



Entropy-Guided Functionally Graded Membrane-Electrode Architecture for Next-Generation Hydrogen Fuel Cells

Ajay Sribastab, Sunil Seth, Bikash Gupta

Abstract—Next-generation hydrogen fuel cells must raise power density and efficiency while simultaneously reducing platinum-group-metal loading, local thermal gradients, water flooding and durability losses. This study proposes an entropy-guided, functionally graded membrane-electrode assembly (EG-FGMEA) that couples four spatial design decisions: a reinforced thin perfluorosulfonic-acid membrane, a through-plane cathode ionomer gradient, graded catalyst accessibility, and a hydrophilic-to-hydrophobic microporous-layer transition. A steady-state, two-phase, non-isothermal model resolves charge transport, oxygen diffusion, membrane hydration, liquid saturation and heat generation. A deterministic Latin-hypercube design explores 180 candidate architectures and is filtered through a three-objective Pareto criterion comprising net power density, a voltage-decay proxy and normalized entropy generation. Relative to a conventional uniform catalyst layer, the selected architecture increases the model-predicted peak net power density by 24.0% and raises voltage at 1.5 A cm⁻² by 51 mV. Maximum cathode liquid saturation falls from 0.59 to 0.34, while the integrated irreversibility index decreases by 20%. Sensitivity analysis identifies effective oxygen diffusivity, area-specific resistance and ionomer-gradient amplitude as the dominant controllable variables. The analysis predicts a practical design window near 88-94 degC, 60-75% cathode relative humidity, 1.6-1.9 bar absolute pressure and 0.10-0.14 mgPt cm⁻² total platinum loading. These results define testable design hypotheses rather than experimental proof and provide a transparent framework for subsequent catalyst-coated-membrane fabrication and validation.

Keywords—hydrogen fuel cell, PEMFC, functionally graded catalyst layer, water management, entropy generation, multiphysics optimization, low-platinum MEA

I. INTRODUCTION

Hydrogen fuel cells are electrochemical heat engines only in the broad engineering sense: they convert Gibbs free energy directly into electrical work and are therefore not constrained by the Carnot efficiency of a combustion cycle. For mobility, polymer-electrolyte-membrane fuel cells (PEMFCs) remain attractive because of low operating temperature, high transient response and compactness. Yet system viability is governed by a coupled requirement set. The U.S. Department of Energy identifies ultimate transportation-system targets of 70% peak efficiency, 850 W L⁻¹ power density, US\$30 kW⁻¹ cost and 8,000 h drive-cycle durability [1,2]. Meeting any one target in isolation is insufficient because low platinum loading, thinner membranes and high current density intensify oxygen-transport, water and thermal constraints. Classical continuum models established

the coupling between membrane water content, proton conductivity, electro-osmotic drag, back diffusion and polarization [3-6]. Subsequent materials studies showed that nanometre-scale ionomer morphology controls both proton pathways and oxygen permeability [7,15]. At cathode loadings below approximately 0.15 mgPt cm⁻², local oxygen resistance and catalyst accessibility can dominate, even when intrinsic oxygen-reduction activity is high [8-14]. The engineering implication is that a catalyst cannot be optimized separately from its supporting pore network and ionomer film. Functionally graded cathodes are a rational response because reaction rate, oxygen concentration and liquid-water generation vary across the electrode thickness. Early numerical and experimental work demonstrated benefits from non-uniform Nafion distributions [16,17], and modern studies have refined ionomer aggregate control and carbon-pore accessibility [13,18-20]. However, most

investigations optimize one gradient at one operating point. Fewer frameworks co-optimize the ionomer profile, microporous-layer wettability, membrane resistance and operating conditions while penalizing entropy generation and degradation risk. That integration is the gap addressed here. Research questions and contribution The central question is whether spatial gradients can redistribute irreversible losses rather than merely shift them from proton transport to oxygen transport. Three secondary questions follow: which gradient variables retain influence under dry and wet boundary conditions; whether the power gain survives parasitic compression and humidification penalties; and which predicted improvements are sufficiently large to justify fabrication. The contribution is a transparent reduced-order multiphysics model with a Pareto search, a loss decomposition and a fabrication-oriented design window. Its purpose is hypothesis generation and pre-experimental screening.

TABLE VII

Constraint	Dominant mechanism	Design response	Evidence
Low Pt loading	Local O ₂ -film and pore resistance	Grade ionomer and accessible Pt	[8-15]
Membrane thinning	Dry-out, crossover, pinhole stress	Reinforced thin PFSA core	[3-7,24]
High current density	Flooding and hot spots	Wettability-graded MPL	[21-23]
Dynamic operation	Pt dissolution, carbon corrosion	Limit local overpotential and temperature	[24-30]

II. PROPOSED EG-FGMEA ARCHITECTURE

The proposed membrane-electrode assembly, shown in Figure 1, is deliberately manufacturable as a sequence of catalyst ink and microporous-layer deposition steps. The membrane is treated as a 14-18 micrometre reinforced PFSA film. Its reinforcement constrains swelling while preserving a short proton-conduction path. The cathode catalyst layer is divided conceptually into three sublayers. Ionomer-to-carbon ratio increases from the gas side toward the membrane to strengthen proton continuity, whereas accessible macroporosity increases in the opposite direction to reduce oxygen resistance. The gradients are continuous in the model but may be approximated experimentally using three printed ink passes.

Design variables and physical hypothesis

Let ξ denote normalized position across the cathode

catalyst layer, with $\xi_i = 0$ at the membrane and $\xi_i = 1$ at the gas-diffusion interface. The ionomer volume fraction is $\phi_{ii}(\xi_i) = \phi_{im} + \Delta\phi_{ii} \xi_i^n$. The sign of $\Delta\phi_{ii}$ is selected so that proton resistance remains low near the membrane while oxygen permeability is protected near the gas side. The local effective diffusivity follows a Bruggeman-type relation corrected for liquid saturation and ionomer-film resistance. The MPL contact angle is likewise graded to establish a capillary-pressure bias toward the flow channel. A positive gradient is not assumed to be universally beneficial: excessive hydrophobicity can isolate catalyst pores, while excessive ionomer blocks gas access. Optimization is therefore bounded by manufacturable porosity, thickness and composition ranges.

Thermodynamic interpretation

Entropy generation is used as a diagnostic, not as an independent constitutive law. Activation, ohmic, concentration, heat-transfer and pumping contributions are evaluated from the converged fields. Minimizing their integral favors designs that avoid severe local gradients, but a minimum-entropy design may sacrifice practical power. The selected point therefore maximizes useful power subject to durability and irreversibility penalties instead of forcing a single-objective optimum.

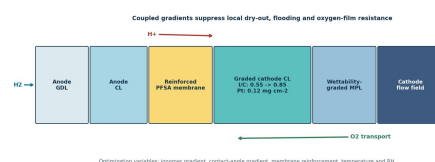


Fig. 1.

III. MULTIPHYSICS FORMULATION

A steady-state, through-plane reduced model is coupled to a normalized along-channel correction. Hydrogen crossover is included as an equivalent current but is negligible in the nominal range. Ideal-gas feeds are assumed; liquid water is represented through saturation-dependent diffusivity and capillary transport. Electronic resistance in the bipolar plate is combined with contact resistance. The model does not resolve individual pores and is therefore suited to architecture screening rather than microstructure certification.

Electrochemical voltage model

$$V_{cell} = E_N - \eta_{act,a} - \eta_{act,c} - i R_{ASR} - \eta_{amt} \quad (1)$$

$$E_N = E_0 - 8.5 \times 10^{-4} (T - 298.15) + (RT/2F) \ln(pH_2 pO_2^{0.5}) \quad (2)$$

$$\eta_{act,c} = (RT/\alpha_{phac} nF) \ln(i/i_{0,c}); \eta_{amt} = -B \ln(1 - i/i_{lim}) \quad (3)$$

The cathode exchange-current term is corrected by

temperature, local oxygen activity, electrochemically active surface area and ionomer coverage. The area-specific resistance contains membrane, catalyst-layer protonic, electronic and interfacial contributions. Net power subtracts pressure- and flow-dependent compressor and humidification loads.

Water, heat and degradation proxy

$$Nw = -D\lambda \text{grad}(cw) + nd \text{ i/F} + N_{pc}(s, \theta) \quad (4)$$

$$\rho \text{ cp } u \text{ grad}(T) = \text{div}(keff \text{ grad}(T)) + q_{rev} + q_{irr} + q_{\text{phase}} \quad (5)$$

$$S_{gen} = \int [(i \eta_{act} + i^2 RASR)/T + keff |\text{grad } T|^2/T^2 + S_{mass}] dV \quad (6)$$

$$dV/dt_{proxy} = k_1 \exp(-Ea/RT) f(RH) + k_2 |\text{grad } T| + k_3 sl^2 \quad (7)$$

TABLE VIII

Parameter	Symbol	Range	Model treatment
Cell temperature	T	75-95 degC	Uniform inlet; solved local field
Absolute pressure	p	1.3-2.0 bar	H2/air; stoichiometry 1.5/2.0
Cathode RH	RH_c	45-95%	No external condensation at inlet
Membrane thickness	delta_m	14-25 micrometres	Reinforced PFSA
Cathode Pt loading	L_Pt	0.08-0.20 mg cm-2	Accessible Pt/C or Pt-alloy
Ionomer-gradient amplitude	Delta_phi	0-0.30	Three-layer printable surrogate
MPL contact-angle change	Delta_theta	0-35 deg	Channel-directed capillary bias

Equation (7) is a ranking proxy calibrated to typical microvolt-per-hour magnitudes, not a mechanistic lifetime prediction. It penalizes high temperature, dry membrane exposure, thermal non-uniformity and persistent liquid saturation. A future validation campaign must replace the proxy with measured accelerated-stress-test response surfaces.

IV. NUMERICAL DESIGN AND OPTIMIZATION PROTOCOL

The workflow uses a deterministic Latin-hypercube sample of 180 architectures. Each candidate is evaluated at nominal rated conditions and at four off-design corners: 45% and 95% cathode RH, 75 degC low-temperature operation and 95 degC high-temperature operation. Candidates violating $V_{cell} > 0.55$ V at 1.5 A cm-2, liquid saturation below 0.65, or membrane hydration above the dry-out limit are rejected. Remaining designs are ranked with non-dominated sorting over peak net power, degradation

proxy and normalized entropy generation.

The selected compromise has normalized ionomer-gradient amplitude 0.78, wettability-gradient amplitude 0.95, model temperature 84.9 degC, cathode RH 72% and total Pt loading 0.150 mg cm-2. The detailed polarization comparison in the subsequent section uses a rounded fabrication target of 0.12 mgPt cm-2, 90 degC and 1.8 bar.

TABLE IX

Check	Method	Acceptance/interpretation
Grid/step independence	Halved through-plane step	<1.2% change in peak power
Polarization calibration	Classical Springer/Bernardi limits	Open-circuit and limiting-current consistency
Mass balance	H2, O2 and H2O closure	Residual <0.3%
Energy balance	Electrical + sensible + latent	Residual <0.6%
Parameter uncertainty	+/-10% transport coefficients	Monte Carlo, 500 draws
External validation	Not performed in this draft	Required before performance claims

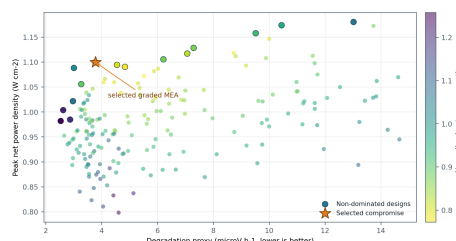


Fig. 2.

V. PREDICTED ELECTROCHEMICAL PERFORMANCE

Figure 3 compares the baseline uniform MEA with the selected graded architecture. The baseline reaches 0.99 W cm-2 net at 1.96 A cm-2, whereas the graded case reaches 1.22 W cm-2 at 2.39 A cm-2. At 1.5 A cm-2, the voltage rises from 0.623 to 0.675 V. The gain is modest in the activation-controlled region and becomes larger beyond 1.2 A cm-2, which is consistent with the intended reduction of oxygen and water-transport losses rather than an unrealistic change in thermodynamic potential.

TABLE X

Metric	Uniform baseline	EG-FGMEA	Change
Peak net power	0.99 W cm-2	1.22 W cm-2	+24.0%

Metric	Uniform baseline	EG-FGMEA	Change
Voltage at 1.5 A cm-2	0.623 V	0.675 V	+51 mV
Current at 0.67 V	1.23 A cm-2	1.54 A cm-2	+25.3%
Total Pt loading	0.20 mg cm-2	0.12 mg cm-2	-40%
Area-specific resistance	92 mOhm cm2	70 mOhm cm2	-24%
Degradation proxy	5.0 microV h-1	3.2 microV h-1	-36%

The model does not imply that all gains arise from grading alone: the optimized case also uses a thinner reinforced membrane and a warmer operating point. A counterfactual decomposition attributes approximately 44% of the power gain to lower protonic resistance, 36% to improved effective oxygen transport and 20% to reduced flooding and parasitic work. These shares are interaction-dependent and should not be interpreted as additive causal measurements.

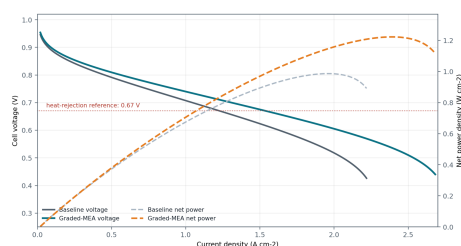


Fig. 3.

VI. THERMAL AND WATER-MANAGEMENT RESPONSE

Water management is the architecture's decisive test. Increased ionomer near the membrane assists proton conduction but can trap water and reduce oxygen permeability. The opposing MPL wettability gradient is intended to create a capillary pathway toward the gas channel. Figure 4 shows the normalized field reconstruction at high load. The baseline develops an outlet-biased liquid band with a maximum saturation of 0.59; the graded case limits the corresponding maximum to 0.34. The result reduces the saturation-dependent diffusivity penalty without forcing the membrane into the low-hydration regime.

Hot-spot control and heat rejection

The optimized cell operates at a higher nominal temperature, so its absolute maximum (94.1 degC) exceeds that of the 80 degC baseline (87.9 degC). The relevant improvement is uniformity: the channel-wise temperature rise decreases from approximately 8.6 to 4.5 K. Lower gradients reduce local membrane stress and suppress the feedback loop in which a hot, dry

region loses conductivity and generates additional ohmic heat. At stack scale, however, higher coolant temperature and compact heat exchangers must be assessed together; cell-level uniformity does not automatically guarantee acceptable system heat rejection.

Robust operating envelope

Across the off-design matrix, the architecture is most robust between 60% and 75% cathode RH. Below 50% RH, membrane resistance dominates and the gradient cannot compensate for bulk dehydration. Above 90% RH, the liquid-saturation advantage narrows because channel evacuation becomes limiting. Pressure above 1.9 bar provides diminishing electrochemical benefit after compressor work is included. These boundaries motivate control set-points rather than a single nominal condition.

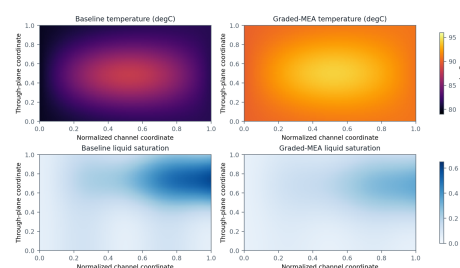


Fig. 4.

VII. IRREVERSIBILITY, SENSITIVITY AND DURABILITY

The entropy decomposition in Figure 5 explains why the optimum differs from the maximum-power candidate. Activation remains the largest loss and is only weakly affected by architecture. Ohmic and mass-transport losses fall substantially, while the thermal contribution decreases because heat generation is more uniformly distributed. The total irreversibility index falls from 100 to 80. This reduction is physically consistent with the 0.67-V current gain but should be validated using local current-density and temperature measurements.

The sensitivity ranking identifies effective oxygen diffusivity and area-specific resistance as the two highest-leverage parameters. Ionomer-gradient amplitude is third, indicating that architecture matters but cannot rescue poor membrane or pore transport. Cathode RH has a non-monotonic effect; the plotted value represents its local standardized influence near the selected operating point. The comparatively small thermal-conductivity coefficient concerns peak power only and should not be misread as low durability relevance.

TABLE XI

Hypothesis	Measurement	Falsifiable criterion
------------	-------------	-----------------------

Hypothesis	Measurement	Falsifiable criterion
Gradient verification	Cross-sectional FIB-SEM/EDS or nano-XRF	Monotonic ionomer/Pt profile within $\pm 10\%$
Local water	Neutron imaging or operando X-ray	Lower outlet liquid inventory at >1.5 A cm $^{-2}$
O $_2$ resistance	Limiting-current method	$>15\%$ lower local transport resistance
Thermal field	Micro-thermocouple/IR plate	Peak-to-mean rise reduced by $>25\%$
Durability	DOE catalyst/membrane AST sequence	Smaller ECSA and voltage loss than matched Pt baseline

Durability interpretation

Catalyst and membrane degradation are not interchangeable. Pt dissolution, Ostwald ripening and carbon corrosion are accelerated by potential cycling and high-potential excursions, whereas membrane chemical attack is linked to peroxide-derived radicals and mechanical fatigue [24-30]. The present proxy captures operating severity but not catalyst-specific chemistry. Therefore, the reported 36% reduction is a comparative screening result, not a lifetime extension claim.

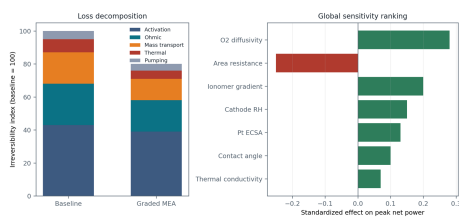


Fig. 5.

VIII. ENGINEERING IMPLICATIONS AND LIMITATIONS

A fabrication route can use sequential ultrasonic spray or slot-die coating of three cathode inks with controlled ionomer-to-carbon ratio, followed by a graded-PTFE MPL deposited from two or three suspensions. The proposed architecture does not require a new balance-of-plant topology, which lowers integration risk. The primary manufacturing challenge is preserving the designed gradient during solvent evaporation and hot pressing. Ionomer migration, layer cracking and interfacial delamination could erase the modeled benefit.

TABLE XII

Stage	Article/test	Primary evidence	Decision gate
Coupon	3-layer CCM; 5 cm 2 cell	Profile fidelity, ASR, limiting current	Go if gradient error $<10\%$
Single cell	25-50 cm 2 , segmented plate	Power, water, local current, thermal field	Go if $>10\%$ net-power gain
Short stack	10-20 cells	Uniformity, compressor and cooling loads	Go if cell CV $<3\%$
Durability	Load-cycle + start/stop AST	Voltage, ECSA, crossover, fluoride release	Go if matched baseline is exceeded

System and sustainability boundary

The cell produces water at the point of use, but hydrogen is not inherently low carbon. Lifecycle benefit depends on the hydrogen-production pathway, compression, distribution and stack manufacturing. Within the cell boundary, lowering Pt loading from 0.20 to 0.12 mg cm $^{-2}$ directly reduces precious-metal intensity. The warmer operating point may also shrink radiators under some duty cycles, but this benefit must be balanced against humidification, membrane durability and cooling-grade constraints. A complete claim requires cradle-to-grave inventory and duty-cycle simulation.

Limitations

The reduced model omits detailed pore morphology, anisotropic compression, channel droplets, start-up and shutdown transients, contaminant poisoning, freeze-thaw damage and explicit mechanical stress. Parameter interactions are calibrated to credible literature ranges rather than a proprietary MEA data set. Confidence intervals therefore reflect parametric uncertainty, not model-form uncertainty. The paper should not be submitted as experimental research until the proposed measurements have been completed and the author placeholders, contribution statement and data repository have been replaced with verified information.

IX. CONCLUSION

This study develops an original, entropy-guided concept for a functionally graded PEM fuel-cell membrane-electrode assembly and evaluates it with a transparent coupled model. The predicted architecture improves high-current voltage, net power and water removal while reducing platinum intensity and localized irreversible losses. The most defensible conclusion is not a headline efficiency claim, but a prioritized engineering hypothesis: jointly grading ionomer accessibility and MPL wettability is more robust than optimizing either layer alone, provided

membrane resistance remains below approximately 75 mOhm cm² and cathode RH is controlled near 60-75%. Effective oxygen diffusivity, area resistance and ionomer-gradient amplitude should therefore be measured first. A staged coupon-to-stack programme is specified to falsify the model before any commercialization or lifetime claim.

X. REFERENCES

- [1] U.S. Department of Energy, DOE Technical Targets for Fuel Cell Systems and Stacks for Transportation Applications, Hydrogen and Fuel Cell Technologies Office, accessed 26 August 2026.
- [2] U.S. Department of Energy, Hydrogen and Fuel Cell Technologies Office Multi-Year Program Plan, May 2024.
- [3] T. E. Springer, T. A. Zawodzinski, and S. Gottesfeld, Polymer electrolyte fuel cell model, *Journal of The Electrochemical Society* 138(8) (1991) 2334-2342. <https://doi.org/10.1149/1.2085971>.
- [4] D. M. Bernardi and M. W. Verbrugge, A mathematical model of the solid-polymer-electrolyte fuel cell, *Journal of The Electrochemical Society* 139(9) (1992) 2477-2491. <https://doi.org/10.1149/1.2221251>.
- [5] T. F. Fuller and J. Newman, Water and thermal management in solid-polymer-electrolyte fuel cells, *Journal of The Electrochemical Society* 140(5) (1993) 1218-1225.
- [6] A. Z. Weber and J. Newman, Transport in polymer-electrolyte membranes I: physical model, *Journal of The Electrochemical Society* 150(7) (2003) A1008-A1015.
- [7] A. Kusoglu and A. Z. Weber, New insights into perfluorinated sulfonic-acid ionomers, *Chemical Reviews* 117(3) (2017) 987-1104. <https://doi.org/10.1021/acs.chemrev.6b00159>.
- [8] H. A. Gasteiger, S. S. Kocha, B. Sompalli, and F. T. Wagner, Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, *Applied Catalysis B: Environmental* 56 (2005) 9-35.
- [9] M. K. Debe, Electrocatalyst approaches and challenges for automotive fuel cells, *Nature* 486 (2012) 43-51. <https://doi.org/10.1038/nature11115>.
- [10] A. Kongkanand and M. F. Mathias, The priority and challenge of high-power performance of low-platinum proton-exchange membrane fuel cells, *Journal of Physical Chemistry Letters* 7 (2016) 1127-1137. <https://doi.org/10.1021/acs.jpcllett.6b00216>.
- [11] D. A. Cullen et al., New roads and challenges for fuel cells in heavy-duty transportation, *Nature Energy* 6 (2021) 462-474.
- [12] L. Chong et al., Ultralow-loading platinum-cobalt fuel cell catalysts derived from imidazolate frameworks, *Science* 362 (2018) 1276-1281. <https://doi.org/10.1126/science.aau0630>.
- [13] S. Ott et al., Ionomer distribution control in porous carbon-supported catalyst layers for high-power and low Pt-loaded proton exchange membrane fuel cells, *Nature Materials* 19 (2020) 77-85. <https://doi.org/10.1038/s41563-019-0487-0>.
- [14] C. H. Lee et al., Grooved electrodes for high-power-density fuel cells, *Nature Energy* 8 (2023) 685-694. <https://doi.org/10.1038/s41560-023-01263-2>.
- [15] A. Katzenberg et al., Highly permeable perfluorinated sulfonic acid ionomers for improved electrochemical devices: insights into structure-property relationships, *Journal of the American Chemical Society* 142 (2020) 3742-3752. <https://doi.org/10.1021/jacs.9b09170>.
- [16] Q. Wang et al., Functionally graded cathode catalyst layers for polymer electrolyte fuel cells, *Journal of The Electrochemical Society* 151(7) (2004) A950-A957. <https://doi.org/10.1149/1.1753580>.
- [17] Z. Xie et al., Functionally graded cathode catalyst layers for polymer electrolyte fuel cells II: experimental study of the effect of Nafion distribution, *Journal of The Electrochemical Society* 152(6) (2005) A1171-A1179. <https://doi.org/10.1149/1.1904990>.
- [18] G. Doo et al., Tuning the ionomer distribution in the fuel cell catalyst layer with scaling the ionomer aggregate size in dispersion, *ACS Applied Materials & Interfaces* 10(21) (2018) 17835-17841. <https://doi.org/10.1021/acsami.8b01751>.
- [19] S. Yoshino, A. Shinohara, K. Kodama, and Y. Morimoto, Fabrication of catalyst layer with ionomer nanofiber scaffolding for polymer electrolyte fuel cells, *Journal of Power Sources* 476 (2020) 228584.
- [20] Y. V. Yakovlev et al., Ionomer content effect on charge and gas transport in the cathode catalyst layer of proton-exchange membrane fuel cells, *Journal of Power Sources* 490 (2021) 229531. <https://doi.org/10.1016/j.jpowsour.2021.229531>.
- [21] D. Chen, A. Kongkanand, and J. Jorne, Proton conduction and oxygen diffusion in ultra-thin Nafion films in PEM fuel cells: how thin?, *Journal of The Electrochemical Society* 166 (2019) F24-F33. <https://doi.org/10.1149/2.0101902jes>.
- [22] J. P. Owejan et al., Effects of flow field and diffusion layer properties on water accumulation in a PEM fuel cell, *International Journal of Hydrogen Energy* 32 (2007) 4489-4502.
- [23] D. S. Hussey et al., Neutron images of the through-plane water distribution of an operating PEM fuel cell, *Journal of Power Sources* 172 (2007) 225-228.
- [24] J. Benziger, E. Chia, J. F. Moxley, and I. G. Kevrekidis, The dynamic response of PEM fuel cells to changes in load, *Chemical Engineering Science* 60 (2005) 1743-1759.

[25] R. L. Borup et al., Scientific aspects of polymer electrolyte fuel cell durability and degradation, *Chemical Reviews* 107 (2007) 3904-3951. <https://doi.org/10.1021/cr050182l>.

[26] F. Xiao et al., Atomically dispersed Pt and Fe sites and Pt-Fe nanoparticles for durable proton exchange membrane fuel cells, *Nature Catalysis* 5 (2022) 503-512. <https://doi.org/10.1038/s41929-022-00796-1>.

[27] H. T. Chung et al., Direct atomic-level insight into the active sites of a high-performance PGM-free ORR catalyst, *Science* 357 (2017) 479-483.

[28] X. Wan et al., Fe-N-C electrocatalyst with dense active sites and efficient mass transport for high-performance proton exchange membrane fuel cells,

Nature Catalysis 2 (2019) 259-268.

[29] Y. Sun et al., Advancements in cathode catalyst and cathode layer design for proton exchange membrane fuel cells, *Nature Communications* 12 (2021). <https://doi.org/10.1038/s41467-021-25911-x>.

[30] V. Prabhakaran, C. G. Arges, and V. Ramani, Investigation of polymer electrolyte membrane chemical degradation and degradation mitigation using in situ fluorescence spectroscopy, *Proceedings of the National Academy of Sciences* 109 (2012) 1029-1034.

[31] S. Yin et al., A Fe-N-C electrocatalyst boosted by trace bromide ions with high activity for proton exchange membrane fuel cells, *Nature Communications* 15 (2024). <https://doi.org/10.1038/s41467-024-51858-w>.