ENHANCING THE CAPACITY OF ALL-IRON FLOW BATTERIES:
UNDERSTANDING CROSSOVER AND SLURRY ELECTRODES

By

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Dedication

This work is for my gorgeous wife. For all of the late nights you fell asleep waiting for me and all the dishes I will do to make up for it.

And to my parents for all the years of support and encouragement. Sorry for not putting a dedication page in my master’s.

……………………………Hey, Mom. I’m a Doctor!
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Nomenclature

\( A \) = Cross-sectional area \([\text{cm}^2]\)

\( A_{Total}^{Active} \) = Battery total active area \([\text{cm}^2]\)

\( a \) = True active area \([\text{cm}^2]\)

\( \dot{a} \) = Active area per volume \([\text{cm}^2/\text{cm}^3]\)

\( B \) = Percolation scaling coefficient

\( C \) = Concentration \([\text{moles/m}^3]\)

\( C_{dl} \) = Capacitance \([\text{F}]\)

\( \epsilon_{dl} \) = Length average capacitance \([\text{F/cm}]\)

\( \tilde{\epsilon}_{dl} \) = Specific capacitance \([\text{F/cm}^2]\)

\( D \) = Diffusion Coefficient \([\text{cm}^2/\text{s}]\)

\( D^* \) = Effective Diffusivity \([\text{cm}^2/\text{s}]\)

\( E \) = Energy Capacity \([\text{Wh}]\)

\( E^o \) = Standard potential \([\text{V}]\)

\( F \) = Faraday Constant \([96,485 \frac{\text{A} \cdot \text{s}}{\text{mole e}^-}]\)

\( f \) = Solid volume fraction

\( f_c \) = Critical volume fraction for percolation

\( f_{cv} \) = Viscosity critical volume fraction

\( I \) = Operating Current \([\text{A}]\)

\( i \) = Current Density \([\frac{\text{A}}{\text{cm}^2}]\)

\( i_o \) = Exchange current density \([\text{A/cm}^2]\)
Metal plating density in felt $[\frac{A}{\text{cm}^2}]$

Partition Coefficient $K$

Rate of Air Oxidation $[\frac{\text{mole}}{\text{cm}^3 \cdot \text{s}}]$ $k$

Particle Interaction Factor $L_j$

Length of tube viscometer [cm] $\ell$

Electrons/Redox Species $[\frac{\text{moles e}^-}{\text{moles Fe}^{2+}}]$ $n$

Power rating [W] $P$

Particle aspect ratio $p$

Charge [A $\cdot$ s] $Q$

Resistance [ÎΩ] $R$

Area resistance [ÎΩ $\cdot$ cm$^2$] $\bar{R}$

Gas constant $[8.314 \frac{\text{V} \cdot \text{C}}{\text{K} \cdot \text{mole e}^-}]$ $R_G$

Length average resistance [ÎΩ/cm] $r$

Length specific resistance [ÎΩ $\cdot$ cm] $\bar{r}$

Temperature [K] $T$

Time [hours] $t$

Electrode reaction potential [V] $U_{ref}$

Electrolyte Volume [m$^3$] $V_\pm$

Voltage [V] $V$

Open Circuit Voltage [1.2 V] $V_{OCV}$

Impedance [ÎΩ] $Z$

Impedance of interface [ÎΩ $\cdot$ cm] $Z_\zeta$
\( z \) = Electron per redox species \([\text{mole e}^-/\text{mole j}]\)

\( \gamma \) = EMT/Percolation Coefficient

\( \delta \) = Length parallel to current \([\text{cm}]\)

\( \varepsilon_{\text{Pump}} \) = Efficiency due to pumping losses

\( \varepsilon_{\text{Rxn}} \) = Coulombic efficiency due to side reactions

\( \varepsilon_{\text{Shunt}} \) = Efficiency due to shunt losses

\( \varepsilon_{\text{Total}} \) = Round trip voltaic efficiency

\( \varepsilon_{\text{Coul}} \) = Coulombic efficiency due to crossover

\( \varepsilon_{\text{Cap}} \) = \% ideal capacity available

\( \zeta \) = Interface between slurry electronic and ionic phases

\( \eta \) = Overpotential \([\text{V}]\)

\( \Theta \) = Impedance phase angle \([\text{degrees}]\)

\( \kappa \) = Ionic conductivity \([\text{S/cm}]\)

\( \xi \) = Current collector roughness \([\text{cm}^2/\text{cm}^2]\)

\( \rho \) = Particle density \([\text{g/cm}^3]\)

\( \sigma \) = Electronic conductivity \([\text{S/cm}]\)

\( \Phi \) = Potential of solid/solution \([\text{V}]\)

\( \omega \) = Frequency \([1/\text{s}]\)

\( \epsilon \) = Void fraction
Enhancing the Capacity of All-Iron Flow Batteries: Understanding Crossover and Slurry Electrodes

Abstract

by

TYLER J PETEK

Flow batteries have been studied for grid-scale energy storage applications because their capacity and power delivery rate can be independently scaled. The all-iron flow battery is particularly attractive because iron, the only active species, is low cost, abundant, and environmentally benign. With conventional electrodes, the capacity is severely limited and coupled to the power rating because the negative electrode involves iron metal. The available capacity is further reduced by ferric ion transferring across the separator from the positive to the negative electrode where they react with iron metal causing chemical self-discharge of the battery. In order to enhance the capacity of the all-iron flow battery, the use of slurry electrodes to decouple capacity from the power rating and the self-discharge by active species crossover are both studied. Analytical models accounting for crossover estimate the iron concentrations during continuous cycling using microporous Daramic separators and cation-selective Nafion separators. With both, the model predicts a buildup of iron in the negative electrolyte and a depletion of iron in the positive electrolyte that limits the capacity. Decreasing the amount of negative electrolyte relative to the positive enhances the electrolyte utilization. Cost models were used to optimize the separator thickness for capacity retention, coulombic efficiency, and voltaic efficiency. Batteries using Nafion are found to be double the cost of those using Daramic. With the optimized separator, the capacity must be enhanced further to reach the full market potential. Slurry electrodes studied herein are flowing suspensions of electrically conductive particles in the electrolyte. The particles form a continuous conductive network that allows the iron metal to plate on the surface of the particles and are then carried out of the battery to be stored in the external reservoirs; decoupling the capacity from the power rate. Techniques for interpreting electrochemical impedance spectroscopy of different slurry configurations are developed. The performance of the all-iron slurry electrode was enhanced as the amount of metal deposition increased, due to enhanced electronic conductivity and plating kinetics. After cycling, less than 5% of the charge was plated on the current collector indicating effective slurry operation.
Chapter 1 Introduction

1.1 The Electric Grid

The peak power of the electric grid in the United States was about 800 GW in 2008.\(^1\) Today, only about 24.6 GW of energy storage exists,\(^2\) constituting \(~3\%\) of the grid capacity.\(^1,3\) Because there is so little energy storage, electricity has to be generated and distributed in real time to match the ever changing demand.\(^3\) Being load following causes energy production to be very inefficient and susceptible to the volatility of the market (fluctuations in both price and demand).\(^3\)

Another present day issue plaguing the electric grid is the environmental effects of energy production.\(^4,5\) In order to move away from conventional fossil fuel based energy to more environmentally benign methods, renewable energy sources such as wind and solar must be integrated into the electric grid. However, these renewable sources are inherently intermittent and cannot be relied upon to supply power when the demand is needed. This uncertainty actually puts an increased onus on the conventional methods of energy production because they must be ready to supply the demand at peak consumption if the renewable sources were to experience drastic, and normally unpredictable, changes in output. It has been estimated that an electric grid could become destabilized if it were to rely upon intermittent renewable sources for > 20% of its load.\(^3\)

Grid scale energy storage has the potential to mitigate all of the challenges currently facing the electric grid by decoupling the end user from the energy producers. There are upwards of 17 different application specific benefits associated with storage.\(^1,3\) Table 1.1 describes one set of these applications along with market analysis and system requirements.\(^1\) The capacity and power values given in this table correspond to those
required of the systems providing energy storage. The market size is the projected amount of installed storage in the next ten year period. Figure 1.1 shows how these different applications require a wide variety of energy storage. The figure describes the amount of storage and time scale of the discharge response necessary for each application. All of the largest potential U.S. markets (> 10 GW) fit in the categories of energy arbitrage (energy time shifting), system capacity firming (smoothing intermittent energy production), and ancillary services (area regulation, load following, reserve capacity, and power quality). These applications typically require storage over the range of 1-10 MW with systems containing 3-8 hours of storage. However, these applications have a wide range of discharge response time.

Figure 1.1: The required energy storage device capacity and discharge response time for a variety of energy storage applications.
Table 1.1: The summary of energy storage requirements for different applications.\textsuperscript{1,6,7} The potential (GW) is the maximum potential for actual sale and installation of energy storage in the U.S. over a 10-year period.

<table>
<thead>
<tr>
<th>Benefit Type</th>
<th>Capacity (hrs)</th>
<th>Power (MW)</th>
<th>Market (GW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric Grid Scale</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area Regulation</td>
<td>0.25 – 0.5</td>
<td>1 – 40</td>
<td>1.0</td>
</tr>
<tr>
<td>Voltage Support</td>
<td>0.25 – 1</td>
<td>1 – 10</td>
<td>9.2</td>
</tr>
<tr>
<td>Load Following</td>
<td>1 – 4</td>
<td>1 – 500</td>
<td>36.8</td>
</tr>
<tr>
<td>Reserve Capacity</td>
<td>1 – 2</td>
<td>1 – 500</td>
<td>6.0</td>
</tr>
<tr>
<td>Supply Capacity</td>
<td>4 – 6</td>
<td>1 – 500</td>
<td>18.4</td>
</tr>
<tr>
<td>Time Shift</td>
<td>2 – 8</td>
<td>1 – 500</td>
<td>18.4</td>
</tr>
<tr>
<td>Transmission &amp; Dist.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Support</td>
<td>2 – 5 sec</td>
<td>10 – 100</td>
<td>13.8</td>
</tr>
<tr>
<td>Congestion Relief</td>
<td>3 – 6</td>
<td>1 – 100</td>
<td>36.8</td>
</tr>
<tr>
<td>Upgrade Deferral</td>
<td>3 – 6</td>
<td>0.25 – 5</td>
<td>6.0</td>
</tr>
<tr>
<td>On-Site Power</td>
<td>8 – 16</td>
<td>0.002 – 0.005</td>
<td>0.25</td>
</tr>
<tr>
<td>Time-of-use $ Mgt.</td>
<td>4 – 6</td>
<td>10\textsuperscript{−3} – 1</td>
<td>64.2</td>
</tr>
<tr>
<td>Demand Charge Mgt.</td>
<td>5 – 11</td>
<td>0.05 – 10</td>
<td>32.1</td>
</tr>
<tr>
<td>Reliability</td>
<td>0.1 – 1</td>
<td>10\textsuperscript{−4} – 10</td>
<td>9.2</td>
</tr>
<tr>
<td>Power Quality</td>
<td>10 – 60 sec</td>
<td>10\textsuperscript{−4} – 10</td>
<td>9.2</td>
</tr>
<tr>
<td>Renewables</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time-Shift</td>
<td>3 – 5</td>
<td>10\textsuperscript{−3} – 500</td>
<td>36.8</td>
</tr>
<tr>
<td>Capacity Firming</td>
<td>2 – 4</td>
<td>10\textsuperscript{−3} – 500</td>
<td>36.8</td>
</tr>
<tr>
<td>Grid Integration</td>
<td>0.01 – 0.25</td>
<td>10\textsuperscript{−4} – 500</td>
<td>2.3</td>
</tr>
<tr>
<td>Grid Integration</td>
<td>1 – 6</td>
<td>10\textsuperscript{−4} – 500</td>
<td>18.4</td>
</tr>
</tbody>
</table>

The capital cost (CAPEX) required of energy storage to have market benefit greatly varies with each specific application.\textsuperscript{1,6,7} The U.S. DOE has given a CAPEX target of $150/kWh ($600/kW with 4 hours of storage) for a range of applications presented in Table 1.1 and Figure 1.1.\textsuperscript{2} However, recent studies have found the break-even CAPEX to be closer $250-350/kW for load leveling, regulation, and capacity firming applications with 300 MW and 8 hours of storage.\textsuperscript{1,6,7}

There are many different types of energy storage technologies suitable for grid scale applications. Figure 1.2 shows discharge capacities and power ratings typical of a variety
of storage devices. Of all of these technologies, redox flow batteries (RFBs) are the most suitable for the widest variety of applications, particularly for the applications predicted to have the largest market potential.  

Figure 1.2: Typical discharge capacity and power ratings of grid scale energy storage technologies.

1.2 Redox Flow Batteries

Redox flow batteries store energy in the electrochemical states of active chemical species in flowable electrolytes. A typical schematic of a RFB during charge is shown in Figure 1.3. The main components are the positive and negative electrolyte, stored in separate reservoirs, and the electrochemical cell (shown in Figure 1.3 between the reservoirs) through which the electrolytes flow. It should be noted that the relative size of the electrochemical cell and the reservoirs in Figure 1.3 are not drawn to scale.

During operation of the battery, the electrolyte is pumped into the electrochemical cell where the chemical energy is directly converted to electrical energy at the electrode-electrolyte interface. On charge, the active species in the positive electrolyte are electrochemically oxidized releasing an electron into the external circuitry. Simultaneously, the active species in the negative electrolyte are electrochemically reduced during charge by consuming an electron from the external circuitry. The opposite
of these reactions occur during discharge of the battery. The potential difference between
the reactions occurring in the positive and negative electrolytes drives the electrons
through the external circuitry. While electrons are being transferred through the external
circuitry, supporting ions must be transported from one side of the battery to the other in
order to balance the change in charge of the active species (not shown in Figure 1.3).
While the battery is being charged, positively charged cations must transport from the
positive to the negative electrolyte or negatively charged anions must transport from the
negative to the positive electrolyte. The transport of supporting ions is reversed during
discharge of the battery.

![Figure 1.3: Schematic of a typical continuously circulated redox flow battery during charge.](image)

The separator in the electrochemical cell is vital to the operation of the RFB. To force
electrons to flow through the external circuitry, the separator must be non-conductive to
electrons. The separator must at the same time allow the supporting ions to transfer
between the positive and negative electrolyte so that charge can be balanced. Also, so that
the electrochemical potential of the battery is not released chemically, the active species must be kept separate. The operation of the separator will be discussed further in Chapters 2 and 3.

In Figure 1.3, the electrolyte is shown to flow across a flat plate current collector, serving as the electrode, in the electrochemical cell. Conventional electrode structures typically used in flow batteries are porous materials that are electrically conductive. These materials are in contact with the current collector affixed in the electrochemical cell either in the path of the electrolyte flow or next to the electrolyte flow. In this configuration, the current collector only serves as the material through which the electrons are conducted into the external circuitry. The advantage of using a porous electrode is that the surface area of the electrode-electrolyte interface can be maximized.

Inherent to the flow battery architecture is the ability to decouple the energy storage capacity from the battery power delivery rate. The amount of energy that the flow battery has the capacity to store is dictated by the amount of the active species in the system; controlled by the concentration of active species in the electrolyte and the size of the reservoirs. The power delivery rate of the battery, the rate that the electrons can be driven through the external circuit, is dictated by the potential difference between the two electrodes and the size of the electrode; controlled by the size of the electrochemical cell. The power delivery rate being decoupled from the energy storage capacity allows RFBs to enjoy flexible operation and design specifications that lead to a better economy of scaling than traditional electrochemical battery systems.

In Figure 1.3, only one reservoir is used on either side of the battery as opposed to two reservoirs. With one reservoir, the electrolyte is continuously circulated through the
battery and back into the well mixed reservoir on its respective side. Each reservoir contains the charged and discharged state of the active species. When two reservoirs are used on either side of the battery, one reservoir contains the discharged state while the other contains the charged state. One disadvantage using only one reservoir on either side is that the inlet concentration changes with the battery state-of-charge (SOC). However, the battery is able to be operated at higher flow rates, and therefore improved performance, since the required conversion rate per pass is lower than when using two reservoirs on either side.

There have been many different chemistries investigated for use in RFBs, including the iron-chromium,\textsuperscript{12} iron-vanadium,\textsuperscript{13-14} bromide-polysulfide,\textsuperscript{15} and all-vanadium\textsuperscript{16} systems. The all-vanadium RFB is one of the most studied systems to date yet the cost, toxicity, and lack of abundance of vanadium has hindered its marketability.\textsuperscript{17-19} An attractive alternative to the traditional RFB chemistries is the all-iron flow battery.\textsuperscript{20,21}

1.3 All-Iron Flow Batteries

The only active element in the all-iron flow battery is iron; a low cost (> 60 times cheaper than vanadium),\textsuperscript{17} abundant (> 600 times more abundant than vanadium),\textsuperscript{22-24} and environmentally benign material (up to 100 times lower acid strength than vanadium).\textsuperscript{25-27} In the all-iron battery during charge, the positive reaction is the electrochemical oxidation of ferrous ions (Fe\textsuperscript{2+}) to ferric ions (Fe\textsuperscript{3+}) while the negative reaction is the electrochemical reduction of ferrous ions to iron metal, as described in Equations [1.1] and [1.2], respectively. The net battery operation is described by Equation [1.3] and has a standard voltage of 1.21 V.\textsuperscript{20,21} Both ferric and ferrous ions are mildly acidic with a pKa of about 2.91 and 5.0, respectively.\textsuperscript{26} There are two main
challenges when operating an all-iron flow battery: the evolution of hydrogen at the negative electrode and the plating of iron metal.

\[
\begin{align*}
2Fe^{2+} & \rightleftharpoons 2Fe^{3+} + 2e^- & E^0 = +0.77 \text{ V vs. NHE} \quad [1.1] \\
Fe^{2+} + 2e^- & \rightleftharpoons Fe^0 & E^0 = -0.44 \text{ V vs. NHE} \quad [1.2] \\
3Fe^{2+} & \rightleftharpoons 2Fe^{3+} + Fe^0 & E^0 = +1.21 \text{ V vs. NHE} \quad [1.3]
\end{align*}
\]

The negative half-reaction of the all-iron battery, Equation [1.2], occurs at -0.44 V vs. NHE. As such, a significant challenge when operating the all-iron flow battery is the evolution of hydrogen at the negative electrode. Hydrogen evolution not only presents itself as a decrease in current efficiency\(^27\) but it also causes the battery to become imbalanced (the Fe\(^{2+/3+}\) redox reaction still occurs on the positive electrode) and the electrolyte pH to rise.\(^{20,21}\) As the pH of the electrolyte rises above about 2.0, the soluble iron species can precipitate as insoluble iron-hydroxides.\(^{20,21,26,27}\) There have been two approaches to mitigating the effects of hydrogen evolution. The first is simply by maintaining the electrolyte pH below 2.0 through the addition of acid.\(^{20,21}\) Any iron that does happen to precipitate is filtered out and then dissolved in the positive electrolyte in order to rebalance the battery.\(^{20}\) However, over long term cycling, the electrolyte is diluted and the energy content will approach zero.

The other approach to mitigating the effects hydrogen evolution is through the use of additive chemistry. By complexing the soluble iron species, typically with organic ligands such as citrates and oxalates, the iron species can be made soluble in more basic electrolytes.\(^{20,26}\) However, the mild success of this method is mitigated by adversely affecting the battery voltage and plating efficiencies.\(^{26,27}\) In contrast, hydrogen evolution can be directly mitigated through the addition of high concentrations of halide ions, i.e. \(> 5 \text{ M } \Gamma, \text{ Cl}, \text{ and Br}^-,\) to the electrolyte.\(^{27}\) By increasing the concentration of chloride ions
in the electrolyte from 0.1 M to 3.0 M, the amount of hydrogen evolution decreased by 95% at a negative electrode potential of -0.57 V vs. NHE.\textsuperscript{27}

Typical RFBs employ stationary porous structures, such as carbon felts and carbon cloths, as electrodes that are fixed in the energy conversion device. When these electrodes are used in the all-iron flow battery, iron metal is plated directly onto the stationary structure during charge and subsequently stored in the conversion device. In this configuration, the all-iron battery is typically referred to as a hybrid flow battery because the capacity, as well as the power rating, is now dictated by the size of the energy conversion device. While effort have been given to increase the plating capacity of stationary electrodes,\textsuperscript{28-31} they are still limited to much less than 4 hours of storage. This constricted storage capacity will greatly limit the market penetration of the all-iron battery (per Table 1.1) despite the cost and safety advantages associated with the all-iron chemistry.

In order to realize the benefits of the all-iron chemistry in the flow battery architecture, the capacity of the resulting device must be improved. The objective of the work presented in this thesis is to enhance the capacity of the all-iron flow battery. Through studying how the capacity losses due to chemical self-discharge via active species crossover affect the performance, the all-iron battery operation can be modeled more accurately which will lead to optimized battery specifications. Also, this thesis will investigate slurry electrodes in order to decouple the plating capacity from the conversion device size by storing the iron metal on particles that can be carried by the electrode and stored in external reservoirs.
Chapter 2 Crossover Effects on All-Iron Flow Battery Performance

2.1 Introduction

In the all-iron battery, the separator must allow transport of supporting ions at sufficiently high rates so that current is able to flow with reasonable efficiencies. At the same time, a separator must keep the active species in the positive electrolyte separate from those in the negative electrolyte to prevent the battery from chemically discharging. Since no separator is perfect, the active species will be transported from one side to the other along with supporting ions. The rate of crossover of active species in vanadium RFB systems have been characterized\textsuperscript{32-35} but the iron system remains relatively unstudied. In the all-iron battery, ferric ions that cross from the positive to the negative electrolyte can react either electrochemically, Equation [2.1], or chemically with iron metal, Equation [2.2], to form ferrous ions.\textsuperscript{20}

\begin{equation}
2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+} \tag{2.1}
\end{equation}

\begin{equation}
2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \tag{2.2}
\end{equation}

While crossover discharges the all-iron battery, it does not cause a charge imbalance because the net reaction as a result of crossover (Equation [2.2]) is the same as the net discharge reaction of the battery (Equation [1.3]). However, discharge of the battery as a result of crossover does lead to a capacity loss; energy is put into the battery that does not remain as separate ferric ions and iron metal. This capacity loss must be understood in order to predict the effective energy storage capacity of an operating battery and optimize the battery specifications.

The aim of this chapter is to predict the rate that crossover of the soluble iron species occurs in an all-iron battery and the effect that crossover has on the energy storage
capacity. In order to complete this investigation, the rate with which the iron species diffuse across the battery separators must be determined. Commercially available Nafion 117 and microporous Daramic 250 have been investigated as part of continuing efforts to develop more cost effective and robust RFB separators.\textsuperscript{14,36,37}

2.2 Crossover Model

2.2.1 Crossover Model Assumptions

Several assumptions have been made in order to simplify the mathematical model describing the crossover of iron species in the all-iron flow battery. These assumptions apply to both the full battery model and the experiments used to determine the effective diffusivities of each species.

1. Electrolytes are well mixed on either side of the system.
2. The volume of each reservoir remains constant, i.e. no bulk transfer of electrolyte via pressure driven flow and water transfer by electro-osmosis is ignored.
3. Partition coefficients are constant.
4. Temperature of the system is constant.
5. If air oxidation of ferrous iron occurs, Equation [2.3],\textsuperscript{38,39} it proceeds at a constant rate.
6. Effective diffusivities are constant with concentration.
7. Iron metal does not exist in the positive electrolyte at any time.
8. Ferric ions that are transported to the negative side instantly react with iron metal by Equation [2.2] or are reduced to ferrous ions by Equation [2.1].
(9) The concentration profiles in the separator are linear and change significantly faster than the concentration of the electrolyte in each reservoir.

(10) Supporting ions diffuse across the separator at least as fast as the iron species.

\[ 4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \]  

[2.3]

The concentration gradient in the separator depends not only on the rate of diffusion but also on the equilibrium between the separator and the electrolyte, described by the partition coefficient, \( K \). This may lead to local concentrations in the separator different than that of the bulk electrolyte.\(^{40,41}\) In the iron system, the only iron species that can exist in the separator are ferrous and ferric ions. Since these species do not react chemically with each other, only the effective diffusivity, \( D \), of the iron species from one side of the battery to the other is considered in determining concentration as a function of time. Equation [2.4] shows the relationship between the effective diffusivity, the partition coefficient, and the diffusion coefficient, \( D \).\(^{35,41}\)

\[ D = KD \]  

[2.4]

### 2.2.2 Crossover Model during Operation of the All-Iron Battery

The rate that the concentration of each iron species present in the all-iron battery changes during normal charge/discharge operation is described in Equation [2.5a] through Equation [2.5d]. In Equations [2.5a]–[2.5c], the first term on the right side represents crossover due to diffusion and is derived from Fick’s Laws,\(^{41,42}\) the second term represents faradaic operation, and the third term represents air oxidation. In Equation [2.5c] and [2.5d], the last term represents the change in concentration due to ferric ions reacting with iron metal in the negative electrolyte. The current density, \( i \), is positive during charging and negative while discharging.
\[
\frac{\partial C_{Fe^{2+}}^+}{\partial t} = -\frac{A \mathcal{D}_{Fe^{2+}}}{V_+} \left[ \frac{C_{Fe^{2+}}^+ (t)}{\delta} \right] + \frac{i A}{z_F V_+} + \kappa_+ \tag{2.5a}
\]

\[
\frac{\partial C_{Fe^{2+}}^-}{\partial t} = -\frac{A \mathcal{D}_{Fe^{2+}}}{V_+} \left[ \frac{C_{Fe^{2+}}^- (t) - C_{Fe^{2+}}^+ (t)}{\delta} \right] - \frac{i A}{z_F V_+} - \kappa_+ \tag{2.5b}
\]

\[
\frac{\partial C_{Fe^{2-}}^+}{\partial t} = -\frac{A \mathcal{D}_{Fe^{2-}}}{V_-} \left[ \frac{C_{Fe^{2-}}^+ (t) - C_{Fe^{2+}}^+ (t)}{\delta} \right] - \frac{i A}{z_F V_-} - \kappa_+ + \frac{3}{2} \left[ \frac{A \mathcal{D}_{Fe^{3+}}}{V_-} \left[ \frac{C_{Fe^{3+}}^+ (t)}{\delta} \right] + \kappa_- \right] \tag{2.5c}
\]

\[
\frac{\partial C_{Fe^{0}}^{-}}{\partial t} = + \frac{i A}{z_F V_-} - \frac{1}{2} \left[ \frac{A \mathcal{D}_{Fe^{3+}}}{V_-} \left[ \frac{C_{Fe^{3+}}^+ (t)}{\delta} \right] + \kappa_- \right] \tag{2.5d}
\]

Equation [2.5d] represents the change in concentration of iron metal. Iron, as a metal, is not soluble and is not normally expressed in terms of concentration but to keep the notation for each iron species consistent, the amount of iron metal present will be presented as moles of iron metal per negative electrolyte volume. When air oxidation is negligible, the “concentration” of iron metal in the negative is equal to the concentration of ferric iron in the positive electrolyte (if \(z_- = 2z_+\) and \(2V_- = V_+\)).

### 2.3 Experimental

#### 2.3.1 Materials and Equipment

All chemicals used in the calibration and crossover experiments were reagent grade. The NaCl and HCl were purchased from Fisher Scientific (Waltham, MA) and the iron salts were purchased from Alfa Aesar (Ward Hill, MA). Nafion 117 was purchased from Ion Power, Inc. (New Castle, DE). Nafion was prepared by soaking in 5% H₂O₂ for 1 hour at 60°C and then rinsing well in DI water. Prior to use, the Nafion was soaked in electrolyte for 30 minutes. Immediately before inserting the Nafion into an electrochemical cell, it is quickly rinsed to remove any iron species on the membrane surface. The Nafion 117 was found to have a thickness of about 210 microns; measured...
after use in experiments. Daramic separators were graciously donated by Daramic, LLC (Charlotte, NC). The Daramic separator supplied was Daramic 250 Flatsheet with an average reported pore size of 0.1 microns and a thickness of about 225 microns measured after use in experiments. The Daramic was soaked in methanol and rinsed in DI water before use.\textsuperscript{14}

All electrochemical measurements were made with a Solartron 1280B potentiostat from Ametek, Inc.. When necessary, Ag/AgCl reference electrodes from Bioanalytical Systems, Inc. (West Lafayette, IN) were used.

\textit{2.3.2 Effective Diffusivity of Ferric and Ferrous Ions}

The experimental design for determining the effective diffusion coefficient of ferric and ferrous ions across battery separators is shown is Figure 2.1. The cell was made in-house. The endplates are made from CPVC. Buna-N and Teflon gaskets were used to create an 11.5 cm\textsuperscript{3} (0.2 cm x 57.8 cm\textsuperscript{2}) volume on either side of the separator. This volume was filled with hydrophilic polyester felt to ensure complete mixing in the cell. The separator had an active geometric area of 57.8 cm\textsuperscript{2} (7.6 cm x 7.6 cm). Upon assembly, the cell was compressed with 8 bolts each under 60 in-lbs. All materials for the cell construction were purchased from McMaster-Carr (Cleveland, OH).

The volume of electrolyte in either reservoir was 135 cm\textsuperscript{3} and was circulated by a peristaltic pump (Cole-Parmer, USA) at 32 cm\textsuperscript{3}/min. Erlenmeyer flasks were used for reservoirs so that the electrolyte volume could be easily monitored. The second model assumption was justified in that, over an 80 hour experiment, < 3\% volume change between reservoirs was observed. Both reservoirs were under a continuous nitrogen
blanket over the course of the experiment to minimize air oxidation of ferrous iron to ferric iron.

![Experimental design for measuring the effective diffusivity of iron salts across battery separators.](image)

**Figure 2.1:** Experimental design for measuring the effective diffusivity of iron salts across battery separators.

The concentrations of ferric and ferrous iron were monitored by measuring the peak reaction current between two platinized platinum wires submerged in the reservoir. The working electrode was a platinized 0.25 mm diameter platinum wire coil and the counter electrode was a platinized 0.5 mm diameter platinum wire coil (Fisher Scientific, USA). The wires were platinized at 10 mA for 10 second pulses followed by 10 seconds at zero current in a solution of 1% chloro-platinic acid, 0.6 g/L lead acetate, and 0.1 M NaCl. This process was repeated until there was a visibly continuous platinized layer on each electrode. Two electrode cyclic voltammograms with platinized platinum electrodes were used to monitor the concentrations because, due to their high surface area, the electrodes were more resistant to poisoning over the length of the experiment. The working electrode had a smaller diameter than the counter electrode to ensure that the current at the working electrode was limiting at all times.
2.4 Results

2.4.1 Calibrating the Platinum Electrode Response

Solutions of 1.0 M NaCl were made with varying ferrous chloride and ferric chloride concentrations in order to calibrate the 0.25 mm platinized platinum electrode. Cyclic voltammograms were performed at 25, 50, and 100 mV/sec scan rates to ±0.5V vs OCV. In all cases, some amount of both ferric chloride and ferrous chloride was present so that the open circuit potential was well defined. An example CV is shown in Figure 2.2 for 0.25 M FeCl₂, 0.25 M FeCl₃, and 1.0 M NaCl at 25 mV/s. Figure 2.3 shows the calibration results of peak current for ferrous and ferric ions at 25 mV/sec and 50 mV/sec for varying concentrations in a stagnant beaker on the 0.25 mm platinized platinum coil.

Figure 2.2: Second cycle of CV on 0.25 mm diameter platinized platinum wire of 0.25 M FeCl₂, 0.25 M FeCl₃, and 1.0 M NaCl at 25 mV/sec.
Figure 2.3: Calibration of ferrous and ferric chloride in 1.0 M NaCl on 0.25 mm platinized platinum. The unfilled symbols are at 25 mV/sec and the filled symbols are at 50 mV/sec. The triangles are Fe$^{2+}$ and the circles are Fe$^{3+}$.

2.4.2 Effective Diffusivity of Ferrous and Ferric Chloride

In order to accurately determine the effective diffusivities of ferric and ferrous chloride across the battery separators, each species was investigated individually. This was accomplished through experiments during which only one iron species and a supporting cation experienced a concentration gradient. All other ions were present in equal concentration on either side of the separator. An example experimental configuration for investigating the effective diffusivity of ferric ions is described in Table 2.1. Measurements of the iron concentrations were made in the “concentrated” reservoir because the open circuit potential is well defined at all times (both ferric and ferrous ions are always present). 1 M HCl was added to each side to effectively buffer the pH of the electrolyte to a change in concentration of either iron species as ferric iron is a stronger acid than ferrous iron.\textsuperscript{26} In the example experiment described by Table 2.1, there is 2.25 M Cl$^-$ on both sides.
Table 2.1: Initial concentrations of both reservoirs in an experiment to measure the ferric iron effective diffusivity.

<table>
<thead>
<tr>
<th>Concentrated Side</th>
<th>Species</th>
<th>Dilute Side</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 M</td>
<td>FeCl₂</td>
<td>0.25 M</td>
</tr>
<tr>
<td>0.25 M</td>
<td>FeCl₃</td>
<td>0.00 M</td>
</tr>
<tr>
<td>0.00 M</td>
<td>NaCl</td>
<td>0.75 M</td>
</tr>
<tr>
<td>1.00 M</td>
<td>HCl</td>
<td>1.00 M</td>
</tr>
</tbody>
</table>

The experiment described by Table 2.1 was repeated to investigate ferric and ferrous ions across both Daramic 250 and Nafion 117. The initial concentration of the iron species of interest in all cases was 0.25 M. An example of the experimental results, for ferric ions across Nafion 117, is shown in Figure 2.4. The concentrations shown were determined through cyclic voltammetry at 25 mV/s between two platinized platinum electrodes as described above. Equation [2.6] is a simplified model for zero current operation derived from Equation [2.5a] that was used to determine the effective diffusivity.\textsuperscript{41,42} The solid line in Figure 2.4 represents the fit of Equation [2.6] to the experimental data. Here, the positive and negative notations represent concentrated and dilute sides, respectively.

\[
\frac{\partial c_{Fe^{3+}}^+}{\partial t} = -\frac{A D_{Fe^{3+}}}{v_+} \left[ \frac{c_{Fe^{3+}}^+(t) - c_{Fe^{3+}}^-(t)}{\delta} \right] + k_+ \quad [2.6]
\]

Table 2.2 summarizes the effective diffusivities determined for each iron species across each separator studied. The effective diffusivity of iron in Nafion 117 was found to be close to the values reported for vanadium.\textsuperscript{35} For these fits, air oxidation is assumed to only occur in the concentrated reservoir. This is due to air entering around the seal on the electrode leads. The average rate of air oxidation during the experiments was found to be about \(1 \times 10^{-10} \text{ mol/cm}^3 \cdot \text{s}\). This is greater than one order of magnitude slower than the change in concentration by diffusion driven crossover.
Figure 2.4: An example of experimental (open circles) and modeling results (solid line) for determining ferric ion diffusivity across a Nafion 117 separator. The initial concentration is slightly lower than Table 2.1 indicates due to water initially entrained in the felts. The true electrolyte volume is accounted for in the models.

Table 2.2: Effective diffusivities for ferric and ferrous ions across Daramic 250 and Nafion 117.

<table>
<thead>
<tr>
<th>Separator</th>
<th>Species</th>
<th>( D \left[ \frac{cm^2}{s} \right] )</th>
<th>Std. Error</th>
<th>( \frac{cm^2}{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daramic</td>
<td>( Fe^{2+} )</td>
<td>( 9.9 \times 10^{-7} )</td>
<td>0.3 ( \times 10^{-7} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Fe^{3+} )</td>
<td>( 12.3 \times 10^{-7} )</td>
<td>1.0 ( \times 10^{-7} )</td>
<td></td>
</tr>
<tr>
<td>Nafion</td>
<td>( Fe^{2+} )</td>
<td>( 4.3 \times 10^{-7} )</td>
<td>0.7 ( \times 10^{-7} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Fe^{3+} )</td>
<td>( 3.5 \times 10^{-7} )</td>
<td>0.4 ( \times 10^{-7} )</td>
<td></td>
</tr>
</tbody>
</table>

2.5 Discussion

2.5.1 All-Iron Battery Cycling Models

The effective diffusivities from Table 2.2 were applied to the full system model described by Equations [2.5a] – [2.5d] in order to predict the concentration of each iron species during continuous charge/discharge cycling of an all-iron battery. The system of equations was solved analytically using Wolfram Mathematica 9 (described in
Appendix B). Figure 2.5a shows the concentration of ferrous ions in the negative and positive electrolyte during maximum state-of-charge swings in a theoretical 1 MW, 4 MWh all-iron battery charging at +200 mA/cm² and discharging at −200 mA/cm². Both the positive and negative electrolytes are initially 2.0 M FeCl₂. The direction of the battery cycling reversed when any species reached a concentration of zero molar; simulating the theoretical maximum capacity. The area of the battery separator is defined by Equation [2.7]. The volume of both the positive and negative electrolytes is defined by Equation [2.8]. $C^\pm_\text{total}$ is the total amount of all iron species per volume in the given electrolyte. If the total concentration of iron in both electrolytes is the same, the volume of the positive will be twice that of the negative due to the ratio of $z_-/z_+ = 2$. In these systems, the concentration change of ferric ions in the positive reservoir mirrors that of the ferrous ion concentration in the positive reservoir; i.e. the concentration of ferric ions in the positive reservoir is at a maximum when the concentration of ferrous ions is at a minimum and vice versa. (The maximum ferrous concentration is higher than the maximum ferric concentration in the positive electrolyte due to coulombic efficiency loss as a result of crossover.) For these full battery cycling models, air oxidation of ferrous to ferric ions was ignored. When air oxidation is negligible, the “concentration” of iron metal in the negative is equal to the concentration of ferric iron in the positive electrolyte (if $z_- = 2z_+$ and $2V_- = V_+$).

$$A = \frac{P}{iV_{OCV}}$$  \[2.7\]

$$V_\pm = \frac{E}{z\pm FE_{C^\pm_\text{total}V_{OCV}}^{-}}$$  \[2.8\]
Figure 2.5a: Concentration of ferrous ions in a 1 MW, 4 MWh all-iron battery during maximum state-of-charge cycling at ±200 mA/cm² with Daramic 250. The black and gray curves represent Fe²⁺ in the negative and positive reservoirs, respectively.

Figure 2.5b: Concentration of ferrous ions in a 1 MW, 4 MWh all-iron battery with Daramic 250. Cycles are at ±200 mA/cm² and are reversed when any species is 0.25 M. The black and gray curves represent Fe²⁺ in the negative and positive reservoirs, respectively.
A decrease in efficiency resulting from an increase in operating overpotentials is typically observed when batteries undergo deep state-of-charge cycling. In order to more aptly represent real battery operation, a theoretical 1 MW, 4 MWh all-iron battery was again modeled at continuous \( \pm 200 \text{ mA/cm}^2 \) operation but this time the direction of cycling was changed when the concentration of any species reached 0.25 M. This cycling limit results in a maximum available capacity that is 75% of the theoretical maximum described above. The results are shown in Figure 2.5b for a battery with a Daramic separator with no air oxidation. The model begins with 1.75 M FeCl\(_2\) and 0.25 M FeCl\(_3\) in the positive electrolyte and 1.75 M FeCl\(_2\) and “0.25 mol/L” iron metal in the negative electrolyte to simulate the results of an initial charging step necessary to begin at the minimum concentrations from which the battery was cycled. During cycling, the concentration of ferric ions in the positive reservoir again mirrors the ferrous ion concentration changes in the same reservoir while iron metal in the negative reservoir is equal to the concentration of ferric ions in the positive reservoir as in the maximum state-of-charge cycling. The models of continuous maximum state-of-charge cycling and cycling bound by 0.25 M were also extended to systems with Nafion separators.

2.5.2 All-Iron Battery Predicted Performance

The analytical cycling model predicts an accumulation of ferrous ions in the negative reservoir and a depletion of ferric and ferrous ions in the positive reservoir. However, after a sufficient number of cycles, a steady state is achieved where subsequent cycles have the same concentration profiles as the previous cycle. As the amount of iron species on either side approaches the steady state, the capacity of the battery also approaches a
steady state value lower than the initial capacity; the decreased amount of iron ions in the positive electrolyte now dictates the capacity of the battery.

The discharge capacity of the battery after the steady state is achieved is shown in Figures 2.6-2.8 as a percentage of the initial theoretical discharge capacity as described by Equation [2.9] for a given current density and concentration. The ideal discharge time is the estimated discharge time based upon the initial total concentration of iron in the positive reservoir assuming cycling with 100% utilization and 100% coulombic efficiency, given in Equation [2.10]. The actual discharge time is found using the model results. In Figure 2.7 and Figure 2.8, because cycling is limited by the 0.25 M minimum concentration criteria, the maximum capacity, with 100% coulombic efficiency, is 75% of the ideal discharge capacity.

\[ \varepsilon_{\text{Cap}} = \frac{t_{\text{Actual}}}{t_{\text{Ideal}}} \]  
\[ t_{\text{Ideal}} = \frac{zFV_+C_{\text{t=0}}}{iA} \]

**Figure 2.6:** The coulombic efficiency (open symbols) and the % of the initial ideal discharge capacity (closed symbols) of an all-iron battery during maximum state-of-charge cycling with Nafion 117 and Daramic 250 with both electrolyte volumes defined by Equation [2.8].
In addition to the capacity loss, there is also a coulombic efficiency loss due to crossover. Some amount of the energy that is used to charge the battery is not available on discharge because ferric ions have crossed from the positive to the negative side of the battery to react and form ferrous ions, discharging the battery. The resulting coulombic efficiency, due only to crossover and ignoring any side reactions (e.g. hydrogen evolution) is described by Equation [2.11] and was investigated after steady state cycling was developed. The results are summarized in Figure 2.6 for maximum state-of-charge swings as well as Figure 2.7 and Figure 2.8 for cycling bound by 0.25 M concentrations.

\[
\varepsilon_{\text{coul}} = \frac{Q_{\text{disch}}}{Q_{\text{charge}}} = \frac{\int_{0}^{t_{\text{disch}}} I_{\text{disch}} dt}{\int_{0}^{t_{\text{charge}}} I_{\text{charge}} dt} \tag{2.11}
\]

The discharge capacity and coulombic efficiency due to crossover were found not to be functions of the energy-to-power ratio (and therefore not by the area-to-volume ratio). This is due to the area and volume being dictated by Equation [2.7] and Equation [2.8], respectively. For instance, if the ratio of energy-to-power changes from a one hour battery to a four hour battery at a fixed current density and separator thickness, the ratio of the battery area relative to electrolyte volume changes proportionally to the discharge time.
Figure 2.7: The coulombic efficiency (open symbols) and the % of the initial ideal discharge capacity (closed symbols) of an all-iron battery with a Daramic separator during cycling bound by 0.25 M as a function of separator thickness for varying current densities with both electrolyte volumes defined by Equation [2.8].

Figure 2.8: The coulombic efficiency (open symbols) and the % of the initial ideal discharge capacity (closed symbols) of an all-iron battery with a Nafion separator during cycling bound by 0.25 M as a function of separator thickness for varying current densities with both electrolyte volumes defined by Equation [2.8].
2.5.3 Varying Negative Electrolyte Volume

In the systems discussed thus far, the volumes of both the positive and negative electrolytes have been defined by Equation [2.8]; the positive volume has been twice the negative volume. However, because an imbalance of iron between the electrolytes develops due to crossover, the actual capacity of the battery is dictated by the decreased steady state concentration of iron in the positive electrolyte. Defining the negative electrolyte volume by Equation [2.8] results in excess iron present in the negative electrolyte that is never cycled. By decreasing the volume of the negative electrolyte relative to the positive, the concentration swings of ferrous ions in the negative can be increased yielding greater utilization of the negative electrolyte. This decreases the total amount of iron necessary and the total electrolyte volume.

The total amount of faradaic charge passed on the positive side of the battery must equal that of the negative side. If \( V_+ / V_- = 4 \) and the positive electrolyte is cycling \( \pm 1.5 \text{ M iron} \), the concentration swing in negative electrolyte must be \( \pm 3.0 \text{ M iron} \) \( (z_- / z_+ = 2) \). Since the amount of iron in the negative electrolyte and the concentration swing are increasing, the solubility limit of iron must be considered. In order to keep the properties of the electrolyte (e.g. conductivity,\(^{21}\) viscosity,\(^{43}\) etc.) favorable, the concentration of both electrolytes should be limited to less than 3.0 M ferric or ferrous chloride.

In order to maximize electrolyte utilization and capacity while minimizing the amount of electrolyte required, battery systems were simulated with varying ratios of positive to negative electrolyte volume. The positive electrolyte volume is defined by Equation [2.8]
and the negative electrolyte volume is defined by the volume ratio. In these subsequent cases, the initial concentration in the negative electrolyte is 3.0 M FeCl₂.

Cycling scenarios were still bound by 0.25 M minimum concentrations in both electrolytes and with it the need for an initial charge to develop a minimum of 0.25M ferric iron in the positive electrolyte and iron metal in the negative when starting with all of the iron in the ferrous state. For instance, 1.775 M initial ferrous chloride in the positive electrolyte only swings between 0.25 M and 1.525 M. If \( \frac{V_+}{V_-} = 4 \) and the initial negative concentration is 3.0 M FeCl₂, this corresponds to ferrous concentration swings between 0.5 M and 2.5 M in the negative electrolyte. During cycling, an accumulation of ferrous ions in the negative electrolyte still occurs until the steady state concentration profiles are achieved. The maximum amount of ferrous ions in the negative (occurring at full discharge) after the steady state is achieved should not exceed 3.0 M.

Table 2.3 indicates the positive electrolyte initial concentration used for each membrane at each volume ratio. The concentrations are different for Nafion and Daramic separators because of the variation in effective diffusivities.

**Table 2.3**: The initial concentration of ferrous chloride in the positive electrolyte used when cycling the all-iron battery with varying electrolyte volume ratios so that ferrous chloride in the negative electrolyte never exceeds 3.0 M. The initial concentration of ferrous chloride in the negative electrolyte is 3.0 M. Cycling is limited so that the concentration of ferrous and ferric ions in both electrolytes is always above 0.25 M.

<table>
<thead>
<tr>
<th>( \frac{V_+}{V_-} )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daramic</td>
<td>2.40 M</td>
<td>2.13 M</td>
<td>1.93 M</td>
<td>1.775 M</td>
<td>1.65 M</td>
</tr>
<tr>
<td>Nafion</td>
<td>2.82 M</td>
<td>2.43 M</td>
<td>2.16 M</td>
<td>1.96 M</td>
<td>1.89 M</td>
</tr>
</tbody>
</table>

Figure 2.9 shows the concentration profiles when cycling a 1 MW, 4 MWh all-iron battery with \( \frac{V_+}{V_-} = 4 \) and Daramic 250 separator at \( \pm 200 \text{ mA/cm}^2 \). The cycling was
bound by minimum concentrations of 0.25 M of ferric and ferrous chloride in both the positive and negative electrolyte. In the case shown in Figure 2.9, the initial concentration of ferrous chloride is 3.0 M in the negative electrolyte and 1.775 M in the positive electrolyte. The model begins with 1.525 M FeCl$_2$ and 0.25 M FeCl$_3$ in the positive electrolyte and 2.5 M FeCl$_2$ and “0.5 mol/L” iron metal in the negative electrolyte to simulate the results of the initial charging necessary to produce the minimum concentrations from which the battery was cycled.

**Figure 2.9:** Concentration of ferrous ions in a 1 MW, 4 MWh all-iron battery with Daramic 250. Cycles are at ±200 mA/cm$^2$ and are reversed when any species is 0.25 M. The black and gray curves represent Fe$^{2+}$ in the negative and positive reservoirs, respectively. The positive electrolyte volume is described by Equation [2.8]. The negative electrolyte volume is 1/4 the positive electrolyte volume.

The simulation shown in Figure 2.9 was extended to systems with varying current densities, separator thicknesses, and electrolyte volume ratios. Figure 2.10 shows the coulombic efficiency for systems with Daramic and Nafion separators at 200 mA/cm$^2$ and varying volume ratios. Figure 2.10 indicates that changing the relative volume of the
negative electrolyte does not significantly affect the achievable cycle-to-cycle coulombic efficiency.

To compare the predicted capacity available for batteries with different volume ratios, Figure 2.11 and Figure 2.12 show the watt-hours actually available \((\varepsilon_{cap} \cdot E)\) on discharge per mole of iron in the entire battery as a function of volume ratio and separator thickness for both Daramic and Nafion, respectively. The results indicate that the available watt-hours on discharge per mole of iron can in fact be increased by increasing the electrolyte volume ratio. When the negative electrolyte volume is 4 times smaller than the positive electrolyte volume (and an initial negative concentration of 3.0 M operated at \(\pm 200\) mA/cm\(^2\)), a 200 \(\mu\)m Daramic separator can achieve 11.5 Wh/mole Fe while a 35 \(\mu\)m thick Nafion separator can achieve 11.2 Wh/mole Fe. Table 2.4 shows a comparison between the different operating conditions with Nafion and Daramic separators.

**Table 2.4**: Summary of the predicted performance of a 1 MW, 4 MWh all-iron flow battery with \(C_{t=0} = 3.0\) M and the positive electrolyte volume specified by Equation [2.8] cycled at \(\pm 200\) mA/cm\(^2\) bound by 0.25 M in both electrolytes.

<table>
<thead>
<tr>
<th>Separator</th>
<th>Thick V+/V.</th>
<th>(C_{t=0}^+)</th>
<th>(\varepsilon_{coul})</th>
<th>(\varepsilon_{cap})</th>
<th>Wh/mol Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>200 (\mu)m</td>
<td>2</td>
<td>2.43</td>
<td>98%</td>
<td>74%</td>
</tr>
<tr>
<td></td>
<td>200 (\mu)m</td>
<td>4</td>
<td>1.96</td>
<td>99%</td>
<td>68%</td>
</tr>
<tr>
<td>Daramic</td>
<td>200 (\mu)m</td>
<td>2</td>
<td>2.13</td>
<td>94%</td>
<td>69%</td>
</tr>
<tr>
<td></td>
<td>200 (\mu)m</td>
<td>4</td>
<td>1.78</td>
<td>95%</td>
<td>63%</td>
</tr>
</tbody>
</table>
Figure 2.10: The coulombic efficiency of an all-iron battery with Daramic separators (closed symbols) and Nafion separators (open symbols) during 200 mA/cm² cycling bound by 0.25 M as a function of separator thickness for varying ratios of the positive to negative electrolyte. In all cases, the positive electrolyte volume is defined by Equation [2.8] and the initial concentration in the negative electrolyte is 3.0 M.

Figure 2.11: Available watt-hours on discharge per mole of iron in an all-iron battery with a Daramic separator during 200 mA/cm² cycling bound by 0.25 M as a function of separator thickness for varying ratios of the positive to negative electrolyte. In all cases, the positive electrolyte volume is defined by Equation [2.8] and the initial concentration in the negative electrolyte is 3.0 M.
Figure 2.12: Available watt-hours on discharge per mole of iron in an all-iron battery with a Nafion separator during 200 mA/cm² cycling bound by 0.25 M as a function of separator thickness for varying ratios of the positive to negative electrolyte. In all cases, the positive electrolyte volume is defined by Equation [2.8] and the initial concentration in the negative electrolyte is 3.0 M.

2.6 Conclusions

The effective diffusivity of ferric and ferrous ions through both Daramic 250 and Nafion 117 was studied and used to model the concentration profiles during continuous cycling operation. The effective diffusivity of ferric and ferrous ions across Daramic 250 was found to be $9.9 \times 10^{-7}$ cm²/s and $12.3 \times 10^{-7}$ cm²/s, respectively. The effective diffusivity of ferric and ferrous iron across Nafion 117 was found to be $4.3 \times 10^{-7}$ cm²/s and $3.5 \times 10^{-7}$ cm²/s, respectively.

The effective diffusivities determined for the iron species were used in a model of the all-iron flow battery under continuous cycling conditions. It was found that, after sufficient cycling, a steady state is achieved in which there is an accumulation of iron species in the negative electrolyte and a depletion of iron species in the positive
electrolyte. This redistribution of iron species in the battery leads to an energy capacity loss because the now reduced amount of iron in the positive electrolyte limits the battery capacity. This capacity loss, along with the coulombic efficiency loss due to crossover, was investigated as a function of current density, separator thickness, and relative electrolyte volume ratio. It was shown that by decreasing the volume of the negative electrolyte relative to the positive electrolyte volume, the available watt-hours on discharge per mole of iron in the system can be increased. Both the coulombic efficiency and the capacity retention were found to be independent of the battery energy and power ratings.

Both the coulombic efficiency and the actual discharge capacity were found to increase as the operating current density increases and as the separator thickness increases. However, for current densities above 200 mA/cm² and Daramic separators greater than 200 μm thick or Nafion separators thicker than 100 μm the advantages of further increasing current density or thickness are small. Also, the amount of energy available during discharge per mole of iron in the system can be increased by decreasing the volume of the negative electrolyte relative to the positive electrolyte. A maximum energy storage value occurs at a specific separator thickness for a given current density. Operating the battery with a Daramic separator 200-250 μm thick should have the maximum amount of energy stored with the least amount of iron, about 11.5 Wh/mole if $V_+/V_- = 4$. To obtain similar advantages with a Nafion separator, the separator should be 25-75 μm thick.

A nominal 4 hour battery with a 200 μm Daramic separator cycling continuously at ±200 mA/cm² bound by 0.25 M of either iron species is predicted to have a coulombic
efficiency due to crossover of 95% and an effective discharge capacity of 2.5 hours (63% of the theoretical four hours) if the positive electrolyte volume is four times larger than the negative electrolyte. A battery under the same operating condition with a 200 μm Nafion separator will have a coulombic efficiency due to crossover of 98% and an effective capacity of 2.9 hours (74% of the theoretical four hours).

This analytical model only takes into account the effects of crossover when cycling the all-iron battery. Using this model, conditions were found to optimize the performance of the battery and it was found that batteries with Daramic or Nafion separators can perform similarly under the appropriate conditions. In order to truly distinguish the merits of both separators, this analysis must be extended to include other aspects of the battery operation, such as voltaic efficiency and cost, which are presented in Chapter 3 of this thesis.
Chapter 3 Crossover Effects on All-Iron Flow Battery CAPEX

3.1 Introduction

A significant hurdle in obtaining market penetration of grid scale energy storage is the cost of redox flow batteries. As discussed earlier, it is expected that the capital cost (CAPEX) required of grid scale energy storage for market penetration is < $250/kW.\textsuperscript{1,6,7} While a number of models have been developed that predict both the capital and operating costs of RFBs, particularly ones based on the all-vanadium chemistry,\textsuperscript{17-19} not much has been published on the all-iron battery or models including crossover effects. In this chapter, the voltaic efficiency and cost associated with the battery separators will be added to the studies presented in Chapter 2 to form a more complete CAPEX analysis of the all-iron flow battery and allow for the optimal specification of battery separators. Both ion exchange membranes (Nafion) and microporous separators (Daramic) are considered.\textsuperscript{14,44-47}

3.2 Experimental

3.2.1 Materials and Equipment

All chemicals used while determining ionic conductivity of the separators were reagent grade. The NH\textsubscript{4}Cl and HCl were purchased from Fisher Scientific (Waltham, MA) and the iron salts were purchased from Alfa Aesar (Ward Hill, MA). Nafion 117 was purchased from Ion Power, Inc. (New Castle, DE). Daramic 250 separators were graciously donated by Daramic, LLC (Charlotte, NC).

Nafion was prepared by soaking in 5% H\textsubscript{2}O\textsubscript{2} for 1 hour at 60°C and then boiling in DI water. Before use, the Nafion was soaked in the indicated electrolyte for one week. The Nafion 117 was found to have a swelled thickness of about 200 microns.
The Daramic separator supplied was Daramic 250 Flatsheet with an average pore size of 0.1 microns, a reported porosity of $58 \pm 7.5\%$, and a compressed thickness of about 225 microns. The Daramic was soaked in methanol and rinsed in DI water before use.$^{14}$

All electrochemical measurements were made with a Solartron 1280B potentiostat from Ametek, Inc. (Oak Ridge, TN). When necessary, Ag/AgCl reference electrodes from Bioanalytical Systems, Inc. (West Lafayette, IN) were used.

### 3.2.2 Ionic Conductivity of Daramic 250 and Nafion 117

Four probe electrochemical impedance spectroscopy (EIS) was conducted between $2 - 2 \times 10^4$ Hz at 0 VDC with an AC amplitude of 25 mV on samples of Nafion 117 in the cell design shown in Figure 3.1 to determine the resistance of the sample.$^{48-51}$ Each Nafion sample, after being equilibrated in electrolyte for at least one week, was rinsed quickly in DI water and was then submerged in fresh DI water ($> 18 \text{M} \Omega \cdot \text{cm}^2$ before exposure to air) during the EIS measurements. The sample was submerged to keep the degree of swelling constant during the experiment. A typical distance between the reference electrodes, $\delta$, was 0.8 cm. Typical samples had a width of 0.5 cm and thickness of 0.02 cm.

![Figure 3.1: Cell for determining conductivity of Nafion 117.](image)

To determine the ionic conductivity of Daramic, a different four probe apparatus was used. A cross section of this design is shown in Figure 3.2. In this apparatus, the
reference electrodes are each 0.025 cm diameter silver wire. The tip of each of these wires was chloridized in 3 M NaCl by first applying 10 mA pulses to the wire for 30 seconds followed by 10 seconds at -3 mA. This process was repeated for at least 10 minutes. The working and counter electrodes in Figure 3.2 are 0.6 cm diameter graphite rods. The area of the separator exposed to the electrolyte was a circular area of 1.25 cm$^2$. EIS was performed in the same manner as the tests investigating the ionic conductivity of Nafion.

![Separator diagram](image)

**Figure 3.2:** Cross section of the cell used to determine the ionic conductivity of Daramic. The cross-hatched area is filled with electrolyte.

### 3.3 Results: Separator Ionic Conductivity

Equation [3.1] shows the relationship between the resistance measured in the separator and the corresponding ionic conductivity, $\kappa$. In this equation, $\delta$ is the length the current flows between reference electrodes and $A$ is the cross sectional area through which the current flows.$^{49,51}$ In the experiments used to measure the resistance in the Nafion membranes, the cross sectional area is the thickness of the sample times the width, $\delta \times w$. In the experiments used to measure the resistance in the Daramic separators, the cross sectional area is the exposed sample area (1.25 cm$^2$) while the length is the thickness of the sample.
\[ \kappa = \frac{1}{\delta RA} \]  

Table 1 shows the ionic conductivity results for samples of Daramic 250 Flatsheet. The ionic conductivity of the Daramic was found to be 40% of the ionic conductivity of the electrolyte in which the separator was equilibrated while tests were performed. Using the Bruggeman approximation,\textsuperscript{52} Equation [3.2], suggests that the porosity of the sample is about 54%. This agrees well with the manufacturer’s reported porosity for the Daramic 250 Flatsheet (58 +/- 7%).

\[ \kappa_{\text{effective}} = \kappa \varepsilon^{3/2} \]  

Table 3.1: Ionic conductivity of flow battery separators.

<table>
<thead>
<tr>
<th>Separator</th>
<th>Electrolyte</th>
<th>( \kappa ) (m S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 117</td>
<td>0.1 M HCl</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>0.1 M NH₄Cl</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>1.0 M FeCl₂ (pH = 2.5)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1.0 M FeCl₃ (pH = 1.0)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1 M FeCl₂, 1 M FeCl₃ &amp; 1 M NH₄Cl</td>
<td>5-10</td>
</tr>
<tr>
<td>Daramic 250</td>
<td>0.1 M HCl</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>0.1 M NaCl</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>1.0 M FeCl₂</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>1.0 M FeCl₃</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>1 M FeCl₂, 1 M FeCl₃ &amp; 1 M NH₄Cl</td>
<td>48</td>
</tr>
</tbody>
</table>

The ionic conductivity found for the Nafion 117 membranes equilibrated in various electrolytes is also reported in Table 3.1. The ionic conductivities of 78 mS/cm and 25 mS/cm in 0.1 M HCl and 0.1 M NH₄Cl, respectively, agree well with the literature.\textsuperscript{49-51} In the presence of iron, the ionic conductivity of Nafion was observed to significantly decrease. When equilibrated in a typical battery electrolyte (1 M FeCl₂, 1 M FeCl₃, and 1 M NaCl) the Nafion had an ionic conductivity of 5-10 mS/cm. This
agrees well with the range presented in the literature.\textsuperscript{53-55} The natural pH of this electrolyte is about 1.2 due to ferric and ferrous iron being weak acids.\textsuperscript{26}

3.4 Discussion

3.4.1 Voltaic Efficiency Estimates

The battery round trip voltaic efficiency is described by Equation [3.3]. The theoretical open-circuit voltage of the all-iron battery is 1.2 V\textsuperscript{21,26} and Equation [3.4] describes the operating voltage of the battery. The sum of the overpotentials, described in Equation [3.5], includes all of the overpotentials at the anode and the cathode as well as the ohmic losses across the separator and is positive during charge and negative during discharge. Each overpotential can be described as an area resistance times the operating current density, Equation [3.6], assuming each is still in the linear region. While the mass transfer, activation, and ohmic overpotentials of each electrode can vary with battery state-of-charge and electrolyte composition, they are not typically affected by the separator properties. To simplify the investigations presented herein, all of the overpotentials except those associated with the separator will be assumed to be constants. A minimum concentration of 0.25 M for either ferrous or ferric iron has been added to the model such that the assumption of constant kinetic and mass transfer overpotentials is realistic. A battery area resistance of 0.5 Ω·cm\textsuperscript{2}, not including the ohmic resistivity of the separator, corresponds to an overpotential of ±0.1 V at ±200 mA/cm\textsuperscript{2}.

\begin{equation}
\varepsilon_{\text{Volt}}^{\text{Total}} = \frac{V_{\text{Disch}}}{V_{\text{OCV}}} = \frac{V_{\text{Disch}}}{V_{\text{Charge}}} [3.3]
\end{equation}

\begin{equation}
V = V_{\text{OCV}} + \Sigma \eta [3.4]
\end{equation}

\begin{equation}
\Sigma \eta = \Sigma \eta^A + \eta^\text{Sep} + \Sigma \eta^C [3.5]
\end{equation}

\begin{equation}
\eta_j = i \cdot \tilde{R}_j [3.6]
\end{equation}
Figure 3.3a: Predicted voltaic efficiency of a battery operating with Nafion (closed symbols) and Daramic (open symbols) separators with the cell resistance, not including the separator ($\bar{R}_{\text{total}} - \bar{R}_{\text{sep}}$), at a constant 0.5 $\Omega$-cm$^2$.

Figure 3.3b: Predicted voltaic efficiency of a battery operating with Nafion (closed symbols) and Daramic (open symbols) separators cycled at 200 mA/cm$^2$. Square, circle, and triangle symbols represent cell resistances ($\bar{R}_{\text{total}} - \bar{R}_{\text{sep}}$) of 0.50, 0.75, and 1.00 $\Omega$·cm$^2$, respectively.
The area resistance of a separator is described in Equation [3.7] and the round trip voltaic efficiency of the battery, as a function of current density and membrane thickness, is shown in Equation [3.8]. Figure 3.3a shows the voltaic efficiency for an all-iron flow battery as a function of separator thickness at varying operating current densities for both Nafion and Daramic when the cell resistance (not including the separator) is 0.5 Ω·cm². Figure 3.3b shows the voltaic efficiency for an all-iron flow battery as a function of separator thickness at varying cell resistances for both Nafion and Daramic at 200 mA/cm² operating current. In both figures, the ionic conductivity of Daramic and Nafion separators is taken to be 48 mS/cm and 5 mS/cm, respectively, and is assumed to be constant with thickness.

$$\bar{R}^\text{Sep}_{IR} = \frac{\delta}{\kappa_{Sep}} \quad [3.7]$$

$$\varepsilon_{\text{Volt}}^{Total} = \frac{V_{OCV} + \left[R^A + C + \bar{R}^\text{Sep}_{IR}\right]j_{\text{Disch}}}{V_{OCV} + \left[R^A + C + \bar{R}^\text{Sep}_{IR}\right]j_{\text{Charge}}} \quad [3.8]$$

Figure 3.3a and Figure 3.3b show that cells with Daramic separators should have significantly better voltaic efficiencies than those with Nafion separators. At 200 mA/cm² and a cell resistance ($\bar{R}_{total} - \bar{R}_{sep}$) of 0.5 Ω·cm², batteries with Daramic separators of 100 µm thick exhibit about 80% voltaic efficiency. The same battery with a 100 µm thick Nafion separator will only have about 40% voltaic efficiency. Comparing Figure 3.3a to Figure 3.3b, the operating current density is shown to have a much larger effect on the voltaic efficiency than the cell resistance.

### 3.4.2 Coulombic Efficiency and Discharge Capacity Estimates

In Chapter 2, the concentration profiles during cycling of an all-iron flow battery were modeled including the effects of active species crossover and self-discharge. The models
predict an accumulation of ferrous ions in the negative electrolyte and a depletion of iron ions in the positive electrolyte that comes to a steady-state after sufficient cycling. The coulombic efficiency due to crossover and the effective discharge capacity due to the redistribution of iron were calculated. The coulombic efficiency and available capacity were found to increase with current density but the additional gains were small above 200 mA/cm$^2$. These efficiencies are functions of current density, separator thickness, and the ratio of the positive electrolyte volume to the negative electrolyte volume but are not functions of the battery power rating or energy storage capacity.

By increasing the ratio of the positive electrolyte volume relative to the negative electrolyte volume, the amount of iron and electrolyte required in the system decreases drastically. The battery’s available watt-hour per mole of iron was found to increase by increasing the volume ratio but the additional gains were minor above $V_{+,}/V.$ of 4. In order to maintain favorable electrolyte properties the concentration of ferrous chloride in the negative should be below 3.0 M. As a result, the initial concentration of the positive electrolyte must decrease as the volume ratio increases. In all cases discussed herein, the initial concentration of the negative electrolyte is 3.0 M FeCl$_2$. The positive concentration was varied depending on the electrolyte volume ratio and is reported in Table 2.4.
3.5 Cost Model

With the voltaic efficiency, coulombic efficiency, and effective discharge capacity reported in Chapter 2, the CAPEX of an all-iron flow battery can be predicted as a function of membrane thickness, operating current density, energy storage capacity, and the electrolyte volume ratio. Only the CAPEX of the all-iron flow battery materials is investigated: no estimates are made of operating costs, labor, taxes, site preparation, assembly costs, or power conditioning. However, pumping and shunt losses, voltaic and coulombic efficiencies, and the effects of crossover are included. The battery is specified for an available discharge power of 1 MW with varying energy storage capacities. The model parameters used are shown in Table 3.2. The estimated pumping, shunt, and reaction efficiencies agree with the range presented in the literature.\textsuperscript{17,27}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Cell Area, $A_{cell}$</td>
<td>1000</td>
<td>cm$^2$/cell</td>
</tr>
<tr>
<td>Nominal Voltage, $V_{OCV}$</td>
<td>1.20</td>
<td>V</td>
</tr>
<tr>
<td>Current Density, $i$</td>
<td>0.20</td>
<td>A/cm$^2$</td>
</tr>
<tr>
<td>Power Rating, $P$</td>
<td>$1 \times 10^6$</td>
<td>W</td>
</tr>
<tr>
<td>Cells per Stack</td>
<td>100</td>
<td>cells/stack</td>
</tr>
<tr>
<td>$Fe^{2+/3+}, n_+$</td>
<td>1</td>
<td>mole e$^-$/mole j</td>
</tr>
<tr>
<td>$Fe^{2+/0}, n_-$</td>
<td>2</td>
<td>mole e$^-$/mole j</td>
</tr>
<tr>
<td>Daramic, $\kappa$</td>
<td>0.048</td>
<td>S/cm</td>
</tr>
<tr>
<td>Nafion, $\kappa$</td>
<td>0.005</td>
<td>S/cm</td>
</tr>
<tr>
<td>$\varepsilon_{Shunt}$</td>
<td>98%</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_{Pump}$</td>
<td>97%</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_{Rxn}$</td>
<td>99%</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.3: CAPEX model component costs.\textsuperscript{17}

<table>
<thead>
<tr>
<th>Component</th>
<th>Near-Term Cost</th>
<th>Cost Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bipolar Plate</td>
<td>35</td>
<td>$/m^2</td>
</tr>
<tr>
<td>Flow Frames</td>
<td>9.88</td>
<td>$/m^2</td>
</tr>
<tr>
<td>Gaskets</td>
<td>100</td>
<td>$/stack</td>
</tr>
<tr>
<td>Collector Plate</td>
<td>97</td>
<td>$/stack</td>
</tr>
<tr>
<td>End Plates</td>
<td>86</td>
<td>$/stack</td>
</tr>
<tr>
<td>Bolts</td>
<td>12.50</td>
<td>$/stack</td>
</tr>
<tr>
<td>PVC Connections</td>
<td>150</td>
<td>$/stack</td>
</tr>
<tr>
<td>Tanks</td>
<td>92</td>
<td>$/m^3</td>
</tr>
<tr>
<td>Pumps</td>
<td>8,000</td>
<td>$/pump</td>
</tr>
<tr>
<td>2 M Iron Electrolyte</td>
<td>130</td>
<td>$/m^3</td>
</tr>
<tr>
<td>Carbon Felt</td>
<td>70</td>
<td>$/m^2</td>
</tr>
<tr>
<td>Daramic</td>
<td>10</td>
<td>$/m^2</td>
</tr>
<tr>
<td>Nafion</td>
<td>350</td>
<td>$/m^2</td>
</tr>
</tbody>
</table>

In order to simplify and better align these efforts with the current literature, the near term cost estimates of the flow battery components from V. Viswanathan et al. were used and are shown in Table 3.3.\textsuperscript{17} The present day cost estimate of the carbon felt electrode material was used so that other novel electrode materials can be compared more accurately (discussed in detail in Chapter 7). The cost of the iron electrolyte is taken to be $130/m^3.\textsuperscript{17} This is the cost of 2 M iron chloride with supporting ions. The cost of the electrolyte with varying iron concentration used in the CAPEX models is defined by Equation [3.9]. The cost of the separators is an area cost and is assumed to be independent of separator thickness. Equation [3.10] and Equation [3.11] describe the required total battery active area and positive electrolyte volume for a specified discharge power rating and discharge energy capacity. The negative electrolyte volume is dictated by the electrolyte volume ratio. These equations assume the overpotentials on charge and
on discharge are the same. The total battery CAPEX is the sum of each component listed in Table 3.3. It is assumed that only two pumps, totaling $16,000, are necessary for a 1 MW system. While the coulombic efficiency due to crossover and capacity efficiency only depend upon current density and separator thickness, the battery capital cost is also dependent on the energy storage capacity. Battery cycles modeled were reversed when the ferric or ferrous concentration is 0.25 M. Assuming 100% coulombic efficiency, this simulates a maximum 75% state-of-charge swing centered around 50% state-of-charge.

\[
\text{Electrolyte Cost} = \frac{\left[130/m^3\right] \Sigma c^\pm}{2000 \text{ mol} / m^3}
\]  

\[
A_{Total}^{Active} = \frac{P}{V_{OCV} \epsilon_{Pump} \epsilon_{Shunt} \epsilon_{Voltaic} \sqrt{\epsilon}}
\]  

\[
V_{+} = \frac{E}{V_{OCV} C_{4+} F} \frac{1}{\epsilon_{Coul} \epsilon_{Coul} \epsilon_{Voltaic} \epsilon_{Capacit}}
\]

Figure 3.4a-3.4c show the predicted battery CAPEX ($/kW) for an all-iron flow battery \((E/P = 4 \text{ hours})\) with Daramic separators as a function of current density, separator thickness, and energy storage capacity. Figure 3.5a-3.5c show the CAPEX analysis for batteries with Nafion separators. In all cases, the negative electrolyte initially contains 3.0 M ferrous chloride. The initial positive electrolyte concentration varies with electrolyte volume ratio so that the steady state concentration of ferrous or ferric ion does not exceed 3.0 M in either electrolyte. In all cases, the capital cost ($/kWh) is equal to the CAPEX ($/kW) divided by the hours of energy stored. The CAPEX of the battery is found to decrease with decreasing storage capacity, increasing current density, and increasing electrolyte volume ratio. However, the CAPEX of the all-iron battery is
constant with energy storage capacity \((E/P \text{[=] hours})\) for a given current density, separator thickness, volume ratio, and cell resistance.

**Figure 3.4a:** CAPEX ($/kW) of an all-iron battery with a 105 \(\mu\)m thick Daramic separator at various current densities and energy storage capacities. The volume ratio \((V_+/V_-)\) is 4 and the cell resistance \((\bar{R}_{total} - \bar{R}_{sep})\) is 0.5 \(\Omega\cdot\text{cm}^2\).

**Figure 3.4b:** CAPEX ($/kW) of an all-iron battery operated at 200 mA/cm\(^2\) at various Daramic thicknesses and energy storage capacities. The cell resistance \((\bar{R}_{total} - \bar{R}_{sep})\) is 0.5 \(\Omega\cdot\text{cm}^2\) and the electrolyte volume ratio \((V_+/V_-)\) is 4.
Figure 3.4c: CAPEX ($/kW) of a 4 hour all-iron battery operated at 200 mA/cm$^2$ at various Daramic thicknesses and volume ratios ($V_+/V_-$). The cell resistance ($\bar{R}_{\text{total}} - \bar{R}_{\text{sep}}$) is 0.5 Ω · cm$^2$.

Figure 3.5a: CAPEX ($/kW$) of an all-iron battery with a 14 µm thick Nafion separator at various current densities and energy storage capacities. The volume ratio ($V_+/V_-$) is 4 and the cell resistance ($\bar{R}_{\text{total}} - \bar{R}_{\text{sep}}$) is 0.5 Ω · cm$^2$. 
Figure 3.5b: CAPEX ($/kW) of an all-iron battery operated at 200 mA/cm$^2$ at various Nafion thicknesses and energy storage capacities. The cell resistance ($\bar{R}_{\text{total}} - \bar{R}_{\text{sep}}$) is 0.5 Ω · cm$^2$ and the electrolyte volume ratio ($V_+/V_-$) is 4.

Figure 3.5c: CAPEX ($/kW) of a 4 hour all-iron battery operated at 200 mA/cm$^2$, cycled continuously and bound by 0.25 M, at various Nafion thicknesses and electrolyte volume ratios. The cell resistance ($\bar{R}_{\text{total}} - \bar{R}_{\text{sep}}$) is 0.5 Ω · cm$^2$. 
For a specified energy storage capacity, operating current density, and electrolyte volume ratio, there is a separator thickness at which a minimum CAPEX value occurs. These minimum CAPEX values are reported in Figure 3.6 and Figure 3.7, along with the corresponding separator thickness, as a function of the $E/P$ while operating at 200 mA/cm$^2$ and $V_+/V_- = 4$ for batteries with Daramic and Nafion separators, respectively. The separator thickness for which the minimum CAPEX value occurs was found to increase with increasing energy storage capacity and decreasing current density. Over the battery capacities investigated, the optimal thickness of the Daramic separator operated at 200 mA/cm$^2$ and an electrolyte volume ratio of 4 is between 60-150 µm. For batteries with Nafion separators operated at 200 mA/cm$^2$, the optimal thickness is between 5-20 µm.

A 4 hour all-iron flow battery operated at 200 mA/cm$^2$ with $V_+/V_- = 4$ has an estimated minimum CAPEX of about $175/kW ($45/kWh) when using a 105 µm thick Daramic separator. Using a Nafion separator with a thickness of 14 µm, the CAPEX of the same battery increases to about $350/kW ($90/kWh). At most storage capacities and operating currents, the CAPEX at the optimal separator thickness with Nafion is predicted to be about double the CAPEX when using Daramic. Figure 3.8 and Figure 3.9 show the component cost breakdown of a 4 hour all-iron battery with optimal Daramic and Nafion separators, respectively.
Figure 3.6: The optimal separator thickness, and the corresponding CAPEX values, for an all-iron flow battery at 200 mA/cm², $R_{total} - R_{sep} = 0.5 \ \Omega \cdot \text{cm}²$, and $V_+/V_- = 4$ at and various energy capacities with a Daramic separator. The initial concentration in the negative and positive electrolytes, respectively, is 1.775 M and 3.0 M ferrous chloride.

Figure 3.7: The optimal separator thickness, and the corresponding minimum CAPEX values, for an all-iron flow battery with Nafion separators. All conditions are the same as Figure 3.6 except that the initial positive electrolyte concentration is 1.95 M FeCl₂.
Figure 3.8: Component cost breakdown of a 4 hour all-iron battery cycled at 200 mA/cm$^2$ with a 105 μm Daramic separator. The cell resistance, $\bar{R}_{total} - \bar{R}_{sep}$, is 0.5 Ω·cm$^2$ and $V_+/V_- = 4$.

Figure 3.9: Component cost breakdown of a 4 hour all-iron battery cycled at 200 mA/cm$^2$ with a 14 μm Nafion separator. The cell resistance, $\bar{R}_{total} - \bar{R}_{sep}$, is 0.5 Ω·cm$^2$ and $V_+/V_- = 4$. 
3.6 Iron Plating Density Considerations

The CAPEX models presented thus far are for an all-iron battery with conventional felts serving as both the positive and negative electrodes. While charging the battery, iron metal is being plated into the negative felt electrode and any plating capacity limitations of these felt electrodes has been ignored. Hawthorne, et al.\textsuperscript{30} and Hoyt, et al.\textsuperscript{31} have reported that the maximum plating capacity of metal into felt electrodes \((z = 2 \text{ mole } e^-/\text{mole } j)\) to be anywhere between 150-560 mAh/cm\(^2\). The effective plating density in the felt when the overpotential and parasitic losses are accounted for is described by Equation [3.12]. As a result, a metal plating density in the felt, \(j_{\text{felt}}\), of 560 mAh/cm\(^2\) corresponds to a battery storage capacity, \(E/P\), of about 3.85 hours with a 105 µm Daramic separator operating at a current density of 200 mA/cm\(^2\). With a 14 µm Nafion separator operated at 200 mA/cm\(^2\), 560 mAh/cm\(^2\) corresponds to a 3.4 hour battery. Novel electrodes structures will be needed to achieve higher energy storage capacity to power ratios so that the all-iron flow battery can penetrate into the largest potential markets (Table 1.1).

\[
    j_{\text{felt}} = \frac{E}{P} \frac{\epsilon_{\text{Pump}} \epsilon_{\text{Shunt}}}{\sqrt{\epsilon_{\text{Voltaic}}}} \quad \text{[3.12]}
\]

3.7 Conclusions

A parametric study of the capital cost of the all-iron flow battery was preformed focusing on the effects of the separator thickness, cycling current density (including their effects on voltaic efficiency and efficiency losses due to crossover), electrolyte volume ratio, and the energy storage capacity. Both Daramic and Nafion separators were considered. In all cases, the CAPEX of the battery is found to decrease with increasing current density, decreasing storage capacity, and increasing electrolyte volume ratio. An
optimal separator thickness, at which a minimum capital cost occurs, has been predicted for each specified current density, electrolyte volume ratio, and energy storage capacity. For each scenario, the battery CAPEX with the optimal Nafion separator was about double the cost with the optimal Daramic separator. The optimal thickness of the separator, for both Daramic and Nafion, increases as the energy storage capacity increases and cycling current density decreases. Also, the capital cost is found to be much less sensitive to separator thickness and cycling current density when using a Daramic separator then Nafion separators. Table 5 shows the different efficiencies and costs associated with an all-iron battery with 2 hours and 4 hours discharge energy storage capacity when operated at 200 mA/cm².

**Table 3.4:** Summary of the CAPEX model for a 4 hour all-iron battery cycled at the optimal separator thickness and ±200 mA/cm². During cycling, no species concentration was ever below 0.25 M. The cell overpotentials ($\bar{R}_{\text{total}} - \bar{R}_{\text{sep}}$) were constant at 0.5 Ω·cm² and $V_+/V_- = 4$.

<table>
<thead>
<tr>
<th>Separator Type</th>
<th>$E/P$ hrs</th>
<th>δ µm</th>
<th>$\varepsilon_{\text{Volt}}^{\text{Total}}$</th>
<th>$\varepsilon_{\text{Coul}}^{\text{over}}$</th>
<th>$\varepsilon_{\text{Cap}}$</th>
<th>$$/kW$$</th>
<th>$$/kWh$$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>2</td>
<td>10</td>
<td>79%</td>
<td>74%</td>
<td>57%</td>
<td>325</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>14</td>
<td>77%</td>
<td>80%</td>
<td>60%</td>
<td>350</td>
<td>90</td>
</tr>
<tr>
<td>Daramic</td>
<td>2</td>
<td>80</td>
<td>80%</td>
<td>89%</td>
<td>61%</td>
<td>155</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>105</td>
<td>79%</td>
<td>91%</td>
<td>62%</td>
<td>175</td>
<td>45</td>
</tr>
</tbody>
</table>
Chapter 4 Slurry Electrodes

In order to truly be able to reach the vast market potential predicted for grid scale storage, the all-iron flow battery must be able to have 4-8+ hours of energy storage available at < $250/kW. The analysis described in Chapter 3 indicates that the all-iron flow battery with conventional stationary electrodes is capable of meeting these cost targets but cannot have sufficiently large energy capacities with conventional electrodes. Slurry electrodes are investigated so that the energy storage capacity can be decoupled from the power delivery rate. For slurry electrodes to be effective, the current distribution must favor the plating reaction to occur on the surface of the slurry particles instead of stationary components in the energy conversion device. One significant factor contributing to voltaic efficiency, discussed in Chapter 5, and the current distribution, shown in Chapter 6, is the electronic conductivity. This chapter will discuss previously studied electrochemical slurry electrodes and will focus on the description of how they are electronically conductive in order to help guide the slurry particle selection.

4.1 Slurry Electrodes

Slurries are flowing suspensions of solid electrically conductive particles in liquid electrolyte (Figure 4.1). The particles form networks that conduct electrons out into the slurry electrode where the redox reaction can occur on the surface of the particles. There are many advantages to using slurry electrodes over conventional stationary electrodes. The use of a slurry allows the electrode (1) surface area to be scaled independently of the separator area, (2) to be easily manufactured and replaced without disassembling the cell, and (3) to be easily recycled with filtration. During charge and discharge, the electrolyte is pumped through the energy conversion cell as in normal RFB operation. However,
when using slurry electrodes, the solid particles are carried by the electrolyte into and out of the electrochemical cell. When slurries are employed as the negative electrode of the all-iron flow battery, iron metal is plated onto the surface of the slurry particles. As the slurry is circulated out of the electrochemical cell back into the external reservoir, the iron metal is carried with the particles, enabling the energy storage capacity to be decoupled from the power rating. The capacity of the flow battery, as in traditional RFBs, only depends on the amount of electrolyte (slurry) in the system.

![Schematic representation of a slurry electrode.](image)

**Figure 4.1:** Schematic representation of a slurry electrode.

Slurries have been studied for their application as electrochemical electrodes for most of the last century. Heydecke and Beck\(^{56}\) cite fundamental work as early as 1928. Originally, electrochemical slurry electrodes were investigated almost exclusively for waste water treatment.\(^{57-62}\) In the late 1970’s, slurry electrodes were used in the zinc-air battery system for energy storage.\(^{63-65}\) In the last few years, particular interest has been given to other energy storage applications, especially non-aqueous lithium-ion batteries\(^{66-70}\) and electrochemical flow capacitors.\(^ {75-80}\) Table 4.1 presents a brief summary
of the systems studied to date. Most of the recent investigations studied slurry electrodes made with suspensions of high surface area carbon black particles.

### Table 4.1: A brief summary of the electrochemical system investigated with slurry electrodes.

<table>
<thead>
<tr>
<th>System</th>
<th>Particles</th>
<th>Size [µm]</th>
<th>vol. %</th>
<th>Electrolyte</th>
<th>σ [mS/cm]</th>
<th>κ [mS/cm]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Treatment</td>
<td>Organic &amp; Inorganic Carbon Black</td>
<td>10^{-2} – 10^{-1}</td>
<td>0.2-20</td>
<td>Aqueous</td>
<td>n/r</td>
<td>n/r</td>
<td>57-60</td>
</tr>
<tr>
<td>Hg</td>
<td>MWCNTs</td>
<td>d: 10^{-2}</td>
<td>0.01-0.1</td>
<td>Aqueous</td>
<td>n/r</td>
<td>n/r</td>
<td>61</td>
</tr>
<tr>
<td>Cap. DI</td>
<td>Activated Carbon</td>
<td>8.8</td>
<td>2.5</td>
<td>Aqueous</td>
<td>n/r</td>
<td>11.5</td>
<td>62</td>
</tr>
<tr>
<td>Zn-Air Battery</td>
<td>Zinc metal</td>
<td>10^2 - 10^3</td>
<td>2-5</td>
<td>Aqueous</td>
<td>n/r</td>
<td>n/r</td>
<td>63-65</td>
</tr>
<tr>
<td>Li-Ion Battery</td>
<td>Li-Oxide &amp; Carbon Black</td>
<td>2-3</td>
<td>10-25</td>
<td>Non-aqueous</td>
<td>10^{-3} – 1</td>
<td>1 - 25</td>
<td>66-70</td>
</tr>
<tr>
<td>Li-S Battery</td>
<td>Carbon Black</td>
<td>&lt; 1</td>
<td>1-3</td>
<td>Non-aqueous</td>
<td>2 – 20</td>
<td>1.5</td>
<td>71</td>
</tr>
<tr>
<td>Metal-Oxide Battery</td>
<td>Polyamide &amp; Polypyrrole</td>
<td>3-30</td>
<td>n/r</td>
<td>Aqueous</td>
<td>n/r</td>
<td>n/r</td>
<td>72,73</td>
</tr>
<tr>
<td>ZnAg Battery</td>
<td>Ag doped Polyamide &amp; Graphite</td>
<td>n/r</td>
<td>5-10</td>
<td>Aqueous</td>
<td>n/r</td>
<td>n/r</td>
<td>74</td>
</tr>
<tr>
<td>Capacitor</td>
<td>Graphite &amp; Carbon Black</td>
<td>10-500</td>
<td>5-15</td>
<td>Aqueous</td>
<td>&lt; 20</td>
<td>60-300</td>
<td>75-80</td>
</tr>
</tbody>
</table>

While the body of literature surrounding engineering applications of electrochemical slurry electrodes is rapidly growing, there is little fundamental understanding of how these slurry electrodes behave electrochemically under flowing conditions. Most work thus far has been rooted in the theory developed for stationary porous electrodes and fluidized or packed bed electrodes, discussed in detail in Chapter 5 and 6.

### 4.2 Electronic Conductivity of Slurry Electrodes

Slurry electrodes are inherently dynamic bicontinuous systems. Particles are constantly moving and are constantly making and breaking contact with each other. In order for a slurry to effectively function as an electrochemical electrode, the particles must form conductive networks so that a maximum number of particles are available to support the electrochemical reaction. Also, for the electrodes to effectively decouple the negative electrode in the all-iron flow battery, the current distribution must be such that the reaction occurs on the particles in the slurry and not on the current collector.
(discussed in Chapter 6). Effective medium theory and percolation theory, developed mostly in parallel to each other, work to describe the conductivity of these two-phase electrodes.

Effective medium theory was first developed by Maxwell in 1892 when he solved the Laplace equation for the potential field around a sphere of a different material embedded in a continuum. He then related the variations in the potential field of the continuum due to the inclusion of this isolated sphere to conduction in the continuum to obtain Equation [4.1a]. In this equation, \( \sigma_c \) is the conductivity of the continuous phase, \( \sigma_d \) is the conductivity of the dispersed phase, \( \sigma_m \) is the effective conductivity of the mixture, and \( f \) is the volume fraction of the dispersed phase. Because Maxwell solved for the exact field around a single element, Equation [4.1a] only applies to very dilute concentrations of spherical inclusions. Also, Maxwell’s model requires that the conductivity of the continuous phase be greater than zero. The dispersed phase can be greater than or equal to zero. If \( \sigma_d = 0 \), the dispersed spheres are non-conductive, Equation [4.1a] becomes Equation [4.1b].

\[
\frac{\sigma_m}{\sigma_c} = \frac{\sigma_d + 2\sigma_c - 2f(\sigma_c - \sigma_d)}{\sigma_d + 2\sigma_c + f(\sigma_c - \sigma_d)} \quad [4.1a]
\]
\[
\frac{\sigma_m}{\sigma_c} = \frac{2(1-f)}{2+f} \quad [4.1b]
\]

Effective medium theory continued to develop in the same manner set forth by Maxwell; solving for the exact field about a single element and then trying to find correlations to extend the analysis to an entire system. The field progressed in this manner until the Bruggeman model was developed in 1935. Bruggeman extended the Maxwell model to include a random dispersion of spherical particles of a wide size-range in the continuum. He did this by assuming that the field around larger particles is
relatively unaffected by the inclusion of smaller particles. From the perspective of the large spheres, the system is dilute. Bruggeman then integrated for the wide range of “dilute” spheres, which yielded Equation (4.2a). If \( \sigma_d = 0 \), the dispersed spheres are non-conductive, Equation (4.2a) becomes Equation (4.2b). In these equations, \( \gamma = 1.5 \) for dispersions with complete disparity in size distribution. (This exponent does not indicate aspect ratio or dimensionality of percolated network as sometimes implied.) As the dispersed spheres become more uniform in size, \( \gamma \to 1.3 \) and the prediction of the Bruggeman model approaches that of the Maxwell model.

\[
\left( \frac{\sigma_m - \sigma_d}{\sigma_c - \sigma_d} \right) \left( \frac{\sigma_c}{\sigma_m} \right)^\gamma = (1 - f) \quad \text{[4.2a]}
\]

\[
\frac{\sigma_m}{\sigma_c} = (1 - f)^\gamma \quad \text{[4.2b]}
\]

The Bruggeman approximation offers mild improvements over the Maxwell model, matching well with experimental data through about 20 vol% dispersed phase. If the volume fraction of the dispersed phase is > 80 vol%, then the conductivity of a conductive dispersed phase can be modeled with a non-conductive continuous phase, akin to modeling the electronic conductivity of a slurry electrode. This effectively assumes that the continuum is now so dilute, it behaves like spheres of varying sizes trapped between the included particles. To invert Equations [4.1a]-[4.2b], \( f \Rightarrow (1 - f) \). Effective medium theory in these forms does not account for particle-to-particle interactions or clustering of particles and therefore cannot predict an onset of conductivity in the dispersed phase other than at 0.0% loading. There were some efforts to apply Maxwell’s equations to dispersions of particles other than spheres and at higher volume fractions but none were able to fit experimental results as well as the Bruggeman approximation.
Broadbent and Hammersley\textsuperscript{91} were the first to put forth percolation theory in 1957 and to describe the critical concentration, $f_c$, of a dispersion. When the volume fraction of a discontinuous phase is above the critical concentration, a continuous network is formed that extends between the system boundaries. Over the following two decades, percolation theory developed (in tandem with computing power) by describing two-phase systems as circuit networks randomly developing either on the bonds or sites of a lattice.\textsuperscript{92} Equation [4.3] describes the conductivity of a two-phase system in which the dispersed phase has some inherent conductivity, $\sigma_d \neq 0$, and $\sigma_c = 0$. In Equation [4.3], $B$ is a scaling factor such that $\frac{\sigma_m}{\sigma_d} = 1$ when $f = 1$. Table 4.2 shows the predicted values of the variables in Equation [4.3] for a variety of different simulations. Different lattices on which the resistor network is formed are used to simulate dimensionality in the percolation networks. If $f_c = 0$, Equation [4.3] equals Equation [4.2] when solved for the dispersed phase.

$$\frac{\sigma_m}{\sigma_d} = B(f - f_c)^\gamma \quad [4.3]$$

<table>
<thead>
<tr>
<th>Ex. Lattice</th>
<th>$d$</th>
<th>$\gamma$</th>
<th>$f_c$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square</td>
<td>2D</td>
<td>1.3</td>
<td>0.50</td>
<td>2.46</td>
</tr>
<tr>
<td>Cubic</td>
<td>3D</td>
<td>1.6-2.0</td>
<td>0.33</td>
<td>2.23</td>
</tr>
<tr>
<td>Hypercubic</td>
<td>4D</td>
<td>--</td>
<td>0.20</td>
<td>--</td>
</tr>
<tr>
<td>Bethe</td>
<td>$\geq$6D</td>
<td>3.0</td>
<td>0.10</td>
<td>1.37</td>
</tr>
</tbody>
</table>

Table 4.2: Variables in Equation [4.3] applied to lattice bond (vs lattice site) percolation.\textsuperscript{92}

In the 1970’s, Kirkpatrick was the first to bring the field approximations of effective mean theory and the computational approximations of percolation theory together to describe the conductivity of multi-phase systems with particle-to-particle interactions.\textsuperscript{93,94} This eventually led to Equations [4.4a]-[4.4d] by Granqvist et al.\textsuperscript{95} and Gao et al.\textsuperscript{96} In this
system of equations, \( L_j \) is an interaction factor that depends upon \( p \), the particle aspect ratio.

\[
(1 - f) \frac{\sigma_m - \sigma_c}{2\sigma_m + \sigma_c} + \frac{\sum (\sigma_m - \sigma_d)}{\sigma_m + L_j (\sigma_d - \sigma_m)} = 0
\]

[4.4a]

\[
L_x = \frac{1}{2(p^2 - 1)^{3/2}} \left[ p \ln \frac{p + (p^2 - 1)^{1/2}}{p - (p^2 - 1)^{1/2}} - 2(p^2 - 1)^{1/2} \right]
\]

[4.4b]

\[
L_y = L_z = \frac{1 - L_x}{2}
\]

[4.4c]

Figure 4.2: Conductivity and critical volume fraction described by Equation [4.5] for various aspect ratios.

If the conductivity of the continuous phase is again set to zero, Equation [4.4a] becomes Equation [4.5]. \( L_x \) approaches 1 as the aspect ratio approaches zero and it approaches zero as the aspect ratio approaches infinity. By solving for the particle volume fraction when \( \sigma_c = 0 \), the critical concentration, \( f_c \), can be estimated for a given aspect ratio. Figure 4.2 shows the conductivity of a two-phase system and the critical percolation concentration predicted by Equation [4.5] for a range of particle aspect ratios. While the magnitude of the mixture conductivity is dictated by the inherent conductivity of the dispersed phase, the conductivity of the system increases drastically at a given volume fraction when the aspect ratio approaches either zero or infinity (for relatively
dilute dispersions). Figure 4.2 shows rod shaped inclusions have lower critical volume fractions but disks have higher conductivities at a given particle loading.

\[
\frac{9(1-f)}{2f} = 4 \frac{\sigma_d-\sigma_m}{\sigma_m(1+L_x)+\sigma_d(1-L_x)} + \frac{\sigma_m-\sigma_{m'}}{\sigma_m(1-L_x)+\sigma_d}
\]  

[4.5]

**Figure 4.3:** The experimentally determined electronic conductivity of three slurry electrodes made with 230U natural flake carbon particles (p = 0.01), Nano27 carbon nano-flake (p = 0.1), and with MWCNTs (p = 100), shown against the conductivity curves predicted by Equation [4.5].

Figure 4.3 shows the electronic conductivity while flowing of select slurry electrodes, described in Appendix A, compared to the corresponding prediction of Equation [4.5]. As the figure depicts, Equation [4.5], while able to describe the general trends in conductivity, fails to accurately describe both the critical concentration and curvature of the electrical conductivity of any particle shown over a range of aspect ratios and volume fractions. It can be concluded from this that further research on conductivity and conductivity mechanisms of conducting particles within a slurry is required in order to understand the critical factors to design an efficient slurry electrode for use in an electrochemical device.
4.3 Conclusions

Models developed in the literature were discussed for describing the electronic conductivity of slurry electrodes; important for predicting the current distribution and voltaic efficiency. Equation [4.5] combines the fields of percolation theory and effective medium theory. This equation predicts the conductivity of a slurry as a function of two variables, the conductivity of the included particles and the aspect ratio of the particles. The magnitude of the slurry conductivity is controlled by the magnitude of the conductivity of the included particles. How the slurry conductivity changes as the volume fraction of the solid particles changes is controlled in Equation [4.5] by a particle-to-particle interaction factor which is a function of the aspect ratio. For the slurry electrodes investigated in the chapters presented herein, the conductivity model described by Equation [4.5] was not able to accurately predict both the critical volume fraction of the included phase at which the onset of conductivity is observed and how the conductivity changes with the volume fraction of the included phase. In order to use these models to appropriately design a slurry electrode, further work is necessary to better describe the particle-to-particle interaction and the pure phase conductivity. However, Equation [4.5] does point to enhanced slurry properties as the particle aspect ratio diverges from one. This has led particles such as MWCNTs (aspect ratio, width/length, of 100-200) and nanoflakes (aspect ratio < 0.01) to be investigated for use in slurry electrodes. With these extreme aspect ratios, Equation [4.5] predicts critical volume fractions, the minimum amount of slurry particles required for electrical conductivity, less than 2% for particles with aspect ratios either < 0.01 or > 100.
Chapter 5 Characterizing Slurry Electrodes Using Electrochemical Impedance Spectroscopy

5.1 Introduction

Electrochemical impedance spectroscopy (EIS) is a versatile technique employed to investigate electrochemical systems. With an understanding of the system, equivalent circuit models can be developed that describe the EIS response and can be used to determine individual properties. These equivalent circuit models have been developed for a variety of macrohomogeneous porous electrodes. This chapter will study how these EIS equivalent circuit models can be applied to slurry electrodes in order to better understand their electrochemical properties leading to better engineered electrodes.

5.2 Experimental

5.2.1 Materials

Three different carbon particles were investigated and their physical properties are described in Table 5.1. Asbury Carbons (Asbury, NJ, USA) graciously provided 230U, a natural flake carbon with an average diameter of 20 µm, thickness of 100 nm, a reported surface area of 6.5 m²/g, and a carbon purity of 99.4%. Asbury also provided Nano27; carbon platelets with an average diameter of 100 nm, thickness of 2.5-10 nm, a reported surface area of 250 m²/g, and a carbon purity of > 99%. MWCNTs were purchased from Nanostructured and Amorphous Materials, Inc. (Houston, TX, USA). These MWCNTs have an OD of 50-80 nm, length of 10-12 µm, reported surface area of 40 m²/g, and a carbon purity of 99.9%. For these studies, all carbon particles were used as received. Before tests were performed, particles were mixed by hand in electrolyte and then pumped through the system for at least 30 min.
Table 5.1: Slurry carbon particle physical properties.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Diameter</th>
<th>Length</th>
<th>Aspect Ratio</th>
<th>( f_{cv} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>230U</td>
<td>20 µm</td>
<td>200 nm</td>
<td>0.01</td>
<td>0.17</td>
</tr>
<tr>
<td>Nano27</td>
<td>100 nm</td>
<td>10 nm</td>
<td>0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>50-80 nm</td>
<td>10-20 µm</td>
<td>125-400</td>
<td>0.06</td>
</tr>
</tbody>
</table>

All salts used in the subsequent experiments were reagent grade and were obtained from Fisher Scientific (USA). All solutions were made with DI water (> 18 MΩ·cm). When using ferrous salts, solutions were made under a continuous nitrogen blanket and experiments were performed with the electrolyte under a continuous nitrogen purge to mitigate the air oxidation of ferrous to ferric iron. All tests were conducted at room temperature (20-25°C).

It was observed that when the volume fraction of the solid particles was above some critical concentration, there was no longer enough liquid in the slurry to fully wet all of the particles. When the volume fraction of solids rose above this critical volume fraction, the slurry transitioned, quite quickly, from a shear thinning fluid to a semi-solid gel. At this point, the slurry is no longer able to flow. This viscosity critical volume fraction, \( f_{cv} \), is given in Table 3.1 and described in detail by Youssry, et al.

5.2.2 Electrochemical Studies

Electrochemical impedance spectroscopy (EIS) was performed using a Solartron 1280B potentiostat (Ametek, UK). Each test was performed at the open circuit potential (OCV) with a sinusoidal perturbation of 10 mV amplitude over the frequency range 20 kHz-0.2 Hz. The EIS experiments were controlled using ZPlot (Scribner, USA). Cell polarization and an oscilloscope (Tektronix, USA) were used in congress to make sure that the response of the system under perturbation remained linear.
The ionic conductivity of the electrolytes used has been characterized using a glass conductivity cell with platinized platinum electrodes. This apparatus has a cell constant of 200 cm$^{-1}$ over a wide ionic conductivity range encompassing all results presented in this paper. The resistance of the electrolyte was measured in this cell with EIS. The real limit of the impedance at high frequency, $R_{HF}$, of the ionically conducting liquid can be used to find the ionic conductivity, shown in Equation [5.1], where $\kappa$ is the ionic conductivity and $\delta/A$ is the cell constant (200 cm$^{-1}$). Table 5.2 shows the ionic conductivity of relevant electrolytes found using this technique.

$$\kappa = \frac{\delta}{R_{HF} A} \quad [5.1]$$

<table>
<thead>
<tr>
<th>FeCl$_2$</th>
<th>FeCl$_3$</th>
<th>NH$_4$Cl</th>
<th>$\kappa$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>M</td>
<td>M</td>
<td>S/cm</td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>1.0</td>
<td>0.10</td>
<td>7.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50</td>
<td>1.0</td>
<td>0.15</td>
<td>1.0</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>1.0</td>
<td>0.13</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The electrical conductivities of the slurry particles were measured dry in a pellet press. This device is constructed of two 1.27 cm diameter aluminum rods set inside a clear polycarbonate sheath. An 850 mg sample of particles was placed between the two aluminum rods (inside the polycarbonate sheath) and was then compressed with a Carver manual press (Wabash, IN, USA) between 1.5-3.5 MPa. EIS was performed between the two aluminum rods while the particles were under compression at intervals of 350 kPa. This technique is similar to those used by Marinho, et al.$^{97}$ The measured resistance is used in Equation [5.2] to determine the electronic conductivity of the particles, $\sigma$. The thickness of the pellet under compression, $\delta$, was calculated as the difference of the distance between the press plates and the length of the aluminum rods without any
particles present. \( A \) is the cross-sectional area of the aluminum rods. Every time a new particle was investigated using this technique, the aluminum rods were cleaned and degreased with methanol and then hexanes before the high frequency resistance was measured without any particles present. These steps were repeated until the resistance between the two rods was \(< 5 \times 10^{-4} \Omega\) and was subsequently considered negligible.

\[
\sigma = \frac{1}{\delta R_{HF} A}
\]  

[5.2]

The electrical conductivity of the slurry electrodes were characterized while flowing in a tubular cell, designated the “flowing conductivity cell”, for suspensions in DI water with no added salts. This cell was constructed from a polycarbonate tube with 1.3 cm inner diameter and a length of 13 cm. Four pieces of platinum wire, each with a diameter of 1 mm, were situated in the tube so that EIS could be performed on the flowing slurry. The two platinum wires that served as the reference electrodes were 1 cm apart and the two platinum wires that served as the working and the counter electrodes were 8 cm apart. All four wires protruded into the flow \(< 1 \) mm and were situated on the same side of the tubular cell. The electrical conductivity of the slurry was determined using Equation [5.2] and the measured real high frequency resistance of each slurry electrode.

To determine the cell constant of the flowing conductivity cell, \( \delta/A \) in Equation [5.2], EIS was performed on solutions with known ionic conductivities (1-100 mS/cm) made with varying concentrations of HCl. The cell constant was found to be 0.76 cm\(^{-1}\) over this conductivity range.

All other electrochemical experiments were conducted in an in-house channel cell through which the slurry electrodes flow. This “channel cell” was defined by two CPVC flow fields containing straight rectangular channels with a width of 1 cm and length of
12 cm (in the direction of flow). The current collectors were 1 cm wide and 6.725 cm long \((A = 6.725 \text{ cm}^2)\) graphite plates that were centered in the middle of the CPVC channel. The gap between the current collect of each channel and the separator was either 0.1 cm or 0.2 cm. A peristaltic pump (Cole-Parmer, USA) was used for pumping the slurries. In all experiments, the slurry was pumped vertically up through the electrochemical channel cell. The inlet and exit ports of the channel cell were at roughly 30° angles (with respect to the current collector face) to minimize any clogging. Current was collected from this cell through two brass plates that were pressed into the back of the graphite current collectors. The cell was held together with stainless steel endplates. Teflon sheets were used to insulate the endplates and Grafoil (Graftech, USA) was used to minimize contact resistances between the brass plates and the graphite plates. The cell assembly was compressed with 8 bolts that were tightened to 90 in-lbs of torque. The reservoirs used to hold the slurry that was pumped through the channel cell were Nalgene bottles modified to be bottom drawn. Unless otherwise noted, all materials were purchased from McMaster-Carr (Cleveland, OH, USA).

The cell constant of the channel cell was determined by performing EIS on solutions with known conductivities \((1-100 \text{ mS/cm})\) made with varying concentrations of HCl without a separator between the two cell halves. The cell constant was found to be 0.029 \text{ cm}^{-1} and 0.058 \text{ cm}^{-1} for cells with 0.2 cm and 0.4 cm total channel depths, respectively. This is in good agreement with the theoretical values of 0.030 \text{ cm}^{-1} and 0.059 \text{ cm}^{-1} determined from the cell geometry.

For the experiments in which a membrane was used to separate the two channels of the channel cell, Nafion 1035 (Ion Power, DE, USA) was used. The Nafion was pretreated by
boiling in 5% H₂O₂ and then in DI water. The membranes were equilibrated in electrolyte prior to use. Each step was for at least one hour. The swelled thickness of Nafion 1035 was measured to be about 100 μm.

5.3 Analytical EIS Models

5.3.1 EIS of Bicontinuous Electrodes

An equivalent circuit model of a slurry electrode, ignoring any dynamic nature, is shown in Figure 5.1 for an electrode between a current collector (left) and an ionically conductive separator (right). Because the dynamic nature is ignored, this equivalent circuit is akin to those of typical porous electrodes. In this figure; \( R_e \) is the resistance of a finite length of the electronic phase (including any particle-to-particle contact resistance); \( R_{ion} \) is the resistance of a finite length of the ionically conductive liquid phase; \( \zeta \) is the impedance of the interface between the slurry electronic and ionic phases; \( R_{c-e} \) is the contact resistance (if any) between the current collector and particles in solution; and \( \zeta_{c-i} \) is the impedance of the interface between the ionic phase and the current collector. \( \zeta_{c-i} \) and \( \zeta \) will always be of the same form (e.g. a capacitor or a capacitor and resistor in parallel) for the systems studied here but the former applies to the real active area of the current collector while the latter corresponds to the active area of the slurry solid phase. From the carbon particle loading in the slurry and the reported active area, the predicted area of the slurry electrode should be on the order of \( 10^4 \text{–} 10^7 \text{ cm}^2 \); at least 2-5 orders of magnitude greater than that of the current collector. For the studies presented in this paper, the impedance associated with the current collector interface will be ignored.
Figure 5.1: General equivalent circuit model of a porous electrode that is terminated electrically at a current collector (left) and ionically at a ionically conductive separator (right).

Equation [5.3a] and Equation [5.3b] describe the impedance, $Z$ [$\Omega$], of a bicontinuous electrode, ignoring the current collector interface, as developed for macrohomogeneous porous electrodes. Assuming the system is macrohomogeneous allows the electronic and ionic phases to be described by length average resistances, $r_e$ and $r_{ion}$, respectively, described by Equation [5.4]. Any particle-to-particle contact resistance is included in $r_e$.

$$Z = \frac{r_e r_{ion}}{r_e + r_{ion}} \delta + \frac{r_e r_{ion}}{r_e + r_{ion} \sinh \left( \frac{\delta}{\lambda} \right)} + \lambda \frac{r_e^2 + r_{ion}^2}{r_e + r_{ion}} \coth \left( \frac{\delta}{\lambda} \right)$$  \hspace{1cm} [5.3a]

$$\lambda = \left( \frac{Z \zeta}{r_e + r_{ion}} \right)^{1/2}$$  \hspace{1cm} [5.3b]

Equation [5.3a]-[5.3b] consist of four different parameters: the length averaged resistance of the electronic and ionic phases, $r_e$ and $r_{ion}$ [$\Omega$/cm]; the impedance of the interaction of the electronic and ionic phases, $\hat{Z}_\zeta$ [$\Omega$ ⋅ cm]; and the electrode length in the direction of current flow, $\delta$ [cm]. The ionic phase impedance and electrode length can easily be measured independently. EIS can be used, as discussed below, to separate the remaining two parameters depending on the system being studied. (In this chapter, the area impedance, $Z \cdot A$ [$\Omega$ ⋅ cm$^2$], is reported.)

$$r = \frac{1}{\delta} \sum R = [\sigma \cdot A]^{-1} \text{ or } [\kappa \cdot A]^{-1}$$  \hspace{1cm} [5.4]
5.3.2 EIS of Slurry Electrodes with Ionically Conducting Electrolyte in the Absence of a Redox Couple

Salt containing electrolytes with suspended particles have both ionic and electronic conductivity. Slurries such as these, in the absence of Faradiac current, are akin to the electrochemical flow capacitor.\(^{75-80}\) Without a redox couple present, current may only pass from the electronic to the ionic phase through the charging of the double layer capacitance of the solid particles. The impedance of this interaction is described by Equation [5.5] and is a function of the frequency of the perturbation, \(\omega [s^{-1}]\), and the length averaged capacitance of the solid phase double layer, \(c_{dl} [F/cm]\). This length averaged capacitance is related to the specific capacitance, \(\tilde{c}_{dl} [F/cm^2]\), by the specific area of the particles active to the electrochemical process per particle volume, \(\dot{a} [cm^2/cm^3]\), the current collector area, \(A [cm^2]\), and the particle volume fraction, \(f \geq f_c\).

\[
\tilde{Z}_t = (j\omega c_{dl})^{-1} = (j\omega \dot{a}\tilde{c}_{dl}A f)^{-1} \tag{5.5}
\]

In the absence of flow, the equivalent circuit model for an electrochemical slurry capacitor electrode with an ionically conducting separator (the right side) terminated by a current collector (left side) is shown in Figure 5.2. Figure 5.3 shows the typical Nyquist plot of the full impedance model of the static electrochemical slurry capacitor, Equations [5.3]-[5.5], in the electrochemical channel cell with and without separators (single channel with thickness of 2\(\delta\), or a channel with thickness \(\delta\) on either side of a separator). A real resistance equal to the separator impedance, 0.5 \(\Omega\cdot cm^2\), was added to the system without a separator to make the high frequency impedance between the two
models congruent. In both cases, the real impedance increases as the frequency of the potential perturbation decreases.

Figure 5.2: Equivalent circuit of an ionically terminated electrochemical flow capacitor electrode. $C_{dl}$ [F] is the double layer capacitance of the solid particles. This model ignores any dynamic nature of the slurry and the current collector interface.

At the high frequency limit, Equation [5.5] approaches zero and, therefore, Equation [5.3a] reduces to Equation [5.6]; the parallel combination of the ionic and electronic paths. As the frequency decreases, the Nyquist plot of the system with an ionically conductive separator tends to negative infinity in the imaginary axis while the Nyquist plot of the system without a separator has a finite low frequency limit. This low frequency behavior exists because without a separator the electronic phase conduction can complete the circuit between the working and counter electrode. The depression of this semi-circle, and the $\approx45^\circ$ region in the system with a separator, are due to the distributed nature of the electrode, discussed below.

$$R_{HF} = R_\parallel = \frac{r_\text{e}r_\text{ion}}{r_\text{e}+r_\text{ion}} \delta$$  [5.6]
Figure 5.3: The Nyquist representation of the static electrochemical slurry capacitor model with and without a separator in the cell. The solid line represents an ionically terminated electrode (one on either side of a separator) while the dashed line represents an electrically terminated electrode (no separator). For these models, $r_e^{-} = 1.75 \, \Omega/cm$, $r_{\text{ion}} = 1.145 \, \Omega/cm$, $c_{\text{dl}} = 15 \, \text{F/cm}$, $\delta = 0.1 \, \text{cm}$ each channel, and $R_{\text{mem}} = 0.5 \, \Omega \cdot \text{cm}^2$. For the model without a separator, $0.5 \, \Omega \cdot \text{cm}^2$ was added to the real impedance so that the $R_{\text{HF}}$ was congruent between the two models.

The EIS model presented in Figure 5.2 and Figure 5.3 describes a stationary two-phase electrode in the absence of faradaic currents. Under non-stationary conditions, there exists additional current that results from the flow of the particles. The current arises because particles with charged double-layers leave the cell at the outlet thereby permitting uncharged particles (that are hence receptive to accepting current) to enter at the inlet. This current could potentially be modeled in the context of Figure 2 with the inclusion of a volume flow rate dependent source/sink. However, this advective capacitive current (also called “hydraulic current”) has multi-dimensional characteristics (e.g. boundary layers of overpotential that grow as the slurry flow proceeds downstream along the electrode) that make analysis with 1-D equivalent circuit models problematic. Thus, impedance analysis of these situations is difficult.
However, it is possible to estimate the impedance response at the high and low frequency limits. At high frequencies (relative to the residence time of the slurry in the cell), the slurry behaves as a quasi-static solid matrix, and therefore has the same EIS behavior as in the static case (although perhaps with an altered electronic conductivity due to shear-rate effects\textsuperscript{67}). At low frequency, the current response tends toward the steady-state, DC charging value that can be predicted using available models\textsuperscript{79,80}. Thus, even in the situation with a separator present, the Nyquist plot still returns to the real axis at low frequency (instead of having its imaginary component diverge to negative infinity as in the stationary case). The evolution of the Nyquist plot at intermediate frequencies is difficult to ascertain though as the advection-diffusion of surface charge combined with sinusoidal perturbations requires time-dependent, two-dimensional numerical simulations of the governing slurry electrode equations\textsuperscript{79,80}. This approach is beyond the scope of this work.

5.3.3 EIS of Slurry Electrodes Supporting Faradaic Current

Slurry electrodes containing electroactive redox species have been of significant interest for electrochemical device applications including energy storage and water treatment. An equivalent circuit representing a slurry electrode, ionically terminated, that supports a redox reaction is shown in Figure 5.4. The impedance of the liquid-solid interface in the presence of a redox couple is described by Equation [5.7]. In this equation, $\tilde{r}_{ct} [\Omega \cdot \text{cm}]$ is the length specific charge transfer resistance.
Figure 5.4: Equivalent circuit of an ionically terminated electrochemical slurry electrode in the presence of a redox reaction. Again, the current collector interface and effects of flow are ignored in this model.

\[
\frac{Z}{\omega} = r_c t + j \omega r_{ct} c dl
\]  

[5.7]

The advected currents from the previous section also simultaneously exist along with the Faradic reaction currents for slurry electrodes in the presence of redox active species. However, if the kinetics are fast enough and the flow rates are slow enough, the advected capacitive current is generally small\(^7\) and can be ignored. Therefore, the subsequent studies do not include any advective effects.

The impedance of slurry electrodes supporting redox couples are the same whether ionically or electronically terminated due to the presence of the charge transfer resistance. At high frequencies, Equation [5.7] approaches zero and the total impedance, Equation [5.3a], reduces to that of the parallel combination of the ionic and electronic resistance, Equation [5.6]. At low frequencies, Equation [5.7] approaches the impedance of the charge transfer resistance. Because the charge transfer resistance is real and finite, it can bridge the solid phase and the ionic phase at low frequencies.

The first term of Equation [5.3a] represents the parallel combination of the conductive paths and is real, finite, and independent of the voltage perturbation. The second and third terms of Equation [5.3a], however, are a combination of the electronic, ionic, and charge transfer resistances that encompass the distributed nature of the electrode. At all finite
frequencies, the second and third term of Equation [5.3a], combined with Equation [5.7], have both real and imaginary components. Figure 5.5 shows an example Nyquist representation of the impedance of a slurry electrode. In this figure, the specific contributions of the second and third term of Equation [5.3a] are shown. The constant real impedance of the first term is added to the second term while the separator impedance is added to the third term. Doing this only shifts the second and third term in the x-axis of Figure 5.5. As Figure 5.5 shows, both the second and third term have unique contributions to the “distributed shape” of the overall impedance response. While the general shape of the total impedance of the redox active slurry electrode (the solid line in Figure 5.5) is similar to that of the electronically terminated electrochemical flow capacitor (the dashed line in Figure 5.3), the loop trending back to the real axis at low frequencies is in fact due to the redox couple active at the electrolyte-solid interface, highlighting the importance of applying the correct model to the system being investigated.

![Nyquist Plot](image)

**Figure 5.5:** The Nyquist representation of a slurry electrode supporting a redox reaction. The charge transfer resistance is \( r_{tx} = 0.01 \, \Omega \cdot \text{cm} \). All other parameters are the same as in Figure 5.3.

Figure 5.6 investigates the effect of the charge transfer resistance on Equation [5.3a] for a slurry electrode supporting a redox reaction. At high frequencies, a near 45° feature is present in the Nyquist plot for all values of the charge transfer resistance. As the
frequency decreases, the real impedance increases and the Nyquist plot begins to roll towards the real axis forming a feature similar to the charge transfer loop of traditional Randles circuits. However, as the charge transfer resistance increases (the reaction kinetics become slower), the low frequency feature begins to separate from the high frequency feature.

**Figure 5.6:** Nyquist plots of slurry electrode models supporting a redox reaction with a range of charge transfer resistances. Curves a-i have $\tilde{r}_{ct}$ of 0.005, 0.01, 0.02, 0.04, 0.1, 1.0, 10, 100, 1000 $\Omega\cdot$cm, respectively. The values of the other model parameters are the same as in Figure 5.3.

As Equation [5.3a] and Figure 5.6 indicate, the total impedance of a slurry electrode approaching low frequencies is more than the sum of the high frequency resistance and the charge transfer resistance typical of Randles circuits. The additional impedance will be described as a distributed resistance, $R_{dist}$. The total impedance of a slurry electrode at the low frequency, or DC, limit can be described by Equation [5.8]. Using the model parameter for the length specific charge transfer resistance, the total charge transfer resistance of a single electrode can be described by Equation [5.9].
\[ Z_{LF} = R_{DC} = R_{HF} + R_{ct} + R_{dist} \] \[ R_{ct} = \bar{r}_{ct} / \delta \]

Combining the low frequency approximations of Equation [5.3] with Equations [5.7]-[5.9] allows for the distributed resistance of the slurry electrode to be determined. Figure 5.7 shows how the distributed resistance depends upon the charge transfer resistance. As the charge transfer resistance decreases, the distributed resistance also decreases. This occurs because, as \( \bar{r}_{ct} \) approaches zero, it shorts out the solid-liquid interface and the impedance of the slurry electrode approaches Equation [5.6] at all frequencies. Conversely, as the charge transfer resistance increases, the slurry electrode behaves more and more like an electrochemical flow capacitor. At this limit, the distributed resistance approaches a constant value. This maximum distributed impedance \( (R_{dist} \text{ for the capacitor}) \) is a function of the ratio of electronic resistance to ionic resistance and is described in Figure 5.8. The distributed resistance, normalized by the high frequency resistance, is at a minimum value of \( 1/3 \) when the electronic resistance equals the ionic resistance. As the electronic and ionic resistances move further apart, the normalized distributed resistance continues to grow. It should be noted that the high frequency “foot” in Figure 6 does not encompass the distributed impedance. As shown in Figure 5.5, both the second and third terms of Equation [5.3a] contribute to the distributed resistance.
Figure 5.7: The distributed resistance of a slurry electrode supporting a redox reaction as a function of the length averaged charge transfer resistance. In this model, all other parameters are the same as those described in Figure 5.3.

Figure 5.8: The ratio of the distributed resistance to the high frequency resistance as a function of the ratio of the electronic resistance to the ionic resistance. In this figure, $\tilde{r}_{ct} = 10^{10}$, e.g. $R_{dist}$ is at the maximum value for each $R_e/R_{ion}$. 
5.4 Results and Discussion

5.4.1 Maximum Slurry Electronic Conductivity

All slurry electrodes investigated in this study are made of electrically conductive particles suspended in an ionically conductive electrolyte. Before attempting to separate the electronic conductivity from the ionic conductivity in a dynamic flowing slurry, the electronic conductivity was first investigated in a system without electrolyte.

The maximum electronic conductivity occurs when the volume fraction of the liquid phase is zero. However, a “slurry” without electrolyte is not flowable. Therefore, the electrical conductivity of the slurry particles, in the absence of any electrolyte, was measured in the pellet press. The results are shown in Table 5.3 and were found to be weak functions of applied compression over the range tested. Each particle type exhibited conductivity $10^3$ times lower than that of pure graphite.\(^97\) This decrease in conductivity can be attributed to particle-to-particle contact resistances and packing efficiencies.\(^97\) In the flowing slurry electrodes, the particles are under no significant force to pack. Even at the lowest pressures, the dry pressed pellet conductivity will over-estimate the electrical conductivity of the flowing slurry electrode. However, it is interesting to note that the conductivity of the packed particles is similar for the three particles considered, despite their different size and shapes.

Table 5.3: The electronic conductivity of the slurry particles in the pellet press. No liquid electrolyte present.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>230U</td>
<td>5.5 ± 0.2</td>
</tr>
<tr>
<td>Nano27</td>
<td>6.1 ± 0.2</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>6.9 ± 0.3</td>
</tr>
</tbody>
</table>
5.4.2 Slurries in DI Water

Evaluating slurries where the liquid contains no supporting ions (DI water) is a useful diagnostic system to isolate the electronic conductivity. This slurry has negligible ionic conductivity and the EIS response, without an ionic separator, is a single point on the real axis of the Nyquist plot and can be modeled as a pure resistor. The electronic conductivity, $\sigma$, can be found using the measured resistance, $R$, and the cell geometry, $\delta/A$, as in Equation [5.2].

![Conductivity graph](image)

**Figure 5.9:** Conductivity of slurries in DI water as a function of the solid phase volume fraction. Conductivity determined from the high frequency real intercept of the impedance for each particle in the flowing conductivity cell.

Figure 5.9 shows the electronic conductivity of slurry electrodes with each particle at varying volume fractions in DI water as determined in the flowing conductivity cell. The conductivity quickly rises with increasing loading of particles above some critical percolation concentration, $f_c$, where the volume fraction of particles is high enough to
create fully percolating conductive networks. The critical percolation concentration and the rate at which the conductivity rises as a function of increased loading is a factor of particle shape and particle-to-particle interactions. As a flowing slurry, the particles exhibit electrical conductivity $10^2$-$10^3$ times smaller than the dry packed pellets. This again can be attributed to particle-to-particle contact resistances and a further decrease in packing efficiencies.

5.4.3 EIS of Slurry Electrodes Supporting Fe$^{2+/3+}$

The ferric/ferrous couple, a common positive couple in redox flow batteries, was used to investigate the performance of the slurry electrodes supporting an aqueous redox couple. The electrolyte used in these studies was 1.0 M FeCl$_2$, 1.0 M FeCl$_3$, and 1.0 M NH$_4$Cl. This electrolyte simulates the composition of iron electrolytes at 50% state-of-charge.

For the following electrochemical experiments, a single reservoir containing the slurry/electrolyte was used to feed both sides of the electrochemical channel cell (divided by a separator; Nafion 1035). The draw from the reservoir was split and fed into two separate heads on the peristaltic pump before entering the cell so that the volumetric flow rate on either side of the cell was directly controlled. After leaving the electrochemical cell, the slurry from both sides of the cell were combined into one stream before reentering the reservoir. The volume of the reservoir used was typically 700 mL.

This experimental design, deemed a symmetric cell configuration, greatly simplifies the analysis of slurry or porous electrodes in the presence of a redox couple. Using a symmetric cell configuration ensures that the composition of the electrolyte will remain constant throughout all electrochemical tests. Ferric ions are reduced to ferrous ions at the
cathode at the same rate that ferrous ions are oxidized at the anode. Since both streams are remixed, the reservoir composition does not change. The other advantage to the symmetric cell configuration is the simplified EIS analysis. The positive and negative slurry entering the cell should be identical. Also, because the ferrous/ferric couple is facile and symmetric (similar polarization whether reducing or oxidizing), the total overpotential of each electrode should be identical. This allows both slurry electrodes in the cell to be modeled by one circuit, Figure 5.4, instead of two on either side of a membrane and therefore reduces the number of fit parameters significantly. To model the entire symmetric electrochemical cell, Figure 5.4 is modeled in series with the separator resistance and hardware inductance. It is necessary to include the hardware inductance because, at $\sim 10^{-7}$ H, the curves have a finite positive slope when the imaginary impedance is zero.

The ferric/ferrous couple was investigated on slurry electrodes made with MWCNTs in the symmetric channel cell. Focus was put on these particles due to their higher electronic conductivity while suspended in a flowing slurry as shown in Figure 5.9 and due to their smaller primary particle size. For application in continuously circulating slurry electrodes, as opposed to pulse flow,\textsuperscript{66} the stability of the slurry is primarily related to the settling of particles. With the MWCNTs in stagnant slurries, no appreciable settling was observed for at least two hours. However, with the larger particles, settling was visibly observed in shorter time frames (<30 minutes). Also, with the MWCNTs, the pumping action has been observed to be enough to keep the slurry well mixed for well over a week without any noticeable settling in the reservoir.
Figure 5.10 shows the EIS response for slurry electrodes of MWCNTs in 1.0 M FeCl$_2$, 1.0 M FeCl$_3$, and 1.0 M NH$_4$Cl. There are three frequency regions to the impedance response dominated by different processes. At high frequencies, above $10^3$ Hz, the impedance is dominated by the hardware inductance and the parallel ohmic resistance, Equation [5.6]. At intermediate frequencies, $10^{-3}$-$10^3$ Hz, the characteristics of the charge transfer reaction are present (akin to Figure 5.5). The third region in the impedance plots of Figure 5.10 are effects due to mass transfer and the advective current at frequencies below $10^2$ Hz. Of these three regions, only the effects due to mass transfer and advective current should depend on the flow rate of the slurry electrode; impedance due to both decreases with increasing flow rate. Comparing the EIS results as a function of flow rate (curves b-d in Figure 5.10) to the analytical model shows that there is non-negligible low frequency effects at all flow rates investigated. Since the impedance models developed earlier do not account for mass transfer or hydraulic current, the model, Figure 5.4 in series with hardware inductance and membrane resistance, was only applied to the data range above $10^2$ Hz. Over this range, the impedance of curves b-d are near identical; confirming that mass transfer and the advective current are only significant at lower frequencies. When the impedance model was fit to the data, the ionic phase resistance, estimated using Equation [5.1] and Table 5.2, and the separator resistance, 0.5 $\Omega \cdot \text{cm}^2$ corresponding to Nafion 1035 in the iron electrolyte, were fixed. The change in ionic conductivity due to the volume of electrolyte displaced by slurry particles should be negligible ($< 5\%$) at 5 vol% MWCNTs.
Figure 5.10: Nyquist (upper) and Bode phase angle (lower) representations of EIS results on MWCNT slurry electrodes supporting the ferrous/ferric redox reaction. The data points represent experimental data while the solid lines are analytical fits without mass transfer or advective effects; Figure 4 in series with hardware inductance and membrane resistance. (The model fits, Table 5, were used to simulate data below $10^7$ Hz.) Triangles (a) represent data for a cell with 1 mm channels at 200 mL/min with 4.8 vol% MWCNTs. Data sets b-d are with 2 mm channels at 25 mL/min (squares), 200 mL/min (diamonds), and 550 mL/min (circles), respectively, with 5.8 vol% MWCNTs. All data is with a Nafion 1035 separator.

Table 5.4 shows the fitting results of the impedance model to the data presented in Figure 5.10. The electronic conductivities of the slurry electrodes estimated in Table 5.4 match very well with the results shown in Figure 5.9. While the difference in electrolyte between Figure 5.9 and Figure 5.10 can change the particle-to-particle interactions, the fact that the electronic conductivity was similar in both electrolytes is thought to be due to the high aspect ratio of the MWCNTs which force long range percolation. In this case, the aspect ratio of the MWCNTs (Equation [4.4a]) is more important to the
conductivity than the interactions between particles due to electrolyte ionic strength. Also, the good agreement between the electronic conductivities in Table 5.4 and Figure 5.9 implies that the contact resistance between the particles and the current collector is negligible.

Table 5.4: Results from the impedance model as shown in Figure 5.4 in series with hardware inductance and membrane resistance, applied to the data shown in Figure 5.10. For these fits, the membrane (Nafion 1035) resistance is fixed at 0.5 Ω·cm² and the ionic phase conductivity is fixed at 130 mS/cm corresponding to the electrolyte as indicated in Table 5.3. Values in the table are for each slurry on either side of the separator.

<table>
<thead>
<tr>
<th>Channel vol%</th>
<th>( r_e ) [Ω/cm]</th>
<th>( \sigma ) [S/cm]</th>
<th>( r_{ct} ) [Ω·cm]</th>
<th>( c_{dl} ) [F/cm]</th>
<th>( a ) [cm²]</th>
<th>( i_o ) [mA/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mm</td>
<td>4.8</td>
<td>2.22</td>
<td>0.067</td>
<td>0.6·10⁻³</td>
<td>16.7</td>
<td>4.2·10⁴</td>
</tr>
<tr>
<td>2 mm</td>
<td>5.8</td>
<td>1.75</td>
<td>0.085</td>
<td>1.0·10⁻³</td>
<td>1.46</td>
<td>1.5·10⁴</td>
</tr>
</tbody>
</table>

Table 5.4 highlights the charge transfer resistance and the double layer capacitance of each fit in Figure 5.10. The symmetric configuration allows the entire cell to be modeled by one equivalent circuit (Figure 5.4) in series with a membrane; each electrode should have the same overlapping EIS response. The total capacitance predicted by this analysis is only half that of each electrode, \( C_{dl} = 2C_{dl,total} \), because they are two identical capacitances in series. Conversely, the total charge transfer resistance is twice the charge transfer resistance of each electrode, \( 2R_{ct} = R_{ct,total} \); two identical resistances in series. Equation [5.10] and Equation [5.11] describe how the double layer capacitance and charge transfer resistance relate to the true active area and the exchange current density. The specific capacitance, \( \tilde{c}_{dl} \), is assumed to be 40 μF/cm².

\[
a = \frac{C_{dl}}{\tilde{c}_{dl}} \quad \text{[5.10]}
\]

\[
i_o = \frac{R_G T}{z F a R_{ct}} \quad \text{[5.11]}
\]
The exchange current density for the ferric/ferrous couple on graphite in chloride medium has been reported previously to be around 4 mA/cm² in 0.1 M iron solutions. If the exchange current density is roughly linear with concentration of iron, then to coincide with literature, the exchange current density should be 20 mA/cm² and 40 mA/cm² for 0.5 M and 1.0 M iron solutions, respectively. While the exchange current densities in Table 5.4 are in mild agreement as measured under two conditions, they are significantly lower than those determined in literature. This could be attributed to differences between carbon surfaces.

5.4.4 Direct Current Operation of an Fe²⁺/³⁺ Slurry Electrode

The EIS analysis developed above can be used to predict the performance of a slurry electrode with a redox reaction at a constant current. Using the results of Table 5.4, Figure 5.7, and Figure 5.8, the different contributions to the overall polarization can be investigated. Figure 5.11 shows the polarization of an individual slurry electrode operated at 550 mL/min with 5.8 vol% MWCNTs in 1.0 M FeCl₂, 1.0 M FeCl₃, and 1.0 M NH₄Cl in the symmetric cell. Assuming the oxidation and reduction reactions occur at a similar rate, the overpotential of each electrode should be equal. The overpotential of the entire cell is then the sum of both electrodes and the membrane. All overpotentials are assumed to be linear and are defined by Ohm’s law (using the resistances in Table 5.4, Figure 5.7, and Figure 5.8). The low frequency overpotential is the combined effects due to mass transfer and the advective current. These were assumed to be the difference between the low frequency limit of the experimental data and the model fits in Figure 5.10.
Figure 5.11: Polarization curve and overpotential breakdown of the symmetric Fe$^{2+/3+}$ slurry electrode consisting of 5.8 vol% MWCNTs in 1.0 M FeCl$_2$, 1.0 M FeCl$_3$, and 1.0 M NH$_4$Cl flowing at 550 ml/min through a 1 mm gap with a Nafion 1035 separator at 200 mA/cm$^2$. The lines are overpotentials as determined from the EIS analysis for an individual electrode and the solid black line (a) is the total overpotential of the symmetric cell as determined by summing the individual overpotentials. The open squares represent average data points taken from cyclic voltammetry at 25 mV/sec.

Table 5.5 shows the overpotential breakdown of the symmetric ferric/ferrous cell at 200 mA/cm$^2$. Using this information, the voltaic efficiency of a MWCNT slurry electrode supporting the Fe$^{2+/3+}$ redox reaction can be estimated using Equation [5.12]. The standard potential of the ferric/ferrous couple, $E^o$, is +0.77 V vs RHE.$^{21}$ A slurry with 5.8 vol% MWCNT flowing through a 1 mm gap at 200 mL/min operating at 200 mA/cm$^2$ has 82% voltaic efficiency.

$$
\varepsilon_{Volt} = \frac{E^o - \eta_{Total}}{E^o}
$$

[5.12]
Table 5.5: Overpotential breakdown and voltaic efficiency of different 5.8 vol% MWCNT slurry electrodes in 1.0 M FeCl₂, 1.0 M FeCl₃, and 1.0 M NH₄Cl. All overpotentials are for 200 mA/cm² operating current density.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Flow [mL/min]</th>
<th>η_{Slurry-IR} [mV]</th>
<th>η_{CT} [mV]</th>
<th>η_{LF} [mV]</th>
<th>η_{Dist} [mV]</th>
<th>η_{tot} [mV]</th>
<th>ε_{Volt}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mm</td>
<td>200</td>
<td>93</td>
<td>8.1</td>
<td>17</td>
<td>21</td>
<td>139</td>
<td>82%</td>
</tr>
<tr>
<td>2 mm</td>
<td>200</td>
<td>186</td>
<td>6.7</td>
<td>51</td>
<td>52</td>
<td>296</td>
<td>62%</td>
</tr>
<tr>
<td>2 mm</td>
<td>550</td>
<td>186</td>
<td>6.7</td>
<td>25</td>
<td>31</td>
<td>248</td>
<td>68%</td>
</tr>
</tbody>
</table>

5.5 Conclusions

Techniques for interpreting electrochemical impedance spectroscopy results to characterize different flowing slurry electrodes configurations were presented based upon models developed for porous electrodes. These models were discussed with regards to three different slurry systems; particles in deionized water, in supporting electrolyte without redox active species (electrochemical flow capacitor), and in electrolytes with redox couples (redox flow batteries). Through investigating each of these systems, the individual properties of slurry electrodes were determined. It was found that traditional overpotential descriptions, (ohmic, activation, and mass transfer) were insufficient to fully describe the impedance and polarization of the slurry electrodes.

In addition to the traditional overpotentials associated with electrochemical electrodes, there exists an overpotential due to the distributed nature of the current between the electronic and ionic phases of the slurry. This overpotential is a significant contribution to the cell polarization on the order of both the charge transfer and mass transfer overpotentials. It was found that this distributed overpotential is a function of the slurry electrode charge transfer resistance as well as the ratio of the electronic and ionic phase conductivities. Reducing the charge transfer resistance of the slurry electrodes to
< 10^{-4} \Omega \cdot \text{cm}^2 \text{ will lower the distributed overpotential significantly (over a factor of three for the MWCNT slurries).}

With the ferric/ferrous redox couple, MWCNT slurry electrodes were found to operate at over 80\% voltaic efficiency at 200 mA/cm^2. The electrode polarization was dominated by the ohmic losses in the slurry electrode. By increasing the slurry electronic conductivity, the performance of these electrodes can be significantly improved.
Chapter 6 Slurry Electrodes for Iron Plating in an All-Iron Flow Battery

6.1 Introduction

The all-iron flow battery has the potential to be a versatile and cost effective energy storage device. However, its operation is complicated by the negative electrode; the electrochemical plating and stripping of iron metal. This chapter investigates the performance of slurry electrodes in the all-iron battery, focusing on the negative slurry electrode. Stationary, porous electrodes (typical in flow batteries) couple the energy storage capacity to the power rating because the iron is plated into the stationary electrode which is stored in the electrochemical conversion device. The all-iron flow battery with these electrodes is limited to < 3.8 hours.\textsuperscript{30,31} In order to increase the capacity of the all-iron battery so that the market potential can be realized, the capacity must be increased.\textsuperscript{1} Slurry electrodes can decouple the all-iron flow battery, leading to increased capacity, by allowing the iron metal to be stored in external reservoirs.

6.2 Analytical Current Distribution Models

Mathematical modeling of the slurry electrode in the negative half-cell was performed in order to permit the selection of viable candidate slurries. The selection of an appropriate particle to use as the flowable slurry electrode was performed with regards to two principal performance metrics.

The first performance metric was related to the achievable current density. As discussed in Chapter 3, cost models have shown that for the all-iron slurry battery to be practical that the battery needs to be able to support a current density of 200 mA/cm\textsuperscript{2} at a voltaic efficiency of at least 70\%.\textsuperscript{17} Given the 1.2 V cell potential of the all-iron battery,
this means that the desired current density must be achieved with at most 212 mV of total overpotential across the entire cell.

The second performance metric is related to the amount of plating that occurs onto the current collector. If plating occurs onto the current collector and not onto the slurry particles, then the energy density and power density of the battery are no longer decoupled. As decoupling is a desirable trait for grid-scale energy storage, a criterion was established demanding that less than 5% of the total metal plating should occur onto the current collector.

The slurry characteristics necessary to match the performance metrics were examined using standard one-dimensional macrohomogeneous porous electrode equations. The governing equations are identical to those used by Fleischmann and Oldfield for fluidized bed electrodes. The kinetics of the plating reaction were assumed to be linear, resulting in the following equations:

\[
\sigma \frac{d^2 \Phi_1}{dx^2} - a_0zf i_0 \eta = 0 \tag{6.1a}
\]

\[
\kappa \frac{d^2 \Phi_2}{dx^2} + a_0zf i_0 \eta = 0 \tag{6.1b}
\]

Here, \(\sigma\) is the electronic conductivity of the slurry phase, \(\kappa\) is the ionic conductivity of the solution phase, \(\Phi_1\) is the potential of the slurry phase, \(\Phi_2\) is the potential of the solution phase, \(a_0\) is the specific area of the slurry electrode, \(z\) is the number of electrons involved in the plating reaction, \(f = F/RT\) is related to Faraday’s constant, \(i_0\) is the exchange current density, \(x\) is the spatial coordinate across the channel gap, \(\eta = \Phi_1 - \Phi_2 - U_{ref}\) is the overpotential, and \(U_{ref}\) is the open-circuit potential of the electrode reaction relative to a suitable reference electrode such that the overpotential is zero at equilibrium. Effects such as mass transfer overpotentials or advectively-induced capacitive currents are
ignored by this model, but it is believed to capture the dominant behavior associated with slurry electrodes in the presence of fast faradaic reactions.

Figure 6.1: Slurry electrode performance maps. The red shaded region represents the combinations of σ and a₀ that satisfy the requirement that the slurry electrode be able to support a 200 mA/cm² current density for 100 mV total overpotential across the negative half-cell. The blue shaded region represents the combinations of σ and a₀ that satisfy the requirement that the slurry electrode be able to plate less than 5% of the total metal onto the current collector. The purple region denotes satisfaction of both metrics.

In order to account for the fact that reactions can occur on both the current collector plate and the slurry particles, the standard boundary conditions used by Fleischmann and Oldfield needed to be altered. The modified boundary conditions at x=0 (the current collector) and x=δ (the location of the separator) take the form:

\[
\begin{align*}
\frac{d\Phi_1}{dx} &= -\frac{(i-\xi z f I_0 \eta_0)}{\sigma} ; \quad \frac{d\Phi_2}{dx} = -\frac{\xi z f I_0 \eta_0}{\kappa} \quad \text{at } x = 0 \quad \text{[6.2a]} \\
\frac{d\Phi_1}{dx} &= 0 ; \quad \frac{d\Phi_2}{dx} = -\frac{i}{\kappa} \quad \text{at } x = \delta \quad \text{[6.2b]}
\end{align*}
\]

Here, \(i\) is the applied current density, \(\xi\) is the roughness factor of the current collector, and \(\eta_0\) is the overpotential at \(x=0\). The total overpotential across the half-cell can be
described as $\eta_{tot} = \Phi_1(0) - \Phi_2(\delta) - U_{ref}$. An additional factor accounting for the area of the current collector that is occluded by the presence of the slurry could also be included in the boundary conditions, but for low volume fraction slurries (like those in this paper), this effect is believed to be negligible.

The slurry properties that affect the achievement of the above performance metrics are the specific interfacial area and the electronic conductivity. Using typical values for cell dimensions, iron plating reaction kinetics, and electrolyte properties (see Table 6.1), Equations [1a] and [1b] were solved in order to generate maps of the combinations of $\sigma$ and $a_0$ that satisfy the metrics. These maps are shown in Figure 6.1. Regions corresponding to the polarization metric (<100 mV of overpotential in the negative half cell at 200 mA/cm$^2$ or higher) and to the current collector plating metric are both included. Any viable slurry must lie within the bounds of both regions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$</td>
<td>0.1 cm</td>
</tr>
<tr>
<td>$z$</td>
<td>$2 \frac{\text{mole e}^-}{\text{mole Fe}^{2+}}$</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>10 cm$^2$ cm$^{-2}$</td>
</tr>
<tr>
<td>$i_0$</td>
<td>1 mA cm$^{-2}$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>200 mS cm$^{-1}$</td>
</tr>
<tr>
<td>$\eta_{tot}$</td>
<td>100 mV</td>
</tr>
</tbody>
</table>

As shown in Figure 6.1, slurries made with MWCNTs are predicted to be able to achieve both performance metrics based upon the results of Chapter 5. It is likely that other less expensive particles can also match the criteria, but, as a proof of concept, the MWCNT slurry was adopted to permit the examination of the slurry battery performance.
6.3 Experimental

6.3.1 Materials

The slurry electrodes in this study were made with MWCNTs purchased from Nanostructured and Amorphous Materials, Inc. (Houston, TX, USA). These MWCNTs have an OD of 50-80 nm, length of 10-20 µm (aspect ratio of 125-400), a reported surface area of 40 m²/g, and a carbon purity of 99.9%. For these studies, the MWCNTs were used as received. Before tests were performed, the particles were mixed by hand into the electrolyte and then pumped through the system for at least 30 min.

All-iron flow batteries were studied with slurries serving as both the positive and the negative electrodes. In all cases presented herein, the slurry electrodes were composed of 4.8 vol% MWCNTs in the electrolyte. The electronic conductivity of these slurries was, in Chapter 5, found to be about 85 mS/cm while flowing. The positive slurry was initially 0.5 M FeCl₂, 0.5 M FeCl₃, and 1.0 M NH₄Cl while the negative slurry was initially 0.5 M FeCl₂ and 1.0 M NH₄Cl. The ionic conductivity of these electrolytes is about 150 mS/cm. Adding ferric chloride to the positive electrolyte ensured that on discharge, the negative slurry would always be limiting.

All salts used were reagent grade and were obtained from Fisher Scientific (USA). All solutions were made with deionized water (> 18 MΩ-cm, Barnstead Milli-Q). When using ferrous salts, solutions were made under a continuous nitrogen blanket and experiments were performed with the electrolyte under a continuous nitrogen purge to mitigate the air oxidation of ferrous to ferric iron. All tests were conducted at room temperature (20-25°C).
6.3.2 Rheological Studies

The slurries in these studies are intended for use as flowing electrodes. As such, the viscosity of the slurry electrodes are of interest and were investigated with an in-house tube viscometer. The tube viscometer consisted of a vertically-oriented clear polycarbonate tube (3/16 in. ID) through which the slurry was run at various flow rates (ranging from 20 mL/min to 130 mL/min). Differential pressure transducers located 100 cm apart along the length of the tube were used to determine the pressure drop. The reference side of each pressure sensor was open to the atmosphere. During each test, the particles were continually mixed in the reservoir to ensure stable results. The length and diameter of the polycarbonate tube were carefully selected in order to achieve a similar range of shear rates to those that are encountered in the electrochemical flow cell (while still maintaining laminar flow within the tube). The tube viscometer was used in order to avoid the settling and shear-history issues that often encountered with, e.g., cone-and-plate rheometers.

The Ostwald–de Waele (power law) model was adopted to describe the non-Newtonian behavior of the slurry over the range of shear rates considered, as has been done in the work of others.\textsuperscript{76} This model describes the shear stress in terms of the shear rate, $\partial u/\partial y$, a flow consistency index, $K$, and a flow behavior index, $n$, as related through Equation [6.3].

$$\tau = K \left[ \frac{\partial u}{\partial y} \right]^n$$ \[6.3\]

The values for $K$ and $n$ can be determined from tube viscometry data through comparison to an analytical prediction of the pressure drop. The equation for the analytically
predicted pressure drop of an Ostwald–de Waele fluid through a circular cylindrical tube is:

\[ Q = \pi \left[ \frac{n}{3n+1} \right] \frac{[-\Delta p]}{2K\ell} \left( \frac{r}{(3n+1)/n} \right) \]  

[6.4]

Here, \( Q \) is the flow rate, \( \Delta p \) is the pressure drop, \( \ell \) is the length of the tube, and \( r \) is the tube radius.\(^{103}\)

**Table 6.2**: Flow consistency index, \( K \), and flow behavior index, \( n \), for various weight percentages of MWCNTs in 1 M ferric chloride.

<table>
<thead>
<tr>
<th>vol%</th>
<th>( n )</th>
<th>( K ) (cP s(^{n-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.99</td>
<td>1.92</td>
</tr>
<tr>
<td>1.9</td>
<td>0.64</td>
<td>59.6</td>
</tr>
<tr>
<td>2.8</td>
<td>0.49</td>
<td>351</td>
</tr>
<tr>
<td>4.3</td>
<td>0.40</td>
<td>1470</td>
</tr>
</tbody>
</table>

Table 6.2 shows the values for \( K \) and \( n \) that were determined for various loadings of multi-walled carbon nanotubes in a 1 M solution of ferric chloride. Similar to the observations in previous studies,\(^{66,67,75}\) the slurries did exhibit shear thinning behavior with smaller flow behavior indices as the volume loading was increased.

It was observed that when the volume fraction of the solid particles was above some critical concentration, there was no longer enough liquid in the slurry to fully wet all of the particles. When the volume fraction of solids rose above this critical volume fraction, the slurry transitioned, quite quickly, from a shear thinning fluid to a semi-solid gel. At this point, the slurry is no longer able to flow. This viscosity critical volume fraction is described in detail by Youssry, et al.\(^{67}\) For slurries made with the MWCNTs used in these studies, the viscosity critical volume fraction was found to be about 6 vol\%.
6.3.3 Electrochemical Studies

The all-iron flow battery investigations were conducted in an in-house channel cell through which the slurry electrodes flow during operation. This channel cell was defined by two CPVC flow fields containing straight rectangular channels with a width of 1 cm and length of 12 cm (in the direction of flow). The current collectors were 1 cm wide and 6.725 cm long ($A = 6.725 \text{ cm}^2$) graphite plates that were centered in the middle of the CPVC channel. The gap between the current collector of each channel and the separator, $\delta$, was 0.2 cm. During operation, a peristaltic pump (Cole-Parmer, USA) was used for pumping the slurry electrodes. In all experiments, the slurry was pumped vertically up through the electrochemical channel cell at a volumetric flow rate of 250 mL/min. The inlet and exit ports of the channel cell were at roughly 30° angles (with respect to the current collector face) to mitigate clogging. Current was collected from this cell through two brass plates that were pressed into the back of the graphite current collectors. The cell was held together with stainless steel endplates. Teflon sheets were used to insulate the endplates and Grafoil (Graftech, USA) was used to minimize contact resistances between the brass plates and the graphite plates. The cell assembly was compressed with 8 bolts that were tightened to 90 in-lbs of torque. The reservoirs used to hold the slurry that was pumped through the channel cell were Nalgene bottles modified to be bottom drawn. Unless otherwise noted, all cell materials were purchased from McMaster-Carr (Cleveland, OH, USA).

Daramic, LLC (Charlotte, NC) graciously donated Daramic 250 Flatsheet for use in these studies. Daramic 250 Flatsheet has a reported average pore size of 0.1 microns, average porosity of $58 \pm 7.5\%$, and a thickness of about 225 microns measured after use
in experiments. The Daramic was soaked in methanol and rinsed in DI water before use.\textsuperscript{14} Chapter 3 found the ionic conductivity of these separators to be 40% of the conductivity of the electrolyte in which they were operating.

All electrochemical studies were performed using a Solartron 1280B potentiostat. Electrochemical impedance spectroscopy (EIS) was performed at varying cell potentials with a sinusoidal perturbation of 10 mV amplitude over the frequency range 20 kHz-0.2 Hz. The EIS experiments were controlled using ZPlot (Scribner Associates, USA). Cell polarization scans and an oscilloscope (Tektronix, USA) were used in congress to make sure that the response of the system under perturbation remained linear. Cyclic voltammetry with a scan rate of 20 mV/s was used to approximate the polarization of the all-iron flow battery and was controlled using CorrWare (Scribner).

6.4 Performance of the All-Slurry All-Iron Battery

Before the initial charging of the all-iron flow battery, EIS measurements were first conducted at the open circuit potential, shown in Figure 6.2. The high frequency resistance of the battery should be the sum of the parallel ionic and electronic resistances of each slurry electrode along with the separator resistance, Equation [5.6]. For a battery with 2 mm channels on either side of Daramic 250 Flatsheet, the total battery high frequency resistance should be about 2.0 \( \Omega \cdot \text{cm}^2 \) based on the independent electrical and ionic conductivity measurements. As seen in Figure 6.2, the initial EIS measurements are in good agreement with this prediction; confirming the conductivities of the slurry electrodes and separator. The EIS results at subsequent states-of-charge (SOC) will be discussed below.
Figure 6.2: The Nyquist representation of the EIS response of the all-iron flow battery at different states of charge.

Figure 6.3 shows the typical behavior of an all-iron flow battery while charging. The initial battery charge cycle was performed at 75 mA/cm$^2$. The battery voltage rose with the SOC before leveling off around 1.5 V. At the end of the initial charge, just over 1.0 Ah of charge had been stored in the battery bringing the 500 mL negative slurry to just over 7% state-of-charge (SOC). At this point, a cyclic voltammogram was performed on the battery. The average of this voltammogram is shown in Figure 6.4. As the voltammogram shows, the open circuit potential of the all-iron flow battery was about 1.2 V. The slope of the curve at charging and discharging potentials is about 3.2 Ω·cm$^2$. 
Figure 6.3: The voltage profiles while charging an all-iron flow battery at constant current with both positive and negative slurry electrodes. The discontinuity in the 75 mA/cm$^2$ curve occurred when the tubing between the cell and reservoir was readjusted.

Figure 6.4: The average results of cyclic voltammetry of the all-iron all-slurry flow battery with 1.0 Ah and 3.0 Ah of charge. The slope of each curve at discharge potentials is 3.2 Ω·cm$^2$ and 2.0 Ω·cm$^2$, respectively.

After the voltammogram was obtained the charge was continued at 150 mA/cm$^2$ for 2 additional hours (constituting a total battery charge of just over 3.0 Ah). During this period, the cell charging voltage fell to 1.45 V after first going through a voltage maximum. This decrease in cell overpotentials at increased current density operation was
corroborated by the EIS response of the battery, Figure 6.2, decreasing as the SOC of the battery increases and by the charging/discharging slope of the voltammogram decreasing to about 2.0 Ω·cm². EIS was performed at a discharge potential so that the results can be more easily compared at different SOCs. During discharge the dissolution of iron metal is directly studied and the effects of the variation of ferrous iron should be mitigated. Also, any additional side reactions that may occur during charging, discussed below, will not occur.

There are two main mechanisms thought to contribute to the improved performance. As the SOC of the negative slurry rises, the amount of metal deposited in the slurry increases and may therefore increase the slurry electronic conductivity. Also, after the carbon nanotubes are seeded with iron metal, the kinetics of iron plating are enhanced because the kinetic hindrance associated with iron nucleation on carbon is no longer a factor.27

The decrease in the overpotential on charge (whether by increased conductivity and/or improved kinetics) has an additional benefit. When charging at large potentials, the negative electrode can become negative enough for hydrogen evolution to occur.27 When this happens, the electrolyte pH will rise, potentially causing ferric or ferrous iron to precipitate out of solution as their respective hydroxides.27 The precipitated iron hydroxide can form a film on the slurry particles making discharge of the battery more difficult.

Figure 6.5 shows the voltage profiles while cycling the all-iron flow battery at ±75 mA/cm². Each half-cycle is 0.5 hours; constituting swings of ±0.25 Ah. The average charging potential is 1.55 V while the average discharge potential is 0.8 V. The average
voltaic efficiency is just above 50%. As Chapter 3 discussed, the voltaic efficiency could be improved by optimizing the separator and cell design. Over the twelve cycles shown, no appreciable capacity fade was observed (each half cycle lasted the 0.5 hours) and the potential profiles were steady.

![Voltage profiles while cycling the all-iron flow battery with MWCNT slurry electrodes at ±75 mA/cm². Each cycle is ±0.25 Ah.](image)

**Figure 6.5:** Voltage profiles while cycling the all-iron flow battery with MWCNT slurry electrodes at ±75 mA/cm². Each cycle is ±0.25 Ah.

After cycling was concluded, the battery was disassembled at the end of a charge. A thin film (< 0.02 cm) of iron was visible on < 25% of the current collector surface area. If all 3.0 Ah put into the battery was plated onto the current collector, the resulting metal plate would have to be approximately 0.07 cm, or 33% of the channel thickness. The iron that had plated onto the current collector was dissolved into a known volume of HCl and the resulting concentration was determined with a platinum microelectrode. From the dissolved iron concentration and the volume of HCl, the amount of iron deposited on the current collector was found to be < 5% of the total charge put into the battery, confirming that most of the metal was plated onto the slurry particles.
6.5 Conclusions

Slurry electrodes were investigated in order to decouple the energy storage capacity from the power delivery rate in an all-iron flow battery. For the slurry electrode to perform effectively, the battery negative reaction must occur on the slurry particles at reasonably high current densities. Mathematical modeling was used to investigate the current distribution in a slurry electrode as a function of the slurry specific area and electrical conductivity in order to achieve > 95% plating in the slurry electrode (not on the flat plate) at > 200 mA/cm$^2$. From the mathematical modeling, MWCNTs were selected as one viable slurry electrode.

All-iron flow batteries were operated with MWCNT slurries as both the positive and negative electrodes. As the battery state-of-charge increased, the voltaic efficiency of the battery also increased. Two mechanisms thought to contribute to the improved performance are an increase in the slurry electronic conductivity (due to metal deposition on the particles) and an increase in plating kinetics. After cycling the battery around 25% state-of-charge, < 5% of the charge of the battery was observed as iron metal on the current collector.
Chapter 7 CAPEX of All-Iron All-Slurry Flow Batteries

7.1 Introduction

Chapters 5 and 6 discussed the performance of slurries made with MWCNTs serving as both the positive and negative electrodes of the all-iron flow battery, respectively. This chapter will take the performance of the iron slurry electrodes and extrapolate to more optimized system specifications. In addition, the effects of plating into the slurry on the particle physical properties and the capital cost analysis will be discussed to assist in particle selection for future studies.

7.2 Predicted performance of the All-Iron Battery

Table 5.5 shows the overpotential breakdown of the Fe$^{2+/3+}$ redox reaction in a slurry electrode. When operating in battery with the channel gap, $\delta$, of 0.2 cm, the total overpotential of a MWCNT slurry at 200 mL/min is about 300 mV. This corresponds to an electrode polarization of about 1.5 $\Omega\cdot$cm$^2$.

Figure 6.4 describes the total battery polarization of an all-iron battery operated at 250 mL/min with MWCNT slurries as both the positive and negative electrodes in a cell with a channel gap, $\delta$, of 0.2 cm. The total polarization at charging and discharging potentials is approximately 2.0 $\Omega\cdot$cm$^2$ with 3.0 Ah of charge stored. In this battery, Daramic 250 was used as the separator. The Daramic has a conductivity of about 60 mS/cm (40% of the electrolyte’s 150 mS/cm ionic conductivity) which corresponds to about 0.38 $\Omega\cdot$cm$^2$ at 200 mA/cm$^2$. By subtracting the area resistance of the Daramic and the positive electrode (which should not significantly change over the cycling SOC swings demonstrated in Chapter 6) from the total battery area resistance, the total area
resistance of the negative electrode after 3.0 Ah of charge has been deposited is found to be about 0.12 Ω·cm².

Decreasing the channel gap in the cell from 0.2 cm to 0.1 cm should decrease the ohmic, distributed, and low frequency overpotentials by about 50% while the activation overpotentials will increase. This is demonstrated in Table 5.5 where decreasing the channel gap from 0.2 cm to 0.1 cm decreased the total positive slurry area resistance from 1.5 Ω·cm² to 0.7 Ω·cm². Adding the approximated negative polarization (0.12 Ω·cm² for a 0.2 cm channel) to the 0.7 Ω·cm² (0.1 cm channel) implies that the all-iron battery should able to operate with a total cell resistance, not including the separator, of less than 0.8 Ω·cm² with both positive and negative slurry electrodes.

7.3 Particle Plating Density at Maximum State-of-Charge

For a slurry to be a truly viable negative electrode in the all-iron battery, it must maintain physical and electrochemical properties over wide SOC swings. As discussed in Chapter 2 and 3, the optimal battery configuration, due to the effects of crossover, is to operate with 4 times less negative volume than positive volume and an initial negative electrolyte concentration of 3.0 M ferrous ions. As the battery cycling achieves steady state, the concentration in the negative reservoir rises. However, due to concentration limitations of ferrous and ferric chloride and performance limitations at extreme SOC, the concentration of all soluble species was bound between 0.5 M and 3.0 M. In this operating configuration, the maximum amount of iron metal predicted to plate is just less than 3.0 moles per liter of electrolyte. This equates to about $1.68 \times 10^5$ g Fe⁰/m³ electrolyte or about $2.13 \times 10^{-2}$ m³ Fe⁰/m³ electrolyte. Figure 7.1 shows the expected change in the slurry particle physical properties if 3 moles
of iron metal is plated per liter of electrolyte. As iron metal is plated on the particles, the particle density will increase. However, as the amount of particles in the slurry increase, the amount of iron plated onto each particle (assuming uniform distribution) decreases. If slurry electrodes are formed with particles that can achieve volume fractions above 20 vol%, the change in particle density can be kept below 20% at the maximum plating density. Also, achieving higher particle loading has the additional benefit of increasing the slurry specific area, described in Figure 6.1.

![Graph](image.png)

**Figure 7.1:** The physical properties of the slurry particles at maximum plating density (assuming uniform distribution) plotted against the initial volume fraction at 0% SOC. Each property is normalized by that of pure carbon. The battery specifications and cycling conditions are the same as that of Figure 2.9.

### 7.4 CAPEX Estimates of the All-Iron Flow Battery with Slurry Negative Electrodes

Besides meeting performance specifications, the slurry must be cost effective in order to be a viable electrode. The difference of using a slurry negative electrode, as opposed to a porous carbon, is that the amount of electrode material now depends on the negative electrolyte volume and not the geometric area of the battery. The CAPEX analysis presented in Chapter 3 was revisited for all-iron batteries with felt positive electrodes and
slurry negative electrodes as well as batteries with both positive and negative slurry electrodes. The slurry cost is investigated as a cost of carbon per volume of electrolyte. This distinction is made because it encompasses the slurry particle material cost as well as the slurry particle volume fraction, \( f \). The relationship is described in Equation [7.1]. Figure 7.2 shows the CAPEX for all electrode configurations as a function of slurry particle cost. In this analysis, battery is specified to be able to deliver 1 MW and 4 MWh at 200 mA/cm². The negative electrolyte is initially 3 M FeCl₂ and is four times smaller in volume than the positive electrolyte. Cell polarization, not including the separator, is 0.8 \( \Omega \cdot \text{cm}^2 \). The separator is Daramic at the optimal thickness for each particle cost. Because the slurry electrode cost is dependent upon electrolyte volume and not geometric area, the optimal separator when using slurry electrodes is thicker when using felt electrodes.

\[
\frac{\text{\$ particles}}{\text{m}^3 \text{ electrolyte}} = \frac{\text{\$ particle}}{\text{kg particle}} \frac{f}{1-f} \rho_{\text{part}} \quad [7.1]
\]

![Figure 7.2: CAPEX of the all-iron battery under varying electrode configurations as a function of slurry particle cost. The battery is specified to be 1 MW, 4 MWh, \( R - R_{\text{sep}} = 0.8 \Omega \cdot \text{cm}^2 \), \( V^+/V^- = 4 \), the initial negative electrolyte is 3 M FeCl₂, and \( i = 200 \text{ mA/cm}^2 \).](image-url)
The CAPEX analysis indicates that the all-iron battery with a negative slurry electrode made of particles < $1000/m^3 electrolyte ($2/kg at 20 vol%) and a felt electrode is more cost effective than the all-felt system. In comparison, the all-slurry battery must be made with particles < $400/m^3 electrolyte ($0.7/kg at 20 vol%). However, slurry electrodes < $3000/m^3 electrolyte ($6/kg at 20 vol%) can still achieve the cost target of $250/kW set forth by the DOE with a felt positive electrode.
Chapter 8 Conclusions

Flow batteries have long been attractive for grid scale energy storage because of their ability to independently scale the energy storage capacity and power delivery rate by storing the active species in reservoirs external to the battery energy conversion device. Market penetration of present day flow battery technologies has thus far been limited by the cost, abundance, and toxicity of the battery chemistries. The all-iron flow battery was investigated in this work as a flexible grid-scale energy storage device because iron is a low cost (> 60 times cheaper than vanadium), abundant (> 600 times more abundant than vanadium), and environmentally benign material (up to 100 times lower acid strength than vanadium). The all-iron battery uses the ferrous/ferric redox couple as the positive electrode reaction and the stripping/plating of iron metal to/from ferrous ions as the negative.

Flow batteries typically employ porous structures as stationary electrodes which are housed in the battery energy conversion device. Iron metal is plated directly onto the negative electrode and is therefore stored in the conversion device when electrodes of this type are used as the negative electrode in an all-iron battery. This couples the energy storage capacity to the power delivery rate (both now dictated by the size of the conversion device and not the reservoir) and limits the capacity to < 4 hours of energy storage. In order to impact the majority of the potential markets for grid-scale energy storage, it is projected that the flow battery will have to have > 4 hours of storage at < $250/kW. Two mechanisms that affect the capacity of the all-iron battery were investigated; capacity reduction through chemical discharge by active species crossover
during operation of the all-iron battery and the ability of slurry electrodes to directly decouple the capacity of the all-iron battery negative electrode.

The effective diffusivity of the soluble iron species across both Daramic and Nafion separators were experimentally measured and used to analytically predict the concentration of the iron species during continuous cycling operation in all-iron batteries. The effective diffusivity of ferrous and ferric ions across Daramic was found to be three times that of Nafion. However, the ionic conductivity of Daramic in the iron electrolyte was found to be ten times that of Nafion. In the investigations of how crossover effects the performance of all-iron batteries, the following conclusions were made.

(1) The electrolyte becomes unbalanced, iron in the positive electrolyte is depleted while iron builds up in the negative, but comes to a steady state with sufficient cycling.

(2) After steady-state cycling is achieved, there is a decrease in electrolyte utilization and an increase in coulombic efficiency losses due to crossover predicted.

(3) The utilization of the electrolyte increases as the ratio of the negative to the positive electrolyte volume decreases below that of the stoichiometric ratio.

(4) The CAPEX of the all-iron battery, a metric encompassing all the effects of the separator, showed that there exists an optimal separator thickness for each current density and storage capacity.

(5) Under most conditions, batteries with Daramic separators are 2x more cost effective than those using Nafion separators and can be < $250/kW with ≤ 10 hours of storage.
Slurry electrodes are flowing suspensions of electrically conductive particles in liquid electrolyte. When the concentration of solid particles is high enough \((f > f_c)\), a continuous conductive network is formed allowing the redox reactions to occur on the surface of the particles. There are many advantages to using slurry electrodes over conventional stationary electrodes. The use of a slurry allows the electrode (1) surface area to be scaled independently of the separator area, (2) to be easily manufactured and replaced without disassembling the cell, (3) and to be easily recycled with filtration. When slurry electrodes are used as the negative electrode in the all-iron flow battery, the iron metal is plated onto the particles which are then carried by the flow of the electrolyte out of the energy conversion cell and into the external reservoir, allowing the energy storage capacity to be scaled independently of the power delivery rate and capacities greater than 4 hours should be achievable. Many slurry electrodes were investigated but, due to its high electronic conductivity, slurries made with MWCNTs were the focus of the electrochemical studies. Electrochemical impedance spectroscopy was specifically investigated for characterizing the performance of the slurry electrodes. The following conclusions were made from the slurry electrode studies.

(1) Using the conventional definitions of the ohmic and activation overpotentials, an additional distributed impedance (which is a function of the ionic, electronic, and charge transfer impedances) is required to accurately predict the performance of an electrochemical slurry electrode.

(2) The polarization of the positive iron reaction on MWCNT slurries was > 65% ohmic losses; the electronic conductivity must be improved to significantly enhance the performance.
(3) All-iron flow batteries with both positive and negative slurry electrodes were successfully cycled and < 5% of the charge was found plated on stationary components in the battery.

(4) The electronic conductivity of the slurry electrode and the exchange current density were increased as iron metal was plated onto the slurry particles, improving the battery polarization to 0.8 $\Omega \cdot \text{cm}^2$, not including the separator.

From the work presented in this thesis, in order for a slurry to be a viable negative electrode of the all-iron battery, it must have the following specifications.

(1) In order to mitigate the change in particle density as the state-of-charge increases (< 20% change in density from bare particles), the loading of the particles in the slurry must be > 20 vol%.

(2) For > 200 mA/cm$^2$ operation and < 5% of the plating to occur on the current collector, > 30 mS/cm electronic conductivity and > $5 \cdot 10^6$ m$^2$/m$^3$ ($> 100$ m$^2$/g at 20 vol%) surface area to volume of slurry is required.

(3) To achieve > 100 m$^2$/g at 20 vol% and create a stable slurry for continuous operation (mitigate settling), the primary particle size should be < 200 nm in two dimensions.

(4) To achieve < $250$/kW with a slurry negative electrode and a conventional porous positive electrode, the slurry must be < $3,000$/m$^3$ (< $6$/kg at 20 vol%).
Chapter 9 Future Investigations

9.1 Crossover Studies

An analytical model was developed describing the concentration profiles of the active species in the all-iron flow battery during continuous cycling operation. These models were based on experimental measurements of the effective diffusivity of each soluble iron species across a specified battery separator. The effective diffusivity describes the rate that the iron species diffuses from one side of the battery to the other encompassing the diffusion coefficient of the iron ions and any partitioning that may occur in the separator. Future studies to help further develop this model should investigate how electrolyte and separator conditions affect the effective diffusivity of the soluble iron species.

The effective diffusivity of each iron species in the studies presented was assumed to be constant with the battery state-of-charge. However, the model was applied to a continuously cycled battery system with one reservoir on either side of the battery. This means that, as the battery is cycled, the concentration of the active species is constantly rising and falling. The change in concentration of ferric and ferrous ions could have a non-negligible effect on the effective diffusivity. The studies presented in Chapter 3 should be extended to a wider range of electrolyte compositions in to better understand how the battery will operate during cycling operation.

Nafion separators are ion exchange membranes with fixed charge species throughout the separator dictating the partitioning of ions in the separator and the ionic conductivity. Due to the difference in charge of the ferric and ferrous ions, the equilibrium of each in the Nafion separators is different, highlighted by the difference in effective diffusivity
reported in Chapter 3. During battery cycling, not only is the concentration of both the ferric and ferrous ions constantly changing, but their ratio relative to each other is also changing. The effect of the ratio of the iron ions was not investigated but could potentially have an effect on the effective diffusivity across the Nafion separators.

### 9.2 Slurry Electrode Investigations

The use of a slurry negative electrode is necessary for the all-iron flow battery to be able to reach the full potential of the market for grid-scale energy storage. However, to be an effective battery electrode, in addition to enhancing the battery capacity, the energy efficiency must be sufficiently high. As discussed in Chapters 5 and 6, the performance of the slurry electrodes are ohmically limited (> 65% of the positive electrode polarization is due to IR-losses). While the electronic conductivity is sufficiently large to decouple the battery (Figure 6.1), the ohmic resistance of the electrode still directly depends on the slurry electronic conductivity (Equation [5.6]). The effects of decreasing the slurry thickness in the energy conversions device were discussed and observed experimentally to decrease the ohmic losses. However, this benefit is limited because it increases the pressure drop (and therefore the parasitic pumping losses). To develop a truly effective slurry electrode, further increases must be made to its electronic conductivity.

Very little is presently understood about the conductivity of slurry electrodes. Chapter 4 discusses efforts made to describe how the particle loading can affect the slurry electrode. However, the magnitude of the conductivity is still dictated by $\sigma_d$, the pure conductivity of the particles. As Chapter 5 indicates, the value of $\sigma_d$ that should be used in the analyses of Chapter 4 is ambiguous. There are orders of magnitude difference
between the conductivity of pure graphite, the conductivity of the packed pellets, and the conductivity of the flowing slurries. The models presented in Chapter 4 acknowledge this complexity but only go as far as utilizing an interaction factor, \( L_j \), which is only a function of the particle aspect ratio. Future studies must be devoted to understanding and enhancing the electronic conductivity of the slurry electrodes and how particle shape, particle size, particle surface treatment, and electrolyte composition affect the particle-to-particle interactions.

In addition to the particle electronic conductivity, the dynamic nature of the slurry electrodes and how it affects the electrochemical properties of the slurry need to be better understood. Some understanding is beginning to come to the field pertaining to flowing effects such as the advected current. However, the effects of the slurry motion on mass transfer and other properties, such as conductivity, are relatively unstudied. All of these are needed to more fully develop the understanding, and engineering, of slurry electrodes.

9.3 CAPEX Model

The CAPEX model presented in Chapter 3 and Chapter 7 was used to help direct the project to key areas of research in order to more effectively enhance the ability of the all-iron battery to obtain its market potential. This model, to be in the scope of this work, made a number of base assumptions. While some of the assumptions will not change the conclusions comparing the different electrode structures, such as only investigating the material cost, others could have a significant impact. One such assumption is that of the shunt currents. For the slurries presented in this work, the electronic conductivity is in most cases significantly lower than the ionic conductivity. As such, there should not be any significant increase in the shunt losses associated with these electrodes. However, as
the electronic conductivity is increased, with new electrodes or even as the state-of-charge increases, the shunt losses could change dramatically. Another such assumption made is in regards to the cost of the separator. While the effects of the separator thickness on the battery performance were investigated, its effects on the battery cost were ignored. Also, all effects in the CAPEX model due to flow are ignored. A constant parasitic pumping loss is assumed and the effect of flow rate on the battery performance is ignored. All of these assumptions could be investigated further in order to produce a more realistic model of the all-iron flow battery.
Appendix A: Slurry Conductivity

In the studies leading up to those discussed in this thesis, the conductivity (and other physical properties) of many different particles were investigated in an attempt to find particles for viable slurry electrodes. The Table A.1 shows the electrical conductivity of the carbon particles under various conditions. All particles were used as received unless the letters “HT” appear after the particle name. Particles distinguished by the “HT” were heat treated at 500°C for > 4 hours in air before being tested. The conductivity reported in the Table A.1 is the electrical conductivity at the maximum flowable particle loading, $f_{cv}$. If no value is given, or “No” future studies are indicated, it is due to non-conducive slurry properties, e.g. excessive viscosities, prone to clogging, excessive settling, did not mix well in electrolyte, too low conductivity, or too low specific area. The specific area of all particles are as reported in the product literature.

Two different methods were used to determine the electrical conductivity of each particle. Conductivities determined using experimental method (Exp.) 1 were done so in 1 M HCl under stagnant conditions. The slurry was made as described in Chapter 5 and Chapter 6. After a stable slurry was pumped through the electrochemical channel cell (Chapters 5 and 6), the flow of the slurry was stopped and EIS was conducted. The low frequency value of the EIS results corresponds to the electrical conductivity (Figure 5.2).

Conductivities determined using Exp. 2 were done so in deionized water while flowing, as described in Chapter 5 in the tubular flowing conductivity cell. The high frequency value of the EIS results corresponds to the parallel combination of the electrical and ionic conductivity. Since the electrolyte is deionized water, initially > 18 MΩ·cm, the ionic conductivity is assumed to be zero. Equation [5.2] was used to determine the electrical conductivity reported.
Table A.1: Properties of slurry electrodes made with a variety of carbon particles.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Source</th>
<th>d [µm]</th>
<th>h [µm]</th>
<th>Shape</th>
<th>(f_{cr})</th>
<th>SA [m²/g]</th>
<th>SA/Vol [m²/m³]</th>
<th>(\sigma) [mS/cm]</th>
<th>Exp.</th>
<th>Future</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regal 660R</td>
<td>Cabot</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3D</td>
<td>14</td>
<td>&gt; 85</td>
<td>2.2 (\times) 10⁷</td>
<td>80</td>
<td>1</td>
<td>Yes</td>
</tr>
<tr>
<td>Regal 400</td>
<td>Cabot</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3D</td>
<td>14</td>
<td>96</td>
<td>2.5 (\times) 10⁷</td>
<td>9</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>Monarch 800</td>
<td>Cabot</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3D</td>
<td>13</td>
<td>254</td>
<td>6.4 (\times) 10⁷</td>
<td>90</td>
<td>1</td>
<td>Yes</td>
</tr>
<tr>
<td>Monarch 905</td>
<td>Cabot</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3D</td>
<td>10</td>
<td>&gt; 85</td>
<td>1.7 (\times) 10⁷</td>
<td>--</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>Vulcan XC72</td>
<td>Cabot</td>
<td>0.05</td>
<td>0.05</td>
<td>3D</td>
<td>10</td>
<td>254</td>
<td>2.5 (\times) 10⁸</td>
<td>&lt; 20</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>Vulcan XC305</td>
<td>Cabot</td>
<td>0.05</td>
<td>0.05</td>
<td>3D</td>
<td>13</td>
<td>112</td>
<td>2.8 (\times) 10⁷</td>
<td>--</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>Black Pearls 2000</td>
<td>Cabot</td>
<td>0.03</td>
<td>0.03</td>
<td>3D</td>
<td>2</td>
<td>1487</td>
<td>1.5 (\times) 10⁸</td>
<td>11</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>Super-P HT</td>
<td>Timcal</td>
<td>0.04</td>
<td>0.04</td>
<td>3D</td>
<td>2</td>
<td>62</td>
<td>3.1 (\times) 10⁶</td>
<td>--</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>KetjenBlack EC-600JD</td>
<td>AkzoNobel</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3D</td>
<td>4</td>
<td>1270</td>
<td>1.0 (\times) 10⁸</td>
<td>--</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>230U Asbury</td>
<td>15-20</td>
<td>0.1</td>
<td>Flake</td>
<td>18</td>
<td>6.5</td>
<td>2.1 (\times) 10⁶</td>
<td>15</td>
<td>2</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>230U HT Asbury</td>
<td>15-20</td>
<td>0.1</td>
<td>Flake</td>
<td>18</td>
<td>6.5</td>
<td>2.1 (\times) 10⁶</td>
<td>13</td>
<td>2</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>3243 Asbury</td>
<td>40</td>
<td>0.1</td>
<td>Flake</td>
<td>22</td>
<td>3</td>
<td>1.1 (\times) 10⁶</td>
<td>11</td>
<td>2</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>3243 HT Asbury</td>
<td>40</td>
<td>0.1</td>
<td>Flake</td>
<td>20</td>
<td>3</td>
<td>1.1 (\times) 10⁶</td>
<td>8</td>
<td>2</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Nano27 Asbury</td>
<td>0.1</td>
<td>0.005</td>
<td>Platelet 8</td>
<td>250</td>
<td>4.0 (\times) 10⁷</td>
<td>12</td>
<td>2</td>
<td>No</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nano27 HT Asbury</td>
<td>0.1</td>
<td>0.005</td>
<td>Platelet 7</td>
<td>250</td>
<td>3.5 (\times) 10⁷</td>
<td>25</td>
<td>1</td>
<td>Yes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nano27 HT Asbury</td>
<td>0.1</td>
<td>0.005</td>
<td>Platelet 9</td>
<td>250</td>
<td>4.5 (\times) 10⁷</td>
<td>40</td>
<td>2</td>
<td>Yes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>xGnP Graphene C300</td>
<td>XGS</td>
<td>&lt; 2</td>
<td>&lt;0.02</td>
<td>Platelet 20</td>
<td>300</td>
<td>1.0 (\times) 10⁸</td>
<td>25</td>
<td>1</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>xGnP Graphene C300</td>
<td>XGS</td>
<td>&lt; 2</td>
<td>&lt;0.02</td>
<td>Platelet 20</td>
<td>300</td>
<td>1.0 (\times) 10⁸</td>
<td>83</td>
<td>2</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>xGnP Graphene C300 HT</td>
<td>XGS</td>
<td>&lt; 2</td>
<td>&lt;0.02</td>
<td>Platelet 20</td>
<td>300</td>
<td>1.0 (\times) 10⁸</td>
<td>33</td>
<td>1</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>xGnP Graphene M15</td>
<td>XGS</td>
<td>15</td>
<td>&lt;0.02</td>
<td>Platelet 5</td>
<td>150</td>
<td>1.5 (\times) 10⁷</td>
<td>62</td>
<td>2</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>1223YJ</td>
<td>NanoAmor</td>
<td>0.05</td>
<td>0.1</td>
<td>MWCNT 6</td>
<td>40</td>
<td>4.8 (\times) 10⁶</td>
<td>85</td>
<td>2</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

For convenience in the laboratory, the wt% of the particles is sometimes used instead of the vol%. Equations [A.1] and [A.2] show the relationship between the slurry wt% and vol%. In these equations, \(\rho_C\) and \(\rho_E\) are the carbon and electrolyte densities, respectively.

\[
wt\% = \frac{\rho_C \cdot \text{vol}\%}{(\rho_C \cdot \text{vol}\% + \rho_E (1-\text{vol}\%))} \tag{A.1}
\]

\[
\text{vol}\% = \frac{\rho_E \cdot wt\%}{(\rho_E \cdot wt\% + \rho_C (1-\text{wt}\%))} \tag{A.2}
\]
Appendix B: Mathematica Crossover Model

The model presented in Equations [2.5a]-[2.5d] of Chapter 2 describing the concentration profiles of the iron species during cycling of the all-iron flow battery was solved using Mathematica 9.0. The code for the Mathematical program is shown below.

```
InitialCond = 
{VoltageValue -> 1.2, PowerValue -> 1000., EnergyValue -> 4000.,
Cp30Value -> 0.25, Cp20Value -> 1.525, Cn20Value -> 2.5,
D2Value -> (9.9*(10^-7)), D3Value -> (12.3*(10^-7)),
dmemValue -> 105., npValue -> 1, nnValue -> 2, CurrentMag -> 200.,
VolRatio -> 4.0};

parameters = 
{BatteryVoltage -> VoltageValue, BatteryPower -> PowerValue,
BatteryEnergy -> EnergyValue, Cp30 -> (C30*1000),
Cp20 -> (C20*1000), Cn20 -> (Cn20*1000),
D2 -> (D2*3600/10000), D3 -> (D3*3600/10000),
Vp -> ((EnergyValue*1000*3600)/(96485*VoltageValue*npValue*(Cp30*1000))),(1000)),
Vn -> ((EnergyValue*1000*3600)/(VolRatio*96485*VoltageValue*npValue*(Cp20*1000))),(1000)),
A -> (PowerValue*1000*1000/(CurrentMag*VoltageValue*100000)), dmem -> (dmemValue/1000000),
np -> npValue, nn -> nnValue,
F -> (96485/3600), icycle -> (CurrentMag*(100^2)/1000)
/. InitialCond;

CycleInfo = 
{{0, Cn20Value /. InitialCond, Cp20Value /. InitialCond, Cp30Value /. InitialCond}};

profiles = 
NDSolve[
{Cp3'[t] == -(D3*A/Vp)*((Cp3[t])/dmem) + (r[t]*A/(np*F*Vp)),
Cp2'[t] == -(D2*A/Vp)*((Cp2[t]-Cn2[t])/dmem) - (r[t]*A/(np*F*Vp)),
Cn2'[t] == -(D2*A/Vn)*((Cn2[t]-Cp2[t])/dmem) - (r[t]*A/(nn*F*Vn)) + ((3/2)*(-D3*A/Vn)*((-Cp3[t])/dmem)),
A'[t] == 0, a'[t] == 0,
Cp3[0] == Cp30, Cp2[0] == Cp20, Cn2[0] == Cn20, r[0] == icycle, a[0] == 0,
WhenEvent[
{Cp2[t] == 0.25*1000, Cp3[t] == 0.25*1000, Cn2[t] == 0.25*1000},
{r[t] -> r[t], a[t] -> t, CycleInfo = Append[CycleInfo, {t, Cn2[t]/1000, Cp2[t]/1000,
Cp3[t]/1000}]}, parameters, 
{Cp3, Cp2, Cn2, r}, {t, 0, 100000000}}/. parameters,
{Cp3, Cp2, Cn2, r}, {t, 0, 100000000}}
```

The first section of the code, InitialCond, sets the initial conditions for the battery system being modeled. The values shown are for an all-iron battery with a 105 µm Daramic separator cycled at 200 mA/cm² with a volume ratio of 4.0. The second section of the code, parameters, sets the value of each parameter in consistent units that are then applied to the model. The third section, CycleInfo, initializes the table that will contain the concentrations of each species at the beginning and end of each charge/discharge cycle. The final section, profiles, solves the system of equations, [2.5a]-[2.5d]. The WhenEvent in this section changes the current from charging to discharging, or vice versa, when the concentration of any species is 0.25 M. When this change occurs, the concentration of each species and the time is added to CycleInfo. The following dictates the nomenclature used in the Mathematica code.

**InitialCond Nomenclature**

InitialCond = Initial conditions for the model

VoltageValue = Battery open circuit voltage [V]

PowerValue = Battery power [kW]

EnergyValue = Battery energy storage capacity [kWh]

Cp30Value = Initial conc. of ferric ions in the positive [mol Fe³⁺/L]

Cp20Value = Initial conc. of ferrous ions in the positive [mol Fe²⁺/L]

Cn20Value = Initial conc. of ferrous ions in the negative [mol Fe²⁺/L]

D2Value = Effective diffusivity of ferrous ions [cm²/s]

D3Value = Effective diffusivity of ferric ions [cm²/s]

dmemValue = Separator thickness [µm]

npValue = Equivalence of positive reaction [mol e⁻/mol Fe]
\[ \text{nnValue} = \text{Equivalence of negative reaction} \quad [\text{mol e}^-/\text{mol Fe}] \]

\[ \text{CurrentMag} = \text{Magnitude of cycling current density} \quad [\text{mA/cm}^2] \]

\[ \text{VolRatio} = \text{Ratio of the electrolyte volume} \quad [\text{Pos. Vol./Neg. Vol}] \]

**Parameters Nomenclature**

\[ \text{BatteryVoltage} = \text{Battery open circuit voltage} \quad [\text{V}] \]

\[ \text{BatteryPower} = \text{Battery power} \quad [\text{kW}] \]

\[ \text{BatteryEnergy} = \text{Battery energy storage capacity} \quad [\text{kWh}] \]

\[ \text{Cp30} = \text{Initial conc. of ferric ions in the positive} \quad [\text{mol Fe}^{3+}/\text{m}^3] \]

\[ \text{Cp20} = \text{Initial conc. of ferrous ions in the positive} \quad [\text{mol Fe}^{3+}/\text{m}^3] \]

\[ \text{Cn20} = \text{Initial conc. of ferrous ions in the negative} \quad [\text{mol Fe}^{3+}/\text{m}^3] \]

\[ \text{D2} = \text{Effective diffusivity of ferrous ions} \quad [\text{m}^2/\text{h}] \]

\[ \text{D3} = \text{Effective diffusivity of ferric ions} \quad [\text{m}^2/\text{h}] \]

\[ \text{Vp} = \text{Positive electrolyte volume} \quad [\text{m}^3] \]

\[ \text{Vn} = \text{Negative electrolyte volume} \quad [\text{m}^3] \]

\[ \text{A} = \text{Separator geometric area} \quad [\text{m}^2] \]

\[ \text{dmem} = \text{Separator thickness} \quad [\text{m}] \]

\[ \text{np} = \text{Equivalence of positive reaction} \quad [\text{mol e}^-/\text{mol Fe}] \]

\[ \text{nn} = \text{Equivalence of negative reaction} \quad [\text{mol e}^-/\text{mol Fe}] \]

\[ \text{F} = \text{Faradays constant} \quad [\text{Ah/mol e}^-] \]

\[ \text{icycle} = \text{Magnitude of cycling current density} \quad [\text{A/m}^2] \]

\[ \text{r} = \text{Current density vs time} \quad [\text{A/m}^2] \]

\[ \text{a} = \text{time when cycle ends} \quad [\text{s}] \]
References


