Lecture 29: Forced Convection II

Notes by MIT Student (and MZB)

As discussed in the previous lecture, the magnitude of limiting current can be increased by imposing convective transport of reactant in a porous media. This is because $I_{lim} \sim \frac{neAD\bar{c}}{L}$ (L is the diffusion length in a porous electrode) and in forced convection, the length scale for diffusion is δ (boundary layer thickness) which is typically much smaller than L. Last lecture, we also examined the transport of reactant carried into the system by a convective fluid stream and obtained a scaling for the boundary layer thickness in two cases: (i) Plug flow of fluid through inert porous media (Figure 1) (ii) Poiseuille flow with Lévêque Approximation (Figure 2). In both cases, reaction takes place only at the interface at y=0.

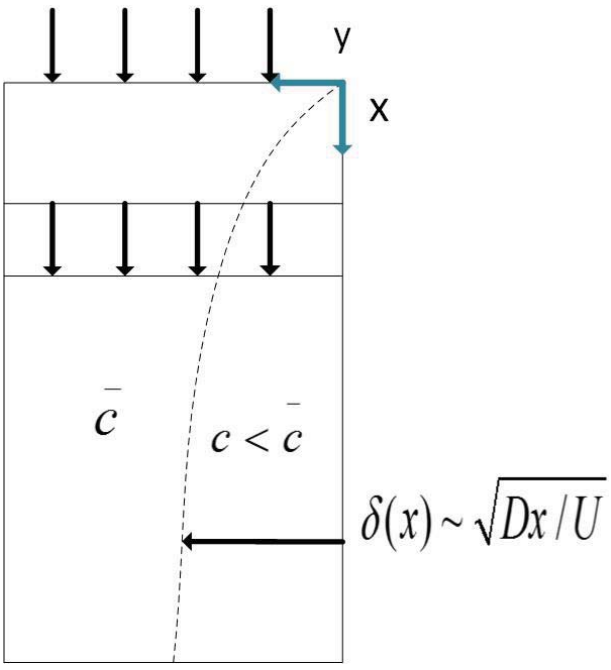

Figure 1: Plug flow through inert porous media

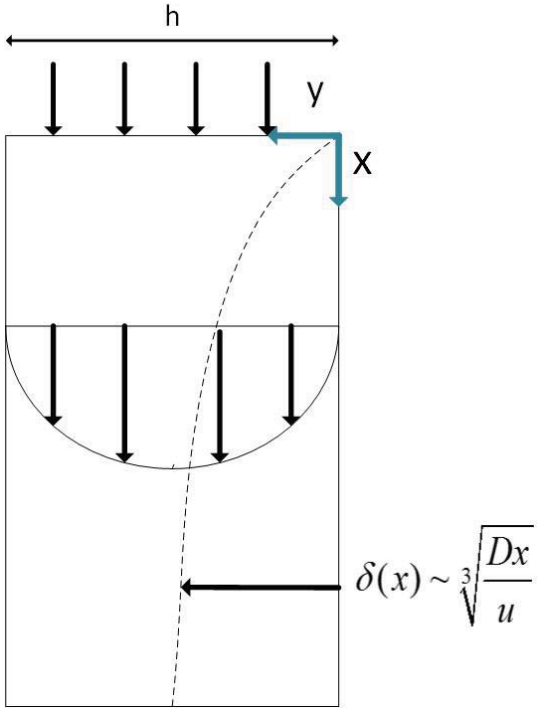

Figure 2: Poiseuille flow with Lévêque Approximation

Membrane-Electrode Assemblies:

Figures 3 and 4 show the side and top views of a membrane-electrode assembly. The reactant gas is forced into inlet channels and drawn out of separate outlet channels and can pass between the two by travelling though the porous electrode. In this way, the reactant gas moves past the catalyst layer and reacts in the presence of the catalyst.

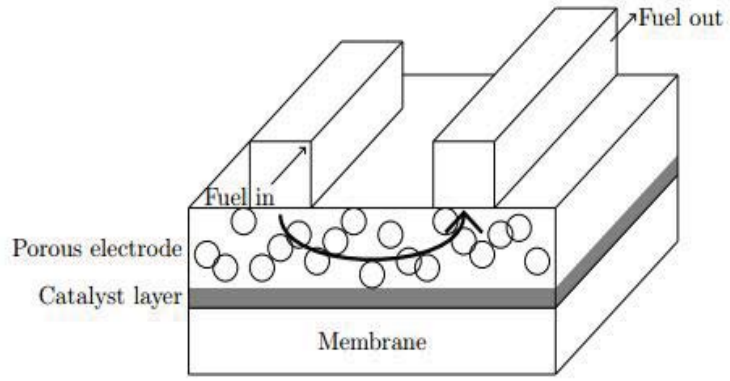

Figure 3: Membrane-electrode assembly

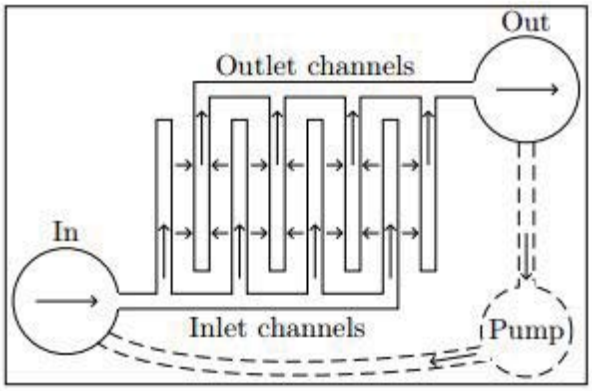

Figure 4: Interdigitated flow channels

General Analysis:

In a porous medium, the flow velocity is related to the pressure gradient by Darcy's law:

$$u = -K\nabla P \tag{1}$$

where K denotes permeability. Using the continuity equation for an incompressible fluid gives:

$$\nabla . u = 0 \tag{2}$$

Combining Eq. 1 and 2, we get:

$$\nabla^2 p = 0 \tag{3}$$

At steady state with no homogenous reaction occurring, the governing equation for transport of reactant (assuming constant diffusivity) is given by:

$$u . \nabla c = D\nabla^2 c \tag{4}$$

Combining Eq. 1 and Eq. 4, we get:

$$-K\nabla P . \nabla c = D\nabla^2 c \tag{5}$$

Different Boundary Conditions are as follows:

- Both the pressure as well as concentration are known at the inlet and outlet. Pressure is P_{in} at the inlet and P_{out} at the outlet. Assume both at the inlet and outlet, $c = \bar{c}$.
- There cannot be any velocity through the walls (no penetration boundary condition), so $\hat{n} . \nabla P = 0$. Also, using no flux boundary condition at the walls, we get: $\hat{n} . \nabla c = 0$ (This is because there is no convective velocity normal to the wall).
- At the membrane surface, $\hat{n} . \nabla P = 0$. However, reaction occurs at the membrane electrode interface. So, $\hat{n} . D\nabla c = R$ where R is the rate of reaction. At limiting current condition, c=0 can be used as the boundary condition.

In those situations where the differential equations become difficult to solve because of complicated geometry, they can be solved using a technique called conformal mapping[1]. This method can be used to map a complex geometry to a simple geometry where the differential equations can be solved easily. Usually, this involves writing the coordinates of a point in the new system as an analytical function of the coordinates of its equivalent point in the old system. The

problem is then solved in the simple geometry. By using an inverse map, we can get back the solution to our original problem. The procedure is demonstrated in Figure 5:

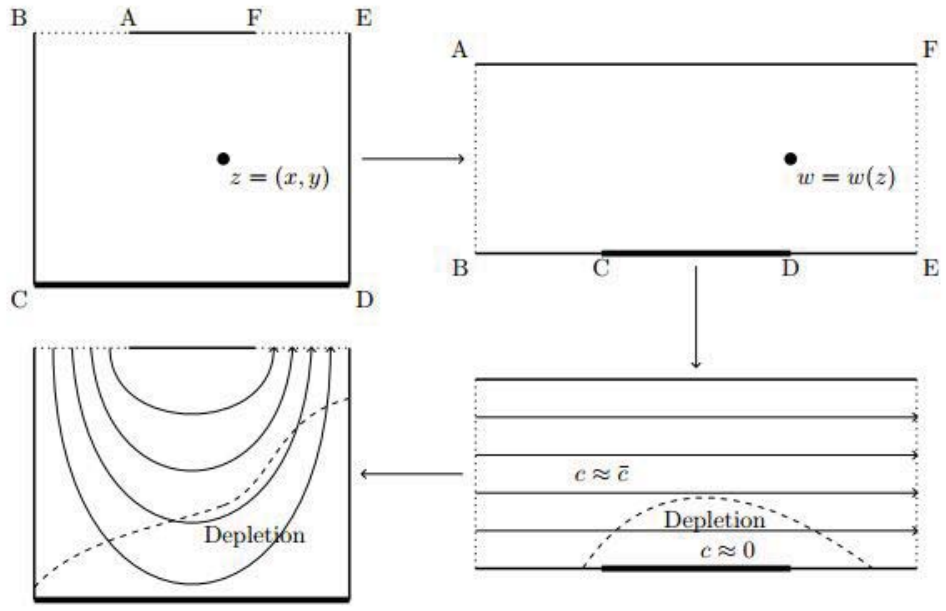

Figure 5: Solving the convection-diffusion problem using conformal mapping

Fuel Efficiency vs. Power Density:

Last lecture, we found using scaling analysis arguments that the boundary layer thickness scales as: $\delta \sim \sqrt{\frac{Dx}{U}}$. Hence increasing the fluid velocity would decrease the boundary layer thickness resulting in an increase in the magnitude of the limiting current. In this section we will use scaling analysis to obtain order of magnitude estimate of the limiting current and the proportion of fuel utilized.

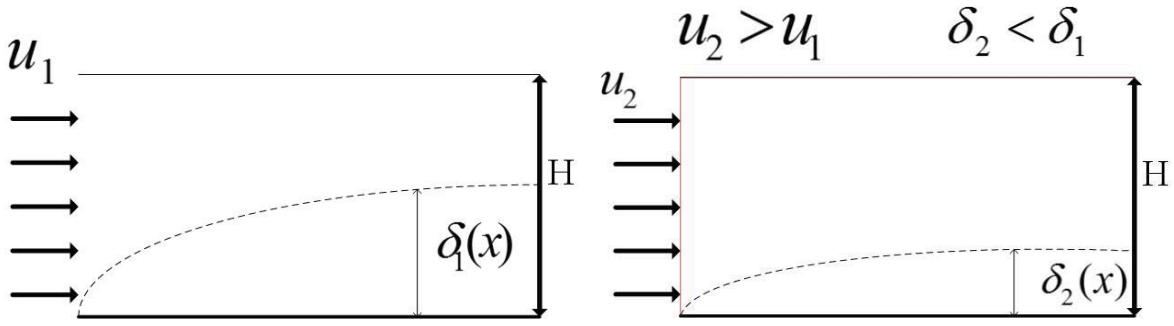

Figure 6: Convective flow of fluid over a reacting surface

We consider the case of plug flow of fluid over a reacting surface. In last lecture, we obtained an order of magnitude estimate of the boundary layer thickness given by:

$$\delta \sim \sqrt{\frac{Dx}{u}} \tag{6}$$

Consider H to be the height of the flowing fluid. Then we can define dimensionless variables $\tilde{\delta}$ and $\tilde{x}$ by dividing δ and x by H. We obtain the relation:

$$\tilde{\delta} \sim \sqrt{\frac{\tilde{x}}{Pe}} \tag{7}$$

where Pe is the Peclet number which signifies the ratio of convective transport rate to diffusive transport rate and is defined as:

$$Pe = \frac{uH}{D} \tag{8}$$

We are interested in getting a scaling for the limiting current. In the case of limiting current, concentration at the reacting surface, $c = 0$.

Flux density, F at the reacting surface:

$$F = D\frac{\partial c}{\partial y}_{(y=0)} \sim D\frac{\bar{c}}{\delta} \tag{9}$$

$\bar{c}$ is the bulk concentration outside the concentration boundary layer.

The limiting current is the flux density integrated over the area of reacting surface, multiplied by the charged transferred in electrode reaction. If we consider a reacting surface with width W and length L, the limiting current is given by:

$$I_{lim} \sim neW\bar{c}\int_0^L \frac{dx}{\delta} \tag{10}$$

Substituting the scaling for δ in (10) from (6), we obtain:

$$I_{lim} \sim neW\bar{c}\sqrt{uDL} \tag{11}$$

If we didn't have convective flow, then the limiting current in the absence of flow (only diffusion) would be given by the relation: $I_{lim,only\ diffusion} = neLW\bar{c}D/H$

We can obtain dimensionless limiting current by dividing the limiting current in the presence of flow by the limiting current in the absence of flow (only diffusion).

$$\tilde{I}_{lim} \sim \sqrt{Pe}\sqrt{\frac{H}{L}} \tag{12}$$

From the above scaling for the dimensionless limiting current, we find that it is possible to enhance the limiting current by increasing the flow velocity. From previous lecture, we know $P_{max} \sim I_{lim} V_o$

So, faster flows generate larger power density due to increased I_{lim}.

Next, we try to find a scaling for the proportion of fuel utilized. We define γ_F as the ratio of fuel consumed to fuel input.

$$\gamma_F = \frac{I_{lim}}{neuHW\bar{c}} \tag{13}$$

$$\gamma_F \sim \frac{neW\bar{c}\sqrt{uDL}}{neuHW\bar{c}} \sim \frac{1}{\sqrt{Pe\ \frac{H}{L}}} \sim \frac{1}{\tilde{I}_{lim}} \tag{14}$$

From the above scaling for the proportion of fuel utilized, we find that there is a tradeoff. Even though it is possible to increase the limiting current by increasing the fluid velocity, this results in a corresponding decrease in the fuel utilization. This means that though I_{lim} can be increased by increasing fluid velocity, less of the fuel is able to diffuse to the reacting surface by the time it reaches the outlet at x=L.

To summarize, increasing the fluid velocity leads to:

- Decrease in boundary layer thickness.
- Increase in the magnitude of limiting current.
- Larger power density because of increased limiting current.
- Less concentration polarization voltage losses because of increase in I_{lim} (Please refer to Figure 7 below).
- Decrease in fuel utilization.

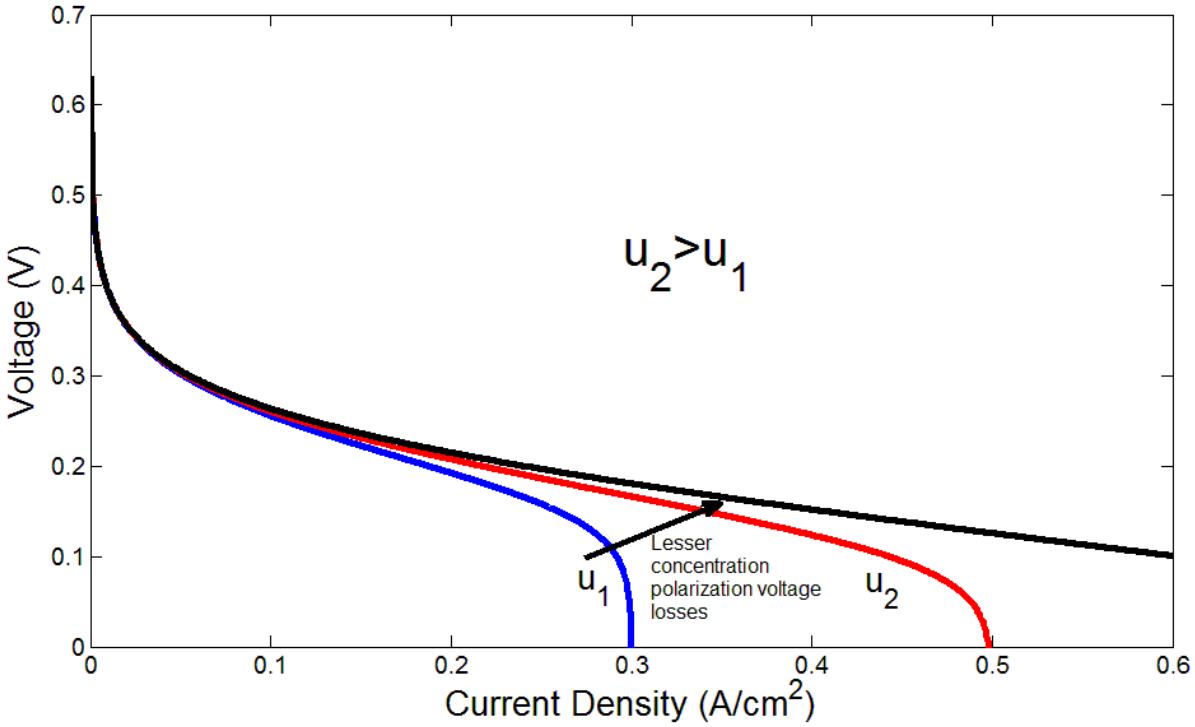

Figure 7: Plot showing decrease in concentration polarization voltage losses with increase in fluid velocity

Hydrogen Bromine Laminar Flow Battery (HBLFB)

Hydrogen bromine laminar flow battery[2] (HBLFB) is an example of a membraneless electrochemical cell. The need for a membrane is eliminated in such systems by relying on laminar flow and slow molecular diffusion of reactants for separation of the two half-reactions.

The two half-cell reactions in HBLFB are the oxidation of gaseous hydrogen at the anode and reduction of aqueous bromine at the cathode. The system is modeled by considering laminar, fully developed flow of electrolyte between two flat electrodes.

We consider the following reactions occurring at the anode and cathode surface:

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $Br_2 + 2e^- \rightarrow 2Br^-$

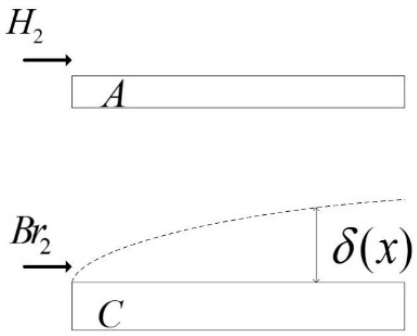

Figure 8: Flow Battery with a depletion layer of Bromine at the cathode surface

The cell voltage can be expressed as:

$$V_{cell} = V_0 + \frac{k_B T}{2e} ln\left(\frac{c_{Br_2,s}(x)}{\bar{c}_{Br_2}}\right) + \eta^c{}_{act}(I) - \eta^a{}_{act}(I) - IR_{el} \tag{15}$$

where V_0 represents the open circuit voltage at the bulk conditions, $\eta^c{}_{act}(I)$ and $\eta^a{}_{act}(I)$ are the activation overpotential at the cathode and anode surface, R_{el} is the electrolyte resistance and $c_{Br_2,s}(x)$ is the concentration of bromine at the cathode surface. From the lecture on "Concentration Polarization" we know the following relation:

$$I(x) = \left(1 - \frac{c_{Br_2,s}(x)}{\bar{c}_{Br_2}}\right) I_{lim}(x) \tag{16}$$

The analytical solution of $I_{lim}(x)$ is known by applying suitable boundary layer theory. The reaction kinetics for both half-cell reactions in the HBLFB are sufficiently fast and reversible, so the activation overpotential at both anode and cathode can be neglected.

In this scenario, the cell voltage can be expressed as:

$$V_{cell}(x) = V_0 + \frac{k_B T}{2e} ln\left(1 - \frac{I(x)}{I_{lim}(x)}\right) - I(x)R_{el} \tag{17}$$

References

1. Conformal mapping of some non-harmonic functions in transport theory, M. Z. Bazant, Proc. Roy. Soc. A. 460, 1433-1452 (2004).

2. Boundary Layer Analysis of Membraneless Electrochemical Cells, W. A. Braff, C. R. Buie and M. Z. Bazant, J. Electrochem. Soc. 160 (11) A2056-A2063 (2013).

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