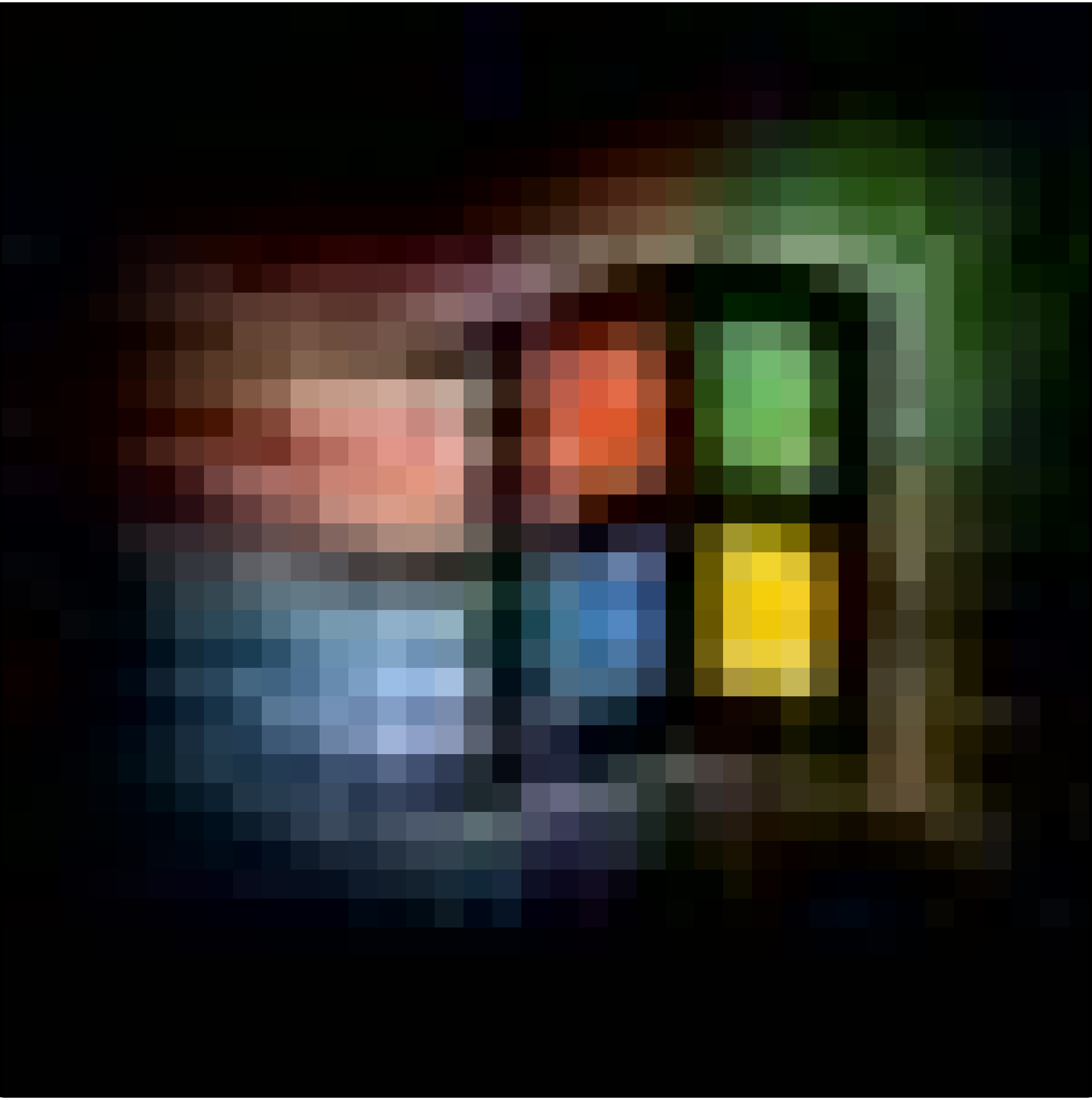
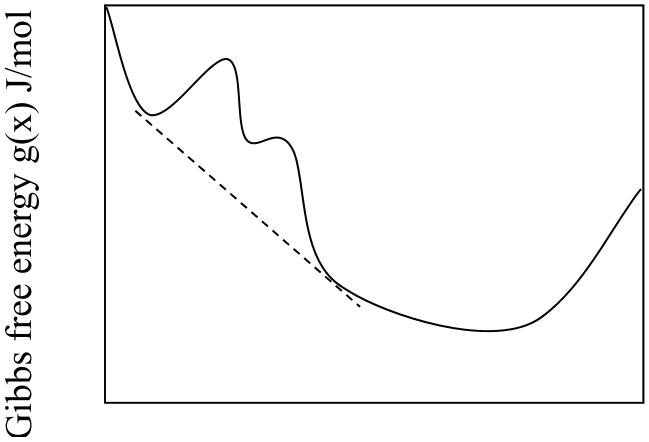
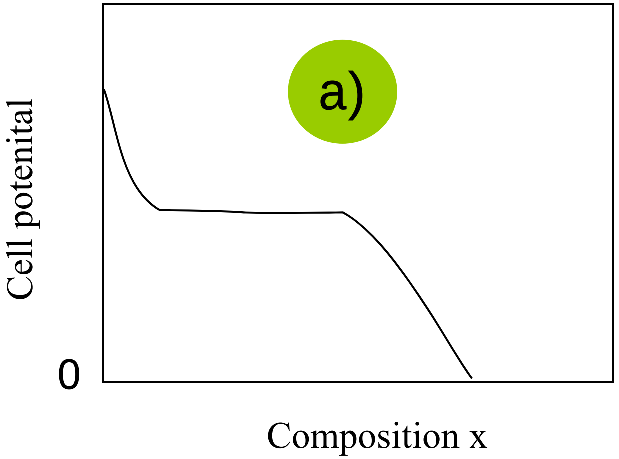
Result

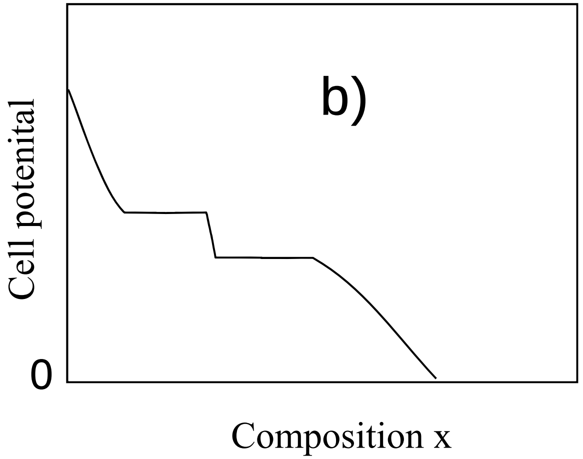


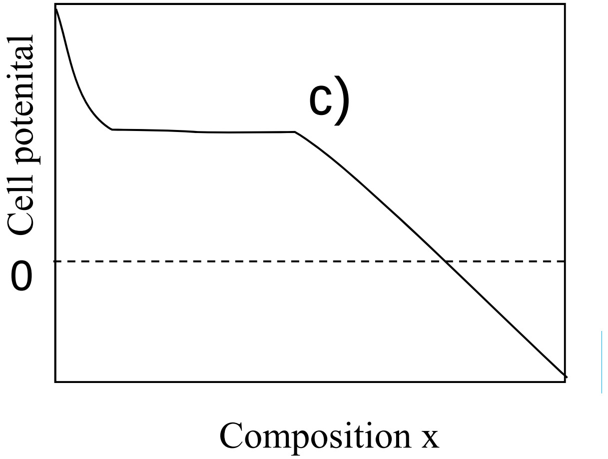
Question Gibbs Free Energy 1

23. Based on the Gibbs Free Energy of the cathode, and assuming Li metal as anode, how does the voltage profile look like?









Practical questions

✓ ✓ What is the direction of a redox reaction?

✓ ✓ What is the voltage that a redox reaction can deliver?

✓ What is the energy density of a battery?

What determines the cycle life of a battery

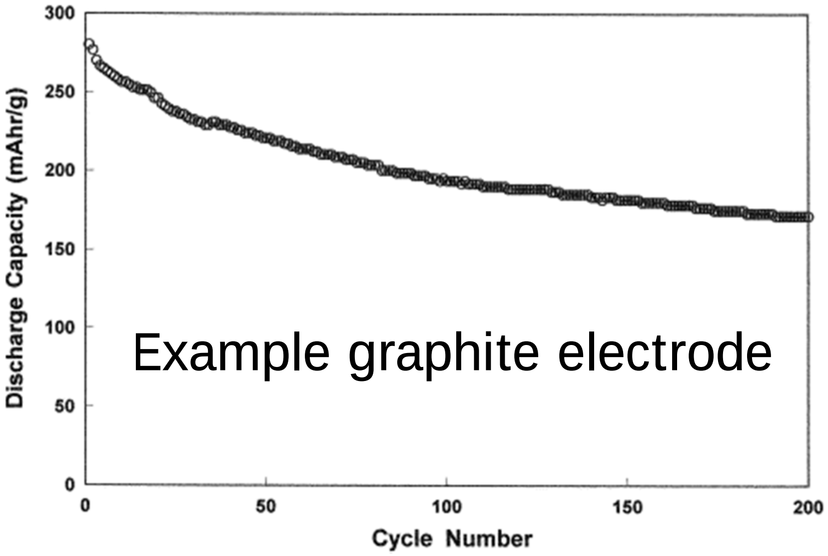
What is the power density of a battery? -> kinetics

Cycle Life of Batteries

Cycle Life of Batteries

Reduced cycle life:

Energy loss due to increasing cell impedance and due loss of active material



Example graphite electrode

Reasons for reduced cycle life:

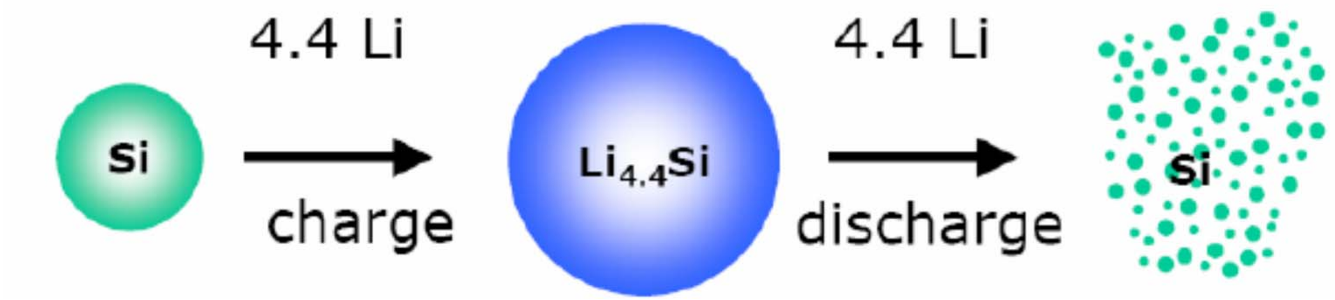
(1) Structural changes in the electrodes upon (dis)charge

(2) Thermodynamic instability electrode-electrolyte leading to decomposition of the electrolyte

-1-

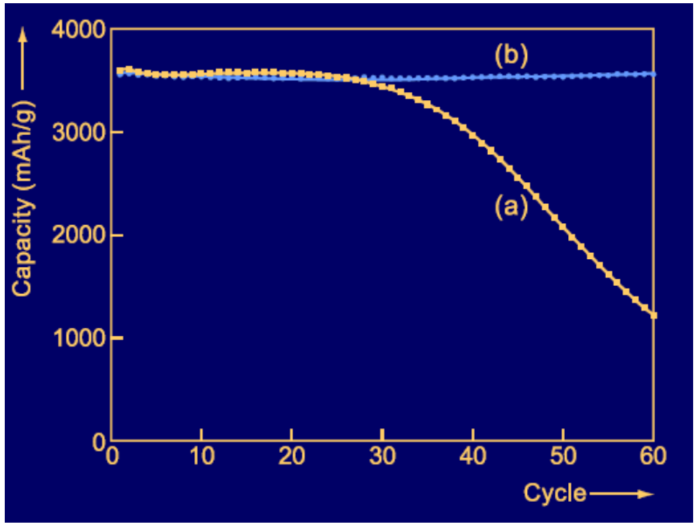
Structural changes of the electrodes upon (dis)charge

Structural changes of the electrode
Reconstitution-Formation reactions



Volume expansion almost 400%
Leads to mechanical failure ->
Loss in capacity.

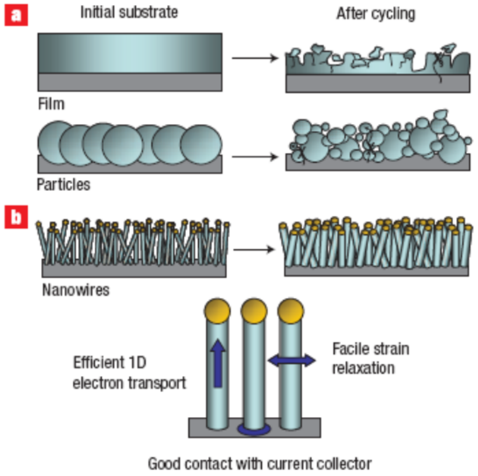
Rule of thumb, less than 10%
Volume expansion will lead to good
mechanical cycle life



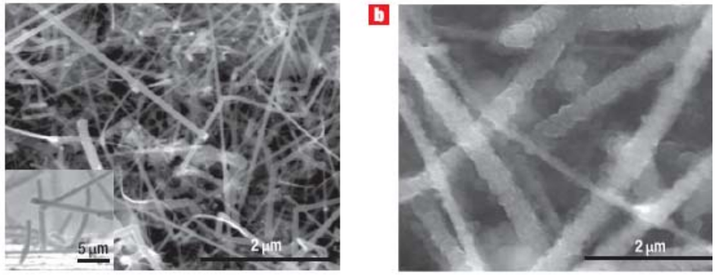
(b) Graphite x 15
(a) Si

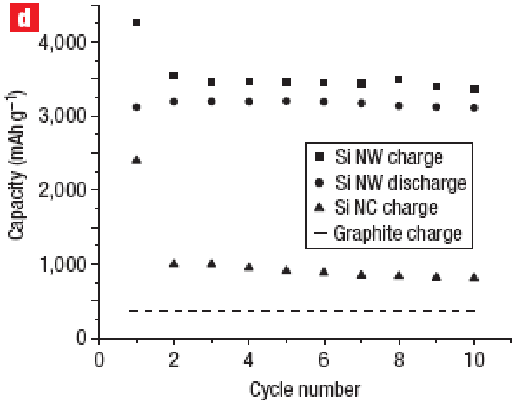
Intermezzo: Strategies Alloy anode

(1) Nano Si wires

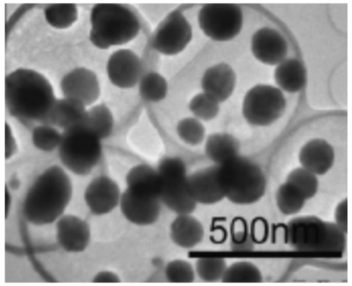


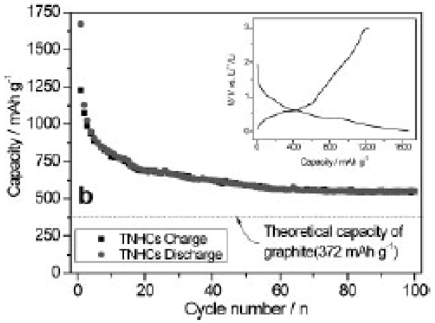
- ➢ Space for $Li_{4.4}Si$ volume expansion
- ➢ Only 10 cycles reported





(2) Nano sized Sn particles encapsulated in hollow carbon sph





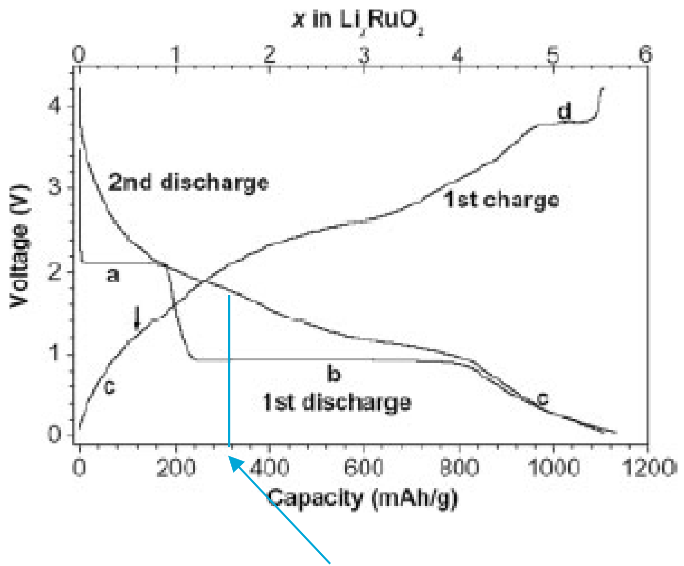
- ➢ Space for $Li_{4.4}Sn$ volume expansion
- ➢ No loss of contact due to confinement in Carbon sphere

Structural changes of the electrode
Reconstitution-Displacement reactions

(a) $Li^+ + e^- + RuO_2 \rightarrow LiRuO_2$	(Li-insertion, see later)
(b) $Li^+ + e^- + LiRuO_2 \rightarrow 2Li_2O + Ru$	(reconsititution-displacement)
(c1) $Li^+ + e^- +$ electrolyte -> SEI(Li)	(supercapacitive behavior, later)

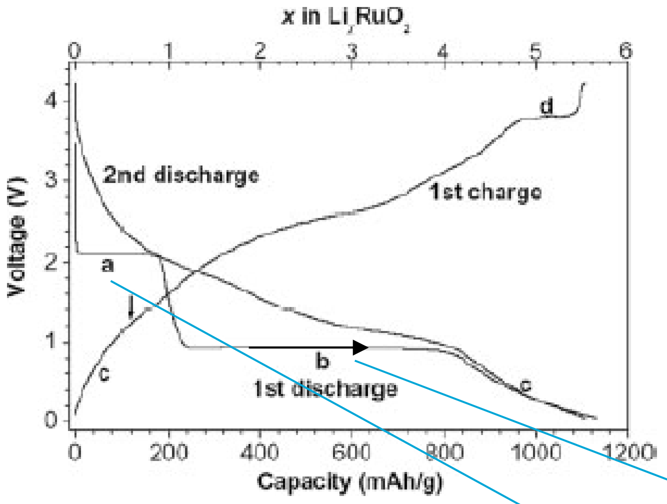
Host material decomposes in Li_2O and metal

SEI: Solid electrolyte interface: forms during first (dis)charge cycles, decomposed electrolyte (later)



Capacity of graphite

Structural changes of the electrode
Reconstitution-Displacement reactions



Host transforms in new compound
⇒ Extra capacity
⇒ Huge structural changes (after first cycle it remains nano-structured)
⇒ Only reversible because of nano distances Ru-O in Li_2O/Ru mixture

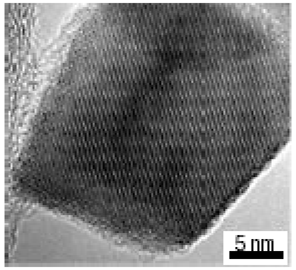
Nano structured RuO_2

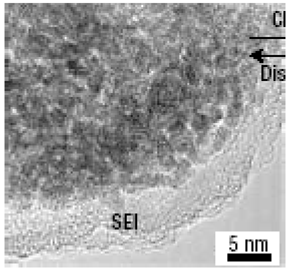
(a) $Li^+ + e^- + RuO_2 \rightarrow LiRuO_2$

(b) $Li^+ + e^- + LiRuO_2 \rightarrow 2Li_2O + Ru$

(c1) $Li^+ + e^-$ + electrolyte -> SEI(Li)

SEI: Solid electrolyte interface: forms during first (dis)charge cycles, decomposed electrolyte





Structural changes of the electrode Insertion-reactions

Electrode material serves as a host, also phase changes possible (structural changes):

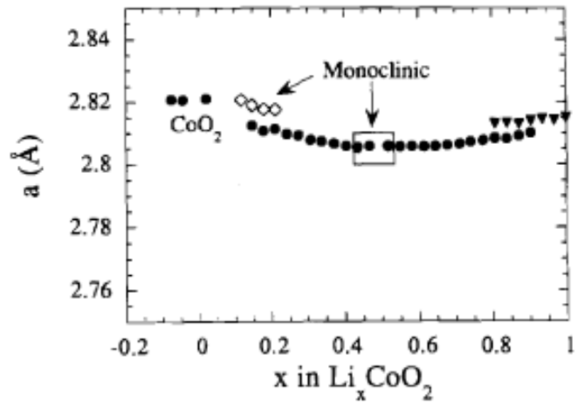
Example: $LiCoO_2$:

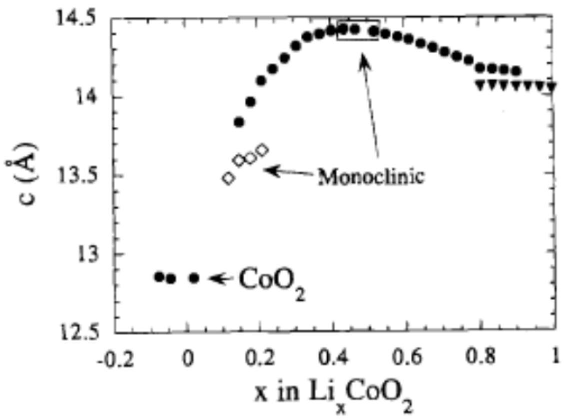
(+) $Li_{0.5}CoO_2(s) + 0.5Li^+ + 0.5e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Li_1CoO_2(s)$ (4 V vs Li/Li^+)

(-) $Li_xC_6 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} 6C + xLi^+ + xe^-$ (1 V vs Li/Li^+)

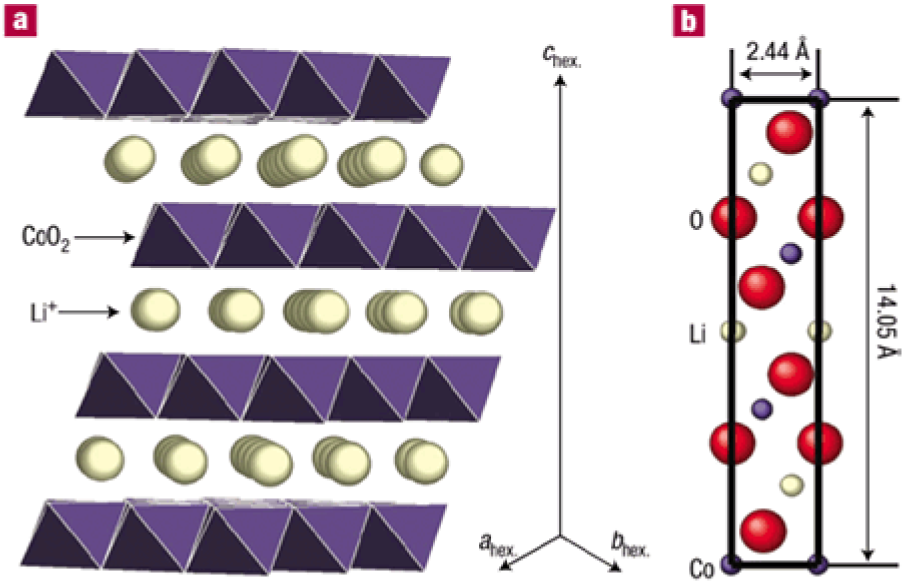
Such reactions lead in most cases to mechanical failure after many cycles due to swelling-shrinking associated with the structural changes.

Structural changes of the electrode Insertion-reactions: $LiCoO_2$

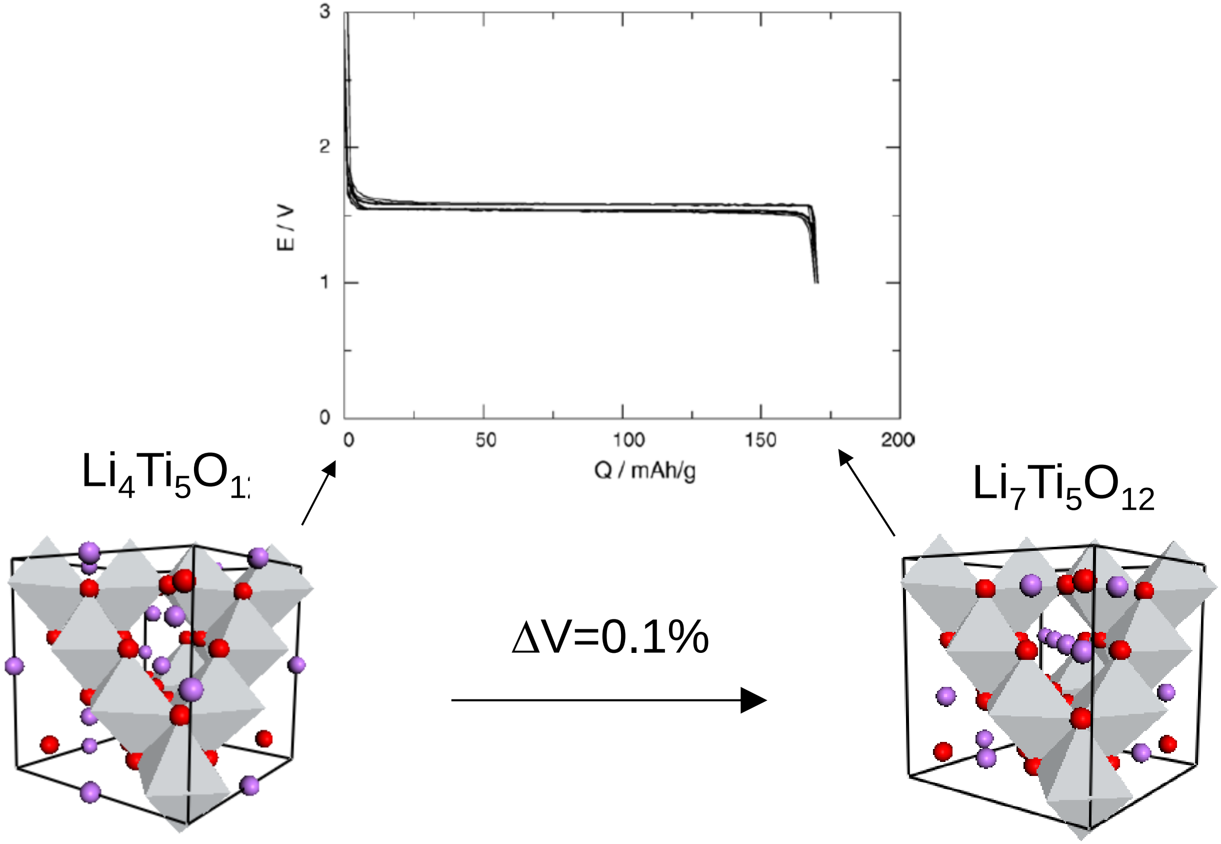




	CoO_2	->	$LiCoO_2$	
a:	2.822		2.819 Å (10^{-10} m)	
b:	2.822		2.819 Å	
c:	12.879		14.05 Å	
V:	102.56		111.65 $Å^3$	**$\Delta V = 8.9\%$**



Structural changes of the electrode
Insertion-reactions: $Li_4Ti_5O_{12}$



$Li_4Ti_5O_1$

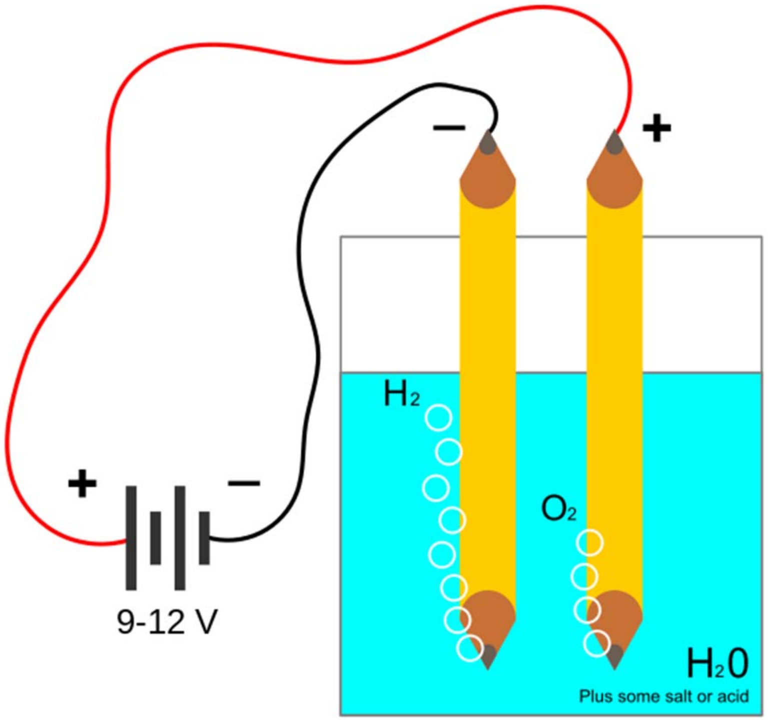
$Li_7Ti_5O_{12}$

$\Delta V=0.1\%$

-2-

Thermodynamic instability electrode-electrolyte leading to decomposition of the electrolyte

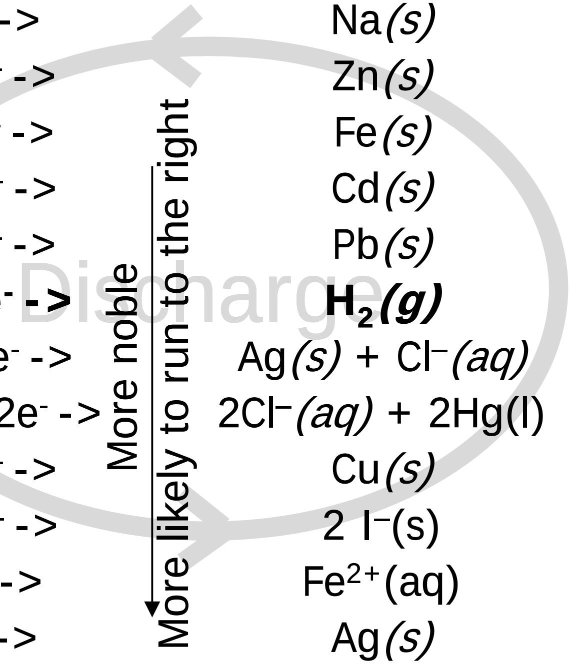
Decomposition of the electrolyte



Electrochemical cells, driving force

Standard reduction potentials are commonly denoted by the symbol ε^o. (means under standard conditions 293 K and 1 bar, 1 molair concentrations) ε^o values for hundreds of electrodes have been determined and are usually tabulated in order of increasing tendency to accept electrons (increasing oxidizing power.)

The more positive the half-cell EMF, the smaller the tendency of the reductant to donate electrons, and the larger the tendency of the oxidant to accept electrons



oxidant (electron acceptor)	**reductant** (electron donor)	**E°, volts**
$Na^+ + e^-$ ->	$Na(s)$	–2.71
$Zn^{2+} + 2e^-$ ->	$Zn(s)$	–.76
$Fe^{2+} + 2e^-$ ->	$Fe(s)$	–.44
$Cd^{2+} + 2e^-$ ->	$Cd(s)$	–.40
$Pb^{2+} + 2e^-$ ->	$Pb(s)$	–.126
$2\ H^+ + 2e^-$ ->	**$H_2(g)$**	**0.000**
$AgCl(s) + e^-$ ->	$Ag(s) + Cl^-(aq)$	+.222
$Hg_2Cl_2(s) + 2e^-$ ->	$2Cl^-(aq) + 2Hg(l)$	+.268
$Cu^{2+} + 2e^-$ ->	$Cu(s)$	+.337
$I_2(s) + 2e^-$ ->	$2\ I^-(s)$	+.535
$Fe^{3+} + e^-$ ->	$Fe^{2+}(aq)$	+.771
$Ag^+ + e^-$ ->	$Ag(s)$	+.799
$O_2(g) + 4H^+ + 4e^-$ ->	$2\ H_2O(l)$	+1.23
$Cl_2(g) + 2e^-$ ->	$2\ Cl^-(g)$	+1.36

What is the potential difference we need to split water? Charge!

$$4H^+ + 4e^- + 2H_2O \rightarrow 2H_2 + O_2 + 4H^+ + 4e^-\ ,\quad E^o_{cell} = 1.23 - 0 = 1.23\ \mathrm{V}$$

Decomposition of the electrolyte

Splitting of water

Red/Cat $2H^{+} + 2e^{-} \rightarrow H_2$

Ox/An $2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-}$

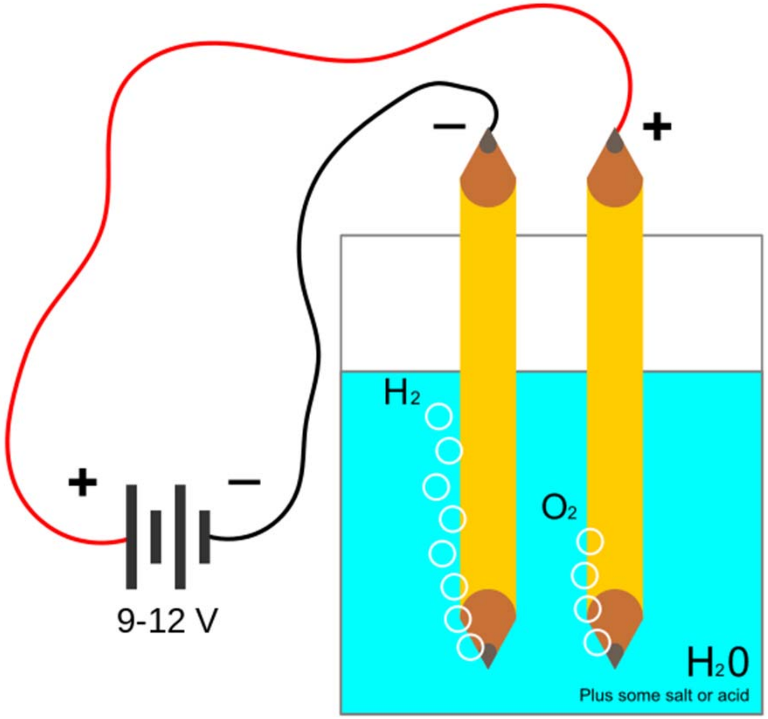
Total $2H_2O \rightarrow 2H_2 + O_2$

$$E^{o}_{Cell} = 1.23\ \mathrm{V}$$

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$$

$$4OH^{-} \rightarrow O_2 + 2H_2O + 4e^{-}$$

$$2H_2O \rightarrow 2H_2 + O_2$$



Decomposition of water

Depends on concentrations H$^+$/OH$^-$ (pH) of water => Nernst

$$E_{Cell} = E^0 - \frac{RT}{zF} \ln \Pi c_j^{\nu} = E^0 - \frac{RT}{zF} \ln(K)$$

$$2H^+ + 2e^- \rightarrow H_2$$

$$E_H = E^o_{H^+/H_2} - \frac{RT}{zF} \ln \frac{[H_2]}{\left[H^+\right]^2} = E^o_{H^+/H_2} - \frac{RT}{zF} \ln \frac{\left[p_{H_2}/p_0\right]}{\left[H^+\right]^2} = E^o_{H^+/H_2} - \frac{2.303RT}{zF} \log \frac{\left[p_{H_2}/p_0\right]}{\left[H^+\right]^2}$$

$$E^o_{H^+/H_2} = 0, \quad \mathrm{p}_{H_2} = p_0, \quad pH = -\log\left[H^+\right]$$

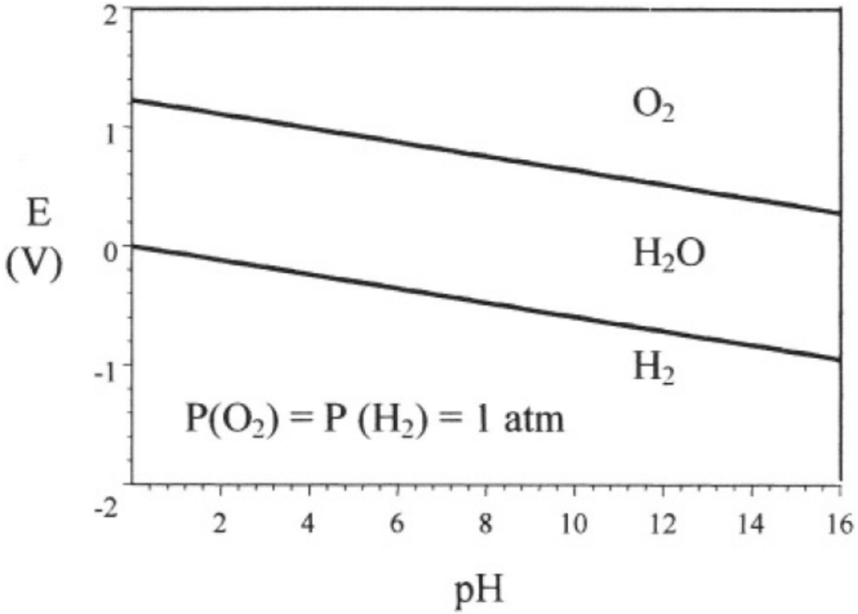
$$E_H = -\frac{2.303RT}{2F}\left[\log\left[p_{H_2}/p_0\right] - 2\log\left[H^+\right]^2\right] = -\frac{2.303RT}{F} pH$$

Decomposition of water

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

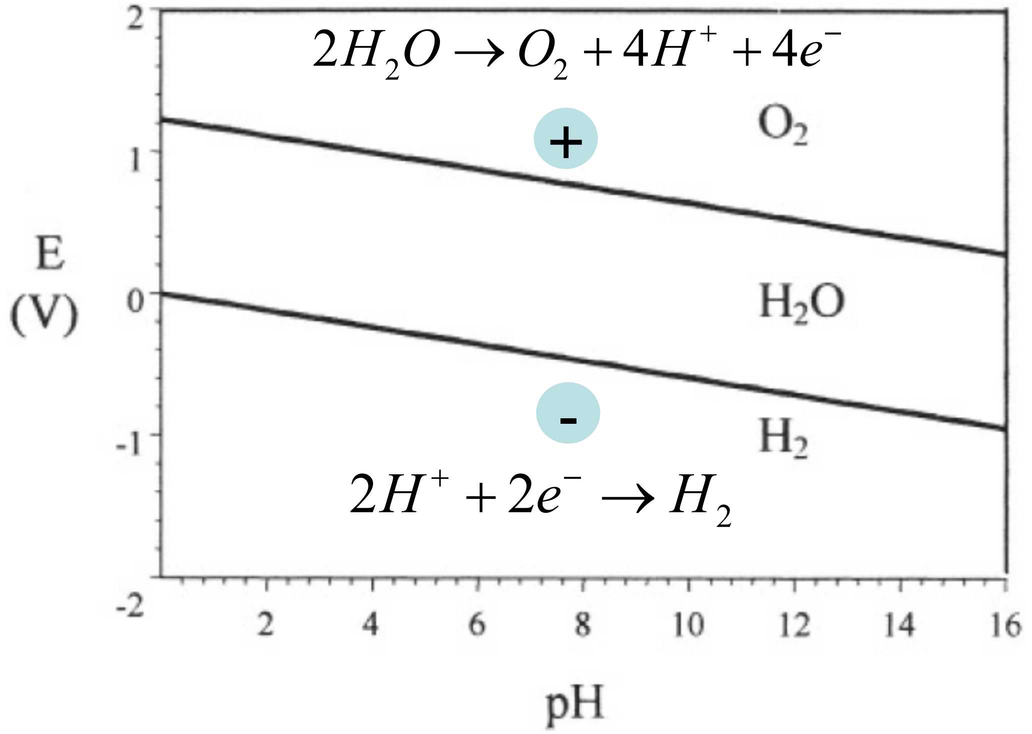
$$E_{O_2} = E^o_{O_2} - \frac{RT}{zF}\ln\frac{[H_2O]^2}{[O_2][H^+]^4} = 1.229 - \frac{2.303RT}{F}pH$$

Pourbaix Diagram



Decomposition of water

Pourbaix Diagram

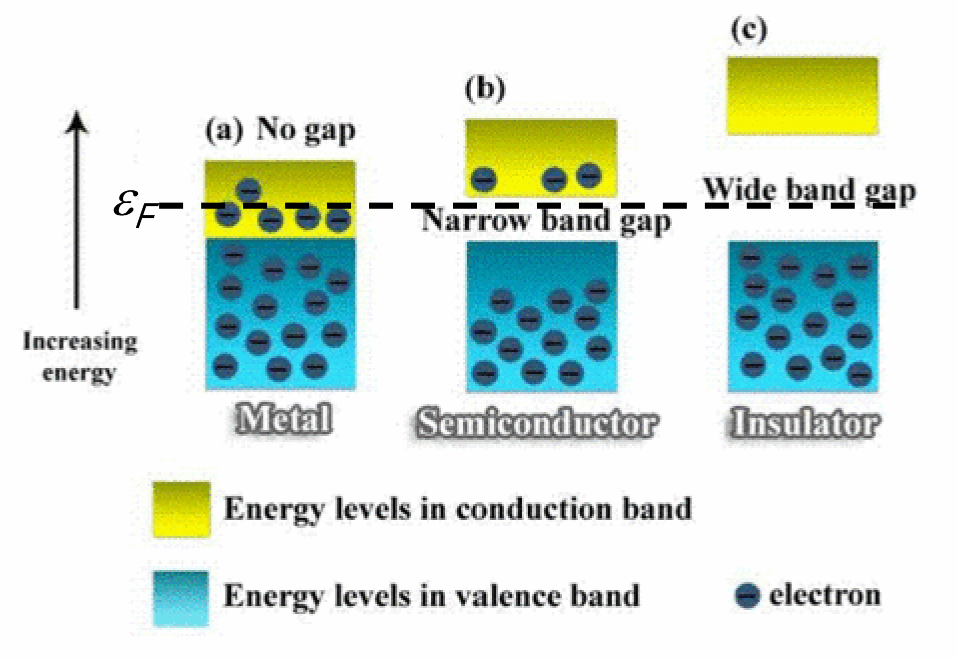


$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$2H^+ + 2e^- \rightarrow H_2$$

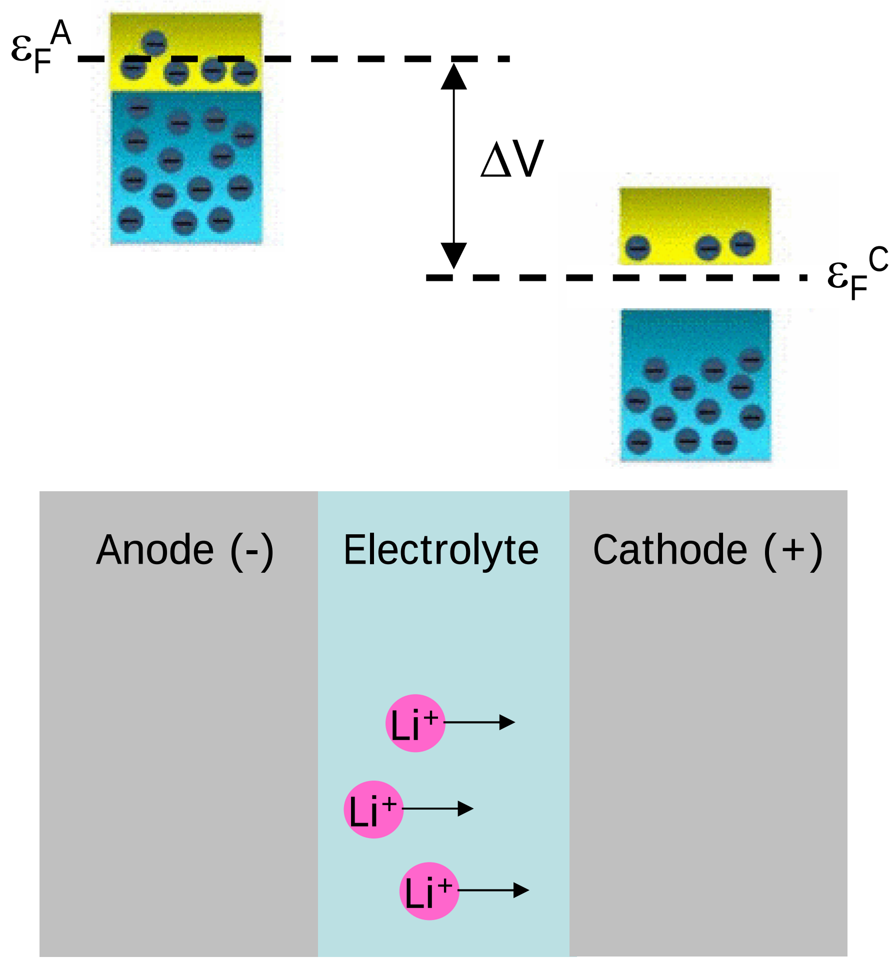
A more general way to look at it: band structure

Band structure of solids



ε_F: Fermi level, potential energy of an electron in a solid defined as the chemical potential of the electron: $\varepsilon_F = \mu_{e^-}$

Relation battery voltage and Fermi level



Difference in Fermi level

⇩

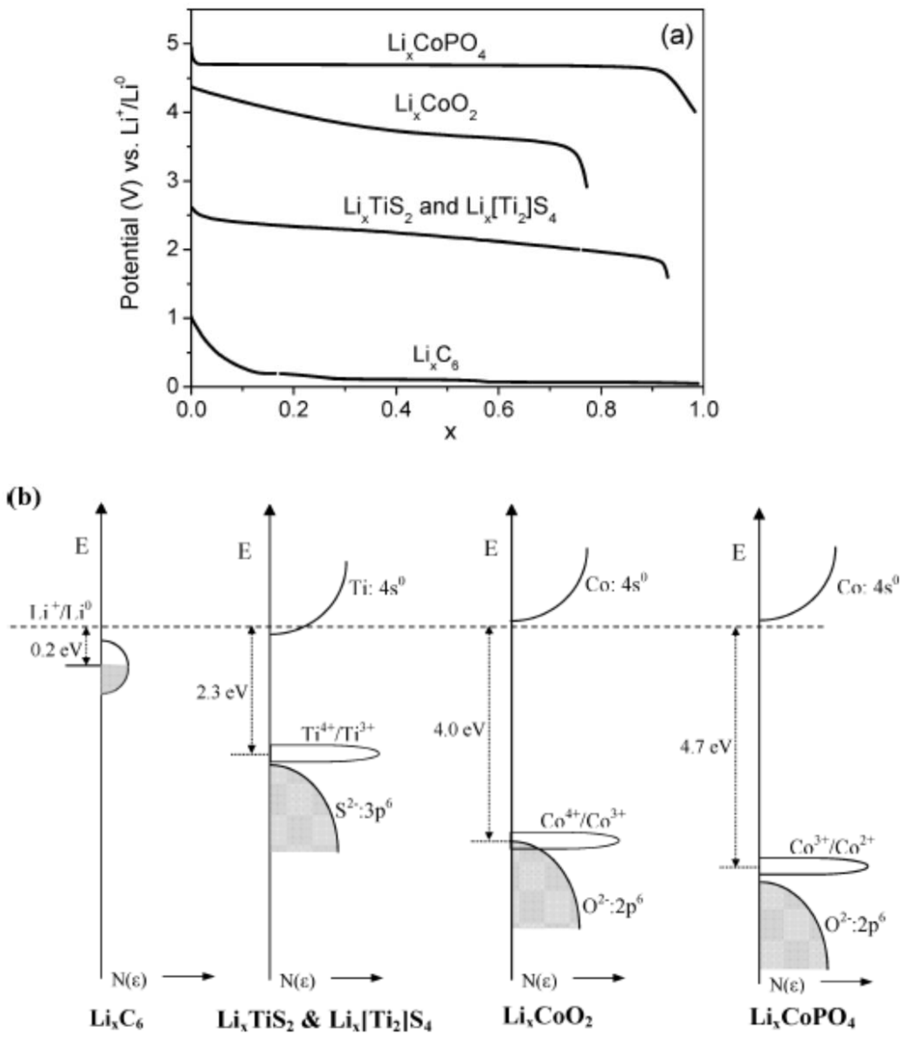
Difference in electron chemical potential

⇩

Difference in potential

$$E_{Cell} = \mu_{e^-}^{A} - \mu_{e^-}^{C} = \varepsilon_F^A - \varepsilon_F^C$$

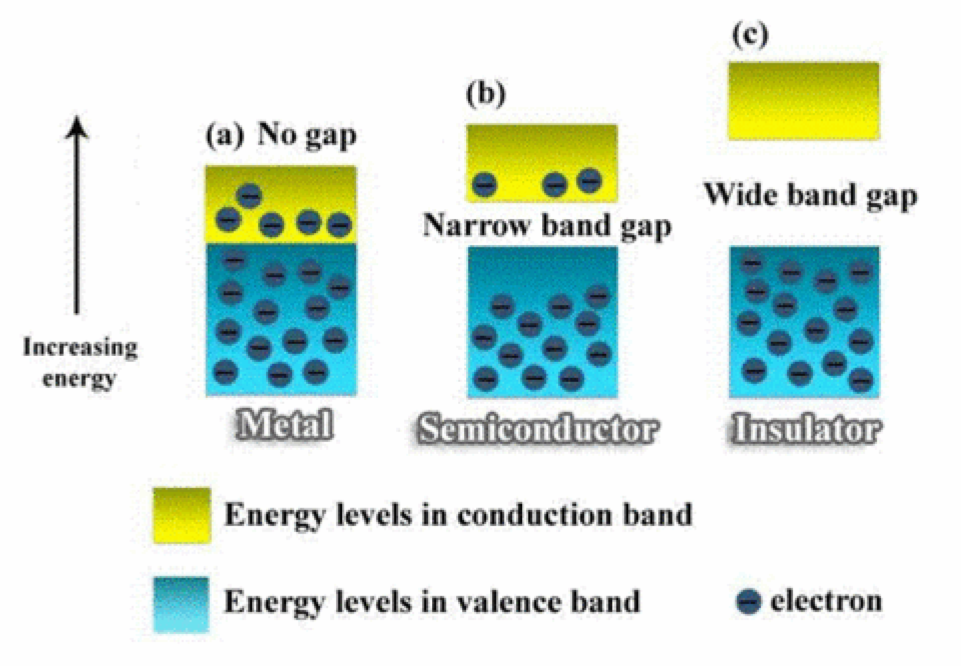
Relation battery voltage and Fermi level



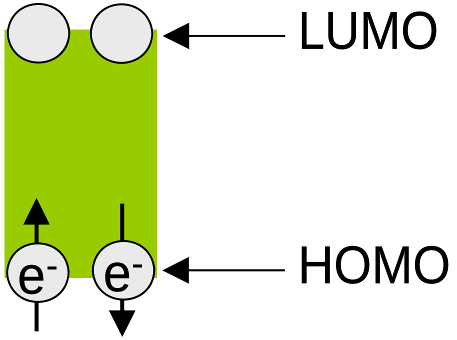
Conduction band

Valence band

LUMO and HOMO inorganic materials

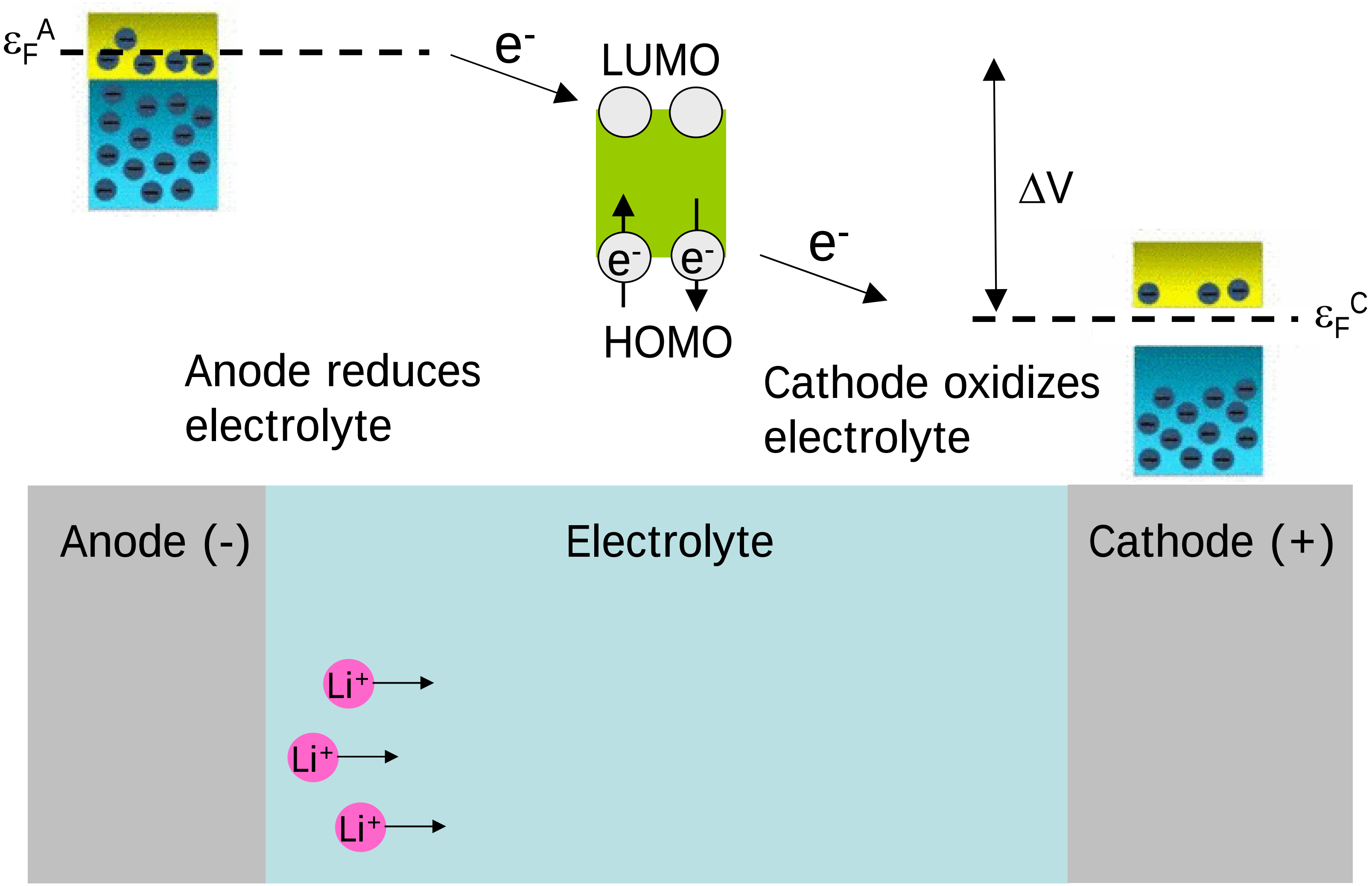


Inorganic material

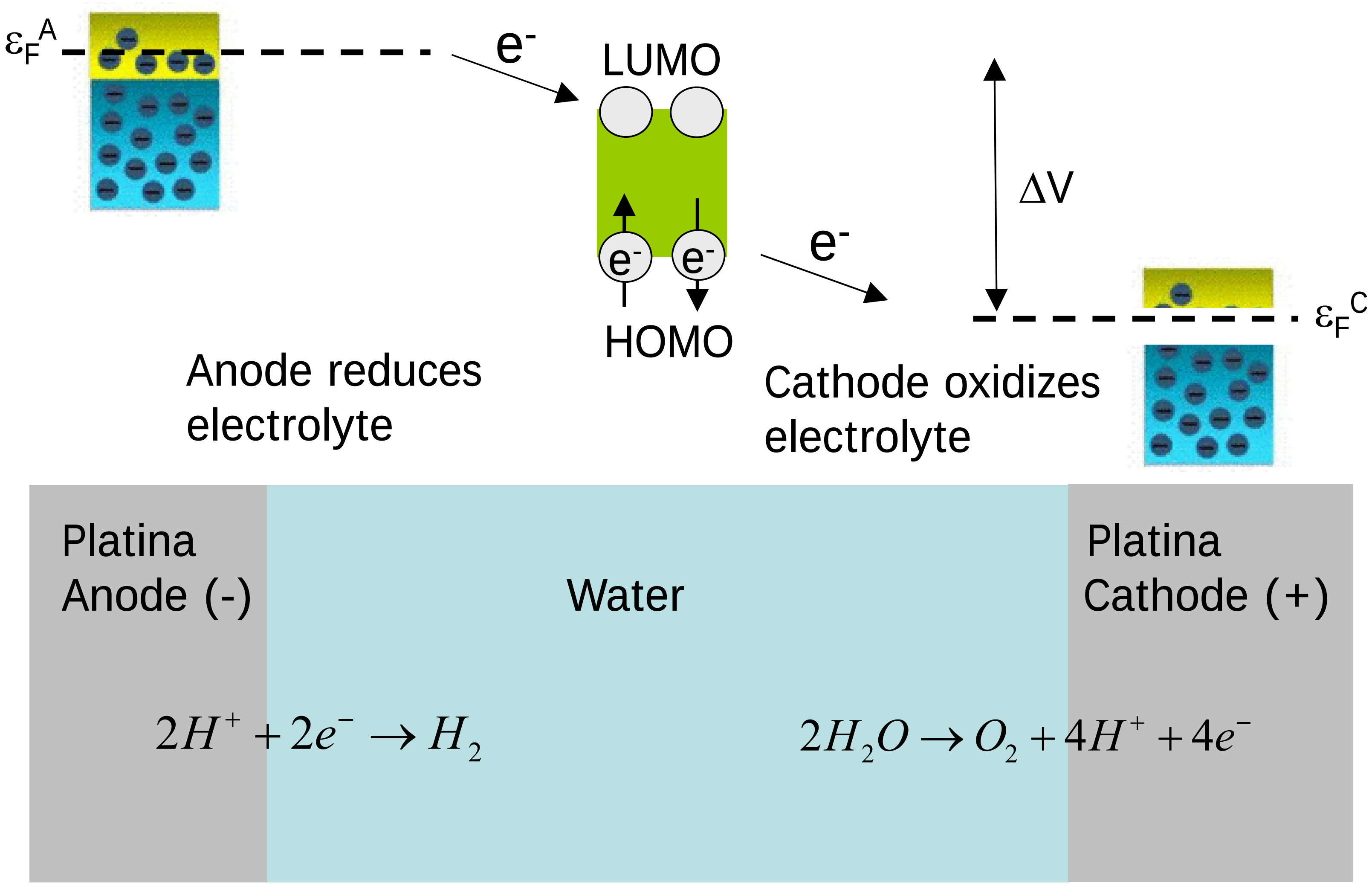


LUMO: Lowest Unoccupied Molecular Orbital (in conduction “band”)
HOMO: Highest Occupied Molecular Orbital (in valence “band”)

Electrolyte stability



Electrolyte stability



Anode reduces electrolyte

Cathode oxidizes electrolyte

Platina
Anode (-)

Water

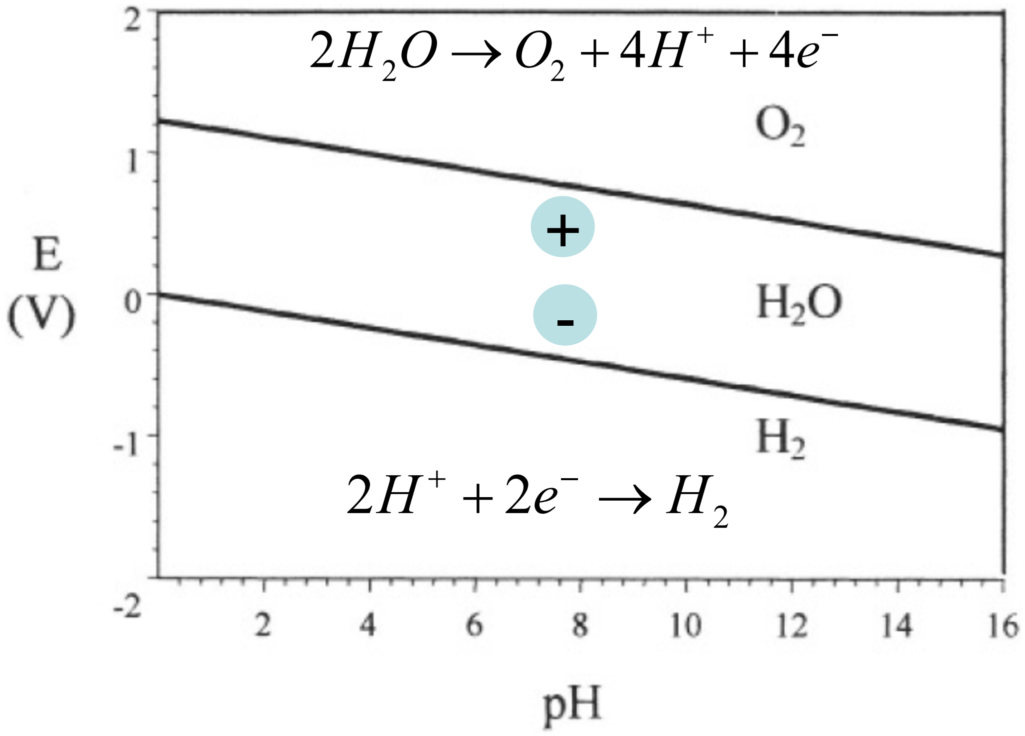
Platina
Cathode (+)

$$2H^+ + 2e^- \rightarrow H_2$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

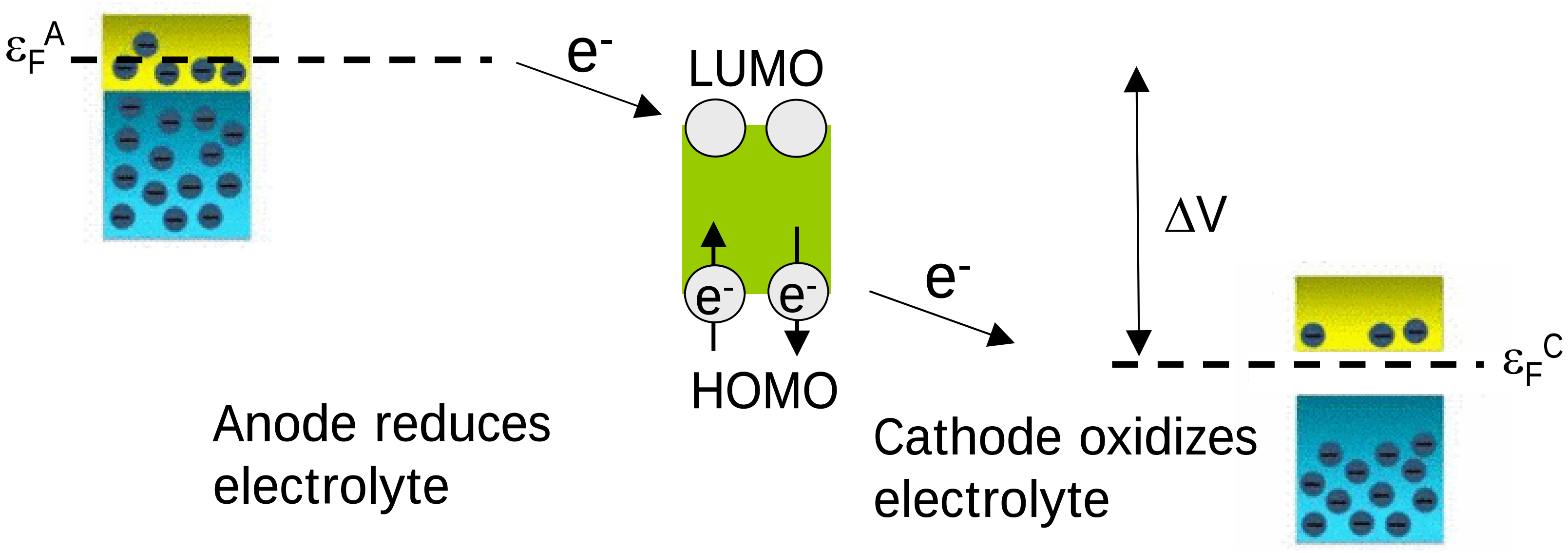
Decomposition of water

Pourbaix Diagram


$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$2H^+ + 2e^- \rightarrow H_2$$

Question electrolyte stability 1



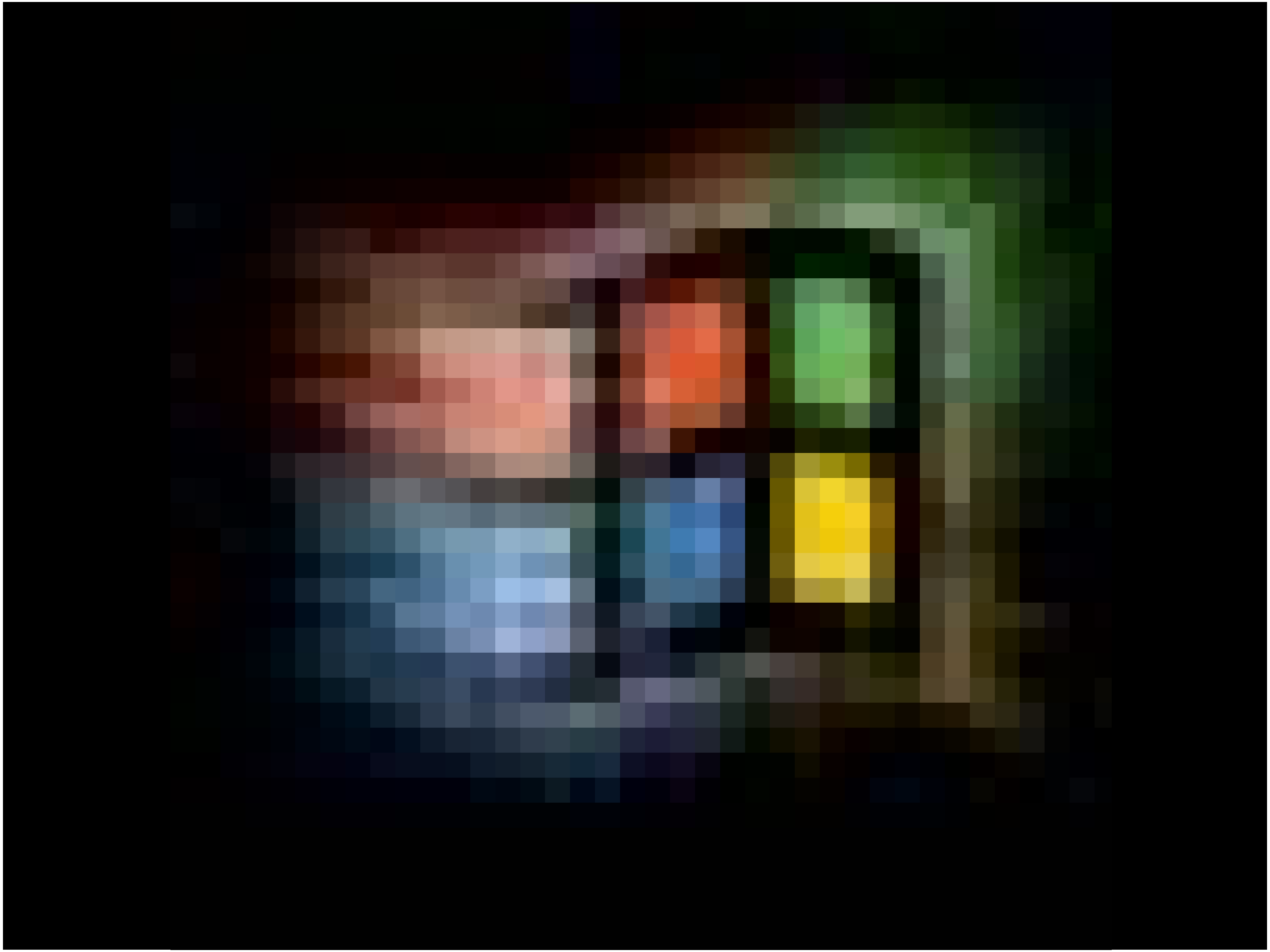
Anode reduces electrolyte

Cathode oxidizes electrolyte

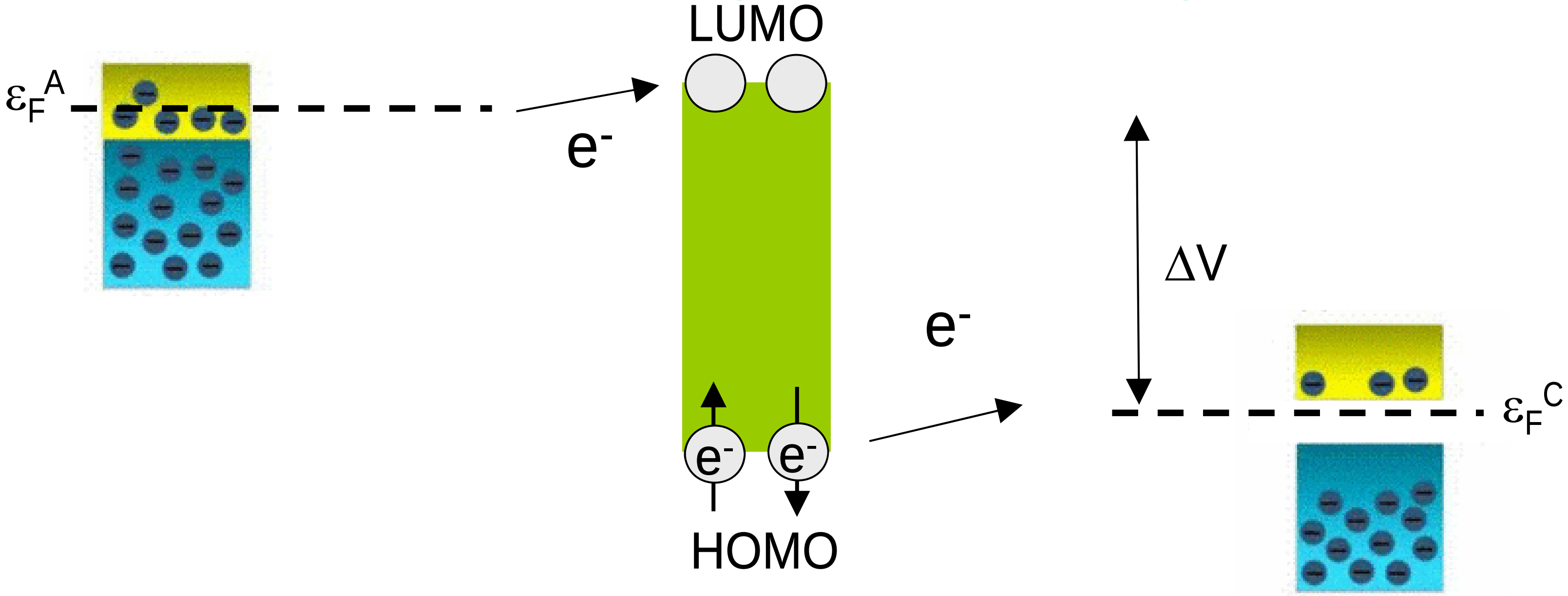
24. To prevent electrolyte decomposition:

a) The difference between the LUMO and HOMO should be as small as possible
b) LUMO-HOMO > $\varepsilon_F^A - \varepsilon_F^C$
c) LUMO-HOMO < $\varepsilon_F^A - \varepsilon_F^C$
d) LUMO>ε_F^A and ε_F^C >HOMO
e) no clue

http://www.edupinion.nl/c619 Result



Question electrolyte stability 1



24. To prevent electrolyte decomposition:

a) The difference between the LUMO and HOMO should be as small as possible

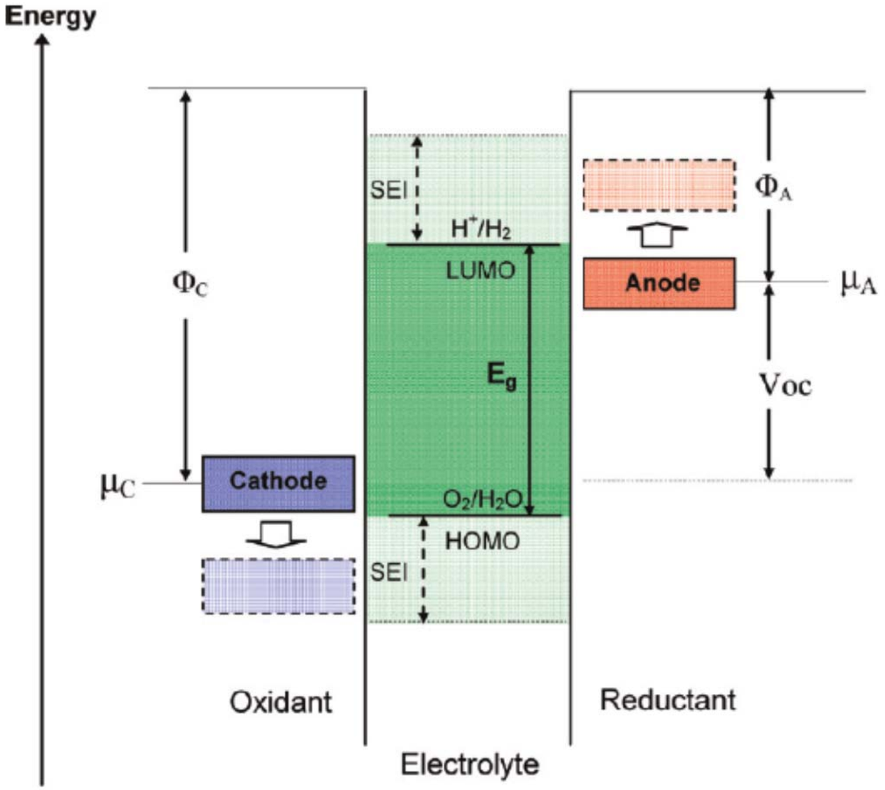
b) LUMO-HOMO > ε_F^A-ε_F^C

c) LUMO-HOMO < ε_F^A-ε_F^C

d) LUMO>ε_F^A and ε_F^C >HOMO

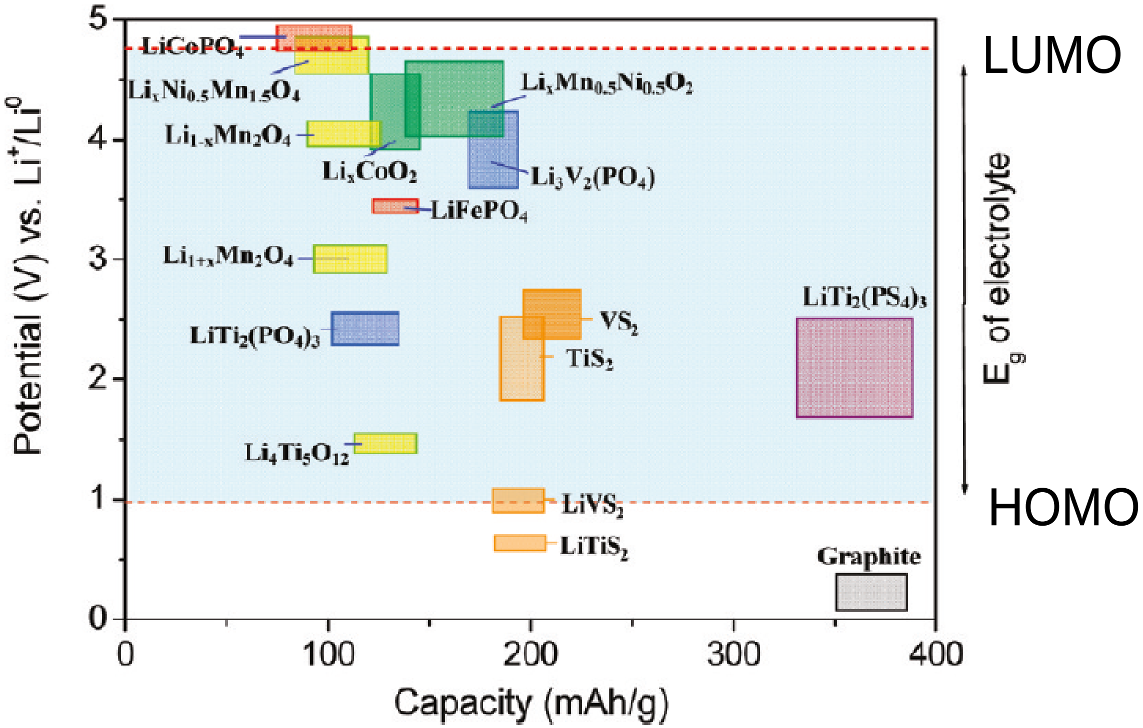
e) no clue

Electrolyte-electrode stability diagram



$$E_{Cell} = \phi_C - \phi_A = \mu_{e^-}^A - \mu_{e^-}^C = \varepsilon_F^A - \varepsilon_F^C$$

Question electrolyte stability 2

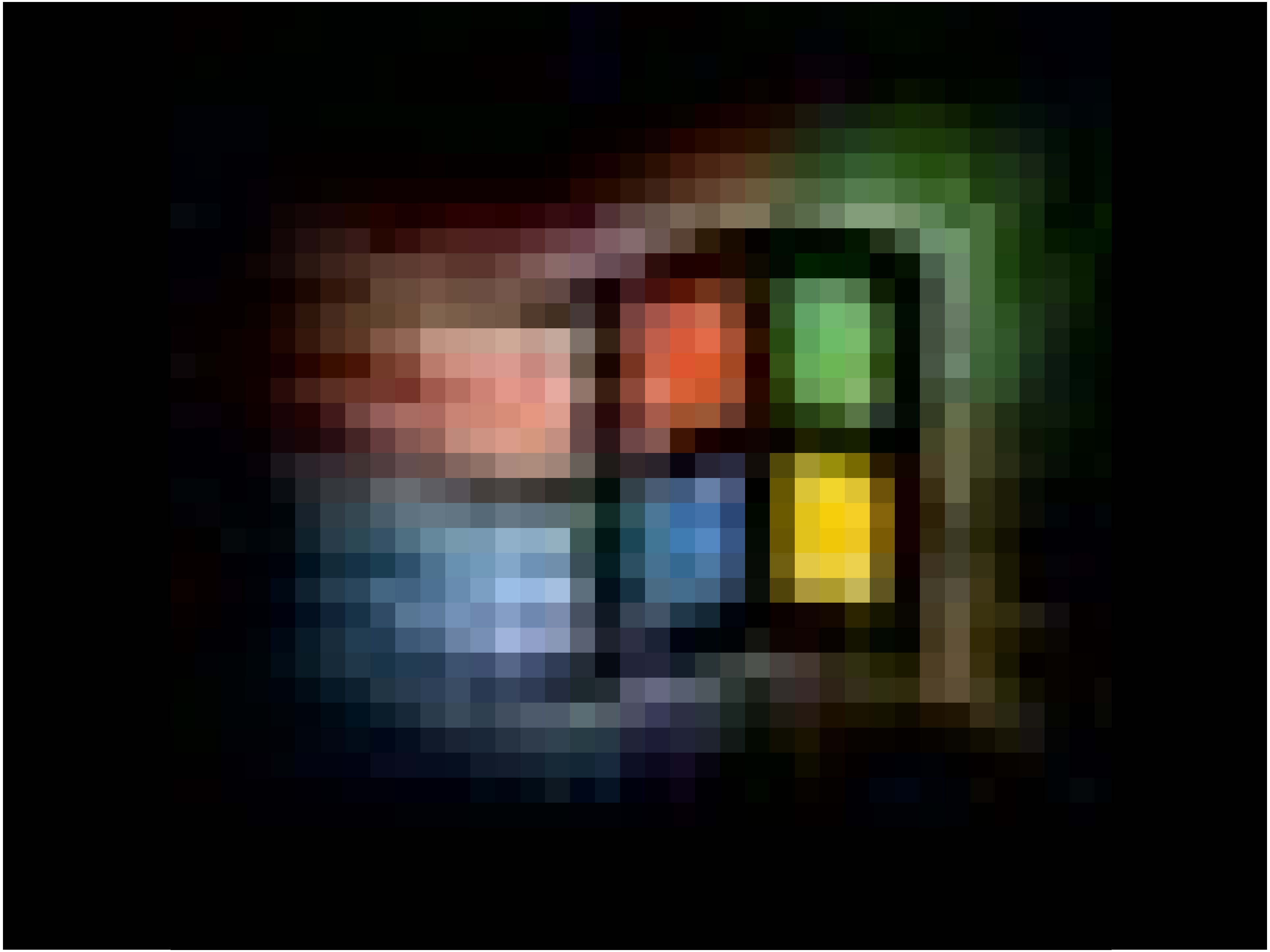


25. The highest energy density electrode combination that will not result in electrolyte decomposition is:

a) $LiCoPO_4$ vs Graphite
b) $LiNi_{0.5}Mn_{1.5}O_4$ vs $LiVS_2$
c) $Li_3V_2(PO_4)$ vs $LiTi_2(PS_4)_3$
d) $LiCoPO_4$ vs $LiVS_2$
e) no clue

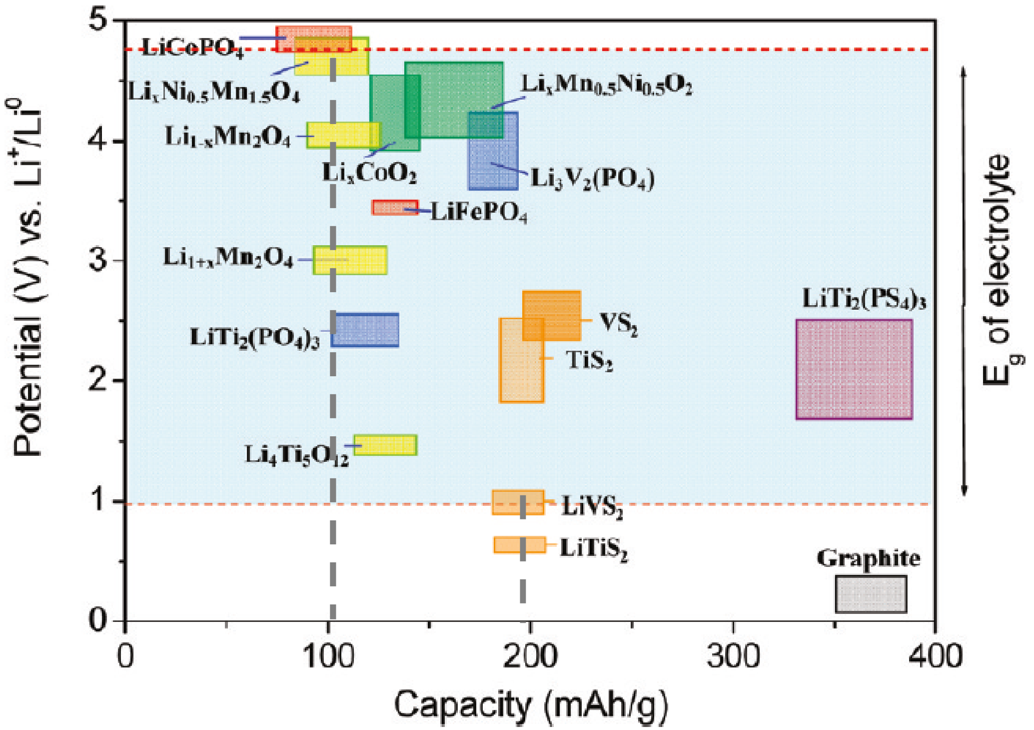
http://www.edupinion.nl/c863

Result



Question electrolyte stability 2

Energy = Capacity x Voltage
(1 mAh/g = 3.6 C, [V] = [J/C])



25. The highest energy density electrode combination that will not result in electrolyte decomposition is:

a) $LiCoPO_4$ vs Graphite:

b) $LiNi_{0.5}Mn_{1.5}O_4$ vs $LiVS_2$: ~150x3.5=525

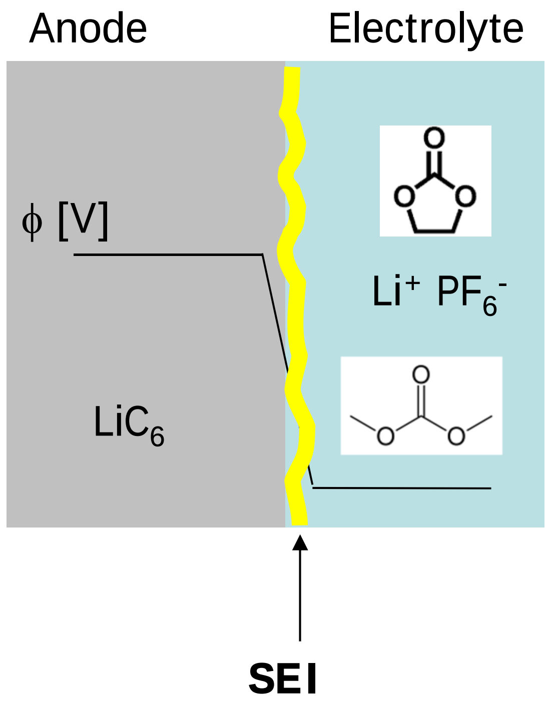
c) $Li_3V_2(PO_4)$ vs $LiTi_2(PS_4)_3$ ~270x2=545

d) $LiCoPO_4$ vs $LiVS_2$

e) no clue

SEI Formation

Formation of the Solid Electrolyte Interface (SEI) at the negative electrode

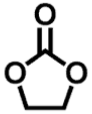


Side reactions take mainly place at the interface between electrolyte and anode

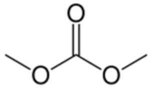
At low voltage (0-0.8 V versus Li metal) the inorganic solvants are thermodynamically unstable versus the anode

Leads to the formation of a Solid Electrolyte Interface (SEI) layer (Li_2CO_3, alkyl-carbonates, polymers…)

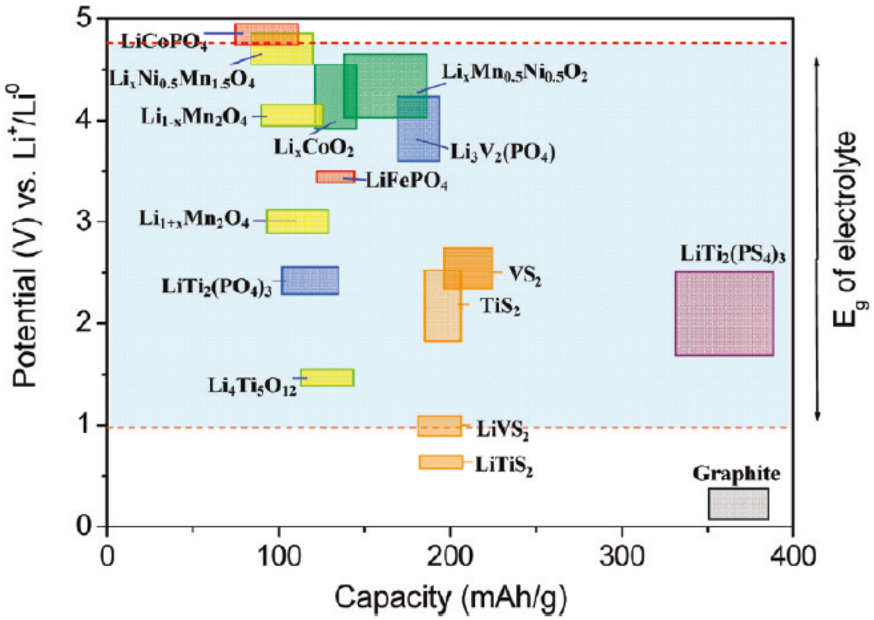
Ethylene Carbonate (EC):

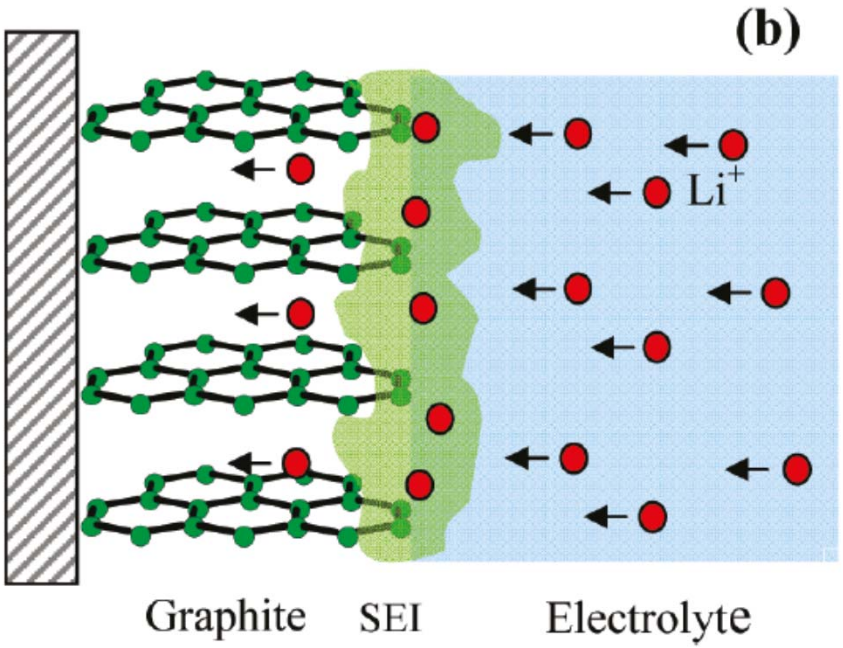


Dimethyl Carbonate (DMC):

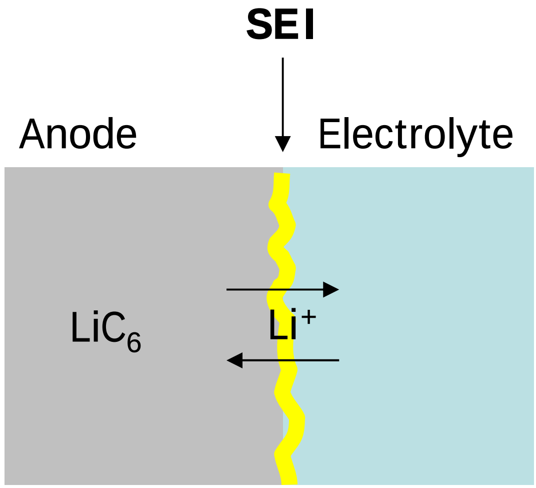


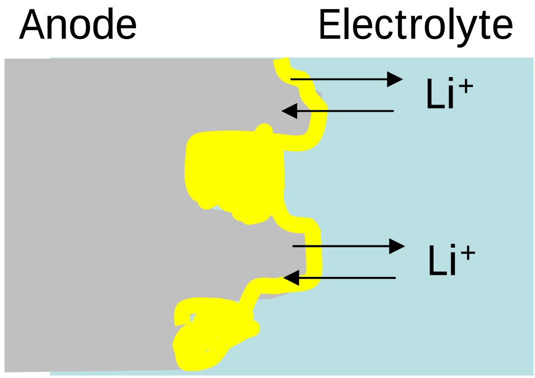
Example SEI Formation: Graphite





SEI Formation

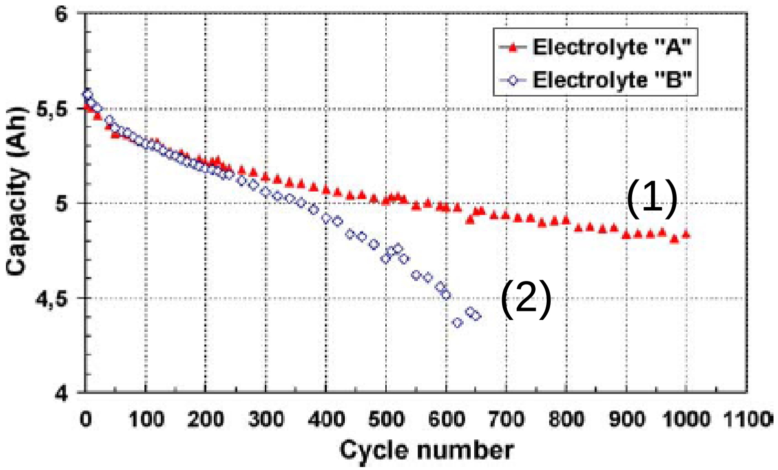




Depending on the electrolyte, interface and salt the SEI can:

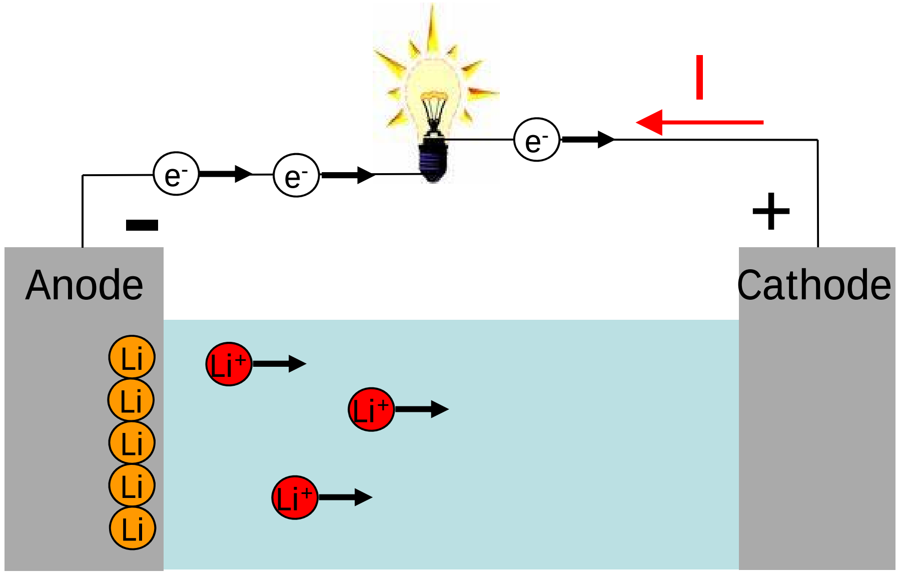
(1) Form a stable electronic isolating layer (but ionic conducting) passivating further side reactions -> long cycle life

(2) Grow extensively blocking Li-transfer and reducing active surface area -> increasing the current density -> higher over potentials -> more SEI formation -> avalanche effect -> short cycle life



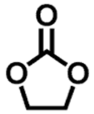
Demands Li-ion Electrolyte

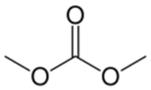
- **Good (Li^+) ionic conductor**
- **Electronic Isolator**
- **Stability window 5 V (depends on sys.)**
- **Stable up to ~ 70 degree celcius**
- **Cheap**
- **Non toxic**



Mostly applied: Non aqueous solvents:

Ethylene Carbonate (EC), Dimethyl Carbonate (DMC)





Good ionic conduction, stability ~ 0.8-4.5 V (vs Li/Li^+)

Medium toxic, flammable, unstable etc -> Casing battery should be very good (=expensive)

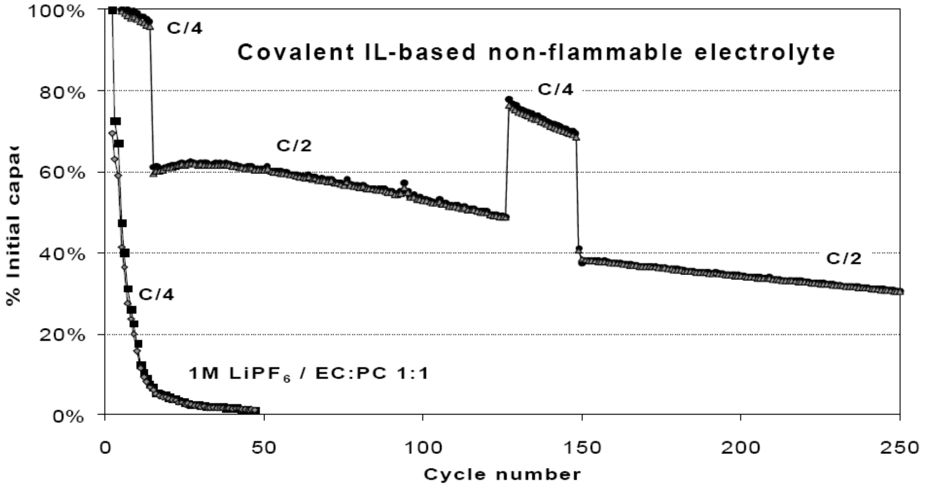
Li salts: $LiClO_4$ or $LiPF_6$: Toxic and expensive

Li-ion batteries, ionic liquids

Ionic liquid: salt in the liquid state:

electronic isolator
good ionic conductor
thermal stability
non-flammable
chemically stable (large stability window)
} safe
cheap?

Li-ion Cycling Performance
at 100°C



Li-ion batteries, solid electrolytes

Solid electrolytes:

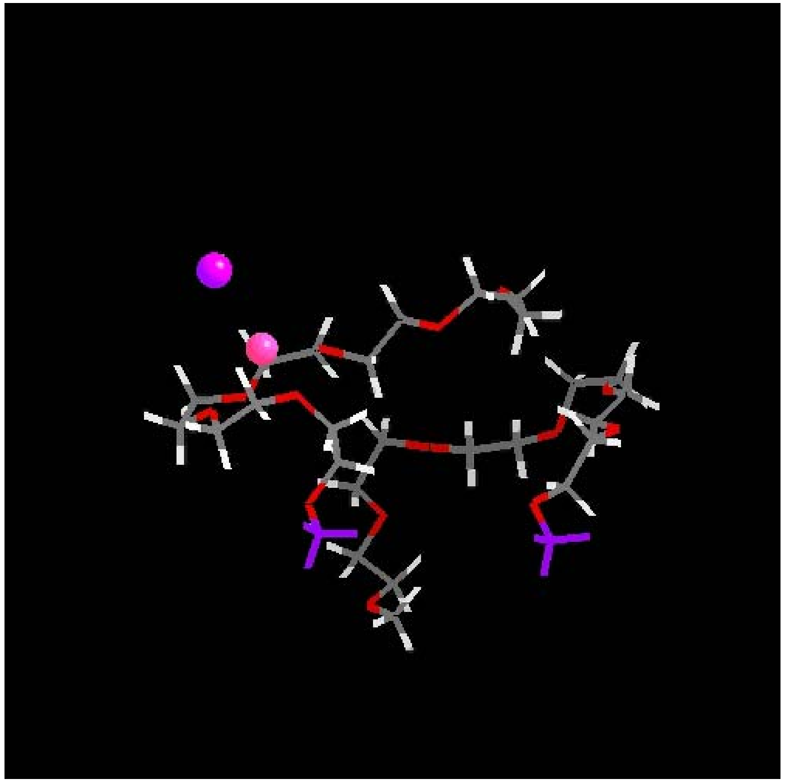
Less difficulty/cost associated with long term encapsulating liquid electrolytes (that may start leaking), freedom design of batteries, high temp.

Example: polymer electrolytes like polyethyleneoxide

Because polymers can have intrinsic mobility of the polymer chains, a dissolved Li salt can also move through it. However, solid electrolytes show much lower Li^+ conductivities (low power density)

Application limited to large systems that can be maintained at high temperatures

Poor ionic mobility, PEO LiI



Li-ion batteries, electrolytes

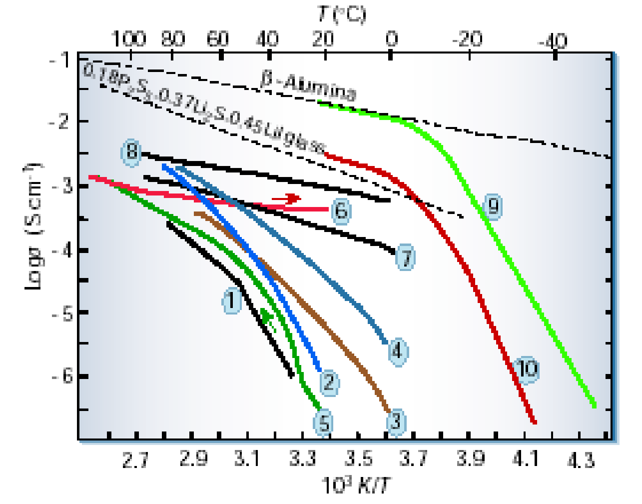
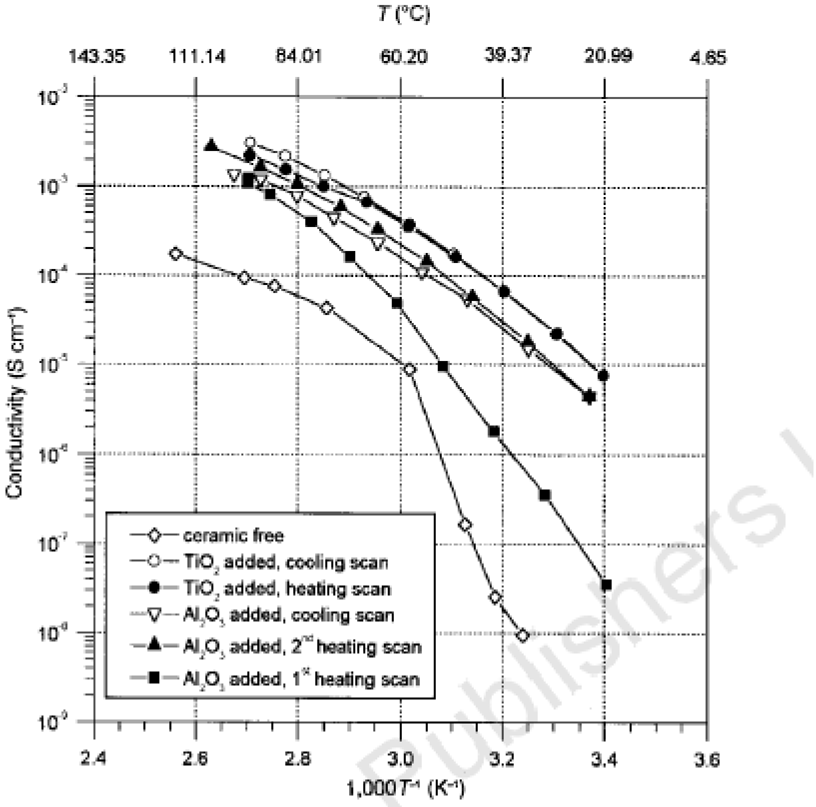


Figure 8 Arrhenius plot of conductivity for various solid electrolytes. 1, First-generation PEO-$LiCF_3SO_3$; 2, new solutes with high-dissociation PEO-$Li[(CF_3SO_2)_2N]$; 3, low-T_g combination polymer; 4, plasticized polymer electrolyte PEO-$Li[(CF_3SO_2)_2N]$ + 25% w/w PEG-dimethylether (molecular weight, 250); liquid crystalline polymer electrolytes; 5, heating curves; 6, cooling curve[54]; 7, gel-type polymer (X-linked PEO-dimethacrylate-$Li[(CF_3SO_2)_2N]$-PC 70%); 8, liquid electrolyte PC/DME $LiCF_3SO_3$; 9, liquid electrolyte EC/DMC-$LiPF_6$ at low temperature[51]; 10, gel electrolyte P(VDF-HFP)/EC/DMC-$LiPF_6$ (ref. 61).

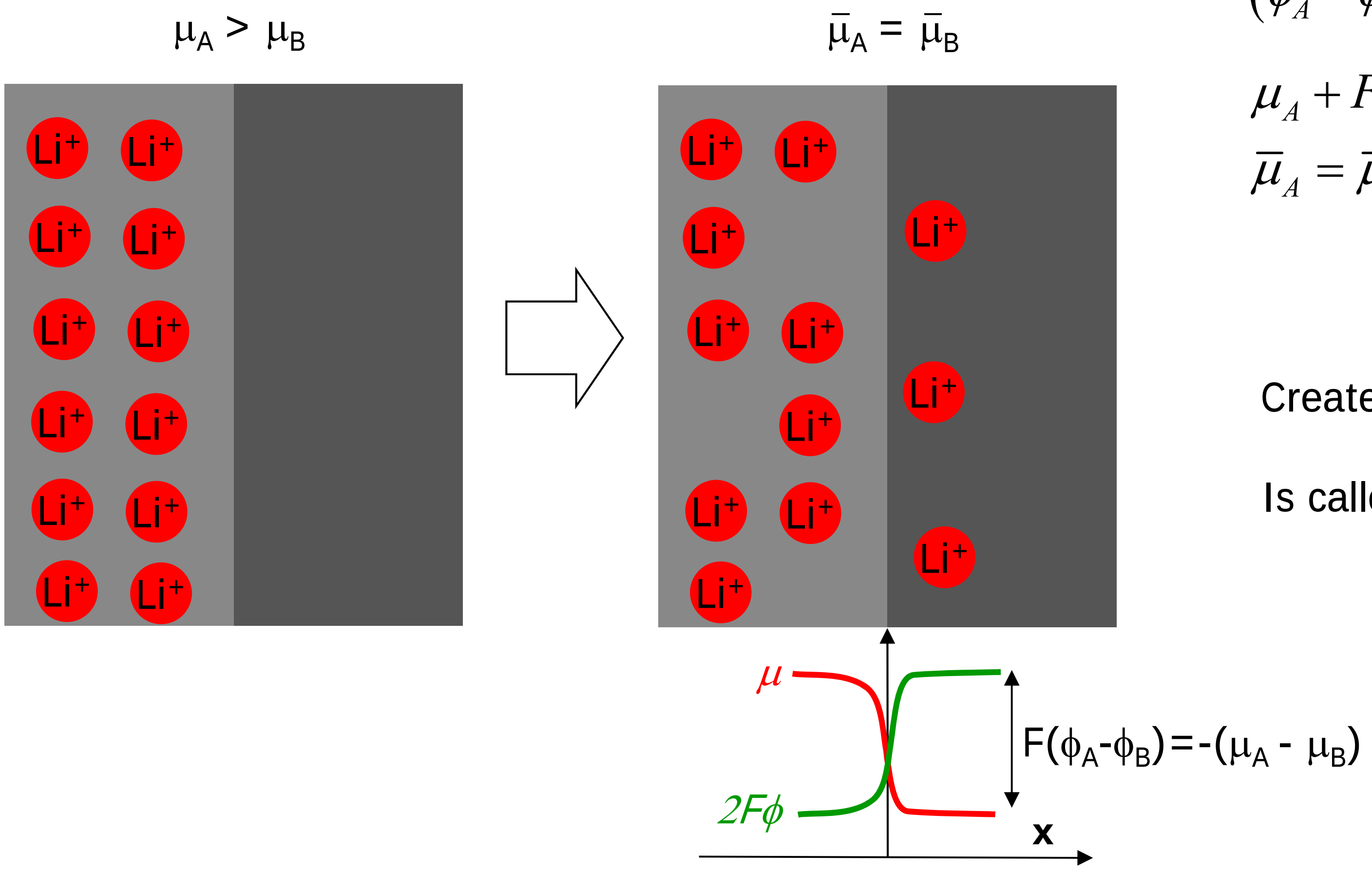
Other strategy:

Adding nano-particles increases the Conductivity in PEO-$LiClO_4$



Space charges

Two ion conductors and poor electronic isolators:



$$(\phi_A - \phi_B) = -\frac{(\mu_A - \mu_B)}{F}$$

$$\mu_A + F\phi_A = \mu_B + F\phi_B$$

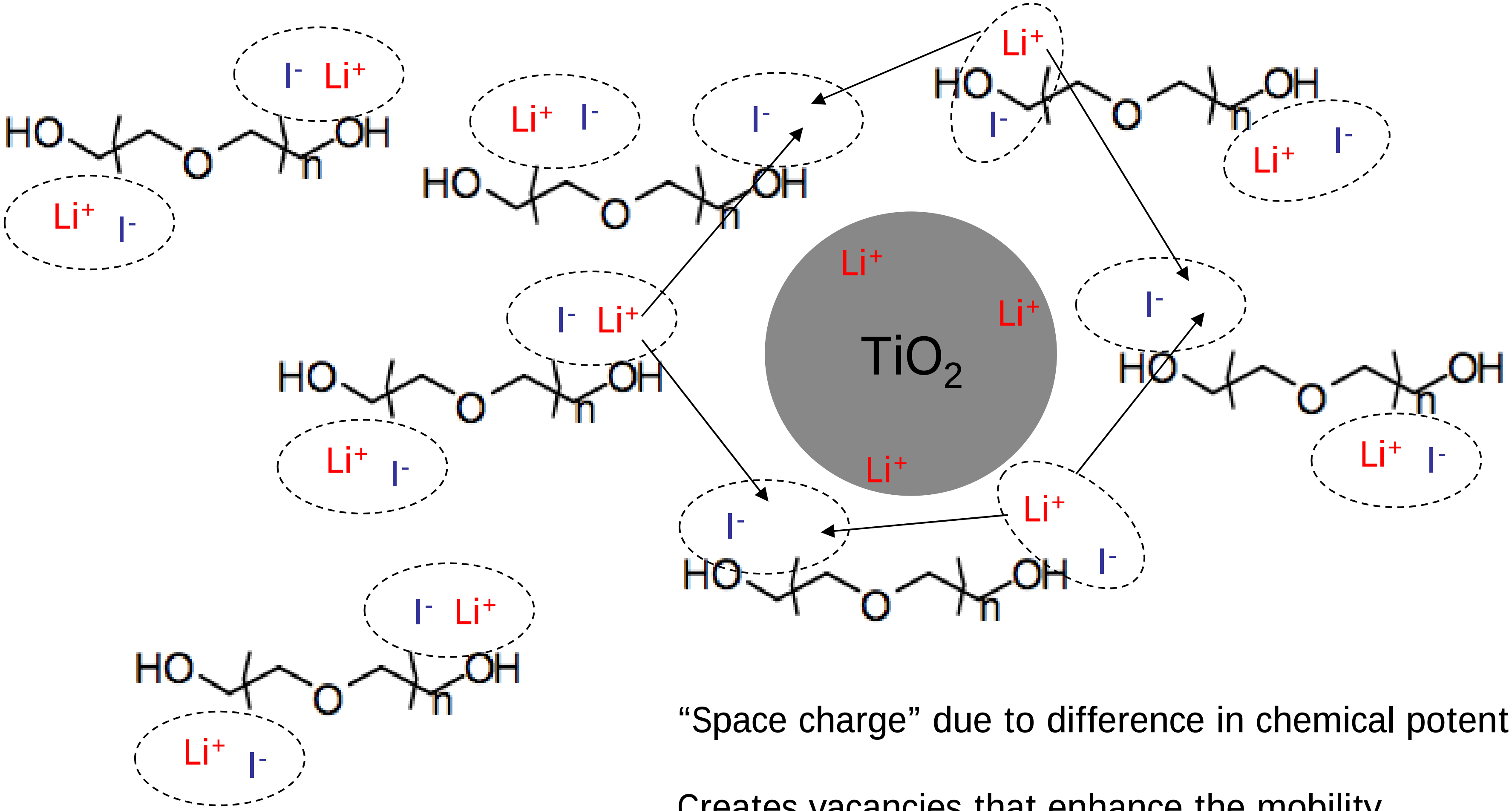
$$\bar{\mu}_A = \bar{\mu}_B$$

Creates vacancies in A!

Is called “Space Charge”

For diffusion you need vacancies

Li-ion batteries, electrolytes



“Space charge” due to difference in chemical potential

Creates vacancies that enhance the mobility

Practical questions

✓ ✓ What is the direction of a redox reaction?

✓ ✓ What is the voltage that a redox reaction can deliver?

✓ What is the energy density of a battery?

✓ ✓ What determines the cycle life of a battery

What is the power density of a battery? -> kinetics

Practical Energy Density

Energy density only exists for a combination of electrodes, 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 (=1 for Li^+*)*
ε_{Cell}*: cell potential [V]*
M: mass of the electrodes (sum of both!) [g/mol]

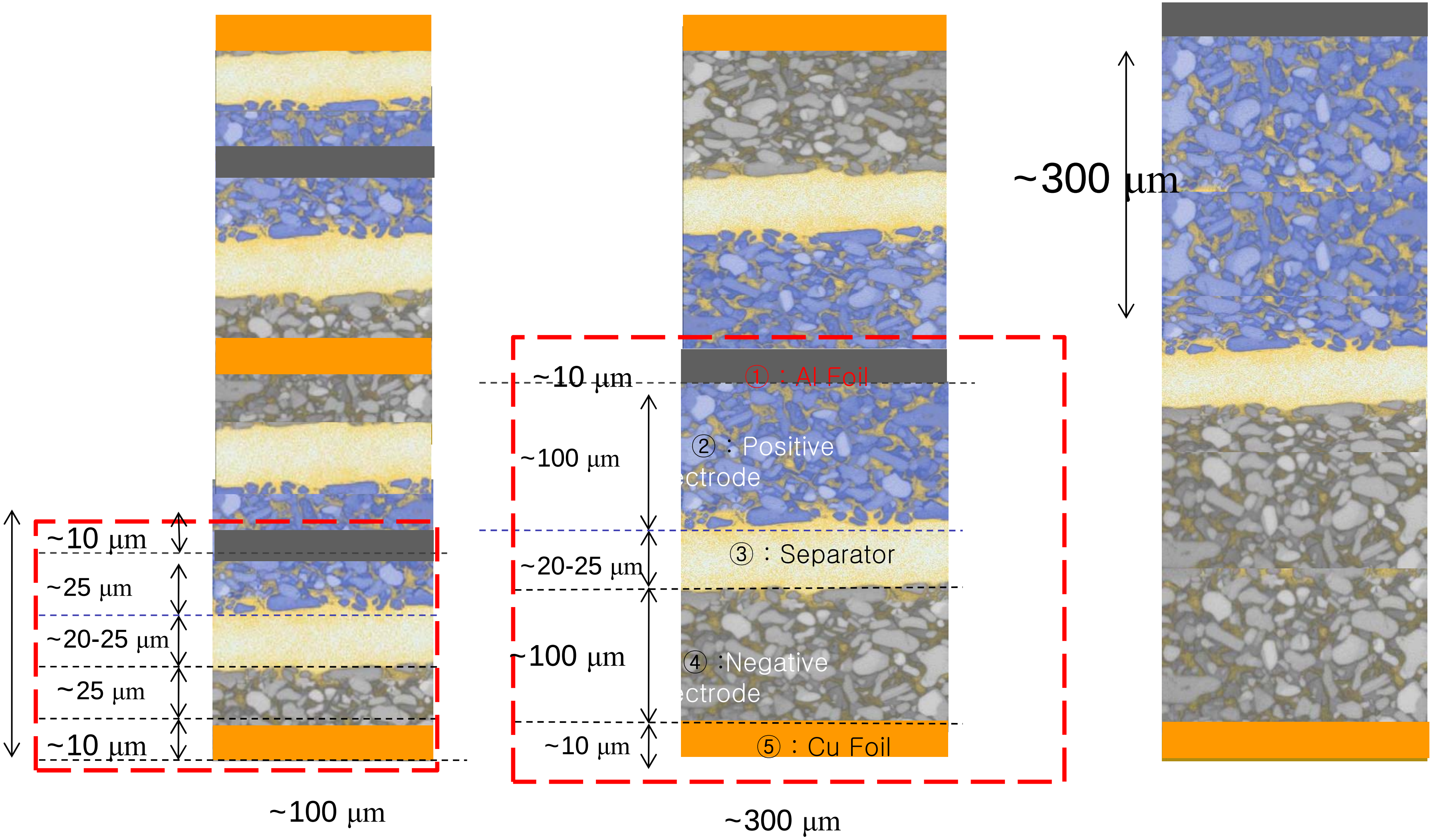
Example:

(+) $Li_{0.5}CoO_2 + 0.5Li^+ + 0.5\ e^- \rightarrow LiCoO_2$
(-) $LiC_6 \rightarrow 6C + Li^+ + e^-$

0.5 Li^+ stored per unit CoO_2, this requires 0.5 C_6
$\Rightarrow$For $x = 0.5$ $M = M_{3C} + M_{CoO2} = 127$ *g/mol*
$\Rightarrow$Using $\varepsilon_{Cell} = 3.6$ *V* it follows that *Energy density = 1370 J/g = 380 Wh/kg*

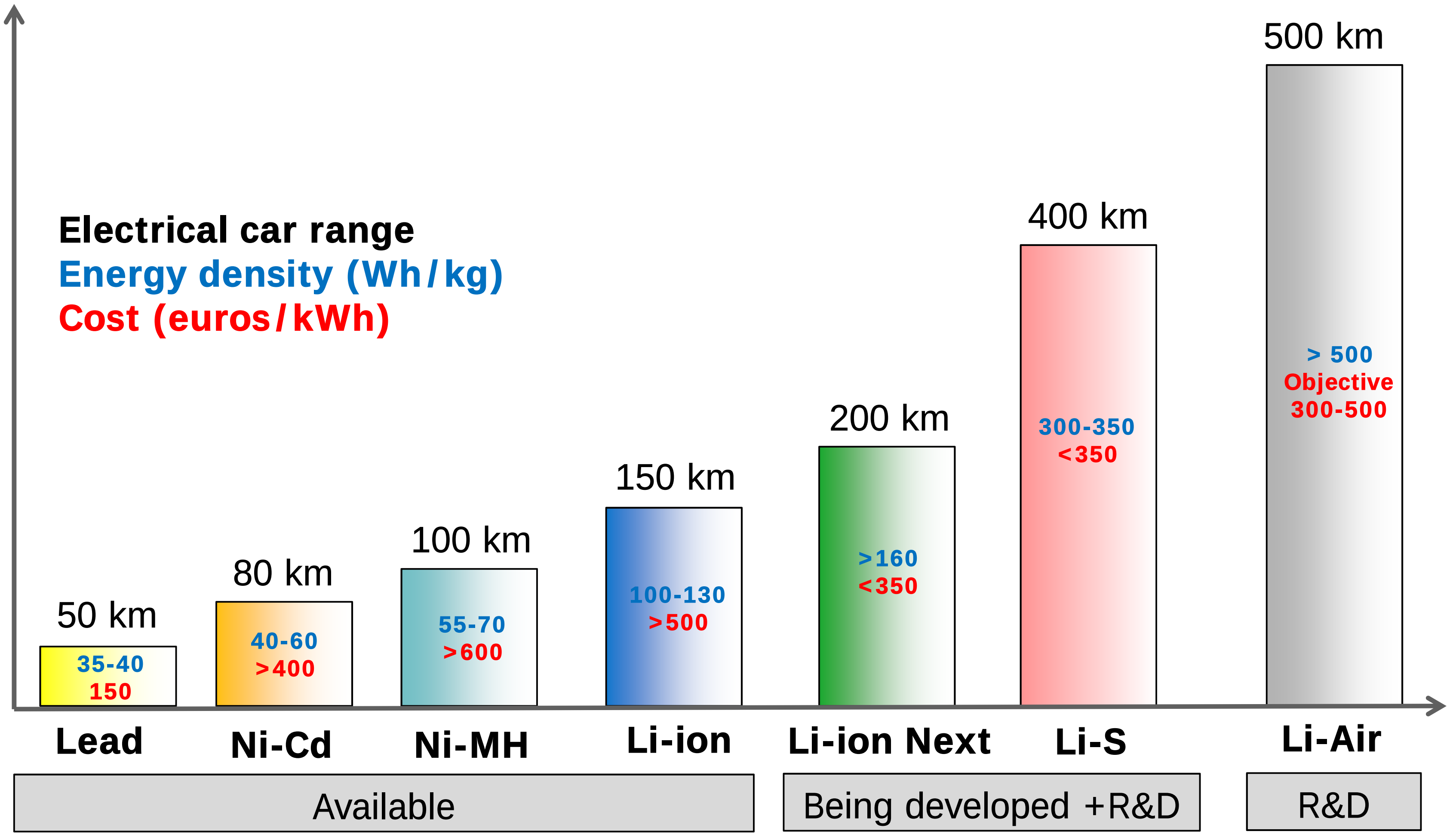
This is only taking into account the weight of the electrodes,
Electrode additives, Electrolyte, separator, current collectors and packing:
Energy density complete battery ~ *110 Wh/kg (~30%)*

Energy density: amount of active material



Increasing Energy Density →

Energy density for mobility



Question Energy Density

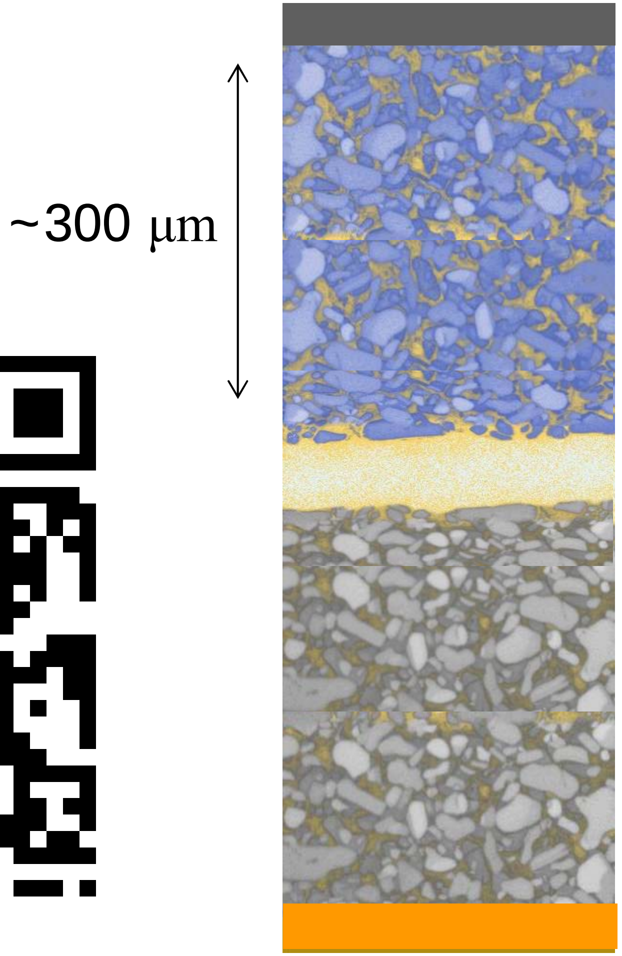
26. Why do you think batteries in practice have relatively thin (~ max 50 μm) electrodes?

a) Difficult to make

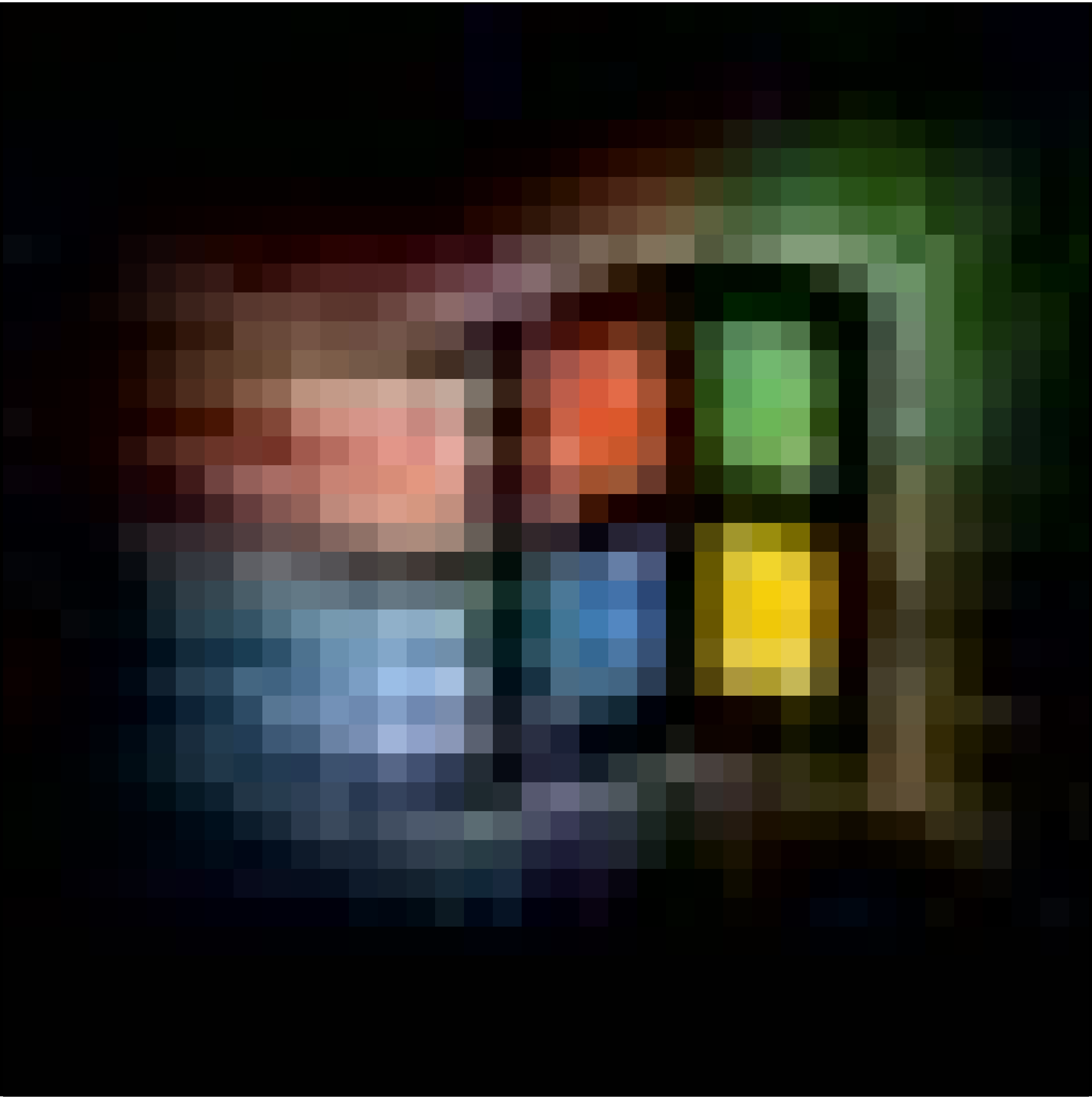
b) Long (dis)charge times

c) Shorter cycle life

d) No clue



http://www.edupinion.nl/c368 Result



Question Energy Density

26 Why do you think batteries have in practice relatively thin electrodes?

a) Difficult to make

b) Long (dis)charge times

c) Shorter cycle life

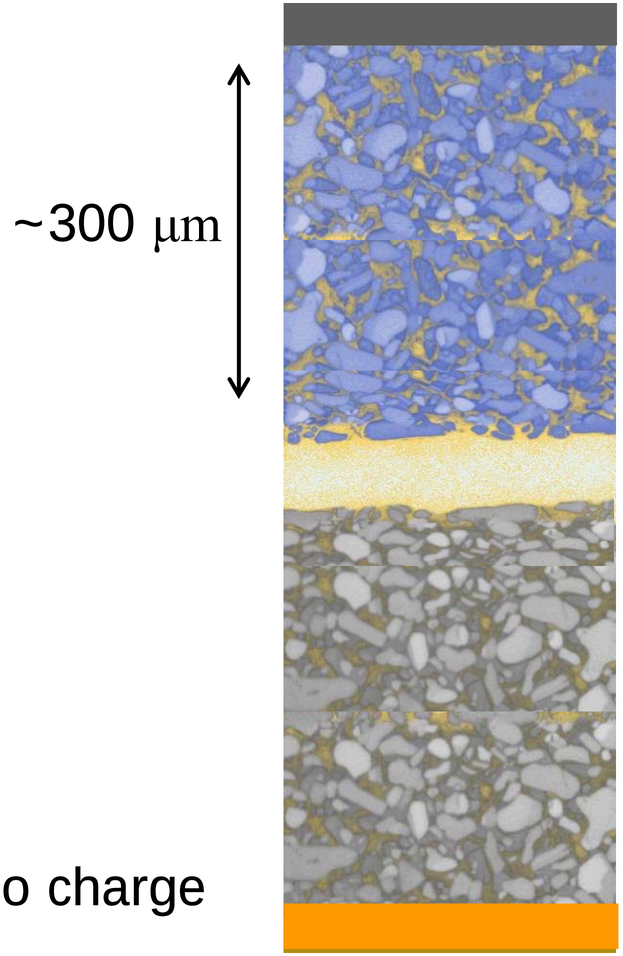
d) No clue

L: diffusion length:
D: diffusion coefficient
t: diffusion time

$$L \approx \sqrt{\pi D t}$$

$$t \approx \frac{L^2}{\pi D}$$

Electrode 6 times thicker => takes 36 times longer to charge



Practical questions

- ✓ ✓ What is the direction of a redox reaction?
- ✓ ✓ What is the voltage that a redox reaction can deliver?
- ✓ ✓ What is the energy density of a battery?
- ✓ ✓ What determines the cycle life of a battery
- What is the power density of a battery? -> kinetics

Program Batteries

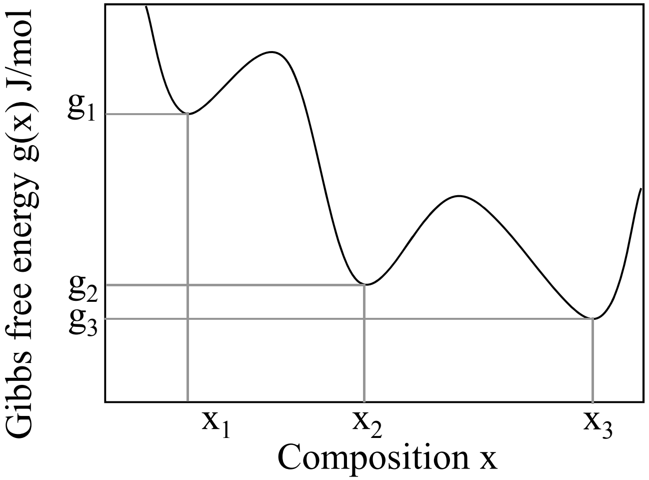
Lecture 1: Feb 27	History, Applications, basic Electrochemistry and thermodynamics of batteries: Redox reactions, Gibbs free energy, chemical potential, Nernst.
Lecture 2: March 6	Solid state electrode reaction mechanisms, phase diagrams, phase rule, Gibbs Free energy, voltage profiles, capacities and 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 systems: Li-air, Li-sulphur Flow-cells Batteries for static storage, NaS, Na aquous. Costs and Performance comparison batteries/systems Material Abundance

Home assignments

Read Chapters 3.1-3.3 Electrochemistry

Read Paper Ceder et al. Science (bb)

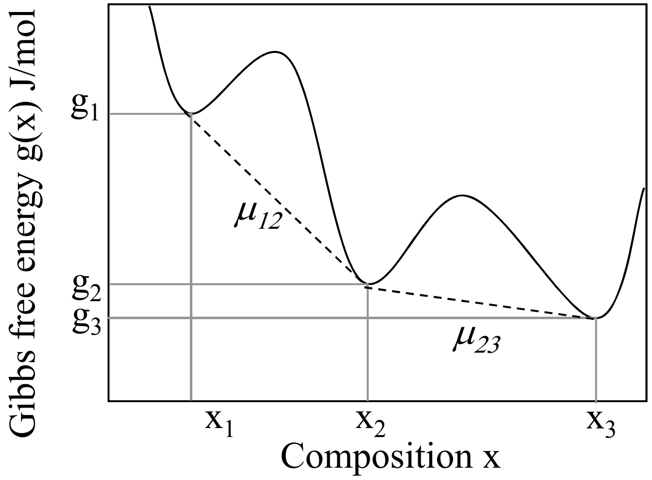
Exercise:



g(x) is the Gibbs Free energy of the cathode during discharge, assume the potential of the anode to be 0 and constant

a) Sketch the voltage profile resulting from the Gibbs Free energy diagram
b) In which direction with this reaction proceed
c) Calculate the voltage of the voltage plateau(‘s) if any.
d) Sketch a phase diagram that could represent this Gibbs Free energy diagram

Home assignment



g(x) is the Gibbs Free energy of the cathode during discharge, assume the potential of the anode to be 0 and constant

a) Sketch the voltage profile resulting from the Gibbs Free energy diagram
b) Which direction will this reaction proceed?
c) Calculate the voltage of the voltage plateau('s) if any.
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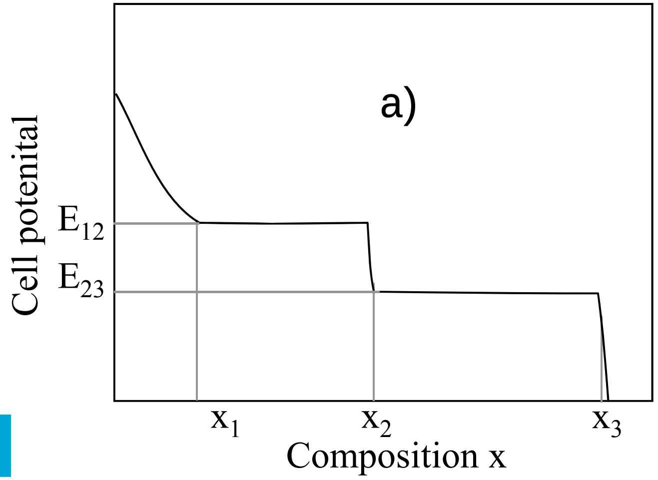

b) In the direction of decreasing Gibbs Free energy: right