Macroscopic Modeling of a One-Dimensional Electrochemical Cell using the Poisson-Nernst-Planck Equations

by

David Yan

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
The Edward S. Rogers Sr. Department of Electrical Engineering
University of Toronto

© Copyright 2017 by David Yan
Abstract

Macroscopic Modeling of a One-Dimensional Electrochemical Cell using the Poisson-Nernst-Planck Equations

David Yan
Doctor of Philosophy
The Edward S. Rogers Sr. Department of Electrical Engineering
University of Toronto
2017

This thesis presents the one-dimensional equations, numerical method and simulations of a model to characterize the dynamical operation of an electrochemical cell. This model extends the current state-of-the art in that it accounts, in a primitive way, for the physics of the electrolyte/electrode interface and incorporates diffuse-charge dynamics, temperature coupling, surface coverage, and polarization phenomena. The one-dimensional equations account for a system with one or two mobile ions of opposite charge, and the electrode reaction we consider (when one is needed) is a one-electron electrodeposition reaction. Though the modeled system is far from representing a realistic electrochemical device, our results show a range of dynamics and behaviors which have not been observed previously, and explore the numerical challenges required when adding more complexity to a model. Furthermore, the basic transport equations (which are developed in three spatial dimensions) can in future accommodate the inclusion of additional physics, and coupling to more complex boundary conditions that incorporate two-dimensional surface phenomena and multi-rate reactions.

In the model, the Poisson-Nernst-Planck equations are used to model diffusion and electromigration in an electrolyte, and the generalized Frumkin-Butler-Volmer equation is used to model reaction kinetics at electrodes. An energy balance equation is derived and coupled to the diffusion-migration equation. The model also includes dielectric polarization effects by introducing different values of the dielectric permittivity in different regions of the bulk, as well as accounting for surface coverage effects due to adsorption, and finite size “crowding”, or steric effects. Advection effects are not modeled but could in future be incorporated. In order to solve the coupled PDE’s, we use a variable step size second order scheme in time and finite differencing in space. Numerical tests are performed on a simplified system and the scheme’s stability and convergence properties are discussed. While evaluating different methods for discretizing the coupled flux boundary condition, we discover a thresholding behaviour in the adaptive
time stepper, and perform additional tests to investigate it. Finally, a method based on ghost points is chosen for its favorable numerical properties compared to the alternatives. With this method, we are able to run simulations with a large range of parameters, including any value of the nondimensionalized Debye length $\epsilon$.

The numerical code is first used to run simulations to explore the effects of polarization, surface coverage, and temperature. The code is also used to perform frequency sweeps of input signals in order to mimic impedance spectroscopy experiments. Finally, in Chapter 5, we use our model to apply ramped voltages to electrochemical systems, and show theoretical and simulated current-voltage curves for liquid and solid thin films, cells with blocking (polarized) electrodes, and electrolytes with background charge. Linear sweep and cyclic voltammetry techniques are important tools for electrochemists and have a variety of applications in engineering. Voltammetry has classically been treated with the Randles-Ševčík equation, which assumes an electroneutral supported electrolyte. No general theory of linear-sweep voltammetry is available, however, for unsupported electrolytes and for other situations where diffuse charge effects play a role. We show theoretical and simulated current-voltage curves for liquid and solid thin films, cells with blocking electrodes, and membranes with fixed background charge. The analysis focuses on the coupling of Faradaic reactions and diffuse charge dynamics, but capacitive charging of the double layers is also studied, for early time transients at reactive electrodes and for non-reactive blocking electrodes. The final chapter highlights the role of diffuse charge in the context of voltammetry, and illustrates which regimes can be approximated using simple analytical expressions and which require more careful consideration.
Acknowledgements

I’d like to acknowledge my co-supervisors, Professors Francis Dawson and Mary Pugh, for their knowledge and guidance over a period of five long years. I’d also like to thank Professor Keryn Lian, Professor Charles Ward, Professor Harry Ruda, Professor John Newman, Jin Chang, Ahmed Huzayyin, and Mario Palasciano for many useful discussions and for their assistance with this thesis. Additionally, I’d like to thank Professor Martin Bazant for his insight and expertise in helping me complete Chapter 5, as well as Professors Maarten Biesheuvel and Keith Oldham for their many helpful comments and suggestions.

Finally, I’m very grateful for the help and support of my parents and my wonderful girlfriend Maddy. I couldn’t have done it without you.
**Contents**

1 Introduction .................................. 1
   1.1 Motivation and Modeling Philosophy .................. 2
   1.2 A Perspective on Electrochemical Cell Modeling ........ 4
   1.3 Review of Battery Models .......................... 10
   1.4 Thesis Objectives and Contributions .................. 14
   1.5 Thesis Layout .................................. 15

2 Equation Development .......................... 16
   2.1 Mass Transport .................................. 18
      2.1.1 Bulk Reactions .......................... 20
   2.2 Poisson Equation .............................. 20
   2.3 Energy Transport .............................. 21
   2.4 Boundary Conditions .......................... 22
      2.4.1 Electrostatics and Current Conservation ........ 24
      2.4.2 Reaction Kinetics ........................ 26
      2.4.3 Energy Conservation .................. 27
      2.4.4 Surface Coverage .................. 29
5.4.3 Unsupported Electrolytes with Thin Double Layers ...................... 78
5.5 Blocking Electrodes ...................................................... 82
  5.5.1 Model Problem ...................................................... 82
  5.5.2 Liquid Electrolytes .................................................. 84
  5.5.3 Solid Electrolytes .................................................. 87
5.6 Liquid Electrolyte Thin Films .......................................... 91
  5.6.1 Model Problem ...................................................... 91
  5.6.2 Low Sweep Rates ................................................... 91
    Thin EDL ............................................................... 91
    Thick EDL ............................................................. 92
  5.6.3 Diffusion versus Reaction Limitation ............................ 92
  5.6.4 Transient Space Charge .......................................... 94
5.7 Solid Electrolyte Thin Films .......................................... 97
  5.7.1 Model Problem ...................................................... 97
  5.7.2 Low Sweep Rates ................................................... 97
    Thin EDL ............................................................... 97
    Thick EDL ............................................................. 97
  5.7.3 Diffusion versus Reaction Limitation ............................ 98
5.8 Leaky Membranes ....................................................... 102
  5.8.1 Model Problem ...................................................... 102
  5.8.2 Negative Background Charge .................................... 103
  5.8.3 Positive Background Charge ..................................... 106

6 Conclusions, Contributions and Future Work .......................... 110
### 6.1 Contributions

### 6.2 Future Work

- **6.2.1 General**
- **6.2.2 Numerics**
- **6.2.3 Dielectric Polarization**
- **6.2.4 Temperature**
- **6.2.5 Surface coverage**

### Appendices

- **A Derivation of Energy Balance Equation**
- **B Derivation of Current Conservation Equation**
- **C The Butler-Volmer Model of Faradaic Reactions**
- **D Derivation of Numerical Extrapolation Formula**
- **E Derivation of Modified Randles-Sevcik Equation**
- **F Matlab Code**
  - **F.1 Double Electrode Code**
    - **F.1.1 concentration.m**
    - **F.1.2 cur.m**
    - **F.1.3 errcomp.m**
    - **F.1.4 extrapolate.m**
    - **F.1.5 main.m**
F.1.6 makemesh.m ................................................................. 155
F.1.7 parameters.m ........................................................... 156
F.1.8 poisson1d.m ............................................................... 158
F.1.9 postprocess.m ........................................................... 160
F.1.10 step.m ................................................................. 161
F.1.11 temperature.m .......................................................... 166
F.1.12 voltage.m ............................................................. 169
F.2 EIS Tool ................................................................. 169
F.2.1 imp_spec_tool.m ...................................................... 170
F.2.2 findZ2.m ............................................................ 171
F.3 Chebyshev Pseudospectral Code ........................................ 171

Bibliography 192
List of Figures

1.1 Charge distribution and the potential $\Phi$ near an electrode in Gouy-Chapman and Stern theories. In Gouy-Chapman theory, there is a region of diffuse charge adjacent to the electrode. The Stern model adds a compact layer of charge on the electrode surface. In the figure, $\lambda_S$ is the width of the Stern layer. ................................................................. 6

1.2 Solution to the one dimensional Poisson-Boltzmann equation (equation (1.6)) with $\phi_0 = 1$. Cation concentration (b) is related to the potential (a) via $c = \exp(-\phi)$. $x$ is scaled to the Debye length $\lambda_D = \sqrt{\frac{e k_B T}{2 e^2 C_0}}$. ................................................................. 8

1.3 (a) Typical cation (solid) and anion (dashed) concentrations in an electrochemical cell with thin double layers and (b) the same plot zoomed onto the right hand side boundary. 13

2.1 A diagram showing the geometry of an electrolyte between two flat electrodes. $\lambda_S$ is the width of the Stern layer, a compact layer of charge on the electrode surface. Adjacent to the Stern layers are the diffuse charge regions which we define to have a rough width of $L_{\text{diff}}$. The (largely) electroneutral bulk makes up the remainder of the electrolyte. $L$ is the distance between the two Stern planes, or the interelectrode width minus $2\lambda_S$. .... 17

2.2 Boundary condition applied to $\Phi$ in the Stern layer. Current balance is shown between $J_{\text{ext}}$, the applied or solved for external electrical current density and the flux of charged species into the electrode. Also shown is the direction of the normal vector relative to the electrode. ................................................................. 25
2.3 A figure showing the Newton’s law of cooling boundary condition for temperature, including the locations of the ambient and boundary temperatures. The section in red is the electrode, the section in yellow is the Stern layer and the section in white is the electrolyte, which includes the diffuse charge region. The heat transfer coefficient $H$ takes into account the geometry and material properties of the electrode.

2.4 Heat flux balance at the Stern layer, as in equation (2.23). Flux balance is shown between the externally applied heat flux $J_{q,\text{ext}}$ and the incoming heat flux in the electrolyte. In this work, we use a mixed convection boundary condition on the electrode side, and approximate $J_{q,\text{ext}}$ using $H(T_{\text{amb}} - T_{\text{stern}})$, where $H$ is a heat transfer coefficient. The heat generated in the Stern layer is given by $\lambda_S \left( J_e \cdot \mathbf{E} + \frac{D}{\varepsilon_0} \frac{\partial \mathbf{P}}{\partial \tau} \right)$.

2.5 Different mechanisms of electrode “coverage” in electrochemistry: (a) Surface adsorption of an aqueous species onto an electrode, (b) Intercalation of lithium into graphite, where lithium molecules are sandwiched between layers of graphite.

3.1 A plot of equation 3.3 (a) and an example of its resulting mesh (b).

3.2 Coarse/fine time stepping scheme. First a two-step coarse time step with step size $dt$ is taken using $u^n$ and $u^{n-1}$ to obtain $u^{n+1}_c$. Then a two-step fine step with step size $dt/2$ is taken using $u^n$ and $u^{n-\frac{1}{2}}$ to create $u^{n+\frac{1}{2}}$, and another is taken using $u^n$ and $u^{n+\frac{1}{2}}$ to create $u^{n+1}_f$. Values of $u$ at half steps are stored at each step in order to allow the next fine step. In the diagram, open circles indicate values from fine half-steps.

3.3 Approximating the solution of $u_t = u_{xx}$ with $u(0,t) = 0$, $u(1,t) = 1$ and $u(x,0) = 1$. The parameters are tol = $10^{-6}$, range = tol/3, $dx = 1/40$, and $dt_{\text{max}} = 1$. (a): $l^2$ norm of $\partial u/\partial t$ as a function of time. (b): $l^2$ norm of the approximation of the local truncation error (3.18). The horizontal dashed lines mark the upper and lower bounds: tol ± range. (c): The time step $dt$ for which the solution $u^{n+1}$ is accepted and the time-stepping scheme advances.
3.4 A diagram of the first three time levels. \( c^1, T^1 \) and \( \phi^1_x \) are the initial conditions, which are used by the elliptic solver to generate for \( \phi^1 \). The four vectors at the first time are then all used to make a Forward Euler step, creating \( c^2, T^2 \) and \( \phi^2_x \). These three vectors are then used to generate \( \phi^2 \), and all eight vectors from the first and second time levels are used in a two-step scheme to create \( c^3, T^3 \) and \( \phi^3_x \).  

3.5 \( dt \) vs time for toy model with adaptive time stepping using the “direct” method and BV-like boundary conditions. \( N = 20, tol = 10^{-2}, u(\cdot,0) = 1 \). The time steps threshold to a value of \( \sim 10^{-1} \).  

3.6 Computed local truncation error vs time for toy model with piecewise constant time steps using the “direct” method for the boundary conditions (3.28)-(3.29) and BV-like boundary conditions. \( N = 20, tol = 10^{-2}, u(\cdot,0) = 1, dt = 0.01 \) for \( t \leq 10 \) and \( dt = 1 \) for \( t > 10 \).  

3.7 \( dt \) vs time for toy model with adaptive time stepping with “ghost point” method and BV-like boundary conditions. \( N = 20, tol = 10^{-6}, u(\cdot,0) = 1 \).  

3.8 Computed error vs time for toy model with piecewise constant time steps with “ghost point” method and BV-like boundary conditions. \( N = 20, tol = 10^{-6}, u(\cdot,0) = 1, dt = 0.01 \) for \( t \leq 10, dt = 1.5 \) for \( t > 10 \).  

3.9 Time steps chosen by adaptive stepper for the toy model using two first-order time stepping schemes: Forward Euler (equation (3.32)) and implicit-explicit (equation (3.33)), and either direct or ghost point method at the boundary (with BV-like boundary conditions). \( N = 40, tol = 10^{-6} \) for ghost point method simulations and \( tol = 10^{-2} \) for direct method simulations.  

3.10 \( dt \) vs time for toy model with adaptive time stepping with \( u(0) = u(1) = 0, N = 40, tol = 10^{-6} \).  

3.11 Time steps chosen by adaptive stepper for the toy model for (a) \( u(0) = 1 \) and \( -(u_x + uv_x)_{x=1} = 0 \), (b) \( u(0) = 0 \) and \( -(u_x + uv_x)_{x=1} = v(1) - 0.1 \) and (c) \( u(0) = 0 \) and \( -(u_x + uv_x)_{x=1} = u(1) \exp(v(1)) - \exp(-v(1)) \). \( N = 40, tol = 10^{-6} \).  

xii
$dt$ vs time for full model with forcing, shown in (b), in response to voltage set to 0.1, 0.2, 0.3 and 0.4 at times 7.5, 8, 8.5 and 9 using a sequence of hyperbolic tangent functions to provide smoothing, shown in (a). $N = 90$, tol = 1e-6, range = tol/3, all parameters set to 1 except $\epsilon = 0.1$. $c_\pm(x, 0) = 1$, $T(x, 0) = 1$.

4.1 $\theta$ and voltage vs time for a reaction at a single electrode with reaction kinetics described by equation (4.2). $\epsilon = 0.001$, $\delta = 1$, $k = 50$, $q_s$ varied.

4.2 Current density vs. time for a voltage ramp of $\theta = -1$ with Langmuir and Frumkin adsorption isotherms, as in equations (4.4) and (4.5), with $w(\theta) = -(1 - 2\theta)$. $\epsilon = 0.001$, $\delta = 1$, $k = 50$, $q_s = 1$.

4.3 Current density vs. time for a voltage step of 1 with $w(\theta) = -(1 - 2\theta)$ for the Frumkin isotherm. $\epsilon = 0.001$, $\delta = 1$, $k = 50$, $q_s = 1$.

4.4 Potential at steady state for cell with jump in $\epsilon$ and without, for various values of $\epsilon_{\text{bulk}}$, with $\delta = 0.01$ and $k_{c,c} = j_{r,a} = 100$, $j_{r,c} = k_{c,a} = 50$.

4.5 Current vs. time with jump in $\epsilon$ and without for a voltage step of 0.1, for various values of $\epsilon_{\text{bulk}}$, with $\delta = 0.01$ and $k_{c,c} = j_{r,a} = j_{r,c} = k_{c,a} = 50$.

4.6 Average temperature with $\alpha = h = 50$, $k = 50$, $\epsilon = 1$, $\delta = 1$ and $\beta = 0.1$ for different values of current.

4.7 Steady-state temperature with $\alpha = h = 50$, $k = 50$, $\epsilon = 0.001$, $\delta = 1$ and $\beta = 0.1$ for different values of current.

4.8 Average temperature with $j = 0.5$, $\epsilon = 0.001$, $\delta = 1$, and $\beta = 0.1$ for different values of thermal conductivity $\alpha = h$.

4.9 Temperature evolution for the low thermal conductivity ($\alpha = h = 0.1$) and high thermal conductivity ($\alpha = h = 100$) cases, with $j = 0.5$, $\epsilon = \lambda_s = 0.001$, $\beta = 0.1$.

4.10 Randles equivalent circuit, where $R_s$ is the solution resistance, $C_{\text{dl}}$ is the double layer capacitance, $R_{\text{ct}}$ is the charge-transfer resistance and $Z_W$ is the Warburg mass-transfer impedance.
4.11 Nyquist plot of the impedance of a parallel RC circuit, with \( R = C = 1 \). High frequency limit is at the origin, and low frequency limit is at \((0, 1)\). ................................................................. 70

4.12 Impedance plot with and without polarization effects. Frequency ranges from 0.1 to 500, \( v_{\text{bias}} = 0, v_{\text{pk-pk}} = 0.01 \). Values for \( \epsilon \) are the same as in Figures 4.4 and 4.5, except with \( \epsilon = 0.1 \). ................................................................. 71

4.13 Impedance plot with Langmuir and Frumkin surface coverage isotherms. Frequency ranges from 0.1 to 500, \( v_{\text{bias}} = 0, v_{\text{pk-pk}} = 0.01 \). Values for \( \epsilon \) are the same as in Figures 4.2 and 4.3, except with \( \epsilon = 0.1 \). Low frequencies are at \( Z = 0 \), increasing clockwise. ............... 72

5.1 Diagram showing electrochemical systems with applied voltage \( v \) and resulting current \( j_{\text{ext}} \) for a system with (a) a single electrode and (b) two electrodes. In the single electrode case, the left hand boundary is modeled as an ideal reservoir with a fixed potential. Also shown is a sketch of the potential inside the cell: dashed line is the potential in the bulk, solid line is the potential in the diffuse double layer. ......................................................... 76

5.2 Simulated current curves for a supported electrolyte with one electrode in response to a voltage ramp with \( \tilde{S} = -50 \), with various values of \( k \). Also shown is the high reaction rate limit in equation (5.4). ................................................................. 79

5.3 Simulated \( j \) vs. \( v \) curves with various values of reaction rate \( k \) for an unsupported electrolyte with one electrode, in response to a ramped voltage with scan rate \( \tilde{S} = -50 \). The \( k = 50 \) simulation gives results which are numerically equivalent to the large \( k \) limit. Also shown is the theoretical result for a supported electrolyte from equation (5.4). ............... 79

5.4 (a) Voltammogram and (b) concentrations with \( k = 0.1 \) (reaction limited) for an unsupported electrolyte with one electrode subjected to a ramped voltage with scan rate \( \tilde{S} = 50 \), with \( \epsilon = 0.001 \) and \( \delta = 100 \). Labels in the concentration plot correspond to snapshots of cation concentration \( c_+ \) at times labeled on the current vs. time plot. ............... 80

5.5 (a) Voltammogram and (b) concentrations with \( k = 100 \) (diffusion limited) for an unsupported electrolyte with one electrode subjected to a ramped voltage with scan rate \( \tilde{S} = -50 \), with \( \epsilon = 0.001 \) and \( \delta = 100 \). Labels in the concentration plot correspond to snapshots of cation concentration \( c_+ \) at times labeled on the current vs. time plot. ............... 80
5.6 (a) Voltammogram for an unsupported electrolyte with one electrode subjected to a triangular voltage with $|\tilde{S}| = 50$, $\epsilon = 0.001$, $k = 50$ and $\delta = 0.01$. (b) Net charge densities $\rho = c_+ - c_-$. Labels on the charge density plot correspond to snapshots of $\rho$ in the double layer at times labeled on the voltammogram.

5.7 Equivalent circuit diagram for system with two blocking electrodes, showing the defined direction of current and polarities of the double layer capacitors. Note that $\tilde{C}$ is a function of $\Delta\phi$.

5.8 Simulated (solid line) and uniformly valid approximation (dashed line) $j$ vs $v$ curves for a thin EDL liquid electrolyte with two blocking electrodes and parameters $\epsilon = 0.001$, $\delta = 0.01$ and various values of the scan rate $\tilde{S}$. Dashed lines are plotted from equation (5.14).

5.9 Simulated (solid line) and uniformly valid approximation (dashed line) $j$ vs $v$ curves for a thick EDL liquid electrolyte with two blocking electrodes and parameters $\epsilon = 0.1$, $\delta = 0.01$ and various values of $\tilde{S}$. Dashed lines are plotted from equation (5.14).

5.10 (a) $j$ vs. $v$ and (b) cation concentrations for a thick EDL liquid electrolyte with two blocking electrodes and parameters $\epsilon = 0.1$, $\delta = 0.01$ and scan rate $\tilde{S} = -0.1$. Labels in (a) correspond to cation concentrations in (b) at various times.

5.11 Simulated (solid line) vs. uniformly valid approximation (dashed line) $j$ vs $v$ curves for a thin EDL solid electrolyte with a single blocking electrode and parameters $\epsilon = 0.001$, $\delta = 0.01$ and $\tilde{S} = \pm 1$. Figure (a) shows the negative part of the sweep and Figure (b) shows the positive part. Dashed lines are plotted from equation (5.16).

5.12 Simulated (solid line) and uniformly valid approximation (dashed line) $j$ vs $v$ curves for a thin EDL solid electrolyte with two blocking electrodes and parameters $\epsilon = 0.001$, $\delta = 0.01$ for various values of $\tilde{S}$. Dashed lines are plotted from equation (5.17).

5.13 Simulated (solid line) and uniformly valid approximation (dashed line) $j$ vs. $v$ curves for a thick EDL solid electrolyte with two blocking electrodes and parameters $\epsilon = 0.1$, $\delta = 0.01$ and various values of $\tilde{S}$. Dashed lines are plotted from equation (5.17).
5.14 Simulated (solid line) and uniformly valid approximation (dashed line) $j$ vs $v$ curves for a thick EDL solid electrolyte with a single blocking electrode and parameters $\epsilon = 0.1$, $\delta = 0.01$ and $\tilde{S} = \pm 1$. Figure (a) shows the negative voltage sweep and Figure (b) shows the positive voltage sweep. Dashed lines are plotted from equation (5.16).

5.15 $v$ vs $j$ curves for a thin EDL liquid electrolyte with two electrodes and with parameters $\epsilon = 0.001$ ($\delta = 1, 10$) and $\epsilon = 0.005$ ($\delta = 0.1, 0.01$), $k_{c,C} = 30$, $k_{c,A} = 1$, $j_{r,C} = 0.1$ and $j_{r,A} = 0.8$ ($v_0 \approx 5.5$). Also shown are the steady-state curves in the GC and H limits from equations (5.18) and (5.19), respectively. Simulated curves were created using a voltage scan rate of $\tilde{S} = 2.5$.

5.16 $j$ vs $v$ for a thick EDL liquid electrolyte with two electrodes, with various values of $k_{c,C}$. $\epsilon = 0.1$, $\delta = 1$, scan rate $\tilde{S} = 2.5$ and other reaction rate parameters the same as in Figure 5.15.

5.17 Faradaic current vs. voltage for a liquid electrolyte with two electrodes with $\tilde{S}$ varied and with parameters $\epsilon = 0.05$, $\delta = 1$ and $k_{c,a} = 50 = j_{r,a} = k_{c,c} = j_{r,c} = 50$ ($v_0 = 0$). Diffusion limitation is seen to set in at higher voltages in the $\tilde{S} = -100$ plot.

5.18 Faradaic current vs. voltage for a liquid electrolyte with two electrodes and with $\tilde{S}$ varied, with parameters $\epsilon = 0.05$, $\delta = 1$, $k_{c,a} = 50$, $j_{r,a} = 100$, $k_{c,c} = 0.1$ and $j_{r,c} = 0.05$ ($v_0 \approx 1.4$). A current response dominated by reaction limitation is seen in the $\tilde{S} = -100$ plot.

5.19 Voltammogram for a thin EDL liquid electrolyte with two electrodes subjected to a triangular voltage with $\epsilon = 0.001$, $\delta = 0.3$, $k = 50$ and $|\tilde{S}| = 100$. Concentrations with development of space charge regions are shown in Figure 5.20.

5.20 (a) Current and (b-d) resulting cation (solid line) and anion (dashed line) concentrations showing space charge regions developed at the cathode and anode from a triangular applied voltage in a thin EDL liquid electrolyte with two electrodes. Parameters used were $\epsilon = 0.001$, $\delta = 0.3$, $k = 50$, and $|\tilde{S}| = 100$.

5.21 $v$ vs $j$ curves for a thin EDL solid electrolyte with two electrodes and with $\epsilon = 0.001$, $k_{c,C} = 30$, $k_{c,A} = 1$, $j_{r,C} = 0.1$, $j_{r,A} = 0.8$ ($v_0 \approx 5.5$) and $\delta$ varied. Also shown are the steady-state curves in the GC and H limits from equations (5.21) and (5.22), respectively. Simulated curves were created using a voltage scan rate of $\tilde{S} = 2.5$. 
5.22 \( j \) vs \( v \) for a thick EDL solid electrolyte with two electrodes, with various values of \( k_{c,C} \).
\( \epsilon = 0.1, \delta = 1, \) scan rate \( \tilde{S} = 2.5 \) and other reaction rate parameters the same as in Figure 5.21. ........................................ 98

5.23 Faradaic current vs. voltage for a solid electrolyte with two electrodes with \( \tilde{S} \) varied and with parameters \( \epsilon = 0.05, \delta = 1 \) and \( k_{c,a} = 50 = j_{r,a} = k_{c,c} = j_{r,c} = 50 \) \( (v_0 = 0) \). No diffusion limitation is allowed in solid electrolytes, and so the \( j \) vs. \( v \) curves are linear for all values of \( \tilde{S} \). ........................................ 99

5.24 (a), (b) \( j \) vs. \( v \) and (c), (d) cation concentrations \( c_+ \) at \( t = 0.025 \) (dashed line), 0.05 (dash-dotted line), 0.075 (dotted line) and 0.1 (solid line) for \( \tilde{S} = -100 \) voltage sweeps on both liquid and solid electrolytes with two electrodes. Other parameters are the same as in Figures 5.17 and 5.23. ........................................ 100

5.25 Faradaic current vs. voltage for a solid electrolyte with two electrodes and with \( \tilde{S} \) varied, with parameters \( \epsilon = 0.05, \delta = 1, \) \( k_{c,a} = 50, j_{r,a} = 100, k_{c,c} = 0.1 \) and \( j_{r,c} = 0.05 \) \( (v_0 \approx 1.4) \). Reaction limitation is prominent in the \( \tilde{S} = -100 \) curve. ........................................ 101

5.26 Sketch of a “leaky” membrane. Left hand boundary is an ideal reservoir with constant concentration \( (c_+ = c_- = 1) \) and zero potential \( (\phi = 0) \). Right hand boundary is an electrode. Mobile charge is shown with a filled circle, fixed charge (negative in this case) is shown without a circle. ........................................ 102

5.27 Current in response to a voltage ramp in a liquid electrolyte with one electrode and constant background charge. Parameters are \( \epsilon = 0.005, \delta = 10, \rho_s = -0.01 \) and \( k = 50 \).
Also shown is the steady state response from equation (5.24). ........................................ 104

5.28 Current from a voltage ramp applied to a liquid electrolyte with a single electrode and constant background charge. Parameters are \( \epsilon = 0.005, \delta = 10, \rho_s = -0.1 \) and \( k = 50 \).
Also shown is the steady state response from equation (5.24). ........................................ 104

5.29 (a) Voltammogram and (b-d) resulting cation (solid line) and anion (dashed line) concentrations from a triangular applied voltage applied to a thin EDL liquid electrolyte with two electrodes and constant background charge. Parameters used were \( \epsilon = 0.005, \delta = 1, k = 50, \rho_s = -0.01 \) and \( |\tilde{S}| = 10 \). Two cycles are shown in Figure (a). ........................................ 105
5.30 (a) Voltammogram and (b-d) resulting cation (solid line) and anion (dashed line) concentrations from a triangular applied voltage applied to a thin EDL liquid electrolyte with two electrodes and constant, negative background charge. Parameters used were \( \epsilon = 0.005, \delta = 1, k = 50, \rho_s = -0.1 \) and \( |\tilde{S}| = 10 \). Two cycles are shown in Figure (a).

5.31 Current from a voltage ramp applied to a liquid electrolyte with a single electrode and constant, small, positive background charge. Parameters are \( \epsilon = 0.005, \delta = 10, \rho_s = 0.01 \) and \( k = 50 \). Also shown is the steady state response from equation (5.24), which is shown not to match the simulations.

5.32 Current from a voltage ramp applied to a liquid electrolyte with a single electrode and constant, large, positive background charge. Parameters are \( \epsilon = 0.005, \delta = 10, \rho_s = 0.1 \) and \( k = 50 \). Also shown is the steady state response from equation (5.24), which is shown not to match the simulations.

5.33 (a) Voltammogram and (b-d) resulting cation (solid line) and anion (dashed line) concentrations from a triangular applied voltage applied to a thin EDL liquid electrolyte with two electrodes and small positive background charge. Parameters used were \( \epsilon = 0.005, \delta = 1, k = 50, \rho_s = 0.01 \) and \( |\tilde{S}| = 10 \). Two cycles are shown in Figure (a).

5.34 (a) Voltammogram and (b-d) resulting cation (solid line) and anion (dashed line) concentrations from a triangular applied voltage applied to a thin EDL liquid electrolyte with two electrodes and large positive background charge. Parameters used were \( \epsilon = 0.005, \delta = 1, k = 50, \rho_s = 0.1 \) and \( |\tilde{S}| = 10 \). Two cycles are shown in Figure (a).

B.1 Gaussian surface around the electrode/electrolyte interface, showing current balance. Left side of the figure is the electrolyte side and right is the electrode side.

C.1 The path of a particle in stochastic rate theory, showing the “energy hump” of the transition state between the initial and final states. \( U_1, U_2 \) and \( U_{TS} \) denote the internal energies of the initial, final and transition states, respectively.
List of Tables

2.1 (a) dimensional parameters from the experiments in silica nanopores from Deng et al., 2013 and (b) computed nondimensionalized parameters ........................................... 36

3.1 Convergence test on toy model with “direct” method implementation of boundary conditions (3.28)-(3.29). Reading the columns from left to right, the boundary conditions are: homogeneous Dirichlet, linear & coupled, nonlinear & uncoupled, and BV-like. We compute six solutions on a uniform mesh \( dx = 1/20 \) using constant time steps up to time \( t = 1 \). The \( i \)th solution \( u_i \) is computed using \( dt = 0.001/2^i \). The ratios are computed using the discrete solutions \( u_i \) at the final time \( t = 1 \); the ratio is defined as \( \|u_i - u_{i+1}\| / \|u_{i+1} - u_{i+2}\| \) with the \( l^2 \) norm. Ratios approaching 4 indicate second order accuracy in time, while ratios approaching 2 indicate first order accuracy. ........................................ 51

3.2 Convergence Test on Toy Model with ghost point method and BV-like boundary conditions. See Caption 3.1 for a full explanation. The mesh width is \( dx = 1/20 \) and the simulation ran to time \( t = 1 \). Ratios tending to 4 indicate second-order accuracy in time. 53

3.3 Convergence test on full model with current boundary conditions and \( j_{ext} = 0 \). L2 Norm and constant time steps. \( N = 300, t_{end} = 0.1, \) all model parameters set to 1 except \( \epsilon = 0.1 \). 58

3.4 Average \( dt \) values chosen by the adaptive stepper for various values of \( \epsilon \) for the full PNP equations with tol=10\(^{-6}\), \( \delta = 1, k = 1, N \) and \( dx \) chosen appropriately. Voltage boundary conditions with \( v = 0 \) are used. .......................................................... 59
List of Symbols

\( \lambda_S, \lambda_s \) Dimensional [m] and nondimensional width of the Stern layer

\( \varepsilon \) Dielectric permittivity [F/m]

\( \varepsilon_{\text{stern}}, \varepsilon_{\text{diff}} \) Dielectric permittivities of the Stern layer and the diffuse charge region [F/m]

\( \varepsilon_r \) Relative permittivity

\( \Phi, \phi \) Dimensional [V] and dimensionless electric potential

\( C, c \) Dimensional [mol/m\(^3\)] and dimensionless concentration

\( C_\pm, c_\pm \) Dimensional [mol/m\(^3\)] and dimensionless cation (+) and anion (-) concentration

\( T, T \) Dimensional [K] and dimensionless temperature

\( k_B \) Boltzmann’s constant [m\(^2\)kg/(s\(^2\)K)]

\( U \) Internal energy [J]

\( a \) Effective diameter of a solvated ion [m]

\( \mu \) Chemical potential [J/mol]

\( \mu_\pm \) Cation (+) and anion (-) chemical potential [J/mol]

\( e \) Electron charge [C]

\( \rho \) Charge density [C/m\(^3\)]

\( C_0 \) Reference concentration [mol/m\(^3\)]

\( \lambda_D \) Debye length [m]

\( D, D_\pm \) Diffusivity and cation (+) and anion (-) diffusivity [m\(^2\)/s]
**D** Electric displacement field [C/m²]

\(J, J_\pm\) Molar flux density and cation (+) and anion (-) number flux density [mol/(m²s)]

\(\eta\) Overpotential [V]

\(I, I_0\) Reaction current density and equilibrium exchange current density [A/m²]

\(R\) Ideal gas constant [J/mol K] (Chapters 1, 2, 5), Resistance (Chapter 4) [Ω]

\(F\) Faraday’s constant [C/mol]

\(\alpha\) Butler-Volmer transfer coefficient, dimensionless thermal diffusivity

\(\tau, t\) Dimensional [s] and dimensionless time

\(X, x\) Dimensional [m] and dimensionless length

\(L\) Distance between the two Stern planes [m]

\(L_{\text{diff}}, \ell_{\text{diff}}\) Dimensional [m] and dimensionless length of the diffuse charge region

\(z, z_\pm\) Charge number, charge number for cations (+) and anions (-)

\(\nu_i\) Stoichiometric coefficient of species \(i\)

\(\nu\) Nondimensional particle size parameter

\(B_r\) Reaction rate of reaction \(r\) [mol/m³s]

\(\mu^{\text{ex}}\) Excess chemical potential [J/mol]

\(K_c, K_a\) Cathodic and anodic reaction rates [mol/m³s]

\(K, k\) General dimensional [mol/m³s] and dimensionless reaction rate parameter

\(k_c, j_r; k_f, k_b\) Nondimensional forward and backward reaction rates

**E, \(E\)** Electric field [V/m]

**P, \(P\)** Electric polarization density [C/m²], pressure

\(\rho_m\) Mass density [kg/m³]

\(c_p\) Specific heat capacity at constant pressure [J/(kg·K)]

\(J_q\) Heat flux density [W/m²]
\textbf{\textit{J}_e} Electric current density \([A/m^2]\)

\textbf{\textit{B}} Magnetic field \([J/(A\cdot m^2)]\)

\textbf{\textit{M}} Magnetization \([A/m]\)

\(H_{i0}^f\) Molar enthalpy of formation of species \(i\) \([J/mol]\)

\(v\) Average bulk fluid velocity \([m/s]\)

\(K_T\) Thermal conductivity \([W/(m\cdot K)]\)

\(n\) Normal vector

\(\sigma_s\) Surface charge density \([C/m^2]\)

\(\textbf{\textit{J}_{ext}}, j_{ext}\) Dimensional \([A/m^2]\) and dimensionless external (applied) electrical current density

\(n\) Number of electrons involved in a reaction

\(\textbf{\textit{J}}_q,\text{ext}, j_{q,ext}\) Dimensional \([W/m^2]\) and dimensionless external (applied) heat flux density

\(\mathcal{T}_{\text{amb}}\) Ambient temperature \([K]\)

\(H, h\) Dimensional and dimensionless heat transfer coefficient \([W/m^2\cdot K]\)

\(\theta\) Fraction of occupied surface sites

\(K_E\) Adsorption equilibrium constant

\(Q_s, q_s\) Dimensional \([mol/m^2]\) and dimensionless surface coverage parameter

\(D_0\) Reference diffusivity \([m^2/s]\)

\(T_0\) Reference temperature \([K]\)

\(j, j_\pm\) Nondimensionalized number flux density for cations (+) and anions (-)

\(\epsilon\) Ratio of Debye length \(\lambda_D\) and device thickness \(L\) (Chapters 1, 2, 4 and 5), numerical error (Chapter 3).

\(\delta\) Ratio of Stern layer thickness \(\lambda_S\) and Debye length \(\lambda_D\)

\(\beta\) Dimensionless Joule heating parameter

\(d\) Dimensionless diffusivity
ω Ratio of $dt_{\text{now}}$ and $dt_{\text{old}}$

LTE Local truncation error

H.O.T. Higher order terms

$\epsilon_c, \epsilon_f$ Coarse and fine error

tol Error tolerance

range Error range

$\eta_{\text{min}}, \eta_{\text{max}}$ Adaptive time stepper search range

$Z$ Electrical impedance [Ω]

$Z_W$ Warburg impedance [Ω]

$V, v$ Dimensional [V] and dimensionless voltage

$S, \tilde{S}$ Dimensional [V/s] and dimensionless voltage scan rate

$\tilde{R}, \tilde{C}$ Nondimensional resistance and capacitance
Chapter 1

Introduction

As global energy consumption increases and reliance on renewable energy grows, policy makers will depend more on energy storage to ensure system efficiency and energy availability. Electrochemical energy storage devices such as batteries, electrolytic capacitors, fuel cells and supercapacitors are some of the most important energy storage technologies and are ubiquitous in modern society.

Electrochemical cells consist of an electrolyte in contact with one or more conducting electrodes. Ions are transported to and interact with the electrodes, changing the composition of the electrode through electron transfer, a process which may either be caused by or give rise to an external electrical current. Electrochemical cells fill a range of roles, from high energy density (fuel cells) to high power density (capacitors). Lithium-ion batteries are perhaps the most important electrochemical storage device today, and see use in everything from cell phones to pacemakers [1]. In the future, users of electrochemical devices will require more detailed information on their characteristics in order to predict how charging and discharging profiles will influence efficiency, state of charge, state of health and lifetime. Mathematical models are created in order to predict time-domain properties of the electrochemical cells such as voltage and current response, small-signal properties such as impedance, and also factors influencing the state of health such as electrode or electrolyte degeneration and capacity fade.

Electrochemical bulk and interface models are used for numerous purposes in science and engineering. Within the field of energy storage, they are used for state-of-charge estimation [2, 3], modeling of charging-discharging cycles in batteries [4, 5], start-up behaviour of fuel cells [6] and lifetime prediction [7] to name a few. These models are used in many important and rapidly developing technologies in
energy conservation such as hybrid electric vehicles [8, 9], photovoltaics and wind power [10]. Outside of specifically modeling energy storage devices, the equations used in this work have broad applicability to describe systems where transport of charged particles are coupled to an electric field. Some important examples are ionic liquids [11, 12], charged membranes [13, 14], liquid junctions and electrokinetic phenomena [15, 16, 17] such as electrodialysis. Many of the models in use are empirical [4, 7, 8, 9, 10] or circuit-based [2, 3]; they are not developed from a first principles approach and greatly simplify or neglect much of the physics by omitting the coupling between fields and ignoring interfacial dynamics and physical processes occurring in the interfacial regions. The regime of operation for which these models can provide predictive capability is therefore limited.

The classical problem of electrical conduction between two flat electrodes was studied by Nernst [18] over a century ago. Since then, many models of electrochemical cells have been proposed, but they ignore many poorly understood details occurring at the interface. Rather than trying to create a three-dimensional model which accounts for all of the details (a challenging task), researchers have worked with one-dimensional models to include additional physics, and also to address the numerical challenges when incorporating complex nonlinear boundary conditions.

Recently, major contributions have been made by Martin Bazant and coworkers [19, 20, 21, 22] towards a modern mathematical model that accounts for the electrode/electrolyte interface as well as electrolyte bulk phenomena in a more self consistent and rigorous fashion. In this thesis, their model is used as a foundation into which additional effects can be incorporated and studied, culminating in a versatile model which comprehensively captures the dynamics of the problem and physical processes occurring at and in the immediate region adjacent to the interface.

1.1 Motivation and Modeling Philosophy

Since the work in this thesis focuses almost exclusively on numerical modeling of a 1-D cell, we wish to justify our work for an end-user, such as an operator of an electrochemical device.

Electrochemical devices are crucial for enabling renewable energy utilization for energy storage (batteries, fuel cells, supercapacitors), hydrogen production, electro-incineration of wastewater or carbon sequestration, and in many other applications. These devices are sometimes integrated within a system that includes power conversion equipment, which enables the integration of electrochemical devices into electrical grids with other energy sources. Energy storage devices connected to the grid or used in
transportation systems are subjected to arbitrary charging and discharging profiles, temperatures, and other factors. The prediction of performance metrics such as available power density at different states of charge under these diverse conditions is currently not well understood. Other end-user concerns could include: weight, cost, safety, and lifetime, which also cannot be accurately predicted based on in-situ measurements alone. A conventional approach amongst manufacturers is to leverage experimental experience to guide the development of new energy storage devices. Experimental results, while essential, can become less relevant when the underlying physics is poorly understood. Mathematical modeling, then, serves to bridge the gap between the fundamental physics behind device operation and experimental results.

A mathematical model that is derived from first principles and is computationally efficient is useful to an end-user in, among other things,

- predicting the electrical, mechanical and thermal properties of the device,
- exploring new manufacturing or material systems that could lead to increased performance or functionality, lower cost, the use of low toxicity materials, lower weight, safe operation and longer operating lifetimes,
- determining the role of electrode surface impurities, surface morphology and structural deformations on device characteristics, and
- designing controllers for the power conversion equipment.

Also, from an engineering perspective, electrochemical devices have different performance metrics and end-user requirements. However, the modelling procedure for various devices often share many things in common, in that the information gained from modeling one system can often be applied to other systems with only minor changes. We do not intend the modeling and simulation work in this thesis to comprehensively cover all of the points listed above, but only to make advances in a few areas and to create a framework (equations, numerical method) from which additional physics can be added, if their mechanisms are known. For example, if electrode state-of-health was known to be a function of total current through the electrode, this could easily be incorporated into the equations if the functional relationship between integrated current and reaction rate was given.

Furthermore, many problems in electrochemistry are three dimensional in nature, especially if effects such as surface coverage and fluid flow are to be fully captured. The creation of a model that incorporates
all of the important physics is still an active area of research on two fronts: incorporation of the relevant physics and development of an efficient numerical scheme. Unfortunately, the system we are considering has many inherent complexities (nonlinearities, complicated physics, numerical instabilities) which make the development of a 3D model impractical as a first step. Instead, our approach is to consider only the 1D problem, while incorporating as much physics as possible. We propose that by solving the technical issues (such as in the numerics and time-stepping) involved in a 1D model, we make the extension to higher dimensions much more tractable.

Finally, it is often difficult to obtain certain transport and thermodynamic parameters, particularly if the system has built-in uncertainties such as impurities or complex surface morphology and structure. For this reason, and for validation purposes, it is important for the model to be capable of matching simulated results to experimental ones. In electrochemistry, the two most important experimental techniques are voltammetry (application of a ramped or stepped voltage to a test electrode and measuring the resulting current) and impedance spectroscopy (application of a frequency sweep, usually in voltage, and measuring the resulting current). The model should be able to easily replicate these experiments using the appropriate boundary conditions and post-processing tools. Difficult to obtain parameters can then be estimated using these tools by fitting simulated values to experimental values.

1.2 A Perspective on Electrochemical Cell Modeling

There is a rich history of modelling electrochemical systems, starting in the 18th century with early galvanic cells [23]. The modern approach originates from the ideas of Gouy [24], Chapman [25] and Stern [26], who were interested in the structure of the electrical double layer. Interest in the structure of the double layer is well justified: almost all of the interesting phenomena occur in this region, since it is where Faradaic reactions (chemical reactions that involve the transfer of electrons) take place and where the largest electric fields are found.

For the purposes of clarity, we will define what we mean when we write “electrical double layer” and “bulk region”. When speaking about the “electrical double layer” or EDL, we are referring to the Stern, (or Helmholtz layer or compact layer) of ions adjacent to the electrode surface as well as the adjacent region of diffuse charge. The “bulk” traditionally refers to the remainder of the electrolyte. However, when modeling, our partial differential equations describe everything except the Stern layer; specifically, we are using continuum methods to model both the bulk region and the diffuse charge regions between
the bulk and the Stern layers. Finally, when we refer to the “electrode”, we refer to the electrically conducting phase in contact with the ionic conductor, which does not include either the diffuse or compact part of the double layer.

A common feature of models found in the electrochemical literature is the assumption of electroneutrality of the bulk electrolyte. Though the electroneutrality assumption ignores the dynamics of the diffuse charge region, it greatly simplifies computations and is valid when the double layers are thin compared to the size of the entire cell. As theoretical and simulation results will show in Chapter 5, however, diffuse charge effects cannot be ignored in regimes with thick double layers relative to the interelectrode width and/or a large applied voltage. Furthermore, we will show that our equations predict the breakdown of the bulk electroneutrality assumption under certain conditions.

Figure 1.1 shows a representation of ion distributions near the electrode in the Gouy-Chapman and Stern theories. In Gouy-Chapman theory, ions near an electrode are arranged in a diffuse manner according to the Boltzmann distribution. This model was later amended by Stern to include a compact layer of ions sitting adjacent to the electrode surface, where \( \lambda_S \) is the Stern width, or open half plane distance. The Stern or Helmholtz plane or is defined as where the Stern layer “ends” and the diffuse charge region “begins”. The scale of interactions near the electrode is usually discussed in terms of the Debye length (\( \lambda_D \)), the length scale for electrostatic screening. Near the electrode we have the Stern layer (\( \sim 1\lambda_D \)) and diffuse region (\( \sim 5\lambda_D \)), and the region further away (\( > 10\lambda_D \)) is classified as the bulk where electroneutrality can be assumed. See Chapters 2 and 3 of Bockris [27] for a discussion of classical ionic-solvent and ion-ion interactions and Gouy-Chapman theory.

The width of the Stern layer, \( \lambda_S \) in Figure 1.1 is a somewhat tricky quantity to define. It is sometimes thought of as the actual width of the compact layer (i.e. less than a few solvation radii) and sometimes thought of primarily as a measure of the capacitance of the compact layer [28]. In the latter case, an effective Stern width \( \lambda_S \) is often defined as

\[
\lambda_S = \frac{\varepsilon_{\text{stern}}}{C_S}
\]

(1.1)

where \( \varepsilon_{\text{stern}} \) and \( C_S \) are the averaged differential permittivity and capacitance per unit area of the compact layer, respectively. This is a key facet of the Gouy-Chapman-Stern model of the double layer, which assumes that the capacitance per unit area of the compact layer is constant. Realistically, \( \lambda_S \) would need to be fitted if it was needed for modeling. However, when computations are performed later, the dimensionless equations only use the dimensionless parameter \( \delta \), which is the ratio between the Stern
Figure 1.1: Charge distribution and the potential $\Phi$ near an electrode in Gouy-Chapman and Stern theories. In Gouy-Chapman theory, there is a region of diffuse charge adjacent to the electrode. The Stern model adds a compact layer of charge on the electrode surface. In the figure, $\lambda_S$ is the width of the Stern layer.

layer width and the Debye length (as discussed later in Section 2.6). In our work we are interested in taking limits of $\delta$, which correspond to regimes where dynamics are dominated by either the compact layer or the diffuse layer.

The literature contains studies of the double layer using different modelling techniques (computational quantum dynamics [29] and molecular dynamics [30]) and experiments (e.g. electron microscopy [31, 32] and spectroscopy [33]). However, one of the most important methods (and most important to the current work) is using a statistical mechanical approach via modifications of the Poisson-Boltzmann (PB) equation. These statistical methods, which result in models we refer to as Modified Poisson-Boltzmann, or MPB models, predict the equilibrium behaviour of the diffuse part of the double layer, and were the first models to incorporate a number of important physics such as excluded volume (the effect of finite ion size, also called steric effects) and polarization (bound charge and dielectric effects) [34].

One way of deriving the basic PB equation for a dilute binary 1-1 electrolyte uses the phenomenological free energy (as detailed in [35]):

$$F = U - TS = \int dx \left( -\frac{\varepsilon}{2} |\nabla \Phi|^2 + eC_+ \Phi - eC_- \Phi - \mu_+ C_+ - \mu_- C_- \right) + \frac{k_B T}{a^3} \int dx \left[ a^3 C_+ \ln (a^3 C_+) + a^3 C_- \ln (a^3 C_-) \right]$$  \hspace{1cm} (1.2)
where $F$, $U$, $S$, and $T$ are the Helmholtz free energy, internal energy, entropy and temperature, respectively. $C_+$ and $C_-$ are the number densities of the positive and negative ions, with associated chemical potentials $\mu_+$ and $\mu_-$, respectively, and $\varepsilon$ and $\Phi$ are the permittivity and electric potential, respectively.

$a$ is a size parameter for ions, generally taken to be the effective solvation diameter, which corresponds to the size of a solvated ion. The minimization of equation (1.2) with respect to $\Phi$ and $C_{\pm}$ gives their equilibrium distributions. Setting the variation of $F$ with respect to $\Phi$ to zero gives the Poisson equation

$$-\nabla \cdot (\varepsilon \nabla \Phi) = \rho := e (C_+ - C_-) \tag{1.3}$$

where $\rho$ represents charge density. Similarly, setting the variation of $F$ with respect to $C_{\pm}$ to zero gives the equilibrium distribution of ions.

$$C_{\pm} (\Phi) = C_0 \exp \left( \frac{\mp e \Phi}{k_B T} \right) \tag{1.4}$$

where $C_0 = \exp (\mu_+ / k_B T) / a^3$ is a reference concentration. Substituting equation (1.4) into (1.3) results in the classical Poisson-Boltzmann equation,

$$-\nabla \cdot (\varepsilon \nabla \Phi) = 2eC_0 \sinh \left( \frac{e \Phi}{k_B T} \right) \tag{1.5}$$

Equation (1.5) was solved analytically by Gouy and Chapman for the 1-D case with a 1-1 electrolyte. The one dimensional nondimensionalized PB equation,

$$\frac{d^2 \phi}{dx^2} = \sinh (\phi) \tag{1.6}$$

can be solved analytically on the half-line $[0, \infty)$ with $\phi(0) = \phi_0$, $\phi(\infty) = 0$, and admits a solution

$$\phi = 2 \ln \left[ \frac{1 - \gamma e^{-x}}{1 + \gamma e^{-x}} \right], \quad \gamma = \frac{e^{-\phi_0 / 2} - 1}{e^{-\phi_0 / 2} + 1} \tag{1.7}$$

Figure 1.2 shows the potential from equation (1.7) with $\phi_0 = 1$ and one of the ion concentrations as a function of the distance from the interface.

The early workers in the field were primarily interested in matching the theory that they had developed to measurements of, among other things, differential capacitance (per unit area), defined as the derivative of surface charge density with respect to the potential difference across the double layer. In the simple
one dimensional flat electrode case, equation (1.5) can be integrated to obtain [36]

$$C_{\text{diff}}(\Delta \Phi) = \sqrt{\frac{2e^2C_0\varepsilon}{k_BT}} \cosh \left[ \frac{e\Delta \Phi}{k_BT} \right]$$

(1.8)

where $\Delta \Phi$ is the potential drop between the electrode and the bulk solution. Equation (1.8) is known as the Gouy-Chapman model of double layer capacitance, and will be revisited later in the thesis when simulations are performed on systems with blocking electrodes (Section 5.5).

The pioneering work of Gouy and Chapman was carried on by Grahame [37, 38] and Eigen and Wicke [39], who continued to expand the theory to create expressions that could be validated by measuring differential capacitance and surface tension. This work was followed by Macdonald [40, 41, 42, 43, 44] and Liu [45], who made significant contributions by including steric and polarization effects by way of a lattice gas model. A number of authors work in this area currently, continuing to extend Poisson-Boltzmann theory to study effects not included in mean-field theory such as overscreening [46, 11], steric [47, 48, 49, 50] and polarization effects [35, 51].

A closely related way of modeling the double layer is using the Poisson-Nernst-Planck (PNP) equations, which is the Poisson equation for the electric potential coupled to conservation equations for the $N$ ionic species. For a dilute electrolyte in steady-state, the $N + 1$ equations can be written as

$$\nabla \cdot \left( -\frac{z_iD_i\varepsilon}{k_BT}C_i\nabla \Phi - D_i\nabla C_i \right) = 0$$

(1.9)
\[ \nabla \cdot \mathbf{D} = -\nabla \cdot (\varepsilon \nabla \Phi) = q \]  
\hspace{1cm} (1.10)  

where \( D_i, z_i \) and \( C_i \) are the diffusion coefficient, charge number and number density for the \( i^{th} \) ionic species, respectively, and \( \mathbf{D} \) is the electric displacement field. Note that equation (1.9) assumes that the Einstein relation, \( \mu_i = \frac{D_i}{k_B T} \), holds. An early and important work using the steady state Poisson-Nernst-Planck equations to model the double layer was by Smyrl and Newman [52, 53], who performed a matched asymptotic expansion to arrive at an approximate solution. Other authors [54, 55] have also taken this approach, and recently Bazant, Chu and Bayly [20, 19] have used the same method as Smyrl and Newman by applying asymptotic expansions to the PNP equations in addition to solving the steady-state equations numerically. PNP models are in fact cousins to MPB models since the Poisson equation can be directly derived from equation (1.2) and the flux density is related to the electrochemical potential \( \mu \) via  
\[ J_i = -\frac{D_i}{k_B T} C_i \nabla \mu_i \]  
\hspace{1cm} (1.11)  

Both the Poisson-Boltzmann and Poisson-Nernst-Planck equations are important to modeling the bulk and the diffuse region of the electric double layer. However, most work assumes static conditions as in equations (1.9)–(1.10) and so cannot model dynamic effects.

Equally important to a model for the diffuse region is a model for electrode reactions. Regardless of whether a single step or multi-step electrode reaction is taking place, modern electrochemistry ubiquitously uses the Butler-Volmer equation to relate current to the electrode potential. The version of the BV equation most commonly seen in the literature is  
\[ I = I_0 \left[ \exp \frac{-\alpha F \eta}{RT} - \exp \frac{(1 - \alpha) F \eta}{RT} \right]. \]  
\hspace{1cm} (1.12)  

where \( \eta = \Delta \Phi - \Delta \Phi_0 \) is the overpotential, or the electrode potential minus the equilibrium electrode potential (both with reference to an ideal reference electrode), \( F \) is Faraday’s constant and \( R \) is the ideal gas constant \((F/R = e/k_B)\). \( \alpha \) is a “transfer coefficient” which is often set to 1/2, and \( I_0 \) is a reference current density.

All versions of the BV equation are based on Eyring’s transition state theory [56] with the application of what’s known as the Butler-Volmer hypothesis: the electrostatic energy of the intermediate reaction state is a weighted average (\( \alpha \) and \( 1 - \alpha \)) of the initial and final states. A good overview of Butler-Volmer reaction kinetics can be found in Chapter 3 of [57], and we provide a summary in Appendix C. There are other theories for reaction kinetics which do not depend on the assumption of a transition
state. A well-known example is Ward’s statistical rate theory [58]. There is also the recently developed Marcus-Hush-Chidsey kinetics [59, 60], which is a microscopic theory of charge transfer at electrodes based on Marcus theory. However, we will elect to use Butler-Volmer kinetics in this work since it is easier to apply and matches many experimental predictions [61].

1.3 Review of Battery Models

It is useful to introduce at this stage a review of battery models since so many developments in electrochemistry and modeling of electrochemical cells were spurred on by the development of batteries. The interest in batteries has taken on a greater sense of urgency given the large energy storage requirements for electrical grids that rely on renewable sources of energy. This review also serves as a gateway to the objectives of this thesis.

Modern battery models which describe an entire battery (as opposed to a single electrode) tend to focus on a particular aspect of battery behaviour or compute a particular property or aspect of cell behaviour (such as lifetime [62, 63, 64] or state-of-charge prediction [65, 66]), and range from multiphysics PDE models to empirical equations. Wenzl et. al. [7] classifies four different types of battery models: electrochemical first-principles (PDE), equivalent circuit (mathematically equivalent to a system of ODEs), empirical (based on experiment) and statistical (eg. artificial neural network). Each approach has its advantages and disadvantages. Empirical (see for example [4]), circuit (see for example [67], [68] and [69]) and “lumped” ODE models (see for example [70] and [71]) can be fairly inclusive of physical effects and are quick and easy to use, but are often fitted to measured results or averaged over more complex equations, making them less representative of the underlying physics. Linear circuit models in particular are popular due to the ease with which small-signal circuit parameters at a given operating point can be identified using impedance spectroscopy [72, 73, 74]. Statistical models are not the focus of this work, but see [75] for an example of an artificial neural network used to predict battery capacity.

The linear circuit approach to battery modeling is perhaps the most popular due to the speed and ease with which circuit values can be obtained; this will be discussed later in the thesis with an example of a linear circuit model. However, difficulty can arise due to the ambiguousness of determining the fitting parameters. More importantly, equivalent linear circuit models are restricted to small-signal regimes due to the nature of their construction, which eliminates access to many useful modes of operation involving larger currents with arbitrary temporal profiles.
PDE models, on the other hand, are first principles models of the bulk and near-interface regions which use statistical and quantum mechanics to compute the transport and thermodynamic parameters. A discretized version of these equations becomes a nonlinear set of coupled ordinary differential equations which could, in principle, also be formulated as nonlinear distributed circuits by modeling first-order time-derivatives as capacitors, second-order space derivatives as resistors and all other terms as dependent sources. This type of transformation, however, has limited value other than perhaps for visualization of the underlying equations.

The earliest electrochemical PDE models such as the Sand system [76] (equations (1.13)–(1.15)), and the Cottrell system, (equations (1.13)–(1.14), (1.16)) model the time-dependent behaviour of the region near the electrode under current and voltage steps, respectively (see Chapter 2 of [77]),

\[
\frac{\partial C}{\partial \tau} = D \frac{\partial^2 C}{\partial X^2} \tag{1.13}
\]

\[
C(X, 0) = C_0, C(\infty, \tau \geq 0) = C_0 \tag{1.14}
\]

\[
\frac{\partial C}{\partial X}(0, \tau > 0) = J_0, \tag{1.15}
\]

\[
C(0, \tau > 0) = 0 \tag{1.16}
\]

In both the Sand and Cottrell systems, an initial concentration profile is subjected to an instantaneous change in current (1.15) or voltage (1.16) at the electrode and the equations model the resulting time-dependent concentration profile (the Sand/Cottrell system will be revisited later in the thesis in Section 5.4). The advantage of PDE models lies in being able to study length and time scales unavailable to micro-scale methods while retaining the ability to trace modeling equations back to first principles. The trade-off is that PDE models are usually more computationally intensive compared to the empirical/statistical/equivalent circuit modeling approaches previously discussed which make simplifying assumptions.

One major school of modern PDE models belongs to the work of John Newman and coworkers on porous electrode batteries [78], starting on lead-acid batteries [79] with Tiedemann and later on lithium-ion batteries [80] with Doyle and Fuller. This work has been extremely influential, as essentially all electrochemical models of the hugely important family of lithium batteries since then have followed Newman’s framework. These models are a system of fully coupled PDEs using concentrated solution transport theory, Butler-Volmer reaction kinetics, and in the case of lithium batteries, an extra diffusion
PDE for the average lithium concentration in the insertion particles. One notable feature of Newman’s model is the assumption of electroneutrality in the electrolyte \((z_+c_+ + z_-c_- = 0)\), which means that Poisson’s equation is not solved in the bulk. The current edition of Newman’s book [81] is recommended to readers interested in the physics of this model. Ferguson & Bazant [82] also presents the mathematics of Newman’s concentrated electrolyte theory.

Another school of PDE models is the family of thin film models developed by Martin Bazant and colleagues. The original model [20, 19] and its time-dependent version [22] is an electrochemical model using the Poisson-Nernst-Planck equations with generalized Frumkin-Butler-Volmer (gFBV) kinetics [83], and models a cell with planar electrodes. The distinguishing characteristic of the Bazant family of models is its handling of the electrical double layer: the diffuse region is modeled explicitly by coupling reaction kinetics to a mixed boundary condition on \(\Phi\), the electric potential. The treatment of diffuse charge dynamics (that is, coupling of Faradaic reactions to the electric potential field) is missing from the Newman family of models, though very recently there have been attempts to add these elements into Newman’s lithium-ion model [84]. It is also fairly straightforward to incorporate steric effects into the Bazant family of models, and this has been done [49, 50, 17]. The PNP-gFBV model has wide applicability in electrochemistry, and has been used to model a large number of different systems, including porous media [85, 86, 87, 88], microelectrodes [89, 90], ion-exchange membranes [13, 14], electrokinetic phenomena [15, 16, 17], ionic liquids [11, 12], electrochemical thin films [20, 19, 21], fuel cells [91], supercapacitors [92], and many more.

In order to elaborate on what exactly is meant by “diffuse charge effects”, and how they affect reaction kinetics, we have plotted a typical concentration distribution for a \(z : z\) electrolyte in Figure 1.3, generated using the model developed in Chapters 2 and 3. The diffuse layer parameter, \(\epsilon\), is chosen so that double layers are thin.

The concentrations in Figure 1.3 are *almost* electroneutral, which is to say that \(c_+ = c_-\) is true for the entire domain except for two narrow regions near the boundaries. The zoomed in region at the right hand side boundary (Figure 1.3b) is a *diffuse double layer*, where concentrations can differ greatly from their bulk values. As a brief aside, Figure 1.3b shows the same type of diffuse double layer which we showed when we plotted a solution of the Poisson-Boltzmann equation in Figure 1.2. The Poisson-Boltzmann equation takes the value of the concentrations outside of the double layer (i.e. at \(x = 0.99\) in Figure 1.3 and enters it as the bulk concentration \(C_0\) in equation (1.5). Note that only one of the two values of the concentration is needed for equation (1.5) since \(c_+ = c_-\) everywhere except in the diffuse region.
Now, when we say that electroneutrality is assumed by a model, what we mean is that the model assumes that the interelectrode width (distance between the two electrodes, $L$) is so large (equivalently, that the diffuse region is so thin) that the bulk can be extended right up to the electrode, and that the diffuse part of the double layer can be ignored. However, the diffuse double layer is present regardless of its size and so there always exists a difference between the concentration’s bulk value and its value at the reaction plane, with a corresponding jump in the potential. This causes an issue when there are reactions at the electrode: since both the concentration and potential enter into the Butler-Volmer equation, there is a difference when using their bulk values versus their values at the reaction plane. This is what’s known as the Frumkin effect, a correction which was first introduced by Frumkin [93] and Levich [94] and later applied by Itskovich, Kornyshev and Vorontyntsev [95, 96] to the modeling of solid electrolytes with one mobile ionic species and fixed background charge. Frumkin was the first to point out that the potential drop which drives reactions is across the Stern layer (i.e. based on local quantities) rather than in relation to a reference electrode far away, although complete mathematical models for dynamical situations were not formulated until much later. The Frumkin effect belongs to a family of additions and modifications to classical theory when diffuse charge dynamics are taken into account, a field which has seen significant contributions from a variety of workers in the past two decades [20, 21, 28, 97, 89]. A further review of historical and recent work in the field of diffuse charge effects as they apply to voltammetry is presented in Chapter 5.

Finally, temperature is an aspect of modeling which, while obviously important, is often neglected or simplified in modern models of electrochemical systems. While there are many models in the literature which consider temperature effects, many use lumped ODE, empirical or linear circuit models. Some
models such as Liu et. al. [98], Fang et. al. [99], Botte, Subramanian and White [100] and Pals and Newman [101] treat the overall temperature of the battery as depending on time only (not on space), and solve the resulting ODE with an empirical source term, while others ([67] or [102] for example) use an equivalent circuit representation of the battery geometry to model heat flow. More complex models which have full coupling between the PDEs for temperature and mass transport do exist [103], but some [104, 105] still use an averaged, or lumped source term in the temperature PDE. In this thesis, our aim is to take the initial steps in including a dynamic energy transport PDE which couples to the PNP-FBV equations.

1.4 Thesis Objectives and Contributions

As discussed in the Section 1.3, modern electrochemical models simplify aspects of the physics including treatment of diffuse charge and temperature coupling. It is too challenging a task to incorporate all of the physics in a 3d model of an electrochemical cell at this stage, so we begin by introducing additional physics in a 1d representation of a electrochemical cell. This cell can not be used to describe the majority of physical systems however it allows us to explore the impact of the additional physics and where warranted we can compare these results to known analytical results or qualitative results obtained from suitable experiments obtained from the literature. More importantly, the simulation of a 1 d electrochemical cell allows one to address the numerical challenges associated with including additional physics and the impact of nonlinear boundary conditions and interfacial dynamic effects. A fully-coupled one-dimensional PDE model for a binary electrolyte with parallel planar electrodes and a thin interelectrode gap (which allows us to ignore advection) is developed in this thesis. We begin by presenting three-dimensional PDEs which describe mass transport coupled to the electric field, temperature evolution and electrode reactions (more complexity could be added in the future), and end with a one-dimensional set of nondimensionalized equations.

We then numerically approximate solutions of the system using an adaptive time step scheme on a nonuniform spatial mesh and analyze both the numerical scheme and the properties of the approximated solutions. In terms of numerical methods, we use a multistep implicit-explicit scheme with adaptive time stepping and we analyze the numerics in detail, along with its suitability for use with systems of coupled parabolic and elliptic PDEs such as the time-dependent PNP equations.

The three main contributions in modeling are (1) the inclusion of polarization effects into the PNP
equations, (2) deriving a new equation to couple temperature to the PNP equations and (3) modeling diffuse charge dynamics. Inclusion of polarization (and steric) effects into electrochemical models has traditionally been outside of the domain of mainstream modeling, but these effects may be important, especially when large and/or high frequency forcings are applied. Although the developed model is immediately relevant to electrochemical thin films, it is quite general (except for the lack of advection) and applicable to a wider variety of systems. The temperature equation developed here comes directly from nonequilibrium thermodynamics, and has been derived specifically to include polarization effects. The predictions from the model may be used to suggest future experiments to illustrate the importance of the added physics.

Using the equations and numerical method, we run simulations to test the inclusion of temperature, polarization and surface coverage effects into the model by varying parameters, and perform frequency sweeps to mimic impedance spectroscopy experiments. We then use the model to apply ramped voltages to a variety of electrochemical cells: single electrode systems with supported and unsupported electrolytes, capacitors with blocking electrodes, thin films and finally in membranes or microchannels with background charge, using the leaky-membrane model.

1.5 Thesis Layout

This thesis contains five chapters. Chapter 1 has provided a background on modeling of the electrolyte/electrode interface and reviewed existing models. In Chapter 2, the modeling equations are developed, along with a discussion of simplifications which were used. Chapter 2 also contains the nondimensionalization of the modeling equations. Chapter 3 shows the development of the nondimensionalized modeling equations and includes a number of numerical tests and a discussion on the numerical properties of the model. Simulation results for temperature, surface coverage and polarization effects are given in Chapter 4, and the impedance spectroscopy tool is discussed. Finally, in Chapter 5, the model is used to study the transient response of cells to ramp voltages in order to mimic electrochemical voltammetry experiments.
Chapter 2

Equation Development

In this chapter, we develop a general system of equations which describe mass and energy transport in an electrochemical system. While we do not restrict ourselves to a liquid electrolyte, we do make the assumption of mechanical equilibrium and that advection does not occur, or that $\mathbf{v} = 0$. This assumption holds for many situations of interest, particularly in sealed batteries and capacitors, and while in principle convection effects could be added, they are not within the scope of this work. We also (along with Biesheuvel et. al. [21]) hold the view that the Poisson-Nernst-Planck equations are valid up to the Stern plane but not to the electrode itself. Specifically, the modeling PDE’s are valid in both the largely electroneutral bulk and in the diffuse charge region of the electric double layer (the region between the bulk and the Stern layer). The link from the electrode, across the Stern layer, to the PDEs is made by using the appropriate boundary conditions, which are approximations based on more accurate quantum-mechanical models.

Figure 2.1 shows the regions relevant to the model. Immediately adjacent to the electrodes are the Stern, or compact layers which have width $\lambda_S$. The Stern and diffuse layers together comprise the electrical double layer. The (largely electroneutral) bulk lies between the two electrical double layers. The definition of the diffuse region compared to the bulk region is somewhat arbitrary because there isn’t a sharp transition to electroneutrality (see Figure 1.2a). Its width $L_{\text{diff}}$, therefore, is not a precise value but a definition of convenience which will be later used to apply different dielectric properties in regions with different mean electric fields.

We take the convention that in the following,
Figure 2.1: A diagram showing the geometry of an electrolyte between two flat electrodes. $\lambda_S$ is the width of the Stern layer, a compact layer of charge on the electrode surface. Adjacent to the Stern layers are the diffuse charge regions which we define to have a rough width of $L_{\text{diff}}$. The (largely) electroneutral bulk makes up the remainder of the electrolyte. $L$ is the distance between the two Stern planes, or the interelectrode width minus $2\lambda_S$.

1. upper case, Greek and script lettering denote the dimensional form of variables and parameters,

2. lower case denote their nondimensional form, introduced in Section 2.6,

3. physical constants and parameters which are already nondimensional retain their traditional case and lettering, and

4. $z_i$, the charge number, retains its sign (so that a negative ion has $z < 0$).

The continuity equations for mass and energy can be derived by taking moment order expansions of the Boltzmann transport equation, where the zeroth order expansion yields the continuity equation for mass and the second order expansion yields the continuity equation for energy, or heat transfer (See Chapter 2 of Shu [106] for this derivation in the context of fluid mechanics). The first order moment is not needed since we do not account for advection. However, it is still used in an indirect way in developing the constitutive relationship between current density and the electric field as well as the diffusion term in the continuity equation for mass.

The general form of a continuity equation for a conserved quantity $U$ is written as

$$ \frac{\partial U}{\partial \tau} = -\nabla \cdot \mathbf{F} + \dot{U} $$

(2.1)
Some model or approximation can then be used to write the flux density $\mathbf{F}$ and the source term $\dot{U}$ in terms of $U$, $\mathbf{X}$ and $\tau$ in order to close the equation. For an electrolyte with $N$ species (indexed by $i$, and not counting the solvent), there are $N + 2$ partial differential equations: $N$ parabolic PDEs for the species $C_i(\mathbf{X}, \tau)$, one additional parabolic equation for the temperature $T(\mathbf{X}, \tau)$ and one elliptic PDE for the potential $\Phi(\mathbf{X}, \tau)$. Along with the appropriate boundary conditions and any extra equations which describe additional physics, these equations fully characterize the behaviour of the bulk, including the diffuse region.

### 2.1 Mass Transport

The continuity equation for conservation of mass for the $i$th species is

$$
\frac{\partial C_i}{\partial \tau} = -\nabla \cdot \mathbf{J}_i + \sum_{r=1}^{M} \nu_{ir} B_r
$$

Equation (2.2) is commonly referred to as the reaction-diffusion equation, where $\mathbf{J}_i$ is the flux of species $i$ with concentration $C_i$. There are $M$ reactions; $\nu_{ir}$ is the stoichiometric coefficient of species $i$ in reaction $r$ ($\nu_{ir} = 0$ if species $i$ is not involved in reaction $r$), $B_r$ is the reaction rate of reaction $r$, and $\tau$ represents time. The flux $\mathbf{J}_i$ is related to the electrochemical potential of species $i$ by

$$
\mathbf{J}_i = -\frac{D_i}{k_B T} C_i \nabla \mu_i
$$

where $D_i$ is the diffusion coefficient for the $i$th species and $\mu_i$ is the electrochemical potential of the $i$th species, defined as

$$
\mu_i = k_B T \ln C_i + z_i e \Phi + \mu_i^{\text{ex}}.
$$

$\mu_i^{\text{ex}}$ in equation (2.4) is the excess chemical potential, related to the activity coefficient via $\mu_i^{\text{ex}} = k_B T \ln \gamma_i$; it’s primarily used to model steric effects [50]. For example, one simple model for the excess chemical potential in a 1-1 electrolyte, first developed by Bikerman in 1942 [107], can be derived by
adding the extra entropy from excluded volumes to the free energy in (1.2):

\[
F = U - TS = \int d\mathbf{r} \left( -\frac{\varepsilon}{2} |\nabla \Phi|^2 + eC_+ \Phi - eC_- \Phi - \mu_+ C_+ - \mu_- C_- \right) \\
+ \frac{kT}{a^3} \int d\mathbf{r} \left[ a^3 C_+ \ln (a^3 C_+) + a^3 C_- \ln (a^3 C_-) \\
+ (1 - C_+ a^3 - C_- a^3) \ln (1 - C_+ a^3 - C_- a^3) \right]
\]

(2.5)

where, compared to equation (1.2), the last term in the second integral of (2.5) accounts for excluded volume effects, and can be derived using a lattice-gas model for electrolyte particles [48]. Taking the variation with respect to \( C_{\pm} \) as in equation (1.4) yields

\[
\mu_i^{ex} = -k_B T \ln \left( 1 - a^3 C_+ - a^3 C_- \right)
\]

(2.6)

where \( a \) is a size parameter which roughly corresponds to the hydration diameter of solvated ions [39, 17]. In equations (2.5) and (2.6), we have chosen \( a \) to be the same for both species for convenience. Equation (2.6) provides a simple approximation of size effects. More sophisticated models such as the virial equation of state for rigid sphere gasses proposed by Carnahan and Starling [108] would provide greater accuracy.

Equation (2.3) relates the flux of the \( i \)th species to the chemical potential of that species, but a more general picture of multicomponent transport can be found using the non-ideal Stefan-Maxwell equations (see Chapter 2 of [109]), where this flux also has contributions from the gradients of the other species’ electrochemical potentials. This generalization of equation (2.3) can be written succinctly as

\[
\begin{bmatrix}
J_1 \\
J_2 \\
\vdots \\
J_N 
\end{bmatrix} = -[B]^{-1} \begin{bmatrix}
\frac{C_1}{k_B T} \nabla \mu_1 \\
\frac{C_2}{k_B T} \nabla \mu_2 \\
\vdots \\
\frac{C_N}{k_B T} \nabla \mu_N 
\end{bmatrix}
\]

(2.7)

where \([B]^{-1}\) is a non-diagonal matrix of diffusion coefficients. However, this introduces the problem of having to obtain more parameters in the form of diffusion coefficients for cross-terms, but in principle, this can be done if required.
2.1.1 Bulk Reactions

The sum in equation (2.2) models chemical reactions in the electrolyte, if they occur. For a chemical reaction written as

\[ \nu_1 A + \nu_2 B = \nu_3 C + \nu_4 D \]

the reaction rate is commonly written for a single-step reaction as

\[ B_r = K_f C_A^{\nu_1} C_B^{\nu_2} - K_b C_C^{\nu_3} C_D^{\nu_4} \quad (2.8) \]

where \( K_f \) and \( K_b \) are temperature-dependent rate constants. These types of reaction rate equations come from kinetic theory and the molecular collision rates are assumed to be proportional to concentration \[110\]. However, a sophisticated model is generally not needed in electrochemical models due to the fact that high concentration and total dissociation of acids are universally desireable in electrochemical devices, meaning that bulk reactions play a minimal role. We do not include bulk reactions in our simulations in this thesis, but leave this area for future work.

2.2 Poisson Equation

Gauss’s law for the electric displacement field is

\[ \nabla \cdot D = e \sum_i^N z_i C_i \quad (2.9) \]

where \( D \) is the electric displacement field. This equation is accompanied by a constitutive relation and a definition of the electric potential:

\[ D = \varepsilon_0 E + P \quad E = -\nabla \Phi \quad (2.10) \]

The polarization\(^1\) \( P \) models the contribution of bound charge to the electric field and current density. Most generally, the polarization should be modeled using a differential equation to account for the inertia when a dipole responds to a change in the orientation of an external field. However, a common simplification, which is valid if the electric field does not change very quickly \[112\], is to assume \( P \)

\(^1\)Not to be confused with a different usage of the term ‘polarization’ in experimental electrochemistry referring to the interdependence of electrode current and potential, as in Chapter 10 of \[111\]
responds locally and instantaneously to $E$, in which case the polarization can be written as a function of the electric field. An example of such a function is the \textit{Langevin function} (see Chapter 4 of [113]) which models dielectric saturation in a polar substance. The Langevin function is

$$P(E) = \mathcal{N} p \left[ \coth \left( \frac{p|E|}{k_B T} \right) - \frac{k_B T}{p|E|} \right] \dot{E}$$

(2.11)

where $p$ is the molecular dipole moment and $\mathcal{N}$ is the number of molecules per unit volume. The Langevin function is sometimes written as a Taylor series, but in general $P(E)$ can be written (using Einstein summation notation) as

$$P_i = P_{0i} + a_{ij} E_j + b_{ijk} E_j E_k + ...$$

(2.12)

where the coefficients $a_{ij}$ and $b_{ijk}$ are components of the electric susceptibility tensors.

In the field of electrochemistry, the effect of polarization, while missing from time-dependent battery models in the literature, has been considered in studies of the structure of the double layer (Grahame [38] and Macdonald [41]). There is both theoretical [45] and experimental [27] evidence confirming that the relative permittivity $\varepsilon_r$ is an order of magnitude smaller next to the electrode ($\sim 6$) than in the bulk ($\sim 80$) because of the high electric field close to the interface. The reduction in the differential permittivity is due to layers of oriented water molecules bound near the electrode surface, causing the dielectric properties of water to dominate in the Stern and diffuse regions [45], while excess polarization due to ionic charge dominates in the bulk [51, 35], where the water dipoles are not oriented.

Regardless of the exact model, as long as $P(E)$ is known, its effect can be included using equations (2.9) and (2.10) along with an appropriate boundary condition at the Stern plane. A discussion of how to handle this required matching condition will be left to Section 2.4 when boundary conditions are discussed.

### 2.3 Energy Transport

The equation describing energy transport can be expressed in terms of pressure, entropy or temperature depending on which parameter is easiest to work with, usually based on the most practical means of representing a boundary condition. In electrochemical cells it is convenient to work with temperature,
for which the energy balance equation is

\[
\rho m c_p \frac{\partial T}{\partial \tau} = -\nabla \cdot J_q + J_e \cdot \mathbf{E} + \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \tau} + \mathbf{B} \cdot \frac{\partial \mathbf{M}}{\partial \tau} - \sum_r \sum_{i=1}^N \nu_{ir} H_{i0}^f B_r
\] (2.13)

where \( \rho_m \) is the mass density of the bulk electrolyte, \( c_p \) is the specific heat capacity at constant pressure, \( J_q \) is the heat flux, \( J_e \) is the electrical current density, \( H_{i0}^f \) is the molar enthalpy of formation for species \( i \), \( \mathbf{B} \) is the magnetic field and \( \mathbf{M} \) is the magnetization. This equation assumes that the center-of-mass averaged velocity \( \mathbf{v} \) is zero and that the system is in mechanical equilibrium. If these assumptions are broken, then additional terms must be added. Equation (2.13) was derived using Chapters 13 and 14 of de Groot and Mazur [114] and Chapters 1, 2 and 4 of Haase [115], and is detailed in Appendix A.

Equation (2.13) is quite general and describes the evolution of temperature in a polarizable medium, with source terms which include Joule heating \( (J_e \cdot \mathbf{E}) \), polarization \( (\mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \tau}) \), magnetization \( (\mathbf{B} \cdot \frac{\partial \mathbf{M}}{\partial \tau}) \), and chemical reactions \( (-\sum_r \sum_{i=1}^N \nu_{ir} H_{i0}^f B_r) \). The heat flux \( J_q \) in equation (2.13) should include the gradient of the electric potential along with the gradient of concentration (i.e. \( J_q = -\gamma_T \nabla T + \gamma_{ET} \nabla \Phi + \gamma_{CT} \nabla C \)). Similarly, the mass flux and electrical current density can depend on all three gradients. The thermal-chemical cross-terms reflect the Soret effect; the thermal-electric cross terms reflect thermoelectric effects [116]. However, these effects are relatively small and less important in electrochemical systems and so we will simply use Fourier’s law to write the heat flux as

\[
J_q = -K_T(T) \nabla T
\] (2.14)

where \( K_T \) is the thermal conductivity, which in general is a function of temperature.

## 2.4 Boundary Conditions

It must be stressed that the PDEs developed so far (equations (2.2), (2.9) and (2.13)) are valid only in regions where gradients of scalar potentials are not too large. Alternatively speaking, they are valid where continuum (i.e. mean field and local density) approximations can be made. To properly model the Stern layer and surface effects, a first-principles quantum mechanical model is needed and matching conditions are required to link the macroscopic equations to the microscopic interface. These matching conditions are implemented as boundary conditions at the Stern plane. The PDE’s model the electrolyte up to the Stern planes and so the boundary conditions must bridge the gap between the the Stern planes...
and the electrodes. The most important information needed from quantum mechanics to establish proper boundary conditions for the PDE model are

1. a relationship between the electric displacement field $\mathbf{D}$ (or equivalently, the surface charge density $\sigma$) and the electric field $\mathbf{E}$ (or equivalently, the voltage difference across the Stern layer),

2. an expression for the Faradaic reaction rate as a function of concentration in the bulk (diffuse region) and the potential difference across the Stern layer,

3. a time-dependent equation for the temperature difference across the Stern layer which links the heat flux through the Stern layer, and

4. an equation describing electromechanical coupling in the Stern layer where the structure of the compact layer can change as a function of the interfacial electric field (electrostriction).

Items 1, 2 and 3 will provide the boundary conditions on Poisson’s equation, the reaction-diffusion equations and the heat equation, respectively. Item 4 includes the electrostrictive effect, or a change in compact layer thickness as a function of the electric field (or more precisely, the polarization, which is closely tied to the differential permittivity). This change in thickness is due to mechanical stress caused by the reorientation of water dipoles in the presence of a strong field. Mathematically, the electrostrictive stress is quadratically related to polarization ($S_{ij} = Q_{ijkl}P_kP_l$) [117] and its effect has been studied by workers such as Grahame [118] and Macdonald, who gave a heuristic expression (equation 15 in [40]) for the relationship between compact layer thickness and electrostrictive pressure. Studies [119] and simulations [120] have shown that electrostrictive forces have a significant and measurable impact on double layer structure, but to our knowledge a satisfactory mathematical model has not been developed for aqueous electrolytes. The effect can, in principle, be included in the current model either by making Stern layer thickness $\lambda_S$ a function of the electric field at the boundary, or by including its effect directly into Poisson’s equation when the actual mechanical stresses are less important than their resulting effect on the field and charge kinetics.

The interface model should, in principle, be treated using a quantum mechanical treatment of the surface. An important element of such a description is an understanding of surface states [121, 122], or Tamm states [123], which are bound states at the surface due to the electronic wavefunction of the electrode extending into the solution. The bound states interact with molecules in solution, affecting the properties of the double layer. However, using a quantum mechanical model to describe relationships pertaining to the interface is beyond the scope of this thesis, so we close the equations by including the first three
boundary conditions via. making idealized continuum approximations, and the fourth can be ignored by assuming no electromechanical coupling.

2.4.1 Electrostatics and Current Conservation

At a device level, the two boundary conditions that we are interested in applying at the electrodes are a time-varying voltage or a time-varying current. To facilitate this, and to have coupling between the concentration and potential in the diffuse layer and reaction kinetics, a condition on the potential $\Phi$ is needed on the boundary as well as an ODE for current conservation, along with the reaction rate equation given in Section 2.4.2, equation (2.18). For the boundary condition on $\Phi$, we propose equation (2.15):

$$n \cdot D = n \cdot (\varepsilon_0 E + P) = \sigma_s$$  \hspace{0.5cm} (2.15)

where $D$ is the electric displacement field in the limit approaching from the electrolyte side of the Stern plane, $\sigma_s$ is the surface charge density on the electrode, and the displacement field in the electrode is assumed to be zero since the electrodes are considered perfect conductors. This assumption cannot be invoked, for example, if the electrode is a semiconductor since diffuse charge effects at semiconductor junctions means that a zero field assumption is invalid, but this is beyond the scope of this thesis.

In principle, if the constitutive relation linking $D$ and $E$ is known from experiment or theory for a particular system, equation (2.15) can be used to model its effect on double layer structure. For example, the ion correlation force [124], an attractive short range van der Waals-like force between charged surfaces (charge at surface of electrode and charge at surface of Stern layer on the electrolyte side), is not predicted by Poisson-Boltzmann theory. However, there has been success in modeling ion correlations in the double layer by using a modified Poisson equation with a fourth derivative [17, 125] by representing $\varepsilon$ as an operator and writing $D = -\varepsilon \nabla \Phi$ where $\varepsilon = \varepsilon_0 (1 - \ell_c \nabla^2)$ [11], where $\ell_c$ is a correlation length parameter such as the Bjerrum length. On the other hand, if $D$ can be approximated as $D = -\varepsilon \nabla \Phi$, where $\varepsilon$ takes on constant values which are not necessarily the same on either side of the Stern plane, then we can write

$$\varepsilon_{\text{diff}} \frac{\partial \Phi}{\partial n} = \varepsilon_{\text{stern}} \frac{\Phi_{\text{stern}} - \Phi_{\text{electrode}}}{\lambda_S}$$  \hspace{0.5cm} (2.16)

where the left hand side is defined to be in the limit approaching from the electrolyte side of the Stern plane and the electric field in the Stern layer has been linearly approximated by a voltage difference (refer to Figure 2.2). In equation (2.16), $\varepsilon_{\text{diff}}$ is the permittivity in the diffuse region and $\varepsilon_{\text{stern}}$ is the
permittivity in the Stern layer. Equation (2.16) is effectively the same as the boundary conditions used in [20] (equations 10 and 11) and its related equations in followup papers [19, 21], except that in equation (2.16), the permittivities have been explicitly separated from the effective Stern width so that $\lambda_S$ can be thought of as the actual physical width of a thin dielectric layer adjacent to the electrode surface. Equation (2.16) assumes that the point of zero charge (pzc) occurs when $\Delta \Phi = 0$ across the Stern layer, so that the electrode potential is defined relative to the pzc. For a single electrode model, an arbitrary offset can be added to the reference potential so as to ignore this effect, but for two electrodes having different pzc’s, an additional potential shift must be added to equation (2.16) for at least one electrode [97, 89] to account for material-dependent pzc’s [126]. More generally, a continuum model could potentially extend into the electrode material to more accurately model its charge distribution and the resulting electric field when coupled to the electrolyte, but this is beyond the scope of this work.

The electric field is solved for using a current conservation equation, as shown in Figure 2.2. Applying the divergence theorem to Ampere’s law gives the result that $d\mathbf{D}/d\tau + \mathbf{J}$ is conserved. On the electrode side we have just $\mathbf{J}_{\text{ext}}$ due to the assumption of good conductivity and on the electrolyte side we have

Figure 2.2: Boundary condition applied to $\Phi$ in the Stern layer. Current balance is shown between $J_{\text{ext}}$, the applied or solved for external electrical current density and the flux of charged species into the electrode. Also shown is the direction of the normal vector relative to the electrode.
\( \frac{dD}{d\tau} \) plus the sum of ionic fluxes, \( \sum_{i}^{N} z_i J_i \). This results in equation (2.17):

\[
\frac{\partial D}{\partial \tau} = J_{\text{ext}} - e \sum_{i}^{N} z_i J_i \tag{2.17}
\]

which models the time-dependent charging of the double layer. \( D \) on the left hand side of equation (2.17) is again defined as being in the limit approaching the Stern plane from the electrolyte. The derivation of this equation can be found in Appendix B, and is the same as equation 8 in [127] and equations 8, 9 and 10 in [22].

2.4.2 Reaction Kinetics

In order to describe reactions at the electrode, we will use the Frumkin-Butler-Volmer (FBV) equation [83] shown in equation (2.18)

\[
I = K_c C_O \exp \left( -\frac{\alpha_c n e \Delta \Phi_S}{k_B T} \right) - K_a C_R \exp \left( \frac{\alpha_a n e \Delta \Phi_S}{k_B T} \right) \tag{2.18}
\]

which is the rate equation for the charge-transfer reaction

\[ \text{O} \quad \rightleftharpoons \quad \text{R} + e^- \]

where \( K_c \) and \( K_a \) are rate constants, \( \alpha \) is a “transfer coefficient”, and \( C_O \) and \( C_R \) are the concentrations of the oxidizing and reducing species at the electrode, respectively, and \( n \) is the number of electrons involved in the reaction. As a convention, \( I \) in equation (2.18) is defined as from the solution (or ionic conductor) into the electrode and \( \Delta \Phi_S \) is defined as the electrode voltage minus the voltage at the Stern plane. When contrasted to the classical Butler-Volmer equation (equation (1.12)), the potential difference \( \Delta \Phi_S \) in equation (2.18) is explicitly defined as being across the Stern layer, as opposed to being in reference to a vague “solution potential”. Specifically, equation (2.18) gives a needed boundary condition on \( \Phi \) at the Stern plane in terms of \( \Phi \) and concentrations at the electrode. This allows a coupling between reaction kinetics and dynamic double layer structure as modeled by Poisson’s equation (with the current conservation ODE, equation (2.17)) and the reaction-diffusion equation (equation (2.2)). This has been shown to predict behaviour and aspects of diffuse charge dynamics not predicted by equation (1.12) (for example, the Frumkin effect is taken into account) [28].
The classical theory, equation (1.12), is recovered with the definition of the overpotential, $\eta$, as

$$\eta = \Delta \Phi_S - \Delta \Phi_{eq}^S$$  \hspace{1cm} (2.19)

where $\Delta \Phi_{eq}^S$ is defined to be the equilibrium (i.e. zero-current steady state) value of $\Delta \Phi_S$ (the potential difference across the Stern layer), which, by setting $I = 0$ in equation (2.18), can be found (assuming $\alpha_c = 1 - \alpha_a$) to be

$$\Delta \Phi_{eq}^S = \frac{k_B T}{ne} \log \left( \frac{K_c C_O^*}{K_a C_R^*} \right)$$  \hspace{1cm} (2.20)

where $C_O^*$ and $C_R^*$ are the equilibrium concentrations of the two species at the electrode. Substituting equation (2.20) and (2.19) into equation (2.18) yields

$$I = I_0 \left[ \frac{C_O}{C_O^*} \exp \left( \frac{-n e \eta}{k_B T} \right) - \frac{C_R}{C_R^*} \exp \left( \frac{n e \eta}{k_B T} \right) \right]$$  \hspace{1cm} (2.21)

which is the form commonly seen in the electrochemistry literature. $I_0 = n e (K_c C_O^*)^{\alpha_a} (K_a C_R^*)^{\alpha_c}$ is the equilibrium exchange current density. The further assumption that $C_O = C_O^*$ and $C_R = C_R^*$, or that the concentrations at the reaction planes do not deviate from their equilibrium values, leads to the form in equation (1.12).

For some of the physics and background behind the Butler-Volmer equation, refer to Appendix C.

### 2.4.3 Energy Conservation

For the boundary condition on the energy conservation (heat) equation, we turn again to nonequilibrium thermodynamics. Albano & Bedeaux [128] extended the thermodynamics of de Groot & Mazur [129] to charged interfaces. We used this work to obtain our boundary condition; the derivation is similar enough to the one in Appendix A that an interested reader should refer to it and to [128]. Since the Stern layer is thin (on the order of several atomic widths), it makes sense to assume the temperature within the Stern layer depends only on time. This allows us to use an ODE to describe its temperature evolution,

$$(\rho_m c_p)_{s\text{tern}} \frac{\partial T_{\text{stern}}}{\partial \tau} = -\mathbf{n} \cdot \left( \frac{J_{q,\text{ext}} - J_q}{\lambda_S} \right) + \mathbf{J} \cdot \mathbf{E} + \frac{D}{\varepsilon_0} \frac{\partial \mathbf{P}}{\partial \tau}$$  \hspace{1cm} (2.22)

where bolded quantities on the right hand side of equation 2.22 are defined to be in the limit as they approach the Stern plane from the electrolyte side and the linear approximation $(J_{q,\text{ext}} - J_q)/\lambda_S$ has been used to replace the divergence of the heat flux. Equation (2.22) is analogous to equation 8 in
Bedeaux & Kjelstrup [130] and equation 12 in Rubi & Kjelstrup [131], which are temperature boundary equations used in similar contexts. Furthermore, the boundary condition on the electrode side may not be known explicitly so there could be a need to extend the domain until a known boundary condition can be applied. In this case, the mixed boundary condition we use mimics a situation with open convection on the electrode side. Finally, if \( J_{q,ext} \) or \( T_{electrode} \) is known (i.e. a constant heat flux or constant temperature boundary condition), it can simply be plugged in to equation (2.22). We will use a simple model for \( J_{q,ext} \) referred to as Newton’s law of cooling, or \( J_{q,ext} = H(T_{amb} - T_{stern}) \), where \( H \) is an area-averaged heat transfer coefficient which takes into account the geometry and material properties of the electrode and \( T_{amb} \) is the ambient temperature, a constant. Figure 2.3 shows a diagrammatic representation of this boundary condition.

\[
\begin{align*}
T_{amb} & \quad \text{Electrode} \quad \bullet \\
& \quad \text{Stern layer} \quad \text{Electrolyte} \\
\text{Flux} & \quad = H(T_{stern} - T_{amb}) \\
\end{align*}
\]

Figure 2.3: A figure showing the Newton’s law of cooling boundary condition for temperature, including the locations of the ambient and boundary temperatures. The section in red is the electrode, the section in yellow is the Stern layer and the section in white is the electrolyte, which includes the diffuse charge region. The heat transfer coefficient \( H \) takes into account the geometry and material properties of the electrode.

Use of equation (2.22) in practice has some ambiguity, since one must decide where to physically place \( T_{stern} \) in order to numerically discretize the fluxes, as well as which values to use for \( \mathbf{J} \) and \( \mathbf{E} \) in the discretization. This is nuanced because the discretization will need values of \( \mathbf{J} \) and \( \mathbf{E} \) within the Stern layer, but this region is not part of the computational domain. As a first approximation, our approach is to treat the Stern layer as a thermally thin layer such that \((\rho c_p)_{stern} \sim 0\) and write instead

\[
\mathbf{n} \cdot (\mathbf{J}_{q,ext} - \mathbf{J}_q) = \lambda_S \left( \mathbf{J}_e \cdot \mathbf{E} + \frac{D}{\varepsilon_0} \frac{\partial \mathbf{P}}{\partial \tau} \right) 
\]  

(2.23)

Figure 2.4 shows the flux balance at the Stern layer from equation (2.23) diagrammatically. The thermal
inertia term \((\rho_m c_p)_{\text{stern}} \frac{\partial T_{\text{stern}}}{\partial t}\) has been set to zero. This treatment of the thermal boundary condition

\[
q_{\text{J,ext}} \quad \text{Electrode} \quad \text{Electrolyte} \\
\begin{array}{c}
J_q,\text{ext} \quad J_q \\
= H(T_{\text{amb}} - T_{\text{stern}}) \\
\text{T}_{\text{stern}} = \text{T}_{\text{boundary}} \\
\text{JE} + E \frac{dP}{dt}
\end{array}
\]

is simply a first approximation, and more work should be done in the future to account for the physics involved.

### 2.4.4 Surface Coverage

The final piece of the model is an ODE to model partial coverage of the electrode surfaces. Theoretical [132], experimental [133] and modeling [134] work has been done on the subject of partial coverage of reaction sites. It’s well known that in galvanic cells, the discharging reaction may cause the electrode material to be altered, either due to occupation of surface sites as is the case for the lead/lead sulfate electrode [135, 136] or due to an intercalation mechanism in the case of lithium-ion batteries [137]. These two mechanisms are shown in Figure 2.5. Knowledge of the surface coverage during operation is key to predicting the state of charge, and can also be used to model physical effects such as pseudocapacitance (see Chapter 10 of Conway [138] for example).

We will consider a simple model involving a single adsorbed species on a flat electrode surface. We also assume that only monolayers can form, but in other systems there can be multilayer or dendritic growth in which case other factors need to be accounted for. Although surface coverage is, in general,
Figure 2.5: Different mechanisms of electrode “coverage” in electrochemistry: (a) Surface adsorption of an aqueous species onto an electrode, (b) Intercalation of lithium into graphite, where lithium molecules are sandwiched between layers of graphite.

a two dimensional phenomenon, one can assume one-dimensional behaviour if the surface coverage at any infinitesimally small region on a surface is replicated at all other infinitesimally small regions on the surface. The model and equations used depend on the material system (combination of electrode surface material and electrolyte), the determination of which is an active area of research. It is important to stress that nearly all modern electrochemical devices involve some kind of porous material (rather than a flat surface) as an electrode. As it stands, the state of the art for modeling of porous electrodes (at a device level) does not consider fine structure but rather treats pore insertion in a volume-averaged sense [82, 99, ?]. Here, we do not intend for our simple model to be a comprehensive model for electrode coverage, but rather only as a first step towards one.

In order to add fractional coverage of a single species to our model, we must first introduce the quantity $\theta$, which is defined to be the surface fraction of occupied sites for an electrode. We will assume that the rate of change of a quantity $\theta$ is proportional to the charge transfer or reaction current,

$$Q_s \frac{d\theta}{d\tau} = J \quad (2.24)$$

where $Q_s$ is a parameter corresponding to the charge required to form a full layer of adsorbate and $J$
is the reaction current associated with the adsorped species. The coverage \( \theta \) must lie between 0 and 1, a condition which is not enforced by equation (2.24) alone, but rather when solved self-consistently the reaction rate and transport equations. Also, by using equation (2.24), we are implicitly assuming that any rearrangement of surface states happens quickly relative to the other time scales in the system, and that the state of the surface at any instant in time is wholly captured by the value of \( \theta \). These are strong assumptions, which can be relaxed in future work.

Next, in order to derive a reaction rate equation which couples to the fractional surface coverage \( \theta \), we use the theory which we briefly explain in Appendix C. For example, a possible model for the initial (solution) and final (adsorbed) states is

\[
\mu_1 = k_B T \ln C
\]

\[
\mu_2 = k_B T \ln \theta - k_B T \ln(1-\theta) + \Delta E_{ads}
\]

where \( \mu_1 \) is the chemical potential of the solution and \( \mu_2 \) is the chemical potential of the surface. Equation (2.26) can be obtained from a simple lattice-gas model [139], and the second and third terms in the equation model excluded area effects and adsorption energy, respectively.

Historically, adsorption has been studied using adsorption isotherms. Adsorption isotherms are equations of state which are equivalent to choosing a particular model for the chemical potential of the initial, transition and final states in Butler-Volmer kinetic theory, as discussed in Appendix C. Surface isotherms relate solution concentration \( C \) (or pressure \( P \) for gas systems) of a species to its concentration on a surface. One of the simplest isotherms, developed by Irving Langmuir in 1916 [140] is the Langmuir isotherm, which was originally created to model monolayer adsorption of gas molecules without interaction between adsorbed molecules. The equilibrium isotherm expression can be written as

\[
\theta = \frac{K_E P}{1 + K_E P}
\]

for a gas or

\[
\theta = \frac{K_E C}{1 + K_E C}
\]

for an aqueous solution, where \( \theta \) is the surface fractional coverage, \( K_E = \exp(-\Delta E_{ads}/k_B T) \) is an equilibrium constant and \( P \) is the pressure of the gas. These expressions can be derived by equating the two chemical potentials (equations (2.25)–(2.26) are representative of an aqueous solution). Alternatively
since our interest is in aqueous solutions we can invert expression (2.28) and obtain (2.28) as

\[ K_E C = \frac{\theta}{1 - \theta} \]  

(2.29)

The Langmuir isotherm is still commonly used in chemistry [141], but there are more advanced models [132]. Using the appropriate models, the reaction rate equation can be modified to include effects such as enthalpy changes, excluded area effects and short-range interactions between adsorbates. In general, equations like (2.25)–(2.26) must be constructed on a problem-specific basis, and in Section 4.1 we test two common monolayer isotherms, namely the Langmuir and the Frumkin models.

The previous discussion dealt with a steady state phenomenon however the objective is to develop equations which are equally valid for transient studies. Therefore, to modify to our reaction rate equation to accommodate the surface coverage models in equations (2.25)–(2.26), we simply substitute the chemical potentials into equation (C.16) from Appendix C. We then obtain a rate equation of the form

\[ R = K_c C_O \exp \left( \frac{-ez\sigma_1 \Delta \Phi}{k_B T} \right) - K_a \frac{\theta}{1 - \theta} \exp \left( \frac{ez\sigma_a \Delta \Phi}{k_B T} \right) \]  

(2.30)

The surface coverage model developed in this section and Appendix C is very simple and is only intended to be a first step towards incorporating surface coverage and similar effects into a full electrochemical cell model. In Section 4.1, we run simulations using the model described here and show that the model generates physically realistic results. However, a more complete model of surface coverage would necessarily be constructed based on a specific reaction, from which the the thermodynamic relationship between coverage and kinetics can be derived [142].

### 2.5 Model Overview and Simplifications

Now that the general set of equations have been developed, we simplify them by making assumptions about the most relevant physics and about the battery geometry. First, we assume the electrodes are flat and parallel and that fringing effects near the edges of the electrodes are negligible. Therefore, we assume that all quantities only depend on \( X \), the direction perpendicular to the electrodes, and \( \tau \), the time. Second, because our primary interests in this study are the effects of temperature and polarization, we assume that there are no reactions in the bulk: there is no sum term in the reaction diffusion equations (2.2) or in the energy equation (2.13). As mentioned in Section 2.1, this is a reasonable
assumption for electrochemical systems. Finally, for these particular simulations we will treat $\varepsilon_r$, the relative permittivity, as piecewise constant in space with different values in the Stern layer, inside the diffuse layer, and in the bulk. This type of layered approach to modeling the polarization has a precedent in older [40, 42] and modern [89, 97] literature, and retains essential features of the physics. It avoids the need to include an extra nonlinear $(\nabla \Phi)^2$ term in the diffusion flux (2.3).

We will now deal with the temperature equation. The one-dimensional energy balance equation (2.13) without chemical reactions is

$$\rho c_p \frac{\partial T}{\partial \tau} = K \frac{\partial^2 T}{\partial X^2} + JE + E \frac{\partial P}{\partial \tau} \tag{2.31}$$

where the final two terms in equation (2.13) ($B \cdot \frac{\partial M}{\partial \tau} - \sum_r \sum_{i=1}^N \nu_{ir} H^f_i B_r$) have been dropped since we are not concerned with magnetic effects or reactions. From (2.31) the rate of change of the temperature depends on the rate of change of the polarization and vice versa. To close the system, one needs an independent ODE for $P$, determined from a constitutive law for $P$ in terms of other quantities. For example, if $P$ is a linear function of $E$, i.e. $P = (\varepsilon_r - 1)\varepsilon_0 E$ and $D = \varepsilon_r \varepsilon_0 E$, then

$$\frac{\partial P}{\partial \tau} = \frac{\varepsilon_r - 1}{\varepsilon_r} \frac{\partial D}{\partial \tau} = -\frac{\varepsilon_r - 1}{\varepsilon_r} J \tag{2.32}$$

by Ampere’s law. Then the second and third terms on the right hand side of equation (2.31) become

$$JE - \frac{\varepsilon_r - 1}{\varepsilon_r} JE = \frac{1}{\varepsilon_r} JE \tag{2.33}$$

That is, the effect of the term $E \frac{\partial P}{\partial \tau}$ is to modify the Joule heating from $JE$ to $\frac{JE}{\varepsilon_r}$.

Models of, for example, the dependence of $\varepsilon_r$ on ion concentration (see Section 6 of [35] for a treatment of this with MPB theory) certainly exist and it is straightforward to include such effects into the model, but we leave this for future work.

### 2.6 Nondimensionalization

Now, we rescale the primary dependent and independent variables as follows:

$$x = \frac{X}{L} \quad t = \frac{D_0 \tau}{L^2} \tag{2.34}$$
\[ c_i = \frac{C_i}{C_0} \quad \phi = \frac{F\Phi}{RT_0} \quad (2.35) \]

\[ T = \frac{T}{T_0} \quad j_i = \frac{L}{D_0 C_0} J_i \quad (2.36) \]

where \( D_0, T_0 \) and \( C_0 \) are a reference diffusion coefficient, temperature and concentration, respectively and \( L \) is the length of the bulk region (the distance between the two electrodes minus \( 2\lambda_S \)). Using these rescaled variables, equations (2.2), (2.9) and (2.13) become

\[ \frac{\partial c_i}{\partial t} = -\frac{\partial}{\partial x} d_i \left[ -\frac{\partial c_i}{\partial x} - \frac{z_i c_i \partial \phi}{T} - c_i \frac{d}{d\xi} \sum \nu c_i \right] \quad (2.37) \]

\[ -\epsilon^2 \frac{\partial^2 \phi}{\partial x^2} = \frac{1}{2} \sum_{i=1}^{N} z_i c_i \quad (2.38) \]

\[ \frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} - \beta \sum_{i=1}^{N} z_i j_i \frac{\partial \phi}{\partial x} \quad (2.39) \]

where \( \epsilon = \lambda_D/L, \lambda_D = \sqrt{\frac{\mu_0\epsilon_0 RT_0}{2F^2C_0}} \), \( \nu = a^3 C_0 \), \( \alpha = \frac{K_T}{\rho_m \tau_F \rho_r \tau_r} \), \( \beta = \frac{RC_0}{\rho_m \tau_F \rho_r \tau_r} \), \( d_i = D_i/D_0 \). Here, \( \lambda_D \) is the Debye length, \( \alpha \) is the (dimensionless) thermal diffusivity, and \( d_i \) is the (dimensionless) diffusivity of the \( i^{th} \) species. Note that we are using units of mols per unit volume for dimensional concentration instead of number density, as the former is more commonly seen in the electrochemistry literature. As a result, \( F \) and \( R \) appear in the rescalings rather than \( e \) and \( k_B \).

Equation (2.17) rescales to

\[ -\frac{\epsilon^2}{2} \frac{\partial \phi_x}{\partial t} = j_{\text{ext}} - \sum_{i=1}^{N} z_i j_i \quad (2.40) \]

where \( j_{\text{ext}} = \frac{L}{4FD_0 C_0} J_{\text{ext}} \). Note that \( J_{\text{ext}} \) is an electrical current density, not a concentration flux, and its rescaling factor \( \frac{4FD_0 C_0}{L} \) is the classical limiting current density of Nernst [18] and Brunner [143, 144].

Equation (2.24) rescales to

\[ q_s \frac{d\theta}{dt} = j \quad (2.41) \]

where \( q_s = \frac{Q_s}{L_C_0} \) and \( \theta \), as a fraction, is already nondimensional.

The boundary conditions on the concentrations, equation (2.30), rescales to

\[ j_i = -z_i c_i \frac{\partial \phi}{\partial x} - \frac{\partial c_i}{\partial x} - c_i \frac{d}{d\xi} \sum \nu c_i = k_c C_0 e^{-\alpha_c \Delta \phi} - (1 - \theta) k_a e^{\alpha_a} \Delta \phi \quad (2.42) \]
where
\[ k_c = \frac{K_O L}{4D_0}, \quad k_a = \frac{K_R L C_M}{4D_0 C_0}, \] (2.43)

Equation (2.16) becomes
\[ \lim_{x \to x^+} \epsilon_{\text{diff}}^2 \frac{\partial \phi}{\partial x} = \frac{\epsilon_{\text{stern}}^2}{\epsilon_{\text{stern}}} \frac{\Delta \phi_{\text{stern}}(t)}{\epsilon_{\text{stern}}^2} \] (2.44)

where \( \delta \equiv \frac{\lambda_s}{\lambda_D} \), the ratio of the Stern layer thickness to the Debye length. The PDEs (2.37)–(2.39) have spatial domain \((0, 1)\) and the boundary conditions are at \(x = 0\) and \(x = 1\). We set the electrode potential to 0 at \(x = -\lambda_s\), and so \(\Delta \phi_{\text{stern}} = \phi(0, t) - 0\). At \(x = 1\) there are two options: 1) a current boundary condition where the current is set in equation (2.40) and \(\Delta \phi_{\text{stern}} := \epsilon \phi_x(1, t)\) or 2) a voltage boundary condition where the rescaled voltage at the right electrode is specified, \(v(t)\), and \(\Delta \phi_{\text{stern}} := v(t) - \phi(1, t)\).

If a voltage boundary condition is used, equation (2.40) is used to post-process for the current \(j_{\text{ext}}\). Since we have chosen to have a different value for \(\epsilon_r\) in the bulk and diffuse region, we need an internal matching condition, and this is simply
\[ \lim_{x \to L_{\text{diff}}/L} \epsilon_{\text{diff}}^2 \frac{\partial \phi}{\partial x} = \lim_{L_{\text{diff}}/L \to x} \epsilon_{\text{bulk}}^2 \frac{\partial \phi}{\partial x} \] (2.45)

Finally, when writing the temperature boundary condition, using the same arguments as for equations (2.32)-(2.33), the thermal boundary condition (2.23) becomes
\[ j_{q, \text{ext}} - j_q = \pm \lambda_s \beta_{\text{stern}} \sum_{i=1}^{N} z_i j_i \Delta \phi \epsilon_{\text{stern}}^2 \delta \] (2.46)

where \(\beta_{\text{stern}} = \frac{R C_0 (2-\epsilon_r)}{\rho_m \epsilon_p} \), and \(\frac{\Delta \phi}{\epsilon_{\text{stern}}^2}\) is defined in equation (2.44).

### 2.6.1 Example Parameter Values

Since our simulations in the rest of this work focuses on parameter regimes rather than any particular physical system, we provide in this section some example parameter values from experimental work which uses the PNP-gFBV equations (specifically, the leaky membrane model used in Section 5.8). We take our experimental values from the work of Deng et al. [145], who performed voltammetry experiments on the copper electrodeposition reaction in silica nanopores.

The first thing worth noting is that the parameter \(\delta\) is not available using experimental data since it depends on the width of the Stern plane, which is hard to measure. Practically, \(\delta\) is set in the range 0.01...
Table 2.1: (a) dimensional parameters from the experiments in silica nanopores from Deng et al., 2013 and (b) computed nondimensionalized parameters

(a) Dimensional Parameters

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference concentration ($C_0$)</td>
<td>1 mol/m³</td>
</tr>
<tr>
<td>Diffusivity ($D$)</td>
<td>$2.15 \times 10^{-10}$ m²/s</td>
</tr>
<tr>
<td>Reaction rate ($K$)</td>
<td>2.8 A/m²</td>
</tr>
<tr>
<td>Interelectrode width ($L$)</td>
<td>1 mm</td>
</tr>
<tr>
<td>Voltage scan rate ($S$)</td>
<td>2 mV/s</td>
</tr>
<tr>
<td>Permittivity ($\varepsilon$)</td>
<td>$8.85 \times 10^{-12}$ F/m</td>
</tr>
<tr>
<td>Surface charge density</td>
<td>-3 mC/m²</td>
</tr>
<tr>
<td>Ambient Temperature ($T$)</td>
<td>293 K</td>
</tr>
</tbody>
</table>

(b) Dimensionless Parameters

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nondim. Debye length ($\varepsilon$)</td>
<td>$1.08 \times 10^{-6}$</td>
</tr>
<tr>
<td>Voltage scan rate ($S$)</td>
<td>$3.68 \times 10^2$</td>
</tr>
<tr>
<td>Background charge ($\rho_s$)</td>
<td>$-8.89 \times 10^{-3}$</td>
</tr>
<tr>
<td>Reaction rate ($k$)</td>
<td>$3.26 \times 10^6$</td>
</tr>
</tbody>
</table>

to 100, depending on whether the diffuse region or compact layer should dominate the electrical double layer; $\delta = 1$ is a balance between the two. The second thing is that in this experiment, and typical of other experiments, $\varepsilon \ll 1$ and $k \gg 1$, indicating that the experiment is in a regime which is nearly electroneutral (thin double layers), with fast reactions. In practice, entering $\varepsilon < 0.005$ and $k > 50$ into the model is enough to guarantee thin double layers and fast reactions.

### 2.7 Time and Length Scales

The equations governing the physics summarized in Section 2.6 have several time scales: the diffusion time scale, $\tau_D = L^2/D$ and the reaction time scale, $\tau_R = L/K$, for a characteristic reaction rate $K$, the temperature time scale $\tau_T = \rho c_p / K T$ and the adsorption, or surface coverage time scale $\tau_{SC} = \frac{Q_s L}{D C_0}$. For the voltammetry simulations performed in Chapter 5, there is also the imposed voltage scan rate time scale, $\tau_S = \frac{RT}{F S}$. Rescaling time to $\tau_D$ results in several dimensionless groups: the nondimensional scan rate

$$\tilde{S} = \frac{\tau_D}{\tau_S} = \frac{S L^2 F}{D R T} \quad (2.47)$$

the nondimensional reaction rate

$$k = \frac{\tau_D}{4 \tau_R} = \frac{KL}{4D} \quad (2.48)$$

also known as the “Damkohler number”. In Eq. (2.43), $k$ takes two forms, $k = k_c$ and $k = j_r$, for the forward (oxidation) and backward (reduction) reactions with the characteristic rates, $K = K_O$ and $K = K_R C_M / C_0$, respectively. Finally, there are also the nondimensional thermal diffusivity

$$\alpha = \tau_D / \tau_T \quad (2.49)$$
and the nondimensional surface factor

\[ q_s = \frac{\tau_D}{\tau_{SC}} \]  

The dimensionless model also contains thermodynamic information about the electrochemical reaction, independent of the overall reaction rate [61, 57, 86]. For any choice of a single reaction rate scaling, there is a third dimensionless group, which can be expressed as the (logarithm of) the ratio of the dimensionless forward and backward reaction rates,

\[ \ln \frac{k_c}{J_r} = \ln \frac{K_0 C_0}{K_R C_M} = \Delta \phi^{\Theta} \]  

This is the dimensionless equilibrium interfacial voltage, where the net Faradaic current (equation (2.42)) vanishes in detailed balance between the oxidation and reduction reactions for the reactive cation at the bulk reference concentration \(C_0\).

There are also two length scales of interest: the cell thickness \(L\) and the Debye length \(\lambda_D\), which is the length scale over which electrostatic screening occurs. In Section 2.6, we chose to scale distance to \(L\), resulting in two dimensionless groups associated with length scales. The first is the nondimensionalized Debye length \(\epsilon = \lambda_D/L\) and the second is the ratio of the Stern width to the Debye length, \(\delta = \lambda_S/\lambda_D\). The dimensionless parameters \(\epsilon\) and \(\delta\) control how the model handles the double layer and diffuse charge dynamics. \(\epsilon\) controls double layer thickness relative to the geometry, whereas \(\delta\), which is effectively a ratio of Stern and diffuse layer capacitance, relates to the competition between the Stern and diffuse layers in influencing overall double layer behaviour.

In Chapters 4 and 5, we will vary some of these parameters and simulate their effect on cell behaviour. We are primarily interested in the limiting behaviour of these nondimensional groups in order to identify regimes of operation. These limits will be discussed in their respective sections, but we will introduce some of the most important limits here.

The first is the “classical” limit of ambipolar diffusion (diffusion of ionic species with electroneutrality), which corresponds to the limit \(\epsilon \to 0\). In this limit, equation (2.38) is simply

\[ c_+ = c_- \]  

which means that equation (2.37) simplifies to a single diffusion equation,

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2}$$  \hspace{1cm} (2.53)

and the potential is calculated via

$$\frac{\partial}{\partial x} \left( c \frac{\partial \phi}{\partial x} \right) = 0$$  \hspace{1cm} (2.54)

There are also two limits of interest on $\delta$. The first is the so-called “Gouy-Chapman” (GC) limit, $\delta \to 0$, which corresponds to a situation where all of the potential drop in the double layer is across the diffuse region, and the second is the so-called “Helmholtz” (H) limit, $\delta \to \infty$, where all of the potential drop is across the Stern layer. Assuming quasi-equilibrium, the Boltzmann distribution for ions is invoked ($c_{\pm} = \exp (\mp \Delta \phi_D)$) and the right hand side of equation (2.42) becomes

$$J = 4k_c c_+ e^{-\Delta \phi_D} - 4 j_r$$  \hspace{1cm} (2.55)

where $\Delta \phi_D$ is the potential drop across the diffuse region. The right hand side of equation (2.42) becomes

$$J = 4k_c c_+ e^{-\Delta \phi_S/2} - 4 j_re^{\Delta \phi_S/2}$$  \hspace{1cm} (2.56)

where $\Delta \phi_S$ is the potential drop across the Stern layer.

Another limit of interest is the fast reaction, or Nernstian limit, where thermodynamic equilibrium is assumed. In the Nernstian limit, the nondimensionalized reaction rate parameters $k_c, j_r \to \infty$ for a fixed ratio, $j_r/k_c$, corresponding to a given equilibrium half-cell potential for the reaction, equation (2.51). In this limit, the left-hand sides of equations (2.42) and (2.55)–(2.56) approach zero, and all three boundary conditions reduce to the Nernst equation,

$$\Delta \phi = \Delta \phi^\Theta + \ln c_+$$  \hspace{1cm} (2.57)

where again the bulk solution is used as the reference concentration. In order to place the Nernst equation in the standard form [57, 61],

$$E = \frac{RT}{nF} \Delta \phi^{eq} = E^\Theta + \frac{RT}{nF} \ln \frac{C_+}{C_{ref}}$$  \hspace{1cm} (2.58)

we must define the equilibrium interfacial voltage relative to a standard reference electrode (e.g. the
Standard Hydrogen Electrode in aqueous systems at room temperature and atmospheric pressure with $C_{\text{ref}} = 1$ M) by shifting the reference potential,

$$E^\Theta = \frac{RT}{nF} \left( \Delta \phi^\Theta - \ln \frac{C_0}{C_{\text{ref}}} \right) = \frac{RT}{nF} \ln \frac{K_0 C_{\text{ref}}}{K_R C_M} \quad (2.59)$$

In this way, tables of standard half-cell potentials can be used to determine the ratio of reaction rate constants, and measurements of exchange current density can then determine the individual oxidation and reduction rate constants.

Finally, there is the “supported” electrolyte limit, which models a situation where a large concentration of inert salt is added to the electrolyte to remove the contribution from electromigration. We choose to model liquid electrolytes in the limit of high supporting salt concentrations by setting $\phi(x, t) = 0$ and removing Poisson’s equation (equation (2.38)) from the model. This has two effects: first, electromigration is no longer a part of the transport equations (equation (2.37)). Second, the voltage difference $\Delta \phi = v - \phi_{\text{stern}}$ which enters into the FBV equation (equation (2.42)) is just the electrode potential since $\phi_{\text{stern}} = \phi(1) = 0$. This results in a time-dependent version of the classical Randles-Sevcik system [57], with Butler-Volmer rather than Nernstian (infinitely fast) reaction kinetics.
Chapter 3

Numerical Method

In general, there are several properties of a numerical method that need to be established so as to allow the solver for the Poisson-Nernst-Planck equations to be stable, provide accurate results and converge quickly. The first is a nonuniform mesh in space, which is useful because the potential and concentration distributions near the electrode can change significantly over short distances. The mesh near the boundaries should be finer than the mesh in the middle of the domain, where the concentration and potential are nearly constant. Secondly, many electrochemical systems of interest are subject to forcings for short durations of time, with long periods of relaxation with constant or no forcing in between. This, along with the transient dynamics driven by the initial data, gives the problem more than one time scale. The numerical scheme we use should be able to detect these changes in time scales and vary the step size accordingly. Numerical methods using implicit or explicit time stepping and finite differencing in space are commonly used as computational methods for the PNP equations [77, 146], and also for the similar drift-diffusion equations in semiconductor physics, where it is usually paired with the Scharfetter-Gummel interpolation method for mesh midpoints [?, ?]. Various other methods of discretizing the PNP equations in space are also seen in the literature, such as finite element, finite volume, and spectral methods [?]. Additionally, in many applications such as modeling of biological ion channels, it is sufficient to solve the steady-state version of the PNP equations [?], and so there is often a limited scope of work on time stepping for a fully dynamic model. In our literature search, we did not become aware of any methods which solve the time-dependent PNP equations using adaptive time stepping. In this chapter then, we will develop and test an adaptive time stepper for the PNP-gFBV equations with error control.
The chapter is structured as follows: Sections 3.1 and 3.2 present the spatial and temporal discretization, respectively. Section 3.3 presents our adaptive stepping and error control algorithm. Finally, Section 3.4 contains the numerical experiments that we run on a simplified set of equations, and contains a discussion of the properties of our numerical scheme.

The numerical simulations in this work were written in MATLAB and run on Debian Linux with 16 cores and 64 GB of RAM. Runtime ranged from a few minutes to two weeks, depending on the time range and parameters. The MATLAB code for the model can be found in Appendix F.

### 3.1 Spatial Discretization

The geometry is divided into a non-uniform mesh, with $x \in [0, 1]$ and parameterized via

$$x(s) : [0, 1] \rightarrow [0, 1],$$

so that $x_i := x(s_i)$, $0 = x_1 < x_2 < ... < x_N = 1$ and $dx(i) := x(s_{i+1}) - x(s_i)$ where $s_i = (i - 1) \, ds$, $i = 1, 2, ..., N$ and $ds = 1/(N - 1)$. The function $x(s)$ may, for example, be piecewise linear as in equation (3.2)

$$x_i = \begin{cases} \frac{L_1(i-1)}{N_1} & i = 1, 2, ..., N_1 \\ \frac{L_2(i-N_1)}{N_2} + L_1 & i = N_1 + 1, ..., N_1 + N_2 \\ \frac{L_3(i-N_1-N_2)}{N_3} + L_1 + L_2 & i = N_1 + N_2 + 1, ..., N_1 + N_2 + N_3, \end{cases}$$

with $N_1 + N_2 + N_3 = N$ and $L_1 + L_2 + L_3 = L$ for a mesh that is uniform in three different regions.

Alternatively, one could use a logistic function, for example, to create a mesh with smoothly varying nonuniformity as in

$$x(s_i) = \begin{cases} 0 & i = 1 \\ \frac{1}{1 + e^{-\gamma(s_i - \frac{1}{2})}} & i = 2, ..., N - 1 \\ 1 & i = N. \end{cases}$$

In either case, parameters can be adjusted in order to place more mesh nodes near the boundaries, as shown in Figure 3.1. In practice, we used equation (3.2) with either two, three or five regions when writing the code.

For the discussion of spatial discretization of the PDE’s and boundary conditions, we first consider
discretizing the model continuity equation

\[ u_t = -(J(u, u_x))_x. \] (3.4)

At internal nodes, \((J(u, u_x))_x\) at node \(x_i\) is discretized using a second-order center-differencing scheme

\[
\frac{du_i}{dt} \approx (u_t)_{x_i} = (J(u, u_x))_{x_i} \approx \frac{J(u, u_x)_{x_{i+1/2}} - J(u, u_x)_{x_{i-1/2}}}{x_{i+1/2} - x_{i-1/2}},
\] (3.5)

where \(x_{i+1/2}\) is the midpoint of \([x_i, x_{i+1}]\) and the approximations

\[
u_{i\pm1/2} \approx \frac{u_{i\pm1} + u_i}{2} \quad \text{and} \quad u_x|_{i\pm1/2} \approx \frac{\pm u_{i\pm1} \mp u_i}{\pm x_{i\pm1} \mp x_i}
\] (3.6)

are used in approximating the flux at the midpoints. At the boundary, we use a three-node, second-order approximation for \(u_x\). For example, the approximation for the left hand boundary is

\[
u_{x|_{x=0}} \approx -\frac{2dx(1) + dx(2)}{dx(1)(dx(1) + dx(2))} u_1 + \frac{dx(1) + dx(2)}{dx(1)dx(2)} u_2 - \frac{dx(1)}{dx(2)(dx(1) + dx(2))} u_3,
\] (3.7)
where \( dx(1) = x_2 - x_1 \) and \( dx(2) = x_3 - x_2 \). Next we consider a model Poisson equation,

\[
\frac{\partial^2 u}{\partial x^2} = f(u).
\]

(3.8)

In the interior, we again use a three point center-differencing scheme

\[
\frac{2u_{i+1}}{dx(i)(dx(i) + dx(i - 1))} - \frac{2u_i}{dx(i)dx(i - 1)} + \frac{2u_{i-1}}{dx(i - 1)(dx(i) + dx(i - 1))} \approx \frac{d^2u}{dx^2}
\]

\[
= f(u)_{x=x_i}.
\]

(3.9)

On the boundaries and internal boundaries, we use a left or right-handed three point stencil to approximate the derivative. For example, a mixed boundary condition on the left hand boundary of the form

\[
u_x|_{x=0} = \frac{u(0) - 0}{\lambda}
\]

(3.10)

would be discretized into

\[
\frac{u_1}{\lambda} = -\frac{2dx(1) + dx(2)}{dx(1)(dx(1) + dx(2))} u_1 + \frac{dx(1) + dx(2)}{dx(1)dx(2)} u_2 - \frac{dx(1)}{dx(2)(dx(1) + dx(2))} u_3.
\]

(3.11)

It is worth noting here that Bazant and coworkers (i.e. in [19] and [21]), used a Chebyshev pseudospectral spatial discretization in their work, where we use a finite difference discretization. We wrote and tested a Chebyshev spectral version of the code using the chebfun package [147, 148] and found that, while the spectral and finite difference codes gave nearly identical results, the finite difference code ran orders of magnitude faster than the spectral code when using the same time stepping scheme. The MATLAB code for our chebfun test script can be found in Appendix F.3.

### 3.2 Time Stepping

Multistep schemes such as backwards differentiation formulae and Adams-Bashforth and Crank-Nicholson methods have long been applied in computational fluid mechanics to time step advection-diffusion equations (see Chapter 4.4 of [149]) where both the diffusion and advection terms are linear. Semi-implicit, or implicit-explicit schemes, are useful when PDEs contain both linear stiff terms and nonlinear terms which are difficult to handle using implicit methods. For our model, we use a variable step size implicit-explicit backwards differencing formula (VSSBDF2) presented by Wang and Ruuth [150, 151]. To present the
method, we consider the ODE
\[ \frac{du}{dt} = f(u) + g(u), \]  
(3.12)

where \( f(u) \) is a nonlinear term (that is best handled explicitly) and \( g(u) \) is a linear term with a fast timescale that is best handled implicitly to avoid numerical instability.

We now present the time stepping scheme, using a superscript notation to denote time levels, so that \( u^n \) approximates the value of the function \( u(\cdot, t) \) at \( t = t^n \). Given the values \( u^{n-1} \) at time \( t^{n-1} = t^n - dt_{\text{old}} \) and \( u^n \) at time \( t^n \), the future value \( u^{n+1} \) at time \( t^{n+1} = t^n + dt_{\text{now}} \) is determined by equation 2.8 in [150]:
\begin{equation}
\frac{1}{dt_{\text{now}}} \left( \frac{1 + 2\omega}{1 + \omega} u^{n+1} - (1 + \omega)u^n + \frac{\omega^2}{1 + \omega} u^{n-1} \right) = (1 + \omega)f(u^n) - \omega f(u^{n-1}) + g(u^{n+1}),
\end{equation}
(3.13)

where \( \omega = dt_{\text{now}}/dt_{\text{old}} \). This second-order scheme was shown to have favorable stability properties compared to the other second order schemes based on numerical experiments on Burger’s equation [150].

If one is using a non-adaptive time stepper then the time steps \( t^n, n = 0, 1, \ldots \) are chosen before computing the solution \( u \). An adaptive time stepper chooses the new time step size \( dt_{\text{now}} \) based on already-computed solutions. For example, using the values \( u^{n-1}, u^{n-\frac{1}{2}} \) and \( u^n \) at times \( t^n - dt_{\text{old}}, t_n - dt_{\text{old}}/2 \) and \( t_n \), respectively, we choose a new time step size \( dt_{\text{now}} \) so that the local truncation error (LTE) is “small enough” but not “too small”: small enough so that the error is within tolerance, but large enough to ensure a reasonable simulation time. First, we choose a candidate time step: \( dt_{\text{now}} = dt_{\text{old}} \), for example. We then take one “coarse” step from \( t^n - dt_{\text{old}} \) and \( t^n \) to \( t^n + dt_{\text{now}} \), creating \( u^{n+1}_c \). Next, we take one “fine” step from \( t^n - dt_{\text{old}}/2 \) and \( t^n \) to \( t^n + dt_{\text{now}}/2 \), creating \( u^{n+1}_f \) and taking a second fine step creating \( u^{n+1}_f \). As discussed in the next section, we use \( u^{n+1}_c \) and \( u^{n+1}_f \) to estimate the local truncation error; if the error is acceptable, then we advance in time. If the error is unacceptable, then we choose a new \( dt_{\text{now}} \) to try. This scheme is shown in Figure 3.2. Note that in the figure, \( dt_{\text{now}} > dt_{\text{old}} \); this would happen in the first attempt if the local truncation error was too small.
3.3 Error Control

Given the two approximations $u_c^{n+1}$ and $u_f^{n+1}$ of the solution at time $t^n + dt_{\text{now}}$, we wish to use them to approximate the local truncation error. By performing a multivariable Taylor expansion of equation (3.13), we can compute the local truncation error associated with the scheme:

$$LTE = u^{n+1} - u(t^{n+1})$$

$$= \frac{1}{6} \left( 3g''(u(t))u'(t)^2 + 3g'(u(t))u''(t) - u^{(3)}(t) \right) dt_{\text{now}}^2 (dt_{\text{now}} + dt_{\text{old}}) + \text{H.O.T.} \quad (3.14)$$

and so

$$u^{n+1} = u(t_{n+1}) + C dt_{\text{now}}^2 (dt_{\text{now}} + dt_{\text{old}}) + \text{H.O.T.} \quad (3.15)$$

The constant $C$ is determined by $u'(t^n)$, $u''(t^n)$, $u^{(3)}(t^n)$, $g'(u(t^{n+1}))$ and $g''(u(t^{n+1}))$. These are not known a priori, and so in building an adaptive time stepper, one needs to approximate $C$ somehow. To do this, we use equation (3.15) to write the local truncation error for the coarse and fine steps, which
are
\[ \epsilon_c = u_c^{n+1} - u(t^{n+1}) = Cdt_{\text{now}}^2 (dt_{\text{now}} + dt_{\text{old}}) + \text{Higher Order Terms} \]  
\[ \epsilon_f = u_f^{n+1} - u(t^{n+1}) = \frac{Cdt_{\text{now}}^2 (dt_{\text{now}} + dt_{\text{old}})}{8} + C \frac{dt_{\text{now}}^4}{4} + \text{H.O.T.} \]  
Using equations (3.16) and (3.17) to approximately solve for \( C \), one finds that the local truncation error can be approximated using \( u_c^{n+1} \), \( u_f^{n+1} \), \( dt_{\text{old}} \) and \( dt_{\text{now}} \):
\[ \epsilon_c \approx \frac{8}{7} dt_{\text{old}} + \frac{5}{7} dt_{\text{now}} \left( u_c^{n+1} - u_f^{n+1} \right). \]  
We will use this approximation of \( \epsilon_c \) when testing whether to use \( dt_{\text{now}} \) or to coarsen or refine it. If \( dt_{\text{now}} \) has been accepted, we then use \( u_f^{n+1} \) and \( u_c^{n+1} \) to construct an approximation \( u^{n+1} \) which has smaller truncation error. Specifically, \( u^{n+1} \) is a linear combination of the form
\[ u^{n+1} = \alpha u_c^{n+1} + \beta u_f^{n+1}, \]  
with coefficients
\[ \alpha = -\frac{dt_{\text{old}} + 3dt_{\text{now}}}{7dt_{\text{old}} + 5dt_{\text{now}}}, \quad \beta = \frac{dt_{\text{old}} + dt_{\text{now}}}{7dt_{\text{old}} + 5dt_{\text{now}}}. \]  
The LTE for \( u^{n+1} \) is one order higher than the LTE for both \( u_c^{n+1} \) and \( u_f^{n+1} \). Note that if \( dt_{\text{now}} = dt_{\text{old}} \) then equation (3.19) reduces to the classic Richardson extrapolation formula commonly used in numerical analysis. The full derivation of equations (3.18) and (3.19)–(3.20) can be found in Appendix D.

### 3.3.1 Adaptive Time Stepping

We now discuss how to use the approximate local truncation error (equation (3.18)) in the adaptive time stepping method used to compute \( u^{n+1} \). There are two parameters in the adaptive scheme, tol and range. The adaptive scheme seeks a time step \( dt_{\text{now}} \) such that the local truncation error \( \epsilon_c^{n+1} \) is in \( (\text{tol} - \text{range}, \text{tol} + \text{range}) \) and in practice we have used a relationship such as \( \text{range} = \text{tol}/3 \) and \( \text{tol} = 10^{-6} \). The following presents the steps in our adaptive stepping and refinement strategy.

1. Set the loop counter, \( i \), to 1 and set \( dt^1 = dt_{\text{old}} \), where \( dt^i \) is the \( i \)th guess at a value for \( dt_{\text{now}} \).
2. (a) Take coarse and fine steps to compute \( u_c^{n+1} \) and \( u_f^{n+1} \) and use (3.18) to approximate \( \epsilon_c^i \). Use the multistep scheme for \( n > 1 \) and equation (3.13) with \( \omega = 0 \) (single-step) for the first time step.
(b) Compute \( \epsilon^i_c \) and check if \(|\epsilon^i_c - \text{tol}| < \text{range} \). If yes, go to step 5.

3. Check the loop counter. If \( i_{\text{max}} \) attempts have been made trying to find an acceptable value for \( dt_{\text{now}} \) and \(|\epsilon^i_c| \geq (\text{tol} + \text{range}) \), then set \( dt_{\text{now}} \) to \( dt_{\text{min}} \). Alternatively, if at any time \( dt_{\text{now}} > dt_{\text{max}} \), then set \( dt_{\text{now}} \) to \( dt_{\text{max}} \). Compute the resulting \( u_{c}^{n+1} \) and \( u_{f}^{n+1} \), and go to step 5.

4. Increment the loop counter by 1 and make a guess at \( dt_{\text{now}} \) based on equation (3.21) and return to step 2

\[
dt^{i+1} = dt^i \min \left( \max \left( \left( \frac{\text{tol}}{\epsilon_c} \right)^{1/p}, \eta_{\text{min}} \right), \eta_{\text{max}} \right) \tag{3.21}
\]

5. Advance in time, setting \( dt_{\text{now}} = dt^i \), \( t^{n+1} = t^n + dt_{\text{now}} \) and use (3.19) to define \( u^{n+1} \).

\( i_{\text{max}} \) is the maximum number of allowed iterations per time step, and \( dt_{\text{min}} \) and \( dt_{\text{max}} \) are the minimum and maximum allowed time steps, respectively. \( dt_{\text{min}} \) is set based on computing time requirements, and we have used values in the range \( 10^{-10} \) to \( 10^{-8} \). \( dt_{\text{max}} \), in practice, is never reached as the system of equations we are studying has an inherent instability which causes the time-stepper to plateau at a relatively small \( dt \). This is discussed in Section 3.4.

Equation (3.21) is a carry-over from refinement strategies for single step schemes, where \( p \) is the order of the LTE. It is based on the idea that the LTE satisfies \( \epsilon^i \approx C \left( dt^i \right)^p \), so setting \( dt^{i+1} = \left( \frac{\text{tol}}{\epsilon_c} \right)^{1/p} dt^i \) will bring \( \epsilon^{i+1} \) closer to \( \text{tol} \). The role of \( \eta_{\text{min}} \) and \( \eta_{\text{max}} \) in (3.21) is to prevent \( dt^{i+1} \) from changing "too much" at once \( (\eta_{\text{min}} \leq dt^{i+1}/dt^i \leq \eta_{\text{max}}) \). \( \eta_{\text{max}} \) and \( \eta_{\text{min}} \) are set to reasonable values, such as 1.2 and 0.8, respectively, as safeguards to guarantee that the adaptive stepper is able to converge. This type of error control strategy is discussed in Chapter II.4 of Hairer, Norsett and Wanner [152]. Since we’re using a two-step time stepping scheme, something different needs to occur for the first time step. For the first step, we use a first order IMEX scheme, i.e. (3.13) with \( \omega = 0 \), which has an LTE \( \sim O(dt^2) \) along with the error control that uses \( p = 2 \) in (3.21) and the extrapolation formula \( u^{n+1} = 2u_f - u_c \).

Above, we described the time-stepping for a single ODE in steps presented above. Given the system of ODEs that would arise from spatially discretizing a parabolic PDE, we would use the same approach but would define the local truncation error using the norm of \( u \). In our simulations, we chose the \( L^2 \) norm. To demonstrate the performance of the adaptive time-stepper, we computed solutions to the diffusion equation \( u_t = u_{xx} \) with Dirichlet boundary conditions \( u(0,t) = 0, u(1,t) = 1 \) using the temporal discretization given by (3.13). The term \( u_{xx} \) is handled implicitly, like the term \( g(u) \), and there is no nonlinear term hence \( f(u) = 0 \). The solution decays exponentially fast to the equilibrium solution \( u(x,t) \to x \). If one had constant time-steps, one would expect that the local truncation error would
decay exponentially fast to zero. Similarly, if the local truncation error is constrained to stay within a fixed interval, one would expect that the time-step size would grow exponentially in order to satisfy this. The left plot in Figure 3.3 shows that as time passes, the norm of $u_t$ is going to zero exponentially fast: the solution is equilibrating. The centre plot shows that at first the approximate local truncation error (3.18) is in the interval $[\text{tol} - \text{range}, \text{tol} + \text{range}]$ but that once $dt$ reaches the maximum value $dt_{\text{max}}$ the local truncation error can no longer be forced to be greater than $\text{tol} - \text{range}$. At this point, the local truncation error decreases to zero exponentially fast. The plot on the right shows that the time-step grows exponentially in time until it reaches the maximum value $dt_{\text{max}}$.

Figure 3.3: Approximating the solution of $u_t = u_{xx}$ with $u(0, t) = 0$, $u(1, t) = 1$ and $u(x, 0) = 1$. The parameters are tol = $10^{-6}$, range = tol/3, $dx = 1/40$, and $dt_{\text{max}} = 1$. (a): $l^2$ norm of $\partial u/\partial t$ as a function of time. (b): $l^2$ norm of the approximation of the local truncation error (3.18). The horizontal dashed lines mark the upper and lower bounds: $\text{tol} \pm \text{range}$. (c): The time step $dt$ for which the solution $u^{n+1}$ is accepted and the time-stepping scheme advances.

In total, the model has $N$ parabolic PDEs for ionic species $c_i$ (2.37), one ODE for the electric field at
the cathode $\phi_x$ (if there are current boundary conditions (2.40)), a parabolic PDE for the temperature (2.39) and one elliptic PDE for the potential $\phi$ (2.38). If the model is extended to include adsorption effects at the electrodes, there would be two additional ODEs describing the dynamics of the fraction of surface coverage at the two electrodes. We now describe how to time-step this system in a way that the global truncation error is $O(dt^2)$ when we take constant time steps ($dt_{\text{old}} = dt_{\text{now}} = dt$). Figure 3.4 shows the scheme for the first and second (and subsequent) time steps. For a solution with one mobile ionic species, for example, the initial data $c$ and $\phi_x$ is discretized resulting in initial vectors $c, T \in \mathbb{R}^N$ and $\phi_x^1 \in \mathbb{R}^1$. Given $c^1, T^1$ and $\phi_x^1$, we solve the elliptic PDE to determine $\phi^1 \in \mathbb{R}^N$. Using forward Euler on the $N + 1$ parabolic PDEs and the ODE, we determine $c^2, T^2$ and $\phi_x^2$ from $c^1, T^1, \phi_x^1$ and $\phi^1$. We then solve the elliptic PDE to determine $\phi^2$. The two-step method is then applied. In general, $\phi^{n+1}$ is solved for using $c^{n+1}, T^{n+1}$ and $\phi_x^{n+1}$. It is important for numerical accuracy that the correct $\phi$ is associated with the correct time level: not doing so will reduce the global truncation error from $O(dt^2)$ to $O(dt)$ when constant time steps are taken. Furthermore, since the elliptic equation is “post-processed” (the potential at time $t^n$ is determined from the other quantities at time $t^n$), its values do not factor into the computation of the local truncation error during adaptive time stepping.
3.4 Numerical Tests

Now that we have described our discretization schemes in space and time, we continue by constructing and exploring the numerical properties of a “toy” version of the PNP-gFBV equations (2.37)–(2.44). We consider the coupled parabolic, elliptic system

\[ u_t = u_{xx} + (uv_x)_x = -(-u_x - u v_x)_x, \quad (3.22) \]
\[ v_{xx} = -u \quad (3.23) \]

on \( x \in (0,1) \) with boundary conditions on the flux of \( u \)

\[ (-u_x - uv_x)_{x=0} = F(t) = -u(0,t) e^{v(0,t)} + e^{-v(0,t)}, \quad (3.24) \]
\[ (-u_x - uv_x)_{x=1} = G(t) = u(1,t) - 1. \quad (3.25) \]

We refer to the functions \( F(t) \) and \( G(t) \) as the “flux constraint functions”. Finally, there are Robin and Neumann boundary conditions on \( v \)

\[ v(0,t) - 0 = v_x(0,t), \quad (3.26) \]
\[ v_x(1,t) = 0. \quad (3.27) \]

In terms of the full system, \( v \) is the analogue of the potential and \( u \) is the analogue of the concentration of a species. This toy system has properties of the full system, most importantly the nonlinear coupled advection term in equation (3.22) and the flux boundary condition on the flux of \( u \), (3.24), is coupled to \( v \). We refer to this boundary condition as “Butler-Volmer-like”, or “BV-like”.

In the interior of the domain, \( x \in (0,1) \), we discretize in space using the methods outlined in Section 3.1 and time step using the time stepper and error control methods in Sections 3.2 and 3.3. The PDE (3.22) is discretized at the interior nodes, \( x_2, \ldots, x_{N-1} \), using the temporal discretization given by (3.13). The term \( u_{xx} \) in (3.22) is handled implicitly, like the term \( g(u) \), and the nonlinear term \( (u v_x)_x \) is extrapolated forward in time, like the nonlinear term \( f(u) \). This results in \( N-2 \) equations involving the \( N \) unknowns, \( u_1^{n+1}, \ldots, u_N^{n+1} \). The boundary conditions provide two additional equations.

It is unclear how the boundary conditions on the flux of \( u \), equations (3.24)–(3.25), should be handled, because not only is the flux, \(-u_x - uv_x\), nonlinear and coupled to \( v \) but so is the flux constraint function
A natural first approach is to extrapolate both the nonlinear term in the flux and the flux constraint function into the future, for example using the equation

\[-(u_x)_1^{n+1} - (1 + \omega)(uv)_1^n + \omega(uv)_1^{n-1} = (1 + \omega) F^n - \omega F^{n-1}\]  

(3.28)

to approximate the boundary condition (3.24). Here, \(F^n = -u_1^n e^{v^n_1} + e^{-v^n_1}\), and \(F^{n-1}\) is defined analogously. Similarly, the boundary condition (3.25) would be approximated as

\[-(u_x)_N^n - (1 + \omega)(uv)_N^n + \omega(uv)_N^{n-1} = (1 + \omega) G^n - \omega G^{n-1}\]  

(3.29)

where \(G^n = u_N^n - 1\) and \(G^{n-1} = u_N^{n-1} - 1\). We refer to equations (3.28) and (3.29) as the “direct” method of handling the boundary conditions. The \(N\) equations are solved, determining \(u_1^{n+1}, \ldots, u_N^{n+1}\). The elliptic equation \(v_{xx} = -u_1^{n+1}\) and the Robin and Neumann boundary conditions (3.26)–(3.27) are then discretized and solved, determining \(v_1^{n+1}, \ldots, v_N^{n+1}\).

As shown in Table 3.1, with constant time steps, we found this method to be second-order accurate in time if the boundary conditions on the flux of \(u\) are replaced with homogeneous Dirichlet boundary conditions on \(u\): \(u(0,t) = u(1,t) = 0\). The method is first-order accurate in time with the BV-like boundary conditions, (3.24)–(3.25). Because the BV-like boundary conditions are nonlinear and coupled to the elliptic equation, we also considered boundary conditions of intermediate complexity. Specifically, the linear, coupled boundary conditions \(u(0,t) = 0\) and \(u(1,t) = v(1,t) - 1\) and the nonlinear, uncoupled boundary conditions \(u(0,t) = 0\) and \(u(1,t) = \cos(u(1,t)) - 1\). The solutions were found to diverge with no-flux boundary conditions on \(u\) (equations (3.24)–(3.25) with zero on the right-hand sides).

<table>
<thead>
<tr>
<th>(dt)</th>
<th>Homog. Dirichlet</th>
<th>linear coupled</th>
<th>nonlinear uncoupled</th>
<th>BV-Like</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>4.01</td>
<td>3.58</td>
<td>2.05</td>
<td>2.43</td>
</tr>
<tr>
<td>0.001/2</td>
<td>4.01</td>
<td>2.89</td>
<td>2.02</td>
<td>2.30</td>
</tr>
<tr>
<td>0.001/4</td>
<td>4.01</td>
<td>4.79</td>
<td>2.01</td>
<td>2.18</td>
</tr>
<tr>
<td>0.001/8</td>
<td>4.00</td>
<td>11.26</td>
<td>2.01</td>
<td>2.10</td>
</tr>
<tr>
<td>0.001/16</td>
<td>4.02</td>
<td>1.14</td>
<td>2.00</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Table 3.1: Convergence test on toy model with “direct” method implementation of boundary conditions (3.28)-3.29). Reading the columns from left to right, the boundary conditions are: homogeneous Dirichlet, linear & coupled, nonlinear & uncoupled, and BV-like. We compute six solutions on a uniform mesh \(dx = 1/20\) using constant time steps up to time \(t = 1\). The \(i^{th}\) solution \(ui\) is computed using \(dt = 0.001/2^i\). The ratios are computed using the discrete solutions \(ui\) at the final time \(t = 1\); the ratio is defined as \(\|ui - ui+1\|/\|ui+1 - ui+2\|\) with the \(l^2\) norm. Ratios approaching 4 indicate second order accuracy in time, while ratios approaching 2 indicate first order accuracy.

We found that with BV-like boundary conditions and adaptive time stepping turned on, the error control
algorithm is unable to make the error arbitrarily small by reducing \( dt \), so that only values of tol larger than some minimum value are possible. Furthermore, when a value of tol larger than this minimum value is used, the adaptive time stepper exhibits a thresholding behavior, where the adaptive stepper will remain near a fixed \( dt \) even though the solution has equilibrated (see Figure 3.5). This appears to be related to some sort of instability as suggested by the following test. First, the simulation is run with a constant time-step \( dt \) that is chosen to be smaller than the threshold value for \( dt \) and the simulation is run until the solution has largely equilibrated: \( |du/dt| \to 0 \), error \( \sim \) roundoff. At this point, the time-step \( dt \) is increased to be larger than the threshold value for \( dt \) and the simulation is run further with this constant time step. We observe that the solution diverges, suggesting that the simulation is unstable for time-steps larger than the threshold value of \( dt \). See Figure 3.6.

The “direct method” for boundary conditions (3.28)-(3.29) had the undesirable properties of: not being able to take the parameter tol to be arbitrarily small, the time-step \( dt \) thresholds, and method is not second-order accurate in time for the BV-like boundary conditions. For this reason, we sought an alternative approach for the boundary. We refer to this alternative method the “ghost point” method (see Section 1.4 of Thomas [?]), since it assumes the PDE (3.22) holds at the two boundaries, \( x = 0, 1 \), and uses the same time stepping scheme as at the internal nodes \( x_2, \ldots, x_{N-1} \). Applying the PDE at \( x_1 \) and \( x_N \) requires the flux, \( -u_x - u v_x \), at the “ghost points” \( x = -dx_1/2 \) and \( x = 1 + dx_{N-1}/2 \) located outside of the spatial domain \([0, 1]\). To this end, we assume that the flux boundary conditions

Figure 3.5: \( dt \) vs time for toy model with adaptive time stepping using the “direct” method and BV-like boundary conditions. \( N = 20, \) tol = 10\(^{-2} \), \( u(\cdot, 0) \equiv 1 \). The time steps threshold to a value of \( \sim 10^{-1} \).
Figure 3.6: Computed local truncation error vs time for toy model with piecewise constant time steps using the “direct” method for the boundary conditions (3.28)-(3.29) and BV-like boundary conditions. 

$N = 20$, $\text{tol} = 10^{-2}$, $u(\cdot, 0) = 1$, $dt = 0.01$ for $t \leq 10$ and $dt = 1$ for $t > 10$.

(3.24)-(3.25) hold at the ghost points. The discretized PDE at $x = 0, 1$ become the two ODEs

$$
\begin{align*}
\frac{\partial u}{\partial t} &= \left(\frac{u_x + uv_x}{x = dx_1/2} - F(t)\right) dx_1 \\
\frac{\partial u}{\partial t} &= G(t) - \left(\frac{u_x + uv_x}{x = 1 - dx_{N-1}/2}\right) dx_{N-1}
\end{align*}
$$

We found the ghost point method to be second-order accurate in time, as shown in Table 3.2 for BV-like boundary conditions (3.24)-(3.25). This is unsurprising since the time stepping scheme is second-order accurate and the ghost point method treats the boundary points in the same manner as the interior points.

<table>
<thead>
<tr>
<th>$dt$</th>
<th>Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>0.001/2</td>
<td>3.47</td>
</tr>
<tr>
<td>0.001/4</td>
<td>3.65</td>
</tr>
<tr>
<td>0.001/8</td>
<td>3.79</td>
</tr>
<tr>
<td>0.001/16</td>
<td>3.89</td>
</tr>
<tr>
<td>0.001/32</td>
<td>3.94</td>
</tr>
</tbody>
</table>

Table 3.2: Convergence Test on Toy Model with ghost point method and BV-like boundary conditions. See Caption 3.1 for a full explanation. The mesh width is $dx = 1/20$ and the simulation ran to time $t = 1$. Ratios tending to 4 indicate second-order accuracy in time.

The ghost point method performs much better with the adaptive time stepper in that the local truncation error can be made arbitrarily small by decreasing $dt$: any value of tol is admissible. However, the method does still have the thresholding behavior with adaptive time stepping, as shown in Figure 3.7, although
the threshold value for $dt$ is larger. Also, the apparent instability for large time-steps persists, as suggested by Figure 3.8.

![Figure 3.7: $dt$ vs time for toy model with adaptive time stepping with “ghost point” method and BV-like boundary conditions. $N = 20$, tol = $10^{-6}$, $u(\cdot, 0) = 1$](image)

Figure 3.7: $dt$ vs time for toy model with adaptive time stepping with “ghost point” method and BV-like boundary conditions. $N = 20$, tol = $10^{-6}$, $u(\cdot, 0) = 1$

![Figure 3.8: Computed error vs time for toy model with piecewise constant time steps with “ghost point” method and BV-like boundary conditions. $N = 20$, tol = $10^{-6}$, $u(\cdot, 0) = 1$, $dt = 0.01$ for $t \leq 10$, $dt = 1.5$ for $t > 10$.](image)

Figure 3.8: Computed error vs time for toy model with piecewise constant time steps with “ghost point” method and BV-like boundary conditions. $N = 20$, tol = $10^{-6}$, $u(\cdot, 0) = 1$, $dt = 0.01$ for $t \leq 10$, $dt = 1.5$ for $t > 10$.

It is natural to ask whether the thresholding behaviour still occurs with adaptive time stepping on a one-step time-stepping scheme, and whether it still occurs when simpler (homogeneous, uncoupled) boundary conditions are used. We considered two one-step schemes for the toy model PDE (3.22): forward Euler,

$$
\frac{u^{n+1} - u^n}{dt} = (u_{xx} + (uv)_x)^n,
$$

(3.32)
and the implicit-explicit scheme,

\[ \frac{u^{n+1} - u^n}{dt} = (u_{xx})^{n+1} + ((uv_x)_x)^n. \] (3.33)

For both time-steppers, we tried both the "direct" and ghost point methods for the boundary conditions, (3.28)-(3.29) and (3.30)-(3.31) respectively. Adaptive stepping is used, with the error at each step calculated via. \( \epsilon = |u_{fine} - u_{coarse}| \). The time stepping results are shown in Figure 3.9. All four of the

(a) Forward Euler, direct  
(b) Forward Euler, ghost point  
(c) Implicit-explicit, direct  
(d) Implicit-explicit, ghost point

Figure 3.9: Time steps chosen by adaptive stepper for the toy model using two first-order time stepping schemes: Forward Euler (equation (3.32)) and implicit-explicit (equation (3.33)), and either direct or ghost point method at the boundary (with BV-like boundary conditions). \( N = 40, \text{tol}=10^{-6} \) for ghost point method simulations and \( \text{tol}=10^{-2} \) for direct method simulations.

order schemes in Figure 3.9 display a thresholding of \( dt \). Additionally, the steppers which used the direct method at the boundaries share the issue of a hard lower bound on the error, as was the case for the two-step direct scheme, which is why a \( \text{tol}=10^{-2} \) was used for the two direct method simulations instead of \( \text{tol}=10^{-6} \). Of the first-order schemes, only the implicit-explicit method with ghost points has similar performance in this test to the multistep scheme, which is the reason we use it to take the first time
The final question to answer is whether the toy model still thresholds with simpler boundary conditions, which might give us some further insight into the nature of the thresholding. First, we tested the VS-SIMEX solver on the toy model with homogeneous Dirichlet boundary conditions on the left boundary, i.e. \( u(0) = 0 \), and a function that decays to 0 on the right boundary, \( u(1) = \exp(-t) \), and found that no thresholding occurs. The time steps chosen by the solver can be seen in Figure 3.10. This would seem to indicate that the thresholding does not occur simply due to solving a coupled parabolic-elliptic system of PDEs.

Figure 3.10: \( \Delta t \) vs time for toy model with adaptive time stepping with \( u(0) = u(1) = 0 \), \( N = 40 \), \( \text{tol}=10^{-6} \)

Next, we tested the solver with various flux boundary conditions at the right hand side and \( u(0) = 0 \) at the left hand boundary (except for the zero flux case, where \( u(0) = 1 \) was used since zero flux and \( u(0) = 0 \) admits the solution \( u = v = 0 \)). Figure 3.11 shows the \( \Delta t \) vs. time plots for these simulations, where the boundary conditions were all set using the ghost point method in equation (3.31).

These tests show that the thresholding somehow comes about due to having coupled boundary conditions and time stepping the boundary node. Even in the homogeneous Neumann case (Figure 3.12a), the term \( uv_x \) must be extrapolated, and so any flux boundary condition involves extrapolating a coupled term regardless of the exact value of the flux. This is a strange behaviour, since a nonlinear coupled term gets extrapolated when every point in the interior of the domain is time stepped, which does not cause thresholding as demonstrated in the homogeneous Dirichlet case (Figure 3.10), but this seems to cause an issue at the boundary, even though we are time stepping the two boundary nodes exactly the same way as interior nodes. In the end however, we have already shown that time stepping the boundary node
and setting the flux via ghost points has superior numerical properties compared to extrapolating the part of the flux containing $v$ as in equations (3.28)–(3.29), and so it is clearly the better alternative.

Having studied the adaptive time stepper for the toy model ((3.22)–(3.27)), we now consider the full model (the nondimensionalized PNP equations with BV boundary conditions). Table 3.3 shows a convergence test on the full model using current boundary conditions and Figure 3.12 shows the step sizes chosen by the adaptive time stepper with a series of voltage jumps at the right-hand boundary.

It should be noted that with the boundary conditions we used, the boundary condition $v = 0$ results in immediate equilibrium since $c_\pm = 1$ and $\phi = 0$ is a solution, and so the adaptive stepper permits a large $dt$ for the first step. However, in Figure 3.12 we used a sequence of step-like shifts of hyperbolic tangent functions instead of hard step functions to raise the voltage, which is why the time steps decreases before plateauing at a step size of roughly 0.02. When the forcings occur, the adaptive stepper reduces
Table 3.3: Convergence test on full model with current boundary conditions and $j_{ext} = 0$. L2 Norm and constant time steps. $N = 300$, $t_{end} = 0.1$, all model parameters set to 1 except $\epsilon = 0.1$.

<table>
<thead>
<tr>
<th>$dt$</th>
<th>Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td>0.005/2</td>
<td>4.43</td>
</tr>
<tr>
<td>0.005/4</td>
<td>4.23</td>
</tr>
<tr>
<td>0.005/8</td>
<td>4.44</td>
</tr>
<tr>
<td>0.005/16</td>
<td>4.71</td>
</tr>
<tr>
<td>0.005/32</td>
<td>4.94</td>
</tr>
</tbody>
</table>

Figure 3.12: $dt$ vs time for full model with forcing, shown in (b), in response to voltage set to 0.1, 0.2, 0.3 and 0.4 at times 7.5, 8, 8.5 and 9 using a sequence of hyperbolic tangent functions to provide smoothing, shown in (a). $N = 90$, tol = 1e-6, range = tol/3, all parameters set to 1 except $\epsilon = 0.1$. $c_{\pm}(\cdot, 0) = 1$, $T(\cdot, 0) = 1$.

dt to $\sim 10^{-5}$ to compensate. Between forcings, the step size can be seen to be increasing. This is a demonstration of the value of adaptive time stepping versus constant time steps: a constant step method would require step sizes of $10^{-5}$ to resolve the forcings, whereas the adaptive stepper has step sizes of $> 10^{-2}$ for most of the duration of the simulation.

Finally, one numerical feature of the full PNP equations which does not exist in the toy model that we have constructed is the parameter $\epsilon$, which controls the dynamics of the boundary layers near the electrodes. Since $\epsilon$ scales with $1/L$ and $t$ (and therefore also $dt$) scales with $1/L^2$, we expect that lowering epsilon by a factor of $a$ should result in $dt$ being smaller by a factor of $a^2$. We tested this by running the full model with six different values of $\epsilon$ and recording the threshold value of $dt$ that the adaptive stepper settles on. The average value is approximated by averaging $dt$ values in a 1 time unit window. The results shown in Table 3.4 confirm this scaling behaviour.

The fact that our method is able run with any value of $\epsilon$ is an important contribution, as previous work on time-dependent solutions to the PNP equations [22, 153] have $\epsilon \geq 10^{-3}$, whereas in principle we are
Table 3.4: Average $dt$ values chosen by the adaptive stepper for various values of $\epsilon$ for the full PNP equations with tol=$10^{-6}$, $\delta = 1$, $k = 1$, $N$ and $dx$ chosen appropriately. Voltage boundary conditions with $v = 0$ are used.

<table>
<thead>
<tr>
<th>$\epsilon$</th>
<th>$dt$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0257</td>
</tr>
<tr>
<td>0.01</td>
<td>0.000241</td>
</tr>
<tr>
<td>0.001</td>
<td>$3.70 \times 10^{-6}$</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>$2.48 \times 10^{-8}$</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>$2.25 \times 10^{-10}$</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>$2.37 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

able to simulate with any value of $\epsilon$. 
Chapter 4

Model Benchmarking

In this chapter, we present and discuss some simulation results from our model. In particular, we want to test the validity of the three additions that we have made to the basic model: surface coverage, polarization and temperature, and the numerical method we have chosen. Only one effect will be active at a time during test runs, and for each effect we will vary relevant parameters and observe their effect on cell behaviour. These simulations are a “sanity-check”, and we are testing to see if the equations and numerical methods we have developed produce sensible results. More in-depth simulations with comparisons to theory can be found in Chapter 5.

Unless stated otherwise for a particular test, the default parameters are $z_+ = -z_- = n = 1$, $D_0 = D_+ = D_- = 1$, $\epsilon = 0.001$, $\delta = 1$, $k_{c, \text{cathode}} = j_{r, \text{anode}} = j_{r, \text{cathode}} = k_{c, \text{anode}} = 50$, $\nu = 0$.

Finally, it is important to validate simulated results experimentally and the two experiments most commonly performed by electrochemists are voltammetry and impedance spectroscopy. Since we would like our model to be able to replicate these two important classes of results, two additional tools have been built which run on top of the base code. The first is a single-electrode model which emulates a three-electrode experimental voltammetry setup, and the second is a frequency sweep tool which emulates impedance spectroscopy. Some proof-of-concept results using the impedance spectroscopy tool are presented in Section 4.4, and a single electrode voltammetry model is presented in Chapter 5.
4.1 Surface Coverage

Of the three new classes of physics that our model includes, surface coverage has the largest and most obvious effect, since it directly modifies the Butler-Volmer equation. The equation that we are using to model the dependence of the surface fraction $\theta$ on the reaction rate is

$$q_s \frac{d\theta}{dt} = j_{c+}$$  (4.1)

where $q_s$ is a parameter that corresponds to the number of total sites, $j_{c+}$ is defined as the Faradaic portion of the current density from the solution into the electrode and $\theta$ is defined as the surface fraction of occupied sites. For our tests, we suppose that only the positive ion takes part in the electrode reaction and requires an empty site on the electrode surface. We also assume that the forward reaction (the ion binding with a surface site) creates an occupied site, and that this process is reversible. The surface fraction of unoccupied and occupied sites are $(1 - \theta)$ and $\theta$, respectively, i.e.

$$c_+ + e^- + \text{unoccupied site} \leftrightharpoons \text{occupied site}$$

so we may naively write the charge-transfer rate as

$$j_{c+} = k_{c+}e^{c+ \text{ electrode}}(1 - \theta)e^{-\alpha_e \Delta \phi} - j_f \theta e^{\alpha_e \Delta \phi}$$  (4.2)

Figure 4.1 shows the evolution of voltage and surface coverage $\theta$ on a system with a single electrode with reaction kinetics governed by equation (4.2), with $\epsilon = 0.001$, $\delta = 1$, $k = 50$, and $q_s$ varied.

![Figure 4.1: \(\theta\) and voltage vs time for a reaction at a single electrode with reaction kinetics described by equation (4.2). \(\epsilon = 0.001\), \(\delta = 1\), \(k = 50\), \(q_s\) varied.](image)
We can see that, as expected, an increase in $q_s$ in equation (4.1) results in a smaller equilibrium value of $\theta$ and a larger equilibrium value of $v$. The latter is due to the fact that the equilibrium value of the voltage across the cell includes the term

$$ v_0 = \log \left( \frac{k_{c,c} j_{r,a}}{j_{r,c} k_{c,a}} \right) \quad (4.3) $$

with the subscripts $a$ and $c$ denoting values at the anode and cathode, respectively. In the surface coverage model, $k_c$ is multiplied by $(1 - \theta)$ and $j_r$ is multiplied by $\theta$. The equilibrium values of $\theta$ at each electrode have slightly different values, which tend towards the same value as $q_s$ gets large, resulting in different equilibrium voltages across the cell.

As discussed in Section 2.4.4, isotherms describe the amount of adsorbate on an interface as a function of pressure or concentration at equilibrium. Equation (4.1) is equivalent to the Langmuir equilibrium isotherm,

$$ \frac{\theta}{1 - \theta} = K_{EC} \quad (4.4) $$

where $K_E$ is an equilibrium constant. Langmuir isotherms are a special case of the more general Frumkin equilibrium isotherm, which is written as

$$ \frac{\theta}{1 - \theta} e^{\frac{w(\theta)}{k_B T}} = K_{EC} \quad (4.5) $$

where a positive $w(\theta)$ corresponds to an increase in energy of the adsorbed state for higher coverages, or repulsion between adsorbed species, and a negative $w(\theta)$ corresponds to attraction between adsorbed species (see Chapter 6.2 of [154]).

Figures 4.2 and 4.3 show a comparison of the two for $q_s = 1$ and $w(\theta) = -(1 - 2\theta)$ with a voltage ramp and a voltage step.

The important behaviour to take away from Figures 4.2–4.3 is that the current eventually relaxes to zero in both cases. With surface coverage effects active, current is not allowed to be non-zero indefinitely since a non-zero current must result in a change in $\theta$. An equilibrium is eventually reached where the reaction current vanishes, and so these simulations agree with what is physically expected.
Figure 4.2: Current density vs. time for a voltage ramp of $\dot{S} = -1$ with Langmuir and Frumkin adsorption isotherms, as in equations (4.4) and (4.5), with $w(\theta) = -(1 - 2\theta)$. $\epsilon = 0.001$, $\delta = 1$, $k = 50$, $q_s = 1$.

Figure 4.3: Current density vs. time for a voltage step of 1 with $w(\theta) = -(1 - 2\theta)$ for the Frumkin isotherm. $\epsilon = 0.001$, $\delta = 1$, $k = 50$, $q_s = 1$.

4.2 Polarization

The effect of polarization on cell behaviour can be studied by varying the nondimensionalized parameter $\epsilon$, which is proportional to the square root of the relative permittivity $\varepsilon_r$, in the bulk, diffuse regions and Stern layer. This parameter appears in the bulk equation (2.38) and the boundary conditions (2.44).
Chapter 4. Model Benchmarking

(2.45), as well as the current conservation equation (2.40). \( \varepsilon_r \) also appears in the parameter \( \beta \) in the temperature equation (2.39), but we are turning off temperature and surface coverage for simulations in this section.

Since the nondimensionalized parameter \( \epsilon \) is proportional to the square root of \( \varepsilon_r \), we assume that \( \epsilon = 0.001, 0.01 \) and 0.1 correspond to the value for unpolarized water (\( \varepsilon_r = 80 \)) and chose values for \( \epsilon \) in the double layers relative to the \( \epsilon \) in the bulk. For these simulations, we used \( \epsilon_{\text{diff}} = \epsilon_{\text{bulk}} \sqrt{\frac{\varepsilon_r}{80}} \). There is also the choice of \( \ell_{\text{diff}} = L_{\text{diff}}/L \), the constant width of the double layer, including the diffuse part. For these simulations, we chose the values \( \ell_{\text{diff}} = 0.01, 0.05 \) and 0.1, respectively. Different values for \( \epsilon \) in different regions are set by altering the value for \( \epsilon \) in equations (2.38), (2.40) and (2.44) and then applying equation (2.45) at the internal boundaries where \( \epsilon \) changes. Figure 4.4 shows the potential at steady state (\( j_{\text{ext}} = 0 \)) for the cell with and without polarization applied, for various values of \( \epsilon_{\text{bulk}} \).

Since having all reaction parameters equal results in immediate equilibrium, we chose the reaction rate coefficients to be \( k_{c,c} = j_{r,a} = 100, j_{r,c} = k_{c,a} = 50 \) for a steady-state cell voltage of \( \sim 1.4 \).

![Graphs showing potential at steady state for cell with and without jump in \( \epsilon \) for various values of \( \epsilon_{\text{bulk}} \).](image)

Figure 4.4: Potential at steady state for cell with jump in \( \epsilon \) and without, for various values of \( \epsilon_{\text{bulk}} \), with \( \delta = 0.01 \) and \( k_{c,c} = j_{r,a} = 100, j_{r,c} = k_{c,a} = 50 \).
Since $\epsilon$ is the characteristic length of the double layer, we can expect a smaller value of $\epsilon$ to result in a thinner double layer, and this is seen in Figure 4.4. In Figure 4.5c, the value of $\epsilon$ is large enough in the simulation without a jump in $\epsilon$ that the double layers for the two electrodes nearly overlap at steady-state, and interestingly, lowering $\epsilon$ in just the region near the electrode but not the rest of the domain restricts the double layer to just the region $L_{\text{diff}}$ from the boundary. Since $\epsilon$ controls the amount of charge separation that is able to occur, or rather the length scale over which the amount of charge separation is able to occur, we would also expect that the potential varies in a smaller region when $\epsilon$ is made smaller in that region, and this matches what is seen in Figure 4.4.

Another demonstration of the effect of different $\epsilon$ in the different regions at a cell level is with voltage driven phenomena, especially with high frequency oscillations or rapid changes in the applied voltage. Figure 4.5 shows the current response a voltage step of +0.1 with and without different values of $\epsilon$ and $k_{c,c} = j_{r,a} = j_{r,c} = k_{c,a} = 50$.

![Graphs showing current vs. time with jump in $\epsilon$ and without for a voltage step of 0.1, for various values of $\epsilon_{\text{bulk}}$, with $\delta = 0.01$ and $k_{c,c} = j_{r,a} = j_{r,c} = k_{c,a} = 50$.]
A further test of polarization effects can be done using a frequency sweep of the system and recording the resulting voltage-current relationships, but we leave this to Section 4.4 when impedance spectroscopy tests are run.

### 4.3 Temperature

For our temperature simulations, we will be using the mixed flux boundary condition

\[ J_{\eta,\text{ext}} = h(T - T_{\text{amb}}) \]  \hspace{1cm} (4.6)

to model the interface between the cell and the ambient, where \( h \) is a nondimensionalized parameter proportional to electrode surface area. We will also remove temperature dependence from the diffusion and electrostatic (Nernst-Planck and Poisson) parts of the model so that the mass flux is coupled to the temperature equation but not vice versa. This allows temperature evolution to be studied in isolation, assuming no temperature dependence in the rest of the model; simulations with temperature dependence in the bulk should be considered in future work.

Figure 4.6 shows the evolution of the average temperature in the cell with \( \alpha = h = 50, k = 50, \epsilon = 1, \delta = 1 \) and \( \beta = 0.1 \) and with various currents. where the bulk averaged temperature in Figure 4.6 is

Figure 4.6: Average temperature with \( \alpha = h = 50, k = 50, \epsilon = 1, \delta = 1 \) and \( \beta = 0.1 \) for different values of current.
calculated using a numerical approximation of the integral of the temperature over the domain:

\[
T_{\text{ave}}(t) = \int_0^1 T(x,t) \, dx \approx T_1 \, dx_1 + \sum_{i=2}^{N-1} T_i \frac{dx_i + dx_{i-1}}{2} + T_N \, dx_N
\] (4.7)

where \(dx_i\) is the width of the \(i^{th}\) mesh element; equation (4.7). \(T_1\) and \(T_N\) are the values of temperature on the left hand side and right hand side boundaries, and so they are scaled by \(dx_1/2\) and \(dx_{N-1}/2\), respectively.

Clearly, from Figure 4.6, larger currents produce higher temperatures. We also see a period of rapid temperature growth for \(t \sim 0.01\) followed by a more gradual plateauing, due to the fact that the rate of temperature diffusion is much faster than the speed of concentration diffusion (\(\alpha, h \gg 1\)).

Figure 4.7 shows the steady state (long time limit) temperature profiles for each of the currents in Figure 4.6. For an ambient temperature of 293 K, these temperature changes correspond to an increase of between 0.1 and 1 degrees.

Figure 4.7: Steady-state temperature with \(\alpha = h = 50, k = 50, \epsilon = 0.001, \delta = 1\) and \(\beta = 0.1\) for different values of current.

Next, Figure 4.8 shows the effect of varying \(\alpha\) and \(h\) with \(j = 0.5\). Varying the thermal diffusivity relative to concentration diffusivity has two effects. First, as \(\alpha\) and \(h\) increase, the relaxation time scale for thermal diffusion decreases, and the temperature relaxes faster. Second, the steady-state temperature increases with a decrease in \(\alpha\) due to a decrease in the thermal conductivity. Both of these are observed in Figure 4.8.
Figure 4.8: Average temperature with $j = 0.5$, $\epsilon = 0.001$, $\delta = 1$, and $\beta = 0.1$ for different values of thermal conductivity $\alpha = h$.

Finally, Figure 4.9 shows the temporal evolution of the temperature for the low conductivity ($\alpha = h = 0.1$) and high conductivity ($\alpha = h = 100$) cases.

Figure 4.9: Temperature evolution for the low thermal conductivity ($\alpha = h = 0.1$) and high thermal conductivity ($\alpha = h = 100$) cases, with $j = 0.5$, $\epsilon = \lambda_s = 0.001$, $\beta = 0.1$.

### 4.4 Frequency Response

Measuring small-signal frequency response as a means of characterizing systems finds uses in many fields. In electrochemistry, the application of this technique is commonly known as electrical impedance
spectroscopy (EIS). EIS generally involves applying a small signal perturbation (usually voltage-driven, sometimes current-driven) to a cell on top of a constant, or DC bias. The amplitude ratio and phase difference between the output and input signals are then measured over a range of frequencies, and the result is the frequency-dependent small-signal impedance of the cell. The impedance data can then be used to fit values for a small-signal equivalent circuit model (see Chapter 17 of Conway [138]). Barsuokov and Macdonald [155] is a good reference for both the theoretical and practical aspects of impedance spectroscopy.

The classical model of impedance spectroscopy is a linearized version of the PNP equations in the limit of high support, subject to a small amplitude sinusoidal voltage at the electrode. With a sinusoidal forcing function, the semi-infinite diffusion equations can be recast into a time-harmonic form and solved to obtain an expression for the Faradaic impedance \( Z = \frac{\hat{V}}{\hat{I}} \), where \( \hat{V} \) and \( \hat{I} \) are the phasors for the applied voltage and resulting Faradaic current (see Chapter 4 of Lasia [156]). For the simple case of semi-infinite diffusion, \( Z \) takes the form

\[
Z = \frac{RT}{n^2F^2} \frac{1}{\alpha k_f C_D(0) + (1 - \alpha) k_b C_R(0)} + \frac{RT}{n^2F^2} \frac{k_f}{\sqrt{j\omega D_D}} + \frac{k_b}{\sqrt{j\omega D_R}} \quad (4.8)
\]

where the first term in (4.8) is referred to as the charge-transfer resistance, \( R_{ct} \), and the second as the Warburg impedance, which arises from mass transfer. In the case of reversible reactions, the second term in equation (4.8) simplifies to

\[
Z_W = \frac{RT}{n^2F^2 \sqrt{j\omega}} \left( \frac{1}{\sqrt{D_D C_D(0)}} + \frac{1}{\sqrt{D_R C_R(0)}} \right) \quad (4.9)
\]

The impedance in equation (4.8) is often represented as a small-signal equivalent circuit model for the electrode, the oldest and most common being the Randles circuit shown in Figure 4.10.

![Randles equivalent circuit](image)

Figure 4.10: Randles equivalent circuit, where \( R_s \) is the solution resistance, \( C_{dl} \) is the double layer capacitance, \( R_{ct} \) is the charge-transfer resistance and \( Z_W \) is the Warburg mass-transfer impedance.
In Figure 4.10, $R_s$ is the solution resistance and $C_{dl}$ is the double layer capacitance, which arise from bulk diffusion and the displacement current term from the left hand side of equation (2.17), respectively.

We now demonstrate using a simple RC circuit example the means by which impedance spectroscopy plots are generated. The complex impedance of a parallel RC circuit can be written

$$Z(\omega) = \frac{1}{1/R + j\omega C} \quad (4.10)$$

where $\omega$ here denotes angular frequency.

The impedance of electrochemical interfaces is usually shown in the form of a Nyquist plot, where the imaginary part is plotted against the real part of the impedance. The Nyquist plot for equation (4.10) is shown in Figure 4.11. The characteristic semicircular shape is due to the parallel RC elements, where the high frequency limit is at the origin and the low frequency limit is at some point on the real axis.

![Nyquist plot](image)

Figure 4.11: Nyquist plot of the impedance of a parallel RC circuit, with $R = C = 1$. High frequency limit is at the origin, and low frequency limit is at (0,1).

In simulation work in the literature, the Poisson-Nernst-Planck equations and its linearized ($\frac{FV}{RT} \ll 1$) counterpart the Debye-Falkenhagen equation [?] have been used to perform model impedance spectroscopy [?]. Notably, the PNP equations have been used along with Chang-Jaffe boundary conditions [157] in the extensive body of work on impedance spectroscopy by J. R. Macdonald [158, ?]. Chang-Jaffe boundary conditions treat Faradaic reactions as first-order boundary conditions independent of the electric field. In the current context, they are equivalent to the our Frumkin-Butler-Volmer boundary
condition in the GC limit with $\Delta \phi_S \rightarrow 0$, equation (2.55). In contrast, our simulations here do use FBV kinetics, which capture diffuse charge dynamics.

From a modeling perspective, in order to allow a frequency sweep using the model, we need to add code to calculate the amplitude and phase difference of two signals. One popular method for EIS systems to compute impedance is to employ the discrete Fourier transform, but since our model uses non-uniform time steps, applying a normal fast-Fourier transform algorithm is impossible. An alternative is a non-uniform FFT, such as the \texttt{NUFFT} package by Greengard and Lee [159, 160]. The base \texttt{NUFFT} code requires a time range from $-\pi$ to $\pi$, which would require rescaling the post-processed current. Although this is certainly possible, we chose to use a simple peak detection algorithm to find the relative amplitude and phase of the current and voltage signals (the code can be found in Appendix F).

Figure 4.12 shows two series of frequency sweeps from 0.1 to 500, with values for $\epsilon$ the same as in Figures 4.4 and 4.5, though only a sweep using $\epsilon_{\text{bulk}} = 0.1$ is shown. Though a smaller value of $\epsilon$ is more physically realistic, we present these plots only as a proof of concept.

![Impedance plot with and without polarization effects.](image)

Figure 4.12: Impedance plot with and without polarization effects. Frequency ranges from 0.1 to 500, $v_{\text{bias}} = 0$, $v_{\text{pk-pk}} = 0.01$. Values for $\epsilon$ are the same as in Figures 4.4 and 4.5, except with $\epsilon = 0.1$.

Figure 4.13 shows two series of frequency sweeps from 0.001 to 100 on the model with surface coverage turned on, employing the Langmuir and Frumkin isotherms. Parameter values are the same as in Figures 4.2 and 4.3, and again $\epsilon = 0.1$ is used.

Both Figures 4.12 and 4.13 display the semicircular shape of a primarily RC small signal response, showing that, in terms of a frequency sweep, our model and numerical method behave as expected.
Figure 4.13: Impedance plot with Langmuir and Frumkin surface coverage isotherms. Frequency ranges from 0.1 to 500, $v_{\text{bias}} = 0$, $v_{\text{pk-pk}} = 0.01$. Values for $\epsilon$ are the same as in Figures 4.2 and 4.3, except with $\epsilon = 0.1$. Low frequencies are at $Z = 0$, increasing clockwise.
Chapter 5

Voltammetry with Diffuse Charge Effects

Note: A modified version of this chapter along with elements of Chapter 2 has been submitted for publication in the journal *Physical Review E* under the title “Theory of linear sweep voltammetry with diffuse charge: unsupported electrolytes, thin films, and leaky membranes”, with co-authors Martin Z. Bazant, P. M. Biesheuvel, Mary C. Pugh and Francis P. Dawson.

5.1 Introduction

Polarography/linear sweep voltammetry (LSV)/cyclic voltammetry (CV) is the most common method of electro-analytical chemistry, pioneered by Heyrovsky and honored by a Nobel Prize in Chemistry in 1959. The classical Randles-Sevcik theory of polarograms is based on the assumption of diffusion limitation of the active species in a neutral liquid electrolyte, driven by fast reactions at the working electrode. [161, 162, 163] Extensions for slow Butler-Volmer kinetics (or other reaction models) are also available (see chapters 5 and 6 of [57]). The half-cell voltage is measured at a well-separated reference electrode in the bulk liquid electrolyte, which is assumed to be electro-neutral based on the use of a supporting electrolyte [81].

Most classical voltammetry experiments and models featured a supported electrolyte: an electrolyte with an inert salt added to remove the effect of electromigration. In many electrochemical systems of
current interest, however, the electrolyte is unsupported, doped, or strongly confined by electrodes with nanoscale dimensions. Examples include super-capacitors, [164], capacitive deionization [85], pseudocapacitive deionization and energy storage [86, 87], electrochemical thin films [20, 19, 21, 83], solid electrolytes used in Li-ion/Li-metal [165, 166], electrochemical breakdown of integrated circuits [167], fuel cells [91, 168], nanofludic systems [169, 170, 171], electrodialysis [172, 173, 14], and charged porous “leaky membranes” [174, 13] for shock electrodialysis [145, 175] and shock electrodeposition [176, 177]. In all of these situations, diffuse ionic charge must play an important role in voltammetry, which remains to be fully understood.

To the author’s knowledge, there has been no comprehensive mathematical modeling of the effects of diffuse charge on polarograms, while fully taking into account time-dependent electromigration and Frumkin effects of diffuse charge on Faradaic reaction rates (literature review in Section 5.2). The goal of this chapter is thus to construct and solve a general model for voltammetry with the effects of diffuse charge included. We consider the simplest Poisson-Nernst-Planck equations for ion transport in dilute liquid electrolytes, dilute solid electrolytes and leaky membranes, coupled with the Frumkin-Butler-Volmer (FBV) kinetics for Faradaic reactions at the electrodes [28, 20, 19, 95, 178] as reviewed by Biesheuvel, Soestbergen and Bazant [21]. The model we have constructed in Chapters 2–3 is well-suited to all of the tests that we run in this chapter. When running these tests, our numerical method will be able to resolve fine details in both time and space without requiring extremely fine meshes.

The chapter is structured as follows. We begin with a brief historical review of voltammetry on systems with weak supporting electrolyte in Section 5.2. We then present voltammetry simulations on a single electrode in a supported and unsupported electrolyte in Section 5.4. Next, in Section 5.5, ramp voltages are applied to systems with one or two blocking electrodes, and simulation results are used to match simulated and theoretical capacitance curves. Sections 5.6 and 5.7 show simulations on electrochemical thin films in the thin and thick electrical double layer limit. Finally, we simulate ramped voltages applied to porous “leaky” membranes with fixed background charge in Section 5.8.

5.2 A Brief Review of Voltammetry on Systems with Weak Support

Interest in voltammetry in low conductivity solvents and dilute electrolytes without little to no supporting electrolyte has slowly grown since the 1970s. Since the work of Buck [54], a variety of PNP-based
microscopic models have been proposed [179, 55, 180, 181], which provide somewhat different boundary conditions than the Frumkin-Butler-Volmer model used in this work. Since the 1980s, various experiments have focused on the role of supporting electrolytes [90]. For example, Bond and co-workers performed linear sweep [182] and cyclic [183, 184] voltammetry using the ferrocene oxidation reaction on a microelectrode while varying supporting electrolyte concentrations. One of the primary theoretical concerns at that time was modeling the extra ohmic drop in the solution from the electromigration effects which entered into the physics due to low supporting electrolyte concentration. Bond [185] and Oldham [186] both solved the PNP equations for steady-state voltammetry in dilute solutions with either Nernstian or Butler-volmer reaction kinetics to obtain expressions for the ohmic drop. While they listed the full PNP equations, they analytically solved the system only with the electroneutrality assumption or for small deviations from electroneutrality, which is a feature of many later models as well [187, 188, 181]. The bulk electroneutrality approximation is generally very accurate in macroscopic electrochemical systems [81, 189], although care must be taken to incorporate diffuse charge effects properly in the boundary conditions, as we show in this chapter. Bento, Thouin and Amatore [190, 191] continued this type of experimental work on voltammetry and studied the effect of diffuse layer dynamics and migrational effects in electrolytes with low support. They also performed voltammetry experiments on microelectrodes in solutions while varying the ratio of supporting electrolyte to reactant, and noted shifts in the resulting voltammograms and a change in the solution resistance [192].

More recently, Compton and co-workers have done extensive work involving theory [193, 194, 195], simulations [89, 193, 196, 197] (and see Chapter 7 of [146] or Chapter 10 of [90]) and experiments [198, 199, 200, 201] on the effect of varying the concentration of the supporting electrolyte on voltammetry. Besides considering a different (hemispherical) electrode geometry motivated by ultramicroelectrodes [202], there are two significant differences between this body of work and ours, from a modeling perspective.

The first difference is that Compton and co-authors consider three or more species in their models in order to account for the supporting electrolyte and the effect of varying its concentration. The additional species in their work are sometimes neutral [198, 199] and sometimes charged [193, 197], depending on the reaction being modeled. Modeling of uncharged and supporting ionic species has also been a feature of older models in the literature [185, 186, 187]. In this work, we only consider the two extremes: either an unsupported binary electrolyte or (briefly, for comparison) a classical fully supported electrolyte.

The second difference lies in their treatment of specific adsorption of ions and a related approximation used to simplify the full model. Although some studies involve numerical solutions of the full PNP
equations with suitable electrostatic and reaction boundary conditions [89], many others employ the “zero-field approximation” for the thin double layers [89, 196], which is motivated by strong specific adsorption of ions. In this picture, the Stern layer [26] (outside the continuum region of ion transport) is postulated to have two parts: an outer layer of adsorbed ions that fully screens the surface charge, and an inner uncharged dielectric layer that represents solvent molecules on the electrode surface. The assumption of complete screening motivates imposing a vanishing normal electric field as the boundary condition for the neutral bulk electrolyte at the electrode outside the double layers. This assertion also has the effect of eliminating the electromigration term from the flux entering the double layers, despite the inclusion of this term in the bulk mass flux. Physically, this model assumes that the electrode always remains close to the potential of zero charge, even during the passage of transient large currents.

Finally, for completeness, we note that Moya et al. [203] recently analyzed a model of double-layer effects on LSV for the case of a neutral electrolyte surrounding an ideal ion-exchange membrane with thin quasi-equilibrium double layers, and no electrodes with Faradaic reactions to sustain the current.

### 5.3 Modeling Domain

In this chapter, we consider ramped voltages applied to electrochemical systems with one or two electrodes. Figure 5.1 shows a sketch of both systems. The two electrode case models a battery or capacitor, whereas the one electrode case models an electrode under test at the right hand side of the domain with an ideal reservoir and potential set to zero at the left hand side.

![Diagram showing electrochemical systems with applied voltage \( v \) and resulting current \( j_{\text{ext}} \) for a system with (a) a single electrode and (b) two electrodes. In the single electrode case, the left hand boundary is modeled as an ideal reservoir with a fixed potential. Also shown is a sketch of the potential inside the cell: dashed line is the potential in the bulk, solid line is the potential in the diffuse double layer.](image)
5.4 Bulk Liquid Electrolytes

5.4.1 Model Problem

The model problem for this section is a single electrode in an aqueous electrolyte with a reference electrode at $x = 0$ and two mobile ions. Voltammetry on a single electrode in solution is one of the oldest problems in electrochemistry; experiments are usually conducted using the “three-electrode setup”, where one electrode acts as a voltage reference while another (the auxiliary electrode) provides current. Computationally, this setup can be mimicked with

$$c_\pm = 1, \quad \phi = 0$$

applied at $x = 0$. This models a cell with only one electrode, with the other approximating an ideal reference electrode or an ideal reservoir.

In order to ensure that dynamics do not reach the reference electrode, we restrict ourselves to the regime $\tilde{S} \gg 1$ and $t \ll 1$. The reaction rate parameter $k$ can either be fast ($k \gg 1$) or slow ($k \ll 1$), which corresponds to a diffusion-limited regime and reaction-limited regime, respectively.

5.4.2 Supported Electrolytes

A supported electrolyte is where an inert (does not take part in electrode or bulk reactions) salt is added in order to screen the electric field so as to render electromigration effects negligible (i.e. $\phi = 0$ in the bulk). Voltammetry with supported electrolytes has classically been treated as a semi-infinite diffusion problem. For an aqueous system at a planar electrode with a reversible electrode reaction (reaction much faster than diffusion) involving two species denoted O (oxidized) and R (reduced), the current resulting from a slow ramped voltage is given, using the present notation, by (see Chapters 5 and 6 of [57])

$$J(\tau) = nFD_O \left( \frac{\partial C_O(X, \tau)}{\partial X} \right)_{X=0} = nFAC_O^* (\pi D_O \sigma)^{1/2} \chi(\sigma \tau),$$

where $\sigma \equiv nFS/RT$ ($S$ is the scan rate) and $\chi$ is the Randles-Sevcik function. The same system of equations is also often considered for irreversible (slow reactions compared to diffusion) and ‘quasi-reversible’ reactions, with the appropriate changes to the boundary conditions.
The reaction we will be considering is

\[ \text{C}^+ + e^- \rightleftharpoons \text{M} \]  \hspace{1cm} (5.3)

where M represents the electrode material. An example of such a reaction is the Cu-CuSO\textsubscript{4} electrode-deposition process. Since the reaction only involves one of the two ions as opposed to both as in the Randles-Sevcik case, the mathematics are simplified somewhat and we are able to obtain an analytical solution. We need to solve the diffusion equation (equation (2.53)) on \( x \in (0, \infty) \) with the fast reaction boundary condition, equation (2.57) with \( \Delta \phi = v(t) \). The applied voltage is \( v(t) = -\tilde{S} t \) since we consider positive current as out of the electrode, and the current is computed via \( j = \frac{\partial c}{\partial x} \bigg|_{x=0} \). These equations admit the solution

\[ j(t) = \sqrt{\tilde{S}} e^{-\tilde{S} t} \text{erfi} \left( \sqrt{\tilde{S} t} \right) \]  \hspace{1cm} (5.4)

where \( \text{erfi}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp x^2 \, dx \) is the imaginary error function. The derivation of equation (5.4) can be found in Appendix E. We term equation (5.4) a “modified” Randles-Sevcik equation, which applies to voltammetry on a fast reaction involving only one ionic species in a supported electrolyte. Figure 5.2 shows simulated \( j(t) \) curves with various values of \( k \) compared to equation (5.4), with \( \tilde{S} = 50 \). The curves in Figure 5.2 exhibit the distinguishing features of single-reaction voltammograms: current increases rapidly until most of the reactant at the electrode has been removed due to transport limitation. The peak represents the competition between the increasing rate of reaction and the decreasing amount of reactant at the electrode. After the peak, the lack of reactant wins out, and there is a decrease in the amount of current the electrode is able to sustain. Also worth noting is that at low reaction rate \( k \), the start of the voltammogram is exponential rather than linear due to reaction limiting.

The simulated curves in Figure 5.2 approach equation (5.4) in the limit of large \( k \), which makes equation (5.4) a good approximation for the current response to a ramped voltage in a supported electrolyte with fast, single-species reaction. Note that due to definition differences, the simulated current must be multiplied by 4 because there is a difference of a factor of 4 between the current in equation (2.40) and the ion flux in equation (2.42).

### 5.4.3 Unsupported Electrolytes with Thin Double Layers

For the single-electrode, thin-EDL, unsupported electrolyte problem, we use a value of \( \epsilon = 0.001 \), and impose the restrictions \( \tilde{S} \gg 1 \) and \( t \ll 1 \) in order to remain in a diffusion-limited regime. Figure 5.3 shows plots of voltammograms for \( v(t) = -50t \) (\( \tilde{S} = 50 \)) with \( \delta = 100 \), and the modified Randles-Sevcik
Figure 5.2: Simulated current curves for a supported electrolyte with one electrode in response to a voltage ramp with $\tilde{S} = -50$, with various values of $k$. Also shown is the high reaction rate limit in equation (5.4).

It is interesting to note that, while the situations leading to the currents in Figures 5.2 and 5.3 may seem superficially similar (both involve voltammetry on a single electrode with fast reactions), they do not produce the same results. The physical difference is that electromigration is included in the latter (i.e.
equation (2.38) is solved along with the anion transport equation), which opposes diffusion, resulting in a slower response. This type of shift in the voltammogram for low support has been well documented in the experimental literature (see [182, 190, 191, 197, 199], among others).

Next, Figures 5.4 and 5.5 show the voltammograms for the \( k = 0.1 \) (reaction limited) and \( k = 50 \) (diffusion limited) cases, with accompanying concentration profiles (\( c_+ \) and \( c_- \) are identical in the bulk but only \( c_+ \) is shown). The current in Figure 5.4 exhibits the initial exponential shape and slower response indicative of reaction limited dynamics compared to Figure 5.5.

The parameter \( \delta \) was chosen to be large for these simulations so that large diffuse double layers do not
form, making it easier to see a correspondence between the slope of the concentration at the electrode and the resulting current. The current and slope of $c_+$ both reach a maximum when the voltammogram peaks, followed by a gradual flattening of the concentration as transport limitation sets in. Furthermore, though we end our simulations in this section after the cation concentration reaches zero at the electrode, we will see in Section 5.6.4 that the PNP-FBV equations admit solutions past this point with the formation of space charge regions.

For completeness, Figure 5.6 shows two voltammetry cycles on the system with $\epsilon = 0.001$, $k = 50$, $\delta = 0.01$ and $\tilde{S} = 50$. Due to the fact there is only one electrode and only one species takes part in the reaction, the voltammogram has a diode-like behavior: diffusion limiting in the direction of positive current and exponential growth in the direction of negative current. Also shown are the net charge densities ($\rho = c_+ - c_-$) in the diffuse double layer ($x > 0.99$) during the first cycle, which are allowed to form since $\delta$ is small, so that the double layer is dominated by the diffuse charge region. The amount of charge separation in the diffuse double layer is very large at large voltages, and highlights the need to use the PNP-FBV equations to capture their dynamics.

![Figure 5.6: (a) Voltammogram for an unsupported electrolyte with one electrode subjected to a triangular voltage with $|\tilde{S}| = 50$, $\epsilon = 0.001$, $k = 50$ and $\delta = 0.01$. (b) Net charge densities $\rho = c_+ - c_-$. Labels on the charge density plot correspond to snapshots of $\rho$ in the double layer at times labeled on the voltammogram.](image)

Finally, an interesting observation is that in Figure 5.6, the current peak is much higher in the second (and subsequent) cycle(s) than in the first. We expect that this is due to charge dynamics near the electrode: concentration distributions do not return their initial distributions when the polarity of $v$ reverses. Due to the fast scan rate, there is still an excess of positive ions near the electrode when the voltage switches polarity at the start of the second cycle, allowing for a much longer time for the current to build before transport limitation occurs.
5.5 Blocking Electrodes

5.5.1 Model Problem

A blocking, or ideally polarizable electrode, is one where no Faradaic reactions take place. From a modeling perspective, this means setting $k_c$ and $j_r$ in the Butler-Volmer equation to zero, so that current is entirely due to the displacement current term in equation (2.40).

Voltammetry experiments are most often used to probe Faradaic reactions at test electrodes; in this application, nonfaradaic, or charging current is undesirable. With that being said however, linear sweep voltammetry is also a standard approach to measuring differential capacitance. In this section we consider ramped voltages applied to both liquid and solid electrolytes, and both thin EDL and thick EDL (thin film) systems. Much of the early work in electrochemistry was centered around matching experimental differential capacitance curves with theory. Gouy [24] and Chapman [25] independently solved the Poisson-Boltzmann equation to obtain the differential capacitance per unit area for an electrode in a liquid electrolyte, which in the present notation can be written as

$$\tilde{C}_{\text{liquid}}(\Delta \phi) = \frac{1}{\epsilon} \cosh \frac{\Delta \phi}{2}$$ (5.5)

where $\Delta \phi$ is across the entire double layer, including the diffuse part. Later, Kornyshev and Vorotyntsev [96] performed a similar calculation for a solid electrolyte to obtain

$$\tilde{C}_{\text{solid}}(\Delta \phi) = \frac{1}{\epsilon} \frac{e^{-\Delta \phi} - 1}{\sqrt{e^{-\Delta \phi} + 1}} \text{sgn}(\Delta \phi)$$ (5.6)

Note that the capacitance for the liquid electrolyte is symmetrical about 0, but the capacitance for the solid electrolyte is not symmetrical due to the fixed charge breaking the symmetry.

In this section, we use ramp voltages to investigate the behaviour of blocking electrodes. Similar work has been done by Bazant et. al. [204], who used asymptotics to study diffuse charge effects in a system with blocking electrodes subjected to a step voltage, and Olesen et. al. [153] who used both asymptotics and simulations to do the same for sinusoidal voltages. The results of this section have applications to EDL supercapacitors [92], capacitive deionization [205, 206] and induced charge electro-osmotic (ICEO) flows [17, 16]. In the simulations in this section, $\delta$ is set to 0.01 so that the capacitance is dominated by the diffuse part of the double layer.
The displacement current in equation (2.40) is related to the nondimensionalized capacitance through

\[ j = \frac{\epsilon^2}{2} \frac{d\phi}{dt} = \frac{\epsilon^2}{2} \frac{dq}{dt} = \frac{\epsilon^2}{2} \frac{dv}{dt} \]  

(5.7)

where \( \frac{dv}{dt} = \tilde{S} \). In other words,

\[ \frac{j}{\tilde{S}} = \frac{\epsilon^2}{2} \tilde{C} \sim \frac{\epsilon}{2} \]  

(5.8)

and therefore \( \epsilon \) is the natural scale for capacitance when relating to the displacement current. We refer to this as our "rescaled" capacitance, which we denote using the symbol \( \tilde{C} \).

Both solid and liquid electrolyte systems with two blocking electrodes behave like the circuit shown in Figure 5.7. For liquid electrolytes, \( \tilde{R} \sim 2 \) and \( \tilde{C}(0) = \epsilon/2 \). For solid electrolytes, \( \tilde{R} \sim 4 \) [20, 21] and

\[ \tilde{C}(0) = \frac{\epsilon^2}{2} \lim_{\Delta \phi \to 0} \tilde{C}_{\text{solid}}(\Delta \phi) = \frac{\sqrt{2} \epsilon}{2}. \]

Figure 5.7: Equivalent circuit diagram for system with two blocking electrodes, showing the defined direction of current and polarities of the double layer capacitors. Note that \( \tilde{C} \) is a function of \( \Delta \phi \).

There are two regimes of operation when a ramped voltage is applied to a capacitive system. The first is the small time \( t \ll \epsilon \) behavior, when the double layers are charged with time constant \( \tau_{\text{RC}} = \tilde{R}\tilde{C}/2 \), where the factor of \( 1/2 \) accounts for the fact that there are two capacitors in series. To predict the behavior during this time, we turn to the ordinary differential equation describing the circuit in Figure 5.7, which is

\[ v(t) - 2\Delta \phi = \tilde{R}\tilde{C}(0) \frac{d\Delta \phi}{dt} \]  

(5.9)

where \( v(t) = \tilde{S}t \). From equation (5.9), the current can be solved in the case of a two electrode liquid electrolyte to be

\[ \frac{2j_{\text{inner}}(t)}{\tilde{S}} = \tilde{C}(0) \left( 1 - e^{-\frac{v}{\tilde{C}(0)\tilde{R}}} \right) \]  

(5.10)

where we have used \( \tilde{R} = 2 \) for a liquid electrolyte. The equivalent expression for solid electrolytes with single and double electrodes will be discussed in Section 5.5.3. The second regime of operation is the
large time \((t \gg \epsilon)\) behavior. After the RC charging time, the current tracks the capacitance based on equation (5.8). The relevant equation is

\[
   j = \frac{\epsilon^2 dq}{2 dt} = \tilde{C}(\Delta \phi) \frac{d\Delta \phi}{dt}
\]

(5.11)

Since we are only able to control to the potential drop across the cell \((v(t))\) and not the potential drop across the double layer \((\Delta \phi)\), we must estimate the value of \(\Delta \phi\) by accounting for the potential drop across the bulk. To do this, we can use the equation \(v(t) = 2\Delta \phi + \tilde{R}j\). In practice however, \(j \ll 1\) for blocking electrodes and so we can instead just use \(\Delta \phi \approx v(t)/2 = \tilde{S}t/2\). Equation (5.11) can then be rewritten as

\[
   \frac{2j_{\text{outer}}}{\tilde{S}} = \tilde{C}(v/2)
\]

(5.12)

From equation (5.10) we have a solution for small times (the inner solution), and from equation (5.12) we have a solution for large times (the outer solution). The long time limit for the inner solution must be equal to the small time limit for the outer solution, and so the two solutions can be combined by adding them and subtracting the overlap,

\[
   j = j_{\text{inner}} + j_{\text{outer}} - j_{\text{overlap}}
\]

(5.13)

where \(2j_{\text{overlap}}/\tilde{S} = \tilde{C}(0)\), thereby creating a uniformly valid approximation of the capacitance for all values of \(v(t)\).

### 5.5.2 Liquid Electrolytes

The uniformly valid approximation (equation (5.13)) for a liquid electrolyte with two electrodes is

\[
   \frac{2j}{\tilde{S}} = \tilde{C} \left(1 - e^{-\frac{v}{\epsilon}}\right) + \frac{\epsilon}{2} \cosh \frac{v}{4} - \tilde{C}
\]

(5.14)

where \(\tilde{C} = \epsilon/2\). Figure 5.8 shows \(j - v\) curves for a thin EDL \((\epsilon = 0.001)\) liquid electrolyte and various values of the nondimensionalized scan rate \(\tilde{S}\).

The theoretical and simulated curves in Figure 5.8 show general agreement, though the simulated curves are consistently lower than the theoretical ones.

Next, Figure 5.9 shows \(j \text{ vs } v\) curves for a liquid electrolyte with thick double layers \((\epsilon = 0.1)\) compared
Figure 5.8: Simulated (solid line) and uniformly valid approximation (dashed line) $j$ vs $v$ curves for a thin EDL liquid electrolyte with two blocking electrodes and parameters $\epsilon = 0.001$, $\delta = 0.01$ and various values of the scan rate $\tilde{S}$. Dashed lines are plotted from equation (5.14).

to the uniformly valid approximation, equation (5.14). For each value of $\tilde{S}$ tested, the two plots show large deviations from the approximation.

The reason for this is that the approximation in equation (5.14) is based on an equilibrium (Gouy-Chapman) picture of the EDL. With thick EDL liquid electrolytes under large voltage forcings, so much charge separation occurs that the system is far from equilibrium for the Gouy-Chapman model to be valid. To investigate further, we plot in Figure 5.10 the current resulting from a voltage sweep of $\tilde{S} = -0.1$ on a liquid electrolyte system with $\epsilon = 0.1$ along with cation concentrations at various points during the sweep.

We can separate the behavior in Figure 5.10 into three regimes. For small voltages (A), the concentrations show near-equilibrium behavior. As the voltage increases (B, C), the diffuse regions become large and the bulk concentration begins to be depleted, and the two double layers begin to overlap - it may be
Chapter 5. Voltammetry with Diffuse Charge Effects

Figure 5.9: Simulated (solid line) and uniformly valid approximation (dashed line) $j$ vs $v$ curves for a thick EDL liquid electrolyte with two blocking electrodes and parameters $\epsilon = 0.1$, $\delta = 0.01$ and various values of $\tilde{S}$. Dashed lines are plotted from equation (5.14).

Figure 5.10: (a) $j$ vs. $v$ and (b) cation concentrations for a thick EDL liquid electrolyte with two blocking electrodes and parameters $\epsilon = 0.1$, $\delta = 0.01$ and scan rate $\tilde{S} = -0.1$. Labels in (a) correspond to cation concentrations in (b) at various times.
possible to model behavior at this stage by accounting for the depletion of bulk concentration as in [204]. Finally, at large voltages (D), we see complete charge separation, with nearly all of the positive charge located at the cathode (and similarly, with nearly all of the negative charge at the anode). This result highlights the need to model of diffuse charge dynamics using the PNP-FBV equations; such a highly nonlinear separation of charge would not be predicted by models which assume electroneutrality or neglect the coupling between diffuse charge dynamics and electrode currents.

5.5.3 Solid Electrolytes

Since the capacitance for a solid electrolyte (equation (5.6)) is not symmetrical about $\Delta \phi = 0$, the capacitance for a solid electrolyte system with two blocking electrodes can be represented using the two capacitors in series,

$$\frac{1}{C_{\text{solid}}(\Delta \phi)} = \frac{1}{C_{\text{solid}}(\Delta \phi)} + \frac{1}{C_{\text{solid}}(-\Delta \phi)}$$  \hspace{1cm} (5.15)

The uniformly valid approximation for a solid electrolyte with one electrode is

$$\frac{j}{S} = \tilde{C} \left(1 - e^{\frac{v}{\tilde{S}}}\right) + e^{\frac{-v}{\sqrt{e^v + v - 1}}} \text{sgn}(v) - \tilde{C}$$  \hspace{1cm} (5.16)

where $\tilde{C} = \sqrt{2} \epsilon$. Using equation (5.15), the approximation for two electrodes is

$$\frac{2j}{S} = \tilde{C} \left(1 - e^{\frac{v}{\tilde{S}}}\right) + \epsilon \left(\frac{e^{-\tilde{S} - 1}}{\sqrt{e^{-v} + v - 1}} \text{sgn}(v) \right) - \tilde{C}$$  \hspace{1cm} (5.17)

where $\tilde{C} = \frac{\epsilon}{2\sqrt{2}}$ and $||$ indicates the reciprocal of the sum of the reciprocals (the parallel circuit symbol), i.e. $A||B = 1/(1/A + 1/B)$. The additional factor of 1/2 in the exponent in the inner part of equation (5.17) is due to the fact that the electrolyte resistance for solid electrolytes is 4 rather than 2.

Figure 5.11 shows the $j$ vs $v$ curve for $\tilde{S} = 1$ compared to the theoretical result for a thin EDL solid electrolyte with a single electrode, and sees good agreement between the simulated results and our approximation from equation (5.16).

Next, Figure 5.12 shows $j$ vs $v$ curves for a thin EDL ($\epsilon = 0.001$) solid electrolyte with two blocking electrodes for various values of $\tilde{S}$, compared to the uniformly valid approximation from equation (5.17), which also sees good agreement.

Finally, Figure 5.13 shows the capacitance curve for a thick EDL ($\epsilon = 0.1$) solid electrolyte with two
Figure 5.11: Simulated (solid line) vs. uniformly valid approximation (dashed line) $j$ vs $v$ curves for a thin EDL solid electrolyte with a single blocking electrode and parameters $\epsilon = 0.001$, $\delta = 0.01$ and $\tilde{S} = \pm 1$. Figure (a) shows the negative part of the sweep and Figure (b) shows the positive part. Dashed lines are plotted from equation (5.16).

electrodes. It is interesting to note that a departure from equilibrium behavior seen in Figure 5.9 is not apparent for this case. However, if we plot the single electrode, thick EDL curves (shown in Figure 5.14a for the negative sweep and Figure 5.14b for the positive sweep), we see that there is indeed a departure from the equilibrium capacitance curve for the positive voltage ($\tilde{S} = 1$) sweep, with the simulated capacitance having non-monotonic dependence on voltage. This disagreement is masked by the fact that for two electrodes (which can be thought of as two capacitors in series, as in equation (5.17)), the smaller, positive voltage sweep capacitance (which agrees with the equilibrium approximation) dominates.
Figure 5.12: Simulated (solid line) and uniformly valid approximation (dashed line) $j$ vs $v$ curves for a thin EDL solid electrolyte with two blocking electrodes and parameters $\epsilon = 0.001$, $\delta = 0.01$ for various values of $\tilde{S}$. Dashed lines are plotted from equation (5.17).
Figure 5.13: Simulated (solid line) and uniformly valid approximation (dashed line) $j$ vs. $v$ curves for a thick EDL solid electrolyte with two blocking electrodes and parameters $\epsilon = 0.1$, $\delta = 0.01$ and various values of $\tilde{S}$. Dashed lines are plotted from equation (5.17).

Figure 5.14: Simulated (solid line) and uniformly valid approximation (dashed line) $j$ vs $v$ curves for a thick EDL solid electrolyte with a single blocking electrode and parameters $\epsilon = 0.1$, $\delta = 0.01$ and $\tilde{S} = \pm 1$. Figure (a) shows the negative voltage sweep and Figure (b) shows the positive voltage sweep. Dashed lines are plotted from equation (5.16).
5.6 Liquid Electrolyte Thin Films

5.6.1 Model Problem

In this section, we study voltammograms of liquid electrolyte electrochemical thin films. General steady-state models for thin films have been previously presented in [20] and [19] as well as in [21], with a time-dependent model considered in [22]. In the present work, we consider voltage ramps on systems with two dissimilar electrodes, i.e. values of \( k_c \) and \( j_r \) such that an equilibrium voltage develops across the cell.

5.6.2 Low Sweep Rates

Thin EDL

At low sweep rates, the current-voltage relationship approaches the steady-state response, which for solid and liquid electrolytes was derived by Bazant et al. [20] (for an electrolytic cell with two identical electrodes) and Biesheuvel et al. [21] (for a galvanic cell with two different electrodes). For a liquid electrolyte, the cell voltage is given in the GC (\( \delta \to 0 \)) limit by

\[
v(j) = v_0 - 4 \tanh(j) + \ln \frac{1 - j/j_{r,A}}{1 + j/j_{r,C}}
\]

(5.18)

and in the H limit (\( \delta \to \infty \)) by

\[
v(j) = v_0 - 4 \tanh(j) - 2 \text{arcsinh} \frac{j}{\sqrt{\beta_A(1+j)}} - 2 \text{arcsinh} \frac{j}{\sqrt{\beta_C(1-j)}}
\]

(5.19)

where \( v_0 = \ln \frac{k_{c,C}j_{r,A}}{k_{c,A}j_{r,C}} \) is the equilibrium voltage, \( \beta_A = 4k_{c,A}j_{r,A} \) and \( \beta_C = 4k_{c,C}j_{r,C} \). The subscripts \( A \) and \( C \) denote parameter values at the anode and cathode, respectively.

Figure 5.15 shows \( v \) vs \( j \) curves for a solid electrolyte for \( k_{c,C} = 30, k_{c,A} = 1, j_{r,C} = 0.1, j_{r,A} = 0.8 \) (the same as Figure 3 in [21]) for an open circuit voltage of \( v_0 = 5.5 \) and various values of \( \delta \) along with the GC and H limits from equations (5.18)–(5.19). The curves were created with a voltage ramp from -10 to +15 with a scan rate of \( \tilde{S} = 2.5 \). The \( \delta = 1 \) and \( \delta = 10 \) curves were generated with \( \epsilon = 0.001 \), while the \( \delta = 0.1 \) and \( \delta = 0.01 \) curves with \( \epsilon = 0.005 \). As expected, the voltage-current response for a liquid electrolyte is seen in Figure 5.15 to have reaction limits at \( j = -j_{r,C} = -0.1 \) and \( j = j_{r,A} = 0.8 \) in the
Figure 5.15: $v$ vs $j$ curves for a thin EDL liquid electrolyte with two electrodes and with parameters $\epsilon = 0.001$ ($\delta = 1, 10$) and $\epsilon = 0.005$ ($\delta = 0.1, 0.01$), $k_{c,C} = 30$, $k_{c,A} = 1$, $j_{r,C} = 0.1$ and $j_{r,A} = 0.8$ ($v_0 \approx 5.5$). Also shown are the steady-state curves in the GC and H limits from equations (5.18) and (5.19), respectively. Simulated curves were created using a voltage scan rate of $\tilde{S} = 2.5$.

GC limit, and diffusion limits at $j = \pm 1$ in the H limit. The limiting cases from equations (5.18)–(5.19) also do not strictly bound the simulated results in Figure 5.15 due to the non-monotonic dependence of the cell voltage $v$ on $\delta$ [21].

**Thick EDL**

Figure 5.16 shows $j$ vs $v$ for a thick EDL liquid electrolyte with two electrodes, with various values of $k_{c,C}$. $\epsilon = 0.1$, $\delta = 1$, scan rate $\tilde{S} = 2.5$, with other reaction rate parameters the same as in Figure 5.15. Since the voltage sweep rate is slow compared to both reaction and diffusion and $\epsilon$ is large enough that the double layers are able to overlap and interact with each other, the current vs. voltage curve straightens out compared to a thin double layer system, becoming effectively Ohmic in nature.

### 5.6.3 Diffusion versus Reaction Limitation

When sweep rates are fast, current-voltage curves will differ from the slow sweep results in Section 5.6.2 due to physical limitation of the speed at which current can be produced at electrodes. This nonlinear interdependence of current and voltage when current flows into an electrode is referred to in electrochemistry by the blanket term **polarization**, not to be confused with the dielectric polarization. Generally speaking, when current flows across a cell, its cell potential, $v$, will change. The difference
between the equilibrium value of \( v \) and its value when current is applied is commonly referred to as the overpotential or overvoltage and labeled \( \eta \).

Very briefly, there are three competing sources of overpotential in an electrochemical cell:

1. **Ohmic polarization** is caused by the slowness of electromigration in the bulk. When a cell behaves primarily Ohmically, it is characterized by a linear \( j-v \) curve which can be written as \( \eta_{\text{ohm}} = r_{\text{cell}}j \).

   When this behavior is modeled by a circuit, it is usually represented as a single resistor between the two electrodes.

2. **Kinetic polarization** is due to the slowness of electrode reactions (\( k \) small). Using the overpotential version of the Butler-Volmer equation as a starting point, and assuming fast transport of species to and from the electrode (\( C_{\text{electrode}} = C_{\text{bulk}} \)), we can invert the equation to find \( \eta_{\text{kin}} = \arcsinh \left( \frac{j}{j_0} \right) \), where \( j_0 \) is the nondimensional exchange current density. Thus, when kinetic polarization is the primary cause of overpotential, the \( j-v \) curve takes on an exponential characteristic. This type of polarization is represented by a charge-transfer resistance in circuit models.

3. **Transport, or concentration polarization** is due to slowness in the supply of reactants or removal of products from the electrode, resulting in a depletion of reactants at the electrode. Concentration polarization is characterized by a saturation of the current-voltage relationship, and is represented by the frequency-dependent Warburg element in circuit models.
Figure 5.17 shows the current vs. voltage characteristic for a two-electrode cell with fast reactions \( k = 50 \) and \( 
abla S \) varied. When \( 
abla S \) is large, diffusion limitation sets in and the current can be seen to approach saturation. When \( 
abla S \) is small, the relationship is Ohmic, i.e. linear response. For plots where the sweep rate \( 
abla S \) varies, we only plot the Faradaic part of the current (the second term on the right hand side of equation (2.40)) since for \( 
abla S \gg 1 \) there is a significant displacement component.

Figure 5.17: Faradaic current vs. voltage for a liquid electrolyte with two electrodes and with \( \nabla S \) varied and with parameters \( \epsilon = 0.05, \delta = 1 \) and \( k_{c,a} = 50 = j_{r,a} = k_{c,c} = j_{r,c} = 50 \) (\( v_0 = 0 \)). Diffusion limitation is seen to set in at higher voltages in the \( \nabla S = -100 \) plot.

Figure 5.18 shows Faradaic current vs voltage for a liquid electrolyte with two electrodes and with \( 
abla S \) varied and parameters \( \epsilon = 0.05, \delta = 1, k_{c,a} = 50, j_{r,a} = 100, k_{c,c} = 0.1, \) and \( j_{r,c} = 0.05 \) (\( v_0 \approx 1.4 \)). As \( \nabla S \) increases, the \( j-v \) curve is seen to take on a more pronounced exponential character, thus showing the effect of reaction limitation.

### 5.6.4 Transient Space Charge

The development of a space charge region, or a region of net charge outside of the double layer where \( \rho = c_+ - c_- \neq 0 \), is a strongly nonlinear effect that was predicted by Bazant, Thornton & Ajdari [204] and solved by Olesen, Bazant & Bruus using asymptotics and simulations for large sinusoidal voltages [153]. Figure 5.19 shows the voltammogram of a system subjected to a triangular voltage with \( \epsilon = 0.001, \delta = 0.3, k = 50 \) and \( 
abla S = 100 \), and Figure 5.20 shows the development of space charge regions.

The current-voltage response during space charge formation is a transient case of a diffusion limited
Chapter 5. Voltammetry with Diffuse Charge Effects

Figure 5.18: Faradaic current vs. voltage for a liquid electrolyte with two electrodes and with $\tilde{S}$ varied, with parameters $\epsilon = 0.05, \delta = 1, k_{c,a} = 50, j_{r,a} = 100, k_{c,c} = 0.1$ and $j_{r,c} = 0.05 (v_0 \approx 1.4)$. A current response dominated by reaction limitation is seen in the $\tilde{S} = -100$ plot.

Figure 5.19: Voltammogram for a thin EDL liquid electrolyte with two electrodes subjected to a triangular voltage with $\epsilon = 0.001, \delta = 0.3, k = 50$ and $|\tilde{S}| = 100$. Concentrations with development of space charge regions are shown in Figure 5.20.

system ($\tilde{S}, k \gg 1$) being driven above the limiting current [19, 172, 53] and the subsequent breakdown of electroneutrality in the bulk. Figure 5.20 shows the current peaking as diffusion limiting sets in ($t = 0.1$) and anion concentration at the cathode reaches zero (Figure 5.20b). After this time, a space charge region begins to form outside of the double layer as seen in Figure 5.20c, and the current ramps up slowly until the voltage reverses direction. Since the cell is symmetrical, the same thing occurs at the anode during the positive voltage part of the cycle, with current flowing in the other direction.
Figure 5.20: (a) Current and (b-d) resulting cation (solid line) and anion (dashed line) concentrations showing space charge regions developed at the cathode and anode from a triangular applied voltage in a thin EDL liquid electrolyte with two electrodes. Parameters used were $\epsilon = 0.001$, $\delta = 0.3$, $k = 50$, and $|\tilde{S}| = 100$.

(Figure 5.20d). The height of the current peak and slope of current during space charge development are dependent on the value of $\tilde{S}$. Also, though the one-dimensional equations predict it, the formation of large space charge regions may not happen in reality due to hydrodynamic instability caused by electro-osmosis [169, 16, 207].

An effect which is not included in the simulation that could prove important is ionic crowding [50], as both concentrations reach large values (i.e. $c_-(x = 0, t = 0.6) \approx 4$) at the electrodes. It may be interesting to extend these simulations to include steric effects in future work.
5.7 Solid Electrolyte Thin Films

5.7.1 Model Problem

In this section, we consider ramp voltages applied to solid electrolyte electrochemical thin films. The counterion concentration is fixed, i.e.

\[ c_-(x, t) = 1 \]  
(5.20)

5.7.2 Low Sweep Rates

Thin EDL

For a solid electrolyte in the thin EDL limit, the cell voltage is given in the GC limit by

\[ v(j) = v_0 - 4j + \ln \frac{1 - j/j_{r,A}}{1 + j/j_{r,C}} \]  
(5.21)

and in the H limit by

\[ v(j) = v_0 - 4j - 2 \arcsinh \frac{j}{\sqrt{\beta} A} - 2 \arcsinh \frac{j}{\sqrt{\beta} C} \]  
(5.22)

Figure 5.21 shows \( v \) vs \( j \) curves for a solid electrolyte for \( \epsilon = 0.001, k_{c,C} = 30, k_{c,A} = 1, j_{r,C} = 0.1, \) \( j_{r,A} = 0.8 \) (the same as [21] Figure 3) and various values of \( \delta \) along with the GC and H limits from equations (5.21)–(5.22). The curves were created with a voltage ramp from -10 to +15 and with a scan rate of \( \tilde{S} = 2.5 \). Compared to the liquid electrolyte case, the two limits on \( \delta \) for fixed countercharge are seen in Figure 5.21 to have a reaction limits at \( j = -j_{r,C} = -0.2 \) and \( j = j_{r,A} = 0.8 \) in the GC limit, but no diffusion limit in the H limit, which is consistent with the expected behavior for a solid electrolyte.

Thick EDL

Figure 5.22 shows \( j \) vs \( v \) for a thick EDL solid electrolyte with two electrodes, with various values of \( k_{c,C}, \) \( \epsilon = 0.1, \delta = 1, \) scan rate \( \tilde{S} = 2.5 \), with other reaction rate parameters the same as in Figure 5.21. As in the liquid case, the sweep rate is too slow for any polarization effects to occur, and the current response remains Ohmic over the voltage range.
Figure 5.21: $v$ vs $j$ curves for a thin EDL solid electrolyte with two electrodes and with $\epsilon = 0.001$, $k_{e,C} = 30$, $k_{e,A} = 1$, $j_{r,C} = 0.8$ ($v_0 \approx 5.5$) and $\delta$ varied. Also shown are the steady-state curves in the GC and H limits from equations (5.21) and (5.22), respectively. Simulated curves were created using a voltage scan rate of $\tilde{S} = 2.5$.

Figure 5.22: $j$ vs $v$ for a thick EDL solid electrolyte with two electrodes, with various values of $k_{e,C}$. $\epsilon = 0.1$, $\delta = 1$, scan rate $\tilde{S} = 2.5$ and other reaction rate parameters the same as in Figure 5.21.

### 5.7.3 Diffusion versus Reaction Limitation

In terms of electrode polarization, the key difference between liquid and solid electrolytes is that the imposed constant counterion concentration associated with a solid electrolyte does not allow diffusion limiting to occur, since the reacting species is not allowed to be depleted at the electrodes. This can be seen in Figure 5.23, where the current remains linear with respect to voltage even at high sweep rates.
Figure 5.23: Faradaic current vs. voltage for a solid electrolyte with two electrodes with $\tilde{S}$ varied and with parameters $\epsilon = 0.05$, $\delta = 1$ and $k_{c,a} = 50 = j_{r,a} = k_{c,c} = j_{r,c} = 50$ ($v_0 = 0$). No diffusion limitation is allowed in solid electrolytes, and so the $j$ vs. $v$ curves are linear for all values of $\tilde{S}$.

Figure 5.25 shows the current vs voltage curve for a solid electrolyte with $\tilde{S}$ varied. $\epsilon = 0.05$, $\delta = 1$, $k_{c,a} = 50$, $j_{r,a} = 100$, $k_{c,c} = 0.1$, $j_{r,c} = 0.05$ ($v_0 \approx 1.4$). As in the liquid electrolyte case, high sweep rates cause the system to become primarily reaction-limited, producing an exponential curve. At lower $\tilde{S}$, the response remains Ohmic, and so the curves approach a straight line.
Figure 5.24: (a), (b) $j$ vs. $v$, Liquid electrolyte and (c), (d) cation concentrations $c_+$ at $t = 0.025$ (dashed line), 0.05 (dash-dotted line), 0.075 (dotted line) and 0.1 (solid line) for $S = -100$ voltage sweeps on both liquid and solid electrolytes with two electrodes. Other parameters are the same as in Figures 5.17 and 5.23.
Figure 5.25: Faradaic current vs. voltage for a solid electrolyte with two electrodes and with $\tilde{S}$ varied, with parameters $\epsilon = 0.05$, $\delta = 1$, $k_{c,a} = 50$, $j_{r,a} = 100$, $k_{c,c} = 0.1$ and $j_{r,c} = 0.05$ ($v_0 \approx 1.4$). Reaction limitation is prominent in the $\tilde{S} = -100$ curve.
5.8 Leaky Membranes

5.8.1 Model Problem

Finally, we consider the classical description of membranes as having constant, uniform background charge density $\rho_s$, in addition to the mobile ions [208, 209, 210, 211]. In this section, we focus on the strongly nonlinear regime of small background charge and large currents in a “leaky membrane” [13, 15]. This situation can arise as a simple description of micro/nanochannels with charged surfaces, as well as traditional porous media, neglecting electro-osmotic flows. In the case of a microchannel with negative charge on its side walls, surface conduction through the positively charged diffuse double layers can sustain over-limiting current (faster than diffusion) [174] and deionization shock waves [212]. This phenomenon has applications to desalination by shock electrodialysis [145, 175], as well as metal growth by shock electrodeposition [176, 177], and the following analysis could be used to interpret LSV for such electrochemical systems with bulk fixed charge.

Figure 5.26 shows a sketch of the model problem. A “leaky” membrane with a uniform background charge (negative in the figure) and with mobile cations and anions lies between an ideal reservoir on the left hand side ($c_+ = c_- = 1, \phi = 0$) and an electrode on the right. We investigate situations with both positive and negative background charge whose concentration is small compared to the mobile ions.

![Sketch of a “leaky” membrane](image-url)

Figure 5.26: Sketch of a “leaky” membrane. Left hand boundary is an ideal reservoir with constant concentration ($c_+ = c_- = 1$) and zero potential ($\phi = 0$). Right hand boundary is an electrode. Mobile charge is shown with a filled circle, fixed charge (negative in this case) is shown without a circle.
The appropriate modification to the Poisson equation for a background charge is

$$-2\epsilon \frac{\partial^2 \phi}{\partial x^2} = z_+ c_+ + z_- c_- + 2\tilde{\rho}_s$$

(5.23)

where $\tilde{\rho}_s = \rho_s/(2C_0 F)$ is the nondimensionalized background charge density. Equation (5.23) is equivalent to the “uniform potential model” and “fine capillary model” [88] and has a long history in membrane science [208, 209, 210]. For example, Tedesco et. al. [213] recently used an electroneutral ($\epsilon \to 0$) version of equation (5.23) to model ion exchange membranes for electrodialysis applications.

The time-independent equations for the bulk charged electrolyte without electrode interfaces can be solved to obtain the steady-state current-voltage relationship [174], which is given by

$$j = \frac{1 - e^{-|v|/2} - \tilde{\rho}_s |v|}{2}$$

(5.24)

where the factor of one half is due to a difference in our definition of the scaling current (in equation (2.40)) from [174]. This expression has been successfully fitted to quasi-steady current voltage relations in experiments [145, 176, 177], which in fact were obtained by LSV at low sweep rates, so it is important to understand the effects of finite sweep rates. In Sections 5.8.2–5.8.3, we present simulation results for ramped and cyclic voltammetry on systems with background charge opposite sign (negative background charge) and the same sign (positive background charge) as the reactive ions.

### 5.8.2 Negative Background Charge

First, we consider the case where the sign of the background charge is opposite to that of the reactive cations, which avoid depletion by screening the fixed background charge. This is the most interesting case for applications of leaky membranes [145, 175, 176, 177], since the system can sustain over-limiting current. Figure 5.27 shows current in response to voltage ramps with $\epsilon = 0.005$, $\delta = 10$, $\rho_s = -0.01$ and $k = 50$, with various values for $\tilde{S}$. The limiting behavior for the current for small $\tilde{S}$ can be predicted by the steady state response from equation (5.24). As observed in multiple experiments [145, 176, 177], a bump of current overshoot occurs prior to steady state for high sweep rates, which we can attribute to diffusion limitation during transient concentration polarization in the leaky membrane. Similar bumps have also been predicted by Moya et al. [203] for neutral electrolytes in contact with (non-leaky) ion-exchange membranes with quasi-equilibrium double layers.
Chapter 5. Voltammetry with Diffuse Charge Effects

Figure 5.27: Current in response to a voltage ramp in a liquid electrolyte with one electrode and constant background charge. Parameters are $\epsilon = 0.005$, $\delta = 10$, $\rho_s = -0.01$ and $k = 50$. Also shown is the steady state response from equation (5.24).

Figure 5.28: Current from a voltage ramp applied to a liquid electrolyte with a single electrode and constant background charge. Parameters are $\epsilon = 0.005$, $\delta = 10$, $\rho_s = -0.1$ and $k = 50$. Also shown is the steady state response from equation (5.24).

Next, Figures 5.29 and 5.30 show cyclic voltammograms and corresponding concentration profiles for background charges of $\rho_s = -0.01$ and $\rho_s = -0.1$, respectively, with $\tilde{S} = 10$. Due to the additional background charge, the concentrations in the bulk are slightly different. For a 1:1 electrolyte, this difference is exactly $-2\rho_s$, as in equation (5.23). For an electrolyte that is not 1:1, the difference can be obtained using $z_+c_+ + z_-c_- = -2\rho_s$. 
Figure 5.29: (a) Voltammogram and (b-d) resulting cation (solid line) and anion (dashed line) concentrations from a triangular applied voltage applied to a thin EDL liquid electrolyte with two electrodes and constant background charge. Parameters used were $\epsilon = 0.005$, $\delta = 1$, $k = 50$, $\rho_s = -0.01$ and $|S| = 10$. Two cycles are shown in Figure (a).

Similar to the cyclic voltammogram in Section 5.4.3, the current-voltage relationship in Figures 5.29 and 5.30 displays diffusion limited behavior in the negative voltage sweep direction and purely exponential growth (reaction limiting behavior) in the other. This is because there is only one electrode in these simulations with only one of the two species taking part in the reaction. Furthermore, as with the space-charge voltammetry simulations in Section 5.6.4, the large voltage and fast sweep rate causes very large concentrations to develop near the electrodes (for example, $c_-(x = 1, t = 3) \approx 30$ in the $\rho_s = -0.01$ run). The addition of steric effects into the model would again make the results more realistic.
Figure 5.30: (a) Voltammogram and (b-d) resulting cation (solid line) and anion (dashed line) concentrations from a triangular applied voltage applied to a thin EDL liquid electrolyte with two electrodes and constant, negative background charge. Parameters used were $\epsilon = 0.005$, $\delta = 1$, $k = 50$, $\rho_s = -0.1$ and $|\tilde{S}| = 10$. Two cycles are shown in Figure (a).

5.8.3 Positive Background Charge

For positive $\rho_s$, equation (5.24) predicts a decreasing current (or negative steady-state differential resistance) after the exponential portion, a behavior which has been observed in some experiments [176, 177] and not others [145]. Interestingly, when double-layer effects and electrode reaction kinetics are considered in the model simulations, the region of negative resistance is also not observed, as shown in Figure 5.31 for $\rho_s = 0.01$ and in Figure 5.32 for $\rho_s = 0.1$. Physically, the interfaces provide overall positive differential resistance, even as the bulk charged electrolyte enters the over-limiting regime with negative local steady-state differential resistance.

Finally, Figures 5.33 and 5.34 show voltammograms and concentrations for $\rho_s = 0.01$ and $\rho_s = 0.1$. For the concentrations shown for these two values of $\rho_s$, the difference between $c_+$ and $c_-$ is $-2\rho_s$, which is
Chapter 5. Voltammetry with Diffuse Charge Effects

Figure 5.31: Current from a voltage ramp applied to a liquid electrolyte with a single electrode and constant, small, positive background charge. Parameters are $\epsilon = 0.005$, $\delta = 10$, $\rho_s = 0.01$ and $k = 50$. Also shown is the steady state response from equation (5.24), which is shown not to match the simulations.

Figure 5.32: Current from a voltage ramp applied to a liquid electrolyte with a single electrode and constant, large, positive background charge. Parameters are $\epsilon = 0.005$, $\delta = 10$, $\rho_s = 0.1$ and $k = 50$. Also shown is the steady state response from equation (5.24), which is shown not to match the simulations $-0.02$ and $-0.2$, respectively.
Figure 5.33: (a) Voltammogram and (b-d) resulting cation (solid line) and anion (dashed line) concentrations from a triangular applied voltage applied to a thin EDL liquid electrolyte with two electrodes and small positive background charge. Parameters used were $\epsilon = 0.005$, $\delta = 1$, $k = 50$, $\rho_s = 0.01$ and $|\tilde{S}| = 10$. Two cycles are shown in Figure (a).
Figure 5.34: (a) Voltammogram and (b-d) resulting cation (solid line) and anion (dashed line) concentrations from a triangular applied voltage applied to a thin EDL liquid electrolyte with two electrodes and large positive background charge. Parameters used were $\epsilon = 0.005$, $\delta = 1$, $k = 50$, $\rho_s = 0.1$ and $|\tilde{S}| = 10$. Two cycles are shown in Figure (a).
Chapter 6

Conclusions, Contributions and Future Work

In this thesis, we developed a system of equations which model the behaviour of a one-dimensional electrochemical cell and added new physics that has not been incorporated in existing models. This included the basic equations such as the Poisson-Nernst-Planck (PNP) equations which model diffusion and electromigration in an electrolyte, as well as generalized Frumkin-Butler-Volmer reaction kinetics at the electrodes. Progress was made in extending the equations to include temperature and surface coverage, and modified the electrostatic and diffusion equations to allow different values of permittivity in different regions of the bulk as well as bulk reactions and steric, or crowding effects. When solving the system of equations, we limited ourselves to a one dimensional geometry with simple electrolyte compositions and electrode reactions. However, we showed that the equations lend themselves easily to the incorporation of new physical effects, and that even our very simple system was able to reproduce analytical results and predict novel behaviour.

We then developed a numerical method for fast and efficient solving of the model equations equations. The numerical method we chose has the properties of being both second order with nonuniform discretization in time and space. This allows the solver to concentrate mesh points near the electrodes and concentrate time steps when boundary conditions are changing quickly. Particular attention was paid to convergence in time and handling of boundary conditions. The numerical method was tested on a simplified “toy” model which retains some key features of the full model, and a stability condition was
found which originates from the “ghost point” method used to ensure second order accuracy in time. Furthermore, our numerical scheme was found to be able to operate with arbitrarily small values of the nondimensional parameter $\epsilon$. Using the numerical method, we benchmarked our model by varying parameters for temperature, polarization and surface coverage with predictable results from simulations.

Finally, we used our model to investigate the role of diffuse charge effects on various systems when ramped voltages are applied. We began with single-electrode voltammograms for supported electrolytes, with an analytical expression in the limit of fast reactions, as well as for unsupported electrolytes in the limit of small $\epsilon$. For these systems, we showed where inclusion of diffuse charge dynamics plays a larger role, i.e. when a system with small $\delta$ has a large voltage applied. Next, we presented analytical expressions for the capacitance of liquid and solid electrolyte systems with blocking electrodes, and compared them to simulations with both thin and thick double layers. We found that our analytical approximations worked well for thin double layers, but in some cases disagreed when double layers were thick. We followed by applying ramped voltages to solid and liquid thin films to obtain current-voltage relationships and discussed the effect of various types of polarization, and how their effect on the current differed between liquid and solid electrolytes. For liquid electrolytes, we also observed the formation of space charge regions at large voltages, another prediction which is made possible by using the PNP-FBV equations. We ended with simulations on the leaky membrane model, where we found that simulations matched a steady-state analytical expression reasonably well when the background charge was opposite in polarity to the reactive ion (negative background charge) but did not match theory with positive background charge. In general, we conclude that diffuse charge dynamics becomes important in voltammetry at large applied voltages and/or with thick double layers. For each type of system we considered, the simulation results we obtained were compared to limiting cases and we showed where simple analytical expressions can be used to predict behavior (such as approximating capacitance curves), and which regimes require more careful analysis and simulation. This is of practical interest for electrochemists and engineers, for whom it can assist in guiding the design of new devices and experiments.

6.1 Contributions

The primary contributions of this thesis are:

- The development of an equation for temperature (a bulk PDE and boundary conditions which are coupled to the other equations) from first principles and incorporation of surface coverage and
dielectric polarization effects into the model. These were tested in simulation and found to give reasonable results.

- The development and testing of numerical methods for solving the PNP equations. Of the methods we tested, the ghost point VSIMEX method was found to have the best numerical properties.

- Simulations using ramped voltage and cyclic voltammetry boundary conditions for a variety of electrochemical systems with diffuse charge effects.

In summary, we consider our work to serve as a stepping stone to developing future electrochemical models with greater geometric complexity and with more accurate physics, as detailed in the next section.

6.2 Future Work

6.2.1 General

In Chapters 2 and 5, we developed the equations for and studied the effect of diffuse charge in batteries and capacitors. There is a lot of room for additional physics. For example, simulations can be performed with recombination bulk reactions (ion-ion, ion-defect, etc) [165] and lattice crowding (steric) effects [49, 50, 12, 17]. Though we developed both bulk reactions and steric effects as part of our model, we didn’t do any tests with them and only limited ourselves to the simplest expressions. We mentioned in Section 2.1 the possibility of coupled mass transport fluxes (Maxwell Stefan, dusty gas, etc) [109], which become important in concentrated electrolytes. This, and extending Poisson’s equation to include electrostatic correlations (an attractive short range van der Waals-like force observed between charged surfaces) [11], would give a more complete picture of the bulk electrolyte. Furthermore, while we used generalized BV kinetics [61] in this work, Marcus kinetics [57, 60] may provide a more accurate model of reaction kinetics. Another important aspect is that most modern electrochemical storage devices involve at least one porous medium, whether it is an electrode or membrane. The model could incorporate porous media in two ways: by adding macroscopic, volume-averaged parameters to the model which affect transport (such as the porosity or tortuosity) [82], or by creating a two or three-dimensional nanoscale model of a single pore. In the latter case, continuum approximations should still be valid down to scales of a few double layer widths [126, 214].
Finally, two major simplifications we made were the choices to ignore any advection and keep the equations one-dimensional. Relaxing these two simplifications would hugely increase the complexity of the model, especially if a three-dimensional model is required, and is a potential area of future research.

6.2.2 Numerics

In Chapter 3, we developed a adaptive-time solver for coupled parabolic-elliptic partial differential equations. The stability condition found in the toy model is worth investigating further, to nail down the exact condition and potentially figure out a way past it. It would be interesting to see if the thresholding in \( \frac{dt}{\epsilon} \) that we observed is a fundamental property of the equations or something artificial that was introduced by the way we handled the boundary conditions and time stepping. A related issue in the PNP model is the fact that, since time is scaled to \( L^2 \), decreasing \( \epsilon \) by a factor of 10 increases the simulation time by a factor of 100. There may be a numerical tool that can be invoked to improve this.

6.2.3 Dielectric Polarization

For future work, it would be interesting to incorporate higher order electrostatic effects into the model. We can start by having a better boundary condition, perhaps using a functional to describe the relationship between the polarization and the electric field. Similarly, in the bulk, it may be possible to incorporate an actual PDE or ODE for the polarization (adding time dynamics) instead of just having it be a function of \( E \), though it may be that time domain effects are not as important in the bulk since the forcing in the system operates on time scales which are relatively long.

On a related note, we briefly discussed modeling of electromechanical effects in Section 2.4, specifically changes in Stern layer properties due to electrostriction. It may be worthwhile to pursue modeling of these electromechanical effects, particularly for thin film systems where they might be more important.

6.2.4 Temperature

In Chapter 2 and Appendix A, we derived a general energy balance equation which models the temperature evolution, but fully coupled simulations were outside the scope of this thesis. Therefore, a first step in improving thermal modeling would be to couple the temperature field into the Poisson-Nernst-Planck equations. A related issue is implementing cross-coupling between diffusion and temperature, which
includes finding and including the temperature dependence of parameters. Finally, it may be possible to use a more accurate boundary condition for heat flow across the electrode-electrolyte interface, since it is known that Fourier’s heat law is not applicable across a boundary.

6.2.5 Surface coverage

We only treated the very basics of surface coverage; this is a wide open area of work. The next steps may be to test simulations against experiment or consider more realistic models of surface coverage.
Appendix A

Derivation of Energy Balance Equation

This appendix covers the derivation of the energy balance equation in the bulk of polarizable media. First we will go through the derivation of the energy balance equation in unpolarized media, then go through what changes when \( P \) and \( M \) are nonzero, followed by a derivation of the temperature equation.

We start from Maxwell's equations:

\[
\nabla \cdot \mathbf{D} = q \quad \text{(A.1)}
\]
\[
\nabla \cdot \mathbf{B} = 0 \quad \text{(A.2)}
\]
\[
\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial \tau} \quad \text{(A.3)}
\]
\[
\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial \tau} \quad \text{(A.4)}
\]

where \( q \) denotes the free charge density because \( \rho \) is reserved for mass density. From Maxwell’s equations, we can derive the energy and momentum balance equations for the electromagnetic field in the absence of polarization:

\[
\frac{\partial}{\partial \tau} \left( \frac{1}{2} \mathbf{E} \cdot \mathbf{D} + \frac{1}{2} \mathbf{B} \cdot \mathbf{H} \right) = -\nabla \cdot (\mathbf{E} \times \mathbf{H}) - \mathbf{J} \cdot \mathbf{E} \quad \text{(A.5)}
\]
\[
\varepsilon_0 \mu_0 \frac{\partial (\mathbf{E} \times \mathbf{H})}{\partial \tau} = -\nabla \cdot \sigma - q\mathbf{E} - \mathbf{J} \times \mathbf{B} \quad \text{(A.6)}
\]
Appendix A. Derivation of Energy Balance Equation

where $\sigma$ is Maxwell’s stress tensor, defined in unpolarized media as

$$
\sigma_{ij} = \varepsilon_0 \left( E_i E_j - \frac{1}{2} \delta_{ij} E^2 \right) + \frac{1}{\mu_0} \left( B_i B_j - \frac{1}{2} \delta_{ij} B^2 \right) \quad (A.7)
$$

and $\nabla \cdot \sigma$ denotes the divergence of a rank two tensor, which returns a vector (i.e. $(\nabla \cdot \sigma)_i = \partial \sigma_{ij} / \partial x_j$).

Now, the momentum balance equation for a material with an electromagnetic field can be written

$$
\frac{\partial}{\partial \tau} \left( \rho \mathbf{v} + \varepsilon_0 \mu_0 \mathbf{E} \times \mathbf{H} \right) = -\nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{T}) \quad (A.8)
$$

where $\mathbf{v} \mathbf{v}$ denotes a dyadic tensor product ($(\mathbf{v} \mathbf{v})_{ij} = v_i v_j$) and $\mathbf{T}$ is the Cauchy stress tensor. Subtracting equation (A.6) from equation (A.8) yields

$$
\frac{\partial}{\partial \tau} (\rho \mathbf{v}) = -\nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{T}) + q \mathbf{E} + \mathbf{J} \times \mathbf{B} \quad (A.9)
$$

Equation (A.9) is the momentum balance equation for matter in an EM field. Multiplying this equation by $\mathbf{v}$ gives us the balance equation for kinetic energy:

$$
\frac{\partial}{\partial \tau} \left( \frac{1}{2} \rho \mathbf{v}^2 \right) = -\nabla \cdot \left( \frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + \mathbf{T} \cdot \mathbf{v} \right) + \mathbf{T} : \nabla \mathbf{v} + q \mathbf{v} \cdot \mathbf{E} - \mathbf{J} \cdot \mathbf{v} \times \mathbf{B} \quad (A.10)
$$

where we have made use of the identities $\mathbf{v} \cdot \partial \rho \mathbf{v} / \partial t = \partial / \partial t \left( \frac{1}{2} \rho \mathbf{v}^2 \right)$, $\mathbf{v} \cdot \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \nabla \cdot \left( \frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} \right)$, $\mathbf{v} \cdot \nabla \cdot \mathbf{T} = \nabla \cdot (\mathbf{T} \cdot \mathbf{v}) - \mathbf{T} : \nabla \mathbf{v}$ and $\mathbf{v} \cdot \mathbf{J} \times \mathbf{B} = -\mathbf{J} \cdot \mathbf{v} \times \mathbf{B}$, and where $\nabla \mathbf{v}$ denotes a vector gradient, which returns a rank two tensor (i.e. $(\nabla \mathbf{v})_{ij} = \partial v_i / \partial x_j$) and $\mathbf{T} : \nabla \mathbf{v}$ denotes a tensor contraction, which returns a scalar (i.e. $S : \mathbf{T} = S_{ij} T_{ij}$).

Combining (A.10) with (A.5), we get

$$
\frac{\partial}{\partial \tau} \left( \frac{1}{2} \rho \mathbf{v}^2 + \frac{1}{2} \mathbf{E} \cdot \mathbf{D} + \frac{1}{2} \mathbf{B} \cdot \mathbf{H} \right) = -\nabla \cdot \left( \frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + \mathbf{T} \cdot \mathbf{v} + \mathbf{E} \times \mathbf{H} \right) + \mathbf{T} : \nabla \mathbf{v} + q \mathbf{v} \cdot \mathbf{E} - \mathbf{J} \cdot \mathbf{E} - \mathbf{J} \cdot \mathbf{v} \times \mathbf{B} \quad (A.11)
$$

At this point, a distinction needs to be made between the two types of free electric currents. This won’t matter for the final final equations because for a sealed battery, $\mathbf{v} = 0$ and $\nabla \cdot \mathbf{T} = 0$, but we will include this for completeness. There are two contributions to total free current density. First there is
the diffusion current (mass flux due to the concentration gradients), defined as

\[ j_d = \sum_{i=1}^{n} = z_i N_i \]  (A.12)

(where we label the individual diffusive fluxes \( N_i \)). There is also the convection current (mass flux due to a bulk velocity \( v \)), defined as

\[ j_c = q v \]  (A.13)

where again, \( q \) denotes charge density. The combination of (A.12) and (A.13) is the total free current density, \( J \):

\[ J = j_d + j_c = \sum_{i=1}^{n} = z_i N_i + q v \]  (A.14)

Using equation (A.14) in equation (A.11) and also using the fact that \( v \cdot (v \times B) = 0 \), equation (A.11) can be rewritten

\[
\frac{\partial}{\partial \tau} \left( \frac{1}{2} \rho v^2 + \frac{1}{2} E \cdot D + \frac{1}{2} B \cdot H \right) = -\nabla \cdot \left( \frac{1}{2} \rho v^2 v + T \cdot v + \varepsilon_0 \mu_0 E \times H \right) \\
+ T : \nabla v + j_d \cdot (E + v \times B) \tag{A.15}
\]

Equation (A.15) means that the combined kinetic and electromagnetic energy isn’t conserved, but has a volumetric generation rate equal to \( T : \nabla v + j_d \cdot (E + v \times B) \). However, the total energy \( E \) must be conserved, i.e.

\[
\frac{\partial E}{\partial \tau} = -\nabla \cdot J_e \tag{A.16}
\]

and so we define

\[ E = \rho u + \frac{1}{2} (\rho v^2 + E \cdot D + B \cdot H) \]  (A.17)

where \( \rho u \) is the density of internal energy and accounts for, at a microscopic scale, thermal agitation and small-range molecular interactions. Similarly, we define an energy flux

\[ J_e = J_q + \left( \frac{1}{2} \rho v^2 v + \rho u v + \sum_k H_{k0} J_k + T \cdot v + \varepsilon_0 \mu_0 E \times H \right) \]  (A.18)

where \( J_q \) is the heat flow and \( H_{k0} \) is the partial molar enthalpy of species \( k \). Substituting equation (A.17) and (A.18) into equation (A.16) and using equation (A.15), we have

\[
\frac{\partial \rho u}{\partial t} = -\nabla \cdot \left( u v + J_q + \sum_k H_{k0} J_k \right) - T \cdot \nabla v + j_d \cdot (E + v \times B) \tag{A.19}
\]
or, using the definition of the substantial derivative \( \frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \) and mass conservation \( \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) \), we can alternatively write

\[
\rho \frac{du}{dt} = -\nabla \cdot \left( \mathbf{J}_q + \sum_k H_{k0} \mathbf{J}_k \right) - \mathbf{T} \cdot \nabla \mathbf{v} + \mathbf{j}_d \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (A.20)
\]

where the last term in equation (A.20) represents the amount of electromagnetic energy transformed into internal energy per unit volume per unit time. From here, in order to formally obtain the forms of the flux equations using thermodynamics, some more work needs to be done, i.e. finding the rate of entropy generation using Gibbs’ equation and then applying the Onsager reciprocal relations. However, these steps are not necessary for deriving the energy balance equation.

Now onto how this derivation changes when the medium is polarized. We begin with how equation (A.6) changes when polarization/magnetization is nonzero. The constitutive relations are now

\[
D = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad (A.21)
\]

\[
B = \mu_0 \mathbf{H} + \mu_0 \mathbf{M} \quad (A.22)
\]

Using equations (A.21) and (A.22), equation (A.6) becomes

\[
\varepsilon_0 \mu_0 \frac{\partial (\mathbf{E} \times \mathbf{H})}{\partial \tau} = \varepsilon_0 \mu_0 \frac{\partial}{\partial \tau} \left[ \left( \frac{\mathbf{D} - \mathbf{P}}{\varepsilon_0} \right) \times \left( \frac{\mathbf{B}}{\mu_0} - \mathbf{M} \right) \right]
= \frac{\partial}{\partial \tau} [(\mathbf{D} - \mathbf{P}) \times (\mathbf{B} - \mu_0 \mathbf{M})]
= \frac{\partial}{\partial \tau} [\mathbf{D} \times \mathbf{B} - \mathbf{P} \times \mathbf{B} - (\mathbf{D} - \mathbf{P}) \times (\mu_0 \mathbf{M})]
= \frac{\partial (\mathbf{D} \times \mathbf{B})}{\partial \tau} - \varepsilon_0 \mu_0 \frac{\partial (\mathbf{E} \times \mathbf{M})}{\partial \tau} - \frac{\partial (\mathbf{P} \times \mathbf{B})}{\partial \tau} \quad (A.23)
\]

Using the tensor identity \( (\nabla \times \mathbf{A}) \times \mathbf{B} = \nabla \cdot (\mathbf{BA} - \mathbf{A} \cdot \mathbf{BU}) - \mathbf{A} \nabla \cdot \mathbf{B} + (\nabla \mathbf{B}) \cdot \mathbf{A} \) where \( \mathbf{U} \) is the identity
tensor $U_{ij} = \delta_{ij}$ as well as equations (A.1)-(A.4), the first term in equation (A.23) becomes

$$\frac{\partial (D \times B)}{\partial \tau} = \frac{\partial D}{\partial t} \times B + D \times \frac{\partial B}{\partial \tau}$$

$$= (\nabla \times H - J) \times B - J \times B + D \times (\nabla \times E)$$

$$= \nabla \cdot (BH - H \cdot BU) - H \nabla \cdot B + (\nabla B) \cdot H - J \times B$$

$$+ \nabla \cdot (DE - D \cdot EU) + (\nabla D) \cdot E - E \nabla \cdot D$$

$$= \nabla \cdot [BH + DE - (B \cdot H + E \cdot D) U]$$

$$+ (\nabla B) \cdot H + (\nabla D) \cdot E - qE - J \times B$$

(A.24)

where again, the quantities $BH$ and $DE$ represent dyadic products and $U$ is the identity tensor. Furthermore, using the chain rule, we have that

$$(\nabla D) \cdot E = (\nabla \epsilon_0 E) \cdot E$$

$$= (\nabla \epsilon_0 E) \cdot E + (\nabla P) \cdot E$$

$$= \nabla \cdot \left[ \left( \frac{1}{2} \epsilon_0 E^2 + P \cdot E \right) U \right] - (\nabla E) \cdot P$$

(A.25)

and similarly

$$(\nabla B) \cdot H = \nabla \cdot \left( \frac{1}{2} \frac{1}{\mu_0} B^2 U \right) - (\nabla B) \cdot M$$

(A.26)

so that equation (A.24) can be written

$$\frac{\partial (D \times B)}{\partial \tau} = \nabla \cdot \left[ DE + BH - \left( D \cdot E + B \cdot H - \frac{1}{2} \epsilon_0 E^2 - \frac{1}{2} \frac{1}{\mu_0} B^2 - P \cdot E \right) U \right]$$

$$- (\nabla E) \cdot P - (\nabla B) \cdot M - qE - J \times B$$

(A.27)

The terms inside the round brackets in equation (A.28) can be rewritten using equations (A.21) and (A.22) as

$$D \cdot E + B \cdot H - \frac{1}{2} \epsilon_0 E^2 - \frac{1}{2} \frac{1}{\mu_0} B^2 - P \cdot E = \epsilon_0 E^2 + P \cdot E + \frac{1}{\mu_0} B^2 - B \cdot M$$

$$- \frac{1}{2} \epsilon_0 E^2 - \frac{1}{2} \frac{1}{\mu_0} B^2 - P \cdot E$$

$$= \frac{1}{2} \epsilon_0 E + \frac{1}{2} \frac{1}{\mu_0} B^2 - B \cdot M$$

(A.28)
so that finally, we have

\[
\frac{\partial (D \times B)}{\partial \tau} = \nabla \cdot \left[ \mathbf{B}H + \mathbf{D}E - \left( \frac{1}{2} \varepsilon_0 E^2 + \frac{1}{2} \frac{1}{\mu_0} B^2 - \mathbf{B} \cdot \mathbf{M} \right) \right] U \\
+ (\nabla \mathbf{B}) \cdot \mathbf{H} + (\nabla \mathbf{D}) \cdot \mathbf{E} - q\mathbf{E} - \mathbf{J} \times \mathbf{B}
\]  
(A.29)

Now for the other two terms in equation (A.23), we can write, using the definition of the substantial derivative and conservation of mass, the conservation equations for \( \rho \mathbf{p} \) and \( \rho \mathbf{m} \) (where \( \mathbf{P} = \rho \mathbf{p} \) and \( \mathbf{M} = \rho \mathbf{m} \)) as

\[
\frac{\partial \mathbf{P}}{\partial \tau} = -\nabla \cdot (v\mathbf{P}) + \rho \frac{d\mathbf{P}}{d\tau} 
\]  
(A.30)

\[
\frac{\partial \mathbf{M}}{\partial \tau} = -\nabla \cdot (v\mathbf{m}) + \rho \frac{d\mathbf{m}}{d\tau} 
\]  
(A.31)

Furthermore, we may write (directly from the definition of the substantial derivative)

\[
\frac{\partial \mathbf{B}}{\partial \tau} = \frac{d\mathbf{B}}{d\tau} - v \cdot \nabla \mathbf{B} 
\]  
(A.32)

\[
\frac{\partial \mathbf{E}}{\partial \tau} = \frac{d\mathbf{E}}{d\tau} - v \cdot \nabla \mathbf{E} 
\]  
(A.33)

Using equations (A.30)-(A.33), we get

\[
\frac{\partial (\mathbf{P} \times \mathbf{B})}{\partial \tau} = -\nabla \cdot [v(\mathbf{P} \times \mathbf{B})] + \rho \frac{d(\mathbf{P} \times \mathbf{B})}{d\tau} 
\]  
(A.34)

\[
\varepsilon_0 \mu_0 \frac{\partial (\mathbf{M} \times \mathbf{E})}{\partial \tau} = -\varepsilon_0 \mu_0 \nabla \cdot [v(\mathbf{M} \times \mathbf{E})] + \varepsilon_0 \mu_0 \rho \frac{d(\mathbf{m} \times \mathbf{E})}{d\tau} 
\]  
(A.35)

Substituting equations (A.34) and (A.35) with equation (A.29) into equation (A.23), we finally obtain

\[
\varepsilon \mu \frac{\partial (\mathbf{E} \times \mathbf{H})}{\partial \tau} = \nabla \cdot \mathbf{\sigma} - \mathbf{F} 
\]  
(A.36)

where \( \mathbf{\sigma} \) is the generalization of Maxwell’s stress tensor in polarized media, given by

\[
\mathbf{\sigma} = \mathbf{D}E + \mathbf{D}H - \left( \frac{1}{2} \varepsilon_0 E^2 + \frac{1}{2} \frac{1}{\mu_0} B^2 - \mathbf{M} \cdot \mathbf{B} \right) U + v(\mathbf{P} \times \mathbf{B}) - \varepsilon_0 \mu_0 v(\mathbf{M} \times \mathbf{E}) 
\]  
(A.37)

and \( \mathbf{F} \) is the generalization of the force vector in polarized media, given by

\[
\mathbf{F} = q\mathbf{E} + \mathbf{J} \times \mathbf{B} + (\nabla \mathbf{E}) \cdot \mathbf{P} + (\nabla \mathbf{B}) \cdot \mathbf{M} + \rho \frac{d(\mathbf{P} \times \mathbf{B})}{d\tau} + \varepsilon_0 \mu_0 \rho \frac{d(\mathbf{m} \times \mathbf{E})}{d\tau} 
\]  
(A.38)
Equation (A.36) simplifies to equation (A.6) in the case when \( P = M = 0 \). The momentum balance equation is again given by equation (A.9) but with equations (A.37) and (A.38) taking the place of the unpolarized Maxwell’s stress tensor and the Lorentz force, respectively. Proceeding as we had previously, multiplying the momentum equation by the velocity \( v \) gives the balance equation for the kinetic energy,

\[
\frac{\partial}{\partial \tau} \frac{1}{2} \rho v^2 = -\nabla \cdot \left( \frac{1}{2} \rho v^2 v + T \cdot v \right) + T : \nabla v + F \cdot v
\]  

(A.39)

where \( F \cdot v \) is

\[
F \cdot v = qE \cdot v + v \cdot (j_d \times B) + v \cdot (\nabla E) \cdot P + v \cdot (\nabla B) \cdot M + \rho v \cdot \frac{d(p \times B)}{d\tau} - \varepsilon_0 \mu_0 \rho v \cdot \frac{d(m \times E)}{d\tau}
\]  

(A.40)

where again we have used the definitions of the two currents in equations (A.12)-(A.14).

We now introduces primed variables for the fields for an observer moving with velocity \( v \):

\[
D = D' - v \times H'
\]  

(A.41)

\[
E = E' - v \times B'
\]  

(A.42)

\[
P = P' + v \times M'
\]  

(A.43)

\[
H = H' + v \times D'
\]  

(A.44)

\[
B = B' + v \times E'
\]  

(A.45)

\[
M = M' - v \times P'
\]  

(A.46)

Through direct substitution of equations (A.41)-(A.46) into equation (A.40), equation (A.40) can be rewritten

\[
F \cdot v = qE' \cdot v + v \cdot (j_d \times B') + v \cdot (\nabla E') \cdot P' + v \cdot (\nabla B') \cdot M'
\]

\[
+ v \cdot (\nabla v) \cdot (P' \times B' - \varepsilon_0 \mu_0 M' \times E') + \rho v \cdot \frac{d(p' \times B')}{d\tau} - \varepsilon_0 \mu_0 \rho v \cdot \frac{d(m' \times E')}{d\tau}
\]  

(A.47)

Now we make use of three complex tensor relations (which can be derived using the chain rule for tensor derivatives, Maxwell’s equations, conservation of mass and the definition of the substantial derivative)
for the middle terms on the right hand side of equation (A.51),

\[
\mathbf{v} \cdot (\nabla E') \cdot \mathbf{P}' = \nabla \cdot (\mathbf{P}' \cdot \mathbf{E}') - \mathbf{E}' \cdot \nabla \cdot (\mathbf{v} \mathbf{P}')
\]
\[
= \nabla \cdot (\mathbf{P}' \cdot \mathbf{E}' \mathbf{v}) + \mathbf{E}' \cdot \frac{\partial \mathbf{P}'}{\partial t} - \rho \mathbf{E}' \cdot \frac{d \mathbf{P}'}{d t}
\quad \text{(A.48)}
\]

\[
\mathbf{v} \cdot (\nabla B') \cdot \mathbf{M}' = \nabla \cdot (\mathbf{M}' \cdot \mathbf{B}' \mathbf{v}) - \mathbf{B}' \cdot \nabla \cdot (\mathbf{v} \mathbf{M}')
\]
\[
= \nabla \cdot (\mathbf{M}' \cdot \mathbf{B}' \mathbf{v}) + \mathbf{B}' \cdot \frac{\partial \mathbf{M}'}{\partial t} - \rho \mathbf{B}' \cdot \frac{d \mathbf{m}'}{d t}
\quad \text{(A.49)}
\]

\[
\mathbf{v} \cdot (\nabla \mathbf{v}) \cdot (\mathbf{P}' \times \mathbf{B}' - \varepsilon_0 \mu_0 \mathbf{M}' \times \mathbf{E}') = \nabla \cdot [(\mathbf{P}' \times \mathbf{B}' - \varepsilon \mu \mathbf{M}' \times \mathbf{E}') \cdot \mathbf{v} \mathbf{v}]
\]
\[
- \mathbf{v} \cdot \nabla \cdot [\mathbf{v} (\mathbf{P}' \times \mathbf{B}' - \varepsilon_0 \mu_0 \mathbf{M}' \times \mathbf{E}')] = \nabla \cdot [(\mathbf{P}' \times \mathbf{B}' - \varepsilon_0 \mu_0 \mathbf{M}' \times \mathbf{E}') \cdot \mathbf{v} \mathbf{v}]
\quad + \mathbf{v} \cdot \frac{\partial \mathbf{P}'}{\partial t} (\mathbf{P}' \times \mathbf{B}' - \varepsilon_0 \mu_0 \mathbf{M}' \times \mathbf{E}')
\quad - \rho \mathbf{v} \cdot \frac{d}{d t} (\mathbf{p}' \times \mathbf{B}' - \varepsilon_0 \mu_0 \mathbf{m}' \times \mathbf{E}')
\quad \text{(A.50)}
\]

Introducing (A.48)-(A.50) into equation (A.51), we can rewrite \( \mathbf{F} \cdot \mathbf{v} \) as

\[
\mathbf{F} \cdot \mathbf{v} = \nabla \cdot [(\mathbf{P}' \cdot \mathbf{E} + \mathbf{M}' \cdot \mathbf{B}) \mathbf{v}] + \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial t} - \mathbf{M} \cdot \frac{\partial \mathbf{B}}{\partial t} + \frac{\partial (\mathbf{B} \cdot \mathbf{M}')}{\partial t}
\quad - \varepsilon_0 \mu_0 \frac{\partial}{\partial t} [\mathbf{E}' \cdot (\mathbf{v} \times \mathbf{M}')] + q \mathbf{E}' \cdot \mathbf{v} - \mathbf{j}_d \cdot (\mathbf{v} \times \mathbf{B}') - \rho \mathbf{E}' \cdot \frac{d \mathbf{P}'}{d t} - \rho \mathbf{B}' \cdot \frac{d \mathbf{m}'}{d t}
\quad \text{(A.51)}
\]

Substituting this expression for \( \mathbf{F} \cdot \mathbf{v} \) into equation (A.39) and adding in equation (A.6) as before, we obtain the generalization for equation (A.11) for polarized media,

\[
\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \mathbf{v}^2 + \frac{1}{2} \mathbf{E} \cdot \mathbf{D} + \frac{1}{2} \mathbf{B} \cdot \mathbf{H} - \mathbf{M}' \cdot \mathbf{B} + \varepsilon \mu \mathbf{E}' \cdot (\mathbf{v} \times \mathbf{M}') \right)
\]
\[
= -\nabla \cdot \left[ \frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + \mathbf{T} \cdot \mathbf{v} - (\mathbf{P}' \cdot \mathbf{E} + \mathbf{M}' \cdot \mathbf{B}) \mathbf{v} + \mathbf{E} \times \mathbf{H} \right]
\quad + \mathbf{T} \cdot \nabla \mathbf{v} - \mathbf{j}_d \cdot \mathbf{E}' - \rho \mathbf{E}' \cdot \frac{d \mathbf{P}'}{d t} - \rho \mathbf{B}' \cdot \frac{d \mathbf{m}'}{d t}
\quad \text{(A.52)}
\]

Equation (A.52) is the analog to equation (A.11) for polarized media, and states that the rate of change of the kinetic plus electromagnetic energy is equal to an energy flux plus a source term, \( \mathbf{T} \cdot \nabla \mathbf{v} - \mathbf{j}_d \cdot \mathbf{E}' - \rho \mathbf{E}' \cdot \frac{d \mathbf{P}'}{d t} - \rho \mathbf{B}' \cdot \frac{d \mathbf{m}'}{d t} \). If we define a total energy \( e \) and energy flux \( \mathbf{J}_e \) as we did previously, but in
the context of equation (A.52), we finally obtain

\[ \rho \frac{du}{d\tau} = -\nabla \cdot \left( J_q + \sum_k H_k J_k \right) - T : \nabla v + j_d \cdot E' + \rho E' \cdot \frac{dp'}{d\tau} + \rho B' \cdot \frac{dm'}{d\tau} \] (A.53)

which is the generalization of equation (A.20) to systems with polarization, which also simplifies to equation (A.20) without polarization.

Speaking now in our case, we have mechanical equilibrium (\( \nabla \cdot T = 0 \)) and no convection (\( v = 0 \)) (though the general equation is here in case we do want to study the effects of thermal expansion, etc) so the primed and unprimed coordinates are the same, and there are is no convective source in the heat flux or generation term. Assuming \( \rho \) is also constant, we can write

\[ \frac{du}{d\tau} = -\nabla \cdot \left( J_q + \sum_k H_k J_k \right) + j \cdot E + E \cdot \frac{\partial P}{\partial \tau} + B \cdot \frac{\partial M}{\partial \tau} \] (A.54)

Where \( u \) now represents the volume density of internal energy instead of the mass density. Next, to go from the balance equation for internal energy to the temperature equation, we turn to the definition of the enthalpy and the partial molar enthalpy. For a system with polarization and magnetization, the volume density of enthalpy is defined as

\[ h = u + P - E \cdot P - B \cdot M = \sum_k H_k c_k \] (A.55)

where \( H_k \) is the specific molar enthalpy, defined as \( H_k = (\partial H/\partial n_k)_{T,P,E,M,n_\gamma \neq k} \), whereas \( h_0 \) and \( H_k \) are the enthalpy density and partial molar enthalpy in the absense of polarization and magnetization, then, using a property of the partial molar enthalpy, we can write

\[ h = h_0 - E \cdot P - B \cdot M = \sum_k H_k c_k + \sum_k [E \cdot (PV)_k + B \cdot (MV)_k] c_k \] (A.56)

By definition, \( \sum_k [E \cdot (PV)_k + B \cdot (MV)_k] c_k = E \cdot P - B \cdot M \), so we just have

\[ u + P = \sum_k H_k c_k \] (A.57)

Taking the derivative with respect to time of both sides of equation (A.57), we have

\[ \frac{du}{d\tau} + \frac{\partial P}{\partial \tau} = \sum_k \frac{\partial H_k}{\partial \tau} c_k + \sum_k \frac{\partial c_k}{\partial \tau} H_k \] (A.58)
Using another thermodynamic identity (Haase, equation 4-6.18), equation (A.54) and the equation of mass conservation for species $k$,

$$\frac{\partial c_k}{\partial \tau} = -\nabla \cdot J_k + \sum_r \nu_{kr} B_r$$  \hspace{1cm} (A.59)

where the second term in equation (A.59) accounts for bulk reactions (i.e. $\nu_{kr}$ is the stoichiometric coefficient for the $k^{th}$ species in the $r^{th}$ reaction and $b_r$ is the reaction rate of the $r^{th}$ reaction), we have, from equation (A.58),

$$-\nabla \cdot \left( J_q + \sum_k H_{k0} J_k \right) + J \cdot E + E \cdot \frac{\partial \mathbf{P}}{\partial \tau} + B \cdot \frac{\partial \mathbf{M}}{\partial \tau} + \frac{\partial P}{\partial \tau}$$

$$= \rho c_p \frac{\partial T}{\partial \tau} + \left[ 1 - \frac{T}{\bar{V}} \frac{\partial \bar{V}}{\partial T} \right] \frac{\partial P}{\partial \tau}$$

$$+ \sum_r \sum_k \nu_{kr} H_{k0} b_r - \sum_k H_{k0} \nabla \cdot J_k$$  \hspace{1cm} (A.60)

where $\bar{V}$ is the molar volume. If it can be assumed that pressure is constant (a reasonable assumption for a closed, aqueous electrolyte in mechanical equilibrium with no vapor phase present), then equation (A.60) can finally be rewritten

$$\rho c_p \frac{\partial T}{\partial \tau} = -\nabla \cdot J_q + J \cdot E + E \cdot \frac{\partial \mathbf{P}}{\partial \tau} + B \cdot \frac{\partial \mathbf{M}}{\partial \tau} - \sum_r \sum_k \nu_{kr} H_{k0} b_r - \sum_k J_k \cdot \nabla H_{k0}$$  \hspace{1cm} (A.61)

which is our temperature equation with polarization and magnetization. As we progressed through this derivation, we made two major simplifications:

- Mechanical equilibrium and no convection: $\mathbf{v} = 0$, constant pressure
- Constant mass density $\rho$

At this point we can briefly shift the discussion to the double summation term in equation (A.61). This term is easier to conceptualize if rewritten as $\sum_r B_r \sum_k \nu_{kr} H_{k0}$, i.e. a reaction rate multiplied by the change in partial molar enthalpy of the reaction. In chemistry it is common to use the standard enthalpy of formation $H^f_{k0}$, which is the enthalpy of formation at standard temperature and pressure, instead of the partial molar enthalpy, i.e.

$$\nu_1 A + \nu_2 B \longrightarrow \nu_3 C + \nu_4 D \hspace{1cm} \Delta H = \nu_3 H^f_C + \nu_4 H^f_D - \nu_1 H^f_A - \nu_2 H^f_B$$

This substitution is valid as long as the reaction that takes place is not too far away from standard conditions, but more importantly values for standard enthalpies can be found for nearly all chemical
species.

The other term is the last term in equation (A.61), which is a left-over term from $\nabla \cdot \sum_k H_{k0} J_k$, is a source term due to species flux against a temperature gradient (since $dH \sim C_p dT$). This is a term sometimes called the “heat of transport”, and is related to the Soret effect, or thermodiffusion (see Chapters 1 and 2 of [215]). Since we are not interested in studying these effects in electrochemical cells, we choose to simplify equation (A.61) by ignoring the last term, and also by replacing $H_{k0}$ with $H^f_{k0}$ for practicality. The energy equation now reads:

$$\rho c_p \frac{\partial T}{\partial \tau} = -\nabla \cdot J_q + \mathbf{J} \cdot \mathbf{E} + \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \tau} + \mathbf{B} \cdot \frac{\partial \mathbf{M}}{\partial \tau} - \sum_r \sum_k \nu_{kr} H^f_{k0} B_r$$  \hspace{1cm} (A.62)
Appendix B

Derivation of Current Conservation Equation

This appendix details the derivation of the current conservation equation used to model the evolution of the potential difference across the Stern layer. This equation comes from conservation of charge,

\[ \frac{\partial \rho_f}{\partial t} = -\nabla \cdot \mathbf{J}, \]  

where \( \rho_f \) is the free charge, given by Gauss’s law by

\[ \nabla \cdot \mathbf{D} = \rho_f. \]  

Now, in order to arrive at the current conservation equation, we now choose one of the boundaries on which we would like to impose a current, and integrate this equation across it, using a thin rectangular volume (or any prism where the sides are perpendicular to the surface), as shown in Figure B.1. This looks like

\[ \frac{\partial}{\partial t} \iiint_V \nabla \cdot \mathbf{D} \, dV = - \iiint_V \nabla \cdot \mathbf{J} \, dV. \]  

Assuming that \( \mathbf{D} \) and \( \mathbf{J} \) are nonzero only in the direction normal to the electrode surface and applying the divergence theorem, we have

\[ \frac{\partial}{\partial t} (\mathbf{D}_{\text{right}} - \mathbf{D}_{\text{left}}) = -(\mathbf{J}_{\text{right}} - \mathbf{J}_{\text{left}}). \]  

126
\[ \sum J_i \rightarrow J_{\text{ext}} \]

Figure B.1: Gaussian surface around the electrode/electrolyte interface, showing current balance. Left side of the figure is the electrolyte side and right is the electrode side.

Now, \( J_{\text{right}} \) is nothing but the externally applied current, \( J_{\text{ext}} \), \( J_{\text{left}} \) is the sum of the currents in the electrolyte (\( \sum J_i \)), \( D_{\text{left}} \) is the electric displacement field at the Stern plane, and we are assuming that the field in the metal is zero (for a perfect conductor). So what results is

\[
\frac{\partial D}{\partial t} = J_{\text{ext}} - \sum J_i. \tag{B.5}
\]
Appendix C

The Butler-Volmer Model of Faradaic Reactions

In this appendix, we will briefly and informally give the reader some background on the keystone of reaction modeling in electrochemistry: the Butler-Volmer equation.

The Butler-Volmer model of Faradaic reactions comes from stochastic rate theory, which posits that a particle is performing a random walk across a potential energy landscape as shown in Figure C.1.

In Figure C.1, $U_1$, $U_2$ and $U_{TS}$ denote the internal energies of the initial, final and transition states, respectively. If $U_{TS} - U_1 \gg k_B T$ and $U_{TS} - U_2 \gg k_B T$, the theory gives the mean first passage time.

Figure C.1: The path of a particle in stochastic rate theory, showing the “energy hump” of the transition state between the initial and final states. $U_1$, $U_2$ and $U_{TS}$ denote the internal energies of the initial, final and transition states, respectively.

respectively. If $U_{TS} - U_1 \gg k_B T$ and $U_{TS} - U_2 \gg k_B T$, the theory gives the mean first passage time.
from the initial state to the final state as

\[ \langle \tau_{12} \rangle = \tau_0 \exp \left( \frac{U_{TS} - U_1}{k_B T} \right) \]  

(C.1)

Therefore, the mean transition rate is

\[ r_{12} = \frac{1}{\langle \tau_{12} \rangle} = r_0 \exp \left( -\frac{U_{TS} - U_1}{k_B T} \right) \]  

(C.2)

Therefore, the net reaction rate for a reversible reaction is

\[ r = r_{12} - r_{21} = r_0 \exp \left( -\frac{U_{TS} - U_1}{k_B T} \right) - r'_0 \exp \left( -\frac{U_2 - U_{TS}}{k_B T} \right) \]  

(C.3)

where \( r_{21} \) is the mean transition rate from state 2 to state 1. Note that this gives us \( r_{12}/r_{21} \propto e^{(U_1-U_2)/k_BT} \), which is a de Donder relation. Next consider the general (non-Faradaic, i.e. no electron transfer) reaction

\[ \sum s_i R_i \rightleftharpoons \sum t_j P_j \]

where \( s_i \) is the stoichiometric number corresponding to species \( R_i \), and \( t_j \) is the stoichiometric number for species \( P_j \). The energies of the initial and final states are \( U_1 = \sum s_i U_{i,1} \) and \( U_2 = \sum t_j U_{j,2} \), respectively, where \( U_{i,1} \) is the energy of species \( i \) in state 1 and \( U_{j,2} \) is the energy of species \( j \) in state 2. The probability of finding species \( i \) in state 1 (per volume) is assumed to be proportional to its concentration \( C_{i,1} \) in a dilute solution, and so the net reaction rate can be written

\[ r = r_f \prod C_{s_i,1}^{s_i} \exp \left( -\frac{U_{TS} - U_1}{k_B T} \right) - r_b \prod C_{t_j,2}^{t_j} \exp \left( -\frac{U_2 - U_{TS}}{k_B T} \right) \]  

(C.4)

Note that at equilibrium, \( r = 0 \), and

\[ \Delta U_{eq} = (U_1 - U_2)_{eq} = k_B T \ln \left( \frac{r_b \prod C_{t_j,2}^{t_j}}{r_f \prod C_{s_i,1}^{s_i}} \right) \]  

(C.5)

which is reminiscent of the Nernst equation. Now, let us examine what happens if an electron is one of the reactants and there is an electric field applied, with the example reaction

\[ \sum t_{R,j} R_j^{z_R,j} \rightleftharpoons \sum s_{O,i} O_i^{z_O,i} + ne^- \]

where \( R \) indicates a reduced species and \( O \) indicates an oxidized species and superscript indicates charge
(where $z$ can be negative). The energies of the initial and final states are

$$U_1 = \sum t_{R,j} U_{R,j} + \sum t_{R,j} z_{R,j} e\Phi = U_1^0 + \sum t_{R,j} z_{R,j} e\Phi \quad (C.6)$$

$$U_2 = \sum s_{O,i} U_{O,i} + \sum s_{O,i} z_{O,i} e\Phi - n e\Phi_e = U_2^0 + \sum s_{O,i} z_{O,i} e\Phi - n e\Phi_e \quad (C.7)$$

where $\Phi$ is the solution potential and $\Phi_e$ is the electrode potential. In order to make progress towards a reaction rate equation, we require a model for the energy of the transition state. The Butler-Volmer hypothesis states that the electrostatic energy of the transition state is a weighted average of the initial and final states, or that

$$U_{\text{TS}} = U_{\text{TS}}^0 + \alpha \sum t_{R,j} z_{R,j} e\Phi + (1 - \alpha) \left( \sum s_{O,i} z_{O,i} e\Phi - n e\Phi_e \right) \quad (C.10)$$

where $\alpha$ is the (usually experimentally fitted) transfer coefficient which appears in the Butler-Volmer equation. Using equations (C.8)–(C.10), we have

$$U_{\text{TS}} - U_1 = \alpha \sum t_{R,j} z_{R,j} e\Phi + \sum i s_{O,i} z_{O,i} e\Phi - \alpha \sum i s_{O,i} z_{O,i} e\Phi - \sum j t_{R,j} z_{R,j} e\Phi - (1 - \alpha) n e\Phi_e$$

$$= -(1 - \alpha) \sum j t_{R,j} z_{R,j} e\Phi + (1 - \alpha) \sum i s_{O,i} z_{O,i} e\Phi - (1 - \alpha) n e\Phi_e \quad (C.11)$$

where for simplification we assume that any constants in equations (C.8)–(C.10) have already been absorbed into a the forward ($k_f$) or backward ($k_b$) reaction rate constant outside of the exponents. Next, we make use of charge conservation,

$$\sum s_{O,i} z_{O,i} - n = \sum t_{R,j} z_{R,j} \quad (C.12)$$

to write

$$U_{\text{TS}} - U_1 = (1 - \alpha) n e\Phi - (1 - \alpha) n e\Phi_e$$

$$= -(1 - \alpha) n e (\Phi_e - \Phi)$$

$$= -(1 - \alpha) n e \Delta \Phi \quad (C.13)$$

With a similar derivation, we find, $U_2 - U_{\text{TS}} = one \Delta \Phi$, which we can substitute along with equation
(C.13) into equation (C.4) to arrive at

\[ R = k_f \prod C_{R,i}^{t_R} \exp \left( \frac{(1 - \alpha)ne\Delta\Phi}{k_B T} \right) - k_b \prod C_{O,j}^{t_O} \exp \left( -\frac{\alpha ne\Delta\Phi}{k_B T} \right) \]  

(C.14)

where traditionally \( \Delta\phi \) is (somewhat ambiguously) defined as the potential difference between the electrode and the solution, \( \Phi_e - \Phi \). However, the generalized Frumkin-Butler-Volmer equation removes most of this ambiguity by strictly defining \( \Delta\phi \) as the potential at the electrode minus the potential at the Stern plane.

In order to extend the Butler-Volmer model to concentrated solutions, we turn to another often misunderstood quantity, the electrochemical potential, which for an aqueous species can be written as

\[ \mu = k_B T \ln C + \mu^{\text{ex}} \]  

(C.15)

The leap of interpretation here to link it to the previous treatment is to argue that the excess chemical potential \( \mu^{\text{ex}} \), which contains contributions from excluded volume effects and external fields, is equivalent or at least similar to the internal energy \( U \). Recall that we never deal with \( \mu \) or \( U \) by itself, only differences, and so any constants carried by either of the two quantities vanish. It’s worth mentioning here that, as with the Butler-Volmer hypothesis, there is no strong theoretical justification for replacing the internal energy with the chemical potential. Like with the Butler-Volmer hypothesis, it is simply something which has been validated by some experiments [57], while others suggest the need for a deeper theory [60].

We rewrite equation (C.4) with chemical potentials as

\[ r = r_f \prod C_{i,1}^{t_{R,i}} \exp \left( -\frac{\mu_1^{\text{ex}} - \mu_1^{\text{ex}}}{k_B T} \right) - r_b \prod C_{j,2}^{t_O} \exp \left( -\frac{\mu_2^{\text{ex}} - \mu_2^{\text{ex}}}{k_B T} \right) \]  

(C.16)

Since

\[ \mu_1^{\text{ex}} = \mu_1 - k_B T \ln \prod C_{i,1}^{t_{R,i}} \]  

(C.17)

and

\[ \mu_2^{\text{ex}} = \mu_2 - k_B T \ln \prod C_{j,2}^{t_O} \]  

(C.18)

equation (C.16) can be written

\[ r = r_f \exp \left( -\frac{\mu_1^{\text{ex}} - \mu_1}{k_B T} \right) - r_b \exp \left( -\frac{\mu_2^{\text{ex}} - \mu_2}{k_B T} \right) \]  

(C.19)
where $\mu_{\text{TS}}$ is often just assumed to be constant (with the weighted sum of electrostatic energy). And so in practice, the electrochemical potential, which can be obtained from thermodynamics from the partial molar free energy, is what ultimately enters into the Butler-Volmer equation. For a complete description using the Butler-Volmer model charge transfer, a model for the chemical potentials of the initial, transition and final states are needed.
Appendix D

Derivation of Numerical Extrapolation Formula

In this appendix, the error approximation and extrapolation formula used in Chapter 3 is derived. We consider time stepping the ODE

\[ \frac{du}{dt} = f(u) + g(u) \]  \hspace{1cm} (D.1)

where the value of \( u \) at time \( n + 1 \) is given by

\[
\frac{1}{dt_{\text{now}}} \left( \frac{1 + 2\omega}{1 + \omega} u^{n+1} - (1 + \omega)u^n + \frac{\omega^2}{1 + \omega} u^{n-1} \right) = (1 + \omega)f(u^n) - \omega f(u^{n-1}) + g(u^{n+1}) \]  \hspace{1cm} (D.2)

By making the substitutions \( u^{n+1} = u(t+dt_{\text{now}}) \) and \( u^{n-1} = u(t-dt_{\text{old}}) \) and performing a multivariable Taylor expansion about \( t \), the local truncation error is found to take the form

\[
\text{LTE} =
\begin{align*}
&(-f(u(t)) - g(u(t)) + u'(t)) dt_{\text{now}} + ((-f'(u(t)))u'(t) - g'(u(t))u'(t) + u''(t)) \\
&\quad + \left( \frac{1}{2} u'(t)^2 g''(u(t)) + \frac{1}{2} g'(u(t))u''(t) - \frac{1}{6} u^{(3)}(t) \right) dt_{\text{old}} dt_{\text{now}}^2 \\
&\quad + \left( -\frac{1}{2} u'(t)^2 f''(u(t)) - \frac{1}{2} f'(u(t))u''(t) + \frac{1}{3} u^{(3)}(t) \right) dt_{\text{now}}^3 + O(dt^4)
\end{align*} \hspace{1cm} (D.3)
\]

where \( O(dt^4) \) denotes terms where \( dt_{\text{now}} \) and \( dt_{\text{old}} \) combined appear four or more times. Assuming that \( u(t) \) is a solution of (D.1), the \( dt_{\text{now}} \) term in (D.3) vanishes. Differentiating (D.1) to find \( u'' \) and \( u''' \) and
using this in equation (D.3), the \(dt^2_{\text{now}}\) also vanishes. This leaves

\[
\text{LTE} = \left( \frac{1}{2} u'(t)^2 g''(u(t)) + \frac{1}{2} g'(u(t)) u''(t) - \frac{1}{6} u^{(3)}(t) \right) dt_{\text{old}} dt^2_{\text{now}} \\
+ \left( -\frac{1}{2} u'(t)^2 f''(u(t)) - \frac{1}{2} f'(u(t)) u''(t) + \frac{1}{3} u^{(3)}(t) \right) dt^3_{\text{now}} + H.O.T. \tag{D.4}
\]

By making the further substitutions

\[
f'(u(t)) = -g'(u(t)) u'(t) + u''(t) \tag{D.5}
\]

and

\[
f''(u(t)) = \frac{u^{(3)}(t) - f'(u(t)) u''(t) - g''(u(t)) u'(t)^2 - g'(u(t)) u''(t)}{u'(t)^2} \tag{D.6}
\]

equation (D.4) simplifies to

\[
\text{LTE} = \frac{1}{6} \left( 3g''(u(t)) u'(t)^2 + 3g'(u(t)) u''(t) - u^{(3)}(t) \right) dt^2_{\text{now}} (dt_{\text{now}} + dt_{\text{old}}) + H.O.T. \tag{D.7}
\]

which means that for \(u^{(3)}(t)\) bounded, \(u^{n+1}_c\) takes the form

\[
u^{n+1}_c = u(t^{n+1}) + C dt^2_{\text{now}} (dt_{\text{now}} + dt_{\text{old}}) + H.O.T. = u(t^{n+1}) + \epsilon_c + H.O.T. \tag{D.8}
\]

And so the local truncation error for the coarse step is

\[
\epsilon_c = u^{n+1}_c - u(t^{n+1}) = C dt^2_{\text{now}} (dt_{\text{now}} + dt_{\text{old}}) + H.O.T. \tag{D.9}
\]

To find the LTE for \(u^{n+1}_c\), we find the LTE for \(u^{n+1/2}_f\) by replacing \(dt_{\text{now}}\) and \(dt_{\text{old}}\) in (D.9) by \(\frac{dt_{\text{now}}}{2}\) and \(\frac{dt_{\text{old}}}{2}\), respectively. We then find the LTE for \(u^{n+1}_f\) by setting both \(dt_{\text{now}}\) and \(dt_{\text{old}}\) to \(\frac{dt_{\text{now}}}{2}\). Adding these LTE’s yields the LTE for \(u^{n+1}_f\),

\[
\epsilon_f = u^{n+1}_f - u(t^{n+1}) = C dt^2_{\text{now}} (dt_{\text{now}} + dt_{\text{old}}) + C \frac{dt^3_{\text{now}}}{4} + H.O.T. \tag{D.10}
\]

From equations (D.9) and (D.10), we can compute \(C\) using \(u_c, u_f, dt_{\text{now}}\) and \(dt_{\text{old}}\):

\[
C \approx \frac{u_c - u_f}{\frac{3}{8} dt^3_{\text{now}} + \frac{7}{8} dt^2_{\text{now}} dt_{\text{old}}} \tag{D.11}
\]
Now that $C$ is known, we plug it into (D.8), resulting in

$$
\epsilon_c \approx \frac{u_c - u_f}{\frac{1}{8} dt_{\text{now}}^3 + \frac{7}{8} dt_{\text{now}}^2 dt_{\text{old}}} \left( dt_{\text{now}}^2 (dt_{\text{now}} + dt_{\text{old}}) \right)
$$

(D.12)

Finally, we subtract $\epsilon_c$ from $u_c^{n+1}$ to create a more accurate approximation of $u(t^{n+1})$. This results in

$$
u(t^{n+1}) \approx u_c^{n+1} - \epsilon_c = \alpha u_c^{n+1} + \beta u_f^{n+1}
$$

(D.13)

where

$$
\alpha = \frac{dt_o + 3dt_n}{7dt_o + 5dt_n}, \quad \beta = 8 \frac{dt_o + dt_n}{7dt_o + 5dt_n}
$$

(D.14)
Appendix E

Derivation of Modified Randles-Sevcik Equation

In this appendix, we solve the semi-infinite diffusion equation with a nonhomogeneous boundary condition; the method is taken from Chapter 5.5 of O’Neil [216]. The equation and boundary conditions are

\[ u_t = u_{xx} \quad \text{(E.1)} \]

\[ u(x,0) = A \text{ for } x > 0 \quad \text{(E.2)} \]

\[ u(0,t) = f(t) \text{ (where } f(0) = A) \quad \text{(E.3)} \]

We begin by considering the same problem with a jump at the boundary at time \( t = t_0 \):

\[ u_t = u_{xx} \quad \text{(E.4)} \]

\[ u(x,0) = A \text{ for } x > 0 \quad \text{(E.5)} \]

\[ u(0,t) = \begin{cases} A & 0 < t < t_0 \\ B & t > t_0 \end{cases} \quad \text{(E.6)} \]

where \( A, B \) are positive constants. \( u(0,t) \) can be written with the Heaviside step function \( H(t) \) as

\[ u(0,t) = A(1 - H(t - t_0)) + BH(t - t_0) \quad \text{(E.7)} \]
The PDE (E.4)–(E.6) can be solved via Laplace transform. The Laplace transform of equation (E.4) is

\[ sU(x, s) - A = \partial_{xx} U(x, s) \]  

(E.8)

where \( U(x, s) = \mathcal{L} u(x, t) \). The general solution of equation (E.8), a constant-coefficient second order ODE for \( U \), is

\[ U(x, s) = a(s)e^{\sqrt{sx}} + b(s)e^{-\sqrt{sx}} + \frac{A}{s} \]  

(E.9)

We impose the condition \( a(s) = 0 \) because we would like the solution to be bounded as \( x \to \infty \). This leaves us to solve for \( b(s) \) using the boundary condition (equation (E.7)). The Laplace transform of equation (E.7) is

\[ \mathcal{L} u(0, t) = \frac{A}{s} - \frac{A}{s} e^{-t_0 s} + \frac{B}{s} e^{-t_0 s} \]  

(E.10)

using equation (E.10), \( b(s) \) can be solved to be

\[ b(s) = \frac{B - A}{s} e^{-t_0 s} \]  

(E.11)

giving us

\[ U(x, s) = \frac{B}{s} - \frac{A}{s} e^{-t_0 s}e^{-\sqrt{sx}} + \frac{A}{s} \]  

(E.12)

We can now take the inverse Laplace transform of equation (E.12) to obtain

\[ u(x, t) = A + (B - A) \text{erfc} \left( \frac{x}{2\sqrt{t - t_0}} \right) \]  

(E.13)

where \( \text{erfc}(z) = 1 - \text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty \exp x^2 \, dx \) is the complementary error function. In other words, the solution to the semi-infinite diffusion problem with a jump of \( \Delta u(0, t_0) \) relative to \( A \) at \( x = 0 \) and time \( t = t_0 \) is

\[ u(x, t) = A + \Delta u(0, t_0) \text{erfc} \left( \frac{x}{2\sqrt{t - t_0}} \right) \]  

(E.14)

Now, using Duhamel’s principle, we have for an arbitrary series of steps at \( t = t_i \) given by \( \Delta u(0, t_i) = f(t_i), \)

\[ u(x, t) = A + \sum_i \Delta f(t_i) \text{erfc} \left( \frac{x}{2\sqrt{t - t_i}} \right) \]  

(E.15)

where \( \Delta f(t_i) = f(t_{i+1}) - f(t_i) \). We can take the continuum limit with \( \Delta f(t_i) = \frac{df}{dt}(t_i) \Delta t_i \), where \( t_i < t_i < t_{i+1} \) to obtain

\[ u(x, t) = A + \int_0^t \frac{df}{dt}(t') \text{erfc} \left( \frac{x}{2\sqrt{t - t'}} \right) \, dt' \]  

(E.16)
and finally we can make the substitution $\tau = t - t'$ to write

$$u(x, t) = A - \int_t^0 \frac{df}{dt} (t - \tau) \text{erfc} \left( \frac{x}{2\sqrt{\tau}} \right) d\tau$$

$$= A + \int_0^t \frac{df}{dt} (t - \tau) \text{erfc} \left( \frac{x}{2\sqrt{\tau}} \right) d\tau$$  \hspace{1cm} (E.17)

Equation (E.17) may be numerically integrated. Alternatively, since the function we are interested in is $f(t) = e^{-St}$ and we wish to compute the resulting current $j = u_x(0, t)$, we can arrive at an analytical expression for $u_x(0, t)$,

$$u_x(x, t) = Se^{-St} \int_0^t e^{S\tau} e^{-x^2/4\tau} \frac{1}{\sqrt{\pi \tau}} d\tau$$  \hspace{1cm} (E.18)

$$u_x(0, t) = \sqrt{S}e^{-St} \text{erfi} \left( \sqrt{St} \right)$$  \hspace{1cm} (E.19)

where $\text{erfi}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp x^2 dx$ is the imaginary error function.
Appendix F

Matlab Code

This appendix contains the MATLAB code for the electrochemical model developed in this thesis. There are many different versions of this code, and the one presented here is one for a double electrode system, with temperature and surface coverage included. Also in this chapter is the code for the frequency sweep tool, which runs the double electrode model at different frequencies.

F.1 Double Electrode Code

F.1.1 concentration.m

centration.m is called by step.m to set up the matrices in order to time step the Nernst-Planck equation.

function [ c_new ] = concentration( z,dx,N1,N2,N3,N4,N5,dt_now,dt_old,D_0,D,lambda_s,nu,
                             j_left_now,j_right_now,j_left_old,j_right_old,c_now,phi_now,T_now,c_old,phi_old,T_old,
                             cp_now,cm_now,cp_old,cm_old )

%concentration.m
%creates c_new depending on value of z (+1 for cp, -1 for cm, etc)
%works for both types of concentrations
%j_left_(old/now) and j_right_(old/now) are calculated in step.m and passed in. They
%represent the values of the fluxes at the previous/current time.
w = dt_now/dt_old;
N = N1+N2+N3+N4+N5;

A = zeros(N,N);
b = zeros(N,1);

% set up A and b
for i = 2:N-1
    A(i,i-1) = -dt_now*D/D_0*2/(dx(i-1)*(dx(i)+dx(i-1)));
    A(i,i) = (1+2*w)/(1+w) + dt_now*D/D_0*2/(dx(i)*dx(i-1));
    A(i,i+1) = -dt_now*D/D_0*2/(dx(i)*(dx(i)+dx(i-1)));
    b(i) = (1+w)*c_now(i) - w^2/(1+w)*c_old(i) ...  
    + dt_now*(1+w)*D/D_0*( ( z*(c_now(i)+c_now(i+1))/(T_now(i)+T_now(i+1))* (phi_now(i+1) - 
                             phi_now(i))/dx(i) - z*(c_now(i)+c_now(i-1))/(T_now(i)+T_now(i-1))* (phi_now(i) - phi_now(i-1))/dx(i-1) ) / ((dx(i)+dx(i-1))/2) ...  
    + ((c_now(i+1)+c_now(i))/2*nu* ( (cp_now(i+1)-cp_now(i))/dx(i) + (cm_now(i+1)-cm_now(i))/dx(i) )/(1-nu* ( (cp_now(i+1)+cp_now(i))/2 + (cm_now(i+1)+cm_now(i))/2 ) ) - (c_now(i-1)+ 
                             c_now(i))/2*nu* ( (cp_now(i)-cp_now(i-1))/dx(i-1) + (cm_now(i)-cm_now(i-1))/dx(i-1) ) /((1-nu* ( (cp_now(i)+cp_now(i-1))/2 + (cm_now(i)+cm_now(i-1))/2 ))/((dx(i)+dx(i-1))/2) 
    ) ...  
    - dt_now*w*D/D_0* ( ( z*(c_old(i)+c_old(i+1))/(T_old(i)+T_old(i+1))* (phi_old(i+1) - 
                             phi_old(i))/dx(i) - z*(c_old(i)+c_old(i-1))/(T_old(i)+T_old(i-1))* (phi_old(i) - phi_old(i-1))/dx(i-1) ) / ((dx(i)+dx(i-1))/2) ...  
    + ((c_old(i+1)+c_old(i))/2*nu* ( (cp_old(i+1)-cp_old(i))/dx(i) + (cm_old(i+1)-cm_old(i))/dx(i) )/(1-nu* ( (cp_old(i+1)+cp_old(i))/2 + (cm_old(i+1)+cm_old(i))/2 ) ) - (c_old(i-1)+ 
                             c_old(i))/2*nu* ( (cp_old(i)-cp_old(i-1))/dx(i-1) + (cm_old(i)-cm_old(i-1))/dx(i-1) ) /((1-nu* ( (cp_old(i)+cp_old(i-1))/2 + (cm_old(i)+cm_old(i-1))/2 ))/((dx(i)+dx(i-1))/2) 
    )
end

% handle boundary conditions via ghost points.
% lhs
A(1,1) = (1+2*w)/(1+w) + dt_now/(dx(1)*(dx(1)/2));
A(1,2) = -dt_now/(dx(1)*(dx(1)/2));
Appendix F. Matlab Code

\[ b(1) = (1+w) \cdot c_{\text{now}}(1) - w^2/(1+w) \cdot c_{\text{old}}(1) \ldots \]
\[ + (1+w) \cdot dt_{\text{now}}/(dx(1)/2) \cdot D/D_0 \ast \left( \frac{z \ast (c_{\text{now}}(2)+c_{\text{now}}(1))}{(T_{\text{now}}(2)+T_{\text{now}}(1))} \ast (\phi_{\text{now}}(2) - \phi_{\text{now}}(1))/dx(1) \ldots \right) \]
\[ + \frac{(c_{\text{now}}(2)+c_{\text{now}}(1))}{2} \cdot nu \ast \left( \frac{(cp_{\text{now}}(2)-cp_{\text{now}}(1))}{dx(1)} + \frac{(cm_{\text{now}}(2)-cm_{\text{now}}(1))}{dx(1)} \right) / \left(1-nu \ast \left( \frac{(cp_{\text{now}}(2)+cp_{\text{now}}(1))}{2} + \frac{(cm_{\text{now}}(2)+cm_{\text{now}}(1))}{2} \right) \right) + j_{\text{left}_{\text{now}}} \ldots \]
\[ \right) \cdot \frac{w \cdot dt_{\text{now}}/(dx(1)/2) \ast D/D_0 \ast \left( \frac{z \ast (c_{\text{old}}(2)+c_{\text{old}}(1))}{(T_{\text{old}}(2)+T_{\text{old}}(1))} \ast (\phi_{\text{old}}(2) - \phi_{\text{old}}(1))/dx(1) \ldots \right) \]
\[ + \frac{(c_{\text{old}}(2)+c_{\text{old}}(1))}{2} \cdot nu \ast \left( \frac{(cp_{\text{old}}(2)-cp_{\text{old}}(1))}{dx(1)} + \frac{(cm_{\text{old}}(2)-cm_{\text{old}}(1))}{dx(1)} \right) / \left(1-nu \ast \left( \frac{(cp_{\text{old}}(2)+cp_{\text{old}}(1))}{2} + \frac{(cm_{\text{old}}(2)+cm_{\text{old}}(1))}{2} \right) \right) + j_{\text{left}_{\text{old}}} \ldots \]
\[ \right) \]
\%rhs
\[ A(N,N) = \frac{(1+2w)/(1+w) + dt_{\text{now}}/(dx(N-1) \ast (dx(N-1)/2))}; \]
\[ A(N,N-1) = -dt_{\text{now}}/(dx(N-1) \ast (dx(N-1)/2)); \]
\[ b(N) = (1+w) \cdot c_{\text{now}}(N) - w^2/(1+w) \cdot c_{\text{old}}(N) \ldots \]
\[ - (1+w) \cdot dt_{\text{now}}/(dx(N-1)/2) \cdot D/D_0 \ast \left( \frac{z \ast (c_{\text{now}}(N)+c_{\text{now}}(N))}{(T_{\text{now}}(N)+T_{\text{now}}(N))} \ast (\phi_{\text{now}}(N) - \phi_{\text{now}}(N-1))/dx(N-1) \ldots \right) \]
\[ + \frac{(c_{\text{now}}(N)+c_{\text{now}}(N-1))}{2} \cdot nu \ast \left( \frac{(cp_{\text{now}}(N)-cp_{\text{now}}(N-1))}{dx(N-1)} + \frac{(cm_{\text{now}}(N)-cm_{\text{now}}(N-1))}{dx(N-1)} \right) / \left(1-nu \ast \left( \frac{(cp_{\text{now}}(N)+cp_{\text{now}}(N-1))}{2} + \frac{(cm_{\text{now}}(N)+cm_{\text{now}}(N-1))}{2} \right) \right) + j_{\text{right}_{\text{now}}} \ldots \]
\[ \right) \cdot \frac{w \cdot dt_{\text{now}}/(dx(N-1)/2) \ast D/D_0 \ast \left( \frac{z \ast (c_{\text{old}}(N)+c_{\text{old}}(N))}{(T_{\text{old}}(N)+T_{\text{old}}(N))} \ast (\phi_{\text{old}}(N) - \phi_{\text{old}}(N-1))/dx(N-1) \ldots \right) \]
\[ + \frac{(c_{\text{old}}(N)+c_{\text{old}}(N-1))}{2} \cdot nu \ast \left( \frac{(cp_{\text{old}}(N)-cp_{\text{old}}(N-1))}{dx(N-1)} + \frac{(cm_{\text{old}}(N)-cm_{\text{old}}(N-1))}{dx(N-1)} \right) / \left(1-nu \ast \left( \frac{(cp_{\text{old}}(N)+cp_{\text{old}}(N-1))}{2} + \frac{(cm_{\text{old}}(N)+cm_{\text{old}}(N-1))}{2} \right) \right) + j_{\text{right}_{\text{old}}} \ldots \]
\[ \right) \]
\[ c_{\text{new}} = A \backslash b; \]
\[ \]
end

F.1.2 cur.m

cur.m defines the current as a function of time.

function \[ j \] = cur( t )
j=0;
end

F.1.3 errcomp.m

ercomp.m approximates the error at each time step.

function [ err ] = errcomp( step,dt_now,dt_old,cp_coarse,cm_coarse,T_coarse,phi_x_right_coarse,
    theta_left_coarse,theta_right_coarse,cp_fine,cm_fine,T_fine,phi_x_right_fine,
    theta_left_fine,theta_right_fine )
%errcomp.m
%computes error value based on richardson extrapolation
%step = 0 means first time step, step = 1 means subsequent steps
%make sure to set phi_x_right_coarse and phi_x_right_fine to 0 if using
%voltage boundary conditions

if step==0
    err=4/3*norm(cp_coarse-cp_fine);
else
    err=norm(cat(1,cp_coarse,cm_coarse,T_coarse,phi_x_right_coarse,theta_left_coarse,
        theta_right_coarse) ... -cat(1,cp_fine,cm_fine,T_fine,phi_x_right_fine,theta_left_fine,theta_right_fine))*8*(dt_old+
        dt_now)/(7*dt_old+5*dt_now);
end
end

F.1.4 extrapolate.m

extrapolate.m applies the extrapolation formula to go from the coarse and fine steps to the next time
step using a variable time step Richardson extrapolation formula.

function [ u_out ] = extrapolate( u_coarse,u_fine,dt_old,dt_now )
%extrapolation formula for a 2 step, 2nd order variable step scheme.
alpha=-(dt_old + 3*dt_now)/(7*dt_old + 5*dt_now);
beta=8*(dt_old + dt_now)/(7*dt_old + 5*dt_now);

u_out=alpha*u_coarse + beta*u_fine;

end

main.m is the main run script which contains the time stepping code, and contains calls to mesh.m which creates the mesh, step.m and poisson.m, which compute values of the variables at time $t + dt$, and errcomp.m and extrapolate.m, which perform error and Richardson extrapolation. Results are saved to a .mat file every $t_{save}$ time units.

**F.1.5 main.m**

```matlab
%main.m
%main script for battery model, Jan 2015, by Dave yan
%contains function calls to makemesh.m to set up geometry and also adaptive
%time stepping code which calls step.m, the main battery stepping function

clc;
clear;

start=tic;

%physical (i.e. not numerical) parameters script
parameters;

%type of boundary condition. bc=0 for current (set current in cur.m)
% bc=1 for voltage (set voltage in voltage.m)
bcc=0;

%set up geometry
N1=120;
```
N2=80;
N3=80;
N4=80;
N5=120;
N=N1+N2+N3+N4+N5;
L1=0.01;
L2=0.09;
L3=0.8;
L4=0.09;
L5=0.01;
%call my meshing function
[x,dx]=makemesh(N1,N2,N3,N4,N5,L1,L2,L3,L4,L5);

%set up timescale
n=1;
t(n)=0;
t_end=3;
dt=1e-6; %initial dt
t_save=0.01; %save every multiple of this parameter
%set up error tolerances for adaptive stepping
tol=1e-6;
range=tol/3;
% range=Inf;
dt_max=0.001; %biggest i'm willing to let dt get
%dt_max=Inf;
dt_min=1e-8; %smallest i'm willing to let dt get
c_max=25; %maximum number of convergence steps before i take dt=dt_min
eta_max=1.1; %eta_min dt_old < dt_new < eta_max dt_old
eta_min=0.9;
c=0; %convergence counter

%set up file name for saving
formatOut = 'mm_dd_yy';
date=datestr(now,formatOut);
file_name=sprintf('%s_eps=%g_delta=%g_D=%g_k=%g_endtime=%g.mat',date,epsilon_1,delta,D_p,
Appendix F. Matlab Code

% set up initial conditions
for i=1:N
    cp(i,n)=1;
    cm(i,n)=1;
    T(i,n)=1;
    debug1(i,n)=1;
end
phi_x_right(n)=0;
theta_left(n)=0;
theta_right(n)=0;
phi(:,n)=poisson1d(bc, dx,N1,N2,N3,N4,N5, lambda_s, epsilon_1,epsilon_2,epsilon_3,
                      epsilon_s_left,epsilon_s_right,cp(:,n),cm(:,n),z_cp,z_cm, phi_x_right(n),voltage(t(n)));

% coarse step
[ cp_coarse,cm_coarse,T_coarse,phi_x_right_coarse,theta_left_coarse,theta_right_coarse,
debug1_coarse = step(bc,t_now,dt,Inf,dx,N1,N2,N3,N4,N5,cp_now,cm_now,phi_now,T_now,
phi_x_right_now,theta_left_now,theta_right_now,ones(N,1),ones(N,1),zeros(N,1),ones(N,1)
0,0,0, lambda_s,D_0,D_p,D_m,kc_left,jr_left,kc_right,jr_right,epsilon_1,epsilon_2,
epsilonion_3,epsilon_s_left,epsilon_s_right,z_cp,z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,
h_right,T_amb,gamma_left,gamma_right,nu,frum);

%fine step
[ cp_half,cm_half,T_half,phi_x_right_half,theta_left_half,theta_right_half,debug1_half ] = step
(bc,t_now,dt/2,Inf,dx,N1,N2,N3,N4,N5,cp_now,cm_now,phi_now,T_now,phi_x_right_now,
theta_left_now,theta_right_now,ones(N,1),ones(N,1),zeros(N,1),ones(N,1),0,0,0, lambda_s,D_0
,D_p,D_m,kc_left,jr_left,kc_right,jr_right,epsilon_1,epsilon_2,epsilon_3,epsilon_s_left,
epsilon_s_right,z_cp,z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,h_right,T_amb,gamma_left,
gamma_right,nu,frum);

phi_half=poisson1d(bc, dx,N1,N2,N3,N4,N5, lambda_s, epsilon_1,epsilon_2,epsilon_3,
epsilonion_s_left,epsilon_s_right,cp_half,cm_half,z_cp,z_cm, phi_x_right_half,voltage(t_now+dt
/2));

[ cp_fine,cm_fine,T_fine,phi_x_right_fine,theta_left_fine,theta_right_fine,debug1_fine ] = step
(bc,t_now+dt/2,dt/2,dt/2,dx,N1,N2,N3,N4,N5,cp_half,cm_half,phi_half,T_half,phi_x_right_half
,theta_left_half,theta_right_half,cp_now,cm_now,phi_now,T_now,phi_x_right_now,
theta_left_now,theta_right_now, lambda_s,D_0,D_p,D_m,kc_left,jr_left,kc_right,jr_right,
epsilonion_1,epsilon_2,epsilon_3,epsilon_s_left,epsilon_s_right,z_cp,z_cm,k,a_left,a_1,a_2,a_3
,a_right,h_left,h_right,T_amb,gamma_left,gamma_right,nu,frum);

%evaluate error
err=errcomp( 0,dt,0,cp_coarse,cm_coarse,T_coarse,phi_x_right_coarse,theta_left_coarse,
theta_right_coarse,cp_fine,cm_fine,T_fine,phi_x_right_fine,theta_left_fine,theta_right_fine
);

while abs(err - tol)>range
  %take a stab at the new dt
  fac=(tol/err)^(.5);
  if fac > eta_max fac=eta_max;
  elseif fac < eta_min fac=eta_min;
  end
  dt=dt*fac;
  %If my calculated dt goes over dt_max, take a step with dt_max and exit
  %the loop.
  if dt>dt_max
dt=dt_max;

[ cp_coarse,cm_coarse,T_coarse,phi_x_right_coarse,theta_left_coarse,theta_right_coarse,
  debug1_coarse ] = step(bc,t_now,dt,Inf,dx,N1,N2,N3,N4,N5,cp_now,cm_now,phi_now,T_now,
  phi_x_right_now,theta_left_now,theta_right_now,ones(N,1),ones(N,1),ones(N,1),ones(N,
  1),0,0,0, lambda_s,D_0,D_p,D_m,kc_left,kr_left,kr_right,epsilon_1,
  epsilon_2,epsilon_s_left,epsilon_s_right,epsilon_s_right,z_cm,k,a_left,a_1,a_2,a_3,
  a_right,h_left,h_right,T_amb,frum );

[ cp_half,cm_half,T_half,phi_x_right_half,theta_left_half,theta_right_half,debug1_half ] =
step(bc,t_now,dt/2,Inf,dx,N1,N2,N3,N4,N5,cp_now,cm_now,phi_now,T_now,phi_x_right_now,
theta_left_now,theta_right_now,ones(N,1),ones(N,1),ones(N,1),ones(N,1),0,0,0,
lambda_s,D_0,D_p,D_m,kc_left,kr_left,kr_right,epsilon_1,
epsilon_2,epsilon_s_left,epsilon_s_right,epsilon_s_right,z_cm,k,a_left,a_1,a_2,a_3,
epsilon_s_right,a_right,h_left,h_right,T_amb,frum );

phi_half=poisson1d(bc, dx,N1,N2,N3,N4,N5, lambda_s, epsilon_1,epsilon_2,epsilon_3,
epsilon_s_left,epsilon_s_right,cp_half,cm_half,z_cm, phi_x_right_half,voltage(t_now+dt/2) );

[ cp_fine,cm_fine,T_fine,phi_x_right_fine,theta_left_fine,theta_right_fine,debug1_fine ] =
step(bc,t_now+dt/2,dt/2,dt/2,dx,N1,N2,N3,N4,N5,cp_half,cm_half,phi_half,T_half,
phi_x_right_half,theta_left_half,theta_right_half,ones(N,1),ones(N,1),ones(N,1),ones(N,1),
lambda_s,D_0,D_p,D_m,kc_left,kr_left,kr_right,epsilon_1,
epsilon_2,epsilon_s_left,epsilon_s_right,epsilon_s_right,z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,h_right,T_amb,frum );

break;
end

%coarse step

[ cp_coarse,cm_coarse,T_coarse,phi_x_right_coarse,theta_left_coarse,theta_right_coarse,
  debug1_coarse ] = step(bc,t_now,dt,Inf,dx,N1,N2,N3,N4,N5,cp_now,cm_now,phi_now,T_now,
  phi_x_right_now,theta_left_now,theta_right_now,ones(N,1),ones(N,1),ones(N,1),ones(N,1),
  0,0,0, lambda_s,D_0,D_p,D_m,kc_left,kr_left,kr_right,epsilon_1,epsilon_2,
  epsilon_3,epsilon_s_left,epsilon_s_right,epsilon_s_right,z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,h_right,T_amb,frum );

%fine step

[ cp_half,cm_half,T_half,phi_x_right_half,theta_left_half,theta_right_half,debug1_half ] =
step(bc,t_now,dt/2,Inf,dx,N1,N2,N3,N4,N5,cp_now,cm_now,phi_now,T_now,phi_x_right_now,
theta_left_now, theta_right_now, ones(N,1), ones(N,1), ones(N,1), ones(N,1), 0, 0, 0, lambda_s, D_0, D_p, D_m, kc_left, jr_left, kc_right, jr_right, epsilon_1, epsilon_2, epsilon_3, epsilon_s_left, epsilon_s_right, z_cp, z_cm, k, a_left, a_1, a_2, a_3, a_right, h_left, h_right, T_amb, gamma_left, gamma_right, nu, frum);

phi_half = poisson1d(bc, dx, N1, N2, N3, N4, N5, lambda_s, epsilon_1, epsilon_2, epsilon_3, epsilon_s_left, epsilon_s_right, cp_half, cm_half, z_cp, z_cm, phi_x_right_half, voltage(t_now + dt/2));

[ cp_fine, cm_fine, T_fine, phi_x_right_fine, theta_left_fine, theta_right_fine, debug1_fine ] = step(bc, t_now + dt/2, dt/2, dt/2, dx, N1, N2, N3, N4, N5, cp_half, cm_half, phi_half, T_half, phi_x_right_half, theta_left_half, theta_right_half, lambda_s, D_0, D_p, D_m, kc_left, jr_left, kc_right, jr_right, epsilon_1, epsilon_2, epsilon_3, epsilon_s_left, epsilon_s_right, z_cp, z_cm, k, a_left, a_1, a_2, a_3, a_right, h_left, h_right, T_amb, gamma_left, gamma_right, nu, frum);

% evaluate error
err = errcomp(0, dt, 0, cp_coarse, cm_coarse, T_coarse, phi_x_right_coarse, theta_left_coarse, theta_right_coarse, cp_fine, cm_fine, T_fine, phi_x_right_fine, theta_left_fine, theta_right_fine);

c = c + 1;

display(sprintf('err=%.3g,time=%.8f,dt=%.3g,c=%d', err, t_now, dt, c));

% perform richardson extrapolation
p = 1; % the first step with dt_old=Inf is equivalent to coarse/fine forward euler, p=1

cp_new = (2^p * cp_fine - cp_coarse) / (2^p - 1);

cm_new = (2^p * cm_fine - cm_coarse) / (2^p - 1);

T_new = (2^p * T_fine - T_coarse) / (2^p - 1);

phi_x_right_new = (2^p * phi_x_right_fine - phi_x_right_coarse) / (2^p - 1); % phi_x_right continues to be 0 for voltage boundary conditions

theta_left_new = (2^p * theta_left_fine - theta_left_coarse) / (2^p - 1);

theta_right_new = (2^p * theta_right_fine - theta_right_coarse) / (2^p - 1);

% solve for phi at this time level
phi_new = poisson1d(bc, dx, N1, N2, N3, N4, N5, lambda_s, epsilon_1, epsilon_2, epsilon_3,
%store values at fine half-step
cp_half_old=cp_half;
cm_half_old=cm_half;
T_half_old=T_half;
phi_x_right_half_old=phi_x_right_half;
phi_half_old=phi_half;
theta_left_half_old=theta_left_half;
theta_right_half_old=theta_right_half;

%advance time
cp_old=cp_now;
cm_old=cm_now;
T_old=T_now;
phi_x_right_old=phi_x_right_now;
phi_old=phi_now;
theta_left_old=theta_left_now;
theta_right_old=theta_right_now;
dt_old=dt;

cp_now=cp_new;
cm_now=cm_new;
T_now=T_new;
phi_x_right_now=phi_x_right_new;
phi_now=phi_new;
theta_left_now=theta_left_new;
theta_right_now=theta_right_new;

if t_now>=t_save*n;
    display('snapshot taken');
t(n+1)=t_now+dt;
    cp(:,n+1)=cp_new;
    cm(:,n+1)=cm_new;
end
\[ T(:,n+1) = T_{\text{new}}; \]
\[ \text{phi}_{\text{x right}}(n+1) = \text{phi}_{\text{x right new}}; \]
\[ \text{phi}(;n+1) = \text{phi}_{\text{new}}; \]
\[ \text{theta}_{\text{right}}(n+1) = \text{theta}_{\text{right new}}; \]
\[ \text{theta}_{\text{left}}(n+1) = \text{theta}_{\text{left new}}; \]
\[ [j_f(n+1), j_d(n+1), j(n+1), v(n+1)] = \text{postprocess}(bc, dx, N1, N2, N3, N4, N5, t(n+1), t_{\text{now}}, \text{cp}(;n+1), \text{cm}(;n+1), \text{phi}(;n+1), T(:,n+1), \text{phi}_{\text{x right}}(n+1), \text{theta}_{\text{left}}(n+1), \text{theta}_{\text{right}}(n+1), \lambda_s, D_0, D_p, D_m, k_{\text{c left}}, j_{\text{r left}}, k_{\text{c right}}, j_{\text{r right}}, \epsilon_1, \epsilon_2, \epsilon_3, \epsilon_{\text{s left}}, \epsilon_{\text{s right}}, z_{\text{cp}}, z_{\text{cm}}, k, a_{\text{left}}, a_1, a_2, a_3, a_{\text{right}}, h_{\text{left}}, h_{\text{right}}, T_{\text{amb}}, \gamma_{\text{left}}, \gamma_{\text{right}}, \nu, \text{frum}); \]
\[ \text{save}(\text{file name}, \text{cp}, \text{cm}, \text{phi}, j_f, j_d, j, v, t, x, T, \text{theta}_{\text{left}}, \text{theta}_{\text{right}}); \]
% print to file
n = n+1;
end

t_{\text{now}} = t_{\text{now}} + dt;

\% reset convergence counter

c = 0; %reset convergence counter

\% subsequent time steps

while t_{\text{now}} < t_{\text{end}} - \varepsilon

\% coarse step (with same dt as previous step)
\[ [\text{cp coarse}, \text{cm coarse}, T_{\text{coarse}}, \text{phi}_{\text{x right coarse}}, \text{theta}_{\text{left coarse}}, \text{theta}_{\text{right coarse}}, \text{debug coarse}] = \text{step}(bc, t_{\text{now}}, dt, dt_{\text{old}}, dx, N1, N2, N3, N4, N5, \text{cp now}, \text{cm now}, \text{phi now}, T_{\text{now}}, \text{phi}_{\text{x right now}}, \text{theta}_{\text{left now}}, \text{theta}_{\text{right now}}, \text{cp old}, \text{cm old}, \text{phi old}, T_{\text{old}}, \text{phi}_{\text{x right old}}, \text{theta}_{\text{left old}}, \text{theta}_{\text{right old}}, \lambda_s, D_0, D_p, D_m, k_{\text{c left}}, j_{\text{r left}}, k_{\text{c right}}, j_{\text{r right}}, \epsilon_1, \epsilon_2, \epsilon_3, \epsilon_{\text{s left}}, \epsilon_{\text{s right}}, z_{\text{cp}}, z_{\text{cm}}, k, a_{\text{left}}, a_1, a_2, a_3, a_{\text{right}}, h_{\text{left}}, h_{\text{right}}, T_{\text{amb}}, \gamma_{\text{left}}, \gamma_{\text{right}}, \nu, \text{frum}); \]

\% fine step (with same dt as previous step)
\[ [\text{cp half}, \text{cm half}, T_{\text{half}}, \text{phi}_{\text{x right half}}, \text{theta}_{\text{left half}}, \text{theta}_{\text{right half}}, \text{debug half}] = \text{step}(bc, t_{\text{now}}, dt/2, (dt_{\text{old}})/2, dx, N1, N2, N3, N4, N5, \text{cp now}, \text{cm now}, \text{phi now}, T_{\text{now}}, \text{phi}_{\text{x right now}}, \text{theta}_{\text{left now}}, \text{theta}_{\text{right now}}, \text{cp half old}, \text{cm half old}, \text{phi half old}, T_{\text{half old}}, \text{phi}_{\text{x right half old}}, \text{theta}_{\text{left half old}}, \text{theta}_{\text{right half old}}, \lambda_s, D_0, D_p, D_m, k_{\text{c left}}, j_{\text{r left}}, k_{\text{c right}}, j_{\text{r right}}, \epsilon_1, \epsilon_2, \epsilon_3, \epsilon_{\text{s left}}, \epsilon_{\text{s right}}, z_{\text{cp}}, z_{\text{cm}}, k, a_{\text{left}}, a_1, a_2, a_3, a_{\text{right}}, h_{\text{left}}, h_{\text{right}}, T_{\text{amb}}, \gamma_{\text{left}}, \gamma_{\text{right}}, \nu, \text{frum}); \]
Appendix F. Matlab Code

epsilon_s_right,z_cp,z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,h_right,T_amb,\gamma_left,\nu,frum);
phi_half=poisson1d(bc, dx,N1,N2,N3,N4,N5, lambda_s, epsilon_1,epsilon_2,epsilon_3,
epsilon_s_left,epsilon_s_right,cp_half,cm_half,z_cp,z_cm, phi_x_right_half,voltage(
t_now+dt/2));
[ cp_fine,cm_fine,T_fine,phi_x_right_fine,theta_left_fine,theta_right_fine,debug1_fine ] =
step(bc,t_now+dt/2,dt/2,dt/2,dx,N1,N2,N3,N4,N5,cp_half,cm_half,phi_half,T_half,
phi_x_right_half,theta_left_half,theta_right_half,cp_now,cm_now,phi_now,T_now,
phi_x_right_now,theta_left_now,theta_right_now, lambda_s,D_0,D_p,D_m,kc_left,jr_left,
kc_right,jr_right,epsilon_1,epsilon_2,epsilon_3,epsilon_s_left,epsilon_s_right,z_cp,
z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,h_right,T_amb,\gamma_left,\gamma_right,\nu,frum );

%evaluate error
err=errcomp( 1,dt,dt_old,cp_coarse,cm_coarse,T_coarse,phi_x_right_coarse,theta_left_coarse,
theta_right_coarse,cp_fine,cm_fine,T_fine,phi_x_right_fine,theta_left_fine,
theta_right_fine );
while abs(err - tol)>range
  %take a stab at the new dt
  fac=(tol/err)^(1/(5));
  if fac > eta_max fac=eta_max;
  elseif fac < eta_min fac=eta_min;
  end
  dt=dt*fac;
  %If my calculated dt goes over dt_max, take a step with dt_max and exit
  %the loop.
  if dt>=dt_max
    dt=dt_max;
    [ cp_coarse,cm_coarse,T_coarse,phi_x_right_coarse,theta_left_coarse,
      theta_right_coarse,debug1_coarse ] = step(bc,t_now,dt,dt_old,dx,N1,N2,N3,N4,N5,
      cp_now,cm_now,phi_now,T_now,phi_x_right_now,theta_left_now,theta_right_now,
      cp_old,cm_old,phi_old,T_old,phi_x_right_old,theta_left_old,theta_right_old,
      lambda_s,D_0,D_p,D_m,kc_left,jr_left,kc_right,jr_right,epsilon_1,epsilon_2,
      epsilon_3,epsilon_s_left,epsilon_s_right,z_cp,z_cm,k,a_left,a_1,a_2,a_3,a_right,
      h_left,h_right,T_amb,\gamma_left,\gamma_right,nu,frum );
    [ cp_half,cm_half,T_half,phi_x_right_half,theta_left_half,theta_right_half,
      ...] = step(bc,t_now,dt,dt_old,dx,N1,N2,N3,N4,N5, ... );
Appendix F. Matlab Code

```matlab
debug1_half ] = step(bc,t_now,dt/2,(dt_old)/2,dx,N1,N2,N3,N4,N5,cp_now,cm_now,
phi_now,T_now,phi_x_right_now,theta_left_now,theta_right_now,cp_half_old,
phi_half,T_half_old,phi_x_right_half_old,theta_left_half_old,
theta_right_half_old, lambda_s,D_0,D_p,D_m,kc_left,kr_left,kr_right,
epsilon_1,epsilon_2,epsilon_3,epsilon_s_left,epsilon_s_right,z_cp,z_cm,k,a_left,
a_1,a_2,a_3,a_right,h_left,h_right,T,amb,gamma_left,gamma_right,nu,frum);
phi_half=poisson1d(bc, dx,N1,N2,N3,N4,N5, lambda_s, epsilon_1,epsilon_2,epsilon_3,
epsilon_s_left,epsilon_s_right,cp_half,cm_half,z_cp,z_cm, phi_x_right_half,
voltage(t_now+dt/2) );
[ cp_fine,cm_fine,T_fine,phi_x_right_fine,theta_left_fine,theta_right_fine,
debug1_fine ] = step(bc,t_now+dt/2,dt/2,dt/2,dx,N1,N2,N3,N4,N5,cp_half,cm_half,
phi_half,T_half,phi_x_right_half,theta_left_half,theta_right_half,cp_now,cm_now,
phi_now,T_now,phi_x_right_now,theta_left_now,theta_right_now,cp_old,cm_old,
phi_old,T_old, phi_x_right_old,theta_left_old,theta_right_old, lambda_s,D_0,D_p,D_m,kc_left,
kr_left,kr_right,epsilon_1,epsilon_2,epsilon_3,epsilon_s_left,epsilon_s_right,z_cp,
z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,h_right,T,amb,gamma_left,gamma_right,nu,
frum );
break;
end
%coarse step (with same dt as previous step)
[ cp_coarse,cm_coarse,T_coarse,phi_x_right_coarse,theta_left_coarse,theta_right_coarse,
debug1_coarse ] = step(bc,t_now,dt,dt_old,dx,N1,N2,N3,N4,N5,cp_now,cm_now,phi_now,
phi_x_right_now,theta_left_now,theta_right_now,cp_old,cm_old,phi_old,T_old,
phi_x_right_old,theta_left_old,theta_right_old, lambda_s,D_0,D_p,D_m,kc_left,
kr_left,kr_right,epsilon_1,epsilon_2,epsilon_3,epsilon_s_left,epsilon_s_right,z_cp,
z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,h_right,T,amb,gamma_left,gamma_right,nu,
frum );
%fine step (with same dt as previous step)
[ cp_half,cm_half,T_half,phi_x_right_half,theta_left_half,theta_right_half,debug1_half ]
= step(bc,t_now,dt/2,(dt_old)/2,dx,N1,N2,N3,N4,N5,cp_now,cm_now,phi_now,T_now,
phi_x_right_now,theta_left_now,theta_right_now,cp_half,cm_half,phi_half,T_half,
phi_x_right_half_old,theta_left_half_old,theta_right_half_old, lambda_s,
D_0,D_p,D_m,kc_left,kr_left,kr_right,epsilon_1,epsilon_2,epsilon_3,epsilon_s_left,epsilon_s_right,z_cp,
z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,h_right,T,amb,gamma_left,gamma_right,nu,frum);
phi_half=poisson1d(bc, dx,N1,N2,N3,N4,N5, lambda_s, epsilon_1,epsilon_2,epsilon_3,
```
epsilon_s_left,epsilon_s_right,cp_half,cm_half,z_cp,z_cm, phi_x_right_half,voltage(t_now+dt/2) );
[ cp_fine,cm_fine,T_fine,phi_x_right_fine,theta_left_fine,theta_right_fine,debug1_fine ]
= step(bc,t_now+dt/2,dt/2,dt/2,dx,N1,N2,N3,N4,N5,cp_half,cm_half,phi_half,T_half,
phi_x_right_half,theta_left_half,theta_right_half,cp_now,cm_now,phi_now,T_now,
phi_x_right_now,theta_left_now,theta_right_now, lambda_s,D_0,D_p,D_m,kc_left,jr_left
,kc_right,jr_right,epsilon_1,epsilon_2,epsilon_3,epsilon_s_left,epsilon_s_right,z_cp
,z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,h_right,T_amb,gamma_left,gamma_right,nu,
frum );
%evaluate error
err=errcomp( 1,dt,dt_old,cp_coarse,cm_coarse,T_coarse,phi_x_right_coarse,
theta_left_coarse,theta_right_coarse,cp_fine,cm_fine,T_fine,phi_x_right_fine,
theta_left_fine,theta_right_fine );
c=c+1;
%display(sprintf('n=%d,err=%.3g,time=%.3g,dt=%.3g,c=%d',n,err,t(n),dt,c));
end
display(sprintf('err=%.3g,time=%.8f,dt=%.3g,c=%d',err,t_now,dt,c));
%extrapolate using extrapolation formula
cp_new = extrapolate(cp_coarse,cp_fine, dt,dt_old);
cm_new = extrapolate(cm_coarse,cm_fine, dt,dt_old);
T_new = extrapolate(T_coarse,T_fine, dt,dt_old);
phi_x_right_new=extrapolate(phi_x_right_coarse,phi_x_right_fine, dt,dt_old); %phi_x_right continues to be 0 for voltage boundary conditions
theta_left_new=extrapolate(theta_left_coarse,theta_left_fine, dt,dt_old);
theta_right_new=extrapolate(theta_right_coarse,theta_right_fine, dt,dt_old);
%solve for phi at this time level
phi_new = poisson1d( bc,dx,N1,N2,N3,N4,N5, lambda_s, epsilon_1,epsilon_2,epsilon_3,
epsilon_s_left,epsilon_s_right,cp_new,cm_new,z_cp,z_cm, phi_x_right_new,voltage(t_now+
dt) );

cp_half_old=cp_half;
cm_half_old=cm_half;
Appendix F. Matlab Code

T_half_old=T_half;
phi_x_right_half_old=phi_x_right_half;
phi_half_old=phi_half;
theta_left_half_old=theta_left_half;
theta_right_half_old=theta_right_half;

% advance time
cp_old=cp_now;
cm_old=cm_now;
T_old=T_now;
phi_x_right_old=phi_x_right_now;
phi_old=phi_now;
theta_left_old=theta_left_now;
theta_right_old=theta_right_now;
dt_old=dt;

cp_now=cp_new;
cm_now=cm_new;
T_now=T_new;
phi_x_right_now=phi_x_right_new;
phi_now=phi_new;
theta_left_now=theta_left_new;
theta_right_now=theta_right_new;

if t_now>=t_save*n;
    display('snapshot taken');
t(n+1)=t_now+dt;
    cp(:,n+1)=cp_new;
    cm(:,n+1)=cm_new;
    T(:,n+1)=T_new;
    phi_x_right(n+1)=phi_x_right_new;
    phi(:,n+1)=phi_new;
    theta_right(n+1)=theta_right_new;
theta_left(n+1)=theta_left_new;
[j_f(n+1),j_d(n+1),j(n+1),v(n+1)]=postprocess(bc,dx,N1,N2,N3,N4,N5,t(n+1),t_now,cp(:,n+1),cm(:,n+1),phi(:,n+1),phi_old,T(:,n+1),phi_x_right(n+1),theta_left(n+1),theta_right(n+1),lambda_s,D_0,D_p,D_m,kc_left,jr_left,kc_right,jr_right,epsilon_1,epsilon_2,epsilon_3,epsilon_s_left,epsilon_s_right,z_cp,z_cm,k,a_left,a_1,a_2,a_3,a_right,h_left,h_right,T_amb,gamma_left,gamma_right,frum);
save(file_name,'cp','cm','phi','j_f','j_d','j','v','t','x','T','theta_left','theta_right'); %print to file
n=n+1;
end

t_now=t_now+dt;
c=0; %reset convergence counter
end

%print runtime
runtime=toc(start);
fprintf('Runtime: %d minutes and %f seconds\n',floor(runtime/60),rem(runtime,60));

F.1.6 makemesh.m

Creates the mesh in one dimension.

function [x,dx]=makemesh(N1,N2, N3,N4,N5, L1, L2, L3,L4,L5)
%makemesh.m
%takes in N1, N2, N3, the number of desired elements in each region and L1, L2, L3, the lengths of each region
%returns dx, the vector of mesh widths and x, the mesh vector

t1=linspace(1,N1,N1);
t2=linspace(N1+1,N1+N2,N2);
t3=linspace(N1+N2+1,N1+N2+N3,N3);
t4=linspace(N1+N2+N3+1,N1+N2+N3+N4, N4);
t5=linspace(N1+N2+N3+N4+1, N1+N2+N3+N4+N5, N5);
Appendix F. Matlab Code

%piecewise linear mesh
x=zeros(N1+N2+N3,1);
x(1:N1) = L1*(t1-1)/(N1-1);
x(N1+1:N1+N2) = L2*(t2-N1)/N2 + L1;
x(N1+N2+1:N1+N2+N3) = L3*(t3-N1-N2)/N3+L1+L2;
x(N1+N2+N3+1:N1+N2+N3+N4)= L4*(t4-N1-N2-N3)/N4 + L1+L2+L3;
x(N1+N2+N3+N4+1:N1+N2+N3+N4+N5)= L5*(t5-N1-N2-N3-N4)/N5 + L1+L2+L3+L4;

%straight up linear, debug
N=N1+N2+N3;
t=linspace (1,N,N);
x=t/N;

dx=diff(x);

end

F.1.7 parameters.m

Defines constant parameters used in the code.

%defines constants as a script called in main.m

%nondimensionalized species transport coefficients
D_0=1;
D_p=1;
D_m=1;

kc_left=50; %butler-volmer charge transfer constants
jr_left=100;
kc_right=100;
jr_right=50;

qs=1;
frum=0;

gamma_left=1/qs; \%coefficients for surface coverage. higher gamma means same current causes faster rise in theta

gamma_right=1/qs;

\%nondimensionalized electrical and polarization coefficients
delta=1;
epsilon=.001; \%bulk epsilon

epsilon_1=epsilon;
epsilon_2=epsilon;
epsilon_3=epsilon;
epsilon_s_left=epsilon;
epsilon_s_right=epsilon;

\%nondimensionalized steric parameter

\%nondimensionalized temperature coefficients
k=1;
a_left=.1; \%coefficient in front of JE for the left stern plane
a_1 = .1; \%coefficients in front of JE for the bulk
a_2 = .1;
a_3 = .1;
a_right=.1; \%coefficient in front of JE for the right stern plane
h_left=1; \%coefficients for temperature boundary condition
h_right=1;
T_amb=1; \%nondimensionalized ambient temperature
F.1.8 poisson1d.m

Solves the 1D Poisson equation subject to different boundary conditions. Here the Robin boundary condition
\[ \lambda_s \frac{\partial \phi}{\partial x} = \phi_{\text{electrode}} - \phi_{\text{stern}} \]  

is used.

function [ phi ] = poisson1d(bc, dx,N1,N2,N3, N4, N5, lambda_s, epsilon_1,epsilon_2,epsilon_3,
                epsilon_s_left,epsilon_s_right,cp,cm,z_cp,z_cm, phi_x_right,v )

%poisson1d.m
%1d poisson solver
%solves epsilon^2 d^2 phi/dx^2 = -1/2 sum_i(c_i)
%internal boundary conditions epsilon_1^2 phi_x_N1 = epsilon_2^2 phi_x_N1+1
%and epsilon_2^2 phi_x_(N1+N2) = epsilon_3^2 phi_x_(N1+N2+1)
%boundary condition epsilon_s_left^2 (phi_1 - 0) = epsilon_1^2 phi_x_1
%and either epsilon_s_right^2 phi_x_right = epsilon_3^2 phi_x_N for current
%boundary conditions or epsilon_s_right^2 (v - phi_N)/(lambda_s) =
%epsilon_3^2 phi_x_N for voltage boundary conditions
%takes geometry vectors and constants, some polarization parameters, the
%cp and cm vectors, and phi_x_right and v for boundary conditions (but only
%uses one of the two depending on the 'bc' flag)

N=N1+N2+N3+N4+N5;

A = zeros(N,N);
b = zeros(N,1);

%set up A and b
A(1,1) = -(2*dx(1)+dx(2))/(dx(1)*(dx(1)+dx(2))) - epsilon_s_left^2/(lambda_s*epsilon_1^2);
A(1,2) = (dx(1)+dx(2))/(dx(1)*dx(2));
A(1,3) = -dx(1)/(dx(2)*(dx(1)+dx(2)));
b(1) = 0;

for i=2:N1-1
    A(i,i-1)=2/(dx(i-1)*(dx(i)+dx(i-1)));

end
A(i,i) = -2/(dx(i)*dx(i-1));
A(i,i+1) = 2/(dx(i)*(dx(i)+dx(i-1)));
b(i) = -1/(2*epsilon_1^2)*(z_cp*cp(i) + z_cm*cm(i));
end
A(N1, N1-2) = epsilon_1^2*dx(N1-1)/(dx(N1-2)*(dx(N1-2)+dx(N1-1)));
A(N1, N1-1) = -epsilon_1^2*(dx(N1-2)+dx(N1-1))/(dx(N1-2)*dx(N1-1));
A(N1, N1) = epsilon_1^2*(2*dx(N1-1)+dx(N1-2))/(dx(N1-1)*(dx(N1-2)+dx(N1-1))) ... 
+ epsilon_2^2*(2*dx(N1)+dx(N1+1))/(dx(N1)*(dx(N1)+dx(N1+1)));
A(N1, N1+1) = - epsilon_2^2*(dx(N1)+dx(N1+1))/(dx(N1)*dx(N1+1));
A(N1, N1+2) = epsilon_2^2 * (dx(N1))/(dx(N1+1)*(dx(N1)+dx(N1+1)));
b(N1)=0;
for i=N1+1:N1+N2+N3+N4-1
   A(i,i-1) = 2/(dx(i-1)*(dx(i)+dx(i-1)));
   A(i,i) = -2/(dx(i)*dx(i-1));
   A(i,i+1) = 2/(dx(i)*(dx(i)+dx(i-1)));
   b(i) = -1/(2*epsilon_2^2)*(z_cp*cp(i) + z_cm*cm(i));
end
A(N1+N2+N3+N4,N1+N2+N3+N4-2) = epsilon_2^2*(dx(N1+N2+N3+N4-1))/(dx(N1+N2+N3+N4-2)*(dx(N1+N2+N3+N4-2)+dx(N1+N2+N3+N4-1)));
A(N1+N2+N3+N4,N1+N2+N3+N4-1) = -epsilon_2^2*(dx(N1+N2+N3+N4-2)+dx(N1+N2+N3+N4-1))/(dx(N1+N2+N3+N4-2)*dx(N1+N2+N3+N4-1));
A(N1+N2+N3+N4,N1+N2+N3+N4) = epsilon_2^2*(2*dx(N1+N2+N3+N4-1)+dx(N1+N2+N3+N4-2))/(dx(N1+N2+N3+N4-1)*(dx(N1+N2+N3+N4-2) + dx(N1+N2+N3+N4-1))) ... 
+ epsilon_3^2*(2*dx(N1+N2+N3+N4) + dx(N1+N2+N3+N4+1))/(dx(N1+N2+N3+N4)*dx(N1+N2+N3+N4+1));
A(N1+N2+N3+N4,N1+N2+N3+N4+1) = -epsilon_3^2*(dx(N1+N2+N3+N4) + dx(N1+N2+N3+N4+1))/(dx(N1+N2+N3+N4)*dx(N1+N2+N3+N4+1));
A(N1+N2+N3+N4,N1+N2+N3+N4+2) = epsilon_3^2*(dx(N1+N2+N3+N4))/(dx(N1+N2+N3+N4+1)*(dx(N1+N2+N3+N4+1)*dx(N1+N2+N3+N4+1)));
b(N1+N2+N3+N4)=0;
for i=N1+N2+N3+N4+1:N-1
   A(i,i-1) = 2/(dx(i-1)*(dx(i)+dx(i-1)));
   A(i,i) = -2/(dx(i)*dx(i-1));
   A(i,i+1) = 2/(dx(i)*(dx(i)+dx(i-1)));
   b(i) = -1/(2*epsilon_3^2)*(z_cp*cp(i) + z_cm*cm(i));
end
% for i=2:N-1
% A(i,i-1) = 2/(dx(i-1)*(dx(i)+dx(i-1)));
% A(i,i) = -2/(dx(i)*dx(i-1));
% A(i,i+1) = 2/(dx(i)*(dx(i)+dx(i-1)));
% b(i) = -1/(2*epsilon_1^2)*(z_cp*cp(i) + z_cm*cm(i));
% end

if bc==0 %current
A(N,N) = (2*dx(N-1)+dx(N-2))/(dx(N-1)*(dx(N-1)+dx(N-2)));
A(N,N-1) = -(dx(N-2)+dx(N-1))/(dx(N-2)*dx(N-1));
A(N,N-2) = dx(N-1)/(dx(N-2)*(dx(N-1)+dx(N-2)));
b(N) = epsilon_s_right^2/epsilon_3^2*phi_x_right;
else %voltage
A(N,N) = (2*dx(N-1)+dx(N-2))/(dx(N-1)*(dx(N-1)+dx(N-2))) + epsilon_s_right^2/(epsilon_3^2*lambda_s);
A(N,N-1) = -(dx(N-2)+dx(N-1))/(dx(N-2)*dx(N-1));
A(N,N-2) = dx(N-1)/(dx(N-2)*(dx(N-1)+dx(N-2)));
b(N) = epsilon_s_right^2/(epsilon_3^2*lambda_s)*v;
end

%compute phi
phi = A \ b;

end

F.1.9 postprocess.m

Called every t save time units in main.m to compute postprocessed values (current when using voltage boundary conditions and voltage when using current boundary conditions). Note that the code for surface coverage is not included in this version of postprocess.m.

function [ j_f, j_d, j, v ] = postprocess( bc,dx,N1,N2,N3,N4,N5,t,t_old,cp,cm,phi,phi_old,T,
                               phi_x_right,theta_left,theta_right,lambda_s,D_0,D_p,D_m,kc_left,jr_left,kc_right,jr_right,
Appendix F. Matlab Code

epsilon_1, epsilon_2, epsilon_3, epsilon_s_left, epsilon_s_right, z_cp, z_cm, k, a_left, a_1, a_2, a_3, a_right, h_left, h_right, T_amb, gamma_left, gamma_right, frum)

%postprocess for either j or v depending on the boundary conditions.
%remember that dx and t aren’t uniform.

N=N1+N2+N3+N4+N5;
if bc==0
    v=phi(N) + epsilon_3^2/epsilon_s_right^2*lambda_s*phi_x_right;
    j=cur(t);
    j_f=0;
    j_d=0;
else
    jpr_now = 4*kc_right*cp(N)*exp(-(voltage(t)-phi(N))/(2*T(N)))... - 4*jr_right*exp((voltage(t)-phi(N))/(2*T(N)));
    jmr_now = 0;
    v=voltage(t);
    j_f=(z_cp*jpr_now + z_cm*jmr_now)/4;
    j_d=- epsilon_s_right^2/(2*(t-t_old))*((voltage(t) - phi(N))/lambda_s - (voltage(t_old) - phi_old(N))/lambda_s);
    j=j_f+j_d;
end
end

F.1.10 step.m

Main function to take an arbitrary sized time step using a variable step size second order backwards differentiation formula. Calls temperature.m and concentration.m to compute those matrices, and computes the stepped value of phi_x_right if current boundary conditions are used.

function [ cp_new, cm_new, T_new, phi_x_right_new, theta_left_new, theta_right_new, debug1 ] = step(bc,t,dt_now,dt_old,dx,N1,N2,N3,N4,N5,cp_now,cm_now,phi_now,T_now,phi_x_right_now,theta_left_now,theta_right_now,cp_old,cm_old,phi_old,T_old,phi_x_right_old,theta_left_old,theta_right_old,lambda_s,D_0,D_p,D_m,kc_left,jr_left,kc_right,jr_right,epsilon_1,epsilon_2,epsilon_3,epsilon_s_left,epsilon_s_right, z_cp, z_cm, k, a_left, a_1, a_2, a_3, a_right, h_left,
% appendf.m

function [ w ] = appendf( h_right, T_amb, gamma_left, gamma_right, nu, frum )

%Steps the vectors cp, cm, phi, T and phi_x_right to the next time step.
%Uses a variable step size, nonuniform mesh implicit-explicit BDF time
%stepper for the concentrations, temperature and phi_x, and an O(dx^2)
%Poisson solver for phi.
%
%bc: 1 for voltage boundary conditions, 0 for current boundary conditions
%t: current time (scalar)
%dt_now: current time step (i.e. t[n+1] = t[n] + dt_now)
%dt_old: previous time step (i.e. t[n] = t[n-1] + dt_old)
%dx, N1,N2,N3: N-1 length vector of mesh widths (vector) and numbers of
%meshes in each region
%<vector>_now: N length vectors (or scalar for phi_x_right) holding current
%values in time
%<vector>_old: N length vectors (or scalar for phi_x_right) holding
%previous values in time (that is, at t[n] - dt_old)

w = dt_now/dt_old;  %omega_(n)
N=N1+N2+N3+N4+N5;
dbg1=zeros(N,1);

%handle stepping of phi_x_right (for current boundary conditions)
%and handle calculations of BV_left and BV_right

if bc==0  %for current boundary conditions
    BV_left_now = 4*kc_left*(1-theta_left_now)*cp_now(1)*exp(phi_now(1)/(2*T_now(1))) ...
                  - 4*jr_left*theta_left_now*exp(-frum*(1-2*theta_left_now))*exp(-phi_now(1)/(2*T_now(1)))
    BV_right_now = 4*kc_right*(1-theta_right_now)*cp_now(N)*exp(-lambda_s*phi_x_right_now/(2*T_now(N))) ...
                   - 4*jr_right*theta_right_now*exp(-frum*(1-2*theta_right_now))*exp(lambda_s*
                       phi_x_right_now/(2*T_now(N)));
    j_p_left_now=-BV_left_now;
end
j_m_left_now=0;
j_p_right_now = BV_right_now;
j_m_right_now=0;
BV_left_old = 4*kc_left*(1-theta_left_old)*cp_old(1)*exp(phi_old(1)/(2*T_old(1))) ...
   - 4*jr_left*theta_left_old*exp(-frum*(1-2*theta_left_old))exp(-phi_old(1)/(2*T_old(1)))
   
   BV_right_old = 4*kc_right*(1-theta_right_old)*cp_old(N)*exp(-lambda_s*phi_x_right_old/(2*T_old(N))) ...
   - 4*jr_right*theta_right_old*exp(-frum*(1-2*theta_right_old))exp(lambda_s*
     phi_x_right_old/(2*T_old(N)));
j_p_left_old=-BV_left_old;
j_m_left_old=0;
j_p_right_old = BV_right_old;
j_m_right_old=0;

phi_x_right_new=(1+w)^2/(1+2*w)*phi_x_right_now - w^2/(1+2*w)*phi_x_right_old ...
   - 2*dt_now/epsilon_s_right^2*(1+w)/(1+2*w)*( cur(t+dt_now) ...
   - (1+w)/4*(z_cp*j_p_right_now + z_cm*j_m_right_now) + w/4*(z_cp*j_p_right_old + z_cm*
     j_m_right_old) )

elseif bc==1

BV_left_now = 4*kc_left*(1-theta_left_now)*cp_now(1)*exp(phi_now(1)/(2*T_now(1))) ...
   - 4*jr_left*theta_left_now*exp(-frum*(1-2*theta_left_now))exp(-phi_now(1)/(2*T_now(1)))
   
   BV_right_now = 4*kc_right*(1-theta_right_now)*cp_now(N)*exp(-(voltage(t)-phi_now(N))/(2*T_now(N))) ...
   - 4*jr_right*theta_right_now*exp(-frum*(1-2*theta_right_now))exp((voltage(t)-phi_now(N)
     )/(2*T_now(N)));
j_p_left_now=-BV_left_now;
j_m_left_now=0;
j_p_right_now = BV_right_now;
j_m_right_now=0;

BV_left_old = 4*kc_left*(1-theta_left_old)*cp_old(1)*exp(phi_old(1)/(2*T_old(1))) ...
   - 4*jr_left*theta_left_old*exp(-frum*(1-2*theta_left_old))exp(-phi_old(1)/(2*T_old(1)))
   
;
BV_right_old = 4*kc_right*(1-theta_right_old)*cp_old(N)*exp(-(voltage(t-dt_old)-phi_old(N)) / (2*T_old(N))) ... 
- 4*jr_right*theta_right_old*exp(-frum*(1-2*theta_right_old))*exp((voltage(t-dt_old)-phi_old(N))/(2*T_old(N))));

j_p_left_old=-BV_left_old;
j_m_left_old=0;
j_p_right_old = BV_right_old;
j_m_right_old=0;
phi_x_right_new=0;
end

%without theta's
% if bc==0 %for current boundary conditions
% BV_left_now = 4*kc_left*cp_now(1)*exp(phi_now(1)/(2*T_now(1))) ... 
% - 4*jr_left*exp(-phi_now(1)/(2*T_now(1)));
% BV_right_now = 4*kc_right*cp_now(N)*exp(-lambda_s*phi_x_right_now/(2*T_now(N))) ... 
% - 4*jr_right*exp(lambda_s*phi_x_right_now/(2*T_now(N)));
% j_p_left_now=-BV_left_now;
% j_m_left_now=0;
% j_p_right_now = BV_right_now;
% j_m_right_now=0;
% BV_left_old = 4*kc_left*cp_old(1)*exp(phi_old(1)/(2*T_old(1))) ... 
% - 4*jr_left*exp(-phi_old(1)/(2*T_old(1)));
% BV_right_old = 4*kc_right*cp_old(N)*exp(-lambda_s*phi_x_right_old/(2*T_old(N))) ... 
% - 4*jr_right*exp(lambda_s*phi_x_right_old/(2*T_old(N)));
% j_p_left_old=-BV_left_old;
% j_m_left_old=0;
% j_p_right_old = BV_right_old;
% j_m_right_old=0;
%
% phi_x_right_new=(1+w)^2/(1+2*w)*phi_x_right_now - w^2/(1+2*w)*phi_x_right_old ... 
% - 2*dt_now/epsilon_s_right^2*(1+w)/(1+2*w)*( cur(t+dt_now) ... 
% - (1+w)/4*(z_cp*j_p_right_now + z_cm*j_m_right_now) + w/4*(z_cp*j_p_right_old + z_cm* 
% j_m_right_old) );
% elseif bc==1
%   BV_left_now = 4*kc_left*cp_now(1)*exp(phi_now(1)/(2*T_now(1))) ...
%           - 4*jr_left*exp(-phi_now(1)/(2*T_now(1)));
%   BV_right_now = 4*kc_right*cp_now(N)*exp(-(voltage(t)-phi_now(N))/(2*T_now(N))) ...
%           - 4*jr_right*exp((voltage(t)-phi_now(N))/(2*T_now(N)));
%   j_p_left_now=-BV_left_now;
%   j_m_left_now=0;
%   j_p_right_now = BV_right_now;
%   j_m_right_now=0;
%   BV_left_old = 4*kc_left*cp_old(1)*exp(phi_old(1)/(2*T_old(1))) ...
%           - 4*jr_left*exp(-phi_old(1)/(2*T_old(1)));
%   BV_right_old = 4*kc_right*cp_old(N)*exp(-(voltage(t-dt_old)-phi_old(N))/(2*T_old(N))) ...
%           - 4*jr_right*exp((voltage(t-dt_old)-phi_old(N))/(2*T_old(N)));
%
%   j_p_left_old=-BV_left_old;
%   j_m_left_old=0;
%   j_p_right_old = BV_right_old;
%   j_m_right_old=0;
%   phi_x_right_new=0;
% end

%step theta_left and theta_right
theta_left_new=(1+w)^2/(1+2*w)*theta_left_now - w^2/(1+2*w)*theta_left_old ...
+ dt_now*(1+w)^2/(1+2*w)*gamma_left*BV_left_now ...
- dt_now*w*(1+w)/(1+2*w)*gamma_left*BV_left_old;
theta_right_new=(1+w)^2/(1+2*w)*theta_right_now - w^2/(1+2*w)*theta_right_old ...
+ dt_now*(1+w)^2/(1+2*w)*gamma_right*BV_right_now ...
- dt_now*w*(1+w)/(1+2*w)*gamma_right*BV_right_old;
% theta_left_new=1;
% theta_right_new=1;

%step cp,cm,T by calling their respective functions
Appendix F. Matlab Code

dp_new=concentration( z_cp,dx,N1,N2,N3,N4,N5,dt_now,dt_old,D_0,D_p,lambda_s,nu,j_p_left_now,
    j_p_right_now,j_p_left_old,j_p_right_old,cp_now,phi_now,T_now,cp_old,phi_old,T_old,cp_now,
    cm_now,cp_old,cm_old );

dm_new=concentration( z_cm,dx,N1,N2,N3,N4,N5,dt_now,dt_old,D_0,D_m,lambda_s,nu,j_m_left_now,
    j_m_right_now,j_m_left_old,j_m_right_old,cm_now,phi_now,T_now,cm_old,phi_old,T_old,cm_now,
    cm_now,cp_old,cm_old );

v_now=voltage(t);
if dt_old==Inf
    v_old=0;
else
    v_old=voltage(t-dt_old);
end

T_new=temperature( bc,dx,N1,N2,N3,N4,N5,dt_now,dt_old,lambda_s,nu,D_0,D_p,D_m,k,a_1,a_2,a_3,
    a_left,a_right,h_left,h_right,T_amb,z_cp,z_cm,cp_now,cm_now,phi_now,T_now,phi_x_right_now,
    cp_old,cm_old,phi_old,T_old,phi_x_right_old,v_now,v_old,j_p_left_now,j_p_left_old,
    j_m_left_now,j_m_left_old,j_p_right_now,j_p_right_old,j_m_right_now,j_m_right_old );

end

F.1.11 temperature.m

Similar to concentration.m, this function computes the values for temperature at the next time step. Called by step.m.

function [ T_new ] = temperature( bc,dx,N1,N2,N3,N4,N5,dt_now,dt_old,lambda_s,nu,D_0,D_p,D_m,k,
    a_1,a_2,a_3,a_left,a_right,h_left,h_right,T_amb,z_cp,z_cm,cp_now,cm_now,phi_now,T_now,
    phi_x_right_now,cm_old,phi_old,T_old,phi_x_right_old,v_now,v_old,j_p_left_now,j_p_left_old,
    j_m_left_now,j_m_left_old,j_p_right_now,j_p_right_old,j_m_right_now,j_m_right_old )

%temperature.m
%returns T_new based on vectors at current and past

w=dt_now/dt_old;
N=N1+N2+N3+N4+N5;

A=zeros(N,N);
b=zeros(N,1);

%handle bulk

for i=2:N-1
    if i<N1
        a=a_1;
    elseif i>=N1 & i < N2
        a=a_2;
    else
        a=a_3;
    end
    i_p_now=-D_p/D_0*(cp_now(i+1)-cp_now(i-1))/(dx(i-1)+dx(i)) ...
    - D_p/D_0*z_cp*cp_now(i)/T_now(i)*(phi_now(i+1)-phi_now(i-1))/(dx(i-1)+dx(i)) ...
    - D_p/D_0*cp_now(i)*nu*((cp_now(i+1)-cp_now(i-1))/(dx(i)+dx(i-1)) + (cm_now(i+1)-cm_now(i-1))/(dx(i)+dx(i-1)))/(1-nu*(cp_now(i)+cm_now(i)));
    j_p_old=-D_p/D_0*(cp_old(i+1)-cp_old(i-1))/(dx(i-1)+dx(i)) ...
    - D_p/D_0*z_cp*cp_old(i)/T_old(i)*(phi_old(i+1)-phi_old(i-1))/(dx(i-1)+dx(i)) ...
    - D_p/D_0*cp_old(i)*nu*((cp_old(i+1)-cp_old(i-1))/(dx(i)+dx(i-1)) + (cm_old(i+1)-cm_old(i-1))/(dx(i)+dx(i-1)))/(1-nu*(cp_old(i)+cm_old(i)));
    j_m_now=-D_m/D_0*(cm_now(i+1)-cm_now(i-1))/(dx(i-1)+dx(i)) ...
    - D_m/D_0*z_cm*cm_now(i)/T_now(i)*(phi_now(i+1)-phi_now(i-1))/(dx(i-1)+dx(i)) ...
    - D_m/D_0*cm_now(i)*nu*((cp_now(i+1)-cp_now(i-1))/(dx(i)+dx(i-1)) + (cm_now(i+1)-cm_now(i-1))/(dx(i)+dx(i-1)))/(1-nu*(cp_now(i)+cm_now(i)));
    j_m_old=-D_m/D_0*(cm_old(i+1)-cm_old(i-1))/(dx(i-1)+dx(i)) ...
    - D_m/D_0*z_cm*cm_old(i)/T_old(i)*(phi_old(i+1)-phi_old(i-1))/(dx(i-1)+dx(i)) ...
    - D_m/D_0*cm_old(i)*nu*((cp_old(i+1)-cp_old(i-1))/(dx(i)+dx(i-1)) + (cm_old(i+1)-cm_old(i-1))/(dx(i)+dx(i-1)))/(1-nu*(cp_old(i)+cm_old(i)));
    A(i,i-1)=-k*dt_now*2/(dx(i-1)*(dx(i-1)+dx(i)));
A(i,i) = (1 + 2*w)/(1 + w) + k*dt_now*2/(dx(i)*dx(i-1));
A(i,i+1) = -k*dt_now*2/(dx(i)*(dx(i-1)+dx(i)));

b(i) = (1 + w)*T_now(i) - w^2/(1 + w)*T_old(i) ...
   - dt_now*(1 + w)*a*(z_cp*j_p_now + z_cm*j_m_now)*(phi_now(i+1)-phi_now(i-1))/(dx(i-1)+dx(i)) ...
   + dt_now*w*a*(z_cp*j_p_old + z_cm*j_m_old)*(phi_old(i+1)-phi_old(i-1))/(dx(i-1)+dx(i));
end

%handle boundaries

% lhs
A(1,1) = (1 + 2*w)/(1 + w) + 2*dt_now*k/(dx(1)*(dx(1)/2));
A(1,2) = -2*dt_now*k/(dx(1)*(dx(1)/2));

b(1) = (1 + w)*T_now(1) - w^2/(1 + w)*T_old(1) ...
     + dt_now*(1 + w)*( 2*h_left*(T_amb - T_now(1))/(dx(1)/2) - a_left*(z_cp*j_p_left_now + z_cm*
                      j_m_left_now)*phi_now(1)-0)/lambda_s ) ...
     - dt_now*w*( 2*h_left*(T_amb - T_old(1))/(dx(1)/2) - a_left*(z_cp*j_p_left_old + z_cm*
                      j_m_left_old)*phi_old(1)-0)/lambda_s );

% rhs
if bc==0
    phi_x_now=phi_x_right_now;
    phi_x_old=phi_x_right_old;
elseif bc==1
    phi_x_now=(v_now-phi_now(N))/lambda_s;
    phi_x_old=(v_old-phi_old(N))/lambda_s;
end

A(N,N) = (1 + 2*w)/(1 + w) + dt_now*2*k/(dx(N-1)*(dx(N-1)/2));
A(N,N-1) = -dt_now*2*k/(dx(N-1)*(dx(N-1)/2));

b(N) = (1 + w)*T_now(N) - w^2/(1 + w)*T_old(N) ...
     - dt_now*(1 + w)*( 2*h_right*(T_now(N)-T_amb)/(dx(N-1)/2) + a_right*(z_cp*j_p_right_now +
                      z_cm*j_m_right_now)*phi_x_now ) ...
     + dt_now*w*( 2*h_right*(T_old(N)-T_amb)/(dx(N-1)/2) + a_right*(z_cp*j_p_right_old + z_cm*
                      j_m_right_old)*phi_x_old );
T_new=A\b;

end

F.1.12 voltage.m

Specifies the voltage as a function of time.

function v=voltage(t)

% voltage.m
% called by step.m for voltage boundary conditions. takes current time t and
% returns voltage v.

if t>0
    v=-t;
else
    v=0;
end

v=0.1*(tanh(100*(t-7.5))/2 + 1/2);

v=0.1*(tanh(100*(t-7.5))/2 + 1/2) + .1*(tanh(100*(t-8))/2 + 1/2) + .1*(tanh(100*(t-8.5))/2 + 1/2) + .1*(tanh(100*(t-9))/2 + 1/2);

end

F.2 EIS Tool

imp_spec_tool.m and findZ2.m are scripts to run a frequency sweep on the model and postprocess for impedance, respectively. This code requires some minor changes to main.m in order to run since some parameters need to be altered in this code rather than in main.m.
**F.2.1 imp_spec_tool.m**

Runs a frequency sweep of the model by running main.m with sinusoidal voltages over a range of frequencies.

```matlab
clear;
clc;

% physical (i.e. not numerical) parameters script
parameters;

formatOut = 'mm_dd_yy';
date=datestr(now,formatOut);
file_name=sprintf('EIS_%s.mat_eps=%g_delta=%g.mat',date,epsilon_1,delta);

v_bias=0; % bias voltage
amp=0.005; % voltage amplitude
t0=20;

freqs=[0.001 0.005 0.01 0.05 0.1 0.3 0.5 0.7 0.9 1.1 2 5 10 50 100];

for asdf=1:length(freqs)
    freq=freqs(asdf);
    cyclelength=10*2*pi/(freq); % want at least 10 cycles. period length is 1/freq
    t_end=t0+cyclelength;
    main;
    Z(asdf)=findZ2(freq,t0,t,v,j); % ramp up in v should correspond to current INTO the battery
    % (I define my current as into the electrode from the electrolyte side)
    % display(sprintf('step %g out of %g done', asdf, length(freqs)));
    save(file_name,'Z'); % print to file
    clear t v j phi cp cm T phi_x_right theta_left theta_right err dt dt_max n;
    clear cp_coarse cm_coarse T_coarse phi_x_right_coarse theta_left_coarse theta_right_coarse;
    clear cp_fine cm_fine T_fine phi_x_right_fine theta_left_fine theta_right_fine;
    clear cp_half cm_half T_half phi_x_right_half theta_left_half theta_right_half;
    clear cp_half_old cm_half_old T_half_old phi_x_right_half_old theta_left_half_old
    theta_right_half_old;
```
% plot(-real(Z),-imag(Z),'-o');

F.2.2 findZ2.m

Function to postprocess for the impedance Z given a current and voltage signal.

function [ Z ] = findZ2( omega,t0,t,v,j )

peak6 = t0 + 2*pi/omega*6 + pi/(2*omega); %exact location of the 6th peak in v(t)
peak7 = t0 + 2*pi/omega*7 + pi/(2*omega); %exact location of the 7th peak in v(t)

[jmax,loc]=findpeaks(j(peak6<t & t<peak7));
window=t(peak6<t & t<peak7);

if min(size(loc))==0 phi=0; else phi=(window(loc)-peak6)*omega; end %detect phase of j
magV=max(abs(v(t>t0) - mean(v(t>t0))));
magJ=max(abs(j(t>t0) - mean(j(t>t0))));

mag=magV/magJ;
Z=mag*exp(-1i*phi);

end

F.3 Chebyshev Pseudospectral Code

This section contains MATLAB code written using the chebfun package which was used to solve the toy model from Chapter 3 using a pseudospectral Chebyshev polynomial method as a comparison to the VSIMEX method which was chosen.

% solves u_t = -(u_x + uv_x)_x subject to 
% u_t + uv_x = u e^v + e^-v at x=0
% u_t + uv_x = -u + 1 at x=1
% and
%v_xx = -u subject to
%v - v_x = 0 at x=0
%v_x = 0 at x=1

%plus
%u2_t = -(u2_x - u2v_x)_x subject to
%u2=1 at x=0
%u_x - uv_x = 0 at x=1

clc;clear;

%set up timescale
n=1;
dt = 0.01;
t(n) = 0;
t_end = 0.5;

%display my current time
display(sprintf('step = %d, time = %.2g', n, t(n)));

%set up initial condition
u{n} = chebfun(@(x) 1, [0,1]);

L_v = chebop(0, 1);
L_v.op = @(v) diff(v, 2);
L_v.lbc = @(v) diff(v)-v;
L_v.rbc = @(v) diff(v,1);

%solve for v at time t=0
v{n} = L_v\(-u{n});

%define what I need for this time step
v_x = diff(v{n}, 1);
NL = diff(u{n}.*v_x, 1);

L_u = chebop(0, 1);
% take my first time step
u{n+1} = L_u\(u{n} + dt*NL);  

% solve for v at this time step
v{n+1} = L_v\(-u{n+1});

% advance in time
t(n+1)=t(n)+dt;
n=n+1;

% display my current time
display(sprintf('step = %d, time = %.2g', n, t(n)));

% subsequent time steps
while t(n)<t_end-eps
    % define what I need for this time step (v_x and NL at i and i-1)
    v_x_now = diff(v{n}, 1);
    v_x_old = diff(v{n-1}, 1);
    NL_now = diff(u{n}.*v_x_now, 1);
    NL_old = diff(u{n-1}.*v_x_old, 1);

    L_u = chebop(0, 1);
    L_u.op = @(u) 3*u/2 - dt*diff(u, 2);
    L_u.lbc = @(u) diff(u,1) + u*v_x_now(0) - u*exp(v{n}(0)) + exp(-v{n}(0));
    L_u.rbc = @(u) diff(u,1) + u*v_x_now(1) + u - 1;

    % take my time step
    u{n+1} = L_u\(2*u{n} - u{n-1}/2 + dt*(2*NL_now-NL_old));

    % solve for v at this time step
    v{n+1} = L_v\(-u{n+1});

% advance in time
\[ t(n+1) = t(n) + dt; \]
\[ n = n + 1; \]

% display my current time
\[ \text{display(printf('step = \%d, time = \%.2g', n, t(n))});} \]
end

figure(1); plot(u{n}); hold on; plot(v{n}, 'r--');
Bibliography


