

Porous Electrodes (I. Supercapacitors)

1. Effective Equations for Thin Double Layers

For supercapacitor electrodes, convection is usually negligible, and we drop out convection terms here. Let's focus on effective equations governing the transports and electrostatics in electrolyte.

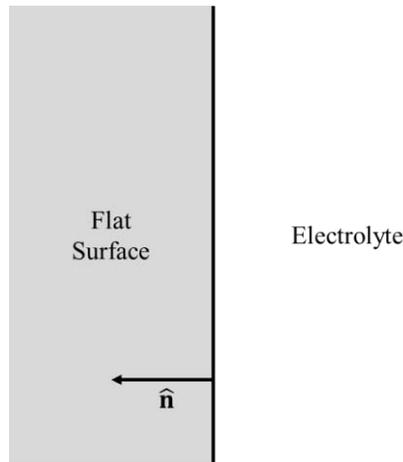


Figure 1. Flat Electrode Surface

Species conservation equations, Nernst-Plank flux constitutive equations, and Poisson equation make up Poisson-Nernst-Plank (PNP) set of equations (bold fonts indicate that the variables are in vector quantity):

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{F}_i = 0 \quad (1)$$

$$\mathbf{F}_i = -D_i c_i \nabla \tilde{\mu}_i \quad (2)$$

$$\rho = \sum_i z_i e c_i = -\epsilon \nabla^2 \phi \quad (3)$$

Electrostatic constrain and flux constrains on the surface specify boundary conditions. Electrostatic constrain can be interpreted differently, given different specified variables. When there is a specified amount of surface charge, we can have *Gaussian law* satisfying the electrostatic constrain:

$$-\hat{\mathbf{n}} \cdot (\epsilon \nabla \phi) = q_s \quad (4)$$

On the other hand, when given a specified surface potential, we can use the following approximation, Equation (5), instead of Equation (4), satisfying the electrostatic constrain. This boundary condition could be more simplified assuming negligible capacity in Stern layer.

$$\begin{aligned} \Delta \phi = \phi_e - \phi(x=0) &= \lambda_s \hat{\mathbf{n}} \cdot \nabla \phi(x=0) \\ \phi_e &= \phi(x=0) \end{aligned} \quad (5)$$

We can use either Equation (4) or (5) to satisfy the electrostatic constrain, depending on specified variables at the surface. In addition, flux constrains of species specify the rest of necessary boundary conditions:

$$\hat{\mathbf{n}} \cdot \mathbf{F}_i = R_i \quad (6)$$

We now apply the above set of equations (PNP) as well as boundary conditions to the porous electrode with double layer thickness far thinner than the pore length scale.

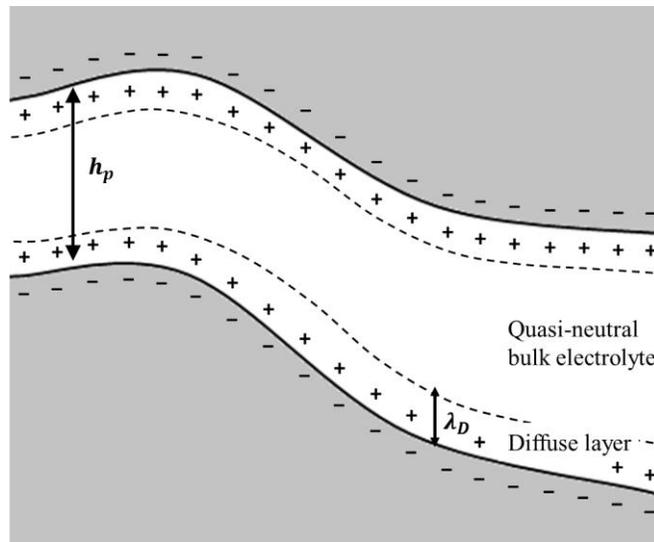


Figure 2. Thin Double Layer in a Pore

When the pore length scale is far larger than the length scale of double layer, $h \gg \lambda$, we have separation of length scales. The mathematical structure of thin double layer problem is well understood from the perspective of *singular perturbation analysis*, in which each of two regions requires a different approximation. Two different approximations are constrained by *matched asymptotic expansions*.

We first assign notations for different variables. From now on throughout this lecture, we use the following notations.

- \hat{c} : Concentration of Species i in Double Layer
- c : Concentration of Species i in Bulk Electrolyte

- $\hat{\mu}$: Chemical Potential of Species i in Double Layer
 μ : Chemical Potential of Species i in Bulk Electrolyte

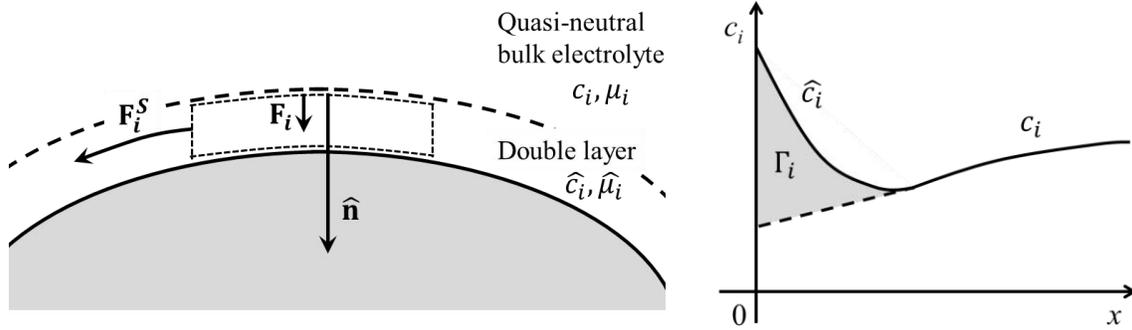


Figure 3. Variables in Two Different Regions

In quasi-neutral bulk electrolyte, we can use the quasi-neutral approximation, and conclude with zero divergence of current density.

$$\rho = \sum_i z_i e c_i \approx 0 \quad (7)$$

$$\nabla \cdot \mathbf{j} = \nabla \cdot \left(\sum_i z_i e \mathbf{F}_i \right) \approx 0 \quad (8)$$

As stated above discussion, asymptotic expansions of approximated variables in two different regions should be matched with the corresponding pair respectively. In a pore, variables are well approximated by the quasi-equilibrium approximation, and chemical potentials in the two regions are approximately constant across the pore.

$$\lim_{\hat{x} \rightarrow \infty} \hat{c}_i = \lim_{x \rightarrow 0} c_i \quad (9)$$

$$\hat{\mu}_i = \mu_i \quad (10)$$

Now, conditions constraining the variables in double layer can be found by defining surface variables as shown in Figure 3 (Stern layer capacity ignored):

$$\Gamma_i = \int_0^\infty \left(\hat{c}_i - \lim_{x \rightarrow \infty} \hat{c}_i \right) dx \quad (11)$$

$$\mathbf{F}_i^S = -D_i \Gamma_i \nabla_s \tilde{\mu}_i \quad (12)$$

Then the effective boundary condition using the variables above is (Chu and Bazant, 2007):

$$\frac{\partial \Gamma_i}{\partial t} + \nabla_s \cdot \mathbf{F}_i^S = R_i^S + \hat{\mathbf{n}} \cdot \mathbf{F}_i \quad (13)$$

where Γ_P : Excess Surface Concentration of Species i per Area
 \mathbf{F} : Surface Flux of Species i
 $\frac{\tilde{\mu}_P}{T_P}$: Dimensionless Chemical Potential of Species i
 R : Net reaction rate of Species i Using Bulk Variables (c ,

Total diffuse charge density can be calculated with excess surface concentrations.

$$q = \sum_i z_i e \Gamma_i \quad (14)$$

2. Porous Electrodes

Formal derivation by volume averaging (homogenization) goes from the thin double layer equations inside pores to macroscopic partial differential equations. An appropriate model would involve volume averages of variables over a volume element small compared to the overall dimensions (L), but large than the pore structure length scale (h_p). Hence, to have this model valid, the following condition is necessary.

$$L \gg h_p \gg \lambda_D \quad (15)$$

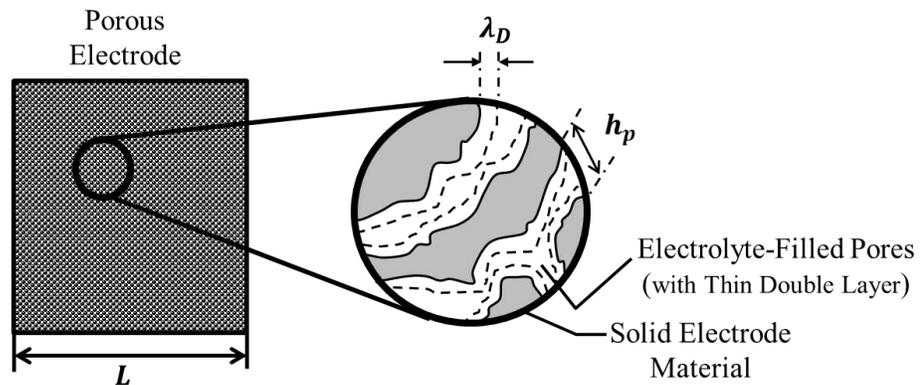


Figure 4. Length Scales in Porous Electrode

Not always, but for supercapacitors, we do not deplete the salt ions in electrolyte. Thus it is a valid approximation to assume that concentrations (c and potentials (ϕ and ψ)) are varying slowly in the macroscopic viewpoint. This assumption justifies the volume-averaging or homogenization.

In this macroscopic treatment, we do not consider the actual geometric details of the pores. Rather, we define macroscopic potential in electrolyte, potential in solid material, and ion concentrations to be continuous and well-defined functions of space coordinates. As a result, the porous electrode in this model is represented by the superposition of two continuous media

without microstructure, one corresponding to the electrolyte solution and the other corresponding to the solid material matrix. In this model both media are defined in the whole domain.

Therefore, in this macroscopic model, potential in electrolyte () as well as potential in conducting solid material () are defined in the whole domain of space, whereas they were only defined in each phase formerly. Volume-averaged concentrations in macroscopic viewpoint are different from and related to the concentrations in bulk electrolyte and in double layers as shown in the following equation (in former lectures, \bar{c} was used for the concentrations in reservoirs or in inlet flows of fuel. In this lecture, \bar{c} is used for volume-averaged concentrations in macroscopic viewpoint). The macroscopic ion concentrations are defined throughout the whole volume as well.

$$\bar{c}_i = \epsilon_p c_i + a_p \Gamma_i \quad (16)$$

The first term on right hand side corresponds to the contributions from bulk electrolyte, and the second term is from excess concentrations in double layers. Newman's book (3rd Ed, 2004) does not take account of the second term. However, this term may have significant effects especially when we consider supercapacitors whose charges are mostly stored in the double layers.

With the variables defined with the macroscopic model, we can construct the species conservation equations, as well as the flux constitutive equations:

$$\frac{\partial \bar{c}_i}{\partial x} + \nabla \cdot \bar{\mathbf{F}}_i = \bar{R}_i \quad (17)$$

$$\bar{\mathbf{F}}_i = -\bar{D}_i \bar{c}_i \nabla \tilde{\mu}_i \quad (18)$$

We could better model the macroscopic flux equation, including the transport in double layers as shown in Equation (19) and Figure 5. Transport in double layer (surface transport) would be significant when the stored diffuse charge is large.

$$\bar{\mathbf{F}}_i = -\bar{D}_i \epsilon_p c_i \nabla \tilde{\mu}_i - \bar{D}_i^s a_p \Gamma_i \nabla \tilde{\mu}_i \quad (19)$$

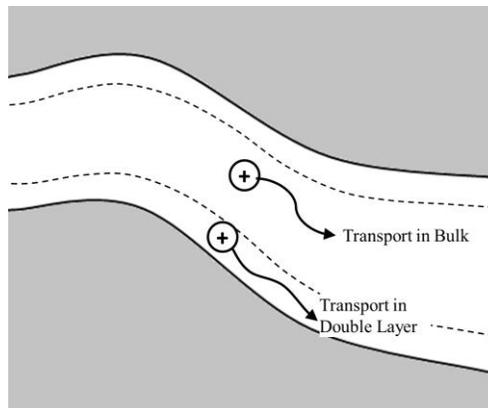


Figure 5. Transport in Double Layer (Surface Transport)

For the macroscopic volume-averaged reaction term (\bar{R}_i), we could model it by using the surface reaction term based on the bulk concentrations and potentials:

$$\bar{R}_i = a_p R_i^S(c_i, \phi, \phi_e) \quad (20)$$

where

- $\frac{\tilde{\mu}_i}{T_P}$: Dimensionless Chemical Potential of Species i
- \bar{D}_i : Effective Diffusivity in porous medium (see Lecture 34)
- \bar{D}_i^s : Effective Surface Diffusivity
- ϵ_p : Macroscopic Porosity
- a_p : Surface Area Density

With the macroscopic concentrations and fluxes above, we can also define macroscopic current density as well as charge density. For the charge density, only excess surface concentrations matter, since bulk electrolyte keeps quasi-neutrality.

$$\bar{\mathbf{j}} = \sum_i z_i e \bar{\mathbf{F}}_i \quad (21)$$

$$\begin{aligned} \bar{\rho} &= \sum_i z_i e \bar{c}_i \\ &= a_p \sum_i z_i e \Gamma_i = a_p q_D \end{aligned} \quad (22)$$

Due to macroscopic neutrality, $\bar{\rho} = -a_p q$. This macroscopic charge density is conserved by the following equation. The negative sign in Equation (23) is due to the definition of current density, which defines anodic currents to be positive.

$$\frac{\partial \bar{\rho}}{\partial t} + \nabla \cdot \bar{\mathbf{j}} = \bar{\mathbf{j}}_F \equiv -\sum_i z_i e \bar{R}_i \quad (23)$$

Now, we define electronic current density in a porous electrode.

$$\bar{\mathbf{j}}_e = -\bar{\sigma}_e \nabla \phi_e \quad (24)$$

Due to macroscopic charge conservation, the divergence of total current is zero.

$$\nabla \cdot (\bar{\mathbf{j}}_e + \bar{\mathbf{j}}) = 0 \quad (25)$$

With the governing equations discussed above, we can now understand what the solutions look like for different applications. In this lecture, we focus on getting and understanding the solution for supercapacitors. The solutions for batteries and fuel cells will be discussed in the next lecture (Lecture 36). In supercapacitor applications, we do not have significant faradaic reactions on the electrode pore surfaces. Thus, we can get the solution, setting the faradaic

transference current to be zero ($\bar{j} = 0$). On the other hand, for batteries and fuel cells, we can neglect capacitance of double layers, and focus on faradaic contributions. Also, it is required to model reaction products, in addition to the reacting ions and electrons.

3. Supercapacitors

In a model for supercapacitors, we can neglect faradaic transference current ($\bar{j} = 0$) and changes in salt concentration due to capacity charging of double layers (*c.f.* salt depletion due to double layer charging is considerable in *capacity desalination* applications). Then, we can define effective ionic conductivity ($\bar{\sigma}_P$, approximated to be constant).

$$\bar{\mathbf{j}} = -\bar{\sigma}_p \nabla \phi \quad (26)$$

The charge conservation equation, Equation (23), then becomes:

$$\frac{\partial \bar{\rho}_s}{\partial t} = -\frac{\partial \bar{\rho}}{\partial t} = \nabla \cdot \bar{\mathbf{j}} \quad (27)$$

Combining Equation (24) and (25),

$$\nabla \cdot \bar{\mathbf{j}} = -\bar{\sigma}_p \nabla^2 \phi = -\nabla \cdot \bar{\mathbf{j}}_e = \bar{\sigma}_e \nabla^2 \phi_e \quad (28)$$

We need to employ a double layer capacitance model (C_D), such as DH model or GC model, to relate the charge densities to the potentials.

$$-\frac{\partial q_D}{\partial t} = C_D(\phi, \phi_e, c_i, \dots) \frac{\partial (\phi_e - \phi)}{\partial t} \quad (29)$$

Plugging in Equation (22) and (28) to the above Equation (29), we now have an equation governing the potentials in electrolyte and solid material.

$$\bar{\sigma}_e \nabla^2 \phi_e = -\bar{\sigma}_p \nabla^2 \phi = a_p C_D \frac{\partial (\phi_e - \phi)}{\partial t} \quad (30)$$

Equation (30) contains two governing partial differential equations for potential in electrolyte (ϕ_e) and potential for solid material (ϕ). To solve the governing equations, we need boundary conditions and initial conditions. The boundary conditions are shown in Figure 6. On the surface contacting with a separator, electron flux is not allowed and the normal component of potential gradient in solid material is zero. In similar manner, on the surface contacting with a current collector, ion flux is not allowed and the normal component of potential gradient in electrolyte is zero. The potential in electrolyte at the surface contacting a separator is set to be the zero reference value. And we set potential (V), may be a function of time, in conducting solid material at the surface contacting a current collector.

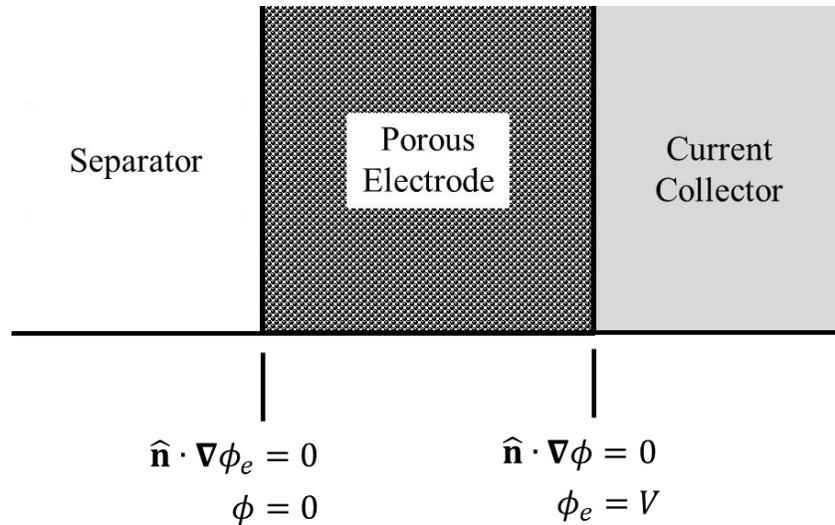


Figure 6. Boundary Conditions for Macroscopic Potentials

For initial conditions, let's start from charge-potential relationship. The charge density (q) is related to the capacitance and the potential difference with the following equation:

$$q(\mathbf{x}, t) = C(\phi_e - \phi) \quad (31)$$

We consider starting from the equilibrium voltage (open circuit voltage, V_o). This leads us to have a uniform initial charge density throughout the porous electrode. In general, this initial condition can be expressed using Equation (32) and (33).

$$q(\mathbf{x}, 0) = \text{uniform} = CV_o \quad (32)$$

$$\phi_e(\mathbf{x}, 0) - \phi(\mathbf{x}, 0) = V_o \quad (33)$$

The governing equations, Equation (30), could be solved for supercapacitor applications with the boundary conditions shown in Figure 6, and the initial condition, Equation (33). The specific solutions will be discussed in the next lecture, Lecture 36.

4. Transmission Line Model

In fact, the governing equations, Equation (30), could be equivalently obtained by using the *transmission line model*. This can be easily seen by manipulating expressions of conductivity and capacitance, using resistances and capacitance per length.

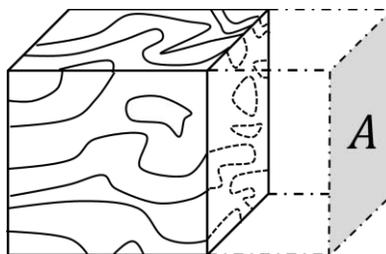


Figure 7. Macroscopic Cross-sectional Area

$$\bar{R}_e = \frac{1}{A\bar{\sigma}_e} \quad : \text{Resistance to Electron Current per Length}$$

$$\bar{R}_p = \frac{1}{A\bar{\sigma}_p} \quad : \text{Resistance to Ion Current per Length}$$

$$C = Aa_p C_D \quad : \text{Total Capacitance of Double Layer per Length}$$

With the newly defined parameters above, we can rearrange the governing equation, Equation (30), and show that this equation is equivalent to the transmission line model. By doing so, we can now understand which physical basis the circuit elements are based on.

$$\frac{1}{\bar{R}_e} \nabla^2 \phi_e = -\frac{1}{\bar{R}_p} \nabla^2 \phi = C \frac{\partial(\phi_e - \phi)}{\partial t} \quad (34)$$

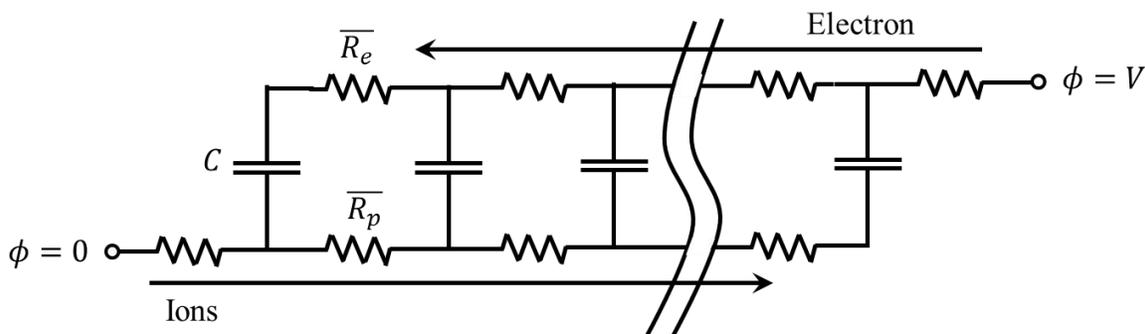


Figure 8. Transmission Line Equivalent Circuit Model

In next lecture, Lecture 36, we will solve the governing equations, Equation (30) or equivalently Equation (34), using the boundary conditions shown in Figure 6, and the initial condition, Equation (33), for supercapacitor applications.