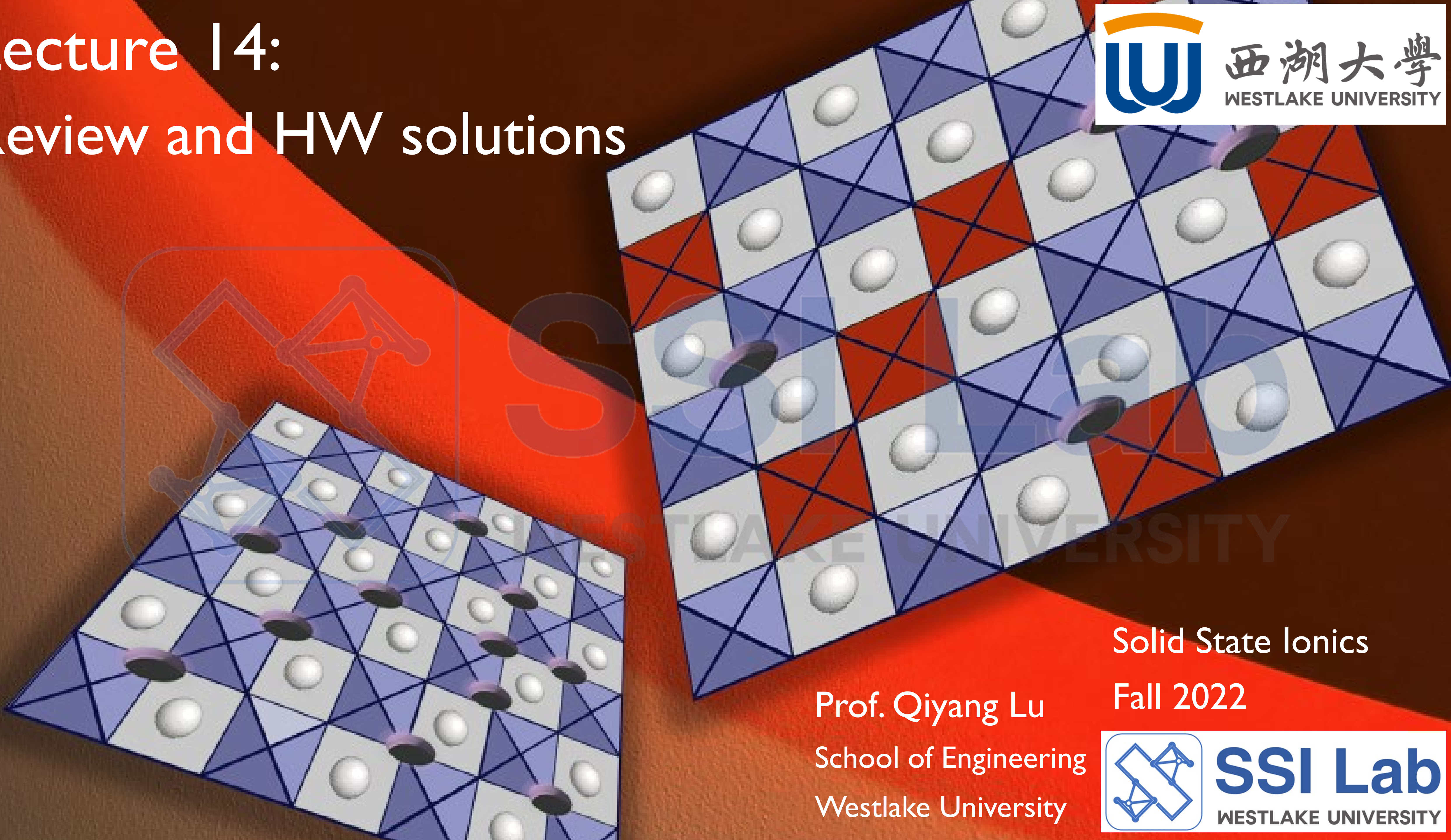
Lecture 14:
Review and HW solutions



Solid State Ionics

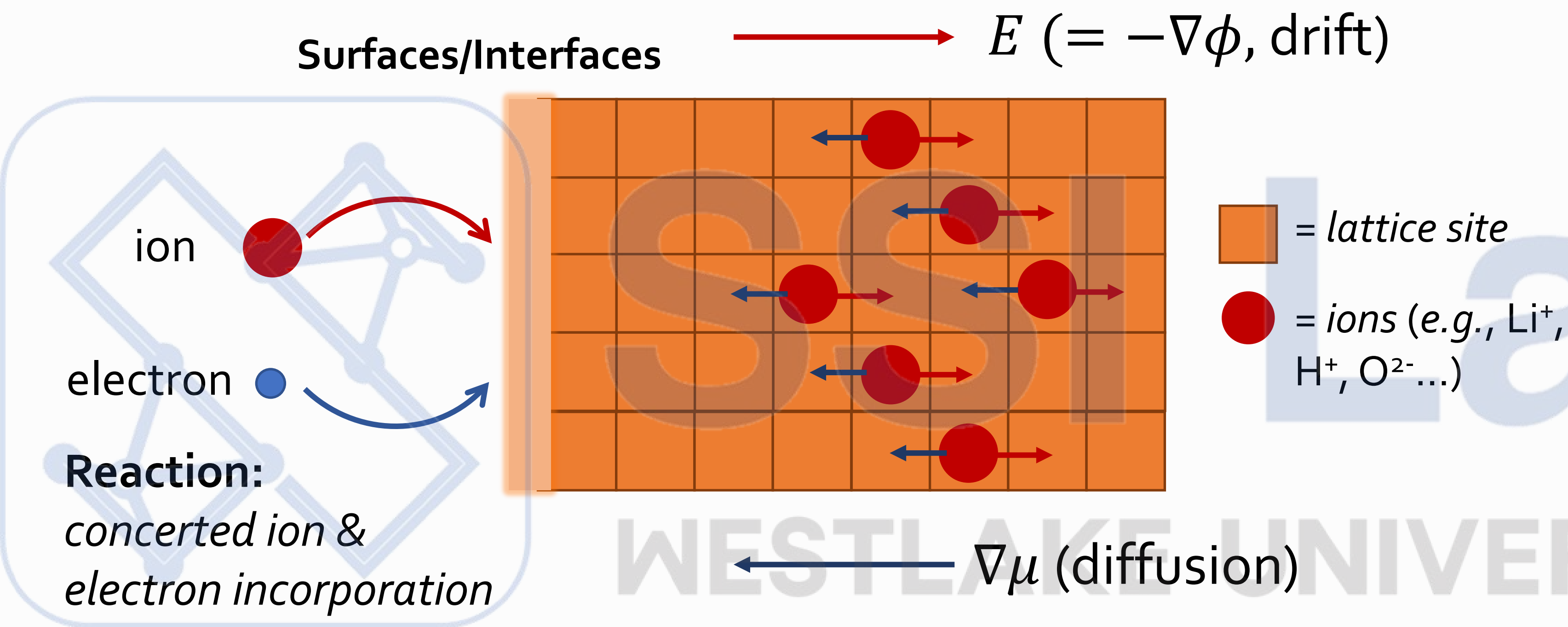
Fall 2022

Prof. Qiyang Lu

School of Engineering

Westlake University

Diffusion & Reactions of ions/ionic defects in solids



Ion motion: *drift + diffusion*

- Similar to electrons/holes in semiconductor physics;
- Ion mobility is much slower → totally different *temp. and time scales*.

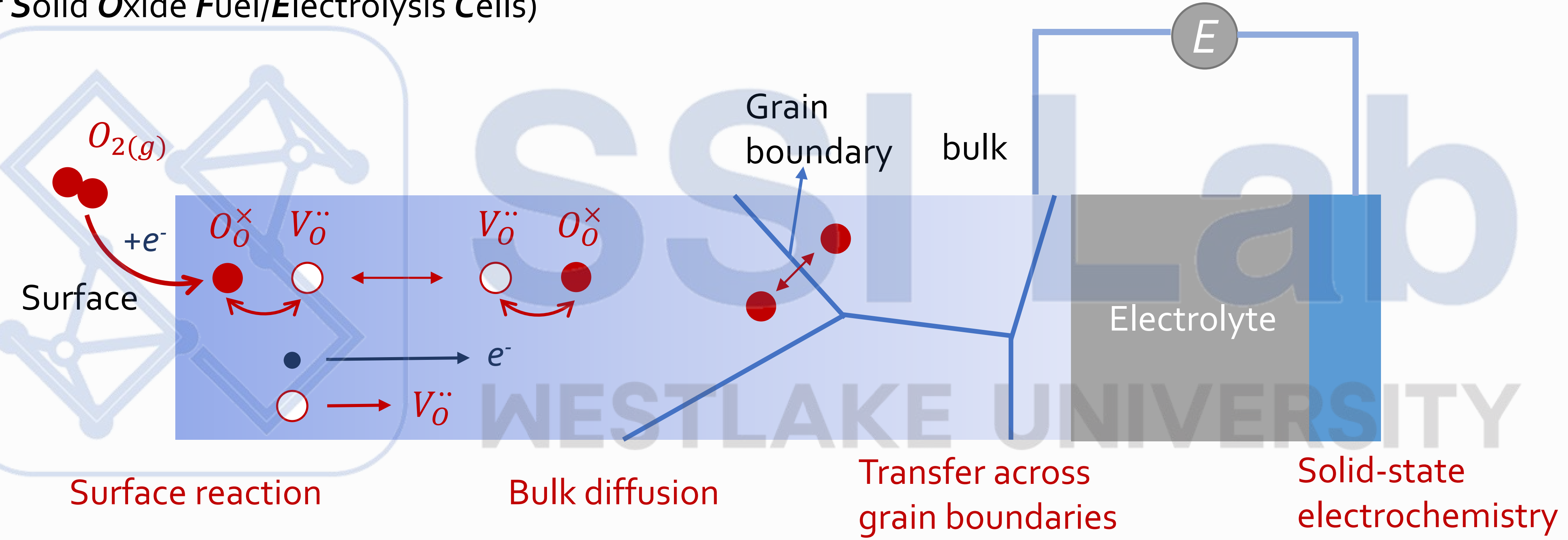
Goal:

By the end of the semester, you will have a clear physical picture on the ***diffusion & reactions*** related with ***ions in solid state*** and have the tools to analyze the *fundamental physical chemistry process*.

Diffusion & Reactions in Solid Oxide Cells (SOCs)

Example:

Mixed ionic and *electronic* conducting oxides at high temperature
(Electrodes for ***S***olid ***O***xide ***F***uel/***E***lectrolysis ***C***ells)



$$j_O = -k_{surf} c_{surf}$$

$$j_O = -D\nabla c$$

Review of course content

Defect chemical equilibrium

Brouwer diagram:

[def] ~ $ln a_i$

i = charge neutral species (*e.g.*, O2, Li)

Space charge layers (SCLs)

$$\phi(x_1) \neq \phi(x_2)$$

$$a_i(x_1) \neq a_i(x_2)$$

- Gouy-Chapman case
- Mott-Schottky case

"frozen" defects

$$\boxed{\frac{\partial \tilde{\mu}_i}{\partial x} = 0}$$

Solid State Ionics:
Transport and *Reaction* of *Ionic defects*

$$\boxed{\frac{\partial \tilde{\mu}_i}{\partial x} \neq 0}$$

$$\boxed{\tilde{\mu}_i = \mu_i^0 + RT ln a_i + z_i F\phi}$$

Ionic defect transport

- Diffusion: $\nabla\mu \neq 0$ ($\nabla c \neq 0$)
- Drift: $\nabla\phi \neq 0$
- Coupled drift-diffusion:

$$J_i = -\frac{\sigma_i}{z^2F^2}\nabla\tilde{\mu}_i$$

Concerted ion-electron transport

Chemical diffusivity:

$$D_O^\delta = \frac{RT}{4F^2}\frac{\sigma_O^\delta}{c_O^\delta}$$

Solid-state electrochemistry

- OCP: $E = (\tilde{\mu}_{e',a} - \tilde{\mu}_{e',c})/\mathrm{F}$
- Kinetics: Butler-Volmer *eqn.*
  Marcus(-Hush-Chidsey)

Review of course content: Homework 1-3

HW1

Defect chemical equilibrium

Brouwer diagram:

[def] ~ $ln a_i$

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HW2

Space charge layers (SCLs)

$\phi\,(x_1) \neq \phi\,(x_2)$

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HW2

Ionic defect transport

- Diffusion: $\nabla\mu \neq 0$ ($\nabla c \neq 0$)
- Drift: $\nabla\phi \neq 0$
- Coupled drift-diffusion:

$$J_i = -\frac{\sigma_i}{z^2F^2}\nabla\tilde{\mu}_i$$

Concerted ion-electron transport

Chemical diffusivity:

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HW3

Solid-state electrochemistry

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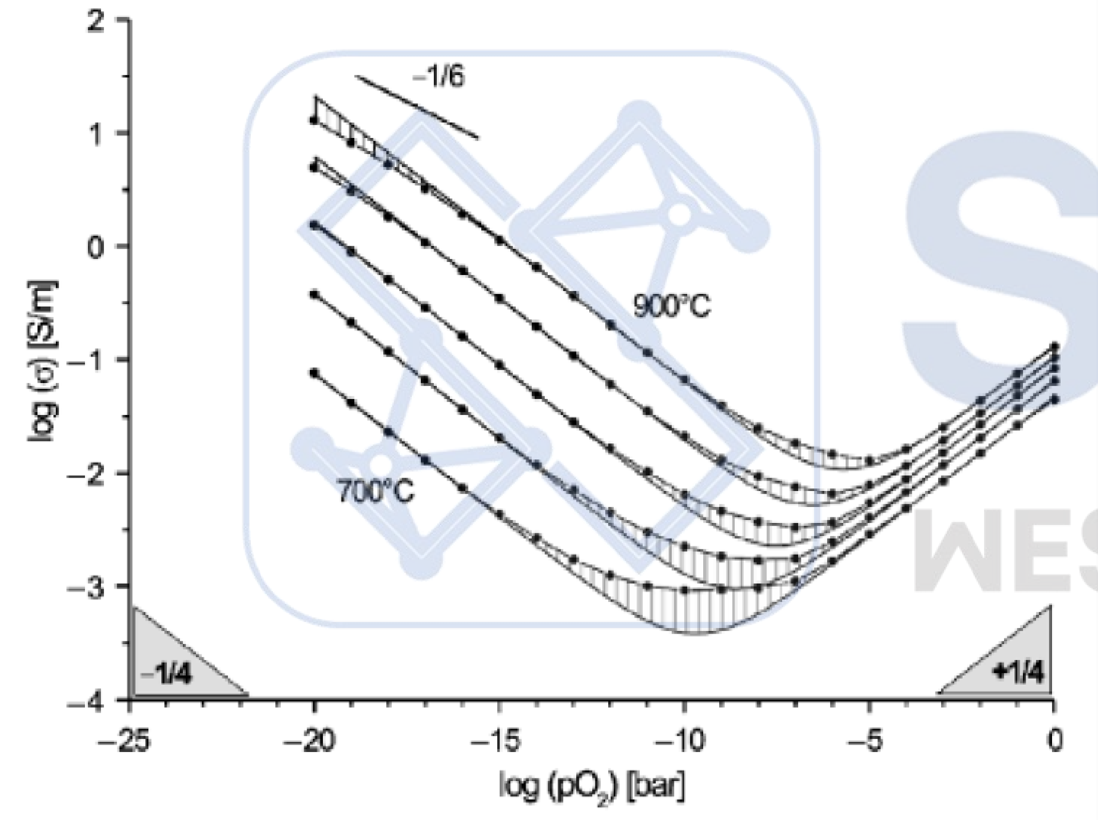
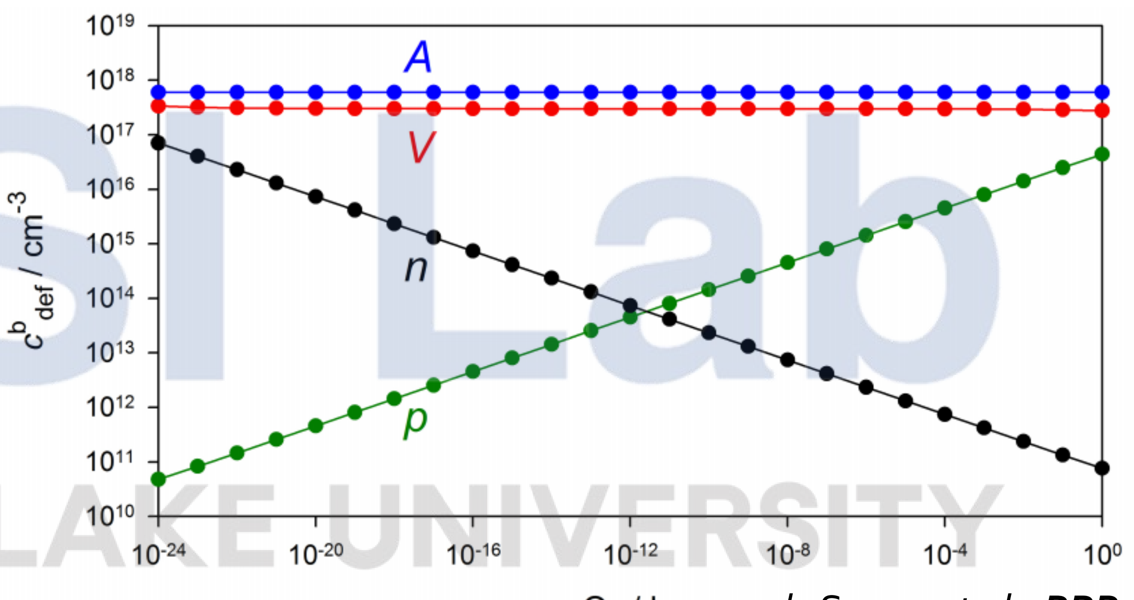
- Kinetics: Butler-Volmer *eqn.*
  Marcus(-Hush-Chidsey)

HW 1, Problem 1: Defect chemistry of $SrTiO_3$

log σ ~ log pO_2 plot of acceptor-doped $SrTiO_3$





de Souza *et al.*, ***PRB***, 2014

p = $[h^{\cdot}] \propto p_{O_2}{}^{1/4}$

n = $[e'] \propto p_{O_2}{}^{-1/4}$

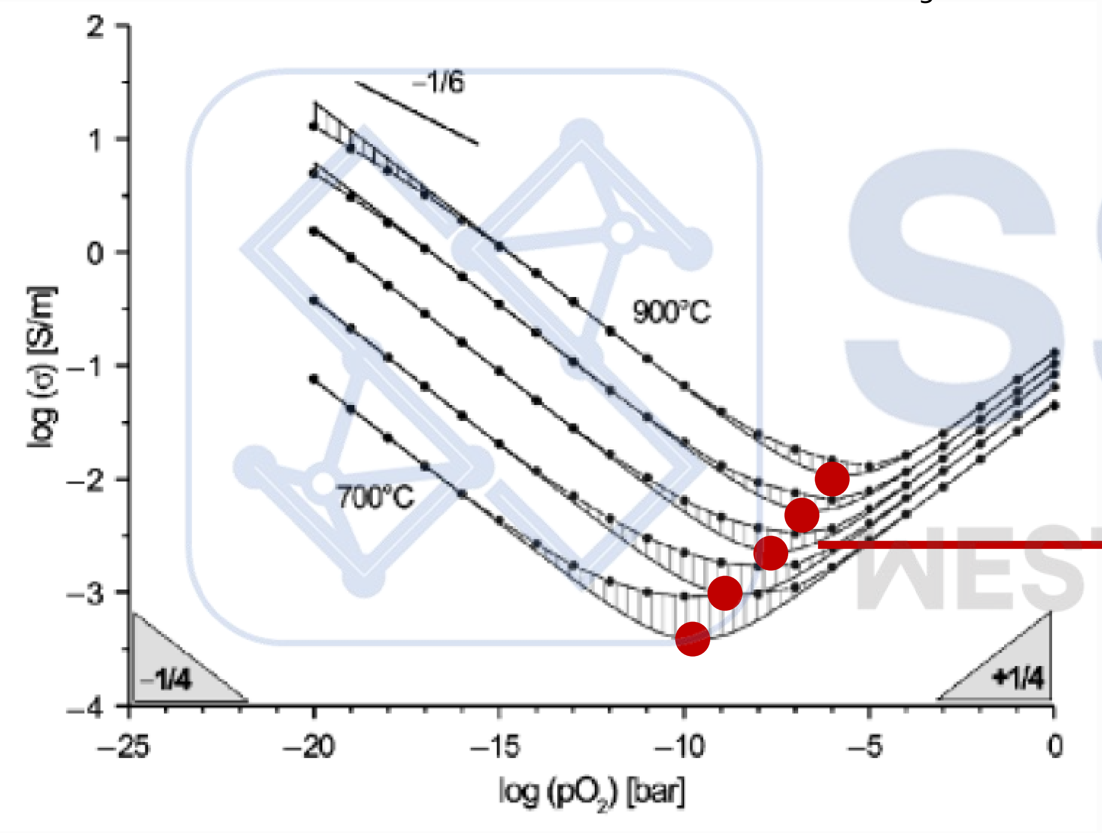
$$\sigma_{tot} = ne\mu_e + pe\mu_h + V(Z_V e)\mu_V$$

At ~973 K for $SrTiO_3$:

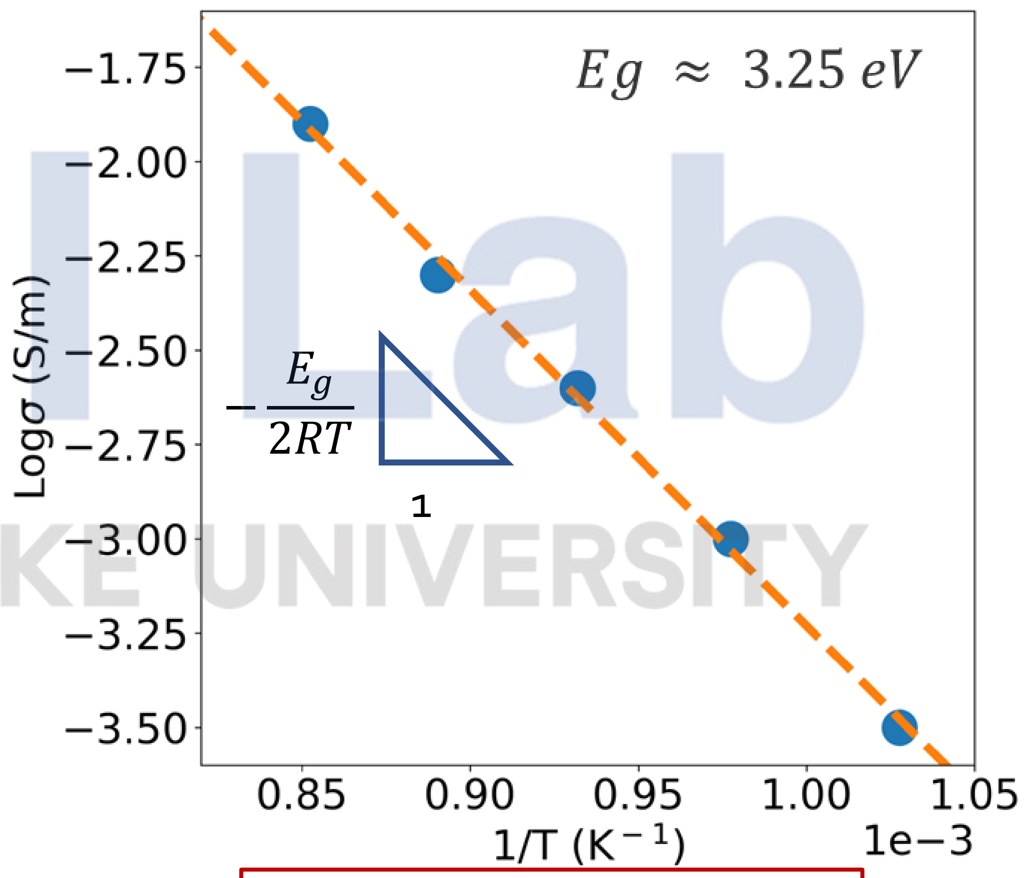
μ_e, μ_h ~ 0.1 cm²/(V·s) vs. μ_V ~ 4 x 10^{-4} cm²/(V·s)

HW 1, Problem 1: Defect chemistry of $SrTiO_3$

log σ ~ log pO_2 plot of acceptor-doped $SrTiO_3$



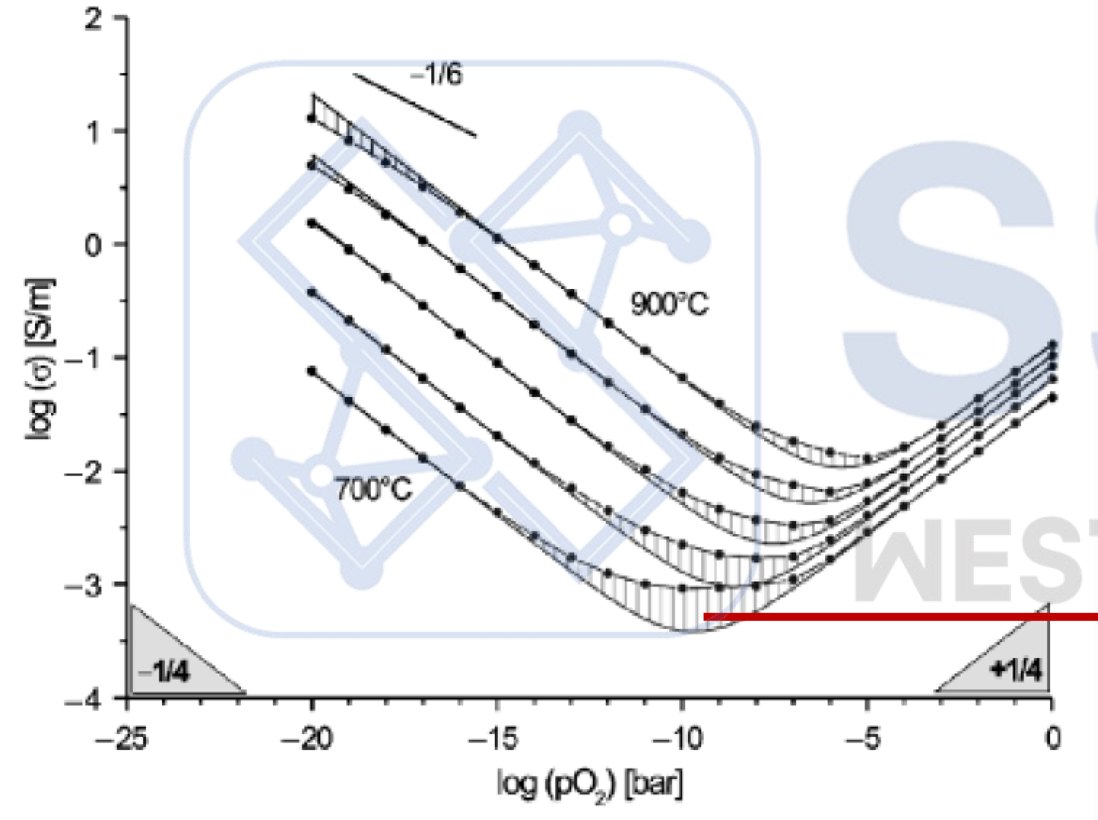
Lowest point in the log σ ~ log pO_2 plots



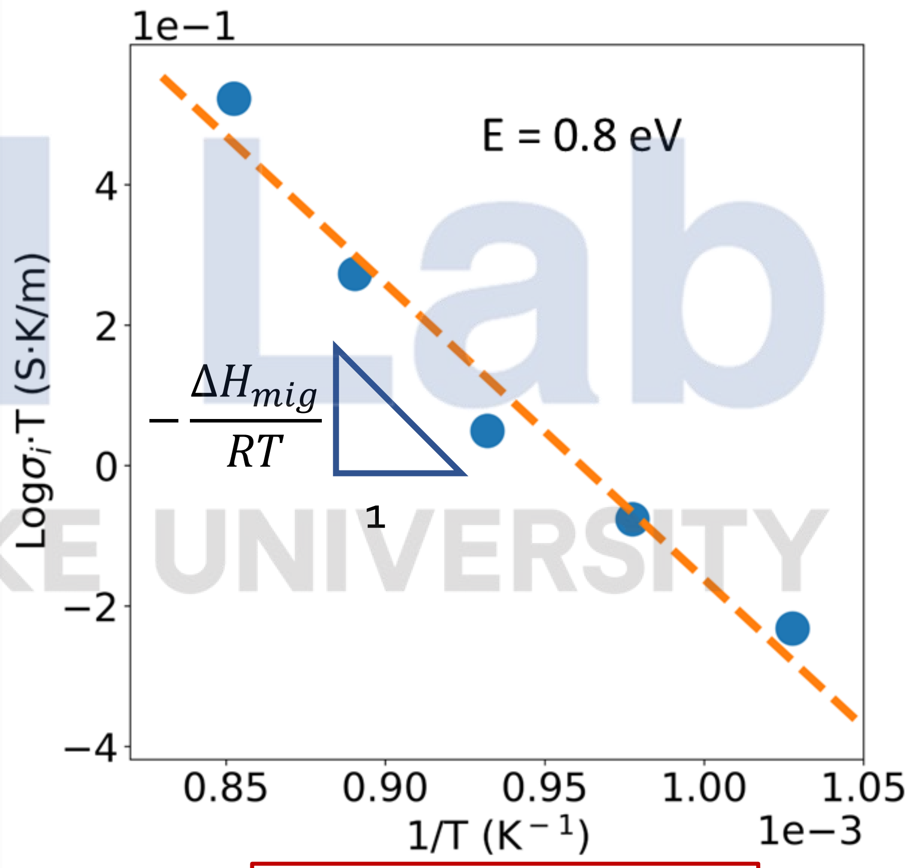
$$[h^{\cdot}] = [e'] \propto \exp(-\frac{E_g}{2RT})$$

HW 1, Problem 1: Defect chemistry of $SrTiO_3$

log σ ~ log pO_2 plot of acceptor-doped $SrTiO_3$

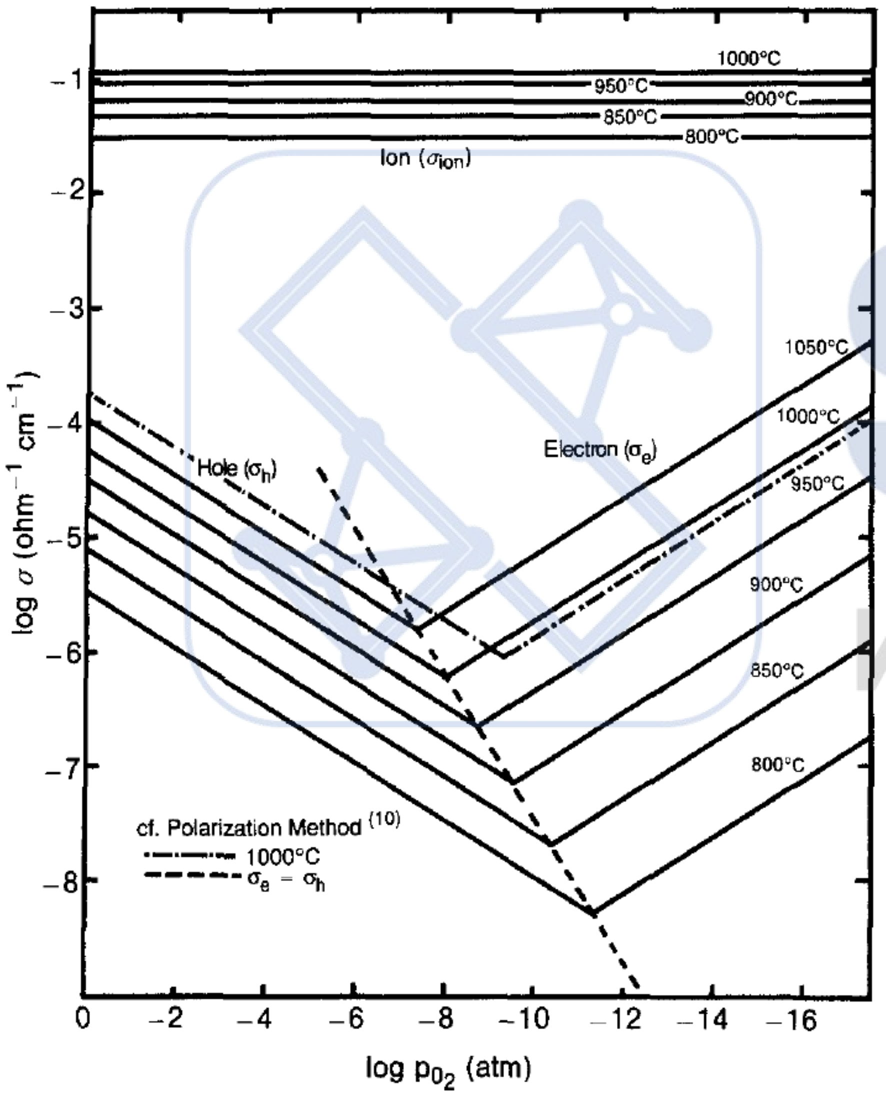


Shaded area in the log σ ~ log pO_2 plots



$$\sigma_{ion} \propto \exp\left(-\frac{\Delta H_{mig}}{RT}\right)$$

HW 1, Problem 11: "p-n junction" in yittria-stablized zirconia (YSZ)



$$\boxed{O_O^{\times} \leftrightharpoons V_O^{\cdot\cdot} + 2e' + 1/2O_2}$$

For $(Y_2O_3)_{0.08}(ZrO_2)_{0.9}$ (so-called 8YSZ), $[V_O^{\cdot\cdot}]$ is fixed by Y dopants

p = $[h^{\cdot}] \propto {p_{O_2}}^{1/4}$

n = $[e'] \propto {p_{O_2}}^{-1/4}$

$$\sigma_{tot} = ne\mu_e + pe\mu_h + [V_O^{\cdot\cdot}](Z_{V_O^{\cdot\cdot}}e)\mu_{V_O^{\cdot\cdot}} \longrightarrow$$ Ionic conductivity dominates

Electronic current density: $j_{e^-} = -F\,J_{e^-} = \frac{\sigma_{e^-}}{F}\nabla\tilde{\mu}_{e^-} \quad (z_{e^-} = -1)$

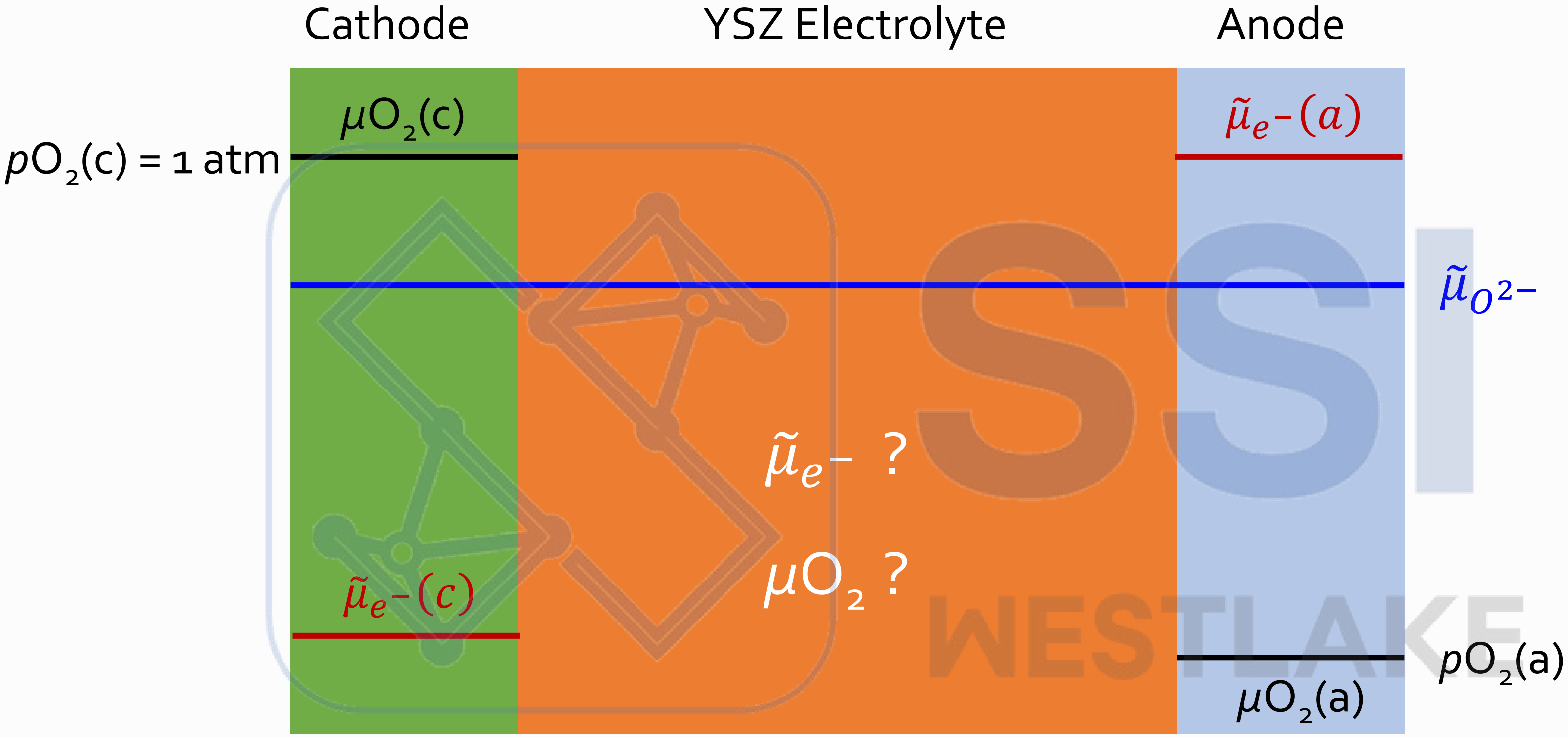
$$j_{h^+} = F\,J_{h^+} = -\frac{\sigma_{h^+}}{F}\nabla\tilde{\mu}_{h^+} \quad (z_{h^+} = 1)$$

$$j_{eon} = j_{e^-} + j_{h^+} = \frac{\sigma_{e^-}}{F}\nabla\tilde{\mu}_{e^-} - \frac{\sigma_{h^+}}{F}\nabla\tilde{\mu}_{h^+} = \frac{\sigma_{e^-} + \sigma_{h^+}}{F}\nabla\tilde{\mu}_{e^-}$$

$$(\tilde{\mu}_{e^-} = -\tilde{\mu}_{h^+})$$

Park *et al.*, *J. Electrochem. Soc.*, **136**(10) 2867 (1989)

HW 1, Problem 11: "p-n junction" in yittria-stablized zirconia (YSZ)



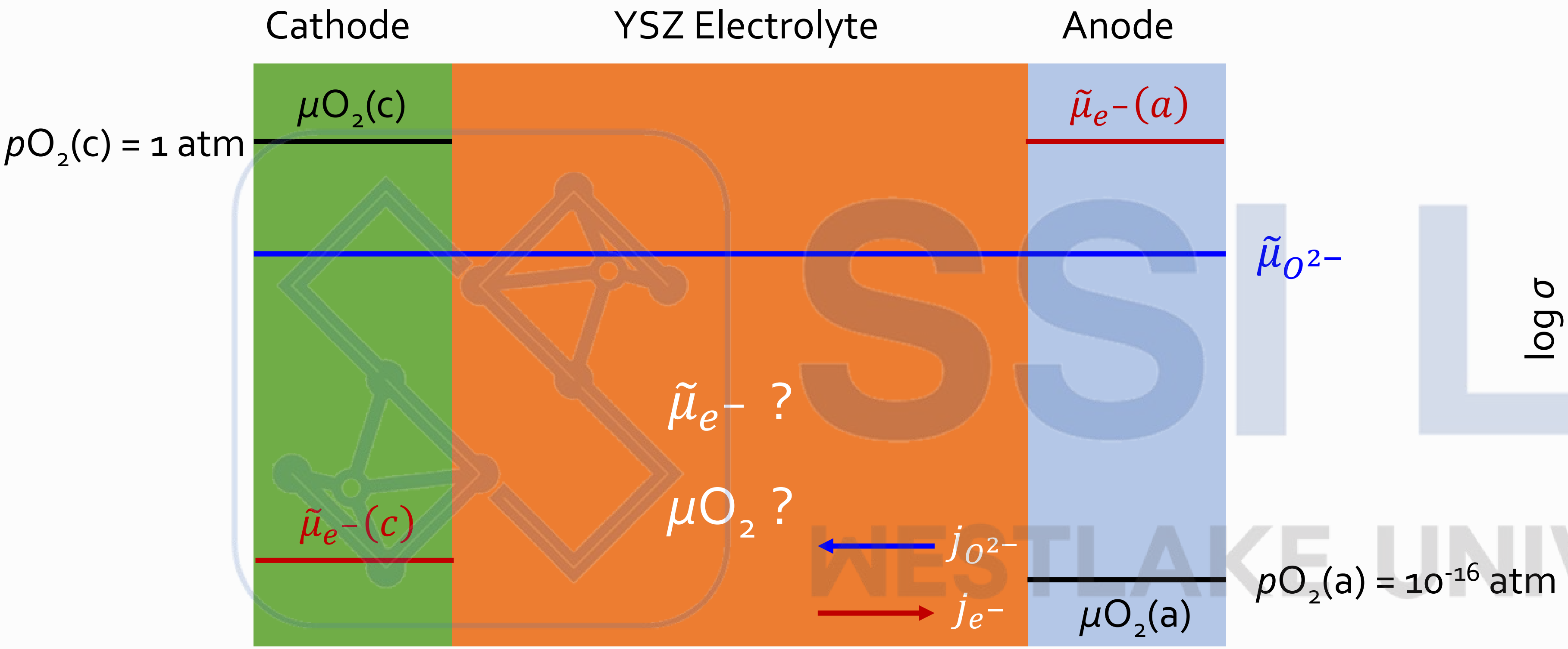
Note:

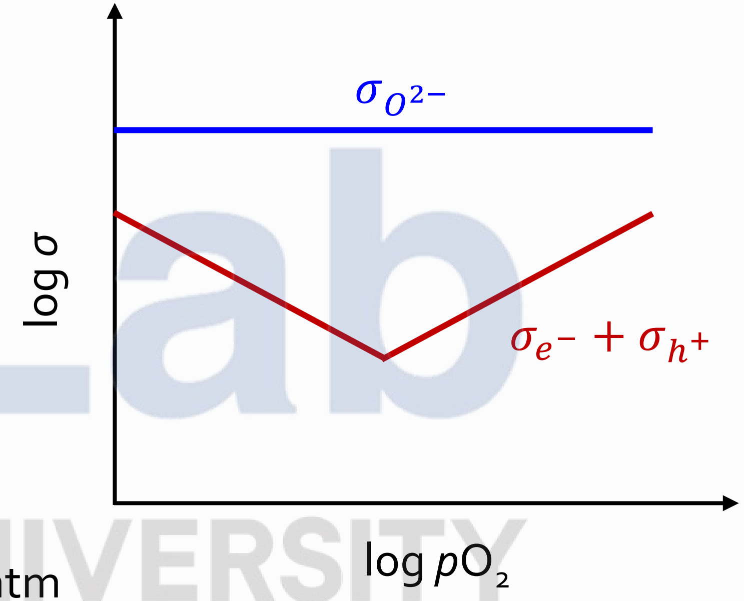
- At open-circuit condition, $\tilde{\mu}_{O^{2-}}$ is uniform across the electrolyte;
- $OCV = -1/\mathrm{F}\left(\tilde{\mu}_{e^-}(c) - \tilde{\mu}_{e^-}(a)\right)$

$\frac{1}{2}\mu_{O_2}(c) + 2\tilde{\mu}_{e^-}(c) = \tilde{\mu}_{O^{2-}}(lyte)$

$\tilde{\mu}_{O^{2-}}(lyte) = \frac{1}{2}\mu_{O_2}(a) + 2\tilde{\mu}_{e^-}(a)$

HW 1, Problem 11: “p-n junction” in yittria-stablized zirconia (YSZ)





$$j_{e^-} = -j_{O^{2-}} = j_0$$

$$\sigma_{O^{2-}} \gg \sigma_{e^-} + \sigma_{h^+}$$

$$\downarrow$$

$$\frac{\partial \tilde{\mu}_{e^-}}{\partial x} \gg -\frac{\partial \tilde{\mu}_{O^{2-}}}{\partial x}$$

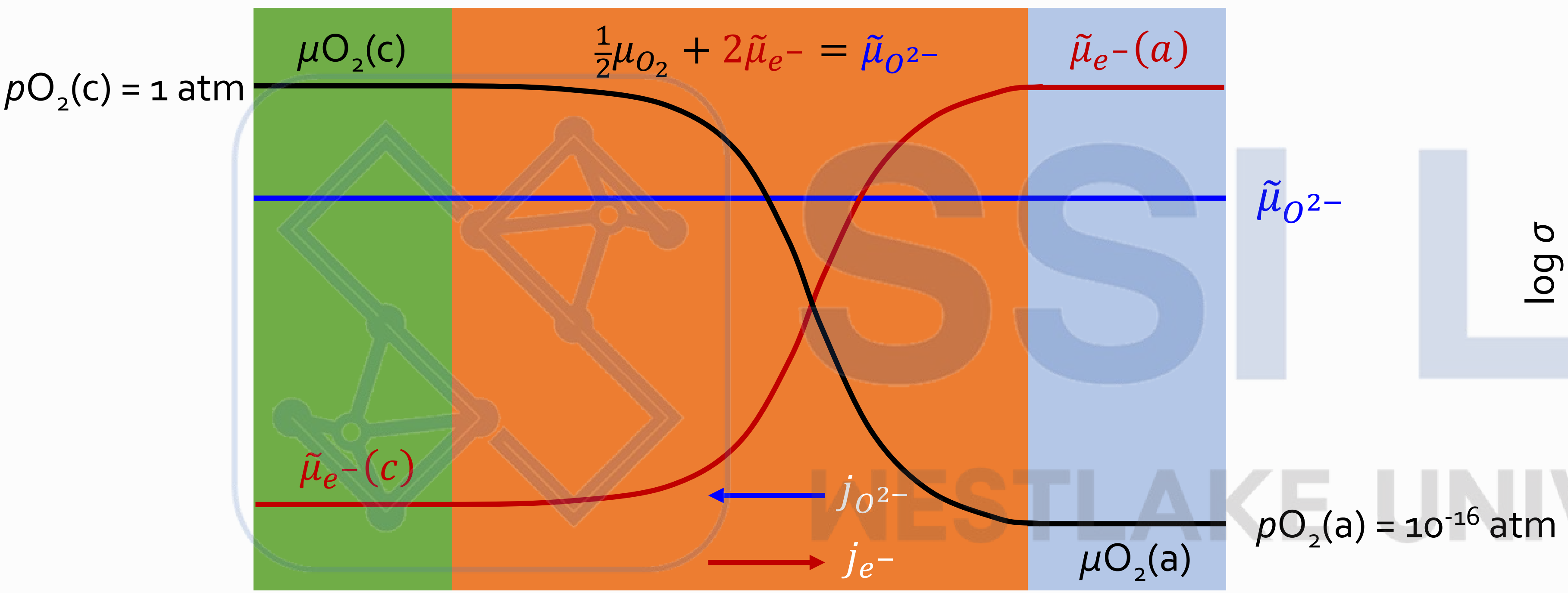
$$j_{eon} = j_{e^-} = \frac{\sigma_{e^-} + \sigma_{h^+}}{F} \nabla \tilde{\mu}_{e^-}$$

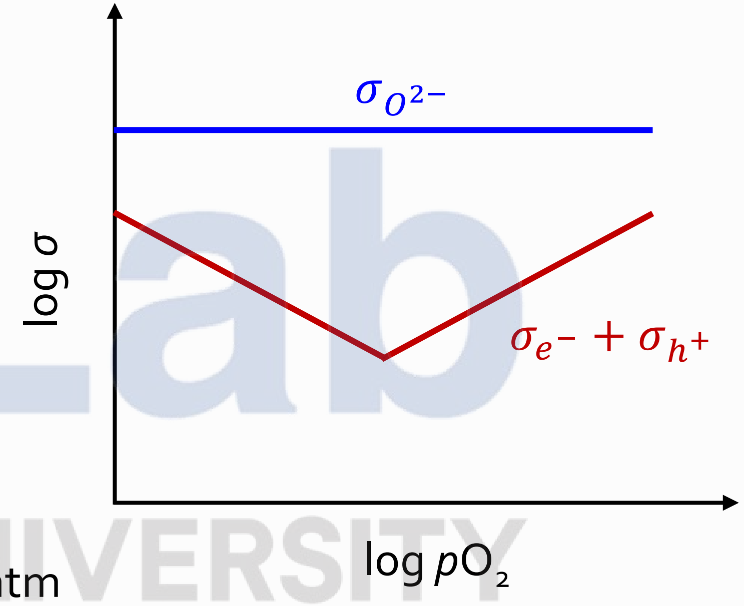
$$j_{ion} = j_{O^{2-}} = \frac{\sigma_{O^{2-}}}{2F} \nabla \tilde{\mu}_{O^{2-}}$$

Constant inside the YSZ electrolyte

Westlake University 西湖大學

HW 1, Problem 11: "p-n junction" in yittria-stablized zirconia (YSZ)





$$j_{eon} = j_{e^-} = \frac{\sigma_{e^-} + \sigma_{h^+}}{F} \nabla \tilde{\mu}_{e^-}$$

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Constant inside the YSZ electrolyte

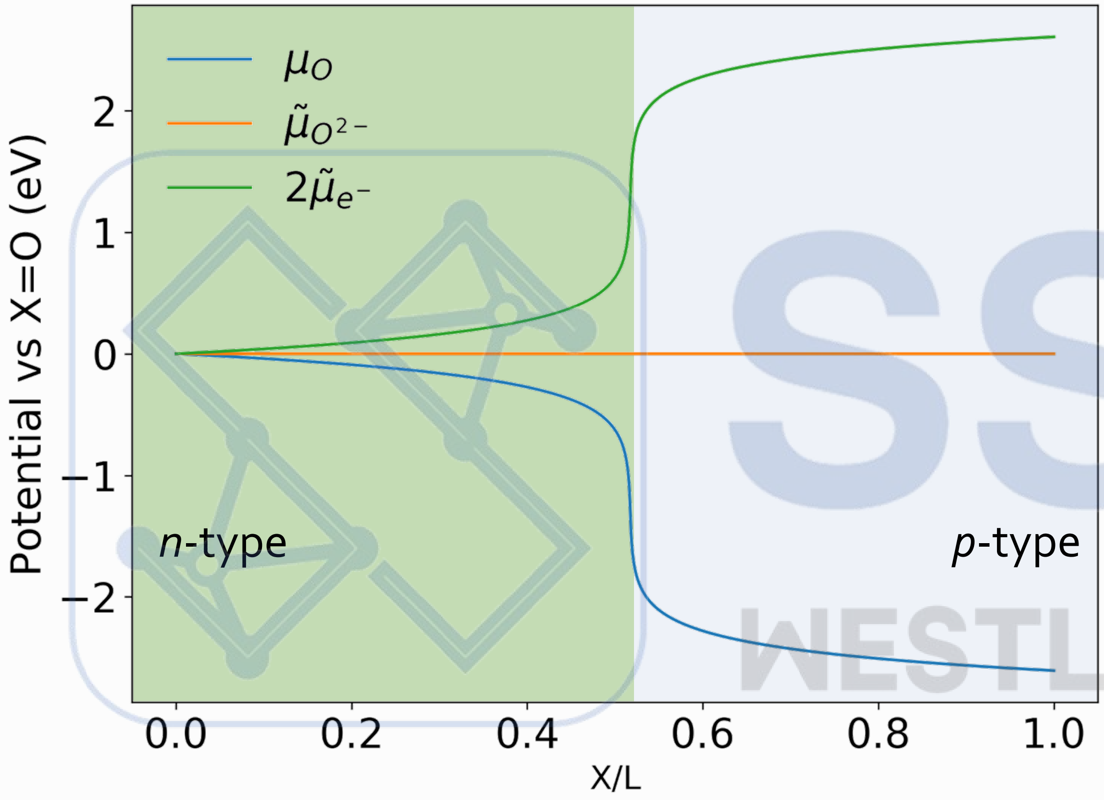
$$j_{e^-} = -j_{O^{2-}} = j_0$$

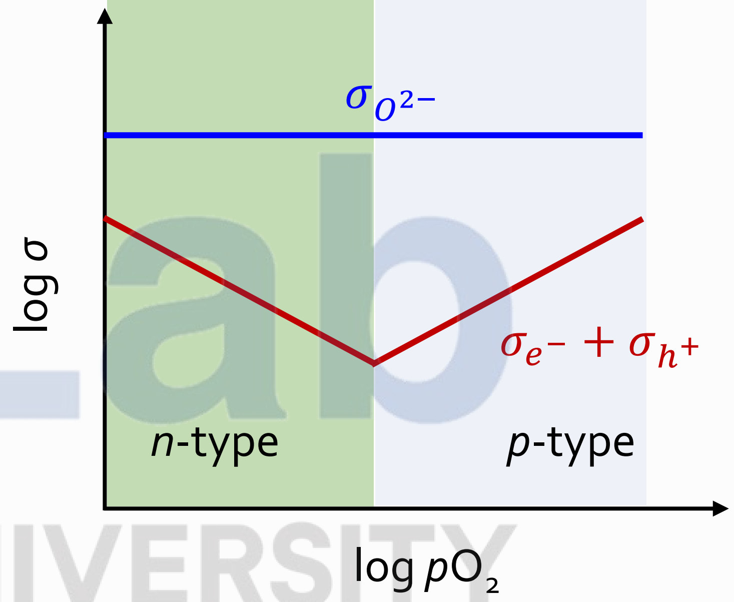
$$\sigma_{O^{2-}} \gg \sigma_{e^-} + \sigma_{h^+}$$

$$\downarrow$$

$$\frac{\partial \tilde{\mu}_{e^-}}{\partial x} \gg -\frac{\partial \tilde{\mu}_{O^{2-}}}{\partial x}$$

HW 1, Problem 11: "p-n junction" in yittria-stablized zirconia (YSZ)





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Constant inside the YSZ electrolyte

$$j_{e^-} = -j_{O^{2-}} = j_0$$

$$\sigma_{O^{2-}} \gg \sigma_{e^-} + \sigma_{h^+}$$

$$\Downarrow$$

$$\frac{\partial \tilde{\mu}_{e^-}}{\partial x} \gg -\frac{\partial \tilde{\mu}_{O^{2-}}}{\partial x}$$

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Defect chemical equilibrium

Brouwer diagram:

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Transport and *Reaction* of *Ionic defects*

$$\boxed{\frac{\partial \tilde{\mu}_i}{\partial x} \neq 0}$$

$$\boxed{\tilde{\mu}_i = \mu_i^0 + RTlna_i + z_iF\phi}$$

HW2

Ionic defect transport

- Diffusion: $\nabla\mu \neq 0$ ($\nabla c \neq 0$)
- Drift: $\nabla\phi \neq 0$
- Coupled drift-diffusion:

$$J_i = -\frac{\sigma_i}{z^2F^2}\nabla\tilde{\mu}_i$$

Concerted ion-electron transport

Chemical diffusivity:

$$D_O^\delta = \frac{RT}{4F^2}\frac{\sigma_O^\delta}{c_O^\delta}$$

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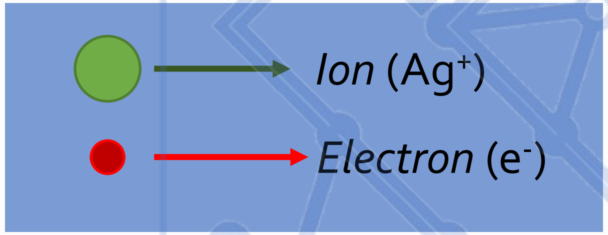
Solid-state electrochemistry

- OCP: $E = (\tilde{\mu}_{e',a} - \tilde{\mu}_{e',c})/\mathrm{F}$
- Kinetics: Butler-Volmer *eqn.*
  Marcus(-Hush-Chidsey)

HW II, Problem I: "Job-sharing" mass transport

Mixed ionic & electronic conductor (MIEC)



Chemical diffusion

$$J_{Ag^+} = -\frac{\sigma_{Ag^+}}{F^2}\nabla\tilde{\mu}_{Ag^+} = -\frac{\sigma_{Ag^+}}{F^2}(\nabla\mu_{Ag^+} + F\nabla\phi)$$

$$J_{e^-} = -\frac{\sigma_{e^-}}{F^2}\nabla\tilde{\mu}_{e^-} = -\frac{\sigma_{e^-}}{F^2}(\nabla\mu_{e^-} - F\nabla\phi)$$

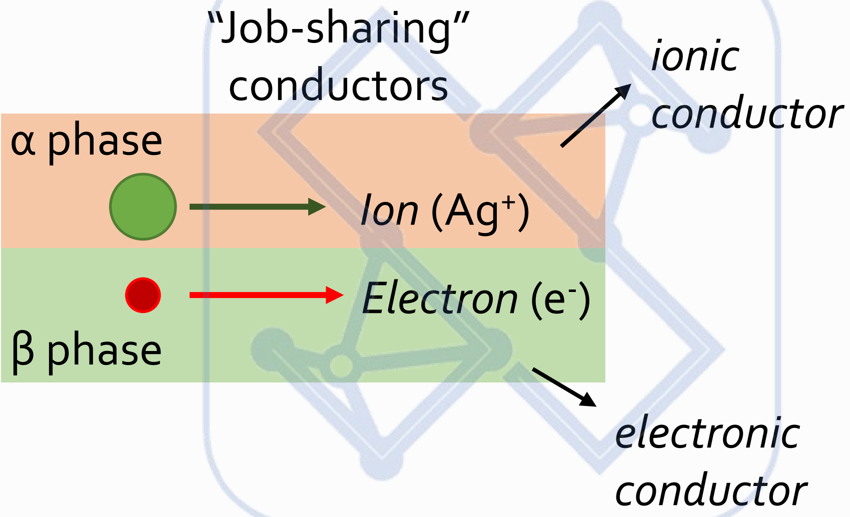
$$J_{Ag} = J_{Ag^+} = J_{e^-} \longrightarrow$$ Ag flux = Ionic flux = electronic flux

$$J_{Ag} = \frac{\sigma_{e^-}}{\sigma_{Ag^+} + \sigma_{e^-}}J_{Ag^+} + \frac{\sigma_{Ag^+}}{\sigma_{Ag^+} + \sigma_{e^-}}J_{e^-}$$

$$= -\frac{1}{F^2}\frac{\sigma_{e^-}\sigma_{Ag^+}}{\sigma_{Ag^+} + \sigma_{e^-}}(\nabla\mu_{Ag^+} + \nabla\mu_{e^-}) \longrightarrow$$ Dilute limit: $\nabla\mu_i = (RT/c_i)\nabla c_i$

$$= -\frac{RT}{F^2}\underbrace{\underbrace{\frac{\sigma_{e^-}\sigma_{Ag^+}}{\sigma_{Ag^+} + \sigma_{e^-}}}_{1/R^\delta}\underbrace{\left(\frac{1}{c_{Ag^+}} + \frac{1}{c_{e^-}}\right)}_{1/C^\delta}}_{D^\delta_{Ag}}\nabla c_{Ag}$$

HW 11, Problem 1: "Job-sharing" mass transport



$$J^{\alpha}_{Ag^+} = -\frac{\sigma^{\alpha}_{Ag^+}}{F^2}\nabla\tilde{\mu}^{\alpha}_{Ag^+} = -\frac{\sigma^{\alpha}_{Ag^+}}{F^2}\left(\nabla\mu^{\alpha}_{Ag^+} + F\nabla\phi^{\alpha}\right)$$

$$J^{\beta}_{e^-} = -\frac{\sigma^{\beta}_{e^-}}{F^2}\nabla\tilde{\mu}^{\beta}_{e^-} = -\frac{\sigma^{\beta}_{e^-}}{F^2}\left(\nabla\mu^{\beta}_{e^-} - F\nabla\phi^{\beta}\right)$$

$$J_{Ag} = J^{\alpha}_{Ag^+} = J^{\beta}_{e^-} \longrightarrow$$

Ag flux = Ionic flux in *α phase*
= electronic flux in β *phase*

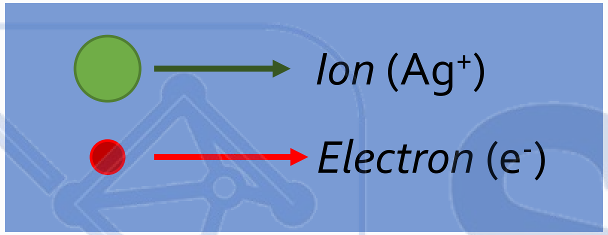
$$J_{Ag} = \frac{\sigma^{\beta}_{e^-}}{\sigma^{\alpha}_{Ag^+} + \sigma^{\beta}_{e^-}} J^{\alpha}_{Ag^+} + \frac{\sigma^{\alpha}_{Ag^+}}{\sigma^{\alpha}_{Ag^+} + \sigma^{\beta}_{e^-}} J^{\beta}_{e^-}$$

$$= -\frac{1}{F^2}\frac{\sigma^{\beta}_{e^-}\sigma^{\alpha}_{Ag^+}}{\sigma^{\alpha}_{Ag^+} + \sigma^{\beta}_{e^-}}\left(\nabla\mu^{\alpha}_{Ag^+} + \nabla\mu^{\beta}_{e^-} + F\nabla(\phi^{\alpha} - \phi^{\beta})\right)$$

$$= -\frac{RT}{F^2}\underbrace{\underbrace{\frac{\sigma^{\beta}_{e^-}\sigma^{\alpha}_{Ag^+}}{\sigma^{\alpha}_{Ag^+} + \sigma^{\beta}_{e^-}}}_{1/R^{\delta}}\Big(\underbrace{\frac{1}{c^{\alpha}_{Ag^+}} + \frac{1}{c^{\beta}_{e^-}} + \frac{F}{RT}\frac{\partial(\phi^{\alpha} - \phi^{\beta})}{\partial c_{Ag}}}_{1/C^{\delta}}\Big)}_{D^{\delta}_{Ag}}\nabla c_{Ag}$$

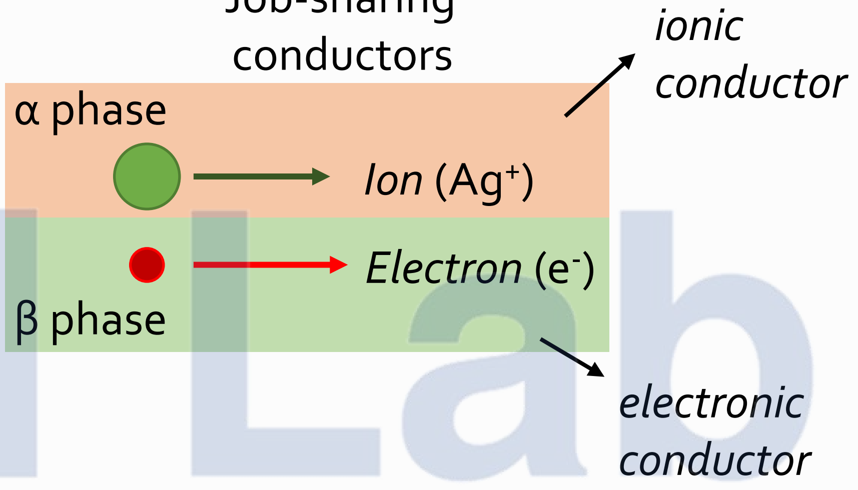
HW 11, Problem 1: “Job-sharing” mass transport

Mixed ionic & electronic conductor (MIEC)



Chemical diffusion

“Job-sharing” conductors



$1/R^{\delta}$	$\dfrac{\sigma_{e^-}\sigma_{Ag^+}}{\sigma_{Ag^+}+\sigma_{e^-}}$	$\dfrac{\sigma_{e^-}^{\beta}\sigma_{Ag^+}^{\alpha}}{\sigma_{Ag^+}^{\alpha}+\sigma_{e^-}^{\beta}}$

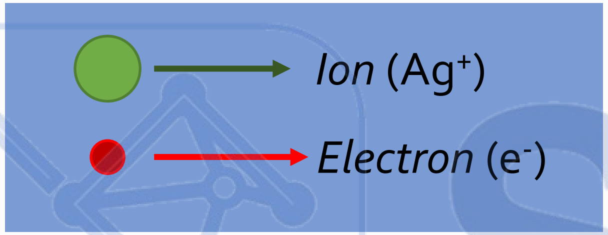
$$\frac{\sigma_{e^-}^{\beta}\sigma_{Ag^+}^{\alpha}}{\sigma_{Ag^+}^{\alpha}+\sigma_{e^-}^{\beta}} \approx \sigma_{Ag^+}^{\alpha}$$

α phase $RbAg_4I_5$ $\sigma_{Ag^+}^{\alpha} = 0.27\ S/cm$, $\sigma_{e^-}^{\alpha} = 3\times10^{-9} S/cm$

β phase graphite, $\sigma_{e^-}^{\beta} = 1250\ S/cm$

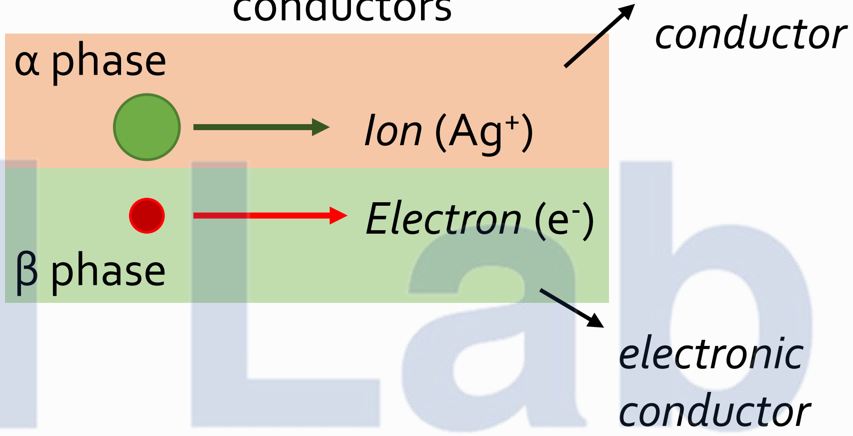
HW 11, Problem 1: "Job-sharing" mass transport

Mixed ionic & electronic conductor (MIEC)



Chemical diffusion

"Job-sharing" conductors



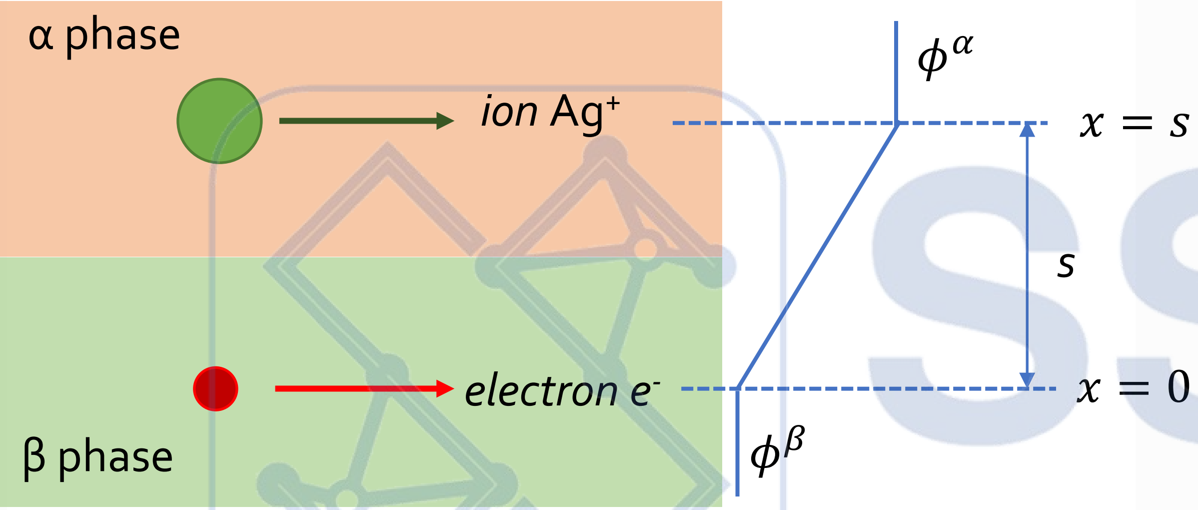
$1/C^{\delta}$	$\frac{1}{c_{Ag^+}} + \frac{1}{c_{e^-}}$	$\frac{1}{c^{\alpha}_{Ag^+}} + \frac{1}{c^{\beta}_{e^-}} + \boxed{\frac{F}{RT}\frac{\partial(\phi^{\alpha} - \phi^{\beta})}{\partial c_{Ag}}} \rightarrow$ *electrostatic term*

$$\frac{1}{c^{\alpha}_{Ag^+}} \ll \frac{1}{c^{\beta}_{e^-}}$$

α phase RbAg$_4$I$_5$, $c^{\alpha}_{Ag^+} \approx 10^{22}\ cm^{-3}$

β phase graphite, $c^{\beta}_{e^-} \approx 10^{19}\ cm^{-3}$

HW 11, Problem 1: "Job-sharing" mass transport



Gauss's Law:

Electric field $\boxed{E = \dfrac{Q_{enc}}{\varepsilon_0 \varepsilon_r}}$ *"enclosed charge"*

At position $x = 0$:

$$\boxed{E(0) = -\frac{d\phi}{dx}\bigg|_{x=0} \approx \frac{\phi^\alpha - \phi^\beta}{s} \approx \frac{c_{Ag} F s}{\varepsilon_0 \varepsilon_r}}$$

$$\frac{F}{RT}\frac{\partial(\phi^\alpha - \phi^\beta)}{\partial c_{Ag}} \approx \frac{F}{RT}\frac{F s^2}{\varepsilon_0 \varepsilon_r} \sim 10^{-17}\ cm^3$$

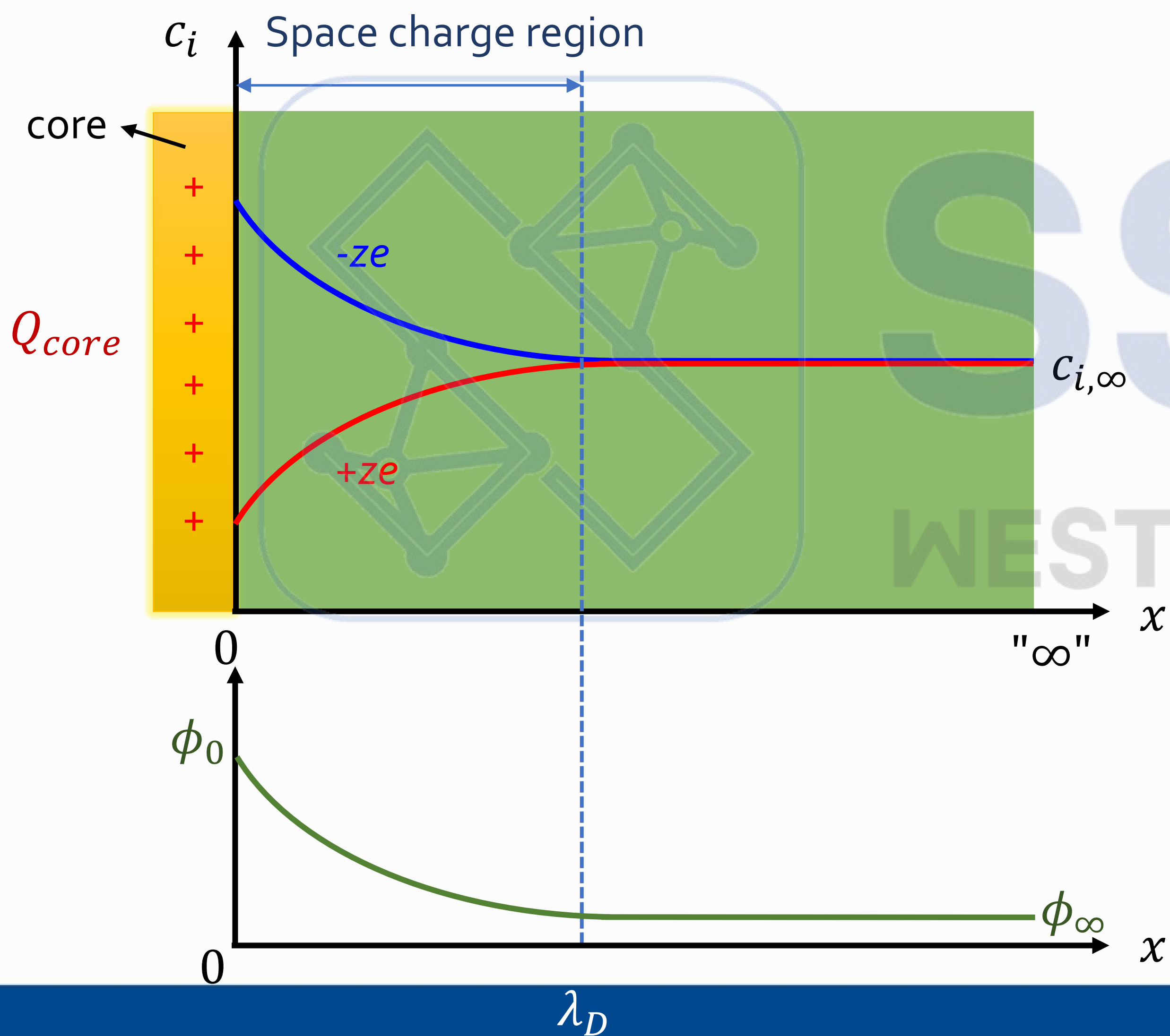
$$\frac{1}{c^\alpha_{Ag^+}} \ll \frac{1}{c^\beta_{e^-}}$$

α phase $RbAg_4I_5$, $c^\alpha_{Ag^+} \approx 10^{22}\ cm^{-3}$

β phase graphite, $c^\beta_{e^-} \approx 10^{19}\ cm^{-3}$

HW II, Problem II: The exact solution of the potential profile in Gouy-Chapman case

Let's consider the Gouy-Chapman case with +ze/-ze defects:



$$\rho(x) = 2zec_{i,\infty}\sinh\left(-\frac{ze\phi(x)}{k_BT}\right)$$

Poisson's equation

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\varepsilon_0\varepsilon_r} = \frac{2zec_{i,\infty}}{\varepsilon_0\varepsilon_r}\sinh\left(\frac{ze\phi(x)}{k_BT}\right)$$

$$\frac{d\phi}{dx} = -\frac{2k_BT}{ze\lambda_D}\sinh\left(\frac{ze\phi(x)}{2k_BT}\right)$$

$$\lambda_D = \sqrt{\frac{\varepsilon_0\varepsilon_r k_BT}{2z_i^2c_{i,\infty}e^2}}$$

$$\frac{\tanh(ze\phi(x)/4k_BT)}{\tanh(ze\phi_0/4k_BT)} = \exp\left(-\frac{x}{\lambda_D}\right)$$

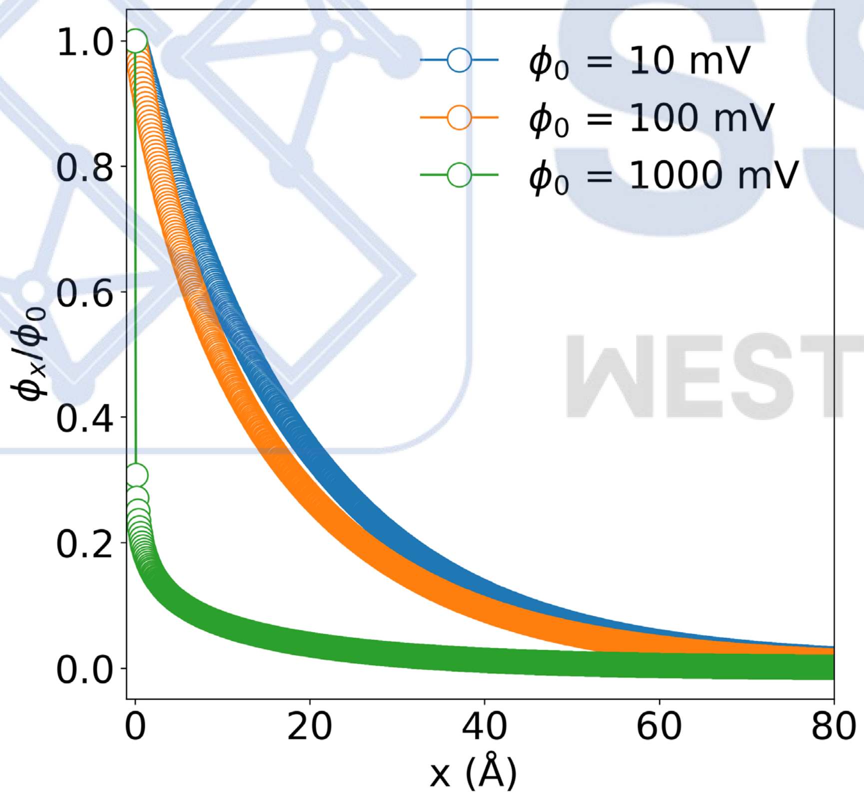
$\phi(x) \sim x$
(universal form)

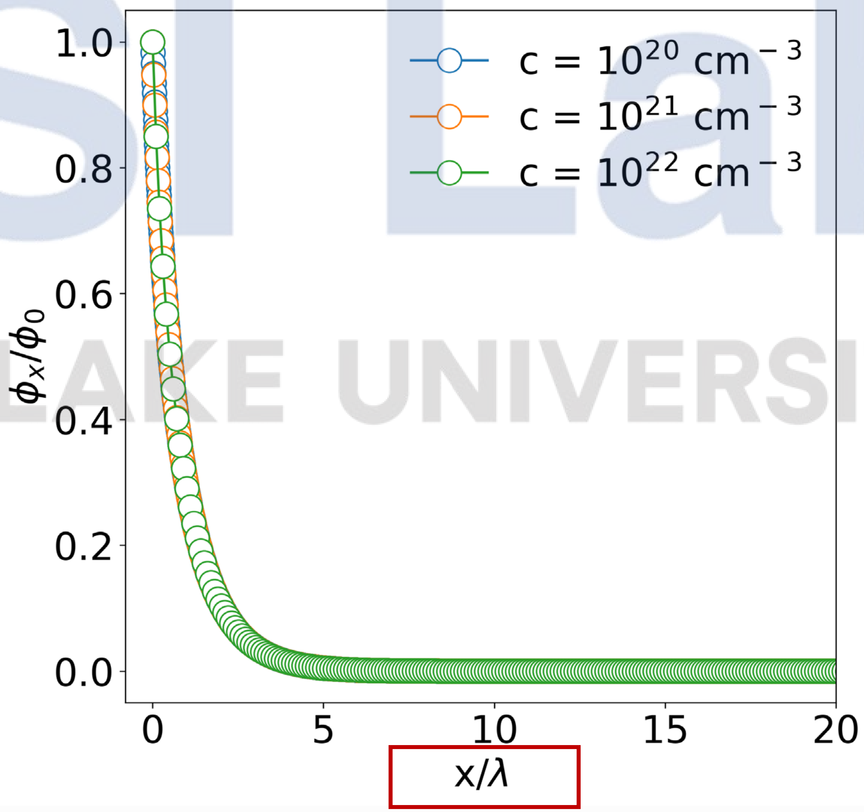
HW II, Problem II: The exact solution of the potential profile in Gouy-Chapman case

$$\boxed{\frac{\tanh(ze\phi(x)/4k_BT)}{\tanh(ze\phi_0/4k_BT)} = \exp(-\frac{x}{\lambda_D})}$$

$\phi(x)\sim x$ (universal form)

If $ze\phi_0 \ll k_BT$, we can linearize the equation by using $\tanh x \sim x$: $\rightarrow$ $\boxed{\phi(x) = \phi_0 \exp(-x/\lambda_D)}$





Review of course content: Homework 1-3

HW1

Defect chemical equilibrium

Brouwer diagram:

[def] ~ lna_i

i = charge neutral species (*e.g.*, O2, Li)

HW2

Space charge layers (SCLs)

$\phi\,(x_1) \neq \phi\,(x_2)$

$a_i\,(x_1) \neq a_i\,(x_2)$

- Gouy-Chapman case
- Mott-Schottky case

"frozen" defects

$$\boxed{\frac{\partial \tilde{\mu}_i}{\partial x} = 0}$$

Solid State Ionics:
Transport and *Reaction* of *Ionic defects*

$$\boxed{\frac{\partial \tilde{\mu}_i}{\partial x} \neq 0}$$

$$\boxed{\tilde{\mu}_i = \mu_i^0 + RTlna_i + z_iF\phi}$$

HW2

Ionic defect transport

- Diffusion: $\nabla\mu \neq 0$ ($\nabla c \neq 0$)
- Drift: $\nabla\phi \neq 0$
- Coupled drift-diffusion:

$$J_i = -\frac{\sigma_i}{z^2F^2}\nabla\tilde{\mu}_i$$

Concerted ion-electron transport

Chemical diffusivity:

$$D_O^\delta = \frac{RT}{4F^2}\frac{\sigma_O^\delta}{c_O^\delta}$$

HW3

Solid-state electrochemistry

- OCP: $E = (\tilde{\mu}_{e',a} - \tilde{\mu}_{e',c})/\mathrm{F}$
- Kinetics: Butler-Volmer *eqn.*
  Marcus(-Hush-Chidsey)

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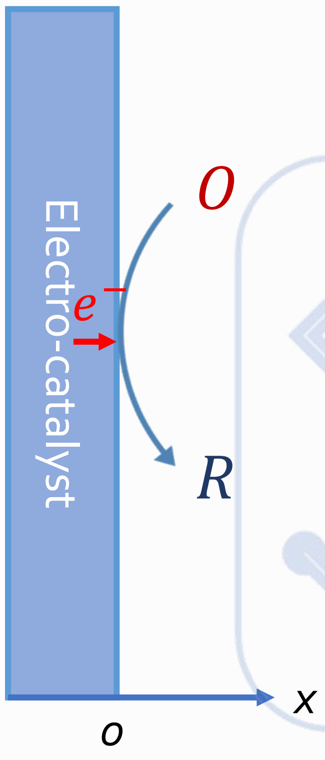
HW III, Problem I: The Nernst term in the Butler-Volmer Equation



$$\boxed{O + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R}$$

$E^{0\prime} = 0\ V$

Non-equilibrium

$$I = FA(\vec{R} - \overleftarrow{R}) = FA\,k^0\left[exp\left(-\frac{\alpha F\Delta E}{RT}\right)[O]_{x=0} - exp\left(\frac{(1-\alpha)F\Delta E}{RT}\right)[R]_{x=0}\right]$$

A ↓ Electrode surface area

$$\boxed{j = Fk^0\left[exp\left(-\frac{\alpha F(E-E^{0\prime})}{RT}\right)[O]_{x=0} - exp\left(\frac{(1-\alpha)F(E-E^{0\prime})}{RT}\right)[R]_{x=0}\right]}$$

Butler-Volmer Equation

"*Sanity check*": at which potential E, $i = 0$?

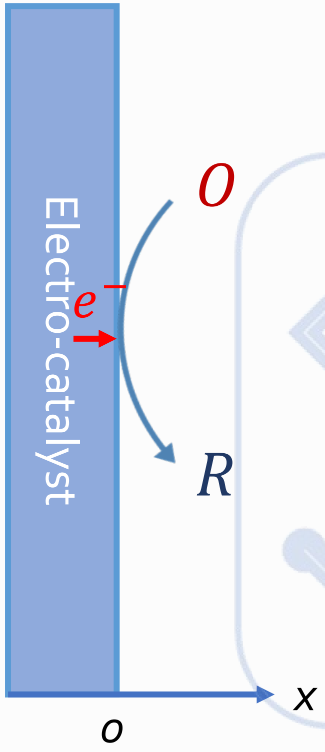
$$exp\left(-\frac{\alpha F(E-E^{0\prime})}{RT}\right)[O]_{x=0} = exp\left(\frac{(1-\alpha)F(E-E^{0\prime})}{RT}\right)[R]_{x=0}$$

➡

$$\boxed{E_{eq} = E^{0\prime} + \frac{RT}{F}\ln\left(\frac{[O]_{x=0}}{[R]_{x=0}}\right)}$$

Nernst Equation!

HW III, Problem I: The Nernst term in the Butler-Volmer Equation



$$O + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R$$

$E^{0\prime} = 0\ V$

We define *overpotential* as extra driving force compared with E_{eq}

Overpotential $\eta = E - E_{eq}$

$$\boxed{j_0 = F\,k^0([O]_{x=0})^{1-\alpha}([R]_{x=0})^{\alpha}}$$

I_0 : *Exchange current*

$$j\ = FA\,k^0\left[exp\left(-\frac{\alpha F(E-E^{0\prime})}{RT}\right)[O]_{x=0} - exp\left(\frac{(1-\alpha)F(E-E^{0\prime})}{RT}\right)[R]_{x=0}\right]$$

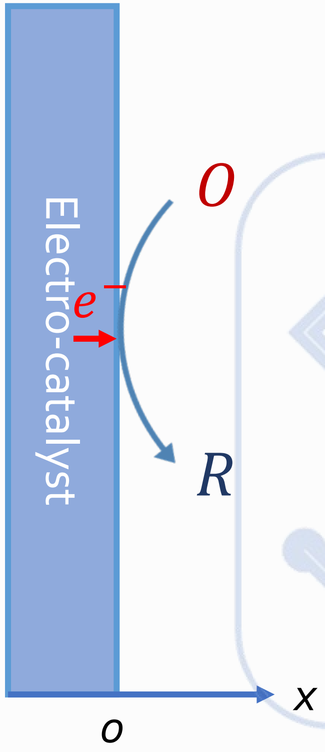
$$\begin{aligned} j\ &= j_0\left[exp\left(-\frac{\alpha F(E-E_{eq})}{RT}\right) - exp\left(\frac{(1-\alpha)F(E-E_{eq})}{RT}\right)\right] \\ &= j_0\left[exp\left(-\frac{\alpha F\eta}{RT}\right) - exp\left(\frac{(1-\alpha)F\eta}{RT}\right)\right] \end{aligned}$$

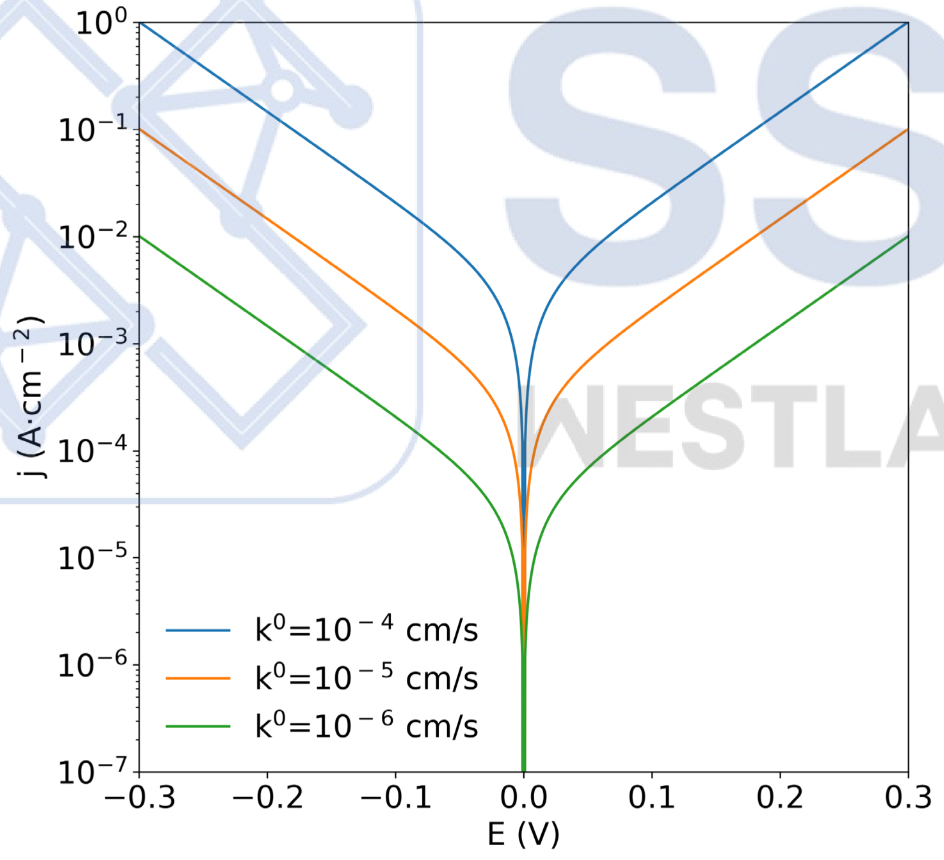
de Donder relation

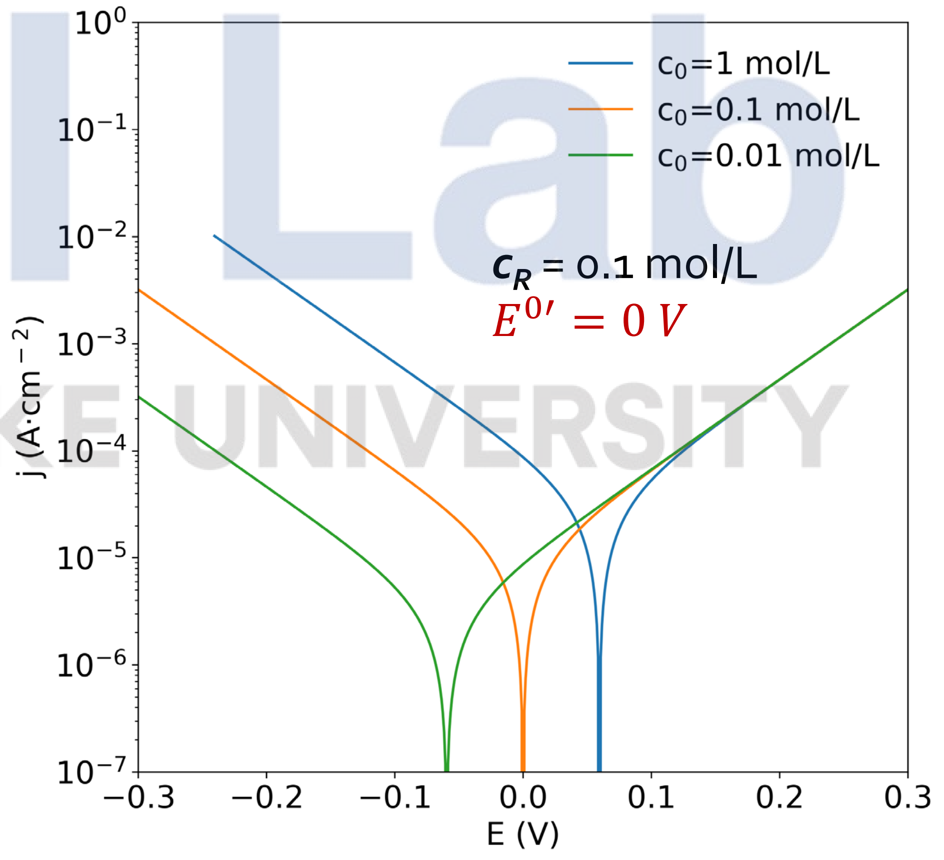
$$\boxed{j_a/j_c = -exp\left(\frac{F\eta}{RT}\right)}$$

HW III, Problem 1: The Nernst term in the Butler-Volmer Equation

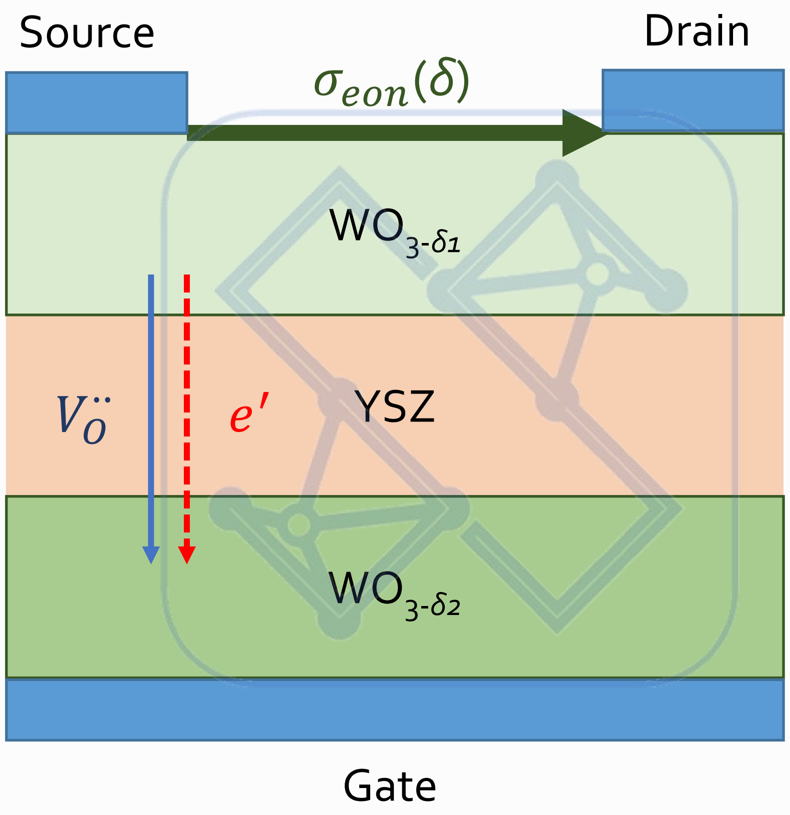
$$j = Fk^0\left[exp\left(-\frac{\alpha F(E-E^{0\prime})}{RT}\right)[O]_{x=0} - exp\left(\frac{(1-\alpha)F(E-E^{0\prime})}{RT}\right)[R]_{x=0}\right]$$





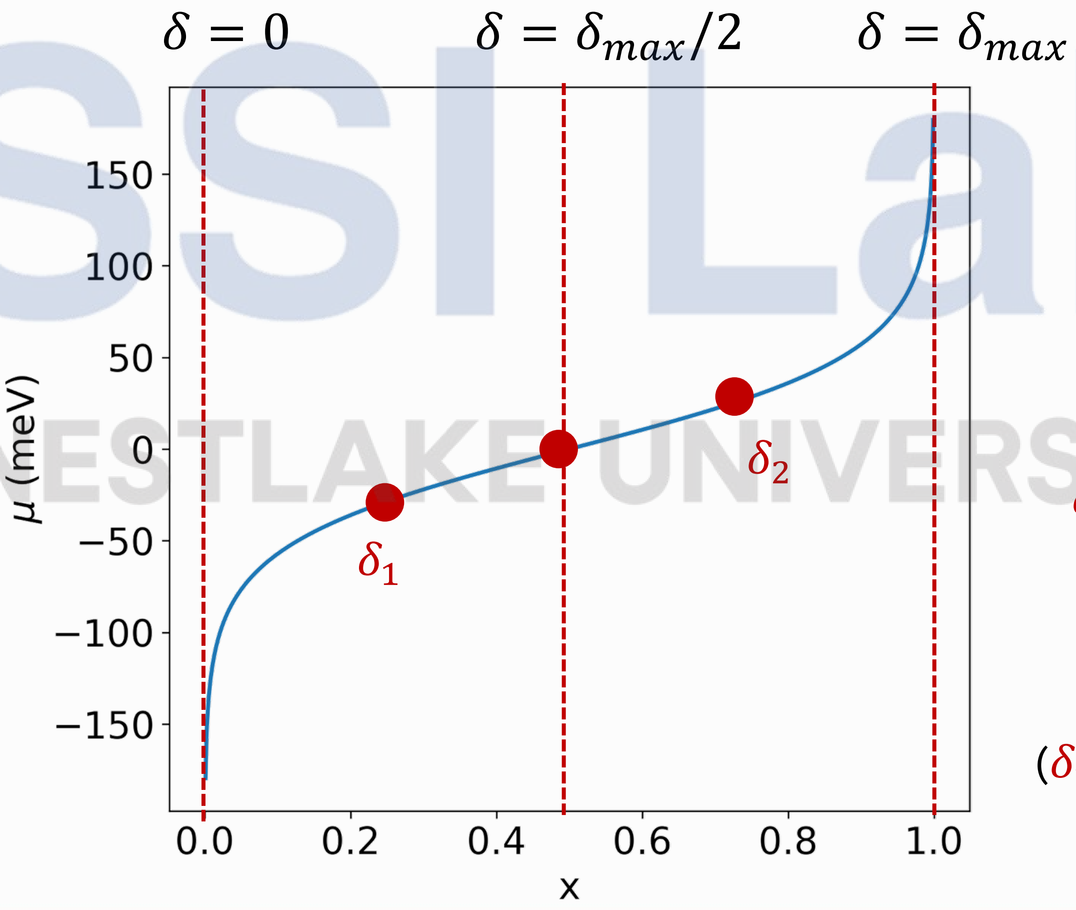


HW III, Problem II: Phase separation in electrochemical ionic synapses



$$\mu(x) = \frac{1}{\delta_{max}}\frac{\partial G}{\partial x} = RTln(\frac{x}{1-x})$$

$(x = \delta/\delta_{max})$



At equilibrium:

$\mu(x_1) = \mu(x_2)$

$\delta_1 = \delta_2 = \delta_{max}/2$

Volatile

($\delta_1 \neq \delta_2$ is not stable)

HW III, Problem II: Phase separation in electrochemical ionic synapses

Electrochemical driving force:

$$\boxed{\eta = \frac{1}{F}(\mu(x_2) - \mu(1/2)) = \frac{RT}{F} k_B T ln(\frac{x}{1-x})}$$

Current density:

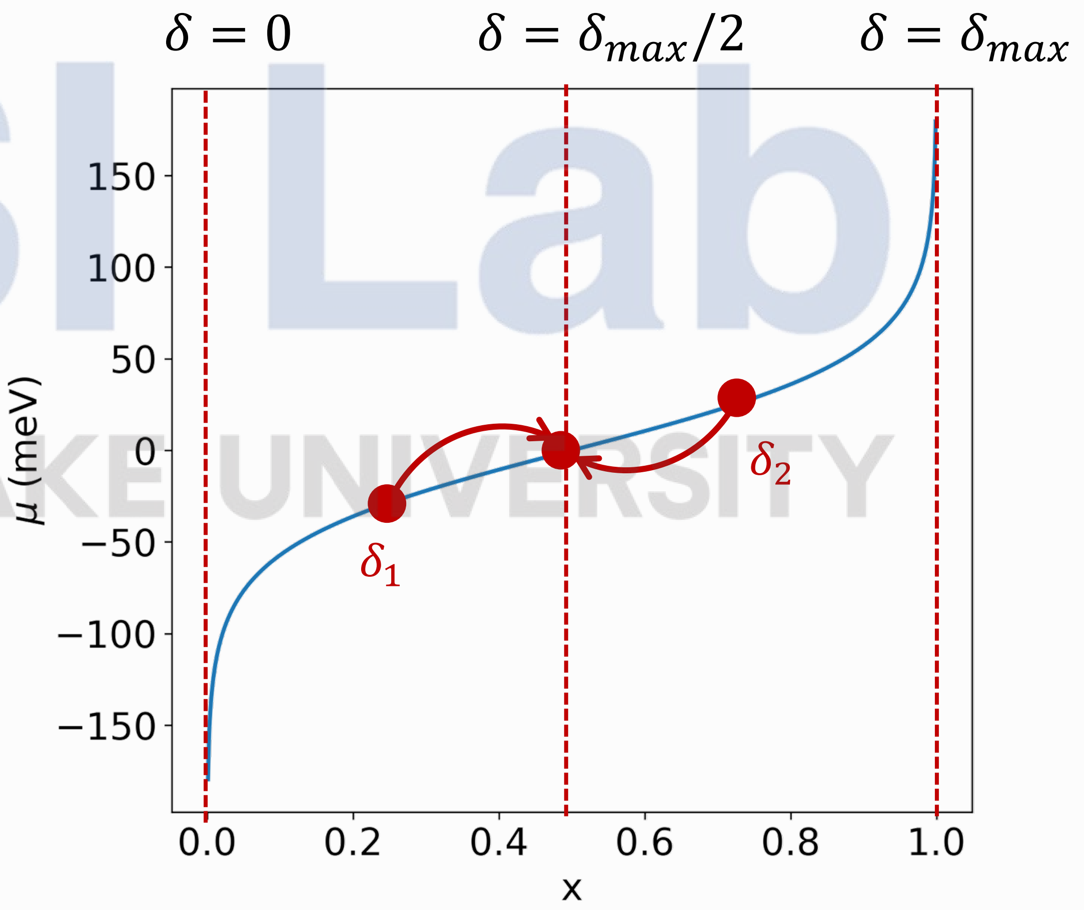
$$\boxed{\begin{aligned} j(x) &= j_0 \left[exp\left(-\frac{\alpha F \eta}{RT}\right) - exp\left(\frac{(1-\alpha) F\eta}{RT}\right)\right] \\ &= j_0 \left[(\frac{x}{1-x})^{-\alpha} - (\frac{x}{1-x})^{1-\alpha} \right] \end{aligned}}$$

Charge $\longrightarrow$ $dQ = j(x)\, A\, dt = (\delta_{max}\, dx) \frac{A \cdot l \cdot 2e}{V}$

$$\int_{x_2}^{1/2} j(x)\; dx = \int_0^{t_{eq}} \frac{V}{\delta_{max} \cdot l \cdot 2e} dt$$

$$\boxed{\mu(x) = \frac{1}{\delta_{max}} \frac{\partial G}{\partial x} = RT ln(\frac{x}{1-x})}$$

$(x = \delta/\delta_{max})$



HW III, Problem II: Phase separation in electrochemical ionic synapses

Electrochemical driving force:

$$\eta = \frac{1}{F}(\mu(x_2) - \mu(1/2)) = \frac{RT}{F} k_B T ln(\frac{x}{1-x})$$

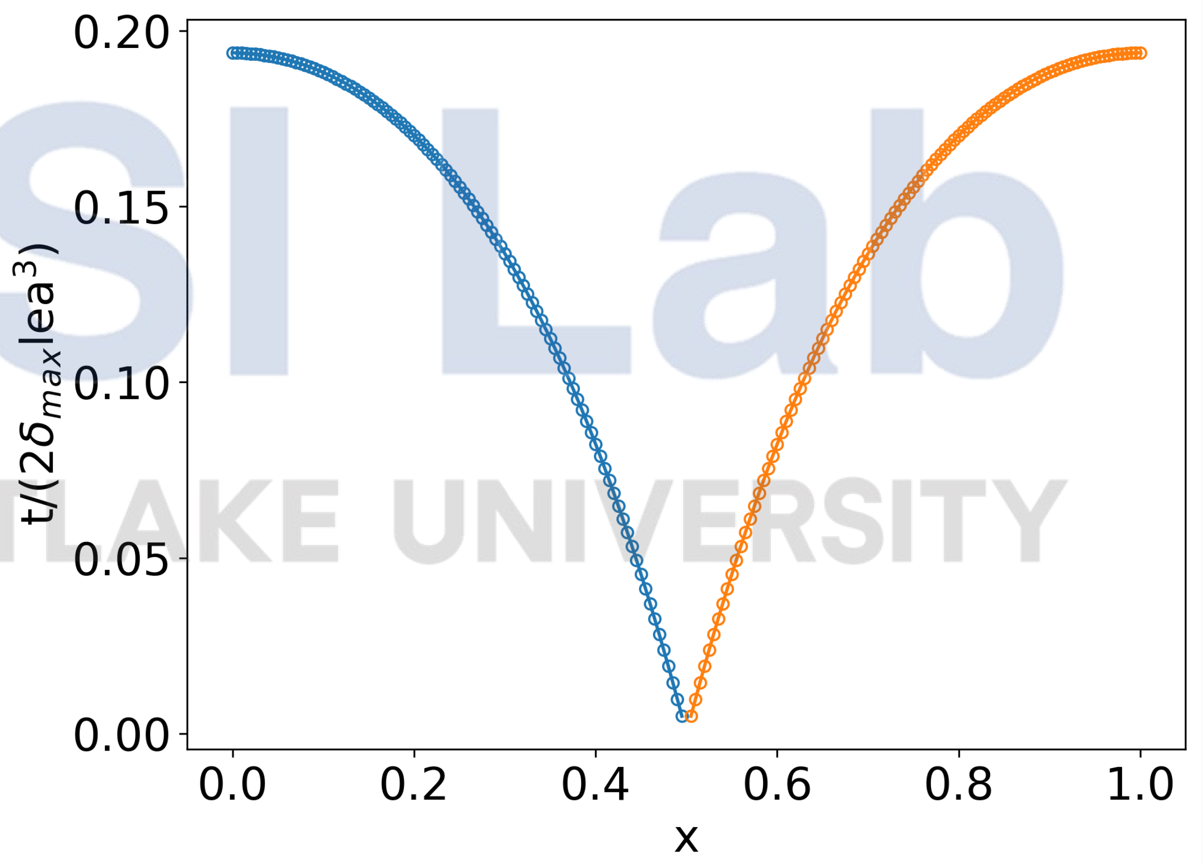
Current density:

$$j(x) = j_0 \left[exp\left(-\frac{\alpha F \eta}{RT}\right) - exp\left(\frac{(1-\alpha)F\eta}{RT}\right)\right]$$
$$= j_0 \left[(\frac{x}{1-x})^{-\alpha} - (\frac{x}{1-x})^{1-\alpha} \right]$$

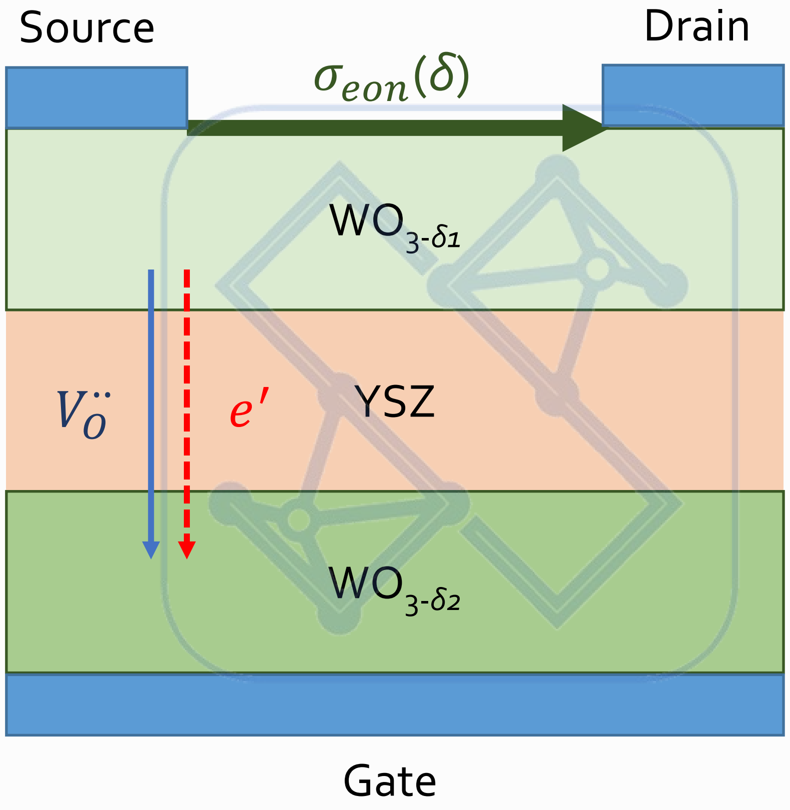
Charge ⟶ $dQ = j(x)\, A\, dt = (\delta_{max}\, dx)\frac{A \cdot l \cdot 2e}{V}$

$$\int_{x_2}^{1/2} j(x)\ dx = \int_0^{t_{eq}} \frac{V}{\delta_{max} \cdot l \cdot 2e} dt$$

t_{eq} increases when further deviates from equilibrium (x = ½)

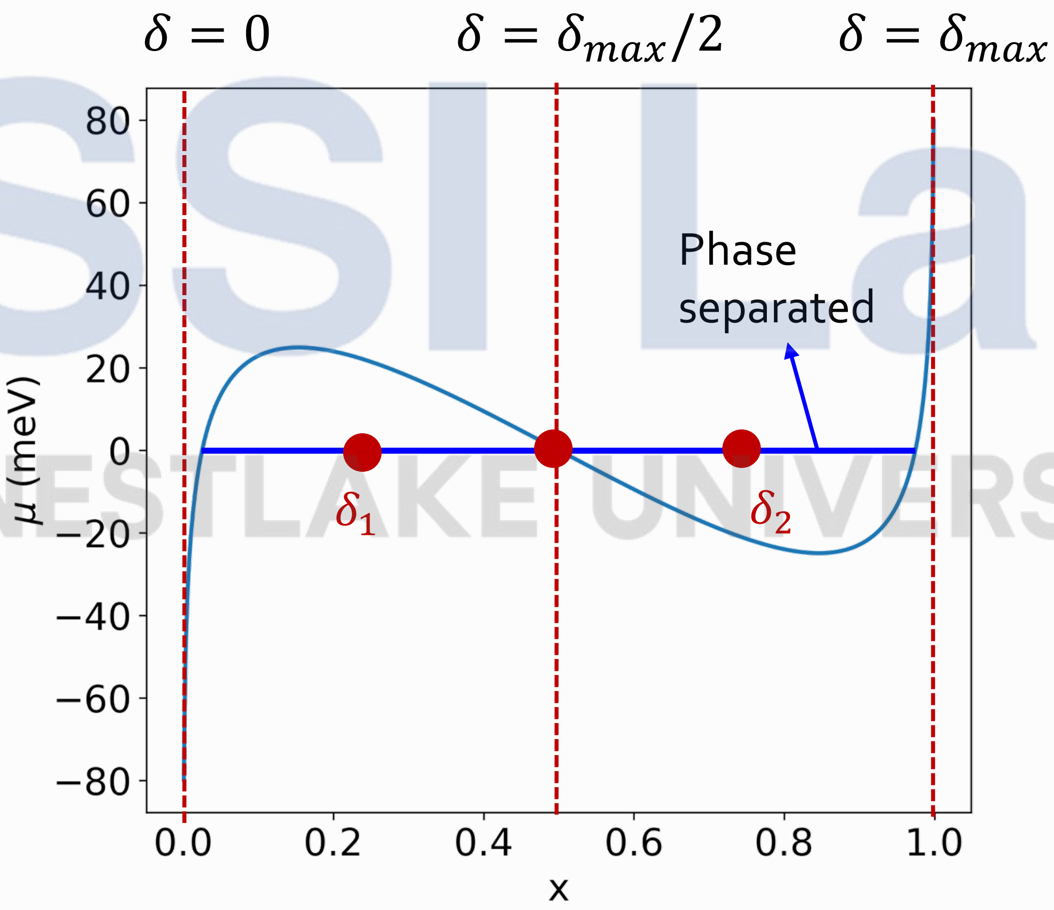


HW III, Problem II: Phase separation in electrochemical ionic synapses



$$\mu(x) = \frac{1}{\delta_{max}}\frac{\partial G}{\partial x} = h_0\,(1-2x) + RT ln(\frac{x}{1-x})$$

$(x = \delta/\delta_{max})$



At equilibrium:

$\mu(x_1) = \mu(x_2)$

$\delta_1 \neq \delta_2 \neq \delta_{max}/2$

Non-volatile

($\delta_1 \neq \delta_2$ is stable)

Review of course content: Homework 1-3

HW1

Defect chemical equilibrium

Brouwer diagram:

[def] ~ $\ln a_i$

i = charge neutral species (*e.g.*, O2, Li)

HW2

Space charge layers (SCLs)

$\phi\,(x_1) \neq \phi\,(x_2)$

$a_i\,(x_1) \neq a_i\,(x_2)$

- Gouy-Chapman case
- Mott-Schottky case

"frozen" defects

$$\boxed{\frac{\partial \tilde{\mu}_i}{\partial x} = 0}$$

Solid State Ionics:

Transport and Reaction of *Ionic defects*

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Ionic defect transport

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- Drift: $\nabla\phi \neq 0$
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  Marcus(-Hush-Chidsey)

End of Lecture 14
Solid State Ionics Fall 2022

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