III. Reaction Kinetics

Lecture 13: Butler-Volmer equation

Notes by ChangHoon Lim (and MZB)

1. Interfacial Equilibrium

At lecture 11, the reaction rate R for the general Faradaic half-cell reaction was derived.

$$R \rightarrow O + ne^-$$

where $R = \sum_i s_{iR} R_i^{Z_{iR}}$ =Reduced state

$O = \sum_i s_{iO} O_i^{Z_{iO}}$ =Oxidized state

Here s_i is the stochiometric coefficient of species i (positive for reduced state and negative for oxidized state), $R_i(O_i)$ is a symbol for chemical formula and Z_i is the charge number of species i.

$$R = k_a C_R e^{(1-\alpha)ne\Delta\phi/k_B T} - k_c C_O e^{-\alpha ne\Delta\phi/k_B T} = R_a - R_c = \frac{\#\,reactions}{time \cdot site}$$

where $C_R = \prod_i c_{iR}^{s_{iR}}$, $C_O = \prod_i c_{iO}^{s_{iO}}$, $\Delta\phi = \phi_e - \phi$ = electrode potential- solution potential, and α is symmetry factor (transfer coefficient).

[Note] $\dfrac{R_a}{R_c} = \dfrac{k_a C_R}{k_c C_O} e^{ne\Delta\phi/k_B T}$

The ratio of anode reaction rate to cathode reaction rate does not depend on α or any properties of the transition state.

In equilibrium, the net reaction rate R is zero. That is, $R_a = R_c$

$$\Delta\phi_{eq} = \frac{k_B T}{ne} \ln\left(\frac{k_c C_O}{k_a C_R}\right) = V^0 - \frac{k_B T}{ne} \ln\left(\frac{\prod_i c_{iR}^{s_{iR}}}{\prod_i c_{iO}^{s_{iO}}}\right) \text{ where } V^0 = \frac{k_B T}{ne} \ln\left(\frac{k_c}{k_a}\right)$$

This is the Nernst equation. And, V^0 is a kinetic definition of the standard potential, related to microscopic reaction rates.

2. Activation Overpotential

In electrochemistry, it is more common to use (activation) overpotential rather than $\Delta\phi$. Overpotential is

$$\eta = \Delta\phi - \Delta\phi_{eq}$$

This is the "extra voltage" which drives a Faradaic current. In terms of overpotential, the reaction rate is

$$R = k_a C_R e^{(1-\alpha)ne(\eta+\Delta\phi_{eq})/k_B T} - k_c C_O e^{-\alpha ne(\eta+\Delta\phi_{eq})/k_B T}$$

Using $\Delta\phi_{eq} = \dfrac{k_B T}{ne}\ln\left(\dfrac{k_c C_O}{k_a C_R}\right)$,

$$R = k_a C_R \left(\frac{k_c C_O}{k_a C_R}\right)^{1-\alpha} e^{(1-\alpha)ne\eta/k_B T} - k_c C_O \left(\frac{k_c C_O}{k_a C_R}\right)^{-\alpha} e^{-\alpha ne\eta/k_B T}$$

$$R = (k_c C_O)^{1-\alpha}(k_a C_R)^{\alpha}\left[e^{(1-\alpha)ne\eta/k_B T} - e^{-\alpha ne\eta/k_B T}\right]$$

$I=neAR$ where A is electrode area. Thus,

$$\boxed{I = I_0\left[e^{(1-\alpha)ne\eta/k_B T} - e^{-\alpha ne\eta/k_B T}\right]}$$

where $I_0 = neA(k_c C_O)^{1-\alpha}(k_a C_R)^{\alpha}$ is the "exchange current" in a dilute solution. This is the Butler-Volmer equation.

3. Limiting Cases of the Butler-Volmer equation

A) Linear Response

For small overpotentials ($|\eta| \ll \dfrac{k_B T}{ne}$), we can linearize the Butler-Volmer equation.

$$I = I_0\left(\frac{ne\eta}{k_B T} + \underbrace{\frac{(1-2\alpha)}{2}\left(\frac{ne\eta}{k_B T}\right)^2}_{\alpha=1/2:vanish} + \frac{(1-2\alpha-2\alpha^2)}{6}\left(\frac{ne\eta}{k_B T}\right)^3 + ...\right)$$

Leading order approximation within which current is linear to overpotential,

$$I \sim I_0 \frac{ne\eta}{k_B T}$$

$$\eta_{act} \sim \frac{I}{R_{act}} \quad R_{act} = \frac{k_B T}{neI_0}$$

R_{act} (>0) is the constant resistance of the Faradaic reaction. Activation overpotential is positive at anode and negative at cathode for a galvanic cell (*I>0*) and electrons flows from anode to cathode.

B) **Tafel Response**

For large overpotentials ($|\eta| \gg \dfrac{k_B T}{ne}$),

$$I \sim \begin{cases} I_0 e^{(1-\alpha)ne\eta / k_B T}, \eta \gg \dfrac{k_B T}{ne} \\ -I_0 e^{-\alpha ne\eta / k_B T}, \eta \ll -\dfrac{k_B T}{ne} \end{cases}$$

"Tafel plot" of $\ln|I|$ .vs. η has a slope $\dfrac{(1-\alpha)ne}{k_B T}$ for anodic current and $\dfrac{\alpha ne}{k_B T}$ for cathodic current, and y-intercept is $\ln|I_0|$.
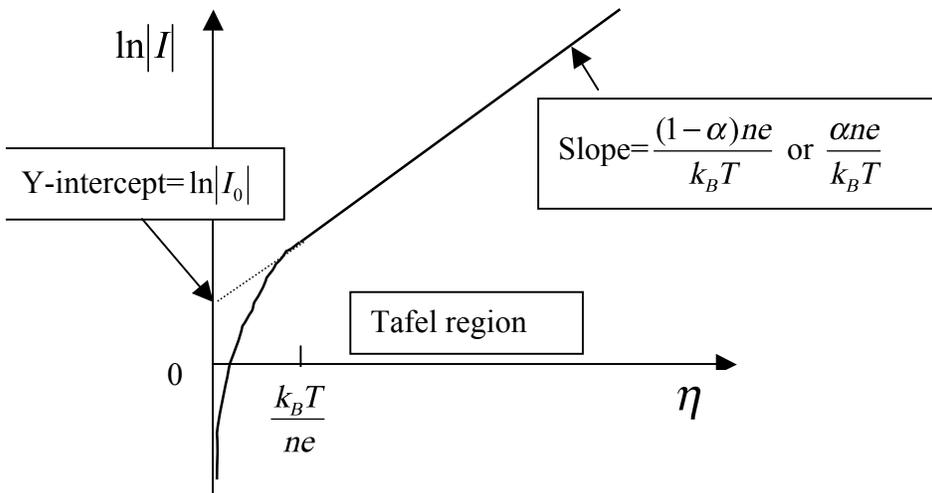

Figure 1. Typical Tafel plot of log(current) versus overpotential. The Butler-Volmer equation predicts a asymptotic linear dependence for large overpotentials, where the slope is related to the transfer coefficient and the y-intercept gives the exchange current.

C) **Symmetric electron transfer** ($\alpha = \dfrac{1}{2}$)

It is common to assume symmetric electron transfer in the Butler-Volmer equation (Fig 2), and this often agrees well with experimental Tafel plots. As we will see in later lectures, this assumption is also mathematically convenient, since the BV equation can be expressed as a hyperbolic sine dependence,

$$I = I_0 \left[e^{ne\eta / 2k_B T} - e^{-ne\eta / 2k_B T} \right] = 2I_0 \sinh\left(\frac{ne\eta}{2k_B T} \right)$$

which can be easily inverted, in terms of the inverse hyperbolic sine

$$\eta = \frac{2k_B T}{ne} \sinh^{-1}\left(\frac{I}{2I_0} \right)$$

We see that activation overpotential is mainly important at small currents and has roughly the magnitude of the thermal voltage kT/e. At larger currents, the activation overpotential grows much more slowly, as a logarithm of the applied current (relative to the exchange current).
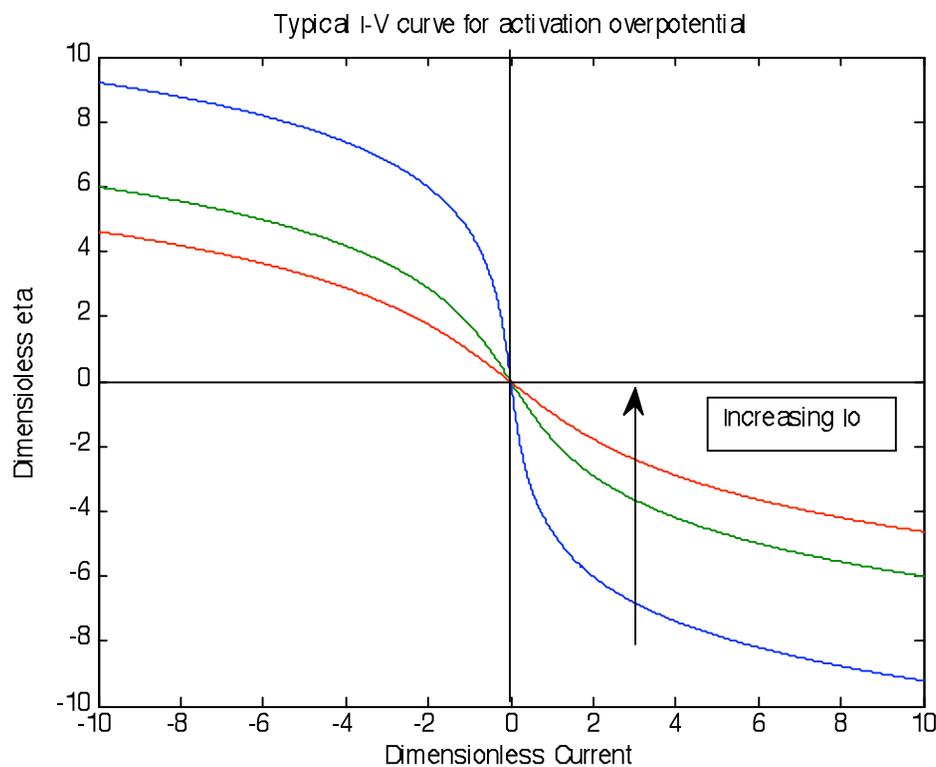

Figure 2. Typical I-V curve for activation overpotential for symmetric electron transfer (alpha=1/2)

D) **Asymmetric electron transfer** ($\alpha = 0,1$)
If the interfacial voltage only biases one direction of a Faradaic reaction, say the positive (oxidation) reaction $\alpha = 0$, and not the other, then the Butler-Volmer takes the simple form

$$I = I_0 \left[e^{ne\eta/k_B T} - 1 \right]$$

which is mathematical identically to the nonlinear I-V response of a semiconductor diode (lecture 2). In this case, for a positive overpotential ("forward bias"), which enhances the oxidation reaction, the current grows exponentially with voltage, while the current saturates to a constant for large negative overpotentials ("reverse bias"), set by the reduction reaction rate. Later in the class (lecture 32), we will see that similar behavior can result from the influence of diffuse charge on Faradaic reaction kinetics (the "Frumkin correction" to the Butler-Volmer equation), similar to a semiconductor p-n junction.
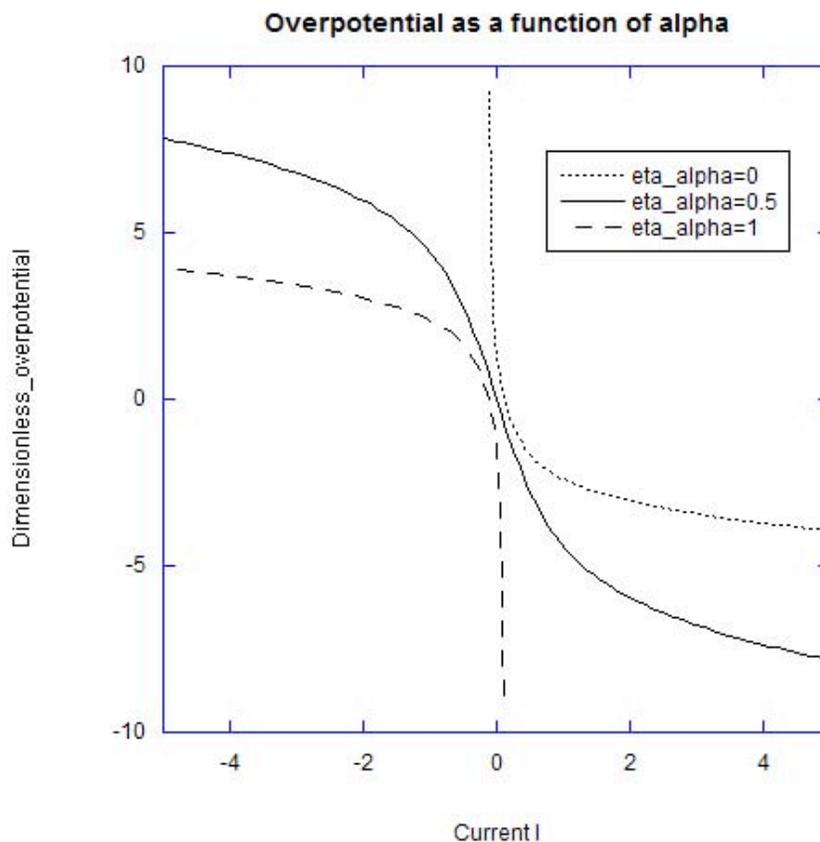

Figure 3. Dimensionless over-potential vs. current for different values of the Butler-Volmer transfer coefficient. In the limits alpha=0 or 1, the interface acts like an ideal semiconductor diode, which passes current preferentially in one direction ("forward bias") with only a small saturation current in the opposite direction ("reverse bias").

For further reading, see Newman, *Electrochemical Systems* (Ch 8) and Bard and Faulkner, *Electrochemical Methods* (Ch 3)

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