III. Reaction Kinetics

Lecture 15: Ion Adsorption and Intercalation

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1. Surface adsorption/intercalation of neutral species

Adsorption on a surface or intercalation in a bulk solid involves strong particle interactions which go beyond dilute solution theory. For example, in fuel cell, the hydrogen molecules need to attach onto the Pt catalyst and then split into two atoms or protons to be further reacted. Similarly, in Li ion battery, Li must be intercalated into the host crystal and then react with the active material. As a first approximation, the adsorption step in these processes can be modeled by lattice gas model (which is equivalent to a Langmuir-type isotherm in equilibrium).

Assume θ to be the mean coverage of the surface by adsorbed species (or filling fraction of intercalated species). Consider the adsorption of neutral species first.

Reaction $M \rightarrow M_{ads}$

Consider the ideal solution of particles and holes. For desorbed species: $\mu = kT\ln(a)$

For adsorbed species, chemical potential $\mu_{ads(\theta)} = kT\ln(\theta) - kT\ln(1-\theta) + h_0(1-2\theta) + \Delta E_{ads}$

The first term describes the dilute coverage, the second term represents the excluded volume effect. The third term considers the short range interactions between adsorbed species using regular solution model. And ΔE_{ads} is the adsorption energy.

A. Equilibrium
In equilibrium, chemical potential of adsorbed equals that of the desorbed species, from which we will get the adsorption isotherm

$$\mu = \mu_{ads(\theta)}$$

$$\Rightarrow \frac{\theta_{eq}}{1-\theta_{eq}} e^{-2h_0\theta_{eq}} = Ka$$

where $K = e^{-\frac{\Delta E_{ads}+h_0}{kT}} = e^{\frac{U_0}{kT}}$.

Note that $U_0 > 0$ favors adsorption. For $h_0 \neq 0$, this is called "Frumkin isotherm"; For $h_0 = 0$, it recovers Langmuir isotherm.
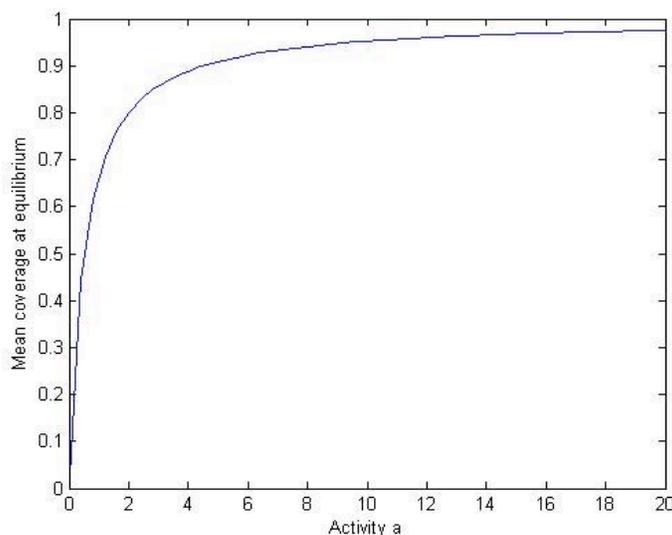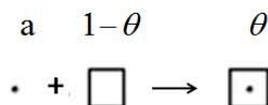
$$\theta_{eq} = \frac{Ka}{1+Ka}$$

Fig. 1 A typical Langmuir isotherm

B. Kinetics

When adsorption is not in equilibrium, standard picture for kinetic process of neutral adsorption can be described as a reaction between neutral species and a vacancy. The activity for neutral species is a, the mean coverage is θ, and the concentration for vacancy is $1-\theta$.

Thus, we can write the reaction rate as $\overline{R} = k_{\rightarrow}a(1-\theta) - k_{\leftarrow}\theta$, but this implicitly assumes a certain form of the activity coefficient γ_A of the activated state. A more general expression for the reaction rate comes from Butler Volmer equation.

$$R = R_0[e^{-(\mu_{TS}^{ex} - \mu_1)/kT} - e^{-(\mu_{TS}^{ex} - \mu_2)/kT}]$$

$$R = \frac{R_0}{\gamma_A}[e^{\mu_1/kT} - e^{\mu_2/kT}]$$

This formulation is consistent with the isotherms obtained from $R = 0 \Leftrightarrow \mu_1 = \mu_2$.

Next, we have to say something about transition state. We know $\mu_{TS}^{ex} = kT \ln \gamma_A$, but what is the activity coefficient γ_A? Reaction rate R corresponds to a certain choice of model for γ_A.

1) One possible model is to only consider excluded volume in transition state. In this case, excess chemical potential of the transition state can be written as $\mu_{TS}^{ex} = -kT\ln(1-\theta) + \Delta E_A$

Substitute this into the Butler Volmer equation, we get:

$$R = R_0(1-\theta)e^{-\Delta E_A/kT}[a - \frac{\theta}{1-\theta}e^{\Delta E_{ads}/kT}]$$

$$= \overline{R} = k_\rightarrow a(1-\theta) - k_\leftarrow \theta$$

$$\text{with} \begin{cases} k_\rightarrow = R_0 e^{-\Delta E_A/kT} \\ k_\leftarrow = R_0 e^{\Delta E_{ads}/kT} \end{cases}$$

This result is same as what we got before assuming a specific transition state model.

2) Another way to treat transition state is to assume $\mu_{TS}^{ex} = -kT\ln(1-\theta) + h_A(1-2\theta) + \Delta E_A$, where there is repulsion or attractive interactions between adsorbed species in transition state.

Then the reaction rate can be expressed as $R = \overline{R} \cdot e^{h_A(2\theta-1)/kT}$. $h_A>0$ means activated (transition) state has lower energy if other adsorbed species are nearby because of two body interactions, and thus reaction rate will be amplified as coverage θ goes to 1. This represents if transition state has attractive interactions, adsorbed species help to catalyze more adsorption.

The above two examples illustrate how to construct a model for neutral species reaction kinetics from a microscopic statistical model. Next we will study the adsorption with electron transfer (Faradaic) reactions.

2. Faradaic Reactions during adsorption/intercalation

In order to describe adsorption process with charge transfer reactions, we can adopt the modified Butler Volmer equation from the previous lectures. For example, consider the Li intercalation process in cobalt oxide particles in a composite Li-ion battery cathode as shown in Fig 2. Solvated Li^+ ions come from $LiPF_6$ electrolyte and electron comes from carbon black. They both adsorb onto the Li_xCoO_2 crystal surface and then react with Li_xCoO_2.

The reaction can be expressed as follows. Note we express reaction from reduced state (solid state) to oxidized state (electrolyte phase) which is the reverse of adsorption process. The reduced state (state 1) is intercalated Li, the oxidized state (state 2) contains Li^+ ion and an electron.

$$Li_{(s)} \rightarrow Li^+ + \bar{e} \quad (R \rightarrow O + \bar{e})$$

$state1 \qquad state2$
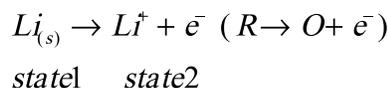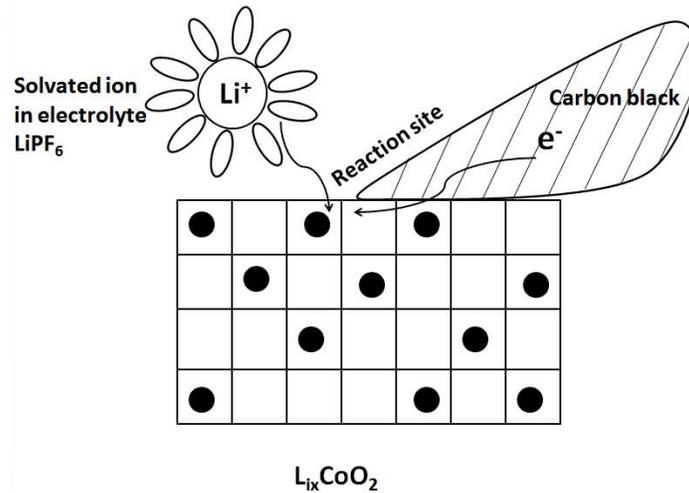
Fig. 2 Demonstration of Li intercalation process in $LiCoO_2$

According to the Butler Volmer equation, current is a function of overpotential:

$$I = I_0 [e^{(1-\alpha)e\eta/kT} - e^{-\alpha e\eta/kT}]$$
$$where\ I_0 = k_0\, a_R^\alpha\, a_O^{1-\alpha} / \gamma_A; \quad k_0 \propto \#\ of\ reaction\ sites$$

Using regular solution model, we can express the electrochemical potential of two states.

$$\mu_R = \mu_{Li} = kT\ln(\frac{\theta}{1-\theta}) + h_0(1-2\theta) + \Delta E_{ads}$$

$$\mu_O = \mu_{Li^+} + \mu_{e^-}$$

$$where \begin{cases} \mu_{Li^+} = kT\ln a_{Li^+} + e\phi \approx kT\ln c_{Li^+} + e\phi \\ \qquad \mu_{e^-} = -e\phi_e \end{cases}$$

In equilibrium, $\mu_R = \mu_O$ leads to

$$kT\ln(\frac{\theta}{1-\theta}) + h_0(1-2\theta) + \Delta E_{ads} = kT\ln a_{Li^+} + e\phi - e\phi_e = kT\ln a_{Li^+} - e\Delta\phi$$

Where $\Delta\phi = \phi_e - \phi$

Then it becomes Nernst equation

$$\Delta\phi_{eq} = \Delta\phi^0 - \frac{kT}{e}\ln(\frac{\theta}{a_{Li^+}(1-\theta)}) + \frac{2\theta h_0}{e} = \frac{kT\ln a_{Li^+} - \mu_{Li}}{e}$$

Now overpotential can be expressed as difference of chemical potential between two states over unit charge:

$$\eta_{act} = \Delta\phi - \Delta\phi_{eq} = \Delta\phi - \frac{kT\ln a_{Li^+} - \mu_{Li}}{e} = \frac{\mu_1 - \mu_2}{e}$$

If we plug this into the Bulter-Volmer kinetics, we will get

$$I = I_0[e^{(1-\alpha)e\eta/kT} - e^{-\alpha e\eta/kT}]$$

$$I = I_0[e^{(1-\alpha)e\eta/kT} - e^{-\alpha e\eta/kT}] = \frac{k_0 a_R^\alpha a_o^{1-\alpha}}{\gamma_A}[e^{(1-\alpha)e\eta/kT} - e^{-\alpha e\eta/kT}]$$

Similarly, we need to provide a model for the transition state. If we ignore interactions with other intercalated Li, and assume that the transition state excludes more than one site because of the solvation shell, the chemical potential for transition state can be expressed as
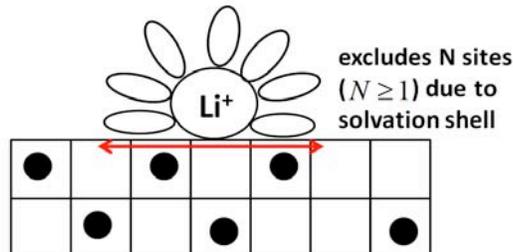
$$\mu_{TS}^{ex} = -NkT\ln(1-\theta) + \Delta E_A$$

Fig. 3 The transition state excludes more than one site because of the solvation shell

Then,

$$\gamma_A = \frac{e^{\Delta E_A/kT}}{(1-\theta)^N}$$

$$I_0 = K a_{Li}^\alpha a_{Li^+}^{1-\alpha}(1-\theta)^N$$

$$I_0 = K'\theta^\alpha (1-\theta)^{N-\alpha} e^{-2h0\theta\alpha} a_{Li^+}^{1-\alpha}$$

In a special case that N=1 and $\alpha = 1/2$,

$$I_0 = K\sqrt{\theta(1-\theta)}e^{-h_0\theta}\sqrt{a_{Li^+}}$$

Note that exchange current vanishes and interfacial resistance diverges for $\theta \to 0$ or $\theta \to 1$. Moreover, $h_0 \neq 0$ breaks symmetry around $\theta = 1/2$, since partial interactions either enhance or reduce the reaction rate.

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