

V. Electrostatics

Lecture 27a: Diffuse charge at electrodes

Notes by MIT Student

We have talked about the electric double structures and corresponding models describing the ion and potential distribution in the double layer. Now we start to investigate the effect of double layer on the reaction kinetics, especially how the diffuse ionic charges affect the Faradaic half-cell reaction kinetics.

1. Frumkin Correction to Butler Volmer Kinetics

First we assume that Faradaic reaction takes place at a reaction plane, which is roughly the same as stern plane. The charge carriers need to hop over this stern layer barrier (with a thickness of one solvent molecule) and pick up an electron to finish the Faradic reaction. This region is basically a solvation shell of the electrode surface. Remember that the Butler Volmer (B-V) kinetics is a molecular scale equation, thus, in order to introduce the Frumkin correction, we apply the B-V equation only across this compact layer and the reaction rate, where the reaction occurs. Then the B-V equation can be described as:

$$R = R_0 [e^{(1-\alpha)ne\eta/kT} - e^{-\alpha ne\eta/kT}]$$

$$\text{prefactor } R_0 = \frac{k_0 a_R^\alpha a_O^{1-\alpha}}{\gamma_A}$$

overpotential across stern layer : $\eta = \Delta\phi_s - \Delta\phi_s^{eq}$

$$\Delta\phi_s^{eq} = \Delta\phi_s^O - \frac{kT}{ne} \ln\left(\frac{a_O}{a_R}\right)$$

Combining all these equations we will get:

$$R = \frac{R_0}{\gamma_A} [a_R e^{\frac{(1-\alpha)ne}{kT}(\Delta\phi_s - \Delta\phi_s^O)} - a_O e^{\frac{-\alpha ne}{kT}(\Delta\phi_s - \Delta\phi_s^O)}]$$

Note that for every charged species, activities or concentrations are all evaluated *locally at the stern plane*, which differs from the corresponding values in the neutral bulk electrolyte as we used in BV equation before.

Now, in order to relate it to the bulk concentrations, we need a double layer model. For example, if the diffuse part of the double layer satisfies dilute solution approximation, then for ionic species i with charge $z_i e$

$$c_{i(x=0)} = c_i^o e^{-z_i e \zeta / kT}$$

where $c_{i(x=0)}$ is concentration at stern plane

c_i^o is bulk concentration

$$\zeta = \phi_{(x=0)} - \phi_{bulk} = -\Delta\phi_{D(x=0)}$$

$e^{-z_i e \zeta / kT}$ is the Boltzman factor for charge across the diffuse layer.

This makes R_0 , $\Delta\phi_s^{eq}$ and thus η and R all depend on zeta potential ζ or surface charge. At surface $x=0$, $\psi_{(x=0)} = \zeta = -\Delta\phi_{D(x=0)}$. This was first noted by Frumkin in the 1930s, but Zeta potential is always related to charge, and ζ or q_s are usually fitted and assumed constants. However, as we seen in the previous lecture, ζ must depend on the current and should be predicted by the model.

2. Complete mathematical model based on Stern boundary condition

After we split double layer into Stern/compact layer and diffuse layer, potential boundary condition at the interface of these two layers is always missing in electrochemical system modeling. To complete the mathematical model, we have to introduce a reasonable boundary condition. To an approximation, since no charge is located within the compact layer, the electric field within it can be treated as constant, so if we denote $x = 0$ to be the Stern plane, our boundary condition can be written in terms of our effective compact layer thickness λ_s as follows based on a linear extrapolation of the potential across the compact layer.

$$\Delta\phi_s = \phi_e - \phi_{(x=0)} = \lambda_s \hat{n} \cdot \nabla \phi_{(x=0)} = -\lambda_s \hat{n} \cdot \bar{E}$$

where \hat{n} is the outward normal pointing from solution to the electrode

$$\lambda_s = \frac{\epsilon}{\epsilon_s} h_s \text{ is the effective thickness of the stern layer}$$

This makes reaction kinetics dependent on normal electric field \bar{E}

Apply Gauss's law, we will figure out that it also depends on surface charge density q_s .

$$-\hat{n} \cdot (\epsilon_{solution} \bar{E}_{solution} - \epsilon_{metal} \bar{E}_{metal}) = q_s$$

$$\Rightarrow -\hat{n} \cdot \bar{E}_{solution} = \frac{q_s}{\epsilon_{solution}}$$

Then we relate q_s to $\Delta\phi_s$: $\Delta\phi_s = -\lambda_s \hat{n} \cdot \bar{E} = \lambda_s \frac{q_s}{\epsilon_{solution}} = \frac{h_s q_s}{\epsilon_s}$

A. Helmholtz limit

Remember the dimensionless group $\delta = \frac{\lambda_s}{\lambda_D}$ is the ratio of stern layer effective thickness and

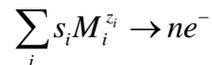
Debye screening length. When δ goes to infinity $\Delta\phi \cong \Delta\phi_s \gg \Delta\phi_D$, and we recover the usual BV kinetics using bulk concentrations without any Frumkin correction for diffuse charge.

But surface charge is not independent. The model predicts surface charge self-consistently by

$$q_s = \frac{\epsilon_s \Delta\phi_s}{h_s}, \quad q_s^{eq} = \frac{\epsilon_s \Delta\phi_s^{eq}}{h_s}$$

B. Gouy-Chapman limit

When δ goes to zero, $\Delta\phi \cong \Delta\phi_D \gg \Delta\phi_s$, and the flux boundary condition loses its explicit voltage dependence. Consider the reaction below:



Flux boundary condition is:

$$\hat{n} \cdot \vec{F}_i = s_i R = \frac{s_i R_o}{\gamma_A} \left[a_R e^{\frac{(1-\alpha)ne}{kT}(\Delta\phi_s - \Delta\phi_s^o)} - a_O e^{\frac{-\alpha ne}{kT}(\Delta\phi_s - \Delta\phi_s^o)} \right]$$

$$R_{\delta \rightarrow \infty} = k_o c_R - k_r c_O \quad (\text{Chang-Jaffe BC})$$

$$\text{where } \left\{ \begin{array}{l} k_o = \frac{R_o}{\gamma_A} \left(r_R e^{\frac{(1-\alpha)ne\Delta\phi_s^o}{kT}} \right) \\ k_r = \frac{R_o}{\gamma_A} \left(r_O e^{\frac{-\alpha ne\Delta\phi_s^o}{kT}} \right) \end{array} \right.$$

In the derivation, it seems that voltage no longer matters for the reaction kinetics, but actually it does. The current or reaction rate still depends implicitly on the total double layer voltage via the concentrations c_R, c_O .

With $k_o, k_r = \text{const}$ this is **Chang-Jaffe' boundary condition** (just standard chemical kinetics applied at the stern plane)

Example: Consider a cathode reaction $M \rightarrow M^+ + e^-$ (M=Li, H, etc)

Assume dilute solution and quasi-equilibrium, c_+ is the stern plane concentration, and c_+^o is the bulk concentration.

$$c_o = c_+ = c_+^o e^{-e\Delta\phi_D/kT}$$

$$\Delta\phi_D \cong \Delta\phi = \phi_c - \phi_{bulk}$$

$$R = \frac{I}{eA} = k_o c_R - k_r c_+^o e^{-e\Delta\phi/kT} \quad (e^{-e\Delta\phi/kT} \text{ is Frumkin correction})$$

This just looks like BV equation with $\alpha=1$

At equilibrium R=0, we get

$$\Delta\phi_{eq} = \frac{kT}{e} \ln\left(\frac{k_r c_+^o}{k_o c_R}\right) = \Delta\phi_S^o - \frac{kT}{e} \ln\left(\frac{a_+^o}{a_R}\right) \quad \text{This is the Nernst equation.}$$

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

$$R = \frac{I}{eA} = k_o c_R - k_r c_+^o \left(\frac{k_o c_R}{k_r c_+^o}\right) e^{-e\eta/kT}$$

$$\Rightarrow I = k_o c_R eA (1 - e^{-e\eta/kT}) = I_o (1 - e^{-e\eta/kT})$$

Based on this current expression, we see **that in the Gouy-Chapman limit, double layer acts like an ideal semiconductor diode** (like p-n junction behavior), and pass current in one direction only. This can be further explained from microscopic point of view in figure 2 and 3.

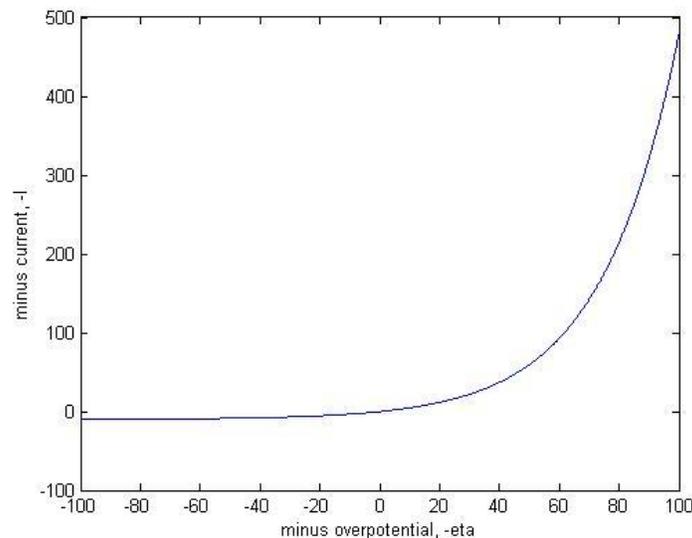


Fig. 1 In Gouy-Chapman limit double layer only allows current in one direction

In the forward bias, voltage keeps increasing the active species (counterions) at surface, and the diffuse layer is biased to accumulate a lot of active species (here cations) at the reaction plane due to the negative voltage relative to the bulk. Therefore, the local resistance is low and it allows a large current.

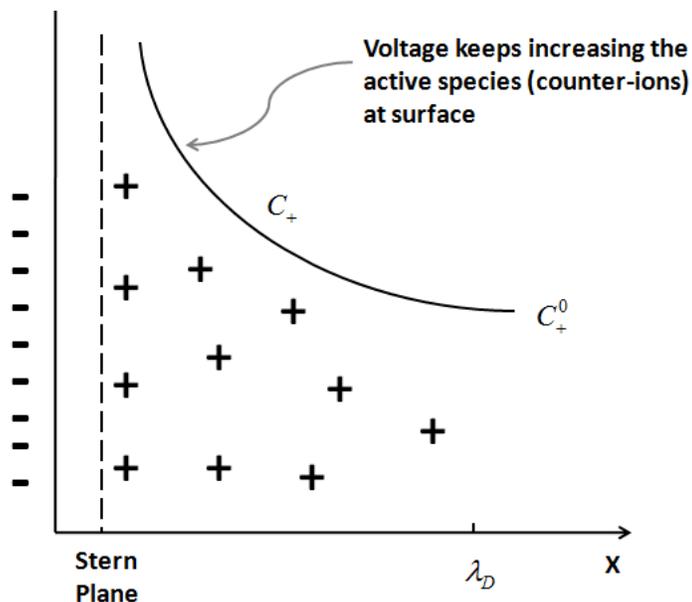


Fig. 2 Ion distribution in forward bias

However, in the reverse bias, the active species (cations) are depleted by the positive potential, thus local resistance becomes large and only a small constant current can go through, since we assume a neutral reduced state, whose concentration is unaffected by the electric field.

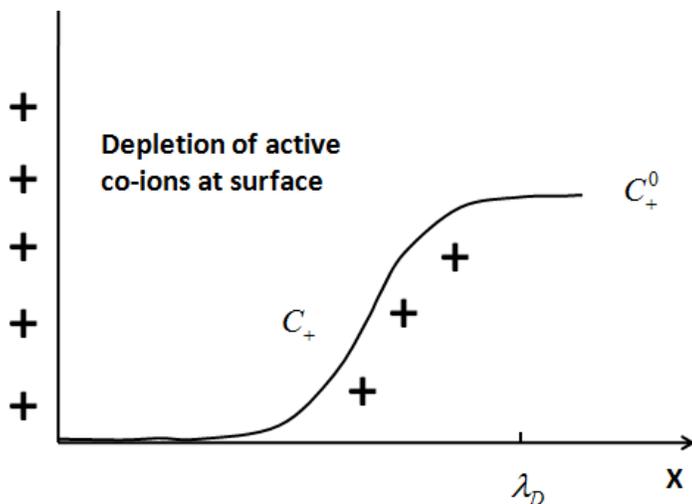


Fig. 3 Ion distribution in negative bias

We can also write overpotential as a function of current for the Gouy-Chapman limit of the Frumkin-Butler-Volmer theory:

$$\eta = -\frac{kT}{e} \ln\left(1 - \frac{I}{I_0}\right)$$

This looks very similar to the diode circuit element for diffusion limitation (ion concentration polarization), but note that here I_0 is actually a **reaction limited current**.

References

1. M. Z. Bazant, K. T. Chu and B. J. Bayly, Current-voltage relations for electrochemical thin films, *SIAM J Appl Math* 65 (2005) 1463-1484.
2. P. M. Biesheuvel, M. van Soestbergen, and M. Z. Bazant, Imposed currents in Galvanic cells, *Electrochimica Acta* 54 (2009) 4857-4871.

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10.626 Electrochemical Energy Systems
Spring 2014

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