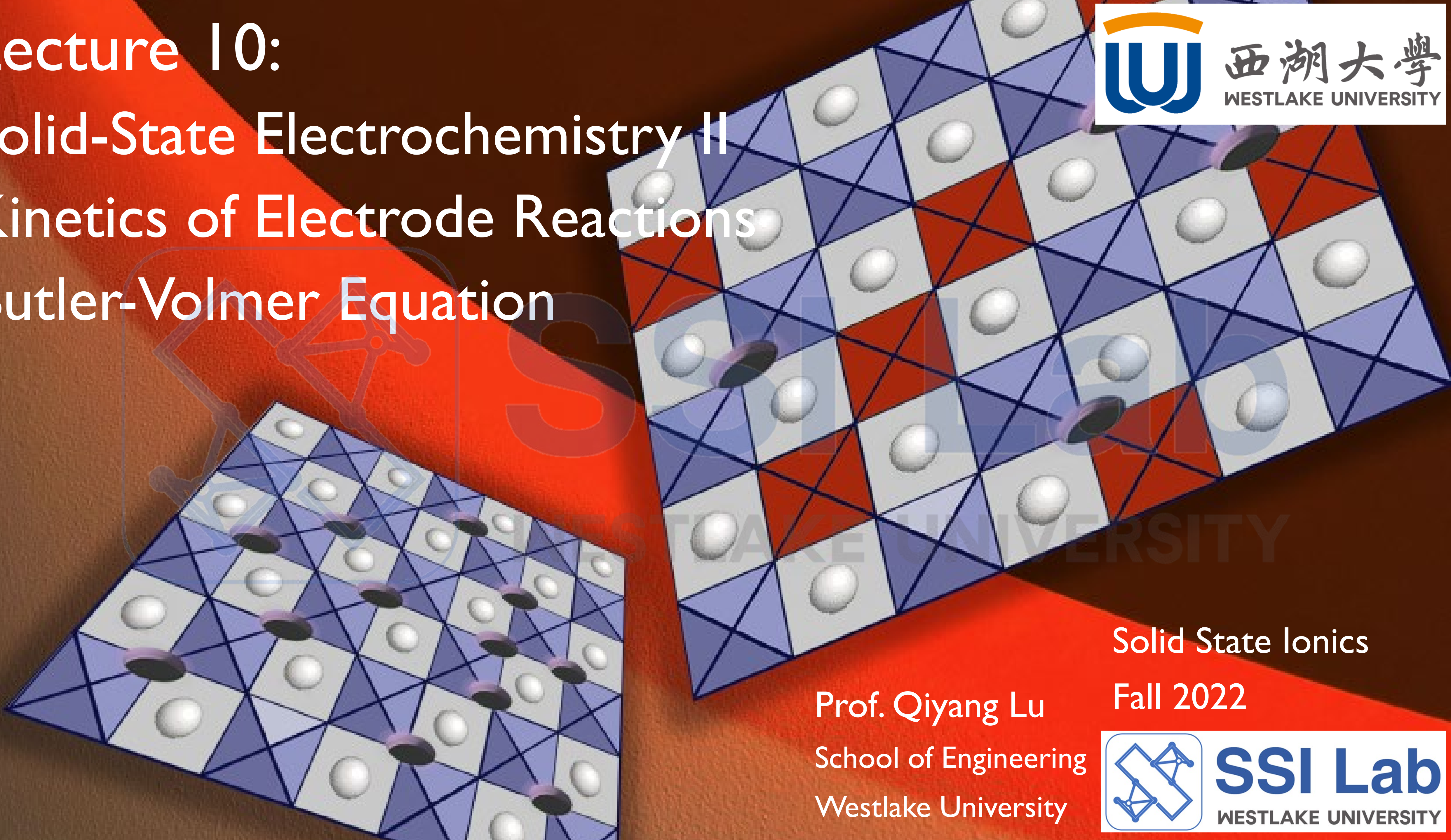
Lecture 10:

Solid-State Electrochemistry II

Kinetics of Electrode Reactions

Butler-Volmer Equation



Solid State Ionics

Fall 2022

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School of Engineering

Westlake University

Things we will discuss in this lecture

Kinetics of Electrode Reactions:

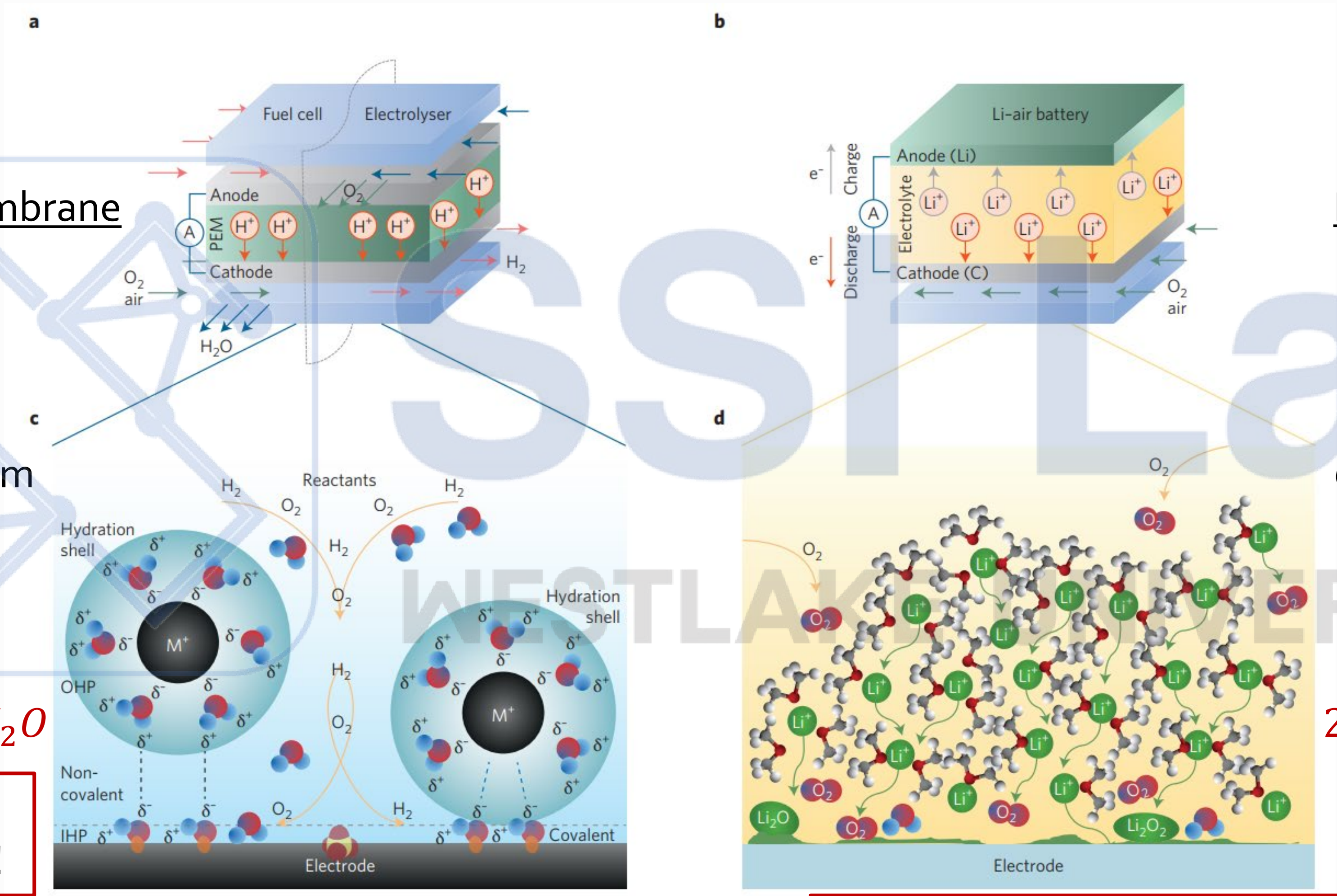
- How to build a model for charge transfer at electrode surfaces?
- What are the key assumptions for Butler-Volmer equations?
- What does the *η-I* curve look like at small/large overpotentials?

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

The importance of electrode kinetics

Proton-**E**xchange **M**embrane **F**uel **C**ell (**PEMFC**)

Lithium-Air Battery



Aqueous solution system

Organic solution system

***O**xygen **R**eduction **R**eaction (**ORR**)*

$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

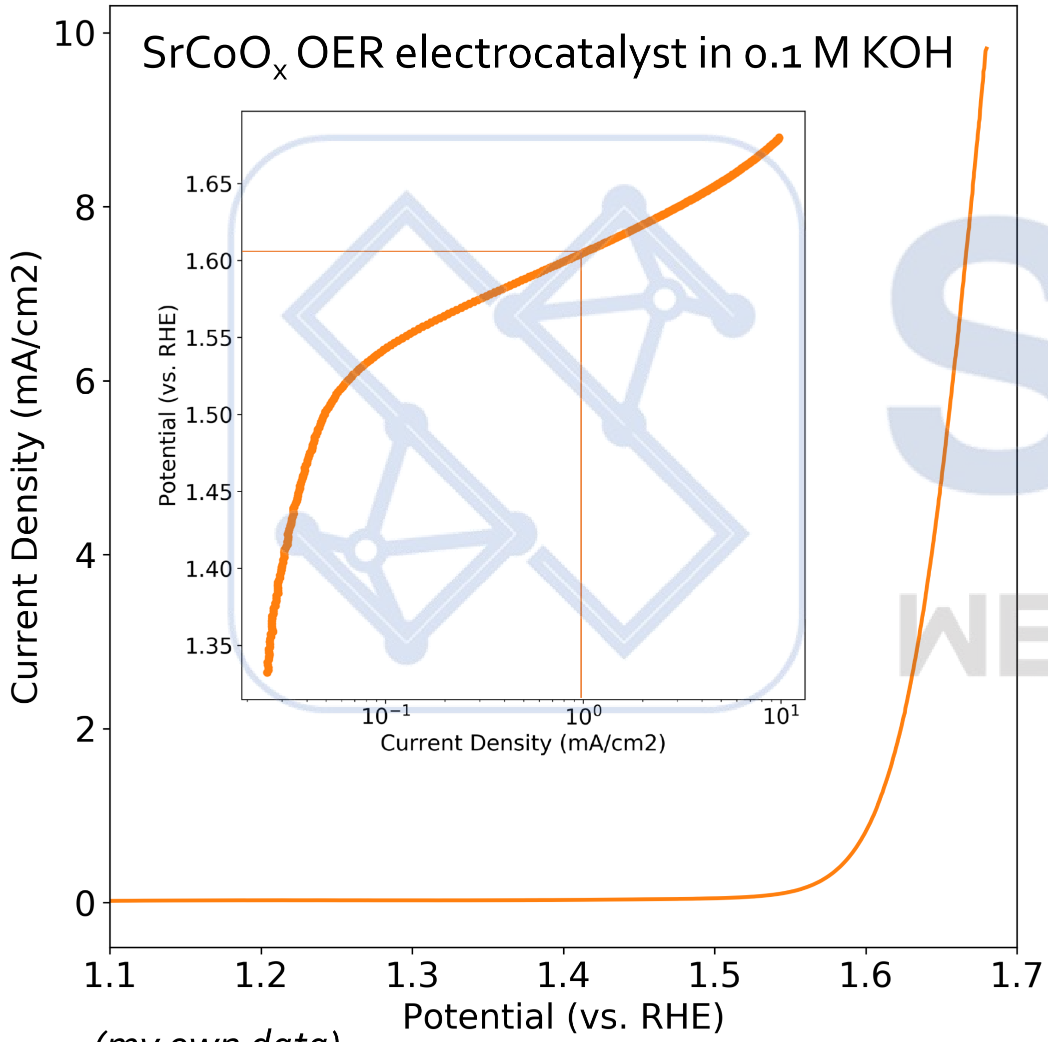
$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$

Electrocatalysis happens at ***interfaces***!

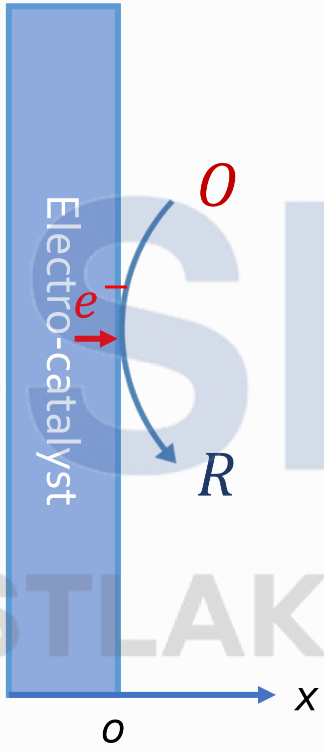
Stamenkovic, Markovic et al., *Nat. Mater.*, **16**, 57–69 (2017)

In either case, ***electro-catalytic*** reaction determines the performance of cells

How to understand the *I-E* characteristics?



(my own data)



$$O + e^- \rightleftharpoons R$$

Equilibrium potential with fixed $[O]_{x=0}$ and $[R]_{x=0}$ (concentrations are only evaluated at interfaces):

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

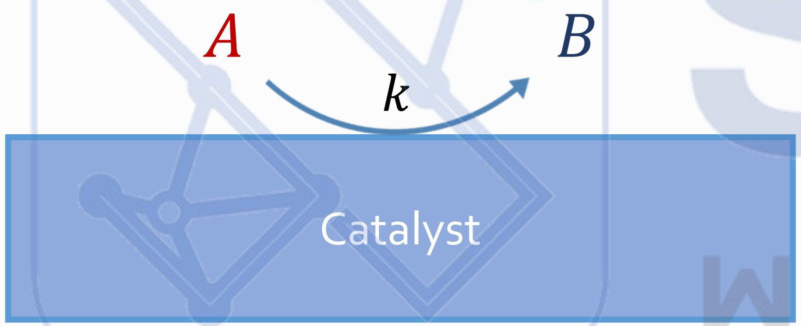
Nernst Equation

- The current (I) is directly related to the rate of the electrochemical *rxn* (so-called Faradaic current);
- The potential applied (controlled) E can be far away from E_{eq};
- We seek a theory to make prediction of I-E curves.

The difference between catalysis (chemical) and electro-catalysis (electrochemical)

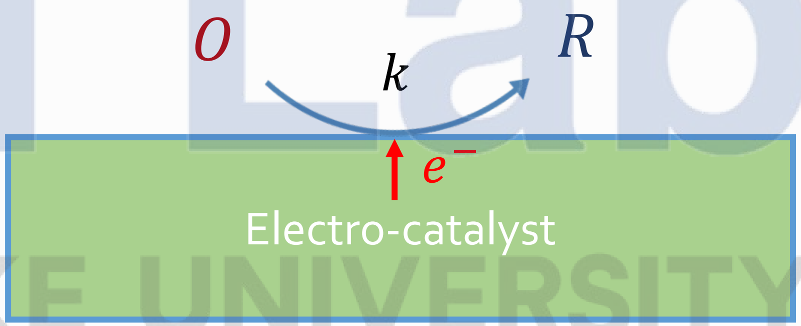
Chemical Reaction (*rxn*)
(Catalysis)

$$A \rightleftharpoons B$$



Electrochemical Reaction
(Electro-catalysis)

$$O + e^{-} \rightleftharpoons R$$



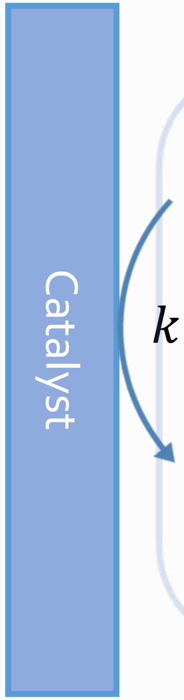
Reaction rate is determined by

- Concentration of reactant and product ($[A]$ and $[B]$)
- Temperature

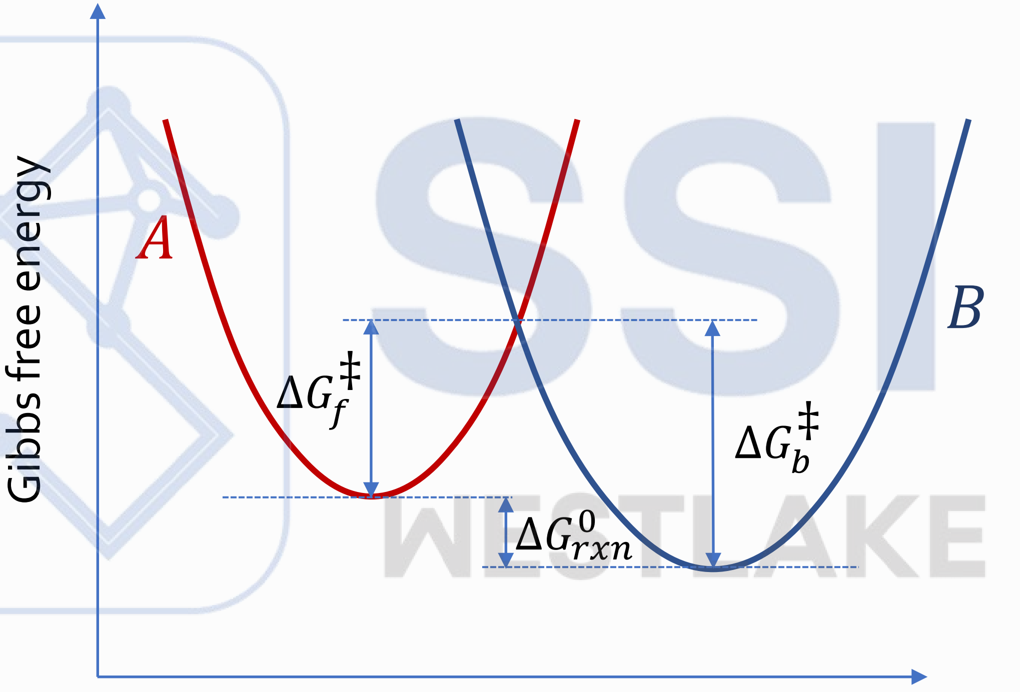
Reaction rate is determined by

- Concentration of reactant and product ($[O]$ and $[R]$)
- Temperature
- Electrode potential (which affects energy of ***electrons***)
- Concentration of electrons (?) → *quantum* effect

Fundamentals on thermal catalysis (chemical reaction)



Transition State Theory



Reaction coordinate*

$$\boxed{A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B}$$

$$k_f = A_f exp(-\Delta G_f^{\ddagger} /RT)$$

$$k_b = A_b exp(-\Delta G_b^{\ddagger} /RT)$$

Prefactor (or **Frequency factor**)

Erying Equation $\boxed{A = \kappa \frac{k_B T}{h}}$

Transmission coefficient
$0 < \kappa < 1$

Planck's constant
$(h = 4.135 \times 10^{-15} eV/Hz)$

At equilibrium: $\boxed{k_f[A] = k_b[B]}$

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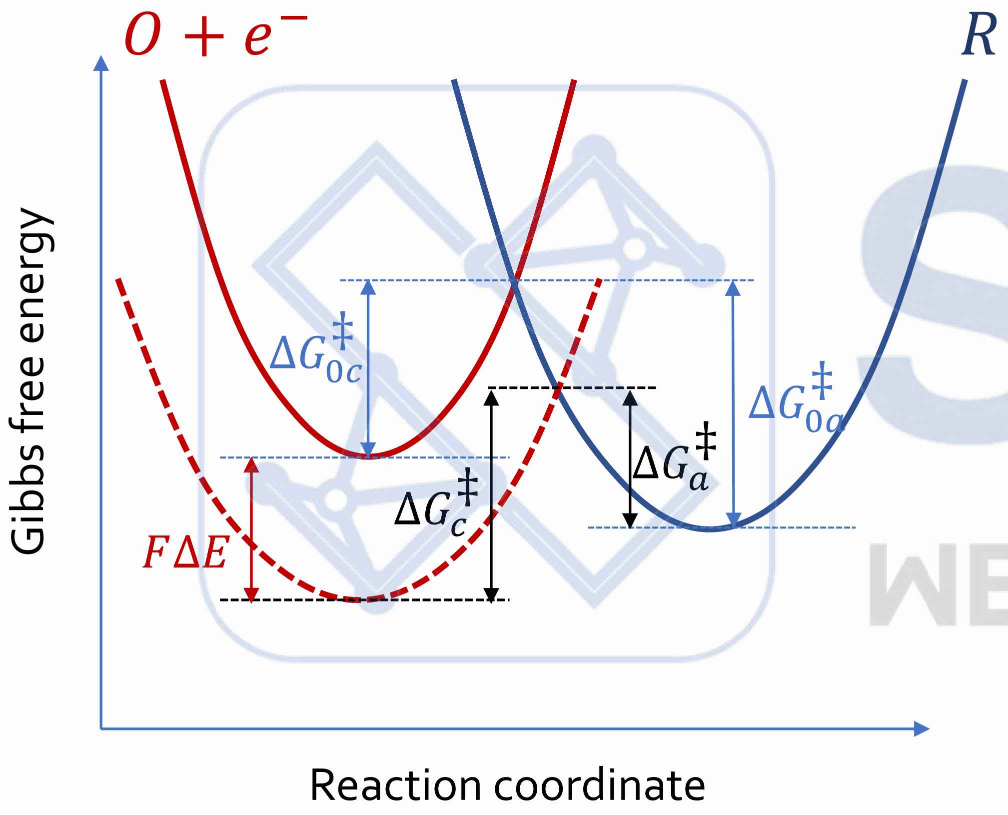
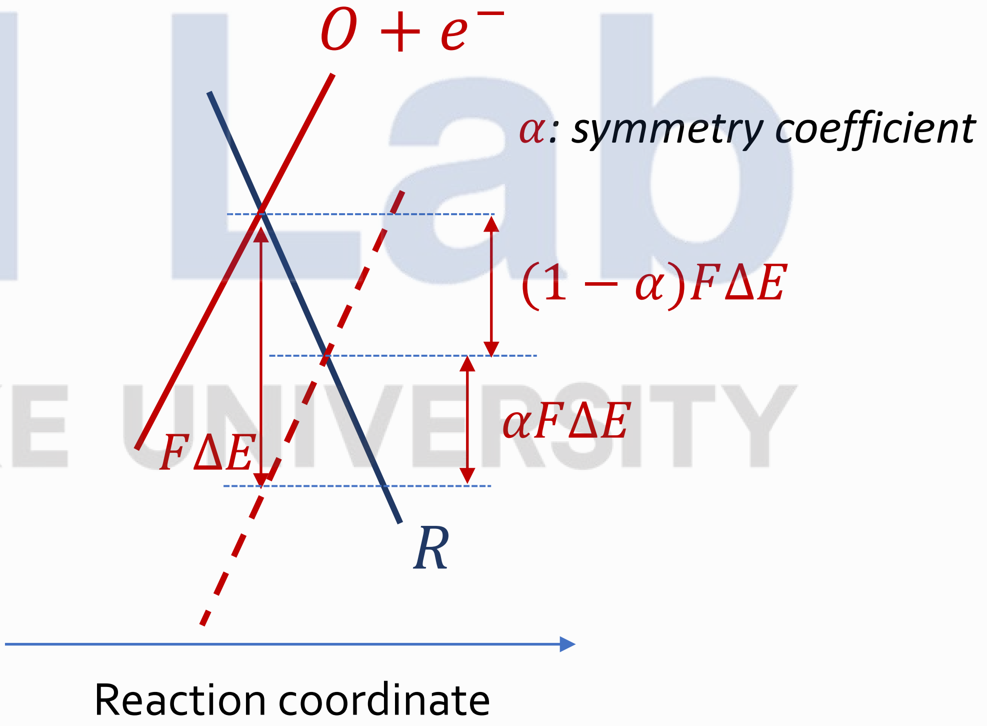
* "*an **abstract** one-dimensional coordinate which represents progress along a reaction pathway*" ***-Wikipedia***

Electro-catalysis: charge transfer reaction



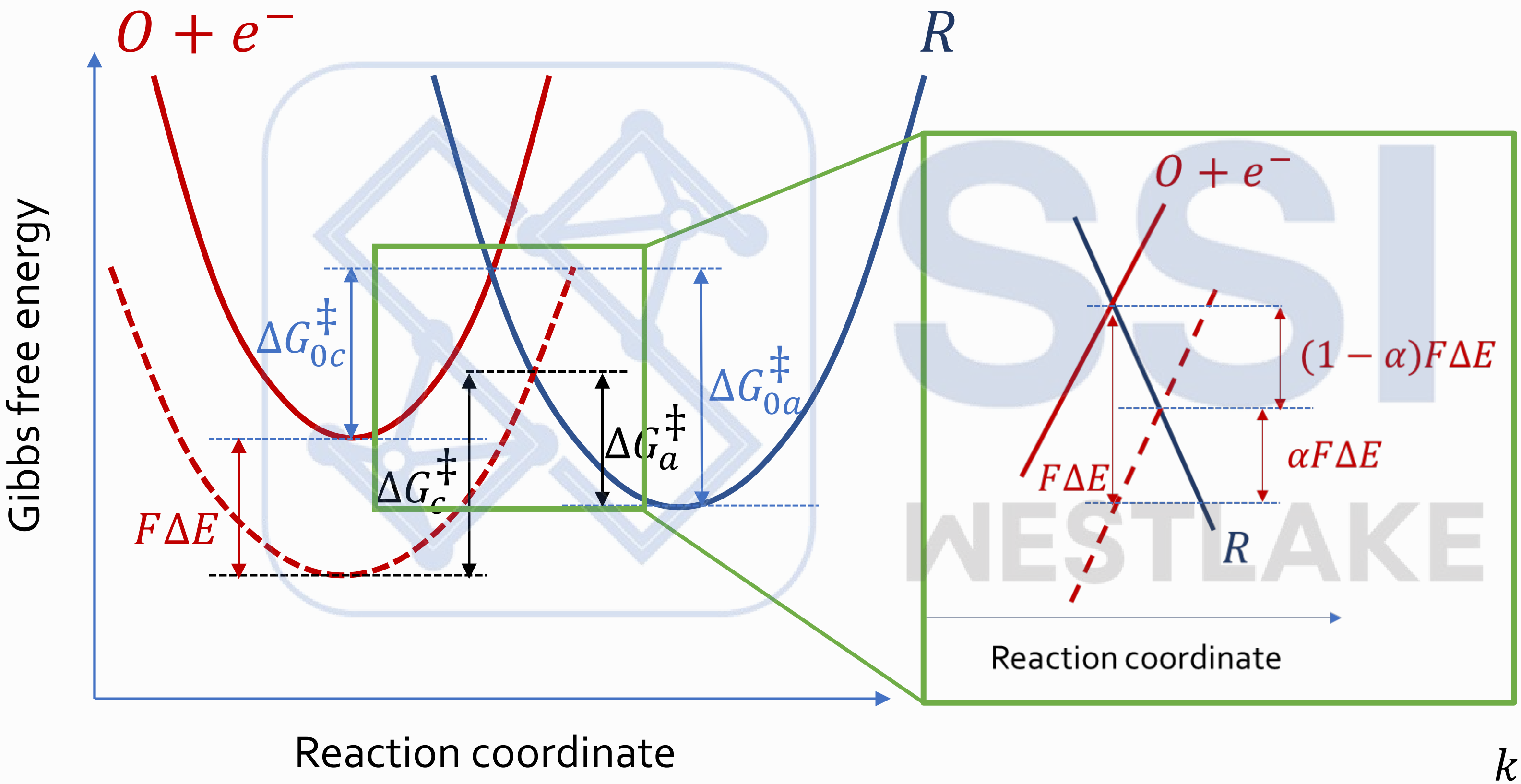
$$O + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R$$



Note: applied electric potential (ΔE) only changes the energy of $O + e^-$ due to the *charge of electrons*

Question: How does applied electric potential (ΔE) change the free energy of activation ($\Delta G^{\ddagger}$)?

Electro-catalysis: charge transfer reaction



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

$$\boxed{\begin{aligned}\Delta G_c^\ddagger &= \Delta G_{0c}^\ddagger + \alpha F\Delta E\\ \Delta G_a^\ddagger &= \Delta G_{0a}^\ddagger - (1-\alpha)F\Delta E\end{aligned}}$$

$$\begin{aligned}k_c &= A_c exp\left(-\Delta G_c^\ddagger/RT\right)\\ &= A_c exp\left(-\Delta G_{0c}^\ddagger/RT\right) exp(-\alpha F\Delta E/RT)\end{aligned}$$

$$\begin{aligned}k_a &= A_a exp\left(-\Delta G_a^\ddagger/RT\right)\\ &= A_a exp\left(-\Delta G_{0a}^\ddagger/RT\right) exp((1-\alpha)F\Delta E/RT)\end{aligned}$$

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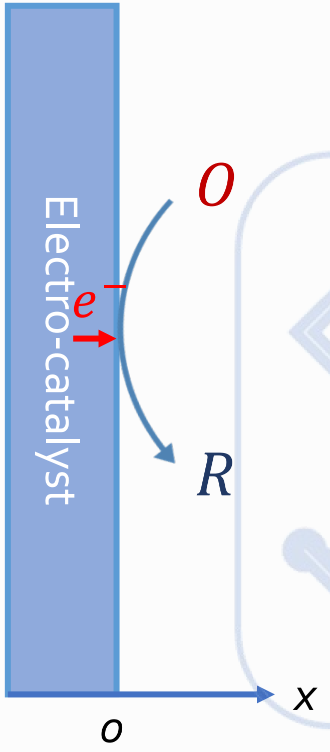
The Butler-Volmer (B-V) equation



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

Note that $\Delta E = E - E^{0\prime}$ is the electrochemical driving force for the reaction

$E^{0\prime}$ is so-called *formal potential* $[O]_{x=0} = [R]_{x=0}$

At equilibrium ($E = E^{0\prime}$, which means ΔE is o)

$$\boxed{k^0 = A_a exp\left(-\Delta G_a^{\ddagger}/RT\right) = A_c exp\left(-\Delta G_c^{\ddagger}/RT\right)}$$

Standard rate constant k^0

Non-equilibrium

Forward rxn (cathodic)

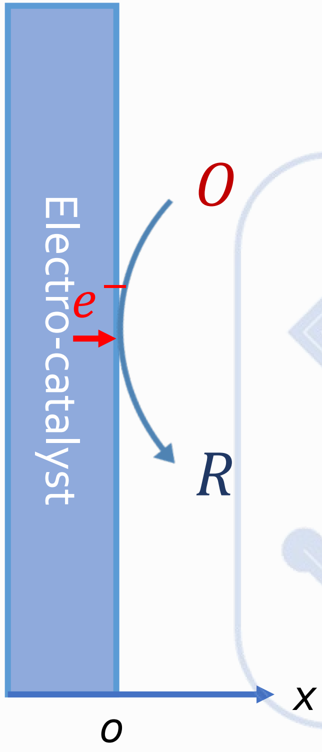
$$\vec{R} = k_c[O]_{x=0} = k^0 exp\left(-\frac{\alpha F \Delta E}{RT}\right)[O]_{x=0}$$

Backward rxn (anodic)

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

Note: Electrocatalytic reaction only happens at the interface ($x = 0$); We assume mass transport (diffusion) is fast ($[O]_{x=0} \approx [O]_{x=\infty}$)

The Butler-Volmer (B-V) equation



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

Non-equilibrium

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

$A \downarrow$ Electrode surface area

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

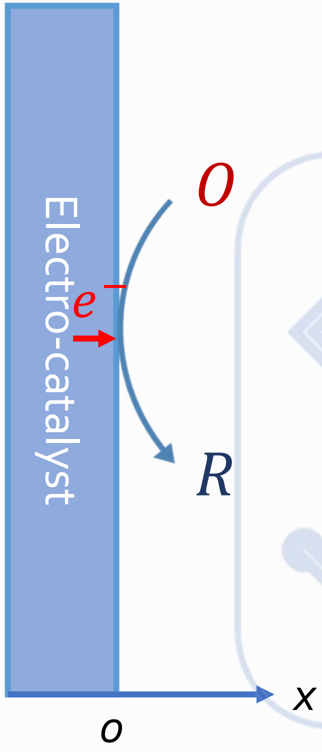
Butler-Volmer Equation

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

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

Nernst Equation!

The Butler-Volmer (B-V) equation



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

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

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

$$\boxed{I_0 = FA\,k^0([O]_{x=0})^{1-\alpha}([R]_{x=0})^{\alpha}}$$

I_0 : *Exchange current*

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

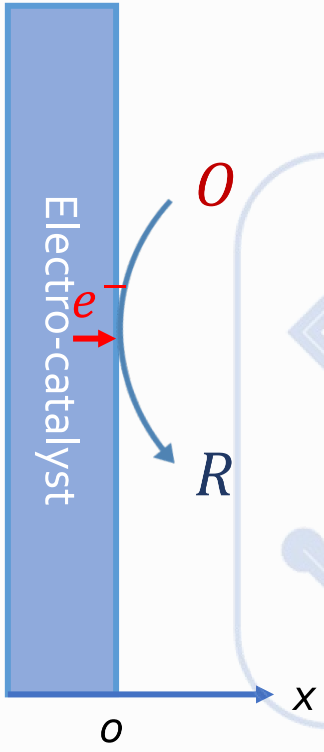
$$\begin{aligned} I &= I_0\left[exp\left(-\frac{\alpha F(E-E_{eq})}{RT}\right) - exp\left(\frac{(1-\alpha)F(E-E_{eq})}{RT}\right)\right] \\ &= I_0\left[exp\left(-\frac{\alpha F\eta}{RT}\right) - exp\left(\frac{(1-\alpha)F\eta}{RT}\right)\right] \end{aligned}$$

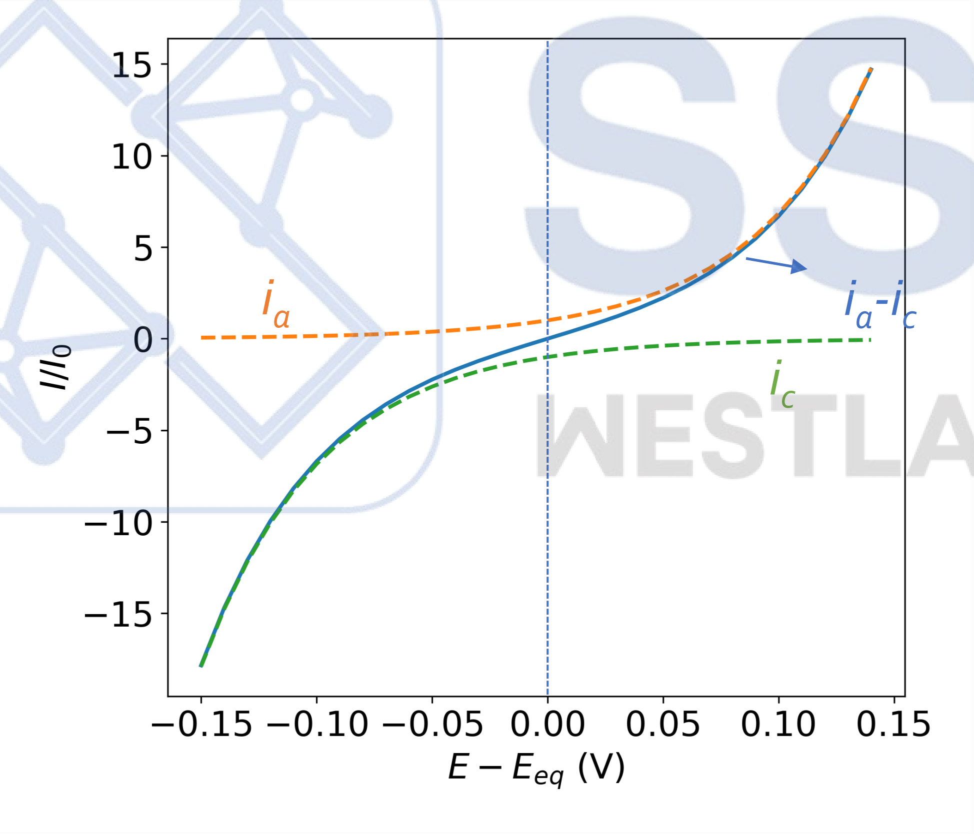
Butler-Volmer Equation
(the most common form)

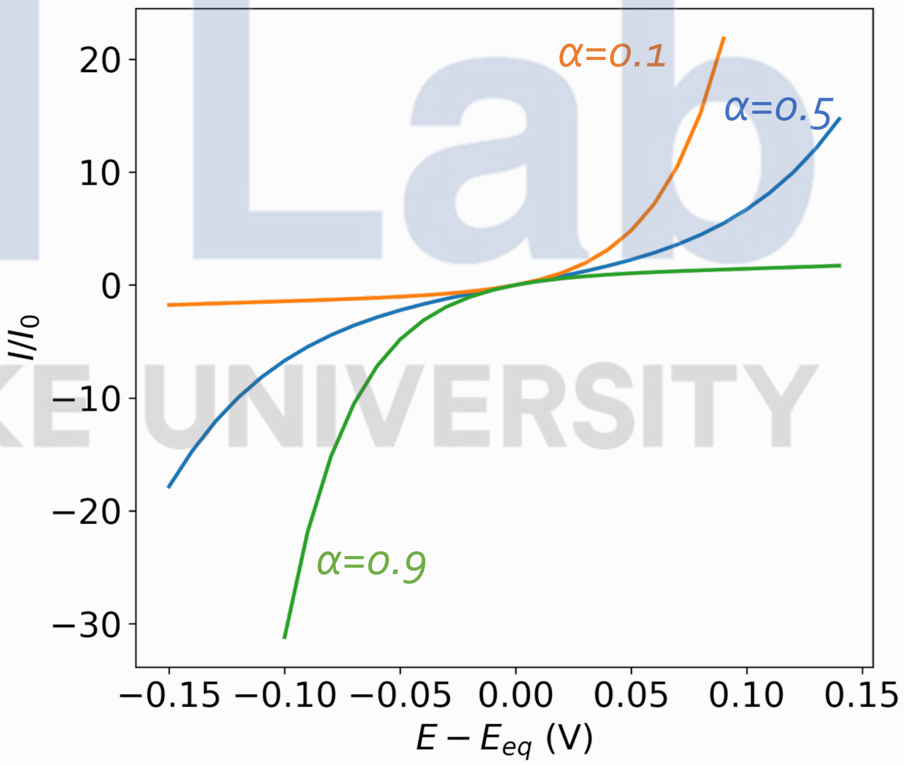
The Butler-Volmer (B-V) equation

$$I = I_0\left[exp\left(-\frac{\alpha F(E-E_{eq})}{RT}\right) - exp\left(\frac{(1-\alpha)F(E-E_{eq})}{RT}\right)\right]$$

Butler-Volmer Equation
(the most common form)







The Butler-Volmer (B-V) equation: approximations

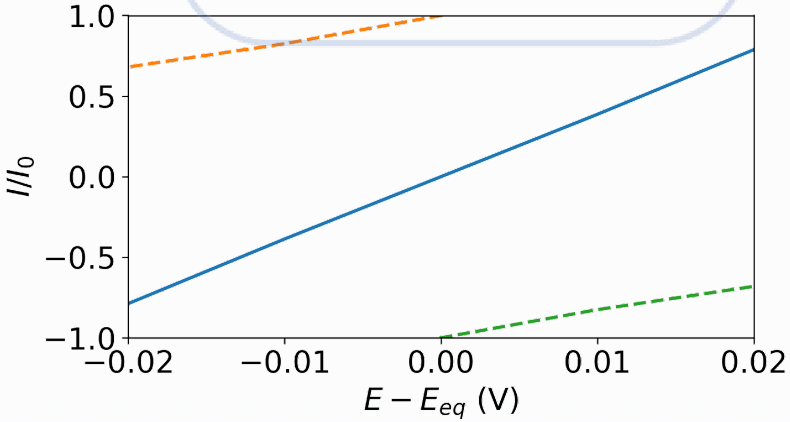
$$\boxed{I = I_0\left[exp\left(-\frac{\alpha F(E-E_{eq})}{RT}\right) - exp\left(\frac{(1-\alpha)F(E-E_{eq})}{RT}\right)\right]}$$

Butler-Volmer Equation

If $E - E_{eq}$ is small ($e^x \sim 1 + x$)

$$\boxed{I = -\frac{I_0 F}{RT}(E - E_{eq})}$$

Charge transfer resistance $R_{ct} = \frac{I_0 F}{RT}$



If $E - E_{eq} \gg 0$ (compared with RT/F)

$$\boxed{I = -I_0 exp\left(\frac{(1-\alpha)F(E-E_{eq})}{RT}\right)}$$

Only ***anodic*** current matters

If $E - E_{eq} \ll 0$ (compared with RT/F)

$$\boxed{I = I_0 exp\left(-\frac{\alpha F(E-E_{eq})}{RT}\right)}$$

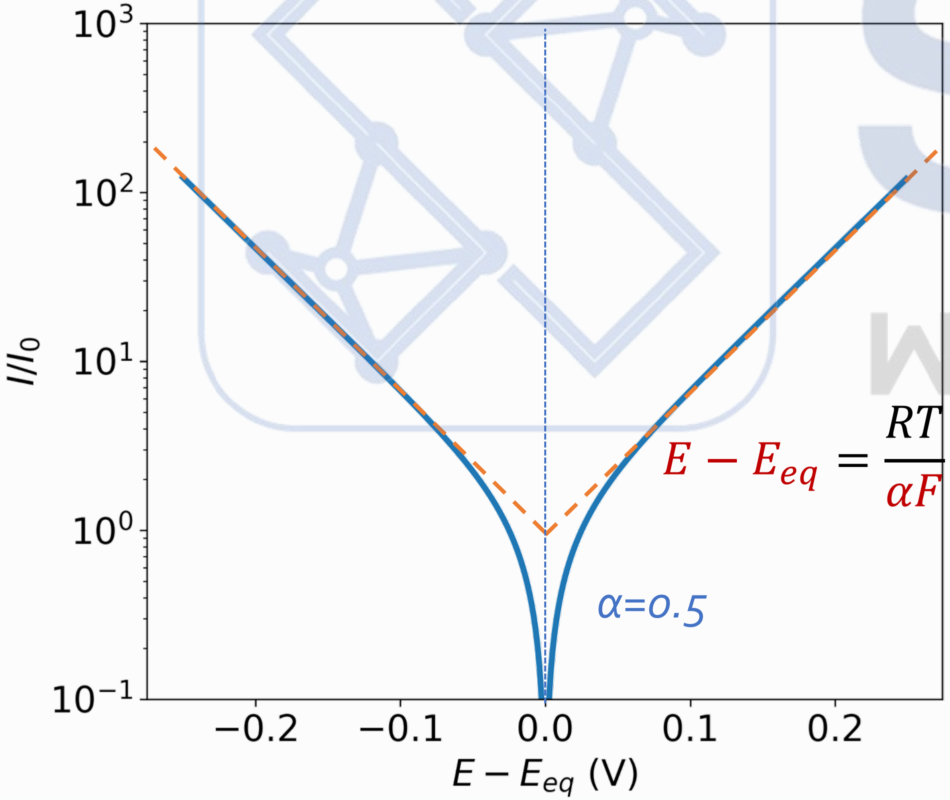
Only ***cathodic*** current matters

Tafel plot: extract α and I_0

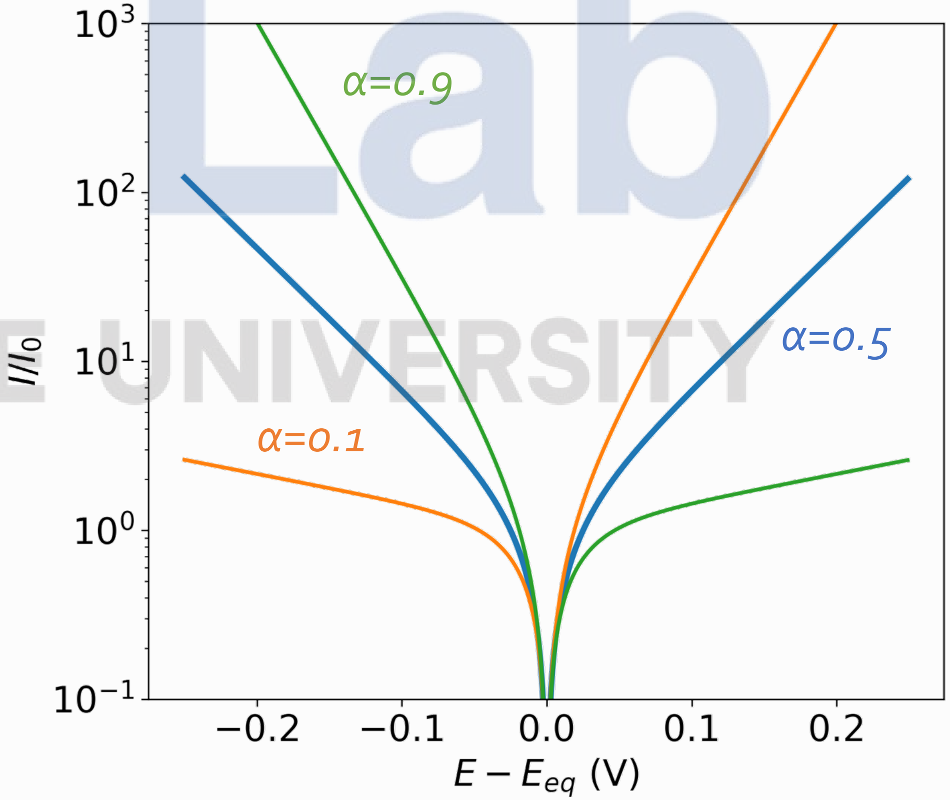
$$\boxed{I = -I_0 exp\left(\frac{(1-\alpha)F(E-E_{eq})}{RT}\right)} \qquad (E - E_{eq} \gg 0)$$

$$\boxed{I = I_0 exp\left(-\frac{\alpha F(E-E_{eq})}{RT}\right)} \qquad (E - E_{eq} \ll 0)$$

$\alpha \neq 0.5$ → Forward and backward current not symmetric any more

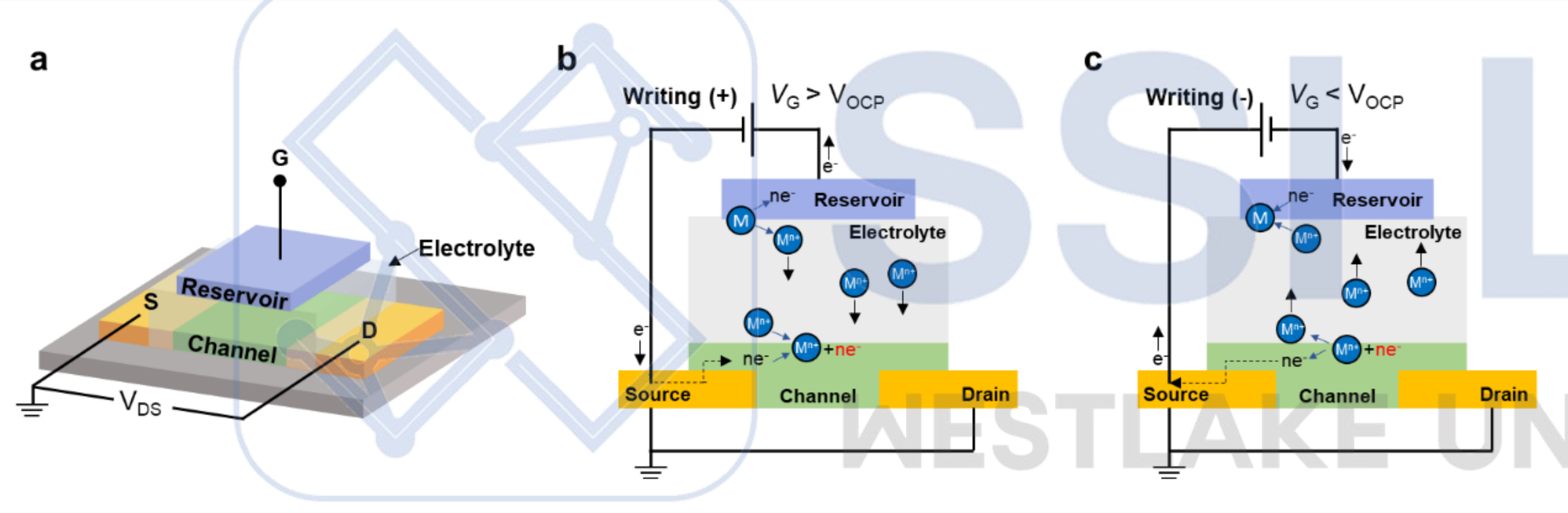


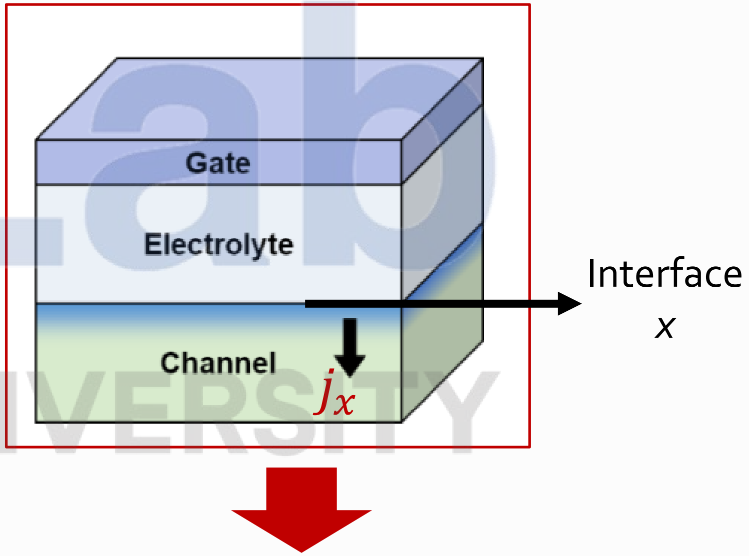
$$E - E_{eq} = \frac{RT}{\alpha F} lnI_0 - \frac{RT}{\alpha F} ln|I|$$



Beyond electrocatalysts: the application of B-V equation

The Butler-Volmer (B-V) equation can be used to describe the kinetics of *charge transfer* at interfaces, not limited to electrocatalysts.





$$j_x = j_{x_0}\ (\exp(-\frac{\alpha_x zFV_x}{RT}) - \exp(\frac{(1-\alpha_x)zFV_x}{RT}))$$

- *Electrochemical Ionic Synapses* use redox rxn to tune the conductivity of the channel material for memory and computing;
- Faradaic current density at interface *x* (electrolyte/channel interfaces) is modeled using B-V.

Huang, del Alamo, Li, Yildiz *et al.*, *Adv. Mater.*, (2022)

Things we have discussed in this lecture

Kinetics of Electrode Reactions:

- How to build a model for charge transfer at electrode surfaces?
- What are the key assumptions for Butler-Volmer equations?
- What does the η-I curve look like at small/large overpotentials?

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

End of Lecture 10
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