Optical Visualization of Two Phase Flow in PEM Electrolyzers

by

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Abstract

Polymer electrolyte membrane (PEM) electrolyzers are ideally suited to pairing with renewable energy sources given the capability to operate at high current densities and transition between different potential loading. To become commercially competitive however PEM electrolyzers require improvements in performance and cost reduction. Much of the technology for PEM electrolysis has comes from PEM fuel cells, leaving room for improvement. The slower reaction kinetics and highly corrosive environment at the anode due to the oxygen evolution reaction (OER) in particular requires research and development to increase efficiency. This study focuses on the behavior of two-phase flow of oxygen in water as it relates to cell performance. Optical visualization with a high speed camera was used to observe oxygen bubbles at the anode during PEM electrolysis.

Images of oxygen bubbles in two-phase flow were successfully recorded using three experimental setups: a sample holder submerged in a water filled tank, a modified channel-less PEM electrolyzer cell and a modified PEM electrolyzer cell with optically accessible channels. Image processing pathways were successfully developed using MATLAB and Fiji to study individual bubbles in all setups. The channel-less electrolyzer setup operated at a much lower performance than standard PEM electrolyzer cells. It is suspected that contact resistance reduces the electrochemical performance either as a result of the in-plane conductivity for the PTL being very high or large ohmic contact losses where the PTL contacts the current distributor. The optically accessible channel design was able to operate at performances comparable to an unmodified cell and bubble images were captured in-situ to observe bubbly to annular flow regimes over a range of current densities. This investigation showed that flow field channel aspect ratio is an important determinant to cell performance.
Acknowledgements

This research was made possible by NSERC Strategic Project Grant funding for designing new materials for electrolyzing clean fuel with Dr. Aimi Bazylak as the principal investigator at the University of Toronto. Material samples of porous transport layers were provided in kind supply by Hydrogenics. A special thanks go to Dr. Jon Pharoah at Queen’s University for his supervision during this research, Dr. Brant Peppley for his support and Chris Saliba and Arshad Mohammed for their assistance with processing images. I would also like to thank with Ela, Nafisa, Rutendo, Elyse, Parisa, and for their technical help and supportive discussions.
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## Nomenclature

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<th>Definition</th>
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<tr>
<td>PEM</td>
<td>Polymer Electrolyte Membrane</td>
</tr>
<tr>
<td>ACL</td>
<td>Anode Catalyst Layer</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
</tr>
<tr>
<td>SOEC</td>
<td>Solid Oxide Fuel Electrolyzer Cell</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid Polymer Electrolyte</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Polymer Electrolyte Membrane Fuel Cell</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen Evolution Reaction</td>
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<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
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<tr>
<td>PTL</td>
<td>Porous Transport Layer</td>
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<tr>
<td>PFSA</td>
<td>Perfluorosulfonic Acidic Membrane</td>
</tr>
<tr>
<td>CCM</td>
<td>Catalyst Coated Membrane</td>
</tr>
<tr>
<td>PtG</td>
<td>Power to Gas</td>
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<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
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<tr>
<td>CFL</td>
<td>Compact Fluorescent Light</td>
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GIF           Graphic Interchange Format
MEA           Membrane Electrode Assembly
MPL           Micro-porous Layer
LHV           Lower Heating Value
HHV           Higher Heating Value
EIS           Electrochemical Impedance Spectroscopy
DAQ           Data Acquisition Unit
HPLC          High Performance Liquid Chromatography
CCL           Cathode Catalyst Layer
TIFF          Tagged Image File Format
ROI           Region of Interest

Symbol

\( F \)               Faraday’s constant              \( \text{C}/(\text{mol e}^-) \)
\( \Delta G_{R}^{o} \) Change in Gibb’s Free Energy for Reaction  \( \text{J}/\text{mol} \)
\( \Delta H_{R}^{o} \) Change in Enthalpy for Reaction          \( \text{J}/\text{kg} \)
\( \Delta S_{R}^{o} \) Change in Entropy for Reaction            \( \text{J}/\text{mol K} \)
\( i \)            Current Density                                \( \text{A}/\text{m}^2 \)
\( W_{el} \)          Electrical Work                             \( \text{J} \)
\( Q \)                Heat Transfer from Cell                        \( \text{J} \)
\( z \)         Electrons transferred in Reaction                    \( (\text{mol e}^-)/(\text{mol reactant}) \)
<table>
<thead>
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<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
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<tr>
<td>$E_{\text{cell}}^o$</td>
<td>Standard Cell Potential</td>
<td>V</td>
</tr>
<tr>
<td>$E_{\text{reduction}}^o$</td>
<td>Standard Reduction Potential</td>
<td>V</td>
</tr>
<tr>
<td>$E_{\text{oxidation}}^o$</td>
<td>Standard Oxidation Potential</td>
<td>V</td>
</tr>
<tr>
<td>$E$</td>
<td>Cell potential</td>
<td>V</td>
</tr>
<tr>
<td>$E_{\text{rev}}^o$</td>
<td>Standard Reversible Cell Potential</td>
<td>V</td>
</tr>
<tr>
<td>$E_{\text{th}}^o$</td>
<td>Standard Thermoneutral Potential</td>
<td>V</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal Gas Constant</td>
<td>J/(mol K)</td>
</tr>
<tr>
<td>$a$</td>
<td>Activity of Species</td>
<td>-</td>
</tr>
<tr>
<td>$P_{\text{act}}$</td>
<td>Probability of Species in Activated State</td>
<td>-</td>
</tr>
<tr>
<td>$V_{\text{cell}}$</td>
<td>Cell Voltage</td>
<td>V</td>
</tr>
<tr>
<td>$V_{\text{rev}}$</td>
<td>Reversible Cell Voltage</td>
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<tr>
<td>$E_a$</td>
<td>Activation Energy of Reaction</td>
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<td>$\eta_{\text{act}}$</td>
<td>Activation Overpotential</td>
<td>V</td>
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<td>$\eta_{\text{ohm}}$</td>
<td>Ohmic Overpotential</td>
<td>V</td>
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<tr>
<td>$\eta_{\text{diff}}$</td>
<td>Diffusion Overpotential</td>
<td>V</td>
</tr>
<tr>
<td>$\eta_{\text{bubb}}$</td>
<td>Bubble Overpotential</td>
<td>V</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
<td>A</td>
</tr>
<tr>
<td>$i_o$</td>
<td>Exchange Current Density</td>
<td>A/m²</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Electron Transfer Coefficient</td>
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<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
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<tr>
<td>( \eta )</td>
<td>Activation Overpotential</td>
<td>V</td>
</tr>
<tr>
<td>( A )</td>
<td>Active Area</td>
<td>m^2</td>
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Chapter 1

Introduction

1.1 The Need for Renewable Sources of Energy

The increasing global demand for energy presents difficulties given our current consumption and reliance of fossil fuels. Limited sources of fossil fuels will eventually be unable to keep up with the demand for energy consumption [5–8]. Coupled with the problems associated with greenhouse gas emissions from the use of fossil fuels, this issue has been gaining an increased awareness and has led to global governmental pressures to reduce the use of fossil fuels by implementing measures to reduce emissions from industry, through initiatives such as carbon pricing [1, 9, 10].

With growing concerns over environmental sustainability and energy conservation, renewable sources of energy are becoming an attractive solution to the problem of growing energy demands [6, 11]. Increased environmental awareness has led to the use of environmentally friendly renewable energy sources such as photovoltaics, hydro-power and wind turbines. A major difficulty in deploying renewables into the energy grid however is the intermittency due to fluctuations in the production of energy from these sources. Since renewable energy generation is dependent on uncontrollable environmental factors that are independent of current demands for energy, integrating renewables into ancillary services for power grids is a key issue [7, 8]. Therefore a method to couple fluctuating supply to electricity grids and current demand for
electricity is vital for the practical application of renewable energy sources.

To address the problems associated with intermittent power production from renewables, hydrogen production through electrolysis is seen as an efficient means of storing this energy to be economically viable and efficient [5,12]. Hydrogen from electrolysis is viewed as a clean source of energy since it does not release carbon and produces virtually no pollution [13–15]. Using electrolyzers therefore pairs well with renewable energy sources since there is no production of greenhouse gas emissions during this process, further moving from carbon-based energy sources such as fossil fuels.

1.2 Renewable Energy Policy and Targets

The transition to renewable energy sources started with Denmark in 2012 with a target of 35% electricity to come from renewables by 2020 and eventually 100% of electricity consumption supplied by renewables by 2050. Germany has since set optimistic targets of having 80% of energy from renewables by 2050 while stop using nuclear power by 2022 as seen in Figure 1.1 [5,12].

The European Union has also set targets of utilizing 20% renewable energy by 2020 with Finland setting a target of 38% supplied by renewables [16]. Nordic countries have been successful in the development of energy production from renewable sources. In Iceland 100% of its total energy generation comes from renewable energy resources primarily from geothermal energy utilization. Norway has the second highest with 98% of its energy supplied from renewable sources, mainly from hydropower [17,18].

1.3 Hydrogen as an Energy Carrier

Hydrogen has many benefits as an energy carrier. It is the third most abundant element on earth and hydrogen gas can be produced in a renewable manner without
the emission of greenhouse gases. Molecular hydrogen however is not found naturally and must be produced by an energy input. To obtain pure hydrogen it must be extracted from compounds with other elements, the greatest quantity of which is water. Hydrogen acting as an energy carrier can be produced from a variety of processes [19,20]. Today the majority of hydrogen production comes from reforming natural gas and by products from chemical production (combined 78%), but does not produce high purity hydrogen [5] Only about 4% of hydrogen production comes from electrolysis, historically used in the agricultural fertilizer industry. Hydrogen is also used in other niche applications such as flushing during the manufacturing of silicon chips, and in the glass and steel industries [1,19,21]. It is estimated that the global hydrogen production is around 40 billion kg per year [19,22].

1.3.1 Transition to a Hydrogen Economy

The hydrogen economy comprises of the production of hydrogen from an energy source, storage and transmission of this hydrogen to where it can be utilized and the end use to produce heat or power [19]. Using hydrogen as an energy carrier has the
advantage of having versatility from the methods which it can be produced. It can be produced by both in industrial processes and transported through pipelines or tankers or in produced where it is used in local decentralized systems. These means of hydrogen implementation on different scales are shown in Figure 1.2 show that hydrogen has the potential to be implemented in many ways for fulfill energy storage requirements [1].

![Figure 1.2: Means of hydrogen implementation as an energy carrier [1].](image-url)

There are three general categories for which hydrogen energy markets could be used: small systems for transportation, medium systems for industrial applications and large systems for energy storage applications [15]. Currently there are no commercial large scale electrolyzer projects coupled with renewable energy sources. A 6 MW PEM electrolyzer Energiepark Mainz project however was conducted for ancillary services for a local power grid in Mainz, Germany to investigate large scale PEM electrolysis power connected to an 8 MW wind power system [10]. Three operating conditions were tested to see which would be the most profitable and it was found that Power to
Gas (PtG) can yield revenues but there is a high dependence on regulatory framework for the economic viability of such projects [10]. This shows that in a political climate with policies charging increased prices for carbon emission energy sources, it would be expected that the economic framework could be adjusted to make energy from renewable sources a more widespread economically viable option. A similar study has been conducted to show that hydrogen technologies could be feasible for the Spanish electricity grid by converting electricity to hydrogen instead of modulating power plant output to meet peak demands [23].

Hydrogen produced from renewable energy has also been explored in the UK to provide greater energy security for the country. The UK based H2FC Supergen project was used to bring together the research in hydrogen and fuel cells for the purpose of looking at implementing hydrogen as an energy carrier across the country. The UK is facing a challenge of depleting fossil fuel reserves and hydrogen serves as a form of energy independence through power to gas and the transportation sector [1]. Transmission and distribution constraints in the UK for example lead to high costs to add hydrogen in the north compared to the south since the bulk of generation occurs in the north [24]. It has been suggested that the implementation of hydrogen as an energy carrier can be established in markets for on-site hydrogen production using existing infrastructure that would eventually lead to a large scale implementation of a hydrogen economy [1]. Promising strides are being made in implementing hydrogen as an energy carrier, an example of which is major car manufacturers such as Hyundai, Toyota and Honda that are now producing commercial hydrogen vehicles [1].

Some hydrogen fueled technologies have been developed by redesigning technologies that operate on natural gas such as vehicle internal combustion engines and through electricity production in gas turbines [1, 14]. Hydrogen can also be used to convert directly to electrical energy through the use of fuel cells. PEM fuel cells are an energy conversion device that electrochemically converts hydrogen and oxygen into electric-
ity, unlike batteries which are energy storage devices.

Storage of hydrogen is complex due to its low specific volume and the high permeability of materials typically used for pipelines and storage tanks. There are three main methods in which to store hydrogen: liquid storage, compressed storage and metal hydrides. Liquid storage is complicated by the fact that the boiling temperature is 20K under standard conditions. Transporting liquid hydrogen is feasible for large scale storage. The boil off of hydrogen is released to the atmosphere by pressure relief valves to prevent high pressures building up in the tank. Metal hydrides are another form of storage where hydrogen atoms are chemically bonded to a host metal lattice such as magnesium and has been explored by the automotive industry \[14,25\]. High pressure hydrogen is currently the method of choice for automobile manufacturers of fuel cell powered vehicles. For acceptable driving ranges the hydrogen requires compression to around 700 bar to provide high enough energy densities \[1\].

Hydrogen can be used both to store energy and used to supplement the energy grid through existing natural gas pipeline infrastructure \[1,2,10,26\]. Hydrogen produced by electrolysis for energy production applications is currently used where it is most cost effective which typically benefits from hydrogen produced near the point of use \[27,28\]. Using hydrogen to supplement hydrocarbons in gas pipelines can provide a pathway for transitioning from fossil fuels to renewable energy sources. As more hydrogen is produced from renewable energy sources it will help to make electrolyzer technology more economically viable as mentioned earlier. Hydrogen storage is a main concern in the H2FC Supergen project to develop the means to implement a hydrogen economy in the UK. This study uses hydrogen system modelling to investigate grid supplementation systems, expected hydrogen demand trajectory as hydrogen technology matures and the development hydrogen networks in the UK \[1,26\].
1.4 Hydrogen Production by PEM Electrolysis

Electrolyzers are devices which use electrical energy to split water into hydrogen and oxygen through the electrolysis reaction. Electrolyzers provide a promising potential for use in the energy sector as a way to produce and store energy from renewable sources as hydrogen. The types of electrolyzers are characterized by their electrolyte. The three main types of electrolyzer technologies are: Alkaline, Solid Oxide (ceramic) and PEM. Alkaline electrolysis is the most mature technology and oldest form of commercial electrolyzer on the market [2]. The implementation of solid oxide electrolyzers (SOEC) are limited due to very high operating temperatures, perhaps favouring a combined heat and power arrangement but is capable of achieving very high efficiencies. Currently there are no commercial hydrogen SOECs in a production electrolyzer, however carbon monoxide SOECs are currently available [2,15,29]. Significant efforts are being made to advance PEM electrolysis technology [1, 2, 5, 10, 11, 28]. General Electric Company was the first to develop solid polymer electrolyte (SPE) for water electrolysis in the 1960’s by using catalyst layers with iridium and platinum supported on carbon black [30]. PEM electrolyzers offer a variety of advantages over alkaline electrolysis including: higher energy efficiency, higher production rates and smaller, more compact system designs [5, 13]. PEM electrolyzers also have faster ion transport through a thin solid membrane and avoid the use of a caustic electrolyte used in many alkaline electrolyzers [2]. PEM electrolysis for large scale hydrogen energy production benefits over other electrolysis types because of the ability to operate intermittently, has a quick startup ability and fast load change capabilities [5,10,27]. While PEM electrolysis is well suited to pair with renewable energy, it is also highly scalable for smaller hydrogen production [1]. PEM electrolyzers typically operate at temperatures between 50-80°C making them attractive especially for standalone applications [5]. As seen in Figure 1.2, electrolysis can be implemented for both local and centralized production of hydrogen making PEM electrolysis an increasingly attractive technology.
PEM electrolyzers are largely based on technology borrowed from PEM fuel cells (PEMFC), which use hydrogen fuel and convert it into electricity in an exothermic reaction. As such, the electrolyzers require additional research to optimize the design. The highly corrosive environment caused by oxygen at the anode in particular requires special material considerations leading to the use of expensive materials [27]. The bulk of cost of electrolyzer stacks comes from the use of rare metals particularly in the MEA, porous electrodes and current collectors [2,13,24,31].

1.5 Motivation and Aim of Research

As mentioned previously, much of the current technology for PEM electrolyzers is borrowed from PEMFC technology. A PEMFC operates differently than a PEM electrolyzer however since gaseous reactants are supplied to the catalyst surfaces with excess gases and product water removed. Electrolyzers require a supply of liquid water as the reactant and the products exit the cell in the gaseous phase in a two-phase mixture with excess reactant water [28]. PEMFCs convert hydrogen and oxygen into water while releasing electrical energy. Although a PEMFC operates on the same electrochemical principles as a PEM electrolyzer run in reverse, research into optimization of performance is required for PEM electrolyzers. High cost of PEM electrolysis stacks limit the economic viability of PEM electrolyzers and consequently the ability of using hydrogen as an energy carrier.

The reaction kinetics of the OER on the anode side is much slower in comparison to the hydrogen evolution reaction (HER) and limits electrochemical performance of a PEM electrolyzer [2,5,31,32]. Better understanding of the formation and distribution of oxygen bubbles at the anode will aid in the development of the connecting interfaces in PEM electrolyzers. Designing this section for optimal electronic and mass transport is critical for developing more efficient and more economically viable PEM
electrolyzer systems.

This study is focused on the emergence and departure of oxygen bubbles at the anode of a PEM electrolyzer. In the cell this research focuses on the interface between the anode catalyst layer (ACL) and the porous transport layer (PTL). The research explores the relationship between two-phase flow on the anode side of an electrolyzer to study the influence on the electrical performance in respect to mass transport, ultimately to be used in material design to improve cell performance.

The objectives of this study are to (1) develop an optical visualization setup to observe bubbles in a PEM electrolyzer and (2) observe oxygen bubbles using the setup to examine two-phase flow in a PEM electrolyzer with respect to performance.

1.6 Thesis Overview

Chapter 2 introduces a brief background into the relevant electrochemical theory through thermodynamics, reaction kinetics and the Nernst Equation. A summary of visualization methods used to study two-phase flow in PEM electrolyzers and methods used to characterize performance in current literature is reviewed. This section also includes a discussion of PEMFC literature related to visualization.

In Chapter 3, the experimental setup and methodology is discussed. This includes the procedure for testing and operating conditions used for testing in both the tank and electrolyzer test station. The three visualization setups developed for this study are discussed here in detail. The image processing pathway for determining bubble statistics is described in this section.

Results from the bubble visualization setups are presented in Chapter 4. This includes the initial results from the tests conducted with the sample holder fully flooded in the
tank. These results were used to gain an understanding of the nature of two-phase flows from a catalyst coated membrane (CCM) and develop techniques to record and process bubble images. Results from the modified electrolyzer cell are presented in this section. This includes results from the channel-less modified electrolyzer cell to visualize bubbles coming directly from the surface of PTL samples. The second modification uses optically accessible flow channels with a modified PEM cell used in the electrolyzer test station where bubbles are visualized in-situ through an optical access point into two flow channels.

Conclusions from this study and recommendations for future work for visualization of oxygen bubbles using the optically accessible modified PEM electrolyzer cell setup is included in chapter 5.
Chapter 2

Background and Literature Review

The operation of PEM electrolyzers with an emphasis on the optical visualization of the mass transport within the cell, particularly at the anode is reviewed. Thermodynamic theory and a brief description of reaction kinetics is discussed in regard to PEM electrolysis, and a description of the operation of a PEM electrolyzer is provided. A discussion on steady-state polarization curves to characterize electrochemical performance is included. Previous works conducted in PEM electrolysis and relevant works coming from visualization in PEM fuel cells is included in this literature review.

2.1 Breakdown of Components in Polymer Electrolyte Membrane Electrolyzers

In a PEM electrolyzer, a solid perfluorosulfonic acidic membrane (PFSA) is used as the electrolyte, commonly Nafion® is used to separate two half cells. The charge carrier through the membrane is H⁺ ion. The full electrolysis reaction, HER half cell reaction and OER half cell reaction with cell potentials are shown in Equations 2.1, 2.2 and 2.3 below.

The full water electrolysis reaction is given by:

\[ H_2O(l) \rightarrow H_2(g) + 1/2O_2(g); \quad E=-1.229V \]  

(2.1)
Anode OER half reaction:

$$
H_2O_{(l)} \rightarrow 1/2O_{2(g)} + 2H^+ + 2e^- , \quad E=-1.229V \tag{2.2}
$$

Cathode HER half reaction:

$$
2H^+ + 2e^- \rightarrow H_2(g) , \quad E=0.00V \tag{2.3}
$$

A membrane electrode assembly (MEA) is manufactured by applying an anode catalyst layer commonly using iridium oxide, and a cathode layer commonly composed of platinum supported on carbon black. A PTL is placed against the anode catalyst layer to manage electrical conductivity and the diffusion of reactants and products to and from the catalyst surface. Carbon paper with a microporous layer (MPL) is usually used pressed in the cathode side to manage gaseous transport from the electrode surface. Flow field plates are used to supply reactant water and remove products from the cell through channels and from the electrode surfaces. Current distributors are placed on the outside of the flow field plates to supply current across the cell. An electrolyzer cell consists of the MEA, PTL, carbon paper/cloth and flow field plates sandwiched between the current collecting plates and compressed together.

In an electrolyzer cell water is supplied to the anode. Reactant water at the anode travels to the catalyst sites where oxygen evolves at the surface of the anode catalyst layer and the $H^+$ ion travels through the SPE to the cathode, as seen in Figure 2.1. At the cathode $H^+$ and electrons combine to form $H_2$ and is released from the catalyst surface. Product hydrogen and oxygen then travel through the PTL at the anode and carbon paper/cloth at the cathode respectively, before traveling into the flow fields so they can be collected and stored.

PEM electrolyzer performance is dependent on the complex interactions between the mass transfer, electrical charge transfer, heat and electrochemical properties of the
cell. Conditions for single cell testing in literature are generally seen at temperatures ranging from 20-100 °C, flow rates from 1-60 mLmin\(^{-1}\) and operating current densities with current cells ranging from approximately 0.1-4 Acm\(^{-2}\) [5, 28, 33].

### 2.2 Thermodynamics

Electrolyzers are electrochemical devices that transform electrical energy into chemical energy, and therefore are limited by the laws of thermodynamics. The decomposition of water to hydrogen and oxygen gas, driven by thermal and electrical energy can be explained by the first law of thermodynamics:

\[
\Delta H_R = Q + W_{el} = \Delta G_R + T \Delta S_R
\]  

In Equation 2.4 \(\Delta H_R\) is the enthalpy of the reaction, \(Q\) is the heat transfer from the cell, \(W_{el}\) is the electrical work in the system, \(\Delta G_R\) is the change in Gibb’s Free Energy and \(T \Delta S_R\) is the entropy term which represents the thermal energy required for the chemical reaction (i.e. the electrolysis of water). As with all reactions, not all the energy in an electrochemical reaction can used to do work by the system. The
minimum amount of electrical energy to drive the electrolysis reaction under standard conditions is given by Gibb’s free energy in Equation 2.5.

\[ \Delta G_R = -zFE^o \]  

(2.5)

The change in Gibb’s free energy for the electrochemical reaction is given by \( \Delta G_R \), \( z \) is the number of electrons involved in the reaction, \( F \) is Faraday’s constant (96 485 C mol\(^{-1}\)) and \( E^o \) is the standard potential [21]. Gibb’s free energy is therefore the thermodynamic equivalent amount of energy to split 1 mole of water to hydrogen and oxygen. From Equation 2.4, the decomposition of water with the temperature and electrical dependence of the total energy demand as a function of temperature is shown in Figure 2.2.

The total energy required to split liquid water will decrease until water reaches a gaseous state where the total energy demand increases but remains below the energy demand in the liquid state. In the gaseous phase more of the total energy demand to split water can be attained from thermal energy input with as the temperature of the system increases. The electrical energy to split water will therefore decrease with
increasing temperature since a lower proportion of the energy needs to be supplied from electrical input. A higher electrochemical efficiency can therefore be attained by running the electrolysis process at higher temperatures.

For \( \Delta G_R > 0 \) the reaction requires an external source of energy to proceed forward, as is necessary for the electrolysis of water. The minimum potential difference for the electrolysis reaction to proceed without losses present is referred to as the reversible cell voltage, \( V_{rev} \) [2]. From the definition of the cell potential for an electrolyzer cell the measured potential between anode and cathode is given by:

\[
E^\circ_{cell} = E^\circ_{reduction} - E^\circ_{oxidation}
\]

Under standard conditions using the lower heating value (LHV) the reversible cell potential for the anode OER reaction and cathode HER reaction is -1.229V and 0V, respectively. This gives a reversible cell potential, \( E^\circ_{rev} \) for the electrolysis of water as -1.229V using the LHV. In the absence of an external heat source all energy must come from electrical energy input, this is called the thermoneutral voltage, \( E^\circ_{th} \). The thermoneutral voltage based on the higher heating value (HHV) of water electrolysis is -1.481V [2, 28]. The equations for the reversible and thermoneutral cell potentials are shown in Equations 2.7 and 2.8.

\[
E^\circ_{rev} = \frac{\Delta G^\circ_R}{zF}
\]

\[
E^\circ_{th} = \frac{\Delta H^\circ_R}{zF}
\]

The Nernst Equation is derived from Gibb’s free energy for an electrochemical reaction, it defines the reversible electrochemical cell potential at non-standard conditions by relating the measured cell potential to the reaction quotient of concentrations of chemicals involved in the reaction [2, 34]. The equation relates the reduction potential to the standard electrode potential and can be used with both full and half cell
reactions. The Nernst equation for the electrolysis of water is given by:

\[ E = E^o - \frac{RT}{2F} \ln \frac{a_{H_2}a_{O_2}^{1/2}}{a_{H_2O}} \]  

(2.9)

E is the cell potential, \( E^o \) is the standard state reversible cell potential, R is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), F is Faraday’s constant (96 485 C mol\(^{-1}\)) and T is the cell temperature. The activity for the reduction and oxidation reactions are raised to the corresponding stoichiometric coefficient. The thermodynamics of a system only provides information on the theoretical limits of the reaction. In an actual electrolyzer cell irreversible losses require the applied potential to be above the reversible cell potential for the reaction [2,34].

### 2.3 Reaction Kinetics

Electrochemical reactions involve a transfer of electrons between the electrode surface and chemical species adjacent to that electrode surface and result in a cell potential due to energy from this chemical reaction [34]. Energy drives all changes in chemical reactions. In a redox reaction electrons are transferred due to the movement of charged particles and results in a potential difference. During this reaction the number of electrons transferred when a reaction is complete can be related to the definite amounts of reactants consumed and products formed from Faraday’s Law [34]. In PEM electrolysis H\(^+\) ions are the charge carrier traveling through the SPE and the electrons flow through the external circuit. Electrochemical reactions occur at interfaces, the current corresponding to the potential difference between electrodes therefore determines the amount of substances involved in the reaction.

The Nernst equation gives the maximum potential difference from the energy released in a reaction. Because electrochemical reactions occur at interfaces, the current produced is directly proportional to the interface area, and therefore allows the activity of different surfaces to be compared per unit area, typically expressed as A cm\(^{-2}\) [34].
All reaction rates are finite due to an activation energy barrier that impedes the conversion of reactants to products. This activation energy determines the reaction rate with the overall reaction being limited by the slowest step in a reaction. The probability of finding a species in the activated state depends exponentially on the size of the activation energy of reaction, $E^*$:

$$P_{\text{act}} = e^{-\frac{E^*}{RT}} \quad (2.10)$$

where $P_{\text{act}}$ is the probability of finding a species in the activated state, $R$ is the universal gas constant and $T$ is the temperature in K [2, 34]. Chemical species must reach this activated state to go from reactants to products. The activation barrier is manipulated by changing the potential through the cell.

Irreversible losses require that a higher potential be applied though the cell than the reversible cell potential calculated by thermodynamics. There are three distinct kinetic loss regions: activation, ohmic and mass transport. The mass transport loss consists of the diffusion and bubble losses. The cell voltage of an operating cell is always higher than the thermoneutral voltage due to these irreversible loses seen in Equation 2.11 [2].

$$V_{\text{cell}} = V_{\text{rev}} + \eta_{\text{act}} + \eta_{\text{ohm}} + (\eta_{\text{diff}} + \eta_{\text{bubb}}) \quad (2.11)$$

Activation losses are a Faradic loss that are kinetically controlled by the ability of the catalyst to proceed the reaction forward. The activation loss can be broken down based on the catalyst interface into the anodic activation overpotential, $\eta_{\text{act, an}}$ and the cathodic activation overpotential, $\eta_{\text{act, cath}}$. This is the first electrochemical barrier which occurs at low voltages. The ohmic region occurs at intermediate voltages and is controlled by the ohmic resistance of the SPE (often Nafion®) to pass H$^+$ and the flow of electrons through the cell components [2]. This loss is governed by Ohm’s law. The mass transport region occurs at higher potentials and is controlled by the trans-
port of reactants and products to and from the catalyst surfaces [2, 34]. If the rate of transport of products away from the catalyst interface is insufficient then there is a resistance that impedes the reaction proceeding forward [2, 28]. The mass transport losses can be broken down into diffusion losses, $\eta_{\text{diff}}$, and bubble overpotential losses, $\eta_{\text{bubb}}$. Diffusion losses result from gaseous oxygen blocking pore networks in porous electrodes, restricting reactant water from reaching the catalyst sites. This causes a concentration resistance that impedes the reaction proceeding forward. Bubble overpotential losses arise from the gas phase shielding the active area and reducing the catalyst utilization [2]. An example of the contribution of losses to the cell potential for a PEM electrolyzer is shown in Figure 2.3. The cell voltage during electrolysis is the combination of the reversible cell potential and the sum of irreversible losses within the cell. Mass transport losses only occur at high current densities when many reactants are evolved into gaseous products.

![Figure 2.3: Performance curve example for a PEM electrolyser showing loss regions [3].](image)

The slow reaction kinetics and high cost of iridium catalyst require research into new materials to make PEM electrolyzers more economically viable while being able
to withstand the highly corrosive environment on the anode side. Currently unsupported iridium oxide catalysts are used with current research focusing on supporting iridium oxide catalysts on a metal oxide to improve catalyst utilization to reduce costs [3, 5, 24]. Iridium has an additional constraint associated with being the rarest element on earth. Additional research is ongoing for sources of lower cost electrolysis catalysts. Ruthenium oxide is a viable alternative for the OER but suffers from instability and needs to be supported by another oxide, such as IrO$_2$ [35].

Ionic resistance from the membrane and the OER activation overpotential dominate efficiency losses [3]. Concentration losses are not generally seen in electrolyzers because of fully flooded conditions, even at high current densities [2]. Diffusion dominates the mass transport losses at low current densities where at higher current densities bubble overpotential arise. The transport of gaseous oxygen and hydrogen in PEM electrolysis greatly affects the performance of PEM electrolyzers. As the rate bubbles leave the surface of the catalyst increases it allows the active area on the membrane to become available to reactant water more quickly. This increases the amount of water that can be split through electrolysis and improves overall cell performance. The membrane therefore must have a high proton conductivity while allowing little gaseous species to pass through.

### 2.3.1 Measuring Performance using a Polarization Curve

A polarization curve is a common technique for measuring the performance of an electrochemical system. The voltage applied through the cell is plotted against the current or commonly the current density, $i$ [Acm$^{-2}$] over the active area of a PEM electrolyzer. A sample polarization curve showing the three regions at low, intermediate and high current density regions is shown in Figure 2.4. The current density relates to the amount of hydrogen produced and the voltage is the energy being applied to the cell [2, 5]. Polarization curves are a measure of the efficiency of an electrolyzer by comparing the overpotentials in the system, with more efficient systems having
lower potential differences at equivalent current density. Potentiostatic polarization curves under steady-state conditions are a common method of characterizing cell performance [2, 34]. The current passing through the cell is measured while the applied potential is held constant.

![Polarization Curve Diagram](image)

**Figure 2.4:** Typical polarization curve showing the kinetic, ohmic and mass transport controlled regions.

### 2.3.2 Butler Volmer Equation and Tafel Slope

Using information from the polarization curve, the Tafel slope and Butler Volmer reaction kinetics can give additional information about the overall cell performance. When both the anode and cathode are considered then the Butler-Volmer equation is used with the probability function in equation 2.10 to determine the [34]. Dynamic equilibrium occurs in the cell when the electrochemical reaction is taking place but the forward and reverse reaction rates are equivalent, this point is called the exchange current density, $I_o$ [34].

\[
i = i_o \left[ e^{\alpha nF\eta/RT} - e^{(1-\alpha)nF\eta/RT} \right] \tag{2.12}
\]
I is the net current through the cell, \( \alpha \) is the transfer coefficient, and \( \eta \) is the activation overvoltage. The Tafel equation is a simplification of Butler Volmer in when either \( \Delta \eta_{\text{act}} \) is either very small or large, 2.14 and 2.13, respectively.

\[
I = I_o(-e^{(1-\alpha)nF\eta/RT}) \rightarrow \ln(-I) = \ln I_o - \eta \frac{\alpha nF}{RT} \tag{2.13}
\]

\[
I = I_o[e^{\alpha nF\eta/RT} \rightarrow \ln I = \ln I_o + \eta \frac{\alpha nF}{RT} \tag{2.14}
\]

At high negative overpotentials, the cathodic current is significantly higher than the anodic current, making this term negligible in equation 2.13 [2]. Usually measurements in the high overpotential region with \( \Delta \eta_{\text{act}} \) large equation 2.14 are used in electrolyzers at high overpotentials where the anodic current is significantly higher than the cathodic current. Since the Tafel equation is in the form:

\[
\eta_{\text{act}} = a + b \ln I \tag{2.15}
\]

it is convenient to use a plot of the overvoltage vs. \( \log \eta \) in the linear region during activation controlled operating conditions at high overvoltages. The exchange current density, \( I_o \) can be determined from the intercept with the y-axis at \( \eta=0 \) where \( b \) is the Tafel Slope. The Tafel slope is often used as a metric to assess catalytic activity at the anode based on the Butler-Volmer equation. The slope of the Tafel slope gives information on the rate determining step.

### 2.4 Literature Review

#### 2.4.1 Bubble Visualization in Polymer Electrolyte Membrane Electrolyzers

Various techniques have been used to study two-phase flow in both PEM electrolyzer and fuel cells. These methods include optical visualization, neutron radiography and
thermal imaging. Electrochemical impedance spectroscopy (EIS) is also a popular method to characterize the performance of a cell in addition to steady-state polarization measurements and cyclic voltammetry performance measurements. Technology borrowed from PEM fuel cells have been adopted for use in PEM electrolyzers, however much of the technology has not yet been adapted directly for electrolyzer cells including the catalyst layer optimization for oxygen removal to obtain higher current densities [2,24].

Two-phase flow in electrolyzers has been observed when gas bubbles produced in the electrolysis reaction detached from the electrode. The flow patterns or flow regimes in a vertical tube or channel may be broken into four regimes: bubbly, slug, churn and annular flow. Figure 2.5 shows a diagram of these flow regimes as bubbles increase in size. In bubbly flows the gas phase exists as discrete bubbles within the liquid. Slug flow occurs when bubble concentration becomes higher and larger bubbles coalesce to diameters the same as the diameter of the channel. These slugs are separated by regions of bubbly flow. Churn flow occurs when the flow becomes disordered and the slugs within the flow become more irregular and narrower. In annular flow the gas flows along the center of the channel and liquid flows as a film along the walls of the channel and as droplets within the channel [36].

The use of transparent cells to study two-phase flow has been explored in multiple studies by the University College London. A study conducted by Dedigama et al. using high speed camera, thermal imaging and EIS with a transparent PEM electrolyser cell looked at the effect of cell temperature and type of two-phase flow on cell performance. The study examined two-phase flow in a single flow channel on the anode side of a cell with transparent end plates. They observed a transition from bubbly to slug flow with increasing current density and tend to be bubbly with higher feedwater flow rates. This research suggests that the transition from bubbly to slug flow actually increases mass transport associated with higher operating current den-
In a study conducted by Ito et al. on the effect of water circulation on PEM electrolyzer performance however found that at low flow rates the performance of the cell decreased. This was a result of the transition to annular or slug flow at lower flow rates [38].

In another study conducted by Dedigama et al. the evolution of gaseous oxygen bubbles at the anode is studied by looking at the effect of the bubbles on the local current density distribution in an optically accessible cell. The cell used a printed circuit board as a segmented current distributor. It was found that in the higher sections of the flow channel there is an increase in the local current density associated with the transition from bubbly flow towards slug flow. This transition tends to fill the channels, causing smaller bubbles to sweep off the surface of the electrode, suggesting there is a increase in the rate of mass transfer and lowering the bubble overpotential [39]. A separate study conducted by the University College London studied flow velocity in flow channels of an optically visible PEM electrolysis cell. Bubbles are characterized from bubbly to slug flow depending on the proximity of bubbles to one another and the liquid phase surrounding it seen in figure 2.5. The study considers the effect of flow rates and temperature on two different flow channel
designs while studying the velocity in the channels of the cell. The study observed that the size of the bubbles was smaller at higher flow water temperatures at the operating current density. At higher water flow rates the transition from bubbly to slug flow was delayed, causing smaller bubbles and fewer slugs [33].

Synchrotron X-ray radiography was used to study gas bubble from the PTL into flow channel analyzed using frequency and gas volumes. It was suggested that selective transport pathways through the PTL occurred with more pathways becoming available at higher current densities [40]. Optical and neutron imaging has been used to study two-phase flow in a PEM electrolyser by Selamet et al. and found that the proximity to the inlet and outlet of water flow as well as gravity and buoyancy forces caused non-uniformities in the water distribution across the cell [41]. The two-phase flow distribution was considered by splitting the image into equal segments and the evolution of individual oxygen bubbles were studied [41]. In an extension of this study conducted by Selamet using a similar experimental setup, higher temperature water is found to produce a higher volume of gaseous oxygen in the anode [42]. Li et al. has studied the evolution of oxygen bubbles from the surface of the MEA using an optically transparent cell with a thin film PTL with uniform circular pores. They found that the growth of oxygen bubbles occurred at the rim of PTL pores and increase in size more rapidly with increasing current density and temperature [43].

A study was conducted by Panchenko et al. using neutron spectroscopy to study the two-phase flow in a PEM electrolyzer cell under water starvation [44]. They found that under the mass transport limitation the gas produced at higher current densities is not properly discharged, hindering the supply of water to the MEA.

Previous work was conducted by Tanaka et al. on hydrogen bubbles at the cathode of a PEM electrolyzer using acrylic plates. They found that the water flow rate changed the bubble radius on the cathode where at increasing flow rates the bubbles
are released from the surface having smaller radius due to the upward force being added to the buoyancy force. It was also shown that at higher current densities the generation of large bubbles increases and the ratio of dissolved hydrogen to total hydrogen decreases [45]. Later work using X-ray contrast imaging and high speed imaging also showed that hydrogen dissolved is directly proportional to the bubble size for a two sided platinum coated SPE [46]. When hydrogen bubbles did not coalescence at lower current densities, bubbles readily dissolved in the water, increasing the inner pressure [46].

Three dimensional modeling of two-phase flow conducted by Nie et al. in the flow field plate found that oxygen distributions vary diagonally across the cell from inlet to outlet. There is a strong non-uniformity in the velocity distribution with higher velocities near the inlet and outlet and the volume fraction of oxygen is not uniform with higher fractions in the center of the flow fields where velocity is lower. It is suggested that higher oxygen volume fractions in certain flow channels can contribute to a reversal in the flow direction as more water is reacted in the center of the cell given a higher residence time [47].

2.4.2 Flow Visualization in Fuel Cells

Much of the technology from PEM electrolysis has been based on PEM fuel cells. Although the operation of PEMFC and PEM electrolyzers are different, relevant work related to two-phase flow in PEMFCs can be beneficial for PEM electrolyzer applications. Similar to electrolyzers, two-phase flow is important for PEMFCs since the product water blocks reactant gases from reaching the catalyst surface impeding the reaction. A study conducted by Liu et al. used a PEMFC with a transparent optical window to view flow at both the anode and cathode while flooded with water to observe two-phase flow in the parallel channels. They found that water drops coalescence in the channels of the cathode formed water channels where oxygen is supplied to the cell. An increase in cell temperature was observed to removes water vapor
from the flow channel and water columns in the channels disappeared. As oxygen flow rates increased the degree of flooding was reduced as excess water was removed and flow transitioned from slug flow to annular flow with an extended phase boundary [48].

Previous work has look at frequency and gas volumes of oxygen bubbles in the flow channel using x-ray radiography [40] however little research has been conducted looking at the origin of the oxygen bubble at the anode and its interaction with the PTL. The transport phenomenon is largely different, especially concerning water and gaseous fluid movement in the devices.

2.4.3 Porous Transport Layer

The PTL serves as an interface between the catalyst layer and flow field. Effective PTLs must provide the following in the cell: they must be (1) highly corrosion resistant due to high oxygen concentrations, (2) provide efficient electronic conductivity, (3) must provide mechanical support in the cell and (4) provide mass transport to effectively move gases away from the catalyst and reactant water to the catalyst surface. There is a balance between electrical conductivity and mass transport, an increase in pore size promotes oxygen bubble transport but reduces electrical conductivity [5]. Porosity is key in the transfer of reactants and products through the PTL since optimization is necessary to have large enough porosity to move gases but will negatively impact electrical conductivity. Conversely very small porosities will limit gas movement through the PTL. The same carbon PTL materials used in PEM fuel cells cannot be used on the anode since the carbon will be oxidized into CO$_2$ through the following reaction:

$$\text{C(s)} + (\text{O}_2(g)) \rightarrow \text{CO}_2(g)$$

The PTL is an expensive component of PEM electrolyzer cells that requires further research to determine what will provide optimal operating conditions and consider
material selections that can be employed to reduce costs. Problems related to the harsh environment are similar for both the PTL and flow field plate for the anode are similar [28]. It is estimated that approximately 48% of electrolyser stack cost comes from the porous PTL materials and separator plates [3]. Bubble flows in the GDL has been conducted by Arbabi et al. for PEM electrolyzers using microfluidic platforms in two dimensional representations of the GDL to felt, sintered and foam PTL materials used for the anode and analyzed using Fiji, looking at volumetric pore space. This study showed that the movement of air bubbles in multiphase flow is capillary dominated throughout the range of air flow rates [49].
Chapter 3

Experimental Design and Method

Three optically accessible testing setups were developed to observe oxygen bubbles at the anode during PEM electrolysis to study their effect on the performance. The study focused on following the evolution of oxygen bubbles from the catalyst layer, through the PTL and in the flow field plate. This was investigated by testing different PTL samples and measuring bubble characteristics through optical visualization while monitoring overall cell performance. Image processing pathways were developed to identify individual bubbles in images captured in each testing setup.

The approach of the study in the PEM electrolysis sample holder involved observing oxygen bubbles through a viewing port cutout in the cell. The electrolysis sample holder was flooded in a tank to ensure two-phase flow occurred and to visualize a larger area than previous literature that had focused on a single flow channel [37]. In this experimental setup bubbles were allowed to vent directly from the viewing port to the atmosphere without going through flow channels where bubbles tend to coalesce [33, 37]. Bubble images were first captured by applying a current through the direct contact from the current distributing plates to the anode catalyst layer to observe bubbles coming off the catalyst surface. Porous titanium PTL samples on the anode was added to observe bubbles coming through the pores of titanium PTL samples. The addition of PTL was intended to follow the evolution of oxygen bubbles to determine if bubbles coalesced while passing through the PTL and to observe how
this is affected by different PTL samples.

Bubbles were then observed in the flow channels of a modified electrolyzer cell with optical access into the flow field plate. An experimental setup to gain optical access through the anode end plate was developed to study bubbles in the two middle flow channels. This experimental setup more realistically replicates the working environment of an electrolyzer cell in which a closed cell has water being pumped through as opposed to sitting in a stagnant flooded environment.

### 3.1 PEM Electrolyzer Cell Materials and Setup

A PEM electrolysis cell was used to condition MEA samples and a separate cell was modified to allow optical access to the anode side to study the movement of oxygen bubbles. Figure 3.1 shows the components within the PEM electrolyzer cell and the unmodified PEM electrolyzer cell used during testing.

![Exploded view of PEM electrolyzer cell.](image1.png)

![Assembled PEM electrolyzer test cell.](image2.png)

(a) Exploded view of PEM electrolyzer cell.  
(b) Assembled PEM electrolyzer test cell.

Figure 3.1: PEM electrolyzer cell used in the electrolyzer test station.

The material breakdown for the unmodified PEM electrolyzer shown in Figure 3.1 is listed in Table 3.1. A description of parts manufactured for optical visualization
within a custom PEM electrolyzer cell is discussed below.

Table 3.1: Materials used in electrolyzer test station cell.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Quantity</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>end plates</td>
<td>2</td>
<td>Machined from a block of aluminum with holes to supply water into the side or the end plates and holes for bolts to compress the cell</td>
</tr>
<tr>
<td>Swagelok quick connectors</td>
<td>4</td>
<td>Connected to the cell and tubing for water delivery pump and product gas removal from cell</td>
</tr>
<tr>
<td>PTFE tubing</td>
<td>8</td>
<td>5mm inner diameter, used to move products and reactants from the cell and within the cell between end plates and flow field plates</td>
</tr>
<tr>
<td>stainless steel bevel washers</td>
<td>16</td>
<td>4.0mm inner diameter</td>
</tr>
<tr>
<td>stainless steel flat washers</td>
<td>8</td>
<td>4.0mm inner diameter</td>
</tr>
<tr>
<td>stainless steel bolts</td>
<td>8</td>
<td>1/4” threaded, 3” length</td>
</tr>
<tr>
<td>graphite composite flow field plate</td>
<td>1</td>
<td>CNC milling machined channels used on the cathode side of the electrolyzer</td>
</tr>
<tr>
<td>gold-coated titanium flow field plate</td>
<td>1</td>
<td>Milled channels cut and gold coated for use on the anode side of the electrolyzer</td>
</tr>
<tr>
<td>current collecting plates</td>
<td>2</td>
<td>Gold coated copper plates to attach cell to power supply</td>
</tr>
<tr>
<td>PTFE rod</td>
<td>2</td>
<td>1/8” diameter, used to align the two flow field plates with gaskets and MEA and cut to 8mm segments</td>
</tr>
<tr>
<td>80mm x 80mm silicone gaskets</td>
<td>2</td>
<td>0.635mm thick, placed between flow field plates and MEA</td>
</tr>
<tr>
<td>105mm x 105mm silicone gaskets</td>
<td>2</td>
<td>0.635mm thick, placed on end plates to provide electrical insulation</td>
</tr>
</tbody>
</table>

The custom built sample holder was designed with similar dimensions to the PEM electrolyzer holder so MEAs and samples could be easily transferred between them. The materials used in the custom Delrin® PEM electrolysis sample holder are summarized in Table 3.2.

HYDRion® N115 MEA samples from IonPower® were used during all tests. The SPE of the MEA is made of 80mm by 80mm Nafion 115 membranes with a thickness of 116.84-137.16 µm. A a 25mm by 25mm active area is one either side of the SPE [50]. Nafion 115 is commonly used in literature while examining cell performance as it provides a good balance between durability and performance [51,52]. The MEAs supplied by IonPower have a cathode loading of 0.3 mg cm$^{-2}$ Pt and anode loading of 1.0 mg cm$^{-2}$ IrO$_2$ accurate to ±0.05 mg cm$^{-2}$ catalyst.
Table 3.2: Materials for Delrin electrolyzer sample holder.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Quantity</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delrin End Plate for anode</td>
<td>2</td>
<td>Machined from 1/2” Delrin with holes for bolts and a square cutout</td>
</tr>
<tr>
<td>Delrin End Plate for anode</td>
<td>2</td>
<td>Machined from 1/2” Delrin with holes for bolts and 2.5mm holes for hydrogen gas to vent</td>
</tr>
<tr>
<td>PTFE tubing</td>
<td>2</td>
<td>5mm inner diameter, used to move product hydrogen between end plates and flow field plates</td>
</tr>
<tr>
<td>M8 stainless steel hex bolt</td>
<td>8</td>
<td>18-8 stainless steel, 1.25mm thread, partially threaded</td>
</tr>
<tr>
<td>stainless steel hex nut</td>
<td>8</td>
<td>18-8 stainless steel, M8 bolt</td>
</tr>
<tr>
<td>stainless steel flat washer</td>
<td>24</td>
<td>8.4mm inner diameter</td>
</tr>
<tr>
<td>graphite composite flow field plate for cathode</td>
<td>1</td>
<td>CNC milling machined channels used on the cathode side of the electrolyzer</td>
</tr>
<tr>
<td>titanium current collecting plate</td>
<td>1</td>
<td>Manufactured from grade 2 titanium</td>
</tr>
<tr>
<td>titanium current collecting plate with square cutout</td>
<td>1</td>
<td>plate, used on the anode side with cutout for optical access</td>
</tr>
<tr>
<td>teflon gasket</td>
<td>1</td>
<td>0.036mm thick, placed between flow field plates and MEA on the anode side</td>
</tr>
<tr>
<td>silicone gasket</td>
<td>1</td>
<td>0.635mm thick, placed between flow field plates and MEA on the cathode side</td>
</tr>
</tbody>
</table>

A 0.5mm carbon paper with a MPL (Sigracet® 10BC) was used in all electrolysisis cells on the cathode side of the MEA, as is common in the literature [2,32]. The microporous layer provides a transition region between large porosity in the PTL (10-30 µm) and fine pores of the catalyst layer (10-30nm) [34]. The MPL reduces contact resistance between cathode catalyst layer and limit the loss of catalyst from the cathode of the MEA [2]. It also can improve the wicking of moisture from the surface of the CCL if water is only circulated on the anode side and decrease electrical contact resistance. The microporous layer on the surface of the carbon PTL on the cathode is made of submicron graphite particles with a PTFE binder. The cell was compressed to 400 psi in the Enerpac. This compression was chosen based previous laboratory knowledge and literature from Siracusano et al. that did not notice significant improvements in electrochemical performance of compressions above 25 kgcm⁻² (356 psi) [52,53].
A titanium plate was machined to produce flow field channels into the plate with holes drilled to allow reactant water and product oxygen to transport through the channels. The titanium plate was etched with a 33% nitric acid and 1.5% wt hydrofluoric acid at 35-40°C for 4 minutes prior to vacuum coating at 400-500°C for one hour. A graphite composite flow field plate was designed for the cathode with the same parallel flow field design as the anode side without the addition of a manifold [53]. The dimensions of the flow field plate design are shown in Figure 3.2. The design of the custom flow field plates with optical access manufactured for use in the electrolyzer test station is discussed below.

![Figure 3.2: Parallel channel flow field plate design.](image-url)

### 3.1.1 Porous Transport Layer Test Samples

Four different PTL samples were used during this study. Two samples were used in the tank with the Delrin sample holder, a 0.5mm Bekeart two sided platinum coated sintered titanium PTL and a 0.5mm expanded titanium mesh with no coating on either side. Two different PTL samples were used for the modified PEM electrolyzer test cell. A 0.2mm titanium fibre and 0.3mm titanium powder PTL provided by
Hydrogenics® were used for this testing arrangement. Figure 3.3 shows the surface structure of the PTL samples.

![PTL samples](image)

(a) Bekeart sintered Ti  
(b) Bekeart expanded Ti  
(c) Hydrogenics Ti fibre  
(d) Hydrogenics Ti powder

Figure 3.3: PTL samples used for tests in the tank and electrolyzer test station.

All PTL samples were cut to 25mm by 25mm to cover the entire catalyst active area on the anode of the MEA. Edges and corners of the PTL samples were treated with a smooth half round file to prevent puncturing the MEA during assembly.

### 3.2 Designing a Cell with Optical Access

Two separate experimental testing setups were used during this study that required different cells for optical access. In the first experimental setup the electrolysis sample holder is submerged in a water filled tank. A cutout in a custom Delrin® end plate provided direct optical access to the surface of the anode side of the MEA/PTL. In
the second experimental setup an existing electrolyzer test station was used with a specially designed electrolyzer test cell with a closed window that allowed water to be pumped through a sealed cell.

### 3.2.1 Sample Holder with Optical Cutout

The cell for testing in the tank was developed using 1/2” Delrin acetal resin (polyoxymethylene) for the end plates [54]. This material was chosen based on its high tensile strength of 9000 PSI and ease of manufacturability. Delrin is a polymer and therefore does not leach ions into the water in the tank while the cell is operating which aided in maintaining water purity. The end plates for the cell were cut to 108mm by 108mm with a waterjet cutter and had holes drilled for 8 M8 stainless steel bolts. The plate for the anode side had a 17mm by 17mm hole cut in the middle of the plate to allow for optical access to the PTL as seen in Figure 3.4.

The sample holder initially accumulated a buildup of bubbles at the top of the viewing port on the anode side. The water level in the tank was lowered to allow for bubbles to vent to the atmosphere however the lower water level refracted light from the free surface making recorded images unusable. To counteract this issue a venting port was added to the anode side so bubbles could more easily vent to the atmosphere. The venting port has a 17mm initial width, the same as the viewing port and then tapers to an 8mm slot, see Figure 3.4. This design was chosen to allow gases to easily vent as buoyancy forces move bubbles upwards from the surface of the catalyst layer. The taper was added to keep material around the top two bolt holes to prevent cracking and to keep the most uniform compression possible within the cell.
Figure 3.4: Electrolysis sample holder showing venting channel on the inside of the anode side end plate.
Titanium current distributors were developed to provide optical access on the anode while also providing electrical contacts for current to pass through in the cell. Although typically gold plated for improved electrical contact and durability, titanium current distributors have been successfully implemented in electrolyser cells [41]. Titanium has shown to be one of the best methods for flow field plate designs given it’s resistance to highly acidic environments, high strength durability, high thermal conductivity and low permeability. A passivation layer however will form over time that increases the contact resistance, increasing the ohmic loss [5, 55]. A titanium plate with a 17mm by 17mm cutout acted as the anode current distributor and used in place of a flow field plate where the surface was in direct contact with the PTL, shown in Figure 3.5.

![Figure 3.5: Anode current distributor design.](image)

### 3.2.2 Modified Polymer Electrolyte Membrane Test Cell

A 25.4mm thick aluminum end plate for the test station was modified by cutting a 30mm by 30mm hole in the middle of the cell to provide optical access to the cell.
The size of this hole would allow a large enough region for viewing bubbles in the cell and to allow sufficient light to enter the cell. A 20mm by 20mm hole was cut in the middle of a gold plated current distributor used with the optically accessible channels modification. This size was chosen to allow sufficient access to the cell while being as small as possible to aid in uniform compression in the cell. Figure 3.6 shows the modified cell with viewing window to look at the two-phase flow on in the two center flow channels.

![Modified PEM electrolyzer cell with optical access to flow channels.](image)

Two separate designs were used to view the inside of the cell: the first with a 17mm by 17mm channel-less cutout to visualize bubbles coming directly off the PTL and the other using a custom built flow field with an acrylic window for optical access.

The cell with the channel-less square cutout was manufactured from a grade 2 titanium plate to function as both the flow flow channel plate and current distributor. The plate was designed with flow channels to supply water from the bottom of the cell and remove water from the top of the cell, however unlike a conventional flow
field plate it did not have flow channels as seen in Figure 3.7. A 17mm by 17mm cutout through the plate allowed bubbles to pass directly from the PTL to a small cavity 0.195" thick. A 1/8” acrylic plate with a 0.010” silicone elastomer (HT6135) gasket was placed on the outside of the plate to prevent the cell from leaking.

Figure 3.7: Titanium plate with channel-less square cutout for visualization directly from PTL surface.

The modified flow field was designed with the same dimensions as the composite graphite flow field plate used on the cathode with the exception of a cutout that allowed an acrylic window to be placed inside the back of the plate for optical access as seen in Figure 3.9. The flow channels were cut using a CNC milling machine and holes drilled for water inlet and outlet. The viewing window was machined from the back side and electrical discharge manufacturing was used to cut the rib on the inside of the plate so as to maintain consistent contact with the PTL surface. An acrylic window was custom made to fit in the hole with the one side at the depth of the 2mm
flow channels and the other flush with the back of the plate. Holes were drilled and tapped for # 2-56 bolts and custom cut to be flush with the surface of the window. Machine marks were removed from the viewing window with an abrasive crystalline silica scratch removing solution. A polishing solution was then applied to remove all crystalline silica particles to clean the surface. A square cutout in an end plate and current distributor was made to gain optical access to the viewing window on the titanium flow field plate.

Figure 3.8: Modified cell with optical access to flow channels.

3.3 Measurement Systems

3.3.1 Power Supply and Data Acquisition Unit

Steady state polarization measurements were used to monitor the performance of the cell. A Xantrex XHR 7.5-130 DC power supply was used to potentiostatically control the power supplied to the cell. The power supply had an operating range between 0-7.5V and 0-130A giving sufficient resolution for PEM electrolysis operating range. The power supply was connected to the cells using 000 AWG wire to minimize ohmic
losses. Measurements were held at a constant voltage for 4 minutes to allow the cell operation to reach steady state at voltages between 1.3 and 2.4V and held for 6 minutes at 2.6V since there is a higher variation in the current density past this point.

An Agilent 34970A data acquisition/switch system (DAQ) is connected to the cell to record all measured values. The polarization measurements were recorded using an Agilent 50mV/100A DAQ with a shunt resistor connected to the power supply so both current and voltage measurements could be recorded. A Fluke model 8840A multimeter was used to verify voltage and current measurements from the DAQ as per the manufacturer’s calibration procedure. Three temperature probes were connected to the DAQ, two to monitor the water temperature and the other to monitor the temperature of the room temperature during the experiments.

3.3.2 Optical Visualization Apparatus

An IDT Vision Motionscope M5 camera was used for image capture at 170 frames per second. The camera was supported by a metal frame to provide a consistent base for imaging and was focused on a fixed area that contained the viewing port. Table
3.3 summarizes the specifications of the camera used in this study. The camera communicates with the computer via a Full Camera-Link connection with 10 taps (8 bit each) to a Dalsa board. The camera was capable of operating up to 170fps and has a maximum resolution of 2320x1728 at this frame rate [56].

<table>
<thead>
<tr>
<th>IDT Vision MotionScope M5</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Max fps @ max resolution</strong></td>
<td>170 fps @ 2320x1728</td>
</tr>
<tr>
<td><strong>Minimum exposure time</strong></td>
<td>1 µs</td>
</tr>
<tr>
<td><strong>Sensitivity ISO (color)</strong></td>
<td>1000</td>
</tr>
<tr>
<td><strong>Sensor Type</strong></td>
<td>CMOS-Orion II</td>
</tr>
<tr>
<td><strong>Sensor Size</strong></td>
<td>16.4 x 12.1 mm</td>
</tr>
<tr>
<td><strong>Array Size</strong></td>
<td>4 Megapixels</td>
</tr>
<tr>
<td><strong>Pixel Size</strong></td>
<td>7 x 7 µm</td>
</tr>
</tbody>
</table>

A Leica Z16 APO 16:1 macroscopic lens with the IDT Vision M5 camera was used for capturing images during testing with the sample holder in the tank. The lens has a fully apochromatic zoom from 0.57-9.2x and a built-in iris diaphragm for adjustable depth of field [57]. A single beam path for parallax-free imaging. A 39mm 2.0x planapochromat objective lens is used with the camera along with a Leica 0.5x C-mount adapter to connect the lens to the camera. The Leica lens was found to have too high a magnification for testing in the modified electrolyzer setup. A Tokina AT-X Pro D 100mm F2.8 macro lens was used for this setup and attached to the camera using a Nikon F-mount adapter. The 100mm focal length provided enough distance from the electrolyzer cell for light to enter the viewing port while the viewing area was in focus. The setup used to capture bubble images is shown in Figure 3.10.

Three lighting options were considered for this study: halogen, light emitting diodes
Figure 3.10: Visualization setup with the Tokina AT-X Pro D lens.

(LEDS) and compact fluorescent lights (CFL). Halogen lighting was found to be bulky and the high heat output caused localized heating that interfered with temperature control for the cell. Light emitting diodes were also considered in the test setup through an arrangement of four 500 lumen bulbs were able to effectively illuminate the viewing area. During analysis of recorded images, flickering produced from the LEDs introduced problems when analyzing the images that proved these lights to be ineffective. Two 42W CFL coupled with a programmed start electronic ballast were chosen to illuminate the viewing region. The CFL lighting was chosen because it was able to output 3200 lumens per bulb to sufficiently illuminate the viewing region with far less heat flux from that generated from the halogen lighting. Coupled with a programmed smart electronic ballast the CFL lighting did not flicker in the recorded images.
3.4 Experimental Setup

Two experimental setups are used in this study: the first with the Delrin® sample holder and the second with a modified test cell in an electrolyzer test station. A description of the two experimental setups is described in the following section.

3.4.1 Sample Holder in Tank

An experimental setup was designed to study two-phase flow in a custom sample holder electrolysis cell with a cutout for viewing bubbles coming directly off the PTL. A 30.2L glass tank surrounded by 3.8cm polystyrene foam insulation was used to provide a fully flooded environment for the sample holder. This experimental test station consists of the measurement system described above and a temperature control system. A schematic of the test setup is shown in Figure 3.11.

![Figure 3.11: Electrolysis sample holder experimental setup.](image-url)
3.4.1.1 Temperature Control

Air temperature variations in the lab without a temperature control system initially caused the temperature of the water in the tank to fluctuate up to ±8 °C over the course of a single test. To manage the temperature fluctuations a Julabo® F12 water bath with heating and cooling capabilities was used to control the temperature of the water in the tank. Stainless steel Swagelock® piping was arranged in the tank to act as a heating and cooling element to control the temperature of the water. Polystyrene foam insulation 3.8cm thick (R:5/RSI:0.88) was attached to the outside of the tank and sealed with polypropylene film adhesive was used to manage heat loss from the system.

3.4.2 Electrolyzer Test Station

A PEM electrolyzer test station was used to condition MEA samples and used with modified cell parts to visualize bubbles within the cell. The test station consists of the measurement system described above, temperature control and water supply systems. Test cells described above were connected to the electrolyzer test station to control testing conditions and record performance measurements. A schematic of the test setup for conditioning and optical visualization is shown in Figure 3.12 and Figure 3.13 respectively.

3.4.2.1 Temperature Control System

Digi-sense® Model 68900 temperature controllers were used to control the temperature of the feed water and the temperature of the cell between 30-60°C. K-type thermocouples were used to record temperatures for the cell and water supply line. Two 75mm heating rods with a diameter of 5mm were used to control the cell temperature by placing them in holes in the aluminum end plates. Inlet water was heated to the same temperature as the cell using an insulated electronic heating strip over stainless steel tubing.
Figure 3.12: Electrolyzer test station setup for MEA conditioning.

Figure 3.13: Electrolyzer test station setup for optical visualization study.
3.4.2.2 Water Supply System

Water was purified with a reverse osmosis filtration system to obtain 15 M-Ohm water required for the electrolysis reaction. A 20L Thermo Scientific® water bath was used to heat water supplied to the cell. A Waters® Model 515 high performance liquid chromatography (HPLC) pump was used to transport water from the water bath to the cell through PTFE tubing. A 45 µm glass frit filter was attached to the end of the PTFE tubing to prevent particles from entering the pump. The pump had a flow rate of 0-10mLmin\(^{-1}\) with a 0.001mLmin\(^{-1}\) resolution. Prior to testing the pump was primed and purged. The pump was calibrated using the calibration pre-set and verified using a 10 mL graduated cylinder to measure water fed at 8mLmin\(^{-1}\) through the HPLC pump over a one minute interval.

The reaction for the breakdown of water and the half reaction that constitute the full electrolysis reaction are used to determine the expected formation of hydrogen and oxygen gases. The amount of water consumed during the electrolysis reaction is dependent on the current used during operation of the cell from Faraday’s Law:

\[
\dot{N}_{H_2O} = \frac{iA}{2F}
\]

where i is the current density, A is the active area and F is Faraday’s constant [2].

3.5 Experimental Method

3.5.1 Cell Assembly for MEA Conditioning

An Enerpac® A258 hydraulic press with an RC1010 piston with an effective area of 2.24in\(^2\) was used to compress the cell in the electrolyzer test station. Bolts were inserted into the cell while under compression and tightened in a crisscross pattern for even cell compression. A pressure of 400psi (2760 kPa) was chosen based on previous experience from a graduate student at Queen’s University and the literature
as discussed above [52]. The resolution of the scale on the Enerpac causes a resolution of ±10psi (70 kPa). Pressure testing was conducted to ensure there was good electrical contact between the catalyst layers, PTL electrodes, flow field plates and the current distributors. Two 0.635mm silicone gaskets were placed between the flow field plates and MEA to prevent products and reactant from leaking. The assembled cell was connected to the output tubing using Swagelock® quick connectors from the HPLC pump to the anode end plate and the output water and gas mixture to both anode and cathode end plates.

### 3.5.2 Study using Sample Holder in Tank Setup

The sample holder was assembled with a 0.036mm teflon gasket on the anode side of the cell and a 0.635mm silicone gasket on the cathode side between the bipolar plate and MEA. Both gaskets had a 25mm by 25mm cutout in the middle that is aligned with the active area of the MEA. A 25mm by 25mm carbon paper with a microporous layer (Sigracet® 10BC) is placed inside the cutout in the gasket, completely covering the cathode catalyst layer (CCL) on the MEA. Similarly a 25mm by 25mm titanium PTL sample is placed on the anode catalyst layer (ACL) with the edges filed to protect the membrane from puncturing. An Enerpac® hydraulic press is used to compress the cell assembly for the setup in the tank at 400 psi. Bolts are tightened to 4.5Nm using an adjustable torque wrench in a crisscross pattern to reduce localized pressure points. The through plane cell resistance is measured using a Hioki® 3560AC HiTester to check for proper electrical contact to ensure an electrical short did not occur during assembly. The sample holder is then run under high purity water to remove and dust or contaminants from entering the tank.

The tank was cleaned and rinsed with 15Mohm DI water before each test. The tank was then filled with 7.5L of 15Mohm DI water. The water in the tank fully covered the viewing port and ACL but provided sufficient room to connect power supply and leads to the DAQ. The water bath temperature was then set and a Swagelock...
stainless steel piping assembly acting as a heat exchanger was placed in the tank for 60 minutes to allow the temperature to come to equilibrium. Two K-type thermocouples are placed at either end of the tank to monitor temperature water temperature and one K-type thermocouple is used to monitor air temperature.

The DAQ and power supply are connected to the current collecting plates and the sample holder is then placed in the tank to hydrate for 15 minutes. A steady state polarization measurement was then taken after which the cell is allowed to cool for 15 minutes from any localized cell heating that occurred at higher current densities to dissipate before bubble images were recorded. One set of images were recorded during a two second interval. The cell was allowed to equilibrate for 5 minutes following a change in current density before images were recorded.

3.5.3 Study using Optically Accessible Cell in the Electrolyzer Test Station

The modified PEM electrolyzer test cell was assembled with a 0.036mm teflon gasket on the anode side of the MEA with tests using the titanium plate with a channel-less square cutout. A 0.635mm silicone gasket on the anode side for tests with the optical flow field plate. A 0.635mm silicone gasket on the cathode side of the MEA. Carbon paper with a MPL and titanium PTL samples are cut to 25mm by 25mm and placed on the cathode and anode side, respectively. The cell was compressed to 300psi in the Enerpac® hydraulic press with bolts tightened to 4.5Nm. The pressure was changed from 400 psi to 300 psi in this test cell because the contact with the PTL is only made around the perimeter of the PTL and there is no support provided by flow channels. An electrical resistance measurement is taken using the Hioki® 3560AC HiTester before the cell is connected to the test station.

After the cell was connected to the HPLC pump a leak test was conducted, then the DAQ and power supply leads were connected. Heating rods were then inserted into
each of the aluminum end plates while the water bath temperature is set. The tem-
perature controllers for the inlet feed water and cell temperature. Water was pumped
through the cell for the MEA to hydrate and the cell temperature to equilibrate for
15 minutes. A steady state polarization measurement is then taken after which the
cell was allowed to operate for 15 minutes before bubble images were recorded. Three
sets of images were recorded in a two second interval taken 5 minutes apart. The
cell was left to equilibrate for 5 minutes following a change in current density before
images were recorded. Performance measurements and results obtained from these
images are discussed in Chapter 4.
Chapter 4

Results and Discussion

4.1 MEA Conditioning for Steady State Operation

MEA samples were required to operate consistently to ensure that any differences in performance measurements were due to changes to the operating parameters (i.e. PTL sample and temperature. Conditioning or activation serves to break-in the MEA so it can reproducibly operate and provide consistent performance. The conditioning process hydrates the Nafion® membrane while increasing performance and helps the carbon PTL attach to the MEA. Although water electrolysis starts at 1.229V in the absence of losses, moderate cell performances are not usually seen until potential differences of 1.6V and above [5,58].

Various techniques for the conditioning or break-in of PEM electrolyzer MEAs was noted in literature. Rau et al. conditioned new MEAs by alternating between current densities of 0.5 Acm⁻² and 1.0 Acm⁻² at room temperature [59]. Majasan et al. first placed the cell in 60°C DI water for 18 hours then rinsed the MEA in DI water before using in-situ activation at a current density of 0.1 Acm⁻² for 18 hours [33].

New MEA samples from IonPower® were conditioned in-situ in the electrolyzer test station at 60°C. The cell was assembled with the fibre PTL and MPL coated carbon cloth at the anode and cathode, respectively. The MEA was first hydrated for
15 minutes while water was supplied to the anode at 8 mL min\(^{-1}\) without a current applied to the cell. During electrolysis a steady supply of reactant liquid phase water maintains hydration in the cell [60]. After this initial hydration period the cell was operated at a current density of 0.7Acm\(^{-2}\) for two hours. At the end of this period a polarization measurement was taken and the cell was run at a current density of 1.2Acm\(^{-2}\) for another two hours, following which a polarization measurement was taken. This was repeated over three cycles so polarization curves could be compared to determine when the MEA performance was consistent. Figure 4.1 shows polarization measurements taken after 2 hour periods of galvanostatically controlled operation. The MEA was considered fully conditioned when the difference between points on the polarization measurement no longer changed over time. This occurred after 12 hours of operation. After the first 2 hours of conditioning the average difference between the galvanostatically controlled measured points was 949mAcm\(^{-2}\). This difference converged to 201mAcm\(^{-2}\) between the 10 hour and 12 hour polarization measurements taken after each 2 hour conditioning period. The MEA was considered to have steady operation after 12 hours of conditioning.

4.2 Image Analysis

4.2.1 Electrolysis Sample Holder in Tank

An image processing pathway was first developed using the sample holder in the tank setup. Identifying bubbles in images was a difficult task because the bubbles have a relatively low contrast in comparison to the background and no technique for image processing in similar circumstances was found in the literature.

Bubble images were analyzed using Fiji (ImageJ) software [61]. Images were recorded as 8 bit RGB colour tagged image file format (TIFF) using the IDT Vision high speed camera. Images are imported to Fiji as a folder containing 340 separate images. Image
Figure 4.1: MEA conditioning with polarization curves with current density switched between 0.7Acm\(^{-2}\) and 1.2Acm\(^{-2}\) every 2 hours with a polarization measurement taken after every switch.

Segmentation was the method employed to observe bubbles as the particles of interest. Segmentation is the process of splitting an image into multiple segments and typically consists of two parts: pre-processing and image analysis [61]. The TIFF images are compiled into a single stack viewing area is cropped and any adjustments to the rotation of the image were made so the square cutout is orientated vertically. The processing pathway for images from the sample holder consists of three main pre-processing steps: splitting color channel, brightness and contrast adjustment and thresholding before particles were analyzed.

For images captured in the sample holder the first image in the stack is taken as the reference image and subtracted from the remaining 339 images in the stack. The stack is then split into RGB base channels. The green channel contained the highest number of features so it was selected for processing for all image analysis. The brightness and contrast was then adjusted according to the image brightness according to the intensity of the reflected light from the PTL surface based on the PTL sample used. Brightness is altered to clarify the background from the bubbles before the
image is enhanced by saturating the pixels to 0.3%.

The final processing step was to binarize the 8-bit images. The local Fiji thresholding function was used with all thresholding methods to determine which worked the best to segment bubbles in the images. The NiBlack thresholding method was selected to work the best for the image stacks. A radius of 15 is used with the close- and fill hole functions in Fiji. The stack is then inverted and the scale is defined based on the length of the 17mm cutout. The image stack is analyzed using ellipses and including holes.

4.2.2 Electrolyzer Test Station Image Processing

The image processing pathway for images from the modified electrolyzer cell with optical access was built based on the processing developed for analyzing bubbles from the sample holder in the tank. Segmentation was again used to identify bubbles from TIFF images. Pre-processing of images from the optical channels started by first converting individual TIFF images into a single TIFF stack. Images were recorded in RGB colour format, however splitting the channels proved to show no details between the three RGB channels. Since there was no advantage in keeping these as RGB images, they were converted to 8-bit grayscale files. This reduced the memory from each file from 3.41GB to 1.39GB, drastically reducing the memory and time spent processing images in Fiji.

Two critical differences in the image processing pathway were used to analyze images captured using the modified test cells in the electrolyzer test station: the Find Edges Fiji function and the creation of a reference image to identify background features. The image processing pathway with example images following key steps in the image processing is shown in Figure 4.2. TIFF stacks were first rotated right 90 degrees so the channels orientated vertically. The Find Edges Fiji function was applied to detect bubbles in the images by identifying high changes in intensity. The filter utilizes a
Sobel edge detector to find sharp changes in contrast in the images [62]. Although the bubbles are a relatively low contrast particle, the Find Edges function was able to detect bubble particles, however since the background has areas of high contrast, particularly the fibre PTL, the background required additional pre-processing before images could be analyzed.

![Fiji image processing pathway for TIFF images.](image)

The creation of a reference image without bubbles present was developed to replace the function of using the first image in the stack as a reference image. Subtracting a reference image was deemed necessary to remove the background features in image stacks (i.e. the PTL surface). The reference image was created using MATLAB. Image stacks are converted into a three dimensional matrix where pixel values are averaged over stacks containing 340 images. A sample of the reference image created with MATLAB and a sample image with bubbles present for comparison is shown in Figure 4.3. The dark spots representing bubbles on the right side of Figure 4.3 (b) are clearly not visible in the MATLAB created reference image in (a).
Figure 4.3: Comparison of the reference image created by the MATLAB code to a sample image with bubbles in the channel-less modified cell. The circled area in (b) shows bubbles that are particularly noticeable in the image.

This time averaged background was used as the reference image that was subtracted from image stacks in Fiji to eliminate background content from contrast on the PTL surface and any uneven lighting. This method relies on the relatively low contrast of bubbles where often only the edges of the bubbles are visible and the PTL surface can often be seen through the bubbles. The objective of the time average reference image was to produce an image of the PTL surface that appeared to have no bubbles present.

4.2.2.1 Images from Channel-less Modified Cell

Image stacks from the channel-less square cutout were first imported as a three dimensional matrix into MATLAB to create a time averaged reference image as described above. The reference image was then added to the image stacks containing 340 images and the difference function was used as the first step to eliminate background features. The Find Edges function was then applied to the stack. The stack was
duplicated and a gauss filter with 40 pixel radius was applied and then subtracted from the modified stack. Using a Gauss filter to blur images and subtract this from the original image is a common technique to washout areas backgrounds with high contrast [61]. The stack is then inverted and the Auto-threshold function is used to binarize the image. The Close- and Fill Holes functions are the last steps to the pre-processing portion of the image processing pathway.

The scale is defined using the left edge of the square cutout as a reference 17 mm in length and was verified it was manufactured to the proper specifications using a digital caliper. The region of interest is set as a 12mm by 17mm region and the particles are then analyzed. The output graphics interchange format (GIF) file was generated showing ellipses representing bubbles. The GIF file was compared to the original TIFF stack to ensure bubbles were properly identified. As seen in Figure 4.3 the large bubbles that accumulate at the top of the viewing port remain in the reference image since they are nearly stagnant, however the 12mm by 17mm region of interest was chosen to avoid these bubbles.

4.2.2.2 Images from Modified Cell with Optical Channels

The image processing pathway follows a slightly different route for the images containing channels because the aspect ratio of the cell changed the lighting, introducing different optical conditions. The Find edge filter is applied to the stack and reference images in Fiji before image stacks are converted to a three dimensional matrix in MATLAB. The reference image is subtracted from all 340 stack images. An enhance contrast filter is then applied to increase the contrast by saturating the greyscale image so 1% of the total pixels are saturated at low and high intensity pixel values. A Gaussian filter is then applied with a sigma value of 2 to blur the image slightly, reducing unwanted areas of high contrast. A second enhance contrast filter with the same 1% pixel saturation is then applied before the image is binarized with a threshold value of 0.15. Once pre-processing of images in MATLAB was complete
the images were rewritten to a TIFF file.

Image stacks were then opened in Fiji and the Close- function is applied which smooths objects and fills in holes by applying the dilation function followed by erosion operation. The scale is calibrated using the outermost edge of the left 17mm channel as a reference, which was verified it was cut to specifications using a digital caliper. The images are measured individually by defining the region of interest (ROI) as each channel using the Analyze Particles function. Similarly an GIF output file was generated showing ellipses and the ellipses were compared to the unaltered TIFF files to ensure bubbles were properly identified.

4.3 Electrolysis Sample Holder

In the initial study a custom built sample holder was used to study oxygen bubbles from the anode in a flooded tank with DI water. Two phase water-oxygen flow was recorded using a high speed camera and the performance of the electrolysis process was measured using a polarization curve. Two PTL samples were studied at room temperature and a sub-study was conducted to determine the effect of temperature on bubble behaviour. Water temperatures of 25°C and 40°C were used to test the effect of temperature. Images were processed using Fiji to determine the average bubbles size, average number of bubbles and area percentage were found.

A Pt coated fibre and expanded Ti mesh PTL are used in the submerged sample holder in the tank. The performance curves at 25°C are shown in Figure 4.4 with sample images of two phase flow behaviour at selected voltages in Figure 4.5. It should be noted that during this first study new Nafion 115 MEAs were only conditioned for two hours operating at 0.7Acm⁻² and did not complete a full break-in cycle. New MEAs were conditioned for two hours for both PTL samples to maintain consistency in the total lifetime testing for each MEA. The performance of the elec-
trolyzer cell was measured with the Agilent DAQ prior to capturing images so that the performance could be correlated with the bubble sizes and distributions over the surface of the PTL on the anode side.

Figure 4.4: Performance curves at 25°C for the expanded mesh PTL with points A-E and fibre PTL with points F-J where bubble images were taken.

As seen in Figure 4.5 (a) and (f) very few bubbles visible on the surface of the PTL since there is a very low current density passing through the cell. Bubble images were analyzed in Fiji using the method described above to obtain statistical data related to the oxygen bubbles at the anode over the 17mm by 17mm viewing port in the sample holder for the Bekeart 2-sided Pt coated Ti fibre and uncoated expanded Ti mesh PTLs. From the TIFF image stacks the bubble size, percent area covered by bubbles on the surface PTL in the viewing port and total bubbles in the viewing port was measured, see Figure 4.6. These plots represent the average bubble statistics over 340 image frames captured continuously over a two second interval at 170fps.

The average bubble size increases with current density as seen in Figure 4.6 (a). At very low current densities few bubbles evolve from the surface of the PTL. Only relatively large bubbles that did not detach from the surface were apparent in the images
(a) 0.003 Acm⁻², (b) 0.10 Acm⁻², (c) 0.31 Acm⁻², (d) 0.45 Acm⁻², (e) 0.66 Acm⁻²,
1.5V 1.7V 2.0V 2.2V 2.6V

(f) 0.005 Acm⁻², (g) 0.15 Acm⁻², (h) 0.36 Acm⁻², (i) 0.49 Acm⁻², (j) 0.81 Acm⁻²,
1.5V 1.7V 2.0V 2.2V 2.6V

Figure 4.5: Two-phase oxygen gas bubbles using the fibre PTL from (a) to (e) and expanded mesh PTL from (f) to (j) at selected current densities at 25°C in sample holder.
Figure 4.6: Two-phase oxygen gas bubble flow statistics over current density for the fibre and expanded Ti mesh PTLs showing the average (a) bubble size; (b) the area percentage covered on the surface of the PTL over the stack of images; (c) total number of bubbles per frame of the image stack.
and very slowly increased in size with time. At 0.005Acm\(^{-2}\) and 0.003Acm\(^{-2}\) (1.5V) the images could not be analyzed and included in the plots since virtually no bubbles evolving from the surface were visible. As expected the percent area of the viewing port covered by bubbles increases with current density as more water is split into hydrogen and oxygen during the electrolysis reaction in Figure 4.6 (b). The average number of bubbles in Figure 4.6 shows a general increase in the number of bubbles on the surface of both PTL samples. At current densities above 0.49Acm\(^{-2}\) (2.2V) for the fibre PTL the average number of bubbles decreases, Figure 4.6 (c). This is likely due to bubbles tending to coalesce at the top of the viewing port as more oxygen is produced that needs to be vented at increased current densities. This would remain consistent with the increase in bubble size and area percentage covered by bubbles in Figures 4.6 (a) and (b), respectively.

The large discrepancy in size, area percentage and average number of bubbles per frame between the PTL samples can be attributed to the performance differences. The expanded PTL developed a passivation layer resulting in higher ohmic losses. In future studies bubble images are taken at identical current densities to look for differences in two phase flow while the same amount of oxygen is being produced from the electrolysis reaction.

### 4.3.1 Effect of Operating Temperature on Two Phase Flow Behaviour

The effect of temperature on bubble size was studied in the tank at temperatures of 25°C and 40°C for the fibre PTL. The cell performance is shown in Figure 4.7 with sample images of the oxygen bubbles shown in Figure 4.8.

It was expected that the performance of the cell would improve with increased temperature, however the performance decreased as seen in Figure 4.7. Damage to the MEA during testing was the reason for this and a further discussion is included below.
Figure 4.7: Performance curves using the fibre PTL at 25°C with points A-E and 40°C with points F-J where bubble images were taken.

(a) 0.005 Acm$^{-2}$, 1.5V
(b) 0.10 Acm$^{-2}$, 1.7V
(c) 0.26 Acm$^{-2}$, 2.0V
(d) 0.38 Acm$^{-2}$, 2.2V
(e) 0.57 Acm$^{-2}$, 2.6V

(f) 0.005 Acm$^{-2}$, (g) 0.15 Acm$^{-2}$, (h) 0.36 Acm$^{-2}$, (i) 0.49 Acm$^{-2}$, (j) 0.81 Acm$^{-2}$

1.5V 1.7V 2.0V 2.2V 2.6V

Figure 4.8: Two-phase oxygen gas bubbles using the fibre PTL at 25°C from (a) to (e) and 40°C from (f) to (j) at selected current densities.
The average size, percent area of the fibre PTL covered and average bubbles present in each frame of the TIFF image stacks is summarized in Figure 4.9. The electrolyzer was run with the same MEA for both the 25°C and 40°C tests. The same fibre PTL on the anode as well as carbon paper on the cathode was used for each temperature since it partially bonded with the MEA during operation in the test station. A similar test was conducted with the expanded Ti mesh PTL at 40°C, however a high degree of damage occurred to the MEA as discussed below. Bubble statistics for the expanded Ti PTL are therefore not included.

![Graphs of bubble statistics](https://via.placeholder.com/150)

**Figure 4.9:** Two-phase oxygen gas bubble flow statistics over current density for the fibre PTL at 25°C and 40°C showing the average (a) bubble size (b) area percentage covered on the surface of the PTL over the stack of images and (c) total number of bubbles per frame of the image stack.
The behaviour of the bubbles with temperature show the average bubble size and percent area of the viewing port covered by bubbles increasing with current density as seen in Figure 4.8 (a) and (b). It is likely bubbles were getting stuck on the surface of the PTL where there is little bubble movement to encourage the detachment from the PTL surface. Bubbles stuck on the PTL over represent the actual size of the bubbles produced. The decrease in the number of bubbles at 0.57 Acm$^{-2}$ (2.6V), 40°C and 0.81Acm$^{-2}$ (2.6V), 25°C may be due to bubbles tending to coalesce at the top of the viewing port while venting from the cell, leaving less surface area for bubbles to be visible.

4.3.2 MEA Performance and Degradation

An issue that occurs with the sample holder setup is that bubbles tend to get trapped on the top edge of the Delrin end plate as buoyancy forces cause the bubbles to rise. This is especially apparent at higher current densities when more oxygen gas is produced as seen in the bubble images in Figure 4.5. The venting port seen in Figure 4.5: Delrin cell was added to eliminate bubbles from coalescing at the top. Although this did drastically improve the issue of bubbles coalescing at the top of the viewing port some bubbles still got caught on the edge of the titanium current distributor.

The performance of the electrolysis reaction in the sample holder is drastically lower than is seen in PEM test cells in literature [5, 33, 37, 52] when using similar Nafion 115 MEAs and Ti PTL samples. The difference in performance can be attributed to being in an open testing environment where the MEA is not contained within the gasketing of a compressed cell, instead the viewing port leaves the cell open so bubbles can be observed during the electrolysis reaction. The viewing port also does not allow for equal compression over the active area of the MEA, having a much higher compression along the 4mm perimeter of the MEA where the end plate surface area overlaps with the MEA active area/PTL.
The performance of the MEA following the conditioning in the electrolyzer test station was determined with a polarization curve. The cell was then disassembled and the MEA was placed in the sample holder with a viewing port on the anode for testing in the tank at 25°C where a second polarization curve was measured. After testing in the tank the MEA was reassembled in a cell used in the electrolyzer test station where a performance curve was also measured to determine if operation in the tank changed the performance of the MEA. This was then repeated for the second test at 40°C for both PTL samples shown in Figure 4.10.

![Figure 4.10: Degradation in performance of the MEA used in the sample holder with (a) Pt coated fibre PTL and (b) uncoated expanded Ti mesh PTL.](image)

The results from testing in the sample holder show a decrease in performance after each test, most noticeably the performance at 40°C is lower than the performance at
25°C, clearly indicating there is a problem with the MEA. It is suspected that while using the sample holder that the presence of ions in the tank due to the lack of circulation damaged the MEA, lowering the cell performance. This performance decline of the MEA through testing in the tank can be seen in Figure 4.10. It is suspected that high compression around the edges of the PTL may have damaged the surface of the MEA during assembly or that standing water accumulated ions in the DI water that degraded the performance. Recommendations for this issue are discussed in chapter 5.

The sample holder submerged in the tank was designed to make an experimental setup that could produce visible oxygen bubbles coming from the anode side of a PEM electrolysis MEA. A method of capturing and processing images of these bubbles was then developed. It was clear the MEA in the sample holder was being damaged for various potential reasons as described above. To advance this study a modified optically accessible electrolyzer test cell was designed to be more similar to a standard electrolyzer test cell so water could circulate through the cell, but with optical visualization at the anode.

4.4 Modified Channel-less Optical Electrolyzer Cell in Test Station

A channel-less modified electrolyzer setup was used to study bubbles coming directly from the surface of two PTL samples. The viewing area is similar in shape to that of the sample holder in the tank, but is used in a closed system with water circulated through a modified PEM electrolyzer. Similarly to the sample holder setup, potentiostatically controlled polarization curves were measured to assess the cell performance. Polarization curves using the fibre and powder PTL samples in the channel-less electrolyzer setup is shown in Figure 4.11. An HPLC pump was used to pump water at 2mLmin$^{-1}$ through the test cell. The flow rate was chosen to ensure the channel-less port had a constant supply of water available for the electrolysis reaction. The flow
was kept on the lower end of the flow rate capability of the HPLC pump so as to not introduce a significant flow that pulled bubbles from the surface of the PTL, similar to the no flow conditions with the sample holder in the tank.

Figure 4.11: Performance curve in the modified channel-less optical test cell at 60°C.

For the channel-less setup, the region of interest was defined as a 12mm by 17mm rectangular area. The entire channel-less square was not defined as the region of interest because of large bubbles that formed at the top of the channel, Figure 4.12. These bubbles would form along the thickness of the top of the square cutout in the titanium current collecting plate. The 12mm height was chosen based on the maximum available height available in all image stacks to ensure no unevacuated large bubbles at the top of the viewing port were included in the region of interest of the bubbles. Sample images from recorded TIFF stacks at each of the six current densities points studied is shown in Figure 4.13.

The performance curves as seen in Figure 4.11 between the powder and square PTLs are very similar. The powder PTL was chosen to examine the effect of temperature on bubble size in the channel-less setup. Cell performance is very low in comparison
Figure 4.12: The 12mm by 17mm region of interest of the used for analyzing bubbles in channel-less cell orientation.

Figure 4.13: Images of channel-less optical viewing port on modified electrolyzer cell with the fibre PTL at (a)-(f) and powder PTL at (g)-(l).
to other electrolyzers in literature [5,37,39]. This can be explained from the difference in electrical contact since the ribs from flow channels provide a much larger surface area to distribute current over the surface of the PTL.

As seen in Figure 4.13 above, there is a tendency for bubbles to form near the edges of the square cutout in the PTL. It is suspected that there is better contact with the titanium current distributor near the edges which causes bubbles to have a tendency to generate in these areas since better electrical contact gives more energy for the electrolysis reaction to occur resulting in oxygen bubbles. The region of interest for the bubble images was a 12mm by 17mm region to avoid analyzing coalesced bubbles that form at the top of the square cutout. TIFF stacks are analyzed to measure statistics relating to oxygen bubble average size, percent area covered by bubbles in the region of interest and average number of bubbles per image slice as summarized in Figure 4.14.

This study was conducted to look for differences in bubble characteristics between PTL samples. At similar current densities it is expected that the oxygen gas produced and hence percent area covered by bubbles on the PTL surface would be similar, however Figure 4.14 (b) indicates there is a higher percentage of the region of interest covered by bubbles from the the fibre PTL than the powder PTL. The average difference between the area percentage covered is 1.27%. It is suspected that the reason for this larger area percentage comes from bubbles getting stuck on the surface of the acrylic window. As observed during experimentation, there is a tendency for larger bubbles to get stuck between the PTL surface and the inside of the acrylic window. This is particularly evident when bubbles were large enough to make contact with the inside of the acrylic window. These large bubbles could explain why the average bubble size using the powder PTL was higher as larger bubbles trapped in the viewing window during testing were unable to exit the cell, as seen in Figures 4.14 (a). Bubbles that emerged from surface of the powder PTL sample may have been
Figure 4.14: Two phase flow statistics over current density for the fibre and powder PTLs at 60°C showing the average (a) bubble size; (b) the area percentage covered on the surface of the channels over the stack of images; (c) total number of bubbles per frame of the image stack for the channel-less setup.
blocked from view of the camera from behind larger bubbles sticking to the surface of the acrylic window. This is supported by Figure 4.14 (c) since the bubble count is less than the bubble count for the fibre PTL. Since TIFF stacks were recorded over three sets of two second videos spaced 5 minutes apart, there may not have been sufficient time for larger bubbles to dislodge from the surface of the acrylic window, particularly at a low flow rate of 2mLmin\(^{-1}\) used during this study.

Figure 4.14 (a) does shows a trend of increasing area percentage covered by the bubbles at increased current density as would be expected as more oxygen is produced at higher current densities. There is a relatively short range of percentage area covered from 0.05Acm\(^{-2}\) to 0.5Acm\(^{-2}\) however, from 4.2% to 6.6% for the powder PTL and 5.9% to 7.7% for the fibre PTL sample. It is suspected that this is due to the high aspect ratio of 1:1 for the square channel-less cutout as bubbles seem to have a tendency to form around the edges of the channel-less design.

4.4.1 Effect of Operating Temperature on Two Phase Flow Behaviour

Performance curves were taken for the modified channel-less cell at three temperatures: 30\(^\circ\)C, 45\(^\circ\)C and 60\(^\circ\)C as seen in Figure 4.15. The performance of the modified test cell with 17mm by 17mm cutout is again much lower than would be expected in a typical electrolyzer cell operating at similar voltages as described above. Figure 4.15 however does show an increase in performance with cell temperature as would be expected as more thermal energy can be utilized to drive the reaction. Sample images corresponding to points a, b and c on Figure 4.15 recorded at 0.3Acm\(^{-2}\) are show in Figure 4.16.
Figure 4.15: Performance curve for the modified cell with channel-less optical cutout using the powder PTL sample.

Figure 4.16: Images at 0.3Acm$^2$ of the channel-less modified electrolyzer setup using the powder PTL sample at 30°C, 45°C and 60°C.

The maximum temperature used for this study was selected as 60°C because the acrylic used to cover the square cutout was rated for use at temperatures below 70°C. A difference in performance is apparent as seen in Figure 4.15 but at a given current density the amount of oxygen produced will depend on the current density and is independent of temperature.

Similarly TIFF images stacks were captured and a 12mm by 17mm region of interest
was analyzed over the same six current densities as with the PTL testing. From the
TIFF stack analysis, oxygen bubble average size, percent area covered by bubbles in
the region of interest and average number of bubbles per image slice is summarized
in Figure 4.17.

There are no significant differences in the average size, area percent covered by gaseous
oxygen in the region of interest or the average number of bubbles per image slice with
a change in temperature, Figure 4.17 (a), (b) and (c), respectively. Since the same
procedure was followed to record bubble images, it is suspected that detached bubbles
that stuck to the inside surface of the acrylic window could have effected the bubble

Figure 4.17: Oxygen bubble statistics using the channel-less modified electrolyzer cell
showing (a) bubble size; (b) the area percentage covered on the surface of the square
cutout over the stack of images; (c) total number of bubbles per frame of the image
stack
characteristics from recorded images during the temperature testing as well.

As expected, the percent area covered by the bubbles increases with current density for all temperatures tested in this study. A small change in percent area was measured with range between the three temperatures from 3.4% to 6.6%, Figure 4.17. The average number of bubbles per slice remain relatively flat over the range of current densities for all temperatures while the bubble size increases, 4.17 (a) and (c), respectively. The area percentage increase with current density is therefore a result of bubble size increasing with current density.

4.4.2 Formation of Bubble at Water Inlet

During the operation of the channel-less cell it was noted a bubble would form at the bottom left corner of the viewing port where the inlet flow water enters the cell as shown in Figure 4.18. This bubble has an average size of 4.5mm and evolves over the span of current densities operated during this study at increasing frequency with current density.

Figure 4.18: Regularly occurring oxygen bubble forming at the inlet water supply of the cell at the anode.
The presence of this bubble during the two second video burst could increase the average bubble size given the amount of data collected in this study. Physical memory limitations of the computer restricted the size of image stacks that could be captured with the high speed camera. Considering the impact of this bubble was outside the scope of this research however in future work the presence of this bubble should be studied further.

4.4.3 Aspect Ratio

The 1:1 aspect ratio of the channel-less cutout means that bubbles that tend to form near the edges will be far apart and be unable to coalesce. Electrical contact with the titanium plate was only along the outer 4mm of the 25mm by 25mm PTL samples. It is suspected that either the in-plane conductivity is very high or there are large ohmic contact losses where the PTL makes contact with the titanium current distributor. A smaller aspect ratio, such as a typical channel design would increase the contact area with the flow channel plate so bubbles don’t appear to be forming only on the edges of the optical cutout. The following section explores bubbles in a setup with channels with a much higher proportion of the surface of the PTL in contact with the current distributor on the anode.

4.5 Modified Electrolyzer Cell with Optically Accessible Flow Channels

The cell with optically accessible flow channels was designed to be as similar to a standard PEM electrolyzer test cell as possible while providing optical access into the flow field channels. The channels follow the progression of gaseous oxygen in two-phase flow through the PTL and into the flow channels of an electrolyzer test cell. Images of the oxygen bubbles were recorded in the two middle channels of the flow field plate with a high speed camera.
Potentiostatically controlled polarization curves were used to measure the cell performance. An average of two performance measurements was averaged using the fibre and powder PTL samples shown in Figure 4.19. Water was circulated through the cell at 6 mLmin\(^{-1}\) and the cell temperature was set to 60°C to replicate normal operating conditions for PEM electrolyzer test cells. After polarization curves were measured bubble images were recorded using the high speed camera. Sample images from the TIFF stacks at each current density testing point is shown in Figure 4.20.

![Graph showing polarization curves](image)

**Figure 4.19:** Performance curve in the optical flow channel test cell at 60°C.

Gaseous oxygen is in the bubbly flow regime at low current densities, 0.1-0.3 Acm\(^{-2}\). In bubbly flow individual bubbles are visible in the two-phase flow and are independent of each other, see Figures 4.20 (a), (b), (g) and (h). At mid range current densities, 0.6 - 1.0 Acm\(^{-2}\) some bubbles tend to coalesce into larger bubbles resulting in slug flow. At the higher current densities operated during this study, 1.5 - 2.2 Acm\(^{-2}\), large bubbles that fill the entire channel begin to form. The presence of these bubbles in two-phase flow indicates the electrolyzer was operating in an annular regime. These bubbles are oblong in shape and tend to stick to the walls of the channels, impeding
Figure 4.20: Images of the optically accessible flow channels using the powder PTL sample (a)-(f) and fibre PTL sample (g)-(k) at selected current densities
bubbles from traveling out of the channels as seen in the left channels in Figure 4.20 (f) and (l). Image stacks were processed to determine the average bubble size, percent area covered by oxygen bubbles in each channel and total bubbles each channel per image slice as shown in Figure 4.21.

Figure 4.21: Two-phase oxygen gas bubble flow statistics over current density for the fibre and powder PTLs at 60°C showing the average (a) bubble size; (b) the area percentage covered on the surface of the channels over the stack of images; (c) total number of bubbles per frame of the image stack

Figure 4.21 (b) shows no clear difference in the area percentage covered by oxygen bubbles between the fibre and powder PTL samples. As expected, the percentage area covered by bubbles increases with increasing current density. The range of the percentage area covered is from 10.3% to 53.7%. The difference in average percentage area covered using the optical channel setup is much higher than that of the channel-
less cell design which used the same MEA and PTL samples. This is an indication that there is a contact problem as a result of the aspect ratio as discussed below.

The bubble size and percent area covered by gaseous oxygen in the channels increases with current density as expected, seen in Figures 4.21 (a) and (b), respectively. As the current density increases bubbles tend to get larger and coalesce into slugs that progress towards the annular flow region at higher operating current densities. The bubble count decreases with current density as shown in Figure 4.21 (c). This is also a result of bubbles coalescing in the channels. This increase in bubble size was not observed in channel-less sample holder and modified electrolyzer cell with a square cutout. The narrow channels with an aspect ratio of 17:2 force evolved oxygen bubbles to be in close proximity to each other. Consequently these bubbles tend to coalesce into a fewer total number of larger bubbles as seen in Figure 4.20 (a) and (c).

4.5.1 Effect of Operating Temperature on Two Phase Flow Behaviour

The effect of temperature is studied in the modified PEM electrolyzer cell. The powder PTL sample was chosen for this test because had a better performance curve than the fibre PTL. A flow rate of 6 mLmin\(^{-1}\) was used during testing. The temperature range from 30-60°C was chosen based on material selection. The acrylic window covering the flow channels had a temperature limit of 70°C. The temperature was kept below this temperature to minimize the chance of the acrylic window deforming at elevated temperatures. The performance and sample bubble images at the specified operating temperatures are shown in Figure 4.22 and Figure 4.23, respectively.
Figure 4.22: Performance curve using the powder PTL in the optical flow channel test cell at 30°C, 45°C and 60°C.

Figure 4.23: Images at 1.0Acm⁻² of the optically accessible flow channels using the powder PTL sample at (a) 30°C, (b) 45°C and (c)60°C.
As expected, there is a performance increase with increasing temperature using the modified optical flow channel cell. From the TIFF images recorded at the three operating temperatures the average bubble size, percent area covered by bubbles in each channel and total bubble count in each channel per frame was measured as shown in Figure 4.24.

![Graphs showing average bubble size, area percentage covered, and total bubble count vs. current density](image)

Figure 4.24: Two-phase oxygen gas bubble flow statistics over current density using the powder PTL at 30°C, 45°C and 60°C showing the average (a) bubble size; (b) the area percentage covered on the surface of the channels over the stack of images; (c) total number of bubbles per frame of the image stack

The average bubble size increases with current density while the average total bubble count per slice decreases with current density as expected, shown in Figure 4.24 (a) and (c), respectively. The plots indicate that temperature has no effect on the transition from bubbly to slug to annular flow based on bubble size or percent area.
covered by oxygen gas.

The closest comparison bubble size in PEM electrolysis was conducted by Li et al. on the evolution of the oxygen bubble from the surface of the MEA using an optically transparent cell with a novel 24 micron thin film PTL with uniform circular pores. They found that the growth of oxygen bubbles increases in size faster with increasing temperature [43]. Bubble growth was not a part of the scope of this research, however the results from this study find no correlation for bubble size with temperature for PEM electrolysis cell in-situ. In another study conducted by Majasan et al. found that more gas bubbles were observed in the entire anode flow field plate at 2.0A$^{-2}$ between 25°C and 80°C at 15 mLmin$^{-1}$. They also found and that flow rate effect on cell performance was dependent on operating temperature since oxygen solubility in water is temperature dependent [33]. Material and equipment constraints limited study with equivalent parameters, however within the scope of this research it was found the number of bubbles has no dependency on temperature. In future studies the modified optical flow channel cell developed for this research could be modified with a silica glass window to operate at higher temperatures to study the effect of flow rate and temperature to advance this study.

4.6 Interpretation of Bubble Characteristics

4.6.1 Contact Resistance

During this study a major challenge that was encountered was passing sufficient current through the MEA in modified setups (i.e. without flow field channels). Only having contact on the edges of channel-less setups drastically lowered the performance of the electrolysis process as observed with the sample holder in the tank and modified channel-less electrolyzer cell setups. In the literature increased contact is used to study the evolution of the bubble directly from the surface of the PTL. This has been achieved in literature using a titanium mesh in place of titanium sinter or fibre PTL
while having sufficient electrical contact with an area to visualize the MEA directly.

Contact resistance also became a challenge using while using PTL samples of different thickness. The Bekaert fibre and expanded Ti mesh PTLs were significantly thicker than the fibre and powder PTL samples provided by Hydrogenics. A study conducted by Siracusano et al. found that there was a reduction in ohmic contact resistance from using a thicker Ti grid PTL [52]. Since it was desirable to keep the gasketing and compression the same when assembling PEM electrolysis cells, only PTL samples of similar thickness were used for each testing setup. PTL samples of different thicknesses could have an influence on the difference in performances due to contact resistance.

### 4.6.2 Bubble Coalescence in Channels

As oxygen bubbles evolve in the channels there is a tendency for some to get caught against the acrylic backing, particularly in the bottom of the channels. The image processing technique used to produce a reference image by averaging stack images aids in removing these bubbles from the analysis. There are however some bubbles that get stuck between the rib separating channels and the acrylic window. These bubbles appear opaque and therefore oxygen bubbles coming from the PTL may get distorted in the image processing as they travel behind these opaque bubbles. For future use of this experimental setup it is suggested to add a thin strip of gasket to attempt to seal the small gap between the flat surfaces of the acrylic and titanium channel.
Chapter 5

Conclusions and Recommendations

The purpose of this research was to develop an experimental setup and image processing pathway to observe gaseous oxygen bubbles at the anode during PEM electrolysis to study the effect of bubble characteristics on performance. Three experimental setups were developed to study two-phase flow at the surface of the PTL on the anode: a Delrin sample holder submerged in a water filled tank, modified PEM electrolyzer cell with a channel-less orientation and PEM electrolyzer cell with optically visible flow channels. Image processing pathways were developed using MATLAB and Fiji to observe individual oxygen bubbles in images recorded in-situ during PEM electrolysis in the experimental setups. Using these image processing techniques individual low contrast bubbles were successfully studied in images from each experimental setup. The channel-less design showed poor performance results in comparison to a typical PEM electrolyzer cell. The current density however was shown to increase with increasing potentials and higher temperatures, and maintained the expected shape of a performance curve. The PEM electrolyzer with visible flow channels was the most similar experimental setup to a typical PEM electrolyzer test cell while allowing for optical access to oxygen bubbles. The modified PEM electrolyzer cell design is desirable because it gives insights into two-phase flow characteristics and flow regime in two channels while temperature and flow rate can be controlled for the cell.

The results of this research in the optically accessible channel orientation suggests
that bubble size increases with current density. The flow regime is seen to move from bubbly, to slug, to annular flow with increasing current density, as is consistent with literature [33, 36, 37]. At current densities used during this study, it was found at 1.0Acm$^{-2}$ slugs begin to form and at 1.5Acm$^{-2}$ annular flow beings to occur in the flow field channels. Cell performance varied drastically with the channel-less and optical flow channel setups. The channel-less cell was only in contact with the current distributing plate on the overlap with the edges of the 25mm by 25mm PTL samples, leaving the middle 17mm by 17mm portion of the PTL sample without electrical contact to the current distributor. It is suspected that either the in-plane conductivity for the PTL is very high or there are large ohmic contact losses where the PTL contacts the titanium plate that account for this lower performance. This shows that the channel aspect ratio is an important determinant to performance. The area of contact between the MEA and current collector drastically affects electrical contact. This also indicates that the flow field design needs to be tailored to the PTL used in a PEM electrolyzer.

This research found no relation between bubble characteristics with PTL selection or temperature. A limitation of this research stems from bubbles formed in different planes and cannot be observed due to overlap on the 2D surface being visualized. This is particularity important at higher current densities where the rate of gaseous oxygen formation is much higher leading to higher percentages of bubbles in the viewing window that need to be evacuated from the cell. Given the constraint of a small 17mm by 17mm flat surface with optical access from a single plane and small size of the bubbles, having a stereoscopic 3D bubble visualization would not be extremely difficult to implement. A more practical method alternative method to study oxygen bubbles in 3D would be to use a different optical approach such as neutron spectroscopy as seen in literature [41, 42, 44].

The Delrin sample holder in the tank served as an introduction for this research.
Water management in the tank used with the sample holder was challenging because the heating coil outputs ions into the water the affect the conductivity and introduced impurities that could have damaged MEA samples during the electrolysis reaction. Since PEM electrolyzer test cells are not flooded, water is typically pumped through the cell and there is little impact on the conductivity of the water. Given the difficulty with water management in an open testing environment and degradation issues it is recommended to use only the modified electrolyzer test cell for further study. Through the development of this study there are valuable additions that could be made to advance this research. These additions are centered around (1) further study with the experimental setup and processed images and (2) improving the modified electrolyzer cell experimental setup.

Next steps in future study for this research are to examine the bubble statistics collected during image analysis, such as the standard deviation of the bubble size to discuss the significance of results. Further research should be conducted on the aspect ratio of channel sizes by manufacturing additional titanium plates with channels of different sizes. A larger variety of PTL samples should be tested to aid in the understanding of how the microstructure effects the formation of oxygen bubbles and influences overall performance of the cell. Additionally, by using a coated Ti mesh to distribute current over the surface of the active area the evolution of bubbles from the surface of the MEA could studied using this setup.

The modified PEM electrolyzer experimental setup could undergo improvements to advance the efficiency and capabilities for further research. The efficiency of testing could be improved by automating polarization measurements using the power supply to save time during testing to allow for more measurement points to be taken. The addition of a silica glass window would allow for temperatures above 70°C to be tested to better study the effect of temperature on oxygen bubbles. Gold plating the titanium flow field plate is recommended to reduce ohmic losses in the cell as if
common in literature \([5,33,37]\). Peristaltic pumps with a flow rate up to 50 mLmin\(^{-1}\) as seen in literature \([33,37,43]\) would allow the effect of flow rate on oxygen bubbles to be studied with a much larger range. This would also provide enough heat flux to sufficiently to control the cell temperature without the addition of heating rods, making this more representative to the operation of commercial PEM electrolyzers.
References


Appendices

A  Electrolysis without the use of a Porous Transport Layer

Initial testing in the tank was conducted without the use of a PTL sample pressed on the ACL. Through testing it was found that small bubbles did not form on the ACL as they did with the PTL present. This was likely due to insufficient electrical contact without the presence of a PTL that can distribute the current over the surface of the CCM surface. Bubbles are visible on the edges of optical port as seen in Figure A.1, but instead of detaching from the surface of the ACL grow in size very slowly and remain on the surface.

Figure A.1: Oxygen bubbles directly on the surface of the ACL operating at 0.02Acm$^2$ at 2.0V.

To distribute the current across the entire surface of the ACL a titanium mesh was
placed on the surface to act as a current distributor. Figure A.2 shows bubbles visible along the mesh/ACL interface.

Figure A.2: Oxygen bubbles on the forming on the titanium mesh on the surface of the ACL operating at 0.05A/cm$^2$ at 2.0V.

Bubbles were produced using the titanium mesh, however a passivation layer quickly formed on the surface of the mesh which required voltages upwards of 3.0V for electrolysis to occur. Voltages this high could cause damage to the MEA. A platinum coated titanium mesh could be used to continue studying two phase flow using the sample holder in the tank or in the modified electrolyzer cell with the channel-less optical access.

B Review of Sample Holder in the Tank

B.1 Development of Experimental Setup

The initial experimental setup went through multiple iterations in the sample holder and the image capture setup. A description of the developments is intended to aid in the improvement of the experimental setup to further this research. Initially viewing ports were located on both the anode and cathode side on the cell, however the relatively fragile carbon paper on the cathode damaged more easily due to the uneven compression around edges of the square cutout. Initially the end plate with square
cutout was used to make the cell symmetrical, however the since optical access was only required on the one side and the carbon paper was easily damaged the cell was altered.

Various lighting options and camera lens were explored during testing. Initially a halogen light was used having a 8750 lumen output, however the lamp produced a high amount of heat. Although the light had a very high lumen output, it still needed to be approximately 25cm from the tank to provide proper directional light to the viewing port which introduced a hot spot around the optical port on the sample holder and altering the controlled temperature of the water. A 250W halogen light with a 4000 lumen output was also used but also had too large a heat output. An array of four 500 lumen LED bulbs was tested to eliminate the heat problem that occurred with the halogen lights. Two lamps with 2700K and 3200K temperatures were tested. The lumen output from the LEDs was found to be sufficient since their smaller size allowed them to be directed at the viewing port. In the image stacks however, a flicker was apparent from the output of the lamps. Compact fluorescent lights were found to be ideal since they did not output a large heat flux but provided a sufficient lumen output using two 42W bulbs.

The setup described in Chapter 2 was the developed as a result of a previous experimentation. The setup seen in Figure B.3 was developed to have a larger viewing area. The cell is made from a 25.4mm Delrin sheet and was suspended in the tank with support legs, also made of Delrin. This setup had a much larger 16 cm$^2$ viewing port. The sample holder required 25cm$^2$ active area MEAs from IonPower with the same Nafion 115 MEA and used copper current distributors to contact the ACL directly. It was determined that the copper corroded during the electrolysis process which would result in failure of the MEA. Experimenting with this setup was difficult since MEA samples needed to be cut to fit in the setup.
Figure B.3: Design of first iteration of the sample holder used in the tank.

The sample holder described in chapters 3 and 4 is a second iteration this design and was developed so MEAs could be transferred directly from the electrolyzer test station from sample holder in the tank. Additionally a smaller viewing area was used to since a larger viewing area did not offer any advantages in viewing bubbles and statistical analysis of bubble distribution on the ACL surface. Consequently this eliminated the need to larger area active areas where a large portion of the active area was not included in the reaction interface.

B.2 Cell Resistance

Cell resistance was measured during assembly as a benchmark test to ensure consistency in the assembly of cells when using a new MEA using the gasketing and other cell components listed in Table 3.1. As the SPE is hydrated during the electrolysis process the resistance of the MEA will change. The cell resistance for new MEAs was measured with a Hioki® HiTester while cells were compressed in the Enerpac. Resistance in table B.1 represent the average resistance measured across current distributors that the cell should be when assembled to ensure consistency when conditioning new MEAs.
Table B.1: Resistance through current distributors for the sample holder compressed to 400psi.

<table>
<thead>
<tr>
<th>Cell resistance, ohm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre PTL</td>
</tr>
<tr>
<td>Expanded Ti mesh PTL</td>
</tr>
</tbody>
</table>

The resistance for the fibre PTL was based on prior knowledge of assembling a PEM electrolyzer cell. The resistance for the expanded Ti mesh PTL was found through experimentally replicating performance results with the PEM electrolyzer test station. Resistances differing from these values could indicate improper assembly.

C  Image Processing Code

C.1  Tank Image Fiji Processing

The following code was used in Fiji to pre-process and analyze image files. The code uses the first image as a reference image.

```plaintext
//Splitting channels and subtracting the first image from the individual channel
//Duplicate the original stack to Test.tif
run("Duplicate...","title=Test.tif duplicate");
selectWindow("Test.tif");
//setMinAndMax(74,184);
//run("Apply LUT", "stack");
run("Split Channels");

//subtracting the first image with the green stack
selectWindow("Test.tif (green)";
run("Duplicate...", "title=Imggreen");
```
imageCalculator("Subtract create stack", "Test.tif (green)", "Imggreen");
selectWindow("Result of Test.tif (green)");
run("Delete Slice");

// using the green channel and setting the B&C
run("Duplicate...", "title=Test_step2.tif duplicate");
selectWindow("Test_step2.tif");
setMinAndMax(0,72);
run("Apply LUT", "stack");
run("Enhance Contrast...", "saturated=0.3 process_all");
run("Brightness/Contrast...");
// setMinAndMax(0,119); // Only for the Expanded PTL

C.2 Reference Image Creation in MATLAB

MATLAB code was used for each 340 slice TIFF image stack to create a reference image used to remove background features where bubbles are not present in the image for both the channel-less and optical channel electrolyzer setups. This technique relies on the high contrast background and the low contrast of the bubbles. By taking the average pixel value of 8-bit images over the stack of images the background is created by effectively washing out the bubbles. The MATLAB code to make a reference image is shown below.

```matlab
im_stack = [];
info = imfinfo('TestImagesShort.tif');
for i = 1:length(info)
    im_stack = cat(3, im_stack, imread('TestImagesShort', i));
end

im_out = [];
```
im_avg = uint8(floor(mean(im_stack, 3)));  
imwrite(im_avg(:,:,1), 'background.tif', 'Compression', 'none')

C.3 Channel-less Cell Fiji Image Processing

Files were pre-processed and particles analyzed in Fiji using the code below.

makeLine(1119, 351, 1128, 1773);
run("Set Scale...");
run("Set Scale...", "distance=1395.05 known=18.5 pixel=1 unit=mm global");

run("Close-", "stack");
// first channel
makeRectangle(777, 351, 141, 1395);
// second channel
// makeRectangle(1062, 354, 129, 1386);

run("Set Measurements...", "area mean standard bounding fit feret's kurtosis area_fraction limit redirect=None decimal=2");
run("Analyze Particles...", "size=8-Infinity pixel circularity=0.05-1.00 show=Ellipses display clear include summarize stack");

C.4 Optical Channels Image Processing

Files were processed in MATLAB and Fiji. Image pre-processing code in MATLAB is shown below.

im_stack = [];
info = imfinfo('TestStack.tif');
for i = 1:length(info)
    im_stack = cat(3, im_stack, imread('TestStack', i));
end
for i = 1:size(im_stack, 3)
    im_raw = im_stack(:,:,i);
    figure
    imshow(im_raw)
    im_diff = im_raw - im_avg;
    figure
    imshow(im_diff)
    im_contrast = imadjust(im_diff);
    figure
    imshow(im_contrast)
    im_filt = imgaussfilt(im_contrast, 2);
    figure
    imshow(im_filt)
    im_contrast2 = imadjust(im_filt);
    figure
    imshow(im_contrast2)
    im_binary = uint8(255*imbinarize(im_contrast2, 0.15));
    figure
    imshow(im_binary)
    im_out = cat(3, im_out, im_binary);
end

v = VideoWriter('myFile.avi');
v.FrameRate = 10;
open(v)
for i = 1:size(im_out, 3)
    writeVideo(v, im_out(:,:,i))
end

close(v)

%%% creating matlab figure
%figure
for i = 1:size(im_out, 3)
    clf
    imshow(im_out(:,:,i))
    drawnow
    pause(0.1)
end

imwrite(im_out(:,:,1), 'out_stack.tif', 'Compression','none')
for i = 2:size(im_out, 3)
    imwrite(im_out(:,:,i), 'out_stack.tif', 'writemode', 'append', 'Compression','none');
end

The code uses in Fiji to pre-process and analyze particles is shown below. The line command uses the length of the right channel as to set the scale of the images. The rectangle command defines each channel as the regions of interest.

makeLine(1119, 351, 1128, 1773);
run("Set Scale...");
run("Set Scale...", "distance=1395.05 known=18.5 pixel=1 unit=mm global");

run("Close-", "stack");
// first channel
makeRectangle(777, 351, 141, 1395);
// second channel
//makeRectangle(1062, 354, 129, 1386);
run("Set Measurements...", "area mean standard bounding fit feret's kurtosis area_fraction limit redirect=None decimal=2");
run("Analyze Particles...", "size=8-Infinity pixel circularity=0.05-1.00 show=Ellipses display clear include summarize stack");