

V. Electrostatics

Lecture 27b: Diffuse charge in membranes

MIT Student

In last lecture we discussed the effect of diffuse charge on Faradaic reaction kinetics at an electrolyte/electrode interface. Today, we start to study diffuse charge effect on membrane/electrode interface.

1. Basic Physics

Membrane allows transport of ions but not of electrons. In membrane, only one type of ion is mobile with the other type of ions fixed as a background charge, e.g., C_- . The background charge ensures a high conductivity (or low resistance) carried mostly by a mobile counterions, e.g. $C^+(x)$. Let's consider a cation exchange membrane Nafion as an example, protons will hop through very small pores in the polymer membrane, with positive transference number $t^+=1$ and negative transference number $t^-=0$. [Transference number denotes the fraction of current carried by a certain type of ion]. The resistance of the membrane is small, and can be treated as a constant R_m .

2. Current –Voltage Relation

First we discuss two limiting cases for membrane-electrode assembly with Frumkin-Butler-Volmer kinetics and stern boundary conditions.

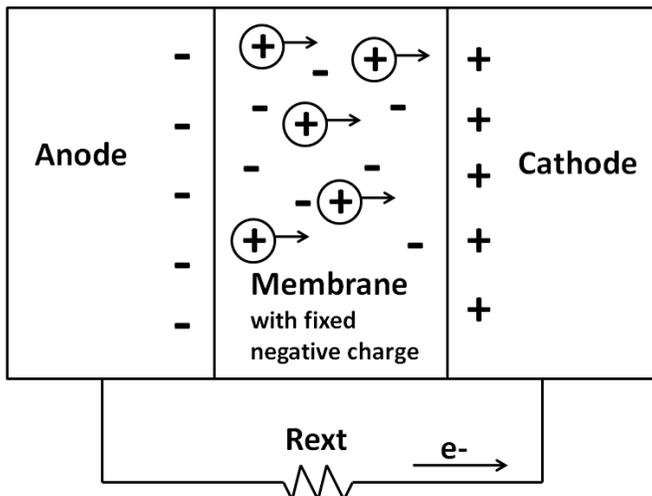


Fig. 1 Membrane-electrode assembly

If $\delta = \frac{\lambda_s}{\lambda_D} \rightarrow \infty$ (Helmholtz limit), we will recover traditional Butler-Volmer kinetics without diffuse charge effect. For example, if symmetry factor is taken to be 1/2, and assume only one active cation participate in the reaction ($n=1$), then voltage can be expressed as

$$V = V^0 - IR_m - \eta_{act}^a(I) + \eta_{act}^c(-I)$$

$$= V^0 - IR_m - \frac{2kT}{ne} \left(\sinh\left(\frac{I}{I_0^a}\right) + \sinh\left(\frac{I}{I_0^c}\right) \right)$$

However, in the Gouy-Chapman limit, $\delta = \frac{\lambda_s}{\lambda_D} \rightarrow 0$, Butler-Volmer becomes Chang-Jaffe's boundary condition and Frumkin effect (concentration correction). According to derivation in last lecture, we know that double layer will act like a diode

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

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

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

where I_0 is the reaction limiting current. In this situation, voltage becomes:

$$V = V^0 - IR_m - \eta_{act}^a(I) + \eta_{act}^c(-I)$$

$$= V^0 - IR_m + \frac{kT}{ne} \ln\left(\frac{1 - I/I_0^a}{1 + I/I_0^c}\right)$$

Now we see that if diffuse charge matters ($\delta = 0$), double layer polarization is dominated by diffuse charge (Frumkin effect) and equivalent circuit is as follows, where each interfacial overpotential acts like a diode and mainly allows current to pass through one direction (out of the electrolyte).

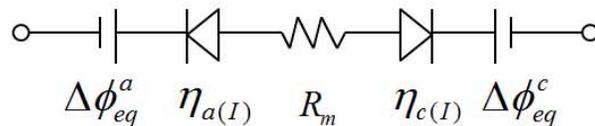


Fig. 2 equivalent circuit for GC limit of the membrane-electrode system.

The interfacial charge is usually neglected in electrochemical modeling, or left as a fitting parameter, but this calculations shows that in general it must depend on the applied current and ionic concentrations in a self-consistent way.

Recall that the reaction limited current is $I_0^a = I_{rxnlim}^{anode} = eA k_0 C_R$ (take anode for example). We can also add diffusion limitation through the concentration.

$$C_R = C_R^0 \left(1 - \frac{I}{I_{diffim}^{anode}}\right), \text{ where } I_{diffim}^{anode} = \frac{DeAC_0}{L}$$

$$\text{Then } I_0^a = I_{rxnlim}^{anode} \left(1 - \frac{I}{I_{diffim}^{anode}}\right)$$

In most situations, diffusion limited current is smaller than reaction limited current, thus we can usually drop it off.

3. General Membrane/Separator Model

Next, we are trying to establish a general model for membrane/separator. Membrane bulk is neutral with constant resistance R_{int} and fixed background charge (negative). Cations are mobile in the membrane and we neglect mobile anions. All the transport equations we need are similar as before except that Nernst Planck equation only applies for cation. Poisson-Boltzman equation becomes:

$$-\varepsilon \frac{d^2\phi}{dx^2} = \rho = e(c_+ - c_-^0)$$

where c_-^0 is a large constant. We assume a dilute solution with Boltzman distribution for the cation: $c_+ = c_+^0 e^{-\frac{e\psi}{kT}}$ with $\psi = \phi - \phi_{bulk}$, and solve for a semi-infinite region at one electrode ($x=0$) Assume thin flat double layer, thus $c_+^0 = c_-^0$. In the bulk, $\psi = 0$.

$$\varepsilon \frac{d^2\psi}{dx^2} = e c_-^0 (1 - e^{-\bar{\psi}})$$

where $\bar{x} = x / \lambda_D$; $\bar{\psi} = \frac{e\psi}{kT}$; $\lambda_D = \sqrt{\frac{\varepsilon kT}{e^2 C_0}}$. This equation can be simplified to be $\frac{d^2\bar{\psi}}{d\bar{x}^2} = 1 - e^{-\bar{\psi}}$

Boundary condition at the bulk is $\bar{\psi}_{(x=\infty)} = \bar{\psi}'_{(x=\infty)} = 0$, and Stern boundary condition is

$$-\delta \frac{d\bar{\psi}}{d\bar{x}} \Big|_{\bar{x}=0} = \bar{\psi}_{(x=0)} - \bar{\psi}_e = -\Delta\bar{\phi}_S$$

$$\bar{\psi}_{(x=0)} = \Delta\bar{\phi}_D$$

Multiply both side with the first derivative, and integrate, we will be able to solve the equation.

$$\frac{1}{2} (\bar{\psi}')^2 = \bar{\psi} + e^{-\bar{\psi}} - 1$$

Finally we will get

$$\Delta\bar{\phi}_s^{-2} = 2\delta^2(\Delta\bar{\phi}_D + e^{-\Delta\bar{\phi}_D} - 1)$$

Parameter δ controls the interplay between stern layer and diffuse layer, and this equation relate $\Delta\bar{\phi}_s$ to $\Delta\bar{\phi}_D$ (or total $\Delta\bar{\phi}$). For general analysis and numerical results, see Ref. 1. Results for solid electrolyte (membrane is one type of solid electrolyte) is shown in figure 3. Reaction limited current I_0 is obtained in the GC limit $\delta = 0$, while Helmholtz limit voltage current curve is close to a linear relationship. All the curves for arbitrary δ value lie between these two limits and show no reaction limiting current since the voltage can bias reactions at the stern plane to achieve any current.

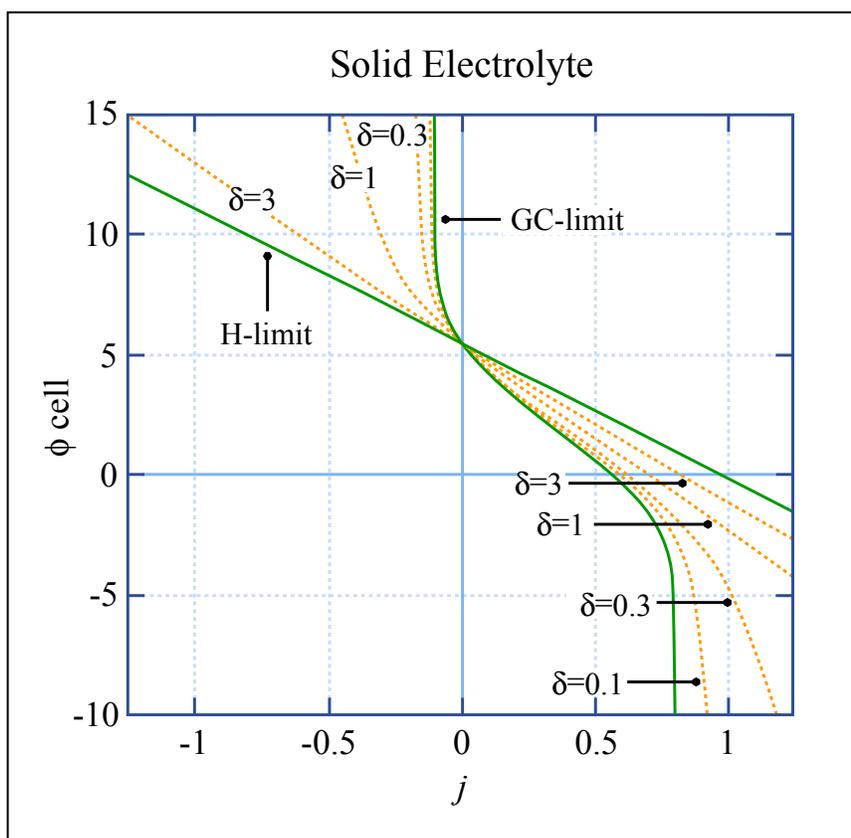


Image by MIT OpenCourseWare.

Fig. 3 Cell voltage vs. current for a galvanic cell with fixed countercharge (membrane model).

4. Differential Capacitance

From the calculation, we also get the capacitance of the membrane/electrode double layer

$$\bar{q} = -\frac{d\bar{\psi}}{dx_{(x=0)}} = -\sqrt{2(\Delta\bar{\phi}_D + e^{-\Delta\bar{\phi}_D} - 1)} \cdot \text{sgn}(\Delta\bar{\phi}_D)$$

$$\bar{C}_D = -\frac{d\bar{q}}{d\Delta\bar{\phi}_D} = -\frac{1 - e^{-\Delta\bar{\phi}_D}}{\sqrt{2(\Delta\bar{\phi}_D + e^{-\Delta\bar{\phi}_D} - 1)}} \cdot \text{sgn}(\Delta\bar{\phi}_D)$$

$$\bar{C} = \frac{1}{\delta + \bar{C}_D^{-1}(\Delta\bar{\phi}_D)}$$

A typical curve for capacitance with $\delta=0.8$ is given below. Note that now differential capacitance has diode effect with symmetry broken. In the positive $\Delta\bar{\phi}_D$ region, capacitance is proportional to $1/\sqrt{\Delta\bar{\phi}_D}$ because of the depletion of counterions, while in the negative $\Delta\bar{\phi}_D$ part, stern cutoff comes from enrichment of counterions.

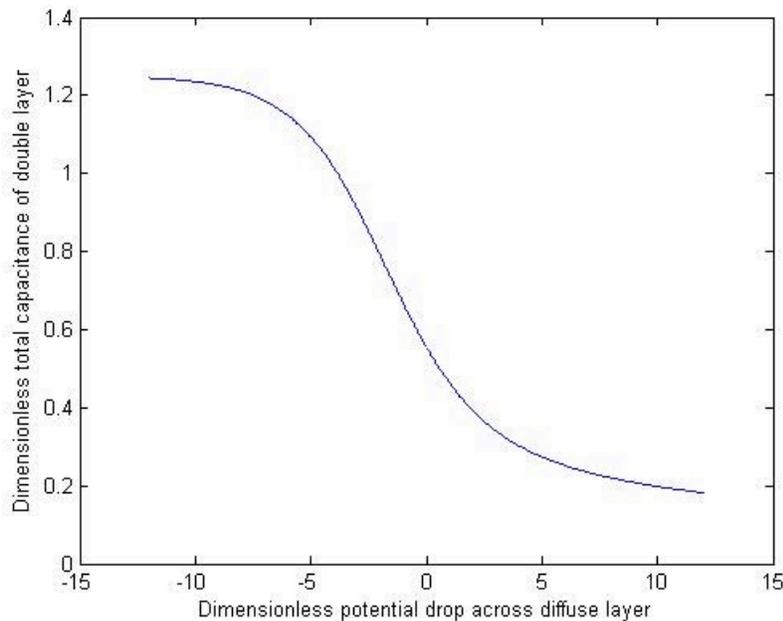


Fig. 4 Dependence of capacitance of double layer on the voltage drop across diffuse layer in membrane/electrode system (figure drawn by taking $\delta=0.8$)

References:

1. Diffuse charge effects in fuel-cell membranes, P. M. Biesheuvel, A. A. Franco, and M. Z. Bazant, *J. Electrochem. Soc.*, **156**, B225-B233 (2009).
2. P. M. Biesheuvel, M. van Soestbergen, and M. Z. Bazant, *Imposed currents in galvanic cells*, *Electrochimica Acta* 54, 4857-4871 (2009).

MIT OpenCourseWare
<http://ocw.mit.edu>

10.626 Electrochemical Energy Systems
Spring 2014

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.