II. Equilibrium Thermodynamics

Lecture 11: Reconstitution Electrodes

MIT Student (and MZB)

"Reconstitution electrodes" undergo phase transformations driven by Faradaic reactions. In equilibrium, the state of charge increases by converting one immiscible phase into another at a constant voltage, which corresponds to the free energy difference between the two phases. Reconstitution electrodes are becoming increasingly common in Li-ion batteries. Typically, there are two immiscible phases, e.g. $LiFePO_4$ and $FePO_4$, with solid solution behavior possible at the extreme concentrations. In other cases, such as $Li_x C_6$, the charge/discharge cycle can pass through two or more reconstitution steps, involving three or more phases.

1 Two Immiscible Phases

1.1 Lithium iron phosphate cathodes

Lithium iron phosphate is a promising cathode material due to safety, low cost and relatively high rate capability and long cycle life, especially in the form of nanoparticles. Unlike most prior Li-ion battery materials, it has a very wide voltage plateau at room temperature, indicating a very strong tendecy to separate into Li rich and Li poor regions. For a given x_1, as shown in Figure 1, there is a phase separation into a fraction $\frac{x_+ - x_1}{x_+ - x_-}$ of x_- and $\frac{x_1 - x_-}{x_+ - x_-}$ of x_+. This means that all x, $x_- < x < x_+$ are linear combinations of x_- and x_+.

1.2 Regular solution model

Simplest Model The simplest model is a regular solution of particles and vacancies. First, we look at the homogenous model. The equations
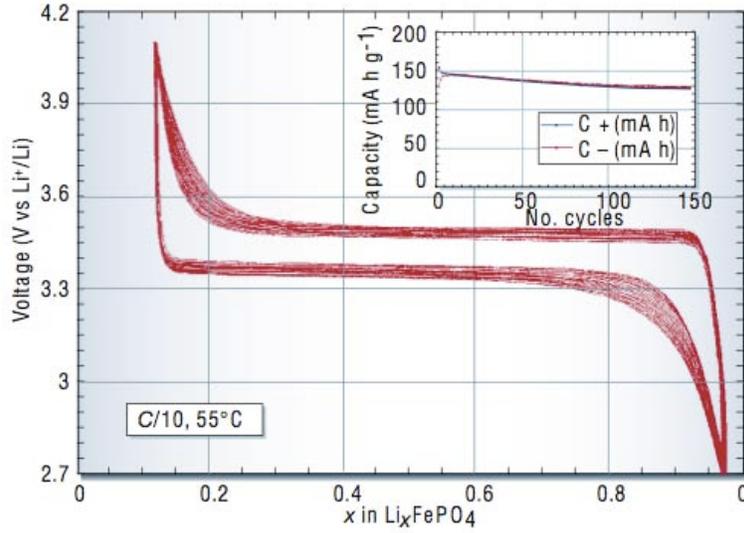
Reprinted by permission from Macmillan Publishers Ltd: *Nature*.
Source: Tarascon, J.-M., and M. Armand. "Issues and challenges
facing rechargeable lithium batteries." *Nature* 414 (2001): 359-367. © 2001.

Figure 1: Charge/discharge cycles of Li/Li$_x$FePO$_4$ near open circuit conditions. [Tarascon et al., Nature (2001).]

describing free energy, chemical potential and open ciruit voltage (per site) are:

$$\bar{g}(x) = h_0 x(1-x) + k_B T(x \ln x + (1-x) \ln 1 - x) \tag{1}$$

$$\bar{\mu}(x) = \bar{g}'(x) = h_0(1-2x) + k_B T \ln \frac{x}{1-x} \tag{2}$$

$$= h_0(1-2x) + k_B T \tanh^{-1} 2x - 1 \tag{3}$$

$$\bar{V}_0(x) = \bar{V}^o - \frac{\bar{\mu}(x)}{e} \tag{4}$$

Dimensionless model We non-dimensionlize the equations by the following variables:

$$\tilde{\mu} = \frac{\bar{\mu}}{2k_B T}$$

$$\tilde{h}_0 = \frac{h_0}{2k_B T} = \frac{T_c}{T}$$

$$y = 2x - 1$$

$$\tilde{\mu} = -\tilde{h}_0 y + \tanh^{-1} y$$

Here T_c is the highest temperature at which phase separation occurs.

1.3 Miscibility Gap

Setting $\tilde{\mu} = 0$ gives us the locations of the minima of $\tilde{g}$.

$$0 = \tanh^{-1} y - \tilde{h}_0 y$$

$$y = \tanh \tilde{h}_0 y \tag{5}$$

Unfortunately, Equation 5 is a transcendental equation, which means we can only solve it numerically, or look at small $\tilde{h}_0 y$ and Taylor expand.

1.3.1 Expansion around T_c

When $|y| << 1$, i.e. x is near $\frac{1}{2}$, we have:

$$\tilde{h}_0 y \approx y + \frac{y^3}{3} + \frac{y^5}{5} + ...$$

$$\tilde{h}_0 \approx 1 + \frac{y^2}{3} + \frac{y^4}{5} + ...$$

$$\frac{T}{T_c} \approx 1 - \frac{y^2}{3} \approx 1 - \frac{4}{3}(x - \frac{1}{2})^2 \tag{6}$$

1.3.2 Expansion near $T = 0$ (or $\tilde{h}_0 \to \infty$)

When $1 - |y| << 1$, x is near 0 or 1. This corresponds to the "edges" of the $\frac{T}{T_c}$ vs x diagram.

We know that

$$\lim_{z \to \infty} \tanh z = \frac{e^z - e^{-z}}{e^z + e^{-z}}$$

$$= \frac{1 - e^{-2z}}{1 + e^{-2z}}$$

$$\approx (1 - e^{-2z})(1 - e^{-2z} + e^{-4z})$$

$$\approx 1 - 2e^{-2z}$$

Thus we can solve for y_+:

$$y = \tanh \tilde{h}_0 y \approx 1 - 2e^{-2\tilde{h}_0 y}$$

Recursively substituting this expansion into itself, we get

$$y_+ \approx 1 - 2e^{-2\tilde{h}_0}$$

Thus,

$$x_+ \approx 1 - e^{-2T_c/T}. \tag{7}$$

We can obtain x_- by noting that $x_+ + x_- = 1$.
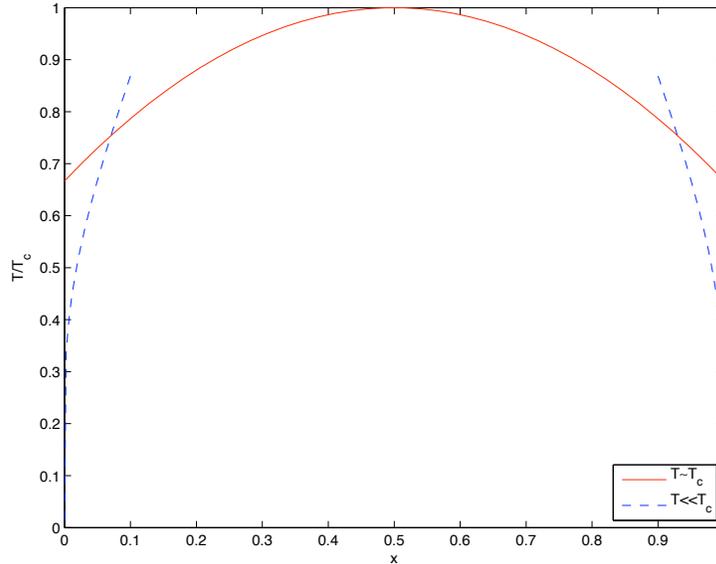
Figure 2: Approximatinos of miscibility gap for different values of $\frac{T}{T_c}$, when $T \approx T_c$ and $T \ll T_c$

1.3.3   Solution by fixed point iteration

Because our equation is of the form $y = F(y0$, we can solve it numerically or generate asymptotic expansions using fixed point iterations. The numerical solution involves guessing a y_0, and then iterating such that:

$$y_{n+1} = F(y_n)$$

This method converges if $F' < 1$ at the fixed point. To use this as an analytic approximation, we observe that substituting the function into itself and then putting in the guess when sufficently close will give us an arbitrarily accurate approximation:

$$y = F(F(F...F(\tilde{h}_0 y))) \approx F(F(F...F(\tilde{h}_0 \cdot 1)))$$

1.4   Spinodal Decomposition

In the miscibility gap, separation fo the two immisible phases is thermodynamically stable (lowest free energy) but phase separation may requre *nu-*

cleation of the second phase inside the first, to facilitate the transformation. However, far enough into the miscibility gap– in the *spinodal region* – spontaneous instability or *"spinodal decomposition"* of the uniform, metastable state will occur.

Imagine some composition fluctuation occurs – see Figure 3. If this lowers the free energy, then the fluctuation will grow, and phase separation is spontaneous. Using common tangent construction, this occurs when the homogenous free energy looses convexity ($\bar{g}'' < 0$):
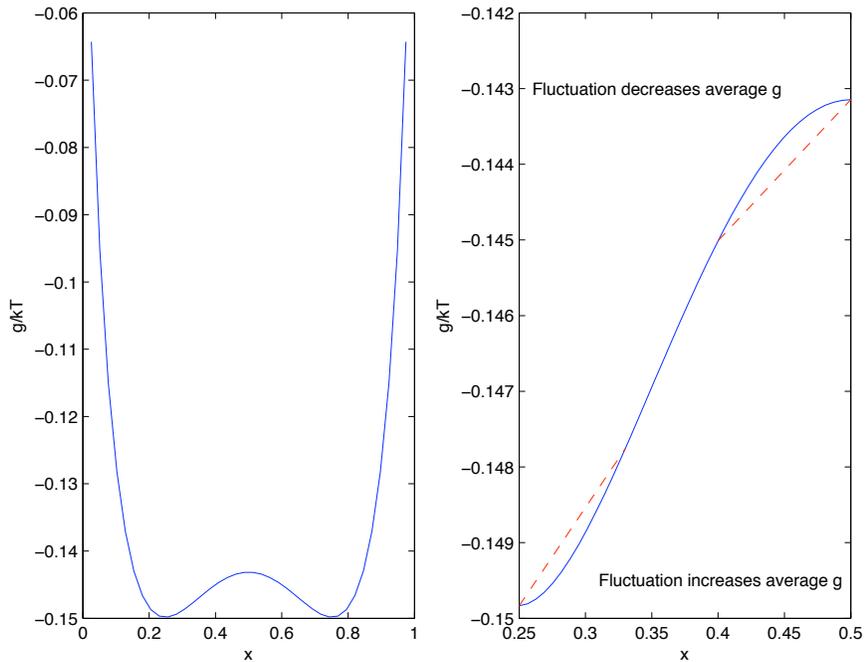
Figure 3: Small fluctuations in composition can raise or lower $\bar{g}$

For the regular solution model:

$$\tilde{g}'' = \tilde{\mu}' = -\tilde{h}_0 + \frac{1}{1-y^2} = 0$$

$$\tilde{h}_{spinodal}^{-1} = \frac{T_c}{T_{sp}} = 1 - y^2 \tag{8}$$

2   Multiple Immiscible Phases

2.1   Graphite anodes

Graphite is the most common anode material for Li-ion batteries, due to its negative voltage and ability to reversibly intercalate lithium (as well as safety and economic factors). Lithium intercalates between graphene C_6 planes but prefers to populate isolated layers. In this case, the different immiscible states correspond to the filling of each layer, every 2nd, every 3rd layer etc. This results in a staircase voltage versus state of charge, with each immiscible, stable phase having every n^{th} layer Li rich, ad the other Li poor, as shown in the Figure.

The Reversible Potential of The Lithium-Graphite Intercalation Compounds vs. The Composition x in Li_xC_6 Plots
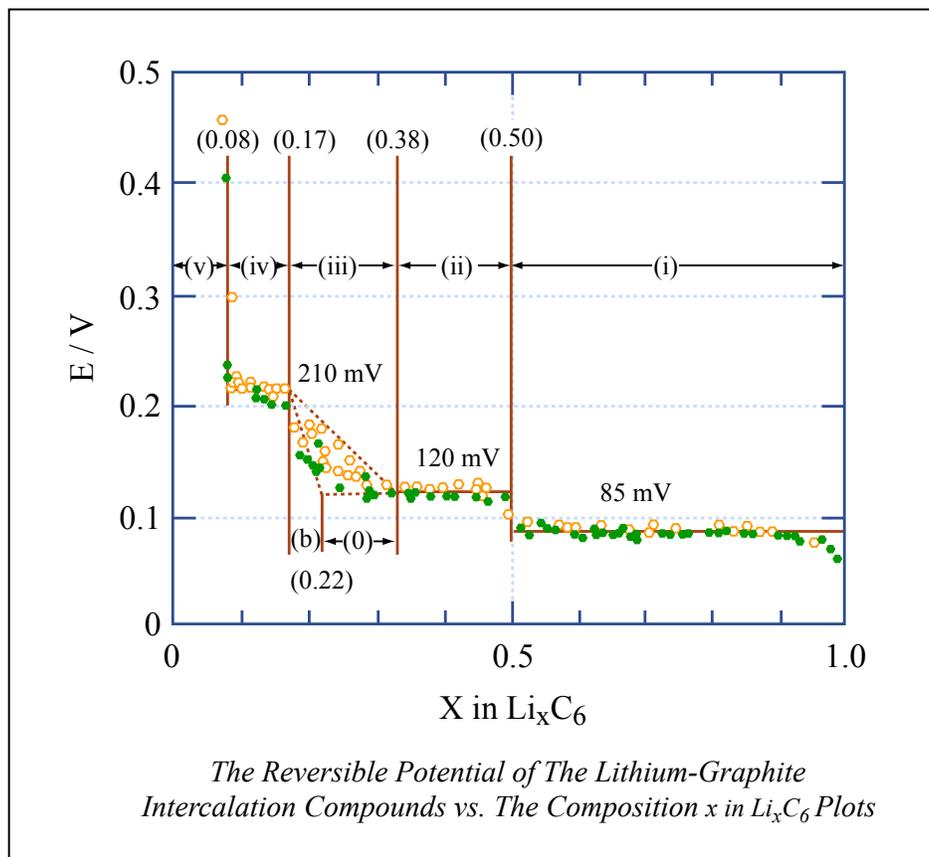
Image by MIT OpenCourseWare.

Figure 4:   Staircase-like open circuit voltage of Li_xC_6 versus Li metal

2.2   Simple model: Two coupled regular solutions

As developed on the homework, a simple model that predicts two stages is that of two layers with filling fraction x_1 and x_2 repeated periodically; $x = \frac{1}{2}(x_1 + x_2)$. Each layer is modeled as a regular solution model $(T < T_c)$ with repulsive enthalpic interactions between adjacent layers.

$$\bar{g}(x_1, x_2) = \bar{g}(x_1) + \bar{g}(x_2) + h_{12}x_1x_2$$

where $\bar{g}(x) = h_0 x(1 - x) + k_B T(x \ln x + (1 - x) \ln(1 - x))$. In $x_1, x_2, \bar{g}$ space, there are minima near $(x_1, x_2) = (0,0), (0,1), (1,0), (1,1)$. Common tangent-plane constructions give us two voltage plateaus in this case.

10.626 Electrochemical Energy Systems
Spring 2014