Electrochemical Equilibrium II

Lecture 12b

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The Electrode Potential

So the conditions for equilibrium are

$$T^\alpha = T^\beta$$ we know this one

$$\mu_1^\alpha + z_1 F \phi^\alpha = \mu_1^\beta + z_1 F \phi^\beta$$
$$\mu_2^\alpha + z_2 F \phi^\alpha = \mu_2^\beta + z_2 F \phi^\beta$$

or equivalently:

$$\eta_1^\alpha = \eta_1^\beta$$

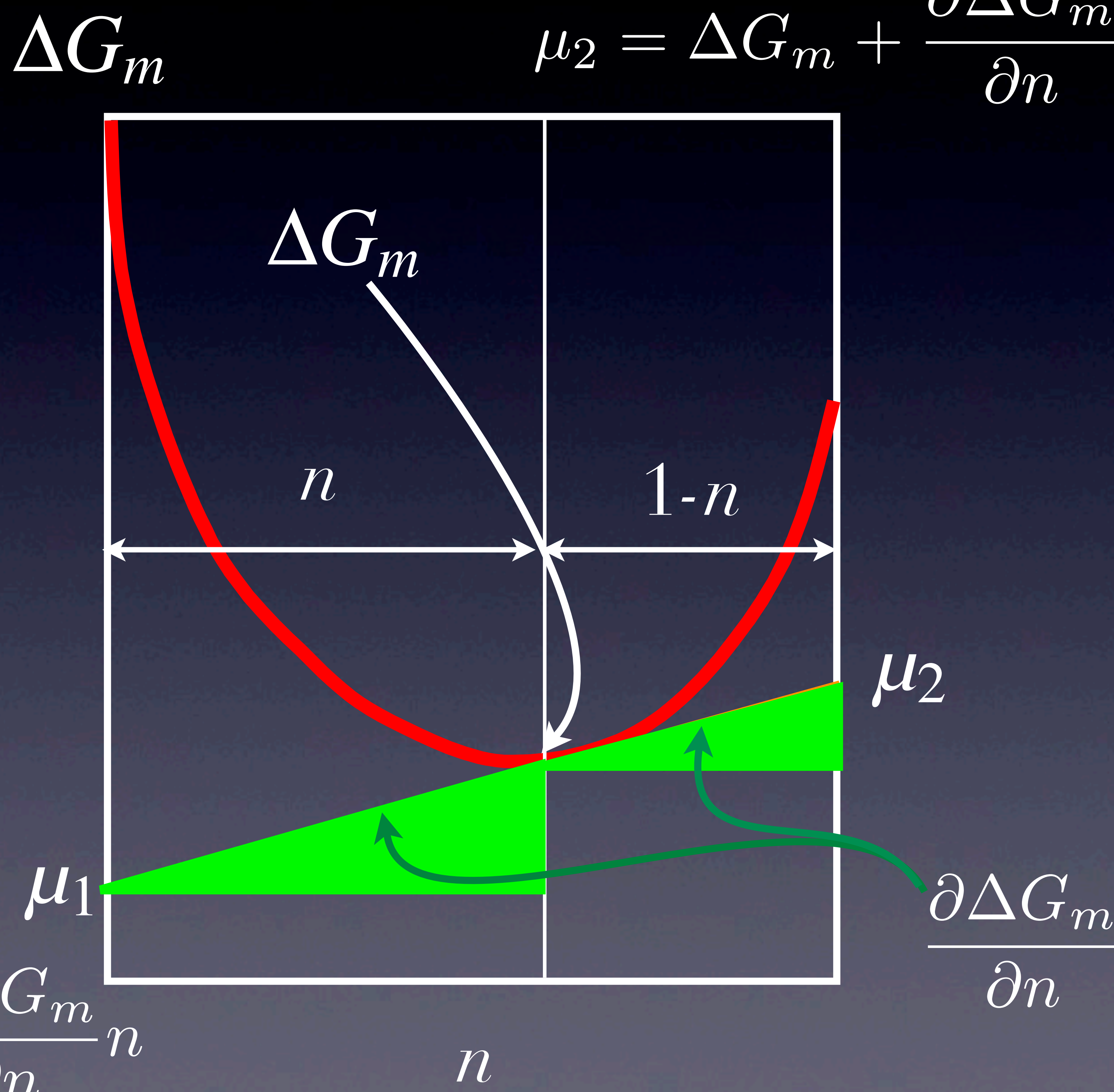
$$\eta_2^\alpha = \eta_2^\beta$$

and yet, another way to look at it:

$$\Delta\phi_1^{\alpha\rightarrow\beta} = \frac{\Delta\mu_1^{\alpha\rightarrow\beta}}{z_1 F} \qquad \Delta\phi_2^{\alpha\rightarrow\beta} = \frac{\Delta\mu_2^{\alpha\rightarrow\beta}}{z_2 F}$$

Method of Intercepts

$$\mu_2 = \Delta G_m + \frac{\partial \Delta G_m}{\partial n}(1 - n)$$



$$\mu_1 = \Delta G_m - \frac{\partial \Delta G_m}{\partial n} n$$

The Common Tangent and Lever Rule

free energy in the miscibility gap:

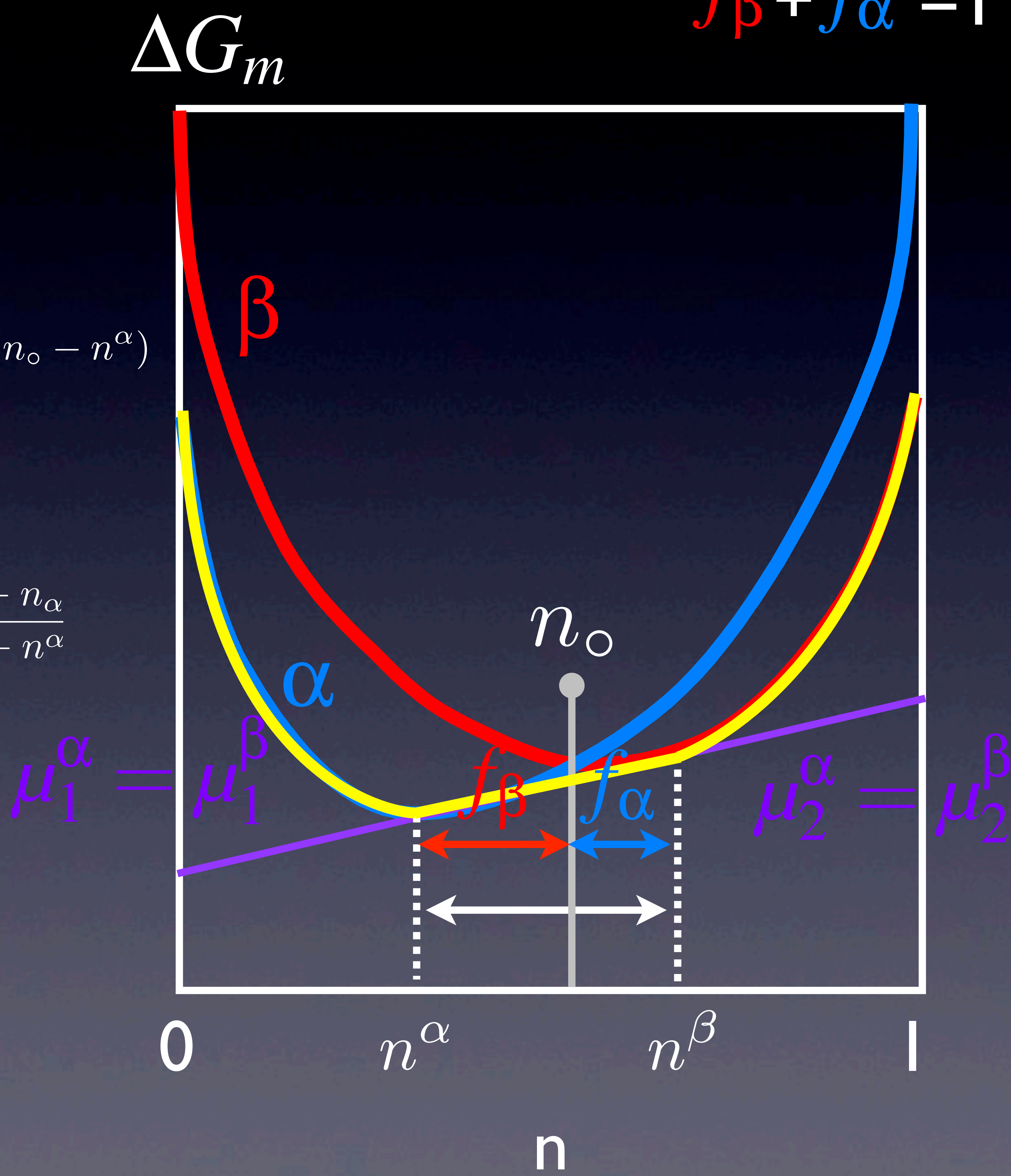
$$\Delta G_m(n_\circ) = \Delta G_m^\alpha(n^\alpha) + \frac{\Delta G_m^\beta(n^\beta) - \Delta G_m^\alpha(n^\alpha)}{n^\beta - n^\alpha}(n_\circ - n^\alpha)$$

$$\Delta G_m(n_\circ) = \Delta G_m^\alpha(n^\alpha)\frac{n^\beta - n_\circ}{n^\beta - n^\alpha} + \Delta G_m^\beta(n^\beta)\frac{n_\circ - n_\alpha}{n^\beta - n^\alpha}$$

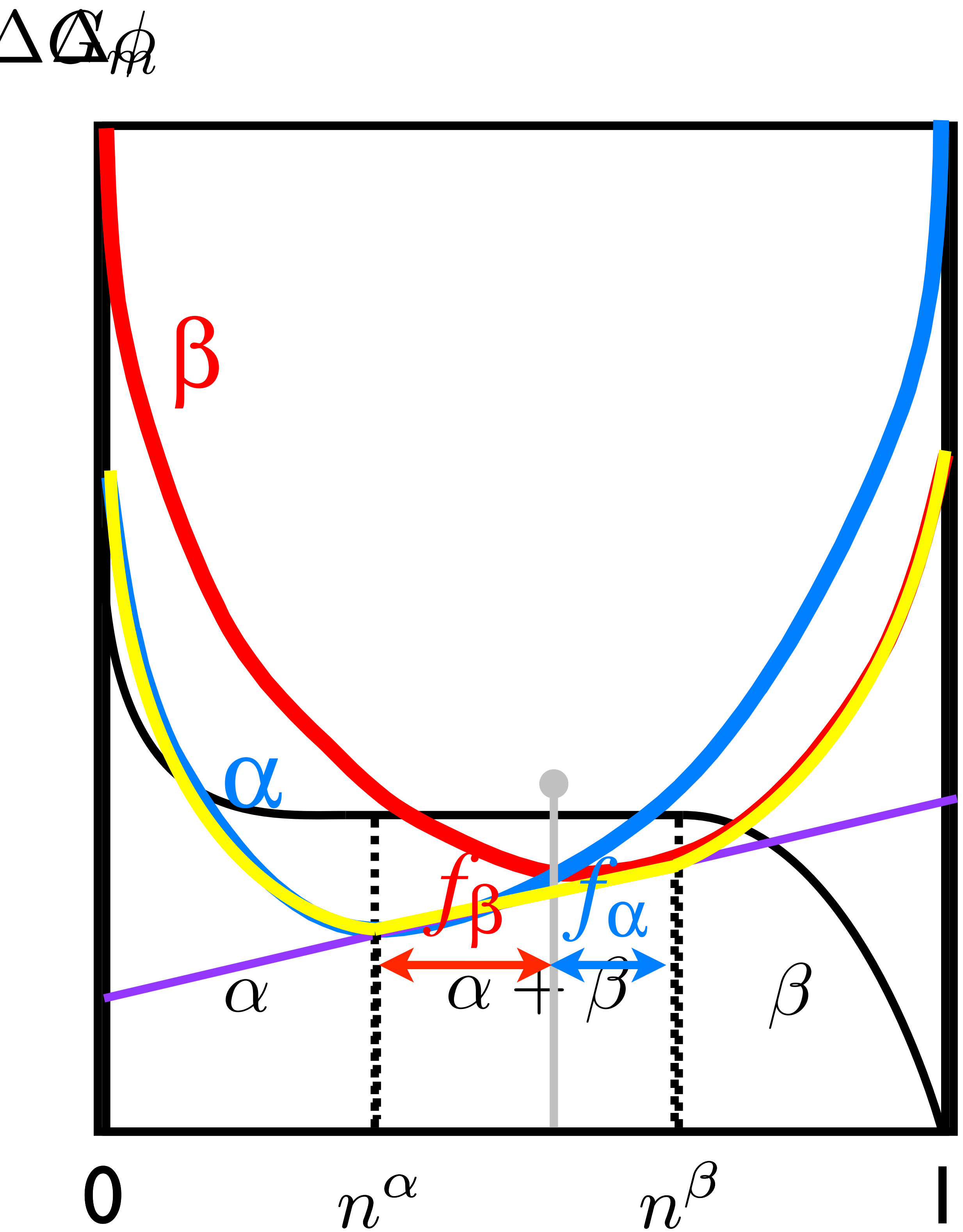
$$f_\alpha = \frac{n^\beta - n_\circ}{n^\beta - n^\alpha}$$

$$f_\beta = \frac{n_\circ - n^\alpha}{n^\beta - n^\alpha}$$

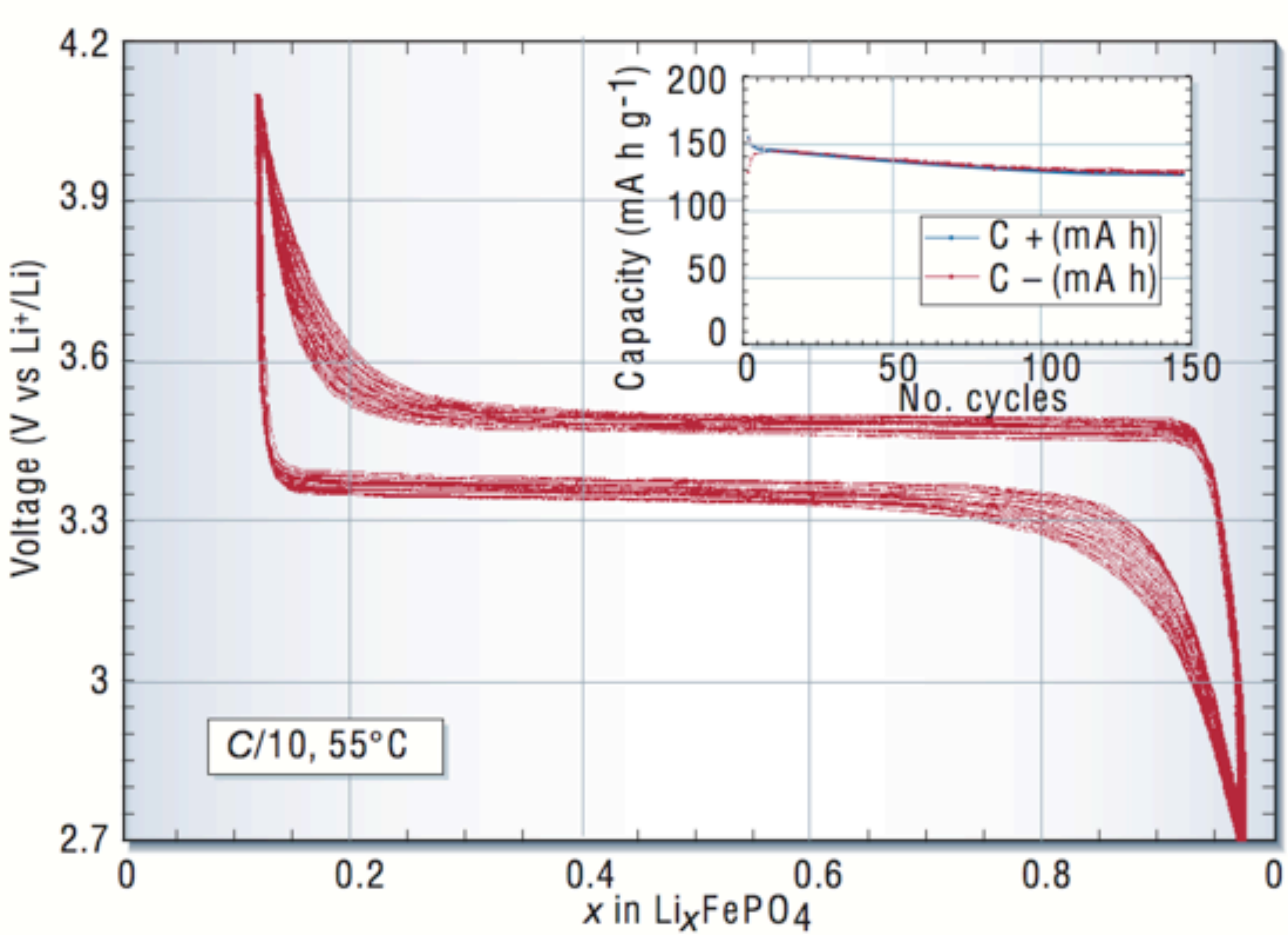
$f_\beta + f_\alpha = 1$



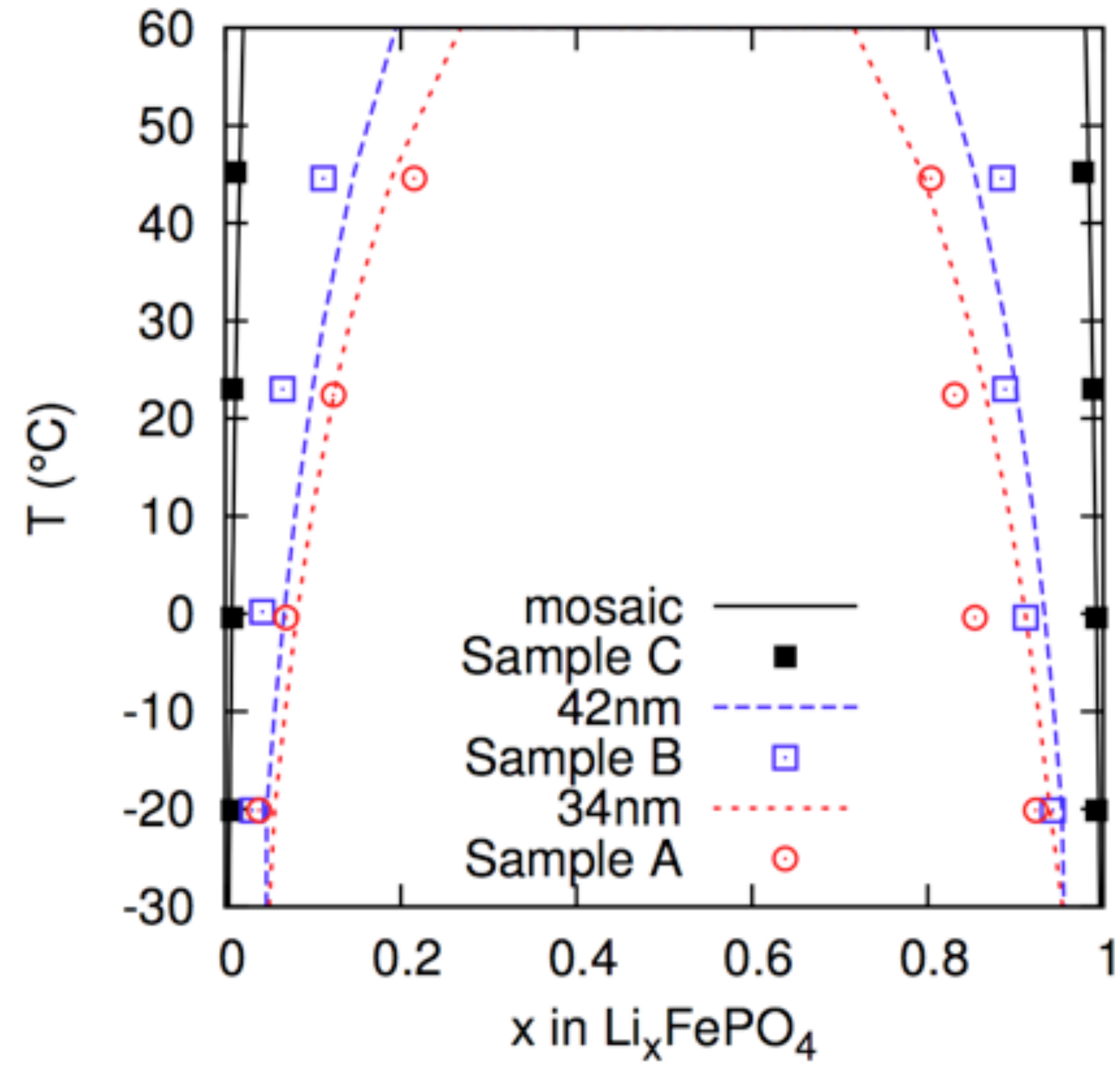
Phase Diagrams and Material Potential



Li-$FePO_4$ System

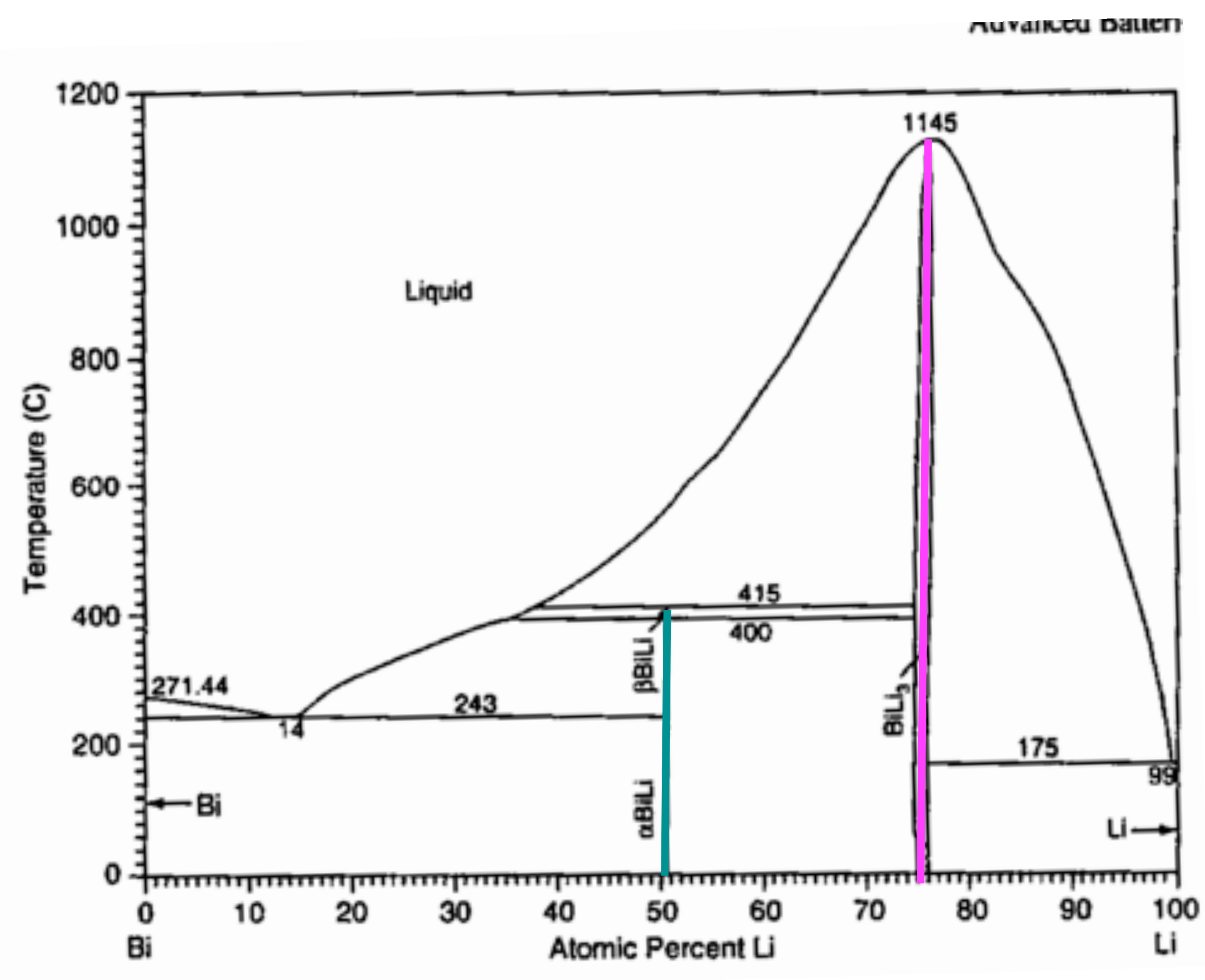


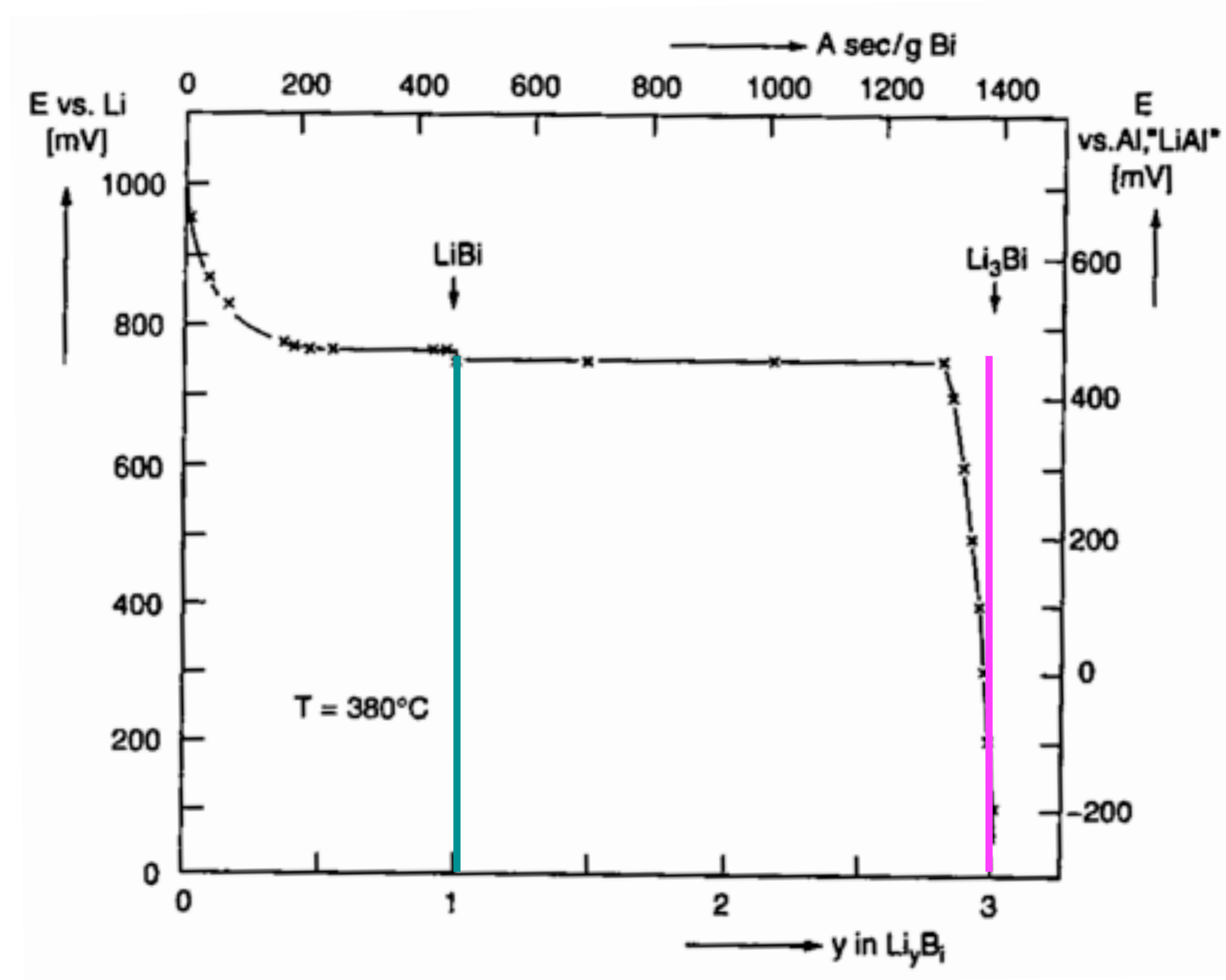
J. M. Tarascon and M. Armand. Issues and Challenges Facing Rechargeable Lithium Batteries. Nature, 414:359–367, 2001.



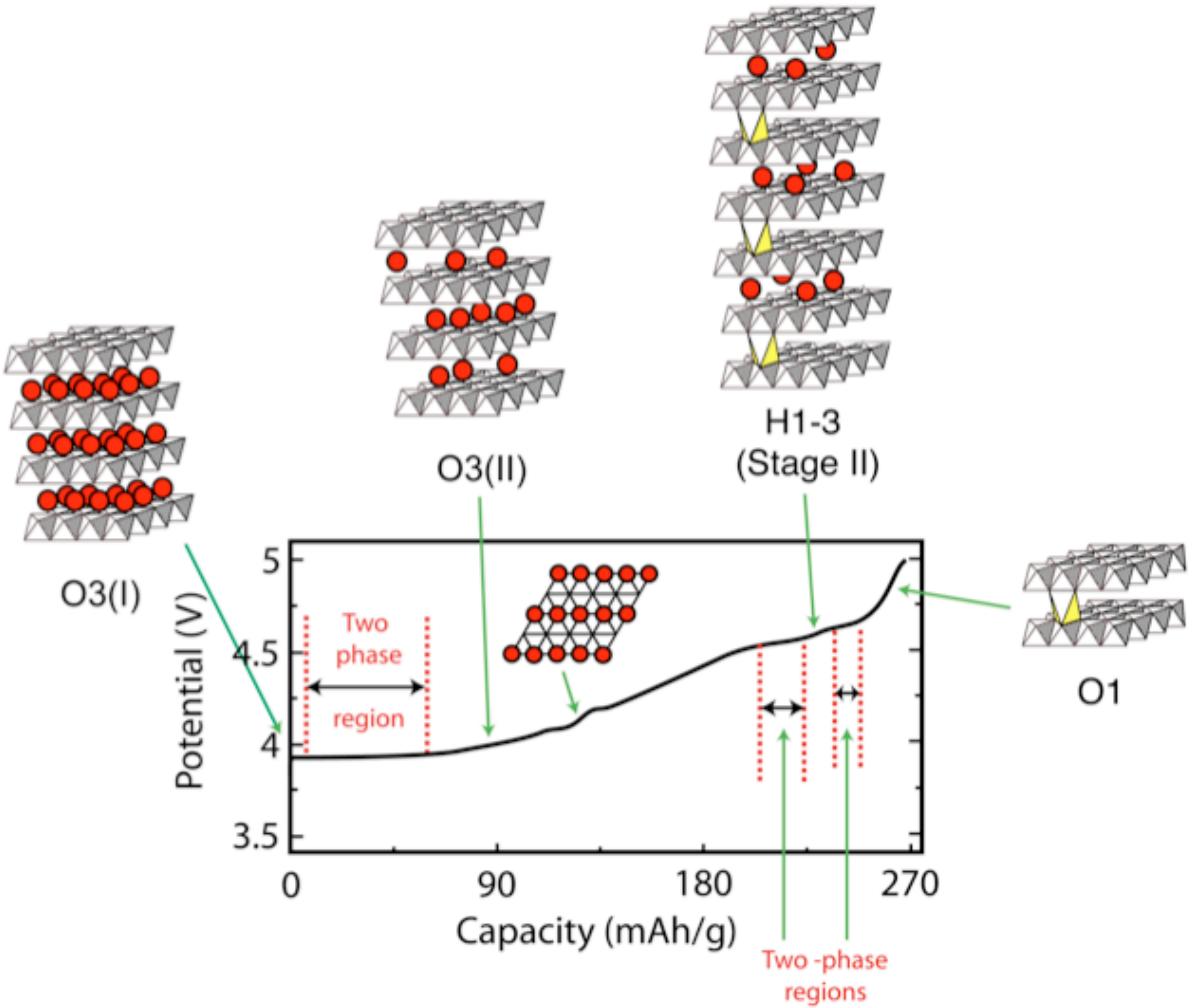
D. Cozwell and M. Bazant, 2012

The Bi-Li System

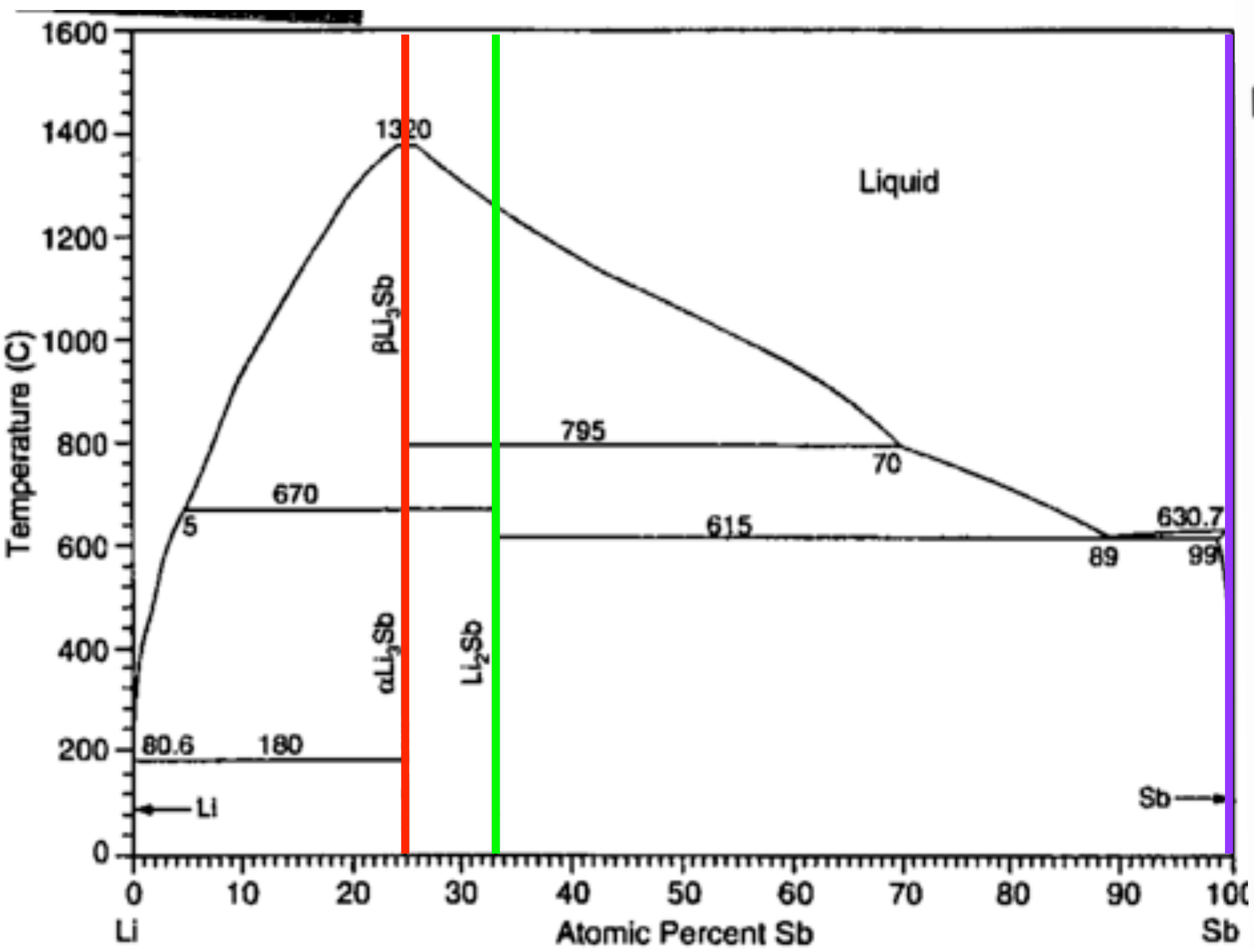




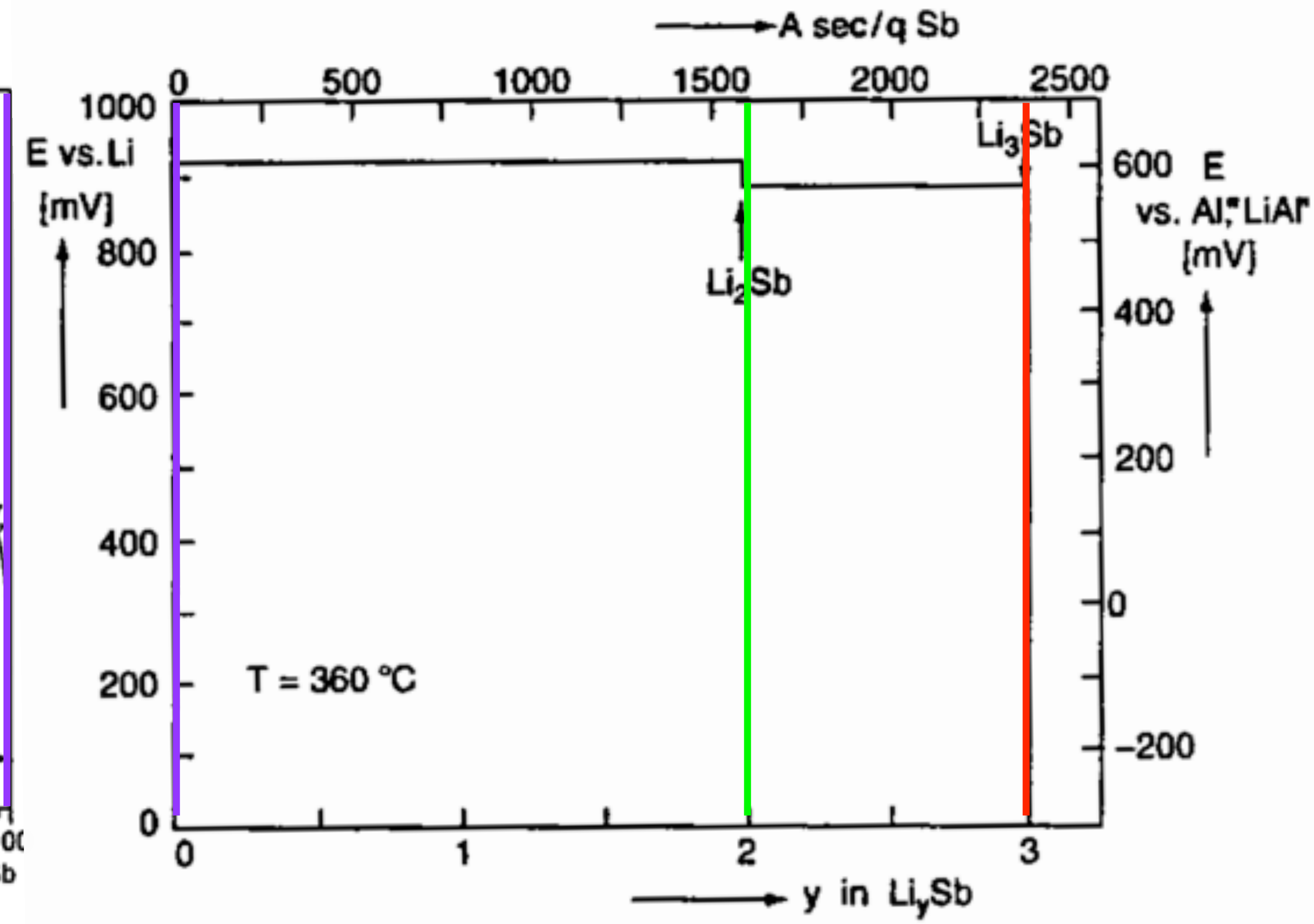
The $LiCoO_2$ System



Sb-Li System



Temperature (C)
1600
1400
1200
1000
800
600
400
200
0
1320
Liquid
βLi3Sb
795
70
670
5
615
630.7
89
99
αLi3Sb
Li2Sb
80.6
180
Li
Sb
0
10
20
30
40
50
60
70
80
90
100
Li
Atomic Percent Sb
Sb



A sec/q Sb
0
500
1000
1500
2000
2500
1000
800
600
400
200
0
E vs. Li
[mV]
Li3Sb
Li2Sb
600
400
200
0
−200
E
vs. Al,"LiAl"
[mV]
T = 360 °C
0
1
2
3
y in LiySb

The C_6-Li System