Novel Carbon-based Electrode Materials for Up-scaled Microfluidic Fuel Cells

by

Dillon Adam Fuerth

A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science

Mechanical and Industrial Engineering
University of Toronto

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Abstract

In this work, a MFC fabrication procedure including two non-conventional techniques (partial baking and cap-sealing) were employed for the development of an up-scaled microfluidic fuel cell (MFC). Novel carbon-based electrode materials were employed, including carbon foam, fibre, and cloth, the results from which were compared with traditionally-employed carbon paper. The utilization of carbon cloth led to 15% of the maximum power that resulted from carbon paper; however, carbon fibre led to a 24.6% higher power density than carbon paper (normalized by electrode volume). When normalized by projected electrode area, the utilization of carbon foams resulted in power densities up to 42.5% higher than that from carbon paper. The impact of catalyst loading on MFC performance was also investigated, with an increase from 10.9 to 48.3 mgPt cm$^{-2}$ resulting in a 195% increase in power density.
Acknowledgments

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To my sister, Stacey Fuerth, who gave me my personality and taught me to laugh at whatever life throws my way, good or bad.

To my roommates, Alex LaPlante, Oren Kraus, and Chris Caputo, thanks for putting up with me and making our house a home. Now that I am finished, I will clean the bathroom, like I promised two years ago.

To Johnny and Mary, thank you for helping me keep food on my plate and provide me with a place to get away.

Thank you to the University of Toronto, NSERC, and the David Sanborn Scott Fellowship for all of your financial support.
Dedication

To my family,

who continually remind me of what is truly important in life.
# Table of Contents

Acknowledgments........................................................................................................ iii

Dedication...................................................................................................................... iv

Table of Contents.......................................................................................................... v

List of Tables ................................................................................................................ ix

List of Figures ................................................................................................................ x

Abbreviations & Nomenclature ....................................................................................... xiii

Chapter 1 Introduction into Microfluidic Fuel Cells ....................................................... 1
  1.1 Microfluidic Fuel Cells in 2012.............................................................................. 1
  1.2 MFC Commercialization Barriers........................................................................ 1
  1.3 Proposal of Novel Electrode Materials for Volumetrically Up-scaled MFCs........... 2
  1.4 Resulting Contributions ....................................................................................... 3
    1.4.1 Submitted Manuscripts .............................................................................. 3
    1.4.2 Oral Presentations ...................................................................................... 3
    1.4.3 Conference Papers ....................................................................................... 3
    1.4.4 Poster Presentations ..................................................................................... 4
  1.5 Thesis Organization ............................................................................................... 4

Chapter 2 Background and Literature Review............................................................... 6
  2.1 Microfluidic Fuel Cell Fundamental Operation.................................................. 6
  2.2 Up-scaling Limitations with the Y-channel Architecture ...................................... 6

Chapter 3 Experimental Setup and Results ................................................................... 9
  3.1 Experimental Setup.............................................................................................. 9
  3.2 Results ................................................................................................................ 9

Chapter 4 Conclusion..................................................................................................... 11
  4.1 Summary ............................................................................................................. 11
  4.2 Future Work ........................................................................................................ 11

Appendices ...................................................................................................................... 13

References ...................................................................................................................... 15

Abstract ......................................................................................................................... 19
3.4.2 Vanadium Impurity........................................................................................................... 23

3.5 Conclusions................................................................................................................................. 23

3.6 Tables............................................................................................................................................. 24

3.7 Figures........................................................................................................................................... 27

Chapter 4 Up-scaled Microfluidic Fuel Cells with Porous Flow-through Electrodes .............. 36

4.1 Introduction.................................................................................................................................. 36

4.2 Motivation and Objectives .......................................................................................................... 36

4.3 Experimental Preparation............................................................................................................ 37
  4.3.1 MFC Fabrication.................................................................................................................... 37
  4.3.2 Fuel and Oxidant Preparation .............................................................................................. 37
  4.3.3 Catalyst Preparation.............................................................................................................. 38
  4.3.4 Electrode Preparation .......................................................................................................... 38
  4.3.5 Fuel Cell Diagnostics.......................................................................................................... 40

4.4 Results and Discussion ................................................................................................................ 40
  4.4.1 Polarization Sweep ............................................................................................................... 40
  4.4.2 Polarization Losses ............................................................................................................. 40
  4.4.3 Projected Electrode Area and Electrode Volume Normalization ........................................ 41
  4.4.4 Normalization by Projected Electrode Area ...................................................................... 41
  4.4.5 Normalization by Electrode Volume .................................................................................... 42
  4.4.6 Validity of Normalizations Based on Electrode Volume ..................................................... 42
4.4.7 Catalyst Loading ................................................................. 42

4.4.8 Electrode Material Evaluation ........................................... 43

4.5 Conclusions ........................................................................ 44

4.6 Tables ............................................................................... 46

4.7 Figures .............................................................................. 49

Chapter 5 Conclusions ............................................................ 57

Chapter 6 Future Work ............................................................ 59

References ............................................................................. 60
List of Tables

Table 2.1  Summary of MFC architecture advancements in literature that influenced the architecture in this thesis.  Pg. 13

Table 3.1  Summary of photolithography fabrication soft bake times, UV energy exposure amounts, and post exposure bake times for each layer of the main master and alternative master.  Pg. 24

Table 3.2  Summary of the physical parameters used to normalize the microfluidic fuel cell performance for Toray carbon paper and 100 PPI carbon foam.  Pg. 25

Table 3.3  Summary of each microfluidic fuel cell performance normalized by projected electrode area and electrode volume.  Pg. 26

Table 4.1  Summary of the physical parameters used to normalize the microfluidic fuel cell performance for each carbon-based electrode material.  Pg. 46

Table 4.2  Summary of each microfluidic fuel cell performance normalized by projected electrode area and electrode volume.  Pg. 47

Table 4.3  Comparison of microfluidic fuel cell power densities previously presented in literature.  Pg. 48
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Schematic of a Y-channel architecture microfluidic fuel cell.</td>
<td>14</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Schematic showing the projected area of an electrode, which is considered the surface of the electrode in the same plane as fuel and oxidant flow.</td>
<td>15</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Scanning electron microscopy (SEM) images of (a) carbon paper and (b) 100 PPI carbon foam at 150X magnification.</td>
<td>27</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Schematic of the microfluidic fuel cell architecture: (a) assembled and (b) expanded.</td>
<td>28</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>Graphical representation of the main master fabrication including (a)-(c) the seed layer, (d)-(f) first feature layer, and (g)-(i) second feature layer.</td>
<td>29</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>Photomasks used to create the (a) first and (b) second feature layers of the microfabricated master.</td>
<td>30</td>
</tr>
<tr>
<td>Figure 3.5</td>
<td>Completed master for the microfluidic fuel cell channel fabrication developed using photolithography techniques.</td>
<td>31</td>
</tr>
<tr>
<td>Figure 3.6</td>
<td>Photograph of a completed microfluidic fuel cell from: (a) bottom view and (b) top view.</td>
<td>32</td>
</tr>
<tr>
<td>Figure 3.7</td>
<td>Photograph of the disassembled electrolytic flow cell used to separate the bulk vanadium solution into respective fuel and oxidant species.</td>
<td>33</td>
</tr>
<tr>
<td>Figure 3.8</td>
<td>Fuel ($V^{2+}$) indicated by purple (left) and oxidant ($VO_2^{+}$) indicated by blue (right) both suspended in a sulfuric acid electrolyte.</td>
<td>34</td>
</tr>
</tbody>
</table>
Figure 3.9  Polarization and power density curves normalized by (a) projected electrode area and (b) electrode volume. Pg. 35

Figure 4.1  Schematic of the microfluidic fuel cell architecture: (a) assembled and (b) expanded. Pg. 49

Figure 4.2  Photograph of a completed microfluidic fuel cell from: (a) top view and (b) bottom view. Pg. 50

Figure 4.3  Fuel (HCOOH) indicated by clear (left) and oxidant (KMnO₄) indicated by purple (right) both suspended in a sulfuric acid electrolyte. Pg. 51

Figure 4.4  Scanning electron microscopy (SEM) images of carbon based electrode materials including: (a) 80 PPI carbon foam and (b) 100 PPI carbon foam, (c) carbon fibre, (d) carbon paper, and (e) carbon cloth at 50X magnification. In (d) and (e), the porous surface of the sample stage is shown but can be ignored. Pg. 52

Figure 4.5  Polarization curves normalized by: (a) projected electrode surface area and (b) electrode volume for: 80 PPI carbon foam, 100 PPI carbon foam, carbon fibre, carbon paper, and carbon cloth. Pg. 53

Figure 4.6  Power density curves normalized by: (a) projected electrode surface area and (b) electrode volume for: 80 PPI carbon foam, 100 PPI carbon foam, carbon fibre, carbon paper, and carbon cloth. Pg. 54

Figure 4.7  Polarization and power density curves for four microfluidic fuel cells employing 80 PPI carbon foam with varied platinum black catalyst loadings. Pg. 55
Figure 4.8 Maximum power density of four microfluidic fuel cells employing 80 PPI carbon foam with varied platinum black catalyst loadings.
Abbreviations & Nomenclature

**Chemical formulas**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>e⁻</td>
<td>Electron</td>
</tr>
<tr>
<td>H⁺</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HCOOH</td>
<td>Formic acid</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>Manganese</td>
</tr>
<tr>
<td>MnO₂(s)</td>
<td>Manganese (IV) oxide</td>
</tr>
<tr>
<td>MnO₄⁻</td>
<td>Permanganate</td>
</tr>
<tr>
<td>V²⁺</td>
<td>Vanadium (II)</td>
</tr>
<tr>
<td>V³⁺</td>
<td>Vanadium (III)</td>
</tr>
<tr>
<td>VO₂⁺</td>
<td>Vanadium (IV) oxide</td>
</tr>
<tr>
<td>VO²⁺</td>
<td>Vanadium (V) oxide</td>
</tr>
<tr>
<td>VOSO₄·XH₂O</td>
<td>Vanadium (IV) sulfate oxide hydrate</td>
</tr>
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</table>

**Acronyms**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDM</td>
<td>Electrode discharge machining</td>
</tr>
<tr>
<td>MFC</td>
<td>Microfluidic fuel cell</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PEM</td>
<td>Polymer electrolyte membrane</td>
</tr>
<tr>
<td>PPI</td>
<td>Pore per inch</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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**Variables**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ</td>
<td>Diffusely mixed region width</td>
</tr>
<tr>
<td>D</td>
<td>Species diffusivity</td>
</tr>
<tr>
<td>h</td>
<td>Centre channel height</td>
</tr>
<tr>
<td>U</td>
<td>Fluid velocity</td>
</tr>
<tr>
<td>x</td>
<td>Position along centre channel</td>
</tr>
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</table>
Introduction into Microfluidic Fuel Cells

1.1 Microfluidic Fuel Cells in 2012

Due to their compact design and high energy densities, microfluidic fuel cells (MFCs) provide a promising solution to the increasing power demand of microscale electronics. Since the initial development of MFCs in 2002 [1, 2], advancements have led to improved quality, positioning them on the brink of commercialization. With continued development, they will be suited for powering many small scale technologies including laptops, cell phones, global positioning system devices, and lab-on-chip systems.

1.2 MFC Commercialization Barriers

Research in the area of MFCs has grown in recent years [3]; however, a few remaining challenges must be addressed before they can be commercialized, such as overcoming: high ohmic resistances, mass transport issues, lack of scalability, and low overall power. These issues stem from the properties of various components of the MFC system, such as: the electrodes, electrical interconnects, choice of fuel and oxidants, catalysts, and architectures.

High ohmic losses result from the combined resistance between the electrolyte, electrodes, and exterior electrical connections [4]. The development of electrodes, which exhibit low electrical resistance while providing an effective platform to connect to external components, will help to reduce these ohmic losses.

The electrode plays a vital role in energy conversion, since MFCs are driven by surface-based chemical reactions and the microstructure of the electrode directly influences the accessibility of internal surface areas to the fuel and oxidant species. Mass transport issues can potentially be alleviated by tailoring the geometry of the electrodes [5].

The electrode also plays a crucial role in the up-scaling of single MFCs. Increasing the electrode size enables leads to an increase in the total active surface area and ultimately an increase in the overall power [6]. Traditionally, carbon paper has commonly employed as a MFC electrode material, which is commercially available at thicknesses of approximately 100 - 370 μm. Electrode materials that allow for a three-dimensional increase in size and can be scaled
volumetrically will lead to a greater overall power.

The most commonly employed MFC architecture is the Y-channel architecture, but as architectures are evolving, a need to develop new evaluation techniques in order to effectively characterize performance between architectures is required. Traditionally, MFC performance has been normalized with respect to the electrode surface area. When employing novel architectures that scale the MFC vertically, it is difficult to use these traditional techniques. A normalization technique based on electrode volume had been previously suggested [7], but not presented.

1.3 Proposal of Novel Electrode Materials for Volumetrically Up-scaled MFCs

The significance of the MFC electrode on performance is evident, as outlined in Section 1.2; however, few authors have conducted research that has employed materials other than carbon paper or graphite [5, 8, 9]. In particular, the use of carbon paper is likely borrowed from their well-established use in polymer electrolyte membrane fuel cells. In this thesis, the employment of carbon foam as a novel MFC electrode material is proposed to address several of the remaining MFC barriers to commercialization, including high ohmic resistance, mass transport issues, lack of scalability, and low overall power. Carbon foam exhibits high mechanical strength and low electrical resistance. Its microstructure may be potentially prescribed, for tailored pore sizes, connectivity, and tortuosity, designed to reduce mass transport limitations. In this thesis, the performance of carbon foam is compared to traditionally-employed carbon paper to validate its applicability as an electrode material in MFCs. The performance is normalized by electrode volume in order to elucidate the impact of up-scaling the MFC. The traditional means of normalizing the performance by electrode area is also presented, and a discussion is provided on the implications of area- versus volume-based normalizations.

Carbon foam is first validated as an appropriate electrode material, after which it is employed in a novel up-scaled architecture to achieve greater overall power. Two additional novel electrode materials employed in this up-scaling study include carbon fibre and carbon cloth. Carbon fibre electrodes are bundles of densely packed fibres. Carbon cloth also has a dense microstructure that contains woven carbon fibres. These electrode materials were selected to support the investigation of the effect of electrode geometry on performance. The effects of catalyst loadings on carbon foam electrodes will also be investigated.
1.4 Resulting Contributions

The work presented in this thesis resulted in the following contributions:

1.4.1 Submitted Manuscripts


1.4.2 Oral Presentations

- Fuerth, D., Bazylak, A. "Partial developing, partial baking, and cap sealing techniques in microfluidic fuel cells." 2011 Foundry Small Talk Seminar, University of Toronto, Toronto, ON, August 26, 2011. (Competition winner)

1.4.3 Conference Papers

- Fuerth, D., Bazylak, A. “Properties and performance of various carbon foam structures in

1.4.4 Poster Presentations


1.5 Thesis Organization

The thesis begins with an explanation of the fundamental principles and components associated with MFCs in Chapter 2. The chapter then leads into the history of MFCs, highlighting notable research in the fields of architecture development, MFC stacks, and electrode materials that are directly related to the work in this thesis.

After an understanding of MFC principles and the state of research have been established, a discussion of previous work is presented in Chapter 3. Preliminary experiments in this chapter were employed to compare the performance of carbon foam with carbon paper and to validate its applicability in MFCs. In addition, a discussion is also provided of the comparison between area- and volume-based performance normalization.

In Chapter 4, carbon foam is employed in a volumetrically up-scaled architecture. Carbon fibre, carbon cloth, and carbon paper are also employed in the up-scaled architecture, and a comparison is performed. The performances of all MFCs are evaluated based on both area-based and volume-based normalization, and the validity of electrode volume normalization technique is critically analyzed. The effects of catalyst loading on MFC performance is also investigated in Chapter 4.
A summary of the thesis and conclusions are presented in Chapter 5, and future work is suggested in Chapter 6.
Background and Literature Review

2.1 Microfluidic Fuel Cell Fundamental Operation

The first microfluidic fuel cells (MFCs) were introduced in 2002 [1, 2], and since then, all MFCs have been governed by common fundamental operating principles, including i) the continual supply of fuel and oxidant dissolved in a liquid electrolyte, ii) micro-scale features that promote laminar flow at low Reynolds numbers, and iii) a liquid-liquid interface that facilitates ionic transport. MFCs are advantageous due to the fact that they may operate with a variety of fuels, such as: vanadium redox species [1, 2, 5-7, 10-13], formic acid [9, 14-25], methanol [8, 26, 27], ethanol [26], hydrazine [26], sodium borohydride [26], hydrogen [18, 28], and formate [29] paired with various oxidants, including: vanadium redox species [1, 2, 5-7, 10-13], potassium permanganate [9, 14, 19], oxygen [15-25, 27, 28], and hypochlorite [29].

The original MFC architecture was the Y-channel architecture, which since originally introduced [1, 2] has been the most replicated architecture in both computational [15-17, 22, 30] and experimental studies [8, 11, 19, 20, 24, 27, 31-33]. The Y-channel architecture consists of two inlet channels connected to a central main channel before leading to a single outlet. Along opposite main channel walls, an anode and cathode are fixed and electrically connected to an external electrical system. Fuel and oxidant are each dissolved in an electrolyte species and fed into the MFC through respective inlets where they meet in the main channel before flowing to the outlet. Due to the micro features of the MFC, the two fluids remain separated in independent laminar streams. The separation between the two fluids eliminates the need for a physical membrane. The physical components are presented in Figure 2.1.

As the fuel and oxidant species react at the electrode surfaces, electrons are collected on the anode, and electrical current passes through external wires to the cathode. As electrons are liberated from the fuel and oxidant species, the liberated ions are free to travel through the electrolyte species before reaching the outlet.

2.2 Up-scaling Limitations with the Y-channel Architecture

The size of the Y-channel architecture has restrictions, such as the depletion boundary layer and
the diffusively mixed region, which will be discussed in this section, that affect the performance, limiting its ability to be up-scaled.

2.2.1 Depletion Boundary Layer

As fuel and oxidant flow through the Y-channel MFC, a depletion boundary layer develops along the electrodes, as seen in Figure 2.1. Since MFCs depend on surface-based chemical reactions, the fuel and oxidant within the immediate vicinity of the electrodes are consumed first. Fresh fuel and oxidant cannot readily replenish these depletion regions due to diffusion limitations. As the fuel and oxidant flow downstream, the depletion boundary layer becomes more prominent and reduces the rate of fuel utilization.

Investigations to mitigate the effects of the depletion boundary layer at the electrode surface have been performed by i) adding multiple inlets to replenish depleted regions [17, 31], ii) adding multiple outlets to remove depleted regions [31], and iii) the induction of irregular flow patterns using herringbone ridges [31] or obstacles [22]. These approaches mitigated the effects of the depletion layer at the cost of complexity, which may pose severe challenges if up-scaled.

2.2.2 Diffusively Mixed Region

As fuel and oxidant flow down the main channel of a Y-channel MFC, the bulk of the fluid remains separated; however, diffusive mixing occurs amongst the species creating a diffusively mixed region, as seen in Figure 2.1. This diffusion region neutralizes the chemical potential between the fuel and oxidant and leads to fuel crossover, both situations hindering the performance of the MFC. The width of this diffusively mixed region, \( \delta \), is governed by the equation [1, 34]:

\[
\delta \approx \left( \frac{DHx}{U} \right)^{1/3}
\]

where \( D \) is the species diffusion rate, \( H \) is the height of the main channel, \( x \) is the position along the main channel and \( U \) is the velocity of the fluid. This equation shows that up-scaling of a Y-channel MFC by increasing channel height or length will lead to a larger diffusive mixing region. Since the electrodes sit on either side of the channel, limiting the physical boundaries of the main
channel also limits the ability to increase electrode size.

The diffusive mixing region has been predominately mitigated through flow channel geometry modifications [9, 15-17, 22, 30]. A decrease in the height of the centre channel has shown to limit the growth of the diffusively mixed region and offers little complications to the fabrication of the MFC [9, 16, 17, 22]. Tapering the height of the centre channel, which leads to a velocity increase towards the outlet, has been shown to control the width of the diffusively mixed region [16, 17]. It has also been proposed that the introduction of a third electrolyte stream between the fuel and oxidant [15, 17, 18, 22, 28] aids in the separation of the species, but at the cost of added complexity.

2.3 Architecture Development: From Y-channel to Flow-through

A novel architecture was presented by Kjeang et al. [6], which illustrated the effect of increased surface area within a single cell. The cell consisted of 29 graphite rod electrodes arranged in a grid formation, parallel to the flow direction of the fuel and oxidant with an active electrode area of 7.3 cm$^2$. The MFC yielded a high maximum overall power of 28 mW but with a low maximum power density of 3.8 mW cm$^{-2}$. Furthermore, the increased active electrode area resulted in a 78\% fuel utilization, which was the highest reported fuel utilization at the time. An additional Y-channel architecture MFC was constructed using identical materials, and a low maximum overall power of 5.8 mW and high maximum power density of 35 mW cm$^{-2}$ were achieved (active electrode area of 0.165 cm$^2$). Their study showed that larger overall power outputs may be obtained from single MFCs with an increased electrode surface area, which may ultimately lead to a more compact MFC stacked system. They also showed that the traditional method of electrode area normalization may not lead to an accurate portrayal of performance. Several Y-channel MFCs would be required to provide the same overall power as a single graphite rod MFC, although the Y-channel cell appears to significantly out-perform the graphite rod MFC, when based on surface area normalization.

Solloum et al. [14] continued the development of the Y-channel architecture with the implementation of a circular pattern, whereby fuel and oxidant flowed radially outward through porous electrodes to capitalize on the active internal electrode surface areas. Fuel was introduced initially in the centre of the MFC, where it diffused through the circular anode. At the outside edge of the anode, the oxidant was introduced. Expired fuel and fresh oxidant passed through the
cathode where a selective catalyst allowed only oxidant reactions to occur. The MFC performance was normalized by a projected electrode area, resulting in a maximum power density of 2.8 mW cm\(^{-2}\) and fuel utilization of 58%. The projected electrode area is considered as a surface of the electrode that is in the same plane as fuel and oxidant flow, as illustrated in Figure 2.2. This normalization technique did not account for the internal surface area of the electrode material, but the internal surface area aided performance due to an increase of reaction sites. This MFC demonstrated the benefits of utilizing the internal electrode microstructure for increased performance.

Kjeang et al. made another significant advancement in architecture development with the presentation of a flow-through MFC architecture [7]. The fuel and oxidant were forced through the anode and cathode, respectively, before reaching the centre channel. Fuel and oxidant flowed in laminar in nature to the outlet of the MFC. The architecture capitalized on the internal surface area of the electrodes and fuel utilization was achieved before the fuel and oxidant made contact. When compared to previously presented architectures at the time, the authors reported significantly high power densities at high flow rates (120 mW cm\(^{-2}\) at 300 μL min\(^{-1}\)) and the highest reported fuel utilization at low flow rates (94% at 1 μL min\(^{-1}\)). The cell was normalized by the projected area of the electrodes, not taking into account the internal surface area of the electrode. The design of this MFC led to a reduction of issues with low power density and mass transport limitations, which had been prevalent in previous MFCs.

Since MFCs are driven by surface-based reactions, performance was improved with the development of the flow-through porous electrode architecture when compared to the original Y-channel architecture (while retaining a similar overall volume). The utilization of internal electrode surface areas to react fuel and oxidant independently prior to converging in the centre channel eliminates issues of mixing regions and depletion boundary layers. Since the majority of chemical reactions take place internally rather than on the electrode outer surface, the microstructure of the electrode is significant; however, the flow-through architectures that have been presented in the literature have dealt exclusively with Toray carbon paper as the electrode material [7, 13, 29, 35]. To the best of the author’s knowledge, there are no other reports in the literature of alternative electrode materials for flow-through architectures.


2.4 Microfluidic Fuel Cell Stacks

Microfluidic fuel cells are limited by their low overall power outputs [36]. One way to increase the power output is to increase the fuel and oxidant flow rate [6, 7, 10, 11, 14, 19, 29]. However, an increase in fuel and oxidant flow rates results in a decrease in fuel utilization [6, 7, 10, 11, 14, 29] since the species pass by the electrodes quickly limiting the diffusion and reaction times needed to fully utilize the fuel contained in the streams.

Salloum and Posner presented a counter-flow MFC architecture that held fuel and oxidant separated by a third electrolyte stream [12]. They operated the MFC at high flow rates to achieve high power densities and low fuel utilizations; however, since the fuel and oxidant remained separated, they may have been reused at a slightly lower concentration. Future work by Salloum and Posner used this third electrolyte stream technique to present the first MFC stacked system [10]. A multi-pass design allowed for two anode and cathode pairs to be electrically connected in parallel while fuel and oxidant flow were directed in series. Fuel and oxidant were reused between electrode pairs by introducing a third inlet electrolytic flow to ensure segregation. The peak power density increased from 7.5 to 16 mW cm$^{-2}$ when the number of passes doubled and fuel utilization increased from 6 to 11%.

Moore et al. presented a plate-frame flow-through MFC stack system [5], which was the first MFC system to expand vertically rather than horizontally on a chip. The stacked system diffused fuel through the anode from the bottom of the cell and oxidant through the cathode from the top of the cell. The fuel and oxidant met in-between the anode and cathode for ionic transport before products exited from a common waste outlet. A single cell of this architecture achieved a peak power density of 5.8 mW cm$^{-2}$ at a flow rate of 50 μL min$^{-1}$ and a fuel utilization of 66% at 16 μL min$^{-1}$. A summary of the MFC architectures which influenced the architectures in this thesis is presented in Table 2.1.

2.5 Tailored Electrodes and Carbon Foam

Previous work in novel single cell architectures and stacked systems have demonstrated the benefits of utilizing the internal surface area of electrodes with flow-through systems [5, 7, 10, 12, 14, 29, 37, 38]. Typically, MFCs have employed either graphite [6, 20, 24, 25, 27], micropatterned electrodes [8, 9], or more commonly, carbon paper [5, 7, 10-12, 14, 21, 26, 29, 37, 38].
as the electrode material, but with the emergence of flow-through architectures, researchers have begun to investigate new electrode materials.

2.5.1 Tailored Electrode Materials for Flow-through Architectures

Moore et al. demonstrated the importance of internal electrode microstructure by tailoring a polyimide precursor for employment in their plate-frame flow-through microfluidic fuel cell [5]. They used a CO₂ laser cutter/engraver to cut the plate electrode into shape before puncturing single holes through the material with the laser. When comparing the performance of the tailored electrode to the commonly employed carbon paper, a 140% increase in power density was observed. They predicted a further increase in power density was possible with an increase of holes through the tailored polyimide as it would decrease pumping losses and increase active surface area.

2.5.2 Carbon Foam as a Potential Electrode Material for Flow-through Architectures

Carbon foam is highly promising as an electrode material when paired with the vanadium redox species, which reacts naturally with bare carbon, eliminating the need for an additional catalyst. Carbon foam exhibits high mechanical strength and conductivity [39]. ERG Aerospace Corporation produces commercially available carbon foam with 520 Pa compressive strength and 0.323 ohm cm bulk resistivity [40]. Preparation of carbon foam requires a carbon-based material, catalyst, bubbling agent (inert gas such as nitrogen or argon), and resin to monitor the bubbling agent [41]. With alterations of the specific materials and concentrations of these materials, the pore sizes can be adjusted. Pores diameters may be as small as 100 – 300 nm [42] or more moderate sizes of 50 – 400 μm [43]. This pore size alterability may reduce mass transport limitations by creating highly permeable pore networks.

2.6 Conclusions

In this chapter, the fundamental operation of the Y-channel MFC was presented, and a discussion of its barriers to commercialization were presented. These barriers included the growth of the depletion boundary layers and the diffusive mixing region. The chronological development of the MFC from the Y-channel architecture to the flow-through architecture was outlined. The performance of MFCs improved with the introduction of the flow-through architecture, due to
the exploitation of internal electrode surface areas. A summary of MFC stacked systems for higher overall power outputs was presented, combined with the potential use of novel carbon foam.
### 2.7 Tables

<table>
<thead>
<tr>
<th><strong>Author</strong></th>
<th><strong>Year</strong></th>
<th><strong>Significance of Contribution</strong></th>
<th><strong>Electrode Material</strong></th>
<th><strong>Fuel and Oxidant</strong></th>
<th><strong>Maximum Power Density (mW cm(^{-2}))</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Kjeang</td>
<td>2007</td>
<td>Graphite rod electrode MFC with increased overall power due to increased electrode surface area</td>
<td>Graphite rods</td>
<td>Vanadium species</td>
<td>3.8</td>
</tr>
<tr>
<td>Salloum</td>
<td>2008</td>
<td>Sequential flow MFC which capitalized on internal electrode surface area</td>
<td>Carbon paper</td>
<td>Formic acid and potassium permanganate</td>
<td>2.8</td>
</tr>
<tr>
<td>Kjeang</td>
<td>2008</td>
<td>Flow-through MFC which capitalized on internal electrode surface area and consumed chemical species prior to ionic transport</td>
<td>Carbon paper</td>
<td>Vanadium species</td>
<td>120</td>
</tr>
<tr>
<td>Salloum</td>
<td>2010</td>
<td>Counter-flow MFC with fuel and oxidant separated by an electrolyte stream</td>
<td>Carbon paper</td>
<td>Vanadium species</td>
<td>5.1</td>
</tr>
<tr>
<td>Salloum</td>
<td>2011</td>
<td>MFC stacked system with fuel and oxidant separated by an electrolyte stream for reuse in successive MFCs</td>
<td>Carbon paper</td>
<td>Vanadium species</td>
<td>16</td>
</tr>
<tr>
<td>Moore</td>
<td>2011</td>
<td>Plate frame flow-through MFC expanded vertically rather than horizontally for incorporation into stacked systems</td>
<td>Tailored polyimide precursor</td>
<td>Vanadium species</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of MFC architecture advancements in literature that influenced the architecture in this thesis.
2.8 Figures

Figure 2.1: Schematic of a Y-channel architecture microfluidic fuel cell.
Figure 2.2: Schematic showing the projected area of an electrode, which is considered the surface of the electrode in the same plane as fuel and oxidant flow.
Validity of Carbon Foam as a Viable MFC Electrode Material

3.1 Introduction

In this chapter, carbon foam is presented as a potential electrode material for microfluidic fuel cells (MFCs) and its performance is compared to carbon paper. An in-depth methodology to fuel cell construction and chemical preparation is established, which encompasses the non-conventional fabrication steps of partial baking and cap sealing. The performance normalization technique based on electrode volume is also presented. This is compared to traditional normalization with respect to the projected electrode area.

3.2 Motivation and Objectives

Microfluidic fuel cells hold the potential to meet our rapidly growing need for micro-scale energy conversion devices due to their high surface area to volume ratios. The MFC electrodes are paramount components, since the performance is driven by chemical reactions that occur at the surface of the electrodes. Therefore, the modification of the conductivity, porosity, permeability, and pore structure of the electrode materials is key for optimizing performance. Traditionally, MFCs have been employed with either graphite [6, 20, 24, 25, 27], or more commonly, Toray carbon paper as the standard electrode material [5, 7, 10-12, 14, 21, 26, 29, 37, 38], with few researchers developing other electrode materials [8, 9]. The motivation of this research is to explore novel MFC electrode materials that exhibit beneficial characteristics to specific applications, such as size limitations or specific power output requirements. Carbon foam is a commercially available, novel MFC electrode material, which may meet these specific requirements since the pore size and distribution may be tailored during the manufacturing process.

The main objective of this chapter is to evaluate whether carbon foam may be used as a novel MFC electrode material by comparing it to commonly employed carbon paper. Both carbon-based electrodes are employed in a previously presented flow-through MFC architecture [7]. This flow through architecture provided high power densities when compared to classical Y-channel architectures as the challenges with mass transport, boundary layer, and fuel crossover were mitigated with increased active electrode surface areas. Vanadium redox species were
employed as fuel and oxidant since they naturally react on bare carbon. This natural reaction eliminates the need for a catalyst.

A secondary objective in this chapter was to introduce a normalization technique based on electrode volume in order to more accurately characterize MFC performance when compared to standard projected electrode area techniques. Standard manufactured sheets of Toray carbon paper reach a maximum thickness of 370 μm [44], while the structural stability of carbon foam allows for a minimal dimension of approximately 1000 μm (100 PPI carbon foam lower limit). In light of these differing material length-scale constraints, the projected electrode area normalization technique does not result in an accurate comparison. In this chapter, both projected electrode area and electrode volume normalizations are presented, and the electrode volume normalization technique is suggested as an additional standard normalization method.

3.3 Experimental Preparation

3.3.1 Electrode Preparation

Toray carbon paper (TGP-H-090 Toray carbon paper, Fuel Cell Earth, Stoneham, MA) was employed as the benchmark electrode material as it has been widely used in MFCs [5, 7, 10-12, 14, 21, 26, 29, 37, 38]. Electrodes were cut with a scalpel from 280 μm thick manufactured sheets to 2 cm x 0.1 cm.

The pore structure of the carbon foam employed was randomly distributed, and the pore size was quantified by the average number of pores per linear inch (PPI). Carbon foam samples with 45 PPI, 80 PPI, and 100 PPI (ERG Materials and Aerospace Corporation, Oakland, CA) were machined to 2 cm x 0.1 cm using electro discharge machining (EDM) to match the projected area of the carbon paper samples. Only 100 PPI carbon foam was successfully machined to 0.1 cm while still maintaining structural stability. The 45 PPI and 80 PPI carbon foams were not used in this experiment due to their fragile structure at 0.1 cm. The 100 PPI electrodes were machined to a thickness of 0.1 cm, since it was not feasible to achieve a thickness similar to carbon paper (280 μm) without compromising the structural integrity of the foam. A summary of the electrode dimensions employed in this work is located in Table 3.1. The microstructures of 100 PPI carbon foam and carbon paper are illustrated in Figure 3.1.
3.3.2 MFC Fabrication

A schematic of the MFC is shown assembled in Figure 3.2 (a) and expanded in Figure 3.2 (b). This MFC consists of two layers on a 1 in x 3 in glass slide support. The top molded layer consists of two inlet channels, two grooves to hold the electrodes in place, and one outlet channel. There are holes pierced through the top molded layer for liquid transport and for electrical connections. The second layer serves as an adhesion layer between the top layer and the supporting glass slide.

3.3.2.1 Master Photolithography Procedure

A main master was created using photolithography techniques that contained a negative imprint of the MFC channels, which are contained in the top molded layer. The fabrication process is outlined in Figure 3.3. Bake times and the amount of ultraviolet (UV) energy exposures of each layer of the master are summarized in Table 3.1.

A seed layer was created to improve the adhesion of the glass slide support of the master to successive feature layers. Approximately 15 mL of SU-8-25 negative photoresist (Micro-Chem, Newton, MA) was poured onto a 1 in x 3 in glass slide and a spin-coater (WS-650SZ-6NPP/LITE, Laurll Technologies Corporation, North Wales, PA) was used to spread the photoresist evenly across the slide to create a seed layer. The rotational speed of the glass slide was ramped for 5 s up to a speed of 500 rpm and held at this speed for 10 s to allow the photoresist to coat the entire glass slide. The rotation speed was increased further over 5 s to a speed of 2000 rpm and held at that speed for 45 s, in order to achieve a 50 μm-thick seed layer [45]. The glass slide and photoresist were soft baked at 65°C for 5 min and 95°C for 15 min to evaporate the solvent and increase the density of the layer [45]. Initially, a lower baking temperature (65°C) was employed in order to minimize large temperature gradients, which typically result in wrinkled surfaces. The seed layer was cured using a flood exposure of 220 mJ cm$^{-2}$ of UV light [45]. The seed layer was post-exposure baked at 65°C for 1 min and 95°C for 4 min to cross-link the exposed layer [45].

The first feature layer was fabricated next, which contained the channel inlets, electrode housing channels, and the centre channel. SU-8-2100 negative photoresist (Micro-Chem, Newton, MA) was spun over the seed layer in a similar fashion. The spinning procedure was identical to the
seed layer, except for the final spin speed was decreased to 1750 rpm to achieve a 150 μm-thick layer [46]. The first feature layer was soft baked at 65°C for 5 min and 95°C for 30 min, exposed to 260 mJ cm⁻² of UV light using the photomask in Figure 3.4 (a) and post-exposure baked at 65°C for 5 min and 95°C for 12 min [46].

The photomask included two crosses (Figure 3.4) used to align the layers of the master that contained channel features; however, these crosses were challenging to identify after successive layers of photoresist had been deposited. In order to overcome this challenge and to easily identify the alignment crosses, each end of the first feature layer was developed using SU-8 developer (MicroChem, Newton, MA), while the channel features remained undeveloped. A black felt tip marker was used to seep ink into the indents of the crosses. These black markings were used to align the channel features through successive photoresist layers.

A second feature layer was fabricated over the first feature layer, which consisted of only the inlet channels and the electrode housing channels. An identical spinning protocol was employed as in the first feature layer to produce another 150 μm-thick layer (300 μm total) to accommodate the carbon paper electrode standard manufactured thickness (280μm). The second feature layer was soft baked at 65°C for 10 min and 95°C for 90 min, exposed to 380 mJ cm⁻² of UV light using the photomask in Figure 3.4 (b), and post-exposure baked at 65°C for 5 min and 95°C for 25 min [46]. The feature layers were developed by submerging the master in SU-8 developer, on an agitating plate, for 15 min to reveal the exposed main master as seen in Figure 3.5.

In conjunction with the main master, an alternative master was designed to accommodate MFCs containing carbon foam electrodes, due to their larger thickness (0.1 cm). A seed layer was spun onto a 1 in x 3 in glass slide and cured in an identical fashion as the main master. Four 150 μm-thick layers of SU-8-2100 negative photoresist were spun over the seed layer, employing the same protocol as the feature layers. After each layer was spun, they were soft baked according to the times and temperatures outlined in Table 3.1. The master was exposed to 600 mJ cm⁻² of UV light with the photomask containing the inlet channels and electrode groove channels (Figure 3.4 (b)) and post exposure baked at 65°C for 5 min and 95°C for 35 min before developing.

3.3.2.2 MFC Assembly

Polydimethylsiloxane (PDMS) (Sylgard 184 Silicone Elastomer Kit, Dow Corning Corporation,
Midland, MI) was mixed to create the top molded layer using a 1:10 weight ratio of base polymer to curing agent. This mixture was poured over the main master to a thickness of approximately 5 - 10 mm. The solution and master were placed in a degassing chamber at -85 kPa for 2 h to remove bubbles formed during the mixing process before curing the PDMS at 75°C for 2 h. The cured PDMS was cut and peeled from the main master in order to access the molded channels. The outlet and inlets were pierced through the top molded layer using a hollow needle. Tubes of 1/16 in inner diameter were inserted into the pierced holes for the inlets and outlet. Two larger holes were pierced for the electrical wiring, and the electrodes were positioned into the molded channels.

A technique called “partial baking” was used to seal the MFC containing carbon paper. For adhesion, a thin PDMS layer of approximately 2 mm was poured over a 1 in x 3 in glass slide for support. The adhesion layer was degassed in a similar fashion to the top layer and baked at 75°C until a tacky consistency was achieved (approximately 40 min). Immediately following this step, the adhesion layer was pressed against the prepared top molded layer. The glass slide, adhesion layer, and top molded layer were baked to fully cure the adhesion layer at 75°C for 1 h. The adhesion layer secures the electrodes within the PDMS and is an effective sealing method for embedding objects (electrodes) into microfluidic devices.

A variation of the partial baking technique called “cap sealing” was used for MFCs containing carbon foam. PDMS was poured over the alternative master to an approximate thickness of 2 mm and allowed to reach a tacky consistency following the same protocol as previously mentioned. The adhesion layer was removed from the alternative master and placed onto a 1 in x 3 in glass slide, with the molded channels exposed. Carbon foam electrodes were placed into the adhesion layer grooves, and the molded top layer was placed onto the adhesion layer by hand. The adhesion layer was cured in a similar fashion to the MFCs containing carbon paper. The cap sealing technique accommodated the 0.1 cm carbon foam electrode thickness.

External electrical connections were established between the electrodes and wire (23 Standard Wire Gauge) using TIGA Silver 920H (Resin Technology Group L.L.C., South Easton, MA). The silver resin was injected through the pre-punched holes of the top molded layer to contact the electrodes, and wires were inserted to create the electrical connection. The MFC was baked at 110°C for 2 h to cure the resin. Epoxy was used to secure the wires and tubes and protect
against leakage. A fully assembled MFC containing carbon paper is shown in Figure 3.6.

3.3.3 Fuel and Oxidant Preparation

The fuel (V$^{2+}$) and oxidant (VO$_2^+$) used in both MFC experiments were prepared from a bulk solution of VO$_2^+$ suspended in sulfuric acid. This ionic species were separated using an electrolytic cell that was designed and constructed in-house (Figure 3.7). Two polycarbonate holders housed the electrolytic cell separated by a Nafion membrane (Fuel Cell Store, San Diego, CA) and liquid sealing rubber gaskets (McMaster-Carr, Robbinsville, NJ). Each polycarbonate holder was machined to create a container to hold the bulk solution for separation. In order to chemically balance the half-cell reactions, the anode compartment was built to hold twice the volume of the cathode compartment. Toray carbon felt electrodes (Fuel Cell Earth LLC, Stoneham, MA) were fixed in each fluid compartment.

A 1 M sulfuric acid electrolyte was derived from concentrated sulfuric acid (University of Toronto, Chemical Stores, Toronto, ON). Vanadium (IV) sulfate oxide hydrate (VOSO$_4$·XH$_2$O, Alfa Aesar, Ward Hill, MA) was dissolved in the prepared electrolyte solution to a concentration of 50 mM VOSO$_4$·XH$_2$O. The presence of VO$_2^+$ was verified by a transparent light-blue solution colour. The solution was poured into the electrolytic cell with a volume ratio of 2:1 for the anode and cathode compartments, respectively. In the electrolytic flow cell, the reaction at the cathode half-cell proceeded in a two-step process [10]:

\[
VO^{2+} + 2H^+ + e^- \leftrightarrow V^{3+} + H_2O \quad E^\circ = 0.337 \text{ V vs SHE}
\]

\[
V^{3+} + e^- \leftrightarrow V^{2+} \quad E^\circ = -0.255 \text{ V vs SHE}
\]

And the anode half-cell reaction was [10]:

\[
VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2H^+ + e^- \quad E^\circ = 0.991 \text{ V vs SHE}
\]

Due to the instability of the fuel (V$^{2+}$) in oxygen, nitrogen flowed continuously in the cathode compartment during the separation with an initial 20 min purge. A 1.9 V potential was applied across the cell [47], resulting in an initial current of 18 mA. During separation, the current declined over 12 h to a value of 1.5 mA. At this point, the fuel (V$^{2+}$) and oxidant (VO$_2^+$) appeared transparent purple and light-blue, respectively, as seen in Figure 3.8.
The fuel cell anodic oxidation reaction is [10]:

\[ V^{2+} \leftrightarrow V^{3+} + e^- \quad E^o = -0.225 \text{ vs } SHE \]

The cathode reduction reaction is [10]:

\[ VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O \quad E^o = 0.991V \text{ vs } SHE \]

### 3.3.4 Fuel Cell Diagnostics

The MFCs were purged with de-ionized water prior to operation, in order to establish wetted flow paths for the fuel and oxidant. A syringe pump (Harvard Pump Plus Dual Syringe, Harvard Apparatus, Holliston, MA) was used to deliver fuel and oxidant to the MFCs at a rate of 60 μL min\(^{-1}\), while MFC performance was monitored with a potentiostat (VersaSTAT 3, Princeton Applied Research, Oak Ridge, TN). The break-in procedure for each MFC was to operate the cell for 15 min before the open circuit voltage (OCV) was recorded. The voltage was incrementally decreased every five minutes and held constant while stable current values were recorded. The results were normalized by projected electrode area and electrode volume using the data presented in Table 3.2.

### 3.4 Results and Discussion

#### 3.4.1 Evaluation of Carbon Foam as a MFC Electrode Material

Polarization and power density curves were normalized by projected electrode area in Figure 3.9 (a) and normalized by electrode volume in Figure 3.9 (b). The OCV, peak power voltage, maximum current density, and maximum power density for each MFC is summarized in Table 3.3. The contrast in performance seen in Figures 3.9 (a) and (b) indicate that normalization techniques have a significant impact on the interpretation of the performance. Normalizing the performance by electrode volume is a more representative approach to characterizing flow-through MFCs, since the increase in the overall MFC housing that accompanies the larger electrode would not otherwise be acknowledged with an area-based normalization calculation. An in-depth discussion of electrode volume normalization will be presented in Chapter 4.

Based on the information presented in Table 3.3 and Figure 3.9, the projected electrode area normalization illustrates that the maximum power density of carbon foam is 228.6% greater than
the maximum power density that resulted from carbon paper. This indicates that carbon foam not only is a suitable material to be used in MFCs, but it is highly effective for improved performance. However, based on the electrode volume normalization, results indicate that carbon paper out-performed carbon foam by 7.5%. Under both normalizations, carbon foam has proven to be a viable electrode material in MFCs with flow-through architectures. Normalizing the results solely on projected electrode area does not enable an accurate representation of the MFC performance, since it does not reflect the additional internal electrode surface area as seen in the discrepancy between Figures 3.9 (a) and (b).

3.4.2 Vanadium Impurity

Non-ideal performance can also be attributed to the lack of vanadium solution separation (fuel and oxidant species) using the apparatus and procedure presented. The fully separated fuel exhibited a purple hue, as indicated in literature; however, the colour of the oxidant was expected to be yellow in colour, rather than the light-blue colour that was observed in this study [48].

It was challenging to obtain a pure form of vanadium; however, since identical fuel and oxidant were employed in both MFCs, the less-than-ideal fuel and oxidant species were effectively employed to compare the relative performances of the MFCs investigated in this study.

3.5 Conclusions

Carbon foam has been shown to be a viable electrode material for MFCs. The performance of MFCs operated with a flow rate of 60 μL min⁻² resulted in carbon foam yielding 228.6% higher maximum power density than the standard carbon paper electrode material when normalized by the projected electrode area. Carbon foam yielded a maximum power density 7.5% lower than carbon paper based on electrode volume normalization. Normalization based on electrode volume rather than traditional projected electrode area allows for a more realistic comparison of performance, as it reflects the internal electrode surface areas and the relative size of a MFC.
3.6 Tables

Table 3.1: Summary of photolithography fabrication soft bake times, UV energy exposure amounts, and post exposure bake times for each layer of the main master and alternative master.

<table>
<thead>
<tr>
<th>Fabrication Layer</th>
<th>Soft Bake Times (min)</th>
<th>UV Energy Exposure (mJ cm(^{-2}))</th>
<th>Post Exposure Bake Times (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65°C</td>
<td>95°C</td>
<td></td>
</tr>
<tr>
<td>Seed Layer</td>
<td>5</td>
<td>15</td>
<td>220</td>
</tr>
<tr>
<td>Main Master 1(^{st}) Feature Layer</td>
<td>5</td>
<td>30</td>
<td>260</td>
</tr>
<tr>
<td>Main Master 2(^{nd}) Feature Layer</td>
<td>10</td>
<td>90</td>
<td>380</td>
</tr>
<tr>
<td>Alt. Master 1(^{st}) Feature Layer</td>
<td>5</td>
<td>30</td>
<td>N/A</td>
</tr>
<tr>
<td>Alt. Master 2(^{nd}) Feature Layer</td>
<td>10</td>
<td>90</td>
<td>N/A</td>
</tr>
<tr>
<td>Alt. Master 3(^{rd}) Feature Layer</td>
<td>10</td>
<td>100</td>
<td>N/A</td>
</tr>
<tr>
<td>Alt. Master 4(^{th}) Feature Layer</td>
<td>10</td>
<td>120</td>
<td>600</td>
</tr>
</tbody>
</table>
Table 3.2: Summary of the physical parameters used to normalize the microfluidic fuel cell performance for carbon paper and 100 PPI carbon foam.

<table>
<thead>
<tr>
<th>Material</th>
<th>Length (cm)</th>
<th>Width (cm)</th>
<th>Area (cm$^2$)</th>
<th>Thickness (cm)</th>
<th>Volume (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGP-H-120 Toray Carbon Paper</td>
<td>1.2</td>
<td>0.1</td>
<td>0.12</td>
<td>0.028</td>
<td>0.00336</td>
</tr>
<tr>
<td>100 PPI Carbon Foam</td>
<td>1.2</td>
<td>0.1</td>
<td>0.12</td>
<td>0.100</td>
<td>0.01200</td>
</tr>
</tbody>
</table>
Table 3.3: Summary of each microfluidic fuel cell performance normalized by projected electrode area and electrode volume.

<table>
<thead>
<tr>
<th>Material</th>
<th>OCV (V)</th>
<th>Voltage at Maximum Power Density (V)</th>
<th>Maximum Current Density (mA cm$^{-2}$)</th>
<th>Maximum Current Density (mA cm$^{-3}$)</th>
<th>Maximum Power Density (mW cm$^{-2}$)</th>
<th>Maximum Power Density (mW cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGP-H-120 Toray Carbon Paper</td>
<td>0.7</td>
<td>0.2</td>
<td>0.547</td>
<td>19.539</td>
<td>0.049</td>
<td>1.737</td>
</tr>
<tr>
<td>100 PPI Carbon Foam</td>
<td>0.5</td>
<td>0.2</td>
<td>1.865</td>
<td>18.650</td>
<td>0.161</td>
<td>1.606</td>
</tr>
</tbody>
</table>
3.7 Figures

Figure 3.1: Scanning electron microscopy (SEM) images of (a) carbon paper and (b) 100 PPI carbon foam at 150X magnification.
Figure 3.2: Schematic of the microfluidic fuel cell architecture: (a) assembled and (b) expanded.
Figure 3.3: Graphical representation of the main master fabrication including (a)-(c) the seed layer, (d)-(f) first feature layer, and (g)-(i) second feature layer.
Figure 3.4: Photomasks used to create the (a) first and (b) second feature layers of the microfabricated master.
Figure 3.5: Completed master for the microfluidic fuel cell channel fabrication developed using photolithography techniques.
Figure 3.6: Photograph of a completed microfluidic fuel cell from: (a) bottom view and (b) top view.
Figure 3.7: Photograph of the disassembled electrolytic flow cell used to separate the bulk vanadium solution into respective fuel and oxidant species.
Figure 3.8: Fuel ($V^{2+}$) indicated by purple (left) and oxidant ($VO_2^+$) indicated by light-blue (right) both suspended in a sulfuric acid electrolyte.
Figure 3.9: Polarization and power density curves normalized by (a) projected electrode area and (b) electrode volume.
Up-scaled Microfluidic Fuel Cells with Porous Flow-through Electrodes

4.1 Introduction

In this chapter, a proof-of-concept up-scaled, flow-through MFC architecture with over nine-times the projected active electrode area than presented in the previous chapter is discussed. Several electrode materials were employed and compared with carbon paper, including 100 PPI carbon foam, 80 PPI carbon foam, carbon fibre, and carbon cloth. Normalization techniques presented in the previous chapter are further investigated and critically discussed. The effect of catalyst loading on MFC performance is also investigated.

4.2 Motivation and Objectives

The development of flow-through MFC architectures alleviated problems associated with mass transport issues, low power densities, depletion boundary layers, and fuel-crossover; however, MFCs are still limited by low overall power output. Before commercialization may be realized, higher overall power outputs must be achieved. This may be done by either developing MFC stacked systems or up-scaling MFCs architectures in order to produce higher overall power from a single MFC. Previous work has investigated MFC stack systems to increase power [5, 10], but no work has been presented to up-scale MFC architectures. When up-scaled single MFC architectures are paired with the stacked system approach, less stacked cells would be required, thus further decreasing volume requirements.

The main objective described in this chapter is the development of a proof-of-concept up-scaled flow-through architecture MFC to achieve large overall power outputs. The presented architecture is an up-scaled version of the MFC presented in Chapter. The materials and techniques developed in this chapter are expected to aid the future development of MFCs towards practical high power single cell MFCs and MFC stacked systems.

A secondary objective of this chapter is to employ novel 100PPI carbon foam, 80 PPI carbon foam, carbon fibre, and carbon cloth in the up-scaled MFC architecture to compare with traditionally employed carbon paper. In Chapter 3, 80 PPI carbon foam exhibited a fragile structure due to large pore size and was not employed; however, since the up-scaled architecture
contains an electrode housing that is double the height of that shown in Chapter 3, both 80 PPI and 100 PPI carbon foams were employed. Carbon fibre and carbon cloth exhibit densely packed microstructures and were chosen to facilitate a comparison with carbon foam, which has highly porous microstructure. The electrode materials were employed with identical projected surface areas, though the thicknesses of each material were varied. This vertical up-scaling investigation further necessitates the use of a volume-based performance normalization. A full discussion and comparison on performance is presented for each electrode material. The effect of catalyst loading on MFC performance was also investigated.

4.3 Experimental Preparation

4.3.1 MFC Fabrication

A schematic of the up-scaled MFC is displayed in Figure 4.1, with an assembled and expanded view to highlight the various components of the design. The operation of the up-scaled MFC is identical to the MFC presented in the previous chapter.

Creation of the main master for the up-scaled MFC followed a similar protocol as the main master presented in Chapter 3, employing 2 in x 3 in glass. New photomasks were developed, which were up-scaled versions of the photomasks presented in the previous chapter. A second master was micro-machined with an identical layout as the up-scaled main master but with an increased height of 2000 μm for the inlet channels and electrode housing channels to account for the up-scaled carbon foam electrodes.

All MFCs were assembled using a similar protocol as Chapter 3. MFCs employing carbon paper, carbon fibre, and carbon cloth were fabricated with the main master, and MFCs employing carbon foam were fabricated with the micro-machined master. All MFCs were sealed using the partial baking technique. A photograph of a fabricated MFC containing 80 PPI carbon foam is shown in Figure 4.2.

4.3.2 Fuel and Oxidant Preparation

Due to the prohibitive challenges of Vanadium species impurities discussed in Chapter 3, for this component of the thesis, 0.04 M formic acid (Formic Acid >95%, Sigma-Aldrich, St. Louis, MO) and 0.01 potassium permanganate (Potassium Permanganate, 98%, Fisher Scientific Group,
Ottawa, ON) were used as fuel and oxidant, respectively. Fuel and oxidant were both suspended in a 1 M sulfuric acid electrolyte solution. The presence of potassium permanganate in sulfuric acid exhibits a distinguishable purple hue, while the formic acid suspended in sulfuric acid appears as a clear liquid, as seen in Figure 4.3. A qualitative tracking of the chemicals through the MFC during operation was optically achieved based on these colours.

The half-cell reactions in the MFC using this fuel and oxidant pair are [14]:

\[
\begin{align*}
HCOOH \leftrightarrow CO_2 + 2H^+ + 2e^- & \quad (E^o = -0.199V \text{ vs. SHE}) \quad (1) \\
MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O(E^o = 1.507V \text{ vs. SHE}) & \quad (2)
\end{align*}
\]

A secondary reaction may also occur when Mn\(^{2+}\) and MnO\(_4^-\) are in the presence of water, which could lead to a solid precipitate that is harmful to MFC performance. The secondary reaction is:

\[
2MnO_4^- + 3Mn^{2+} + 2H_2O \leftrightarrow 5MnO_2(s) + 4H^+(E^o = 0.46V \text{ vs. SHE}) \quad (3)
\]

The theoretical OCV of the MFCs is 1.706V, under the assumption that all reactants are fully oxidized or reduced. This value will be lowered in the case where the secondary reaction takes place [14].

4.3.3 Catalyst Preparation

A catalyst ink was prepared based on a recipe presented by M. S. Wilson and S. Gottesfeld [49]. Nafion (5% wt., Sigma-Aldrich, St. Louis, MO), platinum black (20% Pt, nominally on carbon black, Alfa Aesar, Ward Hill, MA), deionized water, and glycerol (Sigma-Aldrich, St. Louis, MO) were mixed to a mass based ratio of 1:3:20:80, respectively. The ink was ultrasonically mixed for approximately 1 h to achieve a homogenous solution with a homogeneous suspension of particles.

4.3.4 Electrode Preparation

Electrodes were cut from bulk samples of carbon electrode materials including fibre (RPA-TD06P38, Jamestown Distributors, Bristol, RI), cloth (B1B Carbon Cloth Designation B, Plain, BASF Fuel Cell Inc, Somerset, NJ), paper (TGP-H-120 Toray carbon paper, Fuel Cell Earth, Stoneham, MA), and two grades of carbon foam (80 PPI and 100 PPI carbon foam, ERG
Materials and Aerospace Corp, Oakland, CA) to a length of 36 mm and a width of 4 mm. Each material had a unique microstructure (Figure 4.4), which played a significant role in liquid flow patterns and mass transport through the MFC. All materials, excluding carbon foams, were purchased at pre-defined manufactured thicknesses. Carbon fibre and cloth thickness measurements were obtained using an average of 10 electronic caliper measurements. The carbon paper thickness was defined by manufacturer specifications. Both 80 and 100 PPI foams were cut to a thickness of 2 mm (minimal thickness required of 80 PPI carbon foam for structural stability) using EDM.

Electrode pairs (anode and cathode) were immersed in the catalyst ink until they were fully saturated (approximately 30 s) before being placed onto individual pieces of foil. The foil and electrode pairs were completely dried in an oven at 135°C. The catalyzed electrodes were removed from the foil and immediately positioned into the electrode housing grooves (as outlined in Section 4.3.1). Catalyst loadings were calculated using the following formula, where the numerator terms represent the mass recorded at respective stages in the catalyst coating procedure:

\[
\text{Catalyst Loading} = \frac{(Dried \ Electrodes \ and \ Foil) - (Bare \ Electrodes) - (Foil \ and \ Catalyst \ Residue)}{Projected \ Electrode \ Surface \ Area}
\]

Catalyst loadings (normalized by projected electrode area) varied as the electrode materials each exhibited distinct microstructures with variable surface areas (and overall volume) available for catalyst adhesion. The carbon fibre electrode exhibited a densely packed microstructure with minimal pore access, and the smallest volume leading to the lowest catalyst loading of 2.6 mg cm\(^{-2}\). The volume of the carbon cloth was more than twice the volume of carbon fibre, but with a similar tightly-packed microstructure resulting in a catalyst loading of 6.1 mg cm\(^{-2}\). Due to its higher pore accessibility, Toray carbon paper was treated with a catalyst loading of 7.0 mg cm\(^{-2}\). The 100 PPI foam was treated with a catalyst loading of 9.0 mg cm\(^{-2}\), while the 80 PPI carbon foam was treated with a loading of 10.9 mg cm\(^{-2}\) (higher due to its superior pore space accessibility). To investigate the effects of varying the catalyst loading, additional inks were prepared to coat the 80 PPI carbon foam electrodes with loadings of 7.7, 28.1, and 48.3 mg cm\(^{-2}\).
4.3.5 Fuel Cell Diagnostics

The MFCs were operated utilizing the protocol established in Chapter 3 with fuel and oxidants delivered at an increased flow rate of 100 μL min\(^{-1}\). The results were normalized by projected electrode area and electrode volume using the data presented in Table 4.1.

4.4 Results and Discussion

4.4.1 Polarization Sweep

During each polarization sweep, current measurements were collected at every voltage increment at 1-s intervals for a period of 5 min, a period selected for facilitating current stabilization. Immediately following an incremental decrease in voltage, the current values responded with an abrupt increase before slowly converging to a lower, steady-state value. Each current value (shown in Figures 5-8) was an average of the final 60 current measurements at each voltage increment. At high voltages, the data converged quickly, leading to a stable reading, well within the 5-min period. At lower voltages, the fuel cell was generally unstable and current measurements often did not converge within the 5-min period. If the current measurement of the MFC did not converge within the 5-min period, the MFC polarization sweep was terminated. As shown in Figure 5, the MFCs were terminated at a range of voltages due to varying levels of instability. The OCV, voltage at maximum power, and maximum power density for each MFC is summarized in Table 4.2.

4.4.2 Polarization Losses

The polarization curves for each electrode material, normalized by projected electrode area and electrode volume, are presented in Figure 4.5. As seen in Figure 4.5, the MFC with the carbon fibre electrode showed high activation losses, but the main losses present in all MFCs excluding carbon cloth were the ohmic losses. The instabilities mentioned in Section 4.4.1 were attributed to the mass transport limitations, which led to the termination of the voltage sweep. The 80 PPI carbon foam and carbon fibre did not reach the mass transport region of the curve due to an early termination of their operation. Toray carbon paper and 100 PPI carbon foam began to display the characteristics of mass transport limitations before their termination. Carbon cloth was dominated by mass transport limitations throughout its operation.
4.4.3 Projected Electrode Area and Electrode Volume Normalization

Traditionally, current densities in MFCs have been normalized with respect to exposed electrode surface area. This standard was initially used in Y-channel architecture MFCs, where the exposed electrode surface area was defined by the interface between the electrode and liquid. Advancements in MFC architectures, specifically architectures that capitalize on the interior surface of the electrode [5, 7, 10, 12-14, 29, 35, 37, 38], have made it difficult to compare Y-channel architectures with modern architectures. In an attempt to relate performance, researchers have chosen to use a projected electrode surface area; however, this type of normalization did not take into account the added benefit from internal surface areas. It has been previously proposed that normalization based on electrode volume, which takes into account projected electrode area and the thickness of the electrode, would be a more accurate representation of flow-through MFC performance. However, there results of this nature were not available in the literature to facilitate this comparison [7]. In this thesis, MFC performance was normalized by both projected electrode area and by electrode volume.

4.4.4 Normalization by Projected Electrode Area

The maximum power density achieved was 0.402 mW cm$^{-2}$ during operation at 0.5 V when 80 PPI carbon foam was employed, as seen in Figure 4.6 (a). MFCs containing 100 PPI carbon foam, carbon paper, carbon fibre, and carbon cloth achieved 71.0%, 63.8%, 50.2%, and 9.5% of the maximum power density achieved by the MFC with 80 PPI carbon foam, respectively.

Since each MFC employed in this study had the same projected surface area (1.12 cm$^2$), Figure 4.6 (a) illustrates the comparative overall power performance of each MFC, with 80 PPI carbon foam showing the best overall power output. The data reported under this normalization allows for comparison with previous work in the literature; however, there is no literature that utilizes the flow-through architecture paired with the fuel and oxidant employed here.

It is challenging to compare the results in this thesis to previous work in literature since there are several factors that influence the power density of a MFC including architecture, fuel, oxidant, electrolyte, and flow rates. There has not been any literature which has been identical to the operating conditions in this thesis; however, previously presented literature which share common conditions have been outlined in Table 4.3 with their respective power densities.
4.4.5 Normalization by Electrode Volume

The maximum power density acquired, normalized by electrode volume, was 8.40 mW cm$^{-3}$ at 0.6 V in the MFC containing carbon fibre, as seen in Figure 4.8 (b). Cells containing carbon paper, 80 PPI carbon foam, 100 PPI carbon foam, and carbon cloth achieved 80.2%, 23.9%, 16.9%, and 8.3% of the power density obtained by the carbon fibre sample, respectively.

The performance normalized by electrode volume accounts for the impact of electrode thickness on the cell performance. Decreasing the electrode thickness, which governs the cell housing dimensions, leads to an overall reduction in MFC volume. The MFCs containing carbon fibre and carbon paper electrodes greatly outperformed the other cells, primarily due to their small thicknesses (small volumes).

4.4.6 Validity of Normalizations Based on Electrode Volume

By using only traditional projected electrode surface area methods, one cannot accurately compare the overall performance of MFCs when novel architectures utilizing internal electrode surface areas are employed. The limitation of projected electrode area normalization is illustrated when comparing the performance of MFCs utilizing carbon fibre and 80 PPI carbon foam. Based on a projected electrode surface area, it would appear from Figure 4.6 (a) that 80 PPI carbon foam greatly outperformed carbon fibre, providing a power output twice as large. Both MFCs employed an identical architecture layout, but the carbon foam would require over eight times the cavity height due to electrode thickness, ultimately leading to a larger MFC. Thin carbon fibre electrodes achieved a power density four times greater than 80 PPI carbon foam, when based on an electrode volume normalization, as seen in Figure 4.6 (b). Normalization by electrode volume effectively takes the whole electrode into consideration, which is ultimately needed to characterize the performance of the MFC.

4.4.7 Catalyst Loading

The MFC with 80 PPI carbon foam provided the greatest overall power, and the effects of catalyst loadings were investigated by varying the loadings of platinum black from 10.9 mg cm$^{-2}$ to 7.7, 28.1, and 48.3 mg cm$^{-2}$. The resulting polarization and power density curves are presented in Figure 4.7. With a base loading of 10.9 mg cm$^{-2}$, a maximum power density of 0.402 mW cm$^{-2}$ was achieved, as presented in Section 4.4.3. By increasing the catalyst loading to 28.1 mg cm$^{-2}$
and 48.3 mg cm\(^{-2}\), the maximum power density increased by 30\% and 195\%, respectively. Decreasing the catalyst loading to 7.7 mg cm\(^{-2}\) led to a decrease in the maximum power density by 75.8\%. The various catalyst loadings and resulting maximum power densities are presented in Figure 4.8. The drastic variances in performance indicate that there is potential to achieve larger maximum power densities with the up-scaled MFC architecture by varying the catalyst loading.

4.4.8 Electrode Material Evaluation

Upon comparing with traditionally employed carbon paper, it appears carbon cloth was not a suitable electrode material for MFCs. Carbon cloth led to an overall power that was only 15.0\% of carbon paper. In addition, the open circuit voltage was 0.57 V for carbon cloth, which led to a significantly shorter operating range.

The performance of carbon fibre was comparable to carbon paper and was considered a viable electrode material for use in future MFCs. Carbon fibre was advantageous due to its commercial availability as a thinly manufactured material. Based on a projected electrode surface area, the carbon fibre MFC reached 78.7\% of the maximum power density of the carbon paper MFC. On the contrary, based on an electrode volume normalization, the carbon fibre MFC outperformed the carbon paper MFC by 24.6\% in power density, since carbon fibre exhibits a smaller volume than carbon paper. Carbon fibre appears to be a material that is well-suited for applications where lower overall power outputs are needed, and a compact MFC housing cavity design is required.

The 80 PPI and 100 PPI carbon foams were found to be highly promising electrode materials for flow-through MFCs. They outperformed carbon paper when using the conventional projected electrode area normalization technique, achieving 142.5\% (80 PPI) and 111.3\% (100 PPI) of the power density achieved by the MFC containing carbon paper. In contrast, when normalized by electrode volume, 80 PPI and 100 PPI carbon foams only provided 27.1\% and 21.2\% of the power density achieved by carbon paper, respectively, due to their large electrode volumes. Carbon foams are advantageous because they are manufactured in bulk form rather than in sheets, facilitating vertical scalability. Carbon foams are also well-suited for large MFC architectures to allow for large power outputs where size of the housing cavity is not restricted.
4.5 Conclusions

A proof-of-concept microfluidic fuel cell architecture was presented, which demonstrated the ability to up-scale MFCs for high total power outputs. Since MFCs are based on surface reactions, flow-through porous electrodes are highly advantageous for the high surface-area-to-volume ratios. Up-scaling flow-through MFCs with high overall electrode volumes leads to high overall power outputs without compromising the benefits of the microfluidic design. Enlarging the electrodes also facilitated a critical study of how the electrode microstructure affects performance. A comparative study into four novel carbon-based electrode materials, including 100 PPI carbon foam, 80 PPI carbon foam, B1B carbon cloth, and RPA-TD06P38 carbon fibre were compared to traditionally employed TGP-H-120 Toray carbon paper.

On a projected electrode surface area normalization, the cell containing 80 PPI carbon foam produced the highest power density with a value of 0.365 mW cm\(^{-2}\) at a flow rate of 0.1 μL min\(^{-1}\) and voltage of 0.55V. MFCs employing 100 PPI carbon foam, carbon paper, carbon fibre, and carbon cloth achieved 71.0%, 63.8%, 50.2%, and 9.5% of the maximum power density, respectively, of the 80 PPI carbon foam MFC. The 80 PPI carbon foam MFC produced the highest overall power of the electrode materials. When performance was based on electrode volume normalization, the cell containing carbon fibre produced the highest power density, 8.40 mW cm\(^{-3}\), at a flow rate of 0.1 μL min\(^{-2}\) and voltage of 0.6V. MFCs containing carbon paper, 80 PPI carbon foam, 100 PPI carbon foam, and carbon cloth achieved 80.2%, 23.9%, 16.9%, and 8.3% of the power density obtained by the carbon fibre MFC, respectively. The volumetric based normalization accounted for each electrode thickness, which influenced the overall space required to house the electrodes. It is hoped that this method of normalization will be utilized in future work.

The effects of catalyst loading were investigated by varying the amount of platinum black in a MFC employing 80 PPI carbon foam. Under the highest catalyst loading of 48.3 mg cm\(^{-2}\) the cell produced a maximum power density of 1.189 mW cm\(^{-2}\). The increase in performance indicated that there is potential to achieve larger maximum power densities by varying the catalyst loading.

Electrode materials were compared to a MFC using traditionally-employed carbon paper electrodes. Carbon cloth achieved relatively low maximum power densities and was considered an unacceptable material to be used in future MFCs. Carbon fibre performed well when
compared to carbon paper, proving it is a viable MFC electrode material. Based on electrode volume normalization, the MFC containing carbon fibre provided a maximum power density that was 124.6% of the power density achieved by carbon paper. Since carbon fibre is manufactured in thin sheets, its structure is most beneficially employed in MFC applications where electrode cavity size (namely height) is highly constrained. Using the projected electrode area normalization, the 80 PPI and 100 PPI carbon foams outperformed the carbon paper electrode achieving 142.5% and 111.3% of the maximum power density of carbon paper, respectively. Carbon foams are a suitable MFC electrode material for applications that require high power outputs from a single MFC architecture.
4.6 Tables

Table 4.1: Summary of the physical parameters used to normalize the microfluidic fuel cell performance for each carbon-based electrode material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (cm)</th>
<th>Area (cm$^2$)</th>
<th>Volume (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 PPI Carbon Foam</td>
<td>0.200</td>
<td>1.12</td>
<td>0.22400</td>
</tr>
<tr>
<td>100 PPI Carbon Foam</td>
<td>0.200</td>
<td>1.12</td>
<td>0.22400</td>
</tr>
<tr>
<td>B1B Carbon Cloth</td>
<td>0.055</td>
<td>1.12</td>
<td>0.06160</td>
</tr>
<tr>
<td>TGP-H-120 Toray Carbon Paper</td>
<td>0.038</td>
<td>1.12</td>
<td>0.04256</td>
</tr>
<tr>
<td>RPA-TD06P38 Carbon Fibre</td>
<td>0.024</td>
<td>1.12</td>
<td>0.02688</td>
</tr>
</tbody>
</table>
Table 4.2: Summary of each microfluidic fuel cell performance normalized by projected electrode area and electrode volume.

<table>
<thead>
<tr>
<th>Material</th>
<th>OCV (V)</th>
<th>Voltage at Maximum Power Density (V)</th>
<th>Maximum Power Density (mW cm$^2$)</th>
<th>Maximum Power Density (mW cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 PPI Carbon Foam</td>
<td>1.02</td>
<td>0.50</td>
<td>0.4016</td>
<td>1.826</td>
</tr>
<tr>
<td>100 PPI Carbon Foam</td>
<td>0.80</td>
<td>0.40</td>
<td>0.2851</td>
<td>1.426</td>
</tr>
<tr>
<td>B1B Carbon Cloth</td>
<td>0.57</td>
<td>0.35</td>
<td>0.0383</td>
<td>0.697</td>
</tr>
<tr>
<td>TGP-H-120 Toray Carbon Paper</td>
<td>0.98</td>
<td>0.60</td>
<td>0.2562</td>
<td>6.742</td>
</tr>
<tr>
<td>RPA-TD06P38 Carbon Fibre</td>
<td>1.04</td>
<td>0.60</td>
<td>0.2016</td>
<td>8.402</td>
</tr>
</tbody>
</table>
Table 4.3: Comparison of microfluidic fuel cell power densities previously presented in literature.

<table>
<thead>
<tr>
<th>Author (Year)</th>
<th>Architecture</th>
<th>Fuel (Conc.)</th>
<th>Oxidant (Conc.)</th>
<th>Electrolyte (Conc.)</th>
<th>Flow Rate (μL min⁻¹)</th>
<th>Power Density (mW cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuerth (2012)</td>
<td>Flow-Through</td>
<td>Formic Acid (40 mM)</td>
<td>Potassium Permanganate (10 mM)</td>
<td>Sulfuric Acid (1 M)</td>
<td>100</td>
<td>0.402</td>
</tr>
<tr>
<td>Kjeang (2008)</td>
<td>Flow-Through</td>
<td>$V^{3+}$ (2 M)</td>
<td>$VO^{2+}$ (2 M)</td>
<td>Sulfuric Acid (4 M)</td>
<td>300</td>
<td>120</td>
</tr>
<tr>
<td>Kjeang (2008)</td>
<td>Flow-Through</td>
<td>Formate (1.2 M)</td>
<td>Hypochlorite (670 mM)</td>
<td>N/A</td>
<td>60</td>
<td>52</td>
</tr>
<tr>
<td>Salloum (2008)</td>
<td>Sequential Flow (Circular)</td>
<td>Formic Acid (40 mM)</td>
<td>Potassium Permanganate (10 mM)</td>
<td>Sulfuric Acid (1 M)</td>
<td>100</td>
<td>1.0</td>
</tr>
<tr>
<td>Lopez (2011)</td>
<td>Micro Bridge</td>
<td>Formic Acid (1 M)</td>
<td>Potassium Permanganate (144 mM)</td>
<td>Sulfuric Acid (1 M)</td>
<td>60</td>
<td>25.5</td>
</tr>
</tbody>
</table>
4.7 Figures

Figure 4.1: Schematic of the microfluidic fuel cell architecture: (a) assembled and (b) expanded.
Figure 4.2: Photograph of a completed microfluidic fuel cell from: (a) top view and (b) bottom view.
Figure 4.3: Fuel (HCOOH) indicated by clear (left) and oxidant (KMnO₄) indicated by purple (right) both suspended in a sulfuric acid electrolyte.
Figure 4.4: Scanning electron microscopy (SEM) images of carbon based electrode materials including: (a) 80 PPI carbon foam and (b) 100 PPI carbon foam, (c) carbon fibre, (d) carbon paper, and (e) carbon cloth at 50X magnification. In (d) and (e), the porous surface of the sample stage is shown but can be ignored.
Figure 4.5: Polarization curves normalized by: (a) projected electrode surface area and (b) electrode volume for: 80 PPI carbon foam (▲), 100 PPI carbon foam (●), carbon fibre (■), carbon paper (◆), and carbon cloth (●).
Figure 4.6: Power density curves normalized by: (a) projected electrode surface area and (b) electrode volume for: 80 PPI carbon foam (▲), 100 PPI carbon foam (●), carbon fibre (■), carbon paper (◆), and carbon cloth (○).
Figure 4.7: Polarization and power density curves for four microfluidic fuel cells employing 80 PPI carbon foam with varied platinum black catalyst loadings.
Figure 4.8: Maximum power density of four microfluidic fuel cells employing 80 PPI carbon foam with varied platinum black catalyst loadings.
Conclusions

In this thesis, a proof-of-concept up-scaled flow-through microfluidic fuel cell architecture was presented with the goal of advancing the state of the art in MFCs. Novel MFC electrode materials were presented, including 80 PPI carbon foam, 100 PPI carbon foam, carbon fibre, and carbon cloth. A normalization technique based on electrode volume was also presented. This type of normalization allows for a more accurate representation of performance when comparing evolving MFC architectures that utilize internal electrode surface areas. The effect of catalyst loading was also investigated. The main contributions of this thesis are:

- A detailed description of the MFC fabrication processes was presented including a partial baking step and a cap sealing step, which were non-conventional sealing techniques that allowed for embedding foreign objects into MFC architectures.
- An electrolytic flow cell was developed to separate bulk vanadium species suspended in sulfuric acid into fuel and oxidant.
- An electrode volume normalization technique was presented that more accurately represented performance of MFCs which exploited internal electrode surface areas.
- A discussion into the validity and applicability of projected electrode area and electrode volume normalization techniques was presented.
- A proof-of-concept up-scaled flow-through MFC architecture was presented to achieve high overall power. It also served as a platform to evaluate performance of various electrode materials.
- Based on projected electrode area normalization, it was found that the MFC containing 80 PPI carbon foam produced the highest power density of 0.365 mW cm\(^{-2}\). MFCs employing 100 PPI carbon foam, carbon paper, carbon fibre, and carbon cloth achieved 71.0%, 63.8%, 50.2%, and 9.5% of the maximum power density, respectively, of the 80 PPI carbon foam MFC.
- Based on electrode volume normalization, the MFC containing carbon fibre produced the
highest power density of 8.40 mW cm⁻³. MFCs employing carbon paper, 80 PPI carbon foam, 100 PPI carbon foam, and carbon cloth achieved 80.2%, 23.9%, 16.9%, and 8.3% of the maximum power density, respectively, of the carbon fibre MFC.

- Carbon cloth was shown to be an ineffective electrode material to be employed in MFCs. The MFC architecture containing carbon cloth yielded 15.0% the overall power of the MFC containing carbon paper.

- Carbon fibre was proven to be a viable electrode material to be employed in MFCs where there are size restrictions on the MFC housing. The MFC architecture containing carbon cloth yielded a power density based on electrode volume normalization 24.6% higher than the MFC containing carbon paper.

- The 80 PPI and 100 PPI carbon foams appeared as potential electrode materials to be employed in MFCs where large overall powers are required from a single MFC. They yielded power outputs based on projected electrode normalization techniques 42.5% (80 PPI) and 11.3% (100 PPI) greater than the MFC containing carbon paper.

- The effects of catalyst loading were investigated in a MFC employing 80 PPI carbon foam. Under the highest catalyst loading, the cell produced a maximum power density of 1.19 mW cm⁻².

Microfluidic fuel cells have the potential to be commercially available for small scale power applications. The realization of this commercialization hinges on their ability to achieve the necessary power outputs for individual applications while retaining their attractive micro-scale design. In this thesis, a MFC that may achieve high power outputs from a single cell was presented. This up-scaled MFC architecture could be paired with stacked systems or employed individually. Novel materials were presented that will act as building blocks in future work, and normalization techniques were presented to allow researchers to effectively compare performance.
Future Work

The work in this thesis provides a foundation for the continued development of up-scaling MFC architectures with the employment of novel electrode materials. Many future directions are still available for investigation, some of which are listed as follows.

Future work may include the exploration of alternative electrode materials that exhibit microstructures different than those presented in this thesis, such layered or grid-structured pore networks. Computational modeling of electrode surface reactions with bulk fluid movement would allow for materials to be tailored for increased fuel utilization and power densities.

Carbon foam is manufactured in bulk form, allowing for complex shapes and sizes to be achieved. Future work may include the investigation of the effects of varying electrode dimensions for optimal power output.

The up-scaling limits of MFCs architectures may be investigated in future work. Approaching the limits of the microfluidic regime may lead to higher overall power outputs from MFCs.

Employment of up-scaled MFC architectures in stacked systems that are connected both fluidly and electrically may be incorporated in future work. Incorporating up-scaled MFCs in stacked systems would reduce the number of individual MFCs required to achieve an equivalent power output, as each MFC would produce more power, reducing system complexity.

Novel normalization techniques may be investigated in future work that would take into account the system components of the MFC architecture such as housings and channels.
References


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