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Investigation of Pulsed Electrolysis for Hypochlorous Acid Production

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INVESTIGATION OF PULSED ELECTROLYSIS FOR HYPOCHLOROUS ACID PRODUCTION

By

Khoa Van Kieu

B.S. University of Maine, 2021

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Chemical Engineering)

The Graduate School

The University of Maine

May 2023

Advisory Committee:

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INVESTIGATION OF PULSED ELECTROLYSIS FOR HYPOCHLOROUS ACID PRODUCTION

By Khoa Van Kieu

Thesis Advisor: Dr. William J. DeSisto

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
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May 2023

Because of the Covid-19 pandemic along with the delay in the worldwide supply chain, there were disinfectant shortages that lasted for weeks around the world. Therefore, on-site production is a promising solution to satisfy the increasing demand. As more and more people are shifting toward safer and more environmentally friendly products, we are interested in investigating the electrolysis of sodium chloride (NaCl) solution to produce hypochlorous acid (HOCl). Electrolysis is inexpensive as it requires only sodium chloride and electricity, and it does not have any negative impact on the environment. Moreover, electrolysis can be coupled with renewable energy to utilize the excess energy that is hard to store. Meanwhile, hypochlorous acid was proven to be 80-100 times more effective than sodium hypochlorite, commonly known as bleach. Hypochlorous acid was also shown to be a non-toxic, anti-inflammatory, and non-corrosive disinfectant. Since electrolysis is an energy-intensive process, this project will study if using a pulsed direct current to perform electrolysis can improve the current efficiency or electricity requirements of the process. There was evidence showing that pulsed electrolysis was able to improve the electrolysis

efficiency because of the reduction of bubbles coverage, perturbation of the electrical double layer, and enhancement of mass transportation. A flow-through reactor was made with a cathode made from titanium and an anode made from titanium coated with mixed metal oxide (a mixture of Iridium oxide and Tantalum oxide). The squared-shaped pulsed current was generated by utilizing MOSFET. The results showed that pulsed electrolysis increased the number of electrons converted into final products up to 10% more. Pulsed electrolysis also reduced the electricity requirement by 10%-15%. However, it significantly increased the need for sodium chloride because there was no reaction during the off-time. There are several proposed methods to minimize this disadvantage, but more experiments need to be done to assess them. Nevertheless, in the current density range from 2000 to 4500 A/m^2, for the same amount of supplied power, pulsed electrolysis with a duty cycle of 80% required less sodium chloride to produce 1 kg of Cl_2 than conventional constant electrolysis. Although frequency only affected the electrolysis efficiency slightly, operating at the optimized frequency extended the improvement of the pulsed electrolysis compared to the constant electrolysis. Utilizing pulsed electrolysis with the optimized settings can effectively decrease the operating cost of producing disinfectant (hypochlorous acid).

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Bill DeSisto, for all his help and advice through this research and for being so supportive. His sincere guidance leads me to accomplish my research well. I also appreciate all my committee members, Dr. Thomas Schwartz and Dr. Sampath Gunukula, for their support of my research. I also thank Wyatt McDermott and Dr. Andrew Sheaff from the Electrical & Computer Engineering Department at the University of Maine for designing and building the pulsed current generator as well as the control program.

I would like to thank all the members of the Applied Electrolysis Labs for their help and support. I am also grateful to all the graduate students as well as the professors and staff of the Chemical Engineering Department for being so helpful and friendly.

Finally, I would like to express my appreciation to my American and Vietnamese families, especially my mom, for their understanding and assistance, and encouragement.

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CHAPTER 1

INTRODUCTION

1.1 Overview

Due to the Covid-19 pandemic, the global demand for disinfectants increased rapidly.[1] In the meantime, the worldwide supply chain also got interrupted because of several reasons like lockdowns due to the pandemic, war conflicts, etc. In consequence, there were disinfectant shortages that lasted for weeks. One of the main causes is that chemical manufacturers could not get enough raw materials to keep up with the rising demand.[2] Therefore, on-site production of disinfectant is a potential solution. Electrolyzing saline to produce hypochlorous acid as a disinfectant is a promising method because it only requires sodium chloride and electricity, which are inexpensive, and it does not negatively affect the environment. This method also has a broad range of usages like wastewater treatments, water treatments, hand sanitizer, odor control, etc. As researchers suggested that excessive use of disinfectants poses not only several health concerns for humans and animals but also negative impacts on the environment and ecological balance,[3] hypochlorous acid becomes more appealing as an alternative disinfectant. Because hypochlorous acid is a nontoxic and noncorrosive but effective disinfectant.[4] In addition, there is an increase in the demand for environmental-friendly disinfectants, so producing disinfectants by electrolysis may be getting more popular in the future.

Since the electrolysis of saline was discovered and studied for a long time, the thesis will discuss a different approach which is using a pulsed direct current to perform electrolysis instead of a constant direct current in conventional electrolysis. This method is commonly known as pulsed electrolysis. Thanks to the swift improvement of semiconductors and electrical devices in the last few years, we were able to create a low-cost system to generate desired electric pulses. The system allows us to control and monitor closely the behavior of the pulsed current including magnitude, shape, frequency, and duty cycle. Scientists had mixed opinions about whether pulsed current could improve the performance of electrolysis reactions.[5] Hence, this thesis will examine various operating conditions to see if pulsed electrolysis would improve the production of hypochlorous acid.

1.2 Organization

The focus of this thesis is the performance of pulsed electrolysis in terms of the production rate of hypochlorous acid and input requirements (sodium chloride and electricity). This thesis contains the following six chapters. Chapter 1 provides the overview, purposes, and objectives of the research. All the details related to hypochlorous acid, electrolysis of saline, and pulsed electrolysis are reviewed in Chapter 2. Experimental procedures are described in Chapter 3. We will also explain the production system, the reactor design, and the pulse generator. Chapter 4 discusses the comparison between pulsed electrolysis and conventional electrolysis. Chapter 5 reviews the performance of pulsed electrolysis at different frequencies. Finally, the conclusions and future works are summarized in Chapter 6.

CHAPTER 2

ELECTROLYSIS OF AQUEOUS SODIUM CHLORIDE

2.1 Hypochlorous Acid

2.1.1 Overview

The chemical formula of hypochlorous acid is HOCl. Hypochlorous acid is a colorless liquid with a molecular weight is 52.46 g/mol. Although hypochlorous acid is a weak acid (its pKa is about 7.5), it is a strong oxidizing agent.[4] Because HOCl is a weak acid and can be still effective at low concentrations, HOCl is considered a noncorrosive disinfectant.

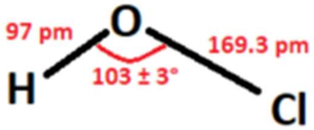

Figure 2.1: Lewis structure of hypochlorous acid

HOCl is produced by white blood cells in mammals to fight effectively against foreign pathogens. In living organisms, HOCl is generated by reacting hydrogen peroxide with chlorine ions and hydrogen ions: $H_2O_2 + Cl^- + H^+ \rightarrow HOCl + H_2O$.[6] Therefore, HOCl is considered nontoxic. HOCl can also be synthesized outside of bodies by using chlorine gas and water: $Cl_2 + H_2O \rightarrow HOCl + HCl$. As HOCl reacts easily with many biological molecules, it can destroy bacteria and viruses in several ways: binding with the unsaturated lipid layer to disrupt cellular integrity, penetrating the cell membrane to damage the nucleic acid of the pathogens, etc.[4]

Despite having many advantages, HOCl is not commonly used nowadays. One of the main reasons is that HOCl is unstable compared to other disinfectants, so it is a challenge to store HOCl for a long time. This research is looking at one of the most promising solutions, which is producing HOCl on-site. By doing so, we can remove the concern about stability as the produced solution can be used up within days or weeks.

2.1.2 pH sensitivity

When dissolved in water, HOCl is always in equilibrium with chlorine gas and hypochlorite ions (OCl^-). In saline solution, the distribution of these chlorine species is a strong function of the solution's pH.

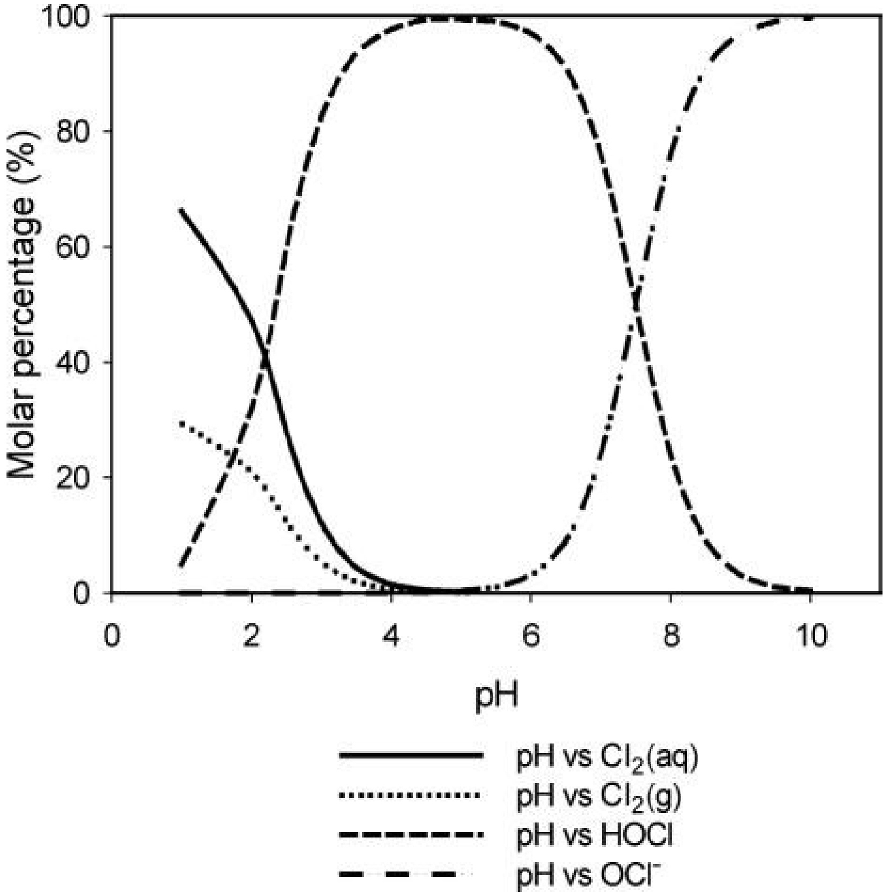

Figure 2.2: Distribution of chlorine species at different pH in NaCl solution[6]

The 3 equations below show the equilibria of HOCl in NaCl solution:

$HOCl \rightleftarrows H^+ + OCl^-$	$pKa = 7.5$
$HOCl + Cl^- + H^+ \rightleftarrows Cl_2(aq) + H_2O$	$K1 = 9.6 \times 10^2\ M^{-2}$
$Cl_2(aq) \rightleftarrows Cl_2(g)$	$K2 = 10.87\ atm\ M^{-1}$

According to Figure 2.2, low pH (<2) favors the formation of aqueous Cl_2. Aqueous Cl_2 can convert to Cl_2 gas and escape out of the solution, resulting in a decrease in active chlorine concentration. For safety purposes, the pH of the solution should not be lower than 4 as dangerous chlorine gas starts to form. The optimized pH range is from 4 to 6 because the molar percentage of HOCl is almost 100%. For pH > 5, there is no more chlorine gas but OCl^- starts forming. The formation of OCl^- does not pose any threat but it reduces the efficacy of the solution as OCl^- is less effective than HOCl. Therefore, the pH of the solution should be maintained below 7 so that HOCl is the predominant species in the solution.

2.1.3 Why is HOCl a better disinfectant than bleach?

Sodium hypochlorite (NaOCl), commonly known as bleach, is another form of HOCl in NaCl solution. Although the two species are very similar and can be easily transformed into each other, HOCl is ideal to use as a disinfectant because it has many advantages over NaOCl. Firstly, HOCl is shown to be 80-200 times more effective at disinfecting than bleach.[7] In other words, HOCl not only can kill more pathogens effectively, which means reducing the bacterial concentration to a lower concentration, but also it can destroy the pathogens much faster than OCl^-.[6] Therefore, HOCl requires a much lower concentration than NaOCl to achieve the same disinfection effect.

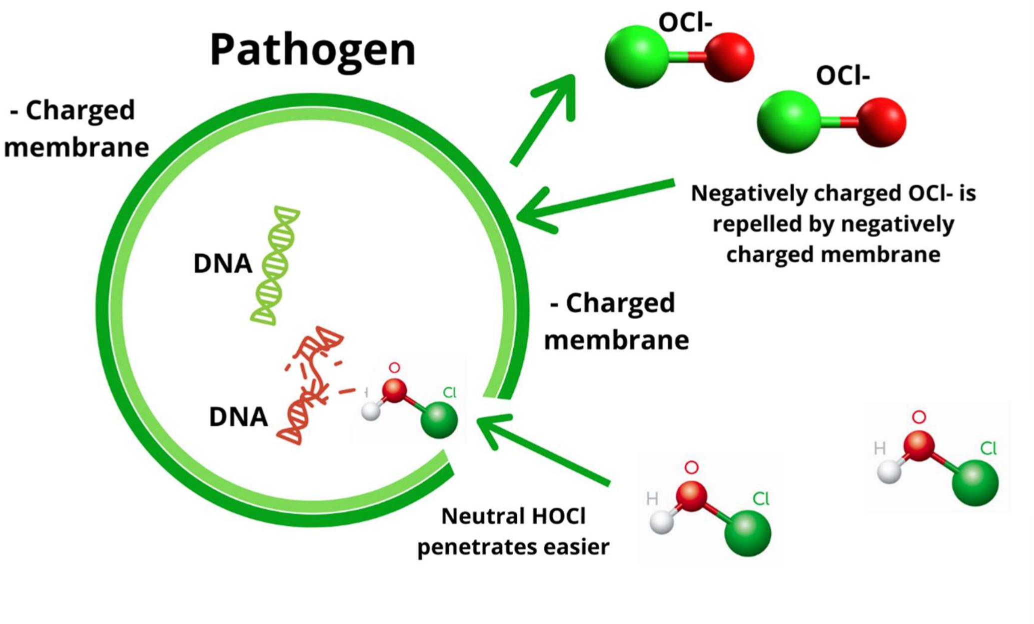

Figure 2.3: Proposed mechanism of the penetration cell walls of HOCl and OCl^-.[8]

One of the main reasons for this advantage of HOCl is the molecular charge. Although both hypochlorous acid and hypochlorite ions have relatively low molecular weight, HOCl is a neutral molecule while OCl^- is negatively charged. In general, the cell walls of pathogens are negatively charged. Therefore, OCl^- is repelled by the cell walls, so it is difficult for OCl^- to get inside bacteria or viruses. On the other hand, HOCl is not repelled by the cell walls as it does not hold any charge. As result, HOCl can easily penetrate the cell walls and kill the pathogens effectively from the inside by disrupting their DNA/RNA.

The second advantage of hypochlorous acid is that it is much safer to use than bleach. Bleach is a highly corrosive solution due to its high concentration, which results in a high pH of about 12-13. Meanwhile, HOCl is not corrosive because of the low required concentration and neutral pH. The low concentration also mitigates the hazards from dangerous side reactions as both HOCl and OCl^- are strong oxidizing agents. One research showed that HOCl has very low cell toxicity and a high therapeutic index.[6] In other words, it is safe to use HOCl for medical purposes. The same research also showed the safe usage of HOCl by using animal models: no irritation, no sensitization, no systemic toxicity for extended usage, and histopathology consistent with wound healing.[6]

As HOCl is more effective and safer than bleach, it has great potential for reducing operating costs. The lower required concentration may not only reduce the material cost but also the cost of dechlorination, especially in water and wastewater treatment. The safety of HOCl can help to reduce the cost of hazard prevention and treatment. For example, users can lessen the requirement of expensive personal protective equipment, decrease the number of high-priced sensors or alarms, or it may be less troublesome to clean up a leakage, etc.

2.2 Conventional Electrolysis

2.2.1 Overview

Conventional (constant) electrolysis is applying constant direct current to drive non-spontaneous chemical reactions. It is used in several industrial processes such as electrometallurgy, electro-refining, and electroplating. The industrial process that produces chlorine by constant electrolysis is called the chlor-alkali process. The required components for electrolysis are an electrolyte, electrodes, and a power supply. Occasionally, a partition, which can be an ion-exchange membrane or a salt bridge, is used to prevent the mixing of products from opposite electrodes.

An electrolyte is a substance or mixture that can conduct electricity and allow ions to move freely. Electrolytes are almost always liquid. The two ways to make liquid electrolytes are mixing compounds with solvent to form mobile ions or melting ionic compounds. The external power source must provide direct current as alternating current cannot facilitate electrolysis reactions. Electrodes are where chemical reactions happen. They are immersed in the electrolyte and connected to the power source. A suitable separated distance between electrodes is needed to allow current to flow through the electrolyte. A great variety of materials can be used for electrodes including metal, graphite, semiconductors, and polymer. Electrode materials can be identified based on chemical reactivity, selectivity, and cost. There are two kinds of electrodes: cathode and anode. A cathode is a negatively charged electrode that attracts cations, while an anode is a positively charged electrode that attracts anions.

The key process of electrolysis is exchanging electrons between atoms and ions due to the applied current. The quantity of the products is proportional to the applied current. At the cathode, reduction reactions occur, in which cations or neutral molecules receive electrons from the cathode to convert to products. On the other hand, at the anode, oxidation reactions happen, in which anions or neutral molecules transform into products by giving up electrons to the anode. Therefore, the electrical circuit consists of the movement of ions in electrolytes and the flow of electrons between the cathode and the anode. Reduction and oxidation reactions are always coupled together, so the product quantity at the two electrodes must follow the overall reaction stoichiometry. In addition, the desired products of electrolysis usually can be separated by mechanical processes as they are formed in different phases (gas or solid) from the electrolyte.

2.2.2 Production of hypochlorous acid by conventional electrolysis

Chemical Reactions:

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ $E° = 1.3583$ V

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E° = -0.8277$ V

Formation of hypochlorous acid: $Cl_2 + H_2O \rightarrow HOCl + HCl$

The production of chlorine using electrolysis, known as the chlor-alkali process, has been commonly used in the industry for a long time. In the chlor-alkali process, pH is purposely kept at a low value to ensure that the produced chlorine gas would not dissolve in water. Therefore, to produce hypochlorous acid, the only difference is to maintain the pH at about neutral, the best range of pH is from 5 to 6. The production of chlorine using electrolysis is an energy-intensive process; the yearly electricity consumption is estimated to be about 150 TWhr.[9] Hence, even small improvements in energy efficiency could help to reduce operating costs significantly.

Nowadays, the most common method to produce hypochlorous acid involves the electrolysis of aqueous sodium chloride (NaCl solution). When dissolved in water, NaCl separates into sodium cations (Na^+ ions) and chloride anions (Cl^- ions). Then, Cl^- ions will be attracted to the anode, where they get oxidized (losing electrons) to form chlorine gas. The gas immediately reacts with water to produce HOCl. Meanwhile, the cathode pulls hydrogen ions from water molecules and reduces them to form hydrogen gas, which can be considered a valuable by-product. An ion-permeable ion-exchange membrane can be used to prevent the OH^- ions from passing through the other side, where they could increase the pH of the HOCl solution. Another way to maintain the desired pH is by adding acids like hydrochloric acid or acetic acid directly into the produced solution.

2.2.3 Important parameters

As the two inputs for the electrolysis process are sodium chloride (NaCl) and electricity, the performance of the process can be evaluated by using only a few parameters. In this project, we will focus on three important parameters:

- Current efficiency: the fraction of electrons converted to product.

- Sodium chloride usage: the ratio between the amount of NaCl in the feed and the amount of HOCl produced. As the system is flow-through, the majority of NaCl in the feed exits the system without converting into the final product. However, the amount of NaCl in the feed also determines the conductivity of the solution in the reactor, which is directly related to the production rate of hypochlorous acid. Therefore, an excess amount of NaCl is needed. NaCl usage is the required amount of NaCl to ensure the desired production rate of hypochlorous acid for a continuous reactor, at a specific current density.
- Electrical usage: the ratio between the amount of supplied power and the amount of produced HOCl.

Both NaCl usage and electrical usage can directly affect the operating costs of the process. Thus, the lower the usage is, the better the performance of the system is. The NaCl usage depends on the concentration of NaCl in the feed. Because NaCl is a strong ionic compound, the higher the concentration of NaCl is, the higher the conductivity of the solution is. The higher conductivity would reduce the required power, which leads to lower electrical usage. On the other hand, the higher the applied current is, the more NaCl in the feed is converted into the HOCl, which results in lower NaCl usage. But the higher current increases the required power. Therefore, NaCl usage and electrical usage are interconnected, changing one will result in a change of the other.

2.3 Pulsed Electrolysis

2.3.1 Pulsed Direct Current

Pulsed direct current (pulsed current) is a direct current that changes in values but never changes direction, in other words, its value is never negative. Because only direct current can be used in electrolysis, it is necessary to clarify that pulsed current is not the same as alternating current. Although both pulsed current and alternating current have changing values, alternating current does change direction, i.e., it has negative values. There are two ways to generate pulsed direct current: pulsing voltage and pulsing current. In this research, only pulsing voltage was studied.

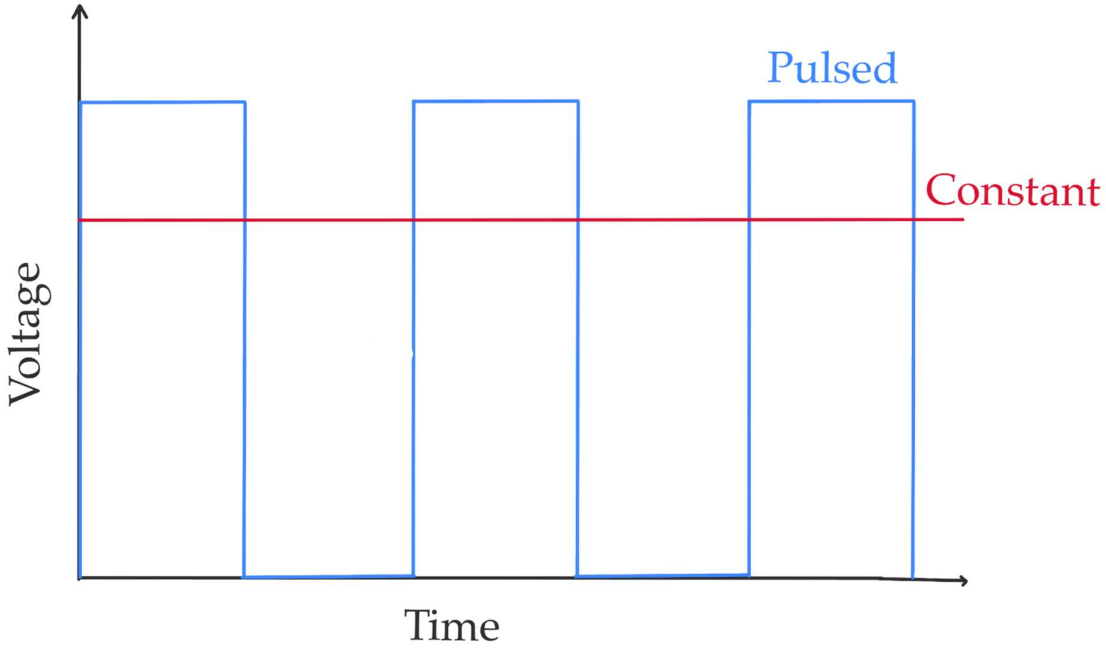

Figure 2.4: Simplified illustration of pulsed direct current

Pulsed current has some important characteristics that this thesis will pay attention to:

- Magnitude of current: the amount of charge (electron) passing through a cross-section of a conductor per unit of time.
- Shape: the shape of voltage/current pulses.
- Frequency: the number of times that current turns on and off per second.

- Duty cycle: the percentage of time that electricity is flowing through the reactor, i.e. the percentage of on-time.

Pulsed electrolysis is simply applying pulsed current instead of constant current to drive non-spontaneous chemical reactions forward.

2.3.2 Overview of pulsed electrolysis

Although pulsed electrolysis technology has been around for a long time, research papers still show conflicting conclusions about its advantages.[5] Majority of researchers agreed that pulsed electrolysis is a promising method to improve the efficiency of electrolysis reactions. But some scientists pointed out that the compensation during off-time outweighed the enhancement during on-time. There are several proposed possible reasons for the improvement of efficiency. Mazloomi et al. studied the many factors that can affect the electrical efficiency of electrolytic hydrogen and one of them was bubble coverage.[10] The paper stated that the accumulation of gas bubbles on the surface of electrodes will reduce their conductivity, which causes bigger ohmic losses. Moreover, the formation of bubbles also reduces the active surface area of electrodes and pushes the electrolyte away from the electrode's surface.[10] Pulsed electrolysis provides the off-period for the bubble to diffuse away from the electrode's surface. Therefore, it has the potential to improve electrical efficiency.

Pulsed current also creates perturbation of the electrical double layer (EDL), which potentially enhances the electrolysis efficiency.[5] Several studies showed that a significant current kept flowing for a short time after disconnecting the applied voltage.[11,12] The proposed cause for this phenomenon was thought to be the discharge of ions from the EDL after the disappearance of the external electric field. Later on, another research showed an observation of a high but short-lived current spike when a voltage was applied to an electrochemical system.[13] This phenomenon was again attributed to the EDL, which increases the current by charging and discharging the first ionic layer.[5] Because of these two effects of EDL, pulsed electrolysis could improve the overall efficiency of the electrolysis system.

Another possible reason is the improvement of mass transfer. The rate of electrolysis depends on the electrolyte transfer rate. One research on alkaline water electrolysis concluded that pulsed current reduces the mass transfer limitation caused by oxygen and hydrogen bubbles, which decreased energy consumption by about 20-25%.[10] Another paper showed that during off-time products moved away from the electrodes while reactants migrated to the surface and built up the concentration. Due to a greater concentration of reactant on the surface of the electrodes, the overpotential of the electrolysis was minimized. As result, the electrolysis efficiency was enhanced by the pulsed current.[14] Another research indicated several folds improvements in the overall rate of the electro-oxidation of formic acid by using pulsed voltage.[15]

However, pulsed electrolysis has a clear disadvantage which is the off-time. Commonly, the voltage of the system during the off-time is 0 V or a value lower than the cell voltage of the electrolysis reactions. Therefore, during the off period, the current does not flow through the system and electrolysis reactions cannot occur. Consequently, the average value of pulsed current can never be higher than the average value of constant current despite the higher value during on-time. In other words, the average rate of pulsed electrolysis cannot be greater than the rate of constant electrolysis.[5] Some results even showed that the electrical enhancement during the on-time was lower than the loss during the off-time.[16]

2.3.3 Pulsed electrolysis production of hypochlorous acid

Currently, we have not found any work that focuses on the production of hypochlorous acid. However, there are quite a lot of publications discussed using pulsed electrolysis to improve the production of hydrogen gas. As mentioned above, the production of H_2 and the production of HOCl are stochiometric. Therefore, improving the efficiency of the production of H_2 should also result in better efficiency of the production of HOCl. In the study about the performance of pulsed electrolysis of alkaline water, Demir et al. concluded that pulse potential created pumping effects that improved the mass transport of hydrogen and oxygen bubbles.[17] As chlorine gas is produced in the electrolysis of sodium chloride solution, improving the mass transport of chlorine bubbles will reduce the corrosion/degradation of the anode because chlorine gas has less contact with the anode. Demir et al. also showed a reduction of 20-25% energy consumption per 1 mol of hydrogen produced thanks to the lower mass transport limitation around the electrode surface.[17] Mandal et al. observed an improvement in hydrogen production rate while using pulsed electrolysis KOH solution with the on-voltage of 12.65 V: pulsed electrolysis has a production rate of 0.31 $ml.min^{-1}.cm^{-2}$ during on-time compared to 0.25 $ml.min^{-1}.cm^{-2}$ of constant electrolysis.[18] Another paper showed that pulsed electrolysis increased the production rate of hydrogen. For a 10% duty cycle at 2 V, the production rate of hydrogen was 1.04 $ml.min^{-1}.cm^{-2}$ during on-time, which was higher than the value of 0.88 $ml.min^{-1}.cm^{-2}$ of constant electrolysis.[19] Therefore, pulsed electrolysis is a promising method to improve the efficiency of the production of HOCl.

CHAPTER 3

EXPERIMENTATION

3.1 Reactor Design

3.1.1 Reactor's components

The reactor was designed to be cost-effective, so most of the parts can be purchased easily in plumping stores, except for the cathode and anode. The reactor was well sealed to make sure there would not be any water leaking. It is easy to assemble with different cathodes and anodes. Moreover, this reactor is easy to connect to the flow system and capable of sizing up to a commercial scale.

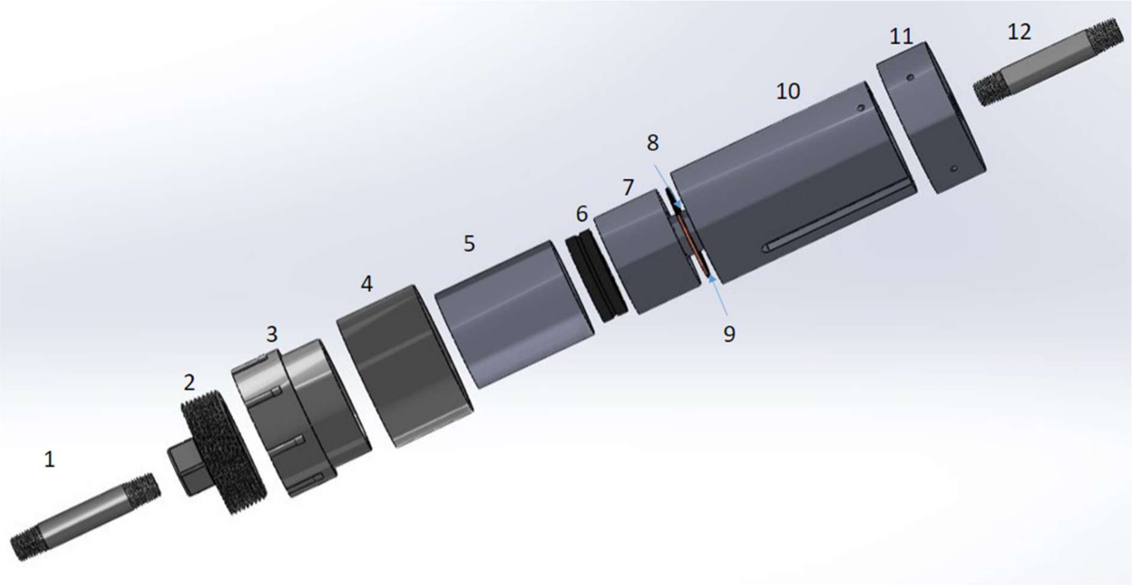

Figure 3.1: Drawing of prototype 1 of the reactor.

Parts List:

1. ¼ inch pipe nipple, 3 inch long, PVC
2. 2 inch pipe threaded plug, PVC

3. 2 inch pipe male cleanout, PVC*
4. 2 inch pipe coupling, PVC*
5. Machined lower flange, chemical resistant PVC
6. 5-hole anode (does not include silver wire connector)
7. Machined upper flange, chemical resistant PVC
8. 1 inch pipe bushing, PVC**
9. Copper ring for cathode electrical contact***
10. Reactor casing, 2 inch pipe, PVC
11. 2 inch pipe cap, PVC
12. ¼ inch pipe nipple, 3 inch long, PVC

*can use 2 inch pipe female cleanout to substitute for 3 and 4

**this bushing is cut to fit to allow room for thread travel

*** cathode pins not shown

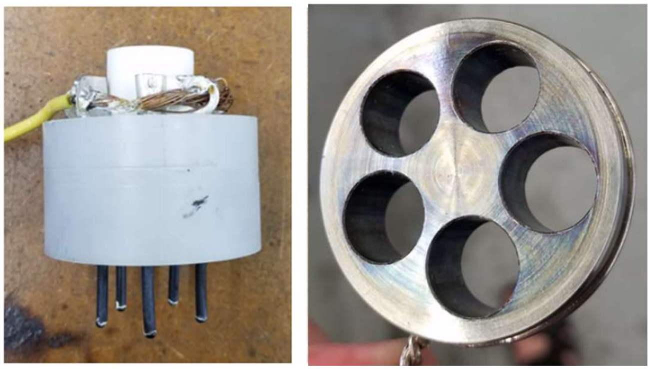

Figure 3.2: Structure of the electrodes

The picture on the left is anodes. The picture on the right is a cathode.

A cathode is simply a piece of material with 5 drilled holes as shown in Figure 3.2. An anode is a pin or ribbon that sits in the middle of one of the 5 holes of the cathode.

3.1.2 Materials of cathode and anode

The cathode was made from titanium. There were several reasons to pick titanium for the cathode. Firstly, titanium has good conductivity, and it is also cheaper than other common conductors like silver, platinum… Secondly, titanium can withstand high current density and high temperature for a long-extended period. Lastly, titanium has great resistance to corrosion and oxidation. This is extremely necessary as the solution in the reactor contains several reactive chemicals such as hypochlorous acid, chlorine gas, sodium hydroxide, etc. On the other hand, the anode was made from titanium coated with mixed metal oxides purchased from Telpro, which is a mixture of Iridium oxide (IrO_2) and Tantalum oxide (Ta_2O_5). This material has the same advantages as titanium. Moreover, mixed metal oxides are commonly used in chloro-alkali technology because it was shown to improve the efficiency of the electrolysis of sodium chloride solution.[20]

3.2 Pulsed current generator

The pulsed current generator was designed and made by an Electrical engineering student (Wyatt McDermott) and an Electrical & Computer Engineering Professor (Andrew Sheaff) at the University of Maine, Orono. Professor Sheaff also provided a computer program that can be used to control and monitor the generator. The pulsed current generator consists of three main components: an external power supply, a reactor driver, and a controller. The three components are indicated in Figure 3.3. The present pulsed current generator is only capable of creating rectangular pulses. The advantages of rectangular pulses include being simple to generate, easy to monitor and measure, and consistent and repeatable. The generator can only create one specific shape of pulses, so to create pulses with another shape, a new generator needs to be built. The external power supply must be a DC power source that can provide up to 20 A or 18 VDC. The reactor driver and the controller are powered by a computer via USB connections.

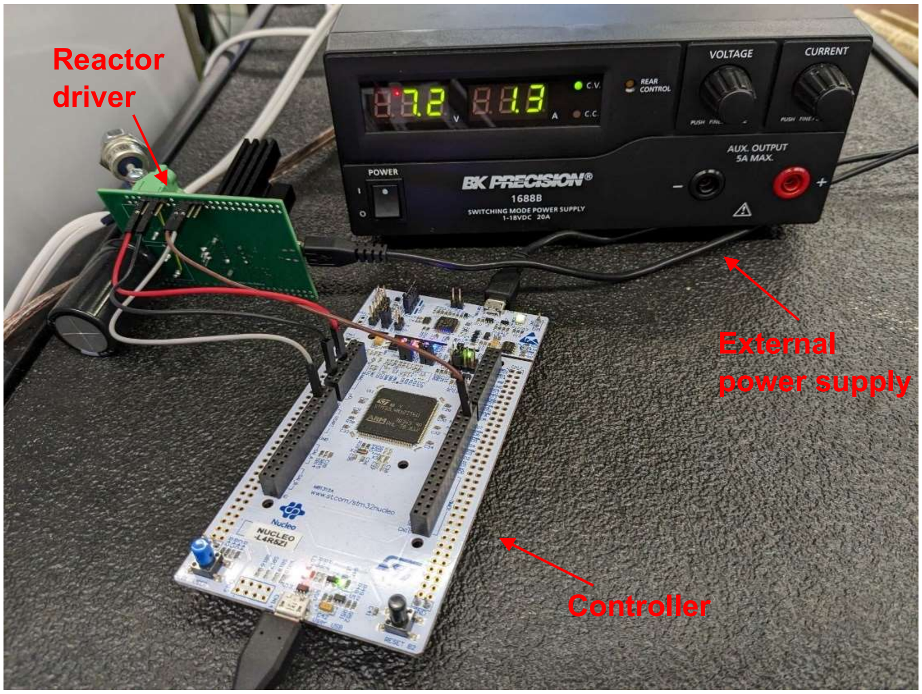

Figure 3.3: Pulsed current generator.

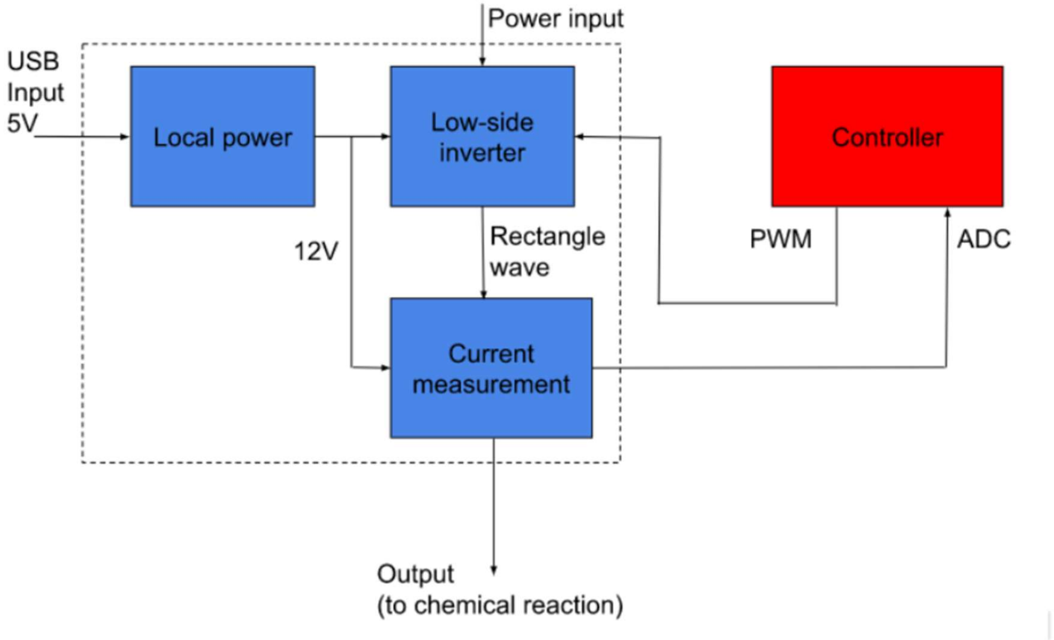

Figure 3.4: Functional block diagram of the pulsed current generator.[21]

The reactor driver was built on a single 5-layer printed circuit board (PCB), which consists of a local power, a low-side inverter, and a current measurement (all are shown as blue components in Figure 3.4). High-side and low-side refer to where components or groups of components are placed in a circuit, in other words, they essentially just specify whether the component is connected to the higher or lower voltage in the circuit. The low-side is between the electrolysis reactor and the ground, while, the high-side is between the power supply and the reactor. The local power was created from a boost converter that takes a 5 V, 2.1 A (max) USB input and outputs 12 V, which powers the gate driver integrated circuit (IC) of the low-side inverter. An analog devices switching voltage regulator was built into the boost converter. The low-side inverter creates the rectangle waveform by connecting and disconnecting the reactor from the ground connection. A low-side inverter is used because it is easier to do electronics-wise. The DC voltage output of the device is set by the external power supply's voltage. The main element of the low-side inverter is metal–oxide–semiconductor field-effect transistor (MOSFET). The rectangular current pulses are created by toggling a MOSFET on and off between the low-side of the load and the ground. Although the reactor only operates at a current lower than 20 A, the MOSFET was designed to withstand a current of up to 60 A for robustness. The MOSFET attaches to a large heat sink to minimize the temperature increase due to the heat loss by switching on-off continuously. The MOSFET needs a 12 V signal to switch, so it requires gate drivers to connect the controller and the MOSFET. It is helpful to describe the system in terms of signal flow. A 3.3 V pulse width modulated (PWM) signal is provided by the controller to set both the frequency and duty cycle of the output rectangular wave. Next, the gate driver IC receives the 3.3 V PWM signal and increases the high-state voltage to 12 V so that it is able to switch the MOSFET. On the other hand, the MOSFET also receives a current flow from the external power supply. Therefore, by switching on and off, the MOSFET can generate rectangular current pulses with the desired magnitude set by the external power supply as well as the same duty cycle and frequency as the PWM signal set by the controller.

Current measurement was implemented with a microcontroller integrated circuit. It amplifies a small differential voltage across a 2 mΩ resistor to a value between 0 and 3.3 V. Then, an analog-to-digital conversion (ADC) input on the controller receives the amplified signal. As we assume chemical reactions in the electrolysis reactor are purely resistive loads, the current magnitude is calculated from the received voltage signal by using Ohm's law.

The controller is a microcontroller integrated circuit connected to a computer that has software written by Dr. Andrew Sheaff. The software is used to set the frequency and duty cycle of the 3.3 V PWM. It is also calibrated to calculate the current measurement of the system. After performing the current calculation, the software displays the results on a python graphical user interface (GUI) via a USB connection to the computer. Thanks to this graph, we can observe how the current may vary during the run time. Moreover, the software also records and stores the results of the current measurement on the hard drive of the computer as an MS Excel file.

3.3 Measuring chlorine concentration

The concentration of hypochlorous acid in the product solution is determined by measuring the total chlorine concentration, which equals the concentration of the free and the combined forms of chlorine. As the raw material is made from only salt and deionized water, there is not any chlorine in the solution before the electrolysis process. Therefore, we assume all of the chlorine in the solution after the reaction is HOCl or OCl^-, which can be converted to HOCl. The total chlorine concentration is measured by using the iodometric method with Hach's digital titrator. Free iodine is released proportionally to the amount of total chlorine present when potassium iodide is introduced to a sample containing chlorine at a pH lower than 8. Then, sodium thiosulfate is used to titrate the iodine.[22]

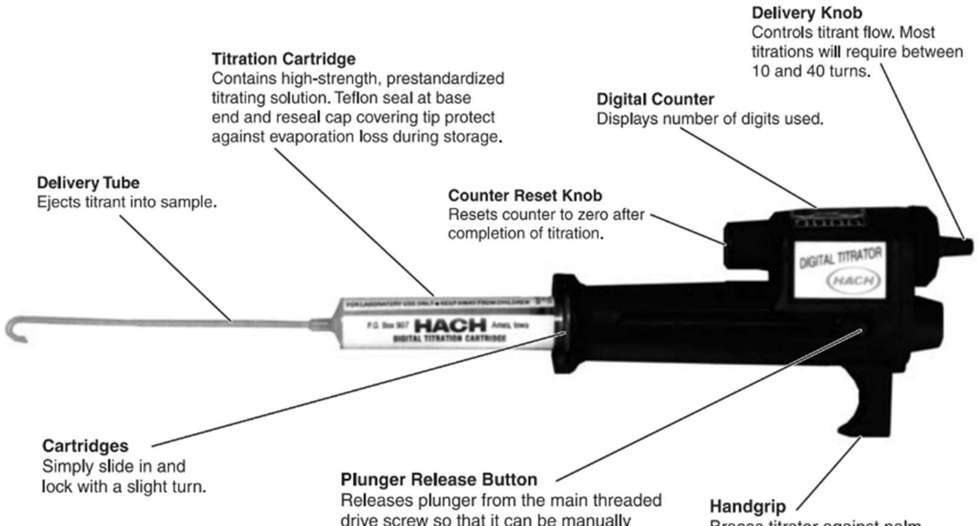

Figure 3.5: Hach Digital Titrator[22]

The test kit purchased from Hach includes a titration body, 0.113 N sodium thiosulfate titration cartridge, dissolved oxygen 3 powder pillows, potassium iodine powder pillows, and starch indicator solution. Based on the expected chlorine concentration, a sample volume can be chosen. The titrator is assembled by connecting a clean delivery tube and the titration cartridge with the titrator body. Then, the delivery tube is flushed with the titration solution. The counter of the titrator should be reset to zero. The chosen amount of sample is mixed with deionized water to make 50 mL of solution in a 125-mL Erlenmeyer flask. One dissolved oxygen 3 powder pillow and one potassium iodine powder pillow are added to the flask and mixed well. The titrator is placed on top of the flask so that the delivery tube tip is immersed in the solution. Then, sodium thiosulfate is added slowly while the flask is being swirled until the solution is a pale yellow. One dropperful of starch indicator solution is added and mixed well. As result, the solution should turn to a dark blue color. Next, the titration continues until the solution changes to colorless. The total chlorine concentration (unit of mg/L) is calculated by multiplying the reading from the titrator with the digits multiplier that matches the chosen sample volume. After finishing the measurement, the titrator should be detached into individual parts for storage, and the delivery tube should be rinsed with deionized water and dried.

3.4 Experiment Setup

All the experiments were carried out in batch mode for better control of the operating conditions. The total volume of the input solution was 6 L, which was fed manually into the system before starting any reaction. The sodium chloride concentration for every run was 2% w/w sodium chloride in water (20 g of NaCl per 1 L of solution). The sodium chloride solution was made by mixing 120 g of NaCl with deionized water such that the final volume was 6 L. Deionized water should be used to minimize the effects of other ions and microorganisms in tap water on the performance of the production of hypochlorous acid. All experiments were run at a constant voltage set by the external power supply. This meant the voltage remained constant during the whole run while the current was varying based on the performance of the reactor. For a constant electrolysis experiment, the reactor was connected directly to the external power supply. For a pulsed electrolysis experiment, the reactor was connected to the external power supply by using the pulsed current generator. The frequency and duty cycle of the pulsed current were controlled by using the software provided along with the pulsed current generator. The run time of every experiment was 1 hour. Temperature and pH were monitored during the run time. The concentration of hypochlorous acid was measured right after the 1-hour run finished. The system was drained and then rinsed with deionized water for about 10-15 minutes between each run.

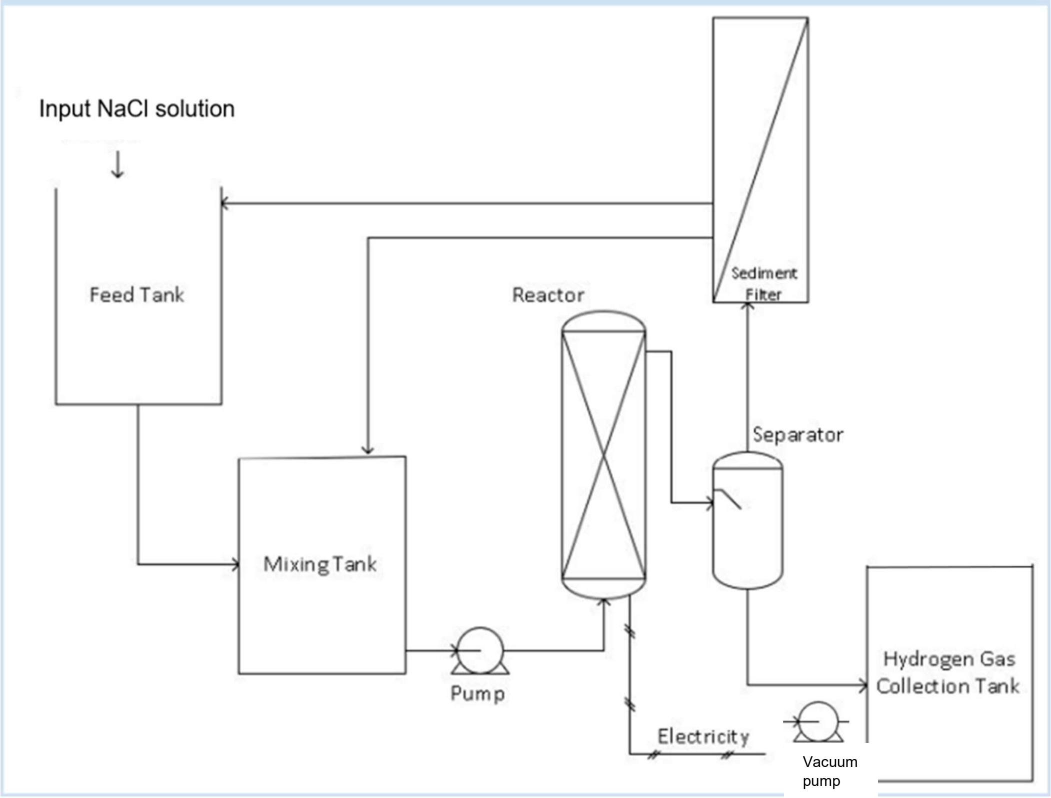

Figure 3.6: Flow diagram of the electrolysis system

This flow diagram helps to visualize flows of raw materials and products in our electrolysis system. The initial NaCl solution was manually fed into the feed tank. Then, the solution flew down to the mixing tank as the feed tank was located higher than the mixing tank. Next, the solution was pumped through the reactor, which connected to the power supply. Here, the electrolytic reactions occurred to form a mixture of hypochlorous solution and hydrogen gas. The product mixture was pushed through a gas separator that contained a gas filtration membrane to separate the hydrogen gas out of the HOCl solution. The hydrogen gas was pulled into a hydrogen gas collection tank by using a vacuum pump. On the other hand, the HOCl solution continued to go through a sediment filter to remove any solid particles in it. Finally, the HOCl solution was recycled back into both the feed tank and the mixing tank. However, the flow from the sediment filter to the feed tank could be redirected to remove part of the produced HOCl solution so that it became a continuous flow system instead of a recycling loop.

The hydrogen gas collection tank could be purged so the tank would not build up pressure that might harm the vacuum pump. Both the gas filtration membrane and the sediment filter should be replaced with new ones every 4-6 months to ensure the performance of the system. Because hydrogen gas is highly flammable and there is a possibility of chlorine gas formation, there should be a running hood/venting system during every experiment. In addition, our electrolysis system contained a hydrogen gas sensor to detect any hydrogen gas leakage in order to prevent fire as electric sparks were created sometimes.

CHAPTER 4

COMPARISON THE PERFORMANCE BETWEEN CONVENTIONAL ELECTROLYSIS AND PULSED ELECTROLYSIS

4.1 Relationship between electrical usage and NaCl usage

As mentioned above, NaCl usage is the required mass of NaCl to produce 1 kg of Cl_2 and electrical usage is the supplied power in kWhr to produce 1 kg of Cl_2 in a continuous reactor. The required electrical power was calculated by multiplying the applied voltage with the average current. According to Ohm's law (V = RI), the average current depended on the applied voltage and the resistance of the system. Since the voltage was always set as constant during a run, the average current of the experiment was determined by the resistance of the system. Several factors that could affect the overall resistance of the system: the reactor, the connections between the power supply and the reactor, and the conductivity of the fed NaCl solution. Because the same reactor and power supply were used for all of the experiments, they should not make any difference between different operating conditions. Therefore, the conductivity of the NaCl solution was the factor that varied the average current the most. The conductivity of the NaCl solution was mainly controlled by the initial concentration of NaCl in the feed. Although temperature could also significantly affect the conductivity, we neglected its effects because the differences in temperature between experiments were small. As NaCl fully dissolved in water, the higher the concentration of NaCl was, the better the conductivity of the solution was. For that reason, the higher the concentration of NaCl in the feed was, the lower the overall resistance of the system was. Consequently, increasing the concentration of NaCl reduced the electrical usage of the system because it would require less voltage to reach the same average current. On the other hand, the NaCl usage depended on the concentration of NaCl in the feed and the average current of the reactor. Because the current was the limiting agent of the electrolysis reaction, the higher NaCl concentration led to a more excessive amount of NaCl in the system, which resulted in higher NaCl usage. Increasing the average current meant increasing the number of electrons flowing through the reactor. Therefore, more Cl^- ions were converted to the HOCl, which resulted in lower NaCl usage. In conclusion, NaCl usage and electrical usage depended on each other, in other words, changing one would result in the change of the other. Both NaCl usage and electrical usage were directly related to the operating cost of the electrolysis system. Hence, to improve the operating cost of the system, we should minimize both NaCl usage and electrical usage.

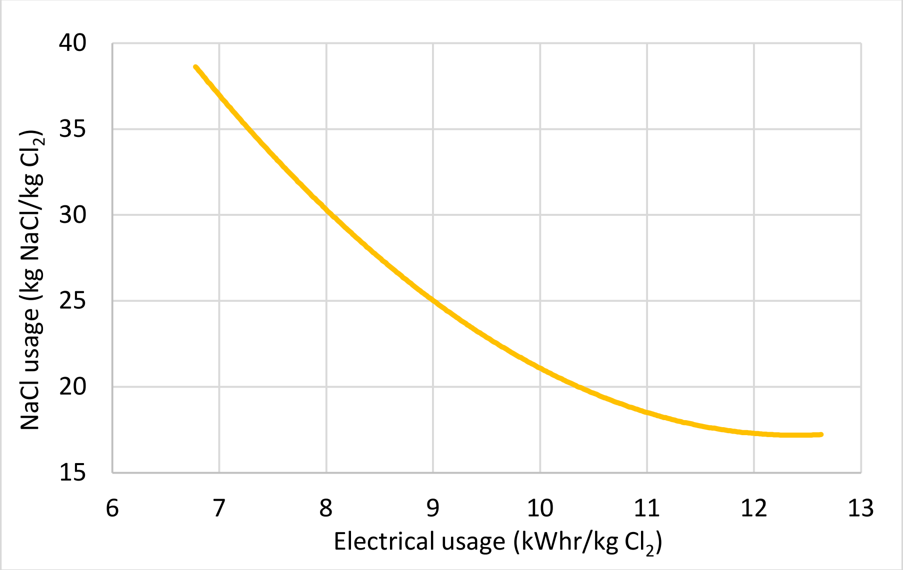

Figure 4.1: The relationship between NaCl usage and Electrical Usage for all experiments of pulsed electrolysis with a duty cycle of 80%.

Figure 4.1 shows the relationship between NaCl usage and electrical usage of pulsed electrolysis with a duty cycle of 80%. We observed that indeed NaCl usage and electrical usage depended on each other. In other words, increasing the electrical usage would decrease the NaCl usage. In addition, this relationship between NaCl usage and electrical usage was observed in both pulsed electrolysis and conventional constant electrolysis. Their relationship was non-linear so there were limits to the trade-off between NaCl usage and electrical usage.

When the NaCl usage was lower than 18 kg NaCl per 1 kg Cl_2, the curve started to flatten out. This meant an extremely large amount of power would be required to reduce the NaCl usage to lower than 18 kg NaCl per 1 kg Cl_2. On the other hand, a similar thing happened when the electrical usage was lower than 7 kWhr per 1 kg Cl_2. A lot of additional NaCl was required to reduce the electrical usage to below 7 kWhr per 1 kg Cl_2. As the price of NaCl and electricity vary from state to state, the location will play an important role in optimizing the operating cost of the system.

4.2 Results

The performance of constant electrolysis was compared to the performance of pulsed electrolysis at various duty cycles. The performances of different duty cycles were also compared to each other. As mentioned above, the three main parameters used to evaluate the performance were current efficiency, NaCl usage, and electrical usage.

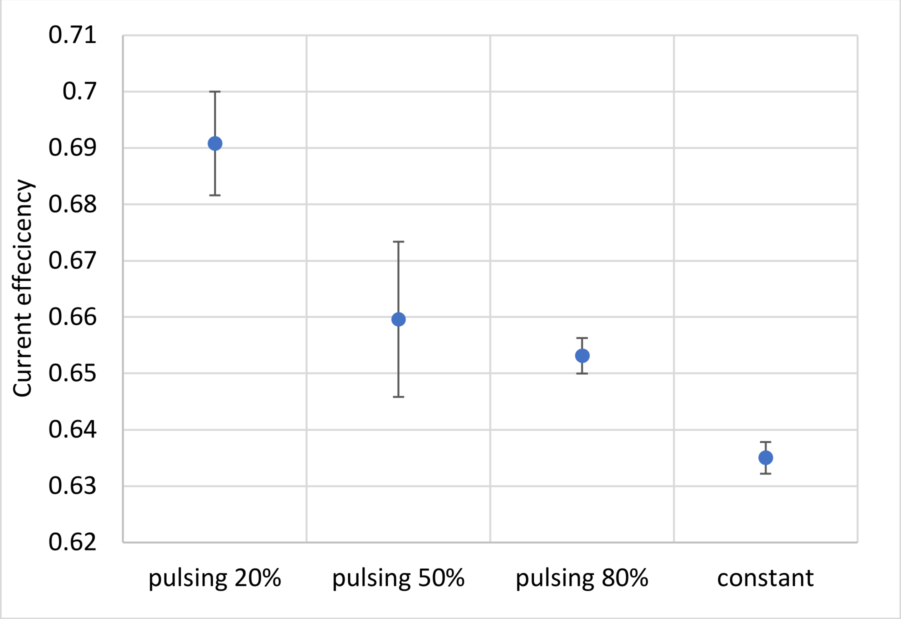

Figure 4.2: Comparison of the current efficiency between different electrolysis conditions (constant and pulsed current with duty cycle of 20%, 50%, and 80%) at current density of about 4000 A/m^2. Error bars represent the 95% confidence interval.

According to Figure 4.2, the pulsed electrolysis increased the current efficiency of the system compared to the constant electrolysis. Moreover, the lower the duty cycle was, the higher the efficiency was. And by looking at the 95% confidence intervals, the differences in current efficiency between pulsed electrolysis and constant electrolysis were statistically significant. The current efficiency of pulsed electrolysis with a duty cycle of 20% increased by 0.06 compared to the constant electrolysis, which was about a 10% relative improvement. For the duty cycle of 50% and 80%, although the improvement was not as high, it was still significant (about 3-4% relative improvement). The higher current efficiency meant that pulsed electrolysis was able to convert more electrons flowing through the reactor to the final product HOCl. This improvement could be attributed to the enhancement of the reduction of the formation of bubbles and improvements in mass transfers.[10] For constant electrolysis, bubbles were continuously formed and covered part of the electrodes, which decreased the chance for electrons to react with Cl^- ions in the solution. However, for pulsed electrolysis, there was an off-time when bubbles were removed away from the electrodes. This increased the active surface area of the electrodes, which resulted in improving the chance of electrons reacting with ions. In addition, it lowered the resistance allowing more current to flow under the same voltage. Moreover, the lower duty cycle also decreased the sizes of bubbles,[5] so it enhanced the solubility of the produced Cl_2 gas in water, which minimized the loss of product into the atmosphere. Besides reducing the mass transfer limitation of bubbles, pulsed electrolysis also lessened the mass transfer limitation of the ions and molecules in the solution. During every off-period, the concentration of the reactants was replenished, which led to a higher reaction rate during the on-time.[14] The lower duty cycle, which had a longer off-period, kept the concentration of reactants relatively high compared to the higher duty cycle or constant current. Because of the two discussed reasons, the pulsed electrolysis greatly improved the current efficiency.

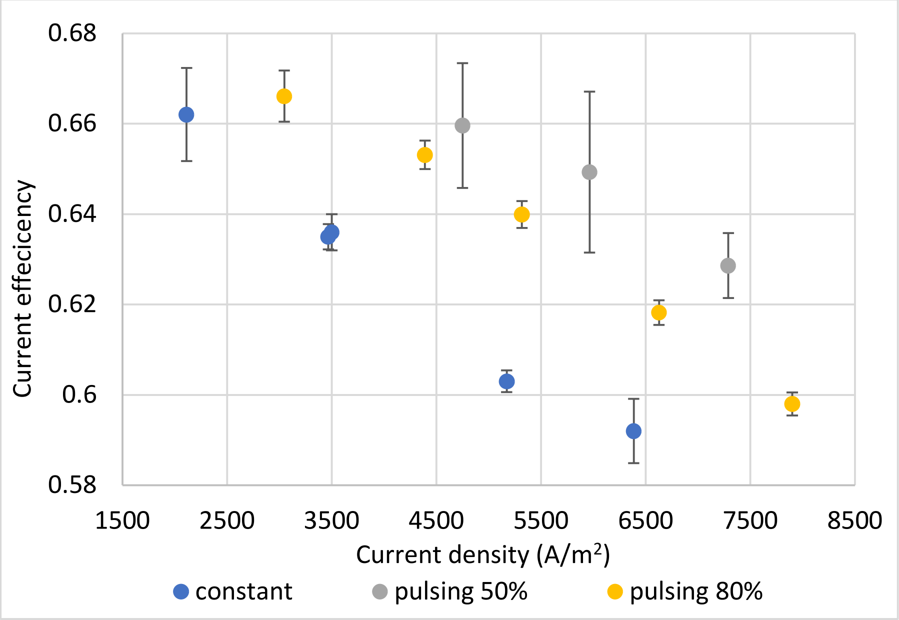

Figure 4.3: The relationship between the current efficiency and the current density at various electrolysis conditions (constant and pulsed current with duty cycle of 50% and 80%). Error bars represent the 95% confidence interval.

Figure 4.3 showed that pulsed electrolysis was able to improve the current efficiency of the system at all current densities. The pulsed electrolysis with a duty cycle of 50% and 80% had an average of 8% and 5% relative improvement compared to constant electrolysis respectively. Figure 4.3 also showed the agreement with Figure 4.2 that the lower the duty cycle was, the better the current efficiency was.

Another observation was that the current efficiency reduced when the current density increased in both pulsed electrolysis and constant electrolysis. The current density was increased by increasing the current flowing through the reactor, which meant more electrons flowing through the electrodes per unit of time. The greater number of electrons sped up the production of gas bubbles, which would cover the more active surface of the electrodes. The high bubbles coverage also increased the overall resistance. Consequently, increasing the current density reduced the current efficiency of the reactor. In addition, the electrodes had a maximum number of active sites. At a certain current density, the number of active sites became the limiting factor instead of the number of electrons. In other words, as the current density was getting higher, there were more and more electrons flowing through the reactor without being converted into HOCl. However, the higher current density also sped up the surface reactions, which sped up the consumption of electrons, so there was not any enormous change in the current efficiency.

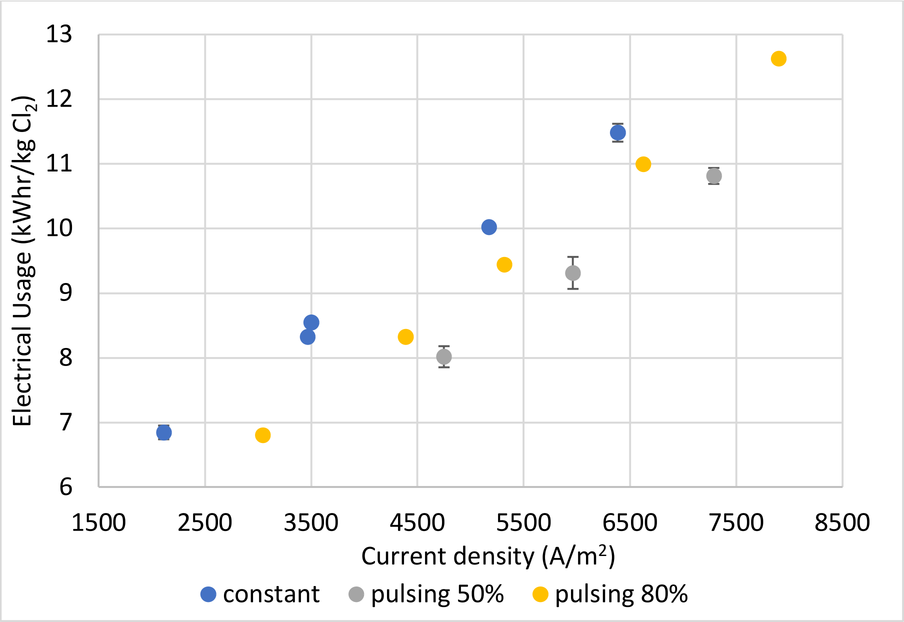

Figure 4.4: The relationship between the current efficiency and the electrical usage at various electrolysis conditions (constant and pulsed current with duty cycle of 50% and 80%). Error bars represent the 95% confidence interval.

Figure 4.4 indicated that pulsed electrolysis had lower electrical usage than constant electrolysis. The pulsed electrolysis with a duty cycle of 80% reduced the electrical current efficiency by about 1 kWhr per kg of Cl_2 produced on average, which was about a 10% improvement. The pulsed electrolysis with a duty cycle of 50% reduced the electrical current by about 1.5 kWhr per kg of Cl_2 produced on average, which was about a 15% improvement. One of the potential causes for this was the improvement of the current efficiency. For the same amount of power supplied to the reactor, the pulsed electrolysis was able to convert more electrons to HOCl. Therefore, it reduced the electrical usage of the system. Another potential cause was that pulsing increased the current during the on-time. This enhancement was attributed to the reduction of gas bubbles that covered the surface of electrodes and the perturbation of the electrical double layer as discussed in Chapter 2.

According to Figure 4.4, when the current density increased, the electrical usage increased. One of the reasons was that the current efficiency was reduced when the current density increased. As a consequence, more power was required to produce the same amount of HOCl. Another reason was that voltage also increased when the current increased. Therefore, the required power increased faster than the production rate of HOCl because power was calculated by multiplying voltage with current.

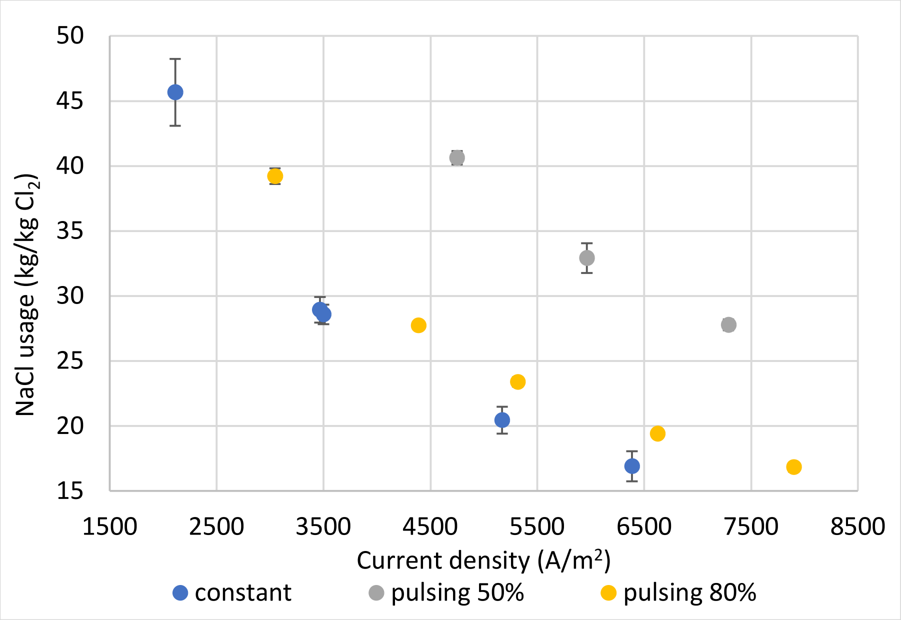

Figure 4.5: The relationship between the current efficiency and the NaCl usage at various electrolysis conditions (constant and pulsed current with duty cycle of 50% and 80%). Error bars represent the 95% confidence interval.

Figure 4.5 pointed out the downside of the pulsed electrolysis, which was a higher NaCl usage than the constant electrolysis. The NaCl usage of the pulsed electrolysis with a duty cycle of 50% was 1.8 times higher than the NaCl usage of the constant electrolysis. The NaCl usage of the pulsed electrolysis with a duty cycle of 80% was about 17%-20% higher than the NaCl usage of the constant electrolysis. As mentioned in Chapter 2, those differences were caused by the off-time when there was no reaction occurred. In other words, during the off-time, there was no NaCl consumed in the reactor. Despite a higher production rate during the on-time, the average overall electrolysis rate of pulsed current was smaller than the rate of constant current because the rate during off-time was zero.

Although the pulsed electrolysis significantly improved the current efficiency and the electrical usage, it inflated the NaCl usage. Therefore, it was difficult to tell which electrolysis method had a better performance when we looked at electrical usage and NaCl usage separately. A better way to assess the electrolysis performance was to study the relationship between NaCl usage and electrical usage. By doing so, we were able to figure out whether the improvement of current efficiency and electrical usage during the on-time could outweigh the increase in the NaCl usage due to the off-time.

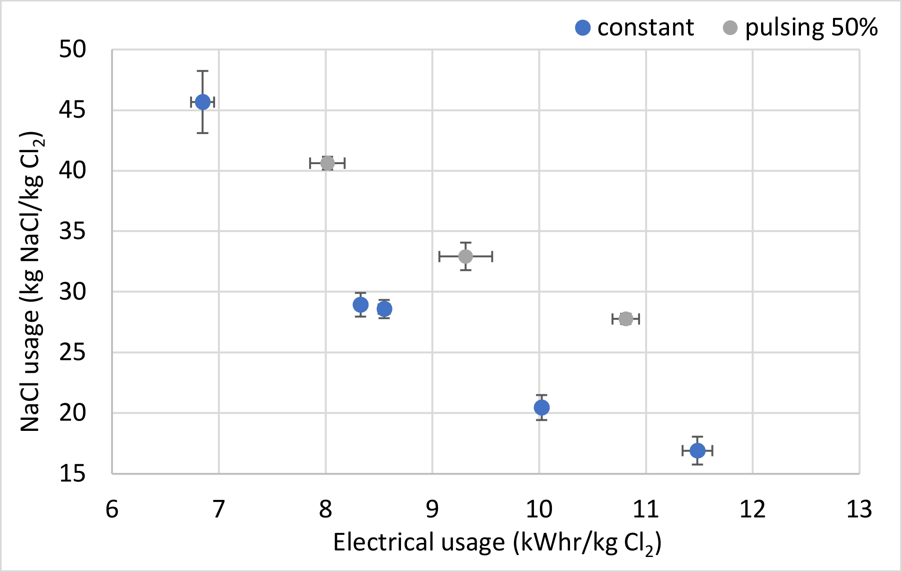

Figure 4.6: The relationship between the electrical usage and the NaCl usage at various electrolysis conditions (constant and pulsed current with duty cycle of 50%). Error bars represent the 95% confidence interval.

Following Figure 4.6, the curve for pulsed electrolysis with a duty cycle of 50% was totally above the curve for constant electrolysis. This meant, for the same amount of power supplied, the pulsed electrolysis always required more NaCl per kg of Cl_2 produced than constant electrolysis. Thus, the improvement of current efficiency and electrical usage during the on-time could not compensate for the disadvantage of off-time. Therefore, the performance of constant electrolysis was better than the performance of pulsed electrolysis with a duty cycle of 50%. In other words, to produce the same amount of hypochlorous acid solution using the same reactor, it would be always more beneficial to use constant electrolysis than pulsed electrolysis with a duty cycle of 50%.

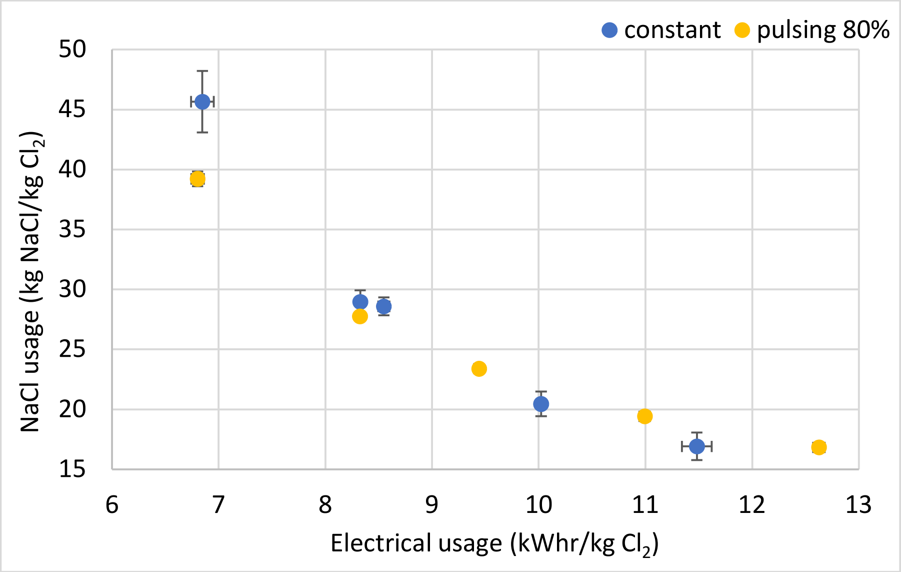

Figure 4.7: The relationship between the electrical usage and the NaCl usage at various electrolysis conditions (constant and pulsed current with duty cycle of 80%). Error bars represent the 95% confidence interval.

Based on Figure 4.7, the performance of pulsed electrolysis with a duty cycle of 80% was more promising than the duty cycle of 50%. When the electrical usage was in the range from 6 to 9 kWhr per kg Cl_2 produced, pulsed electrolysis with a duty cycle of 80% required less kg NaCl per kg Cl_2 produced than the constant electrolysis. The current density for this range of electrical usage was about 2000 to about 4500 A/m^2. In this specific case, the improvement of current efficiency and electrical usage during the on-time was enough to compensate for the disadvantage of off-time. Therefore, it is possible for pulsed electrolysis to outperform constant electrolysis.

4.3 Discussion

All the performances in section 4.2 were discussed regardless of the actual price of NaCl and electricity. However, when the cost of NaCl and electricity are taken into consideration, it is trickier to determine which electrolysis method is really better because the prices of NaCl and electricity vary noticeably from place to place, and they are rarely equal. The difference in the price between NaCl and electricity will play an important role in deciding which electrolysis method is worth using. If the cost of NaCl is higher than the cost of electricity, it will be more necessary to minimize the NaCl usage of the system. In this case, constant electrolysis is most likely to have a better overall performance than pulsed electrolysis. On the other hand, when the cost of electricity is higher than the cost of NaCl, it will be more beneficial to reduce the electrical usage even if it may increase the NaCl usage. In this case, pulsed electrolysis is more likely to have a better overall performance than constant electrolysis as pulsed electrolysis has been proven to significantly improve the current efficiency and electrical usage of the system. For example, we can briefly consider a facility located next to the ocean. Because the system that is in our lab can take oceanic brine as a NaCl solution input, the cost of NaCl for this fictitious facility will be neglectable. Therefore, regardless of the price of electricity, it always makes more sense to optimize the electrical usage of the system. As a result, pulsed electrolysis is most likely to be a more beneficial choice because the showed improvement in electrical usage mentioned above.

Another trade-off that may favor pulsed electrolysis is trading between the operating cost and the capital cost of the system. For the sake of this project, the operating cost is simplified down to the summation of the NaCl cost and the electricity cost, the capital cost includes the cost of the equipment, the initial installation cost, and the cost of maintenance or replacement of any part of the equipment. It is common to increase the upfront capital cost to reduce the annual operating cost of the system, especially if the system is planned to be utilized for a long time. Accordingly, the system can be sized up, which will increase the capital cost, to reduce the operating cost. There are a few ways to scale up the system. One way is expanding the active surface of the electrodes in the reactor. Another way is to add more reactors to the system. Both will raise the cost of the equipment and the initial installation cost. However, by doing so, the production rate should increase proportionally to the increase in the system's size. In other words, more NaCl will be converted into HOCl during the on-time. As a result, the NaCl usage of the system will reduce drastically. For example, two reactors are used for pulsed electrolysis with a duty cycle of 50% instead of one. Since the reactors are the same, individual ones should have similar NaCl usage and electrical usage as the results in section 4.2. However, as the feed stream flows through two reactors now, theoretically, twice the amount of NaCl would be converted to HOCl during the on-time. Therefore, it is enough to cancel out the disadvantaged behaviors of the pulsed electrolysis during the off-time. In this case, because pulsed electrolysis has not only lower electrical usage but also lower NaCl usage, it will surely minimize the operating cost of the system. But more studies are needed to determine whether the drop in operating costs is worth the rise in capital costs. In addition, pulsed electrolysis potentially slows down the corrosion/degradation of the electrodes, so it prolongs the lifetime of the electrodes. Consequently, pulsed electrolysis may decrease the cost of maintenance or replacement of damaged electrodes. Again, more experiments must be conducted to fully understand the trade-off between the capital cost and the operating cost of the pulsed electrolysis method.

CHAPTER 5

THE EFFECTS OF FREQUENCIES ON THE PERFORMANCE OF PULSED ELECTROLYSIS

5.1 Overview

Besides the duty cycle, frequency is another important characteristic of pulsed electrolysis. There was evidence pointing out that frequency affected the efficiency of the electrolysis process. Gopeesingh et al. investigated the concept of dynamic catalytic resonance of the electrocatalytic oxidation of formic acid over Pt. According to them, there was an equilibrium between the surface reaction rate and the mass transportation rate that dictated the maximum overall production rate of the system. It was impossible to have a rate higher than this maximum rate when only static constant voltage was applied. However, they found out that they were able to exceed this maximum rate by using the pulsed voltage at the right frequency. The surface reaction rate was high, but the mass transportation was low when the voltage was large. On the other hand, the surface reaction rate was low, but the mass transportation rate was high when the voltage was small. Therefore, pulsed voltage allowed the system to switch between the high surface reaction and high mass transportation rate so that it maximized the overall production rate of the system.[15] Different frequencies had different effects on various phenomena like electrical double layer formation, bubble formation and transportation, and diffusion layer formation.[5] As mentioned in Chapter 2, those phenomena were related to electrolysis efficiency. Therefore, it was necessary to study how frequency would affect the performance of pulsed electrolysis. This project focused on relatively low frequencies because the pulsed current generator was not as accurate at extremely large frequencies.

5.2 Results

The frequency of the pulsed current mostly affected the current efficiency of the pulsed electrolysis. The effects of frequency on the current efficiency also depended on the voltage at which the system operated. Below, we will look at the behaviors of the current efficiency of pulsed electrolysis with a duty cycle of 80% at various frequencies for set voltages of 6.0 V, 7.2 V, 8.0 V, and 9.0 V.

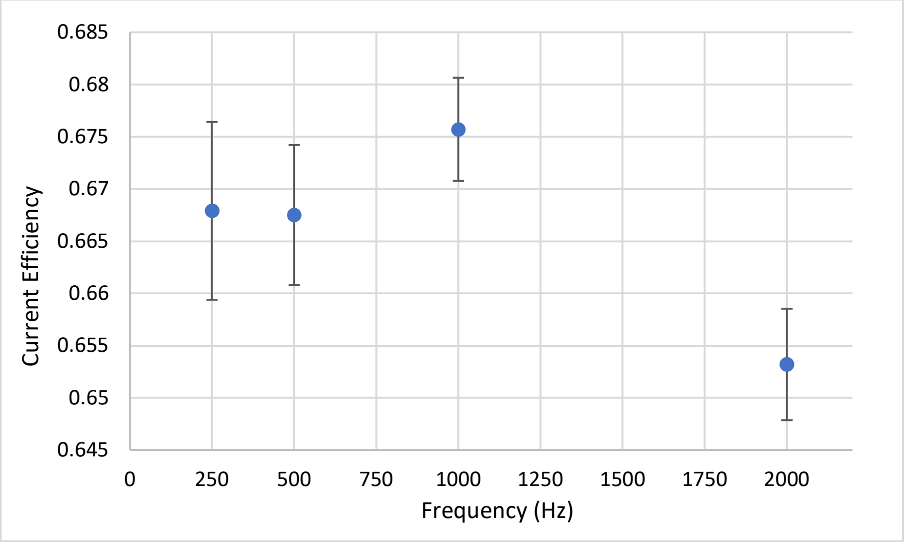

Figure 5.1: The relationship between the current efficiency and the frequency for pulsed electrolysis with duty cycle of 80% at 6.0 V. Error bars represent the 95% confidence interval.

At 6.0 V, the current efficiency increased when the frequency increased until about 1000 Hz, then it decreased when the frequency continued to go up. For this range of frequency, 1000 Hz was assumed to be the optimized frequency for 6.0 V as it gave the greatest current efficiency. This difference was also significant, especially compared to the efficiency at 2000 Hz.

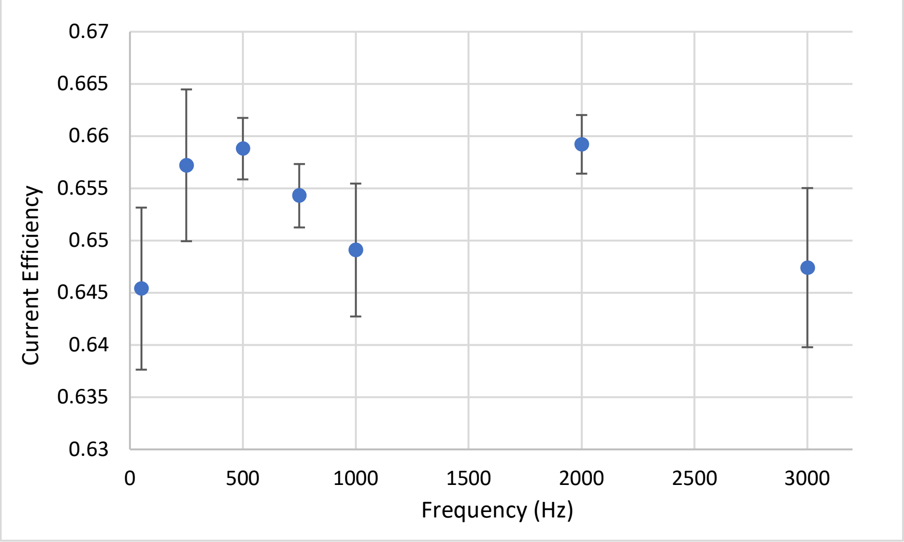

Figure 5.2: The relationship between the current efficiency and the frequency for pulsed electrolysis with duty cycle of 80% at 7.2 V. Error bars represent the 95% confidence interval.

Looking at Figure 5.2, it seemed that there were two maxima (one at 500 Hz and one at 2000 Hz), and the two highest values were almost equal. Although the difference in the current efficiency between different frequencies was quite small (within about 1.5%), the difference between the highest and lowest current efficiency was still statistically significant. Therefore, the optimized frequency for 7.0 V was 2000 Hz.

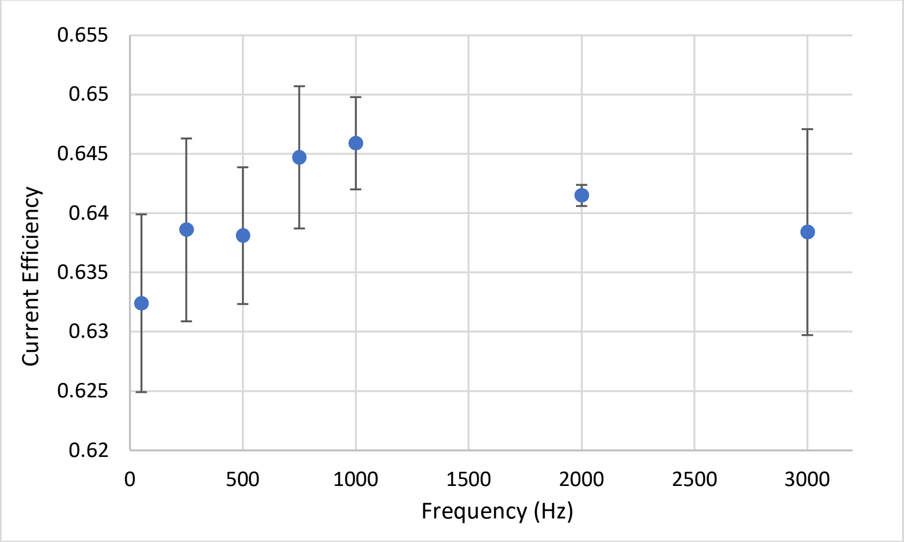

Figure 5.3: The relationship between the current efficiency and the frequency for pulsed electrolysis with duty cycle of 80% at 8.0 V. Error bars represent the 95% confidence interval.

The dependence of the current density on the frequency at 8.0 V was similar to the behaviors at 6.0 V. The current efficiency increased when the frequency increased until about 1000 Hz, then it decreased when the frequency continued to go up. As the voltage increased and the current density increased, the effects of frequency on the current efficiency seemed to get smaller. Following Figure 5.3, although the 95% confidence intervals were small, they still overlapped with each other a lot, especially from 250 Hz to 1000 Hz. However, the difference between the highest value and the lowest value was still statistically significant. Therefore, it was safe to assume that the optimized frequency for 8.0 V was 1000 Hz, despite the overlapping of confidence intervals.

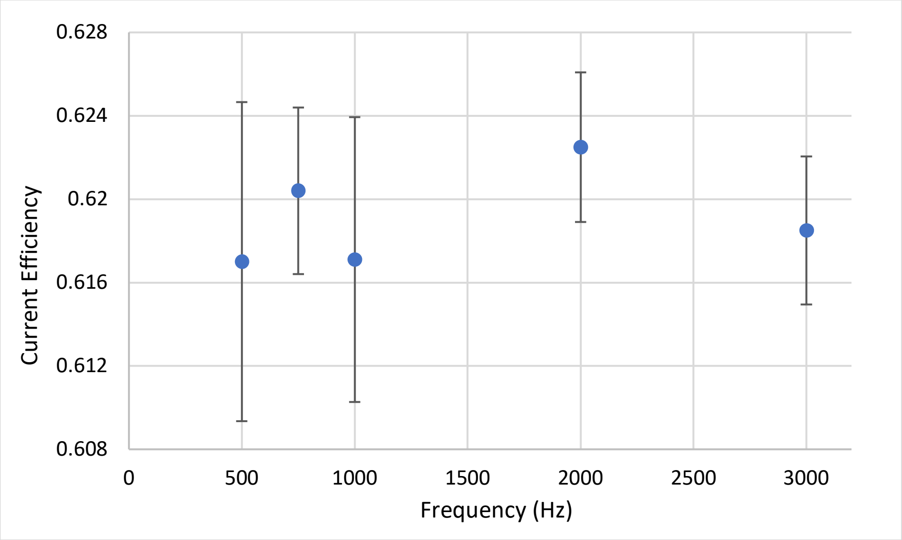

Figure 5.4: The relationship between the current efficiency and the frequency for pulsed electrolysis with duty cycle of 80% at 9.0 V. Error bars represent the 95% confidence interval.

According to Figure 5.4, at 9.0 V, there were not any statistical differences in the current efficiency at various frequencies as all the confidence intervals overlapped with each other. The differences in current efficiency were all less than 1%. However, for the analysis, 2000 Hz was assumed to be the optimized frequency at 9.0 V.

5.3 Optimized Frequencies

Table 5.1: Optimized frequencies with the highest current efficiency at various voltages

Voltage (V)	**6.0**	**7.2**	**8.0**	**9.0**
Frequency (Hz)	1000	2000	1000	2000
Current efficiency	0.676	0.659	0.646	0.623

As the frequency of the pulsed current could affect the current efficiency of the pulsed electrolysis, the goal was to figure out what frequency led to the highest current efficiency. Based on Table 5.1, different voltages had different optimized frequencies. However, they were all in the range of 1000-2000 Hz.

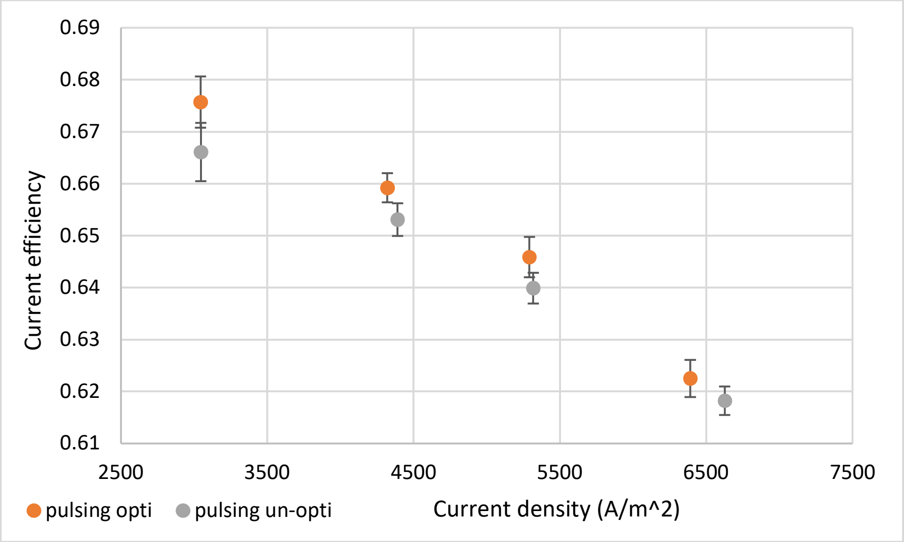

Figure 5.5: Comparison of the current efficiency for pulsed electrolysis with duty cycle of 80% between the overall and the optimized case at various current densities. Error bars represent the 95% confidence interval.

Looking at Figure 5.5, although the difference between the un-optimized and the optimized current efficiencies was small (about 1.4% relative improvement), the difference was still statistically significant for the current density lower than 5000 A/m^2. If the pulsed electrolysis is carried out at those optimized frequencies, it would extend the improvement in performance compared to the constant electrolysis. On the other hand, the low and medium frequencies did not show as much enhancement as expected from the high frequencies as pointed out in some articles.[5] However, some updates have to be done on the pulsed current generator so that it can measure the current accurately at extremely high frequencies (more than 10 kHz). Then, more experiments will be done to investigate more about the effects of frequency on the current efficiency of pulsed electrolysis.

CHAPTER 6

CONCLUSION

6.1 Summary

The Covid-19 pandemic created disinfectant shortages around the world. On-site production of disinfectant is a promising solution. Hypochlorous acid was chosen to be the alternative disinfectant as it is not only much more effective but also much safer than bleach (sodium hypochlorite). The production method is electrolyzing solution of sodium chloride and water because this method is inexpensive and environmentally friendly. However, instead of using conventional constant electrolysis, this project focused on a new approach which is pulsed electrolysis. Pulsed electrolysis was shown to improve the electrolysis efficiency because of the reduction of bubbles coverage, perturbation of the electrical double layer, and enhancement of mass transportation. A reactor was built with a cathode made from titanium and an anode made from titanium coated with mixed metal oxide (a mixture of Iridium oxide and Tantalum oxide). Our colleagues from the Electrical and Computer Engineering Department at the University of Maine designed and made a pulsed current generator. This generator utilizes MOSFET to create square-shaped current pulses. The experiments were carried out at constant voltages in a flow system, which was running in a recycle loop. The NaCl usage and the electrical usage were interconnected, in other words, decreasing NaCl usage would require greater electrical usage. Pulsed electrolysis was able to improve the current efficiency of the system compared to constant electrolysis. The lower the duty cycle was, the better the current efficiency got. Moreover, pulsed electrolysis also reduced electrical usage at various current densities. However, pulsed electrolysis had much higher NaCl usage than constant electrolysis because there was no reaction happened during the off-time. Therefore, running pulsed electrolysis with a low duty cycle was less beneficial than using constant electrolysis. But pulsed electrolysis with a duty cycle of 80% was able to exceed the performance of constant electrolysis. In the current density range from 2000 to 4500 A/m^2, for the same electrical usage, pulsed electrolysis with a duty cycle of 80% required smaller NaCl usage than constant electrolysis. The frequency of the pulsed current only slightly affected the current efficiency of the pulsed electrolysis. Nevertheless, the difference in the current efficiency between optimized and un-optimized frequencies was still statistically significant. By operating at those frequencies, we can enlarge the improvement of the pulsed electrolysis compared to the constant electrolysis.

6.2 Future work

Through this research, pulsed electrolysis showed many potentials to be beneficial for the on-site production of hypochlorous acid. However, all the experiments were carried out in batches, which are difficult to produce large quantities for industrial purposes. Therefore, a continuous production system should be designed and investigated. The main objective would be to determine whether the advantages of pulsed electrolysis mentioned in chapters 4 and 5 hold true for the continuous system. Then, it is necessary to find the best combination of voltage magnitude, frequency, and duty cycle to optimize the operating cost of the continuous production system. The next step will be sizing up the pulsed electrolysis system to an industrial scale and estimating the capital cost.

Although HOCl was proved to be very effective at disinfecting, there were minimal trials to confirm the effectiveness of our product. Therefore, more biological tests should be done to determine the killing microorganism efficacy, rate of disinfecting, and safety of our product. With that information, we can broaden the applications of the system, for example, using it in medical settings or household disinfectants.

The production of hydrogen gas is an important piece of the system, which is barely mentioned in the results. Green hydrogen is a hot topic in the research field and hydrogen produced by electrolysis is one of them. As hydrogen gas is always produced as a by-product in our system, it is crucial to effectively collect it so that we can study more about hydrogen production and its applications.

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APPENDIX:

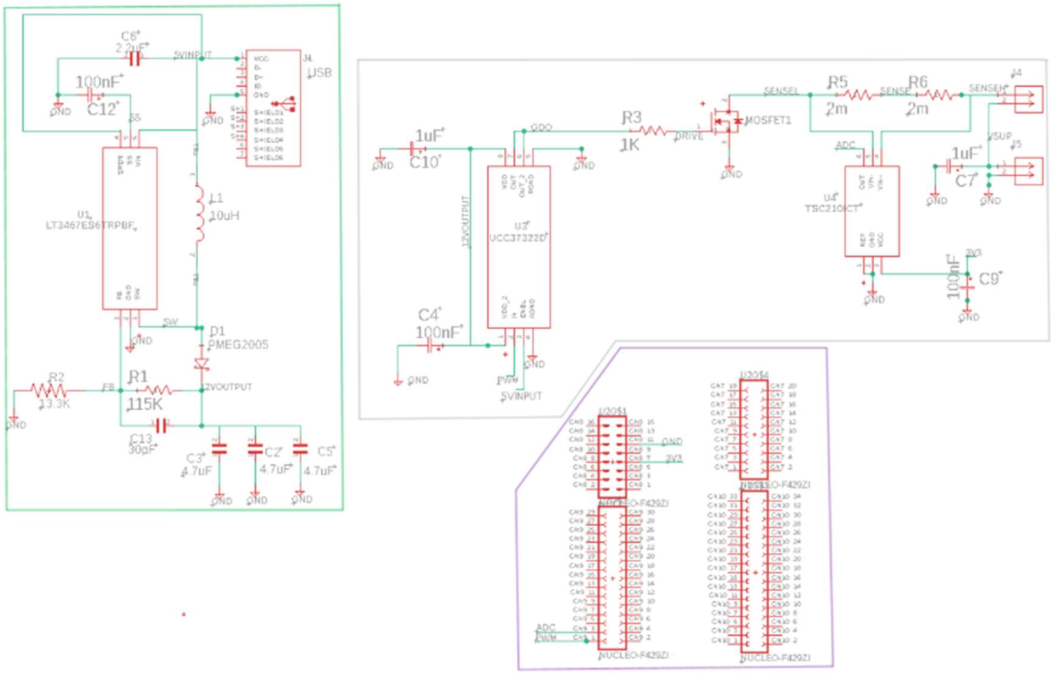

Figure A.1: Complete electrical schematic of the pulsed current generator.[21]

BIOGRAPHY OF THE AUTHOR

Khoa Kieu was born in Da Nang, Vietnam on March 29, 1999. He was raised in Da Nang, Vietnam, and graduated from Le Quy Don High School in 2017. He joined the University of Maine, Orono and graduated in 2021 with a bachelor's degree in Chemical Engineering. He continued to pursue his Master of Science degree in Chemical Engineering at the University of Maine, Orono.

After receiving his degree, Khoa will start looking for a job in the industrial fields. Khoa is a candidate for the Master of Science degree in Chemical Engineering from the University of Maine in May 2023.