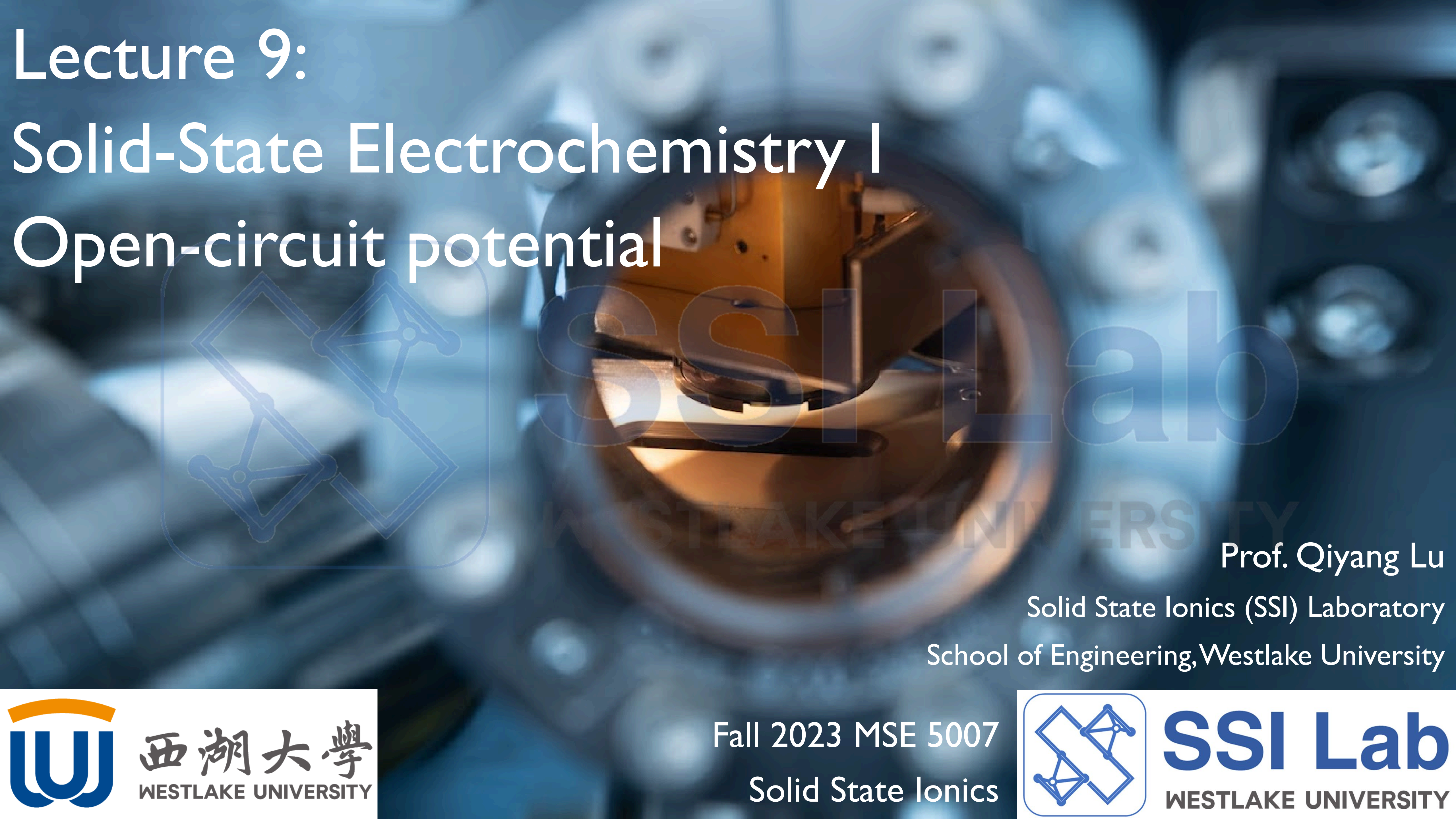

Lecture 9:
Solid-State Electrochemistry I
Open-circuit potential

Prof. Qiyang Lu
Solid State Ionics (SSI) Laboratory
School of Engineering, Westlake University

西湖大學
WESTLAKE UNIVERSITY

Fall 2023 MSE 5007
Solid State Ionics

SSI Lab
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Things we will discuss in this lecture

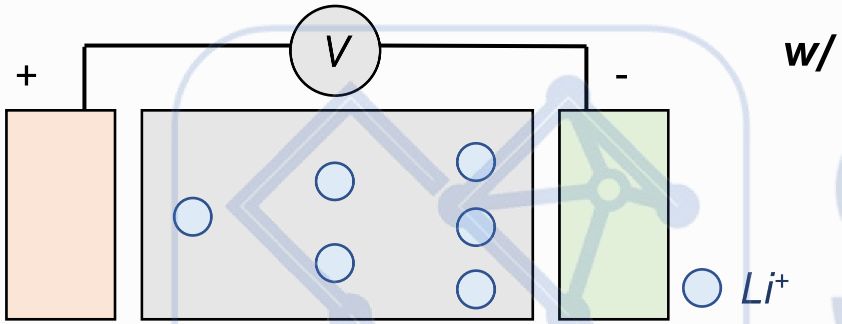
Solid-State Electrochemistry:

- What determines the open-circuit potential of an electrochemical system?
- How to build a model to predict the open-circuit potential for Li-ion battery cathode materials?
- What are the basic assumptions for the lattice gas model?

Goal of this lecture: you should be able to answer the questions above by the end of this lecture :)

The concept of electrochemical potential and equilibrium condition of charged particles

Thought experiment: what happens when a voltage is applied between to parallel electrodes?



w/ an applied voltage: concentration gradient forms

$$J_{tot} = -\frac{cM}{zF}\frac{\partial(\boldsymbol{\mu} + \boldsymbol{zF\phi})}{\partial x} = -\frac{\sigma}{z^2F^2}\frac{\partial(\boldsymbol{\mu} + \boldsymbol{zF\phi})}{\partial x} = -\frac{\sigma}{z^2F^2}\frac{\partial(\tilde{\boldsymbol{\mu}})}{\partial x}$$

$$(\sigma = czFM)$$

$$\boxed{\tilde{\mu} = \mu + zF\phi}$$

Electrochemical potential	Chemical potential	Electrostatic potential
Unit: J/mol (or eV/mol)	Unit: J/mol (or eV/mol)	Unit: V

F: ~96500 C/mol

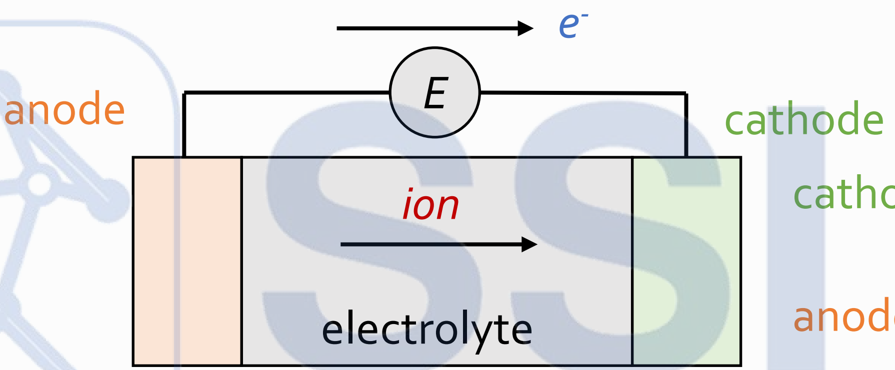
At equilibrium: $J_{tot} = 0 \rightarrow \frac{\partial(\tilde{\boldsymbol{\mu}})}{\partial x} = 0$

For charged species, the equilibrium condition is that *the gradient* of ***electrochemical potential*** $\tilde{\boldsymbol{\mu}}$ is 0

For charge neutral species (such as Li or O_2), $\tilde{\boldsymbol{\mu}}$ is reduced to $\boldsymbol{\mu}$

Applications to Electrochemical Energy Systems

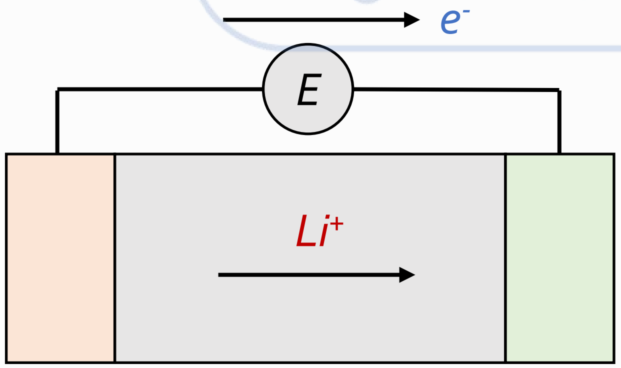
Electrochemical energy systems are based on **concerted motion (transport) of ions + electrons**



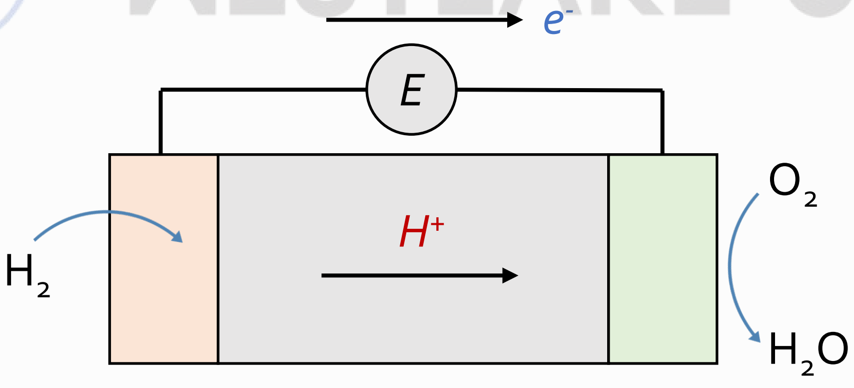
cathode: where ***conventional*** current leaves
reduction reaction

anode: where ***conventional*** current enters
oxidation reaction

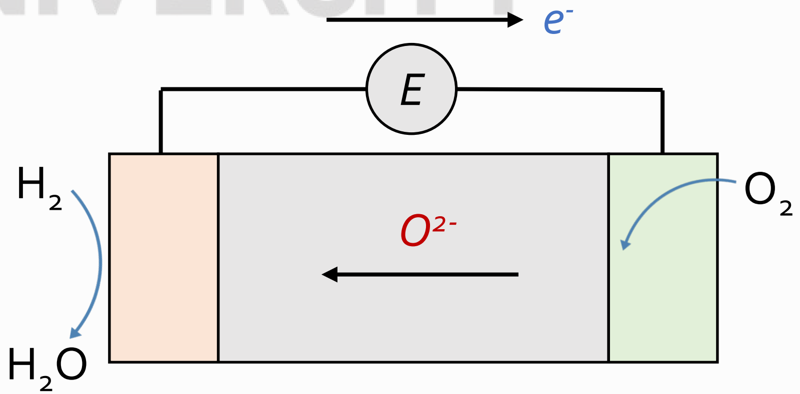
Lithium-ion battery



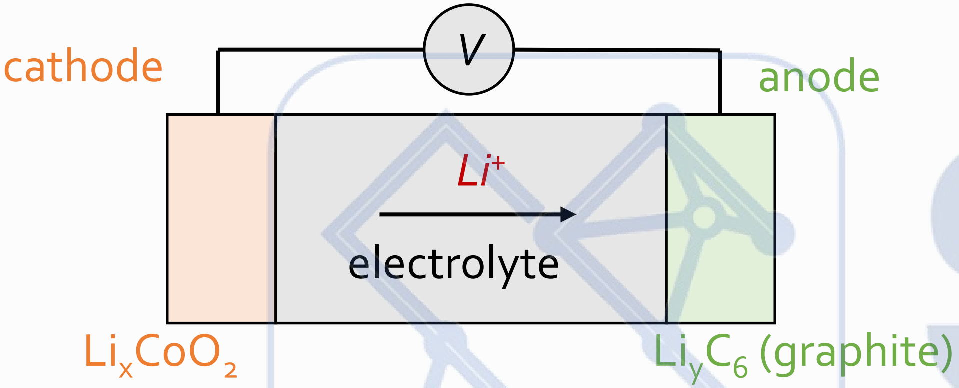
Proton-Exchange Membrane Fuel Cell (PEMFC)



Solid Oxide Fuel Cell(SOFC)



Question: how to understand the open circuit voltage (OCV)?

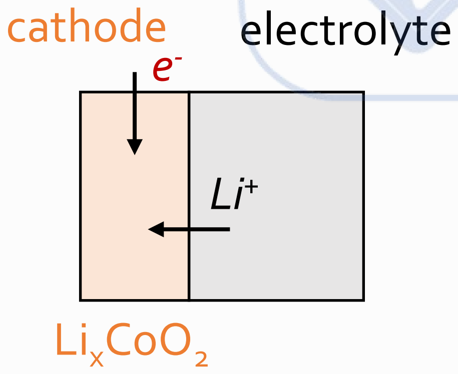


We already know:

1. A voltameter measure the difference of ***electrochemical potential of electrons*** ($\tilde{\mu}_{e^-}$) ;
2. OCV = $(\tilde{\mu}_{e^-}(anode) - \tilde{\mu}_{e^-}(cathode))/\mathrm{F}$

Following question:

What parameters are $\tilde{\mu}_{e^-}(anode)$ and $\tilde{\mu}_{e^-}(cathode)$ *related to?*

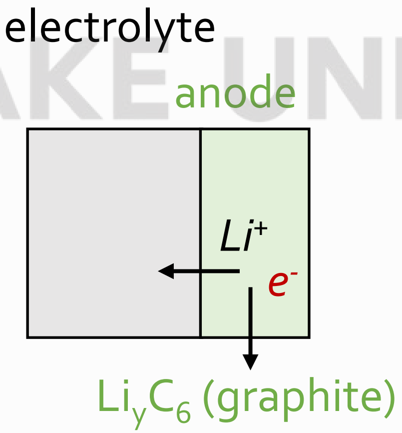


$Li^+ + e^- \rightarrow$ Li (in Li_xCoO_2)

$$\tilde{\mu}_{e^-}(c) + \tilde{\mu}_{Li^+}(lyte) = \mu_{Li}(c)$$

Overall: ("rocking-chair")

Li (in C_6) $\rightarrow$ Li (in Li_yCoO_2)

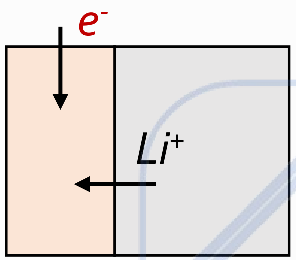


Li (in Li_yC_6) $\rightarrow Li^+ + e^-$

$$\mu_{Li}(a) = \tilde{\mu}_{e^-}(a) + \tilde{\mu}_{Li^+}(lyte)$$

Question: how to understand the open circuit voltage (OCV)?

cathode electrolyte

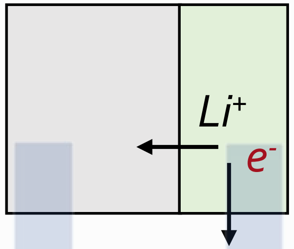


Li_xCoO_2

$Li^+ + e^- \rightarrow Li$ (in Li_xCoO_2)

$$\color{red}{\tilde{\mu}_{e^-}(c)} + \tilde{\mu}_{Li^+}(lyte) = \mu_{Li}(c)$$

electrolyte anode



Li_yC_6 (graphite)

Li (in Li_yC_6) $\rightarrow Li^+ + e^-$

$$\mu_{Li}(a) = \color{red}{\tilde{\mu}_{e^-}(a)} + \tilde{\mu}_{Li^+}(lyte)$$

Overall: ("rocking-chair")

Li (in Li_xC_6) → Li (in Li_yCoO_2)

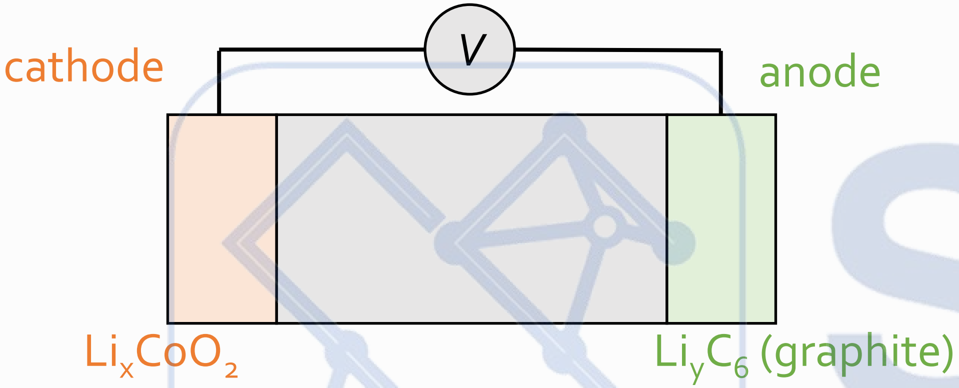
Since the electrolyte can conduct Li^+ (but not e^-), at equilibrium ***electrochemical potential of Li^+*** $\tilde{\mu}_{Li^+}(lyte)$ is ***uniform*** in the electrolyte, *i.e.*, $\frac{\partial \tilde{\mu}_{Li^+}(lyte)}{\partial x} = 0$

Then, we have:

$$\left.\begin{aligned} \mu_{Li}(a) &= \color{red}{\tilde{\mu}_{e^-}(a)} + \cancel{\tilde{\mu}_{Li^+}(lyte)} \\ \color{red}{\tilde{\mu}_{e^-}(c)} + \cancel{\tilde{\mu}_{Li^+}(lyte)} &= \mu_{Li}(c) \end{aligned}\right\}$$

$$\boxed{\begin{aligned} OCV &= -\frac{1}{F}\left(\color{red}{\tilde{\mu}_{e^-}(c) - \tilde{\mu}_{e^-}(a)}\right) \\ &= -\frac{1}{F}\left(\mu_{Li}(c) - \mu_{Li}(a)\right) \end{aligned}}$$

Question: how to understand the open circuit voltage (OCV)?



Overall reaction: ("rocking-chair battery")

Li (in Li_xC_6) → Li (in Li_yCoO_2)

Gibbs free energy (per mole) of the reaction:

$$\Delta G_{rxn}(x,y) = \mu_{Li}(c, Li_xCoO_2) - \mu_{Li}(a, Li_yC_6)$$

$$\boxed{OCV = -\frac{1}{F}\left(\mu_{Li}(c) - \mu_{Li}(a)\right) = -\frac{1}{F}\Delta G_{rxn}(x,y)}$$

If we know how $\mu_{Li}(c)$ changes as a function of composition x and how $\mu_{Li}(c)$ changes as a function of composition y, then we can predict the OCV.

$\Delta G_{rxn}(x,y)$ has to be ***negative*** to make the OCV ***positive***;
In other words, the overall reaction must be ***spontaneous*** to be used in an electrochemical cell for energy extraction.

Brouwer diagram for lithium storage materials

For a lithium-storage material ***LiX*** that can tolerate both ***Li-excess and Li-deficiency***, we consider four point defects: Li_i', $V_{Li}^{\cdot}$, e', $h^{\cdot}$

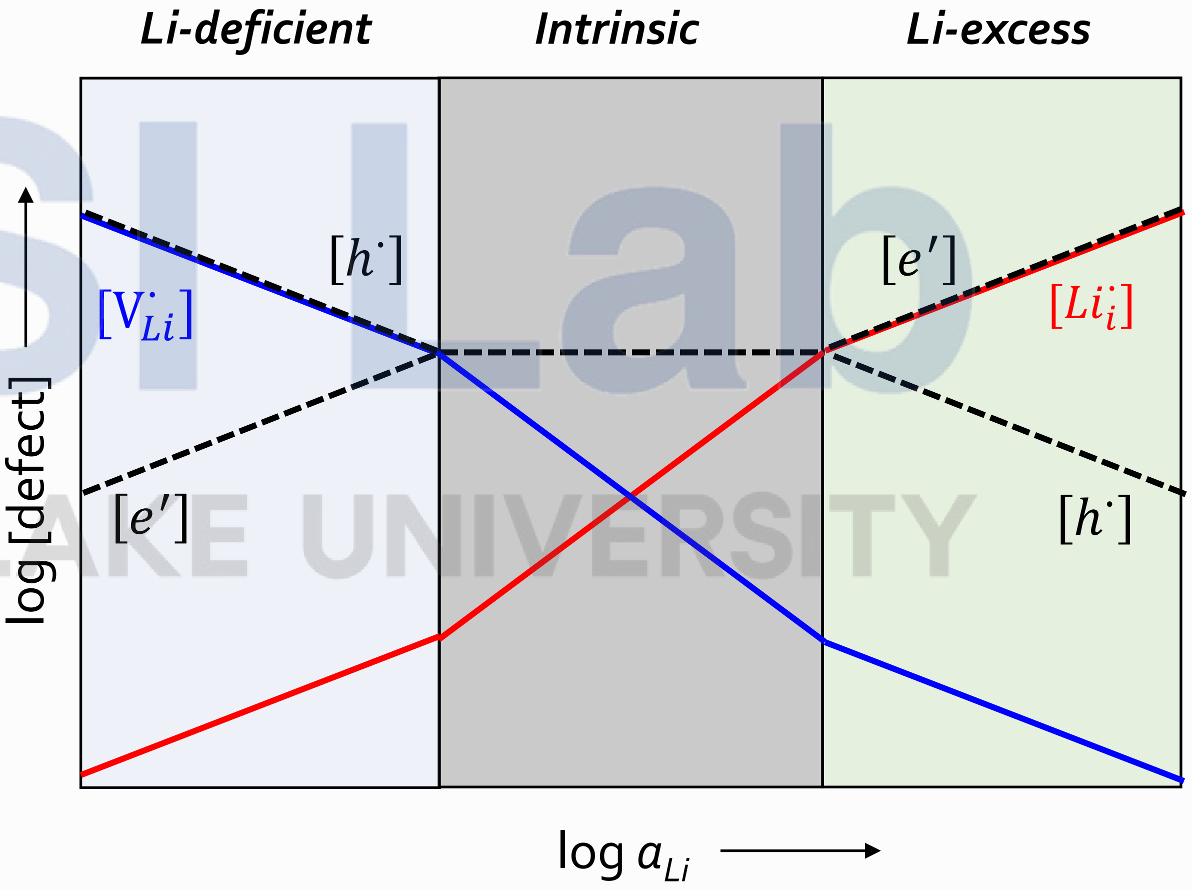
Frenkel pair $\quad null \leftrightharpoons Li_i^{\cdot} + V_{Li}'$ $\quad K_F = [Li_i'][V_{Li}^{\cdot}]$

"Band-to-band" $\quad null \leftrightharpoons e' + h^{\cdot}$ $\quad K_{el} = [e'][h^{\cdot}]$

Li intercalation $\quad Li \leftrightharpoons Li_i^{\cdot} + e'$ $\quad K_{Li} = \frac{[Li_i^{\cdot}][e']}{a_{Li}}$

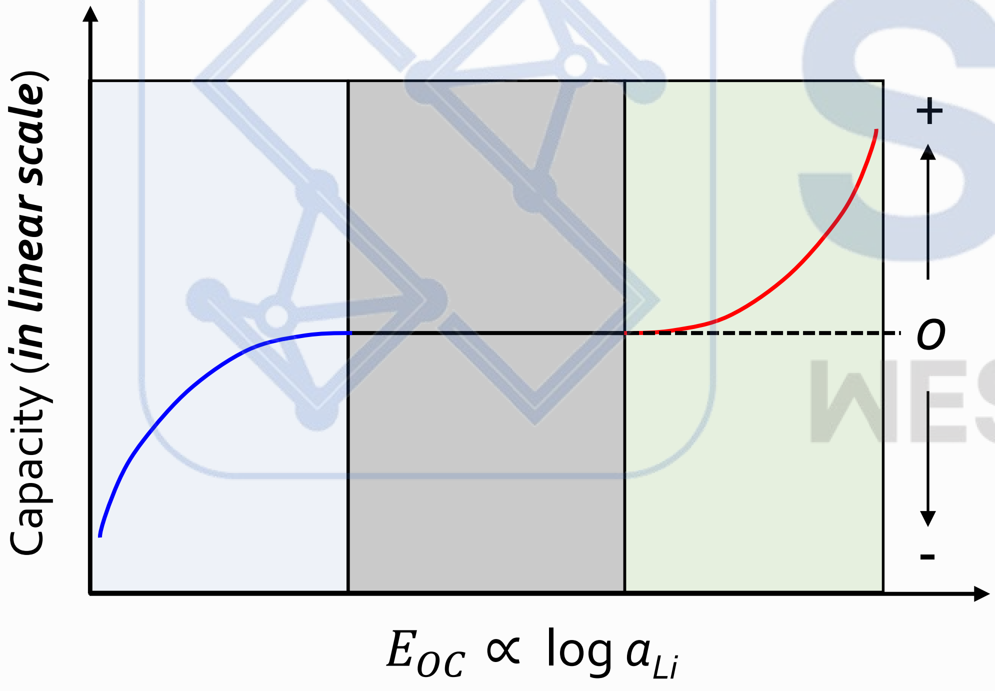
$$\boxed{\mu_{Li} = \mu_{Li}^0 + RTln a_{Li}}$$

We assume $K_{el} \gg K_F$ (small bandgap)

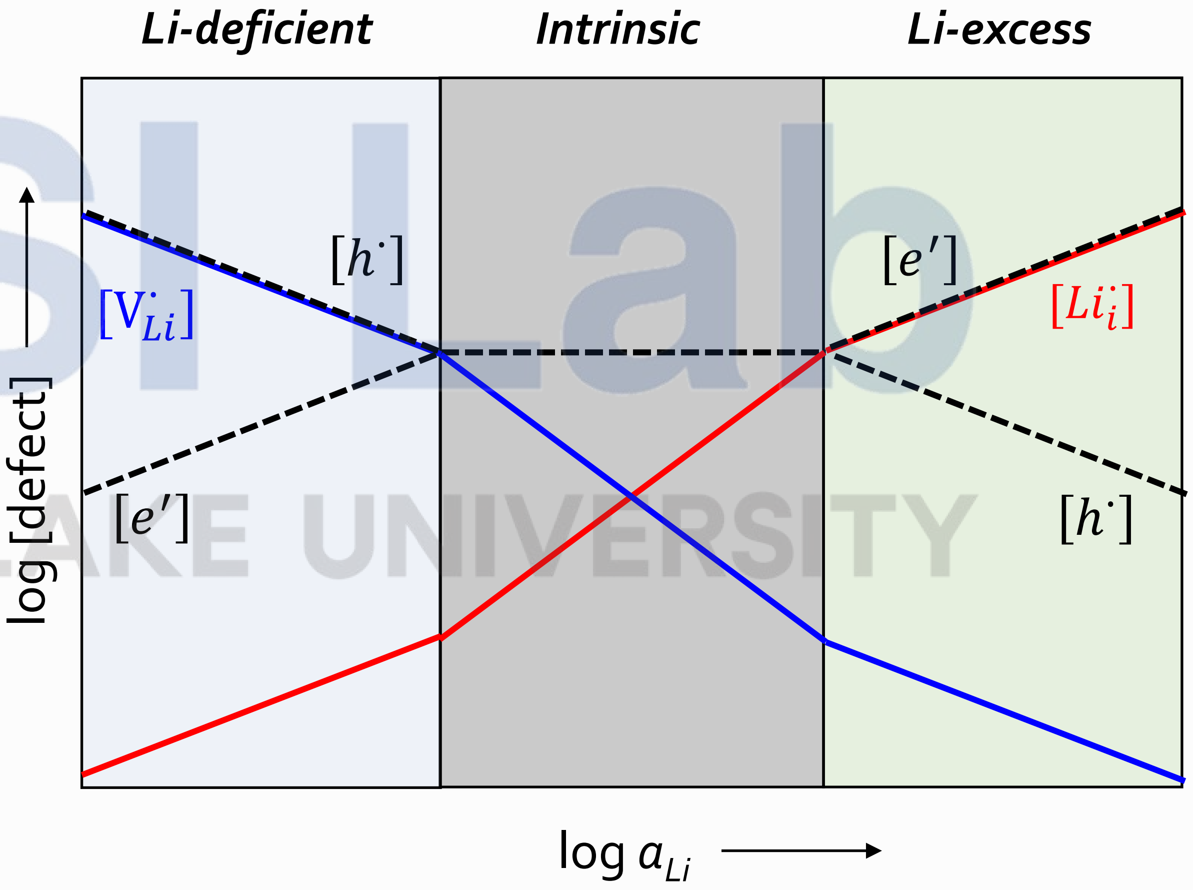


What can we get from such a Brouwer diagram?

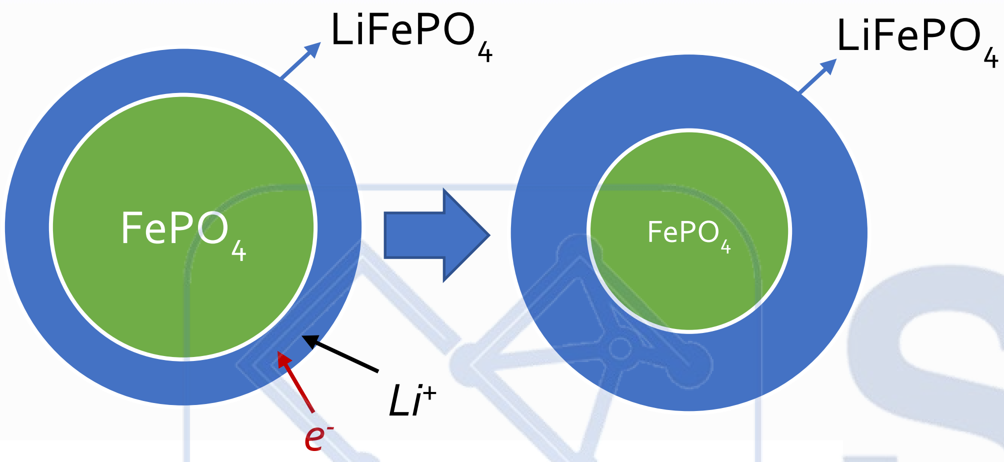
For Li-ion battery materials, we have:
Charge stored: $Q \propto |[Li_i^{\cdot}] - [\mathrm{V}_{Li}^{\cdot}]|$
Open-circuit potential: $E_{OC} \propto \mu_{Li} \propto \ln a_{Li}$

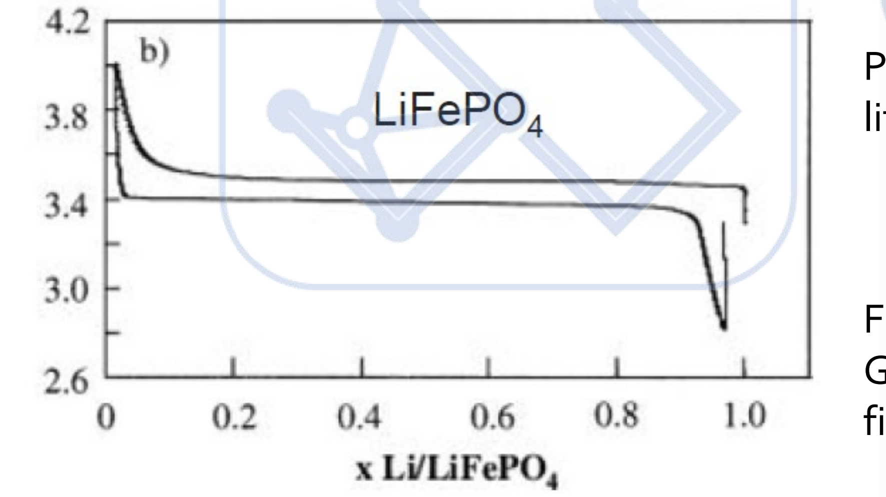


Simulated battery charge/discharge curves (!)



What factors influence the chemical potential of Li in electrodes?

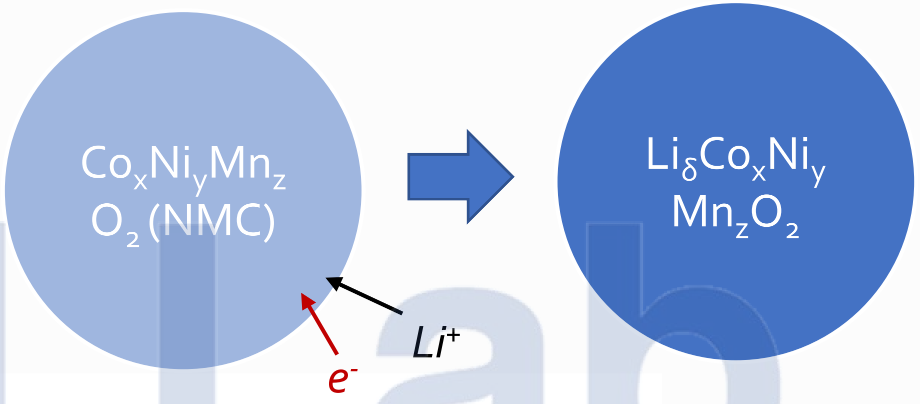


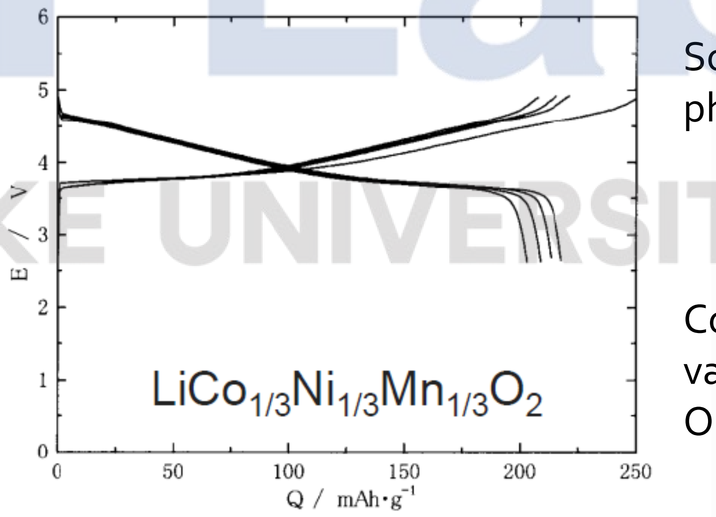


Phase transition induced by lithiation

Fixed μ_{Li} (governed by Gibbs phase rule) resulted in fixed OCV

Huang, Nazar *et al.*, *Electrochem. and Solid-state Lett.*, 2001





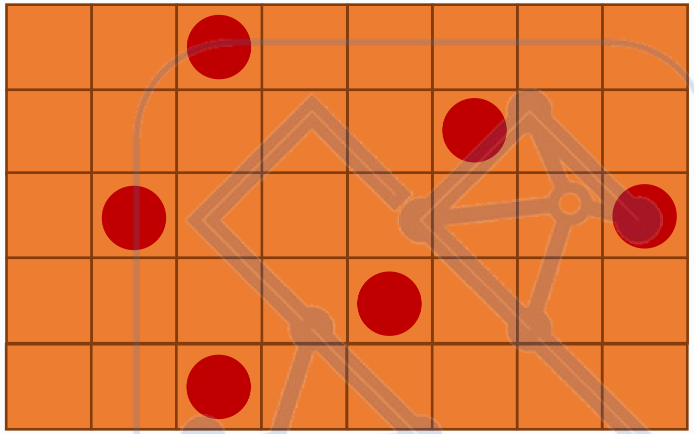
Solid solution (no phase transition)

Continuously varying μ_{Li} and OCV

Yabuuchi *et al.*, *Journal of Power Sources*, 2013

How to model the chemical potential of Li in electrode?

Ideal Lattice Gas Model



🟧 = *lattice site*

● = *Li*

Key assumptions:

- Model intercalated *Li* as ***non-interacting*** gas molecules occupying the lattice sites;
- Concentrated system (*i.e.*, model activity correction);

We use N to denote # of total sites and n to denote *Li*-occupied sites, then:

$G(x) = H - TS$ (where $x = n/N$, and we use $x = 0$ as a reference state)

non-interacting → $H = 0$

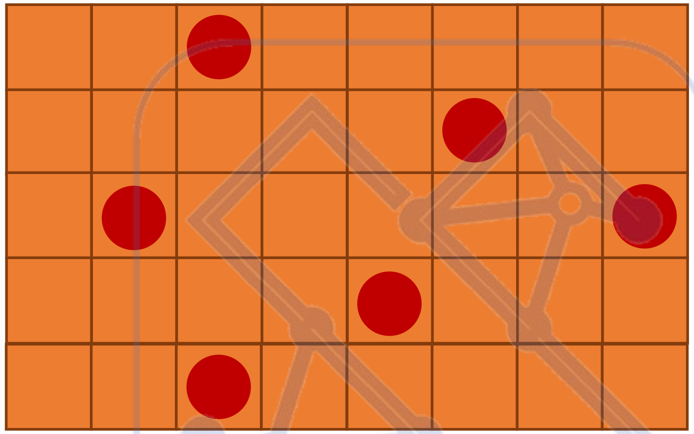
(*or* $H = h_0 x$, the same conclusion)

$$S = S_{cfg} = k_B ln\Omega$$

$$\Omega = \binom{n}{N} = \frac{N!}{n!\,(N-n)!}$$

Calculate configurational entropy and chemical potential

Ideal Lattice Gas Model



🟧 = *lattice site*

● = *Li*

Configurational entropy

$$S_{cfg} = k_B ln\Omega = k_B ln(\frac{N!}{n!\,(N-n)!})$$

Stirling Approximation: $\ln N! \approx N\ lnN - N$, then:

$$S_{cfg} = k_B(N\ lnN \cancel{-N} - n\ln n \cancel{+n} - (N-n)\ln(N-n) + \cancel{(N-n)})$$

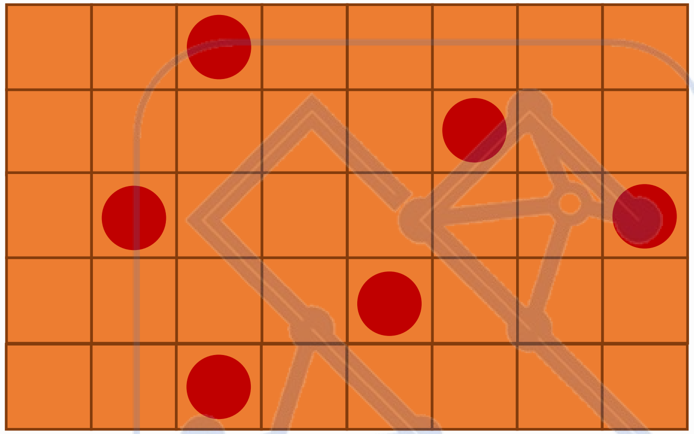
$$G(x) = -TS = -k_BT\ (N ln\frac{N}{N-n} - n\ln\frac{n}{N-n}) \xrightarrow{\boxed{x = n/N}} = -k_BT\ N(ln\frac{1}{1-x} - x\ln\frac{x}{1-x})$$

$$\boxed{G(x) = k_BT\ N(x\ln x + (1-x)\ln(1-x))} \longrightarrow \boxed{\mu(x) = \frac{1}{N}\frac{\partial G}{\partial x} = k_BTln(\frac{x}{1-x})}$$

Expression of ***chemical potential*** using the lattice gas model

Calculate configurational entropy and chemical potential

Ideal Lattice Gas Model



🟧 = *lattice site*

● = *Li*

$$\boxed{\mu(x) = k_B T ln(\frac{x}{1-x})}$$

Expression of ***chemical potential*** using the lattice gas model

Another way to look at this:

$\mu = k_B T ln(\gamma x)$ → *activity coefficient* $\gamma = \frac{1}{1-x}$

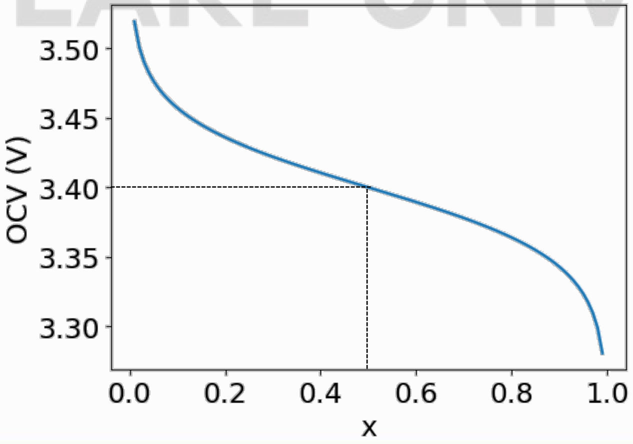
↓

Correction for concentrated solution

If we assume that μ_{Li} of anode stays constant, then we have OCV expression:

$$\boxed{\begin{aligned} OCV &= -\frac{1}{e}(\mu_{Li}(x, cathode) - \mu_{Li,anode}) \\ &= E^0 - \frac{k_B T}{e} ln(\frac{x}{1-x}) \end{aligned}}$$

At room temperature, $\frac{k_B T}{e} = 26\ mV$



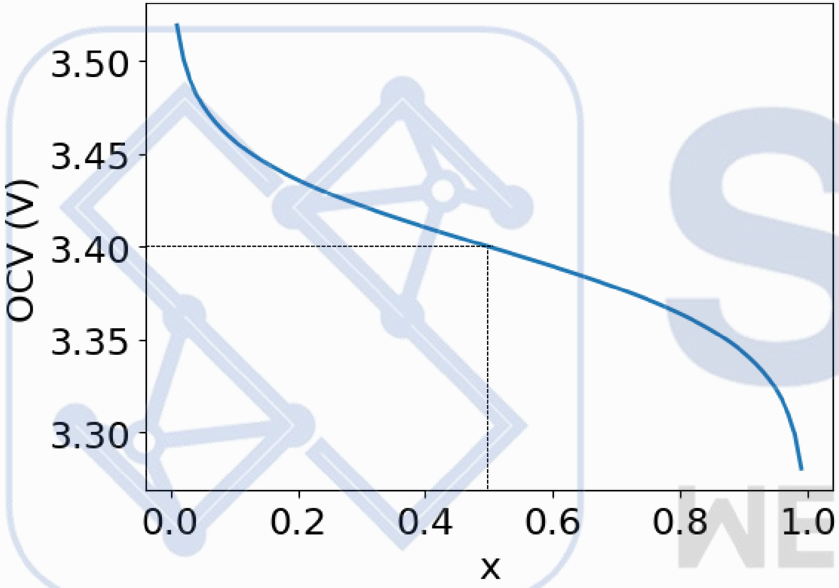
In the plot on the left, we have:

$E^0 = 3.4\ V$

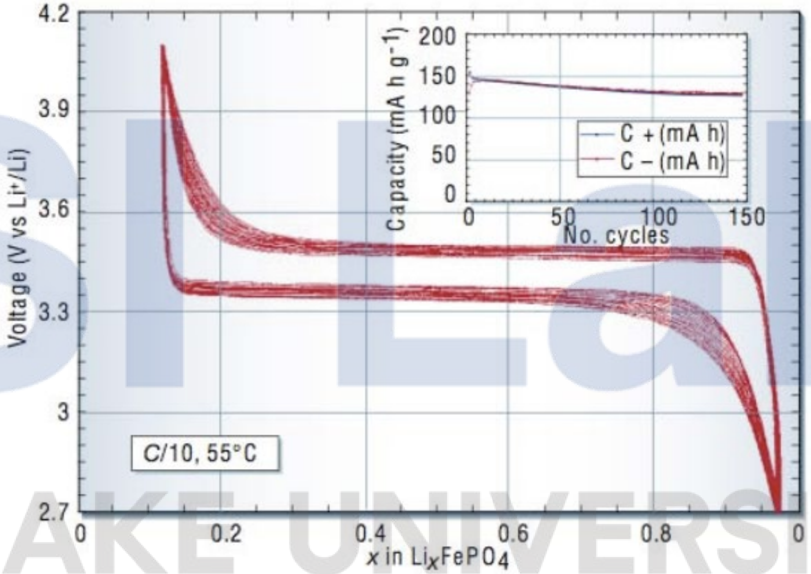
When $x = \frac{1}{2}$, $\mathrm{OCV} = E^0$

Compare predicted OCV~x curve with the real case

Theory



Reality

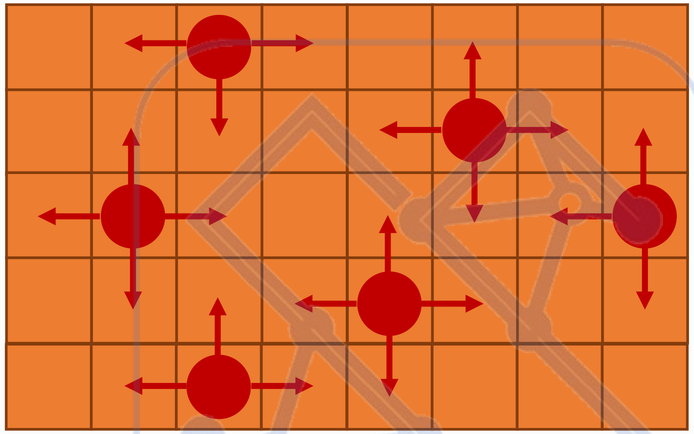


Tarascon, J.-M., and M. Armand. "Issues and challenges facing rechargeable lithium batteries." ***Nature*** 414 (2001): 359-367

- Not too bad for such a simple theory with A LOT of assumptions;
- ***How to explain the plateau in the charge-discharge curves?***

How to model the chemical potential of Li in electrode?

Regular Solution Model



🟧 = *lattice site*

● = *Li*

$$G(x) = H - TS$$

- In the ideal lattice gas model, we assume that there is no interactions between *Li* → $H = 0$
- We can relax this assumption by defining an enthalpy term ***(regular solution)*** → $H = h_0\, N\, x\,(1 - x)$

$$\boxed{G(x) = h_0 N x\,(1 - x) + k_B T\, N(x \ln x + (1 - x)\ln(1 - x))}$$

$$\Downarrow$$

$$\boxed{\mu(x) = \frac{1}{N}\frac{\partial G}{\partial x} = h_0\,(1 - 2x) + k_B T ln(\frac{x}{1 - x})}$$

$$\Rightarrow$$

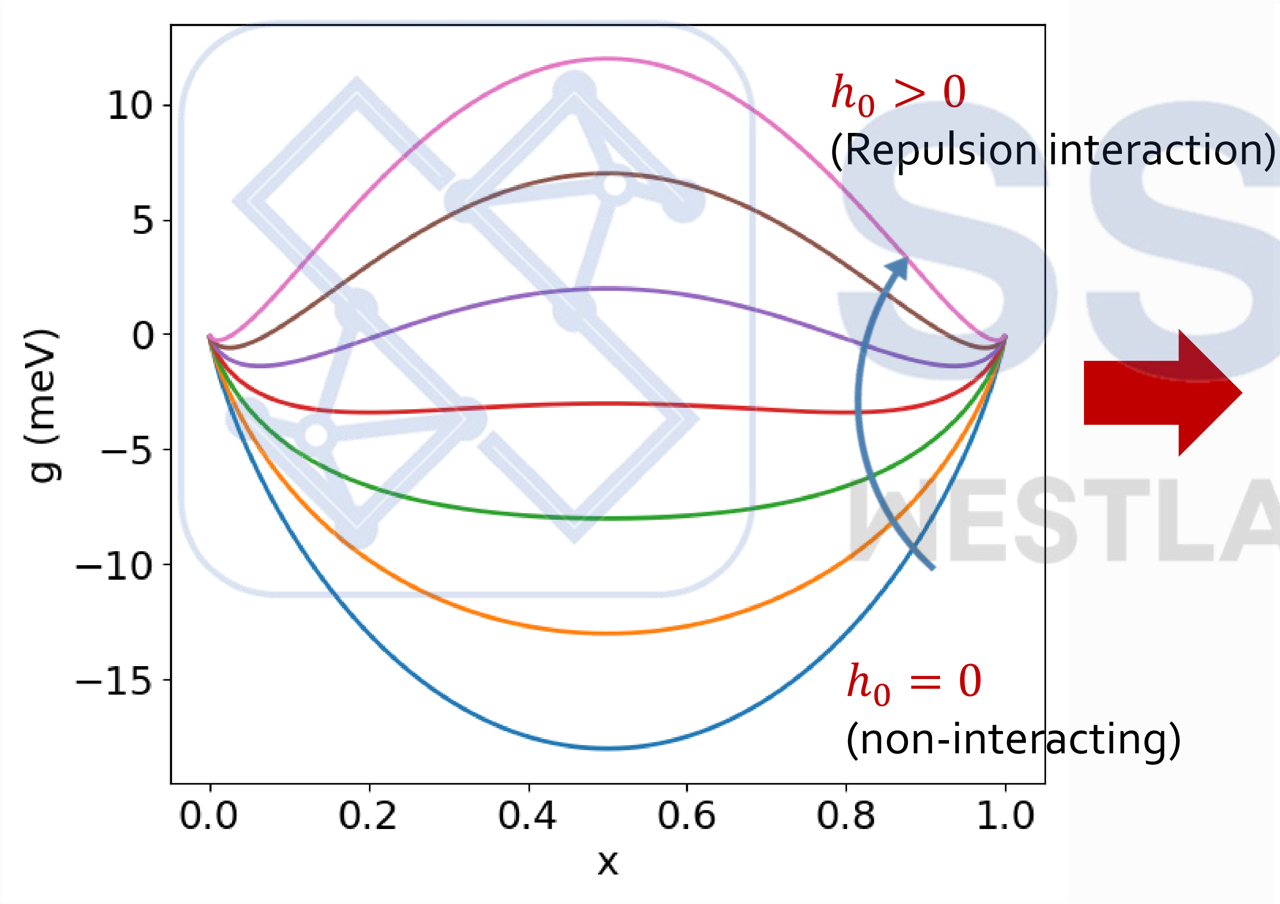
$$\boxed{OCV = E^0 + \frac{h_0}{e}(2x - 1) - \frac{k_B T}{e} ln(\frac{x}{1 - x})}$$

Note: h_0 can be positive (repulsion) or negative (attraction), but the former is more common

The effect of enthalpic and entropic terms in regular solution model

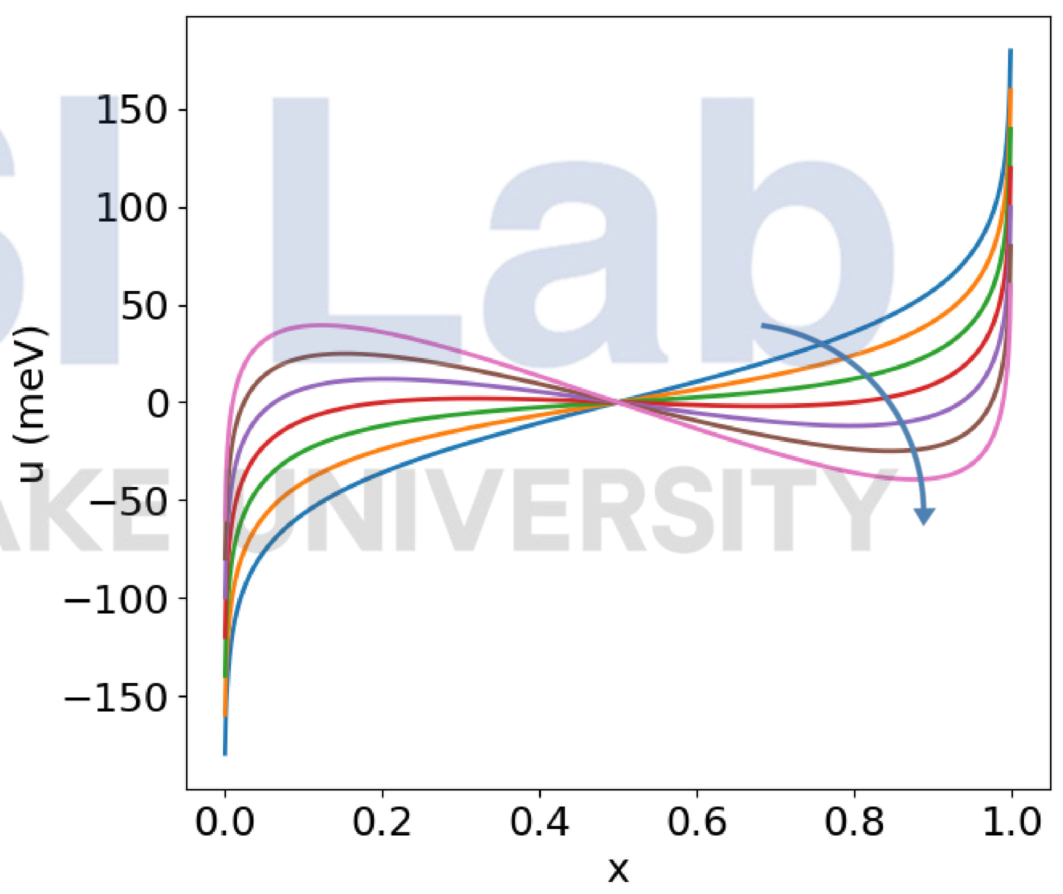
$$g(x) = h_0 x\,(1-x) + k_B T\,(x\ln x + (1-x)\ln(1-x))$$

$$\mu(x) = h_0\,(1-2x) + k_B T ln(\frac{x}{1-x})$$

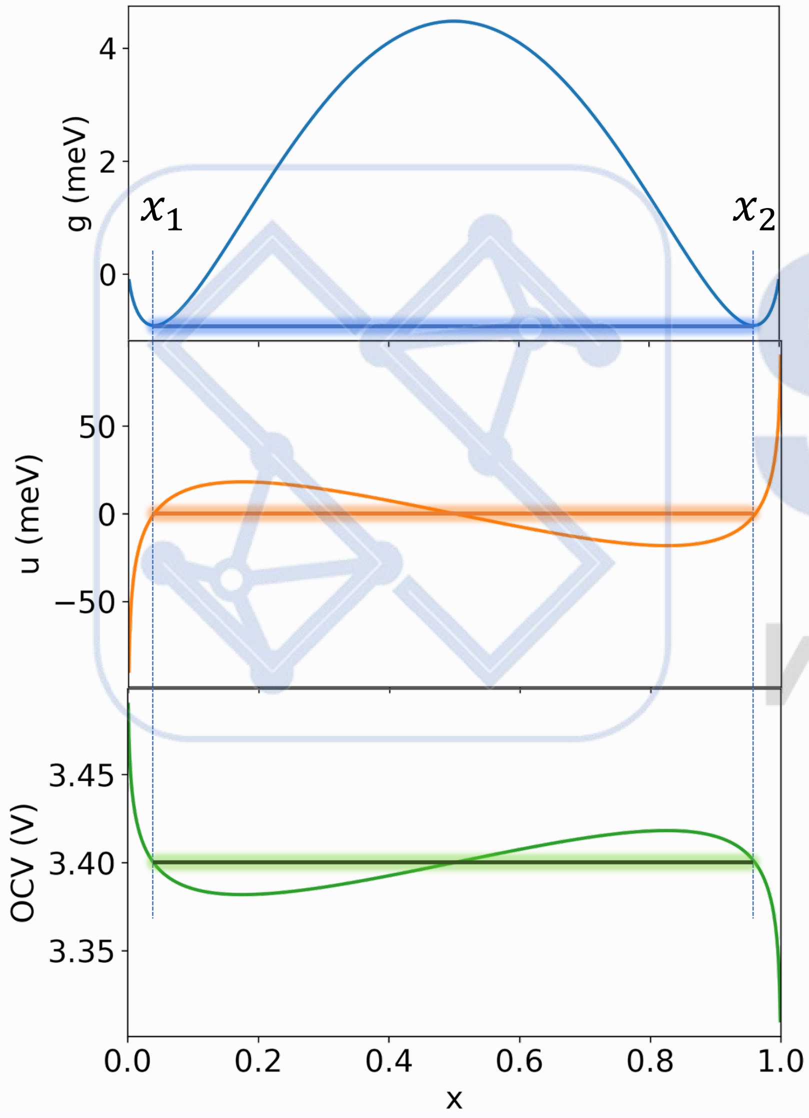


$h_0 > 0$
(Repulsion interaction)

$h_0 = 0$
(non-interacting)



Phase separation and voltage plateau in charge curves



$h_0 > 0$
(Repulsion interaction)

$$\mu(x) = \frac{\partial g}{\partial x}$$

$$OCV = E^0 - \mu(x)$$

At equilibrium, any overall composition between x_1 and x_2 will be decomposed into a mixed phase of x_1 and x_2

Therefore, if there is no kinetic effect (charge/discharge at very slow rate), then μ will be a flat line when $x_1 < x < x_2$

A constant OCV in the charge curve is then indicative of phase transitions in battery electrodes

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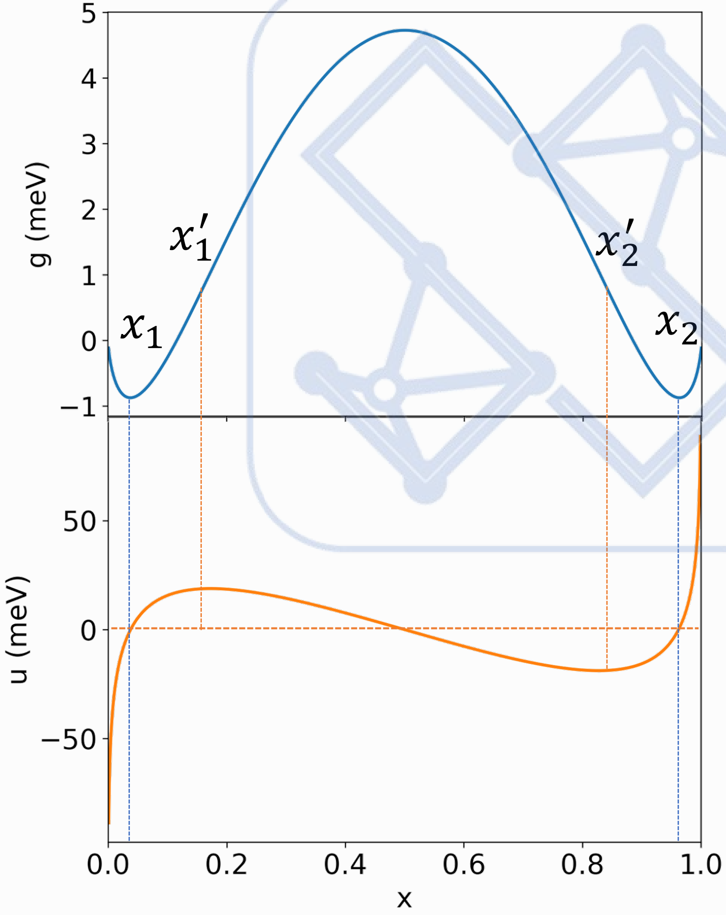
Spinodal decomposition

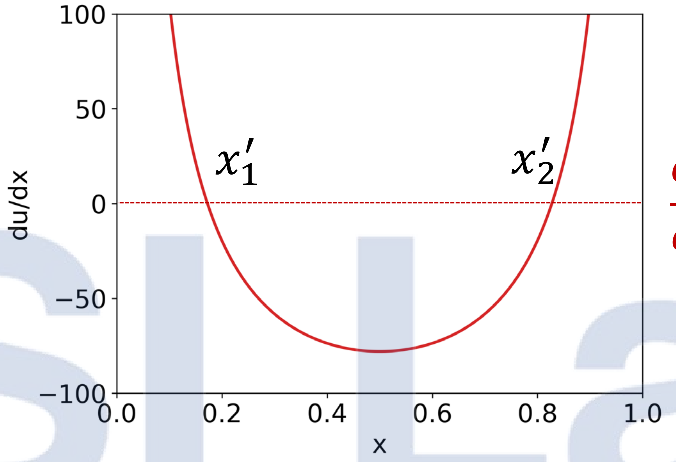
Let's look at the Gibbs free energy curve again

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



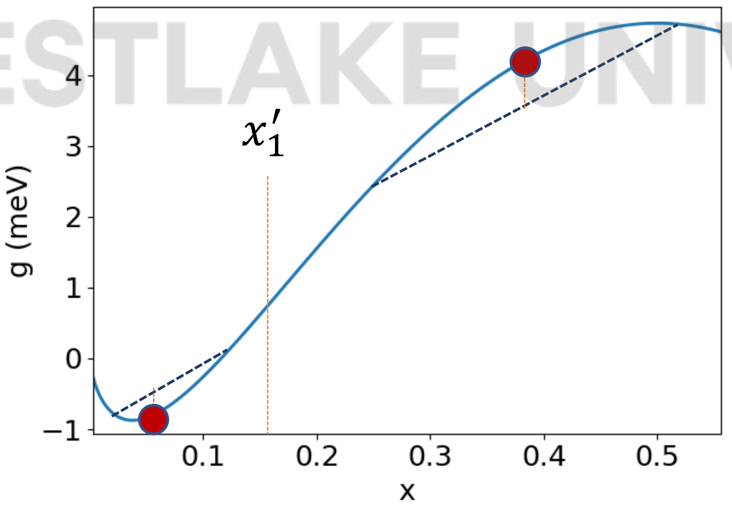
In this case, we set $h_0 = 3.5\,k_B T$

$$\mu(x) = \frac{\partial g}{\partial x}$$



$$\frac{\partial \mu}{\partial x} = \frac{\partial^2 g}{\partial x^2} = 0$$

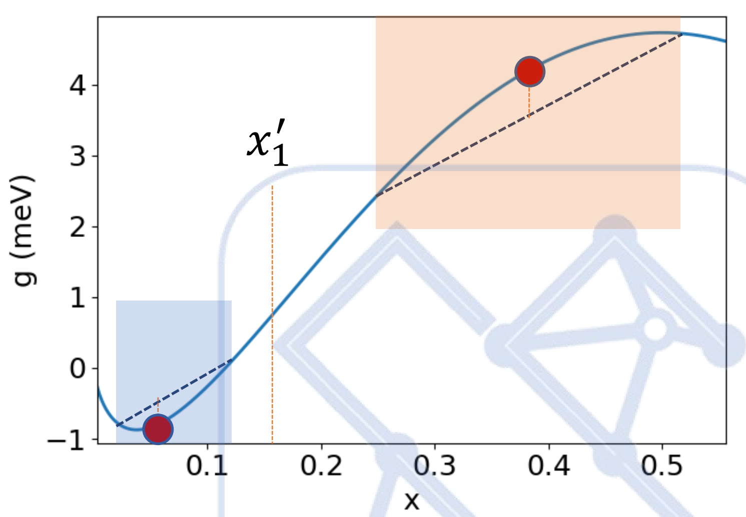
Chemical potential μ is the ***derivative*** of Gibbs free energy g

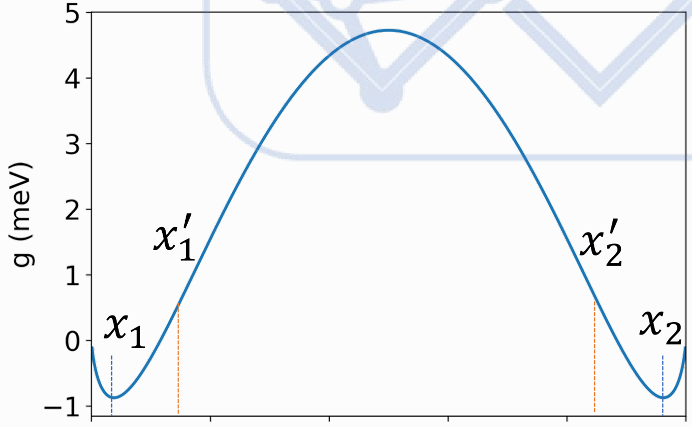


$0 < x < x_1'$: phase separation needs to overcome a ***barrier***;

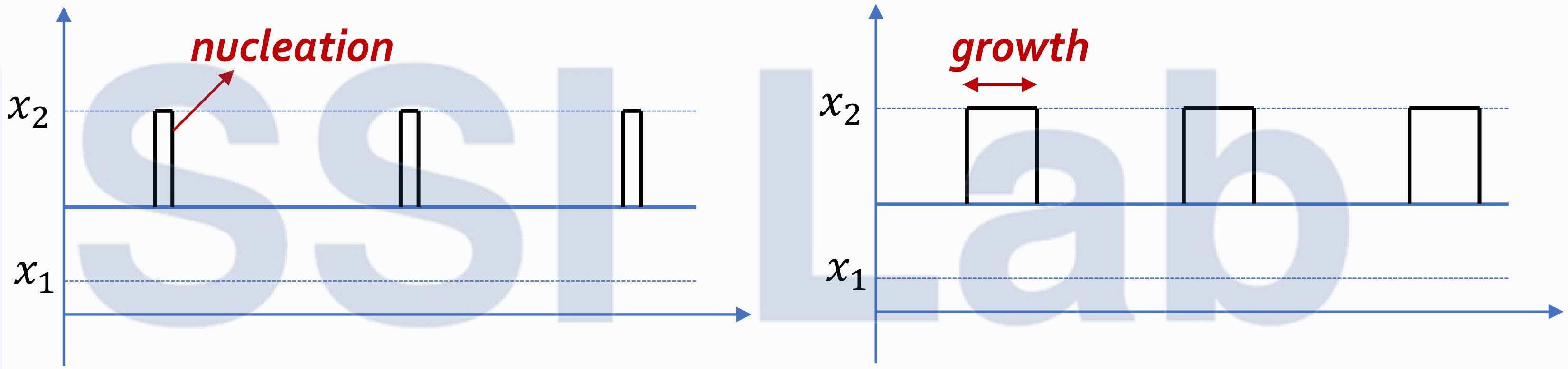
$x_1' < x < x_2'$: phase separation is ***spontaneous***;
so-called spinodal decomposition

Spinodal decomposition: small or large fluctuation in composition

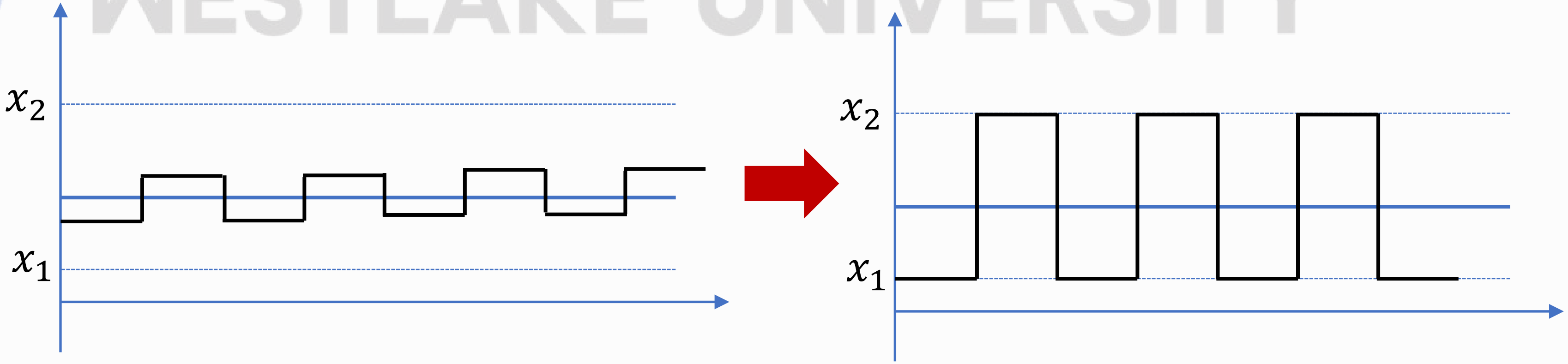




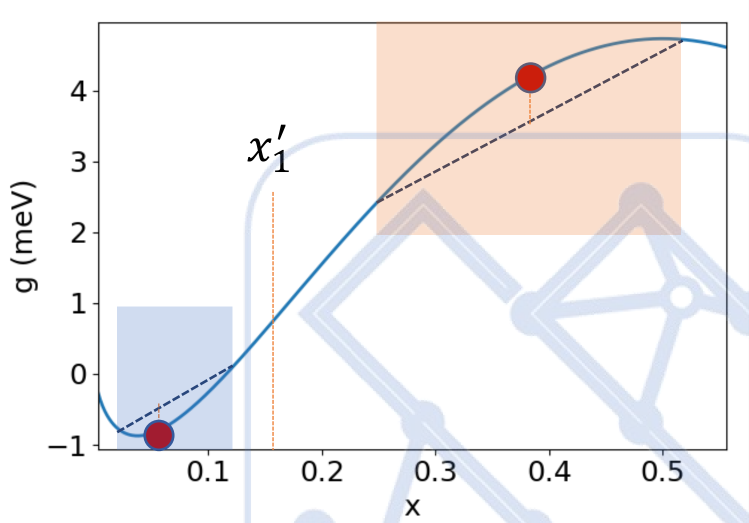
$0 < x < x_1'$: phase separation needs to overcome a ***barrier*** → needs a large fluctuation in composition

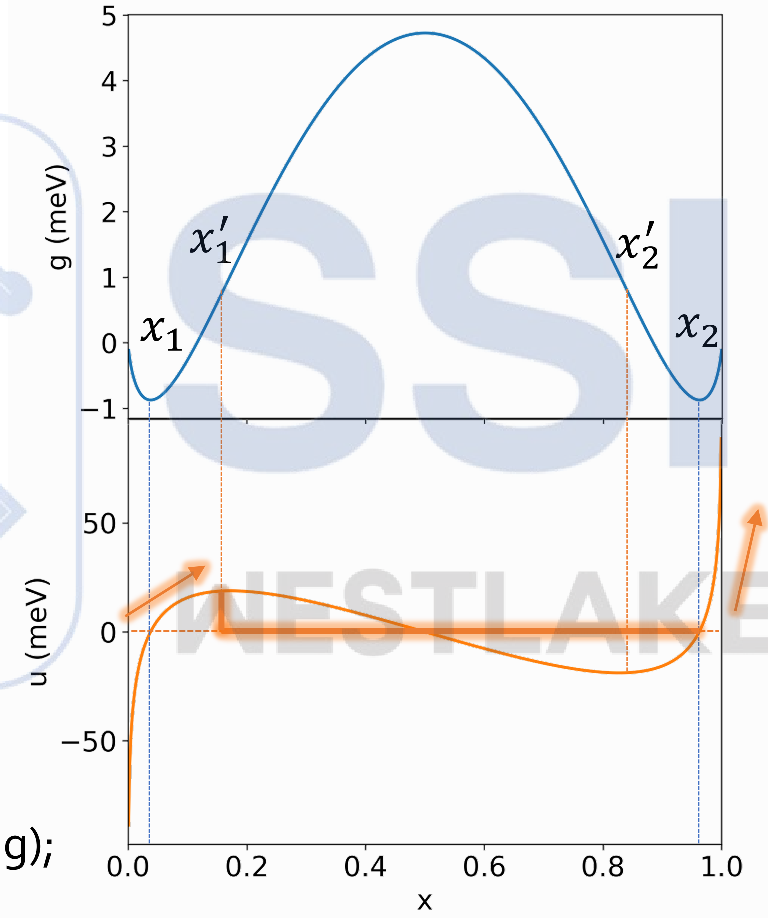


$x_1' < x < x_2'$: phase separation is ***spontaneous***; so-called ***spinodal decomposition***



Coming back to the charge/discharge curves



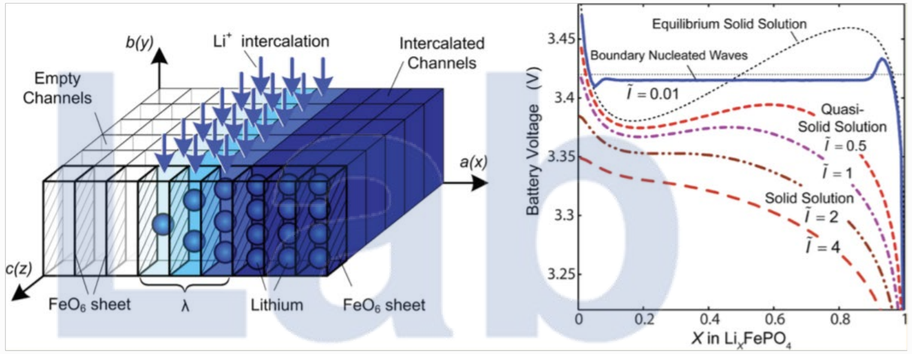


The shape of the charge/discharge curves can be affected by:

- Charging rate (kinetics);
- Direction (charging or discharging);
- Boundary condition ("bounce at walls");

Further reading:

Peng Bai and Martin Z. Bazant, ***Nano Lett.***, 2011, 11, 11, 4890–4896

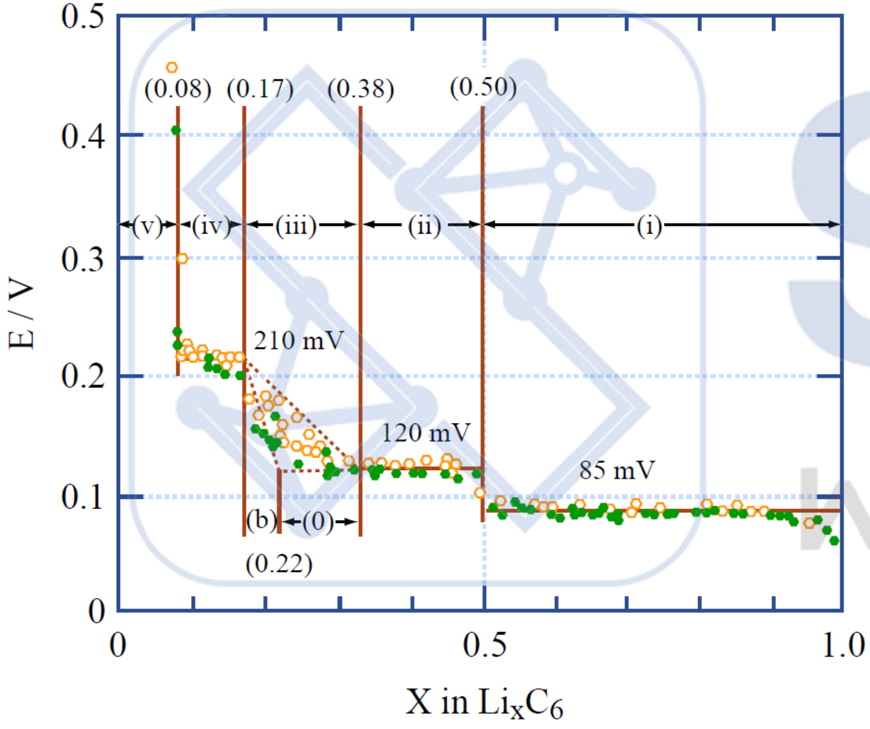


Prof. Martin Z. Bazant
(MIT)
Who taught my echem course :)

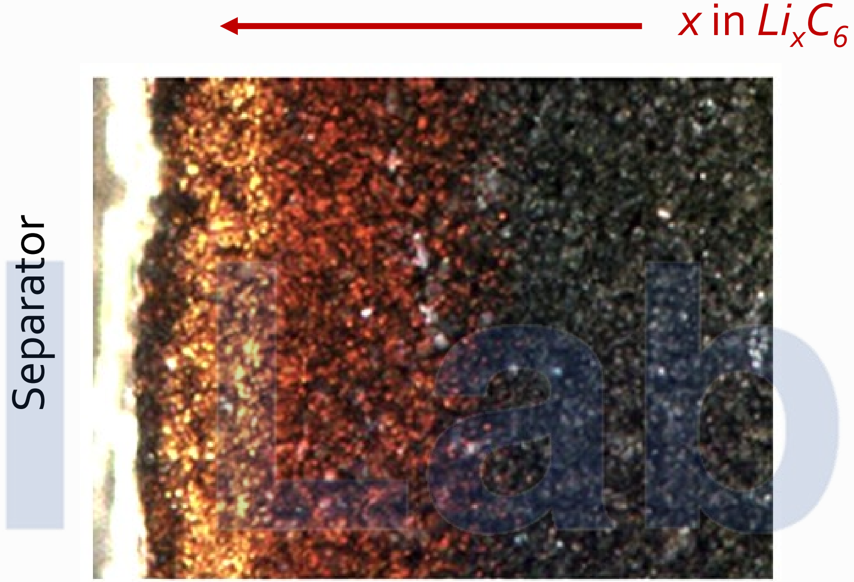
Prof. Peng Bai
(Washington
University in St. Loiuis)

Multiple phase separations: the case of lithiated graphite

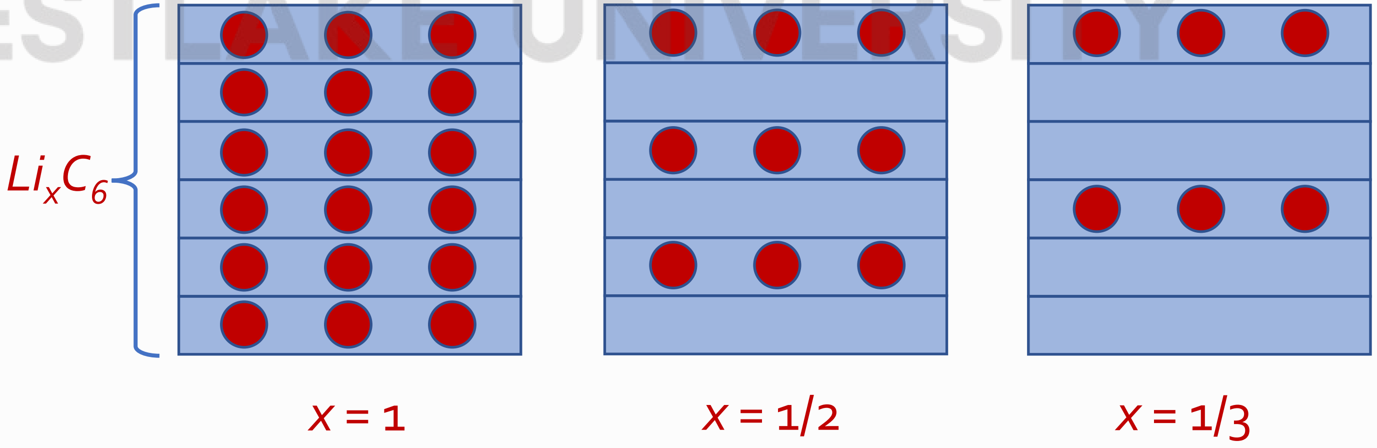
$xLi + C_6 \rightarrow Li_xC_6$



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



Harris et al., *Chem. Phys. Lett.*, 2010



Things we have discussed in this lecture

Solid-State Electrochemistry:

- What determines the open-circuit potential of an electrochemical system?
- How to build a model to predict the open-circuit potential for Li-ion battery cathode materials?
- What are the basic assumptions for the lattice gas model?

Goal of this lecture: you should be able to answer the questions above now (hopefully) :)

End of Lecture 9
Solid State Ionics Fall 2023

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