FLOOD MITIGATION STRATEGIES AND DIAGNOSTIC TECHNIQUES
FOR POLYMER ELECTROLYTE FUEL CELLS

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DOCTOR OF PHILOSOPHY

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ABSTRACT

A persistent challenge in polymer electrolyte membrane fuel cell (PEFC) systems is water management. Membrane humidity must be maximized to ensure good ionic conductivity, while excess product water must be removed to prevent electrode, gas diffusion layer, and flow field channel flooding. This challenge is often addressed by using fully humidified inlet gas streams and incorporating serpentine channel cathode flow fields for air delivery. Although successful in achieving stable performance, the high pressure drops required by such flow fields result in large parasitic power losses (as high as 35% of stack power) and increased system complexity. In the present work, we aim to minimize this loss with novel cathode designs which enable stable, flood-free performance, in parallel channel flow fields.

We first present a detailed study of an active water management system for PEFCs, which uses a hydrophilic, porous carbon cathode flow field as a water transport wick, coupled with an electroosmotic (EO) pump for water removal. We characterize in-plane transport issues and power distributions using a three by three segmented PEFC design. Transient and steady state data provide insight into the dynamics and spatial distribution of flooding and flood-recovery processes. Segment-specific polarization curves reveal that the combination of a wick and an EO pump can effect a steady state, uniform current distribution for a parallel channel cathode flow field, even at low air stoichiometries ($\alpha_n = 1.5$).

Wicks are often an integral part of fluid capacitance and transport in many systems, including not only fuel cells, but also heat pipes, microfluidic chips, and lateral flow chemical assays on cellulose paper. In the second section, we explore porous polymer monoliths as a new wick material and wick fabrication method applicable to fuel cells and potentially other systems. Polymer monolith chemistries, long used for high surface-to-volume ratio separation and filtering media in analytical chemistry, offer tremendous flexibility in resulting monolith pore-structure, chemical composition, and surface chemistry (including wettability). We leverage this flexibility to design, fabricate (including casting), and characterize integrated
hydrophilic porous monoliths, with the aim of achieving high permeability wick materials.

In the third section, we integrate these porous polymer wicks into a metal cathode flow field which is similar to many state-of-the-art architectures (e.g., stamped metal or injection molded). This wick is in situ polymerized to conform to and coat cathode flow field channel walls, thereby spatially defining regions for water and air transport. At the very low air stoichiometry of 1.15, our system delivers a peak power density of 0.68 Wcm$^{-2}$. This represents a 62% increase in peak power over a control case. The open channel and manifold geometries are identical for both cases and we demonstrate near identical inlet-to-outlet cathode pressure drops at all fuel cell operating points. We therefore show significant performance enhancement without introducing additional parasitic losses.
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Chapter 1
INTRODUCTION

1.1. Background

Increasing energy demands of new, high performance portable electronic devices are outpacing advances in battery technology [1] and new high energy density power sources are required. In addition, vehicle power sources represent another important sector which requires sustainable and high energy density power. Presently, the transportation sector relies on petroleum for 95% of total energy used, 60% of which is imported. As a result, transportation accounts for a considerable portion of global greenhouse gas emissions (24% in 2004) and dependence on foreign oil [2].

Over the past decade, increased research and development has gone toward transportation technologies which exploit alternative energy sources. These technologies include bio fuel combustion, hybrid, plug-in hybrid, electric, and fuel cell vehicles. Of these technologies, market penetration models and technological advancement forecasts suggest that fuel cell vehicles may have the most promise for long term CO₂ emission reduction [3, 4].

Polymer electrolyte fuel cells (PEFCs) have been a favored technology as they provide emissions-free power, while operating at high efficiency and low temperatures. Key disadvantages remain, however, which prevent near-term implementation and deployment of fuel cell vehicles. Some disadvantages include current cost of catalyst materials and manufacture, long-term durability issues, and the necessity of a fueling infrastructure [3, 5]. Integration into on-board auxiliary systems also remains a challenge. Air pressurization and delivery are particularly challenging as on-board compressors add to system complexity and can make startup more difficult [6]. Air delivery parasitic losses are also problematic during vehicle idle where air delivery may require a significant portion of the total power required to keep the fuel cell and auxiliary systems operating [7]. In this dissertation we aim to address
1.1.1. Operating principles of fuel cells

Fuel cells leverage the direct conversion of chemical energy into electrical work for highly efficient energy conversion. Figure 1.1 schematically shows this process in a hydrogen fuel cell. A proton conducting membrane (typically Nafion) separates hydrogen and oxygen fuel. Catalyst layers coat each side. In the anode-side catalyst layer, hydrogen gas is oxidized into electrons and protons. Protons are ionically conducted through the membrane, while electrons go through an external circuit (which connects through a load). Both protons and electrons meet with and reduce oxygen in the cathode electrode, producing water.

For a fuel cell operating at standard temperature and pressure, the overall reaction is:

\[
\text{eqn. 1.1} \quad H_2 + \frac{1}{2}O_2 \rightarrow H_2O + 286 \text{ kJ/mol}
\]
As eqn. 1.1 shows, this reaction releases a total of 286 kJ of energy per mol \( H_2 \) (higher heating value). Many losses affect the portion of chemical energy that, instead of being converted to electrical work, is wasted as heat. These include thermodynamic limitations, kinetic losses driving redox reactions at the electrodes, ohmic losses due to ionic transport through the membrane, and mass transport losses. To better elucidate the critical role water management plays in fuel cell performance, we will first briefly discuss each of these losses. Then, in Section 1.2, we will discuss the coupling of fuel cell water management and performance in detail.

1.1.2. Deviations from reversible performance in fuel cells

The Gibbs free energy, \( \hat{g} \), is the total chemical energy available to do work. \( \hat{g} \) is calculated for a particular reaction, and is a function of both temperature and pressure. At STP and for the reaction of hydrogen and oxygen to liquid water, \( \Delta \hat{g} = -237 \text{ kJ/mol} \), which represents a theoretical efficiency of \( \eta_{th} = 0.83 \) (compared to the higher heating value). When operating at \( \eta_{th} \), an ideal fuel cell converts all available energy to electrical work. For this case, we calculate the reversible potential as:

\[
e_{o} = -\frac{\Delta \hat{g}}{nF},
\]

where \( n \) is the number of moles of electrons transferred per \( \Delta \hat{g} \) and \( F \) is Faraday’s constant. For cases of reactant gases at thermodynamic activities, \( a \), less than unity, theoretical potential will deviate from \( E_{o} \) according to the Nernst equation:

\[
e = E_{o} - RT \frac{1}{nF} \ln \frac{\prod a_{\text{products}}^{v_{i}}}{\prod a_{\text{reactants}}^{v_{i}}}
\]

where \( v_{i} \) represents reaction stoichiometric coefficients, \( T \) is reaction temperature, and \( R \) is the universal gas constant.

A common method for characterizing fuel cell performance is the polarization curve. Here, current density (i.e., rate of reaction) is gradually increased and fuel cell operating potential, \( V_{fc} \), is measured. In real fuel cell systems, \( V_{fc} \) decreases from the reversible potential of eqn. 1.3 due to irreversibilities. These irreversibilities, which
include activation ($\eta_{\text{act}}$), ohmic ($\eta_{\text{ohm}}$), and concentration ($\eta_{\text{conc}}$) losses, are characterized by overpotentials and are relate to $V_{fc}$ as:

$$V_{fc} = E - \eta_{\text{act}} - \eta_{\text{ohm}} - \eta_{\text{conc}}.$$  

In the following sections, we detail each overpotential and the corresponding dependence on both reaction rate and water management.

**Activation overpotential and reaction kinetics**

The activation overpotential, $\eta_{\text{act}}$, is the required potential difference to drive anode and cathode oxidation and reduction reactions at a given rate. Reaction rate depends exponentially on $\eta_{\text{act}}$ and is described by the Butler-Volmer relation as:

$$j = j_o \left( \frac{c_R^*}{c_R^o} \exp \left( \frac{\alpha nF \eta_{\text{act}}}{RT} \right) - \frac{c_P^*}{c_P^o} \exp \left( -\frac{(1-\alpha)nF \eta_{\text{act}}}{RT} \right) \right)$$

where $j$ is current density, $j_o$ is the exchange current density, $c$ is species concentration, $\alpha$ is the activation barrier symmetry parameter, subscripts $R$ and $P$ denote reactants and products, respectively, superscript $o$ denotes a reference concentration, and * denotes parameters measured at the catalyst surface [8]. We note that $j_o$ for oxygen reduction is two orders of magnitude smaller than for hydrogen oxidation, and as such, cathode kinetics typically dominate activation overpotential [9]. For even small activation overpotentials (e.g. $\eta_{\text{act}} > 50$ mV in low temperature systems), the second term in eqn. 1.5 becomes negligible and we can solve for $\eta_{\text{act}}$ to obtain the Tafel equation:

$$\eta_{\text{act}} = a + b \log j,$$

where $a$ and $b$ are empirically derived constants.

The total area available within the electrode for reaction is related to the so-called triple phase boundary, where electronic, protonic, and mass transport are all available for the oxygen reduction reaction to take place. As reviewed by Litster *et al.* [10], to maximize these triple-phase regions, a typical electrode is comprised of Pt catalyst, carbon-based support, ionomer (Nafion), and PTFE (for hydrophobicity). Water management within the electrode affects both protonic and mass transport. Liquid water retained in the catalyst layer blocks oxygen diffusion to catalyst sites, thus
reducing active area and leading to higher effective current density. In addition, catalyst layer ionomer dryout reduces protonic transport to catalyst sites, leading to both increased ohmic losses and reduced catalyst utilization.

**Ohmic overpotential and charge transport**

The ohmic overpotential, \( \eta_{\text{ohmic}} \), characterizes losses due to charge transport. These losses can be described by Ohm’s law and are divided into electronic and ionic components as:

\[
\text{eqn. 1.7} \quad \eta_{\text{ohmic}} = i(R_{\text{elec}} + R_{\text{ionic}})
\]

where \( R \) is resistance and \( i \) is current. Typically, proton transport irreversibilities dominate ohmic losses. We therefore rewrite this relation only for protonic conductance in the membrane as:

\[
\text{eqn. 1.8} \quad \eta_{\text{ohmic}} = j \times \text{ASR}
\]

where ASR is area specific resistance, which is the key figure of merit characterizing membrane ion transport. ASR is defined as:

\[
\text{eqn. 1.9} \quad \text{ASR} = AR_{\text{ionic}} = \frac{L}{\sigma}
\]

Here, \( A, L \) and \( \sigma \) are membrane area, thickness, and conductivity, respectively. As eqn. 1.9 shows, thin, highly conductive membranes lead to efficient charge transport. As we discuss in Section 1.2.1, Nafion requires full hydration for good protonic conductivity. As a result, membrane dryout leads to increased ohmic losses and large reductions in fuel cell efficiency.

**Concentration losses**

As reactants are consumed in the catalyst layer, their concentration decreases, resulting in a concentration gradient across the gas diffusion layer. Catalyst layer reactant concentration will continue to decrease until the diffusive flux of reactants from the gas channel is equal to the consumption rate. Using Fick’s law, for a given current density, we can estimate the steady state catalyst layer reactant concentration, \( c_R^* \), as:
eqn. 1.10 \[ c^*_R = c^0_R - \frac{j\delta}{nFD_{\text{eff}}} \]

where \( D_{\text{eff}} \) is the effective diffusion coefficient, \( \delta \) is the gas diffusion layer thickness, and \( c^0_R \) is the channel reactant concentration at the GDL surface. As eqn. 1.10 shows, reactant concentration at the catalyst layer decreases with increasing current density. The effect of this concentration drop on fuel cell performance is twofold: it leads to reduced reversible potential, \( E \), (as described by the Nernst equation, eqn. 1.3) and increased activation overpotential.

As described by O’Hayre et al.[11], \( \eta_{\text{conc}} \) can be written in terms of a limiting current density, \( j_L \):

\[ \text{eqn. 1.11} \quad \eta_{\text{conc}} = c \ln \frac{j_L}{j_L - j} \]

where \( c \) is a constant approximately equal to \( RT/nF(1+1/\alpha) \) and \( j_L \) is the maximum achievable current density as limited by reactant diffusion to catalyst sites. We determine \( j_L \) from eqn. 1.10 by setting catalyst layer reactant concentration, \( c^*_R \), equal to zero:

\[ \text{eqn. 1.12} \quad j_L = nFD_{\text{eff}} \frac{c^0_R}{\delta} \]

Flooding in the cathode can amplify concentration losses in at least two ways. Intrusion of liquid water into the GDL reduces gas permeability and thus \( D_{\text{eff}} \). In addition, flow field flooding leads to flow maldistribution and localized fuel starvation (reduction in \( c^0_R \)).

We note that one way to reduce concentration losses is to maximize the fuel concentration at the GDL/flow field channel interface. If we assume laminar, fully-developed flow (with negligible secondary flows), we can expect reactant concentration in the channel to be minimum near the GDL/channel interface and increase monotonically for increasing transverse distances from the GDL. As a result, we expect \( c^0_R \) to increase as the transverse reactant concentration distribution tends
toward uniformity. To characterize concentration uniformity, we compare diffusive and convective time scales ($\tau_{\text{diff}}$ and $\tau_{\text{conv}}$, respectively), where:

\[
\text{eqn. 1.13} \quad \tau_{\text{diff}} \propto \frac{h^2}{D} \quad \text{and} \quad \tau_{\text{conv}} \propto \frac{L}{\bar{u}}.
\]

Here, $h$ is channel height, $D$ is the binary diffusion coefficient for oxygen in air (for cathode), $L$ is channel length, and $\bar{u}$ is the average streamwise gas velocity in flowfield channels. We can assume well mixed channel conditions when $\tau_{\text{diff}}/\tau_{\text{conv}} \ll 1$. As such, transverse concentration gradients in gas channels are minimal when:

\[
\text{eqn. 1.14} \quad \text{Pe}_{h} \frac{h}{L} = \frac{\bar{u}h}{D} \frac{h}{L} \ll 1.
\]

Figure 1.2 is a contour plot of $\text{Pe}_{h}(h/L)$ versus air flow rate and channel height. All geometric parameters used (except channel height, $h$) were taken from the active water management flow field design discussed in Chapter 2 (namely 23 parallel channels of 1 mm width and length, $L = 5 \text{ cm}$). We assume stoichiometrically controlled experiments (gas flow rate is therefore proportional to $\alpha x j$). Scaling analysis indicates that reduced flow rates and channel heights both tend toward well mixed channel conditions. In our active water management experiments, cathode flow field channel height is 1 mm. In this channel height range, $\text{Pe}_{h}(h/L)$ varies widely over fuel cell operating conditions and increases to order unity at high current densities (and stoichiometries). The plot shows that the effect of channel height on mixing is strongest at high flow rates. For example, at the stoichiometric flow rate required for $\alpha x j = 2.0 \text{ A cm}^2$, decreasing channel height from 0.5 to 0.2 mm reduces the mixing parameter $\text{Pe}_{h}(h/L)$ from 0.28 to 0.11. In contrast, at the flow rate required for $\alpha x j = 0.5 \text{ A cm}^2$, this channel height reduction implies only a 0.04 drop in the mixing parameter.

As we shall see, in our passive water management experiments (see Chapter 4), channel height is 0.5 mm. As Figure 1.2 shows, this relatively small channel height results in fairly uniform reactant concentration and thus improves mass transport to the
catalyst layer. This conclusion is consistent with work by Cha et al. [12], who showed that mass transport limitations may be reduced by using smaller channel sizes.

Figure 1.2: Contours of $\text{Pe}_h(h/L)$ versus flow rate and channel height. When $\text{Pe}_h(h/L) \ll 1$, channel gases are well mixed and GDL/channel interface reactant concentration, $c_{k0}$, is approximately equal to bulk concentration in channels. Reduced flow rates and channel heights both tend toward well-mixed channel conditions.

Increases in hydraulic resistance limit the practical height to which channels can be reduced. White [13] provides an analytical solution relating pressure drop to flow rate for channels of rectangular cross section (see eqn. 3-48 of that reference). Using this relation, we can estimate the power required to deliver air as the product of air flow rate and pressure drop. Normalizing by fuel cell area yields a key figure of merit useful in characterizing air delivery parasitic power:

$$P_{\text{air}} = \frac{\Delta p \times \dot{Q}_{\text{air}}}{A_{\text{fc}}}$$

Here, $P_{\text{air}}$ is the air delivery power per total fuel cell area, $\Delta p$ is pressure drop across flow field channels, $\dot{Q}_{\text{air}}$ is total air flow rate, and $A_{\text{fc}}$ is the area of the fuel cell. Figure
1.3 is a contour plot of $P_{air}$ versus air flow rate and $h$. For the channel heights used in our fuel cell flow fields (0.5 mm and 1.0 mm), this model suggests that air delivery parasitic power is indeed negligible. We observe, however, that reductions in channel height can result in parasitic power losses on the order of fuel cell power (e.g., $P_{air} > 400 \text{ mW cm}^{-2}$ for $h < 30 \mu\text{m}$ at a typical operating point of $\alpha \times j = 2 \text{ A cm}^{-2}$). Results therefore indicate that channel heights should be chosen which simultaneously ensure well-mixed reactant concentration and low flow resistance.

![Figure 1.3: Contours of power required for air delivery, $P_{air}$ (mW cm$^{-2}$), versus air flow rate and channel height. A simple model indicates that $P_{air}$ is minimal for channel heights used in our experiments. Further reduction in channel height, however, can lead to air delivery parasitic power on the order of fuel cell power.](image)

1.2. Water management in PEFCs

A persistent challenge in PEFCs is water management [14]. Membrane humidity must be maximized to ensure good ionic conductivity [15], while excess product water must be removed to prevent electrode, gas diffusion layer (GDL), and flow field channel flooding [14]. As discussed, flooding has multiple impacts on fuel cell performance. At the very least, flooding reduces gas permeability in the GDL and, in effect, the limiting current [16-18]. In addition to GDL flooding, flow field channel
flood can lead to mal-distribution of reagent delivery, localized fuel starvation, and significant spatial non-uniformity in reaction rates [19-22]. These flooding events not only introduce large efficiency losses, but also lead to electrode and long term performance degradation [5]. Flooding poses additional challenges in stacks, where cell flow fields are manifolded in parallel. In such systems, flooding in a single cell has minimal impact on overall inlet-to-outlet pressure drop. As a result, product water can continue to accumulate. This leads to non-uniformity in cell-to-cell potentials, and, in severe cases, cell reversal [23].

In the following sections, we will first briefly discuss the effect of relative humidity on membrane conductivity. We will then give an overview of water transport mechanisms in the membrane and review strategies to leverage such transport to enhance membrane water uptake and conductivity. We will then overview challenges in GDL and flow field flooding and discuss transport mechanisms for water removal.

1.2.1. Membrane water balance

Nafion membranes

Current state-of-the-art PEFCs employ Nafion membranes for high ionic conductivity transport of protons. The chemical structure of Nafion consists of a tetrafluoroethylene backbone (PTFE) with sulfonate terminated perfluorovinyl ether side groups. Proton conduction is attributed to two mechanisms: Grotthus hopping and vehicular transport. Both mechanisms rely on the presence of water and as a result, conductivity is a strong function of membrane water uptake, $\lambda$. Conductivity increases linearly with $\lambda$, which is defined as the number of water molecules per acid group. At complete saturation, $\lambda = \sim 22$, which results in high membrane conductivities of up to $\sim 120 \text{ mS cm}^{-1}$. As shown early on by Springer et al. [24], $\lambda$ is a strong function of relative humidity (RH). Using an empirical fit, they determine the following relation for water uptake as a function of water activity (at $30 \degree C$):

$$\lambda = 0.043 + 17.81a - 39.85a^2 + 36.0a^3$$  

Their results indicate that even for relatively high RH of 80%, conductivity is limited to 50% of its fully saturated value. It is therefore essential that fuel cell gasses remain humidified to prevent membrane dryout and minimize corresponding ohmic losses.

**Water transport mechanisms in the MEA**

Primary mechanisms governing water transport within the membrane include electroosmotic drag and back diffusion, and to a much smaller extent, liquid permeation [25]. As mentioned above, protons travel via both a Grotthus hopping and vehicular mechanism. In the vehicular case, protons, which exist as dynamic aggregates of water molecules, travel in free solution from anode to cathode. During this process, they bring water molecules with them, resulting in what is termed electroosmotic drag (EOD). EOD is quantified by a coefficient identifying the number of water molecules associated with each proton. Many experimental techniques exist to measure EOD coefficient ($c_{EOD}$) directly (e.g., electroosmotic drag cells, radiotracer cells, or even working fuel cells) and, depending on operating conditions, $c_{EOD}$ has been found to range from 0.9 to 4.0 [26]. In general, EOD increases with temperature, $\lambda$ [25] and current density [27].

EOD, coupled with water generation in the cathode-side catalyst layer, often results in anode-side membrane dryout and a gradient in membrane water uptake. This gradient leads to back diffusion (BD) of water from cathode-to-anode. BD is typically quantified with a Fickian diffusion coefficient, which is a strong function of water uptake, changing by up to an order of magnitude with $\lambda$[15].

A convenient and useful metric for membrane water transport is the net water drag coefficient (NDC), which identifies the net number of water molecules transported from anode to cathode, per proton. Both positive and negative values of NDC have been shown [25] and NDC is strongly dependant on MEA materials, gas humidification, and fuel cell operating point. Negative values of NDC indicate net transfer of water from cathode to anode, and are in general, desirable to mitigate anode-side dryout. As such, one approach is to decrease membrane thickness and thereby aid anode-side hydration via enhanced back diffusion. Although this method has been successful [28], concerns remain regarding membrane reliability due to the
formation of pinholes [29]. Another approach is to integrate a cathode-side microporous layer (MPL) between the macroporous GDL and the electrode. This is thought to enhance cathode-side water uptake and liquid permeation, however, there is some disagreement on the actual MPL impact on water transport [30, 31]. While MPL integration consistently affects enhanced fuel cell performance, the exact mechanism for improvement remains an open research topic [25]. We note that membrane water transport largely depends on fuel cell operating point. In general, at low current density, EOD is small and back diffusion successfully aids anode side hydration. At high current density, however, EOD is large and often overcomes back-diffusion, thus resulting in reduced anode-side water uptake.

In addition to these approaches, novel methods have been employed to enhance membrane water balance. For example, Shichun et al. [32] dispersed self-assembled Pt nanoparticles throughout a Nafion membrane. As diatomic hydrogen and oxygen permeate, these catalytic sites enable their combination to water and thus aid internal hydration. In addition, several groups have developed composite membranes with dispersed, hydrophilic, in-organic particles [32]. The integration of these particles results in enhanced water retention and permeability. However, long-term reliability is yet to be shown [25].

It is important to note that, although significant strides in membrane design have enhanced dry-gas performance of PEFCs, membrane water uptake cannot be decoupled from feed-gas humidity. As a result, an often-used approach to achieving high efficiency is to fully humidify feed gases, thus minimizing membrane dehydration, and find ways to remove excess product water. In the following sections, we will explore these methods along with several novel approaches.

1.2.2. Fuel cell flooding and mitigation

To ensure good protonic conductivity, fully humidified feed-gases are often used in PEFC systems. While such operation prevents membrane dryout, this approach exacerbates mass transport issues resulting from liquid water production in the cathode. Such deleterious effects are typically addressed through GDL and flow field design. In this section, we first overview the role of the GDL in flood mitigation. We
then focus on flow field design, water transport mechanisms in flow field channels, and common approaches to product water removal. Finally, we highlight key water removal challenges and introduce the novel methods developed in this dissertation as means to address these challenges.

1.2.3. Gas diffusion layer

The gas diffusion layer (GDL) is situated between the membrane electrode assembly and flow field plates on both the anode and cathode sides. As discussed in Section 1.1.2, GDL materials help minimize mass transport losses by maximizing diffusive transport of reactant gases from flow field channels to reaction sites. Optimal GDL materials are electrically conductive, have high gas permeability, and are of geometries that minimize diffusion path length. In addition, the GDL must effectively transport produced liquid water from the electrode to flow field channels for subsequent removal, while maintaining gas permeability. Considerable work has been done in the development of GDL materials, and a comprehensive review can be found in [33]. Typically, PEFCs employ porous carbon based materials (e.g., carbon cloth or Toray paper) treated with PTFE as GDLs. As discussed by Lin et al. [31], ideal PTFE treatment results in both hydrophilic and hydrophobic pores, thus reducing GDL saturation while allowing effective water transport.

1.2.4. Water transport mechanisms in channels

Liquid product water emerges onto the hydrophobic GDL surface as droplets [34]. Depending on gas velocity, two modes of droplet removal have been observed [35]. At high air velocities, shear forces detach droplets from the GDL surface at sizes much smaller than channel dimensions. This results in water removal via mist flow, with droplet advection at the same speed as the gas. At low air velocities, however, droplet detachment size grows to being on the order of channel dimensions. As a result, droplets grow, come in contact with channel walls, and capillary forces wick water into channel corners. In-channel axial pressure gradients subsequently transport water downstream via corner or annular film flow.
In parallel channel flow fields operated at typical gas flow rates ($\alpha = 2.0$), superficial air velocities are low and capillary wicking and transport in channel corners dominates. This method of liquid water transport, however, is only possible for hydrophilic wall surface chemistry and channel geometry which satisfies the Concus-Finn condition [36]. Concus-Finn establishes a stability condition for corner flow, based on surface contact angle, $\theta$, and the half angle of channel corners, $\beta$. For cases where $\theta < \pi / 2 - \beta$, corner flow is stable, and becomes a primary mechanism for liquid-water removal. For $\theta > \pi / 2 - \beta$, corner flow is not stable and slug formation results. In parallel channel architectures, slug formation leads to channel clogging and is detrimental to fuel cell performance. As such, low contact angle channel surfaces are desirable to enhance water removal and avoid slug formation.

As Zhang et al. [35] show, the existence of corner flow does not ensure liquid water drainage at rates commensurate with water production. They develop an analytical model to estimate corner flow water drainage rate as a function of air stoichiometry. For their geometry of seven 0.5 mm x 1 mm channels, they predict that adequate product water drainage would require air stoichiometries greater than 7.0. In separate visualization experiments using an optically transparent fuel cell, Zhang et al. observed that, for cases where corner flow drainage is insufficient, annular films first develop, become unstable, and subsequently lead to slug formation and channel clogging. As we discuss in the following sections, these visualizations highlight the fundamental need for water management solutions in parallel channel flow fields, as the air flow rates required for adequate water drainage are often prohibitively high in traditional systems.

1.2.5. Water management techniques

Effective water management is critical for stable and long term reliable fuel cell performance [37, 38]. This is often addressed by using fully humidified inlet gas streams and incorporating serpentine channel cathode flow fields for air delivery [39]. Gas humidification prevents membrane dryout, while the long channel length and reduced air channel cross-sectional area of serpentine designs lead to increased
pressure drop and increased air velocities. As discussed in Section 1.2.4, depending on fuel cell operating point, either shear forces will remove liquid product water as a mist or pressure gradients will drive water drainage via corner flow. Although highly successful in achieving stable performance, this approach results in large parasitic power losses (as high as 35% of stack power) and increased system complexity [7, 39, 40]. Required auxiliary compressor and gas humidification systems also reduce power density thru increased system size, sometimes accounting for up to 20% of total fuel cell system volume [41].

Leveraging parallel channel architectures for PEFC cathodes can minimize air delivery parasitic power losses, as parallel channels require lower pressure differentials and thereby eliminate the need for high air compression. Parallel flow fields also offer improved transient performance reliability [42] and simplified flow field manufacturing processes [43]. Despite these benefits, parallel flow fields are seldom used as they are particularly susceptible to flooding [44]. Flooding is addressable in parallel channels, but this is typically accomplished by using very high air stoichiometries ($\alpha_{air} = 4-7$ [35, 43]); and this approach again results in significant parasitic power losses [45].

Several groups have proposed novel methods to minimize air stoichiometry requirements while maintaining effective water management. We here first review largely passive and then active water management strategies. Voss et al. removed excess product water through the anode by enforcing a cathode-to-anode membrane water saturation gradient [46]. This saturation gradient was realized through careful control of anode and cathode gas humidification. In another study, Inoue et al. developed cooling water channel designs to strategically impose thermal gradients, and by extension, saturation pressure gradients. This resulted in approximately uniform relative humidity [47]. Similarly, Li et al. leveraged in channel pressure gradients to maintain gas streams precisely at saturation [39]. As air pressure decreases with distance downstream, water carrying capacity increases. Li et al. used this effect to develop a simple cathode channel design model which matches increased water carrying capacity with water production rate. Although these methods have
shown effective water management, they significantly constrain system design and geometry, and are often not compatible with parallel channel, low-pressure differential, flow field designs.

An alternative approach is to use active flood mitigation for parallel flow field architectures. Yi et al. employed hydrophilic, porous carbon water transport plates as cell separators [48]. These water transport plates remain fully saturated and internally humidify undersaturated gas streams, while a pressure differential applied between gas and internal water transport channels removes excess product water. Buie et al. integrated an electroosmotic (EO) pump directly into a fuel cell cathode [49] and applied an electric field to drive liquid water from the GDL to an external reservoir. Litster et al. extended this idea by externally coupling an EO pump with a porous carbon cathode flow field [50, 51]. In this design, an EO pump generated pressure gradient removed excess product water absorbed by the porous carbon flow field. These active water management strategies all enabled stable, flood free performance in parallel channel flow field architectures, at significantly reduced air stoichiometries.

1.3. Using wicks for water management in fuel cells

Replacing all, or part, of the cathode flow field with porous material can enhance excess product water drainage and removal from the fuel cell. We show this schematically in Figure 1.4. Here, anode flow field, MEA and GDL are typical of traditional fuel cell systems, and we replace the cathode flow field material with a hydrophilic, porous material. Initially, liquid product water emerges from the GDL, is absorbed by the porous cathode flow field, and capillary pressure acts to distribute water throughout. As fuel cell operation continues, the cathode flow field reaches saturation and capillary pressure becomes negligible. As such, channel gas pressure and flow field liquid pressure are similar, and axial gas pressure gradients drive liquid flow downstream within the porous wick material.
Figure 1.4: Schematic of fuel cell design with porous cathode wick material for water management. Porous cathode is hydrophilic and initially acts as a sponge to absorb liquid product water as it emerges from the GDL. As porous material reaches saturation, capillary pressure becomes insignificant, resulting in similar pressure gradients in gas and liquid phases. As a result, axial air pressure gradients in channels drive liquid flow downstream within the wick.

In the following sections, we introduce two main strategies for water management which leverage wicking structures in the cathode. In the first, we couple a porous carbon flow field with an electroosmotic pump for active water removal. In the second, we integrate wicks in a state-of-the-art fuel cell flow field in a geometry designed for gas-pressure gradient driven flow of liquid product water.

1.3.1. Active water removal from PEFCs

Electroosmotic pumping

Electroosmotic (EO) pumps can potentially provide a large range of flow rates and pressure capacities, have no moving parts, and have a high self-pumping frequency [52, 53]. A simple EO pump consists of a porous substrate (often glass), two
electrodes, and a power source. Electrodes are used to create an electric field which imposes a Coulombic force on mobile counterions of electric double layers (EDLs) to create bulk fluid flow [53]. EO pumps have been applied in fuel cells [51, 54], high pressure liquid chromatography[55], and drug delivery [56].

When an electrolyte comes in contact with almost any surface, an EDL forms. In the case of the porous glass frits we use in the present work, surface silanol group donate protons to solution, resulting in a fixed layer of negative charges and a diffuse layer of mobile cations. The thickness of this layer is characterized by the Debye length, \( \lambda_D \), which for a symmetric electrolyte is:

\[
\text{eqn. 1.17} \quad \lambda_D = \left( \frac{\varepsilon k T}{2 \varepsilon^2 z^2 n_\infty} \right)^{1/2}
\]

where \( \varepsilon \) is permittivity, \( k \) is the Boltzmann constant, \( T \) is temperature, \( e \) is the charge of an electron, \( z \) is ion valency, and \( n_\infty \) is number density of ions. Physically, \( \lambda_D \) represents the balance of molecular diffusion, represented by \( kT \) energy, with Coulombic interaction with the wall, the spatial extent of which is related to the amount of charge in solution available to shield the wall’s zeta potential, \( \zeta \).

An applied stream-wise electric field, \( V_{app} \), will exert Coulombic force on net excess charge in the EDL. Viscous interaction with surrounding fluid results in bulk fluid motion and for a single capillary, with both electroosmotic and pressure driven flow, the resulting velocity profile will be:

\[
\text{eqn. 1.18} \quad u(r) = -\frac{a^2}{4 \mu L} \frac{\Delta P}{L} \left( 1 - \frac{r^2}{a^2} \right) - \frac{e \zeta V_{eff}}{\mu L} \left( 1 - \frac{\varphi}{\zeta} \right)
\]

where \( \Delta P \) is the applied axial pressure difference, \( V_{eff} \) is the effective applied potential\(^1\), \( L \) and \( a \) are capillary length and radius, respectively, \( \varphi \) is the radial potential distribution, and \( \mu \) is fluid viscosity.

\[^1\] \( V_{eff} \) is less than \( V_{app} \) and represents the portion of the electric potential dropped across the porous EO pump structure. Both decomposition overpotential and spacing between electrodes and porous structure lead to reductions in \( V_{eff} \).
Figure 1.5: A porous glass EO pump. (a) Schematic of porous glass EO pump modeled as many cylindrical microchannels in parallel (and detailed view of flow in one pore). An electric field, \( E \), is imposed using two electrodes on either side of the porous substrate. (b) A scanning electron micrograph of porous structure showing order 1 \( \mu m \) pores.

As shown schematically in Figure 1.5, an EO pump glass frit can be conceptualized as many tortuous channels in parallel. Using this as a model, Yao et al. [53] predicted EO pump flow rate as:

\[
Q = \frac{\psi}{\tau} \left[ \frac{-\Delta PAa^2}{8\mu L} - \frac{\varepsilon \zeta AV_{eff}}{\mu L} f \right]
\]

where \( \psi \) is porosity, \( \tau \) is tortuosity, \( A \) is pump frit area, and \( f \) is a non-dimensional parameter between 0 and 1, which accounts for finite EDL thickness. From this solution, we obtain maximum pump flow rate and pressure as:

\[
Q_{\text{max}} = -\frac{\psi \varepsilon \zeta A_{\text{EO}} V_{eff}}{\tau \mu L} f \quad \text{and} \quad P_{\text{max}} = -\frac{8\varepsilon \zeta V_{eff}}{a^2} f.
\]

As these expressions show, both flow rate and pressure scale with effective applied potential. In addition, high flow rates require large pump cross-sectional area, while high pressure requires small pores. As discussed in Appendix A, high pressure applications often require EO pumps pore radii on the order of 100 nm [57-59]. In these cases, the EDL carries a significant fraction of total current, which can lead to concentration polarization and propagation of long-range zones of ion depletion and
enrichment. In these cases, significant deviation from the performance predicted by the model of Yao et al. may result [60].

**Coupling EO pumps with cathode flow field for active water management**

We have performed several studies where we couple EO pumps with porous media for active water removal in fuel cells. As mentioned previously, Lister et al. developed and demonstrated an active water management system which coupled an EO pump with a porous carbon, parallel-channel flow-field, to enable flood free performance at low air stoichiometries. Using this system, they achieved a 60% increase in peak fuel cell power with < 0.5% EO pump parasitic. Lister later developed an engineering model which examined coupling of EO pumps with wicks and showed that EO pumps indeed scale favorably for PEFC applications [61]. For example, Lister estimated that parasitic loads of < 1% can be readily achieved so long as EO pump area, $A_{EO}$, is no less than 1% of fuel cell active area. We note that this engineering model is a conservative estimate, as it did not consider passive water drainage mechanisms (e.g. gas-pressure gradient driven flow) and primarily focused on EO pump driven flow.

In Chapter 2, we further elucidate the impact of EO pump/wick systems on fuel cell performance. By segmenting the fuel cell anode, we provide new and significant understanding of flow field flooding and recovery when using parallel channel architectures with active water management.

1.3.2. **Integrated wicks for passive water management**

As Figure 1.4 shows, gas pressure gradients can induce liquid flow in wicks for enhanced water drainage. In Chapter 4, we leverage this passive mechanism to enable stable, flood-free performance in a stamped-metal-type parallel channel architecture, at very low air stoichiometries. We employ in situ polymerized wicks which conform to and coat cathode flow field channel walls, thereby spatially defining regions for water and air transport. Axial in-channel air pressure gradients induce water flow downstream within channel wicks and to a wick header in the outlet manifold. Excess product water then either travels out through the gas outlet or through a porous wall via a slight pressure difference between the outlet manifold and ambient. In effect,
ricks provide a liquid water transport pathway from reaction sites to outside of the fuel cell, along which gas pressure gradients drive flow.

1.4. Scope of dissertation

This dissertation covers the development and characterization of active and passive water management methods for PEFCs. In Chapter 2 we examine transient and steady state performance of a fuel cell with active water management. This study builds on previous work in our lab and employs a segmented fuel cell anode for detailed characterization of spatial variations in fuel cell performance. In Chapter 3, we detail the design and fabrication of porous polymer wick structures. We investigate the relation between polymer chemistry, resulting microstructure, and relevant transport parameters. In Chapter 4, we apply these wicks to a fuel cell cathode for passive water management. Finally, in Chapter 5, we summarize key contributions and conclusions, and make recommendations for further work.
Chapter 2
SEGMENTATION OF AN ACTIVE WATER MANAGEMENT SYSTEM

Unless otherwise noted, this chapter is adapted with minimal modification from “Current distribution in polymer electrolyte membrane fuel cell with active water management,” *Journal of Power Sources*, 174(1), 272–281, 2007.

We here present a detailed study of an active water management system for PEFCs, which uses a hydrophilic, porous cathode flow field, and an electroosmotic (EO) pump for water removal. This active pumping of liquid water allows for stable operation with relatively low air flow rates and low air pressure and parallel cathode channel architectures. We characterize in-plane transport issues and power distributions using a three by three segmented PEFC design. Our transient and steady state data provide insight into the dynamics and spatial distribution of flooding and flood-recovery processes. Segment-specific polarization curves reveal that the combination of a wick and an EO pump can affect a steady state, uniform current distribution for a parallel channel cathode flow field, even at low air stoichiometries (a_w = 1.5). The segmented cell measurements also reveal the mechanisms and dynamics associated with EO pump based recovery from catastrophic flooding. For most operating regimes, the EO pump requires less than 1% of the fuel cell power to recover from near-catastrophic flooding, prevent flooding, and extend the current density operation range.

2.1. Introduction

We recently presented a water management technique that eliminated the need for excessive air flow rates by integrating a low power pump to directly remove water from cathode channels and the gas diffusion layer of PEFCs (see Litster *et al.* [62]).
This system employed a porous carbon cathode flow field and coupled electroosmotic (EO) pump for water removal from a 25 cm² fuel cell. Results showed consistent, flood-free performance at air stoichiometries as low as $\alpha_{\text{air}} = 1.3$, and the EO pump required <1% of fuel cell power. In this chapter, we leverage the segmentation of the anode of the 25 cm² fuel cell described by Litster, to gain new insight into water transport in this active water management system. Cell segmentation provides measurements of local current density within the fuel cell. Such data provides insight into localized phenomena including oxygen depletion at the cathode and flooding events.

Segmentation is a unique diagnostic tool for examining spatially and temporally resolved flooding events. Mench et al. [63] used cell segmentation to observe current density as a function of streamwise length in a serpentine channel cathode flow field. They observed decreased current density near the cathode outlet, with losses intensifying at low air flow rates. These power losses were attributed to liquid water accumulation in the GDL. Yoon et al. [64] investigated flooding effects using a segmented cell (nine by nine segments) with a triple serpentine cathode and single serpentine anode flow field. Yoon induced cell flooding by increasing gas inlet relative humidity. Similar to Mench et al., flooding was observed first near the cathode outlet and then continued toward the inlet until a steady state condition was reached. Although cell segmentation has been conducted in these and other cell configurations [64-79], few studies have examined parallel cathode flow field architecture and, to the best of our knowledge, no studies have investigated current distribution with porous carbon media for cathode flow fields. Our work is therefore the first segmented anode study of a porous carbon cathode, with and without active water management.
2.2. Experimental

2.2.1. Fuel cell assembly and operating conditions

As described above, our design is based on the 25 cm$^2$ PEFC design presented by Litster et al. [62]. The fuel cell assembly, including the segmented anode components introduced in this paper, is shown schematically in Figure 2.1.

![Figure 2.1: Schematic of 25 cm$^2$ PEMFC assembly. Fuel cell features a porous carbon cathode flow field with coupled EO pump for water management, and segmented anode side current collector and flow field for current distribution measurements. Membrane is a commercially available catalyst coated MEA (Ion Power Inc, Newcastle, DE), with Teflon gasket for sealing. Silicone rubber electrically insulates current collectors from aluminum end plates. Four bolts tightened to 35 in-lb provide cell compression. Assembly endplates were machined from aluminum (McMaster – Carr, Atlanta, GA), and were equipped with Kapton heaters and K-type thermocouples for temperature control. Aluminum end plates were electrically insulated from the current](image)
collectors with a 0.5 mm thick silicone rubber layer. The fuel cell was equipped with cathode side water management flow field, and a segmented anode flow field and current collector. We describe the latter components in the next two sections.

We used a commercially available catalyst coated membrane electrode assembly (MEA), obtained from Ion Power Inc. (Newcastle, DE). Four 1/4”-20 bolts tightened to 35 in-lb were used for compression. For all experiments, we operated the fuel cell at a temperature of 55 °C. Inlet gas dew points were also 55°C. Hydrogen flow rate was $\alpha_{H2} = 2.0$. The system components and fuel cell operating conditions are summarized in Table 2.1. Further details regarding the MEA, cathode flow field, and supporting systems (e.g., air and fuel delivery) are given by Litster et al.

Table 2.1: Summary of fuel cell system components and operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane electrode assembly</td>
<td>Ion Power CCM</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>25 µm</td>
</tr>
<tr>
<td>Platinum loading</td>
<td>0.3 mg Pt cm$^{-2}$</td>
</tr>
<tr>
<td>Gas diffusion layer</td>
<td>SGL 10-BB (non-woven w/ MPL)</td>
</tr>
<tr>
<td>Fuel cell active area</td>
<td>25 cm$^2$</td>
</tr>
<tr>
<td>Anode gas</td>
<td>H$_2$ (&gt;99.995%)</td>
</tr>
<tr>
<td>Anode dew point</td>
<td>55°C</td>
</tr>
<tr>
<td>Hydrogen stoichiometry</td>
<td>2.0</td>
</tr>
<tr>
<td>Air stoichiometries</td>
<td>1.3 - 6.0</td>
</tr>
<tr>
<td>Cathode gas source</td>
<td>Air (extra dry)</td>
</tr>
<tr>
<td>Cathode delivered air dew point</td>
<td>55°C</td>
</tr>
<tr>
<td>Endplate temperatures</td>
<td>55°C</td>
</tr>
<tr>
<td>Gas line temperatures</td>
<td>60°C</td>
</tr>
<tr>
<td>Electroosmotic pump area</td>
<td>2 cm$^2$</td>
</tr>
<tr>
<td>Electroosmotic pump voltage</td>
<td>12 V (unless noted otherwise)</td>
</tr>
</tbody>
</table>
2.2.2. Cathode flow field for active water management

We here summarize the design of the cathode flow field with integrated water management; further details are given by Litster. As shown in Figure 2.2a, a parallel flow field was machined from porous carbon (SGL SIGRACET-plate PGP material, SGL Technologies GmbH, Germany), which was then heat treated (baked at 300 °C for 3 min) for increased hydrophilicity. The porous carbon was then seated into a non-porous graphite base. A small (1 cm x 2 cm) tab of the porous carbon layer extends out of the assembly, and this external wick region is coupled to the electroosmotic pump assembly. The electroosmotic pump assembly consists of (starting from above the cathode region and in the major pump flow direction as shown in Figure 2.2b) an acrylic frame, a mesh platinum pump anode, a hydrophilic poly-vinyl alcohol (PVA) filter component, a porous borosilicate glass frit (glass filter from Robu-Glas, Germany), a mesh platinum pump cathode, and a second acrylic frame. The pump hydraulically couples to the porous carbon wick through the PVA filter component, which helps electrically isolate the pump and serves as a filter, keeping particles (e.g., carbon) out of the pump. The acrylic frames add support and the electrodes are attached via wire clamps to external steel wire leads. When dry, the wick and pump initially act as a passive wick, which removes water from the cathode channels and SGL (see Figure 2.2b). Once these porous components are saturated with fuel cell product water, the pump’s electrochemical circuit is automatically closed and the pressure differential generated by the EO pump creates a slight local vacuum in the PVA filter. This local vacuum extracts product water from the fuel cell wick, and this product water is then pumped out by the EO pump.
Figure 2.2: (a) Exploded assembly view of water management system on cathode side featuring 25 cm$^2$ porous carbon flow field and 2 cm$^2$ EO pump, and (b) schematic of water flow through porous carbon wick to the EO pump. The hydrophilic porous carbon flow field absorbs product water from the GDL and functions as a current collector. The EO pump provides a pressure gradient, which pulls water from the flow field, pumps it through the PVA filter, and rejects it externally. White arrows show direction of water flow.
2.2.3. Segmentation

Segmentation Techniques

Segmentation methods were initially developed to examine local effects of evolving gases and mass transport losses in electrolytic cells [80, 81]. Cleghorn et al. [67] first adapted segmentation for current distribution measurements in PEFCs using printed circuit board (PCB) technology to fabricate a segmented anode flow field and current collector. Stumper et al. [77] published an early review paper on three methods of segmentation: partial MEA, sub-cells and current mapping. First, the partial MEA method employs a partially catalyzed membrane that limits electrochemical reaction to specific areas within the fuel cell plane. Several MEAs with progressively more area catalyzed are used. The necessary disassembly and reassembly of the fuel cell, and use of significantly modified MEAs between each step, makes reliable and reproducible results difficult. The second method, the sub-cell method, addresses this repeatability issue by creating a small electrically isolated island within the cell. This island provides spatially precise current density information only for the area it covers. The third method is the current mapping technique, which involves a passive resistor network that is inserted between the flow field plate and the current collecting bus. This technique allows complete mapping of the current distribution in the fuel cell with some loss in accuracy due to lateral current flow through both the flow field plate and GDL.

Bender et al. [65] refined the cell segmentation technique by segmenting the entire anode side of the fuel cell including the electrode, GDL, flow field, and current collector. Bender also carefully calibrated contact resistances throughout the flow field and used Hall sensors for low impedance, ex situ current measurements. These efforts resulted in a reduction of error due to lateral currents; and the group demonstrated real time measurements of current distribution. Continuing work in the area of fuel cell segmentation has focused on stack integration [70, 78], application to larger scale fuel cell systems [82], implementation of segment specific electrochemical impedance spectroscopy [76], and increase of spatial resolution. Recently, Freunberger et al. [68] demonstrated sub-millimeter resolution, providing insight into mass transport issues in
land and channel areas of the flow field plate. In this work, we segment the anode flow field plate and current collector into a three by three array. We leave the MEA and GDL undisturbed and unsegmented to minimize the invasiveness of cell segmentation.

Fabrication

An anode flow field with three by three segmentation was fabricated as shown in Figure 2.3. The process for isolating sections of the anode is similar to that reported by Schneider et al. [76]. Grooves, 1 mm wide x 3 mm deep were machined into a 70 x 70 x 5 mm graphite block (Fuelcellstore.com, Boulder, CO) and then filled with an electrically insulating resin (6366K41, McMaster-Carr, Atlanta, GA). After curing at room temperature for 24 h, the surface was hand sanded to a smooth finish.

Figure 2.3: Fabrication process for segmented anode flow field plate. (1) We machined grooves (1 mm width, 3 mm depth) into a 70 x 70 x 5 mm graphite block. We then filled the grooves with a low viscosity epoxy resin and let set at room temperature for 24 h. (2) Next, we hand sanded the top side to a smooth finish and faced (end milled) the back side to a total thickness of 2 mm, thereby electrically isolating the nine segments. (3) We then machined a three channel serpentine flow field into the top face of the block.
We then faced (end milled) the block from the side opposite the milled sectioning grooves to a thickness of 2 mm, leaving nine electrically isolated segments. A three channel serpentine flow field pattern was then end milled into the front of the block. These channels had channel width, channel depth and rib thickness of 0.75 mm.

A printed circuit board (PCB) segmented current collector was designed and manufactured using a custom, rapid manufacturing protocol (ExpressPCB™) as shown in Figure 2.4. Nine 16.3 x 16.3 mm, 43 µm thick copper pads were printed in a three by three array on the top side of the PCB. Four small thru vias connect each pad to a printed lead on the backside of the board; and these leads electrically join each segment to a connector array (header) for connection to the data acquisition instrumentation. After receiving the PCB from ExpressPCB, we electroplated the copper pads and leads with a 10 µm nickel diffusion barrier and 1 µm gold layer (Electrochem, Inc., Union City, CA). A 0.5 mm thick silicone-rubber layer between the end plate and the PCB board (see Figure 2.1) prevented electrical shorts between leads.

![Figure 2.4: Images of both sides of the printed circuit board segmented current collector. Nine 16.3 x 16.3 mm pads were printed on the front side of the board for contact with graphite flow field segments. Four small thru vias electrically connect each pad to a lead on the backside of the board, which connect to a linear array for connection to instrumentation. We electroplated the PCB leads and contact pads with a 10 µm nickel diffusion layer and 1 µm gold layer.](image)
Flow field configuration

Figure 2.5 shows a schematic of the segmented anode flow field and the porous cathode flow field with a hydraulically coupled, external EO pump. Air entered near segment one, traveled through the porous carbon 23-channel parallel flow field plate and exited near segment nine. Hydrogen entered near segment nine, traveled through the triple serpentine segmented flow field and exited near segment one. The EO pump was positioned near segments six and nine, near the cathode outlet, in order to minimize hydraulic resistance between the pump and the areas most susceptible to flooding.

Figure 2.5: Flow field configuration for all experiments. Shown are the nine segments of the anode plate and the cathode assembly including air flow field channels and the EO pump. The anode and cathode employed a triple serpentine and 23-channel parallel flow configuration, respectively. Also shown are the inlets and outlets for hydrogen and air.
2.2.4. Instrumentation

A schematic of the segmented cell instrumentation is shown in Figure 2.6. Electrical current flows to each of the nine anode segments. We used low impedance (specification by manufacturer of 0.18 mΩ) Hall effect current sensors (LAH-25NP, LEM, Switzerland) to measure current in each channel. Minimizing impedance of the measuring circuit reduces lateral potential differences along the cell area (which can cause unwanted lateral currents).

Figure 2.6: Diagram of cell instrumentation. Electric current travels to the anode current collector thru nine parallel channels, each fitted with a Hall effect current sensor. The Hall sensors output a current proportional to the measured current, which is converted to a measured potential via 1 kΩ precision resistors. The nine channels are connected in parallel to the electronic load, which is connected in series with the fuel cell cathode. Cell potential is measured across the electronic load.
We mounted the Hall sensors on a PCB and electroplated the leads with 180 µm silver (Electrochem, Inc., Union City, CA) to further reduce impedance. These sensors output a measurement current proportional to the conducted signal current, which we converted to a measured potential difference using 1 kΩ precision resistors. We used a PCI-6031E data acquisition card and LabView software for all measurements (National Instrument, Austin, TX). The nine Hall sensor outputs were connected in parallel to the electronic load (Agilent N3301A, Santa Clara, CA), which was in series with the fuel cell cathode.

2.2.5. Impedance calibration

To ensure uniformity of contact resistance, we compressed the current collector in series with the segmented graphite flow field, gas diffusion layer and a copper plate. We then measured impedance through each segment, from PCB lead to copper plate, using the highly sensitive four-wire method and a sourcemeter (Keithley 2400 Sourcemeter, Cleveland, OH). Our mean segment impedance and standard deviation was 15.5 and 2.84 mΩ, respectively. We attribute the variation in segment impedance to differences in current collector PCB trace lengths. The maximum neighboring segment percent voltage difference due to non-uniform impedance was approximately 4.0% at a total-area-averaged current density of \( \bar{j} = 1 \text{ A cm}^{-2} \). The latter is the normalized maximum percent voltage difference between segments due to segment impedance differences (assuming uniform current distribution); calculated as \((\Delta R_{\text{max}}/V_{\text{cell}})(i/N)\cdot100\%\). Here \( \Delta R_{\text{max}} \) is the maximum impedance difference between neighboring segments, \( i \) is the total operating current, \( N \) is the number of segments, and \( V_{\text{cell}} \) is the approximate cell voltage for the given \( i \). Note that actual percentage voltage difference between neighboring segments will in practice exceed the estimate above, as segment voltage difference is also a function of the instantaneous current density in each segment. As shown by our measurements below, neighboring cells often experience relatively large differences in current density (as high as 750 mA cm\(^{-2}\) differences). Accordingly, the metric given above, which assumes uniform current
density, is useful only as a measure of resistance uniformity, and should not be interpreted as the actual voltage difference between segments contributing to cross currents.

Using the current interrupt method, we measured the ohmic impedance of the segmented cell as 8.10 mΩ. This is an increase of 1.25 mΩ over the measured impedance of the same fuel cell without cell segmentation (see Litster et al.). We use this increase as an estimate of the impedance contributed by segmentation (including flow field segmentation, PCB current collector, measurement leads and current sensors). This results in an area specific resistance change due to segmentation of 31.3 mΩ cm² and an average segment measuring impedance increase of 11.3 mΩ.

Overall, we expect some current spreading due to measurement impedance, particularly under non-uniform current distribution operating conditions (see Eckl et al.[83]). However, the degree of error is non-prohibitive in qualitative current distribution characterization.

2.3. Results and discussion

2.3.1. Steady state

Polarization curves for the segmented fuel cell operated at stoichiometries between 1.3 and 6.0 are shown in Figure 2.7. In these first plots, we show the sum total current from all segments in the cell without EO pumping and with EO pumping at \( V_{EO} = 12 \) V. We obtained each polarization curve by increasing overall current density by 0.1 A cm⁻² every 10 min. Voltages shown are the average of the last 2 min of data collected for each 10 min dwell time. Before each polarization curve, we operated the fuel cell at a total-area-averaged current density, \( \bar{j} \), of 0.8 A cm⁻² for 10 min and then purged using high air flow rates to ensure consistent membrane hydration and a flood-free start condition. We terminated polarization curve measurements when the instantaneous cell voltage dropped below 0.2 V. We provide here only a brief description of the performance of the system with EO pumping and refer the reader to Litster et al. [62] for a detailed study of this identical cathode wick and EO pump.
design. Litster includes detailed comparisons between this and two control designs: a second design with a wick but no EO pumping, and a third design with a solid graphite plate cathode (and no EO pumping). Consistent with the work of Litster et al., the present results show that fuel cell operation was flood-free with EO pumping for stoichiometries of $\alpha_{\text{air}} = 2$ to 6, and flooding was significantly mitigated for $\alpha_{\text{air}} \leq 1.5$. Parasitic EO pump power consumption was nominal, ranging between 0.2 and 1% of total fuel cell power production for most operating regimes. This excludes very low operating current densities ($\bar{j} \leq 0.1 \text{ A cm}^{-2}$), where percent power consumption increased to 1 to 2%.

Figure 2.7: Polarization curves showing total fuel cell performance for different stoichiometries, with (a) EO pump off and (b) EO pump on. Data are shown for stoichiometries of $\alpha_{\text{air}} = 1.3$ (○), 1.5 (▼), 2.0 (△), 3.0 (◇), and 6.0 (□). Total cell current was held constant during each 10 min dwell time. Data points represent the time average of the last 2 min of data for each current increment. Without EO pumping, flooding prevents fuel cell operation at $\alpha_{\text{air}} = 1.3$ for all current densities, and prevents operation at $\alpha_{\text{air}} = 1.5$ for current densities above $\bar{j} = 0.2 \text{ A cm}^{-2}$. With EO pumping, fairly robust fuel cell operation is achieved at these low stoichiometries.
Segment-specific polarization curves for air stoichiometries of $\alpha_{air} = 1.5$ thru 3.0 are shown in Figure 2.8. For each operating air stoichiometry, polarization curves without EO pumping and with EO pumping at $V_{EO} = 12$ V are shown. For $\alpha_{air} \leq 2.0$, EO pumping significantly extended the operating range of the fuel cell and/or increased maximum power density. With no EO pumping and $\alpha_{air} = 1.5$, 2.0 and 3.0, the max power densities (averaged over the entire area) were 120, 420 and 470 mW cm$^{-2}$ respectively. In comparison, for EO pumping at 12 V, the respective max power densities were 350, 440 and 470 mW cm$^{-2}$. As expected, pumping had the strongest effect for low stoichiometries. At $\alpha_{air} = 1.5$, the case without EO pumping resulted in severe flooding at low current densities. For example, for the $\alpha_{air} = 1.5$ case, the current density for many of the segments dropped dramatically near current densities of 0.2 A cm$^{-2}$; indicative of catastrophic flooding. In contrast, with EO pumping, the fuel cell performance range was extended past current density values of 0.8 A cm$^{-2}$.

The data also show important spatial trends associated with flooding and the role of the EO pump in preventing flooding. We here first describe global trends and later discuss the specific cases. For $\alpha_{air} \geq 2.0$ and with EO pumping, current densities were highest in upstream segments and lowest in downstream segments. As a result, for each stoichiometry, polarization curves grouped into three distinct regions—high current, mid current and low current density—corresponding to upstream, midstream and downstream (with respect to cathode flow field) segments. We attribute this result to the reduction in oxygen partial pressure as oxygen is consumed at the cathode. Further, as air stoichiometry increased, the differences between segment groups systematically decreased. For $\alpha_{air} = 2.0$, 3.0 and 6.0, the segment-to-segment standard deviations of segment current densities, at a mean current density of 1.0 A cm$^{-2}$, were 0.132, 0.097, 0.070 A cm$^{-2}$, respectively. This trend is consistent with the expected increase in homogeneity of oxygen partial pressure as air stoichiometry increases.
Figure 2.8: Polarization curves with EO pump off (left) and EO pump on at $V_{EO} = 12$ V (right) for air stoichiometries of $\alpha_{air} = 1.5$ (a, b), $\alpha_{air} = 2.0$ (c, d), and $\alpha_{air} = 3.0$ (e, f). Segment locations are shown in Figure 2.5, and are labeled as segments 1 (●), 2 (●), 3 (〇), 4 (■), 5 (□), 6 (△), 7 (◆), 8 (◇), and 9 (◇). EO pumping resulted in significant enhancement (extension) of the range of performance for low air stoichiometry, and flood-free performance at higher stoichiometries.
We next discuss the challenging operation condition of $\alpha_{\text{air}} = 1.5$. At this low stoichiometry and with no EO pumping, nearly all segments clearly experience severe flooding at current densities above 0.1 A cm$^{-2}$. The maximum achievable current density was $\bar{j} = 0.2$ A cm$^{-2}$. Activation of the EO pump extended the operating range and the maximum achievable $\bar{j}$ to 0.8 A cm$^{-2}$. For the latter case, the most severe flooding was limited to segments 4, 7, and (to a lesser degree) 1. These segments are positioned furthest from the EO pump. We conclude that at these current densities, the EO pump was unable to remove all excess product water and, as a result, channels far from the EO pump were left to flood.

At $\alpha_{\text{air}} = 2.0$, the case without EO pumping resulted in severe flooding for current densities between $\bar{j} = 0.2$ and 0.7 A cm$^{-2}$. Flooding effects were less pronounced for current densities beyond $\bar{j} = 0.7$ A cm$^{-2}$. We attribute this mid-range current density flooding and subsequent recovery at higher current densities to the effects of passive water removal by the wick. For these fixed $\alpha_{\text{air}}$ curves, high current density implies higher air flow rate. As discussed by Litster et al., cathode channel flow, the wick, and EO pump system act together to remove water. For the EO pump placement considered here, pressure gradients in the cathode channel translate to in-plane pressure gradients in the wick. These pressure gradients provide a driving force that helps pump water through the wick and toward the EO pump and outlet. At the highest maximum current density value ($\bar{j} = 1.2$ A cm$^{-2}$), the segment current densities again segregated into three groups corresponding to upstream, midstream and downstream segments, suggesting that at this high current operating condition, flooding was not significant. With EO pumping, the fuel cell also achieved a current density of $\bar{j} = 1.2$ A cm$^{-2}$. We note that fuel cell operation was flood free when the EO pump was activated. Accordingly, EO pumping effectively eliminated flooding previously seen during low current density operation. The low current density operating regime is of general interest. For example, low current operation is desirable in automotive applications during vehicle idle, where auxiliary systems are the primary fuel cell load. Accordingly, GM/NIST [84] recently published a paper where they investigate
fuel cell stack flooding at an operating current of 0.2 A cm$^{-2}$. Aluhwalia et al.[7] also show fuel cell performance optimization at low power density to be essential for high overall efficiency. We conclude that EO pumping resulted in a meaningful improvement in fuel cell performance for $\alpha_{\text{air}} = 2.0$.

At $\alpha_{\text{air}} = 3.0$ and without EO pumping, the sharp drops in fuel cell voltage indicative of flooding were observed at current densities of $\bar{j} = 0.2$ and 0.3 A cm$^{-2}$, and primarily in the outlet header and outer channels. For currents higher than about $\bar{j} = 0.4$ A cm$^{-2}$, the fuel cell again recovers from flooding. We again attribute this to advection of water through the wick due to pressure gradients in the cathode channels. At this high $\alpha_{\text{air}}$, high current density regime, product water is largely removed passively by the wick and we therefore expect no significant improvements from EO pumping. Above $\bar{j} = 0.7$ A cm$^{-2}$, the segment current densities again segregate into distinct groups of upstream, midstream and downstream segments. In the case with EO pumping, as with $\alpha_{\text{air}} = 2.0$, we see no signs of flood-related mass transport losses throughout the regime of operation.

Lastly, in Figure 2.9, we present polarization curves for the case of $\alpha_{\text{air}} = 1.3$ and with EO pumping at 12 V. We first note that without EO pumping, this low $\alpha_{\text{air}}$ case resulted in catastrophic flooding at $\bar{j} = 0.1$ A cm$^{-2}$ and therefore no polarization curve could be obtained. These data therefore document fuel cell operation regimes that are accessible only with EO pumping. Operation at $\alpha_{\text{air}} = 1.3$ is possible, but EO pumping provides insufficient water management at the chosen pump voltage. At this extremely low air stoichiometry case, pressure differences in the cathode are negligible (we estimate less than 400 Pa difference between inlet and outlet). Channel regions far from the pump (e.g., segments 4 and 7 and, to a lesser degree, segment 1) are therefore more susceptible to flooding for $\alpha_{\text{air}} = 1.3$ as compared to $\alpha_{\text{air}} = 1.5$. This observed performance improvement at $\alpha_{\text{air}} = 1.5$ suggests that even the small increase in cathode inlet pressures from $\alpha_{\text{air}} = 1.3$ to 1.5 is significant. In Section 2.3.3, we will
present transient studies that confirm that, for low $\alpha_{\text{air}}$, the EO pump has the strongest effect for regions close to the EO pump.

Figure 2.9: Segment-specific polarization curves for $\alpha_{\text{air}} = 1.3$ and EO pumping at 12 V. Segment locations are shown in Figure 2.5, and are labeled as segment 1 (●), 2 (●), 3 (○), 4 (■), 5 (■), 6 (□), 7 (●), 8 (●), and 9 (○). Catastrophic flooding prevented measurement of a polarization curve at this low air stoichiometry, without EO pumping. Accordingly, all of the data shown here represent operating conditions enabled by EO pumping. Segments located far from the EO pump experienced the most significant losses due to flooding. Catastrophic flooding prevented operation beyond $\bar{j} = 0.5$ A cm$^{-2}$.

Although not shown here, we also performed experiments at higher values of $\alpha_{\text{air}}$. At the high stoichiometric ratio of $\alpha_{\text{air}} = 6.0$, the polarization curves with and without EO pumping were consistently nearly identical. In both cases, fuel cell performance was free of flooding in all segments and at all current densities. We again attributed this to relatively high cathode-to-pump pressure differences resulting in the removal of product water passively via the wick. Operation at this high $\alpha_{\text{air}}$ does not require the EO pump.
2.3.2. Current density uniformity and performance

As discussed in Section 2.3.1, when the cathode flow field is free of flooding, segment-specific polarization curves cluster into three distinct groups of upstream, midstream, and downstream segments. We hypothesize that the norm of the current density standard deviations of each of these three clusters can be used as a measure of performance non-uniformity (and by extension, a measure of the presence of flow field flooding). We write this as:

\[ \| \sigma_j \| = \left( \sigma_\circ^2 + \sigma_\square^2 + \sigma_\diamondsuit^2 \right)^{1/2} / j \]

where \( \sigma \) is the standard deviation between current densities of upstream (\( \circ \)), midstream (\( \square \)), and downstream (\( \diamondsuit \)) segments, calculated from polarization curve data in Figure 2.7. We can calculate this non-uniformity parameter for each operating point along polarization curves and use the corresponding \( \bar{j} \) at each point to normalize. Here, \( \| \sigma_j \| \) is defined such that high values indicate increased non-uniformity of fuel cell performance.

We investigate the effect of non-uniformity on fuel cell efficiency by calculating the normalized increase in total overpotential, \( \phi_\eta \), where performance is compared to a flood-free control case at \( \alpha_{\text{air}} = 6.0 \). Here, \( \phi_\eta \), is defined as:

\[ \phi_\eta = \frac{E_{\text{OCV}} - V_{\text{fc}} - (E_{\text{OCV, control}} - V_{\text{fc, control}})}{E_{\text{OCV, control}} - V_{\text{fc, control}}} \]

where total overpotential, \( \eta \), is the difference between operating voltage, \( V_{\text{fc}} \), and open circuit voltage, \( E_{\text{OCV}} \), for each point on a given polarization curve. Physically, this can be interpreted as the fractional increase in irreversibilities over flood-free channel conditions.

Using data from the segment-specific polarization curves in Figure 2.7 where the EO pump is turned off, we plot \( \phi_\eta \) versus \( \| \sigma_j \| \) in Figure 2.10. Data show an approximately linear dependence of \( \phi_\eta \) on \( \| \sigma_j \| \). This result is strong validation that
performance degradation observed while the EO pump is turned off is due to non-uniformity in performance and, by extension, flow field channel flooding.

![Figure 2.10: Flow non-uniformity, $\|\sigma_j\|$, versus normalized performance degradation, $\phi_n$. Data show an approximately linear dependence of $\phi_n$ on $\|\sigma_j\|$. These data indicate that performance degradation observed while EO pump is turned off is due to non-uniformity in performance and, by extension, flow field channel flooding.](image)

In Figure 2.11, we plot $\|\sigma_j\|$ versus $\alpha_{air} \times \bar{j}$ (which we use as a proxy for air-flow rate). Data show that, for operating points of $\bar{j} > 0.1$ A cm$^2$, performance non-uniformity is strongly dependant on air flow rate and decreases as approximately $\|\sigma_j\| \approx 0.45 / (\alpha \times \bar{j})$ (dashed line).

We note that for a given air stoichiometry, water production rate increases proportionally with air flow rate. These data therefore highlight a non-intuitive result that, for constant $\alpha_{air}$ operation, the extent of flow field flooding decreases with increasing current density (and water production rate). As shown by Zhang et al. [35],
stability of channel flow regimes (e.g., corner or slug flow) is related to in-channel superficial velocity and pressure gradients. We hypothesize that the non-linear relation between air-flow rate and performance non-uniformity is likely related to the number of channels that can simultaneously operate without slug formation at a given air flow rate. Further investigation is necessary to elucidate underlying physics governing such multi-phase transport in parallel-channel porous cathode architectures and the corresponding effect on fuel cell performance.

Figure 2.11: Performance non-uniformity versus air flow rate, calculated from polarization curve data for \(a_{\text{air}} = 1.5\) (x), 2.0 (O), and 3.0 (\(\triangle\)), where the EO pump is turned off. Grey symbols are from data at \(\bar{j} = 0.1\) A. For operating points of \(\bar{j} > 0.1\) A cm\(^{-2}\), performance non-uniformity decreases approximately as \(\|\sigma_j\| \equiv 0.45 / (\alpha \times \bar{j})\) (dashed line).

2.3.3. Transient results

We performed a fairly extensive set of start-up and flood recovery experiments with our segmented cell setup. We here summarize the performance of the system as it floods (in the absence of the EO pumping) and as it recovers from severe flooding (upon activation of the EO pump).
Figure 2.12: Power density distribution (and cell potential) of fuel cell operated at $\alpha_{\text{air}} = 1.5$, $\alpha_{\text{H}_2} = 2.0$, and $\bar{j} = 0.5$ A at four instances in time: (a) immediately after purge, (b) after heavy flooding and immediately before EO pump is engaged, (c) at an initial stage of fuel cell recovery and (d) at the approximate steady state end condition. The corresponding cell configuration and orientation is shown in Figure 2.5. Plots show transition from flood-free to near catastrophic flooding operation, and then subsequent recovery once EO pump was engaged at 10V (at $t = 390$ s).

We discuss operation at $\alpha_{\text{air}} = 1.5$ and $\alpha_{\text{H}_2} = 2$, and a constant total-area-averaged current density, $\bar{j}$, of 0.5 A cm$^{-2}$. At these conditions, steady state operation leads to
significant flooding without EO pumping and to flood-free operation when the EO pump is activated. We first purged the fuel cell with a high air flow rate to ensure a flood free start condition. We then operated the fuel cell without EO pumping until flooding caused the cell voltage to drop below about $V_{EO} = 0.2$ V. At this point we activated the EO pump at $V_{EO} = 10$ V to initiate fuel cell recovery. We measured segment current densities and cell voltage continuously for the 15 min duration of the experiment.

Figure 2.12 shows power density distribution plots at four instances in time. The bar heights on each plot represent the power density of each segment. We show segment orientation with respect to the cell configuration in Figure 2.5. The plots chronologically show power distribution at the following four instances: immediately after purge ($t = 0$ s), after heavy flooding and immediately before EO pump is engaged ($t = 390$ s), during fuel cell recovery ($t = 450$ s, about 1 min after activation of the EO pump), and at the approximate steady state end condition ($t \geq 900$ s).

$V_{cell}$ immediately following purge was 0.64 V. As expected, Figure 2.12a shows that this initial fuel cell operating condition resulted in approximately uniform power distribution throughout the cell area. The power density decreased slightly with increased distance downstream. This reduction was expected and was most probably due to oxygen consumption at the cathode. After about 6 min of operation, fuel cell flooding was nearly catastrophic as fuel cell performance deteriorated significantly from the starting condition; resulting in a minimum voltage of $V_{cell} = 0.19$ V and a strongly non-uniform power distribution as shown in Figure 2.12b. At this heavily flooded condition, performance losses were most significant in the outer channels of the cathode flow field and intensified with distance down stream. The manifold cross-sectional area (with respect to flow direction) was 5.0 times larger than the cross-sectional area of each parallel channel, which should result in similar pressure drops across all channels. We attribute this difference between the flooding of interior and exterior channels to the effects of in-plane temperature gradients. For example, the interior channels should experience the highest temperature and will therefore benefit from higher vapor pressure, and a resulting increase in evaporative water removal (see
Hickner et al. [85]). Also, the upstream segments near the inlet header (segment 2, and to a lesser degree segments 1 and 3) produced significantly higher power densities than the remaining segments. We attribute this to the combined effects of downstream flooding and oxygen consumption. For finite power production in all segments, liquid water accumulation is expected to increase with downstream distance, while local stoichiometric ratio decreases—both limiting local reaction rates. This trend is consistent with the work of Mench and Yoon [63, 64] who observed increased flooding with distance downstream in single and triple serpentine cathode flow fields.

Upon activation of the EO pump at $t = 390$ s, recovery was first observed in segments near the EO pump, followed by regions increasingly further from the EO pump. This trend of preferential water removal from areas near the pump is consistent with our steady state experiments for $\alpha_{\text{air}} = 1.3$ and 1.5, where EO pumping was unable to remove product water from far field channels. We conclude that, as anticipated, the EO pump should be located near areas most likely to flood in order to hasten flood recovery and minimize necessary pump voltage. After about 1 min of EO pumping, the fuel cell recovered considerably from the nearly catastrophic flood condition, as shown in Figure 2.12c. At this point in the recovery, $V_{\text{cell}}$ slightly exceeded the initial non-flood voltage, with an operation voltage of 0.65 V. However, current distribution was not nearly as uniform as the starting condition, as segments opposite the EO pump (segments 4 and 7, and, to a lesser degree, segment 1) still showed performance degradations indicative of flooding. The increased power here is most probably due to a minimization of ohmic losses resulting from improved membrane hydration. We hypothesize that the initial purging (to insure no initial flooding) slightly reduced membrane humidity and conductivity.

Full fuel cell recovery was achieved about 3 min after EO pumping was first initiated. This approximate flood-free steady state condition was maintained for the remainder of the 15 min test period. This steady state operation is shown in Figure 2.12d. The final operating voltage increased slightly to $V_{\text{cell}} = 0.66$ V, and revealed a uniform current distribution consistent with the flood-free operation observed initially (shown in Figure 2.12a).
At all stages of the transient experiment, flow channels near the EO pump (by segments 3, 6, and 9) performed consistently better than flow channels opposite the EO pump (by segments 1, 4, and 7). This includes both extremes: the heavily flooded state with EO pump off, and the flood-free steady state end condition with an activated EO pump. At the heavily flooded state, the segment-column-averaged current densities were 0.45 A cm\(^{-2}\) for the near-pump segments and 0.29 A cm\(^{-2}\) for the segments opposite the EO pump. We attribute this to passive, wick-to-pump water removal (see Litster et al. [62] for a more detailed discussion of this issue). With EO pump activated at 10 V, these respective current densities were 0.53 and 0.46 A cm\(^{-2}\).

As shown earlier in this section and in our steady state experiments for \(\alpha_{\text{air}} = 1.3\) and 1.5, the EO pump initially preferentially removes water from nearby areas in the wick flow field. Continuous use of the EO pump for higher \(\alpha_{\text{air}}\) ensures steady state operation of the entire fuel cell without flooding.

2.4. Conclusion

We presented a segmented cell study for a 25 cm\(^2\) PEFC with a cathode-side active water management system. This system used an external EO pump hydraulically coupled to an integrated, hydrophilic porous carbon flow field (wick) for product water removal. This active water management enabled flood-free operation of a 23-channel parallel cathode flow field at low air stoichiometries. Parallel flow field structures greatly reduce the work required to drive forced air convection.

We analyzed water transport issues of the wick/pump system by studying steady state and transient current densities in nine segments. We found that, for moderate air stoichiometries (\(\alpha_{\text{air}} \leq 3.0\)), the fuel cell floods without EO pumping. This flooding resulted in strongly non-uniform and low average power densities. Under partially flooded conditions, performance was best in areas near the cathode inlet header, as losses due to flooding intensified with distance downstream. Inner channels consistently showed better performance than outer channels, which we attribute to in-plane thermal gradients and the resulting increased vapor pressure for interior channels.
Transient experiments showed that upon pump activation, the fuel cell recovered to the flood-free cell voltage within 30 s. Recovery from the heavily flooded state began in regions close to the EO pump, followed by regions increasingly further from the EO pump. Steady state operation of the EO pump ensured flood-free operation for $\alpha_{\text{air}} \geq 2.0$. For these flood-free operating conditions, variations in reactant concentration dominated spatial trends in fuel cell performance, resulting, again, in a slight decrease of fuel cell performance with distance downstream. As expected, as air stoichiometry increased, downstream gradients in oxygen concentration became less significant and performance losses due to concentration reduction were minimized. Parasitic EO pump power consumption was low, ranging between 0.2 and 1% of total fuel cell power production for most operating regimes.
Chapter 3

**DESIGN AND FABRICATION OF POROUS POLYMER WICK STRUCTURES**

Unless otherwise noted, this chapter was adapted with minimal modification from “Design and fabrication of porous polymer wick structures,” under review, *Sensors and Actuators B*, 2010.

3.1. Introduction

In 1990, Tennikova *et al.* [86] first demonstrated highly crosslinked, rigid, microporous polymer monoliths as separation media for high performance membrane chromatography. This initial demonstration has since led to a wide variety of techniques for preparation of porous polymer monoliths, which allow control over pore morphology, mechanical stability, and surface chemistry [87]. Pore size distributions are often bimodal, with large and small pores resulting in materials with both high permeability and high specific surface area. These materials are therefore ideal for many separation applications including liquid chromatography [88], capillary separations [89], capillary electrochromatography [90-92], thin layer chromatography [93] and, more recently, gas chromatography [94]. In addition, polymer monoliths have been used as porous frits in electroosmotic pumps [95], in microfluidic devices for on-chip separations and low Reynolds number mixing [96, 97], as hydrogen storage media [98], and for water management in fuel cells [99]. To our knowledge, outside of the recent effort by Strickland and Santiago [99], there have been no dedicated efforts aimed at realizing high permeability, hydrophilic, porous polymer monoliths suitable for wicking and other multiphase transport applications.

Porous polymer monoliths are synthesized by carrying out free-radical polymerization of crosslinking and monovinyl monomers, in the presence of solvents. Heat, ultraviolet (UV) irradiation, or gamma-rays generate free-radicals by destabilizing an initiating compound [87]. These free-radicals initiate rapid polymer chain growth at what become nucleation sites, which continue to grow as the reaction proceeds. As polymer molecular weight increases, solubility decreases, and a two-phase system of solid polymer and liquid solvent results. The resulting monolith
microstructure consists of an agglomeration of globules, whose size directly impacts resulting pore-size distribution. Globule size is influenced by many factors, including the number of nucleation sites present, monomer concentration, solubility, and degree of cross-linking [100]. Thus, polymer microstructure can be controlled by rate of reaction, monomer/porogen ratio, type of porogenic solvents and fraction of cross-linking monomers. Detailed descriptions of various chemistries and characterization of resulting monoliths can be found in [87] and [100].

In the present work, we designed, fabricated, and characterized porous monoliths of hydroxyethylene methacrylate-co-ethylene glycol dimethacrylate (HEMA-co-EDMA) with the aim of achieving high permeability, hydrophilic, dimensionally and chemically stable materials for use as wicks. In general, wicks are porous, hydrophilic structures that are commonly used to absorb and transport liquids. Wicks are applied to heat pipes and vapor chambers [101], microfluidic systems [102], lateral flow chemical assays on cellulose paper[103], fuel cells [104, 105], and electrospray nozzles [106]. For most applications, an ideal wick has high permeability and can support significant capillary-pressure-induced liquid pressure gradients. Often these two properties are in competition: large pores are required for high permeability, while small pores induce large capillary pressures. In the following sections, we identify key parameters affecting resulting monolith permeability and pore size, discuss competing microstructure properties in detail, and identify strategies to optimize performance for a given application. As an example application, we then discuss a custom injection molding procedure, where we integrated wicks with order 100 μm feature sizes in a polymer electrolyte fuel cell cathode flow field. The latter integration was described as part of a prototype fuel cell system we reported previously [99], however that study centered on the performance of the wick as a component of the system. Here, we present new analysis, methods, and results which specifically focus on the chemistry, process optimization, molding, *in situ* polymerization, and capillary transport properties of the wick structure itself. Our aim is to enable wider applications of such *in situ* polymerized wicks.
3.2. Materials and methods

We here describe materials, discuss choice of chemistry, and present ex situ fabrication methods of polymer monolith samples used for characterization. Characterization included permeability, pore size, and surface area measurements. We describe in situ polymerization of the monolith structures in Section 3.4.

3.2.1. Materials

Ethylene glycol dimethacrylate (EDMA - CAS# 97-90-5), 2-hydroxyethyl methacrylate (HEMA - CAS# 868-77-9), inhibitor removal media (product number: 311332 - CAS 9003-70-7), benzoin methyl ether (CAS# 3524-62-7), and methanol (MeOH) 99.93% were purchased from Aldrich. n-Hexane HPLC grade 95+% was purchased from Alfa Aesar. GE Type 214 quartz tubing (5 mm i.d., 7 mm o.d.) was purchased from National Scientific Company Inc. (Quakertown, PA). GE Type 214 quartz tubing was chosen for its high (>90%) UV 360 nm wavelength transmittance [107].

3.2.2. Polymer chemistry

Wicking structures require hydrophilic surface functionality to absorb water or aqueous solutions. We therefore chose a polymerization chemistry that incorporates the monovinyl monomer, HEMA, which has a polar hydroxyl functional group. Adapting a chemistry from Yu et al. [108], we crosslinked HEMA with EDMA via free radical, UV-initiated polymerization in the presence of MeOH and hexane as solvents. As Yu et al. showed, an MeOH/Hexane binary solvent system provides satisfactory solubility for polymerization and is ideal for large-pore formation (we discuss effect of polymer solubility on pore size in Section 3.3.1) [108].

We photo-initiated polymerization via UV irradiation and destabilization of benzoin methyl ether. We chose photo, rather than thermal initiation, for the present polymerization. Thermal initiators require long polymerization times and elevated temperatures, which can lead to significant evaporative loss of solvents in imperfectly sealed molds. In contrast, photo-initiation can be carried out at room temperature over
shorter polymerization times, thus minimizing evaporative solvent loss. The chemical scheme is depicted in Figure 3.1.

Figure 3.1: Ethylene glycol dimethacrylate (EDMA) reacts with 2-hydroxyethyl methacrylate (HEMA), in the presence of MeOH and hexane, to produce Poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate). UV light destabilizes benzoin methyl ether to produce free-radicals, which initiate rapid polymer chain growth at what become nucleation sites. As polymer molecular weight increases, solubility decreases, and a two-phase system of solid polymer and liquid solvent results. Resulting monolith microstructure consists of an agglomeration of polymer globules, whose size directly impacts resulting pore-size distribution.

To characterize the chemistry and resulting monoliths, we varied two separate ratios: (1) total monomer/solvent and (2) MeOH/hexane. We list recipes in Table 3.1. In all cases, 1.25% (by mass, with respect to monomers) benzoin methyl ether was used.

3.2.3. Ex-situ fabrication for permeability and pore size measurements

Both EDMA and HEMA were received with polymerization inhibitors, which we removed by passing through columns packed with inhibitor removing media. We then mixed the photoinitiator (benzoin methyl ether), HEMA, EDMA, MeOH and n-hexane in the order listed, in glass vials and subsequently purged with nitrogen to minimize oxygen dissolved in solution. Purge was carried out by bubbling nitrogen at 0.3 scfh
for ~2.5 min. In all cases, solution weight change before and after purge was less than 3%.

We transferred solutions into quartz tubes, which we sealed with custom-fabricated Teflon caps. We then irradiated samples using a 100 W, ~365 nm peak wavelength UV lamp, at 8 cm exposure distance, for 1 h. During polymerization, solution changed from transparent to white and visibly opaque in less than 10 min. After polymerization, we flushed samples with methanol to remove unreacted monomers and solvents, and dried at 120°C for 1 h.

3.2.4. Measurement of permeability

Permeability, $k$, of a specific porous material can be interpreted as a material property. Specifically, it is the proportionality constant in Darcy’s law relating pressure difference to superficial fluid velocity in porous media [109]. A form of Darcy’s law is:

$$\text{eqn. 3.1: } \bar{u} = \frac{k}{\mu} \nabla p_l$$

where $\mu$ is fluid viscosity, $\bar{u}$ is the superficial liquid velocity, and $\nabla p_l$ is the pressure gradient in the liquid phase. $\bar{u}$ can be integrated over the cross-sectional area normal to the flow to obtain a linear relationship between pressure gradient and flow rate. Assuming a one dimensional linear pressure distribution and rearranging, this yields $k = \mu (Q/\Delta p) (L/A)$, where $Q$ is the flow rate, $A$ is the cross-sectional area normal to the superficial velocity vector, and $L$ is the distance across which the pressure difference, $\Delta p$, is applied. To measure permeability, we removed the samples from quartz tubing and transferred them into 3/16” heat shrink tubing (SPC Technology, Chicago, IL). Heat shrink sealed around and connected samples to silicone tubes on either end. We observed a good seal around polymer samples with minimal dimensional change due to compression.

We connected samples to a mass flow controller (MC-5SLPM-D, Alicat Scientific, Tucson, AZ) and upstream pressure transducer (PX139 – 030D4V Omega Engineering, Stamford, CT). Permeability was measured by flowing air (ultra zero grade compressed air cylinder, Praxair Inc., San Ramon, CA) through the sample at
seven different flow rates in the range of 20 to 1000 sccm. We set flow rate and measured $\Delta p$ across the sample using a PC with LabView 8.5. To determine $k$, we performed a linear regression fit for each sample to determine the $Q/\Delta p$ slope. $R^2$ values for these fits were higher than 0.98. Since $\Delta p$ depends linearly on $Q$, we determined permeability by directly substituting $Q/\Delta p$ into the above derived one dimensional expression for $k$. We report results in Table 3.1.

3.3. Results

The microstructure of a porous wick material strongly affects its capacity to transport fluids. In this section, we first discuss mechanisms and general trends in resulting monolith microstructure. We then explore the corresponding impact on monolith permeability and capillary transport. Finally, we detail a method for integrating wick structures into a fuel cell as a sample application which requires fine geometric control.

3.3.1. Mechanisms and trends in monolith polymerization

Mechanisms and trends for methacrylate monolith polymerization chemistries are discussed in detail by Vlakh et al. [110]. We summarize here major concepts from Vlakh et al. as we leveraged their study to guide our design and characterization experiments. As mentioned above, four main parameters control resulting monolith structure and properties: (1) rate of reaction, (2) monomer/porogen ratio, (3) solubility and (4) degree of cross-linking.

Rate of reaction

Typically, photo- or thermal-initiators are used to induce polymerization. Initiators form free radicals when exposed to UV radiation or heat, which then induce rapid polymer chain growth by opening and linking monomer vinyl groups. As such, initiator concentration, reaction temperature, and irradiation intensity all influence reaction rate. In general, mean pore size decreases with increasing reaction rate. This relationship is attributed to increased polymer nucleation site concentration, which
affects polymer globules of increased number density and smaller characteristic dimension.

**Monomer-to-porogen ratio**

Porosity is roughly equal to the volumetric fraction of porogenic solvents present [111]. The volumetric ratio of total monomer to total porogenic solvent, therefore, gives fairly direct control over resulting monolith porosity. Physical properties of resulting monoliths limit the range of porosities that can be achieved: non-porous samples typically result at high monomer concentration (roughly $> 0.6 \text{ mL mL}^{-1}$), while samples become friable for low monomer concentration ($< 0.2 \text{ mL mL}^{-1}$).

**Solubility**

A binary solvent system, comprised of a good and poor solvent, is typically used to control polymer solubility. In general, mean pore diameter increases with decreasing solubility of monomers. When a poor solvent is used, polymers can become insoluble at lower molecular weights and therefore precipitate early in the reaction. Remaining monomers are a better solvent than the poor solvent selected, resulting in increased monomer concentration in their vicinity. Polymer growth near existing globules is therefore thermodynamically preferred, and leads to fewer polymer globules of larger characteristic dimension.

**Degree of cross-linking**

Degree of cross-linking is controlled by the ratio of divinyl to mono-vinyl monomers. Changing this ratio affects both the pore size distribution and the chemical composition of the resulting polymer monolith. Pore size typically decreases as degree of cross-linking increases. During reaction, highly cross-linked polymers quickly become insoluble. This results in increased globule number density, and associated polymer globules of smaller characteristic dimension.

**3.3.2. Control and optimization of wick porosity and pore structure**

We limited the present study to exploring the effect of monomer/porogen ratio and solubility on resulting monolith pore structure. We performed a 3 x 3 parametric
study, where we varied both monomer/solvent ratio and solubility (via the binary solvent mixture). We fabricated and characterized monoliths for monomer/solvent ratios of 30/70, 40/60, and 50/50, and MeOH/hexane ratios of 40/60, 50/50, and 60/40 (by mass). In all cases, HEMA/EDMA ratio was 50/50. Resulting monoliths were characterized using mercury intrusion porosimetry to determine pore size distribution and BET analysis to measure specific surface area (Porous Materials, Inc., Ithaca, NY). We measured monolith permeability in-house, as described in Section 3.2.4. Table 3.1 summarizes results. Chemistries for which resulting monoliths were non-porous are indicated with an “n/a” in the porous properties entries.

Table 3.1: Polymer chemistries and corresponding measured properties

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemistry composition</th>
<th>Properties:</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HEMA</td>
<td>EDMA</td>
<td>MeOH</td>
<td>Hex</td>
<td>$\rho$</td>
<td>$d_{mode}$</td>
<td>$d_{median}$</td>
<td>$\bar{d}$</td>
<td>$V_p$</td>
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<td>0.77</td>
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<td>7.6</td>
<td>1.1</td>
<td>3.0</td>
</tr>
<tr>
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<td>0.15</td>
<td>0.35</td>
<td>0.35</td>
<td>0.77</td>
<td>10.1</td>
<td>7.2</td>
<td>1.1</td>
<td>4.6</td>
</tr>
<tr>
<td>HE06</td>
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<td>0.15</td>
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<td>0.28</td>
<td>0.77</td>
<td>9.0</td>
<td>8.4</td>
<td>0.93</td>
<td>3.6</td>
</tr>
<tr>
<td>HE13</td>
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<td>0.20</td>
<td>0.36</td>
<td>0.36</td>
<td>0.68</td>
<td>7.6</td>
<td>6.8</td>
<td>1.1</td>
<td>2.6</td>
</tr>
<tr>
<td>HE14</td>
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<td>0.20</td>
<td>0.30</td>
<td>0.30</td>
<td>0.68</td>
<td>7.9</td>
<td>6.8</td>
<td>1.6</td>
<td>2.5</td>
</tr>
<tr>
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<td>0.20</td>
<td>0.36</td>
<td>0.24</td>
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<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
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<td>6.3</td>
<td>3.3</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>HE23</td>
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<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>HE24</td>
<td>0.25</td>
<td>0.25</td>
<td>0.30</td>
<td>0.30</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

“Concentration by mass fraction (g g$^{-1}$), $^b$porosity, $^c$most common pore diameter, taken as peak of pore size distribution (μm), $^d$median pore diameter, taken as pore size at 50% of total pore volume during mercury intrusion (μm), $^e$characteristic pore size distribution width (μm), $^f$porous volume (mL g$^{-1}$), $^g$specific surface area (m$^2$ g$^{-1}$), $^h$permeability (x 10$^{12}$ m$^2$), $^i$equivalent particle diameter (μm), and $^j$capillary transport parameter (μm).

In Figure 3.2, we plot mean pore size versus the gravimetric fractions $w_{MeOH} = m_{MeOH}/m_{solvents}$ and $w_{solvent} = m_{solvents}/m_{total}$. Data showed a strong increase in pore diameter with increasing solvent fraction. This trend can be seen most clearly for $w_{MeOH} = 0.40$, where polymerizations were successful for all three solvent concentrations. As solvent fraction increases, so does total pore volume. For similar polymer globule formation characteristics (a reasonable assumption for these three
cases, where porogen and monomer compositions are identical) porogenic solvents are expected to occupy volumes of larger characteristic dimension and increased pore size results.

Figure 3.2: Mode pore size as a function of mass fractions $w_{\text{MeOH}}$ ($= m_{\text{MeOH}}/m_{\text{solvents}}$) and $w_{\text{solvent}}$ ($= m_{\text{solvent}}/m_{\text{total}}$). Mode pore diameter increases with both increasing solvent and MeOH fractions. Pore size dependence on solvent fraction is more pronounced.

In addition, the data of Figure 3.2 suggest a maximum in $d_{\text{mode}}$ around $w_{\text{MeOH}} = 0.5$. This is seen most clearly for $w_{\text{solvent}} = 0.70$, where mode pore diameter increased from 8.6 to 10.1 and then decreased to 9.0 μm, for $w_{\text{MeOH}} = 0.4$, 0.5, and 0.6, respectively. This result is consistent with trends observed by Yu et al. [112] who characterized the impact of porogenic solvent composition on median pore size. Yu reported a gradual increase in median pore diameter when increasing $w_{\text{MeOH}}$ from 0.20 to 0.60. At $w_{\text{MeOH}} = 0.60$, pore size reached a maximum and then decreased suddenly upon further increase. We note that porogen composition is a particularly powerful tool for tailoring monolith pore structure for wick applications, as it has minimal impact on monolith chemical composition and porosity.
3.3.3. Designing high performance porous polymer wick material

We elucidate the effect of monolith microstructure on transport characteristics by again considering Darcy’s Law. As eqn. 3.1 shows, holding all else constant, transport rate grows linearly with both permeability and liquid pressure gradient. In general, materials with large pores have high permeability, and therefore, high transport rates. At the same time, capillary transport requires small pores to maximize achievable liquid pressure gradients. In the next two sections, we will consider both permeability and capillary pressure dependency on microstructure in porous polymer monoliths. In addition, we will discuss opportunities to leverage key attributes of monolith microstructure to optimize transport for different applications.

Microstructure and permeability

Pore structure plays a critical role in determining resulting monolith permeability. We here discuss models for permeability, $k$, of eqn. 3.1, presented earlier. An often-used model for relating pore size to macroscopic permeability was developed by Carman and Kozeny [109]. Their model applies Hagen-Poiseuille type flow to an assumed pore structure comprised of many parallel, tortuous channels, of characteristic diameter, $d$. This results in the following relation for permeability:

$$k = \frac{\varepsilon d^2}{16k'},$$

where $\varepsilon$ is porosity, and $k'$ is a geometric parameter describing pore shape and tortuosity. In real systems, there is no single pore dimension, and instead, the hydraulic diameter, $d_H$, is typically used for characteristic diameter. $d_H$ is defined as four times the void volume to surface area ratio. For porous media, the resulting relation is:

$$d_H = \frac{4\varepsilon}{s(1-\varepsilon)},$$

where $s_o$ is specific area (pore surface area normalized by solid phase volume). Substituting into eqn. 3.2, we see that

$$k = \frac{\varepsilon^3}{k'(1-\varepsilon)^2 s_o}.$$
When applied to packed beds of spheres, specific surface area is related to particle diameter, $d_p$, as $s_o = 6/d_p$. Substituting and fitting to experimental data on packed beds, Carman found $k' = 5$, and obtained the result:

$$k = \frac{\varepsilon^3 d_p^2}{180(1 - \varepsilon)^2}$$

Although eqn. 3.5 predicts permeability well for packed beds, its applicability across different types of porous media, including polymer monoliths, is limited [113]. Errors are associated with increased porosity (i.e., porosity significantly greater than interstitial porosity of packed beds of spheres; typically ~0.4), wide distributions in pore sizes, and complex pore shapes and geometries. One approach is to determine an equivalent length scale describing monolith permeability, which can be used for comparison to more traditional porous media (e.g., beds of packed spheres) [113]. For example, by employing eqn. 5, along with permeability measurements and an assumed packed-bed porosity of 0.4, we can determine an equivalent particle diameter, $d_{p,eq}$ [114, 115]. We give calculations of such a $d_{p,eq}$ of polymer monoliths in Table 3.1. Although this is a useful figure of merit for comparisons of hydrodynamic performance of diverse media, the physical significance of $d_{p,eq}$ is difficult to discern, as it neither represents pore size nor correlates well with particle size, as calculated from specific surface area measurements.

Monolith pore structure complexity has limited the success of developing an analytical expression relating permeability to microscale properties. In particular, determining an appropriate length scale characterizing pore structure is difficult, as pore size distributions are often far from monodisperse. For example, Table 3.1 lists characteristic pore size distribution width, $\sigma$, for polymer monoliths. $\sigma$ represents the standard deviation of a Gaussian, fit to the measured pore size distribution. As results indicate, in our polymer monoliths, distribution width is within an order of magnitude of $d_{mode}$.

As an approximation, Guiochon [114] suggests using a length scale related to average through-pore diameter, in conjunction with the Carman-Kozeny relation. Figure 3.3 shows measured versus predicted permeability, when using eqn. 3.2 with $d$
$d_{mode}$ and $k' = 1.3$ for our porous samples and samples of similar structures from the literature. The published data are from three manuscripts and cover a wide range of permeabilities. In addition, the inset of Figure 3.3 shows measured versus predicted permeability using data from the present study only. For these data, $k' = 2.4$ provided the best fit.

![Predicted versus measured permeability for polymer monoliths. Predicted permeability calculated using eqn. 3.2, with $d = d_{mode}$, and with $k' = 1.3$ as a fitting parameter for porous polymer monoliths. Grey symbols (■) represent monolith data from the current study as summarized in Table 3.1. Inset shows fit for these data only, using $k' = 2.4$. Open symbols represent data taken from literature: Viklund et al.[116] (○), [117] (<), and Mehrar et al. [111](>). Data show rough dependence of permeability on $\varepsilon d_{mode}^2$. Significant scatter suggests physics governing hydraulic resistance are not fully captured when using porosity and $d_{mode}$ as a single measured length scale.](image)

Although results roughly show permeability dependence on $\varepsilon d_{mode}^2$, the significant scatter in data suggests that using a single measured length may not capture key physics which arise in polymer monoliths. Although beyond the scope of this paper,
further work is needed to explore specific flow effects associated with polymer monoliths, and reconcile these with porous flow data. Possible fruitful areas include accounting for bi-modal pore size distributions, the topography of these complex pore networks, and effects of broad pore size distributions.

Permeability dependence on polymerization chemistry

In Figure 3.4, we plot measured permeability of monoliths as a function of both \( w_{\text{MeOH}} \) and \( w_{\text{solvent}} \). Measured permeabilities ranged from \( 0.73 \times 10^{-12} \) to \( 1.9 \times 10^{-12} \) m\(^2\). Data show permeability increased with increasing MeOH and total solvent fractions. In general, results are consistent with expected dependence on monolith pore size and porosity. For all samples, except for HE06, mean pore size increased with increasing \( w_{\text{MeOH}} \) and \( w_{\text{solvent}} \). In addition, porosity is approximated by \( w_{\text{solvent}} \). We therefore expect increases in \( w_{\text{MeOH}} \) and \( w_{\text{solvent}} \) both to contribute toward high permeability. For the current chemistry, maximum permeability was achieved for the case of maximum \( w_{\text{MeOH}} \) and \( w_{\text{solvent}} \) (i.e., sample HE06). This result is not expected when using \( d_{\text{mode}} \) to characterize permeability, as \( d_{\text{mode}} \) for HE06 was slightly less than for HE05. We note that \( d_{\text{median}} \), however, was greatest for HE06. These results again highlight the difficulty associated with choosing a single measured length scale to characterize monolith microstructure and predict resulting permeability. In general, however, results confirm that when designing monoliths for high permeability, chemistries which result in high porosity and large pore sizes are desirable.
Figure 3.4: Monolith permeability as a function of \( w_{\text{MeOH}} \) and \( w_{\text{solvent}} \). Permeability ranged from \( 0.73 \times 10^{-12} \) to \( 1.9 \times 10^{-12} \) m\(^2\). Results show permeability increased with increasing \( w_{\text{MeOH}} \) and \( w_{\text{solvent}} \). Monolith permeability is consistent with trends in porosity and pore size (see Figure 3.2).

A note on wick geometry

We note that a wick’s capacity to transport fluids is also highly dependent on wick geometry. Transport capacity increases with cross-sectional area normal to flow and is inversely proportional to characteristic wick length. For example, for the simple cylindrical shapes we fabricated for our permeability measurements (see Section 3.2.4), eqn. 3.1 can be integrated over wick cross-sectional area (normal to direction of flow), \( A \), to obtain flow rate:

\[
Q = \frac{k}{\mu} \left( \frac{A}{L} \right) \Delta P
\]

where \( L \) is cylinder length (along flow direction), and \( \Delta P \) is the total pressure drop across the wick. For more complex geometries, Litster et al. [61] defined a shape factor of the form \((A/L)_{\text{eff}}\) which takes place of the area per length ratio in the equation above. For homogenous and isotropic wick materials (and wick dimensions
significantly larger than pore dimensions) and similar flow distributions, this factor should be only a function of wick geometry and so is a key figure of merit in comparing wicks. Such formulations show how both wick microstructure (which determines $k$) and wick shape (which determine $(A/L)_{\text{eff}}$) are key to maximizing water transport rate.

**Capillary transport**

Capillary pressure arises due to surface tension and can be defined as the difference between gas and liquid pressures across a phase boundary. Capillary pressure is characterized by the Young-Laplace equation:

\[
\Delta p_c = \frac{4\gamma \cos \theta}{d_{\text{eff}}},
\]

where $\gamma$ is surface tension, $\theta$ is contact angle, and $d_{\text{eff}}$ is the effective diameter of a hypothetical capillary.

An important figure of merit in wick systems is the product of the permeability of the material and the capillary pressure that it can sustain. For a given geometry (i.e., for fixed $A/L$ in eqn. 3.6), the maximum flow rate generated by surface tension effects is typically proportional to this product. For example, Ochterbeck [118] discusses the so-called capillary limit of heat pipes, which is defined as when the evaporation rate exceeds the maximum capillary transport rate in the heat pipe wick. Maximum capillary transport rate in these and similar wick systems is estimated using a capillary pressure of $\Delta p_c = 4\gamma d_{\text{eff}}$ (Young-Laplace equation, with $\theta = 0$) and fully saturated wick permeability, $k$. Assuming $d_{\text{eff}}$ scales roughly with mode pore diameter,$^2$ we

---

$^2$ Note that the capillary pressure in a wick is a significant function of saturation, as described by Dullien [119]. Physically, this is associated with the fact that saturating liquid first fills the smallest pores associated with highest capillary pressure. Capillary pressure therefore decreases with increasing saturation percentage. We here take the mean pore diameter simply as a scaling parameter.
expect the maximum sustainable capillary transport rate to scale as $k/d_{mode}$. We therefore include this parameter on the right-hand side of Table 1.

For most applications, an ideal wick has pores small enough for sufficient capillary pressure and high permeability to minimize resistance to transport within the wick. As discussed previously, permeability increases with characteristic pore diameter squared and, in most cases, capillary pressure must therefore be traded for permeability (and vice versa). Advanced wick materials, however, offer opportunity for enhanced capillary transport. For example, Huang et al. developed a micro-structured wick with a spatial gradient in pore size for use in a heat pipe. Pore size decreased from condenser to evaporator, thus simultaneously allowing for high capillary pressure in the evaporator and high permeability for transport in the adiabatic region [120]. Bimodal pore size distribution and spatial variations in microstructure that occur during polymerization [121] may possibly be leveraged for similar, high performance polymer wicks.

3.4. *In situ* fabrication of polymer wicks

We here describe an example application of the current porous polymer monoliths to the molding, synthesis, polymerization, and testing of *in situ* fabricated wicks for the parallel channel structure of a polymer electrolyte fuel cell cathode. We described the performance of this integrated wick and fuel cell system in [122], but here provide new and significant details regarding polymerization, fabrication, and preparation which should be useful to other applications of these porous monoliths. Figure 3.5 shows an overview of the fabrication procedure, which consists of three parts: (1-2) fabrication of a negative mold, (3-4) injection molding of polymer wicks, and (5) removal and cleaning.
Figure 3.5: Schematics of procedure for in situ wick fabrication. Fabrication of negative mold: (1) We placed an aluminum positive template into an acrylic casting base designed to hold the casting resin. This template formed one surface of the resulting wicks by defining a negative image in the resin mold, and the part of interest here (the fuel cell cathode channels) defined the opposite surface. (2) We poured a solvent-resistant polyester resin over the aluminum positive template and allowed to cure for one week. Aluminum template was then removed. Injection molding of wicks: (3) We sandwiched the fuel cell cathode channels between the resin negative mold and a back support plate and compressed. (4) We then injected polymerization solution to fill remaining void space (injection ports not shown and wick layer thickness exaggerated for clarity), sealed the mold assembly, and then irradiated with UV for 1 h. Removal and cleaning: (5) Aluminum cathode channel plate, with attached wicks, was then removed and soaked in an MeOH bath for 24 h. Sample was then dried.

3.4.1. Fabrication of resin negative mold

We first fabricated a resin negative mold which would later define the top surface of the final wick geometry. Steps 1 and 2 of Figure 3.5 schematically show this fabrication procedure. We began with a positive template, whose geometry was precision end-milled from aluminum to match the desired top-surface geometry of the
injection-molded wicks. We then transferred the positive template into a custom acrylic casting base, designed to hold the casting resin. A silicone rubber layer (not shown) between the aluminum positive template and casting base, prevented resin from seeping behind the positive template. We then coated the positive template and casting base with PVA mold-release (TAP plastics, Mountain View, CA) and allowed to dry for 1 h.

For UV initiated, *in situ* polymerization, the resin negative mold must be both UV transparent and solvent resistant. As such, we chose a polyester resin with moderate UV transparency and good solvent resistance (TAP Isophthalic High-Strength Resin, TAP Plastics, Mountain View, CA). We combined resin, catalyst (MEKP Liquid Catalyst, TAP Plastics, Mountain View, CA), and a surface curing agent (TAP Plastics, Mountain View, CA), mixed thoroughly and poured over the positive template. We allowed resin to cure at room temperature for one week. We then soaked the resin negative mold, with embedded positive template, in water to dissolve PVA mold release. We then removed the positive template, thereby leaving behind a negative image in the resin mold.

### 3.4.2. Injection molding of wicks

The fuel cell cathode channels (end milled from aluminum) were roughened to improve wick adhesion, and then sandwiched between the resin negative mold and a back support plate (Figure 3.5, step 3). A silicone layer between negative mold and support plate helped to seal mold assembly. The present fuel cell application required high permeability wick material. We therefore chose solution HE06 for polymerization, which we injected into the mold assembly via two leur-lock fittings (not shown), attached to the support plate. Mold assembly was then sealed and irradiated for 1 h, as described in Section 3.2.3 (Figure 3.5, step 4).

We note that we explored both thermal and UV initiation using AIBN and benzoin methyl ether as initiators, respectively. Thermal initiation required elevated polymerization temperature (~60°C) and long polymerization times (> 12 h). Over this period, evaporative porogenic solvent loss was significant and large voids formed in
the resulting wick material. UV initiation required much shorter polymerization times (< 1 h) at room temperature, and evaporative losses of porogens were insignificant.

3.4.3. Removal and cleaning

Immediately following polymerization, we disassembled the mold assembly and carefully removed the aluminum cathode channels with polymer wicks attached (Figure 3.5, step 5). We placed the newly wick-integrated cathode channels in an MeOH bath for 24 h for diffusive removal of remaining monomers and porogens, refreshing with pure MeOH every 4 h. Figure 3.6 is an image of resulting cathode channels with integrated wicks. Polymerization resulted in high quality, monolithic, surface mounted wicks of ~150 µm thickness. This thickness is ~18 times the mean pore diameter. We note that wick thickness should be substantially greater than pore diameter to ensure good pore connectivity.

Figure 3.6: Image of resulting in situ fabricated wick material integrated into fuel cell cathode channels. Polymerization resulted in high-quality, monolithic wicks, which conform to the surface of the fuel cell cathode channels. The top of the channel-defining “ribs” are purposely left uncoated with wick material to promote good electrical contact for electrical current collection.
3.5. Conclusions and recommendations

We fabricated and characterized porous monoliths of 2-hydroxyethylene methacrylate-co-ethylene glycol dimethacrylate with the aim of achieving high permeability, hydrophilic materials for use as wicks and, once saturated, water transport layers. We characterized the effect of both monomer concentration and porogenic solvent composition on resulting monolith microstructure. Results indicate mode pore diameter increased with decreasing monomer concentration and increasing mass fraction of methanol (with respect to solvents). In addition, we found monolith permeability scaled roughly with porosity times the square of mode pore diameter, and reached a maximum of $1.91 \times 10^{-12}$ m$^2$. We recommend permeability normalized by mode pore diameter as an appropriate figure of merit which approximately captures the wick’s capacity for capillary pressure driven flow. For a given wick geometry, maximum flow rate approximately scales with this figure in systems which leverage capillary pressure for liquid transport.

We then detailed a method to in situ polymerize wicks onto the surface of fuel cell cathode channels. Using a custom fabricated negative mold and UV polymerization, we achieved high quality, monolithic, polymer wicks of $\sim 150$ µm thickness which conformed to the surfaces of the fuel cell cathode channels. We hypothesize that this fabrication procedure can be adapted to other applications where precisely shaped and deposited wicks are advantageous for capillary liquid and/or multiphase transport.

Recommended future directions are numerous. Presently, analytical models do not successfully accurately predict polymer monolith permeability. As such, exploring flow effects specific to polymer monoliths, including those associated with broad and bi-modal pore size distributions, may be a fruitful future research direction. In addition, unique aspects of polymer monolith microstructure, including fabrication of monoliths with macroscopic gradients in pore-structure, could possibly be leveraged for high-performance capillary transport. Finally, the present work represents one of many possible methods for in situ fabrication of polymer wicking structures. Lithographically defined wicks represent a particularly exciting potential fabrication
method that may offer fine geometric control, and also be amenable to batch fabrication processes.
Chapter 4

PASSIVE WATER MANAGEMENT WITH IN SITU POLYMERIZED WICKS

Unless otherwise noted, this chapter was adapted with minimal modification from “In-situ polymerized wicks for passive water management in proton exchange membrane fuel cells,” Journal of Power Sources, 195 (6): 1667-1675, 2010.

4.1. Introduction

In this chapter, we develop a passive water management system to minimize air delivery parasitic power losses by enabling stable, flood-free performance in a parallel channel architecture, at very low air stoichiometries. As part of this work, we also address manufacturability issues. Separator plates typically account for 80% of stack weight and a significant portion of the total stack cost. State-of-the-art separator plates leverage injection molding or stamping manufacture procedures to minimize cost and weight [123]. To the best of our knowledge, current flood mitigation techniques are very difficult to integrate into these new flow field designs, specifically those which utilize parallel channels. In the present work, we develop a passive water management system that enables stable performance in parallel channel flow field designs at extremely low air stoichiometries, and can be integrated with state-of-the-art flow field architectures. We leverage an in situ polymerized wick design which can conform to the shape of existing flow field plates and be used to provide water management while minimizing pressure drop.

We first present the fabrication procedure, which incorporates a flow field plate geometry comparable to many state-of-the-art architectures (e.g., stamped metal or injection molded flow fields). We then experimentally compare water management flow field performance versus a control case with no wick integration. At the very low air stoichiometry of 1.15, our system delivers a peak power density of 0.68 W cm\(^{-2}\). This represents a 62% increase in peak power over the control case. The open channel and manifold geometries are identical for both cases, and we demonstrate near
identical inlet-to-outlet cathode pressure drops at all fuel cell operating points. Our water management system therefore achieves significant performance enhancement without introducing additional parasitic losses. Finally, we investigate the feasibility of integrating an entirely passive pre-humidification structure in an effort to minimize required auxiliary systems for humidification.

4.2. Material and methods

4.2.1. Water management flow field design overview

We in situ polymerized 150 μm thick polymer wicks on the channel walls of a 19 parallel channel, 25 cm² aluminum flow field. The wick is created and integrated using a novel photo-polymerization and molding process which we detail in Section 4.2.2. The wick spatially defines regions for water (wick) and air (open channel) transport. The channel wick is contiguous with a thin “wick header” molded into the top surface of the outlet manifold. This wick header is 150 μm thick and also connects hydraulically to the outside of the fuel cell via a separate porous wick “bridge” which, when saturated, allows water transport while maintaining a gas seal. The wick bridge is 47 mm wide and is made from glass filter paper (Whatman GF/D, UK). The integrated, in situ-polymerized wicks are hydrophilic. We measured a contact angle of ~55° on a non-porous polymer sample (made using the same chemistry and procedure but without adding porogen chemical) using a contact angle analyzer (FTA200, First Ten Angstroms, Portsmouth, VA). The wick structure in the channels therefore initially absorbs liquid product water once it emerges from the GDL. Wick capillary pressure, defined as the surface tension induced difference between gas and liquid pressures, decreases from a maximum value at low water saturations (where only the smallest pores are filled) to zero when the wick is fully saturated. Therefore, capillary forces initially redistribute water by inducing liquid pressure gradients which transport water from high to low saturation regions.

Once the wick is fully saturated, capillary pressure becomes negligible and liquid and gas pressure gradients likely become equal. This is because even a small amount of liquid water on the wick surface is enough to prevent menisci on the wick surface
from supporting a wick-to-channel pressure difference (see Litster et al.[51] for further discussion of wick capillary pressures and wick-to-channel pressure differences). As a result, and as per Darcy’s law [124], axial in-channel air pressure gradients induce water flow downstream within channel wicks and to the wick header in the outlet manifold. Excess product water then either travels out through the gas outlet or through the wick bridge via a slight pressure difference between the outlet manifold and ambient. Consistent with discussion by Litster et al.[51], we assume full wick saturation during steady-state operation. Therefore, in effect, wicks provide a liquid water transport pathway from reaction sites to outside of the fuel cell by leveraging air pressure gradients.

Figure 4.1 shows the passive cathode water management flow field (WMFF) design. Our control (no wick) flow field is shown in the inset. We fabricated both flow fields to have approximately identical open flow areas in both channels and manifold. This resulted in nearly identical inlet-to-outlet pressure drops for both the wick and no-wick cases. Carefully controlling geometry is important, as pressure drop and air velocities relate directly to water removal rate and air compressor parasitic power. We note that the wick material is a di-electric polymer. As a result, the WMFF has a reduced conducting area in contact with the GDL. Conductive rib thicknesses are 370 and 670 μm for the WMFF and control, respectively. Current interrupt measurements revealed a slight increase in area specific resistance, from 100.5 to 101.0 Ωcm² (a difference smaller than the uncertainty of our impedance measurements). For all cases, we used a triple serpentine anode flow field to prevent anode-side flooding.
Figure 4.1: Passive water management flow field (WMFF) design. The main image (top left) and a detail view (bottom left) show the aluminum flow field with integrated wick. Control (no wick) flow field is shown in the inset on the top right. The cross-section of the wick and control case are compared on the bottom right. Both flow fields have equal open channel and manifold geometry to ensure similar gas flow characteristics. ~150 μm thick polymer wicks coat the channel and manifold surfaces of the WMFF. Channel wicks absorb liquid product water ejected from the GDL. Initially, capillary forces distribute water throughout the wick structure. Once fully saturated, in-channel gas pressure gradients induce in-wick pressure gradients and flow of water downstream. Water travels through channel wicks to a wick header in the outlet manifold. Excess product water then leaves the fuel cell through the gas outlet, or through the wick bridge, via a slight pressure difference between outlet manifold and ambient.

4.2.2. Fabrication procedure

Injection molding

In this section, we describe the molding process used to fabricate wicks on the surface of the cathode water management flow field. We first precision end-milled aluminum (McMaster-Carr, Chicago, IL) flow fields for both the water management (wick) and control (no wick) cases. We machined the water management flow field to
have channel and manifold dimensions 150 μm larger to allow room for subsequent polymerization of surface mounted wicks. We then used a solvent resistant, polyester resin (TAP Plastics, Mountain View, CA) to cast the top “negative image” mold for injection molding. The control flow field plate itself served as the casting template for the wick mold to ensure nearly identical open channel geometry of the finished flow field. We note that by leveraging the difference between the control and water management flow field geometries for injection molding, we achieved precisely defined wick geometry. See Appendix B for more details.

Figure 4.2 shows details of the wick fabrication procedure. We assembled the top mold, the water management flow field, a silicone gasket, and a Teflon support plate, using eight 10-32 bolts for compression. Using a glass syringe, we then injected a solution of monomers, solvents, and photo-initiator (chemistry detailed in Section 3.2.2) via luer-lock ports on the back side of the mold assembly, and visually confirmed that the solution displaced all air in voids between the aluminum flow field and top mold. We then sealed the mold and photo-initiated polymerization with a UV-light source (~365 nm peak) for 1 h. During polymerization, the monomer solution turned from transparent to opaque and resulted in a porous polymer monolith. We then removed the flow field from the mold, and soaked it in several baths of methanol for a total of 12 h. To prevent oxide-layer formation and potential ion contamination of the fuel cell, we subsequently electroplated both the water management and control flow fields with a 10 μm nickel diffusion barrier and then 1 μm gold (Electrochem, Union City, CA). The electroplating left the porous polymer surface of wick samples intact.
Figure 4.2: Injection molding procedure for WMFF: We (1) assembled the mold, which includes top “negative image” mold, flow field plate, silicone gasket (not shown) and Teflon support plate; (2) injected monomer solution to fill voids between flow field plate and top mold; (3) sealed mold and photo-initiated polymerization with UV light source for 1 h; and (4) removed and cleaned in a methanol bath.

In situ polymerization of porous materials

We provide here a brief description of the reagents, reactions, and processing of the polymerization procedure. We present a more detailed discussion (and comparison with alternate chemistries) in Chapter 3. Porous polymers are fabricated by combining monofunctional and crosslinking monomers with a solution of porogenic solvents in a closed mold. For the chemistry used here, we use a photo-initiator to carry out free radical polymerization. As polymer chain length increases, the polymer becomes insoluble. As a result, a two-phase system of solid polymer and liquid solvent forms. For sufficiently high monomer concentrations, polymer globules
join together and a porous monolith results. Pore size distribution and porosity of the resulting monolith are influenced by four parameters: solubility of monomers in the chosen solvent mixture, ratio of monofunctional to crosslinking monomers, ratio of total monomers to total solvent, and the rate of reaction (influenced by initiator concentration, temperature, and UV light source intensity).

Figure 4.3: Polymerization chemistry used for flow field wicks. We carried out a free radical polymerization of EDMA and HEMA in a sealed mold with methanol and hexane, using benzoin methyl ether as a photo-initiator. During polymerization, as molecule size increases, the polymers become insoluble. This results in a two-phase system of solid polymer and liquid solvents. For sufficiently high monomer concentrations, polymers join and form a continuous porous monolith. The inset shows a scanning electron micrograph (SEM) of the resulting structure.

Figure 4.3 shows the chemistry we used for the WMFF wicks. We adapted this chemistry from work published by Yu et al. [112]. We used monomers of ethylene glycol dimethacrylate (EDMA – CAS# 97-90-5) for cross-linking and 2-
hydroxyethyl methacrylate (HEMA – CAS# 868-77-9) for hydrophilic functionality, a binary solvent system of methanol (MeOH) and hexane (Hex), and benzoin methyl ether (CAS# 3524-62-7) for photo initiation. We achieved a maximum permeability of $2.65 \times 10^{-12}$ m$^2$ using monomer:solvent, HEMA:EDMA, and MeOH:Hex volumetric ratios of 3:7, 1:1, 3:2, respectively, and 1.25 wt% initiator. The preparation procedure was as follows. We passed EDMA and HEMA through a column packed with an inhibitor remover (Sigma-Aldrich prod # 311332), and then degassed all reagents by bubbling nitrogen gas for 7 min. We then combined reagents in a scintillation vial according to the desired volumetric ratios and respective densities, using a precision scale (Pinnacle PI-225D, Denver Instrument, Denver, CO). Finally, we bubbled nitrogen gas through the solution for 3 min to further reduce oxygen concentration in solution. We then injected this solution into the mold, as described in Section 4.2.2.

4.2.3. Fuel cell assembly

Fuel cell assembly and experimental setup is similar that reported by Litster et al. [51], and we only summarize it here. Figure 4.4 shows fuel cell assembly used for all experiments. Starting at center and moving out, it consists of a membrane-electrode assembly (MEA), gas diffusion layers (GDLs), cathode and anode flow fields, current collectors, silicone layers for electrical insulation, and aluminum support plates for compression.

We used a commercially available catalyst coated membrane (Ion-Power, New Castle, DE) with membrane thickness of 25 μm and total Pt catalyst loading of 0.3 mg cm$^{-2}$. GDLs were Sigracet-10BB with a microporous layer. A 280 μm Teflon gasket, placed around each GDL, sealed gases and prevented over compression. We machined the anode flow field from graphite (fuelcellstore.com, Boulder, CO), and used a triple serpentine flow field with 0.75 mm square channels, and 0.75 mm land widths. The cathode flow field used is as described in Section 4.2.1. We machined current collectors from copper which we then electroplated with 1 μm gold (Electrochem, Union City, CA). Custom machined aluminum support plates and four 10-32 bolts, tightened to 15 in-lb, provided compression. For all experiments, we oriented the fuel cell horizontally and fed gases in counter flow.
Figure 4.4: Exploded view of 25 cm$^2$ fuel cell assembly. The fuel cell features the water management flow field (WMFF) on the cathode side and triple serpentine flow field on the anode. A commercially available catalyst coated membrane is sandwiched between two GDLs with microporous layers and Teflon gaskets for sealing. Custom machined support plates are electrically insulated from current collectors with a 500 µm silicone layer. Four bolts tightened to 15 in-lb provide compression. The assembly was oriented horizontally and gases were fed in counter flow in all experiments.

4.2.4. Experimental setup

Here, we briefly describe the setup used for all experiments. Cylinders of compressed air and hydrogen (Praxair) connected to electronic mass flow controllers (Alicat Scientific, Tucson, AZ), and then to a humidification system (Bekktech, Inc).
Saturator temperature was set equal to fuel cell temperature to ensure full gas humidification. Heated tubes, with temperature 10 °C warmer than saturators to prevent condensation, connected the saturators to the fuel cell gas inlets. A temperature controller (Omega CSC32, Stamford, CT) set fuel cell temperature via two Kapton heaters (McMaster-Carr, Chicago, IL) fixed to fuel cell endplates and a K-type thermocouple which was embedded in the anode flow field plate. We used a pressure transducer at the cathode inlet to measure inlet-to-outlet pressure drop.

All experiments were controlled and data collected using Labview 8.5. We used an electronic load (Agilent N3301A, Palo Alto, CA) with power assist boost (Acopian W3.3MT65, Easton, PA) to galvanostatically control experiments. Air and hydrogen stoichiometry were fixed throughout each polarization curve. Prior to using each membrane, we used a voltage cycling procedure to break in the cell. In this break-in period, we cycled fuel cell voltage from 0.8, 0.5, to 0.3 V for 20 s each, for a total of 8 h. Table 4.1 lists key parameters used in all experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel cell temperature</td>
<td>65°C</td>
</tr>
<tr>
<td>Cathode saturator temperature</td>
<td>65°C</td>
</tr>
<tr>
<td>Anode saturator temperature</td>
<td>65°C</td>
</tr>
<tr>
<td>Gas line temperature</td>
<td>75°C</td>
</tr>
<tr>
<td>Hydrogen stoichiometry ($\alpha_{H2}$)</td>
<td>1.5</td>
</tr>
<tr>
<td>Number of channels (cathode)</td>
<td>19</td>
</tr>
<tr>
<td>Active Area</td>
<td>25 cm$^2$</td>
</tr>
<tr>
<td>MEA</td>
<td>Ion Power CCM</td>
</tr>
<tr>
<td>GDL</td>
<td>Sigracet-10BB</td>
</tr>
<tr>
<td>Anode/cathode outlet pressure</td>
<td>1 atm (abs)</td>
</tr>
</tbody>
</table>

Table 4.1: Experimental parameters for both wick-integrated and control fuel cell systems.
4.3. Results and discussion

4.3.1. In-channel pressure gradients

In-channel pressure gradients and air velocities play a critical role in fuel cell water management, and more specifically, in channel flooding [19, 125]. As a result, maintaining similar pressure drop characteristics for the control and water management flow field designs was necessary to isolate the effect of wick integration on water management. Figure 4.5 shows normalized inlet-to-outlet pressure drop versus current density for both the control and water management flow field cases.

![Pressure vs. Current Density](image)

Figure 4.5: Pressure normalized by stoichiometry vs. current density for control (closed) and WMFF (open) cases and stoichiometries of $\alpha_{air} = 1.15$ ($\bigcirc$), 1.30 ($\blacksquare$), 1.50 ($\triangledown$), and 2.00 ($\bigtriangleup$). The relationship between normalized pressure and current density is linear, indicating constant hydraulic resistance, regardless of current density or air stoichiometry. Both the control and WMFF approximately collapse to the same line, indicating nearly equal hydraulic resistance.

Pressure is normalized by air stoichiometry, $\alpha_{air}$, and plotted for $\alpha_{air} = 1.15$, 1.30, 1.50, and 2.0. As the figure shows, flow field hydraulic resistance is nearly identical for
both the WMFF and control, and at all fuel cell operating points. Because hydraulic resistance is nearly equal, we therefore expect no additional air delivery parasitic loss due to wick integration.

4.3.2. Water transport regime

We here first briefly review some multiphase water transport terms and physics, and the present and discuss our experimental results. In a detailed visualization study, Zhang et al. identified three regimes by which liquid product water is removed from the GDL surface [35]. By balancing surface adhesion and drag forces, Zhang derived a semi-empirical relation for droplet detachment size as a function of air velocity. As air velocity increases, the characteristic diameter of droplets at detachment decreases. For sufficiently high air velocities, droplets detach before contacting channel walls and advect as air-stream-borne droplets (a mist). At lower velocities, droplet detachment size becomes comparable to channel dimensions. For hydrophilic channel walls that satisfy the Concus-Finn condition [36], droplets join a corner flow upon contacting the channel wall. However, at high current densities, corner flow is unable to remove all product water; and this leads to annular film and eventual water slug formation.

For the channel geometry used in the current study, the maximum average channel velocity was 1.5 m s\(^{-1}\) (at maximum air stoichiometry and current density of \(\alpha_{\text{air}} = 2.0\) and \(j = 1.5\) A cm\(^{-2}\), respectively). At these velocities, detachment droplet characteristic dimension is expected to be larger than the channel. Also, channel surface properties and geometry are such that the Concus-Finn condition is not met, so corner flow is not sustained and we expect channel slug formation.
Figure 4.6: Representative voltage versus time for polarization curve measurements at $\alpha_{\text{air}} = 1.3$, for control and WMFF cases. Cell current was increased by 0.1 A cm$^{-2}$ every 600 s. Control case data indicate significant performance degradation due to flooding in the control case. Voltage transients (inset) show performance decline and discrete events of partial recovery. These transients are consistent with liquid water accumulation in channels and manifold, followed by spontaneous, intermittent purging. The WMFF shows significantly improved performance. WMFF data reveal stable performance for most current densities. Low magnitude voltage fluctuations, however, suggest some liquid water may also be present in channels, particularly at low current densities ($j = 0.3\text{-}0.4$ A cm$^{-2}$) and again at the highest current density ($j = 1.4$ A cm$^{-2}$). In this wick case, failure occurred suddenly and immediately after incrementing current to 1.5 A cm$^{-2}$.

Transient voltage yields insight into flooding events [51, 125, 126]. The data in Figure 4.6 indeed suggest slug flow does occur. Figure 4.6 shows representative realizations of fuel cell potential versus time during polarization curve measurements for both control and WMFF, at $\alpha_{\text{air}} = 1.3$. Here, the dynamic fuel cell load is adjusted to increment current density by 0.1 A cm$^{-2}$ every 600 s. The inset details transient performance of the control flow field in the high current density regime (which is
likely partially flooded). Voltage data reveal a characteristic fuel cell response, which involves a gradual decreases in performance followed by sudden, temporary recovery events. We hypothesize that this is due to gradual liquid water accumulation in the flow field channels and/or manifold. Once a critical liquid water content is reached, accumulated product water intermittently purges, and cell performance momentarily recovers.

4.3.3. Engineering model of water transport in wicks

The WMFF case shows significant performance enhancement. The temporal fluctuations of voltage at each current setting are much lower than the control case. At most operating points, channel wicks likely transport enough product water along the wicks to successfully mitigate slug formation and catastrophic flooding. Using a simple Darcy flow model, we can estimate the fraction of product water that the measured pressure drop is capable of transporting through the channel wicks. We estimate the maximum water flow rate in the wick as

\[ Q_{\text{wick, max}} = \frac{A_w - k_w \Delta p}{\mu_{H_2O} L_c}, \]

where \( A_w \) is the channel wick cross-sectional area, \( \mu_{H_2O} \) is the dynamic viscosity of water, \( k_w \) is the wick permeability, \( \Delta p \) is the measured pressure drop from inlet to outlet, and \( L_c \) is the channel length. We measured \( k_w \) ex situ, using a specially fabricated porous monolith sample and the radial flow method [127, 128] (these calibrations used the same polymer chemistry reported in Section 4.2.2). This expression slightly over-estimates pressure induced flow in the wick, as the measured inlet-to-outlet pressure difference is not dropped over the channel length alone (but includes difficult-to-quantify manifold and interconnect losses).

We can normalize \( Q_{\text{wick, max}} \) by the water production rate to obtain a measure of the fraction of product water transported by the wick:

\[ \chi = \frac{Q_{\text{wick, max}}}{Q_{\text{prod}}}, \]

where the volumetric water production rate is \( Q_{\text{prod}} = \left( jA_{fc} / 2Fn_{\text{chan}} \right)(M_{H_2O} / \rho_{H_2O}) \).
Figure 4.7 shows a plot of $\chi$ versus $\alpha_{\text{air}}$. We obtained this data by first analyzing $\chi$ versus current density, $j$, for stoichiometries of $\alpha_{\text{air}} = 1.15$, 1.30, 1.50, and 2.0 (shown in inset). We calculated $\chi$ using eqn. 4.1 and eqn. 4.2, and pressure data measured during polarization curve experiments (which we present in Section 4.3.5). As the inset shows, for each stoichiometry, $\chi$ is roughly independent of current density as expected for relatively flood free channels. We obtain the main plot of Figure 4.7 by averaging $\chi$ for $j > 0.5$ A cm$^{-2}$ (shown in dashed box) for each stoichiometry.$^3$

![Figure 4.7: Maximum fraction of product water transported through wick by measured pressure drop, $\chi$, for stoichiometries of $\alpha_{\text{air}} = 1.15$, 1.30, 1.50, and 2.0. The inset shows $\chi$ vs. current density for each stoichiometry. Error bars represent the standard deviation of temporal fluctuations in $\chi$. We averaged values of $\chi$ for $j > 0.5$ A cm$^{-2}$ (dashed box) to obtain each data point in the main figure. Results indicate that, for stoichiometric flow rates considered, channel wicks transport at most 41% of product water.]

$^3$ In this averaging, we neglect $j \leq 0.5$ A cm$^{-2}$ data, as two phase flow physics dominate pressure measurements in this range. Non-linearities introduced by two-phase fluctuations are not accounted for in our model, and are most prominent in the low current density regime for two reasons. First, flood induced channel shutdown is substantial at the low air flow rates encountered at low current density. Such shutdown results in large changes in system hydraulic resistance. Second, the low current regime is more susceptible to noise in $\chi$, as we normalize $Q_{\text{wick, max}}$ by $Q_{\text{prod}}$. 

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Results suggest that \( \chi \) is independent of current density and increases linearly with air stoichiometry. This functional relationship is expected and can be elucidated by rewriting \( \Delta p \) in eqn. 4.1. We recall from Figure 4.5 that \( \Delta p \) had an approximately linear dependence on flow rate. This suggests that in our experiments, cathode gases remained in a laminar pipe-flow regime. We therefore rewrite \( \Delta p \) as:

\[
\text{eqn. 4.3} \quad \Delta p = R_{\text{chan}} \left( \frac{\alpha_{\text{air}} j A_{\text{fc}}}{4 F n_{\text{chan}} \rho_{\text{air}}} \right) \frac{M_{\text{air}}}{M_{\text{H}_2\text{O}}},
\]

where \( R_{\text{chan}} \) is the effective channel hydraulic resistance and the term in brackets is the approximate air flow rate per channel. We substitute \( \Delta p, Q_{\text{wick,max}}, \) and \( Q_{\text{prod}} \) into eqn. 4.2 to obtain a new relation for \( \chi \):

\[
\text{eqn. 4.4} \quad \chi = \left( \frac{R_{\text{chan}}}{R_{\text{w}}} \right) \left( \frac{\rho_{\text{H}_2\text{O}} M_{\text{air}}}{\rho_{\text{air}} M_{\text{H}_2\text{O}}} \right) \frac{\alpha_{\text{air}}}{2},
\]

where we define a wick hydraulic resistance as \( R_{\text{w}} = \mu_{\text{H}_2\text{O}} L_{\text{w}} / k_w A_w \). In the current study, geometric parameters (first set of brackets) and fluid thermophysical parameters (second set of brackets) remain constant. eqn. 4.4 is therefore consistent with the experimental results for \( j > 0.5 \text{ A cm}^{-2} \) as shown in Figure 4.7. In effect, water transport in the wick automatically responds to increase in \( Q_{\text{prod}} \), as both water production and air pressure drops each scale proportionally with air flow rate.

As eqn. 4.4 indicates, aside from thermophysical fluid properties, three main parameters govern \( \chi \): \( R_{\text{chan}}, R_{\text{w}}, \) and \( \alpha_{\text{air}} \). Increasing \( R_{\text{chan}} \) and \( \alpha_{\text{air}} \) enhances through-wick water transport. However, either of such increases also increases air pressure drop, resulting in additional parasitic power. Parasitic power increase can be avoided by instead minimizing \( R_{\text{w}} \). For our system, \( k_w, A_w, \) and \( L_{\text{w}} \) are 2.65 x 10\(^{-12}\) m\(^2\), 7.50 x 10\(^{-5}\) m\(^2\), and 5 cm, respectively. Using these values, results shown in Figure 4.7 indicate that, for the air stoichiometries considered, the channel wicks likely do not transport all produced water. For example, we estimate that channel wicks transport only 41\% of product water at the highest air stoichiometry of \( \alpha_{\text{air}} = 2.0 \). In future flow
field designs, increasing either channel wick cross-sectional area or permeability would increase this flow fraction.

Complete characterization of secondary water transport mechanisms is not the intent of this study, and would require a more in-depth visualization study. We hypothesize, however, that corner and/or annular film flow may exist. This is supported by the voltage data we present in Figure 4.6. For \( j = 0.3-0.4 \text{ A cm}^{-2} \), slight voltage fluctuations suggest some liquid water may accumulate in the flow field. At higher current densities, however, these transients disappear and performance appears flood-free. Adequate liquid water removal rate at higher current densities could be accounted for by a transition to corner/annular film flow. Such a regime transition is expected when increasing gas superficial velocity [129], as is the case when incrementing to higher current density.

### 4.3.4. Vapor-phase transport of water

Lastly, we note the effect of vapor-phase transport of water. In all our experiments, we set saturator temperature equal to fuel cell temperature to ensure full gas humidification. For high current density operation (\( j > 1.2 \text{ A cm}^{-2} \)), however, temperature near the membrane (measured with thermocouple embedded in anode flow field) increased above the set point by up to 6°C. We attribute this temperature increase to heat generated by reaction and charge transport losses. We therefore expect some evaporative water removal in the high current density region. For the worst-case scenario, where measured fuel cell temperature rose to 71°C, we estimate evaporative removal is limited to less than 15% of produced water (maximum evaporation rate calculated for \( j = 1.5 \text{ A cm}^{-2} \) and \( \alpha_{\text{air}} = 2.0 \)). We expect negligible evaporation for \( j \leq 1.2 \text{ A cm}^{-2} \), as the measured temperature remained at 65°C.

### 4.3.5. Polarization curves

In this section, we present polarization curves for the control and the passive wick water management flow field cases. Before each polarization curve, we operated the fuel cell at 0.8 A cm\(^{-2}\) and \( \alpha_{\text{air}} = 1.8 \) for 10 min to ensure a repeatable start condition. We purged the cathode of any accumulated product water with an 1840 sccm air flow
rate for 10 s. We began each polarization curve experiment by measuring open circuit voltage for 1 min. We then incremented current by 0.1 A cm$^{-2}$ every 10 min and terminated the experiment once the instantaneous voltage dropped below 0.2 V. Each data point represents the time average of the last 2 min of each 10 min dwell period.

Figure 4.8: Polarization curves for control (left) and WMFF (right) for $\alpha_{\text{air}} = 1.15$ (○), 1.30 (□), 1.50 (▼), and 2.00 (▲). Error bars represent ±1 standard deviation of temporal fluctuations in potential. For the control case, we observed pronounced flooding at all air stoichiometries. Flooding was most significant for $\alpha_{\text{air}} = 1.15$-1.50 and restricted the maximum obtainable current density. The WMFF demonstrated considerable performance improvement. For most operating points, performance appeared flood free. An exception was in the mid-current density range ($j = 0.3$-0.6 A cm$^{-2}$), where voltage transients suggested some water slug formation in channels.

Figure 4.8 shows polarization curves for the control and WMFF cases, for stoichiometries of $\alpha_{\text{air}} = 1.15$, 1.30, 1.50, and 2.0. In the control case, flooding affected performance at all stoichiometries. This was expected, as stoichiometries used were significantly less than those typically required for stable performance using parallel channel cathode flow fields [43]. Flooding was most pronounced in the very low stoichiometry cases. For $\alpha_{\text{air}} = 1.15$, 1.30, and 1.50, catastrophic flooding prevented operation above 0.9, 1.1, and 1.3 A cm$^{-2}$, respectively. Flooding is often associated
with high current density operation \((j > 1 \text{ A cm}^{-2}) [18, 130]\)). However, we observed significant performance losses in the low current density region. This is consistent with previous work showing that, when both stoichiometry and current density are small, flooding can be pronounced [50, 131] and lead to mass transport losses resulting from flow mal-distribution and reduced GDL permeability, and kinetic losses resulting from reduced effective active area. We therefore attribute low current density flooding to minimal water removal rates which result from low air flow rates. Performance improved at the increased stoichiometry of \(\alpha_{\text{air}} = 2.0\). Flooding appeared present at nearly all current densities, however, and was most significant in the high current density range. Voltage transients also suggested channel flooding, which eventually led to fuel cell failure.

The WMFF significantly improved fuel cell performance. Polarization curves revealed stable, flood free performance at nearly all operating points. One exception was in the mid-current density range \((j = 0.3-0.6 \text{ A cm}^{-2})\), where voltage transients indicated some channel slug formation. Performance recovered, however, at increased current densities (and, by extension, increased air flow rates) and appeared flood free. The WMFF extended operating range by 0.4, 0.3 and 0.2 \text{ A cm}^{-2} for stoichiometries of \(\alpha_{\text{air}} = 1.15, 1.30 \text{ and} 1.50\), respectively. For each case, fuel cell failure occurred suddenly and immediately after incrementing current for the final time.

Results using the WMFF indicate that the system’s degree of flooding does not increase monotonically with current density. As current is increased, fuel cell performance transitions from near open cell potential, through a short region of flooding, then through a significant region of recovery, and then finally a sudden catastrophic flooding event at termination. Possible factors causing the recovery phase include a change of water transport regime (e.g., slug to corner flow) or increased evaporative removal due to internal heating. Water transport and management is a delicate balance between production and removal, and deserves further investigation in future work. Visualization studies of our system are difficult but would perhaps further elucidate important water transport mechanisms. Other possible diagnostic tools for further investigation include neutron imaging [132-134], X-ray
radiography[135], and magnetic resonance imaging[136] for water distribution measurements or cell segmentation methods to spatially resolve flooding events [20].

4.3.6. Power density performance

Figure 4.9 shows maximum power density as a function of air stoichiometry for control and WMFF cases. As expected, max power increases with air flow rate. At all stoichiometries tested, wick integration significantly increased maximum power. This power increase was most significant at low stoichiometries. For example, the WMFF increased max power from 0.41 to 0.68 Wcm$^{-2}$ for $\alpha_{\text{air}} = 1.15$. To quantify performance enhancement, we also plot the fractional increase in max power, $\phi^*$, which we define as:

$$\phi^* = \frac{P_{\text{max, WMFF}} - P_{\text{max, control}}}{P_{\text{max, control}}}.$$ 

Figure 4.9: Maximum power generated by the fuel cell ($P_{\text{max}}$) as a function of stoichiometry for control and WMFF cases (closed and open circles, respectively). We also plot the (non-dimensional ratio of) fractional power increase, $\phi^*$, due to wick integration. The WMFF significantly increased $P_{\text{max}}$ for all air stoichiometries, and especially for the low $\alpha_{\text{air}}$ cases. Results show a 62% increase in peak power for $\alpha_{\text{air}} = 1.15$. $\phi^*$ decreased with increasing $\alpha_{\text{air}}$, from 0.62 at $\alpha_{\text{air}} = 1.15$ to 0.10 at $\alpha_{\text{air}} = 2.0$. 

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As shown in Figure 4.9, the WMFF increased max power by 62% at the lowest stoichiometry of $\alpha_{\text{air}} = 1.15$. $\phi^*$ decreased roughly as the inverse of air stoichiometry, diminishing to 10% at $\alpha_{\text{air}} = 2.0$. We again note that wick integration introduced no additional hydraulic resistance. Therefore, power measurements can be compared directly, as the WMFF introduced no additional parasitic losses.

4.4. Feasibility of passive humidification for dry gas operation

This section is adapted, with minor modification, from “In-situ polymerized wicks for passive water management and humidification of dry gases,” *ECS Transactions*, 25(1): 303–309.

Figure 4.10: Schematic of flow field design with wick for water management and connection to pre-humidifier. Liquid product water is absorbed from the GDL by a wick layer which is directly cast onto the flow field channel surfaces. Water is transported in the wick along the flow direction to a wick header in the outlet manifold, and then through a wick “bridge.” Water is then evaporated into dry gases in the humidification region.

As shown in Figure 4.10, integrated wicks can be coupled externally with a pre-humidifying hydrophilic porous structure (pre-humidifier) via a wick bridge. Product
water is collected by the channel wicks, travels downstream to the wick header, then through the wick bridge, and into the porous evaporating structure. Dry gases can then be flowed through this structure to pre-humidify inlet streams.

Evaporation from porous media is a complex phenomenon. Significant modeling work has been reported [137, 138]. Here, we present a simple model intended only to estimate the feasibility of pre-humidification of the fuel cell cathode air-stream. The model was developed using a commercial modeling program (COMSOL Multiphysics).

Figure 4.11: (a) Schematic of humidifier geometry and model parameters. Humidifier is composed of a porous glass tube that is fully saturated with water. The outside boundary is set at a fixed temperature equal to the fuel cell temperature \( T_{FC} \). Fully developed flow of dry gas at \( T_{FC} \) enters on the right. (b) Results of model for an equivalent air flow rate for \( j = 0.5 \) A cm\(^{-2}\) and \( \alpha_{air} = 1.3 \). Transverse RH distribution is plotted for ten cross sections.

Figure 4.11a shows geometry and conditions used in the model. The humidifier is a porous glass annulus “fed” by a small tab of negligible flow resistance. We assumed that evaporative mass flux is small compared to capillary wicking, and as a result, the porous glass remains fully saturated. Temperature on the outside boundary \( (r = D_o/2) \) was fixed at the fuel cell operating temperature \( T_{FC} \). We assumed fully developed Poiseuille flow of dry air (dew point of 25°C) at the inlet. Air flow rate was set by the stoichometric air flow rate required by the fuel cell (function of current density, \( j \), and...
At the air/porous glass interface \( (r = D_i/2) \), we assumed water concentration for fully saturated air (based on local temperature). We also assumed that all of the heat required for phase transition is absorbed at this boundary.

Figure 4.11b shows model results for a humidifier length of 5 cm and an equivalent air flow of \( j = 0.5 \) A cm\(^{-2}\) and \( \alpha_{\text{air}} = 1.3 \). Relative humidity (RH) fields at \( T_{FC} \) were calculated for ten cross-sections. As expected, the model shows transverse water concentration gradients which transport water vapor from the porous glass annulus walls, toward the center of the tube. Water vapor is then advected in the axial direction. As a result, average RH increases with downstream distance.

![Figure 3: Area averaged RH at pre-humidifier outlet as a function of flow rate (set by current density, \( j \), for \( \alpha_{\text{air}} = 1.3 \)). Outlet RH increases with increasing humidifier length and decreasing flow rate.](image)

Figure 3 shows average RH at the humidifier exit as a function of fuel cell current density, for four tube lengths. As expected, RH increases with decreasing air flow rate and increasing humidifier length. For all cases, the humidifier significantly increases outlet RH from the dry gas RH of 0.05. We conclude that the integration of a simple, passive pre-humidifier can effect significant improvement in inlet RH. In addition, we also expect in-channel wicks to internally humidify gases through a mass transport effect analogous to the mass transport in heat pipes (as reported by Litster et al. [139]).
4.5. Conclusions

We developed a passive water management cathode flow field that enabled stable, flood-free performance with 19 parallel channels at very low air stoichiometries. We presented a fabrication procedure where we in situ polymerize wicks on the flow field channel walls and manifold surfaces. This resulted in high quality, 150 μm thick, monolithic wick structures, which provided a hydraulically connected pathway from reaction sites to outside of the fuel cell. We used geometry and materials similar to many state-of-the-art flow field designs (e.g., stamped metal flow fields), and hypothesize that the water management system can be affordably integrated into transportation scale fuel cell stacks.

We experimentally compared fuel cell performance using the water management flow field (WMFF) against a control cathode flow field (no integrated wicks) which had identical open channel and manifold geometry. The WMFF significantly improved performance. For $\alpha_{\text{air}} = 1.15, 1.30$ and $1.50$, the WMFF extended operating range by 0.4, 0.3 and 0.2 A cm$^{-2}$, respectively. Performance improvement was most significant for $\alpha_{\text{air}} = 1.15$. At this very low air stoichiometry, integrated wicks increased maximum power from 0.41 to 0.68 W cm$^{-2}$. This represents a 62% increase in peak power. At all operating points, inlet-to-outlet pressure drops were nearly identical for both the WMFF and control flow fields. Performance enhancements were therefore obtained without introducing additional air-delivery parasitic losses.

Even with the WMFF, we observed some mid-current density range flooding at all air stoichiometries. For the low air stoichiometries used, a simple model suggested that the wick alone does not transport all product water. Further investigation is therefore necessary to fully understand any secondary water transport mechanisms. Possible diagnostic tools include neutron imaging and cell segmentation for spatially resolved water content and reaction rates.

We also presented a method for leveraging this water management system to passively pre-humidify dry inlet gases. A simple model suggests that significant improvement in fuel cell inlet relative humidity can be achieved. Suggested future
work includes identifying secondary water transport mechanisms and leveraging integrated wicks to enable high performance dry gas operation.
Chapter 5

CONCLUSIONS, CONTRIBUTIONS, AND RECOMMENDATIONS

We here present major conclusions and contributions of the work presented as a part of this dissertation. We then make recommendations for future directions that could serve as a continuation of this work.

5.1. Conclusions and contributions

5.1.1. Spatial characterization of active water management system

1. We developed and applied anode side segmentation to a polymer electrolyte fuel cell with active water management. This was the first time for segmentation to be applied to porous carbon flow field architectures, and to the best of our knowledge, the first time to characterize flooding in parallel channel flow fields.

2. Anode segmentation was 3 x 3 and allowed for real-time measurement of power distribution. Instrumentation included nine hall effect sensors for low impedance current measurement. Segmentation was minimally invasive, with a total resistance increase of 1.25 mΩ over a similar non-segmented fuel cell with total resistance of 6.90 mΩ. In addition, fuel cell performance was consistent with that of a non-segmented system, previously published by Litster et al. [51].

3. We characterized steady state fuel cell performance with segment-specific polarization curves. In all cases, results indicated significant performance enhancement when the EO pump is on.

4. We observed flood-free performance for $\alpha_{\text{air}} > 1.5$ and EO pumping. In these flood-free cases:
   • Polarization curves grouped into three distinct regions for high current, mid current, and low current density, corresponding to upstream, midstream and downstream segments, respectively. We attribute these groupings to
reduction in oxygen partial pressure in the stream-wise direction, as oxygen is consumed.

- The range over which current densities varied from upstream to downstream segments decreased with increasing stoichiometry, also consistent with expected trends for concentration losses.

5. For lower air stoichiometries ($\alpha_{\text{air}} \leq 1.5$), segmented polarization curves showed significant performance improvement, however, partial flooding remained:

- When EO pumping was insufficient for complete flood mitigation, segments closest to the EO pump showed most improved performance. These results are consistent with transient results indicating increased water removal rate in regions closest to the EO pump.

- Results highlighted the coupling of both passive and active water removal. For example, results indicated flood free performance at $\alpha_{\text{air}} = 1.5$ with the EO pump on. If, however, either passive water removal is reduced (i.e. $\alpha_{\text{air}}$ reduced to 1.3) or the EO pump is turned off, flooding again resulted.

6. Current density measurements without EO pumping highlight coupling of air flow rate with flooding and fuel cell performance:

- Flooding was most prevalent for low to mid current density range.

- For all cases of $\alpha_{\text{air}} \geq 1.5$, performance appeared flood free at high current density, with segment-specific polarization curves again splitting into three distinct groups of upstream, midstream, and downstream segments.

- We proposed a performance non-uniformity parameter to characterize spatial variations in fuel cell performance. This parameter was taken as the norm of the standard deviations between current densities in each grouping of upstream, midstream, and downstream segments.

- Performance losses increased linearly with current density non-uniformity, validating that increased performance losses are due to flow field flooding.
Current density non-uniformity decreased with flow rate as 
\( \sim 0.45 / (\alpha_{air} \times \bar{J}) \), indicating that for most operating conditions, air flow rate, not water production rate, governs parallel channel flow field flooding and non-uniformity of flow distribution.

7. We characterized transient fuel cell performance:
   - EO pumping successfully recovered fuel cell from near catastrophic flooding, and maintained a flood-free steady state condition.
   - Temperature gradients biased flooding toward cooler (outer) channels
   - Performance recovery was in regions near to the EO pump first.

5.1.2. Development of porous polymer monoliths as wick materials

1. This work was the first dedicated effort for realizing high permeability, hydrophilic, porous polymer monoliths suitable for wicking and other multiphase transport applications.
2. We successfully adapted a HEMA-co-EDMA polymer chemistry for fabrication of capillary wicking structures. The polar hydroxyl group on HEMA lended the hydrophilic functionality required for low contact angle wicking structures.
3. We investigated the effect of two key polymer chemistry parameters on resulting monolith microstructure and permeability: monomer fraction and porogen composition:
   - \( \bar{d}_{mode} \) increased with increasing solvent fraction. Solvent fraction served as a proxy for porosity, and thus, for materials of similar pore structure, this trend was expected.
   - \( \bar{d}_{mode} \) increased (roughly) with methanol concentration, \( w_{MeOH} \). We observed a peak in mode pore size at \( w_{MeOH} = 0.5 \), consistent with Yu et al. [112]. However, no such peak in \( d_{median} \) was observed.
   - Permeability increased with both solvent and methanol fraction. This result is consistent with trends in pore diameter and porosity.
4. We identified solvent composition as a powerful means for tailoring pore size distribution, as characteristic pore diameter can be modified while holding porosity and polymer chemistry constant.

5. We developed a Carman-Kozeny type correlation for permeability and identified a rough dependence on $\phi d_{\text{mode}}^2$. Significant scatter in correlation underscored difficulty in linking permeability to a single measured length scale.

6. We suggested $k/d_{\text{mode}}$ as a key figure of merit to characterize capillary transport, which considers bulk fluid transport dependence on both permeability ($k$) and capillary pressure (which scales with pore diameter).

7. We detailed an injection molding procedure for fabrication of polymer wick structures using UV irradiation.

5.1.3. Passive water management with in situ polymerized wicks

1. This work represents the first time wicks have been integrated with state of the art flow fields (e.g., stamped metal or injection molded) for passive water management.

2. We developed a fabrication procedure which resulted in 150 $\mu$m thick, high quality, monolithic wick structures which coat the channels of a metal cathode flow field. Wicks spatially define regions for liquid water (wick) and gas (open channel) transport.

3. We fabricated both wick-integrated and control flow fields with identical open channel geometry. Pressure drops across both flow fields were nearly identical for all operating points. Wick integration therefore introduced minimal increase in air-delivery parasitic.

4. We observed flooding, typical of parallel channel flow fields, in control case:
   - Operation was limited to lower current densities ($j < 1 \text{ A cm}^{-2}$) at lowest air stoichiometry.
   - We observed characteristic voltage fluctuations indicative of flooding, where voltage would gradually decrease and suddenly recover. We
attributed these transients to liquid water accumulation in the manifold or channels, and then sudden purging once a critical volume of water had accumulated.

- Consistent with segmented work, we again identified flooding predominantly in the low-to-mid current density range.

5. Wick integration significantly improved fuel cell performance:
   - Wicks extended the fuel cell operable range by 0.4, 0.3, and 0.2 A cm\(^{-2}\) for stoichiometries of 1.15, 1.30, and 1.50, respectively.
   - Wicks increased peak power density by up to 62% at an air stoichiometry of 1.15. This percent increase reduced to 10% as air stoichiometry increased to 2.0, which was primarily due to significant improvement in control performance.

6. We suggested wick and channel hydraulic resistance, and air stoichiometry as key parameters affecting passive water drainage in wicks.

7. We developed a simple engineering model to estimate water transport within wicks. Model suggested that < 40% of produced water was transported through wicks and we concluded that secondary water transport mechanisms, such as corner flow, are likely significant.

8. We examined the feasibility of a simple pre-humidifier design and hypothesize that humidification of dry inlet gas streams can be achieved with passive wick systems.

5.2. Recommendations

1. Segmented cell work showed a strong dependence of performance uniformity on air flow rate. Further work is required to resolve underlying physics and mechanisms governing stability of multi-phase flow in parallel channel cathode flow fields. Possible fruitful avenues include visualization studies using optically transparent fuel cells and/or the development of models which couple fuel cell performance with multiphase transport and stability in parallel channel architectures.
2. No analytical model currently exists which successfully connects polymer monolith microstructure to bulk hydrodynamic performance. Deviations in microstructure from the Carmen-Kozeny model, including broad distributions in pore size and pore channel necking, may possibly be accounted for using bivariate pore size distribution data to accurately characterize monolith microstructure [140]. This data could then be coupled with a capillaric model which includes both variations in capillary size and periodic capillary constrictions [141].

3. Monoliths with macroscopic gradients in characteristic pore-size are of great interest for high-performance capillary transport. Monolith pore size dependence on polymerization temperature may possibly be leveraged to achieve structures with continuous spatial variations in mode pore diameter, by imposing thermal gradients during reaction.

4. Lithographic definition of wick structures using UV initiated polymerization should be investigated as a possible method for geometric definition of wick structures.

5. Further work is necessary to understand passive water management in parallel channel flow fields with wicks. Our work indicates that secondary transport mechanisms, other than Darcy flow through wicks, are significant. Visualization studies using an optically transparent fuel cell may be a fruitful avenue for further understanding.

6. Work by Zhang et al. [35] suggests that drainage of product water via corner flow increases with decreasing channel surface contact angle. Thin porous polymer layers may possibly be explored as super-hydrophilic coatings for enhanced water transport in parallel channel flow fields.

7. Humidification system complexity and size may possibly be minimized in fuel cell systems by coupling integrated wicks with passive prehumidification structures. Porous polymer monoliths with heterogeneous wetability (both hydrophilic and hydrophobic pores) should be explored as high phase-boundary area structures for compact humidification.
Appendix A

CONCENTRATION POLARIZATION IN EO PUMPS

This appendix is adapted, with minor modification, from “Evidence shows concentration polarization and its propagation can be key factors determining electroosmotic pump performance,” *Sensors and Actuators B*, 143(2):795–798, 2010.

Porous structures with submicron pore diameters and low ionic strength electrolytes yield more efficient electroosmotic (EO) pumps. For these conditions, however, electric double layers may carry a substantial portion of ionic current, creating an imbalance between current carried by anions versus cations. This leads to the formation of net neutral regions of ion depletion and enrichment on opposite sides of the pump. We visualize ionic concentration enrichment and depletion using a custom visualization setup with an embedded porous glass EO pump. Visualizations and conductance measurements indicate that concentration polarization (CP) zones are formed and propagate in EO pump systems with order 100 to 1,000 $\mu$M ionic strength. To date, no EO pump model has taken CP into account and yet CP has a significant effect on pumping rate and power consumed. We propose pore volume to surface area ratio as a new Duhkin number length scale for predicting CP regimes in EO pumps. CP and its propagation can have profound and long-range effects on ionic conductivity and electric fields in EO pumps.

A.1. Introduction

Electroosmotic (EO) pumps can potentially provide a large range of flow rates and pressure capacities, have no moving parts, and have a high self-pumping frequency[52, 53]. A simple EO pump consists of a porous substrate (often glass), two electrodes, and a power source. Electrodes are used to create an electric field which imposes a Lorentz force on mobile counterions of electric double layers (EDL) to create bulk fluid flow [53]. EO pumps have been applied in fuel cells [51, 54], high
pressure liquid chromatography [55], and drug delivery [56]. Challenges to EO pump implementation include achievement of low applied voltage and high flow rate per power, and the effects of electrolysis bubbles [142-145]. These challenges drive designs to pore radii of order of 100 nm [57-59].

Figure A.1: Schematic of propagating CP in an electroosmotic pump device. System consists of a porous glass structure (grey), connecting channels, and electrodes. Top zoom view depicts the flow through a single pore with direction of electroosmotic flow (EOF) indicated by the grey arrow. When in contact with water, pore walls deprotonate to form EDLs of negative stationary wall charges and diffuse mobile cations. Pores contain an increased cation concentration ($c_+$) and there are more mobile cations than anions. Electromigration and advection of charge both cause a net cationic flux ($J_+$) significantly greater than anionic flux ($J_-$). (Here $J$ is the total ion flux of a species due to electromigration, advection, and diffusion.) A control volume analysis (dashed boxes) indicates net flux of total (positive plus negative) charge into the cathode side and out of the anode side regions. These regions of net ion accumulation and depletion are sufficiently far from wall charge (at least a few Debye lengths away) and so they are approximately net neutral. In some cases, the resulting ion enrichment and depletion zones propagate as concentration shocks (black arrows) and can therefore have long-range spatial effects on concentration distribution [146, 147].
When electric fields are applied to systems which incorporate submicron channels, net neutral concentration enrichment and depletion regions may form at interfaces with larger channels; an effect called concentration polarization (CP)[148]. We show CP schematically in Figure A.1. The effects of surface conduction on stationary CP have been modeled and experimentally studied for over 40 years [149]. CP has been visualized experimentally in systems containing nanochannels [147, 150], mesoporous beads [151, 152], packed beads [153] and porous monoliths [153, 154]. In addition, Postler et al.[155] developed a numerical model for electroosmosis in sub-micron channels which captures CP onset and the effect of adverse pressure loads.

In some cases, CP can propagate and induce strong, system-wide spatiotemporal variations in ionic strength[146, 147]. To the best of our knowledge, propagating CP has not been confirmed experimentally in EO pump operation, and models of EO pumps with order 100 nm pore radii do not account for CP [57, 58, 156]. In this work, we therefore document and study the propagation of CP in an EO pump system. We present visualizations and conductance measurements which confirm experimentally the occurrence of propagating CP in an EO pump with mean pore diameter of order 100 nm. Our intent is to provide compelling evidence that propagating CP is important in EO pump performance and motivate studies which investigate CP in EO pumping.

A.2. Theory

CP arises when mobile EDL counterions carry a significant portion of the total ionic current. In an EO pore, the associated flux imbalance between co- and counterions results in net neutral ion enrichment and depletion downstream and upstream of the pump, respectively. CP can be characterized by a Dukhin number, a surface-to-bulk conductance ratio of the form[146, 147, 157]:

\[
Du \equiv \frac{\sigma_{\text{surf}}}{\sigma_{\text{bulk}}} l = -\frac{s z_1}{F z_1 c_r (z_1 - z_2)(r/2)}.
\]
Here, $\sigma_{surf}$ and $\sigma_{bulk}$ are surface and bulk conductance, and $l$ is a characteristic length[157]. $s$ is the surface charge density, $c_r$ is initial electrolyte concentration, $v$ is ionic mobility, $z$ is ionic charge, $r$ is characteristic pore radius, and $F$ is Faraday’s constant. Subscripts 1 and 2 denote counter- and co-ion of the binary electrolyte, respectively. We temporarily use $r/2$ for $l$, consistent with recent CP literature,[146],* but further discuss this scale below. Optimized EO pump designs require submicron pores and low ionic strength electrolytes[53, 59, 144], which result in order unity or higher $Du$ (e.g., 200 nm pore radius silica pump using 1 mM ionic strength has $Du$ of approximately unity).

In some cases, concentration enrichment and depletion zones propagate outwards as shocks. As predicted by Mani et al.[146] and experimentally verified by Zangle et al.[147], propagation is governed by two non-dimensional parameters: a Dukhin number and a co-ion electrophoretic mobility normalized by electroosmotic mobility. When CP propagates, the depletion zone travels upstream against bulk flow, and the enrichment zone propagates downstream. In non-propagating CP, these zones remain local to nanochannel interfaces.

A.3. Material and methods

Figure A.2 shows a schematic of the experimental setup. The device consists of (from A to B) a platinum wire electrode and 3.0 mL well, porous glass frit with 450 nm median pore diameter (EoPlex, Menlo Park, CA), 1 mm x 150 µm x 5 cm visualization channel, and a second electrode and 3.0 mL well. We galvanostatically controlled all experiments at 5 µA DC using a Keithley Sourcemeter (Cleveland, OH), with positive current defined when reservoir A is at high potential. Our chip’s layers are, from bottom to top, a transparent mylar backing, mylar channel layer, acrylic frit mount, and acrylic well support.

* Mani et al. [146] presented a Dukhin number with $l = h/2$ (the half height of an infinitely wide channel). A cylinder with diameter $h$ (e.g., an EO pump pore) has twice the perimeter-to-area ratio as an infinitely wide channel of height $h$ and so we use $l = r/2$ for comparisons.
Figure A.2: Experimental setup used to visualize CP and measure channel conductance. The pump substrate is located just below reservoir A, and the view area of the channel is several millimeters past reservoir A. The inset shows the microfluidic chip design.

We captured images using an inverted epifluorescence microscope (Nikon Eclipse TE300), mercury bulb light source, epifluorescent filter cube, 5x, 0.1 NA objective, and 1.3x demagnifier. We used 10 μM Alexa Fluor 488 succinimidyl ester (Molecular Probes, Eugene, OR) to visualize ionic concentration, and sodium borate decahydrate (Mallinckrodt, Hazelwoo, MO) buffer to set ionic strength.

A.4. Results

A.4.1. Depletion and enrichment visualization

We performed visualization experiments using 100 μM borate buffer (a very weak buffer with measured pH of 6.8). We here give the concentration of all borate buffers used as the Na\(^+\) concentration, where a mole of sodium tetraborate (borax) dissolves to form two moles of Na\(^+\). For our conditions, the concentration of boric acid (buffering ion) is approximately equal to Na\(^+\). Measured conductivity and pH values of all buffers used are given in Table S-1 of the supporting materials. In all cases, we used
applied currents of +5 and -5 μA. Figure A.3 shows spatiotemporal plots of ion concentration measurements, where we plot transversed-averaged Alexa Fluor intensity versus axial distance and time. The data show concentration depletion and enrichment on the upstream (high potential) and downstream (low potential) sides, respectively, as expected from CP models[146, 147].

Figure A.3: Spatiotemporal plots of ion concentration enrichment factor versus axial distance from pump-side of viewing window and time. The color intensity data shown is unfiltered, raw data. The contours are based on data convolved with a two-dimensional Gaussian with 15 s and 300 μm widths. a) Applied current of -5 μA. Data show propagating concentration depletion zone, with front velocity of ~400 μm/s. b) Applied current of + 5 μA. Data show enrichment zone propagation. Concentration reached a final enrichment factor of ~1.9. The enrichment front was significantly more diffuse than the depletion front (this is more clearly apparent in the movies included in the supporting materials).
In the depletion case, ion concentration decreased by an order of magnitude within 90 s. We observed propagation of a depletion concentration front with an approximate front velocity of 400 µm/s. In the enrichment case, characteristic time scales were significantly longer and axial concentration gradients very diffuse; so we were unable to identify clearly an enrichment front or propagation velocity. The final measured enrichment factor was ~1.9.

A.4.2. System conductance

The potential applied at the electrodes is dropped primarily across the viewing channel [158]. We therefore measure applied potential at constant current to characterize variations in viewing channel conductance. When enrichment or depletion zones propagate into the channel, conductance respectively increases and decreases. Figure A.4 shows conductance measurements for borate concentrations of 100 and 150 µM (measured pH = 6.8 and 6.9, respectively), and applied currents of -5 and +5 µA. For both buffer concentrations, conductance respectively decreased and increased for negative and positive applied current. This is consistent with the visualized concentration changes, and a confirmation of CP propagation. Conductance versus time measurements also highlight the long-range effects of CP. For the 100 µM depletion case, conductance did not stabilize until ~1400 s (reaching 95% of final value). This indicates the depletion zone (with velocity of 400 µm/s) propagated through the 5 cm length visualization channel into the upstream well.

Characteristic time scales of conductance transients were significantly longer for the 150 µM cases, where depletion-case conductance stabilized at ~1900 s. We attribute this to the reduced Du associated with the increased initial ionic strength.
Figure A.4: Measurements of channel conductance ($G$) in time for applied currents of -5 $\mu$A (open symbols) and +5 $\mu$A (closed), and borate concentrations of 100 ($\bullet$) and 150 $\mu$M ($\circ$). For both -5 $\mu$A cases, conductance decreased to approximately 50% of the initially measured value. For both +5 $\mu$A cases, conductance change was more moderate, and increased by up to ~50% (for 100 $\mu$M) over the full 2000 s observation period. We attribute these results to depletion zone (former) and enrichment zone (latter) propagation into the visualization channel. This is consistent with visualizations shown in Figure A.3, and is a strong confirmation of propagating CP in our EO pump system.

A.4.3. Propagating CP at higher ionic strength

We measured depletion-case (-5 $\mu$A applied current) conductance transients at higher borate buffer concentrations. Figure A.5 shows conductance measurements for four borate concentrations from 700 to 1000 $\mu$M. As with the lower concentrations, the characteristic time scale of transients increased with increasing concentration.
Figure A.5: Measured conductance transients for borate buffer concentrations of 700 (▲), 800 (▲), 900 (◀) and 1000 μM (▼). We normalized conductance by the initial measured value. The dashed line represents conductance predicted by traditional EO pump models, which assume constant spatial and temporal ionic strength distributions. Characteristic time scales of transients increase with increasing initial concentration. For all cases, results indicate propagating CP, although calculations of Duhkin number using mean pore radius predict non-propagating CP.

Even at 1 mM ionic strength, CP induces long-range concentration changes. If we use median pore diameter to calculate Du, the model of Mani et al.[146] predicts non-propagating CP at these higher borate concentrations. However, predictions for porous media are not straightforward. For example, from porosimetry data (Porous Materials Inc, Ithaca, NY) of a similar porous glass sample, ~25% of the pore volume should be composed of pores small enough to be within the propagation regime. We hypothesize that the total pore-volume-to-surface-area ratio may instead be a better characteristic length scale for Du; as this more accurately describes current carried by EDLs. Porosimetry data indicate our pore-volume-to-surface-area ratio is order 10 nm. Using this length scale, the Mani et al. model predicts propagation at the highest buffer concentration of 1000 μM, in agreement with our observations. Full characterization
of CP propagation in porous media is beyond the scope of this paper and we plan to further investigate this.

A.5. Conclusion

We experimentally observed propagating concentration polarization (CP) in an EO pump system. At an ionic-strength of 100 μM, we observed a depletion shock with front velocity of approximately 400 μm/s (and at least 10-fold drop in ionic strength); and an enrichment front with final enrichment factor of ~1.9. We confirmed enrichment and depletion zone propagation by measuring system conductance. Results indicate that CP propagation rate decreased with increasing initial ionic strength (increased Dukhin number), as expected from established CP theory[146]. The temporal dynamics of conductance indicated that CP fronts propagated through the entire channel.

Conductance measurements suggested CP propagation at an ionic strength of 1000 μM, which is not expected if mean pore radius is used as characteristic length scale. We propose using pore-volume-to-surface ratio for characteristic length, which for our system accurately predicts CP propagation at 1000 μM. In future work, we hope to develop models for CP propagation in porous media, where the distribution of pore-sizes introduces significant complexity.

A.6. Supplementary information

A.6.1. Detailed description of visualization experimental procedure

Before each experiment, we flushed the frit and channel with 5 to 10 mL of 100 μM sodium borate decahydrate (borate concentration specified) buffer (pH = 5.5), and visually inspected the channel to ensure that nearly all bubbles had been purged. We acquired a background image (50 frames) and then flushed the frit and channel with 2 mL of borate buffer and 10 μM Alexa Fluor 488 solution. We then attached the wells, filled each with 2 mL of the same solution, and acquired a flatfield image (50 frames). During visualization, we acquired images at 2 Hz, with 75 ms exposure time. 15 s into each visualization, we applied ±5 μA DC. We continued acquisition until
concentration in the visualization region approximately reached steady state (typically for 20 to 30 min). Data was acquired using a 12-bit CCD camera (fx16 CoolSnap, Roper Scientific, Trenton, NJ).

All data were processed and plotted using MatLab (The Mathworks, Natick, MA). We subtracted the mean of 50 background frames from all images, and normalized using the mean of 50 flatfield frames to obtain spatial plots of the enrichment factor relative to the initial concentration. We averaged each image in the transverse direction to obtain one dimensional axial concentration data.

A.6.2. Detailed schematic of visualization chip

Figure A.6: Image (top left) and drawings of visualization chip used in experiments. On the right, we show top and bottom view drawings of the visualization chip. The bottom-left close-up view shows bottom side of glass frit and viewing channel. Arrows represent direction of bulk fluid flow for applied currents of ± 5 μA. At the top-left is a top-view image of the experimental setup. Image shows chip with luer lock connectors. These are used to connect to 3 mL wells (not shown). Chip consists of (from top to bottom) acrylic support and frit mount layers, a mylar channel layer, and mylar backing. The glass frit is mounted in the frit mount layer using 5 min epoxy (ITW Devcon, Danvers, MA).
A.6.3. Characterization of buffers used

<table>
<thead>
<tr>
<th>Buffer Concentration (Na⁺)</th>
<th>pH</th>
<th>Conductivity (µS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 µM</td>
<td>6.8</td>
<td>14.1</td>
</tr>
<tr>
<td>150 µM</td>
<td>6.9</td>
<td>19.6</td>
</tr>
<tr>
<td>700 µM</td>
<td>9.5</td>
<td>60.9</td>
</tr>
<tr>
<td>800 µM</td>
<td>9.2</td>
<td>72.9</td>
</tr>
<tr>
<td>900 µM</td>
<td>9.4</td>
<td>78.6</td>
</tr>
<tr>
<td>1000 µM</td>
<td>9.3</td>
<td>88.5</td>
</tr>
</tbody>
</table>

Table A.1: Measured pH and conductivity of buffer solutions (Pinnacle 542 pH/conductivity meter, Corning, Lowell, MA). As described by Persat et al.[159], the pH of these low ion concentration buffers is a strong function of the effects of dissolved carbon dioxide. Dissolved carbon dioxide reacts with water to form carbonic acid which dissociates to lower pH values in “pure” water. At 100 µM Na⁺ concentrations, the pH (and ionic strength) is controlled by this effect and reaches a pH of 6.8 as shown in the table.
Appendix B

Details of *In situ* polymerized wick flow field

Figure B.1 and B.2 are adapted, with minimal modification, from the supplemental information published with “*In-situ* polymerized wicks for passive water management in proton exchange membrane fuel cells,” *Journal of Power Sources*, 195 (6): 1667-1675, 2010.

A note on flow field fabrication

We attempted several approaches to fabricate cathode-side metal flow fields. In one approach, we sent designs out for electrochemical etching of stainless steel, but found geometric precision unacceptable. In another, we attempted to end-mill stainless steel. Induced thermal stresses, however, lead to warping of the final flow field. End-milling of aluminum, finally, proved successful. To accomplish the desired angular geometry, we used a custom end-mill (Robb-Jack, Lincoln, CA) with 45° angled sides. Figure B.1 shows final geometry of metal flow field plates.
Figure B.1: Dimensioned drawings of (a) control and (b) WMFF before *in situ* wick polymerization. All dimensions in mm. Detailed views show channel geometry and rib thickness. Channel cross-sectional dimensions are shown on right. Major in-plane dimensions shown for the control flow field are identical for the WMFF. Internal channel dimensions and manifold depth of WMFF, however, are 150 μM larger to allow room for subsequent polymerization of water transport wicks.
Figure B.2: Pore size distribution of *in situ* polymerized wick material. Measured using mercury intrusion porosimetry (Porous Materials Inc, Ithaca, NY) on a specially fabricated polymer sample where we used the same chemistry and process as in the flow field wick fabrication. Scanning electron micrograph of resulting morphology is shown in inset. Results indicate a mean pore diameter of 10 μm. Permeability and porosity of this sample was $2.65 \times 10^{-12}$ m$^2$ and 0.7, respectively.
Appendix C

DESIGN CONSIDERATIONS OF SEGMENTED ANODE INSTRUMENTATION

In this appendix, we discuss design and fabrication considerations for the segmented current collector and current measurement instrumentation. Details on segmented anode flow field can be found in Chapter 2. For details on fuel cell setup and operation strategies, see summary in Appendix E of [160].

Use of printed circuit boards in fuel cell instrumentation

There are many suppliers for rapid and inexpensive production of printed circuit boards (PCBs). Two companies we have used include PCB123 and PCBexpress. For the devices described here, we used PCBexpress. In its simplest form, a PCB consists of a single plastic layer with conductive metal traces on either side. Thru vias (drilled holes which are plated with copper) are used to selectively connect traces from one side to the other.

For fuel cells of the size considered in this dissertation, total current is relatively high (e.g., 30 A is not an uncommon current to be generated by the fuel cell). As such, resistance of circuits designed into PCBs becomes important. In typical fabrication processes, metal traces are copper and ~ 50 µm thick. As an example, for a 1 mm trace width, the resulting resistance is ~ 3.4 mΩ cm⁻¹. To minimize resistance in traces which carry large currents, we used large trace widths (3 mm) and subsequently electroplated them with 430 µm of Ag to increase total conductance. Note that Ag oxidizes and if used, it should be subsequently plated with Au or another inert metal.

Segmented current collector design

Figure C.1 shows the segmented current collector PCB design. On one side (shown in green), nine large copper pads cover the surface. Pad size corresponds to segment sizes of the anode flow field. Five thru vias connect each pad to traces on the opposite side of the PCB, which electrically connect segments to an array of vias. In this array, we mount a MOLEX 39506-1009 PCB header, to connect segments to
current measurement circuitry. Current collector was subsequently nickel and the gold plated, as discussed in Section 2.2.3.

Figure C.1: Design of PCB used for segmented current collection. Nine pads (green), which align with anode flow field segments, cover one side of the PCB. Five through vias connect each pad to a trace on the opposite side, which connects to a header on one end of the board. This header is then used to connect segmented current collector to current measurement instrumentation.

**Instrumentation design**

Because we leave GDL and electrode unsegmented, instrumentation impedance must be minimized to mitigate leakage of current between segments. As a result, we employed hall effect sensors (LEM LAH 25-NP). These sensors are low impedance (0.18 mΩ), offer high temporal resolution (reaction time < 500 ns), and can be mounted on a PCB. Figure C.2 shows hall effect sensors and the PCB design we used for their mount. Several wiring configurations are available for these current transducers (which are described in the technical specifications accompanying the sensors). We chose wiring input current to pins 1, 2, and 3, and output to pins 4, 5 6, as this configuration minimizes sensor impedance and allows for measured current densities of up to 25 A. Traces connect current input and output of each sensor to
respective via arrays (shown as “1” and “2”, respectively, in Figure C.2), which connect to external wiring via MOLEX 39506-1009 PCB header. These headers are designed to carry up to 8 A per channel. In addition, output current of each sensor connects to a separate via array (“3” in Figure C.2) where an additional header connects externally to a bank of precision resistors for voltage measurement. Power is provided to all sensors at “4” using a conventional computer DC power supply.

Figure C.2: Layout of PCB and instrumentation for nine-channel current measurements. PCB is two layer, with traces shown in green on back side, and traces shown in red on top. Yellow outlines demarcate locations where hall effect current transducers and PCB headers are mounted.
Images of instrumentation

Figure C.3: Image of current measurement instrumentation. Nine current transducers (blue) are mounted on PCB (see Figure C.2). Headers allow for connection of board to external segmented anode and load. Transducers output a current proportional to measured current, which is converted to a voltage by precision resistors mounted on breadboard. Nine pairs of leads allow for voltage measurement by DAQ.

Figure C.4: Image of instrumentation connected to the fuel cell. To minimize ohmic losses, ~5 cm long, 18 AWG wire connects segmented current collector to circuit board. Output current from board is combined into a single line, which connects to the electronic load.
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