Modeling a Proton Conducting Ceramic Electrolysis Cell to Determine the Effects of Electrolyte Thickness on Faradaic Efficiency and Ohmic Resistance

Introduction/Motivation:

I would like to model a proton-conducting ceramic electrolysis cell (PCEC), so that I can see how electrolyte thickness effects performance and faradaic efficiency. A PCEC is a solid state device made up of three layers: a positive electrode (positrode), a negative electrode (negatrode), and a dense electrolyte. The positrode is a porous layer of BCFZY. BCFZY is a doped perovskite that has the ability to conduct oxygen ions, protons, and electrons. The electrolyte is a thin layer (~10µm) of proton conducting BCZYYb. BCZYYb does exhibit some electronic leakage on top of proton conduction. The negative electrode is a porous layer of 40% BCZYYb and 60% Nickle.

Research has shown that increasing the thickness of the electrolyte increases ohmic resistance, but also increases faradaic efficiency[1]. I would like to see if I can model a PCEC such that I can find the optimal electrolyte thickens to balance faradaic efficiency and ohmic resistance.

Further, the Colorado Fuel Cell Center has recently obtained an ultrasonic spray coater, which will enable the electrolyte thickness to be tailored with relative ease. Many physical experiments will be done with spray coated cells to not only figure out how to best use the spray coater, but also to maximize performance and faradaic efficiency. A model could assist in maximizing performance, while also saving time and resources by reducing the amount of physical experiments.

Model Formulation:

An interesting detail of PCECs is that they are reversible and can be ran in "reverse" as a fuel cell. This means that the chemical potentials are the main driving force for the electric potential of the cell. For ease of modeling, the model started out as a quasi 2D PCFC model. The phenomena modeled are: gas transport into each electrode, the charge transfer reactions, and the subsequent proton, oxygen ion, and electron diffusion. The model is also a single particle model, no layers are discretized (however there are two different sections of the negatrode). Also, the cell is at 525°C and atmospheric pressure.

Negatrode are commonly called anodes, but in the case of a reversible cell, the anode acts as a cathode when ran in electrolysis mode, thus making the name "anode" confusing. However, regardless of which direction the cell is running in, one electrode will be negative and the other will be positive. Thus the terms "negatrode" and "positrode" are used for the electrodes

The plan was to finish the model as a PCFC, then code in an applied bias to override the chemical potential and run the cell as a PCEC. Then the model would be ran under multiple electrolyte thicknesses from 5µm to 25µm. Unfortunately the model is still in the PCFC stages. The rest of this section will go through each of the three areas of modeling for all three layers of the cell. Figure 1 shows a cross section model of a cell running in fuel cell mode.

Assumptions:

- There are no transport limitations in the gas phase such that the gas phase concentrations are fixed.
- The amount of lattice sites are fixed.
- Each layer is treated as a single particle.
- The whole surface of the BCFZY positrode is active
- There are no side reactions happening. There are only two reactions at each electrode.
- The electrodes are modeled as packed spheres for gas transport.
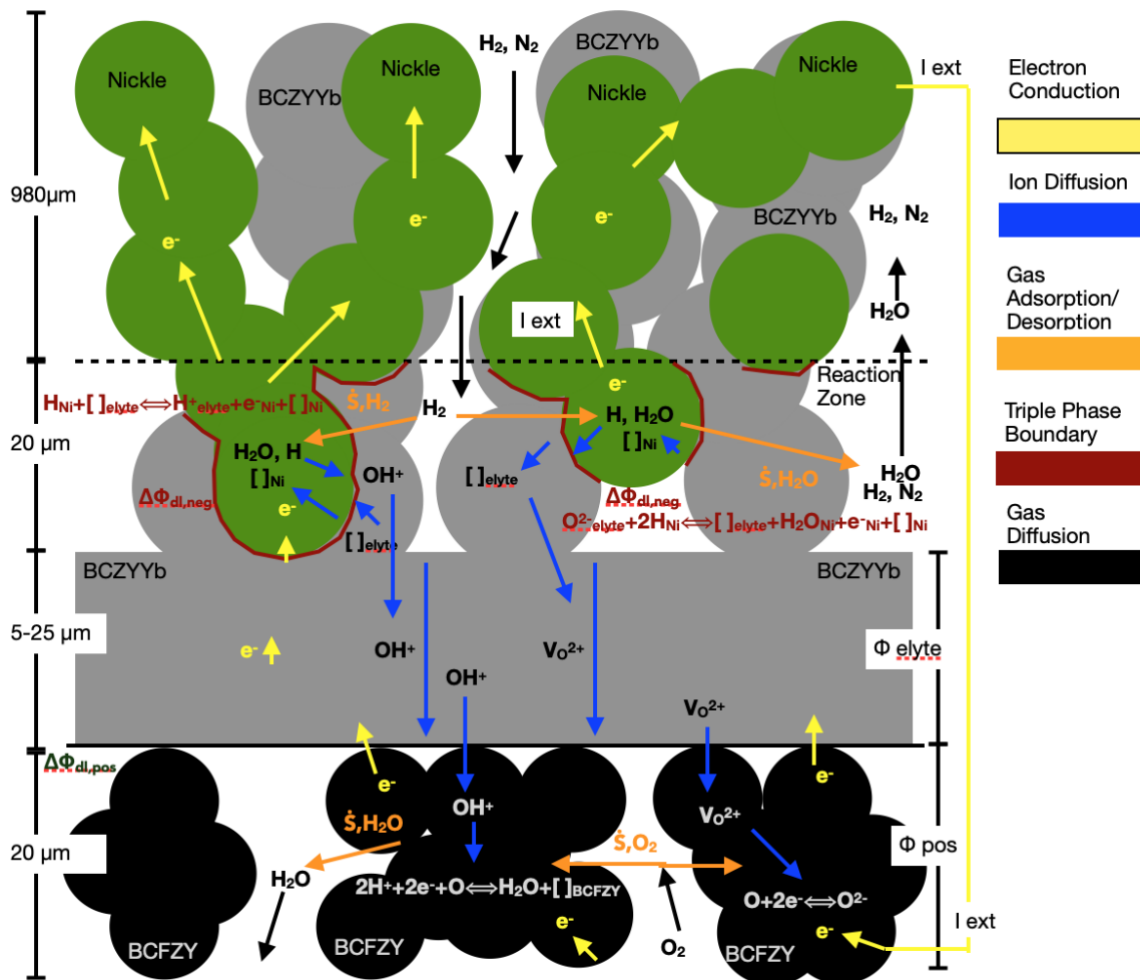- The Bruggeman coefficient is 0.5.

Figure 1. Cross section of a PCFC. This model is not to scale and is to be used to visualize the phenomena to be modeled. Although this model shows the proton and oxygen ion reactions as separate, they happen concurrently at the TPB in the negatrode and at the surface of the positrode.

Negatrode:

The negatrode is a 1mm thick cermet made from 60wt% BCZYYb which is a mixed oxygen and proton conduction and 40% Ni which is electrochemically active and is an electron conductor. The first 980μm of the negatrode are too far from the electrolyte for the species diffusion to have a relevant effect on performance, so it is just modeled as a gas transport zone. In this model there is an abundance of reactants so, the concentration of species in this layer is constant. In the bottom 20μm of the negatrode (reaction zone) gas transport, surface reactions, charge transfer reactions, and species diffusion is modeled.
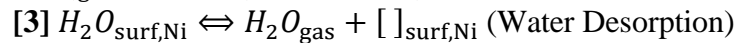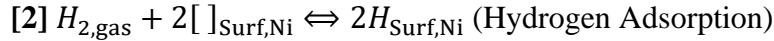
Gas transport between the gas transport layer and the reaction layer is modeled by the gas diffusing down a concentration gradient and down pressure gradients modeled by Darcy's law which is shown in (Eq.1): In the negatrode there will be hydrogen gas, nitrogen gas, and steam (from the surface reactions)

$$[1] \; N_k = C_{int} * X_k * (-\frac{K_g}{\mu}\nabla P + \frac{D_k * \epsilon_{gas}\nabla X_k}{\tau_{fac}X_k})$$

Where N_k is the species molar flux, C_{int} is the average gas concentration at the interface, X_k is the average mol fraction of species k at the interface, K_g is the gas permeability of the

negatrode,μ is the dynamic viscosity of the gas, P is pressure, ε_{gas} is the volume fraction of the gas phase, and τ_{fac} is the tortuosity factor, and $D_{eff,k}$ is the diffusivity of species k. For now μ and D_k at 550°C were taken from HW5, and ε_{gas} is estimated from SEM images. In this model I am assuming an abundant amount of gas flow, such that the gas concentrations in the gas transport layer are constant. Therefore I only need to track the gas concentrations in the reaction layer, which will be in my solution vector as C,k,rxn,neg.

The other component that changes the gas concentrations in the reaction layer is the gas phase surface reactions at the negatrode. Eq. 2 and Eq. 3 are two reactions that occur on the surface of the nickel that effect the molar flux of the hydrogen and steam. These only occur in the reaction zone.

$$[2] \; H_{2,gas} + 2[\,]_{Surf,Ni} \Longleftrightarrow 2H_{Surf,Ni} \text{ (Hydrogen Adsorption)}$$
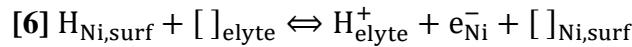$$[3] \; H_2O_{surf,Ni} \Longleftrightarrow H_2O_{gas} + [\,]_{surf,Ni} \text{ (Water Desorption)}$$

Originally the plan was to calculate the molar flux's of the Hydrogen and steam using the reaction rate constants and mass action kinetics. However that proved to be difficult so now the molar fluxes are modeled using the faradaic current of the negatrode seen in Eq. 4 and Eq.5.

$$[4] \; \dot{s}_{H_2 gas,surf} = 0.5 \; \frac{i_{far,neg,p} * \nu_{H,Ni,Neg,p}}{n_{neg,p} * F} + \frac{i_{far,neg,o} * \nu_{H,Ni,Neg,o}}{n_{neg,o} * F}$$

$$[5] \; \dot{s}_{H_2O,gas,surf,neg} = \frac{i_{far,neg,o} * \nu_{H_2O,Ni,Neg,o}}{n_{neg,o} * F}$$

The i_{far} terms are the faradaic current terms at the negatrode. There are two components to i_{far} in the negatrode and they are due to the charge transfer reactions that produce protons (subscript p) and consume oxygen ions (subscript o). The n and ν values are from the half cell equations for the two surface charge transfer reactions Eq.6 and Eq.7 that happen at the triple phase boundary of the Ni and the electrolyte.

$$[6] \; H_{Ni,surf} + [\,]_{elyte} \Longleftrightarrow H^+_{elyte} + e^-_{Ni} + [\,]_{Ni,surf}$$
$$[7] \; O^{2-}_{elyte} + 2H_{Ni,surf} \Longleftrightarrow [\,]_{elyte,surf} + H_2O_{Ni,surf} + [\,]_{Ni} + 2e^-$$

Using Eq. 6 and Eq. 7, the molar fluxes of the 6 charge transfer species can be calculated, as shown in Eq.8-13 (mol/s). In the subscripts there are the letters "p" and "o", which correspond to Eq. 6 (the protonic transfer equation) and Eq.7 (The oxygen ion transfer equation) respectively. Again these equations are only for modeling in the reaction zone.

$$[8] \; \dot{s}_{H,Ni,surf} = \frac{\nu_{H,Ni,p} * i_{far,neg,p}}{n_p F} + \frac{\nu_{H,Ni,o} * i_{far,neg,o}}{n_o F}$$

$$[9] \; \dot{s}_{H^+,elyte} = \frac{\nu_{H^+,elyte,neg,p} * i_{far,neg,p}}{n_p F}$$

$$[10] \; \dot{s}_{O^{2-},elyte} = \frac{\nu_{O^{2-},elyte,o} * i_{far,neg,o}}{n_o F}$$

$$[11] \; \dot{s}_{H_2O,Ni,surf} = \frac{\nu_{H_2O,Ni,o} * i_{far,neg,o}}{n_o F}$$

$$[12] \; \dot{s}_{[\,],elyte} = \frac{\nu_{[\,],elyte,p} * i_{far,neg,p}}{n_p F} + \frac{\nu_{[\,],elyte,o} * i_{far,neg,o}}{n_o F}$$

$$[13] = \dot{s}_{[\,],Ni,surf} = \frac{\nu_{[\,],Ni,surf,p} * i_{far,neg,p}}{n_p F} + \frac{\nu_{[\,],Ni,surf,o} * i_{far,neg,o}}{n_o F}$$

The molar flux equations (Eq. 4-5,8-13) were then needed to calculate the change in concentrations of the species in the negatrode (mol/m²-s). The concentrations of the six surface species will be tracked in the solution vector. The changes in concentration will be calculated

using Eq. 14-19. Where L_{TPB} is the length of the triple phase boundary, and A_{Ni} is the surface area of the Ni, and were calculated using simple geometry based off of SEM images that I have taken. $J_{k,Dif}$ is the diffusion flux

$$[14] \frac{dC_{H,Ni,surf}}{dt} = 2 * \dot{s}_{H_2,gas,surf} - \dot{s}_{H,Ni,surf} * \frac{L_{TPB}}{A_{surf,Ni}}$$

$$[15] \frac{dC_{H^+,elyte}}{dt} = \dot{s}_{H^+,elyte} * \frac{L_{TPB}}{A_{surf,Ni}}$$

$$[16] \frac{dC_{O^{2-},elyte}}{dt} = \dot{s}_{O^{2-},elyte} - \dot{s}_{H_2O,surf} * \frac{L_{TPB}}{A_{surf,Ni}}$$

$$[17] \frac{dC_{H_2O,Ni,surf}}{dt} = \dot{s}_{H_2O,Ni,surf} * \frac{L_{TPB}}{A_{surf,Ni}} - \dot{s}_{H_2O,gas,surf,neg}$$

$$[18] \frac{dC_{[],elyte}}{dt} = \dot{s}_{[],elyte} * \frac{L_{TPB}}{A_{surf,Ni}}$$

$$[19] \frac{dC_{[],Ni,surf}}{dt} = -\left(2 * \dot{s}_{H_2,gas,surf} + \dot{s}_{H_2O,gas,surf,neg}\right) + \dot{s}_{[],Ni,surf} * \frac{L_{TPB}}{A_{surf,Ni}}$$

This is where I had significant trouble getting the model to run well and ultimately as far as I got. I will still hash out the plan for the rest of the model. Anyway, the concentrations of each species are important because the faradaic current is being calculated through mass action kinetics as follows.

$$[20] i_{MA} = nF \left(k_{fwd}^* \exp\left(\frac{-\beta n_{elec}F\Delta\phi}{RT}\right) \prod_m C_{ac,k}^{v_k'} - k_{rev}^* \exp\left(\frac{(1-\beta)n_{elec}F\Delta\phi}{RT}\right) \prod_m C_{ac,k}^{v_k''} \right)$$

The total faradaic current was calculated by adding together the current from the protonic and oxide reactions as seen in Eq. 21. In the negatrode there is an ionic current from the chemical reactions, electric external current, and a double layer current to balance out the other two currents. The external current was hard coded in, and the faradaic current was calculated with Eq.21, so i_{dl} (which is i_{int} in the code) was calculated with Eq. 22. i_{dl} is crucial for calculating the potential difference at the negatrode/electrolyte interface, Eq.23, (which is tracked by the solution vector). $C_{dl,neg}$ is the capacitance at the electrolyte/negatrode interface and is hard coded into the code.

$$[21] i_{far} = i_{far,p} + i_{far,o}$$
$$[22] i_{dl} = i_{ext} - i_{far}$$
$$[23] \Delta\phi_{dl,neg} = \frac{i_{dl,neg}}{C_{dl,neg}}$$

Thus completing the phenomena modeled in the negatrode. $\Delta\Phi_{dl,neg}$ is the cumulation of all processes in the negatrode and is the parameter that is the most sought in this layer. A summary of all parameters tracked in the negatrode, C,k,rxn,neg is a 3x1 vector consisting of H_2, N_2, and steam respectively.

$$[24] SV_{neg} = \begin{bmatrix} \Delta\phi_{dl,neg} \\ C_{k,rxn,neg} \\ C_{H,Ni,surf} \\ C_{H^+,elyte} \\ C_{O^{2-},elyte} \\ C_{H_2O,Ni,surf} \\ C_{[],elyte} \\ C_{[],Ni,surf} \end{bmatrix}$$

Electrolyte:

The electrolyte is being modeled as two separate layers. The first is the porous 20μm of electrolyte in the negatrode. The second is a dense 5-25μm layer that will be varied to see the effect of electrolyte thickness on faradaic efficiency and performance. In the electrolyte the only phenomena to model are electric and ionic conductivity. Although there are only two layers to model, there are three states that will be used in the calculations. The diffusing ionic species will be tracked at the nickel/negatrode interface in the negatrode, the negatrode/solid electrolyte interface, and the electrolyte/positrode interface.

The diffusivities of the protons and oxygen ions in a BCZYYb7111 electrolyte were found in a paper by Zhu et al[2]. In the code, and in Figure 1, diffusing protons and oxygen ions are written as OH^+ and V_O^{2-} (This is actually what is diffusing in reality). Species diffusion flux, N_k, was calculated by:

$$[25] \; N_k = -D_{k,BCZYYb} * \epsilon^{1.5} \nabla C_k - D_{k,BCZYYb} * \epsilon^{1.5} C_k \frac{z_k F}{RT} \nabla \phi$$

Here $D_{k,BCZYYb}$ is the diffusivity of species k in the BCZYYb7111 electrolyte at 550°C and in the code is a three species vector containing OH^+ ,O, and V_O^{2-} respectively. C_k is the concentration of species k, z_k is the charge of species k, and $\nabla \phi$ is the differential of electric potential across the electrolyte. ε is the volume fraction of electrolyte in the layer and is 0.191 in the negatrode layer and 1 in the electrolyte layer. ε is to the power of 1.5 because the Bruggeman factor is assumed to be -0.5 The total ionic conductivity was calculated as:

$$[26] \; i_{ion} = F \sum_k z_k N_k$$

The electronic conductivity is a function of the electrical conductivity of the electrolyte (σ_{el}), the layer thickness (dy), and the potential difference across the layer. σ_{el} for BCZYYb was found in a paper by Somekawa et al[3]. Electrical conductivity was calculated using the equation below:

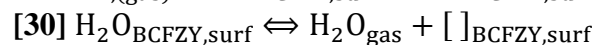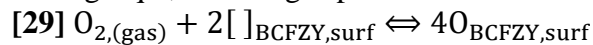$$[27] \; i_e = \frac{-(\phi_2 - \phi_1)\sigma_{el}}{dy}$$

The electric current will be tracked. The base electrolyte code has been made in a jupyter notebook, but it has not been integrated and tested into the main project. Below are the electrolyte variables tracked in the SV:

$$[28] \; SV_{ely} = \begin{bmatrix} C_{k,ion,Ni,ely} \\ C_{k,ion,Neg,ely} \\ C_{k,ion,ely,pos} \\ i_e \end{bmatrix}$$

Positrode:

The positrode is a 20μm thick porous layer of a triple-conducting oxide BCFZY. Like the negatrode gas transport, surface reactions, charge transfer reactions, and species diffusion is modeled. The positrode is different from the negatrode because all the diffusion species and the electrons all flow through the bulk of the BCFZY to the surface. Eq. 25, Eq, 26, and Eq. 27 will be used to model this. The concentrations of the ionic species in the bulk will be tracked The electrical and ionic diffusivity properties of BCFZY were found in a paper by Song et al[4]. Eq. 22 and Eq. 23 can use the ionic current flowing from the electrolyte to calculate the double layer potential between the positrode and the electrolyte.

Gas transport was modeled using Eq.1, and the gas phase surface reactions are:

$$[29] \; O_{2,(gas)} + 2[\,]_{BCFZY,surf} \Longleftrightarrow 4O_{BCFZY,surf}$$
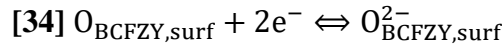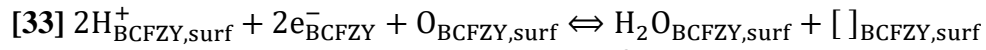$$[30] \; H_2O_{BCFZY,surf} \Longleftrightarrow H_2O_{gas} + [\,]_{BCFZY,surf}$$

The gas species concentration is not being tracked. It is a fixed value due to the assumption that there are no gas transport limitations. The molar flux equations for the gas species can be calculated as:

$$[31] \; \dot{s}_{O_2 gas,surf} = 0.5 \left(\frac{i_{far,pos,p} * \nu_{O,surf,pos,p}}{n_{pos,p} * F} + \frac{i_{far,pos,o} * \nu_{O,surf,pos,o}}{n_{pos,o} * F} \right)$$

$$[32] \; \dot{s}_{H_2 O,gas,surf,pos} = \frac{i_{far,pos,p} * \nu_{H_2 O,BCFZY,pos,p}}{n_{pos,p} * F}$$

Just like in the negatrode the gas phase molar fluxes are modeled using the faradaic current of the positrode. The two surface charge transport reactions are listed below:

$$[33] \; 2H^+_{BCFZY,surf} + 2e^-_{BCFZY} + O_{BCFZY,surf} \Leftrightarrow H_2 O_{BCFZY,surf} + [\,]_{BCFZY,surf}$$

$$[34] \; O_{BCFZY,surf} + 2e^- \Leftrightarrow O^{2-}_{BCFZY,surf}$$

The molar flux of each species due to the gas phase and charge transfer reactions is determined by:

$$[35] \; \dot{s}_{H^+,surf} = \frac{\nu_{H^+,surf,p} * i_{far,pos,p}}{n_{pos,p} F}$$

$$[36] \; \dot{s}_{O,pos,surf} = \frac{\nu_{O,surf,p} * i_{far,pos,p}}{n_{pos,p} F} + \frac{\nu_{O,surf,o} * i_{far,pos,o}}{n_{pos,o} F}$$

$$[37] \; \dot{s}_{O^{2-},surf} = \frac{\nu_{O^{2-}-surf,o} * i_{far,pos,o}}{n_{pos,o} F}$$

$$[38] \; \dot{s}_{H_2 O,pos,surf} = \frac{\nu_{H_2 O,surf,p} * i_{far,p}}{n_{pos,p} F}$$

$$[39] \; \dot{s}_{[\,],BCFZY,surf} = \frac{\nu_{[\,],BCFZY,p} * i_{far,p}}{n_{pos,p} F}$$

The concentrations of each of the 5 charge transfer species are tracked in the solution vector. Calculating the change in concentration for the positrode is easier than in the negatrode because all of the surface is active, so the distance unit on all the molar flux values is the same (just the surface area, calculated from SEM images). Below are the equations that calculate the change in concentration due to the surface species due to the gas phase surface reactions and the charge transfer equations:

$$[40] \; \frac{dC_{H^+ surf}}{dt} = \dot{s}_{H^+,surf}$$

$$[41] \; \frac{dC_{O,pos,surf}}{dt} = \dot{s}_{O,pos,surf} + 2 * \dot{s}_{O_2 gas,surf}$$

$$[42] \; \frac{dC_{O^{2-},surf}}{dt} = \dot{s}_{O^{2-},surf}$$

$$[43] \; \frac{dC_{H_2 O,pos,surf}}{dt} = \dot{s}_{H_2 O,pos,surf} - \dot{s}_{H_2 O,gas,surf,pos}$$

$$[44] \; \frac{dC_{[\,],BCFZY}}{dt} = \dot{s}_{[\,],BCFZY} + \dot{s}_{H_2 O,gas,surf,pos} - \dot{s}_{O_2 gas,surf}$$

Positrode faradaic current is calculated the same way as the negatrode. Eq.21, Eq.22, and Eq.23 are used to calculate the component $\Delta\Phi_{dl,pos}$ from the surface reactions. The positrode contributions to the solution vector are:

$$[45]\ SV_{neg} = \begin{bmatrix} \Delta\phi_{dl,pos} \\ C_{k,ion,ely,pos} \\ C_{H^+,surf} \\ C_{O,pos,surf} \\ C_{O^{2-},surf} \\ C_{H_2O,pos,surf} \\ C_{[\ ],BCFZY,surf} \end{bmatrix}$$

The total ideal solution vector is listed below:

$$[46]\ SV_{neg} = \begin{bmatrix} \Delta\phi_{dl,neg} \\ C_{k,rxn,neg} \\ C_{H,Ni,surf} \\ C_{H^+,elyte} \\ C_{O^{2-},elyte} \\ C_{H_2O,Ni,surf} \\ C_{[\ ],elyte} \\ C_{[\ ],Ni,surf} \\ C_{k,ion,Ni,ely} \\ C_{k,ion,Neg,ely} \\ C_{k,ion,ely,pos} \\ i_e \\ \Delta\phi_{dl,pos} \\ C_{k,ion,ely,pos} \\ C_{H^+,surf} \\ C_{O,pos,surf} \\ C_{O^{2-},surf} \\ C_{H_2O,pos,surf} \\ C_{[\ ],BCFZY,surf} \end{bmatrix}$$

Results/Discussion:

I was not able to get the code to work, so unfortunately there are not much results to discuss. One thing I would like to mention is that changing the solve_ivp method to BDF greatly helped in the calculations. Before it was set to BDF everything I tried went to negative infinity.

I did get some data when I was only modeling charge transfer and only tracking the positrode and negatrode potentials data was obtained. The two double layer potentials quickly move to equlibrium values. This makes sense because in this model the only variables that
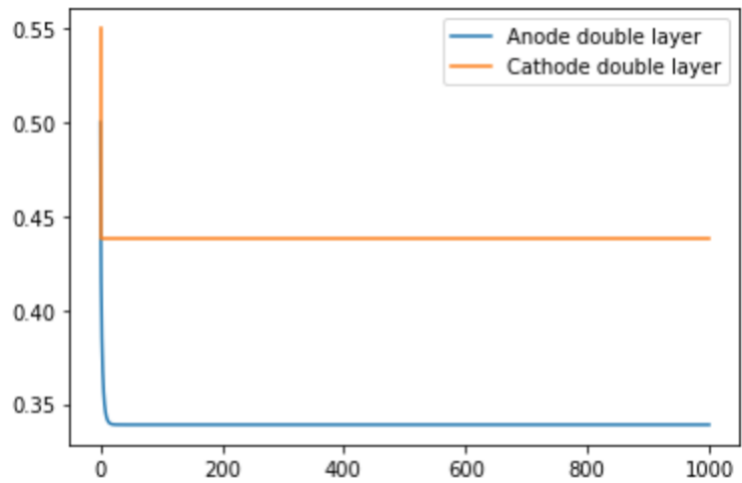

Figure 2. Double layer potentials of the most basic model. Both decrease to an equilibrium point relatively quickly
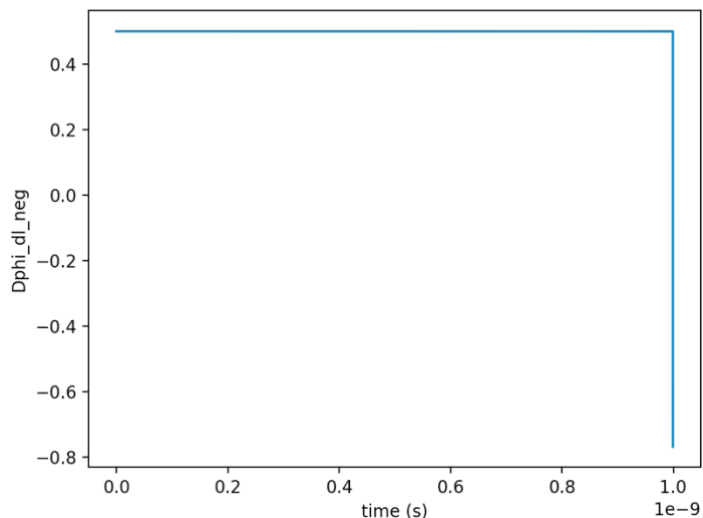
Figure 3. Negatrode double layer potential as a function of time. The model goes to negative infinity quite quickly.
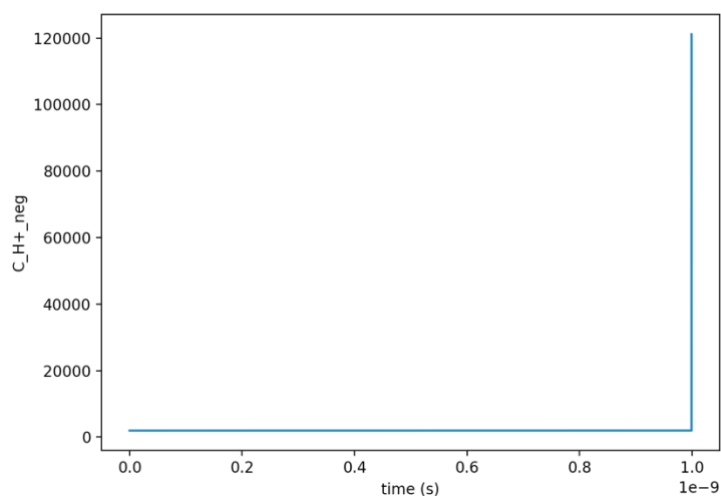

Figure 4. The proton concentration in the negatrode as a function of time. There is no balancing equation, so the concentration will just increase.

are changing are the double layer potentials, so not many things have to allign to form an equlibrium.

I am currently trying to incorporate the gas transport and charge transfer equations for the negatrode into the model. Current process has the solver breaking almost instantly, as seen in Figure 3, the time scale is in 10^{-9}s. This is likely due to the species surface concentrations. When the gas phase reactions were coded in (Eq.4,5), there was then an imbalance, species were being created and none were being destroyed so the equilibrium concentration was then infinity. The charge transfer equations were added in to remedy this problem (Eq.14 – Eq.19). However there is still an imbalance in the species because diffusion out of the negatrode was not accounted for. For example, there is nothing accounting for protons leaving the negatrode, so the concentration will just increase indefinietly, which is seen in Figure 4. Throwing off one species will throw off all other variables in this case since all of the species are intertwined and since the double layer potential is a function of all of the species concentrations.

Conclusions:

Again, unfortunately I was not able to properly form a model and draw conclusions, so really this sections will just be things I thought I did wrong and learned from while doing this project.

One thing I wish I did was look up the physical inputs from literature as I coded in each section into the jupyter notebooks. There were times where I could not tell if there was an error because of my code or because my input variable is throwing off the solver.

This lead to the next thing I wish I did better was that since I did not know if my input variables were any good, I would just try to prematurely code in the next section. This made it really hard to pinpoint where problems were coming from. Stalling progress to a halt.

Memes:
The memes flowed much more freely than the coding, so I was able to finish this section.
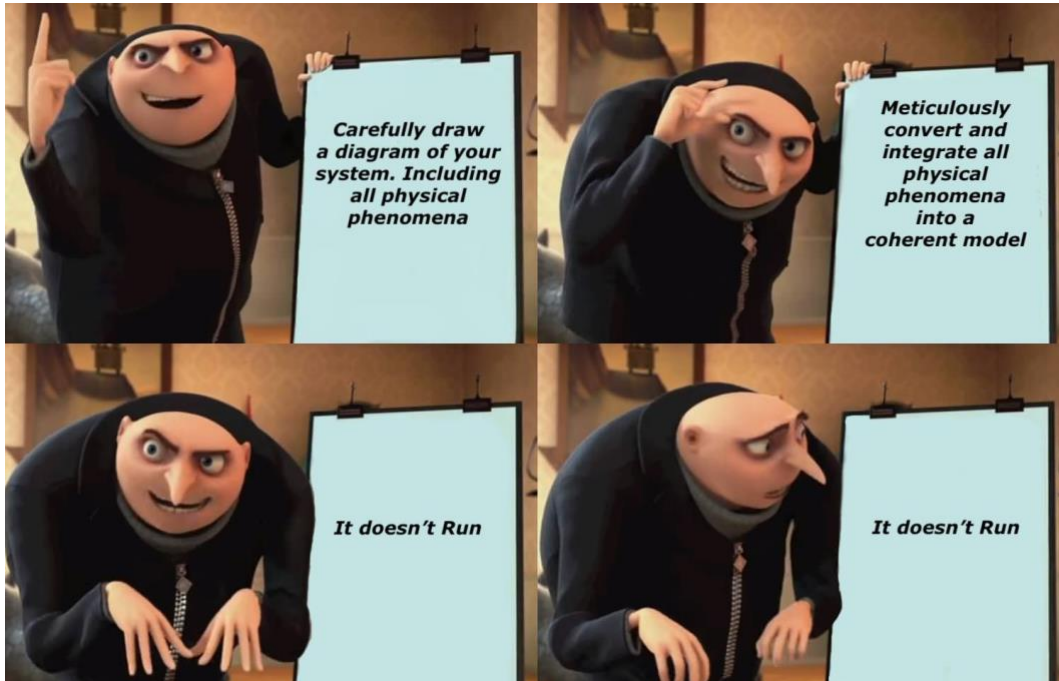
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