

# Hydrogen and Electrical Energy Storage



06 March 2013

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Radiation, Radionuclides and Reactors

# Program Batteries

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

# 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

# From last week...

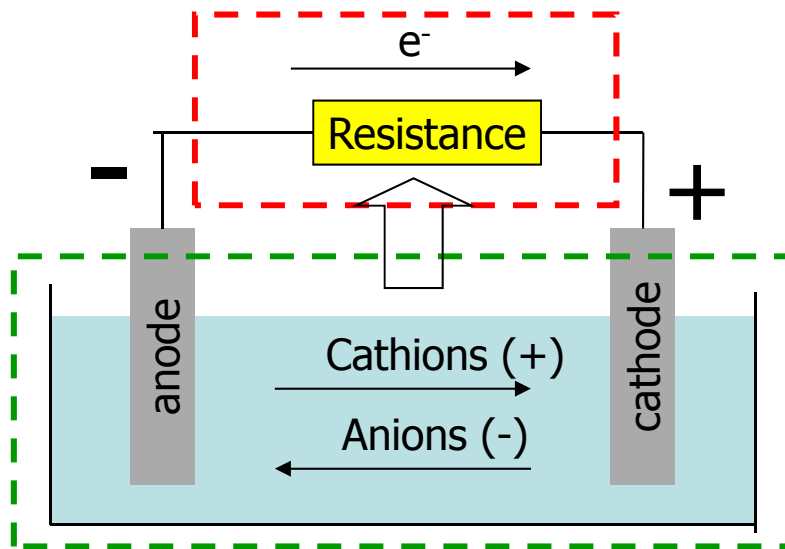
(1) Table of standard reduction potentials

(2) Derivation Gibbs free energy

(3) Homework

# Equilibrium electrochemistry

Think of Battery: we have mass flow in the battery (ions) that cause the charge flow. The mass flow represents chemical work (moving ions) which is converted to electrical work outside the battery.



## During discharge

In the Resistance outside the battery:

$$W_{Elec} = -E_{cell} dQ$$

In the battery:

$$W_{chem} = \sum_j \mu_j dn_j$$

Therefore, besides volume work the battery does chemical work which converted to electrical work outside:

$$W_{Chem} = \sum_j \mu_j dn_j = -E_{cell} dQ = W_{Elec}$$

# Equilibrium electrochemistry

$$E_{Cell} = -\frac{\sum_j \nu_j \mu_j}{zF}$$

Application on Daniel element

Anode (-): oxidation  $Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cathode (+): reduction  $Cu^{2+} + 2e^- \rightarrow Cu(s)$

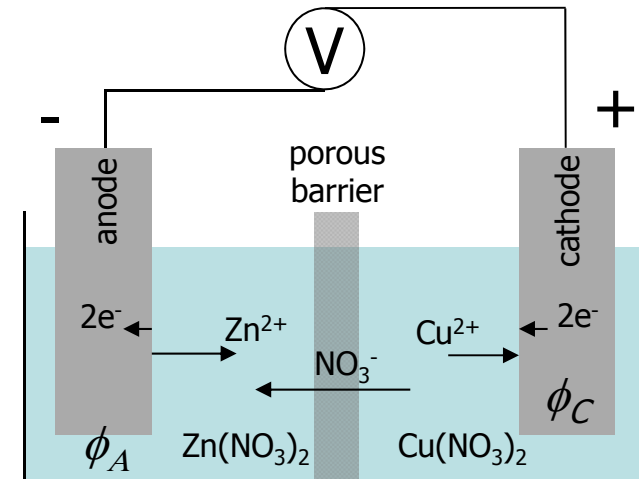
Total:  $Cu^{2+} + Zn(s) \rightarrow Cu(s) + Zn^{2+}$

$$E_{Cell} = (\phi_C - \phi_A) = -\frac{\sum_j \nu_j \mu_j}{zF} = -\frac{(\mu_{Cu} + \mu_{Zn^{2+}} - \mu_{Cu^{2+}} - \mu_{Zn})}{2F}$$

$$E_{Cell} = \frac{(\mu_{Cu^{2+}} - \mu_{Cu})}{2F} - \frac{(\mu_{Zn^{2+}} - \mu_{Zn})}{2F}$$

$$E_{Cell} = \varepsilon_{Cu/Cu^{2+}} - \varepsilon_{Zn/Zn^{2+}} \stackrel{\text{Standard conditions}}{=} \varepsilon_{Cu/Cu^{2+}}^o - \varepsilon_{Zn/Zn^{2+}}^o$$

<sup>o</sup> Standard conditions: concentrations 1 mol/l, p=1 bar, T=20°C



# Electrochemical cells, driving force

Standard reduction potentials are commonly denoted by the symbol  $\varepsilon^\circ$ . (means under standard conditions 293 K and 1 bar, 1 molair concentrations)  $\varepsilon^\circ$  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)	$E^\circ$ , volts
$\text{Na}^+ + e^- \rightarrow$	$\text{Na}(s)$	-2.71
$\text{Zn}^{2+} + 2e^- \rightarrow$	$\text{Zn}(s)$	-0.76
$\text{Fe}^{2+} + 2e^- \rightarrow$	$\text{Fe}(s)$	-0.44
$\text{Cd}^{2+} + 2e^- \rightarrow$	$\text{Cd}(s)$	-0.40
$\text{Pb}^{2+} + 2e^- \rightarrow$	$\text{Pb}(s)$	-0.126
$2 \text{H}^+ + 2e^- \rightarrow$	$\text{H}_2(g)$	0.000
$\text{AgCl}(s) + e^- \rightarrow$	$\text{Ag}(s) + \text{Cl}^-(aq)$	+0.222
$\text{Hg}_2\text{Cl}_2(s) + 2e^- \rightarrow$	$2\text{Cl}^-(aq) + 2\text{Hg}(l)$	+0.268
$\text{Cu}^{2+} + 2e^- \rightarrow$	$\text{Cu}(s)$	+0.337
$\text{I}_2(s) + 2e^- \rightarrow$	$2 \text{I}^-(s)$	+0.535
$\text{Fe}^{3+} + e^- \rightarrow$	$\text{Fe}^{2+}(aq)$	+0.771
$\text{Ag}^+ + e^- \rightarrow$	$\text{Ag}(s)$	+0.799
$\text{O}_2(g) + 4\text{H}^+ + 4e^- \rightarrow$	$2 \text{H}_2\text{O}(l)$	+1.23
$\text{Cl}_2(g) + 2e^- \rightarrow$	$2 \text{Cl}^-(g)$	+1.36

More noble  
More likely to run to the right

What is the potential difference  $\varepsilon$  (Volt,  $V=J/C$ ) build up?

$$\text{Zn}(s) + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}(s), \quad E^\circ_{\text{cell}} = \varepsilon^\circ_{\text{Cu}/\text{Cu}^{2+}} - \varepsilon^\circ_{\text{Zn}/\text{Zn}^{2+}} = 0.337 - (-0.76) = 1.097 \text{ V}$$

# Equilibrium electrochemistry

What is the influence of concentrations (activities) on the electrode potential?

We already found for the potential of a redox reaction:

$$E_{Cell} = -\frac{\sum_j \nu_j \mu_j}{zF}$$

Using  $\mu = \mu^o + RT \ln c$  (derived for ideal gas, dilute solutions) this leads to the Nernst equation:

$$E_{Cell} = E^o - \frac{RT}{zF} \ln \prod c_j^{\nu_j} = E^o - \frac{RT}{zF} \ln(K)$$

Where  $K$  is the equilibrium constant of the redox reaction



# From last week...

(1) Table of standard reduction potentials

(2) Derivation Gibbs free energy

(3) Homework

# Basic thermodynamics

Fundamental equation of reversible thermodynamics (combination laws 0-2 and work):

$$dU = \delta Q + \delta W = TdS + \sum_i Y_i dX_i$$

Relevant for batteries (add pressure volume work and chemical work):

$$dU = TdS - pdV + \sum_i \mu_i dn_i$$

Note: determining  $U$  by integration is not easy because the natural variables of  $U$  are  $S$  and  $V$  which are not easy to control! ( $n$ : number of moles reacted is easy to control)

Change natural (dependent) variables to  $p$  and  $T$  (easy to control and constant during battery operation) by Legendre transformation. Define new state variable Gibbs free energy  $G$ :

$$G = U - TS + pV$$

# Basic thermodynamics

$$dU = TdS - pdV + \sum_i \mu_i dn_i$$

$$G = U - TS + pV$$

$$dG = dU - TdS - SdT + pdV + Vdp$$

$$dG = TdS - pdV + \sum_i \mu_i dn_i - TdS - SdT + pdV + Vdp$$

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

$$dG = Vdp - SdT + \sum_j \mu_j dn_j \quad \text{Constant p and T} = \sum_j \mu_j dn_j$$

$$dG = \delta W_{chem} = \delta W_{elec} = \sum_j \mu_j dn_j = -EdQ$$

Integrate over n moles

$$\Delta G = -E\Delta Q = -znFE(n)$$

$$\Delta G^0 = -zFE^0 \quad \text{Standard conditions, 1 mol, RT, 1bar}$$

# Equilibrium electrochemistry: Relation cell voltage and Gibbs Free energy

$$\delta W_{chem} = dG = \sum_j \mu_j dn_j = -EdQ = \delta W_{elec}$$

$$\Delta G = -E\Delta Q$$

$$\Delta G^0 = -zFE^0 \quad ({}^0 \text{ standard conditions, } p=1 \text{ bar, } T=293 \text{ K, 1 molair concentrations )}$$

Application on Daniel element (standard conditions)



$$\Delta G^0 = -zFE^0 = -2 \cdot 96500 \cdot 1.1 = -212.3 \text{ kJ/mol}$$

$\Delta G < 0$  Reaction occurs spontaneous (battery discharge)

General:  $\Delta G < 0$  :  $E > 0$  : discharge exothermic

$\Delta G > 0$  :  $E < 0$  : charge, endothermic

# From last week...

(1) Table of standard reduction potentials

(2) Derivation Gibbs free energy

(3) Homework

# Home assignments

Read Chapters 1 and 2 Advanced Batteries

Practice Electrochemistry:

Plot the voltage of the daniel element as a function of  $[Zn^{2+}]$  concentration  
Assuming starting concentration  $c_{Zn^{2+}} = 0.1 \text{ mol/l}$  and  $c_{Cu^{2+}} = 1.0 \text{ mol/l}$  (assume  $c_{Zn(s)} = c_{Cu(s)} = 1$ , and the cell volume 0.01 l).

How much chemical energy was converted to electrical energy?

Consider the following redox reaction:  $Cu_{(s)} + Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Ag_{(s)}$   
What is the Gibbs free energy change under standard conditions? (Use standard reduction potentials)

# Equilibrium electrochemistry

Examples of using  $\varepsilon = (\phi_C - \phi_A) = \varepsilon^0 - RT/zF [\ln \prod c_j^{\nu_j}] = \varepsilon^0 - RT/zF \ln(K)$

Example 1: How does the electrode potential of the reaction  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$  depends on the concentration

For  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$  we find:  $c_{\text{Cu}^{2+}}$ ,  $\nu = -1$ ,  $c_{\text{Cu(s)}}$ ,  $\nu = 1$

So:  $K = c_{\text{Cu(s)}} / c_{\text{Cu}^{2+}}$

Hence:  $\varepsilon = \varepsilon^0_{\text{Cu/Cu}^{2+}} - RT/2F [\ln (c_{\text{Cu(s)}}/c_{\text{Cu}^{2+}})] = 0.337 - 0.013 [\ln (c_{\text{Cu(s)}}/c_{\text{Cu}^{2+}})]$

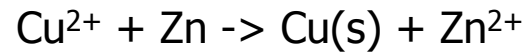
where we used  $R=8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $F=9.65 \cdot 10^4 \text{ C}\cdot\text{mol}^{-1}$

Similar for  $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn(s)}$  :

$\varepsilon = \varepsilon^0_{\text{Zn/Zn}^{2+}} - RT/2F [\ln (c_{\text{Zn(s)}}/c_{\text{Zn}^{2+}})] = -0.76 - 0.013 [\ln (c_{\text{Zn(s)}}/c_{\text{Zn}^{2+}})]$

# Home assignments

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



$$z=2, \nu_{\text{Cu}^{2+}}=-1, \nu_{\text{Zn}}=-1, \nu_{\text{Cu}}=1, \nu_{\text{Zn}^{2+}}=1$$

$$R=8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}, F=9.65 \cdot 10^4 \text{ C}\cdot\text{mol}^{-1}, T=293 \text{ K}$$

$$E^0 = \varepsilon^0_{\text{Cu/Cu}^{2+}} - \varepsilon^0_{\text{Zn/Zn}^{2+}} = 0.337 - (-0.76) = 1.097$$

$$E_{\text{Cell}} = 1.097 - 0.013 \ln \frac{c_{\text{Cu(s)}} c_{\text{Zn}^{2+}}}{c_{\text{Zn(s)}} c_{\text{Cu}^{2+}}} = 1.097 - 0.013 \ln \frac{c_{\text{Zn}^{2+}}}{c_{\text{Cu}^{2+}}}$$



# Home assignments

Plot the voltage of the daniel element as a function of  $[Zn^{2+}]$  concentration  
 Assuming starting concentration  $c_{Zn^{2+}} = 0.1 \text{ mol/l}$  and  $c_{Cu^{2+}} = 1.0 \text{ mol/l}$  (assume  $c_{Zn(s)} = c_{Cu(s)} = 1$ , and the cell volume  $0.01 \text{ l}$ ).

$$E_{Cell}^{Start} = 1.097 - 0.013 \ln \frac{c_{Zn^{2+}}}{c_{Cu^{2+}}} = 1.097 - 0.013 \ln 0.1 = 1.127$$

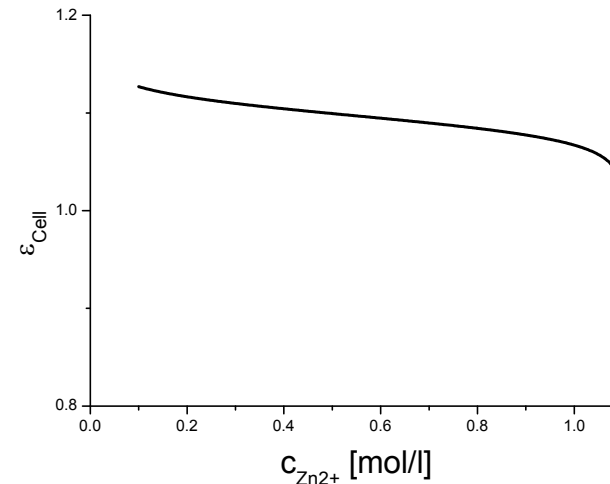
$$c_{Cu^{2+}} = 1.1 - c_{Zn^{2+}} \quad [0.1 \leq c_{Zn^{2+}} \leq 1.1]$$

$$E_{Cell}^{Start} = 1.097 - 0.013 \ln \frac{c_{Zn^{2+}}}{1.1 - c_{Zn^{2+}}}$$

$$dG = -\varepsilon_{Cell} dQ$$

$$dQ = zFVdc_{Zn^{2+}}$$

$$\Delta G = -zFV \int_{0.1}^{1.0} \varepsilon_{Cell} dc_{Zn^{2+}} \approx -2 \times 96500 \times 0.01 \times 1.1 \times 1 \left[ \frac{\text{C} \cdot \text{l} \cdot \text{V} \cdot \text{mol}}{\text{mol} \cdot \text{l}} \right] \approx -2 \text{ kJ}$$



# Home assignments

Consider the following redox reaction:  $\text{Cu}_{(s)} + \text{Ag}^+_{(aq)} \rightarrow \text{Cu}^{2+}_{(aq)} + \text{Ag}_{(s)}$   
What is the Gibbs free energy change under standard conditions? (Use standard reduction potentials)

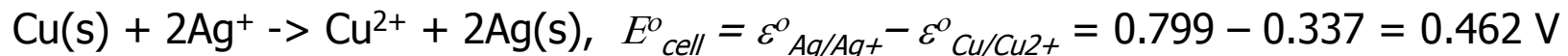
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$\text{Cd}^{2+} + 2e^- \rightarrow$	$\text{Cd}(s)$	-.40
$\text{Pb}^{2+} + 2e^- \rightarrow$	$\text{Pb}(s)$	-.126
$2 \text{H}^+ + 2e^- \rightarrow$	$\text{H}_2(g)$	<b>0.000</b>
$\text{AgCl}(s) + e^- \rightarrow$	$\text{Ag}(s) + \text{Cl}^-(aq)$	+ .222
$\text{Hg}_2\text{Cl}_2(s) + 2e^- \rightarrow$	$2\text{Cl}^-(aq) + 2\text{Hg}(l)$	+ .268
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$\text{Cl}_2(g) + 2e^- \rightarrow$	$2 \text{Cl}^-(g)$	+ 1.36

More noble  
More likely to run to the right



$$\Delta G^\circ = -zFE^\circ = -2 \cdot 96500 \cdot 0.462 = -89.2 \text{ kJ/mol}$$

# Program Batteries

- Lecture 1: History, Applications, basic Electrochemistry and thermodynamics of batteries: Redox reactions, Gibbs free energy, chemical potential, Nernst.  
Feb 27
- Lecture 2: Solid state electrode reaction mechanisms, phase diagrams, phase rule, Gibbs Free energy, voltage profiles, capacities and energy densities. Li-ion batteries  
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# Overview

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

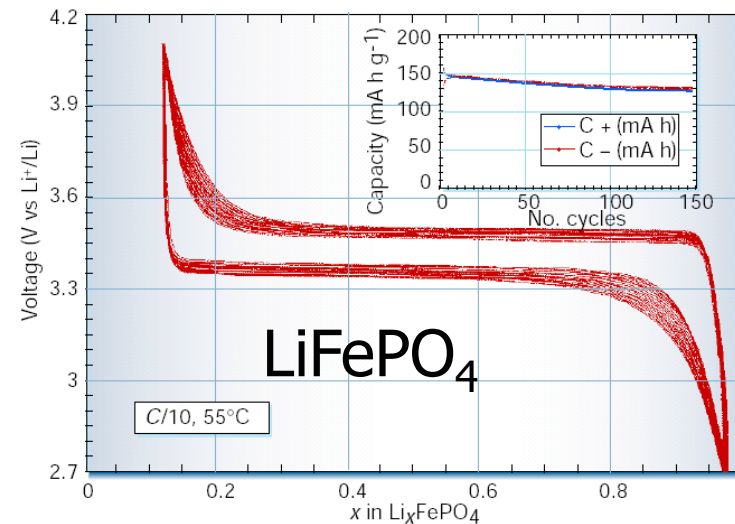
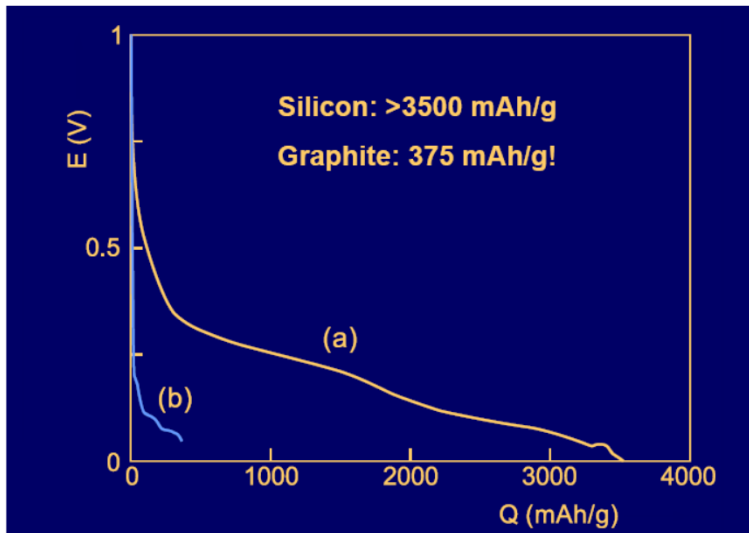
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Review Goodenough et al. Chemistry of Materials and lecture sheets

Lecture 4: Electrochemistry 3.1-3.3, Lecture sheets

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

# Modern batteries: Solid state reaction mechanisms in batteries

- Electrolyte concentrations of charge carrying ions does not change
- => Nernst is useless determining the voltage
- => Structural and morphological changes in the electrodes



# Solid state reaction mechanisms in batteries

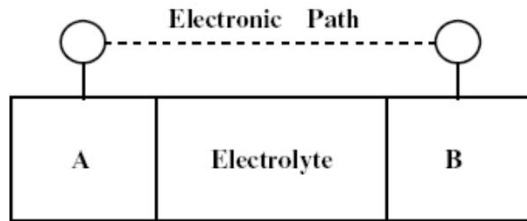
Reconstitution reactions:      Formation reactions:       $A+B = AB$   
Displacement reactions:       $A+BX = AX + B$

Insertion reactions:       $xA + BX = A_xBX$

Apply to Li-ion batteries:

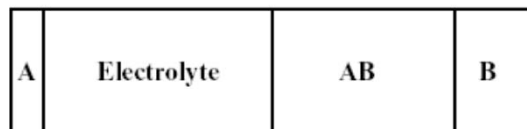
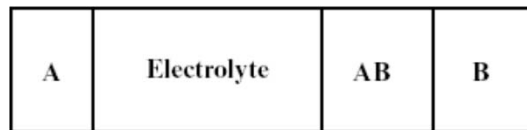
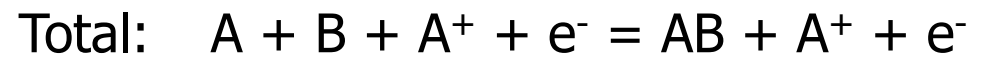
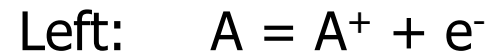
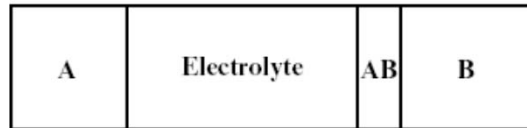
- (1) Morphology change/phase diagrams
- (2) Relation morphology and voltage shape
- (3) Capacity and Energy density

# Solid state reactions



$$\Delta G_f^0 < 0$$

Requires A and B diffusion through AB





## Question electrochemistry 4

Left:  $A = A^+ + e^-$

Right:  $B + A^+ + e^- = AB$

13. What is the anode and what reaction occurs at the anode?

- (a) Right, oxidation
- (b) Right, reduction
- (c) Left, oxidation
- (d) Left, reduction
- (e) no clue



<http://www.edupinion.nl/c954>



## Question electrochemistry 4

13. What is the anode and what reaction occurs at the anode?

Left:  $A = A^+ + e^-$  => oxidation/anode c)  
Right:  $B + A^+ + e^- = AB$

# Reconstitution-formation reactions

$$A + B = AB$$

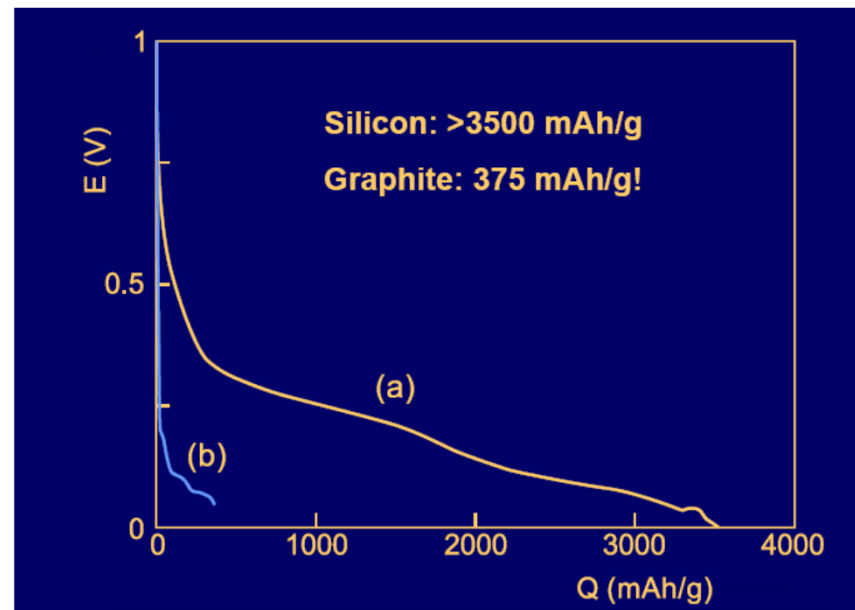
# Reconstitution-formation: Example Si

Discharge

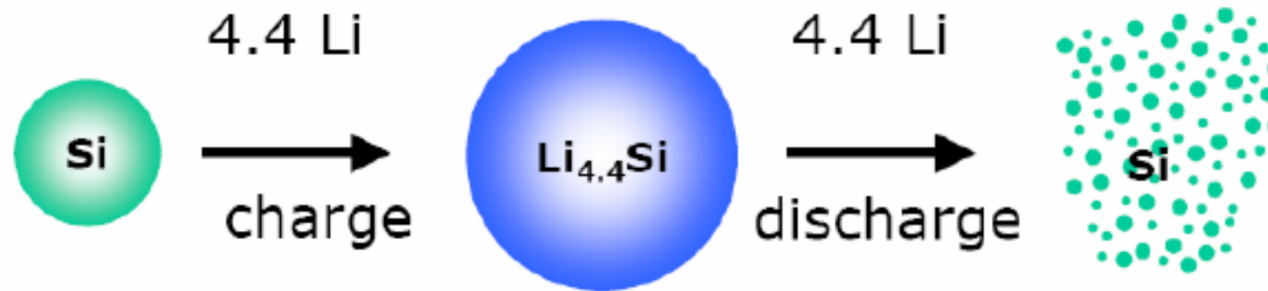
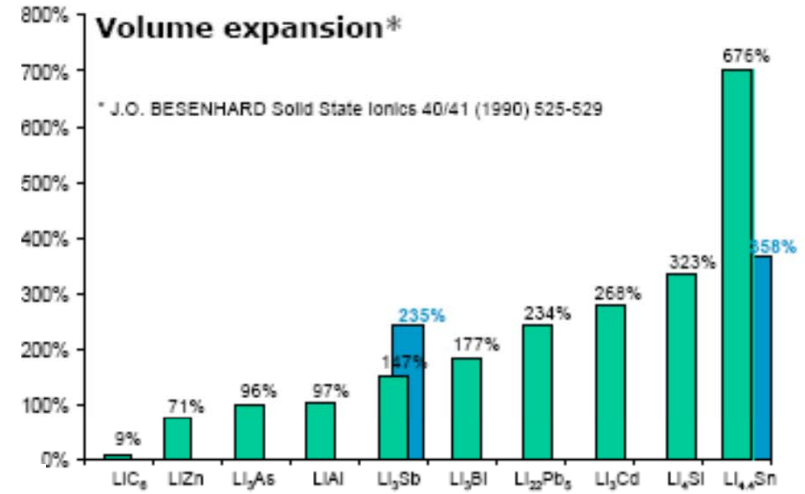
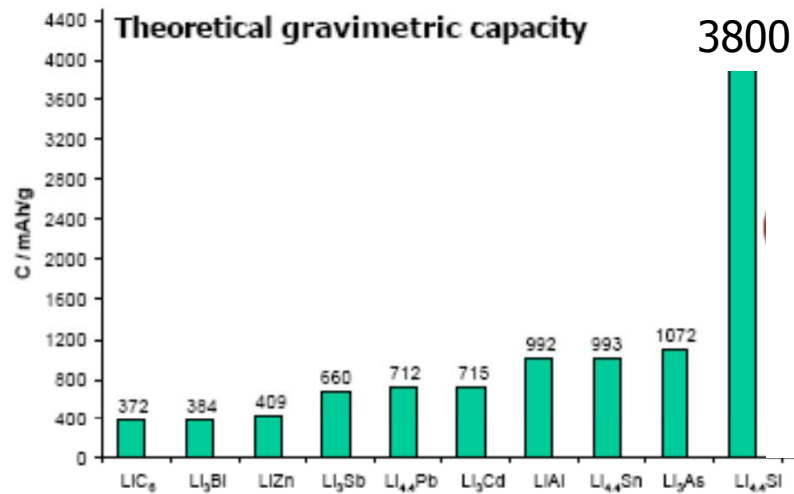
$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$  (oxidation/anode)

$\text{Si} + 4.4\text{Li}^+ + 4.4\text{e}^- \rightarrow \text{Li}_{4.4}\text{Si}$  (reduction/cathode)

Total  $\text{Si} + 4.4\text{Li} \rightarrow \text{Li}_{4.4}\text{Si}$

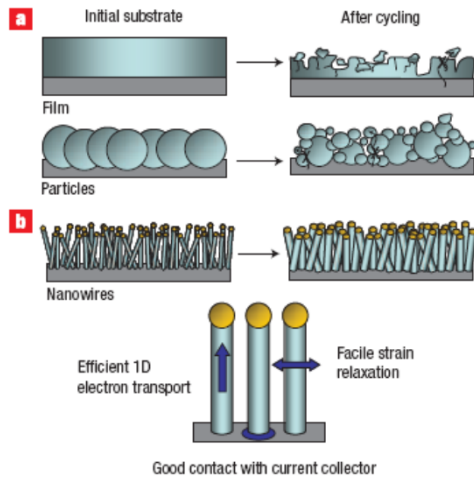


# Reconstitution-formation: Example Si

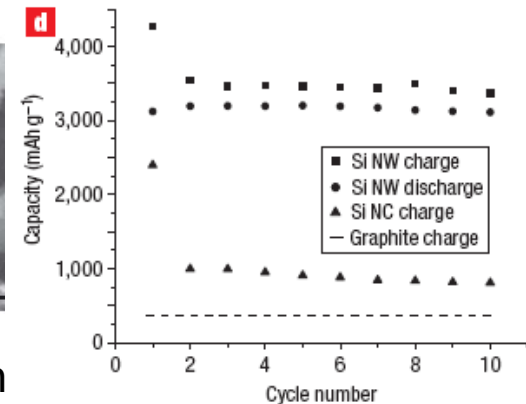
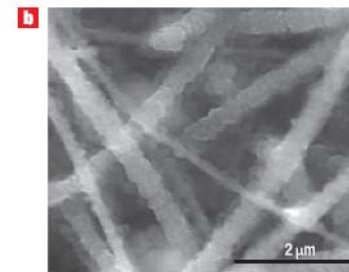
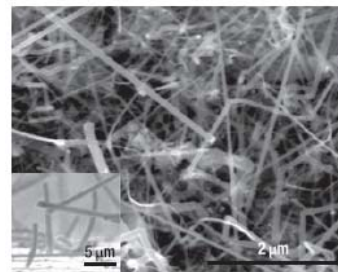


# Intermezzo: Strategies Alloy anode

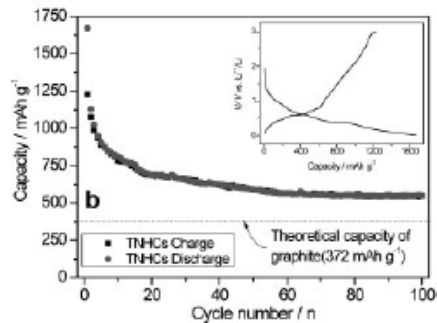
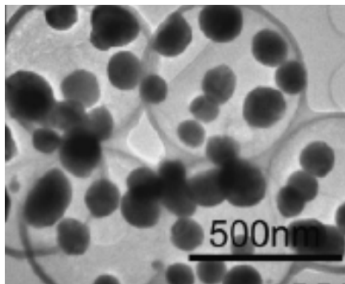
## (1) Nano Si wires



- Space for  $\text{Li}_{4.4}\text{Si}$  volume expansion
- Only 10 cycles reported



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



- Space for  $\text{Li}_{4.4}\text{Sn}$  volume expansion
- No loss of contact due to confinement in Carbon sphere

# Reconstitution-formation reactions

General characteristics:

Host structure is radically changed due to alloying reaction, huge volume changes, short cycle life

Relatively large amount of Li per host atom, relatively high specific capacities (high energy density)

Usually metals (Si, Sb, ...) good electronic conductivity (next lectures)



# Reconstitution-displacement reactions

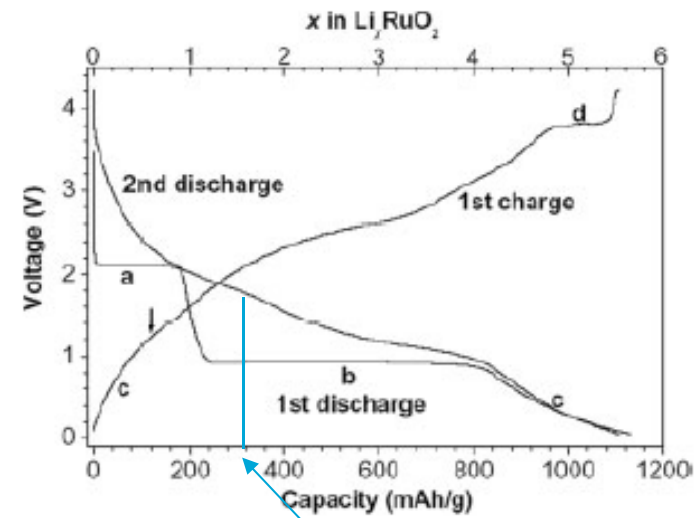
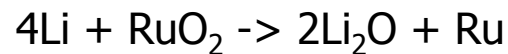


# Reconstitution-displacement reactions: Example: RuO<sub>2</sub>

- (a)  $\text{Li}^+ + \text{e}^- + \text{RuO}_2 \rightarrow \text{LiRuO}_2$  (Li-insertion, see later)
- (b)  $3\text{Li}^+ + 3\text{e}^- + \text{LiRuO}_2 \rightarrow 2\text{Li}_2\text{O} + \text{Ru}$  (reconstitution-displacement)
- (c1)  $\text{Li}^+ + \text{e}^- + \text{electrolyte} \rightarrow \text{SEI}(\text{Li})$  (supercapacitive behavior, later)

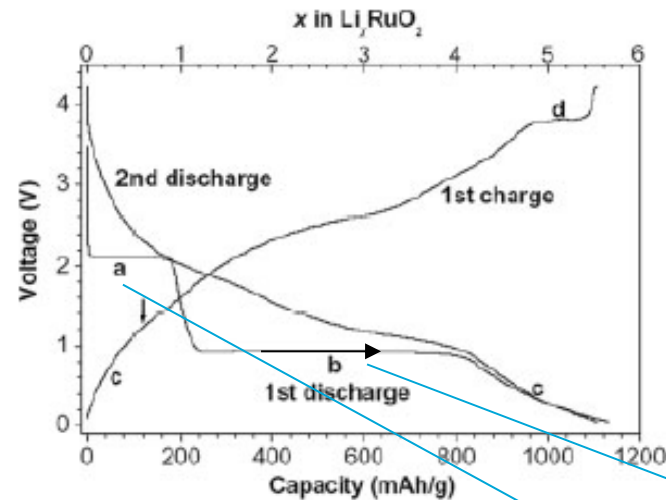
Host material decomposes in Li<sub>2</sub>O and metal

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



Capacity of graphite

# Reconstitution-displacement reactions: Example: RuO<sub>2</sub>

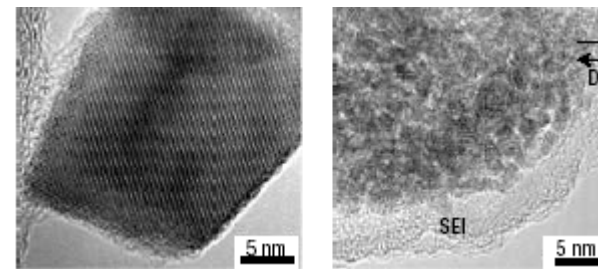


Host transforms in new compound  
 ⇒ Extra capacity  
 ⇒ Huge structural changes (after first cycle it remains nano-structured)  
 ⇒ Only reversible because of nano distances Ru-O in Li<sub>2</sub>O/Ru mixture

Nano structured RuO<sub>2</sub>



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



# Reconstitution-displacement reactions

General characteristics:

Host structure is radically changed due to alloying reaction, huge volume changes, segregation metal and  $\text{Li}_2\text{O}$  short cycle life

Relatively large amount of Li per host atom, relatively high specific capacities (high energy density)

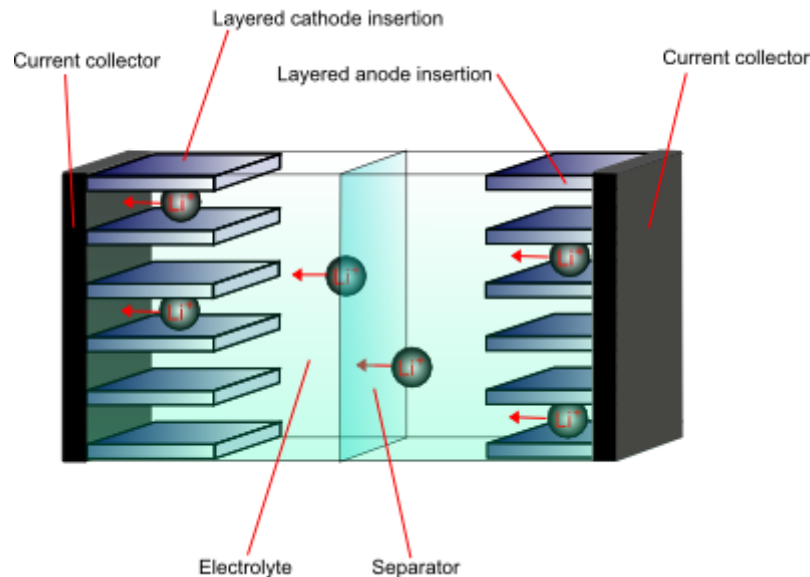
Good electronic conductivity metal, but poor electronic and ionic mobility  $\text{Li}_2\text{O}$ . To make this reversible requires very short Metal- $\text{Li}_2\text{O}$  distances

# Insertion reactions



# Insertion reactions

Anode and Cathode are intercalation compounds  
(rocking chair system):



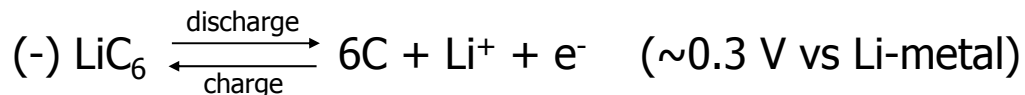
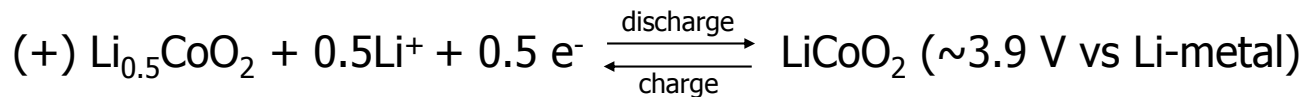
Li-ions intercalate into a host material

Usually host is crystalline transition metal oxide/phosphate/silicate

Transition metal provides redox couple

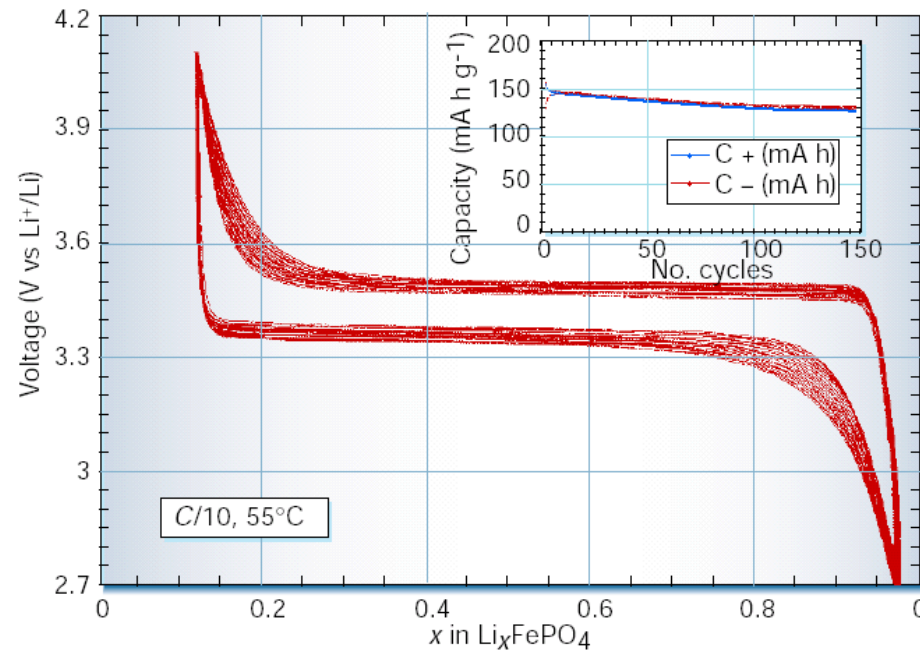
Requirements host material:

- Ionic and electronic conductor
- Large specific Li-ion capacity
- High voltage difference
- Stable
- Cheap
- Abundant
- Non-toxic



~ 3.6 V battery. This is ~3 times higher than that of NiCd and NiMH (-> high energy density)

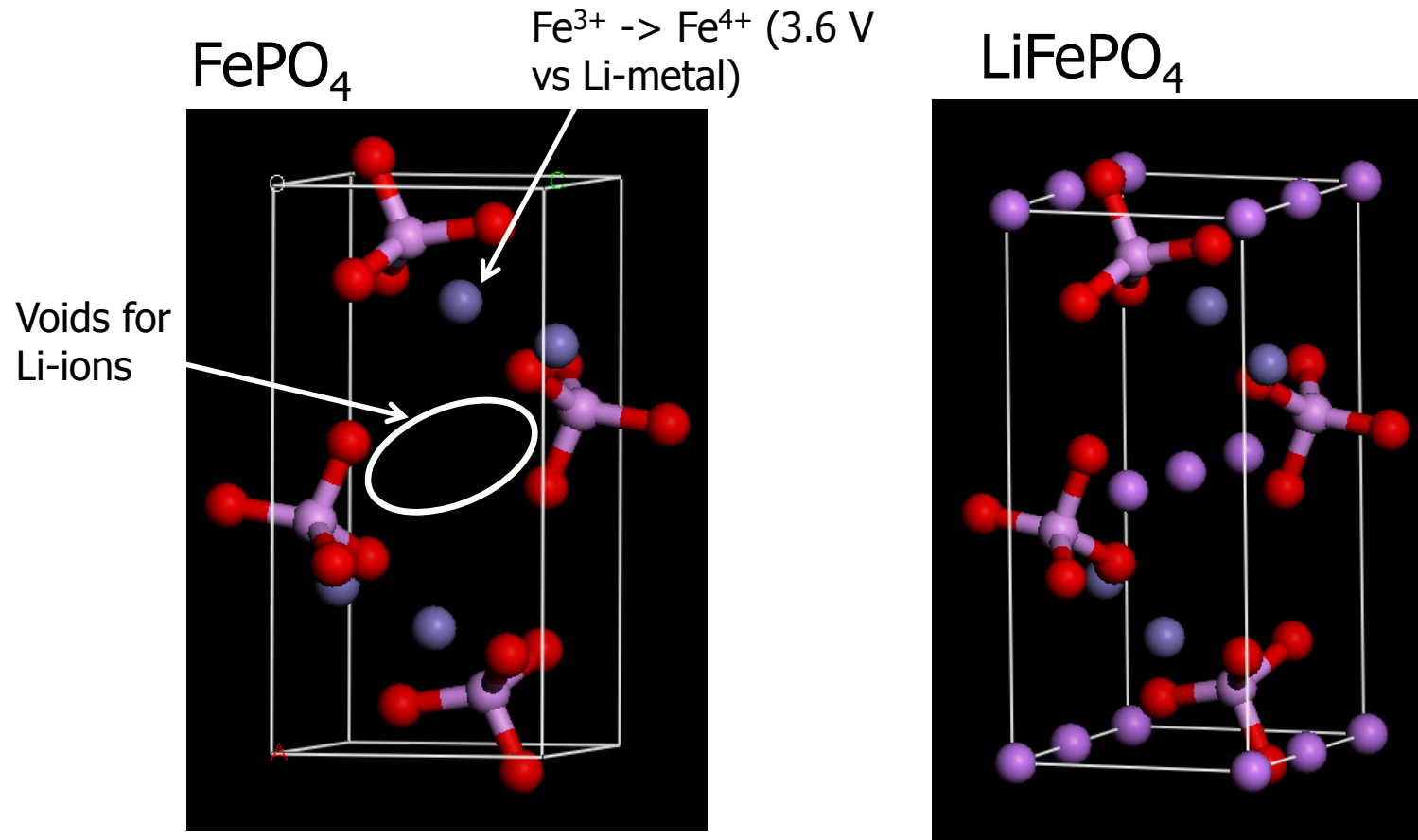
# Insertion Reaction Example: $\text{LiFePO}_4$



$\text{LiFePO}_4$  current alternative for  $\text{LiCoO}_2$

- o Very stable (high cycleability, safe)
- o Cheap, abundant and environmentally friendly
- o High Voltage, but less than  $\text{LiCoO}_2$  (3.6 versus Li-metal)
- o Reasonable capacity
- o Constant voltage

# “Host reaction” Example: $\text{LiFePO}_4$



Volume change:  $\sim 5\%$



# Insertion Reactions

General characteristics:

Host structure provides framework, if volume change is small, long cycle life

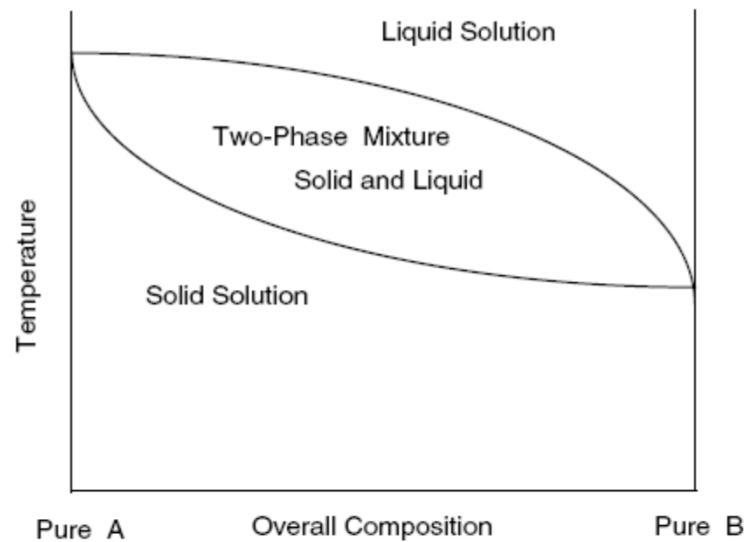
Host structure is extra weight to carry, relatively low specific capacities (low energy density)

Metals have no voids, insertion hosts are usually semi conductors, poor electronic conductivity (next lectures)

# Phase Diagrams

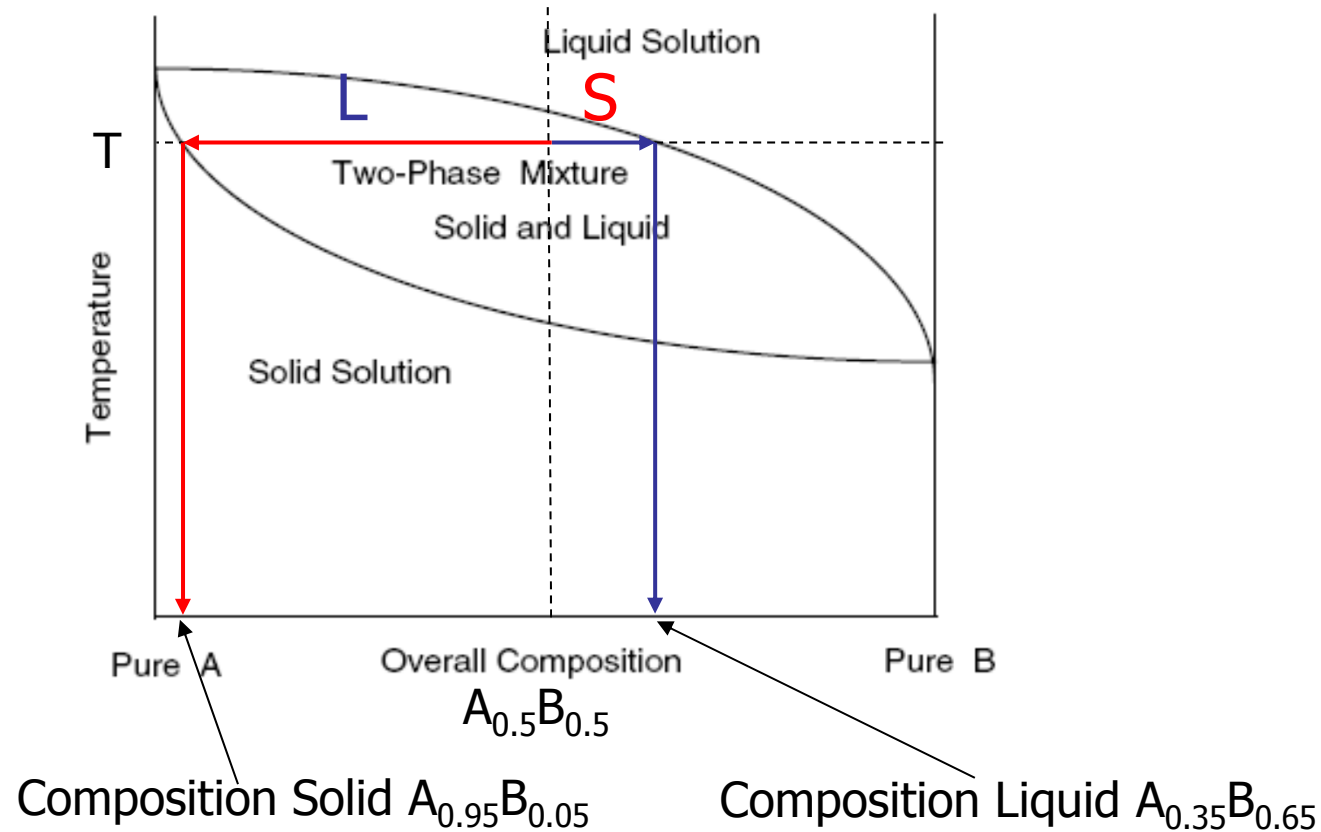
What are they, how they work

# Binary Phase Diagrams



- The components A and B are completely miscible
- A and B have a different melting point

# Binary Phase Diagrams, lever rule



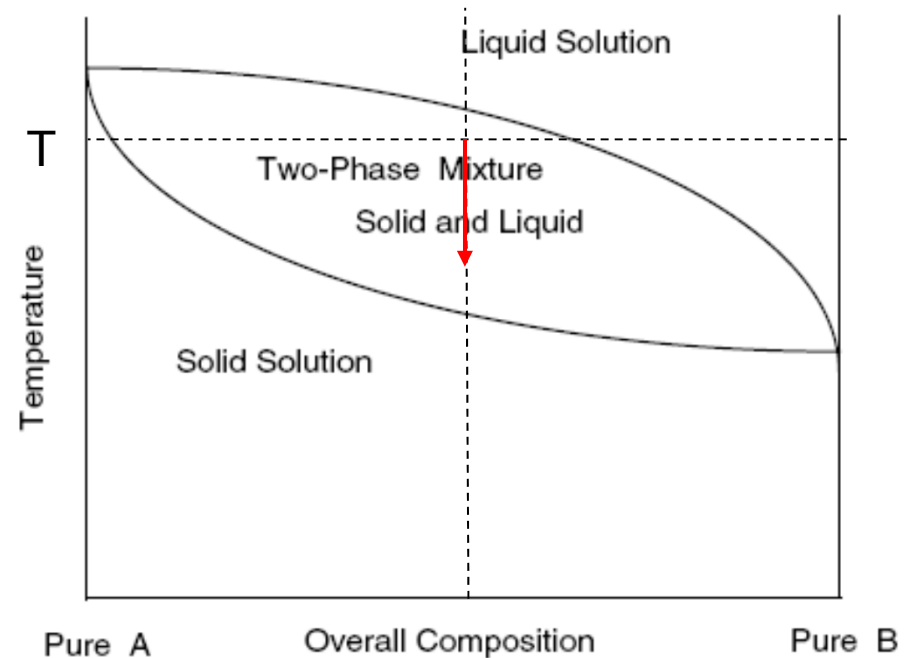
Phase fraction **Liquid**:  $F_L = L/(L+S) \sim 0.75$ , Phase fraction **Solid**:  $F_S = S/(S+L) \sim 0.25$

Back calculation overall composition:  $A_xB_{1-x}$  with  $x = 0.95x_{F_S} + 0.35x_{F_L} = 0.5$

# Question Phase Diagram 1

14. Suppose we cool down what will happen:

- a) nothing
- b) contents A of liquid phase will decrease
- c) contents B of liquid phase will decrease
- d) no clue

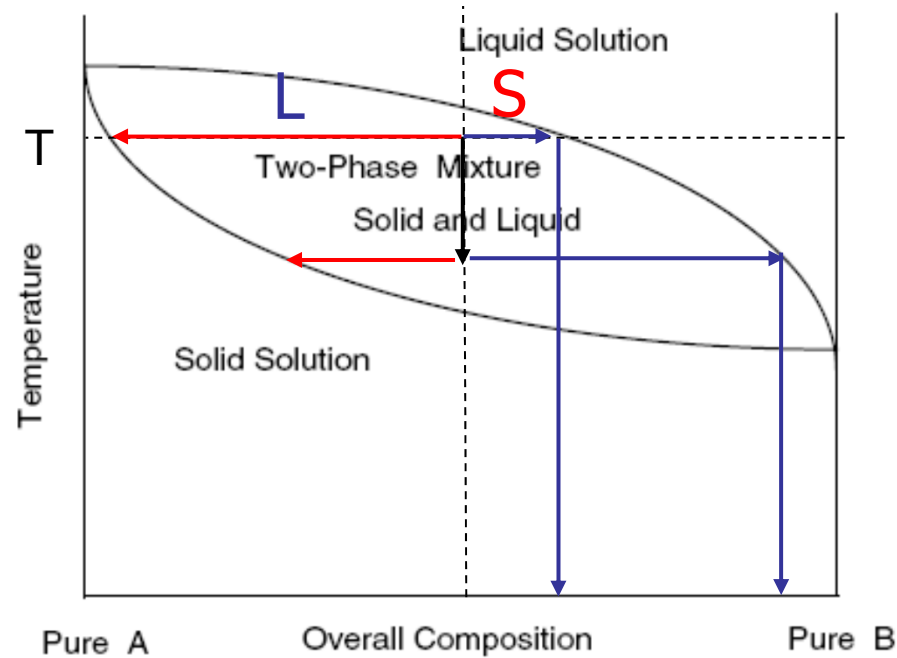


<http://www.edupinion.nl/c474>

Result



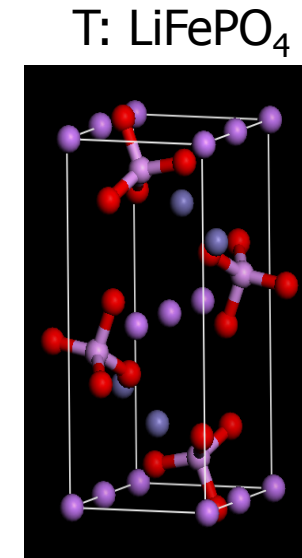
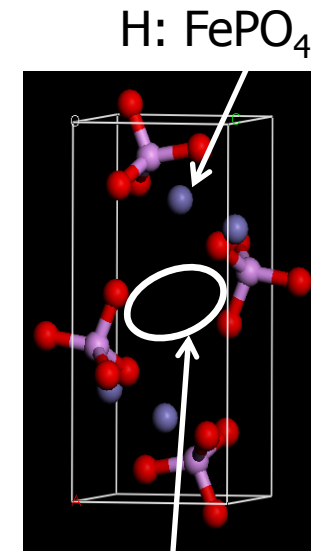
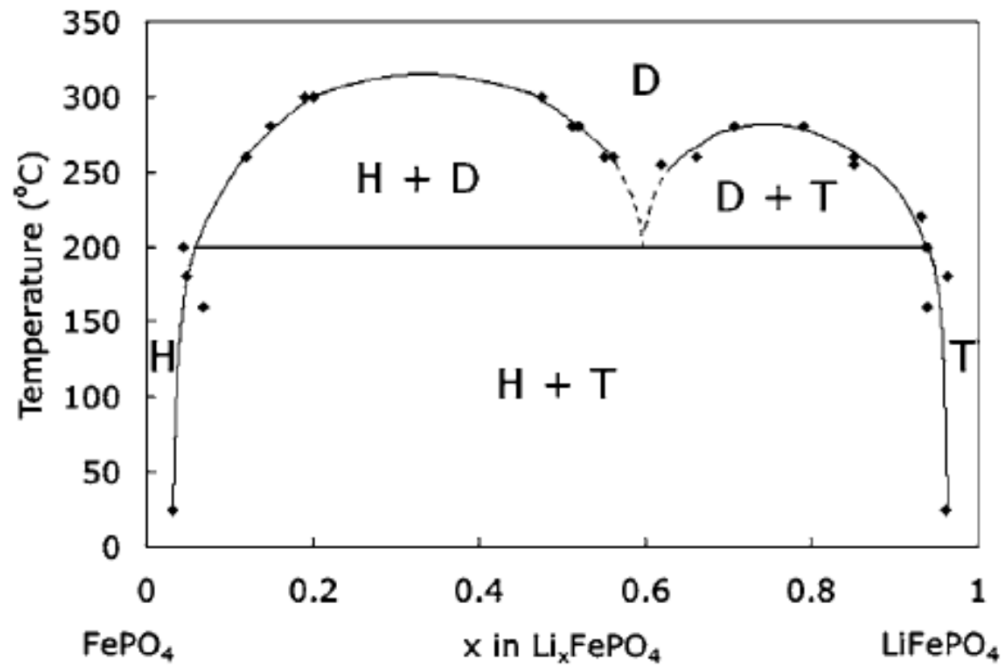
# Question Phase Diagram 1



14. Suppose we cool down what will happen =>

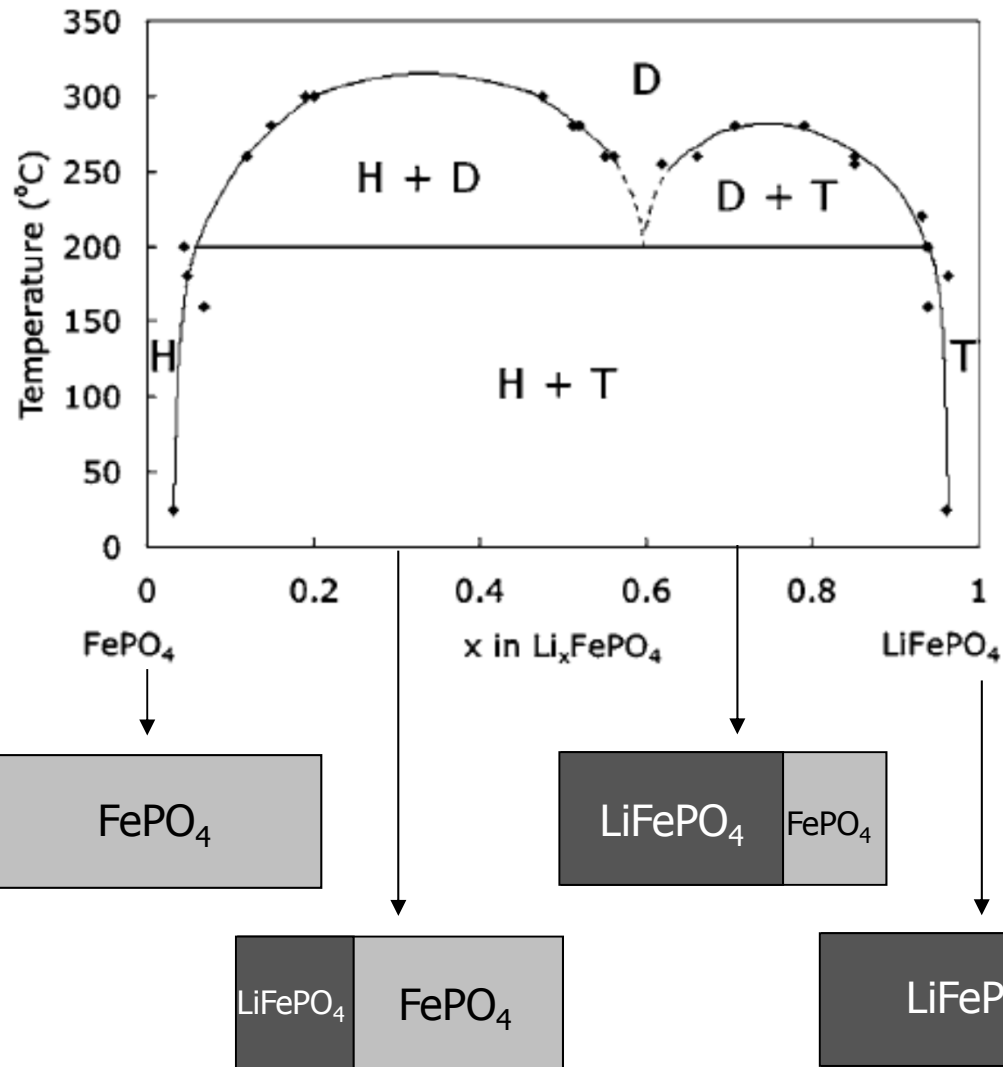
In liquid phase B increases so A decreases (also in the solid phase!) => b)

# Example Insertion Phase diagram: $\text{LiFePO}_4$



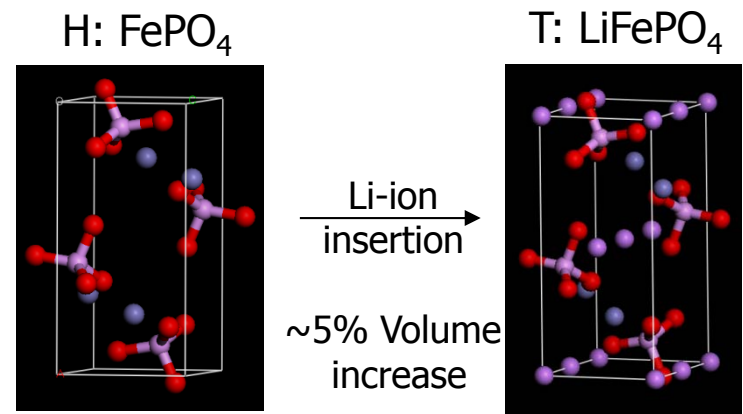
Voids for Li-ions



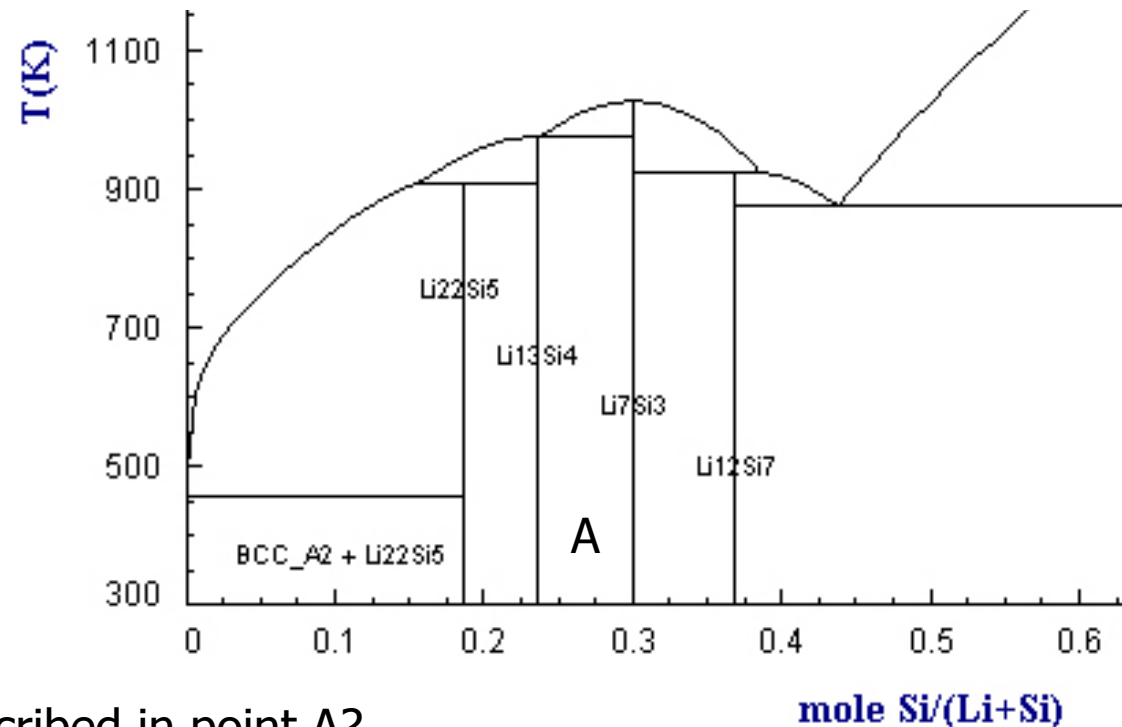
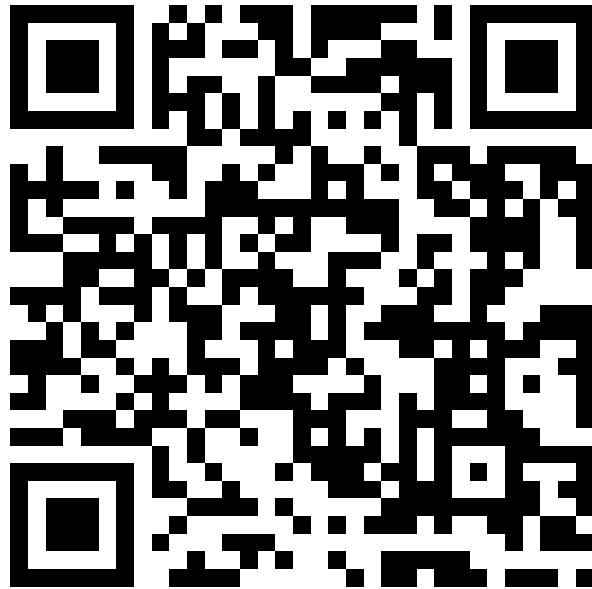


This is a Phase Transition

The two phases coexist



## Question phase diagram 2



15. How is the material best described in point A?

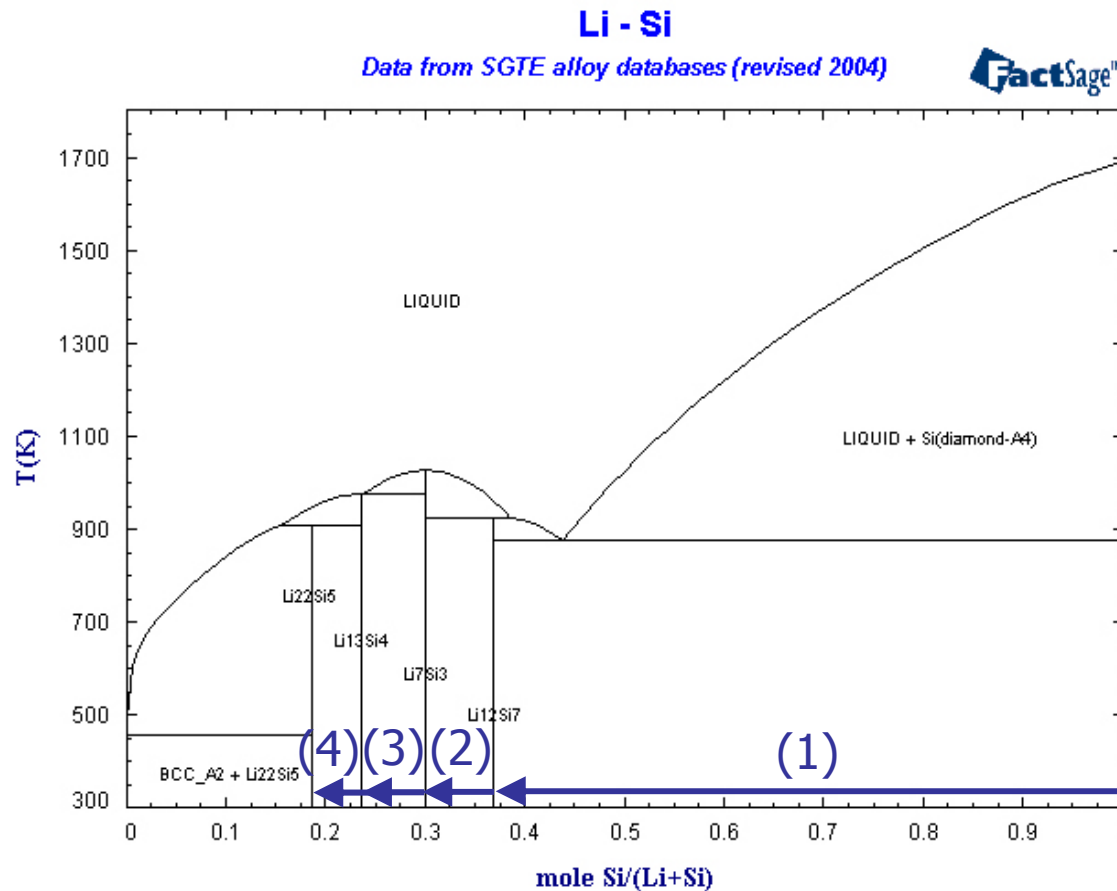
- a) homogeneous composition with  $\text{Si}/(\text{Li}+\text{Si})$  between 0.24 and 0.3
- b) constant composition  $\text{Li}_7\text{Si}_3$
- c) coexisting  $\text{Li}_7\text{Si}_3$  and  $\text{Li}_{13}\text{Si}_{14}$
- d) no clue

<http://www.edupinion.nl/c269>

Result



# Example Reconstitution-formation phase diagram: Li-Si



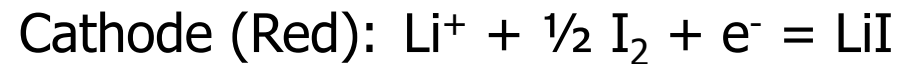
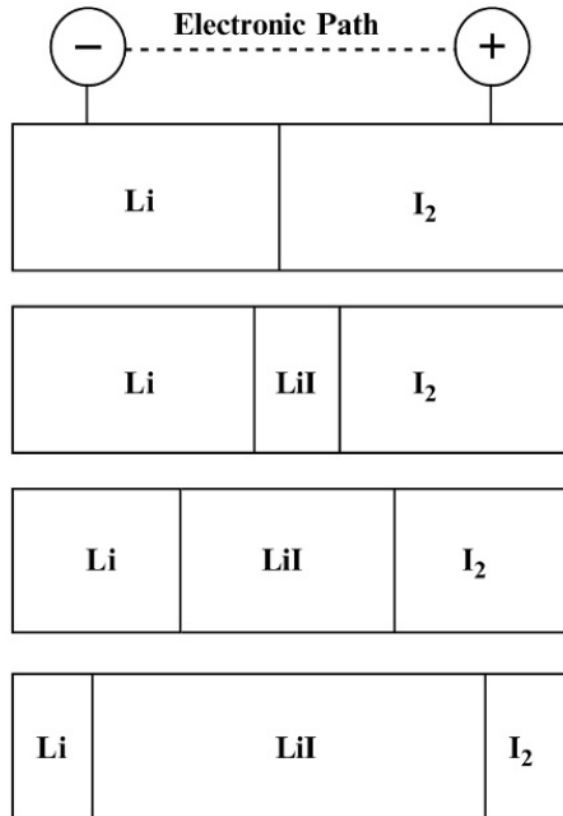
- (1)  $7\text{Si} + 12\text{Li} = \text{Li}_{12}\text{Si}_7$
- (2)  $\text{Li}_{12}\text{Si}_7 + 13/3\text{Li} = \text{Li}_7\text{Si}_3$
- (3)  $\text{Li}_7\text{Si}_3 + 11/4\text{Li} = \text{Li}_{13}\text{Si}_4$
- (4)  $\text{Li}_{13}\text{Si}_4 + 23/5\text{Li} = \text{Li}_{22}\text{Si}_5$

Total:  $\text{Si} + 4.4\text{Li} = \text{Li}_{4.4}\text{Si}$

# Relation Voltage Profile with Phase Diagram

Gibbs phase rule

# Example, the Lithium Iodine Cell



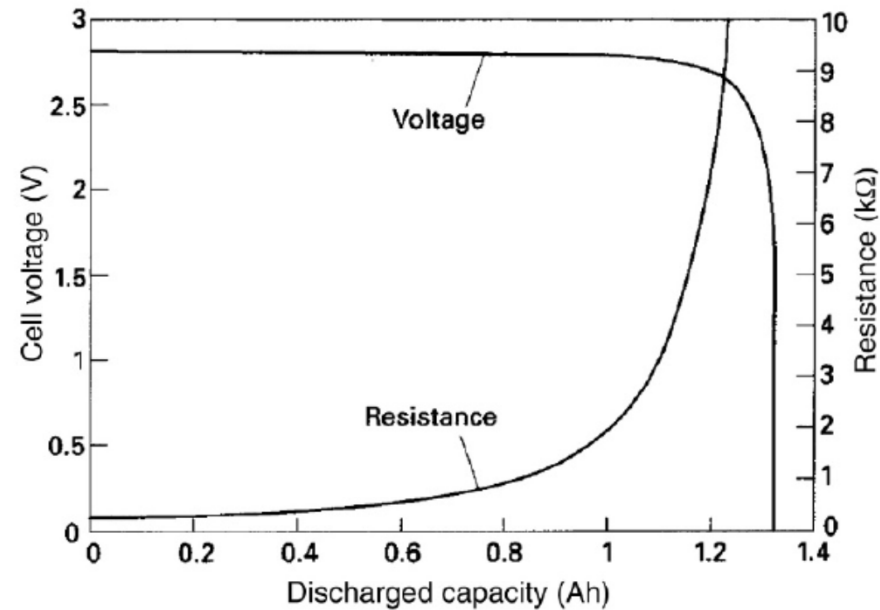
Note LiI is the electrolyte!

$$E_{\text{Cell}} = -\Delta G_r / zF$$

$$\Delta G_r = \Delta G_f(\text{LiI}) = -269.7 \text{ kJ/mol at } 25^\circ\text{C}$$

$$E_{\text{Cell}} = 2.8 \text{ V}$$

# Example, the Lithium Iodine Cell



Why is the voltage constant?

# 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 that must be specified to define the system.



## Question Thermodynamics 3

16. Examples of Intensive thermodynamic parameters are:

- (a)  $G, \mu$
- (b)  $G, S, U$
- (c)  $T, p, \mu$
- (d) no clue



<http://www.edupinion.nl/c573>

Result



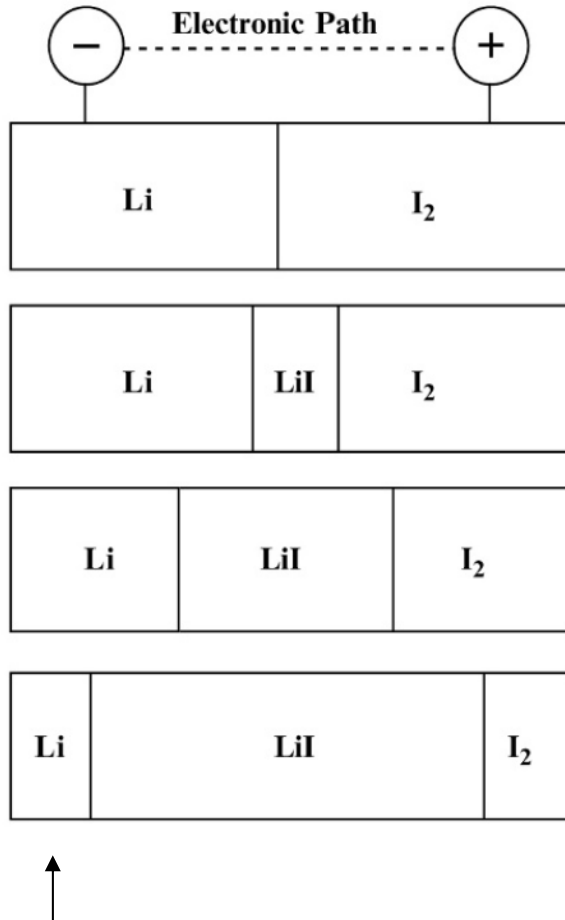
# Question Thermodynamics 3

16. Examples of Intensive thermodynamic parameters are:

- (a)  $G, \mu$
- (b)  $G, S, U$
- (c)  $T, p, \mu$
- (d) No clue

Intensive variables do not scale with the system => c)

# Example, the Lithium Iodine Cell



$$F = C - P + 2$$

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

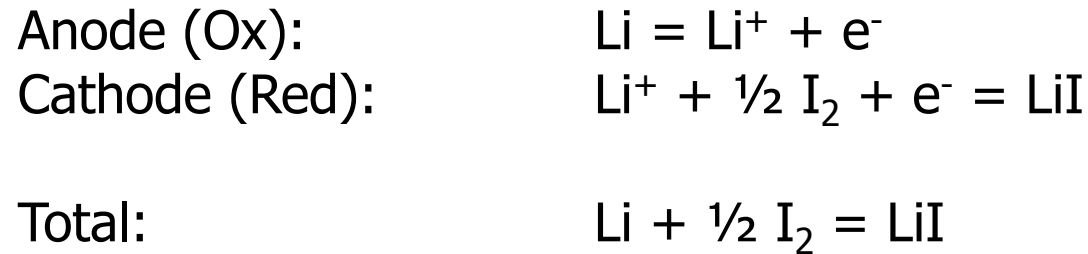
LiI becomes the electrolyte

Li-metal, negative electrode:  $C = 1, P = 1 \Rightarrow F=2$

I<sub>2</sub>, positive electrode:  $C = 1, P = 1 \Rightarrow F=2$

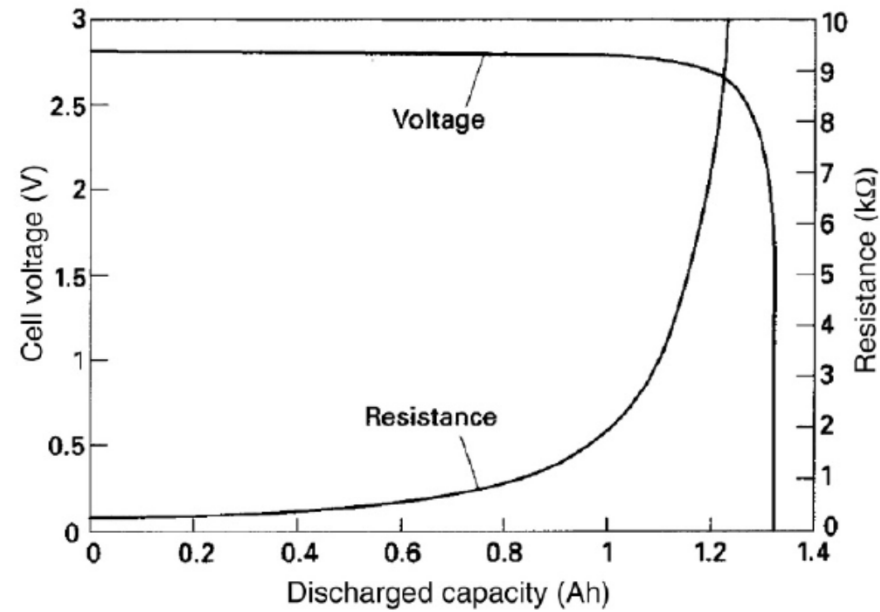
If  $p, T$  are specified, the chemical potential is defined (fixed)

# Example, the Lithium Iodine Cell



$$E_{\text{Cell}} = (\phi_C - \phi_A) = -\frac{\sum_j \nu_j \mu_j}{zF} = -\frac{\left( \mu_{\text{Li}^+} + \frac{1}{2} \mu_{\text{I}_2} - \mu_{\text{Li}} - \frac{1}{2} \mu_{\text{I}_2} \right)}{F}$$
$$E_{\text{Cell}} = \frac{(\mu_{\text{I}_2} - \mu_{\text{I}_2})}{2F} - \frac{(\mu_{\text{Li}^+} - \mu_{\text{Li}})}{F} = \text{constant}$$

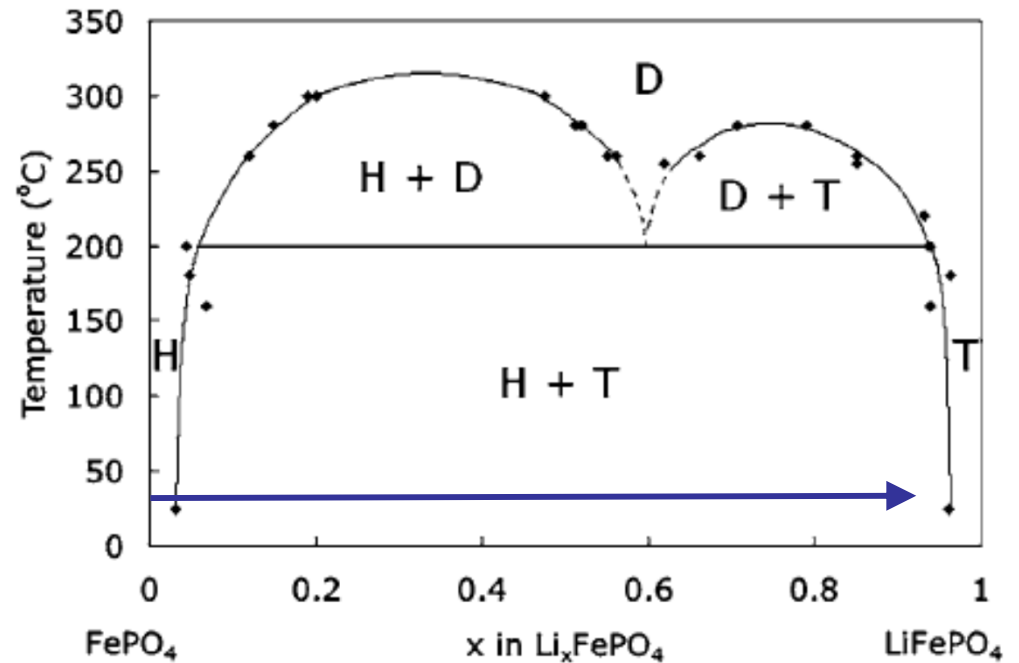
# Example, the Lithium Iodine Cell



# Question Gibbs Phase Rule 1

17. How many relevant components are present in this phase diagram?

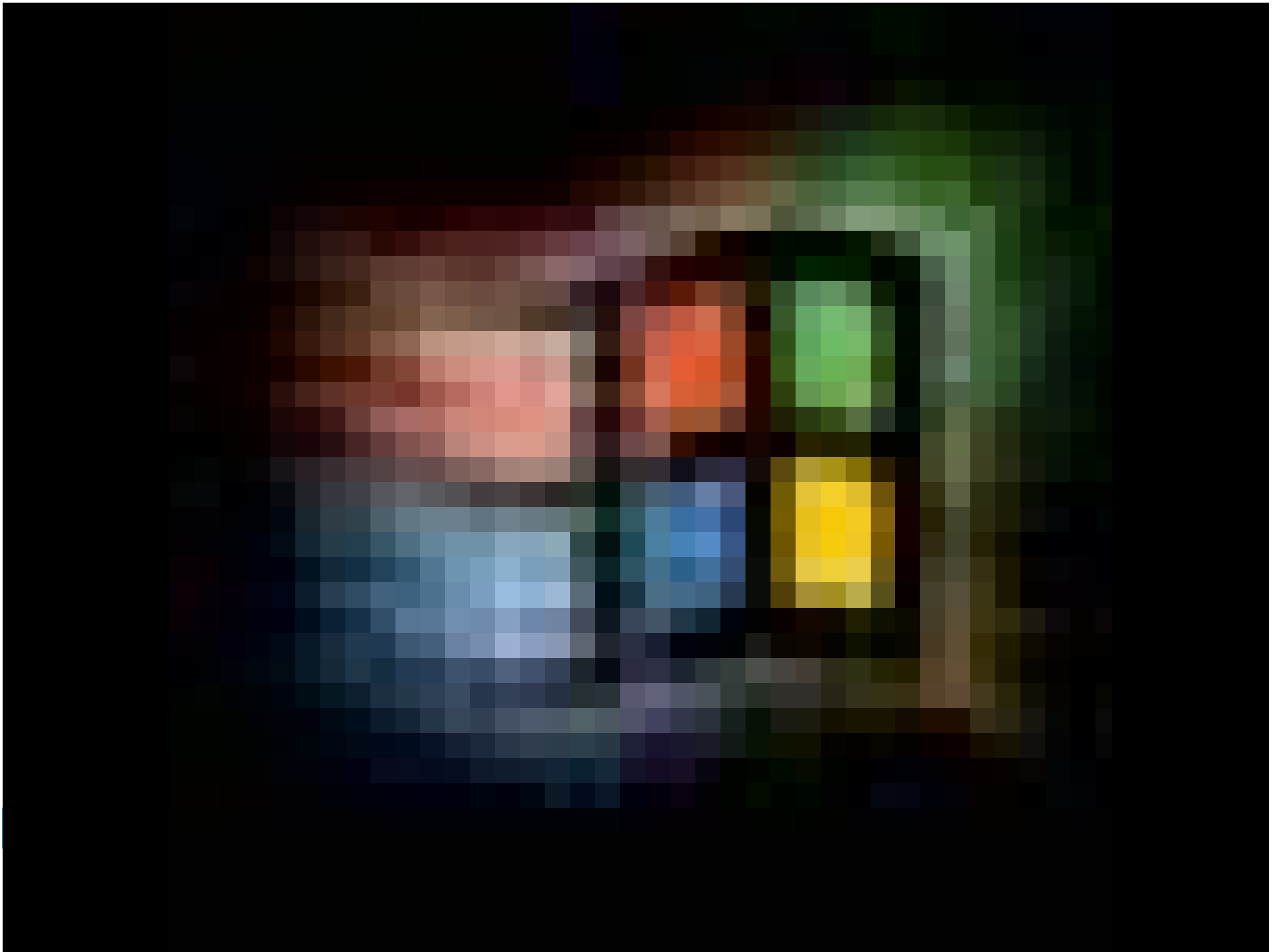
- a) 1
- b) 2
- c) 3
- d) 4
- e) no clue



<http://www.edupinion.nl/c391>

Result



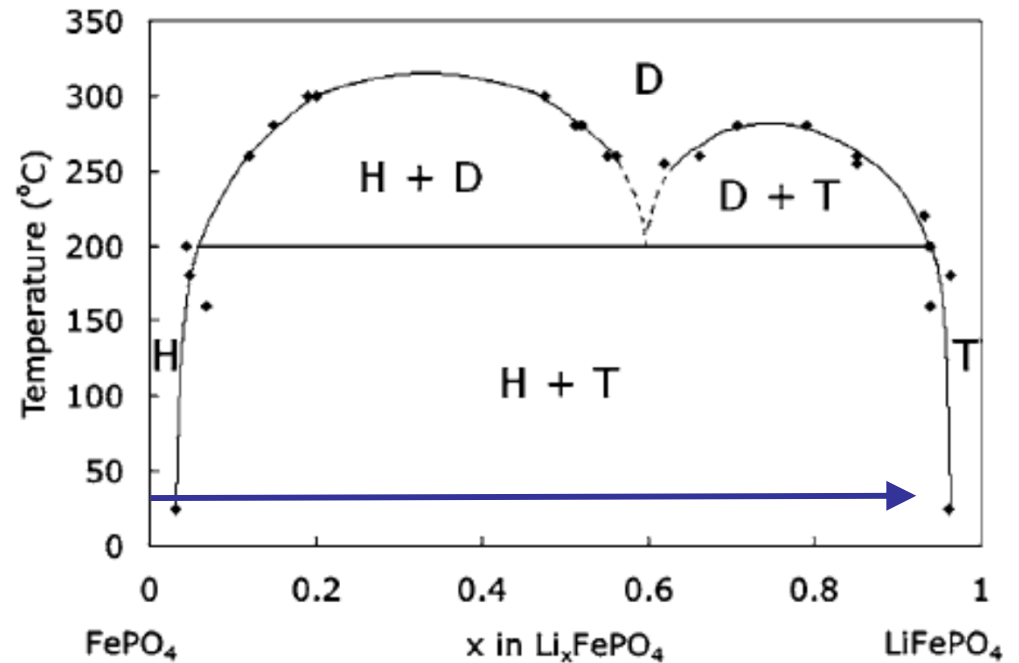




# Question Gibbs Phase Rule 1

17. How many components?

- a) 1
- b) 2
- c) 3
- d) 4
- e) no clue

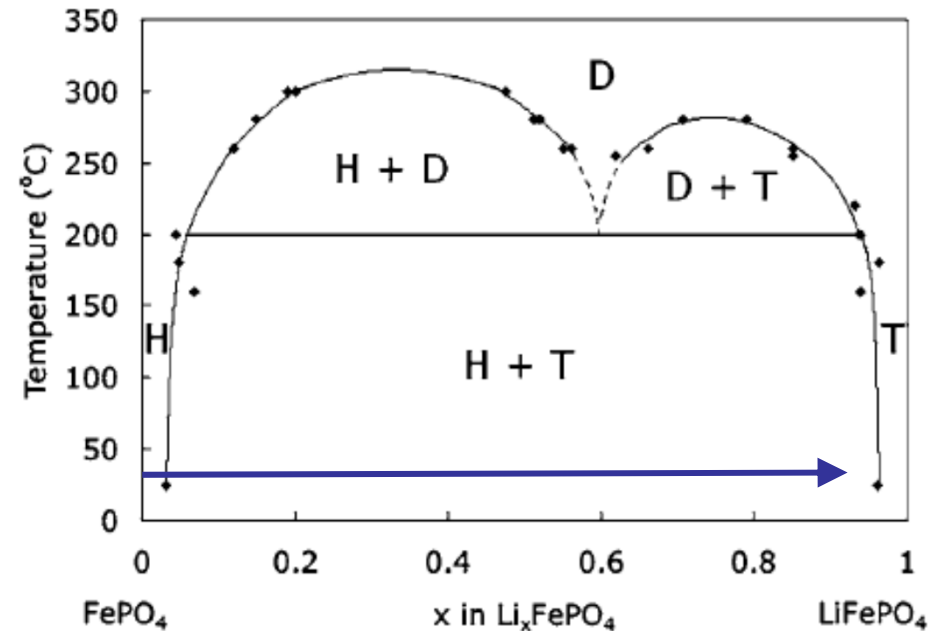


2 components: Li and  $\text{FePO}_4 \Rightarrow$  answer b)

## Question Gibbs Phase Rule 2

18. What is true in the region H+T?

- a) The voltage varies
- b) The voltage is constant
- c) Nothing can be said about the voltage
- d) no clue

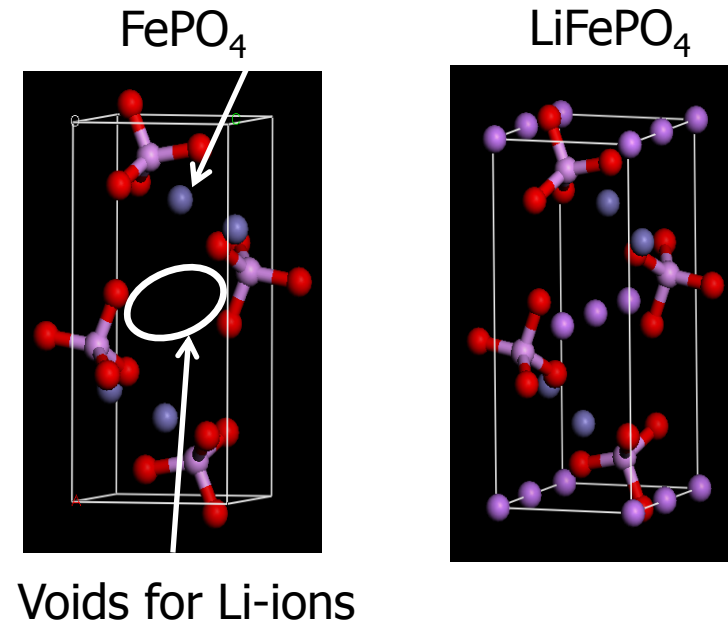
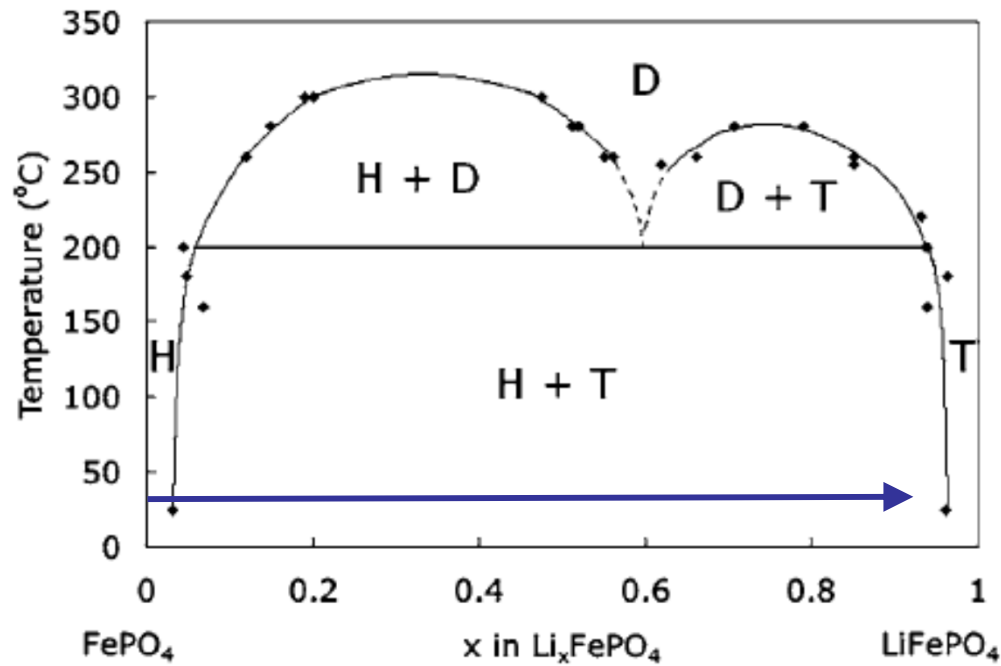


<http://www.edupinion.nl/c195>

Result



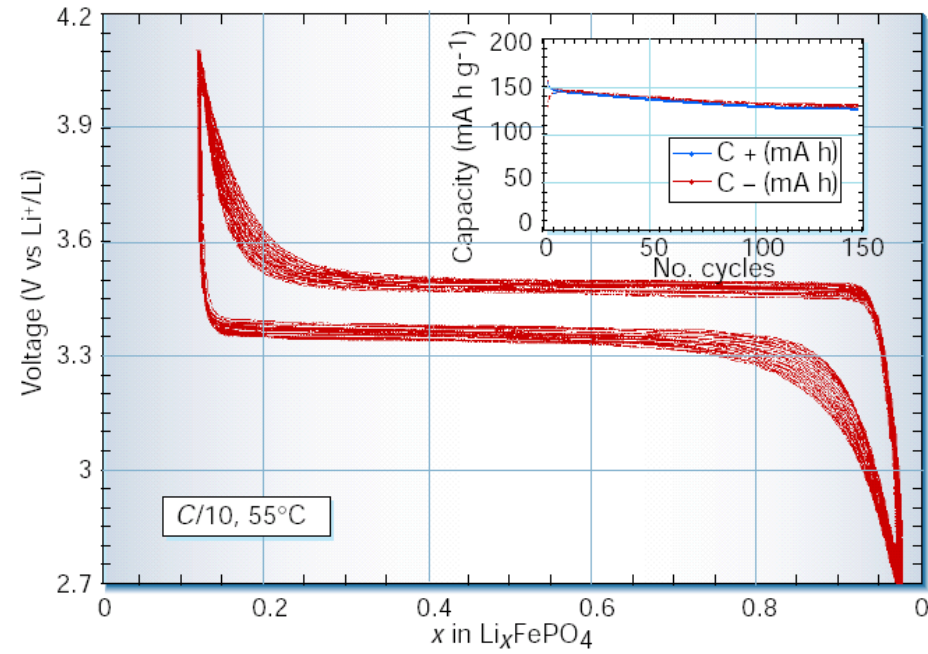
# Question Gibbs Phase Rule 2



$$F = C - P + 2 = 2 (\text{Li and FePO}_4) - 2 (\text{H and T}) + 2 = 2,$$

$T, p$  specified  $\Rightarrow E_{\text{cell}} = \text{constant} \Rightarrow b)$

# Question Gibbs Phase Rule 2



# Program Batteries

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

# 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

# To do for next week

Read Chapters 2.5 and 2.6 Electrochemistry

Read Advanced Batteries Chapter 14.1,14.2,14.B1-4, 16.1-2,16B  
Review Goodenough et al. Chemistry of Materials

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

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

b) Sketch the voltage diagram

