

To the Graduate Council:

I am submitting herewith a dissertation written by Anirban Roy entitled “Investigation of transport phenomena in high-performance PEM Water Electrolyzers.” I have examined the final paper copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Mechanical Engineering.

Dr. Matthew Mench, Major Professor

We have read this dissertation
and recommend its acceptance:

Dr. Matthew M. Mench

Dr. Douglas S. Aaron

Dr. Feng-Yuan Zhang

Dr. Vasilios Alexiades

Dr. Jacob A. Wrubel

Accepted for the Council:

Dixie L. Thompson

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(Original signatures are on file with official student records.)

Investigation of transport phenomena in high-performance PEM Water Electrolyzers

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Anirban Roy

August 2024

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Dedicated to Anita Roy.

মা, যেখানেই থাকো, আশা করি সুখে ও শান্তিতে আছো ...

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যারা তোমাকে সাহায্য করেছে, তাদের কখনও ভুলে যেও না।
যারা তোমাকে ভালোবাসে, তাদের কখনও ঘৃণা কোরো না।
যারা তোমাকে বিশ্বাস করে, তাদের কখনও ঠকিয়ে না।

– স্বামী বিবেকানন্দ

Abstract

The increasing demand for renewable energy sources to replace fossil fuels, requires a growing need for a steady energy supply from source to power distribution. Renewable energy often relies on intermittent natural sources or is geographically bound, necessitating energy storage solutions. Polymer Electrolyte Water Electrolyzers (PEWEs) offer a promising solution but require performance enhancements for economic viability. This study focuses on applying distributed diagnostic techniques for PEWEs to gain insights into improving their performance.

The research aims to investigate transport phenomena in high-performance PEWEs, utilizing a segmented cell approach to probe different aspects of transport within a single cell. This diagnostic tool provides in-situ measurements of local performance, enabling a comprehensive understanding through the analysis of current density and high-frequency resistance distributions. The primary objective of this work is to leverage distributed diagnostics to characterize various diffusion media and flow-field designs, discerning their impact on various transport mechanisms. These findings will inform component redesign and performance optimization for efficiency and catalyst utilization.

Additionally, it introduces the concept of an “effective water transport number”, providing a novel approach for characterizing water transport. Through distributed area specific resistance measurements, the research also seeks to quantify spatial variations of various overpotentials. Furthermore, this work investigates the bottlenecks and assesses the impact of flow-field design and architecture on localized

transport to enhance the next generation designs of high-performance PEWEs. Finally, a LBM framework is presented to simulate the complex multi-scale bubble transport process at the pore-scale within the PTLs of a PEWE.

The successful achievement of these objectives deepens the understanding of high-performance PEWEs and the intricate aspects of various transport phenomena at play. It aims to provide valuable insights for optimizing cell operating conditions and long-term durability solutions. The experimental results not only serve as validation for modeling efforts; but also highlight the complex multi-physics phenomena governing these systems. Furthermore, better understanding of two-phase flow and the phenomenon of bubble detachment for the different type of porous transport layers contribute to the development of new generation, high performance diffusion media which ultimately leads to improved cell performance and reduced levelized cost of hydrogen.

keywords: *PEM Electrolyzer, Porous transport layer, Current distribution, Water transport, Architecture, Diagnostics*

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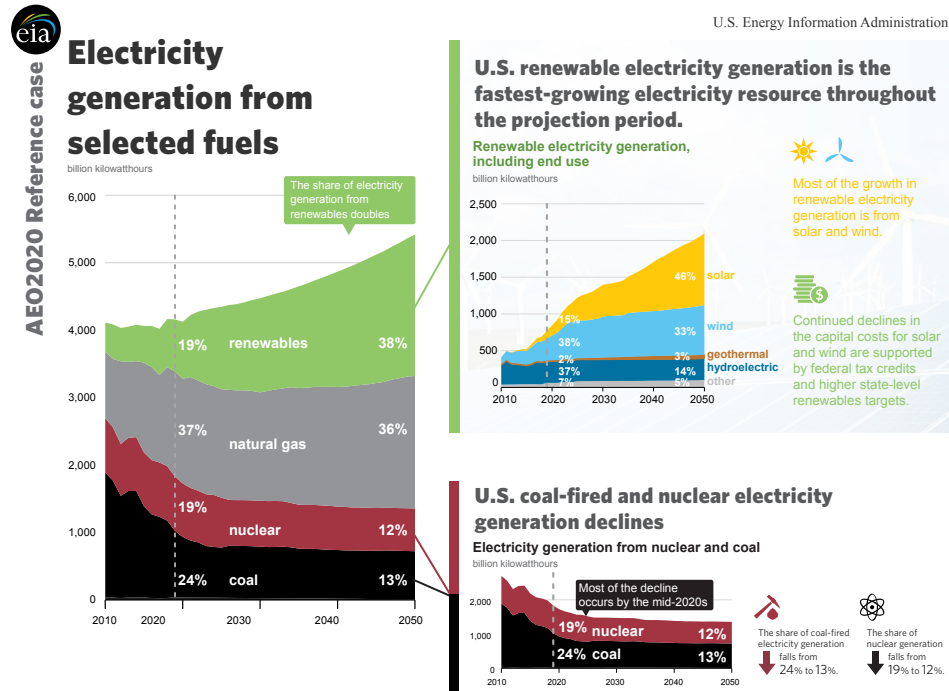
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Chapter 1

Introduction

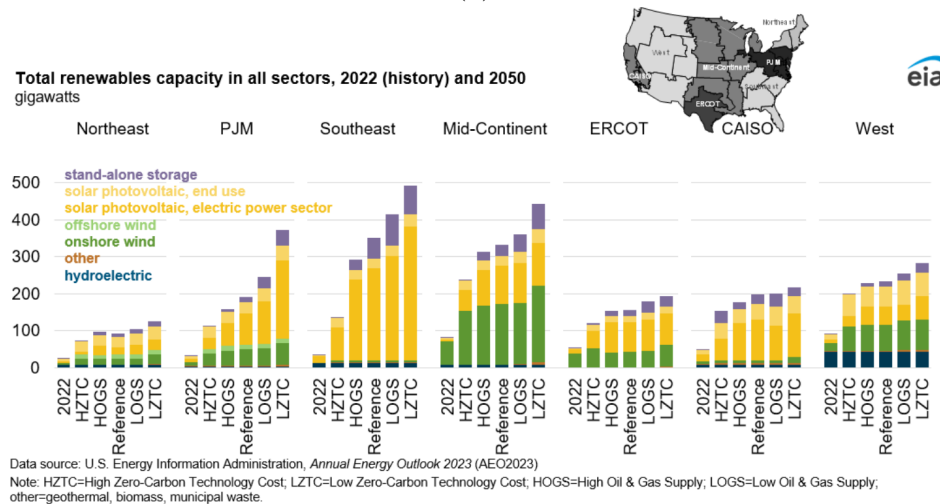
The escalating global demand for energy and the imperative to reduce carbon emissions have become the principal motivation for advancing renewable energy technologies. Over the past few decades, the substantial growth in solar, wind, hydroelectric, and tidal energy sectors has underscored their substantial potential to supplant conventional fossil fuels.

The Annual Energy Outlook 2020 [[U.S.EIA, 2020](#)] published by the U.S. Energy Information Administration (EIA) also presents a discernible shift in the composition of electricity generation within USA. Their findings predict that renewables emerge as the fastest expanding source of electricity production through the year 2050. This trajectory is primarily attributed to ongoing reductions in the capital costs associated with solar and wind energy, which are further incentivized by federal tax credits and the adoption of higher renewable energy targets at the state level, as depicted in Figure [1.1a](#). In their most recent Annual Energy Outlook for 2023 [[U.S.EIA, 2023](#)], the EIA anticipates that renewable power capacity will grow (at-least by a factor of 2) in all regions of the United States. Although, the specific composition of renewable resources in each region will vary due to differences in regional resource availability, as illustrated in Figure [1.1b](#).



Source: U.S. Energy Information Administration, Annual Energy Outlook 2020 (AEO2020) Reference case

(a)



(b)

Figure 1.1: U.S. Energy Information Administration's Annual Energy Outlook predictions of electricity production through 2050: (a) 2020 reference case for power and electricity shows a distinct trend for renewable energy sources being the fastest-growing source of electricity production [U.S.EIA, 2020]; (b) 2023 reference case also projects increased renewable power capacity in all regions of the United States with regional variations [U.S.EIA, 2023].

However, the majority of these energy sources are geographically constrained because of mismatches between regions where energy is produced and regions where it is consumed. Moreover, the intermittent nature of such electricity generation poses challenges in seamless integration with the grid [Hermesmann and Müller, 2022]. Therefore, there is a pressing need for an efficient energy carrier that can facilitate storage and transportation. Hydrogen has emerged as an exceptionally promising candidate for such a role in the future energy landscape. Projections from the International Renewable Energy Agency (IRENA) suggest that hydrogen and its derivatives are poised to significantly contribute and estimated to account for nearly 12% of final energy consumption by 2050 [IRENA, 2021].

Recognized for its high energy density, adaptable conversion processes, and the feasibility of large-scale storage, hydrogen is increasingly acknowledged as a pivotal energy resource in the pursuit of carbon neutrality. Its applications span diverse sectors, encompassing industry, power generation, and transportation. [Yue et al., 2021]

Hydrogen may be produced from a variety of technologies and resources. Presently, the predominant method for hydrogen production heavily relies on reforming and gasifying fossil hydrocarbon sources, with natural gas (76%) and coal (23%) serving as the primary feedstocks. Regrettably, this approach leads to the emission of approximately 830 million metric tons of carbon dioxide annually, as detailed in the 2021 report by the International Energy Agency (IEA) [IEA, 2021]. Nevertheless, alternative hydrogen production technologies, such as water electrolysis, are gaining prominence. According to the IEA’s 2022 report [I.E.A, 2022], global electrolyzer capacity in 2020 was limited to 0.3 GW, predominantly powered by grid electricity to produce hydrogen; which is expected to grow because of planned project pipelines in almost 30 countries indicating that global electrolyzer capacity could reach almost 17 GW by 2026.

Among the array of electrolyzer technologies, alkaline electrolysis currently stands at the forefront of technological readiness levels of TRL 9-11 (TRL, see Figure 1.2 for

legend). In contrast, solid oxide electrolysis and polymer exchange membrane electrolysis are situated at earlier stages of technological readiness, specifically at TRL 3-5 and TRL 8-10, respectively, as outlined in [Schmidt et al., 2018, Varela et al., 2021]. The polymer electrolyte water electrolyzer (PEWE), alternatively known as a proton exchange membrane electrolyzer (PEMEC), is potentially the promising option, due to its high current density, ability to produce high-purity hydrogen, and rapid response time [Wang et al., 2023, Lin et al., 2022, Zhou et al., 2023].

However, more research is needed to reduce the initial cost and the durability of the process. As of 2015, the levelized cost, which encompasses all capital and operational expenses associated with hydrogen production through electrolysis, amounted to \$3.90 per kilogram. Notably, 46% of the capital cost for a PEWE can be attributed to the membrane-electrode-assembly (MEA), while electricity accounts for 45-50% of the overall hydrogen generation cost [Pivovar, 2021]. In an effort to address these challenges and promote the use of electrolysis for hydrogen production, the U.S. Department of Energy (DOE) has set ambitious targets. They aim to reduce the levelized cost of hydrogen generated by electrolysis to \$2.00 per kilogram by the conclusion of 2025, with a further target of \$1.00 per kilogram by 2030 [U.S.DOE, 2024a]. These objectives align with the Hydrogen Earthshot initiative, which seeks to achieve the milestone of reducing the cost of clean hydrogen to \$1 per kilogram within a decade (commonly referred to as "1 1 1") [U.S.DOE, 2024b]. Achieving these targets would signify a more than 50% reduction in costs within a span of five years and a 75% reduction compared to the prices observed in 2011.

Therefore, it is critical for the development of gigawatt-scale PEWEs to have highly effective electrodes that are inexpensive, efficient, and durable [Yu et al., 2022, Kang et al., 2018]. Significant research efforts have been directed toward reducing precious metal catalyst loadings (by 80-90% compared to current loadings of 1 mg/cm^2) [Hegge et al., 2020] to enable ubiquitous PEWE commercialization. Nevertheless, it's essential to recognize that the performance of PEMECs is not

solely contingent upon catalyst loadings. System architecture plays a pivotal role and greatly influences performance due to the intricate interplay between localized architectural features and material interactions [Zhang and Yuan, 2022, Jiang et al., 2023]. Furthermore, to drive down the cost of hydrogen production, there is a consistent preference for operating at high current densities. This choice stems from the potential to significantly reduce the capital investment required for electrolyzer stacks while maintaining a specified hydrogen production rate. High-current operations necessitate efficient transport of reactants and products within PEWEs to ensure optimal performance [Roening et al., 2022].

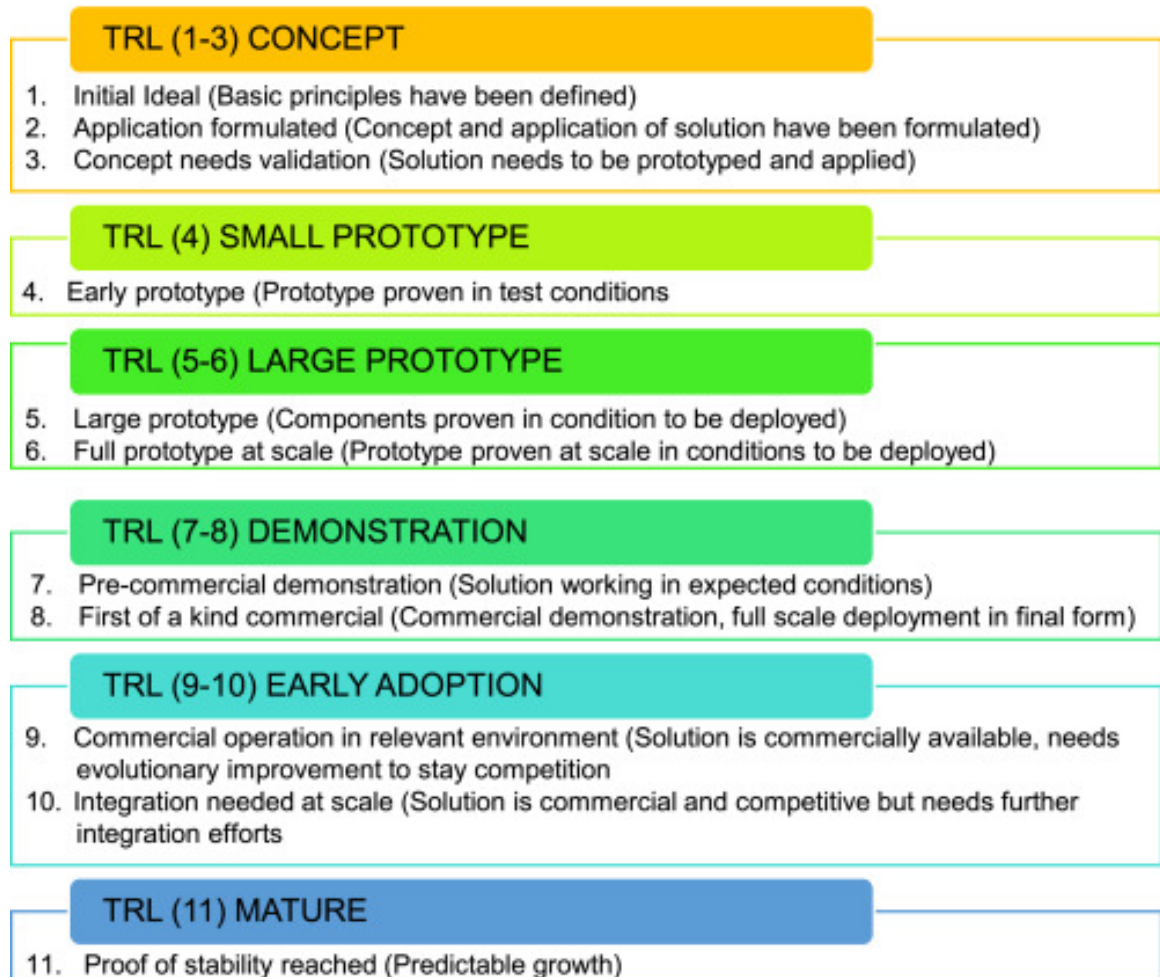


Figure 1.2: Legends and descriptions of technologies' technology readiness level (TRL) [Hassan et al., 2023]

Chapter 2

Technical background on PEWEs

Water electrolysis for hydrogen generation, encompasses three primary techniques: alkaline water electrolysis (AWE), solid oxide electrolysis (SOE), and polymer electrolyte membrane water electrolysis (PEWE), as illustrated in Figure 2.1. Each of these approaches possesses distinct characteristics and challenges.

AWE relies on highly concentrated alkaline solutions and employs diaphragms (viz. materials like asbestos, polyethersulfone, glass reinforced polyphenylene sulfide compounds, and other microporous polymer membrane) to segregate the gases produced at the cathode and anode. Nevertheless, it faces limitations such as low operating pressure, sluggish anion transport kinetics, and restricted current density [Carmo et al., 2013].

SOE operates under high pressure and elevated temperatures, ranging from 500°C to 850°C. However, it grapples with issues concerning catalyst durability and membrane degradation.

In contrast, PEWE is a promising method for high-purity hydrogen production in future industrial applications. It boasts several advantages, including high current density [Carmo et al., 2013], superior energy efficiency, minimal gas crossover, a broad operating temperature range (from 20°C to 80°C). Notably, a PEWE's dynamic performance allows it to operate efficiently at varying loads, from zero to overload

conditions [Buttler and Spliethoff, 2018], and it exhibits rapid cold start times, measured in seconds to minutes [Götz et al., 2016]. Furthermore, PEWEs maintain low cross-permeability, yielding hydrogen of exceptional purity, often exceeding 99.99% after drying [Shiva Kumar and Himabindu, 2019]. Its modular design also supports high-pressure operation, capable of functioning under differential pressure conditions of up to 350 bar [Ayers et al., 2017].

2.1 Working principle

A PEWE is an electrochemical device designed to convert electrical energy into chemical energy by employing water as its primary reactant. Its fundamental operation can be described as the reverse process of a hydrogen polymer electrolyte membrane fuel cell (PEMFC). The PEWE uses electricity to oxidize water, producing oxygen and hydrogen ions (protons) at the anode. The protons pass through the membrane and are reduced at the cathode to produce hydrogen.

Figure 2.2 shows the overall working principle for the PEWE. The design of a PEWE generally consist of two half cells separated by a thin membrane that is both proton conducting and electron insulating. Both sides of the membrane are coated with a catalyst layer (CL) where the reactions occur.

The catalyst-coated membrane (CCM) situated at the center is a crucial component for a PEWE. This CCM serves as the site where the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) occur. It consists of three integral layers: a cathode CL, an anode CL, and a polymer electrolyte membrane (PEM). Adjacent to the CCM, the transport of liquids and gases is facilitated by two porous transport layers (PTL) [Hackemüller et al., 2019, Lee and Bazylak, 2020, Stiber et al., 2021]. In the context of typical anode-circulation operations, where most of the water-gas transport occurs in the anode, some literature refers to the anode porous transport layer as the liquid-gas diffusion layer (LGDL) and designates the cathode PTL as the gas diffusion layer (GDL) [Li et al., 2019, Maier et al., 2020].

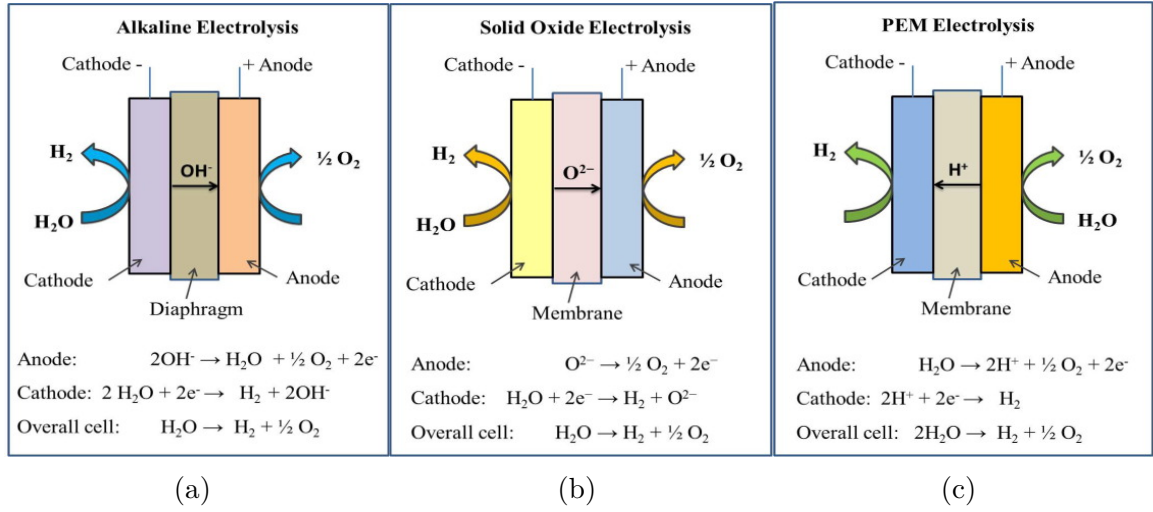


Figure 2.1: Types of water electrolysis process and their schematic diagram: (a) Alkaline water electrolysis; (b) Solid oxide electrolysis; (c) Polymer electrolyte membrane water electrolysis [Carmo et al., 2013]

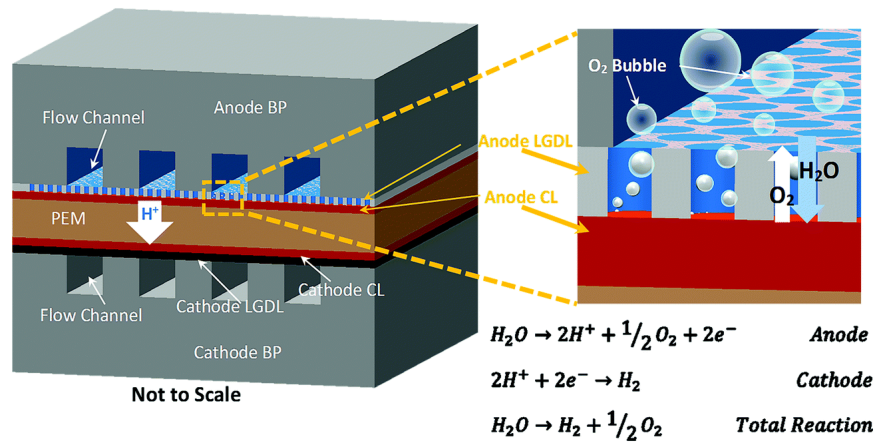


Figure 2.2: Schematic of a working PEWE with thin titanium LGDLs with the overall reactions shown [Kang et al., 2017].

The CCM and PTL are securely held in place by flow fields and end-plates. Flow fields play a crucial role in distributing water and facilitating gas drainage, while the end-plates ensure a secure assembly of components to prevent any leakage. Alternatively, in some PEWEs, catalyst-coated porous transport layers called porous transport electrodes (PTE) may be employed instead of CCM. These PTEs are conceptually akin to gas diffusion electrodes (GDE) used in fuel cells [Pham et al., 2021, Li et al., 2021, Yeo et al., 2022, Chen et al., 2022].

2.2 Literature review

2.2.1 Contextual background

The harsh environment within a PEWE, characterized by low pH at the membrane, operating potentials exceeding 1.5V, and high oxygen concentration at the anode, necessitates the utilization of electro-catalysts primarily from the platinum group metals (PGMs) [Bernt et al., 2020]. Conventionally, carbon-supported platinum (Pt/C) is employed for the cathodic Hydrogen Evolution (HER), while catalysts based on iridium (Ir) are typically chosen for the anodic OER. Strategies to enhance catalyst efficiency include increasing the surface area of traditional iridium oxide materials, which has shown improved catalytic activity. However, maintaining this benefit over time remains a challenge due to potential degradation mechanisms. Extended structures like nanowires and nanostructured thin films have exhibited slightly higher efficiency and better stability [Ayers, 2021]. The form of iridium used also impacts catalytic stability, with blends of different iridium components being researched across various studies. Incorporating additives like ruthenium, nickel, or cobalt can enhance activity and stability [Kumar and Lim, 2023]. Catalyst support structures play a crucial role in stabilizing high surface area forms, with some promising materials such as nano-structured thin film electrodes (NSTF) and titanium sub-oxides. For a more comprehensive understanding of these strategies

for improving catalyst efficiency, the impact of catalyst form on stability, and the use of additives to enhance activity and stability, researchers are encouraged to refer to several review articles [Bernt et al., 2020, Ayers, 2021, Fu et al., 2023, Kumar and Lim, 2023, Wu et al., 2023].

In a similar vein, reviews highlighting the challenges in the development of PEM can be found in articles such as [Perović et al., 2023] and [Javed et al., 2023]. Furthermore, the review by Lou, *et al.* [Luo et al., 2023] delves into the significant challenges associated with materials used to manufacture flow fields/bipolar plates (BP). It emphasizes the necessity for ongoing fundamental research aimed at optimizing crucial factors like interface contact resistance, corrosion resistance, and material cost to facilitate the large-scale commercialization of BP technology.

Current PEWE research focuses on cost reduction through novel catalysts and electrode materials, often overlooking the impact of electrolysis products and gas bubbles on cell performance. Bubbles, while potentially aiding local convection, usually have an adverse effect on electrochemical reactions, especially within PEWEs, where both bubble formation and transport happen concurrently [Yuan et al., 2023]. Bubble evolution takes place on the catalytic surface, while bubble transport involves multi-step processes across various cell components. This area of research remains under-explored, with recent findings indicating adverse consequences such as elevated mass transport losses, reduced catalyst utilization, and unstable cell performance (as described in Figure 2.3).

Nearly all major components within PEMECs impact the journey of bubbles from their generation to removal; a process analogous to water management in PEM fuel cells which is well known to have significant influences on the overall cell performance [Berg et al., 2004, Wang et al., 2021b]. Modifications to these components can yield significant performance enhancements. For instance, an innovative electrode design focusing on efficient bubble management, reported a 24-fold increase in anode catalyst utilization compared to conventional designs [Yu et al., 2022]. Similarly,

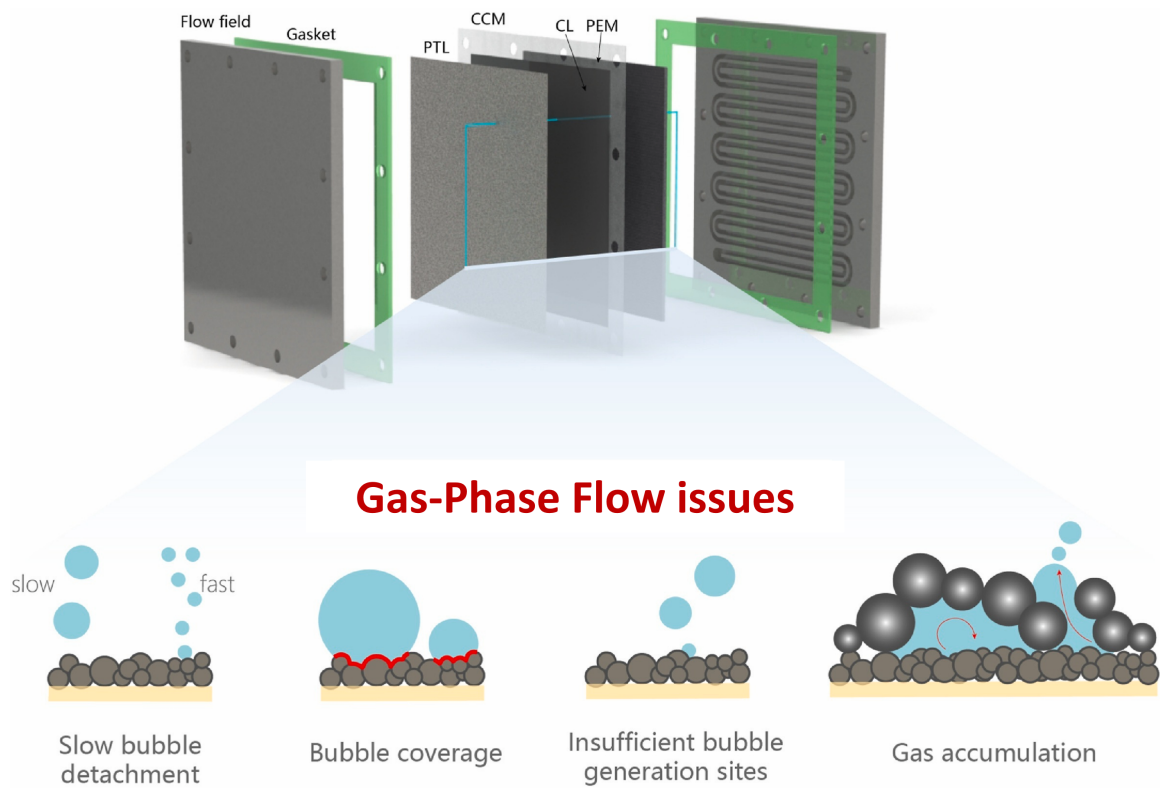


Figure 2.3: The structure of a typical proton exchange water electrolysis cell and the bubble issues within it [Yuan et al., 2023].

a PTL design that effectively addresses gas accumulation observed an estimated reduction in mass transport overpotential by as much as 76.7% [Lee et al., 2020c].

2.2.2 Related work

Mass transport: Bubble dynamics and two-phase flow

Over the past decade ex-situ investigations have been predominantly carried out by multiple authors to better understand the two-phase flow in a PEWE and to optimize the PTL morphology. Ito, *et al.* [Ito et al., 2012] conducted a study on sintered titanium current collectors, varying parameters such as porosity, pore size, and fiber diameter. Their research revealed that changes in porosity had minimal impact on performance, whereas pore diameter exerted a significant influence. By utilizing liquid/gas superficial velocity plots, they were able to categorize the type of two-phase flow experienced within an electrolyzer. Additionally, their findings emphasized the critical role of bubble detachment diameter in determining the operational two-phase flow regime. Consequently, they proposed an optimal pore diameter of approximately $10\mu m$ for such PTLs.

To better understand and effectively characterize two-phase flow in PEWEs different in-situ techniques have been developed and used to better visualize what is happening inside of the electrolyzer cell. Majasan, *et al.* [Majasan et al., 2018a] investigated the gas-bubble dynamics and two-phase flow behavior for two different anodic flow-fields using high-speed optical imaging and related the results to the electrochemical performance. Their findings highlighted that a longer flow path length promotes gas accumulation and results in annular flow regime at a high current density, which degrades cell performance. Dedigama, *et al.* [Dedigama et al., 2014] conducted an in-situ flow characterization study, revealing through their electrochemical impedance spectroscopy (EIS) results a reduction in mass transport limitations when transitioning from bubbly flow to the slug flow regime. However, this finding contrasts with the research of Seweryn, *et al.* [Seweryn et al., 2016], who conducted

an in-operando neutron imaging study to examine water saturation levels within PTLs across current densities ranging from $0.1 - 2.5 A \cdot cm^{-2}$. Their study indicated that water saturation profiles remained consistent and unaffected by changes in current density, suggesting that gas pathways are independent of production rate. Similar experiments using in-operando X-ray computed tomography on a functioning PEWE cell were conducted by Satjaritanun, *et al.* [Satjaritanun et al., 2020]. Their observations revealed that from an in-plane perspective, oxygen followed nearly identical transport pathways under both $1.0 A \cdot cm^{-2}$ and $4.0 A \cdot cm^{-2}$ operating conditions, even when the water feed rate was increased threefold at the lower current density. Similarly, in the through-plane view, the oxygen distribution within the PTL exhibited a consistent pattern across different current densities. Similar transport behavior has also been observed in Angelis’ work [De Angelis et al., 2021], implying that oxygen escapes the cell via preferential routes. Bubble transport routes in PTL are guided by the porous structure. Typically, oxygen generated at the anode tends to follow paths characterized by larger voids, occasionally encountering obstructions at constricted regions. This transport process can be described as a sequence of pressurization and penetration steps. The Bazylak group has developed a microfluidic platform known as PTL-on-Chip, which provides insights into this bubble transport phenomenon [Arbabi et al., 2013, Arbabi et al., 2014, Arbabi et al., 2016, Lee et al., 2017].

The PTL-on-Chip platform is designed to replicate different PTL types, such as felt, sintered powder, and foam, by utilizing volumetric pore space data derived from micro-computed tomography images. In this setup, gas is introduced into the simulated PTL through a gas inlet to mimic the generation of gas bubbles from the CL [Arbabi et al., 2014]. During continuous gas injection, it becomes evident that the total gas saturation within the simulated PTL remains largely consistent over time, occasionally exhibiting abrupt increases. This sustained, unchanging total saturation suggests that gas movement within the PTL is limited, and the gas experiences increasing pressurization. The results clearly show that the bubble flow

in the pressurization state is hindered by the PTL’s limiting throat. Subsequently, a sharp increase in total saturation following an extended pressurization period signifies rapid gas penetration into new voids within the PTL. During this penetration phase, the limited gas flow abruptly overcomes the previous constriction at the limiting throat and expands in the path of least resistance. It’s noteworthy that while the gas flow in various simulated PTLs exhibited the same behavior, it followed distinct flow pathways based on the specific PTL structure. The predominant flow pathway in the PTL is contingent upon the distribution of porosity and throat sizes, and this can vary when subjected to different rates of gas injection. Furthermore, under high gas injection rates, akin to simulating high current operation, the gas flow behavior may transition from capillary fingering to viscous fingering within specific PTL morphologies. This shift can lead to a reduction in local water saturation near the gas inlet [Lee et al., 2017]. These results are in agreement with experiments (reported in [Satjaritanun et al., 2020, De Angelis et al., 2021]) that showed that the oxygen distribution region is slightly wider when a PEWE operates at high current densities. This could mean the original primary transport pathways have been extended.

Oxygen bubble flow within the anode PTL follows a distinct pattern. Initially, the bubbles detach from the CL and occupy voids with low resistance in the PTL near the CL, primarily influenced by PTL morphology rather than ribs and channels. Subsequently, some bubbles migrate towards pathways beneath the channels and are rapidly discharged, releasing the occupied pores. In contrast, certain bubbles become trapped in the PTL under the ribs, resulting in higher oxygen content compared to the PTL under the channel. Hence, the characteristics of the rib and channel features within the flow field significantly influence the pathway of bubble transport in the PTL. At steady-state operation in a PEWE, there is a consistent decrease in water saturation from the PTL/channel interface to the PTL/CL interface [Seweryn et al., 2016, Zlobinski et al., 2020, De Angelis et al., 2021]. This trend holds true across various current densities, although the final water saturation near the PTL-CL interface may vary. In the same vein, [Maier et al., 2020] reports

that the water/gas saturation distribution within various PTLs under the same flow field exhibits a consistent pattern at the cell scale. Due to simultaneous bubble generation throughout the CL and the extended path for their removal from the cell, gas accumulation within the PTL intensifies as it approaches the outlet. With higher current densities, the area of relatively low water saturation within the PTL gradually expands from the outlet to the inlet. Nevertheless, a portion of the PTL volume near the outlet retains adequate water saturation to support some OER.

Electron and mass transport: Interfaces and pore structure

While bubble dynamics and two-phase flow are frequently studied independently within PEWEs, recent research has emphasized that mass transport losses in these cells are significantly influenced by the PTL’s pore structure and its interactions with the CL.

Experimental studies

Schuler, *et al.* [Schuler et al., 2019a, Schuler et al., 2019b] employed postmortem X-ray tomography and revealed that the interface between the PTL and CL has a substantial impact on both mass transport and ohmic losses. The interfacial contact resistance at this boundary is closely linked to mass transport within the PTL. This aligns with the work by Majasan, *et al.* [Majasan et al., 2018a, Majasan et al., 2018b], supporting the idea that contact resistance between the PTL and CL is a key factor in electrolyzer performance. They also found that a smaller pore diameter ($16\mu m$) outperform a larger pore diameter ($60\mu m$) supporting the findings of Ito, *et al.* [Ito et al., 2012]. Furthermore, findings from the optimization studies by Grigoriev, *et al.* [Grigoriev et al., 2006] were in agreement with other studies [Schuler et al., 2019a, Majasan et al., 2018b, Ito et al., 2012], consistently indicated that pore structure is more critical than porosity. A mean pore diameter of approximately $12\mu m$ was identified by [Grigoriev et al., 2006] as yielding optimal electrochemical performance. Lui, *et al.* [Liu et al., 2018] highlighted issues of

surface passivation (titanium oxidation) in titanium PTLs, which increase interfacial resistance. They proposed that a thin layer of iridium (20–150 nm thick) can serve as a protective coating, reducing contact resistance by $60\text{m}\Omega\cdot\text{cm}^2$ which significantly improved performance.

Investigations carried out by Verdin, *et al.* [Verdin et al., 2017] using segmented a 250 cm^2 circular cell into 64 segments revealed a clear correlation between local compression forces and current distribution within a cell, suggesting that such contact heterogeneity can lead to faster localized aging in the PEWE’s active region. Similarly, Parra-Restrepo, *et al.* [Parra-Restrepo et al., 2020] found a heterogeneous distribution of current density between the inlet and the outlet, caused by the changing properties of the PTL along the cell. Investigations carried out by Minnaar, *et al.* [Minnaar et al., 2020] used current distribution and neutron radiography to study two different PEWE flow-fields and found that the flow-field design is important to obtain an even workload distribution across the PEWE cell. They observed that current density tended to be higher at the anode inlet due to gas accumulation towards the outlet. They also found that the pin-type flow-field resulted in better and more equally distributed current and temperature density.

Computational studies

Along with experimental work, full scale CFD modeling have also been done in electrolyzer research to better understand water and temperature distributions within the cell and flow within the PTLs. Nie, *et al.* [Nie and Chen, 2010] developed a CFD model to investigate flow in a parallel flow-field. Their findings suggest that an increase in oxygen gas flow rate creates an increased pressure drop across the flow-field plate. As the mass flow rate of oxygen increases, a local minima in the velocity magnitude can be observed near the outlet. The work also shows that the volume fraction of oxygen is not uniform within the flow-field. It is relatively high at the center region of the plate, which causes reverse flow in some channels. Since the center region of the flow-field experiences lower fluid velocity magnitudes with longer residence time,

more reactions take place in this region. Others like Olesen, *et al.* [Olesen et al., 2016] has developed detailed computational fluid dynamics models to establish the effect of geometry, and the effect of distressed gas bubbles. They found that at low water stoichiometric ratio the presence of gas-phase causes a maldistribution in the liquid face, which leads to non-uniform distribution of reaction sites.

Further computational investigations in transport within the PTL have been carried out by various research groups. Pore network modeling was conducted by J.K. Lee, *et al.* [Lee and Bazylak, 2020, Lee et al., 2020c, Lee et al., 2019b] to study the PTL-CCM interface. They found that PTLs with larger pore and throat size exhibit higher relative permeability, therefore improving liquid water permeation. They also observed that porosity graded PTLs lead to improved transport properties when the low porosity region was positioned next to the CCM. This finding corroborates the outcomes of the study conducted by C.H. Lee, *et al.* [Lee et al., 2017] where they created a PTL-on-chip system capable of measuring gas transport within a well-defined porous media structure. This innovation allowed for the direct visualization of gas/liquid interface dynamics within the PTL-on-chip network. Their investigation identified a critical limiting throat that had a direct impact on breakthrough phenomena and the manner in which bubbles were removed from the PTL, as discussed in subsection 2.2.2.

Monte Carlo pore network studies [Vorhauer et al., 2019, Altaf et al., 2020] were also done where the authors successfully simulated gas/liquid invasion patterns. It was revealed that the pore size distribution could be adjusted independently of the porosity and it would result in different invasion patterns. Their major findings suggest that the pore size distribution affects the invasion pattern more significantly than the porosity. C.H. Lee, *et al.* [Lee et al., 2019a] did another study to investigate compressible-gas into liquid saturated porous media. In this work it was found that the pore scale interfacial velocity is predominately controlled by the pore throat size where the Haines jump occur. The Haines jump is a phenomenon observed during two-phase flow in porous media. It involves the rapid displacement of a meniscus

from a narrow pore throat to a wider pore body, accompanied by a sudden drop in capillary pressure. This occurs when a bubble accelerates swiftly out of a pore throat and the bubble front moves beyond its final equilibrium position because of inertia, resulting in an unsteady velocity profile of the advancing interface. The presence of Haines jumps can cause the redistribution of fluids within the pores, especially during primary drainage processes.

These findings therefore suggest that a micro porous layer (MPL) in the PTL promotes viscous fingering, which results in lower gas saturation in the bulk of PTL. This enables more efficient reactant delivery and improved performance of the PEWE. Lee, *et al.* [Lee et al., 2020b] did a follow up study where they investigated temperature impact on two phase flow with neutron imaging and a 2D CFD model. They showed that an increase in operating temperature results in the reduction of gas saturation in the PTLs (particularly near the catalyst layer CL-PTL interface) and the promotion of uniform gas distribution near the CL-PTL interface which leads to lower mass transport overpotentials. The authors also found that above 60°C the current density has an impact on the saturation of the anodic PTL and hydration of the CCM.

Heat and proton transport: Membrane hydration and ionic resistance

The PEM is made of selective polymer that allows only hydronium ion (proton) transport across its interfaces. The ionic conductivity of such membranes are a function of the temperature and hydration. Therefore, understanding the nature of heat transfer and its influence on membrane hydration is critical. In recent years, Bock, *et al.* [Bock et al., 2020] created a CFD model to study the temperature distribution within the PEWE cell. Their results show that the highest temperature is at the membrane and that there is a non-uniform temperature distribution within the cell. Temperatures were notably elevated on the anode side where the OER takes place and in regions aligned with flow-field channels.

Immerz, *et al.* [Immerz et al., 2018a, Immerz et al., 2018b] conducted a study on strip cell PEWEs using localized current distribution measurements. Employing a segmented cell approach, they examined local current distributions and EIS measurements in various sections of the cell. Their findings showed that the ionic resistance, measured by high-frequency resistance (HFR), increased along the channel length. This was interpreted as a sign of membrane drying, leading to reduced proton transport due to the accumulation of gas bubbles near the outlet. Although the study did not extensively discuss temperature distribution, it hinted at inefficient heat transfer near the outlet, potentially contributing to membrane dryness in that area.

Temperature plays a significant role in influencing gas saturation distribution within PEWE cells [Lee et al., 2020c]. As the temperature increases, it enhances bubble transport under varying current densities. This enhancement effect is particularly pronounced near the PTL-CL interface at low current densities, resulting in a notable decrease in gas saturation, which is advantageous for improving oxygen evolution reaction (OER) performance. Conversely, near the PTL-flow field interface, increasing temperature leads to an increase in gas saturation. Unlike the effect near the PTL-CL interface, this saturation increase intensifies with increasing current. Furthermore, higher temperatures reduce the accumulation of oxygen in the PTL beneath the ribs. These observed phenomena at the PTL-flow field interface align with results within the flow channel, characterized by larger bubble sizes and increased bubble numbers under the same current conditions [Majasan et al., 2018a, Lee et al., 2020c, Hoeh et al., 2015].

2.3 Summary

The PEWE, a promising hydrogen production technology, has gained global attention for its high efficiency, flexibility, and compatibility with renewable energy sources. Significant progress has boosted current densities at constant precious metal catalyst

loadings; but higher current densities pose efficiency challenges due to detrimental bubble effects. Bubbles decrease gas supersaturation near the catalyst, reducing mass transfer losses but concealing the catalytic surface, increasing activation losses.

Transport routes in PEWE are governed by porosity, wettability, and component structure. Bubble accumulation, especially under dynamic loads, hampers water-gas transport and diminishes cell performance. Establishing efficient, low-resistance bubble transport pathways in the CL, PTL, and flow field can mitigate these issues.

2.4 Motivation

Enhancing water electrolyzer performance by effectively managing bubbles remains challenging due to a limited understanding of bubble evolution and transport in PEWEs. Research gaps exist concerning the origin and movement of oxygen and hydrogen bubbles at the CL, PTL and their interfaces, necessitating further investigations to uncover bubble formation sites and dynamics, which can inform CL and PTL structure designs.

Additionally, comprehending the dynamic aspects of bubble transport across the entire PEWE cell requires more attention. Studies reveal gas transport hysteresis in PTL, showcasing gas accumulation during repetitive load changes that lead to performance losses under intermittent loads [Lee et al., 2020a]. Contradictory reports [Demir et al., 2018, Bakker and Vermaas, 2019] suggest that pulse voltage or pressure variations can enhance bubble detachment and improve electrolyzer efficiency. Given the intermittent and fluctuating nature of renewable energy sources powering PEWEs, in-depth research is needed to effectively grasp the dynamic characteristics of bubble transport.

Analyzing mass transport within the PTL is challenging due to complex two-phase flow dynamics. Currently, there is no widely accepted theory capable of describing two-phase flow in PEWE PTLs and directly linking it to various electrochemical

overpotentials for improved performance prediction. This issue remains contentious, with conflicting conclusions arising from different experimental and modeling studies.

Despite some progress in this area, there is significant potential for enhancing water electrolyzer performance, particularly concerning bubble management, given the existing gaps in the knowledge of bubble evolution and transport in PEWEs. To address these challenges, this body of research prioritizes the development of advanced in-situ diagnostics and implementation of effective bubble management techniques for PEWEs. The advancement of bubble management strategies in PEWEs can encompass a range of approaches, including but not restricted to the following areas:

- In-situ characterizations of bubble evolution
- Optimizing CL-PTL interface for more bubble nucleation sites, smaller bubble detachment size, and higher bubble detachment frequency
- Designing PTLs and flow fields for efficient and unobstructed bubble transport throughout the entire PEWE
- Improve PEWE operation strategy to mitigate bubble accumulation during dynamic loads
- Modeling the complex multi-scale bubble transport process and its impact on electrochemical performance

Chapter 3

Thesis statement and objectives

Effective utilization of the CL relies on efficient water and gas transport through PTLs, which also facilitate low-resistance electronic pathways between CLs and current collector plates. In a polymer electrolyte water electrolyzer, the sources of electrochemical losses are kinetic, ohmic, and mass transport overpotentials. As shown in Figure 3.1a, the polarization curve highlights that kinetic overpotential significantly outweighs other overpotentials at lower current densities due to the sluggish anodic OER.

However, when operating at higher current densities, mass transport overpotentials become significant, contributing to nearly 10-20% of total losses. Ohmic losses, resulting from ionic resistance in the PEM, are dependent on temperature and hydration. Although membrane hydration in liquid-fed PEWEs, in most cases, is unaffected by mass transport; specific operational conditions can exacerbate these effects as evidenced in Figure 3.1a. Consequently, a comprehensive understanding and control of transport phenomena are essential for efficient PEWE design and operation. Mass transport overpotentials primarily stem from insufficient water supply to the anodic CL. Effective gas removal from the PTL during the OER is crucial to alleviate these losses.

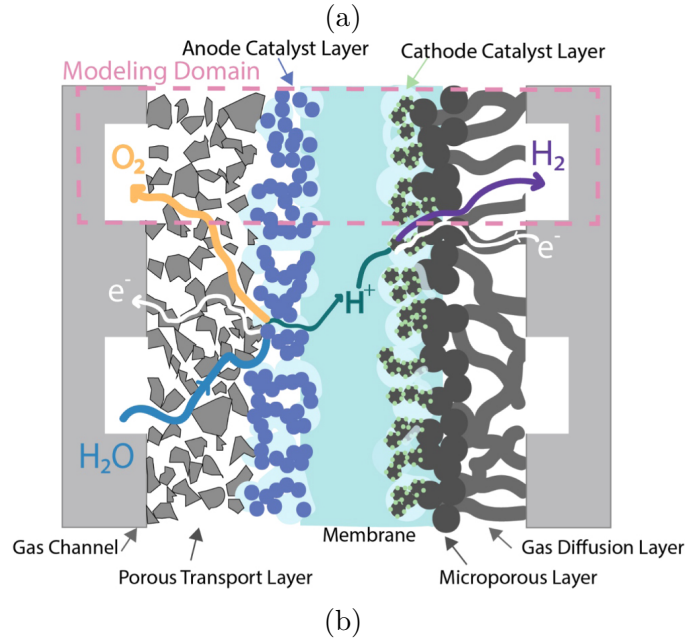
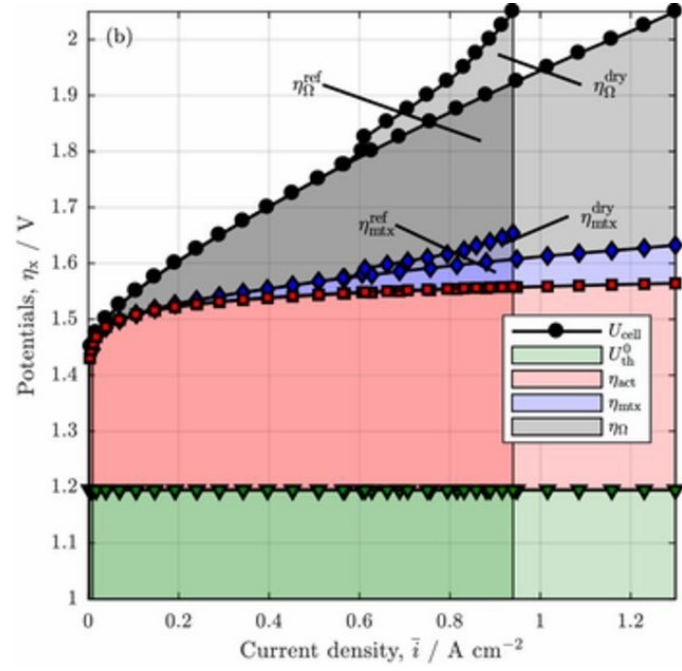


Figure 3.1: (a) Typical polarization characteristic curves for a PEWE showing the different overpotentials separated out [Immerz et al., 2018a]; (b) Schematic showing various aspects of transport occurring inside a PEWE. [Fornaciari et al., 2020]

Tackling mass transport limitations within the PTL presents a challenge characterized by two-phase flow dynamics. Presently, a widely accepted theory for describing two-phase flow in PTLs of PEWEs remains elusive, as divergent conclusions have emerged from various experimental and modeling studies. This work endeavors to achieve a thorough understanding of various transport aspects within PEWE, viz. electron and proton transport, heat transfer, and mass transport (as seen in Figure 3.1b) through the application of in-situ distributed diagnostic techniques. The primary objective is to advance the knowledge regarding mass transport and its intricate interplay within PEWEs. By conducting a rigorous experiments and in-depth analysis, we aim to unveil the intricate dynamics of bubbles and two-phase flow phenomena taking place within these systems. This investigation will not only identify bottlenecks but also shed light on the influence of flow-field design and architectural factors on localized transport, ultimately facilitating improvements in next generation designs for high performance PEWEs. Furthermore, this work aims to underscore the importance of modeling such a multifaceted phenomena at both the pore scale and macro-scale levels.

3.1 Research statement

“This research seeks to provide a detailed understanding of PEWEs through distributed diagnostics, advancing the knowledge of mass transport, bubble dynamics, and two-phase flow, by providing detailed spatially resolved data that are needed to advance state-of-art model development and validation, and also help inform next generation designs for high performance PEWE systems.”

3.2 Research objectives

1. Establish distributed measurement techniques for in-situ characterization of transport in PEWEs.

2. Introduce the concept of an “effective water transport number” for characterizing water transport in PEWEs using current density distribution (CDD) measurements.
3. Quantify spatial variations of various overpotentials through distributed area specific resistance (DASR) measurements to correlate ohmic and mass transport losses related to bubble accumulation and membrane hydration.
4. Identify bottlenecks and assess the impact of flow-field design and architecture on localized transport, aiming to enhance next generation designs of high-performance PEWEs.
5. Establish a framework and construct a CFD model to simulate the complex multi-scale bubble transport process within the PTLs of a PEWE.

The objectives proposed as part of this thesis demonstrates the benefits of distributed diagnostic techniques and offers further insight into mass transport limitations in electrolyzers that are not observable from traditional polarization measurement for different PEWE configurations using various flow fields and diffusion media.

Objective 1 has been achieved and published as a journal article [Roening et al., 2022], with additional details in Chapter 5. Objectives 2 and 4 are addressed together in Chapter 6, which was initially presented at the ECS conference [Roy et al., 2022] and is currently published as a journal article [Roy et al., 2024]. Objectives 3 and 5 are explored separately, resulting in Chapter 7 and Chapter 8 respectively. At the moment of writing this dissertation, manuscripts are being prepared from these chapters and are expected to be submitted to relevant journals for peer-review and publication.

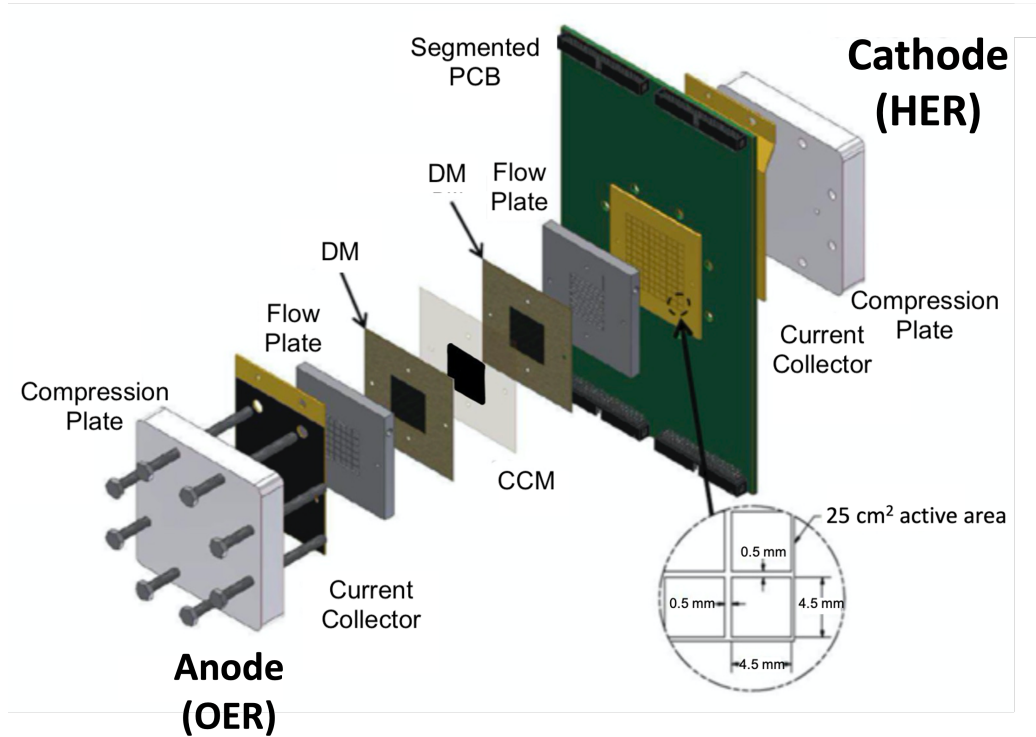
Chapter 4

Diagnostics & methods of approach

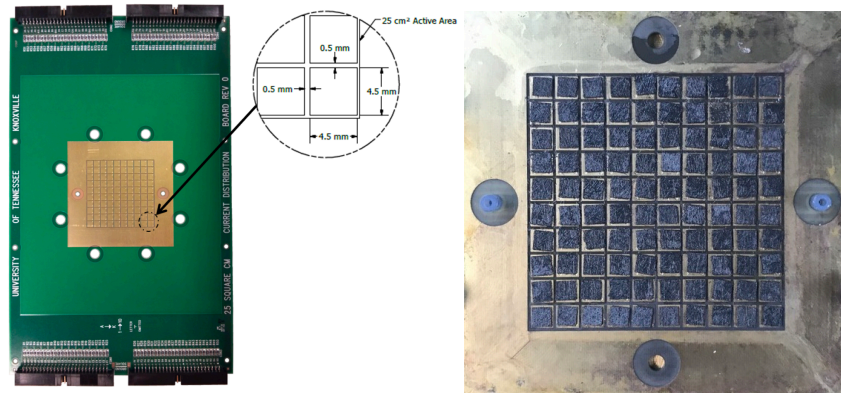
In this work current density distribution (CDD) and distributed area specific resistance (DASR) measurements were used as the primary diagnostic techniques to collect in-situ data across the active area of an operating PEWE.

Although a limited amount of studies on experimental CDD measurements in PEWEs have been conducted to date, local current distribution measurements in PEM fuel cells have been described extensively in the works of Bender *et al.* [Reshetenko et al., 2012b, Reshetenko et al., 2012a, Reshetenko et al., 2013, Phillips et al., 2017] and the Mench group [Mench et al., 2003, Clement et al., 2016, Ertugrul et al., 2019, Roenning et al., 2022, Roy et al., 2022, Roy et al., 2024]. Various methods have been used for CDD measurements, including resistor networks, potential probes, and printed circuit boards (PCB). In this work, the PCB technique was used due to its high spatial resolution and accuracy.

Current distribution provides useful insight for model validation and is used to meet the objectives outlined in (Section 2.3). However, it is essential to exercise caution when working with any such PCB test cells to minimize lateral current spread. This objective is accomplished through the segmentation of the flow fields, resulting in reduced cross-talk between segments and enhanced result accuracy [Eckl et al., 2006].



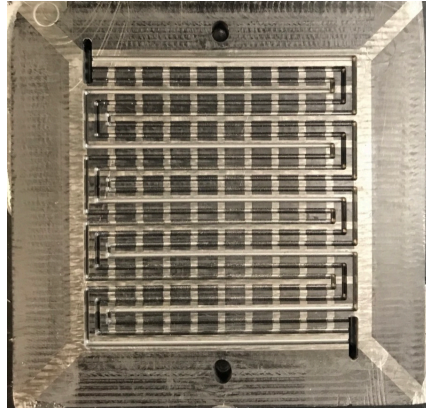
(a)



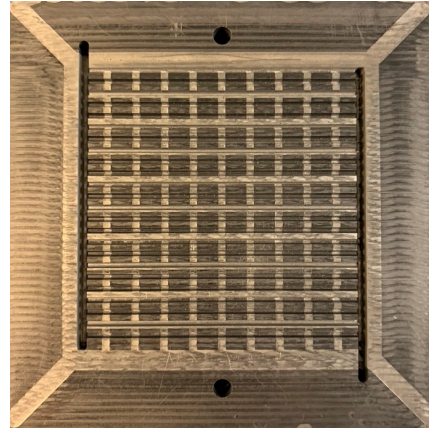
(b)

(c)

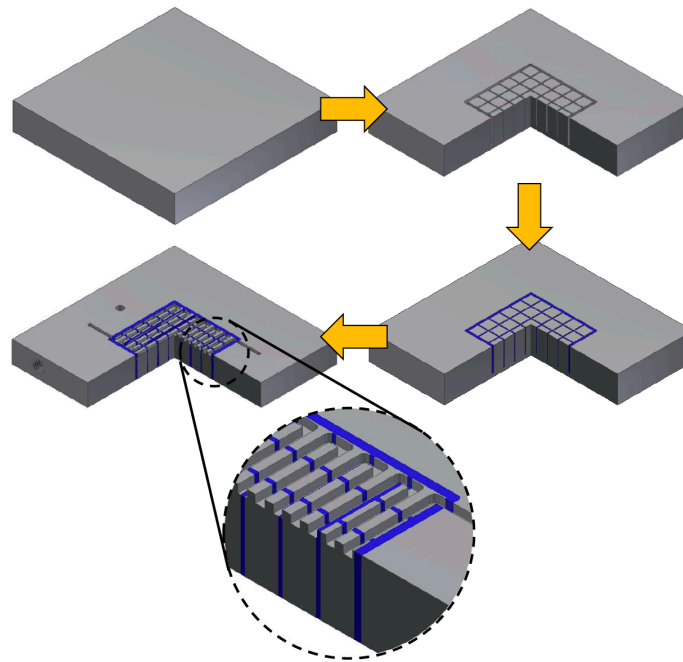
Figure 4.1: Description of current distribution set-up. (a) Current distribution setup (Figure adapted from [Roening et al., 2022]). Images of (b) the PCB board and, (c) segments with pieces of 10AA carbon paper for good contact.



(a) Triple serpentine segmented flow plate



(b) Parallel segmented flow plate



(c) Segmentation Process

Figure 4.2: Segmented 25cm^2 triple serpentine (a) and parallel (b) flow field plates. (c) Representation of the fully segmented cell manufacturing process where the grid represents epoxy [Clement, 2016]

4.1 Experimental test-bench and the PCB

The experimental setup, as illustrated in Figure 4.1a, comprises various components within the PEWE system. This includes a catalyst-coated membrane (CCM), anode and cathode diffusion media (DM), gaskets, flow plates, current collectors, compression plates, and the integration of a printed circuit board (PCB). The PCB was strategically positioned between the flow distribution plate and the current collector. The in-house fabricated flow fields were constructed on graphite plates and play a crucial role in this test system. Specifically, the anode plate was partitioned into 100 electronically isolated segments, each measuring 4.5 mm x 4.5 mm. The PCB incorporates an array of shunt resistors (each of $5m\Omega$), in contact with each 4.5 mm x 4.5 mm segment within the flow field. These shunt resistors enable passive distributed measurements of local current by monitoring voltage drop across the parallel circuit. Distributed measurements occurred passively while a potentiostat controlled the electrolyzer.

The PCB, developed in collaboration with an industry partner, was custom-designed for prior research within the group and subsequently manufactured off-site [Clement, 2016]. The PCB configuration features a 10 x 10 array of segments, with each segment measuring 4.5 mm x 4.5 mm and a 0.5 mm spacing between each segments, as represented in Figure 4.1b. Therefore, this board is capable of accommodating cells with active areas that are evenly divisible up to 25 cm^2 . To establish effective contact between the flow field plate and the PCB, small sections of carbon paper were placed in between the PCB and the segmented flow field plate. These carbon paper sections were compressed to 50%, as depicted in Figure 4.1c. This compression mechanism ensures proper and consistent contact between these components.

The PCB was linked to a National Instruments™ data acquisition system using ribbon cables. This data acquisition system was equipped with custom LabVIEW™

software, allowing passive real-time data collection from the PCB. Simultaneously, a multichannel BiologicTM (Seyssinet-Pariset, France) potentiostat/galvanostat (VSP/VMP3B-100 booster) was used to regulate the PEWE and acquire polarization data. Polarization curves and CDD and DASR measurements were conducted across various cell configurations and flow rates. Electrochemical impedance spectroscopy (EIS) measurements were also performed using the Biologic potentiostat. Frequencies from 10 kHz to 1Hz were applied with the ASR being determined as the intercept of the Nyquist plot at the real axis at high frequencies ($\sim 1000Hz$).

In all cases, cells were potentiostatically controlled with varying voltage holds at regular intervals, typically lasting 60 seconds each. The corresponding current was recorded at each voltage step during these steady-state conditions. The data for distributed current from each segment was generally collected approximately every 0.2 seconds and then averaged over the most recent 30 seconds, ensuring accurate measurements of in-situ localized current distribution. Additionally, a single frequency ($\sim 1000Hz$) AC perturbation with a small (10mV) amplitude is superimposed on top the DC polarization to gather the distributed area specific resistance data from each segment.

4.2 Cell architecture

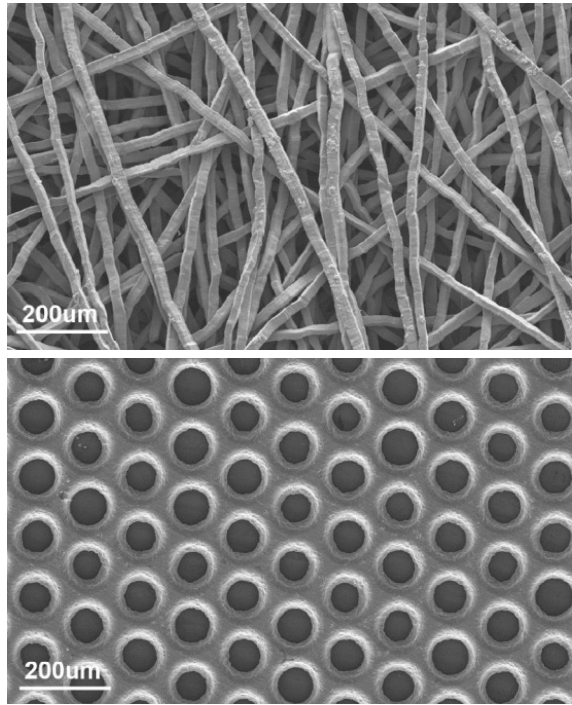
The experimental cell configuration used in this work feature flow fields with an active area of $25cm^2$, incorporating various flow channel architectures such as, parallel, triple serpentine and pin-type flow fields. The fully segmented plates, exemplified in Figure 4.2a and 4.2b, were fabricated in-house using a procedure akin to that employed for fuel cells and VRFBs as outlined in [Clement, 2016]. The segmentation process encompassed four key steps, detailed in Figure 4.2c. Initially, channels were machined into a impermeable graphite plate (obtained from Graphite Store) to correspond with the segments on the PCB. Subsequently, epoxy (DURALCOTM 4540) was applied after machining the channels halfway through the plate. The epoxy was compressed

under pressure and cured, followed by the segmentation of the back half of the plate. Considering the operating temperature of the electrolyzer during these experiments was 80°C (generally higher than that of VRFBs), channels extending to the corners of the plate were introduced and filled with epoxy. This accommodates for thermal expansion under the elevated operating temperature, thus preventing cracking of the segmented plates. Finally, the relevant flow channels were machined into the segmented plate, and inlet/outlet holes were incorporated on the side of the plate to facilitate the placement of the PCB between the flow plate and the current collector.

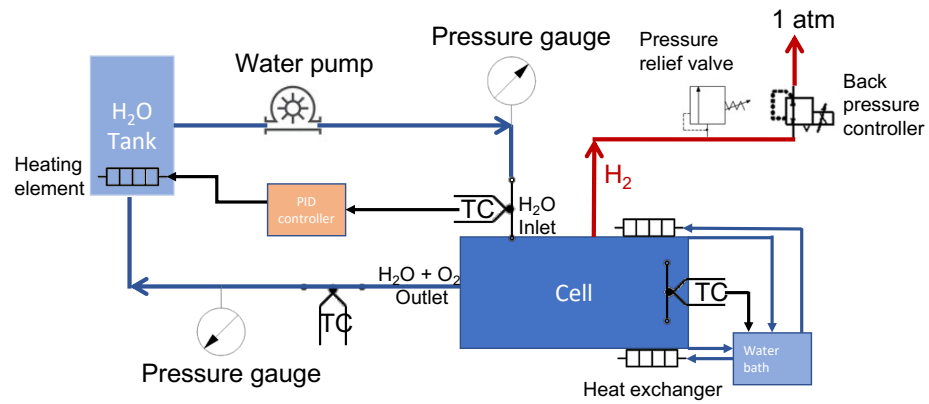
4.3 Cell materials and operating conditions

All materials employed in these experiments were provided either by collaborators involved in DOE project number DE-EE0008426 or were procured from the Fuel Cell Store (URL detailed in [Fuel-Cell-Store, 2024]). The catalyst coated membranes (Nafion-117) with a thickness of 200 μm were furnished by nelTM and featured an Ir-black catalyst on the anode and a Pt/C catalyst on the cathode. Similarly, catalyst coated membranes (Aquivion E98-09S) with a thickness of 90 $\mu m \pm 20\mu m$ were acquired from Fuel Cell Store. The catalysts on these membranes had a loading of 2.0 mg/cm^2 for Ir on the anode side and 0.8 mg/cm^2 for Pt on the cathode.

Two types of anode PTL materials were utilized: conventional titanium felt (baseline PTL) with a thickness of 0.125 mm , and a 50 μm thin titanium foil (LGDL) featuring 80 μm pores. The latter was manufactured by Dr. F. Zhang’s lab at the University of Tennessee, as illustrated in Fig. 4.3a. Both the anode diffusion media were coated with iridium to enhance contact and reduce ohmic losses [Kang et al., 2022]. While Toray carbon paper (TGP120) primarily served as the cathode-side PTL; the influence of various PTLs, including SGL 24AA, 24BA, and 24BC, was investigated in subsequent chapters.



(a) Types of anode PTLs



(b) Schematic of test system

Figure 4.3: **(a)** The two types of PTLs, baseline titanium felt PTL and thin foil titanium LGDL. **(b)** Schematic of the hydraulic and electronic control circuit for the test system.

The experimental cell was subjected to compression using eight bolts each tightened to a bolt torque of 5 $N - m$, while the temperature was consistently maintained at $80^{\circ}C$. Figure 4.3b illustrates a schematic of both the hydraulic and electronic control circuitry for the test system. The feedwater bath formed part of a closed system with a PID control circuit, ensuring the delivery of water at a temperature of $80^{\circ}C$, as monitored by a thermocouple near the anode inlet. The heat exchanger was seamlessly integrated into the compression plates and was actively regulated to remain at $80^{\circ}C$, accomplished through a recirculating water bath. Pressure measurements were also recorded at both the inlet and outlet of the feedwater line. On the hydrogen side, a pressure relief valve and pressure controller were employed to maintain an exit pressure of 1 atm throughout all experiments.

4.4 Data collection and processing

4.4.1 Polarization curves and impedance spectroscopy

Polarization curves are the most common diagnostic tool for fuel cells and electrolyzers due to their simplicity and effectiveness. Galvanostatic polarization involves varying the current while keeping other operating conditions constant and monitoring the resulting voltage response. Similarly, in a potentiostatic polarization curve, the cell potential is held constant at a specific value, and the resulting current is measured.

Polarization curves provide performance assessment for a PEWE across different current densities. Under various current loads, the voltage deviates from the reversible cell potential due to overpotentials, comprising Faradaic (activation i.e. chemical kinetics) and non-Faradaic (viz. ohmic and mass transport) losses. A typical polarization curve exhibits four distinct regions, indicating performance limitations: open-circuit potential reflects crossover and equilibrium conditions, low current densities reveal activation overpotentials, intermediate densities show ohmic resistance, and high densities highlight mass transport resistance.

This study involved measuring polarization curves for different cell configurations and flow rates (ranging from $0.24\text{mL}/\text{min}/\text{cm}^2$ to $4\text{mL}/\text{min}/\text{cm}^2$). All cells were controlled potentiostatically (to minimize corrosion of the carbon bipolar plates), with voltage holds ranging from 1.2 V to 2.4 V in 0.1 V increments, each lasting around 60 seconds. The current corresponding to each voltage step during these steady-state conditions was recorded and subsequently averaged over the final 30 seconds to ensure accurate, transient-free measurements.

Additionally, electrochemical impedance spectroscopy (EIS) measurements were conducted in conjunction with polarization curve measurements. EIS is a technique that assesses a system’s electrical response to an alternating current signal, enabling the study of various electrochemical processes, including charge transfer, chemical kinetics, reaction mechanisms, mass transport, and interfacial interactions. This technique is valuable for investigating a system’s resistance, capacitance, inductance, and its behavior at different frequencies.

During EIS, a small AC perturbation is applied to the system over a range of frequencies, and the resulting AC current or voltage is recorded. The impedance of the system, expressed as a complex number with real (resistance) and imaginary (reactance) components, is measured at each frequency. Impedance data can be represented in various forms, such as Nyquist plots, Bode plots, or equivalent circuits. In a PEWE, EIS is frequently employed to identify the rate-determining steps and quantify the effects of various phenomena on the electrolysis process. This includes assessing charge transfer, mass transport, double-layer formation, and membrane resistances, all of which play a crucial role in the system’s performance.

In this study, a range of frequencies from 10 kHz down to 1 Hz was employed, along with a 10mV AC perturbation for each voltage hold. The obtained impedance data were then analyzed. The ASR was determined by identifying the intercept of the Nyquist plot on the real axis at high frequencies ($\sim 1000\text{Hz}$), and the diameter of the primary semicircle provided information about the charge transfer resistance. Due to the inclusion of the PCB, the segmented flow-field and non-conductive material used

to isolate segments in the segmented flow-field, the system ASR was slightly higher ($\sim 50 \text{ m}\Omega - \text{cm}^2$) than for a typical cell.

4.4.2 CDD measurements

In this thesis, the current density distribution data can be presented in multiple formats as illustrated in Figure 4.4. Figure 4.4a displays the flow field overlaid on the CDD plots. In Figure 4.4b the raw data in a grid format as recorded from the data acquisition system, is presented. Figure 4.4c shows the processed data as smoothed (spatially interpolated) absolute current density contour plots. Finally, Figure 4.4d exhibits the processed data as a fractional deviation from the average CDD plots.

The fractional deviation from average is calculated from the interpolated absolute current density maps, using the following equation,

$$\tilde{i} = \frac{i - \bar{i}}{\bar{i}} \quad (4.1)$$

where $\tilde{i}$ is the fractional deviation from average; i is the absolute current density measured in A/cm^2 ; and $\bar{i}$ is the average current density which corresponds to the current density of the polarization curve for the same voltage hold.

The experimental results demonstrate that each cell build exhibits a unique distribution profile, primarily noticeable at lower voltage holds (ranging from 1.5 to 1.9 V), which remains consistent (i.e., a background distribution). These distribution variations are relatively small, typically within $\pm 15\%$, and likely stem from ohmic disparities associated with each build. To distinguish the CDD linked to mass transport variations that are observed at higher voltages, we define an average background for each build. This average background is computed as the mean of the distributions observed between 1.5 V and 1.9 V as illustrated in Figure 5.3 (refer to section 5.2).

It's important to note that this average background distribution remains consistent even if the inlet and outlet for the anode feedwater are reversed. Moreover, the

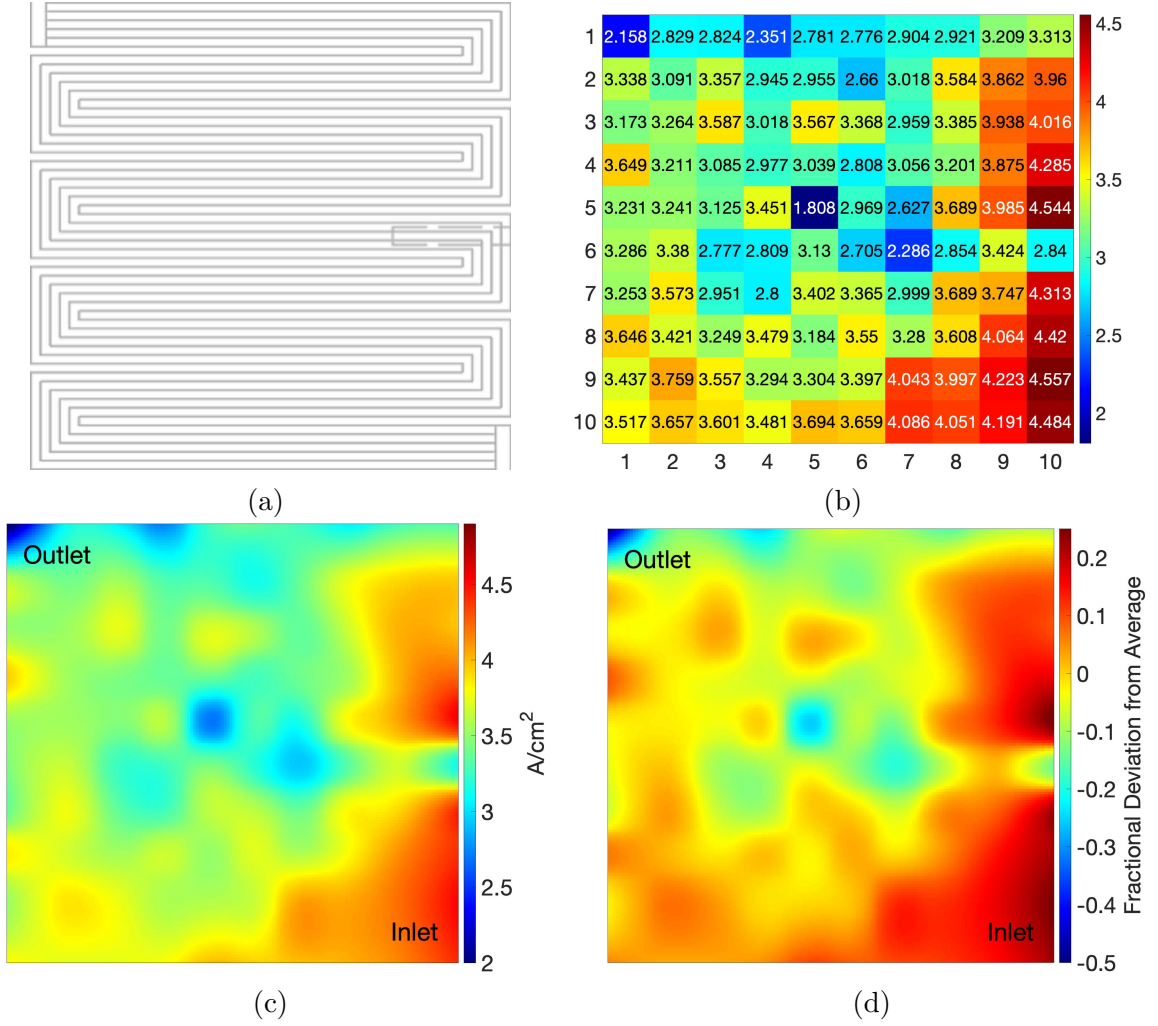
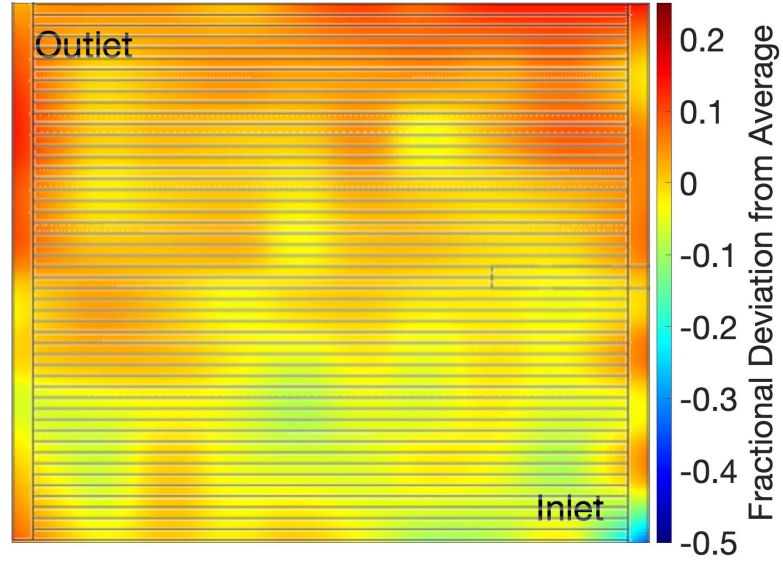


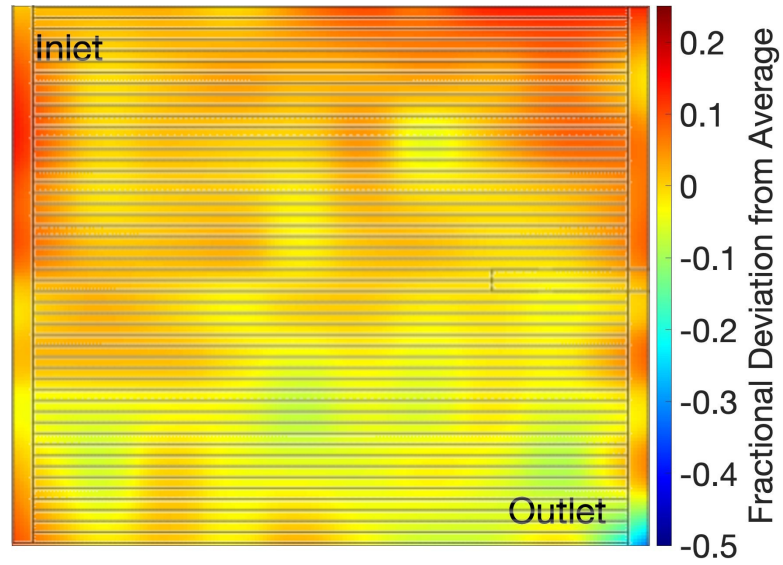
Figure 4.4: Data processing for a data set with triple serpentine, 25cm^2 flow channel design (a) at a voltage hold of 2.3V : (b) raw data, (c) smoothed interpolation data, and (d) smoothed fractional deviation from average.

pattern remains similar when the cell is disassembled and reassembled with the same materials. It can be observed in Figure 4.5 that switching the flow in the opposite direction did not change the current distribution pattern. The distribution pattern was seen to be consistent for a combination of LGDL and CCM. There is little to no difference between Figure 4.5a and 4.5b.

Therefore the fraction deviation from average CDD plot is further processed into the fourth presentation format that represents mass transport isolated fractional deviation from average current density. Figure 4.6 provides an overview of the correction process for an isolated mass transport distribution. Within this figure, 4.6a depicts the smoothed normalized distribution measured for the 2.3 V build, while 4.6b exhibits the average background distribution calculated for this build by averaging distributions from 1.5 V to 1.9 V. Figure 4.6c showcases the resulting distribution after subtracting the average background 4.6b from the measured distribution at 2.3 V 4.6a. A comprehensive explanation is provided in the subsequent chapter (refer to section 5.2).

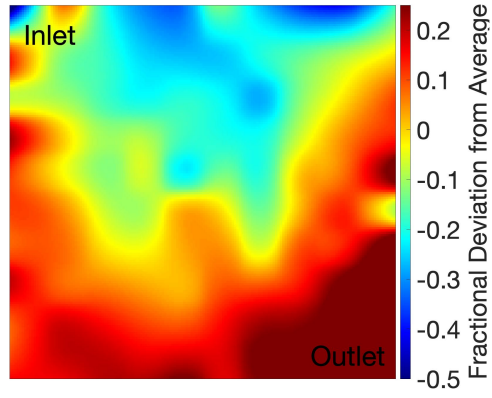


(a) Regular flow configuration

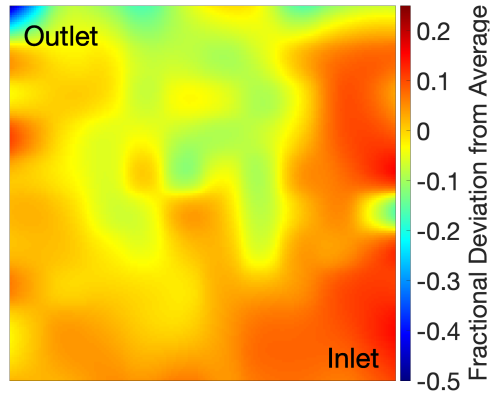


(b) Reversed flow configuration

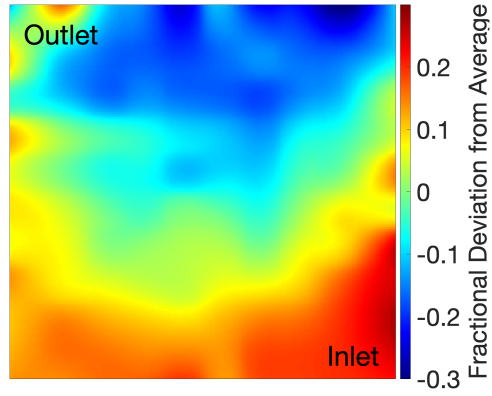
Figure 4.5: Normalized current distribution plots for a thin foil LDGL with: a) original configuration; b) reversed flowing feed water.



(a) Interpolated CDD plots



(b) Background CDD



(c) Mass Transport Isolated CDD plots

Figure 4.6: (a) Fractional deviation from mean current distribution plot for the cell build at $2.3V$, (b) background distribution, (c) Isolated mass transport distribution.

Chapter 5

Mass transport limitations in polymer electrolyte water electrolyzers using spatially-resolved current measurement

*This chapter is revised based on the published paper [Roening et al., 2022]:
Frida H. Roening, Anirban Roy, Douglas S. Aaron, Matthew M. Mench, "Mass
transport limitations in polymer electrolyte water electrolyzers using spatially-resolved
current measurement", Journal of Power Sources, vol. 553, pp. 231749, 2022.*

*My contributions to this work spanned across methodology development, validation
procedures, formal data analysis, extensive investigative work and data collection,
original draft composition, and the creation of visual representations. Other authors
assisted with data curation, review and editing of the manuscript.*

This work utilizes spatially-resolved current measurements to provide insight into
mass transport limitations in electrolyzers that are not observable from traditional

polarization measurement. In this study, two types of flow-fields (parallel and triple-serpentine) and two types of diffusion media (patterned porous thin titanium foil LGDLs and Ir-coated titanium felt PTLs) were examined. A non-uniform current distribution dominated by mass transport limitations was observed to be instigated by the restriction of liquid water transport to catalyst sites. Additionally, conditions are revealed which yield similar polarization performance but dissimilar current distributions. In such cases, the transport limitations for different architectures and porous media affect polarization in different regions of the active area. Furthermore, the triple-serpentine flow-field used in this study performs better than the parallel flow-field under mass transport limited operating conditions. This indicates that the parallel flow-field used in this study is more susceptible to starvation than the triple-serpentine flow-field for the electrolyzer studied.

5.1 Methodology

5.1.1 Experimental setup and cell architecture

An exploded view of the experimental test cell is shown in Fig. 5.1a-5.1b, the PEWE includes a catalyst-coated membrane, anode and cathode diffusion media, gaskets, flow plates, current collectors, and compression plates, along with the addition of a printed circuit board (PCB) as shown in Fig. 5.1b. Two types of PTL material were used at the anode - conventional titanium felt (baseline PTL) of thicknesses 0.125 mm and a 50 μm thin titanium foil (LGDL) with 80 μm pores manufactured by collaborators at the University of Tennessee Space Institute (UTSI) [Mo et al., 2016], are shown in Fig. 5.1c. Both the anode diffusion media (DM) were coated with iridium for better contact and lower ohmic losses [Kang et al., 2022]. Toray carbon paper (TGP120) was used as the cathode-side PTL. The catalyst coated membranes (N117) were fabricated by nel (Oslo, Norway) The catalysts were 2.0mg/cm² Ir/IrO_x on the anode side and 1.0mg/cm² Pt black on the cathode [Wang et al., 2021b,

Wrubel et al., 2021]. For all experimental results reported, experiments were repeated with at least three sets of materials (CCM, CL, DM) for each configuration and operating condition.

The electrolyzer cell had an active area of 25 cm^2 . The effect of flow-field configuration using both triple-serpentine and parallel channel flow-fields (Fig. 5.1d) were also investigated in the experiments. The flow-field channels were 1 mm deep and wide. The flow plates were machined out of impermeable graphite and fully segmented to mirror the spacing of the PCB and filled with epoxy (DURALCO™ 4540) to electronically isolate each segment. Graphite was chosen as a viable material for the flow-fields for its ease of machinability and low cost. Furthermore, the operating voltage was restricted to 2.4V and HFR measurements monitored to avoid oxidation and corrosion. The PCB was placed between the segmented flow plate and the current collector on the anode side. To ensure good contact between the PCB and the flow-field, isolated pieces of carbon paper (TGP 120) were placed in between each segment on the flow-field and the PCB. Fig. S2 shows that uniform contact between the flow-field and the PCB was achieved. This experimental system was of a wet/dry configuration with the anode side experiencing two-phase flow. The oxygen evolution reaction (OER) is the rate limiting process, therefore making the anode of greater interest of study. The in-plane conductivity of the LGDL and PTL has been measured to be 1854 S/cm and 1801 S/cm respectively, showing that the current distributions presented in this work for these two diffusion media are comparable. It is well known that the in-plane electrical conductivity does cause some distortion and smearing of the data while measuring spatial current density distributions. This effect has been discussed in our previous work [Roy et al., 2020].

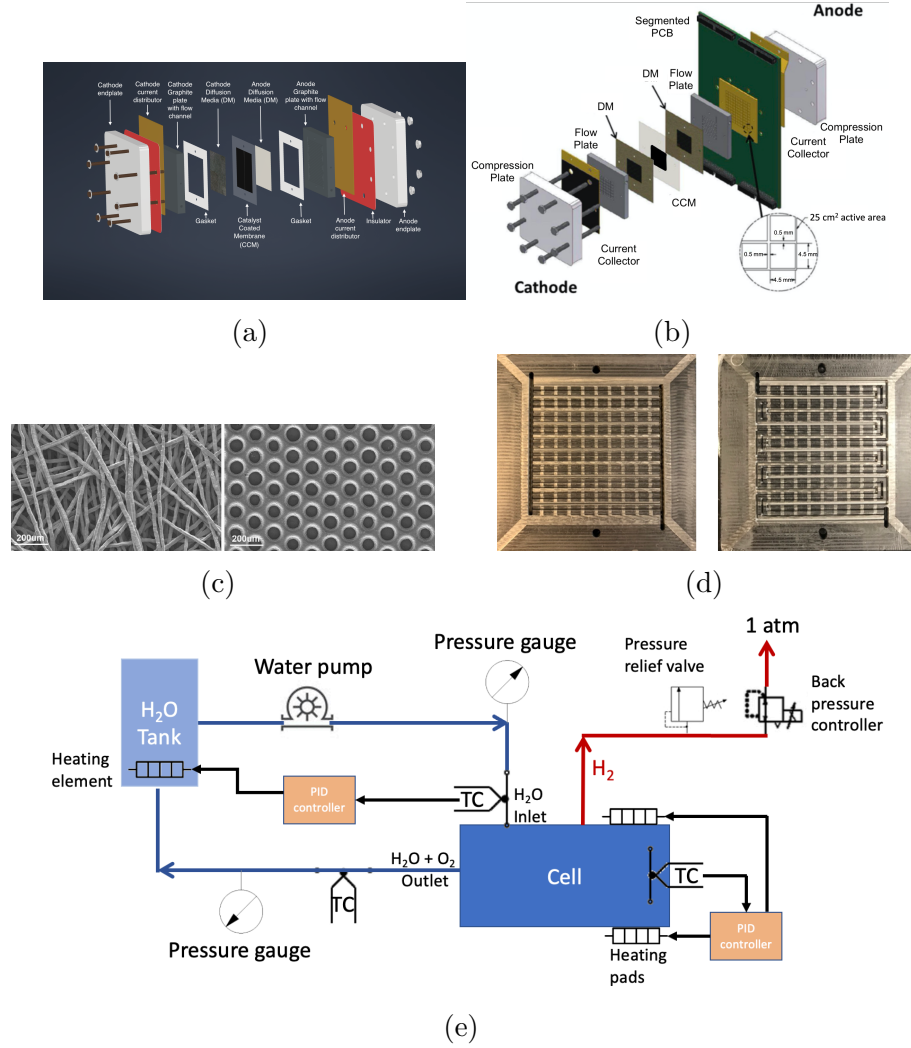


Figure 5.1: Description of current distribution set-up. (a) CAD overview of a typical electrolyzer. (b) Current distribution setup. (c) The two types of PTLs, baseline titanium felt PTL and thin foil titanium LGDL. (d) Image of triple-serpentine and parallel segmented flow-fields. (e) Schematic of the test system.

5.1.2 Polarization curves and in-situ current distribution measurements

Polarization curves and in-situ localized current distribution measurements were performed for both diffusion media on both flow-fields at varying flow-rates from $0.24\text{mL}/\text{min}/\text{cm}^2$ to $2\text{mL}/\text{min}/\text{cm}^2$. The cell was compressed to $5N - m$ bolt-torque, and the cell temperature maintained at 80°C by external heating pads and preheated feed-water.

Fig. 5.1e shows a schematic diagram of the hydraulic and the electrical circuit for the test system. The water bath was part of a closed system PID control circuit that delivered water at 80°C which was sensed by a thermocouple near the anode inlet. A similar closed system PID control circuit with two heating pads was used to regulate the cell temperature. An additional thermocouple was placed in the outlet to measure the difference in temperature of the feed water as it passes through the cell. A FLIR thermal imaging camera combined with the thermocouple in the cell was used to verify the cell temperature. Fig. S1, shows that the cell membrane was maintained at 80°C throughout the experiment. A discussion on thermal effects within the system is provided in the supplementary information as part of Appendices. Furthermore, the pressure on the feed-water line was measured using pressure gauges at the inlet and the outlet. The hydrogen side had one pressure relief valve and a pressure controller that maintained a line pressure at atmospheric 1bar for all experiments.

All cells were potentiostatically controlled from 1.2 V to 2.4 V in 0.1 V increments. Corresponding current was recorded at each steady-state voltage step. By testing at least three sets of materials for each cell configuration and operating condition, all the polarization data were averaged and the maximum error was calculated to be $\sim 7\%$. The highest errors were noted for the most extreme operating conditions (flow-rate of $0.24\text{mL}/\text{min}/\text{cm}^2$ and voltage holds above 2.2V).

While the multichannel potentiostat/galvanostat (Arbin InstrumentsTM, College Station, TX) was used for polarization curves, a National InstrumentsTM data

acquisition system with a custom LabVIEW program capable of measuring current densities between 0.1 to $10 A/cm^2$, collected real time data from the PCB. The PCB consisted of $4.5\text{ mm} \times 4.5\text{ mm}$ segments separated by 0.5 mm . The flow-field has 100 segments that passed current through an array of shunt resistors (0.4 Ohm) present on the PCB; the measured voltage drop across each shunt resistor was used to calculate the current in each segment.

Distributed current data for each segment was collected every 0.2 seconds and averaged over the final 30 seconds of each step. The current distribution data were then interpolated in post-process to obtain a smoothed contour plot (as seen in Figure 4.4 and explained in Chapter 4). Averaged data are presented as local current density distribution and normalized by fractional deviation from the average (detailed discussion can be found in section 5.2. Results and Discussion).

The HFR measurements were carried out with a Biologic VSP potentiostat with a VMP3B 20A booster module. Due to the inclusion of the PCB, the segmented flow-field and non-conductive material used to isolate segments in the segmented flow-field, the system HFR was slightly higher ($\sim 50\text{ m}\Omega - cm^2$) than for a regular cell set-up. Details of the technique were provided in previous work [Clement et al., 2016]. Experimental error for current distribution measurements were assessed via repeated testing and have been determined to be within $\pm 5\%$ of all reported values in this work.

5.2 Results and discussion

The performance of the PEWE system is usually analyzed by measuring polarization data. In order to investigate the changes in its spatial distribution of current density, local current distribution data are obtained for each voltage hold on the polarization curves. It was found that, under certain conditions of relatively low flow-rate, the current densities were non-uniform. Operating under extreme conditions made the mass transport limitations of the system well pronounced and therefore easier to

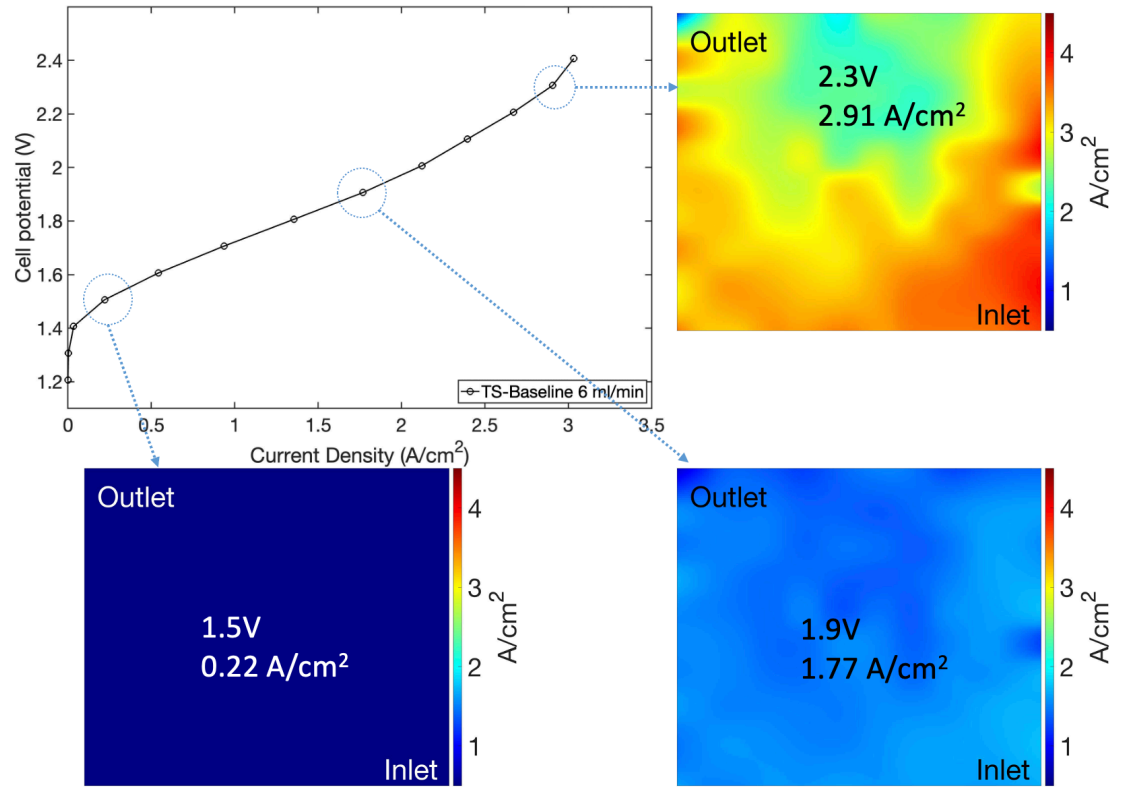


Figure 5.2: Current distributions evolving as voltage increase. Mass transport limitations observed above $2.3V$ for a flow-rate 0.24 ml/min/cm^2 on the triple-serpentine flow-field at $80^\circ C$ with the baseline PTL.

characterize. These insights can be applied to create better design solutions that increase performance and efficiency under normal conditions, as well.

Fig. 5.2 shows the evolution of the local current density distribution at various points on the polarization curve for an electrolyzer operating at low stoichiometric ratio (0.24 ml/min/cm^2). It can be observed that, at lower voltage, current distributions are relatively uniform with an overall low current density. As the polarization increases, the overall current density increases and the spatial distribution remains uniform. At higher voltage holds ($> 2.3V$), mass transport limitations can be observed in the polarization curve, the corresponding current distribution plot is no longer uniform. A region of high current density near the inlet and low near the outlet can be observed.

Analyzing each segment’s deviation from the mean current density helps to better analyze the current distribution maps by normalizing all current distributions to the same scale. Details of these calculations are provided in the supplementary information as part of Appendices.

The experimental results reveal that each cell build, at voltages from 1.5 to 1.9 V, has a distribution profile that is consistent with each specific build. These variations in the distributions are relatively small (within $\pm 15\%$) and can be assumed to be due to interfacial contact resistance and/or heterogeneity in cell compression associated with each build [Kang et al., 2022, Parra-Restrepo et al., 2020]. Therefore, in order to better isolate the mass transport limited current distribution, a background correction is applied. An average background for each build is defined as the mean of the distributions seen between 1.5V to 1.9V, as shown in Fig. 5.3a. This average background distribution does not change if the inlet and outlet are reversed (as shown in Section 4.4, Fig. 4.5). Further details on the nature of this background distribution are discussed in the supplementary information as part of Appendices. Fig. 5.3b depicts how the correction for an isolated mass transport distribution is obtained. Starting with the normalized distribution and subtracting the average background to generate the resulting isolated mass transport distribution.

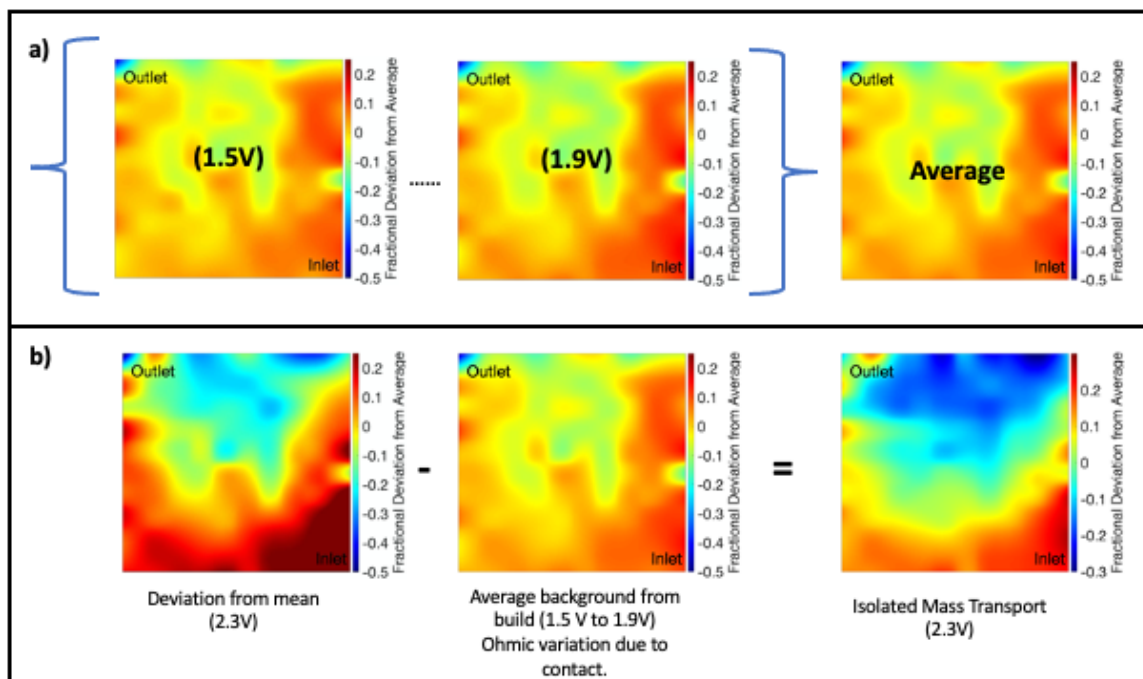


Figure 5.3: Data processing. (a) The average background for each build defined as the mean of the distributions seen between 1.5V to 1.9V. (b) Corrected data (e.g. at 2.3V) defined as the average background subtracted from the deviation from mean distribution.

In this work, all current distribution maps are therefore presented as fractional deviation from the average current density with the applied background correction. The influence of different types of diffusion media and flow-field architecture on mass transport limitations are investigated. To better understand the influence of mass transport within the high performance LGDLs, experiments were carried out near mass transport limited conditions for both the triple-serpentine and the parallel flow-fields.

5.2.1 Triple-serpentine

Fig. 5.4 shows the polarization curves obtained for the thin foil LGDL on the triple-serpentine flow-field with flow-rates varying from 6 *ml/min* (0.24 *ml/min/cm²*) to 50 *ml/min* (2 *ml/min/cm²*) and their corresponding current distributions (up to 20 *ml/min* or 0.8 *ml/min/cm²*). It can be observed from the polarization curve in Fig. 5.4a that mass transport limitations are present at high current densities and low flow-rates. These mass transport limitations are observed to be a function of flow-rate and can be alleviated through increased feedwater flow. The current density distributions at 2.3V are presented in Fig. 5.4b - 5.4e. The mass transport limitations in these distributions manifest as a gradient —relatively high current near the inlet and low near the outlet. At the lowest flow-rate (6 *ml/min*) this gradient is most pronounced. For each flow-rate, two sets of current distribution plots are recorded. These distributions are presented in the supplementary information Fig. S3 as part of Appendices. As the flow-rate increases the intensity of the gradient decreases (Fig. 5.4c) and eventually the distribution transitions to be uniform ($\pm 10\%$) at flow-rates above 20 *ml/min*. A $\sim 70 \text{ m}\Omega \cdot \text{cm}^2$ increased HFR was measured at 2.3V compared to the HFR at OCV, for the cell operating at the lowest flow-rate (6 *ml/min*). At higher flow-rates (20 and above), the HFR increase at 2.3V compared to the HFR at OCV was measured to be significantly lower, $\sim 15 \text{ m}\Omega \cdot \text{cm}^2$. Immerz, et al. [Immerz et al., 2018a, Immerz et al., 2018b] demonstrated that low

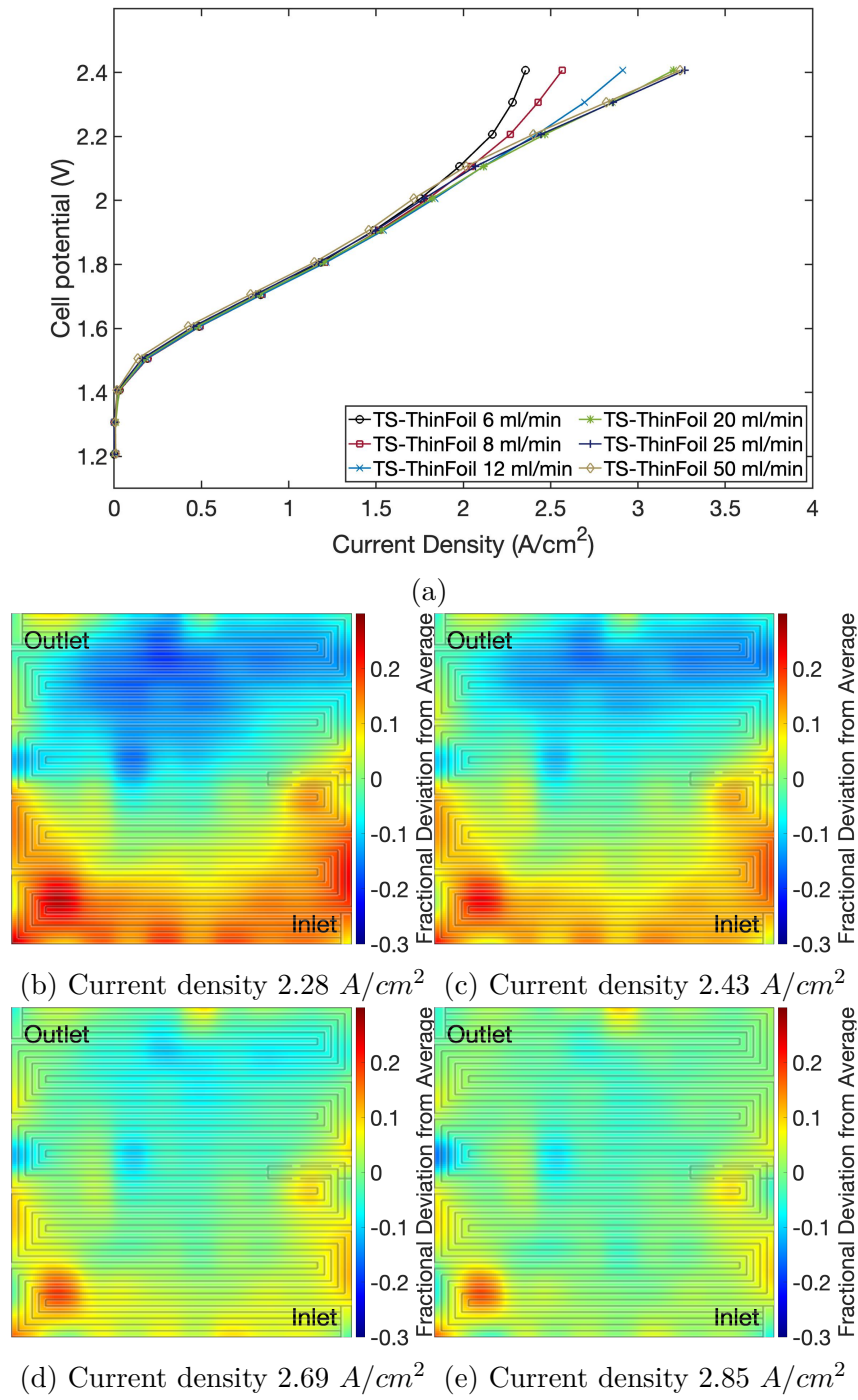


Figure 5.4: Mass transport limitations can be observed to be decreasing with increased flow-rate. **(a)** Polarization curve and mass transport isolated distributions (at 2.3V) for **(b)** 6 ml/min , **(c)** 8 ml/min , **(d)** 12 ml/min , and **(e)** 20 ml/min on the triple-serpentine flow-field with the thin foil LGDL at 80 $^{\circ}C$.

current density region near the outlet may be due to bubble accumulation. Significant bubble accumulation results in a reduced specific heat capacity of the two-phase fluid mixture, which may lead to local dry-out of the membrane. This causes the local HFR of the system to increase under mass transport limited regimes. This is one of the reasons for higher overpotentials and reduced performance.

The triple-serpentine flow-field has long channels where the flow is restricted. Therefore, it can be assumed that the low current density region near the outlet is a result of gas accumulation towards the end of the channels. The stoichiometric ratios were calculated to be around 17 at 6 *ml/min* at 2.3V (Supplementary Fig. S5 presented in Appendices). The calculated stoichiometric ratio is greater than 1, which indicates the system has enough reactants in the bulk flow-field and is locally starved near the catalyst layer. This may cause membrane dry out and increased temperatures near the outlet (refer to discussion in supplementary information as part of Appendices) which contributes to the low current density regions observed in Fig. 5.4b. Increasing the feed water flow-rate therefore helps performance through enhanced bubble removal.

5.2.2 Parallel flow-field

Fig. 5.5 presents the polarization curves obtained for the thin foil LGDL on the parallel flow-field with flow-rates varying from 6 *ml/min* to 50 *ml/min* along with their corresponding current distributions (up to 20 *ml/min*). The investigations reveal a dependence on the flow-field architecture as the parallel flow-field is observed to be more sensitive to the mass transport. Like the triple-serpentine, the parallel flow-field also exhibits non-linearity in the polarization curve at higher voltage holds for lower flow-rates. However, the polarization curves start to deviate from each other around 1 *A/cm²* as opposed to ~ 1.8 *A/cm²* in the triple-serpentine flow-field. The gradient from inlet to outlet still exists in the local current distribution. However, unlike the triple-serpentine flow-field, the region of low current density seems to be

larger and more spread out (Fig. 5.5b - 5.5e). Furthermore, it can even be clearly detected at high a flow-rate of 20 ml/min . Similar to the triple-serpentine operating at the lowest flow-rate (6 ml/min), the parallel flow-field shows a $\sim 100\text{ }mOhm - cm^2$ increase in HFR at 2.3V compared to the HFR at OCV, which is higher than the value measured for the triple-serpentine flow-field. At higher flow-rates (20 and above), the HFR increase at 2.3V compared to the HFR at OCV was measured to be significantly lower, $\sim 3\text{ }mOhm - cm^2$. Interestingly these values correspond with the polarization trends where the parallel outperforms the triple-serpentine at the highest flow-rate.

A possible explanation for this phenomenon could be due to lower flow velocities in the channels of the parallel flow-field. The parallel flow-field has 25 channels that the water flows through, yielding low channel flow velocity (superficial liquid velocity was calculated to be $\sim 0.03\text{ }m/s$ at 6 ml/min compared to $\sim 0.25\text{ }m/s$ in the triple-serpentine flow-field [Ito et al., 2012]). Since bubbles get transported out of the cell with the liquid flow, the lower channel flow-rate may lead to bubble accumulation in the channels [Majasan et al., 2018a, Majasan et al., 2018b]. It is assumed that drag on the gas-phase bubbles is proportional to the channel fluid phase relative velocity; also, removal of product gas from the reaction sites and the channels is a key factor in sensitivity to liquid flow-rate. The stoichiometric ratio for the cell at 2.3V for a flow-rate of 6 ml/min was calculated to be 21, indicating that for the same flow-rate, less overall reactions can be supported in the same active area using the parallel flow-field compared to the triple-serpentine (which had a stoichiometric ratio of 17). A large portion of the catalyst layer (active area) is likely inaccessible to the reactant due to bubble accumulation. This drives membrane dry-out, increased HFR, and local rise in temperature (refer to discussion in supplementary information as part of Appendices). With those assumptions, the relative performance of the two architectures can be explained.

A semi-empirical comparison at mass transport-limited operating conditions for the two flow-fields is presented in Fig. 5.6. The figure shows local current density deviations as a function of area specific flow-rate for the inlet and outlet regions

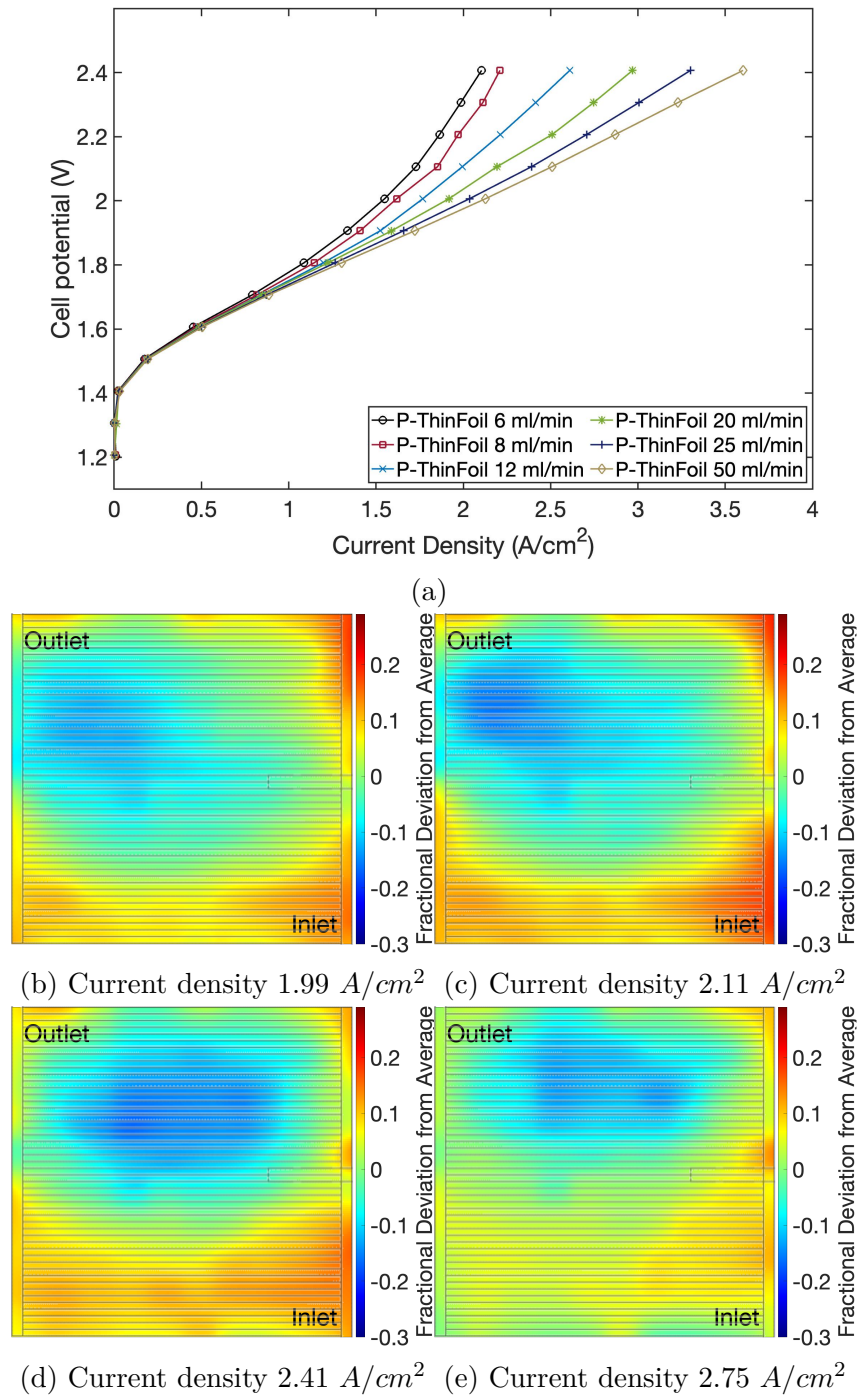


Figure 5.5: Mass transport limitations can be observed to be decreasing with increased flow-rate. (a) Polarization curve and mass transport isolated distributions (at 2.3V) for (b) 6 ml/min, (c) 8 ml/min, (d) 12 ml/min, and (e) 20 ml/min on the parallel flow-field with the thin foil LGDL at 80 °C.

for both flow-fields. The inlet region is defined as the 2x2 square of segments (corresponding to an active area of 10mm x 10mm) closest to the inlet, while the outlet region is the 2x2 square of segments (corresponding to an active area of 10mm x 10mm) closest to the outlet. Fig. 5.6a compares the inlet region for the two flow-fields. It is evident from the exponential curve fits that the triple-serpentine reaches an asymptote at lower flow-rate compared to the parallel flow-field. Similarly, Fig. 5.6b compares the outlet region for the two flow-fields and exhibits similar trends. As the flow-rate increases to 2 ml/min/cm^2 , the inlet and outlet normalized current densities showed negligible deviation from the average (close to zero). This indicates, at flow-rates of 2 ml/min/cm^2 and higher, there was little or no mass transport limitation for the thin foil LGDL on either flow-field.

5.2.3 LGDL/PTL comparison

Fig. 5.7 portrays a combination of polarization data obtained with two different diffusion media – a thin foil LGDL and a baseline PTL, on both parallel and triple-serpentine flow-fields. In the previous sections it is demonstrated that mass transport losses in a PEWE system are a strong function of flow-rate. In this comparison, only the extreme flow-rates of 6 ml/min and 50 ml/min were analyzed. 50 ml/min is chosen on the high end because the cell shows similar current density distribution and performance above 2 ml/min/cm^2 .

Fig. 5.7a is a comparison of the thin foil LGDL on the two flow-fields. At 50 ml/min , the performance is similar on both triple-serpentine and parallel flow-fields. Furthermore, the performance measured at 50 ml/min for all cell combinations at 2 V was around 2 A/cm^2 . At 6 ml/min the performance is significantly better on the triple-serpentine flow-field compared to the parallel flow-field. As seen from Section 5.2.2, it can be theorized that the drag on the gas-phase bubbles is proportional to the channel fluid phase relative velocity squared which is important

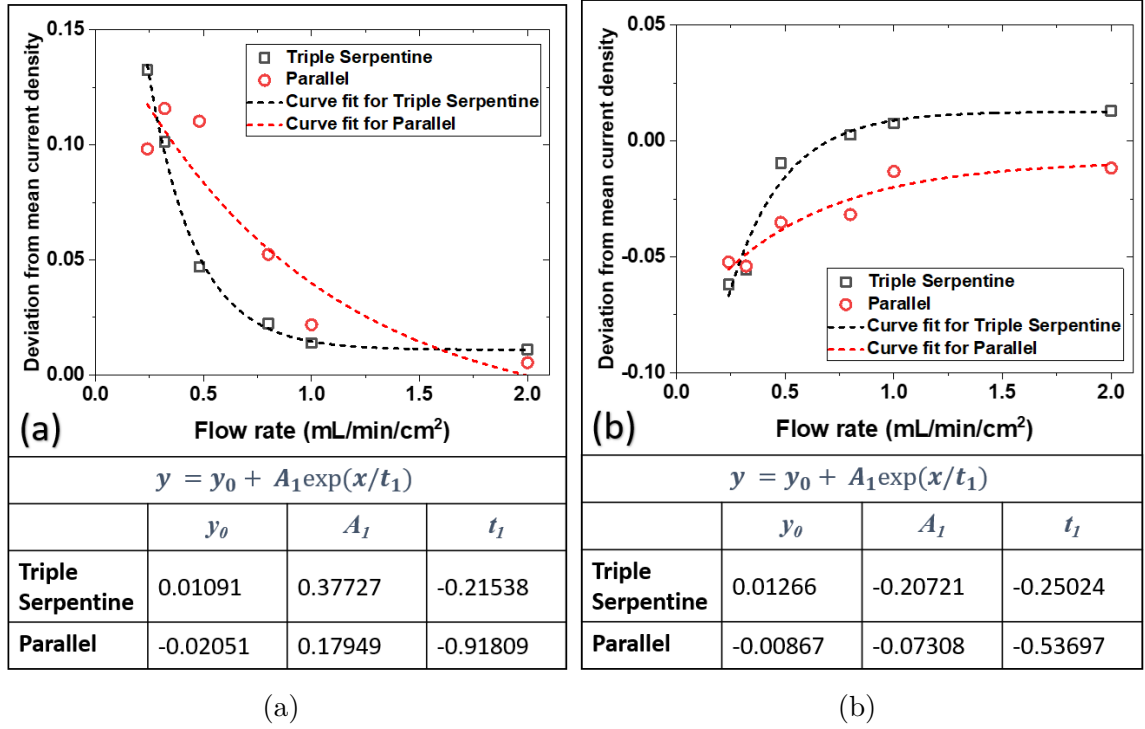


Figure 5.6: Fractional deviation from average current density as a function of flow-rate for parallel and triple-serpentine flow-fields; near the (a) inlet and (b) outlet.

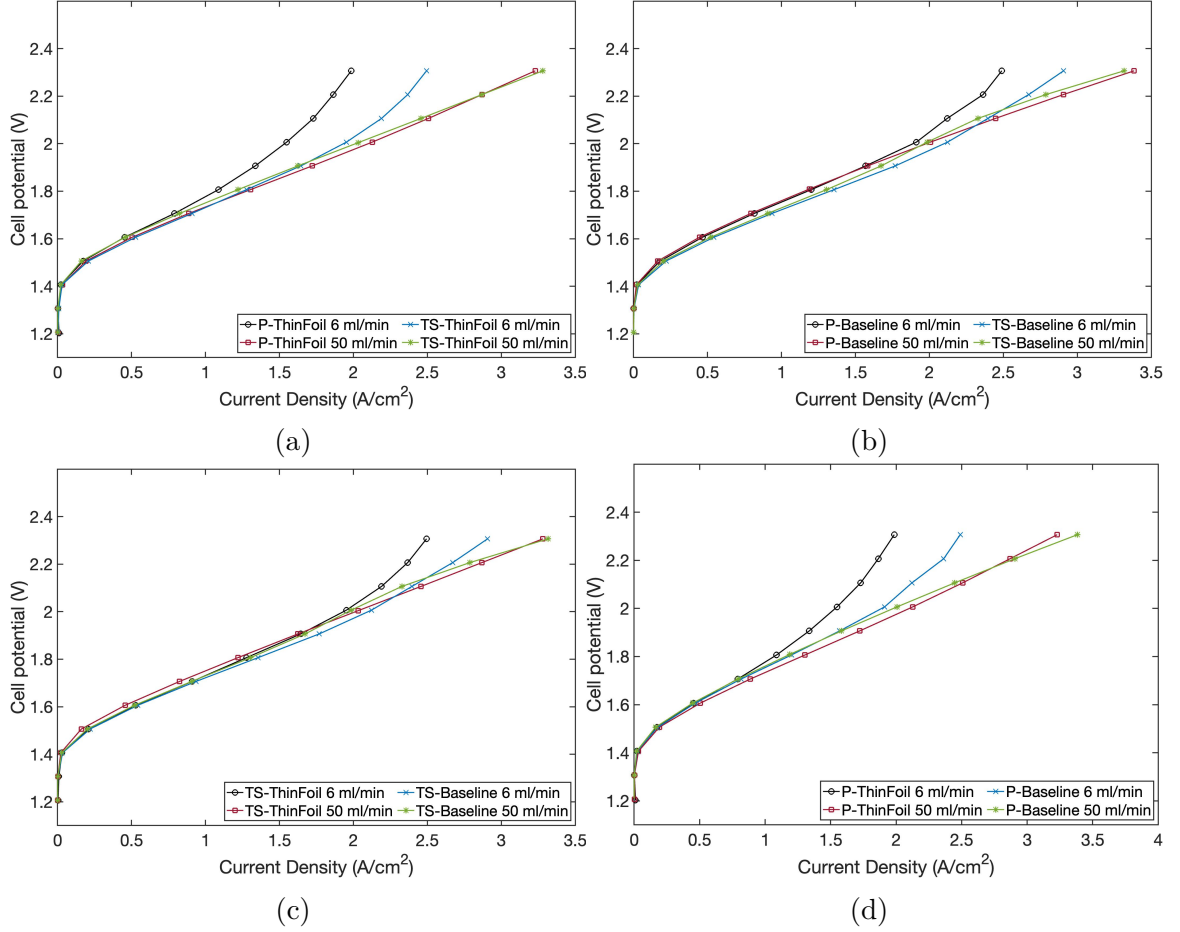


Figure 5.7: Polarization curve comparison between the two flow-fields and diffusion media at 6 *ml/min* and at 50 *ml/min*. **(a)** Thin foil LGDL on the triple-serpentine and parallel flow-field, **(b)** baseline LGDL on the triple-serpentine and parallel flow-field, **(c)** thin foil LGDL and baseline PTL on the triple-serpentine flow-field and **(d)** thin foil LGDL and baseline PTL on the parallel flow-field. All polarization curves were measured at 80 °C.

in removing the gas-phase from the reaction sites. This may explain the relative performances of the two architectures.

A comparison of both flow-fields' influence on a conventional baseline PTL is shown in Fig. 5.7b. It can be observed that the variation of flow-rate has a small impact on performance with this type of diffusion media. The porous morphology (Fig. 5.1c) of the baseline PTL allows for mass transport between channels, underneath the lands. A possible explanation for the improved performance on the triple-serpentine flow-field at 6 *ml/min* may be due to higher in-plane permeability of the baseline PTL. A larger pressure gradient exists in the triple-serpentine flow-field (reported in supplementary Fig. S6 as part of Appendices) because of its longer channel length, thus Darcy's law eq. 5.1, suggests greater mass flux underneath the lands. This translates to better performance of the baseline PTL compared to the LGDL as seen in Fig. 5.7c - 5.7d by effectively utilizing more active catalyst area. Further evidence supporting this hypothesis can be found in the current density distribution measurements presented in Fig. 5.8.

$$q = -\frac{\kappa}{\mu L} \Delta P \quad (5.1)$$

([Bear, 2013] where q is the flux, κ is permeability, μ is the viscosity, ΔP is the pressure drop and L is the given distance)

All these current distributions are measured in a mass transport limited region and the gradients observed in Sections 5.2.1 - 5.2.2 are also present for the baseline PTL. This diffusion media showed the greatest current deviation (Fig. 5.8b,d) under these conditions on both flow-fields. Fig. 5.8a, c shows the current density distributions for the thin foil LGDL on both flow-fields under the same conditions. The triple-serpentine (Fig. 5.8c) is seen to have a high current density zone in the inlet channels and around the bends at each switchback.

Similarly, the parallel flow-field exhibits high current density for the first few inlet channels. This indicates that, under such operating conditions, the flow-rate is not

enough to supply water to the reaction sites for all 25 channels equally; this behavior is exaggerated by the LGDL’s inability to allow transport underneath the lands. Conversely, the PTL allows for transport underneath the lands and facilitates better access to reaction sites at the catalyst layer. Hence, Fig. 5.8b shows more pronounced high current density zone near the inlet.

5.3 Conclusions

The state of the art materials studied in this work exceed the performance benchmarks set by DOE 2020 [U.S.DOE, 2024a]. However, in order to extract higher performance and enhanced efficiency, a better understanding of the mass transport limitations is needed. In order to better characterize this phenomena extreme conditions of low water flow-rate and high current were explored. The results from this work can be translated to optimize system design and architecture for normal operating conditions and gain higher performance. Furthermore, by having systems with efficient mass transport, parasitic pumping losses can be reduced.

Under the operating conditions tested of low relative flow-rate, a large current density gradient was observed for all cell configurations. That is, local high current density can be observed towards the inlet with reduced current density closer to the outlet. The triple-serpentine flow-field performs better than the parallel flow-field under mass transport limited operating conditions, indicating that the parallel flow-field is more sensitive to starvation than the triple-serpentine flow-field for the test cell configurations studied here. This is likely a result of higher liquid velocity in the channels for the triple-serpentine flow-field compared with lower channel velocity in the parallel flow-field, which facilitates product gas removal. All diffusion media perform similarly while operating in lower current density regions, but behave differently under extreme conditions of high current density.

In order to achieve highly compact and efficient PEWE operation, careful consideration of mass transport of the liquid and gas-phases are needed, and through

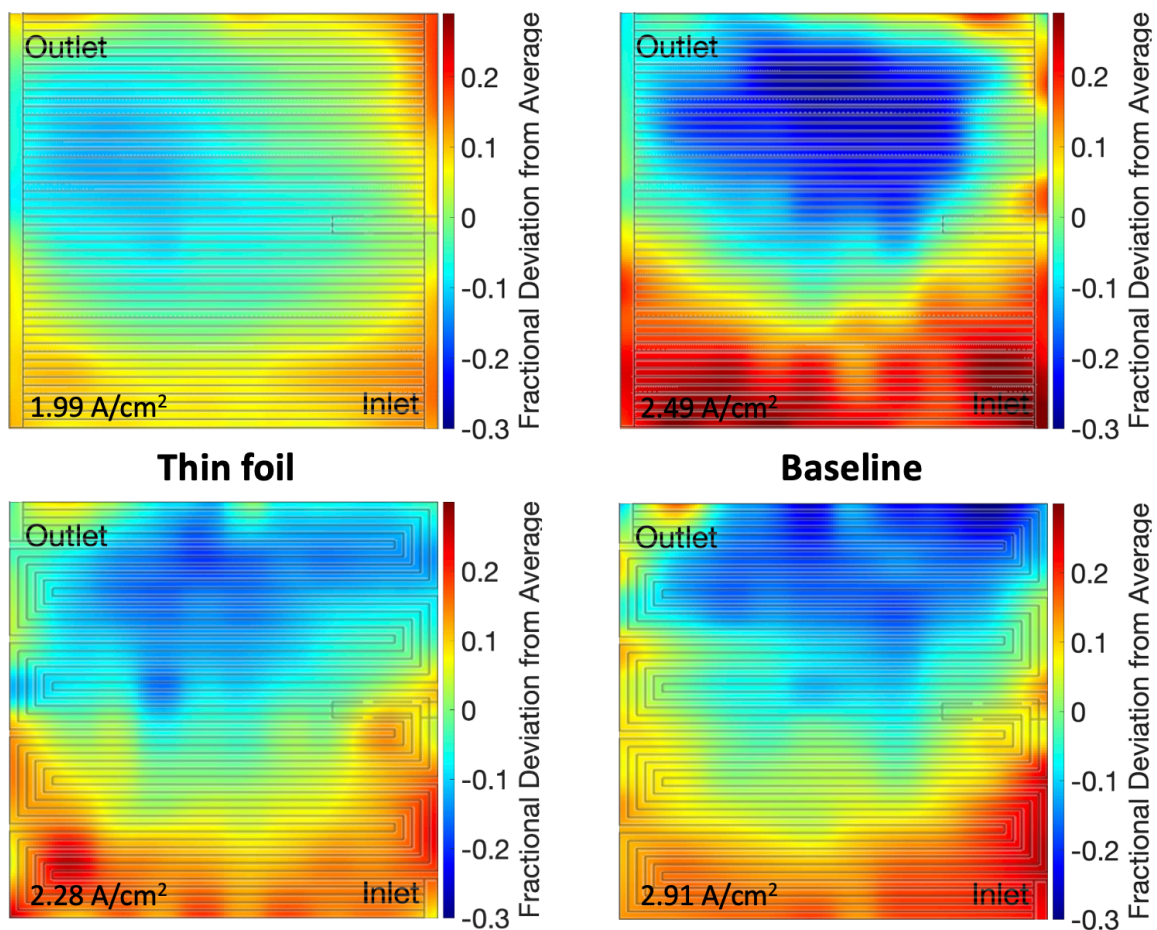


Figure 5.8: Current distribution comparison under mass transport limited conditions (6 ml/min at 2.3 V) for the baseline PTL and thin foil LGDL on both flow-fields at $80 \text{ }^{\circ}\text{C}$.

this understanding higher-performance designs can be conceived, that are the subject of ongoing work. Furthermore this work has provided useful insights and experimental data that can be used for detailed model verification for multiple combinations of cell designs and flow-rates.

Chapter 6

EWTN: Quantifying mass transport to enable water electrolyzer architectures with low flow-rate sensitivity

This chapter is revised based on the published research article in the Journal of the Electrochemical Society under the same name as the title of this chapter [Roy et al., 2024]. The authorship is attributed to:

Anirban Roy, Frida H. Roenning, Douglas S. Aaron, Feng-Yuan Zhang, and Matthew M. Mench.

My contributions to this work spanned across conceptualization of the idea, methodology development, validation procedures, formal data analysis, extensive investigative work and data collection, original draft composition, and the creation of visual representations. Other authors assisted with data curation, review and editing of the manuscript.

To develop cost-effective and high-performing polymer electrolyte water electrolyzers (PEWEs) for gigawatt-scale applications, researchers have focused on

reducing precious metal catalyst loadings and optimizing porous transport layers. However, the performance of PEWEs is also affected by system architecture. Mass transport losses are dependent on localized architecture and material interactions. In-situ measurements, such as current density distribution maps have demonstrated advantages in understanding the intricate characteristics and influence of two-phase flow within PEWEs. This study proposes the parameter of effective water transport number (EWTN) as a quantitative tool to investigate such current density distribution (CDD) measurements for PEWEs. The results show that higher flow-rates have EWTN values of 0.95 and above, indicating no mass transport limitations; while lower flow-rates with large CDD gradients have EWTN values between 0.6-0.8, indicating mass transport limited conditions. The new analysis also identified a correlation between ohmic overpotentials and mass transport losses due to bubble accumulation and membrane hydration. To address these limitations, a unitized pin-type LGDL/flow-field design was developed, which effectively enhance liquid water transport and prevents local gas accumulation, resulting in improved mass transport characteristics. The results of this work show reduced flow-rate sensitivity and $\sim 13\%$ increased performance with the pin-type architecture at $0.24\text{ml}/\text{min}/\text{cm}^2$.

It is critical for the development of gigawatt-scale PEWEs to have highly effective electrodes that are inexpensive, efficient, and durable [Yu et al., 2022, Kang et al., 2018]. Significant research efforts have been directed toward reducing precious metal catalyst loadings (by 80-90% compared to current loadings of $1\text{mg}/\text{cm}^2$)[Hegge et al., 2020] to enable ubiquitous PEWE commercialization. The performance of PEWEs partially depends on the porous transport layers (PTLs), which enable effective catalyst utilization and uniform water distribution to the anode catalyst layer. To enhance mass transport through the anodic PTL, Zhang et al.[Wang et al., 2023, Yu et al., 2022, Kang et al., 2018, Wang et al., 2021b] have developed a thin-foil titanium liquid-gas-diffusion-layer (LGDL). However, optimization of such advanced materials alone are not sufficient for achieving high

performance and durability in PEWEs, as their performance is significantly affected by system architecture and operating conditions.

Mass transport losses in PEWEs, which account for up to $\sim 25\%$ of overall performance loss [Fornaciari et al., 2020], have been the focus of many studies, particularly through optimization of the anodic diffusion media or PTL and flow-field [Lee and Bazylak, 2020, Lee et al., 2020c, Schuler et al., 2019a, Schuler et al., 2019b, Grigoriev et al., 2006, Lee et al., 2020a]. Recent research [Roening et al., 2022] emphasizes the importance of comprehensive analysis of the architectural interactions, including the PTL-land-channel interplay, to optimize mass transport and system performance in electrochemical systems. Furthermore, the use of advanced in-situ diagnostics has demonstrated potential to provide insights on localized limitations resulting from the two-phase flow within PEWEs [Yuan et al., 2023]. One such in-situ technique that has yielded promising results is local current-density-distribution (CDD) measurements. These measurements provide a two-dimensional, real-time visualization of the amount of current generated at the membrane electrode assembly (MEA) and can aid in the investigation of mass transport limitations.

There are many paths to improve mass transport within PEWEs, and the measurement of CDD has been a valuable tool. Although CDD measurements are primarily quantitative in nature, they are often interpreted as a visual reference, making them appear qualitative and challenging to differentiate among test results. Therefore, to further advance the use of current density measurements for optimizing electrochemical systems, an effective water transport number (EWTN) is proposed in this work to further quantify the CDD measurements. This analysis offers an improved method for analyzing CDD measurements and is used to identify and design architecture that yielded performance improvement. Furthermore, the proposed analysis has led to the conceptualization and development of a unitized pin-type LGDL/flow-field aimed at improving mass transport within a PEWE. This research highlights the importance of using quantitative analysis to further advance our understanding of PEWEs and optimize their performance and design.

6.1 Methodology

6.1.1 Experimental setup

The experimental PEWE test bench used in this work is depicted in Figure 6.1. The PEWE comprises a catalyst-coated membrane, anode and cathode porous transport layers, gaskets, flow-plates, current collectors, compression plates, and a PCB as shown in Figure 6.1a. In this study, a thin titanium foil LGDL with a thickness of $50\text{ }\mu\text{m}$ and circular pores of $50\text{--}80\text{ }\mu\text{m}$ diameter patterned in a hexagonal close packing, as shown in Figure 6.1b, was used. The LGDL was developed by Dr. Zhang’s group at UTK [Wang et al., 2021b, Yu et al., 2022, Wang et al., 2023]. For comparison purposes, a baseline titanium felt purchased from the Fuel Cell Store (url in [Fuel-Cell-Store, 2024]) was used (seen in Figure 6.1b). As previously reported in the literature [Roening et al., 2022, Kang et al., 2022], both the anode PTLs were coated with iridium to improve electrical contact and reduce ohmic losses. The cathode-side PTL was Toray™ carbon paper (TGP120). The catalyst coated membranes (Aquivion E98-09S) were sourced from Fuel Cell Store with a thickness of $90\mu\text{m} \pm 20\mu\text{m}$. The catalysts were 2.0 mg/cm^2 *Ir – black* loading on the anode side and 0.8 mg/cm^2 *Pt* loading on the cathode. To ensure consistency, experiments were repeated with at least three sets of materials for each configuration and operating conditions.

Polarization curves and in-situ CDD measurements were performed at varying flow-rates from 0.24 ml/min/cm^2 to 4 ml/min/cm^2 . The experimental cell was compressed using a bolt torque of 5 N – m (as mentioned in previous work [Roening et al., 2022]), and the temperature was maintained at 80°C . Fig. 6.1d shows a diagram of the hydraulic and the electronic control circuit for the test system. The feedwater bath was part of a closed system PID control circuit that delivered water at 80°C , sensed by a thermocouple near the anode inlet. The heat-exchanger was integrated as part of the compression plates and was maintained at 80°C by a

recirculating water bath. The pressure on the feed-water line was measured at the inlet and the outlet. The hydrogen side had one pressure relief valve and a pressure controller that maintained an exit pressure at 1 *atm* for all experiments.

6.1.2 Polarization curves and in-situ current distribution measurements

All cells were potentiostatically controlled from 1.2 *V* to 2.2 *V* in 0.1 *V* increments, with corresponding current density recorded at each steady-state voltage step. The polarization data were averaged and the maximum error was calculated to be approximately $\sim 3\%$, based on at least three sets of materials tested for each cell configuration and operating condition. The highest errors were noted for the most extreme operating conditions (flow-rate of 0.24 *ml/min/cm*² and voltage holds above 2.2 *V*).

While the multichannel Biologic (Seyssinet-Pariset, France) potentiostat/galvanostat (VSP potentiostat with a VMP3B-100 booster) was used for polarization curves, a National InstrumentsTM data acquisition system with a custom LabVIEW program collected real time data from the PCB. Details of the working principle of the CDD are given in previous work [Roening et al., 2022]. Distributed current data for each segment was collected every 0.2 seconds and averaged over the final 30 seconds of each step. Averaged data are presented as local CDD and normalized by fractional deviation from the average (detailed discussion can be found in previous work [Roening et al., 2022]). Electrochemical impedance spectroscopy (EIS) measurements were also performed using the Biologic potentiostat, with the area specific resistance (ASR) being determined as the intercept of the Nyquist plot at the real axis at high frequencies ($\sim 1000\text{Hz}$). It should be noted that the measured ASR is about 50 *mΩ – cm*² higher than that of a regular PEWE without the CDD peripherals, as reported in our previous work. The experimental error for current distribution measurements (i.e. values reported in the histograms) was assessed

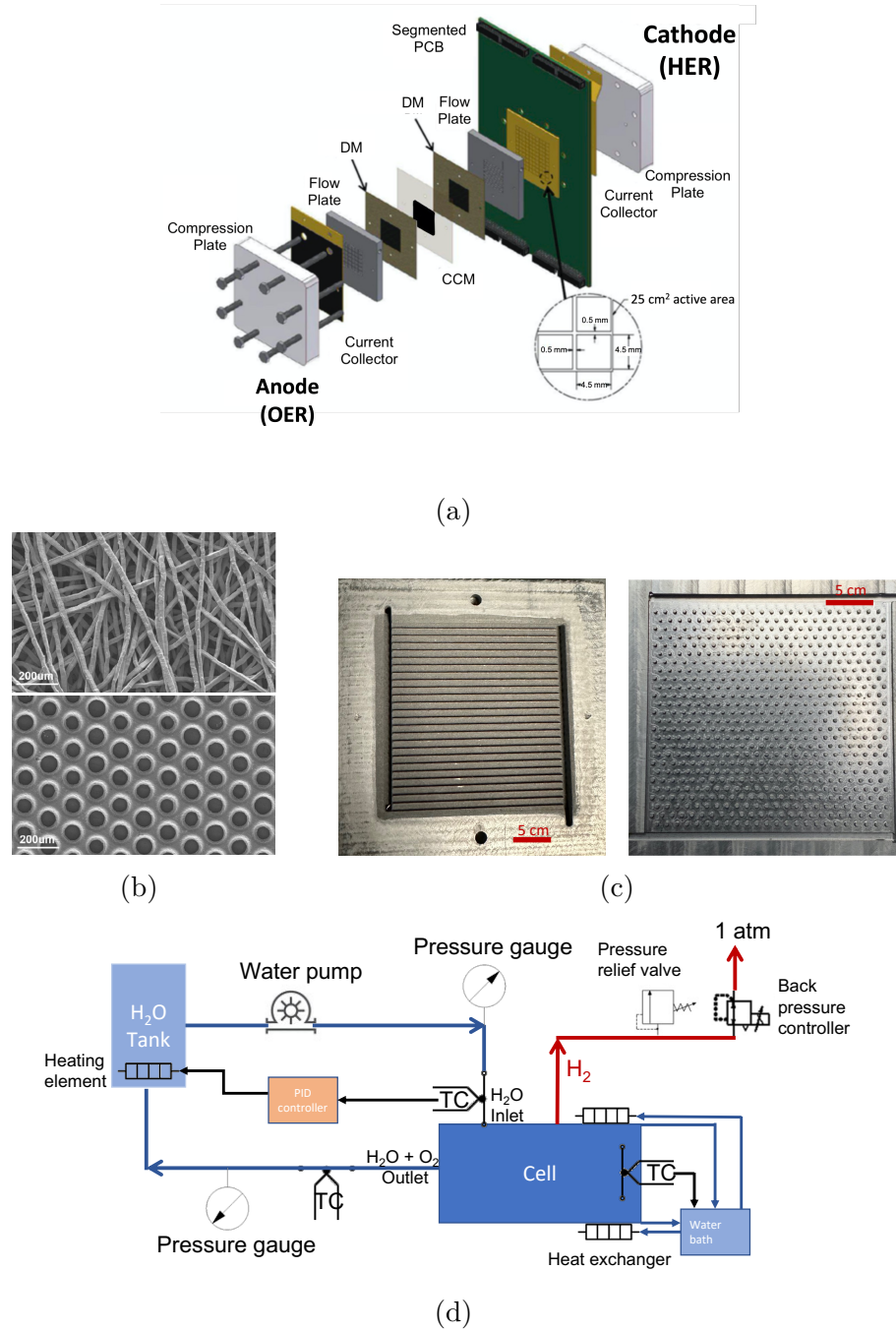
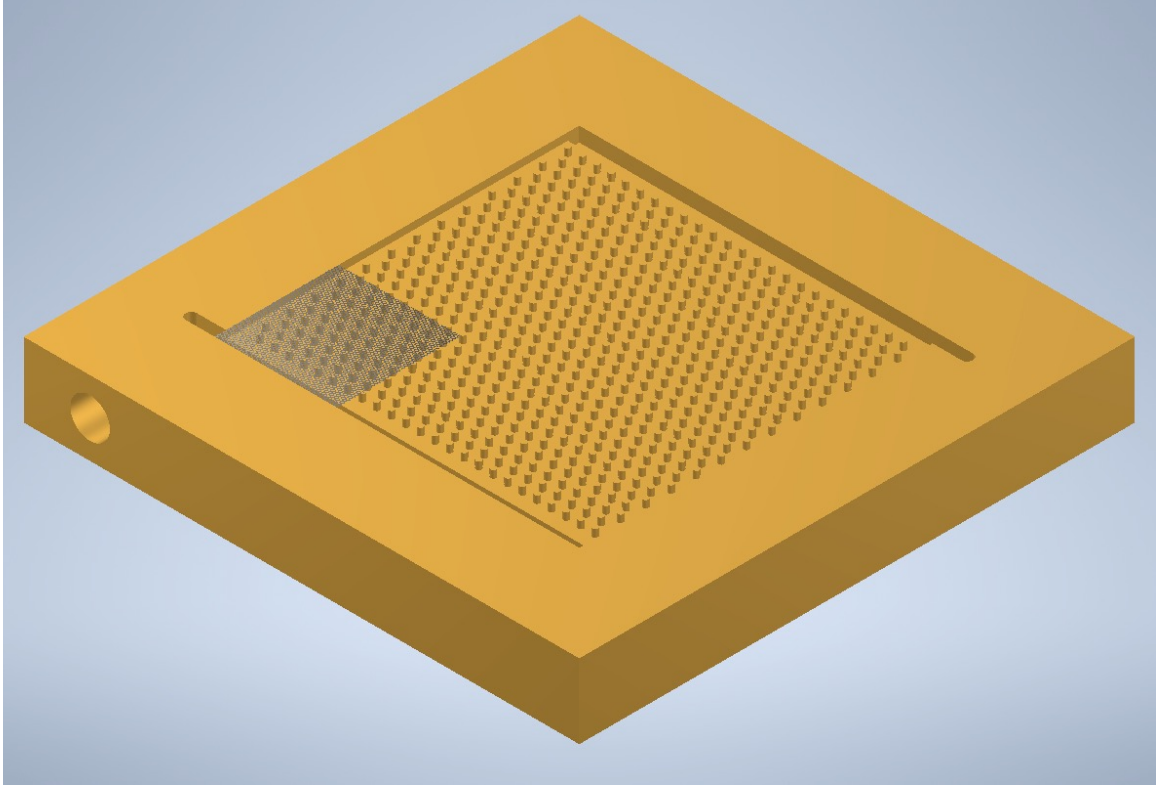
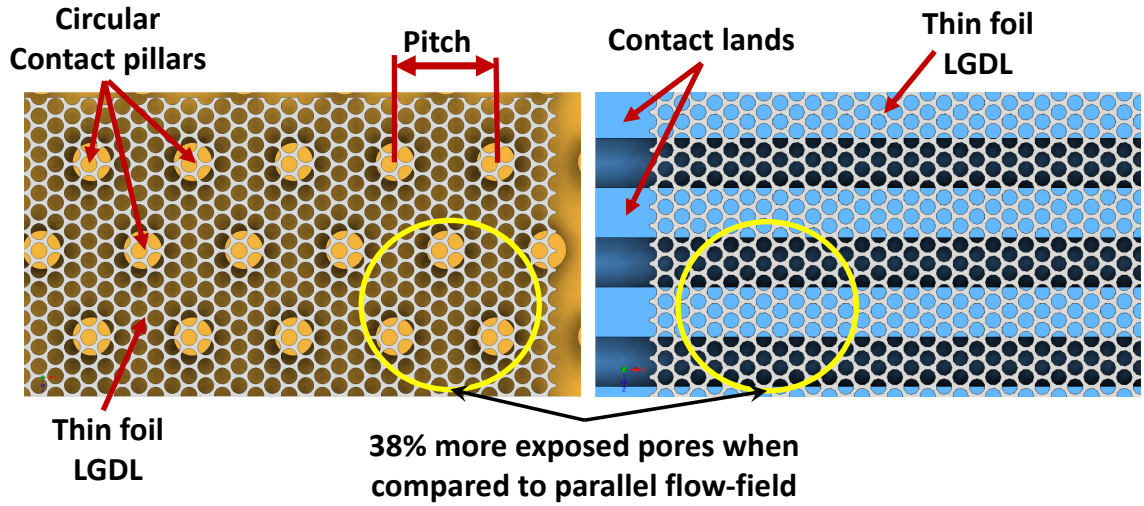


Figure 6.1: Description of PEWE test system. (a) Current distribution setup (Figure adapted from [Clement et al., 2016]). (b) The two types of PTLs, baseline titanium felt PTL and thin foil titanium LGDL. (c) Images of parallel and pin flow-fields. (d) Schematic of the test system.



(a)



(b)

Figure 6.2: Pin-type flow-field: (a) CAD model of a 25 cm^2 pin-type flow-field. (b) Sections of the two flow-fields with a overlaid LGDL. Highlighted features include circular cross-section pins with a diameter of $75\text{ }\mu\text{m}$ arranged with a 2 mm pitch offset (left). A larger channel-land ratio of 0.88 provides more exposed pores at the catalyst interface when compared to a conventional parallel flow-field (right).

through repeated testing and found to be within $\pm 8\%$ of all reported values in this study.

6.1.3 Flow-field designs: parallel and pin-type configurations

In all experiments, a 25 cm^2 active area cell was used. To analyze the impact of flow-field design, a parallel channel and a pin-type configuration flow-field (as depicted in Figure 6.1c) were tested. The parallel channel flow-field had a depth of 1 mm and a width of 1 mm , while the pins featured a circular cross-section with a diameter of $75\text{ }\mu\text{m}$ and were arranged with a 2 mm pitch offset (Figure 6.2). The pin-type configuration is particularly suited to match the design of the LGDL, exposing 35% more pores to increase transport and promoting exchange between channels as shown in Figure 6.2b. Compared to the parallel flow-field with a channel to land ratio of 0.5, the pin-type flow-field has a higher ratio of 0.88. In addition to enhancing transport, the staggered pattern of the pin design helps reduce pressure drops (see supplementary information Figure S7 as part of Appendices), which is beneficial for overall system performance. Additionally, this configuration allows for better customization of the flow-field to align with the patterned LGDL design, thereby minimizing the shadowing of land areas on the LGDL pores. Design parameters, such as the pin’s cross-section, pitch, and aspect ratio, can be adjusted and optimized for each specific LGDL to achieve the best performance. Moreover, the LGDL can be welded or permanently attached to the flow-field to form a unitized component [Zhang et al., 2023]. However, in this work the flow-field version was not integrated into a single component, and it only demonstrates the feasibility.

The flow-plates used in the experiments were fabricated from impermeable graphite, with the cathode-side plates being fully segmented to match the spacing of the PCB and filled with epoxy (DURALCO™ 4540) to electrically isolate each segment. In order to measure CDD, the PCB was positioned between the segmented flow plate and the current collector on the cathode side. To ensure good contact

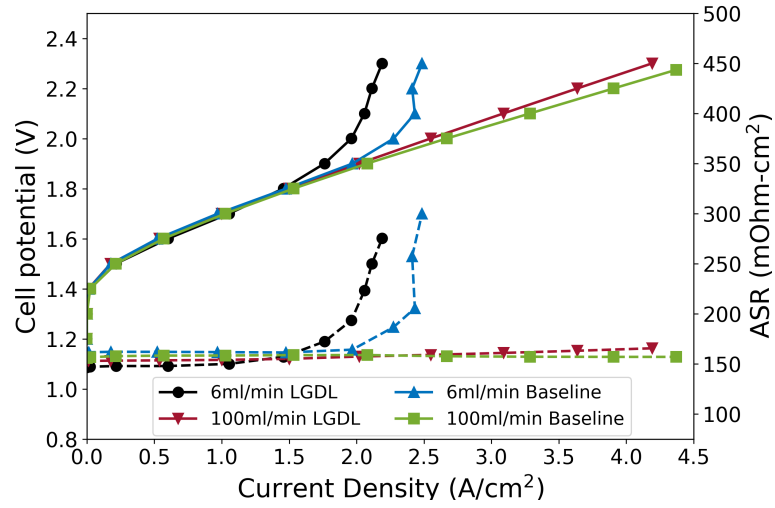
between the PCB and the flow-field, isolated pieces of carbon paper (TGP 120) were placed in between each segment on the flow-field and the PCB. Further details can be found in previous work [Roenning et al., 2022].

6.2 Results and discussion

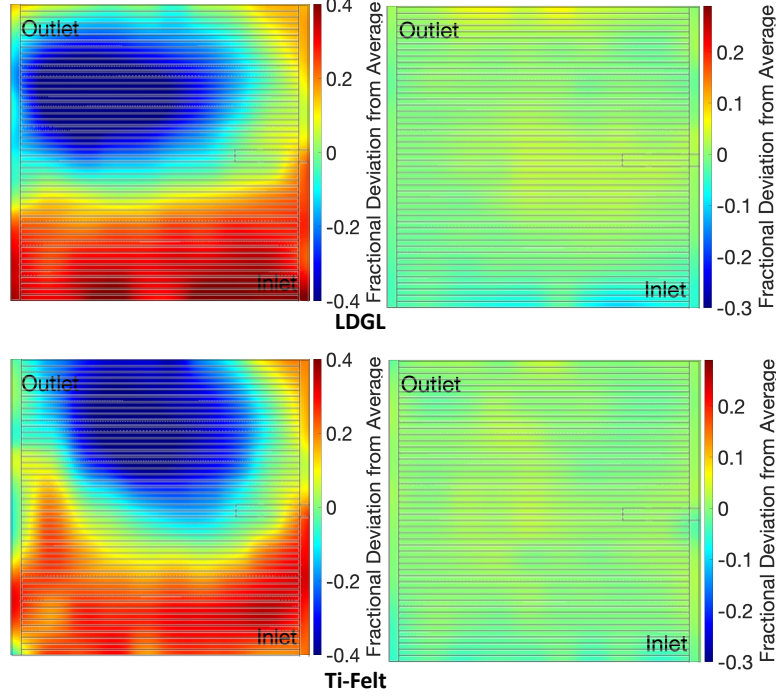
Previous work [Roenning et al., 2022] showed that mass transport limited conditions yielded qualitatively similar current density distributions: gradients with relatively high current towards the inlet and low towards the outlet. Although the contour current distribution plots showed certain dissimilarities, they have been largely qualitatively considered to gauge cell performance and characterize mass transport, as seen in Figure 6.3. By examining the polarization curve, it is evident that there is a significant performance difference (at the lowest flow-rate) between the two configurations (Figure 6.3a), despite having similar current distribution data (as shown in Figure 6.3b). It was observed that the two-phase mass transport limitations (bubble accumulation) were related to the area specific resistance (ASR) of the system (as seen in Figure 6.3a). Locally increased ohmic drop is related to gas-phase accumulation and local dry-out [Immerz et al., 2018a, Immerz et al., 2018b, Weber et al., 2023]. The ASR shows a sharp increase at low flow-rates and higher voltage holds. Since the current distribution measurements give a qualitative sense of bubble accumulation, a quantitative analysis to better characterize the mass transport effects within the electrolyzer was developed.

6.2.1 Effective water transport number: a quantitative analysis of current density distributions

Figure 6.4 shows histograms for four different operating conditions for the thin foil LGDL with the parallel flow-field, each derived from the current density maps (shown inset). The histograms plot bins/intervals (of 0.033) of the fractional deviation from



(a)



(b)

Figure 6.3: PEWE performance for two types of diffusion media (thin foil Ti LGDL and Baseline Ti felt) with a parallel flow-field. **(a)** Polarization curves (solid lines) measured at 6 *ml/min* and 100 *ml/min* along with their corresponding ASR (dashed lines). **(b)** Corresponding CDD maps for 6 *ml/min* (left column) and 100 *ml/min* (right column) recorded at the highest voltage hold of 2.2 *V*. The CDD measurements provides a qualitative sense of bubble accumulation

average current density, and the distribution function is in terms of percentage area. In the absence of mass transport limitations (Figures 6.4a, 6.4b, 6.4d), the observed histograms exhibited normal/gaussian characteristics, with the mean current density accounting for at least 40% of the active area (i.e., very little deviation from the mean). Additionally, these histograms displayed a small standard deviation (~ 0.05), indicating that the current distributions were relatively uniform. As the PEWE transitioned into mass transport limited regions of operation (Figure 6.4c), the histogram flattened out between intervals of -0.5 to 0.5 and the standard deviation increased to 0.217. Since the distribution widened, the percentage of active area occupied for any interval stayed relatively low (below 15%).

To further characterize the nature of mass transport observed within the electrolyzer, an effective water transport number (EWTN) has been defined as the ratio between the observed current density (i) to that of a reference current density (i_{ref}), measured while operating under relatively low mass transport limited conditions, for a given cell configuration. As shown in previous work [Roening et al., 2022], while all other conditions remain constant, an increase in flow-rate alleviated mass transport limitations. Thus, for each voltage hold, i_{ref} was chosen to be the cell average current density measured at the highest flow-rate (4 ml/min/cm^2).

$$EWTN = \frac{i}{i_{ref}} \quad (6.1)$$

The local current densities in the PEWE can be considered as the global mean current density ($\bar{i}$) with some local deviation ($\tilde{i}$) from this average value; this approach was also demonstrated in previous work [Roening et al., 2022]. Hence, the effective water transport number can be rewritten as:

$$EWTN = \frac{\bar{i}}{i_{ref}} \left(1 + \frac{\tilde{i}}{\bar{i}} \right) \quad (6.2)$$

Since the fractional deviation from the mean was defined as the ratio of the $\tilde{i}/\bar{i}$, the effective water transport number essentially acts as a transformation of the current

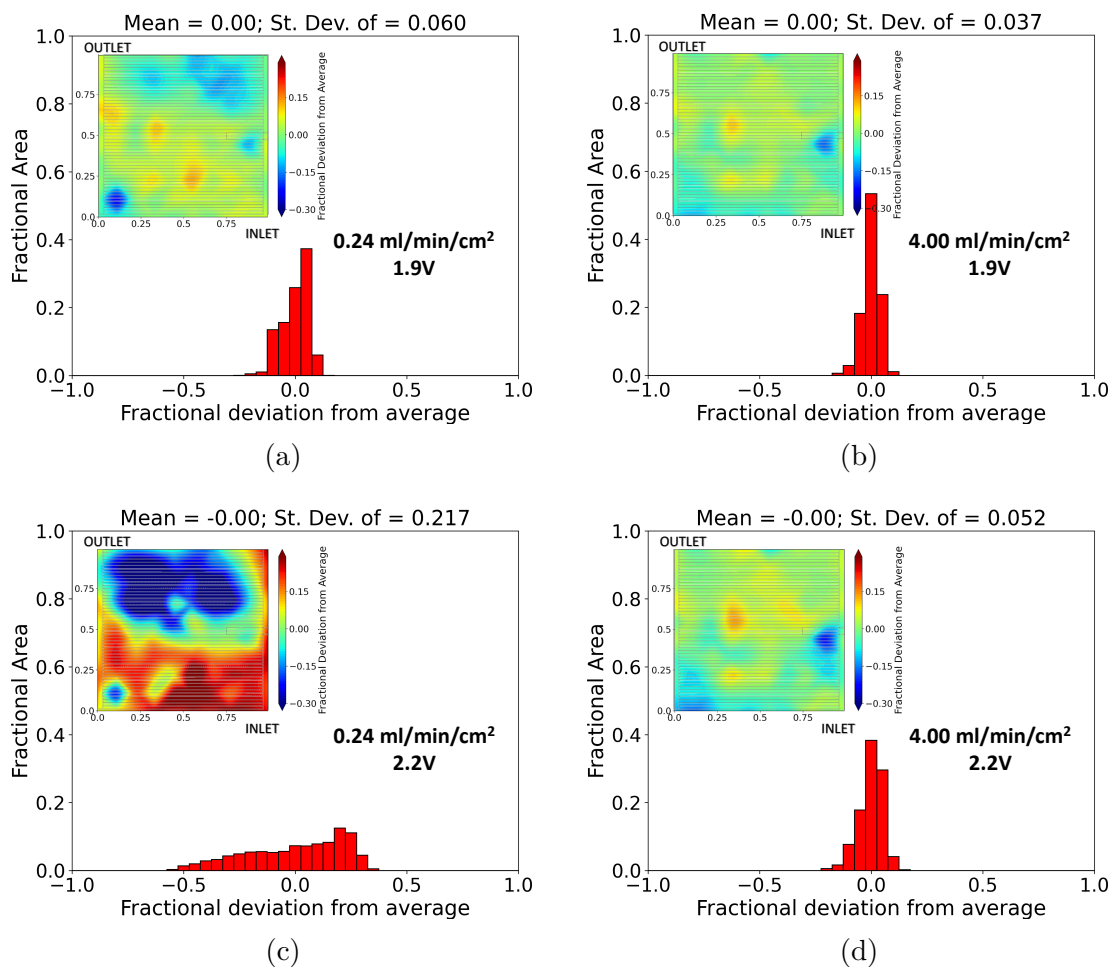


Figure 6.4: Histograms along with corresponding CDD plots as related to fractional active area for the LGDL with the parallel flow-field recorded under four different operating conditions. (a) 0.24 ml/min/cm^2 at 1.9 V (b) 4.0 ml/min/cm^2 at 1.9 V (c) 0.24 ml/min/cm^2 at 2.2 V (d) 4.0 ml/min/cm^2 at 2.2 V

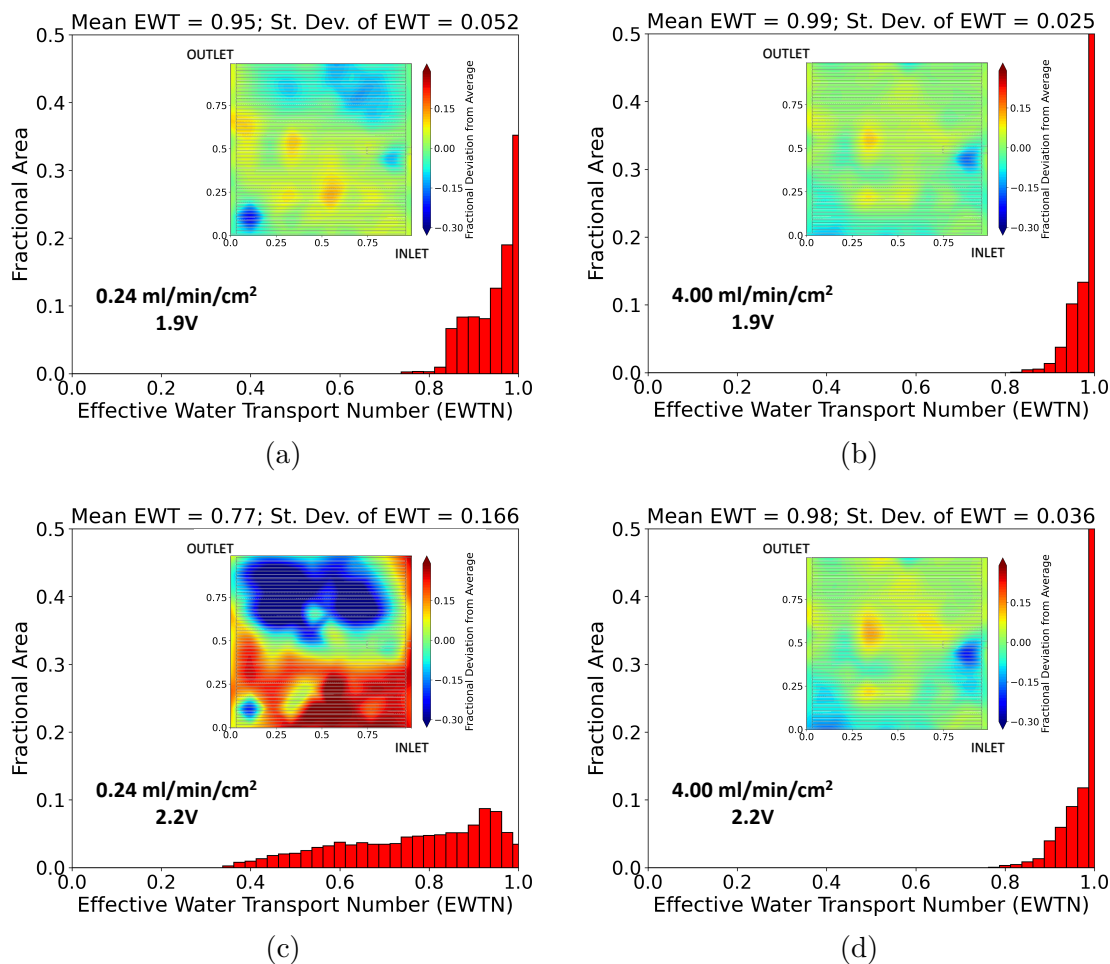


Figure 6.5: Histograms of the Effective Water Transport Number as related to fractional active area, along with corresponding CDD plots for the LGDL with the parallel flow-field recorded under four different operating conditions. (a) 0.24 ml/min/cm² at 1.9 V (b) 4.0 ml/min/cm² at 1.9 V (c) 0.24 ml/min/cm² at 2.2 V (d) 4.0 ml/min/cm² at 2.2 V

distribution that ties together the local performance characteristics of the cell with its polarization curve. Interestingly, the EWTN approaches one as mass transport limitations go to zero since the ratio $\tilde{i}/\bar{i}$ approaches zero and the value of $\bar{i}/i_{ref}$ approaches one. Conversely, as mass transport limitations dominate performance, the ratio of $|\tilde{i}/\bar{i}|$ increases to larger values; however, the value of $\bar{i}/i_{ref}$ approaches zero, thereby bounding the EWTN between 0 and 1.

6.2.2 EWTN-based characterization of mass transport for the parallel flow-field

The polarization curves and their corresponding ASR values are reported in the supplementary information in Figure S8 as part of Appendices. Figure 6.5 presents the EWTN distribution for the LGDL with the parallel flow-field operating at 0.24 $ml/min/cm^2$ and 4 $ml/min/cm^2$ (the complete set of distributions is reported in supplementary Figure S9-S10 as part of Appendices). As anticipated, for higher flow-rates and low voltage holds (Figures 6.5a, 6.5b, 6.5d), the EWTN was close to one for the majority of the active area.

At a voltage of 1.9V and flow-rates of 0.24 and 4 $ml/min/cm^2$, the proportion of active area that exhibits an EWTN above 0.9 is $\sim 70\%$ and $\sim 90\%$, respectively. The corresponding global EWTN (which is the same as the average of the local EWTN) are 0.95 and 0.99, while the EWTN histograms show standard deviations of 0.052 and 0.025 respectively. At a voltage hold of 2.3V and a high flow-rate of 2 $ml/min/cm^2$ (as seen in Figure. 6.5d), the absence of mass transport limitations results in an EWTN distribution resembling that shown in Figure 6.5a and 6.5b, with a mean of 0.98 and a standard deviation of 0.036. However, at the low flow-rate of 0.24 $ml/min/cm^2$ and 2.3V voltage hold (Fig. 6.5c), the EWTN decreases, indicating a greater degree of mass transport limitation. The mean EWTN value is 0.77, with a standard deviation of 0.166, which exceeds the values observed in Figures 6.5a, 6.5b and 6.5d. It is noteworthy from the histogram in Figure 6.5c that the majority of

the active area experiences transport limitations and bubble accumulation as $>60\%$ of the distribution is below an EWTN of 0.9. It has also been shown that these distributions are impartial to changing the direction of flow (refer to Figure S11 in supplementary information as part of Appendices).

It is noteworthy that the overall shape of the histograms remained similar to that in Fig. 6.4, though the EWTN values were transformed and scaled. Additionally, the mean value corresponded to that of the global EWTN. Therefore, the observations made for Fig. 6.4 also applies for Fig. 6.5. It is evident that this new analysis gives a quantitative representation of the percentage of active area experiencing relative mass transport limitation. This provides the opportunity to further investigate and attempt to relate mass transport to other outcomes of interest such as durability, impact of bubble accumulation, operating parameters, and materials used.

6.2.3 New and improved flow-field design for LGDLs

In previous work [Roening et al., 2022], it was demonstrated that the performance of the PEWE utilizing a micro-patterned Ti-Foil LGDLs was highly reliant on the cell architecture and exhibited poor mass transport behavior using conventional channel-based (e.g. parallel) flow-fields. While higher feedwater flow-rates can alleviate mass transport limitations, this may not be feasible in industrial-scale systems due to increased parasitic losses. When compared with conventional PTLs, the LGDLs' lack of in-plane permeability resulted in a more rapid onset of mass transport limitations at lower flow-rates, increased ASR, and poor utilization of the total potential active area of the catalyst. To mitigate these problems, a unitized single flow-field/LGDL component with flow-field optimized for the LGDL design pattern was conceived [Zhang et al., 2023].

Figure 6.6 depicts the polarization curves for the pin-type flow-field with varying flow-rates (0.24 ml/min/cm^2 to 4 ml/min/cm^2) using the thin foil LGDL. The corresponding CDD maps and EWTN histograms are shown in Figure 6.6b-6.6d

(the complete set of distributions is reported in supplementary Figure S12 as part of Appendices). Similar to the behavior observed in the parallel flow-field, the polarization curve for the pin-type flow-field exhibits non-linearity at higher voltage holds for lower flow-rates. Furthermore, a gradient from the inlet to the outlet is still present in the local CDD maps. To further analyze the differences in performance, the EWTN is used. Figure 6.6 shows how, with the same voltage hold of 2.3V, the EWTN shifts from 0.87 at 0.24 ml/min/cm^2 to 0.99 at 4 ml/min/cm^2 and the standard deviation decreases from 0.071 to 0.030 with increasing flow-rate. Additionally, the ASR also demonstrates a similar pattern to that observed for the parallel flow-field. With larger flow-rates, the ASR exhibits a more uniform behavior. However for lower flow-rates, bubble accumulation near the outlet results in local membrane dry-out (as demonstrated by Immerz, et al. [Immerz et al., 2018a, Immerz et al., 2018b]), which manifests as an exponential increase in the ASR towards higher voltage holds. This further leads to limitations in mass transport. The local regions of low CDD corresponding with lower EWTN (in Figure 6.6b), may experience similar dry-out which causes the overall ASR to increase. Therefore, it can be assumed that the low current density region near the outlet is a result of gas accumulation in the region. This hypothesis is further supported by the fact that increasing the feed water flow-rate improves performance through enhanced bubble removal.

Figure 6.7a shows the polarization data comparing the performance of the pin-type with the parallel flow-field at flow-rates of 0.24 ml/min/cm^2 and 4 ml/min/cm^2 . It is evident that the pin type flow-field outperformed the parallel flow-field at lowest flow-rate and maintained similar performance at the highest flow-rates. Furthermore, the parallel flow-field recorded $\sim 25 \text{ m}\Omega\text{-cm}^2$ less ASR when operated at 4 ml/min/cm^2 . This difference was expected, and arises from the poor interfacial contact of the pins with the LDGL. Integrating the LGDL into a single unitized component is expected to reduce interfacial contact resistances and enhance cell performance. However, the maximum recorded ASR at the lowest flow-rate was considerably lower ($\sim 30 \text{ m}\Omega\text{-cm}^2$) for the pin-type flow-field when compared to the parallel flow-field, indicating that

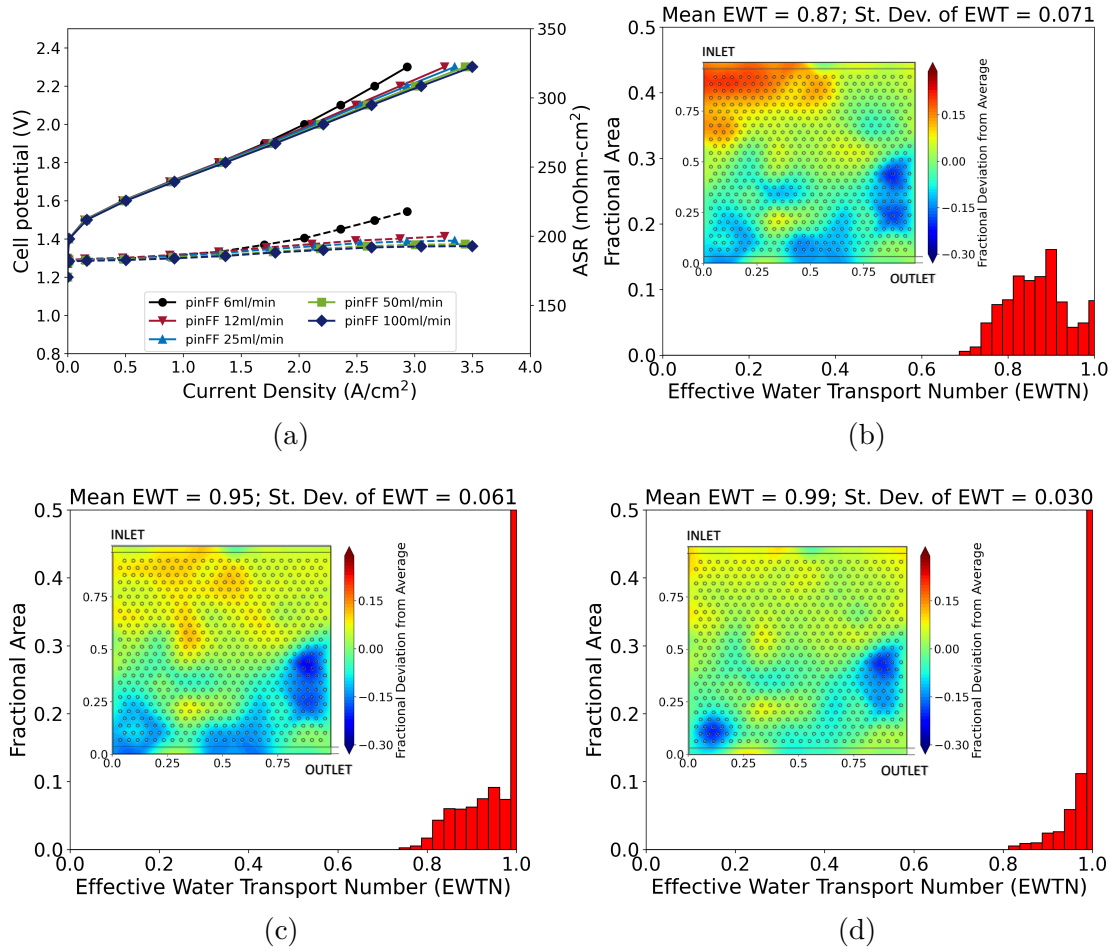
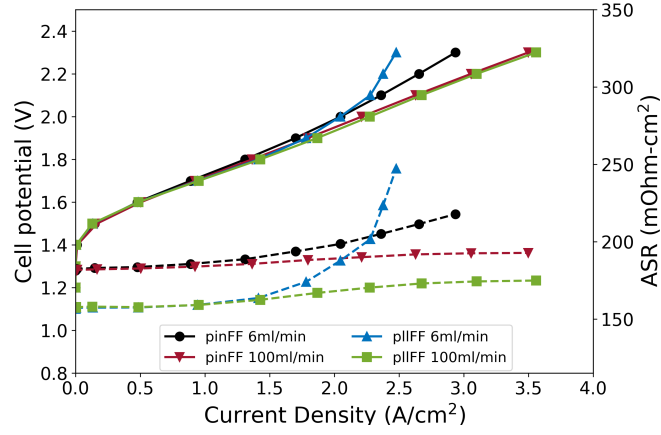
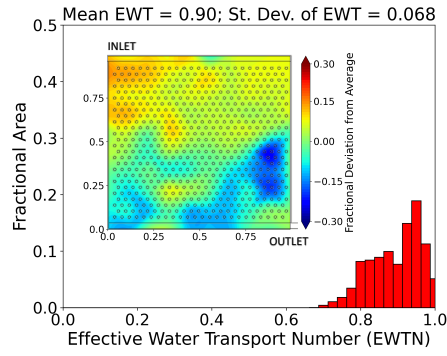


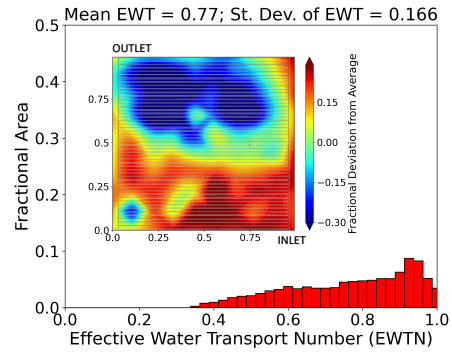
Figure 6.6: PEWE performance for using the LGDL with the pin-type flow-field: **(a)** Polarization curves (solid lines) measured at 0.24 ml/min/cm^2 , 0.48 ml/min/cm^2 , 1.0 ml/min/cm^2 , 2.0 ml/min/cm^2 and 4.0 ml/min/cm^2 along with their respective ASR (dashed lines). Corresponding histograms of the EWTN as related to fractional active area, along with the CDD plots (shown in inset) at 2.2 V under three different flow-rates: **(b)** 0.24 ml/min/cm^2 **(c)** 0.48 ml/min/cm^2 **(d)** 4.0 ml/min/cm^2



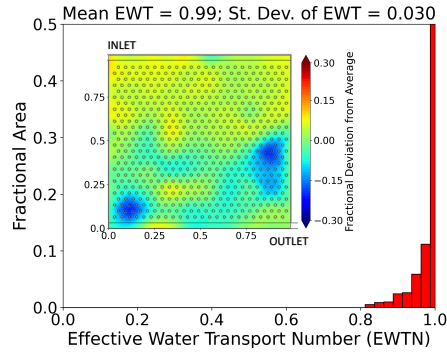
(a)



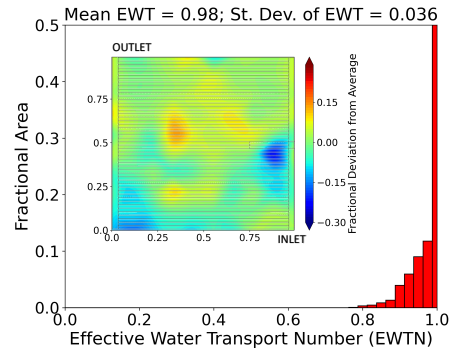
(b)



(c)



(d)



(e)

Figure 6.7: PEWE performance comparison between pin type flow-field and parallel flow-field paired with the LGDL: (a) Polarization curves (solid lines) measured at 0.24 ml/min/cm^2 and 4.0 ml/min/cm^2 along with their respective ASR (dashed lines). Histograms of the EWTN along with the CDD plots (shown in inset) recorded at 2.2 V for: (b) pin-type flow-field operating at 0.24 ml/min/cm^2 , (c) parallel flow-field operating at 0.24 ml/min/cm^2 , (d) pin-type flow-field operating at 4.0 ml/min/cm^2 , (e) parallel flow-field operating at 4.0 ml/min/cm^2

the design enabled more effective bubble removal and reduced local membrane dry-out.

Figures 6.7b, 6.7d and 6.7c, 6.7e shows the CDD map and the local EWTN distribution for the pin type and parallel flow-fields, respectively. Comparing the EWTN histograms for the operating flow-rate of 0.24 ml/min/cm^2 , it is evident that the pin type flow-field (Figure 6.7b) had better area utilization as indicated by 80% of its fractional area distribution being above an EWTN of 0.8; whereas, only $\sim 50\%$ of the active area for the parallel flow-field sustained an EWTN greater than 0.8 (Figure 6.7c). The average or global EWTN for the pin-type flow-field was 0.9 with a standard deviation of 0.068 while parallel flow-field had an EWTN distribution of 0.77 mean with 0.166 standard deviation. The experimental results for the pin flow-field showed a consistent 15-20% improvement in current density at the highest voltage hold (of 2.2V) operating at flow-rates of 0.24 ml/min/cm^2 for all experimental runs. Although, the PEWE performance at 4.00 ml/min/cm^2 using both flow-fields was similar (as seen in Figure 6.7a), the pin-type flow-field had a slightly higher mean EWTN (0.99) than the parallel flow-field (0.98), as shown in Figure 6.7d and 6.7e. The pin-type flow-field also had a lower standard deviation of EWTN, indicating that it facilitated more uniform water transport to the catalyst layer at the highest flow-rate. Table 6.1 summarizes the performance improvements achieved using the pin-type flow-field; while Table 6.2 summarizes the EWTNs for the pin and parallel architectures.

The pin architecture is specifically designed to overcome the challenges associated with mass transport limitations with a LGDL, especially at low stoichiometries (flow-rates). By managing bubbles more effectively, this design reduces the likelihood of local dry-out of the membrane and mitigates the resulting increase in ASR that is typically observed under mass transport limited conditions. As shown in Figure 6.8, the percent change in ASR (normalized with respect to the ASR measured at OCV) as a function of current density for two different flow-rates are compared for both the pin and parallel flow-fields. Figure 6.8 shows that the parallel flow-field exhibits a

greater increase in ASR compared to the pin-type. The maximum percentage change in ASR recorded (at the maximum current density) was 57.9% for the parallel whereas 20.1% for the pin. Interestingly, the experiments have consistently shown that the parallel flow-field continues to exhibit a higher increase in percentage ASR (11.1% vs. 6.8%) compared to the pin flow-field, even at higher flow-rates. This observation is attributed to the greater shadowing of the pores of the LGDL by the parallel flow-field lands. A detailed discussion is provided in supplementary information as part of Appendices. Therefore, the pin architecture can significantly improve membrane hydration, leading to better overall performance and presumably increased durability of the membrane by decreasing local moisture gradients.

6.3 Conclusions

Current density distribution measurements are known to be a useful tool for investigating in-situ performance for PEWEs and other electrochemical systems. However, their semi-quantitative nature limits their effectiveness in investigating mass transport in PEWEs. To address this, an effective water transport number has been proposed in this study to quantify CDD measurements and provide a clear indication of performance. The EWTN scale, ranging from 0 to 1, signifies varying degrees of water transport to the catalyst coated membrane. Values surpassing 0.95 are indicative of exceptional mass transport characteristics, while the range of 0.8 to 0.95 denotes a transitional region. Mass transport effectiveness is considered poor within the range of 0.6 to 0.8, and values falling below 0.6 indicate a critically deficient level of mass transport. Results showed that higher flow-rates have EWTN values of 0.95 and above, indicating no significant mass transport limitations, while lower flow-rates with large gradient CDD maps have EWTN values between 0.6-0.8, indicating mass transport limited conditions. Standard deviations for mass transport limited conditions ranged between 0.1-0.2, while those for higher flow-rates were less than 0.05. This work also identified a direct correlation between ohmic overpotentials

Table 6.1: Performance measured and improvement calculated for the two flow-fields

Flow-rate ($ml/min/cm^2$)	Current (A/cm^2) @ 2.2V		% improvement
	PlIFF	PinFF	
0.24	2.38	2.69	13.29
4.00	3.10	3.09	-

Table 6.2: Recorded EWTN values for the two flow-fields at 2.2V

Flow-rate ($ml/min/cm^2$)	EWTN @ 2.2V			
	PlIFF		PinFF	
	mean	St. dev.	mean	St. dev.
0.24	0.77	0.166	0.9	0.068
4.00	0.98	0.036	0.99	0.030

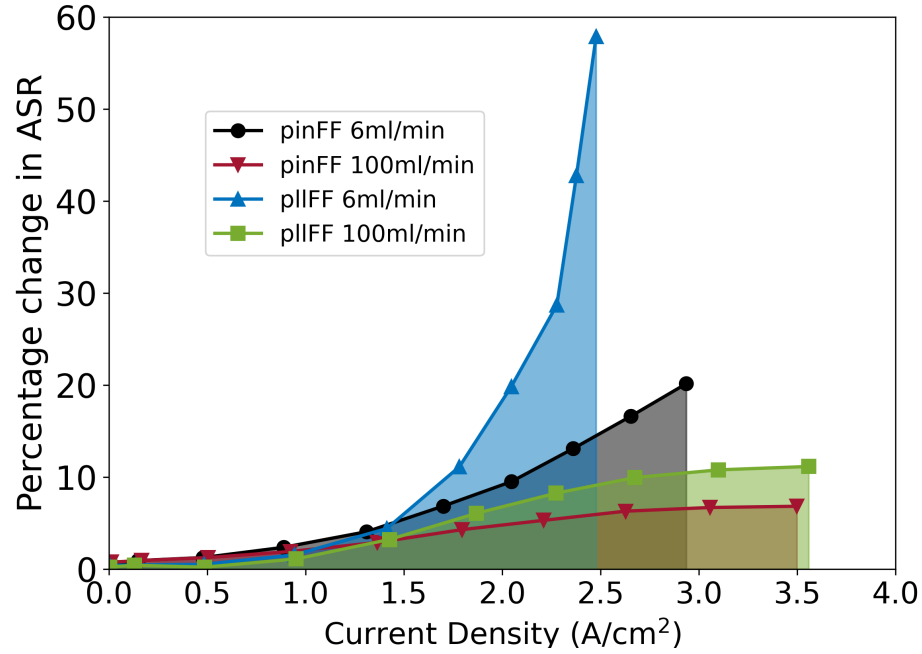


Figure 6.8: Relative change in ASR of the PEWE as a function of current density using the LGDL paired with the parallel and pin-type flow-fields at different flow-rates

and mass transport losses due to bubble accumulation and membrane hydration. Additionally, this study led to the development of a unitized pin-type LGDL/flow-field design which improves mass transport of the gas phase within a PEWE. This design more effectively removed bubbles enhancing low flow-rate performance, as demonstrated by higher overall EWTN values with lower standard deviations for the pin-type architecture. Compared to the parallel flow-field, this design demonstrated a lower percentage change in ASR values (20.1% vs. 57.9%) during high-current-density operations.

The analysis provided in this work not only offers an opportunity to explore and establish connections between mass transport and the outcomes of various critical aspects, including durability, impact of bubble accumulation, and operating parameters. It also provides a framework to further develop state-of-the-art materials and architecture/components for such systems.

Chapter 7

Combining distributed electrochemical measurements with a semi-empirical model to identify local variations in overpotentials for PEM water electrolyzers

This chapter is revised based on the manuscript submitted to the Joule (cell Press) to be considered for publication under the same name as the title of this chapter. If published the authorship would be attributed to:

Anirban Roy, Frida H. Roenning, Douglas S. Aaron, Feng-Yuan Zhang, and Matthew M. Mench.

My contributions to this work spanned across conceptualization of the idea, methodology development, validation procedures, formal data analysis, extensive investigative work and data collection, original draft composition, and the creation of visual representations. Other authors assisted with data curation, review and editing of the manuscript.

Developing gigawatt-scale PEWEs requires electrodes that are high performing, cost-efficient and durable [Yu et al., 2022, Kang et al., 2018]. Key cost drivers include the use of platinum group metals (PGM), such as iridium, for catalyzing the oxygen evolution reaction (OER) [Yuan et al., 2022], and titanium-based porous transport layers (PTL) [Schuler et al., 2020b]. Reducing the use of these materials while increasing power density would significantly lower capital costs. Therefore, recent research has aimed to reduce expensive PGM catalyst loadings by 80-90% from the current standard of 1 mg/cm^2 [Hegge et al., 2020] to enhance the large-scale adoption of PEWEs. In the electrolysis cell, the anode PTL is particularly critical for enabling the use of thin electrolyte membranes and low noble metal catalyst layer (CL) loadings, required for future systems to reduce capital and operational costs. The PTL, which is primarily made of Titanium, is responsible for conducting heat and electrons from the anode catalyst layer, facilitating multi-phase (liquid water/oxygen gas) transport, and providing mechanical support to the catalyst-coated membrane (CCM). The ideal PTL maximizes the contact surface between PTL and the anode CL without sacrificing any transport properties.

Therefore, to achieve the highest catalyst utilization with enhanced mass transport characteristics through the anodic PTL, F.Y. Zhang and co-workers [Kang et al., 2017, Wang et al., 2021b, Yang et al., 2021, Wang et al., 2021a] have developed a thin-foil titanium liquid-gas-diffusion-layer (LGDL). However, optimization of such advanced materials alone are not sufficient for achieving high performance and durability in PEWEs. Their performance is significantly affected by system architecture and operating conditions. Hence, understanding the complexities of various overpotentials within PEWEs is crucial for optimizing their performance and efficiency [Roenning et al., 2022]. The aim is to achieve a highly uniform reaction rate across the entire active surface area of the electrodes with minimal sensitivity to variations in operating conditions. Hence, considering a specific combination of materials and operating parameters, meticulous system design is necessary to maximize efficiency [Roy et al., 2024].

Additionally, durability in PEM water electrolysis is a paramount concern, especially as lower anode loadings are associated with higher degradation rates. For instance, reducing the Iridium loading without altering the catalyst composition results in a thinner CL [Bernt et al., 2018]. This creates a challenging scenario for the in-plane electrical network of the catalyst layer, leading to inactive sections within the anode CL. These inactive sections may manifest as isolated catalyst "islands" or regions with high resistance due to thin conduction pathways or distant catalyst sites far from the triple-phase contacts [Higashi and Beniya, 2023, Bernt et al., 2020].

Reports [Feng et al., 2017, Kuhnert et al., 2023] also indicate that the degradation mechanisms in PEM water electrolyzers are primarily dominated by irreversible efficiency losses. Although reversible degradation in these systems are also present, they are not fully understood [Feng et al., 2017]. Catalyst degradation can be manifested through changes in the electrochemical surface area (ESCA) or the activity of the catalyst. For instance, catalyst dissolution can lead to a rougher surface structure with more active sites, initially maintaining activity but eventually leading to layer damage and catalyst detachment if dissolution and re-deposition occur continuously [Feng et al., 2017]. High voltage operation conditions contribute to performance degradation and material deterioration, challenging the long-term durability of PEM water electrolyzers [Kuhnert et al., 2023]. Moreover, the harsh operating conditions inside a PEWE contribute to catalyst layer degradation through dissolution, migration, agglomeration, detachment, and support passivation [Spöri et al., 2017]. The instability of the membrane and porous transport layers further exacerbates the degradation of both anode and cathode CLs during long-term operation.

This study focuses on investigating the contribution of different overpotential categories and their spatial variations through in-situ analysis. This provides crucial insights that can help understand and mitigate issues caused by non-uniformity in reactions within PEWEs. Employing a segmented cell and printed circuit board (PCB) approach [Roening et al., 2022, Roy et al., 2024], current density

distribution (CDD) and distributed area-specific resistance (DASR) measurements are obtained. A breakdown analysis of the various overpotentials and their spatial variations is also provided by applying a semi-empirical zero-dimensional model to analyze the experimental data.

Through this work, a thorough investigation into the complex nature of two-phase mass transport occurring inside a PEM water electrolyzer is explored. Understanding and optimizing mass-transport phenomena and managing bubble accumulation are critical for enhancing the performance and longevity for PEWEs. Typically, in the fuel cell community, modeling mass transport limitations is thought of as diffusion-limited transport [Weber et al., 2014]. However, for water electrolyzers, oxygen accumulation (i.e. product transport limitation) in the anode PTL is seen to cause membrane dry-out and an increase in the area-specific resistance (ASR) [Immerz et al., 2018a, Immerz et al., 2018b]. The experimental results from this work elucidate the intricate relationship between ohmic and mass transport losses, emphasizing the deep coupling induced by the two-phase nature of the system. The results shown here suggest that, as mass transport limitation grows, the highest increase in overpotential comes from mass transport-coupled ohmic losses. Beyond conventional diffusion limited mass transport losses, bubble dynamics significantly impact local hydration and ASR, highlighting the need for a holistic approach in device optimization.

7.1 Methodology

7.1.1 Experimental setup

The experimental PEWE test bench used in this work is illustrated in Figure 7.1. The PEWE setup includes compression plates, current collectors, a catalyst-coated membrane, anode and cathode porous transport layers along with gaskets, flow plates, and a PCB, as depicted in Figure 7.1a. In this study a thin titanium foil LGDL, developed by Dr. F. Y. Zhang’s group at UTK [Wang et al., 2021b,

Yang et al., 2021, Wang et al., 2023], was used. The thickness of the LGDL was $50\text{ }\mu\text{m}$ and it had circular pores measuring $50\text{--}80\text{ }\mu\text{m}$ in diameter arranged in a hexagonal close-packed pattern, as depicted in Figure 7.1b. For comparison, a baseline titanium felt purchased from the Fuel Cell Store (reference in [Fuel-Cell-Store, 2024]) was used, also shown in Figure 7.1b. Consistent with previous studies [Roening et al., 2022, Roy et al., 2024], both anode PTLs were coated with iridium to enhance electrical contact and reduce ohmic losses. TorayTM carbon paper (TGP120) was used as the cathode-side PTL. The catalyst-coated membranes (Aquivion E98-09S), with a thickness of $90\mu\text{m} \pm 20\mu\text{m}$, were also obtained from the Fuel Cell Store. The catalysts had a loading of 2.0 mg/cm^2 *Ir – black* on the anode side and 0.8 mg/cm^2 *Pt* on the cathode. To ensure reliability, experiments were conducted with at least three sets of materials for each configuration and operating condition.

Electrochemical characterization such as polarization curves and in-situ CDD and DASR measurements were carried out at varying flow-rates, ranging from 0.24 ml/min/cm^2 to 4 ml/min/cm^2 . The experimental cell was compressed using a bolt torque of $5\text{ N} - \text{m}$ (as explained in previous works [Roening et al., 2022, Roy et al., 2024]), and the cell was maintained under isothermal conditions at 80°C (unless specified otherwise). Fig. 7.1d shows a diagram of the hydraulic and the electronic control circuit for the test system. The feedwater bath, part of a closed system PID control circuit, delivered water at the set water temperature, which was monitored by a thermocouple near the anode inlet. Heat exchangers that were integrated into the compression plates, was also used to maintain the cell under isothermal conditions. Pressure was monitored at both the inlet and outlet of the anode feedwater line. On the hydrogen side, a pressure relief valve and a pressure controller maintained an exit pressure of 1 atm for all experiments.

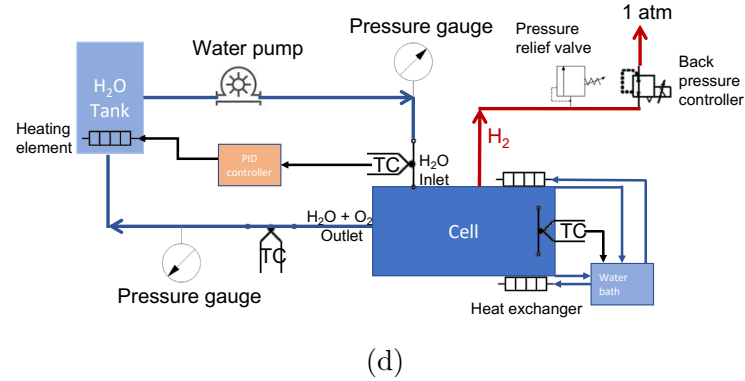
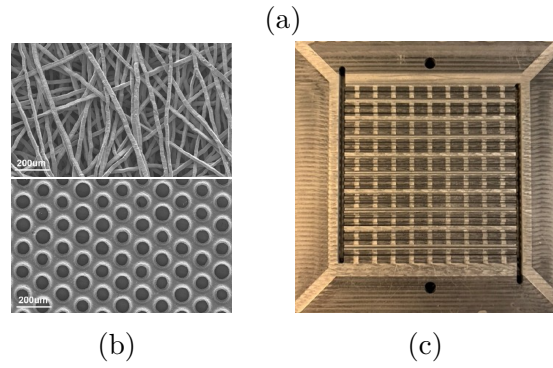
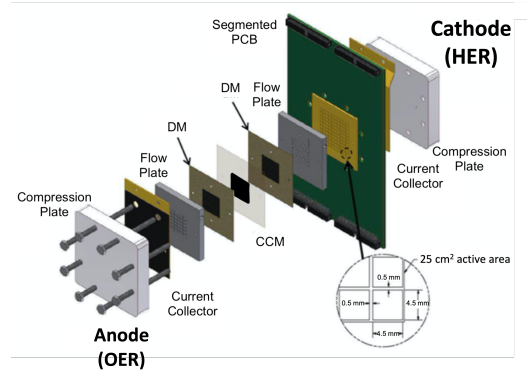


Figure 7.1: Description of PEWE test system. (a) Current distribution setup. (b) The two types of PTLs, baseline titanium felt PTL and thin foil titanium LGDL. (c) Image of a segmented parallel flow-field. (d) Schematic of the test system. (Figures adapted from [Roy et al., 2024])

7.1.2 Polarization curves, EIS and CDD measurements

All cells were potentiostatically controlled from 1.2 V to 2.2 V in 0.1 V increments, with corresponding current density recorded at each steady-state voltage step. The polarization data were averaged and the maximum error was calculated to be approximately $\sim 3\%$, based on at least three sets of materials tested for each cell configuration and operating condition. The highest errors were noted for the most extreme operating conditions (flow-rate of 0.24 ml/min/cm^2 and voltage holds above 2.1 V).

While a multichannel Biologic (Seyssinet-Pariset, France) VSP potentiostat with a VMP3B-100 booster was used for global polarization curve measurements; a National InstrumentsTM data acquisition system with a custom LabVIEW program collected real time data from the PCB for local in-situ measurements. Distributed current data for each segment was collected every 0.2 seconds and averaged over the final 30 seconds of each step. Further details of the working principle of the CDD can be found in previous work [Roening et al., 2022, Roy et al., 2024]. Averaged data are presented as local CDD normalized as fractional deviation from the average (detailed discussion can be found in previous work [Roening et al., 2022]).

Electrochemical impedance spectroscopy (EIS) measurements were also performed using the Biologic potentiostat spanning a frequency range of $2\text{kHz} - 1\text{Hz}$ with an applied voltage perturbation of 10mV . The area specific resistance (ASR) was determined as the intercept of the Nyquist plot at the real axis at high frequencies ($\sim 1\text{kHz}$). It should be noted that the measured ASR is about $50 \text{ m}\Omega - \text{cm}^2$ higher than that of a regular PEWE without the CDD peripherals, as reported in our previous works [Roening et al., 2022, Roy et al., 2024].

7.1.3 Distributed area specific resistance

The distributed area specific resistance measurements were carried out in tandem with the CDD measurements using the same National InstrumentsTM data acquisition

system. A single sinusoidal frequency of ($1kHz$) alternating voltage along with the DC polarization was applied to the system using the potentiostat, such that the AC perturbation amplitude was $10mV$ for optimal signal-to-noise ratio. Each segment in the PCB was equipped with a shunt resistor connected in series, allowing the current flowing through a segment to be determined by measuring the potential drop across the resistor. Since all 100 segments were connected in parallel, a global AC perturbation facilitated local EIS measurements. The built-in frequency analyzer for the data acquisition system was able to isolate the gain or amplitude of the current passing through each segment at the specified frequency, which was then used to calculate the impedance of the individual segments.

The frequency response analyzer built into this data acquisition system was unable to resolve the phase shift in the impedance data. Consequently, the current hardware limitations prevent recording a full spectrum EIS. Therefore, the DASR data presented in this work assumes that for a high-frequency EIS measurement at $1kHz$, the phase shift is negligible (i.e. less than 3 degrees as recorded globally) and is the same for all segments; making the impedance magnitude approximately equal to its real component.

To verify the accuracy of the distributed ASR measurements, the equivalent resistance of the circuit was calculated using the parallel resistor rule. This calculated resistance matched the recorded global ASR for the PEWE within a 8% error margin. The observed error may arise from factors such as loose connections or faulty segments that fail to record data accurately.

7.1.4 0D semi-empirical model

Using a zero-dimensional (0D) semi-empirical model, the total cell overpotential can be deconvoluted into its major components. There are three primary categories of overpotentials: kinetic, ohmic and diffusion limited mass transport losses in PEWEs,

and together with the open circuit potential they sum up to the overall cell operating potential [Falcão and Pinto, 2020],

$$V = E_{OCP} + \eta_{act} + \eta_{Ohm} + \eta_{diff} \quad (7.1)$$

E_{OCP} is the open circuit potential and was calculated using the Nernst equation [Falcão and Pinto, 2020, Han et al., 2017] as follows,

$$E_{OCP} = E_0 + \frac{RT}{2F} \ln \left(\frac{\alpha_{H_2} \alpha_{O_2}^{0.5}}{\alpha_{H_2O}} \right) \quad (7.2)$$

where R is the universal gas constant, T is the operating temperature (in Kelvin) and F is Faraday constant. The reversible potential E_0 was calculated using a temperature dependent expression [Han et al., 2017].

$$E_0 = 1.229 - 0.9 \times 10^{-3}(T - 298.15) \quad (7.3)$$

In Eq. 7.1 η_{act} represents the overall activation overpotential, which includes contributions from both the cathodic and anodic kinetics. Since a reference electrode was not used in the experiments to separate the contributions from the anode and cathode catalyst layers, the overall kinetics of the cell are considered as a whole. The Butler-Volmer equation is commonly used to calculate activation overpotentials. However, under the simplified assumptions that only the oxidation reaction occurs at the anode with negligible contribution from the cathode, the overall activation overpotential can be approximated using the Tafel equation [Mench, 2008],

$$\eta_{act} = \mathbf{b} \log_{10} \left(\frac{i}{i_0} \right) \quad (7.4)$$

where, i is the measured current density and the parameters $\mathbf{b}$ is the Tafel slope and i_0 the exchange current density. These kinetic parameters were estimated by curve-fitting the model to the iR-free polarization curves.

In Eq.7.1 the η_{Ohm} is the ohmic overpotential that accounts for the ionic and electronic resistance within the cell. This follows Ohm's law and was calculated as,

$$\eta_{Ohm} = i \times ASR \quad (7.5)$$

The electronic resistance primarily occurs at the interface contacts between layers, while the main source of ionic resistance is the membrane. The conductivity of the ionomer is highly dependent on temperature and hydration, and bubble accumulation can affect this conductivity, creating a strong correlation with the nature of mass transport within a PEWE. This relationship has been demonstrated in previous studies [Roy et al., 2024, Immerz et al., 2018a, Immerz et al., 2018b].

Therefore in this work, the ohmic overpotential was separated into two components: a background ohmic overpotential $\eta_{Ohm,b}$, calculated from the background resistances (ASR_0) measured as the average ASR during the first four voltage holds (1.2V - 1.5V), and a mass transport coupled ohmic overpotential $\eta_{Ohm,mt}$, calculated from the difference between the resistance measured at higher voltage hold and the background resistance (see Eqs.7.6-7.8).

$$\eta_{Ohm} = \eta_{Ohm,b} + \eta_{Ohm,mt} \quad (7.6)$$

$$\eta_{Ohm,b} = i \times ASR_0 \quad (7.7)$$

$$\eta_{Ohm,mt} = i \times (ASR - ASR_0) \quad (7.8)$$

Finally, η_{diff} is the diffusion overpotential, which arises when the reaction rate is limited by the transport of reactants to the catalyst layer and the removal of products away from the catalyst layer. This is commonly modeled with respect to a limiting current density (i_{lim}) [Han et al., 2017] as,

$$\eta_{diff} = -\frac{RT}{2F} \ln \left(1 - \frac{i}{i_{lim}} \right) \quad (7.9)$$

However, previous experimental studies [Suermann et al., 2016, Schuler et al., 2020a] have shown that the diffusion overpotentials in PEWEs do not follow a such a logarithmic relationship. This discrepancy is an active area of research and is suspected to be due to changes in catalyst layer resistance [Wrubel et al., 2021, Padgett et al., 2023, Weber et al., 2023]. Therefore, in this analysis, the mass transport losses are isolated according to Eq.7.10, which models η_{diff} by subtracting the kinetic and ohmic overpotentials from the total overpotential.

$$\eta_{diff} = V - (E_{OCP} + \eta_{act} + [\eta_{Ohm,b} + \eta_{Ohm,mt}]) \quad (7.10)$$

7.2 Results and discussion

The performance of a PEWE using a parallel flow-field is known to be sensitive to the variation in feedwater flow-rate, as demonstrated by our previous studies [Roening et al., 2022, Roy et al., 2024]. Figure 7.2a-b compares the polarization curves measured using both the baseline PTL and the thin foil LGDL. It is evident that the baseline PTLs exhibit lower sensitivity to variations in anode feedwater flow-rates when compared to the LGDL. Higher current densities were recorded at higher voltage holds when the anode feedwater flow-rate was set at $0.24\text{ml}/\text{min}/\text{cm}^2$ using the baseline PTL.

Additionally, the ASR measured for PEWEs using both baseline PTLs and LGDLs increases at high current density operations (i.e. high rates of gas evolution). This rise in ASR is significantly affected by changes in anode feedwater flow-rate. The sensitivity of ASR to flow-rate variations indicates local dehydration. The thin foil LGDL, lacking in-plane water transport, is more susceptible to ionomer dry-out beneath the flow-field lands. Interestingly, the LGDL, being thin and having high through-plane conductivity, exhibited a lower background ASR compared to the baseline PTL, as shown in Table 7.1.

7.2.1 Estimating overpotentials using 0D semi-empirical model

Using Eq.7.2, the open-circuit-potential for each polarization curve experiment was estimated and is listed in Table 7.2. The E_{OCP} was subtracted from the PEWE operating potential to calculate the total overpotential (i.e. polarization).

To estimate the kinetic parameters, the iR-free polarization curves were constructed by removing the total ohmic contributions (calculated using Eq.7.5) from the total overpotentials and plotted on a semi-logarithmic plot as shown in Figure 7.2c-d. The Tafel slope and exchange current density were then estimated using linear regression based on Eq.7.4. The regression lines were fitted for data points between a current density of $10mA/cm^2$ and $500mA/cm^2$ assuming this range represents the kinetically dominated region for all measurements [Suermann et al., 2016].

The Tafel slopes obtained from the experiments ranged from $60mV/dec$ to $65mV/dec$, aligning well with the values reported in the literature for Iridium catalysts in acidic media up to $80^{\circ}C$ [Suermann et al., 2016, Schuler et al., 2020a]. The diffusion media had little to no effect on the Tafel slope (as seen in Figure 7.2e) as expected; since the CCMs used for all cells were cut from the same batch of materials.

However, morphological interactions between the diffusion media and the catalyst layer interface are known to affect kinetic parameters. The calculated exchange current density showed appreciable differences. The oxygen evolution reaction and hydrogen evolution reaction at the catalyst layers favor sites closer to triple-phase contacts, minimizing in-plane resistance [Mo et al., 2016] and maximizing transport [Weber et al., 2023]. The lower exchange current density recorded for the baseline PTL, as shown in Figure 7.2f, may indicate fewer triple-phase boundaries at the PTL/CL interface compared to the LGDL [Kulkarni et al., 2022].

To gain deeper insights into the experimental results, the zero-dimensional (0D) semi-empirical model (as discussed in section 7.1.4) was applied to the experimental data to perform a breakdown analysis of overpotentials. It can be observed from

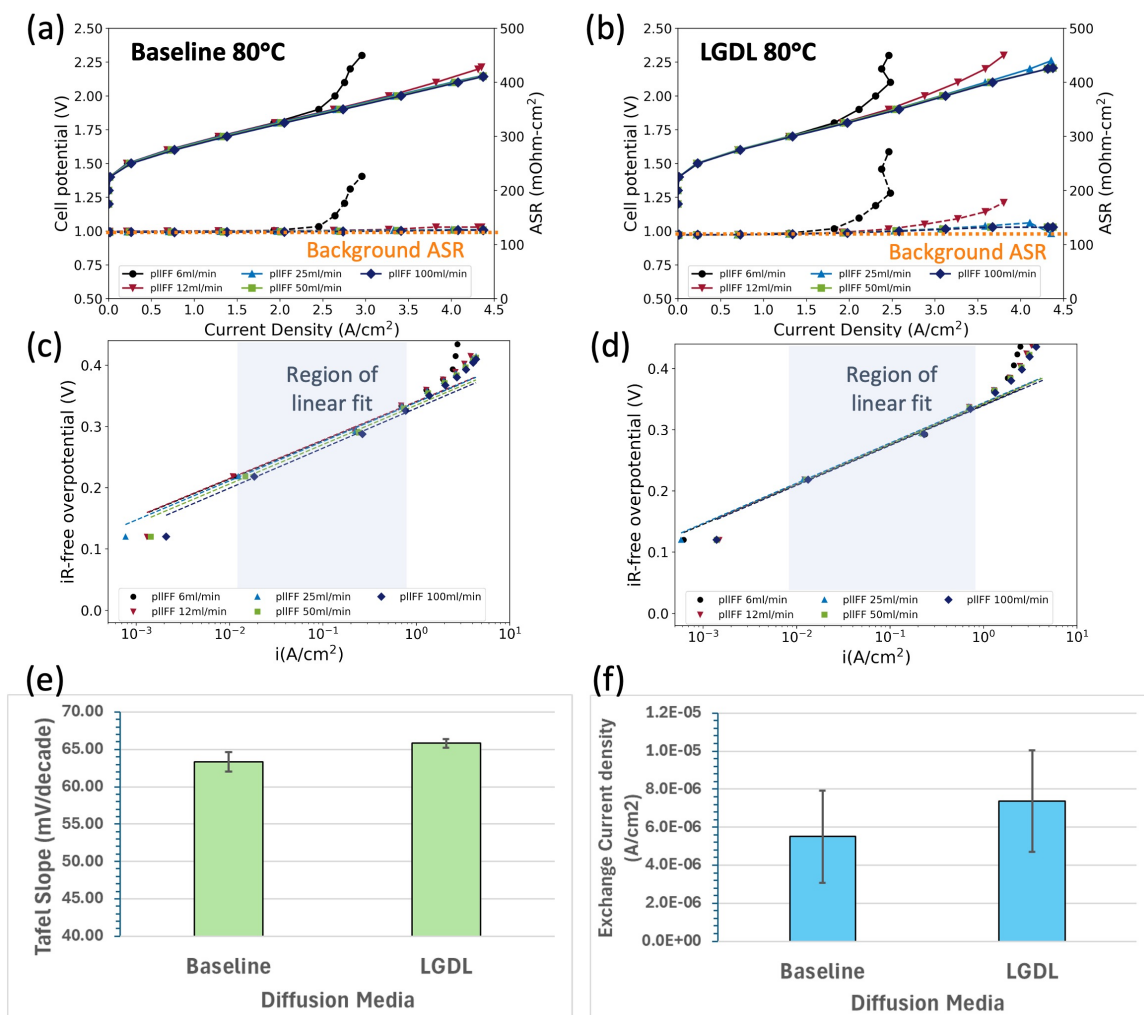


Figure 7.2: PEWE performance for two types of diffusion media with a parallel flow-field operating at 80°C. (a) Polarization curves using baseline PTL for all flow-rates; (b) Polarization curves using LGDL for all flow-rates; (c) iR-free polarization curves for baseline PTL; (d) iR-free polarization curves for LGDL; (e) Tafel slopes for both diffusion media; (f) Exchange current density for both diffusion media.

Figure 7.3, that the kinetic (η_{act}) and background ohmic ($\eta_{Ohm,b}$) contributions to the total overpotential were largely independent of the diffusion media used when comparing the performance at the same anode feedwater flow-rate.

By varying the anode feedwater flow-rate, the mass transport coupled ohmic overpotential ($\eta_{Ohm,mt}$) is observed to increase at the lowest flow-rate of 0.24 ml/min/cm^2 for both diffusion media, when operating at higher voltage holds. However the increase is about 1.5 times higher for the LGDL compared to the baseline. It is interesting to note that, even when the feedwater was set to the highest flow-rate of 4 ml/min/cm^2 , a 5% increase in $\eta_{Ohm,mt}$ at higher operating potentials (of 2.1V) was observed for the LGDL. However, this behavior was not seen in the baseline PTL, indicating that the in-plane mass transport of the baseline PTLs maintains sufficient hydration of the ionomer. Thereby preventing any buildup of mass transport-coupled ohmic resistances.

Similarly, the η_{diff} for both diffusion media followed the same trends, increasing with higher voltage holds and reduced anode feedwater flow-rates. Interestingly, only negligible differences in η_{diff} between the baseline PTL and LGDL was observed. The patterned straight pores of the LGDL offer a short diffusion path for the exchange of liquid water and gas bubbles. However, the steady-state water-gas pathways established inside the baseline PTL offer better access via diffusion to the catalyst sites beneath the flow-field lands compared to the LGDL, which restricts in-plane transport.

Table 7.3 provides a side-by-side comparison of the various categories of overpotentials using both types of diffusion media. The breakdown overpotential analysis for all flow-rates for both diffusion media with additional discussion is provided in the supplementary information.

Table 7.1: ASR measured for the PEWE using both baseline PTL and LGDL diffusion media for different cell temperatures

Temperature ($^{\circ}C$)	ASR ₀ ($mOhm \cdot cm^2$)		ASR @ 2.1V @6ml/min ($mOhm \cdot cm^2$)		ASR @ 2.1V @100ml/min ($mOhm \cdot cm^2$)	
	Baseline PTL	LGDL	Baseline PTL	LGDL	Baseline PTL	LGDL
60	144.7 ± 2.3	133.1 ± 0.2	159.8	186.6	152.3	151.8
70	132.1 ± 0.9	124.2 ± 0.8	167.2	183.5	136.8	139.8
80	124.2 ± 1.2	116.0 ± 1.8	176.6	195.2	126.5	132.0

Table 7.2: Calculated open-circuit-potentials of the PEWE operating at different temperatures

Temperature ($^{\circ}C$)	E_{OCP} (V)
60	1.198
70	1.189
80	1.180

Table 7.3: A side-by-side comparison of overpotentials measured in both mV and % of the total overpotential, for baseline PTL and LGDL operating at $80^{\circ}C$ for flow-rates of 0.24 ml/min/cm^2 and 4.0 ml/min/cm^2

Diffusion Media	Baseline PTL				LGDL			
Flow-rate ($ml/min/cm^2$)	0.24		4.0		0.24		4.0	
Voltage hold	1.7 V	2.1 V	1.7 V	2.1 V	1.7 V	2.1 V	1.7 V	2.1 V
η_{act} mV(%)	348 (67.0)	368 (40.0)	341 (65.6)	370 (40.2)	349 (67.2)	366 (39.8)	349 (67.2)	379 (41.2)
$\eta_{Ohm,b}$ mV(%)	154 (29.6)	322 (35.0)	162 (31.2)	476 (51.8)	146(28.0)	264 (28.7)	150 (28.8)	424 (46.1)
$\eta_{Ohm,int}$ mV(%)	2 (0.3)	146 (15.9)	0 (0.0)	15 (1.6)	5 (1.0)	199 (21.6)	1 (0.2)	47 (5.1)
η_{diff} mV(%)	17 (3.2)	84 (9.1)	17 (3.3)	60 (6.5)	19 (3.7)	92 (10.0)	20 (3.8)	70 (7.6)

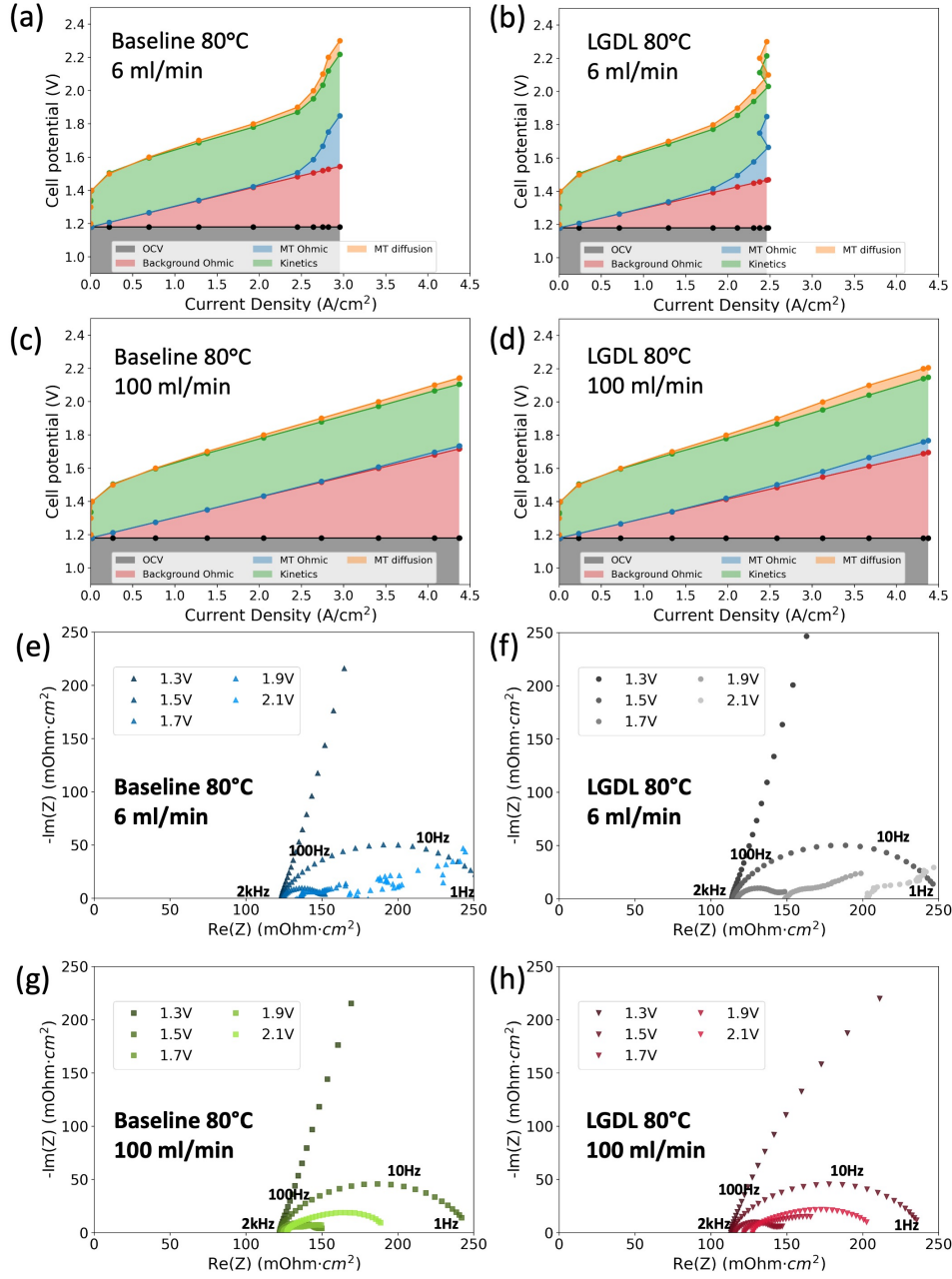


Figure 7.3: Side-by-side performance comparison for two types of diffusion media with a parallel flow-field operating at 80°C. Polarization curves with overpotential breakdowns for: (a) baseline PTL at 0.24 ml/min/cm²; (b) LGDL at 0.24 ml/min/cm²; (c) baseline PTL at 4.0 ml/min/cm²; (d) LGDL at 4.0 ml/min/cm². EIS Nyquist plots measured at various operating potentials for: (e) baseline PTL at 0.24 ml/min/cm²; (f) LGDL at 0.24 ml/min/cm²; (g) baseline PTL at 4.0 ml/min/cm²; (d) LGDL at 4.0 ml/min/cm².

7.2.2 Global EIS characteristics

Each curve in Figure 7.3e-h represents the EIS response of the PEM water electrolyzer as recorded for a specific voltage-hold. A clear trend for plots in Figure 7.3e,f and h is observed, where the ASR increases as the operating voltage increases. These measurements correspond to the ASR values reported in the last row of Table 7.1.

At high to mid frequencies, the impedance arc for all plots tend to decrease with increased operating voltages, reflecting changes in charge transfer resistance. This suggests that the electrochemical reactions at the electrodes become more efficient at higher voltages, likely due to improved reaction kinetics as predicted by the Butler-Volmer (or Tafel) relationship.

Interestingly, for Figures 7.3g-h, when operating at 1.8V or higher the first arc in all the Nyquist plots is seen to increase. This may suggest a loss in ECSA [Yang et al., 2024] or an increased resistance from a secondary process such as changes in the catalyst layer resistance [Padgett et al., 2023] due to dehydration of the ionomer. Both effects could be attributed to the high rates of gas evolution reactions. However, for Figures 7.3e-f, the this increase is not as prominent and the presence of a secondary arc is detected. The data also suggest an increasing trend in impedance at mid to lower frequencies for higher voltages, which could indicate an increase in diffusion or mass transport limitations. Furthermore, the overall shape of the Nyquist plots for both diffusion media are comparable. This indicates that the diffusive mass transport resistances for both diffusion media are similar, even though the water-gas exchange characteristics for the baseline PTL and LGDL are known to be different.

It must be noted that at 0.24 ml/min/cm^2 and higher operating voltages, the high rate of bubble evolution introduces noise to the EIS measurements making them hard to interpret and fit equivalent circuit models. Therefore, further investigations into the EIS characteristics of PEM water electrolyzers (viz. [Hensle et al., 2023,

Li et al., 2023, Yuste-Tirados et al., 2024]) are warranted. However, it is outside the scope of this work.

7.2.3 Local DASR measurements

Prior studies have demonstrated the utility of current distribution measurements [Roening et al., 2020, Roy et al., 2024]. In this work, local distributed area specific resistance was also collected alongside the CDD measurements. The DASR data is processed similarly to the CDD data as described in Roening, et al. [Roening et al., 2022]. Figure 7.4 shows the collected DASR contour plots at 0.24 and 4.00 $ml/min/cm^2$.

Previous works [Roening et al., 2022, Roy et al., 2024] showed that mass transport limited conditions yielded qualitatively similar current density distributions with gradients measuring relatively high current densities toward the inlet and low current densities toward the outlet. As mentioned in prior work [Roy et al., 2024], this is most likely caused due to the local dehydration of the PEM. Figure 7.4c lends irrefutable evidence for the hypothesis as it is clearly evident that the local ASR near the outlet is more pronounced due to the presence of bubble accumulation. Whereas during high flow-rate operations the local ASR distribution presented in Figure 7.4e is fairly uniform and closely matched the background ASR (see supplementary information (FigS3)). As mentioned in the supplementary information, the background ASR distribution pattern was also seen to be consistent for a combination of diffusion media and CCM suggesting that this distribution pattern may primarily capture irregularities that form at the PTL/CL interface.

Although the CDD and DASR contour plots showed certain dissimilarities, they have been largely used qualitatively to gauge cell performance and characterize mass transport, as seen in Figure 7.4b-e. Therefore, by using the EWTN [Roy et al., 2024] as a performance metric, it becomes easier to quantify the differences between the baseline PTL and the LGDL. Table 7.4 shows that the EWTN measured at 2.1V, remains close to 1 with a low standard deviation when using the baseline PTL.

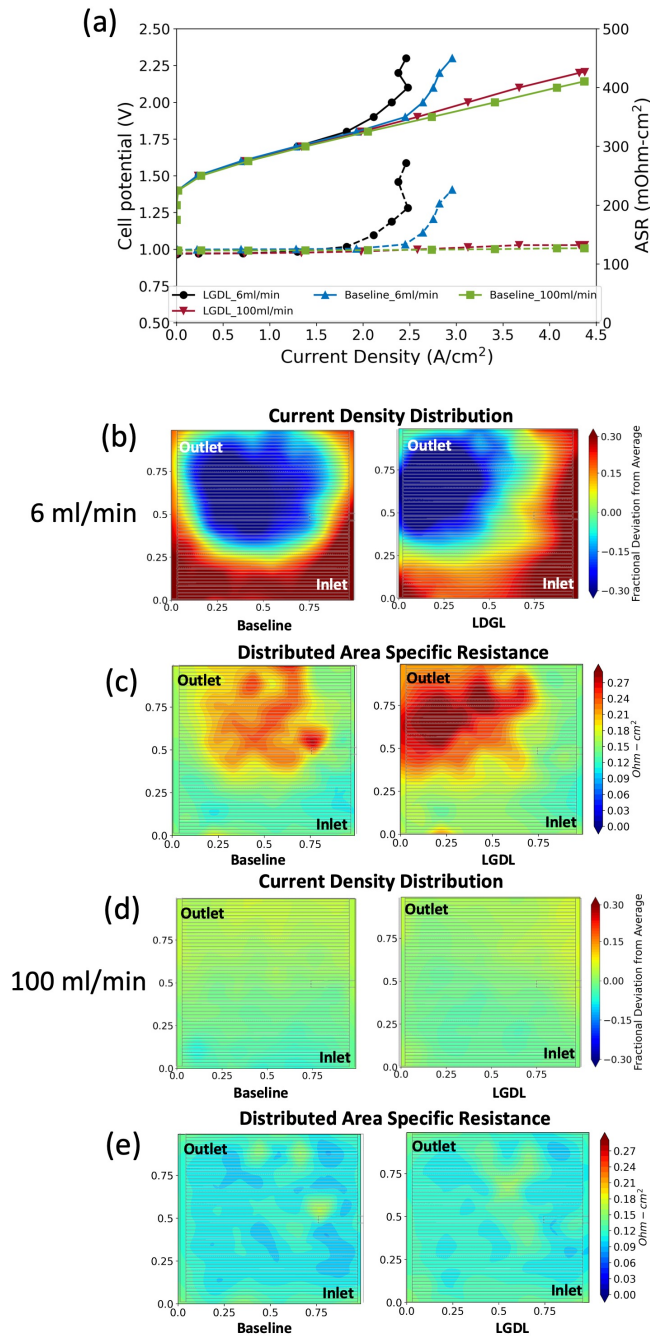


Figure 7.4: Global and local performance response of a PEWE using both diffusion media with a parallel flow-field: (a) Polarization curves (solid lines) measured at 0.24 ml/min/cm^2 and 4.0 ml/min/cm^2 along with their corresponding ASR (dashed lines). (b) CDD maps for 0.24 ml/min/cm^2 (left: Baseline PTL, right: LGDL) recorded at a voltage hold of 2.1 V and (c) corresponding DADR maps. Similarly, (d) CDD maps for 4.0 ml/min/cm^2 with (e) corresponding DADR maps.

Under all conditions, the baseline PTL registers higher mean EWTN values and lower standard deviations compared to the LGDL. Operating at the lowest flow-rate of 0.24 ml/min/cm^2 , the mean EWTN for the baseline PTL is approximately 15% more than that of the LGDL and 10% more when operating at 4.0 ml/min/cm^2 .

However, the question remains: what aspect of mass transport is measured by EWTN? To answer this, an investigation into the local distribution of each component of overpotential is required.

7.2.4 Local distribution of overpotentials

By applying the same semi-empirical model used for global measurements to the distributed measurements (i.e. CDD and DASR) data, spatial variations in overpotentials are revealed. Since all segments are essentially connected in parallel, they experience the same polarization or total overpotential. The spatial variations in $\eta_{Ohm,b}$ and $\eta_{Ohm,mt}$ can be calculated using Eq.7.7 and Eq.7.8. Furthermore, since the catalyst layer is uniform and the experiments are carried out at beginning-of-life these CCMs, the Tafel parameters are assumed to be spatially invariant. Hence, the local η_{act} can be predicted using Eq.7.4. Finally, applying Eq.7.10, η_{diff} is estimated as the residual. A detailed walk-through of the data processing is provided as part of the supplementary information. In order to compare the contributions of each category of overpotential, the values are normalized as percentage with respect to the total polarization. These are then mapped similar to the CDD and DASR plots as shown in figure S1. These contour plots are further converted into histograms and box-and-whiskers plots to gain statistical insights about their distributions and compare their relative contributions as the operating conditions change. A detailed description of the process is provided in the supplementary information.

In Figure 7.5b-e, histograms for local overpotentials are plotted for two operating voltages: 1.7V (shown in Figure 7.5b-c) and 2.1V (shown in Figure 7.5d-e), as indicated by the black dashed lines on the polarization curve in Figure 7.5a.

The corresponding CDD and DASR plots are included along with the histograms. Additionally, the pie charts in Figure 7.5a illustrate the global average percentage contributions of the local overpotentials for each voltage hold.

Figure 7.5 illustrates that moving to higher operating voltages on the polarization curve, the major contributor to the polarization (i.e. limiting conditions), shift from being predominantly kinetic to mass transport limitations. At 1.7V, 67.3% of the total polarization arises from η_{act} , 28% from the $\eta_{Ohm,b}$, 1% from the $\eta_{Ohm,mt}$ and remaining from η_{diff} . Conversely, operating at 2.1V, which simulates mass transport limited conditions, 39.8% of the total polarization is from η_{act} , 28.7% from $\eta_{Ohm,b}$, 21.6% from $\eta_{Ohm,mt}$ and 10% from η_{diff} .

As evident from Figures 7.5b-e the distributions for η_{act} show minimal spatial variations, with a total range measuring less than 4% and an inter-quartile range (IQR) measuring less than 2% for both operating voltages. Additionally, Figure 7.5b-c shows that operating at 1.7V, all categories of overpotential are quite uniformly distributed (as their IQR is less than 2%). Interestingly, $\eta_{Ohm,b}$ shows a left-skewed distribution which suggests that the majority ($\sim 75\%$) of the CL/PTL interface maintains good contact, contributing nearly 25-28% of the total overpotential. However, the histograms for η_{diff} reassembles a normal distribution, with most of the active area contributing 3.8% (on average) to the polarization due to diffusion limitations.

When operating at 2.1V which simulates mass transport limited conditions, significant changes in the distributions for $\eta_{Ohm,b}$, $\eta_{Ohm,mt}$ and η_{diff} are observed. As seen from Figures 7.5d-e, the background ohmic contributions exhibit a larger variation (IQR of 10.3%) with a slightly right-skewed distribution. More than 50% of the active area (lower two quartiles) provided only 18-30% contribution to the total polarization. Significant bubble accumulation near the outlet leads to local dehydration of the PEM, resulting in a left-skewed distribution for $\eta_{Ohm,mt}$, which shows 50% of the active area (represented by the upper two quartiles) contributing 21-34% of the total polarization. This also leads to 10-18% contributions in the form

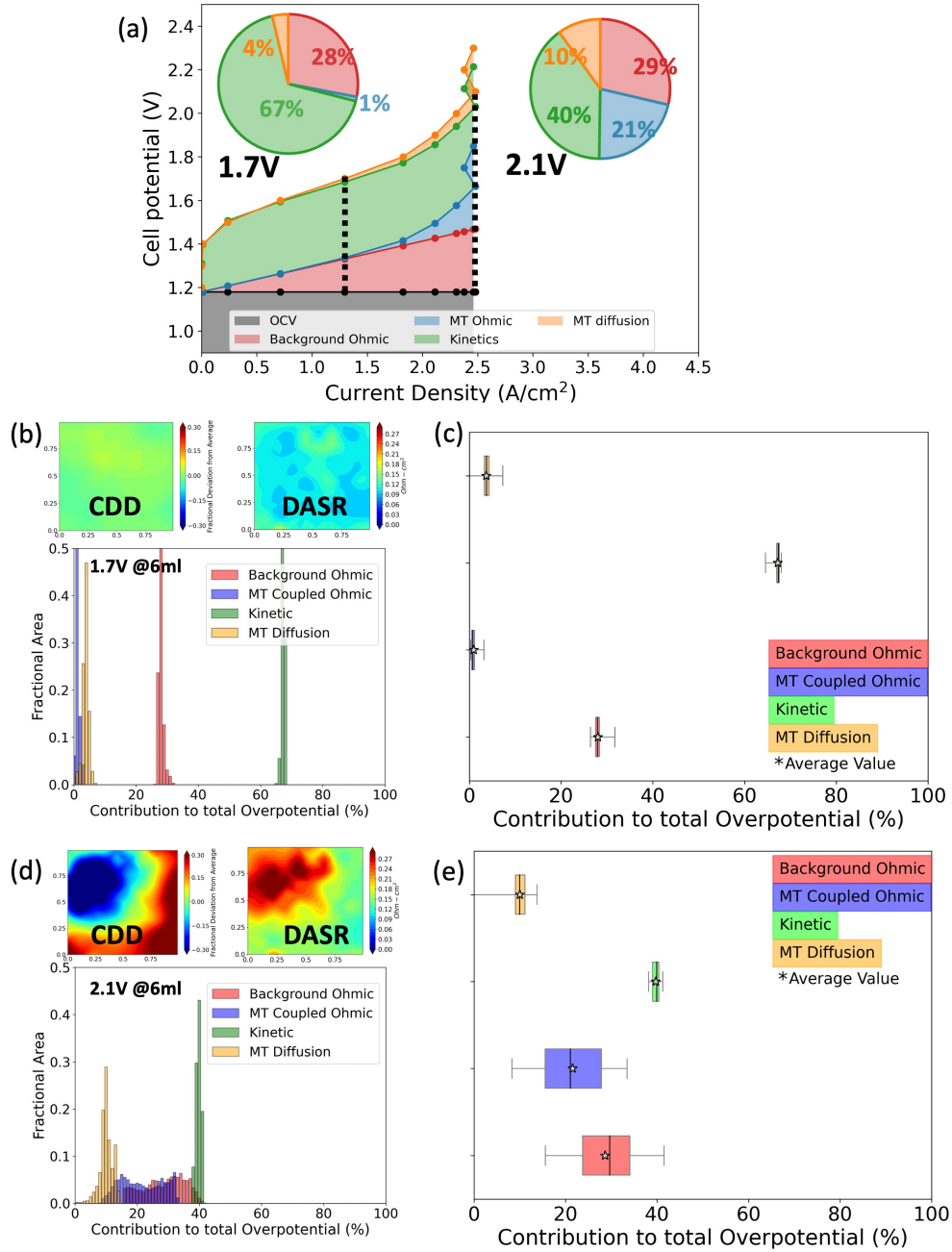


Figure 7.5: Analysis of various overpotentials at the global and local scale: (a) Polarization curve for LGDL at 0.24 $ml/min/cm^2$ at 80°C; (inset) pie-charts represent their % contributions at 1.7V and 2.1V. (b) Histograms showing the spatial variation of each overpotential category for the corresponding CDD and DASR measurements at 1.7V; (c) Box-and-whiskers plots for corresponding overpotential distributions at 1.7V. Similarly, (d) Histograms and (e) Box-and-whiskers plots corresponding to distributed measurements at 2.1V are shown.

of η_{diff} , as reactions in this half of the active area are sustained by diffusive water transport in the vapor phase.

Tabulating the data presented in box-and-whisker plots in Table 7.5, allows for a better appreciation of the statistical differences in the distributions of the local overpotentials. This format facilitates easier comparisons between different operating conditions and will be used henceforth.

7.2.5 Baseline PTL and LGDL comparison

Figure 7.6a-d compares the distributions of the local overpotentials as developed inside the PEM water electrolyzer using baseline PTLs and LGDLs when operating at 2.1V and a flow-rate of 0.24 ml/min/cm^2 . In both cases the kinetic contributions are similar and show very little variations.

The $\eta_{Ohm,b}$ distributions for both diffusion media range in between 20-50%. When using the baseline PTL, 50% (the two upper quartiles) of the active area contributes nearly 35-50% of the total polarization as background ohmics. Whereas, the LGDL manages to contribute 30-43% of the total overpotential as $\eta_{Ohm,b}$. This indicates that using the LGDL the PEM is more susceptible to local dehydration effects when the anode feedwater flow-rate is not effective at removing bubbles. This is also proved by comparing $\eta_{Ohm,mt}$ for both diffusion media, where it can be clearly observed that half of the distribution (represented by the two lower quartiles) contributes at least 9% and up to 21% of the total polarization when using the LGDL and at least 4% up to 17% of the total polarization for the baseline PTL. The IQR for both categories of η_{Ohm} measure about 1.5 times more when using the baseline PTL than the LGDL. This larger variation highlights the fact that the baseline PTL facilitates in-plane water transport. It also suggests that the water-gas transport pathways inside the baseline PTL changes as the local saturation changes which may result in local variations in hydration of the PEM.

Table 7.4: Performance measured using EWTN at 2.1V for baseline PTL and LGDL

flow-rate (ml/min/cm ²)	EWTN mean $\pm$ std.dev	
	Baseline PTL	LGDL
0.24	0.76 $\pm$ 0.178	0.61 $\pm$ 0.145
0.48	0.95 $\pm$ 0.049	0.80 $\pm$ 0.058
1.0	0.97 $\pm$ 0.026	0.88 $\pm$ 0.021
2.0	1.0 $\pm$ 0.006	0.90 $\pm$ 0.024
4.0	1.0 $\pm$ 0.007	0.90 $\pm$ 0.022

Table 7.5: Statics for the distributions of various overpotentials measured at 1.7V and 2.1V

Overpotential	1.7V				2.1V			
	Mean	range	Median	IQR	Mean	range	Median	IQR
η_{act}	67.3%	3.5%	67.4%	0.5%	39.8%	3.1%	40.0%	1.3%
$\eta_{Ohm,b}$	28.0%	5.3%	28.0 %	0.8%	28.7%	26.0%	29.7%	10.3%
$\eta_{Ohm,mt}$	1.0%	2.9%	0.7%	0.6%	21.6%	25.1%	21.1%	12.3%
η_{diff}	3.7%	7.3%	3.8%	1.0%	10.0%	13.8%	10.0%	2.1%

Table 7.6: Statics for the distributions of various overpotentials measured at 2.1V for the PEWE using a baseline PTL and LGDL operating at an anode feedwater flow-rate of 0.24 ml/min/cm² and 4.0 ml/min/cm²

	Overpotential	6 ml/min				100 ml/min			
		Mean	range	Median	IQR	Mean	range	Median	IQR
Baseline PTL	η_{act}	40.0%	3.0%	40.0%	1.3%	44.8%	2.0%	44.8%	0.4%
	$\eta_{Ohm,b}$	35.0%	31.8%	34.6%	15.6%	50.2%	31.7%	50.0%	2.2%
	$\eta_{Ohm,mt}$	15.9%	24.3%	16.9%	14.9%	0.6%	3.8%	0.5%	0.9%
	η_{diff}	9.1%	13.8%	9.1%	3.0%	4.7%	17.8%	4.7%	1.5%
LGDL	η_{act}	39.8%	3.1%	39.9%	1.3%	41.2%	1.6%	41.2%	0.4%
	$\eta_{Ohm,b}$	28.7%	26.0%	29.7%	10.3%	46.1%	12.0%	45.7%	2.9%
	$\eta_{Ohm,mt}$	21.6%	25.1%	21.1%	12.3%	5.1%	4.7%	5.1%	1.3%
	η_{diff}	10.0%	13.8%	10.0%	2.1%	7.6%	8.5%	8.1%	1.8%

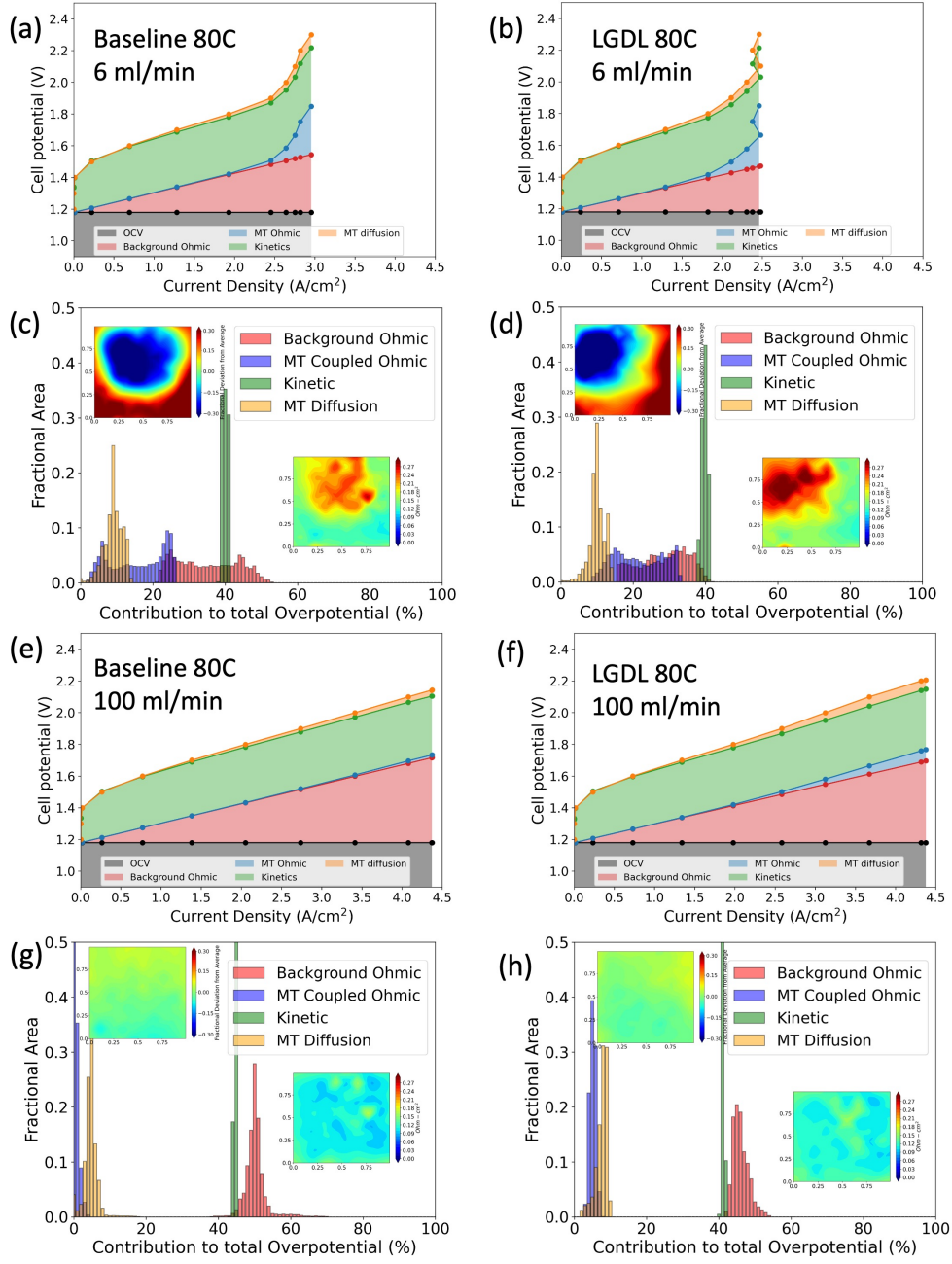


Figure 7.6: Overpotential breakdown analysis: comparing global response for (a) baseline PTL and (b) LGDL operating at a flow-rate of 0.24 ml/min/cm^2 ; Corresponding local distributions at 2.1V for (c) baseline PTL and (d) LGDL are presented. Similarly, global response (e)-(f) along with corresponding local distributions at 2.1V (g)-(h) for baseline PTL and LGDL are also presented.

Interestingly, the distributions for η_{diff} are mostly similar, even though there are significant differences in the nature of fluid transport through the each diffusion media. Only minor differences in the median value and IQR are noted (see Table 7.6). This may suggest that the diffusion limitation is primarily occurring at the micro-porous-scale within the CL. This is further supported by the comparing the distributions of the local overpotentials when operating at 2.1V with a high anode feedwater flow-rate of 4 $ml/min/cm^2$ as shown in Figures 7.6e-h.

The CDD and DASR as presented in Figures 7.6e-h are seen to be uniform and results in a normal distribution for the activation and background ohmic overpotentials. However, negligible contributions from $\eta_{Ohm,mt}$ was observed when using the baseline PTL. Whereas, the LGDL expressed a normal distribution with a mean value of 5.1% (see Table 7.6). Furthermore, the η_{diff} distribution for the LGDL is right-skewed and the lower two quartiles is seen to contribute at least 4% and up to 8% of the total polarization. By the same measure, the baseline PTL only contributes up to 5% of the total overpotential as diffusion limited overpotential and developed a normal distribution.

Since a flow-rate of 4 $ml/min/cm^2$ is high enough to prevent any major bubble accumulation inside the flow-field channels and diffusion media of the PEM water electrolyzer, the source of diffusion limited overpotential must stem from the CL. Using the thin foil LGDL, nearly 50% of the catalyst area is obstructed by the flow-field lands, hindering in-plane transport. However, the baseline PTL is known to establish steady-state pathways within its porous structure for water-gas exchange [Satjaritanun et al., 2020]. As a result, a longer diffusion length and larger η_{diff} is expected to develop for the LGDL when compared to the baseline PTL. Although such a difference is observed, it is less than 5% of the total polarization.

Therefore it is hypothesized that although the geometry and morphology of the diffusion media might primarily impact macro-scale fluid dynamics, their effects on micro-scale diffusion is less pronounced. Hence, the primary limitation to diffusion inside a PEM water electrolyzer occurs at the CL. At these micro-porous scales,

the diffusion path-lengths of the reactants and products within the catalyst layer are relatively short but highly tortuous [Sadeghi et al., 2024]. This increases the effective diffusion resistance, making the overall diffusion process less sensitive to the differences between the baseline PTL and LGDL.

7.2.6 Effect of temperature

Investigations on the effects of temperature on the various overpotentials are presented in this section. Figure 7.7a-b shows the variation in kinetic parameters as temperature is varied for the PEM water electrolyzer using both diffusion media. As previously discussed (see section 7.2.1), there is negligible difference in the Tafel slope measured between the baseline PTL and LGDL. However, as temperature increases, a clear linearly increasing trend of the Tafel slope can be observed for both diffusion media, as seen in Figure 7.7a. This result is expected as the Tafel approximation is derived from the Butler-Volmer model of kinetics. In this derivation, it can be shown that for a constant charge-transfer coefficient with fixed number of electrons (i.e. known reaction and electrode material), the Tafel slope is directly proportional to the temperature [Mench, 2008].

Similarly, Figure 7.7b shows an exponentially increasing trend between temperature and the calculated exchange current density. This is also expected, as the exchange current density is a measure of the reaction rate-constant and follows the Arrhenius' law [Bard et al., 2022]. It is interesting to note that the difference in exchange current densities between the baseline PTL and LGDL are not as pronounced for temperatures lower than $80^{\circ}C$.

Furthermore, the conductivity of the ionomer is known to depend on the temperature and hydration [Zawodzinski et al., 1993]. As the background ASR is measured at the beginning of the polarization curve, the hydration of the ionomer remains unchanged. Therefore, with increase in temperature, the ASR_0 decreases (as reported in Table 7.1). Since the kinetic parameters, rate of reactions and ionomer

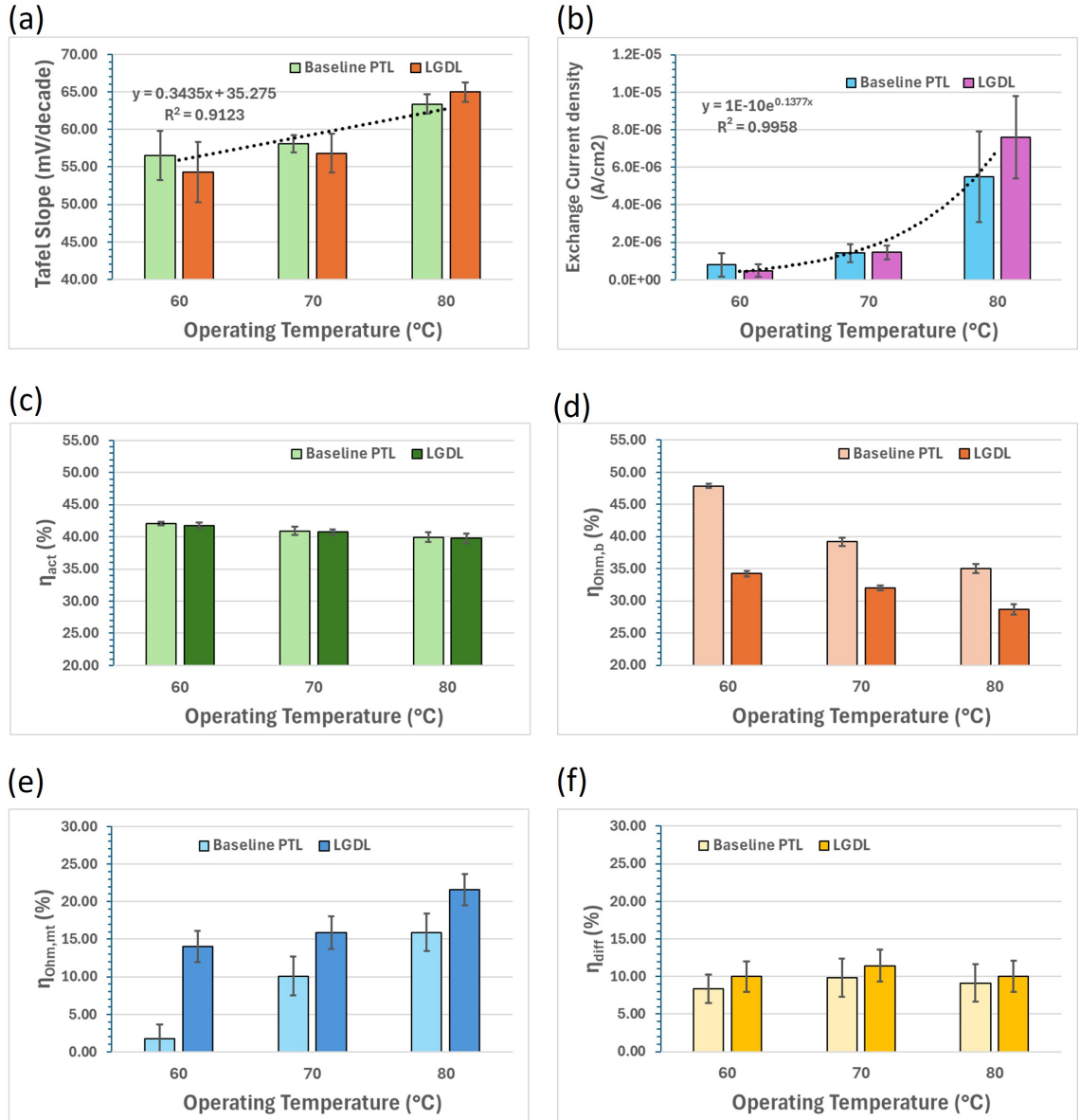


Figure 7.7: Side-by-side performance comparison at 0.24 ml/min/cm² for baseline PTL and LGDL under different operating temperatures — Kinetic parameters like: (a) Tafel slope; (b) Exchange current density. Different overpotentials at 2.1V such as: (c) Kinetic overpotential; (d) Background ohmic overpotential; (e) Mass-transfer coupled ohmic overpotential; (f) Diffusion limited overpotential are also presented.

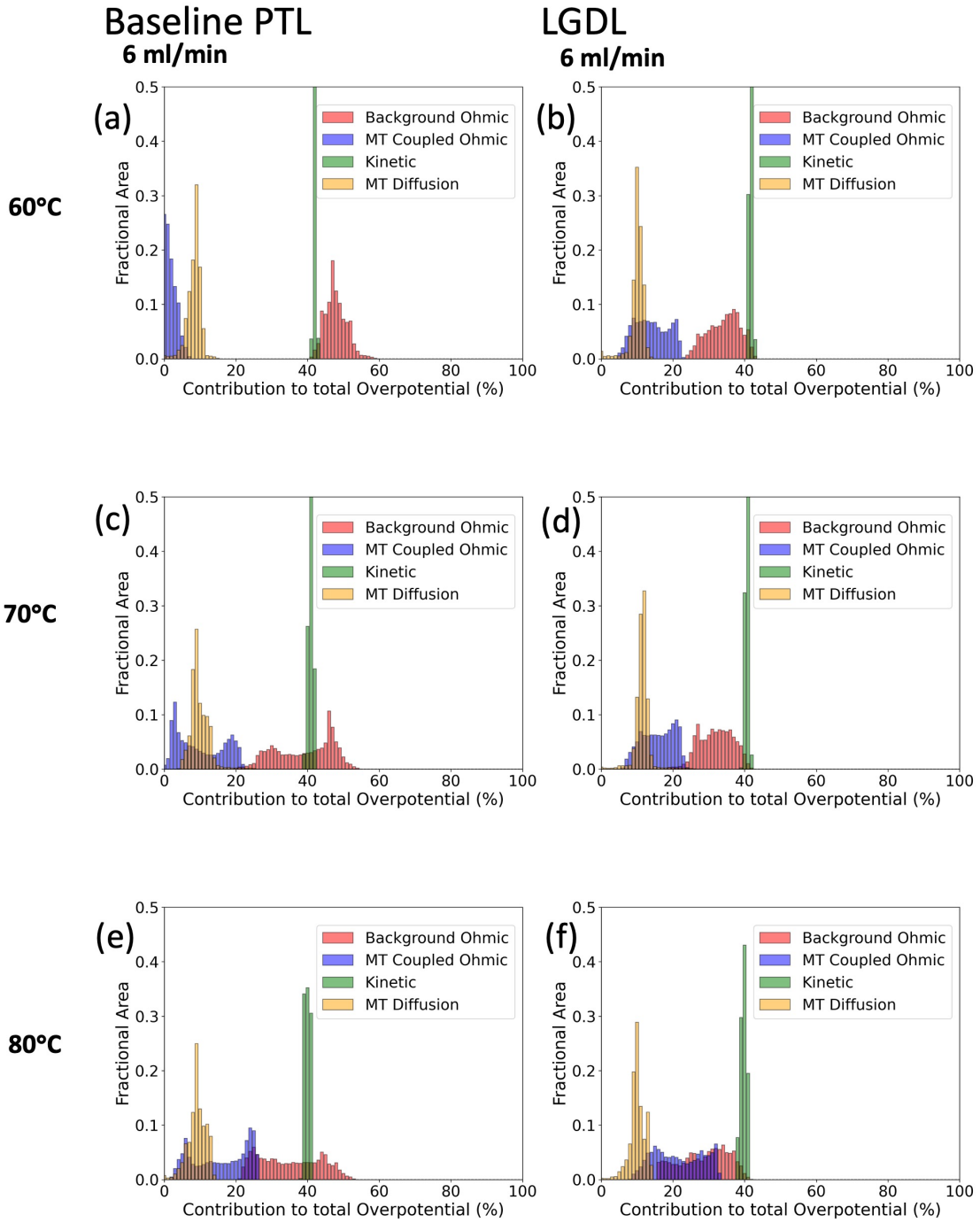


Figure 7.8: Side-by-side comparison of the distribution of local overpotentials at 2.1V for baseline PTL (left column) and LGDL (right column) operating at a flow-rate of 0.24 ml/min/cm², under different operating temperatures.

conductivity all improve with increased temperature, the overpotentials η_{act} and $\eta_{Ohm,b}$ are seen to decrease as shown in Figure 7.7c-d.

Although the cell is kept under isothermal conditions by the test-bench, the overall ASR measured at higher operating voltages shows positive deviation from ASR_0 . This indicates that the change in $\eta_{Ohm,mt}$ must be due to local variation in hydration. Figure 7.7e shows that the rise in temperature also result in an increased $\eta_{Ohm,mt}$ for both diffusion media. This suggests that the rate of local dehydration increases when operating at higher temperatures. Interestingly, there is no significant changes measured in η_{diff} (see Figure 7.7f) as temperature is varied.

Figure 7.8 compares the differences in the distributions of the local overpotentials using both the baseline PTL and LGDL for operating temperatures of $60^\circ C$, $70^\circ C$ and $80^\circ C$, when the anode feedwater flow-rate is set to 0.24 ml/min/cm^2 . Table 7.7 summarizes the data presented in Figure 7.8. The distributions for the kinetic and diffusion limited overpotentials, η_{act} and η_{diff} , exhibit a very small increase in their IQR with increased cell temperature. The biggest change in the distributions is noticed for η_{Ohm} . As the cell temperature increases, $\eta_{Ohm,b}$ for both baseline PTL and LGDL showed a decrease in their median value with an increase in their range and IQR. Similarly, $\eta_{Ohm,mt}$ for both diffusion media also showed a simultaneously increase in their median, range and IQR, with increase in cell temperature. For all distributions the baseline PTL managed to contribute nearly 5-10% less $\eta_{Ohm,mt}$ than the LGDL when comparing the lower two quartiles.

7.3 Conclusion

Through the use of the segmented cell and PCB approach, this study demonstrates an advanced technique for measuring and understanding the electrochemical behavior within PEWEs. Coupled with the application of a semi-empirical model, it allows for the investigation of different overpotential categories and the identification of their spatial variations.

The results show that variations in area-specific resistance of the PEWE are significantly influenced by the anode feedwater flow-rate. Moreover, the DASR measurements indicate that local dehydration of the polymer electrolyte membrane is primarily responsible for increased polarization, behaving similar to mass transport-limited currents at low flow-rates due to ineffective bubble removal from the catalyst surface. To facilitate better quantification and analysis, the overall ohmic overpotential is proposed to be divided into ($\eta_{Ohm,b}$) background and ($\eta_{Ohm,mt}$) mass transport-coupled ohmic overpotentials. The $\eta_{Ohm,b}$ distributions for both diffusion media (baseline PTL and LGDL) range in between 20-50% of the total overpotential. It was also shown that when the anode feedwater flow-rate is not effective at removing bubbles, the PEM is more susceptible to local dehydration effects while using the LGDL. This was supported by the baseline PTL having lower average values for $\eta_{Ohm,mt}$. Furthermore, analyzing EIS results revealed that along with variations in ASR, some secondary processes such as changes in the catalyst layer resistance or decreased electrochemical surface area may occur due to high rates of gas evolution and bubble accumulation.

The effect of cell temperature on the various overpotentials were also presented in this work. An increase in temperature was seen to improve kinetics and background ohmics. However, the increase in temp also caused increased rate of dehydration which lead to an increase in the mass transport coupled ohmic contributions. Although diffusion processes are expected to improve with increased temperature, no such appreciable trends for both the diffusion media were noted.

Interestingly, only negligible differences in the diffusion overpotential were observed when comparing PEWE performance using both baseline PTLs and LGDLs. Even though it is known that there are significant differences in the nature of two-phase fluid transport occurring within each diffusion media. This leads to the hypothesis, that the diffusion limitation is primarily occurring at the micro-porous-scale within the CL. Further evidence may be found by comparing the η_{diff} distributions for each diffusion media operating at flow-rates of 4 ml/min/cm^2 , which

is high enough to prevent any major bubble accumulation inside the PEM water electrolyzer. The baseline PTL can establish steady-state pathways within its porous structure for water-gas exchange. Whereas, the thin foil LGDL prohibits in-plane transport and nearly 50% of the catalyst area gets trapped underneath the flow-field lands. As a result, a longer diffusion length and larger η_{diff} is expected to develop for the LGDL when compared to the baseline PTL. However, the LGDL is observed to contribute at least 4% and up to 8% of the total polarization; whereas, the baseline PTL only contributes up to 5% of the total overpotential. The micro-porous structure of the CL plays a critical role in diffusion processes. Since the difference in η_{diff} is not more than 5%, the diffusion limitations must arise from diffusion of species through the catalyst layer. These micro-structures control the accessibility of reactants to the catalytic sites and the removal of products, leading to localized diffusion limitations which can overshadow the macroscopic differences in larger-scale fluid dynamics inside the anode diffusion media.

This research highlights the complex nature and intricacies of mass transport limitations in PEM water electrolyzers. By providing a deeper understanding of PEWE dynamics, this work offers a foundation for informed engineering decisions. These insights enrich theoretical knowledge and are crucial for enhancing the efficiency and economic viability of PEWEs, thereby advancing the prospect of sustainable hydrogen production.

Table 7.7: Statics comparing the distribution of local overpotentials for baseline PTL and LGDL at a flow-rate of 0.24 ml/min/cm^2 and various cell temperatures

	Overpotential	Baseline				LGDL			
		Mean	range	Median	IQR	Mean	range	Median	IQR
60°C	η_{act}	42.1%	1.8%	42.1%	0.4%	41.8%	2.3%	41.8%	0.7%
	$\eta_{\text{Ohm,b}}$	47.9%	17.7%	47.5%	3.9%	34.2%	19.7%	34.8%	6.8%
	$\eta_{\text{Ohm,mt}}$	1.8%	6.8%	1.4%	2.4%	14.0%	18.5%	13.8%	7.9%
	η_{diff}	8.4%	14.7%	8.7%	2.0%	10.0%	14.1%	10.2%	1.6%
70°C	η_{act}	40.9%	3.0%	41.1%	1.1%	40.7%	2.4%	40.8%	0.7%
	$\eta_{\text{Ohm,b}}$	39.2%	34.4%	40.8%	14.5%	32.0%	23.7%	32.1%	7.5%
	$\eta_{\text{Ohm,mt}}$	10.1%	22.3%	8.7%	13.2%	15.9%	17.8%	16.1%	7.8%
	η_{diff}	9.8%	20.9%	9.2%	2.9%	11.4%	25.7%	11.5%	1.4%
80°C	η_{act}	40.0%	3.0%	40.0%	1.3%	39.8%	3.1%	39.9%	1.3%
	$\eta_{\text{Ohm,b}}$	35.0%	31.8%	34.6%	15.6%	28.7%	26.0%	29.7%	10.3%
	$\eta_{\text{Ohm,mt}}$	15.9%	24.3%	16.9%	14.9%	21.6%	25.1%	21.1%	12.3%
	η_{diff}	9.1%	13.8%	9.1%	3.0%	10.0%	13.8%	10.0%	2.1%

Chapter 8

An advanced Cahn-Hilliard and Navier-Stokes coupled LBM model to predict two-phase flow dynamics at the pore-scale

The lattice Boltzmann method (LBM) of modeling multi-phase flow, has recently emerged as a popular and promising technique. Being one of the mesoscopic numerical methods, the LBM has the capability to address macro-scale simulations similar to a classical Navier-Stokes solver; As well as simultaneously consider the micro-scale interparticle interactions. It is most appreciated because of its ability to handle complex geometries, as well as multi-component multi-phase flows [Lee, 2009, Satjaritanun et al., 2021]. Unlike traditional computational fluid dynamics (CFD) methods that solve macroscopic equations, the LBM simulates fluid flow through the use of microscopic fluid descriptions or mesoscopic kinetic equations. Furthermore, the phase separation and interfacial dynamics, which are essential for simulating multi-phase flows, are known to difficult to model and implement by

traditional CFD methods. However such phenomena can be simulated in LBM by incorporating additional interparticle interactions.

Most of the popular two-phase LBM methods are considered as diffuse-interface models. Here, the phase interface is spread out on grid points and the surface tension is transformed into a volumetric force [Lee and Lin, 2005]. Numerical schemes based on a sharp interface representation, as compared to diffusive interface models, are usually more accurate. However, such models require resolving additional numerical problems in their implementation, especially with high density and viscosity ratios [Banari et al., 2014a]. Sharp interface models face difficulties in accurately computing bubble interface curvature and related surface tension forces. This often leads to the appearance of numerical errors along the interface in their solutions. Such issues can be avoided when using a diffusive interface representation.

Several different LBM models for the simulation of multi-phase flow have been proposed in the past. The first LBM multi-phase model was based on a two-component Lattice-gas automata (LGA) model [Rothman and Keller, 1988, Zanetti, 1988], proposed by Gunstensen et al. [Gunstensen et al., 1991]. This model was later modified by Grunau et al. [Grunau et al., 1993] to allow variations of density and viscosity. In these models, red and blue particle distribution functions were assumed to mimic two different fluids. To maintain interfaces and to separate different phases, a “re-color” step was introduced to force fluid particles with the same color to move towards each other. More recently the color gradient method was modified to accurately characterize the interfacial tension and the geometrical wetting to eliminate the nonphysical transfer of mass [Leclaire et al., 2016, Akai et al., 2018]. This method was further used to study two-phase flow in porous media [Zakirov and Khramchenkov, 2020, Cheng et al., 2023, Jeon et al., 2023]. Zakirov et al. [Zakirov and Khramchenkov, 2020] studied two-phase flow with high density ratios in porous media and reported on permeability coefficients, displacement efficiency, viscous and capillary forces in action.

The most commonly used LBM multi-phase model is the Shan-Chen [Shan and Chen, 1993] (SC) model because of its simple implementation scheme. An interparticle potential is introduced to model the surface tension and phase separation. However, the model has been shown to suffer from numerical instabilities in the form of spurious currents/velocities at the interface between the two phases [Ezzatneshan and Goharimehr, 2021] for fluids with high density and viscosity ratios. He et al. [He et al., 1998] found that the anisotropy reported in the SC model is a consequence of inappropriate interparticle interactions. The non-physical dependence of this interparticle potential on the magnitude of the density and viscosity ratio is also a major restriction of the standard SC model for simulating multi-phase flows. To maintain stability researchers have implemented more realistic equations of state (EoS) [Yuan and Schaefer, 2006, Kupershtokh et al., 2009, Ezzatneshan and Vaseghnia, 2020] and different forcing schemes [Guo et al., 2002, Kupershtokh et al., 2009].

Paliwal et al. [Paliwal et al., 2021] extended the intermolecular forces beyond the nearest-neighboring nodes. Deng et al. [Deng et al., 2019] proposed a modified SC approach, where the Peng-Robinson EoS was used along with the modified Guo forcing scheme [Guo et al., 2002, Li et al., 2012]. Further they were able to change the viscosity dependence on the density, to model more realistic viscosity ratios and the surface tension was determined by the difference between normal and parallel pressures to the interface. They used the model to study bubble detachment in channel with a finite domain.

In 1996, a LBM model proposed by Swift et al. [Swift et al., 1996a, Swift et al., 1996b] used the free-energy approach. In their model, the equilibrium distribution was modified so that the pressure tensor was consistent with the tensor derived from the free-energy function of non-uniform fluids. Similarly, He et al. [He et al., 1998, He and Luo, 1997, He et al., 1999] proposed a novel LBE formulation for non-ideal gases based on the continuous discrete Boltzmann equation (DBE) using a single-relaxation-time approximation.

In this model, the intermolecular interactions simulating non-ideal gas effects are derived from the Enskog extension of the Boltzmann equation. This results in the phase separation to be induced by mechanical instability in the supernodal curve of the phase diagram. Naturally, implementation of the thermodynamical concept is more flexible than some of the previous LBE models such as the SC model. Further, the Galilean invariance troubling the free-energy-based models [Swift et al., 1996a, Swift et al., 1996b] was effectively removed from their formulation. Unfortunately, He et al. [He et al., 1999] also reported numerical stability due to the stiffness of their intermolecular interaction force and its inherent dependency on the density gradient.

Lee et al. [Lee and Lin, 2005, Lee and Lin, 2003, Lee and Fischer, 2006, Lee and Liu, 2008, Lee, 2009, Lee and Liu, 2010] was able to improve upon efforts of He et al. [He et al., 1998] to solve the DBEs describing the pressure and momentum for multi-phase flows. First, they split up intermolecular forces for non-ideal gas into hydrodynamic pressure, thermodynamic pressure, and surface tension force contributions. They also reported [Lee and Lin, 2003] that "parasitic currents" affected numerical results at interfaces, due to the imbalance between thermodynamic pressure and surface tension forces resulting from truncation errors, particularly, in relation to curvature computations. After which Lee and Fischer managed to nearly eliminate the problem by using a thermodynamic identity to recast the intermolecular forcing term from a stress into a potential form [Lee and Fischer, 2006]. Furthermore, they used different discretization patterns (i.e., centered, staggered, and mixed differences) at different steps of the simulation, to make their numerical scheme stable for large density ratios [Lee and Lin, 2005]. With this discretization scheme, Lee et al. [Lee and Liu, 2008, Lee, 2009, Lee and Liu, 2010] were able to simulate two phase flows with density ratio of up to 1000. However, their method was only valid for low Reynolds and Mach numbers. Additionally, numerical efficiency seemed to be quite low, due to the need for calculating various forms of first-order and second-order derivatives of the macroscopic variables. Huang et al. [Huang et al., 2018] later implemented this model on a GPU cluster.

Banari et al. [Banari et al., 2014a, Banari et al., 2014b] developed and implemented a LBM based in part on Inamuro et al.’s approach of removing the pressure gradient from the momentum equation. However, they used a modified primary set of equilibrium functions for the ”pressureless” NS equations, in which viscosity is still present and related to the relaxation time as in a classical LBM. Similarly to Inamuro et al, the velocity field was corrected by solving a Poisson equation for the pressure, but in this model it was done using a third set of LBM equilibrium functions, which led to less efficiency and impaired the inherent simplicity of the LBM. For the interface capture a standard Cahn-Hilliard equation (in which surface tension and equivalent body forces are rigorously derived) was used, and solved for using an LBM scheme.

In conventional multi-phase LBM models that are used to simulate two-phase flows inside the anode diffusion media of a water electrolyzer, challenges arise when dealing with high density and viscosity ratios. These instabilities manifest as spurious velocities at interfaces, large density ratios and gradients, and issues arising from large viscosity ratios due to the direct relationship with the collision operator. Furthermore, the physical properties of surface tension and contact angle cannot be directly implemented in such models.

To address these limitations, the proposed model employs a coupled Cahn-Hilliard and Navier-Stokes approach. This approach adopts a Volume of Fluid-like strategy, wherein the fluids are modeled using one mass and momentum conservation equation for the binary fluid mixture, while another equation describes the two phases (water and air). By doing so, the direct coupling between the density of the fluid and pressure is effectively decoupled, a characteristic of typical LBM models. Furthermore, the model breaks the relationship between the collision operator and fluid viscosity, allowing for successful LBM simulations with high density and viscosity ratios. Another improvement of this model is its capability of simulating two-phase flow in a finite domain. These enhancements significantly improve the stability and accuracy of the simulations in challenging scenarios.

The paper is organized as follows. In Section 8.1, the Cahn–Hilliard model with advection is briefly reviewed. The discrete Boltzmann equation is presented for a general case, as well as for the coupled NS-CH model. In Section 8.2, the discretization of the LBEs, spatial spatial gradients and boundary conditions are described. The model algorithm is also presented. Validation of the present LBE method and the simulations of bubble detachment are presented in Section 8.4. Concluding remarks are given in Section 8.5.

8.1 Mathematical model

The proposed model exhibits its strength in tackling the challenges arising from high-density and viscosity ratios in two-phase flows. By adopting the coupled Cahn-Hilliard and Navier-Stokes approach.

8.1.1 Coupled Cahn-Hilliard Navier-Stokes model

The continuity equation for each species of multi component fluids can be written as [Lee, 2009],

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i \mathbf{u}_i = 0 \quad (8.1)$$

where ρ_i and $\mathbf{u}_i$ denote the local density and velocity of the species i .

For a mixture, the total density is conserved as $\rho = \sum_i \rho_i$. The local velocity $\mathbf{u}_i$ is related to the volume average velocity $\mathbf{u}$, the bulk density ρ and the volume diffusive flow rate $\mathbf{j}$ by the relationship: $\rho \mathbf{j} = \rho_i (\mathbf{u}_i - \mathbf{u})$.

For a binary system $i = 1, 2$, using the previous relationship, Eq. 8.1 can be rewritten for the composition $C = (\rho - \rho_2)/(\rho_1 - \rho_2)$ as,

$$\frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{u}C) = -\nabla \cdot \mathbf{j} \quad (8.2)$$

The local average density is calculated from the composition C as, $\rho = C\rho_1 + (1 - C)\rho_2$. If the diffusive flow rate is related to the local composition of two components [Lee, 2009], $\mathbf{j}_1 = -\mathbf{j}_2 = \mathbf{j}$, it yields $\nabla \cdot \mathbf{u} = 0$. This condition is only approximately satisfied in the LBE method at low mach number.

In the convective Cahn-Hilliard equation the diffusive flow-rate is assumed to be proportional to a thermodynamic driving force, which is also proportional to the gradient of the chemical potential [Jacqmin, 1996]. This is expressed as,

$$\mathbf{j} = -M\nabla\mu \quad (8.3)$$

where $M > 0$ is the mobility coefficient.

Furthermore, it is assumed that the interactions between the liquid-gas interface and the solid surface are of short-range and appear as a surface integral in the total free energy [Genies, 1985], which takes the following form,

$$\Psi_b + \Psi_s = \int_V \left(E_0(C) + \frac{\kappa}{2} |\nabla C|^2 \right) dV + \int_S (\phi_0 - \phi_1 C_s + \phi_2 C_s^2 - \phi_3 C_s^3 + \dots) dS \quad (8.4)$$

where the bulk energy is defined as $E_0(C) = \beta C^2(C - 1)^2$, κ is the gradient parameter and β is a constant. C_s is the composition at the solid surface, and typically differs from the bulk or equilibrium composition. Finally, ϕ_i with $i = 0, 1, 2, \dots$ are constant coefficients.

The equilibrium profile is determined such that the energy is minimized and reads $\mu = \mu_0 - \kappa \nabla^2 C = \text{constant}$, where $\mu_0 = \partial E_0 / \partial C$ is the classical part of a chemical potential.

The solution to above energy minimization problem for a planar interface at equilibrium is given by an interface profile described by the following equation,

$$C(z) = \frac{1}{2} + \frac{1}{2} \tanh \frac{2z}{\xi} \quad (8.5)$$

where z is the coordinate normal to the plane, ξ is the (numerical) interface thickness, which is often chosen based on accuracy and stability of the simulation.

Given ξ and β , the gradient parameter κ and the surface tension force σ can be computed as,

$$\kappa = \frac{\beta\xi^2}{8} \quad (8.6)$$

$$\sigma = \int \sqrt{2\kappa E_0(C)} \cdot dC = \frac{\sqrt{2\kappa\beta}}{6} \quad (8.7)$$

Therefore, the behavior of the system out of equilibrium is dictated by the evolution equation for the composition C ,

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = M \nabla^2 \mu \quad (8.8)$$

The Cahn-Hilliard (CH) equation (Eq. 8.8) describes the two phases and their interfaces. In essence, it characterizes the composition of the binary fluid mixture within the domain across both space and time.

On the other hand, the flow kinematics of the mixture is described by Navier-Stokes (NS) equation described in the following form,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (8.9)$$

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \nabla \cdot \eta [\nabla \mathbf{u} + \nabla \mathbf{u}^T] + \rho \mathbf{g} + \mathbf{F}_\sigma \quad (8.10)$$

Here, p is the hydrodynamic pressure, $\eta = \rho c_s^2 \lambda$ is the dynamic viscosity, $\mathbf{F}_\sigma$ is the surface tension force (modeled as $C \nabla \mu$) and $\rho \mathbf{g}$ is a gravitational force acting on the fluid.

The coupling between the two equations happens through the velocity $\mathbf{u}$, which solved from the NS equations and fed back into the CH equation. The CH equation is then used to solve for the composition C which relates that to the density (ρ), and is fed back into the NS equations. Due to the nature of LBM and kinetic gas theory

where pressure and density are related, to achieve this coupling the NS equations for mass and momentum (Eq. 8.9, 8.10) are transformed into the pressure evolution and momentum equations [He et al., 1999, Lee and Lin, 2005],

$$\frac{\partial p}{\partial t} + \rho c_s^2 \nabla \cdot \mathbf{u} = 0 \quad (8.11)$$

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p - C \nabla \mu + \nabla [\rho c_s^2 \lambda \cdot (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)] \quad (8.12)$$

where $\rho c_s^2 \lambda$ is defined as the dynamic viscosity η . Eq. 8.11 can be derived from the continuity equation with the following relationship of pressure and density, $\partial p / \partial \rho = c_s^2$ and assuming that $\mathbf{u} \cdot \nabla p \sim O(Ma^3)$ is negligible [Lee and Lin, 2003].

8.1.2 Discrete Boltzmann equations

The above described model is based around the LBM framework. The discrete Boltzmann equation (DBE) is used to describe the evolution of the particle distribution function over time and space [He and Luo, 1997, He et al., 1998, He et al., 1999, Lee, 2009],

$$\frac{Df_\alpha}{Dt} = \left(\frac{\partial}{\partial t} + \mathbf{e}_\alpha \cdot \nabla \right) f_\alpha = -\frac{1}{\lambda} (f_\alpha - f_\alpha^{eq}) + \frac{1}{c_s^2} (\mathbf{e}_\alpha - \mathbf{u}) \cdot \mathbf{F} \Gamma_\alpha \quad (8.13)$$

where f_α is the particle distribution function, $\mathbf{e}_\alpha$ is the α -direction microscopic particle velocity, ρ is the mixture density, $\mathbf{u}$ is the volume averaged velocity, c_s is the speed of sound, λ is the relaxation time, $\mathbf{F}$ is source/sink terms to simulate forces.

The equilibrium distribution function f_α^{eq} is described as,

$$f_\alpha^{eq} = w_\alpha \rho \left[1 + \frac{\mathbf{e}_\alpha \cdot \mathbf{u}}{c_s^2} + \frac{(\mathbf{e}_\alpha \cdot \mathbf{u})^2}{2c_s^4} - \frac{(\mathbf{u} \cdot \mathbf{u})}{2c_s^2} \right] \quad (8.14)$$

where w_α is the weights [Qian and Chen, 2000, Sukop and Thorne, 2006], and $\Gamma_\alpha = \Gamma_\alpha(\mathbf{u}) = f_{eq}/\rho$. Applying the Chapman-Enskog expansion on the DBE allows for retrieval of various advection-diffusion equations. For instance, the set of NS

equations is obtained by using the zeroth-order-moment expansion for mass conservation and the first-order-moment expansion for momentum conservation. Typically, The particle collision, $\frac{1}{\lambda} (f_\alpha - f_\alpha^{eq})$, models the effect of viscosity/ diffusivity on the system. The relaxation time (λ), is directly related to the viscosity/ diffusivity based on kinetic theory of gases.

To simulate high viscosity ratios, the equilibrium distribution function f_α^{eq} is modified to decouple the relationship between the collision operator and the fluid's viscosity. This modification is based on the work of Banari et al. [Banari et al., 2014a],

$$f_\alpha^{eq} = w_\alpha \rho \cdot \left[1 + \frac{\mathbf{e}_\alpha \cdot \mathbf{u}}{c_s^2} + \frac{(\mathbf{e}_\alpha \cdot \mathbf{u})^2}{2c_s^4} - \frac{(\mathbf{u} \cdot \mathbf{u})}{2c_s^2} + \frac{1}{2c_s^2} (\lambda - 0.5) \left(\frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial u_\alpha}{\partial x_\beta} \right) \mathbf{e}_\alpha \mathbf{e}_\beta \right] \quad (8.15)$$

For all simulations in this work, the value of λ was chosen to be 1. The introduction of this extra term effectively removes the direct modeling of viscosity through the collisions in the Boltzmann equation. To preserve the NS equation, the viscous forces $\rho\eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)$ must be reintroduced as a separate source term as demonstrated in Eq. 8.17 and 8.19).

By adopting this approach, the model achieves stability while accurately representing high viscosity ratios in the simulation. The decoupling of the collision operator and the reintroduction of the viscosity term as a separate source term strike a balance between stability and preserving the essential features of the NS equation for accurate fluid flow simulations.

8.1.2.1 Navier-Stokes

The transformation of the DBE (Eq. 8.13, 8.14) from simulating the mass and momentum, to simulating the pressure evolution and momentum equations was accomplished by following the approach presented by Lee et al. [Lee and Liu, 2010]. First, a new equilibrium distribution function was considered as,

$$g_\alpha^{eq} = f_\alpha^{eq} c_s^2 + (p - \rho c_s^2) \Gamma_\alpha(0) \quad (8.16)$$

Taking the total derivative $D_t = (\partial_t + \mathbf{e}_\alpha \cdot \nabla)$ of the new variable g_α establishes the new DBE for the NS equations [Lee, 2009],

$$\begin{aligned} \frac{\partial g_\alpha}{\partial t} + \mathbf{e}_\alpha \cdot \nabla g_\alpha = & -\frac{1}{\lambda} (g_\alpha - g_\alpha^{eq}) + (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla \rho c_s^2 (\Gamma_\alpha - \Gamma_\alpha(0)) \right. \\ & \left. - (C \nabla \mu - \rho \mathbf{g} - \nabla \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)) \Gamma_\alpha \right] \end{aligned} \quad (8.17)$$

To derive the above equation, it is assumed that the hydrodynamic pressure, $p \sim O(Ma^2)$, and its gradient $(\mathbf{e}_\alpha - \mathbf{u}) \cdot \nabla p (\Gamma_\alpha - \Gamma_\alpha(0)) \sim O(Ma^3)$ in the case of low Mach number where, $Ma = |\mathbf{u}|/c_s$.

It can be shown that applying the Chapman-Enskog expansion to Eq. 8.17, recovers the governing equations for the pressure evolution and momentum equation as shown in Eqs. 8.11, 8.12.

8.1.2.2 Cahn-Hilliard

The composition (or order parameter) C is calculated using a second DBE, where the particle distribution function h_α is related to f_α as,

$$h_\alpha^{eq} = \left(\frac{C}{\rho} \right) f_\alpha^{eq} \quad (8.18)$$

Taking the total derivative of h_α as well as approximating $f_\alpha^{eq} = \rho \Gamma_\alpha$ and assuming $\nabla \cdot \mathbf{u} = 0$, establishes the new DBE as,

$$\begin{aligned} \frac{\partial h_\alpha}{\partial t} + \mathbf{e}_\alpha \cdot \nabla h_\alpha = & -\frac{1}{\lambda} (h_\alpha - h_\alpha^{eq}) + M \nabla^2 \mu_c \Gamma_\alpha \\ & + (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla C - \frac{C}{\rho c_s^2} (\nabla p + C \nabla \mu + \rho \mathbf{g} + \nabla \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)) \right] \Gamma_\alpha \end{aligned} \quad (8.19)$$

Applying the Chapman-Enskog expansion to the above equation (Eq. 8.19) recovers the Cahn-Hilliard equation (Eq. 8.8). For a detailed description and derivation of DBEs used in the model, please refer to the works of Lee et al. [Lee and Liu, 2010, Lee and Lin, 2005, Lee and Fischer, 2006, Lee, 2009].

8.2 Discretization

8.2.1 Spatial gradients

Spatial gradients were determined following the methodology established by Lee et al. in their work [Lee and Liu, 2010]. The directional derivative of any variable (denoted here as ϕ) was computed at a discrete lattice point represented as $\mathbf{x}$ by considering the values of ϕ at neighboring integer lattice locations. This computation employed a second-order mixed difference (MD) approximation.

The second-order central difference (CD) approximation of the directional derivative of a variable ϕ was expressed as,

$$\delta t \mathbf{e}_\alpha \cdot \nabla^{CD} \phi|_{(\mathbf{x})} = \frac{1}{2} [\phi(\mathbf{x} + \mathbf{e}_\alpha \delta t) - \phi(\mathbf{x} - \mathbf{e}_\alpha \delta t)] \quad (8.20)$$

Lee et al. [Lee and Liu, 2010] introduced a discretization method for ϕ using the biased difference (BD) approach. This was derived using a Taylor series expansion and is represented as:

$$\delta t \mathbf{e}_\alpha \cdot \nabla^{BD} \phi|_{(\mathbf{x})} = \frac{1}{2} [-\phi(\mathbf{x} + 2\mathbf{e}_\alpha \delta t) + 4\phi(\mathbf{x} + \mathbf{e}_\alpha \delta t) - 3\phi(\mathbf{x})] \quad (8.21)$$

The second order MD approximation is an average of the central and biased differences,

$$\delta t \mathbf{e}_\alpha \cdot \nabla^{MD} \phi|_{(\mathbf{x})} = \frac{1}{2} [\delta t \mathbf{e}_\alpha \cdot \nabla^{BD} \phi + \delta t \mathbf{e}_\alpha \cdot \nabla^{CD} \phi]|_{(\mathbf{x})} \quad (8.22)$$

The second order approximation of the second directional derivative of ϕ was also defined in [Lee and Liu, 2010] as,

$$(\delta t \mathbf{e}_\alpha \cdot \nabla)^2 \phi|_{(\mathbf{x})} = [\phi(\mathbf{x} + \mathbf{e}_\alpha \delta t) - 2\phi(\mathbf{x}) + \phi(\mathbf{x} - \mathbf{e}_\alpha \delta t)] \quad (8.23)$$

Furthermore, it is possible to obtain the gradient of ϕ from its directional derivative by taking first-moment of the directional derivatives with suitable weighting to ensure isotropy. These are written as:

$$\nabla^{BD} \phi|_{(\mathbf{x})} = \frac{1}{c_s^2 \delta t} \sum_{\alpha \neq 0} w_\alpha \mathbf{e}_\alpha (\delta t \mathbf{e}_\alpha \cdot \nabla^{BD}) \phi|_{(\mathbf{x})} \quad (8.24)$$

$$\nabla^{CD} \phi|_{(\mathbf{x})} = \frac{1}{c_s^2 \delta t} \sum_{\alpha \neq 0} w_\alpha \mathbf{e}_\alpha (\delta t \mathbf{e}_\alpha \cdot \nabla^{CD}) \phi|_{(\mathbf{x})} \quad (8.25)$$

$$\nabla^{MD} \phi|_{(\mathbf{x})} = \frac{1}{2} [\nabla^{BD} \phi + \nabla^{CD} \phi]|_{(\mathbf{x})} \quad (8.26)$$

$$\nabla^2 \phi|_{(\mathbf{x})} = \frac{1}{c_s^2 \delta t} \sum_{\alpha \neq 0} w_\alpha (\delta t \mathbf{e}_\alpha \cdot \nabla)^2 \phi|_{(\mathbf{x})} \quad (8.27)$$

8.2.2 Lattice Boltzmann equations

To solve the DBEs represented by Eq. 8.17 and Eq. 8.19, a discretization approach is employed along the characteristics with a time step of δt . In a prior works by Lee et al. [Lee, 2009], it was demonstrated that the temporal integration over the interval $[t, t + \delta t]$ is coupled with the spatial integration over the domain $[\mathbf{x}, \mathbf{x} + \mathbf{e}_\alpha \delta t]$. Furthermore, through a Chapman-Enskog analysis, it was established that the trapezoidal rule is necessary for integration to avoid introducing any spurious derivatives into the system while retaining second-order accuracy.

Consequently, the LBE for Eq. 8.17 is derived as follows,

$$\begin{aligned}
g_\alpha(\mathbf{x}, t) = & g_\alpha(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t) - \frac{g_\alpha - g_\alpha^{eq}}{2\lambda} \Big|_{(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t)} - \frac{g_\alpha - g_\alpha^{eq}}{2\lambda} \Big|_{(\mathbf{x}, t)} \\
& + \frac{\delta t}{2} (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla^{BD} \rho c_s^2 (\Gamma_\alpha - \Gamma_\alpha(0)) \right. \\
& \left. - (C \nabla^{BD} \mu - \rho \mathbf{g} - \nabla^{BD} \eta (\nabla^{BD} \mathbf{u} + (\nabla^{BD} \mathbf{u})^T)) \Gamma_\alpha \right]_{(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t)} \\
& + \frac{\delta t}{2} (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla^{BD} \rho c_s^2 (\Gamma_\alpha - \Gamma_\alpha(0)) \right. \\
& \left. - (C \nabla^{BD} \mu - \rho \mathbf{g} - \nabla^{BD} \eta (\nabla^{BD} \mathbf{u} + (\nabla^{BD} \mathbf{u})^T)) \Gamma_\alpha \right]_{(\mathbf{x}, t)}
\end{aligned} \tag{8.28}$$

By defining $\bar{g}_\alpha$ and $\bar{g}_\alpha^{eq}$ as modified particle and equilibrium distribution functions, respectively,

$$\begin{aligned}
\bar{g}_\alpha = & g_\alpha + \frac{1}{2\lambda} (g_\alpha - g_\alpha^{eq}) - \frac{\delta t}{2} (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla^{CD} \rho c_s^2 (\Gamma_\alpha - \Gamma_\alpha(0)) \right. \\
& \left. - (C \nabla^{CD} \mu - \rho \mathbf{g} - \nabla^{CD} \eta (\nabla^{CD} \mathbf{u} + (\nabla^{CD} \mathbf{u})^T)) \Gamma_\alpha \right]
\end{aligned} \tag{8.29}$$

$$\begin{aligned}
\bar{g}_\alpha^{eq} = & g_\alpha^{eq} - \frac{\delta t}{2} (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla^{CD} \rho c_s^2 (\Gamma_\alpha - \Gamma_\alpha(0)) \right. \\
& \left. - (C \nabla^{CD} \mu - \rho \mathbf{g} - \nabla^{CD} \eta (\nabla^{CD} \mathbf{u} + (\nabla^{CD} \mathbf{u})^T)) \Gamma_\alpha \right]
\end{aligned} \tag{8.30}$$

Eq. 8.28 can be recast into a simpler form,

$$\begin{aligned}
\bar{g}_\alpha(\mathbf{x}, t) = & \bar{g}_\alpha(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t) - \frac{1}{\lambda + 1/2} (\bar{g}_\alpha - \bar{g}_\alpha^{eq}) \Big|_{(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t)} \\
& + \delta t (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla^{MD} \rho c_s^2 (\Gamma_\alpha - \Gamma_\alpha(0)) \right. \\
& \left. - (C \nabla^{MD} \mu - \rho \mathbf{g} - \nabla^{MD} \eta (\nabla^{MD} \mathbf{u} + (\nabla^{MD} \mathbf{u})^T)) \Gamma_\alpha \right]_{(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t)}
\end{aligned} \tag{8.31}$$

Similarly, the LBE for Eq. 8.19 is derived as follows,

$$\begin{aligned}
h_\alpha(\mathbf{x}, t) = & h_\alpha(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t) - \frac{h_\alpha - h_\alpha^{eq}}{2\lambda} \Big|_{(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t)} - \frac{h_\alpha - h_\alpha^{eq}}{2\lambda} \Big|_{(\mathbf{x}, t)} \\
& + \delta t M \nabla^2 \mu \Gamma_\alpha \Big|_{(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t)} + \frac{\delta t}{2} (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla^{BD} C - \frac{C}{\rho c_s^2} (\nabla^{BD} p \right. \\
& + C \nabla^{BD} \mu + \rho \mathbf{g} + \nabla^{BD} \eta (\nabla^{BD} \mathbf{u} + (\nabla^{BD} \mathbf{u})^T)) \Big] \Gamma_\alpha \Big|_{(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t)} \\
& + \frac{\delta t}{2} (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla^{BD} C - \frac{C}{\rho c_s^2} (\nabla^{BD} p \right. \\
& + C \nabla^{BD} \mu + \rho \mathbf{g} + \nabla^{BD} \eta (\nabla^{BD} \mathbf{u} + (\nabla^{BD} \mathbf{u})^T)) \Big] \Gamma_\alpha \Big|_{(\mathbf{x}, t)}
\end{aligned} \tag{8.32}$$

The modified particle and equilibrium distribution functions for h are defined as,

$$\begin{aligned}
\bar{h}_\alpha = & h_\alpha + \frac{1}{2\lambda} (h_\alpha - h_\alpha^{eq}) - \frac{\delta t}{2} (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla^{CD} C - \frac{C}{\rho c_s^2} (\nabla^{CD} p \right. \\
& + C \nabla^{CD} \mu + \rho \mathbf{g} + \nabla^{CD} \eta (\nabla^{CD} \mathbf{u} + (\nabla^{CD} \mathbf{u})^T)) \Big] \Gamma_\alpha
\end{aligned} \tag{8.33}$$

$$\begin{aligned}
\bar{h}_\alpha^{eq} = & h_\alpha^{eq} - \frac{\delta t}{2} (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla^{CD} C - \frac{C}{\rho c_s^2} (\nabla^{CD} p \right. \\
& + C \nabla^{CD} \mu + \rho \mathbf{g} + \nabla^{CD} \eta (\nabla^{CD} \mathbf{u} + (\nabla^{CD} \mathbf{u})^T)) \Big] \Gamma_\alpha
\end{aligned} \tag{8.34}$$

Therefore, the LBE for Eq. 8.32 then becomes,

$$\begin{aligned}
\bar{h}_\alpha(\mathbf{x}, t) = & \bar{h}_\alpha(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t) - \frac{1}{\lambda + 1/2} (\bar{h}_\alpha - \bar{h}_\alpha^{eq}) \Big|_{(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t)} \\
& + \delta t M \nabla^2 \hat{\mu} \Gamma_\alpha \Big|_{(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t)} + \delta t (\mathbf{e}_\alpha - \mathbf{u}) \cdot \left[\nabla^{MD} C \right. \\
& - \frac{C}{\rho c_s^2} (\nabla^{MD} p + C \nabla^{MD} \mu + \rho \mathbf{g} + \nabla^{MD} \eta (\nabla^{MD} \mathbf{u} + (\nabla^{MD} \mathbf{u})^T)) \Big] \Gamma_\alpha \Big|_{(\mathbf{x} - \mathbf{e}_\alpha \delta t, t - \delta t)}
\end{aligned} \tag{8.35}$$

8.2.3 Macroscopic equations

The composition, dynamic pressure and momentum can be computed by taking the zeroth and first moments of the modified particle distribution functions.

$$C = \sum_{\alpha} \bar{h}_{\alpha} + \left(\frac{\delta t}{2} \cdot M \nabla^2 \mu\right) \quad (8.36)$$

$$\rho \mathbf{u} = \frac{1}{c_s^2} \sum_{\alpha} \mathbf{e}_{\alpha} \bar{g}_{\alpha} - \frac{\delta t}{2} (C \nabla^{CD} \mu_c + \rho g + \nabla^{CD} \eta (\nabla^{CD} \mathbf{u} + (\nabla^{CD} \mathbf{u})^T) - \nabla^{CD} p) \quad (8.37)$$

$$p = \sum_{\alpha} \bar{g}_{\alpha} + \frac{\delta t}{2} \mathbf{u} \cdot \nabla^{CD} \rho c_s^2 \quad (8.38)$$

The density can be calculated using the following relation,

$$\rho(C) = C \rho_1 + (1 - C) \rho_2 \quad (8.39)$$

8.2.4 Boundary conditions

The most commonly used boundary condition in LBM schemes is the standard bounce-back boundary condition. This boundary condition is particularly straightforward to apply and are thus well-suited for simulating fluid dynamics within domains characterized by intricate geometries [Sukop and Thorne, 2006]. In a standard LBM simulation, the first-order moment is tied to macroscopic velocities. Therefore, to enforce no-slip boundary conditions along solid walls (where velocities are zero), the unknown particle distribution functions are computed using conventional bounce-back schemes. Instead of the regular collision, the distribution function is bounced back (or mirrored) at the boundaries.

However, in coupled two-distribution-function LBM simulations like this CH-NS solver, using standard bounce-back techniques becomes challenging. This is due to the coupling between distribution functions through macroscopic variables. Simply

applying bounce-back to both functions does not adequately satisfy macroscopic boundary conditions.

The Zou-He method enhances the accuracy of wall boundary conditions compared to standard bounce back schemes and also allows for the implementation of inlet and outlet boundary conditions, essential for describing fluid flow within finite domains. The Zou-He boundary condition is rooted in the concept of bouncing back the non-equilibrium part of the distribution function. This approach allows the calculation of unknown particles of the distribution function based on the knowledge of macroscopic variables at the boundaries. These boundary macroscopic variables can be determined using either Dirichlet or Neumann boundary conditions.

8.2.4.1 Wall boundaries

For the wall boundaries, all interior solid nodes are treated as outside-the-domain. The interfacial solid/fluid nodes in the normal direction to the curvature of the solid boundary are then identified and the boundary conditions are applied on these nodes to model the fluid interaction with the solid.

The boundary condition for the CH equation to capture the fluid composition and the behavior of the binary fluid interface at the solid boundary was modeled using the cubic boundary condition defined in the work of Lee et al. [Liu and Lee, 2009, Lee and Liu, 2010, Connington and Lee, 2013]. The solution to Eqs. 8.1- 8.3 requires two boundary conditions. First, the linear boundary condition for $\nabla^2\mu$ ensures no mass flux due to the chemical potential gradient normal to the solid boundary [Yan and Zu, 2007, Briant and Yeomans, 2004],

$$\hat{\mathbf{n}} \cdot \nabla \mu_c|_s = 0 \quad (8.40)$$

where $\hat{\mathbf{n}}$ is the unit normal vector. Second, the boundary conditions for $\nabla^2 C$ can be established by minimizing the total free energy subject to the specified wall free

energy,

$$\hat{\mathbf{n}} \cdot \nabla C|_s = \frac{\phi_c}{\kappa} (C_s - C_s^2) \quad (8.41)$$

The dimensionless wetting potential Ω_c ,

$$\Omega_c = \phi_c / \sqrt{2\kappa\beta} \quad (8.42)$$

which is related to the equilibrium contact angle θ^{eq} due to Young's law, as,

$$\cos \theta^{eq} = \frac{\sigma_{s2} - \sigma_{s1}}{\sigma_{21}} = -\Omega_c \quad (8.43)$$

Once Eq. 8.41 is imposed, $\mu = \mu_0 - \kappa \nabla^2 C$ is treated as a scalar. The derivation of the cubic boundary condition for van der Waals fluids can be found in [Liu and Lee, 2009].

To ensure no slip boundary condition for the NS equations at these interfacial nodes, the other macroscopic variables are specified. All components of velocity are specified as zero (Dirichlet condition). The pressure is calculated as a zero gradient across the interface (Neumann condition),

$$\mathbf{n} \cdot \nabla p|_s = 0 \quad (8.44)$$

8.2.4.2 Inlet and Outlet boundaries

For the constant velocity inflow boundary condition, the composition and velocity were defined using the Dirichlet condition, while the pressure was defined using the zero gradient Neumann condition. On the other hand, for the outflow boundary condition, the pressure was defined using the Dirichlet condition, while the order parameter and velocity were defined using the zero gradient Neumann boundary conditions. By incorporating these boundary conditions, the simulation accurately represents the inflow and outflow dynamics, ensuring that the fluid properties at the domain boundaries are appropriately accounted for, thus providing a more comprehensive and realistic simulation of the fluid system.

8.2.4.3 Treatment of gradients at boundaries

In order to calculate gradients of any variable at boundary nodes, the profile ϕ , of any macroscopic variable, in the solid is taking the mirror image of ϕ in the fluid particle. Calculating the first and second order derivatives at the boundary when $\mathbf{x}_s + \mathbf{e}_\alpha \delta t$ and $\mathbf{x}_s + 2\mathbf{e}_\alpha \delta t$ are located outside the computational domain while $\mathbf{x}_s - \mathbf{e}_\alpha \delta t$ and $\mathbf{x}_s - 2\mathbf{e}_\alpha \delta t$ are not, any unknown variable outside the fluid domain is approximated by,

$$\phi(\mathbf{x}_s + \mathbf{e}_\alpha \delta t) = \phi(\mathbf{x}_s - \mathbf{e}_\alpha \delta t) \quad (8.45)$$

$$\phi(\mathbf{x}_s + 2\mathbf{e}_\alpha \delta t) = \phi(\mathbf{x}_s - 2\mathbf{e}_\alpha \delta t) \quad (8.46)$$

The directional derivatives in the normal direction $\mathbf{e}_\alpha$ are then,

$$\delta t \mathbf{e}_\alpha \cdot \nabla^{CD} \phi|_{(x)} = 0 \quad (8.47)$$

$$\delta t \mathbf{e}_\alpha \cdot \nabla^{BD} \phi|_{(x_s)} = \frac{1}{2} [-\phi(\mathbf{x}_s - 2\mathbf{e}_\alpha \delta t) + 4\phi(\mathbf{x}_s - \mathbf{e}_\alpha \delta t) - 3\phi(\mathbf{x}_s)] \quad (8.48)$$

$$\delta t \mathbf{e}_\alpha \cdot \nabla^{MD} \phi|_{(x_s)} = \frac{1}{2} [\delta t \mathbf{e}_\alpha \cdot \nabla^{BD} \phi + \delta t \mathbf{e}_\alpha \cdot \nabla^{CD} \phi]_{\mathbf{x}} \quad (8.49)$$

8.2.4.4 Zou He boundary conditions for PDFs

The macroscopic variables were determined based on the specific boundary conditions appropriate for each problem. Depending on the nature of the boundary condition, either a Dirichlet or Neumann condition was employed, wherein a prescribed value ($\phi = \text{const}$) or the gradient of the value normal to the boundary is defined ($\mathbf{n} \cdot \nabla \phi = \text{const}$), respectively. When Neumann conditions were used, the values were computed using forward or backward difference schemes. To translate the information to the

distribution functions, the equilibrium functions are recalculated using the updated values.

For an inlet node on a D2Q9 lattice, f_0 to f_5 (see Figure 8.1) are known, after streaming from previous time step, and the unknowns are f_6, f_7, f_8 . It is assumed that the bounce back rule is still applicable for the non-equilibrium part of the particle distribution at the boundary nodes based on the Zou-He boundary condition [Zou and He, 1997]. Hence $f_6 - f_6^{eq} = f_2 - f_2^{eq}$, $f_7 - f_7^{eq} = f_1 - f_1^{eq}$ and $f_8 - f_8^{eq} = f_0 - f_0^{eq}$. This system of equations is then solved to update all values of the distribution function. Using the updated values, regular collision and streaming can be carried out as usual.

8.3 Algorithm

In this work, the CH-NS coupled model solved using LBM is demonstrated for a two-dimensional problem. Therefore, a D2Q9 lattice is used as shown in Figure 8.1. The model's algorithm is presented in Algorithm 1. The boundary conditions consist of constant velocity inlets and zero pressure outflow boundaries based on Zou-He [Zou and He, 1997] conditions. The solid-fluid interactions at walls are defined by the contact angle as described in the works Lee et al. [Lee and Liu, 2010, Liu and Lee, 2009].

8.4 Numerical tests

In this section results from typical bench-marking Computational Fluid Dynamics (CFD) problems involving two-phase flows are presented. These bench-marking cases demonstrate the effectiveness and reliability of the proposed model in accurately simulating complex two-phase fluid interactions and interfaces with high-density and viscosity ratios. The results are categorized into four model validation sections. The initial test shows simulations for a stable bubble. These simulations effectively

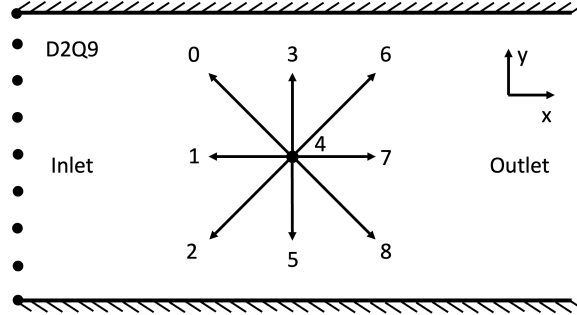


Figure 8.1: Schematic plot of velocity directions of the D2Q9 stencil in a channel.

Algorithm 1 Coupled CH-NS LBM algorithm for two-fluids

Initialize all reference values ($\rho_0, \delta x, U_{LB}, Re, Pe, \sigma, W, \rho_1/\rho_2, \eta_1/\eta_2$)
Initialize domain, identify solid nodes and boundary nodes
Initialize the phase field C , density ρ , velocity $\mathbf{u}$ and pressure p using initial conditions
Calculate chemical potential for the given conditions
Initialize particle distribution functions, g_α and h_α
for $t < t_{end}$ **do**
 Compute collision and streaming for $h_\alpha(\mathbf{x}, t + \delta t)$ using Eq. 8.18, 8.33-8.35
 Compute collision and streaming for $g_\alpha(\mathbf{x}, t + \delta t)$ using Eq. 8.16, 8.29-8.31
 Calculate $C(\mathbf{x}, t + \delta t)$ and $\rho(\mathbf{x}, t + \delta t)$ using Eq. 8.36 and Eq. 8.39
 Calculate $p(\mathbf{x}, t + \delta t)$ and $\mathbf{u}(\mathbf{x}, t + \delta t)$ using Eq. 8.38 and Eq. 8.37
 Update chemical potential for the given conditions
 Set boundary conditions for $p, \mathbf{u}, C$, and ρ
end for

demonstrate how the model minimizes free surface energy of the interface and validates that the pressure reaches an equilibrium to balance surface tension forces. The subsequent test cases illustrate the model’s proficiency in accurately capturing fluid interfaces with solid boundaries, as well as its ability to effectively represent different wetting conditions based on the contact angle. Thereafter, it is the model’s capability to simulate dynamic behavior within a finite domain, featuring an inlet and outlet boundary condition is shown. Finally, the model’s ability to simulate bubble dynamics with fluid-solid interactions is demonstrated by simulating a test case for bubble detachment inside a channel.

8.4.1 Stationary bubble

The first benchmarking test simulated a stationary bubble of lighter fluid inside a heavier fluid and vice versa, in the absence of gravity. These simulations demonstrate how the model minimizes free surface energy of the interface. The simulation was started from an initial state of rest filled with a fluid and a central elliptic region filled with the other fluid of different density. As expected, the elliptic bubble or droplet gradually relaxed to form a circle due to surface tension, as the simulation approaches the steady-state. The transformation from an elliptical shape to a circular shape indicates that the bubble has reached a stable state, and the forces acting on it have reached a balance.

In Figure 8.2, the results show the evolution of the bubble’s shape during the simulation. In Figure 8.2a, the initial shape of the bubble is depicted as elliptical. As the simulation progresses, Figure 8.2b illustrates the final equilibrium shape of the bubble, which has evolved into a perfect circle. This equilibrium shape is observed at a time step of 100000. Figure 8.2c- 8.2d show the density and pressure plots respectively. The dashed lines represent the initial condition while the solid lines represent the final state for the density, hydrodynamic and total pressure. It can be observed that the pressure difference between the inside and outside of the bubble reaches an equilibrium

to balance surface tension forces. This equilibrium state is determined by the Young-Laplace law, which governs the relationship between pressure, curvature, and surface tension at the interface of a fluid system.

For the next simulation the fluids were reversed and a water droplet in air was simulated. Similar to Figure 8.2, Figure 8.3a shows the initial shape of the droplet and Figure 8.3b shows the final shape of the droplet after it has stabilized into a circle at time step 100000. Figure 8.3c-8.3d show the initial and steady state plots across the x-axis through the middle of the domain for density and pressure respectively. For both cases, the pressure inside the bubble/droplet is predicted to be higher than the surrounding. This is expected in order to sustain a spherical structure without imploding. This also verifies that the model is stable for either fluid being dominant.

Young-Laplace's law predicts that, if the two-fluid interface is curved, a pressure jump Δp occurs across it, which is proportional to the radius of the curvature. Therefore, testing multiple simulations with varying bubble diameters allows for the construction of Figure 8.4. This illustrates that Δp increases linearly as $1/r$ increases. The slope of this line gives a value of 2σ , which within 10% error of the simulation input for σ . This validates that the pressure difference obtained from the simulation test cases are accurate.

8.4.2 Contact angle

In this section, a bubble on a solid surface with no gravitational forces was simulated. The fluid interaction with the solid boundary was modeled using the cubic boundary condition described in section 8.2.4 based on the work of Lee et al. [Lee and Liu, 2010, Connington and Lee, 2013]. Figure 8.5 demonstrates three distinct scenarios of contact angles: Figure 8.5a a neutral wetting condition, with a contact angle of 90° , Figure 8.5b a hydrophilic case, with a contact angle close to 45° , and 8.5c a hydrophobic case, with a contact angle close to 135° . This illustrates the model's proficiency in accurately capturing fluid interfaces with solid boundaries,

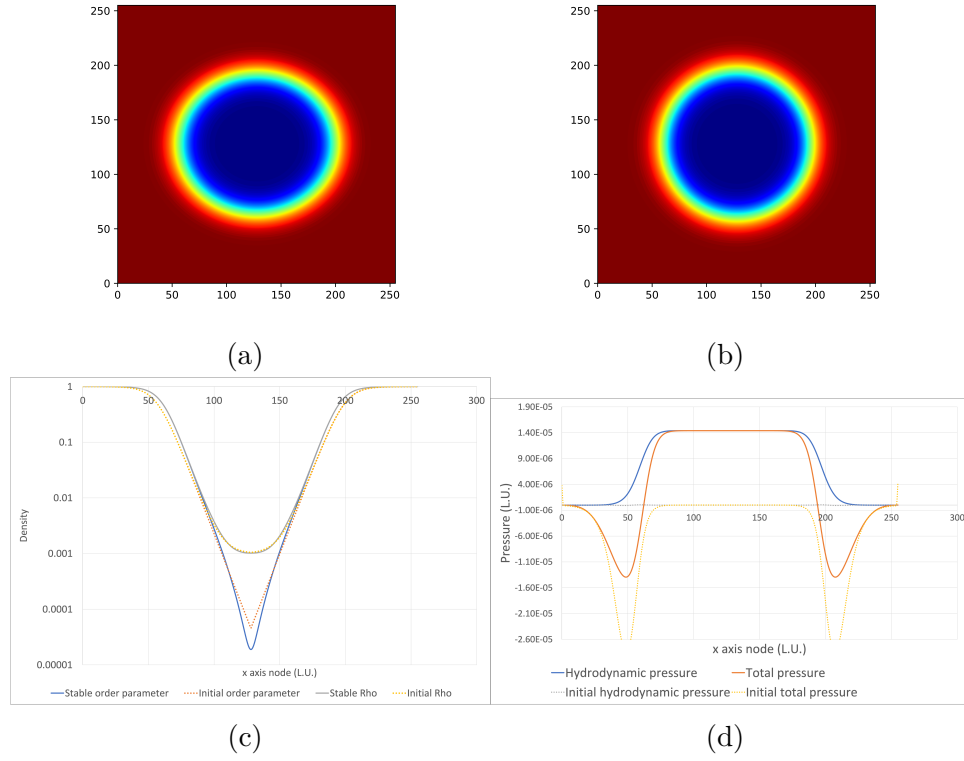


Figure 8.2: Air bubble in water. a) Initial elliptical bubble shape, b) Steady state bubble at timestep 100000, c) initial and steady state density plots along the x-axis through the middle of the bubble, and d) initial and steady state hydrodynamic and total pressure plots along the x-axis through the middle of the bubble.

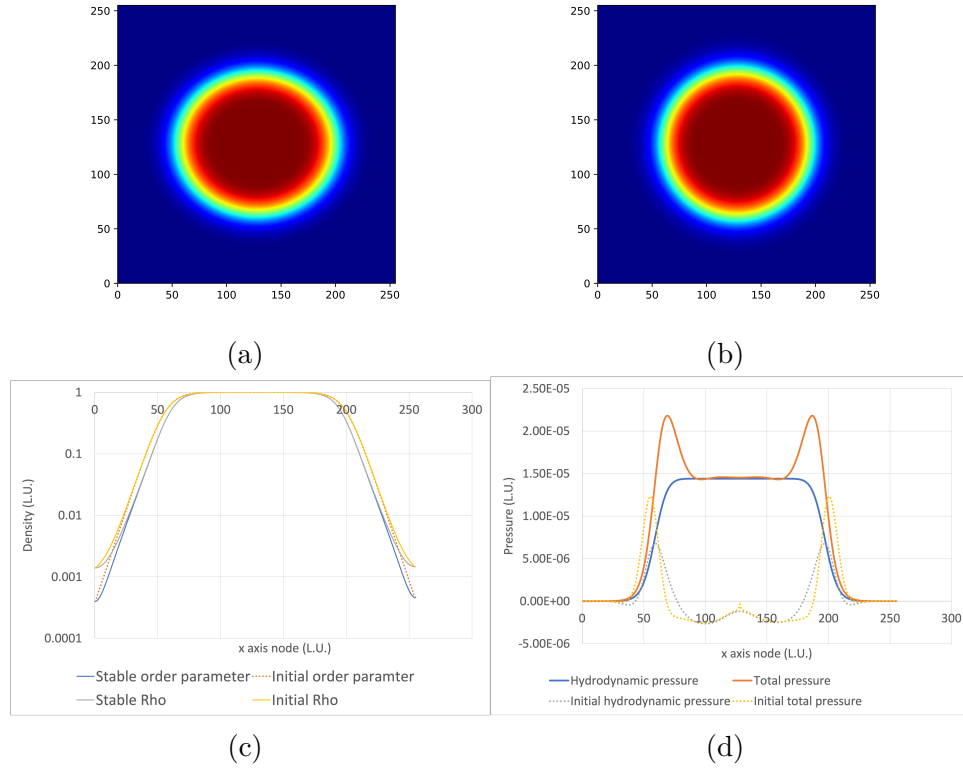


Figure 8.3: Water droplet in air. a) Initial elliptical bubble shape, b) Steady state bubble at time step 100000, c) initial and steady state density plots along the x-axis through the middle of the bubble, and d) initial and steady state hydrodynamic and total pressure plots along the x-axis through the middle of the bubble.

as well as its ability to effectively represent different wetting conditions based on the contact angle input.

8.4.3 A bubble moving across a finite domain

In the following test cases, both an inlet inflow and an outlet outflow boundary condition were introduced. A perfectly circular air bubble was placed into the domain filled with water moving with constant velocity from the inlet (i.e. left hand boundary) and was pushed towards the outlet. For the first case (shown in Figure 8.6) the top and the bottom boundaries had no walls and were set to outflow boundaries along with the outlet on the right hand boundary. The simulation case was for a Reynolds number of 500 with the corresponding Weber number being 1.024. The Péclet number was set to 15041. As the bubble moves forward, the velocity field is seen to stabilize, as the bubble reaches its expected steady state shape [Bhaga and Weber, 1981] of an ellipse, shown in the velocity plots of Figure 8.6. The bubble will continue to exit the domain completely without further change of its shape.

Figure 8.7 shows a similar simulation case – however, the upper and lower boundaries of the domain are replaced with walls. The presence of the walls cause a fully developed boundary layer to form within the domain. Since, the bubble is large enough to where the interface experiences viscous drag forces due the boundary layer, the shape of the bubble now deforms into that of the classic Taylor bubble. This is similar to the slug flow experienced inside the channels of an electrolyzer.

8.4.4 Bubble detachment

The last test case simulates a bubble detaching from the lower wall boundary that is hydrophilic. As shown in Figure 8.8 the bubble initially rests on the surface (Figure 8.8a) and gets washed away by the velocity of the denser fluid in the rest of the domain.

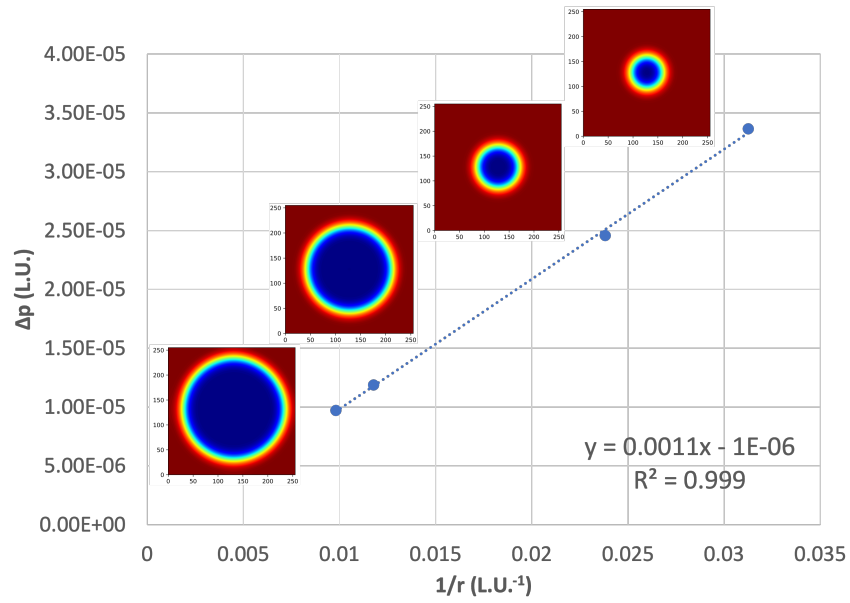


Figure 8.4: Plot of curvature ($1/r$) vs. pressure difference used to determine surface tension in simulations. The data points show a linear trend with a R^2 value of 0.99.

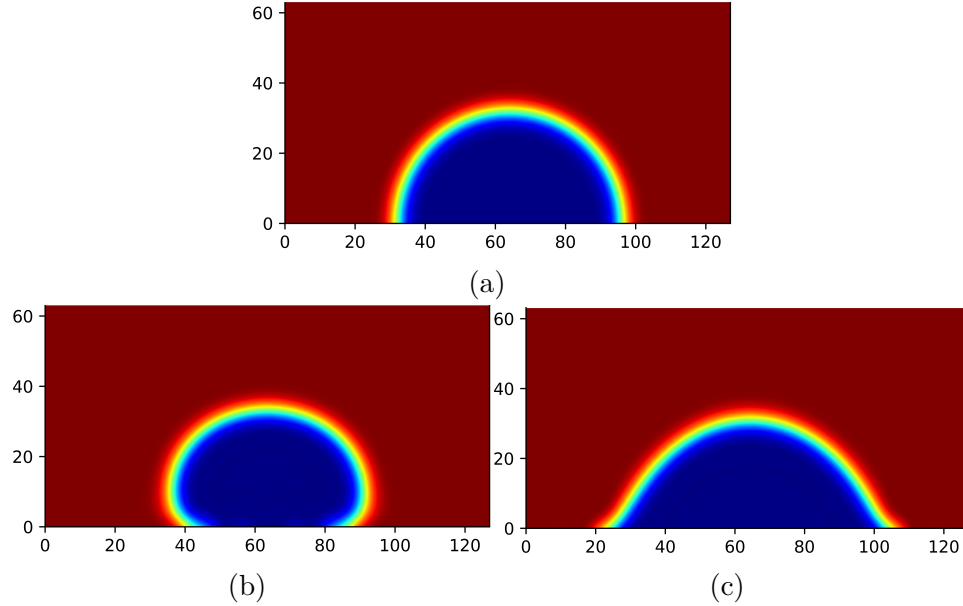


Figure 8.5: Binary fluid wall interaction. Red represents water (denser fluid) and blue represents air (lighter fluid). (a) contact angle of 90° , (b) contact angle close to 45° and (c) a contact angle close to 135°

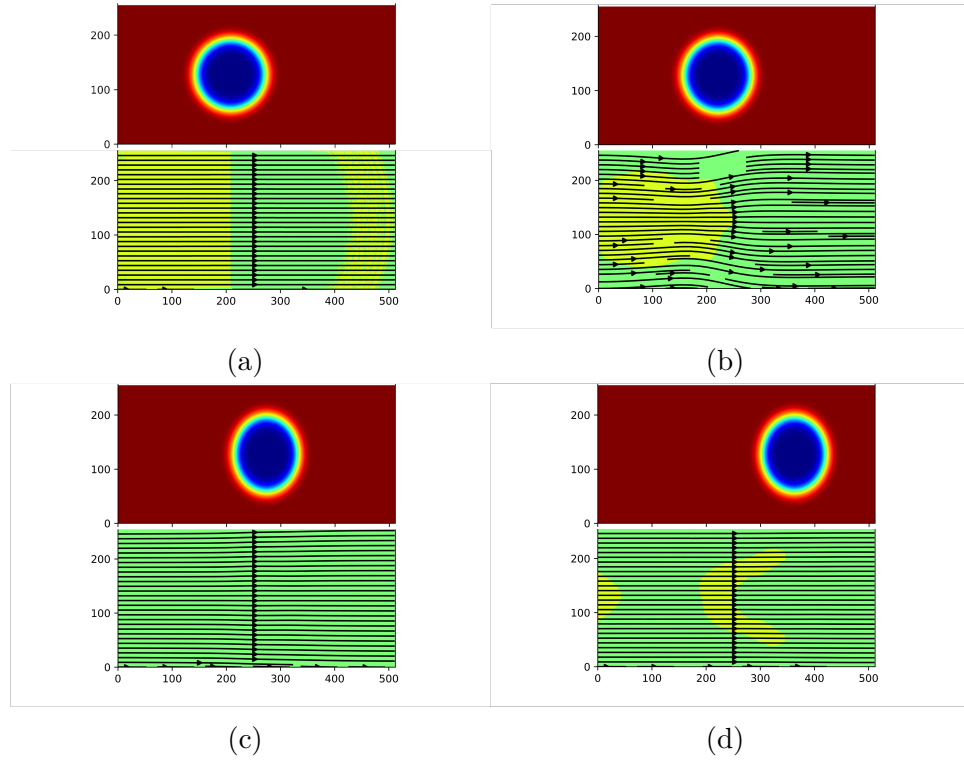


Figure 8.6: Moving bubble through finite domain with no walls in the upper and lower boundary. a) initial time, b) timestep of 6000, c) timestep of 33000 and d) timestep of 78000.

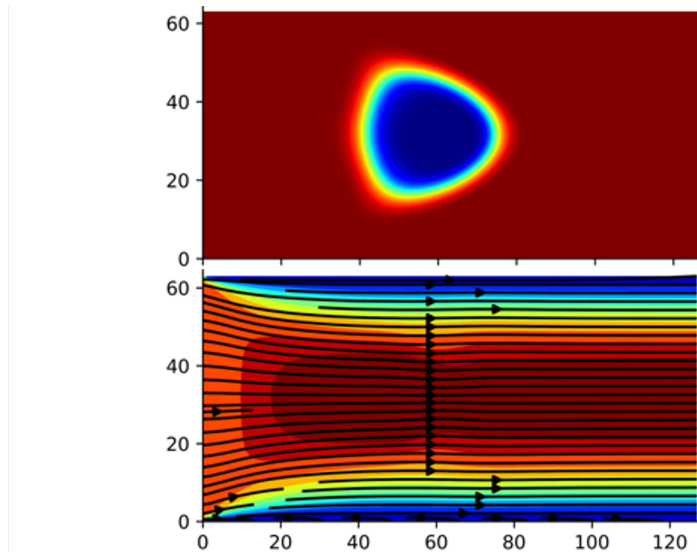


Figure 8.7: A bubble moving through finite domain with upper and lower boundaries as walls.

Overall, the bubble is distorted and inclined at angle through the flow. This sets up two contact angles: α as advancing and β as receding contact angle as seen in Figure 8.8c, 8.8d. In Figure 8.8e, 8.8f the detachment of the bubble from the surface is shown. After the bubble has detached it will exit the domain as in the previous simulations.

The inclination angle and bubble detachment dynamics depends on the forces which act on the bubble while in contact with the initial position on the wall. There are multiple forces acting on the bubble as it detaches [Manthey et al., 2023]. The surface tension force which acts on the contact line between the substrate, the liquid, and the gas is responsible for pinning the bubble to the wall surface. The counter force exerted by the water on the air bubble as it equilibrates and displaces the water. This also pins the bubble in place. Multiple forces pull on the bubble and lead to detachment as water flows across the domain. Some of these are the quasi-steady drag forces along with the shear lift force experienced by the bubble due to the unbounded flow around it. The hydrodynamic pressure contributes as another lift force, arising from the asymmetrical velocity profile on the wall. Lastly, the contact pressure force created by the pressure difference across the bubble interface exerts a force on the substrate, which in turn exerts a reaction force on the bubble. If the lift forces overcome the pinning forces bubble detachment is seen. The bubble is also dragged across the bottom of the wall due to the horizontal components of these competing forces.

8.5 Conclusions

A robust model capable of simulating two-phase flow and wall interactions for fluids with high density and viscosity ratios in a finite domain has successfully developed. By adopting a coupled Cahn-Hilliard and Navier-Stokes approach and incorporating a scheme to decouple the LBM relaxation time with the kinematic viscosity, the model breaks the limitations present in standard LBM models, enabling more accurate and

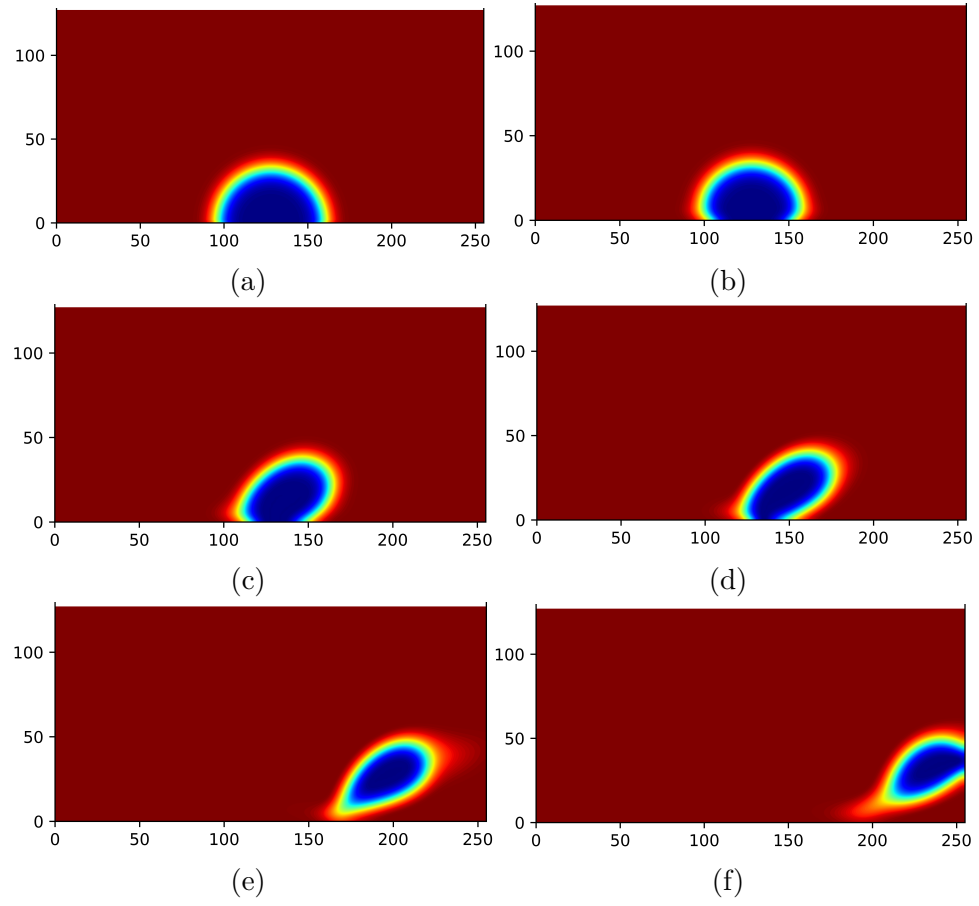


Figure 8.8: Air bubble detachment from a solid wall of a channel caused by water flowing from the inlet (left) to the outlet (right).

stable simulations. This model was verified using various multi-phase bench-marking simulations.

The goal of this work is to apply the model to predict gas saturation inside the porous transport layers and the catalyst layer of a PEM water electrolyzer. The PTL is an essential component for the efficient gas transport to and from the catalyst layer in PEM water electrolyzers. The CH-NS LBM model offers a robust framework for simulating gas diffusion and saturation within its intricate pore structures. By integrating fluid dynamics and gas-phase diffusion, this model is best suited to accurately predicts gas distribution patterns and identify potential blockages or stagnation zones, and optimizes PTL design parameters (such as pore size, tortuosity, and porosity) to enhance mass transport efficiency. Similarly, within the catalyst layer, where electrochemical reactions take place, precise modeling of gas saturation is crucial for understanding diffusion-limited reaction kinetics and optimizing catalyst utilization. The scalable nature of the CH-NS LBM model makes it perfect to simulate gas transport through the catalyst layer as well.

Chapter 9

Conclusion: Mass transport phenomena inside PEWEs is highly complex and interconnected with other forms of transport

A polymer electrolyte water electrolyzer (PEWE) is a promising technology for high-purity hydrogen production in future industrial applications. It has garnered global attention due to its high efficiency, flexibility, and compatibility with renewable energy sources. To reduce the cost of hydrogen production, there is a consistent preference for operating at high current densities. This approach can significantly lower the capital investment required for electrolyzer stacks while maintaining a specified hydrogen production rate.

Significant progress has been made in achieving higher current densities at constant precious metal catalyst loadings. However, operating at these higher current densities introduces efficiency challenges due to detrimental bubble effects. High-current operations in PEM water electrolyzers require efficient transport of reactants and products to ensure optimal performance. Analyzing mass transport within the

porous transport layers is particularly challenging due to complex two-phase flow dynamics. Currently, there is no widely accepted theory capable of comprehensively describing two-phase flow in PEWE PTLs and directly correlating it with various electrochemical overpotentials to improve performance predictions. This the research demonstrated as part of this dissertation attempts to fill this gap in understanding. It also underscores the need for further research and development to better characterize and model the intricate transport phenomena within PEWEs. It has been shown that the state of the art materials studied in this work far surpassed the performance benchmarks set by U.S.DOE for 2020 [U.S.DOE, 2024a]. However, in order to continue improving the system efficiency and engineering new generation of materials, a better understanding of the various aspects of transport is needed.

In Chapter 5, the current density distribution measurement technique is established for in-situ characterization of transport in PEM water electrolyzers (PEWEs). Under the tested conditions of low relative flow-rate, a significant current density gradient was observed across all cell configurations. High local current densities were seen near the inlet, while reduced current densities were noted closer to the outlet. The study reported in this chapter also demonstrated that the triple-serpentine flow-field outperforms the parallel flow-field under mass transport-limited conditions. This suggests that the parallel flow-field is more prone to starvation than the triple-serpentine flow-field for the test cell configurations used in this research. The likely reason is the higher liquid velocity in the channels of the triple-serpentine flow-field, which enhances product gas removal compared to the lower channel velocity in the parallel flow-field. Furthermore, all diffusion media were noted to exhibit similar performance at lower current density regions. However, under extreme high current density conditions, their behaviors diverged significantly.

Although current density distribution (CDD) measurements have proven useful for in-situ performance investigation of PEWEs and other electrochemical systems, their semi-quantitative nature limits their effectiveness in analyzing mass transport within PEWEs.

In Chapter 6, an effective water transport number (EWTN) is proposed to address this limitation. The study aimed to fully quantify CDD measurements and provide a clear indication of performance. The EWTN is scaled from 0 to 1, signifying varying degrees of water transport to the catalyst-coated membrane.

The results from the investigation done in this chapter revealed that higher flow-rates yield EWTN values of 0.95 and above, indicating no significant mass transport limitations. Conversely, lower flow-rates with large gradient CDD maps exhibit EWTN values between 0.6 and 0.8, indicating mass transport-limited conditions. The standard deviations of the distributions under mass transport-limited conditions ranged between 0.1 and 0.2. This is 2-5 times higher than the standard deviations observed for higher flow-rates. The study also identified a direct correlation between ohmic overpotentials and mass transport losses due to bubble accumulation and membrane dehydration.

Additionally, an unitized pin-type LGDL/flow-field design was developed as part of this research. This design enhanced the gas phase transport in a PEWE and removed bubbles more efficiently. This led to improving low flow-rate performance, as shown by higher overall EWTN values with lower standard deviations for the pin-type architecture. Furthermore, the pin-type architecture exhibited a lower percentage change in ASR values compared to the parallel flow-field designs.

In Chapter 7, the use of the segmented cell and PCB was taken a step further. This research done in this chapter demonstrates an advanced technique for measuring both CDD and distributed area-specific resistances (DASR) inside a PEWE. Coupled with the application of a semi-empirical model, this technique enables the investigation of different overpotential categories and the identification of their spatial variations. The results show that variations in area-specific resistance of the PEWE are significantly influenced by the anode feedwater flow-rate. Moreover, the DASR measurements indicate that local dehydration of the polymer electrolyte membrane is primarily responsible for increased polarization, behaving similar to mass transport-limited currents at low flow-rates due to ineffective bubble removal from the catalyst surface.

To improve quantification and analysis, the overall ohmic overpotential was divided into background ($\eta_{Ohm,b}$) and mass transport-coupled ($\eta_{Ohm,mt}$) components. The $\eta_{Ohm,b}$ distributions for both the baseline PTL and LGDL range between 20-50% of the total overpotential. It was also shown that ineffective anode feedwater flow-rate led to local dehydration in the PEM, especially with the LGDL, as evidenced by lower average $\eta_{Ohm,mt}$ values in the baseline PTL. Additionally, EIS results indicated that variations in ASR and secondary processes, such as changes in catalyst layer resistance or reduced electrochemical surface area, may occur due to high gas evolution rates and bubble accumulation.

The effect of cell temperature on the various overpotentials were also explored in this work. Increasing cell temperature in this study enhanced kinetics and background ohmic losses. However, it also accelerated local dehydration rates. Despite expectations for improved diffusion processes with higher temperature, no significant trends were observed for either diffusion medium.

Interestingly, minimal discrepancies in diffusion overpotential were noted when comparing PEWE performance with baseline PTLs and LGDLs, despite their known differences in two-phase fluid transport dynamics. This suggests that diffusion limitations primarily manifest at the micro-porous scale within the catalyst layer. The micro-porous structure of the catalyst layer significantly influences diffusion processes. Given the diffusion limited overpotential differences are minimal (less than 5%), these limitations predominantly arise from species diffusion through the catalyst layer. These micro-structures govern reactant access to catalytic sites and product removal, causing localized diffusion constraints that can outweigh larger-scale fluid dynamics differences within the anode diffusion media.

These experimental investigations serve to demonstrate the complexities of the mass transport processes occurring within PEM water electrolyzers. Given the ongoing nature of this research, there is a clear need to develop theoretical frameworks that can accurately describe and predict these processes. However, the model

needs to be powerful enough to capture two-phase flow dynamics at the pore-scale. Compared to conventional macroscopic continuum-based CFD models, Lattice Boltzmann Method based models are best suited for such applications.

Chapter 8 introduces a robust lattice Boltzmann method (LBM) model designed to simulate two-phase flow and wall interactions for fluids with high density and viscosity ratios within a finite domain. By employing a coupled Cahn-Hilliard and Navier-Stokes approach and a scheme to decouple the LBM relaxation time from the kinematic viscosity, this model overcomes limitations of standard LBM models. This offers more accurate and stable simulations of two-phase fluid dynamics. Although the current model does not predict the electrochemical performance of PEM water electrolyzers, its framework can be expanded and integrated into larger models to explore such simulations in the future.

To achieve highly compact and efficient operation of PEM water electrolyzers, careful consideration of mass transport in both liquid and gas phases is essential. This research highlights the intricate challenges posed by mass transport limitations in these systems. By deepening the understanding of PEM water electrolyzer dynamics, this body of work hopes to build a foundation for making informed engineering decisions. This understanding can pave the way for designing higher-performance next-generation systems. Furthermore, this dissertation provides valuable insights and experimental data that can be used to rigorously verify models across various cell designs and flow rates. These insights not only contribute to advancing theoretical knowledge but are equally important for enhancing the efficiency and economic viability of PEM water electrolyzers, thereby promoting sustainable hydrogen production.

Chapter 10

Final thoughts and suggested avenues of future research

This dissertation showcases the advantages of advanced, in-situ distributed diagnostic techniques and provides valuable insights into transport limitations within PEM water electrolyzers. These findings go beyond what traditional characterization methods can reveal, particularly in exploring different PEWE configurations employing various flow fields and diffusion media.

Five years ago we wanted to find the answer to the question: “*what is the nature of transport inside PEM water electrolyzers?*” Each chapter in this dissertation is seen to build upon the findings of the previous. This led to asking more deeper questions like, “how important is mass transport considerations for PEWEs? What is nature of dehydration occurring inside the cell? How does bubble accumulation and dehydration affect the various losses in the system?” At the time of writing, armed with advanced diagnostic tools and rigorous experimental data, we have unraveled some of the intricacies governing mass transport limitations in these devices. This journey has not only deepened our understanding of electrochemical processes but also illuminated pathways for future advancements in PEM electrolyzer technology.

Moving forward, the following ideas merit consideration as promising avenues for future research:

- **Isolate diffusion related mass transport losses in PEWEs.** This body of research has demonstrated that the actual diffusion limited mass transport losses is most likely occurring inside a PEM water electrolyzers at the micro-porous scale in the catalyst layer. By isolating these diffusion-related losses, researchers can pinpoint specific areas for improvement, such as enhancing the design of PTL/CL interfaces or optimizing catalyst structures to facilitate more efficient transport of reactants and products. This targeted approach not only enhances the fundamental understanding of mass transport phenomena but also holds promise for advancing the performance and scalability of PEM electrolyzer technology.
- **Investigate durability of system and materials.** Ensuring the long-term reliability and robustness of PEWE systems and their components is crucial for advancing their commercial viability and widespread adoption. This involves comprehensive evaluation of their performance over extended periods, considering factors such as operational cycles, load variations, and environmental conditions (temperature, pressure, humidity), which can significantly impact degradation rates. By conducting accelerated aging tests and real-world simulations, researchers can effectively quantify degradation mechanisms and identify critical failure modes. Advanced in-situ diagnostics and non-destructive testing enable real-time assessment of system health and early detection of potential failures. Integrated with predictive modeling, these tools facilitate proactive maintenance strategies and contribute to enhancing the overall reliability of PEM electrolyzer systems. This approach supports the goal of achieving durable, efficient, and economically viable hydrogen production technologies essential for a sustainable energy future.

- **Applying the advanced CH-NS LBM model to predict gas saturation inside PTL and catalyst layer.** The PTL is essential for efficient gas transport to and from the catalyst layer in PEM water electrolyzers. The CH-NS LBM model offers a robust framework for simulating gas diffusion and saturation within the intricate pore structures of the PTL. By integrating fluid dynamics, gas-phase diffusion, and electrochemical reactions, this model accurately predicts gas distribution patterns, identifies potential blockages or stagnation zones, and optimizes PTL design parameters (such as pore size, tortuosity, and porosity) to enhance mass transport efficiency. Within the catalyst layer, where electrochemical reactions take place, precise modeling of gas saturation is crucial for understanding diffusion-limited reaction kinetics and optimizing catalyst utilization. The scalable nature of the CH-NS LBM model makes it a versatile tool to simulate gas transport through the catalyst layer. This capability facilitates accurate prediction of reaction rates, mitigation of mass transport limitations, and improvement of overall electrolyzer efficiency.
- **Integrating pore-scale models with macro-scale continuum models.** This represents a pivotal advancement in computational modeling for PEWEs. This initiative aims to bridge the gap between micro-scale transport phenomena within materials like PTLs and catalyst layers, and the overall performance of PEM electrolyzer systems operating at the macro-scale. At the pore scale, intricate phenomena such as fluid flow, mass transfer, and electrochemical reactions govern processes within these materials. Conversely, macro-scale continuum models describe system-wide behavior, considering bulk flow dynamics, electrochemical reactions across multiple cells, and performance metrics like current density and hydrogen production rate. Integrating these approaches involves coupling pore-scale simulations to inform macro-scale models, enhancing understanding of how micro-scale phenomena impact overall system performance. For instance, insights from pore-scale simulations on

local gas distributions and reaction kinetics can refine boundary conditions and parameters in macro-scale models, thereby enhancing predictive accuracy. Key challenges include managing computational complexity, transferring data across scales, and validating models against experimental data. Future research will focus on refining multi-scale frameworks, incorporating finer physics and chemistry details, and adapting models to meet evolving needs in sustainable energy technologies.

As we continue to refine our models and expand our experimental capabilities, we aim to achieve higher efficiencies, reduced costs, and enhanced durability in PEM water electrolyzers. This pursuit is not just about advancing hydrogen production capabilities; Instead it is about contributing to a sustainable energy future where clean hydrogen plays a pivotal role in decarbonizing our global energy systems.

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Appendices

This chapter is a dedicated repository of supplementary information designed to enhance and complement the content of each preceding chapter. It includes additional details, data, and resources that provide readers with a deeper and more comprehensive understanding of the research presented.

Specifically, it serves as a dedicated space for relevant background information, methodology specifics, extended experimental results, and any other materials that bolster the arguments and findings outlined in the main chapters. By offering this supplemental content, the chapter adds value to the entire dissertation, ensuring that readers have access to all the essential information required to comprehend the intricacies of the study.

Supplementary Information for Chapter 5

Cell temperature

The thermal management system was implemented such that the cell was maintained at 80°C under normal operating conditions. The FLIR image (Fig. S1) and the cell thermocouple showed that the cell was maintained close to 80°C throughout the experiments. As expected the difference in water temperature between the inlet and outlet was found to be highly dependent on the flow-rate. For the highest flow-rate the temperature difference between the inlet and the outlet went from an initial value of 2°C (before polarization begins) to a value of 10°C by the end of the polarization measurements. This indicates some in-plane temperature variability is expected as shown by [Immerz et al., 2018a, Minnaar et al., 2020]. However, the current density distributions and cell HFR measurements stays relatively uniform, indicating that this temperature distribution has relatively low impact on the comparisons made in the paper on cell performance.

For the lowest flow-rate, the long residence time of the feed-water within the system, made it difficult to accurately measure the temperature change between the inlet and the outlet. The cell temperature was noted to increase by $\sim 15^{\circ}\text{C}$ from its initial condition, while operating under the mass transport limited conditions. This indicates a larger variation in temperature across the active area due to ineffective heat removal. The insufficient supply of liquid water coupled with the high oxygen content inside the cell lowers the specific heat capacity of the fluid (two phase mixture of water and oxygen gas) flowing through the system. This leads to poor thermal management of the cell and may contribute to the increased HFR and the lower current density regions observed near the outlet.

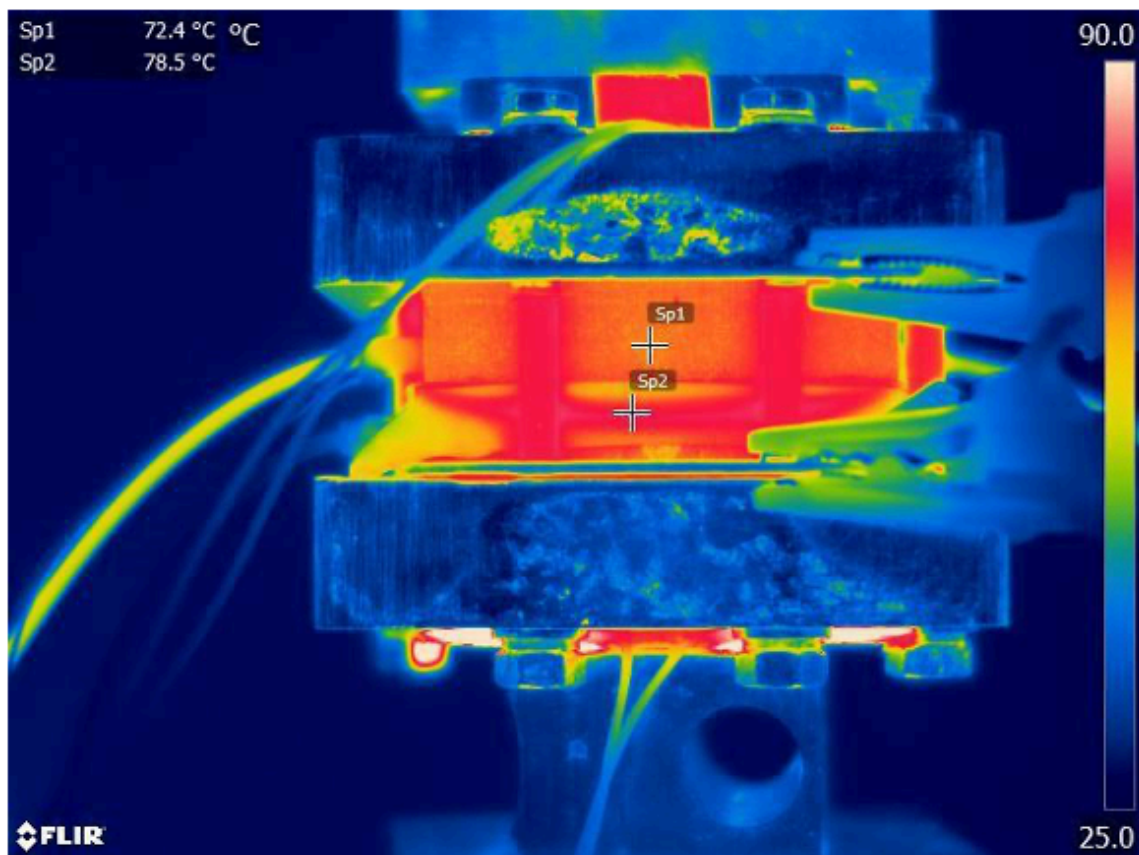


Figure S1: FLIR thermal image of cell showing that the membrane temperature is close to the reported operating temperature

Background correction

Fig. S2 shows that there is relatively uniform compression between the PCB and the flow-field, flow-field and DM, DM and CCM. The small heterogeneities observed in the pressure paper test matches with the background distribution. Therefore, the correction applied to the interpolated data accounts for this discrepancy and eliminates it.

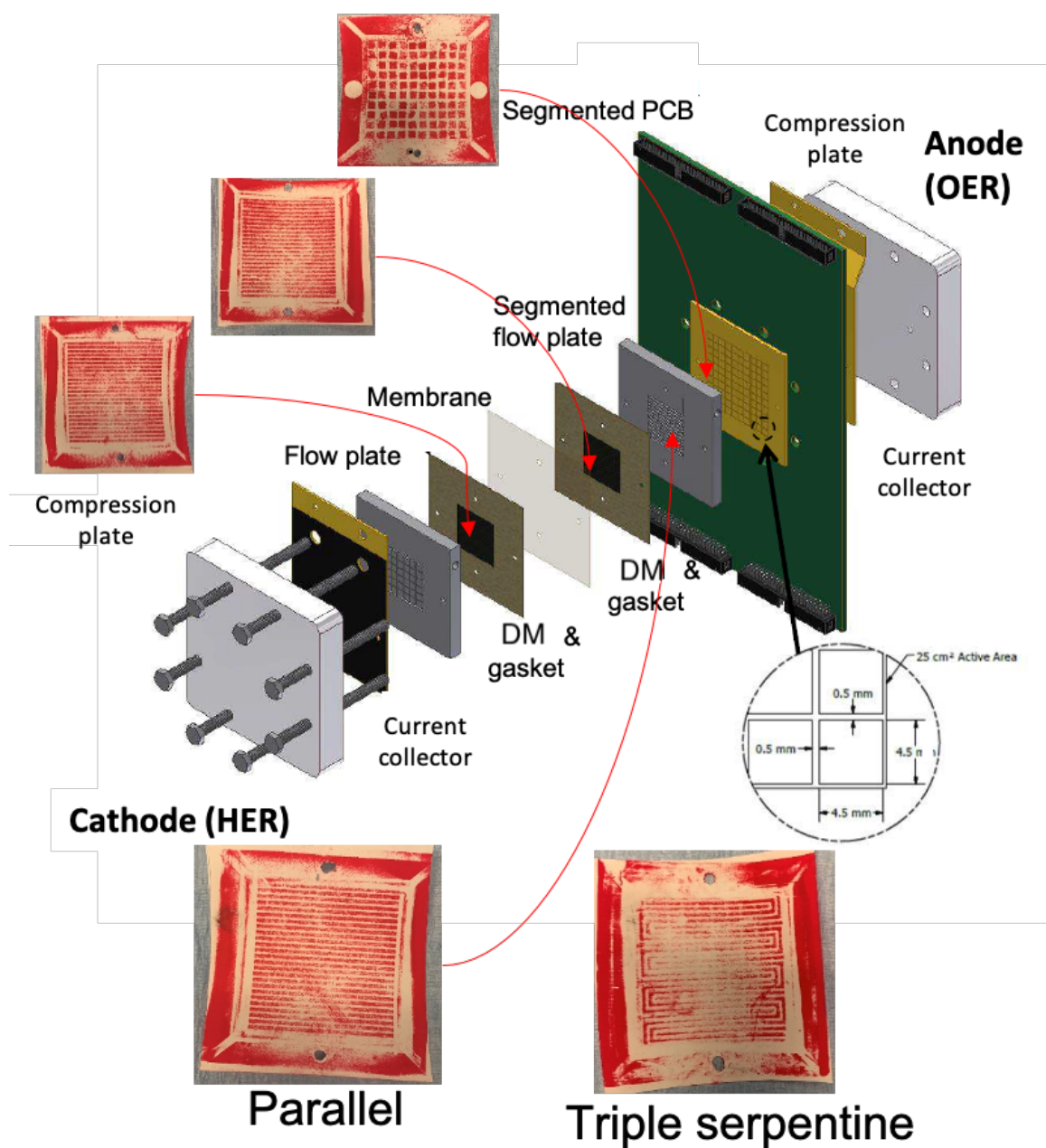


Figure S2: Pressure paper images showing uniform compression between each layer of the cell.

Mass transport isolated distributions and flow-rate dependencies

Two sets of current distribution plots (with flow-rates in opposite direction) were recorded and presented in the following figures. The distributions for the triple-serpentine flow-field are presented in Fig. S3. The figures to the left show the inlet in the bottom right corner, while for the figures to the right the flow is reversed and the inlet is at the top left corner. It can be observed that reversing the flow reverses the current distribution pattern supporting that mass transport limitations is the phenomenon observed. Furthermore, it is seen that the current density is higher around the bends for all flow-rates. It can be hypothesized that the gas phase gets driven away which is facilitated by the greater momentum transfer around these bends.

Similarly, for the parallel flow-field, two sets of current distribution plots were recorded for each flow-rate and presented in Fig. S4. The figures to the left show the inlet in the bottom right corner, while for the figures to the right the flow is reversed and the inlet is at the top left corner.

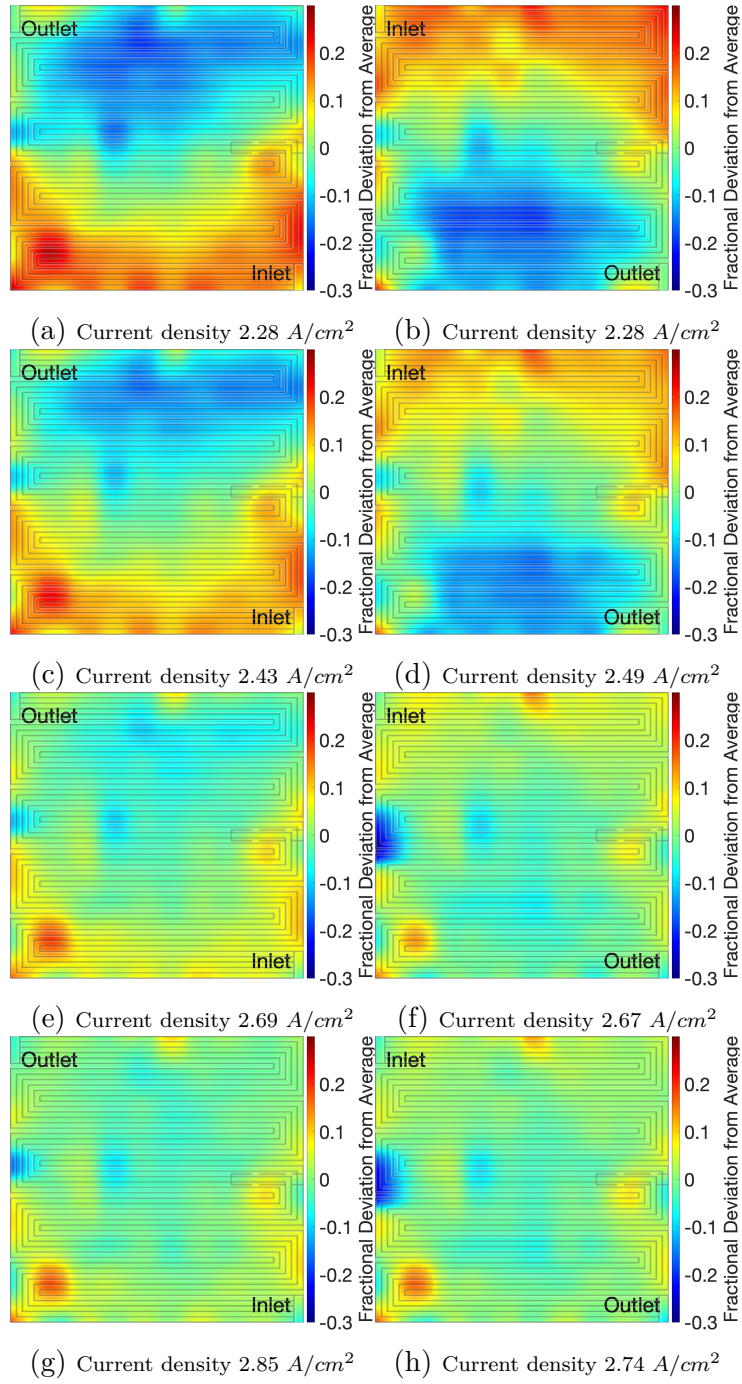


Figure S3: Current density distribution for the thin foil LGDL on the triple-serpentine flow-field at 2.3V at 80°C for a flow-rate of (a) 6 ml/min (b) 6 ml/min reversed (c) 8 ml/min (d) 8 ml/min reversed (e) 12 ml/min (f) 12 ml/min reversed (g) 20 ml/min (h) 20 ml/min reversed

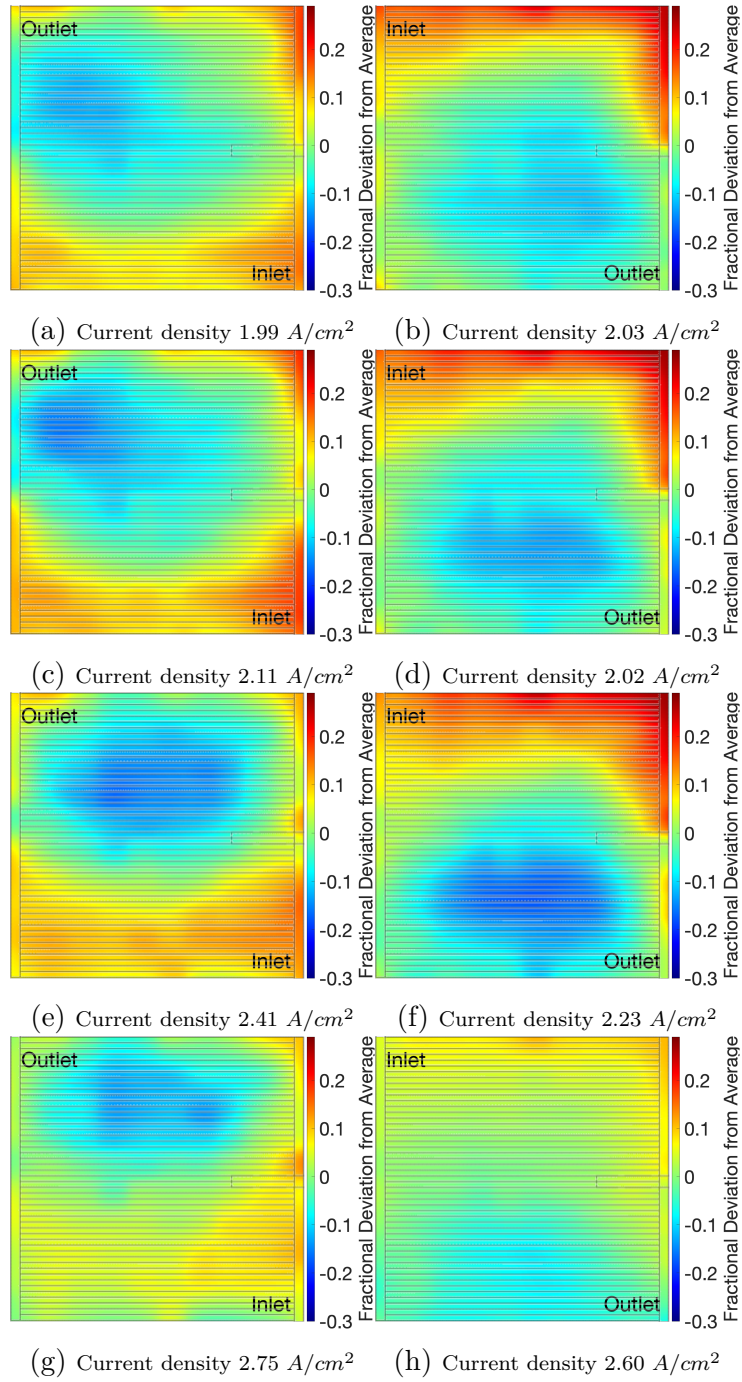
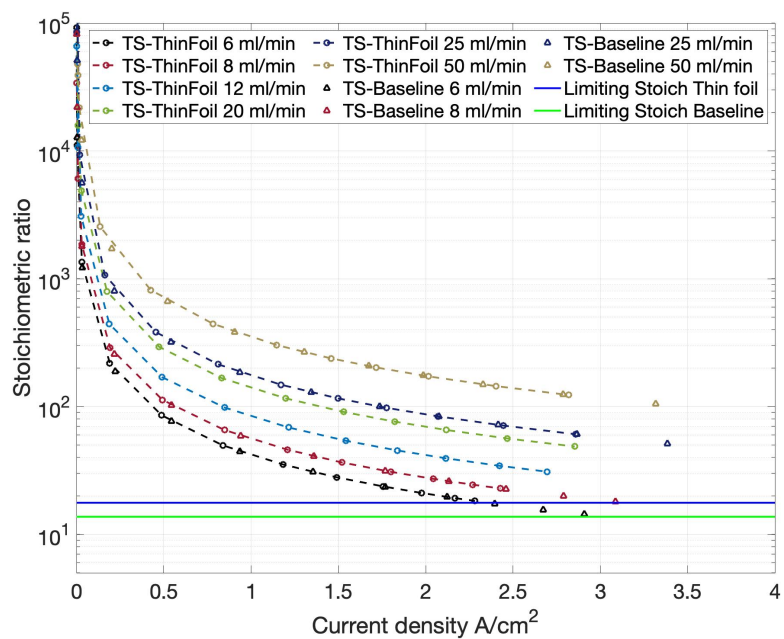


Figure S4: Current density distribution for the thin foil LGDL on the parallel flow-field at 2.3V at 80°C for a flow-rate of (a) 6 ml/min (b) 6 ml/min reversed (c) 8 ml/min (d) 8 ml/min reversed (e) 12 ml/min (f) 12 ml/min reversed (g) 20 ml/min (h) 20 ml/min reversed

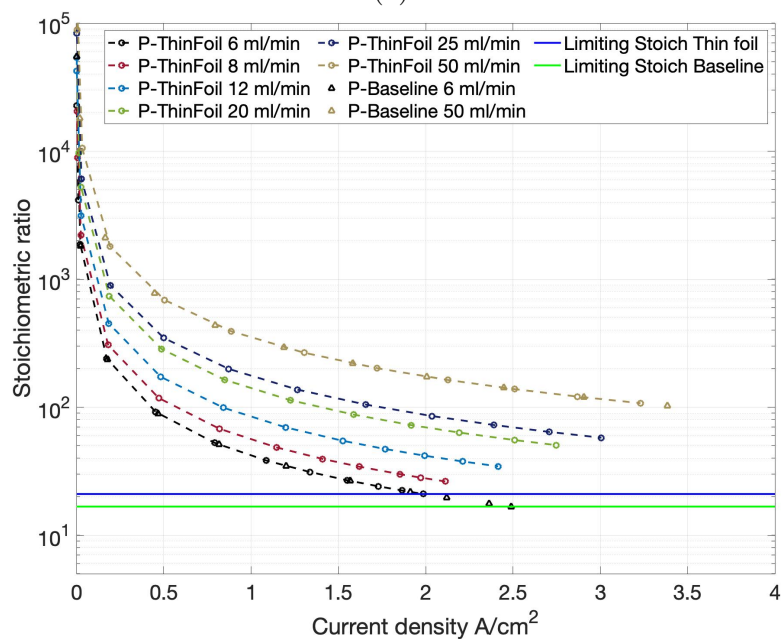
Stoichiometry

Analyzing the stoichiometric ratio as defined in Eq. 1 provides further insights into the mass transport behavior inside the PEWE. Fig. S5 shows the stoichiometric ratio as a function of the current density for both diffusion media on **(a)** the triple-serpentine flow-field and **(b)** the parallel flow-fields. At the lowest flow-rate of 6 *ml/min* for the triple-serpentine flow-field S5a, the thin foil LDGL reaches a limiting current density behavior at a stoichiometric ratio of 17 (blue line) and the baseline PTL reaches a limiting current at a stoichiometric ratio of 14 (green line). Similarly on the parallel flow-field the thin foil LDGL reaches limiting current density behavior at a stoichiometric ratio of 21 (blue line), the baseline PTL which reaches the limiting current at a stoichiometric ratio of 17 (green line). Thus, for all cases the stoichiometric ratios at the limiting current are an order of magnitude greater and 1. In other words, the system has enough reactants not to be mass transport limited in the bulk flow-field away from the reactant sites. Therefore the mass transport limiting behavior exhibited the PEWE is likely due to bubble accumulation, local starvation, local temperature gradients and membrane dry-out.

$$\Lambda = \frac{\dot{n}_{in}}{\frac{iA}{2F}} = \frac{\rho_{H_2O}\dot{Q}_{in}}{\frac{iA}{2F}} \quad (1)$$



(a)



(b)

Figure S5: Stoich for various diffusion media and flow-rates on the (a) triple serpentine and (b) parallel flow-field at $80^\circ C$.

Pressure drop across PEWE

It is evident from Fig. [S6](#) that the pressure drop across the parallel cell is reduced compared to the triple-serpentine flow-field.

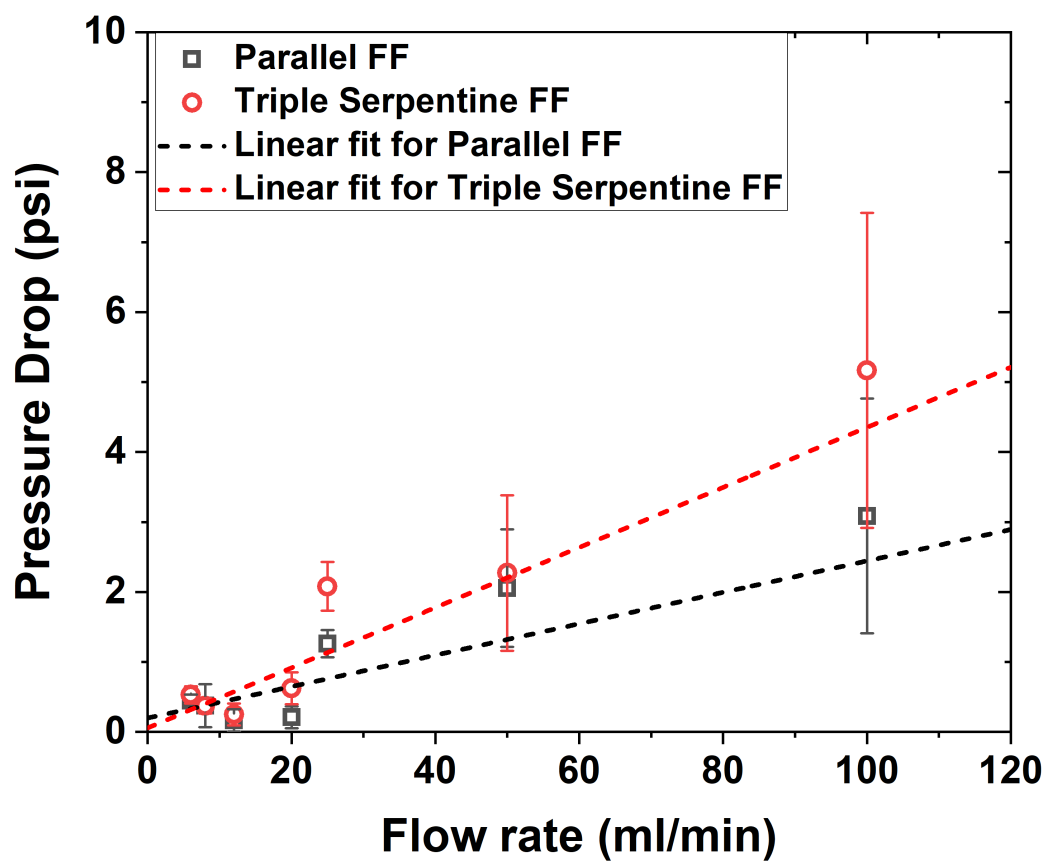


Figure S6: Pressure data for the parallel and triple-serpentine flow-field for flow-rates between 6 ml/min and 100 ml/min operating at $80^{\circ}C$

Supplementary information for Chapter 6

Pressure drop

Figure S7 shows a plot of pressure difference (kPa) vs area specific flow-rate ($ml/min/cm^2$) across the PEWE for the pin and parallel flow-fields. It is evident that the pressure drop is lower for the pin-type for all flow-rates compared to the parallel flow-field. Furthermore, by having systems with lower pressure drop across the cell, parasitic pumping losses can be reduced, increasing system efficiency.

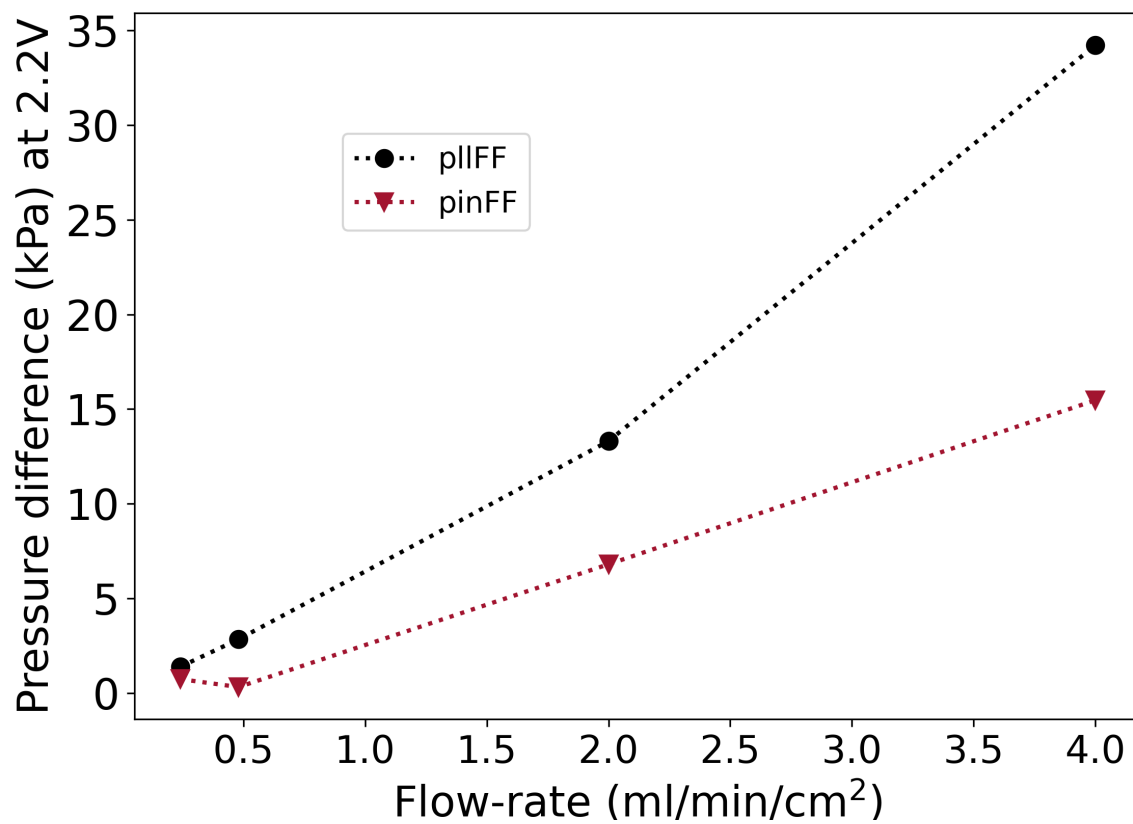


Figure S7: Pressure drop across the PEWE as a function of flow-rate operating at 2.2 V using the parallel and pin-type flow-fields

Supplementary data for the parallel flow-field

Figure S8 shows the polarization curve for the parallel flow-field for flow-rates increasing from 0.24 ml/min/cm^2 to 4 ml/min/cm^2 . The polarization curves exhibit non-linearity at higher voltage holds for lower flow-rates. The polarization curves start to deviate from each other around 1.5 A/cm^2 . This deviation partially a result of an increase in the ASR for higher current densities and lower flow-rates, most likely caused by bubble accumulation.

The corresponding EWTN histograms for the lowest and highest flow-rate of 0.24 ml/min/cm^2 and 4 ml/min/cm^2 measured throughout the various voltage holds ranging from 1.8V to 2.2V (shown in Figure S8) are presented in Figure S9-S10. For a flow-rate of 0.24 ml/min/cm^2 , as the voltage holds increases, the mean value of the histograms decrease, the standard deviation value increases and bubble accumulation is visible in the CDD measurements. For the high flow-rate of 4 ml/min/cm^2 , all mean EWTN values stay at 0.98 or above and no visible transport is evident from the CDD measurements. Interestingly, the standard deviation values for both cases show an increasing trend towards higher voltage holds in the polarization curve. This could be applied to identify the onset off mass transport limitations in a PEWE.

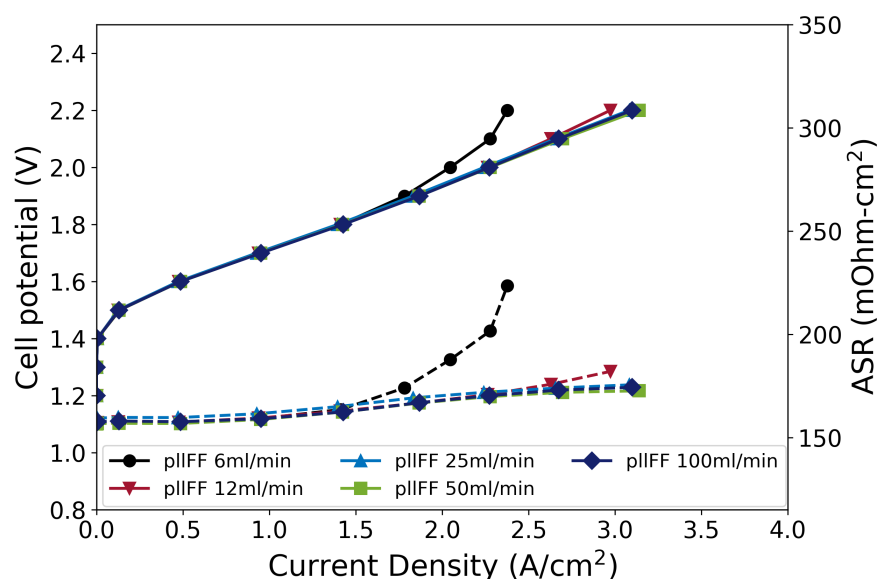


Figure S8: Polarization curves (solid lines) along with the recorded ASR (dashed lines) for a PEWE using a parallel flow-field with the LGDL operating at various flow-rates.

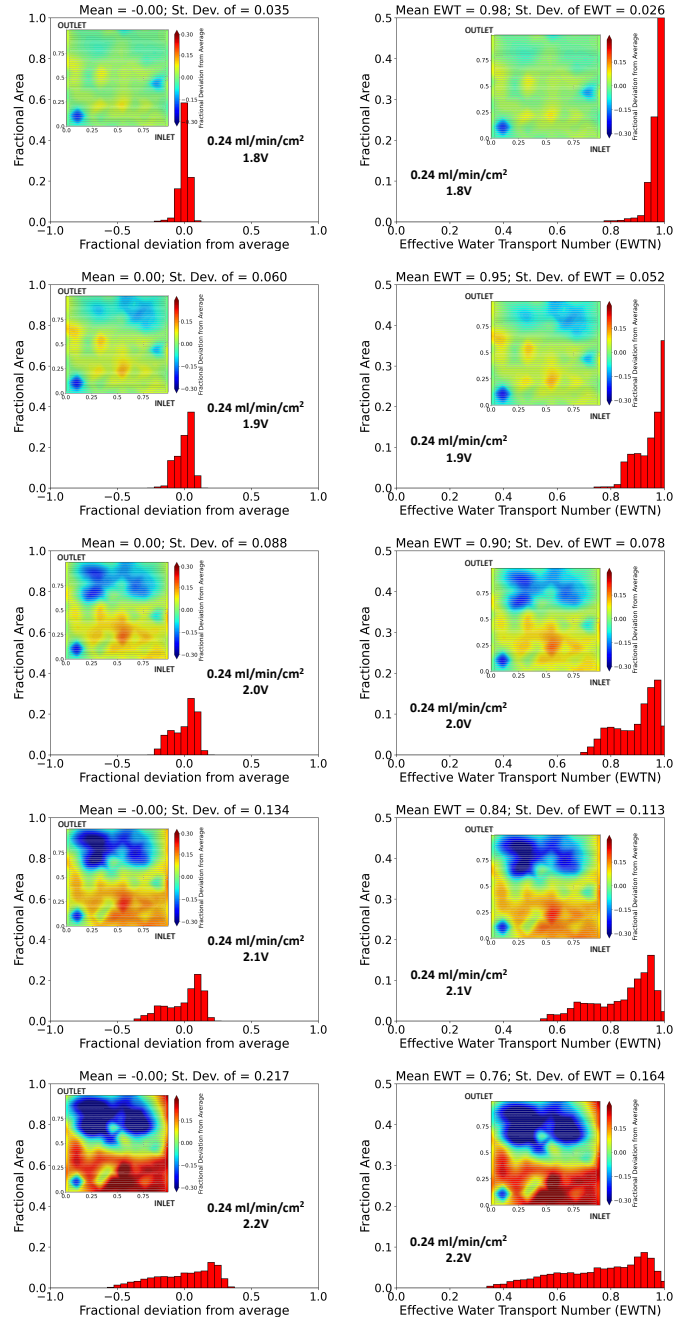


Figure S9: Histograms of the fractional deviation (left column) and EWTN (right column) with corresponding CDDs for the PEWE using the LGDL with a parallel flow-field operating at various voltage holds between 1.8 V and 2.2 V (shown in each row), for flow-rates of 0.24 ml/min/cm^2 .

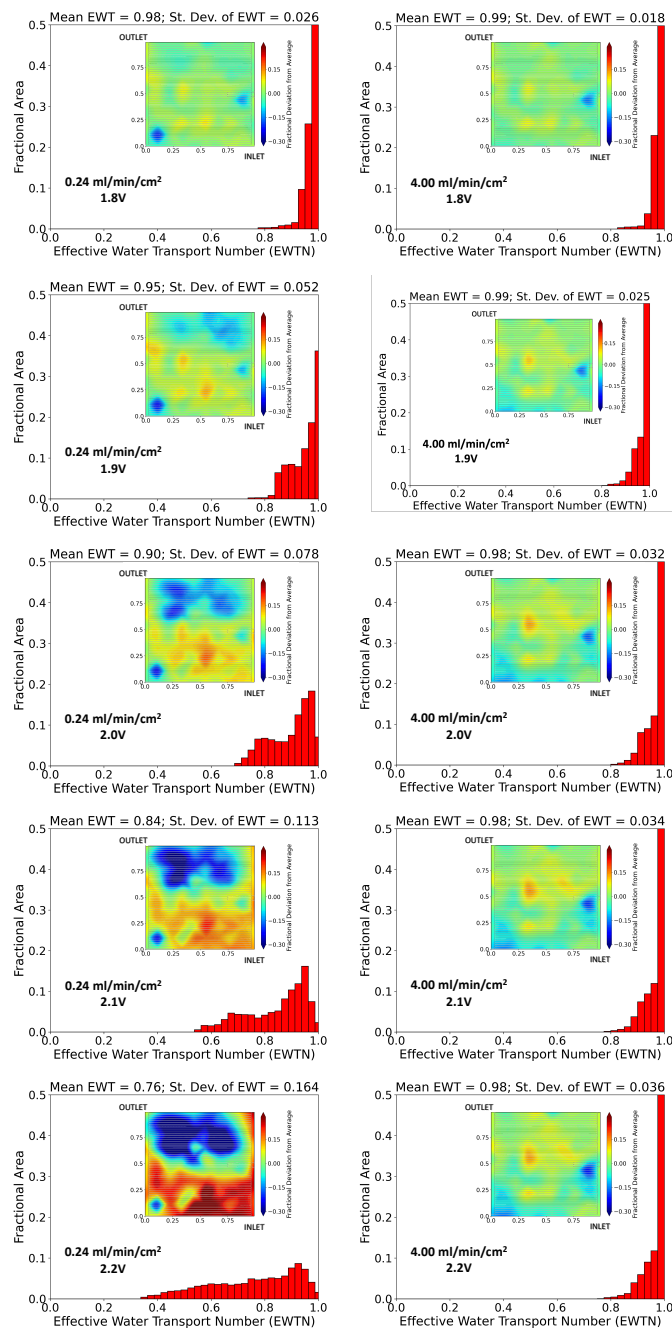


Figure S10: Histograms of EWTN with corresponding CDDs for the PEWE using the LGDL with a parallel flow-field operating at various voltage holds between 1.8 V and 2.2 V (shown in each row), for flow-rates of 0.24 ml/min/cm² and 4 ml/min/cm² (shown in each column).

Two sets of current distribution plots (with counter flow orientation) were recorded and presented in the following figures. At lower flow rates, larger standard deviation and lower mean values are evident. It can be observed that reversing the flow reverses the current distribution pattern but had no significant effect on either the average or standard deviation of the EWTN. This confirms that the CDD data are appropriately represented. The plots show a definite trend as the flow-rate decreases, the mean value of the histograms decrease, the standard deviation value increases and bubble accumulation is visible in the CDD measurements.

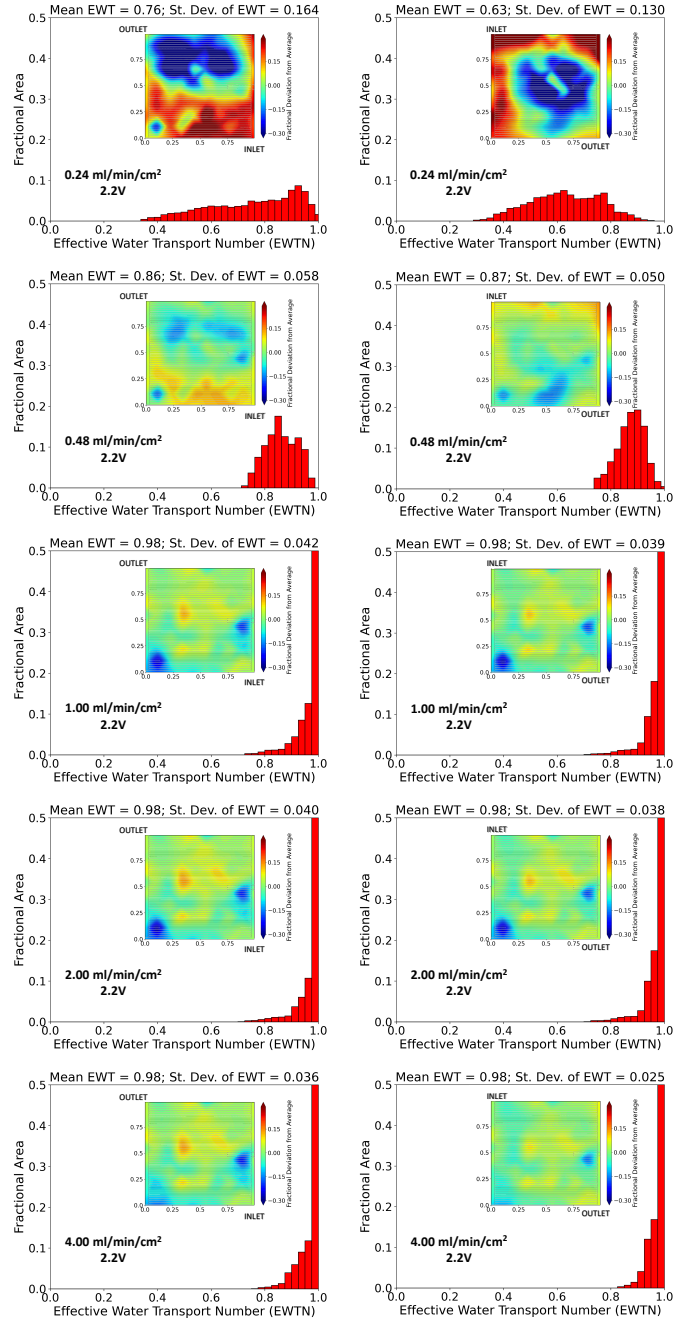


Figure S11: Histograms of EWTN with corresponding CDDs for the PEWE using the LGDL with a parallel flow-field operating at various flow-rates between 0.24 ml/min/cm^2 and 4 ml/min/cm^2 (shown in each row). Each column show the distributions when the inlet and outlet were reversed.

Supplementary data for the pin-type flow-field

Two sets of current distribution plots (with counter flow orientation) were recorded for the pin-type flow-field and presented in Figure S12. This figure is similar to Figure S11, the pin-type flow-field shows the same trends as the flow-rate was varied from 0.24 ml/min/cm^2 and 4 ml/min/cm^2 . However the average of the EWTN consistently recorded higher, while the standard deviations are consistently lower, when compared to the parallel flow-field.

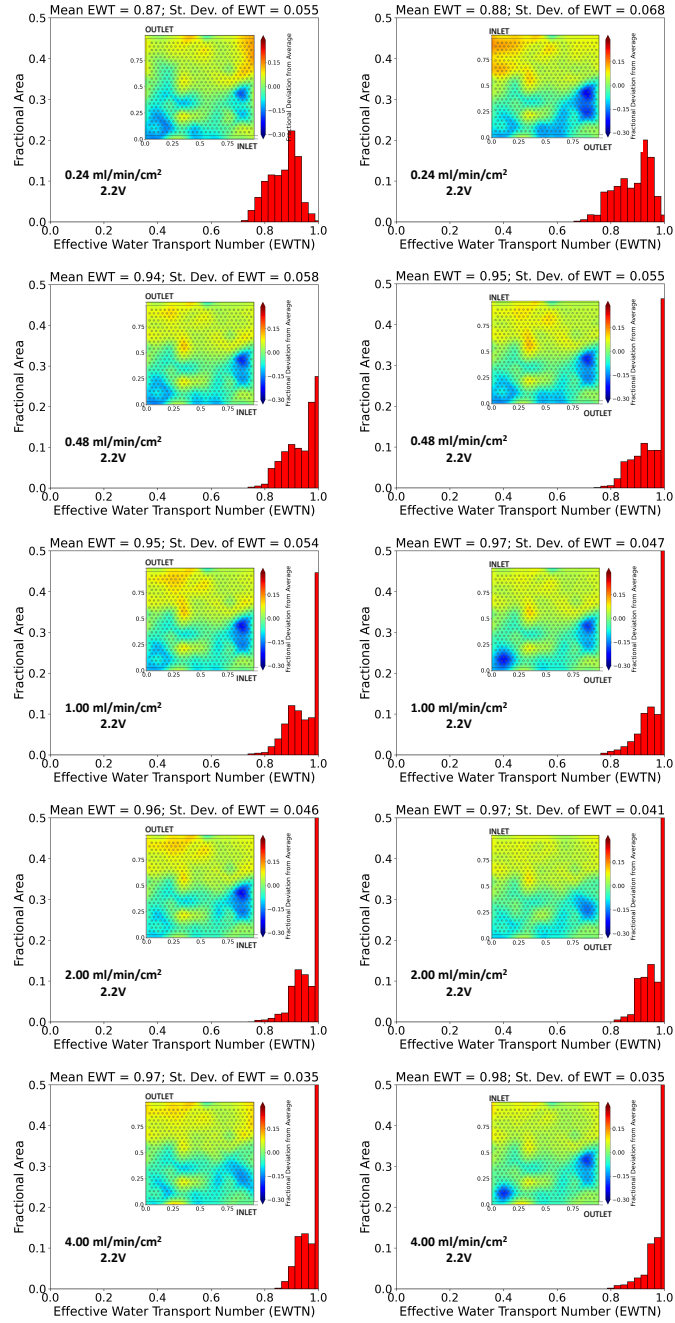


Figure S12: Histograms of EWTN with corresponding CDDs for the PEWE using the LGDL with a pin-type flow-field operating at various flow-rates between 0.24 ml/min/cm^2 and 4 ml/min/cm^2 (shown in each row). Each column shows the distributions when the inlet and outlet were reversed.

Mass transport-induced ohmic behavior

A plot of percentage change in ASR measured at the highest voltage hold of $2.2V$ versus feed-water flow-rate is presented in Figure S13. Below 1 ml/min/cm^2 the percentage change in ASR and the rate at which it decays is sensitive to the flow-field type. The parallel records a higher coefficient for both b and c compared to the pin-type flow-field, indicating that the pin flow-field has better hydration and less dry-out of the membrane.

Figure S13 illustrates the percentage change in ASR measured at the highest voltage hold of $2.2V$ as a function of feed-water flow rate. It is evident from the figure that an exponential decay function can be used to fit the data. Interestingly, for flow-rates less than 1 ml/min/cm^2 , the percentage change in ASR and its decay rate are found to be sensitive to the flow-field type. The parallel flow-field exhibits higher coefficients for both b and c compared to the pin-type flow-field, suggesting that the pin-type flow-field is better at maintaining local membrane hydration, preventing local dry-out and has a lower flow-rate sensitivity overall.

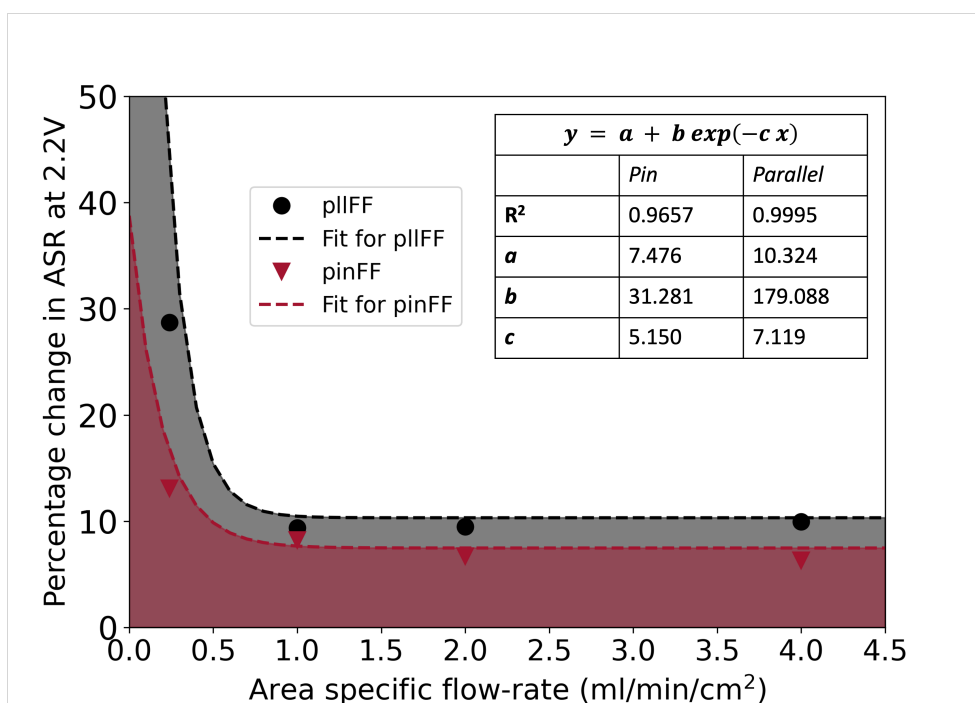


Figure S13: The variation observed for the percentage deviation of the ASR recorded at 2.2 V as a function of feed-water flow-rate. Table in inset shows the equation and coefficients used to fit the data.

Supplementary information for Chapter 7

Global overpotential breakdown analysis with increasing flow-rate

Figure S14 shows the overpotential breakdown polarization curves for increasing flow-rates between 0.24 to 4.00 $ml/min/cm^2$. At the lowest flow-rate of 0.24 $ml/min/cm^2$, it is evident from Figure S14a,b) that there is a high increase in $\eta_{Ohm,MT}$ for both PTLs at higher voltage holds (2.0V-2.3V). However for the baseline PTL, when the flow-rate is increased above 0.48 $ml/min/cm^2$, $\eta_{Ohm,MT}$ is almost negligible, while for the LGDL some contribution from $\eta_{Ohm,MT}$ can be observed for all flow-rates.

Figure S15 shows bar charts for each of the four overpotentials recorded at 2.1V comparing the PTL and the LGDL at various flow-rates. It is evident that the $\eta_{Ohm,MT}$ is high at low flow-rates for both PTLs, and higher for the LGDL across all flow-rates. The kinetic overpotential and the mass transport diffusion overpotential is relatively similar for both PTLs for all flow-rates. Moreover, η_{diff} does show an exponential decrease with increased flow-rate.

Baseline PTL

LGDL

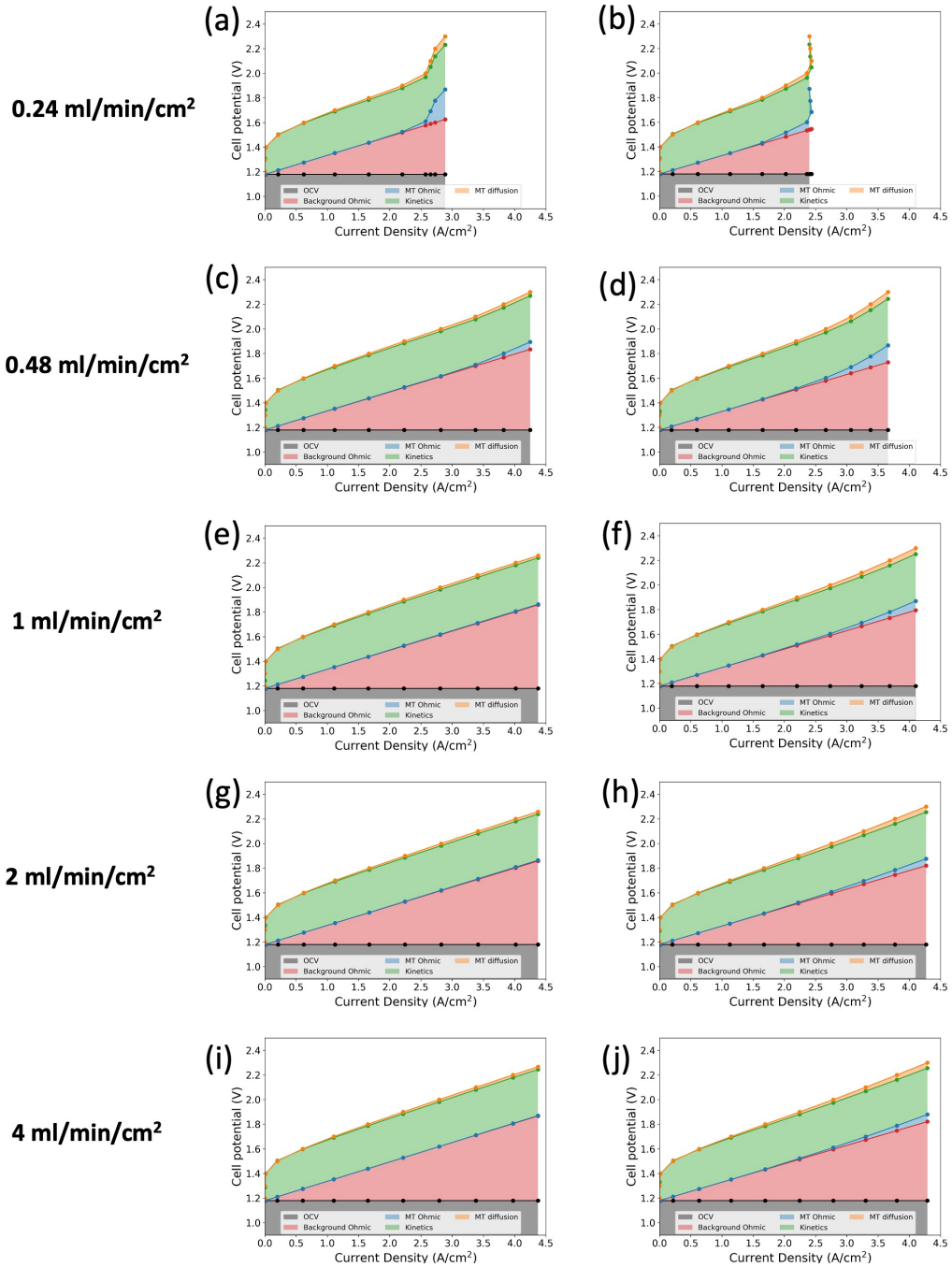


Figure S14: Global overpotential breakdown analysis for both diffusion media as a flow-rate is varied.

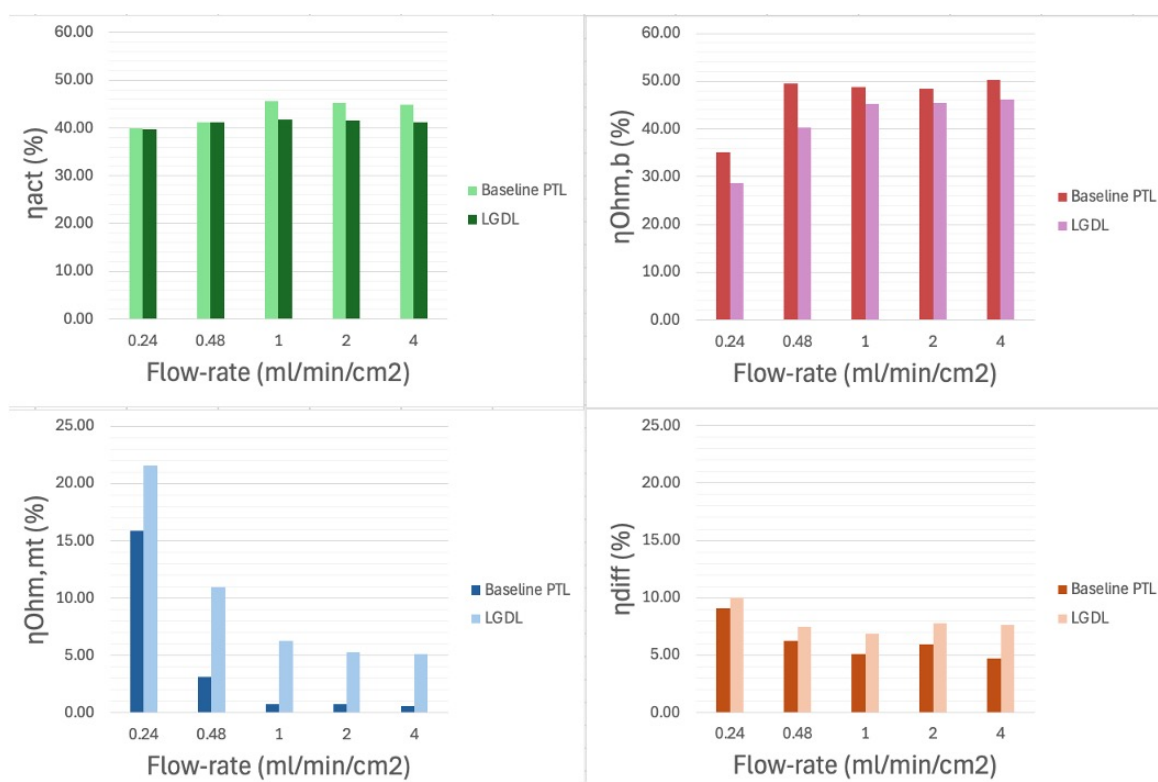


Figure S15: Comparison of contributions of overpotentials at 2.1V for both diffusion media as flow-rate is varied.

Background ohmics and DASR data processing

The experimental results reveal that each cell build has a distribution pattern for the DASR that is consistent with each specific build that remain consistent between operating voltages of 1.2-1.5 V. These variations in the distributions are relatively small (within $\pm 15\%$). Furthermore, increasing the operating voltage for lower flow-rates, a change in the pattern is observed for the DASR distribution.

Therefore, in this work, to calculate the background Ohmic for the each experiment, the DASR for each segment is averaged between voltage holds of 1.2V and 1.5V (as shown in Figure S16). This average background distribution does not change if the inlet and outlet are reversed (see Figure S17). Further, in order to isolate the mass transport coupled ASR distribution, the background DASR is removed from absolute DASR measured at higher voltage holds as shown in Figure S16.

Figure S18 depicts the overall and background DASR at 6 *ml/min* and 100 *ml/min* for both the baseline PTL and the LGDL. It can be observed that for higher flow-rates, where very little $\eta_{Ohm,MT}$ is observed the background ohmic is very similar to the DASR measured. However, for the LGDL a small difference can be seen in between the measured DASR and the background ohmic distribution at 100 *ml/min*. This is expected due to the presence of $\eta_{Ohm,MT}$ observed at 2.1V in the polarization curve in Figure S14j.

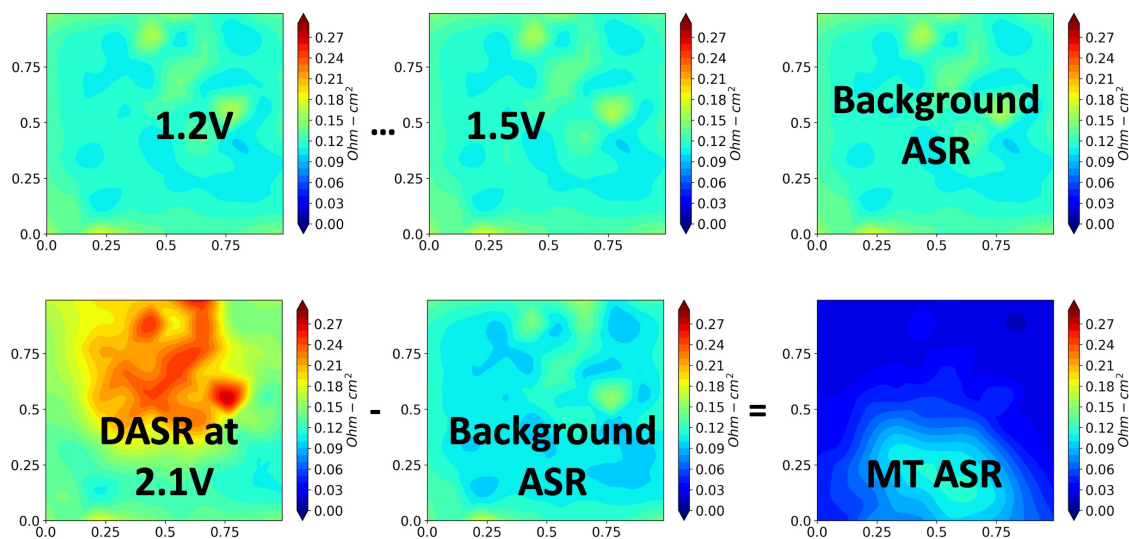


Figure S16: Calculation of the background DADR and mass transport coupled DADR

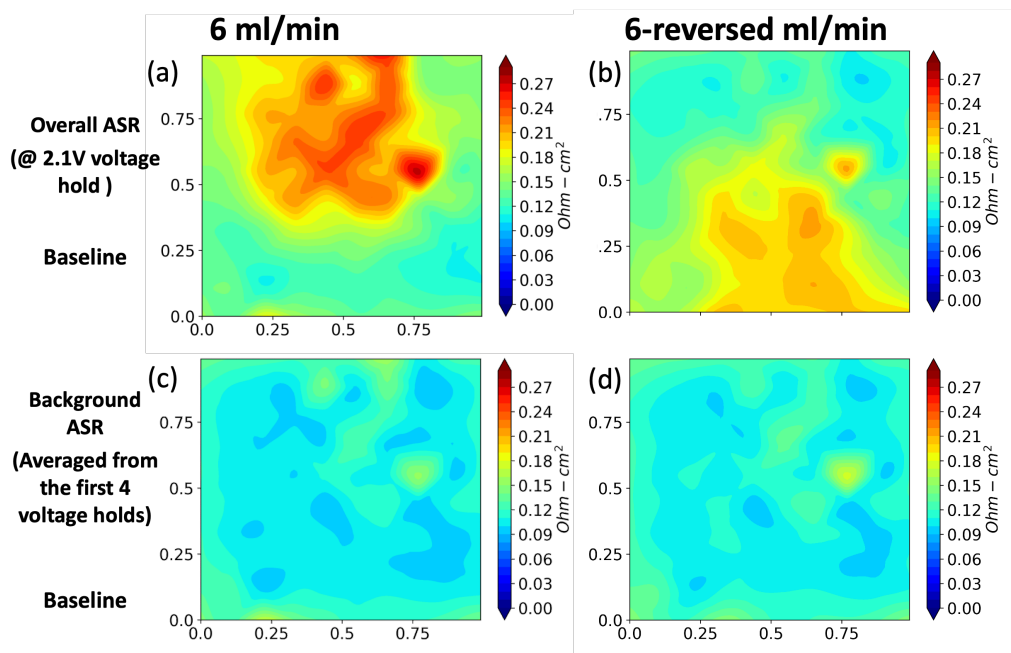


Figure S17: Effect of flow-rate on the background DADR.

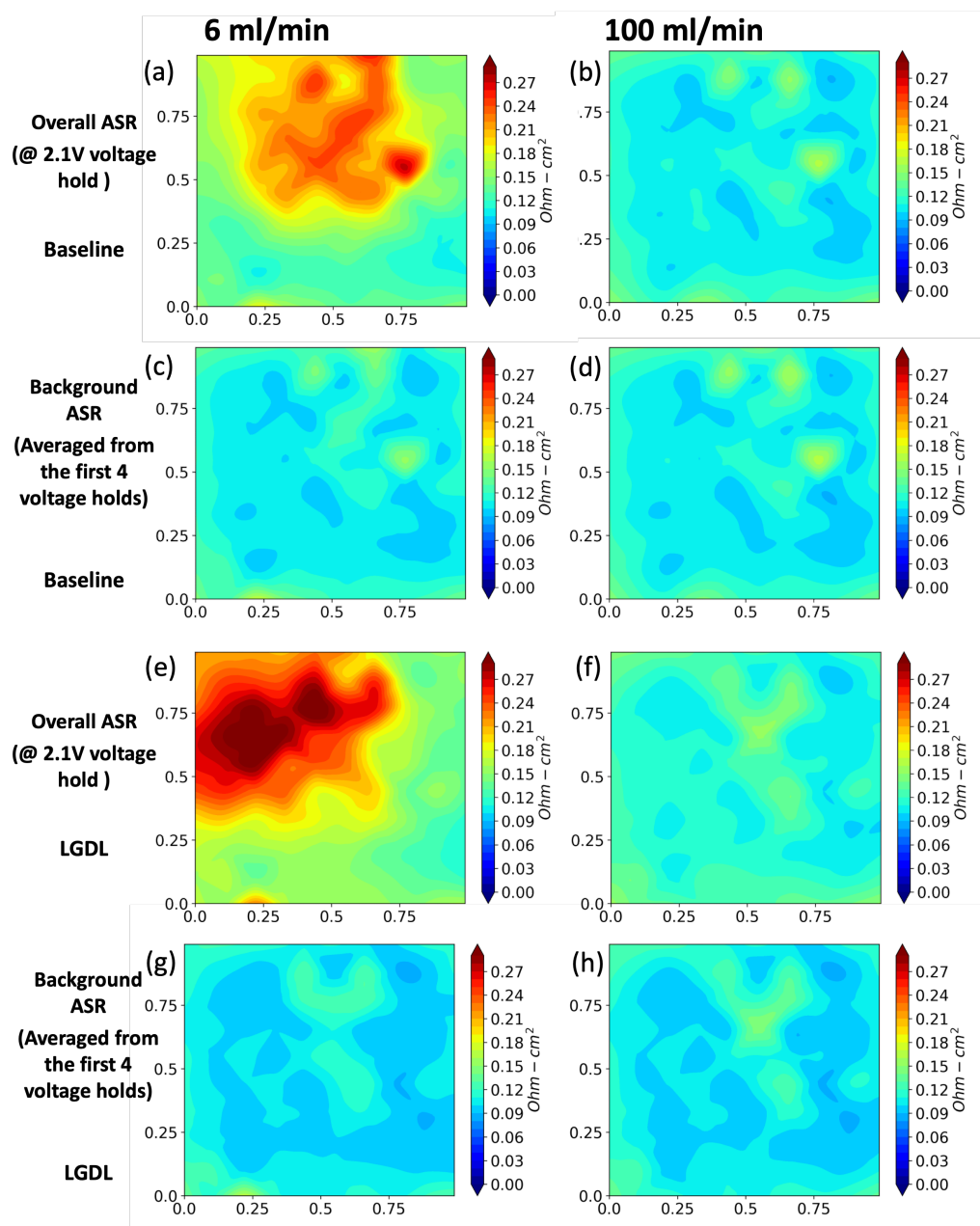


Figure S18: The DARS contour plots along with the background DARS, recorded for Baseline PTL and LGDL operating at 2.1V for 6 and 100 *ml/min*.

Performance characterization using EWTN

Figure S19 depicts the EWTN histograms and corresponding CDD maps for both the baseline PTL and LGDL for increasing anode feedwater flow-rates. It can be observed that all histograms at lower flow-rates start as highly spread out distributions. The histograms move towards 1 for higher flow-rates. For the LGDL at 12 *ml/min* a small gradient can be observed in the CDD map as well as a lower EWTN value compared to the baseline PTL. For flow-rates higher than 25 *ml/min* no gradient can be observed in the CDD maps and the histograms are seen to be shifted towards one. Moreover, all EWTN values are observed to be lower for the LGDL compared to the baseline PTL.

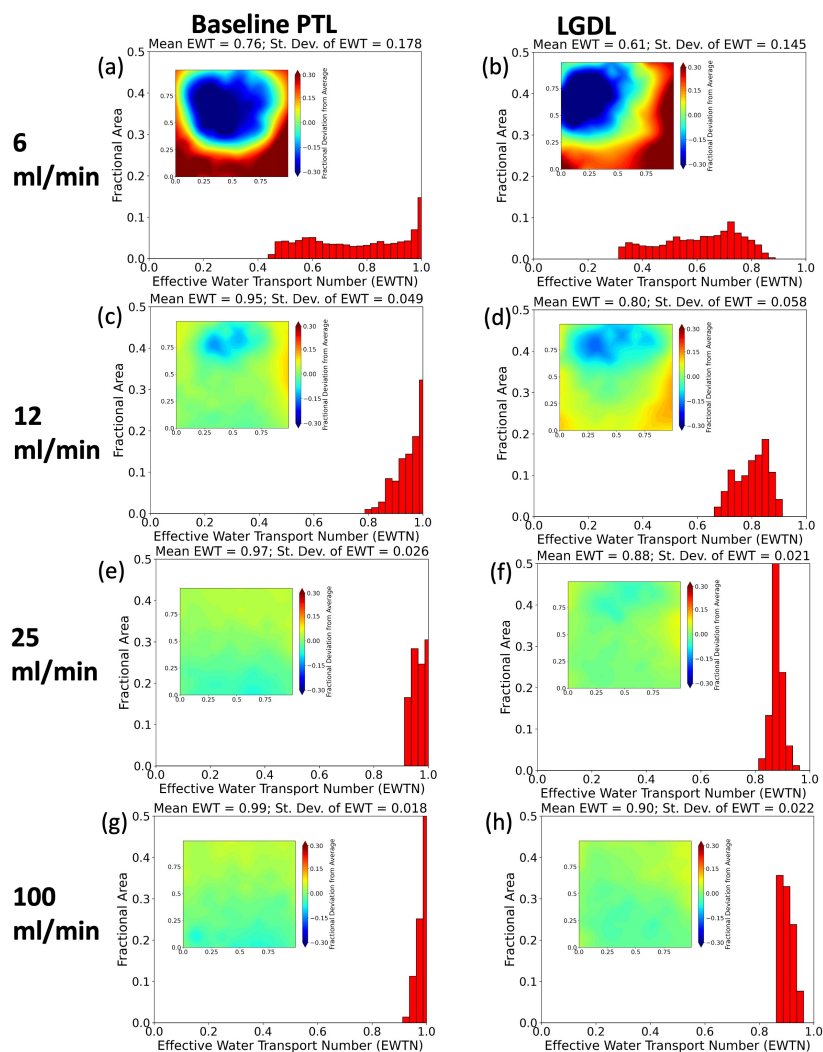


Figure S19: Comparing the performance of the PEWE for the baseline PTL and LGDL using EWTN.

Local overpotential breakdown analysis

The local overpotential analysis is done by applying the 0D model in a similar manner as described in section 7.2.1, but using the spatial current and ASR data. The kinetic parameters $\mathbf{b}$ (the Tafel slope) and i_0 (the exchange current density) were estimated by curve-fitting the model to the global iR-free polarization curves and assumed to be spatially invariant. Figure S20 shows the local distributions used for the calculations for the different overpotentials using the semi-empirical model described in Section 7.1.4. All local overpotentials are normalized as percentages with respect to the total overpotential.

Figure S21 presents the local overpotential plots along with the total iR-free overpotential distribution, for the baseline PTL at 6 *ml/min* and 100 *ml/min*. Similarly, figure S22 shows the same distributions for the LGDL at the same operating conditions.

Histograms, CDD maps and DASR maps for both PTLs

Figure S23 shows the histograms for the baseline PTL and the LGDL operating at 2.1V for flow-rates varying from 6 *ml/min* to 100 *ml/min*. It can be observed from the histograms that the LGDL shows a higher contribution for $\eta_{Ohm,MT}$ compared to the baseline at all flow-rates. For a flow-rate of 12 *ml/min* the baseline PTL shows a close to uniform distribution, while the LGDL still has a clear gradient in the CDD maps and a much larger mean $\eta_{Ohm,MT}$.

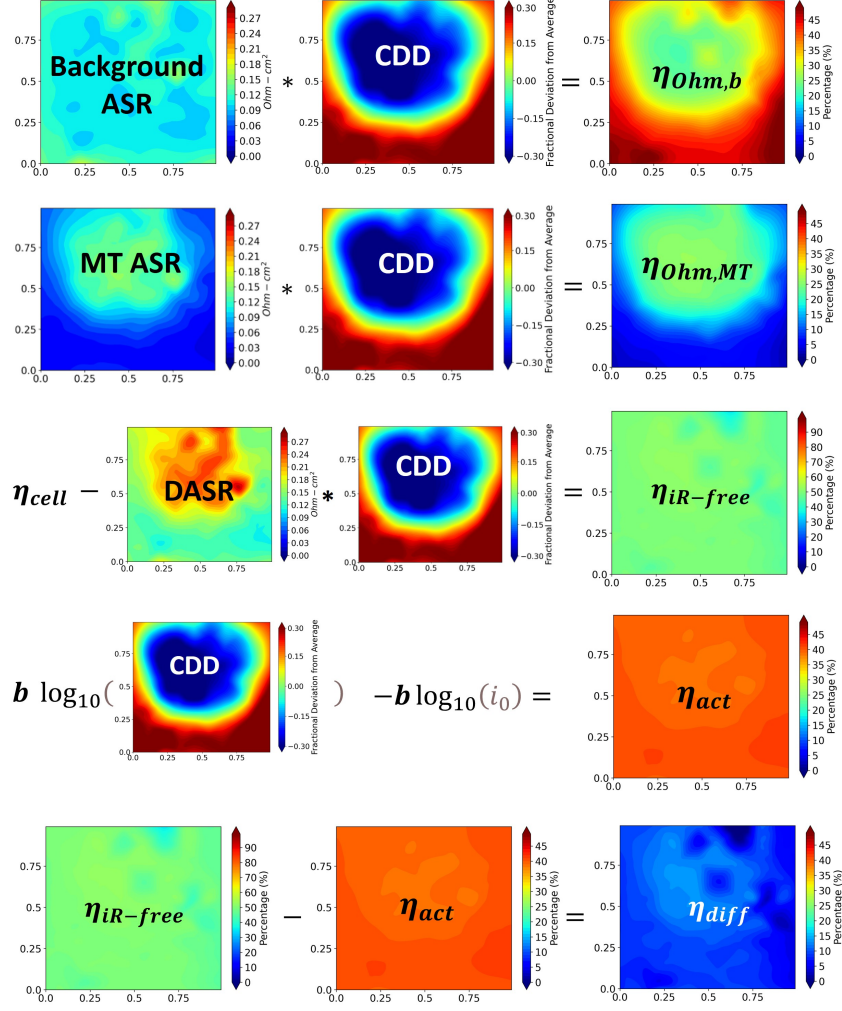


Figure S20: Calculations of local overpotentials using semi-empirical model along with the CDD and DASR measurements.

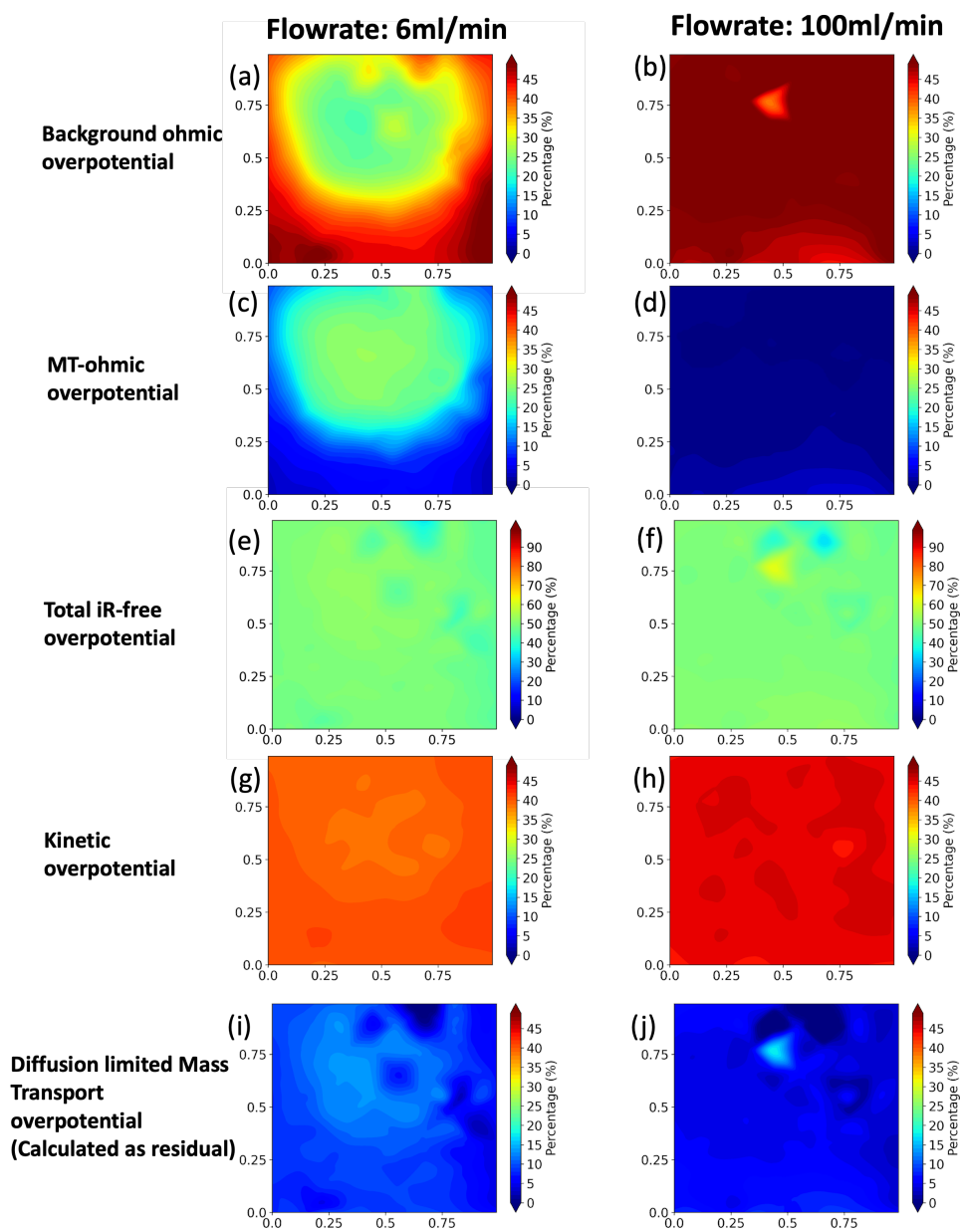


Figure S21: Local overpotential breakdown for a PEWE using a baseline PTL operating at 2.1 V under a flow-rate of 6 ml/min and cell temperature of 80°C.

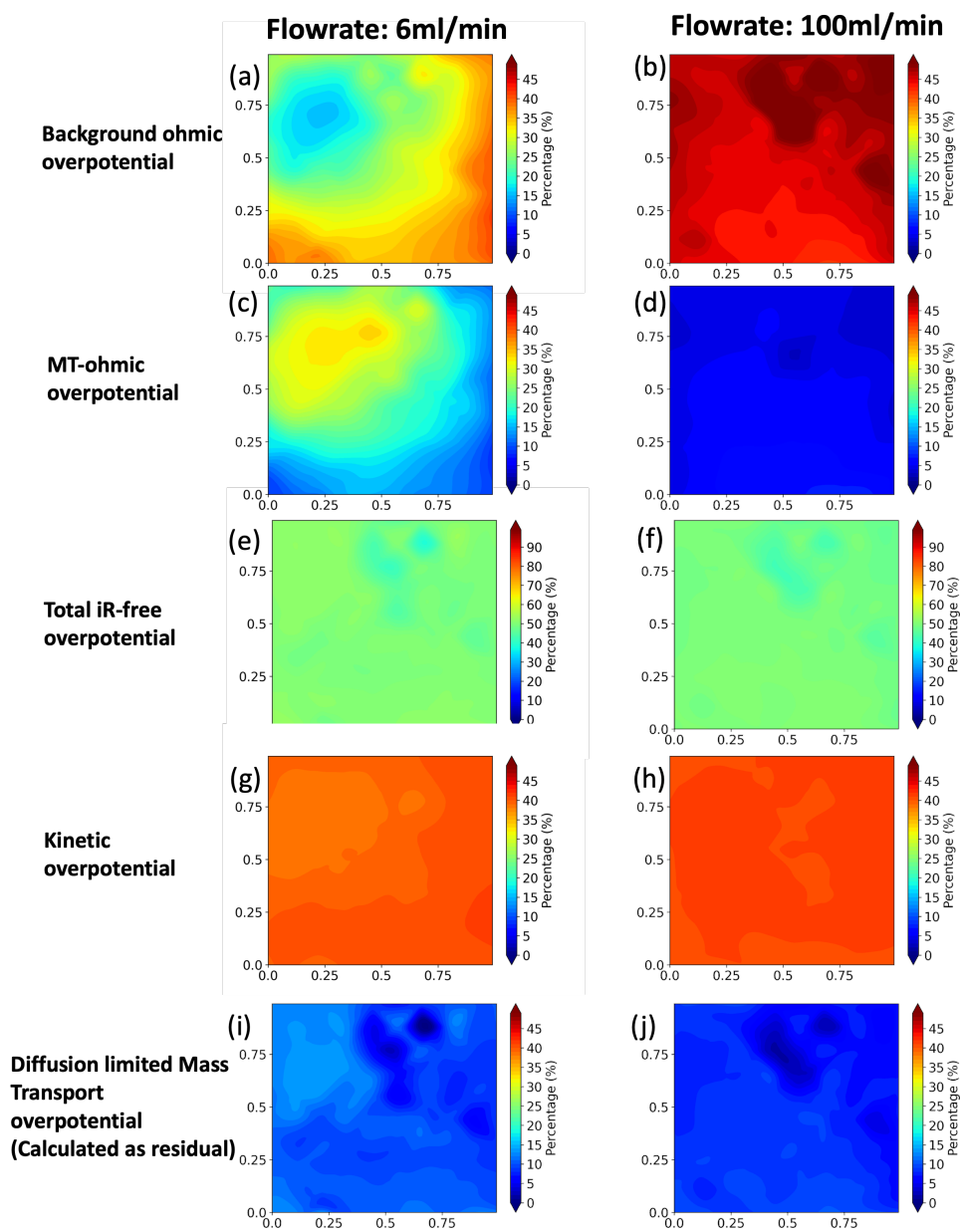


Figure S22: Local overpotential breakdown for a PEWE using a LGDL operating at 2.1 V under a flow-rate of 6 ml/min and cell temperature of 80°C.

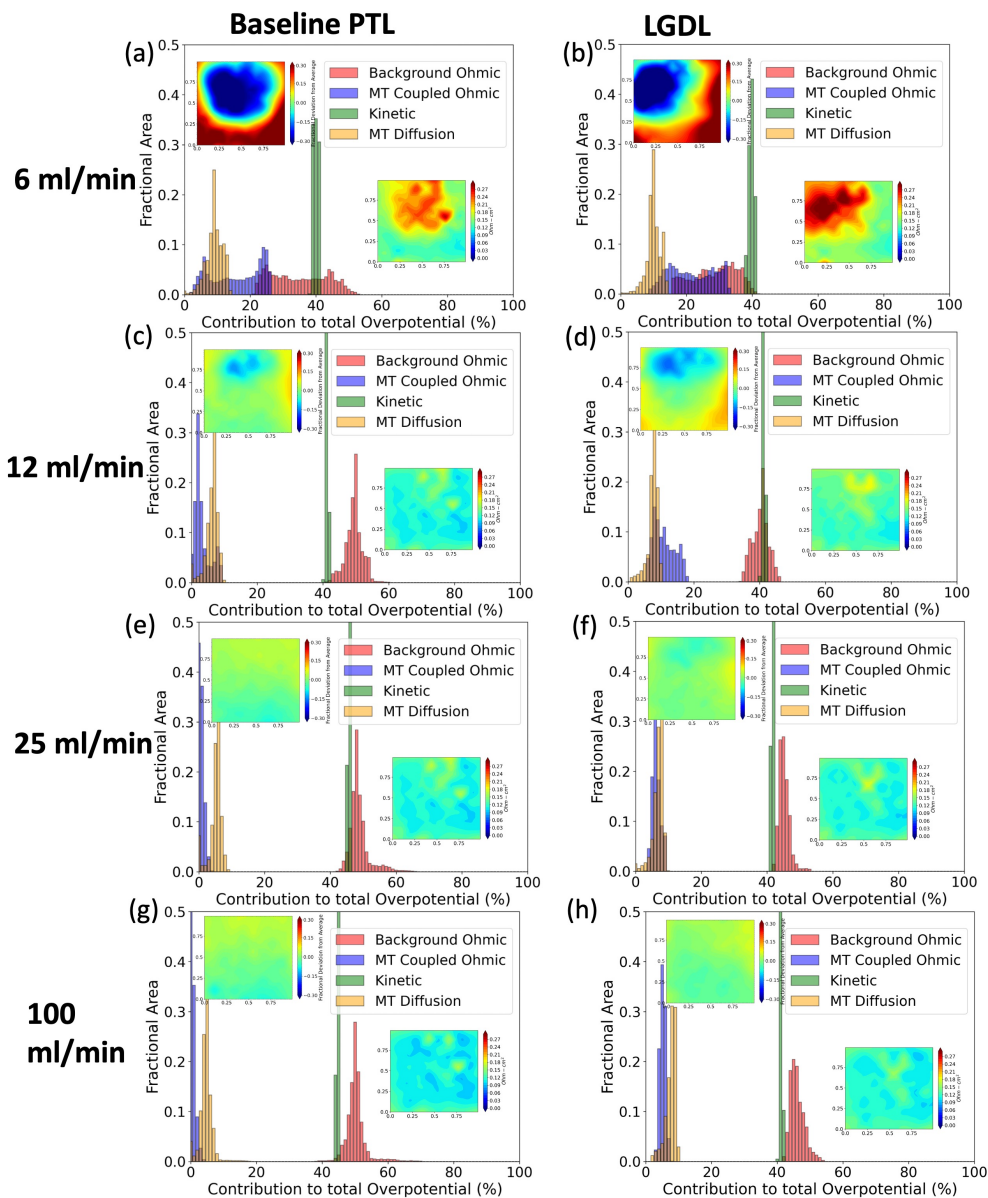


Figure S23: Histograms of all overpotentials for the baseline PTL and the LGDL operating at 2.1V for flow-rates varying from 6 *ml/min* to 100 *ml/min*.

Vita

Anirban Roy, originally from Kolkata, India, completed his high school education in 2010. He then pursued a Bachelor of Technology degree in Mechanical Engineering at MCKV Institute of Engineering, affiliated with the West Bengal University of Technology in India, graduating in 2014. Following his undergraduate studies, Anirban worked as a manufacturing engineer at Tractors' India Pvt. Ltd. for a year, where he was involved in establishing Standard Operating Procedures (SOPs) and prototype implementations. Subsequently, he returned to academia to pursue a Master of Technology degree in Renewable Energy Science and Technology at the Indian Institute of Engineering Science and Technology, Shibpur. In 2019, Anirban embarked on his doctoral journey at the University of Tennessee, Knoxville, under the guidance of Dr. Matthew M. Mench.