

Fabrication and Characterization of Nanoparticle Microporous Layers on Platinized Titanium Fiber Felt for Electrolyzer Anodes

By

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

The electrospraying device was designed and constructed by Dr. Yongwook Kim. The performance test was done at Toronto Metropolitan Univeristy with the support of Prof Chunghyuk Lee and Ms Fazele Bahnamniri. The through-plane electrical conductivity test was done with the support of Dr Saeed Habibpour at the Univeristy of Waterloo.

Abstract

This study is concerned with the incorporation of various nanoparticles in the microporous layers (MPL) on titanium fiber felts for use at the anode in proton exchange membrane (PEM) water electrolyzers. The nanoparticle MPLs were coated onto Ti fiber felt using various methods. Three types of nanoparticles were utilized: indium tin oxide (ITO), tin (Sn) and titanium (Ti). The ITO and Sn nanoparticles were applied using an electrospraying technique, with Nafion as a binder (in the case of ITO) to ensure adhesion to the felt substrate and polyvinylpyrrolidone (PVP) as a surfactant to prevent nanoparticle sedimentation. This method resulted in uniformly smooth coatings. In contrast, Ti nanoparticles were deposited via a solvent evaporation method without a binder. This was followed by sintering of the nanoparticle-coated Ti felt at 750°C for 1 hour under an argon atmosphere. The resulting MPLs underwent comprehensive characterization, including surface imaging via scanning electron microscopy (SEM), assessments of permeability and porosity and measurements of electrical conductivity. The final and critical phase of characterization involved testing the samples in a laboratory-scale water electrolyzer. The electrolyzer setup included titanium bipolar plates with a once-through 2.1 x 2.1 cm – flow field leading to the membrane electrode assembly with an active area of 0.9 x 2.0 cm. All cells used to characterize performance consisted of a commercial carbon fiber cathode coated with an MPL (SGL 22BB) and a Hydrion N-115 catalyst-coated membrane. The tests revealed that the performance using sintered MPLs was superior to that of the electrosprayed MPLs and surpassed that of the baseline case (Ti felt with no coating). The sintered Ti coating with the lowest loading operated the best indicating that the rougher and thinner MPL was the best choice. The poor performance of the electrosprayed MPLs is attributed to the higher interparticle resistance due to the presence of non-conducting materials (dispersant and binder) as reflected in the lower conductivity of these MPL.

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1. Introduction

1.1 An overview of Hydrogen Production

Due to the intermittent nature of the supply of renewable energy from sources such as wind and solar, it is critical that it be stored in an intermediate form. Hydrogen has been recognized and widely accepted as an important intermediate chemical energy carrier that enables the storage and transportation of energy when and where the need arises^[1]. For instance, hydrogen can be used as an alternative fuel in internal combustion engines^[2–4], or used in fuel cells^[5]. The latter are particularly appealing due to their high conversion efficiency providing a pathway for conversion of the chemical energy of hydrogen into electricity.^[6]

The first reported production of hydrogen dates back to 1520 when Paracelsus observed the formation of a flammable gas when metals (iron, zinc, and tin) were dissolved in sulfuric acid.^[7] Today, hydrogen gas production methods can be divided into two broad classes depending on whether the source is a fossil fuel or renewable.^[8] Hydrogen production from fossil fuels is achieved by hydrocarbon reforming or hydrocarbon pyrolysis, while renewable hydrogen production is carried out by water splitting using electrolysis or biomass processes.^[8] Recently, the term blue hydrogen has been used to denote gas produced from fossil sources, while gas produced from renewable power and electrolysis is referred to as green hydrogen.^[9] In August 2022, an agreement between the governments of Canada and Germany was signed on the future site of a green hydrogen production plant in Newfoundland to export hydrogen to Germany potentially by 2025.

Hydrogen production by electrolysis requires the use of electrical energy to split water molecules into hydrogen and oxygen. The electrode reactions involved depend on whether

electrolysis is carried out under acidic or alkaline conditions. In acidic media, the electrode reaction at the anode is:



while at the cathode the following occurs:



In alkaline media the anode and cathode reactions are:



and



The most commonly used water electrolysis methods in industry are carried out in alkaline liquid water electrolyzers (AWE) or in cells operating with ion exchange membranes that serve as solid polymer electrolytes without liquid under acidic or alkaline conditions. Proton exchange membranes are used in acidic electrolyzers (given the acronym PEMWE), while anion exchange membranes are used in alkaline systems (AEMWE). Two other less commonly used methods of water electrolysis are microbial electrolysis (MEC) and solid oxide water electrolysis (SOE).^[10] Other methods of hydrogen production such as photoelectrolysis and low temperature water electrolysis exist although these have not been extensively investigated or applied in industry.^[11,12] A more detailed explanation of the main water electrolysis methods is presented in Chapter 2.

1.2 Electrode Configuration

The internal configuration of the PEMWE is shown in Figure 1. The microporous layer (MPL) is the focus of the present work since a reliable and high-performance solution remains elusive. The MPL acts as a bridging layer between the porous transport layer (PTL) and the catalyst-coated membrane (Figure 1). The porous transport layer is the region where the reactant H_2O flows into the cell and products O_2 and H_2 flow out of the cell, and consists of pores ranging from 10-100 microns in size. The catalyst layer on the CCM by contrast has pores much smaller than 0.5 microns. One of the main purposes of the MPL therefore is to act as a bridge for electrical contact between the porous transport layer and the catalyst layer (CL) by providing smaller pores and a smoother surface. More details regarding the MPL are given in section 2.2.4.

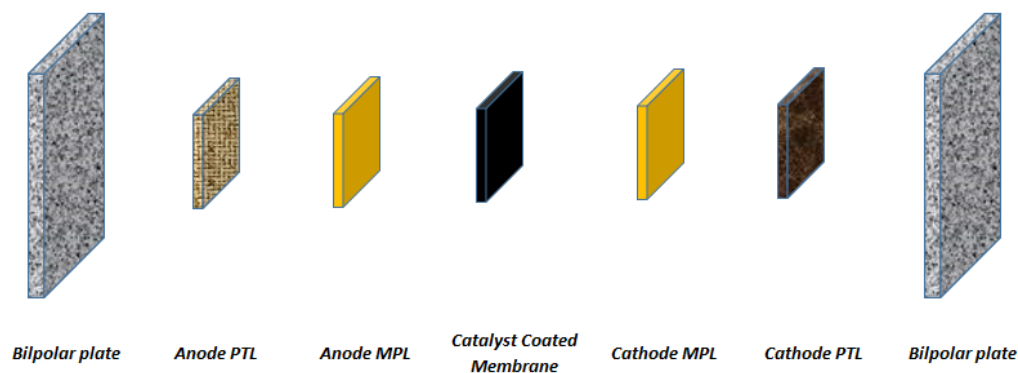


FIGURE 1: VISUALIZATION OF THE INTERNAL STRUCTURE OF A WATER ELECTROLYZER SHOWING THE MPL

1.3 Research Proposal

The research proposal for this study was to investigate the use of different nanoparticles as a microporous layer (MPL) for the anode of a proton exchange membrane water electrolyzer (PEMWE). The choice of materials used was severely limited due to the strongly oxidizing

conditions existing at the anode. The materials had to either be stable against oxidation, or the oxidized form had to be electrically conductive. The nanoparticles examined in this study were tin (Sn), indium tin oxide (ITO) and titanium (Ti). The ITO and Sn nanoparticles were electrosprayed over a platinized Ti felt substrate using a polymer dispersant, isopropanol as the solvent. In the case of ITO, Nafion was used as the binder, while the Sn nanoparticles were sintered under N₂. ITO was considered due to its superior corrosion resistance relative to commonly used pure Ti as it was already in an oxidized form.

The properties of each MPL were first characterized by determining their permeability, porosity and surface morphology. In the second part of the study, the electrochemical performance of the samples were measured in an operating cell.

1.4 Outline of Thesis

This thesis focuses on testing different nanoparticles as MPLs for PEMWE. Chapter 2 gives some background on different types of water electrolyzers, reviews the internal structure and components of electrolyzers, summarizes past studies on the use of MPLs in PEMWE and finally explains the research proposal for this study. Chapter 3 provides details about the materials used, experimental setup, nanoparticle deposition conditions used in each method and characterization techniques used. Chapter 4 discusses the results of the experimental work. Finally, Chapter 5 summarizes the results of this thesis and provides direction for future work.

2. Background

2.1.1 Proton exchange membrane water electrolyzers

One of the older electrolysis methods includes the use of platinum electrodes and separate tubes to collect evolved gases during electrolysis in a liquid solution.^[13] Another early method of hydrogen production was studied by Poul la Cour, who used the produced hydrogen in lamps with a refractory material for illumination.^[13] Modern acidic electrolyzers denoted here as PEMWE are designed with a proton exchange membrane to separate the anode and cathode. Water introduced at the anode is oxidized to produce O_2 and protons (reaction (1)). The protons conduct through the membrane to the cathode where they are reduced to generate H_2 (reaction(2)). A schematic representation of the PEMWE is shown below (Figure 2).

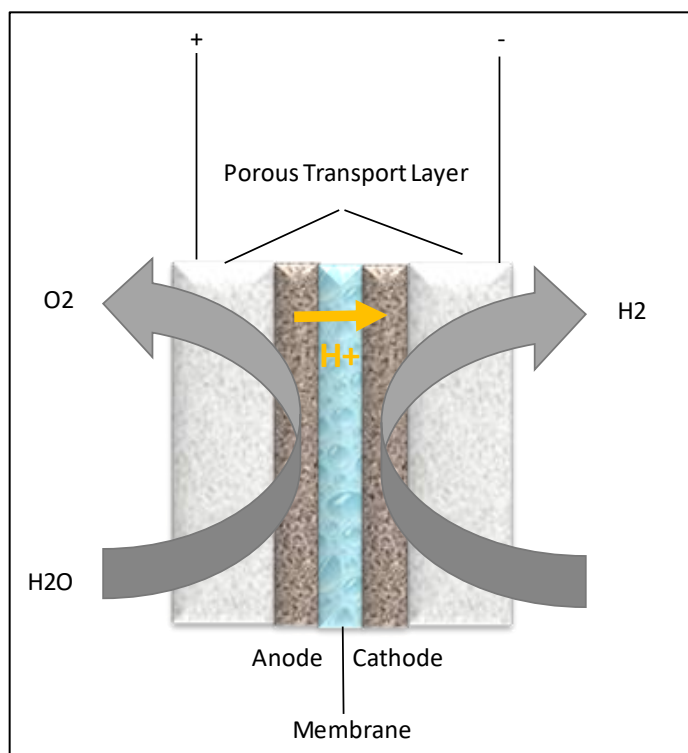


FIGURE 2: INTERNAL STRUCTURE OF PEMWE

An example of a commercial PEMWE is the 20 MW plant in Becancour, Quebec. The main advantages of the PEMWE over earlier methods is the more compact design afforded by the use of very thin ionomeric membranes, which also provide greater energy efficiency and higher production rates for a given footprint.^[14] Research to improve PEMWE technology is ongoing. Some of the key areas identified for improvement are the use of thinner membranes and the application of coatings on the PTL to reduce contact resistance, both of which will increase operational efficiency.^[15]

Based on the research reported to date, the best performing cells can achieve a current density of 2.0 A/cm^2 with a voltage as low as 1.67-1.80 V depending on the different electrocatalyst and membrane combinations used.^[16–18] Of course it would be desirable to operate at even higher current density in commercial operations. Currently, commercial PEMWE can be operated at current densities up to 2.0 A/cm^2 and pressures up to 350 bar, which also reduces operating costs because it produces compressed hydrogen which is the desired form for purposes of transport and storage.^[19] In addition, operation at higher pressures also improves reaction kinetics.^[20] Researchers have been working on improving the current density even further with the development of thinner electrodes/membranes to reduce the ohmic resistance and more durable components using approaches such as platinization of the electrodes.^[21]

2.1.2 Alkaline water electrolyzers/anion exchange membrane water electrolyzers

AWE and AEMWE are variations of the same technique that use an anion exchange membrane to enable the selective transport of OH^- from the cathode to the anode where they are oxidized to form O_2 and water (reaction (3)). AWEs are designed with a circulating solution of KOH or NaOH in two sections separated by an anion exchange membrane. The figure below illustrates an AWE with a circulating KOH electrolyte.^[22]

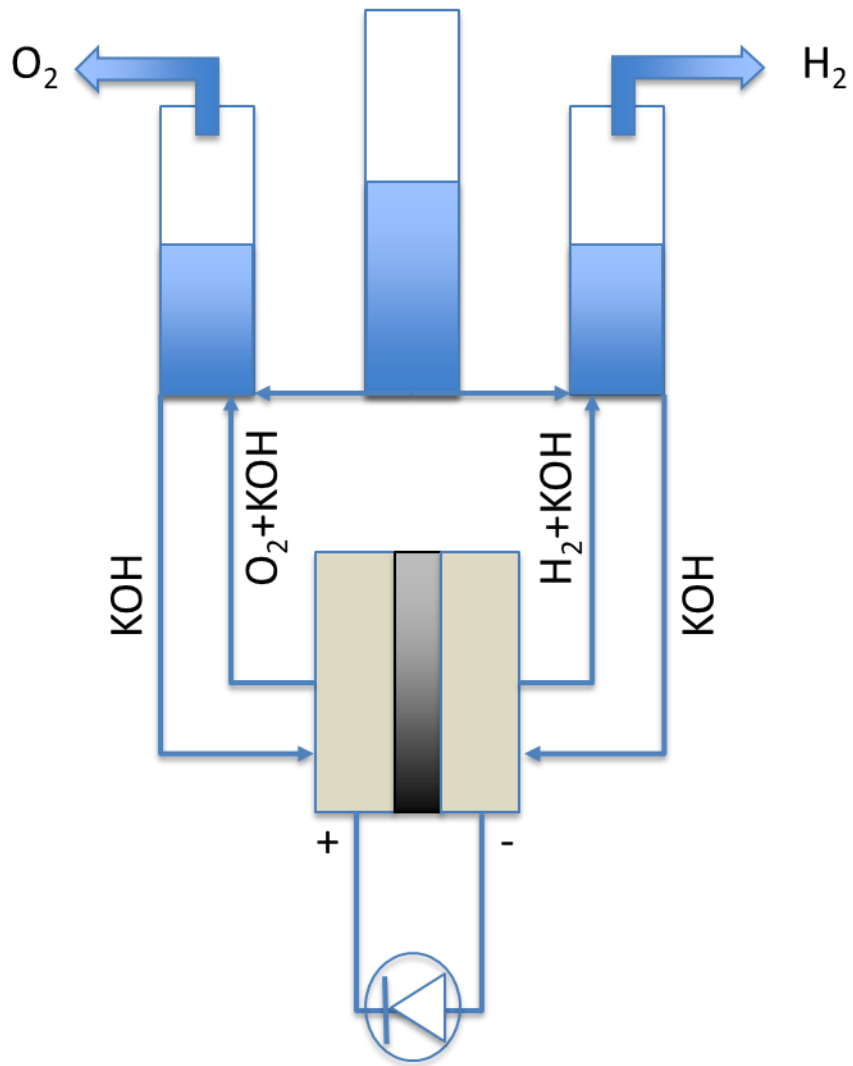


FIGURE 3: A BASIC FLOW DIAGRAM OF AN ALKALINE WATER ELECTROLYZER

Alkaline electrolyzers are now being made into compact designs by placing an anion exchange membrane between the electrodes similar to the design of PEMWEs. These are referred to as anion exchange membrane water electrolyzers (AEMWE).

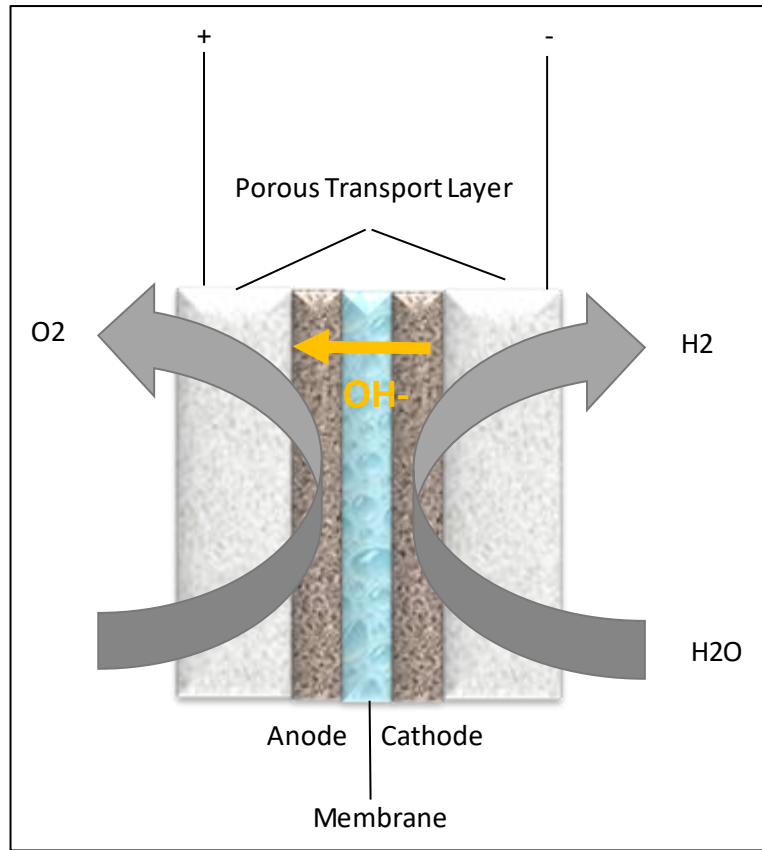


FIGURE 4: INTERNAL STRUCTURE OF AN AEMWE

The incorporation of MPLs in AEMWE has not been extensively investigated although it has been shown by a few researchers that their use at the anode would be beneficial.^[23,24]

2.1.3 Solid oxide electrolyzers (SOE)

In an SOE, steam is fed to the electrolyzer which operates at a high temperature of 750-950°C.^[25] The most common electrolyte used in SOEs is yttria-stabilized zirconia (YSZ).^[26,27] The anode used is strontium-doped lanthanum manganite perovskite (LSM) or LSCF while a Ni/YSZ electrode is used as the cathode.^[26,27] The figure below shows the basic setup of a SOEC.

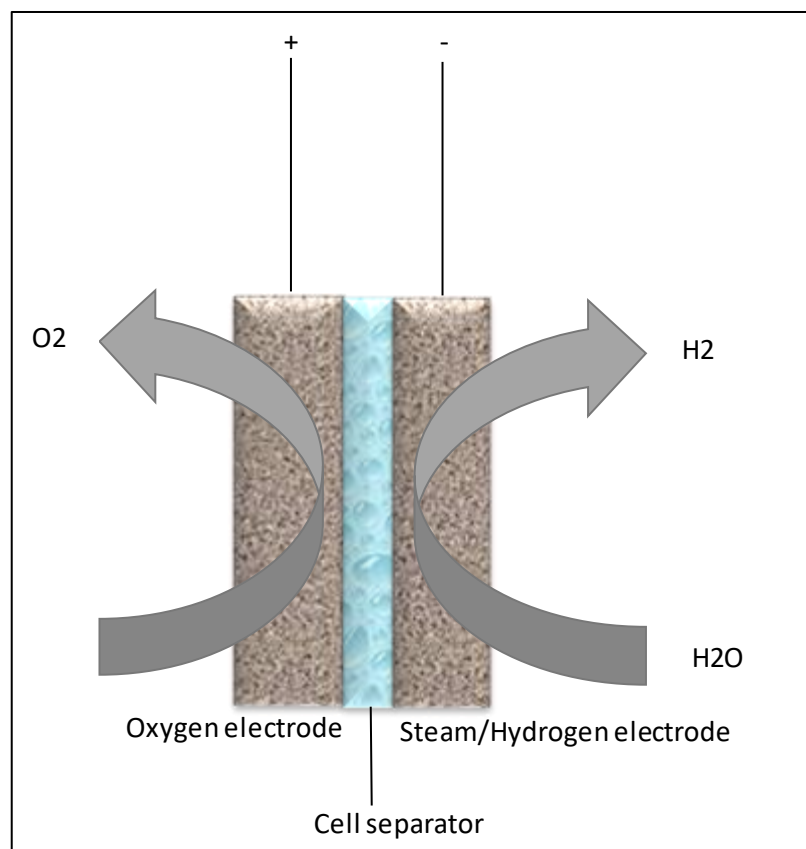


FIGURE 5: INTERNAL STRUCTURE OF A SOE

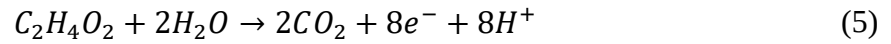
The main disadvantage of SOE is the high production cost of the electrolytes required to withstand the severe operating temperatures.^[28] Secondly, the time taken to reach the high operating temperature during startups is another limitation. Despite these challenges, an important advantage is the high ionic conductivity of the electrolyte at high temperatures which increases their energy efficiency.^[28] In 2022, LSB industries announced plans to build a 10 MW SOE at their Pryor, OK facility in the USA.

2.1.4 Microbial electrolysis (MEC)

In an MEC, organic matter is oxidized using electrochemically active bacteria resulting in the formation of CO₂, electrons and protons.^[29] When an external voltage is applied across the cell,

protons are reduced to hydrogen at the cathode, while the oxidation of organic matter is catalyzed by the bacteria at the anode.^[29] With acetate used as a substrate (organic matter), the reactions are as follows:^[29]

anode:



cathode:



Although an MEC can be operated with the objective of remediating wastewater, such applications are impractical because of the slow degradation of complex substrates and low conductivities of actual wastewater.^[30] The by-product of an MEC is different from that of the other electrolytic methods since it produces CO₂ at the anode instead of O₂. Although several lab-scale research experiments have been conducted on MEC, no industrial-scale MEC units have been installed to date.

2.2 Structure of Electrolyzer Cell

The basic units of the electrolyzer are the membrane, anode/catalyst layer (CL), cathode/catalyst layer and a porous transport layer (PTL) and microporous layer (MPL) on each side. Figure 1 shown earlier in section 1.2 depicts the internal components of the electrolyzer. Whereas MPLs are being investigated for use on the anode side, only about a half of previous studies have investigated their use on the cathode side. Nevertheless, the use of an MPL on the cathode side is still recommended due to the advantages of protecting the catalyst layer and increasing the contact area to enhance electrical conductivity. Obviously, each of these

components has a distinct function that needs to be optimized. Researchers have investigated and attempted to optimize each one individually to understand its impact on and improve the overall performance of the electrolyzer.^[31,32]

The membrane together with the electrocatalyst, porous transport layer and microporous layer is generally referred to as the membrane electrode assembly (MEA). The electrocatalyst can be coated onto the substrate (PTL) or onto the membrane. Both alternatives have been extensively investigated by previous researchers. The structure is referred to as a catalyst-coated membrane (CCM) when the catalyst is coated onto the membrane, while it is termed a catalyst-coated substrate (CCS) when coated onto the PTL. Lim et al have discussed the advantages and disadvantages of the CCM and CCS in a PEM fuel cell.^[33] After reviewing the fabrication procedure for the CCS using the direct spray technique and the CCM using the direct spray and decal transfer techniques, they concluded that the CCM produced by the decal transfer technique achieves better performance.^[33] Ito et al investigated both configurations in an AEMWE and also concluded that the CCM has better mass transport characteristics than the CCS.^[34] Shirvanian et al reached the same conclusion that the CCM is better than the CCS in AEMWE due to better contact with the membrane.^[35] The above conclusions drawn on AEMWE can presumably be applied to PEMWE as well. Although the use of CCM has been shown to exhibit superior performance over that of the CCS, one downside with the CCM configuration is poor electrical contact with the current collectors. However, this problem can be mitigated by the introduction of an MPL between the PTL and CCM.

2.2.1 Membrane

The membranes used in AEMWE and PEMWE are solid hydrocarbon membranes that separate the electrodes, allow ion exchange and prevent the reaction products O_2 and H_2 from

mixing.^[36] A highly performing membrane should have the following characteristics: high chemical stability, cost effectiveness, excellent ionic conductivity, low swelling and easy fabrication.^[36] For proton exchange membranes, water uptake and swelling are major concerns since they directly affect the hydromechanical stability and electrochemical activity of the membrane.^[37] Currently, the fluorinated-based polymer Nafion is the most common membrane used in PEMWE because of its good ionic conductivity and excellent physicochemical properties.^[36] Nafion is the commercial name for a tetrafluoroethylene-based fluoropolymer-copolymer that was invented by DuPont. Pre-fabricated membranes of Nafion are labeled as Nafion-XYZ, with XYZ representing 3 numerical digits that include information about their thickness. Another approach used by researchers employs a liquid Nafion solution of a known weight % mixed with other polymers to manufacture the membrane. For example, Munsur et al mixed polyacrylic acid and polyvinyl alcohol with Nafion and found that the performance of the cell with the modified membrane was better than that obtained using a pure Nafion membrane by attaining higher current density and lower ohmic resistance.^[38] Other polymers that have been used in PEMWE membranes are polybenzimidazole (PBI) and sulfonated polyether ether ketone.^[36]

AEMWE membranes are designed to conduct hydroxide ions (OH^-). Lim et al examined the use of Zirfon, which is a porous composite membrane composed of a polysulfone matrix and ZrO_2 present as a powder.^[39] In another study, Aili et al used a membrane blend based on poly(arylene ether sulfone) (PSU) and poly(vinylpyrrolidone) (PVP).^[40] Fortin et al investigated the effect of varying the thickness of a commercially available anion exchange membrane known as Aemion (produced by Ionomr Innovations Inc) and found that the use of thinner and high ion exchange capacity membranes exhibited good performance at lower electrolyte concentrations.^[41] Cummins Inc. developed a patented anion exchange membrane known as IMET for use in an AWE

that is made up of inorganic materials that are very chemically resistant and do not contain asbestos which is a commonly used separator in AWE.^{[42][43]}

2.2.2 Catalyst layer

Since the catalyst layer is the heart of the cell where all the reactions occur, access to it by all the reactants is essential. The porous structure of the catalyst layer should ensure reactants and products can be exchanged without significant mass transport hindrance. This requires an optimum porosity since water and gas transport will suffer if it is too low whereas the reactive surface area and electrical and ionic conductivity will not be sufficiently high if it is too high. Ionomer solutions are used to bind the catalyst onto the membrane or the substrate. Catalysts are essential for overcoming the kinetic energy barrier for the electrochemical reactions of oxygen evolution and hydrogen evolution that occur in water splitting.^[44] The electrode reactions taking place in PEMWE and AEMWE were given previously in Eqns (1) - (4). In both the PEMWE and AEMWE, the oxygen evolution reaction (OER) occurs at the anode. The slow kinetics (high overpotential) of the OER is a limitation that reduces the efficiency of electrolysis processes.^[45] The OER generally has sluggish reaction kinetics due to the very high overpotential required to break the O-H bond and subsequently form the O-O bond.^[46]

Noble metal oxides are the preferred catalysts for the OER. Although RuO₂ provides excellent electrochemical activity for the OER, it has not been widely used because it is susceptible to corrosion.^[47] IrO₂ is more stable than RuO₂, but has the downside of exhibiting lower electrochemical activity.^[48] Non-metal oxides have also been studied for use as OER catalysts. For example, Du et al used metal chalcogenides partly based on the fact that their high surface area and low particle size make them attractive for use as a catalyst. Their performance tests revealed that the chalcogenides exhibited lower overpotential compared to RuO₂ in the voltage range of

1.25-1.75 V, reflecting improved catalytic activity over that of RuO₂.^[49] Tavakkoli et al explored the use of an organometallic catalyst (Ni(II) bipyridine) and found that it exhibited high stability and activity, leading to a better performance than that achieved using a RuO₂ catalyst.^[50]

On the other hand, platinum catalysts have been utilized extensively for the HER at the cathode. However, due to the high cost of Pt, researchers have investigated approaches to use catalysts free of platinum group metals (PGM-free) or optimize the PGM catalysts to minimize the Pt loading required. For example, a low Pt-loaded Mo co-catalyst was used in both acidic and alkaline media with excellent stability and electrochemical performance.^[51] Esposito et al showed that the activity of a monolayer of Pt on a low-cost substrate was similar to that of bulk Pt as a catalyst.^[52] It is worth noting that Pt-based catalysts exhibit lower performance for the HER in alkaline electrolytes as compared to acidic electrolytes. Thus, higher Pt loading would be required in alkaline electrolytes.^[53] However, it should also be noted that since Pt can be easily recovered from used electrodes, the high loading and cost of Pt usually turns out not to be a major concern nowadays since end users typically lease the precious metal from the supplier over the duration that it is being used and so becomes part of the operating cost rather than being a capital expense.

2.2.3 Porous transport layer

The main role of the porous transport layer (PTL) is to ensure that reactant (i.e. liquid) water can access the regions of the catalyst layer that are located under the flow field ribs. If the ribs are positioned directly against the CL, then only half of the active area would be utilized. Because the PTL is located between the flow field and the reaction sites, it must support every transport process that is occurring in the cell (except for ion transport between the catalyst layers which is confined to the membrane separator). The PTL must enable liquid water flow, gas bubble flow, electron transport and even heat transfer.^[54] Its morphology and pore structure have to be

properly designed to ensure efficient catalyst utilization and enable the provision of a smooth support for ultrathin membranes.^[32] With the introduction of the MPL, however, some of these aspects of the PTL requirements are less important since these functions can be augmented by the MPL.

For the older AWE that operated with a circulating electrolyte, a PTL was not needed due to direct contact of the liquid electrolyte with the electrodes. Newer AEMWE which operate with anion exchange membranes are designed with a PTL. Generally, metals are used as the PTL on the anode in both PEMWE and AEMWE, while carbon is used as the PTL on the cathode side. Metals are required at the anode because of the high overpotential of the OER which leads to a highly corrosive environment that destroys most carbon-based materials. In their study, Park et al tested a nickel/titanium-based PTL at the anode of an AEMWE and a carbon-based PTL at the cathode, concluding that the use of nickel foam in the PTL yielded the best performance and durability followed by that of nickel felt, while the use of titanium felt on its own exhibited the lowest performance.^[55] In another recent study on AEMWE, researchers used Ni foam at the anode and carbon paper at the cathode.^[56]

PEMWE operate similarly with metal-based anodes and carbon-based cathodes for the same reasons as in the case of AEMWEs. Ti-based materials have been the most commonly used in the anode PTL in PEMWEs.^[57] Rakousky et al used two sheets of Toray paper (carbon paper) on the cathode and a porous titanium sinter plate at the anode (platinized and non-platinized) and observed that Pt-coated PTLs exhibited a substantially lower degradation rate (12 $\mu\text{V/h}$) compared to non-Pt coated PTLs (194 $\mu\text{V/h}$).^[58] The use of different forms of Ti PTL (sintered powder, foam, felt and mesh) and their properties have been well studied, but nearly all cases neglected to include

a MPL.^[32] In fact, it remains an open question as to what properties the MPL should possess and what materials are suitable.

2.2.4 Microporous Layer

The PTL can range from 100 to 300 μm in thickness with fibers up to 20-30 μm , while the CL is made of nanometer-size catalyst particles in the range of 20-80 nm. Due to this large difference in the particle size, portions of the CL that are masked by large particles are inactive due to transport resistance or are electrically isolated since they lie far from contact points with the PTL imposing long transport lengths. This is illustrated schematically in Figure 6. Moreover, direct contact between the PTL and the CL can mechanically damage the catalyst layer. As an example, Mandal et al. observed many dents on the CL in the CCM due to the impact of Ti felt fibers.^[59] In order to fill the gaps and ensure a smooth contact between layers, an MPL can be applied to one side of the PTL prior to fixing the PTL onto the CL.

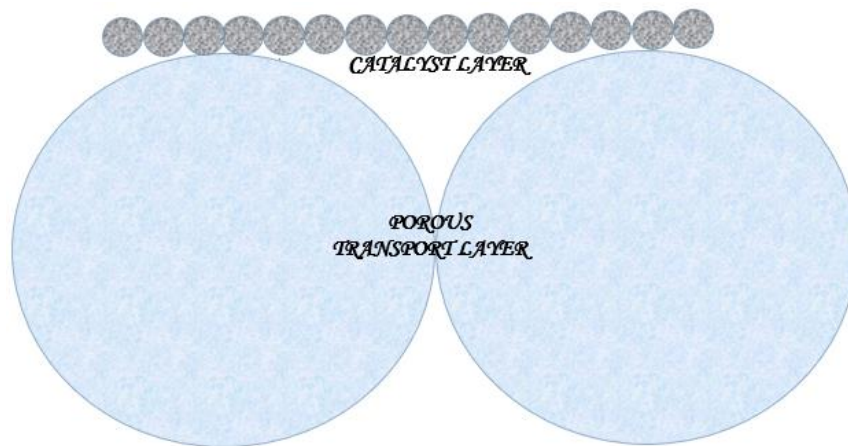


FIGURE 6: REPRESENTATION DEPICTING THE SCALE DIFFERENCE BETWEEN THE PTL AND CL AND HIGHLIGHTING THE NECESSITY FOR THE INCORPORATION OF AN MPL

On the other hand, when an MEA is prepared with a CCS structure, the difference in size between the CCS and the membrane is not that large and therefore the MPL may not be required. However, past studies have indicated that the use of CCM-based MEAs yields better performance than those based on a CCS structure.^[33–35] This performance can be further enhanced by the application of the MPL. The following section describes some studies done in PEMWE designed with anode MPLs.

2.3 Past Studies and Current Research

The application of an MPL in PEM fuel cells has been widely studied whereas examples of applications of the MPL on PEMWEs are much fewer. Lettenmeier et al. used the vacuum plasma spraying (VPS) technique to deposit porous Ti coatings onto sintered Ti filters.^[60] In their procedure, Ti powder was fed to the VPS setup operated at 50 mbar pressure to reduce the exposure to O₂ which would oxidize the Ti. Each sample was tested for leakage rate and interfacial contact resistance, while its cross section was analyzed using SEM. The leakage rate is a measure of the rate at which gases flow through the sample under high pressure and is often used as a rough measure of the sample density. Electrochemical tests were conducted using the Ti filter with and without an MPL, a Nafion 115 membrane, an Ir-based anode and Pt-based cathode. The researchers concluded that the resistance between interconnecting parts of the electrolyzer decreased by $\sim 20 \text{ m}\Omega\text{-cm}^2$ in the presence of the MPL. Also, at higher current densities of 5 A/cm^2 , the overpotential of the electrolyzer was reduced by $\sim 256 \text{ mV}$, corresponding to a 5% increase in voltage efficiency. The voltage required to operate the cell at 2.0 A/cm^2 was $\sim 1.95 \text{ V}$ based on their polarization curve. In another study, Schuler et al. sintered Ti powder onto a substrate at $1150\text{-}1300^\circ\text{C}$ and soaking times of 1-3 h.^[61] A Nafion 115-based CCM was utilized as the electrolyte. A CT scanner was used to examine the structure of the sample. For the electrochemical test, the same PTL/MPL structure was used at the cathode and the anode. They observed that the introduction of the MPL increased the current density by a factor of 2.2-2.8 over the voltage range of 1.4 to 1.9 V, reduced mass transport losses (an average of $\sim 60 \text{ mV}$ lower mass transport overpotential at 2 A/cm^2) and lowered the surface roughness. Again, they did not explicitly state the voltage required to operate the cell at 2.0 A/cm^2 , but it appears to be $\sim 1.7 \text{ V}$ based on their polarization curve.

Hwang et al. used the screen-printing technique to load Ti powder onto a Ti felt.^[62] They used a Nafion 115-based CCM and a carbon paper-based PTL on the cathode. The MEA was then characterized by using it in a unitized reversible fuel cell (URFC). A unitized reversible fuel cell is a unit that can also be operated as an electrolyzer. The performance for electrolysis was studied up to a maximum of 1 A/cm² only. According to the current density-voltage curve they obtained, a voltage of ~1.65 V was required to achieve the maximum current density.

In another URFC, researchers used an MPL prepared using a powder of IrO₂ deposited on Ti by thermal decomposition.^[63] The Ti/IrO₂ powder was then mixed with PTFE in a weight ratio of 65:35 before being spread onto a carbon paper and sintered to make the MPL/PTL at the anode. The cathode was prepared by applying a powder of Vulcan XC-72 carbon black on the carbon paper. The CCM was made of Nafion 112 with electrocatalysts sprayed directly onto the membrane. The MEA was then hot pressed together. When tested in an electrolyzer, a voltage of 1.8 V was required to achieve 2 A/cm².

Kang et al. used a slightly different approach to prepare a thin, well-tuned Ti liquid gas diffusion layer (LGDL) with a highly regular and organized structure for use at the anode.^[64] It should be noted that the terms PTL and GDL are often used interchangeably nowadays, with most researchers now shifting towards the use of PTL since it permits the transport of both water and gases. They manufactured their sample lithographically (using patterned resist masks and chemical wet etching of thin foils). They achieved an excellent performance using this PTL in which a voltage of only 1.66 V was required to operate the cell at 2 A/cm². This could be due to the particularly thin transport layer in their design which reduces mass transport and ohmic resistances. In another study closely related to this research, Hegge et al. used electrospinning to fabricate an MPL.^[65] Their MPL consisted of IrO_x particles, which helped to reduce the overall loading of the

catalyst by 80% due to improved electrical contact between the PTL and the catalyst layer. Deng et al ^[66] investigated the use of TiC as the MPL in their study. They used an 800 μm thick layer of Ti felt and 1-5 μm sized Ti powder for the coating. PVP, PSU and Ti powder were mixed in N-methyl-2-pyrrolidone (NMP) to prepare the solution, which was sprayed using an airbrush onto the Ti felt. The layer was then vacuum-sintered at 1000 °C. The rationale behind their approach was that the carbon produced from the adhesive during the sintering process would react with the Ti powder to form TiC. Based on their polarization curve, the best performance using this sintered MPL was a 1.83 V voltage to operate the cell at 2 A/cm².

In a more recent publication, Schuler et al ^[67] used irregularly shaped Ti particles and spherical Ti particles on commercial Ti felt. Both these particles were tested individually for their performance. The spherically shaped particles are deemed to be superior due to the smoother edges which are essential when using thinner membranes. The irregular shaped particles, on the other hand, have rougher edges that could potentially rupture thinner membranes. Unfortunately, these authors did not specifically report the size of both these particles, but an estimate of ~10-15 μm can be made for both these particles based on their SEM images. The best performance using the spherical Ti particles was a voltage of ~1.77 V for 2 A/cm².

It should be noted that several earlier research studies attempted to use what was labeled as a microprotective layer, although it appears to serve the same purpose as the microporous layer (MPL) described here.^[68,69] It should be noted that in previous studies, the researchers have mainly focused on the use of micron-sized particles in their MPLs.

Building upon the results of previous studies ^[60-67], one of the main focus of this research is on the use of nanoparticles to form the MPL coating. The use of nanoparticles as MPLs has not been actively explored in water electrolyzers as much as it has in the case of fuel cells. This study

is unique in two main respects: i) fabrication of an MPL using nanoparticles and ii) use of novel materials such as ITO and Sn as MPL coatings.

The benefits of using nanoparticles over micrometer-sized particles in the fabrication of the MPL are demonstrated through a simple illustration. The figure below shows the voids that form between layers when micrometer-sized MPL particles are used. These voids can become sites where gas bubbles and water droplets accumulate, leading to mass transport limitations, rendering the catalyst site inactive and, consequently, reduced performance efficiency. Furthermore, incorporating nanoparticles in the MPL enhances electrical contact efficiency by increasing the number of contact points between the MPL and the PTL. Additionally, the nanoparticle-based MPL serves as a protective cushion between the micron-sized PTL particles and the catalyst layer (CL), safeguarding the fragile CL from potential damage

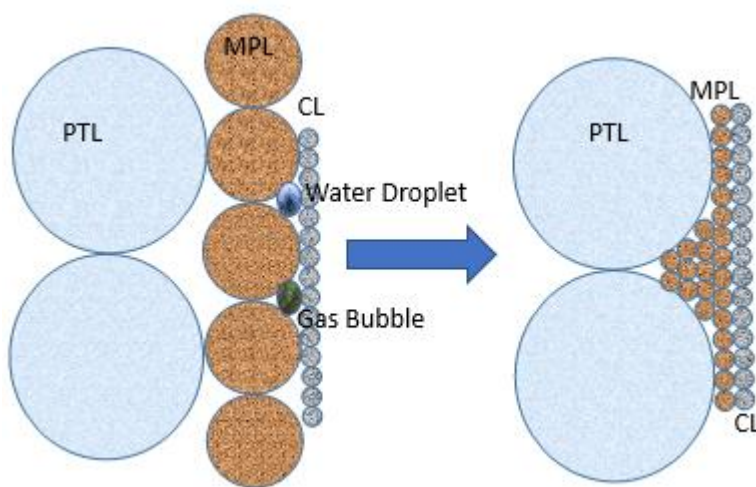


FIGURE 7: ILLUSTRATION SHOWING THE ACCUMULATION OF GAS BUBBLES AND WATER DROPLETS IN THE VOID SPACES FORMED BY MICROMETER-SIZED PARTICLES IN THE MPL, COMPARED TO THE REDUCED VOIDS WHEN NANOPARTICLES ARE USED

Based on research studies in which ITO has been successfully used as a support layer for OER catalysts^[31,70], we explore its use as an MPL in a PEMWE using electrospraying as the deposition technique. In addition, we also investigate the use of Sn as an MPL along with the commonly used Ti nanoparticles. Sn is being tested since SnO₂ was successfully applied in the catalyst layer along with IrO₂ in a study by Datta.^[71] It is therefore expected that the Sn MPL at the anode will oxidize to some form of tin oxide during electrolysis and potentially enhance the OER reaction kinetics.

3. Materials and Methods

MPLs were fabricated using three different types of nanoparticles. Different techniques were employed to ultimately form four MPLs that are labelled as MPL-ITO(10), MPL-Sn(8), MPL-Ti, and MPL-ITO(5). MPL-ITO(10) and MPL-ITO(5) were formed using ITO nanoparticles, while MPL-Sn(8) was made from Sn nanoparticles. The number in brackets in this designation denotes the ITO or Sn loading in units of mg/cm^2 . For example, MPL-ITO(10) contained an ITO loading of $10 \text{ mg}/\text{cm}^2$, while MPL-ITO(5) contained only $5 \text{ mg}/\text{cm}^2$. MPL-ITO(10), MPL-Sn(8) and MPL-ITO(5) were prepared by electrospraying. MPL-Ti was made from Ti nanoparticles and prepared by a solvent evaporation technique. The major differences between these MPLs are summarized in Table 1. Electrospraying offers appealing advantages for the deposition of nanoparticles including a uniform coating, scalability and versatility, making it a superior choice for producing the MPL compared to other deposition techniques such as air spraying or doctor blade methods. Electrospraying is a relatively unexplored method for the fabrication of MPLs in water electrolyzers and so was applied to the formation of the ITO- and Sn-based MPLs with the idea of yielding interesting and useful physical characteristics. In addition, ITO- and Sn-based MPLs have not been previously investigated, making this the first application of these materials. Ti nanoparticles were deposited under binder- and polymer-free conditions to enable a comparison with the results of previous studies that have reported on the effectiveness of Ti-based MPLs.^[60,62] No binder/dispersant was used and sintering was the main method for binding the particles in these earlier studies. Electrospraying requires the use of PVP as a dispersant and therefore could not be used for the Ti-based MPL since this would prevent a direct comparison with previous studies.

All nanoparticles were obtained from US Research Nanomaterials. The ITO nanoparticles contained a mixture of indium oxide and tin oxide at a weight ratio of 95:5 and particle size of 20-

70 nm. Poly(vinylpyrrolidone) (PVP) (purchased from Sigma Aldrich) which was used as a nanoparticle dispersant to form MPL-ITO(10), MPL-Sn(8) and MPL-ITO(5) had a molecular weight of $\sim 1,300,000$. The Sn nanoparticles were 60-80 nm in size, while the Ti nanoparticles were 30-50 nm. A 5 wt% solution of Nafion purchased from Ion Power was used as a binder precursor for MPL-ITO(10) and MPL-ITO(5).

The substrate for each MPL was platinized fiber felt (purchased from the Fuel Cell Store) with a porosity of 53-56% and a thickness of $\sim 266 \mu\text{m}$. The cell used for the performance tests contained the water electrolysis catalyst-coated Hydrion N115 CCM membrane purchased from Ion Power. The loading of catalyst on this membrane was $1.0 \text{ mg IrOx}/\text{cm}^2$ on the anode side and $0.3 \text{ mg Pt}/\text{cm}^2$ on the cathode side. The cathode used for the performance test was Sigracet 22 BB (SGL22BB) which is a non-woven carbon paper with a microporous layer (MPL) that has been treated with 5% PTFE by weight. It has an overall thickness of $215 \mu\text{m}$.

**TABLE 1: DEPOSITION METHODS, COMPOSITION AND LOADING
FOR THE DIFFERENT MPL OF THIS STUDY**

MPL	COMPOSITION	DEPOSITION METHOD	LOADING (mg/cm^2)
MPL-ITO(10)	ITO	Electrospraying	10
MPL-ITO(5)	ITO	Electrospraying	5
MPL-Sn(8)	Sn	Electrospraying	8
MPL-Ti(8)	Ti	Solvent evaporation	8
MPL-Ti(11)	Ti	Solvent evaporation	11
MPL-Ti(12)	Ti	Solvent evaporation	12

3.1 Preparation of electrospaying solution

The solution preparation methods are described below according to the MPL.

MPL-ITO(10) and MPL-ITO(5):

The following procedure for preparing the electrospaying solution was adopted based on previous studies on electrospaying with nanoparticles.^[72,73] The electrospaying solution was obtained by adding PVP and a 5 wt% Nafion solution to isopropanol. The function of PVP was to disperse the nanoparticles in the solution and to reduce the settling tendency. PVP is an excellent stabilizer that prevents clumping of nanoparticles by repulsive forces which are caused by its hydrophobic carbon chains inducing a steric hindrance effect.^[74] Enough PVP was added so that its concentration in the electrospaying solution was 1.71 mg/mL-isopropanol while the amount of Nafion solution used was based on the deposited solids containing 17% of binder at the end of the preparation step. These targets were determined based on different experimental combinations which were evaluated by varying the binder and dispersant concentrations and testing the adhesion of the produced MPL to the felt. Given that the solution containing Nafion was thoroughly stirred overnight, it can be confidently assumed to be well dispersed, ensuring that the final percentage of the binder in the MPL closely matches the initially calculated value. This was an optimum composition that prevented excessive settling of the nanoparticles and still provided good adhesion of the nanoparticles to the felt. The mixture of PVP, Nafion and isopropanol was first stirred using a magnetic stirrer at 800 rpm for 16 h prior to the addition of the ITO nanoparticles. Enough ITO nanoparticles were added to yield a concentration of 12 mg/mL-isopropanol. The solution was then sonicated for 75 min.

MPL-Sn(8):

The procedure to form MPL-Sn(8) differed from that of MPL-ITO(10) and MPL-ITO(5) in that it did not include the Nafion solution since it involved the sintering of the Sn nanoparticles which obviated the need for a binder. The procedure began with the addition of enough PVP to yield a concentration of 3 mg/mL-isopropanol in the spraying solution. One effect of not including Nafion was to significantly reduce the viscosity of the solution, which of course would make it much easier for the Sn nanoparticles to settle out. To counteract this effect, a higher concentration of PVP than that used to make MPL-ITO(10) and MPL-ITO(5) was added to the solution (3 mg/mL compared to 1.71 mg/mL). After PVP and isopropanol were stirred together at 800 rpm overnight for ~16 h, enough Sn nanoparticles were added to yield a concentration of 20 mg/mL and the solution was sonicated for 75 min.

3.2 Preparation of Ti Fiber Felt

The Ti felt was sonicated in deionized water for 5 min to remove all impurities before being etched in HCl at 55 °C for 7 min. The etching was done to eliminate the passivation layer of titanium oxide that forms on the surface of the felt. As shown in a study by Bystron^[75], etching in HCl also leads to the formation of titanium hydride which protects the felt from further oxidation. Another important benefit of the etching is to roughen the surface of the felt to enable good adhesion of the nanoparticles on the surface.^[75]

After being etched, a 3.3 x 3.3 cm sample of the Ti felt was cut for electrospraying and then placed in the middle of the aluminum foil collector of the electrospraying chamber. The collector (onto which the Ti felt was placed) was set to move 2 cm by 2 cm in the x-y direction. The smaller movement area for the collector was chosen because the circular jet covers a larger area than the movement range. The fiber felt was attached to the aluminum foil collector by carefully placing

small pieces of tape on the edges to avoid interfering with the electric field. To produce an MPL for the electrolyzer performance test, a 2.0 x 0.9 cm felt piece was cut out from the electrosprayed sample. This size was selected for electrospraying to match the dimensions required for the electrolyzer set up.

3.3 Electrospraying Setup and Parameters

The electrospraying device is designed to automatically move the collector in an x-y plane while keeping the needle in a fixed position (Figure 8). The speed at which the collector plate moves can be varied from a minimum speed of 10 mm/s to a maximum speed of 15 mm/s. It turns out that 10 mm/s was the optimum speed for the deposition of the nanoparticles since a higher speed led to poor packing of the nanoparticles and a non-uniform coating with valleys and peaks.

The electrospray solution was loaded onto a 10 ml syringe. A 16-gauge needle was used to attain a flow rate of 0.66 mL/h when fabricating MPL-ITO(10) and MPL-ITO(5), while a 24-gauge needle was used to achieve a flow rate of 0.3 mL/h in the case of MPL-Sn(8). A lower flow rate was required in the case of MPL-Sn(8) to avoid the formation of droplets during electrospraying that occurs at higher flow rates, presumably due to the lower viscosity of the binder-free electrospraying solution used to fabricate this MPL. A syringe pump was used to pump the solution to the needle. The pitch (distance that the collector plate traveled after each axis scan) was set to 5 mm. The spraying was done in one batch of 4.5 ml electrospraying solution for MPL-ITO(10), 3.0 ml for MPL-Sn(8) and 2.1 ml for MPL-ITO(5). These batch volumes represent the total sprayed volume onto the felt. A higher volume was used for MPL-ITO(10) to produce a thicker coating of the nanoparticles. The distance between the needle tip and collector was maintained at 2.1 cm for MPL-ITO(10) and MPL-ITO(5) and 4.0 cm for MPL-Sn(8) throughout electrospraying. A shorter distance in each case led to wet regions appearing on the collector during spraying, signifying that

the solution did not have enough time to evaporate. Due to the lower viscosity of the solution used to produce MPL-Sn(8), a lower electric force was needed to form a spray and so the needle distance was increased (i.e., greater separation distance corresponds to a smaller electric field between the needle and collector). An alternative approach would have been to reduce the voltage for the same separation distance used for the other MPLs, but the decision was to maintain the same spray voltage for all samples in this study. The electrospray voltage was maintained at 5.5 kV in all cases. Operation at a higher voltage generally led to bifurcation of the cone jet, resulting in two jets spraying two different areas. Voltages lower than 5.5 kV led to solution drips forming along with the jet. The optimum Taylor cone jet was achieved empirically through a careful balance of the flow rate and voltage.

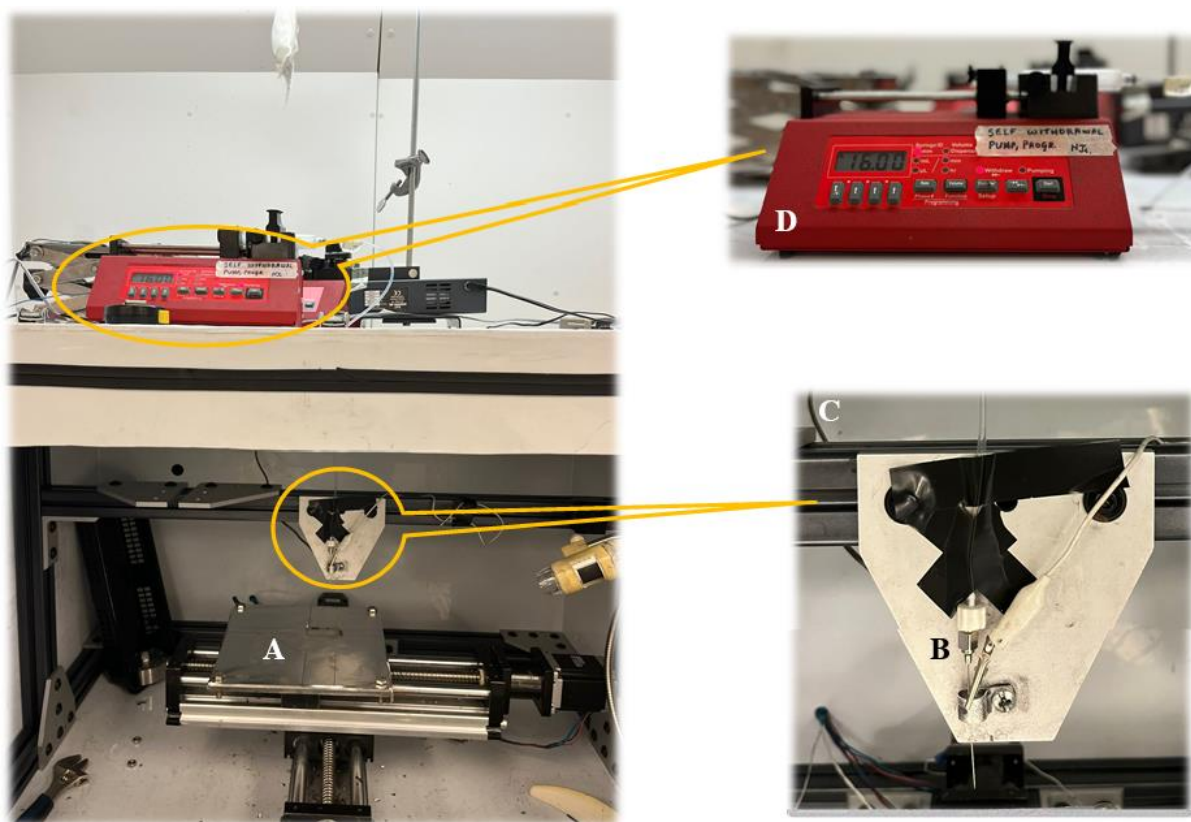


FIGURE 8: ELECTROSPRAYING SETUP: (A) COLLECTOR, (B) NEEDLE, (C) POWER SUPPLY CABLE AND (D) PUMP.

Table 2 below summarizes the main electrospraying parameters used to produce the 3 MPLs:

TABLE 2: ELECTROSPRAYING PARAMETERS

PARAMETER	MPL-ITO(10)	MPL-Sn(8)	MPL-ITO(5)
needle size (gauge)	16	24	16
flow rate (ml/h)	0.66	0.3	0.66
spray volume (ml)	4.5	3.0	2.1
voltage (kV)	5.5	5.5	5.5
tip-to-collector distance (cm)	2.1	4.0	2.1

3.4 Preparation of MPL-Ti by Solvent Evaporation

MPL-Ti was prepared using Ti nanoparticles that were mixed in ethanol at various concentrations to obtain 3 different loadings on the MPL. The nanoparticles were briefly stirred and sonicated for 15 min. Then, a piece of the Ti felt substrate was placed in a petri-dish into which the Ti-laden suspension was poured. The samples were then left to dry overnight at room temperature. The drying conditions were not controlled, and the evaporation was allowed to proceed under the conditions prevailing in the lab at the time of preparation. Once dried, a smooth coating of MPL-Ti formed on the felt. The MPLs produced in this manner were labelled as MPL-Ti(8), MPL-Ti(11) and MPL-Ti(12) according to the loading levels given in Table 3 below:

TABLE 3: TITANIUM LOADING ON FELT

MPL	Loading (mg/cm ²)
<i>MPL-Ti(8)</i>	8
<i>MPL-Ti(11)</i>	11
<i>MPL-Ti(12)</i>	12

3.5 Post-electrospraying Treatment

After electrospraying, MPL-ITO(10) and MPL-ITO(5) were dried in an ISOTEMP 282A oven in air at 105°C for 1 h. This ensured that all the solvent had evaporated and only the solid deposit containing binder, PVP and ITO remained on the surface. Two different versions of MPL-ITO(10) and MPL-ITO(5) were formed. The first was used as is, while the second one was compressed after being removed from the oven. The compressed version was squeezed in a hydraulic press at 2000 kg for 30 s. Once formed, each MPL was characterized by various methods to determine its properties and performance. The uncompressed MPL were denoted as MPL-

ITO(10)_{NC} and MPL-ITO(5)_{NC} while the compressed samples were denoted as MPL-ITO(10) and MPL-ITO(5).

MPL-Sn(8) was placed in the furnace at 500°C for 6 h under N₂ to sinter the Sn. MPL-Sn(8) was also produced in 2 different versions. The first one was uncompressed, while the second was compressed in a hydraulic press at 2000 kg for 30 sec, similar to MPL-ITO(10) and MPL-ITO(5). The compressed sample was labelled as MPL-Sn(8) while the uncompressed sample was labelled as MPL-Sn(8)_{NC}.

MPL-Ti(8), MPL-Ti(11) and MPL-Ti(12) were placed in the furnace at 750°C for 1 h under argon to sinter the Ti nanoparticles. The image below (Figure 9) shows the final prepared samples.

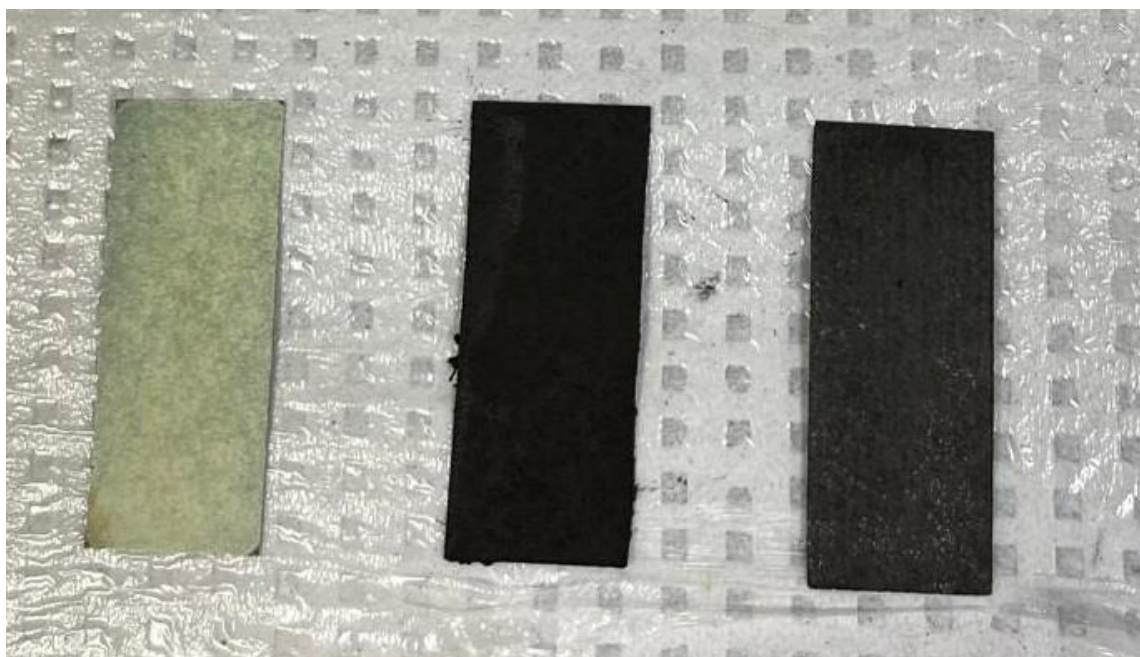


FIGURE 9: FINAL MPL COATINGS (FROM L TO R, MPL-ITO(10), MPL-Ti(8) AND MPL-Sn(8))

3.6 Characterization of MPLs by SEM and AFM

The morphology of the MPLs was examined using a Quanta FEG 250 SEM. The Quanta FEG 250 operates in three modes: high-vacuum, low-vacuum and ESEM (which stands for environmental SEM). It achieves a resolution of 1.2 nm at 30 kV and 2.3 nm at 1 kV with beam deceleration in high vacuum using the in-column detector. All the images for this study were captured under high-vacuum mode at 20 kV. The SEM unit was used to examine the surface morphology of the MPLs. Magnifications of 500x, 250x and 100x were applied to all samples. In order to determine composition of the solids deposited onto the Ti felt, elemental analysis of the MPLs was conducted using energy dispersive x-ray spectroscopy (EDX). Since the ITO and Sn nanoparticles tended to settle in the syringe, the composition of ITO/Sn in the final coating was expected to be lower than the amount that was initially loaded into the spraying solution.

Atomic force microscopy (AFM) was conducted using an Integrated Circuit Scanning Probe Instruments (ICSPI) model using a mobile Redux Atomic Force Microscope operating in contact mode. This unit generated 3D images of the MPLs as well as measuring their roughness. The surface roughness was measured only for MPL-Ti(8), MPL-Ti(11) and MPL-Ti(12). Only the roughness of the MPL-Ti samples was obtained because, as observed later, these samples exhibited the best performance when used in the electrolyzer compared to the other MPLs.

3.7 Through-Plane Permeability

The permeability of the samples was measured using a procedure described in earlier research which involved supplying air on the upstream side of the sample and measuring the upstream pressure, with the downstream side remaining under atmospheric conditions.^[76] As shown in Figure 10, the sample was sandwiched between two rubber gaskets placed inside two smooth metal blocks to achieve an air-tight seal. The sample characterized was circular with the diameter being 1.6 mm (1/16”) larger than the gasket hole diameter. In this set up, the sample was 11.1 mm (7/16”) in diameter, while the inner diameter of each gasket was 9.5 mm (3/8”).

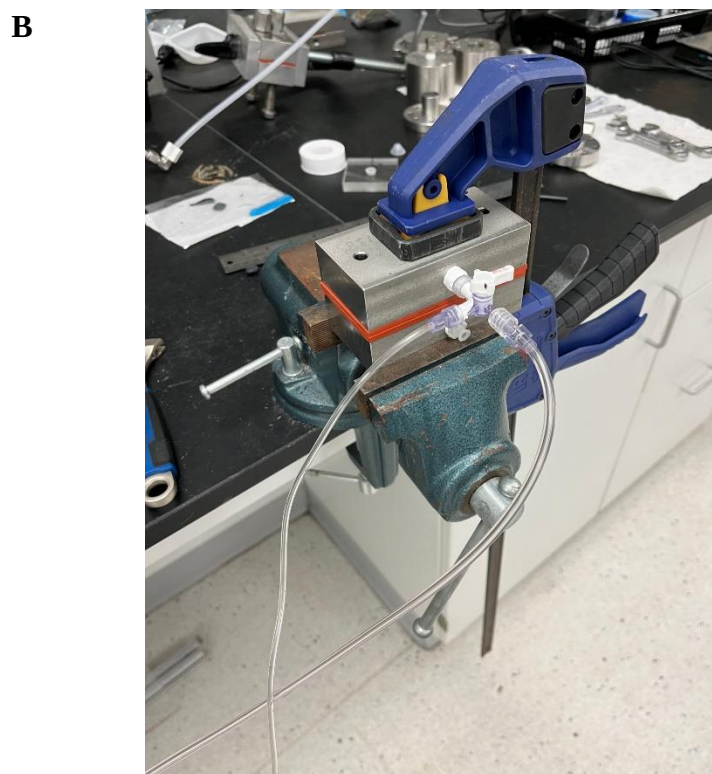
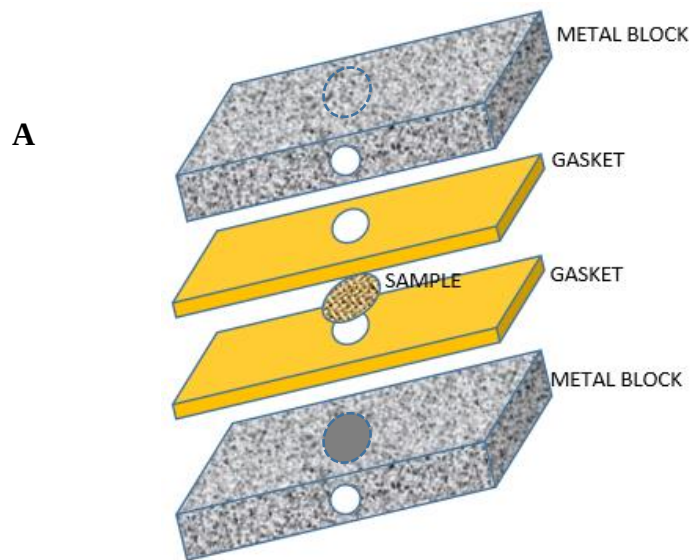


FIGURE 10: A - SCHEMATIC REPRESENTATION OF THROUGH-PLANE PERMEABILITY MEASUREMENT SET UP; B – HOLDER USED IN PERMEABILITY SET UP

Due to the low gas pressure applied, the seal could be confidently considered to be air-tight. To be sure, a leak test was also performed by placing a sample with very low permeability in the setup, shutting off the air supply and then ensuring that the pressure did not drop.

The through-plane permeability was determined by measuring the pressure difference for each of 7 different flow rates over the range from 0 to 80 sccm and Darcy's law modified for compressible gas flow:^[76]

$$\frac{P_{IN}^2 - P_{OUT}^2}{2LRT/MW_{AIR}} = \frac{\mu}{K} m' \quad (7)$$

where

- P_{IN} is the inlet pressure of the gas (Pa)
- P_{OUT} is the exit pressure (atmospheric) (Pa)
- m' is the mass flux of air across the sample ($\text{kg m}^{-2} \text{s}^{-1}$)
- K is the permeability coefficient (m^2) normally reported in units of Darcy. (1 Darcy is equivalent to $0.987 \times 10^{-12} \text{m}^2$)
- MW_{AIR} is the molecular weight of air (kg mol^{-1})
- μ is the kinematic viscosity of air (Pa s)
- L is the thickness of the sample (m)
- R is the universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
- T is the ambient temperature (K)

Mass flow rates were obtained by multiplying the volumetric flow rates by the density of air at the flow pressure and temperature. The mass flux was obtained by dividing the mass flowrate by the area of the sample normal to the direction of air flow. To determine the permeability

coefficient K , the quantity on the left-hand side of Eqn (7) was first plotted versus m' and the statistically best-fit straight line was determined. According to Eqn (7), the slope of this straight line is numerically equal to μ/K , where μ is the known viscosity of air. Once μ/K was determined from the best straight-line plot, K was obtained from the ratio of μ to the slope.

3.8 Porosity

Porosity is defined as the volume fraction of voids present in a sample. Although the porosity is important, the pore size probably has a larger impact on the performance, especially for the MPL which has pore sizes primarily on the order of nanometers. However, in the following analysis, only the overall porosity is evaluated since the pore size and distribution could not be determined using this procedure.

In this study, the porosity of the overall sample (felt with the MPL) was measured using the procedure first developed by Rashapov et al. ^[77] that is based on measuring its buoyancy in a known fluid. First, the sample was cut out into a circular shape with diameter d . Then, the thickness δ_0 of the sample was measured at 3 different locations using a micrometer. The weight of the sample was measured in air by taking the average of 3 measurements. The usual procedure involves submerging the sample in silicon oil and holding it under a vacuum of approximately 1000 Pa overnight to eliminate all trapped air and to fully wet the pores with silicon. However, due to the larger pore size of the samples in this study, this was not necessary and so the sample was kept under a vacuum only as long as it took the evolution of air bubbles to cease (~45 min). The sample weight was then measured while being fully submerged in a silicon bath using the set-up shown in Figure 11 below. In this study, MPL-Ti(8) was the only Ti coating for which the porosity was measured since the porosities of the other Ti samples were expected to be similar.

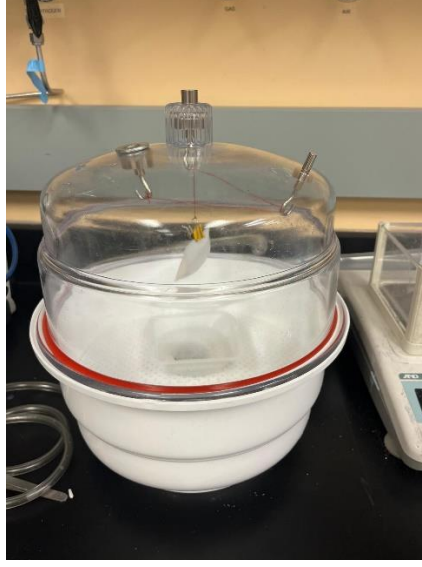


FIGURE 11: SETUP FOR PULLING VACUUM DURING POROSITY MEASUREMENT AND FILLING THE PORES WITH SILICON

Applying the Archimedes principle, the density of the submerged solid is calculated as:

$$\rho_s = \rho_l \frac{m_s}{m_l} \quad (8)$$

where m_s is the mass of the solid, m_l is the mass of liquid displaced by the solid and ρ_l is the density of silicon oil. m_l is determined by taking the difference of the mass of the solid in air and the mass of the solid submerged in the silicon, i.e.,

$$m_l = m_s - m_{s,l} \quad (9)$$

Replacement of Eqn (9) in Eqn (8) yields

$$\rho_s = \frac{m_s}{V_s} = \rho_l \frac{m_s}{m_s - m_{s,l}} \quad (10)$$

which can be rearranged to yield:

$$V_s = \frac{m_s - m_{s,l}}{\rho_l} \quad (11)$$

where V_s is the solid volume of the sample. From the measured value of $m_l = m_s - m_{s,l}$, V_s can be determined. The buoyancy force exerted by air on the sample could be safely neglected due to the low density of air. The porosity was then calculated by the following formula where V_b is the bulk volume obtained from the known thickness and radius of the sample:

$$\varepsilon = 1 - \frac{V_s}{V_b} \quad (12)$$

3.9 X-Ray Tomography Imaging

X-ray computed tomography (XCT) imaging was conducted at a collaborating laboratory to evaluate the internal structure of selected samples. The XCT analysis was specifically performed on the three best-performing Ti-MPL samples. These samples were chosen based on their superior performance (as observed later in section 4.8.2).

To optimize the imaging process, the samples were assembled into a single composite unit. Each Ti-MPL sample was separated by a layer of aluminum foil, so that each sample could be uniquely analyzed. This arrangement allowed for simultaneous analysis of all samples in a single XCT scan, improving the efficiency of the imaging process and providing a comprehensive dataset for comparison.

The diagram below illustrates the stacking configuration of the samples to facilitate effective XCT imaging.

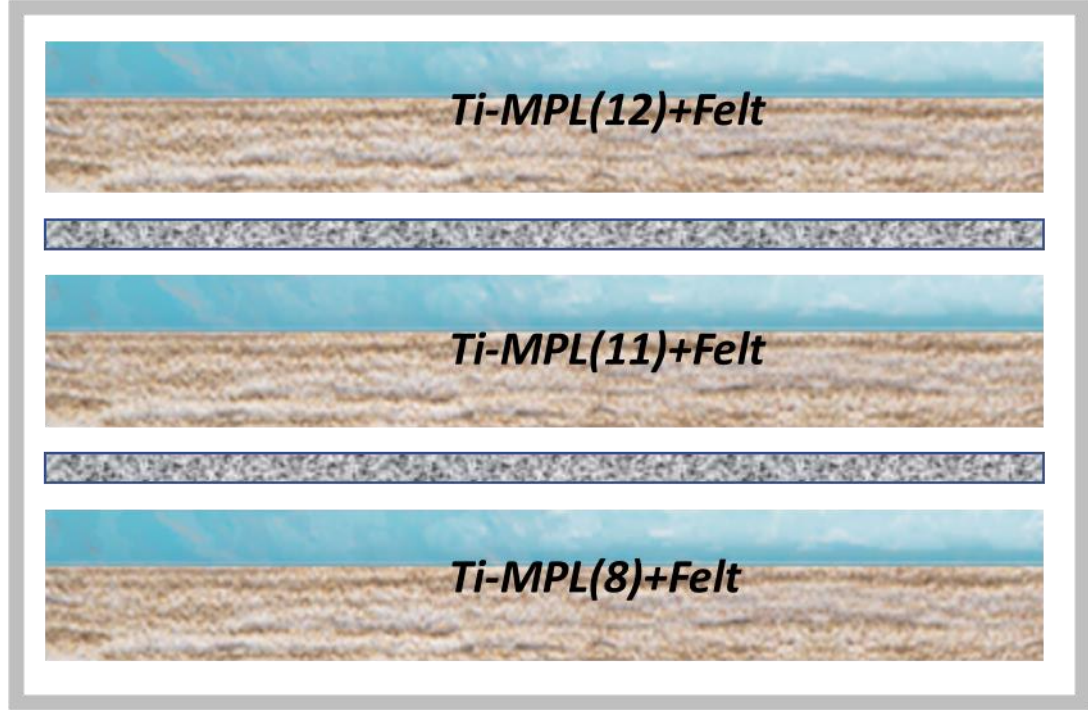


FIGURE 12: TI-MPL SAMPLES ARRANGEMENT FOR XCT IMAGING. THIS IMAGE SHOWS HOW THE SAMPLES WERE STACKED TOGETHER SEPARATED BY AL FOIL

3.10 Through-Plane Electrical Conductivity

The through-plane electrical conductivity was measured using a device in which the sample was sandwiched between 2 copper plates and compressed by applying a constant pressure. The procedure for measurement was to obtain a plot of voltage versus current for the samples with the slope of the curve corresponding to the resistance R of the sample. Voltages of 0.125, 0.25 and 0.50 V were applied and the corresponding currents were measured. Since the area A and the thickness l of the samples are known, the conductivity could be calculated as shown below.

$$\rho = \frac{R A}{l} \quad (13)$$

where ρ is the resistivity ($\Omega\cdot\text{m}$). With ρ known, the conductivity σ in S m^{-1} was obtained as follows:

$$\sigma = \frac{1}{\rho} \quad (14)$$

For each distinct coating type (ITO, Sn & Ti), only one sample was selected (compressed ones - MPL-ITO(10) for ITO and MPL-Sn(8) for Sn, and MPL-Ti(8) for Ti) since the electrical conductivity depends mainly on the material composition.

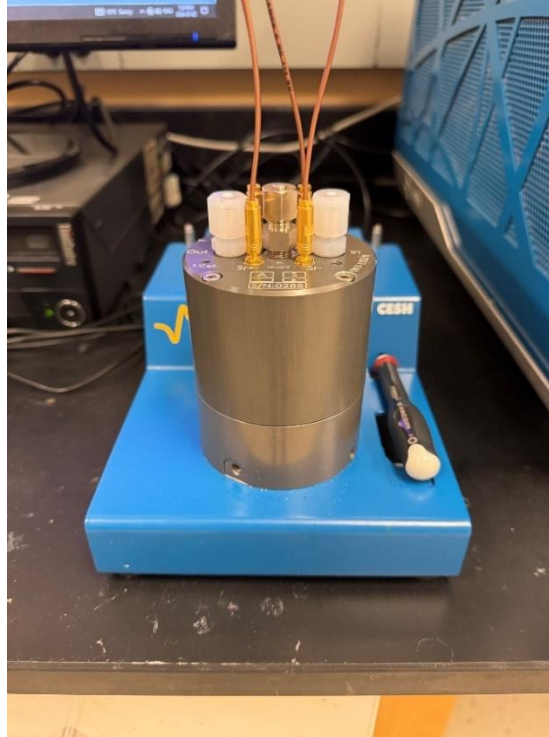


FIGURE 13: DEVICE USED TO MEASURE THE THROUGH-PLANE CONDUCTIVITY

3.11 Electrolyzer Performance Test

For the performance test, the samples were tested using DI water at 75°C on the anode side with no circulation to the cathode. The use of DI water was preferred to prevent scale formation on the membrane and catalyst and thereby reduce maintenance costs. The polarization curves were obtained by applying a voltage from 1.4 – 2.0 V in increments of 0.05 V and measuring the current.

At each applied voltage, the current was measured after a wait time of 3 min to ensure that a stable value was obtained.

The MPL samples were cut to dimensions of 2.0 cm x 0.9 cm to fit the electrolyzer. The flow field area was 2.1 cm x 2.1 cm along a single-pass flow-through serpentine pattern (Figure 14). The bipolar plates were both made of titanium. The performance test was done individually for each MPL as the anode, SGL22BB as the cathode and Hydrion N115 as the CCM.

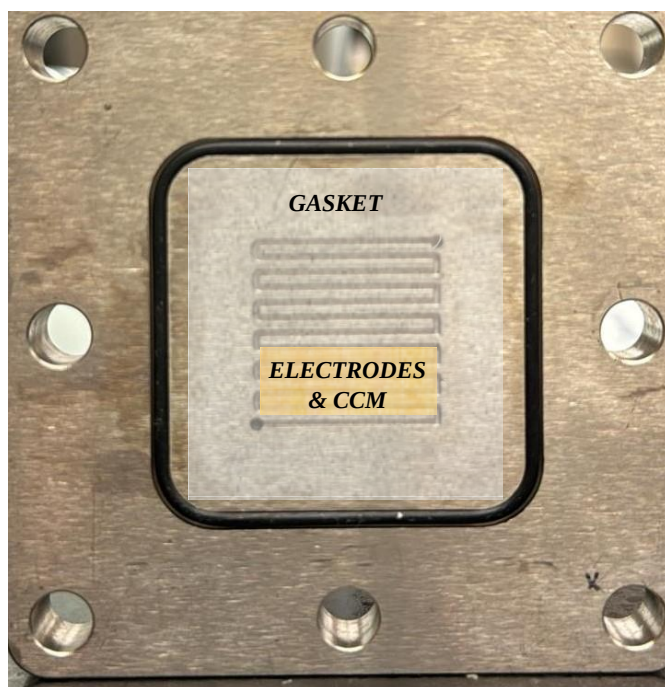


FIGURE 14: TI BI-POLAR PLATE WITH ONCE-THROUGH FLOW FIELD USED FOR PERFORMANCE TEST. YELLOW REGION INDICATES AREA COVERED BY ELECTRODES AND CCM

A KNF Simdos10 pump was used to maintain a constant water supply rate of 25 ml/min through the cell during operation. The temperature of the DI water was maintained at 75°C using an external water bath to yield a final temperature of ~60°C in the electrolyzer.

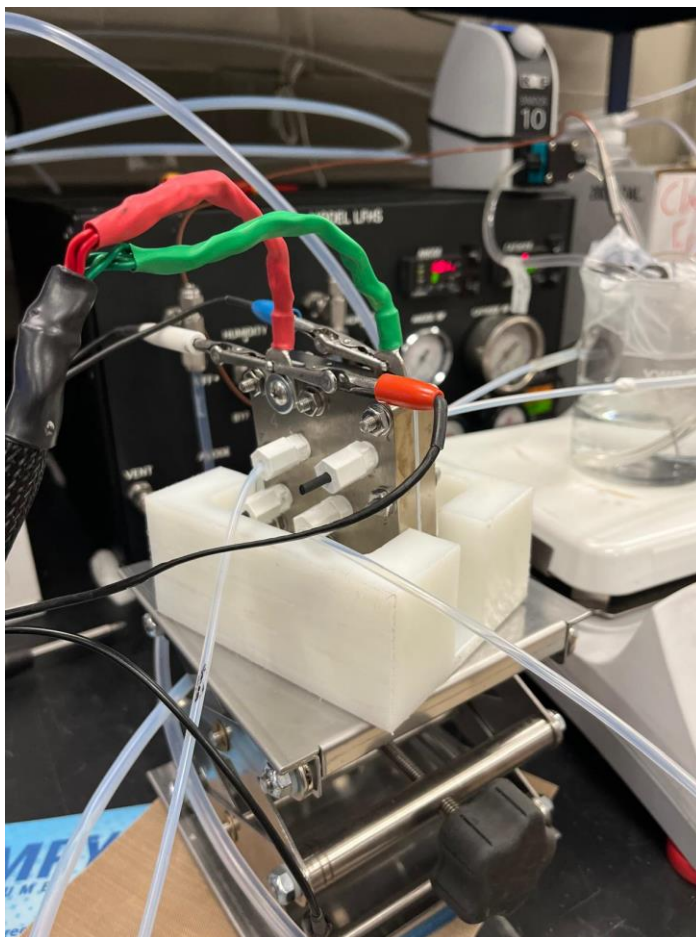


FIGURE 15: ASSEMBLED LAB SCALE ELECTROLYZER

The compression level selected for the anode/cathode was adjusted by using gaskets of different thicknesses. The aim was to compress each sample by $\sim 15\%$ of the original thickness. For example, if the sample had a thickness of $300\ \mu$, a gasket of $255\ \mu$ was used. Figure 16 & Figure 17 below show the anode and the cathode of the electrolyzer with the inlet and outlet streams.

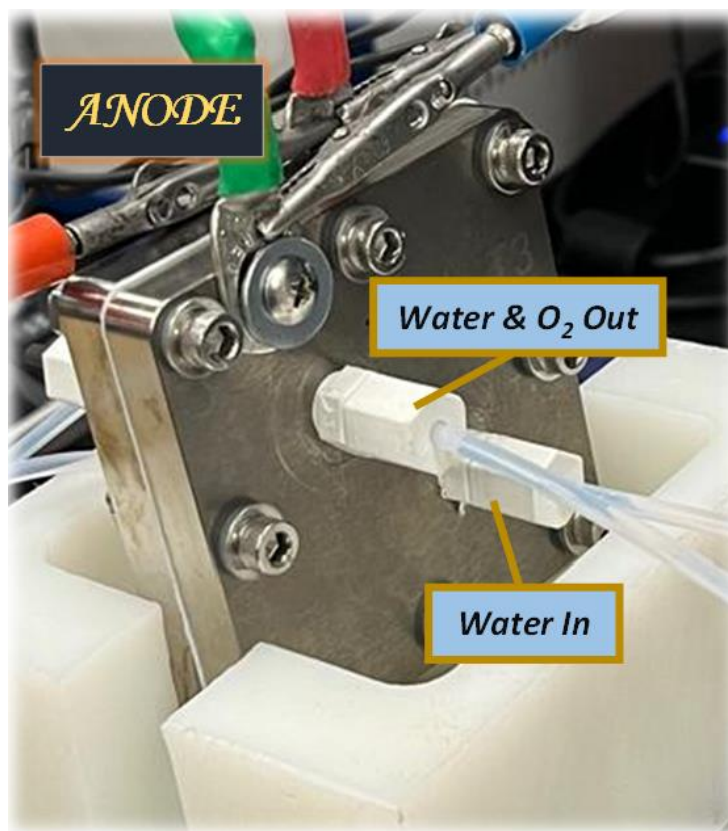


FIGURE 16: INLET AND OUTLET STREAMS TO AND FROM ANODE OF THE LAB-SCALE ELECTROLYZER USED IN THIS STUDY

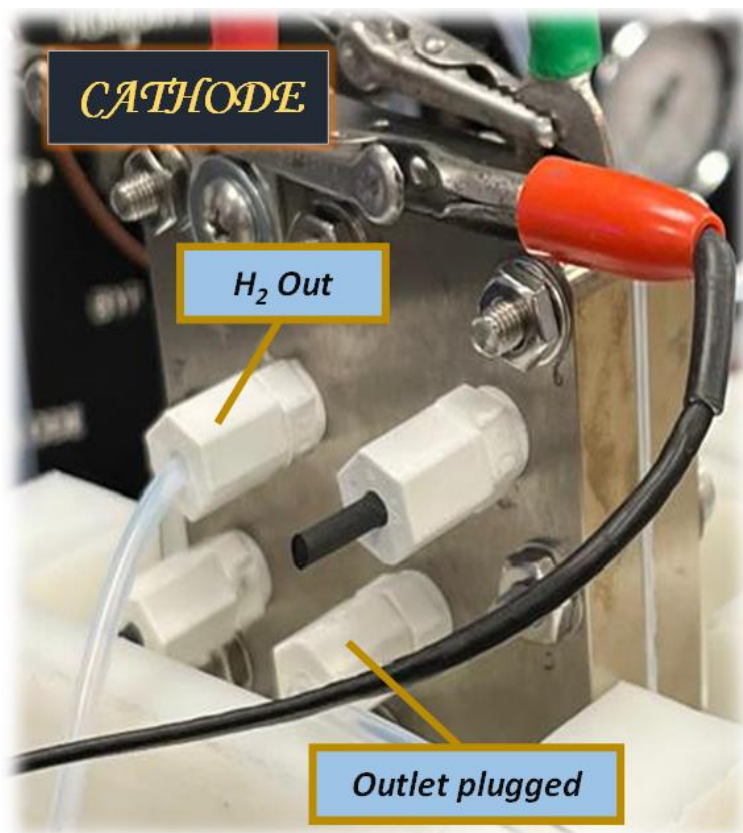


FIGURE 17: GAS (HYDROGEN) OUTLET STREAM FROM CATHODE OF THE LAB-SCALE
ELECTROLYZER USED IN THIS STUDY

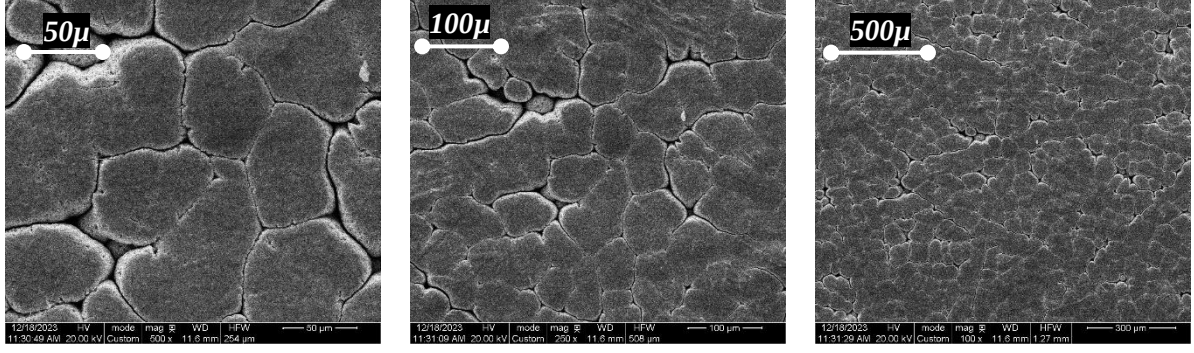
4. Results and Discussion

4.1 SEM Images

SEM images at different magnifications (X500, X250 and X100) of the various MPLs have been obtained using a Quanta FEG 250 SEM. The information gained from these images is discussed below.

4.1.1 MPL-ITO(10) and MPL-ITO(10)_{NC}

As shown in Figure 18 and Figure 19, the coatings for MPL-ITO(10) and MPL-ITO(10)_{NC} cover the felt fibers fully. The coating of MPL-ITO(10) appears flattened due to compression under the hydraulic press. Compression is important because it helps to create a smooth and continuous MPL layer to ensure good contact with the catalyst layer. However, as noted later in section 4.5, this has an impact on its permeability. The overall thickness of the MPL-ITO(10) sample (including the felt substrate) after the compression is measured using a micrometer and found to be 280 μ . In the absence of compression, the overall thickness of the sample (i.e., MPL-ITO(10)_{NC}) is found to be 305 μ .

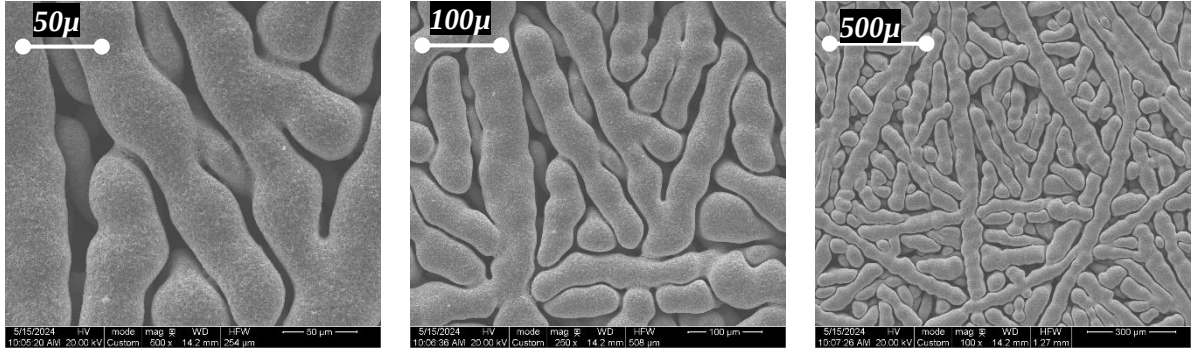


MPL-ITO(10) 10 mg/cm², X500

MPL-ITO(10) 10 mg/cm², X250

MPL-ITO(10) 10 mg/cm², X100

FIGURE 18: SEM IMAGES OF MPL-ITO(10) AT DIFFERENT MAGNIFICATIONS



MPL-ITO(10),NC 10 mg/cm², X500

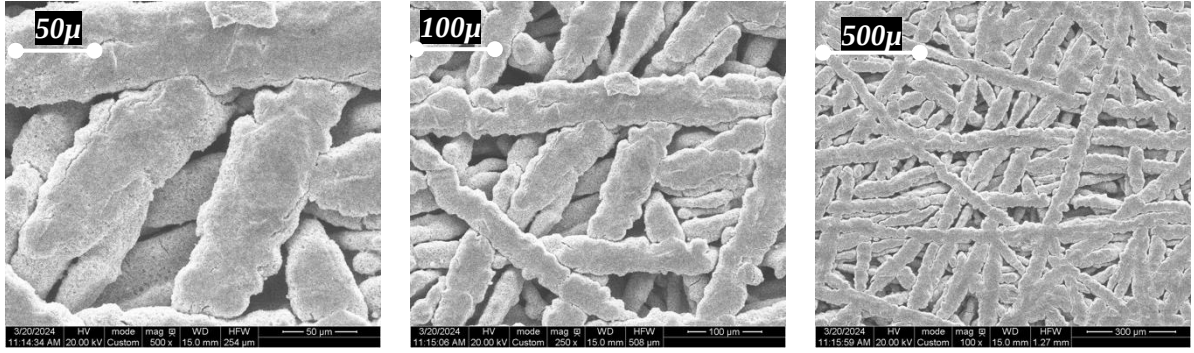
MPL-ITO(10),NC 10 mg/cm², X250

MPL-ITO(10),NC 10 mg/cm², X100

FIGURE 19: SEM IMAGES OF MPL-ITO(10),NC AT DIFFERENT MAGNIFICATIONS

4.1.2 MPL-ITO(5) and MPL-ITO(5),NC

The thickness of MPL-ITO(5),NC (Figure 21) is determined to be 285 μ , while that of MPL-ITO(5) (Figure 20) is 262 μ .

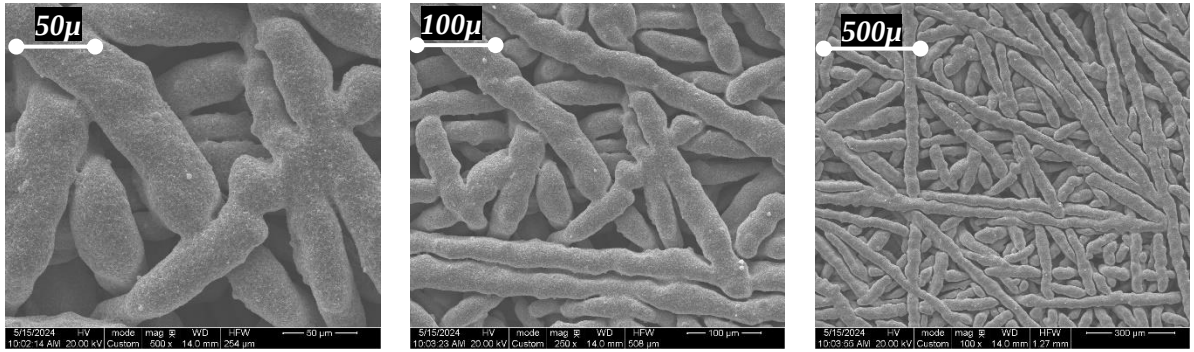


MPL-ITO(5) 5 mg/cm², X500

MPL-ITO(5) 5 mg/cm², X250

MPL-ITO(5) 5 mg/cm², X100

FIGURE 20: SEM IMAGES OF MPL-ITO(5) AT DIFFERENT MAGNIFICATIONS



MPL-ITO(5)_{,NC} 5 mg/cm², X500

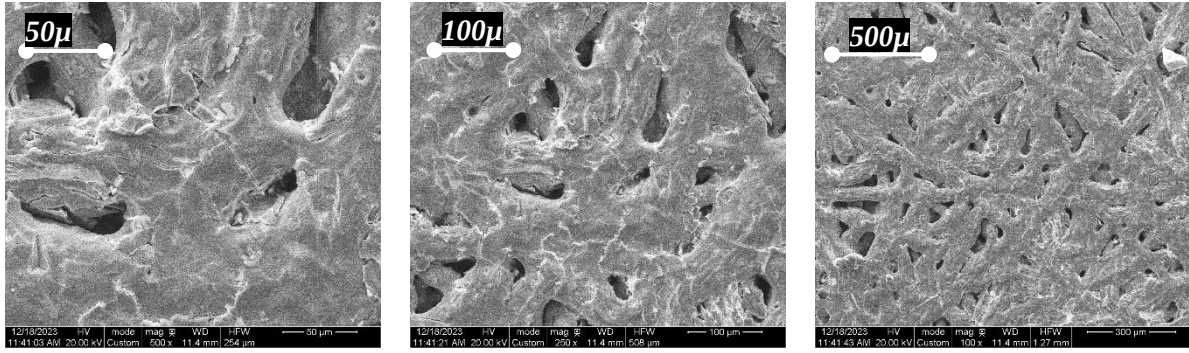
MPL-ITO(5)_{,NC} 5 mg/cm², X250

MPL-ITO(5)_{,NC} 5 mg/cm², X100

FIGURE 21: SEM IMAGES OF MPL-ITO(5)_{,NC} AT DIFFERENT MAGNIFICATIONS

4.1.3 MPL-Sn(8) and MPL-Sn(8)_{,NC}

The SEM images in Figure 22 and Figure 23 indicate a good coverage of the fibers by the Sn nanoparticles. The thickness of the uncompressed MPL-Sn(8)_{,NC} (combined coating and felt substrate) is measured to be 285 μ . If compressed, the thickness of MPL-Sn(8) and the substrate is reduced to 262 μ .

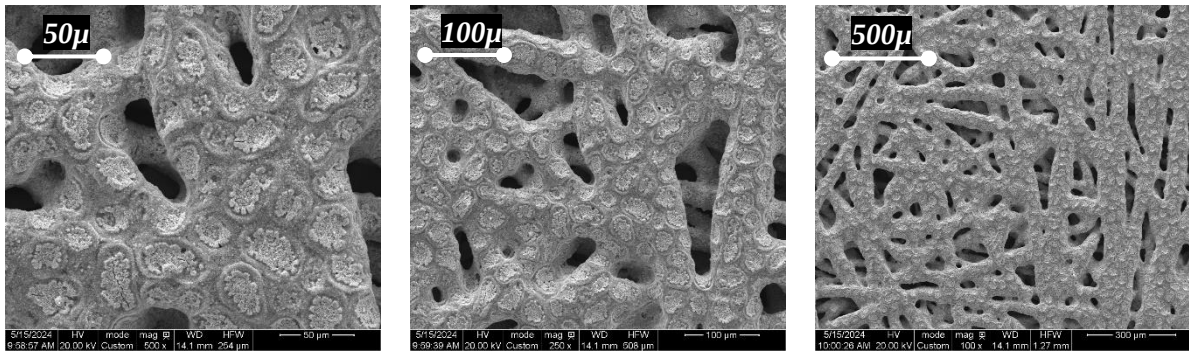


MPL-Sn(8) 8 mg/cm², X500

MPL-Sn(8) 8 mg/cm², X250

MPL-Sn(8) 8 mg/cm², X100

FIGURE 22: SEM IMAGES OF MPL-Sn(8) AT DIFFERENT MAGNIFICATIONS



MPL-Sn(8)_{NC} 8 mg/cm², X500

MPL-Sn(8)_{NC} 8 mg/cm², X250

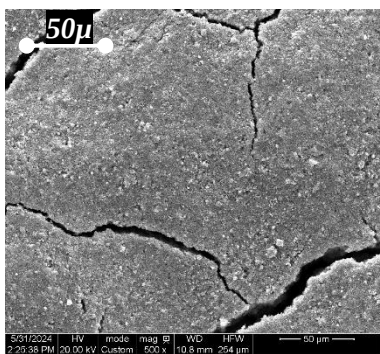
MPL-Sn(8)_{NC} 8 mg/cm², X100

FIGURE 23: SEM IMAGES OF MPL-Sn(8)_{NC} AT DIFFERENT MAGNIFICATIONS

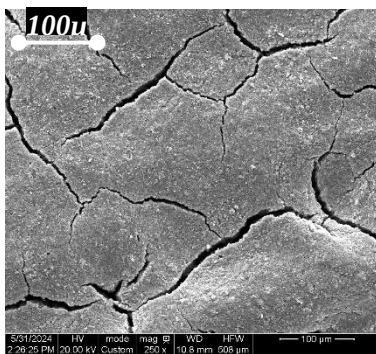
4.1.4 MPL-Ti(8), MPL-Ti(11) and MPL-Ti(12)

The SEM images of MPL-Ti(8), MPL-Ti(11) and MPL-Ti(12) (Figure 24 - Figure 26) show excellent coverage of the fibers with the coating. In each case, the surface seems to have a smooth coating, with cracks appearing on the surface. The formation of cracks in the MPL was unintentional, but highly fortuitous. Since the pores of the MPL are on the same order as the particle size, the low fluid permeability and high capillary breakthrough pressure of the nanoporous regions would be problematic for reactant and product transport. The presence of cracks provides a pathway for these processes. In fact, as seen in PEM fuel cells where

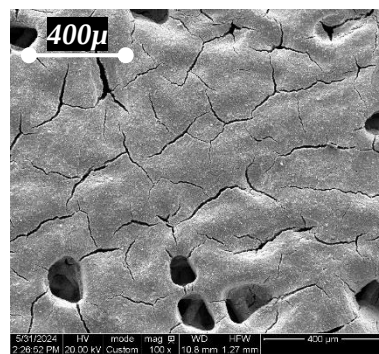
nanoparticle MPLs are common, several researchers have proposed using a laser to create perforations to facilitate the transport.^[78–80] Thus, solvent evaporation not only ensures uniform coverage but also enhances the functional properties of the MPL through the formation of beneficial cracks. After sintering, the thicknesses of these MPL samples vary only over the range from 350 to 365 μ , showing that they are not affected by the loading of the Ti nanoparticles.



MPL-Ti(8), 8 mg/cm², X500

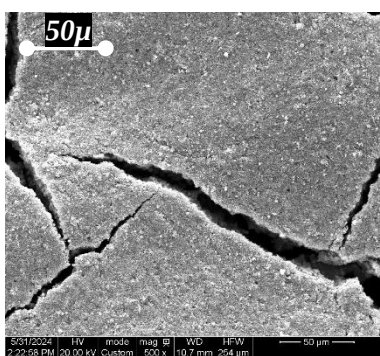


MPL-Ti(8), 8 mg/cm², X250

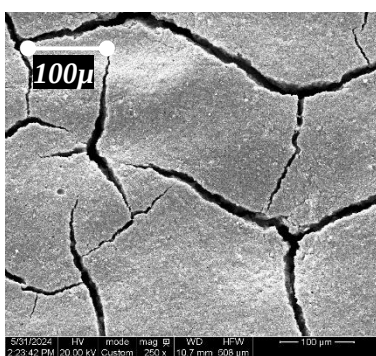


MPL-Ti(8), 8 mg/cm², X100

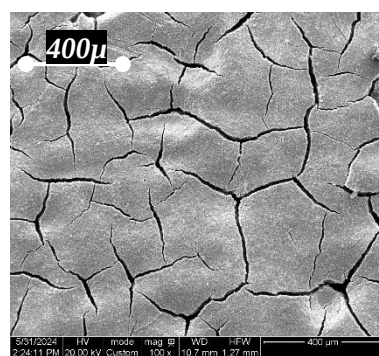
FIGURE 24: SEM IMAGES OF MPL-Ti(8) AT DIFFERENT MAGNIFICATIONS



MPL-Ti(11), 11 mg/cm², X500

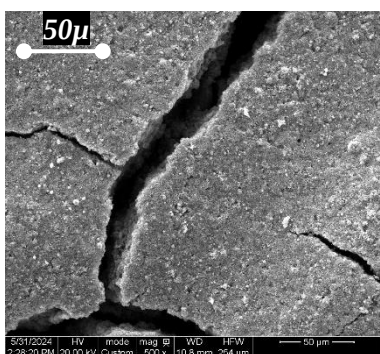


MPL-Ti(11), 11 mg/cm², X250

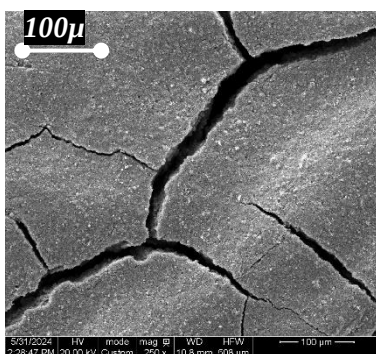


MPL-Ti(11), 11 mg/cm², X100

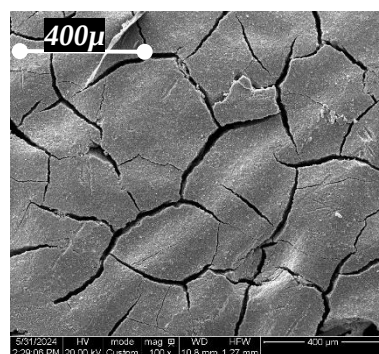
FIGURE 25: SEM IMAGES OF MPL-Ti(11) AT DIFFERENT MAGNIFICATIONS



MPL-Ti(12), 12 mg/cm², X500



MPL-Ti(12), 12 mg/cm², X250



MPL-Ti(12), 12 mg/cm², X100

FIGURE 26: SEM IMAGES OF MPL-Ti(12) AT DIFFERENT MAGNIFICATIONS

In summary, it is observed that the electrosprayed nanoparticles are deposited directly onto the fibers and conform to their shape, resulting in a non-flat coating, unlike the flat sheet coatings observed in MPL-Ti(8) – MPL-Ti(12), which were deposited by solvent evaporation. However, upon compression, the electrosprayed MPLs also become significantly flattened.

4.2 AFM Images

Of all the samples produced, only the MPL-Ti had a visibly smooth surface. Consequently, this sample was investigated further to estimate the nanoscale roughness since this ultimately determines the contact with the CL. The 3D maps of the surfaces of MPL-Ti obtained using AFM are presented below.

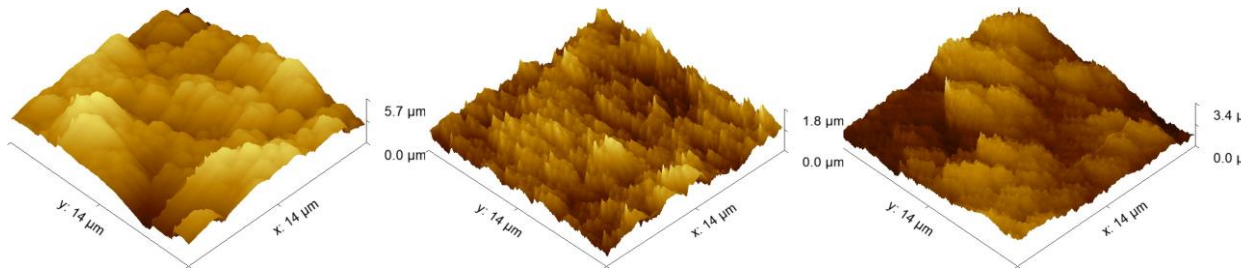


FIGURE 27: AFM IMAGES OF MPL-Ti(8), MPL-Ti(11) AND MPL-Ti(12) (L TO R)

Based on these images, we observe that the maximum peaks of the MPL are $\sim 6 \mu$. The roughness is reduced as the loading of the Ti nanoparticles increases. The root mean square (RMS) roughness for the 2D scans, as calculated using Gwyddion software is:

- MPL-Ti(8): 0.21μ
- MPL-Ti(11): 0.18μ
- MPL-Ti(12): 0.18μ

As expected, the roughness of MPL-Ti(11) and MPL-Ti(12) is similar since the loading only differs by 1 mg/cm^2 . Sample A exhibits the highest roughness in terms of both the average value

and peak heights due to the lower loading of nanoparticles. However, as observed in section 4.8, sample A exhibits the best performance which could be attributed to its rougher surface which should improve the contact with the catalyst layer.

4.3 EDX

EDX was done together with the SEM to yield the results that are summarized below. EDX was used to measure the compositions of MPL-ITO(10), MPL-Sn(8) and MPL-Ti(8). Since the electrospraying solutions for MPL-ITO(5), MPL-ITO(5)_{NC} and MPL-ITO(10) had exactly the same composition, it is expected that MPL-ITO(5) and MPL-ITO(5)_{NC} would have the same composition as MPL-ITO(10) and so were not analyzed.

4.3.1 MPL-ITO(10)

The EDX results are summarized in the table below:

TABLE 4: COMPOSITION OF MPL-ITO(10) AS DETERMINED BY EDX

Element	Weight%
C	8
O	17
F	24
In	51

The analysis indicates that the MPL contains 51 wt % indium. It should be noted that Sn which is a component of ITO was not detected by this analysis. This may indicate that the % of Sn is small and not detected by the EDX.

The presence of carbon, oxygen and fluorine in the sample is expected due to the presence of the Nafion binder and PVP dispersant in the MPL sample.

4.3.2 MPL-Sn(8)

The EDX analysis of MPL-Sn(8) is summarized in the table below.

TABLE 5: COMPOSITION OF MPL-Sn(8) AS DETERMINED BY EDX

Element	Weight%
C	17
O	16
Sn	67

The wt % Sn in the coating is only 67%, while the combined weight fraction of C and O is 33%. Since Sn makes up 87% of the original mixture, this indicates that a significant amount of settling of the Sn nanoparticles (~20%) occurred in the syringe during electrospraying. Some of the carbon and oxygen originate from the PVP in the coating. However, the wt % of oxygen in PVP is ~ 4.5 times less than the weight % of carbon in PVP. The observation of an almost 1:1 mass ratio in the actual coating suggests that a significant amount of the oxygen present in the coating is associated with Sn oxide.

4.3.3 MPL-Ti(8)

EDX analysis shows that it contains 100% Ti.

4.4 Porosity

The results of the porosity test are summarized in Table 6 below.

TABLE 6: POROSITY MEASUREMENT RESULTS

SAMPLE	Porosity
Felt+MPL-ITO(10)	0.29
Felt+MPL-ITO(10) _{,NC}	0.53
Felt+MPL-Sn(8)	0.33
Felt+MPL-Sn(8) _{,NC}	0.54
Felt +MPL-Ti(8)	0.51
Felt+MPL-ITO(5)	0.50
Felt+MPL-ITO(5) _{,NC}	0.53

Not surprisingly, the porosities of the compressed MPL-ITO(10) and MPL-Sn(8) samples are both lower than that of the substrate, which is reported by the manufacturer to be 53-56%. Unlike the situation for MPL-ITO(10) and MPL-Sn(8), no porosity reduction is observed for MPL-ITO(5) possibly due to the lower loading of the nanoparticles.

For the most part, these results are consistent with the previous observation that the MPL coating covers a significant portion of the pores in the felt. On the other hand, the porosity of MPL-Ti(8) and the uncompressed MPLs are very close to the porosity of the bare substrate, indicating that the particles are deposited on the surface only and have not penetrated into the pores of the substrate. This effect is directly visible later in section 4.5 which shows that the permeabilities of MPL-ITO(10) and MPL-Sn(8) are lower than that of the other MPLs due to the compression of these samples. Unfortunately, these measurements do not tell us much about the porosity of the MPL coating itself since it is only the porosity of the combined structure comprising the substrate and coating that is being measured.

4.5 Through-Plane Permeability

The through plane permeability results are reported in units of Darcy (Da) where $1 \text{ Da} = 10^{-12} \text{ m}^2$. The coating covers the top pores of the felt and fills some of the pores so it is expected that the permeability of the combined layer will be lower than that of the plain felt.

This is evident from the SEM images (Figure 18 - Figure 26) where the surface coatings cover the fibers of the felt. As an example, a comparison of the SEM images for uncoated felt and felt coated with MPL-ITO(10) is shown below in Figure 28.

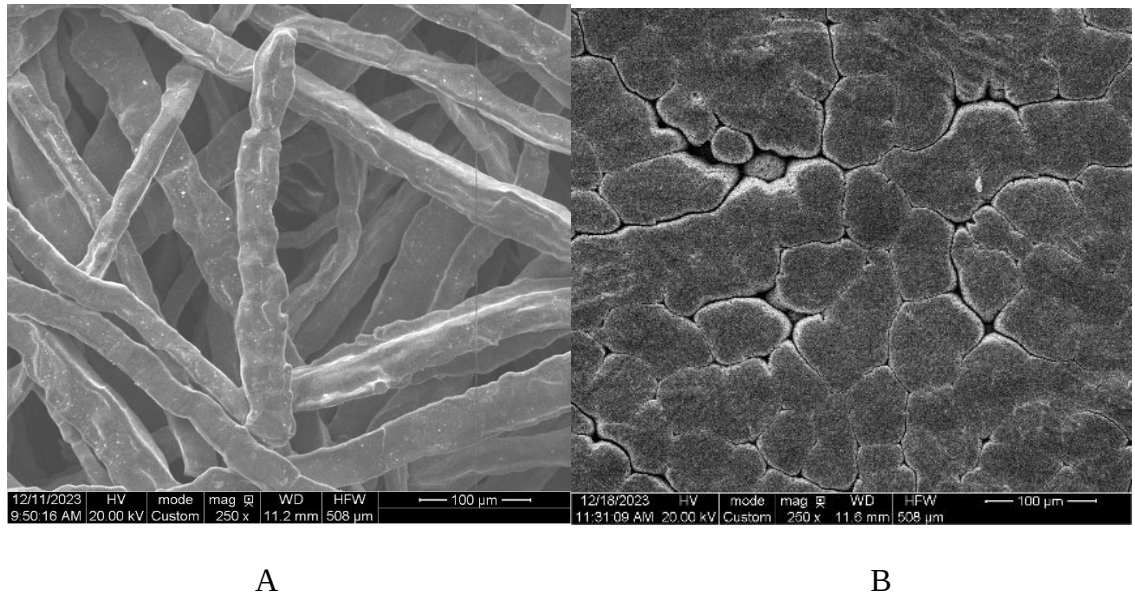


FIGURE 28: DIFFERENCE BETWEEN A COATED SAMPLE – MPL-ITO(10) (B) AND UNCOATED PIECE OF FELT (A)

The permeability results are presented below.

TABLE 7: PERMEABILITY AND POROSITY OF FELT+MPL LAYERS**(PERMEABILITY IS EXPRESSED IN DARCY UNITS [D] WHICH IS $0.978 \times 10^{-12} \text{ m}^2$)**

Sample	Permeability [D]	Porosity
Felt+MPL-ITO(10)	0.40	0.29
Felt+MPL-Sn(8)	1.70	0.33
Felt+MPL-Ti(8)	4.90	0.51
Felt+MPL-Ti(11)	4.80	-
Felt+MPL-Ti(12)	4.90	-
Felt+MPL-ITO(5)	2.50	0.50
Felt+MPL-ITO(10) _{,NC}	4.50	0.53
Felt+MPL-Sn(8) _{,NC}	4.80	0.54
Felt+MPL-ITO(5) _{,NC}	4.90	0.53

Lickert et al reported similar permeability values of 2.3 Da and 5.4 Da for sintered fibrous Ti felt having porosities of 51 and 53%, respectively.^[81] Based on these values, the porosity has a significant impact on the permeability. Comparing the porosities and the permeabilities of the MPL coatings, the increase in permeability with porosity is very noticeable.

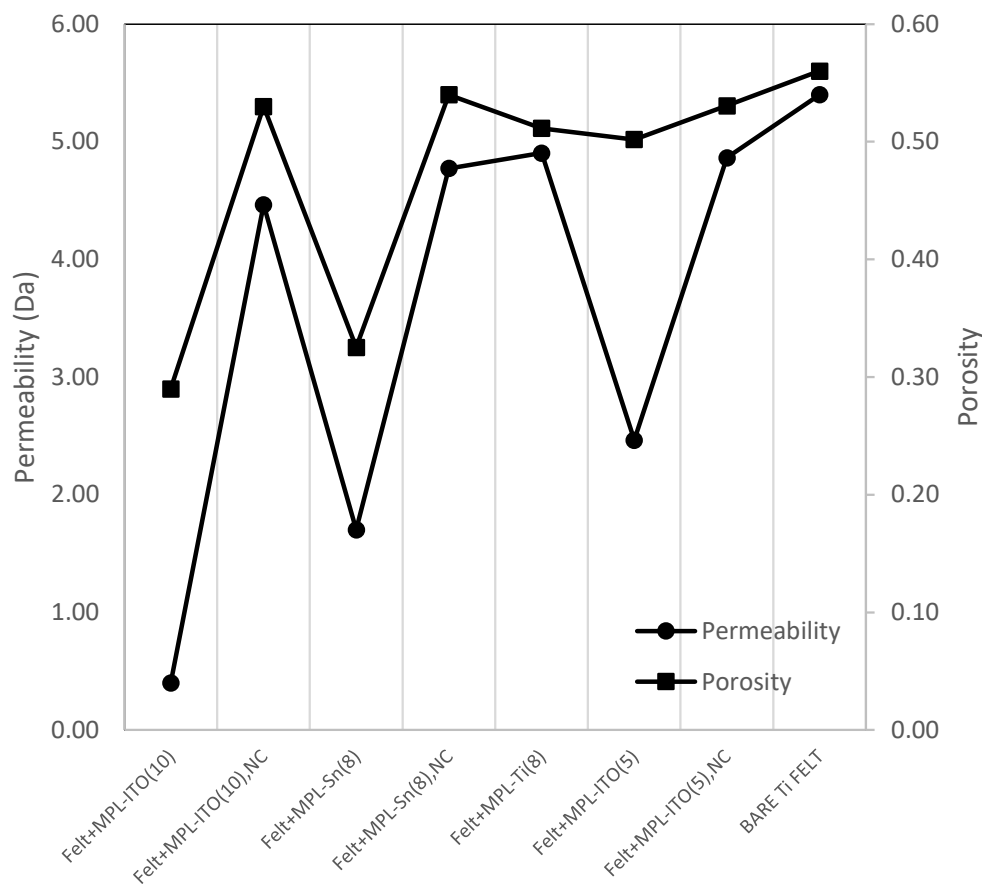


FIGURE 29: CORRELATION BETWEEN PERMEABILITY AND POROSITY OF THE MPL COATINGS FABRICATED IN THIS STUDY

Based on Figure 29 above, we observe that felt+MPL-Ti and all the uncompressed samples have similar permeabilities to that of the uncoated felt. This is due to the loose packing of the nanoparticles over the felt. The deposition method of the Ti nanoparticles is based on simple gravity settling and so it is expected that the particles will be loosely placed and not compacted. This is also consistent with the measured thickness of the MPL+PTL which is $\sim 350 \mu$ for MPL-Ti (compared to $285/305 \mu$ for MPL-ITO(10)_{NC} and MPL-Sn(8)_{NC}) for a similar loading.

Notably, the porosity of the felt+MPL-ITO(5) did not decrease as significantly as its permeability. This may be attributed to the lower nanoparticle loading on the felt, resulting in less invasion of the felt pores compared to the pore invasion of MPL-ITO(10) and MPL-Sn(8).

The permeability of felt+MPL-ITO(10) is the lowest and could be due to the presence of binder which improves the volume packing of the MPL hence and more completely fills the pores. This is also depicted in the SEM image in Figure 18 showing that the ITO coating forms a well compacted layer over the felt.

4.6 Through-Plane Conductivity

The data obtained from the through-plane electrical conductivity experiments are summarized and plotted below.

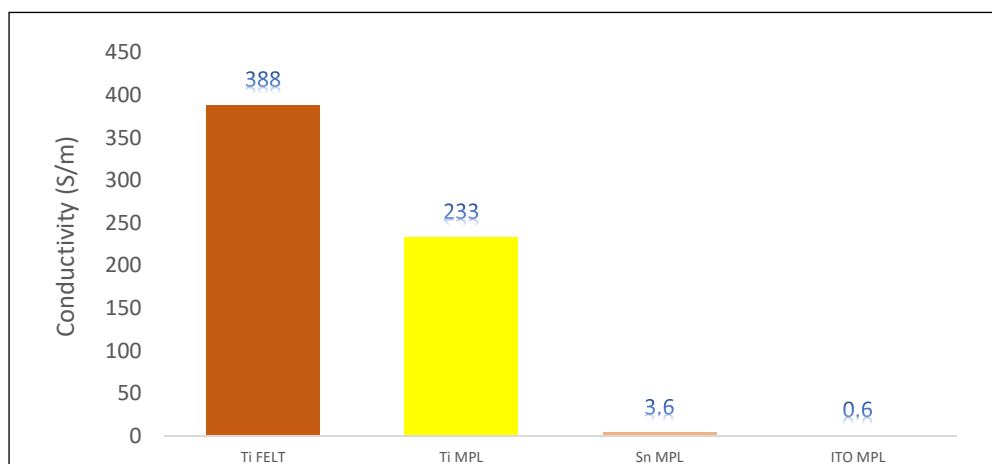


FIGURE 30: THROUGH-PLANE ELECTRICAL CONDUCTIVITIES OF MPL-ITO(10), MPL-SN(8), MPL-TI(8) AND TI FELT.

MPL-ITO(10) exhibits the lowest conductivity presumably due to the presence of binder forming an insulating layer between particles. Next in increasing order is MPL-Sn(8) (Sn), which also has a lower conductivity due to the presence of PVP dispersant. Ti-coated MPL-Ti(8) has the

highest conductivity among the MPLs due to the absence of any non-conductive components. As would be expected, all MPL coatings have conductivities lower than that of the bare Ti felt since the presence of the coating would be expected to reduce the overall electrical conductivity of the sample, although the values for MPL-Ti(8) and bare Ti felt are still within the same order of magnitude ($\sim 10^2$ S/m).

4.7 XCT Imaging

The XCT images offer valuable insights into the morphology of the MPL and its interaction with the felt substrate. The primary purpose of capturing these images was to determine the extent to which the MPL penetrated, if at all, into the pores of the felt. The XCT images were also used to measure the thickness of the MPL.

The XCT images were analyzed using ImageJ. The images were first scaled according to the known thickness measurements obtained in the lab using a micrometer. Based on this calibration, the thickness of the MPL-Ti was measured. The images from the XCT that were analyzed using imageJ are shown below.

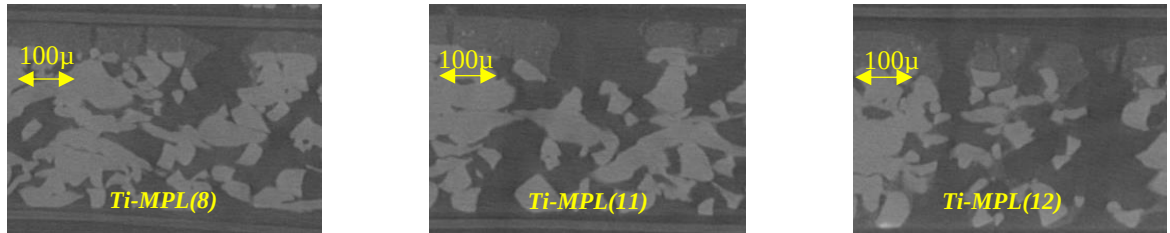


FIGURE 31: XCT IMAGES SHOWING THE INTERNAL STRUCTURE AND THE MPL STRUCTURE FOR ALL 3 Ti-MPL

The lighter regions in Figure 31 indicate the felt while the darker regions represent the MPL. The XCT images reveal noticeable discontinuities within the MPL, which are particularly prominent in regions where voids in the underlying felt provided insufficient support for the

nanoparticle deposition, resulting in voids within the MPL itself. As discussed earlier, although these cracks and voids are seen as defects, they actually contribute positively by enhancing the permeability of the layer.

Another key observation is that the majority of the MPL is deposited on the surface of the felt, with minimal penetration into the felt pores. This deposition pattern is advantageous as it reduces the MPL impact on the gas and liquid transport through the porous transport layer (PTL).

The table below summarizes the total thickness and the MPL thickness as measured using the ImageJ analyzer. Notably, the thicknesses of MPL-Ti(11) and MPL-Ti(12) are very similar, which aligns with the expectation given their comparable nanoparticle loading.

TABLE 8: TOTAL THICKNESS AND MPL THICKNESS FOR THE Ti-MPL AS MEASURED USING IMAGEJ

	TOTAL THICKNESS (μ)	MPL THICKNESS (μ)
<i>MPL-Ti(8)</i>	356	51
<i>MPL-Ti(11)</i>	360	61
<i>MPL-Ti(12)</i>	363	63

4.8 Cell Performance Test Results

Polarization curves were obtained in an electrochemical cell to evaluate the overall performance of each sample. Polarization curves are a good indicator of overall performance since any problems from poor mass transfer to low electronic conductivity all manifest themselves by increasing the cell voltage at a given current density. Depending on what part of the polarization curve is affected, the cause of the problem can be identified. The performance of the samples was evaluated against that of the baseline material which is platinized Ti felt with no MPL coating. Polarization curves exceeding the performance of this baseline material were deemed favorable.

The polarization curves of the various MPLs are presented below in two sections – first those formed by electrospraying (4.8.1) followed by those that are sintered and binder-free (4.8.2).

MPL-ITO(10)_{NC}, MPL-Sn(8)_{NC} and MPL-ITO(5)_{NC} exhibit poor performance with currents almost 50 times less than that of MPL-Ti. The non-conductive parts appear to have a detrimental effect on the performance of the MPL. At even the lowest loading (i.e., MPL-ITO(5)_{NC}), the layer appears non-conductive and the performance is unsatisfactory. The compressed samples perform the worst as the current drops down to almost zero within the first few seconds of the voltage being applied. It is possible that compressed structures tend to trap the evolving oxygen bubbles at the anode catalyst layer. The trapping of bubbles has two main effects which degrade the performance. Firstly, the bubbles can block the active sites (catalyst pores) and reduce the effective surface area for the chemical reaction. Secondly, the accumulation of bubbles can lead to mass transport limitations by blocking passage of the reactant (water) to the catalytic sites and removal of oxygen from the anode. The sintered Ti MPL (MPL-Ti) performed much better than the electrosprayed MPLs and the baseline case.

4.8.1 Electrosprayed MPLs

The electrosprayed MPLs that are functional, but perform poorly, are MPL-ITO(10)_{NC}, MPL-Sn(8)_{NC} and MPL-ITO(5)_{NC}. The compressed versions of these MPLs are not functional as has already been noted. Figure 32 below shows the polarization curves for the binder/dispersant-containing MPLs. Of these, MPL-ITO(5)_{NC} performs best due to the lower loading of the binder/ITO nanoparticles. This suggests that the poor performance is directly related to the relatively low conductivity of the coating so that the thinnest one is the best choice. In a side study, we explored the effect of an even lower binder content of 10% compared to 17% in this study, but this did not lead to a significantly better performance.

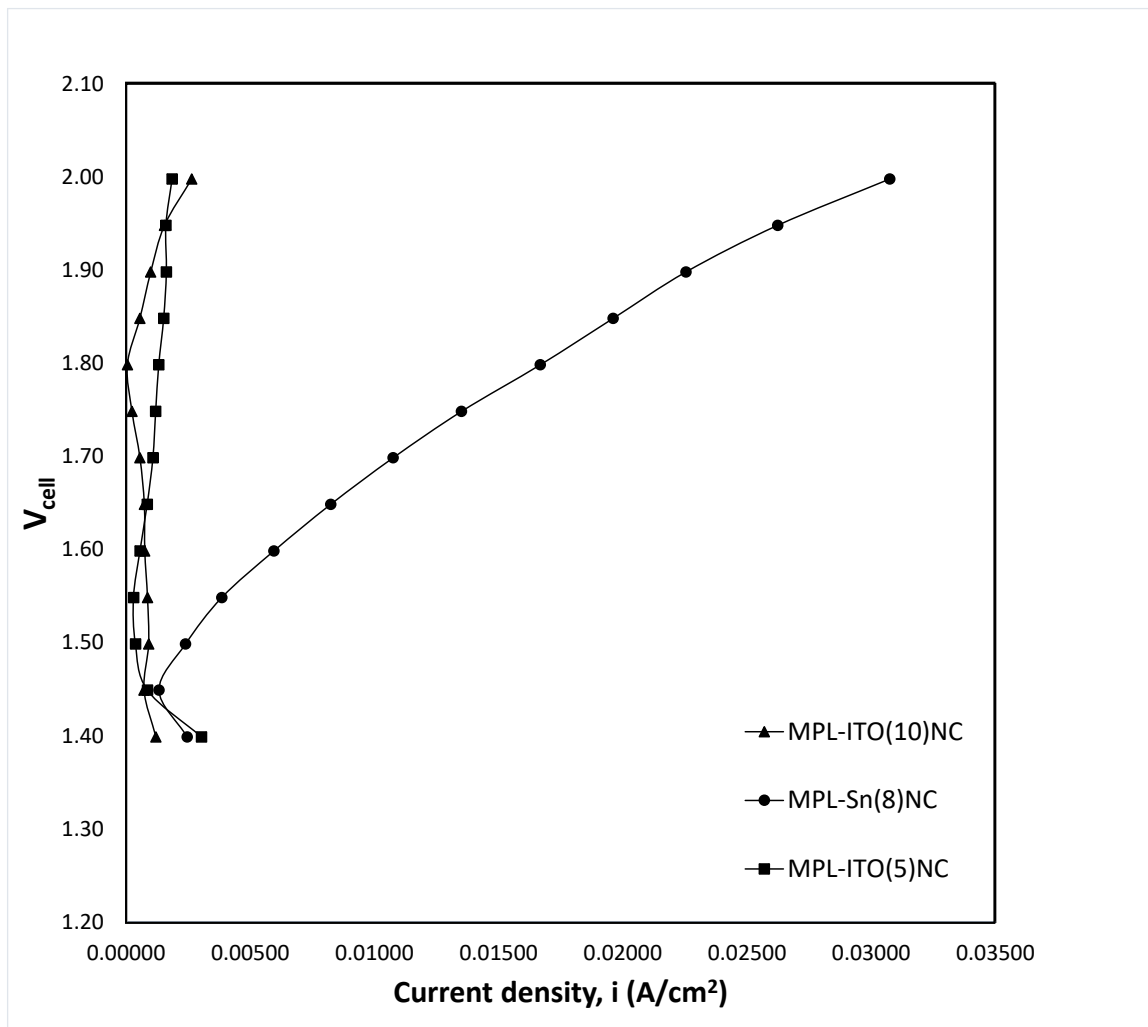


FIGURE 32: POLARIZATION CURVE FOR ELECTROSPRAYED MPL. THE PERFORMANCE TEST WAS DONE AT 75°C WITH WATER FLOW RATE OF 25 ML/MIN AT ANODE AND NO CIRCULATION AT CATHODE

4.8.2 Binder-free sintered Ti MPLs

The sintered Ti MPLs that perform relatively well are MPL-Ti(8), MPL-Ti(11) and MPL-Ti(12). It is observed that the MPL-Ti(8) which contains the lowest loading of the MPL (8 mg/cm²) performs best followed by MPL-Ti(11) and MPL-Ti(12). The better performance of the MPL-

Ti(8) is mainly attributed to the relatively rougher surface which likely improves the contact surface area with the catalyst layer. As shown in Figure 33, the performance of all 3 sintered MPLs surpasses that of the baseline. Although this suggests that the performance may be further improved by applying an even lower loading of the Ti nanoparticles, this is likely limited by the fact that the nanoparticles will not form a smooth continuous and uniform coating if the loading is too low.

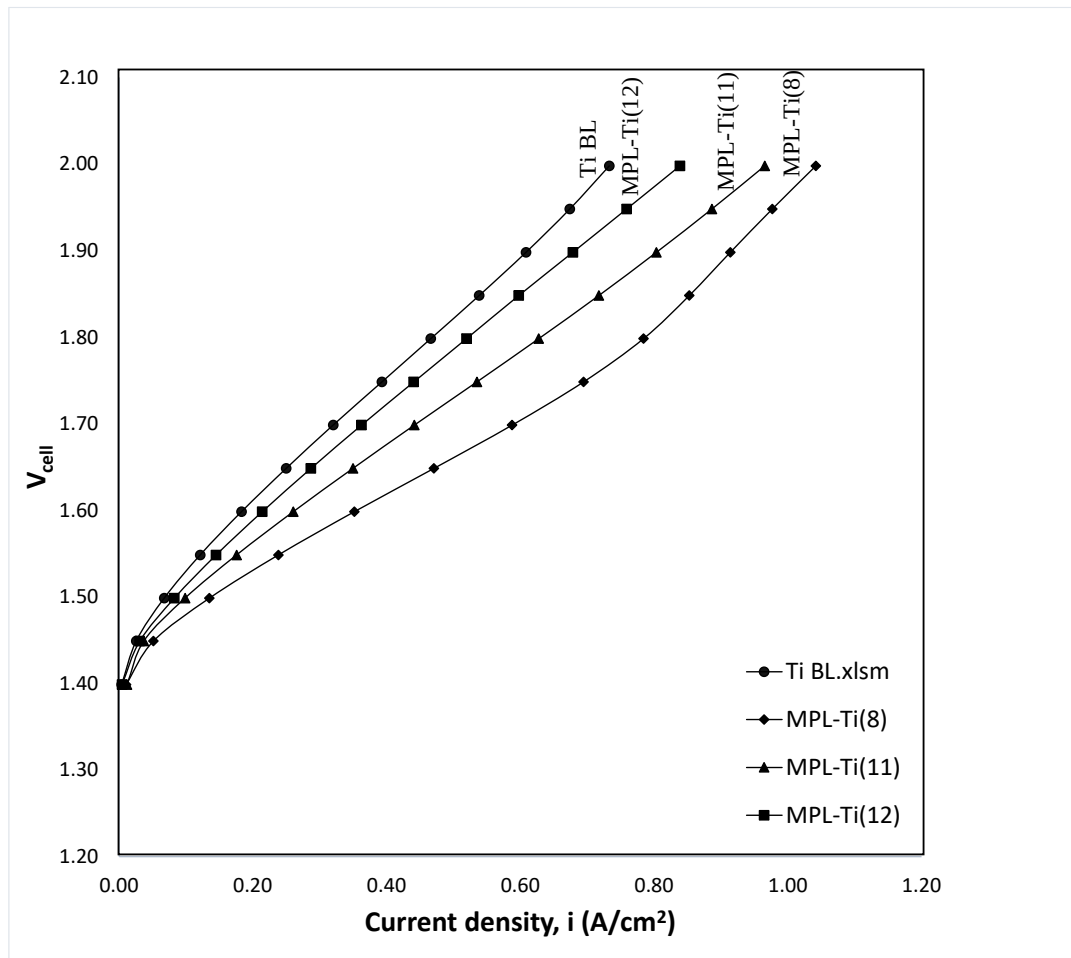


FIGURE 33: POLARIZATION CURVE FOR SINTERED Ti-MPL. THE PERFORMANCE TEST WAS DONE AT 75°C WITH WATER FLOW RATE OF 25 ML/MIN AT ANODE AND NO CIRCULATION AT CATHODE

5. Conclusion and Recommendation for Future Work

The experimental investigation of different nanoparticles and binders as microporous layers (MPLs) for electrolyzers has provided valuable insights into the effect of using Nafion as a binder and performance of various configurations. The MPLs were characterized and tested for performance in a lab-scale electrolyzer. The study investigated the use of ITO, Sn and Ti nanoparticles as MPLs coated over platinized Ti felt. ITO was an attractive alternative due to its resistance to corrosion, although the presence of Nafion binder adversely affected the electrical conductivity leading to poor performance in the electrolyzer. Similarly, the Sn MPL also performed poorly in the electrolyzer and exhibited low electrical conductivity, likely due to the non-conductive PVP dispersant. The MPL that performed the best in the electrolyzer was the sintered Ti MPL.

The key findings are summarized below:

- SEM and AFM imaging provided detailed insights into the surface morphology and coverage of MPLs, showing effective fiber coverage and compression-induced structural changes.
- EDX analysis provided compositional details, including the presence of the binder and dispersant (PVP).
- Porosity and permeability measurements demonstrated that compressed MPLs had lower porosity and permeability, leading to poorer performance in the electrolyzer due to potential blockage of gas (oxygen) and liquid (water) pathways.

- Through-plane conductivity tests highlighted the detrimental effects that binders/dispersants can have on electrical performance. Binder-free, sintered Ti MPLs exhibited significantly higher conductivity.
- Comparison of polarization curves obtained in a lab-scale electrolyzer underscored the superior performance of sintered MPLs over binder-containing ones. In particular, MPL-Ti configurations yielded the best results and surpassed baseline performance. However, it is important to note that the overall performance was lower (by a factor of 2-3) than what other researchers have achieved. This discrepancy could be attributed to several factors: the inability to maintain the electrolyzer temperature consistently at 80°C and the gradual corrosion of the titanium bipolar plates over time. Additionally, the bipolar plates used in the current study had been previously used for CO₂ electrolysis, which may have led to some degradation and affected the cell performance. Comparing the effects of the different loadings of the sintered Ti MPL, the lowest loading of the Ti nanoparticles (MPL-Ti(8)) with the relatively rougher surface exhibited the best performance. It was also observed that the compressed MPLs did not perform at all in the electrolyzer due to total blockage of the gas flow path.

The findings of this study highlight the importance of material selection such as proper binder selection, surface morphology and integrity. Future research should aim to enhance deposition techniques and further optimize the thickness of the microporous layer (MPL) by experimenting with different binders and dispersants. Potential alternatives include conductive polymers as binders and dispersants that can be vaporized. The suboptimal performance of the electrosprayed MPLs is primarily attributed to the non-conductive components, namely the binder (Nafion) and dispersant (PVP). Therefore, substituting these with more suitable materials is recommended. It

should also be noted that since the performance of the MPL-Ti and the baseline Ti felt did not match with what has been reported in the literature, it is also recommended to test the MPL-Ti in an electrolyzer set-up that is properly designed and dedicated for water electrolysis.

Additionally, the performance of sintered Ti MPLs (MPL-Ti) could be enhanced by applying a gold or platinum coating to improve durability through increased corrosion resistance. In this study, MPL-Ti is made of Ti nanoparticles which can form a passive non-conductive oxide layer when exposed to the conditions prevailing in the electrolyzer, resulting in performance degradation. Coating this layer with platinum or gold will help mitigate this degradation. Furthermore, the solvent evaporation deposition method used in this study is not efficient for scale-up and repeatability. Alternative methods such as spray coating or doctor blade techniques should be explored to enhance scalability and efficiency.

To further optimize the experimental procedures, a design of experiments (DOE) approach could be implemented to investigate key parameters such as sonication time, MPL thickness, loading rate, and the percentage of components used in electrospraying. DOE allows for the investigation of multiple factors simultaneously with a minimal number of experiments, providing a more efficient way to explore the parameter space. Additionally, it enables the quantification of interactions between variables, offering deeper insights into how the factors influence each other. This would help identify the optimal combination of variables that yield the best performance.

6. Appendix

6.1 Porosity measurement raw data

	Felt+MPL-ITO(10)	Felt+MPL-ITO(10) _{,NC}	Felt+MPL-Sn(8)	Felt+MPL-Sn(8) _{,NC}	Felt+MPL-Ti(8)	Felt+MPL-ITO(5)	Felt+MPL-ITO(5) _{,NC}
Thickness (um)	273	305	260	285	349	262	262
R (in)	0.1875	0.15625	0.1875	0.15625	0.1875	0.15625	0.15625
Bulk volume (m ³)	1.9E-08	1.5E-08	1.8E-08	1.4E-08	2.4E-08	1.2E-08	1.2E-08
Dry weight (kg)	0.0000617	0.0000312	0.0000602	0.0000296	0.0000562	0.0000298	0.0000289
Wet weight (kg)	0.0000485	0.0000244	0.0000482	0.0000234	0.0000446	0.0000236	0.000023
Density (Liquid)(kg/m ³)	960	960	960	960	960	960	960
Density (Solid) (kg/m ³)	4487	4405	4816	4583	4651	4614	4702
solid volume (m ³)	1.3E-08	7.0E-09	1.2E-08	6.4E-09	1.2E-08	6.4E-09	6.1E-09
Porosity	0.29	0.53	0.33	0.54	0.51	0.50	0.53

6.2 Permeability measurement raw data

MPL-ITO(10) & MPL-ITO(10)_{,NC}

The table below summarizes the experimental results of the permeability test for MPL-ITO(10).

INLET PRESSURE AND FLOW RATE FOR FELT+MPL-ITO(10) AND FELT+MPL-ITO(10)_{,NC}

Q [sccm]	P _{IN} [Pa] – MPL-ITO(10)	P _{IN} [Pa] – MPL-ITO(10) _{,NC}
10	24	7
20	57	12
30	82	19
40	117	25
50	146	31
60	177	38
70	207	43
80	238	49

MPL-Sn(8) and MPL-Sn(8)_{,NC}

The table below summarizes the experimental results of the permeability test for MPL-Sn(8).

INLET PRESSURE AND FLOW RATE FOR FELT+MPL-SN(8) AND FELT+MPL-SN(8)_{,NC}

Q [sccm]	P _{IN} [Pa] – MPL-Sn(8)	P _{IN} [Pa] – MPL-Sn(8) _{,NC}
10	8	3
20	13	5
30	20	8
40	26	11
50	38	14
60	45	16
70	52	19
80	58	21

MPL-Ti(8), MPL-Ti(11) and MPL-Ti(12)

The table below summarizes the experimental results of the permeability test for MPL-Ti.

INLET PRESSURE AND FLOW RATE FOR FELT+MPL-TI

Q [sccm]	P _{IN} [Pa] - A	P _{IN} [Pa] - B	P _{IN} [Pa] - C
10	5	4	5
20	8	8	9
30	10	13	12
40	14	15	16
50	17	16	19
60	21	24	23
70	24	27	26
80	29	28	30

MPL-ITO(5) and MPL-ITO(5)_{NC}

The table below summarizes the experimental results of the permeability test for MPL-ITO(5).

INLET PRESSURE AND FLOW RATE FOR FELT+MPL-ITO(5)_{4-NC}

Q [sccm]	P _{IN} [Pa] – MPL-ITO(5)	P _{IN} [Pa] – MPL-ITO(5) _{NC}
10	4	5
20	9	11
30	13	16
40	18	22
50	22	27
60	27	32
70	33	37
80	37	42

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