

Electric double layer effect (EDL) for the redox species in solution

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In this report I will reformulate the electric double layer effect of bulk redox reaction.

1 Electric double layer effect for the redox species in solution

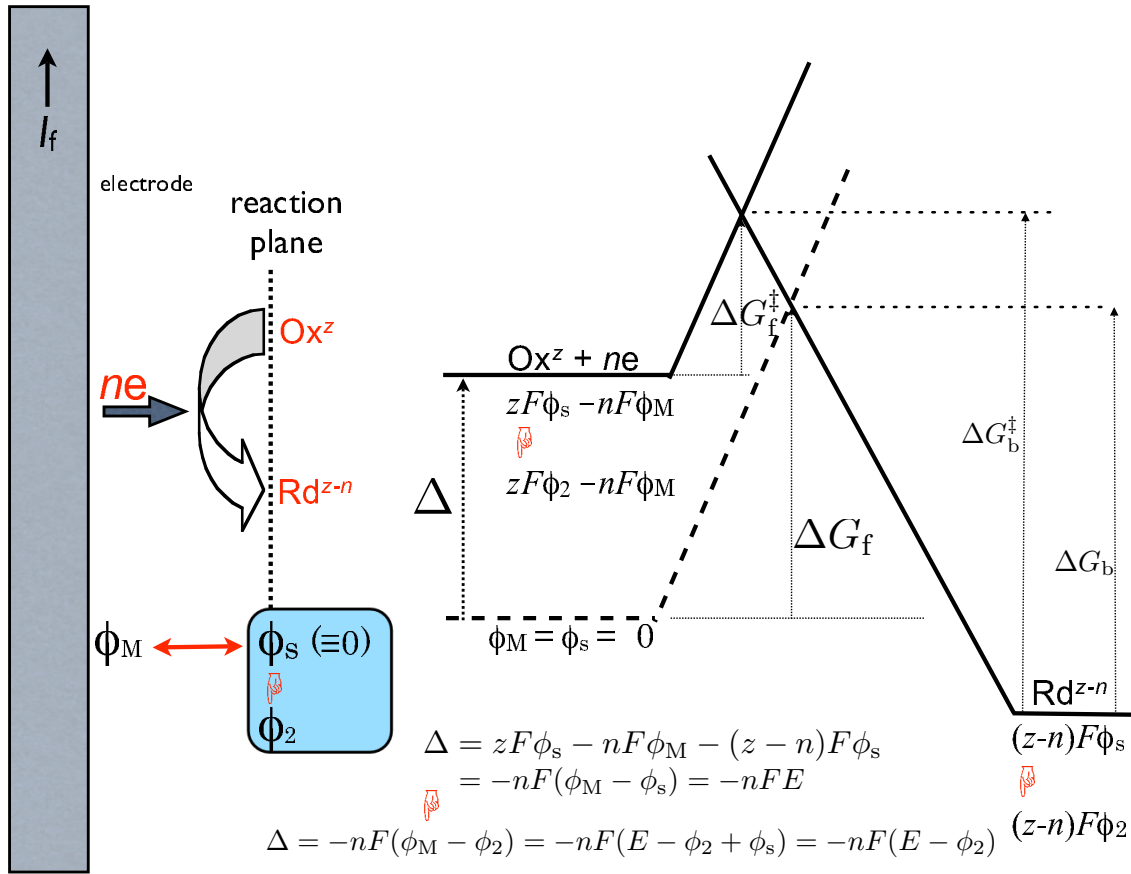


Figure 1: Left: Redox reactions are occurred at the reaction plane $z = z_2$. Right: Energy diagram along the reaction path. In this figure the reduction state is takes as the energy reference.

We assume the redox reaction $Ox^z + ne \rightleftharpoons Rd^{z-n}$ takes place at the reaction plane at $z = z_2$. When the electric double layer effect is not considered (surface charge density is low and the reaction plane is not so close to the electrode), the potential ϕ_2 at the reaction plane can be negligible, and the potential is equal to the potential ϕ_s at bulk solution

$$\phi_2 = \phi_s = 0 \quad (1)$$

When the external potential $E = \phi_M - \phi_s$ is applied to the electrode, the difference Δ_0 of the electrochemical potential of the reactants and the products become

$$\Delta_0 = zF\phi_s - nF\phi_M - (z-n)F\phi_s = -nF(\phi_M - \phi_s) = -nFE \quad (2)$$

Here F is the Faraday constant, ϕ_M is the potential at the electrode, and E is the electrode potential. In Butler-Volmer theory the difference Δ_0 contribute the decrease of the activation barrier for the reaction of $\text{Ox}^z + ne \rightarrow \text{Rd}^{z-n}$ by $\alpha\Delta_0$ from the barrier ΔG_f when $E = 0$, and Δ_0 contribute the increase of the reaction barrier for oxidation by $(1 - \alpha)\Delta_0$.

When the electrode interface is strongly electrified, the potential at the reaction plane is not negligible and the reaction rate will change. In the following formulation, we simply put ϕ_2 into $\phi_s (\neq \phi_2)$ in the reaction rate theory by Butler-Volmer. Then Δ_0 should be replaced by Δ in the following way,

$$\Delta = zF\phi_2 - nF\phi_M - (z - n)F\phi_2 = -nF(\phi_M - \phi_2) = -nF(E - \phi_2) \quad (3)$$

1.1 kinetics

The activation barriers for the forward (reduction) ΔG_f^\ddagger and backward(oxidation) reactions ΔG_b^\ddagger are given by

$$\Delta G_f^\ddagger = \Delta G_f - \alpha\Delta = \Delta G_f + nF\alpha(E - \phi_2) \quad (4)$$

$$\begin{aligned} \Delta G_b^\ddagger &= \Delta G_b - \Delta G_f + \Delta + \Delta G_f^\ddagger = \Delta G_b - \Delta G_f + \Delta + \Delta G_f - \alpha\Delta \\ &= \Delta G_b + (1 - \alpha)\Delta = \Delta G_b - nF(1 - \alpha)(E - \phi_2) \end{aligned} \quad (5)$$

Here ΔG_f and ΔG_b is the activation barrier for the forward(reduction) and backward(oxidation) reaction when $\Delta = 0$.

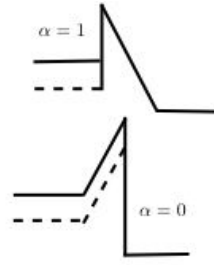


Figure 2: α parameter

The current for the forward (reduction) reaction I_f is

$$I_f = -nFA \frac{kT}{h} \exp\left(-\frac{\Delta G_f^\ddagger}{RT}\right) c_{\text{Ox}}(z_2) \quad (6)$$

Here A is the area of the electrode, k is Boltzman constant, h is Plank constant, R is gas constant, T is temperature, $c_{\text{Ox}}(z_2)$ is the concentration of Ox at the reaction plane $z = z_2$. From the equilibrium condition we have (we will show later)

$$c_{\text{Ox}}(z_2) = c_{\text{Ox}}^0 \exp\left(-\frac{zF\phi_2}{RT}\right) \quad (7)$$

Here c_{Ox}^0 is the concentration of Ox in the bulk phase. We have

$$\begin{aligned} I_f &= -nFA \frac{kT}{h} \exp\left(-\frac{\Delta G_f^\ddagger}{RT}\right) c_{\text{Ox}}(z_2) = -nFA \frac{kT}{h} \exp\left(-\frac{\Delta G_f}{RT}\right) \exp\left(-\frac{nF\alpha(E - \phi_2)}{RT}\right) c_{\text{Ox}}^0 \exp\left(-\frac{zF\phi_2}{RT}\right) \\ &= -nFA k_f^0 \exp\left(\frac{(\alpha n - z)F\phi_2}{RT}\right) \exp\left(-\frac{\alpha nFE}{RT}\right) c_{\text{Ox}}^0 \end{aligned} \quad (8)$$

$$k_f^0 \equiv \frac{kT}{h} \exp\left(-\frac{\Delta G_f}{RT}\right) \quad (9)$$

The current for backward reaction (oxidation) is given by

$$I_b = nFA \frac{kT}{h} \exp\left(-\frac{\Delta G_b^\ddagger}{RT}\right) c_{\text{Rd}}(z_2) = nFA \frac{kT}{h} \exp\left(-\frac{\Delta G_b}{RT}\right) \exp\left(\frac{(1 - \alpha)nF(E - \phi_2)}{RT}\right) \exp\left(-\frac{(z - n)F\phi_2}{RT}\right) c_{\text{Rd}}^0$$

$$= nFAk_b^0 \exp\left(\frac{(\alpha n - z)F\phi_2}{RT}\right) \exp\left(\frac{(1 - \alpha)nFE}{RT}\right) c_{\text{Rd}}^0 \quad (10)$$

$$k_b^0 \equiv \frac{kT}{h} \exp\left(-\frac{\Delta G_b}{RT}\right) \quad (11)$$

$$(12)$$

Here c_{Rd}^0 is the concentration of Rd in the bulk phase. We used

$$\begin{aligned} (1 - \alpha)nF(E - \phi_2) - (z - n)F\phi_2 &= (1 - \alpha)nFE - nF\phi_2 + \alpha nF\phi_2 - znF\phi_2 + nF\phi_2 \\ &= (1 - \alpha)nFE + (\alpha n - z)F\phi_2 \end{aligned}$$

1.2 From equilibrium condition

$$\text{Ox}^z(z_2) + ne(z = 0 : \text{electrode}) \rightleftharpoons \text{Rd}^{z-n}(z_2) \quad (13)$$

$$\tilde{\mu}_{\text{Ox}}(z_2) = \mu_{\text{Ox}}^0 + RT \ln a_{\text{Ox}}(z_2) + zF\phi_2 \quad (14)$$

$$\tilde{\mu}_{\text{Ox}}(z = +\infty) = \mu_{\text{Ox}}^0 + RT \ln a_{\text{Ox}}^0 + zF \underbrace{\phi_s}_{=0} \quad (15)$$

$$\tilde{\mu}_{\text{Ox}}(z_2) = \tilde{\mu}_{\text{Ox}}(z = +\infty), \quad a_{\text{Ox}}(z_2) = a_{\text{Ox}}^0 \exp\left(-\frac{zF\phi_2}{RT}\right) \quad (16)$$

$$c_{\text{Ox}}(z_2) = c_{\text{Ox}}^0 \exp\left(-\frac{zF\phi_2}{RT}\right), \quad (\text{in the case of } \gamma_{\text{Ox}} = 1) \quad (17)$$

$$\tilde{\mu}_e = \mu_e^0 - nF\phi_M \quad (18)$$

$$\tilde{\mu}_{\text{Rd}}(z_2) = \mu_{\text{Rd}}^0 + RT \ln a_{\text{Rd}}(z_2) + (z - n)F\phi_2 \quad (19)$$

$$\tilde{\mu}_{\text{Rd}}(z = +\infty) = \mu_{\text{Rd}}^0 + RT \ln a_{\text{Rd}}^0 + (z - n)F \underbrace{\phi_s}_{=0} \quad (20)$$

$$\tilde{\mu}_{\text{Rd}}(z_2) = \tilde{\mu}_{\text{Rd}}(z = +\infty), \quad a_{\text{Rd}}(z_2) = a_{\text{Rd}}^0 \exp\left(-\frac{(z - n)F\phi_2}{RT}\right) \quad (21)$$

$$c_{\text{Rd}}(z_2) = c_{\text{Rd}}^0 \exp\left(-\frac{(z - n)F\phi_2}{RT}\right), \quad (\text{in the case of } \gamma_{\text{Rd}} = 1) \quad (22)$$

$$\mu_{\text{Ox}}^0 + \mu_e^0 + RT \ln a_{\text{Ox}}(z_2) + zF\phi_2 - nF\phi_M = \mu_{\text{Rd}}^0 + RT \ln a_{\text{Rd}}(z_2) + (z - n)F\phi_2 \quad (23)$$

$$\phi_M - \phi_s - (\phi_2 - \phi_s) = -\frac{\mu_{\text{Rd}}^0 - \mu_{\text{Ox}}^0 - \mu_e^0}{nF} + \frac{RT}{nF} \ln \frac{a_{\text{Ox}}(z_2)}{a_{\text{Rd}}(z_2)} \quad (24)$$

$$E_{\text{eq}} - \phi_2 = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Ox}}(z_2)}{a_{\text{Rd}}(z_2)} \quad (25)$$

$$= E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Ox}}^0}{a_{\text{Rd}}^0} - \frac{z}{n}\phi_2 + \frac{z - n}{n}\phi_2 \quad (26)$$

$$E_{\text{eq}} = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Ox}}^0}{a_{\text{Rd}}^0} \quad (27)$$

$$E_{\text{eq}} = E^{0'} + \frac{RT}{nF} \ln \frac{c_{\text{Ox}}^0}{c_{\text{Rd}}^0} \quad (28)$$

The total current is zero in equilibrium

$$I_f + I_b = 0 \quad (29)$$

and for the potential $E = E_{\text{eq}}$

$$k_f^0 \exp\left(\frac{(\alpha n - z)F\phi_2}{RT}\right) \exp\left(-\frac{\alpha nFE_{\text{eq}}}{RT}\right) c_{\text{Ox}}^0 = k_b^0 \exp\left(\frac{(\alpha n - z)F\phi_2}{RT}\right) \exp\left(\frac{(1 - \alpha)nFE_{\text{eq}}}{RT}\right) c_{\text{Rd}}^0 \quad (30)$$

$$\begin{aligned} k_f^0 \exp\left(\frac{(\alpha n - z)F\phi_2}{RT}\right) \exp\left(-\frac{\alpha nFE^{0'}}{RT}\right) (c_{\text{Ox}}^0)^{1-\alpha} (c_{\text{Rd}}^0)^\alpha &= k_b^0 \exp\left(\frac{(\alpha n - z)F\phi_2}{RT}\right) \exp\left(\frac{(1 - \alpha)nFE^{0'}}{RT}\right) (c_{\text{Ox}}^0)^{1-\alpha} (c_{\text{Rd}}^0)^\alpha \\ k_f^0 \exp\left(-\frac{\alpha nFE'_0}{RT}\right) &= k_b^0 \exp\left(\frac{(1 - \alpha)nFE'_0}{RT}\right) \equiv k_t^0 \end{aligned} \quad (31)$$

1.3 Electric double layer (EDL) effect

Then we have

$$I_f = -nFAk_f^0 \exp\left(\frac{(\alpha n - z)F\phi_2}{RT}\right) \exp\left(-\frac{\alpha nFE}{RT}\right) c_{\text{Ox}}^0 \quad (32)$$

$$= -nFA \underbrace{k_t^0 \exp\left(\frac{(\alpha n - z)F\phi_2}{RT}\right)}_{= k_t^{\text{app}}} \exp\left(-\frac{\alpha nF(E - E^{0'})}{RT}\right) c_{\text{Ox}}^0 \quad (33)$$

$$I_b = nFAk_b^0 \exp\left(\frac{(\alpha n - z)F\phi_2}{RT}\right) \exp\left(\frac{(1 - \alpha)nFE}{RT}\right) c_{\text{Rd}}^0 \quad (34)$$

$$= nFA \underbrace{k_t^0 \exp\left(\frac{(\alpha n - z)F\phi_2}{RT}\right)}_{= k_t^{\text{app}}} \exp\left(\frac{(1 - \alpha)nF(E - E^{0'})}{RT}\right) c_{\text{Rd}}^0 \quad (35)$$

The total current of the system can be written in the same way as Butler-Volmer-like equation

$$I = I_f + I_b \quad (36)$$

$$= -nFAk_t^{\text{app}} \left[\exp\left(-\frac{\alpha nF(E - E^{0'})}{RT}\right) c_{\text{Ox}}^0 - \exp\left(\frac{(1 - \alpha)nF(E - E^{0'})}{RT}\right) c_{\text{Rd}}^0 \right] \quad (37)$$

In the above equation, **please note that the bulk concentrations are used.** If we write the apparent rate constant by

The EDL effect for the redox reaction rate becomes

$$k_t^{\text{app}} = k_t^0 \exp\left(\frac{(\alpha n - z)F\phi_{\text{ad}}}{RT}\right) \quad (38)$$

In the original Butler-Volmer equation the surface concentrations are used

$$I(t) = I_f + I_b \quad (39)$$

$$= -nFAk^0 \left[\exp\left(-\frac{\alpha nF(E - E^{0'})}{RT}\right) c_{\text{Ox}}(z_2, t) - \exp\left(\frac{(1 - \alpha)nF(E - E^{0'})}{RT}\right) c_{\text{Rd}}(z_2, t) \right] \quad (40)$$

$$k^0 \equiv k_f^0 \exp\left(-\frac{\alpha nFE'_0}{RT}\right) = k_b^0 \exp\left(\frac{(1 - \alpha)nFE'_0}{RT}\right) \quad (41)$$

In this sense the concentration profile of redox species should be reconsidered. The double layer region (diffuse layer) is much short-ranged compared to the diffusion layer as shown below. If the electric double layer (EDL) effect is on, the redox concentration is greatly enhanced (or suppressed) at the diffuse layer in such a way $c_{\text{Ox}}(z_2) = c_{\text{Ox}}^0 \exp(-zF\phi(z_2)/(RT))$.

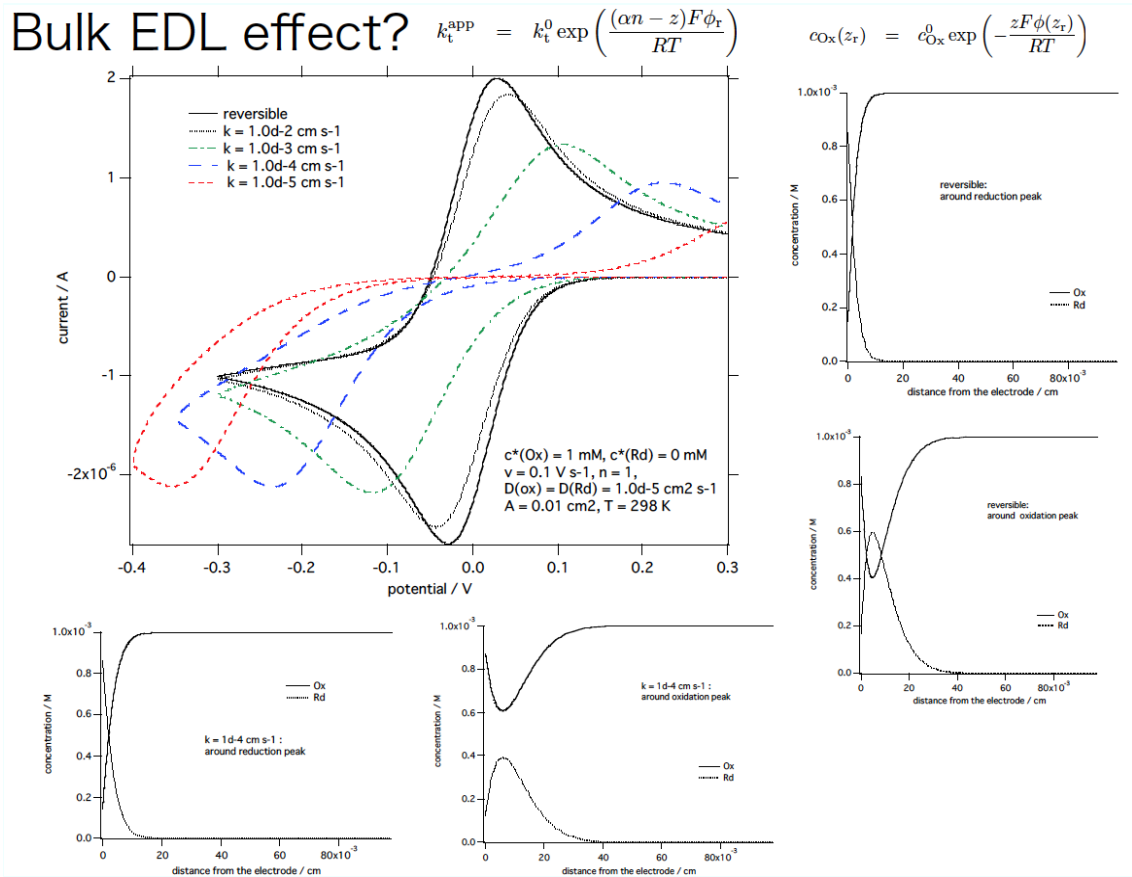


Figure 3: some examples of CV and the concentration profile

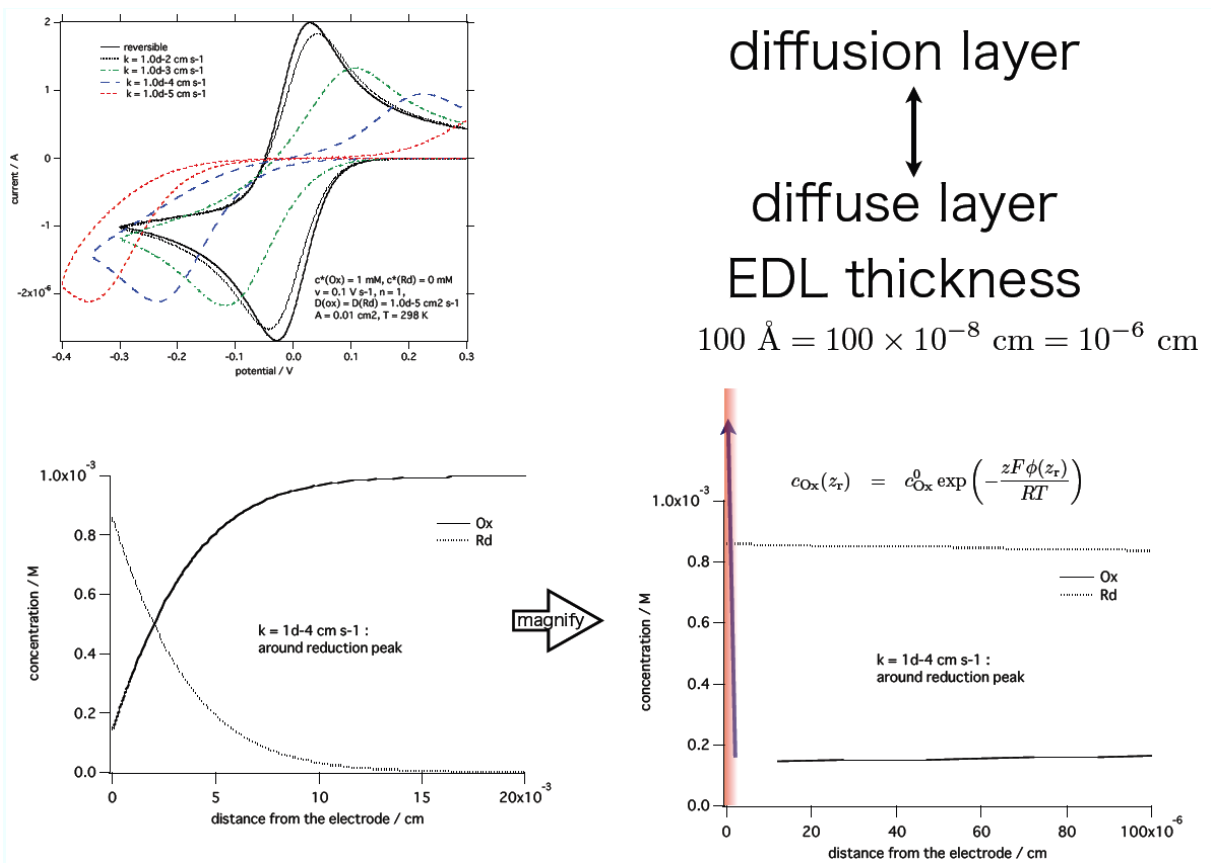


Figure 4: some examples of CV and the concentration profile