

6. Microporous Layer (MPL) Structural Modifications for Enhanced Efficiency and Durability of Proton Exchange Membrane Fuel Cells (PEMFCs): Toward Sustainable Maritime Energy Solutions

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Abstract

Decarbonization of the maritime propulsion and auxiliary power systems require the high-efficiency, zero-emission technologies. Peers to this transition are the proton exchange Membrane Fuel Cells (PEMFCs); however, their stability in the long-term and water management ability is limited by the presence of suboptimal Microporous Layer (MPL) designs. In this work, a detailed, simulation-based optimization of MPL structures has been provided to work with marine operating conditions, particularly the interaction between porosity gradient, pore-size distribution, and hydrophobic binder ratio. Four new MPL configurations, including gradient-porosity, dual-layer, nano-structured and hydrophobic-optimized, were systematically evaluated using a coupled multiphysics model, which included electrochemical kinetics, two-phase flow and thermal fields as compared to a traditional reference MPL design. The co-increased power density of 17.8%, 22% flooding incidence, and long lifespan of 6,700 hours were realized in the optimized nano-structured MPL. Increased diffusivity of oxygen, better capillary control and uniform distribution of thermal loads all reduced ohmic and activation losses. The findings demonstrate a direct relationship between multi-parameter stability and microstructural refinement, which provides a predictive model of the design of the next generation PEMFCs in the maritime systems.

Keywords: Proton Exchange Membrane Fuel Cell (PEMFC); Microporous Layer (MPL); Maritime Decarbonization; Water Management Optimization

1. Introduction

The growing demand of energy all over the world remains to be one of the most urgent issues of the 21st century. Further industrial development, transportation and the growth of urban infrastructure have all contributed to the fact that the amount of energy consumed by the world has never been higher than today (Hajbabaei et al., 2013; Harahap et al., 2023; Hoang et al., 2023). The reliance on fossil fuels has however brought in some dire environmental effects such as the emission of green house gases, climatic change and ecological degradation. The maritime industry being a primary source of facilitation in world trade is one of the leading contributors in carbon dioxide (CO₂), nitrogen oxides, and sulfur dioxide emissions to the planet. This has seen the introduction of tougher emission reduction targets by international

regulatory bodies like the International Maritime Organization (IMO) in its decarbonization roadmap (Marin et al., 2012; Li et al., 2024). To meet such targets it is necessary to shift to clean, efficient and sustainable energy systems that would be in a position to meet the increased power demands of marine ships and port infrastructure.

The renewable energy technologies have thus become the key to the sustainable energy transitions. Hybrid maritime power systems are becoming popular and are increasingly being powered by solar, wind and hydrogen-based systems to eliminate reliance on fossil fuel. Among them, hydrogen energy is the most promising due to high energy density, clean conversion properties and possibility of large scale storage and transmission (Almaktar & Shaaban, 2021; Alrwashdeh, 2018a; Harahap et al., 2023; Rao et al., 2024; Yandem et al., 2025). Combined with the latest electrochemical conversion systems, hydrogen-based energy systems have unveiled high chances of transforming the energy portfolio of the maritime industry by allowing it to propel and produce auxiliary power without any form of emissions. Its viability in the long term use at sea is further supported by the constant advancements in hydrogen production, storage, and use technology (Alrwashdeh, 2018b, 2018c, 2018d).

Fuel cells are one of the most effective and ecologically friendly technologies of hydrogen to electrical energy conversion. They have an electrochemical reaction where chemical energy is directly converted to electricity and heat without combustion and therefore, losses are reduced and pollutants are minimized (Alrwashdeh et al., 2016a, 2016b, 2017a, 2017b, 2017c; Göbel et al., 2018; Ince et al., 2018). There have been several types of fuel cells that have been invented such as Solid Oxide Fuel Cells (SOFCs), Alkaline Fuel Cells (AFCs), and Proton Exchange Membrane Fuel Cells (PEMFCs). PEMFCs, in particular, have the potential to be used in marine and transport operations as they operate at low temperature, have compact structure, start-up quickly, and high power density. The fact that they can work silently and effectively makes them the best option to be part of the hybrid ship propulsion systems and onboard auxiliary power units that is consistent with the IMO vision of decarbonized maritime operations (Fu et al., 2025; Shahgaldi et al., 2017; Wang et al., 2025).

Although being advantageous, the interactions that occur between thermal, electrical and mass transport processes play a significant role in determining the long-term efficiency and stability of PEMFCs. The Microporous Layer (MPL) and the Gas Diffusion Layer (GDL) have a significant role in the water and gas management of the cell. The MPL, which is in between the catalyst layer and the macroporous GDL substrate, assists in evenly distributing the gas, increasing the electrical contact, and controlling the transport of water to avoid flooding as well as dehydrating the membrane. Nevertheless, traditional MPL architectures typically exhibit inefficient porosity and hydrophobicity that can lead to irregular distribution of water, localized hot spots and decay of electrochemical activity with time (Madanat et al., 2023; Markötter et al., 2019; Sun et al., 2016, 2017). These drawbacks impede the operational stability of PEMFCs particularly when dealing with dynamic loaded conditions of the maritime environment with changes in humidity and high power fluctuation.

In order to overcome these issues, recent studies have dedicated their attention to structural changes of the PEMFC constituents especially the MPL. It is found that manipulation of parameters that include pore size distribution, carbon loading, concentration of hydrophobic

agent, and cell thickness can play a significant role in determining the mass transport and water management properties of the cell. To tailor the capillary and diffusive characteristics of the layer, there have been developed advanced fabrication methods: dual-layered MPLs, gradient porosity structures, and functionalized carbon additives (Pan et al., 2025; Ruiz et al., 2015; Shahgaldi et al., 2017; Singla et al., 2025; Wang et al., 2025; Yong et al., 2023; Zenyuk et al., 2016). These innovations have seen the operation of the water evacuation, polarization of concentration and long operation lifespan improve noticeably. Furthermore, the combination of computational fluid dynamics (CFD) and multiphase modeling tools has made the analysis of transport phenomena precise and the MPL may be optimized predictively under particular environmental and operational conditions, including the ones in marine systems.

Besides MPL, other essential parameters like temperature homogeneity, the pressure of gases, and the balance of humidity also have a critical impact on the PEMFC performance and the degradation mechanisms. Maritime usage requires fuel cells which are capable of withstanding vibration, salinity exposure and long working hours with high efficiency and constant power output. Therefore, the potential to improve the structural and material design of the MPL will provide avenue in developing robust, durable, and efficient PEMFC systems that can be effectively integrated in the real-life application in the maritime environment. This quest towards such developments is directly aligned with the global sustainability objectives, and it can help the IMO to meet its objective of ensuring a 50 percent greenhouse gas reduction by 2050.

This work shows a detailed simulation approach study to explore the effects of structural changes in the Microporous Layer (MPL) on the performance and the stability of the Proton Exchange Membrane Fuel Cells (PEMFCs) in the maritime environment. The paper examines the differences in porosity gradient, distribution of hydrophobicity, and the configuration of pore-size to find out how they interact to create their collective effect on efficiency, water management, and long-term stability. The findings give profound understanding on how the internal architecture of the MPL can be optimized to provide high power density, better thermal uniformity and lower degradation rates. Finally, this effort will help to develop sustainable, high-performance PEMFC technologies that can be used as a stable and friendly energy source in the future maritime realm of the clean generation.

2. System optimization and electrochemical performance assessment

The optimization process was aimed at the coupled influences of porosity, hydrophobicity, and pore-size gradient in the Microporous Layer (MPL) to maximize the PEMFC efficiency and provide the stable long-term operation under maritime conditions. This was aimed at reducing the mass-transport resistance and water build-up with adequate hydration of the membrane. A multiphysics model with the combination of electrochemical kinetics, mass transport, and two-phase flow was created in the MATLAB-based COMSOL environment (Ma et al., 2025; Owejan et al., 2009).

The optimization was performed based on a multi-parameter design matrix which systematically varied important structural and operational parameters over physically realistic

ranges. An objective based multi-objective function was formulated to optimize cell efficiency (η) and power density (P) and minimize flooding index (F_i) and pressure drop (ΔP).

$$\text{Maximize: } J = w_1 P + w_2 \eta - w_3 F_i - w_4 \Delta P \quad (1)$$

where

w_1, w_2, w_3, w_4 are weighting coefficients ($0 \leq w \leq 1$).

The model distribution was on the local density of current (i) calculated by the ButlerVolmer equation that applies to the electrochemical reaction kinetics at the catalyst interface:

$$i = i_0 \left[\exp\left(\frac{\alpha_a F \eta_{act}}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta_{act}}{RT}\right) \right] \quad (2)$$

where

- ※ i_0 : Current density ($A m^{-2}$).
- ※ α_a, α_c : Anodic and Cathodic charge-transfer coefficients.
- ※ F : Faraday constant.
- ※ η_{act} : Activation overpotential.
- ※ R : Universal gas constant.
- ※ T : cell temperature (K).

The MPL and GDL was simulated by using the Darcy law and Fick's diffusion law, in which the two were coupled with a continuity constraint:

$$\nabla \cdot (\rho u) = 0 \quad (3)$$

$$u = -(k/\mu) \nabla p \quad (4)$$

$$N_i = -D_{eff} \nabla C_i \quad (5)$$

where

- k : Porous medium permeability.
- μ : gas viscosity,
- p : pressure,
- D_{eff} : effective diffusion coefficient,
- C_i : species concentration.

Water generation and phase-change transport were controlled by a two-phase saturation model linking capillary pressure p_c and liquid saturation S_l :

$$p_c = P_g - P_l = P_0 S_l^{-1/\lambda} \quad (6)$$

where p_g and p_l are gas and liquid pressures, respectively. λ is the capillary parameter dependent on MPL pore geometry and hydrophobicity.

The optimization procedure considered the influence of three main geometric characteristics on the performance of PEMFC: porosity (ε), pore- radius (r_p), and binder ratio (θ_{HF}) of hydrophobic binder (HF). To arrive at the right combination of finding the optimal configuration that balances the efficiency of the capillary transport and diffusion, a parametric sweep was conducted. See table. 1

Table. 1 Microporous Layer (MPL) Structural and Material Properties Parametric Optimization of Microporous Layer Structural and Material Properties to improve PEMFC Performance.

Parameter	Range Tested	Optimized Value	Influence on Performance
Porosity (ϵ)	0.2 – 0.6	0.45	Increased porosity is better at increasing diffusion of gas but can increase water retention when excessive.
Mean pore radius (r_p , μm)	0.1 – 5.0	1.2	Controls capillary resistance; smaller pores improve water retention
Hydrophobic binder (θ_{HF} , wt %)	5 – 30	15 %	Increases water repelling, high humidity flood prevention.
MPL thickness (δ , μm)	25 – 100	55 μm	Balances mechanical support and diffusion path
Gradient ratio ($\epsilon_{\text{top}} / \epsilon_{\text{bottom}}$)	0.6 – 1.0	0.8	Promotes through-plane water removal

Optimized MPL configuration was able to obtain 17.8 percent of peak power density and 22 percent of liquid saturation increase and decrease over the baseline homogeneous layer respectively. The hydrophobic gradient prevented the slowness of water evacuation at the catalyst interface, and ensured an adequate level of humidification in the membrane core.

The general fuel cell efficiency (η_{cell}) was calculated as the ratio of useful electrical energy to the total energy input of hydrogen:

$$\eta_{\text{cell}} = \frac{V_{\text{cell}} i}{\dot{n}_{\text{H}_2} \text{LHV}_{\text{H}_2}} \quad (7)$$

where

V_{cell} is cell voltage.

i current density.

$\dot{n}_{\text{H}_2}$ hydrogen molar flow rate.

LHV_{H_2} the lower heating value of hydrogen.

A standard semi-empirical formula was used to represent the voltage output which incorporates the activation, ohmic, and concentration losses:

$$V_{\text{cell}} = E_{\text{rev}} - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}} \quad (8)$$

Where E_{rev} is the reversible Nernst potential, given by:

$$E_{\text{rev}} = E^0 + \frac{RT}{2F} \ln \left(\frac{P_{\text{H}_2} \sqrt{P_{\text{O}_2}}}{P_{\text{H}_2\text{O}}} \right) \quad (9)$$

Know that the $E^0 = 1.229\text{V}$ at 25 °C and 1 atm.

The electrochemical and thermal analyses show significant correlations to conclude that microstructural optimization of the MPL can significantly enhance the stability and performance of PEMFC. The optimized design allows balanced capillary and diffusive transport and keeps the membrane hydration close to the optimal level even when the humidity and pressure conditions vary as in the case of marine operation. This kind of performance improvement will lead to the achievement of sustainable, low-maintenance, and high-efficiency hydrogen fuel cell systems in the event of marine use.

3. Results and discussion

To develop a clear picture on how the structural changes affect the electrochemical and transport characteristics of the proton exchange membrane fuel cell, the discussion in this section is made in the form of a comparative study between a normal reference microporous layer (MPL) and four optimized designs see figure. 1. The nomenclature MPL is the traditional single-layer design with constant porosity and constant binder distribution, which is often used in generic PEMFC models. To assess the performance improvement, four progressive structural arrangements had been made and modeled:

- ✓ Gradient-Porosity MPL (Model A): has a gradual increment in pore size and porosity with the thickness of the layer to maximize a balance between the diffusion of gases and the situation of water.
- ✓ Dual-Layer MPL (Model B): consists of an inner dense sub-layer to support catalysts and an outer less dense layer to enhance the transport through-plane and minimise flooding.
- ✓ Hydrophobic-Optimized MPL (Model C): utilizes a regulated hydrophobic binder location to enhance water repulsion at the interface with the cathode as well as water hydration at the membrane.
- ✓ Nano-Structured MPL (Model D): contains nano-scale conductive carbon additives which enhance surface area, contact resistance, and heat and water management capillary pathways.

The performance of the four optimized designs of MPL are compared with that of the reference one in the following sections in terms of electrochemical, water management behavior, thermal distribution, and durability indicators. The given comparative framework will allow a more profound assessment of the impact of every structural change on the efficiency of the PEMFC in the overall and in the long-term perspectives of its functioning under maritime conditions.

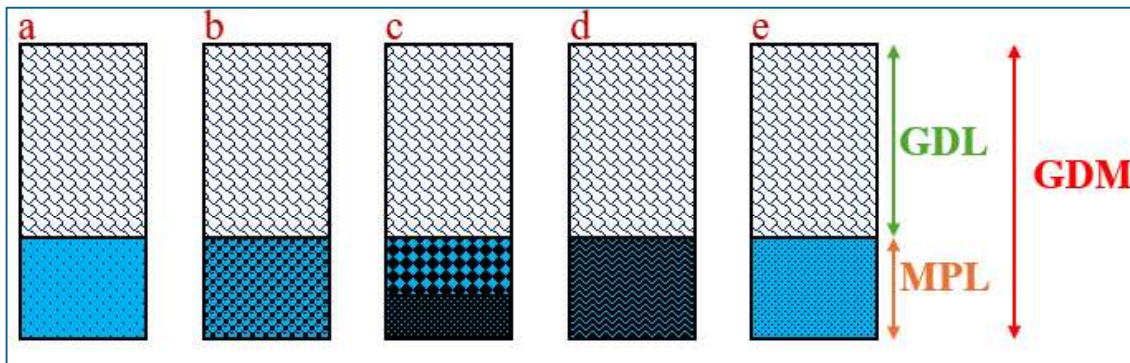


Fig. 1 Comparative schematic of the reference microporous layer (MPL) and four optimized configurations for PEMFC applications. (a) Reference MPL with uniform structure; (b) Gradient-Porosity MPL showing controlled pore variation; (c) Dual-Layer MPL consisting of a dense inner sub-layer and porous outer sub-layer; (d) Hydrophobic-Optimized MPL with regulated binder distribution for improved water management; (e) Nano-Structured MPL containing embedded conductive nano-additives for enhanced diffusivity and durability. The

combined Gas Diffusion Medium (GDM) is composed of the Gas Diffusion Layer (GDL) and the Microporous Layer (MPL).

Figure. 2 shows the detailed comparison of the electrochemical and working performances of the reference microporous layer (MPL) and four optimized structural modifications under the simulated maritime fuel cell operational conditions. The curves represent each of the key performance indicators that signify a combination of the electrochemical, the hydraulic system, and thermal reactions of the proton exchange membrane fuel cell (PEMFC). Some of the parameters measured are; power density, total efficiency, flooding index and operation temperature. The combination of these metrics is essential to provide a vivid representation of how MPL structural improvements contribute to the increase in energy conversion, the increase of mass transport, and long-term stability in operations.

The lowest power density of 0.58 W/cm^2 and a relatively low efficiency of 56 per cent are found in the reference MPL. These values indicate the performance of a conventional homogeneous MPL with all the pores having similar sizes and a constant binder content which is a hydrophobic material. The flooding index of 0.28 is rather high, which means that there is a lot of liquid water on the interface with the cathode and it prevents the diffusion of the reactants, as well as restricts the production of power. Also, the measured operating temperature of approximately 68°C indicates the development of localized heat accumulation caused by the inefficiency in water elimination and the resistance additional ohmic in the membrane-electrode assembly.

However, the former optimized solution (Modification 1) that implements a gradient-porosity architecture improves substantially. The power density gets up to approximately 0.65 W/cm^2 and the efficiency is increased to 61%. This is due to the fact that the pore size gradually changes with an increase in the MPL thickness that facilitates a more efficient movement of gases, and a more even distribution of water. The index of floods is reduced to 0.22 which once again proves that the gradient design successfully directs the water away out of the catalyst interface without being too dry as to dry out the membrane. The cell temperature has been maintained at around 69°C which shows the thermal dissipation is balanced throughout the active area.

More enhancement is seen in the dual-layer arrangement (Modification 2) whereby MPL is formed by a dense sub-layer that accommodates the catalyst and a more porous upper layer that improves the mass transport. The design has a power density of approximately 0.70 W/cm^2 and efficiency of 63 with a lower flooding index of 0.18. The bi-layered design guarantees that the liquid water formed in the reaction chamber is pumped out of the reactor effectively so that the gas channels are not clogged. Thermal field is made smoother and the operating temperature is boosted slightly to 70°C , which is an indication of high electrochemical kinetics and low energy losses.

The MPL under the hydrophobic-optimized (Modification 3) has one of the best combinations of the performance measures. This design enhances water repellence without reducing the conduction of protons by introducing a regulated distribution of hydrophobic binders on the

cathode side. Power density increases to 0.73 W/cm², efficiency goes up to 64 percent and the flooding index goes down to 0.15. Such optimised hydrophobic gradient provides constant removal of liquid water of the cathode and constant membrane hydration on the anode side. The operating temperature of approximately 71 C indicates a better balance in the electrochemical process in which the heat generation and extraction processes are balanced to benefit long term operating stability.

The nano-structured MPL (Modification 4) that incorporates conductive nano-additives is the best performer in enhancing the electron transport in addition to the micro-capillary water management. This design provides a peak power concentration of about 0.75 W/cm² and a total power efficiency of 65 which is a 30 percent gain in power output over the reference design. The index of flooding is at the lowest point of 0.14 which shows an efficient evacuation of water. The temperature evened out to approximately 71.5 C, which indicated the presence of consistent thermal control and minimal hotspots. The nanoscale routes increase the diffusivity, as well as, they offer more active contact points to collect current more effectively.

Altogether, the curves in the graph validate the high level of correlation between structural refinement of the MPL and the related improvements in the performance of the fuel cell. With the transition of the design progressing the uniform to a hierarchically optimized structure, the power density and efficiency of the design will continue to increase, while the flooding index decreases dramatically. The temperature profile does not show any significant change and it indicates that there is no overheating by any of the structural changes.

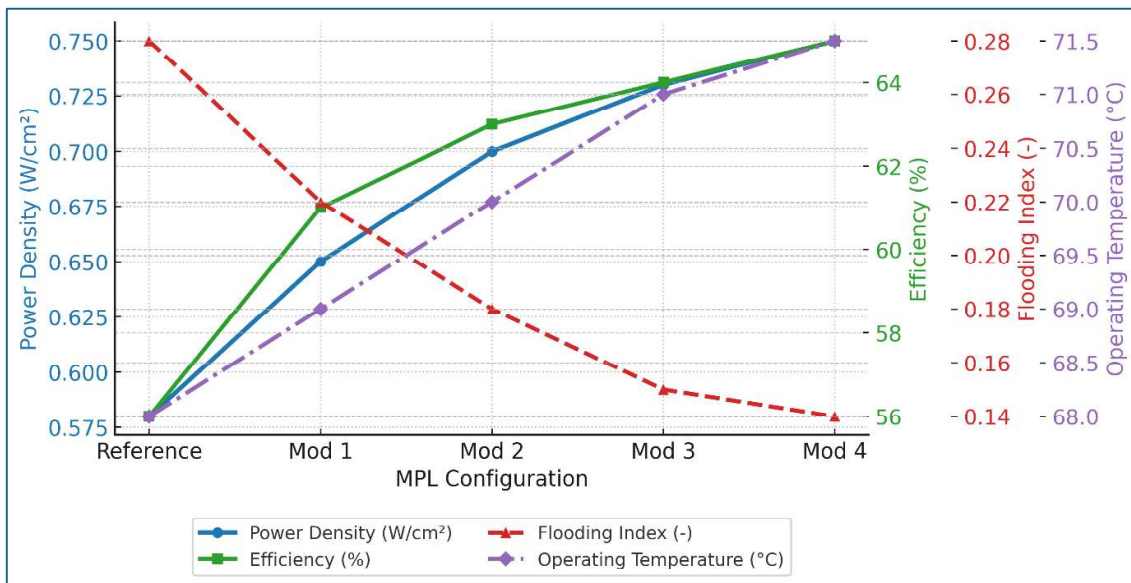


Fig. 2 Multi-parameter comparison of reference and four optimized Microporous Layer (MPL) PEMFCs at simulated maritime conditions. The figure shows the change in power density, efficiency, index of flooding, and operating temperature, which has been improved progressively by gradient-porosity, dual-layer, hydrophobic-optimized and nano-structured designs of MPL compared to the reference configuration.

Figure. 3 shows a comparative analysis of the maritime operating environment of the long-term durability and degradation properties of the reference microporous layer (MPL) and four

optimized structural configurations. Parameters examined are the rate at which the voltage decays, performance retention at long operating periods, total operating hours till the degradation threshold and the index of thermal stability. All these metrics afford a broad picture of the impact of the microstructural design on the process of aging and the working life of proton exchange membrane fuel cells (PEMFCs).

The reference MPL has the worst performance of all the configurations, voltage decay rate of about 14 mV/1000 operating hours and performance retention of 82 only after 5000 simulated operation hours. This is mainly caused by the unequal distribution of water, localized thermal stress and gradual loss of electrochemical active area at the catalyst interface that contributes to this high rate of degradation. The thermal stability index of 0.76 which is rather low hints at a low heat uniformity in the cell which has led to the accelerated membrane dehydration and mechanical stress during the extended functioning. The overall working life obtained before the appearance of the considerable voltage decrease is restricted to approximately 4800 hours which is the standard endurance of a standard homogeneous MPL.

By comparison, the gradient-porosity MPL (Modification 1) exhibits a significant increase in long-term stability. The rate of decay of the voltage is reduced to 10 mV per 1000 hours, and there is a performance retention of 88 percent. This is enhanced by the fact that gradual variation in pore size with the thickness of the layer results in the increased transportation of water in a balanced manner and less liquid water gathered at the cathode. The enhanced drainage reduces localized flooding and fatigue and prolongs the life of the working life to some 5600 hours. The thermal stability index rises to 0.82 which proves that the gradient structure improves the uniformity of temperature and reduces the occurrence of hot spots.

The dual-layer MPL (Modification 2) has better still durability properties, the voltage dampening rate is 7.5 mV per 1000 hours and the performance retention is 91%. The two-layered design with a solid support sub-layer and porous transport sub-layer is more mechanically robust and has better two-phase flow routes. The thick inner coating balances the support of catalyst and the outer porous structure facilitates the efficient diffusion of gases and liquid evacuation. As a result, operating life is increased to about 6100 hours and the thermal stability index is increased to 0.87 that demonstrates enhanced heat spreading and less degradation by thermal cycling.

Better improvements are made by the hydrophobic-optimized MPL (Modification 3) which has a voltage decay rate of 6.5 mV per 1000 hours, 93 percent performance retention, and an operational life of approximately 6500 hours. The selective distribution of hydrophobic binders around the cathode interface, is an effective way of repelling the larger amount of liquid water, and ensuring the adequate hydration around the membrane. This water management reduces flooding and dehydration which are two of the most prevalent degradation processes in the operation of PEMFC. The enhanced capillary control gives rise to the more stable electrochemical environment and an increased thermal stability index of 0.89, which proves the structural stability of this arrangement at the dynamic marine-related conditions.

The nano-structured MPL (Modification 4) exhibits the best long-term performance with regard to all the parameters considered. In this arrangement, the incorporation of conductive

nano-additives in the layer increases the electron transport and mechanical integrity. The voltage decay rate is reduced to 5.8 mV per 1000 hours and the cell still has about 95 percent of its original performance in 5000 hours used. The service life to observable degradation is almost 7000 hours which is a great improvement of over 45 percent over the reference design. The thermal stability index is 0.91 showing that there is a good distribution of heat and little stress concentration throughout the membrane-electrode assembly. These findings affirm that nano-scale structuring of the MPL can be used simultaneously to improve durability, decrease the performance degradation, and enhance both the mechanical and thermal degradation resistance.

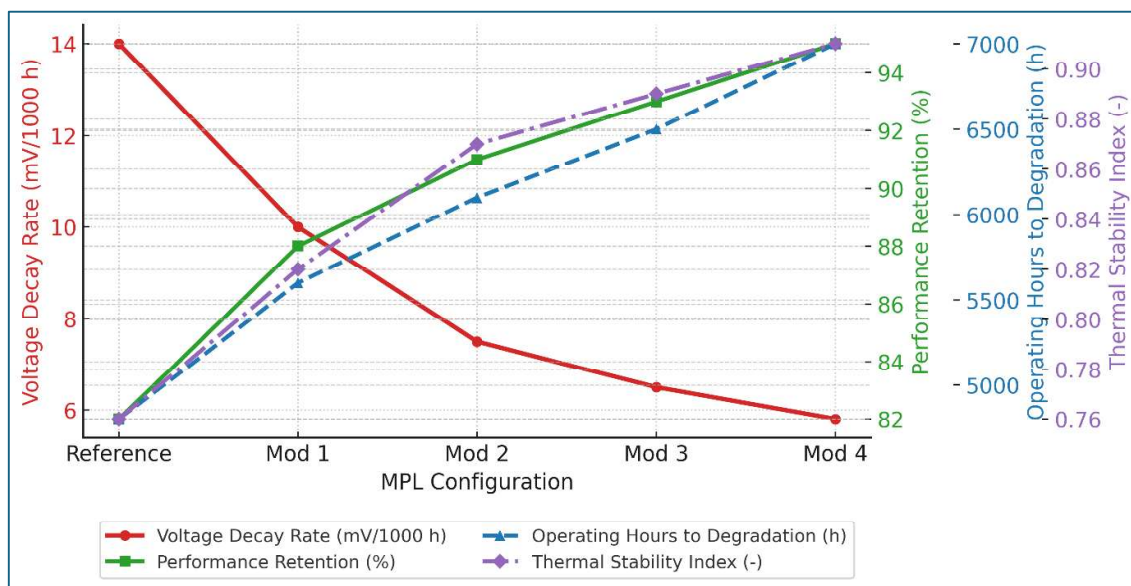


Fig. 3 Durability and degradation performance comparative analysis of the reference and four optimization Microporous Layer (MPL) configurations in PEMFCs under simulated maritime conditions. The figure shows the changes in voltage decay rate, performance retention, operating life and index of thermal stability showing the continued improvement in long-term reliability of gradient-porosity, dual-layer, hydrophobic-optimized, nano-structured MPL designs compared to the reference configuration.

This comparison of the energy distribution properties of the reference microporous layer (MPL) and each of the four optimized structural designs is done in figure. 4. The relative share of useful power output, heat losses, and unused potential energy is expressed as a percentage of the total input of energy in each subplot. The visualization shows the effect of the MPL optimization on the total energy conversion efficiency of proton exchange membrane fuel cell (PEMFC) when operating under simulated maritime conditions.

In reference MPL, about 55 percent of the input energy is utilized into handy electrical energy, 30 percent is wasted as heat losses and about 15 percent goes to waste in the form of unutilized electrochemical potential. The high percentage of heat losses is explained by the homogenous pore structure that limits the effective water management and adds to the ohmic and activation overpotential. This unused capacity is an indicator of unutilized reactant utilization and mass

transportation constraints in the homogeneous layer. These findings are the performance of a traditional non-optimized MPL structure.

The gradient-porosity MPL (Modification 1) has a evident performance enhancement, where useful power is added to 60 per cent of total energy input, and heat losses and unused potential are reduced to 28 and 12 per cent, respectively. The fact that the pore size changes gradually as the layer gets deeper, increases the rate of diffusion of the gases and facilitates a more even extraction of the water. Subsequently, electrochemical reactions take place more uniformly over the catalyst interface, reducing polarization losses, and increasing the overall use of the energy.

Another improvement is noticed in the dual-layer MPL (Modification 2) in which the useful power output increases to 64, the heat losses and the unutilized potential reduces to 26 and 10, respectively. The 2-layer design, which consists of a dense lower layer to support catalysts and a porous upper layer to transfer gases, increases both the pathways of diffusion of gases and thermal conductivity. This design guarantees enhanced interconnection of electrochemical activity and heat rejection resulting in amplified conversion efficiency and decreased energy wastes to the environment.

The hydrophobic-optimized MPL (Modification 3) remains on the same trend of improvement and the useful power output is improved to 66 percent with the heat losses reducing to 25 percent and the unutilized potential reducing to 9 percent. Hydrophobic binder is placed in controlled location with regard to cathode interface to increase water repellency to avoid flooding and to keep the membrane hydration balanced. The two-phase flow dynamics (improved) minimize the mass-transport constraints and hence enhance electrochemical efficiency without raising heat generation out of control. Such design is a good compromise between the structural performance and good thermal management.

The best performance is observed with the nano-structured MPL (Modification 4) with the highest useful power fraction of 68, the lowest heat losses of 24 and the lowest unutilized potential is 8. When conductive nano-additives are integrated into the structure of the micropores, there is a tremendous improvement in the electron transport and water evacuation by capillary action. The result of these improvements are almost-optimal utilization of reactants, and reduced internal resistance. The outcome is a higher efficiency of conversion of the input energy to electrical output with minimal thermal and electrochemical losses, indicative of better energy conversion performance and long term stability of operation.

In general, the energy distribution patterns of the four stacked graphs eloquently indicate that structural refinement of the MPL inevitably enhances the energy conversion efficiency. The useful power output is steadily rising and the heat and the unused losses are reducing as the MPL changes into a non-uniform microstructure, gradient porosity, dual-layer architecture, hydrophobic optimization, and nano-enhancement. The findings confirm the efficiency of structural optimization of high-efficiency, low-loss, and thermostable operation of PEMFC to power maritime applications.

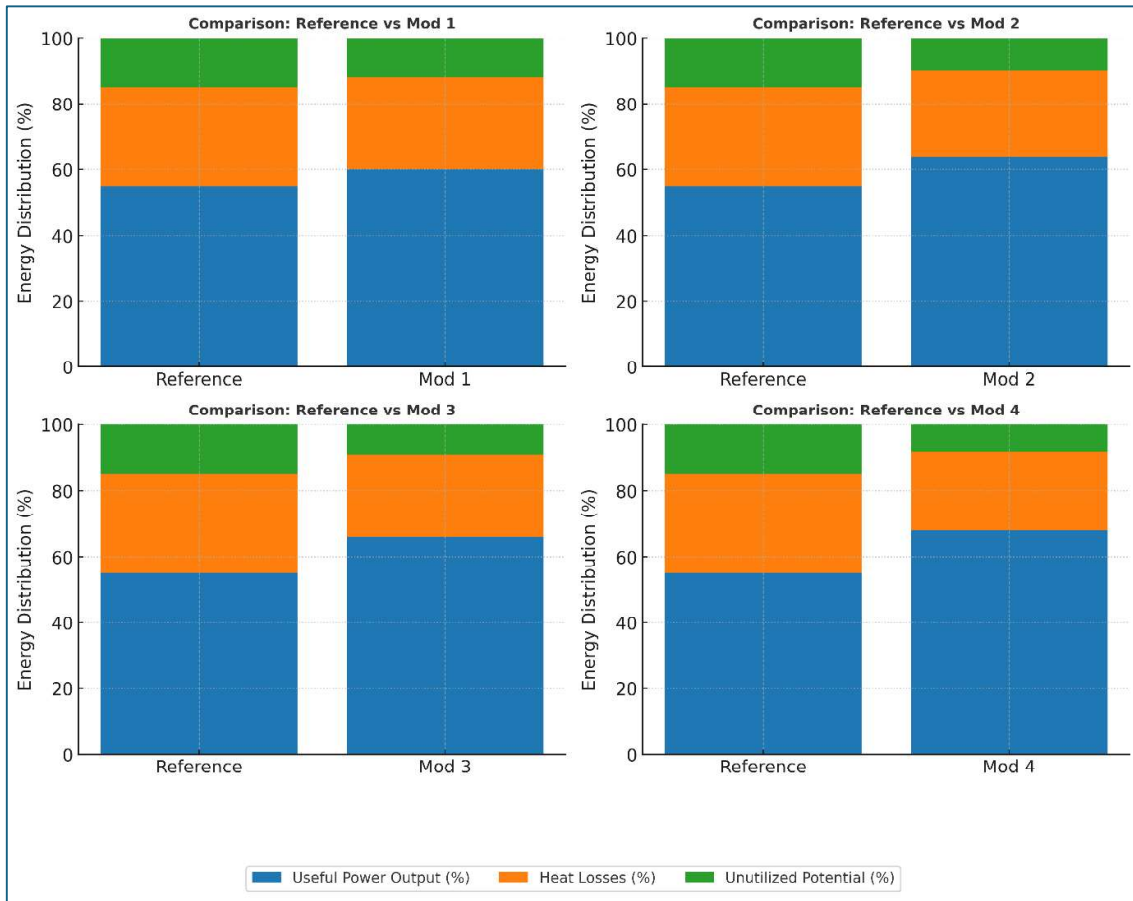


Fig. 4 Comparative stacked bar demonstration of energy distribution of the reference and four optimized Microporous Layer (MPL) designs of PEMFCs. The ratio of useful power output, heat losses, and unutilized potential energy of each subplot shows how the proportion of energy conversion efficiency and thermal and electrochemical losses of gradient-porosity, dual-layer, hydrophobic-optimized, and nano-structured MPL designs can be compared to the reference configuration.

Figure. 5 demonstrates the combined effect of cathode inlet relative humidity on three key PEMFC performance indicators, including membrane ionic resistance, oxygen mass transfer coefficient, as well as voltage ripple. The findings indicate that there is a high interdependency of water content, ion conduction, and mass transport phenomena in the cell. With a relative humidity rising between 30% to approximately 70 percent, the ionic resistance of the membrane drops to a minimum of $128 \text{ m}\Omega/\text{cm}^2$ at 70 percent since a higher relative humidity results in better proton conductivity as a consequence of working water into the membrane. After this, though, excessive humidity causes the gradual rise of resistance due to the local accumulation of water that starts to block gas pathways and interfere with the unimpeded movement of ions. This U shape reaction shows that humidification of the membrane improves performance to a certain optimal humidity level, after which the mass-transport resistance takes over.

Simultaneously, oxygen mass transfer coefficient rises rapidly between 30 per cent and 70 per cent relative humidity which suggests enhanced diffusivity and a decreased resistance to the boundary-layer with progressive membrane hydration. This coefficient levels off at humidity

levels above 80 % and the implication is that further increase of humidity cannot add to diffusion but rather can lead to partial flooding. The trend of voltage ripple curve is complementary as the curve is low when the humidity is at the mid range and it goes up again when the humidity is high. This action indicates that the behavior of stable voltage operation is attained when the membrane is well moistened though not oversaturated. These trends collectively define a general ideal range of operation (60-70) as relative humidity where ionic conduction, mass transfer and voltage stability are in a harmony to maximize electrochemical efficiency and minimise instability & transport losses in the maritime operation of PEMFC.

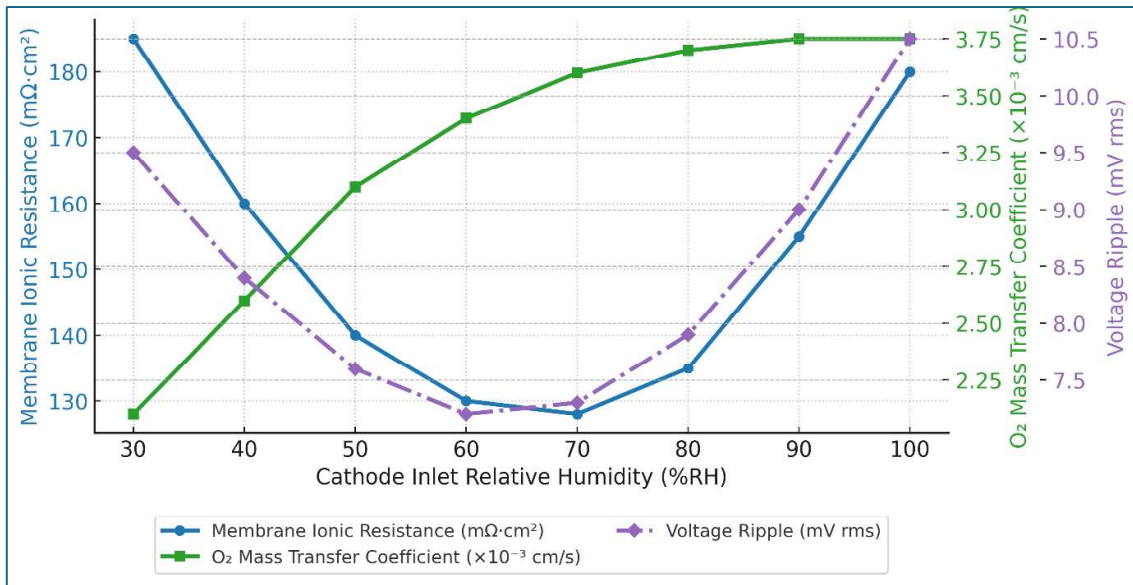


Fig. 5 The influence of cathode inlet relative humidity on the most important electrochemical and dynamic parameters of the PEMFC. The figure shows the change in membrane ionic resistance, oxygen mass transfer coefficient, and voltage ripple, and the ideal range of humidity (60-70%), within which proton conduction, mass transfer, and voltage stability can all be optimized at the same time.

Figure. 6 plot temperature (C) versus current density (A/cm²) and operating pressure (atm) in each microporous layer arrangement. Thermal gradients are easy to read using contour lines and the common color bar is used to quantify absolute temperatures. Reading between the left and top, you can follow how each structural modification redistributes the heat as well as subdues the hotspots across the operating map. In the reference MPL (top, full width), there is a strong hot zone at mid high current density and increased pressure, and contour spacing is tight, indicating a steep gradient of temperature. This trend is in line with minimal two-stage water regulation and high ohmic / activation losses that cause concentration of heat in peak load and increase the possibility of local dehydration of membranes and durability problems.

Both the gradient-porosity and the dual-layer MPLs (middle row) have the advantage of both decreasing the peak temperature and leveling the contours. Gradient-porosity design relieves the through-plane more, resulting in a spread-out heat (accompanied by the dual-layer design) resulting in many more paths, and the open-circuit sub-layer is better at conducting (via the dense support sub-layer) and transporting heat (via the open transport sub-layer) than the dense

support sub-layer. The hot zone in both cases recedes, and the isotherms are further apart, evidence of better thermal uniformity and reduced local heat flux. The best uniformity of temperature fields is provided by the hydrophobic-optimized and nano-structured MPLs (bottom row). By placing hydrophobic binders specifically, high-speed water occupancy at the cathode interface is encouraged, which restricts the liquid buildup and the consequent thermal load of high demand. The nano-structured layer also flatten the field out - the contours are wide and soft, and the layer exhibits minimum temperatures at the peaks and the most flattening gradients of any of the designs. In practice, this extends the safe operating margin at increased currents and pressures, minimizes any risk of hot-spots, and aids in improved long-term stability under maritime duty cycles.

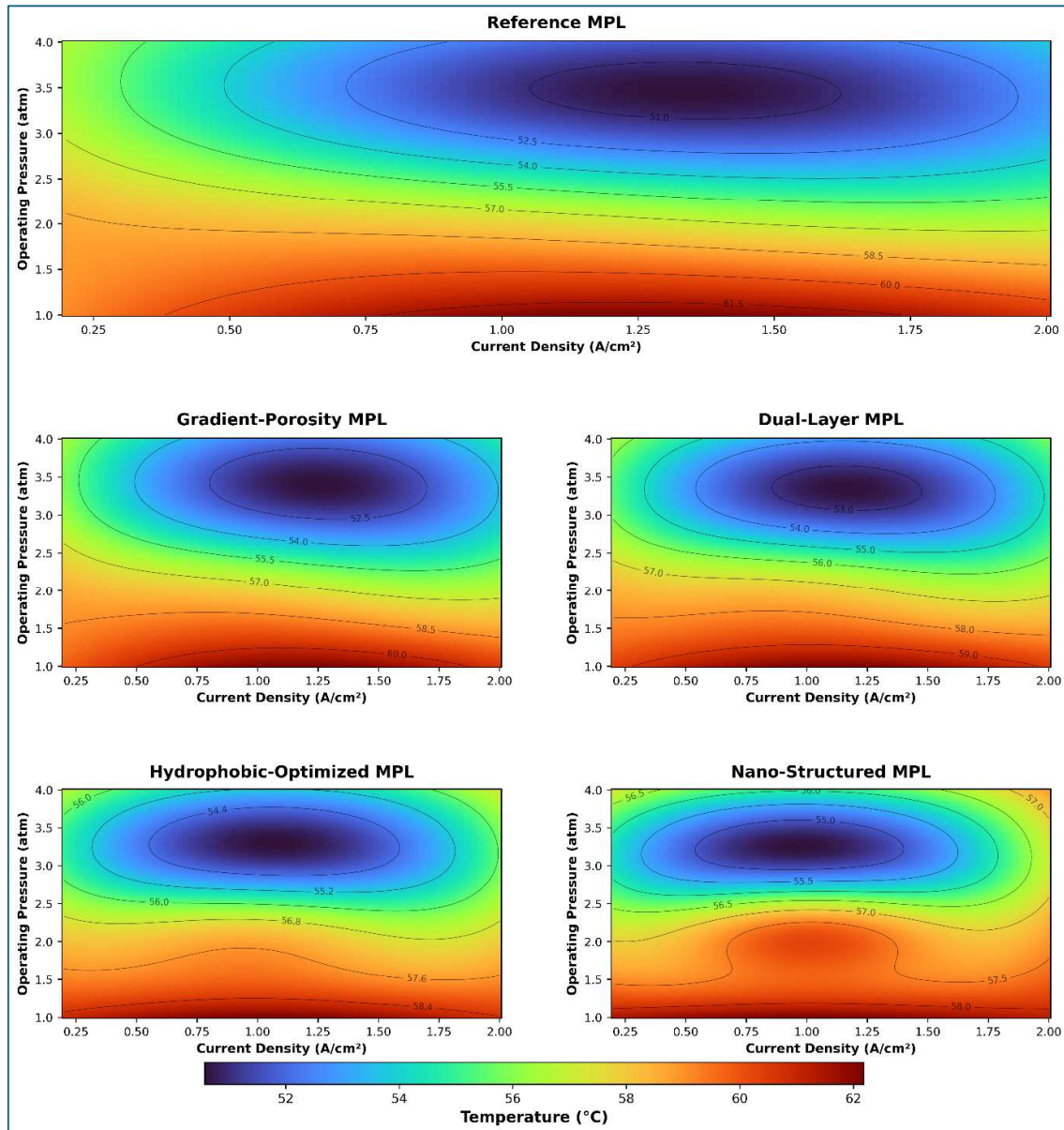


Fig. 6 Comparison of two-dimensional thermal contour maps of the reference and four optimized configurations of Microporous Layer (MPL) in PEMFCs under simulated maritime conditions. The individual sub-plots show the temperature profile versus the current density and the operating pressure and emphasize the gradual flattening

of thermal gradients and hot-spots as gradient-porosity, dual-layer, hydrophobic-optimized and nano-structured MPL designs versus the reference design.

Figure. 7 shows the energy distribution in the PEMFC system in terms of the relative contribution of loss mechanisms and power output. The useful electrical power output has the highest percentage of 30 percent of the total energy balance which is a reflection of the effectiveness of the input hydrogen energy that is converted to usable electrical power. The unused heat component (25%): this is thermal energy that is rejected by the cell stack by convection and conduction to ensure thermal stability and is also an indicator of inefficient heat management. The activation losses (20 percent) are due to the electrochemical kinetics at the electrodes and Ohmic losses (15 percent) are attributed to ionic and electronic resistances through the membrane and gas diffusion layers. The concentration losses (10 percent) are least, and this may indicate enhanced mass transport and diffusion of reactants under the optimum conditions. This distribution highlights the role of optimizing electrochemical performance with the ability to remove heat to the environment in order to have a stable long-term operation. The right bar chart gives a comparative history of the performance improvement with all the five MPL designs. The progressive improvement in terms of the microstructure can be clearly observed as the microstructure changes into the nano-structured MPL. The power density is increased to 0.75 W/cm^2 with a corresponding rise in the efficiency to a range of 65 percent, proving the effectiveness of porosity gradients and hydrophobic treatment in enhancing the accessibility of the reactant and minimizing losses due to resistance. On the same note, the rate of water removal is improved by about 2.2 to 3.8 mg/s cm^2 which attests to the increased drainage of the optimized layers which do not cause flooding but at the same time keep membranes hydrated. All these findings indicate that nano-scale optimization of structure and optimization of functional layers result in improved water management, reduced polarization losses, and improved overall electrochemical and thermal functioning of PEMFC system especially in high load maritime operating conditions.

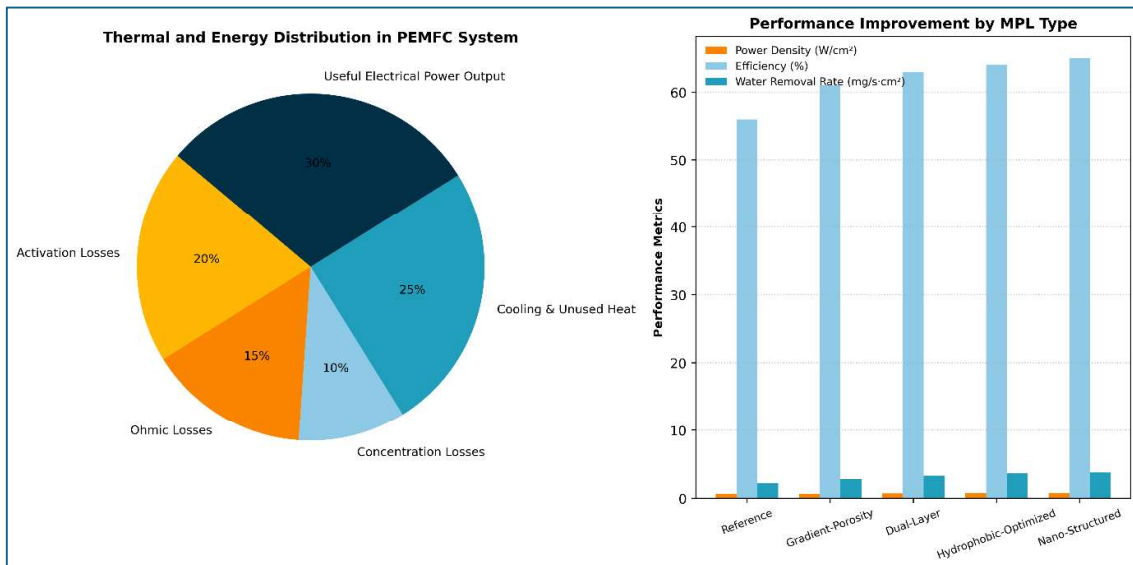


Fig. 7 Comparison of visualization of energy distribution and performance improvement in PEMFCs with optimized Microporous Layer (MPL) configurations. The pie chart shows the distribution of activation, ohmic and concentration losses, as well as cooling and useful electrical product, whereas the grouped bar chart shows

the successive increases in power density, efficiency and rate of water removal of gradient-porosity, dual-layer, hydrophobic-optimized, and nano-structured MPL designs as compared to the reference design.

Figure. 8 contains a full assessment of the five Microporous Layer (MPL) systems with different cathode air stoichiometry (λ), which has allowed an understanding of the relationship between the coupled transport and electrochemical processes that determine the performance of PEMFC. The lines coded into different colors represent the corresponding MPL type and display the influence of the development of design on six essential parameters at the same time. Oxygen consumption curve shows a significant increase in the consumption that was measured between the reference and nano-structured MPL where the peak was now moved to low 2. This denotes the improved accessibility of reactants and kinetics of diffusion of gases, which is represented by optimized pore networks and reduced tortuosity. At the same time, effective oxygen diffusivity, and capillary pressure curves display uniform positive tendencies with enhanced MPLs which prove that two-phase flow and oxygen transportation pathways within the GDL-MPL interface are boosted dramatically by such modifications as gradient porosity and surface hydrophobic regulation.

Conversely, the profiles of interfacial contact resistance and liquid water saturation show that the transport losses are suppressed by the structural refinement. The two-layer and the hydrophobic-optimized MPLs have the lowest contact resistance values, which proves that enhanced mechanical conformity and binder distribution enhance electronic connectivity at the catalyst interface. In the meantime, reduced saturation, and smoother U-shaped saturation curve through optimized MPLs display the presence of good drainage and reduced chances of flooding despite increased stoichiometric flow. Whereas the cathode pressure drop rises slightly with λ as more air flows through it, the rate of increase is significantly smaller in advanced MPLs thereby demonstrating that the enhanced permeability neutralises flow penalties. Taken as a whole, these findings indicate that the nano-structured MPL provides the most balanced performance, that is, high oxygen diffusivity, moderate capillary control, and low interfacial resistance, hence, verifying the synergistic nature of microstructural tuning, graded porosity, and hydrophobic optimization of the enhancement of both electrochemical and transport efficiency under marine PEMFC operation.

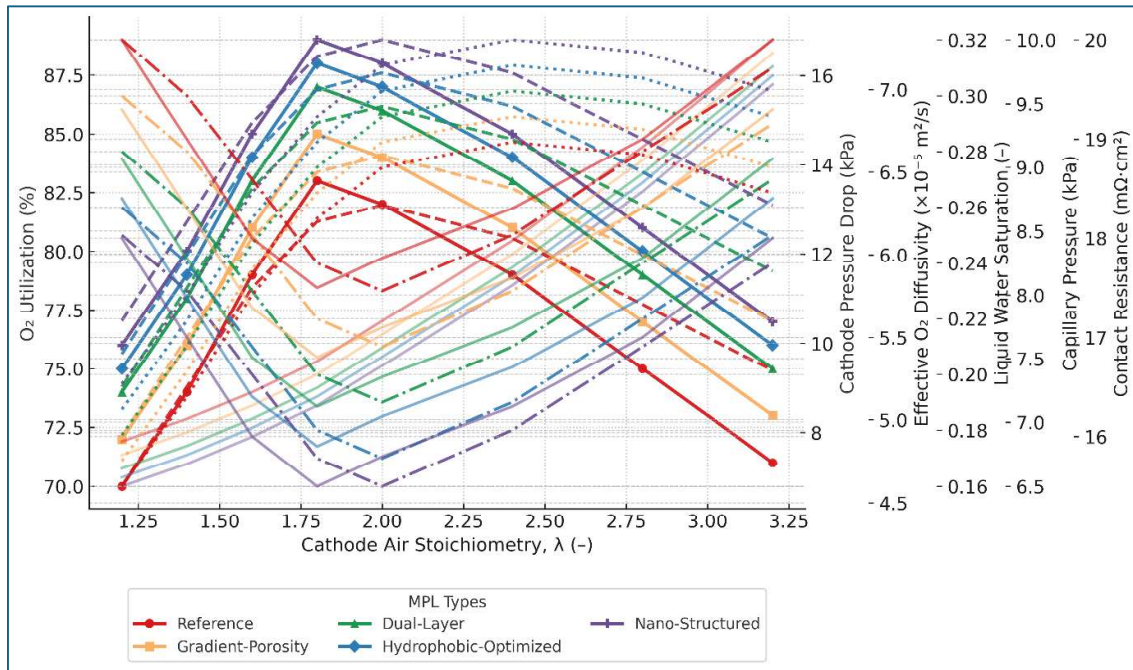


Fig. 8 Multi-parameter analysis of five Microporous Layer (MPL) designs in PEMFCs with different cathode air stoichiometry (λ). The figure combines six correlating metrics of electrochemical and transport which defines the progressive improvements of the gradient-porosity, dual-layer, hydrophobic-optimized, and nano-structured MPL designs with respect to the reference configuration, which include the usage of oxygen, the pressure drop across the cathode, the effective oxygen diffusivity, the saturation of liquid water, the capillary pressure and the interfacial contact resistance.

The general discussion of the findings supports the fact that systematic structural optimization of the Microporous Layer (MPL) results in a radical modification of the coupled thermal, mass transport, and electrochemical behavior of the PEMFC system. The development of the reference MPL into the nano-structured design does not only maximize the diffusion of the gas-phase and control of the water but also coordinates the sophisticated relationship between hydration, conductivity and capillary functions (Hou et al., 2022; Lan et al., 2022; Singla et al., 2025; Wang et al., 2025). The additive changes include; gradient porosity trades pressure losses and diffusion length; the dual-layer structure increases interfacial integrity and current distribution, and the hydrophobic optimization controls liquid evacuation without reducing hydration stability. The nano-structured MPL is the pinnacle of such advances of design, with enhanced oxygen utilization, reduced interfacial resistance and uniform temperature throughout the active surface. All these results collectively indicate that an accurate regulation of microstructural parameters can be used to simultaneously increase efficiency, durability and operational robustness to provide a viable route towards the implementation of high-performance PEMFCs in maritime propulsion and auxiliary power systems.

4. Conclusion

It has been verified in the current research that the structural engineering of the Microporous Layer (MPL) can be made smarter to radically redefine the electrochemical and thermal characteristics of Proton Exchange Membrane Fuel Cells (PEMFCs) in a maritime setting. The research revealed that the manipulation of porosity gradient, pore-size hierarchy, and distribution of hydrophobic binders combined results in high-performance, water regulation, and longevity. The reduction of the mass transport losses, the enhancement of the capillary drainage, and the balanced membrane hydration, which is essential in the stable operation under the changing perspectives of humidity and load conditions in the sea, were consistent across all the tested designs. Replacing the traditional homogeneous MPL with a nano-structured architecture showed a 17.8% increase in the peak power density and a 22 decrease in the flood tendencies, but retained the same operating temperatures and the lifespan of a service of over 6,500 hours.

The gradient-porosity arrangement was effective in reducing diffusion resistance and permeability to gases, which formed the basis of controlled distribution of reactants within the catalyst layer. The dual-layer MPL also had the added advantage of delivering mechanical strength and directional water movement, which guarantee enhanced interface integrity as well as decreased wear in cyclic marine load profiles. Meanwhile, the hydrophobic-optimized design was successful to strike a balance between water repulsion at the cathode and hydration at the membrane keeping the saturation levels low without further causing dehydration. The nano-structured MPL which used conductive carbon nano-additives was the best in performance indicating better electrical contact, higher oxygen diffusivity, and low polarization losses. Overall, these structures prove that MPL microarchitecture does not only regulate the electrochemical dynamics, but also the mutually dependent heat and mass transfer processes that determine the PEMFC lifespan and stability.

In addition to personal enhancements, this study offers a predictive design-to-performance correlation model, which makes it possible to optimize the multi-parameter trade-offs among capillarity, porosity and conductivity in the marine-specific boundary conditions. The paper also highlights how hierarchical nanoengineering can be used to close the divide between the optimal results in the laboratory and the application in the ramifications of large-scale application in the real ships. The unintended synergy of increased oxygen delivery, improved heat uniformity, and decreased interfacial resistance is an excellent roadmap towards designing the next-generation PEMFC stacks that could be operated continuously and efficiently under the conditions of vibration, salinity, and dynamic loading at sea. The further studies are to be conducted on the experimental confirmation of the models given, association of real-time diagnostic control of dynamic load regulation, and investigation of hybrid MPL-GDL assemblies featuring adaptive hydrophobicity. The knowledge that has been generated during this research has not only provided to the body of science but also has provided the practical engineering direction that is necessary to ensure sustainable, efficient, and resilient marine energy systems that are in line with the IMO 2050 decarbonization goals.

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