Homogeneous Reaction Diffusion

Notes by MIT Student (and MZB)

This lecture will focus on the homogeneous reaction diffusion regime in which diffusional transport is coupled with homogeneous reactions. Before this lecture, our focus has been on trying to understand transport and reactions separately. In this lecture we will examine them together. The 1-D governing equation for such a phenomenon is given by:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + k(C_0 - C) \tag{1}$$

The rightmost term in the above equation is the contribution of the homogeneous reaction which was not considered before this lecture. Some examples where this equation is applicable follow:

1. Electrocatalysis: This is one of the direct examples of the homogeneous reaction diffusion regime. This involves multiple steps, *i.e.* diffusion, adsorption and a possible charge transfer at the surface ($x = 0$). As shown in the schematic of Fig(1), species will adsorb on the catalyst surface, then diffuse along the surface to the right/left surfaces where a charge transfer reaction can occur. The center of such system has a symmetry boundary condition. The edges are described by the reaction which relate the potential and current to the concentration.
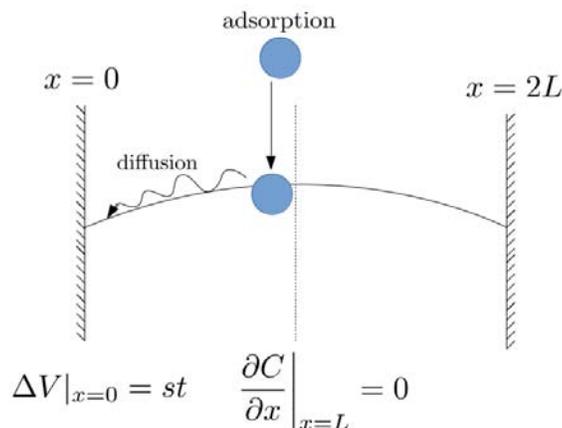

Figure 1: Schematic of electrocatalysis mechanism involving reaction diffusion

2. Pseudocapacitor porous electrode: In the approximation of a linear RC transmission line (introduced earlier in the class), this system follows the exact same formulation

above for a homogeneous reaction diffusion system. In a standard supercapacitor porous electrode, we have already shown that the interfacial double layers on the metallic surface stored charge electrostatically and provide an effective capacitance per unit length (C_P) in the equivalent circuit. There is also pore resistance for ion transport per unit length (R_P). In the case of a "pseudocapacitor" there is also the possibility of a Faradaic reaction at the surface (e.g. due to adsorbed redox molecules, or battery nanoparticles), which provides additional "pseudocapacitance" that increases C_P via electrochemical (as opposed to electrostatic) charge storage as well as a parallel interfacial resistance (per length per area) R_i for charge transfer reactions (e.g. from the linearized Butler-Volmer equation). The equivalent circuit of such a system as shown in Fig(2).
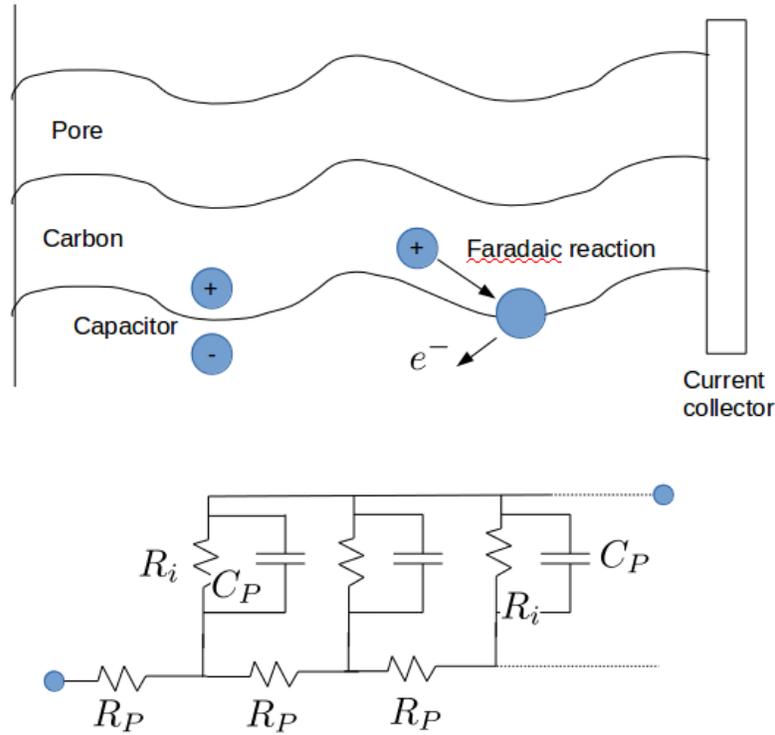

Figure 2: Schematic of pseudocapacitor electrode and its equivalent circuit

We also derived the following governing equation:

$$C_P \frac{\partial \phi}{\partial t} = \frac{1}{R_p} \frac{\partial^2 \phi}{\partial x^2} - \frac{\phi}{R_i} \tag{2}$$

If we compare Equation (2) with Equation (1), it is clear that they have the same form, such that we can easily define equivalent concentration, diffusivity and reaction rate constants.

3. Semiconductors: This is another example for which we get a similar governing equation because holes and electrons combine with each other, coupling diffusion and reactions.

The rest of the lecture will be divided into two parts: Linear sweep voltammetry and Impendence problem.

1 Linear Sweep Voltammetry

As mentioned before, the governing equation for the current system is as follows:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + k(C_0 - C)$$

wherein C_0 is the initial concentration and C is the current concentration on ions. Because the reaction is electrochemical, we can relate the change in potential (ΔV) to concentration using the Nernst equation as follows:

$$\Delta V = \frac{k_B T}{ne} \ln\left(\frac{C}{C_0}\right) = \frac{k_B T}{ne} \ln\left(\frac{C_0 + \Delta C}{C_0}\right) \tag{3}$$

Now, if we assume small changes in voltage and concentration, the log term can be linearized and we obtain:

$$\Delta V = \frac{k_B T}{ne}\frac{\Delta C}{C_0} \tag{4}$$

For linear sweep voltammetry, we know that $\Delta V = st$. The boundary condition for solving the diffusion reaction equations are as follows:

$$st = \frac{k_B T}{ne}\frac{\Delta C}{C_0}\bigg|_{x=0} \tag{5}$$

$$\frac{\partial C}{\partial x}\bigg|_{x=L} = 0 \tag{6}$$

The initial condition for the system will be as follows:

$$C|_{t=0} = C_0 \tag{7}$$

The trick to solve this equation is to transform the variable from C to its derivative u because in that case we will be able to use Equation (5) as a simpler boundary condition. Hence, differenting Equation (1) w.r.t. time and defining $u = \dfrac{\partial C}{\partial t}$, we get:

$$\frac{\partial u}{\partial t} = D\frac{\partial u}{\partial x^2} - ku \tag{8}$$

The boundary conditions and initial will change for this equation as follows:

$$\frac{\partial u}{\partial t}\bigg|_{x=0} = \frac{nesC_0}{k_B T} \tag{9}$$

$$\frac{\partial u}{\partial x}\bigg|_{x=L} = 0 \tag{10}$$

$$u|_{t=0} = 0 \tag{11}$$

To solve the equation for earlier times, we can assume that $t \ll \dfrac{1}{k}$, which means that system hasn't had enough time to "feel" the reactions. This can also be understood in terms of length scales, i.e. the diffusion length scale which scales as $\sqrt{Dt}$ is much smaller than the steady state length scale of $\sqrt{\dfrac{D}{k}}$. This has been shown in the Figure(3).
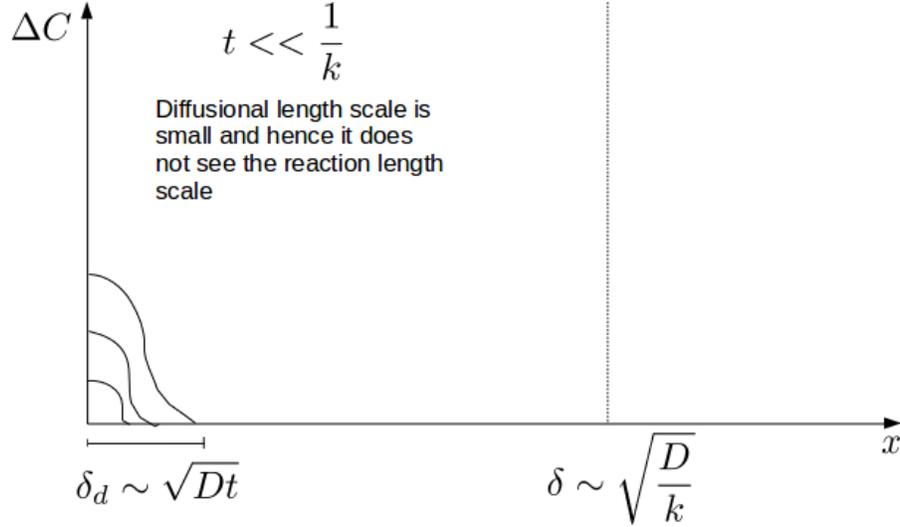

Figure 3: Schematic of concentration profiles for early time

This also implies that the boundary condition mentioned in the Equation (10) will change to following:

$$\left.\frac{\partial u}{\partial x}\right|_{x=\infty} = 0 \tag{12}$$

Hence, now we can easily solve Equation (8) with Equation (9,10,12) to get the following result:

$$u = \frac{nesC_0}{k_B T} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{13}$$

Calculating the exact solution for C from Equation (13) by integrating w.r.t. x was omitted from this lecture and covered in the solution of HW-5. However, we can still use scaling analysis to get a good approximate solution and relate current and voltage. From Equation (13) it is clear that we can safely assume:

$$\Delta C = \frac{nesC_0 t}{k_B T} \operatorname{f}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{14}$$

We know that:

$$I = -neAD \left.\frac{\partial C}{\partial x}\right|_{x=0} \tag{15}$$

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Hence, differentiating Equation (14) w.r.t. x and using Equation (15), we can arrive at:

$$I = \text{Const.}\frac{(ne)^2 AC_0 s}{k_B T}\sqrt{Dt} = \text{Const.}\frac{(ne)^2 AC_0 s}{k_B T}\sqrt{D\frac{\Delta V}{s}} \qquad (16)$$

To find the value of constant, we would have to go through the math, but we find that scaling analysis gives a very good method to understand the relationship between current and voltage for linear sweep voltammetry in reaction diffusion system. However, these results only apply for early times. In order to solve for later times, we make a new approximation. We assume most concentration gradients will be confined in a boundary layer region and the concentration gradient at $x = 0$ can be calculated by a linear approximation as shown in Fig(4). The boundary layer thickness is that set by the competition between diffusion and bulk reactions which were neglected in the preceding analysis for early time.
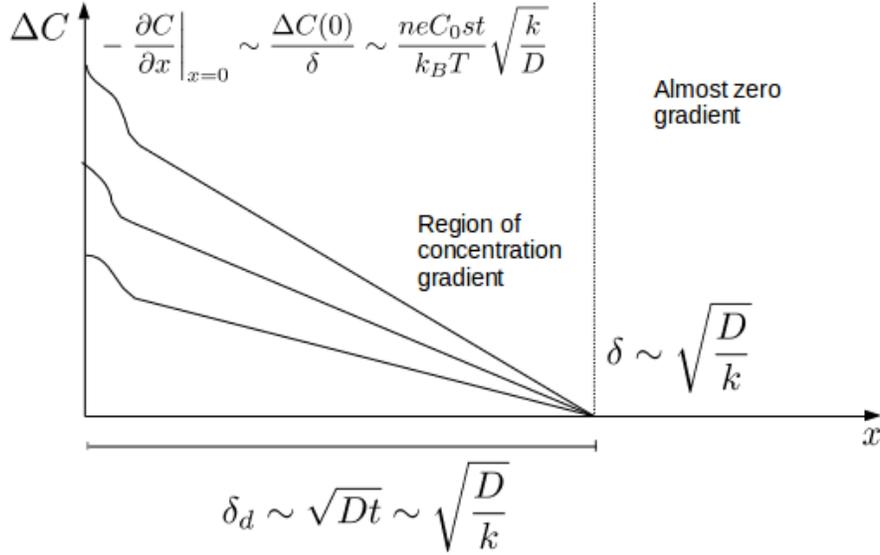

Figure 4: Schematic of concentration profiles for late time

Hence, as earlier, using equation (15), we can calculate I as follows:

$$I = \text{Const.}\frac{(ne)^2 ADC_0 st}{k_B T}\sqrt{\frac{k}{D}} = \text{Const.}\frac{(ne)^2 ADC_0 \Delta V}{k_B T}\sqrt{\frac{k}{D}} \qquad (17)$$

We can now plot equation (16) and (17) together to get a response for I as a function of ΔV. The response has been shown in Fig(5).

The response goes as square root initially and linear at later times. The dotted lines show the response without reaction.
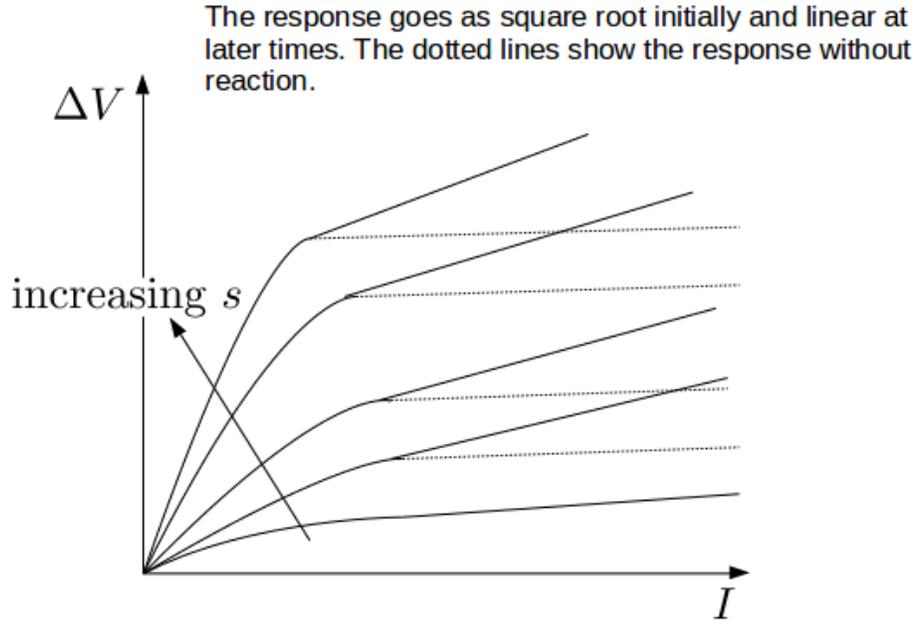
Figure 5: Response of I to linear sweep voltammerty i.e. $\Delta V = st$

2 Impedance Problem

This problem is very similar to the solution we discussed in few lectures back for Warburg impedance. This solution was founded by Greisher. To calculate the impedance, we will substitute, $\Delta C(x,t) = \mathrm{Re}(\Delta C^* e^{i\omega t})$ in Equation (1). Doing that we get the following result:

$$i\omega \Delta C^* = D\Delta \frac{\partial^2 C^*}{\partial x^2} - k\Delta C^* \tag{18}$$

which can be rearranged:

$$(k + i\omega)\Delta C^* = D\Delta \frac{\partial^2 C^*}{\partial x^2} \tag{19}$$

We can see that Equation (19) is very similar to Warburg's impedance equation except $i\omega$ has been replaced by $k + i\omega$. Therefore we can use the previous solution for a semi-finite system:

$$\frac{Z(ne)^2 AC_0\sqrt{D}}{k_B T} = \frac{1}{\sqrt{k + i\omega}} \tag{20}$$

We can make these equations dimensionless by defining $\widetilde{k} = \dfrac{kL^2}{D}, \widetilde{\omega} = \dfrac{\omega L^2}{D}, \widetilde{Z} = \dfrac{Z(ne)^2 ADC_0}{k_B TL}$. In addition, we had previously arrived at the solution for a finite system. Using the nondimensional parameters:

1. Semi-infinite system: $\widetilde{Z} = \dfrac{1}{\sqrt{\widetilde{k} + i\widetilde{\omega}}}$

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Table 1: Limiting cases of finite-length reaciton-diffusion (Gerisher) impedance

System	Limits	$\widetilde{Z}$	Discussion
Finite	$\widetilde{k} \gg 1$	$\dfrac{1}{\sqrt{\widetilde{k} + i\widetilde{\omega}}}$	Same as semi-infinite system at $\widetilde{k} \gg 1$ because $\delta \sim \sqrt{\dfrac{D}{k}} \ll L$
Finite	$\widetilde{k} \ll 1, \widetilde{\omega} \gg k$	$\dfrac{\coth\sqrt{i\widetilde{\omega}}}{\sqrt{i\widetilde{\omega}}}$	Converts to a finite-length Warburg element as reaction is so slow that $\delta \sim \sqrt{\dfrac{D}{k}} \gg L$
Finite	$\widetilde{k} \ll 1, \widetilde{\omega} \ll k$	$\dfrac{\coth\sqrt{\widetilde{k}}}{\sqrt{\widetilde{k}}}$	Relatively flat concentration profile and hence constant resistance (real impedance)

2. Finite system: $\widetilde{Z} = \dfrac{\coth\sqrt{\widetilde{k} + i\widetilde{\omega}}}{\sqrt{\widetilde{k} + i\widetilde{\omega}}}$

The above relations have been looked into more details in extreme cases in Table(1) and the Nyquist plot has been shown in Fig(6).
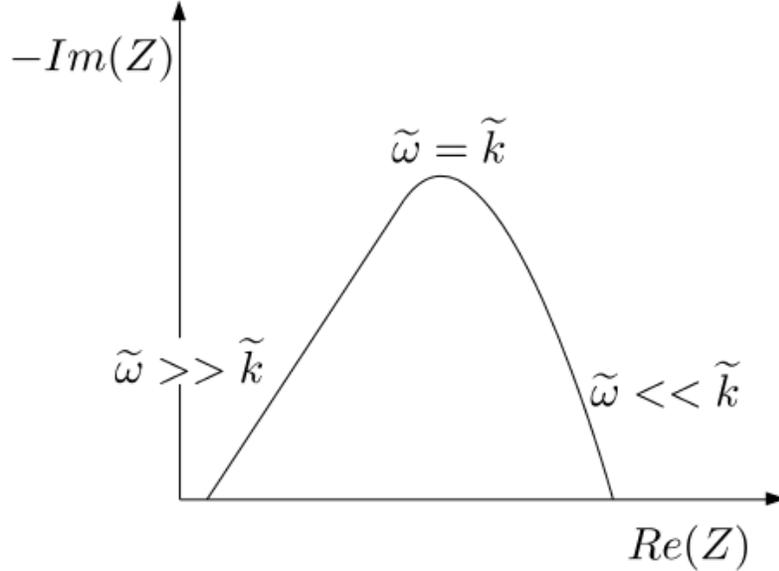

Figure 6: Nyquist plot for the frequency response

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