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Evaluation of Anodes and Modular Membrane-Less Single Cell Reactor Designs for On-Site Hypochlorous Acid Generation

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EVALUATION OF ANODES AND MODULAR MEMBRANE-LESS SINGLE CELL REACTOR DESIGNS FOR ON-SITE HYPOCHLOROUS ACID GENERATION

By

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B.S. Kazan National Research Technological University, Russia, 2021

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Thesis Advisor: Prof. DeSisto William Joseph

An Abstract of the Thesis Presented
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Ensuring safe drinking water and effective sanitation remains a global priority. The shortages of disinfectants experienced during the COVID-19 pandemic further underscore the importance of reliable disinfection methods. Chlorine-based disinfection is widely used but poses safety hazards and logistical challenges in its traditional production and transportation forms. Alternately, on-site chlorine generation using electrochemical conversion of aqueous sodium chloride offers a promising solution, mitigating these risks and providing a flexible approach to disinfection. This thesis investigates the performance of various anode materials and modular, membrane-less, single-cell reactor designs to optimize on-site chlorine generation. Optimization included minimizing specific electrical consumption for chlorine generation and maximizing chlorine current efficiency. Operating conditions of applied voltage, sodium chloride concentration, reactor geometry and flow rate were investigated. For specific reactor designs, optimizing these conditions is important for commercial applications. A preliminary techno-economic analysis is also presented.

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CHAPTER ONE

1 INTRODUCTION

1.1 Chemistry Of Chlorine Species (Chlorine Gas, Hypochlorous Acid, Hypochlorite Ions) And Their Disinfectant Properties

Chlorine-based disinfectants have played a pivotal role in global public health, particularly in the purification of drinking water and wastewater treatment. The effectiveness of chlorine disinfection stems from the unique chemistry of chlorine species in aqueous solutions. These species—including chlorine gas (Cl_2), hypochlorous acid (HOCl), and the hypochlorite ion (OCl^-)—engage in multifaceted reactions that ultimately lead to the inactivation of pathogens[1].

Chlorine chemistry with an emphasis on the species involved in disinfection. It examines their formation, equilibria, reactivity, and how these factors influence disinfection performance. Understanding the chemical basis of disinfection is critical for engineers to optimize chlorination processes, address operational challenges, and assess the potential formation of undesirable byproducts.

1.1.1 Chlorine Chemistry Fundamentals

Chlorine is a highly reactive halogen occupying group 17 of the periodic table. Chlorine gas (Cl_2), the elemental form, is a dense, greenish-yellow gas with a pungent odor. When dissolved in water, chlorine gas undergoes a rapid hydrolysis reaction:

$$Cl_2\ (g) + H_2O\ (l) \rightleftharpoons HOCl\ (aq) + H^+\ (aq) + Cl^-\ (aq)$$

Hypochlorous acid (HOCl) is a weak acid that partially dissociates in water:

$$HOCl\ (aq) \rightleftharpoons H^+\ (aq) + OCl^-\ (aq)$$

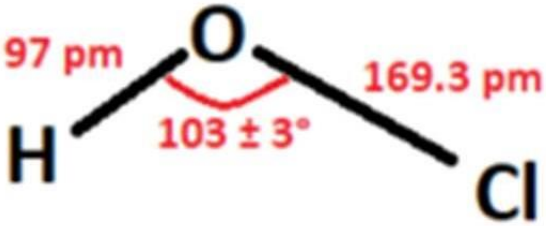


Figure 1-1: Lewis's structure of hypochlorous acid.

The hypochlorite ion (OCl^-) is the conjugate base of hypochlorous acid. The relative concentrations of HOCl and OCl^- are highly pH-dependent, governed by the following equilibrium constant (pKa) relationship:

$$pKa\ (HOCl) = 7.5 \text{ at } 25°C$$

At pH values below 7.5, HOCl predominates, while OCl^- is the major species at pH values above 7.5.[2]

Chlorine-based disinfectants have played a critical role in ensuring safe drinking water and sanitation for decades. The remarkable disinfectant properties of chlorine arise from its diverse and reactive chemistry in aqueous solutions. This section explores the fundamental chemistry of chlorine species, including chlorine gas (Cl_2), hypochlorous acid (HOCl), and hypochlorite ion (OCl-), and delves into the mechanisms that make them powerful disinfectants.

1.1.2 Chlorine Chemistry in Water

1.1.2.1 The Pourbaix diagram

A Pourbaix diagram is a powerful tool that visually represents the stability of various chemical species of an element in an aqueous solution.[3] It charts the dominant species as a function of potential (redox strength) and pH (acidity). In the case of chlorine, the Pourbaix diagram is especially insightful. It reveals that hypochlorous acid (HOCl), the primary disinfectant, is most stable under slightly acidic conditions. At higher pH, hypochlorite ions (OCl-) dominate, and at very high potentials, undesirable species like chlorite (ClO2-) and perchlorate (ClO4-) can form. Understanding the Pourbaix diagram is crucial in chlorine-based disinfection, as it guides the optimization of pH for maximum HOCl and minimizes byproduct formation. Additionally, in electrochemical chlorine generation, the Pourbaix diagram aids in the selection of anode materials stable within the desired operating conditions. It even helps predict the potential for corrosion of metals exposed to different chlorine species. While the Pourbaix diagram reflects thermodynamic equilibrium, it provides invaluable insights into real-world systems where chlorine chemistry plays a crucial role in water treatment and industrial processes.

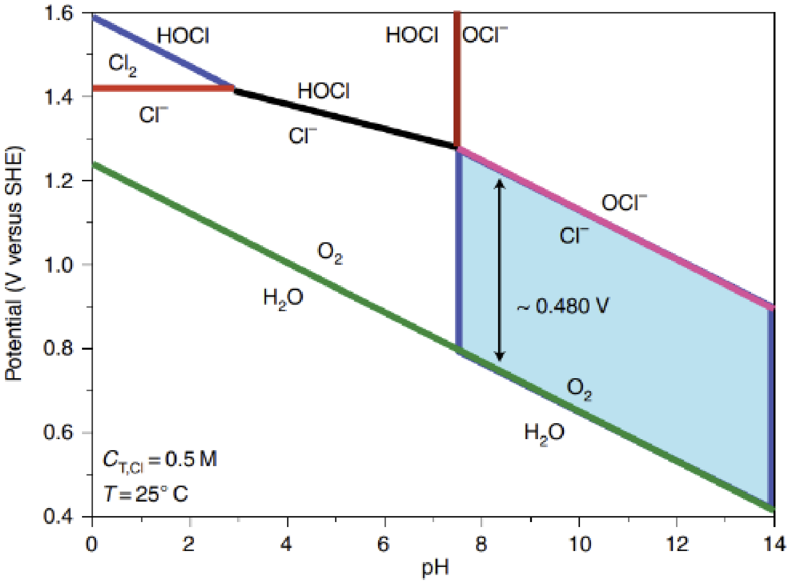


Figure 1-2: Pourbaix diagram for Chlorine species[4]

1.1.3 Chlorine Species and Disinfection Mechanisms

Both hypochlorous acid and hypochlorite ions, collectively known as "free chlorine," possess disinfectant properties. However, HOCl is a significantly more potent disinfectant than OCl-[1].

1.1.3.1 The superior biocidal activity of HOCl stems from several factors:

Smaller Size and Neutrality: HOCl is a small, uncharged molecule, allowing it to penetrate microbial cell walls more easily than the negatively charged OCl- ion[5].

Higher Oxidizing Power: HOCl exhibits a higher oxidation potential than OCl-, making it more effective in oxidizing key cellular components within microorganisms[6].

The primary mechanisms through which chlorine species inactivate microorganisms include:

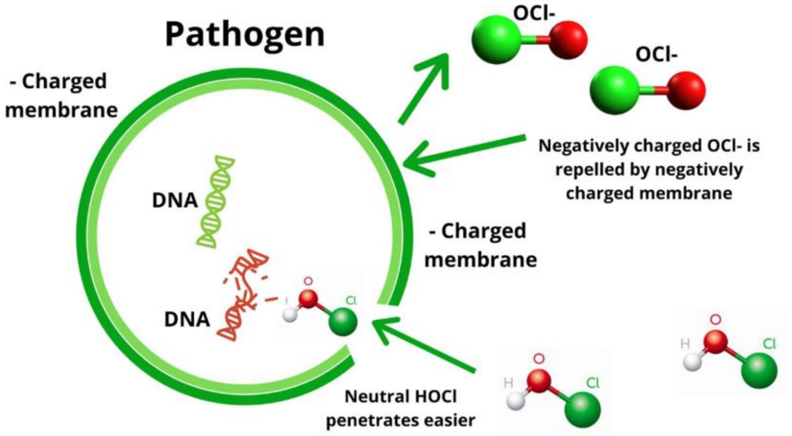


Figure 1-3: Proposed mechanism of the penetration cell walls of HOCl and OCl-[7]

Oxidation of Cellular Components: Chlorine species act as powerful oxidizing agents, disrupting vital cellular structures such as proteins, lipids, and nucleic acids. This oxidative damage compromises essential cellular functions[5,6].

Sulfhydryl Group Inactivation: Chlorine species react with sulfhydryl (-SH) groups present in enzymes and other proteins. This reaction inactivates the proteins, hindering vital metabolic processes.

DNA Disruption: Chlorine species can disrupt the structure of DNA and interfere with DNA replication, preventing cell growth and reproduction.

1.1.4 Factors Influencing Disinfection Efficacy

The efficacy of chlorine-based disinfection is influenced by several factors, including:

i. pH: As discussed earlier, pH significantly affects the distribution of HOCl and OCl-. Since HOCl is the more potent disinfectant, maintaining a slightly acidic pH optimizes disinfection efficiency. However, HOCl is somewhat unstable, and its efficacy is strongest at slightly acidic pH (around 5-6). At higher pH values, chlorite ions (ClO2-) and perchlorate ions (ClO4-) can form through further oxidation[1]. Concentration: The concentration of free chlorine directly impacts disinfection efficacy. Higher concentrations generally lead to faster inactivation of microorganisms.
ii. Contact Time: Disinfection requires sufficient contact time between chlorine species and the target microorganisms. Longer contact times result in greater microbial inactivation.
iii. Temperature: Disinfection rates tend to increase with increasing temperature due to enhanced chemical reaction rates[8].
iv. Organic Matter: The presence of organic matter can interfere with chlorine-based disinfectants by consuming free chlorine and shielding microorganisms[9].

1.1.5 Chlorination Byproducts

While chlorine-based disinfection offers numerous advantages, it is important to acknowledge the potential formation of disinfection byproducts (DBPs)[10]. When chlorine reacts with organic matter present in water, it can generate a range of byproducts, including trihalomethanes (THMs) and haloacetic acids (HAAs). Some DPBs are classified as potential carcinogens, requiring careful monitoring and control in water treatment systems[10].

1.1.6 Alternative Chlorine-Based Disinfectants

To address concerns about DBP formation, other chlorine-based disinfectants have been developed and adopted in water treatment:

i. Chloramines: Chloramines are formed by the reaction of chlorine with ammonia. They are weaker disinfectants than free chlorine but are more persistent and less likely to produce DBPs[11].

ii. Chlorine Dioxide (ClO2): Chlorine dioxide is a powerful disinfectant and oxidant that forms fewer DBPs compared to traditional chlorine. It is effective against a broad range of microorganisms[11].

1.1.7 Engineering Considerations for Chlorine-Based Disinfection Systems

The design and operation of chlorine-based disinfection systems within a chemical engineering context require careful consideration of various factors:

i. Disinfectant Dosage and Contact Time: Determining the appropriate chlorine dosage and contact time is essential for logarithmic inactivation of target microorganisms while considering water chemistry and regulatory limits.

ii. Process Control and Monitoring: Real-time monitoring of free chlorine residual, pH, and temperature is crucial for ensuring effective disinfection and process optimization.

iii. DBP Control and Mitigation: Strategies to minimize DBP formation may include optimized chlorine dosing, organic matter removal before chlorination, and alternative disinfectants where applicable.

iv. Safety and Handling: Chlorine is a hazardous chemical, requiring strict safety protocols and appropriate engineering controls during storage, handling, and application.

Chlorine-based disinfectants have revolutionized the way we ensure water safety and sanitation. The chemistry of chlorine in water, generating potent disinfecting species like hypochlorous acid and hypochlorite ion, is fundamental to its efficacy. Understanding the mechanisms of microbial inactivation, factors influencing disinfection, potential formation of byproducts, alternative chlorine-based disinfectants, and associated engineering considerations is crucial for the responsible implementation of chlorine-based disinfection in water treatment processes.

1.2 Applications: Water Treatment (Drinking, Wastewater, Pools), Industrial Uses, Agriculture, Healthcare

Hypochlorous acid (HOCl), a potent oxidant formed through the hydrolysis of chlorine in water, offers specific advantages as a biocidal agent. In drinking water systems, HOCl serves as a primary disinfectant. Its superior inactivation capability against a wide range of pathogens, including bacteria, viruses, and protozoa, ensures the elimination of waterborne disease threats. In wastewater treatment, HOCl effectively reduces microbial loads in effluent before discharge. This safeguards aquatic ecosystems and protects public health by minimizing the dissemination of harmful microbes. Recreational water settings like pools and spas benefit from HOCl's fast microorganism inactivation rate, preventing the transmission of illnesses in environments subject to fluctuating contamination levels[12].

Beyond water, HOCl finds diverse industrial applications. The food processing sector uses HOCl's potent yet safe properties for sanitizing surfaces, equipment, and even rinsing fresh produce. This reduces contamination risks, enhances food safety, and can extend product shelf life. HOCl is also employed in various industrial processes like cooling water treatment for biofouling control. Its oxidative power disrupts microbial growth, preventing inefficiencies and potential corrosion associated with biofilm formation[13]. Agriculture benefits from HOCl as well, with applications including the disinfection of irrigation systems to combat plant pathogens and sanitation of livestock facilities to maintain animal health.

The healthcare field recognizes the advantages of HOCl. Due to its compatibility with human tissues at appropriate concentrations, HOCl is increasingly used in wound care[14]. Its antimicrobial action accelerates healing and reduces the risk of infection. While exploration of alternative disinfection technologies continues, the efficacy, versatility, and relative safety profile of HOCl ensure its ongoing importance in numerous applications where reliable sanitation is critical.

1.3 Hypochlorous Acid and Effects of Name on Acceptance and Adoption

Hypochlorous acid (HOCl), the active biocidal species in various chlorine-based disinfection solutions, offers advantages due to its rapid inactivation of microorganisms and favorable safety profile at appropriate dilutions. Yet surprisingly, the name "hypochlorous acid" itself poses challenges for its wider acceptance and adoption[15]. Understanding this complexity requires examining the interplay of scientific accuracy, traditional nomenclature, and end-user perceptions.

From a chemical engineering standpoint, the term "hypochlorous acid" is scientifically precise and critical for process design and optimization. In electrochemical generation, parameters such as solution pH, chloride concentration, and current density directly influence the equilibrium between HOCl and the less potent hypochlorite ion (OCl^-). Control of these variables is essential in maximizing HOCl yield, ensuring disinfection efficacy while minimizing byproduct formation. Moreover, thorough characterization and modeling of chemical kinetics require accurate species identification, making the term "hypochlorous acid" indispensable for technical communications and research within this field.

However, beyond specialized engineering disciplines, potential barriers to acceptance arise. The word "acid" may evoke concerns about corrosivity and harshness, even though HOCl in typical disinfection concentrations exhibits milder effects than strong acids[16]. Additionally, the public and certain industries are more accustomed to terms like "chlorine," "bleach," or "chlorinated water." This disparity between the scientifically correct term and common language creates potential friction in technology transfer, adoption in emerging applications, and even regulatory approval processes where precision in terminology is paramount. Strategies for Enhancing Acceptance and Adoption.

To bridge this gap, several approaches hold promise:

i. Targeted Education and Communication: Clear, accessible information about HOCl, its generation, properties, and safe handling practices is crucial. Emphasizing the relative advantages of HOCl over traditional chlorine delivery methods (e.g., on-site generation reducing safety hazards) can further bolster its appeal.
ii. Data-Driven Case Studies: Compelling demonstrations of HOCl's efficacy in various applications, supported by robust scientific data, can further solidify its position as a viable alternative. This strategy is particularly impactful when showcasing successes in industries where traditional chlorine uses faces limitations or challenges.
iii. Contextualized Terminology: While upholding the importance of "hypochlorous acid" in technical settings, adapting language for different audiences is valuable. For example, emphasizing the specific benefits of HOCl-based disinfectants (like reduced odor or suitability for sensitive materials) can resonate better with end-users.
iv. Standards and Regulations Alignment: Proactive engagement with regulatory bodies and industry standard-setting organizations can facilitate the adoption of precise terminology. Consistency in nomenclature across guidelines and safety documents enhances clarity and streamlines approval processes for novel HOCl-based technologies.

1.3.1 Outlook for the Future

The adoption of "hypochlorous acid" as a mainstream term is likely to increase alongside the growth of on-site generation systems, which necessitate a greater understanding of the underlying chemistry for successful design and operation. Moreover, as HOCl continues to gain traction in diverse applications due to its safety and efficacy, more widespread familiarity with the correct scientific term becomes inevitable. The key lies in proactive communication strategies that acknowledge the technical importance of "hypochlorous acid" while making it accessible and understandable to the diverse stakeholders involved in its implementation and acceptance.

1.4 On-Site Generation (OSG) Basics

On-site generation (OSG) of chlorine-based disinfectants like hypochlorous acid gained popularity after supply chain disruptions during COVID-19. This concept led to the development and integration of an OSG at a small wastewater treatment plant (WWTP) in Maine located in Biddeford Pool.[17] At the Biddeford Pool WWTP the OSG system has been integrated within the plant to displace concentrated bleach which is delivered regularly to the plant. The production of chlorine disinfectant is accomplished by electrolysis. Unique to this work is the use of wastewater effluent to produce disinfectant. This places additional challenges to the system regarding reliability, reproducibility, and longevity. The long-term goal of OSG systems is on-demand disinfectant production which responds to fluctuating demand under process control. [18]

1.5 Principles Of Electrochemical Chlorine Generation (Electrolysis of Brine)

The generation of chlorine-based disinfectants occurs through the electrolysis of brine (saltwater). Within an electrolytic cell, an electric potential is applied across two electrodes immersed in a solution of sodium chloride[19]. At the positively charged anode, chloride ions (Cl^-) undergo oxidation, surrendering electrons and transforming into chlorine gas (Cl_2). This chlorine gas is highly reactive and rapidly undergoes hydrolysis within the aqueous environment, forming a mixture of hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) depending upon pH. Simultaneously, at the negatively charged cathode, the reduction of water takes place. This process produces hydrogen gas (H_2) and hydroxide ions (OH^-). Oxygen can also form at the anode. The primary electrochemical reactions of interest are:

Anode: $2Cl^- \rightarrow Cl_2 + 2\bar{e}; 2H_2O \rightarrow O_2 + 4H^+ + 4\bar{e}$

Cathode: $2H_2O + 2\bar{e} \rightarrow 2H_2 + 2OH^-$

Several key factors dictate the efficiency and output of the chlorine generation process. The choice of anode material influences not only chlorine production rates, but also the potential formation of byproducts and the overall longevity of the system.[20] Commonly used dimensionally stable anodes (DSAs) consist of mixed metal oxides (e.g., RuO_2, IrO_2), known for their durability, conductivity, and high selectivity for chlorine evolution reaction (CER).[21] However, ongoing research actively explores new materials to further optimize performance and minimize costs.[22] One consideration is developing materials that provide better selectivity between chlorine and oxygen formation.[23–25] Furthermore, parameters like the electrolyte's salt concentration, the applied current density, and the operating temperature all play critical roles in shaping the reaction kinetics and equilibrium within the cell. Finally, cell design itself, including the physical arrangement of electrodes, flow patterns, and the presence or absence of a membrane separator, introduces further variables that can influence the generation of the desired chlorine-based disinfectant.

1.6 Advantages Of OSG (Safety, Reduced Logistics, Environmental)

On-site generation (OSG) of chlorine-based disinfectants offers a compelling solution for wastewater treatment plants (WWTPs) like the Biddeford facility, delivering advantages across key operational, safety, and environmental considerations. Primarily, OSG significantly enhances safety by sidestepping the risks of transporting, storing, and handling concentrated chlorine chemicals.[17] This translates directly to protecting workers at the WWTP and minimizing potential hazards to the surrounding Biddeford community. Additionally, OSG can streamline operations and potentially reduce costs. By relying on readily available salt and electricity, WWTPs can lessen their dependency on external suppliers of pre-formed chlorine, simplifying logistics and potentially reducing expenses related to bulk chemical transport and storage.

OSG aligns with sustainability goals relevant to Maine's environmental policies, making it particularly appealing from an ecological standpoint. Reducing the transport of hazardous chemicals minimizes the WWTP's carbon footprint.[26] On-site generation also helps prevent wastage associated with the degradation of pre-formed hypochlorite solutions, supporting responsible resource management. Furthermore, OSG gives precise control over disinfectant dosage. Operators at the Biddeford WWTP can tailor chlorine output to match fluctuating wastewater loads or specific disinfection requirements, ensuring reliable treatment efficacy while optimizing chemical use.

Additional context-specific benefits are worth noting. In the event of emergencies or infrastructure disruptions affecting supply chains in Maine, the self-sufficiency granted by OSG for disinfection at the Biddeford WWTP would bolster operational resilience. The flexibility to generate dilute hypochlorous acid solutions on-site may also reduce potential wear and tear on equipment compared to utilizing more concentrated chlorine products, extending infrastructure lifespan. Importantly, the advantages synergize – for instance, safety improvements stemming from OSG also contribute to reduced environmental risks due to minimized chemical transport.

While the precise impact of OSG adoption at the Biddeford WWTP would depend on the existing infrastructure and specific system design, the potential for enhanced safety, operational efficiency, environmental responsibility, and control over disinfection makes OSG a technology worthy of serious consideration in the ongoing modernization of wastewater treatment practices in Maine and globally.

1.7 Advantages Of Membrane-Less Electrochemical Reactors

Membrane-less electrochemical reactors hold significant advantages for my thesis research. By eliminating the ion-exchange membrane, these reactors reduce fabrication costs, minimize internal resistance, and enable the utilization of liquid electrolytes with superior ionic conductivity compared to solid-state counterparts. This simplified design is particularly valuable for applications such as water electrolysis and brine electrolysis, where high current density operation is desired. While membrane-less systems require careful management of product streams to prevent cross-contamination, their inherent efficiency and cost-effectiveness make them compelling candidates for scaled electrochemical processes relevant to renewable energy storage and chemical synthesis.[27]

1.8 Current Knowledge Gaps, Performance Limitations, Room for Optimization in OSG Anodes and Reactors

Despite the clear advantages of OSG, ongoing research and development seek to overcome remaining challenges and push the boundaries of performance and efficiency. Anode materials play a vital role in chlorine generation, yet current selections often involve trade-offs and limitations. While mixed-metal oxide (MMO) anodes, typically based on ruthenium or iridium oxides, offer reasonable durability, their high cost and potential for the formation of undesirable byproducts (such as perchlorate) are ongoing concerns.[28] This drives a continuous search for novel materials that balance factors like chlorine production efficiency, longevity under the often-harsh electrochemical conditions, cost-effectiveness, and environmental safety. Promising avenues of research include exploring new combinations of mixed metal oxides, alternative catalyst compositions entirely, and innovative surface coatings or treatments to enhance existing materials' properties.

Reactor designs present another frontier for optimization and innovation in OSG. Maximizing chlorine yield, while minimizing energy consumption and ensuring ease of maintenance, requires intricate engineering considerations. Cell geometry, electrode spacing, flow patterns through the reactor, and the choice between divided or undivided cell configurations all influence disinfectant output, energy efficiency, and the system's overall footprint. Innovations such as three-dimensional electrodes are emerging, designed to increase surface area and boost reaction rates within a given reactor volume. Additionally, integrating computational modeling and simulation tools is becoming invaluable for predicting complex flow and reaction dynamics within cells, allowing for virtual prototyping and optimization before costly physical fabrication.

Beyond the core components of anodes and reactors, other areas of OSG hold potential for process improvements. Membrane technologies play a crucial role in divided cells. The development of more durable and selective membranes can improve efficiency by preventing unintended mixing of products while promoting ion transfer crucial for the electrochemical reactions.[27] Furthermore, power supply and control systems present opportunities for refinement. Optimization of current density profiles, potentially using advanced control algorithms, could tailor the chlorine generation rate to precisely match fluctuating disinfection needs, maximizing energy efficiency and minimizing unnecessary chemical production.

The primary objective of this thesis was to evaluate the performance of different anode materials and single-cell reactor designs for efficient on-site chlorine generation, with a focus on optimizing chlorine production, energy consumption, and product quality.

The research addressed included anode material evaluation for on-site disinfection generation. The performance of various anode materials, including dimensionally stable anodes (DSAs), mixed metal oxides (MMOs) exploring RuO_2, TiO_2, and others, were investigated. Metrics included chlorine generation efficiency, current density, and long-term stability. The research also addressed the impacts of membrane-less reactor concepts such as electrode configuration and separation distance. Reactor performance was characterized with respect to energy and salt use required to produce chlorine. The impact of operating parameters like current density, applied voltage, brine concentration, active surface area, and flow rate were investigated.

This research impacts successful development of efficient and reliable on-site chlorine generation technology to improve resource use, community safety, community protection against supply disruptions, and improve the local economy through job creation.

The thesis is structured as follows:

Chapter 2: Literature Review: A review of chlorine chemistry, disinfection mechanisms, challenges of traditional chlorination, and the principles of electrochemical chlorine generation are presented. Existing research on anode materials and reactor designs is examined.

Chapter 3: Methodology: This chapter will detail the experimental methods, including the selection and fabrication of anode materials, design of single-cell reactors, and testing procedures for evaluating chlorine generation performance.

Chapter 4: Results and Discussion: This chapter will present research findings, including the performance evaluation of different anode materials and reactor designs. The impact of operating parameters on the quality of chlorine production/product will be analyzed and discussed. A preliminary techno-economic analysis is presented.

Chapter 5: Conclusion: Summarizes key findings and their implications for on-site chlorine generation technology. Recommendations for future research and development are presented.

This thesis contributes to the advancement of on-site chlorine generation technology. The development of safe and efficient systems has the potential to revolutionize water treatment practices, enhance access to safe drinking water globally, and provide versatile disinfection solutions across various applications.

CHAPTER 2

2 LITERATURE REVIEW

2.1 State-Of-The-Art Materials: Mixed Metal Oxides (MMO), Platinum, Ruthenium, Iridium, Tantalum, And Iridium Mixed Oxides

Extensive research has propelled the development of state-of-the-art materials for electrochemical reactors, aiming to enhance efficiency, selectivity, and durability. Nanostructured electrodes featuring high surface areas and tailored active sites have emerged as a significant focus.[2921] These designs promote enhanced electrochemical kinetics and can be engineered for specific reactions. Mixed metal oxides (MMOs) have emerged as a versatile and promising class of materials for electrochemical reactors, offering enhanced durability and cost-effectiveness compared to traditional noble metal catalysts.[30,31]Platinum, ruthenium, iridium, tantalum, and their combinations as iridium mixed oxides have been traditionally favored due to their excellent electrocatalytic activity and stability, particularly in demanding acidic environments.[32,33] However, their high cost and potential scarcity pose a barrier to large-scale deployment. Researchers are actively exploring strategies to enhance MMO performance for applications like water electrolysis and chlorine production to rival or surpass these noble metals.[34]

While materials science has advanced significantly in developing high-performance electrocatalysts, a substantial gap remains in translating these advancements to optimal reactor design and operation. Most studies focus on material synthesis and characterization at the laboratory scale, offering limited insights into their performance within large-scale electrochemical reactors.[35] A critical need exists for systematic studies that evaluate catalyst integration, reactor geometry, and operating conditions in concert to maximize the potential of mixed metal oxides and other emerging materials[36]. Such investigations are crucial to address challenges like long-term stability in aggressive environments and to inform the engineering of practical and economical electrochemical systems. These materials hold promise for reducing overpotentials and minimizing undesirable side reactions, leading to improved overall energy efficiency.

Addressing this gap can unlock the full potential of advanced materials, enabling cost-effective and sustainable electrochemical processes. Titanium dioxide (TiO_2) has gained attention due to its inherent corrosion resistance, dimensional stability, relative electrical conductivity, and cost-effectiveness compared to traditional noble metals.[37] While not intrinsically conductive, doping TiO_2 with noble metals (e.g., Ru, Ir) can significantly enhance its conductivity, making it a highly attractive electrocatalyst candidate.[24,38,39] These characteristics make TiO_2 coatings a valuable strategy to improve the durability and affordability of electrocatalysts.

Ruthenium dioxide (RuO_2) boasts high electrical conductivity and catalytic activity, especially for the chlorine evolution reaction (CER). However, its poor corrosion resistance in the harsh chlor-alkali environment limits its standalone use as an anode material.[23] Mixed metal oxides (MMOs) provide an alternative, offering improved durability and cost-effectiveness compared to pure RuO_2.[23] Despite commercial availability (e.g., Telpro), inconsistencies in MMO anode performance necessitate in-house synthesis and production for quality control and reproducible results.

A crucial aspect of chlor-alkali electrolysis is the selectivity of chlorine production at the anode. The competing oxygen evolution reaction (OER) can decrease efficiency and product yield. Anode material significantly influences this selectivity. RuO_2 and other noble metal oxides have traditionally been favored for CER[21,34], but their high cost and potential scarcity drive research toward alternatives.

The strategy of applying TiO_2 coatings aims to balance desirable CER activity with enhanced durability. While TiO_2 coatings might potentially reduce CER performance compared to pure RuO_2, they offer a more sustainable and practical long-term solution for systems requiring extended cycle life.

This thesis project addresses a critical need by exploring TiO_2-based coatings for improved electrocatalysts specifically designed for chlor-alkali electrolysis. The goals are to achieve:

Dimensionally stable anodes: Titanium-based anodes offer excellent dimensional stability, reducing wear and maintenance.

Cost-effectiveness: The use of TiO_2 and strategic doping strategies aim to decrease reliance on expensive noble metals.

Reproducibility: In-house synthesis and coating processes will ensure consistent quality and performance.

Further research is needed to optimize the TiO_2 coating composition and application methods to achieve the ideal balance between CER activity, OER suppression, durability, and cost-effectiveness. This will contribute to the development of more efficient and sustainable electrochemical processes for chlorine production.

2.2 Challenges In Practical Reactor Design

While extensive research drives the development of state-of-the-art materials for electrochemical reactors, a comparative lack of focus exists on translating these breakthroughs into practical reactor performance. Most studies emphasize material-level improvements, with limited systematic investigations on how these advancements impact overall reactor efficiency, scalability, and cost-effectiveness for industrial implementation.[22] This gap hinders the transition of promising lab-scale technologies into the real-world arena.

2.2.1 Tradeoffs and Practical Challenges

Designing electrochemical reactors for practical applications involves navigating complex tradeoffs between capital expenses (CAPEX) and operating expenses (OPEX). Strategies to reduce CAPEX, such as modular designs and membrane-less configurations, offer significant potential.[40–42] However, these designs introduce their own sets of challenges. Optimizing modularity for flexibility while ensuring efficiency remains an engineering hurdle. Similarly, membrane-less reactors need precise flow and electrolyte management to maintain product purity.

2.2.2 Durability Concerns

Ensuring the longevity of electrochemical reactors in demanding industrial environments poses a substantial challenge. Electrode degradation, corrosion, and fouling in harsh conditions (e.g., acidic, alkaline, or high-salinity electrolytes) can severely compromise long-term performance and economic viability. Developing robust materials, coatings, and operational strategies to withstand these aggressive environments is essential for widespread adoption of electrochemical technologies.[34]

2.3 Membrane-less electrochemical reactors

Membrane-less electrochemical reactors offer a promising avenue for reducing capital costs (CAPEX) and improving efficiency in electrochemical processes.[36] By eliminating the traditional ion-exchange membrane, these reactors reduce internal resistance, simplify fabrication, and can utilize a wider range of liquid electrolytes with superior conductivity. This design choice can lead to higher current densities and enhanced reaction rates, making membrane-less reactors particularly attractive for applications like water splitting and brine electrolysis.[43,44]

However, membrane-less systems pose unique challenges. Managing product streams to minimize cross-contamination and prevent the formation of unwanted byproducts is crucial. Precise control of flow dynamics and electrolyte distribution within the reactor becomes essential to maintain separation and selectivity. Additionally, careful design and materials selection are necessary to mitigate potential issues like electrode corrosion in these membrane-less environments.

2.4 My Approach

My thesis work aims to bridge the existing gap between state-of-the-art materials development and practical electrochemical reactor engineering. Recognizing the need to translate materials-level advancements into tangible process improvements, my research centers on reactor optimization and performance evaluation under real-world constraints. I will systematically investigate how electrode materials and reactor designs function within the context of an integrated reactor system.

My primary objectives include optimizing reactor design parameters, conducting rigorous performance evaluations, and establishing design guidelines tailored for practical applications. I will focus on engineering metrics of paramount industrial relevance, such as energy efficiency, scalability, durability, and cost-effectiveness. Ultimately, my research seeks to develop a holistic understanding of the interplay between materials, reactor configuration, and overall process performance, providing valuable insights for the deployment of efficient and sustainable electrochemical technologies.

Our goal is to avoid such a situation; as in Figure 2-1.

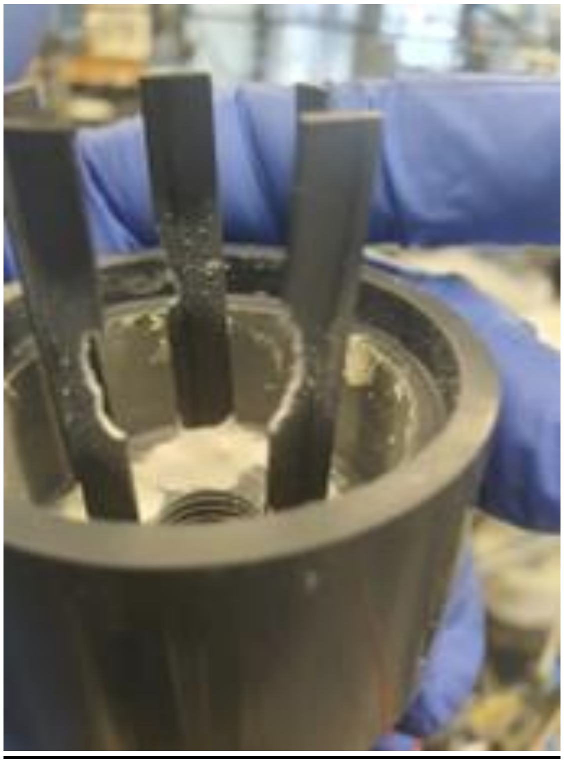


Figure 2-1: Corroded anode ribbons.

CHAPTER 3

3 METHODOLOGY

3.1 Cathode And Anode Materials

The cathode material chosen for the reactor was titanium, primarily due to its advantageous properties. Firstly, titanium exhibits excellent conductivity, making it suitable for facilitating efficient electron transfer during electrolysis.[45,46] Moreover, titanium is comparatively more cost-effective than other common conductors like silver or platinum, contributing to overall cost-efficiency in reactor construction. Secondly, titanium demonstrates exceptional durability, withstanding high current density and elevated temperatures over extended periods without compromising its performance. This resilience is crucial for maintaining consistent operation and longevity in electrochemical processes. Lastly, titanium possesses remarkable resistance to corrosion and oxidation, which is particularly essential in environments containing reactive chemicals such as hypochlorous acid and chlorine gas. This corrosion resistance ensures the integrity and longevity of the cathode, minimizing the risk of material degradation and contamination of the reactor solution.[30]

Similarly, the anode material comprised titanium coated with mixed metal oxides obtained from Telpro, consisting of Iridium oxide (IrO_2) and Tantalum oxide (Ta_2O5), lab-synthesized RuO_2-coated anodes, and modifications of Telpro MMO. This choice offers several advantages akin to those of titanium. Firstly, the titanium substrate provides a robust foundation, while the mixed metal oxides coating enhances the anode's electrocatalytic properties, promoting efficient electrolysis. Moreover, like titanium, the mixed metal oxides coating exhibits resilience to harsh operating conditions, including high current density and corrosive environments. This durability ensures the long-term performance and stability of the anode, crucial for sustained reactor operation. Additionally, mixed metal oxides are widely recognized for their effectiveness in chloro-alkali technology, where they have been shown to improve the efficiency of sodium chloride electrolysis.[34,47] By leveraging the combined benefits of titanium substrate and mixed metal oxides coating, the anode material enhances the overall performance and efficiency of the electrochemical reactor, contributing to its effectiveness in various industrial applications, particularly in wastewater treatment and disinfection processes.

3.2 NANOPARTICLE SLURRY PREPARATION AND SYNTHESIS

3.2.1 The procedures and materials used for TiO_2 and RuO_2 nano-catalysts preparation and synthesis are described below.

3.2.1.1 Materials used:

Titanium (IV)butoxide (≥ 97%)

H_2O_2

Ammonium Hydroxide (NH_3OH)

Deionized Water

3.2.1.2 Equipment used:

- Stir plate.
- 250 mL beaker
- Magnetic Stirrer
- Filter paper or screen
- Water bath (20 C)
- pH strips
- Brown bottle for storage

mM- 1/1000th of a mole per liter

3.2.2 Procedure For Low Temp TiO_2 (Titanium Dioxide) Nano-Catalyst Preparation and Synthesis

The procedure for low temp titanium dioxide nano-catalyst preparation was obtained from[47–49] with some modifications.

1. Weigh uncoated electrode.
2. Immediate precipitation of hydrolyzed titanium species occurs when TiB precursor (4 mL) is added to deionized water (100 mL) under vigorous stirring.
   a. Reacts with water to form butanol and titanium dioxide.
3. These hydrolysis reactions continued for 5 to 10 min, after which the resulting precipitate was filtrated and washed with distilled water.
4. Prepare 45 mL of 35% H_2O_2 solution in water.
5. The dry precipitate was dissolved by adding H_2O_2 (45 mL, 35% in water, Sigma-Aldrich), resulting in a very exothermic reaction.
   a. Very exothermic, safe beaker and gloves
   b. Done in water bath. Control of the temperature in a thermostatted water bath at 20 °C is necessary to guarantee a reproducible synthesis route towards a stable precursor solution.
   c. A controlled addition of H_2O_2 until the reaction diminishes is therefore most appropriate. Adding 1 mL at a time
   d. At the bottom of the recipient a translucent, red phase appears, while the foam is formed in the top part.
   e. Slowly add 1 mL of H_2O_2 until complete red solution
6. Immediate dilution with water by a factor of 3 is necessary to avoid the development of a highly viscous polymeric gel phase.

a. Triple volume with water (DI water)

b. A clear, orange to the yellow solution of low viscosity appears. The current solution characteristics, with a pH of 3, will cause an increase in viscosity over time.

c. Check pH.

7. When a viscosity of 20 mPa.s is attained, the pH is increased to 7 by adding ammonia (25 wt.%, Chem-Lab). This inhibits any further viscosity increase. Slowly add 1 mL at a time
    a. Instead of controlling viscosity watch pH.
    b. This step can be varied for desired coating thickness.
8. Storage in a dark vessel allows for extended stability of the precursor solution for up to several months.

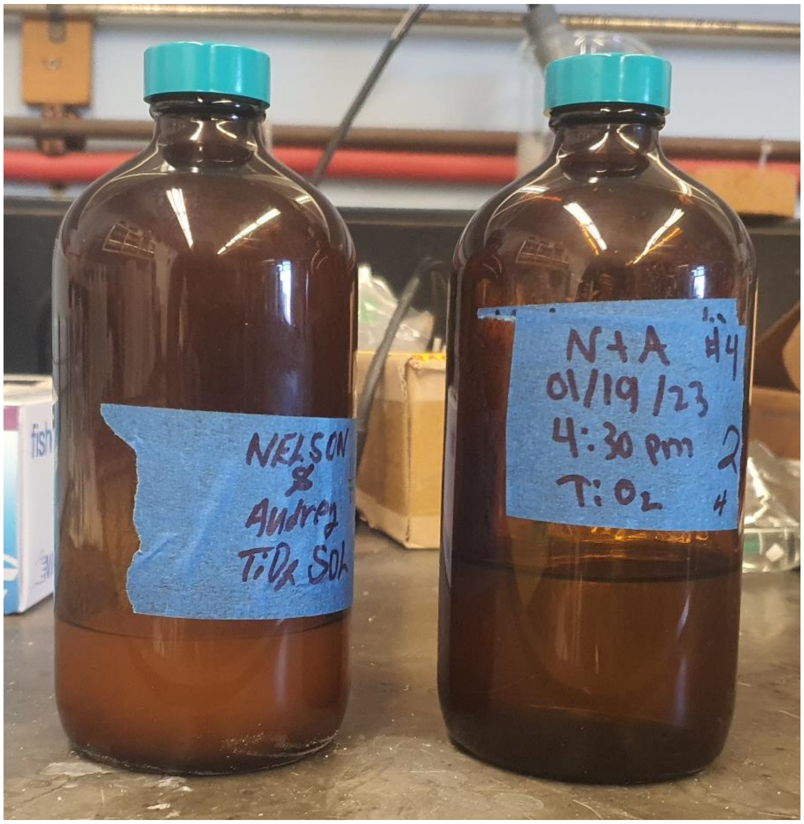


Figure 3-1: Lab-Synthesized TiO_2 Solution

3.2.3 Procedure For Low Temp RuO_2 (Ruthenium Dioxide) Deposition on Blank (Rough Surface) Titanium

The procedure for low temp ruthenium dioxide nano-catalyst preparation was obtained from[25] with some modifications.

3.2.3.1 Materials used:

Ruthenium (III) chloride ($RuCl_3$)

Deionized Water

3.2.3.2 Equipment used:

i. Ceramic Oven (furnace)

ii. Acetone (99.5%)

iii. Gloves

iv. Tweezers

v. Blank Ti wires (of desired shape and size)

vi. 50ml Beaker (Tailor to desired solution size)

3.2.3.3 Electrode (Anode Material) Preparation

1) Clean gloves must be worn throughout the procedure.
2) Make a mixture of acetone and water (50V/V%)
    i) 50 mL Acetone
    ii) 50 mL DI Water
3) Immerse tweezers in mixture.
4) clean crucibles with the mixture
5) Using the clean tweezers, immerse the anode materials in the mixture.
    a) Place in the crucible and allow to air dry.

3.2.3.4 RuO_2 Nanoparticle Slurry Preparation

1) Make a mixture of $RuCl_3$ and DI water (1/20 wt/wt%)
    a) 1g $RuCl_3$
    b) 20g DI water
2) Weigh a gram of $RuCl_3$ and pour it into a beaker.
3) Weigh and add 20g of DI water and shake mixture mildly for 5 mins.
4) Pour the prepared solution into preferred container, use immediately or store for future use.

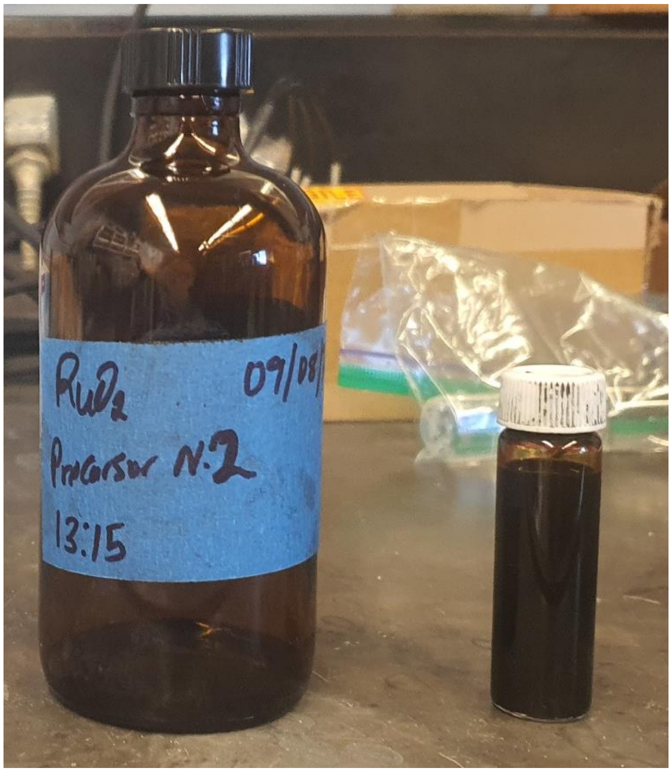


Figure 3-2: Lab-Synthesized RuO_2 Solution

3.3 Coating Process

Similar coating procedures and methods were used for the deposition of RuO_2 and TiO_2 nano-catalysts on the desired substrates, mostly thin blank titanium wires and ribbons.

3.3.1 Dip Coating

1. Clean gloves and tweezers must be used throughout the procedure.
2. Using clean tweezers, soak anode materials in the slurry for 24hrs.
3. Set ovens to 80 C and 425 C (2 ovens are preferred for this process)
4. Take out and place anode materials in crucibles. Use gloves and crucible tongs to safely put in oven.

5. Anneal in the 80C oven for 10mins. Place immediately and anneal in 425C oven for 10mins.
6. Repeat process 9 times (optimal loading number) or vary for different deposition thickness and layer (Quickly remove from the 425C oven and place anode materials into the solution)
7. Finally, anneal at 425C for 1hr.
8. Allow to cool for 2hrs and use!

Figure 3-3: Furnace for annealing/coating processes.

Figure 3-4: Anode Wires Inside a Crucible for Coating.

3.4 <u>Chlorine Concentration Measurement</u>

The determination of hypochlorous acid concentration in the product solution relies on measuring the total chlorine concentration, encompassing both free and combined chlorine forms. As the raw material consists solely of salt and deionized water, no chlorine is present in the solution prior to the electrolysis process. Thus, it is assumed that all chlorine in the solution post-reaction exists as either HOCl or OCl-, which can be converted to HOCl. The total chlorine concentration is quantified using the iodometric method with Hach's digital titrator "Digital Titrator | Hach.".

This method involves the introduction of potassium iodide to a chlorine-containing sample at a pH below 8, leading to the proportional release of free iodine. Subsequently, sodium thiosulfate is employed to titrate the iodine.

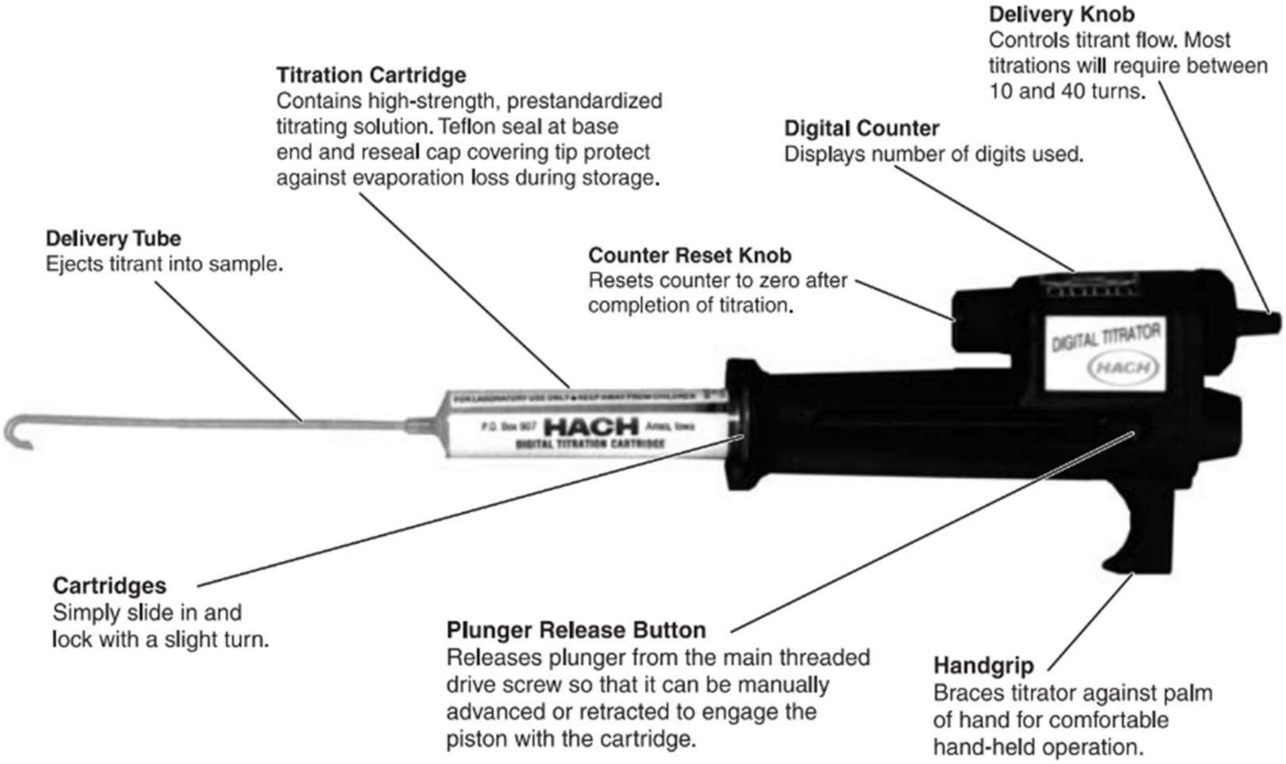


Figure 3-5: Hach Digital Titrator (Digital Titrator Manual, Model 16900, 2013)"Digital Titrator | Hach."

https://www.hach.com/p-digital-titrator/1690001.

Figure 3-6: Hach Digital Titrator showing dark purple color before titration.

The Hach test kit comprises essential components such as a titration body, 0.113 N sodium thiosulfate titration cartridge, dissolved oxygen 3 powder pillows, potassium iodide powder pillows, and starch indicator solution. Determination of the chlorine concentration dictates the selection of an appropriate sample volume. The titrator assembly involves connecting a clean delivery tube and the titration cartridge to the titrator body, followed by flushing the delivery tube with the titration solution and resetting the titrator counter to zero. A chosen sample volume is mixed with deionized water to create a 50 mL solution in a 125-mL Erlenmeyer flask, to which dissolved oxygen 3 powder pillows and potassium iodide powder pillows are added and thoroughly mixed. Placing the titrator on top of the flask with the delivery tube tip immersed in the solution, sodium thiosulfate is gradually added while swirling the flask until the solution turns pale yellow. The addition of starch indicator solution should result in a dark blue color, with titration continuing until the solution becomes colorless. The total chlorine concentration in mg/L is calculated by multiplying the titrator reading with the corresponding digits multiplier based on the chosen sample volume. Upon completion of the measurement, the titrator components are detached for storage, and the delivery tube is rinsed with deionized water and dried for future use.

3.5 Experimental Setup

A system for producing hypochlorous acid by sodium chloride/water electrolysis was purchased from Maine Manufacturing Partners (MMP). The unit recirculates the NaCl/water solution through a reactor, where electricity is applied to produce hypochlorous acid and hydrogen. The hydrogen is collected by filtration through a ceramic hollow fiber membrane and quantified by water displacement. The circulating solution also passed through a bag filter.

Figure 3-7: MMP Unit 1 (Hypochlorous acid generator)

MMP unit 1 is one out of the three system units that were used in this project.

MMP unit 2: Is a simple flow through unit designed for the testing of hypochlorous acid yield and quality.

See Figure 3-8.

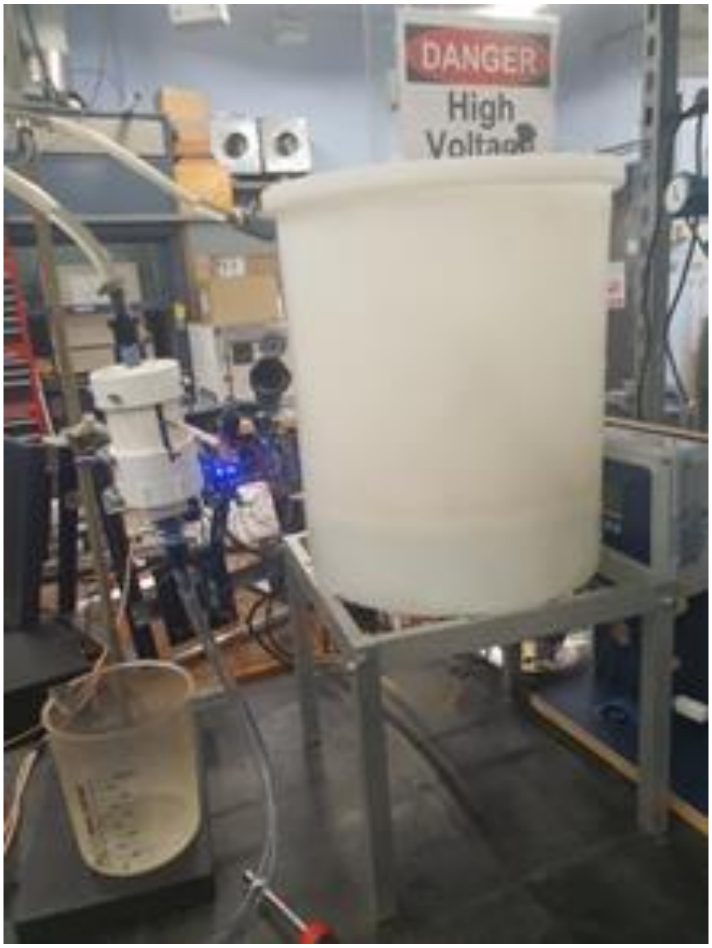


Figure 3-8: MMP Unit 2

MMP unit 3: Is an equally simple flow through unit for quick testing and evaluation of anode materials. See Figure 3-9.

Figure 3-9: MMP Unit 3

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 solution run was 2% w/w sodium chloride in water (20 g of NaCl per 1 L of solution). The sodium chloride 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.

3.6 Generic Reactor Components

The reactor's design prioritizes cost-effectiveness and simplicity, sourcing most components from plumbing stores, except for specialized cathode and anode materials. Its robust construction ensures effective sealing against water leakage. Versatile assembly capabilities accommodate diverse cathode and anode configurations, enhancing flexibility in experimentation and optimization. Furthermore, seamless integration into existing flow systems simplifies setup and operation, facilitating swift deployment in wastewater treatment applications. With scalability to commercial proportions, the reactor exemplifies adaptability and efficiency, poised to meet the demands of diverse industrial settings with ease and effectiveness.

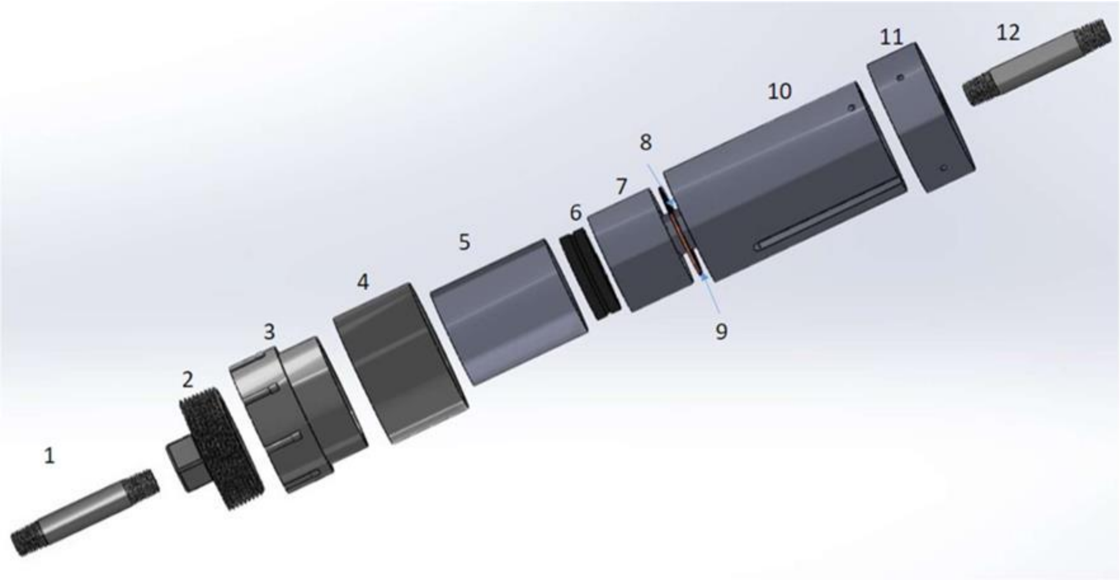


Figure 3-10: Drawing of prototype 1 of the reactor.

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

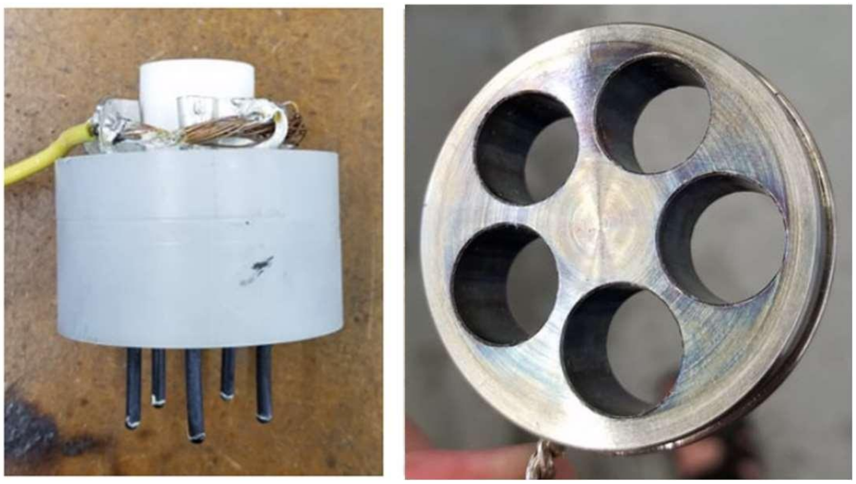


Figure 3-11: Structure of the electrodes.

The picture on the left shows anode wires while the picture on the right is a cathode. A cathode is simply a piece of material with 5 or more drilled holes as shown in Figure. An anode is a pin or ribbon that sits in the middle of one of the 5 or more holes of the cathode.

3.7 Variables To Manipulate: Cell Geometry, Flow Rates, Electrode Configuration

As pointed out earlier, in the field of electrochemical engineering, optimizing reactor performance involves manipulating key variables: cell geometry, flow patterns, and electrode configuration. Cell geometry, including electrode spacing and reactor volume, affects mass transfer and reactant distribution, influencing reaction kinetics and selectivity. Varying flow patterns, such as laminar or turbulent regimes, impact mixing efficiency and transport phenomena, allowing engineers to tailor flow velocities for optimal mass transport. Electrode configuration, encompassing size, shape, spacing, and material composition, determines electric field distribution and reaction rates. Manipulating electrode geometry controls reaction kinetics and energy utilization, with advancements in materials enhancing selectivity and durability. By adjusting these variables systematically, engineers achieve precise control over reaction kinetics and product quality in diverse industrial applications.

The reactors were designed with different number of holes and sizes to increase the proximity of the wires and provide more active surface areas for reaction. Optimum flow rates and patterns are required for these reactors to ensure optimum performance of the entire system. We carried out our experiments at different flow rates and recorded different chlorine selectivity at variable flow rates.

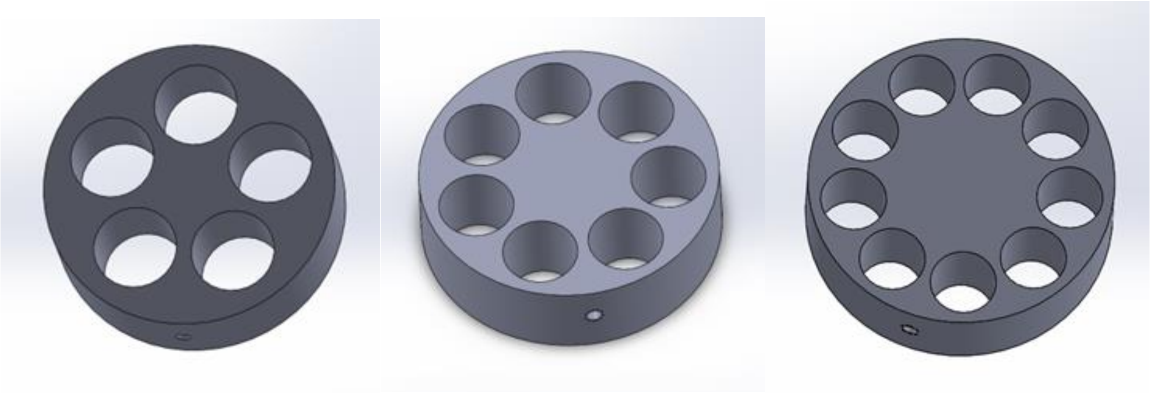


Figure 3-12: Different Cathode Configurations

Figure 3-12 show different cathode configurations of 5, 7, and 9 holes respectively.

CHAPTER 4

4 RESULTS AND DISCUSSION

4.1 Anode Performance Data

Performance evaluation for different anode materials were carried out primarily in two different reactor/system set-ups. The first reactor set up, referred to as a test reactor, was simplified for rapid evaluation of anodes. The second reactor set up, referred to as a production reactor, allowed testing in a production-like environment, like the treatment plant at Biddeford Pool, are brief descriptions of the two reactor types, followed by key metrics used in the analysis of this research project.

Test Reactor: This is a simple electrolysis reactor comprised of single anode and a cathode immersed in a flowing solution connected directly to a power source. The cathode was a 0.0625 in. diameter titanium wire. The anode was also a 0.0625 in. diameter coated titanium wire. This reactor is designed and fabricated for quick electrode material analysis and validation.

Figure 4-1: Test reactor prototype 3.

Production Reactor: A production reactor on the other hand is a more complex unit with anodes and cathode materials housed in a compartment (see component descriptions in Chapter 3). The production reactors are fabricated with components from the test reactor after evaluation for further analysis and experiments mimicking the wastewater treatment facility conditions. Production reactor cathodes consisted typically of 1.75 inch by 0.5-inch titanium disc with five 0.5-inch holes whose inner surfaces were the reaction site. Anodes were either 0.0625-inch diameter coated titanium wires or 0.25 in by 0.025 in thick coated ribbon. Elongated single ribbon and single wire reactors were also investigated. These reactors were 5 inches long and fabricated from titanium tubing, 0.5-inch OD, which served as the cathode.

Chlorine Selectivity: Chlorine selectivity, a critical aspect of electrochemical processes, compares the theoretical production rate of chlorine with the actual production rate achieved during electrolysis. The theoretical production of chlorine assumes all available electrons participate in the oxidation of chloride ions to chlorine gas. This was determined using Faraday's equation $r = \frac{I}{nF}$, where I is the current, n is the reaction constant (2 for this reaction) and F is Faraday's constant. The actual chlorine production rate was determined by measuring total chlorine concentration over a known time interval. This number is also referred to as current efficiency, or the efficiency of electron conversion to desired product. Higher chlorine selectivity signifies a greater proportion of desired chlorine gas relative to byproducts. In this system the major by-product is oxygen gas. Understanding chlorine selectivity is vital for optimizing reactor design and material selection to enhance process efficiency and reduce costs. Factors such as electrode composition, surface morphology, and operating conditions influence selectivity, necessitating systematic analysis. By correlating selectivity trends with parameters like current density and electrolyte concentration, researchers can optimize production rates while minimizing energy consumption and waste generation. Advancing knowledge of chlorine selectivity holds promise for improving electrochemical technologies in water treatment, chemical synthesis, and other industries.

Current Density: Current density is defined as the current normalized to the surface area of the electrode. In this study surface area was determined by the bulk physical measurement of the electrodes. Surface roughness, particle size and particle shape were not considered.

Specific Energy Consumption: The energy required to generate chlorine was determined by calculating the power delivered to the electrodes (from current and voltage measurement) and dividing by the chlorine production rate as described above. The units typically given are $\frac{kW\cdot hr}{kg}$. Minimizing this value leads to more energy efficient processing.

Current density, a crucial parameter in electrochemical processes, refers to the amount of electrical current flowing through a given area of the electrode surface. It plays a significant role in determining reaction kinetics, product selectivity, and energy efficiency. Higher current densities generally lead to increased reaction rates and higher production rates of desired products. However, excessively high current densities can result in undesirable side reactions, decreased selectivity, and electrode degradation. Therefore, optimizing current density is essential to balance production efficiency with electrode durability and product quality. Understanding the relationship between current density and electrode performance is vital for designing efficient electrochemical systems with enhanced productivity and longevity. Experimental analysis and computational modeling are commonly employed to study the effects of current density on electrochemical reactions and inform process optimization strategies.

Parameters: The effect of anode material, current density, applied voltage, sodium chloride concentration, and reactor geometry on chlorine selectivity and specific energy consumption were evaluated.

4.1.1 Surface Morphology of Anodes:

Several anodes were evaluated for chlorine production. These anodes were either purchased (MMO, from Telpro) or fabricated with some combination of RuO_2 or TiO_2 layers whose synthesis procedures are detailed in Chapter 3. Scanning Electron Microscopic images were obtained to examine the surface morphology before and after coating.

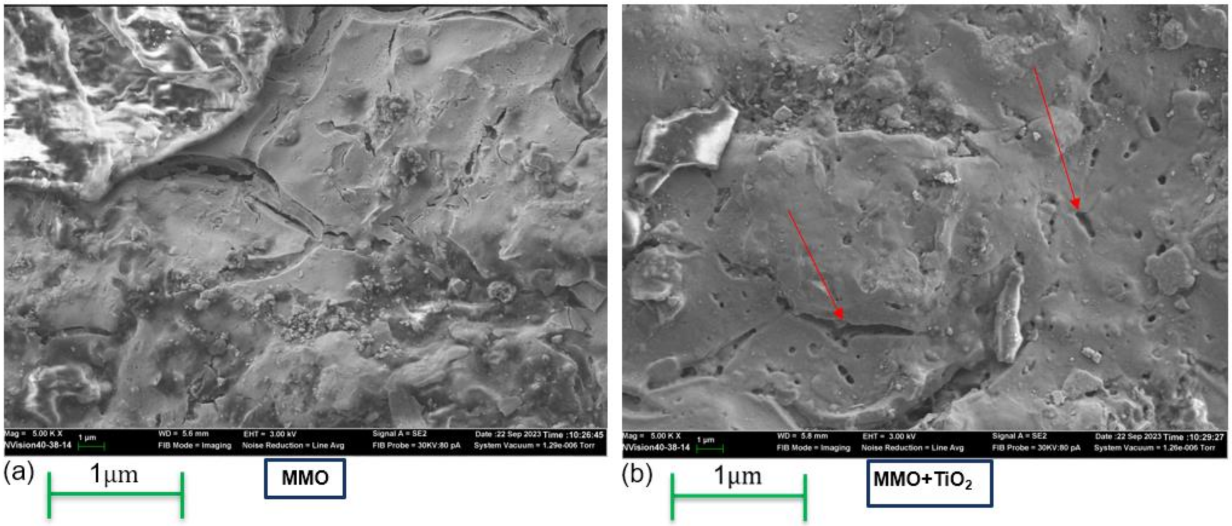


Figure 4-2: A 1 micrometer scale view of an MMO wire (a) before and (b) after Ultrathin TiO_2 doping.

Figure 4-2 shows a one micrometer scale view of an MMO wire before and after ultrathin TiO_2 deposition respectively. Literature suggests that the cracks and tiny holes depict the presence of titania particles on the substrate.[50,51]

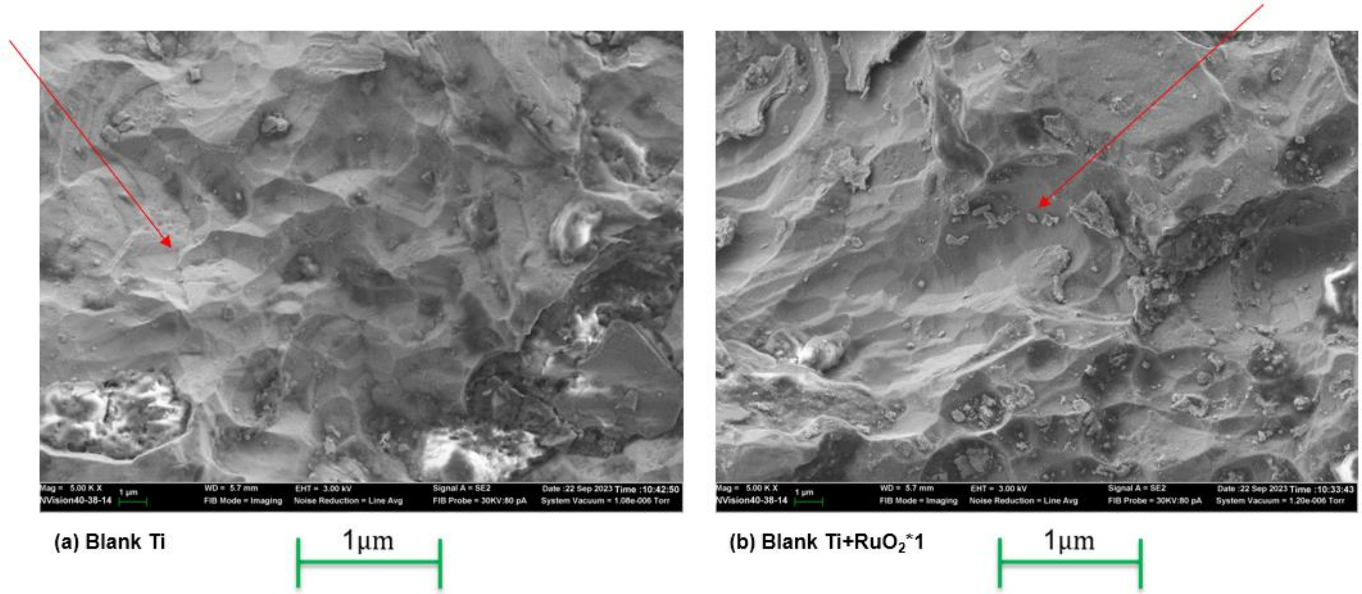
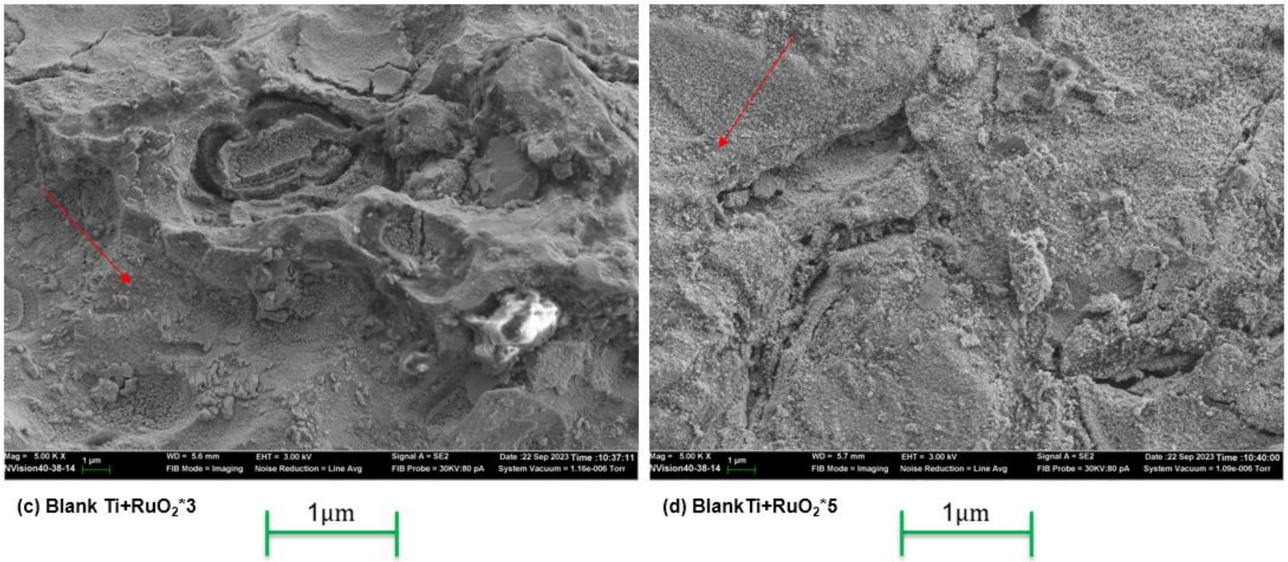


Figure 4-3: A 1 micrometer scale view of blank Ti wire before and after variable dip cycles.



(c) Blank Ti+RuO_2*3

(d) BlankTi+RuO_2*5

Figure 4-4 A 1 micrometer scale view of blank Ti wire before and after variable dip cycles.

Figure 4-3 and Figure 4-4 show a one micrometer scale view of a blank titanium wire before and after thin RuO_2 coating of 1, 3, and 5 dips respectively. There is a visible increase in the quantity and coverage of particles on the wires with increasing dip cycles. It is assumed these particles are RuO_2 however further analysis is required to confirm that.

4.1.2 Anode materials comparison:

MMO anode material is a mixed metal oxide consisting of Iridium oxide (IrO_2) and Tantalum oxide (Ta_2O_5) obtained from Telpro. RuO_2 and TiO_2 nanoparticles were deposited on the MMO to improve its catalytic activity and dimensional stability, respectively. Several anode configurations were fabricated and tested. These were: mixed metal oxide (MMO), titania coated MMO (MMO + TiO_2), titania (first layer) and Ruthenia (second layer) coated MMO (MMO + TiO_2 + RuO_2), Ruthenia coated titanium (Ti + RuO_2), and Ruthenia coated MMO (MMO + RuO_2). Although the thickness and uniformity of the nanoparticles' coating weren’t determined, the coating was typically carried out at 5 dips and annealed as described in Chapter 3.

4.1.2.1 Test Reactor anode material analysis:

Experiments were carried out with the test reactor for analysis and are described below. For these experiments the sodium chloride concentration was 20 g/L. The experiments were run at constant flow rate, roughly 1500 mL/min. The experiments were conducted at constant voltage of 6V.

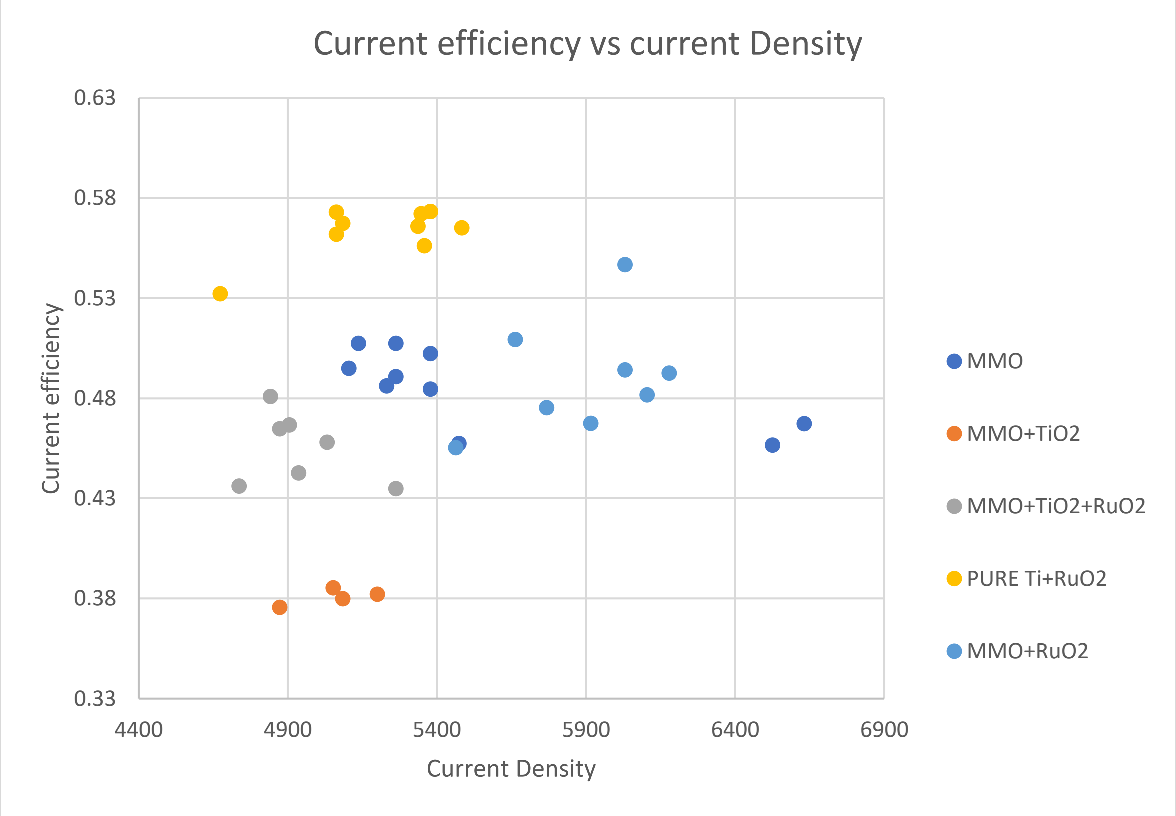


Figure 4-5: Different MMO anode modifications and RuO_2 Comparisons

Figure 4-5 above shows a comparison of current efficiency (chlorine selectivity) vs current density of different anodes against the control anode material (MMO). TiO_2 coated MMO portrays a weaker affinity for the chlorine evolution reaction hence a decreased chlorine selectivity. And a RuO_2 deposition on the same material improved its chlorine selectivity from 38% to 48%. The effect of Ruthenia coating on MMO on current efficiency was unclear and appears to have no effect. The deposition of RuO_2 on a blank titanium wire shows a significant improvement in chlorine selectivity relative to the MMO anode, from an average of 49% to 56%. This quick and inexpensive reactor design and experiments helped establish the superior affinity of Ruthenia to chlorine evolution reactions. This is consistent with the literature.[52] Considering that the Ruthenia-coated anode used in the test reactor was produced at 5 dips, we tried to further analyze the effect of coating thickness on the material's chlorine selectivity. More dip cycles were considered due to the lack of complete surface coverage seen in the SEM images. It was thought prudent to increase the dip cycle to ensure total coverage of the substrate surface. 7-dip and 9-dip Ruthenia-coated anode wires were produced for this cause. Results are shown in Figure 4-6.

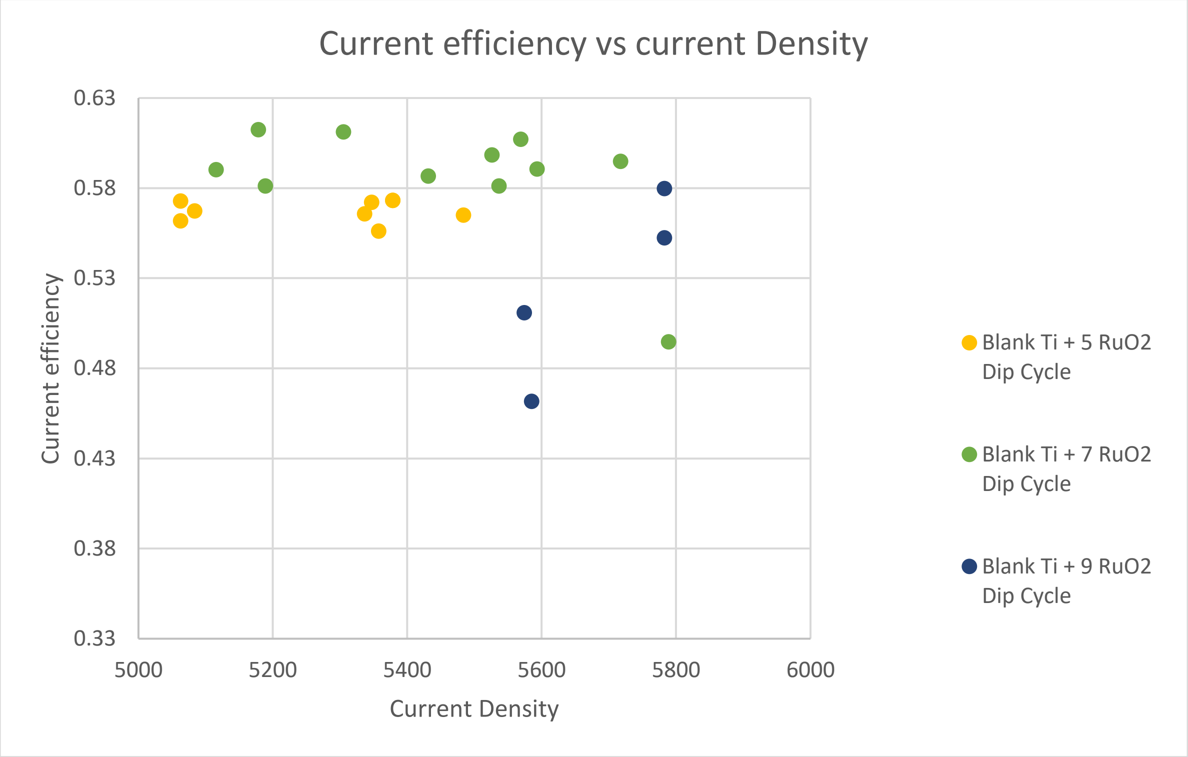


Figure 4-6: RuO_2 Anode Dip Cycles Comparison on Chlorine Selectivity

As seen in Figure 4-6, the effect of the increase in layer thickness through increased dip cycles appears mixed. Increasing to 7 dip cycles increased chlorine current efficiency, however 9 dip cycles resulted in a slight decrease in chlorine current efficiency. These results are preliminary and further investigation is required to optimize Ruthenia layer thickness for maximum chlorine current efficiency. Increasing the dip cycle from 5 to 9 could decrease chlorine selectivity for a few reasons. Firstly, the excess ruthenium deposition might over-saturate the anode surface, blocking the very active sites that are crucial for chlorine evolution. Secondly, too much ruthenium could cause the catalyst to restructure in a way that changes its surface morphology, making it less efficient for chlorine-specific reactions. Finally, the increased number of dip cycles raises the risk of introducing impurities from the solutions. These impurities can potentially poison the active sites on the catalyst, hindering chlorine production and reducing selectivity. To address this, we will consider optimizing the dip cycle, ensuring solution purity, and analyzing the anode surfaces using characterization techniques.

4.1.2.2 Production Reactor Anode Material Analysis:

To further evaluate the test reactor results, production reactors were fabricated with three anodes: MMO, MMO + TiO_2 and Ti + RuO_2. The results and analysis are detailed below for the 5-pin reactor type in Figure 4-7. These experiments were typically run at 6.5 V. The experiments with MMO were run at constant current of 5 Amps.

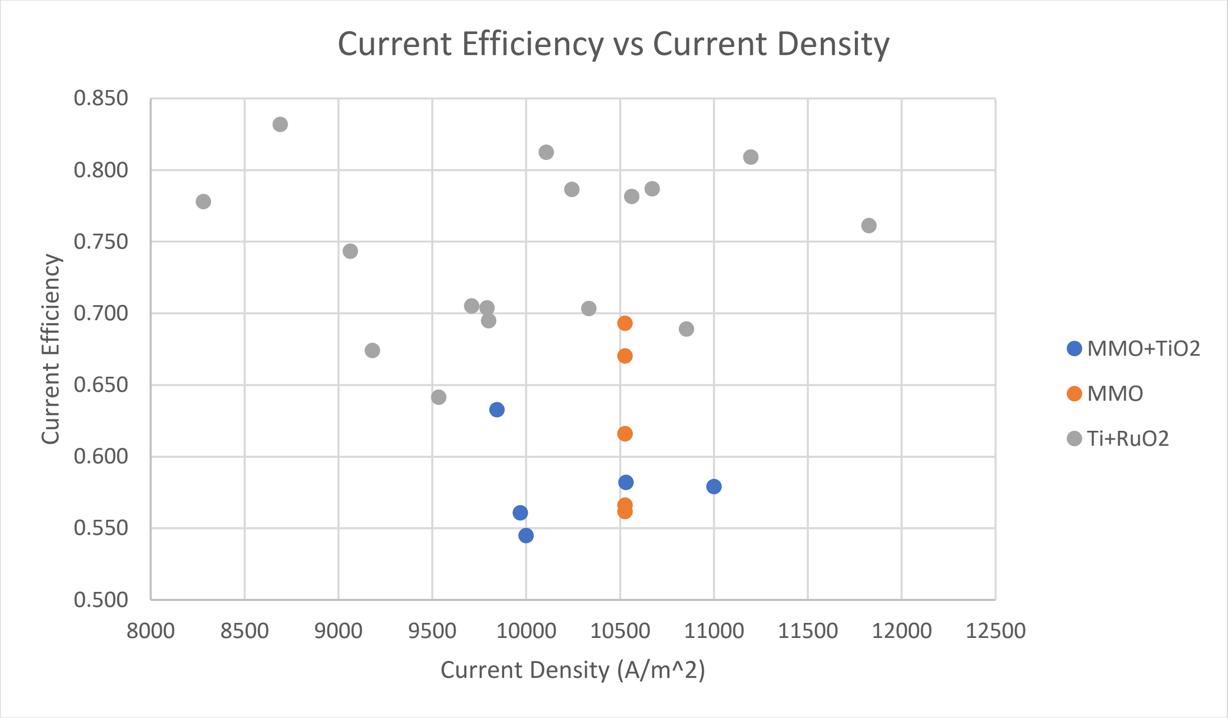


Figure 4-7: RuO_2 *and MMO Anodes Comparison*

These results confirm the results from the test reactor regarding Ruthenia coated titanium. Current efficiency was improved roughly 20% relative to MMO anodes. A slight decrease in current efficiency was observed with titania coated MMO, also consistent with the test reactor results. Figure 4-8 plots the current efficiency results relative to MMO anodes for the test and production reactors, highlighting the improvement measured with Ruthenia coated titanium anodes.

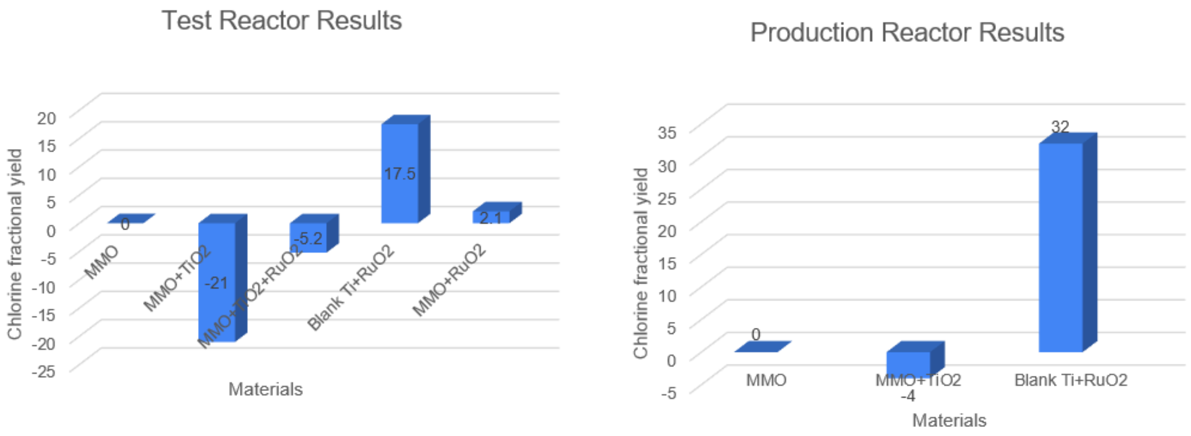


Figure 4-8: Test and Production Reactors Analysis

4.1.2.3 Specific Energy Consumption Analysis for Variable Anode Materials:

Figure 4-9 shows the improvements in specific energy usage when using Ruthenia coated titanium anodes in the production reactors. This advantage could be attributed to RuO_2 superior CER proclivity and higher electrical conductivity over MMO, and titania coated MMO. However, titania coated MMO shows better specific energy consumption for chlorine production regardless of its high OER affinity. The use RuO_2 coated titanium anodes supports the goal of minimizing high energy consumption encountered in chloro-alkali processes.

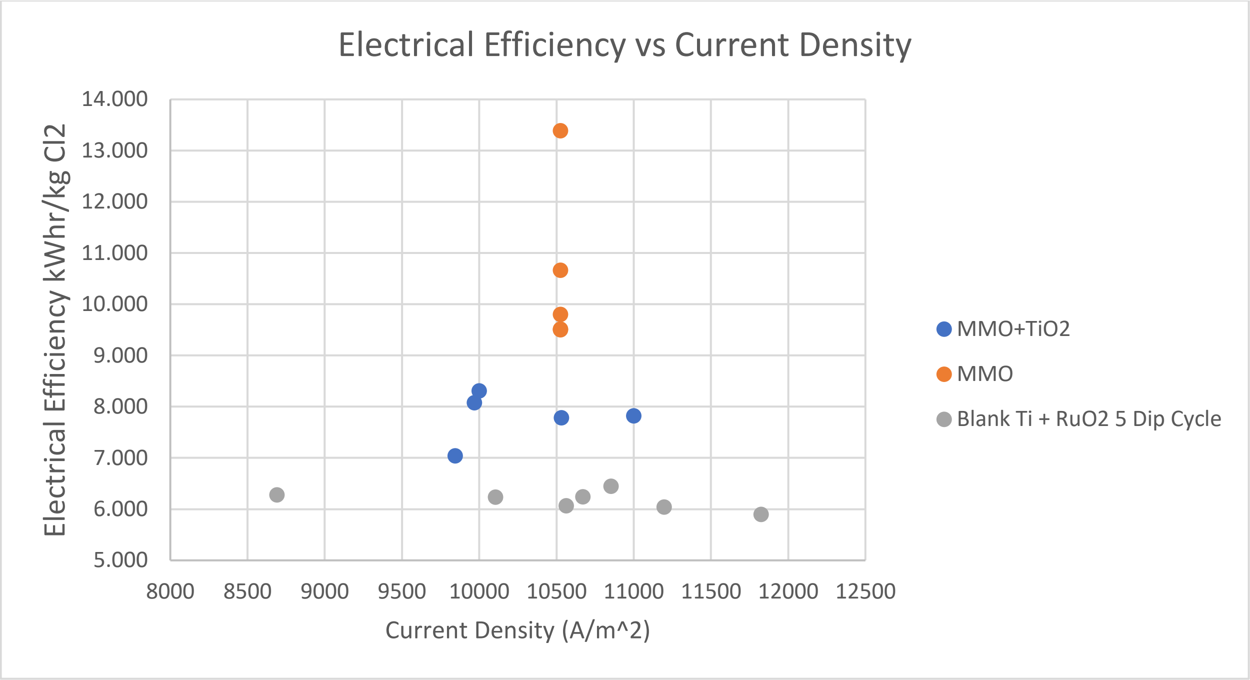


Figure 4-9 Specific energy usage kWhr/kg Cl_2 vs Current Density.

4.1.2.4 Effects of Applied Voltage on Current Efficiency:

Figure 4-10 shows the effect of applied voltage on current efficiency. This data is shown for MMO anode only. Current efficiency decreases significantly and progressively as voltage increases indicating that increased potential favors increased oxygen production relative to chlorine production. Minimizing operating voltage is important in maximizing chlorine production.

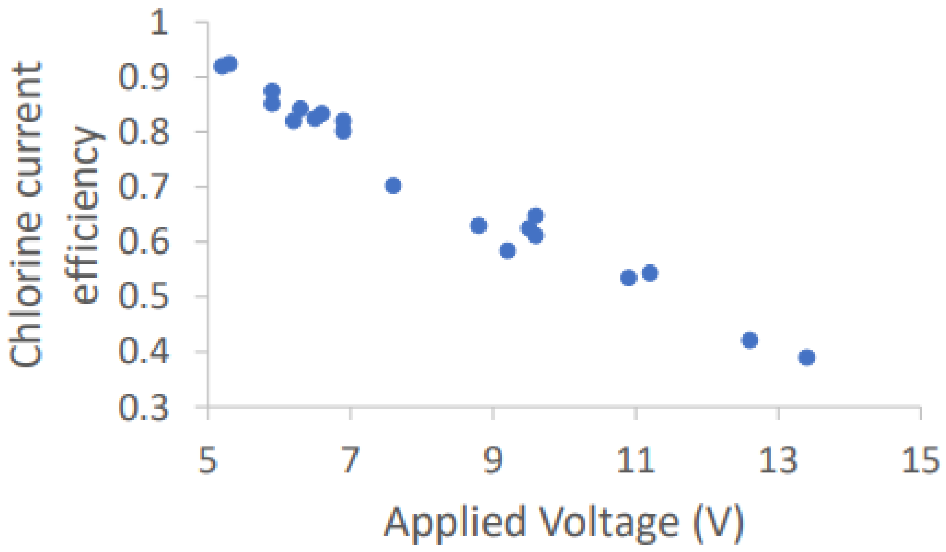


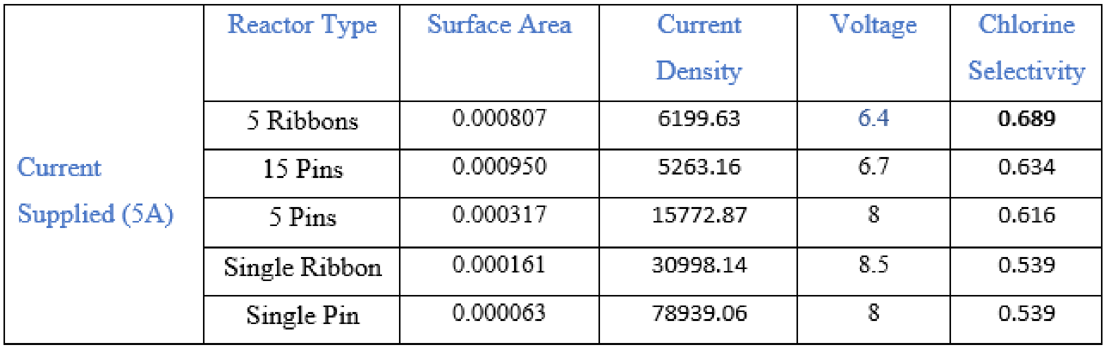
Figure 4-10 The effect of applied voltage on chlorine current efficiency at 5 A current flow.

4.2 Reactor Design Outcomes: Effects Of Active Surface Area on Reactor Performance

Five different reactor configurations using MMO anodes were evaluated with respect to specific energy consumption. The reactor types were described above. The changes in reactor configurations changed the surface area of the anode and the distance between the anode and cathode. Increasing surface area under constant current reduces current density. Decreasing the electrode separation distance reduces the ohmic resistance in the reactor and can improve specific energy use.

Table 1 shows physical data and results from experiments conducted on the five different reactor types. Chlorine selectivity decreases with applied voltage, consistent with Figure 4-10 above. For the constant current run in these reactors, ohmic resistance determines the required applied voltage. Ohmic resistance in a reactor combines resistances from contacts, electrode material, electrode separation distance and salt concentration. Increasing voltage will also increase resistance due to internal heat generation. The first two reactors have larger surface areas and shorter electrode separation distances which could contribute to lowering ohmic resistance in the reactor. This trend is also reflected in the specific energy consumption favoring reactor designs that minimize ohmic resistance. Figure 4-11 shows the increase in specific energy use as applied voltage is increased for all reactor types. Figure 4-12 shows results for reactors running under constant current of 5 A. This analysis is more practical and reflects basic knowledge to minimize ohmic resistance in electrochemical reactors. It is acknowledged that the reaction system is quite complex and dependent on many variables that were not considered.

Table 1: The current density of different anode surface areas



	Reactor Type	Surface Area	Current Density	Voltage	Chlorine Selectivity
Current Supplied (5A)	5 Ribbons	0.000807	6199.63	6.4	**0.689**
	15 Pins	0.000950	5263.16	6.7	0.634
	5 Pins	0.000317	15772.87	8	0.616
	Single Ribbon	0.000161	30998.14	8.5	0.539
	Single Pin	0.000063	78939.06	8	0.539

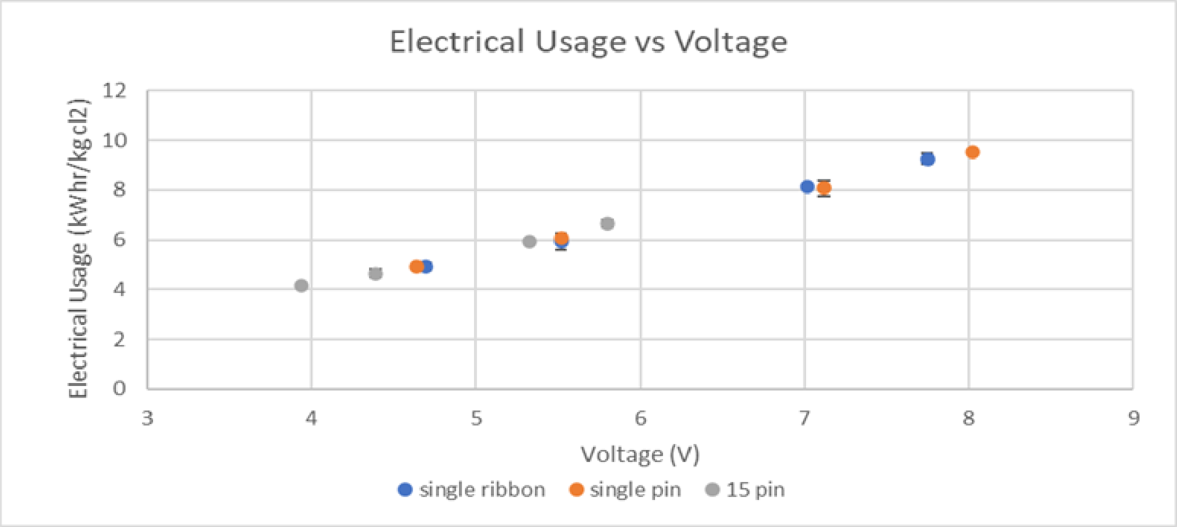


Figure 4-11: Electrical usage vs voltage for variable active surface areas.

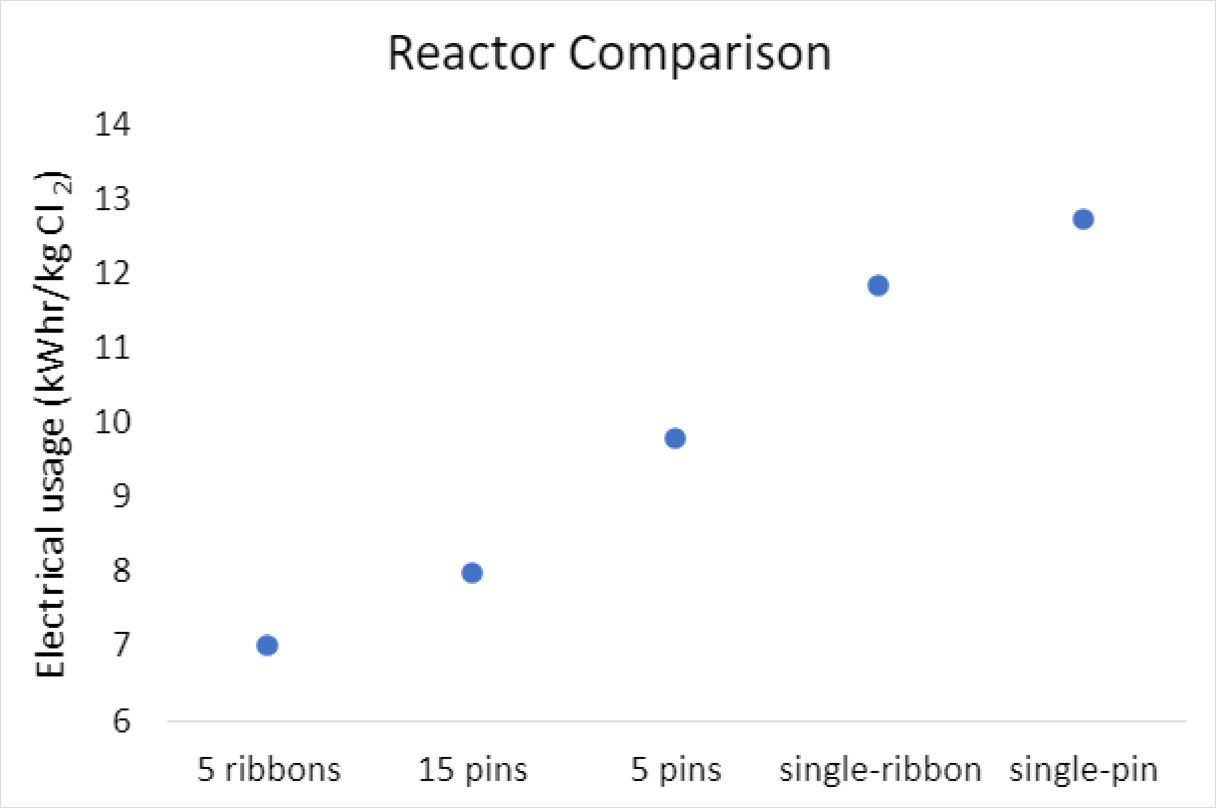
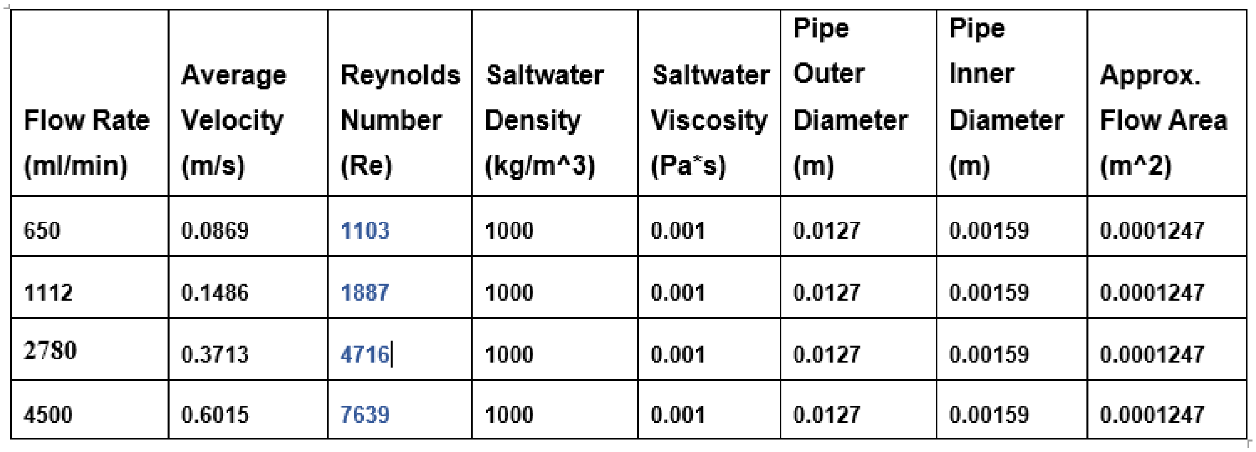


Figure 4-12: Electrical Usage vs Reactor surface area comparison.

4.3 The Effects of Flow Rate on Reactor Performance

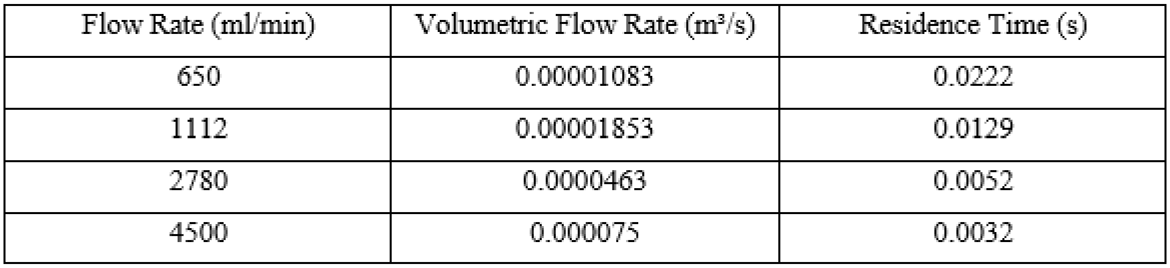
For continuous-flow through electrolysis reactors, it is expected that flow rate through the reactor is an important variable to understand. Flow rate can impact multiple variables and is complex to analyze the effect on reactor performance. Flow rate directly impacts the residence time of reactants within the active zone of the reactor, influencing the extent of electrochemical reactions at the electrodes. Additionally, it dictates the mass transport of reactants to the electrode surface and the removal of products, ensuring a continuous supply of reactants and preventing the buildup of products that can hinder reaction efficiency. Furthermore, flow dynamics play a crucial role in influencing mixing patterns within the reactor, promoting homogeneity, preventing localized depletion of reactants, and aiding in heat distribution to avoid hotspots that can degrade performance or damage components. Flow rate also influences bubble management, with optimal flow rates facilitating the dislodgement of gas bubbles (e.g., hydrogen) from the electrode surface to maintain electrode accessibility. From an engineering perspective, manipulating flow rate requires careful consideration of energy consumption, as increased flow rates can lead to higher pressure drops and greater pumping costs. Thus, optimizing flow rate necessitates a delicate balance between maximizing reaction efficiency, ensuring effective mass transport, and minimizing energy consumption. Because of the complexity of the reaction environment, it is prudent to experimentally determine the effects of flow rate on performance metrics for each reactor type.

Table 2: Flow rate and other vital parameters



Flow Rate (ml/min)	Average Velocity (m/s)	Reynolds Number (Re)	Saltwater Density (kg/m^3)	Saltwater Viscosity (Pa*s)	Pipe Outer Diameter (m)	Pipe Inner Diameter (m)	Approx. Flow Area (m^2)
650	0.0869	1103	1000	0.001	0.0127	0.00159	0.0001247
1112	0.1486	1887	1000	0.001	0.0127	0.00159	0.0001247
2780	0.3713	4716	1000	0.001	0.0127	0.00159	0.0001247
4500	0.6015	7639	1000	0.001	0.0127	0.00159	0.0001247

Table 3: Flow rate and Residence time



Flow Rate (ml/min)	Volumetric Flow Rate (m³/s)	Residence Time (s)
650	0.00001083	0.0222
1112	0.00001853	0.0129
2780	0.0000463	0.0052
4500	0.000075	0.0032

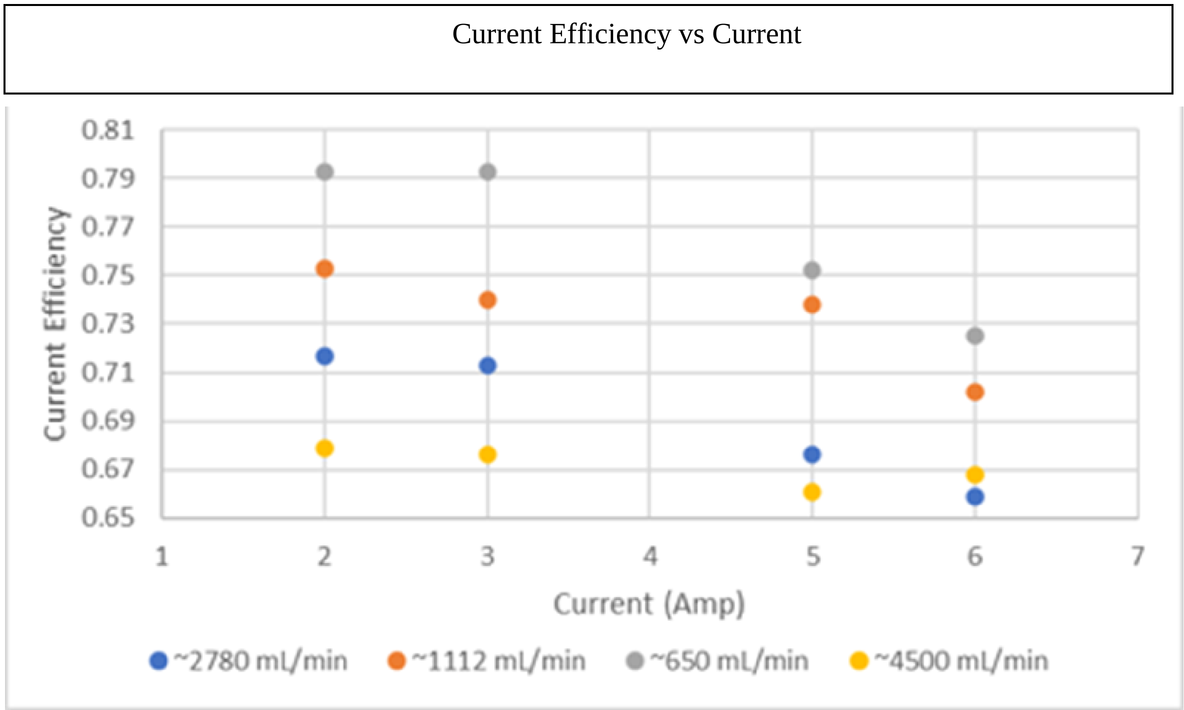


Figure 4-13: Flow rate vs chlorine selectivity.

Flow rate dependent performance data was obtained from our lab-fabricated 15-pin annular type, modular, flow-through, single-cell electrolysis reactor with MMO anode wires. Experiments explored chlorine generation performance at various flow rates under constant current densities. Table 2 shows data used to calculate fluid velocity and Reynolds numbers for different flow rates used. Table 3 shows residence time values within the reactor for different flow rates. Generally, increasing the flow rate (650 ml/min to 4500 ml/min) appears to decrease chlorine selectivity across all current densities as shown in Figure 4-12. From a practical viewpoint, operating this reactor at lower flow rates increases current efficiencies at constant current flow. Increases of approximately 16% in current efficiency were measured when lowering the flow rate from 4500 to 650 mL/min.

4.4 The Trade Off Between Electrical and Salt Usage

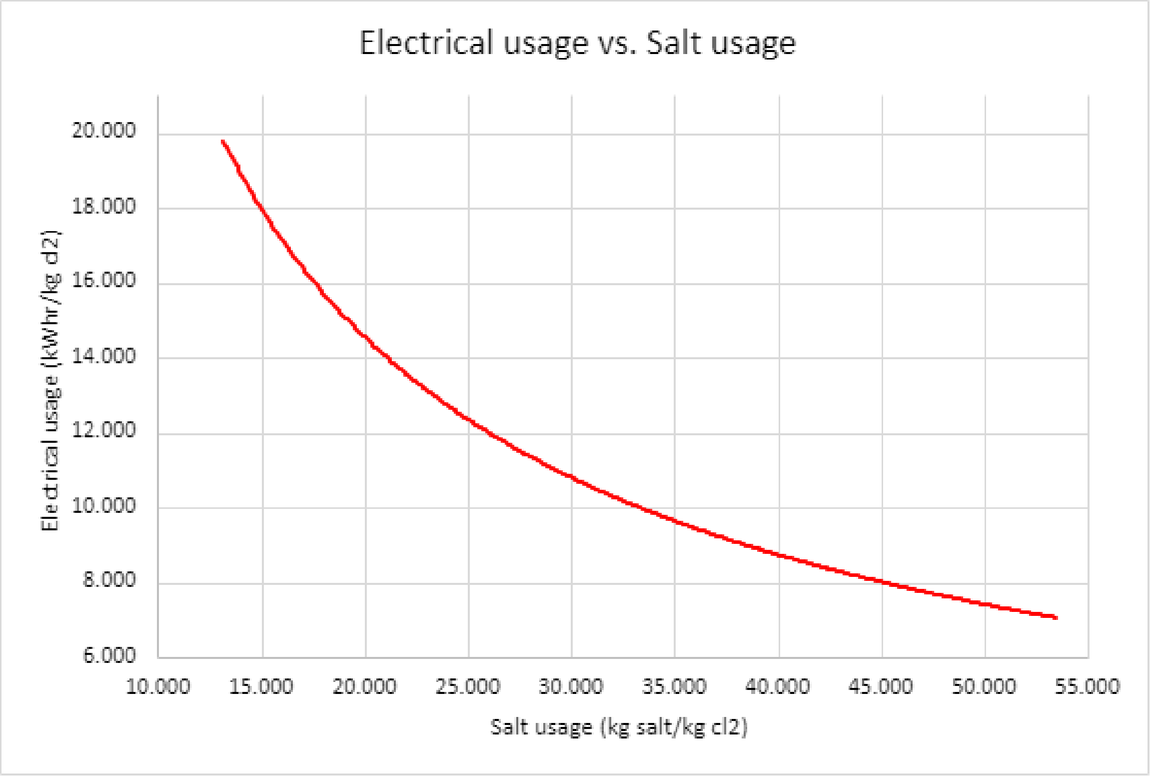


Figure 4-14: The Tradeoff Between Electrical and Salt Usage

The interplay between NaCl usage and electrical usage underscores the complex dynamics inherent in electrolysis processes. Higher NaCl concentrations increase solution conductivity, reducing electrical resistance and, consequently, electrical usage. However, higher current densities also lead to increased NaCl conversion to HOCl, reducing NaCl usage but simultaneously increasing electrical usage. Balancing these factors requires careful optimization to achieve optimal performance and cost-effectiveness. Because there is a tradeoff between the two operational costs it is worthwhile to examine preliminary technoeconomic analysis of our system.

4.5 Preliminary Techno-economic analysis:

Figure 4-16 shows the integration of an OSG disinfectant unit into a WWTP. A buffer tank containing concentrated HOCL is maintained by continually electrolyzing salt water to match the plant demand. Plant demand is controlled by maintaining a slight excess amount of chlorine in the plant disinfection tank prior to discharge. Hence, F_{out} is balanced by F_{in} and chlorine is produced to replace chlorine used.

Preliminary technoeconomic analyses of relative changes in operating costs (electricity and NaCl) were made comparing the MMO anode-based reactors against the RuO_2 anode-based reactors and buffer tank concentrations. The lower specific energy usage and higher production rate of the RuO_2-based reactor reduces electricity costs directly. Taking data from Figure 4-9, the specific energy use of RuO_2-based reactors reduces by approximately 40% at the conditions of those experiments. Further reduction could be obtained by operating at lower applied voltages, although this could require more reactors and increase capital costs. Additionally, further reductions could be obtained by operating at recirculating flow rates through the reactor. The NaCl cost is only dependent on the buffer tank concentration under constant plant demand. Doubling the buffer tank concentration will reduce the makeup NaCl flow in half (for constant NaCl concentration), thereby reducing NaCl costs.

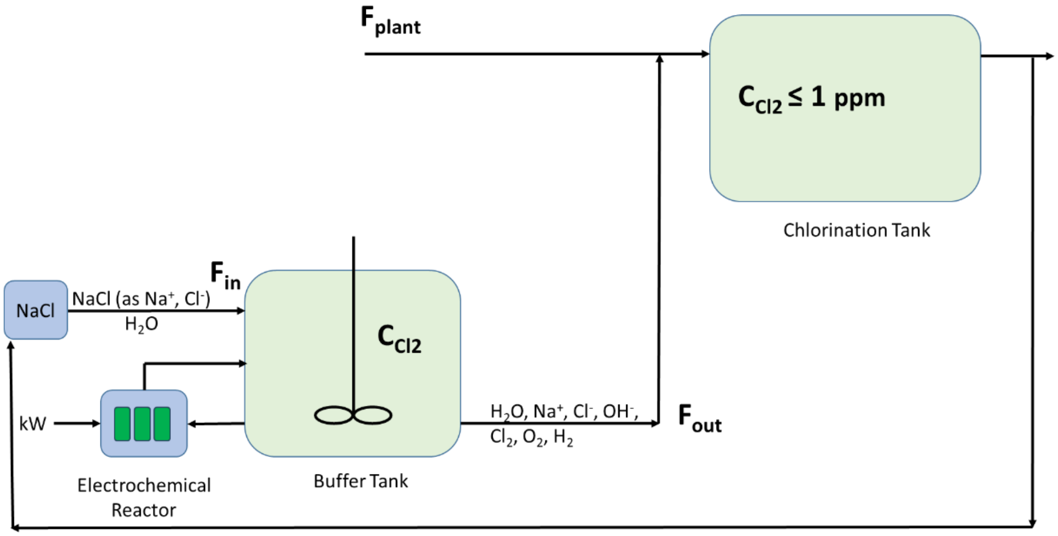


Figure 4-15: Preliminary techno- economic analysis of project work.

CHAPTER 5

5 CONCLUSION

5.1 Practical Implications

This research project delves into the optimization of electrochemical chlorine generation for water treatment applications. Anode material selection and reactor design were identified as crucial factors determining reactor performance. Experiments using a modular, flow-through, single-cell reactor revealed that RuO_2-coated anodes demonstrate superior chlorine selectivity compared to mixed metal oxides (MMOs) or TiO_2-coated variants. While RuO_2 catalysts offer promising potential, addressing dimensional stability is essential for long-term practical applications. Economic analysis suggests substantial cost savings (up to 30%) when employing RuO_2 catalysts alongside optimized operating conditions. Reactor design parameters, particularly active surface area and electrolyte flow rate, were systematically investigated. Larger active surface areas generally correlate with enhanced chlorine production and decreased energy consumption due to lower current densities. Furthermore, the data gotten highlight a complex relationship between flow rate, residence time, and chlorine selectivity. A delicate balance exists between ensuring sufficient reaction time while managing potential side reactions at excessively low flow rates. Understanding the interplay between anode materials, reactor configuration, flow dynamics, and energy efficiency is vital for developing cost-effective on-site chlorine generation systems.

To optimize reactor performance and ensure efficient utilization of RuO_2 catalyst, a modeling approach may be employed. This model would allow for the rapid adjustment of flow rates and reactor parameters across different reactor configurations, enabling the identification of optimal operating conditions for maximizing productivity and cost savings. By integrating economic considerations with performance metrics, such as chlorine selectivity and material durability, researchers can develop robust electrochemical systems that deliver both economic and environmental benefits in diverse industrial settings. Continued research and development efforts are essential to unlock the full potential of RuO_2 catalysts and advance the field of electrochemical engineering towards sustainable and cost-efficient solutions for water treatment, chemical synthesis, and beyond.

I would like to mention that a Dirigo Stream Unit from Maine Manufacturing Partners is currently integrated into the disinfection process at the Biddeford Pool WWTP managed by the City of Biddeford.

To date, over 1.3 million gallons of wastewater have been treated. Over 6000 gallons of effluent have been repurposed to produce chlorine disinfectant by electrolysis.

5.2 **Future Work**

Further research will focus on establishing the dimensional stability and cycle life of RuO_2-based anodes, which is crucial for long-term applications. Efforts will be directed towards enhancing the RuO_2 coating quality and processes for optimal electrochemical reactor (CER) performance. Utilizing advanced characterization techniques, such as mass spectrometry, will be essential to determine the composition and quality of produced gases. Investigating the effective collection and potential utilization of produced hydrogen gas is a priority to maximize the sustainability impact of this technology. Leveraging TiO_2 as a protective layer for anodes shows promise for improved robustness, making it a valuable research avenue. Continuous refinement of reactor designs and the overall system is essential for optimizing performance, addressing potential side reactions, and ensuring process efficiency. This comprehensive approach will drive ongoing innovation in electrochemical chlorine generation for water treatment and various industrial applications.

BIBLIOGRAPHY

1. Clayton GE, Thorn RMS, Reynolds DM. The efficacy of chlorine-based disinfectants against planktonic and biofilm bacteria for decentralised point-of-use drinking water. *NPJ Clean Water*. 2021;4(1). doi:10.1038/s41545-021-00139-w

2. de Sousa Filho JW, Lenza GA, Tonhela MA, de Araújo KS, Fernandes DM, Malpass GRP. Full-scale application of an electrochemical disinfection solution in a municipal drinking water treatment plant. *Water and Environment Journal*. 2022;36(1):86-95. doi:10.1111/wej.12763

3. pubmed-31701964.

4. Mohammed-Ibrahim J, Moussab H. Recent advances on hydrogen production through seawater electrolysis. *Mater Sci Energy Technol*. 2020;3:780-807. doi:10.1016/j.mset.2020.09.005

5. Kwon N, Chen Y, Chen X, Kim MH, Yoon J. Recent progress on small molecule-based fluorescent imaging probes for hypochlorous acid (HOCl)/hypochlorite (OCl−). *Dyes and Pigments*. 2022;200:110132. doi:10.1016/J.DYEPIG.2022.110132

6. Bocklage J, Miller C, Salerno A, Stocum J. *Evaluation of Hypochlorous Acid Fogging: An Alternative Disinfection Method*.

7. Kieu K Van. *INVESTIGATION OF PULSED ELECTROLYSIS FOR HYPOCHLOROUS ACID PRODUCTION*.; 2023.

8. Zeng JS, Tung HH, Wang GS. Effects of temperature and microorganism densities on disinfection by-product formation. *Science of the Total Environment*. 2021;794. doi:10.1016/j.scitotenv.2021.148627

9. Kong Q, Ye L, Pan Y, et al. *Supplementary Information: Photochemical Transformation of Free Chlorine Induced by Triplet State Dissolved Organic Matter*.

10. Stefán D, Balogh J, Záray G, Vargha M. Comparison of Disinfection By-Product Formation and Distribution during Breakpoint Chlorination and Chlorine-Based Disinfection in Drinking Water. *Water (Switzerland)*. 2022;14(9). doi:10.3390/w14091372

11. How ZT, Kristiana I, Busetti F, Linge KL, Joll CA. Organic chloramines in chlorine-based disinfected water systems: A critical review. *Journal of Environmental Sciences*. 2017;58:2-18. doi:10.1016/J.JES.2017.05.025

12. Ashby L V., Springer R, Hampton MB, Kettle AJ, Winterbourn CC. Evaluating the bactericidal action of hypochlorous acid in culture media. *Free Radic Biol Med*. 2020;159:119-124. doi:10.1016/J.FREERADBIOMED.2020.07.033

13. He Y, Hu X, Jiang J, Zhang J, Liu F. Remediation of PAHs contaminated industrial soils by hypochlorous acid: performance and mechanisms. *RSC Adv*. 2022;12(17):10825-10834. doi:10.1039/d2ra00514j

14. jcad_11_11_36.

15. Natarelli N, Nong Y, Maloh J, Sivamani R. *Hypochlorous Acid: Applications in Dermatology*.

16. Mehendale F V., Clayton G, Homyer KM, Reynolds DM. HOCl vs OCl−: clarification on chlorine-based disinfectants used within clinical settings. *J Glob Health Rep*. 2023;7. doi:10.29392/001c.84488

17. Digitalcommons@umaine D, Sebagisha DN. *Disinfection Applications of On-Site Hypochlorous Acid Disinfection Applications of On-Site Hypochlorous Acid Production Production*. https://digitalcommons.library.umaine.edu/etd/3775

18. Dénis JM, Donzé G, Willen S, Darioly M, Andlauer W, Piantini U. Monitoring of On-site Generated Hypochlorite for Water Disinfection. *Chimia (Aarau)*. 2022;76(10):871-875. doi:10.2533/chimia.2022.871

19. Perry SC, Ponce de León C, Walsh FC. Review—The Design, Performance and Continuing Development of Electrochemical Reactors for Clean Electrosynthesis. *J Electrochem Soc*. 2020;167(15):155525. doi:10.1149/1945-7111/abc58e

20. Vos JG, Liu Z, Speck FD, et al. Selectivity Trends between Oxygen Evolution and Chlorine Evolution on Iridium-Based Double Perovskites in Acidic Media. *ACS Catal*. 2019;9(9):8561-8574. doi:10.1021/acscatal.9b01159

21. Deng Z, Xu S, Liu C, Zhang X, Li M, Zhao Z. Stability of dimensionally stable anode for chlorine evolution reaction. *Nano Res*. 2024;17(3):949-959. doi:10.1007/s12274-023-5965-7

22. Perry SC, Ponce de León C, Walsh FC. Review—The Design, Performance and Continuing Development of Electrochemical Reactors for Clean Electrosynthesis. *J Electrochem Soc*. 2020;167(15):155525. doi:10.1149/1945-7111/abc58e

23. Mirseyed SF, Jafarzadeh K, Rostamian A, Abbasi HM, Ostadhassan M. A new insight on the mechanisms of corrosion deactivation of a typical Ti/IrO2 + RuO2 +TiO2 coating in the presence of Ta2O5 in chlor-alkali medium. *Corros Sci*. 2023;214:111005. doi:10.1016/J.CORSCI.2023.111005

24. Basavarajappa PS, Patil SB, Ganganagappa N, Reddy KR, Raghu A V., Reddy CV. Recent progress in metal-doped TiO2, non-metal doped/codoped TiO2 and TiO2 nanostructured hybrids for enhanced photocatalysis. *Int J Hydrogen Energy*. 2020;45(13):7764-7778. doi:10.1016/J.IJHYDENE.2019.07.241

25. Nazir R, Basak U, Pande S. Synthesis of one-dimensional RuO2 nanorod for hydrogen and oxygen evolution reaction: An efficient and stable electrocatalyst. *Colloids Surf A Physicochem Eng Asp*. 2019;560:141-148. doi:10.1016/J.COLSURFA.2018.10.009

26. Ruggerio CA. Sustainability and sustainable development: A review of principles and definitions. *Science of The Total Environment*. 2021;786:147481. doi:10.1016/J.SCITOTENV.2021.147481

27. Talabi OO, Dorfi AE, O'Neil GD, Esposito D V. Membraneless electrolyzers for the simultaneous production of acid and base. *Chemical Communications*. 2017;53(57):8006-8009. doi:10.1039/c7cc02361h

28. *Ideal Crop Marks Manual of Water Supply Practices*.; 2015.

29. Pomerantseva E, Resini C, Kovnir K, Kolen'ko Y V. Emerging nanostructured electrode materials for water electrolysis and rechargeable beyond Li-ion batteries. *Adv Phys X*. 2017;2(2):211-253. doi:10.1080/23746149.2016.1273796

30. Lim HW, Cho DK, Park JH, et al. Rational Design of Dimensionally Stable Anodes for Active Chlorine Generation. *ACS Catal*. 2021;11(20):12423-12432. doi:10.1021/acscatal.1c03653

31. Hong S, Lee T kyu, Hoffmann MR, Cho K. Enhanced chlorine evolution from dimensionally stable anode by heterojunction with Ti and Bi based mixed metal oxide layers prepared from nanoparticle slurry. *J Catal*. 2020;389:1-8. doi:10.1016/J.JCAT.2020.04.009

32. Ullah N, Omanovic S. Large charge-storage-capacity iridium/ruthenium oxide coatings as promising material for neural stimulating electrodes. *Mater Chem Phys*. 2015;159:119-127. doi:10.1016/J.MATCHEMPHYS.2015.03.061

33. Gao G, Sun Z, Chen X, et al. Recent advances in Ru/Ir-based electrocatalysts for acidic oxygen evolution reaction. *Appl Catal B*. 2024;343:123584. doi:10.1016/J.APCATB.2023.123584

34. Singla J, Thakur I, Sangal V, Verma A. Dimensionally stable anode (Doped-MMO) mediated electro-oxidation and multi-response optimization study for remediation of urea wastewater. *Chemosphere*. 2021;285:131498. doi:10.1016/J.CHEMOSPHERE.2021.131498

35. Petrović N, Malviya BK, Kappe CO, Cantillo D. Scaling-up Electroorganic Synthesis Using a Spinning Electrode Electrochemical Reactor in Batch and Flow Mode. *Org Process Res Dev*. 2023;27(11):2072-2081. doi:10.1021/acs.oprd.3c00255

36. Hashemi SMH, Karnakov P, Hadikhani P, et al. A versatile and membrane-less electrochemical reactor for the electrolysis of water and brine. *Energy Environ Sci*. 2019;12(5):1592-1604. doi:10.1039/c9ee00219g

37. Ayorinde T, Sayes CM. An updated review of industrially relevant titanium dioxide and its environmental health effects. *Journal of Hazardous Materials Letters*. 2023;4:100085. doi:10.1016/J.HAZL.2023.100085

38. Zhou J, Gao Z, Xiang G, et al. Interfacial compatibility critically controls Ru/TiO2 metal-support interaction modes in CO2 hydrogenation. *Nat Commun*. 2022;13(1). doi:10.1038/s41467-021-27910-4

39. Yoo H, Oh K, Lee YR, Row KH, Lee G, Choi J. Simultaneous co-doping of RuO2 and IrO2 into anodic TiO2 nanotubes: A binary catalyst for electrochemical water splitting. *Int J Hydrogen Energy*. 2017;42(10):6657-6664. doi:10.1016/J.IJHYDENE.2016.12.018

40. Talekar G V. Electrode-based reactors in modular wastewater treatment. *Modular Treatment Approach for Drinking Water and Wastewater*. Published online January 1, 2022:149-170. doi:10.1016/B978-0-323-85421-4.00009-7

41. Mehrkhah R, Park SY, Lee JH, Kim SY, Lee BH. Prospective performance assessment of enhanced electrochemical oxidation technology: Insights into fundamentals and influencing factors for reducing energy requirements in industrial wastewater treatment. *Environ Technol Innov*. 2023;32:103336. doi:10.1016/J.ETI.2023.103336

42. Nami H, Rizvandi OB, Chatzichristodoulou C, Hendriksen PV, Frandsen HL. Techno-economic analysis of current and emerging electrolysis technologies for green hydrogen production. *Energy Convers Manag*. 2022;269:116162. doi:10.1016/J.ENCONMAN.2022.116162

43. Noël T, Cao Y, Laudadio G. The Fundamentals behind the Use of Flow Reactors in Electrochemistry. *Acc Chem Res*. 2019;52(10):2858-2869. doi:10.1021/acs.accounts.9b00412

44. Hadikhani P, Hashemi SMH, Schenk SA, Psaltis D. A membrane-less electrolyzer with porous walls for high throughput and pure hydrogen production. *Sustain Energy Fuels*. 2021;5(9):2419-2432. doi:10.1039/d1se00255d

45. Medeiros MC, de Medeiros JB, Martínez-Huitle CA, et al. Long-chain phenols oxidation using a flow electrochemical reactor assembled with a TiO2-RuO2-IrO2 DSA electrode. *Sep Purif Technol*. 2021;264:118425. doi:10.1016/J.SEPPUR.2021.118425

46. Chun D, Lim CR, Lee HS, Yoon WS, Lee TK, Kim DK. Electrochemical treatment of urine by using Ti/IrO2/TiO2 electrode. *Journal of Water Process Engineering*. 2018;26:1-9. doi:10.1016/j.jwpe.2018.06.004

47. Sharma RK, Bandichhor R, Mishra V, et al. Advanced metal oxide-based nanocatalysts for the oxidative synthesis of fine chemicals. *Mater Adv*. 2023;4(8):1795-1830. doi:10.1039/D2MA00977C

48. Improve efficiency by using ALD TiO2 - Supplemental Material.

49. Kangwoo Cho_2015_thesis_entire.

50. Cabrera-Rodríguez O, Trejo-Valdez MD, Torres-SanMiguel CR, et al. Evaluation of the performance of TiO2 thin films doped with silver nanoparticles as a protective coating for metal prostheses. *Surf Coat Technol*. 2023;458:129349. doi:10.1016/J.SURFCOAT.2023.129349

51. Feng Z, Zhang X, Li H, et al. Enhancing the properties of metal-composite interface by a nano-TiO2 coating. *Ceram Int*. 2024;50(1):1764-1776. doi:10.1016/J.CERAMINT.2023.10.275

52. Adiga P, Nunn W, Wong C, et al. Breaking OER and CER scaling relations via strain and its relaxation in RuO2 (101). *Mater Today Energy*. 2022;28:101087. doi:10.1016/J.MTENER.2022.101087

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