

On the Development of a Molten Salt Electrorefining Simulation

Dakota S. Banks*

Chemical Engineering Department, Brigham Young University, Provo, Utah

E-mail: dakotasb@byu.edu

Abstract

This document provides instructions for making an *outline* of a paper. The instructions here correspond to Step 3 of the process described in the README and in Whitesides article. Once you have an outline (and data of course), writing a paper is a relatively straightforward (but often time-consuming) process.

At the outline stage, do not write an abstract. Writing the abstract is typically the last step before you submit a paper.

Introduction

Molten salt electrorefining is an area of significant interest in the production and purification of many of the worlds important metals including aluminum, uranium, titanium and many others. Electrorefining in general is fairly well understood in aqueous systems however there is much more uncertainty in molten salt systems due to the difficulty of accurate measurements and testing. One means to overcome this obstacle is to develop simulations of the process and systems involved.

These simulations come in several different flavors and varieties. The simplest form are pure thermodynamic models which focus on understanding the equilibrium behaviour of the metal in the electrolyte. Other simulations utilize full 3D geometric information to capture the full breadth of mass transfer information. Still other models strike a middle ground by simulating mass transfer in one dimension only.

The ultimate goal of these models is to obtain information that can be used to improve and understand the experimental and applied processes currently in use in many different industries. To obtain such information a model needs several different features and abilities. It needs to be fast enough to return information of a shorter time scale than the operation of an electrorefining cell. It needs to capture the most important aspects of physics and chemistry that could affect the electrorefining process. Finally it needs to be experimentally validated so we know that the model adheres to reality.

A 1D model fits the criteria nicely. It is fast, while still capturing enough information about mass transfer and geometry to compare to experiments. Current 1D electrorefining models trace their origin to the TRAIL model with the most recent model coming from Cumberland in 2014. This model, dubbed ERAD, is focused on the potential development of passivation layers in Uranium electrorefining but is lacking key areas. Most notably the model uses simple guesses as to the thickness of the diffusion layers which according to the authors of TRAIL is the "most important parameter of the model". ERAD was developed as a general ER model and thus has limited ability to be experimentally validated. Our efforts seek to develop an ER model that has closer ties to a specific system, allowing for direct experimental validation without a total sacrifice of generality.

This simulation was developed in an effort to create a better bridge between experimental results and simulation models. Specifically, we have developed a connection between experimental parameters and the diffusion layer thickness which is a key parameter in the rate of diffusion.

Methods

Kinetics

The kinetics of the surface reactions at each electrode are handled using a variation of the Butler-Volmer equation for metal dissolution which is given by:

$$i = i_0 \left[\frac{X_s}{X_b} \exp \left(\frac{-\alpha n F \eta}{RT} \right) - \frac{X_{m,s}}{X_{m,b}} \exp \left(\frac{(1 - \alpha) n F \eta}{RT} \right) \right] \quad (1)$$

where $i_0 = n F k (X_b)^{(1-\alpha)} (X_{m,b})^\alpha$, X represents a mass fraction with the subscript s for surface and b for bulk. The m subscript is for the mass fraction in the metal on the electrode. η represents the surface overpotential, α is the charge transfer coefficient which we have fixed at 0.5 for the time being.

Mass transfer

In an ER cell there are three mass transfer vehicles; diffusion, migration, and convection. This model is concerned with ER cells that are continuously stirred. This causes two regions to form, a well-mixed inner region that comprises the majority of the cell and a pair of narrow regions near the surface of each electrode where convection is negligible. The diffusion layers can be modeled with the following set of equations:

$$\frac{dC_i}{dt} = z_i u_i F \nabla (C_i \nabla \phi) + D_i \nabla^2 C_i, \quad (2)$$

$$\sum_i z_i C_i = 0 \quad (3)$$

where the subscript i refers to components $1 \dots n$, z is the charge number of each component and ϕ is the local electropotential (which is different than the applied potential). These equations are all coupled through ϕ which is implicitly governed by Equation 3, the elec-

troneutrality condition. These equations are written with the assumption that the mobility, u , and the diffusion coefficients are constant with respect to space and is only strictly correct in diffuse systems. In a future paper this system will be revisited assuming a concentrated system but for this version of the model these equations suffice.

Diffusion layer thickness

To solve the mass transfer equations in the previous section, one must know the thickness of the diffusion layers. This value is one of the most important parameters in the model since it directly controls the rate of diffusion. Other authors have estimated this value based on a range of assumptions and guesses but to validate the model experimentally it is important to tie this value to physically measurable parameters.

In the broader transport discipline much work has been done on the boundary layers that form in flowing fluids. Correlations have been developed for many different geometries and flow parameters. For this model two correlations have been used based on a commonly used geometry for critical material processing.

The first correlation describes the boundary layer formed on the surface of a disk with a fluid in rigid body rotation above it.[?]

$$\delta = \left[\ln \left(\frac{b}{r} \right) \right]^{\frac{1}{3}} \frac{b}{\left(-\frac{F0}{9} \right)^{\frac{1}{3}} Re^{\frac{1}{2}} Sc^{\frac{1}{3}}} \quad (4)$$

In this correlation $Re = vb/\nu$ and $Sc = \nu/D$. ν is the kinematic viscosity, v is the velocity, b is the radius of the disc, r is the position on that radius, $F0$ is a model parameter, D is the diffusion coefficient, and δ is the diffusion layer thickness. This equation is then averaged over the size of the disk to get a value for the diffusion layer thickness at the surface of the disk. This correlation represents the anode.

The second correlation is for rigid body rotation of a fluid inside of a hollow cylinder.[?]

$$\delta = \left(\frac{\nu z}{v R^2} \right)^{\frac{2}{5}} R \quad (5)$$

In this equation R is the cylinder radius, and z is the vertical position in the cylinder. Again, this equation is averaged over the length of the cylinder to find a single value for the 1D mass transfer model. This correlation represents the cathode.

Despite their simplicity, these correlations serve as a good approximation of the diffusion layers formed in this geometry. Additionally, these correlations can be replaced with others for a different geommetry, making this method capable of simulating a range of different cell designs.

Anode activity model

Since the anode is molten metal alloy with a changing composition over time it makes sense that the activity of the analyte in the anode will also change over time. The model we are using to represent this change in activity is the Miedema model.[?]

$$\ln \gamma_i = \frac{1}{RT} a_{ij} \Delta H_{ij} \left[1 + (1-x) \left[\frac{(1-2x)}{x(1-x)} - \frac{[u_i(\phi_i - \phi_j)]}{(1 + (1-x)u_i(\phi_i - \phi_j))} + \frac{[u_j(\phi_j - \phi_i)]}{(1 + xu_j(\phi_j - \phi_i))} - \frac{V_i [1 + (1-2x)u_i(\phi_i - \phi_j)] + V_j [-1 + (1-2x)u_j(\phi_j - \phi_i)]}{V_j(1-x)(1 + xu_j(\phi_j - \phi_i)) + V_i x(1 + (1-x)u_i(\phi_i - \phi_j))} \right] \right] \quad (6)$$

where

$$\Delta H_{ij} = f_{ij} \frac{x(1-x)(1 + xu_j(\phi_j - \phi_i))(1 + (1-x)u_i(\phi_i - \phi_j))}{V_j(1-x)(1 + xu_j(\phi_j - \phi_i)) + V_i x(1 + (1-x)u_i(\phi_i - \phi_j))} \quad (7)$$

and

$$f_{ij} = \frac{2pV_iV_j \left\{ q/p \left[n_i^{1/3} - n_j^{1/3} \right]^2 - (\phi_i - \phi_j)^2 - b(r/p) \right\}}{n_i^{-1/3} + n_j^{-1/3}}. \quad (8)$$

Additionally, x is the mass fraction of one component, V_i and V_j are molar volumes, u_i , u_j , n_i , n_j , ϕ_i , ϕ_j , q , p , and b are model parameters, and a_{ij} is a parameter related to the entropy. One major limitation of this model is that it is unable to handle phase changes so if the anode solidifies at any point this model will not capture that.

Numerical methods

Results and Discussion

Diffusion layer model

- The diffusion layer is the portion of the model with the most happening
- Various factors impact how this region behaves and what impacts it.
- Key diffusion layer parameters/behaviours are thickness, migration, concentration

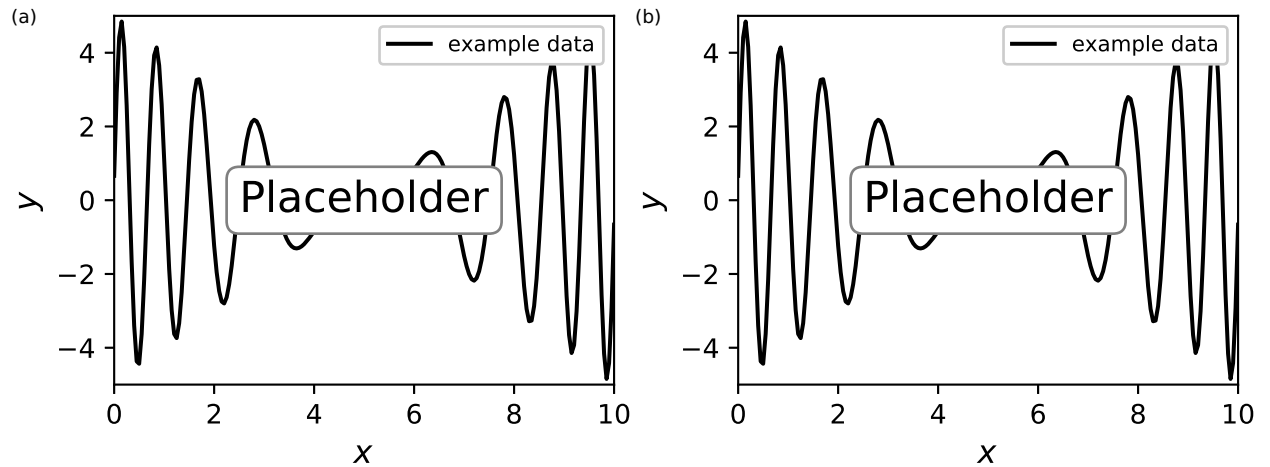


Figure 1: Boundary layer thickness is dictated by the correlations used. Side by side figure with each of the correlations. One side shows anode. Other side shows cathode

Depending on the correlation, different parameters will have greater or lesser effects on the boundary layer thickness. When developing an ER cell it is important to know these

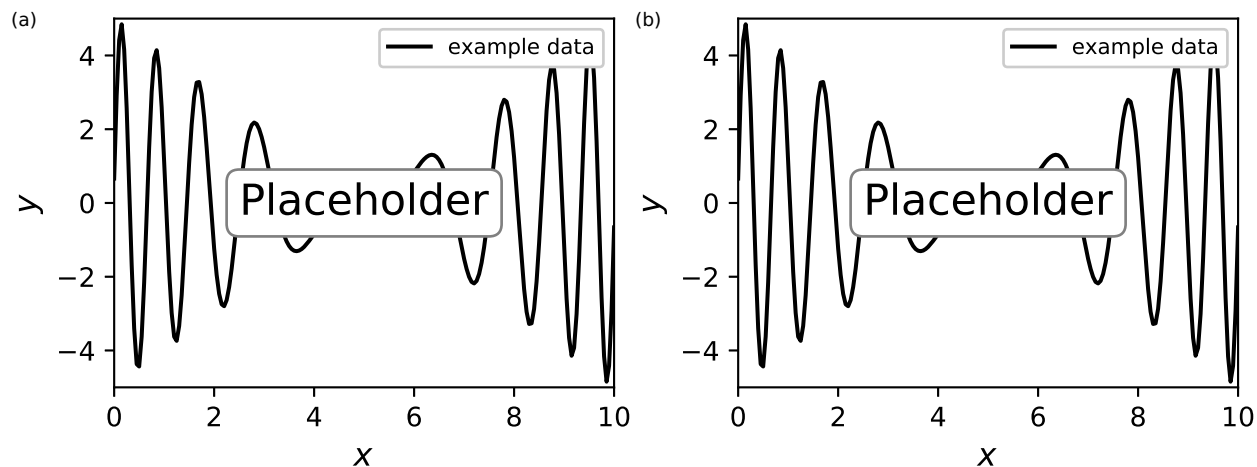


Figure 2: Sensitivity from correlations to actual parameters such as velocity and viscosity

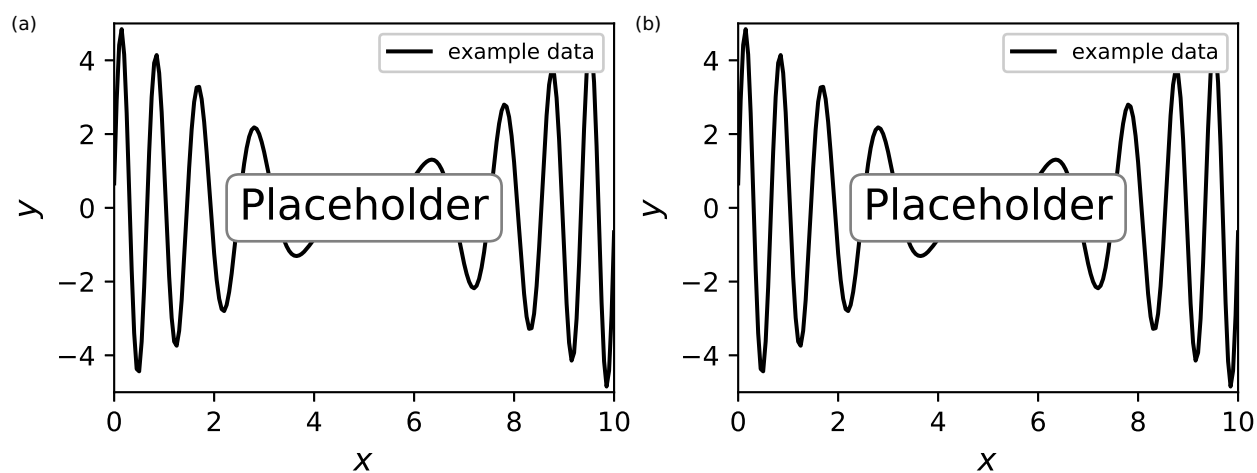


Figure 3: Impact of migration on time to steady state?

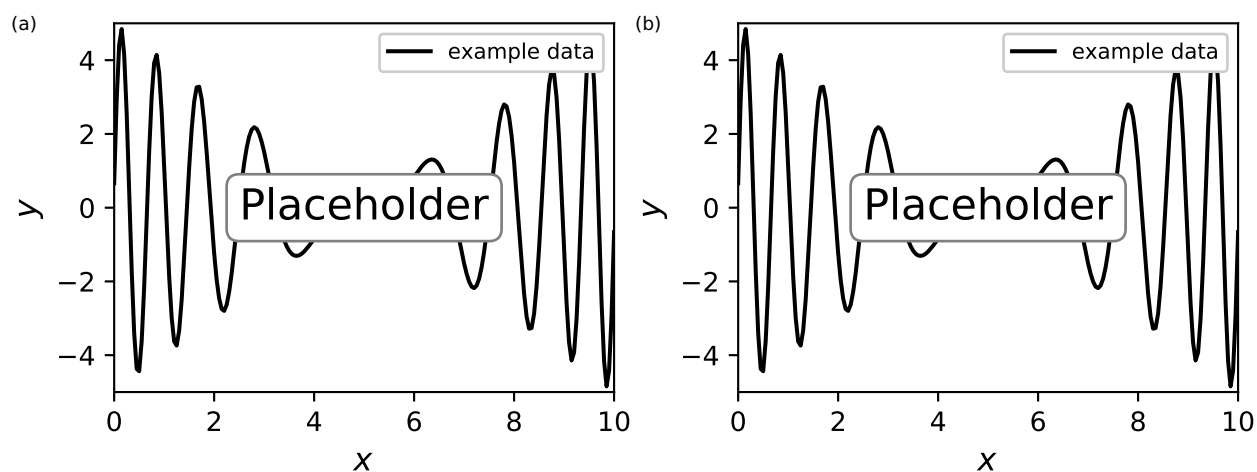


Figure 4: Results of CV compared to real world?

dependencies because they will dictate what parameters are most important to the running of the cell and the optimization thereof.

It could also be useful to make figures of CV matching with and without migration

Electrorefining model

- Electrorefining model includes pseudosteady treatment of anode
- Also needs pseudosteady for bulk
- Doesn't need anything for cathode because of system design for critical metals
 - critical metals don't want to concentrate metal anywhere. For no critical metals this is not important and the simulation could be adapted to compensate.

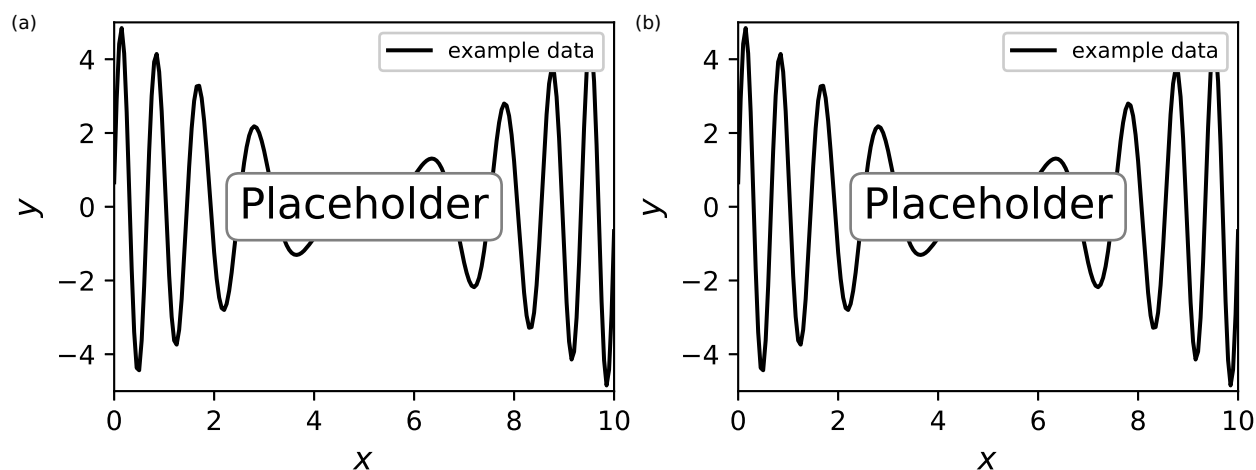


Figure 5: Figure that shows process? Somehow show time scales, maybe series of cells

- Several distinct time scales
- Diffusion layer transient
- Steady diffusion layer, pseudosteady bulk
- steady diffusion layer and bulk, pseudosteady anode

- Steady anode, steady diffusion, pseudosteady bulk
- steady anode, steady bulk, transient diffusion layer

Figure for each of these scales?

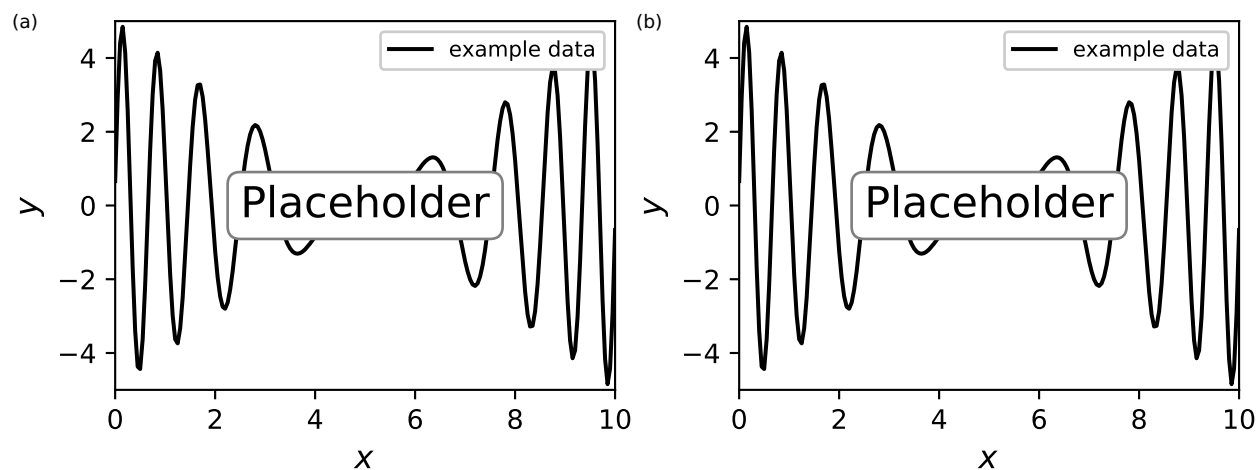


Figure 6: Absolute boundary layer thickness impact

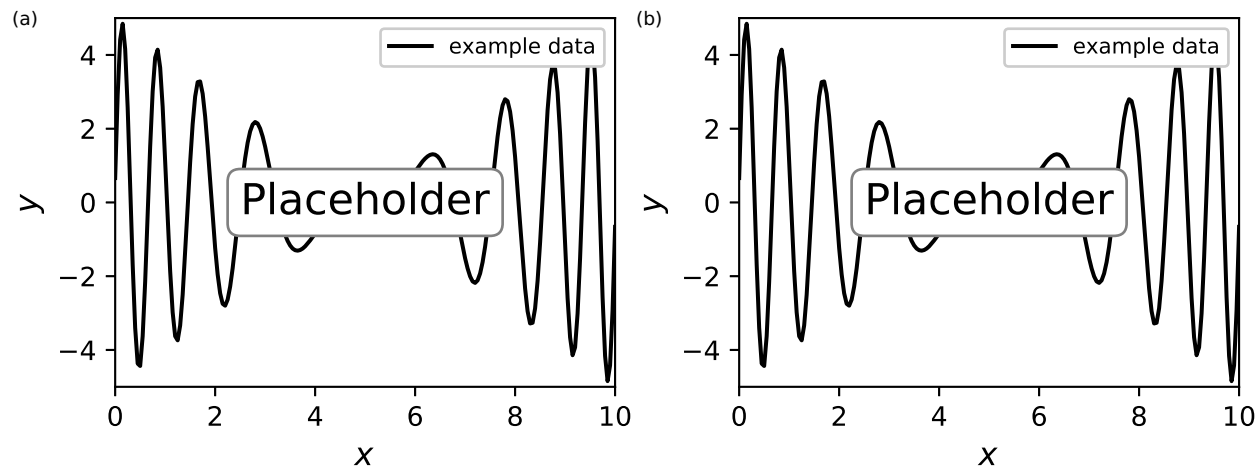


Figure 7: Relative boundary layer impact

I am imagining these compared to either the time to completion for the cell or even on the current output of the cell at a fixed potential.

Any one of these figures might balloon out to two or three if not more. It kind of depends on how easy it is to present the concept with a figure.

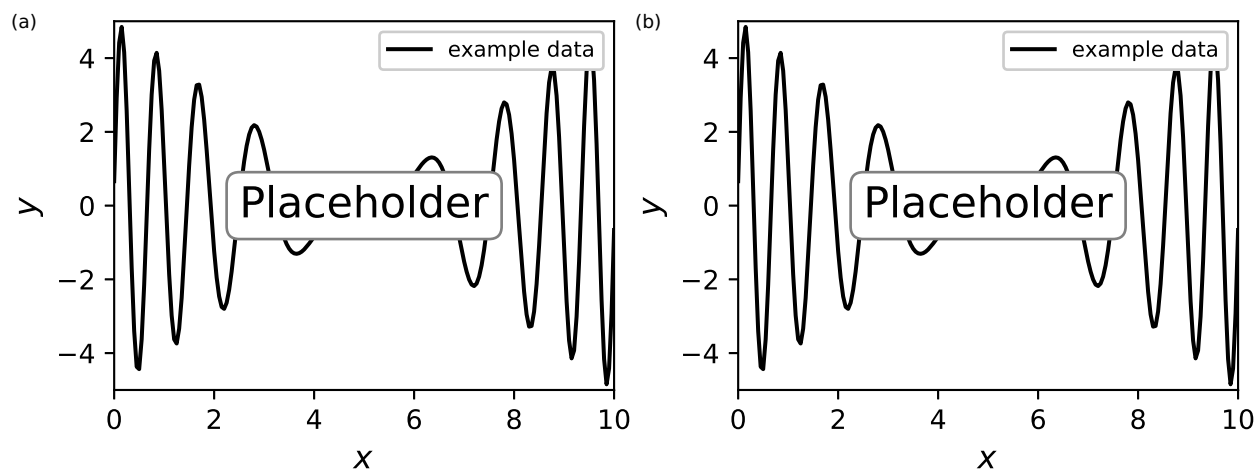


Figure 8: Sensitivity on overall simulation from design parameters assuming the current boundary layer correlations

Other potential ideas to talk about

- Look at various geometries and find the one most optimal based on some parameters
 - Can do this for both diffusion layer and overall cell operation
- Could also potentially sweep temperature
- I may add to this list as I do more research

Conclusion

Limitations of this method

- Assuming dilute pretty strictly. Hard to relax this assumption
- multiple reactions aren't implemented yet
- No experimental results yet

Conclusions for real this time

- We have developed a simulation method that is capable of connecting experimental parameters to simulation parameters using correlation derived from real physics

- The simulation presents the importance of the diffusion layer thickness
- We present our ability to match CV results
- We show the various stages of an ER cell run based on the different time scales that things operate on
- We show how the boundary layer affects the ER cell run itself alongside its general impact and effect from physical parameters

Future work: Implement activity model for electrolyte Match directly to experimental results.
Loosen the dilute assumption before getting rid of it entirely.

Acknowledgement

We would like to acknowledge financial support from Brigham Young University and computational resources from the BYU Office of Research Computing.