

IV. Transport Phenomena

Lecture 16: Concentration Polarization

Notes by MIT Student

We have previously discussed open circuit voltage, which can be derived from the Nernst equation, and activation overpotentials, which can be derived from the Butler-Volmer equation. This can accurately describe the behavior of electrochemical cells at low currents, but for sufficiently large currents, the transport of reactants to the reaction sites begins to become limiting, and the concentration at the reaction sites will be significantly lower than the bulk concentration. As the current gets even larger, the reaction will completely run out of reactants, and the voltage required to push the reaction will diverge as the current approaches a limiting current, I_{lim} . This behavior is commonly described by a concentration polarization. For this lecture, we will examine how the diffusion of reactants can be modeled to describe this process.

1 Linear Diffusion and Convection

In a dilute (quasi-binary) solution, the transport of solutes can be described in terms of a flux density \vec{F} , which in the absence of convection can be described by Fick's Law: $\vec{F} = -D\nabla C$, where D is the diffusivity of the particles, and C is their concentration. In the presence of fluid velocity \vec{u} , the more general expression for Fick's Law becomes:

$$\vec{F} = -D\nabla C + \vec{u}C. \quad (1)$$

Note that a more accurate model of gas transport in porous media is the Dusty Gas Model, as has been shown for the case below of a solid oxide fuel cell¹, but Fick's Law is a reasonable simple model for most electrochemical systems.

¹Y. Fu et al., J. Electrochem. Soc. 162, F613 (2015).

The diffusivity D can be derived from a molecular random walk, which yields a result of the form

$$D = \frac{\Delta x^2}{2\Delta t}, \quad (2)$$

where Δx is the mean free path of the solute and Δt is the mean time between collisions of the solute. Keep in mind that this expression would need to be modified for concentrated solutions because it relies upon the fact that there are no interparticle interactions in order to obtain independent random walks.

In order to apply Fick's law, we need a final relationship between flux and concentration, which we obtain from conservation of mass. There are many good derivations of the conservation of mass relation available in textbooks, [?] but for our purposes, it is adequate to observe that for a point in space, the flux inwards plus any local particle generation must be equal to the flux outwards, or else there will be a change in local concentration. For the case where there are no volumetric sources, this relationship is described by:

$$\frac{\partial C}{\partial t} + \nabla \cdot \vec{F} = 0. \quad (3)$$

If we assume a constant diffusivity and incompressible flow, so that $\nabla \cdot (D\nabla C) = D\nabla^2 C$ and $\nabla \cdot \vec{u} = 0$, we can combine equations 1 and 3 to obtain the linear convection-diffusion equation:

$$\frac{\partial C}{\partial t} + \vec{u} \cdot \nabla C = D\nabla^2 C, \quad (4)$$

which is the primary tool for describing mass transport in many systems.

2 Limiting Current Density

Concentration polarization can be defined as the loss of voltage due to concentration changes out of equilibrium, or while current is passing. There are three basic ways for this to occur. The first is that the local equilibrium voltage depends on the local concentration, as described by the Nernst Equation. The second is that the local exchange current, and therefore the activation overpotential, also depend on local concentration, as described by the Butler-Volmer equation. The third process, which is often described on its own as the concentration polarization, is that the conductivity of the electrolyte will also change as a function of local concentration, as described by the Nernst-Planck equation. The first two of these effects are commonly referred to as "external" effects because they are dependent upon the reactant

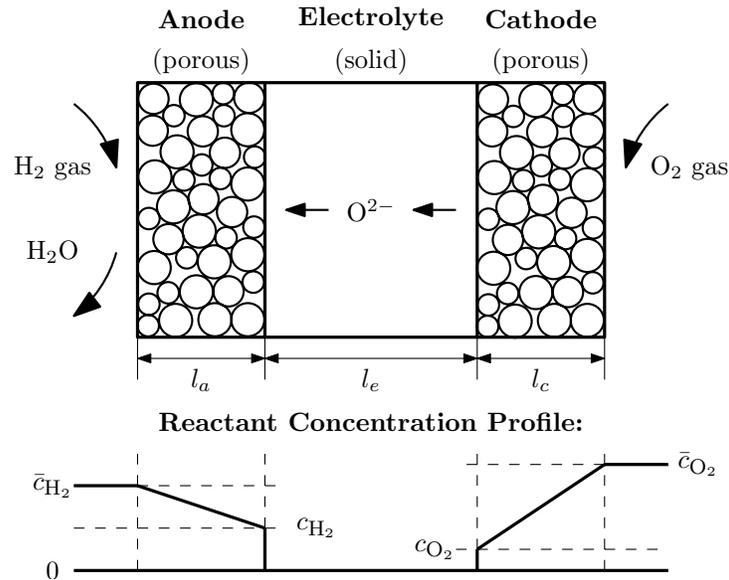


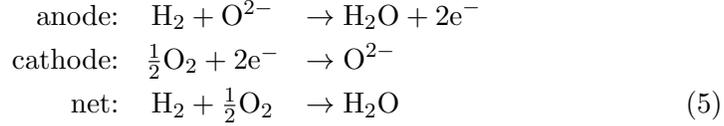
Figure 1: (Image taken from 2009 10.95 Scribe notes by Charles Moore.) Schematic of a solid oxide fuel cell. Oxygen is supplied to the cathode, where it is reduced to oxygen ions that migrate across the electrolyte to the anode, where they oxidize hydrogen that has adsorbed onto the anode. At steady state for $I > 0$, the concentration profiles of oxygen and hydrogen in the cathode and anode electrodes will be as shown in the lower part of the figure.

and product concentrations outside of the electrolyte, while the third effect is an “internal” effect because it stems from changes taking place inside the electrolyte.

3 Example: Solid-Oxide Fuel Cell

Consider the case of a solid oxide fuel cell. This system, with parameters as shown in figure 1, consists of two porous gas diffusion electrodes (typically nickel anode and LSM cathode) on either side of a solid oxide electrolyte (typically YSZ, yttrium stabilized zirconia) that can be treated as ideally permeable to O^{2-} ions, and impermeable to everything else. In practice, these systems are comprised of three ceramic layers, and generally operate

at temperatures between 600 and 1000 °C. The half reactions are as follows:



For the simple case of steady state diffusion in the porous electrodes where we neglect diffusion, the transport equations simplifies to $\partial^2 c / \partial x^2 = 0$, which has a linear solution. If we let the 'bulk' concentrations be \bar{c}_i and the concentrations at the surface of the electrodes facing the electrolyte be c_i , then the problem is fully defined, and it is trivial to specify the flux $F = D\Delta c_i / l_i$. The current is connected to the particle flux by $I = 2eA_a F_{H_2} = eA_c F_{O_2}$, so the current can be written in terms of the flux across either the anode or the cathode:

$$\begin{aligned}
 \text{anode reactant: } & I = D_{H_2} \frac{\bar{c}_{H_2} - c_{H_2}}{l_a} 2eA_a \\
 \text{cathode reactant: } & I = D_{O_2} \frac{\bar{c}_{O_2} - c_{O_2}}{l_c} 4eA_c.
 \end{aligned} \tag{6}$$

Physically, concentrations must always be positive, so the particle flux through the porous electrode cannot exceed the value it achieves when the reactant concentration at the electrode surface reaches zero. This corresponds to anode and cathode limiting currents, which occur when one or the other reactant cannot diffuse fast enough to allow for any more current to pass. These can be written as

$$\begin{aligned}
 I_{lim}^c &= \frac{4eA_c D_{O_2} \bar{c}_{O_2}}{l_c} \\
 I_{lim}^a &= \frac{2eA_a D_{H_2} \bar{c}_{H_2}}{l_a}
 \end{aligned} \tag{7}$$

We can now express c in terms of I and I_{lim} :

$$\begin{aligned}
 I &= I_{lim}^c \left(1 - \frac{c_{O_2}}{\bar{c}_{O_2}}\right) = I_{lim}^a \left(1 - \frac{c_{H_2}}{\bar{c}_{H_2}}\right) \\
 \frac{c_{O_2}}{\bar{c}_{O_2}} &= 1 - \frac{I}{I_{lim}^c}, \quad \frac{c_{H_2}}{\bar{c}_{H_2}} = 1 - \frac{I}{I_{lim}^a}
 \end{aligned} \tag{8}$$

We can also relate the current to the outward flux of the water vapor reaction product at the anode,

$$\text{anode product: } I = D_{H_2O} \frac{c_{H_2O} - \bar{c}_{H_2O}}{l_a} 2eA_a$$

and thus relate the water concentration at the anode surface to the current

$$\frac{c_{H_2O}}{\bar{c}_{H_2O}} = 1 + \frac{I}{I_{lim}^w}, \quad (9)$$

where

$$I_{lim}^w = \frac{2eA_a D_{H_2O} \bar{c}_{H_2O}}{l_a} \quad (10)$$

which is the limiting current, $I = -I_{lim}^w$, when the cell is run in reverse as an electrolyzer, splitting water electrochemically into hydrogen and oxygen gases, by applying a reverse voltage and putting energy into the system.

Now that we have expressions for $c(I)$ at either electrode, we can plug them into our model:

$$V(I) = \Delta\phi_{cathode} - \Delta\phi_{anode} - \Delta\phi_{electrolyte} \quad (11)$$

where

$$\begin{aligned} \Delta\phi_{cathode} &= \phi_{metal}^c - \phi_{electrolyte}^c = \Delta\phi_{eq}^c + \eta_{act}^c(I) \\ \Delta\phi_{anode} &= \phi_{metal}^a - \phi_{electrolyte}^a = \Delta\phi_{eq}^a + \eta_{act}^a(I) \\ \Delta\phi_{electrolyte} &= IR_{el}. \end{aligned}$$

From the Nernst equation (assuming dilute gases), we have

$$\begin{aligned} \Delta\phi_{eq}^c &= U_c^\ominus - \frac{kT}{2e} \ln \left(\frac{c_{O_2^{2-}}}{\sqrt{c_{O_2}}} \right), \\ \Delta\phi_{eq}^a &= U_a^\ominus + \frac{kT}{2e} \ln \left(\frac{c_{H_2O}}{c_{H_2} c_{O_2^{2-}}} \right) \end{aligned} \quad (12)$$

so if we let V_0 correspond to the open circuit voltage at the 'bulk' conditions \bar{c}_{O_2} and \bar{c}_{H_2} , and then plug our result from equation 8 into the Nernst equation, we get:

$$\begin{aligned} V_0 &= U_c^\ominus - U_a^\ominus - \frac{kT}{2e} \ln \left(\frac{c_{H_2O}}{\bar{c}_{H_2} \sqrt{\bar{c}_{O_2}}} \right) \\ V_{eq}(I) &= V_0 + \frac{kT}{2e} \ln \left(\frac{c_{H_2}}{\bar{c}_{H_2}} \right) + \frac{kT}{4e} \ln \left(\frac{c_{O_2}}{\bar{c}_{O_2}} \right) - \frac{kT}{2e} \ln \left(\frac{c_{H_2O}}{\bar{c}_{H_2O}} \right) \\ &= V_0 + \frac{kT}{2e} \ln \left(1 - \frac{I}{I_{lim}^a} \right) + \frac{kT}{4e} \ln \left(1 - \frac{I}{I_{lim}^c} \right) \\ &\quad - \frac{kT}{2e} \ln \left(1 + \frac{I}{I_{lim}^w} \right) \end{aligned} \quad (13)$$

As $I \rightarrow I_{lim}^i$, the equilibrium voltage diverges because diffusion cannot supply enough reactants to the reaction sites to maintain a steady state. Note

that the voltage will diverge at the minimum of I_{lim}^c and I_{lim}^a . As noted above, the voltage also diverges to $+\infty$ as $I \rightarrow -I_{lim}^w$ due to diffusion limitation of water vapor during electrolysis in reverse operation.

As we discussed earlier, variations in concentration also affect reaction kinetics, as manifested in the Butler-Volmer equation. We will limit our analysis to symmetric ($\alpha = 1/2$) reactions in a dilute gas for now, but one could obtain similar results for more complicated models. In our simple case, Butler-Volmer takes the form:

$$\eta_{act}^a = \frac{kT}{e} \sinh^{-1} \left(\frac{I}{2I_0^a} \right)$$

$$\eta_{act}^c = \frac{kT}{e} \sinh^{-1} \left(\frac{I}{2I_0^c} \right)$$

where:

$$I_0^a = K_0^a \sqrt{\frac{c_{H_2} \bar{c}_{H_2O}}{\bar{c}_{H_2} c_{H_2O}}} = K_0^a \sqrt{\frac{1 - \frac{I}{I_{lim}^a}}{1 + \frac{I}{I_{lim}^w}}}$$

$$I_0^c = K_0^c \sqrt[4]{\frac{c_{O_2}}{\bar{c}_{O_2}}} = K_0^c \sqrt[4]{1 - \frac{I}{I_{lim}^c}}. \quad (14)$$

All the parameters that are not a function of current are folded into the K_0^i constants so that we can focus on the limiting current behavior. When we plug these results back into equation 11, we obtain a full model for the effect of concentration, which has a current versus potential relationship shown in figure 2. It is worth mentioning that for $I \rightarrow I_{lim}^i$, we can take asymptotic expansions of the activation overpotentials to obtain simpler expressions. [Note: For large z , $\sinh^{-1}(z) \sim \ln(2z)$]

$$\eta_a \sim \frac{kT}{e} \ln \left(\frac{I}{K_0^a \sqrt{1 - I/I_{lim}^a}} \right) \sim \frac{kT}{2e} \ln \left(1 - \frac{I}{I_{lim}^a} \right)$$

$$\eta_c \sim \frac{kT}{e} \ln \left(\frac{I}{K_0^c \sqrt[4]{1 - I/I_{lim}^c}} \right) \sim \frac{kT}{4e} \ln \left(1 - \frac{I}{I_{lim}^c} \right). \quad (15)$$

The last comment to make about this result is that although concentration polarization is often only significant for relatively large currents, in many real world systems it can be a major concern in system design. If we look at power rather than voltage, as shown in the lower part of figure 2, we obtain a result with a sharp peak power near the limiting current followed by a steep drop in output as the system approaches super galvanic operation

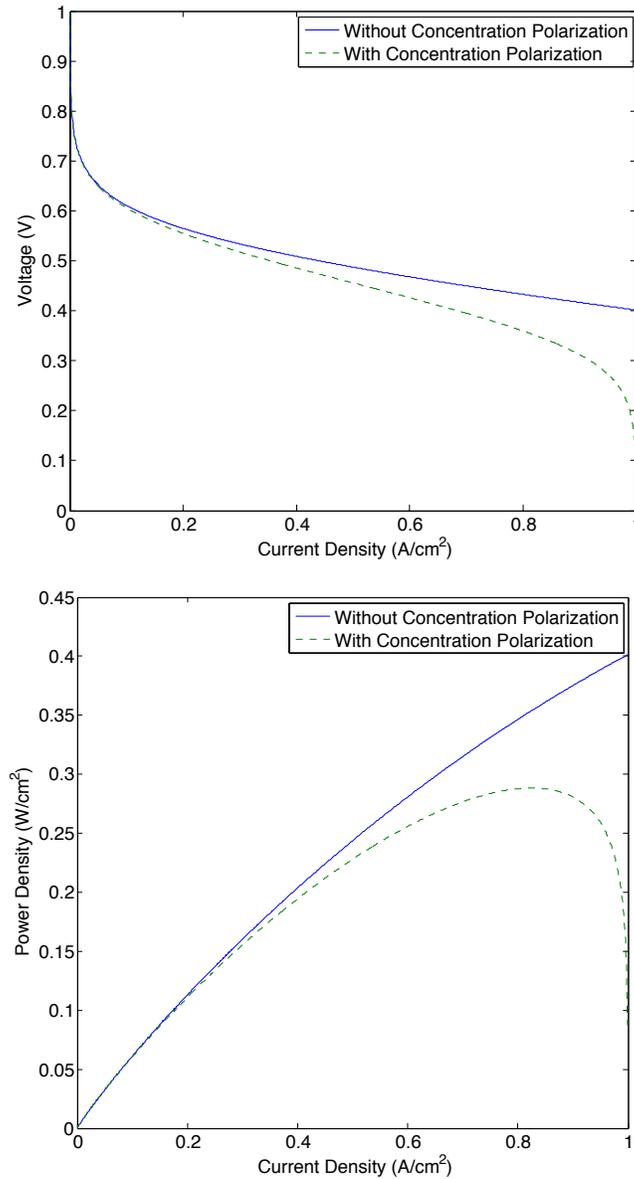


Figure 2: Voltage and power versus current under simplified fuel cell conditions. ($R_{el} = 0.1 \Omega \cdot \text{cm}^2$, $I_{lim}^c = I_{lim}^a = 1 \text{ A/cm}^2$, $K_0^c = K_0^a = 10^{-5} \text{ A/cm}^2$) When concentration polarization effects are included, voltage diverges as current approaches the limiting current. Peak power occurs quite near to limiting current density, so concentration polarization becomes the main limitation on maximum power density.

($V < 0$). For many mobile systems, power density is often of greater importance than efficiency, so the hard limit on power density that concentration polarization imposes can be a significant design limitation.

For further reading, see O'Hare et al., *Fuel Cell Fundamentals*, Ch. 5.2.

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