# A Nature-Inspired Approach to Robust Fuel Cell Design with Water Management

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## Declaration

I, In Sung Cho, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

.....

Signature

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Date

## Dedication

Thank you, God, for it was by your grace I was able to finish my PhD. I love you, Lord, my strength, and to you, I dedicate this dissertation.

"Naked I came from my mother's womb, and naked I will depart. The Lord gave and the Lord has taken away; may the name of the Lord be praised."

Job 1:21

### Abstract

Polymer electrolyte membrane fuel cells (PEMFCs) are a promising alternative source of energy conversion for a wide range of transport, portable, and stationary power applications, due to their high efficiency, low operating temperature, and high power density. However, there remain challenges to broader commercialisation of this technology, including high electrocatalyst cost, performance limitations associated with unoptimised flow-field designs, and water management. Here, a lung-inspired approach is employed to overcome reactant homogeneity issues in PEMFCs. The characteristics of the lung that allow uniform gas distribution *via* an optimised fractal structure linking bronchi to alveoli, and realising a remarkable combination of minimal entropy production, low pressure drop, and scale-invariant operation, serve as a guide towards the proposed design of fractal flow-fields for PEMFCs.

A theoretical model is developed and simulations are conducted to determine the number of generations required to achieve uniform reactant distribution and minimal entropy production. Guided by the simulation results, three flow-fields with N = 3, 4, and 5 generations are fabricated using 3D printing *via* direct metal laser sintering. The lung-inspired flow-field with N = 4 generations outperforms the conventional serpentine flow-fields while maintaining lower pressure drop. The fractal flow-field with N = 5 generations on the other hand, exhibits excess flooding at high humidity operating conditions. *In situ* water visualisation *via* neutron radiography reveals susceptibility to flooding of the fractal flow fields, due to the lack of convective gas flow requisite for effective liquid water removal, resulting in significant water accumulation in the interdigitated outlet channels. Hence, a novel water management strategy is developed that uses capillaries to control liquid water in PEMFCs. The proposed mechanism serves as a simple and effective means of achieving robust and reliable fuel cell operation. Implementation of this water management strategy is expected to circumvent remaining problems of high-generation fractal flow-fields.

### **Impact statement**

A nature-inspired engineering methodology is presented to solve engineering challenges associated with the reactant distribution in PEMFCs. Here, lung-inspired flow-fields are designed guided by the structure of a lung. While the study investigates the lung-inspired approach specifically for PEMFC applications, we also point to potential applications of the proposed nature-inspired approach to other electrochemical and fluid distribution systems. In particular, redox flow batteries, electrolysers, and different types of fuel cells (high temperature, direct methanol, alkaline, *etc.*) should benefit from the proposed nature-inspired approach, as flooding is mitigated in these systems.

One of the defining characteristics of the fractal approach is scalability. Scalability poses a significant engineering challenge to commercial electrochemical systems. The current approach to system scale-up (*e.g.*, increasing channel number/length) leads to an inevitable consequence of excessive pressure drop or exacerbated reactant maldistribution, factors that contribute to depreciated overall system performance and efficiency. Using the nature-inspired approach, the characteristics of the lung structure are retained irrespective of scale (that is to say, uniform gas distribution is maintained without incurring excessive pressure drop). Thus, adoption of the proposed approach in the design of industrial-scale electrochemical systems should permit scale-invariant operations, thereby allowing system efficiency to be maintained during system scale-up.

The water management mechanism pioneered in this study is also expected to have a significant impact on research fields related to separation of liquid from a multiphase mixture. Microseparators, for instance, currently rely on conventional semi-conductor processing technique for fabrication of the separator chips. The technique entails multiple processing steps (*e.g.*, coating, aging, baking of the photoresist layer, and ion etching), making it undesirable for mass production. The proposed one-step capillary fabrication process serves as a simple, fast, and cost effective means of manufacturing these separator chips, and should foster mass production of microseparators for industrial applications.

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## List of publications

#### Journal papers

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- J. I. S. Cho, T. P. Neville, P. Trogadas, J. Bailey, P. Shearing, D. J. L. Brett, M.-O. Coppens, "Capillaries for Water Management in Polymer Electrolyte Membrane Fuel Cells", *International Journal of Hydrogen Energy*, 2018, 43, 21949-21958.
- J. I. S. Cho, T. P. Neville, P. Trogadas, Q. Meyer, Y. Wu, R. Ziesche, P. Boillat, M. Cochet, P. Shearing, D. J. L. Brett, M.-O. Coppens, "Visualization of Liquid Water in a Lung-Inspired Flow-Field based Polymer Electrolyte Membrane Fuel Cell via Neutron Radiography", *Energy*, 2019, 170, 14-21.
- Y. Wu, J. I. S. Cho, T. P. Neville, Q. Meyer, R. Ziesche, P. Boillat, M. Cochet, P. R. Shearing, D. J. L. Brett, "Effect of serpentine flow-field design on the water management of polymer electrolyte fuel cells: An in-operando neutron radiography study", *Journal of Power Sources*, 2018, 399, 254-263
- J. O. Majasan, J. I. S. Cho, I. Dedigama, D. Tsaoulidis, P. R. Shearing, D. J. L. Brett, "Two-phase flow behaviour and performance of polymer electrolyte membrane electrolysers: Electrochemical and optical characterisation", *International Journal of Hydrogen Energy*, 2018, 43, 15659-15672

- J. O. Majasan, J. I. S. Cho, M. Maier, I. Dedigama, P. R. Shearing, D. J. L. Brett, "Effect of Anode Flow Channel Depth on the Performance of Polymer Electrolyte Membrane Water Electrolyser", *ECS Transactions*, 2018, 13, 1593-1603
- X. Lu, T. Li, A. Bertei, J. I. S. Cho, T. M. M. Heenan, M. F. Rabuni, K. Li, D. J. L. Brett, P. R. Shearing, "The application of hierarchical structures in energy devices: new insights into the design of solid oxide fuel cells with enhanced mass transport", *Energy Environ. Sci.*, 2018.

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1.2 and 3, respectively, which corresponded to flow rates of 0.056 1 min <sup>-1</sup> and 0.335 1
min <sup>-1</sup> at 1 A cm <sup>-2</sup> . The dew point of inlet gases was set to 70°C. No backpressure was
applied to the system
Figure 5.10 The rate of change of water mass in water transport channels with respect to
current density for a parallel flow-field modified with capillaries (6.25 cm <sup>2</sup> surface area).
Experiments were conducted at cell temperature of 70°C using hydrogen and air at 100%
RH and a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow
rates of 0.056 l min <sup>-1</sup> and 0.335 l min <sup>-1</sup> at 1 A cm <sup>-2</sup> . The dew point of inlet gases was set
to 70°C. No backpressure was applied to the system
Figure 5.11 Change in pressure drop across the cathode with respect to current density
for different flow-fields (6.25 cm <sup>2</sup> surface area). Experiments were conducted at cell
temperature of 70°C using hydrogen and air at 100% RH and a stoichiometric ratio of
1.2 and 3, respectively, which corresponded to flow rates of $0.056 \ 1 \ min^{-1}$ and $0.335 \ 1$
min <sup>-1</sup> at 1 A cm <sup>-2</sup> . The dew point of inlet gases was set to 70°C. No backpressure was
applied to the system
Figure 6.1 " $xz$ " orthoslice from tomogram of the cross-section of a 0.5 mm thick 3D
printed stainless steel layer with a capillary array. The small 'globules' at the top and
bottom of the layer are the metal particles that has not been fully sintered by the laser.
Small irregular pores reveal the internal structure of the printed steel exhibits a slight
porosity from incomplete metal sintering

### Chapter 1

### Introduction

Sections of this work have been adapted from "A lung-inspired approach to scalable and robust fuel cell design," *Energy Environ. Sci.*, 2018, 11, 136-143

Polymer electrolyte membrane fuel cells (PEMFCs) have tremendous potential as an energy technology with zero emissions at point of use.[1] The rapid start-up time, low weight, and high efficiency make PEMFCs particularly attractive for portable and applications.[2] However, there remain challenges automotive to broader commercialisation of this technology, including high electrocatalyst cost, durability issues, and performance limitations associated with unoptimised flow-field designs. For example, poor flow-field design can lead to channels becoming clogged with liquid water and non-uniform reactant distribution.[3, 4] Such mass transport issues can lead to the accumulation of excess water in the pores of the gas diffusion layer (GDL)[5] and reactant starvation, which, in turn, can lead to corrosion of carbonaceous support material,[6] electrocatalyst sintering, and facile membrane degradation,[5] all of which are detrimental to fuel cell longevity. Reactions of bulk and crossover gases at each electrode[7] result in the formation of harmful radicals,[8] which significantly hinder the oxygen reduction kinetics and oxygen/air transport through the polymer electrolyte.[9]

Thus far, there have been two prevalent strategies reported in the literature to overcome the uneven reactant distribution issue in PEMFCs. The first approach is based on empirical alteration of the channel configurations (such as channel path length,[10] land width,[11, 12] and land/channel ratio[13, 14]), whereas the second approach imitates the apparent structure of biological organisms.[15-19] The consensus to the first strategy is that the utilisation of flow-fields with wider rib spacing, narrower and shorter channels and path length improves reactant distribution.[10, 11, 14] However, these modifications tend to result in lower membrane hydration and membrane conductivity,[13] a higher pressure drop[20] as well as ineffective water and heat management.[10]

These drawbacks to the first strategy have led to the exploration of an alternative route, taking "inspiration" from biological systems. The term "inspiration" is purposely enclosed within parentheses, since all reports to date imitate the apparent structure of a natural fluid distribution system (such as leaves, lungs, veins, *etc.*) without being fundamentally grounded in the underlying physical phenomena.[15-19] Lack of a formal mathematical description and a methodology to inform the design of such flow-fields leads to difficulties in reproducing those designs, optimising their channel geometries, and scaling them up.



Figure 1.1 Inspired by nature: the unique characteristics of the lung (fractal structure and minimum entropy production) are implemented into the design of lung-inspired flow-fields for PEMFCs.[21]

Here, a more systematic nature-inspired approach[22-24] is used to design flow-fields guided by the structure of the human lung (Figure 1.1), which ensures uniform gas distribution *via* an optimised fractal structure linking bronchi to alveoli, and realising a remarkable combination of minimal entropy production, low pressure drop, and scale-

invariant operation. In the following sections, the utilisation of this approach for engineering lung-inspired flow-fields is presented step-by-step, followed by experimental validation.

Another important aspect of fuel cell operation is water management. Managing water within the cell, not only to ensure proper membrane hydration but also to minimise transport resistance arising from excess liquid water in the system, is a critical issue for high efficiency PEMFCs. Water management is particularly challenging for flow-field geometries designed to distribute gaseous reactant across multiple channels.[25, 26] Thus, a portion of this work is dedicated to addressing flooding issues associated with the lung-inspired flow-fields. Liquid water formation and transport across the lung-inspired flow-field based PEMFCs are evaluated using neutron radiography to gain indepth understanding of water management in lung-inspired flow-fields. Lastly, a novel water management strategy is presented that uses capillary arrays to control liquid water in PEMFCs for potential integration with the fractal flow-fields.

#### 1.1 Inspiration from nature

The major role of the flow-field in a PEMFC is to achieve effective reactant distribution across the catalyst layer, perform water and heat management, as well as transfer of electrical current between individual cell components in a fuel cell stack.[1] The lung serves a purpose in nature that is similar in several aspects: air is drawn from the atmosphere and transported through its fractal architecture into the bloodstream to oxygenate the blood cells. Its fractal geometry obeys Murray's law, which states that the cube of the diameter of the parent vessel is equal to the sum of the cubes of the diameters of the daughter vessels at each level of bifurcation, hereby leading to minimal mechanical energy losses.[27] The repeatedly branching fractal structure of the lung ensures uniform distribution of oxygen throughout the given volume.[28-30] The upper generations (~14-16) of branches (bronchi) are proportioned so as to optimally slow down the gas flow from the bronchial (convection driven flow) to the acinar airways (diffusion driven flow; ~7-9 lower generations), resulting in constant entropy production in both regions and, thus, in minimal global entropy production over the entire

structure.[31, 32] Hence, the condition for thermodynamic optimality is directly associated with the pressure drop in the lung, which must be the same across every branch, according to:[28]

$$\frac{V_{i,j}}{T \cdot L_{i,j}} = \frac{-\Delta P_{i,j}}{T} = \text{constant}$$
(1.1)

where  $V_{i,j}$  (m<sup>3</sup> s<sup>-1</sup>) and  $\Delta P_{i,j}$  (Pa) are the individual gas flow rate and pressure drop for each branch, respectively,  $L_{i,j}$  (m<sup>4</sup> s kg<sup>-1</sup>) is the associated Onsager coefficient[28] (which depends on the length and radius of each branch), and T (K) is the temperature.[28] Using this criterion for each branch, the self-similar architecture of the lung preserves thermodynamic optimality, irrespective of scale.

Another important characteristic of the fractal structure of the lung is the harmonisation of convection and diffusion driven flow between bronchial and acinar airways.[33] This feature prompts the following question: why should an optimal design decrease the flow in the bronchial airways, and aim to achieve this through the minimum number of bifurcations? The answer lies in the Péclet number, Pé, which is the ratio of convective to diffusive transport rate.[30] For Pé numbers larger than 1 (Pé > 1), transport by convection is faster than transport by diffusion, resulting in significant oxygen concentration gradients and, thus, suboptimal oxygen transport to acini. Reduction of the flow *via* a minimum number of bifurcations is optimal, since the "units" needed to build *N* bifurcations grow exponentially with *N*.[33] Thus, a Pé number close to 1 after *N* bifurcations is not only necessary for efficient transport, but also sufficient.[33]

#### 1.2 Polymer electrolyte membrane fuel cells (PEMFCs)

The PEMFC converts chemical energy of hydrogen and oxygen directly into electrical energy by exploiting the electrochemical potential difference arising from two spontaneous half-cell reactions at the electrodes; the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR).[34]

At the core of a PEMFC lie two electrodes, separated by a polymer electrolyte membrane, which are collectively called the membrane electrode assembly (MEA). The

membrane serves to facilitate proton transport while preventing gas crossover and shorting circuiting. The electrode comprises porous gas diffusion and catalyst layers. The MEA is sandwiched between two electrically conducting flow-fields which deliver gaseous reactants through gas channels. When unit cells are stacked in series for a higher voltage output, a single flow-field typically acts as both the anode and cathode plate for adjacent cells (bipolar plate).



Figure 1.2 A schematic of a PEMFC and electrochemical reactions that occurs within.

Two oxidation-reduction reactions are involved in electrochemical energy production in a PEMFC:  $H^+/H_2$  at the anode and  $O_2/H_2O$  at the cathode (Figure 1.2). The hydrogen is oxidised (Equation 1.2) at the anode while the oxygen is reduced at the cathode (Equation 1.3), giving rise to the overall reaction (Equation 1.4). The operation of PEMFC produces electricity, heat, and water.

$$H_2 \to 2H^+ + 2e^- \tag{1.2}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{1.3}$$

$$2H_2 + O_2 \to 2H_2O \tag{1.4}$$

#### 1.2.1 Membrane

The development of a chemically stable cation-exchange perfluorosulfonic acid (PFSA) membrane by DuPont as Nafion in the mid to late 1960s, has led to a large scale adoption of this membrane in PEMFCs. The PFSA membrane is a polytetrafluorethylene (PTFE) polymer backbone with sulfonic acid (SO<sub>3</sub>H) groups on side chains.[35] Although the PTFE backbone is hydrophobic, clusters of sulfonic acid groups form highly hydrophilic regions within the membrane that are able to absorb large amounts of water. In the presence of water, the PFSA membrane develops a high concentration of charged SO<sub>3</sub><sup>-</sup> sites that allow the membrane to conduct protons.

The electrolytic conductivity of the membrane is highly dependent on its water content. Water content is defined as the number of water molecules per sulfonic acid group,  $\lambda = N(H_2O)/N(SO_3H)$ . Figure 1.3 illustrates the strong dependences of membrane water content and conductivity on water activity (the relative humidity of an environment that is in equilibrium with the membrane). An exponential dependence of conductivity on water activity accentuates the importance of maintaining high membrane hydration level to minimise performance losses from electrolytic resistance.



Figure 1.3 Conductivity and membrane water content as a function of water activity.[36]

Another important aspect of the PFSA membranes is the effect of elevated temperature on their material properties and ability to absorb water. If the Nafion dries out at temperatures above 100°C, the membrane undergoes morphological changes that reduce the maximum water content upon rehydration.[37, 38] For this reason, PEMFCs are typically operated at 80°C or less. This upper bound to the operating temperature carries several undesirable consequences, such as sluggish ORR kinetics and the requirement of a sophisticated cooling system, which introduces additional parasitic losses and system cost. A significant research activity is currently being undertaken in the development of membranes that can tolerate higher operating temperatures with reduced dependence on humidity.[38-40]

#### 1.2.2 Gas diffusion layer

The gas diffusion layer (GDL) is a carbon fibre sheet that is treated with PTFE to make it waterproof and prevent the blockage of pores with liquid water. A micro-porous layer (MPL) made of carbon carrier modified with hydrophobic agent, is often added between the GDL and catalyst layer (CL) to alleviate flooding.[41, 42] The main functions of the GDL are to allow gas and electrical transport to and from the catalyst layer, remove liquid water from the electrode, and dissipate heat produced at the catalyst layer.[43] It also provides structural support to the MEA.

Although the GDL is a seemingly minor component of a PEMFC stack, studies report that altering the structural properties such as porosity, PTFE content, thickness, and morphology can lead to substantial improvement in fuel cell performance.[43-45] Changing the GDL thickness in particular, has a significant impact on fuel cell performance, as it has a much greater influence on reaction diffusion path in comparison to other parameters. Thinner GDL facilitates reactant mass transport by decreasing reactant concentration gradient[46, 47] and retaining less liquid water within the electrode;[45] beneficial traits that could be used to increase power density and alleviate flooding predominant in fractal flow-fields, especially at high humidity operating conditions.[21]

#### 1.2.3 Catalyst layer

Key electrochemical reactions and various transport phenomena occur inside the catalyst layer, including gas and liquid water transport, dissolution of reactant in the electrolyte, diffusion and reaction of the dissolved reactant within the agglomerate, ionic and electronic conduction.

The catalyst layer typically consists of carbon support, ionomer, and platinum particles, which are randomly dispersed within a porous matrix. Supporting catalyst onto carbon supports is crucial, as it reduces agglomeration and enhances stabilisation of the catalyst nanoparticles.[48] The catalyst layer is deposited on either the membrane or GDL surface by spraying the catalyst ink. The membrane-catalyst layer-GDL assembly is then hot pressed together to allow the electrolyte material to 'flow' at the interface and create the required bonds and connections between the layers.[49]

Numerical modelling of such catalyst layers has been widely researched over the past decades. Mathematical models with varying levels of complexity have emerged to improve the understanding of the complex transport phenomena occurring inside the catalyst layer. These models are broadly classified into three different categories depending on the degrees of resolution: the interface model,[36, 50-52] the homogeneous model,[53-55] and the agglomerate model.[56-62] Agglomerate models are usually employed as it captures most closely the composition and morphology of carbon black supported platinum particles,[63] and the mass transport losses occurring within the catalyst layer.[51] A common element in agglomerate models is that the catalyst layer consists of small spherical agglomerates of carbon supported platinum particles that are evenly coated with a thin ionomer film.[60, 62, 64] Such models have shown remarkable agreement with experimental data.[65-67]

A defining feature of an agglomerate model is how the two-phase liquid transport inside a PEMFC is handled. Consideration of liquid water in the model is important for accurate depiction of actual PEMFC operating environment, where gas transport within the electrode is inhibited by the presence of liquid water. The two-phase agglomerate models have been extensively developed and applied in numerical studies. Many early models, like those developed by Pasaogullari and Wang,[68] utilised capillary pressure data based on capillary flow through sand, mainly Udell's correlation.[69, 70] However, Udell's correlation often leads to a vast underestimation of the liquid water saturation level in the electrode. [68, 71-73] These issues have led Nguyen *et al.* to experimentally determine the capillary pressure function of the gas diffusion and catalyst layers[74] using the volume displacement technique.[75] Wang and Nguyen developed a two-phase PEMFC model based on the experimentally determined capillary pressure properties of the GLD and CL, and evaluated the effect of the capillary pressure properties of the electrode on the liquid water transport rate. [76, 77] The liquid water saturation level jump condition at the GDL | CL interface was also correctly accounted for, by introducing a constant capillary pressure boundary condition at the interface. Building on these studies, Marquis and Coppens have developed a comprehensive onedimensional agglomerate model that accounts for the formation and transport of liquid water within the cathode.[78] This model will be adopted in this thesis to develop and simulate a two-dimensional model of fractal flow-field based PEMFCs.

#### 1.2.4 Flow-field plate

Flow-field is a vital component of a PEMFC as it performs numerous essential functions that dictate the overall system performance, such as reactant distribution across the active area, heat and water management, current collection, and providing mechanical support to the MEA. Flow-field channel configuration in particular, has a huge impact on PEMFC performance, with reported improvement in output power density as much as 50% from appropriate gas distribution alone.[79] Also, bipolar plates comprise the majority of the volume and weight of a PEMFC stack.[79] Thus, the power density (W  $L^{-1}$ ) and specific power (W kg<sup>-1</sup>) of a fuel cell stack can be significantly increased by the use of lightweight materials and improving the layout configuration of flow-fields.



Figure 1.4 Schematics of serpentine (left), parallel (middle), and interdigitated (right) channel architectures for flow-field plates. Red and green arrows represent inlet and outlet channels, respectively.

Three of the most conventional flow-field geometries reported in the literature are parallel, serpentine, and interdigitated (Figure 1.4). The simplicity of parallel flow-field design and the low pressure drop across the channel[80, 81] make them ideal for use in PEMFCs. However, the use of parallel geometry is impractical at high humidity operating conditions, since this design leads to excessive flooding when there is a lack of convective gas.[82, 83] For this reason, commercial parallel flow-field based PEMFCs utilise air with little or no humidification to pre-empt flooding in the cathode.[84, 85] Serpentine flow-field is designed to direct the reactant gas through a single path comprised of one or more flow channels. The higher gas flow rate associated with this design makes the serpentine configuration more suitable for use in high humidity operating environments.[86, 87] However, the high gas flow rate and longer channel path of the serpentine design lead to much higher channel pressure drop than the parallel flow-fields.[25] Interdigitated flow-fields have been investigated in depth for their potential to improve reactant delivery and water management.[88, 89] These flow-fields comprise dead-ended gas channels designed to alleviate mass transport losses by forcing the reactant gas directly into the electrode. However, the excessive pressure drop arising from this forced convection renders its use prohibitive for commercial PEMFCs.[25] High channel pressure drop is undesirable from the viewpoint of system efficiency, as it increases parasitic energy consumption by air blowers.[90, 91] Thus, the development of a flow-field design that accomplishes effective water management and uniform gas distribution at low pressure drop is instrumental for the development of high efficiency PEMFCs.

#### 1.3 PEMFC performance

Theoretically, the voltage output of a PEMFC should be invariable to the changes in current density loading at fixed operating conditions. However, in reality, the voltage output decreases as current loading increases, due to irreversible cell voltage losses arising from several electrochemical phenomena occurring within the cell. The three major causes of overpotential in a PEMFC are activation, Ohmic, and mass transport losses. The fuel cell performance is dictated by the extent of contribution of each type of losses.

#### 1.3.1 Reversible potential

The maximum electrical work that a PEMFC can generate in a constant temperature and constant pressure process is given by the negative of the Gibbs free energy change of the process. The reversible voltage ( $E_{rev}$ ) can be obtained by relating the work available from the Gibbs free energy change to the electrical work done by moving a charge through an electrical potential difference. Accounting for the variations in temperature and reactant concentration, the reversible voltage of a PEMFC is expressed by the Nernst equation:

$$E_{rev} = \frac{-\Delta G^0}{2F} + \frac{\Delta S^0}{2F} (T - T_0) - \frac{RT}{2F} \ln \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}}$$
(1.5)

where  $\Delta G^0$  (J mol<sup>-1</sup>) and  $\Delta S^0$  (J mol<sup>-1</sup> K<sup>-1</sup>) are the change in Gibbs free energy and entropy for the reaction at the reference state, R (J mol<sup>-1</sup> K<sup>-1</sup>) is the universal gas constant, T (K) is the temperature, p (Pa) is the partial pressure, F is the Faraday constant (C mol<sup>-1</sup>), and E (V) is the electrochemical potential. Equation (1.5) indicates that the gain in reversible voltage by increasing the partial pressure of reactants is small due to natural logarithm. Nevertheless, it is advantageous to operate the fuel cell at higher pressure, due to kinetic reasons associated with activation and mass transport losses. The equation also implies that the theoretical efficiency of a fuel cell is higher at lower temperature. However, real fuel cell performance typically increases with increasing temperature, as the reaction kinetic improves with increasing temperature.[1]

#### 1.3.2 Activation overpotential

Activation overpotential ( $\eta_{act}$ ) is characterised by a rapid drop in cell potential at low current densities. Activation losses stem from the rate parameters and activation energy of one or more rate-limiting electrochemical reaction steps,[34] and it is defined as the voltage that is sacrificed to overcome the activation barrier associated with the electrochemical reaction. The majority of activation losses in a PEMFC occur at the cathode due to slow electrode kinetics of the ORR attributed to many individual reaction steps and significant molecular reorganisation.[34] The current-overpotential relation for activation loss is given by the Butler-Volmer equation

$$j = j_0 \left( \frac{c_o^*}{c_o^0} e^{\alpha n F \eta / (RT)} - \frac{c_R^*}{c_R^0} e^{-(1-\alpha)n F \eta / (RT)} \right)$$
(1.6)

where *j* represents electrode current density,  $j_0$  is the exchange current density,  $\alpha$  is the transfer coefficient,  $c_0^*$  and  $c_R^*$  are the actual surface concentrations of the rate-limiting species in the reaction,  $c_0^0$  and  $c_R^0$  are the reference bulk reactant and product concentrations, *n* is the number of electrons transferred in the electrochemical reaction, and  $\eta$  is the overpotential. The first and second term describe the cathodic and anodic contribution, respectively. The Butler-Volmer equation states that the current produced by an electrochemical reaction increases exponentially with increase in activation overpotential, and it generally serves as an excellent approximation for most single-step electrochemical reactions.[34]

At high overpotential, the cathodic term is dominant and Equation (1.6) reduces to the Tafel equation expressed as:

$$\eta_{act} = \frac{RT}{\alpha F} \ln \left(\frac{j}{j_0}\right) \tag{1.7}$$

#### 1.3.3 Ohmic overpotential

Ohmic overpotential ( $\eta_{ohm}$ ) is characterised by a linear decrease in cell voltage with increasing current density. Ohmic losses within a PEMFC occur as a result of ionic resistance of the membrane, electronic resistance of fuel cell components, and contact

resistance between each component. The resistance of a fuel cell is usually represented by area-normalised resistance, also known as area-specific resistance,  $R_{ohm}$ , which is given by:

$$R_{ohm} = R_T A \tag{1.8}$$

where  $R_T$  and A represent the total resistance and area of the catalyst layer, respectively. Since both ionic and electronic resistance obey Ohm's law, Ohmic overpotential can be expressed by:

$$\eta_{ohm} = R_{ohm} j \tag{1.9}$$

Area-specific resistance accounts for the fact that fuel cell resistance scales with area, thus allowing fuel cells of different active area to be compared.

#### 1.3.4 Mass transport overpotential

Mass transport overpotential ( $\eta_{conc}$ ) stems from diffusion limitation within the electrode at elevated reaction rate, where finite mass transport rates limit the supply of fresh reactant and removal of product. Depletion of reactant at the reaction site leads to a reduction in reversible thermodynamic potential, reaction kinetics, and exchange current density. At steady state, the diffusive flux of a reactant can be estimated by the Fick's first law of diffusion

$$j = -nFD^{eff}\left(\frac{c_R^* - c_R^0}{\delta}\right) \tag{1.10}$$

where  $D^{eff}$  is the effective reactant diffusivity and  $\delta$  is the diffusion layer thickness. The limiting current density,  $j_L$ , is a measure of the maximum diffusion rate at which a reactant can be supplied to an electrode, and it is characterised by a sudden drop in cell voltage as a result of zero reactant concentration at the catalyst layer. Equation (1.10) is modified to calculate  $j_L$  by setting  $c_R^* = 0$ :

$$j_L = nFD^{eff} \frac{c_R^0}{\delta} \tag{1.11}$$

An expression for the mass transport overpotential is derived from the Nernst equation by using the definition of the limiting current density, and this is given by:

$$\eta_{conc} = c \ln\left(\frac{j}{j_L - j}\right) \tag{1.12}$$

where c is a constant with an approximate form:

$$c = -\frac{RT}{nF} \left( 1 + \frac{1}{\alpha} \right) \tag{1.13}$$

The equation implies that the mass transport overpotential is minor for  $j \ll j_L$ ; however,  $\eta_{conc}$  will rise sharply as j approaches  $j_L$ . In reality, a fuel cell usually yields a larger value of c than what the equation predicts, as the limiting current density is predominately determined by external factors such as reactant depletion along the channels and flooding.

#### 1.3.5 Polarisation curve

Polarisation is the most universal characterisation technique used to evaluate the overall fuel cell performance. Polarisation curve is a plot of the current density versus the electrode potential for a specific electrode-electrolyte combination. Polarisation curve reveals the sum of potential losses due to activation, Ohmic, and mass transport overpotentials at a given current density:

$$V = E_{rev} - \eta_{act} - \eta_{ohm} - \eta_{conc}$$
(1.14)

A typical polarisation curve of a PEMFC is presented in Figure 1.5. The dashed lines illustrate the extent of contribution of each irreversibility at different operating regions.



Figure 1.5 Typical polarisation curve of a PEMFC. The dashed lines depict the representative distribution of overpotentials.

The loss in fuel cell performance in the low to mid current density region is dominated by activation overpotential, primarily due to the sluggish ORR at the cathode. Significant mass transport overpotential arises at the high current density region because of elevated reactant consumption and water generation, prompting a rapid drop in cell potential.

#### 1.3.6 Electrochemical impedance spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a widely used perturbative characterisation technique used to differentiate major sources of impedance of an electrochemical system. Electrochemical impedance is the response of an electrochemical system to an applied potential or current, and the frequency dependence of the impedance allows the internal dynamics of the system to be revealed. When applied to a PEMFC, sources of overpotential such as reaction kinetics, Ohmic resistance, and mass transport can be independently quantified.

Impedance is a measure of the ability of a system to impede the flow of electrical current when a voltage is applied. Impedance (Z) is given by the ratio between a time-dependent voltage and a time-dependent current:

$$Z = \frac{V(t)}{I(t)} \tag{1.15}$$

Impedance measurements are made by applying a small sinusoidal voltage perturbation, V(t), and recording the system's resultant current response, I(t). The expressions for the input and response signals are given by

$$V(t) = V_0 \cos(\omega t) \tag{1.16}$$

$$I(t) = I_0 \cos(\omega t - \phi) \tag{1.17}$$

where  $V_0$  (V) and  $I_0$  (A) are the amplitudes of the voltage and current signals, respectively. The angular frequency,  $\omega$  (s<sup>-1</sup>), is defined as a function of frequency, f (s<sup>-1</sup>):

$$\omega = 2\pi f \tag{1.18}$$

The response signal may be shifted in phase compared to the input signal by  $\phi$ . A graphical representation of the relationship between an input signal and a phase-shifted response signal is shown in Figure 1.6.



Figure 1.6 Depiction of the response to a sinusoidal voltage perturbation of the current with a phase shift ( $\phi$ ) at a given angular frequency,  $\omega$ .  $I_0$  and  $V_0$  are the signal amplitudes of current and voltage, respectively.

Substituting Equations (1.16) and (1.17) into Equation (1.15), the sinusoidal impedance response of a system can be written as
$$Z = \frac{V_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)}$$
(1.19)

The impedance response can be written in terms of real and imaginary component using the complex notation

$$Z = \frac{V_0 e^{i\omega t}}{I_0 e^{i(\omega t - \phi)}} = Z_0 e^{i\phi} = Z_0 (\cos \phi + i \sin \phi)$$
(1.20)

where *i* is the imaginary unit. The impedance of a system can be expressed in terms of a phase shift  $\phi$  and a magnitude  $Z_0$  (Bode plot). However, it is more common practice to represent the system impedance in terms of a real ( $Re(Z) = Z_0 \cos\phi$ ) and an imaginary component ( $Im(Z) = iZ_0 \sin\phi$ ). Such graphical representation of system impedance is known as Nyquist plot.

The physiochemical processes occurring within a PEMFC can be modelled using a network of circuit elements. This circuit based representation of fuel cell behaviour is known as equivalent circuit models. An effective equivalent circuit model allows accurate interpretation of the reaction kinetics, Ohmic resistance, mass transport, and other properties of a PEMFC.



Figure 1.7 A representation of resistive and capacitive phenomena at the membrane | cathode catalyst layer interface (top) modelled with a simplified Randles circuit (bottom).

One of the most commonly employed equivalent circuit model used to describe the combination of the Ohmic resistance ( $R_{\Omega}$ ) in series with a parallel combination of the double layer capacitance ( $C_{dl}$ ) and Faradaic resistance ( $R_{CT}$ ) is known as the Randles circuit (RC). Here, the Ohmic resistance represents the combination of electrolytic and electric resistance of a system. The Faradaic resistance models the kinetics of the electrochemical reaction. The double layer capacitance reflects the separation of charge that occurs across the reaction interface during the electrochemical reaction (Figure 1.7). The charge separation causes the interface to behave like a capacitor. The transfer function of the Randles circuit shown in Figure 1.7 is given by

$$Z = R_{\Omega} + \frac{1}{\frac{1}{R_{CT}} + i\omega C_{dl}}$$
(1.21)

EIS separates impedances arising from electrochemical reaction  $(R_{ct})$ and proton/electron conduction ( $R_{\Omega}$ ), by exploiting the time lag associated with charging and discharging of the double layer. At high frequencies (1-10 kHz), the capacitor acts as a short circuit and the current is completely shunted through the capacitor. This allows  $R_{\Omega}$ to be isolated and its value to be revealed by the high frequency (leftmost) x-intercept of the Nyquist plot. In contrast, at low frequencies (50-500 mHz), the capacitor fully discharges and it acts as an open circuit. All of the current is forced to flow through the resistors and the total impedance of the system is given by the impedance of the resistors. The value of the total impedance is given by the low frequency (rightmost) x-intercept of the Nyquist plot. For intermediate frequencies, the impedance response of the model exhibits both resistive and capacitive nature of the system. This is because the charge stored in the capacitor cannot fully support the current which causes some of the current to pass through the resistors. This gives rise to the phase-shift between voltage and current, causing the impedance to become complex. The Nyquist representation of the Randles circuit in Figure 1.7 is displayed in Figure 1.8.



Figure 1.8 Example of Nyquist plot for a Randles circuit.

Mass transport in PEMFCs is generally modelled by Warburg circuit elements. One of the commonly used Warburg models for a PEMFC is 'porous bounded Warburg model', which is a modification of 'infinite' Warburg model used to describe the mass transport phenomena for an infinitely thick diffusion layer. Porous bounded Warburg model is used to model finite diffusion processes with diffusion occurring through a fixed diffusion layer thickness from an inexhaustible bulk supply of reactants, and it is given by the form

$$Z = \frac{\sigma_j}{\sqrt{\omega}} (1 - i) \tanh\left(\delta_{\sqrt{\frac{i\omega}{D_j}}}\right)$$
(1.22)

where  $\omega$  is the frequency,  $D_j$  is the diffusion coefficient of species j,  $\delta$  is the diffusion layer thickness and i is the imaginary unit. The Warburg coefficient for a species j is given by the term  $\sigma_j$ , and it is defined as

$$\sigma_{j} = \frac{RT}{(n_{j}F)^{2}A\sqrt{2}} \left(\frac{1}{c_{j}^{0}\sqrt{D_{j}}}\right)$$
(1.23)

where A is the electrode area and  $c_j^0$  is the bulk concentration of species *j*. The Warburg coefficient describes the effectiveness of transporting species *j* to or away from a reaction interface; if the bulk concentration or the diffusion coefficient is high, faster diffusion will occur which diminishes the Warburg coefficient and the mass transport impedance. The frequency of the potential perturbation also determines the value of the Warburg impedance. The Warburg impedance only appears at the low frequency region

of the Nyquist plot, as the reactants must diffuse further at low frequencies, thereby increasing the Warburg impedance.



Figure 1.9 Example of Nyquist plot for a porous bounded Warburg element.

Figure 1.9 gives an example of the Nyquist plot for a porous bounded Warburg element. The porous bounded Warburg impedance displays the characteristic of an infinite Warburg at high frequency ( $\omega > 10D_j/\delta$ ) with a slope of 1. However, the Warburg impedance behaves like a resistor at low frequency and it returns to the real impedance axis. The intercept gives information about the diffusion layer thickness. Figure 1.10 shows a Nyquist plot for Randles circuit diagram with the porous bounded Warburg model. The small semicircle on the left is due to the cathode RC element, while the large semicircle on the right comes from the porous bounded Warburg element.



Figure 1.10 An example of a Nyquist plot for Randles circuit diagram with the porous bounded Warburg element.

Figure 1.11 shows the equivalent circuit model used for data fitting of the Nyquist plots presented in this study. The equivalent circuit consists of two parallel RC elements to

model the anode  $(R_{CT,A})$  and cathode  $(R_{CT,C})$  activation kinetics, a porous bounded Warburg element  $(Z_w)$  to describe the mass transport effect at the cathode, and an Ohmic resistor  $(R_{\Omega})$  to describe the Ohmic losses. The Ohmic resistor is a sum of Ohmic losses from various parts of the fuel cell (membrane, electrode, component interface, *etc.*). The conventional double-layer capacitance is replaced by a constant phase element (*CPE*) in order to improve the quality of the fit and to correctly account for the highly porous nature of the fuel cell electrode.[92]



Figure 1.11 Equivalent circuit diagram used for impedance analysis in this study.  $R_{\Omega}$  is the Ohmic resistance, *CPE* is the constant phase element,  $Z_w$  is the Warburg element, and  $R_{CT,A}$  and  $R_{CT,C}$  are the anodic and cathodic charge transfer resistance, respectively.

# 1.4 Water transport mechanisms

The two-phase transport in flow-field channels occurs predominantly in the form of droplet, film, or slug flow.[93] At high gas flow rates, shear forces detach droplets from the GDL surface at sizes much smaller than channel dimensions, resulting in a mist flow in the gas channel. This is an effective mode of liquid water removal as it mitigates mass transport arising from excess liquid water in the channel. However, high parasitic associated with pumping renders such mode of water removal impractical in PEMFCs. For common air stoichiometric ratios ( $\alpha_{air} = 2$  or 3), the droplet detachment diameter is larger and the influence of channel dimension and surface property on the two-phase flow pattern becomes more prominent. In this situation, capillary wicking of liquid water occurs from the hydrophobic GDL onto the channel walls, resulting in corner[93, 94] or annular film flow.[93] The water is then transported downstream by the channel pressure gradient. This mode of liquid water transport is, however, only observed when the channel surface is sufficiently hydrophilic to satisfy the following Concus-Finn condition:[95]

$$\theta < \pi/2 - \alpha \tag{1.24}$$

where  $\theta$  is the contact angle, and  $\alpha$  is the half-angle of the channel cross-section corner. For cases where  $\theta < \pi/2 - \alpha$ , corner or annular film flow becomes a primary mechanism for liquid water removal. For cases where  $\theta > \pi/2 - \alpha$ , the liquid water cannot be sustained in the form of film on the channel wall due to the lack of surface tension, and slug formation results. Water slugs can only be removed when gravity or shear forces overcome the surface tension.[96-98] Formation of slug is detrimental to fuel cell performance, especially when flow-field geometries with multiple channels (*e.g.*, parallel and lung-inspired flow-fields) are used, as it creates path of least resistance between channels and renders the gas distribution across the electrode highly nonuniform. Therefore, multi-channel flow-fields often requires implementation of water management strategies, as leveraging gas flow alone for water removal leads to prohibitively high parasitic loss from pumping.

# 1.5 Liquid water visualisation

Visualising liquid water in PEMFCs is critical to understand the water formation, transport, and removal mechanisms, and gain insight into possible modifications to be made to the flow-field design and surface properties for improved water management. Several experimental techniques have been developed in the past decades that allow in situ visualisation of the water content in both the MEA and flow-field channel. These include optical visualisation,[99-101] X-ray tomography, [102, 103] X-ray radiography, [104, 105] and neutron radiography. [106-108] Each technique entails its merits and challenges, [25, 109] and the suitability of a visualisation technique should be determined on the basis of the spatial and temporal resolution required by the experiment.

Direct optical visualisation is a well-developed and relatively inexpensive technique that provides superior spatial and temporal resolution of the water droplet formation, growth, and movement.[110-112] However, the technique requires substitution of conventional fuel cell components with transparent materials such as quartz glass[113] or plastic,[114]

which can lead to completely different surface wetting and thermal properties. Moreover, the results obtained using optical technique is often qualitative, due to limited depth perception from the top of the transparent window.[25, 114] Integration of the technique with the lung-inspired fractal flow-fields is also unfeasible, because of the internal three-dimensional (3D) network of fractal branches.

X-ray tomography has been employed to gain three-dimensional insight on the water distribution in PEMFCs.[2, 115, 116] The sub-micron resolution capacity of X-ray synchrotron beam lines allows even small water clusters to be precisely localised in the GDL pores and gas flow channels. However, the limited penetration depth of X-ray through fuel cell components restricts its application to cells with active area of less than 1 cm<sup>2</sup>. Also, it remains a challenge to combine high temporal and spatial resolution to capture the rapid evolution and transport of liquid droplets.[117]

Synchrotron X-ray radiography allows *in situ* observation of water transport in a PEMFC with spatial and temporal resolution of 1  $\mu$ m and 1 s frame<sup>-1</sup>, respectively.[118, 119] Liquid water visualisation has been conducted both in the in-plane and throughplane directions of the fuel cell.[119] However, since X-ray is not as sensitive to liquid water as other PEMFC components, the cell has to be made very thin in the direction of the beam, resulting in a cell design that significantly deviates from the conventional PEMFC architecture. Also, synchrotron radiation for imaging is known to induce radiation damage to the polymer electrolyte membrane,[120] which limits tests to an exposure time of about 30 minutes.[117]

Neutrons on the other hand, penetrate deeply through many common metals, and have a high sensitivity to light elements. The higher attenuation by light elements is due to the fact that neutrons interact predominately with the nucleus, rather than the electron density, as in the case of X-rays.[117] These traits allow evaluation of the effect of different cell designs and operating conditions on liquid water transport and distribution across the entire fuel cell active area,[121-123] with minimal modification to the material and design of cell components. When coupled with a charge coupled device (CCD) camera, data acquisition rates as high as 30 Hz are achievable, although at these

high rates, the signal to noise in the images may be too low to attain detailed spatial information.[124] Typically, a longer single-frame exposure time is used (1 - 25 s) and images are averaged to reduce noise and improve image quality.[121, 125-127]

## 1.6 Water management strategies

Water management remains a persistent challenge for PEMFCs, especially those using perfluorosulfonic acid (PFSA) type membranes, which require effective hydration to ensure good ionic conductivity[128, 129] and longevity.[130, 131] If performed properly, humidifying the inlet gases can ensure proper humidification of the membrane, while any excess water that is produced from the electrochemical reaction has to be continuously removed to ensure efficient fuel cell operation. Water droplets accumulating in flow-field channels can cause system instability,[83, 132, 133] flow maldistribution,[134, 135] and increase in pressure drop across the flow-field,[21, 132, 136] potentially resulting in long-term performance degradation,[5, 21, 137-139] and depreciated fuel cell efficiency.[21, 87] Maintaining an adequate water balance in the system is, therefore, imperative for enhanced fuel cell performance, efficiency, and control.

A common strategy to address flooding in PEMFCs is *via* the incorporation of different flow-field designs in the bipolar plates, such as serpentine and interdigitated designs.[79] Serpentine flow-fields generate high gas velocity and pressure drop to convectively remove liquid water from the gas channels and the electrode.[86, 87] However, the high back-pressure associated with this serpentine design increases the parasitic power losses associated with blowers or compressors[80, 81] and lowers the overall fuel cell system efficiency. The gas channels of interdigitated flow-fields are dead-ended, forcing gas to flow through the gas diffusion layer (GDL), thus effectively removing any liquid water that accumulates under the land.[140, 141] However, similar to the serpentine configuration, interdigitated geometry also results in high pressure drop across the channel, due to forced convection through the GDL. Furthermore, interdigitated flow-fields sustain significant water retention in the channels due to slow gas velocity.[82,

141] For these reasons, serpentine remains the preferred configuration for flow-fields in commercial fuel cell systems.

Despite significant efforts into the development of flow-field channel configurations, such as 3D fine-mesh flow-fields of Toyota Mirai,[142-144] a design that accomplishes effective water management at low pressure drop has not yet emerged, primarily due to the closely intertwined nature of these two elements; effective liquid water removal necessitates a high pressure drop to convectively remove liquid water droplets.[87] The inherent difficulty in managing liquid water by using flow-field geometry alone has led to the development of various advanced water management strategies, such as flow-fields with triangular microchannels or microgrooves.[145, 146] Wicks mounted[147, 148] or directly engineered[149, 150] on the channel surface of a flow-field to avoid the formation of liquid slugs have also been tested. Although the implementation of wicking elements improves fuel cell performance thanks to better water management, flooding persists in the mid-current density range, suggesting that the wicks alone do not transport all product water under certain operating regimes, possibly due to an insufficient gas pressure gradient.[149, 150]

Porous carbon flow-fields with integrated water transport channels for cooling and water removal have also been tested.[151-153] The generated liquid water is directed from the gas channels into internal water transport channels, due to the pressure gradient between the two channels. Under dry operating conditions, the porous carbon flow-fields work in reverse, providing internal humidification as the water in the pores evaporates into the gas channel.[154, 155] The main drawback towards commercialization of these flow-fields, though, is the higher interfacial contact resistance of the porous carbon (~70 m $\Omega$  cm<sup>2</sup>[154]) and the requirement for additional components, namely, a solid graphite frame[152, 154] in the fuel cell setup, which increases the overall cost and complexity of the device.

In the present work, a water management strategy for fuel cells is presented based on the incorporation of capillaries in flow-fields. Capillaries are laser drilled into the land of a parallel flow-field and allow direct removal (wicking) or supply of water (evaporation)

depending on the local demand across the electrode. The proposed mechanism serves as a simple and effective means of achieving robust and reliable fuel cell operation, without incurring additional parasitic losses associated with high pressure drop associated with conventional serpentine flow-fields.

### 1.7 Scope of thesis

This dissertation presents a systematic nature-inspired approach to design and evaluate against conventional serpentine flow-field based PEMFCs, the performance of PEMFCs with flow fields guided by the structure of a lung. This approach is based on the mechanistic understanding of the structure of the respiratory organ, applied in the context of fuel cell technology. It also aims to address flooding issues prevalent in lung-inspired flow-fields using neutron radiography for water visualisation and water management mechanism based on the incorporation of capillaries in flow-fields.

This thesis starts with an introduction to the main essential fuel cell components and various underlying phenomena that occur during cell operation. Numerical models for PEMFC are introduced, followed by a summary of liquid water visualisation techniques and water management strategies developed for PEMFCs. In Chapter 2, a theoretical fractal flow-field based PEMFC model is developed, and simulations are conducted to determine the number of generations required to achieve uniform reactant distribution and minimal entropy production. Chapter 3 details the experimental validation of the lung-inspired flow-fields fabricated using 3D printing *via* direct metal laser sintering (DMLS). Chapter 4 investigates the *in situ* transport and removal of liquid water across the channels of a fractal flow-field with N = 4 using neutron radiography. Chapter 5 presents a novel water management strategy that uses laser-drilled capillaries to manage water in PEMFCs. Lastly, Chapter 6 contains a summary of the work presented in this thesis, and it closes with suggestions on the directions of future work.

# **Chapter 2**

# Modelling and optimising the lung-inspired fractal fuel cells

Sections of this work have been adapted from "Optimizing the Architecture of Lung-Inspired Fuel Cells," *Electrochimica Acta* (submitted) and "A lung-inspired approach to scalable and robust fuel cell design," *Energy Environ. Sci.*, 2018, 11, 136-143

# 2.1 Introduction

The beneficial characteristics of the lung detailed in Chapter 1.1 serve as a guide towards the proposed design of new fractal flow-fields for PEMFCs. A theoretical model is developed that includes the distribution of reactants and liquid water transport, and simulations are conducted to determine the number of generations required to achieve uniform reactant distribution and minimal entropy production. Lung-inspired flow-fields perform some of the tasks of the GDL, such as homogenising reactant concentration and reducing flow velocity prior to entering the catalyst layer. As a result, thinner GDLs can be used, allowing for a higher concentration of oxygen to reach the catalyst layer. To investigate the effect of number of generations N on platinum utilisation, the finite-element model is combined with a two-phase agglomerate model[78] with optimised cathode catalyst layer microstructure.

# 2.2 Mathematical model of flow-field

#### 2.2.1 Modelling domain

The modelling domain consists of the GDL and CL at the anode and cathode, as well as the polymer electrolyte membrane (Figure 2.1). The MEA is located in between fractal flow-fields with surface area of  $10 \text{ cm}^2$ , which are represented by arrows that correspond to the location of the fractal inlet and outlet channels.



Figure 2.1 Schematic of the modelling domain of the lung-inspired flow-field based PEMFC at various generations, *N*. The rectangular box shows what is actually being modelled.[21]

The model captures the effects of varying the number of branching generations N on fuel cell performance by "zooming in" on the flow-field outlets, such that the number of inlets and outlets being modelled remains the same for any given number of generations. However, the size of the modelling domain, along with the size of the inlets, outlets, and land area, changes with each additional generation (Figure 2.1). The thickness of the GDL, CL, and polymer electrolyte membrane remain constant, regardless of the number

of generations being modelled. Due to the symmetry associated with the fractal design, the results from the modelled section can be extrapolated to locally resolve fuel cell performance throughout the entire cell.

#### 2.2.2 Model assumptions

The main modelling assumptions are as follows[56, 64, 156]:

- Steady state
- Ideal gases
- Fully hydrated polymer electrolyte membrane
- Uniform catalyst nanoparticle size and uniform Nafion film thickness on these nanoparticles
- No gas crossover
- No liquid water present in the anode
- High enough electrical conductivity of the electrode to neglect electric resistance

#### 2.2.3 Incorporation of fractal flow-field design into the model

The fractal flow-fields comprise self-similar, repeatedly branching "H" shaped channels designed to uniformly distribute reactant across the catalyst layer surface[21, 157] (Figure 2.2). This channel geometry allows a single inlet to branch into  $4^N$  outlets with each flow path being equal in length. The fractal dimension, *D*, is expressed by:[158]

$$D = \frac{\log(n)}{\log\left(\frac{1}{s}\right)} = \frac{\log(4)}{\log(2)} = 2$$
(2.1)

where n is the number of daughter shapes per parent, and s is the contraction ratio between daughter and parent. A fractal dimension of 2 indicates that, for an infinite number of generations, the structure will become plane-filling. Reactant depletion over the channel path is eliminated with this fractal structure, as only the outlets of the fractal distributor are open to the active area.



Figure 2.2 Fractal structures of different generations N for gas distribution networks in PEMFCs. Red and blue dots represent fluid inlet and outlet, respectively, and dashed boxes represent active membrane area.

Similar to the lung, the channel width of the fractal flow-field networks was scaled by adopting Murray's law, which dictates a cubic relationship between hydraulic diameters of parent and daughter branches, leading to minimum mechanical energy and thermodynamic losses:[28, 30, 158-160]

$$r_p^3 = \sum_{i=1}^n r_{d_i}^3$$
(2.2)

Here,  $r_p$  (m) and  $r_d$  (m) are the radii of the parent and daughter branches, respectively. By following Murray's law, the scaling of the channel diameters leads to a reduction in flow velocity at each generation, due to a net increase in cross-sectional area. Similar scaling of the channel lengths leads to constant pressure drop over each generation of the branching network, which minimises the pressure drop required to drive the flow across the system.[28] This resembles the transition in flow regimes between bronchial tree (convection) and alveoli (diffusion) in the human lung, where gas transport has been shown to be optimal based on irreversible thermodynamics.[28]

The ratio of convective and diffusive fluxes in the last generation of the fractal flowfield is characterised by the dimensionless Péclet number, defined below:

$$P\acute{e} = \frac{L \cdot U}{D} \tag{2.3}$$

where L (m) is the GDL thickness, U (m s<sup>-1</sup>) is the average flow velocity within the GDL, and D (m<sup>2</sup> s<sup>-1</sup>) is the diffusivity. The flow velocity at the flow-field | GDL interface is calculated using:

$$U = \frac{Q_0}{A_N \cdot 4^N} \tag{2.4}$$

where  $Q_0$  (m<sup>3</sup> s<sup>-1</sup>) is the volumetric flow rate of gas at the inlet, and  $A_N$  (m<sup>2</sup>) is the crosssectional area of a single fractal outlet at the  $N^{\text{th}}$  generation. It is important to note that Pé is calculated within the GDL based on the GDL thickness. The optimal number of fractal generations, N, in the flow-field is such that transport transitions from convective to diffusive, corresponding to a local Pé ~ 1. For Pé numbers less than 1 (Pé < 1), transport resistance in the finer channels would increase unnecessarily.

#### 2.2.4 Governing equations for saturated agglomerate model

A steady-state, two-phase, two-dimensional saturated agglomerate model has been employed to model transport and reaction in the catalyst layer,[156] while a modified reaction term[78] is incorporated to account for the spherical geometry of the catalyst agglomerates (Figure 2.3).



Figure 2.3 Summary of governing equations in each domain of the PEMFC. All the terms are presented in detail in the following sections. Domains are not drawn to scale.

#### 2.2.4.1 Transport of gas species within the GDL and CL

The continuity equation (Equation 2.5) and Darcy's law (Equation 2.6) are used to evaluate the velocity and pressure profiles of the gaseous mixture inside the porous media:

$$\nabla . \left( \rho_{g} \cdot u_{g} \right) = 0 \tag{2.5}$$

$$u_g = \frac{-k_p}{\mu_g} \cdot \nabla P \tag{2.6}$$

where  $\rho_g$  (kg m<sup>-3</sup>),  $u_g$  (m s<sup>-1</sup>), and  $\mu_g$  (Pa s) are the density, velocity, and viscosity of the gaseous mixture, respectively,  $k_p$  (m<sup>2</sup>) is the permeability of the porous medium, and *P* (Pa) is the pressure. The Stefan-Maxwell equations are used to describe the multi-component diffusion:

$$\nabla x_i = \sum_{j=1, j \neq i} \frac{1}{C \cdot D_{ij}^{eff}} \cdot \left( x_i \cdot N_j - x_j \cdot N_i \right)$$
(2.7)

where  $D_{ij}^{eff}$  (m<sup>2</sup> s<sup>-1</sup>) is the effective binary diffusivity of species *i* in species *j*,  $x_i$  is the mole fraction of species *i*,  $N_i$  (mol m<sup>-2</sup> s<sup>-1</sup>) is the molar flux of species *i*, and *C* (mol m<sup>-3</sup>) is the total molar concentration of gas. The transport of each gaseous species is governed by a general convection-diffusion equation in conjunction with the Stefan-Maxwell equation to account for multispecies diffusion:

$$\nabla \cdot \left\{ \frac{-\rho_g \cdot w_i \cdot \sum_j D_{ij}^{eff} \left[ \nabla x_j + \left( x_j - w_j \right) \cdot \nabla P \right] }{P} \right\} = M_i \cdot S_i - \rho \cdot u_g \cdot \nabla w_i \qquad (2.8)$$

where  $w_i$  and  $S_i$  (kg m<sup>-3</sup> s<sup>-1</sup>) are the mass fraction and source term of species *i*, respectively. A step by step derivation of Equation (2.8) is given in Appendix C.

The Bruggeman correlation is used to calculate the effective gas diffusion coefficient,[156] which accounts for the reduction in pore space available due to the presence of liquid water within the porous media:

$$D_{ij}^{eff} = D_{ij} \cdot \left[ \varepsilon^{\nu} \cdot (1-s) \right]^{1.5}$$
(2.9)

where  $\varepsilon^{y}$ , *s*, and  $D_{ij}$  (m<sup>2</sup> s<sup>-1</sup>) are the void fraction of the porous medium, saturation, and binary diffusivity, respectively. Saturation is defined as the volume fraction of liquid water occupying the void space of porous medium.

#### 2.2.4.2 Transport of liquid water through the GDL and CL

Liquid water transport inside the GDL and catalyst layer is driven by capillary force and, hence, Darcy's law is used to describe the flow of liquid inside the porous medium:[156]

$$N_{w} = -\frac{\rho_{w}}{M_{w}} \cdot \left[\frac{K_{w}(s)}{\mu_{w}} \cdot \nabla P_{l}\right]$$
(2.10)

where  $P_l$  (Pa),  $\rho_W$  (kg m<sup>-3</sup>),  $K_W$  (m<sup>2</sup>),  $M_W$  (kg mol<sup>-1</sup>), and  $\mu_W$  (Pa s) are the pressure, density, permeability, molecular weight, and viscosity of liquid water, respectively. Analytical equations (Equations 2.11-2.15) for the description of capillary pressure ( $P_c$ ), and permeability of the porous medium ( $K_W$ ) are listed below.

The capillary pressure is expressed by the following empirical correlation:[161]

$$P_{c}(s) = P_{g} - P_{l} = d \cdot \left[ e^{-a_{1}(s-c)} - e^{-a_{2}(s-c)} \right] + b$$
(2.11)

where s is the saturation level,  $P_g$  (Pa) is the gas phase pressure, which is assumed to be constant, and  $a_1$ ,  $a_2$ , c, and d are fitting parameters (Table 2.1). The capillary pressure term in Equation (2.11) is integrated into Equation (2.10) by differentiating both sides of the equation such that

$$\nabla P_c = -\nabla P_l \tag{2.12}$$

where  $\nabla P_g$  is considered negligible due to isobaric operating condition assumed in this study. The  $\nabla P_l$  term in Equation (2.10) is substituted with  $-\nabla P_c$  as shown in Equation (2.14).

Table 2.1 Parameters for the capillary pressure correlation in the GDL and CL.[156]

Capillary function	$a_1$	$a_2$	b (Pa)	С	d (Pa)
GDL	-17.3	-25.1	32.3	0.350	-4.06
Catalyst layer	-23.5	-17.4	477	0.460	-3.58

The permeability of the porous medium depends on the liquid water saturation[161] as given by Equation (2.13):

$$K_{w}(s) = K_{w,0} \cdot s^{4.5} \tag{2.13}$$

where  $K_{w,0}$  (m<sup>2</sup>) is the permeability of liquid water at 100% saturation level.[162] Substituting Equations (2.11) and (2.13) into Equation (2.10) yields the following expression for the liquid water flux:

$$N_{w} = -\frac{\rho_{w} \cdot K_{w,0}}{M_{w} \cdot \mu_{w}} \cdot s^{4.5} \cdot \nabla P_{c} = -D_{c} \cdot \frac{\rho_{w}}{M_{w}} \cdot \nabla s$$
(2.14)

where the capillary diffusion coefficient,  $D_c$  (m<sup>2</sup> s<sup>-1</sup>), is defined as:[156]

$$D_c = -\frac{K_{w,0}}{\mu_w} \cdot \frac{dP_c}{ds} \cdot s^{4.5}$$
(2.15)

#### 2.2.4.3 Transport of dissolved water through the membrane

The transport of dissolved water in the membrane is driven by electro-osmotic drag, diffusion due to the concentration gradient, and hydraulic permeation. However, since the model assumes fuel cell operation under isobaric condition, the hydraulic permeation term is neglected. Hence, the water flux in the membrane can be simplified to:

$$N_w^N = \frac{i_N \cdot n}{F} - D_w^N \cdot \nabla C_w^N$$
(2.16)

where  $i_N$  (A m<sup>-2</sup>) is the electrolyte current density vector, n is the electro-osmotic drag coefficient,  $D_W^N$  (m<sup>2</sup> s<sup>-1</sup>) and  $C_W^N$  (mol m<sup>-3</sup>) are the diffusivity and concentration of water in membrane, respectively. By assuming a fully hydrated membrane, the concentration gradient term can be neglected as well; at steady state, the flux of water is constant, so that, using Equation (2.16):

$$\nabla \left(\frac{i_N \cdot n}{F}\right) = 0 \tag{2.17}$$

#### 2.2.4.4 Transport of charge

The governing equations for the electronic and ionic charge transport are described using Ohm's law as:

$$i_s = -\sigma_s \cdot \nabla \phi_s \tag{2.18}$$

$$i_N = -\sigma_N \cdot \nabla \phi_N \tag{2.19}$$

where  $\sigma_s$  and  $\sigma_N$  (S m<sup>-1</sup>) are the electronic and ionic conductivities,  $\phi_s$  and  $\phi_N$  (V) are the solid and electrolyte phase potentials, respectively. The charge balance equations (Equations 2.18 and 2.19) are solved to obtain solid and electrolyte phase potentials:

$$\nabla \cdot \left(-\sigma_N \cdot \nabla \phi_N\right) = S_\phi \tag{2.20}$$

$$\nabla \cdot \left(-\sigma_s \cdot \nabla \phi_s\right) = -S_\phi \tag{2.21}$$

In the catalyst layer, the source term  $S_{\phi}$  represents the local rate of reaction.  $S_{\phi}$  is zero in the polymer electrolyte membrane and GDL, as no reaction takes place in these domains.

#### 2.2.4.5 Local rate of reaction in the catalyst layer

Assuming that the catalyst layer comprises a continuum of individual spherical catalyst agglomerates, the oxygen reduction reaction rate (mol  $m^{-3} s^{-1}$ ) can be described by:[78]

$$R_{O_2} = \left[\frac{\frac{R \cdot T}{H_{O_2}}}{\frac{\delta_N \cdot \left(\delta_N + r_{agg}\right)}{r_{agg} \cdot a_r \cdot D_{O_2}^N} + \frac{\delta_w \cdot \left(\delta_w + \delta_N + r_{agg}\right)}{\left(\delta_N + r_{agg}\right) \cdot a_r \cdot D_{O_2}^W} + \frac{1}{\xi \cdot k_t}}\right] \cdot C_{O_2}$$
(2.22)

where R (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) is the universal gas constant,  $H_{O2}$  (atm m<sup>3</sup> mol<sup>-1</sup>) is Henry's constant of oxygen between air and electrolyte,  $\delta_N$  and  $\delta_W$  (m) are the ionomer and water film thicknesses surrounding an agglomerate,  $r_{agg}$  (m) is the agglomerate radius,  $D_{O_2}^N$  and  $D_{O_2}^W$  (m<sup>2</sup> s<sup>-1</sup>) are the diffusivity of oxygen in ionomer and water,  $a_r$  (m<sup>2</sup> m<sup>-3</sup>) is the effective agglomerate surface area,  $\xi$  is the agglomerate effectiveness factor, and  $k_t$  (s<sup>-1</sup>) is the reaction rate constant. The first and second term in the denominator describe the diffusion of oxygen through the water and ionomer film, while the final term accounts for diffusion and reaction inside the agglomerate. The reaction rate constant  $k_t$  is expressed by:

$$k_{t} = \left(1 - \varepsilon_{v}^{CL}\right) \cdot \frac{a_{Pt}^{agg} \cdot i_{0,c}}{4 \cdot F \cdot C_{O_{2}}^{ref}} \cdot \exp\left[\frac{-\alpha_{c} \cdot F}{R \cdot T} \cdot \left(V_{A} - \phi_{m} - U_{eq}\right)\right]$$
(2.23)

where  $\varepsilon_v^{CL}$  is the catalyst layer porosity,  $i_{0,c}$  (A m<sup>-2</sup>) is the reference exchange current density for cathode,  $C_{0_2}^{ref}$  (mol m<sup>-3</sup>) is the reference oxygen concentration in the catalyst layer,  $\alpha_c$  is the cathodic transfer coefficient,  $V_A$  (V) is the applied cell voltage,  $U_{eq}$  (V) is the standard equilibrium potential of the oxygen reduction reaction, and  $\phi_m$  (V) is the membrane potential. The effect of the catalyst morphology is taken into account by the active catalyst surface area per unit volume of agglomerates,  $a_{Pt}^{agg}$  (m<sup>2</sup> m<sup>-3</sup>), which is defined as:

$$a_{Pt}^{agg} = \frac{a_{Pt} \cdot m_{Pt}}{t_{CL} \cdot \left(1 - \varepsilon_{v}^{CL}\right)}$$
(2.24)

where  $m_{Pt}$  (g<sub>Pt</sub> m<sup>-2</sup>) is platinum loading,  $t_{CL}$  (m) is the catalyst layer thickness, and  $a_{Pt}$  (cm<sup>2</sup> g<sup>-1</sup>) is the surface area per unit mass of platinum particle, which is estimated from the empirical correlation for platinum supported catalyst:[64]

$$a_{Pt} = 2.2779 \cdot 10^{6} \cdot (Pt \mid C)^{3} - 1.5857 \cdot 10^{6} \cdot (Pt \mid C)^{2} - 2.0153 \cdot 10^{6} \cdot (Pt \mid C) + 1.5950 \cdot 10^{6}$$
(2.25)

where Pt|C is the platinum to carbon ratio in a catalyst agglomerate.

The effectiveness factor,  $\xi$ , for a spherical agglomerate in Equation (2.22) is given by:

$$\xi = \frac{1}{\varphi} \cdot \frac{3 \cdot \varphi \cdot \coth(3 \cdot \varphi) - 1}{3 \cdot \varphi}$$
(2.26)

where the Thiele modulus,  $\varphi$ , is equal to:[78]

$$\varphi = \frac{r_{agg}}{3} \cdot \sqrt{\frac{\left(1 - \varepsilon_{v}^{CL}\right)}{D_{O_{2},eff}^{N}}}$$
(2.27)

The Bruggeman correlation is used to describe the effective oxygen diffusivity inside the agglomerate:

$$D_{O_2,eff}^N = D_{O_2}^N \cdot \frac{\varepsilon_N^{agg}}{\tau_{agg}}$$
(2.28)

Liquid water forms a film on top of the Nafion film, and its thickness can be estimated by:

$$\delta_w = \frac{\varepsilon_v^{CL} \cdot s}{a_r} \tag{2.29}$$

The effective agglomerate surface area,  $a_r$  (m<sup>2</sup> m<sup>-3</sup>), is defined as the outer surface area of the agglomerates per unit volume of the catalyst layer, and is given by:

$$a_r = \frac{3}{r_{agg} \cdot \left(1 - \varepsilon_v^{CL}\right)} \tag{2.30}$$

where  $r_{agg}$  (m) is the catalyst agglomerate radius. The effectiveness factor of the hydrogen oxidation reaction (HOR) is set to 1.0, because hydrogen dissolves rapidly into the electrolyte, and the Butler-Volmer equation is used to define the HOR kinetics as:[35]

$$R_{H_2} = a_{P_l}^{agg} \cdot i_{0,a} \cdot \left(\frac{P_{H_2}}{C_{H_2}^{ref} \cdot H_{H_2}}\right)^{0.5} \cdot \left[\exp\left(\frac{-(1-\alpha_a)\cdot F \cdot \eta_a}{R \cdot T}\right) - \exp\left(\frac{\alpha_a \cdot F \cdot \eta_a}{R \cdot T}\right)\right] \quad (2.31)$$

where  $i_{0,a}$  (A m<sup>-2</sup>) is the reference exchange current density for the anode,  $P_{H2}$  (Pa) is the partial pressure of hydrogen,  $C_{H_2}^{ref}$  (mol m<sup>-3</sup>) is the reference oxygen concentration in the catalyst layer,  $H_{H2}$  (atm m<sup>3</sup> mol<sup>-1</sup>) is Henry's constant of hydrogen between air and electrolyte,  $\alpha_a$  is the anodic transfer coefficient, and  $\eta_a$  is the anodic overpotential.

#### 2.2.4.6 Water phase change

The rate of water phase change (mol  $m^3 s^{-1}$ ) in the porous medium is expressed by:[156]

$$S_{phase} = \begin{cases} k_c \cdot \frac{\varepsilon_i^v \cdot (1-s) \cdot y_v}{R \cdot T} \cdot (y_v \cdot P - P_v^{sat}) & y_v \cdot P \ge P_v^{sat} \\ k_v \cdot \frac{\varepsilon_i^v \cdot s \cdot \rho_w}{M_w} \cdot (y_v \cdot P - P_v^{sat}) & y_v \cdot P < P_v^{sat} \end{cases}$$
(2.32)

where  $y_v$  is the mole fraction of liquid water,  $\rho_w$  (kg m<sup>-3</sup>) is the density of liquid water,  $M_w$  (kg mol<sup>-1</sup>) is the molar weight of water, P (Pa) is the total pressure,  $k_c$  and  $k_v$  (s<sup>-1</sup>) are the condensation and evaporation rate constant, respectively. The vapour saturation pressure,  $P_v^{sat}$  (Pa), is calculated using the Antoine equation:[163]

$$P_{\nu}^{sat} = \exp\left[16.3872 - \frac{3885.7}{(T - 273.15) + 230.17}\right]$$
(2.33)

#### 2.2.5 Boundary conditions (BCs)

BC at the anode gas channel | anode GDL interface:

$$C_{H_2}^s = C_{H_2}^{in} \tag{2.34}$$

BCs at the cathode gas channel | cathode GDL interface:

$$C_{O_2}^g = C_{O_2}^{air} \tag{2.35}$$

$$C_v^g = C_v^{g,air} \tag{2.36}$$

BCs at the anode GDL | anode catalyst layer interface:

$$N_{H_2}^g |_{GDL} = N_{H_2}^g |_{ACL}$$
(2.37)

$$i_N \mid_{ACL} = 0 \tag{2.38}$$

BCs at the cathode GDL | cathode catalyst layer interface:

$$N_{O_2}^{g}|_{GDL} = N_{O_2}^{g}|_{CCL}$$
(2.39)

$$N_{N_2}^{g}|_{GDL} = N_{N_2}^{g}|_{CCL}$$
(2.40)

$$N_{v}^{g}|_{GDL} = N_{v}^{g}|_{CCL}$$
(2.41)

$$i_N \mid_{CCL} = 0 \tag{2.42}$$

$$P_c \mid_{GDL} = P_c \mid_{CCL}$$
(2.43)

BCs at the anode catalyst layer | membrane interface:

$$N_{H_2}^g |_{ACL} = 0 \tag{2.44}$$

$$i_N \mid_{ACL} = i_N \mid_{MEM} \tag{2.45}$$

$$C_{H_2}^g = 0 (2.46)$$

$$\phi_N = 0 \tag{2.47}$$

BCs at the cathode catalyst layer | membrane interface:

$$N_{O_2}^g |_{CCL} = 0 (2.48)$$

$$N_{w}^{g}|_{ccl} = 0 (2.49)$$

$$i_N \mid_{CCL} = i_N \mid_{MEM} \tag{2.50}$$

$$N_w|_{CCL} = N_w^N|_{MEM}$$
(2.51)

$$C_{O_2}^s = 0 (2.52)$$

$$C_{\nu}^{g} = 0$$
 (2.53)

## 2.3 Simulation procedure

#### 2.3.1 Inlet fractal flow-field

The domain described in Figure 2.1 was modelled using the finite element solver COMSOL v.5. Simulations were conducted using a DELL Precision T3500 workstation with 24 GB of RAM and a 3.2 GHz Intel Xeon processor. The gas diffusion and catalyst layers were described by the parameters listed in Table 2.2. A series of parametric sweeps over the number of branching generations and GDL thickness was used to determine the effect of the fractal flow-field architecture on the overall cell performance. The stoichiometry ratio of 2 was used for both cathode and anode, and the simulation was performed at an operating voltage of 0.4 V throughout, unless otherwise stated. Such operating conditions were chosen to represent a regime of operation expected to be limited by reactant access to the electrode, so that the advantages of the fractal flow-field could be expected to become important.

# 2.3.2 Model parameters

Table 2.2 summarises the various parameters used in the aforementioned model including bulk transport parameters.

Geometry	Value	Units	Source	Parameter	Value	Units	Source
Α	10 <sup>-3</sup>	$m^2$		$t_{GDL}$	$350 \times 10^{-6}$	m	[64]
<i>r</i> <sub>agg</sub>	$150 \times 10^{-9}$	m	[78]	$t_{CL}$	$40 \times 10^{-6}$	m	[164]
$W_{c, 1}$	$0.25 \times 10^{-2}$	m		t <sub>mem</sub>	$150 \times 10^{-6}$	m	[64]
Operating of	conditions						
Р	1.1	atm	[165]	<i>x</i> <sub>02</sub>	0.11	-	[78]
Т	353	K	[64]	$x_{N2}$	0.42	-	[78]
$S_{Cathode}$	2.0	-	[166]	$X_w$	0.47	-	[78]
SAnode	2.0	-	[167]	$U_{\it ref}$	1.0	V	[156]
Physical pr	operties						
$C_{O2,ref}$	0.85	mol m <sup>-3</sup>	[64]	$i_{0,c,273}$	$1.0 \times 10^{10}$	$A m^{-2}$	[156]
$C_{H2,ref}$	$5.64 \times 10^{-11}$	mol m <sup>-3</sup>	[168]	$i_{0,c}$	$i_{0.273} \times 2^{(T-273)/10} \times 10^{-4}$	A $m^{-2}$	[169]
$\alpha_c$	1.0	-	[166]	<i>i</i> <sub>0,a</sub>	$1 \times 10^{-4}$	A $m^{-2}$	[170]
$\alpha_a$	0.5	-	[56]	$\mu_w$	$3.5 \times 10^{-4}$	Pa s	[171]
$H_{H2}$	$4.5 \times 10^{-2}$	atm <sup>3</sup> mol <sup>-1</sup>	[168]	$ ho_C$	$2.0 \times 10^{-6}$	g m <sup>-3</sup>	[64]
$H_{O2}$	$3.56 \times 10^{4}$	atm <sup>3</sup> mol <sup>-1</sup>	[172]	$\rho_{Pt}$	$21.5 \times 10^{-6}$	g m <sup>-3</sup>	[64]
n	0.11 x λ	-	[36]	$\mathcal{E}_{V,GDL}$	0.75	-	[173]
λ	$C_{W,N}$ / $C_f$	-	[156]	$\mathcal{E}_{V,CL}$	0.5	-	[78]
$C_{W,N}$	$4.2 \times 10^{-3}$	mol m <sup>-3</sup>	[156]	$\mathcal{E}_{agg,N}$	0.66	-	[78]
$C_f$	$1.2 \times 10^{-3}$	mol m <sup>-3</sup>	[156]	$m_{pt}$	$0.4  imes 10^{-4}$	mg m <sup>-2</sup>	[78]
$k_v$	100	atm <sup>-1</sup> s <sup>-1</sup>	[156]	$k_c$	100	s <sup>-1</sup>	[156]
$Pt \mid C$	0.28	-	[78]				
Transport p	properties						
$k_{p,CL}$	$2 \times 10^{-15}$	$m^2$	[166]	$D_{O2,H2O}$	$2.82 \times 10^{-5} \times (T/308.1)^{1.5}$	$m^2 s^{-1}$	[174]
$k_{p,GDL}$	$2 \times 10^{-15}$	$m^2$	[166]	$D_{O2,N2}$	$2.2 \times 10^{-5} \times (T/293.2)^{1.5}$	$m^2 s^{-1}$	[174]
$K_{w,0-GDL}$	$2.0 \times 10^{-15}$	$m^2$	[156]	$D_{N2,H2O}$	$2.56 \times 10^{-5} \times (T/307.5)^{1.5}$	$m^2 s^{-1}$	[174]
$K_{w,0-CL}$	$5.0 \times 10^{-17}$	$m^2$	[156]	$D_{H2,H2O}$	$9.15 \times 10^{-5} \times (T/307.5)^{1.5}$	$m^2 s^{-1}$	[174]
$\sigma_m$	8.9	$S m^{-1}$	[78]	$D_{O2.N}$	$8.45 \times 10^{-10}$	$m^2 s^{-1}$	[64]
$\sigma_{\rm s}$	1000	$S m^{-1}$	[175]	$D_{O2.w}$	$4.73 \times 10^{-9}$	$m^2 s^{-1}$	[78]

Table 2.2 Parameters used in the model.

#### 2.3.3 Optimisation of the microstructure

Parameters optimised with respect to power density  $(P_D)$  and platinum utilisation  $(P_U)$  were obtained using objective functions proposed in previous studies.[78, 176] The objective function for  $P_D$  optimisation aims to maximise the current density within the cathode catalyst layer, and is defined as follows:[176]

$$\max_{(m_{Pt},Pt|C,\varepsilon_{v}^{CL})} 4FV \int_{(L-t_{CL})}^{L} R_{O_{2}} dx \qquad (2.54)$$

$$0.12 < \varepsilon_{s}^{CL} < 1$$

$$0.12 < \varepsilon_{N}^{CL} < 1$$

$$0.25 < \varepsilon_{v}^{CL} < 1$$

The objective function for  $P_U$  optimisation seeks to achieve high power density at low platinum loading, and is expressed as follows:[78]

$$\max_{\substack{(m_{P_{t}},P_{t}|C,\varepsilon_{v}^{CL})}} \left[ \frac{4FV \int_{\substack{(L-t_{CL})}}^{L} R_{O_{2}} dx}{m_{P_{t}}} \right]$$
(2.55)  
$$0.12 < \varepsilon_{s}^{CL} < 1$$
$$0.12 < \varepsilon_{N}^{CL} < 1$$
$$0.25 < \varepsilon_{v}^{CL} < 1$$
$$P_{D} > 0.20 \frac{W}{cm^{2}}$$

The constraints on volume fractions ensure proper percolation in each phase (solid, ionomer, gas). The constraint on minimum power density ensures that the microstructure can generate sufficient power density while keeping the platinum loading low. The interior-point algorithm with the default tolerances was used for the constrained optimisations. The constraints were implemented as a series of nonlinear constraints.

# 2.4 Simulation results and discussion

#### 2.4.1 Effect of the number of generations on fuel cell performance

Increasing the number of branching generations, *N*, has two effects on the resultant concentration distribution in the porous medium. Firstly, with each additional generation, the distance between adjacent "inlet channels" (outlets of the fractal inlet channel) is reduced, leading to an increasingly uniform boundary condition along the flow-field | GDL interface. Secondly, each subsequent generation increases the total cross-sectional area of the outlets of the fractal inlet channels, thereby slowing the velocity of the reactant gas and ultimately, allowing the convective flux at the channel outlet to approach the diffusive flux in the GDL.



Figure 2.4 (a) A computer generated image of a close-up view of the cathode side of the modelling domain, where red and blue arrows represent the inlet and outlet flow of oxidants to, and oxidants plus formed H<sub>2</sub>O from the catalyst layer, respectively, and (b) change in average current density with respect to the number of generations, N, and, (c) oxygen mass fraction distribution in catalyst layer using fractal N = 4, N = 6, and N = 8

flow-fields, where  $x_{O2}$  is the mass fraction of O<sub>2</sub>.[21] The interdigitated outlet channels are not shown in this figure for ease of visualisation. Readers are directed to Figure 4.4 (b) for full visualisation of the fractal inlet and interdigitated outlet channels.

Figure 2.4 illustrates the performance of the lung-inspired flow-field based PEMFC as a function of the number of generations. At low generation levels (N = 1 to 4), the spacing between adjacent distributor inlets is large (>> GDL thickness) and the flow velocity exiting the final generation is convection dominated (Pé > 1; Table 2.3). Therefore, only sub-sections of the active area directly in the projection of the inlet are exposed to an appreciable amount of oxygen for reaction.[21] This leads to a highly non-uniform gas distribution across the plane of the catalyst layer and low fuel cell performance.

An increase in fuel cell performance occurs between N = 4 and N = 7 generations, as the convective flux becomes equal to the diffusion flux at the exits (Pé ~ 1; Table 2.3), and the spacing between inlets is sufficiently small to engender more uniform concentration profiles at the GDL | CL interface.

At higher generations ( $N \ge 8$ ), the spacing between adjacent inlets becomes very small (~ 100 µm) and diffusion takes over as the dominant transport mechanism in the GDL (Pé < 1; Table 2.3). The resultant concentration profile at the catalyst layer interface is essentially completely uniform. As a result, a plateau in fuel cell performance is observed and additional generations (higher *N*) provide little benefit. Table 2.3 summarises key geometric parameters for the simulation conducted in this study.

N	Number of outlets	Outlet spacing (µm)	Outlet width ( $\mu m$ )	Pé
3	64	4000	992	3.89
4	256	1800	625	2.45
5	1024	823	394	1.54
6	4096	378	248	0.97
7	16384	170	156	0.61
8	65536	74.7	98.0	0.39
9	262144	30.9	62.0	0.24

Table 2.3 Summary of fractal flow-field simulations with standard composition cathode catalyst layer.

## 2.4.2 Effect of the number of generations on GDL thickness

The incorporation of a fractal flow-field to homogenise reactant concentration at the catalyst layer | GDL interface makes the GDL partially redundant, since they serve the same purpose. Therefore, the GDL does not need to be as thick to provide the same degree of homogenisation. By reducing its thickness, additional concentration losses (resulting from the concentration gradient across the GDL) can be avoided. As a result, utilising a thinner GDL would provide higher concentration of reactant gas to the catalyst layer, further enhancing fuel cell performance.



Figure 2.5 Effect of GDL thickness on fuel cell performance.

A similar trend in fuel cell performance is observed up to N = 5 generations for different GDL thicknesses (Figure 2.5). At these low generations, a decrease in GDL thickness merely exacerbates the variation in current density across the GDL | CL interface and does not enhance the fuel cell performance. The increased local current density in the region adjacent to the inlet is offset by a sharp decline in local current density under the land and outlet channels due to diminished transverse reactant transport in thinner GDLs (Figure 2.6 (a)).[177-179]

At higher generations ( $N \ge 5$ ), an improvement in fuel cell performance is observed, as reactant mass transport is facilitated by increasing the reactant concentration gradient across the catalyst layer. This result is consistent with previous reports in the literature demonstrating an increase in fuel cell performance *via* the utilisation of thinner GDLs,[43, 177, 180, 181] due to enhanced mass transport.



Figure 2.6 Effect of gas diffusion layer thickness on local cell current density for (a) N = 3 and (b) N = 6 (inlet positions at  $x \sim 0.33$  and 1; outlet positions at  $x \sim 0$  and 0.67).

Additionally, thinner GDLs enhance local current density as a direct consequence of higher oxygen concentration across the catalyst layer (Figure 2.6 (b)). This observation is in slight contrast with previous reports exhibiting a small drop in current density under the land and outlet channels with thinner GDLs, as a result of reduced lateral mass transport.[177-179] However, the reported aggravated reactant depletion near the outlet channels with thinner GDLs is circumvented for higher generation ( $N \ge 5$ ) fractal flow-fields due to their shorter path length between inlet and outlet channels, which subjects

the entire catalyst layer to higher reactant concentration and current density. The reduction in lateral mass transport with thinner GDLs is not completely attenuated, though, as suggested by the suppressed improvement in current density in areas adjacent to the outlet channels, compared to the inlet channels (Figure 2.6 (b)).

#### 2.4.3 Fractal flow-field with optimised cathode catalyst layers

Apart from the thickness of the GDL, the cathode catalyst layer (CCL) also plays a pivotal role in determining the performance of PEMFCs. From the perspective of fuel cell performance and cost, generating sufficient power density, while lowering the catalyst loading and improving catalyst utilisation, are key criteria to design an efficient catalyst layer. Here, fractal flow-fields are coupled with the CCL microstructures, which were independently optimised with respect to maximum platinum utilisation  $(P_U)$  and power density  $(P_D)$  under the assumption of uniform reactant concentration profile across the flow-field | GDL interface, as proposed by Marquis and Coppens (Table 2.4).[78, 176] While the ionomer fraction in the  $P_D$  and  $P_U$  optimised CCL are higher than values typically reported in the literature, the higher Nafion content is accounted for by a much thinner catalyst layer. Also, in the case of a  $P_U$  optimised CCL, the lower reaction rate (due to ultra-low platinum loading) diminishes the effect of diffusion limitations and, therefore, allows for a higher ionomer fraction in the catalyst layer. The radius of the catalyst agglomerates is known to significantly dictate the performance of the CCL. While not included as a design variable in this work, a value of 100 nm is chosen to minimise any diffusion limitations occurring within the agglomerates themselves.[78]

Table 2.4 Results of microstructure optimisation to maximise power density ( $P_D$ ) and platinum utilisation ( $P_U$ ) in the cathode catalyst layer.

Cathode catalyst	$m_{Pt} (\mathrm{mg}_{Pt}\mathrm{cm}^{-2})$	$t_{CL}$ (µm)	Pt/C	$\varepsilon_s^{CL}$	$\varepsilon_v^{CL}$	$\varepsilon_N^{CL}$	E <sub>N,agg</sub>
Base design	0.40	40	0.28	0.13	0.50	0.37	0.66
$P_D$ optimised	0.18	18	0.29	0.13	0.25	0.62	0.78
$P_U$ optimised	0.01	1.0	0.27	0.14	0.25	0.61	0.77

Figure 2.7 compares the fractal flow-field performance of  $P_U$  and  $P_D$  optimised CCL microstructures to the base design at different generations *N*. The trend in fuel cell performance improvement is similar to previous results, differing only in the magnitude of change in the average current density.

The  $P_D$  optimised CCL microstructure displays the highest average current density at  $N \ge 5$ , despite its lower platinum loading than the base (non-optimised microstructure) CCL (Table 2.4). Its optimised microstructure alleviates the diffusion limitations inside the catalyst layer and agglomerates, resulting in a ~ 20% increase in average current density (Figure 2.7). With less branching generations (N < 5), the  $P_D$  optimised CCL microstructure performance improvement over the base microstructure is lower, indicating that non-uniform gas distribution limits mass transport towards the catalyst layer and, hereby, catalyst utilisation. A significant portion of the catalyst layer adjacent to the outlet channels is oxygen-depleted, and, thus, the optimised catalyst layer in these regions does not result in higher current density.



Figure 2.7 Simulation results showing the effect of number of fractal branching generations on average cell current density for the base and optimised CCL (cathode catalyst layer) microstructures. The operating conditions are  $S_{Anode} = 1.5$  and  $S_{Cathode} = 2$ , and  $r_{agg} = 100$  nm.

On the contrary, the  $P_U$  optimised CCL exhibits the lowest average current density due to its low platinum loading (~ 40 times lower than the base design) resulting in a low

reaction rate.[78] Despite its low intrinsic performance, the  $P_U$  optimised CCL as a whole surpasses the DoE target for platinum utilisation of ~ 8 kW/g<sub>Pt</sub>[182] at N = 4 generations, and plateaus at approximately 36 kW/g<sub>Pt</sub> at N = 6 generations (Figure 2.8). The ultra-low platinum loading of a  $P_U$  optimised CCL allows exposure of appreciable oxygen concentration to platinum catalyst along the radius of the agglomerates, enhancing platinum utilisation. Its significantly thinner catalyst layer (Table 2.4) also facilitates gas diffusion and proton conduction across the CCL, improving mass transport across the CCL and subsequent platinum utilisation.



Figure 2.8 Simulation results showing the effect of number of fractal branching generations on platinum utilisation for the base and optimised CCL microstructures. The operating conditions are  $S_{Anode} = 1.5$  and  $S_{Cathode} = 2$ , and  $r_{agg} = 100$  nm.

The base and  $P_D$  optimised cathode CL designs demonstrate substandard platinum utilisation for all generations, since metal nanoparticles situated towards the centre of an agglomerate are subjected to extremely low oxygen concentrations, due to significant diffusion limitation arising from surplus catalyst loading. A small improvement in platinum utilisation with respect to the number of generations indicates that platinum utilisation is not limited by reactant distribution across the electrode, but by reactant transport within the catalyst agglomerate. Collectively, these results show that proper design of catalyst layer microstructure and platinum loading, factors that predominantly determine oxygen concentration profile within an agglomerate, is indispensable to realise enhanced platinum utilisation from a uniform gas distribution.

A finite-element model of a lung-inspired flow-field based PEMFC was presented. Numerical simulations reveal that the ideal number of branching generations, N, for minimum entropy production lies between N = 5 and 7 for a flow field plate with surface area of 10 cm<sup>2</sup>. For lower numbers of generations (N = 1 - 4), the spacing between adjacent distributor inlets is large and the flow leaving the final generation is convection driven. Beyond this (N = 5 - 7), as oxidant moves through successive generations with decreasing diameter, the convection driven flow becomes similar in magnitude to the diffusion driven flow at the exits. At higher generations ( $N \ge 8$ ), the spacing between adjacent inlets becomes very small (~ 100 µm) and the flow leaving the outlets of the final generation is diffusion driven.

Introduction of a fractal flow-field to homogenise reactant concentration at the flowfield | GDL interface allows for a thinner GDL to be used. Fuel cell performance is enhanced further with a thinner GDL, as a result of higher oxygen concentration across the catalyst layer for a higher number of branching generations, *N*. However, the reduction in lateral mass transport with thinner GDLs only leads to minimal improvement in fuel cell performance for lower numbers of generations ( $N \le 5$ ).

The finite-element model of the lung-inspired flow-field based PEMFC was coupled with cathode catalyst layer (CCL) microstructures optimised with respect to platinum utilisation ( $P_U$ ) and power density ( $P_D$ ). Despite its lower platinum loading, the  $P_D$ optimised CCL yields a higher average current density than the base design, because of a microstructure that facilitates diffusion within the catalyst layer. In the case of a  $P_U$ optimised CCL, the ultra-low platinum loading significantly lowers the reaction rate, resulting in inferior fuel cell performance.

In terms of platinum utilisation, the  $P_U$  optimised CCL surpasses the 2020 DoE target for platinum utilisation of ~ 8 kW/g<sub>Pt</sub> for N = 4 generations, and achieves a value of ~ 36 kW/g<sub>Pt</sub> when N = 6. The base and  $P_D$  optimised microstructures demonstrate extremely low platinum utilisation, due to substantial oxygen deprivation towards the centre of the catalyst agglomerates from surplus platinum loading. A multi-objective optimisation involving platinum loading and power density may be beneficial to evaluate the tradeoff between the objectives for the design of efficient and robust fuel cell catalyst layers.

# **Chapter 3**

# Experimental testing of lung-inspired flow-fields

Sections of this work have been adapted from "A lung-inspired approach to scalable and robust fuel cell design," *Energy Environ. Sci.*, 2018, 11, 136-143.

# 3.1 Introduction

The promising modelling results emphasised the need to engineer lung-inspired, fractal flow-fields and evaluate their performance under fuel cell operating conditions. Threedimensional (3D) fractal flow-fields with multiple generations have not previously been validated experimentally, due to complications associated with the manufacturing of objects with a controlled 3D internal structure; conventional fabrication methods, such as machining or stamping, are limited to two-dimensional structures.

These limitations can be circumvented through the exploitation of 3D printing *via* Direct Metal Laser Sintering (DMLS), which is used to create 3D objects from successive layers of sintered stainless steel.[183, 184] Three flow-fields with N = 3, 4, and 5 were fabricated and assembled in PEMFCs and their performance compared against conventional, serpentine flow-field based PEMFCs.
# 3.2 Experimental

#### 3.2.1 Fractal flow-field design

The fractal structure begins with one "H" and it expands by the addition of smaller "H's" at the tips of the precedent generation as shown in Figure 1.1 and Figure 3.1 (a). Such geometry allows the distribution of gas from a single inlet to the  $4^N$  number of outlet holes with equal hydraulic length which ensures uniform gas distribution. Fractal geometry has been applied to flow-field designs in the past.[18] However, our design is fundamentally different, as the three-dimensional branching structure allows only the "inlet channels" (outlets of the fractal inlet channel) to be exposed to the MEA, eliminating the reactant depletion along the channel, and thus providing uniform local conditions on the surface of the catalyst layer. Between each column of gas inlet channels is an interdigitated outlet channel for excess gas/water removal connected by a main discharge channel (Figure 3.1 (c)). The inlet and outlet channel geometries of each fractal flow-field are outlined in Table 3.1.

Number of generations	Inlet channel dimension (mm)	Number of outlet channels	Outlet channel dimension (mm)	Distance between outlets (mm)
3	$2.16 \times 2.16$	64	0.7  imes 0.8	3.85
4	0.74  imes 0.97	256	0.5  imes 0.75	1.93
5	$0.30 \times 0.60$	1024	0.3  imes 0.5	1.20

Table 3.1 Fractal flow-field inlet and outlet channel geometries.

#### 3.2.2 Manufacturing of fractal flow-fields

The fractal prototype with N = 3 (Concept Laser GmbH, Germany), N = 4, and N = 5 (FineLine Prototyping, USA) generations were 3D printed in stainless steel *via* Direct Metal Laser Sintering (DMLS). The prototypes were designed using Siemens NX 7.5 (Siemens PLM Software, Germany) or Rhino 4.0 (Robert McNeel & Associates, USA) software and the designs were rendered to .stl files before being discretised into thin layers to be printed. The prototypes were printed through a repeated process of stainless

steel powder layering, followed by selective laser sintering, in locations defined by the 2D slice data. A temporary support structure was included to maintain the structural integrity during the build.



Figure 3.1 The promising modelling results guided the engineering of lung-inspired flow-fields: (a) 3D network of the inlet (red) and outlet (blue) branches used in these flow-fields; (b) X-ray radiography is employed to inspect the flow-fields for structural defects and (c) the engineered flow-fields with different numbers of generations, N.[21] The main outlet channels are indicated with red arrows.

Figure 3.1 illustrates the 3D network of the interdigitated inlet and outlet fractal branches, as well as the final generation of the inlet and outlet channels for the three different prototypes. The final generation of H-shaped branches of the N = 3 and N = 4 flow-fields were left open to create additional contact area between the gas channel and the GDL. However, due to fabrication limitations, only the tips of the fifth-generation H-shaped branches were open to the GDL for the N = 5 prototype. All fractal flow-field prototypes were tested against a single and double graphite serpentine flow-field with channel width, land, and depth of 1 mm. A double-serpentine flow-field with channel width, land, and depth of 1 mm was used at the anode.

#### 3.2.3 Fractal flow-field characterisation using X-ray

Prior to experimental testing, X-ray radiography (Zeiss Xradia Versa 520, Zeiss USA) was used to inspect the flow-field channels for structural defects and blockages caused by various process parameters, such as laser energy density, layer thickness, and hatch distance.[185] A video based on X-ray tomography of a flow-field with N = 5 can be found online as supplementary material to reference.[21] The samples were mounted on to the sample holder and imaged at 16 kV with a pixel size of 33 x 33 µm and beam power of 10W. The outlet aperture of the N = 5 flow-field is the smallest at 200 x 300 µm; with a resolution of 33 x 33 µm, large blockages of the outlets would be observable. Radiographs (Figure 3.1 (b)) reveal that the internal structure of the flow-field is well defined and defect-free, especially in the early branching generations, allowing for uniform gas distribution.

# 3.2.4 Gold electroplating of fractal flow-fields

The engineered, fractal flow-fields are gold-plated prior to any fuel cell polarisation measurement to minimise their corrosion under fuel cell operation. Prior to gold electrodeposition, all 3D printed flow-fields were cleaned with acetone, followed by sonication in DI water for 1 minute. These flow-fields were then immersed into 0.02 M gold potassium cyanide solution (KAu(CN)<sub>2</sub>) and a titanium coated stainless steel mesh was used as counter electrode. The electroplating solution was continuously stirred at 100 rpm to minimise local variation in gold concentration throughout the electroplating process. A Gamry potentiostat (Reference 3000) was used to hold the current density at 10 mA cm<sup>-2</sup> for 525 s to electroplate 1 µm of gold onto the 3D printed flow-fields. The fractal flow-field with N = 3 generations had a submerged surface area of 38 cm<sup>2</sup> (I<sub>electrodeposition</sub> = 380 mA), while the fractal flow-fields with N = 4 and 5 generations had a submerged surface area of 30 cm<sup>2</sup> (I<sub>electrodeposition</sub> = 300 mA) each. After electroplating of each flow-field, the concentration of the solution was adjusted by adding 0.08 M KAu(CN)<sub>2</sub> gold replenisher solution.

It is important to note that when the fractal flow-fields were submerged in the electroplating solution, gas bubbles were trapped inside the 3D fractal structures and prevented the wall of the internal structure from being coated. By virtue of the highly acidic condition of PEMFCs and back-flow of generated (acidic) liquid water into the fractal "inlet channels" as shown in Figure 4.6, we anticipate corrosion to occur over time causing structural deformation of the fractal inlet structure and membrane poisoning by metal ions, the latter of which is known to decrease membrane conductivity. However, given the relatively short experiment time for each flow-field (< 30 h) and constant Ohmic resistance observed throughout the long-term tests, we anticipate minimal impact of metal corrosion on the overall fuel cell performance.

#### 3.2.5 Serpentine flow-field fabrication

The  $10 \text{ cm}^2$  and  $25 \text{ cm}^2$  single and double channel serpentine flow-fields were machined in-house from a 6 mm thick graphite plate (Schunk, Germany) using a CNC machine (Roland 40A, UK). All serpentine flow-fields used in this study had channel width, spacing, and depth of 1 mm. A single serpentine flow-field was used on the anode side for all experiments to mitigate flooding on the anode which could otherwise interfere with polarisation and impedance measurements.



Figure 3.2 Single and double channel serpentine flow-field designs. The serpentine channels were orientated horizontally as shown in the figure.

#### 3.2.6 Membrane electrode assembly (MEA) fabrication

10 and 25 cm<sup>2</sup> MEAs were fabricated in-house by hot pressing Nafion HP membrane (DuPont, USA) and ELE0201 gas diffusion electrodes (Johnson Matthey, UK) using a thermal press (Carver, 4122CE). The membrane was used without any pre-treatment and the MEA was pressed at 130°C for 4 minutes with an applied pressure of 400 psi.

#### 3.2.7 Test station operation

Fuel cell temperature, inlet gas flow rate and relative humidity were regulated using an 850e fuel cell station (Scribner Associates, USA). The stoichiometry of anode and cathode were kept constant at 1.2 and 3, respectively. At 1 A cm<sup>-2</sup>, these values corresponded to flow rates of 0.090 l min<sup>-1</sup> and 0.536 l min<sup>-1</sup> for 10 cm<sup>2</sup> active area fuel cell, and 0.224 l min<sup>-1</sup> and 1.339 l min<sup>-1</sup> for 25 cm<sup>2</sup> active area fuel cell for anode and cathode, respectively. The total catalyst loading was 0.4 mg Pt cm<sup>-2</sup>. Inlet air and hydrogen were humidified using bubbler type humidifier tanks. Each gas was fed through a bubbler at the bottom of the water tank and dew points were regulated by controlling the temperature of the water. The inlet gas relative humidity of the anode and cathode was kept the same and the cell temperature was set to 70°C. The outlet of both the anode and cathode was at atmospheric pressure. Gas line temperature was kept higher than the humidifier temperature during operation to prevent any condensation prior to entering the fuel cell.

#### 3.2.8 Electrochemical Impedance Spectroscopy (EIS)

EIS was performed using a Gamry Reference 3000 and Gamry Reference 30K Booster (Gamry Instruments, USA). Prior to the impedance measurement, the fuel cell was conditioned at a constant current to reach steady state. Data points were recorded at a frequency range of 5 kHz to 0.1 Hz (10 frequency points/decade) and AC modulation amplitude was kept below 10% of the DC input signal to ensure a linear system response. EIS was conducted by keeping the stoichiometry of anode and cathode constant at 1.2 and 3, respectively. The cell was maintained at 70°C and the inlet gases were humidified to 50% RH. Back pressure was not applied.

# 3.3 Results and discussion

# 3.3.1 PEMFC performance ( $10 \text{ cm}^2$ surface area)

These flow-fields are assembled in the cathode of a PEMFC (a conventional double serpentine flow-field is mounted on the anode, where there are no notable transport limitations) and high-frequency resistance measurements (Figure A.1, Appendix A) are conducted to ensure that membrane hydration is similar for fractal and serpentine flowfield based PEMFCs under operating conditions. At 50% RH, we expect significantly less condensation to take place across the active area than at 75% RH and 100% RH. This is reflected in the optimal fuel cell performance attained at 50% RH for all flowfields, as it appears to provide near flood-free PEMFC operating conditions with small Ohmic losses (Figure 3.3 (a)).[186, 187] Flooding still appears to occur across the channels of N = 5 flow-field at 50% RH as suggested by a higher mass transport impedance than that of N = 4 in Table 3.2, despite more uniform gas distribution expected across the active area of fractal N = 5 flow-field based PEMFC. The "N = 3design" (fractal with three generations of branching) exhibits the worst performance due to the large spacing between adjacent outlets, [176] which, in turn, leads to insufficient oxygen concentration on the electrode surface and, hence, sluggish kinetics.[5] On the contrary, the N = 4 design demonstrates a ~20% increase in performance (at current densities higher than 0.8  $Acm^{-2}$ ) and ~25% increase in maximum power density compared to serpentine based PEMFCs, due to the enhanced uniformity in reactant distribution across the catalyst layer.



Figure 3.3 Polarisation and power density curves for fractal and serpentine flow-field based PEMFCs (10 cm<sup>2</sup> surface area) at (a) 50% RH, (b) 75% RH, and (c) 100% RH. Experiments were conducted at cell temperature of 70°C using hydrogen and air at a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.090 l min<sup>-1</sup> and 0.536 l min<sup>-1</sup> at 1 A cm<sup>-2</sup>. The dew point of inlet gases was set to 54.9°C, 63.6°C, and 70.0°C for fuel cell operation at 50% RH, 75% RH, and 100% RH, respectively. No backpressure was applied to the system.

A similar trend in performance of fractal and serpentine flow-field based PEMFCs is observed at higher humidity levels (75% RH). PEMFC performance is slightly lower, despite better membrane hydration, due to the presence of more liquid water in the system[188] that impedes effective gas diffusion into the catalyst layer (Figure 3.3 (b)). This is because the any liquid water present in the catalyst and gas diffusion layer reduces the pore space available for gaseous reactant to diffuse through. The effective gas diffusion coefficient is also reduced by the presence of liquid water in the porous media as suggested by Equation (2.9). Nevertheless, the N = 4 design exhibits a ~20% increase in performance (at current densities higher than 0.8 A cm<sup>-2</sup>) and  $\sim$ 30% increase in maximum power density compared to conventional serpentine based PEMFCs.

However, at 50% RH and 75% RH, fractal flow-field based PEMFCs with N = 5 demonstrate lower performance than expected (fractal N = 5 flow-field could not be tested due to excess flooding at 100% RH). Although it is thermodynamically favourable to operate the PEMFC at this state (minimum entropy production of the system),[28] the performance results indicate that operation at Pé > 1 under high humidity conditions requires methods for the efficient removal of liquid water to avoid flooding.

The above statement is verified by fuel cell performance measurements at fully humidified conditions (Figure 3.3 (c)). At 100% RH, additional generation of water vapour (after complete membrane hydration) supersaturates the PEMFC, resulting in water condensation in the electrode and flow-field channels, increasing the mass transport resistance. This is evident by the lower performance (~10%) of the N = 4 design compared to serpentine based PEMFCs (Figure 3.3 (c)). Fractal flow-field based PEMFCs with N = 5 could not be tested due to excess flooding at 100% RH; the gas flow rate from individual fractal channels is insufficient to effectively remove liquid water.

# 3.3.2 EIS measurements ( $10 \text{ cm}^2$ surface area)

Electrochemical impedance spectroscopy (EIS) was used to elucidate the performance improvement of the fractal flow-field based PEMFCs by differentiating major sources of impedance occurring during cell operation (Figure 3.4). EIS was conducted at 0.75 A cm<sup>-2</sup> (50% RH) to represent a regime of operation expected to be limited by reactant transport to the electrode without the effect of flooding. The measured impedance spectra were fitted using the Simplex method in Gamry EChem Analyst, based on the equivalent circuit diagram in Figure 1.11, to deconvolute the extent of the contribution of each phenomenon to the overall fuel cell performance losses.



Figure 3.4 Nyquist plots taken for fractal and serpentine flow-field based PEMFCs (10 cm<sup>2</sup> surface area and 50% RH) at 0.75 A cm<sup>-2</sup>. Dotted lines are fitted results. Blue, red, yellow, purple, and orange circles correspond to perturbation frequencies of 2000 Hz, 200 Hz, 20 Hz, 2 Hz, and 0.2 Hz, respectively. Experiments were conducted at cell temperature of 70 °C using hydrogen and air at a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.067 1 min<sup>-1</sup> and 0.402 1 min<sup>-1</sup> at 1 A cm<sup>-2</sup>. The dew point of inlet gases was set to 54.9°C, 63.6°C, and 70.0°C for fuel cell operation at 50% RH, 75% RH, and 100% RH, respectively. No backpressure was applied to the system.

The values of charge transfer ( $R_{CT}$ ) and mass transport ( $R_{MT}$ ) impedances for the lunginspired and serpentine flow-field based PEMFCs are outlined in Table 3.2. The fractal flow-fields demonstrate lower  $R_{CT}$  and  $R_{MT}$  values than the single-serpentine flow-field. Since flooding is largely mitigated at 50% RH (Figure 3.3 (a)), the improvement in reaction kinetics and mass transport is primarily attributed to better reactant distribution across the electrode. Mass transport within the electrode is improved from reduced diffusional losses, as catalytic sites are exposed to a higher and more uniform reactant concentration profile across the plane. Improved reactant distribution also increases catalyst utilisation and enhances reaction kinetics, as active sites are generally exposed to higher reactant concentration across the active area. A higher mass transport impedance is recorded for fractal flow-field with N = 5 than that of N = 4, despite more uniform gas distribution expected across the active area of fractal N = 5 flow-field based PEMFC. This may be attributed to greater degree of flooding occurring inside the fractal N = 5 flow-field based PEMFC than N = 4, due to significantly slower gas velocity across the fractal inlet and interdigitated outlet channel. Flooding increases mass transport impedance across porous medium as liquid water hinders gas diffusion by blocking the available pore space for gas to travel.

Table 3.2 Fitted values of charge transfer and mass transport at 0.75 A cm<sup>-2</sup> for lung-inspired and serpentine flow-field based PEMFCs ( $10 \text{ cm}^2$  surface area and 50% RH).

Flow-field design	$R_{CT} (\Omega \text{ cm}^2)$	$R_{MT} (\Omega \text{ cm}^2)$
Single serpentine	0.458	0.535
Fractal 4 gen	0.344	0.204
Fractal 5 gen	0.370	0.333

# 3.3.3 Current hold measurements

Fractal and serpentine flow-field based PEMFCs were subjected to a 24 h current hold experiment at 1 A cm<sup>-2</sup> to further evaluate the effect of reactant distribution across the electrode. The positive effect of uniform reactant distribution on fuel cell performance is evident (Figure 3.5). Fractal flow-fields with N = 4 exhibit the lowest voltage decay (~5 mV h<sup>-1</sup>) compared to the serpentine flow-field design (~6.2 mV h<sup>-1</sup>). Assuming that the initial catalyst loading is uniform, the increased voltage decay rate of the serpentine flow-field based PEMFCs shows that uneven reactant distribution leads to higher particle agglomeration and carbon support loss across the channel.[189] The highest voltage decay rate (~11 mV h<sup>-1</sup>) is observed for fractal flow-fields with N = 3, in which the insufficient reactant concentration may have caused local reactant deprivation and cell reversal.[5]



Figure 3.5 Extended current hold measurements (24 h) at 1 A cm<sup>-2</sup> for 10 cm<sup>2</sup> surface area are conducted to evaluate the effect of uniform reactant distribution on fuel cell performance. Experiments were conducted at cell temperature of 70 °C using hydrogen and air at a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.090 l min<sup>-1</sup> and 0.536 l min<sup>-1</sup> at 1 A cm<sup>-2</sup>. The dew point of inlet gases was set to 54.9°C, 63.6°C, and 70.0°C for fuel cell operation at 50% RH, 75% RH, and 100% RH, respectively. No backpressure was applied to the system.

# 3.3.4 Pressure drop ( $10 \text{ cm}^2$ surface area)

In terms of pressure drop (Figure 3.6), fractal flow-fields with N = 3 and 4 exhibit the lowest values (respectively ~75% and ~50% lower than conventional serpentine flow-field design for all RH tested) reducing the power requirements for pressurisation and recirculation of the reactants.[190] On the contrary, fractal flow-fields with N = 5 exhibit a similar pressure drop to serpentine flow-field designs due to the constricted air flow through smaller hydraulic diameters of the inlet and outlet channels.[191, 192]



Figure 3.6 Pressure drop in the cathode for fractal and serpentine flow-field (10 cm<sup>2</sup> surface area) based PEMFCs at (a) 50% RH, (b) 75% RH, and (c) 100% RH. Experiments were conducted at cell temperature of 70 °C using hydrogen and air at a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.090 1 min<sup>-1</sup> and 0.536 1 min<sup>-1</sup> at 1 A cm<sup>-2</sup>. The dew point of inlet gases was set to 54.9°C, 63.6°C, and 70.0°C for fuel cell operation at 50% RH, 75% RH, and 100% RH, respectively. No backpressure was applied to the system.

# 3.3.5 PEMFC performance ( $25 \text{ cm}^2 \text{ surface area}$ )

The obtained experimental results at  $10 \text{ cm}^2$  active area show that the proposed natureinspired approach can be successfully used to resolve uneven reactant distribution issues in PEMFCs. The defining characteristic of the fractal approach, though, is scalability, which is an important feature in nature. This characteristic makes the proposed natureinspired approach stand out among other, bio-mimetic techniques reported in the literature, even though advancements in 3D printing technology *via* DMLS are required to mass produce large fractal flow-fields with a high number of generations.



Figure 3.7 Polarisation and power density curves for fractal and serpentine flow-field based PEMFCs (25 cm<sup>2</sup> surface area) at (a) 50% RH, (b) 75% RH, and (c) 100% RH. Experiments were conducted at cell temperature of 70 °C using hydrogen and air at a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.224 1 min<sup>-1</sup> and 1.339 1 min<sup>-1</sup> at 1 A cm<sup>-2</sup>. The dew point of inlet gases was set to 54.9°C, 63.6°C, and 70.0°C for fuel cell operation at 50% RH, 75% RH, and 100% RH, respectively. No backpressure was applied to the system.

Fractal flow-fields can bridge multiple length scales by adding further generations, while preserving the building units and microscopic function of the system.[22, 193] Larger, 3D printed fractal flow-fields (25 cm<sup>2</sup> surface area) with N = 4 are compared to conventional, serpentine flow-field based PEMFCs. Performance results (Figure 3.7) show that fractal and serpentine flow-field based PEMFCs have similar polarisation curves, which is attributed to the significantly higher pressure drop (~25 kPa) of large

serpentine flow-fields compared to fractal flow-fields (Figure A.2, Appendix A). The increased mass flow rate enhances the overall reaction rate and greatly reduces the resident water in the serpentine channels, resulting in a more uniform reactant distribution across the electrode and thus, improved performance.[194] On the contrary, large fractal flow-fields with N = 4 have minimal pressure drop (< 2 kPa) under all RH conditions tested, revealing their difficulty to purge the produced liquid water from the fuel cell at the same pace as the serpentine flow-fields. Hence, to further improve the design of these fractal flow-fields, it is required to implement different outlet channel designs to remove the unreacted gas and product water, while operating the PEMFC at a Péclet number close to unity. The combination of these two design parameters will achieve maximum fuel cell efficiency from uniform entropy production and minimal parasitic loss, leading to a maximum power density.

# 3.4 Summary

3D printed, lung-inspired fractal flow-fields with N = 4 generations outperform the serpentine flow-fields at high current densities (at 50% and 75% RH) due to more uniform reactant distribution across the catalyst layer. At higher humidity levels (100% RH), though, the performance of N = 5 fractal flow-fields significantly deteriorates; the reduced air flow rate within the fractal flow-fields hampers effective gas diffusion within the porous medium, resulting in insufficient convective liquid water removal. Even though modelling results suggest that a N = 5 design delivers optimum PEMFC performance, in practice, the utilisation of a fractal flow-field above N = 4 is not currently feasible. The identification of the shortcomings of fractal flow-fields pertaining to water management provides a rationale for design improvements, mainly on the land and outlet channels. The closely intertwined nature of these two factors emphasises the need to implement alternative outlet channel geometry or engineered water removal strategies to alleviate flooding and parasitic loss, especially at higher generations.

The uniform gas distribution across the catalyst layer is preserved when these fractal flow-fields are scaled-up ( $25 \text{ cm}^2$  surface area). The fuel cell performance of the large-scale fractal flow-field remains almost unchanged on a per area basis, compared to its

smaller active area counterpart. On the contrary, larger, conventional serpentine flow-fields (25 cm<sup>2</sup> surface area) exhibit improved relative performance over 10 cm<sup>2</sup> ones due to an order-of-magnitude higher pressure drop than that of a fractal flow-field, resulting in faster overall reaction rates and better liquid water removal. However, such excessive pressure drop renders the use of a large-scale serpentine flow-field prohibitive, thus favouring the fractal flow-field. Implementation of effective water removal mechanisms should circumvent remaining problems of high-generation fractal flow-fields.

# Chapter 4

# In situ visualisation of liquid water using neutron radiography

Sections of this work have been adapted from "Visualization of Liquid Water in a Lung-Inspired Flow-Field based Polymer Electrolyte Membrane Fuel Cell *via* Neutron Radiography," *Energy*, 2019, 170, 14-21

# 4.1 Introduction

The concept of lung-inspired flow-fields was numerically validated, and the number of branching generations (N) was found to be the key parameter for reactant uniformity. However, these lung-inspired flow-fields are susceptible to flooding under high humidity conditions, especially at high generation numbers, where the channels become very narrow, due to slow gas flow across each channel.[21]

In contrast to conventional flow-fields, investigation of the dynamics of liquid water in lung-inspired flow-fields using existing visualisation techniques is limited, partly due to the inherent difficulty in accessing liquid water through the 3D printed stainless steel structure with complex internal channel networks. In-depth understanding of the two-phase flow across the lung-inspired flow-field channels would serve to identify the shortcomings of the current design pertaining to water management, and improve it *via* 

an alternative outlet channel geometry or implementation of an engineered water management strategy.

In this study, through-plane neutron imaging results are presented for the lung-inspired flow-field with N = 4 generations, and compared to results for a conventional double-serpentine flow-field. The fuel cell is operated at ambient temperature in the absence of gas humidification. A series of galvanostatic measurements are performed and the corresponding transient changes in fuel cell potential are presented along with neutron images to investigate the effect of liquid water formation and transport on fuel cell performance.

# 4.2 Experimental

#### 4.2.1 MEA fabrication

A 10 cm<sup>2</sup> MEA was fabricated in-house by hot pressing a Nafion 212 membrane (DuPont, USA) and ELE0070 gas diffusion electrodes (Johnson Matthey, UK) using a 12-ton thermal press (Carver, 4122CE). The membrane was used without any pre-treatment, and the assembly was pressed at 130°C for 3 minutes with an applied pressure of 400 psi.[49] The membrane has a thickness of 50  $\mu$ m, and the catalyst layers have a platinum loading of 0.4 mg Pt cm<sup>-2</sup>.

#### 4.2.2 PEMFC components

Figure 4.2 shows an exploded view of a PEMFC using a lung-inspired flow-field at the cathode. Both end-plates were made of 8 mm thick aluminium plates, which were electroless plated in gold to prevent corrosion. The same fractal flow-field as introduced in Chapter 3 was used in this study. The fractal flow-field consists of 3D network of branching inlet channels and interdigitated outlet channels, which are connected by a manifold (Figure 4.4). The flow-field was electroplated in-house in gold (Spa Plating, UK) to 1  $\mu$ m thickness. A detailed description of the dimensions and configuration of the plates and gold electroplating procedure is outlined in Chapter 4.2.3. The fractal flow-field was assembled in the cathode of a PEMFC, in which notable transport

limitations occur. A 2 mm thick gold-coated aluminium plate was used as a cathode current collector for the lung-inspired flow-field and a 0.8 mm thick graphite sheet (RS pro, UK) was placed in between for a gas-tight seal. The current collector was used only for the fractal flow-field. Current was drawn directly from the serpentine flow-fields at the anode and cathode. At the anode, a single-channel serpentine flow-field was used with channel width, spacing, and depth of 1 mm, 1 mm, and 0.7 mm, respectively. The anodic serpentine flow-field was made of a 2 mm thick aluminium plate, which was electroless plated in gold.



Figure 4.1 Schematics of the single (left) and double (right) channel serpentine flowfields used for the anode and cathode, respectively.

The behaviour of the above-mentioned setup was compared to a PEMFC using a serpentine flow-field at the cathode. The cathodic double-serpentine flow-field was fabricated by milling channels into a 1.6 mm thick printed circuit board (PCB) plate (35  $\mu$ m copper layer) to achieve channel width and spacing of 1 mm, and depth of 0.8 mm. At the anode, again, a single-serpentine flow-field was used with channel width, spacing, and depth of 1 mm, 1 mm, and 0.7 mm, respectively. The anodic flow-field was made of a 0.8 mm thick PCB plate (35  $\mu$ m copper layer). The PCB flow-fields were electroplated to 0.5  $\mu$ m in nickel (Balco Engineering, UK) and 5  $\mu$ m in gold (Spa Plating, UK). A 70  $\mu$ m thick sheet of Tygaflor was used as a gasket at the interface between flow-fields/current collector and end-plates for electrical insulation. The same material was used as a gasket to seal the perimeter of the MEA.

Since anode flow-field was made entirely of metal, current was drawn directly at the top of the plate. The fractal N = 4 flow-field was electrically connected with the anode flow-field using a gold plated aluminium current collector. An electrically conductive graphite sheet was placed between the fractal flow-field and current collector to ensure proper gas seal across the metal interface. Any current that was generated at the anode was passed to the cathode current collector, graphite sheet, and fractal flow-field before reaching the MEA, giving rise to the oxygen reduction reaction.



Figure 4.2 Exploded view of individual PEMFC components used in this study. Green (pointing the back of the fractal flow-field) and red arrows indicate the position of fractal inlet and interdigitated outlet channels, respectively.

## 4.2.3 Gold electroplating of fractal flow-fields

The fractal flow-fields are gold-plated to minimise corrosion during operation. The flow-fields were electroplated by immersing them into 0.02 M gold potassium cyanide solution (KAu(CN)<sub>2</sub>) and a titanium coated stainless steel mesh was used as counter electrode. A Gamry potentiostat (Reference 3000) was used to hold the current density at 10 mA cm<sup>-2</sup> for 525 s to electroplate 1  $\mu$ m of gold onto the 3D printed flow-fields. The fractal flow-field with *N* = 3 generations had a submerged surface area of 38 cm<sup>2</sup> (I<sub>electrodeposition</sub> = 380 mA), while the fractal flow-fields with *N* = 4 and 5 generations had a submerged surface area of 30 cm<sup>2</sup> (I<sub>electrodeposition</sub> = 300 mA) each. After electroplating

of each flow-field, the concentration of the solution was adjusted by adding 0.08 M KAu(CN)<sub>2</sub> gold replenisher solution.

#### 4.2.4 PEMFC operation

A simplified schematic of the experimental setup is displayed in Figure 4.3. The test station supplied dry hydrogen (purity 99.995%) and air at a stoichiometric ratio of 1.2 and 3, respectively, by controlling the gas flow rate using mass flow controllers (EL-FLOW, Bronkhorst). The current drawn from the cell was regulated using a DC electronic load (PLZ664WA, Kikusui). An in-house computer controlled system (LabVIEW, National Instruments) controls the components of the rig and records data with a data acquisition card (USB 6363, National Instruments). The PEMFC was operated without external heating. Table 4.1 lists the key operating conditions used in all experiments. These conditions were chosen to reproduce a regime of operation expected to be limited by flooding, while preventing condensation in the fractal distribution network, which could otherwise obstruct the through-plane view.



Figure 4.3 Simplified schematic for through-plane fuel cell imaging in NEUTRA, facing the LiF/ZnS scintillator.[195] MFC stands for mass flow controller.

Parameter	Value	
Fuel cell temperature	Ambient	
Cathode RH	Dry	
Anode RH	Dry	
Hydrogen stoichiometry ( $\alpha_{H2}$ )	1.2	
Air stoichiometry ( $\alpha_{air}$ )	3	
Active area	$10 \text{ cm}^2$	
Membrane	Nafion 212	
Electrode	ELE0070	
Cathode/anode outlet pressure	1 atm (abs)	

Table 4.1 Operating conditions used during PEMFC operation.

Experiments were conducted by incrementally changing the current density every 10 minutes at 0.1 A cm<sup>-2</sup> intervals until the potential dropped below 0.2 V. In cases where a rapid decline in fuel cell potential occurred at low current density, the fuel cell was subjected to 1 L min<sup>-1</sup> of air flow for 30 s to purge excess liquid water from the system before moving on to the next current density. The anode stream was directed from the upper right to the lower right corner of the MEA for the lung-inspired flow-field. The anode flow direction was reversed for the conventional double-serpentine flow-field to achieve counter-current flow orientation with air (Figure 4.5). The fractal N = 4 flow-field was horizontally orientated as shown in Figure 4.4 (a).



Figure 4.4 (a) Optical image of the gold plated engineered flow-field with N = 4 generations and (b) a schematic showing the fractal geometry. Blue and red arrows indicate the location of the fractal inlet and interdigitated outlet channels, respectively.

# 4.2.5 Neutron imaging facility

Neutron radiography was conducted at the neutron imaging facility NEUTRA of the SINQ spallation source (Paul Scherrer Institute, PSI, Switzerland).[195] Thermal neutrons provided by the source are extracted from a moderator tank in the thermal energy range of  $1 \times 10^{-3}$  to 10 eV with a Maxwellian spectrum energy of  $25 \times 10^{-3}$  eV. The second position was used inside the shielded area along the beam line with a maximum field-of-view of  $15 \times 15$  cm<sup>2</sup>. The fuel cell was placed in through-plane orientation to the beam to visualise liquid water across the electrode (Figure 4.3). A LiF/ZnS neutron scintillator screen converts the neutron flux of the beamline into light emission, which is then reflected by a mirror to be recorded by a CCD camera with a pixel size of 0.104 mm and a resolution of 0.2 mm.

Images were taken with an exposure time of 20 s, which provides enough temporal resolution to capture dynamic changes in liquid water distribution during a current hold. The exposure time is within the range typically used for neutron imaging of PEMFCs (1 - 25 s).[121, 125-127] The intensity images are generated in FITS format, which are post-processed using PSI's in-house software written in Interactive Data Language (IDL).

### 4.2.6 Contact angle measurements

The contact angle of the fractal flow-field surface was measured using a drop shape analyser (Kruss DSA 100, Germany). An 8  $\mu$ L drop of deionised water was placed on the surface of a sample and the static contact angle was measured using built-in fitting software. The 3D printed stainless steel, gold plated aluminium plate, and milled PCB surface exhibited hydrophilic surface properties with a measured contact angle of 75.3°, 81.0°, and 56.6°, respectively.

# 4.2.7 Quantification of the water thickness from neutron images

After applying necessary corrections to the resulting images (filtering, subtraction of the neutron scattering background, alignment of "operating" and reference images), images

taken during cell operation were normalised to a reference image of the dry fuel cell (Figure 4.5) before operation to obtain only the attenuation corresponding to the water content in the system. The thickness of water,  $t_{water}$ , is calculated from the relative neutron transmission ( $I/I_0$ ) by inverting Lambert-Beer's law:

$$t_{water} = -\frac{\ln\left(\frac{I}{I_0}\right)}{\mu_{water}}$$
(4.1)

where *I* is the intensity of the beam in operation,  $I_o$  is the intensity of the beam for the dry fuel cell,  $t_{water}$  is the thickness of water, and  $\mu_{water}$  is the attenuation coefficient of water. The attenuation coefficient of neutrons in liquid water was measured in the NEUTRA beamline for the given setup at 3.5 cm<sup>-1</sup>.[196] In the following sections, the water content will be expressed as the effective water thickness in mm.



Figure 4.5 Radiograph of a dry cell with (a) double-serpentine and (b) fractal N = 4 gen. Green and red arrows indicate the flow direction of air and hydrogen, respectively. For the fractal flow-field case, air was directed perpendicular to the plane.

# 4.3 Results and discussion

### 4.3.1 Lung-inspired flow-field with N = 4 generations

Neutron images of the lung-inspired flow-field based PEMFC (N = 4) were taken during a galvanostatic operation at 0.3 A cm<sup>-2</sup>. Images are displayed in chronological sequence to reveal the evolution and transport of liquid water across the channel. The blue band around the rectangular opening of the graphite sheet (red arrow in Figure 4.6 (c)) is water that has penetrated into the interface between the flow-field and the graphite sheet due to incomplete sealing. The white region on the bottom right (red arrow in Figure 4.6 (a)) is a result of liquid water that was present in the end-plate when the dry image was taken, but was later purged using high gas flow prior to operation.



Figure 4.6 (a) - (d) Neutron images showing water distribution across the lung-inspired flow-field based PEMFC with N = 4 (10 cm<sup>2</sup> surface area) at different times and (e) variation in potential during galvanostatic operation at 0.3 A cm<sup>-2</sup>. The time at which each image was taken is marked on the curve. Experiments were conducted at ambient cell temperature using dry hydrogen and dry air at a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.026 l min<sup>-1</sup> and 0.159 l min<sup>-1</sup> at 0.3 A cm<sup>-2</sup>. No backpressure was applied to the system.

A gradient in liquid water distribution is observed at the start of PEMFC operation with greater water content towards the bottom of the electrode. Dry hydrogen gas flows from the top to the bottom on the opposite side of the MEA, causing a portion of the liquid water generated near the top of the cathode catalyst layer to be transported across the membrane via back-diffusion. Back-diffusion of liquid water occurs due to concentration gradient of water across the membrane (Equation 2.16). Since dry gas was used for both electrode and water is only generated at the cathode, a water concentration gradient is established across the membrane with higher water concentration towards the cathode side. This causes the generated water at the cathode to be transported across the membrane to the anode. Water droplets appear on the channel wall as they emerge from under the land (channels indicated with green arrows). This observation is in line with previous X-ray and neutron imaging studies showing liquid water to preferentially accumulate at the bottom of the land and start bulging into the channel once the region is saturated.[105, 106] These emerged droplets grow in size and coalesce with neighbouring droplets to form slugs, causing channel blockages. The overall quantity of liquid water increases over time with significant water accumulating in the interdigitated outlet channels, which leads to an exponential decay in cell potential, as a greater region of the electrode is progressively deprived of reactant gas. This result is consistent with a previous report demonstrating flooding to occur at low current densities, caused by slow gas velocity.[197] The substantially slower gas flow across the channels of fractal flowfields in comparison to most conventional flow-field designs makes fractal flow-fields particularly susceptible to flooding at low current density. Channel flooding in fractal flow-fields is highly undesirable, as it creates low resistance paths, redistributing the gas within the fractal distributor network, such that more gas flows out in the vicinity of the outlet channels with less liquid water, thus starving the region underneath the flooded channels of reactant gas.[25, 134, 198]

A significant portion of liquid water is found in the "inlet channels" (outlets of the fractal distributor). Since inlet gas supply is dry, all liquid water found in the inlet channels is the product of the electrochemical reaction. The generated liquid water enters the inlet channels by capillary pressure. The narrow dimensions of the final generation and the hydrophilic channel wall cause the generated liquid water to be

wicked into the inlet channels. Additionally, the hydrophobic gas diffusion layer (GDL) generates capillary pressure, which forces liquid water into the channel.[71, 199, 200] We assume that these interacting forces prompt backflow of generated liquid water into the inlet channels, where gas flow is partially impeded due to minor structural imperfections within the fractal network. The finding underscores the importance of ensuring a high degree of resolution of the fractal network; especially channels in close proximity to the final generation where feature size is small, and even a minor structural defect can locally disrupt the gas distribution.



Figure 4.7 (a) - (d) Neutron images showing water distribution across the lung-inspired flow-field based PEMFC with N = 4 (10 cm<sup>2</sup> surface area) at different times and (e) variation in potential during galvanostatic operation at 0.5 A cm<sup>-2</sup>. The time at which each image was taken is marked on the curve. Experiments were conducted at ambient

cell temperature using dry hydrogen and dry air at a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.044 1 min<sup>-1</sup> and 0.267 1 min<sup>-1</sup> at 0.5 A cm<sup>-2</sup>. No backpressure was applied to the system.

A more dynamic liquid water movement is observed across the channel at 0.5 A cm<sup>-2</sup> from faster gas flow and higher channel pressure drop. Hence, flooding is substantially alleviated as indicated by a slower decline in potential (Figure 4.7; note the different scale of the Y-axis, compared to Figure 4.6). The process of liquid water transport and removal is captured and highlighted with arrows.

As water droplets get expelled into the manifold (red arrow in Figure 4.7 (a)), small remnants of the droplet are left behind in the channel downstream (red arrow in Figure 4.7 (c)). The remnants form as a result of a breakup of the primary slug caused by the combined effects of air velocity and surface tension,[94] and these exist in the form of a film.[94, 114, 201] Some liquid droplets spontaneously appear in the channel downstream, also in the form of a film (green arrows in Figure 4.7 (c)). Since there was no involvement of a primary slug, we anticipate wicking of liquid water to have occurred from the hydrophobic GDL onto the hydrophilic channel wall.[93, 94] Film flow allows gas to flow around it and so these droplets remain static until they grow by encountering another slug, vapour condensation or expulsion of generated liquid water from the GDL. Abrupt, temporary recovery in PEMFC potential may be indicative of liquid droplet movement across the interdigitated outlet channel into the manifold, sweeping away stationary droplets attached to the GDL and momentarily enhancing reactant transport to the catalyst layer.[82, 114, 202]

Some liquid water droplets, on the other hand, continue to grow without advective movement (green arrows in Figure 4.7 (a)). The channel pressure drop at 0.5 A cm<sup>-2</sup> appears to be insufficient to remove these slugs, as larger droplets sustain greater adhesive force with the channel wall, requiring greater pressure drop for convective removal.[83] The remaining liquid droplets plug the channel of any gas flow and divert it from neighbouring inlet channels to unfilled contiguous outlet channels, resulting in inhomogeneous gas distribution and local reactant starvation.[25, 134, 198]



Figure 4.8 (a) - (d) Neutron images showing water distribution across the lung-inspired flow-field based PEMFC with N = 4 generations (10 cm<sup>2</sup> surface area) at different times and (e) variation in potential during galvanostatic operation at 0.6 A cm<sup>-2</sup>. The time at which each image was taken is marked on the curve. Experiments were conducted at ambient cell temperature using dry hydrogen and dry air at a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.053 l min<sup>-1</sup> and 0.320 l min<sup>-1</sup> at 0.6 A cm<sup>-2</sup>. No backpressure was applied to the system.

A similar pattern emerges in the growth and discharge of liquid droplets at 0.6 A cm<sup>-2</sup> (Figure 4.8). The decline in potential is more pronounced, despite similar liquid water content as at 0.5 A cm<sup>-2</sup>, as elevated reactant consumption rate causes greater mass transport losses within the electrode. The liquid slug of the order of the outlet channel

length (red arrow in Figure 4.8 (a)) starts seeping and spreading into the manifold as the channel cannot accommodate any more liquid water. The implication of excess liquid water emerging and expanding inside the manifold is significant in terms of removal of lengthy liquid slugs. As a liquid slug protrudes into the manifold, the radius of the emerging liquid expands and the curvature of the surface decreases. This causes a local drop in liquid pressure at the interface, inducing liquid flow in the direction of the expanding surface.[199, 200] The slug is slowly pulled out of the channel in the process, as suggested by the weakening neutron signal near the channel upstream, before being completely removed. The emerged water may have joined the slug in the adjacent channel during the expansion (red arrow in Figure 4.8 (c)), facilitating the removal of this slug. It is anticipated that the elevated gas pressure in the channel upstream at 0.6 A cm<sup>-2</sup> also contributed to the expulsion of liquid water into the manifold. Removal of liquid water slugs is met by an instantaneous jump in the potential of over 200 mV. Such drastic performance improvement underscores the importance of maintaining outlet channels clear of liquid water in lung-inspired flow-fields for efficient and stable operation. The potential continues to gradually decline following the slug removal, due to the presence of smaller slugs across the outlet channels, which also results in lower average cell potential compared to the serpentine flow-field at the same operating condition (Figure 4.10). The decline is much more subtle, though, possibly as a result of alleviated flooding and no significant formation of liquid water following the slug removal; any additionally generated liquid droplets are effectively swept away by the gas flow.

# 4.3.2 Conventional double-serpentine flow-field

The water removal mechanism of a double-serpentine flow-field is assessed and compared against the fractal flow-field. The similar anode and cathode channel geometries make it difficult to distinguish the electrode to which the liquid water is associated. However, differentiation is possible with careful observation of the droplet movement and location across the electrode.



Figure 4.9 (a) - (d) Neutron images showing water distribution across a conventional double-serpentine flow-field based PEMFC (10 cm<sup>2</sup> surface area) at different times and (e) variation in potential during galvanostatic operation at 0.3 A cm<sup>-2</sup>. The time at which each image was taken is marked on the curve. Experiments were conducted at ambient cell temperature using dry hydrogen and dry air at a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.026 1 min<sup>-1</sup> and 0.159 1 min<sup>-1</sup> at 0.3 A cm<sup>-2</sup>. No backpressure was applied to the system.

Figure 4.9 shows the evolution of liquid water distribution in the channel of a conventional double-serpentine flow-field at 0.3 A cm<sup>-2</sup>. The counter-current flow orientation of dry air and hydrogen causes the top and bottom region of the active area to be drier than the rest as a result of evaporation and back-diffusion, respectively. The

majority of liquid water at the start of the current hold is observed in the corners of the channel in the form of droplets and film.[114, 203] Liquid accumulates in corners as a result of the decreasing channel-to-channel pressure gradient near the bends.[197, 204, 205] This is because a gradient in pressure is established across the gas channel with higher pressure towards the inlet when there is gas flow. This leads to a pressure difference between adjacent gas channels causing a portion of gas to flow through the porous GDL underneath the flow-field land perpendicular to the direction of main flow. This effect is least pronounced at the channel bend where the channel pressure drop is minimal due to short distance for the gas to travel. Momentary changes in the neutron attenuation signal in the anode outlet manifold following the removal of these droplets at  $0.6 \text{ A cm}^{-2}$  (Figure 4.10) confirms that most of these droplets are present in the anode. Liquid water in the anode remains stagnant through the current hold at  $0.3 \text{ A cm}^{-2}$ , due to slow gas flow and a lack of large enough liquid droplet formation required to initiate water movement across the channel. Water droplets in the corners of the cathodic flow channel (red, blue, and orange arrows in Figure 4.9) exhibit more dynamic movement and tend to spread across the channel surface in the direction of flow - a combined effect of surface hydrophilicity and faster gas flow. Some droplets (orange and blue arrows in Figure 4.9 (a)) spread across the channel top before being discharged across the channel, sweeping away any droplets (green arrow in Figure 4.9 (b)) along the way, thereby facilitating liquid water removal.

A stable PEMFC potential is recorded for the duration of the current hold in spite of fluctuating water content across the active area at 0.3 A cm<sup>-2</sup>. This is ascribed to proper gas flow across the channel and cross flow created by the pressure difference between adjacent channels, allowing for convective reactant transport within the electrode. In the lung-inspired flow-field case, PEMFC performance deteriorated mainly as a result of static slugs in its interdigitated outlet channels that impeded effective reactant transport to the catalytic sites underneath. Such stagnation of water droplets does not occur for the double-serpentine flow-field because of a much lower number of channels that fosters faster gas flow and a smaller likelihood for the path of least resistance to be established between channels.

In contrast to the fractal flow-field, liquid water is observed in the anode of the serpentine flow-field based PEMFC. One plausible cause is the difference in physical properties of the channel wall. The anodic flow-fields used with the serpentine and fractal flow-fields were fabricated from PCB and aluminium plate, respectively. The contact angle of the milled PCB is significantly lower (56.6°) than that of the gold-coated aluminium plate (81°). We anticipate the higher channel surface wettability of the PCB flow-field to cause greater adherence of water to the wall, which hinders convective droplet movement across the channel, so that anodic flow channels become more susceptible to water accumulation.[94, 204]



Figure 4.10 (a) - (d) Neutron images showing water distribution across the doubleserpentine flow-field based PEMFC (10 cm<sup>2</sup> surface area) at different times and (e) variation in potential during galvanostatic operation at 0.6 A cm<sup>-2</sup>. The time at which

each image was taken is marked on the curve. Experiments were conducted at ambient cell temperature using dry hydrogen and dry air at a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of  $0.053 \ 1 \ min^{-1}$  and  $0.320 \ 1 \ min^{-1}$  at 0.6 A cm<sup>-2</sup>. No backpressure was applied to the system.

Water droplets no longer emerge from the GDL onto the channel wall at 0.6 A  $\rm cm^{-2}$ (Figure 4.10). This is due to significant cross flow created by a greater pressure difference between adjacent channels, which sweeps away any generated liquid water under the land, before it accumulates and surfaces into the channel. As previously mentioned, most liquid water located in the corners is present in the anodic flow channel. Liquid water droplets in the corners gradually spread towards the centre in the direction of the hydrogen flow, before being intermittently removed (Figure 4.10 (d)). The overall quantity of liquid water in the channels of the serpentine flow-field drops significantly when transitioning to a higher current density in comparison to the fractal flow-field. This is primarily due to much higher gas velocity across the channel fostering effective convective liquid water removal. This agrees well with the neutron imaging results reported by Trabold *et al.* that demonstrated a reduced overall quantity of water in the flow-field channels with an increase in current density due to a higher gas velocity.[197] Lastly, erratic fluctuations in potential observed with the fractal N = 4 flow-field at 0.6 A cm<sup>-2</sup> do not occur for the double-serpentine flow-field, which corroborates the excellent water management ability of the serpentine channel geometry.

# 4.4 Summary

Neutron imaging has been employed to visualise liquid water distribution across lunginspired and serpentine flow-field based PEMFCs. The serpentine flow-field based PEMFC exhibits the most stable performance as faster gas flow facilitates effective liquid water removal. On the contrary, the lung-inspired flow-field based PEMFC sustain significant liquid water accumulation in the interdigitated outlet channels, due to limited convective liquid removal from substantially slower gas flow and narrow channel dimensions, resulting in significantly higher overall water content and early

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onset of flooding. Flooding is alleviated at higher current densities, as faster gas flow and increased channel pressure drop yields more dynamic liquid water removal.

The importance of a well-defined, three-dimensional internal structure is identified from the observation of clogged fractal inlet channels. Any minor defects in the fractal channel network, especially in the vicinity of the final generation, render inlet channels prone to clogging with liquid water from improper gas flow.

Without condensation and channel clogging, fractal flow-fields lead to highly uniform gas transport and catalyst utilisation, and, thus, exceptional fuel cell performance.[21] However, flooding in the channels of the fractal flow-field is highly undesirable as it leads to redistribution of the gas within the fractal network, resulting in non-uniform gas distribution across the electrode, which hampers system efficiency and can potentially expedite fuel cell component degradation. Modification of the outlet channel geometry and implementation of water removal strategy should forestall the evolution of liquid slugs in the channels, ensuring robust and reliable operation of fractal flow-field based PEMFC.

# Chapter 5

# Capillaries for water management in PEMFCs

Sections of this work have been adapted from "Capillaries for Water Management in Polymer Electrolyte Membrane Fuel Cells," *International Journal of Hydrogen Energy*, 2018, 43, 21949-21958

# 5.1 Introduction

The lack of convective water removal due to slow gas velocity and narrow channel dimension of the fractal flow-fields prompted the need for development of new water management strategy. Current water management strategies for commercial flow-fields cannot be easily employed into these engineered fractal flow-fields, since they require the installation of a porous carbon plate or implementation of wicking elements on the channel surface to wick out the generated liquid water.

In the present work, a water management strategy for fuel cells is presented based on the incorporation of capillaries in flow-fields. Capillaries are laser drilled into the land of a flow-field and hydraulically connected to water transport channel. Liquid water fills the capillaries, and capillary pressure blocks reactant gas entry into the water transport channel. Depending on the local condition of the membrane electrode assembly (MEA), capillaries either remove excess generated water from the electrode *via* wicking or humidify undersaturated gas streams *via* evaporation. Contrary to porous carbon plates, capillaries impose negligible additional interfacial contact resistance and can be

integrated with a broader range of flow-field designs, including state-of-the-art plates that leverage stamping manufacture procedures.[84, 206, 207] The proposed mechanism is tested on a 6.25 cm<sup>2</sup> active area parallel flow-field, and its performance is evaluated against conventional flow-fields.

# 5.2 Experimental

# 5.2.1 Flow-field plate fabrication

The anode and cathode flow-fields were machined from a 1.6 mm thick printed circuit board (PCB) with a 70  $\mu$ m copper layer. PCB-based fuel cells offer the advantage of being low-cost, light-weight, and easily tailored to specific design requirements,[133, 208-210] which makes the proposed water management strategy highly cost effective in comparison to other previously proposed approaches for water management. A singleserpentine channel was used as the anode flow-field with channel width, spacing and depth of 1 mm. Double-serpentine and parallel flow-fields were used in the cathode with channel width, spacing and depth of 1.2, 1.2, and 0.8 mm, respectively, resulting in channel/active area ratio of 0.54 (double-serpentine) and 0.53 (parallel flow-field).



Figure 5.1 Schematic of the parallel flow-field with capillary elements. The front-side (top left) of the plate has parallel gas flow channels and the back-side (top right) features bifurcating gas manifolds and water transport channels. The bifurcating gas manifolds are hydraulically connected to the parallel gas channels and ensure that gas is uniformly
distributed across the channels. The inset is a close-up view of the cross-section of the plate with the water transport channel and cylindrical capillaries filled with liquid water. Excess liquid water in the GDL under the land is wicked into the water transport channel through the capillaries, perpendicular to the direction of the gas transport. Where the gas stream is undersaturated, capillaries work in reverse, providing internal humidification as the water in the capillaries evaporates into the GDL.

Water transport channels were embedded in the cathode flow-fields by milling 1.4 mm deep parallel channels on the back-side of these flow-fields in such a way that the resulting land thickness is ca. 200  $\mu$ m (inset of Figure 5.1). The ends of the channel were connected by milling 0.5 mm deep perpendicular channels to attain the serpentine configuration.

In the case of parallel flow-fields, bifurcating gas manifolds were introduced at the backside to ensure uniform gas distribution across the parallel channels on the front-side. Capillaries were laser-drilled into the lands using a Compact Laser Micromachining System (Oxford Lasers, USA). A single laser pulse (0.1 s laser drill time) was sufficient to drill through the 200  $\mu$ m thick copper/FR4 composite layer. A 13 × 310 capillary array was drilled into each land, which equates to a capillary spacing of ~50  $\mu$ m. Increasing the capillary number is beneficial in terms of water management, as it increases the total rate of wicking/evaporation. However, the number of capillaries explored in this study was sufficient to mitigate flooding for the investigated fuel cell operating range, as is shown further on (Figure 5.5). Also, capillary spacing of less than 50  $\mu$ m resulted in structural failure of the flow-field land upon cell compression during assembly. Therefore, the 13 × 310 capillary array was deemed suitable for use in this study. The drilling process took a total of 260 min for 40300 capillaries. A SC4000 abrasive sheet was used to remove burr and melt zones[211, 212] created on the surface from the laser drilling.

#### 5.2.2 Ni and Au electroplating

Flow-fields were electroplated in-house in nickel (Balco Engineering, UK) and gold (Spa Plating, UK), prior to laser drilling. The composition of the nickel and gold electroplating solutions were  $0.13 \text{ M H}_4\text{N}_2\text{NiO}_6\text{S}_2$  and  $0.02 \text{ M KAu}(\text{CN})_2$ . A platinum coated stainless steel mesh electrode was used as the counter electrode. The active area region of the flow-field with a 7.5 mm margin around the perimeter was exposed to the electroplating solution (total submerged surface area of 16 cm<sup>2</sup>). The copper layer was electroplated in nickel by applying a current of 0.2 A for 3 min. Gold electroplating was accomplished by applying a current of 0.08 A for 94 min to deposit a 5 µm thick gold layer. The current was reduced for gold plating to prevent tarnishing of gold at high potential.

### 5.2.3 Characterisation of capillaries

The laser drilled capillary structure was evaluated using scanning electron microscopy (SEM; Zeiss EVO10, USA) and X-ray tomography (Zeiss Xradia Versa 520, Zeiss, USA). Sample dimensions were 5 mm  $\times$  5 mm  $\times$  200 µm. The sample for SEM measurement was sputter coated with gold for 60 s before imaging, to reduce charging. SEM images were generated at 15 kV. The sample for X-ray tomography was imaged at 80 kV using a beam power of 7 W with an exposure time of 45 s per radiograph. The optical magnification was 4× with a pixel size of 2.0 µm. The High Aspect Ratio Tomography (HART) mode was employed to improve the image quality of the flat sample.

The solid bright region in the tomogram (Figure 5.2 (b)) corresponds to the metal layer, whereas the bundles of strings and circles in dark grey, indicating a woven fiberglass structure, is the FR4 layer. The epoxy resin that binds the fiberglass is not detected by X-ray tomography, owing to its low attenuation of the beam. Tomogram and SEM image reveal that the capillaries are cylindrical with a slight taper at the top of the copper layer where the laser entered[211-213] and have penetrated all the way through the copper/FR4 composite layer. The capillaries measure ~12.8  $\mu$ m at the entrance

diameter and ~6.4  $\mu$ m at the exit diameter, accounting for a total loss of less than 1% in the land area. The capillary pressure generated by the capillaries is 30.2 kPa, which is calculated using [214]:

$$\Delta P_c = \gamma \kappa = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{5.1}$$

where  $\gamma$  (N m<sup>-1</sup>) is the surface tension of liquid water at 70 °C and  $\kappa$  (m<sup>-1</sup>) is the interface curvature, which can be expressed in terms of  $r_1$  (m) and  $r_2$  (m), the principal radii of curvature of the interface. Increasing the capillary diameter may be advantageous in terms of water management, as it increases the rate of wicking and evaporation. However, given the inversely proportional relationship, increasing the capillary diameter leads to a rapid reduction in the capillary pressure, rendering gas breakthrough into the water transport channel more likely. Thus, the capillary diameter of ~12.8 µm was used, which was the smallest capillary diameter achievable with the laser system.



Figure 5.2 (a) SEM image of the capillaries on the copper layer and (b) "xz" orthoslice from a tomogram of a cross-section of a PCB layer with a capillary array. The solid bright region of the tomogram corresponds to the copper layer and the dark grey region underneath is the FR4 layer.

#### 5.2.4 Fuel cell assembly

A detailed view of the fuel cell assembly is shown in Figure 5.3. It consists of the MEA, anode and cathode flow-fields, gaskets for sealing, a heating plate, an acrylic plate for liquid water transport, and end-plates.

A 6.25 cm<sup>2</sup> MEA was prepared in-house by hot-pressing a Nafion 212 membrane (DuPont, USA) and ELE0070 gas diffusion electrodes (Johnson Matthey, UK) at 130 °C for 3 minutes with an applied pressure of 400 psi.[49] The membrane has a thickness of 50  $\mu$ m and the catalyst layers have a platinum loading of 0.4 mg Pt cm<sup>-2</sup>. Tygaflor gaskets (280  $\mu$ m), placed around each gas diffusion layer (GDL), sealed gases and prevented over-compression.

1/8" PTFE tubing was connected to blind holes ( $\phi = 5.5$  mm) on each side of the 12 mm thick acrylic plate using flangeless fittings and ferrules (IDEX, USA). The acrylic plate allowed the water transport channel of the cathode flow-field to be hydraulically connected to a syringe pump (Harvard Apparatus, USA) and a weighing balance (HR-100AZ, A&D, UK), as shown in Figure 5.4. The weighing balance could weight a minimum of 0.1 mg and had a recording rate of 10 Hz, which provided sufficient measurement resolution and frequency for accurate quantification of the change in water mass in the water transport channel over a period of 250 s per current density increment of 0.1 A cm<sup>-2</sup>. The cell temperature was controlled using a K-type thermocouple (RS pro, UK) and cartridge heaters (RS pro, UK), which were inserted into the stainless steel heating plate. The fuel cell was held together using stainless steel end-plates and was tightened to a torque of 1.8 N m. The assembly was oriented horizontally and reactant gases were fed in co-current orientation during operation.



Figure 5.3 Exploded view of the  $6.25 \text{ cm}^2$  fuel cell assembly. The green, red, and blue arrows represent the direction of air, hydrogen, and liquid water, respectively.

### 5.2.5 Test station operation

A schematic of the experimental setup is outlined in Figure 5.3. Fuel cell temperature, inlet gas flow rate, relative humidity, and electronic load were regulated using a commercial fuel cell test station (850e, Scribner Associates, USA). The anode ( $\alpha_{H2}$ ) and cathode ( $\alpha_{air}$ ) stoichiometric ratio were maintained at 1.2 and 3, respectively, by controlling the gas flow rate. The fuel cell temperature and relative humidity (RH) of the inlet gas were set to 70 °C and 100%, respectively. During operation, the gas line temperature was kept higher than the humidifier temperature to prevent any condensation prior to entering the fuel cell. Table 5.1 lists the key experimental parameters used in all experimental measurements.

Parameter	Value
Fuel cell temperature	70 °C
Cathode RH	100%
Anode RH	100%
Hydrogen stoichiometry ( $\alpha_{H2}$ )	1.2
Air stoichiometry ( $\alpha_{air}$ )	3
Number of cathode parallel channels	11
Number of cathode serpentine channels	2
Active area	$6.25 \text{ cm}^2$
Membrane	Nafion 212
Electrode	ELE0070
Cathode/anode outlet pressure	1 atm (abs)

Table 5.1 Experimental parameters used for fuel cell operation.

The fuel cell operating pressure was measured at the gas inlet using a differential pressure transducer (PX139-005D4V, Omega, UK). An in-house computer controlled system (LabVIEW, National Instruments) was used to record data using a data acquisition card (USB 6363, National Instruments).



Figure 5.4 Schematic of the experimental setup.

Polarisation curves were obtained by taking data points every 60 s at 0.1 A cm<sup>-2</sup> intervals until either a sudden drop in fuel cell performance occurred or the potential fell below 0.4 V. Pressure drop was recorded during polarisation at a data requisition rate of 5 Hz, and the data were averaged to obtain the mean pressure drop. Transient changes in

cell potential were recorded over a period of 250 s at each current density with a data requisition rate of 1 Hz for each current hold experiment.

#### 5.2.6 Water balance measurements

Changes in the mass of water in the water transport channel were measured at the outlet of the 1/8" PTFE tubing immersed in a 10 ml beaker placed on top of a balance (Figure 5.4). Data were recorded over a period of 250 s at each current density with a data requisition rate of 10 Hz. At the start of each experiment, a syringe pump (10 ml min<sup>-1</sup> flow rate) was used to fill the PTFE tubing and water transport channel with liquid water. Once capillaries were filled, capillary pressure prevented breakthrough of reactant gas into the water transport channel. Any water that penetrated the gas channel was purged by flowing air at a rate of 0.5 l min<sup>-1</sup>. Water was not pumped across the water transport channel at a higher pressure than the water transport channel. The pressure difference between the two channels caused excess liquid water in contact with the capillaries to be wicked and transported to the adjacent water transport channel.

### 5.2.7 Electrochemical impedance spectroscopy (EIS)

EIS was performed using a Gamry Reference 3000 and Gamry Reference 30K Booster (Gamry Instruments, USA). Prior to the impedance measurement, the fuel cell was conditioned at a constant current to reach steady state. Data points were recorded at a frequency range of 5 kHz to 0.1 Hz (10 frequency points/decade) and AC modulation amplitude was kept below 10% of the DC input signal to ensure a linear system response.

### 5.3 Results and discussion

### 5.3.1 Polarisation curves

Polarisation experiments were carried out to evaluate the performance of different cathode flow-fields (Figure 5.5). The conventional parallel flow-field experiences inhibited performance, even at a low current density ( $0.2 \text{ A cm}^{-2}$ ), due to the accumulation of excess liquid water in the electrode and gas channels, as a result of the absence of convective gas flow into the electrode[82, 215] and across the channel.[80, 81] On the contrary, integration of capillaries in parallel flow-fields dramatically enhances fuel cell performance as liquid water is wicked away from the electrode before it emerges into the channel. Thus, stable and flood-free performance is achieved at all operating points. The parallel flow-field modified with capillaries exhibits a peak power density of 0.46 W cm<sup>-2</sup> at 1 A cm<sup>-2</sup>. This represents ~95% and ~7% improvement in peak power density over conventional parallel and serpentine flow-fields obtained at 0.5 A cm<sup>-2</sup> and 1 A cm<sup>-2</sup>, respectively.



Figure 5.5 Polarisation and power density curves obtained for parallel, serpentine, and parallel modified with capillary-containing flow-fields (6.25 cm<sup>2</sup> surface area). Experiments were conducted at cell temperature of 70°C using hydrogen and air at 100% RH and a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.056 l min<sup>-1</sup> and 0.335 l min<sup>-1</sup> at 1 A cm<sup>-2</sup>. The dew point of inlet gases was set to 70°C. No backpressure was applied to the system.

#### 5.3.2 Galvanostatic testing and EIS measurements

The above-mentioned improvement in fuel cell performance by the implementation of capillaries in parallel flow-fields was verified by galvanostatic measurements (Figure 5.6). Stable fuel cell performance is achieved with the serpentine flow-field. This is attributed to the faster gas flow and higher pressure drop, which facilitate convective water removal in the porous media and channel. By comparison, the fuel cell performance of the parallel flow-field is highly unstable, as indicated by erratic potential fluctuations at low current density. Such transient potential yields insight into flooding events.[87, 216] A gradual decline in fuel cell performance, followed by abrupt, temporary recovery alludes to liquid water accumulation in the channel or manifold, which intermittently purges, once it exceeds the critical liquid water content.[217-219]



Figure 5.6 Current hold experiment conducted for different flow-fields (6.25 cm<sup>2</sup> surface area). Experiments were conducted at cell temperature of 70°C using hydrogen and air at 100% RH and a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.056 1 min<sup>-1</sup> and 0.335 1 min<sup>-1</sup> at 1 A cm<sup>-2</sup>. The dew point of inlet gases was set to 70°C. No backpressure was applied to the system.

The introduction of capillaries greatly improves the transient stability of the parallel flow-field based fuel cell. Stable fuel cell performance indicates that flooding in the gas channel is mitigated throughout the investigated operating region, as the liquid water is removed directly from the electrode before the formation of droplets in the channel. This result suggests that water management using capillaries reduces the dependence of the modified flow-field on convective gas flow for liquid water removal. As a result, the parallel flow-field modified with capillaries shows greater improvement in fuel cell performance over a serpentine flow-field at higher current densities, implying enhanced mass transport, despite the lack of convective gas transport within the electrode.

Electrochemical impedance spectroscopy (EIS) was conducted to elucidate this improvement in performance (Figure 5.7). The measured impedance spectra were fitted using the Simplex method in Gamry EChem Analyst, based on the equivalent circuit diagram in Figure 5.8, to deconvolute the extent of the contribution of each phenomenon to the overall fuel cell performance losses.



Figure 5.7 Nyquist plots taken at 0.5 A cm<sup>-2</sup> for different flow-fields (6.25 cm<sup>2</sup> surface area). EIS was not conducted on the parallel flow-field, due to excessive fluctuations in data points, as a result of system instability. Dotted lines are fitted results. Blue, red, yellow, purple, and orange squares correspond to perturbation frequencies of 2000 Hz, 200 Hz, 20 Hz, 2 Hz, and 0.2 Hz, respectively. Experiments were conducted at cell temperature of 70°C using hydrogen and air at 100% RH and a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.028 l min<sup>-1</sup> and 0.167 l min<sup>-1</sup> at 0.5 A cm<sup>-2</sup>. The dew point of inlet gases was set to 70°C. No backpressure was applied to the system.

The values of the charge transfer ( $R_{CT}$ ) and mass transport ( $R_{MT}$ ) resistances for the parallel flow-field modified with capillaries are 0.16  $\Omega$  cm<sup>2</sup> and 0.41  $\Omega$  cm<sup>2</sup>, and for the serpentine flow-field, they are 0.18  $\Omega$  cm<sup>2</sup> and 0.44  $\Omega$  cm<sup>2</sup>, respectively. Thus, the

improvement in reaction rate and mass transport is attributed to better liquid water removal in the porous media facilitated by capillaries. Improved liquid water removal increases catalyst utilisation and enhances the overall reaction rate, as more active sites are made available. Mass transport within the electrode is also improved from reduced diffusional losses, as fewer pores are blocked with liquid water and catalytic sites are more readily available. Although the serpentine geometry is known to achieve superior water removal, local flooding is anticipated in regions around the channel bends,[86, 220] which could have contributed to its higher overall system impedance.



Figure 5.8 Equivalent circuit diagram for impedance analysis.  $R_{\Omega}$  is the Ohmic resistance, *CPE* is the constant phase element,  $Z_w$  is the Warburg element, and  $R_{CT,A}$  and  $R_{CT,C}$  are the anodic and cathodic charge transfer resistance, respectively.

### 5.3.3 High-frequency resistance (HFR)

High-frequency resistance (HFR) measurements were conducted to ensure that membrane hydration and interfacial contact resistance are similar for all flow-fields (Figure 5.9). Maintaining adequate membrane hydration is imperative for proper proton conduction and oxygen mass transport.[221-223] The HFR value is highest at 0.1 A cm<sup>-2</sup>, and it gradually declines as the membrane becomes more hydrated from liquid water generation. The membrane starts to dehydrate slightly at high current densities (> 0.9 A cm<sup>-2</sup>), due to the increased local temperature of the MEA,[85, 224, 225] fostering water evaporation.



Figure 5.9 Change in high-frequency resistance (HFR) with respect to current density for different flow-fields (6.25 cm<sup>2</sup> surface area). Experiments were conducted at cell temperature of 70°C using hydrogen and air at 100% RH and a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.056 1 min<sup>-1</sup> and 0.335 1 min<sup>-1</sup> at 1 A cm<sup>-2</sup>. The dew point of inlet gases was set to 70°C. No backpressure was applied to the system.

A slight discrepancy in HFR values between parallel and serpentine flow-fields may have stemmed from the difference in channel configuration, such as land/channel ratio and channel spacing. The presence of capillaries in the parallel flow-field leads to a small reduction in the contact area between GDL and land, which slightly increases its interfacial contact resistance. However, such marginal difference in the value of HFR is negligible, as it only accounts for a potential drop of 2.7 mV and 1.6 mV at 0.5 A cm<sup>-2</sup> for the serpentine and parallel flow-field modified with capillaries, in comparison to the parallel flow-field.

### 5.3.4 Rate of wicking and evaporation

To investigate the influence of current density on the water balance, the mass change of water in the water transport channel was used as a measure of the rate of wicking or evaporation through the capillaries (Figure 5.10). A positive rate of mass change indicates that there is a net excess of water transported from the electrode to the water

transport channel (wicking), while a negative value indicates a net excess transport of water from the water transport channel to the cathode flow-field (evaporation).

At low current densities ( $\leq 0.5$  A cm<sup>-2</sup>), the generated liquid water is wicked into the water transport channel through capillaries *via* the pressure differential between gas and water transport channels. The rate of wicking increases with current density, due to the larger amount of water generated at the cathode. Although cathode flooding is typically associated with high current density operation, due to increased water production and electro-osmotic drag from the anode,[87] flooding has been shown to occur at a relatively low current density of 0.1 A cm<sup>-2</sup> due to low gas velocity.[197] Unoptimised water management is one of the main causes of irreversible performance degradation and is an issue across the full range of current density. Here, wicking through capillary channels is shown to be an effective means of mitigating flooding at low current density.



Figure 5.10 The rate of change of water mass in water transport channels with respect to current density for a parallel flow-field modified with capillaries (6.25 cm<sup>2</sup> surface area). Experiments were conducted at cell temperature of 70°C using hydrogen and air at 100% RH and a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.056 l min<sup>-1</sup> and 0.335 l min<sup>-1</sup> at 1 A cm<sup>-2</sup>. The dew point of inlet gases was set to 70°C. No backpressure was applied to the system.

The net rate of water transfer in the wicking direction declines with current density at mid-range values ( $0.6 \le j \le 0.8 \text{ A cm}^{-2}$ ). Increased current heats the fuel cell and causes

more water to evaporate from the capillaries. This is not a homogeneous effect and will be most pronounced in regions where local saturation pressure is higher, due to heat generated in the catalyst layer.[85, 225-227] In this operating window, capillaries internally humidify undersaturated gas streams, while removing excess generated water in the electrode. The capillaries remain saturated with liquid water by movement of water from the water transport channel. Since MEA temperature tends to increase towards the gas channel outlet,[227, 228] a gradual transition in water management mechanism from wicking to evaporation is expected along the flow path.[151, 226]

Beyond 0.8 A cm<sup>-2</sup>, evaporation takes over as the dominant form of liquid water transport mechanism for the cell as a whole, due to the rise in cell temperature. This phenomenon agrees with the HFR results, which show membrane dehydration above 0.8 A cm<sup>-2</sup>. Studies report a typical cell temperature rise of 10°C or more at high current densities, which can lead to significant membrane dehydration.[85, 225] A simplified water mass balance calculation in the cathode suggests that a 10°C rise in MEA temperature vastly increases the evaporation rate, satisfying the overall water mass balance without the need for wicking (Figure B.1 in Appendix B). This finding is consistent with neutron imaging work that has shown that at high current densities, flooding is partly mitigated by a temperature increase due to internal heating.[229] These results suggest that such a capillary system could be used to deliver internal gas humidification for fuel cells operating on dry inlet gases. Elimination of the gas humidification system potentially simplifies the overall fuel cell system and is beneficial both in terms of maintenance and operating cost. This will be the subject of future work.

### 5.3.5 Pressure drop

Finally, in terms of pressure drop (Figure 5.11), the unmodified parallel flow-field exhibits the highest value at low current densities (prior to flooding). This observation is in contrast to previous reports displaying significantly higher pressure drop for a serpentine channel than a parallel one, due to faster gas flow and a longer channel path.[80-82] We attribute this anomaly to the constriction and blockage of the gas flow path arising from excess liquid water in the gas channels and bifurcating manifolds.[80]

A similar pressure drop recorded for the parallel and serpentine flow-fields at  $0.1 \text{ A cm}^{-2}$ , where flooding is largely mitigated, suggests that the additional hydraulic resistance stemming from the bifurcating manifolds also significantly adds to the pressure drop over the parallel flow-field.



Figure 5.11 Change in pressure drop across the cathode with respect to current density for different flow-fields (6.25 cm<sup>2</sup> surface area). Experiments were conducted at cell temperature of 70°C using hydrogen and air at 100% RH and a stoichiometric ratio of 1.2 and 3, respectively, which corresponded to flow rates of 0.056 1 min<sup>-1</sup> and 0.335 1 min<sup>-1</sup> at 1 A cm<sup>-2</sup>. The dew point of inlet gases was set to 70°C. No backpressure was applied to the system.

The parallel flow-field modified with capillaries displays the lowest pressure drop, reducing the parasitic energy consumption by air blowers.[90, 91] Hence, the inherent advantage of the parallel flow-field is preserved, owing to the unobtrusive design and superior water management of the capillaries. The ability of the parallel flow-field modified with capillaries to manage liquid water and deliver a low-pressure drop is therefore highly desirable from the perspective of operating cost.

### 5.4 Summary

An approach to achieve efficient water management in PEM fuel cells using capillaries has been presented. The stability and operating range of a parallel flow-field have been shown to markedly improve with this advanced water management mechanism, as channel flooding is mitigated against by direct liquid removal from the channel. This mechanism combines water removal in areas and impeded conditions liable to flooding with a humidification role in regions where the gas stream has a lower water vapour pressure, due to higher temperature or supply of dry gas. Thus, the capillaries allow redistribution of liquid water within the cell by removing or supplying water, depending on the local demand across the MEA. This demonstrates the excellent adaptability of the mechanism to different operation conditions. The parallel flow-field modified with capillaries exhibited ~95% and ~7% improvement in peak power density over the conventional parallel and serpentine flow-fields, respectively.

The proceeding work will focus on testing of flow-fields modified with capillaries under dry operating conditions to validate the gas humidification capacity of the mechanism. This would allow efficient and robust fuel cell operation across a wide range of operating conditions expected to be confronted by a PEM fuel cell during its lifetime. Further work will concentrate on the scalability of these flow fields, making local measurements of current, temperature, and water; optimisation of capillary size, density, and location; and effect of cell orientation and the nature of channel wall materials (hydrophobic/hydrophilic). With respect to scalability, the capillary diameter explored in this study may not be sufficiently small to prevent gas breakthrough into the water transport channel for larger fuel cell systems, as gas pressure significantly increases during scale-up. Fabrication of narrower capillaries is therefore desirable, which will be investigated in the following work, possibly with the use of a more advanced laser system (*e.g.*, femtosecond laser). However, the principles are similar to those discussed here.

### **Chapter 6**

### Research summary and future directions

### 6.1 Research summary

This research introduces a nature-inspired engineering methodology, which is utilised step-by-step to solve the uneven reactant distribution issue in PEMFCs. The fractal geometry of the lung is used as the model to design flow-fields of different branching generations. A theoretical model is developed, and simulations are conducted to determine the number of generations required to achieve uniform reactant distribution and minimal entropy production. The results reveal that the ideal number of generations for minimum entropy production lies between N = 5 and 7. For lower numbers of generations (N = 1 to 4), the spacing between adjacent distributor inlets is large and the flow leaving the final generation is convection driven (Pé > 1), leading to a highly non-uniform gas distribution. At higher generations ( $N \ge 8$ ), the spacing between adjacent inlets becomes very small (~ 100 µm) and the flow leaving the outlets of the final generation is diffusion driven (Pé < 1). Fuel cell performance reaches a plateau at this point, demonstrating that the incorporation of additional branching generations is no longer beneficial.

The effect of the number of generations N on the thickness of the GDL and fuel cell performance is also numerically investigated. Thinner GDL improves fuel cell performance by providing higher concentration of reactant gas to the catalyst layer. However, improvement in cell performance is minimal at lower generations ( $N \le 5$ ), due to diminished transverse reactant transport with thinner GDLs. The model is coupled with an optimised cathode catalyst layer microstructure with respect to platinum utilisation ( $P_U$ ) and power density ( $P_D$ ). The  $P_D$  optimised cathode catalyst layer, despite its lower platinum loading, yields a higher average current density than the base design, because of a microstructure that facilitates diffusion within the catalyst layer. The  $P_U$ optimised cathode CL surpasses the 2020 DoE target for platinum utilisation of ~ 8 kW/g<sub>Pt</sub> at N = 4 generations, and achieves a value of ~ 36 kW/g<sub>Pt</sub> at N = 6. The base and  $P_D$  optimised microstructures demonstrate extremely low platinum utilisation due to substantial oxygen deprivation towards the centre of catalyst agglomerates from surplus platinum loading.

Based on the promising modelling results, three lung-inspired flow-fields with N = 3, 4, and 5 are fabricated using 3D printing *via* direct metal laser sintering (DMLS), and their performance is compared against conventional, serpentine flow-fields. X-ray radiography is used to inspect the flow-field channels for structural defects and blockages caused by various process parameters of laser sintering. The lung-inspired fractal flow-field with N = 4 generations outperforms the serpentine flow-fields at high current densities (at 50% and 75% RH) due to more uniform reactant distribution across the catalyst layer. The performance of N = 5 fractal flow-field significantly deteriorates at 75% RH, due to excessive flooding arising possibly as a result of insufficient convective liquid water removal. The lung-inspired fractal flow-field with N = 3 exhibits the worst performance at 50% RH, due to highly non-uniform gas distribution across the active area.

In order to address the flooding issues of fractal flow-field based PEMFCs at high RH operating conditions, neutron radiography is employed for *in situ* visualisation of liquid water, to identify the shortcomings of the current design pertaining to water management. Fractal flow-field with N = 4 generally exhibits greater overall water content across the active area than the serpentine flow-field, due to significant liquid water accumulating in the interdigitated outlet channels from limited convective liquid removal. The narrow channel dimension of the fractal flow-field is also found to instigate back-flow of liquid water into fractal inlet channels, preferentially clogging channels with improper gas flow

from minor structure defects within the fractal channel network. Inlet channel clogging redistributes the gas within the fractal network, rendering the gas distribution across the electrode highly non-uniform.

The susceptibility to flooding of the fractal flow-fields has prompted the need to engineer a new water management strategy. Current water management strategies for commercial flow-fields cannot be easily integrated with the fractal flow-fields, since they require the installation of a porous carbon plate or implementation of wicking elements on the channel surface to wick out the generated liquid water. Thus, a novel water management strategy that uses capillaries to control liquid water in PEMFCs is developed. The gas channel and water transport channel are hydraulically connected by laser drilling capillaries into the land of a parallel flow-field. By filling the capillaries with liquid water, reactant gas entry into the water transport channel is prevented, while allowing for water transport across the capillaries. The stability and operating range of a parallel flow-field is shown to markedly improve with this advanced water management mechanism, as channel flooding is mitigated against by direct liquid removal from the channel. The net rate of water transfer in the wicking direction varies with respect to current density due to the competing effect of liquid water generation and internal cell heating. At high current densities (>  $0.8 \text{ A cm}^{-2}$ ), evaporation takes over as the dominant form of liquid water transport mechanism for the cell as a whole, due to the rise in cell temperature. EIS reveals an improvement in reaction kinetics and mass transport over the conventional serpentine flow-field, attributed to better liquid water removal in the porous media. The parallel flow-field modified with capillaries exhibits  $\sim 95\%$  and  $\sim 7\%$ improvement in peak power density over the conventional parallel and serpentine flowfields, respectively.

### 6.2 Future directions

- 1. A 3D theoretical model should be developed to fully assess the effect of the fractal flow-field channel geometries on water removal. Despite its high computational demands, such a model will be able to fully simulate flooding at high RH conditions. These modelling results, in combination with experimental neutron radiography measurements, will provide valuable information towards the development of alternative outlet geometries.
- 2. The proceeding work should focus on testing of flow-fields modified with laserdrilled capillaries under dry operating conditions to validate the gas humidification capacity of the mechanism. This would allow efficient and robust fuel cell operation across a wide range of operating conditions expected to be confronted by a PEMFC during its lifetime. Further work should also concentrate on the scalability of these flow fields, making local measurements of current, temperature, and water; optimisation of capillary size, density, and location; and effect of cell orientation and the nature of channel wall materials (hydrophobic/hydrophilic).
- 3. Further work should concentrate on making local measurements of current, temperature, and water of fractal flow-field based PEMFCs. This could be achieved using a PCB based segmented current collector (as currently offered by S++ Simulation Services). Localised current measurements will have to be taken from the anode, since the technique requires the segmentation of flow-field plate or the use of thin flow-field plate to minimise lateral electrical and thermal conduction.
- 4. The susceptibility of fractal flow-fields to flooding remains an obstacle to achieving the full potential of this flow-field design under high RH operating conditions. Effective liquid water removal would not only reduce parasitic loads from pumping, but ensure uniform gas distribution across the active area. Implementation of the water management strategy into fractal flow-fields would

combine the benefits of both, thereby overcoming the challenges specific to the fractal design. Implementation of capillaries into a 0.5 mm thick 3D printed metal plate has been successfully demonstrated as shown in Figure 6.1.



Figure 6.1 "xz" orthoslice from tomogram of the cross-section of a 0.5 mm thick 3D printed stainless steel layer with a capillary array. The small 'globules' at the top and bottom of the layer are the metal particles that has not been fully sintered by the laser. Small irregular pores reveal the internal structure of the printed steel exhibits a slight porosity from incomplete metal sintering.

However, such mechanism requires the integration of water transport channel adjacent to lands and interdigitated outlet channels of the fractal flow-fields with a wall thickness of  $\leq 0.5$  mm. Such intricate design requirement calls for a careful consideration of build orientation, laser parameters, and possible modification to the channel geometry to prevent the wall (between gas and water transport channels) from collapsing during laser sintering.

5. The potential impact of manufacturing tolerance on flow distribution across the 3D inlet network of the fractal flow-fields has to be addressed. The current state-of-the-art metal 3D printers that employ DMLS have a typical minimum accuracy of  $\pm 50 \ \mu\text{m}$ . Despite the seemingly high resolution, given the small dimensions of individual fractal flow-field "inlet" channel of 300  $\mu\text{m}$  x 500  $\mu\text{m}$  or less (for  $N \ge 5$ ), an inconsistency in individual channel dimensions (and hence unequal gas flow rate across individual inlet channel) may arise that could prompt flow maldistribution across the active area. The issue is compounded by

the aforementioned problems arising from the manufacturing process (*e.g.*, partially sintered particles on the surface, thermal deformation during build *etc.*) that can lead to minor structural deformations. One of the ways that could be used to assess the impact of manufacturing tolerance is by cropping a section of the fractal flow-field (using techniques such as electrical discharge machining) and running X-ray tomography on the sample. The numerical model discussed in Chapter 2 can then be used to simulate the flow across the reconstructed sample and a sensitivity analysis can then be conducted to assess whether 3D printing technique is indeed a suitable means of constructing fractal flow-fields.

6. Many of the experimental studies outlined in this thesis compares different flowfields of different designs and active areas. All experiments in this study were conducted using a fresh MEA and same initial conditioning process to ensure (almost) identical starting conditions and each experiment was repeated at least 3 times to ensure the results were statistically relevant. Also, except for the case of fractal flow-field with N = 5 in Chapter 3 and parallel flow-field in Chapter 5 where flooding was prevalent across the channels at 100% RH, repeatable and stable fuel cell performance was attained for all flow-field designs.

Although care was taken to ensure repeatable experimental conditions, experimental error arising from human error which extends from MEA hot pressing to application of torque for cell assembly has not been taken into account in the experimental results. One way in which the experimental error may be minimised is by repeating experiments with a set of at least 3 different MEAs for each flow-field. However, this was not investigated in this study due to time constraint. The potential variability between different MEA/test assemblies also has to be investigated. The future study should therefore focus on repeating experiments using fractal flow-fields across a much broader range of parameters than investigated in this study (e.g., cell compression, different MEA, different cell component design *etc.*).

7. The proposed nature-inspired approach is not limited to PEMFCs, but should lead to performance improvements in other electrochemical systems as well. Redox flow batteries, electrolysers, and different types of fuel cells (alkaline, high temperature, direct methanol, *etc.*) could thus benefit from the proposed nature inspired approach, as flooding is mitigated in these systems. It is strongly encouraged, therefore, that the beneficial effects of achieving uniform gas distribution in these systems through the use of fractal flow-fields be explored for reliable and robust system performance.

## **Appendix A**



Figure A.1 High frequency resistance values for fractal and conventional serpentine flow-field (10  $\text{cm}^2$  surface area) based PEMFCs at (a) 50% RH, (b) 75% RH, and (c) 100% RH.



Figure A.2 Pressure drop in the cathode for fractal and serpentine flow-field ( $25 \text{ cm}^2$  surface area) based PEMFCs at (a) 50% RH, (b) 75% RH, and (c) 100% RH.

## **Appendix B**

Figure B.1 illustrates a break-down of the simplified liquid water mass balance in the cathode for a parallel flow-field modified with capillaries using fully humidified inlet air at 70 °C. The graph outlines the rate of liquid water removed or supplied through capillaries (Figure 5.10), and the theoretical maximum evaporation rate of generated water that can be achieved at elevated MEA temperatures of 75 °C and 80 °C. The assumptions for the simplified water balance calculation are the following:

- Uniform gas and cell temperature profile across the electrode
- Air is immediately heated to the MEA temperature at the inlet
- Fully hydrated polymer electrolyte membrane
- No back-diffusion of liquid water to the anode
- Water is generated in liquid form

The theoretical maximum evaporation rate  $m_{evap}$  (g s<sup>-1</sup>) that can be achieved at a given elevated MEA temperature, T (°C), is given by:

$$m_{evap} = \left( D_{sat,T} - D_{sat,70} \right) \cdot m_{air}$$
(S1)

where  $D_{sat,T}$  (g m<sup>-3</sup>) is the saturated vapour density,  $D_{sat,70}$  (g m<sup>-3</sup>) is the saturated vapour density at 70 °C, and  $m_{air}$  (m<sup>3</sup> s<sup>-1</sup>) is the volumetric air flow rate. Since stoichiometric ratio is maintained during operation,  $m_{air}$  increases linearly with current density. The theoretical total liquid water generation rate  $m_{H2O}$  (g s<sup>-1</sup>) is given by:

$$m_{H_2O} = \frac{I \cdot A \cdot M_{H_2O}}{2F} \tag{S2}$$

where I (A m<sup>-2</sup>) is the current density, A (m<sup>2</sup>) is the active area,  $M_{H2O}$  (g mol<sup>-1</sup>) is the molar mass of water, and F is the Faraday constant.



Fig. B.1 A break-down of the simplified liquid water mass balance in the cathode with respect to current density using fully humidified inlet air at 70 °C. The curve is the measured rate of change in water mass in a water transport channel with respect to current density for a parallel flow-field modified with capillaries, as shown in Figure 5.10. The red and blue lines represent the theoretical maximum evaporation rate of generated water,  $m_{evap}$ , that can be achieved to fully humidify the inlet gas at different MEA temperatures. The black line represents the theoretical total rate of liquid water generation at each current density,  $m_{H2O}$ .

## **Appendix C**

Using the mass conservation equation, the species transport for an individual species, i, is given by:

$$\rho \frac{\partial}{\partial t} (w_i) + \rho \cdot u \cdot \nabla w_i = -\nabla \cdot j_i + R_i$$
(S3)

where  $\rho$  (kg m<sup>-3</sup>) is the mixture density, u (m s<sup>-1</sup>) is the mass averaged velocity of the mixture,  $w_i$  is the mass fraction,  $j_i$  (kg m<sup>-2</sup> s<sup>-1</sup>) is the mass flux relative to the mass averaged velocity, and  $R_i$  (kg m<sup>-3</sup> s<sup>-1</sup>) is the rate expression describing its production or consumption. Assuming steady state condition, the equation can be simplified to

$$\rho \cdot u \cdot \nabla w_i = -\nabla \cdot j_i + R_i \tag{S4}$$

In a multicomponent mixture, the mass flux relative to the mass average velocity,  $j_i$ , can be defined by the generalized Fick equations.[230]

$$j_i = -\rho \cdot w_i \cdot \sum_j \left( D_{ij}^{eff} \cdot d_j \right) - D_j^T \cdot \nabla ln(T)$$
(S5)

where  $D_{ij}^{eff}$  (m<sup>2</sup> s<sup>-1</sup>) is effective binary diffusivity of species *i* in species *j*, *T* (K) is the temperature,  $D_j^T$  (kg m<sup>-1</sup> s<sup>-1</sup>) is the thermal diffusion coefficients, and  $d_j$  (m<sup>-1</sup>) is the diffusional driving force acting on species *i*. Assuming isothermal fuel cell operating condition, the equation can be simplified to

$$j_i = -\rho \cdot w_i \sum_j \left( D_{ij}^{eff} d_j \right) \tag{S6}$$

For ideal gas mixtures the diffusional driving force is[230]

$$d_j = \frac{1}{cRT} \left[ \nabla p_j - w_j \nabla P - \rho_j g_j \right]$$
(S7)

where  $c \pmod{m^{-3}}$  is the total molar concentration, R (J mol<sup>-1</sup> K<sup>-1</sup>) is the universal gas constant, P (Pa) is the total pressure,  $p_j$  (Pa) is the partial pressure, and g (m s<sup>-2</sup>) is an external force such as gravity which is considered negligible in this study. Using the ideal gas law,  $p = c \cdot R \cdot T$ , and the definition of the partial pressures,  $p_j = x_j \cdot p$ , the equation can be written as

$$d_j = \nabla x_j + \frac{1}{P} \left[ \left( x_j - w_j \right) \cdot \nabla P \right]$$
(S8)

Combining equations S4, S6, and S8, the Maxwell-Stefan equation for the transport of the species' mass is given as

$$\nabla \left\{ \frac{-\rho \cdot w_i \cdot \sum_j D_{ij}^{eff} \left[ \nabla x_j + \frac{1}{p} \left[ (x_j - w_j) \cdot \nabla P \right] \right]}{P} \right\} = R_i - \rho \cdot u \cdot \nabla w_i$$
(S9)

# Nomenclature

Α	active area, m <sup>2</sup>
$A_N$	cross-sectional area of a single outlet at the $N^{\text{th}}$ generation, m <sup>2</sup>
$a_r$	effective agglomerate surface area, $m^2 m^{-3}$
$a_{Pt}$	effective catalyst surface area, $\text{cm}^2 \text{g}^{-1}$
С	total gas concentration, mol m <sup>-3</sup>
$C_{f}$	fixed charge site concentration in membrane, mol m <sup>-3</sup>
$C_{H2}^{ref}$	reference concentration of hydrogen, mol m <sup>-3</sup>
$C_{O2}$	concentration of oxygen in catalyst layer, mol m <sup>-3</sup>
$C_{O2}^{ref}$	reference concentration of oxygen, mol m <sup>-3</sup>
$C_{02}^{air}$	concentration of oxygen in inlet air, mol m <sup>-3</sup>
$C_v^g$	concentration of vapour, mol m <sup>-3</sup>
$C_v^{g,air}$	concentration of water vapour in inlet air, mol m <sup>-3</sup>
$C_w^N$	water concentration in membrane, mol m <sup>-3</sup>
D	fractal dimension / diffusivity $(m^2 s^{-1})$
$D_c$	capillary diffusion coefficient, m <sup>2</sup> s <sup>-1</sup>
$D_{ij}$	element of the Maxwell-Stefan diffusion coefficient matrix, m <sup>2</sup> s <sup>-1</sup>
$D_{O2}^N$	oxygen diffusivity in Nafion, m <sup>2</sup> s <sup>-1</sup>
$D_{O2,N}^{eff}$	effective oxygen diffusivity in Nafion, m <sup>2</sup> s <sup>-1</sup>
$D_{O2}^w$	oxygen diffusivity in water, $m^2 s^{-1}$
$D_w^N$	diffusivity of water in Nafion, m <sup>2</sup> s <sup>-1</sup>
F	Faraday's constant, 96500 C mol <sup>-1</sup>
Н	Henry's constant, atm m <sup>3</sup> mol <sup>-1</sup>
$i_N$	electrolyte current density, A m <sup>-2</sup>
$i_d$	current density, A m <sup>-2</sup>
$i_s$	electronic current density, A m <sup>-2</sup>
$i_0$	exchange current density, A m <sup>-2</sup>
$k_c$	condensation rate constant, s <sup>-1</sup>
$k_p$	electrode permeability, m <sup>2</sup>
$k_v$	evaporation rate constant, atm <sup>-1</sup> s <sup>-1</sup>
$k_t$	reaction rate constant, s <sup>-1</sup>
$K_w$	water permeability, m <sup>2</sup>
$K_{w,0}$	water permeability at 100% saturation, m <sup>2</sup>
L	width of fractal outlet at the final generation, m
$m_{pt}$	platinum loading per unit area of catalyst layer, $g_{Pt}$ m <sup>-2</sup>
$M_i$	molecular weight, kg mol
N M <sup>g</sup>	electro-osmotic drag coefficient
Ni	flux of gaseous species i, mol m <sup>2</sup> s <sup>2</sup>

$N_v^{g}$	flux of vapour, mol $m^{-2} s^{-1}$
$N_w$	flux of liquid water, mol $m^{-2} s^{-1}$
$N_w^g$	flux of water vapour, mol $m^{-2} s^{-1}$
$N_w^N$	flux of liquid water in membrane, mol m <sup>-2</sup> s <sup>-1</sup>
Р	total pressure, Pa
$P_c$	capillary pressure, Pa
$P_D$	power density
$P_g$	gas pressure, Pa
$P_i$	partial pressure, Pa
$P_l$	liquid pressure, Pa
$P^{sat}$	saturation pressure, Pa
$P_U$	platinum utilization
Pt C	mass percentage of platinum catalyst on carbon black, kg Pt / (kg C + kg Pt)
$Q_o$	volumetric flow rate of gas at the inlet, m <sup>3</sup> s <sup>-1</sup>
<i>r<sub>agg</sub></i>	agglomerate radius, m
R	ideal gas constant, 8.314 J mol <sup>-1</sup> K <sup>-1</sup>
$R_i$	reaction rate, mol $m^{-3} s^{-1}$
SAnode	anode stoichiometry ratio, 1.2
$S_{Cathode}$	cathode stoichiometry ratio, 3
$S_{phase}$	evaporation/condensation rate, mol m <sup>-3</sup> s <sup>-1</sup>
S	liquid water saturation
S	source term
Т	temperature, K
$t_{CL}$	catalyst layer thickness, m
$t_{GDL}$	gas diffusion layer thickness, m
<i>t<sub>mem</sub></i>	membrane thickness, m
$u_g$	gas phase velocity, m s <sup>-1</sup>
$U_{eq}$	standard equilibrium potential, V
V	voltage, V
$V_A$	operating voltage, V
$W_{c,1}$	initial channel width, m
Wi	mass fraction of species i
$x_i$	mole fraction of species i
$y_v$	mole fraction of liquid water

### <u>Greek</u>

α	charge transfer coefficient
$a_{Pt}^{agg}$	specific catalyst surface area, m <sup>2</sup> m <sup>-3</sup>
$\delta_N$	Nafion film thickness, m
$\delta_W$	water film thickness, m

$\varepsilon_N^{agg}$	agglomerate-ionomer	volume	fraction, m <sup>3</sup>	ionomer m <sup>-3</sup>	agglomerate
1.	66				00

- $\varepsilon^{\nu}$  void phase volume fraction
- $\eta$  overpotential, V
- $\mu$  viscosity, Pa s
- $\xi$  effectiveness factor
- $\rho$  density, kg m<sup>-3</sup>
- $\sigma_m$  ionic conductivity, S m<sup>-1</sup>
- $\sigma_s$  electronic conductivity, S m<sup>-1</sup>
- *τ* tortuosity
- $\phi$  potential, V
- $\varphi$  Thiele modulus
- $\phi_N$  membrane phase potential, V

### **Superscripts and subscripts**

0	intrinsic
a	anode
agg	agglomerate
c	cathode
CL	catalyst layer
eff	effective
eq	equilibrium
g	gas
GDL	gas diffusion layer
$H_2$	hydrogen
i	species i
j	species j
mem	membrane
Ν	Nafion
$N_2$	nitrogen
<b>O</b> <sub>2</sub>	oxygen
Pt	platinum
ref	reference
S	solid phase
v	void phase / vapour
W	liquid water

### **Abbreviation**

ACL	Anode catalyst layer
BC	Boundary condition
CCD	Charge coupled device

CL	Catalyst layer
CCL	Cathode catalyst layer
CPE	Constant phase element
DMLS	Direct metal laser sintering
DoE	Department of Energy
EIS	Electrochemical impedance spectroscopy
GDL	Gas diffusion layer
HFR	High frequency resistance
HOR	Hydrogen oxidation reaction
MEA	Membrane electrode assembly
MEM	Membrane
MFC	Mass flow controller
MPL	Micro-porous layer
ORR	Oxygen reduction reaction
PEMFC	Polymer electrode membrane fuel cell
RC	Randles circuit
RH	Relative humidity
SEM	Scanning electron microscopy
PCB	Printed circuit board
PFSA	Perfluorosulfonic acid
PTFE	Polytetrafluorethylene

### References

[1] J. Larminie, Fuel Cell Systems Explained, 2nd ed., Wiley & Sons, Chichester, West Sussex, 2003.

[2] R.T. White, F.P. Orfino, M.E. Hannach, O. Luo, M. Dutta, A.P. Young, E. Kjeang, Journal of The Electrochemical Society, 163 (2016) F1337-F1343.

[3] S. Ge, C.-Y. Wang, Journal of The Electrochemical Society, 154 (2007) B998-B1005.

[4] Z. Tayarani-Yoosefabadi, D. Harvey, J. Bellerive, E. Kjeang, Journal of Power Sources, 303 (2016) 208-221.

[5] A. Taniguchi, T. Akita, K. Yasuda, Y. Miyazaki, Journal of Power Sources, 130 (2004) 42-49.

[6] P. Trogadas, T.F. Fuller, P. Strasser, Carbon, 75 (2014) 5-42.

[7] V.O. Mittal, H.R. Kunz, J.M. Fenton, Journal of The Electrochemical Society, 154 (2007) B652-B656.

[8] P. Trogadas, J. Parrondo, V. Ramani, Chemical Communications, 47 (2011) 11549-11551.

[9] T. Okada, Y. Ayato, H. Satou, M. Yuasa, I. Sekine, The Journal of Physical Chemistry B, 105 (2001) 6980-6986.

[10] S. Shimpalee, S. Greenway, J.W. Van Zee, Journal of Power Sources, 160 (2006) 398-406.

[11] A.P. Manso, F.F. Marzo, J. Barranco, X. Garikano, M. Garmendia Mujika, International Journal of Hydrogen Energy, 37 (2012) 15256-15287.

[12] P. Wawdee, S. Limtrakul, T. Vatanatham, M.W. Fowler, International Journal of Hydrogen Energy, 40 (2015) 3739-3748.

[13] D.H. Ahmed, H.J. Sung, Journal of Power Sources, 162 (2006) 327-339.

[14] S.-W. Cha, R. O'Hayre, S.J. Lee, Y. Saito, F.B. Prinz, Journal of The Electrochemical Society, 151 (2004) A1856-A1864.

[15] N. Guo, M.C. Leu, U.O. Koylu, International Journal of Hydrogen Energy, 39 (2014) 21185-21195.

[16] J.P. Kloess, X. Wang, J. Liu, Z. Shi, L. Guessous, Journal of Power Sources, 188 (2009) 132-140.

[17] R. Roshandel, F. Arbabi, G.K. Moghaddam, Renewable Energy, 41 (2012) 86-95.

[18] B. Ramos-Alvarado, A. Hernandez-Guerrero, F. Elizalde-Blancas, M.W. Ellis, International Journal of Hydrogen Energy, 36 (2011) 12965-12976.

[19] K. Tüber, A. Oedegaard, M. Hermann, C. Hebling, Journal of Power Sources, 131 (2004) 175-181.

[20] S. Shimpalee, J.W. Van Zee, International Journal of Hydrogen Energy, 32 (2007) 842-856.

[21] P. Trogadas, J.I.S. Cho, T.P. Neville, J. Marquis, B. Wu, D.J.L. Brett, M.O. Coppens, Energy & Environmental Science, 11 (2018) 136-143.

[22] P. Trogadas, M.M. Nigra, M.-O. Coppens, New Journal of Chemistry, 40 (2016) 4016-4026.

[23] M.M. Lynch, J. Liu, M. Nigra, M.-O. Coppens, Langmuir, 32 (2016) 9604-9610.

[24] M.-O. Coppens, Current Opinion in Chemical Engineering, 1 (2012) 281-289.

[25] M. Ji, Z. Wei, Energies, 2 (2009) 1057.

[26] J. Wang, Applied Energy, 157 (2015) 640-663.

[27] C.D. Murray, Proceedings of the National Academy of Sciences of the United States of America, 12 (1926) 207-214.

[28] S. Gheorghiu, S. Kjelstrup, P. Pfeifer, M.-O. Coppens, Is the Lung an Optimal Gas Exchanger?, in: G.A. Losa, D. Merlini, T.F. Nonnenmacher, E.R. Weibel (Eds.) Fractals in Biology and Medicine, Birkhäuser Basel, Basel, 2005, pp. 31-42.

[29] B. Mauroy, M. Filoche, E.R. Weibel, B. Sapoval, Nature, 427 (2004) 633-636.

[30] B. Sapoval, M. Filoche, E.R. Weibel, Proceedings of the National Academy of Sciences, 99 (2002) 10411-10416.

[31] S. Kjelstrup, M.-O. Coppens, J.G. Pharoah, P. Pfeifer, Energy & Fuels, 24 (2010) 5097-5108.

[32] P. Trogadas, V. Ramani, P. Strasser, T.F. Fuller, M.-O. Coppens, Angewandte Chemie International Edition, 55 (2016) 122-148.

[33] C. Hou, S. Gheorghiu, M.-O. Coppens, V.H. Huxley, P. Pfeifer, Gas Diffusion through the Fractal Landscape of the Lung: How Deep Does Oxygen Enter the Alveolar System?, in: G.A. Losa, D. Merlini, T.F. Nonnenmacher, E.R. Weibel (Eds.) Fractals in Biology and Medicine, Birkhäuser Basel, Basel, 2005, pp. 17-30.

[34] R. O'Hayre, S.-W. Cha, W. Colella, F. B. Prinz, Fuel Cell Fundamentals, 2nd ed., John Wiley & Sons, Hoboken, NJ, 2009.

[35] F. Barbir, PEM fuel cells: theory and practice, 2nd ed., Academic Press, Amsterdam, 2013.

[36] T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, Journal of The Electrochemical Society, 138 (1991) 2334-2342.

[37] U. Beuscher, S. J. C. Cleghorn, W. B. Johnson, International Journal of Energy Research, 29 (2005) 1103–1112.

[38] A. Kraytsberg, Y. Ein-Eli, Energy & Fuels, 28 (2014) 7303-7330.

[39] J. Jalili, M.B. Coltelli, V. Tricoli, G. Orsini, The Journal of Physical Chemistry C, 121 (2017) 17129-17136.

[40] C. Sun, L. Chen, S. Shi, B. Reeb, C.A. López, J.A. Alonso, U. Stimming, Inorganic Chemistry, 57 (2018) 676-680.

[41] J.H. Nam, K.-J. Lee, G.-S. Hwang, C.-J. Kim, M. Kaviany, International Journal of Heat and Mass Transfer, 52 (2009) 2779-2791.

[42] J.T. Gostick, M.A. Ioannidis, M.W. Fowler, M.D. Pritzker, Electrochemistry Communications, 11 (2009) 576-579.

[43] L. Cindrella, A.M. Kannan, J.F. Lin, K. Saminathan, Y. Ho, C.W. Lin, J. Wertz, Journal of Power Sources, 194 (2009) 146-160.

[44] S. Park, J.-W. Lee, B.N. Popov, International Journal of Hydrogen Energy, 37 (2012) 5850-5865.

[45] J. Lee, S. Chevalier, R. Banerjee, P. Antonacci, N. Ge, R. Yip, T. Kotaka, Y. Tabuchi, A. Bazylak, Electrochimica Acta, 236 (2017) 161-170.

[46] C.-H. Cheng, H.-H. Lin, G.-J. Lai, Journal of Power Sources, 165 (2007) 803-813.

[47] L. Xing, Q. Cai, X. Liu, C. Liu, K. Scott, Y. Yan, Chemical Engineering Science, 146 (2016) 88-103.

[48] S. Ye, M. Hall, P. He, ECS Transactions, 16 (2008) 2101-2113.

[49] Q. Meyer, N. Mansor, F. Iacoviello, P.L. Cullen, R. Jervis, D. Finegan, C. Tan, J. Bailey, P.R. Shearing, D.J.L. Brett, Electrochimica Acta, 242 (2017) 125-136.

[50] U. Pasaogullari, C.-Y. Wang, Electrochimica Acta, 49 (2004) 4359-4369.

[51] D. Harvey, J.G. Pharoah, K. Karan, Journal of Power Sources, 179 (2008) 209-219.

[52] T. Berning, D.M. Lu, N. Djilali, Journal of Power Sources, 106 (2002) 284-294.

[53] S.-H. Han, N.-H. Choi, Y.-D. Choi, International Journal of Hydrogen Energy, 39 (2014) 2628-2638.

[54] N. Limjeerajarus, P. Charoen-amornkitt, International Journal of Hydrogen Energy, 40 (2015) 7144-7158.

[55] Y. Zhang, A. Verma, R. Pitchumani, International Journal of Hydrogen Energy, 41 (2016) 8412-8426.

[56] W. Sun, B.A. Peppley, K. Karan, Electrochimica acta, 50 (2005) 3359-3374.

[57] D. Song, Q. Wang, Z. Liu, T. Navessin, S. Holdcroft, Electrochimica Acta, 50 (2004) 731-737.

[58] K.-M. Yin, B.-S. Cheng, K.-W. Chiang, Renewable Energy, 95 (2016) 191-201.

[59] A. Jo, G. Gwak, M. Moazzam, J. Lee, H. Ju, International Journal of Hydrogen Energy, 42 (2017) 3731-3747.

[60] R.M. Rao, D. Bhattacharyya, R. Rengaswamy, S.R. Choudhury, Journal of Power Sources, 173 (2007) 375-393.

[61] L. Fan, G. Zhang, K. Jiao, Energy Conversion and Management, 150 (2017) 763-774.

[62] S. Li, J. Yuan, M. Andersson, G. Xie, B. Sunden, International Journal of Energy Research, 41 (2017) 2034-2050.

[63] R. Madhusudana Rao, R. Rengaswamy, Journal of Power Sources, 158 (2006) 110-123.

[64] M. Secanell, K. Karan, A. Suleman, N. Djilali, Electrochimica Acta, 52 (2007) 6318-6337.

[65] M. Moein-Jahromi, M.J. Kermani, International Journal of Hydrogen Energy, 37 (2012) 17954-17966.

[66] N. Khajeh-Hosseini-Dalasm, M.J. Kermani, D.G. Moghaddam, J.M. Stockie, International Journal of Hydrogen Energy, 35 (2010) 2417-2427.

[67] M. Secanell, R. Songprakorp, N. Djilali, A. Suleman, Structural and Multidisciplinary Optimization, 40 (2009) 563.

[68] U. Pasaogullari, C.-Y. Wang, K.S. Chen, Journal of The Electrochemical Society, 152 (2005) A1574-A1582.

[69] H. Meng, C.-Y. Wang, Journal of The Electrochemical Society, 152 (2005) A1733-A1741.

[70] T. Berning, N. Djilali, Journal of The Electrochemical Society, 150 (2003) A1589-A1598.

[71] J.H. Nam, M. Kaviany, International Journal of Heat and Mass Transfer, 46 (2003) 4595-4611.

[72] Y. Wang, C.-Y. Wang, Journal of The Electrochemical Society, 153 (2006) A1193-A1200.

[73] H. Ju, G. Luo, C.-Y. Wang, Journal of The Electrochemical Society, 154 (2007) B218-B228.

[74] T.V. Nguyen, G. Lin, H. Ohn, D. Hussey, D. Jacobson, M. Arif, ECS Transactions, 3 (2006) 415-423.

[75] H. Ohn, T.V. Nguyen, D. Jacobson, D. Hussey, M. Arid, ECS Transactions, 1 (2006) 481-489.
[76] T.V. Nguyen, G. Lin, H. Ohn, X. Wang, Electrochemical and Solid-State Letters, 11 (2008) B127-B131.

[77] X. Wang, T. Van Nguyen, Journal of the Electrochemical Society, 155 (2008) B1085-B1092.

[78] J. Marquis, M.-O. Coppens, Chemical Engineering Science, 102 (2013) 151-162.

[79] X. Li, I. Sabir, International Journal of Hydrogen Energy, 30 (2005) 359-371.

[80] S.-S. Hsieh, B.-S. Her, Y.-J. Huang, Energy Conversion and Management, 52 (2011) 975-982.

[81] S.-S. Hsieh, Y.-J. Huang, B.-S. Her, International Journal of Heat and Mass Transfer, 52 (2009) 5657-5659.

[82] D. Spernjak, A.K. Prasad, S.G. Advani, Journal of Power Sources, 195 (2010) 3553-3568.

[83] J. Bachman, M. Charvet, A. Santamaria, H.-Y. Tang, J.W. Park, R. Walker, International Journal of Hydrogen Energy, 37 (2012) 17172-17179.

[84] S. Haase, M. Moser, J.A. Hirschfeld, K. Jozwiak, Journal of Power Sources, 301 (2016) 251-260.

[85] Q. Meyer, K. Ronaszegi, G. Pei-June, O. Curnick, S. Ashton, T. Reisch, P. Adcock, P.R. Shearing, D.J.L. Brett, Journal of Power Sources, 291 (2015) 261-269.

[86] J. Park, X. Li, Journal of Power Sources, 163 (2007) 853-863.

[87] H. Li, Y. Tang, Z. Wang, Z. Shi, S. Wu, D. Song, J. Zhang, K. Fatih, J. Zhang, H. Wang, Z. Liu, R. Abouatallah, A. Mazza, Journal of Power Sources, 178 (2008) 103-117.
[88] W. He, J. Yi, T. Nguyen, Materials, Interfaces, and Electrochemical Phenomena 46 (2000) 2053-2064.

[89] L. Wang, H. Liu, Journal of Power Sources, 134 (2004) 185-196.

[90] D. Xue, Z. Dong, Journal of Power Sources, 76 (1998) 69-80.

[91] R.S. Gemmen, C.D. Johnson, Journal of Power Sources, 159 (2006) 646-655.

[92] N. Fouquet, C. Doulet, C. Nouillant, G. Dauphin-Tanguy, B. Ould-Bouamama, Journal of Power Sources, 159 (2006) 905-913.

[93] F.Y. Zhang, X.G. Yang, C.Y. Wang, Journal of The Electrochemical Society, 153 (2006) A225-A232.

[94] D. Lorenzini-Gutierrez, S.G. Kandlikar, A. Hernandez-Guerrero, F. Elizalde-Blancas, Journal of Power Sources, 279 (2015) 567-580.

[95] P. Concus, R. Finn, Proceedings of the National Academy of Sciences, 63 (1969) 292-299.

[96] E. Kimball, T. Whitaker, Y. Kevrekidis, J. Benziger, Reactors, Kinetics, and Catalysis 54 (2008) 1313-1332.

[97] E. E. Kimball, J. Benziger, Y. Kevrekidis, Fuel Cells, 10 (2010) 530-544.

[98] Z. Lu, C. Rath, G. Zhang, S.G. Kandlikar, International Journal of Hydrogen Energy, 36 (2011) 9864-9875.

[99] R.M. Aslam, D.B. Ingham, M.S. Ismail, K.J. Hughes, L. Ma, M. Pourkashanian, Journal of the Energy Institute, (2017).

[100] K. Inman, X. Wang, International Journal of Hydrogen Energy, 39 (2014) 19691-19700.

[101] A. Bozorgnezhad, M. Shams, H. Kanani, M. Hasheminasab, G. Ahmadi, International Journal of Hydrogen Energy, 41 (2016) 19164-19181.

[102] S.S. Alrwashdeh, I. Manke, H. Markötter, M. Klages, M. Göbel, J. Haußmann, J. Scholta, J. Banhart, ACS Nano, 11 (2017) 5944-5949.

[103] J. Eller, T. Rosén, F. Marone, M. Stampanoni, A. Wokaun, F.N. Büchi, Journal of The Electrochemical Society, 158 (2011) B963-B970.

[104] J. Hinebaugh, J. Lee, C. Mascarenhas, A. Bazylak, Electrochimica Acta, 184 (2015) 417-426.

[105] S. Chevalier, N. Ge, J. Lee, M.G. George, H. Liu, P. Shrestha, D. Muirhead, N. Lavielle, B.D. Hatton, A. Bazylak, Journal of Power Sources, 352 (2017) 281-290.

[106] Q. Meyer, S. Ashton, P. Boillat, M. Cochet, E. Engebretsen, D.P. Finegan, X. Lu, J.J. Bailey, N. Mansor, R. Abdulaziz, O.O. Taiwo, R. Jervis, S. Torija, P. Benson, S. Foster, P. Adcock, P.R. Shearing, D.J.L. Brett, Electrochimica Acta, 211 (2016) 478-487.
[107] Q. Meyer, S. Ashton, S. Torija, C. Gurney, P. Boillat, M. Cochet, E. Engebretsen, D.P. Finegan, P. Adcock, P.R. Shearing, D.J.L. Brett, Electrochimica Acta, 203 (2016) 198-205.

[108] H. Murakawa, K. Sugimoto, N. Kitamura, M. Sawada, H. Asano, N. Takenaka, Y. Saito, Physics Procedia, 69 (2015) 607-611.

[109] A. Bazylak, International Journal of Hydrogen Energy, 34 (2009) 3845-3857.

[110] K. Tüber, D. Pócza, C. Hebling, Journal of Power Sources, 124 (2003) 403-414.

[111] X.G. Yang, F.Y. Zhang, A.L. Lubawy, C.Y. Wang, Electrochemical and Solid-State Letters, 7 (2004) A408-A411.

[112] A. Theodorakakos, T. Ous, M. Gavaises, J.M. Nouri, N. Nikolopoulos, H. Yanagihara, Journal of Colloid and Interface Science, 300 (2006) 673-687.

[113] D. Spernjak, S.G. Advani, A.K. Prasad, Journal of The Electrochemical Society, 156 (2009) B109-B117.

[114] D. Spernjak, A.K. Prasad, S.G. Advani, Journal of Power Sources, 170 (2007) 334-344.

[115] P. Krüger, H. Markötter, J. Haußmann, M. Klages, T. Arlt, J. Banhart, C. Hartnig, I. Manke, J. Scholta, Journal of Power Sources, 196 (2011) 5250-5255.

[116] A.D. Shum, D.Y. Parkinson, X. Xiao, A.Z. Weber, O.S. Burheim, I.V. Zenyuk, Electrochimica Acta, 256 (2017) 279-290.

[117] M. Hickner, D. Hussey, Neutron Radioscopy: Industrial and Scientific Applications, 2010.

[118] T. Sasabe, S. Tsushima, S. Hirai, K. Minami, K. Yada, ECS Transactions, 25 (2009) 513-521.

[119] T. Sasabe, S. Tsushima, S. Hirai, International Journal of Hydrogen Energy, 35 (2010) 11119-11128.

[120] J. Eller, J. Roth, F. Marone, M. Stampanoni, A. Wokaun, F.N. Büchi, Journal of Power Sources, 245 (2014) 796-800.

[121] A. Iranzo, P. Boillat, P. Oberholzer, J. Guerra, Energy, 68 (2014) 971-981.

[122] P. Oberholzer, P. Boillat, R. Siegrist, R. Perego, A. Kästner, E. Lehmann, G.G. Scherer, A. Wokaun, Journal of The Electrochemical Society, 159 (2011) B235-B245.

[123] J.M. LaManna, S. Chakraborty, J.J. Gagliardo, M.M. Mench, International Journal of Hydrogen Energy, 39 (2014) 3387-3396.

[124] R. Mukundan, R.L. Borup, Fuel Cells, 9 (2009) 499-505.

[125] Q. Meyer, S. Ashton, R. Jervis, D.P. Finegan, P. Boillat, M. Cochet, O. Curnick, T. Reisch, P. Adcock, P.R. Shearing, D.J.L. Brett, Electrochimica Acta, 180 (2015) 307-315.

[126] P. Boillat, P. Oberholzer, A. Kaestner, R. Siegrist, E.H. Lehmann, G.G. Scherer, A. Wokaun, Journal of The Electrochemical Society, 159 (2012) F210-F218.

[127] H. Murakawa, K. Sugimoto, K. Miyata, H. Asano, N. Takenaka, Y. Saito, Physics Procedia, 43 (2013) 277-281.

[128] B.R. Matos, E.I. Santiago, F.C. Fonseca, Materials for Renewable and Sustainable Energy, 4 (2015) 16.

[129] T.A. Zawodzinski, C. Derouin, S. Radzinski, R.J. Sherman, V.T. Smith, T.E. Springer, S. Gottesfeld, Journal of The Electrochemical Society, 140 (1993) 1041-1047.

[130] V.A. Sethuraman, J.W. Weidner, A.T. Haug, L.V. Protsailo, Journal of The Electrochemical Society, 155 (2008) B119-B124.

[131] L. Karpenko-Jereb, C. Sternig, C. Fink, R. Tatschl, International Journal of Hydrogen Energy, 41 (2016) 13644-13656.

[132] X. Liu, H. Guo, F. Ye, C.F. Ma, Electrochimica Acta, 52 (2007) 3607-3614.

[133] Y. Wu, J.I.S. Cho, T.P. Neville, Q. Meyer, R. Zeische, P. Boillat, M. Cochet, P.R. Shearing, D.J.L. Brett, Journal of Power Sources, 399 (2018) 254-263.

[134] S.G. Kandlikar, Z. Lu, W.E. Domigan, A.D. White, M.W. Benedict, International Journal of Heat and Mass Transfer, 52 (2009) 1741-1752.

[135] L. Zhang, H.T. Bi, D.P. Wilkinson, J. Stumper, H. Wang, Journal of Power Sources, 195 (2010) 3231-3239.

[136] F. Barbir, H. Gorgun, X. Wang, Journal of Power Sources, 141 (2005) 96-101.

[137] W. Schmittinger, A. Vahidi, Journal of Power Sources, 180 (2008) 1-14.

[138] J.P. Meyers, R.M. Darling, Journal of The Electrochemical Society, 153 (2006) A1432-A1442.

[139] R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J.E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K.-i. Kimijima, N. Iwashita, Chemical Reviews, 107 (2007) 3904-3951.

[140] D.L. Wood, J.S. Yi, T.V. Nguyen, Electrochimica Acta, 43 (1998) 3795-3809.

[141] J.P. Owejan, T.A. Trabold, D.L. Jacobson, D.R. Baker, D.S. Hussey, M. Arif, International Journal of Heat and Mass Transfer, 49 (2006) 4721-4731.

[142] N. Konno, S. Mizuno, H. Nakaji, Y. Ishikawa, SAE International Journal of Alternative Powertrains, 4 (2015) 123-129.

[143] Y. Nonobe, IEEJ Transactions on Electrical and Electronic Engineering, 12 (2017) 5-9.

[144] T. Yoshida, K. Kojima, The Electrochemical Society Interface, 24 (2015) 45-49.

[145] T. Metz, N. Paust, C. Müller, R. Zengerle, P. Koltay, Sensors and Actuators A: Physical, 143 (2008) 49-57.

[146] R. Koresawa, Y. Utaka, International Journal of Hydrogen Energy, 40 (2015) 8172-8181.

[147] S.-H. Ge, X.-G. Li, I.-M. Hsing, Journal of The Electrochemical Society, 151 (2004) B523-B528.

[148] S. Ge, X. Li, I.M. Hsing, Electrochimica Acta, 50 (2005) 1909-1916.

[149] D.G. Strickland, J.G. Santiago, Meeting Abstracts, MA2009-02 (2009) 819.

[150] D.G. Strickland, J.G. Santiago, Journal of Power Sources, 195 (2010) 1667-1675.

[151] J.S. Yi, J.D. Yang, C. King, AIChE Journal, 50 (2004) 2594-2603.

[152] Z. Wang, Y. Zeng, S. Sun, Z. Shao, B. Yi, International Journal of Hydrogen Energy, 42 (2017) 21922-21929.

[153] A.Z. Weber, R.M. Darling, Journal of Power Sources, 168 (2007) 191-199.

[154] S. Litster, C.R. Buie, T. Fabian, J.K. Eaton, J.G. Santiago, Journal of The Electrochemical Society, 154 (2007) B1049-B1058.

[155] T. Fabian, R. O'Hayre, S. Litster, F.B. Prinz, J.G. Santiago, Journal of Power Sources, 195 (2010) 3640-3644.

[156] X. Wang, T.V. Nguyen, Journal of The Electrochemical Society, 155 (2008) B1085-B1092.

[157] S. Kjelstrup, M.-O. Coppens, J. Pharoah, P. Pfeifer, Energy & Fuels, 24 (2010) 5097-5108.

[158] B.B. Mandelbrot, The Fractal Geometry of Nature, Macmillan, 1983.

[159] C.D. Murray, Proceedings of the National Academy of Sciences of the United States of America, 12 (1926) 207.

[160] B. Mauroy, M. Filoche, E.R. Weibel, B. Sapoval, Nature, 427 (2004) 633.

[161] Q. Ye, T. Van Nguyen, Journal of the Electrochemical Society, 154 (2007) B1242-B1251.

[162] D. Natarajan, T. Van Nguyen, Journal of Power Sources, 115 (2003) 66-80.

[163] J.M. Smith, H.C. Van Ness, M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, 2005.

[164] A.Z. Weber, J. Newman, Journal of the Electrochemical Society, 154 (2007) B405-B412.

[165] B. Zhou, W. Huang, Y. Zong, A. Sobiesiak, Journal of Power Sources, 155 (2006) 190-202.

[166] A.Z. Weber, R.M. Darling, J. Newman, Journal of the Electrochemical Society, 151 (2004) A1715-A1727.

[167] S. Qu, X. Li, M. Hou, Z. Shao, B. Yi, Journal of Power Sources, 185 (2008) 302-310.

[168] D.M. Bernardi, M.W. Verbrugge, Journal of the Electrochemical Society, 139 (1992) 2477-2491.

[169] U. Pasaogullari, C.-Y. Wang, Journal of The Electrochemical Society, 152 (2005) A380-A390.

[170] C. Marr, X. Li, Journal of Power Sources, 77 (1999) 17-27.

[171] Y. Wang, X. Feng, Journal of The Electrochemical Society, 155 (2008) B1289-B1295.

[172] R. Sander, Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry, in, Max-Planck Institute of Chemistry, Air Chemistry Department Mainz, Germany, 1999.

[173] T. Berning, M. Odgaard, S.K. Kær, Journal of Power Sources, 196 (2011) 6305-6317.

[174] E.L. Cussler, Diffusion: Mass Transfer in Fluid Systems, 3rd ed., Cambridge University Press, 2009.

[175] D. Bevers, M. WO, K. Yasuda, K. Oguro, Journal of Applied Electrochemistry, 27 (1997) 1254-1264.

[176] J. Marquis, Nature-inspired hierarchically structured high-efficiency PEM fuel cell, in: Chemical & Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY,, , 2013, pp. 202.

[177] J.-H. Jang, W.-M. Yan, C.-C. Shih, Journal of Power Sources, 156 (2006) 244-252. [178] W. Sun, B.A. Peppley, K. Karan, Journal of Power Sources, 144 (2005) 42-53.

[179] M.-S. Chiang, H.-S. Chu, Journal of Power Sources, 160 (2006) 340-352.

[180] K.T. Jeng, S.F. Lee, G.F. Tsai, C.H. Wang, Journal of Power Sources, 138 (2004) 41-50.

[181] J.-H. Jang, W.-M. Yan, C.-C. Shih, Journal of Power Sources, 161 (2006) 323-332.
[182] in: The US Department of Energy (DOE), Energy Efficiency and Renewable Energy. <u>http://energy.gov/sites/prod/files/2016/10/f33/fcto\_myrdd\_fuel\_cells.pdf</u>, 2016.

[183] J.C. Ruiz-Morales, A. Tarancon, J. Canales-Vazquez, J. Mendez-Ramos, L. Hernandez-Afonso, P. Acosta-Mora, J.R. Marin Rueda, R. Fernandez-Gonzalez, Energy & Environmental Science, 10 (2017) 846-859.

[184] R.L. Truby, J.A. Lewis, Nature, 540 (2016) 371.

[185] S. Seyed Farid Seyed, G. Samira, M. Mehdi, Y. Hooman, M. Hendrik Simon Cornelis, K. Nahrizul Adib, O. Noor Azuan Abu, Science and Technology of Advanced Materials, 16 (2015) 033502.

[186] J.R. Atkins, S.C. Savett, S.E. Creager, Journal of Power Sources, 128 (2004) 201-207.

[187] T.F. Fuller, J. Newman, Journal of The Electrochemical Society, 139 (1992) 1332-1337.

[188] I.S. Hussaini, C.-Y. Wang, Journal of Power Sources, 187 (2009) 444-451.

[189] J. Chen, J.B. Siegel, T. Matsuura, A.G. Stefanopoulou, Journal of The Electrochemical Society, 158 (2011) B1164-B1174.

[190] H. Kahraman, M.F. Orhan, Energy Conversion and Management, 133 (2017) 363-384.

[191] D.-H. Chang, S.-Y. Wu, International Journal of Hydrogen Energy, 40 (2015) 11659-11667.

[192] M. Mortazavi, K. Tajiri, Renewable and Sustainable Energy Reviews, 45 (2015) 296-317.

[193] M.-O. Coppens, Industrial & engineering chemistry research, 44 (2005) 5011-5019.

[194] A.B. LaConti, M. Hamdan, R.C. McDonald, Mechanisms of Membrane Degradation, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.) Handbook of Fuel Cells: Fundamentals, Technology, and Applications, vol. 3, John Wiley & Sons, New York, 2003, pp. 647–662.

[195] E.H. Lehmann, P. Vontobel, L. Wiezel, Nondestructive Testing and Evaluation, 16 (2001) 191-202.

[196] A. Iranzo, P. Boillat, International Journal of Hydrogen Energy, 39 (2014) 17240-17245.

[197] T.A. Trabold, J.P. Owejan, D.L. Jacobson, M. Arif, P.R. Huffman, International Journal of Heat and Mass Transfer, 49 (2006) 4712-4720.

[198] K. Jiao, B. Zhou, P. Quan, Journal of Power Sources, 157 (2006) 226-243.

[199] S. Litster, D. Sinton, N. Djilali, Journal of Power Sources, 154 (2006) 95-105.

[200] C. Quesnel, R. Cao, J. Lehr, A.-M. Kietzig, A.Z. Weber, J.T. Gostick, The Journal of Physical Chemistry C, 119 (2015) 22934-22944.

[201] M.J. Cheah, I.G. Kevrekidis, J.B. Benziger, Langmuir, 29 (2013) 9918-9934.

[202] M.A. Hickner, N.P. Siegel, K.S. Chen, D.S. Hussey, D.L. Jacobson, Journal of The Electrochemical Society, 157 (2010) B32-B38.

[203] J.H. Jo, W.T. Kim, International Journal of Hydrogen Energy, 40 (2015) 8368-8383.

[204] R.B. Ferreira, D.S. Falcão, V.B. Oliveira, A.M.F.R. Pinto, Applied Energy, 203 (2017) 474-495.

[205] P.V. Suresh, S. Jayanti, A.P. Deshpande, P. Haridoss, International Journal of Hydrogen Energy, 36 (2011) 6067-6072.

[206] D.J.L. Brett, N.P. Brandon, Journal of Fuel Cell Science and Technology, 4 (2006) 29-44.

[207] S.-P. Jung, C.-I. Lee, C.-C. Chen, W.-S. Chang, C.-C. Yang, Journal of Power Sources, 283 (2015) 429-442.

[208] Q. Meyer, K. Ronaszegi, J.B. Robinson, M. Noorkami, O. Curnick, S. Ashton, A. Danelyan, T. Reisch, P. Adcock, R. Kraume, P.R. Shearing, D.J.L. Brett, Journal of Power Sources, 297 (2015) 315-322.

[209] Q. Meyer, A. Himeur, S. Ashton, O. Curnick, R. Clague, T. Reisch, P. Adcock, P.R. Shearing, D.J.L. Brett, International Journal of Hydrogen Energy, 40 (2015) 16760-16766.

[210] D.J.L. Brett, S. Atkins, N.P. Brandon, V. Vesovic, N. Vasileiadis, A.R. Kucernak, Electrochemistry Communications, 3 (2001) 628-632.

[211] M.R.H. Knowles, G. Rutterford, D. Karnakis, A. Ferguson, The International Journal of Advanced Manufacturing Technology, 33 (2007) 95-102.

[212] A. Gruner, J. Schille, U. Loeschner, Physics Procedia, 83 (2016) 157-166.

[213] M. Ghoreishi, D.K.Y. Low, L. Li, International Journal of Machine Tools and Manufacture, 42 (2002) 985-995.

[214] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, E. Rolley, Reviews of Modern Physics, 81 (2009) 739-805.

[215] J. Bachman, A. Santamaria, H.-Y. Tang, J.W. Park, Journal of Power Sources, 198 (2012) 143-148.

[216] N.S. Siefert, S. Litster, Journal of Power Sources, 196 (2011) 1948-1954.

[217] P. Deevanhxay, T. Sasabe, S. Tsushima, S. Hirai, Electrochemistry Communications, 34 (2013) 239-241.

[218] P. Deevanhxay, T. Sasabe, S. Tsushima, S. Hirai, International Journal of Hydrogen Energy, 36 (2011) 10901-10907.

[219] T.J. Mason, J. Millichamp, T.P. Neville, P.R. Shearing, S. Simons, D.J.L. Brett, Journal of Power Sources, 242 (2013) 70-77.

[220] K.B.S. Prasad, S. Jayanti, Journal of Power Sources, 180 (2008) 227-231.

[221] J. Zhang, Y. Tang, C. Song, Z. Xia, H. Li, H. Wang, J. Zhang, Electrochimica Acta, 53 (2008) 5315-5321.

[222] D. Novitski, S. Holdcroft, ACS Applied Materials & Interfaces, 7 (2015) 27314-27323.

[223] K.C. Neyerlin, H.A. Gasteiger, C.K. Mittelsteadt, J. Jorne, W. Gu, Journal of The Electrochemical Society, 152 (2005) A1073-A1080.

[224] T. Fabian, J.D. Posner, R. O'Hayre, S.-W. Cha, J.K. Eaton, F.B. Prinz, J.G. Santiago, Journal of Power Sources, 161 (2006) 168-182.

[225] V.A. Raileanu Ilie, S. Martemianov, A. Thomas, International Journal of Hydrogen Energy, 41 (2016) 15528-15537.

[226] T.-F. Cao, H. Lin, L. Chen, Y.-L. He, W.-Q. Tao, Applied Energy, 112 (2013) 1115-1125.

[227] T.-F. Cao, Y.-T. Mu, J. Ding, H. Lin, Y.-L. He, W.-Q. Tao, International Journal of Heat and Mass Transfer, 87 (2015) 544-556.

[228] A.P. Sasmito, J.C. Kurnia, A.S. Mujumdar, Energy, 44 (2012) 278-291.

[229] M.A. Hickner, N.P. Siegel, K.S. Chen, D.N. McBrayer, D.S. Hussey, D.L. Jacobson, M. Arif Journal of The Electrochemical Society, 153 (2006) A902-A908.

[230] C.F. Curtiss, R.B. Bird, Industrial & engineering chemistry research, 38 (1999) 2515-2522.