LOW-COST and METAL-FREE AQUEOUS FLOW BATTERY with ULTRAFILTERED LIGNIN ELECTROLYTE

A Thesis Presented

By

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ABSTRACT

As the number of generation sources from intermittent renewable technologies on the electric grid increases, the need for large scale energy storage devices is becoming essential to ensure grid stability. Flow batteries offer an advantage over conventional sealed batteries, as their energy and power can be scaled independently from one another. This allows flow batteries with properly developed electrolytes to increase their storage durations without needing to increase the capacity of expensive power equipment necessary to scale-up conventional batteries. In this work, a novel flow battery electrolyte is developed meeting the market demands of low cost, sustainability, non-toxicity, and eco-friendliness, which are required to enable energy storage at large scales. The electrolyte uses ligninsulfonate extracted from the waste of biofuel and paper manufacturing as the primary active material.

Various candidate lignins are screened for proper physical and electrochemical properties that enable practical use in a flow battery. A single cell flow battery system is built to quantify the performance of this new electrolyte. This flow battery system is designed for the inexpensive, renewable lignin electrolyte, and does not require any precious metal catalysts or expensive materials of construction to operate properly. The ligninsulfonate electrolyte was shown to have reversible redox behavior with low capacity decay over multiple cycles in half-cell testing. The ligninsulfonate battery was able to achieve current densities of up to 20 mA cm\(^{-2}\), and charge polarization resistance of 14.20 ohm cm\(^{-2}\). This technology presents a unique opportunity for a low cost, metal-free, battery capable of multiple charge-discharge cycles for safe, large scale energy storage.
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NOMENCLATURE

Abbreviations

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<td>Br₂</td>
<td>Bromine</td>
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<tr>
<td>HBr</td>
<td>Hydrobromic acid</td>
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<tr>
<td>H⁺</td>
<td>Hydrogen (ionic form)</td>
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<tr>
<td>e⁻</td>
<td>Electron</td>
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<td>OCV</td>
<td>Open Circuit Voltage</td>
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<td>E⁰</td>
<td>Standard thermodynamic potential</td>
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<td>NHE</td>
<td>Normal hydrogen electrode</td>
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<td>V</td>
<td>Volts</td>
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<td>t</td>
<td>Time</td>
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<td>I</td>
<td>Current</td>
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<td>SOC</td>
<td>State of charge</td>
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<tr>
<td>r</td>
<td>Resistance</td>
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<td>Cycle number</td>
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<td>E</td>
<td>Electrode potential</td>
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<td>z</td>
<td>Number of electrons</td>
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<td>DI</td>
<td>De-ionized</td>
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<td>L</td>
<td>Liter</td>
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<td>P NMR</td>
<td>Phosphorus nuclear magnetic resonance</td>
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<td>m</td>
<td>Meter</td>
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<td>SEC</td>
<td>Size exclusion chromatography</td>
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<td>UV</td>
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</table>
C  Celsius
s  Second
CV  Cyclic voltammogram
M  Molar
AgCl  Silver chloride
FS  Flex stak
FBH  Flow battery hardware
W  watt
U  Energy
F  Faraday’s constant
A  Ampere

Greek letters
η  Efficiency
α  Charge transfer coefficient
Ο  Overpotential

Superscripts/ Subscripts
°  Degrees
c  Coulomb / Charge
d  Discharge
p  polarization
V  voltage
eq  Equilibrium
el  Electrolyte
Chapter 1 – Introduction

1.1 Background

The need to reduce dependence on carbon emitting forms of electricity generation has led to a recent increase in the integration of environmentally friendly energy sources. Two of the most rapidly growing forms of renewable energy, solar and wind, present demand response issues for electrical infrastructure due to their intermittent nature. During high demand periods these intermittent sources require supplemental power output in the form of either peaking power plants or electricity energy storage. Solid electrode batteries have been deployed for short duration load deferment, however since power and energy cannot be scaled independently from one another in these batteries, they cannot be cost-effectively designed to sustain peak power output for long enough durations to effectively defer wind and solar.

Redox flow batteries do not suffer from this limitation, and therefore provide a viable path for long duration grid scale load deferment. However, redox flow battery development has historically been burdened by the high costs of their materials of construction, high cost of electrolytes, and precious metal catalysts required to drive the desired redox reaction. Recently, ligninsulfonate has been investigated as a low cost, earth abundant material that is redox active due to its naturally forming phenol groups. Ligninsulfonate is a very common biopolymer, comprising approximately 20 to 30% of the biomass of most types of wood. Lignins are produced as a byproduct of the pulping process during paper manufacturing, and due to limited industry demand for lignin derivatives they are often burned at a low heating value to recover their waste energy for the paper manufacturing process. Because of the abundance of this lignin byproduct, an estimated 9.8 x 10^5 tons per year, and its limited use, lignin is a low cost and sustainable material.

The redox functions of lignin are used in energy conversion processes in plants. Because of this known redox activity, lignin has seen some precedence being studied as a redox active species for manmade materials. Lignin has been used as a doping agent with polypyrroles to make electrodes, and was shown to increase the stability of the polymer
while also improving the charge storage capacity. However, until now lignin has not been used as an active species in an aqueous flow battery electrolyte. This work puts ultrafiltered lignin sulfonate solutions in a flow battery system using carbon electrodes with no expensive precious metal catalyst. The redox behavior of the lignin is shown to be relatively stable and repeatable, with the ability to be charged and discharged multiple times, and the potential for high energy densities.

1.2 Advantages of a lignin flow battery

In this work, for the first time, we investigate the use of lignin as an electrolyte in a redox flow battery. Unlike many existing flow battery technologies, lignin is sustainable, renewable, and earth abundant as it is a naturally occurring biopolymer. It is non-toxic to animals, contains no heavy metals, and is environmentally friendly. Some lignins have even been approved for use as a dust control dispersant on dirt roads, which speaks to the lack of adverse effects that lignins have on the environment. Lignin flow batteries have an advantage over other redox chemistries, as they could potentially be deployed at energy capacities large enough for grid-scale load deferment without posing any significant health or environmental hazards to their surroundings.

During pulping processes for paper manufacturing, the useful pulp is extracted and separated from the rest of the material in the feedstock, leaving behind a waste product known as black liquor. This black liquor contains high concentrations of lignin, up to approximately 43 wt% depending on the feedstock and pulp extraction method used. Figure 1 shows a simplified schematic of lignin extraction from a typical pulping process. After the pulp is removed, the lignin-rich black liquor waste product is most often dried and sent back to the plant to recover the energy from this material in the form of heat. The black liquor does not have a high heating value compared to more common forms of carbon based heating fuel, and therefore is not generally regarded as a useful fuel. Rather than being burned, the lignin material can easily be separated from the other black liquor constituents using ultrafiltration methods. When these methods are used on the black liquor byproduct of the sulfite wood pulping process, sulfonated lignins are produced and can be dried to yield a fine brown powder, which is shown below on the right side of
Figure 1. These sulfonated lignins, also called ligninsulfonate, are highly water soluble and can also be dissolved in many acids.

Figure 1: Simplified flow diagram of a typical lignin extraction process. Lignin powder is derived from black liquor, a waste product of pulping processes used in the manufacture of paper.

Because the extraction process of useful lignins from black liquor is so simple, and since both are waste products of a high volume process, they are produced at very low cost. Because of the limited commercial uses for lignin there is not a well-established supply chain for this material. Still, in 2013 Arkell et al determined that ultrafiltered lignin could be produced at a concentration of 230 g L⁻¹ for as little as $180 per ton.¹⁷ This combination of low cost, sustainability (waste to energy), earth abundance, and non-toxicity makes lignin a very appealing flow battery chemistry.

1.3 Theory of Operation

A typical flow battery system contains two electrolytes, one positive and one negative, which are each stored in electrolyte tanks, outside of the battery cell itself. Each tank has a pump to deliver the liquid electrolytes to the battery cell, where they are kept separate by a membrane, and back to the return of each tank. This allows the electrolyte to constantly be circulated through the cell during operation. The cell itself has carbon electrodes to facilitate electrochemical reactions, and is connected to a power source and sink, allowing electric power to move in and out of the flow battery system. Figure 2 shows a simplified version of such a flow battery system.
Figure 2: Schematic of the lignin flow battery system assembly

The battery cell itself consists of a series of layers mirrored about a central membrane, as shown in Figure 3. The membrane keeps the electrolytes separate and is electrically insulative and ionically conductive. This allows free ions to move between the two electrolytes, while encouraging free electrons to find a lower-resistance path out of the cell. Next, on either side of the membrane are one or more layers of electrode material, often in the form of carbon paper, cloth, or felt, to facilitate electrochemical reactions within the electrolytes. After this are some seals and solid graphite plates with flow fields machined or cast into them. These allow the liquid electrolytes to flow freely through the battery while also coming into contact with the electrodes and the membrane so that ion exchange between the electrolytes can take place. On the other side of each flow field is a current collector to connect the cell to an electrical source and load, and a set of pressure plates to keep the entire assembly under compression. Oftentimes, such as in
one of the cells used in this research, the function of the pressure plate and current collector are combined into the same plate.

Figure 3: Flow battery cell assembly. The flow battery cell comprises multiple flat layers held together by tie rods.

Ligninsulfonates contain naturally occurring phenol groups, which undergo a reversible two electron, two proton charge transfer when dissolved in a suitable charge carrying electrolyte and put under elevated electric potential on a carbon electrode. Figure 4 illustrates part of the lignin molecule undergoing this phenol/quinone reaction, releasing two electrons and two hydrogen ions in the process. The lignin molecule itself is much larger than what is shown in the figure, and in fact the exact chemical structure of lignin is not known, despite it being one of the most abundant biopolymers on earth.\textsuperscript{18, 19} Still, the phenol groups are assumed to be the only part of the lignin molecule that participate in the redox reaction, and the rest of the molecule shows no signs of degradation even under repeated redox cycling.
In this study, the ligninsulfonate solution was used as the negative electrolyte, and a solution of bromine (Br₂) and hydrobromic acid (HBr) was used as the positive electrolyte. The ion and electron exchange reactions in each half cell are shown in Equation 1.

$$\text{Positive half cell: } \quad \text{Charge} \quad 2\text{HBr} \rightleftharpoons \text{Br}_2 + 2\text{H}^+ + 2\text{e}^-$$
$$\text{Discharge}$$

$$\text{Negative half cell: } \quad \text{Charge} \quad (\text{Lig})-2\text{OH} \rightleftharpoons (\text{Lig})-2\text{O} + 2\text{H}^+ - 2\text{e}^-$$

In all aqueous flow batteries, there also exists the potential for unwanted side reactions where water is split into its constituents.

$$\text{Hydrogen evolution: } \quad 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$
$$\text{Oxygen evolution: } \quad 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$$

These hydrogen and oxygen evolution reactions, shown in equation 2, are harmful for several reasons. Perhaps the most obvious reason is that the water splitting causes water
to exit the system as the battery operates, which leads to loss of water, and increase in electrolyte concentration. This can, in turn, increase the viscosity of the electrolyte, thus leading to overpressure and clogging problems in the flow field, and in extreme cases can even lead to the active materials dropping out of solution. These side reactions also must be avoided as they are driven by electrical energy, which would otherwise be going to charging and discharging the desired redox reaction, and therefore decrease the performance and efficiency of the battery. In some cases, gas bubbles have even been known to form and stay on the electrode surfaces, thus decreasing the contact area of the electrodes and decreasing overall efficiency. These side reactions occur when the battery is operated outside of certain voltage boundaries, which are dependent on the pH and presence of catalysts in the system. In this work, the voltage boundaries have been limited in order to minimize the hydrogen and oxygen evolution side reactions.

1.4 Major Factors Driving Performance
Flow batteries are complex systems, with many chemical, electrical, and mechanical factors driving their overall performance. The most impactful of these factors are discussed in this section.

1.4.1 Open Circuit Voltage
The Open Circuit Voltage (OCV) of the battery is the voltage difference between the two half cells when no electric current is passing through the external circuit. This voltage is of great importance to flow battery systems because it determines the amount of energy that is supplied or stored per unit charge passed. In thermodynamic terms, this is the difference between the standard potential for the anode and cathode, or:

\[ E^{0}_{\text{cell}} = E^{0}_{\text{anode}} - E^{0}_{\text{cathode}} = E^{0}_{\text{positive}} - E^{0}_{\text{negative}} \]  

(3)

The Br\(_2\)/HBr reaction on the positive side is well known to have a standard potential of +1.06 V vs. normal hydrogen electrode (NHE)\(^1\) whereas the lignin reaction on the negative side was measured to be between +0.36 and +0.66 V when corrected for NHE depending on the specific lignin material used. Determination of this standard potential will be discussed later.
It is important to note that equation 3 leads to OCV’s of the lignin/bromine battery between approximately 0.4 and 0.7 volts depending on the lignin used. This is relatively low for flow battery technologies, and therefore in a commercial application bromine would not necessarily be an ideal counterpart to the lignin electrolyte half-cell. The Br₂/HBr half-cell was chosen for this study because it is well understood, and therefore is useful to help quantify the lignin redox behavior in a flow battery.

1.4.2 Current and Voltage Efficiency
There are many ways to express the efficiency of battery systems. Two of the most common are the current and voltage efficiency. Current efficiency (also referred to as coulombic efficiency) is defined as the ratio of discharge capacity to charge capacity per cycle, or

$$\eta_c = \frac{\int_{t_0}^{t_d} i_d \, dt}{\int_{t_0}^{t_c} i_c \, dt}$$

Where $i$ is the current, and $t$ is the time of charge or discharge.\(^{22}\) In this work the current efficiency is calculated during constant current cycling, by dividing the discharge time by the charge time of the previous half cycle.

The voltage efficiency is also of fundamental importance to battery systems. Voltage efficiency varies with state of charge (SOC) and current density, and is given for a certain SOC and current density as

$$\eta_V = \frac{V_{OC} - i_d r_p}{V_{OC} + i_c r_p}$$

Where $V_{OC}$ is the OCV at the given SOC, and $r_p$ is the polarization resistance.\(^{23}\)

1.4.3 Capacity Retention/Crossover
Capacity retention throughout multiple charge discharge cycles is another important metric in flow battery qualification. The primary cause of capacity decay for most flow
batteries is active material crossover through the membrane. Another potential way to lose capacity, which the lignin battery appears to be susceptible to, is degradation of the organic electrolyte due to unwanted oxygen bonding. During cyclic tests at constant current density, the capacity retention of the battery per cycle can be determined by dividing the discharge time of the nth cycle by the discharge time of the n-1 cycle.

Flow batteries also experience another, less damaging form of membrane crossover known as “water transport.” Water transport, as its name implies, is the migration of water molecules across the membrane mainly due to the differential pressure driven osmosis of water through the membrane, and the electroosmotic convection caused by the viscous interactions between the water and the migrating hydrogen ions. This can lead to unwanted changes in the concentration of the two electrolytes during each cycle, and over time can lead to the complete depletion of one tank and overflow of the other if there is a net amount of water transport after each complete cycle.

1.4.4 Cell Resistance

Electrochemical battery theory breaks battery cell resistance into four major components, which are activation, mass transport, ionic, and electronic resistance. The bulk resistance of the battery cell is defined by its polarization curve, which is the slope of the voltage vs current density as shown in Figure 5. This is because, unlike many conventional resistors, battery resistance changes with current.
Figure 5: Example of a polarization curve. The overall cell resistance is determined by the slope of the curve.

Activation losses cause overpotential in the battery due to the electrochemical kinetics of the electrolyte solutions on the electrodes. Essentially, activation losses are the physical resistance of the electrolyte/electrode pair to perform the desired redox reaction, due to the speed of the reaction.\(^{27}\) In any flow battery system, a potential higher than the thermodynamic equilibrium value needs to be applied in order to transfer electrons and ions between the electrolytes. Typically, the activation overpotential can be calculated using the Butler-Volmer equation:

\[
i = i_o \times \left\{ \exp \left[ \frac{\alpha_a z F}{RT} (E - E_{eq}) \right] - \exp \left[ \frac{\alpha_c z F}{RT} (E - E_{eq}) \right] \right\} \tag{6}
\]

Rearranging gives:

\[
O_{\text{activation}} = \frac{RT}{\alpha_a z F} \ln(i) - \frac{RT}{\alpha_c z F} \ln(i_o) \tag{7}
\]
Where E is the electrode potential, $E_{eq}$ is equilibrium potential, $\eta_{activation} = (E - E_{eq})$ is the activation overpotential, $z$ is the number of participating electrons, $\alpha$ is the charge transfer coefficient, and $i$ and $i_o$ are the electrode current density and exchange current density, respectively. 28

Mass transport losses are the result of concentration gradients of the active materials in the electrolyte at the electrode surfaces. As the redox reaction occurs on the surface of the electrode, areas where the reaction has taken place are depleted of ions that can participate in the reaction, and thus the products need to be removed from the reaction zone so that they can be replaced with fresh reactants. Furthermore, electron transfers will only occur on a thin reaction layer, usually less than 1 nanometer thick, between the surface of the electrode and the electrolyte. 27 A schematic of this is shown in Figure 6. As ions travel across the membrane and into the other electrolyte, and electrons travel through the electrode and out of the battery system, they are replenished via diffusion of unreacted electrolyte through the electrode. If the reaction occurs faster than the reactive species are being replenished, then mass transport overpotential will occur. 27 As current density increases this resistance to diffusion becomes more and more limiting.
Figure 6: Schematic of mass transport limitation mechanism (not to scale). The reaction at the electrode surface is limited by the rate at which active materials can be removed and replaced.

There are many ways to mitigate the effects of these diffusion limitations, however most of these have other adverse effects on the battery system performance. For instance, the flow field design can be modified to encourage diffusion towards the reaction zone. Interdigitated flow field designs with tapered flow channels and multiple passes have been shown to have a positive effect on mass transport resistance, but these designs often lead to higher liquid pressure drop through the flow field.²⁹ Similarly, increasing electrolyte flow rate will have the same effect of encouraging active materials to contact the membrane, while in turn increasing pressure drop through the cell, parasitic pumping loads on the flow battery system, and wear on the system components.
The other major cause of overpotential is IR loss, which are losses due to electrical and ionic resistance in the various parts of the flow battery. In order to do useful electrical work outside of the battery systems, the electrons need to travel through essentially all of the solid parts of the cell in order to make their exit, including the electrode, carbon plate, and current collector. They encounter electrical resistance while travelling through each one of these zones, although often times the graphite plates and current collectors are sufficiently designed so that their imposed electronic resistance is negligible. There are also contact losses between all of these parts, which must be taken into consideration when determining materials of construction, machining tolerances, and assembly methods of the battery cell. Ionic losses are due to the ionic resistances in the electrolyte and the ion exchange membrane. Figure 7 shows a summary of IR losses for a full cell.

![Figure 7: Summary of IR losses in a full redox flow cell. While electronic resistance through the solid parts of the battery are negligible, electronic and ionic resistances through the electrolytes and soft goods can be substantial.](image)

In a well-designed flow battery cell, ionic losses dominate electronic losses. Ionic losses in the membrane can easily be combated by decreasing the thickness of the membrane. However, as the membrane thickness decreases the mechanical strength of the membrane...
also decreases, and active material crossover generally increases. Thus a balance between these factors must be achieved along with appropriate pretreatment methods in order to optimize the membrane design.

Because the differences between mass transport overpotential and ionic overpotential can be difficult to measure directly, this work focuses on the polarization curve of the various battery/electrolyte configurations in order to quantify the overall battery performance. Electronic resistance is easily measured by assembling cell hardware without an ion exchange membrane in place, while activation overpotential and reaction kinetics are determined via half-cell measurements of the electrolytes.

1.4.5 Cyclic Stability

The cyclic stability of a flow battery system is of critical importance. Most commercial applications for flow batteries require that they last for several years in order to recuperate the relatively high setup cost of installing a flow battery system. During this time the batteries are usually cycled at least daily, requiring tens to hundreds of thousands of cycles over the life of the device. Cyclic stability can be measured using a number of metrics, with perhaps the most important being loss of current efficiency and capacity retention.

Although the definition of current efficiency was discussed earlier, the various mechanisms that may lead to loss of current efficiency have yet to be explored. Some of the known mechanisms that will lead to both current efficiency and capacity retention loss do so by deactivating the redox active species. This can occur from decomposition of the lignin molecules, active material crossover through the ion exchange membrane, or from external leakage. Losses to both of these metrics can also be induced from unwanted side reactions, such as the water splitting reactions mentioned earlier. Like other organic battery electrolytes, there also exists the potential for loss of current efficiency due to other side reactions that involve unwanted bonding with the organic active material. These can occur from Br₂ crossover into the lignin electrolyte, or from oxygen permeating the flow battery system. An example of this is shown in Figure 8,
where the phenol group undergoes halogenation even in the absence of a catalyst because of the presence of the highly activating hydroxyl group.\textsuperscript{33}

![Figure 8: An example of possible phenol halogenation](image)

In both the bromine crossover and oxygen permeation cases a reduction reaction occurs, which leads to current efficiency loss as the electrons involved do not need to travel through the external circuit.\textsuperscript{23}

1.4.6 Other Performance Considerations

There are other variables that have a significant impact on the overall performance of the flow battery, mostly having to do with the physical and mechanical properties of the electrolytes and materials of construction. These include the wettability and pretreatment methods used for the electrodes and ion exchange membrane, the physical properties of the electrolytes, and the fluidic pressure drop in the flow battery system.

Flow battery electrodes are most often built out of porous carbon materials, in the form of carbon cloth, paper, or felts. There are various methods of mechanical, thermal, and chemical treatments that have been studied, which can have a strong impact on the electrode performance.\textsuperscript{34} In particular, increasing the wettability helps improve electrolyte accessibility and can have a marked effect on performance.\textsuperscript{35} The ion exchange membranes have also shown the benefits of improved ionic conductivity and decreased active material permeability when subjected to certain pretreatment methods.\textsuperscript{36}

The physical properties of the electrolytes, besides their redox characteristics, will also affect the performance and cost of the battery system. The pH of both electrolytes needs to be kept in a range where they will not be overly corrosive or incompatible with
common materials. The use of electrolytes with extreme pH values or overly corrosive characteristics would require that the wetted materials in the battery be built out exotic materials that can withstand these properties. This is not cost effective in most battery systems. Furthermore, the conductivity of the electrolyte needs to be kept in a range where it will allow the flow of electricity and ions, while not being overly conductive. If an electrolyte is too conductive, excessive parasitic shunt currents will form in the battery, which are the result of voltage differences between each cell and each electrochemical stack in the battery system. These currents, although almost always present in electrochemical stacks, increase as the conductivity of the electrolyte increases.  

Finally, density and viscosity of the electrolytes need to be optimized with respect to the parasitic losses encountered in flow battery systems. When designing a flow battery, it is tempting to push the electrolytes to their solubility limits in order to get the best energy density possible. However, this can also lead to increases in the viscosity and density of the solution, which in turn will require more pumping power to deliver reactants to and from the electrochemical stack. The pumping power in any flow battery system is considered to be a complete loss to the system efficiency, as this power does not generate useful electricity able to do work outside of the system. These losses are especially prevalent in an unmodified, organic molecule like lignin, where the useful phenol groups are only a small part of the larger lignin structure. Although highly soluble, the large molecular structure of the ligninsulfonate rapidly increases the density and viscosity of the solution as the concentration is increased, in turn increasing the viscous drag through the system and requiring more parasitic motive power. Thus, a balance must be achieved between the abundance of active groups in the solution, and the overall physical characteristics of the pumped fluid.
2.1 Material Qualification

Dissolution experiments were carried out on various lignins in order to determine types of lignin that could be candidates for inclusion in a flow battery. CleanFlow black ligninsulfonate, unfiltered ligninsulfonate, and Kraft lignin from KTH Royal Institute of Technology as well as commercially available sodium ligninsulfonate from TCI America were each dissolved in solvents of DI water, hydrochloric acid, perchloric acid, and sodium hydroxide. The Kraft lignin was also dissolved in acetic acid. Each sample was comprised of 10 mL of solvent with various weights of lignin powder. After shaking, the solutions were stirred using a magnetic stirrer for approximately 1 hour at room temperature. The solutions were then left to rest at room temperature for 48 hours, after which they were visually inspected for sediment dropout.

Viscosity testing was performed on candidate solutions by a Discovery HR-2 Rheometer (TA Instrument, USA) at 25 °C. The samples were measured at a shear rate from 0.01 to 100 s\(^{-1}\).

Analysis of functional groups was performed through quantitative \(^{31}\)P NMR analysis with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane as a derivatization reagent and eHNDI (Endo-N-Hydroxy-5-norbornene-2,3-dicarboximide) as an internal standard. Sample preparation was carried on according to Areskogh et al.\(^{38}\) Signal assignment and quantification was performed as described elsewhere.\(^{39}\)

Molecular weight distributions of the samples were investigated by dissolving 5 mg of lyophilized samples in 2 ml of DMSO+0.5% LiBr (w/w) solution. After filtration of the samples through 0.45 um PTFE filters, size exclusion chromatography (SEC) was performed on an SEC 1260 Infinity instrument (Polymer Standard Services, Germany). The equipment consisted of an isocratic pump (G1310B), a micro degasser (G1379B) and a standard autosampler (G1329B). The detection system included a UV detector (G1314B) in series with a refractive index detector (G1362A). The mobile phase was DMSO+0.5% LiBr set to a constant flow rate of 0.5 ml/min for a total run time of 65
minutes. The injection volume was 100 μL. The separation system consisted of PSS GRAM Precolumn, PSS GRAM 100 Å and PSS GRAM 10000 Å analytical columns thermostated at 60 °C and connected in series. The pullulan standards with nominal masses of 708 kDa, 337 kDa, 194 kDa, 47.1 kDa, 21.1 kDa, 9.6 kDa, 6.1 kDa, 1.08 kDa and 342 Da were used for standard calibration.

pH and conductivity measurements were taken using an Oakton pH/CON Portable Meter (PC 450). Calibration was done at room temperature using Oakton 1413 and 12880 µS conductivity standards (WD-00653-18, WD-00606-10), and Oakton 4 and 7 pH buffers (EW-00654-00, EW-00654-04)

2.2 Electrochemical Testing

Half-cell measurements were performed on a BioLogic SP150 single channel potentiostat controlled by BioLogic EC-Lab software. Voltage and current were logged at 0.1 mV increments. Generally the voltage was ramped between 0.1 V and 0.7 V. However some of the voltammogram traces presented in this work are trimmed for clarity and to emphasize the redox peaks. Constant scan rates of 25 and 60 mV/s were used on all of the presented data.

For cyclic voltammogram (CV) measurements on lignin solutions, 60 mg of dried lignin powder was dissolved in 50 mL of 0.1 M perchloric acid and stirred at room temperature for 5 minutes. For measurements on dried lignin, solutions of 0.1 M lignin in DI water were dropped on 10 x 20 mm AvCarb carbon paper (P50) working electrodes and allowed to dry for 24 hours. The working electrode with the dried lignin was then immersed in 50 mL of 0.1 M perchloric acid for CV measurements.

All CV experiments used a single-junction Fisher Scientific Accumet Glass Body Ag/AgCl Reference Electrode (1362053) with 4 mol/L KCl filling solution, and a platinum foil counter electrode. A variety of working electrodes were used, including the aforementioned carbon paper, gold foil, and a 5 mm diameter glassy carbon electrode. Prior to each use, the glassy carbon electrode was polished on 600 grit paper with polishing compound, sonicated for 10 minutes in methanol, followed by a 10 minute
sonication in DI water. The CV’s were performed in a 125 mL 3-neck flask and purged with argon gas unless otherwise noted. A photo of this CV setup is shown in Figure 9.

Figure 9: CV test apparatus. The chamber was sealed and put under an inert gas headspace.

2.3 Electrolyte Preparation

For the positive electrolyte, 200 mL solutions of 0.5 M bromine and 0.25 M hydrobromic acid in DI water were used in the fully charged state. Both the bromine and hydrobromic acid were commercial material obtained from Sigma-Aldrich.

The negative electrolyte solution was made by heating 50 mL of DI water to 50 °C and stirring in 0.1 M of dry ligninsulfonate powder. After the powder was thoroughly dissolved, the solution was spiked with enough 70% (w/w) perchloric acid (Sigma-Aldrich) to bring the acid concentration of the solution to 0.1M. The solutions where then loaded into 250 mL electrolyte “tanks” for use in the flow battery system.
A Photograph of each electrolyte in the charged state is shown in Figure 10.

![Figure 10](image)

Figure 10: (Left) positive electrolyte comprised of 0.5 M bromine and 0.25 M hydrobromic acid in DI water; (Right) negative electrolyte comprised of 0.1 M ligninsulfonate in 0.1 M perchloric acid

2.4 Flow Battery Test Apparatus

The flow battery system consisted of a single battery cell assembly, two electrolyte tanks, peristaltic pumps for electrolyte circulation, temperature control equipment, and pressure monitoring equipment. The electrolyte tanks used were 250 mL glass flasks. For temperature stability they were submersed in water and placed on a Fisher Scientific Isotemp Stirring Hot Plate (SP88857200). The negative electrolyte tank was sealed from the atmosphere and constantly purged with nitrogen to limit oxygen interaction with that electrolyte. Prior to entering the tank, this nitrogen was hydrated with 0.1 M perchloric acid in a liquid trap in order to prevent excessive electrolyte evaporation. The electrolyte pumps were MasterFlex L/S heads (HV-07516-02) powered by a L/S economy variable speed drive (HV-07554-80). Cell inlet pressures were monitored by analog pressure gauges with CPVC gauge guards. All interconnections were made with flexible PVC tube and barbed PVDF tube fittings. The flow battery cell was placed above the rest of
the system for easy draining between tests. A photo of the flow battery system can be seen in figure 11.

![Flow battery test system](image)

Figure 11: Flow battery test system

Two cell assemblies were used to qualify the lignin flow battery. The first assembly was a Fuel Cell Store Flow Battery Flex Stak (FS) (3101603). This consisted of a single cell with a 10 cm² active area, and a machined interdigitated flow field on the solid graphite plates. Soft goods were held in place and sealed by 2 layers 1/64” PTFE gaskets on each side. The current collectors were copper, and were encased in machined PVC pressure
plates. The eight machine screws along the outside of the cell were torqued to 15 in-lbs to hold the assembly together. Figure 12 shows the FS assembly (left) and the interdigitated flow field (right).

Figure 12: (Left) FS Cell Hardware assembly; (Right) interdigitated flow field used in this hardware.

The other cell used was a Fuel Cell Store Flow Battery Hardware (FBH) assembly (72108114), consisting of a single cell, 5cm$^2$ active area. This cell had column flow patterns machined into the solid graphite plates, with separate terminals for direct voltage referencing directly on the plate. The cell was sealed by 1/16” or 1/32” gaskets depending on the soft goods configuration used. End plates were ¼” thick, gold plated aluminum, which also served as the current collectors. Each end plate included a 60W heater to regulate cell temperature. The assembly was held together by 8 machine screws torqued to 15 in-lbs. Figure 13 shows the FBH assembly (left) and column flow field (right).
Figure 13: (Left) FBH cell hardware; (Right) column flow field used in this hardware.

For certain tests, FKM o-ring material was inserted into the column flow field, in order to simulate an interdigitated flow field. This modification is indicated by the red arrows in Figure 14.

Figure 14: Column flow field with FKM inserts

Various soft goods were used on the flow battery builds. Carbon felts and carbon papers were pre-treated using a Unaxis Plasma Therm 790 system at 13.56 MHz frequency for
the plasma excitation. During the oxygen plasma treatment, system pressure and oxygen flow rate were kept constant at 2 mT and 25 sccm, respectively. RF plasma power was 150 W and the exposure time was 15 secs.

The membrane pretreatment method involved a 24 hour soak in 0.1 M perchloric acid at room temperature, followed by triple rinsing in DI water prior to loading in the cell. The various cell builds used in these experiments are summarized in Table 1.

![Table 1: Flow battery cell build summary](image)

The temperature of the flow battery electrolytes was maintained at 30 °C, and the 2x 60 W heaters on the FBH cell were plugged in during tests on that assembly. Flow rates remained constant at approximately 250 mL/min. The flow fields of all cells were configured in a co-flow pattern, with the inlet at the bottom of the cell and the outlet at the top in order to mitigate the potential for hydrogen gas vapor locking. Inlet pressures were maintained below 0.5 bar gauge, and differential pressure across the membrane was maintained below 0.1 bar differential. The battery was powered by a BioLogic MPG2 16 channel potentiostat controlled with BioLogic EC-Lab data acquisition and control software.

2.5 Theory and Methods

Theoretical energy density of the lignin electrolyte was calculated based off of the concentration of useful phenol groups in the lignin material. The concentration of phenol groups in the lignin can be related to theoretical energy density via the equation:

\[
U_{el} = F \times V_{oc} \times M_{phenol}
\] (8)
with $U_{el}$ equal to the energy density of the electrolyte, $F$ as Faraday’s constant, $V_{oc}$ as the OCV of the battery at its average state of charge, and $M_{phenol}$ the concentration of phenol groups per unit mass.

OCV was measured by monitoring voltage with no load on the battery system besides the voltage of self-discharge for long periods of time. Usually, this was at least one hour. For measurements where an OCV hold could not be held for such a long period of time, such as during OCV sweeps at various states of charge, the cell was taken to be at its OCV once the rate of voltage change was less than 0.01 mV/s.

Polarization curves, used to measure charge and discharge resistance, were taken by charging and discharging the battery at different rates, with 1 mA/cm$^2$ steps between measurement points. The voltage was allowed to equilibrate for 60 seconds at each current density prior to proceeding to the next step. Plots of voltage versus current were made out of this data, and a linear best fit line was plotted using graphical analysis software. The slope of this line was used to calculate the polarization resistance.

Current efficiency and capacity retention were measured over multiple galvanostatic charge discharge cycles with constant voltage limits. Current efficiency was defined as the discharge time divided by the charge time of the previous half cycle. Capacity retention was defined as the discharge time divided by the discharge time of the previous cycle.
3.1 Lignin Material Qualification

The physical properties of various candidate lignins were studied to determine the best electrolyte formulation to use in the lignin battery. The organic structure, molecular weight, and phenol content of ligninsulfonate varies widely depending on the feedstock it was extracted from, the extraction process used, and the methods of filtration and drying. CleanFlow black ligninsulfonate, unfiltered ligninsulfonate, and Kraft lignin from KTH Royal Institute of Technology as well as commercially available sodium ligninsulfonate from TCI America were each dissolved in solvents of DI water, hydrochloric acid, perchloric acid, and sodium hydroxide. Concentrations were increased until the solution started to become noticeably more viscous, indicating that they would not perform well in the flow battery.

The unfiltered ligninsulfonate became highly viscous and formed a mud-like consistency even at low concentrations. Flow battery electrolytes typically have viscosity similar to that of water, and thus the unfiltered material was eliminated as a candidate. The Kraft lignin was soluble in sodium hydroxide, but not water or any of the acidic solvents. It was also tested in various concentrations of acetic acid, but was only soluble in very high concentrations of this solvent. An electrolyte comprised of concentrated acetic acid would require flow battery hardware made out of expensive materials in order to avoid compatibility problems, so an acetic acid solvent was ruled out. Likewise, a basic solution was not viable at this stage in the lignin battery development, and therefore Kraft lignin was ruled out entirely as a candidate material. The CleanFlow lignin and TCI lignin both stayed relatively inviscid even at concentrations of up to 400 g/L, and therefore we studied in the battery further.

KTH Royal Institute of Technology in Stockholm, Sweden supported this work by supplying candidate lignins and performing size exclusion chromatography and P NMR analysis. Size exclusion chromatography was performed on the CleanFlow ligninsulfonate sample, and yielded a molecular weight of 4,000, which is on the lower end of the molecular weight range for lignins. An analysis of functional groups was
performed through quantitative P NMR analysis, showing an average phenol group concentration of 1.11 mmol g\(^{-1}\) for this material, as seen in Figure 15. This combination of high phenol concentration and low molecular weight is critical for the success of the battery. The high phenol concentration ensures the presence of active materials to facilitate the redox reaction even at modest electrolyte flow rates, while the low molecular weight ensures that the viscosity of the electrolyte solution stays in a range where the material can move freely through the flow field without using excess pump power or risking damage to the ion exchange membrane. Based on these results a solution of 0.1 M lignin dissolved in 0.1 M perchloric acid was formulated for the negative electrolyte, with an approximate energy capacity of 7 Wh L\(^{-1}\) when used with Br\(/\)HBr as a redox couple. Higher concentrations with higher energy densities can easily be made as the ligninsulfonate material is very soluble in water and mild acids;\(^\text{42}\) however for this proof of concept the concentration was intentionally kept low in order to facilitate flow through the battery chamber.

Figure 15: P NMR spectra of best performing lignin. The useful phenol groups show an average concentration of 1.11 mmol g\(^{-1}\).
3.2 Cyclic Voltammetry

To gain further insight into the redox reaction in the lignin phenol groups, half-cell measurements were performed on the ligninsulfonate raw material and diluted negative electrolyte. Figure 16a-c show cyclic voltammetry of the CleanFlow ligninsulfonate material in 0.1 M perchloric acid with various working electrodes. All show a single step electron transfer with high symmetry centering at 0.5 V vs Ag/AgCl. This is consistent with the open circuit voltage against Br₂/HBr in the flow battery (opposing half reaction \( \text{Br}_2 + 2e^- \leftrightarrow 2\text{Br}^- \ 0.86V \text{ vs Ag/AgCl} \)).\(^{43}\) The symmetry and apparent redox reversibility are attributed to the stability of the oxidized lignin product in acidic conditions.

Figures 16a and 16b were tested at a scan rate of 25 mV s\(^{-1}\) with the lignin material in solution at a concentration of 0.3 mM. Both of these show ends which are not second peaks, but are inherent from the background trace of the supporting electrolytes. Due to the limited amount of phenol groups available in such a dilute solution the reduction and oxidation peaks are not very large, but still clearly show reversible redox behavior. Figure 16a shows a trace of the lignin material being cycled 15 times on a gold foil working electrode without any substantial indications of irreversibility, aside from the first cycle. This reduction in peak size after the first cycle was observed consistently over a number of trials, and is likely due to dissolved oxygen in the solution oxidizing the ligninsulfonate before it is depleted. This first-cycle irreversibility is not observed in the flow battery, where the experimental setup allowed easier removal of dissolved oxygen prior to battery operation.
Figure 16: CV scans of lignin material with; (a) multiple cycles on a gold electrode; (b) diluted electrolyte on a carbon electrode; (c) dried active material on a carbon electrode, and; (d) commercially available lignin showing a second set of redox peaks.

Figure 16d is a CV of the TCI ligninsulfonate on a gold foil working electrode. This lignin shows a second, larger set of peaks centering around 0.2 V. The smaller peaks centered around 0.5 V that were present in the CleanFlow lignin can also be seen in the TCI lignin trace. The redox peaks at lower voltage created a larger OCV for the battery, which is beneficial to the battery performance, however this particular lignin did not show cyclic performance that was as strong as the CleanFlow material. Thus, both types of lignin continued to be tested in the flow battery system.

The peak separations of these CV’s are all approximately 100 mV, which is larger than the 59/n mV = 29.5 mV (with n being the number of electrons involved in the redox process) expected for this reaction. This implies that equilibrium is not being established rapidly at the surface of the electrode. The effects of this slow equilibrium behavior are apparent in the flow battery testing.
A trace of the CleanFlow lignin on a gold foil working electrode without an inert gas purged headspace is shown in Figure 17. This voltammogram was cycled 4 times, and shows clear redox decay over each cycle. The numbers on the chart indicate which peaks correspond to which sweep, and the decay is consistent over each cycle. With inert gas purging on the headspace of the CV cell this behavior disappears and the redox peaks are much more stable. This led to the aforementioned oxygen decay theory, and thus inert gas purging was implemented on all subsequent CV tests, and on the flow battery system.

Figure 17: CV scan with no inert gas purging. The cycle number is indicated on the plot, and the intensity of the redox peaks decreases each cycle.

3.3 Initial Cycling and Performance Improvement
The ligninsulfonate flow battery was first setup for operation on cell build number 1 as described in Table 1. This initial build of the battery suffered from high resistance and poor performance, with best polarization resistances of 72.25 and 47.8 ohm cm² on charge and discharge, respectively. Therefore current densities needed to be kept low,
under 5 mA/cm², in order to keep voltages out of the range of oxygen and hydrogen evolution.

During these initial tests the setup did show signs of the lignin redox reactions occurring and the system operating as a battery, albeit with poor performance. The OCV decreased as the battery was discharged and increased on charge. As the battery cycled, the color of the positive electrolyte changed from a dark red color to a pale orange and back to dark red at the beginning of the next cycle. This is shown in Figure 18, and is a result of the positive electrolyte solution containing a high concentration of bromine at top of charge, and using that bromine and protons from the lignin to form hydrobromic acid as it discharges.

![Figure 18: Positive electrolyte at approximately 50% (left), 0% (center), and 100% (right) states of charge](image)

Unfortunately because of the dark color of the negative electrolyte solution it was not possible to notice an appreciable color change on that material. Because of its oxygen sensitivity it also could not be tested using spectral techniques such as UV-vis.

With the knowledge that the fundamental theory of the lignin battery worked properly, but with poor performance, an effort to improve battery performance was initiated. In
order to confirm that the flow battery cells had proper electrical and mechanical contact, dry cell builds were assembled. Dry electrical resistance was measured by assembling the cells without the ion exchange membrane, and measuring the ohmic resistance between the two current collectors. The FS hardware generally had results in the range of 1-2 ohms, depending on the electrodes used and the torque applied on the cell compression hardware. This is relatively high for a dry cell assembly of this size, and it was hypothesized that this high resistance was the result of corrosion on the current collectors, and poor contact in the active area of the cell due to mechanical deformation of the end plates.

In order to verify compression uniformity across the cell, mechanical loading studies were done by placing Fujifilm Prescale Extreme Low Pressure (4LW) pressure sensitive paper between the membrane and positive side electrodes, and assembling the battery as usual. After 10 minutes the cells were disassembled and the pressure paper examined. The result of one of these tests is shown below in Figure 19, and appears to exhibit non uniform compression across the cell and low loading in the cell active area.

![Figure 19: Pressure paper results of FS hardware exhibiting poor loading and uneven distribution.](image-url)
Because of these apparent limitations in the FS battery cell hardware, the FBH cell was acquired. This cell features gold plated current collectors to increase electrical conductivity and resist corrosion, as well as machined aluminum endplates to minimize mechanical deformation when compared with the PVC end plates on the FS hardware. Dry cell resistance measurements of this cell had much lower values of approximately 0.2 ohms, and pressure paper tests showed much better uniformity, an example of which is shown in Figure 20.

Figure 20: Pressure paper results of FBH hardware showing uniform loading.

Although the pressure paper still indicated relatively low loading in the active area, this had to be optimized against fluidic pressure drop through the cell. Thicker electrodes were inserted into the cell in order to increase compression and decrease contact resistance, and this led to a rise in pressure drop especially in the more viscous negative side of the battery. Thus, in this case lower compression was chosen over excessively high pressure drop.

After iterating on various cell and pretreatment configurations (page 24, Table 1), a more optimized combination of materials and methods was found in build #8. This configuration was built on the FBH platform, with 2 plasma pretreated AvCarb G100
felts on either side, a Nafion 212 membrane pretreated as described earlier, and the 5 cm² column flow field. This configuration was able to achieve much lower resistances, as low as 14.20 ohm cm² on charge and 17.75 ohm cm² on discharge (Figure 21), with good repeatability. Thus, this configuration was used for the majority of the remaining performance testing.

![Figure 21: Polarization curve for cell build #8 using CleanFlow lignin electrolyte](image)

**3.4 Cell Performance Data**

Voltage traces of the best performing lignin battery are shown below in Figure 22. This trace was taken at a current density of 10 mA cm⁻² on the CleanFlow ligninsulfonate. The charge curve is limited to the amount of coulombs that were discharged, and because the positive side of the battery was not configured to be capacity limiting, the voltage remains on the plateau throughout the entire charge, and does not increase rapidly prior to being cutoff. More interesting is the discharge curve, which shows a clear plateau at 150 mV, and also shows a more rapid voltage decrease as the lignin runs out of phenol groups that have not yet been oxidized.
In Figure 23, cell voltage is plotted against current density at various states of charge. The power density of the battery shows a significant decrease at lower states of charge, specifically below 60%. This confirms that limitations in the reactants mass transport have a significant impact on the cell voltage. The ends of the best fit lines for each SOC diverge as current density increases, as expected with mass transport limitations. The inset shows a modest increase in OCV, from 0.42 to 0.48 V, with good linearity as the SOC increases.
Figure 23: Cell voltage vs current density at various states of charge, (Inset) OCV at various states of charge

Voltage traces for galvanostatic charging and discharging at various current densities are shown in Figure 24, alongside calculated voltage efficiencies. There is no substantial reduction in voltage efficiency between these small current density steps, however the low overall efficiency beyond current densities of 10 mA cm$^{-2}$ adds further evidence of negative mass transport effects at high current densities.$^{44}$ The relatively low OCV of the battery system, particularly with the CleanFlow lignin that this data was collected from, is also a contributing factor to the drop on voltage efficiency.
Figure 24: (left) Cell voltage vs time at various current densities, (right) calculated voltage efficiencies at various current densities.

Although the indications of mass transport limitations are profound, the current densities that the lignin flow battery was able to achieve are in line with, if not greater than, some of the other organic flow battery materials that have been published. Mass transport effects can be mitigated by optimizing the electrode material, pretreatment method, and flow field, and do not necessarily indicate a fundamental issue with the flow battery electrolyte.

Durability data for the ligninsulfonate battery prototype is shown in Figure 25. The capacity fade observed in the first several cycles is one of the major challenges that the lignin flow battery will need to overcome. Besides a couple of outlier data points at cycles 6 and 9, the ligninsulfonate flow battery shows a steady, exponential, capacity decay from cycle to cycle, indicating that it is losing about the same percentage of capacity per cycle. There could be several reasons for this, including oxygen or bromine reduction of the lignin electrolyte, fouling of the electrodes causing an increase in overall cell resistance, or the loss in current efficiency, which is also plotted in Figure 25. The current efficiency appears to recover around cycle 20, but this recovery is unlikely and may be artificial due to the short duration of each charge-discharge cycle after such an extreme loss of capacity.
Figure 25: Current efficiency and capacity retention over 30 charge/discharge cycles

Although the observed capacity decay was a disappointing result, it is still remarkable that the ligninsulfonate flow battery is able to go through multiple charge cycles with an active material that is derived from nature and not synthesized in a lab.
Chapter 4 – Conclusions and Future Work

4.1 Conclusions

The purpose of this work was to research and prototype a flow battery electrolyte that meets the energy storage industry demands of low cost, sustainability, and low toxicity. Lignin was identified as a substance meeting all of the aforementioned criteria and is also known to have naturally occurring phenol groups able to participate in a theoretically reversible redox reaction. Prior to this work lignin had been researched as a useful material for various parts of energy storage devices, and had never before been investigated as a flow battery electrolyte.

Various lignins were qualified for use as an energy storage medium. An array of candidate electrolytes was synthesized using ligninsulfonate as the primary active material, and electrochemical testing was performed on these electrolytes to fine tune them for optimal performance and durability in a flow battery system. The lignins used were extracted from a common pulping process and did not require any precious metal catalyst or exotic materials to operate. The ligninsulfonate material showed reversible redox peaks capable of going through multiple reduction/oxidation cycles without any appreciable decrease in activity. A flow battery system comprised of a single battery cell was constructed using the best candidate lignin based solutions as the negative electrolyte, and using a well-understood redox active bromine/hydrobromic acid mixture as the positive electrolyte.

The initial lignin flow battery prototypes were able to store energy successfully, albeit with poor performance. A series of tests were run on the flow battery system, and modifications were made to the battery hardware and electrolytes to increase the overall performance of the ligninsulfonate battery. The battery was able to reach current densities of up to 20 mA cm\(^{-2}\), and polarization resistance as low as 14.20 ohm cm\(^2\), which was a significant improvement compared to the polarization resistance of 600 ohm cm\(^2\) achieved by the initial build of the flow battery system. It also achieved voltage efficiencies as high as 85%, and was able to charge and discharge over 30 times using the same battery hardware and electrolytes while retaining some energy storage capacity.
4.2 Future work

There are many factors that need to be investigated in order to truly optimize a flow battery system. This work demonstrated an exciting proof of concept for a flow battery using a novel, low cost, sustainable electrolyte, though some of the characteristics of the current design could use improvement.

The ligninsulfonate flow battery was hampered by poor cyclic durability, including loss of charge capacity and a decrease in current efficiency as the battery cycled. Although there were no directly observable indications of active material crossover during operation, it is likely that there was at least some amount of crossover contributing to the loss of capacity. Finding ways to mitigate crossover could have a highly beneficial impact on the ligninsulfonate battery system. This could be achieved by testing an array of membranes and membrane pretreatment methods to find the most suitable commercially available ion exchange membrane for this application. Oxygen ingress was also identified as a potential cause of capacity decay, and could be minimized in future builds by building a system with materials that are less prone to oxygen diffusion, and by increasing the electrolyte volume to surface area ratio of the negative side of the system.

Targeting the mass transport limitations and overall polarization resistance would also greatly improve the performance of the ligninsulfonate flow battery. In this work the polarization resistance was reduced by more than an order of magnitude from the first build to the last, and mass transport, while harder to quantify exactly, likely improved from the first build where the resistance was in excess of 600 ohm cm\(^2\). There are many aspects of the design that can continue to be improved in order to decrease the resistance and mass transport effects even more. These include changes to the electrode selection and pretreatment methods, optimizing the flow fields for each electrolyte, designing for increased electrolyte flow rates, formulating electrolytes with higher conductivities, operating at elevated temperatures, and increasing the concentration of active materials in the lignin electrolyte.
Perhaps the most important research that could continue on the ligninsulfonate flow battery involves finding a more suitable electrolyte couple than the bromine and hydrobromic acid solution used in this work. As mentioned previously, this positive electrolyte was selected because it is cheap, relatively available, and most importantly has well understood redox properties, which was beneficial for qualifying the lignin solution as an electrolyte. This positive electrolyte does, however, have many drawbacks such as high toxicity, poor material compatibility, and low OCV against the ligninsulfonate electrolyte. Now that the ligninsulfonate has been proven to work in a flow battery, it can continue to be tested against other electrolytes that do not suffer from these issues, and would therefore be more appealing in large scale flow battery systems.
REFERENCES


