Effect of Electrolyte pH on the Electrosynthesis of Hydrogen Peroxide on Carbon Black-based Gas Diffusion Electrodes

Spencer Lindsay
Clemson University, ot.slindsay@gmail.com

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EFFECT OF ELECTROLYTE PH ON THE ELECTROSYNTHESIS OF HYDROGEN PEROXIDE ON CARBON BLACK-BASED GAS DIFFUSION ELECTRODES

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Engineering and Earth Science

by
Spencer Clark Lindsay
August 2020

Accepted by:
Dr. Sudeep C. Popat, Committee Chair
Dr. David L. Freedman
Dr. David A. Ladner
ABSTRACT

The electrochemical synthesis of H₂O₂ by the cathodic reduction of O₂ is an on-site alternative to the current industrial scale method of production. Carbon-based gas diffusion electrodes (GDEs) are selective to H₂O₂ synthesis and inexpensive compared to their precious metal counterparts. The research presented here examines the role electrolyte pH in the cathode has on the efficiency of H₂O₂ electrosynthesis, particularly as it pertains to the rate of H₂O₂ production on the electrode and subsequent degradation in the cathode chamber. From these results, the optimization of the cathode surface and environmental conditions is then considered.

The overall performance was dependent on the recirculation rate of the electrolyte in 4-hour batch experiments. Increasingly turbulent conditions at the surface of the cathode decreased the diffusion layer thickness and accelerated the mass transport of co-synthesized H₂O₂ and OH⁻ with peak performance occurring at a catholyte recirculation rate of 60 mL/min with a maximum cathodic coulombic efficiency (CCE) of 68%. Minimal residence time on the surface of the cathode reduces the chance for the deleterious electrochemical reduction of H₂O₂ to H₂O. High recirculation rates were favored at initial reaction times (t < 2 hour) but the rising bulk electrolyte pH caused by the diffusion of OH⁻ resulted in a larger drops in CCE over time. Alkaline environments yielded the highest H₂O₂ concentrations with a maximum concentration of 1.78 g/L in pH 13.5 after a 4-hour reaction time. The highest concentrations of H₂O₂ synthesized at pH 13.5 were in spite of the rapid degradation that occurred in alkaline conditions. Bulk, pH-driven degradation rates peaked at pH 12 while concurrent bulk and electrochemical reduction was rampant
and nearly uniform across all pH regimes. A Tafel analysis demonstrated a mechanistic shift in the catalytic reaction taking place at pH ≥ 11.5 and is hypothesized to be in favor of the 2-electron reduction pathway, thus demonstrating that pH also influences the selectivity of the reaction. High overpotential Tafel slopes transitioned from ~240 mV/decade to 120 mV/decade at acidic and neutral to alkaline conditions. Stable production efficiencies were achieved in concentrated buffer solutions that effectively neutralized the bulk degradation pathway that appears with increasing pH.
ACKNOWLEDGEMENTS

I am first and foremost particularly grateful for my exceptional advisor Dr. Sudeep Popat for the opportunity to pursue this research. The completion of a thesis-based master’s degree has been as rewarding personally as it has been professionally. Dr. Popat introduced me to a field of science I had never been exposed to before and electrochemistry had me initially asking the question, “Did I make the right decision?” However, it has been an absolute privilege to learn something novel and collaborate with a professor whom I hold in such high regard. I would also like to extend my deepest gratitude to the other members of my committee. I credit the decision to become an environmental engineer to Dr. David Freedman whose first introductory lecture grabbed my attention and has ceased to let go. Dr. Freedman has been a role model for me and countless others that pass through this program for his enthusiasm, wealth of knowledge, and willingness to guide students outside of the classroom. Furthermore, Dr. David Ladner has been integral in my development at Clemson with his passion for teaching and connecting students to industry through the networking opportunities he creates. Through business connections that he has made possible, the work experience I’ve obtained in internships have been as educational as my coursework.

I am also grateful to Dr. Negin Kananizadeh, a brilliant researcher and engineer, for her assistance, encouragement, and friendship during my first year in the group. Dr. Kananizadeh and I started experimenting with H$_2$O$_2$ electrosynthesis together and the extent of this research would not have been possible without her. I would also like to thank
Rodney Merck and Rodney Morgan for constructing and machining the materials for the electrochemical cell reactors.

Finally, I am forever blessed with the unwavering support system of my family and friends. The freedom to pursue what is useful and interesting is the greatest blessing a young person can have and I am indebted to pay that chance forward when it is my time to do so.
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<td>AEM</td>
<td>Anion exchange membrane</td>
</tr>
<tr>
<td>Ag/AgCl</td>
<td>Silver/Silver Chloride</td>
</tr>
<tr>
<td>AO</td>
<td>Anthraquinone oxidation</td>
</tr>
<tr>
<td>AOP</td>
<td>Advanced oxidation process</td>
</tr>
<tr>
<td>ARB</td>
<td>Anode-respiring bacteria</td>
</tr>
<tr>
<td>CCE</td>
<td>Cathodic coulombic efficiency</td>
</tr>
<tr>
<td>CEM</td>
<td>Cation exchange membrane</td>
</tr>
<tr>
<td>CI</td>
<td>Current interrupt</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>CP</td>
<td>Chronopotentiometry</td>
</tr>
<tr>
<td>DDI</td>
<td>Distilled deionized</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>EAOP</td>
<td>Electrochemical advanced oxidation process</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>EF</td>
<td>Electro-Fenton</td>
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<tr>
<td>GC</td>
<td>Glassy carbon</td>
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<tr>
<td>GDE</td>
<td>Gas diffusion electrode</td>
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<tr>
<td>H₂</td>
<td>Hydrogen gas</td>
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<tr>
<td>H₂O₂</td>
<td>Hydrogen peroxide</td>
</tr>
<tr>
<td>HO₂⁻</td>
<td>Hydroperoxide anion</td>
</tr>
<tr>
<td>HPC</td>
<td>Hierarchical porous carbon</td>
</tr>
<tr>
<td>HPPO</td>
<td>Hydrogen peroxide to propylene oxide</td>
</tr>
<tr>
<td>LCA</td>
<td>Life cycle assessment</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>MEC</td>
<td>Microbial electrolysis cell</td>
</tr>
<tr>
<td>MET</td>
<td>Microbial electrochemical technologies</td>
</tr>
<tr>
<td>MFC</td>
<td>Microbial fuel cell</td>
</tr>
<tr>
<td>MPL</td>
<td>Microporous layer</td>
</tr>
<tr>
<td>MPPC</td>
<td>Microbial peroxide producing cell</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen gas</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>Sodium phosphate dibasic anhydrous</td>
</tr>
<tr>
<td>NaH₂PO₄</td>
<td>Sodium phosphate monobasic monohydrate</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen gas</td>
</tr>
<tr>
<td>O-CNT</td>
<td>Oxidized carbon nanotubes</td>
</tr>
<tr>
<td>OH⁻</td>
<td>Hydroxyl radical</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
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<tr>
<td>PBS</td>
<td>Phosphate buffer solution</td>
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<tr>
<td>PEM</td>
<td>Proton exchange membrane</td>
</tr>
<tr>
<td>POP</td>
<td>Persistent organic pollutants</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
</tr>
<tr>
<td>RRDE</td>
<td>Rotating ring disk electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
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<tr>
<td>TPI</td>
<td>Three phase interface</td>
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1.0 INTRODUCTION

Hydrogen peroxide (H₂O₂) is an attractive inorganic chemical for a number of industries due to its use as a chemical oxidant and bleaching agent. A decomposition profile that results in harmless by-products, water and oxygen, H₂O₂ is a green and environmentally benign oxidizing agent that has earned a ranking among the 100 most important chemicals in the world.¹ Its versatile properties are sought after in paper and pulp, textile, chemical, cosmetic, semiconductor, and water and wastewater industries.² The current method of H₂O₂ manufacturing yields exceptionally high strength concentrations that are inherently hazardous to store and transport, thereby unnecessarily raising consumer costs. For a number of the applications, especially in water and wastewater, only dilute concentrations are required. Low strength H₂O₂ concentrations can be alternatively synthesized in-situ at the point of application by the cathodic reduction of O₂ to H₂O₂ on a carbon-based gas diffusion electrode (GDE).

Decentralized production of H₂O₂ is particularly appropriate for water resource recovery facilities. The organic matter found in wastewater contains 1.93 kWh per cubic meter.³ Microbial fuel cells (MFCs) utilize microbially catalyzed oxidation of this organic matter, or chemical oxygen demand (COD), to produce electrical current. Pairing the anodic oxidation of wastewater with a catalyst at the cathode that is capable of reducing O₂ to H₂O₂, such as a carbon-based GDE, instead of H₂O is the operational framework of a microbial peroxide producing cell (MPPC), shown in Figure 1. A life cycle assessment (LCA) of an MPPC, equipped with such an electrode, demonstrated a significantly positive environmental impact by displacing the traditional manufacture of H₂O₂ for on-site use at
a wastewater treatment plant. A deeper understanding of how operational cell parameters affect the performance of gas diffusion electrodes is necessary in order to foresee a technology such as the MPPC be implemented at a wastewater treatment facility or an abiotic cell powered by solar energy be deployed at a paper mill for bleaching.

Irrespective of the application, maximizing the coulombic efficiency of electrosynthesis of $\text{H}_2\text{O}_2$ at a minimal power input is a critical goal. The following research examines how experimental conditions, such as electrolyte pH, alter the performance of

![Diagram of a MPPC](image)

**Figure 1.** The general processes of a MPPC.
H$_2$O$_2$-producing electrochemical cells and how these parameters may be optimized. In an ideal scenario, an efficiently operated MPPC may be powered solely by the chemical energy found in wastewater resulting in the net-neutral production of a valuable chemical.
2.0 BACKGROUND

2.1 Industrial Production and Use

Over the past several decades, increased global production of H$_2$O$_2$ has been largely driven by the replacement of chlorine-based chemicals with H$_2$O$_2$ for the delignification of cellulose and the bleaching of cellulose and pulp. This practice eliminates toxic halogenated constituents from industrial waste streams that require additional treatment challenges. Furthermore, use of H$_2$O$_2$ in the chemical industry accelerated in 2008 when it was implemented in a novel method of propylene oxide synthesis, the hydrogen peroxide to propylene oxide (HPPO) process, based on findings from two decades prior. The HPPO process is an alternative to the traditional chlorohydrin route of propylene oxide production with benefits that include a totally closed solvent and the absence of chlorine and coproducts. Propylene oxide is predominantly used in the production of polyurethane: a multipurpose polymer in escalating demand. Accordingly, the global capacity of H$_2$O$_2$ production increased from 1.5 million metric tons per year in 1991 to 5.5 million metric tons in 2015.

Supplying this demand currently is the anthraquinone oxidation (AO) process originally described by Riedl and Pfleiderer in 1939. The AO process is the predominant industrial-scale practice used for concentrated H$_2$O$_2$ manufacturing that accounts for more than 95% of global production. Despite being able to meet the current demand for H$_2$O$_2$, the drawbacks of the centralized AO process include an excess use of solvents, hazardous solvent and alkylated hydroquinones as waste products, and associated environmental costs of being an energy-intensive process. The AO process is sustainable only at a centralized,
full-scale operation due to the capital demand of industrial equipment necessary to produce vast quantities of concentrated H₂O₂. Therefore, the AO process is unable to be scaled down in size and performed at the point of application. Centralized production also requires the costly transport of hazardous, high grade (70% w/w) H₂O₂ to the consumer. This has led researchers to investigate more practical and sustainable methods of producing H₂O₂ on-site through catalytic electrochemical methods for decentralized applications, most of which only require concentrations up to 8 wt % and some, such as water treatment (WT), less than 0.1 wt %.¹⁰,¹¹ Typical doses required in applications pertaining to water and wastewater treatment are shown in Table 1.

Table 1. H₂O₂ dosage in water and wastewater treatment

<table>
<thead>
<tr>
<th>Technology</th>
<th>Dosage (%)</th>
<th>Reference</th>
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<tr>
<td>Graywater Disinfection</td>
<td>0.01 – 0.013</td>
<td>Murawski¹²</td>
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<tr>
<td>H₂S Control</td>
<td>0.00015 – 0.0004</td>
<td>Young et al.¹¹</td>
</tr>
<tr>
<td>Fenton Process - AOP</td>
<td>0.001 – 2</td>
<td>Yang et al.¹³</td>
</tr>
<tr>
<td>UV/H₂O₂ - AOP</td>
<td>0.005 – 0.015</td>
<td>USP Technologies¹⁴</td>
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Spearheading the decentralized synthesis route is the electrochemical synthesis of H₂O₂. The direct synthesis via molecular H₂ and O₂, the electrochemical oxidation of H₂O, and the electrochemical reduction of O₂ dominate the literature as alternatives to the AO process. Since original reports of Henkel and Weber’s 1914 experiment that initially reported production of peroxide from hydrogen and oxygen, the direct synthesis method uses noble metals, predominantly palladium or a palladium-base, as an electrocatalyst to perform the parallel redox reactions necessary.¹⁵,¹⁶ Ranganathan et al. provide a thorough review on the research status of the direct synthesis method.⁹ Unfortunately, direct
synthesis suffers from inherent safety hazards associated with maintaining molecular H₂ and O₂ outside of their explosive concentration range. To account for this, hydrogen and oxygen gas are diluted in N₂ or CO₂ which limits the process efficiency. Furthermore, the cost and scarcity of these precious metal catalysts are not sensible when considering a modular system on-site.

On the contrary, the electrochemical synthesis of H₂O₂ via the oxidation of H₂O or the reduction of O₂ do not suffer from chemical safety hazards and operates under ambient temperature and pressure. The 2-electron water oxidation simultaneously produces H₂O₂ and H₂ but suffers from low electrocatalyst activities, outside of high cost metal oxides such as BiVO₄, and has a narrow outlook at this time.¹⁷ However, the selective 2-electron oxygen reduction reaction (ORR) is an extensive area of past and current research especially that is now focused on the widely available and affordable non-metal electrocatalysts (e.g. carbon). Therefore, the research here explored the ORR.

2.2 Electrochemical Reduction

The ORR proceeds through a 2- or 4-electron reduction of gaseous O₂ to H₂O₂ or H₂O as shown below.

\[
(1) \quad \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- \quad E^\circ = +0.695 \text{ V}_{\text{SHE}}
\]

\[
(2) \quad \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \quad E^\circ = +1.229 \text{ V}_{\text{SHE}}
\]

Determining the oxygen reduction mechanism has been historically difficult due to the complications in probing the reaction intermediates to elucidate the reaction. Density functional theory (DTF) calculations have demonstrated particularly accurate steps that
correspond with experiments performed in acidic media. The proposed mechanism proceeds as:

\[ \text{O}_2 + * + (\text{H}^+ + e^-) \rightarrow * \text{OOH} \]

where adsorbed *OOH may follow three separate pathways:

\[ * \text{OOH} + (\text{H}^+ + e^-) \rightarrow \text{H}_2\text{O}_2 \]
\[ * \text{OOH} + (\text{H}^+ + e^-) \rightarrow * \text{O} + \text{H}_2\text{O} \]
\[ * \text{OOH} + * \rightarrow * \text{O} + * \text{OH} \]

and the 4-electron reduction may be completed by subsequent reductions

\[ * \text{O} + (\text{H}^+ + e^-) \rightarrow * \text{OH} \]
\[ * \text{OH} + (\text{H}^+ + e^-) \rightarrow \text{H}_2\text{O} + * \]

where * denotes an active site and *OOH, *OH, and *O are adsorbed reaction intermediates.\(^{13}\)

The 4-electron reduction has historically been desirable in fuel cells, such as the proton exchange membrane (PEM) fuel cell, to optimize electricity production; synthesis of H\(_2\)O\(_2\) that is not reduced to H\(_2\)O represents an inefficiency in this configuration and catalysts that suppressed its net production were desirable. However, the 2-electron reduction is no longer being overlooked due to the aforementioned demand for a green, decentralized approach to produce H\(_2\)O\(_2\). Widespread investigation is being done to understand the specific electrosynthesis mechanisms in acidic and alkaline environments.
and to design robust, selective catalysts that subdue the additional two-electron reduction of H$_2$O$_2$ to H$_2$O.$^{13,17,18}$

Berl introduced the first commercial concept of electrochemical reduction of O$_2$ to H$_2$O$_2$ in 1939 using an activated carbon cathode.$^{19}$ Furthermore, Dow Chemical and Huron Chemical commercialized a trickle-bed electrolytic cell in the 1980s that produced an alkaline H$_2$O$_2$ solution that is ideal for wood pulp bleaching where it is not necessary to separate H$_2$O$_2$ from NaOH.$^{20}$ For pulp and paper industries, the Huron-Dow process is a practical method for on-site production of H$_2$O$_2$ and is used today; however, niche applications of an alkaline electrolyte solution eliminate its potential for widespread adoption in other markets.

2.3 Electrocatalysts

Noble metals catalysts, such as gold, platinum, and palladium, account for the highest performance recorded thus far in electrochemically synthesizing H$_2$O$_2$ via the ORR. Similar to the direct synthesis route, Pd-based catalysts, specifically the Au-Pd alloy, have been a focal point for metal-based catalysis.$^{10,17}$ Siahrostami et al. screened for potentially new metal alloy catalysts using DTF calculations and identified Pt-Hg alloy as a highly active and selective catalyst for the 2-electron reduction to H$_2$O$_2$.$^{21}$ Activity describes the readiness of a catalyst to proceed with an electrochemical reaction. Selectivity is a ratio of desired products formed per reactants consumed. In the case of the 2-electron ORR, a selective catalyst will favor the synthesis of H$_2$O$_2$ rather than H$_2$O. Following the discovery of the potential of Hg-modified catalysts, Pd-Hg exhibited activity that was two orders of magnitude higher than that of Au-modified catalysts.$^{22}$ Despite the high
efficiencies and activities achieved by these noble metal catalysts, their cost, scarcity, and toxicity (e.g., Hg) hinder their scalability.

Carbon-based materials show promise in the electrochemical reduction of O₂ to H₂O₂ due to their abundance, robustness, and possibility to fine-tune their chemical structure to attain high selectivity. The large specific surface area, low cost, and resistance to corrosion of these carbon-based electrocatalysts have led researchers to envision their application outside of industry but also for modular water disinfection units in economically deprived regions.²³ This chemical and economic versatility has popularized carbon as a catalyst for H₂O₂ production and has researchers striving to solve the main pitfall of carbon: low activity attributed to the weak interaction between carbon and *OOH.¹³ To combat this weakness, researchers have had varied success with tuning the surface with heteroatoms such as nitrogen, oxygen, fluorine, boron, and iron, and experimenting with more porous starting materials (e.g. graphite) that have a higher density of defect sites.¹³,¹⁸,²⁴ For example, studies done by Sun et al. exploit the favorable characteristics of nitrogen-doped mesoporous carbon catalysts, a high surface area and less restrictive mass transport, by reporting H₂O₂ production efficiencies of ~95% and ~70% in acidic and alkaline solutions.²⁵ Hierarchical porous carbon (HPC) was prepared as a catalyst by carbonization of a metal organic framework and produced ~90% efficiencies at an electrolyte pH 1-4.²⁶ The hierarchical structure of micro-, meso-, and macropores provide ample catalytically active sites and permit unencumbered transport of H₂O₂ from the catalyst layer. Optimizing the mass transport of synthesized H₂O₂, either by designing
favorable catalyst structures or creating hydraulic conditions for conducive diffusion, appears to be a viable method of increasing efficiency.

### 2.4 Electrode Configuration

While identifying and characterizing new catalysts for the selective ORR to \( \text{H}_2\text{O}_2 \), the experimental setup usually used is rotating-ring disk electrodes (RRDE). In this configuration, the electrocatalyst being tested is deposited on a disk electrode, usually as an electrocatalyst ink, to synthesize proportionate amounts of \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O} \) from an air-saturated electrolyte solution. As the disc electrode rotates, the newly synthesized \( \text{H}_2\text{O}_2 \) is rapidly transferred to the ring electrode, typically Pt, for instantaneous oxidation to \( \text{O}_2 \). The selectivity, or what percentage of the electrons are proceeding by the 2- or 4- electron reduction, of the electrocatalyst can be quantified by relating the disk and ring currents observed.\(^{17,27}\) Simple, powerful and very reproducible, RRDE configurations provide ideal conditions and an upper limit to performance when identifying novel electrocatalysts for \( \text{H}_2\text{O}_2 \) production.\(^{13}\)

While the RRDE configuration is particularly useful, its application is limited to microscale laboratory experiments. Therefore, studies touting the selectivity of a novel electrocatalyst are specific to ideal and unrealistic conditions. Alternatively, GDEs provide a scale-up configuration that are representative of a real-world peroxide producing unit. In a typical GDE, there are two distinct layers manufactured on a carbon-based material. On one side, a hydrophobic microporous layer (MPL) allows passive diffusion of \( \text{O}_2 \) to the electrocatalyst under ambient conditions and eliminates the need of costly aeration to saturate the electrolyte.\(^{28}\) This “air-facing” layer is treated with layers of
polytetrafluoroethylene (PTFE) to create a hydraulic barrier to prevent electrolyte leakage yet allowing gaseous diffusion. Hydrophobic polymers, PTFE or Nafion, are also applied to the “electrolyte-facing” catalyst layer in lesser concentrations as a support and binder for the electrocatalyst ink being tested. The electrocatalyst is deposited on this opposing side of the GDE. This results in a steady three-phase interface (TPI) among the electrolyte, catalyst, and O₂.

Experiments performed by Sim et al. have demonstrated that the method in which O₂ is introduced to the GDE dictates performance in peroxide-producing electrochemical cells. Passive diffusion of gaseous O₂ via ambient air conditions, compared to saturating the electrolyte with aqueous O₂ via aeration, is more effective for the 2-electron ORR. Similarly, Li et al. tested the difference in H₂O₂ yield of a carbon black graphite hybrid cathode between O₂ transport limited to electrolyte or air diffusion. Over four different applied potentials to the cathode, the rate of H₂O₂ formation for air diffusion was 0.9 – 12 times higher than for dissolved O₂ diffusion. This accelerated diffusion of O₂ from the gas phase is an extraordinary advantage for GDEs versus heterogeneous electrodes in solution that are undergoing the ORR. The energy and costs associated with aeration would diminish the outlook of H₂O₂-producing electrochemical cells and highlight the utility of GDEs.

2.5 Decomposition

The rate of H₂O₂ decomposition is equally important in electrochemical reactors. Without stable concentrations, the yield of even the most optimal catalyst will be negligible. The
deteriorating performance of a GDE may be attributed to $\text{H}_2\text{O}_2$ decomposition that may proceed in several pathways:

**Electrochemical Reduction**

$$\text{H}_2\text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad E^0 = +1.760 \text{ V}_{\text{SHE}}$$

**Self-decomposition**

$$\text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{OH}^-$$

**Disproportionation**

$$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$$

$\text{H}_2\text{O}_2$ disproportionation is an exothermic reaction ($\Delta H = 100.4 \text{ kJ/mol}$) that produces $\text{O}_2$ and heat. In concentrated solutions, high-test peroxide ($>70\% \text{ w/w}$) is used as a liquid propellant and was first used as such in German weaponry (rocket designs and submarines) during World War II.\(^{33}\) Trace metals and other impurities that catalyze the decomposition reaction include heterogeneous metals Ag, Pt, Au, and Pd\(^{34}\), Fe and Cu\(^{35}\), and metal oxides such as iron and manganese\(^{36,37}\). Decomposition derived from impurities in the chemical structure of container walls and rising temperature was also demonstrated by Schumb.\(^{35}\) Qiang et al. tested the stability of $\text{H}_2\text{O}_2$ in plastic bottles diluted in distilled water over a pH and temperature range of 1 to 13 and 10 – 50°C respectively. Results indicated that above pH of 9, $\text{H}_2\text{O}_2$ decomposition increases with pH, temperature, and time.\(^{38}\) Concentrated lab-grade stock solutions of $\text{H}_2\text{O}_2$ contain stabilizers, such as sodium pyrophosphate, sodium stannate, or ethylenediaminetetraacetic acid (EDTA), that act as chelating agents to inhibit catalysis and minimize decomposition.\(^2\) Nonetheless, minor
catalytic decomposition is unavoidable as trace level impurities are present in reactor materials, electrodes, and inorganic salts required to make electrolyte solutions.

The reactivity between reactor materials and H₂O₂ may also contribute to degradation. Contaminants and functional groups that exist on the ion exchange membrane of a dual-chamber electrochemical cell, electrocatalyst, and GDE may contribute to H₂O₂ degradation. Some experiments reported in literature inspected the percent reduction in membrane mass for anion and cation exchange membranes (CEM) for 45-day batch experiments inoculated with 1% w/w H₂O₂ at pH 12. CEM exhibited lower weight loss, indicating less reactivity with H₂O₂, than anion exchange membranes (AEM) suggesting that the charge of the functional groups on the surface of the ion exchange membrane influences the decomposition kinetics when H₂O₂ is in the deprotonated state.¹¹

2.6 Applications in Water Treatment

H₂O₂ is sought after in water and wastewater treatment technologies as an oxidant and disinfectant that inactivates pathogens of wastewater effluent and reacts with otherwise recalcitrant organics when used in advanced oxidation processes (AOP).³⁹ AOPs function by using the non-selective, highly reactive hydroxyl radicals (OH·) that can be derived from H₂O₂.⁴⁰ Ozone, ultraviolet light, and ferrous iron are commonly used to catalyze the reactions necessary to yield OH· from H₂O₂.⁴¹ The hydroxyl radicals are second only to fluorine in its oxidizing capabilities and mineralize most organic and organometallic pollutants into CO₂, H₂O, and inorganic ions.²

$$\text{(OH·)} + e^- + H^+ \rightarrow H_2O \quad \quad \quad E^o = +2.8 \ \text{V}_{\text{SHE}}$$
2.6.1 Fenton’s Reaction

Fenton’s reaction, an AOP that utilizes the catalytic activity of ferrous iron with H$_2$O$_2$, is particularly effective at removing COD via toxic and persistent organic pollutants (POP), organic synthetic dyes, and pharmaceutical and personal care products from contaminated water. This is achieved by the oxidizing power of the hydroxyl radical and the enhanced coagulation of suspended particles with ferrous and ferric iron.$^{42}$ The formation of hydroxyl radicals from peroxide is catalyzed by Fe$^{2+}$ by the reaction shown below.

\[
\text{(7)} \quad \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + (\text{OH} \cdot) + \text{OH}^- 
\]

An acidic medium of pH ~ 3 is optimum where only a miniscule amount of initial Fe$^{2+}$ is needed due to the cyclical reaction between generated Fe$^{3+}$ and Fe$^{2+}$ at this regime.$^{43}$ Furthermore, acidic environments discourage the precipitation of iron hydroxides.

\[
\text{(8)} \quad \text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + (\text{HO}_2 \cdot) + \text{H}^+ 
\]

When the source of H$_2$O$_2$ for Fenton’s reaction is an electrochemically generated process, such as the cathodic reduction of O$_2$ at a carbon-based catalyst, the system is referred to as the electro-Fenton (EF) method and is an example of an electrochemical advanced oxidation process (EAOP). The electro-Fenton method generates peroxide in-situ, doses catalytic Fe$^{2+}$, and aids regeneration of Fe$^{2+}$ by the simultaneous electrochemical reduction of Fe$^{3+}$ at the cathode surface.$^{44}$

\[
\text{(9)} \quad \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} 
\]

The EF method is a viable means of removing synthetic dyes (i.e. azo dyes), commercial pesticides and antimicrobials, pharmaceuticals, and other environmentally
toxic pollutants such as aniline and phenols. An extensive review by Moreira et al. highlights the current status of EAOP’s effectiveness of treating synthetic and real wastewaters specifically highlighting the EF method.\textsuperscript{44} Even more notable, of all electrochemical configurations of the EAOP studied, carbon-PTFE air-diffusion electrodes, or GDES, used for the electrosynthesis of H\textsubscript{2}O\textsubscript{2} were predominantly used as the cathode. A consistent finding among researchers studying the EF method is the stark contrast of H\textsubscript{2}O\textsubscript{2} accumulation using carbon-PTFE air-diffusion versus carbon felt electrodes. While the rate of peroxide generation is accelerated using a GDE, the catalytic regeneration of Fe\textsuperscript{2+}, steady-state OH\textperiodcentered concentrations, and overall pollutant removal are subsequently reduced. Carbon felt electrodes produce H\textsubscript{2}O\textsubscript{2} at a lesser extent but favor the regeneration of Fe\textsuperscript{2+} and mineralization of the targeted pollutant.\textsuperscript{43} An ideal balance between these parallel reduction reactions looks to be necessary.

One study comparing traditional Fenton’s reagent and the EF process to treat industrial wastewater containing morpholyne and diethylethanolamine, persistent corrosion inhibitors used in industrial processes, found a 64.5\% savings on operational costs when H\textsubscript{2}O\textsubscript{2} is electrogenerated versus purchased and transported on-site. However, treatment efficiency favored the traditional Fenton’s reagent due to the associated iron hydroxide precipitation that occurred within the pore structure of the GDE of the EF configuration.\textsuperscript{45} As discussed previously, the synthesis of H\textsubscript{2}O\textsubscript{2} is accompanied by the synthesis of OH\textperiodcentered at the cathode surface. Local cathode pH is inevitably alkaline despite the bulk conditions. Iron hydroxide precipitation caused by alkaline pH within the pore spaces of a GDE is not the only operational challenge EF will face. A major hurdle for energy
efficient H$_2$O$_2$ electrosynthesis is the cathodic overpotential of the ORR caused by accumulation of OH$^-$ at the catalyst layer. Overpotential is the potential difference between the theoretical and applied potential needed to achieve a specific current density. Further analysis of this universal limitation of cathodic electrosynthesis of H$_2$O$_2$ will be discussed in Section 2.3.

Studies have shown the efficacy of combined H$_2$O$_2$-based AOPs, such as the photoelectro-Fenton process, for the treatment of colorants, such as azo dyes, from textile wastewater. UV radiation augments the electro-Fenton process by increasing the hydroxyl radical yield from peroxide.$^{39,46}$ Encouraging technologies such as this are dependent on the cathodic synthesis of peroxide.

2.6.2 Disinfection

The biocidal properties of H$_2$O$_2$ are used in food, medical, and water industries primarily due to the lack of toxicity following peroxide degradation and the oxidative efficacy on a cellular level towards biomolecules. The antiseptic is found in 3-6% (v/v) concentrations to treat open wounds and surfaces.$^{47}$ Wagner et al. tested H$_2$O$_2$ as a disinfectant on municipal wastewater and determined an average concentration of 195 mg/L was needed for a 2- to 3-log fecal coliform reduction over a two hour contact window.$^{48}$ In-situ synthesis of H$_2$O$_2$ via electrochemical reduction of O$_2$ in a carbon cathode electrochemical cell demonstrated similar results with coliform inactivation with estimated H$_2$O$_2$ concentrations of 100 mg/L.$^{12}$

The selective electrochemical reduction of O$_2$ to H$_2$O$_2$ on a GDE may be part of the solution to the limited access of a basic drinking water service, suffered by 780 million
people, and the 2.1 billion people drinking from source water contaminated with feces.49 Abiotic synthesis of \( \text{H}_2\text{O}_2 \) from intermittent renewable power sources, such as wind and solar, would empower developing countries in remote regions to the access of a powerful oxidant and vital disinfectant. Inspired by the cause, Jaramillo et al. discuss the potential of using a carbon-based electrode in modular electrochemical cells to address this global public health issue.50 An important transition in work such as this, and in many other studies that utilize a RRDE to characterize the selectivity of various catalysts for the 2-electron electrochemical reduction, is to implement the findings into a real-world electrochemical cell structure such as the GDE. GDEs, as discussed previously, allow the passive diffusion of \( \text{O}_2 \) into the electrochemical cell that provides the financial flexibility that developing countries need to implement an EAOP or disinfection reactor. Prior research that uses high purity \( \text{O}_2 \) to saturate their electrolyte in contact with the catalyst is simply not feasible in low-income countries. Furthermore, implementing a GDE as is from a commercial fuel cell manufacturer broadens the scope of this technology. Structural tuning and elemental doping of manufactured GDE diminish the economic benefits of using a widely available material such as carbon.

2.6.3 Microbial Electrochemical Technologies

Parallel oxidation and reduction half-reactions proceed simultaneously in an electrochemical cell. An oxidation and reduction occur on the anode and cathode electrodes respectively. Microbial electrochemical technologies (MET) produce bioenergy and chemicals by catalyzing one or both of these electrochemical half-reactions with microorganisms. In particular, a microbial fuel cell (MFC) harvests bioelectricity from
chemical energy found in organic molecules. Bruce Logan, the pioneer of this multidisciplinary blend of environmental engineering and electrochemistry, envisioned using MFCs as a sustainable platform to capture the energy in wastewater organics to supplement the power requirements of wastewater treatment processes. At the anode, a class of bacteria known as exoelectrogens transfer electrons extracellularly to insoluble electrode acceptors or heterogeneous electrodes. In nature, these species have been found to respire using iron or manganese oxide minerals. Under anaerobic conditions, a biofilm of electroactive bacteria will form on the anode of the MFC, typically a carbon-based electrode such as a graphite plate, brush, or rod, as the electroactive bacteria oxidize molecules such as acetate, ethanol, or glucose that are fed to the anode chamber. The extracellular electron transfer to a heterogeneous electrode occurs via indirect or direct mechanisms, as described by Logan. Anode-respiring bacteria (ARB), most commonly a *Geobacter* or *Shewanella* species, transfer electrons from the organic molecules to the anode creating a negative anode potential. Pairing a negative anode potential with a sustainable electron acceptor, such as O$_2$, with a more positive cathode potential generates electricity.

Over the past two decades, low power density and a lack of cost-effective materials has limited the scalability of MFC technology as a source of bioenergy for wastewater treatment plants. However, a more promising application in the wastewater arena is coupling the electrochemical reduction of O$_2$ to synthesize H$_2$O$_2$ by the oxidation of high-strength wastewater feeds (total COD $> 1,000$ mg/L), such as blackwater or primary sludge. Although the thermodynamics do not require an additional power source to be
applied to the system, the cathodic overpotential of the ORR are consistently high and applying electrical power is typically needed for this reaction. By supplementing with an external power source, the nature of the electrochemical cell shifts from a MFC to a microbial electrolysis cell (MEC).55

Instead of harnessing electrical current from the 4-electron reduction of O₂ to H₂O, a microbial peroxide producing cell (MPPC) synthesizes H₂O₂ in-situ from the 2-electron reduction of O₂ to H₂O₂. Processes that separate higher organic load waste (blackwater), such as solid fecal material, and lower organic strength (graywater), such as sink and shower runoff, represent potential areas for MPPC application. Potable water recovery on space vessels, recreational vehicles, and on remote military bases can reduce blackwater COD while simultaneously disinfecting their graywater for reuse with a MPPC.12 Concentrations of H₂O₂ achieved with MPPCs have reached upwards of 3 g/L with minimal power input; meanwhile, pairing H₂O₂ with Fenton’s process or acting as a disinfectant alone required H₂O₂ concentrations of 550 and 100 mg/L to remove 92% COD and 100% color removal from wastewater and effectively inactivated pathogens.12,56,57 A review of the performance and operational parameters of MPPCs are summarized in Table 2.
Table 2. Literature review of MPPCs that employ a GDE

<table>
<thead>
<tr>
<th>Reference</th>
<th>Cell Type</th>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Reaction Time [hr]</th>
<th>Conc. of H$_2$O$_2$ [g/L]</th>
<th>Overall Coulombic Efficiency [%]</th>
<th>Current Density [A m$^{-2}$]</th>
<th>Potential Applied [V]</th>
<th>Power Applied [W hr/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young et al. (2017)</td>
<td>AEM; serpentine</td>
<td>0.5 mg/cm$^2$ carbon - Nafion binder</td>
<td>200 mM NaCl</td>
<td>4</td>
<td>3.1 (18 mL)</td>
<td>37</td>
<td>10.1</td>
<td>0.31</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>cathode chamber</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Rozendal et al.</td>
<td>CEM</td>
<td>Manufactured ETEK-ELAT</td>
<td>50 mM NaCl</td>
<td>8</td>
<td>1.3 (336 mL)</td>
<td>84.4 (CE)</td>
<td>5.3</td>
<td>0.5</td>
<td>0.93</td>
</tr>
<tr>
<td>(2009)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>98.4 (AE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wells et al. (2018)</td>
<td>AEM</td>
<td>5 mg/cm$^2$ carbon black - Nafion binder</td>
<td>200 mM citric acid:phosphate buffer</td>
<td>24</td>
<td>3.1 (100 mL)</td>
<td>66 (CE)</td>
<td>0.9</td>
<td>0.78</td>
<td>1.86</td>
</tr>
<tr>
<td>Modin et al. (2013)</td>
<td>CEM</td>
<td>Carbon fiber paper with carbon nanoparticles; PTFE binder</td>
<td>50 mM NaCl</td>
<td>21</td>
<td>9.7 (5 mL)</td>
<td>78 (CE)</td>
<td>66 (CE)</td>
<td>5.3</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21.1 (AE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ki et al. (2017)</td>
<td>AEM; serpentine</td>
<td>0.5 mg/cm$^2$ carbon - Nafion binder</td>
<td>50 mM NaOH</td>
<td>6</td>
<td>0.23 (120 mL)</td>
<td>35 (CE)</td>
<td>1</td>
<td>0.2</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>cathode</td>
<td></td>
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</tr>
<tr>
<td>Li et al. (2016)</td>
<td>CEM</td>
<td>Carbon black - graphite (1:5 mass ratio)</td>
<td>50 mM NaSO$_4$</td>
<td>0.023</td>
<td>8.5 x 10$^{-3}$ (14 mL)</td>
<td>72 (CE)</td>
<td>6.1</td>
<td>0.6</td>
<td>56</td>
</tr>
<tr>
<td>Arends et al. (2014)</td>
<td>AEM</td>
<td>Carbon felt (not a GDE)</td>
<td>50 mM NaCl - O$_2$ saturated</td>
<td>4</td>
<td>0.34 (500 mL)</td>
<td>40 (CE)</td>
<td>10</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Sim et al. (2015)</td>
<td>CEM</td>
<td>AvCarb GDS2230 carbon fiber paper</td>
<td>Tap water</td>
<td>6</td>
<td>0.85 (70 mL)</td>
<td>47 (CE)</td>
<td>7.7</td>
<td>0.4 (vs Ag/AgCl)</td>
<td>Not Reported</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Modin et al. (2012)</td>
<td>CEM</td>
<td>Carbon fiber paper coated with 30% PTFE and carbon black ink</td>
<td>50 mM NaCl</td>
<td>9</td>
<td>2.3 (5 mL)</td>
<td>61 (CE)</td>
<td>25.2</td>
<td>-0.11 (NHE)</td>
<td>1.01</td>
</tr>
<tr>
<td>Dong et al. (2018)</td>
<td>CEM</td>
<td>Oxidized graphene</td>
<td>50 mM NaSO$_4$</td>
<td>6</td>
<td>0.082 (7 mL)</td>
<td>Not Reported</td>
<td>Not Reported</td>
<td>Not Reported</td>
<td>Not Reported</td>
</tr>
</tbody>
</table>
2.7 Knowledge Gap

The electrochemical O₂ reduction via the 2-electron pathway to H₂O₂ has the key challenge of establishing efficient, cheap, and selective catalysts and exploring parameters that facilitate the synthesis and stability of peroxide. Mechanistic studies of the ORR on different catalysts and applications of in-situ generated H₂O₂ are found throughout peer-reviewed journals. However, there is a gap in the literature that focuses on understanding the production and stability of in-situ generated H₂O₂ as the final product in an economically feasible and scalable electrochemical cell such as the one shown in Figure 2. Here, a cheap, robust material that is capable of achieving significant H₂O₂ concentrations functions as the working cathode: a carbon black-based GDE. The cathodic current distributed to the GDE may derive from a variety of anode configurations that are coupled to different power sources. The electron sink in a biotic configuration, such as a MPPC, is the chemical energy of biodegradable organic molecules oxidized by ARB; whereas an abiotic modular system connects to a traditional or renewable energy source. In this configuration, a pH gradient originates at the cathode surface because of the co-synthesis of OH⁻ in an initially neutral electrolyte solution.
Figure 2. Peroxide-producing electrochemical cell

The electrolyte pH of electrochemical cells designed to produce H$_2$O$_2$, specifically in the cathode chamber, is a parameter that impacts a multitude of processes that influence performance. Alkaline solutions have been demonstrated to be more selective of the 2-electron reduction to H$_2$O$_2$ than the 4-electron reduction to H$_2$O on carbon electrodes; however, H$_2$O$_2$ is known to degrade rapidly at high pH values. Furthermore, the electrosynthesis of H$_2$O$_2$ raises the pH of the electrolyte as co-synthesized OH$^{-}$ diffuses to the bulk solution. Therefore, the purpose of this work was to conduct experiments on the
electrosynthesis of H₂O₂ using a carbon black-based gas diffusion cathode under a variety of conditions and operational parameters to understand the interplay of electrolyte pH and H₂O₂ production.
3.0 RESEARCH OBJECTIVES

The scope of this thesis originates from the findings of a previous study where the results on the effect of electrocatalyst loading on gas diffusion cathodes were underscored by the dynamic pH of the electrolyte as H₂O₂ was electrosynthesized.¹² By manipulating operational parameters that will influence pH, the following research objectives were designed to answer the question, “How will electrolyte pH affect the rate of in-situ production and decomposition of H₂O₂ in a carbon-based gas diffusion electrode?”

The specific objectives are as follows:

1. Investigate the role of catholyte recirculation rate on H₂O₂ production and electrolyte pH;
2. Determine the effect of initial electrolyte pH on the electrochemical synthesis of H₂O₂;
3. Explore the effect of electrolyte pH on in-situ chemical and electrochemical degradation of H₂O₂; and
4. Examine the influence of electrolyte buffer concentration on the electrochemical synthesis of H₂O₂ and electrolyte pH.

3.1 Research Objective #1: Electrolyte Recirculation

To be measured in the bulk electrolyte and therefore able to be used for in-situ applications, H₂O₂ and deprotonated HO₂⁻ must diffuse from the catalyst loading layer through the electrochemical double layer and interphase boundary layer to reach the bulk solution as depicted in Figure 3. Catalyst characteristics such as structure, porosity, surface charge, loading thickness, and electrolyte recirculation have an impact on the retention time...
of synthesized H$_2$O$_2$ and potential further conversion on the cathode surface. Mass transfer of synthesized H$_2$O$_2$ influences the observed efficiencies as a hindered diffusion pathway from the cathode, due to a thick, and therefore less porous, catalyst layer, provides a sufficient retention time for further electrochemical reduction to H$_2$O.$^{58}$ Aside from induced diffusion, shorter retention times of synthesized H$_2$O$_2$ are promoted by more hydrophobic surfaces using PTFE in the catalyst ink and has been investigated by other research groups.$^{59}$ Previous studies done using an identical electrochemical setup indicate an optimal loading of 1.5 mg/cm$^2$ carbon black ink to minimize porosity related issues in the diffusion of H$_2$O$_2$. Murawski demonstrated that higher catalyst loadings decreased the porosity of the electrocatalyst layer and led to lower efficiencies for H$_2$O$_2$ production as H$_2$O$_2$ was presumably degraded electrochemically. At a 1 mA/cm$^2$ current density, a 3.3 mg/cm$^2$ catalyst loading produced 2-hour coulombic efficiencies of 30-33%. In comparison, a 1.5 mg/cm$^2$ loading yielded efficiencies of 55-60%.$^{12}$ Efficiencies dropped after a 2-hour retention time, when pH-related decomposition dominated performance as the bulk electrolyte became alkaline. Scanning electron microscopy (SEM) images and X-ray computed tomography showed the deposited carbon ink had permeated within the bare carbon cloth fibers and decreased the porosity of the GDE. As the loading increased, the path for synthesized H$_2$O$_2$ to diffuse became more tortuous. With inadequate diffusion of electro-synthesized peroxide from the electrocatalyst layer, further electrochemical reduction of H$_2$O$_2$ to water is more likely to occur. In other words, the rate of in-situ degradation exceeds the rate of diffusion away from the electrocatalyst layer, thus leading
to decreased performance. Ideally, a superficial electrocatalyst layer would have been formed on top of the bare carbon cloth to create a distinct TPI.

This work confirmed trends seen previously in RRDE experiments where minimal catalyst loadings improved selectivity for $\text{H}_2\text{O}_2$ on the following non-noble metal catalysts: nitrogen-containing nanostructured carbon (CN$_x$)$^{60}$, Co$^{61}$, and Fe$^{62,63}$. While experiments focused on the mass transfer $\text{H}_2\text{O}_2$ exist for RRDE assemblies, there are few studies using GDE and none that study the specific effect of electrolyte recirculation rate in the cathode chamber. One study revealed that higher mixing rates increased $\text{H}_2\text{O}_2$ production using a carbon felt cathode in an undivided electrochemical cell. A 3-hour residence time with a mixing rate of 300 and 800 rpm resulted in $\text{H}_2\text{O}_2$ concentrations of $\sim 1$ mM and 4.2 mM, respectively.$^{64}$ However, an undivided cell enables the possibility of anodic $\text{H}_2\text{O}_2$ oxidation in addition to the electrochemical reduction of $\text{H}_2\text{O}_2$. A thorough investigation of electrolyte recirculation rate in a dual-chambered electrochemical cell eliminates the possibility of anodic $\text{H}_2\text{O}_2$ oxidation; so, performance will be directly influenced by the turbulent conditions, or lack thereof, resulting in changes in the diffusion layer thickness. By increasing the recirculation rate, the transport of synthesized species from the electrocatalyst layer to the bulk solution is expedited. Mass transport rates aided with convective forces will be faster than by diffusion alone.

The first objective is to investigate the role that electrolyte recirculation rate has on $\text{H}_2\text{O}_2$ production and final electrolyte pH values. I hypothesize that increasing the linear velocity at the cathode surface will decrease the thickness of the diffusion layer and result in higher in-situ $\text{H}_2\text{O}_2$ concentrations. In addition, the impact on the diffusion of co-
synthesized OH\(^-\) on bulk pH will likely vary. Sequential chemical degradation of H\(_2\)O\(_2\) in a more alkaline solution may be consequential in a batch system with higher recirculation rates.

![Diagram of diffusion pathway of H\(_2\)O\(_2\) from gas diffusion electrode](image)

**Figure 3.** Diffusion pathway of H\(_2\)O\(_2\) from gas diffusion electrode

### 3.2 Research Objective #2: Electrolyte pH

As stated previously and emphasized further in MFC studies, the parameters that influence the production and mass transport of synthesized species at the cathode need to be further understood.\(^{56,58,65}\) Synthesis and degradation of H\(_2\)O\(_2\), HO\(_2^-\) and OH\(^-\) species are
directly tied to operational pH values. With a \( pK_a \) of 11.8, the protonated or deprotonated states of \( \text{H}_2\text{O}_2 \) result in the two ORR scenarios described below based on the local pH of the cathode surface.

\[
\begin{align*}
\text{pH} \leq 11.8 & \quad \text{O}_2 + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- \\
\text{pH} > 11.8 & \quad \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HO}_2^- + \text{OH}^-
\end{align*}
\]

It is well understood that \( \text{H}_2\text{O}_2 \) is more reactive, and therefore less stable, in its deprotonated state occurring in alkaline environments above its \( pK_a \) of 11.8.\(^{11}\) However, the selectivity for the 2-electron ORR on carbon black-based cathodes has been suggested to be favored in basic solutions because of the role high concentrations of \( \text{OH}^- \) have on \( \text{O}_2 \) adsorption. The result is a compromise of production and stability.\(^{24}\)

Further understanding of this relationship is required to optimize cathodic efficiencies (i.e., \( \text{H}_2\text{O}_2 \) yield) on carbon-based GDEs. Therefore, the second objective is to determine the effect of initial electrolyte pH on the electrochemical synthesis of \( \text{H}_2\text{O}_2 \). I hypothesize that the CCE will be optimized at acidic pH regimes where there is miniscule \( \text{H}_2\text{O}_2 \) degradation; however, I assume the rate of production on carbon-based GDEs are consistent irrespective of the pH regime.
3.3 Research Objective #3: Chemical and Electrochemical Degradation

As discussed, it is known that in more alkaline solutions, \( \text{H}_2\text{O}_2 \) will readily decompose due to the non-selective nature of the \( \text{HO}_2^- \) anion and accelerated disproportionation. The potential decomposition pathways for synthesized \( \text{H}_2\text{O}_2 \) were discussed previously. The bulk pH of the cathode chamber does not stay constant in dual-chamber setups over the duration of a batch experiment because of the diffusion of the synthesized \( \text{OH}^- \) ion. Auto-decomposition due to pH may occur in the bulk and on the electrode surface before it diffuses through the distinct layers. Electrochemical reduction of synthesized \( \text{H}_2\text{O}_2 \) to \( \text{H}_2\text{O} \) will occur in concert with the previously described chemical degradation. The reaction is thermodynamically favorable on a carbon electrocatalyst when \( \text{H}_2\text{O}_2 \) is present. The standard reduction potential of the electrochemical reduction of \( \text{H}_2\text{O}_2 \) is significantly more positive than the desired 2-electron oxygen reduction as shown by the \(~1.1 \text{ V (vs SHE)}\) difference in Equations 1 and 3. Therefore, the third objective is to determine the effect of electrolyte pH on the chemical and electrochemical degradation of in-situ \( \text{H}_2\text{O}_2 \). I postulate that more alkaline conditions will demonstrate rapid chemical and electrochemical degradation.

Insight on the rate of chemical and electrochemical degradation at different conditions will differentiate the processes behind the electrochemical cell’s efficiency. High decompositions rates would overshadow a very selective cathode for the 2-electron reduction to \( \text{H}_2\text{O}_2 \) if the rate of degradation severely exceeded the rate of production. On the other hand, if rates of degradation are minimal and the cell is still inefficient, then the cathode would not be selective for \( \text{H}_2\text{O}_2 \) at that electrolyte pH.
3.4 Research Objective #4: Electrolyte Buffer Concentration

Applications of GDEs in electrochemical cells that depend on the sustainable growth of microorganisms in the anode chamber for electrical current typically use buffers to maintain the bulk pH close to neutral – optimal conditions for ARB. Phosphate buffer solution (PBS) has been demonstrated to be effective at neutralizing OH⁻ ions as they diffuse from the surface of the cathode while also being stable in the presence of H₂O₂.¹¹ Phosphoric acid has a second pKₐ value of 7.21. During batch production experiments in a dual-chamber setup, the bulk pH will rapidly rise from initially neutral conditions and exceed the pH 7.21 buffering threshold at lab-scale cathode volumes. Popat et al. performed LSVs with a Pt-based gas diffusion cathode in 100 mM PBS solution that indicated at a pH of 8.3 or higher, “A favorable gradient for transport of OH⁻ cannot be obtained through the deprotonation of H₂PO₄⁻ to HPO₄²⁻.”⁶⁵

The final objective is to examine the effect of PBS buffer concentration on electrolyte pH and subsequent H₂O₂ production. Based on previous literature, I hypothesize that a more buffered electrolyte will result in stable performance due to negligible pH change over time. The results on varying buffer concentration will contribute another level of understanding to the interplay between electrolyte pH and H₂O₂ production.
4.0 MATERIALS AND METHODS

4.1 Electrochemical Cell

Multiple electrochemical cells with identical dimensions were constructed to perform the experiments described here. The anode and cathode chambers were constructed with 0.5” and 0.25” thick Plexiglas frames, respectively. Each of these plates are 4”x4” with a 2”x2” hollowed center that served as the electrolyte chambers. Electrolyte volumes of the anode and cathode chamber are approximately 45 and 20 mL but vary slightly for each experiment. These volume variations are noted, specifically in the cathode chamber, because the concentration of synthesized H$_2$O$_2$ and subsequent efficiency calculations depend on accurate volume measurements. In addition, the concentration of OH$^-$ ions, and thus the pH of the bulk solution, depends on the cathode volume and is hypothesized to profoundly influence H$_2$O$_2$ production experiments. A hydraulic connection between the anode and cathode chambers must be present to allow the transport of ions. As electrons transfer to the cathode, electroneutral conditions are maintained by the ion transport across an ion exchange membrane. To accomplish this, a 127 µm Chemours Nafion CEM separated the anode and cathode chambers to facilitate the transfer of cations from the anode to the cathode. In the particular arrangement of circumneutral pH, Na$^+$ ions transferred across the CEM from the anode to the cathode to satisfy this principle of electroneutrality. A CEM was chosen, instead of an AEM, as it has shown to be less susceptible to H$_2$O$_2$ degradation.$^{11}$ An inert, woven carbon cloth functioned as the counter electrode, anode, while the working electrode, cathode, was a 410 µm CeTech carbon cloth with a hydrophobic MPL and a hydrophilic bare carbon cloth layer on which
a carbon catalyst loading was deposited. The bare carbon cloth anode catalyzed the oxidation of water while the desired ORR occurs on the CeTech GDE. To prevent leaks from the resulting hydraulic pressure experienced by the GDE from the cathode chamber, a 2.5 mg/cm² layer of PTFE was applied to the hydrophobic MPL of the CeTech carbon cloth.66 This was a safety precaution necessary for turbulent conditions at high recirculation rates. The carbon electrocatalyst applied to the cathode was a Vulcan XC 72R carbon-based ink which is discussed further in the following section. A stainless steel plate was machined with a 2”x2” hollow center to evenly distribute current across the GDE while permitting gas diffusion. To prevent leaks between sections, silicon gaskets were placed in between each adjacent Plexiglas plate. The Plexiglas, silicone gasket, and stainless steel plate had eight holes drilled along the perimeter to insert stainless steel screws through. Zinc plated wing nuts capped the ends of the screws and were tightened to close off the flat-plate style electrochemical cell as seen in Figure A-2.

A RE-5B Ag/AgCl reference electrode with a flexible connector from Bioanalytical Systems was placed within the anode chamber through a hole drilled through the top side of the Plexiglas. The anode, cathode, and reference electrode were connected to a BioLogic VMP3 Multi-Channel Potentiostat to apply electrochemical techniques and monitor experimental data. The anode connector was joined directly to the bare carbon cloth. The cathode connector was clamped to one of the conductive wing nuts. Circumneutral PBS was the electrolyte used for all experiments unless specified otherwise. A 0.1 M PBS was made with 32 mM of sodium phosphate dibasic anhydrous (Na₂HPO₄) and 68 mM of sodium phosphate monobasic monohydrate (NaH₂PO₄·H₂O). In electrolyte pH
experiments, pH adjustments were made to the standard PBS composition to reach desired pH values with 5 M NaOH or 36% w/w hydrochloric acid.

4.2 Catalyst Preparation

The carbon catalyst loading was constant for all production experiments and was chosen based off the findings of work previously done by Murawski.12 A 1.5 mg/cm² Vulcan Carbon loading was applied on the hydrophilic side of a flat-sheet CeTech carbon cloth with a carbon black-based catalyst ink as seen in Figure A-1. Activated carbon is used as an electrode support for its high surface area to volume ratio and is known to be a selective catalyst for the 2-electron ORR. On the opposing side of the CeTech carbon cloth is a hydrophobic MPL that is characteristic of gas diffusion electrodes. Together, the total thickness of the cathode is 410 µm. To apply the Vulcan carbon catalyst, a 83.3 mg/mL ink was prepared by adding 0.5 g of Carbon Black Vulcan XC-72 to 1 mL of distilled deionized (DDI) water to a sterile scintillation vial. Five mL of the alcohol-based Nafion Dispersion (1100 equivalent weight, 5% w/w) from Fuel Cell Store was added to the mixture and placed in an ultrasonic bath for 30 minutes. A magnetic stirrer was added to the vial which was stirred for 24 hours before the ink was applied to the electrode. To achieve a 1.5 mg/cm² carbon loading, 0.45 mL of the 83.3 mg/mL ink solution was pipetted in 0.05 mL increments to the hydrophilic side of the CeTech carbon cloth. The carbon ink was spread with a paintbrush over a 25 cm² area and allowed to air dry for 24 hours before being placed into the electrochemical cell. Cathode conditioning was performed by recirculating a 1000 mg/L stock solution of H₂O₂ in DDI water for 30 to 60 minutes in the cathode chamber to remove any trace contaminants on the electrode or that may have
appeared during preparation and handling of the materials. The recirculation was achieved with a Fisher Scientific FH100M multichannel peristaltic pump as discussed further in the production experiment methodology.

4.3 Electrochemical Techniques

Linear sweep voltammetry (LSV) and chronopotentiometry (CP) were used in this research using EC Lab® software by Biologic to characterize and measure the electrochemical reactions taking place on the surface of the cathode. LSV is a powerful technique used to generate polarization curves that provide information on the redox reaction(s) occurring at the electrode of interest.67 In this research, the reaction of interest is the 2-electron ORR at the surface of the carbon GDE and LSVs are used to compare the polarization curves at the various conditions tested. The settings of the LSV experiments are described here. First, the current interrupt (CI) technique is applied to accommodate for ohmic loss, a summation of the ionic, electronic, and contact resistances, between the working electrode and the reference electrode in an electrochemical cell. If not compensated for, experimental results can vary significantly because the applied potential and the potential received by the cathode are not equivalent. This resistance to current is unique for each experiment and needs to be accounted for. As recommended by the EC Lab® software manual, the compensation is set to 85% for the CI technique.68 LSVs were performed, unless otherwise mentioned, at a scan rate of 5 mV/s from a 0.5 to -0.5 V potential range.

CP is an electrochemical technique that applies a constant current to the working electrode while measuring the working electrode potential over time. The working
electrode potential changes to a value where the flux of the reactant to the electrode is sufficient to meet the current chosen.\textsuperscript{69} As before, ohmic loss is first determined using the CI technique at an 85\% compensation. A constant current of 25 mA is applied to the cathode yielding a current density of 1 mA/cm\(^2\). It has been shown in MFCs that ARB are capable of oxidizing organics reaching current densities up to 1 mA/cm\(^2\) and thus the current density used here was chosen accordingly.

### 4.4 Tafel Analysis

LSVs portray the relationship between an applied potential and the observed current at the cathode. Results from an LSV can be used to elucidate the rate-limiting step in the oxygen reduction mechanism and the activity of the carbon electrocatalyst.\textsuperscript{70} This procedure, known as a Tafel analysis, provides insight in the form of a Tafel slope and the exchange current density, \(j_0\). The former is an indication of the ORR mechanism and the latter of catalytic activity.\textsuperscript{71} The exchange current density is defined as the current observed when the net current density of oxidation and reduction reactions is zero due to the forward and reverse reactions being in equilibrium. Larger exchange current densities are associated with lower activation energy requirements and ease of electron transfer. This activation barrier that exists for electrochemical reactions is manipulated by a function of applied potential. Charged species partaking in the reaction of interest are subject to free energy changes based on voltage. The kinetic equation that relates current density with overpotential is the Butler-Volmer equation. Simplifying the Butler-Volmer equation with the assumption that the overpotential is not insignificant, when \(j > j_0\), and the forward-reaction direction dominates yields the Tafel equation:
\( \eta = a + b \log(j) \)

where \( a \) can be converted into \( j_0 \) and \( b \) is equal to the Tafel slope. By plotting \( \log(j) \) vs \( \eta \), the linear regions of the graph can be isolated and individual trendlines plotted. From these linear trendline equation, the y-intercept is the \( j_0 \) and the inverse of the slope is the Tafel slope.\(^7\)

4.5 H\(_2\)O\(_2\) Production Experiment

H\(_2\)O\(_2\) electrosynthesis was studied over a variety of design conditions. A steady-state flux of electrons to the cathode was achieved by applying the CP technique described previously. To ensure adequate mixing in the cathode, the electrolyte in the cathode chamber was recirculated using a Fisher Scientific FH100M multichannel peristaltic pump that was calibrated at various recirculation rates with the pump’s rotations per minute. Samples were taken and measured for H\(_2\)O\(_2\) every 30 minutes over the course of triplicate 4-hour experiments. The cumulative volume removed from sampling was recorded over time to accurately calculate the H\(_2\)O\(_2\) concentration and corresponding CCE. The initial and final pH in the anode and cathode chambers were measured using a Thermo Scientific Orion STAR A211 pH meter. While the focus of this research was on the cathode conditions, anode pH values are not discussed but are found in summarized tables in Appendix D. A 4-hour reaction time was chosen to observe phenomenon that may occur at different rates throughout the experiment. The volume removed from the cathode for each sampling, usually 0.3-0.4 mL, was recorded at each sampling time. The H\(_2\)O\(_2\) concentration and cathodic coulombic efficiency (CCE) are dependent on the total electrolyte volume so minor changes in a ~20 mL cathode chamber due to sampling have
an effect. The CEM is a flexible material that changes shape with hydraulic pressure in the electrochemical cell; therefore, contingent upon its installation and sequence of filling the anode and cathode chambers, the effective cathode volume is variable. The CCE is determined from the theoretical H₂O₂ concentration that assumes all electrons transferred are used in the 2-electron ORR. Thus, a CCE of 100% would mean the theoretical and measured H₂O₂ concentration for a given reaction time is equal. The theoretical H₂O₂ concentration is determined by the cumulative charge transferred to the cathode, as determined by the following equation:

\[
\text{Cathodic Coulombic Efficiency (\%) } = \left( \frac{H_{2O_2}}{H_{2O_2}^{th}} \right) \times 100
\]

where, \( H_{2O_2}^{th} = \frac{I \cdot \text{time} \cdot 3600 \text{ s}}{V \cdot h \cdot 3} \text{ mol H}_2\text{O}_2 \cdot 2 \text{ e}^- \cdot 34 \text{ g H}_2\text{O}_2 \text{ mol H}_2\text{O}_2 \)

where I is current in mA, F is Faraday’s constant (96,485 C/mol*e⁻), V is the cathode volume (mL), and time is the reaction time of the experiment (hours).

4.6 H₂O₂ Measurement

A 0.1 mL sample was taken from the cathode chamber and added to 1 mL of titanium (IV) oxysulfate-sulfuric acid solution (27-31% H₂SO₄ basis) and 0.9 mL of DDI water in a 2 mL plastic cuvette as seen in Figure A-3. A new pipette tip was used to sufficiently disperse the reagent throughout the sample. After 10 minutes, the absorbance was read in a VWR UV-1600PC spectrophotometer at a wavelength of 405 nm which had been zeroed with a cuvette filled with 2 mL of DDI. Because of the acidic nature of the reagent, any HO₂⁻ anions present are protonated, so the effective concentration measured
includes both protonated and deprotonated species of H$_2$O$_2$. This method is based on initial experimentation done with potassium titanium (IV) oxylate by Sellers in 1980. A calibration curve with known H$_2$O$_2$ concentrations was created by diluting 35% w/w stock H$_2$O$_2$; concentrations used were 0, 50, 100, 250, 500, 1000, 1500, and 2000 mg/L. Experiments that measured H$_2$O$_2$ at concentrations exceeding 2,000 mg/L correlated the absorbance to a separate calibration curve with stock concentrations reaching 2,500 mg/L. At concentrations exceeding 2,500 mg/L, the variance surpassed acceptable values and dilutions were made. The calibration curve is shown in Figure 4.

![Calibration curve for the spectrophotometric determination of H$_2$O$_2$](image)

**Figure 4.** Calibration curve for the spectrophotometric determination of H$_2$O$_2$

### 4.7 H$_2$O$_2$ Degradation

To understand the impact that synthesized H$_2$O$_2$ degradation has on the production experiments, 4-hour batch experiments with a 1,200 mg/L initial concentration of H$_2$O$_2$
were performed to investigate the degradation of peroxide at various electrolyte pH without current supplied to the cathode. The experiment was performed in cathode chambers with a 1.5 mg/cm² Vulcan carbon catalyst and Nafion CEM in contact with the electrolyte and recirculated at 60 mL/min to model the H₂O₂ synthesis experiments. Thus, the H₂O₂ degradation pathways are restricted to: 1) auto-decomposition of H₂O₂ due to pH, 2) reaction of H₂O₂ with the carbon electrocatalyst, bare carbon cloth, or ion exchange membrane or 3) disproportionation of H₂O₂ catalyzed by electrolyte, catalyst, or electrochemical material impurities. This experiment eliminates the degradation pathway of further electrochemical reduction of H₂O₂ to H₂O and is referred to as chemical degradation. Electrolyte buffers with initial in-situ H₂O₂ were made by adding 102 µL of 35% w/w hydrogen peroxide to 30 mL of 0.1 M PBS. Titrations of 5 M NaOH or 36% w/w hydrochloric acid were done as needed to cover a wide spectrum of pH values. Concentrations were measured at t = 0 for each trial and degradation rates were determined based off the initial concentration.

To go one step farther, an electrochemical cell was set up to restrict the passive diffusion of O₂ to the cathode while passing a 1 mA/cm² current density to the cathode via the CP technique using the potentiostat. Another stainless steel plate was machined but without the hollowed center as seen in Figure A-2. The GDE still received electrical current but was not exposed to the passive diffusion of air by covering the GDE with the stainless steel plate. To ensure the electrolyte was void of O₂, the cathode chamber was sparged with ultra-high purity N₂ gas throughout the experiment. The absence of O₂ restricts further H₂O₂ production despite receiving an electrical current. In addition to
chemical degradation, this configuration allows H$_2$O$_2$ degradation via the 2-electron electrochemical reduction of H$_2$O$_2$ to H$_2$O. Recirculation rate was held constant at 60 mL/min for a shorter duration of 120 minutes due to the faster kinetics of electrochemical degradation.

The degradation pathways from the pH degradation experiments without current are still possible in this setup. This way, the contribution of H$_2$O$_2$ degradation from electrochemical reduction vs chemical degradation can be determined at various electrolyte pH values.

4.8 Electrolyte Recirculation

Recirculation rate experiments were performed using the standard 0.1 M PBS solution at pH 6.6 while varying the recirculation rate of the electrolyte in the cathode chamber by altering the rotations per minute of the Fisher Scientific peristaltic pump. 1, 5, 20, 40, 60, and 80 mL/min recirculation rates for the cathode chamber were used to determine the effect of the linear velocity across the cathode surface and how convective diffusion plays a role in the mass transport of synthesized H$_2$O$_2$ and OH$^-$ ions, and final electrolyte pH. With these variations, the typical H$_2$O$_2$ production experiment methodology was used.

4.9 Electrolyte Buffer Composition

Phosphate buffer concentrations of 10, 25, 50, 100, and 500 mM at near neutral pH were used as the electrolyte in the cathode chamber for 4-hour production experiments. The 100 mM PBS was made as previously described and appropriate dilutions were made as necessary to achieve 10, 25, and 50 mM solutions. A 500 mM PBS was made with the
same proportions of sodium monophosphate and sodium diphosphate. The initial pH across experiments was not constant due to the dilutions and slight variations in sodium phosphate salt additions; pH ranged from 6.3 to 6.7. Lower ionic strength buffer concentrations increase the electrolyte resistance, accounted for by ohmic loss, and create unfavorable ion transport across the cation exchange membrane as the pH disparity between the anode and cathode chambers increases during the experiment. To restrict the transport of protons to the cathode chamber and neutralizing pH when using low buffer concentrations, the anode electrolyte used when testing 10 and 25 mM PBS in the cathode chamber was 100 mM PBS. This ensures Na\(^+\) transport rather than proton transport. With the purpose of the electrolyte buffer experiments being to investigate the effect of pH, ensuring protons do not transfer across the CEM and neutralize the electrolyte is imperative. H\(_2\)O\(_2\) concentration, cathodic coulombic efficiency, and final electrolyte pH were measured.
5.0 RESULTS AND DISCUSSION

5.1 Electrolyte Recirculation

Effective mass transport of electrosynthesized H$_2$O$_2$ is critical for H$_2$O$_2$-producing electrochemical cells. Without facile diffusion, the further 2-electron electrochemical reduction of H$_2$O$_2$ to H$_2$O will occur as it is thermodynamically favorable. As discussed before, the reduction of O$_2$ to H$_2$O$_2$ has a more negative standard reduction potential than the reduction of H$_2$O$_2$ to H$_2$O; therefore, when both O$_2$ and H$_2$O$_2$ are present, the latter reaction is favored and CCE will diminish. As discussed previously, one way research groups approach this mass transfer limitation is by designing electrodes with porous structures that facilitate the diffusion of H$_2$O$_2$, such as with HPC. To the best of my knowledge, there are no systematic studies investigating the role of electrolyte recirculation rate on H$_2$O$_2$-producing cells with a GDE. This approach will shift the spotlight from the structural properties of the electrocatalyst to the diffusion layer. Popat et al. highlighted the role that the diffusion layer thickness has on the concentration overpotential of a Pt-based GDE, a fuel cell application, by performing LSV with different mixing speeds. Their results showed that even a mild stirring rate improved cathode performance (greater current density for a given cathode potential) by reducing the overpotential caused by an accumulation of OH$^-$ ions at the electrode-electrolyte interface. More alkaline pH values at the cathode surface create a larger overpotential; the Nernst equation depicts a 59 mV potential drop in the ORR per pH unit as shown in the general equations below:

\[
E_{cell} = E^0 - \frac{RT}{nF} \ln Q
\]
\begin{align}
E_{\text{cell}} & = E^0 - 2.303 \frac{RT}{nF} \log Q \quad (13) \\
E_{\text{cell}} & = E^0 - \frac{0.059}{n} \log Q \quad (14)
\end{align}

where \( Q \) is the reactant coefficient, \( R \) is the universal gas law constant, \( T \) is the temperature at standard conditions (25°C), \( F \) is Faraday's constant, and \( n \) is the number of electrons participating in the reaction. Thus, a more neutral cathode, facilitated by the adequate diffusion of OH\(^-\) from the electrocatalyst to the bulk solution, has a lower overpotential. To stress the importance of this anion on the ORR, Popat et al. indicate the significant cathodic potential losses that stems from inefficient OH\(^-\) transport.\(^{65}\)

As shown by Figure 5, electrolyte recirculation rate has a large impact on the CCE of the H\(_2\)O\(_2\)-producing half-cell. Initial coulombic efficiencies at a 30 minutes vary widely from 1 mL/min to 80 mL/min (Figure 5b). At 1 mL/min, the minimum condition that ensures adequate mixing, the CCE was 34%. As recirculation rates increased, efficiencies plateaued above 60 mL/min where 60 and 80 mL/min yielded near equivalent initial efficiencies of 61% and 59%, respectively. At shorter reaction times there was minimal bulk decomposition of H\(_2\)O\(_2\) because cathode pH is still circumneutral; the phosphate buffer solution buffers the introduction of newly synthesized OH\(^-\) ions.
Figure 5. Effect of recirculation rate on peroxide electrosynthesis over a 4-hour batch experiment. a) $\text{H}_2\text{O}_2$ concentration. b) CCE. Error bars represent triplicate trials.
The predominant difference between the performances of these different conditions at 30 minutes is the residence time of H$_2$O$_2$ on the electrocatalyst layer. Without adequate diffusion, more H$_2$O$_2$ is reduced to H$_2$O at low recirculation rates and peroxide production is less efficient. The transport mechanism that induced overpotential changes in Popat’s study is identical to how the electrolyte recirculation rate caused rapid H$_2$O$_2$ transport and increase efficiencies here.$^{65}$

Over the course of the 4-hour batch experiment, efficiencies with recirculation rates of 20 mL/min and above decrease after a 2-hour reaction time. Optimal performance was seen at 60 mL/min with a 4-hour cumulative concentration of 1.46 g/L (Figure 5a). Peaking at 68% efficiency, a recirculation rate of 60 mL/min results in an efficiency decrease to 47% over the duration of the experiment. Meanwhile, performance with a 1 mL/min recirculation rate stayed stable within a range of 34-39% efficiency. The efficiencies seen at lower recirculation rates were more consistent but overall lower than higher recirculation rates.

As displayed in Figure 6, experiments performed at 20 mL/min and above had a final cathode pH~10 and above. The stable recirculation rates of 1 and 5 mL/min had a final cathode pH value of 9 or below. Furthermore, the recirculation rates with a final cathode pH of 10 or higher, except for 40 mL/min plateaued with respect to their overall concentration of H$_2$O$_2$ in the cathode chamber as the experiment progressed. At this point, the rate of production and degradation are equal as the bulk pH degradation occurs. If one could extrapolate to reaction times greater than 4-hours, it will likely display the rate of degradation will exceed the rate of production and the overall concentration will begin to
decline for all conditions as the bulk pH becomes too alkaline. It is clear that electrolyte recirculation rate has an effect on bulk pH and consequently the performance of \( \text{H}_2\text{O}_2 \)-producing cells.

![Graph of final cathode pH vs. recirculation rate](image.png)

**Figure 6.** Relationship between final cathode pH and cathode recirculation rate. Error bars represent triplicate trials.

Equation 1 demonstrates how the 2-electron ORR simultaneously produces \( \text{H}_2\text{O}_2 \) and OH- ions, leading to an alkaline catholyte in dual-chamber electrochemical cells. It is well known that \( \text{H}_2\text{O}_2 \) decomposition is accelerated at high pH which puts a limitation on peroxide yield.\(^{35,74}\) As it is proven here to be crucial, the role electrolyte pH on \( \text{H}_2\text{O}_2 \) production performance dictates further investigation as it pertains to the rate of production and degradation in acidic, neutral, or alkaline environments. From these results, an optimal
recirculation rate of 60 mL/min facilitated rapid diffusion and suggests lower rates of electrochemical reduction at the surface of the cathode. A higher recirculation rate above 60 mL/min appears to have limiting returns in this reactor; although residence time of \( \text{H}_2\text{O}_2 \) is minimal, which limits reduction on the cathode surface, the decomposition that occurs from a more alkaline bulk solution drops the efficiency. Hereafter, the 60 mL/min mixing regime of the cathode chamber was applied to all further experiments.

### 5.2 Electrolyte pH

The batch \( \text{H}_2\text{O}_2 \) production experiments with varying recirculation rates demonstrated that increasingly alkaline catholytes, caused by the coincident production of \( \text{OH}^- \) during the ORR, deteriorates performance over time. The previous experiments were conducted at neutral pH, ideal electrolyte conditions for microbial electrochemical cells, but other applications that utilize \( \text{H}_2\text{O}_2 \) may call for acidic or alkaline environments. For example, Fenton’s reaction is more effective at acidic conditions between pH 2.8-3 while alkaline environments at a pH > 10 are necessary for paper and pulp bleaching.\(^{42}\) In order to accomplish this, phosphate buffer solutions were used to ensure constant electrolyte pH throughout the duration of the experiment. Without a PBS, such as low alkalinity graywater or NaCl solutions commonly used, the pH of the cathode chamber would rapidly approach a pH of 12 as \( \text{OH}^- \) are synthesized and a detailed analysis on electrolyte pH would not be plausible. Therefore, a closer look at the performance in specific pH conditions was performed here.

Contrary to the hypothesis derived from recirculation rate experiments, alkaline environments were favorable for \( \text{H}_2\text{O}_2 \) electrosynthesis. As shown in Figure 7a, an
alkaline electrolyte pH of 13.5 (1.78 g/L) yielded a 244% increase in H$_2$O$_2$ concentration than an acidic electrolyte pH of 1 (0.52 g/L) over the 4-hour batch experiment. Initial CCE linearly increase with electrolyte pH from 26% to 62%, pH 1 and pH 13.5 respectively, and plateau at pH 13 (Figure 7b). As seen previously during the recirculation rate experiments, H$_2$O$_2$ concentrations at neutral pH increase linearly and begin to level off after a 2-hour reaction time as bulk pH assuming approaches the pK$_a$ of H$_2$O$_2$. Electrolyte pH experiments of 11.5 and 12 represent conditions near the pK$_a$ of H$_2$O$_2$ and displayed the largest drop in efficiency over time. The most extreme conditions of pH 1 and 13.5 had stable performance throughout but did result in slight deterioration over time. From initial CCEs of 62% for the alkaline environments of pH 13 and 13.5, final CCE after the 4-hour experiment were 54% and 61% respectively. Similarly, for pH 1 experiments, there was a decrease from an initial CCE of 26% to 17%. The reasoning behind this decline is likely due to the electrochemical reduction of synthesized H$_2$O$_2$ becoming more significant as concentrations rise in the cathode chamber. As was discussed earlier, the thermodynamics favor this undesirable reaction particularly when the concentration of the reactant, H$_2$O$_2$, increases.
Figure 7. Effect of initial electrolyte pH on peroxide electrosynthesis over a 4-hour batch experiment. a) \( \text{H}_2\text{O}_2 \) concentration and b) CCE. Error bars represent triplicate trials.
It has been shown in the literature that the reaction mechanism for the ORR changes depending on the pH of the electrolyte for a nitrogen-doped carbon electrocatalyst.\textsuperscript{75} Wan et al. determine that at low potentials alkaline electrolyte pH decreases the electron transfer number, or the number of electrons that the O$_2$ molecule receives, which favors the production of H$_2$O$_2$ versus direct reduction to H$_2$O. The mechanism of ORR is not fully understood and one group suggests that the varying electrolyte pH results in different electron transfer mechanisms at the Helmholtz planes of the electrochemical double layer.\textsuperscript{27} Their speculation indicates that alkaline environments promote an outer-sphere electron transfer process. This electron transfer mechanism favors the formation of the H$_2$O$_2$ by being a more “indirect” route that avoids the direct chemisorption of O$_2$ to the electrocatalyst surface. Another explanation by Perry et al. symbolizes OH\textsuperscript{-} as a “poison” that blocks and lowers the total number of catalytic active sites. With lower overall active sites, the O$_2$ molecule is more likely to undergo end-on rather than side-on adsorption which encourages a reduction mechanism favoring the 2-electron reduction. In addition, lack of active sites dampens the reduction of H$_2$O$_2$ to H$_2$O as well.\textsuperscript{24} Although an explanation of the effect of pH is not explicit, the pH regime undoubtedly altered performance in this research as it does across the previously cited scientific literature.

The effect of pH on H$_2$O$_2$ production is not uniform across electrocatalysts. The general consensus is that weak-binding catalysts, such as carbon-based electrocatalysts, are more selective for H$_2$O$_2$ in alkaline conditions.\textsuperscript{13} Glassy carbon (GC) electrodes used in an RRDE configuration were compared to in 0.1 M HClO$_4$ and 0.1 M KOH solutions for selectivity; across a potential range of 0.1 – 0.6 V (RHE), the experiments done in alkaline
conditions exhibited high activity (measured ring current), without compromising on selectivity (2-electron pathway efficiency). Contrarily, a phosphorus-doped carbon nanotube GDE was tested for H$_2$O$_2$ production at initial pH values of 3, 7, and 14. Cathodic H$_2$O$_2$ concentrations at 60-minutes were 1.26, 1.29, and 0.85 g/L respectively – significantly favoring neutral and acidic mediums. The selectivity of mesoporous nitrogen-doped electrocatalysts for H$_2$O$_2$ varied strongly with electrolyte pH and applied potential at the working electrode in a RRDE setup. At a low potential regime, less than 0.2 V (vs RHE), a 0.1 M KClO$_4$ (pH 1) electrolyte exhibited the highest selectivity for H$_2$O$_2$. However, when the linear voltage scan increased to potentials between 0.4 – 0.8 V (vs RHE), a 0.1 M KOH (pH 13) electrolyte was the most conducive to H$_2$O$_2$ formation.

LSV data for each electrolyte pH is shown in Figure 8. The results suggest that regardless of the bulk electrolyte pH, the carbon catalyst surface pH is very high (11-12) and H$_2$O$_2$ is predominantly synthesized in the deprotonated state. As discussed, the Nernst equation predicts a 59 mV drop in reduction potential for each unit increase in pH. At a current density representative of this research, or 1 mA/cm$^2$, the difference in potential between pH 1 and 13 is 0.17 V. Theoretically, the Nernst potential predicts a potential difference of ~0.7 V. The modest difference indicates the local pH at the surface is very similar for all of the bulk electrolyte solutions.
Figure 8. LSV data for a range of electrolyte pH conditions performed at a 5 mV/s scan rate

Typical ORR kinetics exhibit a two-step Tafel slope dependent on the applied potential. Pt electrodes portray a 60 and 120 mV/decade Tafel slope for the 4-electron ORR at low and high overpotential ranges. As shown in the Tafel plot in Figure 9, a two-step Tafel slope also exists for ORR on the carbon black-based GDE which vary with electrolyte pH. The Tafel slopes representative of the potential applied during the H₂O₂ production experiments in this research is the high current density region slope where a distinct shift from acidic to alkaline environments can be noted. As shown in Table 3, the Tafel slopes at pH 1 and 6.6 hover around ~240 mV/decade whereas all alkaline environments were close to ~120 mV/decade. These slopes suggest under acidic environments the 4-electron reduction at high overpotentials is dominant and performs poorly as indicated by the larger
Tafel slope. Meanwhile, in alkaline environments the 2-electron reduction is dominant at a Tafel slope range similar to values reported in the literature as discussed below. At the potentials relevant for the cathodic reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2}, the Tafel analysis strongly suggests a mechanistic shift of the ORR favoring the synthesis of H\textsubscript{2}O\textsubscript{2} at alkaline conditions.

![Figure 9](image_url)

**Figure 9.** Two-step Tafel plot at various electrolyte conditions for an ORR on a carbon-based GDE

**Table 3.** Tafel analysis for varying electrolyte pH at high overpotentials

<table>
<thead>
<tr>
<th>pH</th>
<th>Slope</th>
<th>Intercept</th>
<th>mV/decade</th>
<th>j\textsubscript{0} (A/cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>4.19</td>
<td>-3.26</td>
<td>238.7</td>
<td>5.49E-07</td>
</tr>
<tr>
<td>6.6</td>
<td>4.15</td>
<td>-2.39</td>
<td>240.7</td>
<td>4.03E-06</td>
</tr>
<tr>
<td>11.5</td>
<td>7.65</td>
<td>-2.75</td>
<td>130.7</td>
<td>1.78E-06</td>
</tr>
<tr>
<td>12.0</td>
<td>7.58</td>
<td>-2.58</td>
<td>131.9</td>
<td>2.64E-06</td>
</tr>
<tr>
<td>13.0</td>
<td>8.04</td>
<td>-2.26</td>
<td>124.4</td>
<td>5.56E-06</td>
</tr>
<tr>
<td>13.5</td>
<td>8.20</td>
<td>-2.07</td>
<td>122.0</td>
<td>8.55E-06</td>
</tr>
</tbody>
</table>
Changing Tafel slopes designate a shift in the elementary and rate-determining steps of the complicated, multi-step ORR. Even with an exact mechanism still not fully understood or accepted for the state-of-the-art Pt electrode, let alone across the plethora of materials being constructed and tuned for the ORR, a shift in itself of the Tafel slope may represent the transition to the 2-electron reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2}. Research comparing oxidized carbon nanotubes (O-CNT) and CNT for H\textsubscript{2}O\textsubscript{2} production attributed a lower Tafel slope for O-CNT to fast ORR kinetics that favored H\textsubscript{2}O\textsubscript{2} production. The O-CNT and CNT Tafel slopes in a basic solution were 47 and 79 mV/decade respectively. The former corresponded to a ~30% increase in selectivity for H\textsubscript{2}O\textsubscript{2} at a lower Tafel slope.\textsuperscript{78} Lu et al. did not report a two-step relationship but it is assumed that the values reported are representative of the high overpotential region. Lopes et al. attributed the two-step Tafel slope for a Metal-C-N catalyst of 48 and 132 mV/decade at low and high current densities to a transition from the 4- to the 2-electron reduction.\textsuperscript{79} A study that manipulated the extent of amorphous carbon layers deposited on a Pt electrode correlated the catalysts selectivity for H\textsubscript{2}O\textsubscript{2} to adsorption mechanism of O\textsubscript{2}. Higher carbon loadings suppressed the 4-electron pathway by favoring the end-on adsorption of O\textsubscript{2} to the catalyst which was theoretically validated by an ~70 mV/decade increase in Tafel slope.\textsuperscript{80}

Due to the complexity of the ORR and the majority of studies in the literature focused on fuel cell applications, there is sparse reporting of Tafel slopes for H\textsubscript{2}O\textsubscript{2} production. However as mentioned previously, variations of the Tafel slope are tied to a mechanistic shift in the reaction and may be correlated to the performance of GDE in a peroxide producing electrochemical cell.
5.3 Chemical and Electrochemical Degradation

\( \text{H}_2\text{O}_2 \) yield in an electrochemical cell is a function of the efficiency and selectivity of the electrocatalyst, which utilizes electrons for the ORR with \( \text{H}_2\text{O}_2 \) as a product, and the rate the synthesized \( \text{H}_2\text{O}_2 \) is degraded. The degradation routes and mechanisms were discussed in Section 2.5. Degradation that occurs as a result of an electrochemical reduction at the surface of the electrode is known as electrochemical degradation. Otherwise, decomposition that is driven by the hydroperoxide anion, auto-decomposition by means of disproportionation, or reactions between \( \text{H}_2\text{O}_2 \) and materials in the electrochemical cell is referred to as chemical degradation. Understanding the role of electrolyte pH on chemical and electrochemical degradation provides an idea of what pathway is dictating the results of the \( \text{H}_2\text{O}_2 \) production experiments.

As expected and shown in **Figure 10a**, chemical degradation of \( \text{H}_2\text{O}_2 \) in the electrochemical cell displayed a strong dependence on electrolyte pH. At acidic and neutral conditions, \( \text{H}_2\text{O}_2 \) remained stable throughout the duration of the experiment with less than 3% degradation. Minor degradation occurred instantaneously at these pH conditions and leveled off. Trace levels of organic contamination are likely the cause. Alkaline environments exhibited faster degradation of \( \text{H}_2\text{O}_2 \) with peak degradation occurring near the \( \text{pK}_a \) value (≈11.8) of \( \text{H}_2\text{O}_2 \). At an initial pH of 12, 87% of the initial \( \text{H}_2\text{O}_2 \) degraded in the cathode chamber after 240 minutes. Interestingly, the rate of decomposition slowed for pH 13 with 50% of the peroxide remaining by the experiments completion. This may suggest the operative role of trace metal catalyzed disproportionation. At very alkaline conditions (pH≥13) the speciation of metals to high-valent metal complexes may hinder or
eliminate the degradation that transpires from catalytic auto-decomposition. Galbács and Csányi explored the rate of alkali-induced decomposition of H$_2$O$_2$ induced by trace level contaminants found in metal-hydroxides. The study revealed that a maximum decomposition rate occurred between pH 11-12 in purified, or solutions where heavy metal impurities were removed by precipitation, and unpurified NaOH solutions and with systematic additions of Fe(III), Mn(II), and Cu(II). The decomposition kinetics significantly slowed as pH approached 13.$^{74}$

With the electrochemical reduction pathway enabled, degradation was more uniform as a function of pH (Figure 10b). Nearly 100% of the initial H$_2$O$_2$ degraded in alkaline solutions at pH 12 and 13 after 120 minutes. In these experiments, the transition in working electrode potential highlights the gradual depletion of H$_2$O$_2$ and the shift to the electrochemical reduction of H$_2$O to H$_2$(g). The standard reduction potential is more negative as shown by Equation 15 below. An example of this is attached in Figure B-1.

\[
2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^- \quad E^\circ = -0.830 \text{ VSHE}
\]

Unlike chemical degradation at acidic and neutral pH, rapid degradation occurred with 91% and 88% degradation at pH 6.6 and 1. The delta between pH 1/6.6 and 12/13 is explained by the simultaneous chemical degradation in alkaline environments.
Figure 10. a) Chemical and b) Electrochemical + Chemical degradation of H$_2$O$_2$ in an electrochemical cell. Error bars represent triplicate (a) and duplicate (b) trials.
The rate of H₂O₂ decomposition measured by chemical and electrochemical degradation experiments follow first-order kinetics at an initial concentration of ~1,200 mg/L H₂O₂. Chemical degradation in acid and neutral conditions did not follow first-order kinetics due to the miniscule degradation and variability in measuring precise H₂O₂ concentrations. Rate constants and variability for each condition are displayed in Table 4. Associated figures are found in Figure C-1.

<table>
<thead>
<tr>
<th>pH</th>
<th>Chemical k (hr⁻¹)</th>
<th>Chemical R²</th>
<th>Electrochemical + Chemical k (hr⁻¹)</th>
<th>Electrochemical + Chemical R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.011</td>
<td>0.52</td>
<td>0.784</td>
<td>0.98</td>
</tr>
<tr>
<td>6.6</td>
<td>0.013</td>
<td>0.46</td>
<td>0.691</td>
<td>0.98</td>
</tr>
<tr>
<td>12</td>
<td>0.523</td>
<td>0.99</td>
<td>1.032</td>
<td>0.97</td>
</tr>
<tr>
<td>13</td>
<td>0.167</td>
<td>0.99</td>
<td>0.997</td>
<td>0.99</td>
</tr>
</tbody>
</table>

By taking the difference of the overall degradation rate (electrochemical + chemical) and the chemical degradation rate, the rate of electrochemical reduction to H₂O was found to be 0.773, 0.679, 0.509, and 0.830 hr⁻¹ for pH 1, 6.6, 12, and 13 respectively. The results suggest that when electrochemical and chemical degradation are possible, significant degradation occurs irrespective of the electrolyte pH. Despite the absent chemical degradation at pH 1, when current was applied to the electrode there was considerable H₂O₂ loss that narrowly matches results in alkaline conditions. This confirms the universal efficiency loss during electrolyte pH experiments as H₂O₂ accumulates in the cathode chamber. The drop in efficiency over time for pH 1 is due to the electrochemical reduction pathway as it is seen that negligible degradation occurs by chemical degradation.
Results also indicate that the discrepancies between performance at acidic and alkaline pH are related to the rate of synthesis versus the rate of degradation. If overall degradation is prominent and comparable in all environments, as seen by the electrochemical + chemical degradation experiments, then performance dependent upon on the varying rates of synthesis that occur for at each electrolyte pH. The Tafel slopes reported previously at alkaline pH (≥11.5) indicate a separate reaction pathway for the ORR and was hypothesized to be more selective for the 2-electron reduction. It is important to note the uncertainty that exists for the rate of electrochemical degradation when O2 is not restricted to the cathode and there is simultaneous reductions occurring on the catalyst’s active sites.

However, then why does pH 13 and 13.5 yield considerably higher concentrations of H2O2 and coulombic efficiencies than pH 12 if Tafel slopes indicate a similar rate of synthesis and total degradation appears constant? I hypothesize that at minimal retention times at the surface of the cathode, which is achieved by adequate mixing of the cathode chamber, H2O2 degradation is controlled by chemical degradation in the bulk solution when O2 is not restricted to the cathode. If H2O2 is readily transported away from the cathode surface then H2O2 has to diffuse back to GDE and reattach to a catalytic site for further reduction to occur. In this scenario, O2 is instantaneously diffusing and occupying active sites from the GDE exposure to air which outcompetes the rate of diffusion, adsorption, and reduction of in-situ H2O2.

It is important to note capability of PBS to stabilize H2O2 versus unbuffered electrolyte solutions, such as NaCl, commonly used in MPPCs. Young et al. demonstrate the effectiveness of PBS stabilizing H2O2 at circumneutral conditions while NaCl permits
considerable degradation over a period of days. \(^{56}\) Depending on the reaction time of the application and chemical composition of the electrolyte used in the cathode chamber, such as graywater, the stability of any synthesized \(\text{H}_2\text{O}_2\) will unquestionably vary.

### 5.4 Electrolyte Buffer

The buffering capacity of the electrolyte will directly impact the extent of pH rise in the cathode chamber. The \(\text{H}_2\text{PO}_4^-\) species neutralizes synthesized \(\text{OH}^-\) in neutral conditions at the second \(pK_a\) value of phosphorus, 7.2. A concentrated buffer solution will not only maintain a pH near this value but lowers the ionic resistance, or ohmic loss, of the electrolyte resulting in less overpotential.

As shown by Figure 11a, a concentrated PBS of 500 mM resulted in the highest concentration of \(\text{H}_2\text{O}_2\) produced of 1,220 mg/L and exhibited consistent production throughout the duration of the experiment with CCE ranging from 39-44%. Dilute PBS of 10, 25, and 50 mM yielded 724, 730, and 765 mg/L of \(\text{H}_2\text{O}_2\). Initial CCE increased as the PBS concentration of the electrolyte decreased as displayed in Figure 11b. At 30-minutes, 25 mM was 28% more efficient than 500 mM. However, significant loss in efficiency was seen in dilute PBS solutions as the batch experiment progressed. Unlike the consistent CCE of 500 mM, the loss of CCE for 10 and 25 mM was 34 and 40%, respectively. Previously demonstrated in the recirculation rate experiments, the drop in performance over time is closely correlated to a rise in bulk pH. To be expected, the final cathode pH are directly connected to the electrolyte’s ability to neutralize hydroxide ions as shown in Figure 12. Steady performance was paired with neutral pH in 500 mM PBS; the initial and final cathode pH values were 6.22 and 6.79. On the contrary, the performance of 10 mM PBS
dropped 34% as the pH increased from 6.73 to 11.34. The decelerating net rate of production is seen in the curve of the overall H$_2$O$_2$ concentration graph. As the buffer concentration decreases the onset of a plateau, characteristic of the buffer capacity of the electrolyte being reached, occurs at shorter reaction times.
Figure 11. Effect of electrolyte buffer strength on peroxide electrosynthesis over a 4-hour batch experiment. a) $\text{H}_2\text{O}_2$ concentration and b) CCE. Error bars represent triplicate trials.
Figure 12. Relationship between phosphate buffer strength and final cathode pH. Error bars represent triplicate trials.

Inferior performance at 30-minutes for high-strength buffer solutions suggest active site interference on the electrocatalyst by phosphate anions. Strongly adsorbing electrolyte species have been shown to poison electrode surfaces and impede the ORR. For example, increasing Cl\textsuperscript– electrolyte concentrations have been shown to inhibit ORR kinetics on a polycrystalline Pt electrode due to electrocatalyst coverage.\textsuperscript{81} Furthermore, Mamtani et al. tested pristine and poisoned CN\textsubscript{x} in 0.1 M HClO\textsubscript{4} and 0.1 M H\textsubscript{3}PO\textsubscript{4} accordingly. The presence of dihydrogen phosphate resulted in significantly lower ORR activity with the specific kinetic current at 0.7 V (vs SHE) decreasing from 0.97 to 0.19 mA/mg\textsubscript{catalyst}.\textsuperscript{82}
5.5 Other Considerations

Facile mass transport of synthesized $\text{H}_2\text{O}_2$ on carbon-based gas diffusion electrodes was proven to be crucial in achieving optimal CCE. Achieving this by catholyte recirculation in full-scale reactors may demand unnecessary energy requirements; therefore, tuning the electrolyte-facing surface hydrophobicity to expedite the diffusion of synthesized $\text{H}_2\text{O}_2$ is an area of future investigation. As discussed, an optimal GDE contains a distinct TPI that eliminates further electrochemical reduction of $\text{H}_2\text{O}_2$, which this research has demonstrated to contribute to $\text{H}_2\text{O}_2$ degradation. A preliminary examination of the implications of a hydrophobic electrode surface was done.

SEM images were taken of the manufactured GDE used in this research, the CeTech carbon cloth with MPL, to portray the contrast in structure and porosity between the differing sides of the electrode. SEM images at 30x and 400x magnification of the hydrophilic bare carbon cloth, 1.5 mg/cm$^2$ catalyst loading of Vulcan carbon ink on the hydrophilic bare carbon cloth, and the opposing hydrophobic MPL are shown in Figure 13.
Figure 13. SEM imagery at x30 and x400 magnification of hydrophilic bare carbon cloth (red), hydrophilic bare carbon cloth with 1.5 mg/cm² Vulcan catalyst ink (green), and hydrophobic MPL as manufactured (blue).
Unlike previous experiments, an additional PTFE coating was not applied to the hydrophobic MPL but is pictured and experimented with as manufactured. The hydrophilic bare carbon cloth surface with and without ink applied exhibits a considerably different framework than the hydrophobic MPL. The woven carbon threadwork creates a porous matrix for the catalyst ink to become entrenched in as shown by the coating of carbon fibers deep within the surface. Conversely, the MPL enriched with PTFE has a superficial and impermeable surface with slight cracks in the hydrophobic coating. Each of the electrode surfaces were tested in peroxide production experiments as previously described in Section 3.3. The operational parameters were as follows: 1 mA/cm² current density, 25 mL/min recirculation rate, and a 240 minute experiment duration. The results are shown in Figure 14.
Figure 14. Comparison of a hydrophilic carbon cloth with and without 1.5 mg/cm² Vulcan catalyst ink and the hydrophobic MPL as manufactured over the course of a 2-hour batch experiment on: a) H₂O₂ concentration and b) CCE. Error bars represent duplicate trials.
First, it is evident the application of an electrocatalyst ink to the surface of the bare carbon cloth significantly improves peroxide yield. Furthermore, the hydrophobic MPL outperformed the standard method utilized for this research in terms of yield and efficiency. Without detailed information of the properties of the manufactured carbon-PTFE MPL no conclusions can be drawn from these results. Although to what degree is uncertain, the MPL is undoubtedly more hydrophobic than the bare carbon cloth surface typically used and suggests the hydrophobic nature of the surface affects efficiency.

An issue with the CeTech carbon cloth used is the configuration where the MPL acts as the electrolyte-facing catalyst surface and the hydrophilic carbon cloth is oriented to the air. In turbulent hydraulic conditions, electrolyte leakage becomes a risk. FuelCellEtc’s ELAT® line of GDEs features one- and double-sided MPLs treated on a traditional carbon cloth that offer a solution to this issue. H₂O₂ production experiments were conducted with three configurations: 1) ELAT 1400 – 1.5 mg/cm² Vulcan catalyst ink applied to the hydrophilic bare carbon cloth, 2) ELAT 2400 – double-sided MPL with no ink applied, 3) ELAT 2400 – double-sided MPL with 0.5 mg/cm² Vulcan catalyst ink applied to the electrolyte-facing side. To eliminate pH-related decomposition, trials were performed with 250 mM PBS at a 2 mA/cm² current density for 120 minutes. Performance data is summarized in Table 5 and experimental results are shown in Figure 15. The E’we is the average working electrode potential characteristic of the experiment accounting for the ohmic loss and adjusted by 0.24 V per the Ag/AgCl conversion in 250 mM PBS to a SHE. A 60 minute steady-state potential was chosen and averaged between 30 and 90 minutes.
Table 5. Summary of preliminary experimentation on ELAT GDEs.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Catalyst Loading mg/cm²</th>
<th>E'we (vs SHE) V</th>
<th>Max. H₂O₂ mg/L</th>
<th>Avg. CCE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELAT 1400</td>
<td>1.5</td>
<td>-0.07</td>
<td>840</td>
<td>57</td>
</tr>
<tr>
<td>*ELAT 2400</td>
<td>0.5</td>
<td>-0.06</td>
<td>1003</td>
<td>66</td>
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<tr>
<td>ELAT 2400</td>
<td>-</td>
<td>-0.22</td>
<td>1109</td>
<td>78</td>
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</table>

*One trial

While the double-sided ELAT 2400 exhibited the highest performance in terms of peroxide yield, the overpotential required was 0.15 V (vs SHE) more for the ORR than the catalyst loading of 1.5 mg/cm². Thus, a 0.5 mg/cm² catalyst loading was applied on the one side of the MPL of ELAT 2400 to reduce the energy input required to overcome activation. Performance nearly matched the top performing ELAT 2400 without ink and reduced the overpotential by 0.16 V (vs SHE). The porosity specifications reported by the manufacturer for ELAT 1400 and 2400 are 63% and 31%. The results support that a less porous, and more hydrophobic cathode surface, produces greater results. Catalyst ink will lower the overpotential required at a minor cost of efficiency. It should be noted that only one trial was run with 0.5 mg/cm² on ELAT 2400.
Figure 15. Preliminary experiments comparing ELAT GDEs for peroxide electrosynthesis over a 2-hour batch experiment on a) H₂O₂ concentration and b) CCE. Error bars represent triplicate trials.
6.0 CONCLUSION

Synthesizing H$_2$O$_2$ by cathodic O$_2$ reduction in an electrochemical cell is a decentralized alternative to the energy-intensive anthraquinone process. A power source is typically required to overcome the cathodic overpotential that is characteristic in the ORR but microbial technologies have been shown to catalyze the reaction without any additional energy input in a MFC.$^{84,85}$ A MFC that converts the chemical energy in wastewater to electrical energy is a particularly promising area to electrochemically synthesize H$_2$O$_2$ that water industries and niche applications, such as potable water recovery on space vessels, may take advantage of. To efficiently synthesize H$_2$O$_2$ on GDEs, the effect of operational parameters and design conditions on the rate of synthesis and degradation need to be further understood. The fundamental study performed here investigated the interplay between electrolyte pH and cathodic H$_2$O$_2$ production. The summarized results of each research objective below will guide future studies intended to optimize a H$_2$O$_2$-producing electrochemical cell equipped with a carbon black-based GDE.

(1) Research Objective #1: Electrolyte Recirculation

Increasing the recirculation rate accelerates initial CCE (t $<$ 2 hour) with peak performance at 60 mL/min. By inducing turbulent conditions at the surface of the cathode, the diffusion layer thickness decreases and the increased rate of H$_2$O$_2$ diffusion from the cathode surface to the bulk solution limits electrochemical reduction of H$_2$O$_2$. A threshold was met for the trend of increasing initial CCE with catholyte recirculation rate above 60 mL/min; I speculate the electrosynthesis of H$_2$O$_2$ becomes rate-limiting at these
conditions. Increased recirculation simultaneously increases the diffusion of OH\textsuperscript{-} ions from the electrocatalyst layer and creates a more alkaline bulk solution that decreases the stability of H\textsubscript{2}O\textsubscript{2} and reduces performance at longer reaction times.

(2) Research Objective #2: Electrolyte pH

Alkaline environments are favorable for H\textsubscript{2}O\textsubscript{2} production on a carbon black-based GDE with a pH 13.5 electrolyte yielding the highest CCE and cumulative H\textsubscript{2}O\textsubscript{2} concentration. A Tafel analysis performed for each pH suggests a different ORR mechanism is rate-limiting for alkaline conditions that results in a more selective cathodic reduction to H\textsubscript{2}O\textsubscript{2}.

(3) Research Objective #3: Chemical and Electrochemical Degradation

Chemical degradation peaked at pH conditions near the 11.8 pK\textsubscript{a} of H\textsubscript{2}O\textsubscript{2} with pH 12 exhibiting the fastest degradation kinetics. At further alkaline conditions, chemical degradation slowed potentially due to the hindered disproportionation that happens when trace metal speciation to metal hydroxide complexes occurs at pH 13. Concurrent electrochemical and chemical degradation was rampant and nearly uniform across all pH regimes; alkaline pH portrayed slightly faster decomposition due to simultaneous chemical degradation. The degradation experiments alone do not plainly explain the contrasting performances between acidic and alkaline environments. The selectivity of the cathode at different pH regimes as well as how the
electrochemical degradation rates change when O₂ is no longer restricted add to the complexity of the results.

(4) Research Objective #4: Electrolyte Buffer Concentration

Increasing the buffer concentration of the PBS electrolyte yielded consistent performance by eliminating the chemical degradation of synthesized H₂O₂ caused by rising pH. As electrolyte buffer strength increased, the rising phosphate anion concentration is hypothesized to have interfered with the electrosynthesis of H₂O₂ by covering catalytic active sites resulting in lower initial efficiencies.

(5) Other Considerations: Cathode Hydrophobicity

The preliminary results indicate the potentially significant factor of cathode hydrophobicity on the CCE of H₂O₂-producing electrochemical cells using a carbon-based GDE. The following hypothesis is to be tested in future experiments: Tuning the hydrophobicity of the electrolyte-facing cathode surface will ensure facile mass transport of electrosynthesized H₂O₂ to the bulk solution, decrease deleterious electrochemical reduction, and increase net H₂O₂ yield.
7.0 FUTURE WORK

In addition to the hydrophobicity and porosity of the cathode, the electrolyte pH is imperative to consider in the optimization of the electrosynthesis of \( \text{H}_2\text{O}_2 \) on carbon-based GDEs to be done in future studies. As demonstrated here, a higher buffer concentration neutralizes the co-synthesized OH\(^-\) and eliminates the chemical degradation that occurs in the bulk solution. Especially in biological applications such as a MPPC, studies should look to optimize the cathode structure by experimenting with catalyst loading and hydrophobicity while maintaining an environment conducive to microbial growth. With an application that is indifferent or demands a basic solution, such as paper bleaching, the combination of a hydrophobic catalyst surface and an alkaline environment that shifts the ORR mechanism to favor the 2-electron pathway may be ideal.

I recommend that future studies characterize the hydraulic conditions in the cathode chamber. Conducting a hydraulic model with a program such as COMSOL Multiphysics will detail flow patterns, dead zones, and potential short-circuiting that is occurring when the catholyte is recirculated. This would provide a comprehensive analysis to support the recirculation rate data presented in this work. Furthermore, defining the cathode chamber fluid mechanics by way of a Reynolds number or a “G-factor” velocity gradient would allow the experiments to be reproduced more effectively.
APPENDICES
Appendix A – Pictures of electrochemical cell reactor and materials

Figure A-1. a) Vulcan carbon black XC-72 and b) applied carbon black electrocatalyst ink to a carbon-based GDE

Figure B-2. a) Configuration for typical H$_2$O$_2$-production experiment with electrodes connected to potentiostat b) configuration for electrochemical degradation experiments to restrict O$_2$ to cathode
Figure C-3. Spectrophotometric measurement of H₂O₂ using titanium oxysulfate method – increasing concentration proceeds left to right

Figure D-4. Expanded 3D model of electrochemical reactor
Appendix B – Working potential of electrochemical degradation

Figure E-1. Measured working electrode potential during an electrochemical degradation experiment (pH 12 trial) where all in-situ peroxide is degraded.
Appendix C – H$_2$O$_2$ degradation rate constants

Figure F-1. First-order rate constants for H$_2$O$_2$ degradation in chemical and electrochemical experiments starting with 1,200 mg/L peroxide.
Appendix D – Summarized working electrode potentials and pH data

Table D-1. Experimental data from recirculation rate experiments.

<table>
<thead>
<tr>
<th>Recirculation Rate (mL/min)</th>
<th>Initial pH</th>
<th>Final Anode pH</th>
<th>Final Cathode pH</th>
<th>Ewe' (V) vs SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.6</td>
<td>2.6</td>
<td>8.8</td>
<td>-0.10 ± 0.008</td>
</tr>
<tr>
<td>5</td>
<td>6.6</td>
<td>2.8</td>
<td>9.1</td>
<td>-0.08 ± 0.004</td>
</tr>
<tr>
<td>20</td>
<td>6.6</td>
<td>2.7</td>
<td>9.9</td>
<td>-0.10 ± 0.008</td>
</tr>
<tr>
<td>25</td>
<td>6.6</td>
<td>2.5</td>
<td>10.3</td>
<td>-0.09 ± 0.011</td>
</tr>
<tr>
<td>40</td>
<td>6.6</td>
<td>2.8</td>
<td>10.1</td>
<td>-0.15 ± 0.030</td>
</tr>
<tr>
<td>60</td>
<td>6.6</td>
<td>2.6</td>
<td>10.1</td>
<td>-0.17 ± 0.034</td>
</tr>
<tr>
<td>80</td>
<td>6.6</td>
<td>2.7</td>
<td>10.6</td>
<td>-0.18 ± 0.046</td>
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</tbody>
</table>

Table D-2. Experimental data from electrolyte pH experiments.

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Final Anode pH</th>
<th>Final Cathode pH</th>
<th>Ewe' (V) vs SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.2</td>
<td>1.1</td>
<td>-0.01 ± 0.026</td>
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<tr>
<td>6.7</td>
<td>4.9</td>
<td>10.2</td>
<td>-0.09 ± 0.029</td>
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<tr>
<td>11.5</td>
<td>7.1</td>
<td>12.2</td>
<td>-0.15 ± 0.170</td>
</tr>
<tr>
<td>12.0</td>
<td>7.3</td>
<td>12.6</td>
<td>-0.13 ± 0.051</td>
</tr>
<tr>
<td>13.0</td>
<td>12.1</td>
<td>13.1</td>
<td>-0.10 ± 0.010</td>
</tr>
<tr>
<td>13.5</td>
<td>13.0</td>
<td>13.2</td>
<td>-0.10 ± 0.015</td>
</tr>
</tbody>
</table>

Table D-3. Experimental data from electrolyte buffer experiments.

<table>
<thead>
<tr>
<th>PBS Buffer (mM)</th>
<th>Initial pH</th>
<th>Final Anode pH</th>
<th>Final Cathode pH</th>
<th>Ewe' (V) vs SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.6</td>
<td>2.8</td>
<td>11.3</td>
<td>0.20 ± 0.020</td>
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<tr>
<td>25</td>
<td>6.6</td>
<td>2.6</td>
<td>10.9</td>
<td>-0.09 ± 0.091</td>
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<tr>
<td>50</td>
<td>6.7</td>
<td>2.6</td>
<td>9.8</td>
<td>-0.09 ± 0.084</td>
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<tr>
<td>100</td>
<td>6.5</td>
<td>3.9</td>
<td>9.9</td>
<td>-0.08 ± 0.044</td>
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<tr>
<td>500</td>
<td>6.2</td>
<td>6.0</td>
<td>6.8</td>
<td>-0.09 ± 0.013</td>
</tr>
</tbody>
</table>
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