VII. Porous Media

Lecture 36: Electrochemical Supercapacitors

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1. Transmission Line Model for Linear Response

Last time, we took the 'supercapacitor limit' of a general porous medium theory for thin double layers based on three assumptions:

1) The electrolyte concentration remains nearly constant during charging of the electrode, (ionic conductivity $\overline{\sigma}_P \approx const$ in pores).
2) Faradaic reactions are negligible or can be lumped together with double-layer capacitance as an additional "pseudocapacitance", as we will discuss in the next lecture.
3) Voltage applied is small enough ($V \leq \dfrac{kT}{e}$), that the total interfacial capacitance per area is roughly constant $C_D \approx const$.

Under these conditions, the model reduces to two elegant linear PDEs:

$$\overline{\sigma}_e \nabla^2 \phi_e = -\overline{\sigma}_P \nabla^2 \phi_P = a_P C_D \frac{\partial}{\partial t}(\phi_e - \phi_P)$$

where $\phi_e(x,t)$ is the electron potential, $\phi_P(x,t)$ is ion potential, $\overline{\sigma}_e$ is macroscopic electron conductivity in conducting phase, $\overline{\sigma}_P$ is macroscopic ionic conductivity in pores, a_P is double layer area per volume. Then we define resistance and capacitance as sketched in Fig .1. Electron resistance per length is $R_e = \dfrac{1}{A\overline{\sigma}_e}$, ion resistance per length $R_P = \dfrac{1}{A\overline{\sigma}_P}$, and double layer capacitance per length $C = Aa_P C_D$, where A is the macroscopic electrode area, and L is the electrode length, from separator to current collector.

Substituting these definitions above, we arrive at a pair of linear PDES

$$\frac{1}{R_e}\nabla^2 \phi_e = -\frac{1}{R_P}\nabla^2 \phi_P = C\frac{\partial}{\partial t}(\phi_e - \phi_P)$$

which can be interpreted as an *RC transmission line*, as shown in Fig .2.
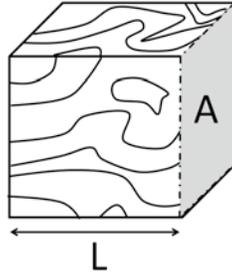
Fig. 1 Geometric parameters of the porous electrode
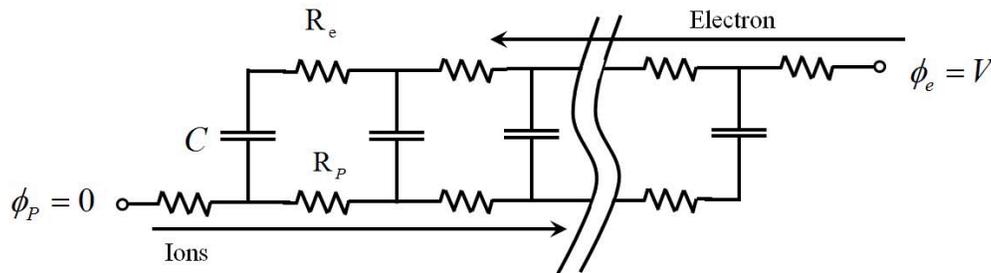
Fig. 2 Transmission Line Equivalent Circuit Model

Once these PDEs are solved for the potentials of ions and electrons, the charge density (per length) stored in the double layer capacitors is given by $q_S(x,t) = C(\phi_e(x,t) - \phi_P(x,t))$

Boundary conditions for these two PDEs are as follows: We set reference pore potential at the separator $\phi_P(0,t) = 0$, ions carry current from separator, thus $\dfrac{1}{R_P}\dfrac{\partial \phi_P}{\partial x}(0,t) = I(t)$. Similarly, at the back side of the electrode (current collector) $\phi_e(L,t) = V(t)$, where $V(t)$ is the half of the total voltage if symmetric electrodes are used for the whole cell. At the current collector, the current is totally carried by electrons, therefore $\dfrac{1}{R_e}\dfrac{\partial \phi_e}{\partial x}(L,t) = I(t)$.

Initial condition: suppose electrode is in equilibrium with I=0, and charge density is constant $q_S = const = C(\phi_e - \phi_P) = CV_0$.

2. Analysis of the Model

Next we go back to the 2 PDEs to do some change of variables, and solve for an example of the supercapacitor which is suddenly applied to a voltage V (i.e., $\phi_e(x,0) = V_0 \Rightarrow \phi_e(L,t) = V$). Although the PDEs look simple (two diffusion-like equations), the boundary conditions are quite nontrivial and couple opposite sides of the electrodes.

1.1 Total current (subtracting the 2 PDEs)

Subtract these 2 PDEs,

$$\frac{1}{R_e}\nabla^2\phi_e = -\frac{1}{R_P}\nabla^2\phi_P = C\frac{\partial}{\partial t}(\phi_e - \phi_P)$$

We will have $\dfrac{\partial^2}{\partial x^2}\left(\dfrac{\phi_e}{R_e} + \dfrac{\phi_P}{R_P}\right) = 0$, integrate once we get $\dfrac{\partial}{\partial x}\left(\dfrac{\phi_e}{R_e} + \dfrac{\phi_P}{R_P}\right) = const$. Actually, this constant is the total current, which is carried by both ions and electrons inside the electrode.

$$\frac{\partial}{\partial x}\left(\frac{\phi_e}{R_e} + \frac{\phi_P}{R_P}\right) = I(t)$$

Using boundary conditions to integrate again, we will get the following expression which is valid for all time and space.

$$\frac{\phi_e}{R_e} + \frac{\phi_P}{R_P} = I(t)x + K(t)$$

$$\text{Where } K(t) = \frac{\phi_e(0,t)}{R_e}$$

Using boundary condition we will get:

$$\frac{V}{Re} + \frac{\phi_P(L,t)}{R_P} = I(t)L + K(t)$$

$$\frac{\phi_P(L,t)}{R_P} = I(t)L + \frac{\phi_e(0,t) - V}{R_e}$$

1.2 Charge density (adding the 2 PDEs)

Adding the original 2 PDEs, we will get: $(R_e + R_P)C\dfrac{\partial}{\partial t}(\phi_e - \phi_P) = \dfrac{\partial^2}{\partial x^2}(\phi_e - \phi_P)$.

Charge stored in the double layer is also a function of space and time as $q_S(x,t) = C(\phi_e - \phi_P)$, so the above equation can be equivalently written as

$$(R_e + R_P)C\frac{\partial q_S}{\partial t} = \frac{\partial^2 q_S}{\partial x^2}$$

Since we know after suddenly applying the voltage V to $\phi_e(L,t)$, $q_S(x,t)$ has not started to change and needs some time to diffuse through the transmission line, we still have $q_S(x,0) = CV_0$, therefore from $q_S(x,t) = C(\phi_e(x,t) - \phi_P(x,t)) = CV_0$ we get

$$\phi_P(x,0) = \phi_e(x,0) - V_0$$

Thus, $\dfrac{\partial \phi_e}{\partial x}(t=0) = \dfrac{\partial \phi_P}{\partial x}(t=0)$. Recall $\dfrac{\partial}{\partial x}\left(\dfrac{\phi_e}{R_e} + \dfrac{\phi_P}{R_P}\right) = I(t)$, finally we will have

$$\frac{\partial \phi_e}{\partial x}(t=0) = \frac{\partial \phi_P}{\partial x}(t=0) = \frac{I(0)}{\dfrac{1}{R_e} + \dfrac{1}{R_P}}$$

So the initial conditions are:

$$\phi_P(x,0) = \frac{I(0)}{\dfrac{1}{R_e} + \dfrac{1}{R_P}} x$$

$$\phi_e(x,0) = \frac{I(0)}{\dfrac{1}{R_e} + \dfrac{1}{R_P}} x + V_0$$

The linear initial profiles of the two potentials correspond to the *initially uniform electric field* in both phases, due to the sudden imposition of a voltage across the electrode, from the separator to the current collector.

And $\phi_e(L,0) = V$ implies $V = \dfrac{I(0)}{\dfrac{1}{R_e} + \dfrac{1}{R_P}} L + V_0$, or equivalently $I(0) = \dfrac{V - V_0}{L}\left(\dfrac{1}{R_e} + \dfrac{1}{R_P}\right)$. This is the initial total current induced by applying the voltage V.

1.3 Numerical simulation results

Following are numerical simulation results when we set initial, equilibrium voltage V_0 to zero and apply a constant voltage V starting at t=0.

From Fig.3 we see that pore potential $\phi_P(x,t)$ and ion potential $\phi_e(x,t)$ both change from their linear initial conditions to the final uniform profile those are consistent with the boundary conditions. Charge stored in the double layer gradually increases with time, until it is fully charged. The charge profile is symmetric in space when $R_e = R_p$(Fig.4). And Fig. 5 shows consistency with the expression we got before ($\dfrac{\phi_e}{R_e} + \dfrac{\phi_P}{R_P} = I(t)x + K(t)$), that is, the weighted summation of two potentials are always linear in space.
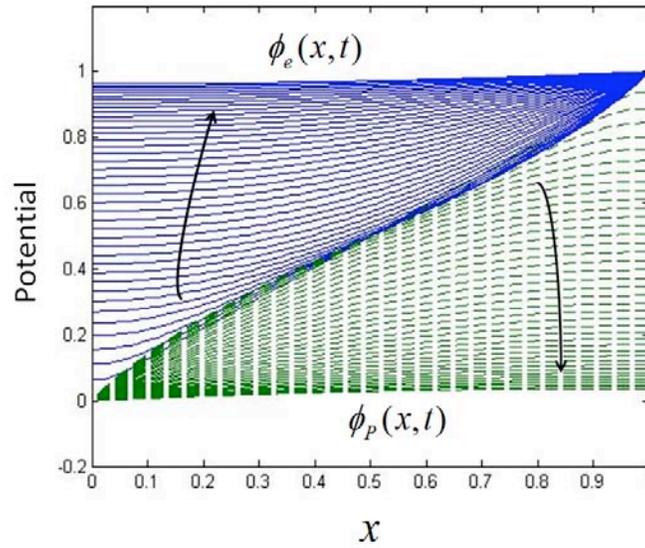
Fig. 3 Numerical simulation of electron potential and pore potential development as time progresses. ($V = 1, V_0 = 0, L = 1, \mathrm{R}_e = R_p$ are used for this plot)
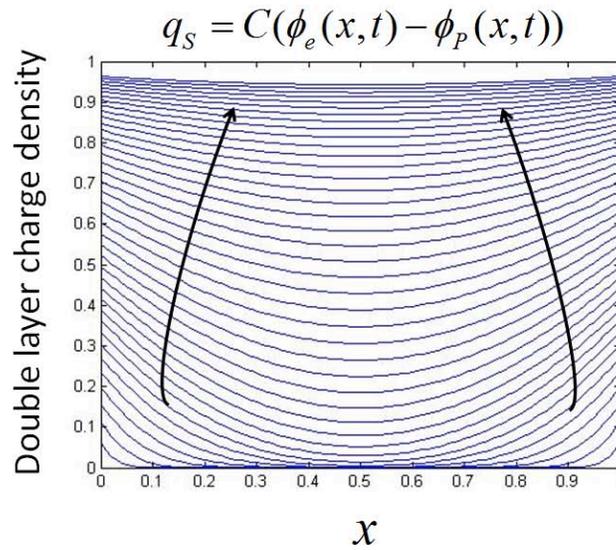
Fig. 4 Numerical simulation of double layer charge density as time progresses. ($V = 1, V_0 = 0, L = 1, \mathrm{R}_e = R_p, C = 1$ are used for this plot)

$$\phi_e(x,t) + \phi_P(x,t)$$
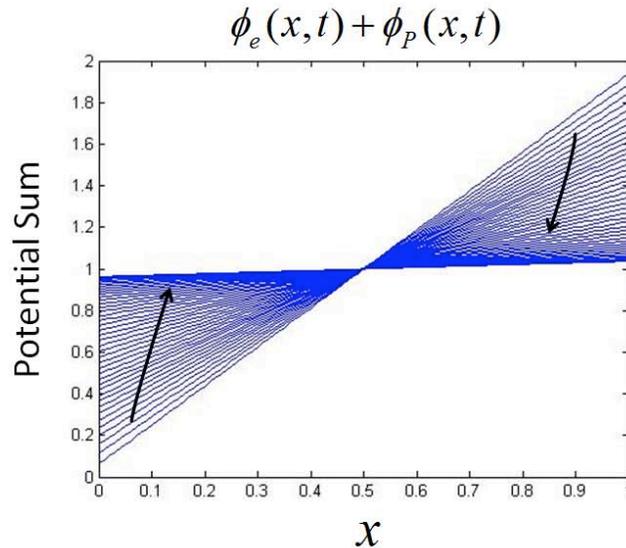
Fig. 5 Numerical time evolution of sum of the electron and ion potentials, whose gradient is proportional to the total current. ($V = 1, V_0 = 0, L = 1, \mathrm{R}_e = R_p$ are used for this plot)

2. Voltage Sweep

Now we consider cyclic voltammetry, where a periodic linear voltage sweep is applied to the system ($V(t) = St$), with τ_S to be the voltage scan time scale.
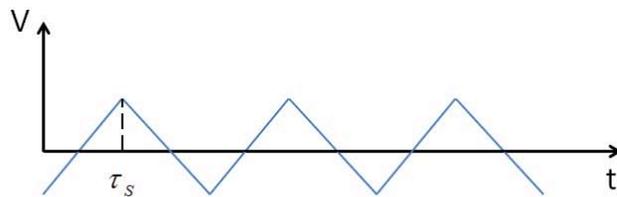
Fig. 6 Voltage applied for a cyclic voltammetry

2.1 Slow sweep

If the voltage scans slowly, there will be no transient effects ($\tau_S \gg L^2 / D_e, L^2 / D_P$), then $q(x,t) \approx const = L \cdot CV(t) = L \cdot C \cdot St$ (where L is the length of the electrode, and C is double layer capacitance per length). In this case, current which reflects capacitance is simply a constant, and the cyclic voltammetry will be rectangles (Fig. 7).

$$I = \frac{dq}{dt} = LC \cdot S = const$$
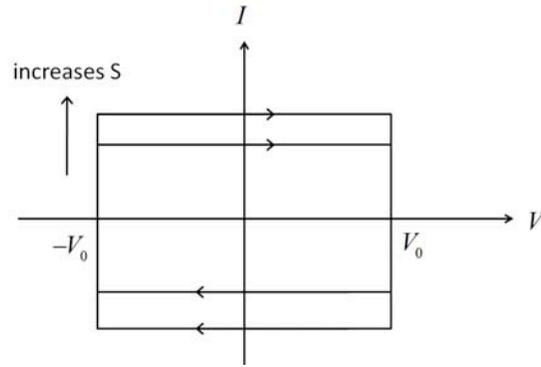
Fig. 7 Cyclic voltammetry in slowly scanned case when differential capacitance is a constant.

When the scan rate S increases, the CV window becomes a larger rectangle with large height.

If the double layer capacitance is a function of voltage applied rather than a constant, $C_{tot}(V) = L \cdot A \cdot a_P C_D(V)$, then the current reflects the $C_{tot}(V)$ information:

$$I = C_{tot}(V)\frac{dV}{dt} = C_{tot}(V) \cdot S$$

For example, in GCS model we have $\dfrac{1}{C_{DL}} = \dfrac{1}{C_D} + \dfrac{1}{C_S}$ where $C_D = L \cdot A \cdot a_P \dfrac{\varepsilon}{\lambda_D}\cosh(\dfrac{zeV}{2kT})$ and

$C_S = L \cdot A \cdot a_P \dfrac{\varepsilon_S}{h_S}$.
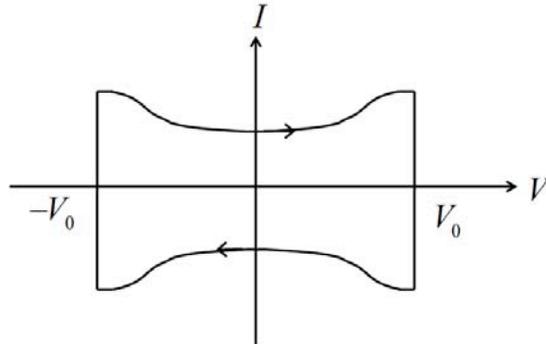
Fig. 8 Cyclic voltammetry in slowly scanned case when double layer differential capacitance follows GCS model.

2.2 Fast sweep

If the voltage scans fast, pore ion dynamics will typically be slower than the relatively fast electron relaxation in conducting phase ($L^2 / D_P \gg \tau_S \gg L^2 / D_e$), and we can safely assume $\phi_e(x,t) = V$. Then the governing equation becomes:

$$D_P\nabla^2\phi_P = \frac{\partial}{\partial t}(\phi_P - V) = \frac{\partial\phi_P}{\partial t} - S \quad where \ D_P = \frac{1}{R_P C}$$

$$BC: \phi_P(0,t) = 0 \qquad IC: \phi_P(x0) = 0$$

This is simply a diffusion problem, with the solution shown in Fig. 9.
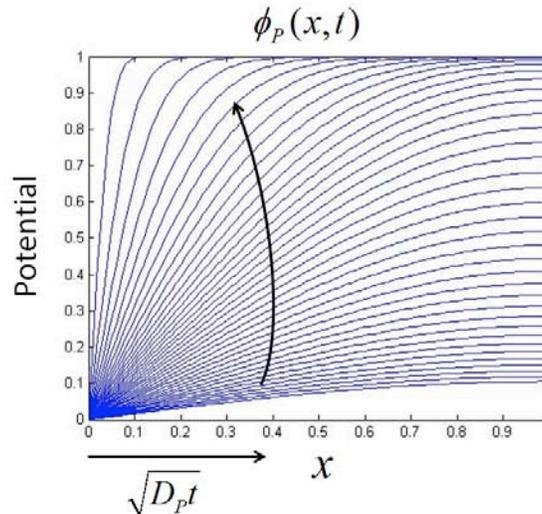
Fig. 9 Pore potential ϕ_P evolution when electrons quickly relaxed in the conducting phase. We can also do a scaling analysis for the current.

$$I = \frac{1}{R_P}\frac{\partial\phi_P}{\partial x}(0,t) \propto \frac{1}{R_P}\frac{V}{\sqrt{D_P t}}$$

$$I \propto \frac{1}{R_P}\frac{V}{\sqrt{\dfrac{V}{S\cdot R_P C}}} \propto \sqrt{\frac{VSC}{R_P}} \propto S\sqrt{\frac{tC}{R_P}}$$

We can easily see that for $t << {L^2}/{D_P} = L^2 R_P C$, voltage $V << L^2 R_P CS$, which is transient effects in the CV scan curves Fig. 10).

If the voltage sweeps fast and the double layer differential capacitance follows GCS model, the cyclic voltammetry will be a combination of the transient effects with the differential double layer capacitance shape (Fig. 11). In the CV curve, there is a peak after the transient region which might be easily treated as a Faradaic reaction peak, but actually, it can just come from the differential double layer capacitance and the transient effect. Thus, it is really hard to identify peaks in complicated cases, especially for pseudocapacitors when double layer capacitance and Faradaic capacitance coexist.
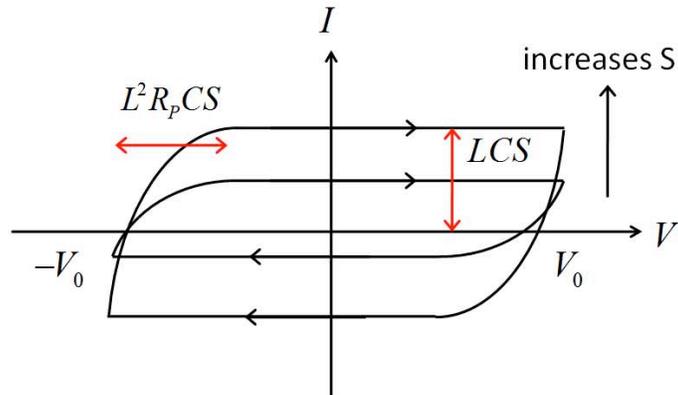
Fig. 10 Cyclic voltammetry in fast scanned case when differential capacitance is a constant.
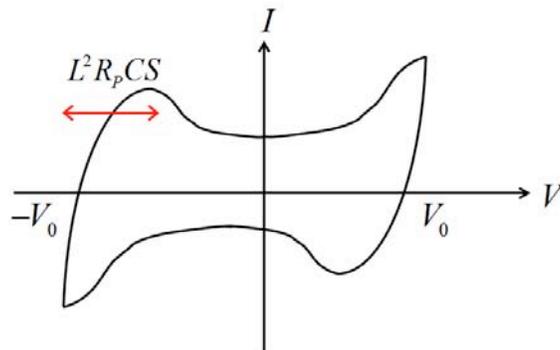
Fig. 11 Cyclic voltammetry in fast scanned case when double layer
differential capacitance follows GCS model.

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