Introduction to the Materials Science of

Rechargeable Batteries

Week 2: Thermodynamics of Battery Materials
Lecture 2.2: The Electrochemical Potential

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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:

\[ \eta_1^\alpha = \eta_1^\beta \]
\[ \eta_2^\alpha = \eta_2^\beta \]

Define this as the **electrochemical potential**

and yet, another way to look at it:

\[ \Delta \phi_1^{\alpha \rightarrow \beta} = \frac{\Delta \mu_1^{\alpha \rightarrow \beta}}{z_1 F} \]
\[ \Delta \phi_2^{\alpha \rightarrow \beta} = \frac{\Delta \mu_2^{\alpha \rightarrow \beta}}{z_2 F} \]
Electrochemical Driving Forces

\[ \varphi_a = \frac{\mu_a^{Li}}{zF} \]

\[ \varphi_c = \frac{\mu_c^{Li}}{zF} \]

\[ \Delta \varphi = \frac{\mu_c^{Li}}{zF} - \frac{\mu_a^{Li}}{zF} \]
Method of Intercepts

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

\[ \mu_1 = \Delta G_m - \frac{\partial \Delta G_m}{\partial n} n \]

\[ \Delta G_m \]

\[ n \quad 1-n \]

\[ \frac{\partial \Delta G_m}{\partial n} \]
Graphical Solution

The Common Tangent Construction
The Common Tangent and Lever Rule

\[ \Delta G_m \]

free energy in the miscibility gap:

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

\[ f_\beta + f_\alpha = 1 \]

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

\[ f_\beta = \frac{n_\circ - n^\alpha}{n^\beta - n^\alpha} \]
Building a Phase Diagram

\[ \Delta G_m \]

\[ T \text{ (K)} \]

\[ \alpha \]

\[ \beta \]

\[ \alpha + \beta \]

\[ n^\alpha \]

\[ n^\beta \]

\[ n \]

\[ 0 \]

\[ 1 \]

\[ \mu_1^\alpha = \mu_1^\beta \]

\[ \mu_2^\alpha = \mu_2^\beta \]
Phase Diagrams and Material Potential

\( \Delta \mathcal{G}_\phi \)

\[0\quad n^\alpha \quad n^\beta \quad 1\]

\( \alpha \quad \alpha + \beta \quad \beta \)

\( f_\beta \quad f_\alpha \)