Use of Viologens in Mediated Glucose Fuel Cells and in Aqueous Redox Flow Batteries to Improve Performance

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Use of Viologens in Mediated Glucose Fuel Cells and in Aqueous Redox Flow Batteries to Improve Performance

Meisam Bahari

A dissertation submitted to the faculty of Brigham Young University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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ABSTRACT

Use of Viologens in Mediated Glucose Fuel Cells and in Aqueous Redox Flow Batteries to Improve Performance

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Doctor of Philosophy

This dissertation presents my efforts to use viologens to improve the performance of glucose fuel cells and aqueous redox flow batteries. These two electrochemical systems have the potential to efficiently exploit renewable sources of energy. The contributions and significance of this work are briefly described below.

Glucose Fuel cells. For glucose fuel cells, viologens were adopted as an electron mediator to facilitate the transfer of electrons from glucose to electrodes for power generation. Use of a mediator circumvents the need for precious metal electrodes to catalyze glucose oxidation. Both the oxidation efficiency and rate of glucose oxidation are important to the viability of glucose fuel cells. Oxidation efficiency is defined as the extent to which the carbons of a carbohydrate (glucose for instance) are oxidized relative to full oxidation to carbon dioxide. The efficiency measured in this study depended on the initial molar ratio of viologen to glucose and also on the rate of the regeneration of the mediator. The maximum conversion efficiency observed was ~22%, which is about three times larger than the values observed for precious-metal-based fuel cells. Rate performance is another important aspect of a glucose fuel cell. Detailed simulations demonstrated that rate performance of viologen-mediated cells was limited principally by mass transfer. The maximum obtainable current density was ~200 mA/cm², which is significantly higher than the rates available from biological fuel cells and comparable to the values observed for precious-metal-based fuel cells. Viologen-mediated fuel cells offer the potential for higher oxidation efficiency and high current densities at a significantly lower cost. This makes viologen-mediated cells an appealing option for future development of glucose fuel cells.

Redox Flow Battery. An asymmetric viologen called MMV was assessed for potential use in aqueous flow batteries to improve performance. With an asymmetric structure, MMV demonstrated one of the most negative redox potentials reported to date for organic electroactive compounds. MMV also showed a relatively high solubility in neutral electrolytes. The electrochemical reaction of MMV involved a reversible single electron transfer with fast kinetics. These characteristics support MMV as a promising anolyte for flow battery applications to improve capacity, energy density, and cell potential. MMV, however, exhibited poor cycling performance at elevated concentrations since it underwent irreversible or partially reversible side reactions. Signs of dimerization and precipitation were observed during cycling. These undesired reactions can be potentially mitigated by synthesizing asymmetric MMV derivatives that possess a higher charge than that possessed by MMV (+1). This modification can reduce the extent of dimerization by increasing repulsive forces between the monomers, and it also has the potential to reduce precipitation by increasing the solubility limit of the compounds.

Keywords: viologens, mediated glucose fuel cells, mathematical modeling, aqueous flow battery
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1 INTRODUCTION

1.1 Motivation

The rapid growth of worldwide energy demand, along with environmentally related concerns such as global warming, has driven a transition from fossil fuels to renewable and sustainable sources of energy. One source of sustainable energy is carbohydrates. Glucose, for instance, has a high energy density and is one of the most abundant, clean, and nonhazardous fuels [1, 2]. Other renewable sources of energy are solar, wind, and hydroelectric power. In fact, the rapidly falling cost of energy generation from solar and wind has led to their large-scale development [3].

Glucose fuel cells and redox flow batteries (RFBs) are the electrochemical systems of interest to this study, and have the potential to enable more effective and efficient use of renewable sources of energy as our society transitions away from fossil fuels. Glucose fuel cells, as their name implies, take advantage of glucose as the energy source for generating electricity [4]. RFBs, on the other hand, have been recognized as a promising option for energy-storage purposes, mitigating the intermittency of renewable sources of energy in order to more effectively harness them to meet the needs of our society [5-7].

Despite the promises in utilizing glucose fuel cells and redox flow batteries, these systems encounter a few challenges. The main challenges of glucose fuel cells are related to the extent of glucose oxidation and the rate at which the oxidation reaction takes place. For flow batteries, on the other hand, the cell potential is one of the factors that may be further improved to provide
higher output powers and energy densities. The challenges of these electrochemical systems, in fact, motivated this research.

In this study, the potential of viologens for improving the performance of the electrochemical systems of interest is evaluated. Viologens have been recognized as a potentially attractive electroactive species owing to their relatively fast electrochemical reaction kinetics on inert electrodes [8]. For glucose fuel cells, viologens are adapted as an electron mediator to facilitate the transfer of electrons from glucose to the electrodes and improve the rate and extent of glucose oxidation. For redox flow batteries, a new viologen that is not commercially available is synthesized and utilized as an electroactive compound. This compound has the potential to increase the cell voltage, improve output power, and increase the energy density of redox flow batteries.

1.1.1 Glucose Fuel Cells

Efforts have been made to exploit glucose as a potential source of energy for fuel cell applications [9-11]. The two most developed types of glucose fuel cells are biological and precious-metal-based abiotic fuel cells; however, significant challenges remain that include low stability, low oxidation efficiency, and high cost [12-16].

Mediated glucose fuel cells represent another type of fuel cell in which a mediator facilitates the oxidation of glucose. In these cells, the transfer of electrons from the fuel to the anode takes place through multiple steps. First, the mediator homogeneously oxidizes the fuel and is reduced in the process. The reduced mediator is, then, transported to the anode surface where it electrochemically releases its electrons, turning back into its oxidized form. Next, the oxidized mediator is transported away from the surface and is once again available to oxidize glucose [17].
Viologens appear promising mediators for glucose fuel cell applications [18]. Both the extent and rate of glucose oxidation are important to the viability of these fuel cells as discussed briefly below.

**Oxidation Efficiency**

Oxidation efficiency or conversion efficiency is defined as the extent to which the carbons of a carbohydrate are oxidized relative to full oxidation to carbon dioxide. This can be characterized as the ratio of electrons released per mole of carbohydrate to the maximum electrons that can be released under complete oxidation. Glucose has 6 carbons that can each be oxidized by +4, corresponding to the possible release of 24 electrons per molecule (24 equivalents per mole). In precious-metal-based fuel cells, glucose commonly releases only 2 electrons, leading to an oxidation efficiency of 8%. Although viologens have been shown to promote high levels of glucose oxidation (even higher than 75%) under aerobic conditions [18, 19], the oxidation efficiency has been surprisingly low in electrochemical cells [20, 21]. Therefore, this study explores possible reasons for the reported low efficiencies. The principal focus of the work is the improvement of oxidation efficiency in an electrochemical cell for fuel cell applications. The mechanism by which glucose transfers electrons to viologens is also examined to gain insight into the pathways that maximize conversion efficiency.

**Oxidation Rate**

Oxidation rate, the speed at which the oxidation reaction proceeds, is another important aspect of glucose fuel cells and determines the generated current in these cells. In a viologen-mediated cell, the transfer of electrons from glucose to the electrode involves multiple processes namely: homogeneous reaction, mass transfer, and electrochemical reaction at the electrode surface. The homogeneous reaction between viologens and glucose occurs at a reasonable rate
Additionally, the electrochemical reaction of viologens takes place with relatively fast kinetics [24]. As a result, a high current density (the current normalized by the area of the cell) is expected from viologen-mediated glucose fuel cells. Nonetheless, the maximum reported current density for these cells in the literature is disappointingly low [20, 21]. Therefore, in this study, the relative significance of the key physical processes is evaluated to understand and mitigate the factors that limit rate performance. Such a study enables us to determine the operating conditions that maximize the current density of viologen-mediated glucose fuel cells.

1.1.2 Redox Flow Battery

A redox flow battery (RFB) is an electrochemical device that is used to store energy from renewable sources of energy such as solar and wind. The stored energy in flow batteries is then used to generate electricity and power. The capacity, energy density, and output power of flow batteries depend on the properties of the electroactive species used. Viologens are attractive for flow battery applications owing to their high solubility, fast kinetics, and tunability. The redox potential of viologens has not received much attention, and the viologens that have been developed show redox potentials significantly higher than what is desired for a flow battery. This provides an opportunity to tailor viologens with lower redox potentials in order to improve battery performance. In this study, we suggest a viologen-based electroactive compound that is not commercially available, but can be synthesized with a simple procedure. This compound possesses a very negative redox potential and high solubility under neutral conditions, offering the possibility of improved aqueous flow battery performance.
1.2 Objective, Scope, and Approach

This study aims to accomplish three objectives that are based on the opportunities mentioned above. The first objective is to quantify glucose oxidation efficiency in a viologen-mediated cell under aerobic conditions and also in an electrochemical cell in the absence of oxygen. The focus, of course, is the oxidation efficiency in electrochemical cells for glucose fuel cell applications. The influence of operating conditions on the conversion is investigated, and the conditions that impact the efficiency are identified. Identification of glucose oxidation products is another important aspect of the study. The product distribution provides insight into the oxidation reaction and the mechanism by which it proceeds.

To accomplish the goals of this objective, we rely on experimental measurements. NMR is used to identify the oxidation products and gain insight into the glucose oxidation mechanism. Chapter 2 presents the results obtained and is based on a manuscript entitled “Oxidation efficiency of glucose using viologen mediators for glucose fuel cell applications with non-precious anodes” published in the Journal of Applied Energy [17].

The second objective is to investigate rate performance of viologen-mediated fuel cells, which is also critical to the viability of viologen-mediated glucose fuel cells. The key physical processes in the cell are homogeneous reaction, mass transfer, and electrochemical reaction. The relative significance of these rates is evaluated to better understand how individual processes contribute to the overall cell behavior and to identify rate-limiting processes. The impact of operating conditions on the rate-limiting processes is also evaluated in order to determine the maximum obtainable current density. The maximum obtainable current density and the required polarization are determined. Finally, practical implications and limitations associated with viologen-mediated fuel cells are discussed.
To accomplish the goals of this objective, a mathematical model is developed and validated experimentally. Chapter 3 includes the experimental and modeling results associated with this objective and is based on a manuscript entitled “Mathematical and experimental analysis of the rate performance of viologen-mediated glucose fuel cells” submitted to the Journal of Electrochemical Society.

The third objective is to examine the potential of MMV (mono-methyl viologen) as an electroactive compound for flow battery applications. MMV was previously used at BYU as an electron mediator for oxidizing carbohydrates. In this study, however, MMV is adapted for aqueous flow batteries. Therefore, this objective aims to evaluate MMV characteristics including solubility and electrochemical kinetics to determine its suitability for flow batteries. More importantly, I also examined its redox potential that can improve the cell potential, energy density and output power of flow batteries. Finally, the performance of MMV is evaluated under cycling conditions.

This third objective is accomplished through experimental work. First, the synthesized MMV is examined by liquid chromatography-mass spectroscopy, and its solubility in water is measured. The properties of MMV are then quantified with various electrochemical techniques such as CV (cyclic voltammetry) and LSV (linear sweep voltammetry) with an RDE (rotating disk electrode), to evaluate its suitability for flow battery applications. Finally, the cycling performance of MMV is evaluated in a flow battery. Chapter 4 includes the results associated with this objective and is based on a manuscript entitled “A viologen-based anolyte with a very negative redox potential for neutral aqueous flow batteries”, which will be submitted to the Journal of Electrochemical Society.
The final chapter of this dissertation summarizes the main conclusions drawn from this work and suggestions for future work.

1.3 Background

To understand the research presented in this dissertation, this section briefly summarizes the fundamentals of glucose fuel cells. This is followed by a brief description of the two main aspects of glucose fuel cells: oxidation efficiency, and rate performance. Finally, a short description of flow battery fundamentals and operating principals are presented.

1.3.1 Glucose Fuel Cells

A fuel cell is a device that directly converts the chemical energy of a fuel and an oxidizing agent into electrical power. To accomplish this conversion, two electrochemical reactions occur: oxidation at the anode and reduction at the cathode. These two electrodes are separated by a membrane, which is an ionically permeable medium that prevents mixing of the electrolytes of the anode and cathode compartments. Membranes that are permeable to cations or anions are called cation exchange membranes (CEM) and anion exchange membranes (AEM), respectively. The electrons released at the anode travel to the cathode via an external circuit. Figure 1-1 provides a schematic diagram of a glucose fuel cell in which an AEM is incorporated.
Fuel cells are commonly categorized by the type of electrolyte used and operating temperature. However, mediated-glucose fuel cells, which are the focus of this work, are not well-described by these categories. These cells use glucose as the fuel, run at low temperatures, and may utilize either an acidic or a basic electrolyte. Glucose fuel cells are sometimes called direct glucose fuel cells (DGFCs). In DGFCs, glucose is directly oxidized inside the cell as opposed to being transformed into another type of fuel before entering the fuel cell. Figure 1-2 shows a classification scheme for DGFCs.

Figure 1-1: A schematic diagram of a glucose fuel cell with an AEM (adapted from [25]).

Figure 1-2: Direct glucose fuel cell classification. The focus of this work is specified in red.
Glucose fuel cells can be divided into two categories based on the type of process used for oxidizing the fuel: biological or non-biological. In biological fuel cells (also known as biofuel cells), either an enzyme or a microorganism is used to oxidize the fuel. When an enzyme is the oxidizer, the fuel cell is an enzymatic fuel cell; when a microorganism is the oxidizer, then it is a microbial fuel cell [14, 26]. Non-biological fuel cells, which are also referred to as abiotic fuel cells, most commonly rely on precious metals to oxidize glucose [27-29]. In cells with precious metal catalysts, glucose oxidation occurs on the anode through contact of the fuel with the electrode. In other abiotic fuel cells, however, the oxidation reaction does not occur directly at the anode; instead, advantage is taken of an electron mediator [30]. Mediated glucose fuel cells are the focus of this work and are identified by the red color in Figure 1-2. Figure 1-3 shows schematically the role of a mediator in a glucose fuel cell.

![Figure 1-3: Schematic view of the anode compartment in a mediated abiotic glucose fuel cell. The electron mediator (EM) transfers electrons from glucose to the anode. Path 1 and 2 represent homogeneous and electrochemical (heterogeneous) reactions, respectively.](image)

As shown in Figure 1-3, glucose oxidation occurs indirectly with the aid of an electron mediator in mediated cells. Specifically, the oxidized electron mediator (EMo) reacts
homogeneously in solution to oxidize glucose, and is reduced in the process. This process is shown as Path 1 in Figure 1-3 and occurs in the bulk electrolyte. Subsequently, the reduced mediator (EMr) is re-oxidized electrochemically at the anode, transferring electrons to the electrode. This process is shown as Path 2 in Figure 1-3. The two reactions (homogeneous and electrochemical) are coupled, and changes in one may influence the other.

The electrochemical oxidation of the mediator does not require a precious metal catalyst. Thus, mediated cells have the potential to significantly reduce cost. A suitable mediator should meet the following requirements [8]

- Its oxidation/reduction reactions are reversible.
- Both the oxidized and reduced forms are stable and soluble in the electrolyte.
- Its reaction with the fuel (homogeneous reaction) is reasonably fast.
- It offers a fast electrochemical reaction at the electrode.

Viologen species meet all these requirements and have been suggested as suitable electron mediators for glucose fuel cell applications. In particular, methyl viologen (MV), has been previously studied in the literature for glucose oxidation [18, 22]. Another viologen that is of interest is mono-methyl viologen (MMV). MMV is a monosubstituted viologen and is evaluated in this study for flow battery applications. A brief discussion of flow batteries is presented later in this chapter. The structures of MV and MMV are shown in Figure 1-4.
Both oxidation efficiency and rate of glucose oxidation impact the performance of a glucose fuel cell. Each of these two aspects is briefly discussed here.

**Oxidation Efficiency**

Oxidation efficiency is defined as the extent to which the carbons of a carbohydrate are oxidized relative to full oxidation to carbon dioxide. This is characterized as the ratio of electrons released per mole of carbohydrate to the maximum electrons that can be released under complete oxidation. Glucose contains six carbons that can release four electrons, corresponding to the possible release of 24 electrons per molecule. Exploiting all the available electrons from glucose is one of the challenges of glucose fuel cells. For instance, enzymatic and precious-metal-based glucose fuel cells utilize only two of the available electrons, equal to an efficiency of 8% [26, 31].

The glucose oxidation mechanism determines the species that are produced from the oxidation reaction, which thereby determines the oxidation efficiency. The oxidation products of glucose include carbon dioxide, the product that corresponds to 100% oxidation efficiency, as well as various carboxylic acids such as formic acid, glycolic acid, glyceral acid, gluconic acid, etc., which correspond to lower efficiencies. The relative amounts of each of these products under
various operating conditions will change based on the glucose oxidation pathway, which in turn changes the conversion efficiency. Therefore, it is important to understand the oxidation mechanism. Understanding the oxidation mechanisms and directing the reaction toward more efficient pathways leads to improvement of the oxidation efficiency.

**Oxidation Rate**

At the anode of a mediated fuel cell, the electron mediator electrochemically reacts and releases electrons. However, just releasing electrons does not ensure a fast reaction. In fact, leaving aside manufacturing issues and materials expenses, the rate of the electrochemical reaction is one of the fundamental challenges in designing this type of fuel cell since a slow electrochemical reaction rate leads to low power [32].

Power, which is a key measure of overall fuel cell rate, is the product of cell voltage and current. Current is commonly reported per unit area of the cell, known as current density. The cell voltage is defined as [33]

\[
V_{cell} = U_{cell} - \eta_{act, anode} - \eta_{conc, anode} - \eta_{act, cathode} - \eta_{conc, cathode} - \eta_{ohmic} \quad (1-1)
\]

where \(U_{cell}\) is open-circuit voltage (OCV) of the cell, \(\eta_{anode}\) and \(\eta_{cathode}\) represent the potential losses at the anode and cathode, respectively. The subscripts \(act\). and \(conc\). represent the activation and concentration polarizations, respectively, at each electrode. Activation polarization reflects the energy needed to drive the electrochemical reactions; and concentration polarization reflects losses due to the concentration gradients near each electrode. \(\eta_{ohmic}\) represents the ohmic losses through the electrolyte and membrane.
The Green line in Figure 1-5 shows a typical cell potential vs. current density plot for a hypothetical fuel cell. In this figure, the activation loss (blue dashed line) and the activation plus the ohmic losses (red dotted line) are plotted to demonstrate that each of the losses affects the cell differently. Determining the magnitude of each type of loss provides insight into approaches for improving performance [34-36].

In viologen-mediated fuel cells, the situation is complicated due to the presence of a homogeneous reaction. In mediated cells, the homogeneous reaction supplies the electrochemical reaction with reactants (see Figure 1-3). Therefore, besides the surface reaction and mass transfer, which impact electrochemical cells, the homogeneous reaction is another process that impacts the performance of mediated cells. In this study, a mathematical model is developed to quantify the relative significance of key physical processes and evaluate the extent to which a process limits rate performance. Subsequently, the impact of operating conditions on the rate-limiting process is evaluated to maximize performance.
1.3.2 Redox Flow Batteries

A redox flow battery (RFB) is an electrochemical device that is used to store and release energy. Unlike fuel cells in which a fuel, such as glucose, has to be consumed continuously to generate electricity, flow batteries generate power from the energy that has been previously stored. Flow batteries can be used to store energy from a variety of sources that include renewable sources such as solar, wind, and hydroelectric energy.

In RFBs, energy is converted from electrical to chemical form and vice versa with the use of two electroactive compounds that are in liquid form. The electrolyte that contains the compound with a more negative redox potential is called anolyte, and the electrolyte that contains the compound with the more positive redox potential is called catholyte. The electrolytes are stored in separate tanks and are pumped through the cell where energy conversion takes place at the electrodes. RFBs have the advantage of decoupling energy and power [33, 37]. A schematic diagram of a redox flow battery is shown in Figure 1-6.

![Figure 1-6: A schematic diagram of a redox flow battery. The labeled components are: 1. graphite plates, 2. porous electrode for the negative side, 3. porous electrode for the positive side.](image)
RFBs are similar to secondary batteries in the sense that they undergo charge and discharge. During the charge step, electrons are nonspontaneously transferred from the catholyte to the anolyte. This nonspontaneous reaction proceeds with the aid of an external power source. The opposite is true for the discharge step, meaning that electrons are spontaneously transferred from the anolyte to the catholyte, generating power [38-40]. RFBs can be categorized into two major groups based on the solvent used: non-aqueous and aqueous. Aqueous redox flow batteries (ARFBs), which is the focus of this research, take advantage of water as the solvent. Due to high conductivity, relatively low cost, and safe nature of aqueous electrolytes, ARFBs are very attractive for large-scale energy storage applications [41-43].

Theoretical capacity and theoretical energy density are two important factors that characterize flow battery performance. The first factor represents the maximum capacity in terms of coulombs of charge available, the second in terms of energy available. The two factors are related by the potential of the cell. The theoretical capacity (normalized by the volume) can be determined for an electrode as [33]

$$\text{theoretical normalized capacity} = \frac{nCF}{3600} \frac{\text{A.h}}{\text{L}}$$  \hspace{1cm} (1-2)

where $C$ is the concentration of the anolyte or catholyte, $n$ is the number of equivalents per mole of the compound that reacts electrochemically, and $F$ is Faraday’s constant. The theoretical capacity (normalized by volume) and energy density can be determined for the entire cell as [44]

$$\text{theoretical normalized cell capacity} = \frac{nC_{\text{min}}F}{3600} \frac{\text{A.h}}{\text{L}} \frac{1 + \frac{C_{\text{min}}}{C_{\text{max}}}}{\text{L}}$$  \hspace{1cm} (1-3)
Theoretical energy density:

\[ \text{theoretical energy density} = \frac{nC_{\text{min}}F}{3600} \left(1 + \frac{C_{\text{min}}}{C_{\text{max}}} \right) V \left[ \frac{\text{W.h}}{\text{L}} \right] \]  

(1-4)

where \( C_{\text{min}} \) and \( C_{\text{max}} \) are the minimum and maximum concentrations of two electrolytes, respectively, and \( V \) is open-circuit voltage (OCV) of the cell.

It is clear from these relationships that the theoretical capacity and theoretical energy density of a flow battery depend on the concentration of electroactive species and the OCV of the cell. The OCV is determined by the redox couple and is a function of the state-of-charge. Anolytes and catholytes with high solubility and a large difference between their redox potentials help to improve the performance of flow batteries.

Viologens are organic compounds with very appealing properties. Viologens show very high solubility in aqueous electrolytes, and more importantly, have properties, such as the redox potential that can be tuned with modifying their structure \[8\]. In this study, a viologen-based anolyte is developed for flow battery applications. This compound, which is called MMV (mono-methyl viologen), has high solubility. Additionally, it has a significantly lower redox potential than viologens that have been previously developed in the literature. With these two properties and a simple synthesis procedure, MMV appears a promising anolyte candidate for improving the performance of aqueous redox flow batteries.

1.4 Summary

In summary, glucose fuel cells and redox flow batteries are electrochemical systems of interest that have the potential to help with the transition away from fossil fuels. Viologens have the potential to promote high levels of glucose oxidation at a reasonable rate for fuel-cell applications. However, the reported oxidation efficiency and current densities for viologen-
mediated glucose fuel cells reported to date have been disappointingly low. In this work, a systematic study is performed to evaluate the factors that impact the oxidation efficiency and rate performance of these fuel cells. Both the oxidation efficiency and rate performance are important for the viability of these fuel cells, making the significance of this study twofold. The optimum operating conditions that maximize oxidation efficiency are determined. Additionally, the mechanism by which glucose transfers its electrons to viologens is also examined to gain insight into the pathways that lead to higher efficiency. Finally, the relative significance of the key physical processes in the cell is quantified to identify limiting-rate processes. Such an analysis enables us to determine the operating conditions that maximize rate performance of viologen-mediated glucose fuel cells.

Redox flow batteries, on the other hand, are promising for storing energy from renewable sources such as solar and wind. Theoretical capacity and energy density are important characteristics of flow batteries and depend on the properties of the electroactive species such as solubility and redox potential. Viologens are attractive for flow battery applications due to their appealing properties. Additionally, viologens can be modified to optimize those properties. The redox potential of viologens is one of the properties that has not received much attention, and the viologens that have been previously developed show redox potentials significantly higher than what is desired. In this study, we suggest a viologen-based electroactive compound that is called MMV. This compound has a very negative redox potential and high solubility under neutral conditions, offering the possibility of improved aqueous flow battery performance.
2 OXIDATION EFFICIENCY OF CARBOHYDRATES USING VIOLOGENS

2.1 Introduction

As our technologically-dependent world faces ever-increasing energy demands, concerns with fossil fuel availability and with environmental issues such as global warming have brought about a search for renewable and sustainable sources of energy. Biomass offers a source of sustainable energy that has the potential to reduce our reliance on fossil fuels. Carbohydrates, produced from biomass, have received considerable attention as potential fuels [1, 2]. For example, glucose is theoretically capable of providing a large specific energy, 4430 Whr kg⁻¹, through the release of its 24 electrons [45]. Due to its high specific energy [4], efforts have been made to exploit glucose as a fuel in electrochemical systems such as fuel cells. However, in spite of these efforts, relatively little progress has been made [9]. This lack of progress is attributed, at least in part, to the low oxidation efficiency of glucose. Oxidation efficiency (or conversion efficiency), defined as the fraction of the theoretical maximum number of electrons released as a result of carbohydrate oxidation, is the focus of this chapter.

For glucose oxidation, biological fuel cells, also known as biofuel cells, have received a great deal of attention. Biofuel cells can be classified as either enzymatic or microbial [13]. In enzymatic fuel cells, oxidation of the fuel is catalyzed by an enzyme. The resulting oxidation reaction is commonly a two-electron process that yields gluconic acid (glucose → gluconic acid + 2e⁻) [12, 46-48]. This oxidation process utilizes only 8% (2 of 24) of the total available electrons...
in glucose. In addition to low oxidation efficiency, poor stability, high cost and short enzyme lifetimes are other drawbacks of enzymatic fuel cells [12, 26, 49, 50]. Microbial fuel cells, in which a whole microorganism oxidizes glucose, have multiple advantages over enzymatic cells. Specifically, microbial fuel cells are less prone to degradation, which leads to greater longevity. They also have the capability of oxidizing the fuel almost completely, thereby releasing most of the available electrons from glucose. However, the transfer of those electrons from the microorganisms to an electrode is difficult and represents the principal challenge for microbial fuel cells [13, 14].

Non-biological fuel cells, also known as abiotic fuel cells, have also been investigated extensively for glucose oxidation. These cells most commonly rely on precious-metal catalysts to oxidize the glucose [27-29, 51]. Use of such catalysts significantly increases the cost of the electrodes, and hence, the fuel cell cost. In addition, such electrodes are susceptible to poisoning due to adsorbed intermediates from the oxidation reaction(s) [16, 27, 49]. Furthermore, these electrodes are not capable of effectively breaking C-C bonds in carbohydrates at moderate temperatures [15, 16, 52, 53]. Rather, a C-H bond is broken to form gluconic acid. Therefore, electrochemical oxidation of glucose in abiotic fuel cells produces mostly gluconic acid, utilizing only two of the available electrons [10, 54, 55]. This two-electron conversion has been reported for a broad range of electrocatalysts including platinum [28, 45, 47], gold [4, 50], palladium [29, 52], and even bi-metallic electrodes [16, 27, 49, 53, 54, 56]. The same oxidation efficiency has been observed with electrolytes at pH values ranging from acidic [29, 51, 57] to neutral [12, 47] and alkaline [16, 49, 50, 58]. This implies that the oxidation pathway of glucose on noble metals does not change with the pH of the electrolyte.
In mediated glucose fuel cells (MGFCs), which are the subject of this study, the glucose oxidation reaction does not occur directly on the anode; instead, an electron mediator is utilized [30]. In this type of fuel cell, the oxidized form of the mediator homogeneously oxidizes glucose and is reduced in the process. Subsequently, the reduced mediator is oxidized electrochemically at the anode, transferring its electrons to the electrode. In this manner, the electron mediator facilitates electron transfer from the fuel to the electrode. Since the electrochemical reaction of the mediator does not usually require a precious-metal catalyst, MDGFCs have the potential for significant cost advantages. In contrast, use of non-precious metal electrodes without a mediator leads to very slow electrochemical reaction of glucose, much slower than rates observed for mediated reactions on the anode [21]. A schematic diagram of the electrochemical system is shown in Figure 2-1.

![Figure 2-1: Schematic illustration of glucose oxidation via an electron mediator (EM). Reaction 1 is the homogeneous oxidation of the fuel by the EM, and Reaction 2 is electrochemical oxidation of the EM on the electrode (heterogeneous). EMr and EMo represent the reduced and oxidized form of EM, respectively.](image)

Viologens such as dimethyl viologen (MV) represent possible electron mediators for glucose oxidation with the potential to increase both the extent and rate of oxidation. The electrochemical
behavior of viologens has been reported in the literature and it is known, for example, that MV presents an elementary single-electron reaction on an electrode [24]. Wheeler and coworkers [18, 59] reported that MV in a strong alkaline environment is capable of oxidizing 75% or more of the glucose to yield products that consist of mostly carbonate and formic acid. In contrast, other similar studies indicated significantly lower conversion efficiencies, although the conversion efficiency of the fuel has often not been reported explicitly [21, 60-62]. However, the detected product distribution containing gluconic acid, glucaric acid, glyceric acid was consistent with a much lower overall conversion efficiency. A possible explanation for the observed differences is that the oxidation efficiency may depend on the specific operating conditions used in the experiments.

One important operating condition is the presence or absence of oxygen. The experiments of Wheeler et al. [18] that resulted in high conversion efficiencies were performed in an aerobic environment, and it was assumed that the only impact of the oxygen was to reoxidize the mediator. A schematic view of the processes that take place in the aerobic environment is shown in Figure 2-2. In this figure, the reoxidation of MV\textsubscript{r}, the reduced form of methyl viologen, occurs by reaction with oxygen. Eventually, when all of the initial glucose has been oxidized, the methyl viologen remains in its oxidized form due to the reoxidation reaction with oxygen. In the electrochemical system, however, reoxidation takes place on the electrode as shown in Figure 2-1. Thus, it is possible that the presence of oxygen not only reoxidizes MV\textsubscript{r} but also impacts the glucose oxidation pathway and enhances the oxidation efficiency.
Another important condition that may impact the oxidation efficiency of glucose is the initial molar ratio of viologen to glucose. At very low ratios, glucose is believed to take reaction pathways that produce unreactive intermediate species, diminishing oxidation efficiency [18, 19, 22, 59, 63].

The conversion efficiency may also be influenced by the rate of the reoxidation reaction of MVr molecules. In the aerobic environment, the rate constant for the reaction between oxygen and MVr is $6.5 \times 10^8 \text{M}^{-1}\text{s}^{-1}$ [64], which assures that reoxidation of MVr is not kinetically limited. In contrast, electrochemical reoxidation of MVr may be significantly slower depending on the specific operating conditions and the design of the electrochemical cell.

The objective of this study was to examine and quantify the conversion efficiency of viologen-mediated carbohydrate oxidation, which is needed in order to evaluate the potential of mediated systems for use in carbohydrate fuel cells. As part of this effort, the influence of operating conditions on the conversion was investigated, including the impact of oxygen, and the conditions that maximize the conversion were identified. We first report results for the efficiency
of viologen-mediated oxidation of various carbohydrates under aerobic conditions, where the highest conversions have been observed. Here, the conversion efficiency of glucose and that of a few other carbohydrates with fewer than six carbon atoms are reported. In previous studies [23, 65] we have observed that the smaller carbohydrates react faster than glucose and may also represent potential fuels. In addition, the conversion efficiency of a few disaccharide and polysaccharide carbohydrates are reported. These carbohydrates contain more carbons than glucose and represent additional potential fuels [65].

We next examine the oxidation efficiency of glucose, as a model carbohydrate, in an electrochemical system. The results of this section are applicable to a glucose fuel cell because the electrochemical cell resembles the anode compartment of such a fuel cell. The impact of the viologen to glucose ratio and the rate of the electrochemical reoxidation reaction on the conversion efficiency under anaerobic conditions are reported. The observed conversion efficiencies are compared to those from the aerobic system to provide insight into the impact of oxygen on glucose oxidation in a viologen-mediated system.

Identification of glucose oxidation products is another important aspect of this chapter. The product distribution provides insight into the oxidation reaction and the mechanism by which it proceeds. Of particular interest are differences observed between the product distribution in the aerobic environment and that present under anaerobic conditions in the electrochemical system.

2.2 Materials and Methods

All of the carbohydrates used in the study, as well as both methyl and ethyl viologen (1, 1’-dialkyl-4, 4’-dipyridine dichloride), were obtained from Sigma-Aldrich. Mono-methyl viologen (MMV) was prepared by refluxing 4, 4, bipyridine with a stoichiometric amount of alkyl iodide in
acetone at 60 °C as described elsewhere [8]. Potassium phosphate dibasic from EMD Millpore Corporation and sodium hydroxide from Mallinckrodt Chemicals were used in buffer preparation. A VersaSTAT-3 electrochemical workstation (Princeton Applied Research) was used for the electrochemical measurements. In the electrochemical cell, nickel foam (thickness, 1.5 mm, porosity ~96%, area density, 300 g/m², from Ebay.com) was used as the working electrode and platinum gauze or wire as the counter electrode. An anion exchange membrane (type, FAA-3, Fumatech, Germany) and a Hg/HgO reference electrode (ALS Co. Ltd, Japan) were also used in the electrochemical cell. 13C1 or all 13C-labeled D-glucose from Sigma-Aldrich were used in a 13C-NMR Spectrometer (Varian INOVA 500 or 300 MHz) for product identification after the reaction experiments were complete. For the 13C-NMR sample preparation, about 80% of the solvent was evaporated by exposing the sample to the environment, either in a nitrogen glovebox or in air for anaerobic and aerobic tests, respectively. Then, sufficient D2O was added to yield a mixture that was at least 20% D2O.

The pH of the solution for all the conversion experiments was controlled with the use of a 1 M phosphate buffer. Temperature was controlled with the aid of a circulating water bath (PolyScience, USA). Various procedures were used to determine the conversion efficiency under anaerobic or aerobic conditions as discussed below.

2.2.1 Aerobic Conversion Measurements

For experiments performed under aerobic conditions, the viologen-mediated glucose conversion was measured with the vial method as described elsewhere [18]. Briefly, a solution of the buffer, viologen, and carbohydrate was prepared, inserted into a septum-sealed reaction vial containing air, and allowed to react to completion. Oxygen was consumed as a result of reaction
with MVr, which was formed by the homogeneous reaction between glucose and MVo. The consumption of oxygen reduced the pressure inside the vial. After 24 hours, which was sufficiently long for the homogeneous reaction to reach completion and for all of the carbohydrates initially present to be consumed, the capped vial was placed underwater and the septum was punctured to allow water to enter. The mass of the entering water was measured and its corresponding volume was used to calculate the moles of oxygen consumed during the reaction.

The number of equivalents (moles of electrons) consumed by oxygen reduction was determined by multiplying the moles of consumed oxygen by four \((O_2 + 2H_2O + 4e^- = 4OH^-)\). The number of equivalents was then divided by the initial moles of the relevant carbohydrate to yield the number of equivalents per mole of sugar. Note that reference to the number of electrons per carbohydrate throughout the chapter is more accurately a reference to the number of equivalents per mole. Finally, no hydrogen peroxide was detected in the final solution, consistent with oxygen reduction involving four electrons [66-70]. This test was conducted using peroxide test strips.

### 2.2.2 Anaerobic Conversion

**Anaerobic Conversion with the Electrochemical Reoxidation**

The anaerobic conversion experiments were conducted in an inert (nitrogen) environment in an electrochemical cell. In this cell, MVr was continuously oxidized electrochemically at the anode rather than by direct reaction with oxygen. A three-electrode set-up was used to perform experiments under potentiostatic conditions while measuring the current as a function of time. Figure 2-3 shows a schematic view of the electrochemical cell that used nickel foam as the working
electrode (WE), platinum wire as the counter electrode (CE), and a Hg/HgO reference electrode (RE). The potential was set between the working and reference electrodes.

![Schematic of the electrochemical cell](image)

**Figure 2-3:** Schematic of the electrochemical cell. WE is the cylindrical nickel foam piece connected to a wire, the RE is in the center, and the CE compartment is isolated except through the anion exchange membrane at the tip of the clear tube on the right.

For the measurements, a viologen solution at the desired pH was placed into the cell with the mediator in the oxidized state. The cell temperature was controlled at the desired value using a water bath that circulated hot water through the cell jacket. Experiments were initiated prior to glucose addition by applying a potential and monitoring the current. Glucose was then injected to the cell.

In the cell, glucose was homogeneously oxidized to form MVr. Subsequently, the MVr was electrochemically oxidized at the working electrode (anode). Figure 2-1 illustrates the reactions that take place simultaneously at the anode. An anion exchange membrane was used to separate the working and counter electrodes. This separation ensured that there was no transport
of the mediator between the WE and CE. Experiments were conducted at constant potential for applied potentials ranging from -0.5 to -0.1 V vs. the RE (the standard redox potential of the reaction $MVo + e^- \rightarrow MVr$ is -0.609 V vs. Hg/HgO, reported vs. SCE in [8]). The potential of the WE was set to a value more positive than the MV redox potential, ensuring oxidation of MVr. Recording of the current was initiated before the glucose injection while MV was present in the cell. Tests continued for several hours after glucose addition until the measured current decreased to ~1% of its peak value. A sample plot of the measured current as a function of time is provided in Figure A-1. In this plot, the measured current was essentially zero prior to the glucose injection. The resulting current was integrated over time to obtain the total coulombs transferred to the WE, and this enabled the calculation of the glucose conversion efficiency. A sample calculation of the glucose conversion efficiency is also included in Appendix A. This calculation corresponds to the data shown in Figure A-1.

**Anaerobic Conversion without the Electrochemical Reoxidation**

For comparison, additional conversion measurements were performed under anaerobic conditions, but without continuous electrochemical reoxidation. The inert environment ensured that oxygen did not impact the conversion results. To do the measurements, the reactive glucose/viologen solution at the desired pH was placed in a vial and kept at the desired temperature until the homogeneous reaction between MVo and glucose went essentially to completion. After 24 hours, which was sufficiently long for the homogeneous reaction to reach completion, the final concentration of MVr was measured by potentiostatic coulometry. To do this, a small amount of the solution, about 200 µl, was taken from the vial and injected into an electrochemical cell similar to that described above (Anaerobic Conversion with the Electrochemical Reoxidation), which was set up inside the glove box. The current due to MVr oxidation was measured as a function of time.
for the sample. These data were integrated to give the amount of charge passed, which was used to calculate the concentration. The concentration was then used for the conversion efficiency calculation. Note, again, that there was no reoxidation of the MVr during the experiment. Rather, coulometry was used for measurement of the MVr concentration once the experiment was complete.

2.3 Results

This section presents the conversion efficiencies of different carbohydrates, including glucose, in an aerobic environment. The conversion efficiency of glucose under anaerobic conditions both with and without in situ electrochemical oxidation is also reported.

2.3.1 Aerobic Conversion Efficiency

The viologen-mediated conversion efficiencies for different carbohydrates in air at pH 11.0 and 50 °C are shown in Figure 2-4. The reaction between the carbohydrate and MV proceeds only under alkaline conditions [22]. Moreover, the homogeneous reaction of six-carbon carbohydrates such as glucose proceeds relatively slowly at room temperature [18, 22]. Hence, the temperature for these experiments was chosen to increase the rate of the homogeneous reaction, which permitted experiments to be completed within a few hours. The carbohydrates were fully utilized upon completion of the experiment. However, as shown in Figure 2-2, MV was transformed back into the oxidized form by reaction with oxygen. Therefore, the final measurements were taken when the carbohydrate and MV utilizations were 100% and 0%, respectively.
The carbohydrates tested included 3-carbon carbohydrates such as dihydroxy acetone (DHA) and glyceraldehyde; 5-carbon carbohydrates such as xylose, arabinose, and ribose; 6-carbon carbohydrates such as glucose, mannose, galactose and rhamnose; and a 1.0:1.0:1.0 mixture of xylose, arabinose, and glucose. The numerical values in parentheses are the number of carbon atoms in each carbohydrate.

Wheeler and coworkers [18, 59] showed that the ratio of initial viologen to carbohydrate influences the oxidation efficiency of carbohydrates. The values reported in Figure 2-4 are the maximum observed conversion efficiencies at initial MVo/carbohydrate ratios ranging from 10 to 20, depending on the specific carbohydrate.
In Figure 2-4, the values on the vertical axis are the number of electrons released through oxidation per carbohydrate where the measured values (blue) are displayed alongside the maximum theoretical values (orange). The percentage above each blue bar is the measured conversion efficiency (as a percentage) relative to the corresponding theoretical maximum. For instance, DHA shows a measured number of electrons released of 7.7 versus a maximum of 12, which corresponds to 64% conversion.

As Figure 2-4 shows, all the carbohydrates tested except for DHA and glyceraldehyde underwent viologen-mediated oxidation at ~70% or greater of the theoretical value in an aerobic environment. The lower efficiency observed for DHA and glyceraldehyde is likely due to oxidation mechanisms that favor less efficient pathways. A discussion of the oxidation pathway is presented later in the chapter.

The carbohydrate mixture (a 1.0:1.0:1.0 mixture of xylose, arabinose, and glucose) also exhibited extensive oxidation. Nearly identical results were found using other viologen-based mediators. According to Figure A-2, MMV, which has a significantly more negative standard redox potential than MV, oxidized DHA, arabinose, ribose, mannose, and rhamnose to the same extent as MV. This suggests that the standard redox potential of the mediator has little effect on aerobic carbohydrate oxidation. A similar conclusion is evident from Figure A-3, which shows the oxidation efficiency of DHA using various viologen-based mediators such as MV (-609 mV), MMV (-985 mV), di-isopropyl (-685 mV), and di-ethyl (-612 mV) (numbers in the parenthesis are the standard redox potential of the viologen compounds vs. Hg/HgO, reported vs. SCE in [8]).

Figure 2-5a shows the aerobic oxidation efficiencies for disaccharides such as cellobiose, lactose, and maltose, relative to their maximum theoretical values. Figure 2-5b presents the conversion efficiencies for polysaccharide carbohydrates such as amylose, maltodextrin, and
Operating conditions for these sets of measurements were the same as those in Figure 2-4, except that the initial MVo/disaccharide ratio was set to 20. Because the degree of polysaccharide polymerization varies widely, definition of an initial MVo/polysaccharide ratio was not feasible. To deal with this challenge, the monomer unit of the polysaccharide was used. In other words, the degree of polysaccharide polymerization was ignored and the initial MVo/polysaccharide ratio was based on the molecular weight of the monomer unit.

As shown in Figure 2-5a, viologen-mediated aerobic oxidation of disaccharides such as cellulose, maltose (with the structure shown in Figure 2-6) and lactose yielded efficiencies of around 50%. According to the suggested oxidation mechanism for disaccharides in the literature [71, 72], these species contain a non-reducing and a reducing end, and only the reducing end undergoes degradation/oxidation reactions. This mechanism provides a possible explanation for
the lower oxidation efficiencies observed for the disaccharides (Figure 2-5a), since only the reducing end (green) would undergo viologen-mediated oxidation, leaving the carbohydrate at the non-reducing end unreacted.

![Figure 2-6: Structure of the Disaccharide Maltose with the Reducing End Highlighted in Green.](image)

Cellulose, the most abundant organic material on earth, is a linear glucose polymer that contains up to 10,000 glucose units that are linked by β-1, 4 glycosidic bonds. Similar to disaccharides, only the reducing end of cellulose is reactive. In an alkaline environment, cellulose can be degraded by various types of reactions that include peeling, stopping and scission. In peeling, short-chain molecules detach from the reducing end of cellulose. This, in turn, creates a new reducing-end group for cellulose that subsequently undergoes further degradation. However, the peeling reaction does not continue to completion; instead, the reducing end of cellulose becomes stable towards alkali via the stopping reaction. This stability results from the conversion of the reducing end into a non-reducing end that contains carbonyl groups. Alkali scission usually occurs at high temperatures (≥150 °C) and can significantly reduce the degree of cellulose polymerization to form more reducing ends [60, 71-73]. The sission reaction, however, is not likely to happen in our system due to the low operating temperature of 50 °C, which was chosen to limit the extent of undesired decomposition of the mediator [59].
The observed oxidation efficiency of 11% for cellulose indicates that the oxidation of cellulose proceeds to a lesser extent in a viologen-mediated system. It is likely that the stopping reaction prevents cellulose from further degradation. Since the scission reaction does not occur to any appreciable extent at our operating temperature, oxidation is limited and most cellulose remains unreacted.

Amylose and maltodextrin (a mixture of amylose hydrolysis fragments) are branched glucose polymers with 1,4-glycosidic bonds that undergo 18% and 25% oxidation, respectively. It has been reported in the literature [72] that the rate of polysaccharide degradation in an alkaline environment is inversely related to the degree of polymerization. That is, a lower degree of polymerization results in increased degradation. This is consistent with our observation that maltodextrin, with the lowest degree of polymerization, provides the largest oxidation efficiency. In contrast, cellulose provides the lowest conversion efficiency due to its higher degree of polymerization.

2.3.2 Anaerobic Conversion Efficiency

In this section, we report conversion efficiency in an anaerobic environment. In this environment, oxygen was completely removed from the system and the conversion efficiency was investigated with or without in situ electrochemical oxidation. The results of this section, especially the latter case, can be applied to an electrochemical system such as a viologen-mediated glucose fuel cell. This is possible because the WE side of our electrochemical cell resembles the anode compartment of a direct glucose fuel cell. Experimental values of the potential at the WE ranged from -0.5 to -0.1 V vs. Hg/HgO for the following reasons. The standard redox potential of the MV mediator is \(-0.609\) V vs. RE [43]. Therefore, potentials more positive than -0.5 V vs. RE
were chosen to ensure that the current at the WE was anodic. Moreover, the redox potential of oxygen, the most common oxidizer, can be as low as 0.25 V vs. RE in the alkaline systems of interest. Therefore, a maximum potential of -0.1 V vs. RE was chosen to be significantly below the redox potential of oxygen; potential values more positive than this maximum are not feasible from an operational perspective as the cell potential would be too low to be practical.

Instead of examining all of the carbohydrates for which the results were reported in an aerobic environment, we focused on glucose as a model carbohydrate and evaluated only the glucose oxidation efficiency under anaerobic conditions. As noted by Isbell et al. [52], various carbohydrates tend to undergo oxidation by the same mechanisms; therefore, investigation of a single carbohydrate, glucose in our case, is used to enhance our understanding of carbohydrate behavior in an anaerobic environment. An understanding of the factors that impact the glucose conversion efficiency will be used to direct us toward the conditions that yield the maximum conversion.

As described earlier in the Materials and Methods Section, two sets of experiments were performed in order to evaluate the conversion efficiency under anaerobic conditions. In the first set, glucose reacted with viologen without reoxidation of the resulting MVr. In the second set, MVr was reoxidized electrochemically throughout the experiment.

**Anaerobic Conversion without Electrochemical Reoxidation of MVr**

Figure 2-7 shows the conversion efficiency of glucose at 50 °C under anaerobic conditions without continuous reoxidation of MVr. Changing the pH from 11 to 12 resulted in an increase in the rate of the homogeneous reaction between glucose and MV, but did not impact the measured conversion efficiency. Therefore, anaerobic experiments were conducted at pH 12 to take
advantage of the faster rate. The glucose concentration was held constant at 2 mM and the initial concentration of MVo was varied to produce the desired initial MVo/glucose ratio. A theoretical maximum efficiency curve is also shown in the figure, in addition to the measured conversion efficiency values that are represented by the green circles. The theoretical curve shows the maximum conversion efficiency of glucose when all the initial MVo is reduced. Once MVo is reduced by glucose, it remains in its reduced form and cannot react further with glucose. Therefore, the theoretical maximum curve presents the maximum obtainable conversion efficiency of glucose when the oxidation efficiency is limited by the initial amount of MVo.

As shown in Figure 2-7, increasing the initial MVo/glucose ratio from 1.8 to 15 increased the oxidation efficiency of glucose from 6% to 22%, which represents a change from about 1.5 to 5.3 electrons. Most of the improvement in the conversion occurs for ratios up to approximately 10, after which the efficiency appears to level off somewhere between 20 and 25%. At very low MVo/glucose ratios, the measured conversion efficiency is very close to the theoretical maximum curve, meaning that the conversion efficiency is limited by the amount of MVo available. Consistent with this, most of the MV is in the reduced form for low initial MVo/glucose ratios as shown in the inset of Figure 2-7. Hence, the low conversion at low ratios is due to an insufficient amount of MVo in solution and not to limitations associated with the glucose oxidation reaction.
Figure 2-7: Anaerobic conversion efficiency of glucose with MVo as a function of the initial MVo/glucose ratio, at pH 12, T=50 °C with no reoxidation of MVr. Green circles are the measured conversion values. The dashed line (theoretical maximum curve) is the calculated maximum conversion if all the MVo is reduced. Results are shown with 95% confidence interval. Inset: percent of MVo that is converted into MVr at different initial MVo/glucose ratios.

**Anaerobic Conversion with Continuous Electrochemical Reoxidation of MVr**

In this section, we report the oxidation efficiency of glucose in an anaerobic environment with continuous electrochemical reoxidation of MVr. An anion exchange membrane was used to separate the anode (WE) and cathode (CE) compartments of the cell in order to prevent the reduction of methyl viologen on the cathode. Both glucose and MV were present on the anode side of the membrane where the working electrode was located. It was found that the membrane effectively eliminated MV crossover. However, according to the literature [74-76], glucose in a basic electrolyte converts into an enediolate anion, which is able to move through the anion exchange membrane. Significant crossover of glucose would lead to loss of the “fuel” and, therefore, underestimation of the conversion.
To minimize the crossover, we implemented two features in the design of the electrochemical cell. First, we made the area of the membrane very small (around 2 mm in diameter). This reduced the rate at which the enediolate ions were able to transport between the WE and CE compartments due to a concentration gradient. Second, we reduced the volume of the CE compartment to approximately 1/15 that of the WE compartment. This size reduction of the CE compartment decreases the magnitude of the concentration gradient between the WE and CE compartments and, consequently, the transport rate of the enediolate ions. The measured conversion value at pH 12, 50 °C and initial MVo/glucose ratio of 1 increased from 13% to 19% due to these changes. This 31.5% increase in the conversion indicates that the fuel crossover was a significant source of error in the conversion measurements prior to improvement of the cell design. Further decreases in the CE-compartment size did not noticeably change the observed conversion value, suggesting that the implemented modifications successfully controlled the crossover issue.

A simple calculation shows that the maximum possible error due to crossover is 6% with the final cell design (details of this calculation are shown in Appendix A). However, the maximum error is not likely in practice. First, equilibrium between the two compartments takes place slowly since the membrane is a barrier that reduces the transport rate of the enediolate ions. On the other hand, the potential gradient in the electrolyte, which is due to the electrochemical reactions on the WE and CE, forces the anions to move toward the WE. Therefore, the potential gradient also reduces the transport rate of the enediolate ions to the CE side. Moreover, consumption of glucose during the experiment reduces the enediolate concentration in the WE compartment. This causes a reverse concentration gradient that drives any enediolate that may have crossed over back toward
the WE side. Hence, it is safe to conclude that the error in the conversion measurements due to the fuel crossover will definitely be lower than 6%.

Figure 2-8 shows the oxidation efficiency of glucose as a function of the initial MVo/glucose ratio (with glucose concentration held constant). This figure also includes the results from Figure 2-7 in order to compare the conversion both with and without continuous electrochemical oxidation of MVr. The rate of electrochemical oxidation has an impact on the conversion efficiency as demonstrated in Figure 2-8.

![Figure 2-8: Anaerobic conversion of glucose with MVo at pH 12, 50°C. Blue squares and red triangles represent the measured conversion efficiencies in the electrochemical cell for the homogeneously and electrochemically limited cases, respectively. The results for the No-Electrochemical-Oxidation case (green circles) are from Figure 2-7 and are only shown for comparison purpose. Results are shown with 95% confidence interval.](image)

When the rate of the electrochemical reaction is slow, electrochemical reoxidation of MVr is the limiting step. Hence, MVr accumulates in the solution, turning the solution color to violet. In contrast, when the electrochemical oxidation is fast, the system is limited by the rate of
homogeneous reaction between the mediator and glucose. Under this condition, MV remains in the oxidized state and the solution remains clear. Therefore, the color of the electrolyte provides a qualitative indication of whether the system is homogeneously or electrochemically limited.

In order to shift from the homogeneously limited case (fast electrochemical oxidation rate) to the electrochemically limited case (slow electrochemical oxidation rate), we changed the rate of the electrochemical reaction by varying the potential and the anode size. A more positive potential at the anode provides a larger driving force for the electrochemical reaction, which results in a faster rate. Increasing the surface area of the anode while maintaining a constant electrolyte volume also increases the MVr oxidation rate. The applied potential was -0.1 and -0.5 V vs. RE for the fast and slow electrochemical oxidation rates, respectively. The anode consisted of a nickel foam with the dimensions of either $0.5 \times 2 \times 0.15$ cm or $5.5 \times 2 \times 0.15$ cm.

It should be noted that the fast electrochemical reaction consumes all the reduced species right at the anode surface. To ensure that the concentration of MVr is zero everywhere and the solution is entirely clear, rapid mass transfer is necessary. We accomplished this by stirring the solution at a very high rate. For the homogeneously limited case, varying the stir speed between 70% and 100% of the maximum rpm of the stir plate did not show any changes in the conversion. To be safe, the stir speed was set at the maximum rpm to ensure that the mass transfer was as fast as possible. For the electrochemically limited case, the speed of stirring was set at 5-10% of the maximum value.

Figure 2-8 shows the conversion efficiencies for a reaction that was conducted at glucose concentration of 2 mM in a pH 12 buffer at 50 °C with initial MVo/glucose ratios ranging from 0.1 to 10. As shown in the figure, the glucose oxidation efficiency varied from 16% to about 22% when the electrochemical reaction was fast and the system was homogeneously limited; this
corresponds to 3.8-5.3 out of the 24 available electrons. Since the reoxidation rate is at its maximum, this represents the maximum glucose conversion efficiency that can be obtained in an electrochemical cell. As shown in Figure 2-8, the conversion increased with increasing the initial MVo/glucose ratio. An increase of 6% in the conversion was observed when the ratio increased 100-fold from 0.1 to approximately 10. The highest rates of change were observed for ratios ≤ 2.

In Figure 2-8, when the electrochemical reaction rate was not at its maximum and the system was electrochemically limited, the conversion efficiency of glucose was lower, ranging from 12% to 20% (2.9-4.8 electrons). The difference was noticeable at low MVo/glucose ratios; in contrast, the difference was less significant for initial ratios greater than about 10. Clearly, the electrochemical reaction rate had a significant influence on glucose oxidation efficiency. Moreover, it was necessary to reoxidize MVr at a rate that was sufficiently rapid to result in a homogeneously limited system in order to obtain the maximum oxidation efficiency.

Figure 2-8 also compares the conversion efficiency in the absence of reoxidation with the results for both fast and slow electrochemical reoxidation. The results are similar at high MVo/glucose ratios. However, for low values of the initial MVo/glucose ratio, the difference observed in the conversion efficiency was significant. Therefore, the reoxidation reaction plays a significant role in enhancing the conversion efficiency at low MVo/glucose ratios. In other words, in situations where the conversion efficiency of glucose is limited by the availability of MVo, reoxidation leads to higher efficiencies as expected.

2.4 Discussion

Viologens are efficient mediators for the oxidation of different carbohydrates, including glucose, due to the relatively fast reaction of viologens with glucose at moderate temperatures in
alkaline solution [22]. In a few studies, a high conversion efficiency was observed for glucose in a viologen-mediated system [18, 59]. In contrast, other similar studies reported a lower conversion efficiency when glucose was oxidized by MV in an electrochemical cell [21, 60-62]. One possible explanation is that the low conversion efficiency was the result of the specific operating conditions used in the experiment.

In previous studies [18, 59], the large observed conversion efficiency was attributed to the reoxidation role of oxygen. The observed behavior was ascribed to the following primary reactions for glucose

\[
\text{glucose} + \text{MV}_o \rightarrow \text{MV}_r + \text{oxidation products} \tag{2-1}
\]

\[
\text{MV}_r \xrightarrow{\text{O}_2} \text{MV}_o \tag{2-2}
\]

In the above sequence, \(\text{MV}_o\) is reduced to \(\text{MV}_r\) (Reaction 2-1) by reacting with glucose to yield oxidation products consistent with the conversion efficiency. Then, oxygen preferentially reacts to oxidize \(\text{MV}_r\) (Reaction 2-2), and not the carbohydrates, which seems reasonable given the rate constant of \(6.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}\) for the reaction of oxygen with \(\text{MV}_r\) [64]. The above sequence implies that oxygen impacts the system solely by reoxidizing \(\text{MV}_r\), which can then further oxidize glucose. If this explanation is valid, it should be possible to replace oxygen with an alternative method for reoxidizing \(\text{MV}_r\), such as an electrode in an electrochemical cell, in order to achieve the same conversion efficiency. Thus, this work investigated the possibility of optimizing the operating conditions in the electrochemical cell in order to obtain a conversion efficiency similar to that observed in an aerobic environment, with the goal of understanding the actual impact of oxygen on glucose oxidation in viologen-mediated systems.
Based on the results presented in Figure 2-4 and Figure 2-8, it is clear that the maximum conversion efficiency in the aerobic environment is significantly larger than that observed for the system with the electrochemical reoxidation. This suggests that the impact of oxygen is not limited to its reaction with MVr. Instead, oxygen may directly oxidize carbohydrates or intermediates that form during the oxidation process and, consequently, enhance the conversion efficiency. Given the observed difference in the conversion efficiency, a different product distribution was expected for the aerobic and anaerobic (electrochemical) environments.

2.4.1 Oxidation Process in the Anaerobic Environment

Prior to presenting the product distribution observed for the anaerobic environment, we first discuss the potential products of glucose oxidation. Although the glucose oxidation can produce a variety of species, literature [18, 20, 21, 77] shows that the most prevalent oxidation products are carbonate, oxalic acid, formic acid, glycolic acid, glyceric acid, arabionic acid, gluconic acid, and a few other acids typically found in small quantities. Of these, carbonate is the most desirable and gluconic acid is the least desirable from a conversion efficiency perspective.

If each of the above-mentioned species is the only product of glucose oxidation, the resulting conversion efficiency would be 100%, 75%, 50%, 25%, 17%, 17%, and 8% respectively. In practice, a mixture of species will be present and the relative concentration of each will determine the overall conversion efficiency. In the anaerobic environment, the maximum conversion efficiency of glucose appears to be 22% or 5.3 electrons, as shown in Figure 2-8. This efficiency suggests that glycolic acid may be the main product of the glucose oxidation in the viologen-mediated system.
In order to identify the major products, such as glycolic acid, $^{13}$C-NMR studies for the oxidation of $^{13}$C$_1$ glucose were performed. The oxidation products formed are shown in Figure 2-9. The peaks observed in this figure were compared against $^{13}$C-NMR results for standard samples. Formic acid and carbonate each have a single peak (at $\delta=170$ ppm and $\delta=167$ ppm, respectively). The $^{13}$C-NMR spectra for glycolic acid and glyceric acid contain multiple peaks. Glycolic acid has two peaks that appear at around $\delta=61$ ppm and 180 ppm. For glyceric acid, the peaks appear at $\delta=64$ ppm, 74 ppm, and 178 ppm. Figure A-4 shows the $^{13}$C-NMR spectrum of a standard sample containing carbonate, formic acid and glycolic acid. Figure A-5 shows the $^{13}$C-NMR spectrum of a standard sample containing glyceric acid.

![Image](image.png)

Figure 2-9: $^{13}$C-NMR spectra of viologen-catalyzed oxidation of $^{13}$C$_1$-labeled glucose at 50 °C, pH 12, in the anaerobic environment (the homogeneously limited case).

In the oxidation of labeled-$^{13}$C$_1$ glucose, the labeled carbon can be incorporated into various products; however, only one of the carbons in each of these products is the labeled carbon. Since the labeled carbon has a dramatically higher intensity than a natural-abundance carbon, only one peak is observed for each of the products. The three peaks in Figure 2-9 represent three...
different oxidation products. Specifically, the peaks observed in the figure correspond to formic acid, glycolic acid and glyceric acid based on a comparison with the relevant standard spectra for the oxidation products of glucose.

The relative concentration of the products was estimated by comparing the observed intensities with the intensities from a standard sample that contained the products at equal concentrations. The relative concentration is defined against the concentration of formic acid. For products that have multiple peaks, the peaks that appear in the oxidation of labeled-\textsuperscript{13}C\textsubscript{1} glucose were chosen as the reference peaks. These are the peaks at $\delta=61$ppm and $\delta=74$ppm for glycolic and glyceric acid, respectively. Details of the relative-concentration calculation for Figure 2-9 are shown in Appendix A.

After obtaining the relative concentration of the major species, a carbon balance was used to estimate the product mole fractions, which requires the total moles of carbon in the oxidation products to be equal to the total moles of carbon in the initial carbohydrate. The resulting estimated mole fractions for the product distribution in Figure 2-9 are 0.27, 0.63, 0.11 for formic acid, glycolic acid, and glyceric acid, respectively. Thus, the main product is glycolic acid consistent with the hypothesis suggested above.

We now examine the measured product distribution and conversion from a mechanistic perspective. Prior to reacting with MVo, glucose in alkaline solution transforms into three different enediolate species with various relative concentrations [78]. The detection of three major products from the oxidation of \textsuperscript{13}C\textsubscript{1}-glucose is consistent with an enolization process that produces three different enediolate species. The enediolate species undergo reactions via various fragmentation pathways as shown in Figure 2-10. Note that this figure is focused on pathways that lead to the observed products and is not intended to be comprehensive. Also, Figure 2-10 excludes
direct (non-mediated) oxidation pathways of glucose on the WE, which was made of nickel. Direct oxidation of glucose was not observed on the WE in the potential range of interest. This is in agreement with the literature in which direct oxidation was reported on nickel only at potentials more positive than 0.15-0.25 V vs. RE [79, 80], well beyond the range of anode potentials feasible for MV-mediated fuel cell operation.

According to Figure 2-10, after β-elimination [81], enediolate species are converted into α-dicarbonyl species that undergo different reactions. Retro-aldolization is an alternative pathway that has been suggested for carbohydrates and involves C-C cleavage to form two aldol species. However, questions have been recently raised about its validity and there is a lack of persuasive experimental results in support of that mechanism [82]. The $^{13}$C-NMR results of this work are not consistent with retro-aldolization.

For glucose, β-dicarbonyl fragmentation of the enediolates through the first pathway results in formic acid, glycolic acid and glyceric acid plus their counterpart aldehydes in their enediolate forms. The second pathway, however, leads to threonic acid, glyceric acid, and glycolic acid plus the counterpart aldehydes in their enediolate forms. These counterpart aldehydes from the first and second pathways also undergo the same fragmentation reactions to form new products. The fragmentation process continues to glyceraldehyde, and finishes by the fragmentation of glycolaldehyde. For the oxidation experiments performed with glycolaldehyde, the last aldehyde in the oxidation chain of glucose, our NMR results showed only two peaks at δ=61 ppm and 180 ppm; these peaks represent glycolic acid as the only product of the glycolaldehyde oxidation.
Figure 2-10: Glucose fragmentation pathways with viologen in the anaerobic environment. 1: enolization and anion isomerisation, 2: β-elimination and transferring electron to MVo molecules, 3: re-arrangement into β-dicarbonyl, 4: β-cleavage.
It should be noted that acids formed in the viologen-mediated system do not undergo further oxidation. For example, when acids such as glycolic acid or glyceric acid were reacted with viologen, the $^{13}$C- NMR results showed only the peaks corresponding to the reactants. Hence, carboxylic acids represent terminal or end-of-the-line products for glucose oxidation under anaerobic conditions.

In Figure 2-10, the first pathway involving $\beta$-dicarbonyl cleavage appears to be the major reaction pathway for glucose oxidation. Support for this comes from the oxidation of $^{13}$C-labeled glucose, which would form formic, glycolic and glyceric acids that contain the $^{13}$C-labeled carbon if the oxidation occurred via the first pathway. The counterpart aldehydes formed via the first pathway would not contain the labeled carbon and, therefore, would not show up in the $^{13}$C-NMR results. Consequently, the observed product distribution shown in Figure 2-9 is in agreement with oxidation by the first pathway. In contrast, oxidation by the second pathway would form threonic acid, glyceric acid, and glycolic acid that would not include the labeled carbon and would not show up in the $^{13}$C-NMR results. Instead, the aldehydes formed would include the $^{13}$C-labeled carbon. When these aldehydes undergo the additional fragmentation, the only species with the $^{13}$C-labeled carbon would be glycolic acid. Since the second pathway does not form formic and glyceric acids with the $^{13}$C-labeled carbon, the second pathway is not in agreement with the observed product distribution (Figure 2-9).

The suggested mechanism from this work is in general agreement with the literature[21, 60, 63, 83, 84]; however, there are a few differences. Watt [63] suggested that the oxidation of carbohydrates with viologen takes place in a step-wise fashion to yield principally carbonate rather than formic acid. In contrast, the NMR results presented in Figure 2-9 shows formic and glycolic acid as the main products. Isbell et al. [83, 84] mentioned that formic acid is the only oxidation
product from glucose in an alkaline environment. This is not consistent with our observations and may be due to the presence of hydrogen peroxide in the study of Isbell et al. According to their proposed mechanism, hydrogen peroxide directly decomposes aldehydes into formic acid and the next aldose through a free-radical mechanism.

Hao et al. [60] and Liu et al. [21] suggested a mechanism for viologen-catalyzed glucose oxidation that included gluconic and glucaric acids, which were observed in a noticeable amount in their experiments. These acids are the least desirable products from the standpoint of oxidation efficiency. Therefore, their presence in those studies is indicative of an oxidation process that is significantly less efficient. The low oxidation efficiency in the study of Hao et al. and Liu et al. may have been due to a very low initial MVo/glucose ratio and a low rate of viologen reoxidation. In the study of Liu et al. [21], the maximum initial MVo/glucose ratio was 0.015, which is almost 7 times smaller than the minimum initial MVo/glucose ratio used in this work. As shown in Figure 2-8, very small initial MVo/glucose ratios and slow reoxidation rates of viologen adversely affect the oxidation efficiency. In particular, the rate of the reoxidation reaction has a profound impact at low initial MVo/glucose ratios. It appears that slow reoxidation rates at low initial MVo/glucose ratios result in glucose oxidation by less efficient pathways. In fact, the lowest extent of conversion was observed for the system without the reoxidation as shown in Figure 2-7.

From the results of this work, it is apparent that the initial MVo/glucose ratio impacts the reaction pathway and, therefore, the conversion efficiency. This conclusion is supported by the measured efficiencies and product distributions. In contrast, if the initial MVo/glucose ratio is sufficiently high and/or the reoxidation rate sufficiently fast, the conversion is not limited by MVo and tests both with and without reoxidation reach the same maximum conversion of approximately 22%. Under these conditions, the product distribution (NMR results of $^{13}$C$_1$ labeled glucose
oxidation) at the maximum conversion efficiency is independent of the reoxidation rate as shown in Figure 2-11.

2.4.2 Oxidation Process in the Aerobic Environment

In Figure 2-4, conversion values of 70% were observed for glucose under aerobic conditions. This efficiency is more than three times larger than the maximum conversion observed in the anaerobic environment, which was ~22%. The difference in conversion requires the product distribution in the aerobic and anaerobic environments to be very different. Figure 2-12 shows the product distribution of $^{13}$C$_1$ labeled glucose oxidation in the aerobic environment for a reaction that was conducted at 50 °C and pH 12.
In Figure 2-12, we observe formic acid, glycolic acid, glyceric acid, and carbonate. Comparison of Figure 2-12 with Figure 2-9, which is the product distribution in the anaerobic environment, demonstrates that formic acid, glycolic acid and glyceric acid form under both aerobic and anaerobic conditions. However, carbonate is only evident as a product under aerobic conditions. Given that carbonate is the result of a high extent of oxidation, its presence is consistent with the higher oxidation efficiency measured for the aerobic environment.

Wilt et al. [85] reported the formation of carbonate from glucose in alkaline electrolyte, which is consistent with our observations. To understand the source of carbonate formation, we combined formic acid, glycolic acid, or glyceric acid with MVo in the presence of oxygen. No oxygen consumption was observed for any of these acids; this implies that these acids do not
undergo oxidation reactions in an aerobic environment, so these compounds cannot be the source of the observed carbonate. Therefore, the carbonate in Figure 2-12 must come from the direct involvement of oxygen in the glucose oxidation pathway. One possibility is the direct oxidation of an enediolate species. 1,2 enediolate is the only species capable of forming a product with only one carbon; thus, it appears that carbonate is the product of 1,2 enediolate fragmentation, and the carbonate formation is in competition with formic acid production. However, the exact mechanism by which the carbonate is formed is not fully understood.

The second important distinction between oxidation under aerobic and anaerobic environments is the concentration of formic acid. Figure 2-12 shows that the concentration of formic acid is larger than that of glycolic and glycERIC acids in the aerobic environment. According to the observed peak intensities in Figure 2-12 and an overall carbon balance, the mole fractions of carbonate, formic acid, glycolic acid, and glycERIC acid are approximately 0.05, 0.60, 0.31, and 0.04, respectively, for oxidation performed under aerobic conditions. However, under anaerobic conditions, based on the product distribution in Figure 2-9, the approximate mole fractions of carbonate, formic acid, glycolic acid, and glycERIC acid are 0, 0.27, 0.63, and 0.11, respectively. Thus, glycolic acid is the major product measured under anaerobic conditions. Since formic acid is the result of a greater extent of oxidation than either glycolic or glycERIC acid, a higher fraction of formic acid is another indication of more efficient oxidation under aerobic conditions.

Figure 2-13 illustrates the product distribution from an all $^{13}$C labeled glucose measured by NMR for oxidation conducted at 50 °C, pH 12 under aerobic conditions. This figure shows the same products as were observed for the oxidation of $^{13}$C1-labeled glucose (only the C1 carbon labeled), except that all of the corresponding peaks are now apparent for each product. Figure 2-13 confirms the formation of carbonate as one of the oxidation products of glucose in
the aerobic environment. Moreover, it shows that formic acid (with an approximate mole fraction of 0.59) is the main product of glucose oxidation under aerobic conditions, along with some glycolic acid, and negligible amount of glyceric acid.

As Figure 2-4 shows, most of the carbohydrates tested oxidize to a significant extent under aerobic conditions. This seems reasonable since various carbohydrates tend to undergo oxidation by the same mechanisms [86]. However, the extent of oxidation was lower for the two three-carbon carbohydrates, DHA and glyceraldehyde. Figure A-6 demonstrates the product distribution from an all $^{13}$C-labeled glyceraldehyde measured by NMR for oxidation conducted at 50 °C, pH 12 under aerobic conditions. This figure demonstrates that the same oxidation products form during the oxidation of glyceraldehyde, indicating similar oxidation pathways. However, the relative concentration of carbonate in Figure A-6 for glyceraldehyde oxidation is lower than that shown in Figure 2-13 for glucose, which is consistent with a lower extent of oxidation. Therefore, the oxidation mechanism for glyceraldehyde likely favors pathways that are less efficient toward full oxidation to carbonate. Since DHA and glyceraldehyde interconvert through the enolization step in alkaline solution [87, 88], DHA is expected to behave similarly to glyceraldehyde, also presenting a lower oxidation efficiency than glucose.
The significant difference in the maximum conversion efficiencies and product distributions measured for glucose oxidation under aerobic and anaerobic conditions clearly shows that oxygen participates directly in the oxidation process. Therefore, its role is not limited to simple reoxidation of MV\textsubscript{r} as initially proposed [18, 59]. Rather, the presence of oxygen favors reaction pathways that result in the formation of formic acid. Additionally, oxygen makes carbonate formation possible, whereas carbonate was not observed in the anaerobic environment.
These differences are consistent with the mechanisms suggested in the literature [71, 81, 89]. In an aerobic environment, oxygen can impact glucose molecules both directly and indirectly. For example, an oxygen atom can be added directly to 1,2 enediolate to form a hydroperoxide intermediate. This intermediate can then undergo C-C cleavage to produce formic acid [71, 81]. The cleavage of the hydroperoxide intermediate is in competition with double-bond migration that produces 2,3 enediolate or 3,4 enediolate. However, when the oxygen concentration in the electrolyte is high, oxidation of 1,2 enediolate that results in the formation of formic acid is favored [85].

In addition to the direct reaction, oxygen can indirectly influence the carbohydrates through the formation of hydrogen peroxide. It has been shown that in the presence of an electron mediator such as anthraquinone-2-sulfonate or methylene blue, 1,2 enediolate form of glucose reacts with the mediator. The product of this reaction is the reduced form of the mediator and D-arabinohexos-2-ulose (glycosulose), which is a dicarbonyl compound. Oxygen first reacts with the reduced form of the mediator and forms the hydrogen peroxide anion. Subsequently, hydrogen peroxide reacts with glycosulose and C-C cleavage of this compound yields formic acid and the next lower aldose with a one-atom-shorter carbon chain [71, 75, 84, 89-94]. This mechanism can also occur in our system in which methyl viologen is the electron mediator. Therefore, formic acid is the favored product in the aerobic environment, in contrast to the anaerobic environment in which glycolic acid is the dominant product.

2.5 Conclusions

Glucose oxidation efficiency was investigated in a viologen-mediated system under both aerobic and anaerobic conditions. Experiments were performed with and without reoxidation of
the mediator. In the aerobic experiments, reoxidation was performed by reaction with oxygen. In contrast, the electrochemical reoxidation was used under anaerobic conditions. The results from the electrochemical cell are directly applicable to a mediated carbohydrate fuel cell since the anode of the electrochemical cell functionally mimics the fuel cell anode. The conversion efficiency in the electrochemical cell depended on the rate of the electrochemical reaction and was higher at the faster reaction rates. The conversion efficiency also depended on the initial molar ratio of viologen to glucose and was observed to increase with increasing the initial ratios up to a value of about 2. Beyond that point, the ratio did not have a significant impact. In the aerobic system, the conversion efficiency was much larger than the maximum conversion efficiency measured in the electrochemical cell, and the principal product was formic acid rather than glycolic acid. Carbonate was also observed in the aerobic system, but not in the electrochemical system. These results show that oxygen used to reoxidize the mediator in aerobic experiments directly impacted the glucose oxidation pathway, leading to efficiencies in excess of those possible with the electrochemical reoxidation as would be found in a fuel cell. Thus, based on our experiments, the maximum conversion efficiency obtainable with viologen-mediated glucose oxidation for fuel cell applications is approximately 22%. This oxidation efficiency is about three times larger than the values observed for precious-metal-based fuel cells. Therefore, viologen-mediated fuel cells offer a significantly higher oxidation efficiency without the additional cost associated with precious metals. This makes viologen-mediated cells an attractive option for large-scale developments of glucose fuel cells.
3 RATE PERFORMANCE OF VIOLOGEN-MEDIATED GLUCOSE FUEL CELL

3.1 Introduction

There is a need for renewable and sustainable sources of energy in order to address environmental concerns, such as global warming, as well as long-term supply and availability issues. Carbohydrates, produced from biomass, represent a sustainable source of energy that has the potential to decrease our reliance on fossil fuels [1, 2]. Glucose, for instance, can provide a theoretical specific energy of 4430 Wh kg\(^{-1}\) if oxidized completely [45]. Glucose not only has a high energy density, but is also one of the most abundant, clean and nonhazardous fuels. All of these advantages make glucose an attractive fuel for electrochemical systems such as fuel cells. Both the extent and rate of conversion are important to the viability of glucose fuel cells, and progress to date has been limited [10, 11]. We recently examined the factors that influence the extent of conversion for a viologen-mediated cell [17]. This study explores the physical processes and interactions between those processes that control the rate at which the glucose can be reacted and, hence, the current density available from a viologen-mediated fuel cell. Both dimensional analysis and detailed simulations are used to identify and quantify the processes that limit the rate behavior of the cell. A similar approach can be used for process development and optimization of any mediated system in which several physical processes interact.

Glucose fuel cells can be categorized as either biological or non-biological [13]. In a biological fuel cell, glucose is oxidized via an enzymatic reaction or by microorganisms. While
these fuel cells do not require precious metal electrodes, several challenges exist with respect to their stability and longevity [12, 46-48]. Furthermore, biological fuel cells exhibit very low rates of glucose oxidation, resulting in low power densities [12-14, 26, 49, 50].

Non-biological fuel cells, also known as abiotic fuel cells, have received considerable attention over the last couple of decades. Abiotic fuel cells can either be mediated or non-mediated. Non-mediated cells commonly use precious metal electrodes such as platinum, gold, palladium or other noble metals to oxidize glucose. Compared to biological cells, non-mediated abiotic cells offer much higher stability, durability and power density [27-29, 51]. Despite these advantages, non-mediated cells have some serious drawbacks. Due to the use of precious metals in the electrodes of these cells, cost represents an obstacle to further development. Electrode poisoning, which leads to deactivation of the electrode over time, is another issue that limits cell development. In fact, poisoning may require the use of larger electrodes and more frequent replacement of the electrodes, which would further increase costs. Strategies for overcoming these obstacles include the use of catalyst supports such as carbon and the use of bimetallic or even trimetallic electrocatalysts [95-97]. In spite of advances, obstacles have not been completely eliminated [4, 16, 49, 54, 58, 97, 98].

Recently, Torigoe et al. [11] obtained a maximum power density of 96 mW/cm2 with use of an Au-Pt anode catalyst, which is the largest reported power density for a non-mediated fuel cell reported to date. To achieve this power density, the authors optimized operating conditions, such as temperature and reactant concentration, and electrocatalyst parameters, such as the composition of the catalyst, catalyst loading and the ionomer to support ratio. Unfortunately, the Au-Pt electrocatalyst used in the study is still susceptible to poisoning, especially at the strongly alkaline conditions under which the experiments were performed [99].
Another drawback associated with the use of precious metals for glucose oxidation is low oxidation efficiency [15, 16, 52, 53]. The primary oxidation product for these catalyzed electrodes is gluconic acid, which corresponds to an efficiency of only 8% [10, 54, 55]. Complete oxidation of the glucose produces 24 electrons per glucose molecule, in contrast to the two-electrons (8%) observed for a variety of electrolytes over a broad pH range for non-mediated abiotic fuel cells [27, 29, 54, 56-58]. Therefore, in spite of the power densities that have been achieved with these cells, important challenges remain that may prevent their use in practice.

Mediated abiotic fuel cells are the principal type of fuel cells of interest to this work. In these cells, glucose oxidation occurs indirectly with the aid of an electron mediator [30]. Specifically, the electron mediator reacts homogeneously in solution to oxidize glucose, and is reduced in the process (see Figure 3-1). Subsequently, the reduced mediator is re-oxidized electrochemically at the anode. Since the electrochemical oxidation of the mediator occurs even on inert electrodes such as graphite, mediated cells have the potential for significant cost savings.

Figure 3-1: An illustration of the reactions that occur in the mediated glucose fuel cell. EMo and EMr represent the oxidized and reduced form of the electron mediator, respectively.
Organic-based mediators, such as the viologens that are the focus of this study, have recently received some attention. It has been reported that the viologen mediators can oxidize up to 22% of glucose in electrochemical cells [17], which is almost three times the conversion possible with precious metal catalysts. Hence, viologen mediators present a significant advantage over precious metals from the standpoint of oxidation efficiency. The rate of oxidation is also critical. According to a kinetic study done by Watt et al. [22, 23], the homogeneous reaction of glucose with viologens proceeds relatively fast in alkaline electrolytes at moderate temperatures. In addition, the electrochemical oxidation of viologens occurs readily on inert electrodes. For example, the oxidation of methyl viologen (MV) is an elementary single-electron reaction with reasonably fast kinetics [24]. This implies the possibility of reasonably high power performance from viologen-mediated fuel cells. In contrast, the reported power performance of MV-mediated cells in the literature is 2.5 mW/cm² [9, 21, 62, 100, 101], which is disappointingly low. Clearly, additional work is needed to explore and mitigate the factors that limit the power performance of viologen-mediated fuel cells.

As mentioned previously, mediated fuel-cell anodes involve both homogeneous and electrochemical reactions. In MV-mediated cells, the homogeneous reaction between glucose and MVo (the oxidized form of MV) forms MVr (the reduced form of MV). After it is formed, MVr is transported to the anode where it is oxidized. The oxidized mediator then moves back to the bulk where it again reacts with glucose. Hence, the rates of the homogeneous reaction, electrochemical reaction, and mass transfer are all potentially important. Depending on the operating conditions in the cell, each of these rates may influence cell performance to a different extent. These rate processes may also interact in different ways under different conditions. Thus, it is crucial to determine how these rates interact and the specific factors that limit cell performance.
The objective of this study was to investigate the performance of a viologen-mediated anode, which is critical to the potential application of viologens in glucose fuel cells. To accomplish this goal, a mathematical model was developed and validated. The model was then used to investigate the coupled rate processes that govern cell performance. As mentioned above, key physical processes included the homogeneous reaction, mass transfer, and electrochemical reaction. The relative significance of these rates was evaluated using dimensional analysis in the form of Damköhler numbers, an approach that has broad application for mediated systems. The maximum obtainable current density and the required polarization were determined for the electrode configuration considered in this work. Finally, practical implications and limitations associated with MV-mediated fuel cells were considered.

3.2 Mathematical Model

The anode side of a viologen-mediated cell was modeled to better understand the factors that control cell performance. Figure 3-2a shows a simplified schematic diagram of the cell of interest, the anode side of which was modeled in this study. Figure B-1 displays a 3-D diagram of the cell used for experiments, which consisted of three regions: the cathode side, the anion exchange membrane (AEM), and the anode side.

The model includes a description of the physical processes that take place in the anode and their influence on the rate of glucose conversion (Figure 3-1). Briefly, homogeneous reaction between the oxidized form of the mediator (MVo) and glucose produces the reduced form of the mediator (MVr). After it is formed, MVr is transported from the bulk to the electrode surface where it is oxidized electrochemically. The oxidized mediator (MVo) is then transported back to the bulk, where it again reacts homogeneously with glucose.
The rates of the homogeneous reaction, electrochemical reaction, and mass transfer are all potentially important and may impact cell performance differently, depending on the operating conditions. Thus, the anode is modeled to determine how these rates are coupled and identify the specific factors that control cell performance under different operating conditions.

Figure 3-2: a) a simplified schematic drawing of the cell (a more detailed drawing of the cell was shown in Figure B-1, b) a 2-D representation of the anode side as was modeled in this study.

The anode is modeled using a 2-D geometry, as shown in Figure 3-2b, and anode performance is predicted in terms of current density. Despite the actual serpentine pattern of the flow channel (see Figure B-1), the flow channel is considered to be straight in the model for simplicity. The flow channel in the anode contains a porous electrode that is characterized by a constant uniform porosity and specific surface area. As listed in Table 3-1, the width and depth of the channel are 5.5 mm and 1.1 mm, respectively. Given the aspect ratio of 5 (5.5/1.1), the model
can reasonably be simplified by assuming that the current density is uniform across the width (z-direction). The electrolyte flows in the x-direction through the porous electrode.

The governing equations used to describe the anode behavior include: species material balances, the Nernst-Planck transport expressions, electroneutrality, conservation of charge, and the Butler-Volmer kinetic expression. These expressions are derived for the 2-D geometry and control volume shown in Figure 3-2.

We begin with the material balance for MVr:

\[
\frac{\varepsilon \partial c_{\text{MVr}}}{\partial t} = -\nabla \cdot N_{\text{MVr}} - R_{1\text{MVr}} + R_{2\text{MVr}}, \tag{3-1}
\]

where \( \varepsilon \) is the porosity of the porous electrode and accounts for the fact that the control volume contains both electrolyte and solid phases, \( c_{\text{MVr}} \) is the concentration of MVr based on the electrolyte volume, \( R_{1\text{MVr}} \) is the consumption of MVr by the electrochemical reaction, \( R_{2\text{MVr}} \) is the generation of MVr by the homogeneous reaction, and \( N_{\text{MVr}} \) is the flux of MVr. A similar material balance with appropriate terms and coefficients is applied to MVo.

The flux, \( N_{\text{MVr}} \), is described by the Nernst-Planck equation:

\[
N_{\text{MVr}} = -\varepsilon z_{\text{MVr}} u_{\text{MVr}} F c_{\text{MVr}} \nabla \phi_2 - \varepsilon D_{\text{MVr}} \nabla c_{\text{MVr}} + \varepsilon c_{\text{MVr}} v \tag{3-2}
\]

where \( \phi_2 \) is the potential in the electrolyte phase, \( z_{\text{MVr}} \) is the charge number for MVr (+1), \( F \) is Faraday’s constant, \( u \) is the mobility, \( D \) is the diffusivity, and \( v \) is the electrolyte velocity as defined in Table 3-1. As shown in Figure 3-2, we assume that convection occurs in the x-direction only. In that direction, MVr is transported by diffusion, migration, and convection. In the y-direction, transport of MVr occurs only by migration and diffusion. The transport coefficients, such as diffusivity, mobility, conductivity, etc., are effective coefficients, which are corrected for porosity and tortuosity, as defined later in this study.
\( \mathcal{R}_1 \) and \( \mathcal{R}_2 \) in Equation (3-1) represent the electrochemical consumption and the homogeneous generation terms, respectively. Both of these source terms are volumetric and are determined based on the superficial volume that includes both the solid and electrolyte phases.

\( \mathcal{R}_1 \) for \( MVr \) is defined as

\[
\mathcal{R}_{1_{MVr}} = \frac{a}{nF} j
\]  
(3-3)

where \( a \) is the specific surface area of the porous electrode and \( n \) is the number of equivalents per mole of MV that reacts electrochemically according to the following half-cell reaction

\[
MVr \rightarrow MVo + e^- \]  
(3-4)

\( j \) in Equation (3-3) is the electrochemical reaction rate of MV described by the Butler-Volmer equation

\[
j = i_0 \left[ e^{\frac{\alpha a F \eta_s}{RT}} - e^{\frac{-\alpha a F \eta_s}{RT}} \right] \]  
(3-5)

Note \( j \) is positive for oxidation (anodic current). \( \eta_s \) is the overpotential and \( i_0 \) is the exchange-current density. For porous electrodes, it is commonly assumed that the concentration is uniform in each control volume. However, the surface concentration can be different from the local pore concentration, depending on the surface reaction rate. Thus, \( i_0 \) is defined at the surface concentration rather than the pore concentration as follows

\[
i_0 = i_{0_{ref}} \left( \frac{c_{MVr_{surf}}}{c_{MVr_{ref}}} \right)^{0.5} \left( \frac{c_{MVo_{surf}}}{c_{MVo_{ref}}} \right)^{0.5}, \]  
(3-6)

where the subscript \( surf \) refers to the electrode surface, and \( ref \) refers to a reference concentration.

The local pore-wall flux from the flowing solution is related to the mass transfer coefficient (\( k_m \)) [102-104]:

63
\[ \mathcal{R}_{1_MVr} = k_m a (c_{MVr} - c_{MVr_{sur}}) \]  

(3-7)

An empirical model of the form \( k_m a = A_1 Sc^{\frac{1}{3}} Re^{A_2} \), where \( Sc \) and \( Re \) are the Schmidt and Reynolds numbers, respectively, was developed for \( k_m \) in this study as described in Appendix B. The overpotential, \( \eta_s \), in Equation (3-5) is defined as

\[ \eta_s = \phi_1 - \phi_2 - U \]  

(3-8)

where \( \phi_1 \) is the potential of the solid phase, and \( U \) is the redox potential of MV defined by the Nernst equation

\[ U = U_o - \frac{RT}{nF} \ln \left( \frac{c_{MVr_{sur}}}{c_{MV_{o,sur}}} \right) \]  

(3-9)

where \( U_o \) is the standard redox potential of the MV half-cell reaction, -0.609 V vs. the Hg/HgO reference electrode used in this study (adapted from [8]). The homogeneous generation term, \( \mathcal{R}_{2_MVr} \), in Equation (3-1) is

\[ \mathcal{R}_{2_MVr} = K_1 (\varepsilon c_g)(\varepsilon c_{OH})(\varepsilon c_{MVo}) \frac{K_2 + (\varepsilon c_{MVo})}{K_2 + (\varepsilon c_{MVo})} \]  

(3-10)

where subscripts \( g, OH, \) and \( MVo \) represent glucose, hydroxide ion, and the oxidized form of MV, respectively [23]. The rate constants for the homogeneous reaction are represented by \( K_1 \) and \( K_2 \). The material balance equation for glucose is

\[ \frac{\varepsilon \partial c_g}{\partial t} = -\nabla \cdot N_g - \mathcal{R}_{2_g} \]  

(3-11)

where \( N_g \) is the glucose flux and \( \mathcal{R}_{2_g} \) is the rate at which glucose is consumed by the homogeneous reaction. Since glucose is essentially unreactive electrochemically in our system, its material balance does not include \( \mathcal{R}_1 \).
Previously [17], we showed that the oxidation efficiency of glucose, which reflects the number of electrons transferred to the mediator per mole of glucose reacted, depends on the initial molar ratio of the mediator to glucose. This ratio is defined as

\[ \beta = \frac{\text{initial moles of MVo}}{\text{initial moles of glucose}} \]  

(3-12)

We now write the following expression for the reaction of glucose with the mediator

\[ \text{glucose} + \alpha \text{ MVo} \rightarrow \alpha \text{ MVr} + \text{products}, \]  

(3-13)

where \( \alpha \) represents the number of electrons transferred to MVo per mole of glucose that reacts. The following empirical relationship is used to estimate \( \alpha \) as a function of \( \beta \) in the range \( 1 < \beta < 15 \) [17]

\[ \alpha = \frac{7.5 \beta}{6.5 + \beta} \]  

(3-14)

Equation (3-14) estimates \( \alpha \) assuming that the mediator undergoes homogeneous reaction without regeneration at the electrode. In contrast, the electrochemical reaction in the actual system regenerates MVo by oxidizing MVr (see Figure 3-1), making it available for further homogeneous reaction. The availability depends upon the transfer rate of MVo from the surface to the reaction site. For simplicity, the impact of MVo regeneration is not considered in the expression used for \( \alpha \), which represents a conservative assumption.

The homogeneous reaction rate of glucose is related to that of MVr as follows

\[ \mathcal{R}_g^2 = -\frac{\mathcal{R}_{MVr}^2}{\alpha} \]  

(3-15)

We assume that the OH\(^-\) concentration remains constant, consistent with experiments that controlled the pH (see Section 3.3.2).
The charge balance for the current in solution is

$$\nabla \cdot \mathbf{i}_2 = aj,$$  \hspace{1cm} (3-16)

which assumes that capacitive effects are not important. The interfacial current, $j$, is defined as positive for oxidation. The current collector is at the back of the porous electrode ($y=0$), as shown in Figure 3-2. At any point in the electrode,

$$\nabla \cdot \mathbf{i}_1 + \nabla \cdot \mathbf{i}_2 = 0$$  \hspace{1cm} (3-17)

For the electrode (solid) phase, ohm’s law applies, resulting in

$$\mathbf{i}_1 = -\sigma \nabla \phi_1$$  \hspace{1cm} (3-18)

For the electrolyte phase, the current is related to the flux of the ions as follows

$$\mathbf{i}_2 = F \sum_i z_i N_i = -\kappa \nabla \phi_2 - F \sum_i z_i D_i \nabla c_i$$  \hspace{1cm} (3-19)

where the subscript $i$ refers to the specific ion. The concentrations of Cl$^-$ and Na$^+$, unreactive ions of the supporting electrolyte used, are obtained from electroneutrality and a material balance similar to Equation (3-1) presented above but without the generation/consumption source terms, respectively. $\kappa$ is assumed to be independent of the local ion concentration and is treated as a fixed parameter based on experimentally measured values for the desired electrolytes. The rationale behind this assumption is discussed in Appendix B. As noted above, $z_i$ and $D_i$ represent the charge number and diffusivity of individual ions in solution. The diffusivities of MVr and MVo are different due to their different degree of association (interaction) with anions and the solvent in aqueous electrolytes [8, 105].

The transport properties in previous expressions, such as mobility, conductivity, and diffusivity, are effective properties within the pores. These effective properties, which are
assumed to be independent of local concentration, are related to the intrinsic properties by the Bruggeman relationship

\[ u = u_{\text{intrinsic}} e^{1.5} \]  
(3-20)

\[ \kappa = \kappa_{\text{intrinsic}} e^{1.5} \]  
(3-21)

\[ D = D_{\text{intrinsic}} e^{1.5} \]  
(3-22)

The intrinsic mobilities were estimated by the Nernst-Einstein relationship. The intrinsic conductivity for each of the electrolytes used, as listed in Table 3-1, was measured with EIS (Electrochemical Impedance Spectroscopy) at the operating conditions of interest. A description of the EIS technique can be found in Section 3.3.2 (Experimental procedure). Intrinsic diffusivities were taken from the literature [24] and corrected for concentration and temperature with use of the following relation [106]

\[ D_{\text{intrinsic}} \mu \propto T \]  
(3-23)

### 3.2.1 Transient Inlet

The model presented in the previous section is sufficient for describing the behavior of the anode if the inlet conditions to the cell are known. However, in the experiments used for the model verification, the reactants were added to a mixing tank placed upstream of the anode as illustrated schematically in Figure 3-3. As a result, the homogeneous reaction initiated in the tank immediately after mixing, and the concentrations of glucose, MVr, and MVo entering the anode compartment varied with time. Therefore, a mixing tank was added to the model to capture the transient nature of the inlet condition present in the experiments.
The material balances for glucose and MVr in the mixing tank are

\[
\frac{dc_{MVr}}{dt} = \mathcal{R}T_{MVr} = \frac{K_1 c_g c_{OH} c_{MVo}}{K_2 + c_{MVo}}
\]

\[
\frac{dc_g}{dt} = \mathcal{R}T_g = -\frac{\mathcal{R}T_{MVr}}{\alpha},
\]

where \( \mathcal{R}T_{MVr} \) and \( \mathcal{R}T_g \) represent the generation of MVr and consumption of glucose, respectively, due to the homogeneous reaction in the mixing tank.

### 3.2.2 Model Parameters

All relevant parameters for the model are presented in Table 3-1
Table 3-1: Model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total length of channels (L, dimension in the x-direction)</td>
<td>cm</td>
<td>40</td>
</tr>
<tr>
<td>Width of each channel (W, dimension in the z-direction)</td>
<td>cm</td>
<td>0.55</td>
</tr>
<tr>
<td>Depth of each channel (Dep, dimension in the y-direction)</td>
<td>cm</td>
<td>0.11</td>
</tr>
<tr>
<td>Porosity of the electrode (ε)</td>
<td></td>
<td>0.93</td>
</tr>
<tr>
<td>Exchange current density (i₀)</td>
<td>A/cm²</td>
<td>2.7×10⁻⁵ [24]</td>
</tr>
<tr>
<td>Operating temperature (T)</td>
<td>°C</td>
<td>50</td>
</tr>
<tr>
<td>Specific area of the electrode (a)</td>
<td>l/cm</td>
<td>61 (calculated)</td>
</tr>
<tr>
<td>Diffusivity coefficient of MVo at bulk condition (D_MVo)</td>
<td>cm²/s</td>
<td>0.86×10⁻⁵ [8]</td>
</tr>
<tr>
<td>Ratio of Diffusivity coefficient of MVr to MVo</td>
<td></td>
<td>3.86 [8]</td>
</tr>
<tr>
<td>Diffusivity of glucose at bulk condition (D_g)</td>
<td>cm²/s</td>
<td>6.5×10⁻⁶ [107]</td>
</tr>
<tr>
<td>Homogeneous reaction rate constant (K₁)</td>
<td>1/(M.s)</td>
<td>0.084 [23]</td>
</tr>
<tr>
<td>Homogeneous rate constant (K₂)</td>
<td>mM</td>
<td>0.38 [23]</td>
</tr>
<tr>
<td>Homogeneous reaction activation energy</td>
<td>kJ/mol</td>
<td>122 [108]</td>
</tr>
<tr>
<td>The electrolyte conductivity for the tests at 8 and 17 mM glucose</td>
<td>S/cm</td>
<td>0.165 (measured)</td>
</tr>
<tr>
<td>The electrolyte conductivity for the test at 0.2 M glucose</td>
<td>S/cm</td>
<td>0.245 (measured)</td>
</tr>
<tr>
<td>Viscosity of the electrolyte for the test at 0.2 M glucose</td>
<td>cP</td>
<td>0.68</td>
</tr>
<tr>
<td>Charge of MVo (z_MVo)</td>
<td></td>
<td>+2</td>
</tr>
<tr>
<td>Charge of MVr (z_MVr)</td>
<td></td>
<td>+1</td>
</tr>
<tr>
<td>Standard redox potential for MV (U₀), vs. Hg/HgO</td>
<td>V</td>
<td>-0.609 [8]</td>
</tr>
<tr>
<td>Graphite fiber size (d)</td>
<td>um</td>
<td>20 (measured)</td>
</tr>
<tr>
<td>Superficial velocity of the electrolyte (v)</td>
<td>cm/s</td>
<td>Q/W×Dep×ε</td>
</tr>
<tr>
<td>Reynolds number (based on the electrode fiber size)</td>
<td></td>
<td>ρdv/μ</td>
</tr>
</tbody>
</table>

3.2.3 Initial and Boundary Conditions

Two different types of simulations were performed. The first type included a mixing tank in order to match the configuration used experimentally. The results from simulations of this type are discussed in Section 3.3 (Model validation). The initial concentrations of glucose, MVo, and OH⁻ in the tank were set as described in Section 3.3. These concentrations determine the inlet
conditions for the anode. The initial current was assumed to be zero, and the initial potential was at the open-circuit voltage (OCV).

In the second type of simulation, steady-state operation without the mixing-tank was considered. The results from these simulations are presented in Section 3.4 (Cell analysis and discussion). For these simulations, the inlet concentrations of glucose, MVo, and OH\textsuperscript{-} at the anode were fixed based on the desired operating conditions, as explained in Section 3.4.

The following boundary conditions were used for both the transient and steady-state simulations. The current collector was treated as impermeable to ions. Also, the AEM was assumed to be impermeable to viologen species, which are positively charged. In an alkaline electrolyte, glucose is converted into an enediolate, which is negatively charged and may permeate through the membrane [17]. Nevertheless, due to the low diffusivity of glucose in AEMs [107], our analysis showed that the fraction of glucose that permeates through the AEM is very small at less than 1.7%. Hence, glucose transport across the AEM was neglected.

The electronic current (\( \mathbf{i}_1 \)) was set to zero at the membrane-electrode interface. Similarly, ionic current (\( \mathbf{i}_2 \)) was specified as zero at the current collector. The electrolyte-phase potential (\( \phi_2 \)) was also set at zero at the membrane-electrode interface (front of the electrode). Finally, the electric potential at the current collector was specified to reflect the applied potential as described in Section 3.3 or 3.4.

### 3.2.4 Numerical Procedure

The equations that constitute the model were solved simultaneously with COMSOL Multiphysics 5.3 for \( c_g, c_{MVr}, c_{MVo}, \phi_1, \phi_2, c_{MVr_{sur}}, c_{MVo_{sur}}, \mathbf{i}_1, \mathbf{i}_2 \). The finite element mesh consisted of 3840 quadrilateral elements that utilized quadratic basis functions. Refinement of the
mesh had no significant impact on the results. The equations at each time step were solved using the direct solver, PARADISO, which utilizes LU decomposition. COMSOL’s Backward Differentiation Formula (BDF) solver, which is an implicit method, was applied for time-stepping with a tolerance of $10^{-6}$. For simulations performed at steady-state where the conditions entering the electrode were assumed constant, Newton’s method was used to solve the coupled equations to a specified relative tolerance of $10^{-6}$.

### 3.3 Model Validation

The above model was validated by comparison against the experimental results of the present study. In what follows, the materials, instrumentation and experimental procedure are first described. Next, experimental results are presented. Finally, results from the experiments and the simulations are compared, and an assessment of the model is made.

### 3.3.1 Materials and Instrumentation

Glucose and methyl viologen dichloride (MV) were obtained from Sigma-Aldrich. Potassium phosphate dibasic from EMD Millpore Corporation and potassium hydroxide from Mallinckrodt Chemicals were used for preparation of the electrolyte. Either an SP-240 (Biologic Science Instruments, France) or a VersaSTAT-3 (Princeton Applied Research) electrochemical workstation was used for electrochemical measurements and control. The pH of the solution was controlled with use of either a 1 M phosphate buffer or manually, as explained in greater detail later in the experimental procedure section. The temperature of the mixing tank was controlled with aid of a circulating water bath (PolyScience, USA).
A viologen-mediated fuel cell was assembled with stainless steel endplates and current collectors, two fuel-cell-grade graphite plates (FC-GR347B, Graphitestore, USA), and an anion exchange membrane (FAA-3-PK-130, fuelcellstore.com). A Teflon gasket (0.002” thick from McMaster-Carr) was placed between the graphite plates to prevent shorting. Potentials were referenced to a Hg/HgO reference electrode (ALS Co. Ltd, Japan) placed just upstream of the anode. Channels on the graphite plates had a serpentine design and were 5.5 mm wide and 1.1 mm deep. The channels were filled with a graphite felt (AvCarb G100, fuelcellstore.com). A schematic drawing of the cell is provided in Figure B-1. Masterflex L/S peristaltic pumps (Cole-Parmer, USA) were used to flow the electrolyte inside the channels. The active area of the membrane was 22 cm². The temperature of the cell was controlled by a power supply/temperature controller (series 2500, Love Controls, USA) and 6 × 250W hot-rod heating elements (by Twidec from amazon.com) that were inserted into holes in the endplates.

3.3.2 Experimental Procedure

Conductivity measurements were conducted at 300 kHz in a cuboid-shaped Teflon cell with two 0.97 cm² stainless-steel electrodes placed 10 cm apart. Glucose oxidation experiments were conducted in the viologen-mediated cell described above. The cell was placed in an inert (nitrogen) environment glove box to prevent oxidation of MVr by oxygen in the air. The electrolyte for each test was added to the mixing tank and its temperature was controlled at the desired value. Glucose and MVo were then added to the tank. After a short amount of time to ensure mixing, the feed pump was used to deliver the solution into the anode. The cell temperature was also controlled to ensure isothermal operation.
The experiments were a series of potentiostatic tests. In these tests, the anode potential was set vs. a Hg/HgO reference electrode (RE) and the current was recorded. The potentials were set more positive than the open-circuit voltage (OCV) of the anode, which was measured at the beginning of each experiment. Each experiment included multiple potentiostatic steps. The minimum duration of each step was at least 30% longer than the fluid residence time at the tested flow rate. After completion of each potentiostatic measurement, the anode potential was switched to the next value in the positive direction as specified in Section 3.3.3 (Experimental results).

The experiments were conducted at low glucose concentrations of 8mM and 17mM, and at a high glucose concentration of 200mM. At the low concentrations, a 1M phosphate buffer adequately controlled the pH of the electrolyte. In contrast, the buffer was not adequate at the high concentration and the pH was controlled manually by syringe pump injection of OH⁻ into the tank during the experiment. Manual adjustment to maintain a pH of 13 was successful in keeping the pH between 12.86 and 13.02.

3.3.3 Experimental Results

Figure 3-4 shows the current density as a function of time at various anode potentials. The current density was based on the active area of the membrane. The experiment was conducted at 50⁰C and a pH of 12.3 for an initial glucose concentration of 17mM and an initial MVo/glucose molar ratio (β) of 1.5. The reaction between the carbohydrate and MV proceeds reasonably fast under alkaline conditions and at elevated temperatures, consistent with the operating conditions selected. The electrolyte flow rate was 3 ml/min. The potentials examined were -0.575, -0.55, -0.5, -0.45, -0.4, -0.3, -0.2 V vs. RE, which were changed in succession and resulted in an increasing anodic current.
The sharp peaks in Figure 3-4 were the result of a problem with the experimental procedure. As mentioned earlier, the potential steps were performed in sequence. In the setup used, the potentiostat inadvertently relaxed potential control immediately before moving to the next step in the sequence. Thus, the peaks resulted from relaxation at the end of each potential step followed by application of the potential for the next step. Because of this, the peaks represent artifacts that resulted from the way the experiments were performed and will not be considered further.

Figure 3-4: Experimental current density versus time at various anode potentials. The green and red lines represent the current density and the anode potential, respectively. Operating conditions were: 17 mM glucose, β 1.5, pH 12.3, electrolyte flow rate of 3 ml/min, and temperature of 50°C.

Excluding the initial transient behavior associated with switching, two interesting observations are evident from Figure 3-4. First, the current density varied with time during each potential step. For instance, the current density increased from 0.8 to 0.9 mA/cm² and from 1.2 to 1.34 mA/cm² during the steps at -0.55V and -0.5 V vs. RE, respectively. This behavior was due to the changing concentration at the anode inlet. As time went on, the MVr concentration in the
tank increased due to homogeneous oxidation of glucose, which increased the concentration at the anode inlet and resulted in a higher anodic current.

The second observation is that the response of the current density with potential changed as the magnitude of the potential increased. Ignoring the transient behavior associated with switching, the current density jumped from 0.3 to 0.8 mA/cm² and 0.9 to 1.2 mA/cm² when the potential was changed from -0.575 to -0.55 V and from -0.55 V to -0.5 V, respectively. Clearly, the current was potential dependent in this range. However, after -0.5 V, again excluding the peaks due to switching, the current followed a continuous line that was independent of potential. In other words, the current-density trend remained unchanged as the potential was increased for potentials greater than -0.5 V. This is consistent with mass transfer (MT) limited current at the higher potentials. Note that the continuing potential-independent increase of the current at these potentials was due to the changing MVr concentration at the anode inlet. Figure B-5 shows the concentration of MVr and glucose versus time at the inlet. The current density increased by 52%, from 1.2 to 1.8 mA/cm², in the MT limited region at times between 450 and 750 seconds. The MVr inlet concentration increased by 49%, from 7.9 to 11.8 mM, during that same time period. Given that the mass transfer limited current is expected to be proportional to concentration, this simple calculation supports the conclusion that the continued variation in the mass transfer limited current was due to changes in the MVr inlet concentration.

Figure 3-5 shows the measured current density at various glucose concentrations. Unlike Figure 3-4, this figure only shows the current density at the end of each potential step. In Figure 3-5a, the blue and red dots represent the current density at glucose concentrations of 8 mM and 17 mM, respectively. The other operating conditions were the same as those for Figure 3-4. The results are shown with 95% confidence intervals.
Figure 3-5: Experimental current densities at three glucose concentrations. The values shown are the current densities at the end of each potential step. The relevant anode potentials are also shown on the plot. a) Blue and red dots represent current densities at 8mM and 17 mM glucose, respectively, at pH 12.3, and an electrolyte flow rate of 3 ml/min. b) the current density at 200 mM glucose, pH 13, an electrolyte flow rate of 10 ml/min. For both a) and b), β was 1.5 and the temperature was 50 °C. Results are shown with 95% confidence intervals.

Figure 3-5b shows the current density at a glucose concentration of 200 mM, more than an order of magnitude higher than the concentrations shown in Figure 3-5a. The flow rate and the pH were also changed to 10 ml/min and 13 in order to obtain higher current densities. The rationale behind this will be explained in detail in Section 3.4 (Cell analysis and discussion).

The maximum current density at the conditions of Figure 3-5b was 120 mA/cm², much higher than the maximum current densities observed for glucose concentrations of 8 mM and 17 mM. Clearly, operating conditions had a significant impact on cell performance; however, it was not clear which conditions had the greatest impact. One of the principal contributions of this study is a quantitative assessment of how various physical processes interact to influence and control cell performance.
3.3.4 Comparison of Model Results with Experimental Data

In this section, results from the model are compared to experimental data to assess the accuracy of the model. The simulations included the transient behavior associated with the tank in order to accurately represent the experimental conditions. Both experiments and simulations were performed at constant potential for various values of the applied potential. No parameter fitting was performed.

Figure 3-6: Comparison between the model predictions and the experimental results at various glucose concentrations. a) blue line and dots represented the model prediction and the experimental results, respectively, at 8mM glucose concentration. Likewise, the red line and dots were at 17mM glucose concentration. The operating conditions were pH 12.3, temperature of 50 °C, β 1.5, and the electrolyte flow rate of 3 ml/min. b) purple line and dots corresponded to the modeling and experimental results, respectively, at 200mM of glucose. The operating conditions were β 1.5, pH 13, temperature 50 °C, the electrolyte flow rate of 10 ml/min.
Figure 3-6 shows the predicted current densities (lines) and corresponding experimental data (points) at various glucose concentrations. The other operating conditions were the same as those for Figure 3-5. As shown in Figure 3-6a, reasonable agreement between the predictions and experimental results was observed for low glucose concentrations with an average, maximum, and minimum deviation of 8%, 13%, and 3%, respectively. The predicted current density increased with time during each potential step, consistent with the experimental results. This transient behavior, as was explained earlier, was due to the changing concentration at the anode inlet. Moreover, the model predictions and the experimental results agreed with respect to the potential at which a mass transfer limit was reached. In Figure 3-6a, no significant jump in the current density was present at potentials more positive than -0.5 V, also in agreement with the experimental results presented above. A similar agreement between predicted and measured results can be observed in Figure 3-6b for a glucose concentration of 200 mM, although the average, maximum, and minimum deviations were slightly higher at 6%, 14%, and 5%.

The above results validate the ability of the model to predict the behavior of the anode with reasonable accuracy over a range of glucose concentrations. The model will now be used to provide insight into the factors that influence and control cell performance for a variety of operating conditions.

### 3.4 Cell Analysis and Discussion

Viologens appear promising as mediators for glucose oxidation owing to their reasonably fast reaction with carbohydrates at moderate temperatures in alkaline electrolytes [22, 23]. In addition, the electrochemical reaction of viologens takes place on inert electrodes with relatively fast kinetics [24]. As a result, the possibility exists for reasonably high performance from
viologen-mediated glucose fuel cells. In contrast, the maximum reported current density for such cells in the literature is less than 10 mA/cm² [9, 21, 62, 100, 101], which is disappointingly low. Therefore, it is important to understand and mitigate the factors that limit cell performance.

The performance of MV-mediated cells is influenced by a number of interacting phenomena that include the homogeneous reaction between glucose and MVo, transport of MVr to the electrode surface, the electrochemical oxidation of MVr, and transport of MVo back to the bulk where it can again react with glucose. The rates of these processes are all potentially important and, depending on the operating conditions, each may influence cell performance to a different extent. In this section, the mathematical model described above is used to understand the impact of each of these rates on anode performance. Of particular interest is the improvement of anode performance in terms of current density. Note, in contrast to Section 3.3, the results presented in this section do not include the transient behavior associated with the tank. Hence, the focus is on what is happening in the anode, and the inlet conditions to the anode remain fixed.

Damköhler numbers derived from dimensional analysis of the system are used to evaluate the relative importance of different physical processes on cell performance. The procedure used applies to any mediated cell in which several processes may interact. The next section describes the dimensionless numbers derived and the factors that they represent. More detailed information on the derivation of the appropriate Damköhler numbers can be found in Section 3.6 (Derivation of Dimensionless Numbers).

### 3.4.1 Dimensional Analysis

The equations of the model can be made dimensionless with use of the following definitions.
\[
\begin{align*}
x^* &= \frac{x}{L} \quad & y^* &= \frac{y}{Dep} \quad & c_g^* &= \frac{c_g}{c_{g, in}} \quad & c_{MVr}^* &= \frac{c_{MVr}}{c_{MVo, in}} \\
c_{MVo}^* &= \frac{c_{MVo}}{c_{MVo, in}} \quad & c_{OH}^* &= \frac{c_{OH}}{c_{OH, in}} \quad & \phi^* &= \frac{nF}{RT} \phi \quad & \tau &= \frac{v}{L} t
\end{align*}
\]

where \(x^*\) and \(y^*\) are dimensionless distances, \(c_i^*\) is the dimensionless concentration of species \(i\), \(\phi^*\) is the dimensionless potential either in the solution or solid phase, and \(\tau\) is the dimensionless time, \(L\) is the total channel length of the channel and \(Dep\) is the depth of the channel (dimension in the \(y\)-direction). \(c_{g, in}\), \(c_{MVo, in}\), and \(c_{OH, in}\) are the inlet concentrations of glucose, MVo, and OH\(^-\), respectively.

The first Damköhler number \((Da_1)\) is the ratio of the rate of the homogeneous reaction to the mass transfer rate and is defined as follows:

\[
Da_1 = \frac{K_1(c_{g, in})(c_{OH, in})}{c_{MVo, in} k_m a}
\]  

(3-27)

The second Damköhler number \((Da_{II})\) represents the ratio of the rate of the surface reaction to the mass transfer rate, as was reported previously in the literature \([109, 110]\). Assuming \(c_{MVr, ref} = c_{MVo, ref} = c_{ref}\), the following equation is obtained for \(Da_{II}\).

\[
Da_{II} = \frac{a_i c_{ref}}{nF c_{ref} k_m a}
\]  

(3-28)

The ratio of the homogeneous reaction rate to the surface reaction rate can be obtained by dividing the first Damköhler number by the second to give \(\Gamma\). \(\Gamma\) can be used to evaluate the relative significance of the homogeneous and electrochemical reaction rates.
\[ \Gamma = \frac{D_a_I}{D_a_{II}} = \frac{\text{Homogeneous reaction rate}}{\text{Electrochemical reaction rate}} = \frac{K_1(e \epsilon_{g, \text{in}})(e \epsilon_{OH, \text{in}})}{\frac{c_{MV_o, \text{in}}}{a_{i_0\text{ref}}} \frac{a_{i_0\text{ref}}}{nF c_{\text{ref}}}} \tag{3-29} \]

In deriving \( Da_{II} \) and \( \Gamma \) that involve the rate of electrochemical reaction, the exponential term in Equation (3-42) is assumed to be of order one. The term, itself, is equal to one at an overpotential of \(~30 \text{ mV}\), and its magnitude varies with the applied potential. At high overpotentials, the magnitude of this dimensionless term can be much greater than one. Under these conditions, the relative rate of the electrochemical reaction is underestimated in both \( Da_{II} \) and \( \Gamma \). In contrast, the impact of the overpotential is accurately included later in this study where cell performance is predicted using detailed simulations.

The derived dimensionless numbers, \( Da_I, Da_{II}, \) and \( \Gamma \), are used in the following sections to explore the relative importance of physical processes involved in the cell. The procedure used and the discussion presented can be applied to any mediated cell in which multiple processes interact and have the potential to influence performance.

### 3.4.2 Comparison of the Homogeneous Reaction Rate to the Surface Reaction Rate

The process that generates the current in a viologen-mediated cell is the electrochemical oxidation of MVr. This reaction consumes the MVr that is formed by the homogeneous reaction of MVo with glucose; hence, the homogeneous reaction provides the feed for the electrochemical reaction. This section examines the coupling between the homogeneous reaction and the reaction on the surface without the impact of mass transfer.

Figure 3-7 shows the impact of glucose concentration and pH on \( \Gamma \). The analysis considers a variation in pH from 12 to 14, which represents a 100-fold change in the \( \text{OH}^- \) concentration. The
glucose concentration is varied from 100mM to 2M. The initial MVo concentration is specified as 1.7M, which is half the solubility limit of MVo in water, to prevent precipitation [24] and to ensure sufficient MVo to react with glucose [17].

![Graph showing Γ vs glucose concentration at various pH values.](image)

Figure 3-7: $\Gamma$, which determined the ratio of the homogeneous reaction rate to the surface reaction rate, versus glucose concentration at various pH values. Inlet conditions are 1.7 M of MVo and the temperature of 50°C.

As shown in the figure, $\Gamma$ varies linearly with glucose concentration at each pH as expected (see equation (3-29)). $\Gamma$ is almost zero at pH 12, independent of the glucose concentration. Such a small $\Gamma$ indicates that the homogeneous reaction does not provide sufficient reactant for the surface reaction, precluding a high current density. Although raising the pH to 13 increases $\Gamma$ to some extent, it remains small, reaching a maximum value < 0.2 at a glucose concentration of 2 M. In contrast, the value of $\Gamma$ increases significantly to near unity at a pH of 14 for most of the glucose concentration range, indicating that the homogeneous reaction is no longer the dominant resistance.
Thus, strong alkaline electrolytes can be used to speed up the homogeneous reaction rate so that it is no longer the dominant factor that limits performance. However, mediator decomposition can be a problem when utilizing strong alkaline conditions in a mediated cell. For example, the decomposition of MV can change its structure and reduce its reactivity toward carbohydrates [59, 111]. One possible way to overcome this problem is by using other viologens that are more stable under alkaline conditions, as discussed later in this study.

Glucose oxidation efficiency, which determines the number of electrons released per mole of glucose, was not considered in the above dimensional analysis. The efficiency is needed to properly quantify the moles of MVr that form per mole of glucose as a result of the homogeneous reaction. The initial MVo/glucose ratio (β) was reported to strongly affect the efficiency. At ratios as high as 10, the efficiency was 22%; nonetheless, it dropped significantly for ratios as low as 1.0 [17]. Therefore, it is important to include the effect of efficiency in the dimensionless numbers that involve the homogeneous reaction rate. This effect is considered by multiplying the rate of the homogeneous reaction by the oxidation efficiency. Therefore, \( I' \) is defined as

\[
I' = \alpha I \\
(3-30)
\]

Figure 3-8 shows the impact of glucose concentration on \( I \) and \( I' \) at pH 14. \( I' \), which includes the impact of oxidation efficiency, initially increases sharply with the concentration, and then remains almost unchanged. In contrast, \( I \), which was taken from Figure 3-7 and does not include the impact of the efficiency, varies linearly. The largest deviation between the two cases is observed at low concentrations and reflects the variation of \( \beta \) with glucose concentration. \( \beta \) is very large at low concentrations, leading to a high oxidation efficiency (\( \beta \) is 17 at 0.1 M of
glucose). In fact, the glucose oxidation efficiency approaches 22% at large values of $\beta$, and almost 6 moles of MVr are formed per mole of glucose. However, $\beta$ decreases as the glucose concentration is increased while the mediator concentration is kept constant ($\beta$ becomes 1.0 at 1.7 M of glucose). At a $\beta$ value of unity, the glucose oxidation efficiency is only 4%. This significant decline in efficiency adversely impacts the conversion process, offsetting the positive impact of glucose concentration on the homogeneous reaction rate.

Figure 3-8: $\Gamma$ and $\Gamma'$ at pH14 versus the glucose concentration. The blue line represents $\Gamma$ and the red curve represents $\Gamma'$. Inlet conditions are 1.7 M of MVo and the temperature of 50°C.

Figure 3-8 indicates that $\Gamma'$ for the MV-mediated cell approaches a maximum and does not exceed 2 for the feasible range of concentrations considered. Thus, the dimensional analysis shows that the rates of the homogeneous reaction and the surface reaction both remain important, even at high concentrations of glucose and OH-. Furthermore, the impact of glucose concentration is much less significant at concentrations above 1M because of the counteracting influences of rate and oxidation efficiency.
3.4.3 Impact of Mass Transfer

In the previous section, the relative significance of the homogeneous and surface reactions was evaluated. In doing so, the impact of mass transfer was not considered. We now evaluate the effect of mass transfer in order to understand its significance relative to the rates of the homogeneous reaction and the electrochemical reaction. This is done by examining the value of the first and second Damköhler numbers ($Da_I$ & $Da_{II}$)

![Figure 3-9: a) First Damköhler number and b) second Damköhler number versus the electrolyte flow rate. The primary and secondary horizontal axes are the flow rate and $k_m a \times 10$. Inlet conditions are pH 14, 1 M glucose concentration, 1.7 M of MVo, and temperature of 50°C.](image-url)
Figure 3-9a demonstrates the impact of the flow rate on $Da_I$. The flow rate affects $Da_I$ through its impact on the mass transfer coefficient. An empirical model for the mass transfer coefficient was developed in this study and is presented in Appendix B. In Figure 3-9a, the primary and secondary horizontal axes are the flow rate and $k_m a \times 10$. A change in the flow rate from 1 to 28 ml/min increases $k_m a$ from 0.007 to 0.11 s$^{-1}$. As a result, $Da_I$ changes from about 8.2 at a flow rate of 1 ml/min, where mass transfer is more limiting than the homogeneous reaction rate, to a value of less than one at the higher flow rates. The same trend is observed for $Da_{II}$, as shown in Figure 3-9b. $Da_{II}$ is approximately 5.3 at a flow rate of 1 ml/min, consistent with mass transfer that is slow relative to the surface reaction rate, and decreases with increasing flow to a value less than one.

Dimensional analysis was used to explore a possible explanation for the low current densities reported for MV-mediated cells in the literature [21, 60, 101]. In the study of Yang et al. [101], for instance, a maximum current density of 5 mA/cm$^2$ was reported at the optimum operating concentrations of 1.5 M glucose, 3M OH$,^-$, and 0.1M MVo. At the optimum operating conditions, the rate of homogeneous reaction and $T''$ were estimated to be 0.0267 mol/(lit.s) and 7.8, respectively. Accordingly, a current density of 56 mA/cm$^2$ was estimated for the porous electrode used in their study, which had a thickness of 0.17cm. This estimated current density is almost an order of magnitude higher than the reported value from the study. It is likely that mass transfer had a significant impact on the performance; however, no information was provided for the flow rate or the mass transfer coefficient, which precluded further evaluation. As an aside, the OH$^-$ concentration of 3M would lead to significant MV decomposition, which may also have impacted performance.
The dimensional analysis presented in this section provided insight into the relative importance of coupled processes in mediated glucose oxidation, and has led to a set of conditions expected to enhance performance. However, it does not provide a complete view of the concentration profiles, local reaction rates, and operational trade-offs needed to optimize the reactor. The detailed model that was developed and validated as part of this study is now used to address these issues, as documented in the following sections.

3.4.4 Rate Comparisons Based on Detailed Simulation

The dimensional analysis in the previous section was used to provide an estimate of the relative significance of rate processes in the cell without the need for detailed calculations. Such estimates are, of course, approximate. In addition, the magnitude of the applied potential was not included in the dimensional analysis and represents a factor that will undoubtedly influence the relative importance of the electrochemical reaction. In this section, we use detailed simulations to evaluate the impact of coupled processes in greater detail.

We begin the analysis re-examining mass transfer. Figure 3-10 shows the impact of the flow on the mass transfer rate and the mass transfer coefficient. Each rate in this figure represents the average mass transfer rate for the corresponding flow obtained by integrating the MVr concentration over the cell assuming a zero concentration at the electrode surface. As shown in the figure, the trends for $k_m a$ and for the mass transfer rate are different. While $k_m a$ increases steadily with flow, the mass transfer rate increases initially until the flow rate reaches about 10 ml/min, after which the changes are less pronounced.
Figure 3-10 suggests that the increase in $k_m a$ is offset to a large degree by a decrease in the average MVr concentration at higher flow rates. As a result, the mass transfer rate, which is the product of the mass transfer coefficient and the average MVr concentration, eventually becomes nearly independent of the flow rate. To confirm this reasoning, the effect of flow on the concentration is evaluated. Of particular concern is how the conversion changes with flow. This includes glucose conversion due to the homogeneous reaction and MVr conversion via the electrochemical reaction. Note that the homogeneous conversion represents the fraction of the initial glucose that is converted in the reactor and is not the same as the glucose oxidation efficiency. At higher flow rates, both glucose and MVr experience a shorter residence time in the cell, leading to lower homogeneous and electrochemical conversions.

Figure 3-11a shows the impact of flow on the dimensionless glucose concentration for the operating conditions indicated. At each flow rate, the glucose concentration decreases due to the reaction in the cell. An increase in the flow rate reduces the residence time in the cell and,
consequently, the fraction of the entering glucose that is oxidized, consistent with a decline in the fractional conversion of glucose shown in Figure 3-11b. Specifically, an increase in the flow rate from 1 to 15 ml/min decreases the conversion from ~100% to 25%, and results in almost 75% of the glucose exiting unreacted at 15 ml/min. Further increase in the flow continues to decrease the conversion but at a much slower rate.

Figure 3-11: a) Dimensionless glucose concentration versus the dimensionless anode length at flow rates of 1 to 14 ml/min with 1ml/min increment, b) glucose conversion as a function of flow rate. Inlet conditions are 1 M glucose, 1.7 M MVo, pH14, and temperature of 50°C.

The flow rate also affects the electrochemical conversion, which is defined as the ratio of electrochemically oxidized MVr to that formed homogeneously in the reactor. Figure 3-12a shows the variation of the dimensionless MVr concentration for the operating conditions stated. At very slow flow rates, such as 1 ml/min, the concentration reaches a maximum and then decreases. In contrast to glucose, which is only influenced by the homogeneous reaction, the MVr concentration is influenced by both the homogeneous and the surface reactions. At 1ml/min, the formation rate of MVr is initially faster than its consumption rate at the surface; as a result, the MVr concentration increases. The consumption rate eventually exceeds the formation rate, leading to a decreasing
trend. The MVr formation rate remains faster than the consumption rate at fast flow rates, yielding a rising trend for the MVr concentration. Figure B-2 shows the ratio of the MVr formation rate to the consumption rate at various flow rates, confirming the observation from Figure 3-12a.

Figure 3-12: a) Dimensionless MVr concentration versus the dimensionless anode length at flow rates of 1 to 14 ml/min with 1 ml/min increment, b) MVr electrochemical conversion versus the flow rate. Inlet conditions are 1 M glucose, 1.7 M MVo, pH14, and temperature of 50°C.

Figure 3-12b shows the impact of flow on the electrochemical conversion. The conversion reaches ~ 50% at 1 ml/min, meaning that half of the formed MVr leaves the cell unreacted. An increase in the flow rate to 15 ml/min reduces the conversion to ~ 30%. Thus, the flow rate has a dramatic impact on the electrochemical conversion.

The simulations show that increasing the flow rate adversely impacts the fractional conversion of both the homogeneous and electrochemical reactions. As a result, the increase in $k_m a$ is counteracted to a large degree by a decrease in the average MVr concentration at higher flow rates, resulting in a mass transfer rate that eventually becomes nearly independent of flow (as shown in Figure 3-10). Despite the negative impact of flow on conversion, the absolute amount
of glucose converted in the reactor, for example, increases with flow due to the higher average concentration.

Figure 3-13: a) Homogeneous reaction rate (averaged over the entire cell) versus the flow rate, b) the ratio of the homogeneous reaction rate to the mass transfer rate at various electrode potentials. Inlet conditions are 1M glucose, 1.7M MVo, pH14, and temperature of 50 °C. The potentials are versus Hg/HgO RE.

Figure 3-13a shows the impact of flow on the homogeneous reaction rate. The rates in this figure are average values obtained by integrating over the entire cell. The rate increases from 10 to 50 mol/m³s as the flow rate is increased from 1 to 15 ml/min, after which the changes to the rate
are much more gradual. The effect of flow on the homogeneous reaction rate reflects the
dependence of the rate on the glucose concentration, which increases with increasing flow (see
Figure 3-11).

The ratio of the homogeneous reaction rate to the mass transfer rate is shown in
Figure 3-13b. This ratio is similar to $Da_t$ except that the actual integrated rates simulated for the
reactor are compared. The ratio in Figure 3-13b is shown versus the flow rate at various anode
potentials to illustrate explicitly the impact of potential, which changes the surface concentration
and, subsequently, the mass transfer rate. The ratio of the homogeneous reaction rate to the mass
transfer rate varies from 2 to ~ 4, depending on the electrode potential, but is always greater than
one. While both rates are of the same order of magnitude and hence both contribute to reactor
performance, consistent with the dimensional analysis presented earlier, the increasing trend
presented in Figure 3-13b is different than the decreasing trend shown previously in Figure 3-9 for
the same ratio of rates based on $Da_t$. This is because the detailed simulations include
concentration variations through the electrode that influence both the individual rates and coupling
between the rates. Two important conclusions can be drawn from these results. First, the
dimensional analysis, as expected, only provides an approximate assessment of the relative
significance of important physical processes, especially when multiple processes are important and
complex coupling exists. In cases where a single process clearly controls behavior, this simple
analysis is likely all that is needed. However, where multiple coupled processes are important,
additional information can be obtained from detailed simulations. Second, the system of interest
is limited more by mass transfer than by the homogeneous reaction rate, even at high flow rates.
This agrees with mass transfer limitations observed experimentally in this study (Figure 3-4 and
3-5).
The important role of mass transfer is illustrated in Figure 3-14, which shows the ratio of the current density to the limiting current density \( \frac{i}{i_{\text{lim}}} \). At a ratio of one, the current is controlled completely by mass transfer. The system operates at the mass transfer limit over the entire range of flows considered for anode potentials greater than \(-0.35\) V. The system also operates at the mass transfer limit at low flow rates for all the potential values considered. However, some deviation from the mass transfer limit is observed at the lower potentials and high flow rates where the ratio drops as low as \(~0.8\). Mass transfer is still important under these conditions, although some potential dependence is also observed.

While the detailed analysis of this section generally agrees with the results of the dimensional analysis, it provides additional insight that helps us to better understand the influence of coupled processes in the cell. For example, the simulations show that the impact of flow on concentrations in the reactor limits the extent to which flow can be used to increase the mass.
transfer rate. It also demonstrates that the electrochemical reaction rate is faster than that of mass transfer under almost all conditions considered, resulting in \( i/i_{\text{lim}} \) values of or close to unity.

3.4.5 Current Density from MV-Mediated Cells

In previous sections, we examined the relative rates of the homogeneous reaction, mass transfer, and the electrochemical reaction for a range of flow rates and potentials, and explored the factors that limit performance. With this background, we now explore the maximum current density that can be obtained from MV-mediated glucose fuel cells. The current density based on the membrane active area is shown in Figure 3-15 as a function of flow and anode potential. The maximum obtainable current density is 187 mA/cm\(^2\), which is not further improved by increasing the flow or the potential. The potential dependency of the current density is consistent with the results of Figure 3-14. At potentials as negative as -0.45 and -0.4 V vs. RE, the ratio of the current to the limiting current (\( i/i_{\text{lim}} \)) drops with increasing flow. Under these conditions, both the surface reaction and the mass transfer contribute to performance. However, at more positive potentials, \( i/i_{\text{lim}} \) remains unity regardless of the flow rate, and the current is controlled solely by mass transfer. Note also that the maximum current density in Figure 3-15 does not continue to increase with flow, consistent with the mass transfer results shown previously in Figure 3-10, which reflects the offsetting effects of flow on the mass transfer coefficient and the concentration.
Figure 3-15: Current density versus the flow rate at various anode potentials. Inlet conditions are 1M glucose, 1.7 M MVo, pH14, and temperature 50 °C. The potentials are versus Hg/HgO RE.

The current density as a function of anode polarization is shown in Figure 3-16. This figure includes overpotentials for the surface reaction, ohmic losses in the electrolyte, and the concentration overpotential. The flat lines in Figure 3-16 at flow rates up to 3 ml/min are consistent with Figure 3-15, indicating that the current density is mass transfer limited over the entire polarization range. The limiting current densities at flow rates of 1, 3, and 5 ml/min are 62, 130, and 158 mA/cm², respectively. As the flow rate is increased, the current density approaches a maximum of 187 mA/cm². The trend for current density remains almost unchanged at flow rates higher than 10 ml/min. Therefore, this flow rate can be considered as the optimum flow rate and corresponds to a superficial fluid velocity of 2.96 cm/s and the Reynolds number of 81.6 (based on the channel hydraulic diameter) or 0.9 (based on the electrode fiber diameter). At high flow rates, a slight dependency on potential is observed; this dependency, however, disappears at polarization values of 300 mV or greater where the rate reaches its maximum value as determined by mass transfer.
3.4.6 Limitations and Practicality of MV-Mediated Cells

In previous sections, the relationship between the mass transfer, homogeneous reaction, and surface reaction was explored. It was found that mass transfer is the major factor that limits performance. In addition, the maximum obtainable current density in an MV-mediated cell was evaluated. The predicted maximum current density is more than an order of magnitude higher than the reported current densities for similar cells in the literature [9, 21, 62, 100, 101], and similar in magnitude to current densities reported for precious-metal-based glucose fuel cells [11]. Despite their advantages, viologen-mediated cells also have a few shortcomings, as discussed here.

One of the main limitations of an MV-mediated cell is MV decomposition (i.e., decomposition of the mediator). The decomposition reaction, which occurs under severe operating conditions, changes the MV structure and reduces its reactivity toward carbohydrates [59, 111]. As was discussed earlier, a high pH value of 14 is needed to obtain reasonably fast homogeneous reaction rates (Figure 3-7). High glucose concentrations are also needed (Figure 3-8), which requires a commensurately high MV concentration. Therefore, the MVo concentration was chosen.

Figure 3-16: Current density versus the anode polarization at various flow rates. Inlet conditions are: 1M glucose, 1.7 M MVo, pH 14, and temperature of 50 °C.
to be 1.7 M, which is half the solubility limit of MVo. Under such severe operating conditions, MV likely undergoes significant decomposition. One way to overcome this problem is to use a viologen mediator that is more stable under alkaline conditions. An alternative to MV is mono-methyl viologen (MMV), which was reported to be noticeably more stable [59]. However, stability alone does not ensure that MMV will be a suitable mediator. For example, as discussed in this study, the homogeneous reaction rate impacts cell performance. The homogeneous reaction rate of MMV with glucose was reported to be slower than that of MV [22]. Thus, the possible use of MMV as a mediator requires a more thorough assessment.

Another important limitation is the glucose oxidation efficiency. In viologen-mediated cells, the efficiency was reported to depend upon the initial molar ratio ($\beta$) of the mediator to glucose. In laboratory experiments, the efficiency dropped from a maximum of 22% at ratios as high as 10 to only 4% at a ratio of unity [17] in cells without regeneration. In this work, the concentration of glucose was raised to 1M in order to increase the rate of the homogeneous reaction. The MVo concentration was also increased to a maximum value of half its solubility limit. The ratio, $\beta$, is only 1.7 at these concentrations, which corresponds to an efficiency as low as 7% in the absence of regeneration. Regeneration of the mediator in the electrochemical cell tends to counteract this effect. However, the availability of the regenerated (oxidized) MV is limited by mass transfer. Both an additional understanding of the factors that influence oxidation efficiency and strategies for improving mass transfer are needed to address possible limitations.

Another concern related to viologen-mediated fuel cells is recycling of the mediator. In a practical cell, the mediator should be recycled and reused to reduce costs and avoid environmental concerns since viologens are hazardous. One option is to simply reuse the exit stream containing the mediator and oxidation products without separation or further treatment. Initial indications are
that the products do not adversely affect the oxidation rate. This assessment is supported by the fact that our model, which did not account for the impact of product buildup, successfully predicted experimentally measured results with reasonable accuracy over a wide range of glucose concentrations. This conclusion, however, should not be extended to concentrations and conditions beyond the verified range. It seems inevitable that oxidation products will eventually build up to the point where they have an adverse impact. Consequently, viable options for the recycle stream include intermittent separation after product buildup or continuous separation. One might also consider further oxidation of the reaction products in a suitable downstream reactor or collocation with a chemical plant that has an existing separation process that can handle additional load. This is an area where additional work is clearly needed.

Mass transfer was found to be the principal limiting factor in the cell. Initially, the mass transfer rate was enhanced by the flow rate, but the increase in the mass transfer coefficient with flow was offset by reduced MVr concentrations in the cell at high flow rates. Cell designs that enhance mass transport would be potentially beneficial. Another approach would be to separate the homogeneous reaction from the electrochemical reaction by pre-reacting the glucose and MV in a separate tank reactor prior to reoxidation of the MV in the electrochemical reactor to produce power. This would maximize the MVr concentration in the electrochemical cell and decouple the glucose conversion from the residence time in the electrochemical cell. It would also permit separate optimization of the conditions for the homogeneous reaction, which may even be coupled with a separation strategy. The pre-reacting strategy was previously examined for a different glucose oxidation system in the literature [112].
3.5 Conclusion

The rate performance of viologen-mediated glucose fuel cells was investigated with use of a mathematical model that was validated by experiments. The relative significance of the key physical processes, including the homogeneous reaction, mass transfer, and the electrochemical reaction, was determined by dimensional analysis and by detailed simulation. The dimensional analysis provided important insight without the need for complex simulations. The simulations, in turn, offered insight not available from the simple analysis. Although all processes were important under certain conditions, mass transfer was the principal factor that limited the maximum current density for the system examined. The mass transfer rate initially improved with flow; however, this effect was offset by decreased reactant concentrations in the cell at high flow rates. The maximum obtainable current density was ~200 mA/cm², which corresponded to an anode polarization of 300 mV. This maximum current density is significantly higher than the current densities available from biological fuel cells and comparable to the rates observed for carbohydrate fuel cells that utilize precious-metal electrodes. Therefore, viologen-mediated glucose fuel cells offer the potential of high current densities at a lower cost, making them an attractive option for the development of glucose fuel cells. Finally, the methods presented can be applied to any mediated system to evaluate the relative importance of multiple coupled processes as a basis for process development and optimization.

3.6 Derivation of Dimensionless Numbers

The equations of the model were made dimensionless with the definitions presented in Equation (3-26). Each term in Equation (3-1) is expanded separately and defined in terms of the dimensionless variables.
\[ -\nabla \cdot N_{MVr} = -\nabla \cdot (\varepsilon z_{MVr} u_{MVr} F c_{MVr} \nabla \phi_2 - \varepsilon D_{MVr} \nabla c_{MVr} + \varepsilon c_{MVr} \mathbf{v}) = \varepsilon z_{MVr} u_{MVr} F \nabla \cdot (c_{MVr} \nabla \phi_2) + \varepsilon D_{MVr} \nabla \cdot \nabla c_{MVr} - \varepsilon \nabla \cdot (\varepsilon c_{MVr} \mathbf{v}) \]  

(3-31)

Assuming constant values for \( \varepsilon, u_{MVr}, D_{MVr}, \) and \( \mathbf{v} \), Equation (3-31) becomes:

\[ -\nabla \cdot N_{MVr} = \varepsilon z_{MVr} u_{MVr} F \left( \frac{\partial c_{MVr}}{\partial x} \frac{\partial \phi_2}{\partial x} + \frac{\partial c_{MVr}}{\partial y} \frac{\partial \phi_2}{\partial y} + c_{MVr} \left( \frac{\partial^2 \phi_2}{\partial x^2} + \frac{\partial^2 \phi_2}{\partial y^2} \right) \right) + \varepsilon D_{MVr} \left( \frac{\partial^2 c_{MVr}}{\partial x^2} + \frac{\partial^2 c_{MVr}}{\partial y^2} \right) - \varepsilon \mathbf{v} \left( \frac{\partial c_{MVr}}{\partial x} + \frac{\partial c_{MVr}}{\partial y} \right) \]  

(3-32)

Now, the substitution of the dimensionless variables and also the Nernst-Einstein relationship results in

\[ -\nabla \cdot N_{MVr} = \varepsilon c_{MVo, in} \left[ z_{MVr} D_{MVr} \left( \frac{1}{L^2} \frac{\partial c_{MVr}^*}{\partial x^*} \frac{\partial \phi_2^*}{\partial x^*} + \frac{1}{Dep^2} \frac{\partial c_{MVr}^*}{\partial y^*} \frac{\partial \phi_2^*}{\partial y^*} \right) + \frac{c_{MVr}^*}{L} \left( \frac{\partial^2 \phi_2^*}{\partial x^*} + \frac{\partial^2 \phi_2^*}{\partial y^*} \right) + D_{MVr} \left( \frac{\partial^2 c_{MVr}^*}{\partial x^*} + \frac{\partial^2 c_{MVr}^*}{\partial y^*} \right) \right] \]  

(3-33)

Expanding \( \mathcal{R}_{1\text{MVr}} \) in Equation (3-1) leads to:

\[ \mathcal{R}_{1\text{MVr}} = \left( \frac{a}{F} \right)^j \left( \frac{a}{F} \right)^i \frac{a}{F} \left[ \exp \left( \frac{\alpha_a F}{RT} \eta_s \right) - \exp \left( -\alpha_c F \frac{RT}{RT} \eta_s \right) \right] = \frac{ai_{0, ref} c_{MVr, sur} \left( \frac{c_{MVr, sur}}{c_{MVr, ref}} \right)^0.5 \exp \left( \frac{\alpha_a F}{RT} \eta_s \right)}{F} \left( \frac{c_{MVr, ref}}{c_{MVr, sur}} \right) \left( \frac{c_{MVr, sur}}{c_{MVr, ref}} \right) \left[ \exp \left( \frac{\alpha_a F}{RT} \eta_s \right) - \exp \left( -\alpha_c F \frac{RT}{RT} \eta_s \right) \right] \]  

(3-34)

Assuming \( c_{MVr, ref} = c_{MVo, ref} = c_{ref} \) and substitution of the dimensionless variables results in

\[ \mathcal{R}_{1\text{MVr}} = \frac{ai_{0, ref} c_{MVo, in} \left( c_{MVr, sur} \right)^0.5}{F c_{ref} \left( c_{MVr, sur} \right)^0.5 \left( 1 - c_{MVr, sur} \right)^0.5 \left[ \exp \left( \alpha_a (\phi_1 - \phi_2) \right) \right)} \]  

(3-35)

If we assume that \( c_{MVo} \gg K_2 \), which is a reasonable assumption considering the small value for \( K_2 \), the expanded form of \( \mathcal{R}_{2\text{MVr}} \) becomes
\[
\mathcal{R}_{2 MV} = \frac{K_1(\varepsilon c_g)(\varepsilon c_{OH})(\varepsilon c_{MVo})}{K_2 + (\varepsilon c_{MVo})} = \frac{K_1(\varepsilon c_g)(\varepsilon c_{OH})(\varepsilon c_{MVo})}{(\varepsilon c_{MVo})} = K_1(\varepsilon c_g)(\varepsilon c_{OH})
\]

(3-36)

The substitution of Equations (3-33), (3-35), and (3-36) into Equation (3-1) and also using the dimensionless variables gives:

\[
\frac{\varepsilon c_{MVo,in}\partial c_{MV}^*}{L \partial \tau} = \varepsilon c_{MVo,in} \left[ z_{MVr} D_{MV} \left( \frac{\partial c_{MV}^*}{L \partial x^*} \frac{\partial \phi^*_2}{L \partial y^*} + \frac{\partial c_{MV}^*}{Dep \partial y^*} \frac{\partial \phi^*_2}{Dep \partial y^*} \right) + c_{MV}^* \left( \frac{\partial^2 \phi^*_2}{L^2 \partial x^* \partial y^*} + \frac{\partial^2 \phi^*_2}{Dep^2 \partial y^* \partial y^*} \right) \right] + D_{MV} \left( \frac{\partial^2 c_{MV}^*}{L^2 \partial x^* \partial y^*} + \frac{\partial^2 c_{MV}^*}{Dep^2 \partial y^* \partial y^*} \right)
\]

\[
- \left( \frac{\partial c_{MV}^*}{\partial x^*} + \frac{L}{Dep \partial y^*} \right) - \frac{a i_{\theta ref} c_{MVo,in}}{F c_{ref}} \left( c_{MVr,sur}^* \right)^{0.5} \left( 1 - c_{MVr,sur}^* \right)^{0.5} \left[ \exp(a c(\phi^*_1 - \phi^*_2)) \right] + K_1 e^2 (c_g, in c_g^*) (c_{OH, in} c_{OH}^*)
\]

Rearranging Equation (3-37) leads to:

\[
\frac{\partial c_{MV}^*}{\partial \tau} = \frac{z_{MVr} D_{MV} \left( \frac{\partial c_{MV}^*}{\partial x^*} \frac{\partial \phi^*_2}{\partial y^*} + \frac{L}{Dep} \frac{\partial c_{MV}^*}{\partial y^*} \frac{\partial \phi^*_2}{\partial y^*} \right)}{L v} + c_{MV}^* \left( \frac{\partial^2 \phi^*_2}{L^2 \partial x^* \partial y^*} + \frac{D_{MV} \frac{\partial^2 c_{MV}^*}{\partial x^* \partial y^*} + (L^2 \partial y^*)}{Dep^2 \partial y^* \partial y^*} \right)
\]

\[
- \left( \frac{\partial c_{MV}^*}{\partial x^*} + \frac{L}{Dep \partial y^*} \right) - \frac{a i_{\theta ref} c_{MVo,in}}{F c_{ref}} \left( c_{MVr,sur}^* \right)^{0.5} \left( 1 - c_{MVr,sur}^* \right)^{0.5} \left[ \exp(a c(\phi^*_1 - \phi^*_2)) \right] + K_1 e^2 (c_g, in c_g^*) (c_{OH, in} c_{OH}^*)
\]

The following dimensionless numbers appear in the above equation:

\[
P_e = \frac{v L}{D_{MV}} \quad D N_1 = \frac{L}{Dep} \quad D N_2 = \frac{D_{MV}}{(v)} = \frac{1}{P_e D N_1^2}
\]

(3-39)
where $Pe$ is the Péclet number, $DN_1$ represents the aspect ratio of the channels, $DN_2$ represents the longitudinal to transversal time constant, $DN_3$ represents the advection time constant to the electrochemical-reaction time constant, and $DN_4$ represents the advection time constant to the homogeneous-reaction time constant. Substitution of these dimensionless numbers in Equation (3-38) and some rearrangements gives:

$$
\frac{\partial c_{MVr}^*}{\partial \tau} = \frac{Z_{MVr}}{Pe} \left[ \left( c_{MVr}^* \frac{\partial^2 \phi^*_2}{\partial x^* \partial x^*} + \frac{\partial c_{MVr}^*}{\partial x^*} \frac{\partial \phi^*_2}{\partial x^*} \right) + DN_1 \left( c_{MVr}^* \frac{\partial^2 \phi^*_2}{\partial y^{*2}} + \frac{\partial c_{MVr}^*}{\partial y^*} \frac{\partial \phi^*_2}{\partial y^*} \right) \right]
+ \frac{1}{Pe} \left( \frac{\partial^2 c_{MVr}^*}{\partial x^{*2}} + DN_2 \frac{\partial^2 c_{MVr}^*}{\partial y^{*2}} \right) - \left( \frac{\partial c_{MVr}^*}{\partial x^*} + DN_1 \frac{\partial c_{MVr}^*}{\partial y^*} \right)
- DN_3 \left( c_{MVrsur}^* \right)^{0.5} \left( 1 - c_{MVrsur}^* \right)^{0.5} \left[ \exp \left( \alpha_a \left( \phi^*_1 - \phi^*_2 \right) \right) \right]
- \exp \left( -\alpha_c \left( \phi^*_1 - \phi^*_2 \right) \right) + DN_4 c_g^* c_OH
$$

(3-40)

For the following relationship

$$
\mathcal{R}_{1,MVr} = k_m a (c_{MVr} - c_{MVrsur}),
$$

(3-7)

substitution of Equation (3-35) and the dimensionless variables give

$$
k_m a c_{MVo, in} (c_{MVr}^* - c_{MVrsur}^*) = \left( \frac{a_i \ref c_{MVo, in}}{nF c_{ref}} \right) \left( c_{MVrsur}^* \right)^{0.5} \left( 1 - c_{MVrsur}^* \right)^{0.5} \left[ \exp \left( \alpha_a \left( \phi^*_1 - \phi^*_2 \right) \right) \right] \left[ \exp \left( -\alpha_c \left( \phi^*_1 - \phi^*_2 \right) \right) \right]
$$

(3-41)

Then,
\[
\left(c_{MVR} - c_{MVR_{\text{sur}}}\right) = \left(\frac{a_{l_0 \text{ref}}}{nF c_{\text{ref}}}\right) \left(c_{MVR_{\text{sur}}}\right)^{0.5} \left(1 - c_{MVR_{\text{sur}}}\right)^{0.5} \left[\exp\left(a_{\alpha} (\phi^*_1 - \phi^*_2)\right) + \exp\left(-a_{\alpha} (\phi^*_1 - \phi^*_2)\right)\right]
\]

From the above equation, the second Damköhler number \((Da_{\text{II}})\), which represents the ratio of the rate of the surface reaction to the mass transfer rate, is obtained.

\[
Da_{\text{II}} = \frac{a_{l_0 \text{ref}}}{nF c_{\text{ref}}} \frac{k_m a}{a_{\alpha}}
\]  

(3-28)

The first Damköhler number \((Da_1)\), which represents the ratio of the rate of the homogeneous reaction to the mass transfer rate, is obtained by

\[
Da_1 = \frac{DN_4 \times Da_{\text{II}}}{DN_3} = \frac{K_1 (e_{c_{B,\text{in}}}) (e_{c_{D,\text{H,in}}})}{c_{MVO,\text{in}}} \frac{k_m a}{a_{l_0 \text{ref}}}
\]

(3-27)

The ratio of the first to the second Damköhler number defines the ratio of the homogeneous reaction rate to the surface reaction rate and has the following form.

\[
\Gamma = \frac{Da_1}{Da_{\text{II}}} = \frac{K_1 (e_{c_{B,\text{in}}}) (e_{c_{D,\text{H,in}}})}{c_{MVO,\text{in}}} \frac{k_m a}{a_{l_0 \text{ref}}} \frac{nF c_{\text{ref}}}{a_{l_0 \text{ref}}}
\]

(3-29)

### 3.7 Nomenclature

Table 3-2 summarizes all the symbols used in the model.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Subscript/Superscript</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c)</td>
<td>Concentration</td>
<td></td>
</tr>
<tr>
<td>(T)</td>
<td>Operating temperature</td>
<td></td>
</tr>
<tr>
<td>(D)</td>
<td>Diffusivity</td>
<td></td>
</tr>
<tr>
<td>(N)</td>
<td>Flux of the species</td>
<td></td>
</tr>
<tr>
<td>(\mathcal{R}_1)</td>
<td>Volumetric source term due to the electrochemical reaction</td>
<td></td>
</tr>
<tr>
<td>(\mathcal{R}_2, \mathcal{R}_T)</td>
<td>Source terms due to the homogeneous reaction in the cell or mixing tank</td>
<td></td>
</tr>
<tr>
<td>(K_1)</td>
<td>Rate constant for the homogeneous reaction</td>
<td></td>
</tr>
<tr>
<td>(K_2)</td>
<td>Rate constant for the homogeneous reaction</td>
<td></td>
</tr>
<tr>
<td>(\beta)</td>
<td>Initial molar ratio of MVo to glucose</td>
<td></td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Conductivity of the solid phase</td>
<td></td>
</tr>
<tr>
<td>(\kappa)</td>
<td>Conductivity of the electrolyte phase</td>
<td></td>
</tr>
<tr>
<td>(\phi)</td>
<td>Electronic or ionic potential</td>
<td></td>
</tr>
<tr>
<td>(i_0)</td>
<td>Exchange current density</td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>Current density</td>
<td></td>
</tr>
<tr>
<td>(j)</td>
<td>The electrochemical reaction rate</td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>Specific area of the porous electrode</td>
<td>anodic, cathodic</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>Transfer coefficient</td>
<td></td>
</tr>
<tr>
<td>(\eta)</td>
<td>Overpotential</td>
<td>ref</td>
</tr>
<tr>
<td>(F)</td>
<td>Faraday’s constant</td>
<td>sur</td>
</tr>
<tr>
<td>(R)</td>
<td>Universal gas constant</td>
<td>1</td>
</tr>
<tr>
<td>(n)</td>
<td>Number of electrons transferred</td>
<td>2</td>
</tr>
<tr>
<td>(k_m)</td>
<td>Mass transfer coefficient</td>
<td>g</td>
</tr>
<tr>
<td>(U)</td>
<td>Redox potential</td>
<td>(\text{MVr})</td>
</tr>
<tr>
<td>(U_o)</td>
<td>Standard redox potential</td>
<td>(\text{MVo})</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Porosity of the electrode</td>
<td>intrinsic</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Density of the electrolyte</td>
<td>in</td>
</tr>
<tr>
<td>(\mu)</td>
<td>Mobility of the ionic species</td>
<td>*</td>
</tr>
<tr>
<td>(\nu)</td>
<td>Viscosity of the electrolyte</td>
<td></td>
</tr>
<tr>
<td>(z)</td>
<td>Charge of the ionic species</td>
<td></td>
</tr>
<tr>
<td>(v)</td>
<td>Superficial velocity of the electrolyte</td>
<td></td>
</tr>
<tr>
<td>(t)</td>
<td>time</td>
<td></td>
</tr>
<tr>
<td>(\tau)</td>
<td>Dimensionless time</td>
<td></td>
</tr>
<tr>
<td>(Da_1)</td>
<td>First Damköhler number, the ratio of homogeneous reaction to mass transfer</td>
<td></td>
</tr>
<tr>
<td>(Da_{II})</td>
<td>Second Damköhler number, the ratio of the surface reaction to mass transfer rate</td>
<td></td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>Ratio of the first to second Damköhler number</td>
<td></td>
</tr>
</tbody>
</table>

**Subscripts/Superscripts**

- \(\text{MVr}\): Reduced form of methyl viologen
- \(\text{MVo}\): Oxidized form of methyl viologen
- \(\text{anodic}\), \(\text{cathodic}\)
- \(\text{ref}\), \(\text{sur}\), \(\text{in}\)
- \(\text{g}\): glucose
- \(\text{OH}\): Hydroxide ions
- \(\text{intrinsic}\)
- \(\text{at the inlet of the cell}\)
- \(\text{dimensionless quantity}\)
4 ASSYMETRIC VIOLOGEN-BASED REDOX FLOW BATTERY

4.1 Introduction

The ever-increasing energy demands of the world, along with concerns related to fossil fuel availability and environmental issues, have driven a transition to alternative sources of energy such as solar, wind, and hydroelectric power. Due to the intermittent nature of these sources, redox flow batteries (RFBs) have been recognized as an energy-storage technology with the potential to enable effective use of renewable energy. Compared to stationary, rechargeable batteries, such as Li-ion batteries, RFBs have several advantages that include the decoupling of energy storage and power output, design flexibility, scalability and modularity, and high energy efficiency [113-115].

In RFBs, energy is converted from electrical to chemical form and vice versa with the use of two electroactive compounds in liquid form. These liquid electrolytes are referred to as the anolyte or catholyte, depending on whether the electroactive compound they contain tends to be oxidized or reduced during discharge. The electrolytes are stored in separate tanks and pumped through the cell where energy conversion takes place at the electrodes [37]. Figure 4-1 shows a schematic diagram of an RFB. To improve the performance of RFBs, various redox couples have been proposed. In this study, we suggest a viologen-based anolyte, where the electroactive component can be formed via a simple synthesis procedure. This anolyte offers appealing characteristics for aqueous-flow-battery applications.
RFBs can be categorized into two major groups: non-aqueous and aqueous. Non-aqueous redox flow batteries (NARFBs) offer cell voltages higher than 4.0 V due to the electrochemical stability of the non-aqueous solvent [116]. Nevertheless, NARFBs suffer from serious drawbacks such as low solubility and slow kinetics of the active redox couples, and low conductivity of the organic electrolyte. Thus, NARFBs typically offer low energy and power densities [117-119]. NARFBs also suffer from a low cycling performance since they lack membranes with suitable selectivity and electrolyte compatibility. Specifically, polymeric membranes, common for aqueous electrolytes, undergo serious swelling in organic solvents, enlarging the pore size and reducing the selectivity [40, 120-125]. Additionally, the flammability of organic solvents raises serious safety concerns [126, 127]. Finally, a key obstacle for large-scale development of NARFBs is that they are expensive due to the high cost of the organic solvents and salts, as well as increased pumping costs associated with high viscosity solvents [128, 129].
Aqueous redox flow batteries (ARFBs) have several appealing characteristics that include high conductivity, relatively low cost of aqueous electrolytes, and increased safety. Therefore, ARFBs are viewed as an attractive option for large-scale energy storage applications [41-43]. However, the electrochemical stability window of water (1.23 V) limits the cell potential of ARFBs. This potential window can be widened to 2.5 V by taking advantage of the sluggish kinetics of HER (hydrogen evolution reaction) and OER (oxygen evolution reaction) on carbon electrodes [130-132].

Aqueous flow batteries with various redox couples have been developed to date. Vanadium-based batteries have been studied extensively. However, the cost of these batteries is almost three times the DOE target cost of 150 $/kWh. While zinc-based batteries are also attractive due to their energy density (>50 Wh/L), their operation requires expensive electrodes, membranes, and fluid-handling equipment due to corrosion issues. The metal deposition in these batteries precludes complete separation of energy from power, limiting design flexibility. Moreover, dendrite growth may occur, causing major safety hazards [133-135].

Table 4-1: Bulk prices of a few electroactive species in $/kAh (adapted from [134])

<table>
<thead>
<tr>
<th>Species</th>
<th>Methyl viologen (MV)</th>
<th>Quinone</th>
<th>Anthraquinone</th>
<th>Vanadium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price</td>
<td>9</td>
<td>25-50</td>
<td>18.4</td>
<td>68-81</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>TEMPO</th>
<th>TEMPOL</th>
<th>Ferrocene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price</td>
<td>29-41</td>
<td>45</td>
<td>7</td>
</tr>
</tbody>
</table>
Organic redox couples for use in flow batteries have received increased attention. The majority of these couples are synthesized from abundant species in nature, making them relatively inexpensive. Table 4-1 compares the price of a few species; viologens, for instance, are almost an order of magnitude less expensive than vanadium. Additionally, organic materials offer the potential of tuning properties such as redox potential, solubility, stability, and kinetics [136-139].

Quinone and its derivatives represent a group of organic compounds that have been extensively studied in the past few years. The first quinone-based flow battery was demonstrated by utilizing 1,2-dihydrobenzoquinone-3,5-disulfonic acid (BQDS) or 1,4-dihydrobenzoquinone-2-sulfonic acid (BQS) paired with a lead sulfate catholyte [140]. Since then, a series of quinone-based compounds have been proposed in the literature. For example, Aziz et al. [136, 141, 142] paired 9,10-anthraquinone-2,7-disulphonic acid (AQDS) as the anolyte with bromine. However, the use of bromine in these cells raises safety concerns due to its toxicity and tendency to promote corrosion. The bromine crossover to the anolyte side also degraded quinone species, leading to a high capacity fade rate [134].

In 2014, Yang et al. [143] reported the first total quinone-based ARFB with an acidic electrolyte. However, most of the compounds examined showed low solubility (less than 1M), as the solubility of quinone species depends strongly on the pH [144, 145]. In strong alkaline electrolytes, the OH groups of quinones become deprotonated, leading to a higher solubility [146]. Nonetheless, strong alkaline electrolytes may cause serious corrosion problems [147, 148]. Additionally, under alkaline conditions, quinones undergo a degradation reaction that adversely impacts the cycling performance, especially at elevated concentrations. As a result, a temporal capacity fade as large as 5 to 8% per day was reported [149-152]. Recently, Aziz et al. designed a new compound called 2,6-DPPEAQ to improve the cyclability. At moderately alkaline
conditions, the cell showed a capacity fade rate of only 0.014% per day [153], the lowest ever reported for any flow battery; nevertheless, the solubility and redox potential still need improvement. 2,6-DPPEAQ showed solubility of only 0.75 M and a redox potential of -0.49 V vs. SHE, which is higher than desired for aqueous flow batteries.

Viologens are organic species of interest for use in flow batteries owing to their high solubility, fast kinetics, low price (see Table 4-1), and synthetic tunability. Unlike quinones, viologens offer high solubility even in neutral electrolytes, making them a desirable option for neutral pH flow batteries [135]. In 2015, Schubers et al. [154] first reported an ARFB with a viologen-based polymer. The same group later developed an ARFB in which dimethyl viologen (MV) was paired with a catholyte called TEMPTMA [155]. Since then, MV has been utilized as an anolyte in a few studies. Liu et al. coupled MV with either TEMPOL [24] or one of two ferrocene-based catholytes called FcNCl and FcN2Br2 [44, 156]. Recently, Aziz et al. [157] and Liu et al. [158] independently synthesized a similar MV derivative, called BTMAP-Vi or ((NPr)2V), respectively. In spite of its improved cyclability, the compound was less efficient than MV in two ways. Its solubility dropped to 2M (instead of 3.4M for MV) and its redox potential was even higher than that of MV. Both properties adversely impact the energy density, an important characteristic of flow batteries.

Therefore, despite their appealing characteristics, viologens have been explored in only a handful of studies, the majority of which have utilized MV. Although MV was modified to some extent in a few of the studies, the main focus was on improving the cycling performance. The redox potential of MV and its derivatives was higher than -0.5 V vs. SHE. These potentials are almost 0.6 V more positive than the potential at which HER commences on carbon electrodes under neutral conditions [24]. Thus, there is an opportunity to tailor viologens so that they offer
more negative redox potentials to provide a higher flow battery cell potential. In this study, we synthesized and investigated a viologen-based anolyte called MMV (1-Methyl-4,4′-bipyridylium iodide). MMV was demonstrated to have a high solubility, high diffusivity, and fast electrochemical kinetics. More importantly, MMV presented a redox potential that was 0.36 V lower than that of MV. All of these properties are attractive for the anolyte of aqueous-flow-batteries. Finally, the cycling performance of MMV was examined. To do so, MMV was coupled with BTMAP-Fc, a ferrocene-based catholyte that was reported to be very stable under cycling conditions [157].

4.2 Material, Instrumentations, and Methods

Chemicals: 4,4′-bipyridine, acetone, iodomethane were obtained from Sigma-Aldrich and used for the synthesis of 1-Methyl-4,4′-bipyridylium iodide (MMV). Sodium chloride from EMD Millpore Corporation was used in electrolyte preparation. 1,1′-Bis[3-(trimethylammonio)propyl]ferrocene Dichloride (BTMAP-Fc) was purchased from TCIchemicals. Milli Q water with a resistivity of 18.2 MΩ.cm was used to make all of the solutions. An Agilent mass spectrometer (Agilent Technologies, USA) with ESI ionization was used to characterize MMV. An SP-240 (Biologic Science Instruments, France) or a VersaSTAT-3 (Princeton Applied Research) electrochemical workstation was used for the electrochemical measurements. The cycling experiments were conducted using a Maccor 4300-battery cycler (Maccor Inc., USA). Potentials are referenced to an SCE reference electrode (ALS Co. Ltd, Japan). An Oakton pH 700 was used for pH measurements. All the experiments and measurements were conducted in an inert environment (nitrogen) glove box.
Cyclic voltammetry (CV) tests: CV experiments were performed in 2M NaCl supporting electrolyte. Various sweeping rates and concentrations of MMV and BTMAP-Fc were examined as described in the Results and Discussion section (Section 4.3). The working electrode was a glassy-carbon (GC) rod (SPI-Glass 11, SPI SUPPLIES, USA) with a diameter of 5 mm embedded in Teflon. Platinum foil and an SCE reference electrode were used as the counter and reference electrodes, respectively. All the CV results have been IR-corrected.

Electrochemical RDE tests: Linear sweep voltammetry (LSV) experiments were conducted in a three-electrode configuration with the same electrodes described above for the CV tests. The electrolyte consisted of 1mM MMV in 2M NaCl. The working electrode was rotated at different speeds ranging from 500 to 3000 rpm with an increment of 250 rpm controlled by a Pine MSR X rotation controller (Pine research, USA). The potential was ramped from -0.75 V to -1.3 V vs. the reference electrode (RE) at a rate of 20 mV/s. Each LSV scan was repeated at least four times to assure repeatability.

Flow battery tests: A flow battery was assembled with aluminum endplates, copper (from McMASTER-CARR) current collectors, and two graphite plates (FC-GR347B, Graphitestore, USA). Various anion exchange membranes were used. Fumasep-FAA-3-PK-75 and Fumasep-FAA-3-PK-130 were purchased from fuelcellstore.com. An AF1-HNN8-25-X (IONOMER Innovation Inc., Canada) was also used. The membranes are referred to as Fumasep-75, Fumasep-130, and IONOMER, respectively, in this study. The active area of the membrane in the assembled cell was 5 cm². A Teflon gasket (0.002" thick from McMASTER-CARR) was placed between the graphite plates to prevent shorting. The graphite plates were machined in-house. Channels on the graphite plates had a serpentine design and were 3.0 mm wide and 1.0 mm deep. The channels were filled with a graphite felt (AvCarb G100, fuelcellstore.com). A schematic drawing of the
Two Masterflex L/S peristaltic pumps (Cole-Parmer, USA) circulated electrolyte inside the channels at a flow rate of 20 ml/min. The total volume of the negative electrolyte was 10 ml. The volume of the positive side electrolyte was 15ml to ensure that the catholyte did not limit cycling behavior.

EIS tests: EIS tests were conducted to measure the internal resistance of the cell. The resistance was measured at 300 kHz in the same cell used for flow battery tests.

4.3 Results and Discussion

4.3.1 Synthesis of 1-Methyl-4,4'-bipyridylium iodide

Mono-methyl viologen (1-Methyl-4,4'-bipyridylium iodide), abbreviated as MMV, was synthesized as reported elsewhere [59, 159]. Briefly, 4,4' -bipyridine was first dissolved into acetone in a round bottom flask. Next, iodomethane was added to the flask and the solution was stirred continuously under nitrogen at 60°C for 8 hours. The temperature of the mixing tank was controlled with the aid of a circulating water bath (PolyScience, USA). The precipitate was filtered, and then washed with acetone and dried. 1-Methyl-4,4'-bipyridylium iodide salt with a molecular weight of 298.11 was formed as a red-orange powder. As shown in Figure 4-2, the mass/charge spectrum of an MMV sample included only one peak at 171.1, which represents the molecular weight of the compound after ionization (MMV+1). No other peaks were detected, confirming that the product had a high purity.
4.3.2 Solubility

The solubility of MMV was measured in both water and a 2M NaCl electrolyte. In these solutions, MMV showed a solubility of 2.95 M and 2.55 M, respectively, both of which are relatively high, but less than that of MV (3.4 M [44]). The somewhat lower solubility is likely due to the higher molecular weight of MMV (including the counterion) and the fact that MMV forms a monovalent cation as opposed to the divalent cation formed by MV when fully dissociated in an aqueous electrolyte. The impact of charge on viologen solubility has been reported in the literature [160, 161]. Finally, while commercially-available MV includes Cl\(^-\) as its counterion, MMV was synthesized with I\(^-\) in order to simplify the synthesis procedure. The larger counterion has also been reported to negatively impact solubility [8].
Figure 4-3: a) The chemical structure of MMV and its charge transfer during its electrochemical reaction, b) cyclic voltammograms (10th cycle) at various scan rates, c) CV voltammograms recorded for 40 cycles at 10mV/s. Conditions: 1mM MMV in a 2M NaCl electrolyte.

4.3.3 Electrochemical Characteristics

Figure 4-3a shows the chemical structure of MMV and its charge transfer during its electrochemical reaction. The MMV$^{+1}$ cation is reduced by a single electron to form a neutral radical (MMV$^0$). The opposite reaction occurs during the oxidation. Figure 4-3b displays cyclic
voltammograms of MMV at various scan rates. The CV measurements were conducted for 1mM MMV in a 2M NaCl supporting electrolyte. Two peaks appear at each scan rate and the ratio of the maximum oxidation current density \(i_{pa}\) to the maximum reduction current density \(i_{pc}\) is very close to unity \(i_{pa}/i_{pc} = 1.06\). The separation of the peaks is 51mV, very close to the ideal value of 59mV for a reversible reaction [33]. Moreover, the position of the peaks does not change with changing the scan rate. These observations confirm a reversible electrochemical reaction for MMV. CV results at a sweep rate of 10 mV/s were recorded for 40 cycles as shown in Figure 4-2c. No significant changes in the results were observed after the third cycle, implying that MMV is stable in aqueous electrolytes at the concentration used in these experiments.

The equilibrium potential is an essential characteristic of the anolyte, and it is desirable to have a potential as low as possible without disrupting the stability of the solvent. According to Figure 4-3b, the half-wave potential of MMV is \(~ -1.05\) V vs. SCE. This potential provides an estimate of the formal redox potential of MMV, assuming identical diffusivities for both the reduced and oxidized forms. Table 4-2 lists the redox potential and solubility of several quinone- and viologen-based species, including MMV. Only a few quinone-based compounds, such as DHBQ and DMBQ, have redox potentials close to that of MMV, but they require strongly basic electrolytes. \([(NPr)_2V]Br_4\) and \([(Me)(NPr)V]Cl_3\) are viologen-based anolytes that were shown to undergo two successive one-electron-transfer reactions, which have different redox potentials as listed in Table 4-2 as 1st and 2nd [162]. These species can be compared with MMV under two different operating scenarios. In the first scenario, the advantage is taken from the two-electron transfer. Therefore, the average potential of the two successive reactions is appropriate for comparison. Since the first electron transfer does not offer much improvement in terms of redox potential, the average potentials are \(- 0.78\) and \(- 0.83\) V vs. SCE, which are \(0.28\) and \(0.23\) V higher
than the potential of MMV. In the second scenario, only the second electron transfer is utilized because it offers a significantly lower potential. Despite the low potential, the solubility of those compounds is approximately half that of MMV. Consequently, both the redox potential and the solubility of MMV look very promising from a flow battery anolyte perspective, and would lead to an ARFB with increased cell potential and energy density.

Table 4-2: redox potential and solubility of several electroactive species (adapted from [133, 163])

<table>
<thead>
<tr>
<th>Species</th>
<th>Redox potential vs. SCE (V)</th>
<th>Solubility (M)</th>
<th>Electrolyte (pH)</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQDS</td>
<td>-0.02</td>
<td>1.0</td>
<td>(0)</td>
<td>Quinone</td>
</tr>
<tr>
<td>DHAQDS</td>
<td>-0.12</td>
<td>1.0</td>
<td>H₂SO₄(0)</td>
<td>Quinone</td>
</tr>
<tr>
<td>DHAQDMS</td>
<td>-0.22</td>
<td>1.0</td>
<td>H₂SO₄(0)</td>
<td>Quinone</td>
</tr>
<tr>
<td>AQS</td>
<td>-0.09</td>
<td>0.2</td>
<td>H₂SO₄(0)</td>
<td>Quinone</td>
</tr>
<tr>
<td>ARS</td>
<td>-0.16</td>
<td>0.05</td>
<td>H₂SO₄(0)</td>
<td>Quinone</td>
</tr>
<tr>
<td>AQDS</td>
<td>-0.04</td>
<td>(0)</td>
<td></td>
<td>Quinone</td>
</tr>
<tr>
<td>2,6-DBEAQ</td>
<td>-0.78</td>
<td>(12)</td>
<td></td>
<td>Quinone</td>
</tr>
<tr>
<td>2,6-DPPEAQ</td>
<td>-0.71</td>
<td>(9-13)</td>
<td></td>
<td>Quinone</td>
</tr>
<tr>
<td>DHAQ</td>
<td>-0.92</td>
<td>0.6</td>
<td>(14)</td>
<td>Quinone</td>
</tr>
<tr>
<td>DHBQ</td>
<td>-0.96</td>
<td>&gt; 4</td>
<td>KOH (14)</td>
<td>Quinone</td>
</tr>
<tr>
<td>ACA</td>
<td>-0.86</td>
<td>2.0</td>
<td>KOH (14)</td>
<td>Quinone</td>
</tr>
<tr>
<td>DMBQ</td>
<td>-0.99</td>
<td>(14)</td>
<td></td>
<td>Quinone</td>
</tr>
<tr>
<td>DMOBQ</td>
<td>-0.94</td>
<td>(14)</td>
<td></td>
<td>Quinone</td>
</tr>
<tr>
<td>2,3-HCNQ</td>
<td>-0.77</td>
<td>(14)</td>
<td></td>
<td>Quinone</td>
</tr>
<tr>
<td>AQDS</td>
<td>-0.41</td>
<td>0.8</td>
<td>NH₄Br</td>
<td>Quinone</td>
</tr>
<tr>
<td>MV</td>
<td>-0.69</td>
<td>3.4 (water)</td>
<td>(7)</td>
<td>Viologen</td>
</tr>
<tr>
<td>BTMAP-Vi</td>
<td>-0.6</td>
<td>1.9 (water)</td>
<td>(7)</td>
<td>Viologen</td>
</tr>
<tr>
<td>(SPr)₂V</td>
<td>-0.67</td>
<td>2.0 (water)</td>
<td>[164]</td>
<td>NaCl (7)</td>
</tr>
<tr>
<td>[(NPr)₂V]Br₄</td>
<td>-0.59 (1ˢᵗ), -0.96 (2ⁿᵈ)</td>
<td>1.3</td>
<td>NaCl (7)</td>
<td>Viologen</td>
</tr>
<tr>
<td>[(Me)(NPr)V]Cl₃</td>
<td>-0.63 (1ˢᵗ), -1.02 (2ⁿᵈ)</td>
<td>1.4</td>
<td>NaCl (7)</td>
<td>Viologen</td>
</tr>
<tr>
<td>MMV</td>
<td>-1.05</td>
<td>2.55</td>
<td>NaCl (7)</td>
<td>This study</td>
</tr>
</tbody>
</table>

Rotating disk electrode experiments were performed to determine the diffusivity of MMV. The results are shown in Figure 4-4a and correspond to an electrolyte containing 1mM MMV at rotation speeds that varied from 500 to 3000 rpm in 250 rpm increments. The common mass-transfer limited curves were observed at all rotation speeds, and a Levich plot was used to estimate
the diffusion coefficient of MMV (Figure C-1a). A diffusivity of $2.26 \times 10^{-5}$ cm$^2$/s was obtained, which is very similar to the diffusivity reported for MV [24]. The measured diffusivity of MMV is almost an order of magnitude higher than that of other electroactive organic species, such as quinones [143], TEMPO-based [165], and ferrocene-based compounds [44, 166].

![Figure 4-4: a) LSV results of MMV, b) plot of reduction overpotentials versus the logarithm of kinetic current densities, and the relevant Tafel fit. Conditions: 1mM of MMV in a 2M NaCl supporting electrolyte, rotation speeds from 500 to 3000 rpm with an increment of 250 rpm.](image)

The kinetic parameters for the MMV surface reaction were also determined. Figure 4-4b shows a plot of the reduction overpotentials versus the logarithm of the current under kinetically limited conditions. These currents were obtained from the Koutecky-Levich plot (see Figure C-1b). The red line in Figure 4-4b represents a fitted Tafel plot, providing an exchange-current density ($i_0$) of 0.12 mA/cm$^2$. Assuming a first-order dependency of $i_0$ on the concentration, a rate constant of $1.2 \times 10^{-3}$ cm/s was estimated. The MMV rate constant is more than four times higher than that reported for MV ($2.8 \times 10^{-4}$ cm/s) [24], and also noticeably higher than the values reported for common organic redox couples such as TEMPOL [24], quinones [143], and also ferrocene-based compounds [44]. The higher rate constant represents another desirable characteristic for application in a flow battery.
A reduction transfer coefficient of 0.79 was obtained for MMV from the slope of the Tafel plot. In aqueous electrolytes, viologens usually form a charge-transfer complex with their counterions. Dissociation of the complex prior to its electrochemical reaction is the reason for transfer coefficients that differ from the expected value of 0.5 for an elementary, single-electron reaction [8, 105]. The properties of MMV are summarized in Table 4-3. This table also includes the properties of a few other compounds for comparison.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility, M Water</th>
<th>2M NaCl</th>
<th>E₁/₂, vs. SCE V</th>
<th>Diffusivity cm²/s</th>
<th>Rate constant cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMV</td>
<td>2.95</td>
<td>2.55</td>
<td>-1.05</td>
<td>2.3 × 10⁻⁵</td>
<td>1.2 × 10⁻³</td>
</tr>
<tr>
<td>MV [24]</td>
<td>3.4</td>
<td>-</td>
<td>-0.69</td>
<td>0.9 × 10⁻⁵</td>
<td>2.8 × 10⁻⁴</td>
</tr>
<tr>
<td>[(Me)(NPr)V]Cl₃ [162]</td>
<td>1.8</td>
<td>1.4</td>
<td>-0.63 (1ˢᵗ)</td>
<td>5.4 × 10⁶</td>
<td>3.6 × 10⁻¹</td>
</tr>
<tr>
<td>BTMAP-Fe [157]</td>
<td>1.9</td>
<td>-</td>
<td>0.15</td>
<td>3.1 × 10⁶</td>
<td>1.4 × 10⁻²</td>
</tr>
</tbody>
</table>

The results presented above demonstrate that MMV is an anolyte with appealing properties. These properties include a reversible electrochemical reaction on inert electrodes with fast kinetics, a high solubility, and more importantly, a very negative redox potential. Because of these characteristics, MMV has the potential to increase the cell voltage, capacity, and energy density of aqueous redox batteries.

4.3.4 Cycling results

In the previous sections, the electrochemical properties of MMV were evaluated with analytical techniques at very low concentrations. Another essential characteristic of MMV for flow battery application is its cyclability in a battery setup at high concentrations as is presented in this section.
To examine the cyclability of MMV in a flow battery, it should be paired with a catholyte. Numerous catholytes have been developed for aqueous flow batteries. A desirable catholyte needs to present fast kinetics, good stability under cycling conditions, high solubility, and a very positive redox potential but lower than the stability limit of the solvent. FcNCl \[44\], TEMPTMA \[155\], and BTMAP- Fc \[157\] have been reported to be promising catholytes. Table 4-4 summarizes the characteristics of cells containing MMV and each of those catholytes. If MMV is paired with FcNCl with a redox potential of 0.37 V vs. SCE and solubility limit of 4 M \[44\], the estimated OCV, theoretical capacity, and energy density are 1.4 V, 45.5 Ah/L and 64.4 Wh/L, respectively. In the case of TEMPTMA with the redox potential of 0.76 V vs. SCE and the solubility limit of 3.2 M \[155\], the cell can deliver an OCV of 1.81 V with the theoretical capacity and energy density of 41.1 Ah/L and 74.5 Wh/L. The energy density of these two cells is higher than that of vanadium flow batteries (41.8 Wh/L \[167\]). However, these catholytes are not commercially available yet to the best of our knowledge and were developed by research groups.

Table 4-4: Estimated OCV, theoretical capacity and energy density of MMV with various catholytes

<table>
<thead>
<tr>
<th>Cell</th>
<th>Catholyte Solubility in water (M)</th>
<th>Catholyte ( E_{1/2}) vs. SCE (V)</th>
<th>Cell OCV (V)</th>
<th>Cell theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMV- BTMAP-Fc</td>
<td>1.9</td>
<td>0.15</td>
<td>1.2</td>
<td>31</td>
</tr>
<tr>
<td>MMV- FcNCl [44]</td>
<td>4</td>
<td>0.37</td>
<td>1.4</td>
<td>45.5</td>
</tr>
<tr>
<td>MMV- TEMPTMA [155]</td>
<td>3.2</td>
<td>0.76</td>
<td>1.8</td>
<td>41.1</td>
</tr>
</tbody>
</table>

To investigate the cycling performance of MMV, it was paired with BTMAP-Fc. This catholyte was chosen since it is commercially available and shows excellent cycling performance in the literature \[157, 158\]. An MMV/BTMAP-Fc cell can deliver an OCV of 1.2V, given the redox potential of 0.15 V vs. SCE for BTMAP-Fc. The theoretical volumetric capacity and energy density of the cell are 31 Ah/L and 37.1 Wh/L, respectively, taking into account the solubility
limits in water for both the species. This energy density is fairly close to that of vanadium flow batteries (41.8 Wh/L [167]); however, the energy density can be further increased by choosing catholytes with higher solubility and higher redox potentials than those for BTMAP-Fc as discussed above.

The cycling performance of an MMV/BTMAP-Fc cell was initially tested at an MMV concentration of 50mM. This concentration corresponds to a maximum capacity of 1.34 Ah/L if all of the MMV were to react. A 2M NaCl supporting electrolyte was used to increase the electrolyte conductivity, although it could adversely impact the power capability of the cell by eliminating ion migration. An IONOMER anion exchange membrane was incorporated in the cell to block the crossover of redox couple owing to their cationic nature. The cutoff potentials were set to 1.4 V and 0.8V for charging and discharging steps, respectively. Figure 4-5a shows cycling performance at 10 mA/cm². Figure 4-5b and the inset show the polarization of the cell during the first and last cycles, respectively. The anolyte changed the color from light yellow to purple and then to rich crimson during the charge. The reverse occurred during the discharge. The delivered discharge potential of the first and last cycles were 1.17 and 1.16, which are very close to the estimated OCV of the cell (1.2 V).

As shown in Figure 4-5a, the discharge capacity decreases from 0.63 Ah/L to 0.15 Ah/L within 35 cycles, equal to a capacity fade rate of 2.17%/cycle. The initial measured capacity is almost half the theoretical capacity and possible reasons for this deviation are explained later in the study. We first discuss the observed capacity fade. To ensure the observed fade rate was due to the chemistry of the redox couples, the capacity fade of MV that was reported in the literature to be very small [24], was measured in an MV/BTMAP-Fc cell in this study. Consistent with the
literature, a slow capacity loss, 0.25%/cycle, was observed for this cell (Figure C-2). Therefore, the high fade rate observed for the MMV/BTMAP-Fc cell was due to the chemistry of MMV.

Figure 4-5: Cycling results at 10mA/cm², with an anolyte and catholyte containing 50mM of MMV and BTMAP-Fc, respectively, both in a 2M NaCl supporting electrolyte. The IONOMER membrane was placed in the cell. a) The orange and blue plus signs represent the charge and discharge capacities, respectively. The green diamonds, red circles, and blue triangles represent coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE), respectively. b) polarization plot of the first charge/discharge cycle. The inset shows the polarization plot of the last cycle.

There are several possible explanations for the observed high rate of capacity fade. First, capacity fade may be due to the crossover of reactive species through the membrane. Given the
very small permeability reported for BTMAP-Fc \((6.2 \times 10^{-10} \text{ cm}^2/\text{s} \text{[157]})\), the problem is not likely due to BTMAP-Fc crossover. In contrast, MMV forms a monovalent cation \((\text{MMV}^{+1})\) upon dissolution in aqueous electrolytes. \(\text{MMV}^{+1}\) ions are subsequently reduced to form neutral \(\text{MMV}^0\) during charge. Therefore, it is possible that the anion exchange membrane, which is designed to block cations, was not effective in suppressing \(\text{MMV}^0\) crossover.

Figure 4-6: CV voltammograms of cycled electrolytes from a cell that initially contained 50 mM of the redox couples and was cycled 35 times. a) cycled anolyte, b) cycled catholyte. The green boxes show the peaks from the crossed catholyte or anolyte. The CV experiments were recorded at 100mV/s.
Electrolytes were examined after cycling to evaluate the extent of crossover. Figure 4-6 shows CV results for electrolytes from a previously cycled cell. The anolyte and catholyte initially contained 50mM of the respective redox couples. Figure 4-6a shows a CV scan of the cycled anolyte and demonstrates that no significant BTMAP-Fc crossed the membrane to the anolyte. The small peaks for BTMAP-Fc that were placed in a green box in Figure 4-6a, correspond to a current density of 0.16 mA/cm², representing a concentration of 0.33 mM (a linear correlation between CV peak current densities and the concentration is presented later in Figure 4-10). Such a small concentration of BTMAP-Fc in the anolyte degrades the initial cell capacity by only 0.7% (or 0.02% per cycle).

Similarly, Figure 4-6b shows a CV scan of the cycled catholyte. As clearly seen in the figure, there are not any noticeable peaks related to MMV in the catholyte (the green box in Figure 4-6b). Thus, MMV did not cross the membrane to any appreciable extent during the 35 cycles tested (approximately 6 hours). These results do not preclude the possibility of crossover in a practical cell that is designed to be operated for several years, which may contribute to some small degree to the capacity loss.

Given the lack of crossover, other possible mechanisms for capacity fade include the loss of reactive species due to irreversible or only partially reversible side reactions. While this was not observed at the low concentrations at which the CV experiments were performed, such reactions are more likely at higher concentrations. In particular, reduced viologens are radicals and may undergo dimerization [163, 168], the extent of which depends on several factors that include the charge of the reduced viologen [168] and the properties of the solvent [169]. If a radical compound has a lower charge, the extent of dimerization increases due to weaker repulsion forces [163]. Thus, neutral MMV⁰ may undergo significantly more dimerization than other
viologens, such as MV, which remain charged in their reduced form. Additionally, the extent of
dimerization is also higher in aqueous electrolytes. As a result, aqueous electrolytes containing
reduced viologens appear purple due to the presence of crimson dimers and blue radicals [105,
170]. Thus, electrolyte color is qualitatively indicative of the extent of dimerization and may range
from blue (slight dimerization) to crimson (high dimerization). During the charging step of the
MMV/BTMAP-Fc cell, the anolyte initially turned purple and then a rich crimson color. The
crimson color is consistent with the substantial dimerization of MMV$^0$.

Another possible side reaction for MMV is precipitation. MMV precipitation was not
previously observed when utilized as a mediator for carbohydrate-fuel-cell applications [22]
probably due to a low concentration range used ($\leq$ 12 mM). However, precipitation is more likely
at higher concentrations. Reduced viologens and dimers are less soluble than the oxidized
monomers in aqueous electrolytes and may precipitate at high concentrations. The precipitation
issue for MMV is probably more concerning since the reduced form of MMV (MMV$^0$) is neutral.
Additionally, the solubility of viologens are affected by the size of counterions and are less severe
with Cl$^-$ than I$^-$ [105, 171]. Both of these reasons suggest that there is a chance of MMV
precipitation in the cell. Significant precipitation was observed in the cell. After disassembling a
cycled cell, the membrane color changed into crimson as shown in Figure C-3. Noticeable
precipitate was also observed on the porous electrode itself, which probably facilitates the
precipitation process by providing a large surface area.

The observations noted above point to reactions involving MMV$^0$ as the primary cause of
capacity fade. Experiments were performed to determine the extent to which MMV$^{+1}$ may also
contribute. The electrolyte containing MMV$^{+1}$ was circulated in the cell for several hours without
charge or discharge. No signs of color change or precipitation on the porous electrode were
observed. In another experiment, the charge/discharge steps were initiated after circulating the electrolytes for several hours. The observed initial capacity and capacity fade rate were the same as that observed when the cycling was started immediately. These observations confirm that dimerization and precipitation do not occur to any observable extent in the absence of MMV$^0$ and that MMV$^0$ was responsible for the capacity fade.

CV scans of fresh and cycled electrolytes were compared to quantify the variation of the electrolytes upon cycling. A fresh and a cycled catholyte showed almost identical CV results, confirming that BTMAP-Fc remained stable during cycling. However, this observation was not true for a cycled anolyte. Figure 4-6a shows the CV result of a cycled anolyte that initially contained 50mM of MMV. The maximum reduction current density ($i_{pc}$) of the cycled anolyte was 35% of that for the fresh anolyte. Therefore, almost 65% of MMV was lost during cycling. The rest of the capacity loss, which corresponds to a fade rate of 0.26%/cycle, remains unexplained. This portion of the capacity fade is identical to that observed for the MV/BTMAP-Fc cell, suggesting that a similar mechanism may be active in both systems.

Figure 4-5a shows that the coulombic efficiency (CE) stays higher than 92% during cycling except during the first few cycles. A coulombic efficiency lower than 100% suggests that the solvent undergoes side reactions. Typical side reactions in aqueous electrolytes are HER and OER. OER is not probable since the redox potential of BTMAP-Fc is almost 0.9 V lower than the potential at which OER takes place on inert electrodes under neutral conditions. HER, on the other hand, mainly occurs at potentials lower than -1.4 V vs. SCE (Figure C-4); however, this reaction may take place to a limited amount at higher potentials, leading to CE values lower than 100%.

As shown in the inset of Figure 4-5a, CE increases from 88% to 93% during the first few cycles. Most likely, HER occurs to a larger extent during the first few cycles, but diminishes later.
Consistent with this hypothesis, some gas bubbles were observed at the exit of the anolyte side during the first few cycles. The pH of the anolyte also rose from 6.95 for a fresh electrolyte to 10.9 for the cycled one, confirming the HER incidence. However, the increase in the pH lowers the HER redox potential by almost 240 mV, which in turn, reduces the driving force for the HER reaction.

Figure 4-7: Cycling results at 10 mA/cm², with an anolyte and a catholyte containing 50 mM of the redox couple in a 2M NaCl supporting electrolyte and a Fumasep-75 membrane. a) Orange and blue plus signs represent the charge and discharge capacities, respectively. Green diamonds, red circles, and blue triangles represent CE, VE, and EE, respectively. b) polarization plot of the first charge/discharge cycle. The green dashed line represents the charging capacity at the cutoff potential of 1.4 V. The inset is the polarization plot of the last charge/discharge cycle.
Figure 4-5a also shows a high voltage efficiency (VE) that remained higher than 90% during cycling. The high VE is consistent with low potential losses in the cell. The measured internal resistance of the cell with the IONOMER membrane was 1.5 $\Omega$.cm$^2$, resulting in ohmic losses of only 15 mV at 10 mA/cm$^2$. Moreover, since the redox couples have relatively fast kinetics (see Table 4-3), the potentials during charge and discharge were close to the cell OCV as shown in Figure 4-5b.

The cycling performance of MMV was also examined with a different membrane to determine if cycling properties are a function of the membrane used. Figure 4-7a shows the results for a cell that contained a Fumasep-75 membrane.

The initial discharge capacity with the Fumasep-75 membrane was 0.67 Ah/L and decreased at a rate of 2.1%/cycle. Both the initial capacity and the capacity fade rate are similar to those observed for the IONOMER membrane. Therefore, the capacity fade was not influenced by the membrane for the membranes considered in this study. Despite identical initial capacities and capacity fade rates, a few important differences were observed in the performance of cells with the different membranes. The initial CE for the cell with Fumasep-75 was 71%, noticeably lower than that of the IONOMER due to the higher resistance of the Fumasep-75 membrane (7.8 $\Omega$.cm$^2$ versus 1.5 $\Omega$.cm$^2$ for the IONOMER membrane as shown in Figure 4-8). Hence, the anolyte potential during charging shifted to lower values that made the HER side reaction more favorable; consequently, a lower CE was observed. Consistent with this assessment, the pH of the anolyte increased to 11.9, almost one pH unit higher than that of the cycled anolyte in the cell with the IONOMER membrane. Again, OH$^-$ formation during the HER reaction shifts the redox potential of HER to lower values, making HER less favorable. The effect of pH on the hydrogen evolution reaction caused the gradual increase in CE observed for subsequent cycles.
The VE of the cell also depended on the membrane used. While the VE for the cell with IONOMER was over 90%, the cell with Fumasep-75 showed a VE of 66%. The low VE is also a result of the higher resistance of the Fumasep membrane and is consistent with the large gap observed between the potential profiles for charge and discharge shown in Figure 4-7b. Due to the higher resistance, the cutoff potential was adjusted to 1.6 V to improve cell capacity by allowing more complete charging. At an inappropriate cutoff potential, such as 1.4 V as specified by the green dashed line in Figure 4-7b, the measured charge capacity would have been only 0.57 Ah/L, which is 17% lower than the capacity measured at 1.6 V. The potential plots for the first and last cycles presented in Figure 4-7b and the inset confirm the suitability of the chosen cutoff potentials. This observation demonstrates the impact of membrane properties and other cell losses on the choice of cutoff potentials. These potentials must be chosen carefully in order to optimize cell performance.

Figure 4-8: Internal resistance of the cell with various membranes versus the concentration of the redox couple in a 2M NaCl supporting electrolyte. The purple diamonds, blue squares, and red triangles represent the resistance of the cell in which an IONOMER, a Fumasep-75, and a Fumasep-130 were incorporated, respectively. The results are the average of at least three repeats.

As mentioned above, the lower CE and VE values for the cell with Fumasep membrane were related to its higher resistance. To explore this effect further, the internal resistance of the
cell with various membranes was measured. The measurements were performed at different concentrations of the redox couple in a 2M NaCl supporting electrolyte (see Figure 4-8). The purple diamonds, blue squares, and red triangles represent the cell resistances corresponding to the IONIMER, a Fumasep-75, and a Fumasep-130 membrane, respectively. Interestingly, independent of the membrane used, the internal resistances increased with increasing concentration of the electroactive species. This observation is likely due to the presence of I⁻. Iodide, which is the counterion for MMV in this study, is larger than the anion of the supporting electrolyte (Cl⁻) and has a lower permeability through the membrane. As a result, the resistance increased with increasing amounts of MMV due to an increased concentration of I⁻ in the system.

The relative resistances of the individual membranes reflect the membrane thickness, as would be expected. The thicknesses of the membranes used in this study were 25µm (IONOMER), 75±5µm (Fumasep-75) and 120±10µm (Fumasep-130). The resistance of the IONOMER increased by 75% from 1.2 to 2.1 Ω.cm² at an MMV concentration of 100mM. That of the Fumasep-130 changed by 130% from 5.7 to 13.1 Ω.cm² for the same change in concentration. At a concentration of 50 mM, at which cycling performance was evaluated, the resistance of the IONOMER was only 19% and 14% of the resistance corresponding to the Fumasep-75 and Fumasep-130 membranes, respectively.

The cycling performance of MMV was also examined at a higher current density of 30mA/cm², as shown in Figure 4-9. The capacity fade rate at 30mA/cm² differs from that at 10mA/cm² in two aspects. First, a sharper initial decrease was observed at 30 mA/cm², followed by a shift to a more gradual decrease; in contrast, a more gradual change was observed for the entire range of cycles at 10 mA/cm². The fade rate at 30 mA/cm² was initially 3.7%/cycle, but dropped to 0.5%/cycle between Cycles 10 and 15. These two regions are specified with two purple
The change occurred when the cell capacity was \( \sim 0.3 \, \text{Ah/L} \), corresponding to an MMV concentration of 11 mM.

Figure 4-9: Cycling results at 30 mA/cm\(^2\), with an anolyte and a catholyte each containing 50 mM of their respective redox couple in a 2M NaCl supporting electrolyte separated by Fumasep-75 membrane. The orange and blue plus signs represent the charge and discharge capacities, respectively. The green diamonds, red circles, and blue triangles represent CE, VE, and EE, respectively.

Secondly, the initial fade rate of 3.7% at 30 mA/cm\(^2\) is substantially higher than the fade rate at 10 mA/cm\(^2\), suggesting that the capacity fade depends upon the current density. As discussed earlier, the capacity fade is due to irreversible or partially reversible reactions involving the reduced form of MMV. The time required to charge the cell at 30 mA/cm\(^2\) is three times shorter than that at 10 mA/cm\(^2\); yet, it results in a higher capacity fade. Thus, the fade rate does not depend on the charging duration itself. Instead, it depends on the rate at which MMV\(^0\) forms.

In another experiment, a long rest period was set between the charge and subsequent discharge steps during which the reduced MMV was circulated in the cell at zero current. The rest period did not impact the capacity fade rate. This means that the capacity only fades during charging. Since the formation rate of MMV\(^0\) is faster at 30 mA/cm\(^2\), the capacity fades more quickly.
is presumably due, at least to some degree, to a higher local MMV\(^0\) concentration. However, further study will be required to define the details of the capacity fade mechanism.

The initial discharge capacity of the cell was about 0.63-0.68 Ah/L at an MMV concentration of 50mM. The theoretical capacity of such a cell should be 1.34 Ah/L \((0.05 \times 96485/3600)\). Thus, the measured capacity was only 49% of the theoretical value. A capacity lower than the theoretical value is expected due to losses in the cell; however, the losses are relatively small at 10 mA/cm\(^2\). Additionally, the initial capacity at 30 mA/cm\(^2\) was identical to that observed at 10mA/cm\(^2\). Thus, the difference between the measured and theoretical capacities cannot be explained by cell polarization. This conclusion is supported by the observation that the measured capacity with MV rather than MMV was 89% of its theoretical value for the same electrochemical cell. All of these observations suggest that the initial capacity for the MMV/BTMAP-Fc cell is limited by factors other than losses in the cell. To explore possible reasons, the electrochemical behavior of the redox couple was examined by CV at various concentrations.

Figure 4-10: Cyclic voltammetry peak current densities versus concentrations. a) \(i_{pa}\) BTMAP-Fc and b) \(i_{pc}\) for MMV. The electrolytes contained 2M NaCl and the potential was scanned at 100mV/s.
The electrochemical reactivity of MMV and BTMAP-Fc was examined by CV at various concentrations. This analysis was performed for the electrochemical reactions that occurred during the charging step, which resulted in the capacity fade as discussed earlier. Figure 4-10a shows the maximum oxidation current density ($i_{pa}$) at various concentrations of BTMAP-Fc. As expected, $i_{pa}$ linearly increases with concentration. The linear relationship is valid for concentrations up to 50 mM without any deviation. Figure 4-10b shows the maximum reduction current density ($i_{pc}$) versus the MMV concentration. The concentration was varied from 0.3 mM to 100 mM. A linear relationship exists at concentrations up to 10 mM, beyond which the behavior changes unexpectedly. $i_{pc}$ at 20 mM, for instance, is substantially lower than that at 5 mM. The different behavior at concentrations greater than or equal to 20 mM was not expected and will clearly impact flow-battery performance.

The trend in Figure 4-10b shows that the electrochemical behavior of MMV at high concentrations deviates from expectations. As discussed earlier, one possible reason for this deviation is the dimerization reaction, which is more likely to occur at higher concentrations. The dimers are less soluble and also less electroactive than the monomers and may lead to such behavior. Another possibility is precipitation of the reduced monomer (MMV$^0$) at the electrode surface [105, 171]. A precipitate was observed to form on the electrode during the CV test of a concentrated solution (100mM MMV), while no precipitation occurred at 1 mM (Figure C-5). Figure 4-11 shows the cyclic voltammogram of an electrolyte containing 100 mM MMV in which the oxidation peak is almost 3 times higher than the reduction peak. This observation can be also explained by precipitation of the reduced species on the electrode, which subsequently leads to a higher oxidation peak [8]. Although the irreversible reactions at higher concentrations of MMV
lead to the unexpected behavior presented in Figure 4-10b and Figure 4-11, further study is needed to determine the extent to which the dimer or MMV\(^0\) is responsible for the observed behavior.

Figure 4-11: CV of an electrolyte containing 100mM MMV and 2M NaCl at a scan rate of 100 mV/s.

It appears that the electrochemical reactivity of MMV is limited at high concentrations. This, of course, presents a problem for flow battery development. Moreover, the capacity of a flow battery with MMV as the negative electrode decreases quickly and the fade rate increases at higher current density. These observations, unfortunately, indicate that MMV has poor cyclability. However, this issue can be mitigated by modifying the MMV structure. Asymmetric MMV derivatives can be synthesized with a higher charge to reduce the extent of dimerization by increasing repulsion forces between the reduced radicals. Viologens with a higher charge show a higher solubility as well [171]. Additionally, synthesizing MMV-derivatives with Cl\(^-\) counterion rather than I\(^-\) also seems beneficial in terms of solubility.

Therefore, MMV derivatives can be synthesized to mitigate the drawbacks of MMV. While the modifications suggested above improve the cyclability, the asymmetric structure of the compounds enables them to offer a very low redox potential. Moreover, these viologens have a lower molecular weight than their symmetric counterparts, possibly enhancing the solubility. All
these characteristics provide asymmetric MMV derivatives the capability to improve the performance of ARFBs over what has been previously reported with symmetric viologens.

4.4 Conclusions

An asymmetric viologen-based electroactive compound called MMV (1-Methyl-4,4'-bipyridylium iodide) was synthesized and assessed for use in aqueous flow batteries. MMV can be produced from inexpensive starting materials via a simple synthesis procedure to produce a low cost material as required for flow battery development. MMV has a solubility of ~ 3 M in water and ~ 2.6 M in a 2M NaCl supporting electrolyte, both of which are high relative to other organic compounds, such as quinones, especially in neutral electrolytes. Analytical experiments at low concentrations revealed that the electrochemical reaction of MMV involves the reversible transfer of one electron with fast kinetics. Additionally, MMV, with an asymmetric structure, demonstrated a redox potential of ~ -1.05 V vs. SCE, which is one of the most negative potentials reported to date for organic electroactive species in neutral electrolytes. Based on these characteristics, MMV is a promising anolyte candidate for flow battery applications with improved capacity, energy density, and cell potential. MMV, however, exhibited poor cycling performance at high concentrations and underwent irreversible or partially reversible reactions. Signs of dimerization and precipitation were observed during cycling, resulting in a capacity fade rate of 2.1%/cycle at 10 mA/cm², which increased at higher current density. Approaches to improve cycling performance include the synthesis of asymmetric MMV derivatives with a higher charge to limit the extent of both dimerization and precipitation. These asymmetric MMV derivatives have the potential to improve cycle life while maintaining a low redox potential and high solubility, which will potentially enhance the performance of ARFBs.
5 CONCLUSIONS AND FUTURE WORK

This chapter presents the principal conclusions from the work described in this dissertation. Recommendations for future work in each of the areas studied are also provided.

5.1 Conclusions

5.1.1 Viologen-Mediated Glucose Fuel Cell

In this work, two important aspects of viologen-mediated glucose fuel cells were studied. Chapters 2 and 3 provided a detailed discussion of the study; the main conclusions drawn are presented here.

**Oxidation Efficiency.** In Chapter 2, the viologen-mediated oxidation efficiency of glucose was discussed under aerobic conditions and in an electrochemical cell in the absence of oxygen. Oxidation efficiency in the electrochemical cell depended on the rate of the electrochemical reaction, and was higher at faster rates. The efficiency also depended on the initial molar ratio of viologen to glucose ($\beta$) and reached a maximum at an optimum $\beta$. The optimum $\beta$ was affected by the rate of mass transfer, which determined the availability of the regenerated mediator for further glucose oxidation. At very fast rates of mass transfer and electrochemical reaction, all the initial mediator remained in its oxidized form and available for oxidizing glucose. In this situation, the optimum $\beta$ was observed to be $\sim 2$. The maximum glucose oxidation efficiency in the
electrochemical cell approached 22%. The maximum oxidation efficiency is about three times higher than the values reported for precious-metal-based fuel cells. Therefore, viologen-mediated fuel cells offer a significantly higher oxidation efficiency without the additional cost associated with precious metals.

Oxidation efficiency was also examined in the presence of oxygen. Under aerobic conditions, oxidation efficiency of glucose was greater than 75%. NMR results revealed that the principal product under aerobic conditions was formic acid rather than the glycolic acid observed for the electrochemical cell. Additionally, carbonate was detected only under aerobic conditions. Therefore, this study resolved inconsistencies in the literature related to the extent of oxidation possible in MV-mediated cells. Although the possibility of oxidation efficiencies of 75% or greater exists in the presence of oxygen, the maximum oxidation possible under anaerobic conditions, required for fuel cell operation, is approximately 22%. Clearly, the presence of oxygen directly impacted the glucose oxidation pathway, leading to efficiencies greater than those possible in an electrochemical cell.

**Oxidation Rate.** In Chapter 3, rate performance of viologen-mediated glucose fuel cells was investigated. The relative significance of the key physical processes, including homogeneous reaction, mass transfer, and electrochemical reaction, was determined. This study was accomplished with both the use of dimensional analysis and a detailed mathematical model. The dimensional analysis provided important information on the relative significance of the processes. The detailed simulations, on the other hand, offered insight not available from simple dimensional analysis. All processes were important under certain conditions; however, mass transfer was the principal factor that limited rate performance. The mass transfer rate initially improved with flow. However, this effect was counterbalanced by decreased reactant concentrations in the cell at high
flow rates. The maximum obtainable current density was $\sim 200$ mA/cm$^2$, which corresponded to an anode polarization of 300 mV. Cell designs that enhance mass transfer will potentially improve rate performance further. The maximum current density is significantly higher than the current densities available from biological fuel cells and comparable to the rates observed for carbohydrate fuel cells that utilize precious-metal electrodes. Therefore, viologen-mediated glucose fuel cells offer the potential of high current densities at a lower cost, making them an attractive option for the development of glucose fuel cells. Finally, the analysis and methodology presented are not limited to viologen-mediated cells; instead, they can describe any mediated system and used to assess the relative importance of coupled processes as a basis for process development and optimization.

5.1.2 MMV-Utilized Redox Flow Battery

In Chapter 4, an asymmetric viologen-based electroactive compound called MMV (1-Methyl-4,4'-bipyridylium iodide) was synthesized and assessed for potential use in aqueous flow batteries to improve performance. MMV, with a simple synthesis procedure and inexpensive starting materials, can reduce the cost of flow battery development. MMV showed a solubility of $\sim 3$ M in water and $\sim 2.6$ M in a 2M NaCl electrolyte; thus, the solubility of MMV is relatively high compared to other organic electroactive compounds. Analytical experiments at low concentrations revealed that the electrochemical reaction of MMV involved a reversible single electron transfer with fast kinetics. Additionally, MMV, with an asymmetric structure, demonstrated a redox potential of $\sim -1.05$ V vs. SCE, which is one of the most negative redox potentials reported to date for organic electroactive species. These characteristics support MMV as a promising anolyte candidate for flow battery applications to improve capacity, energy density, and cell potential. MMV, however, exhibited poor cycling performance at high concentrations
and underwent irreversible or partially reversible side reactions. Signs of dimerization and precipitation were observed during cycling. The irreversible reactions led to a capacity fade rate of 2.1%/cycle at 10 mA/cm², which increased at higher current density.

5.2 Future Work

5.2.1 Viologen-Mediated Glucose Fuel Cell

Oxidation Efficiency. The study presented in Chapter 2 demonstrated the oxidation efficiency as a function of the initial molar ratio of the mediator to glucose. The initial ratio may not be appropriate since it only represents the available mediator for glucose oxidation at the onset of the process. Instead, a dynamic ratio based on the mediator and glucose concentrations in realtime and space as the oxidation reaction proceeds seems more appropriate. This dynamic ratio may be significantly different from the initial ratio, depending on the relative significance of the homogeneous reaction, electrochemical reaction, and mass transfer. A fast electrochemical reaction rate provides fast regeneration of the mediator at the surface of an electrode; however, mass transfer determines the availability of the regenerated mediator for further glucose oxidation. Therefore, evaluating the efficiency as a function of the dynamic ratio provides more accurate insight into the impact of the mediator concentration on the efficiency.

In this study, ¹³C-NMR was used qualitatively to investigate the impact of the operating conditions on oxidation efficiency. An estimation of the concentration of the products was then obtained using a relative intensity of the observed peaks in ¹³C-NMR results. It is suggested that the exact concentration of the products be determined with use of a quantitative ¹³C-NMR technique in which an internal standard with a known concentration is added to the sample.
Another hurdle with the $^{13}$C-NMR technique was time-intensive and challenging sample preparation. Additionally, expensive $^{13}$C-labeled glucose was necessary to obtain a spectrum with a high resolution. These challenges prevented us from a comprehensive product-distribution analysis that could provide more insight into the oxidation mechanism. Therefore, other identification techniques such as Ionic Chromatography may be worth exploring.

**Oxidation Rate.** In Chapter 3, a mathematical model was developed to determine the relative significance of the key physical processes on the anode side of a viologen-mediated fuel cell. In the model, the oxidation efficiency was estimated as a function of the initial molar ratio of the mediator to glucose rather than a dynamic ratio as discussed above. Additionally, an empirical relationship, which did not have a mechanistic basis, was used to estimate oxidation efficiency. These approaches can be improved in a future study to develop a mathematical model with higher accuracy over an extended range of conditions.

In this study, it was assumed that viologens did not undergo decomposition. However, decomposition of the mediator is inevitable in a real viologen-mediated cell under the conditions proposed to obtain a high current density. The decomposition reaction changes the structure of viologens and makes them less reactive toward glucose, affecting oxidation efficiency and the homogeneous reaction rate. In a future study, a rate model can be developed for the decomposition reaction and its impact on the performance of viologen-mediated glucose fuel cells can be examined.

The mathematical model was developed only for the anode side of a viologen-mediated cell. Moreover, the serpentine design of the electrode was simplified to a straight channel. It is recommended to develop a model of the actual geometry. Additionally, the model can be extended to include the performance of the cathode and membrane of a viologen-mediated fuel cell. Such
a comprehensive model determines the total polarization and output power density, and can be used for optimizing the entire cell rather than just the anode.

Lastly, the mathematical model can be extended to contain momentum balance in order to evaluate velocity variations and also pressure drop through the channels. Although such an extended model requires intensive computation time, it can provide additional insight into optimizing the flow rate. To further improve mass transfer, which was the major limiting factor in the cell, alternative electrode designs can be taken into consideration. Using porous electrodes with a higher specific area may also improve mass transfer and the overall rate.

5.2.2 MMV-Utilized Redox Flow Battery

The results presented in Chapter 4 demonstrated the potential of MMV as an anolyte for flow battery applications. Improving cycling performance of MMV can be the subject of a future study. This goal can be accomplished by modifying the structure of MMV to limit the extent of its irreversible reactions, which include dimerization and precipitation. One approach is the synthesis of asymmetric MMV derivatives that possess a higher charge. This modification can reduce the extent of dimerization by increasing repulsive forces between the monomers, and also has the potential to reduce precipitation by increasing the solubility limit of the compounds. Another approach is the synthesis of MMV derivatives with a chloride counterion instead of iodide in order to increase the solubility of the compounds, which will improve cycling performance.

In a future study, MMV derivatives can be paired with catholytes other than BTMAP-Fc that have higher redox potentials and also higher solubility. In this study, the cycling performance of MMV was evaluated by using BTMAP-Fc, a commercially available cathode material with good cycling performance. However, the redox potential and solubility of BTMAP-Fc are lower
than those desired for the catholyte of an aqueous redox battery. FcNCI and TEMPTMA appear to be attractive alternatives, but are not yet available commercially. These compounds may be obtained through collaboration with the research groups that developed them.
APPENDIX A. SUPPORTING INFORMATION FOR CHAPTER 2

Figure A-1: A sample plot of the measured current versus time at a constant potential in the electrochemical cell. The operating conditions are 2mM glucose, MVo/glucose ratio of 5, pH 12, 50 °C, and a working electrode potential of -0.1V vs. RE.

The slight increase in the current prior to the jump is due to the insertion of the needle of a syringe that contained glucose. The immediate increase (jump) in the current is because of the glucose injection to the cell.

A sample calculation of the glucose conversion efficiency for the result shown in Figure A-1:

Integrating the area under the curve yields the total coulombs transferred:

Transferred coulombs (Coul) = 7.389 C
Then, the number of moles of MVr that formed during the homogeneous reaction with glucose is calculated using Faraday’s law:

\[ n_{MVr} = \frac{Coul}{n \times F} = \frac{7.389}{1 \times 96485} = 7.66 \times 10^{-5} \text{ moles} \quad (A-1) \]

where \( F \) is Faraday’s constant and \( n \) is the number of electrons involved in the MV electrochemical reaction, which is one. Considering the initial amount of glucose that was added to the electrolyte, the glucose oxidation efficiency is calculated as:

\[ n_{MVr} \times \frac{24 \times V \times C_g}{24 \times V \times C_g} \times 100 = 21.3\% \quad (A-3) \]

Since a maximum of 24 electrons can be released as a result of glucose oxidation, the moles of glucose is multiplied by 24 in the denominator of the above equation to correctly calculate the conversion efficiency.
Figure A-2: Number of the released electrons from various carbohydrates in the aerobic environment with MV or MMV at pH 11 and 50 °C. The percentage values are the conversion efficiencies. 95% confidence intervals are shown for three cases, and the conversion efficiency for the other cases are average of at least 3 repeats.

Figure A-3: Number of the released electrons from DHA in the aerobic environment with various viologen species at pH 11 and 50 °C. The percentage values are the conversion efficiencies. 95% confidence intervals are shown for MV and MMV, and the conversion efficiency for the other viologen species are average of at least 3 repeats.
Figure A-4: $^{13}$C-NMR spectrum for a standard sample containing carbonate, formic and glycolic acid at the concentration of 0.2 M each, and pH11.
Calculation of the maximum error involved in the conversion measurements due to the fuel crossover:

When the WE and CE sides reach an equilibrium, the concentration of the enediolate species become the same; therefore, we have the following equation:

\[ C_{WE} = C_{CE} \]  \hspace{1cm} (A-4)

in which, \( C \) is the concentration of the enediolate in the WE or CE side. Based on the definition of concentration:
\[
\frac{n_{\text{WE}}}{V_{\text{WE}}} = \frac{n_{\text{CE}}}{V_{\text{CE}}}
\] (A-5)

in which \( n \) and \( V \) represent the number of moles of the enediolate species and volume of the electrolyte, respectively, in the WE or CE side.

\[
\frac{n_{\text{CE}}}{n_{\text{WE}}} = \frac{V_{\text{CE}}}{V_{\text{WE}}}
\] (A-6)

\[
\frac{V_{\text{CE}}}{V_{\text{WE}}} = \frac{1}{15}
\] (A-7)

\[
\frac{n_{\text{CE}}}{n_{\text{WE}}} = \frac{1}{15}
\] (A-8)

\[
\frac{n_{\text{CE}}}{n_t} = \frac{n_{\text{CE}}}{n_{\text{CE}} + n_{\text{WE}}} = \frac{n_{\text{CE}}}{n_{\text{CE}} + 15 \times n_{\text{CE}}} = \frac{1}{16} = 6.2\%
\] (A-9)

where \( n_t \) is the total number of moles of the enediolate species.

**Calculation of the relative concentration of species for the \(^{13}\text{C}-\text{NMR} \) spectrum presented in Figure 2-9:**

As glycolic and glyceric acid each have more than one peak, one of their peaks was chosen as the reference peak. We chose the peaks that appeared in the oxidation of labeled-\(^{13}\text{C} \) glucose (shown in Figure 2-9), which are the \( \delta=61\text{ppm} \) and the \( 74\text{ppm} \) peaks for glycolic and glyceric acid, respectively.

In this work, the relative intensity (RI) of species “A” is defined as the \(^{13}\text{C}-\text{NMR} \) peak intensity of the species “A” divided by the \(^{13}\text{C}-\text{NMR} \) peak intensity of formic acid. In a standard sample containing equal concentrations of formic acid, glycolic acid, and glyceric acid, the relative
intensities are 1, 0.4 and 1.8, respectively. That is, for glycolic acid as an example, its intensity will be 0.4 times the intensity of formic acid at the same concentration.

\[ RI_A = \frac{^{13}C - \text{NMR peak intensity of the species } "A"}{^{13}C - \text{NMR peak intensity of formic acid}} \] \hspace{1cm} (A-10)

In this work, the relative concentration (RC) of species “A” is defined as the concentration of the species “A” divided by the concentration of formic acid. Calculation of the relative concentration can be accomplished by dividing the relative intensity of species “A” in a desired sample to the relative intensity of the species in a standard sample.

\[ RC_A = \frac{RI_A \text{ in a desired sample}}{RI_A \text{ in a standard sample}} \] \hspace{1cm} (A-11)

The relative-concentration calculation for the result shown in Figure 3-9 is as follows:

For glycolic acid:

\[ RI_{glycolic\ acid, \ sample} = \frac{101.68}{108.5} = 0.94 \] \hspace{1cm} (A-12)

\[ RC_{glycolic\ acid} = \frac{RI_{glycolic\ acid, \ sample}}{RI_{glycolic\ acid, \ standard}} = \frac{0.94}{0.4} = 2.35 \] \hspace{1cm} (A-13)

Values of 101.68 and 108.5 are the peak intensities from the $^{13}$C-NMR result presented in Figure 2-9. For glyceralic acid:

\[ RI_{glyceric\ acid, \ sample} = \frac{78.74}{108.5} = 0.73 \] \hspace{1cm} (A-14)
\[
R_{glyceric\text{ acid}} = \frac{R_{I_{glyceric\text{ acid, sample}}}}{R_{I_{glyceric\text{ acid, standard}}}} = \frac{0.73}{1.8} = 0.4 \tag{A-15}
\]

Again, 78.74 and 108.5 are the peak intensities from the $^{13}$C-NMR result presented in Figure 2-9.

Figure A-6: $^{13}$C-NMR spectra of viologen-mediated oxidation of all $^{13}$C-labeled glyceraldehyde at T50 °C and pH 12 in the aerobic environment.
APPENDIX B. SUPPORTING INFORMATION FOR CHAPTER 3

Figure B-1: a) a 3D schematic diagram of the cell for conducting the experiments, b) an enlarged view of the graphite plate.

Figure B-2: The ratio of the MVr consumption rate to the MVr formation rate versus the dimensionless anode length at flow rates of 1 to 14 ml/min with 1ml/min increment. Inlet conditions are 1 M glucose, 1.7 M MVo, pH14, and temperature of 50°C.
Mass Transfer Coefficient

An empirical model was developed for the mass transfer coefficient. The electrochemical technique of limiting current measurements for the reaction of MV was used to characterize the mass transfer. Thus, potentiostatic experiments were performed and the generated current was recorded as a function of the potential at various flow rates. Since MV initially existed in its oxidized form, the applied potential was set lower than the open-circuit voltage (OCV) of the anode side, which contained MV, to ensure a cathodic current. The potential was gradually switched to more negative values until the measured current remained unchanged as shown in Figure B-3. The potential independent current represents limiting current ($I_{lim}$).

Figure B-3: Measured currents versus the anode potential vs. a Hg/HgO reference electrode (RE) at various flow rates. The blue squares and green triangles represent the currents at 3 and 10 ml/min, respectively. The electrolyte contained 10 mM MVo in a 2M NaCl supporting electrolyte. The operating temperature was 50 °C. Results are shown with 95% confidence intervals.

Figure B-3 shows the measured currents versus the anode potential at the operating conditions mentioned. The blue squares and green triangles represent the currents at flow rates of
3 and 10 ml/min. At these flow rates, limiting currents were -45.4 and -127.6 mA. The mass transfer coefficient was estimated from the limiting currents at each flow rate and was fitted to the following empirical model [172-174].

\[ k_m a = A_1 S C_3 Re^{A_2} \]  

(B-1)

The parameters \( A_1 \) and \( A_2 \) were obtained to be 0.0095 (1/s) and 0.82, respectively, through a non-linear regression technique. Figure B-4 shows the experimental limiting currents and the relevant fitted curve.

![Figure B-4: Limiting current versus the flow rate. The orange triangles represent the experimental results and the green line represents the model prediction.](image)

Electrolyte Conductivity Evaluation

In Equation (3-19), the conductivity of the electrolyte was assumed to be independent of local concentration of ions. Instead, it was treated as a fixed parameter based on the experimentally measured values for the desired electrolytes. The rationale behind this assumption is the deviation of the experimental conductivities from the calculated concentration-dependent values. When the
mediator (MV) is added to an electrolyte, it is expected to dissociate and form MV$^{++}$ cation and Cl$^-$ counterion. Although it was expected that adding viologens to aqueous electrolytes may increase the conductivity due to increasing the ion concentration, the measured conductivity remained almost unchanged. As reported in Table B-1, the addition of 300 mM MV, which adds 300 mM MV$^{++}$ and 600 mM Cl$^-$, to an electrolyte containing 2M NaCl and 0.1M KOH did not change the measured conductivity. Consistent with our observation, it was reported that the addition of up to 1M of MV to a 2M NaCl electrolyte did not noticeably change the conductivity [44]. However, conductivities calculated using the Nernst-Einstein equation deviate from the measured values, especially when MV was added. The deviation may be related to the formation of a charge-transfer complex between MV$^{++}$ and the counterion [8], which perhaps prevents the ions from contributing to the conductivity as the Nernst-Einstein equation predicts.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>MV concentration (M)</th>
<th>Measured conductivity (S/cm)</th>
<th>Calculated conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M NaCl-0.1M KOH</td>
<td>0.0</td>
<td>0.16 (this work)</td>
<td>0.28</td>
</tr>
<tr>
<td>2M NaCl-0.1M KOH</td>
<td>0.3</td>
<td>0.16 (this work)</td>
<td>0.40</td>
</tr>
<tr>
<td>2M NaCl</td>
<td>0.0</td>
<td>0.16 [44]</td>
<td>0.25</td>
</tr>
<tr>
<td>2M NaCl</td>
<td>1.0</td>
<td>0.17 [44]</td>
<td>0.66</td>
</tr>
</tbody>
</table>

**Transient Inlet Condition**

Figure B-5 shows the glucose and MVr concentrations at the inlet of the anode compartment with the mixing tank included. The results of this figure were obtained from the mathematical model at the operating conditions mentioned.
Figure B-5: Glucose and MVr concentrations versus time at the inlet of the anode compartment. Operating conditions are: 17mM glucose initial concentration, β of 1.5, pH 12.3, and the temperature of 50 °C.

COMSOL CODE

GLOBAL DEFINITIONS

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFC</td>
<td>40[cm]</td>
<td>0.4 m</td>
<td>length of channel in fuel cell</td>
</tr>
<tr>
<td>DFC</td>
<td>1.1[mm]</td>
<td>0.0011 m</td>
<td>Depth of channel in fuel cell</td>
</tr>
<tr>
<td>porous</td>
<td></td>
<td>0.93</td>
<td>porosity of the electrode</td>
</tr>
<tr>
<td>cstd</td>
<td>0.5[mmol/L]</td>
<td>0.5 mol/m³</td>
<td>reference concentration</td>
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<tr>
<td>Temp</td>
<td>273.17 + 48[K]</td>
<td>321.17 K</td>
<td>operating temperature</td>
</tr>
<tr>
<td>sa</td>
<td>61.07[1/cm]</td>
<td>6107 1/m</td>
<td>specific area of the electrode</td>
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<tr>
<td>ks</td>
<td>0.245[S/cm]</td>
<td>24.5 S/m</td>
<td>conductivity of the electrolyte at T 50</td>
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<tr>
<td>i0s</td>
<td>2.7e-5[A/cm²]</td>
<td>0.27 A/m²</td>
<td>exchange current density</td>
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<td>alfaa</td>
<td>0.25</td>
<td>0.25</td>
<td>anodic charge transfer coefficient</td>
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<tr>
<td>alfac</td>
<td>1 - alfaa</td>
<td>0.75</td>
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<tr>
<td>R</td>
<td>8.314472[J/(mol*K)]</td>
<td>8.3145 J/(mol·K)</td>
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<tr>
<td>Far</td>
<td>96485[C/mol]</td>
<td>96485 C/mol</td>
<td>Faraday's constant</td>
</tr>
<tr>
<td>Q</td>
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<td>1.6667E−7 m³/s</td>
<td>volumetric flow rate of the electrolyte</td>
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<tr>
<td>Name</td>
<td>Expression</td>
<td>Value</td>
<td>Description</td>
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<tr>
<td>---------------</td>
<td>-----------------------------------</td>
<td>------------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>vel</td>
<td>Q/Area_c</td>
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<tr>
<td>Area</td>
<td>LFC*DFC</td>
<td>6E−4 m²</td>
<td>area for current</td>
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<tr>
<td>Area_c</td>
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<td>cross section area for the flow</td>
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<td>0.0055 m</td>
<td>width of the channels of the fuel cell</td>
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<tr>
<td>diffmvbulk_25</td>
<td>0.85e-5[cm^2/s]</td>
<td>0.85E−9 m³/s</td>
<td>Diffusion of MVo species at 25 C and 0.5M NaCl bulk electrolyte</td>
</tr>
<tr>
<td>diffmvbulk</td>
<td>(diffmvbulk_25<em>Vis_0.5_NaCl/RT)</em>(Tref/Vis_2M_NaCl)</td>
<td>3.8184E−9 m³/s</td>
<td>Diffusion of MVo species at 50 C and 2M NaCl bulk electrolyte</td>
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<tr>
<td>diffmv</td>
<td>diffmvbulk<em>porous^1.5</em>diff_MVr_MVo</td>
<td>1.3219E−8 m³/s</td>
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<tr>
<td>cgo</td>
<td>1000[mmol/l]</td>
<td>1000 mol/m³</td>
<td></td>
</tr>
<tr>
<td>MVratio</td>
<td>1.7</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>cmvo</td>
<td>1700[mmol/l]</td>
<td>1700 mol/m³</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>14</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>EP</td>
<td>-0.2[V]</td>
<td>−0.2 V</td>
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</tr>
<tr>
<td>k1k50</td>
<td>0.084[L/mol/s]</td>
<td>8.4E−5 m³/(s·mol)</td>
<td>rate constant at 50 degC</td>
</tr>
<tr>
<td>Ea</td>
<td>122[kJ/mol]</td>
<td>1.22E5 J/mol</td>
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</tr>
<tr>
<td>Tref</td>
<td>273.15 + 50[K]</td>
<td>323.15 K</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>LFC<em>DFC</em>WFC</td>
<td>3.3E−6 m³</td>
<td>volume of the fuel cell</td>
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<tr>
<td>Zmvr</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Zmvo</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>diffmvo</td>
<td>diffmvbulk*porous^1.5</td>
<td>3.4245E−9 m³/s</td>
<td>Diffusion of MVo species</td>
</tr>
<tr>
<td>diffGbulk</td>
<td>6.5e-6[cm^2/s]</td>
<td>6.5E−10 m³/s</td>
<td>Diffusion of glucose in bulk solution</td>
</tr>
<tr>
<td>diffG</td>
<td>diffGbulk*porous^1.5</td>
<td>5.8296E−10 m³/s</td>
<td>Diffusion of glucose</td>
</tr>
<tr>
<td>diff_MVr_MVo</td>
<td>3.86</td>
<td>3.86</td>
<td>Ratio of diffusion of MVr to MVo</td>
</tr>
<tr>
<td>Vis_2M_NaCl</td>
<td>0.6757[centipoise]</td>
<td>6.757E−4 Pa·s</td>
<td>Viscosity of 2 M NaCl electrolyte at T 50</td>
</tr>
<tr>
<td>Vis_0.5_NaCl</td>
<td>0.92625[centipoise]</td>
<td>9.2625E−4 Pa·s</td>
<td>Viscosity of 0.5 M NaCl electrolyte at T 25</td>
</tr>
<tr>
<td>RT</td>
<td>273.15 + 25[K]</td>
<td>298.15 K</td>
<td>room temperature</td>
</tr>
<tr>
<td>ke</td>
<td>i0s/Far/cstd</td>
<td>5.5967E−6 m/s</td>
<td></td>
</tr>
<tr>
<td>CNaCl</td>
<td>2[M]</td>
<td>2000 mol/m³</td>
<td></td>
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### FUEL CELL

#### Chemical Reaction Variables

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<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>cmvrin</td>
<td>epsilon</td>
<td>mol/m³</td>
<td>Glucose initial concentration to the fuel cell</td>
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<tr>
<td>cgin</td>
<td>cgo</td>
<td>mol/m³</td>
<td>cgin</td>
</tr>
<tr>
<td>cmvoin</td>
<td>cmvo</td>
<td>mol/m³</td>
<td>cmvoin</td>
</tr>
<tr>
<td>beta</td>
<td>cmvo/cgo</td>
<td></td>
<td>molar ratio of the initial mvo to glucose</td>
</tr>
<tr>
<td>alfa</td>
<td>7.5*beta/(6 + beta)</td>
<td></td>
<td>empirical coefficient for conversion of glucose</td>
</tr>
<tr>
<td>OH</td>
<td>10^(-14 - pH)[mol/L]</td>
<td>mol/m³</td>
<td>concentration of OH ions</td>
</tr>
<tr>
<td>k1k</td>
<td>k1k50<em>exp(-Ea/R</em>(1/Temp - 1/Tref))</td>
<td>m³/(s·mol)</td>
<td>rate constant 1 for the homogenoeus reaction</td>
</tr>
<tr>
<td>kp</td>
<td>0.38[mmol/L]</td>
<td>mol/m³</td>
<td>rate constant 2 for the homogenoeus reaction</td>
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<tr>
<td>Rhomo</td>
<td>k1k*(porous<em>OH)</em>(porous<em>Cmv o)</em>/(porous<em>cg)/(kp + (porous</em>Cmvo))</td>
<td>mol/(m³·s)</td>
<td></td>
</tr>
</tbody>
</table>
## Electrochemical reaction variables

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>USTD</td>
<td>-0.609[V]</td>
<td>V</td>
<td>STD redox potential vs. Hg/HgO</td>
</tr>
<tr>
<td>termc</td>
<td>alfac<em>Far/(R</em>Temp)</td>
<td>1/V</td>
<td>cathodic coefficient of overpotential in exponential term of the BV kinetics</td>
</tr>
<tr>
<td>terma</td>
<td>alfaa<em>Far/(R</em>Temp)</td>
<td>1/V</td>
<td>anodic coefficient of overpotential in exponential term of the BV kinetics</td>
</tr>
<tr>
<td>epsilon</td>
<td>0.0000015[mmol/L]</td>
<td>mol/m³</td>
<td></td>
</tr>
<tr>
<td>epsilon2</td>
<td>0.0000015[mmol/L]</td>
<td>mol/m³</td>
<td></td>
</tr>
<tr>
<td>crmvs</td>
<td>(max(Cmvr, epsilon)/cstd)^0.5</td>
<td></td>
<td>MVr corrected surface concentration</td>
</tr>
<tr>
<td>crmvos</td>
<td>(max((Cmvo1, epsilon)/cstd)^0.5</td>
<td></td>
<td>MVo corrected surface concentration</td>
</tr>
<tr>
<td>i0</td>
<td>i0s<em>crmvs</em>crmvos</td>
<td>A/m²</td>
<td>Corrected exchange current density</td>
</tr>
<tr>
<td>ksef</td>
<td>ks*porous^1.5</td>
<td>S/m</td>
<td>Modified conductivity of the electrolyte</td>
</tr>
<tr>
<td>U</td>
<td>USTD - R<em>Temp/Far</em>log(max(Cmvr, epsilon2)/max(Cmvo1, epsilon2))</td>
<td>V</td>
<td>Modified redox potential of MV</td>
</tr>
<tr>
<td>overpotential</td>
<td>phig - phis - U</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td>i_n</td>
<td>if(overpotential&gt;0, i0*(exp(terma<em>overpotential) - exp(-termc</em>overpotential)), 0)</td>
<td>A/m²</td>
<td>Electrochemical consumption term</td>
</tr>
<tr>
<td>Relect</td>
<td>sa*i_n/Far</td>
<td>mol/(m³·s)</td>
<td>Volumetric consumption of the electrochemical reaction</td>
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<tr>
<td>kk</td>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>A1</td>
<td>0.006666[1/s]</td>
<td>1/s</td>
<td>MT coefficient model, A1x(Q^A2)</td>
</tr>
<tr>
<td>A2</td>
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<td></td>
<td>MT coefficient model, A1x(Q^A2)</td>
</tr>
<tr>
<td>K_mt_a</td>
<td>A1*(Q/1[ml/min])^A2</td>
<td>1/s</td>
<td>MT coefficient times specific area of electrode</td>
</tr>
<tr>
<td>K_mt</td>
<td>K_mt_a/sa</td>
<td>m/s</td>
<td>Mass transfer coefficient</td>
</tr>
<tr>
<td>NO_MVr</td>
<td>intop1(genproj1(Cmvr))<em>WFC</em>Far</td>
<td>C</td>
<td>charge of the not oxidized MVr in the cell</td>
</tr>
<tr>
<td>AvgCD</td>
<td>intop1(genproj1(i_n))*sa/LFC</td>
<td>A/m²</td>
<td>average current density</td>
</tr>
<tr>
<td>Total_curr</td>
<td>AvgCD<em>WFC</em>LFC</td>
<td>A</td>
<td>Total generated current in the cell</td>
</tr>
<tr>
<td>ChargePass</td>
<td>Total_curr*V/Q</td>
<td>C</td>
<td>Total passed charge</td>
</tr>
<tr>
<td>Name</td>
<td>Expression</td>
<td>Unit</td>
<td>Description</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------------------------------------</td>
<td>----------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>n_MVr_FC</td>
<td>V*(aveop1(Cmvr) - cmvrin)</td>
<td>mol</td>
<td>change in MVr moles inside the fuel cell</td>
</tr>
<tr>
<td>epsilon_i</td>
<td>1e-15 [A/m²]</td>
<td>A/m²</td>
<td></td>
</tr>
<tr>
<td>coeffic</td>
<td>pw1(t[1/s])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCI</td>
<td>Zmvo<em>Cmvo + Zmvr</em>Cmvr + ZNa*CNa</td>
<td>mol/m³</td>
<td>electroneutrality</td>
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<tr>
<td>CE1</td>
<td>(k1k<em>porous^2</em>cgo*OH/cmvo)</td>
<td>1/s</td>
<td>homogeneous reaction pseudo rate</td>
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<tr>
<td>CE2</td>
<td>(sa*K_mt)</td>
<td>1/s</td>
<td>mass transfer pseudo rate</td>
</tr>
<tr>
<td>CE3</td>
<td>(i0s*sa/Far/cstd)</td>
<td>1/s</td>
<td>electrochemical pseudo rate</td>
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<td>resg</td>
<td>2[mm/S]</td>
<td>Ω·m</td>
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</tr>
<tr>
<td>ksg</td>
<td>1/resg</td>
<td>S/m</td>
<td>intrinsic conductivity of the graphite phase</td>
</tr>
<tr>
<td>kg</td>
<td>ksg*porous^1.5</td>
<td>S/m</td>
<td>conductivity of the graphite phase</td>
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**Geometry 1**

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<th>Value</th>
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<tr>
<td>Number of boundaries</td>
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<td>Number of vertices</td>
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</table>

**Rectangle 1 (r1)**

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<th>Description</th>
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<tr>
<td>Width</td>
<td>LFC</td>
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<td>Height</td>
<td>DFC1</td>
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**MVr CONCENTRATION**

<table>
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</thead>
<tbody>
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<td>Lagrange</td>
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<tr>
<td>Element order</td>
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</tr>
<tr>
<td>Compute boundary fluxes</td>
<td>On</td>
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<tr>
<td>Apply smoothing to boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Frame</td>
<td>Spatial</td>
</tr>
<tr>
<td>Dependent variable quantity</td>
<td>Concentration (mol/m³)</td>
</tr>
<tr>
<td>Source term quantity</td>
<td>Reaction rate (mol/(m³·s))</td>
</tr>
</tbody>
</table>
Coefficient Form PDE 1

\[ e_\delta \frac{\partial^2 C_{mvr}}{\partial t^2} + d_\delta \frac{\partial C_{mvr}}{\partial t} + \nabla \cdot (\epsilon \nabla C_{mvr} - \alpha C_{mvr} + \gamma) + \beta : \nabla C_{mvr} + \alpha C_{mvr} = f \]

\[ \nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right] \]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Diffusion coefficient</td>
<td>{\text{diffmv}, 0}, {0, \text{diffmv}}</td>
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<tr>
<td>Source term</td>
<td>\text{Rhomo} - \text{Relect} + kk<em>porous</em>Far<em>Zmvr</em>(diffmv/(R<em>Temp))</em>(phisy<em>Cmvry + phisx</em>Cmvrx + Cmvr*(phisyy + phisxx))</td>
</tr>
<tr>
<td>Convection coefficient</td>
<td>{\text{vel}, 0}</td>
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</tbody>
</table>

Zero Flux 1

Selection Boundaries 2, 5–7

\[-n \cdot (\epsilon \nabla C_{mvr} - \alpha C_{mvr} + \gamma) = 0\]

\[ \nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right] \]

Initial Values 1

Selection Domains 1–2

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<td>Initial time derivative of Cmvr</td>
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</table>

Dirichlet Boundary Condition 1

Selection Boundaries 1, 3

\[ C_{mvr} = r \]
\[ g_{\text{reaction}} = -\mu \]

<table>
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<tr>
<th>Description</th>
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</thead>
<tbody>
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</tr>
<tr>
<td>Apply reaction terms on</td>
<td>Individual dependent variables</td>
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<tr>
<td>Constraint method</td>
<td>Elemental</td>
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</table>

MVo CONCENTRATION
<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape function type</td>
<td>Lagrange</td>
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<td>Element order</td>
<td>Quadratic</td>
</tr>
<tr>
<td>Compute boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Apply smoothing to boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Frame</td>
<td>Spatial</td>
</tr>
<tr>
<td>Dependent variable quantity</td>
<td>Concentration (mol/m^3)</td>
</tr>
<tr>
<td>Source term quantity</td>
<td>Reaction rate (mol/(m^3*s))</td>
</tr>
</tbody>
</table>

Coefficient Form PDE 1

\[
\begin{align*}
\epsilon \frac{\partial^2 C_{mvo1}}{\partial t^2} + \eta \frac{\partial C_{mvo1}}{\partial t} + \nabla \cdot (-c
\nabla C_{mvo1} \cdot \alpha C_{mvo1} + \gamma) + \beta \cdot \nabla C_{mvo1} + \alpha C_{mvo1} &= f \\
\nabla &= \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right]
\end{align*}
\]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coefficient</td>
<td>{{diffmvo, 0}, {0, diffmvo}}</td>
</tr>
<tr>
<td>Source term</td>
<td>-Rhom + Relect + kk<em>porous</em>Far<em>Zmvo</em>(diffmvo/(R<em>Temp))</em>(phisy<em>Cmvo1y + phisx</em>Cmvo1x + Cmvo1*(phisyy + phisxx))</td>
</tr>
<tr>
<td>Convection coefficient</td>
<td>{vel, 0}</td>
</tr>
</tbody>
</table>

Zero Flux 1

\[
\begin{align*}
-n \cdot (-c \nabla C_{mvo1} \cdot \alpha C_{mvo1} + \gamma) &= 0 \\
\nabla &= \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right]
\end{align*}
\]

Initial Values 1

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial value for Cmvo1</td>
<td>cmvo</td>
</tr>
<tr>
<td>Initial time derivative of Cmvo1</td>
<td>0</td>
</tr>
</tbody>
</table>

Dirichlet Boundary Condition 1

\[
C_{mvr} = r
\]
\[ g_{\text{reaction}} = -\mu \]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value on boundary</td>
<td>0</td>
</tr>
<tr>
<td>Prescribed value of Cmvo1</td>
<td>On</td>
</tr>
<tr>
<td>Apply reaction terms on</td>
<td>Individual dependent variables</td>
</tr>
<tr>
<td>Constraint method</td>
<td>Elemental</td>
</tr>
</tbody>
</table>

**GLUCOSE CONCENTRATION**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape function type</td>
<td>Lagrange</td>
</tr>
<tr>
<td>Element order</td>
<td>Quadratic</td>
</tr>
<tr>
<td>Compute boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Apply smoothing to boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Frame</td>
<td>Spatial</td>
</tr>
<tr>
<td>Dependent variable quantity</td>
<td>Concentration (mol/m^3)</td>
</tr>
<tr>
<td>Source term quantity</td>
<td>Reaction rate (mol/(m^3*s))</td>
</tr>
</tbody>
</table>

**Coefficient Form PDE 1**

\[
e^a \frac{\partial^2 cg}{\partial t^2} + d^a \frac{\partial cg}{\partial t} + \nabla \cdot (c \nabla cg - \alpha cg + \gamma) + \beta \cdot \nabla cg + \alpha cg = f
\]

\[ \nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right] \]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coefficient</td>
<td>{diffG, 0}, {0, diffG}</td>
</tr>
<tr>
<td>Source term</td>
<td>-Rhomo/alfa</td>
</tr>
<tr>
<td>Convection coefficient</td>
<td>{vel, 0}</td>
</tr>
</tbody>
</table>

**Zero Flux 1**

\[-n \cdot (c \nabla cg - \alpha cg + \gamma) = 0\]

\[ \nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right] \]

**Initial Values 1**

<p>| Selection | Domains 1–2 |</p>
<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial value for cg</td>
<td>cgo</td>
</tr>
<tr>
<td>Initial time derivative of cg</td>
<td>0</td>
</tr>
</tbody>
</table>

**Dirichlet Boundary Condition 1**

<table>
<thead>
<tr>
<th>Selection</th>
<th>Boundaries 1, 3</th>
</tr>
</thead>
</table>

\[
\begin{align*}
\text{Dirichlet Boundary Condition 1} \\
\text{Selection} & \quad \text{Boundaries 1, 3} \\
\frac{\partial c_g}{\partial t} &= r \\
g_{\text{reaction}} &= -\mu \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value on boundary</td>
<td>cgo</td>
</tr>
<tr>
<td>Prescribed value of cg</td>
<td>On</td>
</tr>
<tr>
<td>Apply reaction terms on</td>
<td>Individual dependent variables</td>
</tr>
<tr>
<td>Constraint method</td>
<td>Elemental</td>
</tr>
</tbody>
</table>

**SURFACE CONCENTRATION EQUATION Cmvsrs**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape function type</td>
<td>Discontinuous Lagrange</td>
</tr>
<tr>
<td>Element order</td>
<td>Quadratic</td>
</tr>
<tr>
<td>Value type when using splitting of complex variables</td>
<td>Complex</td>
</tr>
<tr>
<td>Frame</td>
<td>Spatial</td>
</tr>
<tr>
<td>Dependent variable quantity</td>
<td>Concentration (mol/m^3)</td>
</tr>
<tr>
<td>Source term quantity</td>
<td>Reaction rate (mol/(m^3*s))</td>
</tr>
</tbody>
</table>

**Distributed ODE 1**

\[
\begin{align*}
\frac{e_d}{d^2 t^2} \frac{\partial^2 \text{Cmvsrs}}{\partial x^2} + d_d \frac{\partial \text{Cmvsrs}}{\partial t} &= f \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source term</td>
<td>(K_{mt}*(\text{Cmvr} - \text{Cmvsrs})*sa - \text{Relct})</td>
</tr>
</tbody>
</table>

**Initial Values 1**

<table>
<thead>
<tr>
<th>Selection</th>
<th>Domains 1–2</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial value for Cmvsrs</td>
<td>0</td>
</tr>
<tr>
<td>Initial time derivative of Cmvsrs</td>
<td>0</td>
</tr>
</tbody>
</table>
SURFACE CONCENTRATION EQUATION Cmvos1

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape function type</td>
<td>Discontinuous Lagrange</td>
</tr>
<tr>
<td>Element order</td>
<td>Quadratic</td>
</tr>
<tr>
<td>Value type when using splitting of complex</td>
<td>Complex</td>
</tr>
<tr>
<td>variables</td>
<td></td>
</tr>
<tr>
<td>Frame</td>
<td>Spatial</td>
</tr>
<tr>
<td>Dependent variable quantity</td>
<td>Concentration (mol/m^3)</td>
</tr>
<tr>
<td>Source term quantity</td>
<td>Reaction rate (mol/(m^3*s))</td>
</tr>
</tbody>
</table>

Distributed ODE 1

\[ e_0 \frac{\partial^2 C_{mvos1}}{\partial t^2} + d_0 \frac{\partial C_{mvos1}}{\partial t} = f \]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source term</td>
<td>( K_{mt} (C_{mvo1} - C_{mvos1}) \cdot sa + \text{Relect} )</td>
</tr>
</tbody>
</table>

Initial Values 1

<table>
<thead>
<tr>
<th>Selection</th>
<th>Domains 1–2</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial value for Cmvos1</td>
<td>0</td>
</tr>
<tr>
<td>Initial time derivative of Cmvos1</td>
<td>0</td>
</tr>
</tbody>
</table>

SOLUTION POTENTIAL

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape function type</td>
<td>Lagrange</td>
</tr>
<tr>
<td>Element order</td>
<td>Quadratic</td>
</tr>
<tr>
<td>Compute boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Apply smoothing to boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Frame</td>
<td>Spatial</td>
</tr>
<tr>
<td>Dependent variable quantity</td>
<td>Electrolyte potential (V)</td>
</tr>
<tr>
<td>Source term quantity</td>
<td>Current source (A/m^3)</td>
</tr>
</tbody>
</table>

Coefficient Form PDE 1
\[ e_0 \frac{\partial^2 \phi_{is}}{\partial t^2} + d_{3} \frac{\partial \phi_{is}}{\partial t} + \nabla \cdot (-c \nabla \phi_{is} - \alpha \phi_{is} + \gamma) + \beta \cdot \nabla \phi_{is} + \phi_{is} = f \]

\[ \nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right] \]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coefficient</td>
<td>{(ksef, 0), (0, ksef)}</td>
</tr>
<tr>
<td>Source term</td>
<td>Relect<em>Far + Far</em>(Zmvrxvdiffmv*(Cmvryy + Cmvryx) + Zmvorifmvo*(d(d(Cmvo1, x), x) + d(d(Cmvo1, y), y)) + ZNa<em>diffNa</em>(CNaxx + CNayy) + ZCl<em>diffCl</em>(d(d(CCl, x), x) + d(d(CCl, y), y))</td>
</tr>
</tbody>
</table>

Zero Flux 1

<table>
<thead>
<tr>
<th>Selection</th>
<th>Boundaries 1, 3, 5–7</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-n \cdot (-c \nabla \phi_{is} - \alpha \phi_{is} + \gamma) = 0 )</td>
<td>[ \nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right] ]</td>
</tr>
</tbody>
</table>

Initial Values 1

<table>
<thead>
<tr>
<th>Selection</th>
<th>Domains 1–2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Value</td>
</tr>
<tr>
<td>Initial value for ( \phi_{is} )</td>
<td>EP - USTD</td>
</tr>
<tr>
<td>Initial time derivative of ( \phi_{is} )</td>
<td>0</td>
</tr>
</tbody>
</table>

Dirichlet Boundary Condition 1

<table>
<thead>
<tr>
<th>Selection</th>
<th>Boundary 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi_{is} = r )</td>
<td>( g_{\text{reaction}} = -\mu )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value on boundary</td>
<td>0</td>
</tr>
<tr>
<td>Prescribed value of ( \phi_{is} )</td>
<td>On</td>
</tr>
<tr>
<td>Apply reaction terms on</td>
<td>Individual dependent variables</td>
</tr>
<tr>
<td>Constraint method</td>
<td>Elemental</td>
</tr>
</tbody>
</table>

GRAPHITE POTENTIAL

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape function type</td>
<td>Lagrange</td>
</tr>
<tr>
<td>Description</td>
<td>Value</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Element order</td>
<td>Quadratic</td>
</tr>
<tr>
<td>Compute boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Apply smoothing to boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Frame</td>
<td>Spatial</td>
</tr>
<tr>
<td>Dependent variable quantity</td>
<td>Electric potential (V)</td>
</tr>
</tbody>
</table>

Coefficient Form PDE 1

\[ e \frac{\partial^2 \phi_{ig}}{\partial t^2} + d \frac{\partial \phi_{ig}}{\partial t} + \nabla \cdot (-c \nabla \phi_{ig} - \alpha \phi_{ig} + \gamma) + \beta \cdot \nabla \phi_{ig} + a \phi_{ig} = f \]

\[ \nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right] \]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coefficient</td>
<td>{kg, 0}, {0, kg}</td>
</tr>
<tr>
<td>Source term</td>
<td>-Relect*Far</td>
</tr>
</tbody>
</table>

Zero Flux 1

Selection: Boundaries 1–3, 6–7

\[-n \cdot (-c \nabla \phi_{ig} - \alpha \phi_{ig} + \gamma) = 0\]

\[ \nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right] \]

Initial Values 1

Selection: Domains 1–2

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial value for ( \phi_{ig} )</td>
<td>EP</td>
</tr>
<tr>
<td>Initial time derivative of ( \phi_{ig} )</td>
<td>0</td>
</tr>
</tbody>
</table>

Dirichlet Boundary Condition 1

Selection: Boundary 5

\[ \phi_{ig} = r \]

\[ g_{\text{reaction}} = -\mu \]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value on boundary</td>
<td>EP</td>
</tr>
<tr>
<td>Prescribed value of ( \phi_{ig} )</td>
<td>On</td>
</tr>
<tr>
<td>Apply reaction terms on</td>
<td>Individual dependent variables</td>
</tr>
<tr>
<td>Description</td>
<td>Value</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>Constraint method</td>
<td>Elemental</td>
</tr>
</tbody>
</table>

**SUPPORTING ELECTROLYTE CONC.**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape function type</td>
<td>Lagrange</td>
</tr>
<tr>
<td>Element order</td>
<td>Quadratic</td>
</tr>
<tr>
<td>Compute boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Apply smoothing to boundary fluxes</td>
<td>On</td>
</tr>
<tr>
<td>Value type when using splitting of complex variables</td>
<td>Complex</td>
</tr>
<tr>
<td>Frame</td>
<td>Spatial</td>
</tr>
<tr>
<td>Dependent variable quantity</td>
<td>Concentration (mol/m^3)</td>
</tr>
<tr>
<td>Source term quantity</td>
<td>Reaction rate (mol/(m^3*s))</td>
</tr>
</tbody>
</table>

**Coefficient Form PDE 1**

\[
e_d \frac{\partial^2 \text{Na}}{\partial t^2} + d_0 \frac{\partial \text{Na}}{\partial t} + \nabla \cdot (-c \nabla \text{Na} \cdot \alpha \text{Na} + \gamma) + \beta \cdot \nabla \text{Na} + a \text{Na} = f
\]

\[
\nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right]
\]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coefficient</td>
<td>{diffNa, 0}, {0, diffNa}</td>
</tr>
<tr>
<td>Source term</td>
<td>\text{ZNa} \cdot \text{uNa} \cdot \text{Far} \cdot (d(CNa*(\text{phisx + phisy}), x) + d(CNa*(\text{phisx + phisy}), y))</td>
</tr>
<tr>
<td>Convection coefficient</td>
<td>{vel, 0}</td>
</tr>
</tbody>
</table>

**Zero Flux 1**

\[
- \mathbf{n} \cdot (-c \nabla \text{Na} - \alpha \text{Na} + \gamma) = 0
\]

\[
\nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right]
\]

**Initial Values 1**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial value for CNa</td>
<td>CNaCl</td>
</tr>
<tr>
<td>Description</td>
<td>Value</td>
</tr>
<tr>
<td>------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Initial time derivative of CNa</td>
<td>0</td>
</tr>
</tbody>
</table>

**Dirichlet Boundary Condition 1**

- **Selection**: Boundaries 1, 3
- **Equation**: 
  \[ C_{Na} = r \]
  \[ g_{\text{reaction}} = -\mu \]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value on boundary</td>
<td>CNaCl</td>
</tr>
<tr>
<td>Prescribed value of CNa</td>
<td>On</td>
</tr>
<tr>
<td>Apply reaction terms on</td>
<td>Individual dependent variables</td>
</tr>
<tr>
<td>Constraint method</td>
<td>Elemental</td>
</tr>
</tbody>
</table>

**Mesh 1**

**Size (size)**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum element size</td>
<td>0.025</td>
</tr>
<tr>
<td>Minimum element size</td>
<td>4.0E-4</td>
</tr>
<tr>
<td>Curvature factor</td>
<td>0.2</td>
</tr>
<tr>
<td>Predefined size</td>
<td>Extremely fine</td>
</tr>
<tr>
<td>Custom element size</td>
<td>Custom</td>
</tr>
</tbody>
</table>

**Free Quad 1 (fq1)**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-direction scale</td>
<td>0.3</td>
</tr>
<tr>
<td>y-direction scale</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**STUDY**

**Parametric Sweep**

<table>
<thead>
<tr>
<th>Parameter name</th>
<th>Parameter value list</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>range([ml/min], 1[ml/min], 25[ml/min])</td>
</tr>
<tr>
<td>EP</td>
<td>range(-0.45[V], 0.05[V], -0.2[V])</td>
</tr>
<tr>
<td>pH</td>
<td>range(12, 1, 14)</td>
</tr>
<tr>
<td>cgo</td>
<td>range(0.1[mol/l], 0.2[mol/l], 1[mol/l])</td>
</tr>
<tr>
<td>Description</td>
<td>Value</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>Sweep type</td>
<td>All combinations</td>
</tr>
<tr>
<td>Parameter name</td>
<td>{Q, EP, pH, cgo}</td>
</tr>
<tr>
<td>Parameter value list</td>
<td>{([\text{range}(1,[\text{ml/min}], 1,[\text{ml/min}], 25,[\text{ml/min}]), \text{range}(-0.45[V], 0.05[V], -0.2[V]), \text{range}(12, 1, 14), \text{range}(0.1[\text{mol/l}], 0.2[\text{mol/l}], 1[\text{mol/l}])})</td>
</tr>
</tbody>
</table>

**Stationary**

<table>
<thead>
<tr>
<th>Physics interface</th>
<th>Discretization</th>
</tr>
</thead>
<tbody>
<tr>
<td>MVr concentration (c)</td>
<td>physics</td>
</tr>
<tr>
<td>MVo concentration (c)</td>
<td>physics</td>
</tr>
<tr>
<td>Glucose concentration (c3)</td>
<td>physics</td>
</tr>
<tr>
<td>MVo Surface concentration equation (dode)</td>
<td>physics</td>
</tr>
<tr>
<td>Surface concentration equation (dode)</td>
<td>physics</td>
</tr>
<tr>
<td>Solution potential (Ps)</td>
<td>physics</td>
</tr>
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<td>Supporting electrolyte Na conc. (c2)</td>
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**Solver Configurations**

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**Stationary Solver 1 (s1)**

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APPENDIX C. SUPPORTING INFORMATION FOR CHAPTER 4

Figure C-1: Results obtained from rotating disk electrode experiments. a) Levich plot (the limiting current densities versus the square root of the rotation speed), b) Koutecky-Levich plot (only a few potentials were shown for demonstration purpose). Conditions: 1mM of MMV in a 2M NaCl electrolyte, rotation speeds from 500 to 3000 rpm with an increment of 250 rpm.

Figure C-2: Cycling results of a cell that contained an anolyte with 10mM of MV, a catholyte with 10mM of BTMAP-Fe, and a Fumasep-75 membrane. The current density was 10mA/cm². a) Orange and blue plus...
signs represent the charge and discharge capacities, respectively. Green diamonds represent coulombic efficiency (CE).

![Figure C-3: Photos of a) an IONOMER, b) a Fumasep-75 membrane after being used](image)

Figure C-3: Photos of a) an IONOMER, b) a Fumasep-75 membrane after being used

![Figure C-4: CV voltamogram of an electrolyte containing 1mM BTMAP-FC and 2M NaCl. The blue dashed line represents the potential region in which HER significantly takes place. The result was recorded at 100mV/s.](image)

Figure C-4: CV voltamogram of an electrolyte containing 1mM BTMAP-FC and 2M NaCl. The blue dashed line represents the potential region in which HER significantly takes place. The result was recorded at 100mV/s.
Figure C-5: Photos of the electrode during CV tests. a) the electrolyte contained 100mM MMV, b) the electrolyte contained 1mM MMV. The red circle shows the space around the electrode.
6 REFERENCES


