ME 370B
Energy Systems II:
Modeling and Advanced Concepts

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An Alternative Approach to Fuel Cell Analysis

Analysis of fuel cell performance under finite-rate operating conditions is normally performed following a phenomenological approach based on use of the *Bulter-Volmer* equation. In this approach, the ability of the reactant gases to generate a driving electrical potential is evaluated and then partitioned between the set of transport processes that it is thought to drive and the output electrical potential of the cell. The loss of driving electrical potential associated with the chemical reactions at the anode and cathode are prescribed in terms of electrical *overpotentials* that are partitioned between the forward and reverse reaction processes by use of a prescribed *symmetry factor* (a.k.a., *transfer coefficient*) for the transition state. The definition of these overpotentials is facilitated by the availability of exchange current density data—measurements of the rate at which current is transported across the anode or cathode due solely to thermochemical processes, i.e., in the absence of a driving electrical potential. By using experimental exchange rate data, the requirement of knowing the activation energy of the anode and cathode reactions is removed (actually just subsumed into the exchange rate) and a simplified analysis path exists.

While there is nothing really wrong with this approach, and it has certainly been successful in treating practical problems in fuel cell analysis for decades, there are two deficiencies that suggest use of a different approach. The first is the basic premise that the driving potential for transport and reaction in a fuel cell is the electrical potential. This is not the general case. The driving potential for all of the processes in the fuel cell is the *electrochemical potential*, not the electrical potential. The need for this distinction is obvious in the case of the neutral gas species supplied to the reactant channels of the cell—they are uncharged and therefore cannot be driven by an electrical potential. But that can be handled in a Butler-Volmer type of approach by separating their transport into an outer problem (that sets up the electrical potential available within the cell) and an inner problem (partitioning that potential between the finite-rate losses and the electrical output) that are solved jointly to determine the overall cell performance. The real objection occurs internal to the cell where the key transport problem involves ions and electrons that are charged and can therefore respond to changes in both their chemical potential and the local electrical potential.

In the traditional approach, all transport and activation are prescribed to be driven by the electrical potential. That this is not the case becomes evident when more general electrochemical problems are considered in which significant quantities of reactants are created or consumed at the electrodes of the cell. In such problems, it is inescapable to notice that the change in driving potential concomitant with enriching one species at the expense of another is not an electrical effect. But perhaps more important than this, assigning the loss of electrochemical potential within the cell to electrical potential only can lead to serious confusion in cases where it is not possible to see an intuitive picture of the electrical potential changes

within the cell. While there are many cases where a clear picture of the electrical potential of the cell can be developed—traditional electrode-in-solution cells with well defined, geometrically simple electrical double layers, for example—there are other cases in which a clear picture of the local electrical potential is not as easily developed—e.g., a porous, distributed, cermet-style anode in a solid-oxide fuel cell—such that reliance upon a clear view as to how the electric field drives the reaction is just not possible. Finally, and perhaps most important, the fact is that without additional information —something that allows us to separate the chemical and electrical components—the division among the two driving potentials simply cannot be known. And as we will see below, making this distinction is just not necessary.[1]

We will therefore take an alternative approach.

Tracking Electrochemical Potential through a Fuel Cell

Simply stated, the approach we will take is to track the electrochemical potential through the fuel cell from anode to cathode. We will do this in two passes: In the first we will assume that the cell is in equilibrium (a.k.a., has an open electrical circuit at its terminals) such that no net current flows and only the intrinsic (exchange) processes within the cell are active. Since these processes provide the information needed about the height of the free energy barrier that must be surmounted at the transition states for the anode and cathode, it is no surprise that the equilibrium values of electrochemical potential have a role to play in the finite-rate analysis.

The second pass will be with a prescribed net rate of reaction (a.k.a., reaction velocity) within the cell. This, and the (known) charge number for the overall cell reaction, determines the current generated by the cell. Stated another way, we will march through the cell on the second pass assuming that we know the current output from the cell *a priori*. The advantage of taking such an approach—choosing the reaction velocity as the primary variable around which to construct the analysis—is that the analysis becomes completely explicit. Note that this presents no particular complication since analysis for any other desired condition (e.g., a prescribed electrical output potential instead of current density) can be performed by wrapping the present approach in an outer layer that solves the resulting implicit problem iteratively.

Setting up the Problem

Consider a small area element of a fuel cell with the anode and cathode connected by the electrolyte, but at equilibrium by virtue of open electrical connections. Let us assume that the cell is sufficiently small, or its reactant/product supply/removal flows are configured in such a way as to eliminate lateral gradients (making transport in the cell one dimensional). We will also assume that the rate of heat transfer in the cell is sufficient that the cell may be assumed to be isothermal, and that the pressure of the gases within each gas diffusion layer is uniform.

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[1] This situation is analogous to that in gas turbine analysis when trying to differentiate changes in kinetic energy from changes in enthalpy. In the absence of information about the flow geometry and local state, it is not possible to separate these two, hence analyses must be conducted in terms of the stagnation enthalpy—the joint combination of these energy transfers—not one or the other.

Because the fuel cell is a source of potential difference (not absolute potential), we are free to choose a reference potential for the cell. Since the anode lead is the "negative terminal" of the cell, we will choose the electrochemical potential (not the electrical potential) of an electron at the anode terminal as our fixed reference value.[2] While it is not necessary to actually assign a numerical value to this electrochemical potential—all of the analysis can be done in terms of differences from this reference value—in actually writing computer code to track the potential through a cell, setting this value to zero proves to be convenient since it makes all other electrochemical potentials available immediately as you march through the cell. In the development that follows, we will take this value as being known, but we will not eliminate it from the equations (by setting it equal to zero) since we would like to be able to follow it through the analysis. We reiterate, however, that the fact that this can be arbitrarily fixed is important because it allows us to determine the set of electrochemical potentials in the cell explicitly, in a step-by-step fashion, as we proceed from the anode terminal to the cathode terminal of the cell.

Pass 1: The Cell in Equilibrium

Having set the electrochemical potential of an electron at the anode terminal to zero, and knowing that the cell is in equilibrium, the remainder of the potentials in the cell may be determined as follows:

Since the cell is in equilibrium, no net current, chemical reaction, or species transport occurs within the cell. The gas supplies adjacent to the anode and cathode gas diffusion layers are present, but no net diffusion occurs in the gas diffusion layers, hence no concentration (or chemical potential) gradient exists within them. Similarly, since there is no net current flow, there is no electrical potential gradient along either electrode from the triple-junction sites to the terminal connection, and the electrical potential (and hence the electrochemical potential) along these leads is uniform. The result of holding the cell under these *no-net-flow* conditions is that the values of the electrochemical potentials of the gases at the anode and cathode are known explicitly—each corresponds to the *chemical* potential of the gas flowing in the supply stream adjacent to its gas diffusion layer. This, plus having chosen the electrochemical potential of the electron at the anode terminal to be zero, allows us to move directly to analysis of the anode reaction.

Equilibrium conditions for a hydrogen-fueled, solid-oxide fuel cell requires zero electrochemical affinity for the reaction $H_2(g,a) + O^=(YSZ,a) \rightleftharpoons H_2O(g,a) + 2e^-(Ni,a)$ at the anode

$$\tilde{A}_{eq}^a \equiv \tilde{G}_{P,eq}^a - \tilde{G}_{R,eq}^a = \mu_{H_2O,eq}^{g,a} + 2\tilde{\mu}_{e^-,eq}^{Ni,a} - \mu_{H_2,eq}^{g,a} - \tilde{\mu}_{O^=,eq}^{YSZ,a} = 0$$

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[2] Perhaps a more comfortable alternative would be to set the electrical potential to zero, in effect doing what is often done with a floating power supply. But note that if you accept that the reference electrical potential can be set arbitrarily, then it is always possible to select a value that corresponds to the opposite of the chemical potential of the electrode material, in effect, setting the electrochemical potential to zero.

where superscripts denote the phase or location, subscripts denote the particular species and the conditions under which the quantity is evaluated (e.g., in equilibrium), and R and P stand for reactants and products (of the specified reaction) respectively.

Since the potentials of the hydrogen and water at the anode are imposed externally and the potential of the electron has been fixed, the only unknown is the potential of the oxygen ion, given explicitly by

$$\tilde{\mu}_{O^=,eq}^{YSZ,a} = \mu_{H_2O,eq}^{g,a} + 2\tilde{\mu}_{e^-,eq}^{Ni,a} - \mu_{H_2,eq}^{g,a}$$

Similarly, equilibrium requires zero affinity for $\frac{1}{2}O_2(g,c) + 2e^-(Ni,c) \rightleftharpoons O^=(YSZ,c)$ at the cathode

$$\tilde{A}_{eq}^c \equiv \tilde{G}_{P,eq}^c - \tilde{G}_{R,eq}^c = \tilde{\mu}_{O^=,eq}^{YSZ,c} - \frac{1}{2}\mu_{O_2,eq}^{g,c} - 2\tilde{\mu}_{e^-,eq}^{Ni,c} = 0$$

Again the potential of the gaseous reactant, oxygen, is imposed externally, and the potential of the oxygen ion must be the same as for the anode (since there is no net transport)

$$\tilde{\mu}_{O^=,eq}^{YSZ,c} = \tilde{\mu}_{O^=,eq}^{YSZ,a}.$$

The only unknown is then the potential of the electron, given explicitly by

$$\tilde{\mu}_{e^-,eq}^{Ni,c} = \frac{1}{2}\tilde{\mu}_{O^=,eq}^{YSZ,c} - \frac{1}{4}\mu_{O_2,eq}^{g,c}$$

Note that the equilibrium (open circuit) electrical potential difference of the cell is then immediately available, since the chemical part of the electrochemical potential of the electron is identical for the two electrodes (as long as they are made of the same material and at the same temperature) and therefore cancels out.

$$\tilde{\mu}_{e^-,eq}^{Ni,c} - \tilde{\mu}_{e^-,eq}^{Ni,a} = \left(\mu_{e^-,eq}^{Ni,c} + z_{e^-}F\phi_{eq}^{Ni,c}\right) - \left(\mu_{e^-,eq}^{Ni,a} + z_{e^-}F\phi_{eq}^{Ni,a}\right) = -F\left(\phi_{eq}^{Ni,c} - \phi_{eq}^{Ni,a}\right)$$

Collecting electrochemical potentials from above, the equilibrium electrical potential at the terminals is then given by the not-too-surprising relationship

$$\phi_{eq}^{Ni,c} - \phi_{eq}^{Ni,a} \equiv \Delta\phi_{eq} = \frac{1}{2F}\left(\mu_{H_2,eq}^{g,a} + \frac{1}{2}\mu_{O_2,eq}^{g,c} - \mu_{H_2O,eq}^{g,a}\right)$$

which shows that the overall chemical affinity of the reactants impinging on the gas diffusion layers has been made available as electrical potential energy at the output terminals of the cell.

Pass 2: The Cell with a Prescribed Reaction Velocity

Now consider the same area element of the cell, but with a specified current flowing. The current specification can be converted into the area-specific net reaction rate v (a.k.a., *reaction velocity*) required at each electrode since

$$i = v\,v_{e^-}^c F = v\,v_{e^-}^a F = v2F \implies v = \left(\frac{1}{2F}\right)i$$

The dynamic balance of the potential in the cell can again be written using the electrochemical potential of an electron at the anode terminal as the reference value, but now the effects of finite-

rate transport must be included. In the first pass through the cell there was no net current flow—and hence no reactant flow—and the electrochemical potential of the electrons at the anode triple-junction sites was identical to the value at the anode-side terminal. That is no longer the case; now a conduction loss corresponding to the material, cross-sectional geometry, and length of the electrode interconnection path should be included in the analysis.

In a similar fashion, the chemical potentials of the hydrogen and water at the anode triple-junction sites no longer corresponds to their reactant supply values, and the amount of chemical potential expended to drive the required fluxes (corresponding to the prescribed value of reaction velocity) must be determined.

Fortunately that is not too difficult to do. In the case of the electrons we have already seen that the current that corresponds to reaction velocity v is $i = 2vF$ where F is Faraday's constant. In terms of the flux of electrons (as particles, not electric charge), the electron flux rate is $J_{e^-} = 2v$ since the stoichiometric coefficient of the electron in the overall cell reaction is 2. Similarly, the flux of each of the other species at the anode is given by the product of its stoichiometric coefficient and the reaction velocity

$$J_{H_2}^a = v\,v_{H_2}^a = v, \text{ and } J_{H_2O}^a = v\,v_{H_2O}^a = v$$

These fluxes, in turn, determine the amount of chemical potential consumed (and therefore lost) to drive each flux to, or from, the anode. Deferring until later the details of how to determine that loss, at this point we simply need to recognize that as long as the supply-side composition imposed at the outer edge of the gas diffusion layer is known, the concomitant loss of electrochemical potential, as well as the anode-side mole fractions (in fact, their complete profile through the GDL) can be determined from force-flux conductivity/diffusivity relationships of the kind discussed in class.

The results of that analysis yield the following expressions for the magnitude (absolute value) of the chemical potential difference required to drive each flux at the anode:

$$\Delta\tilde{\mu}_{e^-}^{Ni,a} = J_{e^-}^a\, L_{Ni,a}\big/\kappa'_{Ni,e^-}$$

$$\Delta\mu_{H_2}^{GDL,a} = -\overline{R}T \ln\left(1 - \frac{J_{H_2}^a L_{GDL,a}}{x_{H_2}^{g,a}cD_{H_2-H_2O}}\right)$$

$$\Delta\mu_{H_2O}^{GDL,a} = \overline{R}T \ln\left(1 + \frac{J_{H_2O}^a L_{GDL,a}}{x_{H_2O}^{g,a}cD_{H_2-H_2O}}\right)$$

Accepting for the moment that the right-hand-side of each of these expressions is known, these potential drops provide both the linkage between the supply-side chemical potentials and the values we need at the anode triple junction, but also the linkage we need between our first-pass equilibrium analysis and the current finite-rate analysis of the cell. The reason is that the GDL supply-side values of chemical potential (which form part of the $\Delta\mu's$ above) are the same values that existed during our equilibrium analysis—they are values supplied by the reactant streams. In essence the $\Delta\mu's$ listed above provide the link between the chemical potentials

available to the anode under equilibrium conditions and those available during finite-rate operation. As we will see shortly, this is the key to finding the activation electrochemical potential requirement of the anode.

But just before we go there, let's be very explicit about the fact that, with these $\Delta\mu's$ in hand, we can solve for the potential of each species at the anode triple junction. The potential of the electron at the anode triple junction must exceed its (fixed) value at the anode-side terminal

$$\tilde{\mu}_{e^-}^a = \tilde{\mu}_{e^-,eq}^{Ni,a} + \Delta\tilde{\mu}_{e^-}^{Ni,a}$$

while the potential of the hydrogen at the triple-junction sites is reduced from its equilibrium value

$$\mu_{H_2}^a = \mu_{H_2,eq}^{g,a} - \Delta\mu_{H_2}^{GDL,a}$$

and, like the electron, the potential of the water formed at the anode must increase in order to drive it away from the anode

$$\mu_{H_2O}^a = \mu_{H_2O,eq}^{g,a} + \Delta\mu_{H_2O}^{GDL,a}$$

Using transition state theory, it can be shown that the reaction velocity at the anode is related to the difference between the Gibbs function of the reactants and products (of the anode reaction) and their equilibrium values by

$$v = R_{eq}^a \left\{ \exp\left[\frac{\left(\tilde{G}_R^a - \tilde{G}_{R,eq}^a\right)}{\overline{R}T} \right] - \exp\left[\frac{\left(\tilde{G}_P^a - \tilde{G}_{P,eq}^a\right)}{\overline{R}T} \right] \right\}$$

where R_{eq}^a is the equilibrium (exchange) reaction rate at the anode (obtainable from measured exchange-rate current density data),[3] and the Gibbs functions of the reactants and products are based on electrochemical potentials (for charged species): $\tilde{G}_R^a = \sum_{R,i} v_i^a \tilde{\mu}_i^a$, $\tilde{G}_P^a = \sum_{P,i} v_i^a \tilde{\mu}_i^a$.

Writing this out explicitly gives

$$v = R_{eq}^a \left\{ \exp\left[\frac{\left(\mu_{H_2}^a - \mu_{H_2,eq}^{g,a}\right) + \left(\tilde{\mu}_{O^=}^a - \tilde{\mu}_{O^=,eq}^{YSZ,a}\right)}{\overline{R}T} \right] - \exp\left[\frac{\left(\mu_{H_2O}^a - \mu_{H_2O,eq}^{g,a}\right) + 2\left(\tilde{\mu}_{e^-}^a - \tilde{\mu}_{e^-,eq}^{Ni,a}\right)}{\overline{R}T} \right] \right\}$$

Grouped in this way, it is immediately apparent that three of the terms correspond precisely to the electrochemical transport-loss terms determined above. Rewriting this expression in terms of these (known!) values yields

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[3] If we designate the measured exchange current density of an electrode by i_{eq}, the equilibrium reaction rate is then given by $R_{eq} = i_{eq}/(2F)$. This applies to both the anode and the cathode.

$$v = R_{eq}^a \left\{ \exp\left[\frac{-\Delta\mu_{H_2}^{GDL,a} + \left(\tilde{\mu}_{O^=}^a - \tilde{\mu}_{O^=,eq}^{YSZ,a} \right)}{\bar{R}T} \right] - \exp\left[\frac{\Delta\mu_{H_2O}^{GDL,a} + 2\Delta\tilde{\mu}_{e^-}^{Ni,a}}{\bar{R}T} \right] \right\}$$

This may be rearranged to obtain the potential of the oxygen ion at the anode in terms of its (known) equilibrium value explicitly

$$\tilde{\mu}_{O^=}^a = \tilde{\mu}_{O^=,eq}^{YSZ,a} + \Delta\mu_{H_2}^{GDL,a} + \bar{R}T \ln\left\{ \frac{v}{R_{eq}^a} + \exp\left[\frac{\Delta\mu_{H_2O}^{GDL,a} + 2\Delta\tilde{\mu}_{e^-}^{Ni,a}}{\bar{R}T} \right] \right\}$$

Continuing down through the cell, we know that the electrochemical potential of the oxygen ion at the cathode must exceed its value at the anode by the amount required to drive the ion flux across the electrolyte. As before, the magnitude of this potential difference can be found in terms of YSZ conductivity data as

$$\Delta\tilde{\mu}_{O^=}^{YSZ} = J_{O^=} L_{YSZ} / \kappa'_{YSZ,O^=}$$

such that the electrochemical potential of the ion on the cathode side of the YSZ is then known

$$\tilde{\mu}_{O^=}^c = \tilde{\mu}_{O^=}^a + \Delta\tilde{\mu}_{O^=}^{YSZ}$$

We are almost in a position to tackle the cathode triple junction. The only thing we still need is to establish the transport potential loss for the oxygen

$$\Delta\mu_{O_2}^{GDL,c} = -\bar{R}T \ln\left(\frac{x_{O_2}^c}{x_{O_2}^{g,c}} \right)$$

where the cathode oxygen mole fraction $x_{O_2}^c$ is given in terms of its supply-side value $x_{O_2}^{g,c}$ and flux $J_{O_2}^c$ by

$$x_{O_2}^c = 1 - \left(1 - x_{O_2}^{g,c} \right) \exp\left(\frac{J_{O_2}^c L_{GDL,c}}{c D_{O_2-N_2}} \right)$$

yielding the cathode oxygen potential

$$\mu_{O_2}^c = \mu_{O_2,eq}^{g,c} - \Delta\mu_{O_2}^{GDL,c}$$

The cathode triple-junction reaction rate expression follows the same form as that for the anode

$$v = R_{eq}^c \left\{ \exp\left[\frac{\left(\tilde{G}_R^c - \tilde{G}_{R,eq}^c \right)}{\bar{R}T} \right] - \exp\left[\frac{\left(\tilde{G}_P^c - \tilde{G}_{P,eq}^c \right)}{\bar{R}T} \right] \right\}$$

Written explicitly for the cathode reaction, this becomes

$$\mathrm{v} = R_{eq}^c \left\{ \exp\left[\frac{\frac{1}{2}\left(\mu_{O_2}^c - \mu_{O_2,eq}^{g,c}\right) + 2\left(\tilde{\mu}_{e^-}^c - \tilde{\mu}_{e^-,eq}^{Ni,c}\right)}{\bar{R}T} \right] - \exp\left[\frac{\left(\tilde{\mu}_{O^=}^c - \tilde{\mu}_{O^=,eq}^{YSZ,c}\right)}{\bar{R}T} \right] \right\}$$

Substituting in the oxygen transport loss, yields

$$\mathrm{v} = R_{eq}^c \left\{ \exp\left[\frac{-\frac{1}{2}\Delta\mu_{O_2}^{GDL,c} + 2\left(\tilde{\mu}_{e^-}^c - \tilde{\mu}_{e^-,eq}^{Ni,c}\right)}{\bar{R}T} \right] - \exp\left[\frac{\left(\tilde{\mu}_{O^=}^c - \tilde{\mu}_{O^=,eq}^{YSZ,c}\right)}{\bar{R}T} \right] \right\}$$

Since both the cathode-side, oxygen-ion potential and its equilibrium value are known, this may be rearranged to give the cathode electron potential in terms of its (known) equilibrium value

$$\tilde{\mu}_{e^-}^c = \tilde{\mu}_{e^-,eq}^{Ni,c} + \frac{1}{4}\Delta\mu_{O_2}^{GDL,c} + \frac{1}{2}\bar{R}T \ln\left\{ \frac{\mathrm{v}}{R_{eq}^c} + \exp\left[\frac{\left(\tilde{\mu}_{O^=}^c - \tilde{\mu}_{O^=,eq}^{YSZ,c}\right)}{\bar{R}T} \right] \right\}$$

All that remains is to add the electrochemical potential loss associated with drawing electrons from the cathode-side terminal to the triple junction

$$\Delta\tilde{\mu}_{e^-}^{Ni,c} = J_{e^-}^c \, L_{Ni,c} \big/ \kappa'_{Ni,e^-}$$

such that the electrochemical potential at the cathode-side terminal is

$$\tilde{\mu}_{e^-,t}^{Ni,c} = \tilde{\mu}_{e^-}^c + \Delta\tilde{\mu}_{e^-}^{Ni,c}$$

Subtracting the anode-side terminal electrochemical potential ($\tilde{\mu}_{e^-,t}^{Ni,a} = \tilde{\mu}_{e^-,eq}^{Ni,a}$, our reference value) from that of the cathode yields the electrochemical potential difference of electrons at the output terminals of the cell, which, for electrodes made of the same material and operating at the same temperature, gives the output electrical potential difference of the cell

$$\tilde{\mu}_{e^-,t}^{Ni,c} - \tilde{\mu}_{e^-,t}^{Ni,a} = \left(\mu_{e^-,t}^{Ni,c} + z_{e^-}F\phi_t^{Ni,c}\right) - \left(\mu_{e^-,t}^{Ni,a} + z_{e^-}F\phi_t^{Ni,a}\right) = -F\left(\phi_t^{Ni,c} - \phi_t^{Ni,a}\right)$$

$$\phi_t^{Ni,c} - \phi_t^{Ni,a} \equiv \Delta\phi_t = -\frac{1}{F}\left(\tilde{\mu}_{e^-,t}^{Ni,c} - \tilde{\mu}_{e^-,t}^{Ni,a}\right)$$

This, along with the set of intermediary electrochemical potentials, is what we were after. From this set of potentials, any of the conventional fuel cell performance metrics—including stage-by-stage analysis of the loss of electrochemical potential—can be easily assembled.

Transport in Terms of Electrochemical Potential

There are two types of transport problem encountered in a solid-oxide fuel cell: ionic transport (including electrons) and transport of gaseous species. Because the first problem involves unalterable concentrations of charged particles (electrons, ions) within the transport medium, the driving force requirement for a specified flux is usually expressed in terms of an electrical

conductivity. That being the case, the only thing we need to do is to shift from that view to the more general view that these fluxes are driven by electrochemical potential. In the second problem—gaseous transport—the concentration of particles within the medium varies, and the driving force is expressed in terms of gradients in either concentration or mole fraction by a diffusion coefficient or a diffusivity. In that case we will need to deal with both the complications introduced by the variable concentration of carriers (i.e., solve for the mole fraction profile) as well as shift our viewpoint to one based on chemical potential as the driving force. That is what we address below.

Ionic/Electronic Transport

Shifting viewpoints from one of ionic-conduction/electrical-potential to one of species-conduction/electrochemical-potential requires that we find both the appropriate force-flux relationship and how property data are converted for use with that relationship. This can be done by recognizing the equivalence of the two forms. In other words, that driving a flux of a certain amount of charge $\vec{j}_i$, by use of an electrical potential gradient $\nabla \phi$, is equivalent to driving the corresponding flux of the species $\vec{J}_i$, by the corresponding gradient in its electrochemical potential $\nabla \tilde{\mu}$. In symbolic form

$$\vec{j}_i = \kappa_i \left(-\nabla \phi \right) \Leftrightarrow \vec{J}_i = \kappa_i' \left(-\nabla \tilde{\mu} \right)$$

where κ_i is the electrical conductivity, and κ_i' is the corresponding species conductivity. The magnitude of these fluxes are related by the charge on the species and Faraday's constant

$$J_i = \frac{j_i}{|z_i| F}$$

For conduction in a homogeneous, incompressible solid, the electrical and electrochemical potentials are related by

$$\tilde{\mu}_i \left(T, \phi \right) = \mu_i \left(T, \phi = 0 \right) + z_i F \phi$$

If the conductor is isothermal this implies that

$$\nabla \tilde{\mu}_i = z_i F \nabla \phi$$

Equating the magnitude of the species flux in both frames of reference

$$J_i = \frac{j_i}{|z_i| F} = \frac{1}{|z_i| F} \kappa_i |\nabla \phi| = \frac{1}{|z_i| F} \kappa_i \left| \frac{\nabla \tilde{\mu}}{z_i F} \right| = \frac{1}{\left(z_i F \right)^2} \kappa_i |\nabla \tilde{\mu}|$$

This shows that the conductivity in the electrochemical frame of reference is given in terms of the electrical value by

$$\kappa_i' = \kappa_i / \left(z_i F \right)^2$$

Since the conductor is uniform, and the flux through it is constant, the drop in electrochemical potential across it is given by the product of the gradient and the distance over which the conduction must occur. The resulting expression for the magnitude of the potential drop is

$$\Delta \tilde{\mu}_i = L\left|\nabla \tilde{\mu}\right| = J_i \, L/\kappa_i'$$

which is the result we require for the driving electrochemical potential of electrons and ions in our fuel cell analysis.

Transport in the Gas Diffusion Layers

The other transport problem we must solve is that of gas diffusion through the porous layers adjacent to either electrode. While multicomponent gas diffusion is a challenging topic, we are fortunate in that, for both the anode and cathode, only two species are present: hydrogen and water at the anode, and oxygen and nitrogen (assuming binary air) at the cathode. As such we have a simplified problem of binary diffusion to deal with, and this is further simplified since the high temperatures involved ensure that all the species are well modeled as ideal gases.

The binary diffusivity of an ideal gas is defined implicitly by the expression for its associated flux rate

$$\vec{J}_i = cD_{ij}\left(-\nabla x_i\right)$$

This states that the diffusive flux of species i in the presence of species j is proportional to the total concentration of species, $c = P/(\bar{R}T)$, the binary diffusivity, $D_{ij} = D_{ij}(T,P)$, which is independent of composition but depends on temperature and pressure, and (minus) the gradient in mole fraction of the species of interest. Note that it is the total concentration that appears in this expression, not the concentration of species i. This is particularly useful in the case of ideal gases since the total concentration does not depend upon the particular species involved—all species occupy the same volume at a fixed temperature and pressure. As a consequence of the total concentration remaining fixed, we also know that if one of the two species is depleted, then its contribution to the local concentration must be exactly compensated by the other species. As such, pure binary diffusion at a fixed temperature and pressure becomes a relatively simple problem: If you solve for the composition profile of one of the species, you automatically know the profile for its complement. (This is also the reason why the binary diffusivity must be symmetric, $D_{ij} = D_{ji}$.)

Considering the case of hydrogen/water diffusion through the anode-side GDL, we see that this is a case of simple counterdiffusion—because each hydrogen molecule produces a single water molecule upon reaction, the flux rate of hydrogen moving towards the anode is exactly matched by an equal/opposite flux of water moving away from the anode. The matched fluxes result in there being no net flow (on a molar basis) in the anode GDL such that transport occurs only by diffusion.

Focusing attention on the hydrogen flux moving inward from the supply-side of the GDL we can write the flux expression as

$$\frac{\vec{J}_{H_2}}{cD_{H_2-H_2O}} = -\nabla x_{H_2}$$

For a specified flux rate, at uniform temperature and pressure (and in steady state), the left side of this expression is a constant. This immediately tells us that the mole fraction profile for hydrogen is linear (constant gradient) and declining in the direction of the anode with a slope of magnitude $J_{H_2}/(cD_{H_2-H_2O})$. Conversely, the mole fraction profile of the counter-diffusing water must also be linear, have the same magnitude for its slope, but in the opposite direction. These observations—it is not necessary to formally solve this problem—lead us to values of the mole fraction of hydrogen and water at the anode triple-junction side of the GDL as

$$x_{H_2}^a = x_{H_2}^{g,a} - J_{H_2} L_{GDL,a}/(cD_{H_2-H_2O})$$

$$x_{H_2O}^a = x_{H_2O}^{g,a} + J_{H_2O} L_{GDL,a}/(cD_{H_2-H_2O})$$

where $x_{H_2}^{g,a}$, $x_{H_2O}^{g,a}$ are the mole fractions at the supply-side of the GDL imposed by the reactant streams, and $L_{GDL,a}$ is the thickness of the anode gas diffusion layer.

With the mole fractions on each side of the GDL known, the losses of chemical potential are easily shown to be

$$\Delta\mu_{H_2}^{GDL,a} = -RT \ln\left(\frac{x_{H_2}^a}{x_{H_2}^{g,a}}\right), \quad \Delta\mu_{H_2O}^{GDL,a} = RT \ln\left(\frac{x_{H_2O}^a}{x_{H_2O}^{g,a}}\right)$$

with the mole fraction ratios given by

$$\frac{x_{H_2}^a}{x_{H_2}^{g,a}} = 1 - \frac{J_{H_2} L_{GDL,a}}{x_{H_2}^{g,a} cD_{H_2-H_2O}}, \quad \frac{x_{H_2O}^a}{x_{H_2O}^{g,a}} = 1 + \frac{J_{H_2O} L_{GDL,a}}{x_{H_2O}^{g,a} cD_{H_2-H_2O}}$$

Moving to the case of oxygen diffusion through the cathode-side GDL, we find a similar situation, but with a small twist. Now instead of having pure counterdiffusion—brought about by the matched return flux of species from the electrode—we have a net flow of species into the cathode. What this does is to add an additional component to the transport of oxygen through the gas diffusion layer, and instead of a purely diffusive flux, the flux is now mixed advection and diffusion:

$$\vec{J}_{O_2} = x_{O_2} \vec{J}_{total} + cD_{O_2-N_2}\left(-\nabla x_{O_2}\right)$$

In this expression, ordinary diffusion still occurs by virtue of the composition gradient within the GDL, but added to this is a bulk flux $\vec{J}_{total}$ carrying mole fraction x_{O_2} at any location. Fortunately we know the total flux rate: It is the rate at which oxygen is removed from the stream at the cathode. Making this substitution, we come to the slightly odd-looking expression for the flux-mole fraction relationship

$$\vec{J}_{O_2} = \frac{cD_{O_2-N_2}}{\left(1-x_{O_2}\right)}\left(-\nabla x_{O_2}\right)$$

In effect, presence of the bulk flow modifies the local mole fraction gradient to compensate for the bulk motion. Note that this effect is particularly important from the perspective of the counterdiffusing nitrogen, since it must now diffuse against the bulk flow to exit the GDL.

Writing this expression out in one dimension using y as the distance from the supply-side of the GDL, and separating variables we get

$$\left(\frac{J_{O_2}}{cD_{O_2-N_2}} \right) dy = \frac{-dx_{O_2}}{\left(1 - x_{O_2} \right)}$$

The term in the leading parentheses is again a known constant. Integrating from $y = 0$ to any specified value of y gives

$$x_{O_2}(y) = 1 - \left[1 - x_{O_2}(0) \right] \exp\left(\frac{J_{O_2} y}{cD_{O_2-N_2}} \right)$$

Recognizing that the oxygen concentration at $y = 0$ is the reactant supply value, and choosing $y = L_{GDL,c}$ gives the cathode triple-junction mole fraction as

$$x_{O_2}^c = 1 - \left(1 - x_{O_2}^{g,c} \right) \exp\left(\frac{J_{O_2} L_{GDL,c}}{cD_{O_2-N_2}} \right)$$

Again, with the mole fractions on each side of the GDL known, the loss of chemical potential is

$$\Delta\mu_{O_2}^{GDL,c} = -RT \ln\left(\frac{x_{O_2}^c}{x_{O_2}^{g,c}} \right)$$

Since the mole fraction ratio in the last term is neither particularly compact, nor informative, we will not write it out explicitly, but assume that you will program it directly.