

III. Transport Phenomena

Lecture 17: Forced Convection in Fuel Cells (I)

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Last lecture we examined how concentration polarisation limits the current that can be drawn from a fuel cell. Reducing the thickness of the porous electrode will increase this limiting current, but we want to increase the limiting current without changing the geometry of the cell. We can do this by imposing a fluid flow, as convection can work faster than diffusion alone. We are interested in the case of high power, i.e. $P_{max} \sim I_{lim}V_O$.

1 Membrane-Electrode Assemblies

Figures 1 and 2 show side and top views of a membrane-electrode assembly used to produce a convective flow.

The reactant gas is forced into inlet channels and drawn out of separate outlet channels, and can only pass between the two by travelling through the porous electrode. This moves gas past the catalyst layer, and some of the gas will reach the catalyst and react.

2 General Analysis

Flow velocity is related to the pressure gradient by Darcy's law:

$$\mathbf{u} = -K\nabla p. \tag{1}$$

K is the permeability of the fluid, just a constant. For incompressible flow, we also have

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

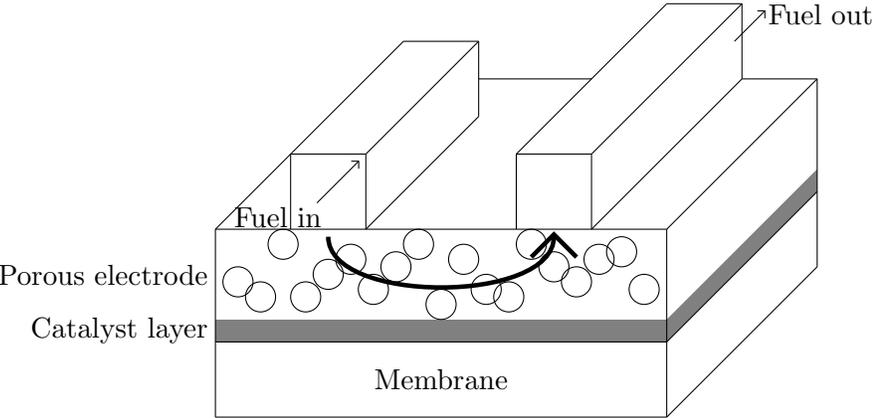


Figure 1: Membrane-electrode assembly

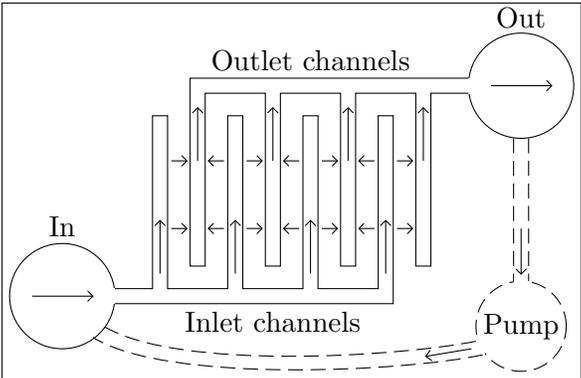


Figure 2: Interdigitated flow channels

Even if the fluid is actually compressible, this equation must hold in the steady state where the amount of fluid at a particular location is not changing in time. Combining these two equations, we have

$$\nabla^2 p = 0. \quad (3)$$

To maintain a steady state, the total rate at which concentration is changing due to convection and diffusion must be zero, i.e.

$$\mathbf{u} \cdot \nabla c = D \nabla^2 c \quad (4)$$

$$\Rightarrow -K \nabla p \cdot \nabla c = D \nabla^2 c. \quad (5)$$

There are different boundary conditions at the inlet and outlet, on the walls and on the membrane.

- At the inlet and outlet, pressure and concentration are both fixed. Pressure is p_{in} at the inlet and p_{out} at the outlet, while we can take concentration to be the same in both places, \bar{c} .
- On the walls, $\hat{n} \cdot \nabla p = 0$, i.e. there cannot be any velocity through the walls. Additionally, $\hat{n} \cdot \nabla c = 0$: this is required in the steady state because any gradient in this direction would be destroyed by diffusion, because there is no convective velocity in this direction that could oppose diffusion.
- On the membrane as on the walls, $\hat{n} \cdot \nabla p = 0$. In this case, however, $\hat{n} \cdot D \nabla c = R$. $\hat{n} \cdot D \nabla c$ is the rate at which particles are hitting the membrane, while R is the rate at which they are reacting: these must be the same in equilibrium. If we are running at limiting current, we will also have $c = 0$. If, on the other hand, we wanted to find the voltage at some sub-limiting current, we would have to solve the equations numerically.

Figure 3 shows what the flow will look like. The solid lines are streamlines, showing the direction of the velocity field, while the dashed line is a concentration contour. It marks the edge of the depletion layer, where concentration goes from approximately \bar{c} outside the layer to less than \bar{c} within the layer.

The differential equations can be solved by conformal mapping (as proven in [1]). The procedure is demonstrated in figure 4. We begin by making a conformal map from the real geometry to one where the problem is much simpler. A conformal map is one where we can write the coordinates of a

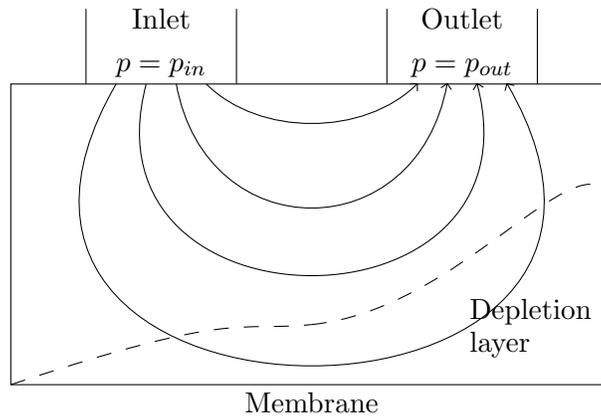


Figure 3: Flow profile in equilibrium

point in the new system as a function of the coordinates of the equivalent point in the old system, and this function is analytic. We then solve the problem in the simple geometry, in this case a rectangle with the inlet and outlet at the two ends, and use the inverse map to go back to the original geometry.

See [2] for the solution of the problem in the simple geometry. Alternatively, we can discover a lot about the solution with some simple scaling analysis.

3 Scaling Analysis

The problem is plug flow (flow at a constant velocity) of concentrated fluid over an absorbing surface. Given that a depletion layer forms, we're interested in the thickness of this layer as a function of distance from the beginning of the absorbing surface, $\delta(x)$ in figure 5.

The convection-diffusion equation describing this situation is

$$u \frac{\partial c}{\partial x} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right). \quad (6)$$

We treat the problem using a dominant balance: considering the two terms that are most significant. Far from the beginning of the absorber, convection dominates diffusion in the x direction, and since the layer is long and thin, concentration will change more rapidly in the y direction than in the x

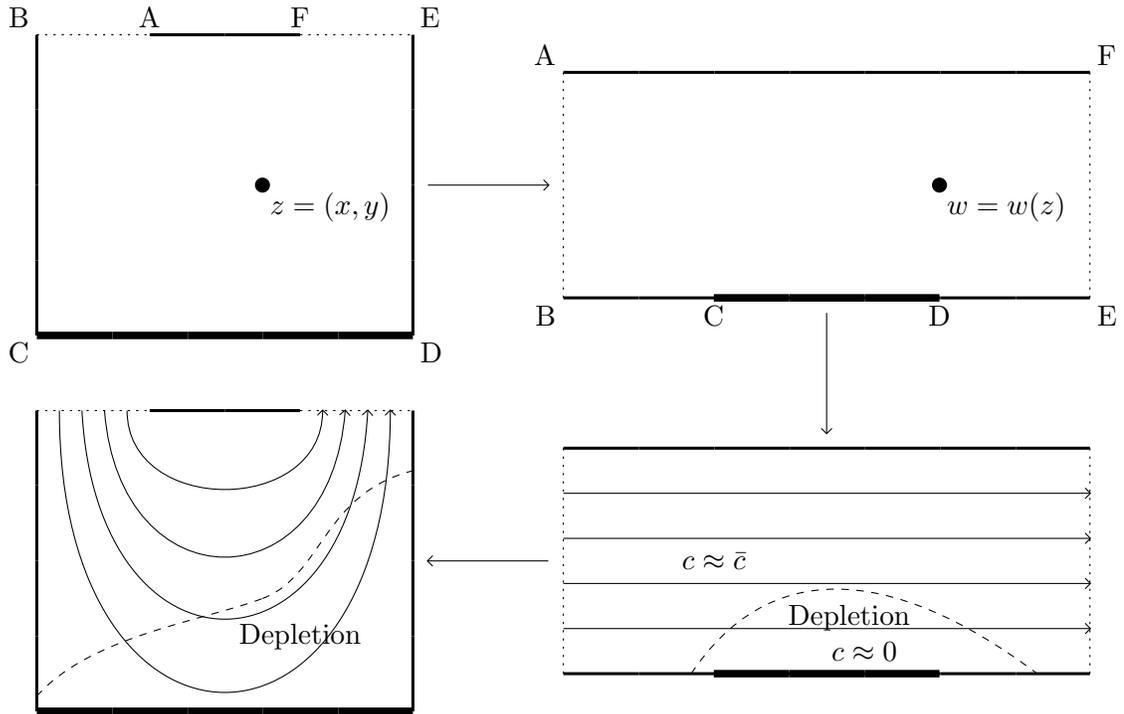


Figure 4: Solving the convection-diffusion problem by conformal mapping

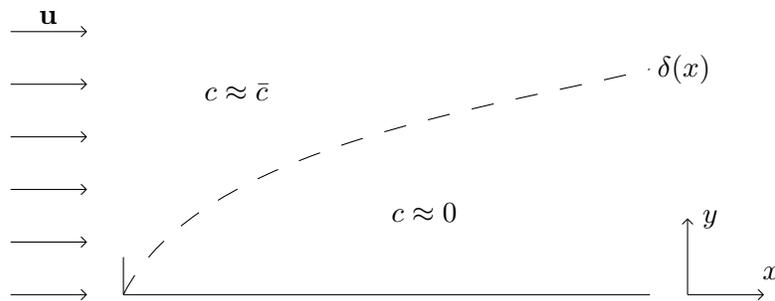


Figure 5: Convection-diffusion boundary layer thickness

direction. Thus

$$u \frac{\partial c}{\partial x} \approx D \frac{\partial^2 c}{\partial y^2}. \quad (7)$$

We can estimate the size of these terms: the gradient of concentration in the x direction must be around \bar{c}/x , while the second derivative of concentration in the y direction will be around \bar{c}/δ^2 . Substituting these values, we have

$$u \frac{\bar{c}}{x} \sim D \frac{\bar{c}}{\delta^2} \quad (8)$$

$$\delta \sim \sqrt{\frac{Dx}{u}}. \quad (9)$$

We can define dimensionless variables $\tilde{\delta}$ and \tilde{x} by dividing δ and x by H , the height of the flowing fluid. We then have the relation

$$\tilde{\delta} \sim \sqrt{\frac{\tilde{x}}{\text{Pe}}}, \quad (10)$$

where Pe is the Peclet number, which measures the relative importance of convection and diffusion and is defined by

$$\text{Pe} = \frac{uH}{D}. \quad (11)$$

Flux density is

$$R = D \frac{\partial c}{\partial y} \quad (12)$$

$$\sim D \frac{\bar{c}}{\delta} \quad (13)$$

$$\sim \bar{c} \sqrt{\frac{uD}{x}}. \quad (14)$$

The dimensionless flux is known as the Sherwood number and is defined by

$$\text{Sh} = \frac{R}{D\bar{c}/H}. \quad (15)$$

From equation 14, we find

$$\text{Sh} \sim \sqrt{\frac{\text{Pe}}{\tilde{x}}}. \quad (16)$$

We are particularly interested in the limiting current, which is the flux integrated over the area of the absorbing surface, multiplied by the charge

transferred in each absorption reaction. If the surface has width W and length L , the limiting current is

$$I_{lim} \sim neW\bar{c}\sqrt{uDL}. \quad (17)$$

If we make this dimensionless by dividing by $neA\bar{c}D/H$ ($A = LW$ is the area of the absorbing surface), which is the limiting current in the absence of flow, we find

$$\tilde{I}_{lim} \sim \sqrt{\text{Pe}}\sqrt{\frac{H}{L}}. \quad (18)$$

It is thus possible to boost the limiting current by increasing the flow velocity.

There is a trade off: the proportion of fuel utilised. If we define γ_F to be the ratio of fuel consumed to fuel input, we find

$$\gamma_F = \frac{I_{lim}}{ne u H W \bar{c}} \quad (19)$$

$$\sim \frac{1}{\sqrt{\text{Pe}H/L}} \quad (20)$$

$$\sim \frac{1}{\tilde{I}_{lim}}. \quad (21)$$

We therefore see that even though it is possible to increase the limiting current, this results in a corresponding decrease in the fuel utilisation.

4 Similarity Solution

Although our scaling analysis was very useful, it is also possible to solve equation 7 exactly. If we define $\tau = x/u$, we get

$$\frac{\partial c}{\partial \tau} = D \frac{\partial^2 c}{\partial y^2}, \quad (22)$$

the diffusion equation. The boundary conditions are $c(y, 0) = \bar{c}$ and $c(0, \tau) = 0$. There is a similarity solution, $c(y, \tau) = f(y/\sqrt{\tau})$. This solution, which can be found by various methods such as substituting the similarity form into the partial differential equation to get a (separable) ordinary differential equation, is

$$c = \bar{c} \operatorname{erf} \left(\frac{y}{2\sqrt{D\tau}} \right) \quad (23)$$

$$= \bar{c} \operatorname{erf} \left(\frac{y}{2\sqrt{Dx/u}} \right). \quad (24)$$

The exact reaction flux is

$$R = D \frac{\partial c}{\partial y}(0, \tau) \quad (25)$$

$$= \bar{c} \sqrt{\frac{uD}{\pi x}}. \quad (26)$$

Comparison with equation 14 shows that solving the equation exactly only changed the approximate result by a factor of $1/\sqrt{\pi}$.

It is also possible to solve the full convection-diffusion equation, Eq. (6), analytically for geometries of interest for fuel cells. Near the leading edge of a membrane (where the flow impinges), there is a similarity solution, which can be mapped to different geometries (Fig. 2 of Ref. [1]). There are also accurate asymptotic approximations of the solution for a finite membrane, which can also be mapped to other geometries [2]. These analytical solutions also have interpretations in viscous fluid mechanics (where the Reynolds number plays the role of the Peclet number); for example, the "Burgers vortex sheet" (Fig. 1 of [3]) is analogous to the concentration profile near the stagnation point where the fluid impinges on the membrane, and "vortex fishbones" (Fig. 4c-d of [3]) correspond to periodic recirculating flows over a membrane, as in the fuel cell assembly sketched above.

References

- [1] Conformal mapping of some non-harmonic functions in transport theory, M. Z. Bazant, Proc. Roy. Soc. A. 460, 1433-1452 (2004).
- [2] Steady advection-diffusion around finite absorbers in two-dimensional potential flows, J. Choi, D. Margetis, T. M. Squires, and M. Z. Bazant, J. Fluid Mech. 536, 155-184 (2005).
- [3] Exact solutions of the Navier-Stokes equations having steady vortex structures, M. Z. Bazant and H. K. Moffatt, J. Fluid Mech. 541, 55-64 (2005).
- [4] O'Hare et al., Fuel Cell Fundamentals, Ch. 5.3.
- [5] J. Newman, K. Thomas-Alyea, Electrochemical Systems, Ch 17.
- [6] W. M. Deen, Analysis of Transport Phenomena, Ch 10.

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