IRON-LIGAND ELECTROKINETICS TOWARDS
AN ALL-IRON HYBRID REDOX FLOW BATTERY

by

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*We also certify that written approval has been obtained for any proprietary material contained therein.
Dedication

To my family. To my sisters and brother, Alexandria, Jessica, and Matthew, for always believing in me, being ready with a goofy story, and keeping life in perspective. You are not only siblings, but also best friends. To my parents, Paul and Mary Hawthorne, for all of their support and encouragement. And to my grandparents, who I know would have been proud.

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List of Symbols

\( a \) – Dimensionless velocity into a porous disk

\( a_s \) – Specific surface area

\( C_B \) – Bulk concentration of the reactive species

\( D_o \) – Diffusion coefficient of the reactive species

\( E' \) – Open circuit potential

\( \Delta E_{pp} \) – Peak separation in a cyclic voltammogram

\( F \) – Faraday’s constant

\( i_o \) – Exchange current density

\( i_k \) – Kinetic current density

\( i_L \) – Limiting current density

\( k \) – Permeability

\( k_{m,avg} \) – Average mass transfer coefficient

\( K_a \) – Acid dissociation constant

\( h \) – Disk thickness

\( L_o \) – Characteristic depth of penetration

\( n \) – Number of electrons

\( pK_a \) – Acid dissociation constant, log

\( r \) – Position along the radial axis

\( R \) – Universal gas constant

\( R_{HF} \) – High frequency resistance, measured using electrochemical impedance spectroscopy
\( Re \) – Reynolds number

\( T \) – Temperature

\( \Delta S^0_{re} \) – Entropy difference of a redox couple

\( Sc \) – Schmidt number

\( v_r \) – Velocity in the radial direction

\( v_z \) – Velocity in the z direction

\( z \) – Position along the z axis

\( \varepsilon \) – Void fraction

\( \eta_A \) – Activation overpotential

\( \kappa_o \) – Conductivity of electrolyte

\( \nu \) – Kinematic viscosity

\( \sigma_E \) – Electronic conductivity

\( \sigma_I \) – Ionic conductivity

\( \psi \) – Empirical shape factor for mass transfer correlation

\( \omega \) – Angular rotation rate
Iron-Ligand Electrokinetics towards an All-Iron Hybrid Redox Flow Battery

Abstract

by

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Flow batteries as a large scale energy storage technology have seen a renewed interest in recent years with the implementation of renewable energy sources on the grid. One such flow battery is the all-iron chemistry. The all-iron flow battery utilizes the Fe II/III redox couple as the positive electrode and the Fe II/0 reaction as the negative electrode. Iron plating in the negative electrode occurs in the cell stack, necessitating intelligent design of the porous electrode structure to maximize plating density, and thus energy storage density. Due to the negative potential of the iron plating reaction, hydrogen evolution is a main concern in long term operation of the all-iron flow battery. As hydrogen evolves the electrolyte pH will rise, causing precipitation of the ferric ions in the positive electrolyte.

This research addresses three critical aspects of the chemistry and design of the all-iron flow battery. First, to increase the ferric ion solubility in relatively high pHs (pH 2 – 3), complexing ligands are considered as an electrolyte additive. Kinetic and mass transfer behavior of several iron-ligand complexes are examined. An electrolyte containing a 0.5:1 glycine to iron ratio showed Fe$^{3+}$ solubility at pHs greater than 2.5 and
reasonable kinetic performance on a glassy carbon electrode. Modeling of the equilibrium species in an iron-glycine solution is used to design an electrolyte with the desired solubility and concentration of Fe$^{3+}$. Second, the iron deposition reaction is considered in conjunction with added ligand. Further suppression of hydrogen evolution was also considered through the use of various supporting electrolytes. High concentrations of chloride ions were found to hinder hydrogen evolution in the negative electrolyte, both on an iron rod electrode and in an all-iron flow battery. Third, the plating capacity of the negative deposition electrode is considered. Six three dimensional electrode structures are presented, and an achievable plating density of 150 mAh/cm$^2$ is demonstrated in two separate electrode structures. Cycling of an all-iron flow battery with a voltaic efficiency of 80% is demonstrated.
Chapter 1
Introduction and Background

1.1 Introduction

Implementation of renewable energy sources on the power grid has increased attention on grid-scale energy storage (1). Though wind and solar power decrease the dependence on fossil fuels, they often produce energy intermittently and must be used in conjunction with an energy storage device. Several energy storage technologies exist, all with advantages and disadvantages (2). In Figure 1-1, a Ragone plot of different energy storage technologies is shown, comparing the energy storage capacity and power output of each. Techniques such as pumped hydro and compressed air energy storage are relatively inexpensive, but are highly dependent on the geography near the energy storage site. Supercapacitors are a relatively high power device, but as of yet are still low in energy density. Another widely studied energy storage system is the hydrogen fuel cell. Fuel cells use hydrogen and oxygen as reactants, with water as the product. However, fuel cells are still relatively low efficiency and often contain expensive catalyst materials. Redox flow batteries, another possibility for energy storage, are both moderate power and moderate energy density.

Redox flow batteries (RFBs) have seen a renewed interest as a method for large scale energy storage, specifically for grid applications such as storage for intermittent energy sources and load leveling (3, 4). Flow batteries operate by storing the dissolved reactive species in external tanks (Figure 1-2). The electrolyte flows through the battery stack, where the electrochemical reactions take place, then back to the external reservoirs.
Figure 1-1. Ragone plot of energy storage technologies, as reported by Ibrahim, et al. (2).

Storing the electrolyte externally eases scaling of the batteries to the grid scale, as the energy storage capacity is solely dependent on the size of the reservoir (5, 6). Several flow battery chemistries exist, including all-vanadium (7) and iron-chromium (8). Additionally, it is possible to operate a flow battery in a hybrid configuration. Hybrid flow batteries, such as the all-iron system (9) and zinc-halide systems (10-12) involve plating/stripping of metal deposits at the negative electrode. This limits the amount of energy that can be stored and the energy capacity is directly related to the amount of metal that can be plated within the stack (10). The all-iron chemistry is advantageous due to the low cost of the reactants and the use of a single species as the reactant. In single
species flow battery electrolytes (all-vanadium, all-iron) crossover of the electrolyte can be easily dealt with: the electrolytes can be remixed and then brought back to their original states (6).

The objectives of this work are focused on two fronts within the all-iron flow battery. First, to understand the electrochemistry of iron-ligand complexes using ligands that enhance iron solubility in an aqueous electrolyte. Both the positive and negative reactions are considered. Secondly, to develop a porous electrode configuration that increases plating current density and energy storage capacity in the all-iron flow battery.

**Figure 1-2.** Schematic of an all-iron flow battery. Dissolved reactive species are stored in external reservoirs, and the electrolyte is pumped through a battery stack.

### 1.2 Background – The All-Iron Flow Battery

An all-iron flow battery was proposed in 1981 as a possibility for redox flow battery applications (9). The all-iron chemistry utilizes a single element in several oxidation states for both the anode and cathode, similar to the all-vanadium RFB (with V(II/III) on the negative electrode and V(IV/V) on the positive electrode). As with the
traditional flow batteries, the electrolyte is stored in external tanks and pumped through a battery stack, where the reactions occur (Figure 1-2). The ferric/ferrous redox couple is employed as the positive electrode reaction, shown for battery charging in Equation 1-1. Fe II/III is a reasonably fast redox couple with a formal reduction potential of 0.77 V vs. NHE (13). The negative reaction of the iron RFB involves plating and stripping of Fe⁰ to Fe²⁺ solution at -0.44 V vs. NHE, shown for battery charging in Equation 1-2. Because this reaction involves plating within the battery stack, this chemistry must be considered a hybrid RFB.

\[
Fe^{2+} \leftrightarrow Fe^{3+} + e^- \quad E^0 = 0.77V \tag{1-1}
\]

\[
Fe^{2+} + 2e^- \leftrightarrow Fe^0 \quad E^0 = -0.44V \tag{1-2}
\]

The energy stored is now tied to the amount of iron that can be plated in the stack, which no longer decouples the energy and power of the battery (one of the advantages of a traditional RFB). A detailed schematic of the reactions, ion transport, and electron flow during discharge is shown in Figure 1-3. The main charge carrying ion is Cl⁻, and the supporting electrolyte is shown as NH₄Cl.

Hruska and Savinell (9) investigated cell performance of an all-iron flow battery as a function of electrolyte composition, cell membrane, and operating temperature. Using iron chloride salts with an ammonium chloride supporting electrolyte, they achieved an electrolyte resistivity of 4 Ω-cm at 22 °C and 2 Ω-cm at 77 °C, reducing the voltaic loss from electrolyte resistivity to 4%. The iron deposit from ammonium chloride
containing electrolyte was highly stable, without the poor adherence and powdery deposits seen when plating from sodium chloride or potassium chloride electrolytes. It was found that the largest voltage loss occurred at the plating electrode, both on charge and discharge. Hydrogen evolution and corrosion of the iron plate was also noted. Hydrogen evolution was mitigated by maintaining a pH gradient across the cell, and with the addition of a small concentration of manganese ions to the electrolyte.

**Figure 1-3.** Detailed schematic of the ion and electron transport within the battery stack for an all-iron flow battery.

For the separator, two materials were considered: Celgard and Daramic. Ferric ions that cross over the membrane directly reacts with the plated iron to form Fe$^{2+}$, leading to a decrease in coulombic efficiency. The Daramic separator was found to more effectively prevent Fe$^{3+}$ crossover; however the IR drop across the Daramic separator was higher than across the Celgard separator (Figure 1-4). Hruska and Savinell report a coulombic efficiency of above 90% in a redox cell containing the Daramic separator. Due to the efficiency loss from ferric ion crossover, an anion exchange membrane was also
considered; however the membranes deteriorated in the ferric chloride electrolyte. Overall, Hruska and Savinell report round trip current efficiencies of 90% and energy efficiencies of 50% for an all-iron flow battery operated at 60 °C. Though the most significant losses occurred at the negative electrode due to slow plating/stripping kinetics with hydrogen evolution and the associated pH change in the electrolyte, the technology still shows promise as a large scale energy storage device.

**Figure 1-4.** (Left) Fe$^{3+}$ crossover as a function of time for two cell separators, Daramic W0733 and Celgard 5511. (Right) IR drop across a Daramic and a Celgard separator as a function of current density. Figures are as reported by Hruska and Savinell (9).

1.2.1 Advantages of the all-iron flow battery

The all-iron flow battery has some inherent advantages over other flow battery chemistries, particularly the all-vanadium redox flow batteries. Most prominent of these advantages is the cost of and availability of materials. A report in October 2013 valued iron at $0.39/kg iron metal and vanadium (as ferrovanadium) at $13.25/kg vanadium
metal (about 34 times more than the cost of iron), with 3,000,000 metric tons of iron and 63 metric tons of vanadium produced globally in 2012 (14). An all-iron flow battery uses domestically available materials as its active species. Additionally, the iron RFB operates at mildly acidic pHs (around 2 – 3). The vanadium RFB operates at highly acidic pHs, usually with a 3 M to 4 M sulfuric acid supporting electrolyte (15). Strong sulfuric acid solutions are highly corrosive, and vanadium is toxic in moderate quantities. The components of the all-iron RFB are environmentally benign, with low toxicity and low acidity. The chemical considerations combined with the low cost of iron make the all-iron RFB an ideal choice as a flow battery chemistry.

1.2.2 Disadvantages of the all-iron flow battery

One disadvantage of the all-iron flow battery is the possibility of unwanted side reactions on the negative electrode, particularly hydrogen evolution. The iron plating potential is -0.44 V vs. NHE, well negative of the hydrogen evolution potential. Increasing the pH of the electrolyte will shift the equilibrium potential of hydrogen evolution more negative and decrease the diffusion limited current due to hydrogen evolution (16); however, Fe$^{2+}$ will precipitate as a hydroxide species before the pH is sufficiently high to completely avoid hydrogen evolution at the iron plating potential. If the hydrogen evolution current is large enough, bubbles can cling to the electrode surface and cause the deposit to form around the bubble (17). Maintaining the electrolyte at a mildly acidic pH, around 2 – 3, will help mitigate hydrogen evolution. Additionally, hydrogen can be suppressed through electrolyte additives such as bismuth (8, 18), sulfide (19), lead, and other heavy metals (9, 20).
Maintaining the electrolyte pH between 2 and 3 may be sufficient to decrease coulombic losses in the negative electrolyte, but will then cause problems in the positive electrolyte. Not only will raising the pH of the battery electrolyte cause precipitation of the ferrous species on the negative electrode, it will especially cause precipitation of the ferric ions in the positive electrolyte. Fe(III) will precipitate as ferric hydroxide at pHs greater than about 2 (21). A method of maintaining ferric solubility at these relatively high pHs is needed. To prevent precipitation of Fe(III), we examine the use of a complexing ligand in the positive electrolyte.

A secondary disadvantage of the all-iron flow battery is the hybrid nature of the electrodes. The negative electrode products are no longer carried to the external reservoir: plated iron must be stored in the battery stack. This limits the amount of energy that can be stored, which is directly related to the amount of metal that can be plated within the stack (10). To maximize energy storage capacity, the amount of iron that can be plated in the negative electrode must be maximized.

The all-iron flow battery is approached on three separate fronts for the purposes of this dissertation. The first is an investigation into the use of complexing ligands in the positive electrolyte and the iron-ligand electrokinetics. A method for estimating kinetic parameters on the porous flow battery electrodes was also tested for applicability. The second approach involves maximizing the plating density in the negative electrode through design of a porous three dimensional electrode structure. The third approach explores the effect of the supporting electrolyte on hydrogen evolution and on the iron plating kinetics. Two promising ligands were also tested in the negative electrolyte in the interest of maintaining a single electrolyte composition in the all-iron flow battery.
1.2.3 Ligand Chemistry in Flow Batteries

Ligand-metal electrochemistry in flow batteries is well established for many ligands including EDTA (22, 23), phenanthroline (23, 24), triethanolamine (25), and DTPA (22, 23, 26, 27), among others. Modiba, et al., investigated ligand complexes for the Ce(III/IV) redox couple, including EDTA, EDDS, NTA, and DTPA, to increase reversibility and electron transfer rate of the reaction (22). The same group further studied the effect of DTPA ligands on the electrokinetics of Ce(III/IV), Cr(II/III), and V(IV/V) for flow battery electrodes (27). Ibanez, et al., combined several redox couples, Fe(II/III), Co(II/III), and Cr(III/IV), and Ru(II/III), with ligands such as EDTA, DPTA, phenanthroline, tetraethyl acetate, bipyridine, ethylene diamine, and diethylene triamine, for application in flow batteries as well as photoelectrochemical cells (23).

The Fe(II/III) redox couple was complexed with o-phenanthroline type ligands by Chen, et al., to shift the redox potential more positive, though the solubility of the iron-ligand complexes was below 1 M in 0.5 M H$_2$SO$_4$ (as low as 0.3 M in the case of Fe-terpyridine) (24). The specific ligand used also influenced the rate of reaction, as shown for 4-cyano-pyridine, bipyridine, and terpyridine in Figure 1-5. The kinetics of the Fe-4-cyano-pyridine complex are sluggish, with a peak separation of almost 0.8 V. The cyclic voltammetry for both the Fe-bipyridine and the Fe-terpyridine are fast, and both shifted positive, to about 1.1 V vs. NHE. Though the redox couples are kinetically acceptable, some instability of the ferric complex was observed, which may contribute to a loss in battery capacity.
Figure 1-5. Cyclic voltammetry curves for the ferrous ion coordinated with 1) 4-cyano-pyridine, 2) bipyridine, and 3) terpyridine on a graphite electrode, as reported by Chen, et al. (24).

The Fe(II/III) redox couple complexed with triethanolamine (TEA) was examined, for use as a negative electrode in an iron-bromine RFB (25). Solubility of the Fe(III)-TEA complex was of concern, with a maximum solubility of 0.6 M in a solution of 3 M NaOH and 1.4 M TEA. Complexing the iron with triethanolamine shifts the Fe(II/III) reaction potential to around -0.8 V vs. NHE (Figure 1-6). The cyclic voltammetry is reversible, similar to that of the Fe-bipyridine and Fe-terpyridine complex in Figure 1-5. The reported open circuit voltage of the Fe-TEA/Br₂ flow cell was 1.9 V. Though the redox potential shift in the cyclic voltammetry makes TEA an unsuitable ligand for the purposes of this application, it might be possible to use the Fe-TEA complex as a negative couple in a double-redox flow battery. However, the basic electrolyte needed for high Fe-TEA solubility is incompatible with the acidic pH of the
uncomplexed ferric/ferrous electrolyte, so an alternate positive couple would be needed. Murthy, et al., also examined the Fe(II/III) couple with ligand complexes that shift the reaction potential in the negative direction, specifically EDTA, DTPA, and nitrilotriacetic acid (26).

![Cyclic voltammetry of the Fe^{2+/3+}-TEA complex at TEA concentrations of 1) 0.01 M TEA, 2) 0.15 M TEA, 3) 0.27 M TEA, and 4) 0.40 M TEA, as reported by Wen, et al. (25).](image)

**Figure 1-6.** Cyclic voltammetry of the Fe^{2+/3+}-TEA complex at TEA concentrations of 1) 0.01 M TEA, 2) 0.15 M TEA, 3) 0.27 M TEA, and 4) 0.40 M TEA, as reported by Wen, et al. (25).

Though several iron-ligand complexes have been reported in the literature, many are unsuitable for the present purpose. Ligands that shift the potential negative (EDTA, DTPA, triethanolamine, etc.) will lower the FeFB cell potential. If the ligand shifts the redox potential negative enough, it is possible to use the iron-ligand redox couple as the negative electrode in a separate flow battery chemistry, though such an investigation is beyond the scope of this work. Other ligands, for example the phenanthroline type
ligands, are too expensive to maintain the low cost electrolyte, one of the primary benefits of using an iron chemistry.

Chemically, there are several other criteria that the ligand must meet. To be effective in an iron flow battery, the desired energy storage capacity of flow batteries necessitates a high solubility of the iron-ligand complex. The iron-ligand complex may have a different solubility than either the ferric ions or the ligands separately. An iron-ligand solubility of at least 1 M will be comparable to the solubility of other flow battery chemistries. The complex must also be soluble at pHs around three (the pH needed to minimize H₂ evolution on the negative electrode). Additionally, the ligand itself must be electrochemically inert in the potential window of the iron flow battery. Finally, the iron-ligand complex must maintain the fast, reversible electrokinetics of the Fe(II/III) redox couple, and have an open circuit potential the same or greater than that of the uncomplexed Fe(II/III) reaction.

1.2.4 Deposition Reaction Electrode Structures

One of the most common examples of a hybrid flow battery negative electrode involves the Zn²⁺/Zn⁰ couple (10, 12, 28), usually with a bromide or chloride positive electrode, though other redox couples such as cerium (29) have been proposed. The simplest negative electrode design for a zinc flow battery is a flat plate electrode structure, where the zinc plates and strips on a second metal substrate (12, 29, 30). The boundary layer on a flat plate in laminar flow is relatively thick (about 85 µm at 2.5 cm/s), meaning the limiting current density is low (≈ 65 mA/cm² for 1 M reactant concentration and n = 1). Consequently, current densities reported in the literature on flat
plate electrode designs are often between 15 mA/cm$^2$ (12) and 45 mA/cm$^2$ (11). Cheng, et al. (30) compared a flat plate with a three dimensional nickel foam electrode for use in a Zn-Ni flow battery, and were able to operate at 80 mA/cm$^2$ with a round trip energy efficiency of 80%. A flow cell with the nickel foam electrode structure cycled at a lower overpotential than one with the flat plate electrode at high current densities, and a similar performance as the flat plate electrode at low current densities (Figure 1-7). The cell with the nickel foam electrode structure was cycled for over 200 cycles, higher than previously reported for Zn-Ni cells with a flat plate electrode structure.

![Figure 1-7. Charge-discharge curves of a Zn-Ni flow battery at varied current densities for a nickel foam electrode structure (NF, solid line), and a nickel sheet electrode structure (NS, dashed line), as reported by Cheng, et al. (30).](image)

More recently, a soluble lead-acid chemistry (using lead (II) methanesulfonate as the dissolved species) has been considered for use in a flow battery configuration, with Pb(0)/Pb(II) as the negative electrode and Pb(II)/PbO$_2$ as the positive electrode (31). Both
reactions in this case involve deposition of solid materials in the battery stack from a liquid electrolyte. Soluble lead-acid battery operation has been reported at currents between 10 and 60 mA/cm$^2$ using a flat Ni plate electrode structure, and demonstrated charge/discharge behavior similar to a traditional lead-acid battery (32, 33). Cell performance at currents between 10 and 100 mA/cm$^2$, using a reticulated vitreous carbon electrode structure, has also been reported for the soluble lead chemistry with round trip energy efficiencies of up to 70 % (31).

Use of a three dimensional electrode structure in Zn and Pb flow cells increased the operating current densities. It should be possible to apply similar designs to an all-iron flow battery. In the literature, an all-iron flow battery was reported having a flat plate negative electrode operating at 60 mA/cm$^2$ and a current efficiency of 90 % (9). In designing an electrode structure, the limiting current density and the void fraction are both of concern. Hybrid flow batteries are also limited by the amount of metal that can be deposited into the electrode structure, thus controlling the amount of discharge time at power available. For example, an economic current density might be 100 mA/cm$^2$, and a typical plating density might be 200 mAh/cm$^2$, thus resulting in a two hour discharge. Employing a three dimensional porous electrode instead of a flat plate will increase active surface area and apparent mass transport rates, thus increasing the limiting current density. In addition, three-dimensional electrodes may also increase the effective plating density that can be obtained.

1.2.5 Iron Plating Kinetics

The iron deposition and dissolution reactions are also of interest. The plating density limits the energy storage capacity of the battery (5, 34), and the main source of
loss occurs at the negative electrode, in the form of hydrogen evolution (9). As hydrogen evolves, the pH of the electrolyte will increase, causing precipitation of the reactants and decreasing the lifetime of the iron flow battery. Additionally, the kinetics of iron plating will depend on the pH of the electrolyte and the pH at the electrode surface (16, 35). In Figure 1-8, polarization curves of iron deposition are reported in electrolytes of varying pH. Curves 1, 2, and 3 (at pHs below 3) in Figure 1-8 are linear. At pHs greater than 3, a shift in the polarization behavior is observed. Curves 4, 5, and 6 in Figure 1-8 show a distinct increase in current around -800 mV, with relatively linear regions on either side of the increase. Two separate mechanisms for iron deposition are supported by the separate polarization behavior, dependent on the electrolyte pH. Hilbert, et al., report the electrochemical reaction order as a function of the electrolyte pH (Figure 1-9). Two separate reaction orders are observed, further indicating that the iron deposition mechanism changes as the electrolyte pH is raised.

Figure 1-8. Polarization curves for iron deposition on a platinum RDE in electrolytes of varying pH, as reported by El Miligy, et al. (35).
Figure 1-9. Electrochemical reaction orders of iron deposition at as a function of pH. As reported by Hilbert, et al. (16).

Increasing the pH of the electrolyte was suggested in section 1.2.2 as a method for mitigating the hydrogen evolution, although the ferric ion solubility is an issue at raised pHs. As discussed in section 1.2.3, addition of a complexing ligand to the electrolyte can increase the solubility of the ferric ions at higher pHs, provided the ferric/ferrous redox kinetics are not significantly altered (23). Even if the ligand is only added to the positive electrolyte, crossover will occur throughout the life of the battery and the ligand will eventually appear in the negative electrolyte as well. In the interest of mitigating crossover effects, a single electrolyte composition is desired (36).

It is likely that ligands will affect the iron plating reaction (37, 38). The ferric-citrate complex can exist at pHs greater than 5, though the Fe$^{2+/3+}$ redox reaction potential is shifted negative by about 600 mV (39). When the plating reaction with citrate was studied, it was found that the open circuit potential for the Fe$^{2+/0}$ reaction was shifted
about 400 mV more negative (37). Plating from an iron(II)-EDTA complex did not shift the plating potential negatively; however the EDTA is electrochemically reduced at about 300 mV more positive than the iron plating (38).

Another avenue of preventing hydrogen evolution is through selecting an appropriate supporting electrolyte. Corrosion literature on iron dissolution has investigated the effect of anions on the kinetics of iron corrosion (40, 41). At low overpotential, iron dissolution proceeds through the adsorption of water on the surface and the formation of Fe(OH)_{ads}, which desorbs into solution. At high overpotential, the dissolution reaction is catalyzed by Fe(OH)_{ads} forming Fe(FeOH), then proceeding to Fe^{2+}\text{aq}. The mechanism at a given overpotential depends both on the chloride concentration and pH of the electrolyte (42). The mechanism of iron plating in the presence of halide ions is less well studied, though plating from sulfate containing electrolytes is well established (16, 35, 43). Iron plating most likely occurs as a simple reversal of the iron dissolution reactions (16).

Two separate mechanisms for iron dissolution exist, one of which involves the direct participation of adsorbed chloride (42, 44, 45). The presence of specifically adsorbed halide ions was found to alter the mechanism by which iron corrodes (40). Iron and the adsorbed chloride form FeCl^{-}\text{ads}, which then reacts with water to form Fe(ClH^{+})_{ads} and then becomes FeCl^{+}\text{aq}. Addition of a low concentration of halide ions (2 mM) to a sulfuric acid electrolyte inhibited corrosion of steel through adsorption of the halide ions on the metal surface (46). Adsorption of both chloride and sulfate ions is pH dependent (47) Also, chloride adsorbs on the metal sites in a monolayer while sulfate adsorbs on metal oxide sites with less than a monolayer surface coverage (47, 48). At high
overpotentials, increasing the chloride concentration lowered the hydrogen evolution current, due to increased surface coverage of chloride and decreased surface coverage of proton (49). A similar decrease in hydrogen evolution has been observed using other halide ions (50). The concentration of halide ions in electrolyte was shown to affect the dissolution kinetics, with iodide being the most inhibiting at concentrations of 5 mM I\(^{-}\) (41). Altering the anion species and its concentration in the supporting electrolyte of an iron flow battery may lower the hydrogen evolution occurring and increase the plating efficiency.

The thesis structure is as follows:

- In Chapter 2, the experimental methodologies for this work are described.
- In Chapter 3, electrokinetics of the ferric/ferrous redox couple and the effect of complexing ligands on the electrokinetics are examined.
- In Chapter 4, a method for evaluating redox electrokinetics on flow battery electrodes is evaluated. This method is based on thin film rotating disk electrode techniques used in the analysis of fuel cell electrocatalysts.
- In Chapter 5, three dimensional porous electrode structures are described for use in the iron plating electrode. A plating capacity of 150 mAh/cm\(^{2}\) is demonstrated in two porous electrode structures.
- In Chapter 6, the effect of the supporting electrolyte composition and complexing ligands on the iron plating/stripping reaction is analyzed. Cycling behavior of an all-iron flow cell is also described.
2.1 Iron-Ligand Electrokinetics

2.1.1 Materials and Reagents

All chemicals were of reagent grade. Dimethyl sulfoxide (DMSO), hydrochloric acid, glycerol, sodium chloride, sodium hydroxide, and trisodium citrate were obtained from Fisher Scientific (Waltham, MA). Ferrous chloride hydrate, ferric chloride hydrate, glycine, malic acid, malonic acid, and xylitol were obtained from Alfa Aesar (Ward Hill, MA).

2.1.2 Solubility and pH Experiments

Solutions were prepared by dissolving 0.1 M FeCl$_3$ in deionized water, then dissolving 0.3 M of the intended ligand in the solution. A concentrated NaOH solution was slowly dripped into the solution under constant mixing to adjust the pH. The pH was continually measured with a pH meter. Precipitation was observed qualitatively while adding the NaOH solution.

Subsequent experiments with glycine were performed by dissolving a specified concentration of glycine, from 0.1 M to 0.9 M in deionized water, and the corresponding FeCl$_3$ or FeCl$_2$ concentration, so the sum of the iron and glycine concentrations was 1 M. In experiments with both ferric and ferrous chlorides, the desired iron concentration was split into equimolar amounts of ferric and ferrous ions (so a 0.05 M solution of glycine...
would contain 0.05 M total iron, which is 0.025 M of Fe$^{2+}$ and 0.025 M of Fe$^{3+}$). The pH was then measured for each solution under constant mixing.

2.1.3 Electrochemical Experiments

Half-cell experiments were performed on a glassy carbon rotating disk electrode (Pine Instruments, Grove City, PA, area = 0.196 cm$^2$), with a platinum mesh counter electrode and Ag/AgCl reference electrode (BASI, West Lafayette, IN). The glassy carbon RDE was polished using 1 µm and then 0.05 µm alumina micropolish and polishing pads (Buehler, Lake Bluff, IL), then sonicated in D.I. water for one minute. Electrolytes were prepared with 1 M NaCl, 0.1 M FeCl$_2$, and 0.1 M FeCl$_3$, unless otherwise noted. Ligand concentrations were 0.8 M for the 4:1 ligand to iron electrolyte and 1.6 M for the 8:1 ligand to iron electrolyte, based on the total iron concentration (both ferrous and ferric). If the pH was adjusted, adjustment was done using concentrated solutions of either NaOH or HCl. The additional volume from adjusting the pH was accounted for, and concentrations were adjusted as appropriate. Polarization curves and electrochemical impedance spectroscopy measurements were done at 3000 rpm. Cyclic voltammetry was performed at 50 mV/s, unless otherwise stated. Limiting current values for Levich calculations were obtained at 200, 500, 1000, 1500, 2000, 2500, and 3000 rpm.

Symmetric cell experiments were performed in a 5 cm$^2$ redox flow battery cell. The graphite current collectors had a serpentine flow channel milled into them, and two pieces of carbon fiber paper (Fuel Cell Store, College Station, TX, Spectracarb 2050-L, 260µm thick) were placed on top of each current collector (Figure 2-1). The membrane
was Daramic (Daramic, Charlotte, NC, 175 SLI Flatsheet Membrane). All experiments were performed at a flow rate of 30 mL/min, unless otherwise noted. Electrolytes contained 1 M NaCl, 0.2 M FeCl₂, 0.2 M FeCl₃, and 2 M ligand, for a 5:1 ligand to total iron ratio, unless otherwise noted. Cell resistance was measured using Electrochemical Impedance Spectroscopy (EIS), from 20 kHz to 0.2 Hz, and taken to be the high frequency intercept of the Nyquist plot. Polarization curves were performed by holding a potential and measuring the steady state current.

**Figure 2-1.** Schematic drawing of a redox flow battery cell used in the symmetric cell experiments. Redrawn based on Figure 3 by Weber, *et al.* (10).

### 2.2 Fiber Mat Rotating Disk Electrodes

#### 2.2.1 Reagents

All chemicals were of reagent grade. Hydrochloric acid, sulfuric acid, and sodium chloride were obtained from Fisher Scientific (Waltham, MA). Ferrous chloride hydrate and ferric chloride hydrate were obtained from Alfa Aesar (Ward Hill, MA).
2.2.2 FMRDE Preparation

The fiber mat rotating disk electrodes (FMRDEs) were prepared using Graftech felt (Cleveland, OH) and glassy carbon rotating disk electrodes (active area 0.196 cm$^2$, obtained from Pine Instruments, Grove City, PA). The felt was separated through a combination of shearing and grinding. For the ink preparation, 5 mg of felt was added to a solution of 5 wt % Nafion® solution, obtained from Sigma-Aldrich (St. Louis, MO). The amount of Nafion solution in the ink was varied from 1.7 mL to 2.3 mL in order to obtain different fiber concentrations in the ink. The solution was sonicated for 5 minutes, after which an aliquot of the ink was pipetted onto the glassy carbon RDE and allowed to dry overnight in air. The aliquot varied in volume from 12 µL to 20 µL, in order to vary the fiber loading on the electrode. Figure 2-2 depicts the process of FMRDE preparation.

**Figure 2-2.** Preparation of a FMRDE. A known concentration of fibers is suspended in a Nafion® solution and ultrasonicated to ensure an even suspension. A known volume is then deposited on a glassy carbon rotating disk electrode and dried in air. If needed, an additional drop of Nafion solution is placed over the thin film to ensure adhesion.
2.2.3 Electrochemical Measurements

Half-cell experiments were performed on a glassy carbon rotating disk electrode (Pine Instruments, Grove City, PA, area = 0.196 cm²), with a platinum mesh counter electrode and Ag/AgCl reference electrode (BASi, West Lafayette, IN). The glassy carbon RDE was polished using 1 µm and then 0.05 µm alumina micropolish and polishing pads (Buehler, Lake Bluff, IL), then sonicated in D.I. water for one minute. Cyclic voltammetry on all FMRDEs was performed in 1 M H₂SO₄ at 20 mV/s to ensure good contact between the fibers and the electrode. Cyclic voltammetry was also performed in a 0.1 M FeCl₂, 0.1 M FeCl₃, and 1 M NaCl electrolyte at 10 mV/s.

Limiting current data was taken in an electrolyte containing 0.01 M FeCl₂, 0.01 M FeCl₃, and 1 M NaCl at rotation rates of 200, 400, 600, 800, and 1000 rpm. The potential was swept at 5 mV/s to obtain an accurate limiting current.

Pulse voltammetry was performed in two different electrolytes: 0.01 M FeCl₂, 0.01 M FeCl₃, and 1 M NaCl; and 0.05 M FeCl₂, 0.05 M FeCl₃, and 1 M NaCl. Pulse voltammetry was taken at pulse times of 500, 250, and 100 ms. High frequency resistances from EIS measurements were used to IR correct pulse voltammetry data. Mass transfer overpotential was corrected for using an experimentally determined limiting current.

2.3 Negative Electrode Structure

2.3.1 Materials and Reagents

All chemicals were of reagent grade. H₂SO₄, HNO₃, CuSO₄, Na₂SO₄, and methanol were obtained from Fisher Scientific (Waltham, MA). FeSO₄ was obtained
from Acros Organics (Geel, Belgium). FeCl$_2$, FeCl$_3$, NH$_4$Cl, and glycerol were obtained from Alfa Aesar (Ward Hill, MA). All electrolytes were made with deionized water (Millipore MilliQ-UV Plus).

For the flow battery experiments, carbon felt was obtained from GrafTech (Cleveland, OH) in 4 mm and 2 mm thicknesses. Carbon cloth (AvCarb Grade – 1071HCB, 380 µm thickness) and carbon paper (Spectracarb 2050-L, 260 µm thick) were obtained from the Fuel Cell Store (College Station, TX). Carbon cloth and carbon felt materials were all pre-treated with nitric acid (51) to improve wettability. The felt or cloth was soaked in 1M HNO$_3$ for one hour and then rinsed with deionized water until the pH of the rinse water reached 6. The non-conducting (non-electrically conductive) felt used was a polyester filter felt with a 5 µm pore diameter and 2 mm thickness (#6376T31, McMaster-Carr, Aurora, OH). A 220 µm thick Daramic (175 SLI Flatsheet Membrane) separator material was obtained from Daramic (Charlotte, NC). Nafion 117 (Proton Power, Lenoir City, TN) was also used as a separator. Conductive carbon ink (Electrodag 421 SS) was obtained from Acheson (owned by Henkel, Dusseldorf, Germany). Unless otherwise stated, all experiments with flow battery hardware used graphite flow fields (38.5 cm$^2$ active area) obtained from TDM Inc. (Ashtabula, OH).

2.3.2 Bonding Procedure

Some of the carbon felts and non-conducting felts were bonded to the graphite flow fields used in the flow batteries to improve the interfacial electrical conductivity. Bonding was done by applying a thin layer of conductive carbon ink to the flow field,
gently pressing the desired felt or cloth into the wet ink, and then curing at 70 °C for 30 minutes in air.

2.3.3 Rotating Cylinder Electrode

Rotating cylinder experiments were performed using a copper rod (99.9 % pure, 5 mm diameter, Alfa Aesar, Ward Hill, MA) masked to a 1 cm² active area. Any surface oxides were removed from the copper surface by soaking the rod in 1 M H₂SO₄ overnight before use. Bonded non-conducting felt rotating rod experiments were performed by bonding a piece of the non-conducting felt over the active area (Figure 2-3). The non-conducting felt was cut to 150 % of the active area, overhanging the exposed copper by 1.5 mm on each side to prevent preferential plating due to any exposed conductive ink. Experiments were performed in 0.2 M FeCl₂ and 1 M NH₄Cl, with an iron rod counter electrode (99.9 % pure, 5 mm diameter, Alfa Aesar, Ward Hill, MA) and a Ag/AgCl reference electrode (BASi, West Lafayette, IN). The cell was purged with nitrogen for the duration of the experiments, and the electrode was rotated at 1500 rpm for both cyclic voltammetry and constant plating experiments. Cyclic voltammetry was performed at 50 mV/s on a fresh electrode, after deposition of 20 mAh/cm² of iron, and after deposition of 480 mAh/cm² of iron. Iron was deposited at -20 mA/cm² to obtain the targeted plating density. All electrochemistry was performed on a Solartron Analytical Modulab 2101A Potentiostat (Farnborough, Hampshire, United Kingdom).
Figure 2-3. Bonded non-conducting felt rotating rod electrode. The active area of the copper rod is defined using Kapton tape, and the non-conducting felt is bonded to the active area using the conductive carbon ink.

2.3.4 Symmetric Cells

Four 38.5 cm$^2$ flow battery cells were run as symmetric Fe$^{2+/3+}$ redox cells. A single reservoir of electrolyte was used, consisting of 0.2 M FeCl$_2$, 0.2 M FeCl$_3$, and 1 M NaCl. The electrolyte was controlled at 50 mL/min in series through the anode (working electrode) and cathode (counter electrode) of the cell. One electrode oxidizes Fe$^{2+}$ to Fe$^{3+}$, the other electrode reduces Fe$^{3+}$ to Fe$^{2+}$. Since a single reservoir is used, there is no change in the concentration of either species. Flow cell hardware consisting of CPVC end plates, graphite flow fields, and a Daramic separator with a 38.5 cm$^2$ area was used in a flow-through configuration (52). The flow fields included an inlet and outlet header 100 µm deep. Four electrode structures were tested in the symmetric cells: A, bonded carbon felt; B, non-bonded carbon felt; C, bonded non-conducting felt; and D, non-bonded non-conducting felt. The electrode structure on each side of the battery was the same. Electrochemical Impedance Spectroscopy (EIS) was performed on each cell around the open circuit potential with a ±10 mV perturbation, from 20,000 Hz to 0.2 Hz.
2.3.5 Flow-by Flow Battery Experiments

An initial flow battery experiment was performed in 5 cm$^2$ serpentine hardware (Fuel Cell Technologies, Albuquerque, NM) (10). Both the positive and negative electrodes consisted of two pieces of carbon paper, and the cell had a Nafion 117 membrane. The flow rate was controlled at 50 mL/min. The same electrolyte composition was used on both the positive and negative side of the battery, consisting of 1 M FeSO$_4$, 1 M CuSO$_4$, and 1 M Na$_2$SO$_4$, with the pH adjusted to 1 by addition of H$_2$SO$_4$. The cell was charged at 40 mA/cm$^2$ for 110 min.

2.3.6 Cu Sulfate Flow Battery Experiments

Cu-sulfate flow battery experiments were performed in the 38.5 cm$^2$ flow-through cell hardware with a Nafion 117 membrane. All experiments were performed with electrolyte flow rates of 50 mL/min. The Cu-Fe sulfate positive electrolyte contained 500 mL of 1 M FeSO$_4$ and 1 M Na$_2$SO$_4$, adjusted to a pH of 1 with H$_2$SO$_4$. For the positive electrode, a piece of carbon felt was treated using nitric acid as previously stated, and bonded to the graphite flow field. Before use, the carbon felt was wetted using methanol for 10 minutes, which was then exchanged with deionized water. The negative electrolyte consisted of 250 mL of 1 M CuSO$_4$ and 1 M Na$_2$SO$_4$, adjusted to a pH of 1 with H$_2$SO$_4$. Six negative electrode configurations were tested, as outlined in Figure 2-4. Electrodes with a single piece of carbon felt used the 4 mm thick felt. Electrodes with multiple layers containing carbon felt used the 2 mm thick felt. All carbon felts and cloths used in the negative electrodes were treated with nitric acid and wetted with methanol, as with the positive electrode. Bonding was performed using the same method as described for
the positive electrode (both for carbon felts/cloths and the non-conducting felts). Layers in the negative electrodes were not bonded to each other, rather the battery relied on compression (to 80 % of the initial electrode thickness) to maintain contact.

Figure 2-4. Electrode structures tested in the Cu-Fe sulfate battery. Structures A-C were also tested in symmetric cells, with a separate naming convention (the third structure tested in symmetric cells, non-bonded non-conducting felt, is not shown). Structures E and F were also tested in all-Fe batteries.

Unless otherwise noted, all batteries were charged at 40 mA/cm² for 3.75 hours, for a total plating density of 150 mAh/cm². Electrochemical Impedance Spectroscopy
was performed after the initial charge at the open circuit potential with a ± 10 mV perturbation, from 20,000 Hz to 0.2 Hz.

2.3.7 All-Iron Flow Battery Experiments

All-iron flow battery experiments were performed in the 38.5 cm² flow-through cell hardware with a Nafion 117 membrane. The flow fields consisted of an inlet and outlet header 100 µm deep, and the electrodes were in a flow-through configuration (52). All experiments were performed at 50 mL/min. Additionally, the all-Fe batteries were run at 60 °C instead of room temperature. Electrolyte for both the positive and negative electrodes consisted of 1.5M FeCl₂, 1.5 M NH₄Cl, and 2.5 M glycerol used as a complexing agent for maintaining Fe(III) solubility (21, 24). In the positive electrolyte, 0.5 M FeCl₃ was added for stability of the ferric/ferrous redox couple potential. The positive electrode was prepared in the same manner as for the Cu-Fe sulfate batteries, by bonding a piece of nitric acid treated carbon felt to the flow field, wetting with methanol for 10 minutes, then exchanging the methanol with deionized water. Only two negative electrode configurations were tested in the all-Fe batteries, designated E and F in Figure 2.

All batteries were charged at 40 mA/cm² for 3.75 hours, for a total plating density of 150 mAh/cm². Electrochemical Impedance Spectroscopy was performed after the initial charge at the open circuit potential with ± 10 mV perturbations, from 20,000 Hz to 0.2 Hz. Charge-discharge cycling for the all-Fe batteries were performed at -40 mA/cm² for 30 minutes on discharge and +40 mA/cm² for 30 minutes on charge, with a total of 6 cycles.
2.4 Iron Plating Electrokinetics

2.4.1 Materials and Reagents

All chemicals were of reagent grade. NaCl, KCl, H$_2$SO$_4$, (NH$_4$)$_2$SO$_4$, and HCl were obtained from Fisher Scientific (Waltham, MA). NH$_4$Cl, FeCl$_2$, glycerol, and glycine were obtained from Alfa Aesar (Ward Hill, MA). FeSO$_4$ was obtained from Acros Inorganic (Geel, Belgium). Copper rod (99.9 % pure, 5 mm diameter) and iron rod (99.9 % pure, 5 mm diameter) were obtained from Alfa Aesar (Ward Hill, MA). All half-cell electrochemical experiments were performed using a Ag/AgCl reference electrode (BASi, West Lafayette, IN) unless otherwise noted.

2.4.2 Electrochemical Experiments

Experiments were performed using a Solartron Modulab 2101A potentiostat, with a Ag/AgCl reference electrode and an iron rod counter electrode. Graphite and copper rods were both used as working electrodes. The rod was masked so a 1 cm$^2$ active area was exposed. The copper rod was soaked in 1 M H$_2$SO$_4$ overnight before use to ensure a clean electrode surface. All electrolytes were prepared under nitrogen, and the electrochemical cell was sealed and kept under nitrogen for the duration of the experiments. Cyclic voltammetry was performed at 50 mV/s unless otherwise noted. Experiments with the copper rod working electrode were never performed above -0.3 V vs. Ag/AgCl, so as to prevent any copper stripping.
2.4.3 Hydrogen Evolution Experiments

Hydrogen evolution experiments were performed on an iron rod masked to 1 cm$^2$ active area as the working electrode, a platinum mesh counter electrode, and a Ag/AgCl reference. The working electrode was held under potential control at -0.7 V vs. Ag/AgCl while being placed in the electrolyte to prevent any iron dissolution. Cyclic voltammetry was run at 25 mV/s, with the working electrode rotated at 400 rpm to prevent any hydrogen bubbles adhering to the electrode surface.

2.4.4 Plating Efficiency Experiments

Plating efficiency experiments were performed using a copper rod masked to 1 cm$^2$ active area as the working electrode, an iron rod counter electrode, and a Ag/AgCl reference. A given plating potential was held for 5 min, then the rod was stripped at -0.35 V vs. Ag/AgCl for 5 min. Charge during deposition versus charge during metal stripping was used to calculate coulombic efficiency. The iron was completely stripped between consecutive experiments in order to ensure accuracy of the metal plate density estimate.

2.4.5 Iron Flow Battery Experiments

Iron flow battery experiments were performed in a 38.5 cm$^2$ flow cell with a Nafion 117 (Proton Power, Lenoir City, TN) membrane. Carbon felt electrodes obtained from GrafTech (4 mm thick, Cleveland, OH) were treated using Fenton’s reagent for 1 hour, then rinsed with deionized water before use. The positive electrode felt was bonded to the current collector using a conductive carbon ink (Electrodag 421 SS) obtained from Acheson (owned by Henkel, Dusseldorf, Germany) to improve electrode contact, as
described in Section 2.3.2. Before cell assembly, the positive electrode was soaked in methanol for 10 min, then rinsed with deionized water to ensure wetting of the felt. Cells were charged at 40 mA/cm$^2$ for 3.75 hr. Cycling was performed at -40 mA/cm$^2$ for 0.5 hr and +40 mA/cm$^2$ for 0.5 hr.
3.1 Background

Solubility of the ferric ion in electrolytes at the pHs required for the iron flow battery (FeFB) is low. To prevent precipitation of the ferric ion as Fe(OH)$_3$, complexing ligands were investigated for use in the FeFB electrolyte. Chemically, there are several criteria that the ligand must meet. To be effective in a FeFB, the desired energy storage capacity of flow batteries necessitates a high solubility of the iron-ligand complex. The iron-ligand complex may have a different solubility than either the ferric ions or the ligands separately. An iron-ligand solubility of at least 1 M will be comparable to the solubility of other flow battery chemistries. The complex must also be soluble at pHs around three (the pH needed to minimize H$_2$ evolution on the negative electrode). Additionally, the ligand itself must be electrochemically inert in the potential window of the FeFB. Finally, the iron-ligand complex must maintain the fast, reversible electrokinetcs of the Fe(II/III) redox couple, and have an open circuit potential the same or greater than that of the Fe(II/III) reaction. These criteria and the metrics used to quantify them are outlined in Table 3-1. Seven ligands were identified that met most of the metrics: citrate, dimethyl sulfoxide (DMSO), glycerol, glycine, malic acid, malonic acid, and xylitol.
Table 3-1. Criteria for Ligand Selection

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Metric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron-ligand solubility</td>
<td>Greater than 1 M</td>
</tr>
<tr>
<td>pH effect on complex</td>
<td>Soluble up to pH 3</td>
</tr>
<tr>
<td>Electrochemically inactive</td>
<td>No oxidation or reduction of ligand (neat in supporting electrolyte)</td>
</tr>
<tr>
<td>No effect on Iron II/III kinetics</td>
<td>$E^\circ &gt; 0.44$ vs. Ag/AgCl</td>
</tr>
<tr>
<td></td>
<td>Symmetrical CV</td>
</tr>
<tr>
<td></td>
<td>High $i_o$ (similar to ferric/ferrous couple in acidic media)</td>
</tr>
</tbody>
</table>

Figure 3-1. Proposed structures for iron-ligand complexes for a) citrate (53), b) DMSO (54), c) glycine (55), d) malic acid (56), and e) malonic acid (57). No structures were found in the literature for glycerol or xylitol.
Of these seven ligands, six contain a carbon chain of 2 to 4 carbons, and carboxylic acid or alcohol groups. Literature reports structures of the iron-ligand complexes for citrate, DMSO, glycine, malic acid, and malonic acid, illustrated in Figure 3-1 (53-57). A ligand may bind the iron at several sites, as in the citrate-iron structure, or it may bind to several different iron ions creating a polymer-like chain, as in the malic acid structure. The complex structure is also affected by pH and electrolyte composition, such as the presence of acid or other salts. The structure will of course play an important role in the properties of the iron-ligand complex, but a thorough structural investigation is beyond the scope of this research.

3.2 Kinetics on a Rotating Disk Electrode

The iron-ligand complexes in Figure 3-1, along with iron-glycerol and iron-xylitol, were evaluated for their effect on the electrokinetics of the ferric/ferrous redox couple through cyclic voltammetry (an example is shown in Figure 3-2). The exchange current densities were estimated in the Tafel region of polarization curves. Though not reported, exchange current densities were also estimated from the EIS charge transfer resistance, and were in good agreement with those estimated from the Tafel region of the polarization curves. Open circuit potentials were estimated from the cyclic voltammetry as the midpoint potential between the oxidation and reduction peaks. The kinetic measurements were performed both at the natural pH of the electrolyte (no adjustment), and at a pH of about 2.5, adjusted with the addition of NaOH. In the case of citrate and glycine, the natural pH of the electrolyte is already above 2.5 (5.25 and 2.85, respectively), so the adjusted pH electrolytes were achieved by the addition of HCl. The
**Figure 3-2.** Cyclic voltammetry of the 4:1 ligand to iron complexes, as compared to a ferric/ferrous only electrolyte, in Fe-DMSO and Fe-Xylitol. All electrolytes consisted of 0.1 M FeCl$_2$, 0.1 M FeCl$_3$, and 1 M NaCl. Electrolytes with a ligand contained 0.8 M of the specified ligand. Cyclic voltammetries for the remaining ligands are reported in Appendix A.

**Table 3-2.** Calculated kinetic parameters for the iron-ligand complexes on a glassy carbon RDE

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Fe ratio</th>
<th>pH</th>
<th>$E_{pp}$ (mV) vs. Ag/AgCl</th>
<th>$i_o$ (mA/cm$^2$)</th>
<th>Natural pH</th>
<th>$E_{pp}$ (mV) vs. Ag/AgCl</th>
<th>$i_o$ (mA/cm$^2$)</th>
<th>pH Adjusted</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>--</td>
<td>1.71</td>
<td>269</td>
<td>498</td>
<td>2.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Citrate</td>
<td>4:1</td>
<td>5.25</td>
<td>426</td>
<td>-239</td>
<td>0.9</td>
<td>2.5</td>
<td>451</td>
<td>-27</td>
</tr>
<tr>
<td>DMSO</td>
<td>4:1</td>
<td>1.78</td>
<td>239</td>
<td>481</td>
<td>1.2</td>
<td>2.2</td>
<td>274</td>
<td>485</td>
</tr>
<tr>
<td>Glycerol</td>
<td>4:1</td>
<td>1.5</td>
<td>292</td>
<td>491</td>
<td>0.8</td>
<td>2.4</td>
<td>308</td>
<td>507</td>
</tr>
<tr>
<td>Glycine</td>
<td>4:1</td>
<td>2.85</td>
<td>548</td>
<td>317</td>
<td>0.2</td>
<td>2.5</td>
<td>462</td>
<td>366</td>
</tr>
<tr>
<td>Malic Acid</td>
<td>4:1</td>
<td>0.67</td>
<td>579</td>
<td>502</td>
<td>0.4</td>
<td>2.6</td>
<td>457</td>
<td>-31</td>
</tr>
<tr>
<td>Malonic Acid</td>
<td>4:1</td>
<td>0.73</td>
<td>358</td>
<td>458</td>
<td>0.9</td>
<td>2.5</td>
<td>640</td>
<td>160</td>
</tr>
<tr>
<td>Xylitol</td>
<td>4:1</td>
<td>1.67</td>
<td>308</td>
<td>498</td>
<td>1.3</td>
<td>2.3</td>
<td>435</td>
<td>500</td>
</tr>
</tbody>
</table>
data calculated from the cyclic voltammetry and polarization curves (natural and adjusted pH, exchange current densities, equilibrium potentials, and peak to peak separation) is summarized in Table 3-2.

The exchange current density measured for an equimolar (0.1 M Fe$^{2+}$ and 0.1 M Fe$^{3+}$) iron only electrolyte (no ligand present) was found to be 2.3 mA/cm$^2$. Literature reports an exchange current density of 4 mA/cm$^2$ on a pyrolytic graphite electrode, at a concentration of 0.094N ferric and 0.06N ferrous chloride (58). Considering the differences in measurement conditions, these exchanges current densities are in good agreement. All of the ligands lower the value of the exchange current density, which appears to be independent of the natural pH of the solutions. In most cases, adjusting the pH further lowers the exchange current density (malic acid and malonic acid were unmeasurable at adjusted pHs due to significant depression of the reaction rate). Glycine, however, seems to slightly increase the rates of reaction when the pH is adjusted: an $i_0$ from 0.2 mA/cm$^2$ at natural pH (2.85) to 0.4 mA/cm$^2$ at adjusted pH (2.5). Malic acid and malonic acid have similar OCVs as the others above at natural pHs, however they shift negative when the pH is adjusted to 2.5 (to -0.031 V and 0.160 V vs. Ag/AgCl, respectively). Citrate shifts the equilibrium potential very negative, to -0.239 V vs. Ag/AgCl, even at its natural pH (pH=5.25), ruling out citrate as a viable choice for a ligand for the positive electrode of the all iron flow battery.
Figure 3-3. Exchange current densities as a function of the complex molecular weight for electrolytes containing 0.1M FeCl₂, 0.1M FeCl₃, 1M NaCl, and 0.8M Ligand. Adjusted pH electrolytes were adjusted to pH 2.5 with NaOH. Citrate and glycine electrolyte pHs were adjusted with HCl.

The electrokinetics of the iron-ligand complexes may depend on factors such as the size of the complex, the number of ligands bonded to each ion, the polarity of the ligand, the pKₐ of the ligand, etc. In Figure 3-3 the exchange current density is plotted as a function of the molecular weight of the iron-ligand complex, both at natural pHs and at pH 2.5. Here, the complex molecular weight was taken to be the iron molecular weight plus the molecular weight of the ligands in the complex, based on the number of ligands reported in the literature (Figure 3-1). As no literature was found for the glycerol or the xylitol complexes, they were assumed to bind in a 2:1 ligand to iron ratio for the present purpose. It would be intuitive that the exchange current density will decrease with increasing complex size, due to the increased shielding of the cation by the relatively
large ligands (59). At natural pHs, the exchange current density actually increases with increasing complex size (Figure 3-3). At pHs adjusted to 2.5, the exchange current density is relatively independent of complex size.

Figure 3-4. Peak separation as a function of the ligand pKₐ, at both natural and adjusted pHs. Calculated from cyclic voltammetry in a 0.1M FeCl₂, 0.1M FeCl₃, 1M NaCl, and 0.8M Ligand electrolyte. Adjusted pH electrolytes were adjusted to pH 2.5 with NaOH. Citrate and glycine electrolyte pHs were adjusted with HCl.

As the pH plays some role in the electrokinetics, the pKₐ of the ligand may shed light on the how the ligand affects the electrokinetics. In this case, the peak separation (ΔEₚₚ) estimated from cyclic voltammetry was plotted as a function of the pKₐ of the ligand (Figure 3-4). The peak separation is a measure of the electrokinetics (peak separation decreases with increasing exchange current density). The peak separation decreases (and electrokinetics increase) with increasing pKₐ, both at natural and adjusted
pHs (the exchange current density also increased with increasing pK\textsubscript{a}, though the
correlation was not as strong as that of the peak separation).

A study by Yee, et al., reports the effect of ligands on the entropy difference
(\Delta S\textsubscript{0rc}) of redox couples (59), which can be used to estimate the rate constant of a redox
reaction using Marcus Theory (60). The literature reports that \Delta S\textsubscript{0rc} is highly dependent
on the ligands surrounding the cation, rather than the cation itself, and that even a single
substitution (such as a complex with five ammine groups and one aquo group, versus a
complex with six ammine groups) affects the interactions between the ligands and
surrounding water molecules, causing a change in the entropy difference. The study
reported by Yee, et al., uses a systematic substitution of ligands in order to understand the
effect on the solvent structuring and the \Delta S\textsubscript{0rc}. The iron-ligand complexes presented here
have too many variables (including size, functional groups, remaining aquo ligands in the
complex, pK\textsubscript{a}, etc.) to effectively understand why the reaction kinetics increase with the
complex size and with the pK\textsubscript{a} of the ligand. Further systematic study using Marcus
Theory as a basis, similar to that of Yee, et al., might provide for a deeper understanding
of the iron-ligand complexes.

3.3 Effect on Diffusion Coefficient

Complexing iron ions with ligands in solution will increase the size of the ion in
the electrolyte, as compared to the iron hydration shield in the absence of ligand. This in
turn could decrease the diffusion coefficient, which will increase mass transfer
overpotentials in the FeFB. Diffusion coefficients were experimentally estimated from
limiting current data (Appendix A) for both the ferrous and ferric ions at natural and
adjusted pHs (Table 3-3). In the absence of ligand, the ferric ion diffusion coefficient was estimated to be $4.8 \pm 0.2 \times 10^{-6}$ cm$^2$/s, which agrees with values found in the literature (between $3 \times 10^{-6}$ and $5.5 \times 10^{-6}$ cm$^2$/s (13)). The ferrous ion diffusion coefficient was estimated to be $5.7 \pm 0.2 \times 10^{-6}$ cm$^2$/s. Literature values have been reported at $1.1 \times 10^{-6}$ cm$^2$/s (61), somewhat lower than the experimentally estimated diffusion coefficient here, however the literature value is for FeSO$_4$ instead of FeCl$_2$.

### Table 3-3. Diffusion coefficients for the ferric and ferrous iron-ligand complexes

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ligand:Fe ratio</th>
<th>D Fe$^{2+}$ (cm$^2$/s)</th>
<th>D Fe$^{3+}$ (cm$^2$/s)</th>
<th>D Fe$^{2+}$ (cm$^2$/s)</th>
<th>D Fe$^{3+}$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>--</td>
<td>5.7E-06</td>
<td>4.8E-06</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Citrate</td>
<td>4:1</td>
<td>1.7E-06</td>
<td>1.4E-06</td>
<td>3.9E-06</td>
<td>2.8E-06</td>
</tr>
<tr>
<td>DMSO</td>
<td>4:1</td>
<td>4.4E-06</td>
<td>3.8E-06</td>
<td>4.2E-06</td>
<td>1.3E-08</td>
</tr>
<tr>
<td>Glycerol</td>
<td>4:1</td>
<td>4.0E-06</td>
<td>4.0E-06</td>
<td>4.8E-06</td>
<td>2.9E-06</td>
</tr>
<tr>
<td>Glycine</td>
<td>4:1</td>
<td>4.0E-06</td>
<td>2.3E-06</td>
<td>4.2E-09</td>
<td>1.9E-06</td>
</tr>
<tr>
<td>Malic Acid</td>
<td>4:1</td>
<td>3.6E-06</td>
<td>2.7E-06</td>
<td>3.2E-06</td>
<td>3.8E-06</td>
</tr>
<tr>
<td>Malonic Acid</td>
<td>4:1</td>
<td>4.3E-06</td>
<td>3.1E-06</td>
<td>3.2E-06</td>
<td>2.8E-07</td>
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<tr>
<td>Xylitol</td>
<td>4:1</td>
<td>2.8E-06</td>
<td>2.4E-06</td>
<td>3.2E-06</td>
<td>2.8E-07</td>
</tr>
</tbody>
</table>

At natural pHs, all of the ligands lower the diffusion coefficients for the ferrous and ferric ions (Table 3-3). The decrease in diffusion coefficient is mainly due to the formation of the iron-ligand complex, and not simply an increase in the electrolyte viscosity due to the added ligand. Glycerol is by far the most viscous of the ligands tested. At 0.8 M, an aqueous glycerol solution will have a viscosity of about 1.2 cp (62). By comparison, a 1 M NaCl solution (the supporting electrolyte used for these studies) has a viscosity of 1.1 cp (62). Based on these viscosities, a 10% decrease in the diffusion coefficient would be expected when glycerol is added to the electrolyte. All of the
diffusion coefficients calculated from ligand containing electrolytes are decreased from the iron only diffusion coefficients by more than 10%. Since the diffusion coefficient values estimated for the iron only electrolytes are comparable to literature values obtained without added salts, it can be inferred that the small increase in viscosity due to the added ligands is not the only contributing factor in the decrease of the diffusivity.

**Figure 3-5.** Calculated diffusion coefficients for the ferrous and ferric ions as a function of the molecular weight of the complex, in a 0.1M FeCl$_2$, 0.1M FeCl$_3$, 1M NaCl, and 0.8M Ligand electrolyte.

When the diffusion coefficient is plotted as a function of the complex molecular weight (Figure 3-5), a general trend of decreasing diffusion coefficient with increasing molecular weight is observed. The correlation between diffusion coefficient and molecular weight is not as strong as expected, however the molecular weight only roughly estimates the size of the iron-ligand complex in solution, and the charge of the complex is not taken into account. Citrate in particular depresses the diffusion
coefficients by 30%. When the pH was adjusted to 2.5, the diffusion coefficients for Fe(II)-citrate, Fe(III)-glycerol, and Fe(II)-malic acid could not be measured due to irreversibility in the electrokinetics. Fe-DMSO and Fe-malonic acid both showed a slight decrease in diffusion coefficient. Fe-glycine, however, showed an increase in the diffusion coefficient with adjusted pH for both the ferrous and ferric complex, suggesting glycine as a better choice for a flow battery electrolyte additive. The diffusion coefficients estimated from the adjusted pH electrolytes are shown in Figure 3-6 as a function of the complex molecular weight. The diffusion coefficients again decrease with increasing molecular weight, with some outlying points at low molecular weights and low diffusion coefficients.

Figure 3-6. Calculated diffusion coefficients for the ferrous and ferric ions with adjusted pH as a function of the molecular weight of the complex, in a 0.1M FeCl₂, 0.1M FeCl₃, 1M NaCl, and 0.8M Ligand electrolyte. Adjusted pH electrolytes were adjusted to pH 2.5 with NaOH. Citrate and glycine electrolyte pHs were adjusted with HCl.
3.4 Symmetric Cell Behavior

The results presented in section 3.1 and 3.2 assessed the iron-ligand properties on a glassy carbon electrode for ease of quantifiable evaluation. Previous literature has shown that there may be differences in performance of flow battery redox couples evaluated on a glassy carbon RDE as compared to evaluation in a flow battery configuration (63, 64). To assess the performance of the iron-ligand complexes in a flow battery, a symmetric cell configuration was used. The symmetric cell utilizes flow battery hardware with a single reservoir of electrolyte: the electrolyte flow is directed in series through the anode and then the cathode of the cell. Because the electrodes in this structure are porous (carbon paper), kinetic information cannot be calculated directly due to current distribution effects. However, relative information can still be obtained.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Fe$^{3+}$ Concentration (M)</th>
<th>Ligand Concentration (M)</th>
<th>pH</th>
<th>$R_{hf}$ (Ω-cm$^2$)</th>
<th>pH</th>
<th>$R_{hf}$ (Ω-cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.2</td>
<td>--</td>
<td>1.52</td>
<td>0.2</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Citrate</td>
<td>0.2</td>
<td>2</td>
<td>5.38</td>
<td>0.21</td>
<td>2.52</td>
<td>0.13</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.2</td>
<td>2</td>
<td>1.85</td>
<td>0.25</td>
<td>2.16</td>
<td>0.31</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.2</td>
<td>2</td>
<td>1.45</td>
<td>0.26</td>
<td>1.94</td>
<td>0.31</td>
</tr>
<tr>
<td>Glycine</td>
<td>0.2</td>
<td>2</td>
<td>3.09</td>
<td>0.22</td>
<td>2.51</td>
<td>0.17</td>
</tr>
<tr>
<td>Malic Acid</td>
<td>0.2</td>
<td>2</td>
<td>0.81</td>
<td>0.2</td>
<td>2.5</td>
<td>0.18</td>
</tr>
<tr>
<td>Malonic Acid</td>
<td>0.2</td>
<td>2</td>
<td>0.72</td>
<td>0.26</td>
<td>2.5</td>
<td>0.14</td>
</tr>
<tr>
<td>Xylitol</td>
<td>0.2</td>
<td>2</td>
<td>1.39</td>
<td>0.28</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

High frequency resistance values for the symmetric cells are small, on the order of 0.3 Ω*cm$^2$, as estimated from EIS (Table 3-4). This corresponds to an iR loss of 150 mV in overpotential at 500 mA/cm$^2$. Since a porous separator was used, the high frequency
resistance is determined by the electrolyte conductivity. Although the various ligands do affect the ionic conductivity, the proton concentration (as shown by the pH values) has a much stronger effect on the conductivity than the nature of the ligand.

![Graph showing polarization curves](image)

**Figure 3-7.** Membrane IR corrected polarization curves for the iron only, Fe-DMSO (natural pH 1.85), and Fe-glycine (pH corrected to 2.5) electrolytes in a symmetric cell configuration at a flow rate of 30 mL/min, with 0.2 M FeCl₂, 0.2 M FeCl₃, 1 M NaCl, and 2 M Ligand, when present.

Example iR corrected polarization curves for the iron only, the 5:1 Fe-DMSO, and the 5:1 Fe-glycine electrolytes are reported in Figure 3-7, corrected using the high frequency resistances in Table 3-4. The polarization curves for the symmetric cells are quite linear, even after IR correction, to current densities up to 0.7 A/cm² (a cell overpotential of 2 V). As the ferric/ferrous redox potential is at 0.77 V vs. NHE, a symmetric cell overpotential of 2 V approximately means a potential of 1.77 V vs. NHE on the anode and a potential of -0.23 V vs. NHE on the cathode. If the mass transfer and
activation overpotentials were significant, the polarization curves would not be linear at such high overpotentials, indicating an ohmically controlled current density in the flow cell.

A linear polarization curve at such high current densities combined with the small high frequency resistances suggest that a significant amount of iR loss exists for which the high frequency resistance does not account. Electrochemical impedance spectroscopy was performed on a cell with no ligand present at the open circuit potential, and also at 100 mA/cm² and 300 mA/cm² (Figure 3-8). The impedance around open circuit is typical: a slightly depressed semicircular charge transfer loop and a finite Warburg impedance. The impedance spectra around 100 mA/cm² and 300 mA/cm² have significantly depressed charge transfer loops, indicating a more distributed current throughout the electrode. In the Bode plot (Figure 3-8b), the charge transfer process is shifted to lower frequencies by an order of magnitude or more relative to the EIS measurement around the open circuit potential, consistent with a larger double layer capacitance. The distributed nature of the current is surmised to be part of the iR that cannot be estimated from the high frequency resistance, and therefore cannot be accounted for in an iR correction of a polarization curve. Although a mass transfer resistance is seen in the EIS even at open circuit, the linear polarization curve up to 700 mA/cm² suggests that the limiting current density is more than 1 A/cm². The mass transfer resistance is not negligible in the open circuit EIS, however it does not significantly increase at higher currents as might be expected, as seen in the EIS around 100 mA/cm² and 300 mA/cm². This again is consistent with a more distributed reaction at higher current density; more of the electrode’s surface area is involved at higher current
densities, so the apparent limiting current density also increases. Because the mass transfer and kinetic overpotentials are comparable as compared to the distributed ohmic overpotentials, the iron-ligand complexes that have reasonable exchange current densities and diffusion coefficients are promising for use in a flow battery. The open circuit potential is still a significant factor for battery’s power density and voltaic efficiency, and a ligand that shifts the OCP more than 100 mV negative would likely not be acceptable, even if its kinetic performance were excellent.

**Figure 3-8.** Electrochemical impedance spectroscopy (Nyquist plot, left, and Bode plot, right) of a symmetric cell containing 0.2 M FeCl$_2$, 0.2 M FeCl$_3$, and 1 M NaCl. EIS was taken at open circuit potential (black), at 100 mA/cm$^2$ (red), and at 300 mA/cm$^2$ (blue). Each spectrum is offset by 0.2 ohm in $Z''$ for clarity.

### 3.5 Glycine-Iron Complex

The results presented above suggest glycine to be the best candidate for an FeFB out of the seven ligands; therefore further studies of this system were carried out. The open circuit voltage of a 4:1 ratio of glycine to iron electrolyte was estimated to be 317 mV vs. Ag/AgCl (Table 3-2). If the amount of glycine is reduced from a 4:1 glycine to
Figure 3-9. Cyclic voltammetry on a glassy carbon electrode for the glycine-iron complex at varying ratios of glycine to iron for (—) iron only, (−−) 1:1 glycine to iron, and (−··) 4:1 glycine to iron. CVs were performed in an electrolyte of 0.1 M FeCl$_2$, 0.1 M FeCl$_3$, 1 M NaCl, and 0.2 M and 0.8 M glycine for the 1:1 and 4:1 electrolytes, respectively.

Iron ratio to a 1:1 glycine to iron ratio, the open circuit voltage shifts positive to 468 mV vs. Ag/AgCl, approaching the iron only OCV, and the peak heights of the cyclic voltammogram are higher than those in the 4:1 glycine to iron electrolyte (Figure 3-9). The pH of the 1:1 glycine to iron electrolyte is 2.05. When the pH is raised to 2.5, the open circuit voltage remains unchanged, and there is only a slight decrease in the peak heights of the CV (Figure 3-10). The pH and concentration of glycine clearly effect the Fe-glycine complex and its electrokinetics, though the interaction between the glycine and iron is not well understood. A better understanding of the relationship between the free iron ions, free glycine, and the iron-glycine complexes can be developed based on a
model of the equilibrium concentrations of the aqueous species in the system. Similar models have been employed in the literature to determine the equilibrium concentrations of iron-citrate complexes used in iron plating baths (37).

Figure 3-10. Cyclic voltammetry on a glassy carbon electrode for (—) iron only, (— –) 1:1 glycine to iron at natural pH, and (— ··) 1:1 glycine to iron at pH adjusted to 2.5. CVs were performed in an electrolyte of 0.1 M FeCl₂, 0.1 M FeCl₃, 1 M NaCl, and 0.2 M glycine (when present). The pH was adjusted with NaOH.

Table 3-5. Coordination constants for iron-glycine complexes

<table>
<thead>
<tr>
<th>Ion</th>
<th>Equilibrium</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>[H₆Gly]/[H⁺][Gly]</td>
<td>9.54</td>
</tr>
<tr>
<td>H⁺</td>
<td>[H₂Gly]/[H₆Gly][H⁺]</td>
<td>2.36</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>[FeGly]/[Fe²⁺][Gly]</td>
<td>3.83</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>[FeGly₂]/[Fe²⁺][Gly]²</td>
<td>7.65</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>[FeGly]/[Fe³⁺][Gly]</td>
<td>10</td>
</tr>
</tbody>
</table>
Literature values of coordination constants for both Fe(II)-glycine and Fe(III)-
glycine (65) are reported in Table 3-5. In addition, glycine (abbreviated gly) has the
ability to be in a positively charged state, a negatively charged state, or a neutral,
zwitterion state. Equations 3-1 and 3-2 represent the protonation and deprotonation of
glycine into its negative and positive states, respectively. Equation 3-3 represents the
three equilibrium states of glycine (negative, zwitterion, and positive). Coordination
constants for glycine and protons in the negatively charged state and positively charged
state (65) are also reported in Table 3-5. Literature reports the pKₐ value for Fe(II) as
6.93 (Equation 3-4) (66). The pKₐ for Fe(III) losing the first proton is 2.74 (Equation 73-
5, and for the second proton is 3.31 (Equation 3-6) (67).

\[
\begin{align*}
NH_2CH_2COOH & \leftrightarrow NH_2CH_2COO^- + H^+ \\
NH_2CH_2COOH + H^+ & \leftrightarrow H_3N^+CH_2COOH \\
NH_2CH_2COO^- & \leftrightarrow H_3N^+CH_2COO^- \leftrightarrow H_3N^+CH_2COOH \\
[Fe(H_2O)_6]^{2+} & \leftrightarrow [Fe(H_2O)_5(OH)]^+ + H^+ \\
[Fe(H_2O)_6]^{3+} & \leftrightarrow [Fe(H_2O)_5(OH)]^{2+} + H^+ \\
[Fe(H_2O)_5(OH)]^{2+} & \leftrightarrow [Fe(H_2O)_5(OH)_2]^+ + H^+
\end{align*}
\]
In addition, Fe(III) can also form a dimer in aqueous solutions, where the full equilibrium is

\[ 2[\text{Fe}(\text{H}_2\text{O})_6]^{3+} \leftrightarrow [\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2\text{Fe}(\text{H}_2\text{O})_4]^{4+} + 2\text{H}^+ \]  (3-7)

The pK\text{a} of the Fe(III) dimer is 2.91 (68). Using the coordination constants, as well as the pK\text{a} values for Fe(II) and Fe(III), a model of the pH as a function of iron and glycine concentration can be written, and used to determine an optimum concentration ratio of glycine to iron for flow battery operation (The Mathematica code used in development of the iron-glycine equilibrium model is presented in Appendix B).

It was assumed that only glycine in its negatively charged form can bond to iron ions. Chelation of metallic ions by carboxyl groups after the loss of the alcoholic hydroxyl proton is well established (53, 69). In addition, a structural investigation of the Fe(II)gly complex indicates that the amino group does not form a bond with the ferrous iron (55). Based on the pHs in question (between 1 and 4) and the pK\text{a} of glycine protonation, it was also assumed that all free glycine molecules were protonated at the ammonium group. The glycine-iron complexes were assumed to form in a 2:1 ratio (Figure 3-1c), with 4 aquo ligands in the remaining sites around the iron (55). Though a coordination constant was not reported in the literature for the 2:1 glycine to Fe(III) complex, the cyclic voltammetry in Figure 3-9 indicates that the 2:1 glycine to iron complexes more strongly than a 1:1 complex. The coordination constant for Fe(III)Gly\textsubscript{2} was assumed to be the same as that for the Fe(III)Gly compound found in literature. Fe\textsuperscript{3+} has a strong positive charge, so it was assumed that the Fe(III)gly complex can lose a proton with the same pK\text{a} as that of Fe(III) losing a proton. Equations 3-8 through 3-17 represent the equilibrium model and include eight equilibrium equations and three mass
balances. A preliminary calculation was done using all of the equilibriums for Fe(II), Fe(III), glycine, and their combinations. Based on the results of the preliminary calculation, it was determined that the protons due to Fe(II) losing a proton, Fe(III) losing a second proton, and Fe(II)Gly losing a proton were not significant, therefore those equilibria were ignored in subsequent calculations.

\[
    K_{\text{Gly}} = [\text{Gly}^-][H^+]/[\text{Gly}] \quad (3-8)
\]

\[
    K_{\text{Fe}^{3+},1} = [\text{Fe}^{3+}(H_2O)_5(OH)][H^+]/[\text{Fe}^{3+}(H_2O)_6] \quad (3-9)
\]

\[
    K_{\text{dif}e} = [\text{Fe}^{3+}(H_2O)_4(OH)_{2}\text{Fe}^{3+}(H_2O)_4][H^+]^2/[\text{Fe}^{3+}(H_2O)_6]^2 \quad (3-10)
\]

\[
    K_{\text{Fe}^{3+}\text{Gly}} = [\text{Fe}^{3+}\text{Gly}_2]/[\text{Fe}^{3+}][\text{Gly}^-]^2 \quad (3-11)
\]

\[
    K_{\text{Fe}^{2+}\text{Gly}_2} = [\text{Fe}^{2+}\text{Gly}_2]/[\text{Fe}^{2+}][\text{Gly}^-]^2 \quad (3-12)
\]

\[
    K_{\text{Fe}^{3+}\text{Gly}} = [\text{Fe}^{3+}\text{Gly}_2(OH)][H^+]/[\text{Fe}^{3+}\text{Gly}_2] \quad (3-13)
\]

\[
    \text{Fe(III)_{Total}} = [\text{Fe}^{3+}\text{Gly}_2(OH)] + [\text{Fe}^{3+}\text{Gly}_2] + [\text{Fe}^{3+}(H_2O)_6] + \\
    [\text{Fe}^{3+}(H_2O)_5(OH)] + 2[\text{Fe}^{3+}(H_2O)_4(OH)_{2}\text{Fe}^{3+}(H_2O)_4] \quad (3-14)
\]

\[
    \text{Fe(II)_{Total}} = [\text{Fe}^{2+}\text{Gly}_2] + [\text{Fe}^{2+}(H_2O)_6] \quad (3-15)
\]
\[
Gly_{\text{Total}} = 2[Fe^{3+}Gly_2(OH)] + 2[Fe^{3+}Gly_2] + 2[Fe^{2+}Gly_2] + [Gly^-] + [Gly] \tag{3-16}
\]

\[
H^+_{\text{Total}} = [Fe^{3+}Gly_2(OH)] + [Gly^-] + [Fe^{3+}(H_2O)_5(OH)] + 2[Fe^{3+}(H_2O)_4(OH)_2Fe^{3+}(H_2O)_4] - ([Gly] + [Gly^-]) \tag{3-17}
\]

The pH of solutions containing equimolar Fe(II) and Fe(III) with glycine were measured experimentally as a function of concentration, where the total concentration of glycine and iron was unity (so a 0.5 M solution of glycine would contain 0.5 M total iron, which is 0.25 M of Fe\(^{2+}\) and 0.25 M of Fe\(^{3+}\)). A comparison of the model to the experimental pH data is reported in Figure 3-11. The calculated pH matches the experimental pH values quite closely. We also estimated with the model the equilibrium concentrations of the various species in solution, and the results are shown in Figure 3-12. The Fe(III)Gly\(_2\) concentration is maximized at a 1:1 glycine to total iron ratio, and is equal to the Fe(II)Gly\(_2\) concentration at a 1.85:1 glycine to total iron ratio (about 0.7 M glycine in Figure 3-12). Below the 1.85:1 ratio, the Fe(III)Gly\(_2\) concentration is larger than the Fe(II)Gly\(_2\) concentration. This result agrees with the cyclic voltammetry, indicating that both Fe(II) and Fe(III) strongly complex glycine in equimolar concentrations at approximately a 2:1 glycine to iron ratio. As the reason for using a ligand in the electrolyte is to keep the ferric ions soluble, it would be desirable that glycine bonds to the ferric ions and not the ferrous ions, which means operating at a ratio of less than 1.85:1. At low glycine concentrations, the free Fe(III) concentration is significantly higher than the Fe(III)Gly\(_2\) concentration. Once a ratio of approximately 0.5:1 glycine to total iron (0.33 M glycine in Figure 15) is reached, the free Fe(III)
concentration and the Fe(III)Gly$_2$ concentration are equal. This result suggests the glycine to iron ratio should be not less than 0.5:1 glycine to total iron. An electrolyte ratio in between 0.5:1 and 1.85:1 glycine to total iron may be practical for use in a FeFB.

**Figure 3-11.** Model of the pH of glycine-iron solutions as a function of glycine concentration, where the total iron concentration (of equimolar Fe(II) and Fe(III)) is one minus the glycine concentration. Plotted are experimental data (▲) and results from the model (– –).

It is useful to understand the change in free iron species in a solution containing a specific concentration of ferric chloride, ferrous chloride, and glycine at a fixed pH. The calculation used in Figure 3-12 limits the total concentration to 1 M (glycine and total iron). As the pH and iron concentrations are raised, the amount of free ferric ions will change, and may be higher than the solubility limit of aqueous ferric species. The solubility of aqueous iron species as a function of pH has been reported by Pourbaix (70). Using this data a limit can be drawn, above which the ferric ions will precipitate as
Fe(OH)₃. In Figure 3-13, this limit is designated by the dotted line, to the right of which Fe³⁺ is insoluble. The free ferric ion concentration was calculated for several ratios of glycine to total iron as a function of pH, and is also plotted in Figure 3-13 (with the total concentration of iron held at 0.5 M), with the diamonds representing the natural pH of each solution. A similar plot can be made for varied concentrations of iron, at a constant glycine to iron ratio. Using Figure 3-13, it can be determined that a solution containing a 4:1 ratio of glycine to total iron will be stable up to a pH of 4, and a solution of 1:1 glycine to total iron will only be stable up to a pH of about 2. The balance between pH, iron concentration, glycine concentration, and reaction kinetics can thus be optimized. A 1:1 solution of glycine to total iron shows reasonably fast kinetics (Figure 3-9), and maintains an equilibrium potential of 468 mV vs. Ag/AgCl, within 100 mV of the equilibrium potential for an iron only electrolyte (498 mV vs. Ag/AgCl). A 1:1 ratio of glycine to total iron has the greatest concentration of complexed Fe³⁺ (Figure 3-12), and if the concentration of the electrolyte is 0.5 M total iron, the pH of the electrolyte can be maintained at about 2 (Figure 3-13), thus meeting the requirements set forth for a positive electrolyte in an all-iron flow battery.
Figure 3-12. Calculated theoretical equilibrium concentrations of the free Fe(II), free Fe(III), Fe(II)Gly₂, and Fe(III)Gly₂ as a function of glycine to iron ratio.

Figure 3-13. Free Fe³⁺ concentration as a function of pH and the ratio of glycine to total iron, for a 0.5 M total iron (0.25 M FeCl₂ and 0.25 M FeCl₃) solution. The dotted line represents the solubility limit of aqueous Fe³⁺, and the diamonds represent the natural pH for each solution.
3.6 Conclusions

Citrate, DMSO, glycerol, glycine, malic acid, malonic acid, and xylitol were evaluated as ligands for the Fe(II/III) reaction for use in an all-iron flow battery. These seven ligand maintain the solubility of iron(III) up to a pH of 3 at a 3:1 ligand to iron ratio in solution. Considering the electrochemical performance, the iron-glycine complex shows the best performance of all these candidate complexes, with kinetics and diffusion coefficients near those of the ferric/ferrous ions without ligand. The calculated exchange current densities appeared to depend both on the ligand pKₐ and on the size of the iron-ligand complex, though further evaluation (through a rigorous study of the ligand, the complex, and its electrochemistry) is needed to draw definite conclusions.

Symmetric flow cell performance indicates an ohmically controlled current distribution within the cell, and that kinetic and mass transfer overpotentials are modest within the flow battery. Electrochemical impedance spectroscopy indicates that the reaction becomes more distributed at high current densities. The distributed ohmic resistance cannot be directly corrected for in the polarization curves, so a direct calculation of kinetic parameters in the flow cell is difficult. The open circuit potential becomes a major factor in determining which complex will optimize the performance in a flow battery, as less than optimal kinetic and diffusion parameters will not significantly affect the cell overpotential.

Cyclic voltammetry experiments on the glycine-iron complex show the cell potential and reaction kinetics can be controlled by varying the electrolyte pH and by varying the ratio of glycine to iron. Theoretical calculations indicate an ideal operating range for an all iron flow battery between 0.5:1 and 1:1 glycine to total iron in the
electrolyte, and that an electrolyte with a 1:1 ratio of glycine to total iron will be stable at a pH of 2. With an open circuit potential of 468 mV vs. Ag/AgCl and the electrolyte pH of 2, a 1:1 glycine to iron electrolyte is promising for use in an all-iron flow battery.
4.1 Introduction and Background

The literature investigating flow battery kinetics, specifically the all-vanadium RFB, shows significant discrepancies between the vanadium reaction kinetics in a flow battery and on a glass carbon RDE. The polarization curves for the full vanadium flow battery, reported by Skyllas-Kazacos and Menictas (71), with graphite felt electrodes show quite reversible and fast behavior (Figure 4-1). However, polarization curves reported by Gattrell, et al. (63) for the vanadium IV/V reaction on glassy carbon electrodes illustrate severely non-symmetric and slow kinetics (Figure 4-1). The vanadium II/III kinetics remained quite reversible on the glassy carbon electrode.

Previous research has attempted to explain this discrepancy through variables such as the electrolyte pH, mass transport to the electrode, a resistive surface film, or surface oxide formation, but as of yet no satisfactory explanations have been offered (64). More recently, literature examining the vanadium redox reaction kinetics in situ found the opposite: that the vanadium IV/V reaction was fast and reversible, while the vanadium II/III reaction showed high polarization (72). It is possible that similar discrepancies will exist in an iron-ligand chemistry, therefore development of a method of studying interfacial kinetics at carbon fiber electrodes was undertaken.
Figure 4-1. (Left) Polarization curve for an all-vanadium redox flow battery using felt electrodes, as reported by Skyllas-Kazacos and Menictas (71). (Right) $V^{2+/3+}$ and $V^{4+/5+}$ polarization curves on a glassy carbon electrode as reported by Gattrell, et al. (64).

The rotating disk electrode (RDE) has become a common method for testing fuel cell catalyst performance through the use of a deposited thin film of catalyst/binder onto a smooth glassy carbon disk electrode surface. Preparation of the thin film rotating disk electrode (TFRDE) involves deposition of an ink onto a glassy carbon RDE, which is then either dried in air or under low heat. Two common methods of ink preparation are presented in the literature. The first suspends the catalyst particles in an aqueous Nafion solution for deposition on a RDE (73). The second creates an ink by suspending the particles in either water or low weight alcohols, and deposits a layer of Nafion on the thin film after the ink is deposited on the RDE (74). Both preparation methods have been well characterized and are accepted as a catalyst evaluation technique. To evaluate kinetic parameters of flow battery redox reactions, adaptation of this technique to carbon felt fibers was attempted. Such a fibrous material presents specific challenges in preparation, and the Fiber Mat RDE (FMRDE) must be evaluated for viability before being implemented as a research tool.
4.2 FMRDE Preparation

Figure 4-2 details the preparation of the FMRDEs. To prepare the fiber ink, the carbon felt electrodes were broken down into individual fibers through a combination of grinding and shearing. Once separated, the fibers were suspended in a Nafion® solution and ultrasonicated. A known concentration of fiber ink was deposited onto a glassy carbon RDE and dried in air overnight. By changing the concentration of fibers in the ink and the volume of ink placed on the RDE, the fiber deposit loading (and thus the thickness of the fiber mat) was controlled as precisely as possible. Due to the cylindrical nature of the fibers, placement of the aliquot was difficult and the mat quality (uniform coverage, adhesion to the RDE, any mud-cracking, etc.) was highly variable in nature.

Figure 4-2. Preparation of a FMRDE. A known concentration of fibers is suspended in a Nafion® solution and ultrasonicated to ensure an even suspension. A known volume is then deposited on a glassy carbon rotating disk electrode and dried in air. If needed, an additional drop of Nafion solution is placed over the thin film to ensure adhesion.
Figure 4-3. Cyclic voltammetry in 1 M H₂SO₄ for a glassy carbon RDE and fiber mat RDEs with 3.75 mg, 8.82 mg, and 11.5 mg fiber loadings. Cyclic voltammetry was performed at 20 mV/s.

4.3 FMRDE Characterization

Cyclic voltammetry measurements on the FMRDEs show a typical carbon response in sulfuric acid (Figure 4-3). The peak seen around 0.4 V vs. Ag/AgCl is common in carbon electrodes, and frequently associated with hydroquinone functional groups on the electrode surface (75). The electrode capacitances were calculated from cyclic voltammetry measurements, such as those in Figure 4-3, at several different loadings in order to assess the electrical connectivity of the felt fibers in the FMRDE form (Figure 4-4). An approximately linear trend was observed between the capacitance and felt fiber loading (and thus the fiber mat surface area). The measurements indicate a specific capacitance of 4.6 µF/cm² (using an area based on the fiber diameter, density, and loading) for the graphite fibers. Glassy carbon literature reports a specific
capacitance of 16 µF/cm² (76). Considering the differences in materials, the values are in fairly good agreement, indicating that the fibers are reasonably accessible to electron transport from the glassy carbon disk surface.

![Figure 4-4](image)

**Figure 4-4.** Estimated capacitance values for FMRDEs of varied loading. The point at 0 mg corresponds to the measurement on a glassy carbon electrode, and the dashed red line is a linear fit to the data.

In addition to being the reaction of interest for the iron flow battery, the ferric/ferrous couple is an ideal choice for evaluating the experimental technique as the reaction is a simple, single electron transfer with fast kinetics. Cyclic voltammetry of the ferric/ferrous redox couple is presented in Figure 4-5 on a glassy carbon electrode and on FMRDEs with two different loadings (3.75 mg and 11.5 mg). The peak potentials seen on the FMRDEs are quite close to the peak potentials on the glassy carbon electrode. The peak height also increases with the fiber loading. It is expected that the peak separation should decrease with increased loading as compared to the CV on glassy carbon,
indicating faster surface kinetics associated with the extended fiber surface area. Indeed the data of Figure 4-5 is consistent with this reasoning. As the performance of the FMRDEs in the ferric/ferrous electrolyte is similar to that of a glassy carbon electrode, the same system can be used to understand the mass transfer effects in a FMRDE.

![Figure 4-5. Cyclic voltammetry of the ferric/ferrous couple on a glassy carbon electrode, a FMRDE with 3.75 mg loading, and an FMRDE with 11.5 mg loading, at a sweep rate of 10 mV/s. Electrodes were not rotated during cyclic voltammetry. Electrolyte contained 0.1 M FeCl$_2$, 0.1 M FeCl$_3$, and 1 M NaCl.](image)

Using a confocal microscope, the topography of three FMRDE films (3 mg, 3.8 mg, and 6.8 mg) was examined. For the purpose of the microscope, a glass slide was masked to resemble the RDE surface, exposing only a circular area 0.25 cm in diameter, and the fiber mat was cast in the exposed glass area. A stack of images was taken with the confocal microscope and flattened into a topographical map for each film, an example of which is shown in Figure 4-6. The relative thickness of each film was taken across a
**Figure 4-6.** Confocal image of a 3 mg FMRDE.

**Figure 4-7.** Topography of fiber mats with 3 mg, 3.8 mg, and 6.8 mg loadings. Confocal images of each film were combined into a topographical map, and the relative thickness was measured across the center of the film. On the y axis, 0 µm corresponds to the glass slide.
distance of about 600 μm in the center of the film, and is shown for each loading in Figure 4-7. The topography is highly variable, with thicknesses ranging from 10 μm to 150 μm in the 3 mg fiber mat. The 3.8 mg and 6.8 mg fiber mats show similar behavior. The cylindrical shape of the fibers does not allow them to stack neatly on the electrode, resulting in the disordered surface seen in the topography. This will have some effect on the mass transfer characteristics of the FMRDE, as the mat will disrupt the diffusion boundary layer of the RDE. To accurately calculate kinetic parameters, the mass transfer overpotential, and thus the limiting current behavior, must be well defined.

4.4 Mass Transfer Effects

Under normal experimental conditions, the limiting current density for a redox reaction using an RDE is defined by the Levich equation:

\[ i_L = 0.620nFD_o^{2/3}v^{-1/6}C_B\omega^{1/2} \]  

(4-1)

where \( i_L \) is the limiting current density, \( n \) is the number of electrons transferred in the reaction, \( F \) is Faraday’s constant, \( D_o \) is the diffusion constant of the reactant species, \( v \) is the kinematic viscosity, \( C_B \) is the concentration of the reactant species in the bulk electrolyte, and \( \omega \) is the angular rotation rate. For a specific rotating disk electrode system, the only variables are the limiting current density and rotation rate, therefore a plot of the limiting current density versus the square root of the rotation rate should be linear, and yield a slope equal to the collection of constants in Equation 4-1. The Levich equation was shown to accurately describe the fuel cell TFRDE system, as the catalyst
thin films (~10 µm) are smaller than the diffusion boundary layer of the rotating electrode (35 µm for a rotation rate of 200 rpm). Upon calculating the thickness of the fiber mats of our electrodes (using the loading and a carbon density of 2.2 g/cm³), a 3 mg felt loading is estimated to be 70 µm thick, which could disturb the diffusion boundary layer. However, if the film is uniform, with the fibers lying flat, the FMRDE may behave as a typical RDE, but with a porous electrode character. The fiber diameter is 8 µm, less than a fourth of the 35 µm thick boundary layer.

Figure 4-8. Levich plots of several FMRDE loadings as well as a glassy carbon RDE. Limiting current density is based on the geometric area of the RDE (0.196 cm²). Limiting current data was taken in an electrolyte containing 0.01 M FeCl₂, 0.01 M FeCl₃, and 1 M NaCl.

FMRDE experiments with several loadings do show a linear trend when fitted to Equation 4-1 for each individual electrode with different fiber loadings (Figure 4-8). Limiting current data for a glassy carbon RDE is also included in Figure 4-8. The limiting
current data for all FMRDEs was normalized to the geometric area; that is, the area of the glassy carbon RDE (0.196 cm$^2$). All of the FMRDE limiting currents are greater than that of the glassy carbon RDE and there is a general trend of increasing limiting current density with increased loading, indicating an increase in active surface area on the FMRDEs. The $y$-intercept of a Levich plot for a well behaved system can be extrapolated to zero. Levich plots for the fiber mats extrapolate to a variety of $y$-intercept values; however, the values are fairly close and there is no correlation between the intercept and felt loading, indicating that the discrepancies may fall within the error in the system (specifically the variability inherent in the FMRDE preparation process). As can be seen, the slopes of the data sets in Figure 4-8 are not constant with loading as should be expected for a well-behaved limiting current density. This suggests that there is a more complex mass transfer mechanism within the fiber mat than simple linear diffusion. Two extreme cases exist for the mass transfer dependent current distribution across the thin film rotating electrode. In the first case, the reaction may occur only at the exterior surface of the film, with no fluid penetration into the FMRDE. In the second case, the fiber mat is completely penetrated, and the entire surface area is active. If the reaction occurs entirely on the surface of the fiber mat, as in the first case, then the Levich plots should not show a dependence on the thickness (and thus fiber loading) of the mat, and the limiting currents in Figure 4-8 would collapse into a single line independent of mat thickness. The dependence of limiting current on fiber loading in Figure 4-8 indicates that the fluid velocity profile penetrates into the mat as well as flows across the surface. If the second scenario is true, where the entire fiber mat surface area is being utilized, the Levich plots should show a clear dependence on fiber loading. The same data was further
normalized by dividing the limiting currents by the fiber loading of the mat (Figure 4-9). If all the fibers throughout the disk volume had equivalent access to reactant, then we would expect a single line representing the data independent of film thickness. The resulting Levich plots did not collapse into a single line, nor is the correlation between loading and increasing slope seen in Figure 4-9 maintained. Combined with the behavior seen in Figure 4-8, the results of Figure 4-9 lead to the conclusion that the flow profile is in between the two extremes, with fluid only partly penetrating through the fiber mat (Figure 4-10). The extent of the flow through the mat is not intrinsically known.

**Figure 4-9.** Levich plots of the experimentally measured limiting current density, normalized by the loading of the film. Limiting current data was taken in an electrolyte containing 0.01 M FeCl₂, 0.01 M FeCl₃, and 1 M NaCl.
Figure 4-10. Schematic of a fiber mat rotating disk electrode, with velocity streamlines across and through the mat.

A characteristic depth of penetration, $L_o$, is often used in porous electrode modeling as an approximation of the current distribution within the electrode, though it does ignore mass transfer effects. If the characteristic depth is significantly less than the thickness of the electrode, then the distribution is ohmically controlled and most of the reaction will occur on the outer surface of the electrode disk. If $L_o$ is greater than the thickness of the electrode, then the current distribution is kinetically controlled and the current will be well distributed throughout the electrode. Grens (77) defines the characteristic depth of penetration as

$$L_o = \left( \frac{RT \kappa_o \varepsilon}{nFA_s i_o} \right)^{1/2}$$  \hspace{1cm} (4-2)$$

where $\kappa_o$ is the conductivity of the electrolyte, $\varepsilon$ is the void fraction of the electrode, $a_s$ is the specific surface area, and $i_o$ is the exchange current density. This depth is defined as
the point where the current density within the porous electrode has decreased by a factor of $1/e$. For the conditions used in the fiber mat rotating disk experiments, with $\kappa_o = 0.13 \text{ S/cm}$, $\varepsilon = 0.75$, $a_s$ equal to 4 divided by the fiber diameter (8 $\mu$m), and $i_o = 1$ mA/cm$^2$, $L_o$ is on the order of 150 $\mu$m. The thickness of the mat varies with loading, from 70 $\mu$m to 270 $\mu$m, meaning that the current distribution becomes more non-uniform as the loading is increased, with most of the current occurring near the surface of the mat. Accounting for mass transfer effects within the electrode would further decrease $L_o$. As the Levich plots do not show any simple mass transfer dependences, further investigation is needed for understanding the effect of mass transfer within the fiber mat electrodes.

4.5 Flow Profile in the FMRDE

The data used in Figures 4-8 and 4-9 was taken at rotation rates between 200 and 1000 rpm, corresponding to the low end of the data presented by Nam and Bonnecaze (78). They postulated that for the porous RDE, the variations in the limiting currents depended on the ratio of the reaction time to the residence time of the reactant. At low rotation rates, the reaction rate is much faster than the residence time of the ions within the porous electrode, and the reactant is consumed at the surface of the electrode. As the rotation rate is increased, the mass transfer rate is increased, so ions penetrate partway into the electrode as well as reacting on the surface. Finally, at high rotation rates (greater than 2000 rpm), the mass transfer happens much faster than the reaction rate, so the ions fully permeate the porous electrode. It is possible that at the rotation rates used in the FMRDE experiments led to a situation similar to that described for the porous RDE, with a non-uniform current distribution throughout the film. An example of such a velocity
profile is demonstrated in Figure 4-10, with some flow through the film and some across the surface of the film.

The velocity profile to a flat rotating disk with a permeating flow into the disk was first described by Stuart (79) as an expansion on Von Kármán’s solution for flow to a rotating disk. Stuart assumed a constant z-direction dimensionless velocity “a” as the flow into the disk surface. Joseph (80) defined a using properties of a porous disk (Equation 4-3).

\[
a = \frac{\sqrt{\nu \omega} 2kh (\omega \nu)^{3/2}}{1 + 4 \left( \frac{k \omega}{\nu} \right)^2}
\]

(4-3)

In Equation 4-3, \( k \) is the permeability of the disk and \( h \) is the thickness of the disk. In the FMRDE system, \( a \) can be taken as a boundary condition at the interface between the fiber mat and the electrolyte, at thickness \( h \). Combined with the continuity equation, a first approximation of the velocity profile in the FMRDE can be written based on the coordinate system in Figure 4-8 as

\[
\nu_r = \frac{ar}{2h}, \quad \nu_z = \frac{-az}{h}
\]

(4-4)

where \( \nu_r \) is the velocity in the r direction, \( \nu_z \) is the velocity in the z direction, \( r \) is the position along the radial direction, and \( z \) is the position along the z direction. The
resulting velocity profile shows that the majority of the flow is in the \( r \) direction (Figure 4-11).

**Figure 4-11.** Theoretical velocity in the \( r \) and \( z \) directions as a function of \( r \) and \( z \), respectively, in a FMRDE electrode at varied rotation rate. Calculation was done for \( h = 0.007 \text{ cm} \), \( k = 3 \times 10^{-5} \text{ cm}^2 \), and a disk radius of 0.25 cm. In the \( r \) direction, 0 cm corresponds to the center of the mat, and 0.25 cm corresponds to the edge of the mat. In the \( z \) direction, 0 cm corresponds to the interface between the RDE and the fiber mat, and 0.007 cm corresponds to the interface between the fiber mat and the electrolyte.

Based on the dimensionless velocity \( \alpha \) (Equation 4-3), the approximated velocity profile (Equation 4-4), and a mass transfer correlation, a FMRDE limiting current model can be derived (the MATLAB code used for the model calculations is presented in Appendix B). Mass transfer correlations exist for many different systems. The mass transfer correlation most closely matching the FMRDE system is that of a packed bed (\( \text{Re} > 40 \)), defined as

\[
k_{m,avg} = \frac{1}{\sqrt{\nu\omega}} \int Re^{0.51} Sc^{2/3} \psi_r \frac{v_r}{dr} \, dr \tag{4-5}\]
where \( k_{m,\text{avg}} \) is the average mass transfer coefficient, \( \psi \) is the empirical shape factor \((\psi = 0.91 \text{ for a packed bed of cylinders})\), \( Re \) is the Reynolds number, and \( Sc \) is the Schmidt number (81). As \( v_z \) was not significant as compared to \( v_r \) (Figure 4-11), only the velocity in the r direction was considered in the mass transfer coefficient calculation. The limiting current density of an FMRDE at a given rotation rate can then be calculated according to Equation 4-6.

\[
i_L = nFCE_k_{m,\text{avg}}
\]  

(4-6)

The FMRDE limiting current model was used to estimate the limiting current density of two FMRDEs at varied rotation rates, and is compared to experimentally measured limiting current densities in Figure 4-12. The model agrees quite well with the experimentally measured limiting current densities for the 11.7 mg FMRDE. At lower loadings, such as the 3.5 mg FMRDE, the model is not a good fit for the experimental data. However, the inconsistency in the fiber mats (as seen in the topography in Figure 4-7) means a true fit for the data is difficult at best. As such, extraction of kinetic data is difficult, since the mass transfer overpotential is ill defined.
Figure 4-12. FMRDE limiting current model calculation as compared to experimentally measured limiting current densities for a 3.5 mg FMRDE and an 11.7 mg FMRDE.

Electrolyte contained 0.01 M FeCl$_2$, 0.01 M FeCl$_3$, and 1 M NaCl. Model parameters include $k = 1800$ Darcy, $D_{Fe} = 4.7 \times 10^{-6}$ cm$^2$/s, $\nu = 0.01$ cm$^2$/s, $h = 83$ µm for the 3.5 mg FMRDE, and $h = 269$ µm for the 11.7 mg FMRDE. Disk radius was 0.25 cm.

4.6 Pulse Voltammetry

Estimating kinetic data from traditional polarization curves requires a well-defined limiting current and mass transfer overpotential, which has proven difficult on the FMRDEs. Therefore we considered the use of pulse voltammetry as an alternative method of calculating kinetic parameters on the FMRDEs. Pulse voltammetry utilizes a succession of potential pulses at increasing amplitudes, held at a short time, with a baseline potential held between each pulse. The short pulse times are not long enough for a diffusion boundary layer to develop, so the mass transfer overpotential is naturally small. However, when pulse voltammetry was performed on the FMRDEs, a limiting
current was still observed, therefore all pulse voltammetry data was corrected for the limiting current, so the remaining current density is solely kinetic current ($i_k$). In Figure 4-13, an example of this correction is shown for a FMRDE with a 3.8 mg loading. Pulse voltammetry on FMRDEs of several different loading were performed, an example of which is shown in Figure 4-14. All pulse voltammetry polarization was corrected for the ohmic overpotential using the high frequency resistance obtained through EIS. The current density was calculated using the geometric surface area of the RDE. Even with the pulse voltammetry technique, the current response in the FMRDEs is highly variable. The 2.4 mg and 3 mg electrodes have similar polarization curves and the current density increases from 2.4 mg to 3 mg, however, the 7.6 mg FMRDE current density was much lower than that of the 6 mg FMRDE (Figure 4-14). Additionally, the 6 mg and 7 mg FMRDE polarization curves show limiting currents, even after correcting to the kinetic current density.
Figure 4-13. Pulse voltammetry polarization of a 3.8 mg FMRDE in 0.01 M FeCl₂, 0.01 M FeCl₃, and 1 M NaCl. Both the raw data and the limiting current corrected data ($i_k$) are shown. Both curves were IR corrected using the high frequency resistance obtained from EIS.

Figure 4-14. Pulse voltammetry polarization of FMRDEs at four different loadings, in 0.01 M FeCl₂, 0.01 M FeCl₃, and 1 M NaCl. Pulses were held for 250 ms, and the baseline was the open circuit potential.
Figure 4-15. Exchange current densities estimated from pulse voltammetry on FMRDEs at two different iron concentrations. Dashed lines represent the exchange current density estimated from pulse voltammetry on a glassy carbon RDE, in the same electrolytes. Both electrolytes contained 1 M NaCl and equimolar concentrations of FeCl$_2$ and FeCl$_3$ (either 0.01 M or 0.05 M of each salt).

Exchange current densities were estimated from the Tafel region of the pulse voltammetry polarization at two different concentrations, based on the geometric surface area of the RDE (Figure 4-15). Additionally, the exchange current densities estimated on a glassy carbon electrode are shown in Figure 4-15 as dashed lines. The exchange current densities in the higher concentration electrolytes are larger for all FMRDEs, as is expected. Since the exchange current densities were calculated using the geometric surface area of the electrodes, a trend of increasing exchange current density with increasing fiber loading (and thus active surface area) is expected. No clear trend emerges in Figure 4-15, though the exchange current densities on the FMRDEs are all larger than
the exchange current density estimated on glassy carbon. The result is similar to that of the limiting current densities (Figures 4-8 and 4-9), in that the observed behavior is highly variable, and that there is no correlation between fiber loading and current. Though pulse voltammetry does decrease the mass transfer effects on the current, the FMRDEs still appear to be too varied in their performance for consistent use in evaluating redox reaction electrokinetics. A different electrode, such as a single carbon fiber electrode, may prove to be less variable in performance.

4.7 Conclusions

The fiber mat rotating disk electrodes’ Levich behavior is not apparent due to complex ohmic and mass transfer within the fiber mat. Correcting for the theoretical flat disk limiting current did not serve to simplify the Levich plots, and no dependence of mass transfer on the full thickness of the mat was observed. Topographical measurements showed a highly disordered surface. The flow profile through a rotating FMRDE was estimated based on a suction velocity through a rotating porous disk, and was able to successfully predict the limiting current behavior at high fiber loadings of the FMRDE. The model was unsuccessful in predicting the limiting current behavior for low fiber loadings.

Pulse voltammetry experiments and exchange current density estimates on the FMRDE also showed no clear dependence on fiber loading. In addition, the current response was not consistent across electrodes. Both the Levich plots and polarization behavior of the fiber mat RDEs point to a non-uniform current distribution. As the FMRDEs are not consistent in topography or in current response, estimation of true
electrokinetic behavior is difficult. A different technique, such as a carbon fiber microelectrode, may prove more uniform in preparation and in electrochemical behavior.
Chapter 5

Negative Electrode Structure

5.1 Background

Hybrid flow batteries are limited by the amount of metal that can be deposited into the electrode structure, thus controlling the amount of discharge time at power available. In hybrid flow batteries using zinc as the negative electrode, current densities of 80 mA/cm$^2$ were achieved by using a porous foam electrode structure instead of a flat plate (30) Employing a three dimensional porous electrode instead of a flat plate will increase active surface area and apparent mass transport rates, thus increasing the limiting current density. A three-dimensional electrode with a high void fraction and appropriately designed current distribution may be able to increase the effective plating density that can be obtained.

Six different three-dimensional structures were examined for their performance as a negative electrode substrate for a metal deposition and dissolution reaction. Combinations of conductive and non-conductive porous materials were examined for their energy storage capacity. For this study we used copper plating from sulfate electrolytes to examine the effectiveness of the electrode structures. This reaction is kinetically fast and about 370 mV positive of hydrogen evolution, therefore it any avoids complications from hydrogen evolution as a side reaction. Two of the better performing electrodes were also incorporated into an all-iron flow battery to evaluate their efficacy in this hybrid flow battery system.
**Figure 5-1.** Calculated current distribution in a porous conductive electrode, at varying ratios of electronic conductivity to ionic conductivity. Parameters used in the calculation include: bulk $\text{Fe}^{3+}$ concentration = 0.25 M, $\text{Fe}^{3+}$ diffusion coefficient = $4.76 \times 10^{-6}$ cm/s, ionic conductivity = 0.1 S/cm, exchange current density = 1.5 mA/cm$^2$, anodic alpha = 0.4, cathodic alpha = 0.6, local limiting current density = 100 mA/cm$^2$, void fraction = 0.8, felt roughness factor = 360 cm$^2$/cm$^3$, temperature = 298 K.

### 5.2 Porous Electrode Current Distribution

Plating density in the hybrid RFB is dependent on the current distribution within the porous electrode. Models for the current distribution in porous electrodes are well studied, with the distribution dependent on the physical structure of the electrode, the electronic and ionic conductivities of the electrode and electrolyte phases, and on the mass transfer and kinetic resistances (82-84). In the case of a flow battery, the velocity of the electrolyte through the porous electrode minimizes the mass transfer resistances. The current distribution can then be calculated based on the Butler-Volmer equation and the
ohmic resistances for both the solid and electrolyte phases, as a function of depth in the porous electrode (the MATLAB code for the current distribution model is presented in Appendix B). Figure 5-1 shows the one dimensional current distribution with varying electronic conductivities ($\sigma_e$), where a depth of 0 cm corresponds to the current collector and a depth of 0.5 cm corresponds to the electrode/membrane interface. The ionic conductivity was held constant at 0.1 S/cm in these calculations. The distribution where $\sigma_e = 1$ S/cm reflects that of a typical flow battery having a carbon felt or carbon paper electrode, where the electrode conductivity is much higher than that of the electrolyte (85). In this case, the majority of the current is concentrated near the membrane. For a negative electrode involving electrodeposition of a metal, the bulk of the plating will then occur near the membrane surface. As plating occurs, the porosity of the electrode decreases. Once the pores of the felt are full with metal deposit, ion transport is restricted into the porous network, resulting in a significant increase in the overpotentials and

![Graph](image)

**Figure 5-2.** Initial charge of the flow-by copper sulfate battery at 40 mA/cm$^2$. Membrane area was 5 cm$^2$, with serpentine flow fields and carbon paper electrodes.
eventual failure of the battery. This is demonstrated in Figure 5-2 for copper deposition from a sulfate electrolyte using a serpentine flow field and carbon paper electrodes (Fe$^{2+}$/Fe$^{3+}$ couple on the positive electrode). The battery started charging at about 0.55 V (120 mV total overpotential), and reached 0.63 V (a 200 mV overpotential) within one hour of charging at 40 mA/cm$^2$. The cell ultimately failed when the cell voltage reached 1.14 V (total overpotential of 710 mV). The total density of copper deposited was 73 mAh/cm$^2$, however the amount of copper deposited at reasonable overpotentials (under 200 mV) was closer to 20 mAh/cm$^2$. When the cell was taken apart, the face of the carbon paper that was against the membrane was filled with copper (Figure 5-3a), while the current collector side of the paper showed very little copper deposition (Figure 5-3b), as expected by the current distribution predicted in Figure 5-2. Copper deposition was also observed along the edges of the carbon paper. As the mass transfer resistance and overpotential increased, the edges of the paper were more likely to be accessed by ions to be plated.

If the electronic conductivity is reduced in magnitude, the maximum in the current distribution can be shifted away from the membrane and towards the current collector (Figure 5-1). When the ratio of electronic conductivity to ionic conductivity equals unity, there is a symmetric current distribution. Significantly lowering the ratio of electronic conductivity to ionic conductivity, say to 0.05, shifts the maximum in the current distribution moves towards to the current collector. In the extreme of very low ratio of electronic conductivity to ionic conductivity, the current density concentrates near the current collector much like that of a flat plate electrode. However, even in this case, the low-conducting electrode structure may provide some benefit by increasing the
mass transfer rates over those of a flat plate, allowing operation at higher current densities. The low-conducting electrode structure does increases the ionic resistance in the region between the membrane and the current collector, but also serves as a membrane support.

![Image](image1.png)

**Figure 5-3.** Plated copper in the flow-by copper sulfate battery, using 5 cm² serpentine hardware (deposition rate of 40 mA/cm², with a total deposit of 73 mAh/cm²) at a) the membrane face of the carbon paper, showing uniform copper deposit and b) the current collector face of the carbon paper, showing essentially no copper deposit in the paper. Copper is observed around the edges of the paper in both pictures, most likely due to the high overpotential and mass transfer resistances near the end of the cell life.

To explore the resistive losses with conducting and non-conducting electrode materials further, symmetric cell experiments were carried out with four different electrode configurations: A, bonded carbon felt; B, non-bonded carbon felt; C, bonded non-conducting felt; and D, non-bonded non-conducting felt. Electrochemical impedance spectroscopy (EIS) measurements were performed on all configurations using a single
reservoir with Fe(II) and Fe(III), flowing in series through the RFB anode and cathode (Figure 5-4). The charge transfer resistances for cases A and B (the carbon felts), are small, and no mass transfer resistance is observed. Bonding the felts serves to decrease the interfacial resistances and lower the high frequency resistance. For cases C and D (the non-conducting felts), the high frequency resistance is increased over cases A and B (about 5 \( \Omega \text{cm}^2 \) for case D versus 2.9 \( \Omega \text{cm}^2 \) for case B). A significant charge transfer and mass transfer resistance are observed in case D (non-bonded non-conducting felt).

Though the non-conducting felt will somewhat break up the boundary layer, the active electrode area in case D is limited to the flat graphite plate. When the non-conducting felt was bonded to the current collector, the high frequency resistance decreased to 3 \( \Omega \text{cm}^2 \), and the charge transfer resistance also decreased. The conductive carbon ink will have a somewhat higher surface area than that of the flat plate current collector (the wet ink is partly forced into the pores of the non-conducting felt), most likely the reason for the decreased charge transfer resistance. The similarities in high frequency resistance values between the bonded carbon felt and the bonded non-conducting felt demonstrates that an electrode of bonded non-conducting felt will not significantly increase ohmic losses in a flow battery.
Figure 5-4. Nyquist plots around OCV for symmetrically run flow cells with A: bonded carbon felt, B: non-bonded carbon felt, C: bonded non-conducting felt, and D: non-bonded non-conducting felt electrode configurations. Electrolyte was 0.2 M FeCl$_2$, 0.2 M FeCl$_3$, and 1 M NaCl.

5.3 Rotating Rod Experiments

To further investigate the use of a non-conducting felt bonded to a current collector as an electrode for a plating reaction, a rotating rod configuration was used, as described in Chapter 2 (2.3.3). Cyclic voltammetry measurements of iron plating and stripping were recorded with the bonded non-conducting felt rod electrode rotated at 1500 rpm, and after plating 20 mAh/cm$^2$ and 480 mAh/cm$^2$ (Figure 5-5). The CVs are compared to the iron plating/stripping cyclic voltammetry on a bare copper rod (1 cm$^2$ active area) within the same electrolyte. As the plating density increased, the CVs indicate that iron deposition occurs at lower overpotentials. Also, the rotating rod with the attached non-conducting felt enabled iron metal deposition at lower overpotentials as
compared to plating on the bare copper rod. It is important to note that the plating
densities calculated on the rotating rod do not take into account any hydrogen evolution
occurring (plating density was estimated based on the applied current and plating time).
The true plating density of iron plated is most likely somewhat less than the estimated
values presented here. Even so, these results indicate that using a non-conducting felt
bonded to the current collector as an electrode structure can lower the plating
overpotential and enable a high plating density (possibly as high as 480 mAh/cm$^2$).

**Figure 5-5.** Cyclic voltammetry of iron deposition and stripping on a bonded non-
conducting felt rotating rod after 0, 20, and 480 mAh/cm$^2$, and compared to a cyclic
voltammogram on a copper rod. Electrolyte was 0.2 M FeCl$_2$ and 1 M NH$_4$Cl.
Figure 5-6. Electrode structures tested in the Cu-Fe sulfate battery. Structures A-C were also tested in symmetric cells, with a separate naming convention (the third structure tested in symmetric cells, non-bonded non-conducting felt, is not shown). Structures E and F were also tested in all-Fe batteries.

5.4 Copper Sulfate Flow Batteries

Six negative electrode structures, shown in Figure 5-6, were tested in the Cu-Fe sulfate battery. The copper negative electrode was chosen for these plating capacity studies to minimize the effects of hydrogen evolution as a competing reaction. Electrodes A and B are traditional flow through carbon felt electrodes. In electrode A, the felt is bonded to the current collector, where as in electrode B the felt is non-bonded. Electrode C is the bonded non-conducting felt. Electrodes D and E use the non-conducting felt on
top of a bonded conductive electrode, either carbon cloth (D) or carbon felt (E). The porous carbon materials in electrodes D and E are used to decrease the kinetic overpotentials while the layer of non-conducting felt prevents plating directly onto the membrane. Electrode F consists of three layers: bonded carbon felt, a Daramic porous non-conducting separator, and a second layer of carbon felt. The Daramic initially isolates the layer of carbon felt bonded to the current collector from the layer of carbon felt near the membrane surface.

![Charging potential-time curves for various electrodes](image)

**Figure 5-7.** Charging potential-time curves for electrodes A (bonded carbon felt), B (non-bonded carbon felt), C (Bonded non-conducting felt), D (Bonded carbon cloth and non-conducting felt), E (bonded carbon felt and non-conducting spacer), and F (bonded carbon felt-Daramic-carbon felt) in a Cu-Fe sulfate battery. Charged at 40 mA/cm² for 230 minutes, or until the voltage sharply increased, indicating failure.

Each battery was charged at 40 mA/cm² until either reaching 150 mAh/cm² (220 minutes) or failing, as indicated by a sharp spike in the potential (Figure 5-7). A summary
of the plating density achieved before failure and the cell voltage during plating for each configuration is presented in Table 5.1. Of the six batteries, electrodes A, B, C, and D failed before reaching the targeted plating density of 150 mAh/cm². Electrodes A and B charged at the lowest overpotentials as expected. Both A and B contain only carbon felt: a layer of non-conducting felt (as in electrodes C, D, and E) adds a gap of zero electronic conductivity (so the ohmic overpotential will depend entirely on the ionic conductivity) and the ohmic overpotential will increase. Electrode C failed at 124 mAh/cm², the lowest plating density of the six electrode configurations. Electrode C corresponds to the configuration used in the rotating rod experiments, of which iron was plated to an estimated 480 mAh/cm². Two explanations for the discrepancy in plating density exist. First, the rotation rate used in the rotating rod experiments provided a much higher solution velocity than what was used in the Cu-Fe sulfate battery. The higher velocity would be expected to result in a higher limiting current density which should yield a smoother, more conformal deposit. Second, the iron plating potentials on the rotating rod are well within the boundaries of hydrogen evolution, while the copper plating potential is more positive than hydrogen evolution and will therefore have a higher current efficiency. These results suggest that use of a bonded non-conducting felt as the plating electrode structure will not provide a high plating density. Electrode D charged at a lower potential than electrode E (0.7 V versus 1.0 V), but ultimately failed at 145 mAh/cm². The carbon cloth in electrode D provides a thin layer of conductive porous media, increasing the plating density over electrode C, however the electrode structure is still not able to provide 150 mAh/cm² of plating capacity. The bonded carbon felt and non-conducting felt (E) and the bonded carbon felt-Daramic-carbon felt (F) electrodes both
successfully reached the targeted 150 mAh/cm² of copper deposit. The charging-time profile for both of these electrodes showed a relatively constant potential, and there was not a rapid rise in charging potential for either electrode.

Table 5-1. Summary of Fe-Cu sulfate batteries.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$R_{HF}$ ($\Omega$*cm²)⁹</th>
<th>Charging Potential (V)⁶</th>
<th>Plating Density (mAh/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Bonded carbon felt</td>
<td>N.D.</td>
<td>0.66</td>
<td>145</td>
</tr>
<tr>
<td>B. Non-bonded carbon felt</td>
<td>N.D.</td>
<td>0.62</td>
<td>128</td>
</tr>
<tr>
<td>C. Bonded non-conducting felt</td>
<td>3.85</td>
<td>0.75</td>
<td>124</td>
</tr>
<tr>
<td>D. Bonded carbon cloth and non-conducting felt</td>
<td>2.31</td>
<td>0.93</td>
<td>145</td>
</tr>
<tr>
<td>E. Bonded carbon felt and non-conducting felt</td>
<td>3.08</td>
<td>1.08</td>
<td>150+ ⁷</td>
</tr>
<tr>
<td>F. Bonded carbon felt-Daramic-carbon felt</td>
<td>1.93</td>
<td>0.79</td>
<td>150+ ⁷</td>
</tr>
</tbody>
</table>

⁹$R_{HF}$ calculated from the high frequency intercept from the EIS in Figure 9
⁶Charging potential refers to the potential measured near the end of the charging curves, either just before cell failure began or at 230 minutes (if failure did not occur)
⁷Electrode did not reach full plating capacity (experiments stopped at 150 mAh/cm²)

The EIS results for electrodes C, D, E, and F are reported in Figure 5-8, and the high frequency resistance calculated from the EIS is reported in Table 5-1. EIS for electrodes A and B could not be measured due to a high density of copper along the membrane, blocking ion transport in the porous network (EIS measurements were taken at the end of the initial charge). Electrode C has the largest high frequency resistance, but a low charging potential (3.85 $\Omega$*cm² and 0.75 V, respectively). As the electrode structure consists only of the non-electrically conducting felt, a large high frequency resistance is expected, and the low charging potential indicates that plating kinetics and
mass transfer are not hindered. Electrode F contained the smallest thickness of non-electrically conductive media (a single piece of Daramic), and had both the lowest high frequency resistance and lowest charging potential (1.93 $\Omega \cdot \text{cm}^2$ and 0.79 V, respectively). Electrode D had a lower high frequency resistance than electrode C due to the layer of carbon cloth (2.31 $\Omega \cdot \text{cm}^2$ versus 3.85 $\Omega \cdot \text{cm}^2$). Electrodes D and E contained a layer of conductive media and a layer of non-conducting felt, contributing to their higher resistances and charging potentials. The mass transfer resistance in all electrode structures can be considered to be small, as indicated by the impedance spectra, due to the relatively high flow rate of electrolyte through the cell. All of the charge transfer semicircles in the EIS results are depressed, indicating a distributed ionic resistance through the electrode. As a result, the charge transfer resistance cannot be directly calculated; rather, an electrode resistance (the combined charge transfer resistance and distributed ionic resistance) can be estimated by the width of the depressed semicircle and used to compare the negative electrode structures. The EIS for electrode C has the largest electrode resistance, due to the absence of any conductive porous media (carbon felt or carbon cloth). This configuration would be expected to have the lowest surface area and thus the highest charge transfer resistance. The electrode resistances for electrodes D, E, and F are much closer in size, as they all contain at least one layer of conductive, high surface area media.
Figure 5-8. Nyquist plots around OCV for negative electrodes C (bonded non-conducting felt), D (bonded carbon cloth and non-conducting felt), E (bonded carbon felt and non-conducting felt), and F (bonded carbon felt-Daramic-carbon felt) in the Cu-Fe sulfate batteries after charge. EIS for electrodes A and B was unable to be determined. Each spectrum is offset by 0.1 ohm in $Z''$ for clarity.

When cells D and E were taken apart, copper deposit was observed throughout the conductive media. In electrode E (bonded carbon felt and non-conducting felt), no copper was observed in the non-conducting felt, only throughout the carbon felt layer (Figure 5-9a). These results are in agreement with the current distribution discussed in the previous section: the majority of the current will be concentrated at the interface between the electrode and the adjacent region of purely ionically conducting material (in this case, the non-conducting felt). In electrode F, the bonded carbon felt-Daramic-carbon felt, a copper deposit was observed in both layers of carbon felt. In the bonded carbon felt layer, the copper was concentrated on the side next to the Daramic layer (Figure 5-9b), and in
the carbon felt layer between the Daramic and membrane, copper was concentrated on the side of the felt facing the membrane (Figure 5-9c). The plating distribution in electrode F suggests that copper plated first in the carbon felt layer near the current collector, and once electrical contact was established through the Daramic, copper then deposited into the carbon felt layer closest to the membrane. The dark areas observed in the carbon felts in Figure 5-9 are spaces where copper was not deposited. Uneven distribution of the copper plate across the surface is most likely due to variability in electrolyte wetting of the carbon felts. Copper deposit in both pieces of carbon felt in electrode F and the absence of copper deposit in the non-conducting felt in electrode E implies that each carbon felt can contain a finite plating density. If a higher plating density is desired, another layer can be added to electrode F, however this will further reduce the voltaic efficiency of the cell. An approach along these lines has been employed for Zn batteries (86, 87). The balance of power delivered and energy capacity in a hybrid flow battery are coupled, and must be tailored to the specific application. It should also be noted that these results were obtained for plating at a single current density.
(40 mA/cm²). It is likely that the maximum plating density that can be achieved within a porous electrode will be a function of the current density. A more rigorous investigation into the maximum plating density, as a function of the applied current, is required to fully characterize the electrode behavior.

5.5 All-Iron Hybrid Flow Batteries

Electrode designs E (bonded carbon felt and non-conducting felt) and F (bonded carbon felt-Daramic-carbon felt) both achieved a plating density of over 150 mAh/cm² in the Cu-Fe sulfate battery. These electrode designs were then tested in an all-iron flow battery. Each battery was charged to 150 mAh/cm², at a current density of 40 mA/cm² (Figure 5-10). The potential and iR corrected potential for both batteries also shown in Figure 5-10, the latter corrected from the high frequency resistance of the EIS (Figure 5-11). The cell with electrode design E charged at a higher potential than the cell with electrode F (1.51 V versus 1.4 V respectively, at the end of charge). The 100 mV difference in overpotential is mostly explained by the differences in high frequency resistance: the cell with electrode E was 4.2 Ω*cm², while the cell with electrode F was 3.3 Ω*cm². When the charging-time plot of each cell is corrected for IR, the two charging curves are initially quite close, however begin to diverge after about one hour of charging, with cell F having a lower iR-corrected charging voltage as compared to cell E. EIS for both electrodes indicate a significant mass transfer resistance and relatively small charge transfer resistance. The EIS measured mass transfer resistances are significant in these cells, though mass transfer impedances were not present in the Cu-Fe sulfate cells.
**Figure 5-10.** Initial charge of all-iron hybrid flow batteries with the bonded felt and non-conducting felt negative electrode (electrode E) and the bonded felt-Daramic-felt (electrode F) negative electrode. IR free curves were calculated using high frequency resistances from EIS.

**Figure 5-11.** Nyquist plots of the all-iron hybrid flow batteries around the open circuit potential with electrode E (bonded felt and non-conducting felt) and electrode F (bonded carbon felt-Daramic-carbon felt) negative electrodes.
with the same electrode configurations (Figure 5-8). Due to the cell design and high porosity of the carbon felts, it is likely that hydrogen bubbles are trapped in the electrode structures and hindering mass transfer. Because the EIS was measured at the end of the initial charge, when the density of plated iron is the highest, the area of electrolyte flow and diffusion of ions to the electrode surface are reduced, again increasing the mass transfer resistances. The current distribution in electrode F is clearly non-uniformly distributed, making quantitative analysis of the charge transfer impedance difficult. Electrode E also shows distributed behavior, and the mass transfer semicircle somewhat overlaps the charge transfer semicircle.

After being charged to 150 mAh/cm², the cells were cycled at ±40 mA/cm² for 30 minutes discharge and 30 minutes charge. The first six cycles are shown in Figure 5-12a, iR-corrected, along with the voltaic efficiency of each cycle (Figure 5-12b). The iR correction was done to directly compare the performance of the two electrodes without the inherently larger iR of Electrode E (due to the presence of the non-conducting felt). In the first cycle, electrode F shows a higher average voltaic efficiency (86.3%) than electrode E, but the voltaic efficiency declines on each subsequent cycle (to 66.8% by cycle 6). Electrode E started at a slightly lower voltaic efficiency (81.6%), but only decreased by 1.6% over six cycles. Coulombic efficiency is not considered here as each cycle was performed over a shallow depth of discharge, and coulombic losses caused by hydrogen evolution could not be estimated. An investigation of the hydrogen evolution in the all-iron flow battery is presented in Chapter 6.
Figure 5-12. a) IR corrected potential during cycling of all-iron batteries with electrodes E (bonded carbon felt and non-conducting spacer) and F (bonded carbon felt-Daramic-carbon felt) at ±40 mA/cm², and b) average voltaic efficiency per cycle number for the iR corrected cycles with electrode E and electrode F.

The two separate carbon felts in electrode F, and thus two separate iron plates, may contribute to the decline in voltaic efficiency of electrode F. Plating in the layer closest to the membrane relies on electrical contact through the Daramic between the two carbon felt. Once that contact is made, the plating and stripping occurs in the carbon felt next to the membrane. Ion transport to the plated iron along the membrane is difficult, as is suggested by the large mass transfer resistance in the EIS results of electrode F (Figure 5-11). As the metal in electrode E was shown to deposit into the carbon felt instead of the non-conducting felt, electrolyte flow can more easily support ion transport through the porous media, lowering the mass transfer resistance. Electrode E can be further optimized by using a thinner non-conducting felt to minimize the cell resistance and by tailoring the current density to maximize plating density, though there will be an inherent limit to the amount of metal that can be plated in a single piece of carbon felt. The stability of
electrode E throughout the cycling suggests it is better suited as a negative electrode than electrode F, even though electrode F had the lower cell resistance.

5.6 Conclusions

Traditional flow battery electrode configurations are difficult to use for negative electrode electrodeposition reactions, as non-uniform current distribution will deposit metal along the membrane-electrode interface, eventually blocking ion transport to the active surface. Non-electrically conductive porous materials were explored as components of a negative electrode structure to shift the current distribution away from the cell membrane and facilitate achieving a higher plating density. Bonding the porous electrode materials to the graphite flow field using a conductive ink reduced the interfacial resistance for both conductive and non-conductive porous materials. Plating results using a Cu-Fe sulfate chemistry indicate a maximum plating density in a bonded carbon felt electrode without a non-conductive region of 145 mAh/cm² before cell failure. Adding non-conducting porous materials to the negative electrode configuration increased the achievable plating density. Two negative electrode structures achieved at least 150 mAh/cm² in the Cu-Fe sulfate chemistries: the bonded carbon felt and non-conducting felt, and the bonded carbon felt-Daramic-carbon felt electrodes. Electrochemical impedance spectroscopy showed little to no mass transfer resistance in the Cu-Fe sulfate cells, indicating that mass transfer does not play a large role in flow battery operation.

In the all-iron chemistry, the negative electrode with a bonded carbon felt and a porous non-conducting felt maintained a voltaic efficiency of 81% over at least six
cycles. The cell resistance in this battery was larger than in the battery with the bonded carbon felt-Daramic-carbon felt negative electrode. To reach a higher energy capacity, more layers of felt and the non-conducting materials can be added, however this will increase the cell resistance, reducing the power and energy storage capability of the battery. Tailoring the energy capacity versus the power towards each specific application of the battery will be necessary. Reduction of hydrogen evolution will further increase energy efficiency of the all-iron battery.
Chapter 6
Iron Plating Electrokinetics

6.1 Background

Hruska and Savinell reported that the main loss of efficiency in the all-iron flow battery was from hydrogen evolution (9). Two methods for suppressing the hydrogen evolution are pursued in this chapter. The first involves raising the pH of the electrolyte. Increasing the pH of the electrolyte will shift the equilibrium potential of hydrogen evolution more negative and decrease the diffusion limited current due to hydrogen evolution (16). The second involves the effect of the supporting electrolyte, in particular the anion, on the hydrogen evolution. The presence and concentration of specifically adsorbed halide ions was found to alter the mechanism by which iron corrodes (40, 41). Altering the anion species and its concentration in the supporting electrolyte of an iron flow battery may lower the hydrogen evolution occurring and increase the plating efficiency. Effect of anion concentration was evaluated both on an iron rod electrode and in an all-iron flow battery cell.

The first method, increasing the electrolyte pH, requires use of a ligand in the positive electrolyte. Using a complexing ligand in the all-iron flow battery electrolyte was shown in Chapter 3 to improve the ferric ion solubility at mildly acidic pHs without suppressing the ferric/ferrous redox kinetics. Similarly, a ligand may or may not affect the iron plating kinetics on the negative electrode (37, 38). Even if the ligand was only added to the positive electrolyte, crossover will occur throughout the life of the battery and the ligand will eventually appear in the negative electrolyte as well. Results from
plating with glycine and with glycerol are presented in this chapter. The effect of the ligand on the hydrogen evolution is also investigated.

6.2 Hydrogen Evolution

Due to the negative potential of the iron deposition/dissolution reaction, evolution of hydrogen can be a significant source of efficiency loss in the all-Iron flow battery. Hydrogen evolution unbalances the electrolyte by raising the pH. Ultimately, the higher pH will cause precipitation of the reactants and cause failure in the battery. The hydrogen evolution reaction, in absence of iron plating, was measured directly through cyclic voltammetry as a function of pH on an iron rod working electrode (Figure 6-1). At pH 1 \( \text{H}_2 \) evolution is an appreciable current density, even at -0.7 V vs. Ag/AgCl (about -0.5 mA/cm\(^2\)). As the pH is raised, the onset of hydrogen evolution is pushed more negative at pH 2, to about -0.75 V vs. Ag/AgCl. At -0.8 V vs. Ag/AgCl (approximately 200 mV overpotential for iron plating) the current density for hydrogen evolution was -15 mA/cm\(^2\) at a pH of 2 (a decrease of about 41 mA/cm\(^2\) from the voltammetry at pH 1). Raising the pH to 3 further reduces the \( \text{H}_2 \) evolution to a current density of -3 mA/cm\(^2\) at -0.8 V vs. Ag/AgCl, though the difference between pH 2 and pH 3 is not as significant as that between pH 1 and pH 2.
Figure 6-1. Cyclic voltammetry of hydrogen evolution on iron as a function of pH, with a constant 3 M Cl\textsuperscript{-} (with HCl and the remaining chloride from NH\textsubscript{4}Cl). Cyclic voltammetry was IR compensated using 90% of the high frequency resistance measured with EIS.

In addition to the pH, the supporting anion may affect the hydrogen evolution. Chloride and sulfate have different adsorption properties on iron surfaces (47, 48). Cyclic voltammetry to measure hydrogen evolution was performed in electrolytes containing chloride or sulfate at a pH of 2 (Figure 6-2). Total anion concentration in the electrolyte was 3 M using either NH\textsubscript{4}Cl or (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}. The hydrogen evolution current density is much larger in the sulfate electrolyte. Even at low overpotentials, there is almost an order of magnitude difference in current density for the sulfate electrolyte over the chloride electrolyte (-25 mA/cm\textsuperscript{2} in the sulfate electrolyte versus -2 mA/cm\textsuperscript{2} in the chloride electrolyte, at -0.8 V vs. Ag/AgCl). Chloride adsorbs to electrodes surfaces much more strongly than sulfate, and requires a large negative potential to desorb (41).
Figure 6-2. Cyclic voltammetry (compensated to 90% of $R_{HF}$) of hydrogen evolution on iron in chloride and sulfate electrolytes. Electrolyte was maintained at pH 2 with either HCl or $H_2SO_4$, with the anion concentration brought to 3 M with either $NH_4Cl$ or $(NH_4)_2SO_4$.

Figure 6-3. Cyclic voltammetry (compensated to 90% of $R_{HF}$) of hydrogen evolution on an iron rod as a function of the chloride concentration. Electrolyte contained 0.1 M HCl, with the remaining chloride concentration from $NH_4Cl$. 
Due to the strong adsorption characteristics of chloride, increasing the anion concentration further may even more attenuate the amount of hydrogen evolution at a given overpotential. A higher concentration will shift the chloride desorption potential more negative, forcing the hydrogen evolution onset potential more negative. Cyclic voltammetry of hydrogen evolution on an iron rod was performed in three chloride concentrations (Figure 6-3). At a constant pH of 1, increasing the chloride concentration from 0.1 M to 5 M decreases the hydrogen evolution current by 95% at -0.8 V vs. Ag/AgCl.

6.3 Supporting Electrolyte Effect on Iron Plating

Not only does the choice of supporting electrolyte affect the hydrogen evolution present during iron plating, it can also affect the iron plating kinetics. Again examining the effect of chloride versus sulfate anions, cyclic voltammetry of iron plating and stripping was performed in NH₄Cl and (NH₄)₂SO₄ electrolytes (Figure 6-4). The current density of the iron plating in sulfate electrolyte is much lower than that in chloride electrolyte, and peak separation in the chloride electrolyte is smaller than in the sulfate, indicating plating kinetics in the chloride electrolyte are faster. Thus chloride electrolytes enhance iron plating kinetics while attenuating hydrogen evolution. Increasing rates of iron electrodissolution in chloride solutions is well established in the literature (40, 42, 45). Two mechanisms for iron dissolution are proposed, one of which involves the direct participation of adsorbed chloride (45). The mechanism at a given overpotential depends both on the chloride concentration and pH of the electrolyte (42). Iron plating can occur
with two different mechanisms as well, most likely simple reversals of the iron dissolution reactions (16).

Figure 6-4. Cyclic voltammetry of iron plating/stripping in chloride and sulfate electrolytes on a copper rod. Electrolyte contained 0.2M of Fe$^{2+}$ and 1M of NH$_4^+$, of either the chloride or sulfate salts.

The cation effect on the plating reaction was also investigated (Figure 6-5). NaCl, KCl, and NH$_4$Cl were all examined as possible supporting electrolyte salts. Cyclic voltammetries with all three of the cations show a flat region of no current between the plating and stripping peaks. This flat region is due to coverage of chloride on the electrode. Once the potential is sufficiently negative enough to remove the chloride, iron will deposit (40). Additionally, the voltammetry shows less plating on the cathodic sweep, and faster plating on the anodic sweep. This is due to an initial kinetic hindrance due to iron nucleation on the copper. Once the iron nucleates, the plating overpotential decreases. The onset of plating in the NH$_4$Cl electrolyte at -0.96 V vs. Ag/AgCl, is more
negative than in NaCl or KCl electrolytes (-0.84 V vs. Ag/AgCl and -0.86 V vs. Ag/AgCl, respectively). All of the cyclic voltammetries show reasonably fast kinetics, with NaCl having the lowest plating potential and very little hysteresis in the plating peak.

![Cyclic voltammetry of iron plating/stripping in supporting electrolytes of NH₄Cl, NaCl, or KCl on a copper rod. Electrolyte contained 0.2 M FeCl₂ and 1 M supporting electrolyte.](image)

**Figure 6-5.** Cyclic voltammetry of iron plating/stripping in supporting electrolytes of NH₄Cl, NaCl, or KCl on a copper rod. Electrolyte contained 0.2 M FeCl₂ and 1 M supporting electrolyte.

Plated iron morphology varies with the supporting electrolyte as well (Figure 6-6). Adhesive quality of the iron deposit and iron oxidation in air were considered when evaluating the morphology. The iron deposited from an (NH₄)₂SO₄ bath was rough and chalky (Figure 6-6a). Iron deposit from a KCl electrolyte had a wavy quality, and oxidized quickly in air, as indicated by the yellowed portions in Figure 6-6c. Electrolytes containing NH₄Cl and NaCl produced the most mechanically and chemically stable deposits (Figure 6-6b and 6-6d, respectively). The deposit from NaCl is highly pitted,
most likely due to considerable hydrogen bubble formation on the electrode surface, though the deposit was adhesive and did not oxidize in air.

![Image](image.png)

**Figure 6-6.** 20 mA/cm² of plated iron from electrolytes containing 0.2M FeCl₂ and 1 M of a) (NH₄)₂SO₄, b) NH₄Cl, c) KCl, and d) NaCl. Iron was plated on a copper rod electrode rotated at 1500 rpm. Pictures were taken at 10x magnification under an optical microscope.

The coulombic efficiency as a function of plating potential was estimated for plating from each of the three supporting chloride electrolytes (Figure 6-7). The plating efficiency reaches a maximum in each electrolyte: a potential that is negative enough to remove chloride from the electrode surface, but positive enough where hydrogen evolution is not yet significant. The maximum efficiency from plating in the NH₄Cl electrolyte is lowest (91.5%) and occurred at a more negative plating potential than the other two electrolytes (-1 V vs. Ag/AgCl), in good agreement with the cyclic voltammetry (Figure 6-5). Iron plated at the highest efficiency in the NaCl electrolyte, 97.7% at a plating potential of -0.95 V vs. Ag/AgCl. If the iron plating mechanisms are simple reversals of the iron deposition reactions (16), it is likely that the chloride
adsorption will directly affect the plating kinetics. Competition between chloride and hydrogen adsorption will also affect the plating kinetics in all electrolytes.

**Figure 6-7.** Coulombic plating efficiency as a function of plating potential for electrolytes containing 0.2 M FeCl₂ and 1 M of either NH₄Cl, NaCl, or KCl on a copper rod electrode (1 cm²). Iron was plated at a given potential for 5 min, then stripped at -0.35 V vs. Ag/AgCl for 5 min. The coulombic efficiency was calculated from the charge plated versus the charge stripped.

### 6.4 Plating with Ligands

The results of the hydrogen evolution in various electrolytes indicate that maintaining an electrolyte above a pH of 3 in the battery will help in mitigating the hydrogen evolution. Complexing the ferric ions with a ligand increases the iron solubility and prevents precipitation in the positive battery electrolyte. In the interest of maintaining a single electrolyte composition, the ligand will also be present in the negative flow...
battery electrolyte. Glycerol and glycine were investigated for their effect on the iron plating/stripping.

Figure 6-8. Cyclic voltammetry of iron plating/stripping on a copper rod in electrolytes containing glycine, as compared to a ligand free electrolyte. All electrolytes contained 0.2 M FeCl₂ and 1 M NaCl. The 1:1 glycine to iron electrolyte contained 0.2 M glycine, and the 0.5:1 glycine to iron electrolyte contained 0.1 M glycine.

Cyclic voltammetry of iron plating/stripping in NaCl electrolytes containing either 0.2 M or 0.1 M glycine as compared to an electrolyte containing only NaCl (ligand free) are reported in Figure 6-8. This corresponds to a 1:1 and a 0.5:1 glycine to ferrous ion ratio, respectively. Both the 0.2 M and the 0.1 M glycine electrolytes shift the plating potential more negative. Iron plating in the 0.1 M glycine electrolyte begins at -0.86 V vs. Ag/AgCl, 25 mV more negative than in the ligand free electrolyte, though the reaction kinetics appear to be similar to those in the NaCl electrolyte. The higher concentration of glycine shifts the plating potential further negatively. When the same experiments were
performed in glycerol containing electrolytes (Figure 6-9), the opposite effect was observed. The low concentration of glycerol (0.1 M) severely depressed the plating reaction, and only a small stripping peak is observed at -0.55 V vs. Ag/AgCl. The cyclic voltammetry in the 0.2 M glycerol electrolyte was very similar to that of the non-ligand containing NaCl electrolyte, with only a 15 mV difference in plating potentials.

**Figure 6-9.** Cyclic voltammetry of iron plating/stripping on a copper rod in electrolytes containing glycerol, as compared to a ligand free electrolyte. All electrolytes contained 0.2 M FeCl₂ and 1 M NaCl. The 1:1 glycerol to iron electrolyte contained 0.2 M glycerol, and the 0.5:1 glycerol to iron electrolyte contained 0.1 M glycerol.
Figure 6-10. Coulombic plating efficiency as a function of plating potential for electrolytes containing 0.2 M FeCl₂ and 1 M NaCl, with 0.2 M of either glycine or glycerol. The Fe only data is repeated from Figure 6-7 to aid as a comparison with the ligand containing electrolytes. Experiments were performed on a copper rod electrode (1 cm²). Iron was plated at a given potential for 5 min, then stripped at -0.35 V vs. Ag/AgCl for 5 min. The coulombic efficiency was calculated from the charge plated versus the charge stripped.

Coulombic efficiency estimates as a function of plating potential were also performed for iron-ligand electrolytes containing 0.2 M ligand (Figure 6-10). Both glycine and glycerol lower the iron plating efficiency. The maximum plating efficiency from the glycine containing electrolyte was 90.7% at -1.1 V vs. Ag/AgCl, 7% less than the maximum efficiency in the NaCl electrolyte. The low plating efficiencies due to chloride adsorption also appear to persist at more negative overpotentials in the glycine electrolyte. When hydrogen evolution in ligand containing electrolytes was studied
Figure 6-11. Hydrogen evolution on an iron rod (1 cm$^2$ active area) in ligand containing electrolytes. Electrolyte contained 1.4 M NaCl, 0.2 M of either glycerol or glycine, and adjusted to pH 3. A NaCl only (no ligand) electrolyte is presented as a comparison.

(Figure 6-11), it was found that glycine containing electrolyte increased the hydrogen evolution over a neat NaCl electrolyte by almost a factor of 4 (from -0.6 mA/cm$^2$ to -2.4 mA/cm$^2$ at -1 V vs. Ag/AgCl). Plating efficiency in the glycerol electrolyte reached 97.8% at -1 V vs. Ag/AgCl. However, during the experiments it was observed that the iron plated from the glycerol electrolytes would not fully strip. A separate stripping potential had to be applied between each plating efficiency experiment to ensure the plated charge was as accurate as possible. The variation in the plating efficiencies observed in Figure 6-10 may also be explained by the difficulty in stripping iron plated in the presence of glycerol. Hydrogen evolution in electrolyte containing glycerol was actually decreased from neat NaCl electrolyte, so the bulk of the inefficiency is most likely due to the difficulty of stripping iron in the glycerol electrolyte. Plating with a
ligand requires either dissociation of the ferrous ion and the ligand or incorporation of the ligand into the plated metal. Either will increase the activation overpotential. While use of a ligand would increase the ferric ion solubility in the positive electrolyte, the addition of glycine or glycerol to the negative electrolyte lowers the coulombic efficiency. Another ligand may be able to both increase the ferric ion solubility in the positive electrolyte and maintain a high iron plating efficiency in the negative electrode.

**6.5 All-Iron Flow Battery Results**

High chloride concentration prevented hydrogen evolution on an iron rod electrode. Similarly, a high chloride concentration should decrease the hydrogen evolution in a flow battery cell. Two electrolytes were examined in flow cells: one cell with 4.5 M Cl\(^-\) and one cell with 7 M Cl\(^-\). Both cells contained 1.5 M FeCl\(_2\), with NH\(_4\)Cl added to provide the remaining chloride ions. NH\(_4\)Cl was chosen as supporting electrolyte as its solubility is higher than NaCl (though NaCl did exhibit a slightly higher plating efficiency on the copper rod in section 6.). Both cells were charged at 40 mA/cm\(^2\) for 3.75 hours, for a total of 150 mAh/cm\(^2\) (Figure 6-12). The 7 M Cl\(^-\) cell had an initial electrolyte pH of 1.88, higher than the 4.5 M Cl\(^-\) cell (initial pH = 1.13). Over the course of charging, the pH in the negative electrolyte increased in both cells to above a pH of 3. As the cells were charged, the gas flow from the negative electrode was measured periodically, and used to estimate an average hydrogen flow rate and the apparent hydrogen evolution current density. The cell with 4.5 M Cl\(^-\) on average exhibited a hydrogen evolution current density of 12 mA/cm\(^2\) (69% coulombic efficiency), while the 7 M Cl\(^-\) cell exhibited an average hydrogen evolution current density of 4.5 mA/cm\(^2\)
(88% coulombic efficiency). The pH of the negative electrolyte was also monitored as the cells charged. The results of current efficiency observed with the rod electrode indeed was observed in the flow battery tests, though over 10% of the current going to hydrogen evolution is still too high for an operational flow battery.

Figure 6-12. Initial potential-time curve for an iron flow battery containing 1.5 M FeCl₂ and either 1.5 M NH₄Cl or 4 M NH₄Cl, for a total chloride concentration of 4.5 M and 7 M, respectively. Cells were charged at 40 mA/cm² for 3.75 hours.

After charging both cells, they were cycled at a shallow depth of discharge (±40 mA/cm², 0.5 hr discharge and 0.5 hr charge) for 14 cycles (Figure 6-13). The voltaic efficiency for each cycle was also estimated (Figure 6-14). The first cycle in both batteries was similar, however the voltaic efficiency of the 4.5 M Cl⁻ cell progressively declined (from 70% to 52% over 14 cycles). Voltaic efficiency in the 7 M Cl⁻ cell declined at a slower rate, 5% over 14 cycles. Though increasing the chloride concentration to 7 M did lower the hydrogen evolution current, it was not eliminated, and
Figure 6-13. Cycle data for an iron flow battery containing either 4.5 M or 7 M total Cl\(^-\). Cells were cycled at -40 mA/cm\(^2\) for 0.5 hr and +40 mA/cm\(^2\) for 0.5 hr, for 14 cycles. The electrolyte contained 1.5 M FeCl\(_2\) with the remaining Cl\(^-\) concentration from NH\(_4\)Cl.

Figure 6-14. Voltaic efficiency of charge/discharge cycles for iron flow batteries containing 1.5 M FeCl\(_2\), with either 4.5 M total Cl\(^-\) or 7 M total Cl\(^-\) (with the remaining chloride from NH\(_4\)Cl).
the pH of the electrolyte slowly increased to above a pH of 4 during operation. Ferrous oxide and hydroxide species formed at these pH levels hinder iron plating kinetics, leading to the decrease in voltaic efficiency, even in the 7 M Cl\(^-\) electrolyte.

### 6.6 Conclusions

Supporting electrolyte composition and pH were investigated with the objective of maximizing plating efficiency in an all-iron flow battery through both minimizing hydrogen evolution rates and enhancing iron plating reaction kinetics. The hydrogen evolution current decreased by a factor of about 4 when the electrolyte pH was increased from 1 to 2. Increasing the concentration of chloride also decreased the hydrogen evolution current. A combination of a pH greater than 2 and a high chloride concentration (up to 5 M) will further reduced the hydrogen evolution current.

Use of chloride as a supporting anion also increased iron plating/stripping kinetics as compared to use of sulfate as a supporting anion. The cation also affected the iron plating kinetics, with an ammonium containing electrolyte shifting the plating potential slightly more negative. Plating from a NaCl supporting electrolyte had the highest coulombic efficiency at 97\%, though the deposit quality with NH\(_4\)Cl was smoothest. The NaCl deposit was much less smooth, however both the deposit from NH\(_4\)Cl and NaCl plating baths were stable in air. Complexing the ferrous ions with a ligand both decreased the plating efficiency and shifted the plating potentials more negative. Though use of a ligand may be feasible in the positive electrolyte of an all-iron flow battery, the negative electrolyte must be free of glycine or glycerol. Another ligand may be able to complex the active species without hindering the iron plating reaction.
Increasing the chloride concentration in an all-iron flow battery decreased both
the charging overpotential and current due to hydrogen evolution. The battery was stable
over 14 shallow cycles, operating at a voltaic efficiency of about 67% at ±40 mA/cm².
Even though the increased chloride concentration reduced the coulombic loss due to
hydrogen evolution, further effort is needed to minimize the hydrogen evolution reaction
in the plating electrode of the all-iron flow battery.
Chapter 7
Conclusions and Future Directions

7.1 Conclusions

One of the main impairments towards use of an all-iron hybrid flow battery (FeFB) is the presence of hydrogen evolution at the negative electrode. Two methods for improving the performance of the FeFB were investigated: complexing the ferric ions with ligands to increase the solubility at mild pHs, and use of supporting electrolyte, particularly the anion species, to suppress hydrogen evolution. The electrokinetics of both the complexed ferric/ferrous redox couple, the coulombic efficiency of the iron plating reaction in varied electrolytes, and the effect of a ligand on the iron plating reaction were all of specific interest.

Citrate, DMSO, glycerol, glycine, malic acid, malonic acid, and xylitol all passed the initial metrics set out for the iron-ligand complexes. Addition of any of these ligands to the positive electrolyte was shown to maintain Fe$^{3+}$ solubility at a pH greater than 2.5. Both the iron-glycine and iron-glycerol complexes displayed the fast, reversible electrokinetics of the ferric/ferrous redox couple. The electrokinetics and equilibrium reaction potential of the iron-glycine complex depends strongly on the electrolyte pH and on the ratio of glycine to iron. A model based on the dissociation constants of glycine, Fe$^{2+}$, and Fe$^{3+}$, and on the equilibrium rate constants of the iron(II)-glycine and iron(III)-glycine complexes was developed to predict the electrolyte properties and solubility limits of iron(III). Based on this model and the electrokinetics observed, a 1:1 ratio of glycine to iron is an ideal composition for the positive electrolyte in the FeFB.
However, when glycine was added to the negative electrolyte, the plating potential was shifted more negative, and the hydrogen evolution increased. The plating reaction is accompanied by a dissociation of the iron(II)-glycine complex, whereas in the redox reaction on the positive electrode, both redox species are complexed with glycine. This dissociation is most likely the cause of the negative shift in the plating potential. A similar experiment with glycerol showed only a slight negative shift in plating potential, however the plated iron was difficult to strip for unknown reasons. It is possible that the glycerol is incorporated into the plated iron. Though it is feasible to improve ferric ion solubility on the positive electrode of the FeFB, the negative reaction cannot tolerate either the addition of glycerol or glycine. Another ligand may be able to maintain both ferric ion solubility and a reasonable plating potential on the negative electrode without increasing the hydrogen evolution current as glycine did.

Hydrogen evolution is affected both by the electrolyte pH and by the type and concentration of supporting anions. Due to its adsorption properties, chloride is an effective inhibitor of hydrogen evolution. Chloride adsorbs on metal sites, while sulfate adsorbs on metal oxide sites in less than a monolayer. The open metal sites in the sulfate electrolyte are free for proton adsorption and thus hydrogen evolution. Increasing the chloride concentration from 0.1 M to 5 M decreased the hydrogen evolution current on an iron rod electrode by 95% in a pH 1 electrolyte. Increasing the pH will further decrease hydrogen evolution. In an FeFB cell, a similar result was observed: by increasing the total chloride concentration to 7 M, the average hydrogen evolution current was reduced to 4.5 mA/cm² from 12.5 mA/cm². Though using a high chloride concentration does improve
battery performance, the hydrogen evolution is not sufficiently suppressed for a fully operational FeFB.

In addition to the investigation into the flow battery electrokinetics, hybrid flow batteries present unique challenges in energy storage capacity and 3-dimensional electrode design. The porous carbon electrodes used in flow batteries cause the current distribution within the porous electrode to be concentrated near the membrane. In addition, at high current densities the reaction becomes highly distributed. The kinetic and mass transfer overpotentials therefore are not controlling the current distribution, as long as the exchange current densities are not low and the diffusion coefficients are reasonable for a species diffusing through a liquid. A negative electrode with alternating layers of carbon felt and non-conducting materials is able to achieve a high plating capacity, with additional layers increasing the capacity. The number of layers will need to be optimized for both energy storage capacity and power, as additional layers of non-conducting material will increase the cell resistance and decrease the power output.

7.2 Future Directions

The ligands initially chosen as possible electrolytes additives were ligands are known to complex metal ions, that were highly soluble, and that were inexpensive and widely available. Though an effort was made to maintain similar structures between ligands (i.e. dicarboxylic acids with 3 carbon, 4 carbon, or 5 carbon chains), the ligands that passed the initial metrics did not necessarily follow such a pattern. Of the seven ligands further studied in Chapter 3, no clear trend emerged between the iron-ligand properties and the electrokinetics. The electrokinetic parameters presented in this
dissertation were estimated using Butler-Volmer kinetics. In the Marcus Theory of electrokinetics, the ligands surrounding a cation play the most significant role in the kinetic parameters (59, 60, 88). For example, a cation with six ammine ligands may have a vastly different exchange current density than that same cation with five ammine ligands and one aquo ligand. The cation itself is of little importance.

For a deeper insight into how a ligand changes the behavior of the Fe^{2+/3+} redox couple, a set of experiments that uses a systematic design of complexes should be undertaken. Firstly, the number of ligands bound to a cation should be tested, with the substitutions made by aquo ligands. Secondly, the ligand structure should be varied, with the number of ligands bound to a given iron ion held constant. In this manner, the effect of increasing the carbon chain in the ligand, or addition of a third carboxylic chain as in citrate, may be considered. A set of experiments such as these may lead to an iron-ligand complex that can be customized to a specific application within the flow battery.

Of the negative electrode structures tested in Chapter 5, two structures reached the target of 150 mAh/cm^2: a carbon felt with non-conducting felt, and a carbon felt-Daramic-carbon felt layered electrode. In both cases, the majority of the plated metal was in the carbon felt, with very little metal observed in the non-conductive layers. These results pose two ideas. One, that the addition of the non-conducting felt layer does not significantly increase the plating capacity: the metal will always plate into the conductive layer. Two, that the true plating capacity of a carbon felt electrode is not well understood. A further study that evaluates the maximum plating capacity of a felt electrode as a function of current density may lead to insight into design of hybrid flow batteries with high energy storage densities. Additionally, if the cell resistance can be reduced to a level
where the current distribution is kinetically controlled instead of ohmically controlled, the plating capacity may also change. Use of a thicker membrane or separator, thin carbon felts, low reactant concentrations, or a highly acidic supporting electrolyte may all shift the current distribution to a kinetically controlled regime.

Progress was made in the reduction of hydrogen evolution through a combination of high chloride concentration and a mild increase in electrolyte pH, to between 2 and 3. However, the hydrogen evolution was not eliminated altogether. An FeFB run with a 7 M Cl\(^{-}\) concentration still exhibited an average hydrogen evolution current density of 4.5 mA/cm\(^2\), about 10% of the total applied current density. Use of another anion, such as bromide or iodide, may be a possibility for further decreasing the hydrogen evolution. Other electrolyte additives exist as well: heavy metals such as lead and chromium (9) have been shown to hinder hydrogen evolution. Heavy metals are toxic, however, which may not be suitable for certain applications of the FeFB. If the hydrogen evolution can be overcome, the all-iron flow battery is a realistic chemistry for use as a grid-scale energy storage device.
Appendices

Appendix A: Supplemental Data, Chapter 3

*Cyclic Voltammetry – Natural pH*

0.1 M FeCl₂, 0.1 M FeCl₃, 1 M NaCl, 0.8 M Ligand, glassy carbon electrode, 50 mV/s

![Graph of Cyclic Voltammetry](image)

**Figure A-1.** Iron only (black), iron-citrate (red), and iron-DMSO (blue).

![Graph of Cyclic Voltammetry](image)

**Figure A-2.** Iron only (black), iron-glycerol (red), and iron-glycine (blue).
Figure A-3. Iron only (black), iron-malic acid (red), and iron-malonic acid (blue).

Figure A-4. Iron only (black) and iron-xylitol (red).
Cyclic Voltammetry – pH adjusted to 2.5

0.1 M FeCl$_2$, 0.1 M FeCl$_3$, 1 M NaCl, 0.8 M Ligand, glassy carbon electrode, 50 mV/s.

**Figure A-5.** Iron only (black), iron-citrate (red), and iron-DMSO (blue).

**Figure A-6.** Iron only (black), iron-glycerol (red), and iron-glycine (blue).
Figure A-7. Iron only (black), iron-malic acid (red), and iron-malonic acid (blue).

Figure A-8. Iron only (black) and iron-xylitol (red).
Limiting Current Data

0.1 M FeCl₂, 0.1 M FeCl₃, 1 M NaCl, 0.8 M Ligand, glassy carbon electrode.

Figure A-9. Iron-only limiting current data. Arrows indicated increasing rotation speed (from 200 rpm to 3000 rpm).

Figure A-10. Levich plot for ferrous ion oxidation with citrate, DMSO, and glycerol at natural pH.
Figure A-11. Levich plot for ferrous ion oxidation with glycine, malic acid, malonic acid, and xylitol at natural pH.

Figure A-12. Levich plot for ferric ion reduction for citrate, DMSO, and glycerol at natural pH. Limiting current values are absolute.
**Figure A-13.** Levich plot for ferric ion reduction for glycine, malic acid, malonic acid, and xylitol at natural pH. Limiting current values are absolute.

**Figure A-14.** Levich plot for ferrous ion oxidation with DMSO, glycerol, and glycine at pH adjusted to 2.5. Iron-citrate was unmeasurable due to suppression of the oxidation reaction.
**Figure A-15.** Levich plot for ferrous ion oxidation with malic acid, malonic acid, and xylitol at pH adjusted to 2.5.

**Figure A-16.** Levich plot for ferric ion reduction for citrate, DMSO, and glycerol at pH adjusted to 2.5. Limiting current values are absolute.
Figure A-17. Levich plot for ferric ion reduction for glycine, malic acid, malonic acid, and xylitol at pH adjusted to 2.5. Limiting current values are absolute.
Appendix B: Mathematica and MATLAB Code

Iron-Glycine pH Model, Chapter 3 – Mathematica

```
[62] AllFeDat = Table[
   {GlyTot, {H, Fe2, Fe3, Fe2G, Fe3G, G, x, a, dife} /. FindRoot[{K1G = x + H / (G),
   KFe2G = KFe2G / ((Fe2) * (x)^n),
   KFe3G = KFe3G / ((Fe3) * (x)^m),
   K1Fe3 = a + H / (Fe3),
   KdiFe = dife + (H)^2 / ((Fe3)^2),
   K1H = w + H / (Fe2G),
   K2H = u + H / (Fe3G),
   Fe2Tot = Fe2 + Fe2G + w,
   Fe3Tot = Fe3 + Fe3G + a + u + 2 * dife,
   GlyTot = G + x + n * Fe2G + m * Fe3G + n * w + m * u,
   H = x + w + a + 2 * dife - (G + x) /. {K1G -> .005, KFe2G -> 45000,
   KFe3G -> 1000000, K1Fe3 -> 0.0063, KdiFe -> 0.00123, K1H -> 0.000001, K2H -> 0.006,
   n -> 2, m -> 2, Fe2Tot -> (1 - GlyTot) + 0.5, Fe3Tot -> (1 - GlyTot) + 0.5),
   {x, .01}, {H, .003}, {Fe2G, .05}, {Fe3G, .06}, {Fe2, .09}, {w, 0.0001},
   {u, 0.0001}, {G, .01}, {Fe3, .08}, {a, 0.0001}, {dife, 0.00002}),
   MaxIterations -> 100000, DampingFactor -> 0.1}, {GlyTot, .05, .9, .05}];

[63] Hconc = Table[
   {AllFeDat[[i]][[1]], AllFeDat[[i]][[2]]}, {i, 1, Length[AllFeDat], 1}];
   Fe2Conc = Table[{AllFeDat[[i]][[1]], AllFeDat[[i]][[2]]}, {i, 1, Length[AllFeDat], 1}];
   Fe3Conc = Table[{AllFeDat[[i]][[1]], AllFeDat[[i]][[2]]}, {i, 1, Length[AllFeDat], 1}];
   Fe2Gly = Table[{AllFeDat[[i]][[1]], AllFeDat[[i]][[2]]}, {i, 1, Length[AllFeDat], 1}];
   Fe3Gly = Table[{AllFeDat[[i]][[1]], AllFeDat[[i]][[2]]}, {i, 1, Length[AllFeDat], 1}];
   GlyConc = Table[{AllFeDat[[i]][[1]], AllFeDat[[i]][[2]]}, {i, 1, Length[AllFeDat], 1}];
   GlyMinConc = Table[{AllFeDat[[i]][[1]], AllFeDat[[i]][[2]]}, {i, 1, Length[AllFeDat], 1}];
   Fe30HConc = Table[{AllFeDat[[i]][[1]], AllFeDat[[i]][[2]]}, {i, 1, Length[AllFeDat], 1}];
   difeConc = Table[{AllFeDat[[i]][[1]], AllFeDat[[i]][[2]]}, {i, 1, Length[AllFeDat], 1}];
```

157
In[1]: AllSpec = ListPlot[{H conc, Fe3 conc, Fe2 conc, Gly conc, GlyMn conc, 
diFe conc, Fe2 Gly, Fe3 Gly, Fe30H conc}, Joined -> True, PlotRange -> {0, 0.8}, 
AxesLabel -> {"Total Gly Conc (M)", "Concentration (M)"}, PlotLegends -> 
{"H", "Fe3", "Fe2", "Gly", "Gly-", "diFe", "Fe2 Gly", "Fe3 Gly", "Fe30H"}, 
PlotMarkers -> {Automatic, Medium}]

In[2]: FeSpec = ListPlot[{Fe3 conc, Fe2 conc, Fe2 Gly, Fe3 Gly}, Joined -> True, 
PlotRange -> {0, 0.5}, AxesLabel -> {"Total Gly Conc (M)", "Concentration (M)"}, 
PlotLegends -> {"Fe3", "Fe2", "Fe2 Gly", "Fe3 Gly"}, 
PlotMarkers -> {Automatic, Medium}]

In[3]: GlySpec = ListPlot[{Gly conc, GlyMn conc, Fe2 Gly, Fe3 Gly}, Joined -> True, 
PlotRange -> {0, 0.7}, AxesLabel -> {"Total Gly Conc (M)", "Concentration (M)"}, 
PlotLegends -> {"Gly", "Gly-", "Fe2 Gly", "Fe3 Gly"}, 
PlotMarkers -> {Automatic, Medium}]}
In[4] = `FeExSpec = ListPlot[{{Fe3Conc, Fe2Conc, diFeConc, Fe3OHConc}}, Joined -> True, PlotRange -> (0, 0.5), AxesLabel -> ("Total Gly Conc (M)", "Concentration (M)"), PlotLegends -> ("Fe3", "Fe2", "diFe", "Fe3OH"), PlotMarkers -> (Automatic, Medium)]

\[\text{Out}[4]=\]

\[
\begin{array}{c}
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\text{0.4} \\
\text{0.3} \\
\text{0.2} \\
\text{0.1} \\
\text{0.0} \\
\text{0.2} \\
\text{0.4} \\
\text{0.6} \\
\text{0.8} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Total Gly Conc (M)} \\
\text{Fe3} \\
\text{Fe2} \\
\text{diFe} \\
\text{Fe3OH} \\
\end{array}
\]

In[5] = `pH = Table[{{AllFeDat[[1]][[1]], -Log10[AllFeDat[[1]][[2]]][[1]]}}, {1, 1, Length[AllFeDat], 1}];
expData = {{{1, 1.09}, {.25, 1.29}, {.33, 1.33}, {.5, 1.5}, {.66, 2.22}, {.75, 2.57}, {.9, 3.45}}];

In[6] = `ListPlot[(pH, expData), Joined -> True, PlotRange -> (0, 4), AxesLabel -> ("Total Gly Conc (M)", "pH"), PlotLegends -> ("Model", "Exp"), PlotMarkers -> Automatic, PlotStyle -> (Red, Thick), (Blue, Dashed)]

\[\text{Out}[6]=\]

\[
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\text{3} \\
\text{2} \\
\text{1} \\
\text{0} \\
\text{0.2} \\
\text{0.4} \\
\text{0.6} \\
\text{0.8} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Total Gly Conc (M)} \\
\text{Model} \\
\text{Exp} \\
\end{array}
\]

In[7] = `Output = Table[{{AllFeDat[[1]][[1]]}, NumberForm[Fe3Conc[[1]]][[2]], 3, NumberForm[Fe2Conc[[1]]][[2]], 3, NumberForm[Fe2Gly[[1]]][[2]], 3, NumberForm[Fe3Gly[[1]]][[2]], 3, NumberForm[GlyConc[[1]]][[2]], 3, NumberForm[GlyMinConc[[1]]][[2]], 3, NumberForm[diFeConc[[1]]][[2]], 3, NumberForm[Fe3OHConc[[1]]][[2]], 3, NumberForm[Hconc[[1]]][[2]], 3}, {1, 1, Length[AllFeDat], 1}];

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<td>0.0481</td>
<td>0.652</td>
<td>4.2×10&lt;sup&gt;-13&lt;/sup&gt;</td>
<td>1.16×10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>0.0003&lt;sup&gt;°&lt;/sup&gt;</td>
<td></td>
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<tr>
<td></td>
<td>10&lt;sup&gt;-6&lt;/sup&gt;</td>
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<td></td>
<td>69</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\texttt{\textbf{In[2]} = \textbf{AllFeDat} = Table\{\{\text{pH, \{Fe3, Fe3G, G, x, a, diFe\}}, \text{FindRoot\{\{K1G = x + H / (G), KFe3G = Fe3G / ((Fe3) \times (x)^m), K1Fe3 = a + H / (Fe3), KdiFe = diFe \times H / (Fe3), K2H = u + H / (Fe3G), Fe3Tot = Fe3 + Fe3G + a + u + 2 \times diFe, GlyTot = G + x + m + Fe3G + m + u\}\}}, \{x, .09\}, \{Fe3G, 0.2\}, \{u, 0.0001\}, \{G, .11\}, \{Fe3, 0.1\}, \{a, 0.0001\}, \{diFe, 0.0002\}, MaxIterations \rightarrow 100000, DampingFactor \rightarrow 0.1\}];}

\texttt{\textbf{In[3]} = \textbf{Fe3Conc} = Table\{\{AllFeDat[[1]][[1]], AllFeDat[[1]][[2]][[1]]\}, \{1, 1, Length[AllFeDat], 1\}]; \textbf{Fe3Gly} = Table\{\{AllFeDat[[1]][[1]], AllFeDat[[1]][[2]][[2]]\}, \{1, 1, Length[AllFeDat], 1\}]; \textbf{GlyConc} = Table\{\{AllFeDat[[1]][[1]], AllFeDat[[1]][[2]][[3]]\}, \{1, 1, Length[AllFeDat], 1\}]; \textbf{GlyMinConc} = Table\{\{AllFeDat[[1]][[1]], AllFeDat[[1]][[2]][[4]]\}, \{1, 1, Length[AllFeDat], 1\}]; \textbf{Fe3OHConc} = Table\{\{AllFeDat[[1]][[1]], AllFeDat[[1]][[2]][[5]]\}, \{1, 1, Length[AllFeDat], 1\}]; \textbf{diFeConc} = Table\{\{AllFeDat[[1]][[1]], AllFeDat[[1]][[2]][[6]]\}, \{1, 1, Length[AllFeDat], 1\}]; \textbf{Output} = Table\{\{AllFeDat[[1]][[1]], Log10[Fe3Conc[[1]][[2]] + 2 \times diFeConc[[1]][[2]] + Fe3OHConc[[1]][[2]]\}, \{1, 1, Length[AllFeDat], 1\}];}

\texttt{\textbf{Out[3]} = \textbf{AllSpec} = ListPlot\{\{Fe3Conc, GlyConc, GlyMinConc, diFeConc, Fe3Gly, Fe3OHConc\}, Joined \rightarrow True, PlotRange \rightarrow \{0, 0.02\}, AxesLabel \rightarrow \{"pH", "Concentration (M)"\}, PlotLegends \rightarrow \{"Fe3", "Gly", "Gly-", "diFe", "Fe3Gly", "Fe3OH"\}, PlotMarkers \rightarrow \{Automatic, Medium\};}
The code shown was used to calculate the 2:1 glycine to iron pH in Figure 3-13. The process was repeated for other ratios of glycine to iron to generate the plot.
% This program calculates the flow field through a TFFRDE, based on the velocity profile calculated from the continuity equation and boundary conditions. The constant 'a' is from Joseph's solution for flow to a porous disk. The program plots the vector field for the velocity in the $r$ and $z$ directions.

\begin{verbatim}
function Flow_field

n = 14; % number of slices
H = .00716; % TF height, in cm
h = H/n; % height of one slice, in cm
d = 0.0010; % fiber diameter, cm
DFe = 10e-6; % diffusion coefficient, cm²/s

rpm = [200;400;600;800;1000]; % rde rotation rate, rpm
[m,~] = size(rpm);
R = 0.25; % disk radius, cm
rad = R/(n/2);
k = .3*10^-5; % permeability, cm²
nu = 0.0105; % kinematic viscosity, cm²/s

r = zeros(1,n);
z = zeros(1,n);

z(1) = 0;
r(1) = -R;
for i = 1:n
    z(i+1) = z(i) - h;
r(i+1) = r(i) + rad;
end

a = zeros(m,1);
qr = zeros(m,n+1);
qz = zeros(m,n+1);
om = rpm.*(2*pi()/60); % angular velocity, rad/s

for j = 1:m
    a(j,:) = (sqrt(nu*om(j))*2*k*H*(om(j)/nu)^(3/2))/(1+4*(om(j)*k/nu)^2);
    qr(j,:) = a(j).*r./(2*H);
    qz(j,:) = -a(j).*z./H;
end

mag = sqrt(qr.^2+qz.^2);
\end{verbatim}
These (kmr and kmz) solve the mass transfer coefficient, based on the correlation from BSL for a packed bed.

\[
kmr = 0.91 \times 0.91 \times (qr) / ((d \times (qr) / nu) \times (0.51) \times (nu / DFe) \times (2/3))
\]

\[
kmz = 0.91 \times 0.91 \times (qz) / ((d \times (qz) / nu) \times (0.51) \times (nu / DFe) \times (2/3))
\]

function TFFRDE_i_lim

This program calculates the local limiting current distribution for a TFFRDE. This solution is based on the flow field solution from the continuity equation (see Flow_field.m).

The limiting current is calculated for several different film heights, and for several rotation rates. The mass transfer correlation is from BSL, for a packed bed reactor. The local limiting current values are exported to a spreadsheet (TFFRDE.xls).

n = 10;
rpm = [200;400;600;800;1000;0];
[m,~] = size(rpm);
m = m-1;
b = 1;
d = 0.001; %fiber diameter, cm
DFe = 4.73e-6; %diffusion coefficient, cm2/s
F = 96500; %faraday's constant, C/mol
nu = 0.0105; %kinematic viscosity, cm2/s
cb = 1e-5; %bulk conc Fe, mol/cm3
R = 0.25;

heights = [.00716,.00832,.01182,.02342,.02689];
perms = [2000,1000,5000,4000,1800];
perms = perms.*10^-8; %For 200-1000rpm
limit = zeros(m+1,n,b);
vel = zeros(m+1,n);
i_levich = (0.62*F*cb*DFe^(2/3)*nu^(-1/6)).*rpm.^((1/2));

for b = 1:5
    H = heights(b);
    h = H/n;
    rough = 360;
    SA = rough*H;
    om = rpm(1).*(2*pi() / 60); %TF height, in cm
    %height of one slice, in cm
    %felt roughness factor, cm2/cm3
    %surface area of a slice, cm2/cm2
    %angular velocity, rad/s
end
rad = 0.25/n; % disk radius steps, cm
k = perms(b); % permeability, cm

i_lim = zeros(1,n);
r = zeros(1,n);
z = zeros(1,n);
z(1) = h;
r(1) = rad;

for i = 1:n-1
    z(i+1) = z(i)+h;
    r(i+1) = r(i)+rad;
end

a = sqrt(nu*om).*(2.*k.*H.*(om/nu)^(3/2))./(1+4*(om*k/nu)^2);
qr = a.*r./(2*H);
qz = -a.*z./H;
vector = sqrt(qr.^2+qz.^2);
vel(1,:) = vector;

km = (0.61*0.91/((R/nu)^(0.5)*(nu/DFe)^(2/3))).*(a./(2*H))^(0.5).*(r.^1.5)./1.5;
kmT = 0.91*0.91.*(qr)./((d.*(qr)./nu).^(0.51).*(nu/DFe).^(2/3));

for l = 1:n
    i_lim(l) = km(l).*cb.*F./(sqrt(nu*om));
end

limit(1,:,b) = i_lim.*SA;

for j = 1:m
    om2 = rpm(j+1).*(2*pi()/60);
    a = sqrt(nu*om2).*(2.*k.*H.*(om2/nu)^(3/2))./(1+4*(om2*k/nu)^2);
    qr2 = a.*r./(2*H);
    qz2 = -a.*z./H;
    vector2 = sqrt(qr2.^2+qz2.^2);
    km = (0.61*0.91/((R/nu)^(0.5)*(nu/DFe)^(2/3))).*(a./(2*H))^(0.5).*(r.^1.5)./1.5;
    KmT = 0.91*0.91.*(qr2)./((d.*(qr2)./nu).^(0.51).*(nu./DFe).^(2/3));
    for l = 1:n
        i_lim(l) = km(l).*cb.*F./(sqrt(nu*om2));
    end
    limit(j+1,:,b) = i_lim.*SA;
    vel(j+1,:) = vector2;
end
function felt_allcond_1D

% This program solves the 1D current distribution in a felt electrode for a set of electronic conductivities at a single overpotential. Slices proceed horizontally, from the current collector to the membrane. The limiting current is found using a mass transfer correlation for flow over a cylinder.

% The program uses butler volmer kinetics for the activation overpotential, the classical mass transfer overpotential, and both the ionic and electronic conductivities for the ohmic overpotential.

% Plots include the current distribution and the limiting current distribution as a function of step and slice.

sigma_e = [1;0.1;0.01;0.005]; % electrode conductivity, S/cm
[g,~] = size(sigma_e);

goal = .150; % goal overpotential in Volts
n = 30; % number of slices thick
slice = 1:n; % slice 1 = end plate, slice n = membrane
X = .5; % electrode thickness, in cm
x = X/n; % thickness of one slice, cm
Y = 7; %electrode length, cm
rough = 360 %felt roughness factor, cm2/cm3
SA = rough*x %surface area of a slice, cm2/cm2
d = 0.0010; %fiber diameter, cm

cb = .25e-3 %Fe concentration, mol/cm3
nu = 0.0105 %kinematic viscosity, cm2/s
DFe = 4.73e-6 %diffusion coefficient, cm2/s
q = 25 %volumetric flow rate, cm3/min
v = q/(x*Y*60); %fluid velocity, cm/s
M = 55.845; %Fe molecular weight, g/mol

io = .00001; %exchange current density, A/cm2
ioc = (io/.01e-3)*cb %exchange current density @ conc, A/cm2
ios = ioc*SA %exchange current density per slice, A/cm2
iLimf = 0.1 %limiting current density at slice n, A/cm2

sigma_b = 0.1 %electrolyte conductivity, S/cm
sigma = sigma_b*0.85^(3/2) %Sigma in the electrode, S/cm
Rs = x/sigma; %electrolyte resistance, ohm*cm2
Re = x./sigma_e %electrode resistance, ohm*cm2

F = 96500; %faraday's constant, C/mol
R = 8.314; %gas constant, J/mol*K
T = 298; %temperature, Kelvin
ne = 1; %number of electrons transferred
alpha_a = 0.4 %charge transfer coefficient, anodic
alpha_c = 1-alpha_a %charge transfer coefficient, cathodic

i_local = zeros(g,n); %local current density, A/cm2
i_lim = zeros(g,n); %limiting current density, A/cm2
i_sumI = zeros(g,n); %local i sum, ionic direction
i_sumE = zeros(g,n); %local i sum, electronic direction

for e = 1:g %local current density at each slice, A/cm2
    i_local(e,:) = (slice).*(ios./(goal.*22));
end

km = (.61*DFe/d).*(d.*v./nu).^(1/2).*(nu/DFe)^(1/3); %mass txfr coef
iLimf = km.*cb.*F; %limiting current, A/cm2
i_lim(:,:, :) = iLimf;

eta_a = zeros(g,n); %activation overpotential, V
eta_c = zeros(g,n); %concentration overpotential, V
eta_o = zeros(g,n); %ohmic overpotential, V

eta_a bv = 0:.00001:.500; %Solved butler-volmer kinetics
i bv = ios.*exp((alpha_a*ne*F/(R*T)).*eta_a bv) -
     exp(- (alpha_c*ne*F/(R*T)).*eta_a bv));
for e = 1:g
    %Solve for eta_a
    for k = 1:n
        i_slice = i_local(e,k);
        num_i1 = find(i_bv>=i_slice);
        placevalue = num_i1(1);
        eta_a(e,k) = eta_a_bv(placevalue);
    end
end

eta_c = abs((R*T/(ne*F)).*log(1-(i_local)./i_lim)); %solve for eta_c

for e = 1:g
    %sum i up to the slice, A/cm2
    for i = 0:n-1
        i_sumI(e,n-i) = sum(i_local(e,1:n-i));
        i_sumE(e,n-i) = sum(i_local(e,n-i:n));
    end
end

RI = Rs.*i_sumI; %Solve for eta_o
RE = zeros(g,n);
for e = 1:g
    RE(e,:) = Re(e).*i_sumE(e,:);
end
for e = 1:g
    for i = 0:n-1
        sumeta = sum(RI(e,n-i:n));
        sumetaII = sum(RE(e,1:n-i));
        eta_o(e,n-i) = sumeta + sumetaII;
    end
end

etaT = eta_a + eta_c + eta_o;
error = zeros(g,n);
for e = 1:g
    error(e,:) = etaT(e,:) - goal;
end

max_each = max(abs(error'));
max_e = max(max_each); %maximum etaT error

while max_e > 0.0001 %iteration solving for etaT
    i_localnew = i_local-0.0005.*error;
    for e = 1:g
        for k = 1:n
            i_slice = i_localnew(e,k);
            num_i1 = find(i_bv>=i_slice);
            placevalue = num_i1(1);
            eta_a(e,k) = eta_a_bv(placevalue);
        end
    end

    eta_c = abs((R*T/(ne*F)).*log(1-(i_localnew)./i_lim));
end
for e = 1:g
    for i = 0:n-1
        i_sumI(e,n-i) = sum(i_localnew(e,1:n-i));
        i_sumE(e,n-i) = sum(i_localnew(e,n-i:n));
    end
end

RI = Rs.*i_sumI;         % Solve for eta_o
for e = 1:g
    RE(e,:) = Re(e).*i_sumE(e,:);
end
for e = 1:g
    for i = 0:n-1
        sumeta = sum(RI(e,n-i:n));
        sumetaII = sum(RE(e,1:n-i));
        eta_o(e,n-i) = sumeta + sumetaII;
    end
end

etaT = eta_a + eta_c + eta_o;
error = zeros(g,n);
for e = 1:g
    error(e,:) = etaT(e,:) - goal;
end

max_each = max(abs(error'));
max_e = max(max_each)
i_local = i_localnew;

s = zeros(1,n);
s(1) = x;
for i = 1:n-1
    s(i+1) = s(i) + x;
end
il = i_local.*1000;

figure(1)
plot(s,il(1,:),s,il(2,:),s,il(3,:),s,il(4,:))
title('Current Distribution')
xlabel('Depth (cm)')
ylabel('Current Density, mA/cm^2')
legend('1','0.1','0.01','0.005')

end
References


