

Lecture 19: Electrocatalysis
Notes by MIT Student (and MZB)

1 The Concept of Electrocatalysis

In chemistry, the concept of a catalyst is defined as a substance that can alter the velocity of a certain chemical reaction without any chemical change. This definition can be directly extrapolated for electrocatalysis. An electrocatalyst is an electrode material that interacts with some certain species during a Faradaic reaction but still remain unaltered. Since electrode reactions are heterogeneous, so electrocatalysts are usually heterogeneous catalysts, which means that the reactions take place on the surfaces of catalysts, and there exist adsorption/desorption steps on the surfaces of electrocatalysts.

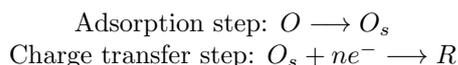
In order to compare the catalytic activity of different electrode materials, one can compare the current density at a constant overpotential, or measure the overpotential at a constant current density. A good electrocatalyst should show high current density at low overpotential.

2 Sabatier Principle

Sabatier Principle (named after French chemist Paul Sabatier) is a qualitative way to predict the activity of heterogeneous catalysts. The principle states that in order to have high catalytic activity, the interaction between reactants and catalysts should neither be too strong nor too weak. If the interaction is too weak, then there will be no reaction on the surface because it is difficult for catalyst surface to bind the reactants. If the interaction is too strong, then the reaction reactant or product is difficult to get desorbed from catalyst surface, which also lowers the activity. This principle also applies to electrocatalysis, basically “some” adsorption is favored, but not too much. Sabatier principle usually gives rise to so-called volcano plot, such as an example shown in Figure 1. Volcano plots were first introduced by Balandin in 1969. The basic idea is that if plotting rate of chemical reaction on a heterogeneous catalyst with some adsorption property, for instance adsorption enthalpy, then according to Sabatier’s principle, the plot will have a maximum, showing the shape like a volcano.

3 Faradaic Reaction with a Surface Adsorption Step

Now let us consider a Faradaic reaction on the surface of an electrocatalyst, which means the charge transfer step follows a surface adsorption step and can be expressed as below:



In which O is the oxidized state, O_s represents the surface adsorbed oxidized state, and R represents the reduced state. Let a_O, a_s, a_R be the activities of O, O_s and R , respectively, then the chemical potentials of

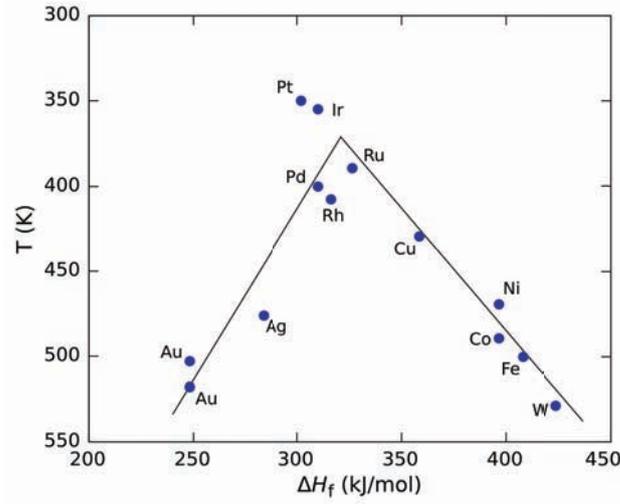


Figure 1: An example of volcano plot, showing the rate of decomposition of formic acid on transition metal surfaces. The y axis is the temperature needed to have a certain decomposition rate. The x axis is the formation enthalpy of metal formate salt. (Research shows the reaction intermediate involves metal formate salt, so the formation enthalpy is an indicator of the ease of formic acid surface adsorption.) Source: http://en.wikipedia.org/wiki/Sabatier_principle/

each species can be expressed as below: (To simplify, assume that the charges of O and O_s equal to zero (i.e. $Z_O = Z_s = 0$) and R has the charge of Z_R .)

$$\mu_O = k_B T \ln a_O + \mu_O^\ominus \quad (1)$$

$$\mu_s = k_B T \ln a_s + \mu_s^\ominus \quad (2)$$

$$\mu_R = k_B T \ln a_R + \mu_R^\ominus + Z_R \phi \quad (3)$$

If we assume that the adsorption step is fast and the charge transfer step is the rate-limiting step, then the chemical potential of oxidized state O should equal to the chemical potential of adsorbed oxidized state O_s , i.e.:

$$\mu_O = \mu_s \quad (4)$$

$$k_B T \ln a_O + \mu_O^\ominus = k_B T \ln a_s + \mu_s^\ominus \quad (5)$$

Let K_{ads} be the equilibrium constant of the adsorption reaction, then we have:

$$a_s = K_{ads} a_O \quad (6)$$

$$K_{ads} = \exp\left(\frac{\mu_O^\ominus - \mu_s^\ominus}{k_B T}\right) = \exp\left(\frac{\Delta H_{ads}}{k_B T}\right) \quad (7)$$

In which $\Delta H_{ads} = \mu_O^\ominus - \mu_s^\ominus$ is the enthalpy change of the adsorption reaction. If we apply the lattice gas model for the electrocatalyst surface, then by the assumption of the lattice gas model, we have: (Θ is the surface coverage ratio of O_s .)

$$a_s = \frac{\Theta}{1 - \Theta} = K_{ads} a_O \quad (8)$$

Then we can get the surface coverage of O_s at the equilibrium state Θ_{eq} :

$$\boxed{\Theta_{eq} = \frac{K_{ads} a_O}{1 + K_{ads} a_O}} \quad (9)$$

Equation 9 is called Langmuir isotherm (or Langmuir adsorption equation).

For the rate-limiting step, namely the charge transfer on the surface of the electrocatalyst surface, we assume the reaction kinetics follow the Butler-Volmer equation, which yields:

$$I = I_0 \left(\exp\left(\frac{-\alpha ne\eta}{k_B T}\right) - \exp\left(\frac{-(1-\alpha)ne\eta}{k_B T}\right) \right) \quad (10)$$

η is the overpotential with the expression $\eta = \Delta\phi - \Delta\phi_{eq}(a_s, a_R)$. The exchange current I_0 in the Butler-Volmer equation can be expressed as a function of concentration of reaction species and activation coefficient of the transition state γ_{TS} :

$$I_0 = \left(\frac{ne\nu}{\gamma_{TS}}\right) (a_s a_e^n)^{1-\alpha} a_R^\alpha \quad (11)$$

Then we need to find the expression for γ_{TS} . Firstly, if we again apply the lattice gas model to the adsorbed oxidized species, then we have:

$$\mu_s = k_B T \ln a_s + \mu_s^\ominus = k_B T \ln \Theta - k_B T \ln(1 - \Theta) + \mu_s^\ominus \quad (12)$$

Compare Equation 12 to the expression $\mu_s = k_B T \ln(\tilde{c}\gamma_s) + \mu_s^\ominus = k_B T \ln(\Theta\gamma_s) + \mu_s^\ominus$, we have the expression for the activation coefficient of O_s :

$$\gamma_s = \frac{1}{1 - \Theta} \quad (13)$$

Based on this observation, if we assume that the transition state excludes s sites, then γ_{TS} can be expressed as: (the origin for $s > 1$ could be due to the solvation shell.)

$$\gamma_{TS} = \left(\frac{1}{1 - \Theta}\right)^s \quad (14)$$

For simplicity, we assume $s = 1$, also let $a_e = a_R = 1$, then the expression for the exchange current becomes:

$$\begin{aligned} I_0 &= \frac{k}{\gamma_{TS}} a_s^{1-\alpha} \\ &= k(1 - \Theta) \left(\frac{\Theta}{1 - \Theta}\right)^{1-\alpha} \\ &= k \frac{(K_{ads} a_O)^{1-\alpha}}{1 + K_{ads} a_O} \end{aligned} \quad (15)$$

($k = ne\nu$ is a pre-factor. We also have $\Theta = \Theta_{eq}$ since we assume the surface adsorption step is fast.)

Finally, let's use Equation 15 to investigate the relationship between reaction rate and surface adsorption equilibrium constant. We know that the current density represents the velocity of the reaction. If we fix the overpotential η , then the total current is proportional to the exchange current, namely $I \propto I_0$. Then we only need to study the relationship between I_0 and K_{ads} . If we plot $\ln I_0 \sim \ln K_{ads}$, we get a curve with the familiar volcano shape, just as the Sabatier's principle predicts (Figure 2). Also, the effect of symmetry factor α is shown in Figure 3. As α deviates $1/2$, the peak position of the volcano plot shifts and also the shape is not symmetric any more.

Notice that:

$$K_{ads} = \exp\left(\frac{\Delta H_{ads}}{k_B T}\right) \quad (16)$$

$$\ln K_{ads} = \frac{\Delta H_{ads}}{k_B T} \quad (17)$$

Therefore, the x axis of these volcano plots is actually proportional to the enthalpy change of adsorption K_{ads} , which again, highlights the Sabatier's principle, i.e. the adsorption should neither be too strong nor too weak to maximize the electrocatalytic activity.

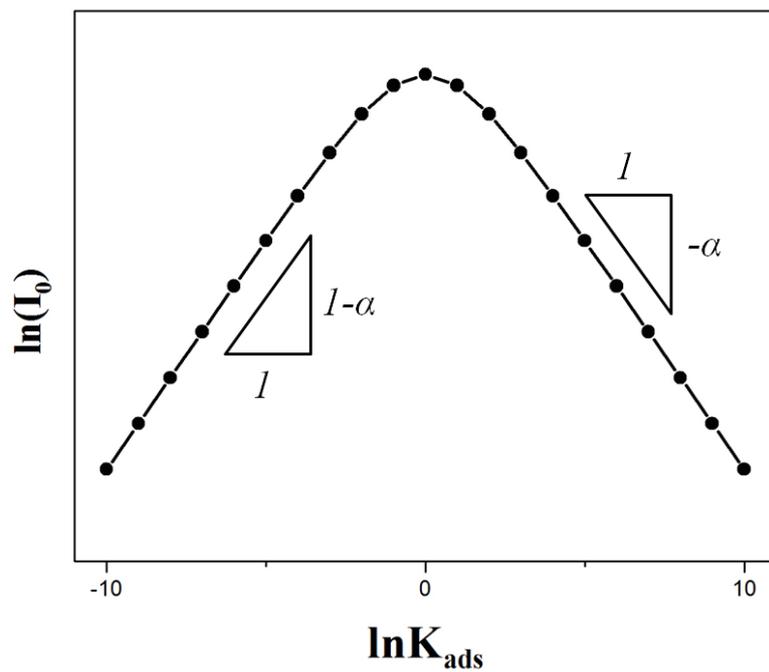


Figure 2: Volcano plots generated from Equation 15. The plot of $\ln I_0 \sim \ln K_{ads}$ has a maximum, the slopes on the left and right of the maximum are $-\alpha$ and $1 - \alpha$, respectively.

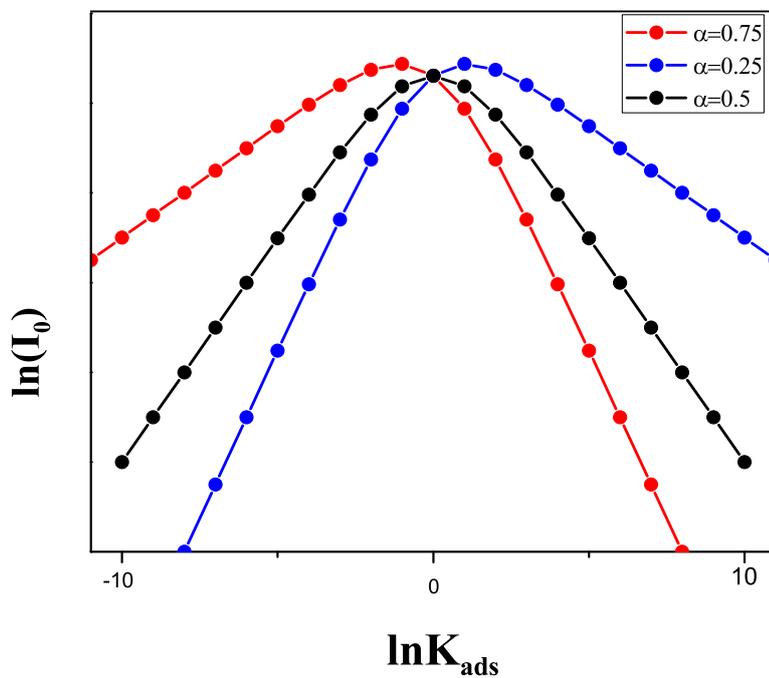


Figure 3: The effect of symmetry factor α on the shape of volcano plots.

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