

IV. Transport Phenomena

Lecture 23: Ion Concentration Polarization

MIT Student (and MZB)

Ion concentration polarization in electrolytes refers to the additional voltage drop (or “internal resistance”) across the electrolyte associated with ion concentration gradients, which exists in addition to the Ohmic voltage drop associated with the mean conductivity. We focus on consider quasi-neutral “bulk” electrolytes.

1. Nernst-Plank equations

Assume there is no convective transport ($\vec{u} = \vec{0}$).

General Nernst-Plank equations:

$$\frac{\partial C_i}{\partial t} = \nabla \cdot (M_i C_i \nabla \mu_i) = \nabla \cdot (D_i C_i \nabla \tilde{\mu}_i)$$

, where $\tilde{\mu}_i = \mu_i / k_B T$, $D_i = M_i k_B T$ (Einstein relation)

For dilute solution (with neglecting electrostatic correlations):

$$D_i = \text{constant}$$

$$\tilde{\mu}_i = \ln C_i + z_i e \tilde{\phi}, \quad \tilde{\phi} = e \phi / k_B T$$

Then, Nernst-Plank equation goes to

$$\boxed{\frac{1}{D_i} \frac{\partial C_i}{\partial t} = \nabla^2 C_i + z_i \nabla \cdot (C_i \nabla \tilde{\phi})}$$

To determine $\tilde{\phi}$, we can use electroneutrality/charge conservation.

$$\boxed{\sum_i z_i e C_i = 0 \Leftrightarrow \nabla \cdot J = 0} \quad (\text{Condition of “quasi-electroneutrality”})$$

$$J = \sum_i z_i e F_i = -e(z_+ D_+ + z_- D_-) \nabla C - e(z_+^2 D_+ - z_-^2 D_-) C \nabla \tilde{\phi}$$

2. Dilute Binary Electrolyte

From quasi-electroneutrality, for a binary salt, we can define salt concentration C via $z_+ C_+ = z_- C_- = C$ which satisfies a simple diffusion equation with a certain average or “ambipolar” diffusivity, as derived in the last lecture:

$$\boxed{\begin{aligned} \frac{\partial C}{\partial t} &= D_{eff} \nabla^2 C \\ D_{eff} &= \frac{(z_+ + z_-) D_+ D_-}{z_+ D_+ + z_- D_-} \end{aligned}}$$

For dilute binary electrolyte, $z_+ = z_-$, the effective diffusivity goes to harmonic mean of the ion diffusivities, weighted by the charge of the opposite species ($\langle \rangle$ denotes the harmonic mean).

$$D_{eff} = \frac{1}{\left(\frac{z_+}{z_+ + z_-}\right) \frac{1}{D_-} + \left(\frac{z_-}{z_+ + z_-}\right) \frac{1}{D_+}} = \langle 1/D \rangle$$

Generally, the effective diffusivity for ambipolar electrolyte D_{eff} is an average of D_+ and D_- giving more weight to smaller diffusivity D and smaller charge z . The diffusion is dominated by the smaller mobility. As an analogy, consider “teacher” with a small “student” traversing a room. Even though the student has the tendency to move much faster than his/her accompanying teacher, he/she is limited in the extent of this mobility by the teacher’s speed and position. That is, highly mobile “student” ions could not stray far from its less mobile “teacher” ion to be maintained electroneutrality of bulk electrolyte. It is the reason why the equation of effective diffusivity expresses the coupling of the positive and negative species. It is noted that this equation is only effective at describing bulk solution, which satisfy electroneutrality assumption. The equation no longer valid when the electroneutrality assumption breaks down, such as near charged surfaces.

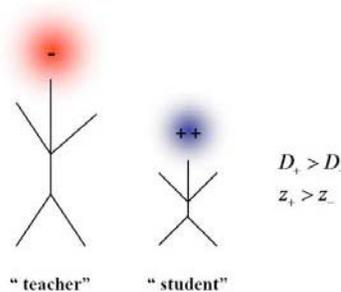


Fig 1. Interpretation of the effective ambipolar diffusivity of a dilute binary electrolyte where the anions are the “students” (or children) and the cations are the “teachers”, who strive to maintain a fixed “teacher-student ratio” consistent with electroneutrality. The ambipolar diffusivity gives more weight to the slower/larger ion with smaller charge (the teacher) since other ion (the student) responds more quickly to electric fields, not only the applied external electric field (which attracts students to different boundaries, as below), but also the internal “diffusion field” which helps the ions to maintain electro neutrality when their diffusivities are different.

3. Steady-State Ion Concentration Polarization

Reservoir/electrolyte/membrane system:

Let's consider 1-D system consisting of a dilute quasi-neutral electrolyte of thickness L passing current from a reservoir through an ideally cation-selective surface, such as an electro dialysis membrane, metal electrode undergoing electroplating...). The cation selective membrane/electrode consumes cations only. Since anions cannot go through this surface, their concentration is depleted by electromigration in the opposite direction, and quasineutrality then implies that the cation concentration also becomes depleted near the surface, leading to concentration polarization. When we section by three region (reservoir, electrolyte, membrane), ion concentration of the reservoir is constant as C_0 . Also, salt concentration C can be defined from quasi-electroneutrality in the electrolyte.

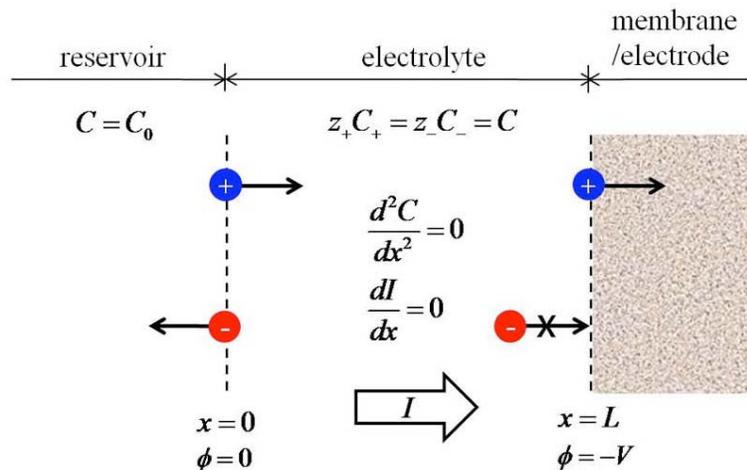


Fig 2. Model problem for ion concentration polarization: One dimensional steady current through a dilute binary electrolyte from a reservoir at fixed concentration at $x=0$ through an ideal cation-selective surface (membrane or electrode) at $x=L$.

In this system, gradient of the flux of cation and the flux of anion should be zero due to cation selective membrane. From constant zero anion flux, we can induce the salt concentration C follows Boltzmann distribution because its chemical potential should be constant.

$$\frac{dF_+}{dx} = 0, F_- = 0 \quad \left(\because \frac{dF_-}{dx} = 0, F_-(x=0) = 0 \right)$$

$$\Rightarrow \mu_- = \mu_0 = k_B T \ln C_- - z_- e \phi = \text{constant}$$

$$\Rightarrow C_- = \frac{C_0}{z_-} \exp(z_- \tilde{\phi})$$

$$\Rightarrow \tilde{\phi} = \frac{1}{z_-} \ln \tilde{C}, \text{ where } \tilde{C} = \tilde{C}_- = z_{\pm} C_{\pm} / C_0$$

Calculate the current I from the flux of cation (set the membrane/electrode area: A),

$$F_+ = \text{constant}$$

$$I = z_+ e F_+ A = -z_+ e A \left(\frac{dC_+}{dx} + z_+ C_+ \frac{d\tilde{\phi}}{dx} \right)$$

Set $z_+ C_+ = \tilde{C} \cdot C_0$, $\tilde{x} = x/L$, and substitute $\tilde{\phi}$

$$\begin{aligned} I &= -\frac{eAC_0}{L} D_+ \left(\frac{d\tilde{C}}{d\tilde{x}} + z_+ \tilde{C} \frac{d\tilde{\phi}}{d\tilde{x}} \right) \\ &= -\frac{eAC_0}{L} D_+ \left(1 + \frac{z_+}{z_-} \right) \frac{d\tilde{C}}{d\tilde{x}} \end{aligned}$$

Limiting current I_{lim} (due to electrolyte depletion only) can be defined by combination of the diffusion term and the electromigration term.

$$I_{\text{lim}} = \frac{eAC_0}{L} D_+ \left(1 + \frac{z_+}{z_-} \right)$$


Now, salt concentration and potential can be expressed for steady ambipolar diffusion with non-dimensionalized current.

$$\tilde{I} = \frac{I}{I_{\text{lim}}} = -\frac{d\tilde{C}}{d\tilde{x}}, \quad \tilde{C}(x=0) = \text{constant}$$

$$\begin{aligned} \Rightarrow \tilde{C} &= 1 - \tilde{I}\tilde{x} \\ \Rightarrow \tilde{\phi} &= \frac{1}{z_-} \ln(1 - \tilde{I}\tilde{x}) \end{aligned}$$

Now we see the limiting current I_{lim} as $\tilde{I} \rightarrow 1$, $\tilde{C}(\tilde{x}=1) \rightarrow 0$, $\tilde{\phi}(\tilde{x}=1) \rightarrow \infty$. Physically, the value of non-dimensionalized current \tilde{I} cannot be larger than 1 because the sign of salt concentration should be positive.

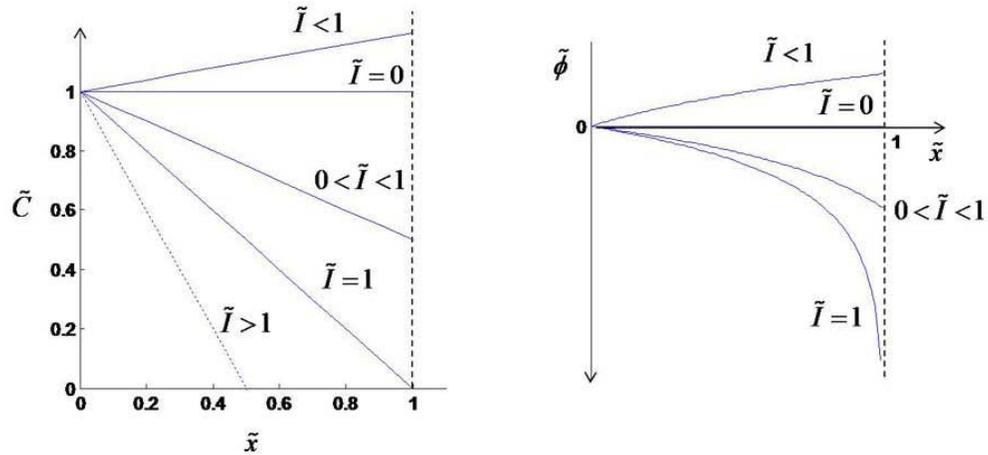


Fig 3. Profiles of neutral salt concentration (left) and electrostatic potential (right) in the model problem of Fig 2 for different currents. At the diffusion-limited current (scaled to 1), the salt concentration vanishes at the cation-selective surface, and the electrostatic potential diverges. Larger currents in this model lead to unphysical negative concentrations. More complete models taking into account diffuse charge, solvent dissociation, and electroconvection provide a number of possible mechanisms to sustain “over-limiting currents” exceeding diffusion limitation. [1-3]

For current-voltage curve,

$$\tilde{\phi}(\tilde{x}=1) = -\tilde{V} = \frac{1}{z_-} \ln(1 - \tilde{I}), \text{ where } \tilde{V} = eV/k_B T \quad \Rightarrow \tilde{I} = 1 - e^{-z_- \tilde{V}}$$

The electrolyte has the same I-V characteristic as an ideal diode (not a constant resistor) due to concentration overpotential by salt depletion (concentration gradient in electrolyte).

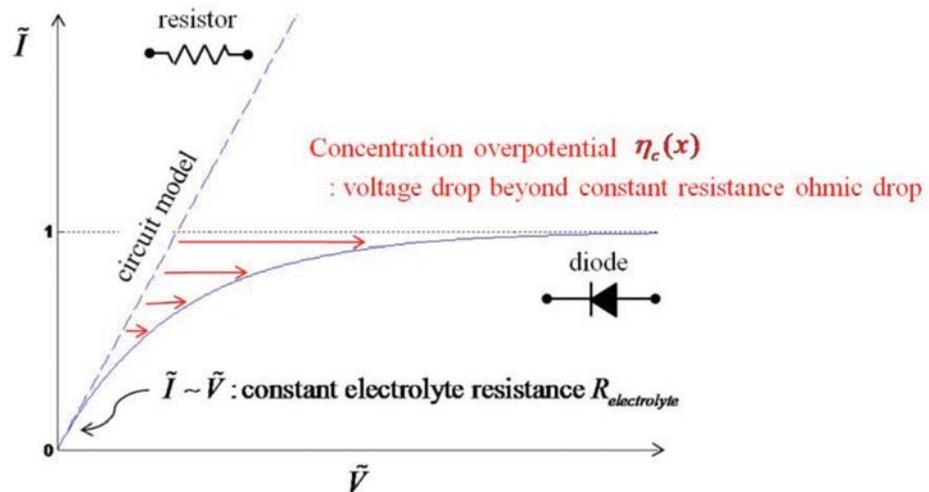


Fig 4. Current-voltage relation for the model problem showing the “concentration overpotential” (additional internal resistance) associated with ion concentration polarization, which lowers the voltage at a given current relative to the prediction of Ohm’s law (constant internal resistance) based on the initial conductivity of the electrolyte. As a result, the electrolyte layer behaves like an ideal semiconductor diode, rather than a constant resistance.

Although it seems like neutral salt is diffusing as ion pairs, this is not the case. The anion flux is zero, while cation flux is not. Instead, the cations move through the anions only roughly maintaining an equal concentration locally. As an analogy, anions are “teachers” who must maintain a fixed “teacher-student ratio” as the cation “students” pass through the system.

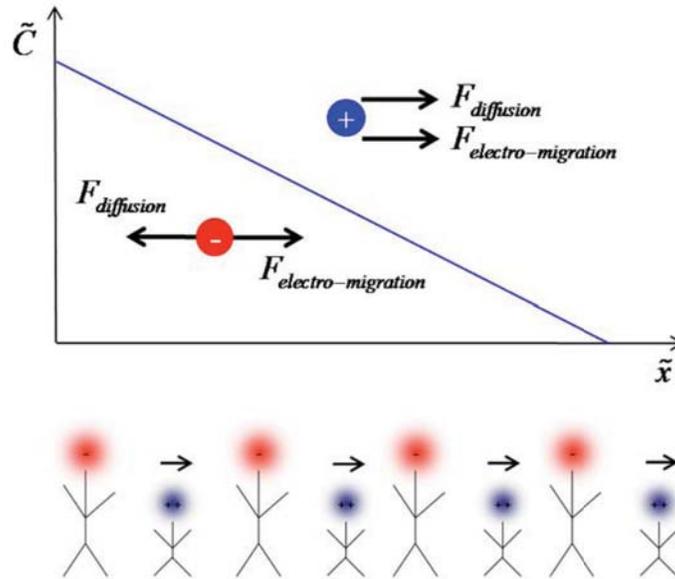


Fig 6. Interpretation of steady conduction in a binary electrolyte, using the teacher-student analogy of Fig. 1. The students (fast cations) pass through the system from the reservoir to the membrane, driven by the applied voltage. (This might represent students entering the classroom from outside and leaving to go to the cafeteria.) Neutrality is maintained with a steady concentration gradient, so that the forward diffusion of the anions is precisely balanced by their electromigration in the opposite direction, yielding zero total flux, while the cations move by a combination of diffusion and electromigration acting in the same direction.

Membrane/electrolyte/membrane system:

Another example is the system with electrolyte between two cation exchange membrane (or electrodeposition / dissolution cell).

The equivalent circuit of this system would be combination of two diodes with opposite directions. Then, ion concentration profile and current-voltage relation go to (set $z=1$),

$$\boxed{\tilde{C} = 1 - \tilde{I}x}, \quad (-1 < \tilde{x} < 1)$$

$$2\tilde{V} = -\ln(1 - \tilde{I}) - (-\ln(1 + \tilde{I}))$$

$$\tilde{V} = \frac{1}{2} \ln\left(\frac{1 + \tilde{I}}{1 - \tilde{I}}\right) = \tanh^{-1}(\tilde{V})$$

$$\boxed{\tilde{I} = \tanh(\tilde{V})}$$

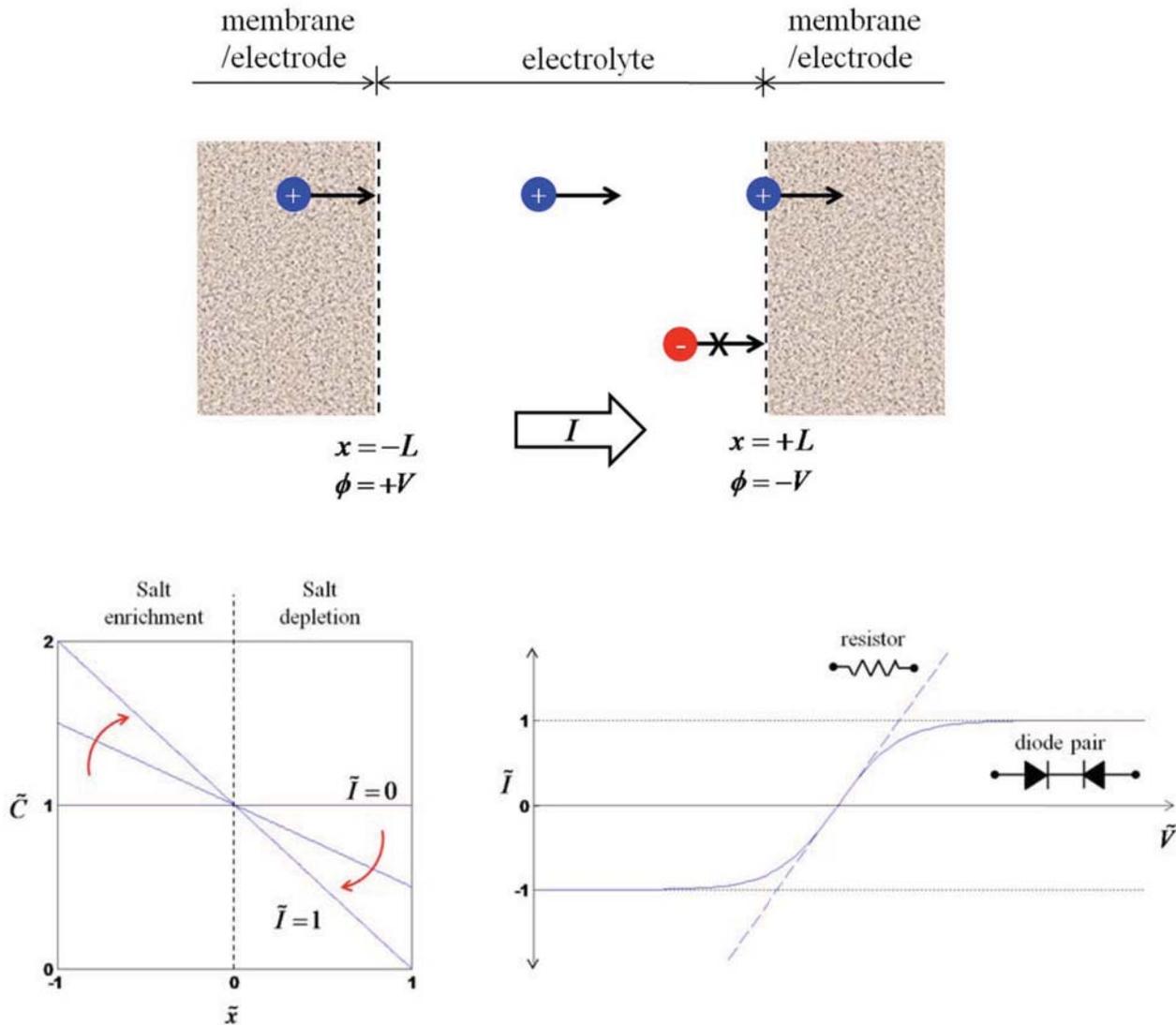


Fig 7. Concentration profile and current-voltage relation for an electrolyte passing steady current between two cation selective surfaces, e.g. cation-selective membranes or electrodes undergoing dissolution (anode on the left) and electrodeposition (cathode on the right).

4. Over-Limiting Current

The preceding theory of concentration polarization and limiting current in an electrolyte has fundamental importance in electrochemical systems and can be traced back at least a century to Nernst. Avoiding such limitations for active ions undergoing desired reactions at surfaces is the main reason that supporting electrolytes (large numbers of additional ions) are widely used to maintain Ohmic behavior of the solution. The theory, however, is oversimplified and loses validity near the limiting current, as pointed out by Levich in the 1950s in his classic book, *Physicochemical Hydrodynamics*, since the quasi-electroneutrality assumption breaks down as the salt concentration goes to zero near the ion-selective surface.

It is now understood that there are a number of physical mechanisms for over-limiting current, exceeding diffusion limitation in an electrolyte:

1. **Extended space charge.** Smyrl and Newman (1967) first pointed out that the double takes on an extended non-equilibrium structure at the limiting current, and Rubinstein and Shtilman (1979) showed that such non-equilibrium space charge can in principle extend far into the bulk up to arbitrarily large currents. This may be relevant for submicron-scale thin films, where convection and electrochemical reactions might not be possible, but otherwise it is believed that this situation is unlikely to be realized in practice.
2. **Electro-osmotic instability.** In bulk liquid electrolytes, Rubinstein and Zaltzman (2000-2007) showed that the extended space charge is hydrodynamically unstable to so-called 2nd kind electro-osmotic flows along the surface, which lead to vortices that bring ions to the surface by convection, once the current exceeds diffusion limitation.
3. **Electrochemical reactions.** Under some conditions (especially at near anion exchange membranes in aqueous solutions), electrochemical reactions, such as water splitting, can produce additional ions once the concentration of the original electrolyte becomes strongly depleted, and this additional conductivity allows the system to sustain over-limiting current.

For a review of these phenomena in the context of electrodialysis for water desalination, see Nikonenko et al, *Advances in Colloid and Interface Science* 160 (2010) 101-123.

Later in the class, we will study ion transport in microchannels and porous media, where the presence of charged walls leads to two additional mechanisms for over-limiting current, circumventing ion concentration polarization:

4. **Surface conduction.** As the quasi-neutral electrolyte becomes depleted in a microchannel or pore, it is possible to sustain larger, over-limiting currents by passing current through the double layers, driven by the large electric field in the depleted region acting on the counterions that remain to screen the wall charge.
5. **Electro-osmotic flow.** The large field in the depleted region also drives electro-osmotic flows along the side walls, which provide another pathway for over-limiting current carried by convection. This mechanism was first noted by Yaroshchuk and Zholkovskiy (2011).

A unified theory of over-limiting current in the microchannel was recently developed by Dydek, Zaltzman, Rubinstein, Deng, Mani, and Bazant (2011), showing a transition from surface conduction to electro-osmotic flow to electro-osmotic instability with increasing channel size. These phenomena may have applications in boosting the power density of batteries or supercapacitors or in a new approach to desalination (“shock electrodialysis”)

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