High voltage quinone flow battery with hybrid acid and base electrolytes

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High voltage quinone flow battery with hybrid acid and base electrolytes

by

Mohsen Torabi Dizaji

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Chemical Engineering

Program of Study Committee:
Wenzhen Li, Major Professor
Eric Cochran
Jean-Philippe Tessonnier
Robbyn K. Anand

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2019

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DEDICATION

This thesis is dedicated to my wife and my parents who have always supported me selflessly.
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ABSTRACT

Performance of an all quinone redox flow battery is enhanced via using electrolytes with contrasting pH on both sides of the proton exchange membrane. This performance increase includes elevation of the open circuit voltage by 300 mV to 1.5 V at SOC of 50% and augmentation of energy density by a factor of three to 20.6 Wh/Kg in reference to the previous redox flow battery developed earlier. The battery is able to operate at current densities up to 80 mA/cm² and meeting columbic efficiency of 99.9% and energy density of 70%. Moreover, the battery with contrasting pH was able to operate for more than 140 hours continuously. Final system pH was similar to the initial system pH. Furthermore, durability of the referenced flow battery comprising of Dihydroxy Anthraquinone and ferricyanide ion was enhanced by using this technique. Electrolyte pH might affect redox reaction of the analytes significantly. For example, redox potential of quinone compounds that entail protonation step in their electrochemical reaction might change by pH and some compounds such as ferricyanide ion or TEMPO compounds might not be able to demonstrate reversible reaction at specific pH. Capability of manipulation of the pH of each half cell independently from the other half cell can bring various advantages such as coupling half reactions that operate at completely different pH and affect redox potential, durability or energy density according to such applications which can prevent the boundaries of the redox flow batteries. Moreover, the battery with contrasting pH was able to operate for more than 140 hours continuously. Final system pH was similar to the initial system pH. Furthermore, durability of the referenced flow battery is enhanced by using this technique via maintaining a neutral pH on the cathode side of the flow battery comprising of Dihydroxy Anthraquinone and ferricyanide ion. Single-cell tests for both systems have been performed and the results as well as half-cell characteristics of the catholyte such as redox potential, reversibility, stability and performance of all quinone redox flow battery is enhanced via using electrolytes with contrasting pH on both sides of the proton exchange membrane.
well as the test conditions and methods are displayed. The systems include the DHAQ (pH=14) vs Ferricyanide ion (pH= 7) redox flow battery that is discussed in chapter 3 as well as DHAQ (pH=14) vs HQDS (pH=0.3) (hydroquinone disulfonic acid) flow battery that is discussed in chapter 4.
CHAPTER 1. RENEWABLE ENERGY AND REDOX FLOW BATTERIES

1.1. Renewable Energy

Renewable energy which is harnessed through sources that can be replenished by the nature not only provide an immense free source of energy but also, they prevent environmental emissions that are concomitants of fossil fuels. Renewable energy is mostly harnessed through sources such as hydroelectricity, geothermal energy, solar energy, wind and biomass. It is rapidly improving field providing a lot of jobs and shaping a very promising future. Countries such United States and China are heavily investing in this field and will harness more energy from renewables in the future.

Renewable energy provides energy security for the world due to the fact that renewable resources are accessible to all people in contrast to the fossil fuels that are not distributed evenly in the world and in addition to that the only solution to stop and mitigate the effect of the greenhouse gases is through utilization of renewable energy in a larger extent. Here, various sources of renewable energy are discussed in summary:

Hydroelectricity: This source still produces the largest proportion of the renewable energy in the world and is mainly harnessed through hydroelectric dams. These dams can be either in large size, small size (producing up to 50MW) or the run-of-the-river dams that do not require construction of large reservoirs. Besides these, hydroelectric power can also be produced by wave power (using energy of the ocean waves) as well as tidal power (using energy difference of the tides.)

Geothermal Power: Geothermal energy relies on the high temperature inside the core of earth that might reach even to 5000 C which is even able to melt the rocks. This immense heat can be
transferred to the upper layers and is able to heat water sometimes up to 370°C. It is a very reliable source of energy and there are tax credit policies in support of them. This source of renewable energy might be area specific and not accessible or economic in all areas.

Biomass Energy: This source of energy relies on the energy derived from bio organisms such as plants. Biomass can either be directly converted to energy by burning or by first conversion to biofuels and then conversion to energy. This technology can benefit from various kinds of cellulosic compounds such as wood chips, corn stoves…. Even though it is a reliable source of energy, it is limited and still problem of emissions exists.

Wind power: wind turbines convert wind energy to electricity and their sizes and efficiencies are increasing rapidly. Power of wind turbines has reached 9MW and will pass 13MW soon. Wind power is not the same in all areas and is usually higher in offshore areas and high altitudes and this affects the full load hours of the turbines. Wind energy is the leading source of new renewables energy in Europe.

Solar Energy: solar energy can be utilized through various means such as solar heating (converting solar energy to heat and using the heat), photovoltaics (converting solar energy directly to electricity), concentrated solar power (solar power is concentrated by mirrors and lenses to a small area, generating heat, driving a heat engine and producing power), solar architecture and artificial photosynthesis. Among these technologies, photovoltaics and concentrated solar power have the highest potential of growth and technologies are growing very fast in this field.

Among these sources of energy, wind and solar have the higher potential from growth.
1.1.1. Rapid growth of Renewable Energy

Wind energy is growing very rapidly in the world. The net energy harnessed through wind has doubled in US since 2011 to 2017\(^1\). The wind turbines are getting larger and are able to produce more energy and also their efficiencies increase. Global growth in the field of wind energy is more than 20% per year and this percentage is even considerably higher for the solar energy reaching 60% growth per year\(^2\). There are reasons for such rapid growth but the most important are the force towards reduction of greenhouse emissions as well as reduction in the cost of solar panels and wind turbines. For example, in US the policy is to produce at least 12% of the energy from renewable resources.

For example, total wind turbine energy installed in United States by the year 2007 was 16.7GW while this figure passed 100GW by the year 2018. There is a similar inclination in the installed solar energy in US. By 2010, the installed capacity of solar energy was very low while by the year 2018, the capacity of the total installed photovoltaic solar cells has surpassed 56GW\(^3\).

![U.S. Installed Wind and Solar Capacity](image)

**Figure 1.1.** US Installed Wind and Solar Capacity\(^4\)
1.1.2. Intermittency in renewable energy and necessity for storage

Solar energy and wind form the most promising sources of renewable energy for future, however, there is a downside with these valuable sources of energy and that is related to their intermittent nature. Sunshine doesn’t exist during all the day and also its intensity various throughout the year. There is a similar case for the wind energy and it is even more intermittent.

This intermittency imposes a problem for the widespread use of the renewable energies in the power grids. Power grids have strict regulations for the power supplied to the grid. Source of power shall be steady and predictable and it is not possible for large power grids to accept any intermittent source of energy because it messes with their network frequency which is a very major issue. Thus, it is needed to mitigate this intermittency.

Figure below demonstrates the intermittency of various sources of renewable energy including wind, solar, hydroelectric, combined heat and power (CHP), anaerobic digestion units (AD) and landfill gas. Solar and wind are demonstrated to have high degrees of intermittency.

![Daily renewable energy generation in the UK](image)

Figure 1.2 Daily renewable energy generation in UK
1.2. Types of Energy Storage

1.2.1. Pumped Hydroelectric Energy Storage (PHES)

This method of energy storage requires pumping of water to a reservoir in a higher elevation at the time of surplus of energy and recovering the potential energy by the aid of a water turbine that is located in the route of the water flowing from the reservoir at the higher elevation to the reservoir at the lower elevation at the time of demand for energy. During the time of low demand, the higher reservoir is filled by pumps and during the time of high demand, water flows from the higher reservoir, rotates the turbine and fills the lower reservoir. Energy system can be reversible and during charging it can be in the form of pump and motor and during discharge it can be in the form of turbine and generator\(^6\).

These systems are highly efficient and their efficiency might even reach higher than 80%. Currently more than 40 PHES systems are operating in the united states and they are very effective in large scale energy storage. However, this forms their main disadvantage for application in small size energy storage. They are geographically dependent and they can only exist when the geographical profile allows their existence and they are not justifiable for small size energy storage which is the main topic of this research.\(^6\)

![Figure 1.3. Pumped Hydroelectric Energy Storage](image)
1.2.2. Compressed Air Energy Storage (CAES)

Another method to store electrical energy is to compress air and store it in natural caverns and retrieve the energy later at the time of demand by the aid of heating the stored compressed air and expanding it through a turbine. Air becomes heated during compression and its temperature needs to be reduced prior to storage and stored compressed gas is heated prior to expansion. This can be optimized via recuperators installed upstream of turbines.

Efficiency of CAES can reach to 60-80% but the problem about them is that they are applicable when natural caverns are present and this limits their applicability for all places and in addition to that installation of compressors, turbines, generators and other facilities necessitates large investment that makes them inappropriate for small size energy storage.

Figure 1.4. Compressed Air Energy Storage
1.2.3. Electrochemical Energy Storage

1.2.3.1. Supercapacitors

Supercapacitors benefit from both the electrical double layer capacitance as well as the electrochemical pseudocapacitance to store energy, benefiting from both the capacitance as well as faradaic redox reaction. They fill the gap between the electrical capacitors and the batteries. Electrical double layer capacitance is achieved through using carbon electrodes with very high surface areas that are able to store a considerable amount of charge thanks to their high surface areas. On the other hand, pseudocapacitance is attained by using metal oxide or conducting polymer electrodes that are able to get pseudocapacitance via redox reactions or electrosorption. Intercalation can also be a process for pseudocapacitance by storing reduced species in layered materials such as graphite.

Even though energy density of supercapacitors is considerably higher than electrical capacitors, it is lower than the energy density of the batteries and this issue makes them infeasible for energy storage derived from renewable resources such as wind and sunshine. They become very expensive and they cannot store sufficient energy. Supercapacitors are more suitable for applications in which higher power ratings are required. Application of the supercapacitors are usually divided into four different groups:

1. Applications for electronic devices such as computers and memory banks
2. Energy storage for devices with short time of operation
3. High power requirements
4. Instantaneous power such as automobile applications, trains, etc.
The above Ragone plot illustrates applicability of various forms of energy storage techniques. While higher power requirements will benefit from supercapacitors, higher energy density applications such as storage of renewable energy will require options such as batteries. Fuel cells are not applicable for this case because they require fuels for operation and they are not applicable to store energy from renewable resources such as wind and sunshine.
1.2.3.2. Stationary Batteries

Stationary batteries are operated through a redox reaction that takes place by transferring electrons from anode to cathode during discharge. Both anode and cathode are placed in electrolytes that are separated by separators or membranes and ions are transferred through this separator to keep the electrolytes electrically neutral during redox reaction.

Stationary batteries can be either in the form of primary batteries that cannot be recharged or secondary batteries that can be charged and used several times. During charging, cathode loses electron(s) to the anode while during discharge, it gets that electron(s) back. Several of voltaic cells are connected together to provide the desired voltage and energy.

In order for a battery to be useful for the renewable energy storage it is necessary to have some attributes. The battery must have high capacity (the amount of energy stored in the battery Kwh), good power rating (amount of energy that a battery can deliver in a specific time Kw), high Depth of Discharge (DoD), good Energy Efficiency, high life time and low cost. Usually it is difficult to satisfy all these requirements together. For example, lead acid batteries that have been tested for a long time and are a cheap source of energy storage, have lower energy efficiency and life cycle. On the other hand, lithium ion batteries are more expensive while they have better efficiency, life time and DOD.

Application of stationary batteries for renewable energy storage requires stacking a lot of batteries together as well as considering system parameters such as power rating... this imposes a lot of unnecessary cost to the energy storage system while the system cannot deliver 100% depth of discharge.10
Figure 1.6. Stationary Batteries

Stationary batteries can be stacked in parallel and series mode to meet the energy storage requirements. Number of cells in parallel and series configuration will depend on the energy storage as well as power requirements of the system. Lead acid batteries as well as lithium ion batteries are among the main options for batteries for storage of renewable energies.
1.2.3.3. Flow batteries

Flow batteries are a type of rechargeable battery in which the redox media are dissolved in electrolytes and stored in separate tanks from which they are pumped to the electrochemical cell to carry out the electrochemical reaction by the aid of which they are capable of storing or discharging energy. Electrochemical cell has a structure similar to the fuel cell in which ion exchange membrane is sandwiched between electrodes and current collectors that are finally fixed by the aid of end plates. Energy capacity of the system depends on the size of the storage tanks and the power rating depends on the size of the electrodes.

Flow batteries provide the possibility of engineering on the battery component, a possibility that did not exist with the stationary batteries. For example, if higher capacity is needed the tanks can become larger and if higher power ratings are needed, electrodes with larger areas will be used. Pumps and lines will be designed according to the tank size and flow requirements. Furthermore, flow batteries can have complete discharge which was impossible with the stationary batteries due to intercalation or other issues. Also, flow batteries provide a chance to update or even change the electrolyte of the system with another compatible electrolyte while it is completely impossible in stationary batteries which provide a black box preventing any kind of manipulations inside them.

All these possibilities enable the redox flow batteries to become considered as a potential choice for the storage of renewable energy. There are different types of flow batteries and some of the main types are explained briefly afterwards.

As illustrated below there are two tanks for each of the redox media dissolved in its electrolyte and these tanks are connected to the electrochemical cell by means of tubing and the flow is sustained in the system by the aid of pumps. Details of the electrochemical cell are explained in the next page.
This picture provides a brief overview of the cell structure of the flow batteries. Ion exchange membranes that can be in the form of cation exchange membranes or anion exchange membranes are sandwiched between electrodes that might be comprised of several layers. Usually both the ion exchange membrane as well as the electrodes are processed prior to being used in the flow battery cell structure. Flow channel plates sandwich the electrodes. On the body of the flow channel plates there are grooves that enable flow and distribution of the redox media on the electrode. There are different types of flow channel plates such as serpentine, interdigitated, dotted…. That can be used in the flow batteries. Flow channel plates or bipolar plates are electrically conductive and receive the electricity from the current collector on one side and transfer the electricity to the electrodes. This current will be later on completed via transfer of ions through the ion exchange membrane. Current collectors are usually made of gold-plated copper and they are insulated in one side to prevent transfer of electricity to end plates in case they are made of a conductive material such as stainless steel. Potentiostat ends are connected to the top of the current collector by means of cables.
and provide the possibility of controlling the experiment via potentiostat interface. Finally end plates are bolted together and tightened sufficiently to keep the whole cell components robust and in place. 11

Figure 1.8. Cell Structure of flow battery
1.2.3.3.1. All Vanadium Redox Flow Battery

These types of flow batteries are probably the most developed type of flow battery. They utilize different valences of ions on both sides of the flow battery. During discharge, $\text{V}^{+2}$ is converted to $\text{V}^{+3}$ in anode while $\text{V}^{+5}$ is converted to $\text{V}^{+4}$ at cathode. The membrane used for this type of flow battery is usually Nafion and both electrolytes are concentrated sulfuric acid. Electrical circuit is completed via transferring of H+ through the membrane from anode to cathode side during discharge and vice versa during charging mode. Operating voltage is around 1.4V and the energy density is between 10-20 Whr/Kg.

These types of batteries have some advantages over other type. The first and the most important is their high durability that can last for very long cycles. The other main advantage is that they are tolerant against crossover which forms one of the main capacity fades in various kinds of flow batteries.

However, there are shortcomings with this technology. The first one is the high cost of the redox media. Vanadium is an expensive element which needs to be used in high quantities in this technology, increasing its price. The other problem is the corrosive electrolyte used in this technology. Concentrated sulfuric acid (4M) is usually used as the electrolyte which limits the materials that can be used for construction of the battery system. Furthermore, this concentrated electrolyte increases the viscosity of the system and thus imposing higher energy for the pumps. This battery is temperature sensitive and in high and low temperatures, precipitation occurs.
All vanadium redox flow batteries are probably the most developed technology in the field of redox flow batteries. Their main advantage lies in their very high durability and their stability against crossover. They have been used in MWh scale and also their application for residential and mobile cases are being developed. The main barrier is the cost of vanadium which has show an upwards trends.
1.2.3.3.2. Iron Chromium Redox Flow Battery

Iron chromium redox flow batteries are another type of flow battery technology that has reached stage of maturity and has experienced large capacities. In this technology, during discharge Cr+2 is oxidized to Cr+3 at anode and Fe+3 is reduced to Fe+2 at cathode. The redox reaction entails one electron and the type of membrane used is usually Nafion. Both metal ions are dissolved in concentrated (3M) hydrochloric acid electrolyte. Iron and chromium ions are susceptible to crossover through the membrane and cause irreversible capacity loss. Thus, both ions are used in both sides of the flow battery to prevent this problem. One of the advantages of this technique is possible elimination of the ion exchange membrane that constitutes one of the major cost components in redox flow batteries.

One of the main advantages of this battery is the low cost of both of the redox media (iron and chromium) thus reducing the total cost of the battery. However, there are down sides with this technology. In the chromium side there is a high possibility of HER side reaction which reduces the overall efficiency of the battery.

![Figure 1.10. Schematic of an Iron-Chromium Redox Flow Battery](image)
1.2.3.3. Zinc Bromium Redox Flow Battery

Zinc bromine flow battery is a type of hybrid flow battery. In contrast to the previous two types of flow batteries in which the redox components remain completely in solution during the redox reaction, in this flow battery, anode active component (zinc) deposits on the electrode upon reduction, thus increasing the electrode weight. Zinc bromide forms the main chemical component used in these batteries. During charging process, zinc is deposited on the anode and bromine is produced in the cathode. During discharge, zinc loses two electrons and bromine is reduced to bromide ion.

Zinc bromine flow battery has a high voltage and entails two electrons in the zinc side which increases the energy density of this system. However, there are challenges to keep the bromine in the liquid phase during charging of the battery. Therefore, it is needed to use some forms of amine or methansulfonic acid which increases the cost. In addition to that, cooling system is needed to prevent evaporation of the formed bromine in the cathode tank. Bromine is highly toxic material and it shall be taken care of seriously. Another problem is related to the formation of zinc dendrite during charging which might puncture the membrane and create short circuit in the flow battery. It is needed to use special procedures routinely to make the surface of the anode electrode smooth.

Figure 1.11. A schematic of a zinc bromine redox flow battery\textsuperscript{14}
1.2.3.3.4. Organic Redox Flow Battery

The three mentioned technologies are among the most developed redox flow battery technologies. All of them have reached stages of commercial development and probably the most developed technology is the all vanadium flow batteries. Despite its good performance and high durability, it has a very corrosive environment and it is not environmentally friendly. More important than that is the high price of vanadium which is a main barrier in the route of wide commercialization of this battery. On the other hand, iron-chromium flow battery suffers from some technical problems such as considerable hydrogen evolution reaction in the anode part which sacrifices the columbic efficiency of the battery. On the other hand, zinc flow batteries suffer from serious dendrite formations that enhance the risk of short circuits and deactivation of the battery as well as serious environmental issues related to utilization of bromine in the cathode. Even though, these batteries have good voltage range and their energy density is also good, such problems impose limitations for the operation of the battery and risk of short circuit that might render the membrane useless, is always present and also complex chemical components are needed to keep the oxidized bromine soluble in the electrolyte which increase the cost accordingly.

Organic components on the other hand have a significant characteristic that inorganic compounds lack it and it is capability of functionalization. This attribute, enables us to modify their various characteristics such as redox potential, solubility, kinetics…. It is possible to synthesize organic chemicals with considerable redox potential, fast kinetics and high solubility. Furthermore, abundance of the raw material of the organic compounds renders the cost of organic chemicals to be considerably less than components such as vanadium and there is a fair probability of reduction of organic prices mainly owing to improvement of new and more efficient technologies such as discovery of new synthesis paths as well as development of new catalysts
with higher selectivity, making organic compounds more competitive against their inorganic counterparts.

Organic compounds can be aqueous or non-aqueous. Non aqueous systems do not deal with the parasitic reactions of HER and OER and thus can operate under higher voltage spans. This attribute makes such systems very interesting. However, there is a downside with these systems and it is related to the low electrical conductivity of non-aqueous flow battery systems. This issue imposes great deal of resistance to the systems and makes it almost inefficient in the cases where higher power rating is needed. In addition to that cost of non-aqueous systems is higher and presence of supporting electrolyte to increase the conductivity will jack up the costs further. On the other hand, aqueous systems benefit from high conductivity of the aqueous systems and the cost of water or the supporting electrolytes is much less and they own better power ratings. Three of the main organic groups that have been used are discussed hereafter.

1.2.3.3.4.1. Alkoxybenzene based

Alkoxybenzene compounds specially the 2,5-di-tert-butyl-1,4-bis(2-methoxyethoxy) benzene or simply DBBB is well known in battery industry due to its usage in lithium ion batteries to prevent against overcharging as well as forming a cathode active component. Alkoxybenzene own a very good redox potential which is higher than the other two main organic redox families (TEMPO, quinone). For example, redox potential of ANL-8(2,5-di-tert-butyl-1- methoxy,4-bis(2-methoxyethoxy) benzene) is 1.34 V vs SHE which is a considerable cathode potential. Other components of this family (ANL-9, ANL 10) have similar redox potentials while their other physical properties are different\textsuperscript{15,16} and turn from a solid state (DBBB) to a semi-liquid (ANL-10) and to a liquid (ANL-8).
These cathode materials can reach a voltage of 4.0 V when coupled with lithium anodes, however, they require organic solvents instead of aqueous solvents and this issue imposes
considerable cost impact in addition to low current density. Furthermore, sterical hinderance of such molecules prevents high concentrations of them in the solvent and this leads to lower energy densities\(^{17}\). Even when chemical structure was modified to reduce the structural hindrance and increase the solubility, the chemicals displayed irreversible chemical decomposition and their capacity faded after less than 50 cycles\(^{18}\). Even though such chemicals show very good half-cell behavior, they are not successful in single-cell tests and this undermines their capability to be used in redox flow batteries. Furthermore, cost of the supporting electrolyte (LiPF\(_6\)) is a major drawback for such systems.

1.2.3.3.4.2. TEMPO based

2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) has been demonstrated to be an organic redox active chemical that can be used for the lithium flow batteries\(^{19}\). TEMPO forms a heterocyclic free radical that can remain stable during redox reactions and displays fast-reversible reactions in half cell tests.

![Figure 1.14. CV of TEMPO vs Li/Li\(^+\)](image)

In this system, TEMPO is coupled with Li in organic electrolyte (propylene carbonate/ethylene carbonate), supported with LiPF\(_6\) and can reach concentrations as high as 2.0M which will display an energy density of 126 WhL\(^{-1}\) which is the highest energy density in all organic flow batteries.
and even higher solubilities which lead to higher energy densities are reported, however the current density was low (5 mA/cm²) and this low current density is not feasible for daily use. A higher energy was derived upon functionalization of TEMPO to reach 4-methoxy TEMPO with a LiTFSI supporting electrolyte however the viscosity of the electrolyte became so high that caused serious doubts about pumppability of this system. On top of that such systems that are based on organic electrolytes (instead of water) are not feasible for industrial applications due to high cost of chemicals, electrolyte (main and supporting) as well as safety concerns.

On the other hand, TEMPO has a successful record of operating in aqueous solutions. Another TEMPO based compound, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-HOTEMPO), was coupled with methyl viologen (MV) in aqueous electrolytes. 4-HO-TEMPO can even reach concentrations as high as 2.1M, however it needs a supporting electrolyte and presence of supporting electrolyte (in this case NaCl) seriously reduces its solubility to 0.5M²¹. The couple illustrates a good potential difference of 1.25V.

Figure 1.15. CV of MV and 4-HO-TEMPO and cycling graphs

The battery was able to operate at high current densities owing to the good conductivity of NaCl solution in water and reach energy efficiency of 62% and an energy density of 8.4 WhL⁻¹. Energy efficiency as well as energy density are not very high. The main reason for low energy density is related to the concentration of cathode active material in presence of supporting electrolyte (NaCl).
Also, TEMPO has been functionalized using sulfonic acid group to form e TEMPO-4-sulfate potassium salt to be coupled to zinc chloride in a semi organic redox flow battery\textsuperscript{16}. The synthesis was a one-step reaction of 4-hydroxy TEMPO with sulfuric acid and then neutralized by potassium hydrogen carbonate. The system utilized a combination of zinc chloride as well as ammonium chloride as supporting electrolyte. The concentration of the cathode active material reached to 1.0M in presence of supporting electrolyte which was a progress since the previous work. The battery was able to reach charge density of 20 AhL\textsuperscript{-1} as well as a current density of 80 mAcm\textsuperscript{2}. This battery has a potential difference of 1.69V which is considerable for aqueous systems. This system benefits from a proton exchange membrane with the Zn\textsuperscript{+2} to be the ions to be transferred through the membrane.

![Schematic of a TEMPO/Zinc flow battery and the capacity/efficiency plot](image)

Figure 1.16. Schematic of a TEMPO/Zinc flow battery and the capacity/efficiency plot

In another effort, TEMPO was functionalized with three methyl ammonium groups to yield N, N, N-2,2,6,6-heptamethylpiperidinyl oxy-4-ammonium chloride (TEMPTMA) coupled with dimethyl viologen dichloride in a flow battery equipped with anion exchange membrane\textsuperscript{21}. The new functional group (three methyl ammonium) significantly increases the solubility of the TEMPO compound and reaches it to the range of 2.3M with presence of 1.5M NaCl as supporting electrolyte. This achievement enhanced the capacity of this battery to 38 AhL\textsuperscript{-1} and its energy
density to 54 WhL\(^{-1}\). The system was tested at the high current density of 200 mA/cm\(^2\). Energy efficiency of the system was over 70\% with the current density of 50 mA/cm\(^2\). However, the authors do not provide any information about the long-term stability of the anode active material (Dimethyl Viologen Dichloride) which is an important criterial for the life cycle of a redox flow battery. Furthermore, viscosity of the synthesized chemical is around 7 mPa.S at room temperature which is almost 7 times the viscosity of water at the same temperature and this issue will have negative effect on the pumping energy requirement of the system. Even at lower temperatures the viscosity might even reach 20 mPaS which is high and might necessitate installation of heating system that will further enhance cost and reduce efficiency.

![Redox Reaction of MV/TEMPMA and the related cycling plot](image)

Figure 1.17. Redox Reaction of MV/TEMPMA and the related cycling plot

TEMPO based compounds have high capability of being used in aqueous flow batteries however, even after overcoming the concentration issues, they might face other side effects such as higher viscosity and finally they involve one electron per each electrochemical reaction. Furthermore, these compounds have the limitation of being used at pH of higher than 2.5. Even though this might be considered as an advantage, if it is desired to benefit from pH reduction of the anode side due to utilization of an anode material that is more stable than viologen compounds, this cathode may not be used due to decomposition.
1.2.3.3.1. Quinone based

Electrochemical behavior of quinone compounds is not new, specially anthraquinone has been well used as cathode\textsuperscript{22} and anode\textsuperscript{23} active material for lithium ion batteries and their characteristics are studied. A functionalized form of anthraquinone (2,6 dimethoxy triethylene glycol anthraquinone) was coupled with lithium in propylene carbonate electrolyte supported by LiPF\textsubscript{6}\textsuperscript{24}. The main problem with this system was the low current density of 10 mA/cm\textsuperscript{2} besides the expensive and hazardous organic electrolyte. Quinone compounds have been tested successfully against Cadmium\textsuperscript{25} and Lead\textsuperscript{26}, showing 1.1 V and 1.09 V potentials respectively. Both of the mentioned systems used aqueous electrolytes.

Tiron vs Lead flow battery:

\[
Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^- \quad \text{E}_0^\circ = -0.35 \, V
\]

Tetra Chloro p-benzoquinone vs Cadmium:

\[
QCl_4 + 2H^+ + 2e^- \rightleftharpoons H_2QCl_4 \quad \text{E}_0^\circ = 0.71 \, V
\]

\[
Cd \rightleftharpoons Cd^{+2} + 2e^- \quad \text{E}_0^\circ = -0.40 \, V
\]

Figure 1.18. Redox reaction of two Quinone Compounds (BQDS/Pb, TCQ/Cd)

Quinone compounds have the ability of performance both in organic electrolytes as well as aqueous electrolytes. Proper functionalization will add to the solubility of the system. In 2014, an all organic quinone flow battery was reported comprising of 1,2-benzoquinone-3,5-disulfonic acid (BQDS) as cathode and anthraquinone-2-sulfonic acid (AQS) as anode active materials respectively\textsuperscript{27}. 
The system reached a theoretical voltage of 0.76 V which is not very high and its long-term durability is shadowed by the durability of the cathode active material. This is a successful demonstration of aqueous quinone flow battery. In another work, another type of quinone compound, 1M 9,10-anthraquinone-2,7-disulphonic acid (AQDS).

Both half cell reactions are displayed as following:

Figure 1.19. Redox Reaction of BQDS and AQS

The battery benefits from quinone compounds in both sides in sulfuric acid electrolyte with a proton exchange membrane.

Figure 1.20. Cycle plots of the BQDS vs AQS flow battery
AQDS in 1M sulfuric acid was coupled with Br₂/2Br⁻ in 3M HBr. This system, in addition to meeting all efficiency criteria, was operated at a high current density of 0.5 A/cm². Energy density of the system reached 9.4 WhL⁻¹. The authors performed power testing on their system in a subsequent work and reached a power density of 1W/cm² which is a high value for the flow batteries.

Figure 1.21. Polarization Curves of the AQDS vs Br₂/2Br⁻ flow battery

A new quinone based anode active materials was introduced in another work. 2,6-dihydroxyanthraquinone (2,6-DHAQ) with a redox potential of -0.67 V was coupled to ferricyanide ion both in alkaline media using potassium as the ion to be transferred through proton exchange membrane. The nonvolatile ferricyanide ion replaced the toxic Br₂/2Br⁻ redox couple and reducing the hazards significantly. On the other hand, 2,6-DHAQ dissolved in alkaline media displayed a much more negative redox potential than AQDS dissolved in acidic media and overall increasing the battery voltage to 1.2V. DHAQ displays fast reactions in alkaline media and its redox potential becomes constant at pH above 12.8. The battery had an energy efficiency of more than 80% with current density of 100 mA/cm² for more than 100 cycles.
Figure 1.22. Cycling plot as well as Capacity/Efficiency plots of DHAQ vs ferricyanide ion

Even though alkaline media is less corrosive than the acidic counterpart, it is still corrosive. Furthermore, alkaline media limits solubility of the ferricyanide ion and thus limits the overall energy density of the flow battery (6.8 WhL⁻¹). Moreover, both components show deactivation symptoms in the long run in the media that they were used (alkaline).

Solubility of DHAQ was further increased by functionalization of this component to form 4,40-((9,10-anthraquinone-2,6-diyl) dioxy)dibutyrate (2,6-DBEAQ) in which the protons of the hydroxyl groups were replaced with butyrate groups. This functionalization increased the solubility of DHAQ six folds in pH 12 and twice in pH 14 and in addition to that enhanced the durability of the material and the capacity fade was reduced to < 0.01%/day. However, this functionalization reduced the redox potential from -0.67 V for DHAQ to -0.51 V for 2,6-DBEAQ.
This component was further functionalized via phosphate groups and its durability was enhanced accordingly. Via this functionalization, the compound was soluble in near neutral pH and reached solubility of 0.75 M at pH=9. This is almost a neutral pH. However, redox potential still is reduced due to this functionalization to -0.47 V and reducing the open circuit potential to 1.02 V.
Quinone compounds are can become reliable redox media in aqueous solutions. They can have good solubilities and they do not necessarily require supporting electrolyte in the system similar to the Tempo compounds and this issue enables them to sustain their high level of concentration. Also, they are able to incorporate two electrons in each reaction which doubles their energy density. Furthermore, through proper functionalization, quinone compounds can be used both as the cathode as well as the anode. Based on these attributes, in our system we have used 2,6 anthraquinone disulfonic acid as the anode and 1,2 hydroquinone 3,5disulfonic acid as the cathode active materials.  

1.3. References

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CHAPTER 2. TESTS USED FOR REDOX FLOW BATTERIES

2.1. Half Cell Tests

2.1.1. Cyclic Voltammetry

It is necessary to monitor the changes in the current vs changes in the potential. Cyclic voltammetry is performed for this purpose. It is comprised of two linear sweeps of potential in opposite direction. First voltage of the working electrode is increased versus the potential of the reference electrode and then it is decreased. Both increase and decrease are in linear mode versus time.

\[ E = E_l \pm vt \]
\[ E = E^0 + \frac{RT \ln(0x)}{nF \text{ Red}} \]
\[ E_{pa} - E_{pc} = \frac{56.5}{n} \text{ mV} \]

Plot of changes of current versus potential (voltammetry) is drawn and because it is repeated for some cycles to get more precise results it is a “cyclic” voltammetry. During the first ramp when the potential is increased the chemical is oxidized and when the potential is reduced the chemical is reduced. During each of these processes (oxidation, reduction), initially the change in the current versus voltage is low and almost linear and then suddenly jumping and getting rate and finally reaching a maximum and coming down to a limit that start the next step. This relation is justified by the Butler-Volmer equation and in part by the Cottrel equation (even though voltage is not constant) and mass transfer limitation induces a maximum in the shape of the voltammetry (minimum in the case of reduction).

\[ i = i_0 \left[ \left( \frac{C_0(0,t)}{C_0^*} \right) e^{-\alpha f \eta} - \left( \frac{C_R(0,t)}{C_R^*} \right) e^{(1-\alpha)f \eta} \right] \]
There are two peaks in the CV test and the average of them will show the redox potential of the electrochemical reaction and the difference of those peaks is a sign of irreversibility of the system. However, a better judgement on the reversibility of the system can be made after consideration of the uncompensated resistance.

\[ E^0 = \frac{E_{pa} + E_{pc}}{2} \]

There is a charging current related to the capacitance of the system according to the following equation which increases with the scan rate and reduces with the concentration of the redox active component. 30

\[ |i_c| = AC_d v \]
\[ \frac{|i_c|}{i_p} = \frac{(2.4 \times 10^{-8})v^{1/2}}{n^{3/2}C_0} \]

Figure 25 A sample CV of an organic flow battery test is illustrated.
2.1.2. Electrochemical Stability

In any electrochemical test it is needed to ensure that the redox media is not going to react with the electrode or is not going to precipitate on the electrode, otherwise the electrochemical reaction will not be reversible and the test will be very difficult to interpret. Randles-Sevcik test is used to verify whether the system is stable to not. This test relies on a series of cyclic voltammograms during which the scan rate is increased and the peak current density is measured and based on the following equation peak current density shall be a linear function of the square root of scan rate if the electrochemical species is stable.

\[ i_p = 0.446nFAC^0\left(\frac{nfVD_0}{RT}\right)^{1/2} \]

Hereunder a sample electrochemical stability test for an organic chemical is illustrated from an article\textsuperscript{16}.

Figure 26 A sample stability analysis for components in a flow battery
2.1.3. Rotating Disc Electrode Tests

Analysis of an electrochemical system requires much more information just than the redox potential, reversibility and stability such as information about the kinetics, diffusivity, reaction constant and exchange current density. This information can be provided by the aid of the Rotating Disc Electrode.

During cyclic voltammetry, there are peaks (maximum for oxidation and minimum for reduction) in the voltammogram that are induced by mass transfer limitations. If mass transfer limitations are overcome then the voltammograms will reach a plateau. This is performed by rotating the working electrode by the aid of a device (RDE). Rotation of the working electrode will induce movement of the fluid around the electrode which will result in introduction of fresh electrolyte to the surface of the working electrode that will bring with it the electroactive material thus preventing mass transfer limitations. Shape of the rotating disc electrode is designed in a manner to minimize any kind of mis-distribution of the redox chemicals on the surface of the electrode and to ensure presence of laminar flow in the system. As the rotation speed of the rotating disc electrode is increased more electrolyte is introduced to the surface of the electrode thus raising the current level of the final plateau. By performing similar LSVs at different rotation speeds it become possible to draw a Levich plot which is a limiting current (Plateau Current) as a function of square root of rotation speed of the electrode. Slope of Levich plot will provide us with the diffusivity of the active chemical in the electrolyte.

\[
\begin{align*}
    i_{l,c} &= 0.62nFAD_o^{2/3} \omega^{1/2}v^{-1/6}C_o^* \\
    i_{l,a} &= 0.62nFAD_R^{2/3} \omega^{1/2}v^{-1/6}C_R^* \\
    E &= E_{1/2} + \frac{RT}{nF} \ln \left( \frac{i_{l,c} - i}{i_{l,a} - i} \right)
\end{align*}
\]
\[ E_{1/2} = E^0 + \frac{RT}{nF} \ln \left( \frac{D_R}{D_O} \right)^{2/3} \]

\[ i_k = F A k_f (E) C_O^* \]

\[ \frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{l,c}} = \frac{1}{i_k} + \frac{1}{0.62 n F A D_O^{2/3} \omega^{1/2} v^{-1/6} C_O^*} \]

Figure 27 RDE and Levich Plots of and organic polymer

In addition to the plateau current, there is the normal current that is a function of the applied potential. By plotting inverse of the measured current versus inverse of square root of rotation speed at various overpotentials we can get the Levich-Koutecky plot which enables us to calculate the kinetic current for each overpotential. Finally plot of logarithm of kinetic current versus overpotential provides us with Tafel plot which will provide us with kinetic data such as exchange current density, Tafel Slope, kinetic constant and charge transfer coefficient.

Figure 28 LK plot and Tafel Plot of and organic polymer in a redox flow battery

\[ \text{slope} = (1.12 \pm 0.08) \times 10^4 \text{A rad}^{-1/2} \text{s}^{-1/2} \]

\[ \log [i_k] = 4.65 \pm 0.01 \]
2.1.4. Pourbaix Diagram

Redox potential of the system might be a function of PH and have different values at different PHs. Change of redox potential versus PH might be accompanied by phase changes (such as the case in Iron) or just become a linear function. This diagram is of a thermodynamic diagram type and doesn’t include kinetics or transport information. In order to derive a Pourbaix diagram for the latter case, a series of cyclic voltammograms are performed with electrolytes at different PHs and the redox potential is measured in each PH and finally the redox potential is plotted versus PH. This plot can give valuable information about the behavior of the redox active component versus PH and our expectations from the voltage derived of the flow battery.

Hereunder pourbaix diagram of the Dihydroxy Anthraquinone (that is used in this research) is extracted from an article and illustrated. 30

\[ aA + bB \rightleftharpoons cC + dD \]

\[ E_H = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

Figure 29 A sample of Pourbaix Diagram
2.2. Single Cell Tests

2.2.1. Galvanostatic Charge and Discharge

The first and foremost responsibility of a flow battery is to become charged and discharged successfully. This test is performed under constant current. According to the convention, when the current is positive, the system is being charged to the set voltage and when the current is negative, the system is becoming discharged to the second voltage defined in the settings. When battery is charging at a constant current, after initial jump in the voltage, as the charging potential is approached slope of the of current vs voltage plot becomes reduced and it becomes similar to a plateau (charging plateau) and at this stage the battery keeps charging unit the desired SOC (state of charge) is reached and then the plot becomes steeps till the voltage reaches the upper limit for the voltage. The same phenomena happen during discharging of the system and the discharge plateau is formed.

\[
\frac{i \tau^{1/2}}{C_O^*} = \frac{n F A D_0^{1/2} \pi^{1/2}}{2}
\]

\[
E = E_{c/4} + \frac{RT}{nF} \ln \left( \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \right)
\]

\[
E_{c/4} = E^0 - \frac{RT}{2nF} \ln \left( \frac{D_O}{D_R} \right)
\]

These two curves are the main representative of the performance of the battery. They can show the columbic efficiency, voltage efficiency and also energy efficiency. Location of the plateaus (charging/discharging) is highly dependent on the volume of the electrolytes and charging/discharging current. 30
Galvanostatic cycling graphs can provide us with valuable information regarding the battery operation both during short term as well as the long term. It becomes possible to study the charging and discharging plateaus, analyze the voltaic efficiency and also study the long term durability of the battery. This test is an indispensable part of battery performance test.
2.2.2. Polarization Curve

Power rating of a flow battery is also important and it needs to be measured. Power rating defines the ability of the flow battery to deliver specific amount of energy during a specific period of time. Polarization curves demonstrate the power rating of a flow battery. Polarization curves are distinct for each state of charge and also, they are function of temperature. At higher temperatures we can get higher powers due to increase in the solubility of the system and also enhancement of the kinetics of the electrochemical reaction. In order to plot polarization curves, we have to first charge the battery to the desired state of charge and then run linear sweep voltammetry on the battery and measure the current at each voltage. By multiplication of current and voltage, we can calculate the power and finally plot the polarization curves.\textsuperscript{3,30}

\[
V_{cell} = E_{theo.} - (|\eta_{act,c}| + \eta_{act,a}) - \eta_{ohmic} - (\eta_{conc,c} + \eta_{conc,a})
\]

\[
V_{cell} = E_{theoretical} - |b_c \log(i)| - a - i \cdot R_{membrane} - 2.303 \left(\frac{RT}{nF}\right) \ln \left(\frac{i_{lim}}{i_{lim} - i}\right)
\]

Figure 31 A sample polarization curve for a flow battery
2.2.3. Electrical Impedance Spectroscopy

Resistance of the battery plays a vital role in the performance of the battery. During the cycling of the flow battery, resistance of the battery will increase the potential difference between charging and discharging plateaus thus reducing the energy efficiency of the system. During the polarization tests, it directly adds to the system resistance and reduces the output voltage and thus the output power of the system. Thus, it is needed to monitor the resistance of the battery carefully.

There are two major types of resistance in the system. Ohmic resistance and kinetic resistance. Also, there are different methods to measure the resistance of the system but the most frequently used and popular method is Electrical Impedance Spectroscopy. During this test, the voltage frequency of the system is changed and imaginary as well as the real part of the system Impedance(resistance) are measured. When these two impedances are plotted versus each other, a Nyquist plot is formed. Intersection of the Nyquist plot with the horizontal (real impedance) axes will give the ohmic resistance and the summation of the ohmic resistance and the kinetic resistance. Frequency of the Nyquist plot is increased as we move from right to left. Correspondingly, we move from the mass transfer-controlled area to the kinetics-controlled area.

\[
Z_{lm} = Z_{Re} - R_\Omega - R_{ct} + 2\sigma^2 C_d
\]

\[
\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left( \frac{1}{D_O^{1/2} C_O^*} + \frac{1}{D_R^{1/2} C_R^*} \right)
\]

![Figure 32 A sample EIS plot of a vanadium redox flow battery](image)
2.2.4. OCV Testing

Open circuit voltage is the potential when battery is not in a closed electric circuit and the system components are provided with enough time to reach equilibrium. Most of the times, OCV is the reported voltage of a battery and its value depends on the amount of charge present in the system or in other words how much the system has been charged. Quantity of the open circuit potential can be calculated using Nernst equation and it can be verified by experiments in lab. Crossover through membrane affect the open circuit potential negatively.

\[
aA + bB \rightleftharpoons cC + dD
\]

\[
E_H = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}
\]

![Sample Open Circuit Voltage as a function of State of Charge](image)

Figure 33 Sample Open Circuit Voltage as a function of State of Charge\(^5\)
2.2.5. Capacity/Efficiency Calculations

Capacity is equal to the amount of charge that is stored in or retrieved from a battery or in other words how many coulombs are in a battery. There are main three types of efficiencies for a battery and they provide important metrics for evaluation of battery performance. Columbic efficiency is the ratio of retrieved charge versus stored charge. Voltaic efficiency is the ratio of discharge voltage to the charge voltage and energy efficiency is the multiplication of the two.

\[
CE = \eta_c = \frac{Q_D}{Q_C}
\]

\[
VE = \eta_V = \frac{\int_{0}^{T_D} E_D(t)dt / T_D}{\int_{0}^{T_C} E_C(t)dt / T_C}
\]

\[
EE = \eta_{EE} = \eta_c \cdot \eta_V
\]

Figure 34 Efficiency/Capacity charts vs cycle number for a flow battery
2.3. References


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CHAPTER 3. INCREASING DURABILITY OF ALKALINE QUINONE REDOX FLOW BATTERY

3.1. Durability Tests

Durability tests are an important element of the redox flow batteries. In this section, a reference paper has been chosen and the results are repeated and the durability tests have been performed on it and finally some mechanisms for deactivation are proposed. During the tests all the milestones such as columbic efficiency, energy efficiency and cycle numbers at a specific charging current density are satisfied.

Various tests have been carried out and three of them are mentioned here. During two of these tests, all of the requirements have been fulfilled:

1. Cycling test with the conditions identical to the science paper: The potential vs Capacity curves at various C-Rates are included and it was not possible to reach the milestones (efficiencies) with these conditions (such as current density).

2. Cycling test (N212 was used as membrane): During 250 cycles with charging current density of 100mA/cm², columbic efficiency of higher than 98% and energy efficiency of higher than 75% was attained. This test took around 2.5 days. States of charge were ~42% for the initial 140 cycles.

3. Cycling test (N211 was used as membrane): During more than 400 cycles with charging current density of 100mA/cm², columbic efficiency of higher than 94% and energy efficiency of higher than 76% was attained. Energy efficiency was higher than 80% during the first 200 cycles and then it dropped to a minimum of 76%. This test took around 6 days. States of charge were ~72% for the initial 60 cycles.
During one of the tests, cathode active material was replaced with fresh materials (instead of the anode that is usually considered to be less durable) and a revival of the performance was witnessed and it is corroborated by a recent published paper that has studied durability of ferrocyanide ion in alkaline media and had concluded decomposition of this ion through redox reactions carried out in alkaline conditions, converting to potassium cyanide. Changing cathode media from alkaline to DI water accompanied by potassium chloride as supporting electrolyte enabled us to sustain high efficiencies at high current densities for longer periods of time. This issue can answer part of our questions regarding the durability of the anthraquinone based redox media in alkaline flow batteries that the rapid decline in the battery capacity was mainly due to the decomposition of the ferrocyanide ion in alkaline media and not the Dihydroxy Anthraquinone. However, DHAQ also deactivates however the related mechanism is not clear for us. This part has been discussed in the related section.

Results of the conditions 1,2&3 are mentioned together.
Differences in the conditions

Table 1. Conditions of the cycling test for the alkaline quinone flow battery

<table>
<thead>
<tr>
<th>Conditions in the Reference Paper</th>
<th>Conditions used here.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate</td>
<td>60 ml/min</td>
<td>100, 120 ml/min</td>
</tr>
<tr>
<td>Quantity of the Anode</td>
<td>4ml, 0.5M DHAQ solution</td>
<td>5ml/8ml, 0.5M DHAQ solution</td>
</tr>
<tr>
<td>Quantity of the Cathode</td>
<td>15 ml, 0.4M Ferricyanide solution</td>
<td>15/25 ml, 0.4M Ferricyanide solution</td>
</tr>
<tr>
<td>Cathode Electrolyte</td>
<td>1M KOH</td>
<td>1M KCl in DI water</td>
</tr>
<tr>
<td>Anode Electrolyte</td>
<td>2M KOH</td>
<td>2M KOH</td>
</tr>
<tr>
<td>Membrane used</td>
<td>N212, pretreated</td>
<td>N212, N211, pretreated</td>
</tr>
<tr>
<td>Electrode</td>
<td>3 Layers of 10AA SGL, pretreated</td>
<td>3 Layers of 39AA SGL, pretreated</td>
</tr>
</tbody>
</table>
3.2. Cycling with the Identical Conditions with the Science Paper

At exactly the same conditions as the reference paper, it was possible to reach an energy efficiency of higher than 75% with current densities around 70mA/cm². A galvanostatic charge and discharge of the system at various current densities is illustrated in the figure below. It was needed to make some modifications in the system to be able to run with the same efficiencies at higher charging current densities.

![Graph showing voltage vs capacity at various C-rates](image)

Figure 35 Galvanostatic charging-discharging of the alkaline quinone flow (70 mA/cm²)
3.3. Cycling Test Using N212 as Membrane

This cycling test was performed with N212 membrane. Charging Current density was 100mA/cm². Columbic efficiency was above 98% and energy efficiency was above 75%. Top picture: cycling samples from 2hr to 4hr. Mid picture: cycling samples from 50hr to 52hr. The Bottom Picture: all Cycles. This test was able to meet all requirements (CE>98%, EE>75%, 100mA/cm², 250cycles, 2.5days).
Figure 36 Charging/Discharging Cycles for the system with N212 membrane

Cylindrical, Voltaic and Energy Efficiencies for the alkaline quinone flow battery during all 250 cycles. Stable columbic efficiency of higher than 98% and voltaic/energy efficiencies of higher than 75% throughout battery operation of 250 cycles (2.5 days).

Figure 37 Columbic, Voltaic and Energy Efficiencies for the alkaline quinone flow battery
3.4. Cycling Test Using N211 as Membrane

This test was also able to meet all requirements (CE>94%, EE>75%, 100mA/cm², 400 cycles, EE >80% during the first 200 cycles). In addition to meeting the requirements, this test was also a durability test of the redox active materials in the system. While the conditions are maintained, some changes in the redox materials has been done to check for the durability. Each plot corresponds to one day of test.
Figure 38 Cycles for the alkaline quinone flow battery with N211 membrane.

During the fourth day, there was a tube rupture inside the peristaltic pump due to long and continuous pump operation which transfer the fluid by squeezing the tube. Tube was replaced and the cathode material was replenished.
Figure 39 Cycles for the alkaline quinone flow battery with N211 membrane.

Sample cycles for the alkaline quinone flow battery with N211 membrane from 2hr to 4hrs of operation. Charging starts at 1.2V and discharge starts at voltage higher than 1.2V, leading to higher voltaic efficiency. This trend is maintained during battery operation (6days).

Columbic, Voltaic and Energy Efficiencies for the alkaline quinone flow battery with N211 membrane. Spikes in the efficiency curves are related to the replacement of the cathode material. Battery has a consistent columbic efficiency during span of six days and a very small reduction in the energy efficiency that can be related to the deactivation of the redox material leading to increasing of the charging voltage and reduction of the discharging voltage.
Capacity for the alkaline quinone flow battery with N211 membrane is displayed in the figure below. This test helps us in verifying the stability of the anode active material (DHAQ) through longer life cycling test. After 75000 seconds, the cathode was replaced with a new material (point 1). At 182000 seconds, the cathode was replaced again (point 2). Tube rupture occurred also in the cathode part and it was replaced at 285000 seconds since start of the test (point 3). Each cathode replacement is identified by a spike in the capacity curve which shows that even though the cathode system has been changed to KCl and DI water, it is not completely stable and still has a role in the overall capacity fade of the battery. However, if the anode was supposed to be completely stable, we would face the initial capacity of the system while this doesn’t happen and the capacity increases partially, thus deactivation of the anode is a fact and we can make sure that DHAQ deactivates in the long run. So, the overall capacity fade can be ascribed to three factors: cathode deactivation, anode deactivation as well as crossover. Elimination/reduction of crossover is only possible by using thicker membranes which will increase the system resistance and sacrifice the energy efficiency which was one of the main milestones of the current research, so thicker membranes are not utilized.

Figure 41 Columbic, Voltaic & Energy Efficiencies of alkaline quinone flow battery (N211)
3.5. Electrochemical Stability

3.5.1. Results of NMR tests

Nuclear Magnetic Resonance (NMR) spectra of the anode active material (DHAQ) was prepared for the fresh material as well as the material at the end of the battery operation. NMR was carried out in the AVIII 600Hz device. NMR spectra are similar for both of the chemicals and do not indicate decomposition.

The top picture is the spectra prior to the start of the test and the bottom picture is the spectra after the end of the test. Numbers on the peaks show the related Hydrogen atom in the DHAQ molecule. The spectra are the same.

![NMR Spectra for the Dihydroxy Anthraquinone.](image)

Figure 3.9.: NMR Spectra for the Dihydroxy Anthraquinone.
3.5.2. Deactivation Mechanisms

NMR test has been performed for both fresh DHAQ as well as used DHAQ and they are included. NMR results show no sign of anthraquinone decomposition because the graphs are similar. Small amount of shift in the peaks might be attributed to neutralization or testing conditions but the materials are the same and this is corroborated with the finding that cathode was the main culprit for battery deactivation in our tests versus the widely suspected anode that had in fact remained more stable than the cathode in alkaline media. However, deactivation of the DHAQ has been verified in the current durability test during which fresh cathode has been injected to the system several times and never the capacity of the system reached the initial capacity, furthermore, deactivation of the quinone compounds has been verified in other papers also\(^1\) and the fact that the NMR results don’t show such phenomena (in my test as well as in the literature\(^1\)), the deactivation shall have occurred in routes that their products are not distinguishable from the original material through NMR and this issue is ascribed to nucleophilic mechanisms initiated by water molecule adding hydroxyl groups to the quinone structure which are not discernible through NMR. In the literature two major mechanisms have been reported as following:

- **Gem-Diol Formation**: This is a reversible mechanism but sacrifices the kinetics of the redox reaction. This mechanism will lead to the changing of the discharge plateau of the battery as well as reduction in the discharging voltage.
- Michael Mechanism: Michael Mechanism is irreversible and completely deactivates the chemical ending in capacity loss of the battery.

![Diagram of Michael Mechanism]

Deactivation takes place for the quinone compounds but not very quickly and while anthraquinones are considered to be more stable than quinones, this cannot be deduced from the published single cell results in flow batteries. Rate of deactivation depends first on the chemical structure of the compound and then on the operating parameters such as state of charge, charging rate…. Interaction of various parameters, especially structural attributes are still under study.

In a recent work the stability of the quinone compounds has been studied through DFT calculations as well as experimentally. A vast pool of quinone compounds has been selected and the calculations are run and some experimental tests have been carried out to verify the calculations. In this work the main deactivation source is ascribed to the nucleophilic addition of water to the carbonyl containing compounds via gem-diol formation (reversible but reduces the kinetics) and Micheal addition accompanied by a tautomerization which is irreversible and completely deactivates the redox capability of the material. According to their analysis, as the redox potential increases, the electrophilicity also increases which enhances the possibility of the nucleophilic attack from water molecules. Based on this paper, my understanding is that species with less redox potential seem to possess more stability.

Despite the comprehensiveness of the work, some points are ambiguous for me regarding this analysis. First, according to this work, it is expected that the quinone compounds do not seem to
be susceptible to deactivation when their carbonyl groups are converted to their corresponding hydroxyl groups because there is no chance of Gem-Diol or Micheal addition, while this doesn’t seem to be in agreements with other publications proposing that deactivation increases with the time that these compounds spend during their reduced state. My other question is related to their experimental section that is limited to four compounds, three of them are sulfonyl containing anthraquinones and the other is anthracene brown (hydroxyl containing) and DHAQ as a strong candidate is not included there. I think we will see more publications of this kind from this group in future covering more aspects.

A rather more experimental approach has been selected in another work to assess the chemical and electrochemical stability of some of the redox media frequently used in flow batteries including DHAQ, via utilization of unbalanced compositionally symmetric cell method and imposing capacity limitation on one side. This research demonstrates that capacity fade of DHAQ is 1%/day when utilized in at 50%SOC and reduces as lower SOC is utilized which magnifies importance of the operating parameters as well.

PH effects are also considered to be effective in the decomposition rate of the quinone compounds and this was the main incentive for synthesizing 4,4’-((9,10-anthraquinone-2,6-diyl)dioxy) dibutyrate (2,6-DBEAQ) in which the end hydrogens of DHAQ are replaced by butyrate carboxylic groups, enabling it to gain higher solubility although sacrificing part of the redox potential due to placing carboxylic groups at the end of the functional group, however they are also responsible for higher solubility. This material can operate in pH 12 but has lower potential than DHAQ but will last much longer.
3.6. References


CHAPTER 4. HIGHER VOLTAGE IN FLOW BATTERIES WITH HYBRID ACID AND BASE ELECTROLYTES

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ABSTRACT

An organic redox flow battery with hybrid acid and base electrolytes using a single cation exchange membrane has been successfully developed to demonstrate higher operation voltage and long durability. An organic redox flow battery with hybrid acid and base electrolytes using a single proton exchange membrane has been developed and tested successfully. This technique has been able to improve the voltage span of the previous quinone flow battery by 300 mA and the energy density is raised three folds to reach 22.11 Wh/Kg. Also, it has been used for another flow battery system to evidence the applicability of this technique to other types of redox flow batteries. This technique has been demonstrated to be advantageous to using two membranes economically.

4.1. Introduction

Intermittency is one of the main barriers in the route of widespread harvesting of the immense amount of renewable energy that mother nature provides us freely. While technologies like pumped hydroelectric and compressed air energy storage might be feasible for very large scale, imminent decentralization of power grids will vitalize importance of efficient small-scale energy
storage systems such as batteries\textsuperscript{2,1}. In contrast to traditional batteries that provide a black box precluding any further modifications on their internal properties, they suffer from various hardships such as dendrite formation in solid state deposition batteries or mechanical electrode damage in intercalation battery systems, flow batteries furnish us with valuable capabilities such as modification of energy and power sections independently via changing the size of storage tanks to increase the stored energy or by modifying cell elements to manipulate the output power\textsuperscript{2}.

Metal ion flow batteries have been developed for a while and technologies such as all vanadium, iron chromium and zinc bromine flow batteries have become well established, however they face challenges such as material cost\textsuperscript{3}, kinetic\textsuperscript{5,38}, precipitation\textsuperscript{4} and corrosion (All vanadium flow batteries), side reaction\textsuperscript{5}, kinetics\textsuperscript{6}, efficiency\textsuperscript{5} and corrosion (Iron chromium), Dendrite formation\textsuperscript{7}, environmental hazards related to keeping all components in solution phase\textsuperscript{8} and requirement for cooling\textsuperscript{9} (Zinc bromine flow batteries). On the other hand, organic flow batteries can provide a reliable alternative by lowering material cost and improving kinetics. Organic compounds have the capability of tunability and it is possible to modify their redox potential, solubility as well as other attributes through proper functionalization\textsuperscript{10}. Sensitivity analysis of capital cost of the vanadium flow batteries has demonstrated importance of the cost of electrolyte\textsuperscript{11}, a conclusion that can be generalized to other flow batteries as well. Finding cheaper alternatives for the vanadium-based electrolytes can reduce the cost of the stored energy\textsuperscript{12} and low cost of organic compounds is their other advantage to other types of redox flow batteries\textsuperscript{13} and provides an alternative for cost problem. Aqueous organic flow batteries are able to operate at higher current densities. However, organic redox flow batteries mostly suffer from low energy density\textsuperscript{14,15,16,18,17}.

Quinones by providing two electrons in each reaction and exhibiting high kinetic rates as well as solubilities, appear to be one of the promising candidates for organic redox flow
batteries\textsuperscript{18,19,20,21}. Low cost, fast kinetics as well as 2 electrons per reaction make them a good candidate for high power requirement systems\textsuperscript{22}. Proper functionalization, makes quinone compounds more soluble in water\textsuperscript{30,23} and enables them to be used both as cathode and anode in aqueous flow batteries. Redox potential of the quinone compounds depends on the pH of the electrolyte thus, in a flow battery that benefits from quinone compounds on both the anode side and the cathode side, upon increasing the system pH, redox potential of the anode will become more negative while the pH of the cathode will become less positive and by reducing the pH the opposite will happen. Therefore, any fixed pH will bring a potential gain from one side and a potential sacrifice from the other side, and this issue renders utilization of the whole potential range of the quinones infeasible, leading to a lower voltage as well as a lower energy density. As a result of that, usually quinone compounds are coupled to other components to have a better voltage at a specific pH.

In a work done by Yan et al\textsuperscript{24}, two ion exchange membranes were utilized in flow batteries. Their system included one anion exchange membrane (AEM) and one cation exchange membrane (CEM) with an electrolyte between the two membranes. This technique can successfully couple various redox groups together and reach higher voltage, however, high cost of the extra membrane will become more pronounced as the flow battery is intended to become scaled up, necessitating utilization of a large amount of ion exchange membranes and imposing more fixed capital cost to the system.

In this paper, we introduce a methodology that enables us to utilize electrolytes with contrasting pH on both sides of the membrane, enabling us to make the best use of the redox potential of both the cathode and the anode. Cathodic quinone will have more positive redox potential at lower pH. Simultaneously, the anodic quinone will have more negative redox at higher pH and this will
increase voltage of the battery and its energy density accordingly. This system provides a redox potential of 1.5 V and an energy density of 22.11 Wh/kg. 2,6-dihydroxy anthraquinone (DHAQ) and 1,2-hydroquinone-3,5-disulfonic acid (HQDS) are used as the anode and the cathode respectively with the following half reactions:

\[
\text{Dihydroxy Anthraquinone: } \text{HSO}_3^- + \text{H}_2\text{O} + 2e^- + 2\text{H}^+ \rightleftharpoons \text{SO}_3^- + 2\text{OH}^- \quad E^0 = 0.85 \text{ V vs SHE} \quad [1]
\]

\[
\text{Hydroquinone-3,5-disulfonic acid: } \text{O} + \text{H}_2\text{O} + 2e^- + 2\text{H}^+ \rightleftharpoons \text{OH}^- + \text{OH}^- \quad E^0 = -0.67 \text{ V vs SHE} \quad [2]
\]

Dihydroxy Anthraquinone has proven to be a reliable anode for alkaline quinone flow batteries showing a good redox potential of -0.67 V as well as good reversibility when coupled to Potassium Ferricyanide\textsuperscript{30}. Redox potential of DHAQ will increase by raising the solution pH (till 12.6), however, reaching concentrations as high as 0.55 M, necessitates using solutions with higher alkalinity (2 M KOH) which also, provides sufficient capacity for the alkalinity of the system, preventing the necessity for a buffer solution at the anode side.

1,2-Hydroquinone-3,5-disulfonic acid (HQDS) has displayed a good redox potential (+0.85 V) when coupled to Anthraquinone sulfonic acid in acidic environment\textsuperscript{25,26} and also it presents a better reversibility as the system pH is reduced (pH<1). Hydroquinone disulfonic acid is very safe in comparison to the hazardous bromine and displays advantages over ferricyanide ion. First, due to presence of two sulfonic acid groups in HQDS it has a high solubility (>1.7 M) in aqueous systems even in neutral pH. Second, it entails two electron transfers per its redox reaction and also, its redox potential can be as high as 0.86 V in acidic solutions. In contrast to ferricyanide ion which
its solubility is limited to 0.4M in alkaline media and is not stable in acidic media, incorporates just one electron in its reaction and its redox potential is independent of pH thus, rendering the potential benefits accrued by pH reduction infeasible and moreover, ferricyanide ion has been proven to be unstable during electrochemical reactions in alkaline environments\textsuperscript{27}. Utilization of HQDS as catholyte significantly increases the energy density of the system due to its higher concentration and entailing two electrons per redox reaction.

Potassium is the main ion to be transferred through charging and discharging cycles of the battery. Anode electrolyte is 2 M KOH and the cathode buffer solution is made with KCl and HCl. This configuration ensures presence of sufficient amount of potassium ion on both sides of the proton exchange membrane that has also been treated in 0.1 M KOH solution overnight ensuring that the sulfonic acid tails in Nafion structure are saturated with potassium. Potassium is the main ion that is transferred through membrane. Also, when there is no injection, intermittent pH measurement of both the cathode and anode tanks by a portable pH meter displays a reduction of pH in the anode side and an increase of pH in the cathode side which is an indication of proton being carried through the membrane as well, necessitating intermittent addition of KOH to the anode side as well as intermittent injection of small volume (0.6 ml/hr) of supporting electrolyte to the cathode side via a HPLC pump. Repeated checking of the pH on both sides of the battery that is equipped with addition system, ensures that the pH of the anode and cathode sides have remained constant at 14.0 and 0.3 respectively during operation for more than 140 hours.

This system demonstrates that all quinone flow batteries can be modified to incorporate an alkaline solution in the anode side and an acidic solution in the cathode side, using one proton exchange membrane to benefit the most from pH dependence of the quinone compounds that rely on deprotonation. Using a high capacity buffer solution with pH=0.3 on the cathode side as well
as electrolyte makeup injection (e.g. via a HPLC pump) will prevent potential drop of the battery
and similarly addition of KOH to anode electrolyte will ensure sustaining high pH levels in the
anode and prevent precipitation of DHAQ.

4.2. Experimental

Materials

All materials were used as received. Anthraflavic acid (2,6-dihydroxy anthraquinone) 90% and
Potassium Hydroxide 85% were purchased from Sigma. Dibasic potassium phosphate 99.4%,
Potassium Chloride 100% and Hydrochloric Acid 36.9% were purchased from Fisher Scientific.
1,2-Dihydroxybenzene-3,5-disulfonic acid disodium salt monohydrate 97% was purchased from
Alfa Aesar. Nafion 212, Carbon paper (Sigracet 39 AA) as well as Single cell hardware including
end plates, collectors, POCO graphite flow channel plates were purchased from fuel cell
technologies.

Cyclic Voltammetry

All half-cell tests were purged by argon during operation to prevent any oxidation with air. A
three-electrode cell was used to carry out cyclic voltammetry. Platinum wire and Ag/AgCl in 3 M
KCl (0.210 V vs. SHE) were used as the counter and reference electrodes respectively. Working
electrode was glassy carbon electrode with diameter of 5 mm. Scan rate was 100 mV/s in all CV
tests except the Randles-Sevcik test that the scan rates were as following: 25,50,75,100,125,150,175,200,250,300,350,400,450,500 mV/s. 2 mM DHAQ in 1 M KOH was
tested from -1.1 V to -0.1V vs Ag/AgCl and 2mM of HQDS in a buffer solution made of 0.5 M
KCl and 1 M HCl with PH=0.3 was tested from 0 V to 1.2 V vs Ag/AgCl. Different mixtures of
(0.2 M) Potassium Phosphate Dibasic (K$_2$HPO$_4$) and (1 M) Hydrochloric Acid were used to
prepare a series of buffer solutions with pHs ranging from 1-7 to run cyclic voltammograms with
5 mM HQDS to prepare the pourbaix diagram. Pourbaix, RDE tests were only performed for the
cathode active material (HQDS) because the similar tests for DHAQ were performed and reported by Aziz et al (2015).

**Rotating Disc Electrode**

Rotating disc electrode tests were performed using a Pine MSR rotator instrument using similar setup as the one used in cyclic voltammetry. The following rotation speeds were used in this test: 300, 400, 600, 800, 900, 1000, 1200, 1400, 1600, 1800, 2000, 2200 and 2400 RPM. RDE testes were performed for two cases. 2 mM HQDS dissolved in a buffer solution with pH=0.3 made of KCl (0.5 M) & HCl (1 M) and also for the buffer solution alone to measure the background currents for subtraction from the main measured currents.

**Galvanostatic charge/discharge**

Cell was assembled according to the improved no-gap structure. The cell design was in a manner to minimize dead zones and optimize flow distribution. Pretreatment of Nafion212 (&211) was performed first by boiling it in DI water at 85°C for 35 minutes, then soaking it at 5% H₂O₂ solution at 85°C and soaking it overnight at 0.1 M KOH. POCO graphite serpentine flow channel plates sandwiched between gold plated copper current collectors were used on both sides. Carbon paper (Sigracet 39AA) was baked in oven at 400°C for 24 hrs and three layers of 39 AA, compressed to 80% of the initial thickness with area of 4 cm² were used on both sides of the membrane. Compression and sealing are guaranteed by the number and thickness of PTFE gaskets used between current collectors and flow channel plates. All tests were performed using a Biologic VSP-300 potentiostat. Flow rate was controlled to be 100 ml/min using Cole-Palmer Masterflex pumps. Further increase of flow rate didn’t show noticeable decrease in the mass transfer resistance of the system. The batteries were charged to 2 V during charging and 0.3 V during discharging (0.5 V for case of HQDS with N211). Cathode pH is sustained via injection of 0.6 ml/hr of 1 M
HCl by the aid of a ChromTech hplc pump equipped with PEEK head that is tolerant against this concentration of hydrochloric acid. 20% of isopropanol in DI water was used as the flushing liquid. pH of anode is maintained by intermittent checking and modifying the pH via adding KOH to anode tank. Both tanks were purged by argon gas throughout the experiment to avoid any reactions with oxygen. Efficiencies were calculated according to the following equations\textsuperscript{31}:

\[
CE = \eta_C = \frac{Q_D}{Q_C} \quad \text{[3]}
\]

\[
VE = \eta_V = \frac{\int_{0}^{T_D} E_D(t)dt / T_D}{\int_{0}^{T_C} E_C(t)dt / T_C} \quad \text{[4]}
\]

\[
EE = \eta_{EE} = \eta_C \cdot \eta_V \quad \text{[5]}
\]

CE, VE & EE are columbic, voltaic and energy efficiency respectively. C, D & T(t) stand for charging, discharging and time respectively. η is efficiency.

4.3. Results and Discussion

4.3.1. Cyclic Voltammetry

Cyclic voltammetry enabled us to observe and compare the redox potential and the reversibility of both quinone compounds used in this system. Cyclic Voltammogram of 2mM DHAQ in 2M KOH (orange curve) and 2mM HQDS in buffer solution pH=0.3 (with 0.5M KCl and 1M HCl) (dark blue curve) are displayed. Scan rate was 100mV/s and the test was performed on glassy carbon electrode. Direction of scans is exhibited by arrows. Dashed lines represent the redox potentials. Oxidized and reduced chemicals forms are illustrated on the CVs. Anode and cathode were sustained at both ends of the pH spectra (14, 0.3) to get maximum benefit from pH. Redox potential of both DHAQ and HQDS are at -0.67 V and 0.85 V, respectively. Both systems displayed good redox potentials as well as good reversibility, however, reversibility (kinetics) of DHAQ was higher than the reversibility of HQDS, which might be attributed to its chemical structure and also partly related to the alkaline reaction media of DHAQ that doesn’t necessitate
protonation steps between redox reactions, which affect the electrochemical kinetics in acidic media\textsuperscript{33}.

![Cyclic Voltammogram of both redox components (DHAQ, BQDS)](image)

Figure 42 Cyclic Voltammogram of both redox components (DHAQ, BQDS)

4.3.2. Electrochemical stability

This test demonstrated the electrochemical stability of the cathode active material (hydroquinone disulfonic acid) as well as its compatibility with the components of the buffer solution in the potential range of the battery operation. These attributes were construed by a linear correlation between the peak current densities and the square root of the scan rates. Randles-Sevcik test was performed with 2 mM of HQDS in a buffer solution comprising of 0.5 M KCl and 1 M HCl with pH=0.3. Cyclic Voltammograms were performed from 0 V to 1.1 V vs Ag/AgCl with scan rates ranging from 20 mV/s to 500 mV/s yielding a linear plot of peak current densities (oxidation) vs square root of scan rates. Cycle #6 is considered as the basis of the calculations.
Even though redox potential of the anode (DHAQ) becomes pH independent in pH values above 12, due to full deprotonation of the reduced species, the discharge plateau of the system becomes steep upon reduction of the pH of the anode solution from 14 to 12. Using 2M KOH at the anode provides sufficient capacity for the alkalinity of the system to prevent reduction of anode pH due to carryover of protons from cathode to anode, thus preventing utilization of some buffer solutions at the anode side which might interfere with the redox reaction. Furthermore, 2M KOH provides a good solubility for the anode material (DHAQ).

4.3.3. Pourbaix analysis

This analysis provided us with the evidence of how much it was possible to gain in the system potential through reduction of pH in the cathode side. Theoretically, it is expected to have gains by lowering pH of the system due to participation of protons in the redox reactions, however this might not be true for some kind of Quinone compounds and a Pourbaix analysis becomes helpful. Pourbaix Diagram was performed by running CVs of 5 mM HQDS in buffer solutions of various pHs made up of varying proportions of K2HPO4 (0.2 M) and HCl (1 M). Scanning is performed with rate of 100 mV/s from 0 V to 1.2 V vs Ag/AgCl. Cycle #6 is considered as the basis of calculation.
Result of the analysis clearly illustrated the gains in redox potential of the system by reducing system pH, thus emphasizing the benefit of using electrolytes with contrasting pH on both sides of the membrane. Furthermore, a reduction in reversibility of the system was witnessed upon increasing of the pH from 1 to 2, which provided us with another benefit accrued by keeping the cathode system as low as 0.3. By comparing the reversibility, it was noticed that the decrease in reversibility is less serious when pH is increased from 2 to 7. This sudden reduction in reversibility upon changing pH from 1 to 2 which might impose higher kinetic overpotential in single cell tests, and it can be attributed to the change in the mechanism of redox reaction. At high proton concentrations (pH<1), redox reaction initiates with the protonation step while in higher pH values (lower proton concentrations), the onset reaction is the electron transfer which is rate limiting in this case. This change of paradigm seems to happen at around pH=2 for HQDS based on this observation. Furthermore, significant reduction in proton concentration might also negatively affect the rate of the second proton transfer which reduces the overall reaction rate. Injection of cathode active material successfully prevented this problem. Pourbaix analysis of the DHAQ has been performed by Aziz et al. (2015) demonstrating reduction of the redox potential with increase of the system pH till 12.8 and after that redox potential remains constant at -0.67 V. However, reaching a concentration of 0.55 M for DHAQ necessitates dissolving it in 2 M KOH. Thus, it is necessary to keep the anode at pH=14 and the cathode at pH=0.3.
4.3.4. Rotating Disc Electrode Analysis

Rotating disc electrodes provided us with the kinetic information of the redox components used in the battery and to identify the kinetically limiting component. Rotating Disc Electrode is performed for 2 mM of HQDS dissolved in buffer solution with pH=0.3 made of 0.5 M KCl & 1 M HCl. Potential was scanned from 0 V to 1.1 V vs. Ag/AgCl reference electrode. Water oxidation reaction becomes noticed as the potential approaches 1.2V in acidic environment, necessitating reduction of the background currents from the derived results prior to making L-K calculations. Scanning is done at the rate of 100 mV/s by varying the rotation speeds from 300 RPM to 2800 RPM with the catholyte and without it and the results are displayed after subtraction of the background currents, thereafter, via LK & Tafel calculations, exchange current density as well as reaction constant are extracted. Slope of Levich plot was calculated to be 0.012 mA/(Rad^{0.5} s^{0.5}) and by considering the kinematic viscosity as 1.08*10^{-6} m^{2}/s, the diffusivity coefficient was calculated to be 2.9*10^{-6} cm^{2}/s which was close to the reported value in the acidic environment^{25}. L-K plots were derived by plotting the inverse of the current vs the inverse of the square root of the rotation speed at various overpotentials. Exchange current density and the reaction rate constant were calculated to be 6.3 * 10^{-5} A/cm^{2} and 1.63 * 10^{-4} cm/s respectively. Rate

Figure 44 Pourbaix Diagram for HQDS
constant of HQDS is lower than the rate constant of the DHAQ published in literature ($7 \times 10^{-3}$ cm/s) which makes the cathode kinetically limiting component.

![Graph showing current vs rotation rate for different potentials](image)

Figure 45 Rotating Disc Electrode is performed for HQDS.

4.3.5. Galvanostatic Cycling

Cell testing was performed at ambient conditions (20°C) with 8ml of 0.55 M DHAQ dissolved in 2 M KOH and 5 ml of 0.9 M HQDS dissolved in buffer solution with pH=0.3 made of 0.5 M KCl and 1M HCl with various charging/discharging currents. The cell comprises of gold covered copper plates, graphite flow channel plates, treated carbon paper as well as Nafion (211&212) membrane.

Galvanostatic cycling of the battery was performed successfully with Nafion 211, displaying the highest voltaic efficiency as well as an open circuit voltage of 1.5V when charging/discharging...
with current of 300 mA. Cycling tests were repeated with Nafion N212 which shows a higher
columbic efficiency probably due to lower crossover resulting from higher thickness of the
membrane. This battery was able to reach OCV higher than 1.5 V and EE higher than 70%. Long
term stability test was performed with an excess amount of cathode active material. 8ml of 0.55 M
DHAQ dissolved in 2 M KOH and 8 ml of 0.9 M HQDS dissolved in buffer solution with pH=0.3
made of 0.5 M KCl and 1 M HCl. Due to deactivation of HQDS, this material was added to the
cathode during intervals to prevent battery dying. 1 M HCl was added via a Hplc pump to the
side while solid KOH was added intermittently to the anode side. The kinetically limiting
current density of 80 mA/cm^2 and discharged with current density of 40mA/cm^2. Columbic
with current of 300 mA. Cycling tests were repeated with Nafion N212 which shows a higher
columbic efficiency probably due to lower crossover resulting from higher thickness of the
membrane. This battery was able to reach OCV higher than 1.5 V and EE higher than 70%. Long
term stability test was performed with an excess amount of cathode active material. 8ml of 0.55 M
DHAQ dissolved in 2 M KOH and 8 ml of 0.9 M HQDS dissolved in buffer solution with pH=0.3
made of 0.5 M KCl and 1 M HCl. Due to deactivation of HQDS, this material was added to the
cathode during intervals to prevent battery dying. 1 M HCl was added via a Hplc pump to the
cathode side while solid KOH was added intermittently to the anode side. The kinetically limiting
current density of 80 mA/cm^2 and discharged with current density of 40mA/cm^2. Columbic
efficiency was raised to 99.99%. Battery was cycled for more than 140 hours with this scheme and
the system pH was measured intermittently, demonstrating that the final system pH (pH=0.3) was
similar to the initial system pH (pH=0.3). Two sample cycles are represented in the figure 5. This
is a successful manifestation of the long-term applicability of flow battery system utilizing
electrolytes with contrasting pHs on both sides of the membrane.
Figure 46 Galvanostatic charging curves for DHAQ vs HQDS system

(Galvanostatic charging curves for DHAQ vs HQDS system using hybrid system made of electrolytes with contrasting pH. a) Cycles done with Nafion 211, b) Cycles done with Nafion 212, c) Durability test for the system with N212, charging current 80mA/cm² and discharging current 40mA/cm² d & e) two selected sample cycles.)
4.3.6. Electrochemical Impedance Spectroscopy

Dissection of the system resistance will enable us to identify high impedance areas inside the system and seek for probable remedies. High frequency resistance (ohmic) is mainly due to ionic movement in membrane as well as ionic, electronic and contact resistance in electrodes and electric resistance through 3D porous structure of the electrode. On the other hand, low frequency impedance will allow us to calculate kinetic polarization. Battery is charged with 1C-rate incrementally (10%) from zero charge to full charge. 100% charging of the system is attained through potentiostatic holding of the system at 2 V until the current fell below 50 mA. In each increment, electrical impedance spectroscopy (EIS) is performed in the range of 200 KHz to 20 Hz and the high frequency resistance is measured as the x-intercept of the graph and the polarization resistance is estimated by extrapolation of the interface of the falling data in the reaction zone of the graph with the x axis. Both ASRs (high frequency, polarization) are plotted against SOC%. Due to porous structure of the electrodes, ohmic resistance is partially higher when it is dry but the ohmic resistance of the battery during other state of charge are similar. The battery shows a kinetic polarization that increases gradually with state of charge which is attributable to the cathode material. Further dissection of resistance elements necessitates using voltage probes to subtract the current of each electrode layer and quantify each resistance independently\textsuperscript{32}.

Similarly, through incremental charging, open circuit voltage of the battery is measured. For measuring OCV, sufficient time was given to the system to reach a stable potential. An OCV of 1.52 V and 1.66 V were attained at SOC of 50% and 100% respectively. High OCV of the system during incremental charging also demonstrates that the system is able to provide a high potential difference.

\begin{align*}
\textit{Cathode:} & \quad \text{BQDS} + 2H^+ + 2e \rightleftharpoons \text{HQDS} \quad E^0 = +0.85 \text{ V vs SHE}\end{align*} \textsuperscript{[6]}
Anode: \[\text{DHAQ} + 2H^+ + 2e^- \rightleftharpoons \text{THAC} \quad E^0 = -0.67V \text{ vs SHE} \]  

\[
E_{\text{Cell(OCV)}} = \left( E_{\text{Cathode}}^0 - E_{\text{Anode}}^0 \right) - \frac{RT}{nF} \ln \left( \frac{[\text{HQDS}] [\text{DHAQ}]}{[\text{BQDS}] [\text{THAC}]} \right)
\]

\[
\text{SOC(\%)} = \frac{[\text{BQDS}]}{[\text{BQDS}]+[\text{HQDS}]} = \frac{[\text{THAC}]}{[\text{THAC}]+[\text{DHAQ}]} \]

THAC stands for 2,6,9,10 tetrahydroxy anthracene which is the reduced form of DHAQ. The above formulation enables us to calculate the theoretical Nernstian potential changes at difference state of charges.

Battery is charged incrementally (10% increments) from 0% SOC to 100% SOC and via performing EIS and OCP, the high frequency ASR (ohmic resistance), polarization ASR as well as open circuit voltage of the system are calculated and plotted.

Figure 47 EIS, OCP and ASR for the battery

(a) EIS @ different state of charges (SOCs) for the system b) ohmic and polarization area specific resistances (ASR) & open circuit voltage (OCV) vs SOC%
4.3.7. Analysis of columbic efficiency of HQDS

Quinone compounds have fast electron transfer kinetics; however, their rate of reactions does not follow the same path when they are dissolved in acidic or alkaline environment. Base on the mechanism called “scheme of squares” first studied by J. Jacq\textsuperscript{33} and also cited by McAuley\textsuperscript{34}, Wedege\textsuperscript{35}, in alkaline media charge transfer follows two consecutive electron transfer steps while in acidic media each electron transfer reaction is accompanied by a proton transfer step which might precede or succeed the corresponding electron transfer step depending on the system pH.

Fig. 6. Scheme of square for benzoquinone disulfonic acid (BQDS). Red arrows show the predominant reaction pathway for BQDS at acidic media. a) Assumed reaction mechanism for DHAQ b) Proposed reaction mechanism for HQDS at pH<2, c) proposed reaction mechanism for HQDS at pH>2. Change in reaction mechanism is accompanied by reduction in overall electrochemical reversibility.

Thus, for DHAQ dissolved in highly alkaline 2 M KOH solution follows the first route\textsuperscript{34} while HQDS that is dissolved in acidic media follows the second mechanism comprising of two consecutive steps each containing one protonation and one electron transfer and their order varies depending on the system pH. thus, overpotential losses and the reversibility of the components are different in acidic and alkaline media. All these factors, lead the charge transfer kinetics of the DHAQ to be higher than HQDS and this kinetic loss in the cathode side will show itself in the potential loss in the galvanostatic graph similar to the polarization graph\textsuperscript{36} and can be further verified by utilization of a dynamic hydrogen electrode and running EIS\textsuperscript{37, 38}. However, still the rate constants of both components are considerably higher than the reactions involved in all
vanadium flow batteries\textsuperscript{39}. Both sides of the battery are excluded from air via argon gas blanketing to prevent re-oxidation of hydroquinone bonds to quinone bonds and loss of columbic efficiency.

DHAQ (anode) is reacting according to the following reactions during charging \[10\] and discharging \[11\]:

\[
\begin{align*}
\text{DHAQ} & \quad +2e + 2H^+ \\
\text{E}^0 & = -0.67 \text{ V vs SHE} \quad \text{[10]}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{OH} \quad \text{OH} \\
\text{HO} & \quad \text{HO} \\
\text{OH} & \quad \text{OH} \\
\text{HO} & \quad \text{HO} \\
\end{align*}
\]

The media is alkaline and the side reactions are:

\[
2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^- \\
E^0 = -0.82 \text{ V vs SHE} \quad \text{[12]}
\]

\[
O_2(g) + 2H_2O + 4e^- \rightleftharpoons 4OH^- \\
E^0 = +0.40 \text{ V vs SHE} \quad \text{[13]}
\]

DHAQ is competing hydrogen evolution reaction during charging and oxygen evolution reaction during discharging. OER is a sluggish reaction due to entailing 4 electrons and seems to be farfetched at this environment. At the time of charging, potential of the anode is reduced to lower than -0.67 V and it passes -0.8277 V, however, HER doesn’t have appreciable kinetics on carbon paper in alkaline media which makes side reactions unable to compete the main redox reaction. Thus, DHAQ is not dealing with serious side reactions and it has high columbic efficiency in addition to its fast kinetics. This phenomenon was also witnessed when DHAQ is coupled to ferricyanide ion in a flow battery\textsuperscript{30}.

On the other hand, HQDS (cathode) is reacting according the following reactions during charging \[14\] and discharging \[15\]:
In addition to that Michael Reaction which is the main deactivation mechanism of the cathode active material (HQDS) and leads to its permanent deactivation and reduces its durability, also affects the columbic efficiency adversely in the long run, necessitating addition of cathode active materials to the battery. Schematic of Michael reaction is illustrated as following:

![Michael Reaction Schematic](image)

The media is acidic and the side reactions are:

\[ \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \quad E^0 = 1.23 \text{ V vs SHE} \quad [18] \]

Similarly, HQDS is also competing hydrogen evolution reaction during charging and oxygen evolution reaction during discharge. However, during charging, cathode voltage will become considerably lower than \(-0.85\) V and such as low potential provides a good margin from HER potential in acidic media even though the HER reaction has to overcome the overpotential of reaction on carbon paper. Even though kinetics of HQDS is higher than HER, in higher status of charge, when less amount of HQDS ions are covering the electrode surface and more protons have access to the electrode surface in acidic media, there is fair chance for HER which lowers CE at higher SOC %.

This phenomenon was successfully prevented in the current system by considering a higher charging rate versus the discharging rate. Exchange current density of HQDS is almost three orders of magnitude
higher than the one for HER which renders side reactions unlikely when the battery is not fully charged (SOC<60%). Based on these, it was possible to reach CE of 99.9% at EE of higher than 70%.

4.3.8. Another demonstration of this technique

This technique has been used successfully with another couple comprising Fe$^{2+}$/Fe$^{2+}$ vs. DHAQ, displaying a start of discharge plateau at a voltage of 1.4 V and columbic efficiency of higher than 99%. Half-cell tests of the half reactions are not repeated as they are mentioned in literature and both of the redox sides are well known. In this cycling test, Iron chloride was dissolved in 3 M hydrochloric acid and supported by 1 M potassium chloride and dihydroxy anthraquinone was dissolved in 2 M KOH, thus having a concentrated acid in one side of the ion exchange membrane (cathode side) and a concentrated base in its other side (anode side). Potassium ion is transported through the ion exchange membrane (N212). The reactions are as following:

\[
\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+} \quad E^0 = 0.77 \text{ V vs SHE} \quad [20]
\]

Cell structure including membrane (N212), carbon paper electrodes (SGL 39AA), flow channel plates (POCO graphite) and the rest of component were similar to the previous tests. Also, system was argon blanketed throughout the experiment. The battery was charged and discharged with 100 mA/cm$^2$ and 60 mA/cm$^2$ respectively, displaying a columbic efficiency of 99.99% and energy efficiency of 70%. This test provides us with another case of utilizing electrolytes with contrasting pH on both sides of the membrane, one being completely in acidic media and the other in alkaline media, and reaching a higher discharge voltage and energy density.
Figure 48 Galvanostatic cycling of Fe/DHAQ flow battery

The battery was tested successfully showing high columbic efficiency as well as good round trip efficiency. This test is a demonstration of the successful applicability of the flow battery using electrolytes with contrasting pH on both sides of a cation exchange membrane which can be further generalized to other systems as well.
4.3.9. Technical aspects of this technique

Even though in this technique it is needed to use two extra pumps which will impose both fixed cost as well as operating cost for the whole system, advantage of the technique can be easily demonstrated in larger scale flow batteries where large amounts of energy storage as well as power ratings are required. In such circumstances, size and flow rate of the injection pumps will become much smaller than the main circulating pumps, thus, having much less energy consumption. On the other hand, high power ratings demand several numbers of large cells to be connected to each other in series to provide the desired voltage and power rating and high energy storage will necessitate utilization of larger tanks accordingly. Increasing number and size of cells is equivalent to higher requirement of ion exchange membranes that take up to 40% of the fixed capital cost of the redox flow batteries, while injection of concentrated acid and base will require two injection pumps that their cost is not considerable to ion exchange membrane.

Operation cost of this technique is also less than using an extra membrane. Even though membrane doesn’t consume electricity directly, it accounts for 70% of the ohmic loss in a battery. Thus, an extra membrane will impose further ohmic potential loss to the system and this issue will be repeated for each cell, reducing the overall output voltage as well as voltage efficiency. However, the energy consumption by the pumps are going to be dependent on the volume of the injected material that will be low due to high concentration of the added materials and pumps will not have any effects on cell efficiencies.

Maintenance cost of this technique is way less than using an extra ion exchange membrane. Even though life cycle of such membranes is considered to be 20 years, such durability is very optimistic. Ion exchange membranes specially anion exchange membranes have low mechanical toughness in contrast to other mechanical items used in a battery. A small hole will make that
membrane completely useless and it becomes necessary to stop the battery and replace the membrane which might not be an easy task for an operating battery. Impact resistance of membranes is not high and a dendrite or a mishandling will break it while pumps are robust and even, they face abrasion or corrosion, the related spare part will be easily replaced while the whole pump can be used.

Injection of chemicals is mainly needed during the time of operation of the battery due to continuous replenishing of the boundary layer with fresh electrolyte which initiates and enhances the carrying process through membrane and at the time that the battery is left idle, injection is not needed.

Amount of chemical injected to the system is dependent on the membrane active surface area rather than the amount of energy stored in the tanks. Thus, estimation of the chemical consumption requires determination of the limiting current density of the system with the type of membrane used. Limiting current density is a function of mass transfer coefficient which is also a function of the velocity through system. By using the models derived for the all vanadium redox flow batteries\textsuperscript{41,42}, it is possible to make an estimation of the amount of chemical used per Kwh of the energy.

\[ i_l = nFk_mC_b \]
\[ k_m = 1.6 \times 10^{-4}v^{0.4} \]
\[ v = \frac{QL_{avg}}{A_pL_p\varepsilon} \]

By considering electrode active area to be 4cm2, electrode porosity (\(\varepsilon\)) to be 93% after compression, assuming a tortuosity \(L_{avg}/L_p\) of 1.09 from literature\textsuperscript{43} and flow rate (Q) of 100
ml/min, mean electrolyte velocity will become 29.3 cm/min, yielding a mass transfer coefficient of $1.2 \times 10^{-4}$ cm/s and finally a limiting current density of 1.27 A/cm$^2$ for the current through membrane. Considering operation to be at 80% from limiting current density, storing 1 Kwh in this system will consume 85 ml of 1 M HCl and 39.6 mgr of KOH with purity of 85%. Based on the current price of HCl (35%) and KOH to be 165 $/MT$ (Kemcore, USA) and 350 $/MT$ (Qingdao Sansino, PRC) respectively, the total chemical cost with this technology will be 0.006 $/kwh$. It is possible to optimize such values as well as operating conditions and even reduce the related costs upon good engineering practices.

Large scale implementation of this technique will require installation of online pH meters on both tanks and connecting them to the injection pump control systems. Alkaline active material (such as KOH) can be added to the system in solid form by replacing the related pump with a solid handling and metering system. Acid will be used in a concentrated form and pumped through an intermittent volumetric injection pump due to the small quantity of injected materials.

4.3.10. Conclusion

In this work, a technique based on using hybrid acid and base electrolytes on both sides of an ion exchange membrane has been used successfully for two different types of flow battery systems. In the DHAQ vs HQDS system, an energy density of 22.11 Wh/kg at an open circuit voltage of 1.5V with a columbic efficiency of 99.9% at charging current density of 80 mA/cm$^2$ and a discharge current density of 40 mA/cm$^2$ and energy efficiency of 70% has been attained. Furthermore, durability of the system including electrolytes with contrasting pH has been tested for more than 140 hours and proved to be successful. Besides half-cell tests of the cathode active material (HQDS) in the used buffer solution have been performed and the results are reported. In the DHAQ vs. Fe$^{2+}$/Fe$^{3+}$ system, a concentrated acid (3 M HCl) and a concentrated base (2 M KOH) have been used on both sides of the membrane and a columbic
efficiency of 99% with a charging current density of 100 mA/cm² and a discharging current density of 60 mA/cm² has been reached.

Using two electrolytes with contrasting pH on both sides of the membrane, enables us to utilize wider potential range and couple various kinds of redox active components together and devise new batteries with higher voltage and energy density. This technique can be specifically useful for those redox media that highly rely on deprotonation during their redox reactions and therefore enhance the voltage span as well as the energy density harnessed from the flow battery.

Hydroquinone disulfonic acid (HQDS) has been chosen for this test because it has the highest redox potential of all quinone compounds (0.86 V vs. SHE) and also owns a very high solubility of 1.7 M in aqueous systems and is also able to be used at pH=7, however more of its redox span is used if it is utilized in acidic media. In this configuration, HOMO of DHAQ is lowered by presence of 2 OH groups while LUMO of HQDS is raised by presence of two sulfonic acid groups, finally raising the cell potential.

Filling the empty locations in HQDS with more electron withdrawing groups will not only raise the redox potential even further, but also it will lower the deactivation of this chemical that is mainly due to Michael mechanism. Simultaneously, higher solubility and diffusion coefficient of HQDS will result in a smaller Nernst diffusion layer and a more effective mass transport coefficient. Possibility of side reactions (HER) can be reduced by operating at lower state of charge (SOC) as well as modification of electrode materials that can increase HER overpotential even further. All these attributes make HQDS a very powerful candidate to be used as cathode materials in redox flow batteries and also provide future opportunities to further work on its structure and augment its characteristics.

Online monitoring of the SOC of this system via UV-vis similar to the case that was used for vanadium flow batteries is not applicable here due to very high absorbance of the components specifically the anode material. However, effect of electrode material, structure and its degradation in preventing side reactions such as hydrogen evolution reaction which reduce the energy efficiency can be considered by measuring the in situ charge transfer kinetics via electrical impedance spectroscopy and constructing the related Tafel
plots, analyzing ECSA effect, benefiting from series technique, utilization of a printed board circuit between flow channel plate and current collector or placing potential probes between electrodes and connecting them to a dynamic hydrogen electrode.

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CHAPTER 5. GENERAL CONCLUSION

Organic redox flow batteries are one of the promising means for the energy storage that is harnessed via renewable resources such as wind and sunshine. These components eliminate various problems imposed by metal flow batteries such as dendrite formation, toxicity, etc. Among various compounds, quinone compounds by involving two electrons in each electrochemical reaction, display a very good candidacy for organic redox flow batteries. Unfortunately, the problem with organic redox flow batteries is their low energy density that limits their chance to be used in flow batteries.

During this thesis, it was demonstrated that by utilizing electrolytes with contrasting pH on both sides of a cation exchange membrane, it is possible to increase the voltage span as well as energy density of this group of redox flow batteries and reach energy densities as high as 27 Wh/L. It is possible to further elaborate this technique to other components and increase the voltage span even more than this amount. Also it will become possible to increase the battery voltage span via proper functionalization.