# Textile-based Sensors for In-situ Monitoring in Electrochemical Cells and Biomedical Applications

by

Sadegh Hasanpour
B.Sc., University of Tehran, 2013
M.Sc., The University of British Columbia, 2016

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## ABSTRACT

This work explores the blending of e-textile technology with the porous electrode of polymer electrolyte membrane fuel cells (PEMFCs) and with smart wound patches to allow monitoring and in-situ diagnostics. This work includes contributions to understanding water transport and conductivity in the carbon cloth gas diffusion layer (GDL), and further developing thread-based relative humidity (RH) and temperature sensors, which can be sewn on a cloth GDL in PEMFCs. We also explore the application of the developed RH and temperature sensors in wearable biomonitoring.

First, an experimental prototype is developed for evaluating water transport, thermal conductivity and electrical conductivity of carbon cloth GDLs under different hydrophobic coatings and compressions. Second, we demonstrate the addition of external threads to the carbon cloth GDL to (1) facilitate water transport and (2) measure local RH and temperature with a minimal impact on the physical, microstructural and transport properties of the GDL. We illustrate the roll-to-roll process for fabricating RH and temperature sensors by dip-coating commodity threads into a carbon nanotubes (CNTs) suspension. The thread-based sensors response to RH and temperature in the working environment of PEMFCs is investigated. As a proof-of-concept, the local temperature of carbon cloth GDL is monitored in an ex-situ experiment.

Finally, we optimized the coating parameters (e.g. CNTs concentration, surfactant concentration and a number of dipping) for the thread-based sensors. The response of the thread-based sensors in room conditions is evaluated and shows a linear resistance decrease to temperature and a quadratic resistance increase to RH. We also evaluated the biocompatibility of the sensors by performing cell cytotoxicity and studying wound healing in an animal model. The novel thread-based sensors are not only applicable for textile electrochemical devices but also, show a promising future in wearable biomonitoring applications.

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# DEDICATION

To my parents (Safoura and Ghorbanali), they were there for me when I needed them the most.

# Chapter 1

# Introduction

Freedom of thought is best promoted by the gradual illumination of men's minds which follows from the advance of science.

Charles Darwin

This dissertation describes new contributions to (i) characterize transport properties in carbon cloth gas di usion layers (GDLs) and (ii) develop textile sensors for monitoring relative humidity (RH) and temperature in polymer electrolyte membrane fuel cells (PEMFCs) and evaluate the sensors for wearable biomonitoring applications. Section 1.1 discusses the research background and motivation of this study. The literature review section is organized into ve subsections: Sections 1.2.1 and 1.2.2 review the characterization methods for GDL water transport and conductivity; Section 1.2.3 and 1.2.4 provide an overview of water management strategies and in-situ temperature and RH diagnostics for PEMFCs; and Section 1.2.5 is a brief overview of the development of bre-based RH and temperature sensors. The objectives and structure of the thesis are presented in Section 1.3 and 1.4.

## 1.1 Background and Motivation

PEMFCs use hydrogen and oxygen in the anode and cathode side and produce electricity and water in the cell. Figure 1.1 illustrates the geometry of a single cell of a membrane electrode assembly (MEA) with ow elds on the cathode and anode sides. A stack of PEMFCs consists of several cells connected in parallel to provide the desired power output. Each cell consists of ve main constituent layers. Reactant

gases travel through these layers from the ow eld to the reaction zone. Each constituent has speci c functions ensuring optimum performance of the cell. Each layer is described below.

Membrane : The core of each cell is a proton conductive membrane responsible for conducting protons and blocking electrons. Na on membranes are widely used materials that have high protonic conductivity in a hydrated environment.

Catalyst Layer (CL) : This thin porous layer consists of catalyst particles (i.e. platinum), ionomers (i.e. per uorosulfonic acid (PFSA)) for transferring protons, conductive support particles (i.e. carbon) for transferring electrons and pores for transporting the reactant and by-product. The amount of catalyst particles is higher on the cathodic side due to sluggish cathode reaction kinetics. The CL is typically around 5-10µm thick and is either coated on the membrane or the microporous layer (MPL) side.

Microporous layer (MPL) : MPL has carbon particles combined with a hydrophobic polymer (e.g. polytetra uoroethetylene (PTFE)), which are sintered on top of the GDL to provide an interface between the CL and the GDL, reduce the contact resistance between GDL and CL, and provide uniform distribution of reactants in the CL and e ectively remove water from the CL to the GDL. This layer has a porosity around 25% and pore size distribution in order of 20 to 500 nm. Depending on the manufacturing process, it might have cracks on the surface.

Gas di usion layer (GDL) : this highly porous layer (porosity 70 to 90%) provides pathways for reactants, by-products and electron transport in and out of the cell. The thickness of this layer is in the range of 100 to 300µm with pore sizes of around 10-100µm. Carbon-based GDLs are widely used and they are coated with hydrophobic polymers mainly PTFE or in some cases with uoroethylenpropylene (FEP). Two main groups are woven and non-woven GDLs. Woven GDLs are also known as carbon cloth are fabricated by weaving carbon bers. Non-woven GDLs are fabricated with a random distribution of carbon bers with a binding that improves the mechanical stability of the GDLs. The GDL is an ortothropic material that has di erent transport properties in the in-plane and through-plane directions. The former is the direction across the thickness of the GDL and the latter is the direction in the plane of GDL.

Flow eld plate : The ow eld consists of channels to uniformly distribute reactant over the whole active area of the cell; it is also a pathway to collect electrons and remove by-products (i.e. water) out of the cell. Di erent designs of channels

exist such as parallel, straight line, interdigitated or serpentine. Each has pros and cons due to di erent modes of transport or pressure drops from the inlet to the outlet of the cell.

This work is motivated by the need to better understand the carbon cloth GDL transport properties and to explore potential opportunities for developing textile-based sensors not only for electrochemical devices such as PEMFCs but also for wearable biomonitoring applications. A exible carbon cloth GDL is suitable to embed bers for enhancing water transport or sensing for further improving the performance and integrate in-situ PEMFCs diagnostics.

Figure 1.1: Schematic of the main components of a single cell PEMFCs with reactants directions and electrochemical reactions.

## 1.2 Literature Review

This section reviews the progress in the literature toward developing experimental procedures for (1) evaluating water transport, thermal conductivity and electrical conductivity of GDLs; (2) improving water management within GDLs through different physical modi cations, addition of external components, or chemical modi cations; (3) monitoring local temperature and RH within PEMFCs; and (4) developing bre-based RH and temperature sensors.

### 1.2.1 Water Transport and Conductivity Analysis of GDLs of PEMFCs

Various studies show that coating GDLs with hydrophobic polymer improves the performance of PEMFCs [6, 7]. Hydrophobic coating facilitates water removal from the cell, speci cally in high current density. Since the operating temperature is commonly between 60 C and 90 C, a combination of liquid water and water vapour exists within GDLs. The vapour phase is transported predominantly by di usion due to concentration and temperature gradients between GDLs and channels. The liquid phase transport is dominated by capillary transport, which is a function of the structure and internal wettability of the GDLs pores [8]. Liquid water leaves the GDL through minimal pressure pathways [5]. Commercial GDLs are made out of carbon bres and are treated with hydrophobic polymers to avoid the accumulation of water within GDL pores, a phenomenon known as ooding". Common industrial practice is to coat GDLs with PTFE via dipping, spraying or brushing; this is known as a bulk treatment. The amount of PTFE is usually between 5% to 30 wt% [9]. Based on the coating procedure, the distribution of PTFE in GDLs varies. Mathias et al. [9] showed that slow drying (e.g. air drying) results in uniform PTFE distributions with more PTFE in the center of the GDL and fast drying (e.g. convective oven) results in more accumulation of PTFE near the surface of the GDL. Bazylak et al. [10] combined scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis to monitor the distribution of PTFE in the through-plane for three types of commercial GDLs (paper, felt and cloth) with 10 wt% PTFE added to the GDLs. The results show that the paper GDL have higher accumulation of PTFE near the surface resulting in a 5% porosity drop near the surface; however, PTFE distributes more evenly in carbon cloth GDLs due to the transverse structure

of carbon bres [11]. PTFE distribution changes the properties of the materials and a ects transport properties, thermal and electrical conductivity and water transport behaviours within the microstructure.

GDLs in an operating fuel cell are under compression. The compression reduces contact resistances and provides sealing, resulting in optimum performance for the cell [12]. This compression has a direct impact on porous structure and on the effective transport properties. As a result of the collector plates geometry, the GDL in an operating fuel cell experiences non-uniform compression. It is, therefore, essential to characterize the properties of the GDL under non-homogenous compression, particularly for thermal conductivity, electrical conductivity and water transport.

Water management is a complex process that needs to be carefully considered in di erent components of the PEMFCs. On the one hand, the polymer membrane requires su cient hydration, and on the other hand, the porous structure of GDLs, MPLs and CL need to remain fully opened (i.e. free of liquid water) under a variety of di erent operating conditions. The multi-objective aspects of water management have impacts on overall performance, and di erent strategies are necessary for the various PEMFCs components: (1) membrane, (2) CL, (3) MPL, (4) GDL and (5) channels. Since GDL water transport is the focus of this work it is discussed next in more detail [6].

## Pattern of water transport within GDLs

The determination of water transport in the 3D anisotropic structure of GDLs is complicated and has been investigated through numerical [13] and experimental modeling [14, 15, 16]. Innovative methods to track water transport experimentally mainly rely on liquid water visualization techniques [17]. The capability of each imaging technique depends on (1) spatial and temporal resolutions, (2) capability for in-situ testing with minimal invasiveness, (3) compatibility with materials and (4) accessibility. Neutron imaging is capable of detecting water within GDLs due to high sensitivity to hydrogen atoms in water, and is a suitable technique to observe water transport in operating fuel cells [18]. However, the low resolution is not favourable for tracking transport at the microstructural level; also, accessibility to this imaging technique is limited. X-ray microtomography (X-µCT), which has been used widely for analysis of porous structures, has also been used to track water transport in ex-situ [16] and in operando fuel cell [19]. However, for 3D imaging, the technique is not capable of dynamic track-

Table 1.1: Summary of liquid water visualization techniques for GDL.

| Research | Imaging | Spatial resolution | Temporal resolution | Type | Merits | Challenges |
|---|---|---|---|---|---|---|
| Bazylak et al. [15] | FS | 21.4 µm | 0.3 s | Carbon paper | Online tracking of water | Limited depth of eld |
| Zenyuk et al. [21] | X-ray | 1.3 µm | 8 min | Carbon paper | Water distribution in micron level | Scanning time does not allow dynamic monitoring of water |
| Wu et al. [22] | Neutron imaging | 26 µm | 5 s | Carbon paper | Good sensitivity to water | It does not generate water distribution in micron level |
| Gostick et al. [23] | X-ray | 1.3 µm | 2 min | Carbon paper | Water distribution in microstructural level was obtained | Time of scan does not allow dynamic monitoring of water |

ing due to the required imaging time. On the other hand, synchrotron X-ray shows promising results by scanning at the sub-second for tracking dynamic water transport [20]. Florescent (FS) microscopy provides high temporal and special resolutions that can give good descriptive behaviour water transport of GDLs [14, 15]; however, the challenge associated with this imaging technique is the production of 2D images with limited depth of eld. Research has focused on the mechanism of water transport within non-woven GDL which are increasingly used in industry, with relatively little work on woven GDLs. Table 1.1 lists ex-situ techniques for observing water transport with a focus on compression and hydrophobic treatment.

### 1.2.2 Electrical and Thermal Conductivity

Electrical and thermal conductivities are important properties that have direct e ects on ohmic losses and thermal management of the cell, respectively. As a result, high thermal and electrical conductivity are necessary for optimum performance of the cell, and their correct estimation are essential to predicting cell performance.

#### Electrical conductivity measurement methods

Electrons are generated in the CL and transport through di erent constituents of the cell. The ow of electrons is accompanied by ohmic losses that consist of the internal resistances of materials and interfacial contact resistances between components (e.g. the GDL and the CL interface). The protonic current in the membrane also generates

ohmic losses. The internal resistances are a function of morphology, hydrophobic treatment and compression of each component. Here, we examine, brie y, methods to measure the electrical conductivity of the GDL.

The measurement of the in-plane conductivity is performed by a four-point probe to e ectively exclude the e ect of contact resistance, as shown in Figure 1.2. Furthermore, since the conductivity is measured along the bre in the in-plane directions, the impact of compression and hydrophobic treatment is minimal. Conductivity measurement in the through-plane direction is challenging since a four-point probe measurement along a thin layer of GDL is not feasible. In addition, the e ect of compression on the through-plane direction is signi cant as the mechanism of conductivity is due to bre-to- bre connections. In addition, hydrophobic treatment, which covers the outer layer of bres, a ects the through-plane electrical conductivity. The through-plane resistivity for the schematic shown in Figure 1.2(b) is:

$$R_{total} = 2R_e + R_s + R_{GDL} + R_{GDL\ s} + R_{s\ e} \tag{1.1}$$

where $R_e$ is the bulk resistance of the copper electrode, $R_s$ is the bulk resistance of stainless-steel disk, $R_{GDL}$ is the resistance of the GDL, $R_{GDL\ s}$ is the interfacial resistance between the GDL and the stainless steel and $R_{s\ e}$ is the interfacial resistance between the stainless-steel disc and the copper electrode. The apparatus resistance ($R_a$) is measured when no GDL is between the probes.

$$R_a = 2R_e + R_s + R_{s\ e} \tag{1.2}$$

To e ectively nd the interfacial resistance ($R_{GDL\ s}$) and $R_{GDL}$, samples of the GDL with di erent thicknesses are required. Then, by plotting the resistance vs. thickness, the y-intercept represents the interfacial resistance, and two resistances can be e ectively separated. However, this method is not applicable if samples of di erent thicknesses are unavailable (which is the case for some GDL samples). In addition, the e ect of the hydrophobic coating distribution across the through-plane direction is not uniform even for similar GDLs with di erent thicknesses, which causes errors in measurement. For these cases, (1) using a gold plate as an electrode to reduce the contact resistance and (2) stacking the same GDLs to make a thicker sample are approaches to separate the GDL resistance from contact resistances e ectively.

The in-plane electrical conductivity is an order of magnitude higher than the

through-plane conductivity, which allows the proper utilization of the entire GDL [9]. Also, it is shown that the limiting factor in ohmic losses is the through-plane direction [9]. Compression on electrical conductivity is more critical when the sample is coated with hydrophobic coatings, which tend to accumulate near the surface area and also changes the distribution of the hydrophobic polymer in the through-plane direction. Although the contact resistance between GDL and bipolar plates plays a signi cant role in the through-plane conductivity, the e ect of hydrophobic coating on the intrinsic through-plane conductivity of GDL is not well-understood.

Figure 1.2: Schematic of the experimental setup for measuring electrical conductivity in (a) in- and (b) through-plane direction [24].

Thermal conductivity measurement methods

The exothermic reaction of PEMFCs, combined with irreversibilities and losses generate heat that distributes within di erent constituent of the cell. The temperature gradient across the cell impacts the transport mechanism, relative humidity and the durability of the cell. An active cooling system combined with optimized heat management is necessary to achieve a highly e cient cell design. The heat management strategy requires detailed information on the constituents' thermal conductivity properties and interfacial thermal conductivity between components similar to electrical conductivity. Among di erent components, the GDL plays a signi cant role since it

impacts many of the losses within a cell.

The (1) highly anisotropic porous structure of GDL combined with (2) multiphase ow, (3) hydrophobic treatment, and (4) e ect of compression leads to an elaborate analysis of evaluating thermal conductivity of the GDL. As a result, the e ective thermal conductivity is a more accurate term since each parameter, as mentioned earlier, has a signi cant e ect on assessing this parameter. First, methods to obtain thermal conductivity in through-plane will be reviewed, and then we move on to the in-plane direction.

Through-plane : A uniform one-dimensional heat ux must be generated in the through-plane direction to measure the thermal conductivity of the GDL. A high conductivity rod with known thermal conductivity property is connected to the top hot plate and three thermocouples are located along the rod's length with the same interval. The same architecture is in place in contact with the cold plate. This guarded heat ux meter is compatible with the ASTM standard. Steady state conditions are considered to be attained when the temperature at each point remains constant within 0:5 C [25]. Following Fourier thermal conductivity formula, from the top rod, the heat ux is evaluated by:

$$Q = k(T)A_r \frac{dT}{dx} \tag{1.3}$$

where $Q$ is heat ux, $k(T)$ is the thermal conductivity and $A_r$ is the cross-sectional area, and $\frac{dT}{dx}$ is the temperature gradient. Then, the temperature di erences between the top and bottom sample (i.e. GDL) obtained from the thermocouples will be divided by heat ux to get the thermal resistance following the formula:

$$R_t = \frac{T_s}{Q} \tag{1.4}$$

where $R_t$ includes thermal resistance and two contact thermal resistances between the top and bottom plate in contact with the GDL. Thermal resistance and thermal contact resistance both are functions of the compression pressure. To exclude the contact resistance, stacking several samples of GDLs results with thermal resistance vs. the number of layers in which the intercepting line gives the contact resistance (similar to electrical conductivity measurement) [25]. As mentioned earlier, the GDL experiences water saturation that has a direct impact on the thermal conductivity estimation. Xu et al. arti cially soaked the GDL sample and performed the test to evaluate the e ect of water saturation on the thermal conductivity. However, the

study did not provide the level of saturation, which can be investigated in future research [26].

The outcome of extensive research indicates that compression increases the through-plane thermal conductivity for GDLs. However, hydrophobic coating higher than 30 wt% reduces the thermal conductivity by hindering bre to bre connection in GDLs [27]. Future work investigating optimum hydrophobic treatment for thermal conductivity is needed to provide detailed data about the e ect of hydrophobic treatment vs through-plane thermal conductivity.

In-plane : Determination of in-plane thermal conductivity needs a more complex setup. For steady-state thermal conductivity measurement, there are two methods reported in the literature. Sadeghi et al. [28] developed a novel approach to determine the in-plane thermal conductivity by generating constant ux travelling in the in-plane direction of GDL. The second technique, which has some advantages over the rst method, is parallel thermal conductance. The parallel thermal conductance method brings high accuracy with faster data collections. In this method, as shown in Figure 1.3, low conductivity material places parallel with the GDL sample [29]. A direct current supply generates a constant temperature in the heat source. The conductivity of the low conductive material is measured without placing a GDL between two thermocouples. The thermal resistance is:

$$R_0 = \frac{T_h \quad T_c}{IV} \tag{1.5}$$

$T_h$ and $T_c$ are temperatures in hot and cold locations captured by thermocouples, respectively. $I$ and $V$ are current and voltage for generating constant temperature. The captured resistance consists of conductivity of low conductive material and apparatus (thermocouples, wiring) and radiation of surrounding (i.e. $R_0$). The test is performed in a vacuum chamber to mitigate the e ect of natural convection (similar to through-plane measurement). The test is repeated with GDL in place, and the new resistance is captured, following the parallel formula as:

$$\frac{1}{R} = \frac{1}{R_0} + \frac{1}{R_s} \tag{1.6}$$

where $R$ is the thermal resistance from the second experiment, and $R_s$ is the thermal

resistance between two edges. The in-plane thermal conductivity is calculated as:

$$k_{GDL;in} = \frac{L}{Wt}\left(\frac{1}{R} \quad \frac{1}{R_s}\right) \tag{1.7}$$

L, W and t are length, width and thickness of the GDL in the test setup. The reviewed techniques managed to obtain in-plane thermal conductivity. However, the e ect of compression and saturation on the in-plane thermal conductivity has yet to be analyzed.

The in-plane thermal conductivity (e.g. TGP-H-120 5 wt% PTFE = 17.39 $W\,m^{1}K^{1}$) is by order of 10 higher than the through-plane conductivity (e.g. TGP-H-120 5 wt% PTFE = 1.62 $W\,m^{1}K^{1}$), which indicates the bottle-neck is in the through-plane direction [24]. Furthermore, hydrophobic treatment increases the thermal conductivity by lling voids and replacing it with polymers, which has a higher conductivity than air. Quantifying the e ect of hydrophobic treatment vs. in-plane thermal conductivity should be performed to determine the optimal hydrophobic treatment for thermal conductivity.

Figure 1.3: Schematic of experimental setup for measuring thermal conductivity in (a) through-plane and (b) in-plane direction [24].

### 1.2.3 Strategies for Enhanced Water Management

E ective water management in PEMFCs is necessary to obtain optimal performance across a range of current densities and environmental conditions. Water in operating fuel cells is a by-product of electrochemical reactions in the cell and is also introduced by the humidi ed inlet gases. At high current densities and when water and heat management are inadequate, water vapour can condense and form liquid water in the porous electrode blocking the pathways of the reactants to the CL, and causing mass transport limitations [14, 17]. The excess water has other deleterious e ects, such as inhomogeneous current density, membrane swelling, and delamination of PEMFCs components in freeze/thaw processes [30]. On the other hand, membrane hydration is an important factor in optimal performance since a dehydrated membrane results in high ionic resistance and performance degradation [13, 17].

The GDL serves several important functions, including (1) reactant and product permeability, (2) electrical conductivity, (3) thermal conductivity, and (4) mechanical support for the membrane electrode assembly (MEA) [9]. This layer is a prime candidate to employ di erent strategies for water management. These strategies fall into three main categories (1) physical modi cations; (2) addition of external components; and (3) chemical modi cations. Other options have also been explored, such as perforated metallic plates or metallic porous substrate instead of brous carbon-based materials [31].

#### Physical modi cation

Modi cations to enhance water transport have been mainly directed at brous carbon-based GDLs, which are widely used in commercial fuel cells. Gerteisen et al. [1] generated through-plane holes with 80 μm diameter in a carbon paper GDL. These holes were located under the channel of the ow eld and result in improved of water transport dynamics and cell performance, with gain in limiting current density of the cell under humidi ed conditions (Figure 1.4(a)-(c)). The through-plane pores are generated by either electric discharge machining, micro-drilling, or laser perforation. The process of perforating pores melts the binder in GDLs and can close the pores; this can be a severe problem for samples with high binder loading. In addition, the laser perforation and the electric discharge machining alter the hydrophobic surface of the pores into hydrophilic surfaces. Okuhata et al. [32] investigated di erences between electric discharge machining and micro-drilling for generating perforated holes and

achieved better performance with micro-drilling, which maintains hydrophobicity of perforated walls. Th r idea of perforated pores has been studied with samples with MPLs [33, 34, 2]. Manahan et al. [34, 2] made 100 to 300 µm pores with and without hydrophilic heat-a ected zones (HAZs) (Figure 1.4(d) and (e)). The HAZs are hydrophilic and preferential pathways for water removal. The results indicated that at 75% RH, the GDL with 300 µm and HAZs performed better; however, for the over-humidi ed condition (i.e. in cold start-up) the fuel cell performance dropped due to water ooding. Physical modi cations have gained much attention in the literature as they are relatively easy to implement; however, the e ectiveness of this approach is limited to speci c running conditions of the cell (e.g. speci c RH and temperature conditions).

Another promising approach is the development of GDL with graded porosity from the CL to the ow channel. The idea is to decrease the capillary pressure in the through-plane direction and speed up water removal from the reaction zone into the channel. Numerical studies have been carried out to determine the optimal porosity distribution. The results suggest a linear porosity distribution from CL to the ow channel. However, achieving such morphologies with carbon-based GDLs adds extra di culties in the manufacturing process [35]. Other innovative approaches, such as electrospinning [36] or functionally graded materials in powder metallurgy, are promising avenues to pursue [35].

Addition of external components

Another approach to improve water management is adding an external layer. One of the passive methods consists of adding a conductive wicking layer between the GDL and the ow eld. This layer prevents ooding under broad operational conditions for air-breathing PEMFCs (Figure 1.4 (g)) [3]. The wicking layer was combined with an electroosmotic (EO) pump to actively remove excess water from the cell. The pump required less than 2% of the fuel cell power, but eliminated the cathode ooding and helps improve stability and water management (Figure 1.4(h)-(i)). The application of this system was shown for a small-scale fuel cell (less than 5W) [4]. However, it adds an extra layer to the MEA and complexity to the system, and its implementation has not been demonstrated in fuel cells with higher power outputs.

Chemical modi cations

As the nature of the process indicates, water transport is a complex phenomenon and requires adaptive solutions for various conditions. A number of studies have explored chemically altering hydrophobicity of the GDL and pattering hydrophilic/hydrophobic [37]. Paul Scherrer Institute researchers developed a novel method for generating hydrophilic/hydrophobic channels on o -the-shelves GDLs with varying width sizes from 100 µm up to 1000 µm. Figure 1.4(l) shows a schematic of the process. A commercial GDL (i.e. Toray TGP-H-060) was  rst dip-coated with an FEP solution (due to higher water-repelling quality in comparison with PTFE); a mask with pre-de ned patterned was then placed on the coated sample and exposed to an electron beam. Subsequently, the GDL was immersed into hydrophilic monomer, N-vinyl formamide (NVF), to graft pNVF to FEP. This process reduces the contact angle (CA) from 105  to 20  and e ectively alteres the region from hydrophobic to hydrophilic (Figure 1.4(k)). EDS analysis indicated the presence of pNVF in the area exposed to irradiation on both sides of the GDL (Figure 1.4(m)). The e ect of capillary pressure on a di erent area of the modi ed GDLs was observed with neutron radiography and shows that hydrophilic channels need a lower capillary pressure (10 mbar) compares to hydrophobic channels (40 mbar). An in-situ fuel cell with GDLs having 500 µm wide hydrophilic channels and 950 µm wide hydrophobic channels shows a considerable improvement in fuel cell performance(Figure 1.4(n)) [5]. The successful demonstration of the novel GDLs was thoroughly studied from synthetic approach [38], ex-situ water transport analysis [18] and in-situ fuel cell testing [39]. However, a challenge is the degradation of the hydrophobic/hydrophilic pattern at the high temperature required for MPL sintering. The authors suggest alternative MPL sintering approaches such as local heating using infrared. Another challenge is that the method is not suitable for nonuniform porosity GDLs.

Chemically altering hydrophobicity of MPL either by using di erent hydrophobic polymers in MPL materials (ex. per uoroalkoxy (PFA) and  uorinated polyurethane based on per uropolyesther (PFPE) blocks) or adding hydrophobic agents or multiple layers of hydrophilic-hydrophobic structure have also been investigated in the literature and are discussed in Ref [35].

### 1.2.4 In-situ RH and Temperature Measurement

Fuel cell operating parameters such as voltage, current, inlet and outlet RH and temperature, and stoichiometry are parameters to control fuel cell performance and avoid water ooding. However, these properties are averaged out over the entire system and do not necessarily represent local conditions as they are typically non-uniform. Nonuniform conditions accelerate the degradation of the cell and, ultimately, cause performance drop. In-situ measurement of local conditions (e.g. temperature and RH) provides detailed information on RH and temperature distribution in a cell, which facilitates implementation of e ective water management strategies for fuel cell stacks. Furthermore, obtaining local parameters provides pathways for adaptive smart porous materials for controlling reactants and product transport within the cell [40]. Here, we brie y review diagnostics techniques for measuring temperature and RH locally within fuel cells.

The local temperature has a direct e ect on a reaction rate, membrane conductivity and, additionally, the transport properties of the membrane. RH is the second key control parameter. This parameter is closely coupled with temperature and determines membrane conductivity and water balance in PEMFCs. In addition, the membrane thickness is proportional to the RH of the cell, and non-uniform distribution of RH accelerates the mechanical degradation of the membrane. The challenge is to locally measure these parameters as closely as possible to the reaction zone with minimal impact on the performance of the cell.

Commercial probes (ex. thermocouples and capacitive RH sensors), Micro-electro-mechanical-systems (MEMS) device and optical sensors (e.g. bre optics) are commonly used tools for monitoring local temperature and RHs. These sensors are placed on either the ow eld or the membrane or between constituent layers (i.e. membrane and CL or CL and GDL or ow eld and GDL). Zhang et al. [41] placed thermocouples between GDL and CL in the cathode where they were distributed from the inlet to the outlet of the cell and captured the local temperature at di erent operating conditions. The results show that there is a gap between local temperature and back-plate temperature (i.e. nominal test temperature), and also, the local temperature and local current densities are well correlated. The sensors, however, covered valuable areas of the CL. Pei et al. [42] designed an experimental setup to measure temperature distribution in a stack of cells. Thermocouples were placed in the cathode side of the ow eld in contact with the GDL. It shows that not only is there a temperature

distribution in each cell, but also, temperatures are varied in the stack and shows parabola temperature distribution along with the stack. Placing thermocouples on the outside of the ow eld also shows non-homogenous temperature distributions within a single cell [43, 44]. Discssion of use of commercial probes to measure RH is limited in the literature. One successful demonstration uses di erent capacitive RH sensors in the ow eld of both anode and cathode for a single cell. RH gradient formed from the inlet to the outlet for both anode and cathode side along the channel. Although the commercial probes provide detailed temperature and RH maps, their footprint is considerable, and most of them are located at a the distance from the reaction zones and require modi cation of ow eld design for the stack of PEMFCs.

MEMS fabrication techniques bene t from a small footprint, monitoring di erent parameters on a single chip and ability to mount on surfaces. A resistance temperature detector (RTD) in a serpentine pattern with a capacitive humidity sensor in the interdigitated structure was fabricated and located on the ow eld of PEMFCs [45]. In a subsequent study, ve sensors in one MEMS device were combined to obtain local temperature, voltage, pressure, ow rate and current and located on the ow eld of cathode [46]. Embedding sensors on MEA is attractive due to collecting information in a crucial area. Lee et al. [47] fabricated a MEMS device with a footprint of 400 µm 400 µm with the thickness of the 2µm and hot-pressed it on the membrane surface. It shows more than 5C di erence existed between the MEA and a bipolar plate surface. However, this diagnostic technique costs in performance loss due to CL's coverage and reducing the active area of the CL.

Employing optical sensors is another promising avenue for in-situ diagnostic in PEMFCs. Tunable diode laser absorption spectroscopy [48], phosphorescence-based sensors [49, 50], and bre grating sensors(FBG) [51, 52, 53] have been utilized in the literature. Inman et al. [50] employed the principal of phosphor thermometry to measure the surface temperature of the a GDL. Phosphor materials were applied on the surface of the GDL, and an optical bre was located on the channel to provide optical path from the phosphor to the photodetector. That allowed to monitor temperature on the surface of the GDL locally at di erent operating conditions. The implantation of the sensor did not have a negative impact on cell performance. David et al. [52] utilized FBG sensors in the channel of PEMFCs and obtained temperature and RH simultaneously in the ow eld with relatively fast response to RH changes(in order of 10 s). These sensors are mainly suitable for monitoring environmental conditions in the ow eld and also need a signi cant change in the ow eld's design. In addition,

the sensors are delicate and fragile. The more detailed information about the bre optic sensors are provided in Refs [54, 53].

### 1.2.5 Fibre-based Temperature and Humidity Sensors

Conventional techniques to measure the local properties in PEMFCs either require signi cant design changes or cause a drop in performance. To address these drawbacks, embedding sensors that can t within the GDL structure is essential. A promising possibility is use of sensitive fabrics that can be added to carbon cloth GDL to work as embedded sensors without compromising the performance. Flexible bre-like sensors that can be weaved or sewn on to carbon cloth resulting in advanced sensing textiles have shown some promise in wearable technology and advanced health system monitoring.

E-textiles that combine electronics with well-established textile technology enable the development of smart fabrics that can sense and respond to external stimuli such as strain [55], temperature and humidity [56]. This section reviews the development and fabrication of bre-like sensors for measuring RH and temperature.

#### Fabrication process

There are three major routes to make functional textiles: (1) bre making, (2) coating/printing and (3) embedding microelectronics within textiles. The backbone of the bre making and coating/printing process is on blending nanomaterials, and then later takes advantage of high precision microelectronics for developing smart textiles [57].

Fibre-making; in this process functional materials are added into precursors to form bres with methods such as wet-spinning and electrospinning. The bre-making process allows homogenous modi cation with embedding functional materials in a sub-micrometre structure and gives the ability to a more detailed design of the internal structure. However, coarse bre quality and low durability are among the important challenges that need to be overcome for scaling up such methods.

Coating and Printing; this scalable and straightforward process forms an electrically conductive layer on the surface of bres, yarn or textile, thereby transforming them into functional materials. The bene ts are low cost and the ability to mass-produce coated textiles by existing production processes. However, this process dose not allow embedding of functional materials in the inner layer of the bre struc-

ture. Dip-coating, screen printing and inkjet printing are main approaches to form a conductive layer on bre and textiles.

Embedding electronics within textiles; this method takes advantage of existing technology in microelectronics with good accuracy and durability. However, the procedure has high costs and lower exibility.

Fibre-based humidity sensors

Zhou et al. [58] developed a wet-spun single-wall carbon nanotube (SWCNTs)-polyvinyl alcohol (PVA) lament that shows a resistive response to RH changes. The PVA swells by exposing it to humidity and interrupting the connections between SWCNTs within the structure of the bre. The resistance of the thread has a quadratic response when exposed to increasing RH. The developed lament can detect the humidity changes between 60% to 100%. In 2008, Shim et al. dip-coated a cotton thread into SWCNTs suspension for detecting albumin, a protein in the blood. Interestingly, they found that the CNT-coated cotton thread is responsive to humidity changes [59].

Using MEMS fabrication techniques such as chemical vapour deposition (CVD) or vacuum physical vapour deposition (PVD) to deposit graphene and graphene oxide has been used to develop thin- lm sensors for applications such as electronic skin [60, 61]. Comprehensive studies addressing the principles, mechanisms and fabrication technologies for humidity sensors are available in Refs [61, 62]. The developed MEMS device then can be blended into textiles for monitoring humidity [63].

Fibre-based temperature sensors

One of the simplest designs is embedding a metallic wire within textile substrates for temperature monitoring. Li et al. sewed platinum metal wire with a diameter of 20 µm on a piece of cotton fabrics and measured the temperature of the substrates [64]. The wire shows a linear increase in resistance by increasing temperature (0.0039 $R=R_0\%\ C^{1}$). A linear response accompanied by stability and a wide temperature range are favourable for metallic wires. However, the rigidity and low sensitivity restrict the application of such wires in many wearable systems. Furthermore, it is not suitable for conductive substrates such as carbon cloth materials.

Coating and printing nanomaterials ink on textiles, bres, or threads is another promising approach for developing a textile-based temperature sensor. Rosace et al.

[65] coated MWCNT-polyacrylic nanocomposite on cotton fabrics and achieved a linear resistive sensitivity of 8 $R=R_0\%K^{-1}$, but the coated fabric shows a response to humidity changes, which limits the application of such coating. CNT-coated cotton thread via a dip-coating process showed a linear increase in resistance of the coated thread by increasing temperature [66]. Batch-to-batch steps were used to coat polypyrrole on commodity threads (i.e. cotton, nylon and polyester) with stable electrical conductivity under bending and strain cycles show a linear temperature response for the coated fabrics. PEDOT:PSS polymer dyed on cotton fabrics and achieve a linearly negative temperature coe cient from 50 C to 80 C [67]. Although many of the mentioned papers show promising results to detect temperature, poor selectivity in coating and printing process is a formidable challenge to overcome.

Similar to RH development, MEMS fabrication techniques are utilized to deposit temperature-sensitive materials on a exible substrate such as PDMS [60] and exible Kapton [68]. Fixing MEMS devices within textiles by weaving them on the substrate is an approach to measure the temperature of the textile.

## 1.3 Objectives

The main objectives of this thesis are:

(1) To investigate the e ect of hydrophobic coating on water transport and conductivity of the GDLs, Chapter 3.

(2) To develop integrated textiles for water transport and embed RH and temperature diagnostics tool within the textile electrode of PEMFCs, Chapter 4.

(3) To develop thread-based temperature and RH sensors for wearable applications and investigate biocompatibility of these devices, Chapter 5.

## 1.4 Structure of Thesis

This thesis consists of six chapters. Chapter 1 provides the background and motivations with a detailed introductory literature review. A summary of the key results is presented in Chapter 2. Chapters 3 to 5 present in manuscript format the main contributions of this thesis with relevant background, experiments, and results.

Chapter 3 presents the experimental procedure for evaluating water transport, thermal conductivity and electrical conductivity of carbon cloth GDLs. The e ect of

hydrophobic coating (FEP) and compression are evaluated.

Chapter 4 demonstrates the integration of the external threads to facilitate water transport and also monitoring RH and temperature via bre-like sensors within carbon cloth GDLs. Physical, microstructural and transport properties of the modied GDL were evaluated. The process of fabricating sensors was also explained, and sensor response for PEMFCs working conditions was investigated.

Chapter 5 presents the development of hybrid temperature and humidity sensors for application in wearable biomonitoring. The study investigates the coating process with the variable concentration of CNTs and surfactants. Further, it characterizes the CNT-coated thread response to temperature and relative humidity. Finally, the biocompatibility of the sensors was evaluated.

Chapter 6 summarizes the key ndings, contributions and suggestions for future work based on the outcomes of three research studies presented in Chapter 3 to 5.

Figure 1.4: Summary of di erent water management strategies. I. Physical Modi cation; (a) GDL with laser perforated pores, (b) schematic of locations of perforation holes along the ow channel, (c) comparison of fuel cell polarization curve for pristine and perforated GDL [1]. (d) HAZ with perforated pores on the GDL and (e) MPL [2]. (f) Polarization curve under over-humidi ed conditions showing a pristine sample outperforms a modi ed sample. [2] II. Addition of External Component; (g) addition of a conductive wicking layer [3], (h) schematic of additional EO pump, (i) MEA with EO pump and (j) fuel cell polarization curve for MEA with and without EO pump [4]. III. Chemical Modi cations (l) schematic presentation of water transport in conventional GDL and GDL with hydrophobic and hydrophilic pathways, (a) GDL with hydrophilic/hydrophobic channels, (m) EDS analysis is showing existing hydrophilic polymer (pNVF) on carbon paper GDL and (n) fuel cell polarization curve for MEA with and without a patterned in GDL [5].

# Chapter 2

# Summary of Key Findings

This chapter summarizes the key results of the three studies undertaken in this dissertation and discussed in detail in Chapters 3 to 5. The rst study analyzes the trade-o between hydrophobic coating on water transport and conductivity for carbon cloth GDLs. In the follow up work, we explored the addition of external threads into cloth GDLs by integrating textile sensing for water and thermal management in PEMFCs. The last study focuses on the development of thread-based temperature and humidity sensors with emphasis on application in wearable biomonitoring.

## 2.1 Woven gas di usion layer for polymer electrolyte membrane fuel cells: liquid water transport and conductivity trade-o s

Hydrophobic coatings are widely used in the industry to improve water transport in GDLs. The coating alters water transport, thermal conductivity and electrical conductivity of the porous GDL. Previously, the e ect of hydrophobic coating on transport properties for non-woven GDLs was studied thoroughly. This study aims to investigate the impact of such coatings on a woven GDL since the structure provides a suitable substrate for adding functional bres for sensing but is signi cantly di erent from the non-woven counterpart.

A test setup was designed to monitor water transport and water pressure in porous structure using upright uorescent microscopy to track dyed water transport within the porous GDL. Three di erent hydrophobic coated GDLs (0%, 30 wt% and 55

wt% FEP) were evaluated. The results show that the hydrophobic coating led to better usage of pores within GDLs and water transported in the in-plane directions compared to non-coated GDLs. The through-plane conductivity analysis shows that the electrical conductivity reduces by increasing hydrophobic coating; however, the thermal conductivity has an optimum amount of conductivity with FEP loading.

The key contributions and ndings of this study are: (1) a procedure is developed to monitor water transport and capture water pressure in the highly porous structure. (2) FEP loading improves the water transport in woven GDLs and utilizes pores in the in-plane directions more e ectively compared to non-coated samples. (3) The electrical conductivity reduces by increasing the hydrophobic coating; however, thermal conductivity increases rst (up to 30% FEP loading) and then decreases. (4) There is a trade-o between better water transport and conductivity of GDLs while using the hydrophobic coating.

This section of the thesis is presented in detail in Chapter 3.

## 2.2 Integrated textile-based sensors for water and thermal management in polymer electrolyte membrane fuel cells

PEMFCs experiences non-uniform water and heat transfer with a gradient of temperature and humidity within the cell. Smart components that can adapt to a variety of dynamic changes are vital criteria to improve the performance and durability of the cells. Generating water transport pathways and combining real-time measurement of temperature and RH distributions witihn a textile GDL allows improvement in performance and paves the routes toward adaptive materials within PEMFCs. This study aims to (1) generate hydrophilic pathways within woven GDLs and investigate the e ect of that external hydrophilic threads on transport properties, and (2) develop embedded threaded sensors for monitoring temperature and RH locally in woven GDLs. Hydrophobic threads were sewn on woven GDLs for facilitating water removal. We analyzed the e ect of threads on the physical and microstructural properties of GDLs. Our results show that threads embedded well in microstructure of woven GDLs with minimal impact on transport properties. The in-situ fuel cell testing indicates that the GDL with hydrophilic threads has no adverse e ect on the performance.

Temperature and RH sensing threads were developed by dip-coating them with CNT ink and sewing them on a woven GDL. The CNT-coated thread shows RH and temperature sensitivity in the working range of PEMFCs. To be able to use these sensors in the fuel cell environment, PDMS was coated on top of the CNT-coated thread to generate an electrical insulating layer and also achieve water vapour transmission for detecting RH. PDMS+CNT-coated thread is responsive to RH changes. FEP coating provides an electrical and vapour insulating layer and also mitigates the RH sensitivity. FEP+CNT-coated thread is solely responsive to temperature. The RH and temperature sensitivity of both threads PDMS+CNT-coated and FEP+CNT-coated threads) were characterized, and an ex-situ experiment shows the workability of such sensors in woven GDLs.

The key contributions and ndings of this study are: (1) external hydrophilic threads embedded in woven GDL generated water pathways. (2) Physical, microstructural and transport properties of GDLs with external threads were analyzed and showed minimal impact on GDLs properties. (3) Temperature and RH sensing threads suitable for PEMFCs working conditions were developed and tested in an ex-situ experiment.

Chapter 4 explains in detail this section of the thesis.

## 2.3 A hybrid thread-based temperature and humidity sensor for continuous health monitoring

In the previous study, thread-based temperature and RH sensors were developed for the working conditions of PEMFCs. The application of these sensors is not limited to diagnostic tools in woven electrodes. These thread-based sensors have prospective use in a wearable biomonitoring system, which works in a lower temperature range (e.g. room temperature). The main objective of the third study is to investigate the use of these sensors in biomedical applications, particularly wound monitoring.

The CNT ink for dip-coating cotton threads is compromised of functionalized multiwalled carbon nanotubes (fMWCNTs) and sodium dodecyl sulfate (SDS) in distilled water. The e ect of concentration of each component and the number of dipping on the thread resistance are investigated. Furthermore, the CNT attachment on the cotton laments is evaluated with SEM imaging. The response to RH and temper-

ature of the CNT-coated thread are further analyzed and shows the responsiveness to both RH and temperature. FEP coating reduces the RH response and shows only temperature sensitivity for CNT+FEP-coated thread. For the proof of concept, the thread-based temperature sensor is combined with a heating thread to control the local temperature within a textile.

Finally, the cytotoxicity response and compatibility of the CNT-coated (i.e. RH sensor) and FEP+CNT-coated (i.e. temperature sensor) threads are evaluated for potential use in smart wound dressing. The analysis shows that the thread-based sensors do not develop a cytotoxic response to cell growth. Furthermore, placing the sensors on healthy mice wounds did not a ect the wound healing process in mice.

The key contributions and ndings of this study are: (1) dip-coating parameters (i.e. concentration of CNTs, surfactant and number of dipping) are optimized for developing CNT-coated thread. (2) The response of the CNT-coated thread to temperature and humidity is investigated and shows a linear decrease in response to temperature change and quadratic resistance increase to RH changes. (3) FEP coating successfully mitigates the RH sensitivity of the CNT-coated thread and results in solely a thread-based temperature sensor. Combining both CNT-coated and FEP+CNT-coated threads can monitor both temperature and RH in textile substrates. (4) Finally, the cell cytotoxicity and animal results show thread-based sensors are biocompatible for wearable biomonitoring.

Chapter 5 explains in detail this section of the thesis.

# Chapter 3

# Woven gas di usion layer for polymer electrolyte membrane fuel cells: liquid water transport and conductivity trade-o s

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## 3.1 Abstract

Gas di usion layers (GDLs) provide pathways for water removal in a PEM Fuel Cell. Woven GDLs, have shown higher capability to contain water and improve performance under humid conditions compared to non-woven GDLs. In this work, we investigate water transport, distribution and location of breakthrough in woven GDLs using uorescent microscopy. GDLs with no coating, 30, and 55 wt% uorinate ethylene propylene (FEP) were investigated. FEP increases hydrophobicity and a ects thermal and electrical conductivities. The results show that the FEP-treated GDLs have higher breakthrough pressures and water contact angles than non-treated GDLs. For untreated samples, water breakthrough occurs in non-compressed regions; whereas, for FEP-treated samples emergence occurs in the compressed regions. Furthermore, water was observed to rst cover visible pores inside the GDLs prior to breakthrough. Increasing FEP loading promotes the propagation of water inside the GDLs. Thermal conductivity is found to improve with FEP coating and attains a maximum at 30 wt%

FEP loading, whereas electrical conductivity decreases with increasing FEP loading. This analysis shows more pores are engaged in water transport with higher FEP loading. Implementation of woven GDLs in fuel cell design requires a balancing of the water and heat transport bene ts with the reduced electrical conductivity.

Keywords : Woven Gas Di usion Layers, Water Breakthrough, Fluorescent Microscopy, Thermal conductivity, Electrical Conductivity

## 3.2 Introduction

The gas di usion layer (GDL) plays a central role in performance of polymer electrolyte membrane fuel cells (PEMFCs) [9]. The GDL facilitates transport of reactants from the ow channels to the catalyst layer and contributes to the transport of electrons and heat from the membrane electrode assembly (MEA), where the electrochemical reactions occur. Additionally, the GDL helps control the level of moisture in a fuel cell. Proper water management ensures that by-product water is removed from the catalyst layer to prevent ooding while maintaining the catalyst layer and MEA hydrated at the same time [15].

The GDL is a porous structure that is fabricated either by weaving carbon bers into a carbon cloth or randomly distributing carbon bers to form a non-woven carbon paper. Carbon bers are mostly made of polyacrylonitrile (PAN) using a solvent spinning process [9]. Spun PAN yarns, used to make carbon cloth, are produced through the Worsted process, where yarns are generated and wrapped around a bobbin for weaving. The woven carbon ber is then carbonized at a minimum temperature of 1600 °C (often under vacuum) [9]. This manufacturing process leads to a more exible GDL structure. Non-woven GDLs are manufactured using the papermaking technology followed by sintering [9]. This process leads to a di erent microstructure for the non-woven GDLs than their woven counterparts. The pore sizes in woven GDLs vary in a wide range from 2µm to 100 µm, whereas pore sizes in non-woven GDLs range from 10µm to 30 µm. The wide range of pore size distribution in the woven GDLs is due to the multiscale microstructure of the constituent yarns that are formed from packed ne brils with large pores located between the yarns [69, 70]. Moreover, woven GDLs have lower porosity and less tortuous structure compared to non-woven GDLs [69]. In addition, the in-plane porosity distribution in woven GDLs has a sinusoidal shape, which varies between 80 to 90%, whereas non-woven GDLs porosity distribution is more random. GDLs are commonly treated with hydrophobic

polymers such as polytetra uoroethylene (PTFE) or uorinated ethylene propylene (FEP) [5] to improve the hydrophobicity of the GDLs using dipping, spraying, or brushing methods. Another process that improves the performance of the GDL is applying a thin microporous layer (MPL), to the side which is in contact with the catalyst layer (CL), to facilitate the wicking of liquid water from the CL to the GDL. MPLs have a pore size distribution much smaller than GDLs, from 100 to 500 nm [9].

Experimental studies to characterize GDLs have been conducted (1) to understand transport properties, such as permeability, di usivity, breakthrough pressure, electrical conductivity and thermal conductivity; and (2) to analyze the microstructure, including bulk porosity, pore size distribution, and porosity distribution. One of the key properties of GDLs is water breakthrough. Breakthrough analysis [71, 72, 73, 16] provides information about the required pressure to overcome the capillary force and also the location of the water breakthrough in GDLs. Benziger et al. [71] investigated water breakthrough pressure for woven and non-woven GDLs without an MPL and showed that woven GDLs have a lower breakthrough pressure (2 kPa) compared to non-woven GDLs (Toray samples 7 kPa). The lower breakthrough pressure of woven samples is due to larger pores located between yarns of the woven GDLs. Furthermore, increasing the PTFE loading of the GDL slightly increases the breakthrough pressure. Lu et al. [73] investigated non-woven GDLs with and without MPL (SGL 25BA and SGL 25BC). SGL samples are more porous compared to Toray samples and have larger pores and porosity values [74]. A breakthrough pressure of 1.7 kPa was reported for GDLs without MPL and 6.7 kPa for GDLs with MPL [73]. This is due to the smaller pores of the MPL, which are expected to increase the breakthrough pressure.

Visualization of water breakthrough in GDLs has been studied with di erent imaging techniques. Two main techniques are X-ray microtomography and uorescent microscopy. Fluckiger et al. [16] performed X-ray tomography imaging of water breakthrough on non-woven GDLs to observe their water content. The scan time was as low as 5 min with sample size of 2.5 mm in diameter. This study showed the saturation curve in di erent water intrusion pressure. In 2015, Weber et al. [21] designed a new test setup to replicate the land and channel in the ow eld in order to observe the water saturation in GDLs. The scan time was about 8 min with a sample size of 3.2 mm in diameter. Although X-ray microtomography shows high resolution and strong ability to characterize GDLs and interfaces in MEAs (e.g., between GDL and

MPL [74], and between MPL and CL [14]), the small sample size and low temporal resolution were challenges for the breakthrough analysis. However, the recent studies try to improve the 3D µCT in sub second, Eller et al. showed the scan time can reduce to 3.2 s with 1% false water detection [20]. However, uorescent microscopy with high temporal and spatial resolution allows better tracking of the emergence of water. The challenges with optical uorescent microscopy are the depth of eld, which does not allow to observe the whole structure of GDLs, and sample holders should be modi ed to provide access of light to the GDLs structure. Litster et al. [14] visualized water transport through the thickness of non-woven GDLs and found the location of the breakthrough on the surface. Bazylak et al. [15] investigated the e ect of compression on the location of the breakthrough in non-woven GDLs and showed that compression damages the PTFE and ber structure and creates preferential pathways for water removal in the compressed areas.

Previous studies mainly characterized non-woven GDLs. However, a comprehensive study to understand water transport in woven GDLs is warranted since these GDLs have a higher capacity to keep water compared to non-woven GDLs (cf. [75]). The present study aims to investigate water transport in woven GDLs at the microstructure level. For this purpose, carbon cloth GDLs with three di erent FEP loadings (0, 30 wt% and 55 wt%) were used to visualize water transport. The study reveals why woven GDLs have a higher capacity to keep water inside compared to non-woven GDLs, and documents the associated changes in thermal and electrical conductivity.

## 3.3 Experimental

### 3.3.1 Preface

The experimental part of this chapter was performed as follow: I was responsible for performing the water transport experiments, data analysis and writing the article. Dr. Mohammad Ahadi performed electrical conductivity and thermal conductivity testing at Ballard Power Systems.

### 3.3.2 GDL

In this study, a woven GDL, Avcarb 1071 HCB (from Fuelcell Earth), was used. This woven GDL has a thickness of 350 μm and porosity of 65%. FEP solution (Te on FEPD 121 Fluoroploymer Dispersion) was used to treat the AvCarb GDLs with 30 and 55 wt% FEP loadings. GDLs were dipped into the solution for 1 min and then placed on needle-point holders. The holders were kept in the vacuum oven at room temperature for an hour; the temperature was then increased to 100 C for one additional hour. This process allowed evaporation of water and other solvents from the GDLs. To evaporate the surfactant, the GDLs were kept in a mu e oven for 50 min while the oven temperature was ramping up to reach 260 C, and then for an additional 10 min at a constant 260 C. To sinter the polymer, the temperature was ramped up to 280 C over 20 min and kept at 280 C for 20 min (also see [5]).

### 3.3.3 Visualization and Breakthrough Pressure

The apparatus to measure the breakthrough pressure and perform uorescence microscopy to visualize water transport is described below. A dilute water solution of 1 millimolar rhodamine B (excitation: emission 540 nm: 625 nm) was prepared to trace water transport in the plane of the GDLs. Since this solution was dilute, dying the water had negligible e ect on the properties of water (compared to pure water).

#### Apparatus

Samples were placed in an assembly and water was injected with a syringe pump at a rate of 0.02ml:min $^{1}$. The clamping device has a top plate made from Plexiglas to visualize water, and it has a small hole (with diameter of 5 mm) for water removal. The O-ring diameter is 9 mm and the area between O-ring and open hole is under pressure. The test performed in isothermal at room temperature. An upright uorescent microscope (DP 73 Olympus BX51), with CY3 lter and 2X objective having a numerical aperture of 0.06, was used in this experiment. A schematic of the clamping device and microscope is shown in Figure 3.1. Images were all taken in black and white. The sample was illuminated with ber optic, Figure 3.1(a). The acquisition software was Olympus CellSense. Water pressure was measured with a di erential pressure transducer (Honeywell FP2000) connected to a DAQ system. The apparatus to measure the breakthrough pressure and perform uorescence microscopy to

visualize water transport is described below. A dilute water solution of 1 millimolar rhodamine B (excitation: emission 540 nm: 625 nm) was prepared to trace water transport in the plane of the GDLs. Since this solution was dilute, dying the water had negligible e ect on the properties of water (compared to pure water).

Image and Data Acquisition

A cooled CCD (charge-coupled device) camera was used to capture the transient transport of water. The nominal depth of the eld, calculated from $d_{field} = \ = NA^2$, was found to be 150 µm, allowing signals to reveal inside the porous structure. The depth of eld of view for the sample was 100 µm that could cover 7 8 bres as well as the space where the water owed. Intensity of the 8-bit images could be correlated to the height of the water on the surface, using the following formula [14]:

$$= \frac{100\,m}{255\,I} \tag{3.1}$$

where is the observable height and I is the intensity of the image. The eld of view was 6.5 mm 5 mm with a spatial resolution of 4.6 µm. This eld of view was large enough to cover many pores ( 2 to 100 µm [70]) on the surface. Scanning electron microscopy (SEM; Hitachi S-3500N) and energy dispersive X-ray spectroscopy (EDS; Hitachi S-3500N) were employed to observe microstructure of GDLs with di erent FEP loadings, and also to deduce distribution of FEP in the GDLs.

### 3.3.4 Thickness Measurement

The thickness of the GDL samples were measured at di erent pressures using a custom-made testbed (Thickness Under Compression-Resistivity Under Compression, or TUC_RUC) and protocol described in detail in [76].

### 3.3.5 Thermal Conductivity Measurement

Thermal conductivities were measured using a guarded heat ux (GHF) testbed, which was custom-made based on ASTM Standard E1530-11 and described in detail in [76, 25, 77]. The procedure for measuring bulk thermal conductivity relies on the measurement of thermal resistances of at least two material samples with di erent thicknesses and then deconvoluting the bulk and contact thermal resistances by

Figure 3.1: (a) Black and white image of woven GDL (scale bar is 2 mm) (b) Schematic of the uorescent microscopy of GDL.

subtracting the two resistances as follows:

$$k_b = \frac{t_2 \quad t_1}{(R_2 \quad R_1)A} \tag{3.2}$$

where $R_1$ and $R_2$ are the resistances measured inside the testbed; $k_b$ is the bulk conductivity of the sample, and $t_1$ and $t_2$ are the thicknesses of the measured sample. In this study, since only one thickness of GDL was available, di erent thicknesses were simply made by stacking the material. It should be noted that the total thermal resistance measured by the GHF testbed consists of the bulk resistance and two thermal contact resistances (TCRs) between a sample and the apparatus (the GHF uxmeters). However, in a stack of several samples, there is an additional TCR between the samples in contact with each other. Therefore, when subtracting resistances of two stacks of samples ($R_2 \quad R_1$) in Equation 3.2, the two TCRs between the stacks and

the apparatus ( uxmeters) cancel out, and only the di erence in bulk resistances of the samples in the stacks and the TCRs between the samples remain. However, as also shown in refs. [78, 79, 80, 81], TCRs between GDLs in a stack of GDL samples are negligible compared to the bulk resistances of the samples. Therefore, the result of subtraction of resistances in Equation 3.2 (i.e. $R_1$ $R_1$) provides an accurate measure of the di erence in bulk resistances of the samples in the stacks. This stacking method has been widely used in the literature for measuring di erent layers of fuel cells, including porous transport layers [78, 79, 80, 81] and catalyst layers [82].

### 3.3.6 Electrical Conductivity

Measurements of electrical conductivity were performed using a Micro Junior 2 micro ohmmeter (Raytech, USA) comprising four custom-made gold-plated probes. A sample was clamped between the probes, and a clamping pressure of 1500 kPa was applied on the probes. Similarly, to the GIF thermal resistance measurements, the electrical conductivity could be deconvoluted from measurements of at least two sample thicknesses using Equation 3.2. Again, di erent thicknesses were made simply by stacking.

## 3.4 Results and Discussion

The clamping device compressed the GDL under an O-ring at a pressure of 1.6 MPa (the pressure lm, which is provided by sensor products Inc., was used for the test. The lm is sensitive between 400 kPa and 2400 kPa. The photo of the pressure lm is available in supplementary information (FigureA.1). This compression is in a same range of compression that GDLs experience in actual fuel cell operation [15]. In-plane and through-plane SEM images of three di erent woven GDL samples, namely AvCarb 1071 HCB with 0, 30 and 55 wt% FEP loadings, are shown in Figure 3.2. The images show that more FEP material is located on the surface than through the bulk structure of the GDLs. Increasing FEP loading changes the physical properties of the woven GDLs from exible to more rigid. This may be due to lling the pores between bers and yarns by FEP, which increases sti ness. The distribution of this polymer within the sample is important since an even distribution of FEP enhances the whole structure's hydrophobicity. The polymeric coating for the samples was investigated using EDS to map uorine material on the surface and along the in-plane direction

of the GDLs, and the resulting in-plane and through-plane distributions of uorine and carbon are shown in Figures 3.3 (a) and (b), and the enhanced FEP content with higher loading is clearly illustrated, with a relatively even distribution through the two planes; we note that AvCarb without FEP shows trace amount of uorine.

Figure 3.2: SEM images of the in-plane and through-plane of GDLs for di erent FEP loading (0, 30 wt% and 55 wt% FEP).

EDS analysis can also be used to quantify the material content. Table 3.1 shows weight percentage of each element in Figure 3.3 (a) (in-plane) and (b) (through-plane). There are errors associated for the weight percentage of uorine and carbon on the surfaces and the cross sections (the detailed report of the quanti cation analysis are available in the supplementary information FigureA.2). Fluorine accumulates more on the surface, as indicated by the higher percentage of uorine in the in-plane direction than the through-plane direction. Similar results were reported for non-woven GDLs [11]. The higher content of hydrophobic polymer (PTFE or FEP) on

Figure 3.3: EDS analysis mapping (a) in-plane distribution (b) through-plane of carbon (red) and uorine (green) for di erent FEP loading sample (0, 30 and 55 wt%).

the surface results in lower porosity near the surface for the treated GDLs. The measured breakthrough pressures for the samples are shown in Figure 3.4(a). Increasing FEP/hydrophobicity of the GDL can reduce the pore sizes and increase the contact angle, see Figure 3.4(b); these factors in turn result in higher breakthrough pressure with higher FEP loading.

Visualizations at the starting time of the breakthrough and following breakthrough are monitored using uorescent microscopy. Figure 3.5 (a) shows the saturation curve over time, which is obtained by monitoring water emergence from the top plate of clamping device. The transient saturation curve shows the low amount of saturation before the breakthrough. However, after the breakthrough, the saturation increased signi cantly. For both cases, higher percentage of saturation was observed for modi ed GDLs compared to the pristine sample. Figure 3.5 (b) shows four instances

Figure 3.4: (a) Breakthrough pressure and (b) water droplet contact angles of GDLs with di erent FEP loading (number of sample = 3).

of water transport in the woven GDLs. Water  rst  lled the pores under the open window for all samples as the open window is located on the top of the injection hole. For the 0% FEP sample, breakthrough occurred in the circular open window, and water covered the surface. However, samples with 30 and 55 wt% FEP followed a di erent scenario. Water  rst  lled the pores in the circular window and then propagated to other pores in the in-plane direction of the GDLs;  nally, breakthrough occurred in the compressed areas, with water covering the surface. The supplementary video of water transport for three di erent GDLs (without coating, 30 wt% FEP and 55 wt% FEP) can be found in the supplementary information (Figure A.3). To provide reproducibility of this test, the same test was performed on more samples and similar results were obtained, which are available in supplementary information. There are some possible explanations for the di erences in water distribution patterns. The water  ow experienced higher resistance in the through-plane direction.

Table 3.1: Carbon and uorine percentage for 0, 30 and 55 wt% FEP loading GDLs.

| Materials | In-plane [wt%] | | Through-plane[wt%] | |
|---|---|---|---|---|
| | Carbon | Fluorine | Carbon | Fluorine |
| AvCarb 1071-Without Coating | 99.7 | 0.3 | 99.8 | 0.2 |
| AvCarb 1071-30 wt% FEP | 62.2 | 37.8 | 65.5 | 34.5 |
| AvCarb 1071-55 wt% FEP | 29.4 | 70.6 | 41.9 | 58.1 |

As a result, the lower resistance pathways are preferential. The hydrophobicity of the GDLs increases and it a ects the breakthrough pressure and contact angles of the modi ed GDLs (Figure 3.4). More hydrophobic pathways cause more propagation of water towards lower resistance regions. This experiment shows that water moves in the in-plane direction, which might have better pore connectivity and lower tortuosity compared to the through-plane direction. Another hindering fact of water transport in the through-plane direction is the accumulation of more FEP on the surface of GDLs, which causes having the smaller pores near the surface and more pressure requires to overcome this barrier. These aforementioned reasons cause increasing the resistance in the through-plane direction, and consequently, water moves inside the GDL and lls the pores rst and then, breaks through in the region under compression.

The intensity of the grayscale image can be correlated to the water height [14]. In Figure 3.6(a), the circular shape is subtracted from the breakthrough image, and the corresponding water height distribution is illustrated in the 3D map. Emergence of water for the 0% FEP sample occurs in the circular windows. However, for the FEP-loaded samples, water covers pores rst in the areas under compression, and then emerges from the compressed regions. This is attributed to distortion of the GDL microstructure under compression. Compression can open some pathways for water in FEP-loaded woven GDLs, as was also shown for non-woven GDLs [15]. Figure 3.7 illustrates through-plane water transport for untreated and treated GDLs. Water travels toward the open window and with no lateral movement in untreated samples; however, in the treated samples, water is forced to move laterally rst and then emerges on the surface.

The variation of GDL thickness with compression is shown in Figure 3.8 for samples with di erent FEP loadings; the error bars for these measurements are smaller than the data points and are not shown. The measurements show that the samples swell with increasing FEP treatment due to impregnation of bers and the lling of

Figure 3.5: (a) saturation over time (b) four instances of water saturation for GDLs without FEP, 30 wt% FEP and 55 wt% FEP (the scale bar is 2 mm).

gaps between bers. Settling down of FEP material on the surfaces of the samples could also contribute to the increased thickness.

Thermal conductivity results, shown in Figure 3.8(b), indicate that the 30% FEP loading GDL has the optimum thermal conductivity. This is a direct result of impregnation of the samples by the FEP material, which has a higher thermal conductivity than air ( 0.2 W m $^{1}$K $^{1}$ for FEP compared to the value of 0.02 W m $^{1}$K $^{1}$ for air). The optimal value is a result of the trade-o between the higher conductivity of FEP material with the increased thickness of the FEP-treated GDLs which lengthens the conduction path inside the samples. The through-plane thermal conductivity values measured in this study are in the same range as through-plane values reported in the literature for woven GDLs [79]( 0.28-0.32 W m $^{1}$K $^{1}$) and non-woven GDLs [83]( 0.15-2.1 W m $^{1}$K $^{1}$).FEP loading has a signi cant impact on electrical conductivity as shown in Figure 3.8(c). Whereas FEP provide better heat conduction pathways

Figure 3.6: (a) Fluorescent microscopy of the breakthrough location (scale bar is 2 mm) (b) 3D map of water height in GDL and breakthrough location on the surface.

than air, it is an insulator for electric current, and the combination of impregnation of bers, deposition of an insulating layer on the surface, and increased thickness result in a signi cant drop in electrical conductivity. Through-plane electrical conductivity data reported in literature are in the range of 250 - 2500Sm $^{1}$ for non-woven GDLs [84, 85, 86].

## 3.5 Conclusion

Water transport, thermal conductivity, and electrical conductivity of woven GDLs with di erent FEP loadings were investigated in isothermal conditions at room temperature. Fluorescent microscopy visualization of water transport showed that for woven GDLs without FEP loading, water rst lls bigger pores between yarns in

Figure 3.7: Water transport inside of (a) untreated and (b) treated woven GDLs.

the woven GDLs and then, breaks through a pore in the open area of the structure. FEP loaded-GDLs, however, have higher breakthrough pressures due to smaller pores and higher hydrophobicity. As such, water ows more in the in-plane direction of the GDLs. Furthermore, the occurrence of the breakthrough is in the area under compression. As in the case of non-woven GDLs [15], water breakthrough is due to distortion of the bers and FEP material under compression. Higher FEP loading results in the swelling of the GDL due to partial lling of pores, possibly impregnation of bers, as well as coverage of the sample surfaces with FEP material. Thermal conductivity measurements showed the existence of an optimum FEP loading (near 30%) as a result of a trade-o between the partial lling of the pores and increased the thickness of the sample by FEP. On the other hand, electrical conductivity decreased monotonically and signi cantly with FEP loading. In implementing woven GDLs in fuel cells, FEP treatment needs to be carefully determined in terms of trade-o s

Figure 3.8: (a) Thicknesses of GDL samples versus pressure, (b) Thermal conductivity and (c) Electrical Conductivity versus FEP loading (number of sample = 3).

between improved water transport, heat, and electrical conduction, possibly using multi-objective optimization [87, 88].

# Chapter 4

# Electrode-integrated textile-based sensors for temperature and relative humidity monitoring in electrochemical cells

## 4.1 Abstract

Advances in textile technologies for transporting biomarkers and smart sensing are exploited in textile electrodes for electrochemical devices to achieve control of water transport as well as relative humidity and temperature sensing. The concepts are implemented and demonstrated within a textile gas di usion layer (GDL) of the electrode of polymer electrolyte membrane fuel cells (PEMFCs). Ex-situ and in-situ characterization show that threads can be introduced in the GDL structure to inscribe water highways within the GDL with minimal impact on GDL microstructure and transport properties. Furthermore, a low-cost procedure was developed to transform commodity threads into temperature and humidity sensors by coating the threads with carbon nanotubes (CNTs) ink. Fluorinated ethylene propylene (FEP) is coated on top of the CNT coated thread to decouple the response to temperature and humidity; the resulting threads achieve a linear change of resistance with temperature (-0.31 %/ C), while relative humidity (RH) is monitored with a second thread coated with polydimethylsiloxane (PDMS). The combination of both threads allows minimally invasive and dynamically responsive monitoring of local temperature and RH

within the electrode of PEMFCs.

## 4.2 Introduction

Electrochemical energy conversion and storage technologies are central to the decarbonization of the transportation and power sectors. They provide the reliability and exibility required to bring low-cost intermittent renewable energy sources into major energy consumer sectors [89]. Porous electrodes are pivotal components in many electrochemical devices, such as polymer electrolyte membrane fuel cells (PEMFCs) [5] and redox- ow batteries [90, 91]. Electrodes typically consist of a multi-layered porous structure, and their performance is signi cantly in uenced by the structure and wetting properties of the pores2. Porous electrodes of PEMFCs require a water management strategy to ensure adequate durability and performance [5]. A particularly challenging aspects of water management is dealing with the inhomogeneous reaction and water production rates in the catalyst layer (CL) [92, 52] and the non-uniform temperature and humidity distribution.

Water management requires balancing both membrane humidi cation to ensure good ionic conductivity and removal of excess water, which can block the pores and hamper reactant gases transport to the CL, i.e. the \ ooding" phenomenon [6, 7, 14]. Poor water management leads to increase stack size, higher cost and reduced power density [17]. Gas di usion layer (GDL) is a porous structure responsible for the transport of air and hydrogen (reactants), water (by-product), heat and electrical current [14, 9]. Water transport is mainly controlled by capillary pressure, which is a function of pore size and hydrophobicity of the GDL. In high current density, the excess amount of water reduces PEMFCs performance signi cantly due to ooding. Different avenues for GDL water management have been pursued. (1) Using perforated metallic GDLs with di erent pore sizes and distributions shows better performance at high current density. However, the durability of these GDLs is signi cantly reduced by corrosion [93, 94]. (2) Generating through-plane holes (80 µm) in the cathode side of the GDL under the ow channels has been shown to reduce the capillary pressure and remove the excessive water [1, 33, 34, 32]. This approach improved the performance of the fuel cell by reducing the cathode overpotential, particularly, in a low humidity environment. However, a drop in performance was observed at high humidity and current densities [32]. (3) Adding a wicking layer to the back of the GDL to remove excess water by hydraulically linking the entire cathode surface was

practiced [3]. Although this approach alleviates the ooding issue in fuel cells, the performance gain is minimal. (4) Fabian et al. [4, 95] invented an active water management strategy by introducing a micro pump to enhance water removal. Promising results were presented for air-breathing fuel cells, but the application of such pump in large scale stacks has not been studied. Furthermore, this approach would increase cost. (5) Tuning wettability of the GDLs and microporous layers (MPLs) [96] (i.e. a thin layer added to the GDL to achieve more uniform reactant distributions) is a promising avenue that has been studied recently. Forner-Cuenca et al. [5] engineered the hydrophobicity of the GDL by radiation grafting of hydrophilic polymers and generating water channels in o the shelve GDLs. The results indicated better water management and better performance of the cells in low humidity (cathode side) environment. In three consecutive studies, the grafting strategy [38], ex-situ analysis [18] and in-situ fuel cell testing via neutron imaging were studied [39]. However, the large-scale utilization of this improvement requires signi cant changes in manufacturing facilities. The path forward in the enhancement of GDL performance is to devise responsive systems that retain water as needed in speci c locations or at certain operating points, while removing water that accumulates in the porous structure at other locations/conditions; monitoring of local parameters (e.g. temperature and relative humidity) is critical to implementing this approach. This paper describes a new approach that simultaneously allows monitoring and improves water management.

Reducing non-uniformity of temperature and humidity [97] is crucial to maintaining ionic conductivity [98] and alleviating degradation of polymer electrolyte membranes [98]. Accurate knowledge of local temperature and humidity is essential for improving water management as well as for improving the accuracy of performance predictions. Conventional methods of temperature and humidity monitoring lack spatial resolution and typically measure temperature and humidity of reactants at the input and the by-product at the output of the cell [99]. Various methods to access the cell temperature locally have been proposed using thermocouples [41, 100, 101, 42], optical sensors [52, 50] and micro-electro-mechanical systems (MEMS) [47, 46, 102, 103, 104, 102, 45]. Zhang et al. [41] placed 11 thermocouples between the GDL and the CL to monitor temperature distributions. The ow eld was modi ed to place these thermocouples, thus covering valuable area of the CL and reducing the active area for the catalysis. This approach has also been employed by other researchers [100, 101, 42]. Use of optical sensors was demonstrated by David et al. [52, 53, 105] who developed an in- ber Bragg grating (FBG) sensor and imple-

mented it an operating fuel cell to simultaneously measure temperature and relative humidity (RH). In addition to good accuracy, this sensor provides dynamic response up to 1Hz. The size of the bers ( 30 µm) however restricted its deployment to a distance from the reaction zones in the CL. MEMS have paved the way for new sensing techniques. For example, Lee et al. [47] fabricated a MEMS device located between the membrane and the CL that captures local temperature and RH. This device requires MEMS fabrication on the membrane with partial covering, and monitoring of di erent locations requires fabrication of a di erent MEMS-membrane which is both costly and cumbersome.

While non-uniformity of parameters such as temperature and RH in the plane of the electrode is well established, studies also show that there are signi cant through-plane gradients between outer plate temperature and the reaction zone temperature [7]. While several methods have been successful in monitoring these non-uniformities in-situ [104, 106] they have not been adopted for monitoring in commercial stacks due to a combination of (1) requirement for signi cant design changes of the cell, (2) need of additional components, and (3) reduction in active area and negative impact on performance.

The development of appropriate sensing, thermal and water management solutions for electrochemical energy applications can take advantage of innovations in textile technologies that have for instance shown promising results in biomedical applications. One of the avenues relies on wicking property of threads to transport biomarkers through the threads [107, 66, 108]. Threads can be easily patterned on a textile substrate to design a network for transport of di erent stream of ows. Junker et al. [109] showed that a network of threads can be used in a low cost process for designing a micro uidic circuits. In addition to facilitating transport, threads have been used for sensing in biomedical applications by coating commodity threads with novel materials such as carbon nanotubes (CNTs). Such thread-based sensors have been used to monitor physical and chemical properties such as [110], pH [111], temperature [66] and humidity [58]. Akbari et al.[66] demonstrated a process in which a commodity thread was transformed into a temperature sensor by simple dip coating in a CNT ink; the sensor exhibited a simple linear relationship between temperature and thread resistance. Besides temperature, CNT coated substrates are also responsive to change of humidity as has been shown for a variety of substrates such as cellulose papers [112], composite lms [113] laments and fabrics [58]. Zhou et al. [58] developed high strength laments out of CNT and poly(vinyl alcohol) via a wetspinning process. The

lament resistance followed a quadratic response to change of RH between 60% to 100% over a range of temperatures [25°C to 75°C] that coincides with PEMFCs.

Based on the promising results of textile technology in bio-medical application, thread-based temperature and humidity sensors were for the first time developed and integrated within a carbon cloth GDL for continuous temperature and humidity monitoring. Taking advantage of the wicking properties of the thread, water pathways were engineered by patterning GDLs to facilitate transport of excess water. Microstructure analysis, scanning electron microscopy (SEM) and X-ray microtomography (μ-CT), were performed to characterize modified porous GDL. In-situ fuel cell testing was performed on modified samples and pristine samples to evaluate the effect of threads on the performance of the fuel cell over a range of conditions representative of actual fuel cell operation.

## 4.3 Results and Discussion

Integrating multifunctional threads within carbon cloth GDLs provides (1) preferential water \pathways" and (2) sensing capability within the fuel cell membrane-electrode assembly (MEA). Figure 4.1(a) shows the process for treating and sewing hydrophilic threads onto carbon cloth GDLs using a commercial sewing machine. The proposed low-cost process uses roll-to-roll system to coat commodity threads with CNT inks by dipping and drying (Figure 4.1(b)). Threads made of polyester, which has high wicking property compared to other commodity threads (see FigureB.1 ), provided preferred pathways for water to cross carbon cloth GDL (Figure 4.1(a)) with a minimal impact on GDL microstructure. To add sensing within GDLs, the conductive CNT coated threads were functionalized to be temperature and humidity sensors. This requires a layer to insulate the thread from the conductive substrate (carbon cloth GDLs), as well as a protective layer to mitigate the sensitivity to humidity. Polydimethylsiloxane (PDMS) is an insulator with the high water vapor transmissivity required for RH sensitivity. PDMS can be easily wrapped around the CNT coated thread via a dip coating process (Figure 4.1(c)). To achieve temperature sensitivity, fluorinated ethylene propylene (FEP) was used to coat the CNT-coated thread; this provides both insulation and mitigation of water vapor transmission allowing measurement of temperature independently. The thread-based sensors monitor temperature and humidity locally and communicate wirelessly with a personal computer (PC) or smartphone. A schematic of sewing thread-based sensors on a piece of car-

bon cloth GDL is shown in Figure 4.1(d). The detailed analysis of these integrated sensors-textile electrodes is presented in the following gure panels.

Figure 4.1: Schematic of process to modify carbon cloth GDL via sewing hydrophilic, temperature and humidity sensing threads. (a) Polyester threads were sewed on carbon cloth GDL generating hydrophilic pathways for water removal. (b) Roll-to-roll process of dip-coating cotton thread to confer humidity and temperature sensitivity. (c) FEP for temperature sensing and PDMS coating for humidity sensing. (d) Sewing of thread-based sensors for wireless monitoring of temperature and humidity.

We evaluated the e ect of addition of threads on physical properties of the GDL. A carbon cloth GDL has a plain weave of carbon yarns with a size of422 3 µm. The SEM image revealed the two-dimensional (2D) view of the microstructure of a plain GDL in Figure 4.2(a). A piece of polyester thread was treated with a corona discharge to enhance the wicking property of the thread (Figure B.2 showed the wicking test results and the SEM images of the thread in Figure B.3). The treated polyester thread with a diameter of 232± 3 µm was sewed on a piece of cloth GDL,

as depicted in Figure 4.2(b). The SEM image showed the thread was embedded in the pristine GDL with a minimal impact on microstructure. For non-woven GDLs, such as Toray 090, the microstructure was impacted as is shown in Figure B.4. Threads were sewed in a straight line on a GDL with two patterns, 1 mm and 4 mm distance apart with a pitch of 1 mm. An in-house tool, thickness under compression and resistance under compression TUCRUC), was utilized to measure the thickness and through-plane electrical conductivity in di erent compression pressures. This tool has been used and evaluated in previous studies [27, 114]. The thickness increased by 100 µm for the 1 mm distance threaded GDL and 60 µm for the 4 mm at 1500 kPa. It showed that the thickness of the modi ed GDL is in the range of commercial products (Gray area in Figure 4.2(b) 370 m for Toray 120 and 110 µm for Toray 030 are the thickness of these two commercial products). On the other hand, electrical resistance under compression yields similar results compared to the pristine sample, even though the threads are non-conductive (Figure 4.2(b)). Another property is the e ect of thread on the water breakthrough pressure, i.e. the required pressure for water to penetrate a porous structure. This test was performed on pristine and threaded samples. The breakthrough pressure decreased 30% for threaded GDLs (Figure 4.2(c)); however, the breakthrough pressure for non-woven GDL is zero due to signi cant structure alteration (Figure B.4). The reason for lower breakthrough pressure might be due to a change in hydrophobicity of the structure rather than the sewing process. Hydrophobicity and contact angle were characterized using sessile drop tests. A water droplet was placed on the GDL the contact angle remained constant over 6 minutes (115); however, for water droplets on the thread the angle changed (from 101 to zero) and the droplet wicked through the polyester thread in 6 minutes (Figure 4.2(d)). This suggests that the thread wicking property can be used to developed water pathways within GDLs.

In this panel, we investigated the e ectiveness of the thread in creating water transport pathways using uorescent microscopy. High temporal resolution was used to track dynamic water transport through the porous structure [27]. Figure 4.3(a) shows that water rst transported in the in-plane direction and lled pores of the GDL, and then, the breakthrough occurred; however, for the GDL with thread, water transported through the threaded regions with the remaining area open for eventual reactants transport (Figure 4.3(b)). The three-dimensional (3D) view of the water transport con rmed that the threaded area is the main pathway for water transport compared to the pristine sample. In addition, the breakthrough location remained

Figure 4.2: Investigating e ect of threads on physical properties of GDL. SEM image of carbon cloth GDL (a) pristine and (b) with hydrophilic thread (scale bar is 1 mm). (c)Thickness under compression and resistance under compression for pristine carbon cloth, with 1 mm and 4 mm distance with 1 mm pitch distance of the hydrophilic thread. (e) E ect of hydrophobic thread on water breakthrough pressure. (f) Contact angle of sessile water droplet on carbon cloth GDL and thread. Error bars represent standard deviation (SD) (n = 3).

xed for the modi ed GDL, whereas for the pristine GDL, water transport occurred in three di erent locations (shown with yellow arrow) in three consecutive breakthrough tests (Figure 4.3(c)). The e ect of thread hydrophobicity was also analyzed with the blue area corresponding to a hydrophilic thread (polyester) and the red area to a hydrophobic thread (carbon ber yarn); both threads were sewed similarly on the substrate. The water breakthrough test showed the hydrophilic region was wetted and the hydrophobic thread did not show any sign of water. This indicates that the wetting properties are more important than the sewing process in determining preferential water breakthrough location (Figure 4.3(d)). These results demonstrate that threads can be embedded in the structure of GDL to e ectively create water pathways.

The depth of eld of 2D SEM images limits observations to the inner layer of modi ed GDLs. Internal change in microstructural properties were analyzed using X-µCT. High resolution (voxel size of 3.16 µm) tomography resolves the pores and