TRANSPORT DESIGN THROUGH CARBON MATERIAL ENGINEERING

IN PEM FUEL CELLS

by

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B.A.Sc., The University of British Columbia, 2015

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Chemical and Biological Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

August 2019

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Transport Design through Carbon Material Engineering in PEM Fuel Cells

submitted by Rubenthra Govindarajan in partial fulfillment of the requirements for the degree of Master of Applied Science in Chemical and Biological Engineering

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Abstract

With the advancements in fuel cell technology, PEM fuel cells have seen tremendous improvements in terms of durability, enhanced catalytic performance and reliability. The introduction of the microporous layer (MPL) has been proven to be highly beneficial in for water management especially at high current densities. Over the years, MPLs fabricated with various carbon blacks were compared and key relationships were reported based mainly on porosity. However, it is also known that carbon blacks have different properties such as structure and particle size which results in porosity differences.

This work aims to develop a clearer understanding of the impact of surface porosity and pore size in the carbons on the overall MPL performance by attempting to delineate these properties from other properties intrinsic to different carbon blacks. To achieve this, commercial acetylene black (AB) was activated under the presence of CO₂ for different durations to increase porosity. In addition, colloid-imprinted carbons (CICs) with different pore sizes were synthesized to obtain carbons with tunable pore sizes.

Results revealed that AB activated for longer durations resulted in higher surface area and pore volume. Subsequently, fuel cell testing showed that the ABs with increasing porosity had the poorer mass transport polarization performance at 80 °C and 100%RH (hot and the humid conditions). This is attributed to the higher water vapor absorbance shown by higher porosity ABs. CIC synthesis with various colloidal silica (CS) sizes exhibited distinct pore patterns reflecting the diameter of the CS particles. By varying the CS to mesophase pitch (carbon precursor) ratio, CICs with variable pore volume and surface areas were obtained with an increasing ratio generally resulting in increased porosity. Non-heat treated CICs were more hydrophilic than the heat treated CICs due to the higher percentage of surface oxygen functional groups and showed increased water.
vapor sorption. CIC12 (pore diameter of ~15 nm) had the highest water sorption with 93% mass increase. Accordingly, fuel cell polarization performances illustrated that CIC12 had the poorest performance at hot and humid conditions due to enhanced water retention capability. This performance significantly improved when CIC12 was heat treated to increase its hydrophobicity.
Lay Summary

The overaccumulation of water, which is a by-product of PEM fuel cell operation impedes the robustness of the fuel cell operation. A layer called the microporous layer which consists of carbon powder and binder plays a pivotal role with helping product water removal and reactant gas access. This research work studied the effect of the surface features of the carbons on the performance of PEM fuel cells. Results revealed that carbons with more pores resulted in poorer performance due to the enhanced water retaining behavior of the carbons. In addition, smaller pores result in greater water retention compared to larger pores. By altering the chemical properties on the surface of the carbons through heating at high temperatures, the water retention behavior can be suppressed leading to increased performance. The work highlights the contributions of these surface features on the overall PEM fuel cell performance and provides guidance on material selection.
Preface

The materials presented in this thesis including the literature review, experimental work, data collection and analysis and thesis writing was done by Rubenthran Govindarajan under the supervision of Dr. David. P. Wilkinson at the Department of Chemical and Biological Engineering, at the University of British Columbia. Dr. Arman Bonakdarpour and Dr. Baizeng Fang also provided guidance in the experimental planning and data interpretation. Jeanne Payoyo assisted with a portion of experimental work presented in Chapter 3 and Chapter 4 during her co-op term under the supervision of the author.

Two manuscripts are being prepared for a portion of results from Chapter 3 and Chapter 4:


The work has also been presented at the following conferences/symposiums by the author:


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<thead>
<tr>
<th>Symbol</th>
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<td>$A_i$</td>
<td>Acetylene black sample where $i$ denotes the activation time in hr</td>
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<tr>
<td>$C_i$</td>
<td>Colloid-imprinted carbons where $i$ denotes the nominal silica particle diameter used for templating</td>
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<tr>
<td>$K$</td>
<td>Permeability</td>
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## List of Abbreviations

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<td>AB</td>
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Acknowledgements

I would like to extend my utmost gratitude to Dr. David P. Wilkinson for giving me this enriching opportunity to work on this master’s project. His invaluable guidance and trust has allowed me to grow further in the field of research from the time I was an undergraduate student researcher in his lab. I also owe special thanks to Dr. Arman Bonakdarpour, Dr. Baizeng Fang and Dr. Ivan Stostevski for their inputs throughout the project and being there to point me towards the right direction whenever I was having difficulties. Not to forget, the rest of the members of the Wilkinson group; Joe, Liu, Amin, Jason for their help in the lab and discussions. Many thanks to Jeanne Payoyo and Joshua Agarwal for spending their summer co-op terms in the lab to help me further my research.

Dr. Jeannete Leeuwner! Thank you for mentoring me in the lab and having purposeful discussions on issues in the lab and beyond. I have always looked up to your patience and perseverance. My experience in the UBC would have been dull if it was not for the presence of Saad Dara, Adrian Serrano and Sean McBeath, who certainly made it worthwhile with the mix of laughter and very little seriousness. Caroline, Youni and Adhithi, thank you for the conversations and company during this degree.

I would like to thank the various personnel who helped me in my research; Thomas, Jesus, Bryan and Trishank from the Merida group; Lev, Chris and Yitao from the MacLachlan group, Dr. Haiyan Wang from the Smith Group, Dr. Gethin Owen from the Centre for High-Throughput Phenogenomics - UBC Dentistry; Dr. Libin Tong from UBC Mining; Dr. Ken Hu from UBC AMPEL, Dr. Xin Zhang from SFU 4D Labs and countless others who have lent a helping hand along the way.
Mum, Pa and the rest of the family back at home, you have been my best fans who poured endless support and belief in me ever since I was a child. I hope this will be another milestone of achievement that will make you folks proud.

My dear Jon. Thank you for your kind patience while I was toiling away with my thesis. You have my undivided attention now.
Dedication

என் பாட்டி

(My grandma)
Chapter 1: Introduction

1.1 Brief history and background of fuel cell technology

A fuel cell is an energy conversion device which converts the energy stored in the fuel (chemical) to electrical energy. The principle behind the technology was first discovered by Christian Friedrich Schönbein in the middle of the 18th century and later demonstrated by Sir William Grove in a series of experiments in a setup termed the gas voltaic battery. The setup included four cells in series which provided current to perform the electrolysis of water.

Further developments were made by Mond and Langer in 1889 through breakthroughs such as the application of porous electrodes, the use of an electrolyte soaked matrix and achieving 0.73V which is nearly 50% of the total energy in hydrogen. Another great pioneer to the technology was Francis T. Bacon who in addition to several research findings, was able to demonstrate the application of an alkaline fuel cell stack. The stack produced 6 kW and was used to power a fork-lift, welding equipment and circular saw. His contribution led to the licensing of his patents by Pratt and Whitley Aircraft Division of United Technologies Corporation. The company then used Bacon’s design to develop fuel cell power plants for the command and service modules of NASA’s Apollo mission in the 1960s.

With the pioneering contributions of Willard T. Grubb through the invention of the solid ion-exchange membrane electrolyte at General Electric Co. in 1955, a new type of fuel cell termed polymer electrolyte membrane fuel cells (PEMFCs) was born. Subsequently, this technology was developed for the NASA’s Gemini program to serve as the main electrical power source. The adoption of fuel cell technology by NASA subsequently became the impetus for further research and development.
Solid ion fuel cells further saw dramatic developments through the utilization of a specialty polymer now known as Nafion® by Walter Grot in 1975. In addition to allowing proton transfer, it provided superior resistance towards chemical degradation by $\text{H}_2\text{O}_2$ which boosted its lifetime during operation. The introduction of Nafion® in the catalyst layer in the work by Raistrick in 1986 at the Los Alamos National Laboratory resulted in significant drop in catalyst loadings required for comparable performance marking another breakthrough in cost reduction and feasibility.

Ballard Power Systems, a name that is widely known in the fuel cell industry, commercialized the PEMFC in the late 1980s in addition to advancing the state of technology through the use of the Dow Chemical Membrane. Further advancements of the application of the technology were made by Daimler-Benz in their demonstration of the Ballard PEMFC stack to drive a car in 1993.

With the increasing demand for electricity, the PEMFC which produces electrical energy from hydrogen and oxygen has garnered much attention in recent years. The high-energy density of hydrogen, low temperature operating condition, power scalability and high theoretical efficiency of PEMFCs makes it an excellent alternative energy conversion device. Another appealing aspect of PEMFCs is the by-product, water which results in the elimination of harmful emissions which are often found with combustion engines. As a result, PEM fuel cells have been used in transportation, backup power and portable devices such as computers, navigations systems and battery chargers. The intriguing prospect of having a pollution free economy could be realized in a hydrogen economy where the hydrogen used to generate electricity is made via renewable means such as water electrolysis instead of fossil fuels.
1.2 The polymer electrolyte membrane fuel cell (PEMFC)

The PEMFC is a type of low temperature fuel cell which utilizes a proton exchange membrane as the electrolyte. Figure 1.1 illustrates the schematic of PEMFC.

![Figure 1.1 Cross-sectional schematic of the PEMFC (not to scale)](image-url)

The PEMFC consists of two electrodes which are separated by a proton electrolyte membrane (PEM). At the anode, hydrogen is supplied through the flow field (FF) plate which is usually fabricated from either graphite or stainless steel and then passes through the GDL. It is important to note that some GDLs include a thin layer of carbon particles referred to as the microporous layer (MPL) deposited on a substrate layer (SL). Note that other terminologies such as diffusion media and porous transport layer have been used in literature in place of SL. This
thesis will refer to carbon fiber papers as SL herein. The GDL is made from carbon fiber paper or carbon woven cloth which helps to evenly distribute the gas in the GDL to the adjacent layer. Current state of the art GDLs incorporate the MPL between the SL and catalyst layer (CL). The CL is composed of a layer containing catalyst particles (usually Pt) supported on carbon particles and ionomer (commonly Nafton™) which functions as a particle binder and proton conductor. The diffused hydrogen undergoes oxidation at the catalytic sites to produce protons and electrons in the hydrogen oxidation reaction (HOR) as shown by Equation 1.1.

$$H_2 \rightarrow 2H^+ + 2e^- \quad [E^\circ = 0.00 \text{ V}]$$

Equation 1.1

The electrons are conducted from the anode CL to FF and flows through the external circuit to the cathode performing electrical work. The hydrated protons (H$_3$O$^+$) are transported from the anode CL to the cathode CL through the electrically insulating PEM. The protonic conductivity of PEM is highly dependent on the water content and the membrane must be sufficiently hydrated to minimize ionic resistance$^{14}$. At the cathode, oxygen diffuses though the GDL to the cathode CL. The oxygen reduction reaction (ORR) takes place on the catalyst surface and produces water as shown by Equation 1.2.

$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O \quad [E^\circ = 1.23 \text{ V}]$$

Equation 1.2

Hence, the overall reaction in the fuel cell is

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad [E^\circ = 1.23 \text{ V}]$$

Equation 1.3

The product water is then removed either through the cathode GDL to FF or via backdiffusion across the membrane to the anode. Depending on the conditions in the cell, water can exist in either liquid, vapor or both phases. Hence, the GDL plays a crucial role in water
removal in the PEMFC. The assembly comprised of the anode GDL, anode CL, PEM, cathode CL and cathode GDL is called the membrane electrode assembly (MEA).

While the technology has shown great promise, the cathode performance greatly influences the performance of PEMFCs. The two major issues affecting cathode performance are slow oxygen reduction reaction (ORR) kinetics and product water removal. The kinetics of ORR at the cathode is slower by approximately six order magnitude when compared to the hydrogen oxidation reaction (HOR) kinetics at the anode. While rigorous research is focused on the improvement of platinum (Pt) based catalysts for enhanced reaction kinetics, effective water management in the PEMFC is equally crucial for optimal performance. The overaccumulation of water produced at the cathode by the ORR results in “flooding”. This decreases the performance of the fuel cell due to blocked reactant gas access to the catalytic sites. This phenomenon generally occurs at high current densities where the water production rate exceeds the rate at which it is removed. However, it can also occur at low gas flow rates and low temperature conditions (i.e., during start-up). Subsequently, this leads to a sharp voltage drop and possibly cell shut down.

1.2.1 Operational principles of PEMFC

For electrochemical systems, the maximum amount of electrical work, $W_{elec}$ possible is related to the gibbs free energy at constant pressure and temperature as shown by Equation 1.4

$$W_{elec} = -\Delta \hat{g}$$

Equation 1.4

Electrical work can also be written as

$$W_{elec} = nFE$$

Equation 1.5

where $n$ is the number of electrons transferred, $E$ is the potential and $F$ is the Faraday’s constant (96, 485 C/mol). Equation 1.4 and 1.5 can be combined and be written as
\[ E = -\frac{\Delta \theta}{nF} \]  
Equation 1.6

This represents the voltage of the electrochemical reaction. Under standard conditions the equation can be written as

\[ E^\circ = -\frac{\Delta \theta^\circ}{nF} \]  
Equation 1.7

The standard potential for a complete electrochemical system is the sum of all the standard potentials in the system

\[ E_{total}^\circ = \sum E_{half \ reactions}^\circ \]  
Equation 1.8

Since fuel cells operate under non-standard conditions, the impact of temperature, pressure and concentration will have to be considered. The following section describes the necessary equations derived through the laws of thermodynamics to evaluate reversible cell potential at any conditions.

1.2.1.1 Impact of temperature

The reversible cell potential as a function of temperature can be expressed as

\[ \left( \frac{dE}{dT} \right)_p = \frac{\Delta s}{nF} \]  
Equation 1.9

where \( \Delta s \) is the change in molar entropy of reaction. If this quantity is assumed to stay constant, the final reversible cell potential, \( E \) for any temperature, \( T \) is

\[ E = E^\circ + \frac{\Delta s}{nF} (T - T_0) \]  
Equation 1.10

1.2.1.2 Impact of pressure

The reversible cell potential as a function of pressure can be expressed as

\[ \left( \frac{dE}{dp} \right)_T = -\frac{\Delta \theta}{nF} \]  
Equation 1.11
where $\Delta \hat{v}$ is the change in molar volume during the reaction. If the gases are assumed to obey the ideal gas law, Equation 1.11 can be rewritten as

$$\left( \frac{dE}{dp} \right)_T = -\frac{\Delta n_g RT}{nFp}$$

Equation 1.12

where $\Delta n_g$ represents the change in the number of gas molecules during reaction. Integrating Equation 1.12 between $p$ and $p_0$ yields

$$E = E^o - \frac{\Delta n_g RT}{nF} \left( \frac{p}{p_0} \right)$$

Equation 1.13

where $p$ is any arbitrary pressure.

1.2.1.3 Impact of concentration

The change in Gibbs energy in relationship to chemical activity of all the species involved in the reaction is described by the van Hoff isotherm

$$\Delta \hat{g} = \Delta \hat{g}^o - \frac{RT}{nF} \ln \left( \frac{\prod a_{product,i}^{v_i}}{\prod a_{reactant,i}^{v_i}} \right)$$

Equation 1.14

where $a_i$ is the activity of the species and the $v_i$ is the stoichiometric coefficient of the species. By combining Equation 1.4, 1.5 and 1.14, we get the Nernst equation

$$E = E^o - \frac{RT}{nF} \ln \left( \frac{\prod a_{product,i}^{v_i}}{\prod a_{reactant,i}^{v_i}} \right)$$

Equation 1.15

This equation relates the reversible cell potential to the temperature, pressure and concentration of the species in the reaction and is of great importance in the thermodynamics of fuel cells.

1.2.2 Losses in PEMFC\textsuperscript{13}

Losses or overpotentials in general, refer to the voltage penalty that must be paid in order to have a net production of current. In the PEMFC, the types of losses are fuel crossover, activation,
ohmic and mass transport. The regions of these losses in polarization curves are depicted in Figure 1.2.

![Figure 1.2 Typical losses observed in polarization curves in PEMFC](image)

1.2.2.1 Fuel crossover losses

While the role of the electrolyte membrane is to only transport H\(^+\) from the anode to the cathode, a finite amount of H\(_2\) permeates across the membrane. The presence of catalyst and oxygen then pushes the reaction to produce water without producing useful work. This results in a mixed potential at the cathode which lowers the overall equilibrium reversible potential. Internal current density also contributes to the current density to deviate from being zero. These losses result in the open circuit voltage, \(E_{ocv}\) observed to be lower than the theoretical voltage for PEMFC.
1.2.2.2 Activation losses

As for most reactions to occur, the activation barrier must be overcome to promote reactants to the activated state for subsequent conversion into products. Similarly, some potential must be sacrificed for the electrochemical reaction to proceed at the electrodes in PEMFC. The Butler-Volmer equation (Equation 1.16) is the cornerstone of electrode kinetics. Fundamentally, it relates the current density, \( j \) produced in electrochemical systems with the activation overpotential, \( \eta_{act} \):

\[
\eta_{act} = \frac{RT}{\beta nF} \ln j_0 + \frac{RT}{\beta nF} \ln j
\]

Equation 1.18

where \( c = \frac{RT}{\beta nF} \ln j_0 \) is the y-intercept and \( m = \frac{RT}{\beta nF} \) is the slope. This general equation is called the Tafel equation which provides a strong tool to determine kinetic parameters for fuel cell studies.

\[
j = j_0 e^{\beta nF \eta_{act}/(RT)}\]

Equation 1.17

The equation can then be linearized by rewriting in the following form,

\[
\eta_{act} = \frac{RT}{\beta nF} \ln j_0 + \frac{RT}{\beta nF} \ln j
\]

Equation 1.18

\[
\eta_{act} = \left( \frac{c R^*}{c_R^0} e^{\beta nF \eta_{act}/(RT)} - \frac{c_P^*}{c_P^0} e^{-(1-\beta)nF \eta_{act}/(RT)} \right)
\]

Equation 1.16

\( j_0 \) is the exchange current density at standard conditions, \( \beta \) is the symmetry factor which depends on the activation barrier (typically ranges between 0.2-0.5), \( F \) is the Faraday’s constant, \( R \) is the gas constant, \( T \) is the temperature, \( c^* \) is the actual surface concentration for product and reactant and \( c^{0*} \) the concentration for product and reactant under standard conditions. \( j_0 \) is the current density observed when the forward and backward reactions are in dynamic equilibrium and serves as an important parameter for kinetic performance optimization.

When \( \eta_{act} \) is large and the forward reaction dominates, the second exponential term in Equation 1.16 becomes negligible and the equation can be reduced to

\[
j = j_0 e^{\beta nF \eta_{act}/(RT)}
\]

Equation 1.17
1.2.2.3 Ohmic losses

This type of overpotential is caused by the resistance of charge transport in the system. This includes the electronic resistance, $R_{elec}$ through the components such as electrodes, wiring, flow field plates and interfacial contacts. Another type of resistance is the resistance to the movement of ions (i.e., $H^+$) across the membrane from anode to the cathode referred to as ionic resistance, $R_{ionic}$. The hydration of the membrane is pivotal in high conductivity of $H^+$. These resistances are additive and can be represented by the following relationship which follows Ohm’s law

\[ \eta_{ohmic} = i(R_{elec} + R_{ionic}) \]

Equation 1.19

Since the mobility electrons is far higher than that of ions, the ionic resistance of the membrane in PEMFC is a dominant contributor to ohmic overpotential, $\eta_{ohmic}$.

1.2.2.4 Mass transport losses

Mass transport refers to the supply of reactants and removal of products at the electrodes. This type of loss becomes dominant at high current densities where the reactants are unable to reach catalytic sites on the electrodes in time. The cause of impediment of gas transport is the slow diffusion activity through the porous networks in the porous layers and additional barriers posed by the accumulation of water (especially in the cathode) at high current densities. As with activation losses, the losses at the cathode are much more dominant compared to the anode due to the production of water. The limiting current density, $j_L$ is the current density where the reactant is completely consumed at the electrode surface ($c_R^* = 0$) and can be expressed as

\[ j_L = nFDeff \frac{c_R^0}{\delta} \]

Equation 1.20
where \( D_{eff} \) is the effective diffusivity of the species, \( \delta \) is the diffusion layer thickness, \( c_R^0 \) is the bulk concentration of species. In order to increase performance, \( j_L \) should be increased and this can be done through design improvements in the gas diffusion layer and flow supply of reactants to evenly distribute the reactants.

The mass transport overpotential \( \eta_{MT} \) can be expressed as

\[
\eta_{MT} = \left( \frac{RT}{nF} \right) \left( 1 + \frac{1}{\beta} \right) \ln \frac{j_L}{j_L - j}
\]

Equation 1.21

where \( \alpha \) is the symmetry factor of the activation barrier observed in activation overpotentials.

1.3 Literature review

1.3.1 Water management in PEMFC

Figure 1.3 Simplified schematic of the water transport mechanism within a PEMFC. ORR refers to the oxygen reduction reaction. EOD refers to the electroosmotic drag
Figure 1.3 illustrates the different ways in which water moves within the PEMFC. Firstly, the reactant gas feed streams (O\textsubscript{2} and H\textsubscript{2}) are humidified before being supplied to the anode and cathode where they travel through the FF, GDL and CL to humidify the PEM. Electroosmotic drag (EOD) is the movement of water across the PEM as a result of protonic conductivity in the same direction. Water molecules that hydrate the proton are transported simultaneously with the proton to the cathode as hydronium ions (H\textsubscript{3}O\textsuperscript{+}). A high rate of EOD results in the depletion of water in the anode CL which results in the loss of water balance in the cell leading to performance deterioration. The ORR at the cathode CL generates water which results in increased water saturation. At the cathode CL, water is transported through either backdiffusion (BD) and/or regular transport from the CL to the FF through the GDL on the cathode side. In backdiffusion, the positive water gradient forces water to travel in the opposite direction to electroosmotic drag back to the anode side of membrane. Depending on the state of water, the gaseous phase transports via diffusion while liquid water travels via capillary pressure in the porous layers.

1.3.2 Water transport in porous layers

The term GDL generally includes the MPL and the carbon fiber/cloth layer, often defined as the substrate layer, SL. Since the layer is responsible for the transport of water, bulk treatment of materials such as Teflon (PTFE) is often applied to facilitate water transport by increasing hydrophobicity\textsuperscript{16–18}. GDLs play a crucial role in the PEMFC due to the following reasons: (1) provides a network of paths to remove water from the catalyst layer to the flow field; (2) provides the access of reactant gases to the catalyst layer from the flow field; (3) conducts electrons between the catalyst sites and flow field channels; (4) heat conductor between the membrane electrode assembly (MEA) and flow field plates; (5) provides mechanical strength to support the MEA.\textsuperscript{17}
The porous structure of the GDL not only determines the permeability of gases and liquid water but also the liquid saturation profile across the GDL.\textsuperscript{19,20} For water vapor transport, it is mainly governed by convection or diffusion, depending on the flow channel design (i.e., serpentine, parallel and interdigitated).\textsuperscript{21} Convection is influenced by the pressure gradient along the channel while diffusion occurs due to the higher concentration of water produced at the CL. As different flow channel designs have different pressure gradients (i.e., highest for interdigitated flow channels and lowest for parallel designs), water vapor transport due to convection can be varied to different degrees.\textsuperscript{21}

Depending on the local mass and heat transfer conditions in the GDL, condensation of water vapor can occur when the vapor pressure exceeds the saturation level. Liquid water transport is driven by capillary action and liquid pressure gradient.\textsuperscript{20} Liquid water may exist in continuous complex-shaped liquid bodies by filling the network of pores and emerge as droplets at the GDL/FF interface.\textsuperscript{22–24} In this process, the micro droplets merge to form larger droplets which results in a preferential path of water transport. As a result, a tree-like percolation of liquid water forms in the pore network in the hydrophobic GDL as illustrated in Figure 1.4.
In addition to capillary action, the voids in the GDL occupied with water results in the increase in liquid pressure. This brings rise to the liquid pressure gradient which drives liquid water flow to lower liquid saturation sections. By increasing the hydrophobicity of the pores through PTFE addition, the surface wettability of water in the pores can be reduced. Due to the differences in pressure at the interface between water and gas in the small pores, the flow of liquid occurs through capillary motion. This is influenced by the surface tension of liquid water, contact angle, porosity, liquid water volume fraction and the intrinsic permeability.

1.3.3 Water breakthrough and pore network

The minimum capillary pressure, $P_c$ required for liquid water to penetrate a throat or pore in the GDL is given by the Young-Laplace formula

\[ P_c = \frac{2\sigma \cos \theta_c}{r_t} \]

where \( \sigma \) is the surface tension of water, \( \theta_c \) is the contact angle and \( r_t \) is the hydraulic or mean pore radius. \( \theta_c \) can be altered through the PTFE content in the GDL and \( r_t \) is determined by the porosity of the porous layer.

This pressure first comes into play at the interfaces of gas and water where water starts to invade the porous layers, mainly at the CL/GDL interface. It is commonly known as the breakthrough pressure for water in the GDL which is crucial for water transport as it influences the inlet condition for water transport. A pressure build-up is required to push water into the GDL and the ease at which water invasion is initiated will depend on \( \Delta p \). A high \( \Delta p \), would result in overaccumulation of water which results in CL flooding. Upon breakthrough, liquid water undergoes a percolation path through the largest pores.

Since the transport of water in the pores depend on the critical radius for penetration, the narrowing of pores or “bottlenecks” results in trapped water which stops the movement of water from the CL to FF as shown in Figure 1.5. This results in flooded zones in the GDL which can only be flushed when the capillary pressure is increased.
1.3.4 Microporous layer (MPL)

The MPL is essentially a porous layer of carbon particles treated with a hydrophobic agent that offers a smaller pore size distribution than the SL. Typically, the pores in the SL are between 10–100 µm created by the gaps between the fibers while the pores in the MPL are typically below 0.5 µm.\textsuperscript{26,27} It was suggested in the work by Wilson \textit{et al.}\textsuperscript{28} that larger pores in the interface between the SL and CL will result in larger water droplet formation at the cathode, signaling a need for layers with smaller pores at the interface. Current state-of-the-art GDLs incorporate MPLs as it has been shown that these MPLs have better performance at high current densities, indicating that the layer improves water management.\textsuperscript{26,27,29–34}

However, there are many different explanations in the literature on how the MPL impacts water management. Here are some of the possible effects:

\begin{figure}
\centering
\includegraphics[width=\textwidth]{gdl.png}
\caption{The effect of narrowing pores in the GDL on liquid water transport\textsuperscript{25}}
\end{figure}

• **Promotion of backdiffusion of water from the cathode to the anode**

The layer forms a barrier which leads to increased hydraulic pressure at the cathode CL which results in increased water flux across the membrane.\textsuperscript{31,35–38} Blanco \textit{et al.} isolated the role of the cathode MPL in promoting backdiffusion by introducing perforated metal sheet with variable open areas at the GDL/FF interface to introduce a barrier for water transport.\textsuperscript{32} They found that when MPL was absent perforated sheets with lower open areas was required to achieve the same anode pressure drop thus, supporting the hypothesis of the role of MPL in aiding in the cathode to anode backdiffusion of water.

• **Reduced water saturation in the cathode GDL**

Passalacqua \textit{et al.} concluded that the reduction of water droplet size in the MPL leads to enhanced oxygen diffusion.\textsuperscript{33}

• **Reduced saturation level of water in the cathode CL**

Qi \textit{et al.} suggested that the MPL is less likely to be flooded because the formation of stable water droplets in the small hydrophobic pores may not occur, leading to less flooding in the CL as well \textsuperscript{29} Owejan \textit{et al.} concluded that water saturation in the CL is reduced as the MPL prevents the condensed water in the SL from penetrating back to the CL.\textsuperscript{39} The same conclusion was also made by Nam \textit{et al.}\textsuperscript{24} These observations are also in agreement with the modelling work by Pasaogulari \textit{et al.} which showed the water removal is enhanced and liquid water saturation decreases with the introduction of a thin hydrophobic MPL.\textsuperscript{40}

• **Limitation of liquid water entry locations**

It was proposed by Nam \textit{et al.} that the MPL reduces the number density of breakthrough pores through efficient collection of water flux from the CL.\textsuperscript{22} In addition, the percolation
of water through the MPL results in a lower number of invaded zones by liquid water in the GDL.\textsuperscript{41,42} This dramatically decreases the saturation of water and promotes the transport of oxygen via diffusion.

- **Increased vaporization of liquid water**

  Thomas \textit{et al.} showed that the addition of an MPL results in higher heat flux at the anode and cathode which results in higher thermal resistance.\textsuperscript{43} The increased temperature enables more water to be transported in the vapor phase which reduces electrode flooding.

  Hence it can be seen that there is not a general agreement on how MPLs impact water management in the PEMFC. In the work by Atiyeh \textit{et al.} and Karan \textit{et al.} the net water drag coefficients determined from experiments with and without cathode MPLs were not significantly different.\textsuperscript{44,45} This suggests that the obtained results did not support the proposed hypothesis on backdiffusion of water from the cathode to the anode leading to the conclusion that water transport is much more complex than previously concluded.

  Apart from water management, the other impacts of the MPL include, the protection of the membrane from the fibers of the GDL\textsuperscript{17,46}, reducing the electrical contact resistance\textsuperscript{29,46} and increased catalytic activity through the decrease of catalyst penetration depth into the diffusion layer.\textsuperscript{29}

1.3.5 **MPL architecture**

1.3.5.1 **MPL configurations in MEA**

  The most common MPL configuration is the substrate-based approach where the MPL slurry is applied on the carbon paper or cloth. The method of application that has been reported in
literature include spraying\textsuperscript{47–50}, screen printing\textsuperscript{47,49,51}, doctor blading\textsuperscript{26,39,52}, brushing\textsuperscript{53,54} and rolling.\textsuperscript{49,55}

Another configuration where the MPL is applied directly on the catalyst layer of CCMs have been reported. Cipollini found that the resistive voltage is lowered by 15-30\% due to improved electrical contact.\textsuperscript{56} The final and less common configuration is the free-standing MPL approach where MPLs are fabricated separately before incorporated into the MEA.\textsuperscript{57} The employment of commercially produced MPL film (Carbel® MP, W.L. Gore & Associates, Inc.) for MPL studies were also done some studies.\textsuperscript{39,58}

1.3.5.2 Pore structures in MPL

The porous structure of the MPL provides pathways for water and gas transport between the SL and CL. Figure 1.6 illustrates the possible types of pores that are present in the microstructure of MPLs along with the general pore categories. Note that the range of pore sizes for the pore categories are given arbitrarily just for the sake of discussion and do not refer to the IUPAC classification of pores for porous materials. The IUPAC classification for pore sizes are: micropores (d < 2 nm); mesopores (2 nm < d < 50 nm); macropores (d > 50 nm).

![Figure 1.6 Illustration of the types of pores that exist in MPLs comprised of carbons as the conductive material (not to scale)](image)
In the literature, the pore size range for GDLs are classified into three main categories; macro-, meso- and micropores.\textsuperscript{49,52,55} For gas transport, bulk diffusion dominates in macropores and Knudsen diffusion dominates in micropores while both modes of diffusion would be present to varying degrees in mesopores.\textsuperscript{49,52} The introduction of hydrophobic agents in the MPL layer further complicates the distribution of water due to the change in hydrophobicity of the pores. Antolini et al. showed that the addition of PTFE decreased the porosity of the pores in the MPL except for the space in and between the carbon particles in the agglomerates.\textsuperscript{59} As a result, the different sized pores in the MPL could be either hydrophobic or hydrophilic.

According to the Young-Laplace equation (Equation 1.21), the capillary pressure required to invade the pore is influenced by the wettability of the pore surface. This means that smaller hydrophobic pores will less likely be invaded by liquid water due to the higher energy required for breakthrough leaving the pores open for gas transport.\textsuperscript{52} Larger hydrophobic pores would be easier for liquid transport due to lower amount of pressure required. As for hydrophilic pores, smaller pores will be filled with condensed water earlier as governed by the Kelvin equation\textsuperscript{55}

\[
\ln \frac{P}{P_0} = -\frac{2\gamma V_m}{rRT} \cos \theta_s
\]

\textit{Equation 1.23}

where $\gamma$ is the surface tension of water, $\theta$ is the contact angle of water on the pore wall, $V_m$ is the molar volume of condensed water, $r$ is the pore radius, $P$ is the partial pressure of water vapor and $P_0$ is the saturation pressure of water vapor in the pore.

This relationship implies water vapor which transports through the MPL will preferentially condense in the smaller pores as higher saturation of water can be achieved under the same pressure. It is suggested by several authors that water transports simultaneously through the micro-
and macro- pores where the micropores transfer the condensed water towards the flowing water macro-droplets. \cite{24,49}

The previous paragraphs describe the complicated nature of water and gas transport in the GDL due to the presence to two-phase flow, varying porosity in the layers, and varying degree of hydrophobicity of the pores. Importantly, Kong et al. pointed out that the ratio of macropore volume and micropore volume is more important than the overall porosity of the layer. \cite{55}

### 1.3.5.3 Pore types in MPL

MPL cracks and pores in the SL generally fall into the macropore category. The presence of cracks in the MPL was studied by Hizir et al. who found that the areal crack density of the MPL studied varied from 2.8% to 8.9% with large variabilities in crack widths (up to 60 µm). \cite{60} These cracks have been reported to be advantageous by providing preferential breakthrough of water due to decreased breakthrough pressure. \cite{39,42,61,62} The introduction of pore formers in the MPL through materials such as PMMA \cite{26} and Li$_2$CO$_3$ \cite{55} have been shown to create preferential liquid water pathways which reduce mass transport resistances. The effect of MPLs with graded porosity prepared with different content of pore forming NH$_4$Cl \cite{51} was also studied. As the porosity of the MPL increases from the CL/MPL interface to the MPL/SL interface, the liquid transport was facilitated through the larger pores while the small pores were used for gas diffusion.

In addition, perforations were also engineered using laser \cite{63,64} and milling \cite{63} on the MPL layer. Alink et. al. suggested that voids created through milling retain water for MEA hydration at dry conditions while they function as pooling sites for water for water drainage at wet conditions \cite{63}. Lu et al. showed that laser perforated MPLs resulted in a uniform water distribution in the GDL and decreased water breakthrough which lead to improved fuel cell performance. \cite{64}
Interparticle gaps which arise from the interstitial spaces between and within carbon particle agglomerates in the MPL provides smaller pathways for transport. Depending on the method of MPL application and the carbon material, the pore size distribution within the layer would differ as the compactness of the layer changes.\textsuperscript{49,65}

Another type of pore in the pore spectrum are the intraparticle pores due to the textural morphology of the primary carbon particles. The smallest of the pores (<2 nm) referred to as micropores based on IUPAC’s nomenclature, arises from the spaces between turbostratic graphite planes of crystallites or between crystallite edges.\textsuperscript{66} In addition to its size, oxygen-containing functional groups found at these edges also impacts the water adsorption capacity of the material\textsuperscript{67}. Wang et al. reported that Black Pearls 2000, a type of carbon black which has high percentage of microporosity resulted in heavy mass transport losses when used in the MPL.\textsuperscript{68} Hence, it can be understood that while textural pores may not directly provide pathways for gas and water transport, they influence the local saturation in the proximity of the pore and subsequently the overall MPL water saturation.

1.3.6 MPL materials (conductive component)

1.3.6.1 Carbon blacks (CBs)

CBs have been widely used as the conductive component in the MPL as reported in the literature. Kinoshita comprehensively discussed the physicochemical and electrochemical properties of carbon which included carbon blacks.\textsuperscript{69} This type of carbon is formed during either thermal decomposition or partial decomposition of hydrocarbons. It was also described how the manufacturing process and feedstocks impact the properties of CBs. The characteristics of some
carbon blacks commonly used in fuel cell research are shown in Table 1.1. It can be observed that the CBs vary vastly in primary particle size, surface area, and agglomerate structures.

Table 1.1 Physical characteristics of carbon blacks commonly used in PEMFC applications$^a$

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Particle size (nm)</th>
<th>Surface area (m$^2$/g)</th>
<th>DBP Adsorption$^b$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketjenblack EC</td>
<td>30</td>
<td>929</td>
<td>350</td>
</tr>
<tr>
<td>Black Pearls 2000</td>
<td>15</td>
<td>1475</td>
<td>330</td>
</tr>
<tr>
<td>Vulcan XC72R</td>
<td>30</td>
<td>238</td>
<td>193</td>
</tr>
<tr>
<td>Acetylene Black</td>
<td>42</td>
<td>51</td>
<td>262</td>
</tr>
</tbody>
</table>

$^a$ Obtained from Kinoshita

$^b$ Dibutyl phthalate (DBP) adsorption method is used to measure the relative structure of carbon Black (High value – large agglomerations or structure, low value – little agglomeration)

Figure 1.7 shows the structures of CB particles. Micropores form at the spaces between the crystalline domains and carbon layer planes in the primary particle. The particles then fuse together by covalent bonds to form aggregates which subsequently have a strong tendency to form agglomerates.

![Figure 1.7 Schematic representation of the microstructures in carbon black: graphite crystalline domain, primary particle, agglomerate, and aggregate](image)

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$^\dagger$ Reprinted with permission from ACS Applied Materials and Interfaces, Vol. 2 Soboleva, T. et al. On the micro-, meso-, and macroporous structures of polymer electrolyte membrane fuel cell catalyst layers, 375-384. Copyright 2010, American Chemical Society
Over the years, CBs such as Vulcan XC72R\textsuperscript{53,55,72–75}, acetylene black\textsuperscript{26,52,53,65,72,73}, Black Pearls 2000\textsuperscript{52,65}, Mogul L\textsuperscript{72}, Ketjenblack EC\textsuperscript{76}, Hicon Black\textsuperscript{75} have been reported used in the literature. In comparative studies with different carbon blacks in the MPL, acetylene black (AB) showed superior fuel cell performance. In a series of studies by Jordan \textit{et al.}, AB showed a 15% increase in power density when used in the MPL under air and oxygen operation compared to Vulcan XC72R (XC72R).\textsuperscript{53,73} The improvement was attributed to the lower microporosity and overall porosity of AB which avoids the flooding of the CL. Similar observations were also made by Passalacqua \textit{et al.}\textsuperscript{72} The increased performance with the AB MPL was due to the higher overall pore volume and smaller average pore size which improved water transport.

Yan \textit{et al.} found that when air is used as oxidant, AB showed superior performance compared to Black Pearls 2000 (BP) and XC72R attributing it to the low surface area of AB.\textsuperscript{77} Under oxygen, BP showed the best performance due to the efficient removal of excess water. However, the authors did not provide further reasoning for the differences. In both cases, the performance of XC72R was lower than AB. Wang \textit{et al.} reported a composite MPL containing a mixture of BP and AB at certain ratios. They discovered that the GDL with AB had the highest gas permeability and hydrophobic porosity while the GDL with BP had the opposite properties\textsuperscript{52,65}. The layer with 10% BP and 90% AB showed the best performance due to the presence of bi-functional (hydrophilic and hydrophobic) pores to overcome mass transport limitations.

1.3.6.2 Other allotropes of carbons

Carbon nanotubes (CNTs) have gained wide interest due to their excellent thermal and electrical conductivities.\textsuperscript{78} As a result, the application of CNTs in MPL have been investigated either as single component type MPLs composed of only CNTs\textsuperscript{48,79–81} or as composite formulations with CBs.\textsuperscript{82–85} A general consensus on the performance improvement is that the CNTs introduce
larger pores due to the morphology of CNTs in the MPL structures which improves oxygen transport.\textsuperscript{48,79,81,82,85} Excellent performance at both low and high humidity conditions were also observed indicating operational robustness with the use of CNTs in the MPL.\textsuperscript{80,83} Lee et al. studied the in-situ liquid water saturation during operation using x-ray tomography to envisage the transport mechanism of CNT-based MPLs.\textsuperscript{79} They found that the effective porosity of MPLs with CNT was higher even though CNT-based MPLs had a higher liquid saturation compared to conventional MPLs. This was attributed to the shallower intrusion of carbon into the SL, resulting in a thinner overall MPL layer.

Another recently discovered carbon allotrope, graphene is known to possess a high Young’s modulus and excellent thermal and electrical conductivity.\textsuperscript{86} Consequently, its unique properties have warranted investigative work as a potential material for MPLs.\textsuperscript{87–89} In the work by Leeuwner and Najafabadi, lower ohmic losses were observed for graphene-based MPLs due to the high electrical conductivity and improved interfacial contact between the CL and MPL.\textsuperscript{87,88} This complex MPL structure also improves water management in both dry and humid conditions observed through polarization tests and long term drying tests. Similar results were also observed by Ozden et al. who supported the view that the formation of complex tortuous paths in graphene-based MPLs leads to greater water retention compared to more direct pathways in CB-based MPLs.\textsuperscript{89} In addition, a composite MPL consisting of graphene and carbon black showed similar performances at 20\% and 100\% RH in the work by Leeuwner et al.\textsuperscript{90} The composite structure of the resulting MPL benefits from the water retaining capabilities of graphene flakes which forms a dense barrier for low water permeability and the presence of carbon black particles between the flakes introduces additional pathways for water transport. This synergistically improves water management at both high and low humidity conditions.
1.3.6.3 Graphite and graphitized carbons

Passalacqua et al. investigated the use of graphite which had low surface area (13 m$^2$/g) in an MPL and saw comparable performance to that of XC72R when a high loading (5 mg/cm$^2$) was used.$^{72}$

The use of graphitized carbon was reported by General Motors to improve the durability of MPLs.$^{91,92}$ In a series of in-situ accelerated degradation studies, MPL containing AB resulted in a loss of 63% of the current density at 0.6V compared to a 30% loss when graphitized Pureblack® SCD-205-110 was used as the carbon. In the tests, both MEAs were held at 1.2V for specific periods. Accelerated startup/shutdown (SUSD) testing up to 1000 cycles further showed that the graphitized carbon had a 25% improvement in the voltage degradation rate vs cycle number at 1.2 A/cm$^2$. Kannan et al. attributed the excellent fuel cell performance of Pureblack® SCD-205-110 compared to XC72R due to the high hydrophobicity of the material which provided relatively better gas transport.$^{93}$

1.3.6.4 Mesoporous carbons

Sahu et al. synthesized ordered mesoporous carbons (MC) using the sol-gel method with pluronic F127 and found the best performance obtained was for MC treated with 2M HNO$_3$.$^{74}$ The authors suggested that along with the optimal degree of functionalization, the different pore sizes introduced in the GDL allowed water to be removed via capillary action while larger pores were open for gas permeation. Xing et al. also saw mass transport improvements in direct dimethyl ether fuel cells when MC was used in the MPL.$^{94}$ This was ascribed to the introduction of liquid transport pathways through the hydrophilic pores of the MC, leaving the larger pores in the GDL for gas diffusion.
1.3.7 **Colloid imprinted carbons (CICs)**

The family of colloid-imprinted carbons (CICs) has been of great interest to researchers due to tunable pore morphology in terms of pore diameter, pore volume and surface area.\(^{95-102}\) The carbon precursor is mesophase pitch (MP), an anisotropic carbonaceous material obtained after polymerization and condensation of pitch and commonly used in the manufacture of carbon fibers.\(^{103}\) The precursor also yields carbons with large crystallites and can be graphitized.\(^{96,104,105}\)

The synthesis of CICs involves MP and colloidal silica mixed at a certain ratio and heated to the softening temperature of MP to allow the imprinting of the silica onto the surface before carbonization at high temperature (i.e. 900°C). This unique property is ascribed to the ability of the polyaromatic molecules in MP to self-assemble into a liquid crystalline phase instead of having a phase transition temperature or melting point.\(^{97}\) The interstitial pores between the templating silica particles can now be filled by the low viscosity MP, leading to the imprinting of pores based on silica particle morphology. Figure 1.8 illustrates the TEM image of a templated CIC with 24nm pores first reported by Li et al.\(^{95}\) The nanostructure of the CIC is composed of randomly arranged pores with high uniformity in terms of pore size.
The tunability of the CICs were investigated using silica colloids with different particle sizes (12 – 50 nm) where the resulting CICs had narrow pore size distributions with mean pore diameters close to the diameter of the silica colloids and different BET surface area.\textsuperscript{95,98–100} The surface area and pore volume of CICs were also tunable based on the imprinting temperature where the pore volume increases when the temperature is increased from 225 to 420°C.\textsuperscript{100,102} Due to the


Figure 1.8 TEM micrograph of CIC synthesized with MP and colloidal silica\textsuperscript{§}
nature of the precursor, CICs contained low microporosity and the morphology was solely dependent on the imprinting silica colloids.\textsuperscript{95,102}

Li \textit{et al.} graphitized CICs at 2400°C under argon and saw about a 50% drop in BET surface area, pore volume and pore diameter.\textsuperscript{102} Despite this, the values obtained especially the surface area and pore volume was higher than that of commercial Carbopack X along with the presence of uniform spherical pores. Through wettability studies, Li \textit{et al.} showed that CICs were highly hydrophilic due to the large presence of surface oxygen groups (\textasciitilde{} 10 \textmu{}mol/m\textsuperscript{2}).\textsuperscript{106} The hydrophilicity was reduced by heat treatment at 1500°C but the nanostructure of the CICs was preserved.

With the remarkable tunability and properties of CIC, this material has found use as a catalyst support in PEMFCs. Fang \textit{et al.} reported higher ORR activity for Pt loaded CIC with 22nm pores compared to a similar loading Pt-loaded Vulcan catalyst in PEMFC operation.\textsuperscript{107} This was attributed to the large pore volume which facilitated mass transport, high electronic conductivity and high surface area and uniform mesoporosity that enabled even distribution of Pt. Banham \textit{et al.} varied the imprinting temperature to control the depth of the pores for Pt deposition.\textsuperscript{100} They discovered that ORR activity was independent of the depth of Pt in the pores indicating the absence of mass transport limitations.

In a series of work by Banham and Pei, CICs with different pore sizes (15, 26, 50 and 80 nm) were synthesized to be used as Pt supports for ORR studies.\textsuperscript{108,109} The distinct circular pores as a result of imprinting by silica colloids of different sizes are evident in the TEM micrographs in Figure 1.9. It was discovered that all Pt-CICs had uniformly distributed Pt particles with similar sizes (4-6 nm). Other CICs had similar ORR activity except for CIC-26 due to thinner walls. The difference in results between the modelling and experimental work led to the suggestion that the
pore wall thickness must be given careful consideration in addition to pore sizes as thinner walls results in higher electronic resistance.\textsuperscript{108}

**Figure 1.9** Distinct pore sizes evident from the TEM micrographs of 10 wt. % Pt/ (a) CIC-15; (b) CIC-26; (c) CIC-50; and (d) CIC-80. The estimated pore sizes were 15, 26, 50 and 80 nm for the respective CICs\textsuperscript{109}

When compared to XC72R and ordered mesoporous carbons (OMC), CICs showed superior ORR performance in both the high and low overpotential regions.\textsuperscript{110} This was attributed
to the low mass transport limitations from the large open pores in CICs compared to OMC even through both catalysts had uniformly distributed and small Pt particles (3.5-4.5 nm).

It is evident that CICs have favorable properties for electrochemical applications based on several key attributes; tunable pore volumes and surface area based on templating conditions and material, ability to be graphitized and low microporosity.

1.4 Research scope and objective

1.4.1 Objectives

In the literature, comparative work on different types of carbon has been done and key relationships between the carbon porosity and overall PEMFC performance have been reported (See Section 1.3.6). Despite this, the carbons being compared have entirely different morphologies (particle size and structure) as shown in Table 1.1. Therefore, this study aims to delineate the impact of porosity alone without other effects from these different contributions to better establish the impact of carbon porosity on mass transport issues in the PEMFC. In addition, CICs have been widely applied in PEMFCs as a catalyst support for their superior properties compared to commercial carbon blacks but they have not been used in the MPL. No applications of CICs as carbons in the MPL have been found in the literature to the author’s best knowledge. In addition, the controlled nanostructure tunability of CICs makes them an excellent candidate model material to study the impact of carbon porosity in the MPL of PEMFCs.

The main objective of this thesis is to establish an understanding of the impact of carbon porosity of carbons used in the MPL on the performance of the PEMFC. The specific objectives are outlined as follows:
1. Study of the impact of porosity in a systematically modified commercial carbon black of the same type
   - To investigate the impact of physical activation on the carbon black particles at different activation periods
   - To characterize the properties of the activated carbon blacks
   - To characterize the properties of fabricated GDLs containing the activated carbons blacks with varying porosities
   - To study the performance of fabricated MPLs with the carbon blacks of different porosities

2. Evaluate the performance of CICs synthesized with different pore nanostructures as candidate materials in MPLs
   - To synthesize CICs with different pore sizes using different colloidal silica sizes and colloidal silica to MP ratios
   - To characterize the properties of the CICs in powder and MPL form
   - To investigate the impact of heat treatment on the CICs
   - To study the performance of fabricated MPLs with the CICs of different pore size and of different hydrophobicity/hydrophilicity

1.4.2 Thesis layout

This thesis is organized into 5 chapters

- **Chapter 1** provides the background to the development of fuel cells and fundamental theories behind the operation of the PEMFC. The literature review section discusses the current findings on the impact of water management, water transport theories in GDLs and
the importance of MPLs. The types of carbons commonly used in MPLs are also discussed along with the nature and applications of CICs in the PEMFC.

- **Chapter 2** highlights the experimental methods undertaken in this thesis work.
- **Chapter 3** covers the first approach where commercial ABs were modified through physical activation with CO\textsubscript{2}. Characterization results of the AB samples and fabricated MPLs with the different ABs are discussed alongside fuel cell testing results.
- **Chapter 4** covers the second approach of using CICs as model carbon materials with tunable pore sizes. The impact of synthesis parameters on the carbon morphology is discussed along with the CIC properties. Fuel cell testing results of MPLs fabricated with the CICs synthesized are also discussed.
- **Chapter 5** summarizes the research results, discussion, and suggestions for future work.
Chapter 2: Experimental methods

This chapter presents all the experimental methods used to perform all the work in this thesis.

2.1 Physical activation of Acetylene Black using CO$_2$

The physical activation of the acetylene black (AB) powders (Alfa-Aesar) was conducted in a tube furnace over a specified duration. Each alumina boat was loaded with approximately 0.7g of AB and the boats were placed in the middle of the tube furnace (GSL-1100X, MTI Corporation). The ends of the alumina tube were sealed using flanges and CO$_2$ gas was passed through the tube for at least 15 mins before the activation process was commenced. The pressure and flow rate of the CO$_2$ gas was set to 50 cm$^3$/min and 345 kPa (50 psi) respectively.

The temperature rate of increase was set to 5 °C/min where the heating was done from room temperature (20-23 °C) to 900 °C. The tube furnace was then set to dwell at 900 °C for a specific duration (5-25 hr) before heating was stopped. The tube furnace was then cooled back to room temperature in the presence of CO$_2$ gas under ambient cooling conditions. Figure 2.1 illustrates the heating scheme in the activation process of AB.

![Figure 2.1 Heating sequence for the activation of acetylene black powder under CO$_2$](image)

Figure 2.1 Heating sequence for the activation of acetylene black powder under CO$_2$
2.2 Synthesis of colloid imprinted carbon (CIC)

The synthesis of CICs were based on the procedure described in the thesis by Banham. Mesophase pitch pieces from Jining Carbon Group Co. Ltd., China were ground into a fine powder using a mortar and pestle. The fine powder was then sieved through US Standard 230 mesh (63 µm) mesh. The sieved MP powder was then milled further into finer particles using high energy ball milling for 1 h using 2-2.2 mm zirconia balls (Glen Mills Inc.). The ratio of zirconia balls to MP was kept at 5:1 mass ratio and the milling jar was then filled with 30 ml of EtOH. The milled slurry was then dried in an oven overnight at 70 °C.

2.5 g of the ball milled MP was dispersed in 50 mL of EtOH/H₂O (60:40 v/v) and stirred for 1 h in a beaker. Colloidal silica suspension was added dropwise into the beaker while the mixture was stirred vigorously. The information on the types of colloidal silica suspension used is shown in Table 2.1. The mass ratio of silica to MP was set at various ratios in the thesis work (2:1, 5:1, 10:1). The mixture was then stirred vigorously for 30 min before being placed in an oven at 70 °C until all the solvent has evaporated. After drying, the MP/silica composite was ball milled using stainless steel balls for 20 min to reduce the chunky composite into fine powder.

<table>
<thead>
<tr>
<th>Name</th>
<th>Supplier</th>
<th>Silica wt.% (%)</th>
<th>Manufacturer reported SiO₂ size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUDOX® HS-30</td>
<td>Sigma-Aldrich</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>LUDOX® TM-40</td>
<td>Sigma-Aldrich</td>
<td>40</td>
<td>22</td>
</tr>
<tr>
<td>NexSil™ 85-40</td>
<td>NYACOL® Nano Technologies Inc.</td>
<td>39-41 (~ 40)</td>
<td>40 – 60</td>
</tr>
</tbody>
</table>
In the carbonization step, 5-5.5 g of MP/silica powder was added into an alumina boat (approximately ¾ of the volume of the boat) before being loaded into the center of the tube furnace. The flanges were secured at the ends of the alumina tube and N\(_2\) gas was passed through set up for at least 15 min before the heating was commenced. The flow rate and pressure of the gas supply was set to 50 cm\(^3\)/min and 345 kPa (50 psi) respectively. The multistep heating sequence is illustrated in Figure 2.2.

![Figure 2.2 Heating sequence for the synthesis of CICs under N\(_2\)](image)

Briefly, the furnace was heated at 5 °C/min from room temperature (20-23 °C) to 300 °C and subsequently kept constant for 2 h at 300 °C for the imprinting step. Next, the temperature was increased to 900 °C at 5 °C/min before being kept constant for 2 h at 900 °C for the carbonization step. The tube furnace was then cooled back to room temperature in the presence of N\(_2\) gas under ambient cooling conditions.

After synthesis, the carbonized sample was washed with 40\% HF (Sigma Aldrich) to remove silica in two steps. In the first step, 10 mL of H\(_2\)O and 30 mL HF was added and shaken to mix thoroughly. After 24 h, the supernatant was removed from the settled carbon mixture and the process was repeated with 5 mL of H\(_2\)O and 10 mL HF. After another 24 h, the etched sample
was washed with plenty of MilliQ water through multiple centrifuging and washing steps before being dried at 110 °C overnight. To determine the percentage of silica left in the CICs, the samples were analyzed using thermogravimetric analysis (TGA-50, Shimadzu). Samples with under 1 % wt. of silica were used for subsequent steps while samples with a higher silica % wt. were washed with HF again.

2.2.1 Heat treatment of CICs

All the samples were heat treated under N₂ atmosphere at 1100 °C for a duration of 2 h. CIC was placed in an alumina boat before being loaded into the middle of the tube furnace. The furnace was heated from room temperature (20-23 °C) to 1100 °C at 5 °C/min and kept at 1100 °C for 2 h. The furnace was then left to cool back to room temperature under ambient cooling conditions while N₂ was passed through the tube.

2.3 Ball milling of CICs

In order to have similar particle size distribution for the synthesized CICs, the carbon samples were ball milled in a high energy ball mill for 20 min using 2-2.2 mm zirconia balls (Glen Mills Inc.). 1 g of CIC was added into the mill jar and the mass ratio of zirconia balls to CIC used was 80:1. The mill jar was then filled with 30 ml of EtOH and 10 ml of H₂O before milling was started. The milled carbon was then dried at 100 °C overnight to remove the solvents completely. The milling time of 20 min was decided after a study on the impact of milling time with particle size was conducted as described in Appendix A.1.
2.4 Microporous layer (MPL) preparation

2.4.1 MPL slurry preparation

A slurry containing all the components in the MPL was prepared prior to application on substrate layer (SL). Firstly, a stock mixture of Triton X-100 (Fisher Scientific) and methylcellulose (MTC) (Sigma Aldrich) was made by dispersing the components in MilliQ water and sonicated using a sonicator (Q700 Sonicator, QSonica) for a total of 1 h. The carbon powder was then added into the sonicated mixture and sonicated for 4 min for even carbon dispersion. PTFE dispersion (DISP 30, Fuel Cell Earth) containing 60 % wt. of PTFE in water was then added into the slurry before sonication for 16 min. The vial containing the MPL slurry was submerged partially in an ice bath throughout the sonication process to prevent overheating of slurry. MC was added as a thickening agent to increase the viscosity of the slurry while PTFE was added to increase hydrophobicity. The recipe for the slurry was adapted from the work of Simon et al.26 Table 2.2 summarizes the composition of the components used in the slurry according to desired ratio of PTFE to carbon.

Table 2.2 The composition of MPL slurry used

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Triton X-100</th>
<th>PTFE dispersion</th>
<th>Methyl Cellulose</th>
<th>Water</th>
<th>% wt. PTFE to carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (g)</td>
<td>1.5</td>
<td>0.3</td>
<td>0.875</td>
<td>0.18</td>
<td>15.35</td>
<td>25&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mass (g)</td>
<td>1.5</td>
<td>0.3</td>
<td>0.625</td>
<td>0.18</td>
<td>15.35</td>
<td>20&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> PTFE dispersion contains 60 wt% PTFE in water
<sup>b</sup> Used for AB-based MPLs
<sup>c</sup> Used for CIC-based MPLs
2.4.2 Coating and sintering of MPL

The MPL slurry was then coated on a commercial carbon fiber paper (Sigracet 29BA, Fuel Cell Store) using a doctor blade. The carbon fiber paper has a thickness of $183 \pm 10 \, \mu m$ and 5 % wt PTFE. The edges of the paper were taped to a glass plate and placed on a hotplate set at 70 °C. The schematic of the coating set up is shown in Figure 2.3. The gap on the doctor blade was set to $600 \, \mu m$ to give the final GDL thickness of approximately $215 \pm 5 \, \mu m$. The glass plate was removed from the hot plate after the coating process to allow the coated MPL to dry under ambient conditions for at least 1 h. All thickness measurements of GDLs were done using a micrometer.

![Figure 2.3 A schematic of the doctor blade coating set up for MPL fabrication](image)

The GDL was then sintered in a muffle furnace with a heating rate of 5 °C/min from room temperature to 380 °C and kept at 380 °C for 30 min to allow the redistribution of PTFE in the MPL. At the end of the sintering process, the GDL was removed from the furnace and allowed to cool to room temperature.

2.4.2.1 Influence of other components in MPL slurry

For MPLs to function optimally, undesired components in the slurry must be removed through decomposition during the sintering process. Components such as Triton X-100 and MTC
may impede the electrical conductivity of the layer. Figure 2.4 shows the TGA data for the components found in the MPL slurry with the same heating profile as the sintering process.

![TGA data for components in MPL slurry under air](image)

**Figure 2.4 TGA data for the components in MPL slurry under air**

It can be observed that rapid decomposition begins for Triton X-100 and MTC between 250 and 300 °C and falls below 1% mass by the end of the sintering process. However, PTFE shows a lower change over the sintering process with approximately 6% mass drop. Hence, it can be argued the contributions by the decomposed residue of Triton X-100 and MTC would be negligible as the amounts are less than 1% mass of the whole MPL layer.
2.5 Characterization methods

2.5.1 X-ray Diffraction (XRD)

In order to determine the crystallinity of the CICs synthesized from MP, XRD analysis was performed using a D2 Phaser (Bruker Corporation) with a Cu Kα radiation source (λ = 0.15418 nm) and Lynxeye detector. The scans were performed for a scattering angle range of 10 ° < 2θs < 85 ° at a rate of 0.02 °/s. Samples were loaded in a powder specimen holder and a glass slide was used to flatten the layer of powder before analysis.

The interlayer spacing, d was determined using the Bragg’s law (See Equation 2.1) where θ is the incident Bragg angle on the sample and λ is the wavelength of the incident x-ray. The crystalline parameters were determined using the Scherrer equation (See Equation 2.2). The values of stack height, Lc, and layer size, La, were determined using the constants Kc (0.89) and Ka (1.84) respectively. The full width at half maximum, B2θ was determined from the 002 peak of the XRD spectrum. The average number of layers per stack, n̄s was estimated from Equation 2.3.

\[ n\lambda = 2d \sin\theta_s \]  
**Equation 2.1**

\[ L_a = \frac{K_a\lambda}{B_2\theta \cos\theta_s} \quad L_c = \frac{K_c\lambda}{B_2\theta \cos\theta_s} \]  
**Equation 2.2**

\[ \bar{n}_s = \frac{L_c}{d} \]  
**Equation 2.3**

2.5.2 Thermogravimetric Analysis (TGA)

Thermogravimetric measurements were performed to determine the silica content in synthesized CICs. As silica is used as a template for the synthesis, the complete removal of silica is essential as the presence of silica increases the resistivity of the carbons. All measurements were performed using a Shimadzu TGA-50 equipment.
In order to determine % of silica left in the CIC samples, 1–2 mg of powder was added into an alumina pan (Mandel Scientific Company, Inc.) before being loaded into the equipment. The TGA-50 unit was then programmed to heat the sample from room temperature (20-23 °C) to 800 °C at a rate of 15 °C/min.

To account for the buoyancy effect during heating, the same heating sequence was used with empty alumina pans. The data from the run with an empty pan was then subtracted from the data obtained with the pan and sample. This correction was done for all the samples.

2.5.3 Transmission electron microscopy (TEM)

All TEM imaging was performed using the FEI Osiris in the 4D Labs at Simon Fraser University (Burnaby campus). Approximately 2 mg of sample was added into a microcentrifuge tube along with 1.5 mL of EtOH. The tubes were then capped and sonicated in a sonication bath for 10 min. A micropipette was then used to dispense 10 µL of the dispersed sample on to a Lacey Carbon Type-A Cu mesh (Ted Paella). Imaging was performed in bright field and dark field modes for STEM imaging in addition to TEM imaging.

2.5.4 Scanning electron microscopy (SEM)

All SEM imaging was performed using the FEI Helios at the Center for High-Throughput Phenogenomics, Faculty of Dentistry at the University of British Columbia. Powdered samples were directly placed on a carbon tab affixed on an SEM stub.

Cross-sectional samples of the gas diffusion layers were prepared by the freeze-fracturing method. This was done by first submerging the sample wedged in a cross-sectional SEM sample holder in liquid nitrogen for 2 min before being quickly fractured with a sharp blade in a single motion.
2.5.5 Nitrogen sorption analysis

The specific surface area and pore size distribution of carbon samples were determined using the Micromeritics ASAP 2020 equipment. All samples were heated overnight at 110 °C to draw out as much moisture in the samples prior to the outgassing procedure. Approximately 100 mg of sample was outgassed for 4 h at 120 °C in the degassing port prior to analysis using liquid nitrogen (77 K).

To determine the specific surface area, the Brunauer-Emmett-Teller (BET) method was applied to the partial pressure values in the following range: $0.05 < P/P_0 < 0.3$. The total pore volume was determined at $P/P_0 = 0.99$. The pore size distribution of the adsorption and desorption branch was determined using the Barrett-Joyner-Halenda (BJH) method for the characterization of CICs. The Non-localized Density Functional Theory (NLDFT) method was used to characterize the pore size distribution of AB samples as the BJH method is known to underestimate the pore size up to 25% for pore sizes under 10 nm.\textsuperscript{112} The t-plot method was used to determine the micropore surface area and volume of the samples.

2.5.6 Particle size analysis

All the particle size distributions of the carbon samples were analyzed by using the Malvern Mastersizer 2000 Laser Diffraction Particle Size Analyser. Approximately 20 mg of sample was mixed with 10 – 15 ml of DI water in a beaker. To evenly disperse the samples, 10 µL of Triton X-100 was added into the beaker and stirred. The sample was added dropwise into the sampling port until a sufficient amount indicated by the Mastersizer 2000 software was obtained prior to analysis. The particle refractive index was set to 2.42 for carbon samples and water was chosen as the medium.
2.5.7 X-ray photoelectron spectroscopy (XPS)

All the XPS analysis was performed using the Leybold Max200 spectrometer with an Al Kα achromatic X-ray source and a survey pass energy of 192 eV and narrow pass energy of 48 eV. All the measurements were done at the Interfacial Analysis & Reactivity Laboratory (IARL) which is located in the Advanced Materials & Process Engineering Laboratory (AMPEL), UBC.

2.5.8 Wettability measurements

To study the wettability of the fabricated MPL, the contact angle measurement is commonly employed. The contact angle is the angle formed by the intersection of the liquid-vapor interface and liquid solid interface and the classification of contact angles is illustrated in Figure 2.5.

Figure 2.5 Illustration of the different categories of contact angles on a smooth surface

The shape of the droplet is governed by the equilibrium of three interfacial tensions as described by the Young equation (Equation 2.5) where \( \gamma_{lv} \), \( \gamma_{sv} \) and \( \gamma_{sl} \) are the interfacial tensions for liquid-vapor, solid-vapor and solid-liquid, respectively.

\[
\gamma_{lv} \cos \theta_c = \gamma_{sv} - \gamma_{sl}
\]

Equation 2.5

For contact angle measurements, a droplet of MilliQ water (~10 µL) was deposited on the surface of interest and high-resolution images were taken using a DSLR camera (T6i, Canon). The contact angle was then determined at the triple-phase point with the open access image analysis
software ImageJ. The average contact angle was determined from several droplets dispensed on 4-5 locations on the surface.

2.5.9 Gas permeability

The permeability of the gas diffusion layer impacts the transport of oxygen and water across the porous structure. To understand the impact of carbon porosity on the transport of oxygen, the oxygen permeability of different samples can be compared. The permeability of a layer as defined by Darcy’s law can be used to determine the permeability of fluid flow through pore space when the fluid flow velocity is laminar\textsuperscript{116}. The governing equation is described by Equation 2.6 where $\Delta P$ is the pressure drop across the thickness of the sample, $K$ is the permeability, $\mu$ is the viscosity of oxygen ($2.02 \times 10^{-5}$ Pa·s) and $\nu$ is the superficial velocity of oxygen

$$\Delta P = -\frac{K \nu}{\mu}$$

Equation 2.6

The pressure drop values were plotted against the superficial velocity and slope of the fit was used to determine $K$ according to Darcy’s law. The gas permeability measurements were performed in a lab-made sample holder which allows gas to flow through the GDL sample as shown in Figure 2.6. To prevent leakage, the samples were held in place with two o-rings placed above and below the sample before being clasped by the stainless-steel cell.
Oxygen pressure was set at 101.5 kPa (1 atm) and was fed at different volumetric flow rates using a rotameter and the pressure drop across the sample was measured using digital manometer (HHM-2020, Omega). The samples were cut into 3 cm diameter circles using a hole puncher and the thickness of the samples were determined using a micrometer. Due to the presence of o-rings in the cell, the final exposed area for oxygen permeability is 5.07 cm$^2$ (diameter of 2.54 cm).
2.5.10 Elemental analysis

The elemental composition of the samples was determined using an analyzer (2400 series II CHNS/O Analyzer, Perkin-Elmer). Approximately 2 mg of samples were placed into tin capsules before being tightly packed to minimize volume due to air. Cystine was used as the calibration standard for the analyzer while sulfamic acid was used to presulfide the column. Helium was used as the carrier gas for the combusted products for analysis and the temperature for combustion was set at 975 °C while the temperature in the reduction tube was 500 °C.

2.5.11 Through-plane resistance measurements

As the MPL interfaces with the CL and SL, the addition of this layer impacts the overall resistance of the MEA. This property can be determined through ex-situ measurement of the through-plane resistance of the MPL and GDL. The samples were cut into 0.9525 cm (3/8 inch) diameter circles using a hole puncher. The sample was then placed between two gold-plated brass plates in a lab-made apparatus as shown in Figure 2.7. A potentiostat (SP-150, Biologic) connected to the gold-plated brass plates was used in a four-wire Kelvin method set up to determine the resistance.
A pneumatic piston was used to lower the top brass plate to apply compressive pressure on the samples at specific pressures controlled by a gas regulator. The potentiostat applies small currents and measures the corresponding voltage at specific compression pressures. The resistance was then determined and normalized according to the surface area (0.713 cm$^2$).

### 2.5.12 Water vapor sorption (WVS)

To study the water vapor uptake of the carbon powders, the setup as shown in Figure 2.8 was used to provide a sealed environment for absorption. The procedure used was adapted from Li et al.$^{99}$ Prior to the start of the experiment, all carbon powders were heated for 24 hr in an oven at 105°C to remove moisture from the materials. A crystallization beaker with 100 mL of Type 1 water was placed below the ceramic platform as the source of water in the glass desiccator. Vacuum grease was applied on the lips of the desiccator to provide an airtight seal.
Figure 2.8 Experimental setup for the water vapor sorption test a) Top view b) Side view

The mass of empty glass vials was recorded and approximately 100 mg of carbon powder of each sample was weighed before being added into the respective vials. The total mass of the vial plus carbon powder for all the samples was recorded. The glass vials were then placed on the ceramic platform before the chamber is closed. At specific intervals, the glass vials containing the carbon samples were weighed and the mass change of carbon powders was tracked over time.

2.6 Fuel cell testing

2.6.1 Cell information

The fuel cell hardware (TP-50, Tandem Technologies) used in all the experimental work has an active area of 49 cm². Due to material constraints, the active area was masked to expose a 5 cm² active area at the center of the cell (the effect of masking is discussed in the following section). The flow field plates with single pass serpentine flow channels (49 cm²) were used in a cross-flow configuration as shown in Figure 2.9.
Figure 2.9 TP-50 anode and cathode flow field plates used for fuel cell testing

The width of the channels and lands were 1.27 mm and 1.16 mm, respectively, while the depth of the channels was 1.27 mm. The MEAs were placed between the anode and cathode flow field plates and compressed using a N₂ bladder at 724 kPa (105 Psi). The cathode flow field plate is above the MEA in the horizontal cell configuration for testing.

2.6.2 Membrane electrode assembly (MEA) preparation

Catalyst coated membranes (CCM) provided by Johnson Matthey Fuel Cells with catalyst loadings of 0.04mg/cm² and 0.4 mg/cm² for the anode and cathode were used in all the MEAs used in this thesis work. On the anode side, commercial GDL (Sigracet SGL 29BC, Fuel Cell Etc.) which has 5 %wt PTFE and an MPL was used. For the cathode GDL, the homemade MPL coated on SGL 29BA (as described in Section 2.4) was used. To fabricate the MEA, the CCM was held in place using Kapton polyamide films (C2345-1R-10000, Matrix Technology Ltd.) with an exposed area of 5 cm² in the middle of the sheets. The exposed active surfaces of the CCM were then flanked by the anode and cathode GDLs with the MPL side being in contact with the CCM. Holes for alignment pins and gas supply were punched. The final MEA is shown in Figure

50
2.10 where it can be observed that GDLs are cut into sizes which are larger than the 5 cm$^2$ active area.

The MEAs were not hot-pressed in order to reduce the number of variables in the thesis work.

![Image of MEA used in testing]

**Figure 2.10 5cm$^2$ MEA used in testing**

2.6.3 **Masking comparison**

The use of a smaller active area for MEA testing was imperative due to material constraints. The overall masked active area was 5 cm$^2$ compared to the full active area of 49 cm$^2$ as shown in Figure 2.11.
The performance of two MEAs with different active area was compared under similar conditions as shown in Figure 2.12. The polarization performance of the masked 5 cm$^2$ cell is identical to that of the 49 cm$^2$ MEA except for the last point in the polarization. The only difference that can be observed is the higher resistance for the masked MEA. This can be attributed to the increased contact resistance between the CCM and GDL due to the presence of additional thickness contributed by the layers of Kapton underneath the unused regions of the GDL as shown in Figure 2.10. Due to the similar MEA performance, the subsequent tests were conducted with the masked 5 cm$^2$ MEA.
Figure 2.12 Polarization and areal resistance comparison of MEAs with two different sizes: 5 cm$^2$ and 49 cm$^2$

2.6.4 Fuel cell operation

The polarization tests were performed using a 2kW Hydrogenics fuel cell test station (G100, Greenlight Innovation). Figure 2.13 illustrates the fuel cell test station set up with the TP-50 cell. The test station controlled the flow rates, gauge pressure, temperature and relative humidity of the reactant gases. The station also controlled the flow rate and temperature of DI water to regulate the temperature of the cell. Thermocouples were fitted in the inlets and outlets of the gas and DI water lines to help monitor the temperature during operation. Voltage pins were inserted into flow field plates to measure the MEA voltage and voltage clips are positioned on the bus plates to measure the cell voltage.
2.6.5  Testing protocols

2.6.5.1  Leak testing

At the beginning of every test, the cell was leak tested using soapy water (Snoop® Liquid Leak Detector, Swagelok). After the cell was assembled and compressed, the reactant gases were supplied to the cell. The water was squirted at the joints in the fittings of the gas lines and at the plate interfaces in the fuel cell. If bubbles were observed, the test station was shut off sequentially according to the shutdown protocol and the necessary steps were undertaken to mend the leak.

2.6.5.2  Start-up and shut down

The set point values for the flow rates, pressure and temperature were achieved stepwise. As the conditioning step always preceded the testing step, the gas flow rate was set to 0.052 NLPM and 0.167 NLPM for H₂ and air, respectively. The coolant flow rate was increased to 0.4 NLPM through 0.2 NPLM increments. The temperature and pressure were increased in 20 °C and 50 kPa increments up to the set point values of 80 °C and 150 kPa, respectively. The increments
were only done after 2-3 min when the values from the previous settings had stabilized. The shut-down procedure was done in reverse after testing.

2.6.5.3 MEA conditioning

All samples were subjected to the conditioning step prior to testing to ensure that the membrane was well hydrated for optimal proton conductivity. For new MEAs, the current was increased stepwise until the corresponding voltage was about 0.6 V where the cell was left to operate under the same conditions until the voltage plateaus (typically in 5-7 h). Older MEAs that have undergone the initial membrane conditioning were subjected to a similar procedure. These MEAs typically took a shorter time to plateau (1-2 h).

2.6.5.4 Testing protocol

All polarization tests were performed under a stepwise galvanostatic mode in the forward scan direction (lower to higher current density). The stoichiometry for H₂ was 1.5 while the stoichiometry for air was 2. The current density was set at 2 mins for each point in the polarization and only the data in the final 60 s was averaged. For each sample, 3-5 polarizations were performed to ensure repeatability and the average from these repetitions was reported as the final polarization curve. Also, the gas lines were purged with high flow rates of the gaseous reactants after each polarization procedure to help removed any accumulated water in the flow fields, MEA, and gas lines from previous steps.

2.6.5.5 High frequency resistance (HFR) measurements

For iR compensation, HFR measurements were performed using an LCR meter (LCR-819, GW-Instek) at a frequency of 2.5 kHz. The probes were placed at each of the bus plates in the fuel cell. The HFR encompasses the ohmic resistances arising from the ionic membrane, component and the contact resistances. To account for the resistance of the plates, a graphite foil (Graphite
foil, 0.5mm (0.02in) thick, 99.8% (metals basis), Alfa Aesar) was placed between the anode and cathode flow plates and the resistance across the cell was measured at the operating conditions (cell compression pressure of 105 psi and cell temperature of 80°C) for approximately 10 minutes. Figure 2.14 shows the schematic of the two different cell configurations to isolate the resistance contributions of the coolant and flow field plates.

![Schematic](image)

**Figure 2.14** Schematic illustrating the two different configurations to account for the resistance of the flow field and coolant plates a) Configuration with the MEA at the center of the cell assembly b) Configuration with the graphite foil at the center of the cell assembly

The resistance value was then averaged and subsequent HFR measurements during cell operation were then corrected by subtracting the HFR value from the determined cell plate resistance from the graphite foil test. The final reported resistance would include the resistance of the membrane, catalyst layers, gas diffusion layers and the contact resistances between the flow field plates and the GDLs.
Chapter 3: Study on the impact of MPL carbon porosity through physical activation of commercial acetylene black

3.1 Introduction

Based on the discussion in the literature review (Chapter 1.3), the reported impact of carbon porosity in the MPL on the overall impact on the performance of a PEMFC has been a consequence of using different types of carbon blacks. In this chapter, the results of the goal to delineate the impact of carbon porosity on PEMFC performance are discussed. The method employed to vary the porosity of the carbon is through the physical activation of commercial acetylene black particles at different durations. Characterizations results of the carbons in both the powder state and resulting MPLs are discussed along with their effect on the overall performance in a PEMFC.

3.2 Results and discussion

3.2.1 Properties of activated acetylene black (ABs)

In general, the acetylene black (AB) samples exhibit a type II isotherm with H3 hysteresis, which according to the IUPAC classification, indicates the presence of mesopores (Figure 3.1a). The slow rise in the adsorption isotherm, at low partial pressures, indicates the low micropore volume of the ABs, which is consistent with observations reported in the literature. At high partial pressures, no saturation is observed indicating the presence of macropores arising from the voids within the aggregates of primary carbon particles. The variations in the pore volume and surface area of the activated ABs, achieved with different treatment periods, are summarized in Table 3.1.
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>S_{BET}</th>
<th>S_{micro}</th>
<th>V_{total}</th>
<th>V_{meso}</th>
<th>V_{meso}</th>
<th>V_{micro}</th>
<th>V_{micro}</th>
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<td>cm^3/g</td>
<td>%</td>
<td>cm^3/g</td>
<td>%</td>
</tr>
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<td>60</td>
<td>25</td>
<td>0.169</td>
<td>0.157</td>
<td>92.9</td>
<td>0.012</td>
<td>7.1</td>
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<tr>
<td>AB5</td>
<td>99</td>
<td>22</td>
<td>0.242</td>
<td>0.232</td>
<td>95.9</td>
<td>0.010</td>
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<tr>
<td>AB10</td>
<td>122</td>
<td>14</td>
<td>0.237</td>
<td>0.231</td>
<td>97.5</td>
<td>0.006</td>
<td>2.5</td>
</tr>
<tr>
<td>AB15</td>
<td>145</td>
<td>34</td>
<td>0.272</td>
<td>0.255</td>
<td>93.8</td>
<td>0.017</td>
<td>6.3</td>
</tr>
<tr>
<td>AB20</td>
<td>159</td>
<td>22</td>
<td>0.298</td>
<td>0.288</td>
<td>96.6</td>
<td>0.010</td>
<td>3.4</td>
</tr>
<tr>
<td>AB25</td>
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<td>0.423</td>
<td>0.418</td>
<td>98.8</td>
<td>0.005</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\(^a\) Determined in the partial pressure range of 0.07 < P/P_0 < 0.3  
\(^b\) Determined using t-plot method  
\(^c\) Obtained from N\(_2\) isotherm at p/p° = 0.995

The activation process increased the surface area of raw AB from 60 to 206 m\(^2\)/g as the activation period was increased. The total pore volume also increased from 0.169 to 0.423 cm\(^3\)/g. Pore development, resulting from carbon removal from the surface of the carbon black particles during the activation process, increases both the BET surface area and the total pore volume of the AB samples. Figure 3.1b shows that with increasing the activation period, there is a steady rise in mesopores of approximately 3.5 nm pore width. The increase in mesoporosity occurs while the micropore content of the AB samples gradually decreases. This phenomenon could be attributed to the occurrence of mesopore evolution where the creation of micropores is followed by pore coalescence to form mesopores.\(^{117}\)
Figure 3.1 (a) Nitrogen sorption isotherms for activated AB samples (b) Non-localized Density Functional Theory (NLDFT)-calculated pore size distributions of the activated AB samples
Figure 3.2 shows SEM images of the acetylene black particles which highlights the agglomerated nature of the carbon black. The primary particles (~40 nm) fuse together to form agglomerations which then form aggregates. The network of gaps within the agglomerates and aggregates subsequently leads to formation of meso- and macropores as proposed by Soboleva et al. The presence of these two types of porosity is evident through the features of the N$_2$ sorption isotherms (Figure 3.1a) where the hysteresis loop and no saturation high partial pressures indicate the presence of mesopores and macropores, respectively. From the high-resolution TEM micrographs, it is evident that pores which develop in the AB carbon are formed through the controlled oxidation of carbon by the CO$_2$. The AB15 sample exhibits higher levels of microporosity compared to AB25 and its surface microstructure, when observed through TEM, appears to be more heterogenous, also indicating a higher percentage of textural porosity. The AB0 sample, which was not activated, shows a lower level of microporosity compared to AB15 and AB25. All three samples show lattice fringes, which are attributed to the high temperatures (> 1500 °C) used in the manufacturing process of acetylene blacks. At high temperatures, heteroatoms such as hydrogen, sulfur and other elements are gradually removed and the crystalline structure converts to more graphitic leading to more prominent lattice spacings.
Oxygen surface groups, in addition to being present at the edge of basal planes of unsaturated carbons, can also be formed during the reaction of CO\textsubscript{2} with the surface carbon atoms.\textsuperscript{67} Figure 3.3 shows the XPS spectra of C1s and respective oxygen bonds present in AB0, AB15 and AB25. While AB0 and AB25 samples have similar peak intensities, AB15 shows a slightly higher peak intensity for the C-O (~285.5 eV) peak. This could be attributed to the higher number of micropores in AB15 compared to the other samples. Since micropores arise from the spaces between carbon layer planes and gaps between carbon layer stacks\textsuperscript{70}, there is an increased disorder in the structure. The higher number of exposed unsaturated carbons at the edges in AB15 could lead to higher number of oxygen functional groups indicated by the small increase in peak intensity for C-O. While this is plausible, it is important to note that one XPS analysis was performed for
each sample and perhaps more samples must be analyzed to fully elucidate the occurrence of the peak intensity increase for C-O in AB15.

Figure 3.4a shows the mass change of AB samples due to water vapor sorption over time under similar conditions where AB0 showed the lowest uptake of water compared to the activated
AB samples. All the activated AB samples showed a rapid increase in mass in the first 24 h followed by a gradual increase over time. Within the same time interval, AB15 showed the highest uptake of water followed by AB20 and AB25. This occurrence could be explained by the higher micropore volume in AB15 and increased oxygen surface functional group content. The accumulation of water in the pores can be further explained using the Kelvin equation which relates the volume of condensed water to the size of the pores. Assuming that the pores are hydrophilic as there is no PTFE present in the powders, smaller pores will be filled by liquid water sooner, leading to increased water saturation due to condensation. Figure 3.4b shows that the specific volume of water absorbed over time is much lower than the specific pore volumes of the AB samples. Since the samples were only exposed to one relative humidity condition ($T = 21.5 \pm 0.5 ^\circ C$) throughout the experiment, more humid conditions would lead to increased condensation of water in the pores. In addition, as more porous materials generally have a higher sorption capacity, it is possible that higher relative humidity would have been required to observe a larger increase in mass for AB20 and AB25 which have a higher ratio of mesopore to micropore and higher surface area.
Figure 3.4 (a) Water vapor sorption study data of AB samples at $T = 21.5 \pm 0.5^\circ C$ (b) Comparison between specific pore volumes in ABs and specific volume of water absorbed at 584h. Data was obtained from one run.
3.2.2 Characterization of activated AB-based MPLs

Figure 3.5 shows a general increase in oxygen permeability as the porosity of the carbon samples increases. The permeability of the carbon fiber paper (SGL 29BA) is high since there is no additional sublayer with lower overall porosity to restrict the diffusion of oxygen. As the treatment time and surface area increases for the AB particles, there is a clear trend of increasing oxygen permeability. AB25, when used in the MPL, showed the highest oxygen permeability (2.21 × 10^{-12} m^2). As the development of through pores are not indicated through the TEM images and N2 isotherms, the increase in oxygen permeability is likely caused by widening of the spaces within the agglomerates and aggregates of the AB particles as a result of an increase in surface roughness on the AB primary particles.

![Figure 3.5 Oxygen permeability values of GDLs with and without an MPL determined using the Darcy equation](image)

Figure 3.5 Oxygen permeability values of GDLs with and without an MPL determined using the Darcy equation
To study the possibility of the widening of spaces within the agglomerates and aggregates within the structure of activated AB particles, several GDLs were analyzed using mercury porosimetry and the results are shown in Figure 3.6. Overall, the pore size distribution of the samples is similar with the exception of the 0.03 to 0.1µm region where the presence of the MPL introduces a series of new peaks (Figure 3.6b). In this region, no peaks were observed for SGL29BA but peaks were present for both the AB0- and AB25-based MPLs. The magnitude of pores in this range also indicate that these are the pores arising from the spaces within the agglomerates and aggregates of AB.66 Based on Figure 3.6b, there is an additional peak for the AB25-based MPL sample indicating that there is an additional pore size range present in the structure of the carbon black. The presence of this additional pore could be contributing to the increased oxygen permeability through the GDL through the introduction of an additional pathway for oxygen transport which was observed in Figure 3.5.

The broad peak in the 100µm region arises from the pores between the carbon fibers in the SGL 29BA. The introduction of MPL causes partial filling of these pores with MPL material which leads to a slight shift in the peak towards a smaller mean pore size. Another prominent region is the 0.5 to 2 µm region, where more intense peaks are observed for the samples with MPL. The pores in this region can be attributed to the smaller pores between the carbon fibers or pores created by the PTFE coating on the fibers (Figure 3.6e) and the presence of cracks on the MPL (Figure 3.6f).
Figure 3.6 (a) Specific pore size distributions of SGL29BA (No MPL) and AB-based MPLs (b) Zoomed specific pore size distributions of the samples in the pore size range of 0.02 and 0.1 µm (c-d) Cross-section SEM images of SGL29BA and SGL29BA + AB25 (e-f) Surface SEM images of SGL29BA and SGL29BA + AB25 with higher magnified image (inset)
Since the hydrophilic behavior of the AB particles undergo some changes during the activation process, the wettability of the AB-based MPLs was studied using the sessile drop method. Based on the results in Figure 3.7, there was no clear trend observed on the impact of AB carbon porosity on the wettability of the MPLs. As the percentage of PTFE in the MPL slurry was kept constant for all the MPLs in this study, the hydrophobic effect of the PTFE may be likely masking the effect of the changes in hydrophilicity of the AB carbons in the MPL. In addition, this method may also not be sensitive enough to observe the small changes of AB hydrophilicity (Figure 3.4) as illustrated by the error bars.

Figure 3.7 Wettability of the various GDLs (MPL side) used in this study. Contact angles on the left and right side of the droplets are reported.
The study of the wettability of compressed AB samples was also attempted by using the sessile drop method. It was found that the compressed AB powders (36 MPa for 10 min) which formed thin and dense pellets cracked easily upon removal from the die press machine. In addition, Li et al. suggested that the sessile drop method is not suitable to study the wettability of carbon powders due to the relatively weak interaction between carbon powders. The particles can move under an external force which results in inconsistent contact angle values obtained. The authors employed contact angle kinetics (CAK) to observe the contact angles under camera for a period of time instead of an arbitrary time in the sessile drop method. This method could be used in the future to examine the wettability of the activated AB samples.

3.2.3 Single cell PEMFC performance of AB MPLs

Figure 3.8a shows the polarization curves of single cell measurements for the different MPLs examined. The polarization data show similar performance in the kinetic region (<200 mAcm\(^{-2}\)) but noticeable differences in the mass transport region. This is expected as the nano-structural changes, induced in the carbon particles through the activation process, impact the surface morphology of the AB particles. At a current density of ~2000 mAcm\(^{-2}\), the best polarization performance was obtained from the AB5 (~0.64 V) and AB0 (~0.62 V) while the lowest performance was obtained from the AB25 sample (~0.56 V). Figure 3.8b shows that in general performance in the mass transport region degrades with increasing AB activation time of the particles.
Figure 3.8 (a) IR-corrected voltage polarization performance of the different GDLs (b) Summary of voltage at selected current densities. Stoichiometry was set to 1.5 and 2 for hydrogen and air respectively, cell temperature = 80°C, gas and humidifier temperature = 80°C, gas pressure = 150 kPag. Note: Two different MEAs were tested for SGL29BA+AB5 for reproducibility.
The different MPLs studied here have similar microstructure because similar MPL preparation technique and the same carbon type are used. Differences in the performance, therefore, can be largely attributed to the differences in the textural carbon porosity. Black Pearls 2000, which has high micropore content, has shown high mass transport losses when compared to AB and this is attributed to the increased hydrophilic properties. Similarly, the AB samples which have been activated longer have a higher volume of pores which contributes to the increased occurrence of capillary condensation of water according to the Kelvin equation.

It is important to note that the more porous AB samples resulted in increased MPL permeability to oxygen, which would delay the onset of flooding effects in the fuel cell membrane electrode assembly. In this case, the textural pores appear to form water pooling sites which promote further water accumulation to impede the removal of water through the MPL leading to flooding issues. From the water vapor sorption studies, one would expect AB15-based MPL would have experienced the highest mass transport losses. However, AB25 which has the largest effective pore volume has more of these water pooling sites leading to higher water accumulation capacity within the MPL. This subsequently results in flooding and poorer water management under conventional operating condition of 80°C and 100%RH.

3.3 Summary

The impact of textural carbon porosity or surface roughness, created through CO\textsubscript{2} activation, on the polarization performance of a single cell PEMFC was reported. As the MPL carbons used are of the same carbon type, delineation between carbon aggregate morphology and overall surface area was possible. Increasing the 900°C activation time with CO\textsubscript{2} resulted in increasing carbon porosity through increased surface area and pore volume. Pore size distribution
of the samples showed an increase in micropores, followed by a rise in mesopores (~3.5 nm), which indicated the occurrence of micropore widening with a longer activation period. The activated AB samples also showed an increase in hydrophilic behavior with a larger increase in water vapor absorbed under similar conditions. The surface wettability of the AB-based MPLs were similar and no noticeable differences could be observed in terms of the contact angles obtained. However, increasing oxygen permeability was observed for MPLs fabricated with more porous ABs and this is caused by the introduction of additional pore sizes within the agglomerated structure of AB as shown in the mercury porosimetry studies. Fuel cell test results showed that MPLs fabricated from carbons with higher porosity had reduced mass transport performance. Even though higher porosity carbons result in GDLs with higher oxygen permeability, this advantage is offset by the presence of small textural pores which promote water saturation. The present work suggests that lower porosity carbon should be used under these conditions.
Chapter 4: Study on the impact of pore size of carbons in MPL through pore size engineering of colloid imprinted carbons (CICs)

4.1 Introduction

In this chapter, the results from the synthesis of CICs with different pore sizes and application of CICs as the MPL conductive material are discussed. Firstly, the impact of the colloidal silica template size and silica to mesophase pitch ratio on the CIC nanostructure are covered. Next, the chemical and physical properties of the CICs from various characterization methods are discussed along with the single cell fuel cell performance of the CIC-based MPLs.

4.2 Results and discussion

4.2.1 Impact of colloidal silica (CS) diameter on CICs

The structure of the synthesized CICs with different colloidal silica (CS) sizes are shown in Figure 4.1 through SEM and TEM micrographs. Since there were no CS nanoparticles to imprint on the mesophase pitch for CIC0 (Figure 4.1a and Figure 4.1e), no distinct pores were formed in the microstructure of the resulting carbon. As a result, CIC0 has a smooth and low porosity structure as shown in Figure 4.1a. From the images, it is apparent that CICs have nanopores which correspond to the diameter of the CS templates used in the synthesis. MP which is composed of polycyclic aromatic hydrocarbons (PAHs) assembles into a liquid-crystalline state, has softening points which allows the precursor to melt and subsequently fill into interstitial spaces. The arrangement of CS spheres in a packed manner results in a templated ordered pattern on the structure of the resulting CICs. The spherical uniform pores on the CICs observed are the result of the monodispersity of the CS particles involved in the templating process.
Figure 4.1 (a-d) TEM images of CIC0, CIC12 2:1, CIC22 2:1, CIC50 2:1 respectively e-h) SEM images of CIC-12 2:1, CIC-22 2:1, CIC-50 2:1 respectively
Figure 4.2a illustrates the N\textsubscript{2} sorption isotherms of the CICs synthesized with different CS diameters and samples without any silica templates (CIC0). CIC0 has a type II isotherm indicating that the carbon is nonporous. The low porosity of the CIC0 is also indicated by the minimal nitrogen uptake in the sorption process (<32 cm\textsuperscript{3}/g) in addition to the particle morphology seen through TEM imaging (Figure 4.1a). During the carbonization process, CIC0 undergoes a large volume expansion leading to the formation of large pores in the μm and mm range as shown in Figure 4.3a. The volume expansion up to 10 times the initial volume due to gas evolution occurs during the carbonization process.\textsuperscript{120} It is important to note that this did not occur for other CICs which have been templated with CS nanoparticles as black carbonaceous residues were obtained after carbonization (Figure 4.3b). Similar observations on the large volume expansion of mesophase pitch in the absence of templates were also made by Adelhelm \textit{et. al.}\textsuperscript{121}. When the silica template was present, the growth perpendicular to the graphene plane (L\textsubscript{c}) was hindered by the confining geometry of the template and as a result no large volume expansion was observed.\textsuperscript{121}
Figure 4.2 (a) N\textsubscript{2} sorption data for the various CICs synthesized with colloidal silica to mesophase pitch mass ratio of 2:1 (b) BJH pore size distribution for the CICs (adsorption branch). CIC0 was included as a reference for comparative reasons.

CIC12, CIC22 and CIC50 all show a type IV isotherm with H1/H3 hysteresis indicating the presence of mesopores in the structure\textsuperscript{122} similar to the CICs synthesized by Banham et. al.\textsuperscript{123}. The narrow cylindrical shape of the isotherms which is unique to type H1 hysteresis at higher
partial pressures (>0.7) indicates the existence of a narrow range of uniform mesopores in the CICs. As the CS particles with uniform diameter imprint themselves on the surface of the mesophase pitch, this results in uniform pore structure on the CICs. It can also be argued that the CICs have some extent of macroporosity as indicated by the shape of the isotherm at a partial pressure close to 1, where no saturation was observed. This feature is unique for type H3 hysteresis where macropores may be found in the pore networks of the CICs leading to incomplete pore condensation. The presence of macropores may be due to the agglomeration of CS during the imprinting step leading to pores larger than the individual colloidal silica particles or larger cracks in the structure of the CIC. Other factors could also be the collapse of the thin walls between the pores and a range of particle sizes found in the colloidal silica suspensions.119

Figure 4.3 (a) Photographs of CIC0 synthesized without the presence of colloidal silica templates after carbonization. (b) Photograph of CIC12 10:1 after carbonization. Both samples were carbonized under nitrogen at 900°C (2 h)
The BJH pore size distributions of the CICs are shown in Figure 4.2b. The adsorption branch of the BJH pore size distribution was used in this case as the smaller centered peaks for the desorption branch shown in Figure 4.4a arises from the pore necks formed between two adjacent imprinted pores. This results in the formation of a network of interconnected pore necks with a smaller pore size reflected in the desorption phase due to the pore blocking phenomena. Some of these pores can also be observed in the enlarged SEM image in Figure 4.4b for CIC50 2:1.

![Desorption branch of the BJH pore size distribution for CICs synthesized with a mesophase pitch to silica mass ratio of 1:2. (b) Magnified image of CIC50 2:1 illustrating the connecting pores between adjacent templated pores](image_url)
The N\textsubscript{2} sorption data show that these types of pores are present in all the templated CICs. Again, the absence of nanoporosity in the CIC0 is further confirmed by the lack of peaks in the distribution. The peaks of the pore size distribution in Figure 4.2b centers slightly larger than the nominal particle sizes of the colloidal silica templates provided by the manufacturer. To verify the pore sizes of CICs, the particle size distribution of colloidal silica particles used as spherical templates were evaluated using image analysis of TEM images shown in Figure 4.5.

![TEM images of colloidal silica particles](image)

**Figure 4.5** (a-c) TEM images of Ludox\textsuperscript{®} HS-30, Ludox\textsuperscript{®} TM-40 and NexSil™ 85-40 respectively (d-f) The particle size distribution and cumulative percentage of particle size for respective colloidal silica particles

Based on the analysis of 70-100 individual particles using image analysis, the mean particle sizes obtained were 17±2 nm, 30±4 nm and 69±11 nm for Ludox\textsuperscript{®} HS-30, Ludox\textsuperscript{®} TM-40 and
NexSil™ 85-40 respectively. These values deviate slightly from the nominal colloidal silica particle sizes given for the three colloidal silica suspensions were 12 nm, 22 nm and 50 nm respectively by the manufacturers. The peaks of the BJH pore size distribution of the CICs in Figure 4.2b agree with the colloidal silica particle sizes determined through image analysis. However, the pore size obtained from the BJH analysis for CIC50 (~100 nm) was significantly larger than the particle size of the template used for the synthesis which was determined to be 69±11 nm. A possible explanation for this is the applicability of the Kelvin equation that forms the basis of the BJH method which has practical limitations at high partial pressures close to unity. Small changes in conditions at these partial pressures leads to considerable impact on the calculated value of the pore radius which poses a practical limit for the accuracy of obtainable pore sizes. 124,125 As a result, the pore sizes of CIC50 2:1 was determined through the image analysis of 100 pores of Figure 4.1h and the pore size was determined to be 58±8 nm which was close to the template size.

4.2.2 Impact of silica to mesophase pitch ratio on CICs

The colloid-imprinting process depends on the arrangement of CS nanoparticles leaving voids to be filled by the “softened” mesophase pitch during the imprinting process.97 Hence, the amount of silica present during the imprinting step plays a significant role in the resulting structure of CICs. The N₂ sorption isotherm and the BJH pore size distribution of various CICs synthesized with silica to carbon precursor mass ratios of 2:1, 5:1 and 10:1 are shown in Figure 4.6.
Figure 4.6 (a,c,e) N₂ sorption isotherm for CIC12, CIC22 and CIC50 with silica to mesophase pitch mass ratios of 2:1, 5:1 and 10:1 (b,d,f) BJH pore size distribution for the various CICs (adsorption branch).
It can be observed that the nitrogen sorption isotherms (Figure 4.6a,c,e) for the 3 types of CICs show the presence of hysteresis and no saturation at high partial pressures like the isotherms shown in Figure 4.2a indicative of a Type H1 and H3 hysteresis. Again, the mesopores arise from the size of the CS nanoparticles and interconnected pore necks between adjacent templated pores. The macropores shown by the absence of saturation at partial pressures close to 1 may be due to agglomeration of CS nanoparticles or collapse in templated pores. The shape of the isotherm for CIC-50 at different ratios resembles more of a H3 hysteresis. This is because the templated pores are in the macropore range (>50 nm) and the source of mesopores are the pore necks smaller CS particles (Figure 4.5c). With the increase in silica to precursor ratio, the uptake of nitrogen increases for all the CICs, indicating higher total pore volume and surface area. This results from the higher number of CS particles available to participate in the imprinting process leading to greater number of pores being formed.

The BJH pore size distribution of the various CICs synthesized with different silica to precursor ratios are also shown in Figure 4.6b,d,f. The distribution for the 3 types of CICs becomes wider as the ratio of silica to precursor is increased. This could be attributed to the occurrence of CS agglomeration and the collapse of pore walls leading to wider pore size distributions. Also, since the diameter of the CS nanoparticles follows a distribution, a larger sample size would reflect a more accurate particle size distribution of the particles. In this case, the particle size distribution of the CS particles may be wider with a larger sample size. As a result, this is reflected in the size distribution of the pores found in the CICs after the synthesis.

The porosity data of the synthesized CICs in this work are shown in Table 4.1. The contribution of microporosity to the overall pore volume of the CICs is low with the highest percentage being 2.3% for CIC12 2:1. The use of mesophase pitch as a precursor for carbon
synthesis has been shown in literature to yield templated carbons with low microporosity compared to precursors such as furfuryl alcohol, acrylonitrile and phenol-formaldehyde. Therefore, it is evident that the use of mesophase pitch as a carbon precursor is advantageous in engineering carbons with specific pore size distributions avoiding the introduction of microporosity.

Table 4.1 Nitrogen sorption data for the various synthesized CICs with different CS sizes and silica to mesophase pitch ratios

| Sample     | \( S_{\text{BET}} \) \(^{a} \) | \( V_{\text{total}} \) \(^{b} \) | \( V_{\text{meso}} \) | \( V_{\text{meso}} \) % | \( V_{\text{micro}} \) \(^{c} \) | \( V_{\text{micro}} \) % | Pore size | nm |
|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------|
| CIC0       | 15              | 0.050           | 0.047           | 94.0            | 0.003           | 6               | -         |
| CIC12 2:1  | 350             | 1.128           | 1.102           | 97.7            | 0.026           | 2.3             | 14.5      |
| CIC12 5:1  | 439             | 2.175           | 2.149           | 98.8            | 0.026           | 1.2             | 17.7      |
| CIC12 10:1 | 639             | 2.465           | 2.441           | 99.0            | 0.024           | 1.0             | 17.6      |
| CIC22 2:1  | 315             | 1.473           | 1.454           | 98.7            | 0.019           | 1.3             | 28.7      |
| CIC22 10:1 | 367             | 1.754           | 1.746           | 99.6            | 0.007           | 0.4             | 29.3      |
| CIC50 2:1  | 113             | 0.744           | 0.739           | 99.3            | 0.005           | 0.7             | 58.8 \(^{d} \) |
| CIC50 5:1  | 220             | 1.459           | 1.457           | 99.9            | 0.002           | 0.1             | -         |
| CIC50 10:1 | 267             | 0.988           | 0.982           | 99.4            | 0.006           | 0.6             | -         |

\(^{a}\) Determined in the partial pressure range of 0.07 < \( P/P_{0} \) < 0.3
\(^{b}\) Obtained from \( N_{2} \) isotherm at \( p/p_{0} = 0.996 \)
\(^{c}\) Determined using t-plot method
\(^{d}\) Determined through image analysis of SEM image (Figure 4.1h)

For the three types of CICs, the BET surface area increases with an increase in the silica to mesophase pitch ratio (Table 4.1). This is purely due to the presence of a higher number of CS nanoparticles available for imprinting of pores. Theoretically, the highest packing density that can be attained by spheres of the same diameter is 0.74 \(^{128} \). Assuming that the density of carbon is 1.6 g/cm\(^3\) and a packing density of 0.74, the theoretical surface areas of the CICs synthesized can be calculated using the following equations

\[
\text{Specific surface area} = \frac{4 \pi r^2}{3 \pi r^3 \rho} = \frac{3 \left[ m^2 \right]}{r \rho \left[ g \right]}
\]

Equation 4.1
where \( r \) is the radius of the CS particle and \( \rho \) is the density of carbon

For comparative reasons, the carbon density value was chosen based on the same values used in the original work of Li et al.\(^{97} \) and the CIC modeling work of Banham et al.\(^{123} \) The calculated surface area of CIC12, CIC22 and CIC50 are 629 cm\(^2\)/g, 357 cm\(^2\)/g and 155 cm\(^2\)/g respectively. Generally, the CS to mesophase pitch ratio of 10:1 resulted in the surface area values closest to that of the theoretical surface area as shown in Figure 4.7. This indicates that there exists a minimal ratio at which the CS nanoparticles must be present to form the densest packing configuration for the templating process in the CIC synthesis. For CIC12 and CIC22, the silica ratios of 2:1 and 5:1 yielded surface area values that were lower than the calculated values. However, this was not the case for CIC50 where the lowest ratio of 2:1 had a surface area of 113 cm\(^2\)/g which was the closest to the calculated surface area (155 cm\(^2\)/g). A possible explanation is the larger spread of the particle size distribution of the NexSil\(^{TM}\) 85-40 CS which has distinctly smaller particles present in the colloid (Figure 4.5c). The packing of CS spheres then deviates from the maximum packing density of 0.74 as the particles of distinctly different sizes are packing together leading to more tightly packed spheres with less voidage (Figure 4.8). Subsequently, the surface area of the CIC is larger than when uniformly sized CS spheres are present.
Figure 4.7 Theoretical surface area and BET surface area of the various CICs synthesized. Surface area values of CICs are plotted based on the mean CS nanoparticle size determined through TEM.

The paragraph before highlights the importance of the ratio of silica to mesophase pitch in the synthesis of CICs. Loosely packed CS spheres have higher voidage which results in irregular carbon wall thickness and isolated pores in the resulting CICs as illustrated in Figure 4.8. In addition to the lower number of CS particles present for templating, this occurrence also leads to lower surface area of templated carbon.
4.2.3 Impact of heat treatment of CICs

To reduce the number of variables in the study, only CICs with an MP to colloidal silica ratio of 1:2 were heat treated to compare the impact of heat treatment on CICs. The structural morphology data of the CICs are compared in Table 4.2.
Table 4.2 Nitrogen sorption data for the non-heat treated and heat treated CICs at 1100°C for 2h in N₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>SBET(^a)/m²/g</th>
<th>V(_{\text{total}})/cm³/g</th>
<th>V(_{\text{meso}})/cm³/g</th>
<th>V(_{\text{meso}})/%</th>
<th>V(_{\text{micro}})/cm³/g</th>
<th>V(_{\text{micro}})/%</th>
<th>Pore size/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIC12 2:1</td>
<td>350</td>
<td>1.128</td>
<td>1.102</td>
<td>97.7</td>
<td>0.026</td>
<td>2.3</td>
<td>14.6</td>
</tr>
<tr>
<td>CIC12 2:1 HT</td>
<td>360</td>
<td>1.129</td>
<td>1.097</td>
<td>97.2</td>
<td>0.031</td>
<td>2.7</td>
<td>14.5</td>
</tr>
<tr>
<td>CIC22 2:1</td>
<td>315</td>
<td>1.473</td>
<td>1.454</td>
<td>98.7</td>
<td>0.019</td>
<td>1.3</td>
<td>28.8</td>
</tr>
<tr>
<td>CIC22 2:1 HT</td>
<td>322</td>
<td>1.580</td>
<td>1.552</td>
<td>98.2</td>
<td>0.028</td>
<td>1.8</td>
<td>28.7</td>
</tr>
<tr>
<td>CIC50 2:1</td>
<td>113</td>
<td>0.744</td>
<td>0.739</td>
<td>99.3</td>
<td>0.005</td>
<td>0.7</td>
<td>58.8(^d)</td>
</tr>
<tr>
<td>CIC50 2:1 HT</td>
<td>111</td>
<td>0.781</td>
<td>0.777</td>
<td>99.5</td>
<td>0.004</td>
<td>0.5</td>
<td>55.0</td>
</tr>
</tbody>
</table>

\(^a\) Determined in the partial pressure range of 0.07 < P/P\(_0\) < 0.3
\(^b\) Obtained from N\(_2\) isotherm at P/P\(_0\) = 0.996
\(^c\) Determined using t-plot method
\(^d\) Determined through image analysis of SEM images (Figure 4.1)

Generally, the heat treatment process did not result in large changes to the nanostructure of the CICs, with only small increase in microporosity for CIC12 and CIC22. These changes can be attributed to the partial gasification of the surface carbons during the heat treatment process.\(^{129}\)

The composition of the precursor, CICs and heat-treated CICs determined through elemental analysis are shown in Table 4.3. The precursor, MP, is mainly composed of carbon(C) and hydrogen(H) since MP is composed of a complex mixture of PAHs arranged in a liquid crystalline phase or mesophase state.\(^{120}\) The low percentage of sulfur found in the MP is due to the nature of the precursor used for the MP production which is naphthalene.

Elemental analysis also revealed that the resulting CICs have lower H content and higher C content with the addition of oxygen(O). During carbonization, the properties of the precursor vastly changes as reactions such as condensation and dehydrogenation of mesogen molecules forms larger aromatic compounds in the liquid crystal phase.\(^{120}\) This results in the formation of a carbon rich residue with anisotropy. The increase in oxygen content can be attributed to the
formation of oxygen containing functional groups at unsaturated carbon sites at the edge of basal planes in the structure.\textsuperscript{130} Some of these groups include carboxyl, lactone, carbonyl and phenol.\textsuperscript{130}

Subsequent heat treatment of the CICs under nitrogen at 1100°C resulted in the removal of oxygen containing groups reflected by the decrease in the O percentage in the carbons. During this process, the polar groups decompose to form compounds such as CO and CO$_2$. Figueiredo \textit{et al.} concluded from a series of studies that heat treatment of active carbon at different temperatures resulted in the complete removal of specific functional groups; carboxylic anhydrides at 600°C, lactones and phenols at 750°C and carbonyls and ethers at 1100°C.\textsuperscript{131} The presence of O in the heat treated samples may likely be due to the inevitable leak of moisture from the environment forming surface oxygen complexes.\textsuperscript{132}

### Table 4.3 Elemental composition of mesophase pitch (precursor) and the synthesized CICs before and after heat treatment at 1100°C under N$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
<th>O (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesophase pitch (Precursor)</td>
<td>94.86</td>
<td>4.33</td>
<td>0.06</td>
<td>0.74</td>
<td>0.01</td>
</tr>
<tr>
<td>CIC0</td>
<td>96.56</td>
<td>0.00</td>
<td>0.06</td>
<td>0.00</td>
<td>3.38</td>
</tr>
<tr>
<td>CIC12-2:1</td>
<td>96.32</td>
<td>0.00</td>
<td>0.07</td>
<td>0.00</td>
<td>3.61</td>
</tr>
<tr>
<td>CIC12-2:1HT</td>
<td>97.76</td>
<td>0.00</td>
<td>0.20</td>
<td>0.00</td>
<td>2.04</td>
</tr>
<tr>
<td>CIC22-2:1</td>
<td>95.73</td>
<td>0.00</td>
<td>0.09</td>
<td>0.00</td>
<td>4.18</td>
</tr>
<tr>
<td>CIC22-2:1HT</td>
<td>97.89</td>
<td>0.00</td>
<td>0.21</td>
<td>0.00</td>
<td>1.90</td>
</tr>
<tr>
<td>CIC50-2:1</td>
<td>96.07</td>
<td>0.00</td>
<td>0.44</td>
<td>0.00</td>
<td>3.49</td>
</tr>
<tr>
<td>CIC50-2:1HT</td>
<td>98.73</td>
<td>0.00</td>
<td>0.36</td>
<td>0.00</td>
<td>0.52</td>
</tr>
</tbody>
</table>

$^a$ Oxygen percentage was determined by subtracting the C, H, N, and S masses from the sample mass.

As the process of heat treatment results in the removal of oxygen containing functional groups of the CICs, the hydrophilic property of the CICs would shift towards being more hydrophobic as reported by Li \textit{et al.}\textsuperscript{119} Figure 4.9a-b illustrate the change in mass of both heat treated and non-heat treated CICs when exposed to a similar vapor pressure of water at room
temperature (T= 21.5±0.5°C) over time. The non-heat treated CICs are generally more hydrophilic as observed from the larger uptake of water by the samples over time. For all the CICs, CIC12 2:1 has the highest uptake of water with about a 95% increase in mass, and the non-porous CIC0 has the lowest uptake of water. The low surface area and low pore volume nature of CIC0 results in the lowest adsorption capacity of water.

![Graph](image)

**Figure 4.9 (a-b) Water vapor sorption data for non-heat treated and heat treated CICs performed at room temperature ((T= 21.5±0.5°C) (c-d) Comparison of specific total volume of CICs with the specific volume of water absorbed at 600h**

The impact of pore size on the overall accumulation of water in the pores can be explained by the Kelvin equation.
\[
\ln \frac{P}{P_0} = -\frac{2\gamma V_m}{rRT} \cos \theta
\]

Equation 4.2

where \( \gamma \) is the surface tension of water, \( \theta \) is the contact angle of water on the pore wall, \( V_m \) is the molar volume of condensed water, \( r \) is the pore radius, \( P \) is the partial pressure of water vapor and \( P_0 \) is the saturation pressure of water vapor in the pore. From the equation, under the same water vapor pressure, the volume of condensed water varies linearly with pore size for hydrophilic pores (\( \theta < 90^\circ \)). As a result, CIC12 2:1 observed the highest uptake of water under the similar conditions compared to the rest of the CICs. The removal of oxygen containing functional groups on the CIC surfaces during the heat treatment process results in higher \( \theta \) values towards 90\(^\circ\). The heat treated CICs result in a lower volume of adsorbed water vapor in the pores, illustrating a noticeable decrease in hydrophilic behavior as shown in Figure 4.9b.

The specific volume of water absorbed by the CICs was compared with the specific pore volumes based on the porosity data obtained in Table 4.2, and are shown in Figure 4.9c-d. Assuming that the total pore volume in the CICs are available for water uptake, it can be observed that the pores in the CICs are only partially filled under the experimental conditions with the exception for CIC0. Similarly, this is also observed for the more hydrophobic heat treated CICs. For CIC0, the amount of water absorbed was higher than the specific pore volume reported by the N\(_2\) sorption analysis (Table 4.2). Based on the morphology of the sample seen in Figure 4.1a and Figure 4.1e, the smooth texture of CIC0 likely indicates that the water absorbed would reside in the pores between the CIC0 particles after the pores in the CICs are filled up. As this result only reflects the water sorption behavior of the CICs at one temperature and one relative humidity, a further increase in temperature to increase the vapor pressure of water would result in higher accumulation of water in the CICs.
Figure 4.10 shows the XRD patterns for the various CICs with and without heat treatment. From the figure, the heat treated CICs show a small increase in intensity and shift towards a larger angle for the (002) graphite peak which represents the interlayer scattering of the graphene stacks.\textsuperscript{121} The heat treatment process results the removal of heteroatoms as the turbostratic structure transitions towards a graphitic structure. However, the change in peak intensity for the heat treated samples was not pronounced as the carbonization temperature was 900°C and the heat treatment temperature was 1100°C. Truly graphitic structures can only be achieved when graphitizable carbons are heated above 2000°C while full graphitization is attained at 3000°C.\textsuperscript{118} The heating process nevertheless increases the crystallite size of the heat treated CICs as shown in Table 4.4.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.10}
\caption{Figure 4.10 XRD patterns for the CICs studied in this work}
\end{figure}
### Table 4.4 Peak position of (002) and crystalline parameters of the CICs and the heat treated CICs at 1100°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>002 peak position</th>
<th>Interlayer spacing, $d_{002}$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Stack height, $L_c$&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Average layer size, $L_a$&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Average number of layers per stack, $n_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIC0</td>
<td>24.96 °</td>
<td>0.357 nm</td>
<td>0.80 nm</td>
<td>1.66 nm</td>
<td>2.2</td>
</tr>
<tr>
<td>CIC12-2:1</td>
<td>24.74 °</td>
<td>0.360 nm</td>
<td>0.79 nm</td>
<td>1.63 nm</td>
<td>2.2</td>
</tr>
<tr>
<td>CIC12-2:1HT</td>
<td>24.90 °</td>
<td>0.358 nm</td>
<td>0.89 nm</td>
<td>1.85 nm</td>
<td>2.5</td>
</tr>
<tr>
<td>CIC22-2:1</td>
<td>24.51 °</td>
<td>0.363 nm</td>
<td>0.77 nm</td>
<td>1.60 nm</td>
<td>2.1</td>
</tr>
<tr>
<td>CIC22-2:1HT</td>
<td>24.95 °</td>
<td>0.357 nm</td>
<td>0.90 nm</td>
<td>1.87 nm</td>
<td>2.5</td>
</tr>
<tr>
<td>CIC50-2:1</td>
<td>24.49 °</td>
<td>0.363 nm</td>
<td>0.74 nm</td>
<td>1.54 nm</td>
<td>2.0</td>
</tr>
<tr>
<td>CIC50-2:1HT</td>
<td>24.92 °</td>
<td>0.357 nm</td>
<td>0.97 nm</td>
<td>2.01 nm</td>
<td>2.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined using the Scherrer equation  
<sup>b</sup> $K_c$ value of 0.89 was used<sup>69</sup>  
<sup>c</sup> $K_a$ value of 1.84 was used<sup>69</sup>

The heat treated CICs show a shift in the 002 peak towards a larger diffraction angle in addition to the enhanced crystallite parameters ($L_c$ and $L_a$). The growth in crystallite size in the perpendicular direction to the planes (stack height) and parallel to the plane (plane size) indicates the role of heat treatment in transitioning the structure towards a more orderly graphitic structure as discussed previously. This also results in an increased number of layers per stack in the crystallites as the interlayer spacing decreases. Interestingly, the diffraction angle for the 002 peak for CIC0 was close to that of the heat treated CICs (Table 4.4) which indicates that the crystalline structure of CIC0 differs from CICs synthesized with CS templates.

Li <i>et al.</i> reported that CICs with larger pore diameter have a larger degree of crystalinity due to the tighter packing of MP molecules on the CS particles facilitated by the lower curvature of larger spheres.<sup>119,133</sup> This was suggested based on the findings in the literature that MP aligns in an orderly way in a vertical orientation and “anchors” to the silica surface during the imprinting step which leaves packed planar graphene sheets in this orientation upon carbonization.<sup>134–136</sup>
However, this trend of increase in crystalinity with increase in pore size was not observed for the non-heat treated CICs but only seen for the heat-treated samples. The silica to mesophase pitch ratio used for these CICs were 2:1 instead of 10:1 ratio and this could have an impact on the resulting crystalite sizes which warrants further investigation.

To reduce the size of the CIC particles for MPL slurry preparation, the respective samples were ball milled under similar conditions. Figure 4.11 illustrates the particle size distribution of the CICs at different stages prior to, and after being ball milled and heat treated.

![Particle size distribution](image)

**Figure 4.11** Particle size distribution of the CICs prior to ball-milling, after ball-milling and after ball-milling and heat treatment. The mean particle size is taken as the peak of the distribution.

The virgin synthesized CIC particles have a larger spread in particle size with mean particle size being around 700 nm. The process of ball milling reduced the mean particle size for CIC12 2:1 and CIC22 2:1 to approximately 70nm based on the peak observed in Figure 4.11. However,
CIC0 particles were smaller than the virgin CICs even before being ball milled (~300 nm). It can also be observed that the ball-milling process did not impact the particle size distribution for CIC0. This could likely be due to the starting particle size distribution of CIC0 prior to ball milling which was much smaller than the other CIC samples. In addition, the physical appearance (Figure 4.3) and particle morphology (Figure 4.1a and Figure 4.1h) of CIC0 which differs from the other CICs may also indicate that the structure changes differently under similar ball milling conditions. The heat treatment process resulted in an increase in particle sizes for CIC12 2:1 and CIC22 2:1. This could be caused by the agglomeration of CIC particles at higher temperature during the heat treatment process.

4.2.4 Single cell PEMFC performance of CIC MPLs

Figure 4.12 shows the polarization performance of the CIC-based MPLs under conventional hot and humid conditions. Among the CICs tested, CIC12 2:1 resulted in the poorest performance with heavy mass transport losses beginning at a current density of 1400 mAcm$^{-2}$ while both CIC22 2:1 and CIC0 show similar performances. For the CICs templated with CS, CIC22 2:1 showed a better performance with a later onset of mass transport polarization at higher current densities. Since the amount of PTFE, MPL thickness and MPL fabrication method are kept the same, the differences observed can likely be attributed to the pore size of the CICs used in the MPL. As shown in Figure 4.9 where CIC12 2:1 has very hydrophilic properties, the effect of flooding would be more pronounced as the MPL would have a high propensity for water accumulation within the pores of the CICs. Conversely, CIC22 2:1 which has a larger pore size results in lower water accumulation within the pores which delays the onset of mass transport with lower water saturation in the MPL. Both CICs, however, show much poorer mass transport
performance compared to the case of no MPL present in the GDL (SGL29 BA). Subsequently, this can be attributed to the hydrophilic nature of the CICs.

Figure 4.12 Fuel cell performance at 100% RH, cell temperature 80°C of CIC-based MPLs (a) raw voltage (b) IR-compensated voltage (c) area normalized HFR at 2.5kHz
Interestingly, CIC0 showed very similar performance to CIC22 2:1 despite having different particle morphology. The water vapor sorption study (Figure 4.9) showed that CIC0 was less hydrophilic than CIC22 2:1 due to the lack of porosity which decreases its hydrophilic behavior leading to lower accumulation of water suggesting that the saturation of water in the MPL would be lower. However, the loading of CIC0-based MPL was significantly higher than the rest of the CIC-based MPLs even though the thickness of the MPLs were kept constant as shown in Table 4.5 indicating differences in particle density. This suggests that the transport of oxygen and water through the MPL is different between the CIC0 and CICs templated with CS (CIC12 2:1 and CIC22 2:1) as a result of the particle morphological differences which impact the pore structure of the MPL.

**Table 4.5 Properties of gas diffusion layers used in the study**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Average thickness</th>
<th>Standard deviation in thickness</th>
<th>Thickness of MPL</th>
<th>Mass of GDL</th>
<th>Mass loading of MPL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µm</td>
<td>µm</td>
<td>µm</td>
<td>g</td>
<td>mg/cm²</td>
</tr>
<tr>
<td>SGL29BA</td>
<td>183</td>
<td>2</td>
<td>-</td>
<td>0.0534</td>
<td>-</td>
</tr>
<tr>
<td>SGL29BA + CIC0</td>
<td>219*</td>
<td>-</td>
<td>36</td>
<td>0.1158</td>
<td>5.1</td>
</tr>
<tr>
<td>SGL29BA + CIC12 2:1</td>
<td>217*</td>
<td>-</td>
<td>34</td>
<td>0.0771</td>
<td>1.9</td>
</tr>
<tr>
<td>SGL29BA + CIC12 2:1HT</td>
<td>219</td>
<td>3</td>
<td>36</td>
<td>0.0741</td>
<td>1.7</td>
</tr>
<tr>
<td>SGL29BA + CIC22 2:1</td>
<td>217</td>
<td>3</td>
<td>33</td>
<td>0.0791</td>
<td>2.1</td>
</tr>
<tr>
<td>SGL29BA + CIC22 2:1HT</td>
<td>216</td>
<td>2</td>
<td>33</td>
<td>0.0715</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*Samples were measured once as the adhesion of carbon to the carbon fiber paper (SGL29BA) was poor*

The performance of the heat treated CIC-based MPLs were also evaluated in a single cell as shown in Figure 4.13. A significant improvement in performance was observed for both CIC12 2:1HT and CIC22 2:1HT as a result of the heat treatment process. As discussed in Section 4.2.3, the heat treatment process results in the removal of oxygen containing functional groups which
decreases the hydrophilic behavior of the CICs causing a lower degree of water condensation in the pores. Accordingly, both heat treated CIC-based MPLs were able to maintain cell potential above 0.6V up to 2000 mAcm\(^{-2}\). It is interesting to note that both of the heat treated CICs show almost identical performance under the same test conditions. Since the CICs are synthesized from the same precursor, this may suggest that the particle nanostructure (i.e., the pores sizes) plays a negligible role affecting the water saturation in the MPL when the pores are more hydrophobic. The cell resistance for the heat treated CIC-based MPLs was also lower than that of non-heat treated samples as shown in Figure 4.13c. The decrease in resistivity in carbonaceous materials like carbon black and anthracites due to heat treatment under chlorine and nitrogen was reported by Stacy et al.\(^{137}\) This was due to the removal of volatile surface functional groups at the periphery of aromatic carbon atoms and the coverage decrease results in a rise in positive charge carriers which decreases resistivity of the carbons.\(^{137}\) Thus, the loss of surface functional groups in CICs (Table 4.3) through the heat treatment process can explain the decrease in MEA resistance during fuel cell testing due to decreased particle resistivity.
The effectiveness of this type of carbon as an MPL material seems to be poor when compared to the performance of the PEMFC without MPL present in the MEA. As MPLs are expected to improve water management under high current density conditions, this suggests that CICs...
may not be good candidate material for MPL application. Possibly, more optimization work may 
be needed.

4.3 Summary

The synthesis of CICs through the variation of CS diameter and CS:MP ratio resulted in 
CICs with vastly different nanostructures. The monodispersity of CS used in the synthesis leads to 
the formation of templated pores with the diameters corresponding to the diameter of the CS 
particles. As the diameter of the CS increased, the surface area of the CIC decreased. The opposite 
trend was observed when the ratio of CS:MP was increased, resulting in CICs with higher surface 
area due to the presence of a greater number of templates. The nanostructure and morphology of 
CICs were significantly affected by the presence of CS templates used in the synthesis. The size 
distribution and the ratio of CS to MP resulted in CICs synthesized with different nanostructures. 
The CICs studied also showed hydrophilic behavior prior to heat treatment consistent with other 
works in the literature. With heat treatment, the CICs underwent the removal of surface oxygen 
functional groups while the nanostructural properties were retained.

Water vapor sorption studies indicated that these functional groups contribute to this 
behavior whereas the heat treated CICs showed only a very small uptake of water vapor under the 
same conditions as virgin CICs. The fuel cell performance of the CIC-based MPLs confirmed 
some of the observations from the water vapor sorption studies where CIC12-based MPL observed 
heavy mass transport losses compared to CIC22-based MPL. CIC0 which had a nonporous 
structure had similar performance to CIC22 which suggest that carbons used in the MPL should 
either be low porosity or have large pores (>30nm) to reduce mass transport effects in the PEMFC 
under hot and humid conditions. Improved performance was observed for MPLs based on heat
treated CICs where similar performances were observed for both CIC12 and CIC22. This highlights another strategy to reduce the hydrophilicity of the carbons used in the MPL, that is heat treatment to remove surface oxygen containing functional groups and enhance the crystallinity of the carbons. Overall, the findings suggest that the porosity of carbons used in the MPLs has a noticeable influence on the performance of PEMFCs when the CICs are hydrophilic. Upon heat treatment, the impact of pore size is negligible as the CICs become more hydrophobic resulting in lower accumulation of water.
Chapter 5: Conclusions and recommendations

5.1 Conclusions

Chapter 3 describes the impact of carbon porosity modification through physical activation and its effect on the MPLs of PEMFCs. The experimental attempt to delineate the impacts of carbon porosity from the different types of carbons with different physical properties was achieved through the activation of virgin AB using a CO$_2$ activation process at different durations. In order to study the changes that occurred to the ABs, the powders were characterized to obtain information on the porosity and wettability. Further characterizations on the fabricated MPLs based on the activated ABs were done in addition to fuel cell testing. The key findings are:

- Increasing activation time from 5 to 25 hours yielded ABs with increasing porosity in terms of BET surface area and pore volume
  - The changes in nanostructure of ABs occurred through the generation of micropores which coalesced to form mesopores when activated for longer durations

- More porous ABs showed higher water uptake capability under the same condition compared to lower porosity ABs
  - The creation of pores from activation gives rise to more water vapor condensation sites available to increase water saturation. The filling of smaller pores occurs before the larger pores as outlined by the Kelvin equation

- Increased oxygen permeability observed for MPLs with increasing AB porosity
  - The activation process resulted in the introduction of new pores between the interstitial spaces within the agglomerates which enhances the permeability of oxygen through the MPL. Mercury porosimeter analysis of the GDLs revealed the presence of an additional pore in the 50nm region in the MPL
- MPLs fabricated with ABs with higher porosity saw an earlier onset of mass transport loss in the polarizations compared to ABs with lower porosity under hot and humid conditions during FC testing
  - It is hypothesized that the creation of additional pores through activation introduces pooling locations which facilitates the condensation of water vapor within the bulk of the MPL leading to increased water saturation impeding oxygen transport.

The low surface area AB which is reported by various authors to have a superior performance when used as an MPL carbon material also offers a great starting point for porosity modification to study the impact of carbon porosity. Consistent with the observations in the literature with more porous carbon blacks, the more porous samples exhibited an increase in mass transport losses. The experimental findings exemplify that under hot and humid conditions, carbons with lower percentage of intraparticle or textural pores should be preferred to suppress the condensation of water vapor in the pores of the carbons in the MPL. This would lead to the minimization of the water saturation in the GDL and help to delay flooding effects.

Chapter 4 describes the synthesis and application of CICs as model carbons with tunable properties based on templating conditions such as CS diameter and CS to MP ratio. The goal of this chapter was to engineer pores of different sizes on CICs to study the impact of pore size of carbons in the MPL on the overall performance of the PEMFC. Synthesized CICs were characterized for porosity and hydrophilic properties. Post treatment of CICs was conducted by heat treatment to remove surface functional groups and to study the effects on hydrophobicity and
crystallinity. The fabricated GDLs containing CICs in the MPL were tested in a single cell fuel cell to study its impacts on the polarization performance. The key findings are as follows:

- The presence of CS during the synthesis results in templated pores on the CICs reflecting the size of the CS diameters used
  - CICs were observed to have unique templated pore features as a result of the monodispersity of the CS particles imprinting on the surface of MP. The pore types on the CICs are predominantly meso- and microporous with minimal microporosity
- The absence of CS during the synthesis process results in carbons with low surface area and pore volume
  - The physical appearance and crystalline parameters differ from the other CICs indicating that the presence of CS influences the structure and properties of CIC greatly
- The ratio of CS to MP also plays a significant role in determining the nanostructure of the resulting CICs.
  - Increase in surface area and pore volume was generally observed when the ratio of CS to MP was increased for the CICs. The particle size distribution of CS also impacts the arrangement of particles during the imprinting steps where broader distributions result in non-uniform arrangements
- Heat treatment of CICs resulted in the removal of oxygen functional groups rendering the CICs more hydrophobic as observed through water vapor sorption studies.
  - CICs with smaller pores (CIC12) observed the highest uptake of water vapor while the effect of pore size on the adsorption capability diminished when samples were
heat treated. This shows that CICs are intrinsically hydrophilic which was consistent with reports in literature.

- Increased crystallinity of CICs observed from the heat treatment process
  - Enhanced lattice parameters revealed through XRD analysis show that the CIC crystalline structures transition towards being more graphitic during heat treatment.

- MPLs fabricated with CICs with smaller pore size (CIC12) which are more hydrophilic result in greater mass transport losses when compared to CICs with larger pore size (CIC22) or non-porous (CIC0) under hot and humid conditions.
  - Smaller pores have a higher propensity for the condensation of water vapor under the same conditions as governed by the Kelvin equation. This suggests that the water saturation in the MPL would be enhanced when carbons with much smaller pores are utilized (e.g., high surface area carbons such as BlackPearls200).

- Heat treated CICs show enhanced polarization performance especially in the mass transport region due to their more hydrophobic behavior.
  - Later onset of mass transport losses observed for the heat treated CIC-based MPLs as the hydrophobic CICs lead to lower saturation of water in the pores thus decreasing the propensity of flooding in the MPL.

- The effect of the hydrophobic nature of the heat treated CICs masks the contributions of pore size of CICs on the mass transport polarizations.
  - Similar polarization performances of CIC12HT and CIC22HT suggests that the hydrophilic/hydrophobic surface nature of the particles plays a pivotal role in increased water saturation even with the presence of small pores.
The CIC is a versatile family of carbons that offers a great degree of tunability based on synthesis parameters which allows it to be a suitable model material to study the impact of pore size on MPL performance. Although the structure and pore sizes in the CICs differ from carbon blacks, this approach allows for greater control of pore morphology with the same precursor in an effort to minimize the differences between porous carbons. The best polarization performance involving MPLs with CICs were MPLs with heat-treated CICs which showed similar performance to the performance of an MPL-less MEA. This suggests that optimization work may be required to fully elucidate the suitability of CICs as candidate materials for MPL carbons. Nevertheless, this thesis demonstrated for the first-time, application of CICs as an MPL carbon material in PEMFCs to the author’s best knowledge. This thesis also provides some basis for the possible application of CICs for MPLs.

5.2 Recommendations

The findings from this thesis revealed several interesting facets that could be explored to develop a further understanding on this topic. Some of the recommendations for future work are as follows:

- Using more sophisticated characterization techniques like dynamic vapor sorption (DVS) will enable the study to be conducted at different saturation pressures to obtain water vapor sorption isotherms for the carbon materials. This will allow a more detailed elucidation of the impact of porosity on sorption behavior. The wettability of AB and CIC samples were studied using a single saturation pressure of water at 21°C by manually weighing the vials containing the carbon samples. By using the DVS method, tests can also be conducted more accurately and quickly compared to the setup used in this study. In addition, the
fabricated MPLs on the SLs can also be studied in the DVS to characterize the water absorbance capacity of the individual GDLs.

- Performing dynamic contact angle measurements such as contact angle kinetic measurements to study the changes in contact angle over a specific time interval to study the wettability behavior of the powder samples. This method is advantageous over static contact angle measurements as it captures the transient behavior of droplet interactions with the powders.

- Performing fuel cell polarizations under different humidities and temperatures would be beneficial in further understanding the roles of carbon porosity on mass transport under different conditions. The conditions used for testing in this work focused on a hot (80°C) and humid (100%RH) condition which is one of the many different conditions that PEMFCs are subjected to. It would be of great interest to understand the roles of these pores under dry conditions: would these pooling sites be beneficial in retaining moisture in the GDL to minimize ohmic losses?

- Heat treating CICs at higher temperatures (>1100°C) to obtain more graphitized CICs would be of interest. Owejan et al.\textsuperscript{91} highlighted the importance of durable carbons used in the MPL to minimize carbon corrosion especially during start-up and shut-down. Since CICs are graphitizable due to the precursor used, graphitized CICs can be prepared to study this effect on possible improvements on corrosion durability.

- Fabricating composite MPLs containing CICs with other carbon blacks to study if the water retaining capabilities of CICs would be beneficial in water management in the PEMFCs by maintaining the balance between membrane drying and flooding. The loading
of CICs in the MPL can be varied systematically in the composite to study the marginal influence of the addition of CICs in the MPL.

- Studying the effect of CICs synthesized with different ratio of CS to MP on the water vapor sorption capacity and performance in the PEMFC when used as an MPL material. This thesis work compared the characteristics and performance of CICs synthesized with CS to MP ratios of 2:1 while other ratios were only synthesized but not applied in the MPL. As solids with higher porosity have increased absorbance capacity, the CICs synthesized with higher ratios of CS to MP may be more hydrophilic.

- Performing electrochemical impedance spectroscopy (EIS) studies under load in the various polarization regions. EIS is a powerful in-situ fuel cell characterization technique which enables users to identify the different sources of impedance for PEMFCs: interfacial charge transfer, mass transport and ohmic. Since this thesis focuses on the impact carbon of porosity on the water management in PEMFCs, examining MEAs with the different carbon samples at high current densities (mass transport region) would shed important information on the oxygen transport-related resistances.

- Performing conductivity measurement of the activated AB and CIC powders. The MPL which bridges the contact between the CL and SL needs to maintain excellent electronic transport to minimize electron transfer resistance. Since the carbons have different porosity, the changes in the carbon structure could impact the resistivity of the material which would translate to different degrees of ohmic losses.

- Optimizing the MPL slurry ink and coating method for CIC-based MPLs. The current fabricated MPLs form a powdery layer on the SL after sintering which requires careful handling to prevent loss of particles from the MPL. This suggests that either the MPL recipe
or application method must be improved, or CICs will have poor cohesive properties when formed into a layer.

- Characterizing the pore size distribution of the CIC-based MPLs to study the differences in MPL pore structures when different CICs are used in the fabrication. The MPL fabricated from CIC0 revealed a higher loading compared to the MPLs from other CICs with the same thickness. This suggests that the layer might be denser and therefore have a different porous structure for material transport.
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Appendices

Appendix A - CIC preparation for MPL fabrication

A.1 Particle size analysis of milled MP precursor

In order to have a similar particle size distribution for the synthesis of CICs, the precursor was first ground into tiny pieces before passed through a US Standard 230 mesh (63 µm) mesh. The powder was then ball milled under using 5:1 (w/w) zirconia balls to MP in 30 mL ethanol for 1 h. The mean, variance and standard deviation were determined to be 0.51, 0.17 and 0.41 µm respectively. Figure A1.1 shows the particle size distribution of the ball milled MP.

![Particle size distribution of milled MP after 20min used for CIC synthesis. The size distribution of particles peaked at about 350 nm](image)

Figure A1.1 Particle size distribution of milled MP after 20min used for CIC synthesis. The size distribution of particles peaked at about 350 nm
A.2 Ball milling studies on CICs

In order to reduce the particle size of the synthesized CICs, the powders were ball milled in a high energy mixer mill with 2-2.2 mm zirconia balls under the same procedure as described in Section 2.3. Approximately 1-2 ml of sample was removed from the milling jar at specific times. Particle size analysis of the particles milled at different durations were conducted and the distribution of particle sizes are shown in Figure A2.1.

Figure A2.1 (a) Particle size distribution of ball milled CIC with respect to time (b) Mean and standard deviation of ball milled CIC with respect to time

The particle size distribution of the sample starts with a wide distribution initially and shifts towards smaller particle size with increased milling time. The decrease in size “plateaus” after 20 minutes where the mean particle size change is minimal. This indicates that the grinding limit for particles has been achieved under these conditions. As a result, the grinding time was taken as 20 min with the same conditions for all future CIC samples.
A.3 Impact of ball milling on CIC particle morphology

As ball milling is a high energy process, it has the potential to change the nanostructure of the CICs. Figure A3.2 shows the desorption branch of the N₂ sorption isotherm for 4 samples that were part of the study.

![Figure A3.2 BJH desorption curve of CICs to study the impact of ball milling on particle morphology. CICs studied were CIC12, CIC22, CIC12-BM and CIC22-BM](image)

The pore size distribution of the samples being studied did not show much deviation. Other nanostructure properties of the samples are shown in Table A3.1. The surface area and pore volume of the samples saw some changes in the nanostructure from the process. However, since the changes did not result in drastically different pore structure in terms of surface area and pore size distribution, the ball-milling step was included in the sample preparation procedure.
Table A3.1 Comparison of the impact of ball milling on the nanostructure of CIC12 10:1 and CIC22 10:1

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$S_{BET}$</th>
<th>$V_{total}$</th>
<th>$V_{micro}$</th>
<th>$V_{meso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m$^2$/g</td>
<td>cm$^3$/g</td>
<td>cm$^3$/g</td>
<td>cm$^3$/g</td>
</tr>
<tr>
<td>CIC12 10:1</td>
<td>601</td>
<td>1.92</td>
<td>0.0161</td>
<td>0.84</td>
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<td>CIC12 10:1 BM</td>
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<td>2.47</td>
<td>0.0241</td>
<td>0.98</td>
</tr>
<tr>
<td>CIC22 10:1</td>
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<td>1.98</td>
<td>0.0172</td>
<td>0.87</td>
</tr>
<tr>
<td>CIC22 10:1 BM</td>
<td>367</td>
<td>1.75</td>
<td>0.0073</td>
<td>0.42</td>
</tr>
</tbody>
</table>
Appendix B - Supplementary data for Chapter 3

The through-plane resistance of the AB-based MPL samples on SGL29BA shows decrease in total resistance when the compression pressure was increased due to improvements in electrical contact (Figure B.1). The resistance values reach a constant value of approximately $2 \cdot 10^{-6}$ mΩcm$^2$ at compression pressure of 350 kPa. In the higher compression range and including the compression pressure at which the cell is compressed (724 kPa), the resistance values between the samples were similar, suggesting that there were no major differences in electrical conductivity between the MPL samples even though the AB samples differ in porosity. It is likely that this method of determining electrical resistivity in the through-plane direction might not be sensitive enough to measure the differences in conductivity of the activated AB samples which was not reflected in the MPL through-plane resistance data.
Figure B.1 Through-plane resistance of the AB-based MPLs at various compression pressures (gauge). Inset: Resistance values in the range of the cell compression during fuel cell testing.

The polarization performance of the AB-based MPLs shown in Figure B.2 were similar when oxygen is fed to the cathode instead of air with the same stoichiometric ratio. Although there are some differences observed in the 1200-1600 mA/cm² region which is likely due to some flooding effects, the general trend observed for the MPLs are similar. The differences between polarizations for the MPLs observed when air (Figure 3.8) was used can be attributed to concentration losses due to the lower concentration of oxygen in air since the stoichiometric ratio of oxidant was kept at 2.
Figure B.2 (a) Polarization curves for the AB-based MPLs at 100% RH and 80°C (b) Areal resistance measured during polarization tests
Appendix C - Supplementary data for Chapter 4

The through-plane resistance of the CIC-based MPLs shown in Figure C.1 illustrates a significant behavior difference between the MPL based on CIC0 compared to the other samples. The higher resistance obtained for this sample could be attributed to the higher loading of MPL deposited on the SL (Table 4.5) which indicates that this layer was denser. As a result, during compression the resulting layer might be thicker when compared to the other MPLs leading to higher resistance values. For the CIC12- and CIC22-based MPLs, the heat-treated CIC-based MPLs showed lower through-plane resistance at low compression pressure (<100 kPa) compared to the non-heat-treated CIC-based MPLs. This difference in resistivity was also noticeable in the HFR data (Figure 4.12c) where the heat treated samples exhibited lower resistance values. At higher compression pressures, the resistance values of the samples are similar except for CIC0-based MPL.
Figure C.1 Through-plane resistance of the CIC-based MPLs at various compression pressures (gauge). Inset: Resistance values in the range of the cell compression during fuel cell testing.
Appendix D - Fuel cell data

Figure D.1a-b show the polarization performances of MEAs with SGL29BA and SGL29BC on the cathode. Improvements in performance can be observed when MPL is present in the cathode GDL as shown by the higher voltages attained in the ohmic and mass transport regions. The improvements in the ohmic region can be attributed to the reduced contact resistance between the catalyst layer of the CCM with the GDL when MPL is present. The reduced ohmic resistance is also illustrated in Figure D1c where lower HFR values were obtained when SGL29BC is used in place of SGL29BA. The improvements observed in the mass transport region can be attributed to the enhancement in water management in limiting flooding the GDL. This subsequently enables increased voltages to be attained at high current densities. The improvements in performance with the presence of MPLs in the MEA is consistent with observations in literature.26,27,29–34
Figure D.1 Fuel cell performance comparison between SGL29BA and SGL29BC as cathode GDL at 100% RH, cell temperature 80°C (a) raw voltage (b) IR-compensated voltage (c) area normalized HFR at 2.5kHz