Lecture 11-12:
Solid-State Electrochemistry III
Frumkin Effect & Marcus Theory

Solid State Ionics

Fall 2022

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Things we will discuss in this lecture

Frumkin Effect:

- What is the Frumkin Effect? How does the space charge layer affect the kinetics at electrode surfaces/interfaces?

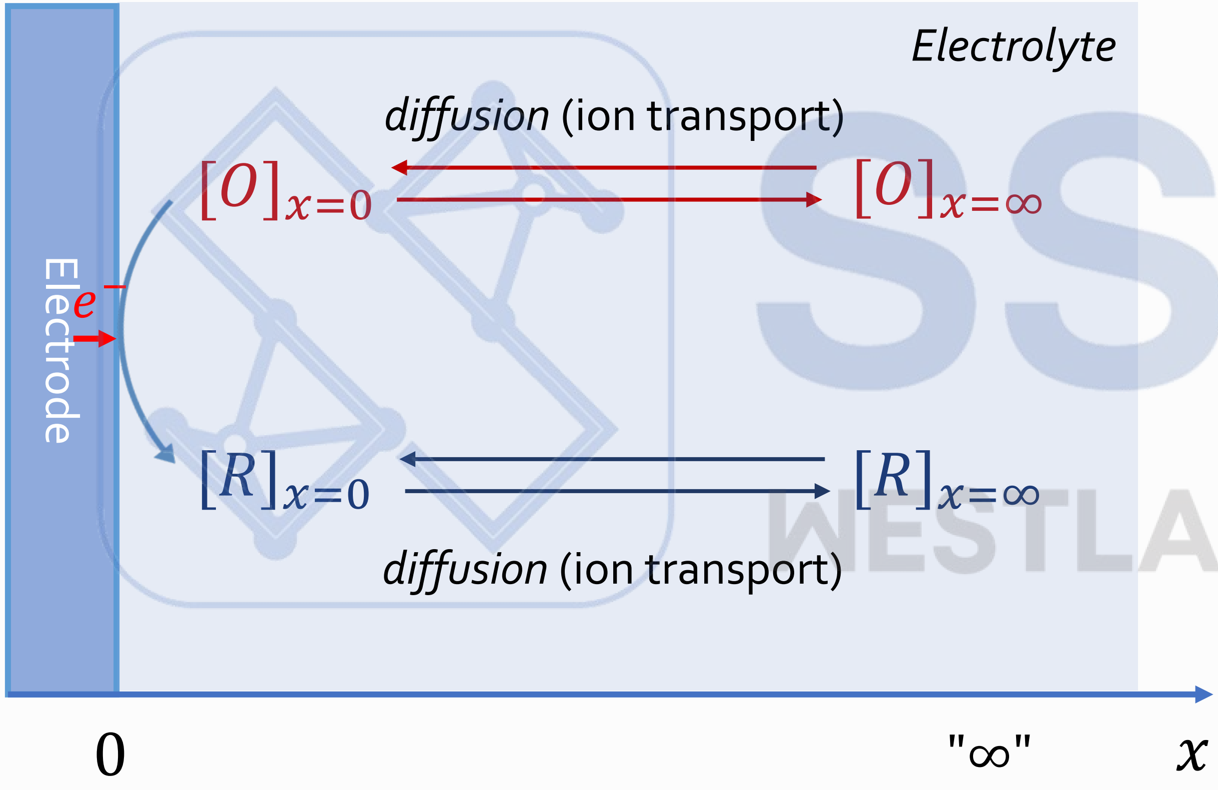
Marcus Theory:

- What does the picture of Marcus Theory for charge transfer look like?

- What is *reorganization energy* and why is it important in the Marcus Thoery?

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

Electrochemical reaction: Nernst equation



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

Equilibrium potential with fixed $[O]_{x=0}$ and $[R]_{x=0}$

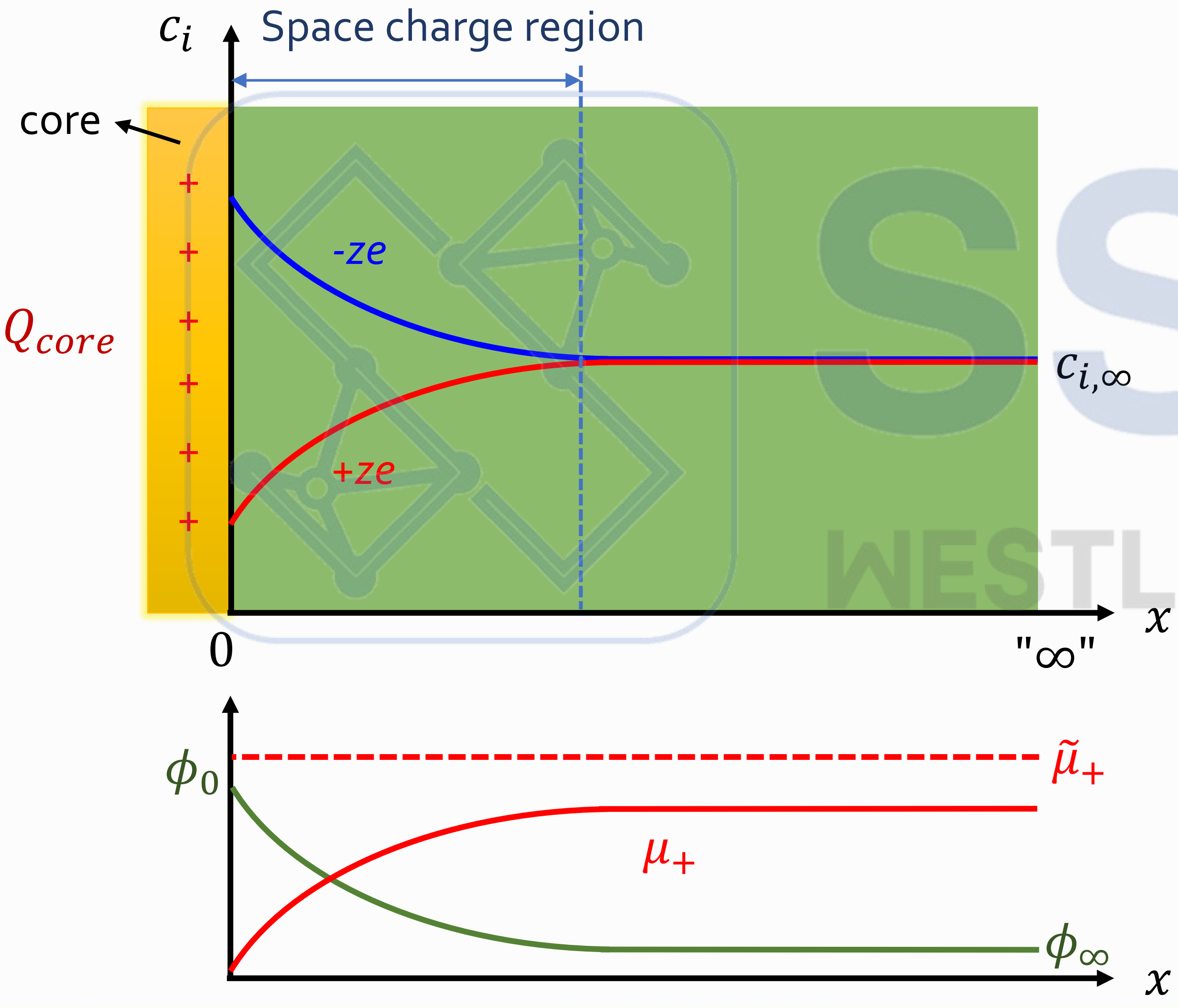
(concentrations are only evaluated *at electrode/electrolyte interfaces*)

Nernst Equation

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

Fast diffusion

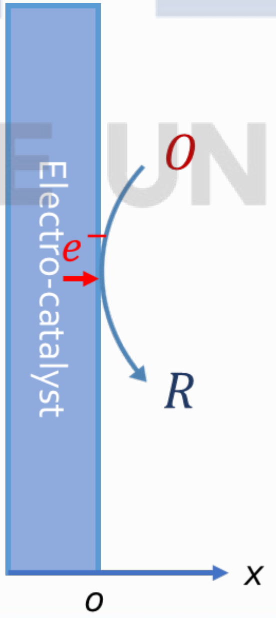
The effect of space charge layer on electrode kinetics



Recall the concentration profile in the space charge layer:

$$c_+(x) = c_{i,\infty}\exp(-\frac{ze\phi(x)}{k_B T})$$

$$c_-(x) = c_{i,\infty}\exp(+\frac{ze\phi(x)}{k_B T})$$



Recall exchange current I_0

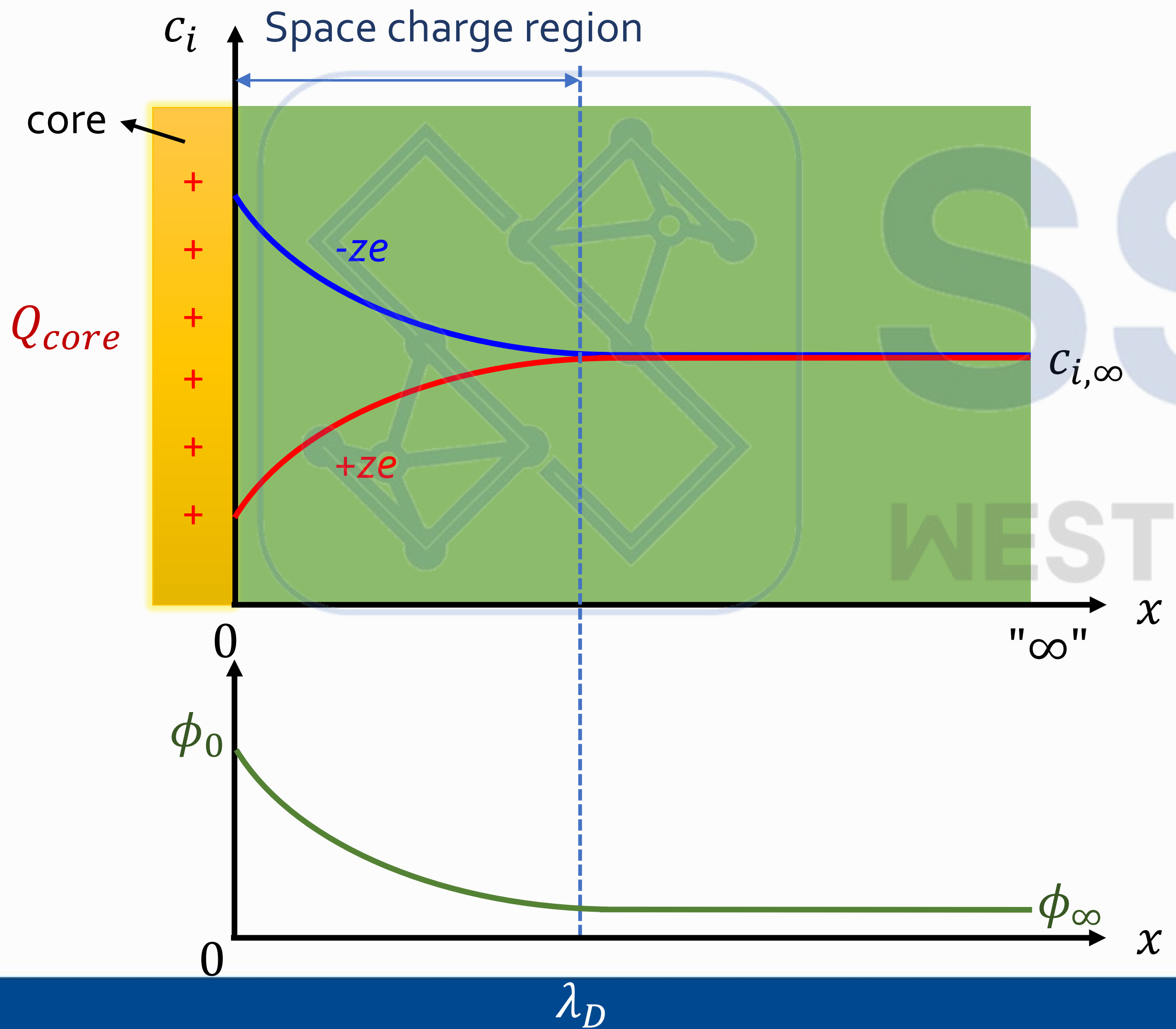
$$I_0 = FA\,k^0([O]_{x=0})^{1-\alpha}([R]_{x=0})^{\alpha}$$

I_0 is dependent on the concentrations at $x = 0$

Space charge effect (so-called Frumkin effect)

Gouy-chapman case: potential profile

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

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

↓

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

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

↓

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

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

Gouy-chapman case: apply Gauss's Law to get Q_{core}

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

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

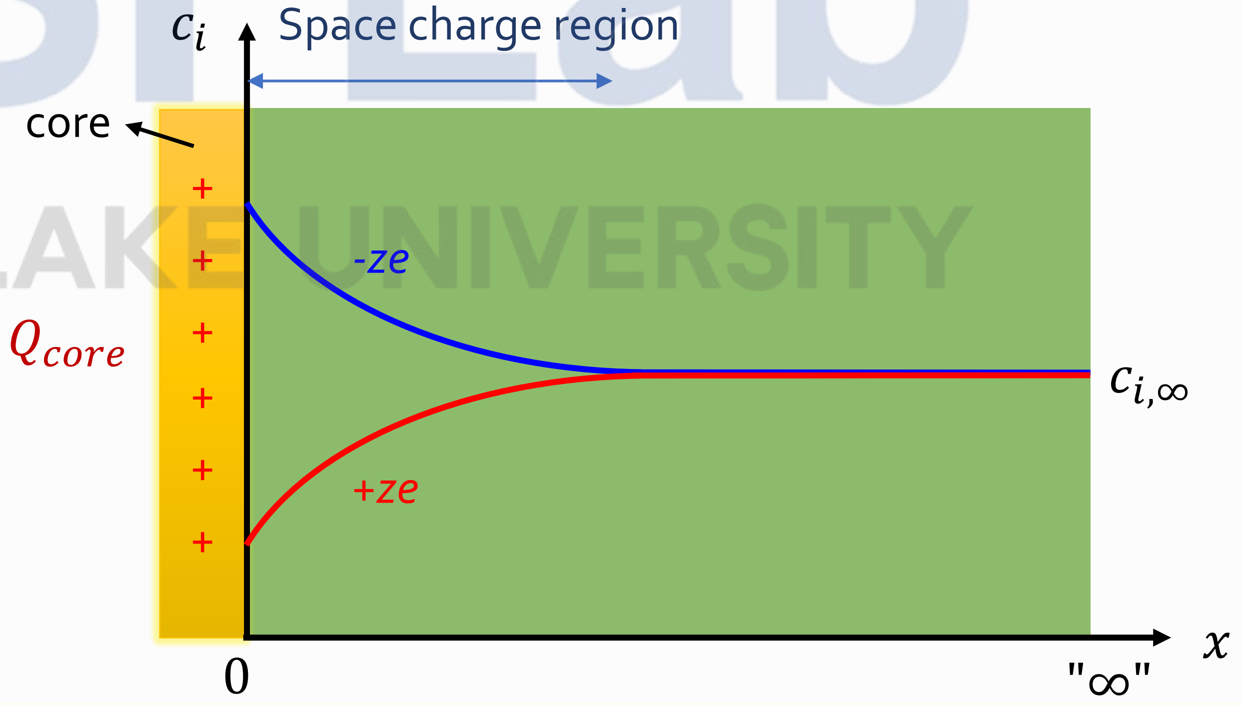
If $ze\phi_0 \ll k_BT$, we can linearize the equation by using $\tanh x \sim x$: → $\phi(x) = \phi_0 \exp(-x/\lambda_D)$

Electric field ← $E = \frac{Q_{enc}}{\varepsilon_0 \varepsilon_r}$ → *"enclosed charge"*

At position $x = 0$:

$$E(0) = -\left.\frac{d\phi}{dx}\right|_{x=0} = -\frac{2k_BT}{ze\lambda_D}\sinh(\frac{ze\phi_0}{2k_BT})$$

$$Q_{core} = \varepsilon_0\varepsilon_r \frac{2k_BT}{ze\lambda_D}\sinh\left(\frac{ze\phi_0}{2k_BT}\right)$$



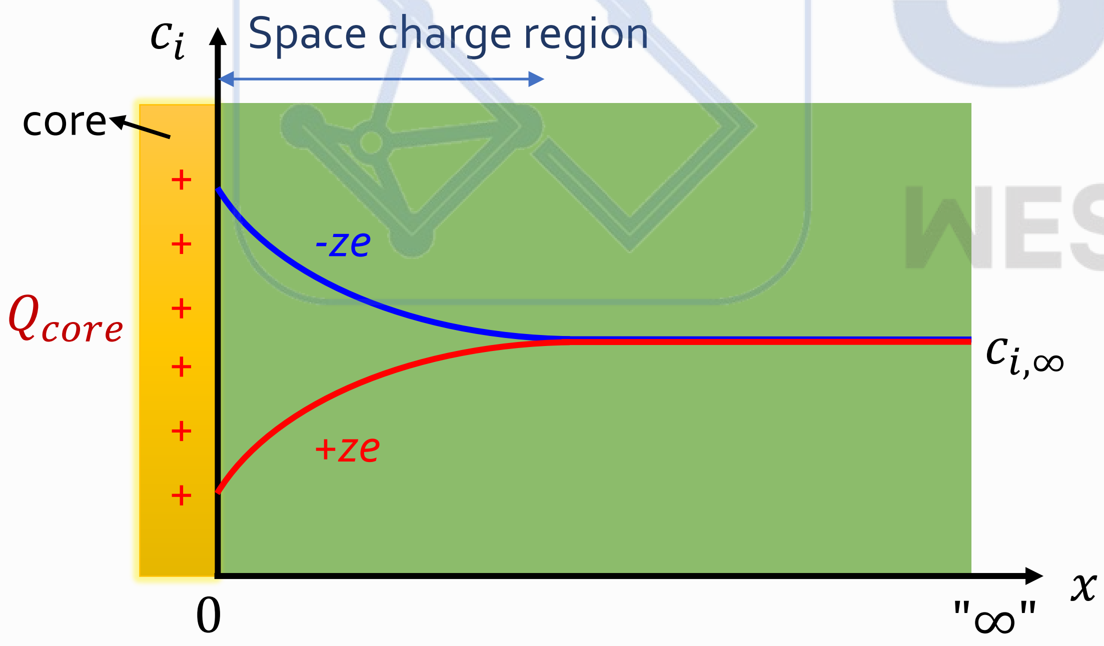
Gouy-chapman case: differential capacitance

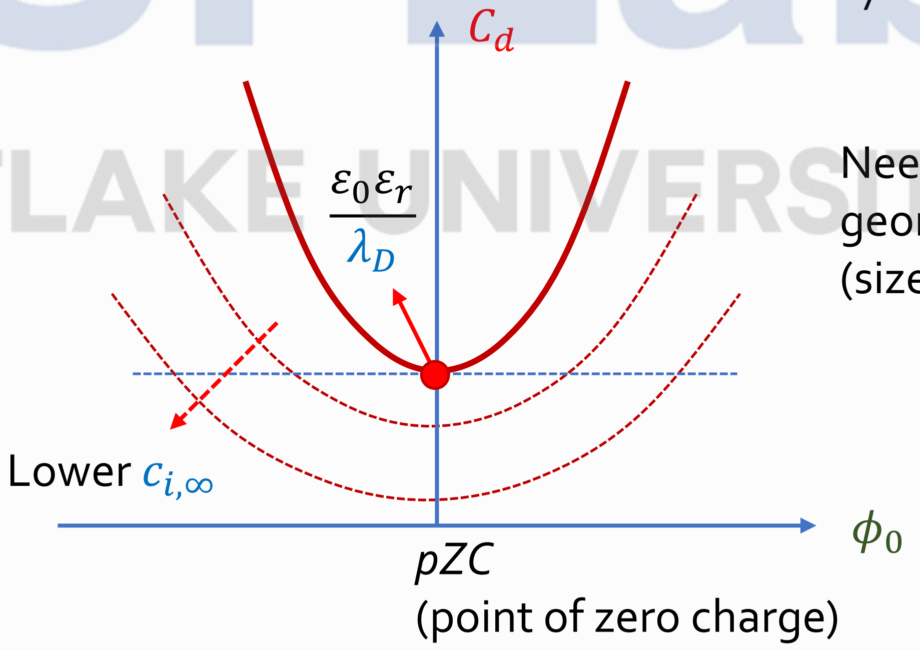
We have established the correlation between charge Q_{core} and potential ϕ_0

$$Q_{core} = \varepsilon_0 \varepsilon_r \frac{2k_BT}{ze\lambda_D} \sinh\left(\frac{ze\phi_0}{2k_BT}\right)$$

We can define differential capacitance:

$$C_d = \frac{dQ_{core}}{d\phi_0} = \frac{\varepsilon_0 \varepsilon_r}{\lambda_D} \cosh\left(\frac{ze\phi_0}{2k_BT}\right)$$





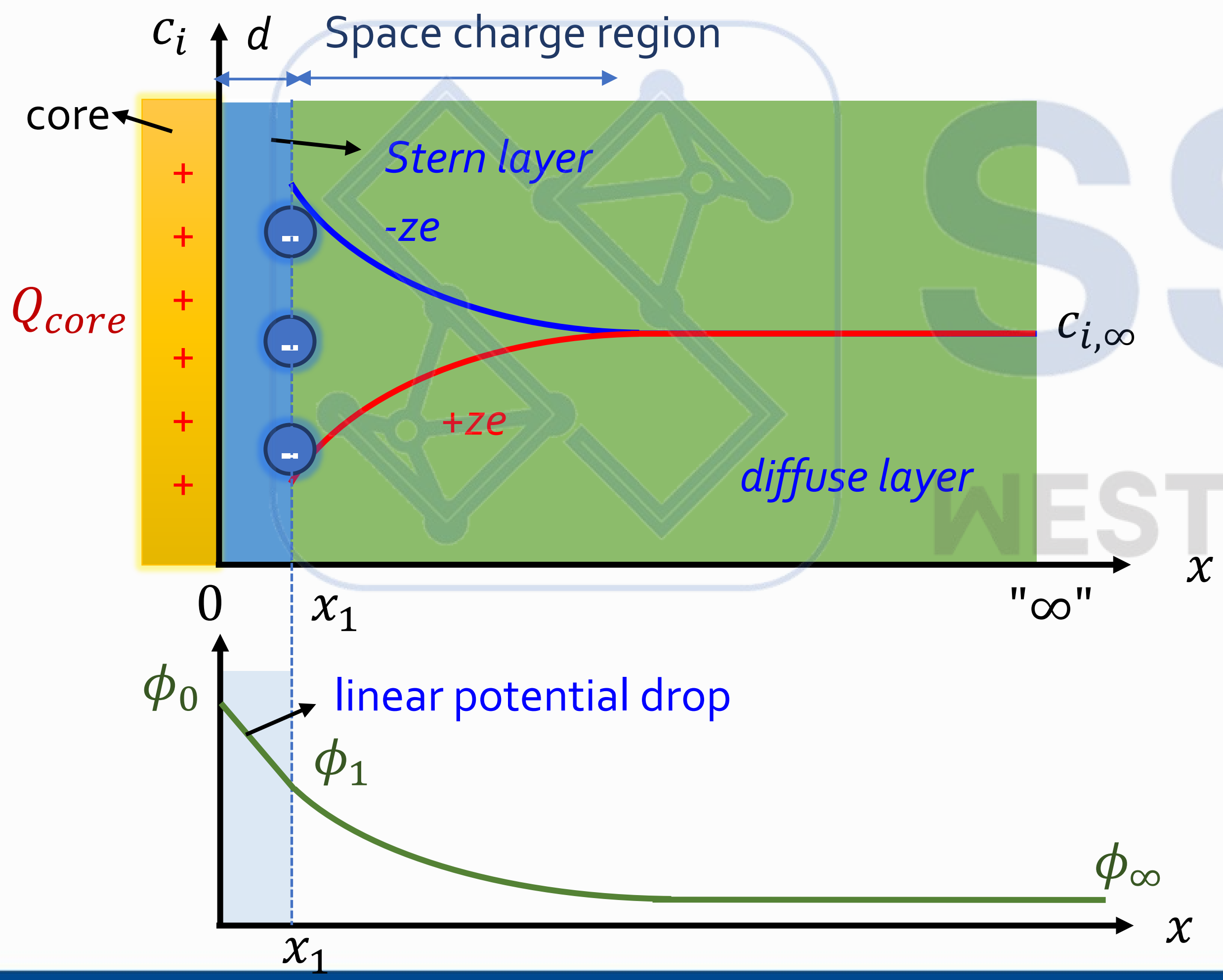
Problem:
Capacitance goes to infinite at high potentials

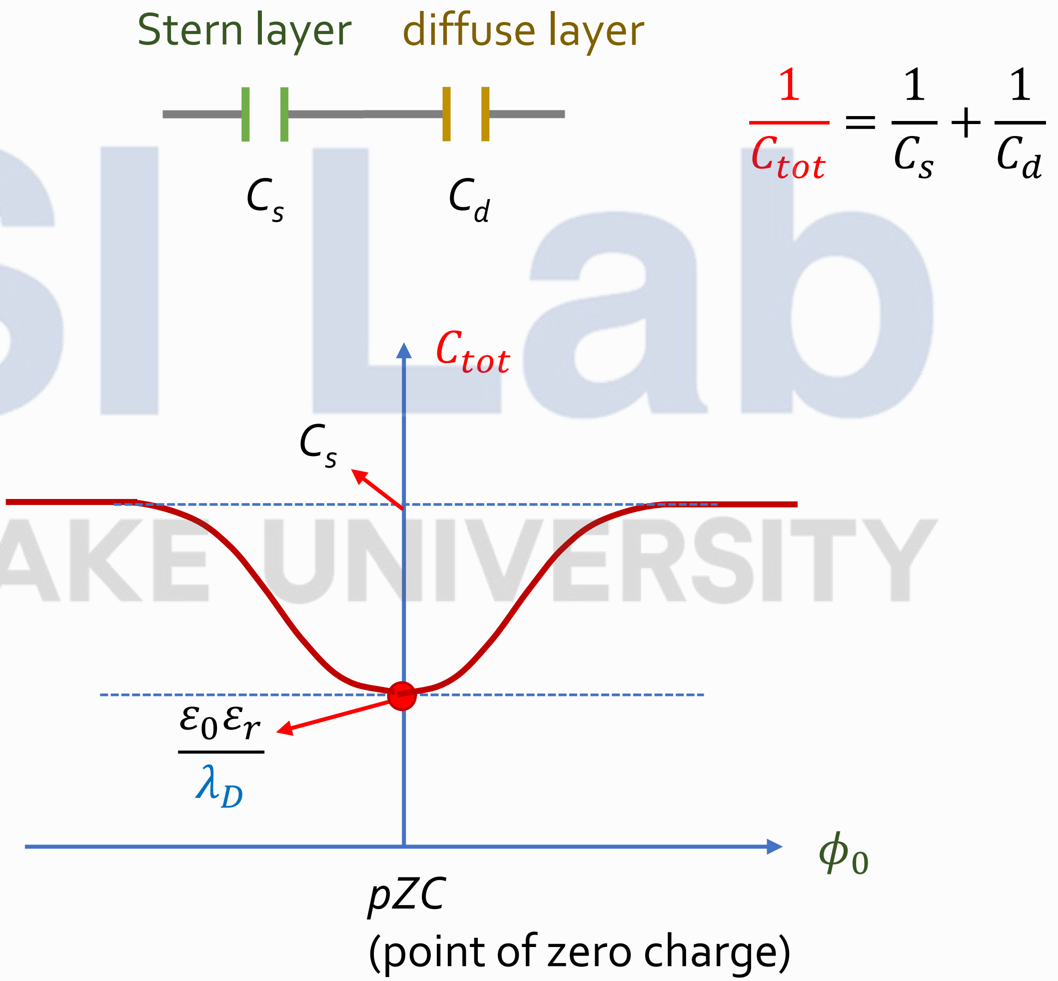
Origin:
Defects are treated as point charges that can be infinitely close to the core.

Need to consider geometry effect (size of defects)

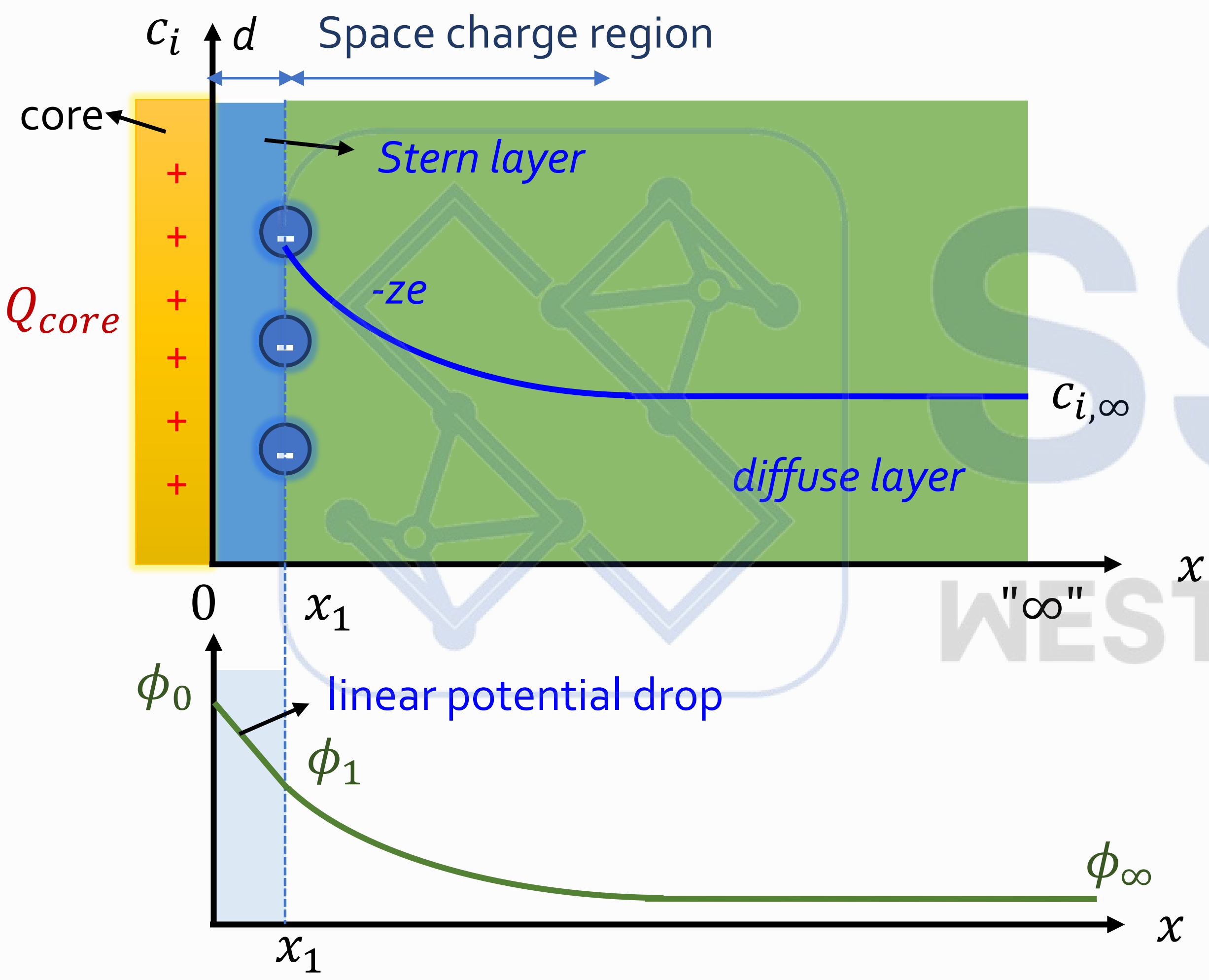
Gouy-chapman case: Stern layer

One must consider the size of defects to solve the capacitance issue:





Frumkin effect: the contribution of Stern and diffuse layers



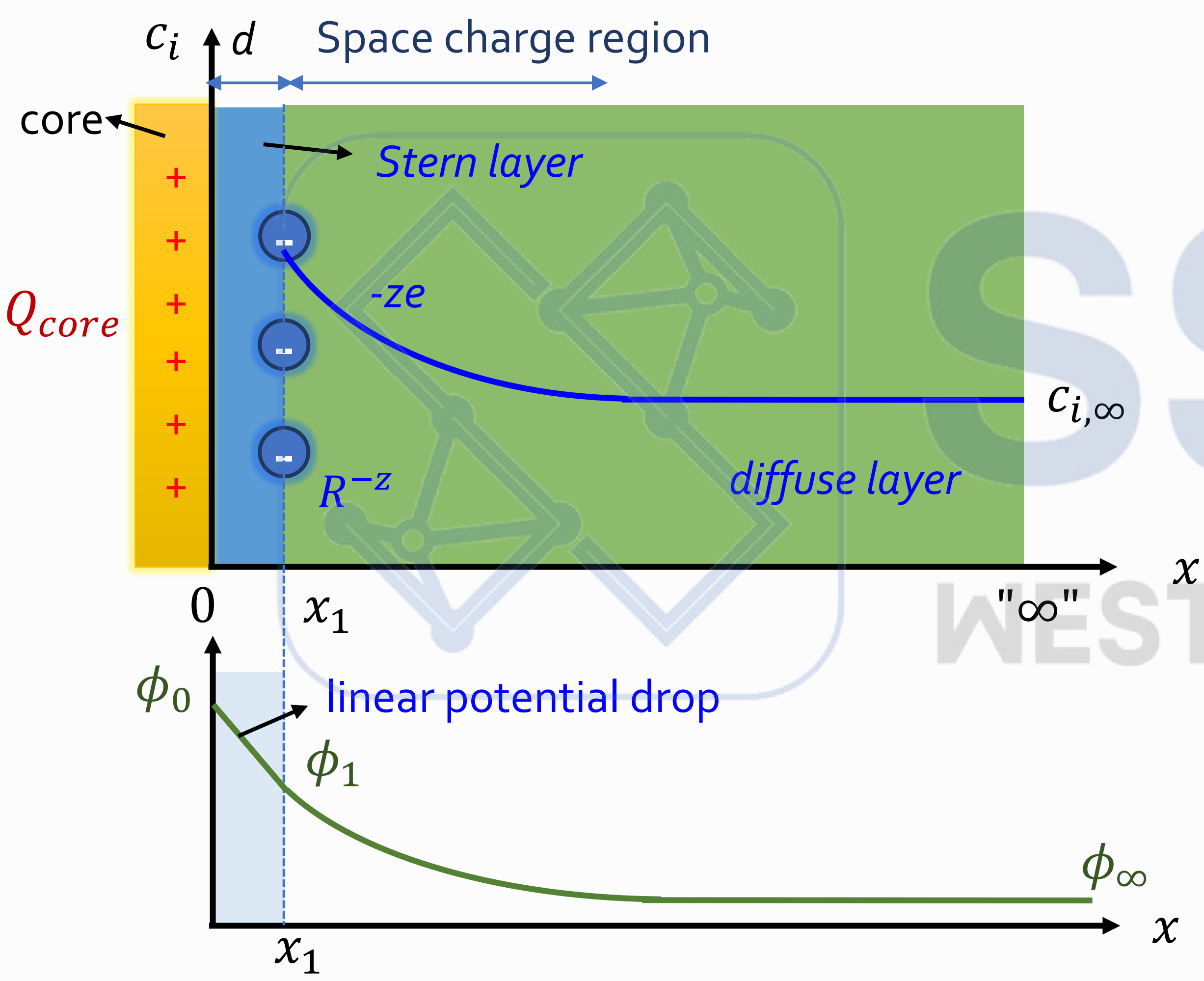
$$O^{-(z-1)} + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R^{-z}$$

$$I_a = FA\overleftarrow{R} = FAk_a[R]_{x=x_1} = FAk^0 exp\left(\frac{(1-\alpha)F\Delta E}{RT}\right)[R]_{x=x_1}$$

- *Concentration effect*: $[R]_{x=x_1} = [R]_{x=\infty}\exp(-zF\phi_1/RT)$
- *Potential effect*:
  w/o Stern layer: $\longrightarrow$ $\Delta E = E - E^{0'}$
  w/ Stern layer: $\longrightarrow$ $\Delta E = E - E^{0'} - \phi_1$

The *Frumkin effect* is the combination of both effects from the change of concentration and potential!

Frumkin effect: the contribution of Stern and diffuse layers



$$I_a = FA\overleftarrow{R} = FAk_a[R]_{x=x_1} = FAk^0 exp\left(\frac{(1-\alpha)F\Delta E}{RT}\right)[R]_{x=x_1}$$

$$[R]_{x=x_1} = [R]_{x=\infty}\exp(zF\phi_1 / RT)$$

$$\Delta E = E - E^{0'} - \phi_1$$

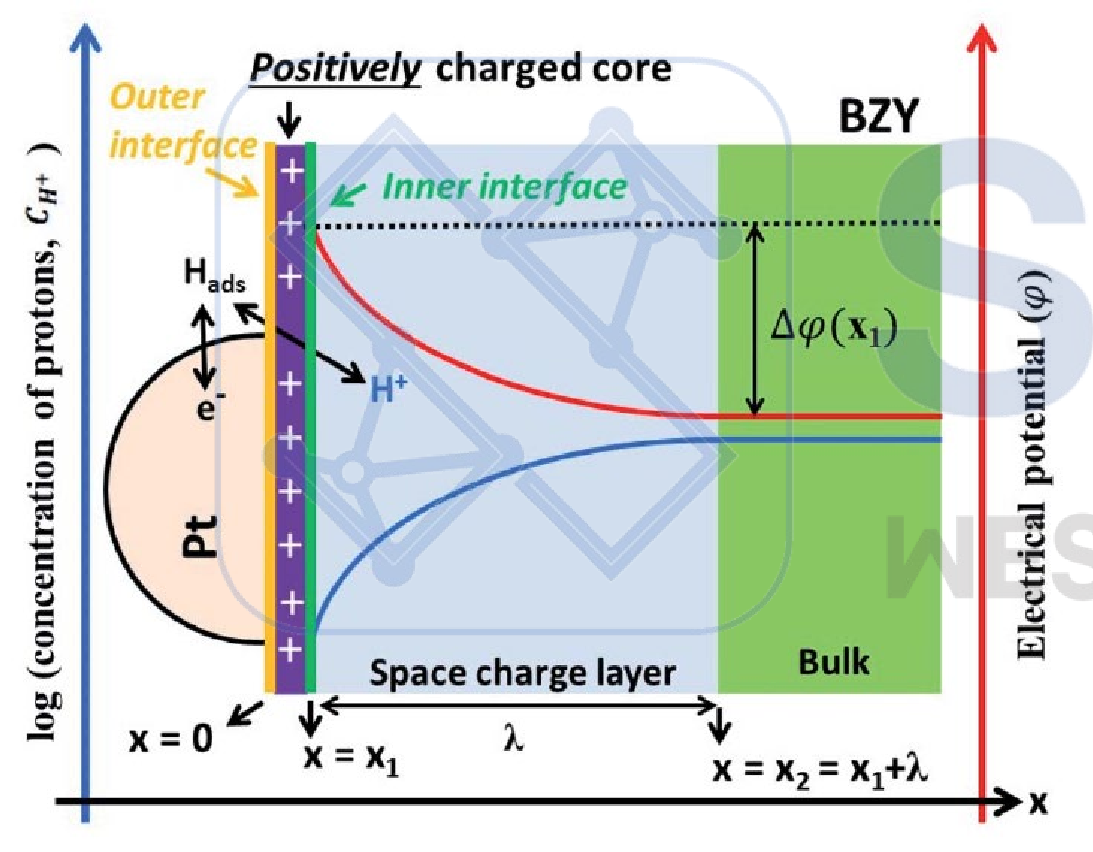
$$I_a = FAk^0 exp\left(\frac{(1-\alpha)F\left(E - E^{0'} - \phi_1\right)}{RT}\right)[R]_{x=\infty}\exp\left(\frac{zF\phi_1}{RT}\right)$$

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

$$\exp\left(\frac{(z-(1-\alpha))F\phi_1}{RT}\right)$$

Modification from *Frumkin effect*

An example: hydrogen oxidation *rxn* (HOR) at Pt/BZY interfaces



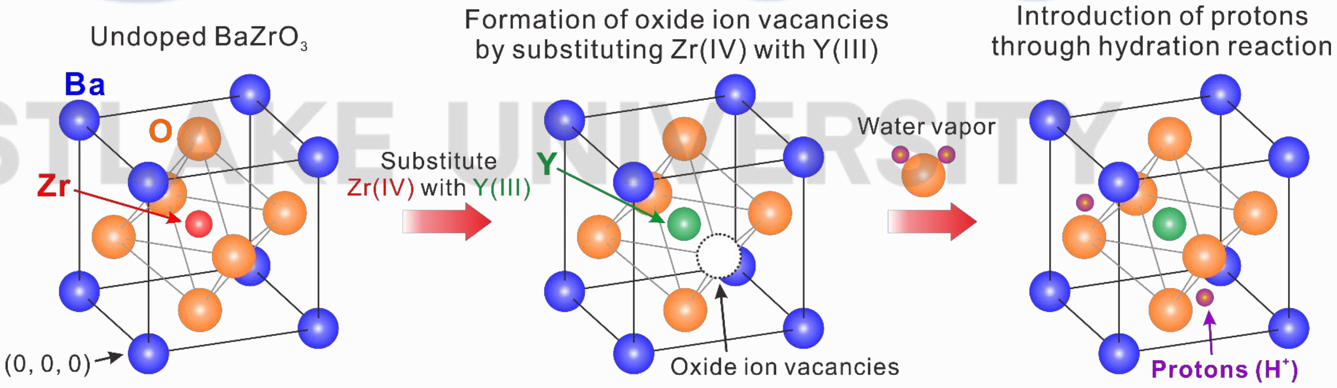
BZY = $BaZr_{0.9}Y_{0.1}O_{3-x}$

$$H_2O + V_O^{\cdot\cdot} + O_O^{\times} \rightleftharpoons 2OH_O^{\cdot}$$

H^+

Electrochemical rxn:

$$H_{ads} \rightleftharpoons OH_O^{\cdot} + e'$$



Courtesy of Prof. Donglin Han (Soochow University)

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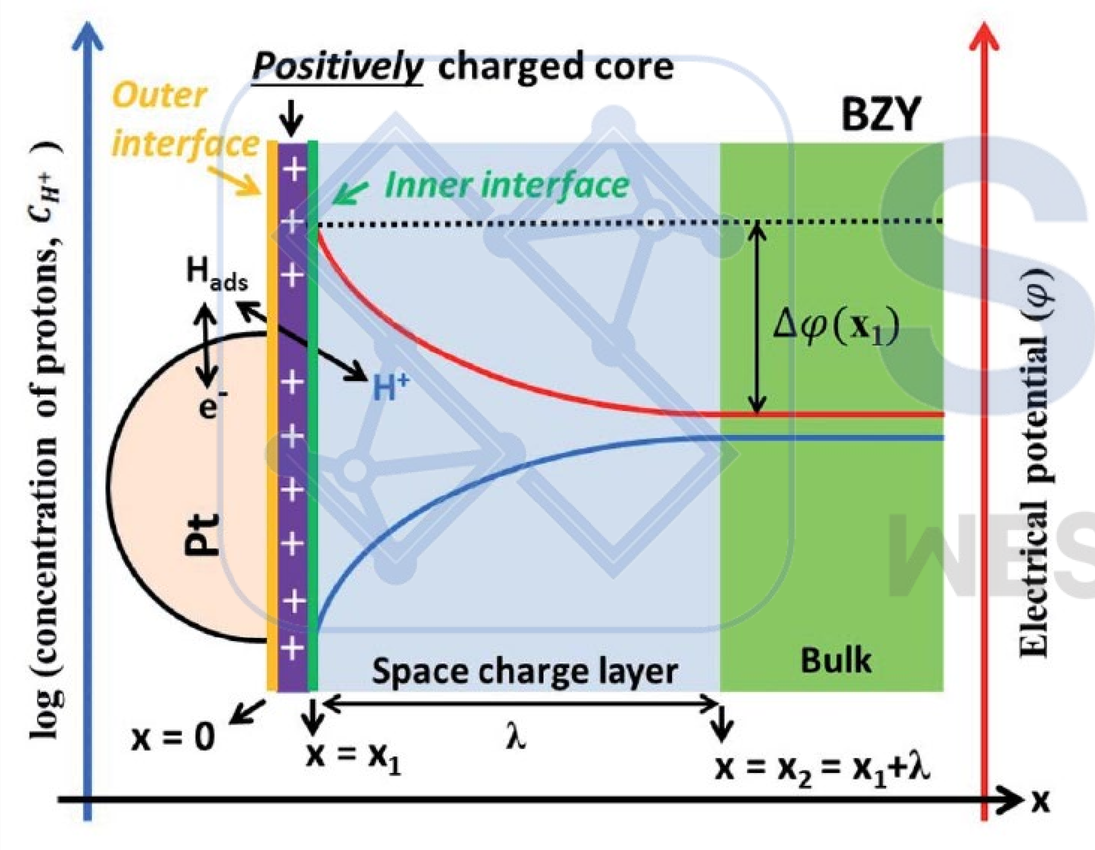

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H^+

Electrochemical rxn:

$$H_{ads} \rightleftharpoons OH_O^{\cdot} + e'$$

- Due to the positive space charge core, the proton ($OH_O^{\cdot}$) concentration at $x = x_1$ becomes depleted;
- This will lead to a modified exchange current density due to the Frumkin effect.

Exchange current

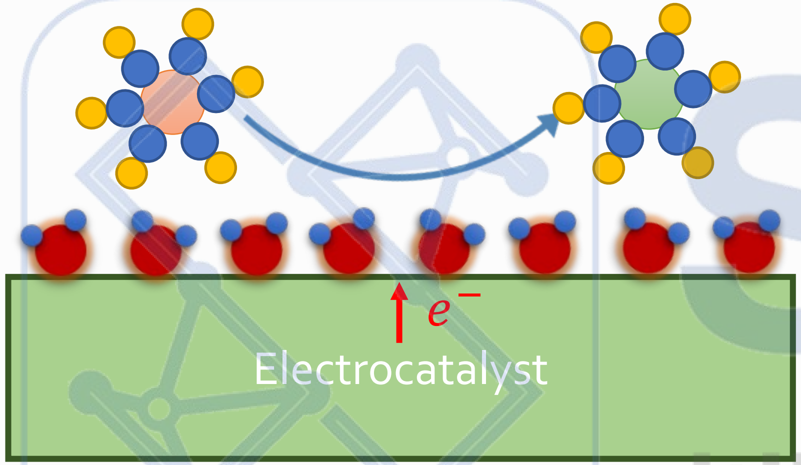
$$I_0 = FA\,k^0([OH_O^{\cdot}]_{x=x_1})^{1-\alpha}\theta_H{}^{\alpha}$$

modified proton conc. *H surf. coverage*

Microscopic picture of charge transfer

Outer Sphere Reaction

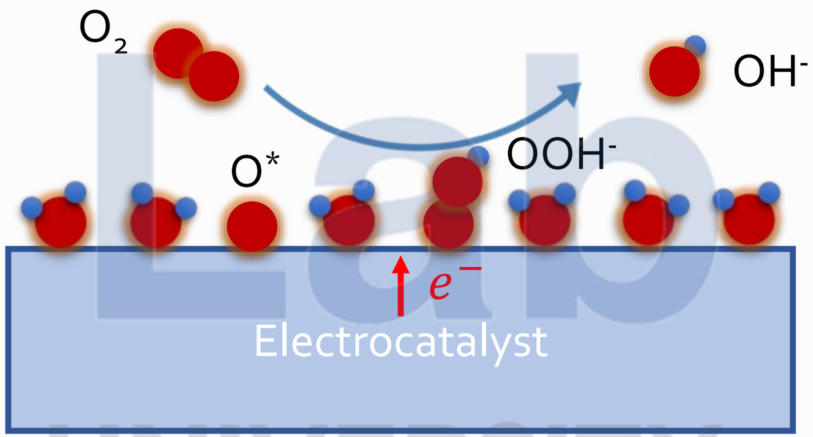
$$Fe(CN)_6^{3+} + e^- \rightarrow Fe(CN)_6^{4+}$$



- The reactant (and the product) does not interact with the electrocatalyst surfaces;
- The original coordinate sphere maintained during the electrochemical reaction.

Inner Sphere Reaction

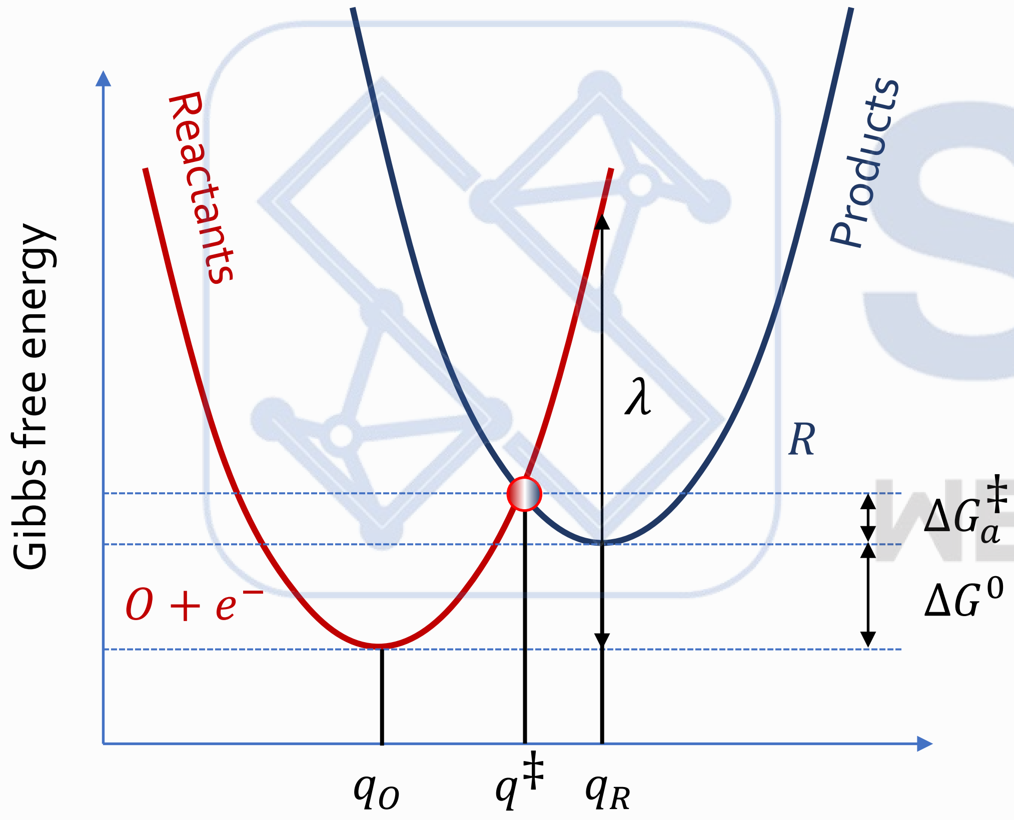
$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$$



- The reactant, product and the ***intermediates*** interact strongly with the electrocatalyst surfaces;
- The original coordinate sphere greatly changed during the electrochemical reaction

Marcus theory: basic assumptions

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



Assumption: the free energy curves have quadratic form as a function of *rxn* coordinates.

$$\Delta G_O(q) = \frac{1}{2}k(q - q_O)^2$$

$$\Delta G_R(q) = \frac{1}{2}k(q - q_R)^2 + \Delta G^0$$

Quadratic (harmonic oscillators)

q: vibrational coordinate

Define *reorganization energy* $\lambda = \frac{1}{2}k(q_R - q_O)^2$

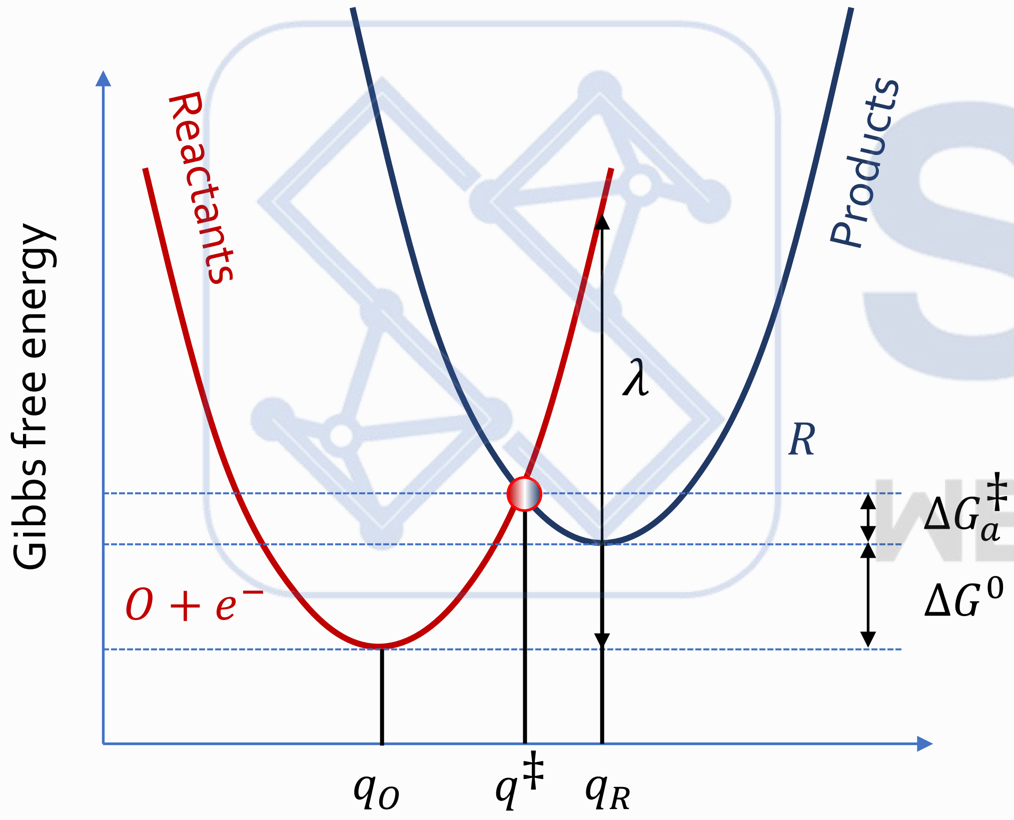
Rudolph A. Marcus

The Nobel Prize in Chemistry 1992

"for his contributions to the theory of electron transfer reactions in chemical systems"

Marcus theory: cross-over point

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



$$\Delta G_O(q) = \frac{1}{2}k(q - q_O)^2$$

$$\Delta G_R(q) = \frac{1}{2}k(q - q_R)^2 + \Delta G^0$$

Quadratic (harmonic oscillators)

q: vibrational coordinate

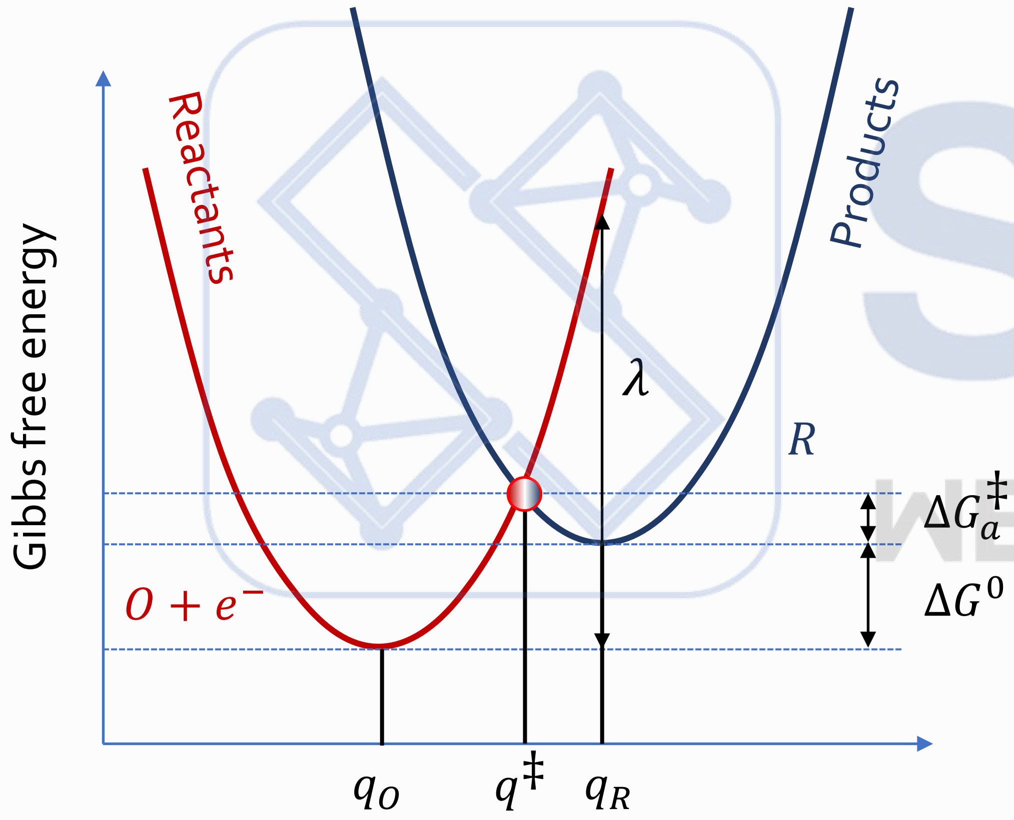
Electron jumping from Reactants ($O + e^-$) to Products (R) must occur at cross-over point because of:

- ***Frank-Condon principle***. Electron transfer occurs so rapidly (in a vibrational frequency) that no change in nuclear configuration can occur during the transfer. This requires that the transfer is a *vertical* line in the diagram.
- ***Conservation of energy*** requires that the transition is a *horizontal* line on the diagram

Cross-over ***point***

Marcus theory: the expression for the barrier

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



Define *reorganization energy* $\lambda = \frac{1}{2}k(q_R - q_O)^2$

$$\Delta G_O(q) = \frac{1}{2}k(q - q_O)^2$$

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Quadratic (harmonic oscillators)

q: vibrational coordinate

At $q = q^\ddagger$ (where the two parabolas intersect)

$$\frac{1}{2}k(q^\ddagger - q_O)^2 = \frac{1}{2}k(q^\ddagger - q_R)^2 + \Delta G^0$$

$$q^\ddagger = \frac{q_R + q_O}{2} + \frac{\Delta G^0/k}{q_R - q_O}$$

$$\Delta G_c^\ddagger = \frac{1}{2}k(q^\ddagger - q_O)^2 = \frac{1}{2}k(\frac{q_R - q_O}{2} + \frac{\Delta G^0/k}{q_R - q_O})^2$$

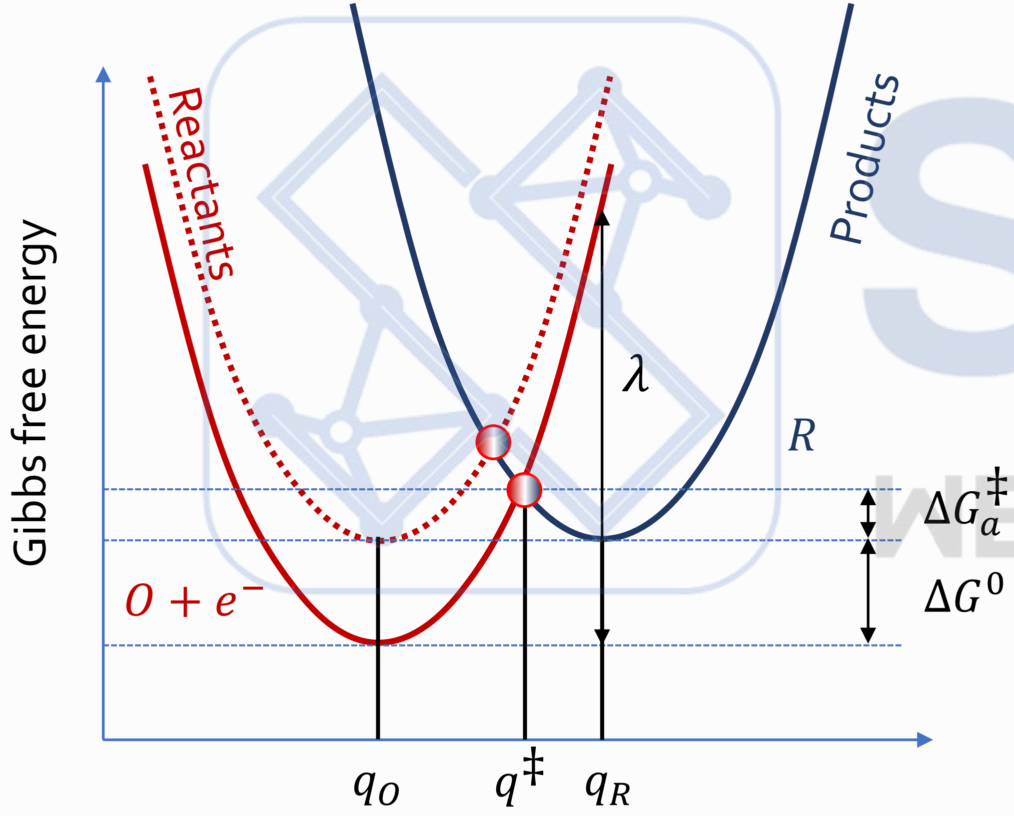
$$= \frac{1}{4}[\frac{1}{2}k(q_R - q_O)^2](1 + \frac{2\Delta G^0}{k(q_R - q_O)^2})^2$$

$$\Delta G_c^\ddagger = \frac{\lambda}{4}(1 + \frac{\Delta G^0}{\lambda})^2$$

$$\Delta G_{c,a}^\ddagger = \frac{\lambda}{4}(1 \pm \frac{\Delta G^0}{\lambda})^2$$

Marcus theory: symmetric coefficient

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

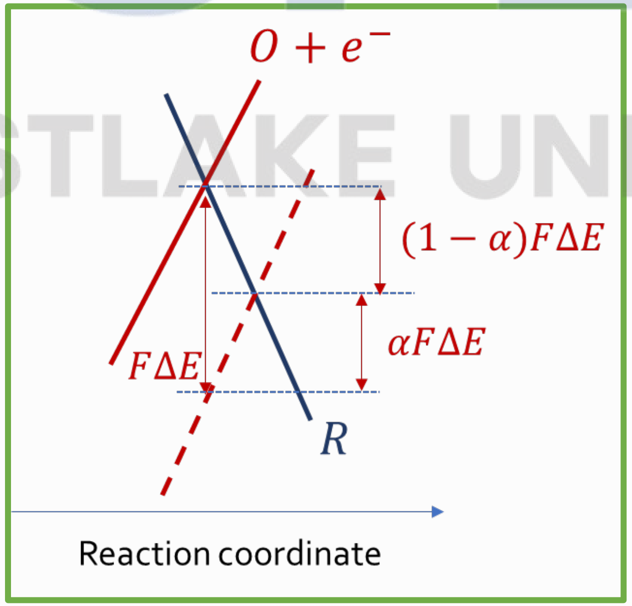


$$\Delta G^{\ddagger}_{c,a} = \frac{\lambda}{4}\left(1 \pm \frac{\Delta G^0}{\lambda}\right)^2 = \frac{\lambda}{4}\left(1 \pm \frac{F(E - E^0)}{\lambda}\right)^2$$

Reorganization energy

$$\lambda = \frac{1}{2}k(q_R - q_O)^2$$

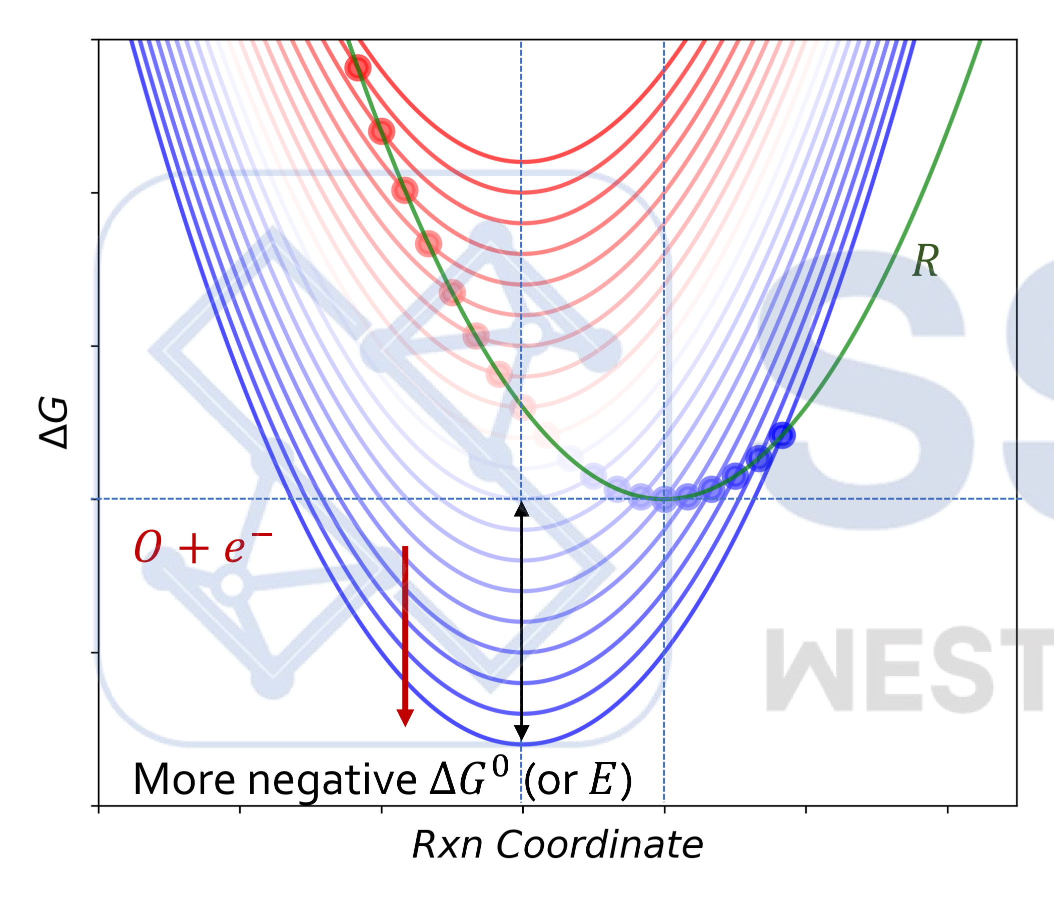
The energy required to transform the ***nuclear configurations*** in the *reactant* to that in the *product*

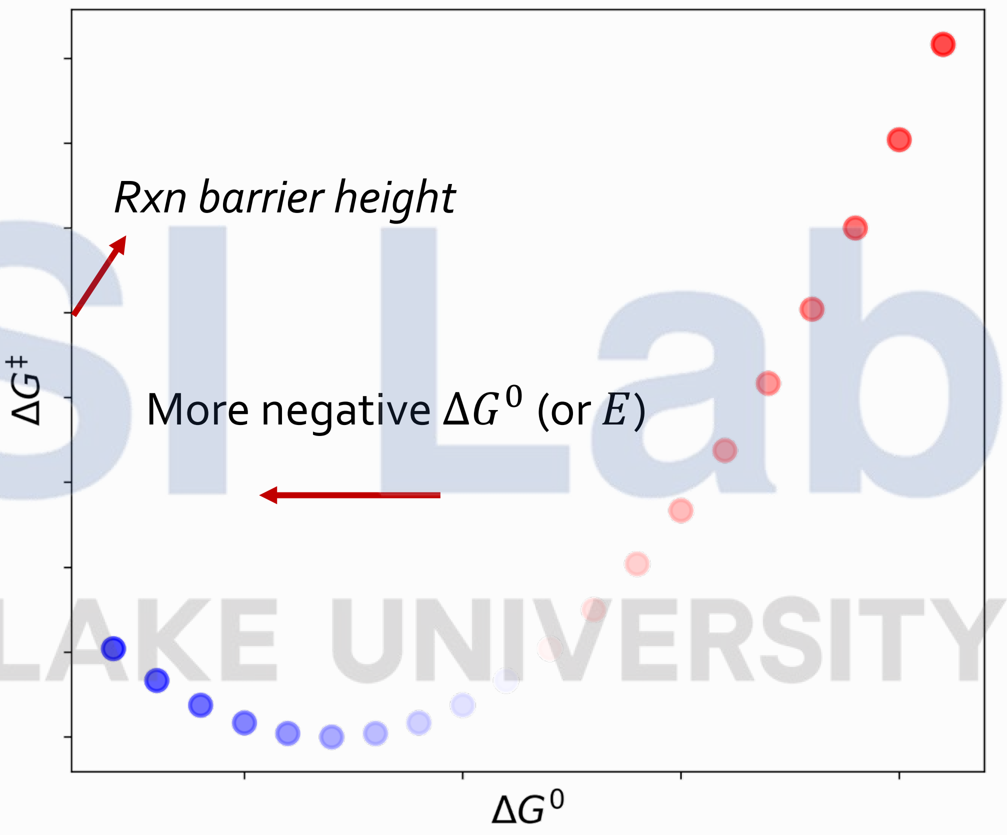


$$\alpha = \frac{1}{F}\frac{\partial \Delta G^{\ddagger}}{\partial E} = \frac{1}{2} + \frac{F(E - E^0)}{2\lambda}$$

Symmetric coefficient α is ***potential-dependent*** predicted by using Marcus Theory

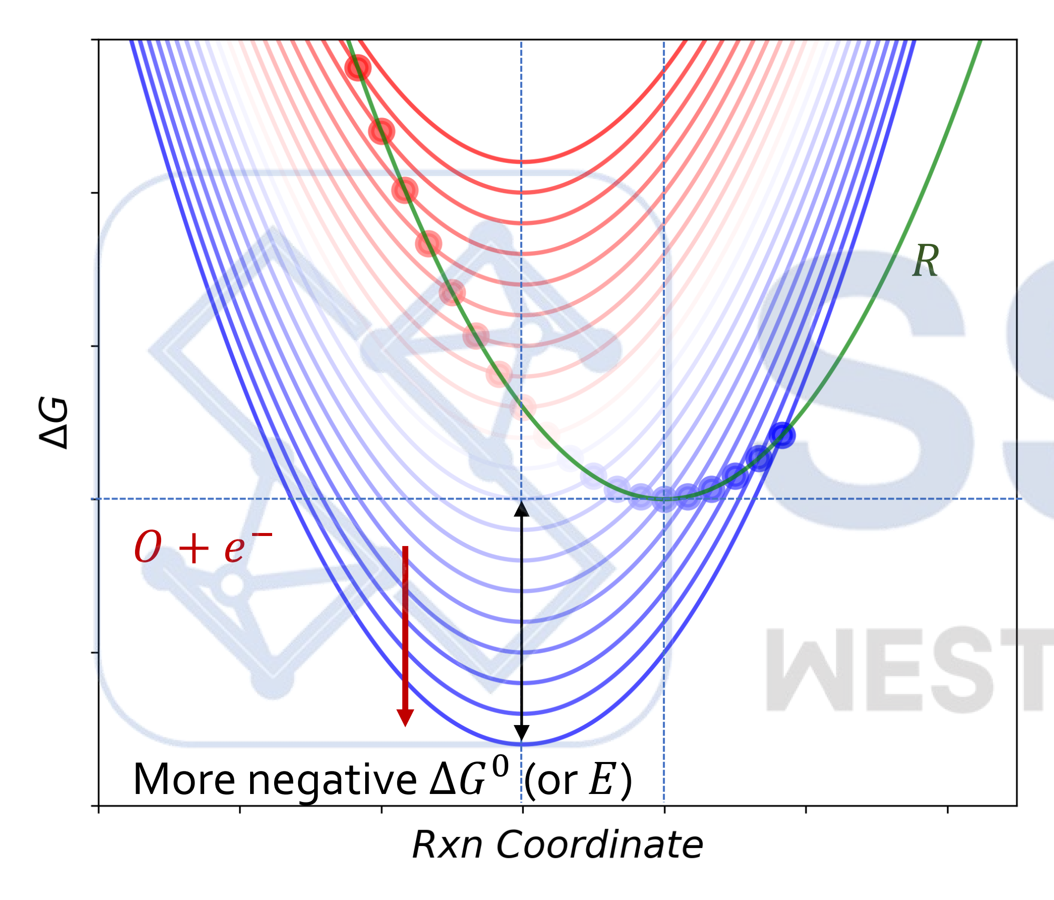
Marcus theory: inverted region

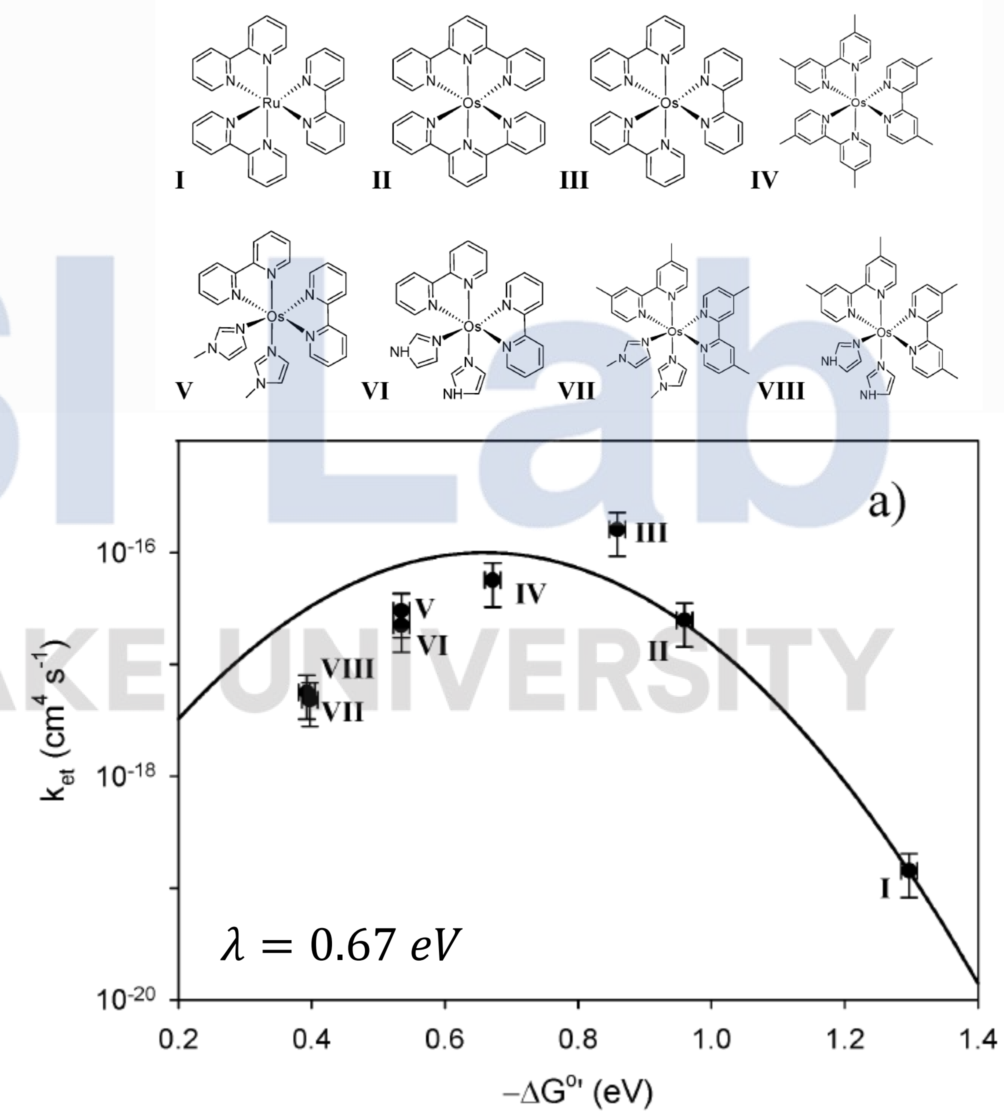




- In B-V *eqn.*, rxn rate change monotonically with E ($\Delta G^0 = F(E - E^0)$);
- Marcus theory predicts the existence of an *inverted region*, *i.e.*, although ΔG^0 becomes more negative, the barrier ($\Delta G^\ddagger$) does not change monotonically.

Marcus theory: inverted region



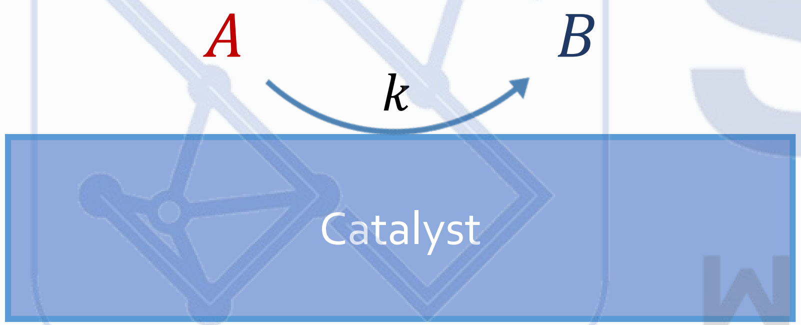


Marcus theory predicts the existence of an *inverted region*, *i.e.*, although ΔG^0 becomes more negative, the barrier ($\Delta G^{\ddagger}$) does not change monotonically.

Go quantum…

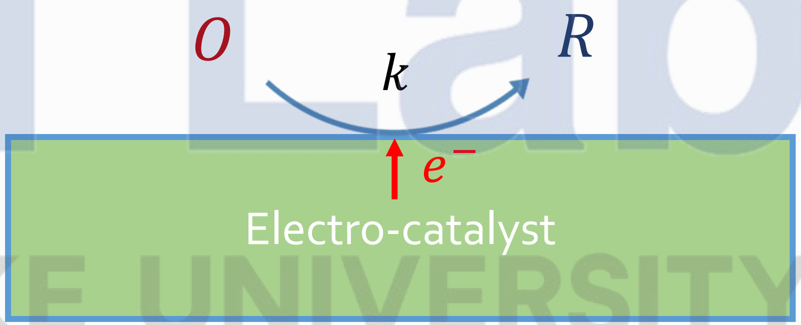
Chemical Reaction (*rxn*)
(Catalysis)

$$A \rightleftharpoons B$$



Electrochemical Reaction
(Electro-catalysis)

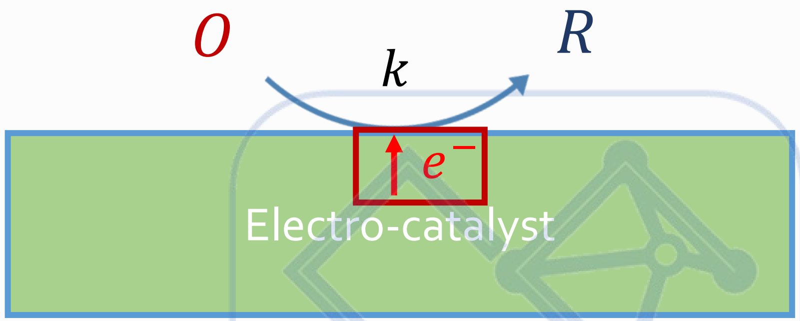
$$O + e^- \rightleftharpoons R$$



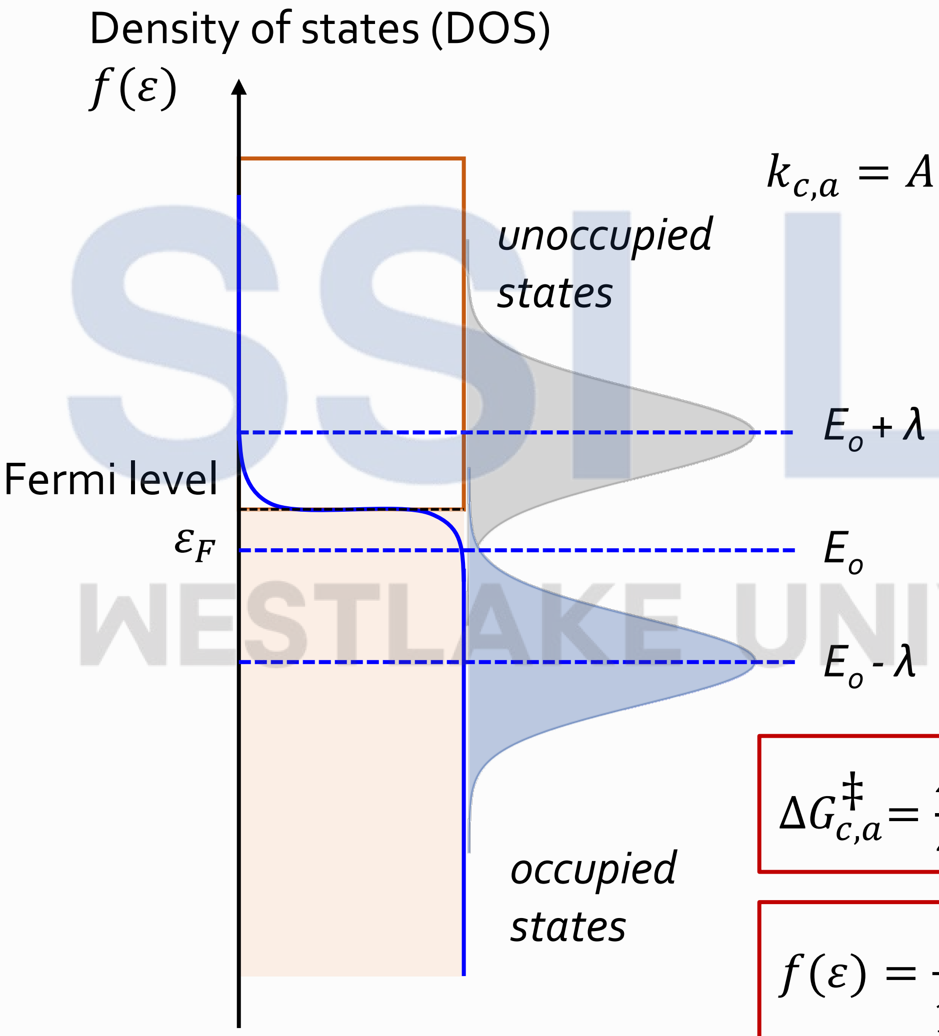
Reaction rate is determined by
- Concentration of reactant and product ($[A]$ and $[B]$)
- Temperature

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

Marcus-Hush-Chidsey Theory: the effect of charge carrier distribution



- Up to now, we have largely ignored the details of electrons in kinetics;
- The availability of electrons (or electron holes) should have a large impact on electrode kinetics
- Fermi-Dirac distribution is used for description of electron/hole density.



Marcus theory

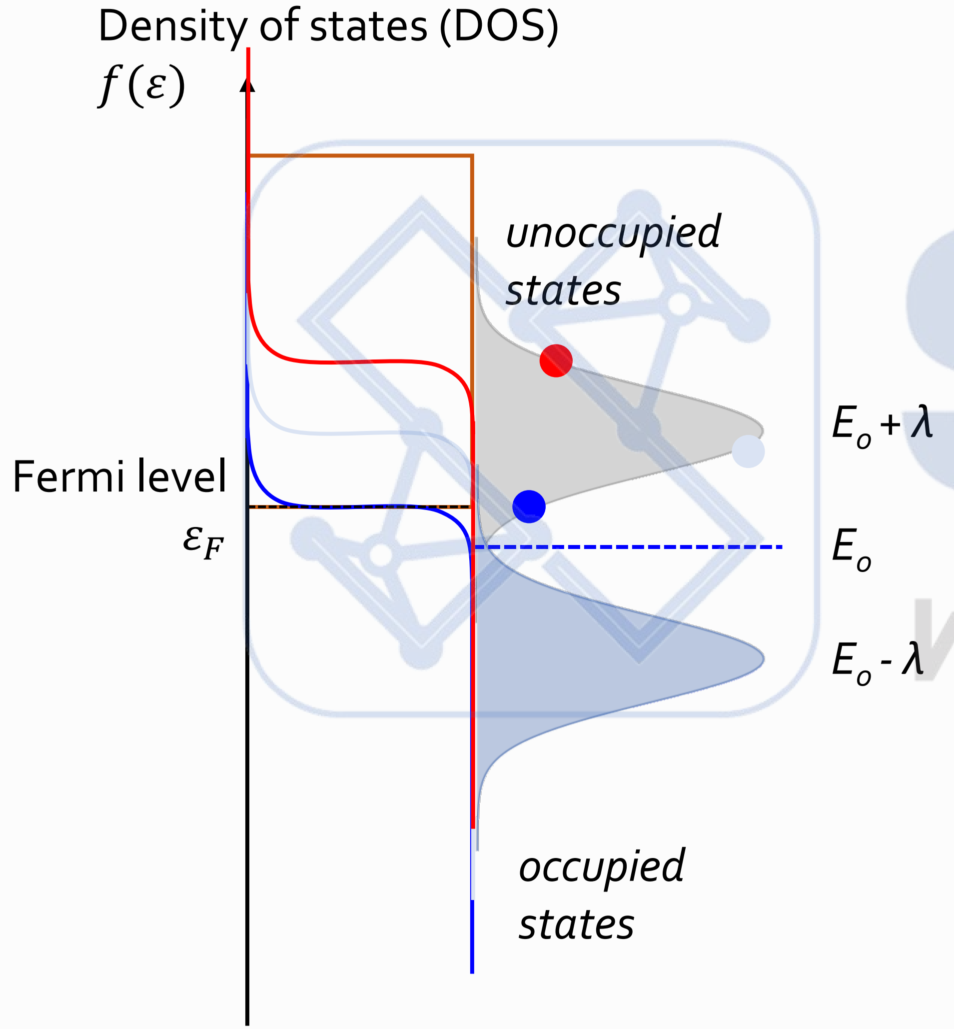
$$k_{c,a} = A \int_{-\infty}^{+\infty} \exp\left(-\frac{\left(\varepsilon - \lambda \pm e(E - E^0)\right)^2}{4\lambda k_B T}\right) \frac{1}{1 + \exp\left(\frac{\varepsilon - \varepsilon_F}{k_B T}\right)} d\varepsilon$$

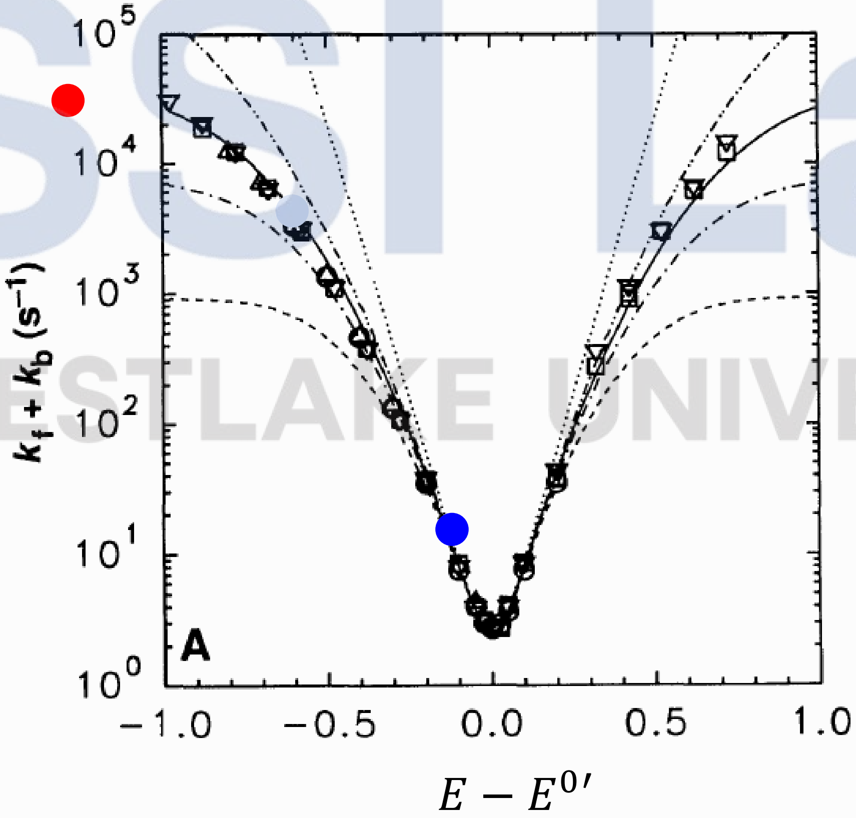
Fermi-Dirac

$$\Delta G^{\ddagger}_{c,a} = \frac{\lambda}{4}\left(1 \pm \frac{\Delta G^0}{\lambda}\right)^2 = \frac{\lambda}{4}\left(1 \pm \frac{e(E - E^0)}{\lambda}\right)^2$$

$$f(\varepsilon) = \frac{1}{1 + \exp\left(\frac{\varepsilon - \varepsilon_F}{k_B T}\right)}$$

Marcus-Hush-Chidsey Theory: the effect of charge carrier distribution

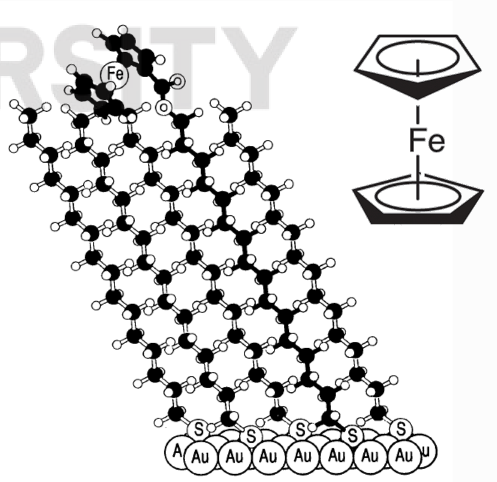




Marcus theory

$$k_{c,a} = A \int_{-\infty}^{+\infty} \exp\left(-\frac{\left(\varepsilon - \lambda \pm e(E - E^0)\right)^2}{4\lambda k_B T}\right) \frac{1}{1 + \exp(\frac{\varepsilon - \varepsilon_F}{k_B T})} d\varepsilon$$

Fermi-Dirac



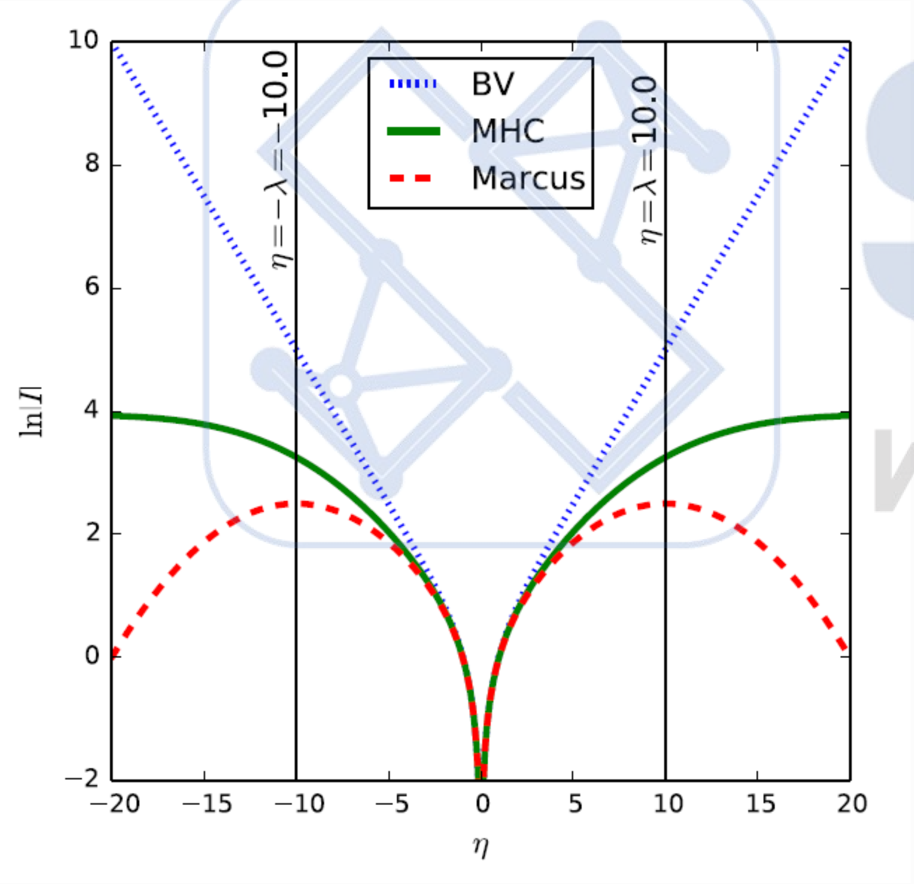
Marcus-Hush-Chidsey Theory: the effect of charge carrier distribution

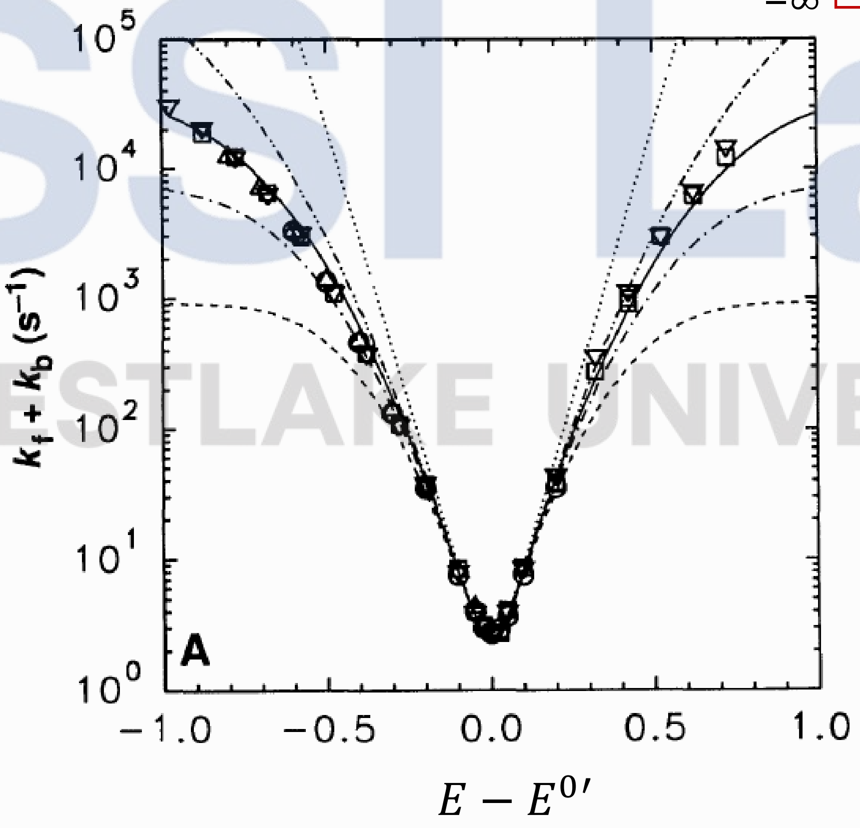
- Marcus-Hush-Chidsey (MHC) theory predicts a flattened *ln I ~ η* curve (no inverted region for metals)
- Inverted region only exists when there is a bandgap (semiconductors)

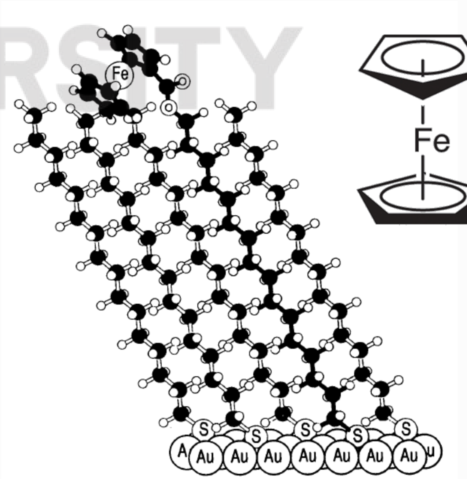
Marcus theory

$$k_{c,a} = A \int_{-\infty}^{+\infty} \exp\left(-\frac{\left(\varepsilon - \lambda \pm e(E - E^0)\right)^2}{4\lambda k_B T}\right) \frac{1}{1+\exp\left(\frac{\varepsilon-\varepsilon_F}{k_B T}\right)} d\varepsilon$$

Fermi-Dirac

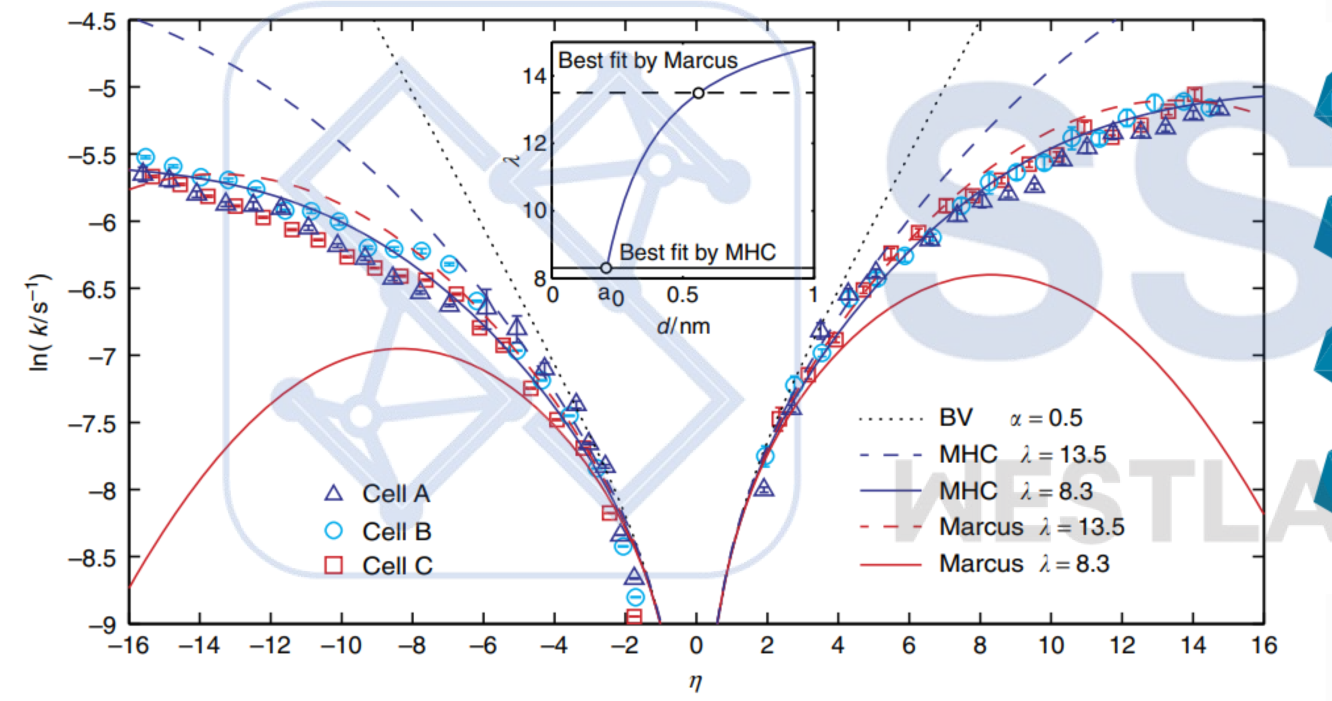


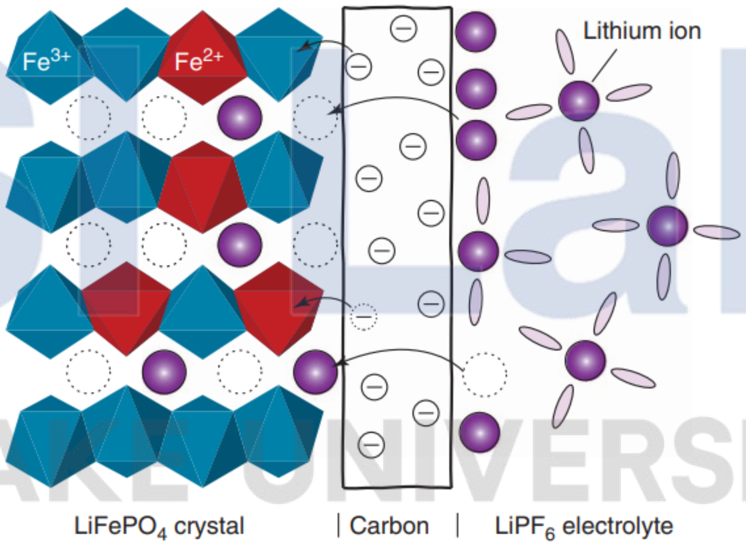


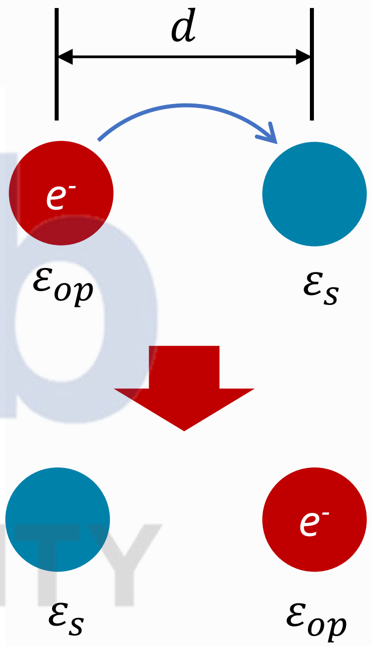


Marcus-Hush-Chidsey Theory: application in solid state

- MHC theory was used to describe the electrode kinetics of Li^+ intercalation into $LiFePO_4$;
- The electrode kinetics obviously deviates from B-V kinetics at higher overpotential.







$\lambda = \lambda_{out} + \lambda_{in}$ → *reorganization of reactant* (short-range)

↓ *reorganization of solvent*

$$\lambda \approx \lambda_{out} = \frac{e^2}{8\pi\varepsilon_0 k_B T}\left(\frac{1}{a_0} - \frac{1}{2d}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)$$

Born Energy of Solvation

a_0: *radii of reactant*; $2d$: *"Jump distance"*

Things we have discussed in this lecture

Frumkin Effect:

- What is the Frumkin Effect? How does the space charge layer affect the kinetics at electrode surfaces/interfaces?

Marcus Theory:

- What does the picture of Marcus Theory for charge transfer look like?

- What is *reorganization energy* and why is it important in the Marcus Thoery?

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

西湖大學
WESTLAKE UNIVERSITY

End of Lecture 11-12
Solid State Ionics Fall 2022

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