

**Efficient PEM Fuel Cell Catalysts Layer
Derived from Biomass**

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List of Abbreviations

Abbreviation	Full Name
CAGR	Compound Annual Growth Rate
CCM	Catalyst Coated Membrane
CL	Catalyst Layer
cryo-TEM	cryogenic Transmission Electron Microscopy
CTAB	Cetyltrimethyl Ammonium Bromide
DFT	Density Functional Theory
DOE	U.S. Department of Energy
ECSA	Electrochemically Active Surface Area
EIS	Electrochemical Impedance Spectroscopy
EISA	Evaporation Induced Self-Assembly
ESRF	European Synchrotron Radiation Facility
FCEV	Fuel Cell Electric Vehicles
FET	Floating Electrode Technique
GCN	Generalized Coordination Number
GDE	Gas Diffusion Electrode
GDL	Gas Diffusion Layer
HAADF-STEM	High-Angle Annular Dark Field-Scanning Transmission Electron Microscopy
HOMC	Highly Ordered Mesoporous Carbon
HOR	Hydrogen Oxidation Reaction
HTC	Hydrothermal Carbonization
ICP-MS	Inductively Coupled Plasma Mass Spectrometry

IL-TEM	Identical-Location Transmission Electron Microscopy
IO	Inverse Opal
MA	Mass Activity
MEA	Membrane Electrode Assembly
MPL	Microporous Layer
NP	Nanoparticle
ORR	Oxygen Reduction Reaction
PEM	Proton Exchange Membrane
PEMFC	Proton Exchange Membrane Fuel Cell
PFSA	Perfluorinated Sulfonic Acid
PGM	Platinum Group Metals
Pt/C	Platinum Nanoparticles deposited on carbon
PTFE	Polytetrafluoroethylene
PV	Photovoltaic
RDE	Rotating Disk Electrode
RHE	Reversible Hydrogen Electrode
R_u	Uncompensated Resistance
SAXS	Small Angle X-ray Scattering
USAXS	Ultra-Small Angle X-ray Scattering
XAS	X-ray Absorption Spectroscopy
XANES	X-ray Absorption Near Edge Structure
μ CP	Micro-Contact Printing
μ TM	Micro-Transfer Molding

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2. **Mengnan Wang**, Jianguang Zhang, Maria-Magdalena Titirici*; Efficient Catalyst Layer for PEMFC Developed from Lignin. in preparation
3. Chantal Glatthaar, **Mengnan Wang***, Lysander Q. Wagner, Frederik Breckwoldt, Zhenyu Guo, Kaitian Zheng, Manfred Kriechbaum, Heinz Amenitsch, Magdalena Titirici*, and Bernd M. Smarsly* Lignin-derived Mesoporous Carbon for Sodium-Ion Batteries: Block Copolymer Soft Templating and Carbon Microstructure Analysis, Chemistry of Materials, accepted
4. Qi Li, Yue Xu, Angus Pedersen, **Mengnan Wang**, Mi Zhang, Jingyu Feng, Hui Luo, Maria-Magdalena Titirici* and Christopher R. Jones*; Investigating the role of Fe-Pyrrolic N4 configuration in the Oxygen Reduction Reaction via covalently bound porphyrin functionalized carbon nanotubes, Advanced Functional Materials, submitted
5. Guangmeimei Yang, Yuxiang Zhou, **Mengnan Wang**, James Murawski, Louise Oldham, Tian Tian, Ifan E.L. Stephens*, and Andreas Kafizas*; Elucidating the Effect of Nitrogen Occupancy on the Hydrogen Evolution Reaction for a Series of Titanium Oxynitride Electrocatalysts, ChemCatChem, 2023, e202300687
6. Aleena Tahir, Tanveer ul Haq, Faria Rafique Basra, Hatice Duran, Joe Briscoe, **Mengnan Wang**, Maria-Magdalena Titirici, Irshad Hussain, and Habib Ur Rehman*; Electronic and surface modifications of Ni-Co-Fe oxides: A catalyst with maximum exposure of Fe active sites for water electrolysis, ACS Applied Engineering Materials, 2023, 1, 7, 1698–1710

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10. Rui Tan, Anqi Wang, Irene Bechis, Charlotte Breakwell, **Mengnan Wang**, Zhiyu Fan, Dezhi Liu, Joshua M. Tuffnell, Alberto Alvarez-Fernandez, Shengming Zhang, Tomas Juergensen, Hannah L. Pilsworth⁷, Tongchao Liu, Stefan Guldin, John V. Hanna, Ifan E. L. Stephens, Maria Magdalena Titirici, Wei Li, Anthony K. Cheetham, Kim E. Jelfs, Thomas D. Bennett, Qilei Song*, Pressure-sintered monolithic metal-organic framework membranes for selective ionic and molecular transport, *Nature*, submitted, 2022
11. Jesús Barrio, Angus Pedersen, Silvia Favero, Hui Luo, **Mengnan Wang**, Saurav Ch. Sarma, Jingyu Feng, Linh Tran, Simon Kellner, Alain Li; Ana Belen Jorge Sobrido, Maria-Magdalena Titirici*, Bio-Inspired and Bio-Derived Aqueous Electrocatalysis, *Chemical Reviews*, accepted, 2022
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13. Hao Zhang, Peng Li, Haochen Zhou, Jiamin Xu, Qianfan Jiang, Joseph H. L. Hadden, Yanying Wang, **Mengnan Wang**, Shengli Chen,* Fang Xie, D. Jason Riley*; Unravelling the Synergy of Oxygen Vacancies and Gold Nanostars in Hematite for Electrochemical and Photoelectrochemical Oxygen Evolution Reaction, *Nano Energy*, 2022, 94, 106968

Abstract

Global warming is a critical issue requiring immediate action towards net-zero emissions. Proton Exchange Membrane Fuel Cells (PEMFCs) are seen as a key technology in this shift by reducing reliance on fossil fuels. The effectiveness of PEMFCs largely depends on the development of catalysts, particularly for the Oxygen Reduction Reaction (ORR) at the cathode. Presently, platinum-based catalysts dominate, but they are expensive and scarce, limiting overall PEMFC efficiency. This thesis addresses three main challenges in PEMFC catalyst development: lack of intermediate testing platforms, understanding of local transport dynamics, and efficient catalyst layer architecture.

The research employs an interdisciplinary approach, combining materials science, electrochemistry, and engineering. A Gas Diffusion Electrode (GDE) was developed for realistic ORR measurement conditions. To enhance ionomer interaction with the catalyst, the study used biomass-derived carbon nanostructures, specifically creating 4nm mesopores in hydrothermal carbonization of xylose. This structure showed improved ORR efficiency, confirmed by operando X-ray Absorption Spectroscopy measurements and structural characterization.

Furthermore, a freestanding carbon film with a hierarchical architecture was designed, using lignin and dual templating techniques for better mass transport and ORR performance. This architecture especially improved performance in mass transport-dominant areas.

In conclusion, the thesis systematically tackles key barriers in PEMFC catalyst layer development. Through experimental innovation and strategic integration of various scientific principles, it offers a rational design strategy for advancing PEMFC technology. This contributes valuable insights and practical solutions for sustainable energy development in the fight against climate change.

Introduction

1.1 Global Warming and its Consequences

The UK Met Office recently confirmed that 2022 was the warmest year on record in the United Kingdom, a tangible manifestation of the severe climate changes that are occurring worldwide.¹ The global mean temperature is now 1.2 °C above pre-industrial levels, signalling a rapidly warming planet (Figure 1). These rising temperatures present a formidable threat to our planet and have a myriad of far-reaching effects. For example, the melting of glaciers and polar ice, one of the most direct consequences of global warming, leads to sea-level rise and the submergence of terrestrial habitats. Changes in the precipitation cycle exacerbate a variety of natural disasters, including storms, floods, and droughts, which poses a significant threat to biodiversity and jeopardizes our food and water security.

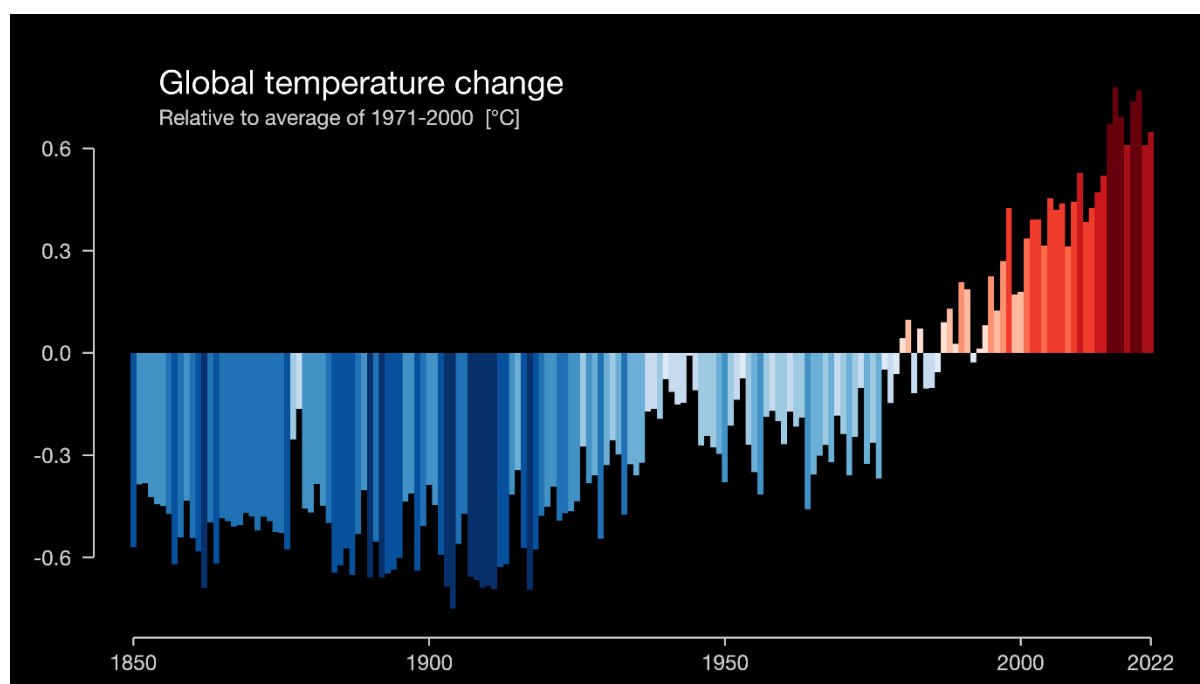


Figure 1. Global mean temperature increase since 1850. Data Source: UK Met Office. Figure reproduced from ²

These global changes were highlighted within the framework of the Paris Agreement of 2015,³ where the international community acknowledged the imperative of constraining global temperature rise to below 2°C, with an even more desirable target of 1.5°C above pre-industrial levels. To achieve this objective, a substantial reduction in greenhouse gas emissions, particularly carbon dioxide (CO₂), is urged within a specified timeframe.

1.2 The Concept of "Net Zero" and its Importance

To effectively curb global warming, the concept of "net zero" is of crucial significance.

'Net zero' is a term that encapsulates a state of equilibrium between the quantity of greenhouse gases introduced into the atmosphere and the amount concurrently removed. In a 'net zero' scenario, anthropogenic emissions are effectively counteracted by the amount being sequestered or offset through various mitigation measures.

Initiatives on a global scale aimed at reaching 'net zero' have been gaining momentum. By the year 2023, a substantial number of countries, over seventy in total, have established a net-zero objective. This group includes the most significant contributors to global emissions: China, the United States, and the European Union. Consequently, these commitments encompass approximately 76% of worldwide emissions.⁴ Beyond national boundaries, this commitment extends to cities, regions, and businesses globally which are all setting 'net zero' targets. Major corporations globally are acknowledging their roles in the fight against climate change and are actively seeking methods to neutralize their carbon footprints.

Nonetheless, the attainment of 'net zero' is a complicated undertaking, extending beyond simple declarations. It necessitates fundamental shifts in energy generation, transportation infrastructure and industrial practices.

1.3 Proton Exchange Membrane Fuel Cell

The predominant reliance on fossil fuel-based energy systems stands as the primary driver of excessive CO₂ emissions. Therefore, it becomes crucial to initiate a transition towards renewable energy sources, thereby displacing the current fossil fuel-dominated paradigm. Several sustainable and environmentally friendly energy technologies have been proposed and implemented to decarbonize the global economy, including solar photovoltaic (PV) systems, wind turbines, geothermal energy, hydroelectric power, and modern use of biomass etc. Among these technologies, the Proton Exchange Membrane Fuel Cell (PEMFC) has garnered significant interest. It utilizes hydrogen (H₂) as fuel and produces electricity and water as the only byproduct. The market for proton exchange membrane fuel cells is expected to experience substantial growth, with its value projected to increase from \$2.10 billion in 2021 to \$22.74 billion by 2028, indicating a compound annual growth rate (CAGR) of 40.6%.⁵ In the year of 2020, 72% of PEMFC was applied in the transportation sector while the rest 28% was used as stationary energy supply.⁵ Other market reports have shown similar prospects. According to

Precedence Research, the global hydrogen fuel cell vehicle market size was estimated at USD 0.65 billion in 2021 and is projected to reach approximately USD 43.19 billion by 2030, with a significant CAGR of 59.4% from 2022 to 2030.⁶

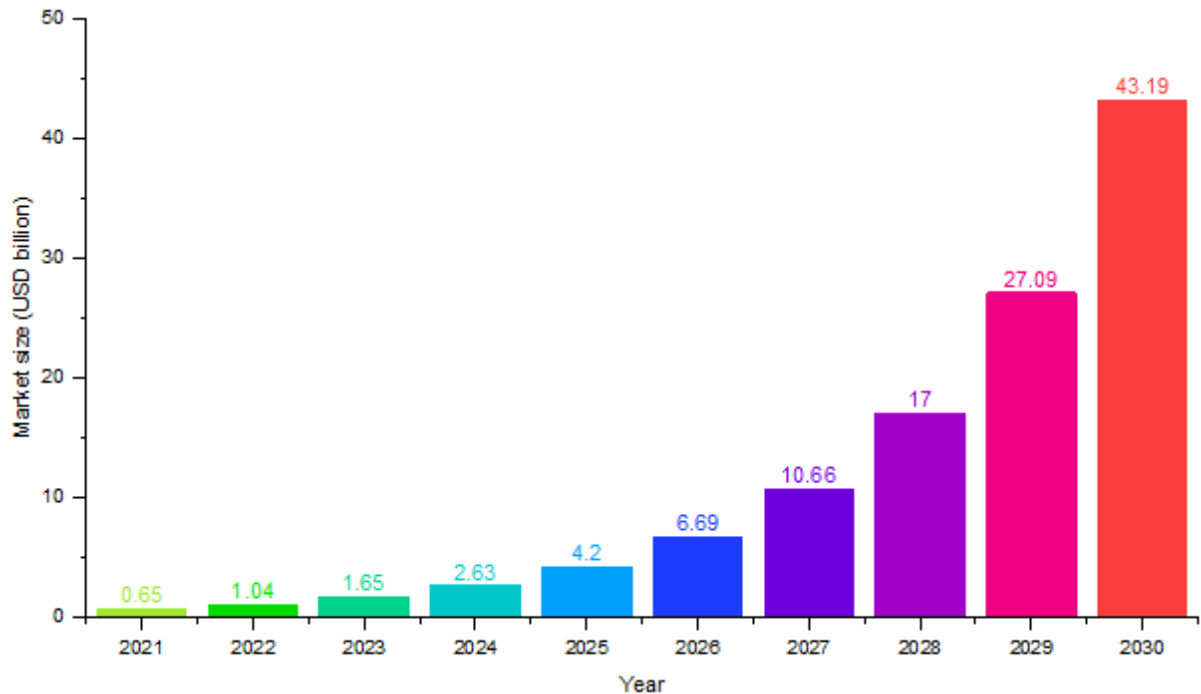


Figure 2. Projected Hydrogen Fuel Cell Vehicle Market size, 2021 to 2030. Replotted with data from Precedence Research⁶

A PEMFC consists of several key components, including a hydrogen fuel stream, an oxygen stream for reacting with the hydrogen, a proton-conducting membrane, an electrolyte, and catalyst-coated electrodes for both the anode and the cathode. As illustrated in Figure 3, hydrogen gas (H_2) is electrochemically oxidized at the anode, producing protons (H^+) and electrons through the hydrogen oxidation reaction (HOR). The electrons flow through an external circuit to provide power for connected devices before eventually reaching the cathode. On the other hand, the protons migrate through the electrolyte and membrane to the cathode side, where the oxygen reduction reaction (ORR) occurs in the presence of oxygen, protons, and electrons. The only byproduct of this process is water.

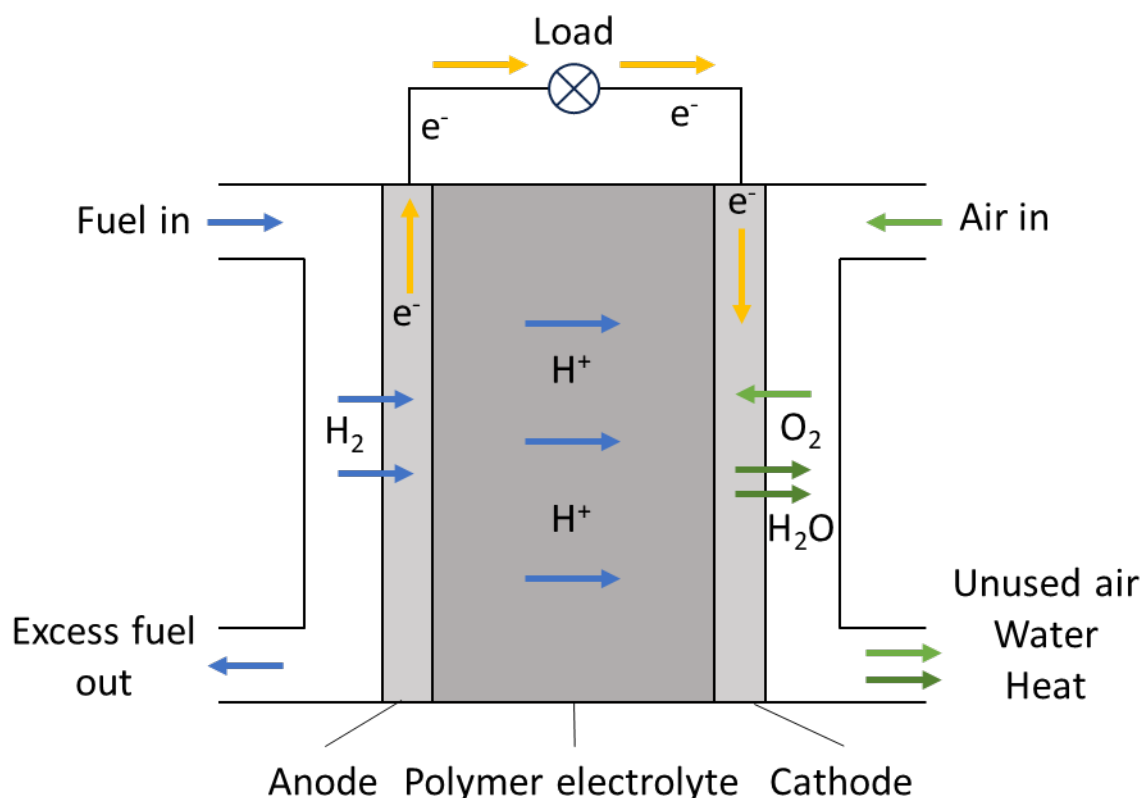


Figure 3. Schematic Diagram of a Typical Proton Exchange Membrane Fuel Cell (PEMFC), illustrating the essential components including the anode, cathode, electrolyte membrane, and the two reactions happening at cathode (ORR) and anode (HOR).

Currently, the most effective catalyst for these two reactions still relies on platinum group metals (PGM)⁷⁸, which poses a major obstacle to the widespread commercialization of PEMFCs due to their scarcity and uneven distribution. For the HOR, the reaction mechanism is simpler, involving the splitting of a hydrogen molecule into two protons and two electrons. This reaction has fewer intermediates, and the hydrogen molecule's interaction with platinum is very favorable. This leads to faster kinetics, fewer complications from intermediates or side reactions, and hence, a vanishingly small voltage loss (less than 5 mV loss at Pt anode loadings of 0.05 mg/cm²).⁹ Compared to HOR, the kinetics of ORR are significantly slower, and challenges with oxygen transport and solubility are more pronounced, resulting in a higher overpotential. The loading required at the cathode is usually around 0.3 mg/cm², much higher than that of the anode. This makes ORR the central focus of fuel cell catalyst development. If we assume that the fuel cell vehicle will make up 10% of the electric vehicle market by 2023, this will mean that there would be approximately 350 million fuel cell electric vehicles (FCEV) on road.¹⁰ This translates into a requirement of at least 1000 tones Pt in the transportation sector

alone, based on an average 30 g Pt loading for an 85-kW electric engine.¹¹¹² This poses a significant challenge to the Pt supply as its current global production in 2022 is recorded less than 200 tones.¹³

1.4 The Promise of Green Carbon from Biomass

Carbon materials play a critical role in energy conversion and storage devices due to their superior electronic conductivity, tailorable surface chemistry, and tuneable porous structures.¹⁴ In particular, carbon is a key component of PEMFC, serving as a catalyst support in the cell's electrode structure, and significantly enhancing the electrochemical reactivity and stability of the catalysts. The use of carbon in PEM fuel cells not only optimizes the electrocatalyst utilization, but also provides an effective medium for electron and mass transport, thus contributing to the cell's overall performance.¹⁵¹⁶

However, the majority of carbon materials currently in use are mostly derived from fossil resources, which raises significant environmental and sustainability concerns due to their finite nature and the associated greenhouse gas emissions as above mentioned.¹⁷ In response, extensive research has been invested into alternative renewable sources of carbon, with a particular focus on the development of sustainable carbon materials derived from biomass.¹⁸¹⁹²⁰²¹

Biomass, typically classified into categories such as plant-derived materials (including grasses, trees, and agricultural crops) and animal waste, possesses the potential to directly replace fossil-based fuels either in its raw form as biomass, or after conversion into biofuels like biodiesel. In a different, yet increasingly prominent capacity, biomass offers itself as an ideal candidate for the production of 'green' carbon. The conversion of biomass into this form of environmentally-friendly carbon, via methods that deviate from the conventional pyrolysis process are of critical importance. Such alternative processes enable precise control over the resulting carbon's chemical structure and morphology, thereby allowing for customization that suits particular applications. This innovative approach towards 'green' carbon synthesis has thus garnered significant interest in both academic and commercial arenas.

1.5 Scope of the Thesis

In the context of escalating climate change and an ever-increasing demand for energy, the overarching goal of this thesis is to present a sequence of projects that emphasize the potential of biomass-derived carbon materials in engineering an efficient PEMFC cathode catalyst layer.

In more specific terms, this research accentuates the potency of these sustainable resources in achieving improved performance acting as the catalysts support for PGM based electrocatalysts for energy conversion.

The thesis is structured as follows:

Chapter 1 - Introduction: This section outlines the critical issues of global warming and the global drive towards achieving net-zero emissions. It offers an overview of PEMFCs, emphasizing their importance in the renewable energy landscape. This chapter also highlights the significance of 'green' carbon derived from biomass resources.

Chapter 2 - Literature Review: This chapter provides a detailed review of the existing literature, with a particular focus on the development of highly active catalysts for PEMFCs and the challenges related to efficient catalyst layers. Three main obstacles for an efficient catalysts layer are identified and reviewed. It further explores the concept of 'green' carbon and its synthesis from biomass.

Chapter 3 - Materials and Methodologies: These methodologies encompass a diverse range of procedures, starting from the preparation of carbon materials and catalysts, followed by the measurement of reaction efficiencies. Additionally, this section delves into the exploration of advanced characterization techniques that have been crucial for the success of the conducted research.

Chapter 4 - Establishment of Gas Diffusion Electrode Half-Cell: This section conveys the findings derived from the initial phases of our investigation, encompassing a detailed discussion on multiple facets associated with the configuration of the gas diffusion electrode. We proceed to benchmark the ORR with an in-depth procedural protocol, thereby establishing a firm foundation for subsequent evaluations of catalyst performance.

Chapter 5 - Optimising the Local Transport via Ionomer/Catalysts Interaction: This chapter thoroughly delineates the development of highly ordered mesoporous carbon, derived from biomass, featuring a rationally designed porous structure and deliberate catalyst deposition. The ideal interaction between the ionomer and the catalysts, regulated by the nanostructure of the carbon, was probed using comprehensive gas sorption analysis and operando X-ray Absorption Spectroscopy.

Chapter 6 - Rationalisation of the Bulk Transport Through Hierarchical Architecture: This chapter builds upon the mesoporous structure developed in the previous section. We

synthesized a hierarchical, bimodal porous carbon film from lignin, another readily available biomass resource, which was subsequently employed as the backbone for the catalyst layer. The continuous and hierarchical architecture of the electrode enables enhanced bulk mass transportation and accessibility of active sites, key factors accentuated in this chapter.

Chapter 7 - Conclusion and Outlook: The final chapter summarizes the key findings of the thesis, provides concluding remarks, and offers future directions for research in this field.

With this well-structured research framework, this thesis strives to showcase the exciting potential of biomass-derived carbon materials in enhancing the performance of PEMFCs and contributing to a more sustainable energy landscape.

Literature Review

1.6 The Development of Catalysts with High Activity for PEMFCs

The Hydrogen and Fuel Cell Technologies Office of the U.S. Department of Energy (DOE) has set specific technical goals for catalysts at the Membrane Electrode Assembly (MEA) level. They aim for an initial mass activity (MA) exceeding 0.44 A/mg_{Pt} at 0.9 V, as measured against the reversible hydrogen electrode (RHE), while the PGM total loading for both electrodes lower than 0.125 mg/cm² and the activity degradation should be less than 40% after undergoing 30,000 voltage cycles.²²

Despite the continuous research activities in developing alternative, Platinum nanoparticles deposited on carbon (Pt/C) remain the mostly used PEMFC electrocatalysts due to the high intrinsic activity and supreme stability in acidic environment.²³ However, due to the high cost and scarcity of platinum, on top of the insufficient activity and stability as per required by the targets, tremendous research efforts are taking place to future boost the activity and stability of Pt-based electrocatalysts.²⁴ The body of research on this topic can be primarily divided into three categories. These include reducing/optimising particle size²⁵²⁶²⁷²⁸²⁹, alloying Pt with a second (usually transition group) metal³⁰³¹ and creating precise or clearly delineated structures³²³³. Pertinent scholarly contributions from these three research areas will be reviewed in the subsequent section.

1.6.1 Particle Size Effect of Pure Pt Nanostructure

In the context of deploying metal nanoparticles as active catalysts, controlling the size and shape of the pure metal nanostructures is an important research direction. Generally, a small particle sizes is favoured for a heterogeneous catalyst due to multiple reason. Segmenting bulk materials into nanoparticles (NPs) brings a substantial proportion of atoms, previously situated in the interior of the bulk material, onto the surfaces where catalytic reactions take place. The smaller these NPs, the larger the surface area to volume ratio becomes. Concurrently, smaller particles are more inclined to harbour a high density of low-coordinated species such as step edges, kinks, and corner atoms, which typically exhibit superior catalytic performance due to their elevated surface free energy.³⁴ In addition, the reduction in particle size dictates the interactions between the metal and the support. This may prompt a rearrangement of the metal species' electronic structure and thereby further expedite the catalytic process.³⁵ Therefore, particle size reduction is widely viewed as one of the most potent strategies to enhance atomic

utilization and catalytic activity. However, the ORR performance is not always increasing with the decrease of Pt particle size.²⁶ Over the past few decades, the size effects of Pt in ORR have been extensively scrutinized and researched²⁵²⁶²⁷²⁸²⁹.

Moreover, the surface facet of the Pt nanostructures, particularly of those with low-index planes (planes characterized by low Miller indices), is profoundly impacted by size manipulation. The catalytic performance of the ORR across these varied facets has been the subject of comprehensive exploration.³⁶ A successful correlation has been established between the binding energies of reaction intermediates on the electrode surface and the resulting catalytic activity³⁷.

This approach has proven effective in predicting the activity of metal electrodes towards ORR. These binding energies are connected to the coordination environment of an active Pt centre. Hence, the nature of the ORR active sites can be pinpointed using the generalized coordination number (GCN), where the coordination number of the Pt atom is extended to its second nearest neighbours.³⁴³⁸

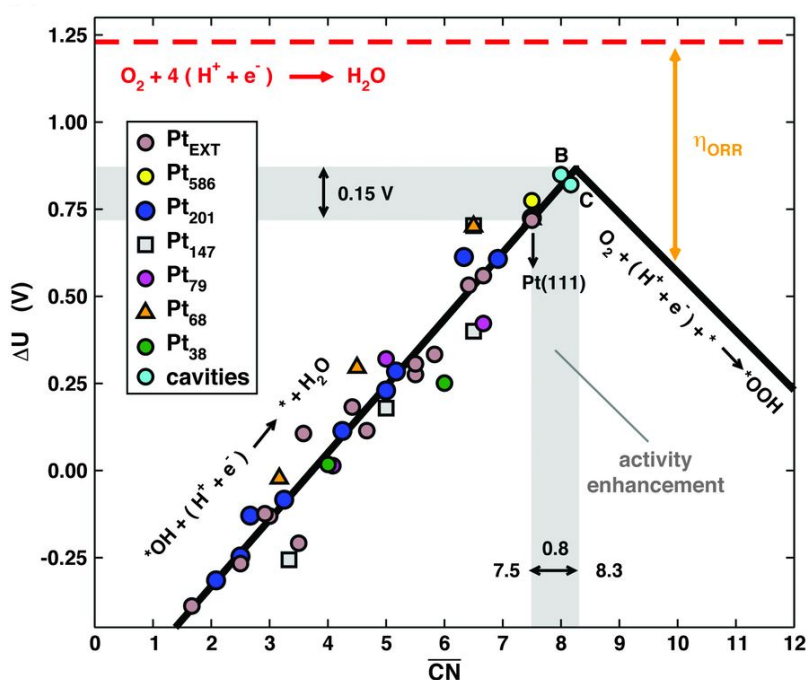


Figure 4. Sabatier analysis of the adsorption energies of competitive intermediate species *OH and *OOH for various Pt species, Reproduced from ³⁴ with permission.

According to Figure 4 extracted from the work published by F. Calle-Vallejo et al.³⁴, a Sabatier analysis of the adsorption energies of competitive intermediate species *OH and *OOH reveals that sites with a GCN between 7.5 and 8.3 possess enhanced activities in comparison to Pt(111).

Experimental ORR activity measurements on model Pt single-crystalline surfaces have indeed confirmed that the GCN can serve as a descriptor for catalytic performance towards the ORR.

In the recent literature, the concept of the GCN has been further expanded to predict the ORR mass activities in absolute units of A/mg_{Pt} for nanostructured Pt electrocatalysts of varying sizes.³⁹ This advancement serves as a testament to the continuously evolving nature of ORR catalysis research, highlighting the potential for size-manipulated nanostructures in enhancing catalytic performance.

In a study conducted by B. Garlyyev and his colleagues, they utilized computational screening to identify the optimal diameters of spherical Pt nanoparticles, which they found to be within the range of approximately 1-3 nm.³⁰ According to their predictions, the highest mass activities were associated with optimal nanoparticles with diameters of 1.1, 2.07, and 2.87 nm (Figure 5). Three nanoparticles with lower activity, represented by green hexagons, are exemplified at diameters of 1.5 nm, 2.5 nm, and 3 nm. The red and blue curves display predicted mass activities for nanoparticles with size distributions of 0.1 nm and 0.17 nm respectively. The ratio between active sites with a GCN range of 7.5 to 8.3 (highlighted in yellow) and the total number of sites is provided for all depicted nanoparticles.

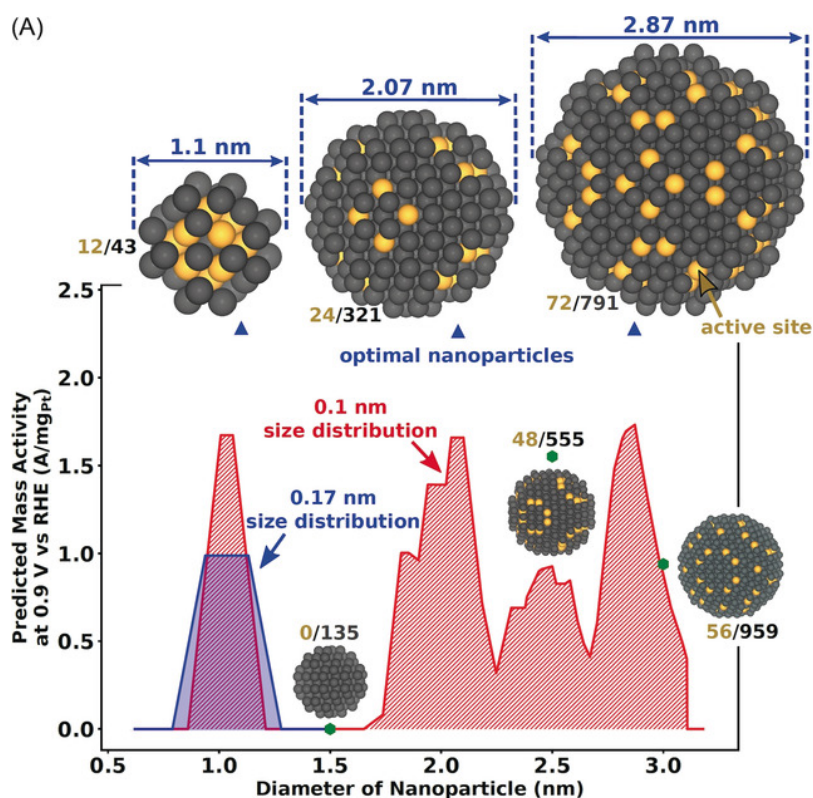


Figure 5. Graphical representation of a computational study, displaying the relationship between spherical Pt nanoparticle diameters and mass activities, suggesting optimal

nanoparticles with diameters of 1.1, 2.07, and 2.87 nm. Figure reproduced from ³⁰ with permission.

Numerous additional studies corroborate that the peak mass activity of Pt nanoparticles is attainable within a particle size range of 2-5nm⁴⁰⁴¹⁴²⁴³. However, when the particle size is further diminished, a decline in mass activity has been observed, seemingly in concert with the reduction in particle size. This is due to the growing proportion of low-coordinated Pt sites that strongly interact with oxygenated species. Additionally, during prolonged operation, smaller particles have a propensity to aggregate or sinter into larger structures, leading to a significant decrease in mass activity.

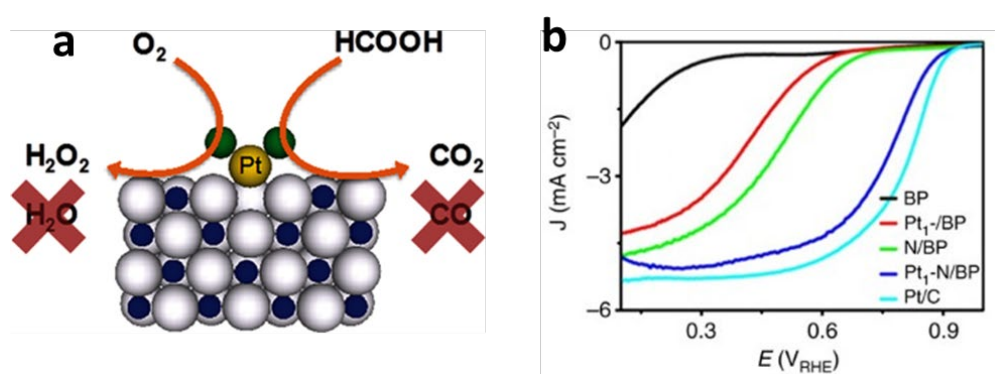


Figure 6. (a) Schematic depiction of a Pt single atom catalyst, highlighting the preference for a 2e⁻ ORR resulting in H₂O₂ production. Figure reproduced from ⁴⁴ with permission. (b) RRDE polarization curves for various Pt-based electrocatalysts in O₂-saturated 0.1 M HClO₄, conducted at a scan rate of 5 mV/s and a rotation speed of 1,600 r.p.m. The outcomes underscore the 4e⁻ ORR capability of Pt₁-N-BP. Figure reproduced from ²⁶ with permission.

Upon further reducing the nanoparticle size to the extreme—representing single Pt sites—an interesting contrast is observed. This can be categorized into two distinct groups based on the type of Pt single atom catalysts (SACs). The first group consists of Pt atoms supported on a catalyst substrate. These catalysts typically demonstrate suboptimal performance in the 4-electron transfer mechanism for the ORR, predominantly producing H₂O₂ through a 2-electron pathway (Figure 6a).⁴⁴ This deviation in behavior is believed to arise from a lack of platinum ensemble sites, redirecting the ORR pathway towards a two-electron route.⁴⁵ The second group is characterized by Pt-N-C coordinated catalysts. While these exhibit commendable 4-electron ORR performance in alkaline conditions, their performance in acidic media remains significantly inferior to conventional Pt/C catalysts.²⁶⁴⁶ Among the broader category of M-N-

C catalysts, Fe-N-C emerges as a more promising candidate, given its relative abundance and cost-effectiveness.⁴⁷ Recent years have witnessed an accelerated surge in research within this domain.^{48,21}

1.6.2 Nanoscale Structure

It is widely accepted that, within nanoparticles (NPs), only surface atoms can interact with reactants and contribute directly to the catalytic activity, while interior atoms are effectively inert. Therefore, the idea of fabricating hollow Pt NPs has gained traction, as removing the interior Pt atoms from solid NPs could retain their catalytic activity whilst simultaneously reducing Pt usage. Wang et al. employed a template-removal method to create hollow NPs which exhibited superior ORR catalytic activity compared to solid Pt NPs of comparable size.⁴⁹ This enhanced catalytic performance was attributed, after comprehensive experimental and density functional theory (DFT) calculations, to lattice contraction induced by the hollow structure. Taking this concept further, Zhang et al. produced Pt nanocages with sub-nanometer thickness, carefully investigating their ORR catalytic performance.⁵⁰ As illustrated in Figure 7, this involved the creation of Pd nanocubes followed by the deposition of four atomic layers of Pt on the surface of Pd cubes via Pt salt reduction at 200°C. The final step was the selective removal of the Pd cube templates, resulting in cubic Pt nanocages covered by {100} facets. This method also enabled the production of Pt octahedral nanocages covered by {111} facets. The specific and mass activities of the octahedral nanocages were found to be five and eight times higher, respectively, than those of commercial Pt/C. Employing a similar synthetic process, He et al. produced icosahedral Pt nanocages, also achieving exceptional ORR performance.⁵¹

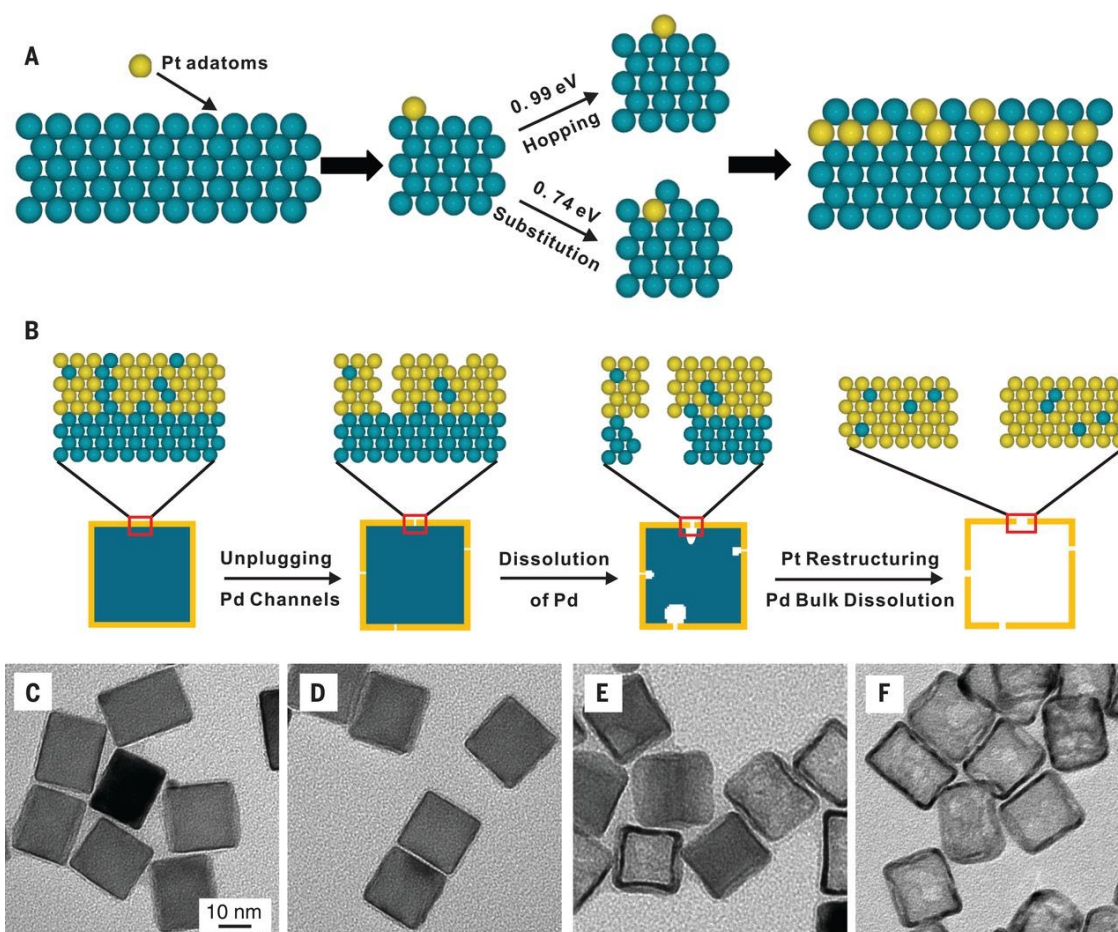


Figure 7. Illustration of the synthesis process of Pt nanocages, developed by Zhang et al., involving the creation of Pd nanocubes, deposition of Pt layers, and selective removal of Pd templates. Figure reproduced from ⁵⁰ with permission.

Other than creasing hollow structure, another strategy to increase the surface to bulk ratio is to generate one-dimensional nanocrystals. Nanowires are considered ideal structures for achieving excellent electrocatalytic performance due to their large surface area and superior stability compared to NPs. Liang et al. synthesized a free-standing membrane of Pt nanowires via a complex templating procedure employing ultrafine Te nanowires. The resultant Pt nanowires displayed higher mass activity and superior durability compared to both the bulk Pt catalyst and commercial Pt/C..⁵² Advancing this, Li et al. engineered ultrafine jagged Pt nanowires with an average diameter of about 2 nm, utilizing a synthetic strategy involving thermal annealing and electrochemical dealloying (Figure 8).⁵³ These Pt nanowires demonstrated exceptionally high ORR catalytic activity with a half-wave potential of 0.935 V versus RHE, markedly more positive by approximately 75 mV than that of Pt/C. They also achieved a mass activity as high as 13.6 A/mg_{Pt}, in addition to excellent long-term durability, which is still believed to be the highest mass activity reported to date. The observed enhancement

in activity was attributed to the atomic stress coupled with the surface's rhombus-configuration, which is particularly conducive to ORR.

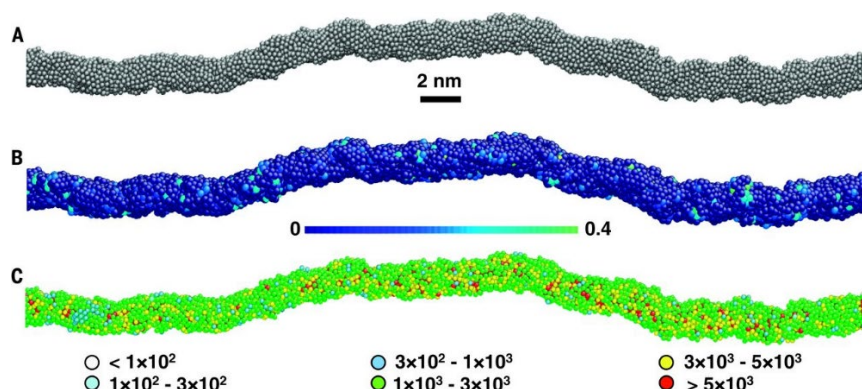


Figure 8. Ultrafine jagged Pt nanowires with an average diameter of about 2 nm, demonstrating the highest mass activity of 13.6 A/mg_{Pt} up to date. Figure reproduced from ⁵³ with permission.

However, while the advancements in producing such nanostructured Pt present promising results, these methodologies come with their own set of challenges. Many of these approaches, such as the fabrication of hollow structures or ultrafine nanowires, can be complex, difficult to replicate, and currently lack scalability for larger industrial applications. Furthermore, the durability, stability, and practical feasibility of these structures in real-world applications remain to be thoroughly evaluated. Though the hollow structures and nanowires offer increased surface areas and potentially better ORR performance, their long-term robustness, especially in varying operational environments, is a subject that warrants further investigation. In conclusion, while these innovative approaches signify strides in catalyst development, a balanced and critical assessment is essential to truly gauge their potential and limitations.

1.6.3 Alloying

The amalgamation of two or more metals through alloying has been extensively studied and proven to endow catalysts with distinct and enhanced properties. Dating back to the early 1990s, scientists have already recognized that the kinetics of ORR could be substantially enhanced by alloying Pt with transition metals, such as Ni, Co, and Cr.⁵⁴ It is commonly held that the atomic and electronic structures of Pt can be enhanced via alloying, which serves to amplify the ORR performance.

Building on this, V R. Stamenkovic et al. systematically evaluated the role of alloying metals using DFT calculations (Figure 9).⁵⁵ The results elucidated a volcano-like correlation between

the specific activities of PtM alloys and the d-band centre, serves as a descriptor in ORR. This relationship demonstrates that both extremely strong and weak adsorptions of oxygen intermediates can hinder the reaction rate, attributable to surface oxide removal and the transfer of electrons and protons to adsorbed O₂, respectively. Notably, Pt₃Co, Pt₃Ni, and Pt₃Fe alloys, residing at the apex of the volcano plot, are predicted to display superior ORR activity relative to other PtM alloys or unalloyed Pt materials.

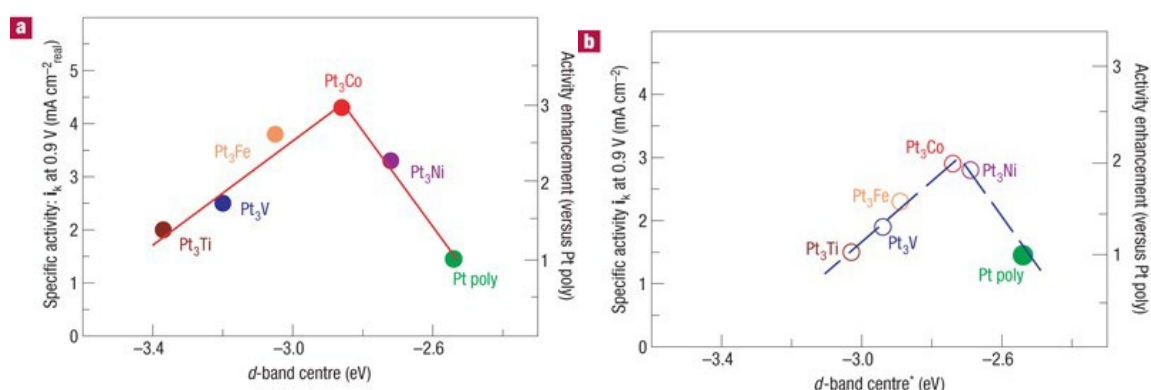


Figure 9. Volcano plot illustrating the systematic evaluation of PtM alloys using DFT calculations, revealing a correlation between specific activities and the d-band centre in ORR. Figure reproduced from ⁵⁵ with permission.

Inspired by these findings, researchers have embarked on further explorations to optimize PtM alloy-based ORR catalysts. This process entails the careful modulation of the composition, morphology, size of the PtM nanostructures and the local interactions. One such example is the platinum-cobalt core-shell nanoparticles reported by L Chong et al.⁵⁶ The catalysts, as depicted in Figure 10, were synthesized employing cobalt or bimetallic cobalt and zinc zeolitic imidazolate frameworks as precursors, yielding platinum-based electrocatalysts with ultralow Pt loading. This process manifested synergistic catalysis involving strained platinum-cobalt core-shell nanoparticles and a PGM free catalytic substrate, resulting in superior fuel cell performance. The two fabricated catalysts demonstrated ORR mass activities of 1.08 and 1.77 A/mg_{Pt}. Computational modelling elucidates that the interaction between platinum-cobalt nanoparticles and PGM-free sites enhances both ORR activity and durability.

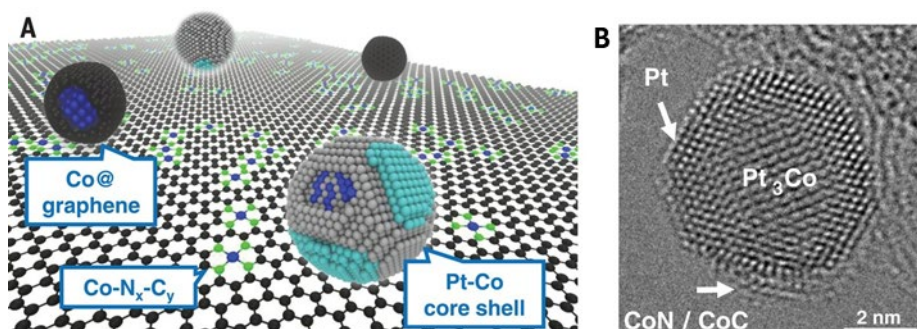


Figure 10. (A) Illustration of LP@PF catalysts, featuring the simultaneous presence of Pt-Co NPs, Co@graphene, and PGM-free Co-N_x-C_y active sites. (B) High-Resolution Transmission Electron Microscopy (HRTEM) image showing a typical Pt-Co alloy NP, composed of a Pt₃Co superlattice core and Pt skin, partially overlaid by CoN and CoC terraces. Figure reproduced from ⁵⁶ with permission.

Other than the transition metals mentioned above, alloying Pt with rare earth elements is another series of studies conducted on various alloys such as Pt₃Y, Pt₅Y, and Pt₃Sc. When characterized under conditions akin to low temperature fuel cell, these alloys displayed varying degrees of ORR activity, with Pt₃Y emerging as the standout, showing an impressive six to ninefold increase in activity over pure Pt at 23°C.⁵⁷ Interestingly, Pt₃Y and Pt₅Y evolved a Pt overlayer under ORR conditions, suggesting an active phase formation that might underpin their superior performance. In contrast, alloys like Pt₃Hf and Pt₃Zr, when exposed to ORR conditions, presented surfaces mixed with Pt and their respective metal oxides, which possibly contributed to their dull performance.⁵⁷

Delving into the Pt_xY alloy, despite its recognized activity and stability, its nanoparticulate synthesis has been challenging. Nonetheless, a breakthrough was achieved with the creation of Pt_xY nanoparticles using the gas-aggregation technique.⁵⁸ These nanoparticles not only exhibited exceptional ORR activity but also confirmed, through exhaustive characterization, that their enhanced performance over elemental platinum was primarily attributed to a compressive strain on the platinum surface atoms by the alloy core.

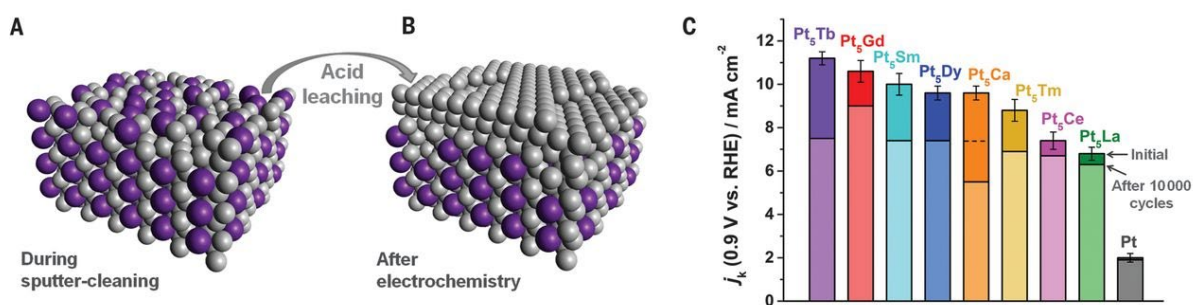


Figure 11. (A) 3D portrayal of the Pt₅M architecture during the sputter-cleaning process. (B) Structure post-electrochemical reactions. (C) Illustration of kinetic current density for Pt₅M and Pt at 23°C, rotating at 1600 RPM in an O₂-saturated 0.1 M HClO₄ environment. This is both before and following a stability assessment that encompasses 10,000 cycles ranging from 0.6 to 1.0 V vs. RHE at a rate of 100 mV/s. Figure reproduced from ⁵⁹ with permission.

Complementing these findings, another pivotal study on platinum alloys with lanthanides and alkaline earth elements highlighted the importance of surface strain in modulating ORR activity.⁵⁹ (Figure 11) Post acid leaching, these alloys developed compressive strain on their pure platinum surfaces, with some, like the one alloyed with terbium, showing up to a 6 fold increase in ORR activity. This phenomenon, in tandem with enthalpy effects, ensured alloy stability under operational conditions.

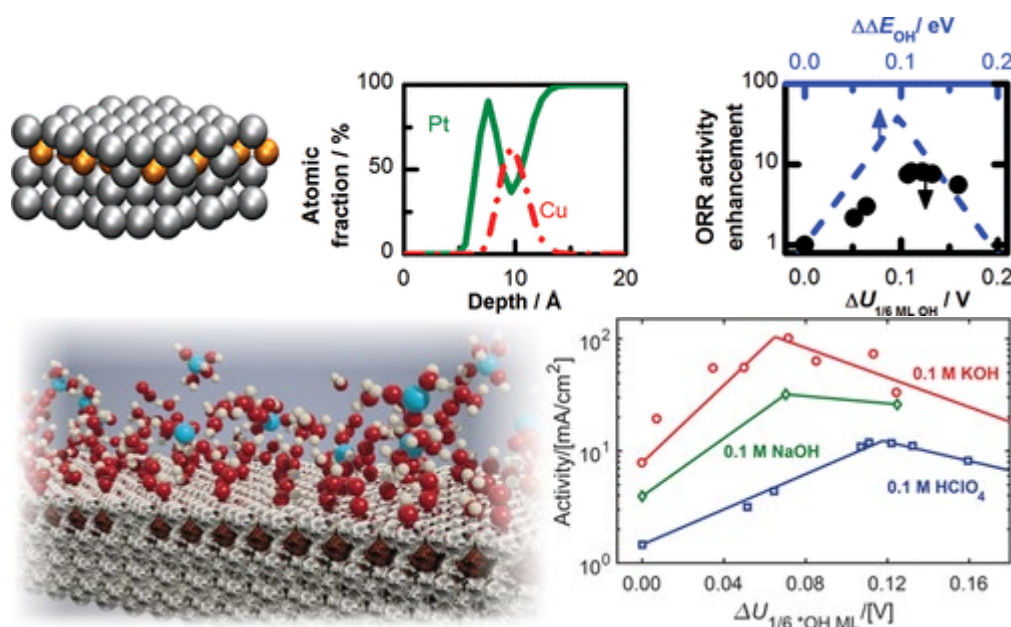


Figure 12. Alloying Cu into the sublayer of Pt(111) modulates the oxygen reduction performance in alkaline solutions. Similar to acidic environments, the primary factor driving the reaction is the binding affinity to the intermediates. Figure reproduced from⁶⁰⁶¹ with permission.

Another stream of research dives deep into the influence of subsurface alloying, specifically focusing on the Cu/Pt(111) near-surface alloy. Ifan et al. introduced the novel concept of near-surface alloys (NSAs) of Cu/Pt(111), where copper atoms are strategically embedded within the subsurface region of a platinum (111) single crystal, thus forming a Pt-skin structure.⁶⁰ They demonstrated the transformative effect of subsurface Cu on the ORR activity, elucidating how this configuration led to an 8-fold enhancement in ORR activity over pure Pt(111) at 0.9 V. The research also underscored the theoretical prediction that an optimal catalyst for ORR would exhibit an OH adsorption energy 0.1 eV weaker than Pt(111). Building upon this, their subsequent work delved deeper into the factors influencing the ORR on metal surfaces in alkaline media, employing the Cu/Pt(111) NSA as their model system.⁶¹ This enabled them to manipulate the binding of reaction intermediates. Through a series of experiments across different electrolytes, they discerned that the ORR activity follows a Sabatier volcano relationship in both alkaline and acidic conditions, refuting earlier contradictory claims. Notably, they also pinpointed the significant effects of changing the electrolyte cation and the presence of surface steps on the ORR activity. They postulated that these observed effects arise from proton transfer and non-covalent interactions at the electrochemical interface, presenting a holistic view of the intricate dynamics at play.

In summary, the field of Pt-based electrocatalysts for the ORR has seen substantial progress, with numerous new catalysts being developed through the strategies previously discussed. While these innovations continue to broaden the landscape of ORR catalysts, nanosized Pt particles remain at the forefront of efficiency, specifically in examining the dynamics of the catalyst layer, especially the transportation phenomena. Therefore, as we transition into the subsequent focus on catalyst layer design, Pt nanoparticles will be the selected active catalysts for further examination. This choice is grounded not only in the impressive performance of Pt NPs but also in the existing profound understanding and the relatively straightforward means of controlling particle size. Such insights and capabilities render Pt NPs an essential foundation upon which to build the next phase of inquiry into catalyst layer design and optimization.

1.7 Challenges for Efficient Catalyst Layer

Despite the substantially enhanced ORR activity and stability of the innovative Pt-based nanocatalysts developed in research laboratories surpassing commercialized Pt/C at rotating disk electrode (RDE) levels (occasionally by a factor of 100), inferring expected MEA-level activities from such ostensibly impressive RDE performance proves challenging.

In their research, J Fan et al. spotlighted several catalysts that displayed exceptional performance under RDE conditions⁶². The comparative analysis of these catalysts under MEA and RDE is adapted and presented in Figure 13. This difficulty arises due to the considerable differences between RDE and MEA testing protocols. Several hurdles persist that must be surmounted for state-of-the-art highly active ORR catalysts to achieve widespread application in commercial PEMFCs. Among these hurdles, one of the most substantial is the effective translation of their superior RDE performance into equivalent MEA performance.

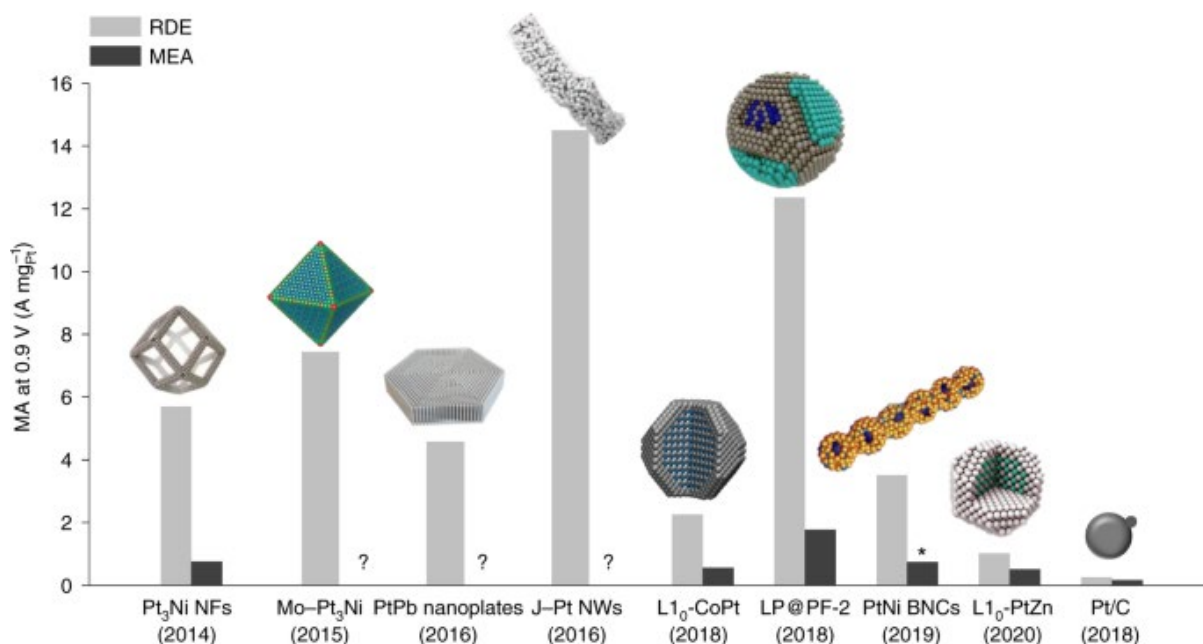


Figure 13. Performance Evaluation of Various State-of-the-Art Catalysts under RDE and MEA Conditions. Details include specific Pt loading, testing environment, and parameters for each catalysts can be found in the respective publications (from left to right): Pt₃Ni NF⁶³, Mo-Pt₃Ni⁶⁴, PtPb nanoplates⁶⁵, J-Pt NWs⁵³, L1₀-CoPt⁶⁶, LP@PF-2⁵⁶, PtNi BNCs⁶⁷, L1₀-PtZn⁶⁸ and Pt/C⁶⁹. Figure reproduced from ⁶² with permission.

The subsequent section delineates the persistent barriers to attaining elevated MEA performance with ultralow Pt loading. These encompass (1) the absence of intermediate testing technologies, (2) the need for a catalyst design that considers local mass transport, and (3) the challenge of designing effective catalyst layers (CLs) architecture.

1.7.1 Intermediate Test Platform

It is incontrovertible that MEA measurements provide the most indicative data of the performance metrics of a fuel cell or electrolyser system. Nonetheless, for preliminary screening of newly synthesized catalysts, which are ordinarily available only in minuscule

quantities, methodologies premised on convective flow within aqueous electrolytes are commonly employed, with the RDE technique being the most ubiquitous. In RDE evaluations, mere tens of micrograms of catalyst per square centimetre of geometric electrode area are layered onto a non-porous conductive substrate electrode, generally composed of glassy carbon or occasionally gold, which is built in the RDE holder. The rotational motion of the RDE creates a distinct diffusion layer, typically spanning a thickness of 5-50 μm depending on the rotating speed. This action facilitates the procurement of kinetic parameters pertinent to the ORR.

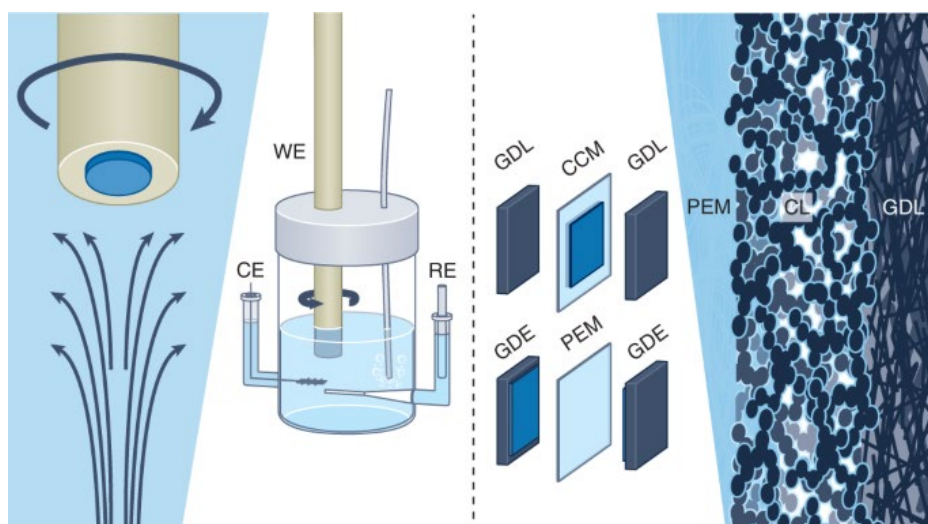


Figure 14. Comparison Between RDE and Five-Layer MEA Configurations: (left) Detail of the local environment surrounding an RDE working electrode in a three-electrode RDE arrangement, encompassing a CE and a RE. (right) Depictions of five-layer MEA structures, either integrating a Catalysts Coated Membrane (CCM) between two Gas Diffusion Layers (GDLs) or a PEM enclosed by two GDEs, with a close-up view of the local setting within an MEA, showcasing the porous CL, composed of catalyst particles (illustrated in black) and ionomer (depicted in light blue). Figure reproduced from ⁷⁰ with permission.

On the contrary, a MEA is composed of 5 different layers including a Proton Exchange Membrane (PEM), anode and cathode catalyst layers, along with their gas diffusion layers. The catalyst layers can be either laminated or spray-coated directly onto the membrane, resulting in a catalyst-coated membrane that is then ensconced by gas diffusion layers. Alternatively, they can be cast onto the gas diffusion layers to form gas diffusion electrodes, with the membrane sandwiched in between. In either scenario, the 5-layered MEA is eventually encapsulated between two flow fields to constitute a single-cell unit. These porous catalyst layers facilitate efficient mass transport through the gas phase. Consequently, high limiting and Pt-specific current densities can be achieved, albeit at the cost of requiring gram quantities of

catalyst powder. Moreover, the fabrication of such MEAs is a labour-intensive process. Their electrochemical testing extends over multiple days per catalyst and additionally necessitates capital-intensive instrumentation capable of exact control of variables such as gas pressure, flow rate, relative humidity, and temperature. Therefore, most novel catalyst designs are predominantly tested in RDEs during the initial development stages and at small-scale synthesis.

Prior to delving into an intermediate testing platform that could facilitate the successful translation of a catalyst's superior RDE performance into comparable MEA performance, it's crucial to comprehend the key differences between these two methods. The most fundamental disparity between the two methodologies is the dominant mass transport limitation, which bears direct consequences on the transferability of RDE results to an MEA setting. In MEAs, reactants predominantly reach the relatively thick catalyst layer (5–20 μm) through brisk gas-phase diffusion via the flow fields, the gas diffusion layers, and the catalyst layer's pores. The final diffusion stage often involves traversing a nanometre-thin film of ionomer covering the catalyst particles.

Contrastingly, in an RDE setup, the substantially thinner catalyst layer (0.1–2 μm) is flooded by the liquid electrolyte, meaning the diffusion length for dissolved O_2 across the liquid diffusion boundary layer spans tens of micrometers.⁷¹ Together with the low solubility of O_2 in aqueous electrolyte solutions⁷², these result in much lower attainable geometric and specific current densities in an RDE setup. This limitation impedes meaningful assessments of high current density ORR performance on PGM catalysts.

A strategy to bridge the performance discrepancy between RDE and MEA is the integration of methodologies that facilitate high mass transport in liquid electrolytes while necessitating significantly lesser amounts of catalyst. The two techniques reported up to date are Floating Electrode Technique (FET)⁷³⁷⁴, wherein the catalyst is cast onto a hydrophobic porous substrate floating on liquid electrolyte, and Gas Diffusion Electrodes (GDEs)⁷⁵⁷⁶, where the electrode is positioned at the liquid/gas interface. These techniques are gradually being incorporated into electrocatalyst research.

Back to 2008, A R Kucernak et al. reported for the first time a FET employing an ultrathin gold grid as a catalyst support, to which a PEM was affixed, thus enabling protons and O_2 to access the catalyst via the grid's 20 $\mu\text{m} \times 20 \mu\text{m}$ pores⁷⁴. This reduction in proton transport resistance further enhanced the FET for assessing ultralow-Pt-loading catalysts in the absence of a

perfluorinated sulfonic acid (PFSA) membrane. In this technique, catalysts were directly deposited onto a hydrophobic, gold-coated porous substrate via a vacuum filtration method, thereby yielding a catalyst layer of more consistent morphology and thickness.

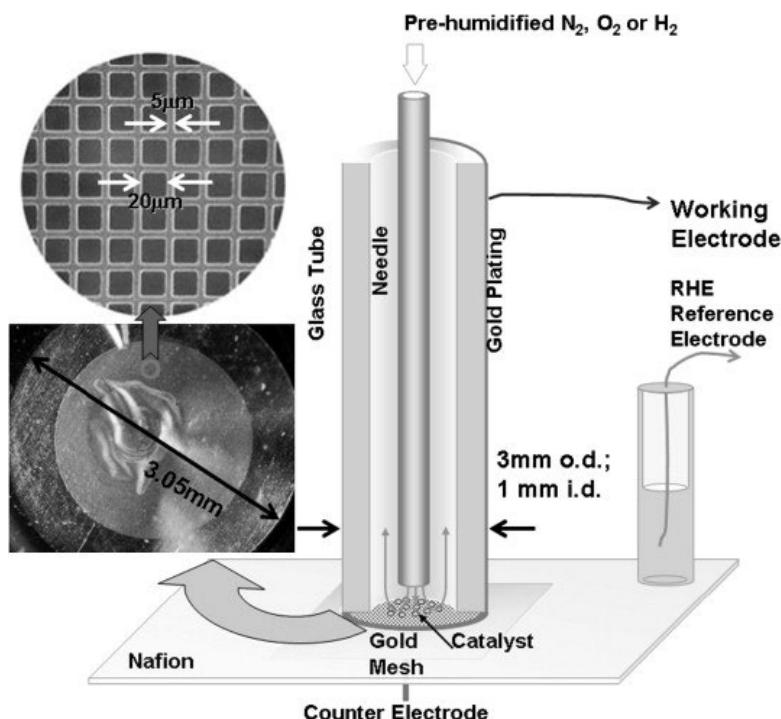


Figure 15. Diagram showing the experimental arrangement for evaluating the electrocatalytic activity of fuel cell electrocatalysts. The setup includes a gold grid with catalyst loaded onto a Nafion₁₁₇ membrane, a gold-plated glass tube touching the mesh, and a needle inside the tube for the flow of pre-humidified gas. A platinum foil counter electrode is located on the other side of the membrane, and a reversible hydrogen electrode in contact with the Nafion₁₁₇ membrane serves as the reference electrode. Figure reproduced from ⁷⁴ with permission.

The hydrophobic substrate was made to float on the HClO₄ electrolyte, with the catalyst side directly exposed to a 4 M HClO₄ electrolyte and the other side exposed to O₂, thus ensuring a surplus of protons and O₂ to meet the high current density demand. Further studies in 2018 explored the effects of various parameters on the Electrochemically Active Surface Area (ECSA) and activity, in addition to different stability assessment protocols to correlate activity and stability values obtained from RDE with those from FET and MEA testing.⁷⁷

Compared to RDE, FET does facilitate the evaluation of catalyst performance over a significantly larger current density region, even though the reproducibility of its results warrants further enhancement. Moving forward, it is necessary to establish standard protocols for FET to increase the cross-laboratory reproducibility of activity and stability outcomes. In a

similar vein to the $\geq 0.44 \text{ A/mg}_{\text{Pt}}$ @ 0.9 V US DOE mass-activity target assessed for MEAs, technical targets for catalysts evaluated using FET should also be thoroughly deliberated and developed as benchmarks to guide future catalyst innovation within the context of large-current-density operation.

Despite the efficiency of FET in providing an initial screening of catalysts for the ORR, one significant constraint of it is the demand for a specific and low loading catalyst architecture that may not accurately mirror a practical fuel-cell catalyst setting. In contrast, the half-cell GDE technique is a versatile testing platform applicable for assessing catalyst-coated GDL or CCM under real PEMFC operating conditions. This setup includes components analogous to those in an actual fuel cell, closely mimicking the local environment and mass transport pathways of an MEA, while demanding lower catalyst mass and retaining a technical complexity akin to the RDE technique. In essence, O_2 can reach one side of the CL, traversing through a monopolar plate and GDL, while the opposing side is either isolated by a PEM or directly confronts the HClO_4 electrolyte.

The concept of a GDE half-cell was pioneered by G. K. H. Wiberg et al. in 2015, constituted by a stainless-steel field and a PEEK plastic cell body that make up the electrochemical cell, which demonstrates a three-electrode arrangement.⁷⁸ In 2018, using a modified cell as illustrated in Figure 16, they proceeded to benchmark a commercial 46.5 wt% Pt/C catalyst (TEC10E50E, Tanaka Kikinzoku Kogyo) for the rapid assessment and testing of low-temperature PEMFC catalysts, aligning the results with those garnered from MEA evaluations.⁷⁶ Compared to measurements using RDE, FET, and MEA, the values at 0.9 vs RHE from the half-cell GDE test were strikingly akin to the results obtained from MEA. More precisely, the ECSA in the half-cell GDE test was marginally lower than in optimized RDE measurements, but almost matched the ECSA values from the MEA. This could be attributed to the variance in the Pt utilization ratio due to differing electrolyte/catalyst interfaces. Despite the intrinsic activity evaluation limitations associated with the half-cell GDE configuration, the I-V curves in this configuration provided a more accurate representation of fuel cell performance.

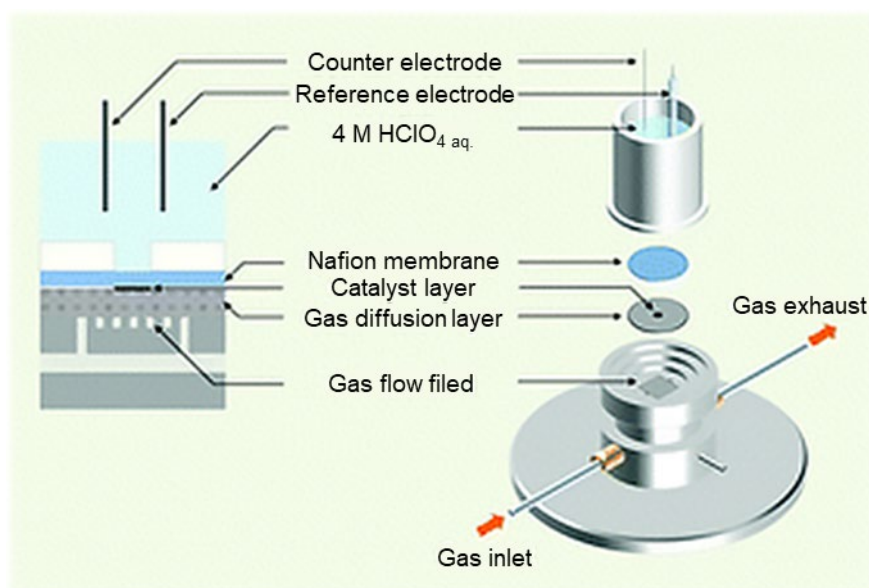


Figure 16. Diagram of the GDE cell developed by M Arenz et al. with detailed cross-section revealing the cell's internal structure. Within the cell, the NafionTM membrane and the GDL, which includes the catalyst layer constructed on it, are nestled between the upper and lower cell bodies. The upper cell body is compressed against the lower one using a clamp (not depicted), and a gas humidifier is attached to the gas inlet. Figure reproduced from ⁷⁶ with permission.

In 2017, another GDE half-cell configuration was presented by B. A. Pinaud et al.⁷⁹, achieving fuel cell current density around 1 A/cm². This report clearly outlined key design considerations, which included cell configuration, electrolyte concentration selection, and iR compensation, thereby underscoring the challenges inherent in the development of such a testing platform. Overcompensation of the potential caused by varying internal resistance was identified and highlighted as a significant concern. The report found that constant current polarizations with iR drop measurements at each step provided a simple and reproducible method for assessing catalyst performance. An optimal electrolyte concentration of 1.0 M HClO₄ was identified, which balanced the necessity for non-limiting H⁺ transport at high currents while minimizing the effect of electrolyte impurities, which could reduce Pt activity. The study concluded that the half-cell configuration used could accurately assess the ORR activity of commercial products, aligning well with measurements made in actual fuel cell hardware, but with significantly reduced testing costs.

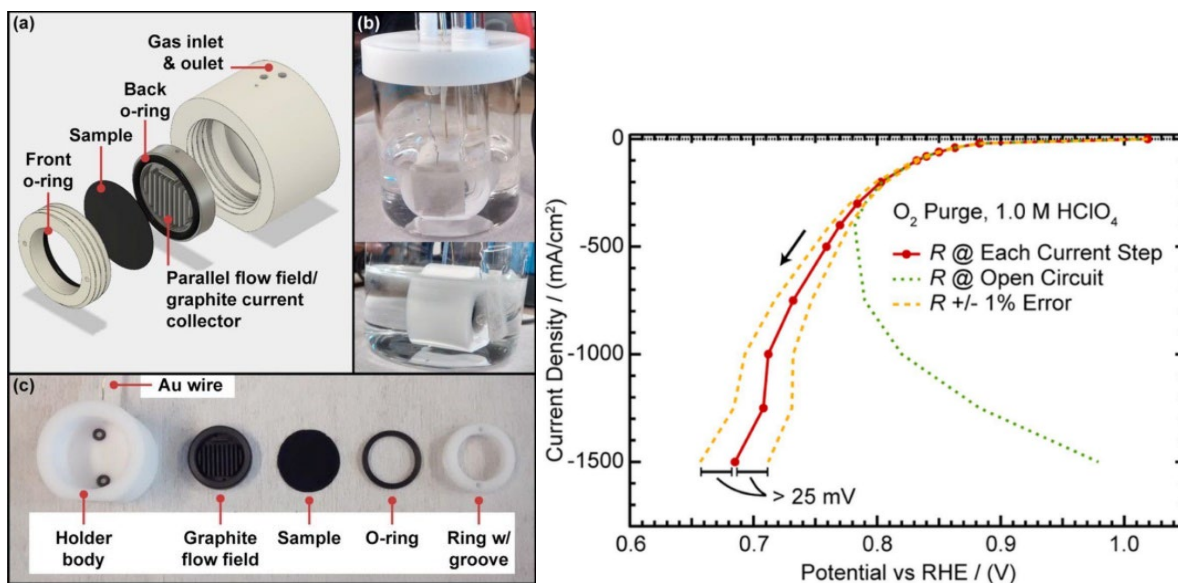


Figure 17. Illustration of the GDE Half-Cell Engineered by B. A. Pinaud et al. To the right, the diagram shows IR-corrected ORR polarization curves obtained through resistance measurements via current perturbation at each step (solid red line), alongside 1% resistance measurements (yellow dashed lines) and open circuit data (green dotted line). This emphasizes the critical role of resistance compensation in this half-cell design. Figures reproduced from ⁷⁹ with permission.

In 2019, a study by K. Ehelebe et al. was reported, which offered critical insights into the impact of Pt loading on the performance of Gas Diffusion Electrodes (GDE) in fuel cells.⁸⁰ One key aspect of their work centered on the effect of Pt loading. The team conducted an in-depth analysis using their tailor-made setup and electrochemical protocol, testing different Pt/C loadings. The outcome exhibited excellent reproducibility, with mass-specific current densities reaching 30 A/mg_{Pt} at 0.6 V vs. RHE. Furthermore, they documented polarization curves over a broad potential window, unencumbered by severe mass transport limitations. This signified an improvement over earlier GDE half-cell studies. A comparison of the ORR performance in GDE half-cell and MEA at high current densities underpinned the effectiveness of the GDE half-cell setup in managing water and mitigating CL flooding issues. The team noted that the performance was largely dependent on the intrinsic catalytic activity of the catalyst, the transport of O₂ to the active catalytic centres, and the accessibility of protons to the catalyst. The study also delved into the importance of ionomer content and distribution. A thin, homogeneous ionomer layer around the Pt particles was suggested to minimize mass transport limitations, ensuring good proton accessibility while simultaneously minimizing the oxygen diffusion pathway length. Furthermore, the research underscored the necessity of strategic Pt

particle positioning in carbon support to minimize mass transport related losses and prevent ionomer poisoning.

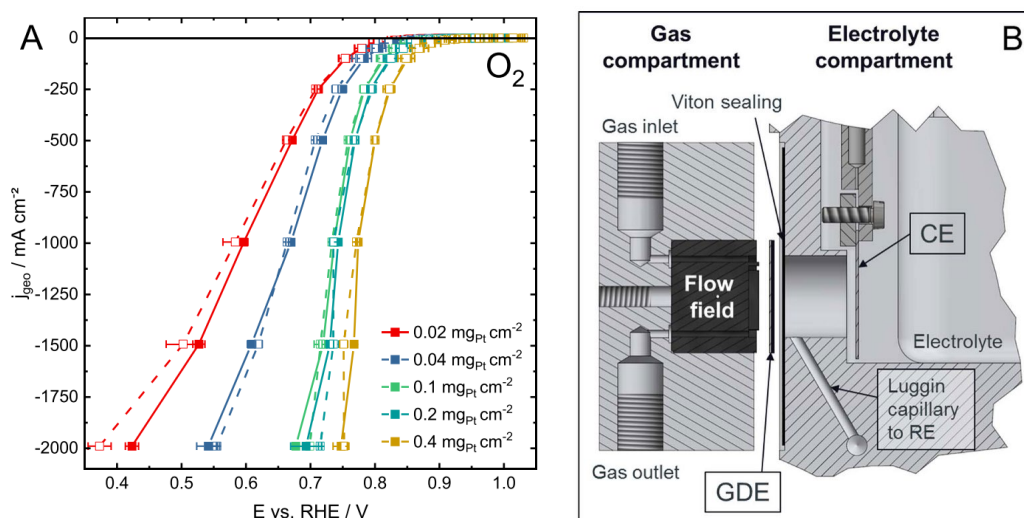


Figure 18. (A) Assessment of ORR activity for various Pt/C loadings on a commercial gas diffusion layer Freudenberg H23C8 in a 1 M HClO_4 solution and (B) scheme of the GDE half-cell setup used with three-electrode assembly. Figure reproduced from ⁸⁰ with permission.

Recognizing the significance of GDE half-cell setups for the advancement of PEMFC, as well as the difficulties encountered when comparing activity data derived from different GDE configurations, a remarkable inter-laboratory collaboration was embarked upon by several research groups specializing in GDE studies.⁷⁵ The main objective of this collective effort was to benchmark the various commercial available electrodes and electrocatalysts including Pt/C GDE (0.3 $\text{mg}_{Pt}/\text{cm}^2$, FuelCellsEtc), spray-coated Pt/C electrocatalysts (40% Pt HiSPEC4000, Johnson Matthey) and spray-coated PtCo/C electrocatalysts (Elyst0690) to facilitate inter-laboratory comparison, and to recommend optimal practices when operating these setups.

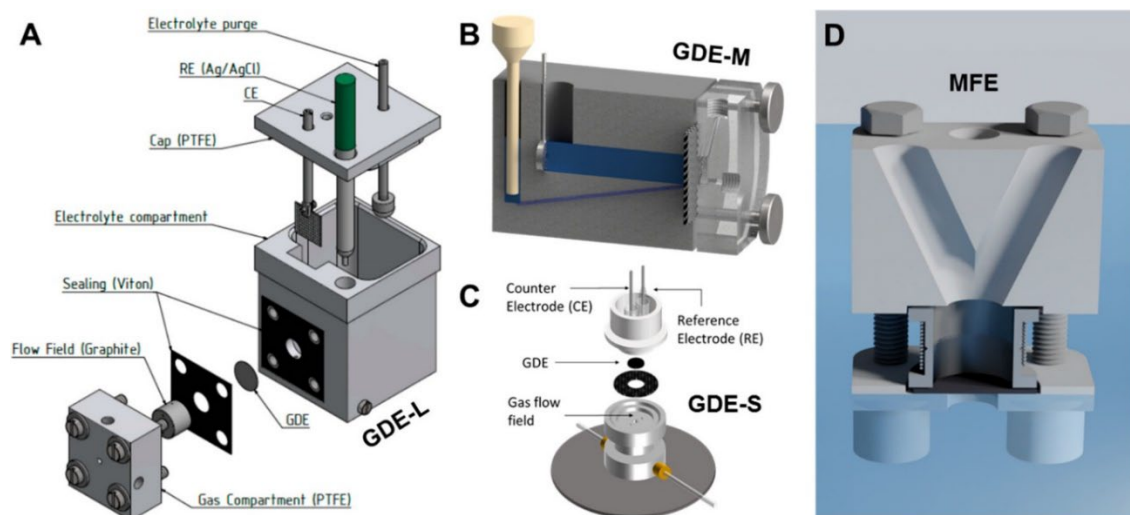


Figure 19. Different GDE half-cell setups used for the inter-lab comparison. (A) GDE setup developed at the Helmholtz-Institute Erlangen-Nürnberg (GDE-L).⁸⁰ (B) Commercial GDE cell from Gaskatel adapted at TU Darmstadt (GDE-M).⁸¹ (C) GDE cell developed by the group of Arenz et al. used in the University of Copenhagen and Leibniz Institute for Plasma Science and Technology (GDE-S).⁷⁶ (D) Modified floating electrode (MFE) setup developed at the National Institute of Chemistry in Ljubljana.⁸² Figure reproduced from ⁷⁵ with permission.

The present inter-laboratory analysis conducted on three different Pt-based GDEs underscores that considerable compatibility can be secured between various configurations and laboratories, given two factors are considered. First, a uniform catalyst layer ought to be fabricated to accommodate the diverse range of geometric surface areas. Disparity in catalyst layer uniformity can create discrepancies in individual measurements, particularly when very small geometric surface area setups are employed. Second, an analogous electrochemical protocol incorporating galvanostatic steps and internal resistance correction at each stage should be implemented. Additionally, upon analysis of the microporous Pt-alloy catalysts, the findings indicate the necessity for an added activation procedure. The ORR generates a specific quantity of water that is essential for facilitating the transport of protons to the catalyst nanoparticles situated within the pores.

The above literature review underlines the irreplaceable role of the GDE in facilitating high performance and optimizing the use of catalysts in PEMFC energy conversion systems. Furthermore, the integration of GDE half-cell designs with external *in situ* online mass spectrometry or *ex situ* analytics, such as Small Angle X-ray Scattering (SAXS)⁸³, ICPMS⁸⁴ or

Identical-Location Transmission Electron Microscopy (IL-TEM)⁸⁵, has been instrumental in gaining unique insights into the impact of catalyst layer properties on stability and selectivity. This holistic approach is crucial in refining our understanding of the stability of catalysts in real electrochemical energy conversion devices and facilitating the scale-up of electrochemical synthesis reactions.

The advancement in GDE and their integration into PEMFC systems epitomize the ongoing evolution and maturation of scientific innovation in this field. While significant strides have been made, the exploration and refinement of these technologies continue to be a dynamic and unfolding process. It is anticipated that future developments will usher in a surge of novel insights and technological enhancements, propelling us toward the realization of a more sustainable and environmentally responsible energy paradigm. In Chapter 4 of this thesis, a comprehensive account will be provided concerning the establishment and benchmarking of a GDE setup. This setup is designed to function as the measurement platform for the development of innovative catalyst supports central to the research presented herein. As such, it forms a pivotal component of the broader endeavour to harness and optimize these advanced technologies for practical application, aligning with the overarching objectives of efficiency and sustainability.

1.7.2 Local Transport – Ionomer/Catalysts Interaction

In the MEA of a PEMFC, the CL is located between the GDL and the PEM, constituting the region where oxygen and protons are transported into the cathode CL. In the case of a GDE half-cell setup, the PEM will be replaced with the liquid electrolyte instead. The mass transport limitation at all interfaces emerges as a significant barrier that must be mitigated. An examination of the CL reveals the presence of ionomer-coated agglomerates and clusters of Pt/C particles.⁸⁶ These form a porous structure encompassing both macropores (>50 nm) and mesopores (2-50 nm).⁸⁷ Optimization is required for the pressure-dependent molecular diffusion in macropores and the pressure-independent local diffusion in mesopores and through interfaces for oxygen and water. In this thesis, these two diffusion scenarios will be optimised in Chapter 4 for local transport and Chapter 5 for bulk transport, respectively.

The local oxygen mass transfer resistance constitutes the most significant portion of the total oxygen transport resistance. As illustrated in Figure 20, the resistance to oxygen mass transfer manifests locally at various interfaces such as the ionomer/gas interface, the ionomer/Pt

interface, and within the bulk ionomer thin film, all closely related to the ionomer content within the CL.

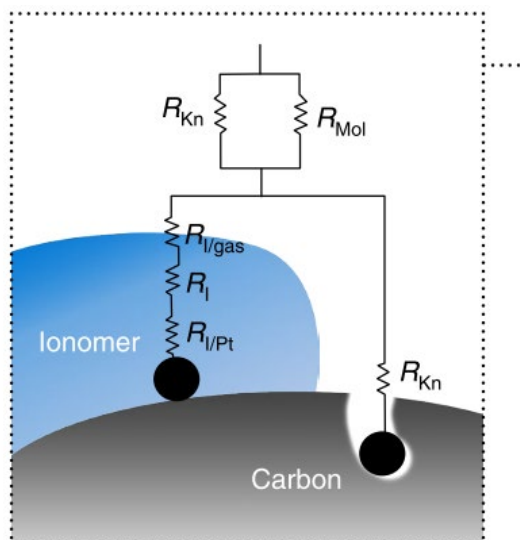


Figure 20. Equivalent circuit model of mass transport of O_2 : The resistance symbols denote Knudsen resistance (R_{Kn} , pressure independent), molecular diffusion resistance (R_{Mol} , pressure dependent), and local oxygen transport resistance including the O_2 transport resistances through the ionomer/gas interface ($R_{I/gas}$) and the ionomer/Pt interface ($R_{I/Pt}$) and local resistance in the bulk ionomer thin film (R_I). Figure reproduced from ⁶² with permission.

Strategies to tailor the ionomer Pt interaction

In the realm of proton conductive ionomers, perfluorinated sulfonic acid PFSA ionomer, notably NafionTM, continues to be the most prevalently utilized.⁸⁸ Decreasing the ionomer content within the CL could have a profound effect in reducing the total oxygen transport resistance, as well as reduce the possible $-SO_3^-$ poisoning of the catalytic sites.⁸⁹ This factor becomes increasingly important in ultralow-Pt-loading MEAs due to the increased ionomer/Pt ratio, implying that a reduction in ionomer content could yield more significant improvements in local oxygen transport. Nevertheless, it is imperative to maintain an adequate level of ionomer to provide adequate proton transport throughout the CL.^{90,91} Therefore, tailoring the ionomer/catalysts interaction within the catalyst layer is much favoured in enhancing local O_2 transport. The strategies can be distilled into two primary approaches: 1) modification of the ionomer's intrinsic properties and 2) strategic manipulation of the ionomer's distribution thus the interaction with the catalysts.

The first fundamental approach to altering O₂ transport dynamics involves modifying the chemistry of the ionomer itself. However, prior to implementing such alterations, it is essential to understand the mechanisms through which the ionomer amplifies local O₂ transport resistance during the ORR. Techniques such as voltammetry utilizing Pt(111) surfaces, and Surface Enhanced Infrared Absorption Spectroscopy (SEIRAS) on a polycrystalline Pt film were employed in this examination.⁹² The ionomer/platinum interface predominantly dictates O₂ permeation fluxes through the ionomer due to the unfavourable adsorption of the sulfonate group onto platinum. Experiments performed with Pt(111) surfaces that were coated with ionomer films demonstrated that the interference with ORR by sulfonate moieties within ionomers becomes less pronounced as the length of the side chain diminishes, ostensibly due to reduced flexibility of the side chains, thereby limiting their orientation to a state where ether groups interact with the Pt surface.

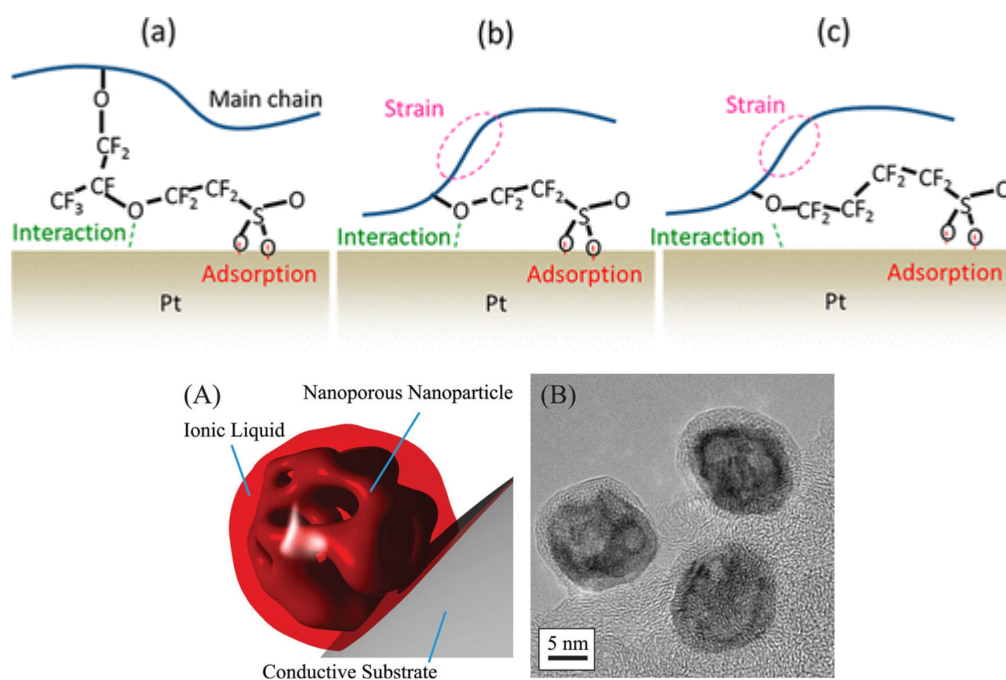


Figure 21. Two strategies for tailoring ionomer chemistry: (1) mitigating sulfonate adsorption by using polymers with short side chains. Figure reproduced from ⁹² with permission; (2) incorporating ionic liquids with high oxygen solubility to improve the availability of oxygen in the catalyst layer. Figure reproduced from ⁹³ with permission.

Beyond the approach of designing polymers with short side chains, the use of a hydrophobic and protic ionic liquid (IL) has been employed to permeate the pores of high-surface-area NiPt alloy nanoparticles, thereby enhancing oxygen transport.⁹³ J. Snyder et al presented the elevated oxygen solubility in the IL, coupled with the confined environment within the pores

of the catalyst, results in improved ORR kinetics. The trends observed in half-cell activity were directly translated into a PEMFC. Properties of the IL such as protonic conductivity, hydrophobicity, equilibrium water content, and oxygen solubility and diffusivity can be synthetically tuned to optimize performance.

Rather than the modification of the ionomer's intrinsic properties, various strategies of manipulating the ionomer's distribution thus the interaction with the catalysts is also reported. It is widely recognized that the surface of Pt nanoparticles exhibits higher hydrophilicity compared to an unmodified carbon support. This increases the propensity of sulfonic acid groups on the ionomer to adsorb on the Pt surface. One approach to directly diminish the extent of ionomer coverage on the Pt surface incorporates the method of molecular masking. Alkanethiol, for instance, can be utilized to veil the Pt surface, subsequently eliminating the potent polar interaction between Pt and the ionomer (Figure 22)⁹⁴. Post fabrication of the electrode, the molecular mask is electrochemically stripped away, revealing an ionomer-deficient Pt surface, consequently reinstating catalytic activity while maintaining optimal proton transport. This molecular masking technique could potentially alleviate local O₂ transport resistance, which is provoked by ionomer coverage. This, in turn, facilitates the reduction of local O₂ transport resistance across the CL, thus enhancing the efficiency of Pt utilization. It is imperative to ensure the complete removal of the mask molecules from the CL, given that even residual quantities of foreign ions may significantly impact the performance and longevity of the MEA.

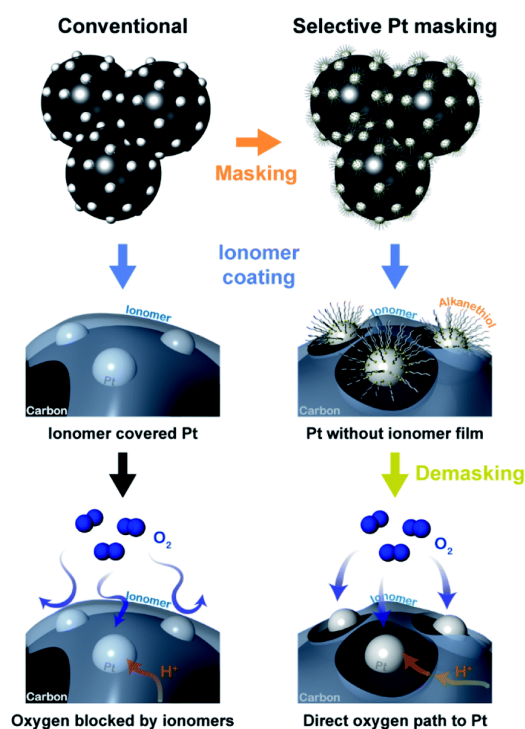


Figure 22. Fabrication process to achieve a targeted nano-scale ionomer distribution via molecular masking. Figure reproduced from ⁹⁴ with permission.

In addition to the masking technology aimed at preventing direct contact between Pt and the ionomer, enhancing the hydrophilicity of the carbon support surface has emerged as a promising approach for attaining homogeneous ionomer distribution, away from the Pt. S. Ott et al prepared a series of N-modified carbon support by firstly pre-oxidizing the pristine carbon in concentrated HNO_3 at 70 °C, followed by pyrolysis in ammonia stream at elevated temperature (200, 400 and 600 °C).⁹⁵ The resulted carbon materials led to homogenous ionomer distribution throughout the catalyst layer by forming ionic bonds between the functional groups of sp^2 pyridinic/pyrrolic/graphitic N with $-SO_3^-$ groups. This not only mitigates O_2 transport resistance but also fosters a more continuous proton transport pathway (Figure 23).

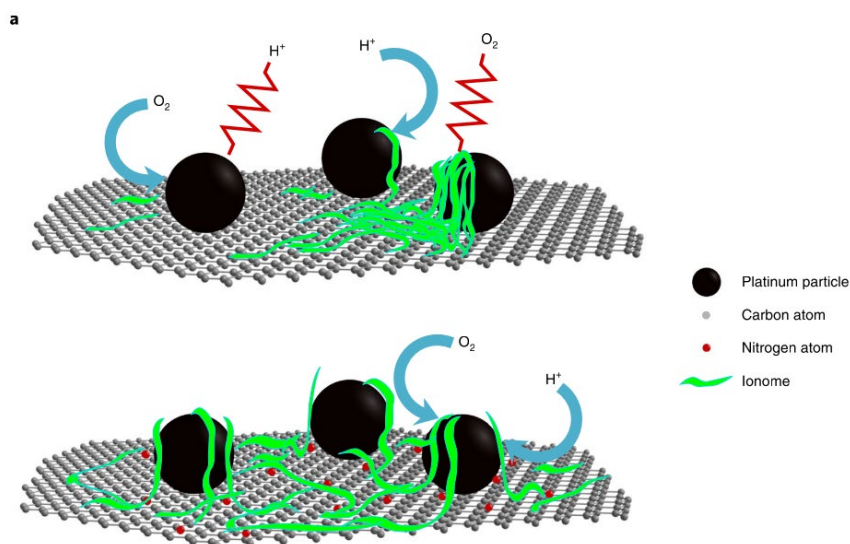


Figure 23. Conceptual representation of the distribution and thickness of the ionomer over both a Pt/carbon surface (upper section) and a modified Pt/N-carbon surface (lower section), in relation to their impacts on proton conductivity and O_2 mass transport. Figure reproduced from ⁹⁵ with permission.

Despite the observed effect of N-doping in creating a uniform ionomer distribution, which theoretically could enhance both the performance and durability of the cathode layer in standard PEMFC operation, the contributions of individual nitrogen species continue to elude complete understanding. E. Hornberger et al. further explored this aspect, specifically emphasizing the analysis of nitrogen-induced changes on catalyst activity and endurance.⁹⁶ Through the use of a specialized fluidized bed reduction reactor, the researchers synthesized highly uniform Pt nanoparticles affixed to N-doped carbons. These demonstrated oxygen reduction reaction efficacy and stability commensurate with state-of-the-art PEMFC catalysts. The team conducted sophisticated operando high-energy X-ray diffraction studies with advanced instrumentation, facilitating a detailed investigation of the impact of N-doping on the degradation behaviour of Pt/N-C catalysts. This involved comparative testing between liquid electrolytes and membrane electrode assemblies in single-cell PEMFCs. The study not only adds to the existing knowledge of N-doped carbon catalyst supports but also uncovers evidence that heteroatom doping, by introducing defects into the carbon backbone, might precipitate carbon corrosion during high-potential cycling (1–1.5 V). This finding implies a complex relationship between N-doping and catalyst performance that warrants further scrutiny.

Rather than introducing heteroatoms, the modification of carbon support can also be done in terms of its nanostructure to provide the desire hosting location for Pt, instead of making it the

overall carbon material more hydrophobic. The significance of the nanostructure of carbon support in affecting ionomer distribution has been acknowledged by researchers for long time, with many proposing that an optimal balance between low and high surface area carbon is necessary.⁸⁶⁹⁷

Yarlagadda et al., in an analysis of 11 distinct Pt/C catalysts deposited on diverse carbon supports, validated this hypothesis through measurements of dry proton availability and local oxygen access.⁹⁸ They reported that carbon supports with a lower surface area tend to cause the ionomer and Pt to come into direct contact, creating local oxygen resistance. Conversely, carbon supports with a higher surface area lacked adequate accessibility to protons and reactant gases. Their research, which included a statistical analysis of the structure of carbon support, led them to conclude that mesopores ranging from 4 to 7 nm offered maximum accessibility and enhanced the performance of ORR.

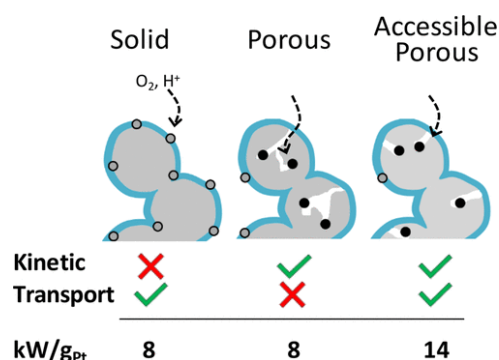


Figure 24. ORR kinetic and transport attributes (including both O₂ and proton) associated with catalyst layer structures derived from three different kinds of carbon (depicted in grey). Tiny black circles are representative of Pt particles that exhibit a relatively high level of activity. Small grey circles denote Pt particles with lower activity, both scenarios attributable to the adsorption of the ionomer (indicated in blue). Figure reproduced from ⁹⁸ with permission.

Despite these findings, the progress and comprehension of carbon supports have been obstructed by the non-uniform nature of carbon materials. In order to foster a more profound understanding of the interactions between catalyst, ionomer, and support, it is essential that catalyst supports are designed and synthesized with uniform pore sizes.

Advanced characterisation of the ionomer Pt interaction.

Besides the various strategies in engineering the ionomer-catalyst interaction, direct characterization of those interactions is integral to further understanding and improvement of fuel cell efficiency. Several methodologies, incorporating morphological, structural, and

electrochemical analysis, have been developed to evaluate the degree of ionomer coverage on Pt catalysts.

For instance, Ultra-Small Angle X-ray Scattering (USAXS) allows the extraction of particle size and its distribution in catalyst aggregates, thereby facilitating the evaluation of changes in ionomer interactions. F. Yang et al. investigated the interaction between NafionTM ionomer particles and XC-72 catalyst aggregates in a liquid medium.⁹⁹ A multiple curve fitting technique was employed to extract particle size and distribution information from the scattering data. To confirm the scattering results, cryogenic Transmission Electron Microscopy (cryo-TEM) was used, offering the capability to observe particle size within a liquid environment. Their results confirmed that the introduction of various functional groups can considerably alter the surface hydrophilicity of the associated carbon blacks. This modification results in two primary outcomes: (1) an enhancement in the dispersion of carbon black particles and (2) the creation of diverse charge groups across the surface of the carbon black particles.

To have more close-up investigations on the interaction, High-Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) imaging could provide a direct visualization of ionomer locations, typically by staining ionomers with caesium to enhance contrast against the carbon support. In 2014, M. Lopez-Haro et al. for the first time analyses the NafionTM layer in fuel cell electrodes obtaining quantitative morphological parameters (average thickness, degree of coverage of carbon support as shown in Figure 25).¹⁰⁰ They found that doubling the amount of NafionTM in the electrode leads to a twofold increase in its degree of coverage of the carbon, while the thickness of the layer, around 7 nm, is unchanged.

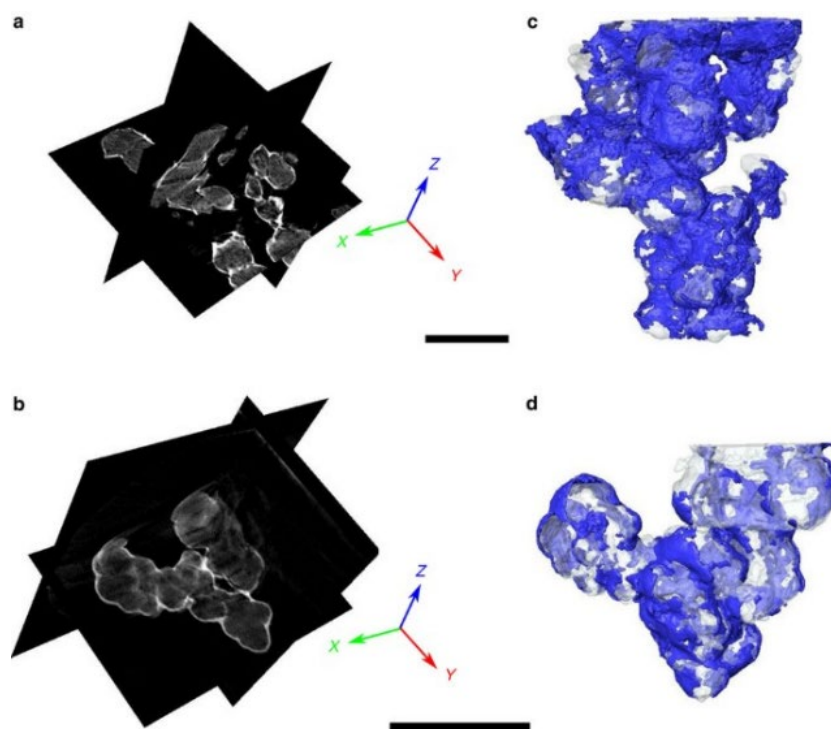


Figure 25. Electron tomography imaging of the NafionTM layer deposited on CB in the electrodes of PEMFCs. Orthoslices from any desired orientation relative to the direction can be extracted, as shown in (a,b) with three distinct orthoslices either parallel or perpendicular to the incident electron beam axis (along the z-direction) for samples 1 (Nafion/CB=0.5w/w) and 2 (Nafion/CB=0.2w/w), respectively. (c) Presents the 3D-rendered volume for sample 1, segmented from the HAADF-STEM-reconstructed tomogram, where blue and grey regions represent the Cs⁺-stained ionomer and CB support, respectively. (d) Illustrates the same for sample 2. The scale bars in the images are equivalent to 200 nm. Figure reproduced from ¹⁰⁰ with permission.

Despite the promising findings using electron microscopy characterization, the accurate mapping of ionomer distribution is still challenging due to potential beam damage induced by high voltage and electron dosage.

Another way to quantify the ionomer coverage is through the electrochemical evaluation, by comparing the electric double layer capacitance or CO stripping current of the ionomer-covered area with the total catalyst area. Ikeda et al.¹⁰¹ and Iden et al¹⁰². have both reported methods for estimating ionomer coverage. Each approach determines ionomer coverage based on the proportion of electric double-layer capacitance for the ionomer-covered area to that of the entire area within the catalyst layers. The techniques employed to measure this capacitance for ionomer-covered areas, however, differ.

Ikeda et al. deployed fluorocarbon fluid to fill pores in cathode catalyst layers, completely obstructing proton conduction to areas not covered by the ionomer.¹⁰¹ Yet, their analysis did not reveal the coverages on Pt and carbon support, but rather investigated the total ionomer coverage on both and its effect on cell performance. On the other hand, Iden et al. implemented a "CO masking" technique to distinguish the contributions from Pt and carbon support, while measuring the capacitance for ionomer-covered areas by presuming that protons do not conduct to non-ionomer-covered areas without adequate water¹⁰². However, their study did not discuss the relationship between ionomer coverage and cell performance.

Recently, T. Takeshita proposed a novel approach, combining the strengths of the two aforementioned methods.¹⁰³ They implemented the fluorocarbon fluid filling method and evaluated the ECSA via CO stripping voltammetry, which is a more accurate method for estimating Pt surface areas compared to the double-layer capacitance. By utilizing this innovative technique, they were able to assess the disparities in ionomer coverages among catalyst samples utilizing both non-porous and porous carbon supports.

The validity of the developed method was confirmed by investigating the relationship between ionomer coverage and specific activity. This was achieved by employing electrodes with Pt catalysts supported on both non-porous carbon (Vulcan) and porous carbon (Ketjen, and Cnovel). As depicted in Figure 26 a and b, the current resulting from CO stripping was calculated under both wet and fluorocarbon-fluid filled conditions. The ratio between these two circumstances represents the coverage of ionomer on Pt. Estimations of the ionomer coverage yielded $90\pm2\%$ for Vulcan, $60\pm7\%$ for Ketjen, and $57.4\pm0.3\%$ for Cnovel, respectively. The lower estimates for the porous carbons (Ketjen and Cnovel) as compared to the non-porous carbon (Vulcan) are attributable to the difficulty of ionomer penetration into carbon pores and the lack of ionomer coverage on Pt nanoparticles within these pores.

The relationship between the ionomer coverage and specific activity was also quantitatively explored, as presented in Figure 26c. Despite the distribution of ionomer coverage being slightly biased, with all samples exceeding 50%, a robust correlation between ionomer coverage and specific activity was established. This underlines the suppression of the ORR by ionomers as a significant issue to be tackled for substantial performance improvement in PEMFC.

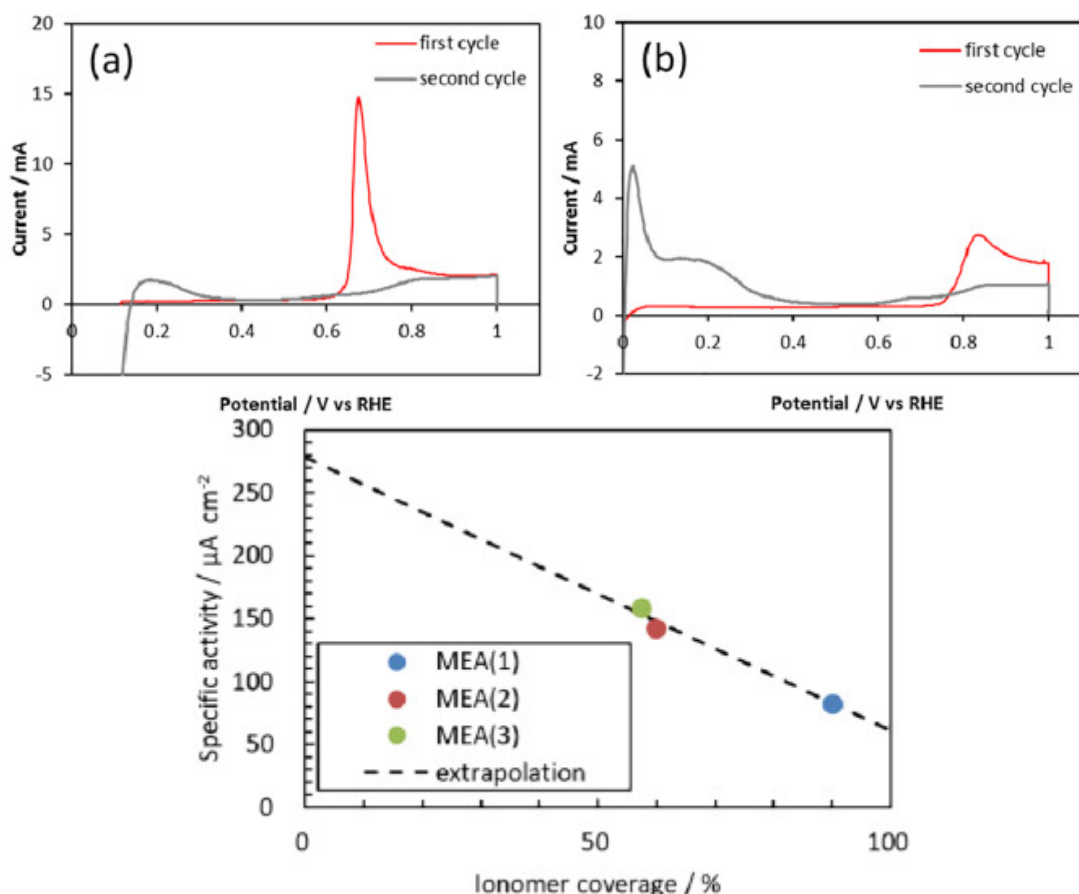


Figure 26. CO stripping voltammograms measured under the (a) wet and (b) fluorocarbon-fluid filled conditions. (c). The relation between the ionomer coverage and the specific activity. Figure reproduced from ¹⁰³ with permission.

The aforementioned electrochemical methods are applicable in MEA tests, given that the conditions must either be dry or inundated with a fluorocarbon fluid. While these methodologies deliver valuable information regarding the degree of ionomer coverage, they fall short in shedding light on the specifics of molecular interactions between Pt and the ionomer. This shortcoming underscores the necessity for more sophisticated characterization techniques such as X-ray Absorption Spectroscopy (XAS). XAS can elucidate changes in electronic structure consequential to the adsorption of sulfonate terminal groups from the NafionTM ionomer, as it monitors spectral shifts in operando.

C. Liu et al applied a quantitative approach to assess the relationship between catalyst activity and the NafionTM coating on the Pt/C catalyst.¹⁰⁴ This approach involved a combination of electrochemical measurements, operando X-ray absorption spectroscopy (XAS), and CO stripping voltammetry. Using operando XAS, they evaluated the specific adsorption during the oxygen reduction reaction (ORR) by gauging the 5d orbital vacancy of the Pt/C catalyst. Their

work established the variations in the electronic structures of Pt at higher potential ranges, in scenarios with and without the ionomer. By comparing the charge displacement of CO and the 5d orbital vacancies in the Pt/C catalysts with I/C ratios of 0.0 and 1.0, they inferred that ionomer-specific adsorption intensifies when the I/C ratio of the Pt/C catalyst reaches 1.0. This increased adsorption results in active site occupation on the surface of the Pt/C catalyst, subsequently reducing the catalyst activity.

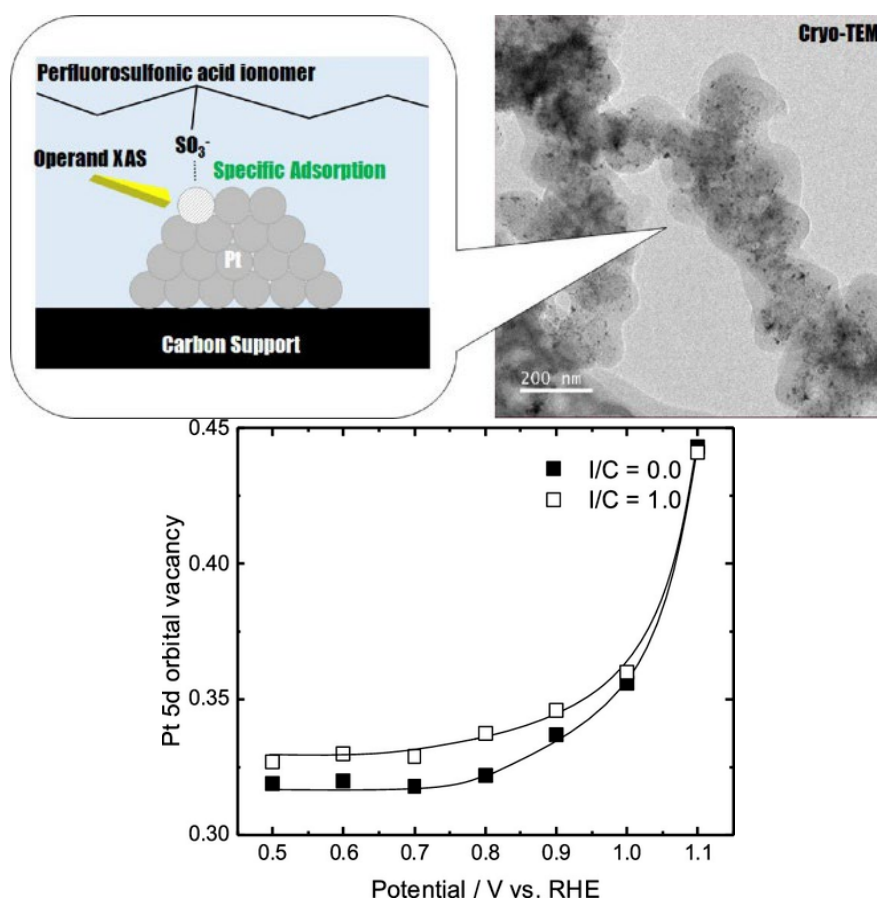


Figure 27. Relationship between potential and the Pt 5d orbital vacancy as measured by specific adsorption of the sulfonate group via X-ray Absorption Spectroscopy, with changes of Pt/C catalysts with I/C = 0.0 and 1.0 from 0.5 to 1.1 V. Figure reproduced from ¹⁰⁴ with permission.

The significant strides researchers have made in optimizing the interaction between the ionomer and catalyst, thereby facilitating local transport, is truly commendable. One notable approach is the nanoengineering of the carbon support. This strategy, unlike the more intensive synthetic approaches involved in molecular masking or new ionomer development, does not require heavy synthesis procedures. Future advancements should be focused on creating more

uniform and ordered pores, combined with sophisticated characterization techniques to deepen our understanding of the carbon support protection effect.

In the forthcoming Chapter 4, we will delve into the production of sustainable highly ordered mesoporous carbon (HOMC) from xylose. This process will be utilized to explore the influence of carbon support structure on Pt-ionomer interactions through advanced characterization techniques. For the first time, operando XAS and gas sorption analysis will be employed in conjunction with ORR catalytic performance in GDE configuration to demonstrate that mesopores enhance performance by fostering a beneficial ionomer/catalyst interaction.

1.7.3 Bulk Transport- Catalyst Layer Architecture

Other than the local transport dominantly effected by the presence of ionomer, transport across the overall catalysts layers (CLs) can also affect the PEMFC performance greatly. As illustrated in Figure 28, the contemporary PEMFC electrodes consist of CLs prepared with ink slurry of platinum catalyst supported on carbon (Pt/C) and an ionomer to form a porous electrode. Often, adjacent to the CL, one can find the microporous layer (MPL). This layer is a carefully constructed blend of carbon nanospheres and polytetrafluoroethylene (PTFE), designed to optimize gas transport and electrical conductivity while concurrently expelling water generated within the CL. Subsequent to the MPL, there is the gas diffusion layer (GDL), a matrix of highly porous carbon fibres, intended to support gas transport and maintain electrical conductivity. This fabrication process results in a haphazardly structured electrode, featuring convoluted pore networks that restrict mass transport and reduce catalyst utilization.¹⁰⁵

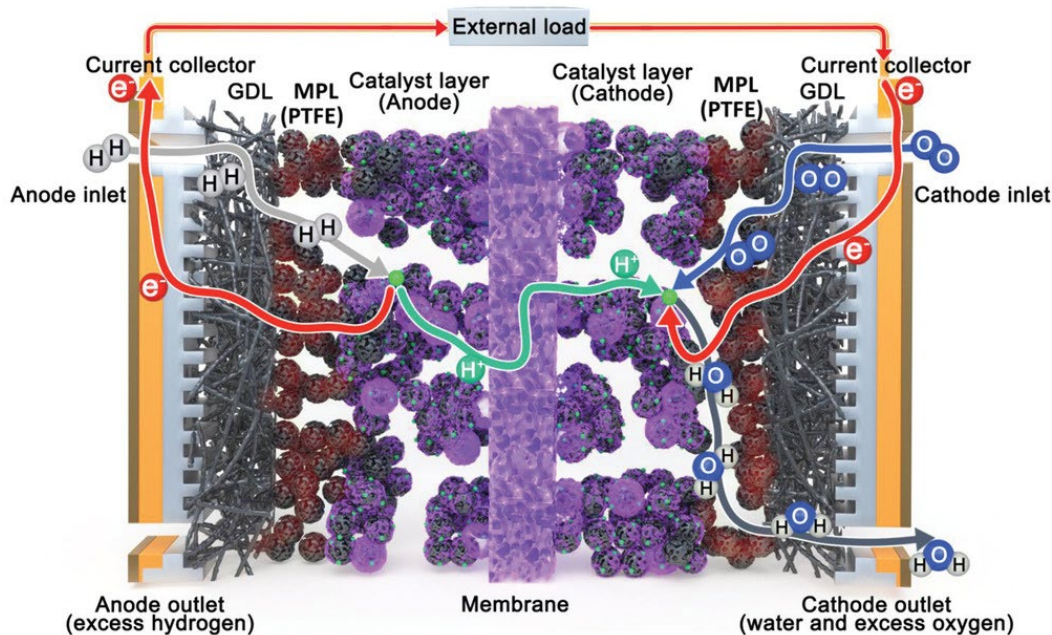


Figure 28. Illustration of a proton exchange membrane fuel cell depicting various layers, their constituents, and the route of reactant transport. Carbon support is represented by black structures, ionomer by purple, PTFE by red, and catalysts by green. Please note that the relative dimensions and distances are not accurately represented, and the catalyst layer, MPL, and GDL exhibit notably differing porosities and support material sizes. Figure reproduced from ¹⁰⁶ with permission.

In order to mitigate the inherent shortcomings of conventional electrode structures, numerous studies have embarked on the quest to engineer alternative architectures. This has been possible due to advancements in various techniques. Broadly, these strategies can be classified into three main categories: inkjet printing techniques, mold (frequently polymethylsiloxane) based patterning, and the construction of nanostructured films. The sections below will explore these advanced catalyst layer fabrication methodologies, shedding light onto their potential to catalyse a paradigm shift in the field of PEMFCs.

The arguably most direct approach to fabricate an efficient electrode architecture is via the inkjet printing process.¹⁰⁷ Using this technique, a variety of electrode configurations can be easily produced. In 2007, inkjet printing was reported for the first time to be successfully demonstrated as a catalyst application method for PEMFCs by A.D. Taylor.¹⁰⁸ The superior precision of inkjet printing enables controlled catalyst deposition, particularly for ultra-low platinum loadings. Such loadings, which prove challenging to realize using traditional methods,

yield some of the most impressive platinum utilizations reported in academic literature. Furthermore, the technique allows the creation of catalyst layers with customizable shapes and even gradations of loading across their thickness. Inspired by this potential, S. Shukla et al. detailed the construction of a thin, patterned electrode with low loading catalyst layers using inkjet printing, as depicted in Figure 29 (right).¹⁰⁹ In comparison to conventional electrodes, these inkjet-printed variants show a significantly enhanced sensitivity to oxygen partial pressures. This finding indicates that macro-scale oxygen and proton transport do not serve as limiting factor for the electrode within the tested NafionTM range of 20 wt% - 40 wt%. Impressively, the inkjet Coated Catalyst Membrane (CCM) exhibited a tenfold increase in Pt mass activity at ambient pressure, compared to a spray-coated CCM. This improved performance is attributed to the reduced thickness of the CL, which consequently minimizes macro-scale transport losses.

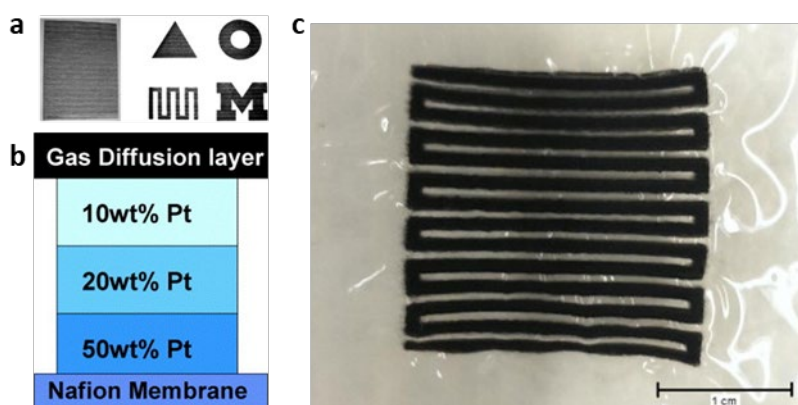


Figure 29. Different electrode configurations produced via the inkjet printing process. (a) catalyst layers with controllable shapes, (b) catalysts layer with graded loading and (c) patterned catalysts layer minimising macro-scale transport losses. Figure reproduced from ¹⁰⁹ and ¹⁰⁸ with permission.

Another method for creating patterned catalyst layers with macroscopic pores is via a molding technique, often employing polymethylsiloxane (PDMS).¹¹⁰ J.K. Koh and his team have innovatively applied this technique for the efficient patterning of large-area platforms with well-defined micro/nanopatterns.¹¹¹ Although their work focused on the fabrication of a polymer electrolyte membrane rather than a catalyst layer, the approach is promising. This cost-effective method utilizes an elastomeric mold at room temperature, thus bypassing the need for hot-pressing (as shown in Figure 30). The patterned structure of the membrane determines the interfacial properties between the membrane and electrode on the cathode side. This, in turn, directly influences the ECSA and Pt utilization of the catalyst. Confirming the effectiveness of

this approach, their innovative technique led to a notable performance improvement in the MEA. Specifically, compared to an MEA constructed without a patterned membrane, the power density was 53% and 59% higher, demonstrating the potential of this fabrication method.

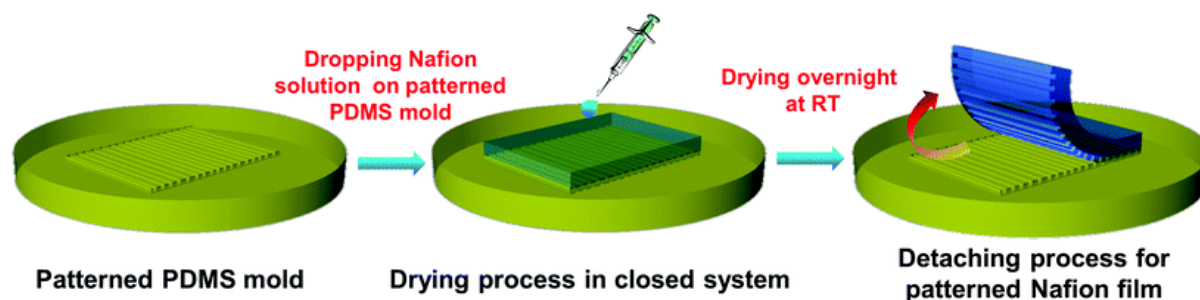


Figure 30. Overview of the fabrication process for patterned NafionTM membranes: from pdms mold design to membrane detachment. The left panel illustrates the PDMS mold design, the middle panel depicts the casting process for preparing a patterned NafionTM membrane using a 5 wt% solution, and the right panel shows the detachment of the dried NafionTM membrane from the PDMS mold. Figure reproduced from ¹¹¹ with permission.

In the light of these encouraging findings, the technique of PDMS molding has been adapted and further used by numerous researchers.¹¹² A study by M.T.Y. Paul et al. highlights the preparation of CLs with hexagonally organized cylindrical features.¹¹³ This was achieved using micro-transfer molding (μ TM) techniques, leveraging PDMS elastomeric templates. (Figure 31) In comparative terms, the CLs patterned through the μ TM method outperformed the standard, unpatterned or continuous CLs in terms of fuel cell performance. This superiority was particularly evident under conditions conducive to a higher water content within the CLs. A downside to this method was the observation of heightened hydrogen crossover and short-circuiting of the MEA. This is likely due to the deformation of the membranes during the process. Furthermore, the PEMFCs containing patterned CLs with arrays of cylindrical discs outperformed those with regular arrays of cylindrical holes, particularly at high current densities. This enhanced performance can be ascribed to a greater proportion of catalyst-free space within the CLs in the samples featuring discrete cylindrical discs of catalyst ink, relative to samples with cylindrical holes in an otherwise uniform film of catalyst ink.

In a remarkable demonstration of PDMS templating, CH Lee and his team recently presented an innovative grooved electrode.¹¹² The researchers ingeniously coupled high ionomer content (to facilitate improved proton transport) with grooves (for rapid O₂ transport), leading to a considerable enhancement in the performance and durability of PEMFCs. The grooved

electrodes showed up to a 50% superior performance compared to state-of-the-art conventional electrodes under standard operating conditions. The enhanced fuel cell performance is attributed to a combination of diagnostics and multiphysics modelling, revealing that the grooved electrodes provide efficient O_2 transport despite their high ionomer content. This, in turn, allows for an improved uniformity in the reaction rate. Furthermore, grooved electrodes demonstrate greater durability, evidenced by less performance loss following carbon corrosion when compared with baseline electrodes. Furthermore, machine learning analysis underscores the potential to further refine these grooved structures for future-generation PEMFCs, offering better performance and durability.

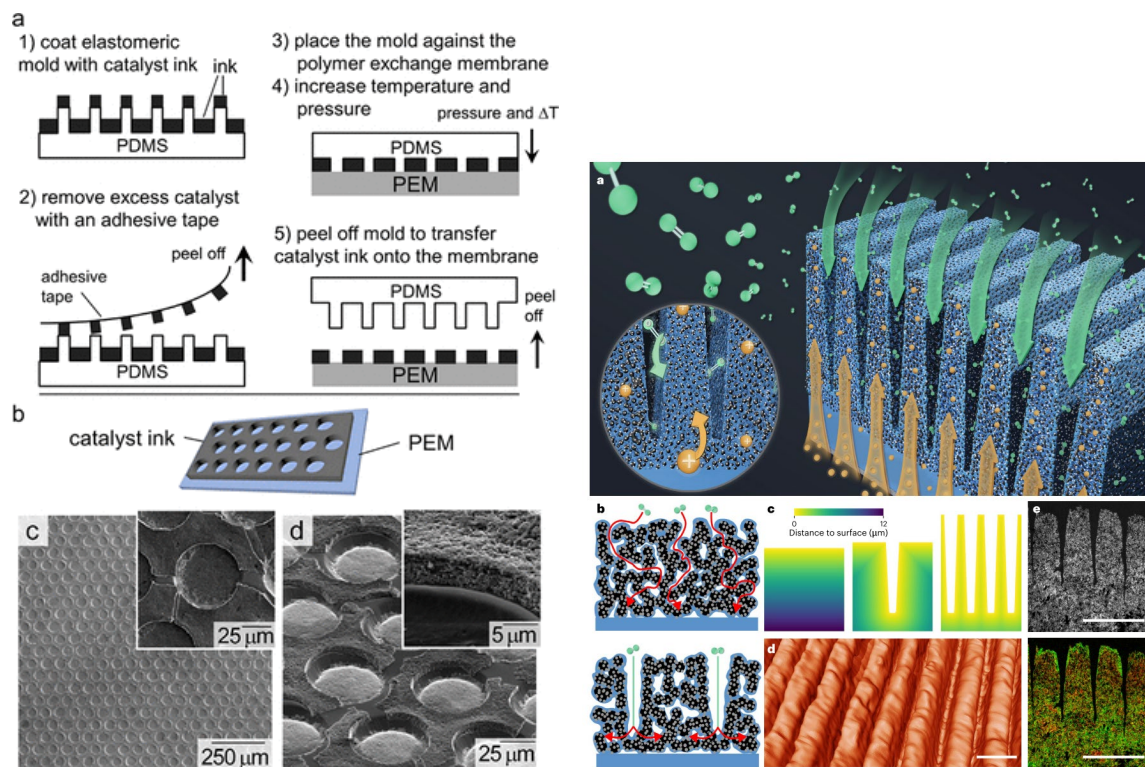


Figure 31. Various patterned catalysts layers leveraging PDMS elastomeric templates.(left).a process to fill catalyst inks into the recesses of a PDMS template, and the transfer of this patterned ink by microtransfer molding (μ TM) to a proton exchange membrane. Figure reproduced from ¹¹³ with permission. (right) the functioning mechanism of grooved electrodes prepared via PDMS molding. The ridges, with a high content of ionomer, enable enhanced transport of H^+ ions (shown in orange), while the grooves facilitate efficient O_2 transport (indicated in green), leading to improved fuel cell performance. It presents a comparison of O_2 transport through flat (top) and grooved (bottom) electrodes, underscoring the reduced O_2 transport resistance in grooved electrodes. Figure reproduced from ¹¹² with permission.

The third and equally significant approach to devising efficient structures for the catalyst layer involves the development of nanostructured films. This typically incorporates the use of intrinsically structured materials such as carbon nanofibers or carbon nanotubes (CNT), as well as a range of nano-sized templates, including silica, alumina, or polymer particles.¹¹⁴¹¹⁵¹⁶ W. Zhang et al. presented a uniquely designed free-standing, sandwich-structured MEA, with nano-Pt loaded ACNT/Nafion/ACNT.¹¹⁶ This was achieved via the attachment of two sets of aligned CNT array electrode structures to the opposite sides of a Nafion PEM membrane. The aligned carbon nanotube array structure fosters an efficient electrical connection between the ion conducting phase and the current collector. Impressively, these innovative ACNT-membrane electrodes exhibit remarkable robustness, preserving their integrity under severe hot-pressing conditions of 5000 psi and 160 °C. Such characteristics position these membranes as a promising future platform technology with potential for reducing the Pt level in fuel cells and enhancing overall fuel cell performance.

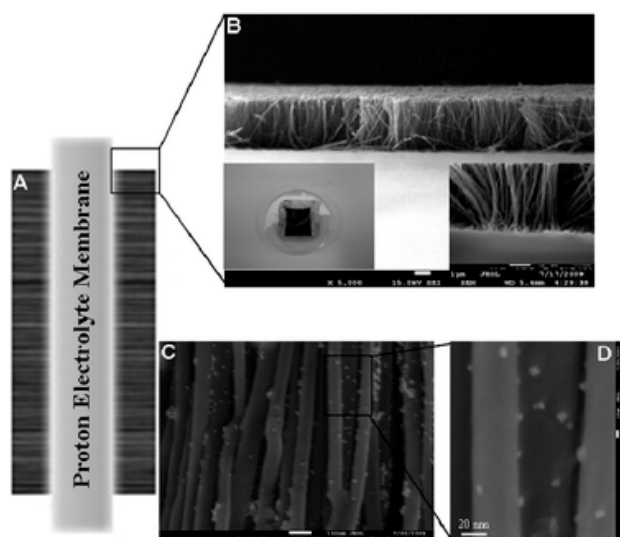


Figure 32. Images of nano-Pt-loaded ACNT/Nafion[™] membrane electrode. Figure reproduced from ¹¹⁶ with permission.

An extensively researched nanostructure for catalyst layers is the three-dimensional, ordered macroporous inverse opal (IO), typically templated by enclosed spherical materials. The IO structure, with its periodic architecture, offers several advantages such as substantial surface area, high voidage, reduced tortuosity, and interconnected macropores. This templating technique can be utilized to fabricate both the carbon support¹¹⁷¹¹⁸ and nanostructured platinum¹¹⁹ directly. As demonstrated in Figure 33, OH Kim et al. presents a method that allows for the straightforward and direct application of a large-area (5 cm² of active area) IO Pt

electrode in a practical MEA device, eliminating the need for any additional transfer process at the electrodes.¹¹⁹ Under equivalent conditions, the current observed for an IO electrode-based MEA with similar Pt loading was 185% higher than a conventional MEA. In contrast, when a thicker electrode is employed, the differences become more noticeable. This disparity arises due to increased concentration losses caused by mass transport of reactants and products in a thicker electrode. Specifically, a thicker electrode mandates a longer diffusion path for reactants to reach the catalyst layer where reactions take place. Similarly, it imposes a greater diffusion distance for the products to be expelled from the fuel cell.

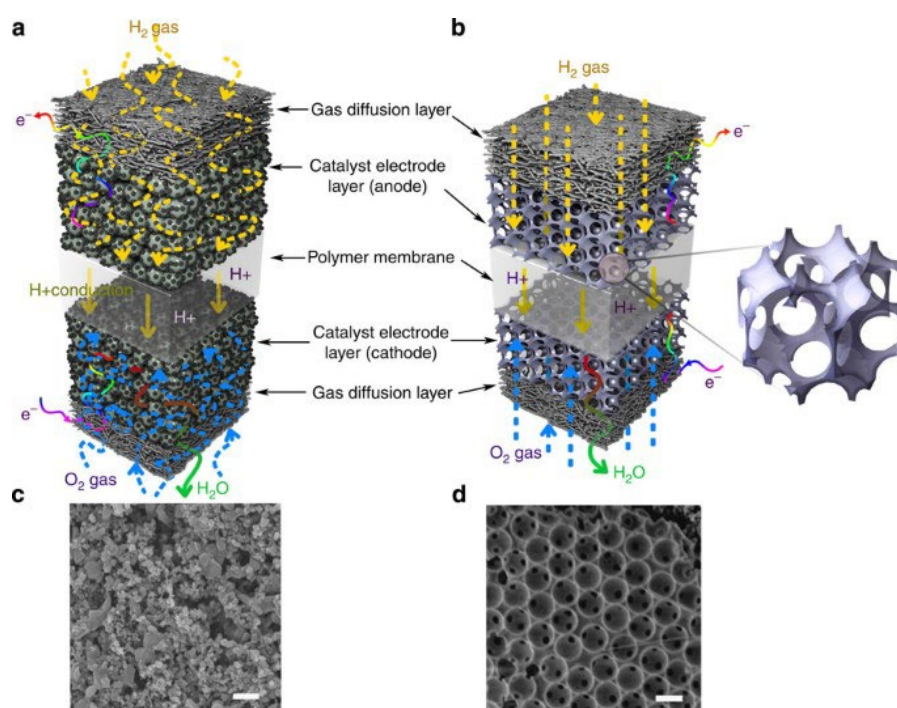


Figure 33. (a) Traditional MEA featuring CCM, (b) Adapted MEA showcasing the inverse-opal-structure (IO) electrode explored in this study. (c) Field Emission Scanning Electron Microscope (FE-SEM) image revealing the surface of a CCM, prepared through the spraying of commercial Pt/C ink. (d) FE-SEM image depicting the surface of an IO electrode, prepared through pulse electrodeposition, following colloidal crystal templating methods. Scale bar represents 500 nm. Figure reproduced from ¹¹⁹ with permission.

The same templating technique and IO structure can also be utilized to form the carbon support using various carbon precursors. As illustrated in Figure 31, mesophase pitch was used as a precursor to generate a series of binder-less, self-supported, nanoporous carbon scaffolds (NCS) characterized by tuneable, monodisperse pores, and three-dimensional scalability.¹²⁰ Notably, catalysts layer with 85 nm pores, emerge as especially promising for hosting the homogeneous

and efficient 3D atomic layer deposition (ALD) of Pt nanoparticles. This is due to the easy penetration of the Pt precursor in gas phase throughout the homogeneous, low tortuosity internal structure. Additionally, the high density of surface defects inherent in the as-synthesized NCS facilitates uniform Pt nucleation while minimizing agglomeration. Fuel cells assembled with an optimal ALD Pt loading of 30 cycles have been demonstrated a specific activity of approximately $0.4 \text{ mA cm}^{-2}_{\text{Pt}}$. This performance is better when compared with commercial catalyst layers carrying comparable Pt mass loadings and tested under similar conditions.

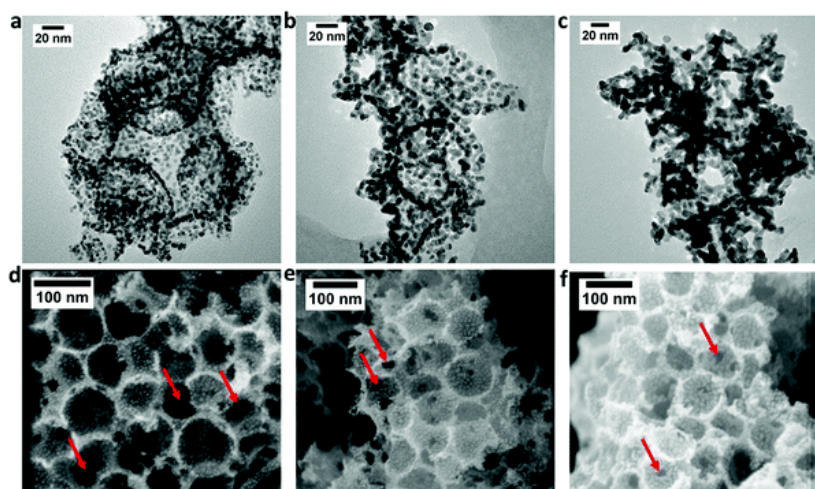


Figure 34. Nanoporous carbon scaffold (NCS) developed from pitch with various macropores and Pt nanoparticles deposited. Figure reproduced from ¹²⁰ with permission.

Despite the considerable progress made with the 3D IO structure, particularly concerning its low tortuosity and interconnected porous design, its limitations are equally significant. Specifically, the absence of a hierarchical structure restricts the effective utilization of Pt active sites. In the subsequent 0 of this thesis, we will elaborate on the development of a hierarchical and continuous catalyst layer. Advancing beyond the IO structure, we introduced a mesoporous level of pores to host the Pt sites, thereby ensuring optimal ionomer interactions. Simultaneously, we constructed the carbon support from a sustainable biomass precursor, further enhancing the ecological footprint of our catalyst design.

1.8 Green Carbon from Biomass

As elaborated in preceding sections, the formulation of a well-defined nanostructure for the carbon support of Pt/C catalysts in PEMFC is of paramount importance, especially for the cathode ORR, which exhibits six orders slower kinetics compared to the anode HOR.¹²¹ In this

context, engineering of mesopores is necessary to provide optimal interaction between the ionomer and catalytic sites, thereby assisting with localized transport. Concurrently, the design must also include interconnected macropores to establish effective pathways for bulk mass transport, thus enhancing the utilization of active sites. Through this meticulously constructed porous network, a multiscale mass transport of protons and reactants can be achieved, leading to an improvement in the overall performance of the fuel cell.

Biomass, recognized as an environmentally friendly, readily available, low-cost, and renewable carbon source, serves as an exemplary candidate for the precursor in the design of nanostructured carbon materials. Such utilization adds extra dimensions of environmental and economic benefits. In this section, we will explore the diverse methodologies to employ biomass for this specific application. These strategies can be primarily classified into two categories based on the choice of the starting materials: top-down fabrication and bottom-up synthesis.

1.8.1 Top-down Fabrication from 3D Natural Materials

Top-down fabrication from 3D natural materials represents a natural and advantageous choice for the preparation of nanostructured carbon as catalyst supports. This method leverages the inherent structural complexities found in natural materials, such as the intricate porous networks within plant tissues or other biological sources. The method typically involves selectively removing components from the native material to create well-defined pores, channels, and structures that are ideally suited for designing catalyst supports. This not only mimics the hierarchical organization of natural systems but also enhances the properties vital for catalyst activity, such as surface area and mass transport efficiency. Additionally, by employing renewable and abundant natural materials as precursors, this approach aligns with sustainability goals, providing an economically viable pathway towards the large-scale production of advanced catalyst supports. There have been several comprehensive reviews regarding the fabrication of carbonaceous materials from biomass.^{122,123} In this thesis, we will be focusing on the recent advances in hierarchical porous carbon development based on top-down fabrication of natural 3D structures.

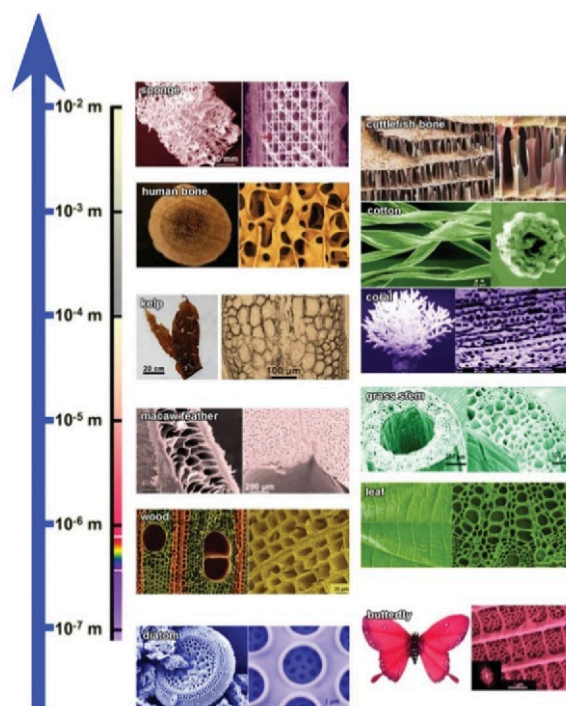


Figure 35. Common hierarchical structured porous natural materials placed alongside the length scale according to their critical dimensions. Figure reproduced from ¹²⁴ with permission.

Many biomass materials, abundant in nature and possessing hierarchical porous structures, present an excellent opportunity for fabricating hierarchical porous carbon. Examples include wood, butterfly wings, leaves, and more, as depicted in Figure 35. These biomass materials have been explored for their potential in this fabrication process, demonstrating a wide array of structural and functional possibilities. Based on the origins, these biomass materials can be categorized mainly into two groups.

The first group includes materials derived from plant sources, which often present well-defined cellular structures, such as wood¹²⁵¹²⁶¹²⁷¹²⁸, sisal leaves¹²⁹, pine needle¹³⁰, rice husk¹³¹, bamboo¹³², loofah¹³³, watermelon¹³⁴, pomelo peel¹³⁵, hemp¹³⁶¹³⁷, clover¹³⁸, peanut skin¹³⁹, fern fiber¹⁴⁰.

Among the various plant materials suitable for fabricating hierarchical porous carbon, wood is particularly appealing due to its natural rigid 3D structure and abundance. Its inherent properties provide an ideal starting point for innovative fabrication techniques. Recently, K P Loh et al. introduced an enzyme-assisted method to harness these qualities, as detailed in their work.¹⁴¹ By treating the wood with a cellulase solution overnight, a significant number of shallow nanopores were generated on the wood's surface. This process notably enhanced the

exposure of the internal structure of the wood, allowing for substantial nitrogen doping onto the carbon skeleton during the subsequent pyrolysis process. This led to the formation of N-doped hierarchical porous carbon materials, effectively retaining the natural 3D porous network of the wood. Such a method not only preserves the intricate architecture of the original material but also introduces functional elements like nitrogen, broadening the potential applications and performance of the resulting carbon materials. The enzyme-assisted approach represents a novel, environmentally friendly pathway to utilize the complex structure of wood, highlighting its promise in the development of advanced catalyst supports.

The second group may encompass materials from animal sources like cattle bone^{142,143}, pig bone¹⁴⁴, sheep bone¹⁴⁵, leather¹⁴⁶, shrimp shell¹⁴⁷. These biomass materials each come with unique nanostructures that lend themselves to specific applications.

Bone, particularly from animal sources, has increasingly drawn research attention due to its unique structural composition of ordered inorganic composites filled with organic collagens, which naturally contain nitrogen. F Wang et al. have explored this structure by developing a 3D hierarchically porous carbon material with self-doped nitrogen through a series of processes including carbonization, KOH activation, and acid etching of cattle bones.¹⁴³ Their subsequent work further demonstrated a successful method for fabricating N,P co-doped carbon by pyrolyzing the obtained porous materials in conjunction with phytic acid and dicyandiamide.¹⁴² Impressively, the original hierarchical porosity of the cattle bones was well preserved in the N,P co-doped electrocatalysts, resulting in a large specific surface. The N, P/C materials exhibited a remarkable ORR performance, with a half wave potential of 0.853 V, and outstanding stability, losing only 1.74% of current density after 10,000 s. These promising results can be attributed to the increased exposure of active sites and the reduced mass transfer barrier in the structure. Such findings underscore the potential of bone-derived hierarchical porous carbon materials as an innovative and efficient approach for catalyst support, highlighting the unique advantages provided by the natural architecture of bone.

The inherent architecture found in these natural resources can be leveraged for various technological advancements. Whether it's the rigid 3D structure of wood or the delicate composition of butterfly wings, these nanostructures offer tailored solutions that can be exploited in areas such as catalyst support, energy storage, and environmental remediation. By aligning the specific characteristics of these materials with corresponding applications,

researchers can develop innovative and sustainable approaches that utilize nature's design to address contemporary challenges.

1.8.2 Bottom-up Synthesis via Templating Small Molecules

The bottom-up approach for synthesizing a hierarchically porous structure typically requires the use of structure guiding through a foreign entity known as a template. This synthesis strategy can be classified based on the specific templates employed. By manipulating the templates, the resultant porous structure can be tailored to achieve the desired characteristics. Compared to the top-down fabrication where the end materials' structure highly depends on the starting biomass, this bottom-up method allows for precise control over the size, shape, and arrangement of the pores, enabling the creation of complex and well-defined hierarchical porous materials. Whether utilizing hard or soft templates, the bottom-up approach provides a robust and versatile pathway toward the design of advanced porous structures for various applications.

Hard Templating

The hard templating method, also known as nano casting, is commonly employed to create porous structures and is notable for its ability to replicate well-defined morphologies. In a typical synthesis procedure, the hard template is integrated with a mixture of carbon precursors, followed by carbonization at a specific temperature. Subsequently, the template is removed by acid leaching or solvent dissolution, resulting in a carbon replica that mirrors the template's structure. Depending on the template size, this process endows the carbon materials with both macropores and mesopores. On the other side of the spectrum, micropores are generated during pyrolysis through the dehydration and dehydrogenation of biomass. These small-scale pores are essential for certain applications and can be further increased through specific chemical activation processes, such as annealing with a carbon corrosion agent (KOH^{148} , CO_2^{149} etc). The simultaneous control of macro (>50 nm), meso (2-50 nm), and microporosity (<2 nm) allows for the customization of the porous structure, making hard templating a powerful tool in the fabrication of tailored carbon materials for various technological applications.

Silica stands out as the most prevalent hard template utilized in the development of various porous structures through nanocasting. Its popularity stems from its ease of synthesis, cost-effectiveness, and the diverse array of available pore sizes and morphologies, including nanospheres, zeolites, and mesoporous silica. Nevertheless, the removal of silica templates

often demands the use of highly toxic chemicals such as hydrofluoric acid (HF) or strongly corrosive alkaline solutions, posing both environmental and safety concerns.

In response, alternative materials like magnesium oxide, zinc oxide (ZnO), and anodized alumina (Al_2O_3) film have been investigated, as they can be removed under relatively mild conditions. A noteworthy example is the work of S. Kubo et al., who reported the preparation of carbon nanotubes through hydrothermal carbonization of furfural, using anodized alumina membrane (with a diameter approximately 200 nm) as the hard template. The resultant nanotubes displayed a highly uniform morphology, coupled with an accessible internal surface afforded by the open-ended structure. This approach represents an innovative and less hazardous alternative to traditional silica-based templating, demonstrating the potential for the advancement of sustainable nanocasting techniques.¹⁵⁰

Metal salts, encompassing both inorganic and organic types, offer another avenue for hard templating in the creation of hierarchically porous structures. Unlike silica and metal oxides, metal salts present a distinct versatility, as they can be tailored to various thermal stabilities. The deployment of metal salts as templates typically involves their integration with carbon precursors. Based on their specific thermal stability characteristics, metal salts can be classified into two main groups, namely thermal stable salts and decomposable salts, thereby broadening the range of possible applications and design configurations.

The stable salt catalogue for hard templating encompasses highly thermally stable ionic compounds, such as combinations of $\text{NaCl}+\text{Na}_2\text{CO}_3$,¹⁵¹ $\text{LiCl}+\text{KCl}$,¹⁵² and $\text{NaCl}+\text{Na}_2\text{CO}_3+\text{Na}_2\text{SiO}_3$.¹⁵³ In scenarios where these salts are soluble in carbon precursor solutions, a uniform distribution can be achieved within the mixture. This uniformity leads to the creation of pores with more consistent sizes and shapes, as the single-phase templating method minimizes variations in the final structure. Such consistency may offer advantages over other types of templates, especially where precise control over pore characteristics is required. An illustrative example of this approach was reported by C. He et al., who developed a 3D hierarchical porous carbon with multi-scale pores (Figure 36). The structure was templated by sodium chloride (NaCl), sodium silicate (Na_2SiO_3), and sodium carbonate (Na_2CO_3), utilizing glucose as the carbon source. The combination of these stable salts with a single-phase templating method resulted in a well-defined porous network, highlighting the efficacy of stable salts in the precise engineering of complex carbon structures. This methodology offers a

promising avenue for further research and applications in areas requiring highly specific porous configurations..¹⁵³

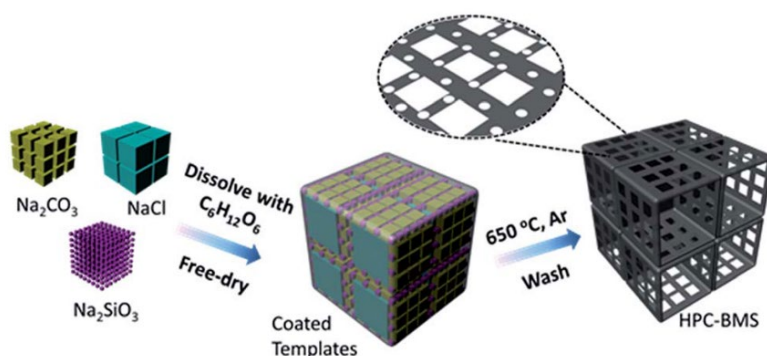


Figure 36. 3D hierarchical porous carbon templated by soluble salt self-assembly. (Extracted from J. Mater. Chem. A, 2015, 3, 22266–22273)

In the process detailed in Figure 36, metal salts, including NaCl, Na₂SiO₃, and Na₂CO₃, are dissolved with glucose and freeze-dried to self-assemble into a 3D hierarchical structure, forming various pore sizes. Upon carbonization and removal of the salt templates by water washing, an interconnected porous carbon structure is produced, with each salt responsible for specific pore sizes (NaCl 1–2 mm, Na₂SiO₃ 5–10 nm and Na₂CO₃ 50–100 nm respectively). The resulting 3D hierarchical porous carbon was tested as a supercapacitor, demonstrating promising enhancements in performance.

The category encompassing decomposable salts pertains to those that are thermally unstable and have the propensity to undergo decomposition into either metal oxides or elemental metals during pyrolysis. This can further include interactions with carbon to metamorphose into metallic configurations. These emergent metal oxides or metals function as tangible templates, which can be extracted through either acid or alkaline washing techniques, leading sequentially to the formation of the targeted porosity. Furthermore, specific salts characterized by their ability to generate gases during decomposition—such as metal carbonates, metal nitrates, and certain organic salts—are preferred in the synthesis of lighter porous carbons. The gases evolved (e.g., CO₂, NH₃) contribute to the activation and structural exfoliation through reactions with carbon. Decomposable salts templates that have been reported recently are sodium phytate (converts to Na₂CO₃ and Na₃PO₄),¹⁵⁴ magnesium nitrate (converts to MgO),¹⁵⁵ magnesium hydroxide (converts to MgO),¹⁵⁶ calcium carbonate (decomposes to CaO),¹⁵⁷ and zinc chloride (decomposes to Zn or ZnO).^{158,159} For example, a study conducted by C. Zhu et al. elaborated on an adaptable method to fabricate porous carbon from cotton fibres using

Mg(NO₃)₂ as the decomposable salt template.¹⁵⁵ The process involved immersing dewaxed cotton in an Mg(NO₃)₂ solution, facilitating the infusion of salts into the cellulose fibres. The saturated fibres were subsequently dried and carbonized, during which MgO was formed in situ, acting as the actual hard template. The acid removal of MgO resulted in a highly porous carbon structure with a substantial specific surface area of 1260 m²/g, accompanied by a blend of macro/mesopores. The ensuing electrochemical analysis of this carbon material as a Li-ion battery anode revealed commendable performance.

This intrinsic adaptability, stemming from the diverse thermal stabilities of metal salts, positions them as an appealing choice for hard templating. Such versatility facilitates the creation of intricate and highly specialized porous structures, which might be elusive or challenging to attain using conventional silica and metal oxide templates.

In addition to inorganic materials, certain organic substances that can be eliminated through non-polar solvent dissolution or thermal decomposition during the carbonization process are also employed as templates to construct porous architectures. Among these, polystyrene (PS) stands as the most commonly utilized organic hard template, owing to its ability to be either combusted away or removed using hot acetone.¹⁶⁰¹⁶¹¹⁶²

R J White et al. detailed an accessible and environmentally responsible method for synthesizing hollow carbon nanospheres, employing polystyrene nanospheres as a template during the hydrothermal carbonization (HTC) of glucose.¹⁶¹ These polystyrene spheres were specifically prepared with hydroxy-terminating groups, facilitating a suitable hydrogen bonding surface for the initial adsorption of glucose. By combining the latex nanoparticles with glucose and subjecting the mixture to an HTC process at 180°C for 24 hours, the template was subsequently eliminated through carbonization of the HTC product at temperatures exceeding the decomposition threshold of polystyrene (>500 °C), thus yielding hollow carbon spheres (Figure 37).

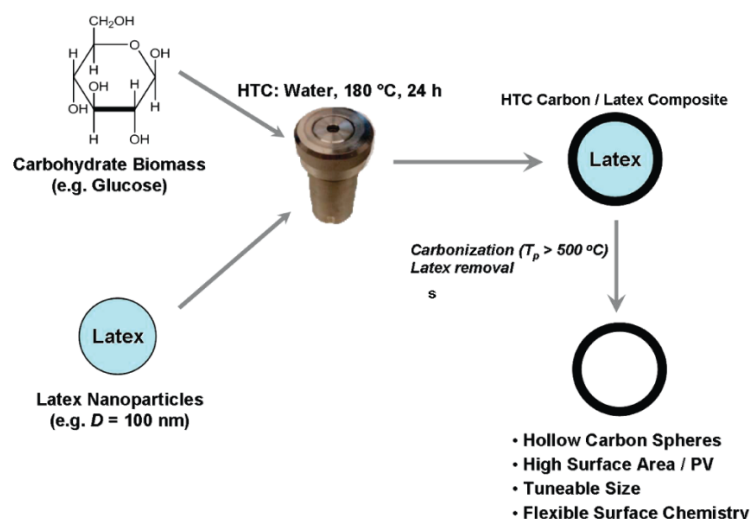


Figure 37. Synthetic strategy for hollow carbonaceous nanospheres templated by polystyrene. (Extracted from J. AM. CHEM. SOC. 2010, 132, 17360–17363)

The last but not least hard templating approach is freeze-casting (ice templating), offering a unique strategy for generating structured carbon materials by harnessing the highly anisotropic solidification behaviour of water. This method has been employed in the fabrication of aerogels, porous ceramics, and hierarchical porous carbons. Typically, an aqueous solution or slurry undergoes a directional temperature gradient, allowing ice crystals to nucleate on the colder side and grow along the gradient, guiding the carbon structure's formation. After solidification, lyophilization (freeze drying) removes the water content by sublimation, and the dried sample is carbonized to yield the final product, often featuring macropores (2–200 μm) due to the ice crystals' size. Combinations with other templating methods or chemical activation are commonly employed to create hierarchically porous structures.¹⁶³¹⁶⁴¹⁶⁵¹⁶⁶

For instance, A. Umar et al. crafted highly porous carbon aerogels via ice templating using cellulose derived from waste bagasse.¹⁶⁴ By treating the bagasse with sodium hydroxide, lignin and hemicellulose were removed, and the remaining cellulose was dissolved using urea and sodium hydroxide. Freeze drying and activation with KOH resulted in macro/mesopores and micropores, respectively, in the carbon materials. These materials, tested as supercapacitor electrodes, demonstrated impressive energy storage capabilities attributed to the specialized pore structure. In a precise control of texture and porosity, F. M. Fernandes et al. manipulated the thermal gradient and polysaccharide concentration to create foams from beet-root pectin.¹⁶⁷ Notably, their subsequent work quantified the pressure generated between ice columns during ice templating by combining in situ synchrotron small-angle X-ray scattering (SAXS) and adiabatic desiccation analysis, marking a pioneering effort in understanding this process.¹⁶⁸

Soft Templating

Contrary to hard templates, soft templates lack a well-defined shape and are predominantly utilized to create mesopores, which are often of significant importance. Soft templates usually consist of organic surfactants or block copolymers capable of self-assembling into micelles. Within aqueous solutions, these micelles generally have their hydrophilic and polar tails oriented outward, enabling interactions with proximal carbon precursors through mechanisms like electrostatic and dipole forces. Consequently, the attracted carbon precursors are incorporated into the micellar assembly, forming carbon precursor-micelle composites that are then subjected to carbonization.

During the elevated temperatures of carbonization, the soft templates are either evaporated or thermally decomposed, leaving behind the carbon formed through pyrolysis of the precursors while preserving the skeleton structure initially created by the spaces among the micelles. Carbon materials obtained in this manner typically feature ordered mesopores, attributed to the organized assembly of soft templates into micelles. The resultant pore pattern varies depending on the micelles' shape; cylindrical micelles yield hexagonally ordered mesopores, while spherical micelles can give rise to cubic arrangements in the derived materials.¹⁶⁹ Soft templates can be classified into two categories based on their interaction forces with the carbon precursors: (1) charged surfactant templates and (2) uncharged surfactant templates.

In the case of charged surfactant templates, their hydrophilic groups carry a charge, either positive or negative. The binding between the carbon precursors and the surfactants in this category occurs through electrostatic interactions, where the charged portions of the surfactants attract oppositely charged or polar regions of the carbon precursors, facilitating the formation of the desired structures..¹⁷⁰¹⁷¹

For example, H Shu et al. developed a one-pot synthesis method for hierarchical porous carbon microspheres, using furfural alcohol and cetyltrimethyl ammonium bromide (CTAB) as a charged surfactant template.¹⁷⁰ As shown in Figure 38 The process involved electrostatic interactions with polyacrylic acid (PAA), the addition of carbon precursors, and the use of tetraethyl orthosilicate (TEOS) as a pore expander, leading to the formation of complex particles. Upon calcination and dissolution of SiO₂ in a 46% HF solution, carbon-SiO₂ composites were obtained. The final carbon material exhibited a hierarchically porous structure, comprising macropores, mesopores, and micropores, templated respectively by phase-separated PAA, CTAB micelles, and in situ-formed silica.

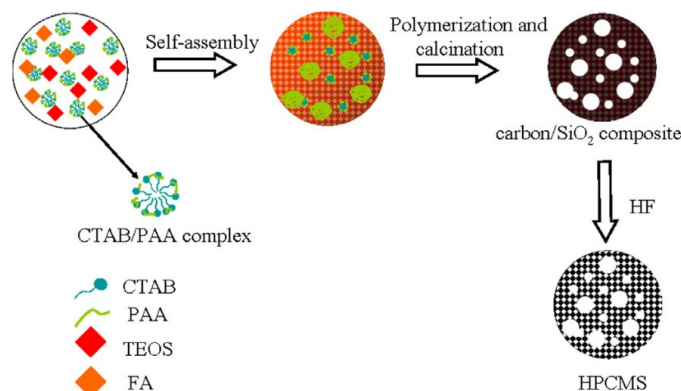


Figure 38. Preparation of hierarchically porous carbon materials with CTAB as soft template. (Extracted from Journal of Power Sources 254 (2014) 10-17)

The other distinct category of soft templates encompasses uncharged surfactant templates, specifically organic block copolymers that exhibit amphiphilic properties due to the coexistence of hydrophobic and hydrophilic components, thus functioning similarly to surfactants. Contrary to charged surfactants, these block copolymers generally establish interactions with carbon precursors through hydrogen bonding rather than electrostatic forces. A prominent example within this classification is Pluronic® triblock copolymers, which include structures such as poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide), with variations like F127¹⁷²¹⁷³¹⁷⁴¹⁷⁵ and P123¹²² etc. In these copolymers, a central hydrophobic block of poly(propylene oxide) (PPO) is flanked by two hydrophilic blocks of poly(ethylene oxide) (PEO), facilitating the formation of hydrogen bonds between the oxygen atoms on the polymer chain and the hydrogen atoms present on the biomass precursors.

Y. Wang et al recently detailed the synthesis of highly ordered mesoporous carbon nano-ellipsoids using xylose, with a triblock copolymer (PEO₇₅-PPO₃₀-PEO₇₅, F127) serving as the soft template (Figure 39).¹⁷⁵ Initially, the xylose formed hydrogen bonds with the copolymer F127, leading to the development of rod-like micelles. These micelles then organized into a hexagonal structure, guided by controlled rates of xylose decomposition and polymerization. If desired, metal precursors could be added to the system, resulting in a metal-cored hexagonal structure. The subsequent carbonization process yielded the final product: highly ordered mesoporous carbon nano-ellipsoids, either with or without encapsulated metal particles.

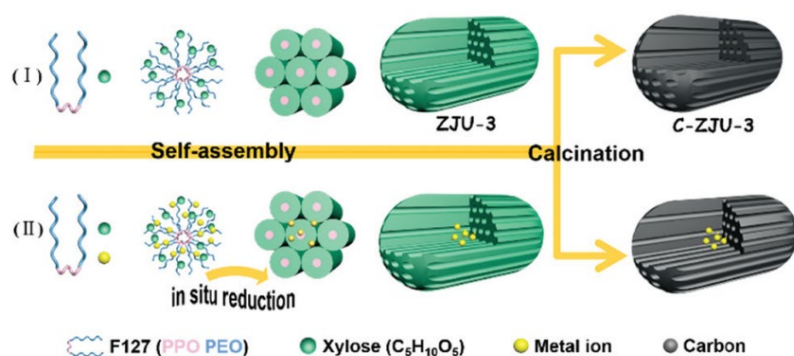


Figure 39. Schematic formation mechanism of the ordered mesoporous nano ellipsoids and their core-shell structures with metal NPs (Pt/Pd). (Extracted from Chem. Commun., 2020, 56, 229--232)

In a different study, Y. Wang et al. described the fabrication of asymmetric flask-like hollow carbon nanoparticles using ribose, templated and interacted with the triblock copolymer (PEO₂₀-PPO₇₀-PEO₂₀, P123).¹²² As shown in the Figure 40, under hydrothermal conditions, a combination of increasing temperature and decreasing pH triggered the formation of oleic acid (OA)-P123 mixed micelles, which subsequently aggregated into nanoemulsions (step 1). As ribose-derived oligomers formed and adhered to the nanoemulsions' surface, further aggregation was obstructed, causing the nanoemulsion to swell and create tensile stress, leading to cracks in the ribose-derived polymer shell (steps 2-1 to 2-4). During the final stage, the ribose derivatives dissolved into the OA phase through the cracks, initiating polymerization along the inner surface. This process caused the outflow of the nanoemulsion and formed a fresh template boundary where further polymerization occurred, culminating in the construction and elongation of the neck of the nanoflasks (steps 3-1 and 3-2).

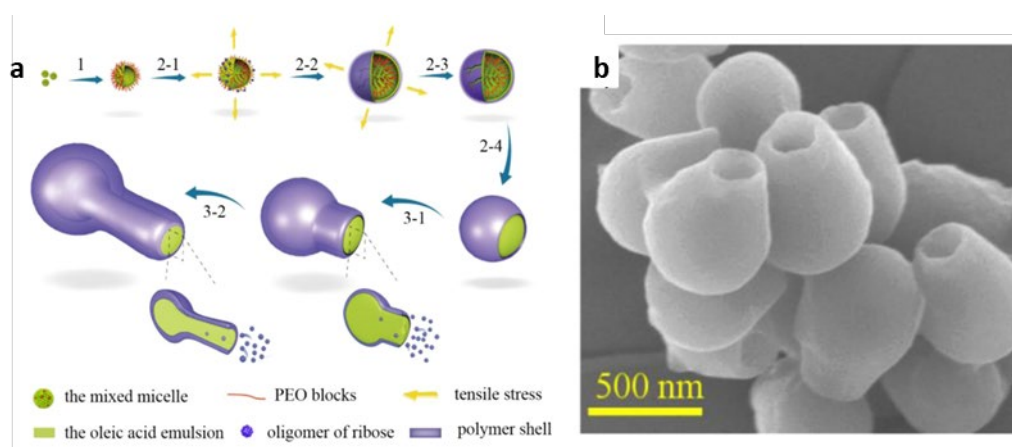


Figure 40. Schematic illustration for the formation of the hollow, open, carbonaceous nanoflask(a), and SEM images of the nanoflask(b). (Extracted from J. Am. Chem. Soc. 2017, 139, 2657–2663)

Apart from the well-known Pluronic® series, other copolymers have also been explored as templates to create hierarchically porous carbon. For example, S Dai et al. devised a technique to produce highly ordered and well-oriented mesoporous carbon films by using a PS-*b*-P4VP block copolymer to template resorcinol–formaldehyde resin.¹⁷⁶ Through a solvent annealing process, they achieved a well-organized structure by arranging resorcinol within the well-defined P4VP domain. Similarly, Y Mai and colleagues utilized a PS-*b*-PEO block copolymer to template the polymerization of dopamine, leading to the formation of mesoporous carbon spheres. Remarkably, the mesopore size could be quantitatively controlled simply by altering the length of the PS block within the copolymer.¹⁷⁷ Recently, C. Glatthaara et al. described the synthesis of a series of lignin-derived carbon materials, employing a soft templating method with self-synthesized PEO-*b*-PHAm block copolymers of varying PEO and PHA chain lengths.¹⁷⁸ This approach facilitated the introduction of isolated spherical pores with diameters ranging from 20 nm to 50 nm. The accessibility of these templated pores can be adeptly tailored through adjustments to the ratio of copolymer to precursor or by modifying the gas atmosphere during pyrolysis (using 1-2% O₂ in N₂). This versatile and controllable pore-structuring method presents significant potential, positioning the resulting carbon materials as highly suitable candidates for various applications including electrocatalyst supports for PEMFC.

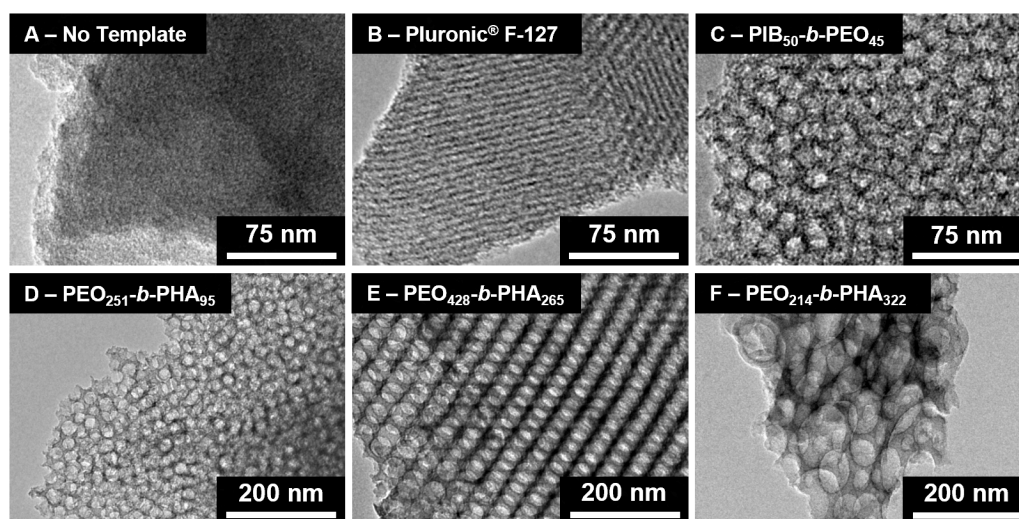


Figure 41. TEM images of obtained carbons after pyrolysis under N₂ at 900 °C: (A) without any template, (B) templated with Pluronic® F-127, and (C) templated with PIB50-*b*-PEO45

and PEO n -b-PHAM polymers with varying block lengths (D) $n = 251$ and $m = 95$, (E) $n = 428$ and $m = 265$, and (F) $n = 214$ and $m = 322$. Figure reproduced from ¹⁷⁸ with permission.

In conclusion, the realm of biomass-derived nanostructured carbon represents a transformative and innovative approach towards achieving efficient PEMFCs. The remarkable advancements in this field have opened new avenues for sustainable energy solutions by harnessing the abundance and cost-effectiveness of biomass. With sophisticated templating methods and chemical activation techniques, complex porous architectures have been realized, leading to enhanced electrochemical performance within PEMFCs.

When the carbon material is developed with the desired characteristics, such as uniform pore size and/or hierarchical porosity, it holds great promise as an advanced electrode material, promoting efficient catalyst utilization and facilitating mass and charge transfer for high-performing fuel cells. The integration of biomass in this context not only showcases remarkable engineering feats but also signifies a crucial step towards aligning energy production with the broader goals of sustainability. As we continue to explore and refine these cutting-edge materials, it becomes evident that biomass-derived nanostructured carbon stands as a beacon of hope in the pursuit of cleaner and greener energy technologies. Embracing such innovations reinforces our commitment to a more sustainable future and inspires us to forge ahead in the quest for environmentally-friendly energy solutions.

Materials and Methodologies

1.9 Materials Preparation

1.9.1 Preparation of Highly Ordered Mesoporous Carbon Particle (HOMC)

0.5 g of xylose (Sigma-Aldrich) and 1.0 g of PluronicTM F127 (PEO₁₀₆PPO₇₀PEO₁₀₆, Sigma-Aldrich) were dissolved in 20 ml 10wt% H₂SO₄ solution (prepared from 95- 98% H₂SO₄, Merck) and left stirring overnight. Then the mixture was transferred into a 30 mL Teflon-lined stainless-steel autoclave for hydrothermal carbonisation for 24 h at 150 °C. The HTC products were collected and filter-washed by water and ethanol for several times until the filtrate became clear. The carbon products were dried in an 80 °C oven overnight, after which they were carbonised at 350 °C for 1 h and then 900 °C for another 1 h with a ramping rate of 1 °C/min under N₂ flow of 300 mL/min to obtain HOMC.

1.9.2 Preparation of Pt/C Catalysts on HOMC and Commercial Carbon Supports

A mixture solution was prepared by mixing 4 mL 0.2 M NaOH in ethylene glycol (anhydrous, 99.8%, Sigma-Aldrich) with 4 mL 0.004 M H₂PtCl₆ in ethylene glycol (prepared from H₂PtCl₆ · xH₂O (~38% Pt basis, Sigma-Aldrich)). 300 mg g of the obtained HOMC was then introduced and well dispersed by sonicating for 30min. The mixture was then refluxed at 160 °C for 3 h, after which the Pt/HOMC catalysts was precipitated by washing with 0.5M HCl solution. The same procedures were repeated using Ketjentblack and Vulcan XC-72 as support to prepare Pt/Kentjenblack and Pt/Vulcan, respectively. All catalysts were washed with 18.2 MΩ.cm water and vacuumed dried at 80 °C for 12 h before testing.

Loading of the Pt is targeted at 1 wt% based on below estimation to fully utilised the mesoporous channels in HOMC.


$$\begin{aligned} Pt \text{ wt\%} &= \frac{\text{mass of Pt NPs on one HOMC}}{\text{mass of carbon in one HOMC}} \\ &= \frac{\text{No. of channels} \times 2 \times V_{PtNP} \times d_{Pt}}{\text{Volume of channels} \div \text{specific mesopore volume}} \\ &\approx 0.2 \text{ wt\%} \sim 1 \text{ wt\%} \end{aligned}$$

No. of channels calculated from the [distance between the ordered mesopores] and [size of the MCS] from TEM

V_{PtNP} Volume of each Pt NP, calculated from the average size of Pt NP from TEM

Volume of channels calculated from the [average length] and [diameter] of the ordered mesopores and *No. of channels* from TEM

specific mesopore volume obtained from accumulative specific pore volume plot in the range of 2-4 nm from N₂ sorption pore size distribution.

1.9.3 Preparation of Polystyrene Nanoparticles

Polystyrene nanoparticles were synthesized through an emulsion polymerization technique.¹⁷⁹ The first step was to purify the styrene (purity $\geq 99\%$, Sigma-Aldrich) from the stabilizer by washing it using a solution of 2 M NaOH. After the complete removal of the stabilizer, the styrene was wash with DI water to ensure a neutral pH. A 3-neck round flask equipped with a stirrer, a reflux condenser, and a thermometer, was first charged with 180 mL DI water. And 0.08g KPS (potassium persulfate, purity $\geq 99\%$, Sigma-Aldrich) was dissolved in 20 mL DI water and was deoxidized for 15 minutes. After the temperature in the flask reaching 80°C, the batch was quickly charged with 11 mL styrene. The polymerization process was initiated by adding KPS. The batch temperature was maintained at 80°C for 24 hours under argon and a white suspension containing polystyrene was obtained.

To collect and wash the polystyrene nanoparticles, the suspension was sent to centrifuge at 10000 rpm for 15 minutes. The resulting precipitation was resuspended in DI water and centrifuged again at the same condition. The washing was repeated for 3 times and white polystyrene particles was obtained, which was subsequently dried in 80 °C for 24 hours.

1.9.4 Preparation of Hierarchical Carbon Film via Dual Templating

To generate a hierarchical and continuous catalyst layer, a dual template consisting of soft template and hard template was incorporated and then removed. Polystyrene microparticles were used as hard templates here while Pluronic F-127 as soft template.

In a typical synthesis, 0.335 g lignin, 0.335 g phloroglucinol (purity $\geq 99\%$, Sigma-Aldrich), 1.1675 g Pluronic® F-127 (Sigma-Aldrich) were dissolved in 32.5 ml methanol and along with 0.6 mL of glyoxal solution (40wt % in H₂O, Sigma-Aldrich).¹⁸⁰ Afterwards, the mixture was sent to sonication bath until the Pluronic® F-127 was dissolved completely to present a brown

suspension. Then 25 mL of suspension was transferred to a container and 1.015 g polystyrene nanoparticles was added into the suspension. Probe sonication was applied to ensure the polystyrene was well dispersed and a brown milky slurry was obtained.

Meanwhile, to explore the reinforcement brought by the additives, PVA (polyvinyl alcohol, 86-89% hydrolysed, Sigma-Aldrich) and MWCNT (carbon nanotubes, multi-walled, Sigma-Aldrich) were added to some of the slurries as shown in table 1.

The original slurries were then divided into two parts, one was left to slow evaporate and the self-assembly is induced during the evaporation, and the other part was air sprayed on the surface of carbon fibre paper (Freudenberg H23C8) using airbrush (Iwata CN gravity feed, 0.35mm nozzle). And slurries with additives were all left to evaporated on the carbon fibre paper. After that, all of the samples were put under 85 °C for 24 hours to induce crosslinking, after which a polymeric film was obtained. In the end, all dried samples were sent to a tube furnace in 300 mL/min N₂ flow with a heating rate of 1°C/min from room temperature to 900 °C, followed by maintenance at 900 °C for 2 hours to carbonise the film and remove all the templates. Afterwards, the samples were cooled to near-ambient temperature in N₂ flow and a catalyst layer of hierarchal mesopores was then obtained.

1.9.5 Preparation of Macroporous-only and Mesoporous-only Carbon Film

To produce carbon films with exclusively macropores or mesopores as control samples, the method described in 1.9.4 was employed with slight modifications. For the sample containing only macropores, Pluronic® F-127 was omitted, whereas for the mesoporous-only sample, the use of PS as hard templates was excluded.

1.9.6 Preparation of Pt/C Catalysts on Hierarchical Carbon Film

After obtaining the hierarchical carbon film from previous step, the preparation of Pt/C electrocatalysts on this freestanding hierarchical carbon film commenced with the formulation of a platinum precursor solution at a concentration of 1 mg_{Pt}/ml using H₂PtCl₆ · xH₂O (~38% Pt basis, Sigma-Aldrich). This solution was meticulously sprayed onto the carbon film using an airbrush (Iwata CN gravity feed, 0.35mm nozzle), taking great care to ensure a comprehensive penetration of the precursor into the structure of the carbon film. The spraying process was performed gradually, allowing the precursor to dry with each application, ensuring an even distribution across the surface and within the pores of the carbon film.

Following the application and impregnation process, the carbon films were subjected to a reduction treatment to convert the platinum precursor into metallic platinum. This reduction was conducted at 350°C for a duration of 2 hours, utilizing a controlled atmosphere with a 5% hydrogen in nitrogen gas flow.

1.10 Physical and Structural Characterisation

1.10.1 Nitrogen Isothermal Sorption

Nitrogen isothermal adsorption/desorption was conducted on a Micromeritics 3flex system at 77 K. Before measurements, ~20 mg samples were degassed at 200 °C for 16 h under vacuum. Gases used were nitrogen (N5.2 CP grade) for adsorption/desorption and He (N5.0 CP grade) for the free-space measurement. The BET equation was used to estimate the total surface area, where the fitting region was determined by the Rouquerol method on 3Flex software version 5.02.¹⁸¹¹⁸² The pore size distribution was calculated using slit geometry and heterogeneous surface-2D-NLDFT model in-built with 3Flex software. Regularization level was selected at the interception point of the error of fit plot and roughness of distribution plot.

1.10.2 Scanning Electron Microscopy

Scanning Electron Microscope (LEO Gemini 1252 FEG-SEM) was used to study the morphologies of samples operating at accelerating voltage of 3 keV and working distance around 3 mm. Before the measurement, the samples were secured onto the alumina sample holders using conductive double-sided carbon tapes. For the sample drop casted on glass substrate, conductive liquid silver paint was used to create effective conductivity path of the sample surface to prevent charge build-up.

Elemental analysis was carried out using the Energy-dispersive X-ray spectroscopy (EDX) inbuilt with the SEM machine. Accelerating voltage was increased to 20 keV and the working distance to 10 mm before the spectra capturing.

1.10.3 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) was carried out for the direct imaging of Pt/C catalysts in a JEOL JEM-2100F at 200 kV and the images analysed with the Gatan software. The catalysts powders were dispersed in ethanol by sonicating for 15min and left settling for 30min. The upper solution was collected and deposited onto the TEM grids (Holey Carbon Films on 300 Mesh Copper Grids, agar scientific). The grid was then left dry overnight and stored in dry conditions before imaging.

1.10.4 Dynamic Light Scattering

Dynamic light scattering measurements were performed using a Malvern Zetasizer MicroV, to determine the polystyrene size synthesized. Since the resulted emulsion were too concentrated for the instrument specifications, they were diluted 100 times. The suspensions were prepared fresh on the day of the measurements. Before each measurement, the suspension was ultrasonicated for 10 minutes to ensure complete dispersion. Each measurement consisted of 10 runs of 10s each. The measurements were repeated at least 3 times. In general, all the suspensions were found to be stable for the duration of the experiment.

1.10.5 X-ray Diffraction

X-ray Diffraction (XRD) measurements were carried out to characterize the crystalline structure and phase composition of the prepared Pt/C electrocatalysts. The XRD analysis was performed using a standard X-ray diffractometer (PANalytical MPD) equipped with a Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$) operated at 40 kV and 20 mA. The diffraction patterns were collected in the 2θ range of 10° to 90° with a step size of 0.02° and a scan rate of 2° per minute.

1.11 Chemical and Electronic Characterization

1.11.1 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) analysis was performed using a Thermo Fisher K-Alpha XPS system to probe the surface composition and electronic state of the samples. Prior to the measurement, the samples were carefully affixed to the sample holders with conductive double-sided carbon tape to ensure stability during analysis. The acquired spectra were analysed using Advantage software, a sophisticated tool that facilitates precise interpretation of the XPS data. To correct for any charging effects that might have occurred during analysis, all spectral peaks were calibrated relative to the carbon C 1s peak at a binding energy of 284.8 eV. This calibration ensures the accurate alignment of the spectral features, thereby providing reliable insights into the surface properties of the investigated samples.

1.11.2 Inductively Coupled Plasma Mass Spectrometry

Before Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis with Agilent 7850 ICP-MS, samples weighing approximately 5 mg were precisely weighed to an accuracy of 0.1 mg. These samples were subsequently digested in 69% HNO₃ (Certified AR, Eur.Ph., for analysis Fisher Chemical™, Fisher Scientific) using a MARS 6 microwave operating at 1800 W for 25 minutes at a temperature of 215 °C. Upon digestion, the solutions were diluted to 2%

HNO₃ to prepare them for analysis. Calibration standards containing platinum (Pt) concentrations of 0, 25, 50, 100, 250, and 400 ppb were utilized to establish a calibration curve. To ensure accuracy and reproducibility, two duplicate measurements were taken for each sample, and the average value was computed. This rigorous methodology enabled a thorough assessment of the Pt content within the analysed samples.

1.11.3 Operando XAS measurements

Operando XAS measurements were performed at room temperature using an in-house designed gas-diffusion-electrode cell placed at 45° to the incident beam. As illustrated below, the gas diffusion electrode was prepared similarly with air spraying onto the Freudenberg H23C8 gas diffusion layer, to obtain a total catalyst loading about 50 to 100 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$. On one side of the GDE is a gas inlet, where oxygen or nitrogen was flowed, on the opposite side is the electrolyte (1 M HClO₄), containing counter electrode (platinum wire) and a capillary tube leading to the reference electrode (RHE).

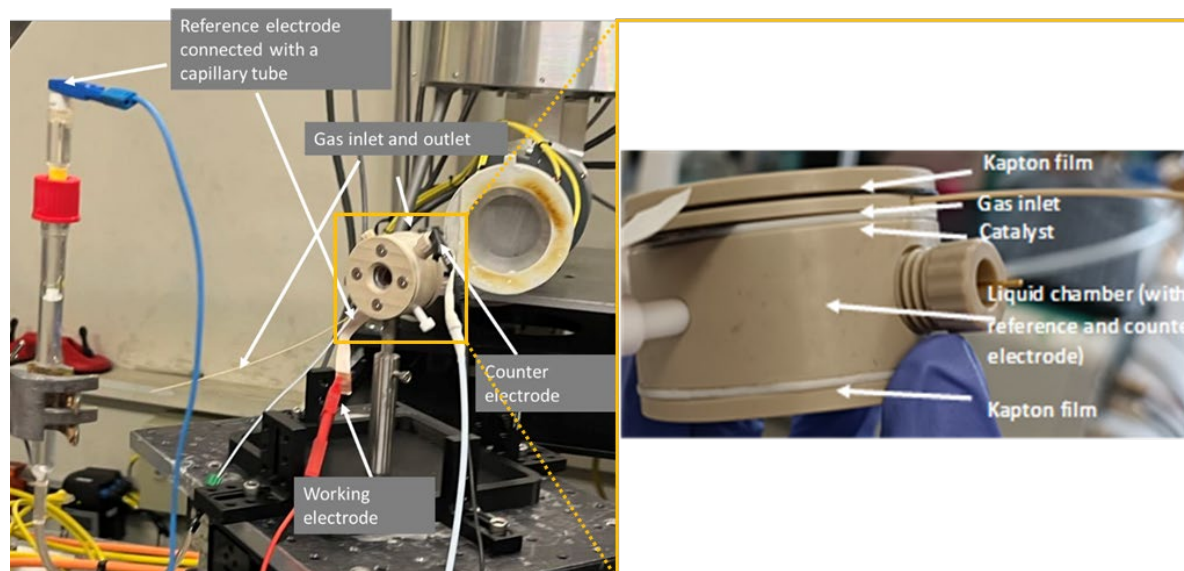


Figure 42. Schematic of the custom-engineered GDE half-cell, specifically tailored for operando X-ray Absorption Spectroscopy (XAS) measurement. Unique design and the integration of specific components are highlighted including the assembly of the cell and the reference electrode connected with a capillary tube.

Operando data were collected at B-18 (Diamond Light Source). The scanning branch of the beamline is equipped with an Si (111) scanning four bounce monochromator. The analyser crystals were aligned to the Pt L2 line and focussed onto a 4 element medipix area detector. Spectra were collected by scanning the monochromator energy over both X-ray absorption near

edge structure (XANES) and extended X-ray absorption fine (EXAFS) region, with a fixed spectrometer energy. Pt foil with 25 μm thickness were used to calibrate the Si (111) double-crystal monochromator and used for data collection as a Pt standard throughout the experiments. The data was normalised to the incident intensity and processed using the Athena software package.

The edge areas were determined from the normalized data by numerical integration. The integration range was from -10 eV to 13 eV relating to the X-ray absorption edge, defined as the inflection point on the absorption edge step. This was done on data from both absorption edges to get A_3 and A_2 for samples, and A_3' and A_2' for Pt foil reference, respectively. The white line intensity difference at each potential was $\Delta A_i = (A_3 + A_2) - (A_3' + A_2')$, which was then normalised by white line intensity difference at 0.5 V for each catalyst to get the relative white line intensity difference $\Delta A_i / \Delta A_{0.5}$.

Pt/Vulcan and Pt/Kentjenblack were also tested at BM28 – XMaS, European Synchrotron Radiation Facility (ESRF) with Si (111) monochromator and the same setup.

1.12 Electrochemical Measurements

1.12.1 Oxygen Reduction Reaction Performance

Gas diffusion electrode (GDE) measurement was carried out in an in-house modified commercial three-electrode half-cell from Gasketel.

When catalysts of powder forms are being tested, the ink for the GDE fabrication is prepared by dispersing 4 mg catalysts and 4 mg NafionTM D-520 (5% w/w in water and 1-propanol, Alfa Aesar), in 2 ml mixture solution compromised of 50 (v/v) % isopropanol ($\geq 99.5\%$, HoneywellTM, Fisher Scientific) and 50(v/v) % 18.2 M Ω .cm water. The ink was homogenised firstly in an ultrasonic bath for 20 mins followed by further processing with a probe sonicator (Fisherbrand model 705, USA) for another 20 min at 0°C, under a 5 s on and 5 s off regime. GDEs were then fabricated by spraying the catalyst ink onto a Freudenberg H23C8 gas diffusion layer (230 μm thick) with an airbrush (Iwata Custom Micron CM-C PLUS) on a hot plate at 70°C. A rubber mask was employed control the catalyst covering area to the desired area. The catalysts loading of the GDEs was measure by the wight differences before and after the spray deposition.

The main and reference chamber was connected with a Haber-Luggin capillary channel and filled up with respective electrolyte for different measurements. A Pt mesh was used as the counter electrode. For acidic measurement, an in-house built RHE was used as the reference

electrode. Electrochemical tests were performed without iR correction employing an AUTOLAB PGSTAT204 coupled with 10A booster in N₂ ($\geq 99.99998\%$ BIP® Plus, Air Products) and O₂ ($\geq 99.9998\%$ UltraPure Plus, Air Products) saturated 1 M HClO₄ (Suprapur®, Merck) electrolyte.

Before each test, N₂ gas was purged to the electrolyte and the main chamber was sealed with tapes. Cyclic voltammetry was then measured for 50 cycles with N₂ supply in the gas chamber in the range of 0.05-1V vs. RHE at 500 mV/s to electrochemically clean the catalysts surface. The gas was then switched to O₂ and the impedance spectroscopy was measured at and the open-circuit potential (OCP) in the frequency range of 10 kHz to 100 Hz to obtain the resistance for iR correction. Lastly the linear sweep voltammetry (LSV) was performed from 1V to 0.05V vs. RHE at 10 mV/s. The polarisation curve was plotted after compensating the working electrode potential with equation $E = E_{\text{measured}} - iR$. All tests were repeated 3 times, reported in the paper are the average and the standard deviation (for LSV measurements).

1.12.2 ECSA Measurement via CO Stripping

CO stripping was carried out to determine the electrochemical surface area (ECSA) of the catalysts as detailed in below diagram. The electrode was firstly cleaned under N₂ by cyclic voltammetry with 50 mV/s between 1.2V and 0.1V. After the cleaning cycles, 0.1 V vs RHE was applied to the electrode with CO (Research grade, BOC) supplied for 5 min, then the gas was switched into N₂ to purge the excess CO for 15mins with the same potential hold at 0.1V. After the purging, the potential was swept from 0.1 V to 1.2 V at 50 mV/s and followed by 2 extra CV scan to testify the complete oxidation of all adsorbed CO. The ECSA was estimated from the CO stripping charge by assuming the specific charge of 420 $\mu\text{C}\cdot\text{cm}^{-2}$.

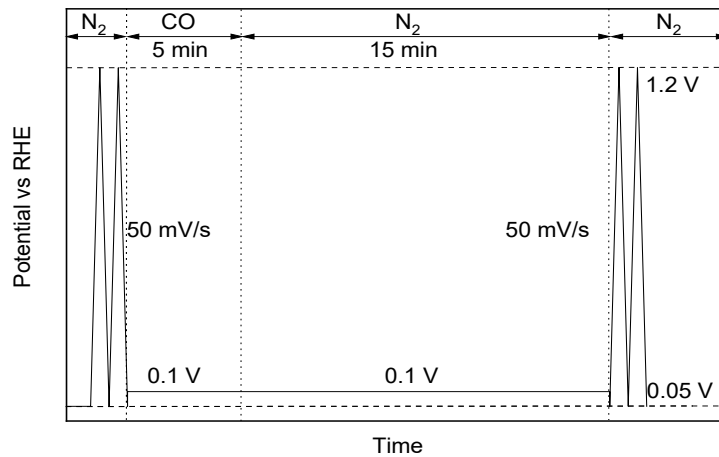


Figure 43. Potential profile and cathode gas compositions in the measurements of ECSA via CO stripping.

1.12.3 ECSA Measurement via Hydrogen Underpotential Deposition (H_{UPD})

ECSA can also be obtained using the current from Hydrogen Underpotential Deposition (H_{UPD}). The electrode was cycled under N_2 by cyclic voltammetry with 50 mV/s between 1.0 V and 0.05V. After subtracting the currents due to the charging of the double layers, the H_{UPD} charge passed over the potential range of 0.08–0.36 V vs. RHE was measured and used to calculate the ECSA, assuming a charge density for one monolayer of adsorbed H atoms (H_{ads}) on Pt of $210 \mu C \cdot cm^{-2}$.

1.12.4 ECSA Measurement via Electric Double Layer Capacitance

Similarly, ECSA can also be obtained using the current from the electrical double layer capacitance, for measuring the none-Pt containing materials. The electrode was cycled under N_2 by cyclic voltammetry with 50 mV/s between 1.0 V and 0.05V. The double layer capacitance region was extracted over the potential range of 0.4–0.6 V vs. RHE to calculate the ECSA.

Establishment of Gas Diffusion Electrode Half-Cell

1.13 Introduction

The development of efficient catalysts remains a key challenge in the advancement of energy technologies, specifically fuel cells. Over the years, numerous efforts have been devoted to enhancing the intrinsic activity of platinum-based catalysts through strategies like alloying and morphological manipulation. However, the task of transferring the high activities measured under the RDE configuration to a technologically relevant MEA poses significant challenges. These disparities mainly arise from the differences in the nature of the electrolyte and the characteristics of the catalyst layer.

In the RDE setup, catalysts are deposited as an ultra-thin layer, ensuring all catalysts are wetted by the liquid electrolyte. On the other hand, the catalyst layer in a MEA, which includes the active catalyst, the support and diffusion layer, and the ionomer, is far more complex. This complexity affects mass transport, a crucial aspect that, due to the idealised thin catalyst layer and the solubility of oxygen in the electrolyte, cannot be effectively studied in the RDE. MEA measurements, while more technologically relevant, demand high material loadings and intricate instrument requirements, making the screening process both costly and time-consuming. Additionally, the combined measurement of the whole fuel cell setup in MEA makes it impossible to separate the different effects arising from the cathode and anode.

In view of these challenges, there is a compelling need for an intermediate testing technology that can provide insights into catalyst performance in a more pragmatic context. This will be a vital tool in guiding future catalyst development strategies. To this end, several GDE setups have been proposed and developed by various research groups, as detailed in the Literature Review (Section 2.2.1). Notable examples include setups developed by Arenz et al.'s group used at the University of Copenhagen and Leibniz Institute for Plasma Science and Technology and the GDE setup developed at the Helmholtz-Institute Erlangen- Nürnberg.⁷⁵

Our study offers a fresh perspective to this ongoing research, having adapted and modified a commercial GDE cell from Gaskatel. It's noteworthy that a similar adaptation was undertaken at TU Darmstadt concurrently. The results from TU Darmstadt, published after our half-cell establishment, offered an excellent benchmark and validation for the protocols we developed.⁸¹

The diagram below (Figure 44) offers a schematic representation of the testing platform of this thesis, which is a modified version of a commercially available half-cell from Gasketel. In our setup, the gas diffusion electrode—catalysts coated on the gas diffusion layer—is installed as the working electrode, while a Pt wire is utilized as the counter electrode. A reference electrode is positioned in a separate chamber but connected closely to the working electrode with a Haber-Luggin-Capillary tube. This setup ensures the accurate measurement of the potential throughout the tests. A critical aspect of benchmarking different half cells involves the use of the same catalyst. Consequently, this study employs the widely-used benchmarking catalyst, HiSPEC4000 (40% Pt/C, Jhonson Matthey), to ascertain that our established half-cell matches up to the performance standard.

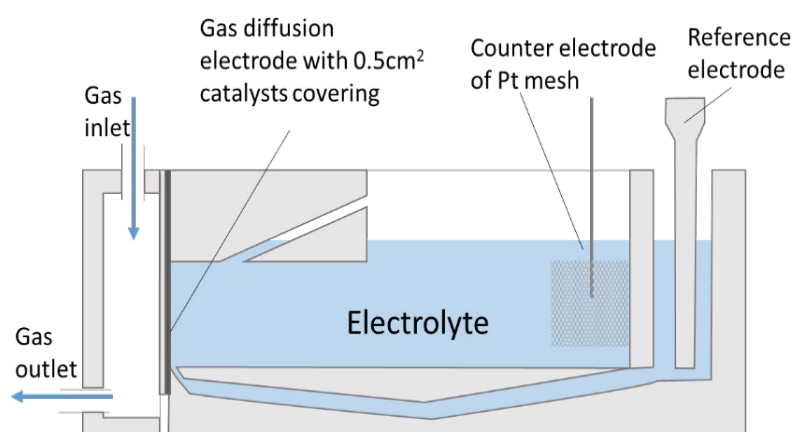


Figure 44. The cross-sectional diagram of the GDE half-cell modified based on commercial Gasketel FlexCell.

Given that the ORR mechanism requires an efficient supply of all reactants for reliable evaluation of catalyst performance, our gas diffusion half-cell is designed to provide the required gas environment, sufficient protons and electrons, and an appropriate evaluation protocol while ensuring a clean cell. In this chapter, we will delve into the intricacies of establishing a GDE and an ORR measurement protocol, ensuring all these critical requirements are met.

The subsequent sections of this chapter will present a detailed analysis of the catalyst performance under various testing conditions, insights into the influence of different variables on catalyst performance in terms of the cell configuration and test protocol. We will also address the challenges and limitations encountered during our study and suggest future development directions. By establishing an intermediate platform for catalysts testing, this

work aims to bridge the existing gap between RDE and MEA measurements, contributing significantly to the broader field of catalyst development and the energy sector as a whole.

1.14 Results and Discussion

1.14.1 Gas Supply

The foremost aspect under our scrutiny was the supply of gas to the electrochemical cell, a pivotal element in creating the intended gas environment. Ensuring a consistent and unimpeded supply of reactant gases is vital to the overall functioning of the electrochemical cell and can significantly impact the resultant ORR measurements.

To probe the effectiveness of our gas supply protocol, we utilized CV measurements under an N₂ environment. This selection was informed by the fact that CV is a standard technique used to study electrochemical systems and offers an insight into the processes occurring at the electrode surface.

Figure 45 presents the findings derived from our investigative efforts. It was crucial to realise the comprehensive filling of the gas chamber with the introduced gas, which necessitated the initiation of gas supply from the top inlet. The initial design of the commercial half-cell features 3 gas openings. However, if the gas was supplied from any of them and allowed to leave the chamber through the other two opening, a mild current of ORR can be observed even under a 200 mL/min N₂ gas supply (Figure 45a red curve). This observation suggests that trace amounts of air could diffuse back into the cell, resulting in this error. To address this issue, one gas opening was sealed, and the other two were utilized as the inlet and outlet. More importantly, after the gas had exited the gas chamber via the bottom outlet, the tubing was then submerged into the electrolyte chamber (Figure 45b, c). This measure ensures that no air can diffuse back into the gas chamber and facilitates the deoxygenation of the electrolyte. This methodology ensures a uniform distribution of gas in both the gas chamber and the electrolyte, thereby mitigating potential disparities in gas concentration or the emergence of an unintended gas environment. This was shown by the black curve in Figure 45a where the reduction peak of oxygen was successfully eliminated. This meticulous attention to detail in creating the desired gas environment strengthens the reliability of our investigative protocol and paves the way for a more accurate analysis of the ORR.

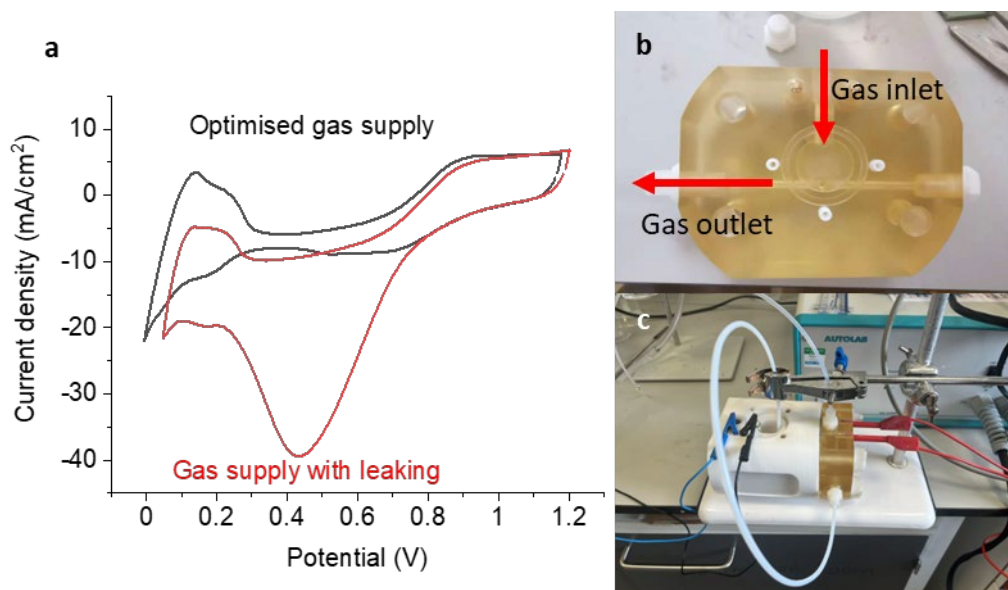


Figure 45. a) Effect of gas supply configuration, demonstrating the differences in CV curves obtained with optimized supply, as compared to an uncompromised supply (where ORR current is observed). b) Configuration of the gas supply, with gas feeding from the top and one bottom outlet sealed, to ensure sufficient filling of the gas chamber. c) Image of the GDE setup, illustrating the arrangements mentioned above.

When introducing the reactant gas to the half-cell, it is critical to ensure an adequate gas supply to circumvent any limitations due to mass diffusion. As documented in prior reports on gas diffusion half cells⁷⁹, an ORR peak current of 1750 mA/cm² has been observed with similar electrode area as in our setup, which translates to a demand of 19 mL/min of O₂. Consequently, for our experiment, the O₂ gas flow rate was established at 200 mL/min. This setting correlates to a stoichiometry of over 10, guaranteeing an abundant supply of O₂ to facilitate the reaction processes effectively. This prudent adjustment of gas flow, based on theoretical predictions and empirical evidence, is vital to optimize experimental conditions and ensure reproducible, reliable results in our study.

To make sure the gas is efficiently delivered to the catalysts later, GDL selection could also make a difference. In this project, both Freudenberg H23C8 and Sigracet 39BB were tested as gas diffusion layers. These two GDLs are both constructed with carbon fibre papers with PTFE treatment and a microporous layer deposited on one side. Their characteristics are listed as below in Table 1 with the primary differences lying in the thickness and air permeability of the GDL. Specifically, Freudenberg H23C8 has been reported to possess an air permeability that is 60 times higher, as determined by a Gurley densometer.

Table 1. Characteristics comparison of Freudenberg H23C8 and Sigracet 39BB. Data extracted from ¹⁸³ and ¹⁸⁴ .

Gas Diffusion Layer Unit	Thickness (microns)	Basic Weight (g/m ²)	Air Permeability (s)	Electrical Resistivity - Through Plane (mΩcm ²)
Freudenberg H23C8	230	135	90	8
Sigracet 39 BB	315	95	1.5	<13

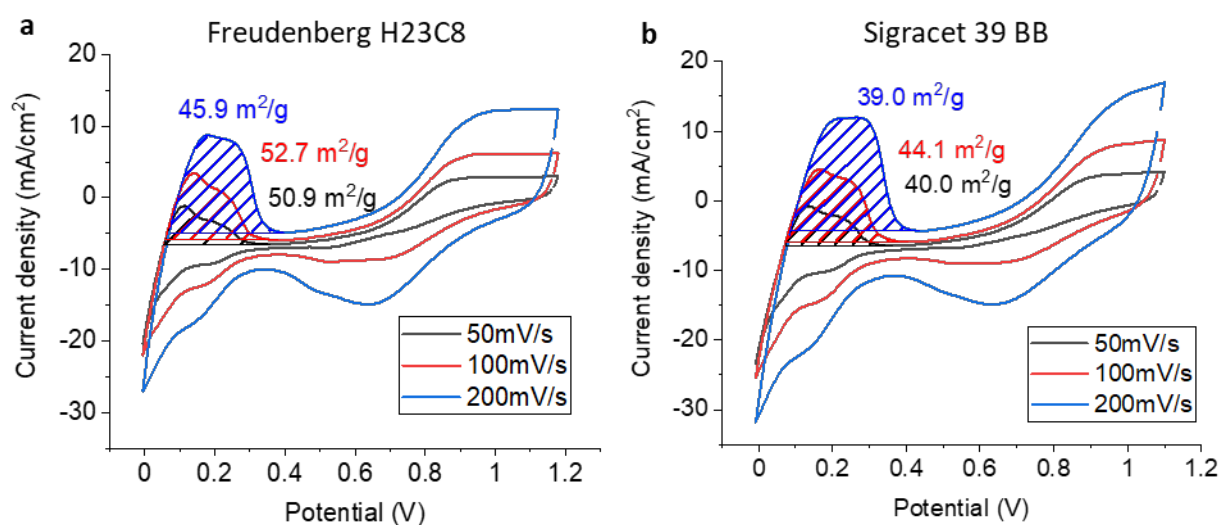


Figure 46. Electrochemical performance comparison of Freudenberg H23C8 and Sigracet 39BB. All data for GDEs with 0.2 mg_{Pt}/cm² (40 wt% Pt/C) in 1M HClO₄ electrolyte.

Utilizing the commercial catalyst HiSPEC4000 from Johnson Matthey, it was deposited onto two distinct GDLs using an identical methodology, and the electrochemical surface area (ECSA) was subsequently calculated through the Hydrogen underpotential deposition region. As depicted in Figure 46, the determined ECSA for both catalysts resides within a closely aligned range, which also agrees very well with other literature and the published information from Johnson Matthey.⁷⁵ However, catalysts deposited on Freudenberg H23C8 yielded a marginally elevated value, suggesting superior reactant interfaces for this GDL. This finding signifies a potential impact on catalytic efficiency, a critical consideration in electrochemical reactions. Hence, given its demonstrated performance, Freudenberg H23C8 was selected as the GDL of choice for this project. It is also worth noting that for both electrodes, the ECSA was calculated to be highest at a 100 mV/s scan rate. This can be attributed to the fact that an overly quick scan rate will result in a non-equilibrium surface, thus reducing the H_{UPD} current. Conversely, when the scan rate is too low, resulting in a small peak area depending on the

catalyst loading, mathematical errors may come into play. Therefore, a scan rate of 100 mV/s was selected to determine the ECSA via H_{UPD} method for this set-up. This decision allows for the maintenance of consistent experimental conditions, thereby improving the reliability of the results obtained in subsequent investigations.

1.14.2 Electrolyte Concentration

Apart from the accessibility of gaseous reactants, the availability and effective supply of another critical element for the ORR, specifically protons, can substantially influence the trajectory of the reaction.

Predominantly, RDE experiments are conducted within the context of either 0.1 or 0.5 M $HClO_4$ environments. Nonetheless, for GDE experiments in anticipation of higher current density, devoid of oxygen concentration as a limiting factor, a higher electrolyte concentration would ideally be adopted to assure proficient proton transport to the catalyst surface.

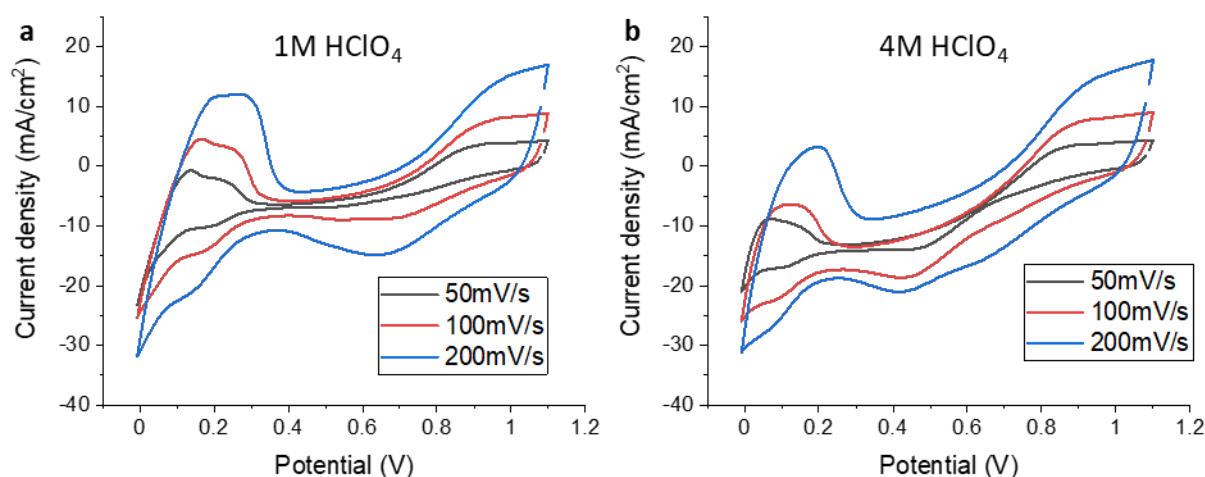


Figure 47. Effect of electrolyte concentration observed with Pt CVs under N_2 in a) 1M and b) 4 M $HClO_4$ electrolyte concentrations, respectively. All data for a GDE with $0.2 \text{ mg}_{Pt}/\text{cm}^2$ (40 wt% Pt/C) on Freudenberg H23C8.

The same GDE (at $0.2 \text{ mg}_{Pt}/\text{cm}^2$) was tested under 1 and 4 M $HClO_4$ environments, respectively, and subsequently recorded the CV under a nitrogen atmosphere, as depicted in Figure 47. Unmistakably, with the upsurge in concentration (from Figure 47a to Figure 47b), the peaks representing hydrogen adsorption/desorption progressively lose their sharpness and exhibit a decrease in peak sizes, indicating a decrease in ECSA, thus loss of active sites. Corroborating evidence for this phenomenon is further provided in Figure 48, where black

curve (1M HClO₄) were observed under the red curve (4M HClO₄) at higher potential region, suggesting better ORR kinetics of the catalysts when in a 1M HClO₄ environment.

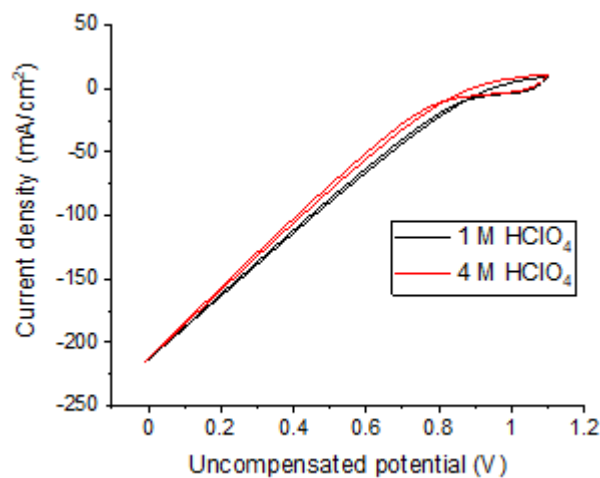


Figure 48. Effect of electrolyte concentration observed with Pt CVs under O₂ in 1M and 4 M HClO₄ electrolyte concentrations. All data for a GDE with 0.2 mg/cm² Pt/C (40 wt%) on Freudenberg H23C8. Potential uncompensated.

The reduction in active sites can likely be attributed to the poisoning effects of adsorbed impurities, in this instance, excessive perchlorate anions that might penetrate the exceedingly thin, or sometimes non-existent, ionomer films covering the Pt catalyst surface. Previous studies have indeed suggested that Cl⁻ anions, a common impurity in HClO₄¹⁸⁵, can cause a pronounced retardation of Pt oxide formation and obstruct the catalytic sites typically available for hydrogen adsorption.¹⁸⁶ Consequently, we opted to proceed with a concentration of 1.0 M HClO₄, aiming to strike a delicate equilibrium between ensuring a non-limiting H⁺ transport and mitigating the noticeable effects of impurity adsorption.

1.14.3 Uncompensated Resistance (R_u)

Given the higher electrolyte concentration used in a GDE, the cell resistance, primarily derived from the electrolyte, is significantly diminished in comparison to an RDE. Typically, electrolyte solution resistance between the reference electrode (RE) and working electrode (WE) has been reported around 20-30 Ω in a 0.1 M HClO₄ environment, yet this value decreases tenfold to below 3 Ω when 1 M HClO₄ is utilised.¹⁸⁷⁷¹

Contrary to measurements using an RDE, the current of the ORR in a GDE setup is not hindered by the oxygen solubility in the electrolyte. Consequently, the current density in a GDE can reach approximately 1 A/cm², marking a significant increase compared to that achieved with

an RDE (circa 6 mA/cm²). This amplified current considerably escalates the potential to be compensated by the electrochemical cell. It is favourable to attain a low resistance, to minimise the temperature rise when operating at high currents.

As such, modifications were made to the GDE half-cell to decrease resistance. Firstly, the distance between the RE and WE was decreased from approximately 7 cm to around 3 cm by securing the counter electrode closer to the working electrode. Secondly, the inclusion of a copper tape on the reverse side of the carbon paper, utilised as the working electrode, was employed. This was done to enhance the contact between the working electrode and the two connecting nodes leading to the potentiostat. As demonstrated in Figure 49, the cell resistance was reduced from 1.20 Ω (black curves) to 0.65 Ω (red curves) following the introduction of copper tape. Moreover, the introduction of Cu layer further prevented the connecting nodes from damaging the delicate working electrodes. It is also worth noting that the Cu layer, attached to the reverse side of the GDE, has no contact with the electrolyte under any circumstances. This arrangement effectively eliminates the concern of introducing Cu impurities into the electrochemical system.

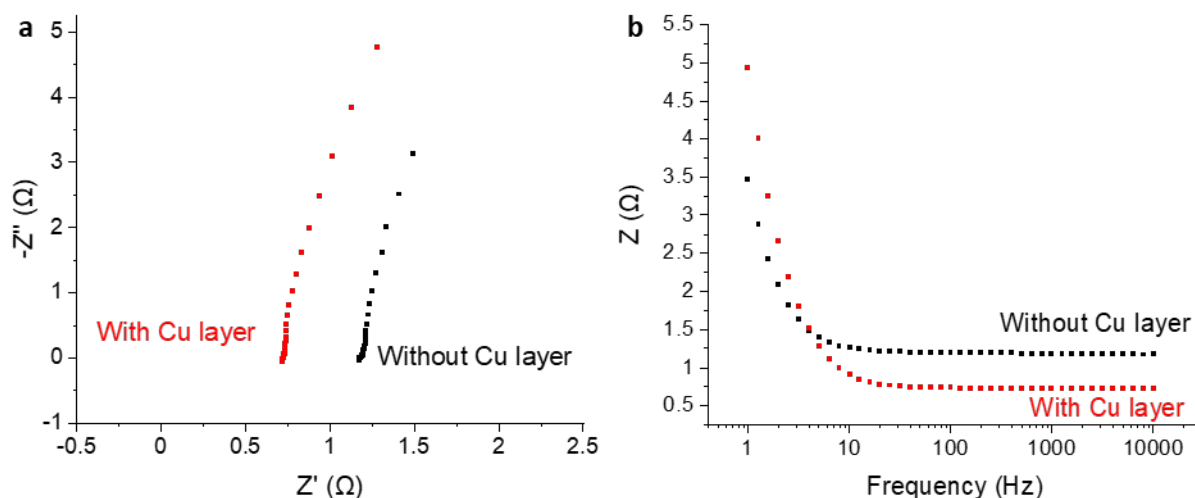


Figure 49. Nyquist and Bode plots showing cell resistance difference with and without the Cu layer insertion.

The relationship between the current density exerted on the electrode and the consequent electrolyte temperature was examined in the subsequent experiment. Here, the entire working electrode area (3.14 cm²) was coated with 0.2 mg Pt/cm² catalysts loading, and the ORR experiment was conducted in a galvanostatic manner. As depicted in Figure 50, the temperature of the electrolyte remains remarkably stable at values under 1A. However, a sharp increase is

observed above 2A, and the electrolyte begins to emit vapour when the cell current reaches 3A (Figure 50b). Notably, the temperature recorded corresponds to the bulk electrolyte; the actual local temperature on the working electrode is likely to be significantly higher.

Given these findings, the cell current for all subsequent experiments was regulated to remain below 1A. This control measure was designed to preclude possible changes in temperature, thereby avoiding any consequent effects on electrolyte resistance and possibly inflated estimations of the kinetics.

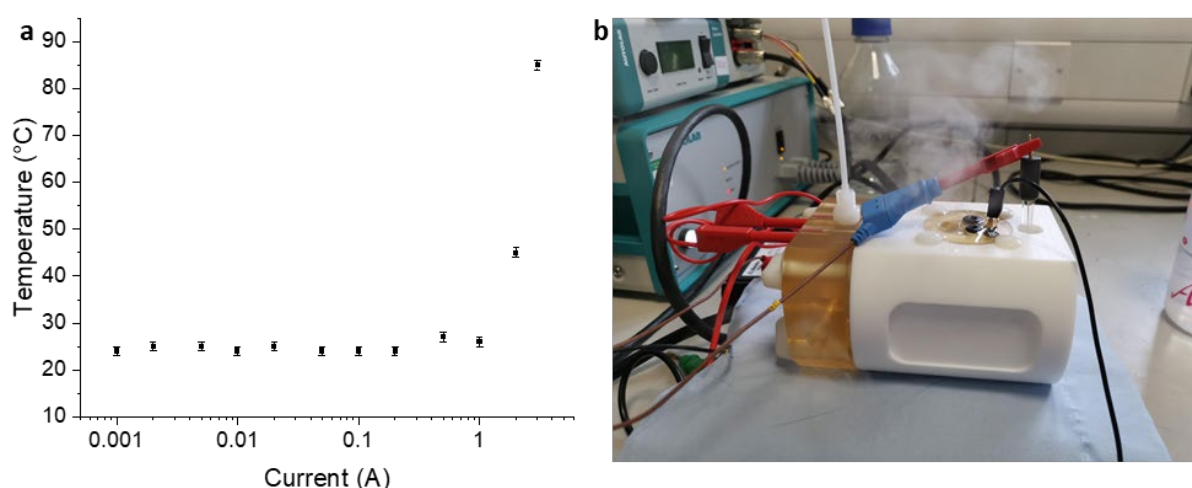


Figure 50. a) Temperature of electrolyte recorded at different current with a sharp increase above 1A. b) Over temperature of the cell when operating at 3A with water vapour observed.

A parameter that frequently provokes discussion in relation to gas diffusion electrodes is the variability of the uncompensated resistance (R_u) at different currents, a phenomenon attributable to the aforementioned temperature increase. Conventionally, researchers perform an Electrochemical Impedance Spectroscopy (EIS) at each distinct current step under galvanostatic measurements and compensate the potential with the true R_u at that current. However, in the context of this study, we opted to maintain a low cell temperature and completely circumvent fluctuations in R_u . This approach was adopted given that even with a stage-wise R_u compensation, modifications in thermal conditions could feasibly influence the ORR results.

As vividly depicted in Figure 51, the R_u read at the high frequency (~ 2000 Hz) on the Bode plot maintains remarkable stability, ranging between 0.0001A and 1A. This clearly demonstrates the effectiveness of our experimental approach in maintaining controlled, consistent conditions for ORR studies.

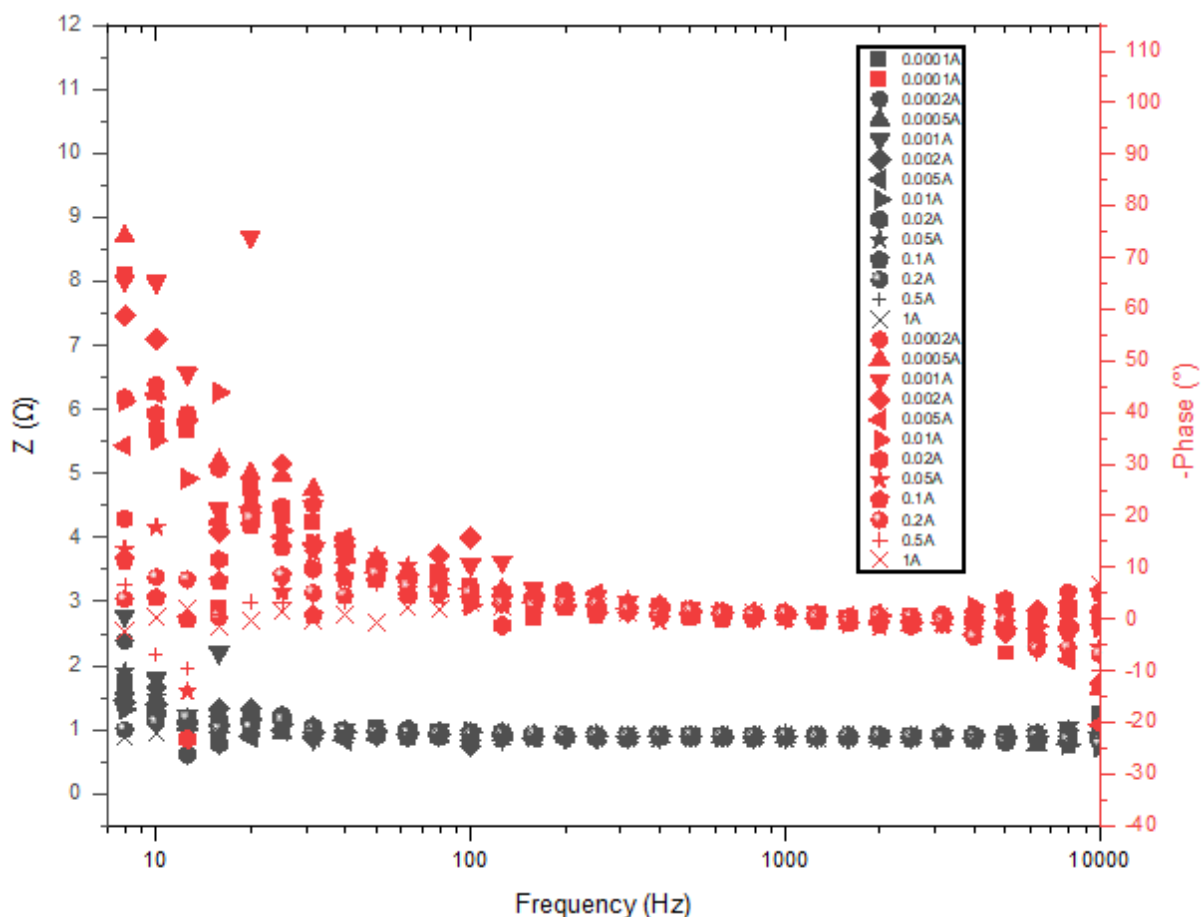


Figure 51. Bode plot of the impedance spectroscopy measurements from 1 mA to 1A indicating no Ru changes.

1.14.4 ORR Measurement and Benchmarking

Prior to evaluating the performance of the catalysts, it is necessary to establish the method for measuring the ORR. While the majority of existing literature on GDE cells employs the chrono-method to ensure a stable operational state, this project conducted measurements using both chronoamperometry and linear sweep voltammetry (LSV) techniques. The same electrode was examined in 1) LSV at 10 mV/s scan rate and 2) potentiostatic staircase of 50 mV step size with current extracted after 15s holding time. The comparison of the results, as depicted in Figure 52, reveals no discernible distinction between the LSV scan and the potentiostatic staircase, suggesting that the 10 mV/s scan rate can reliably maintain a steady operational state for the half-cell. Consequently, a scanning rate of 10 mV/s for LSV was chosen as the preferred method for this project owing to the simplicity of the measurements.

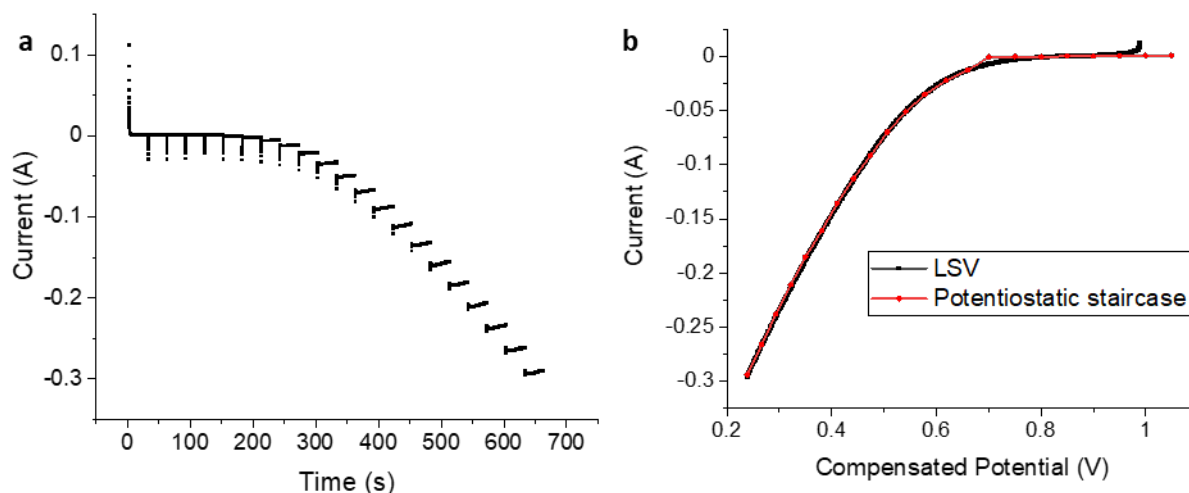


Figure 52. Comparison of chronoamperometry and linear sweep voltammetry measurements. Measurements are done with in-house synthesis Pt/C catalysts ($0.04 \text{ mg}_{\text{Pt}}/\text{cm}^2$ loading) in 1M HClO_4 electrolyte, with Pt mesh as counter electrode. LSV taken at 10 mV/s , chronoamperometry current was extracted after 15s holding time.

Upon establishing the aforementioned methodologies, the widely employed commercial catalyst HiSPEC4000 (40%Pt/C, Jhonson Matthey) was utilised as a benchmark. We subjected a diverse range of catalyst loadings, varying from 0.035 to $0.26 \text{ mg}_{\text{Pt}}/\text{cm}^2$, to testing, and collated these findings with those reported by other researchers.

As depicted in Figure 53, the results from other published works are represented by dashed lines, while the ORR polarization curves obtained in this study are denoted by solid lines. This comprehensive comparison reveals a strong agreement between our results and those previously reported in the literatures, across both low ($\sim 0.03 \text{ mg}_{\text{Pt}}/\text{cm}^2$) and high (0.14 - $0.30 \text{ mg}_{\text{Pt}}/\text{cm}^2$) Pt loading scenarios.

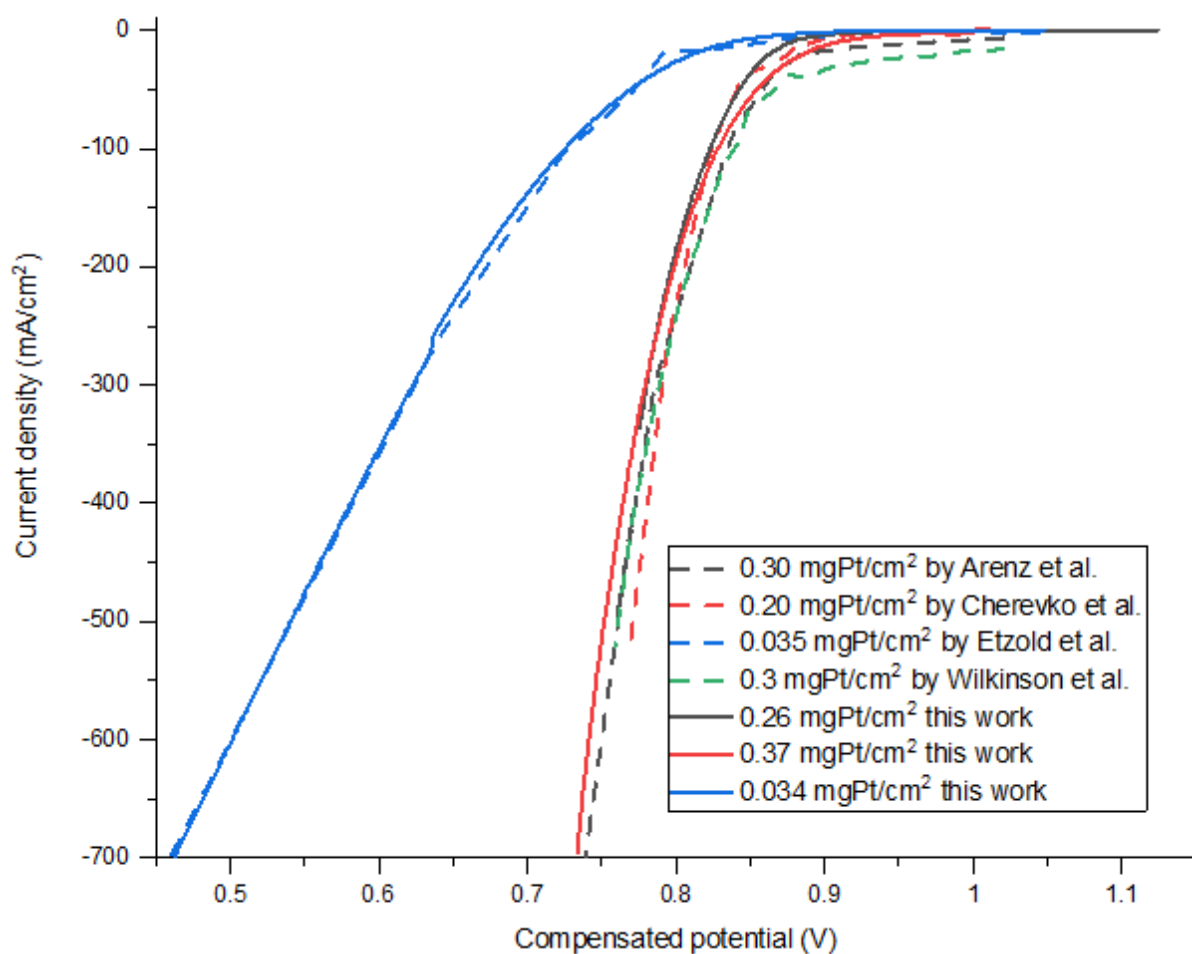


Figure 53. ORR polarisation benchmarking of the half -cell using HiSPEC4000 catalysts. Home measurements were done in 1M HClO₄ electrolyte at room temperature with 200 mL/min oxygen flow and 10 mV/s scanning rate. Literature results were extracted from respective publications.⁷⁹⁸⁰⁸¹

In addition to the ORR polarisation, Figure 54 presents the results of the mass specific activity of HiSPEC4000, indicative of the fact that mass specific activity remains independent of catalyst loading and the type of half-cell employed. This strongly suggests that significant mass transport limitations were absent in any of the tests, thereby validating the utility and consistency of our established methodologies.

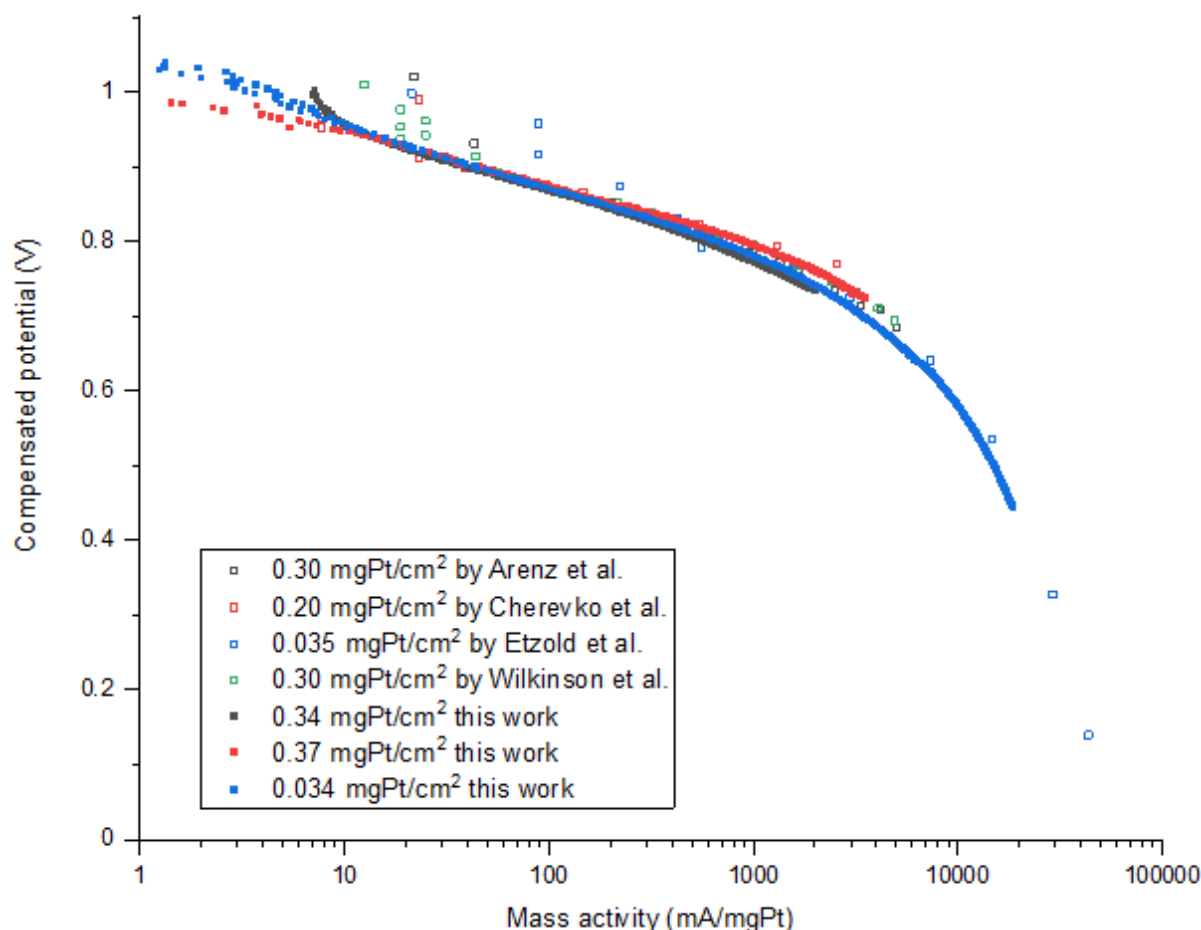


Figure 54. Mass specific activity of HiSPEC4000 catalysts benchmarked in GDE half -cell. Home measurements were done in 1M HClO₄ electrolyte at room temperature with 200 mL/min oxygen flow and 10 mV/s scanning rate. Literature results were extracted from respective publications.⁷⁹⁸⁰⁸¹

1.15 Summary

In summary of this chapter, requisite modifications including the configuration of gas supply, optimization of electrolyte concentration, reduction of cell resistance were executed on the commercially available half-cell to better adapt it to the specific needs of ORR testing. The reengineered design of the half-cell ensured the ORR measurement could be performed with greater consistency and reliability, guaranteeing both the adequacy of reactant delivery and the precision of data collection. A comprehensive test protocol has been summarised in Table 2, which has been adhered to stringently for all GDE experiments conducted within this thesis.

This protocol delineates a comprehensive procedure for assessing the ORR performance of electrocatalysts to be developed in subsequent chapters, commencing with the measurement of R_u , the ECSA and concluding with the precise ORR polarization curve. In instances involving

catalysts with exceedingly low Pt loading, where ECSA calculation via HUPD might pose challenges due to the small peak relative to the double layer capacitance, CO stripping has been included. This is performed after the ORR measurement in order to mitigate potential effects of CO on the electrocatalysts surface structure.¹⁸⁸

Utilizing this protocol in conjunction with the modified GDE half-cell, an intermediate platform has been established to assess the electrocatalysts within an environment that more closely simulates realistic conditions in comparison to the RDE method. This approach facilitates an understanding of multiscale transport phenomena, providing insights that can be leveraged for catalyst development, to be discussed in subsequent chapters.

Table 2. Protocol for the electrochemical characterisations.

Step	Method	Parameter	
1	Determination of iR drop	EIS at OCP	Gas flow N ₂ (~200 mL/min) EIS frequency range 10000-2 Hz EIS amplitude 0.01 V _{RMS} Potential OCP
2	Electrochemical cleaning	CV	Gas flow N ₂ (~200 mL/min) Potential limits 0.05-1.05 V Scan rate 500 mV/s Number of cycles ~100 (until CV constant)
3	ECSA (HUPD)	CV	Gas flow N ₂ (~200 mL/min) Potential limits 0.05-1.05 V Scan rate 100 mV/s Number of cycles 3
4	ORR (O ₂)	Potentiostatic staircase	Gas flow O ₂ (~200 mL/min) Pt-reduction step 0.1V, 5min ORR potential range 1.0 -0.0 V Step size 50 mV Holding time at each point 15s
5	ORR (O ₂)	LSV	Gas flow O ₂ (~200 mL/min) Pt-reduction step 0.1V, 5min ORR potential range 0.0-1.0 V Scan rate 10 mV/s
6	Formation of CO-monolayer	Chronoamperometry	Gas flow CO (~200 mL/min, 5 min), then N ₂ (~200 mL/min, 15min) Potential 0.1 V Time 60 min
7	ECSA (CO)*	CV	Gas flow N ₂ (~200 mL/min) Potential limits 0.1-1.0 V Scan rate 20 mV/s Number of cycles 3

Optimising the Local Transport via Ionomer/Catalysts Interaction

1.16 Introduction

Proton conductive ionomers, such as NafionTM, a perfluorinated sulfonic acid (PFSA) ionomer, are commonly added to the catalyst-support mixture to enhance catalyst binding and proton conduction. However, an often-overlooked aspect is the interaction among the carbon support, proton conductive ionomer, and catalyst, which significantly impacts the local transport of oxygen, protons, and water to the catalyst surface. The presence of ionomer on the catalyst surface improves proton transport and mechanical stability but can also have a poisoning effect¹⁸⁹ and create an additional diffusion layer for oxygen transport⁶².

Several strategies have been employed to manipulate ionomer coverage on the platinum (Pt) surface, including modifying ionomer chemistry⁹², molecular masking⁹⁴, regulating ionomer distribution by introducing nitrogen sites⁹⁵, and engineering the catalyst support⁹⁸. More details on these can be found in the literature review section. Among the different strategies, researchers have long recognized the influence of carbon support nanostructure on ionomer distribution and have suggested that a balance should be achieved between low and high surface carbon.¹⁹⁰ Yarlagadda et al. investigated 11 different Pt/C catalysts deposited on various carbon supports and confirmed this hypothesis by measuring dry proton accessibility and local oxygen accessibility.⁹⁸ They observed that low surface carbon supports suffer from direct contact between ionomer and Pt, resulting in local resistance to oxygen, while high surface carbon supports lack accessibility to protons and reactant gases. Based on statistical analysis of the carbon support structure, the authors concluded that mesopores ranging from 4 to 7 nm would provide the highest accessibility and enhance ORR performance. However, the development and understanding of carbon supports have been hindered by the inhomogeneous nature of carbon materials. To gain a deeper understanding of catalyst-ionomer-support interactions, catalyst supports need to be designed and synthesized with uniform pore sizes.

In addition to the development of catalyst supports with uniform porosity, it is necessary to directly characterize the interaction between ionomers and catalysts. Various methodologies have been developed for evaluating ionomer coverage on Pt catalysts through morphological and structural characterization or electrochemical evaluation. USAXS can be used to extract particle size and size distribution of catalyst aggregates, allowing for the assessment of ionomer interaction changes.⁹⁹ HAADF-STEM imaging enables direct visualization of the location of

ionomers, with ionomers usually stained with caesium to enhance contrast with the carbon support.¹⁰⁰ cryo-TEM has also gained attention for electron microscopy characterization.⁹⁹ However, accurately mapping ionomer distribution remains challenging due to potential beam damage caused by high voltage and electron dosage. Electrochemical evaluation provides a quantitative measurement of ionomer coverage by comparing the electric double layer capacitance or CO stripping current of the ionomer-covered area with that of the total catalyst area.¹⁰³ However, this technique is limited to use in MEA tests, as dry or fluorocarbon-fluid filled conditions are required. Furthermore, the coverage observed with the above methods does not provide insights into the molecular interaction between Pt and ionomer, necessitating closer characterization of the specific adsorption of ionomer ending groups on the Pt surface. X-ray absorption spectroscopy (XAS) can demonstrate electronic structure changes resulting from the adsorption of sulfonate ending groups from the NafionTM ionomer by monitoring spectral changes in operando.

Carbon is the most commonly used electrocatalyst support due to its abundance and good electronic conductivity. However, commercial carbon supports such as carbon black and activated carbon are still largely dependent on petroleum sources. This poses a challenge for the ultimate goal of decarbonisation. Carbon materials need to be prepared from more sustainable resources, and biomass is the natural choice. Among the numerous sources of biomass, xylose is the most abundant pentose derived from hemicellulose and serves as a better choice than other monosaccharides such as glucose due to its suppressed uptake in biological processes.

In this study, we prepared sustainable highly ordered mesoporous carbon (HOMC) from xylose and employed it to rationalize the effect of carbon support structure on Pt-ionomer interactions via advanced characterization techniques. For the first time, operando XAS and gas sorption analysis were employed together with ORR catalytical performance in GDE configuration to prove that mesopores boosted performance by providing optimistic ionomer/catalyst interaction.

1.17 Results and Discussions

1.17.1 Development of Highly Order Mesoporous Carbon from Biomass

The hydrothermal carbonization of biomass represents an economical and sustainable method for creating functional carbonaceous materials. However, the integration of biomass into the synthesis of ordered mesoporous carbon materials has experienced slow progress due to

complex requirements, rendering the preparation of biomass-derived ordered mesoporous carbon materials a challenging endeavour. Recently, an effective strategy for synthesizing ordered mesoporous carbon materials from renewable and environmentally friendly pentose through a one-pot hydrothermal synthesis process has been reported.¹⁷⁴ As depicted in Figure 55, sulfuric acid was utilized as the catalysts and binding agent for the HTC while Plutonic™ F-127 served as a soft template. The acid plays a pivotal role in facilitating the self-assembly of carbon precursors and soft templates, thereby inducing the formation of ordered mesoporous carbonaceous materials under hydrothermal conditions.¹⁷⁵ The acid acts to protonate both the ether moieties in F-127 and the hydroxyl groups in xylose. This process draws them together through electrostatic interactions mediated by the SO_4^{2-} anion. This additional interaction, when combined with the existing hydrogen bonding between the hydroxyl and ether groups, enhances the self-assembly of carbon precursors around the polymer micelles. By the application of this self-assembly mechanism within a biomass system, highly order porous materials with uniform mesopores are synthesised.

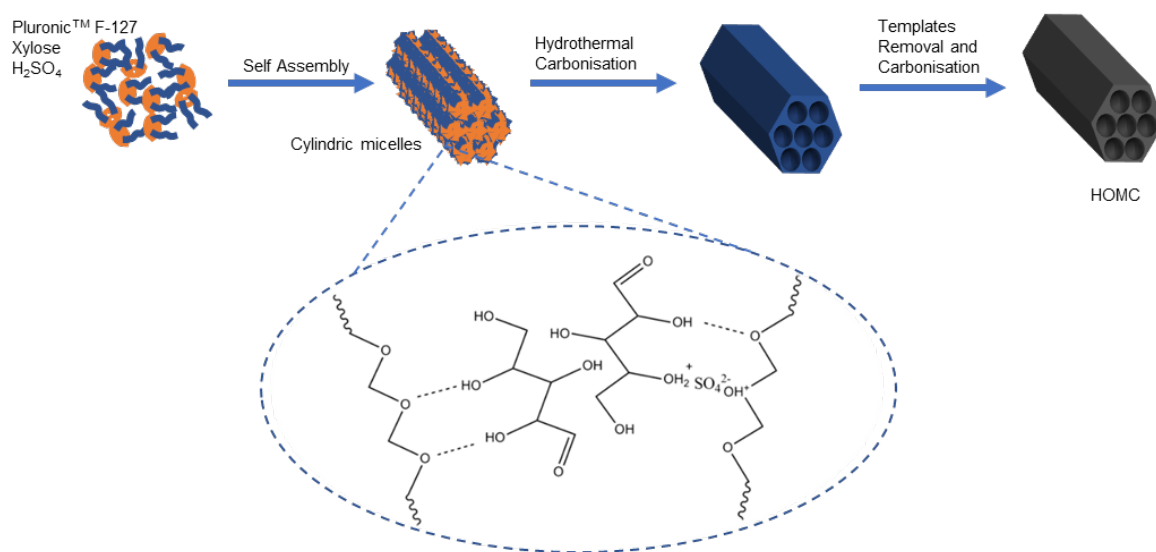


Figure 55. Preparation of highly ordered mesoporous carbon (HOMC) via sulfuric acid mediated hydrothermal carbonisation of xylose with zoomed in interactions of the acid induced self-assembly.

The templates are subsequently eliminated through thermal means during the carbonization process, resulting in the formation of HOMC (Figure 56a&b). The pore size distribution, determined via N_2 sorption (Figure 56c&d), indicates the presence of uniform mesopores measuring approximately 3-4 nm. Corresponding with the sorption analysis, transmission

electron microscopy (TEM) images clearly exhibit primary carbon particles ranging from 300-500 nm in size, featuring uniformly distributed cylindrical pores measuring 3-4 nm (Figure 56a).

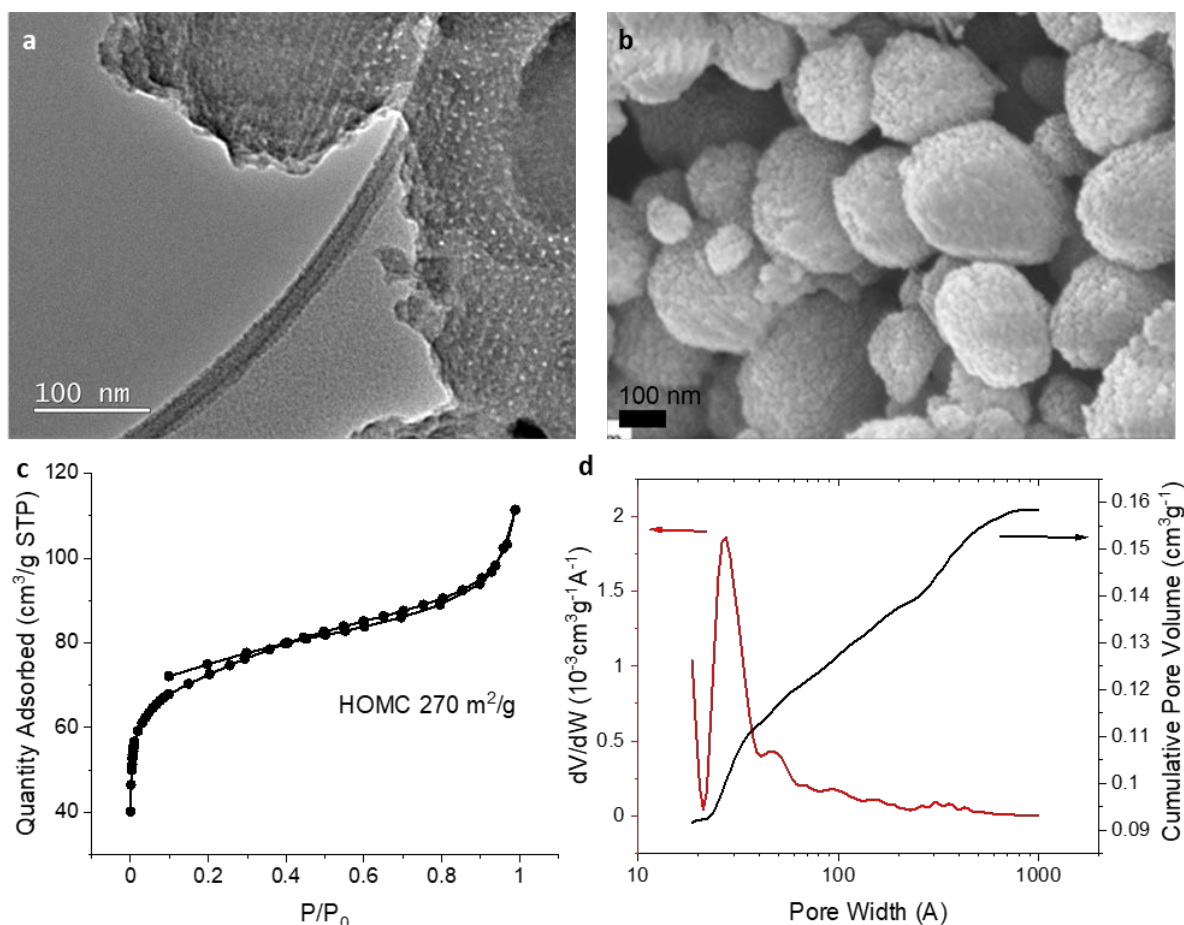


Figure 56. a&b. TEM&SEM images of HOMC. c. N₂ sorption isotherms for HOMC at 77K. d. NLDT pore size distribution for HOMC

1.17.2 Development of Pt/C Catalysts on Different Carbon Supports

In order to examine the impact of carbon structure on the performance of the ORR, nanoscale Pt particles were chosen as a model catalyst due to the extensive understanding of the reaction mechanism and the availability of well-established characterization methods. The polyol method was employed to deposit Pt nanoparticles onto various carbon supports, with precise control over the Pt nanoparticle sizes by adjusting the reaction pH, thus minimizing the influence of the carbon support during this stage. Additionally, Pt/C catalysts were prepared with an extremely low Pt loading to maximize the influence of the carbon structure. Detailed calculation can be found in the experimental section 1.9.2 .

In addition to the synthesized HOMC, two commonly used commercially available carbon substrates, namely Ketjenblack (high surface carbon) and Vulcan XC-72 (low surface carbon), were selected. N₂ sorption measurements were conducted on all three carbon materials before and after Pt nanoparticle deposition. Notably, as shown in Figure 57a, the surface area of HOMC decreased from 308 m²/g to 52 m²/g after the introduction of Pt NPs, experiencing a nearly 90% loss in porosity. The pores size distribution of these two samples also confirmed the loss of porosity (Figure 57b). While for both Ketjenblack and Vulcan XC-72, they retained a significant portion of their porosity after Pt loading with negligible surface area decrease (Figure 57c and e) and consistent pore size distributions (Figure 57 d and f).

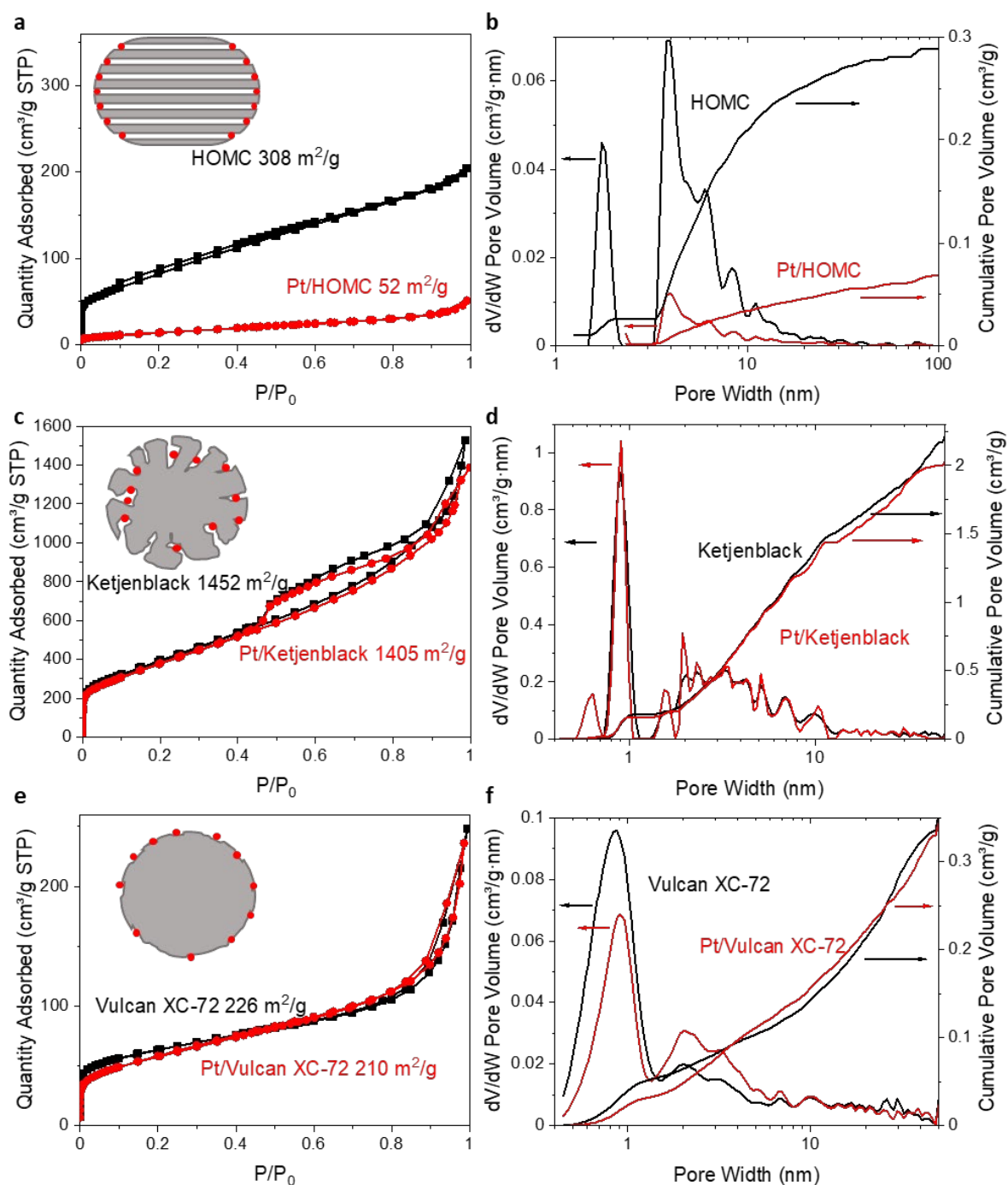


Figure 57. N_2 sorption isotherms and NLDT pore size distribution for Pt/HOMC (a and b), Pt/Ketjenblack (c and d) and Pt/Vulcan (e and f) at 77K, respectively.

Moreover, though all three catalysts have similar Pt content when analysed via ICP-MS after total digestion with microwave assistance (Table 3), when measuring the surface Pt content using XPS, Pt/Vulcan and Pt/HOMC revealed similar contents of 12-15% Pt while Pt/Ketjenblack only has about 0.5% Pt on the surface.

Table 3. Bulk Pt content measured via ICP-MS and surface Pt content measured via XPS for the 3 catalysts.

	Pt/Ketjenblack (wt%)	Pt/Vulcan (wt%)	Pt/HOMC (wt%)
Pt content by ICP	0.58 ± 0.02	0.78 ± 0.03	0.75 ± 0.02
Surface Pt content by XPS	0.49 ± 0.05	14.98 ± 1.50	12.60 ± 1.26

Based on this information, the location of Pt on each catalyst can be inferred. For Vulcan, Pt nanoparticles were found to be deposited on the surface of the support, with no discernible effect on the porosity measured by N₂ sorption (Figure 57e inset). In the case of Ketjenblack, the Pt nanoparticles were situated inside the pores, away from the carbon surface, explaining the low Pt content measured by XPS and the lack of disturbance to the highly porous structure (Figure 57c inset). Finally, on HOMC, Pt nanoparticles were deposited on the surface and positioned at the openings of the mesoporous channels, rendering them inaccessible for nitrogen sorption measurements (Figure 57a inset).

TEM and XPS were employed to systematically characterize the catalysts, affirming that the Pt nanoparticles maintained uniform geometric and electronic structures across the samples. As delineated in Figure 58 (a-c), TEM imaging disclosed that the platinum nanoparticles across the three catalysts were consistently sized with Pt NPs on HOMC of 2.30 ± 0.35 nm, Pt NPs on Vulcan of 2.19 ± 0.51 and Pt NPs on Ketjenblack of 2.08 ± 0.34 nm, which were in a range previously established as optimal for ORR applications.²⁹ Further analysis through High Resolution TEM (HRTEM) revealed that the predominant crystal surface of the nanoparticles was Pt (111), characterized by the interplanar spacing in the interval of 0.224-0.227 nm (Figure 58d). Complementing this, the XPS spectra of Pt yielded identical peak positions and morphologies for the three catalysts, signifying a uniform electronic structure (Figure 59). Collectively, these findings highlight the meticulous control achieved through pH regulation in the polyol synthesis method, resulting in the acquisition of Pt NPs with consistent size and loading. This controlled synthesis facilitated the deliberate differentiation in the positioning of Pt on various carbon supports. The distinction, governed by the nanostructure of the carbon, represents the primary difference among the three catalysts.

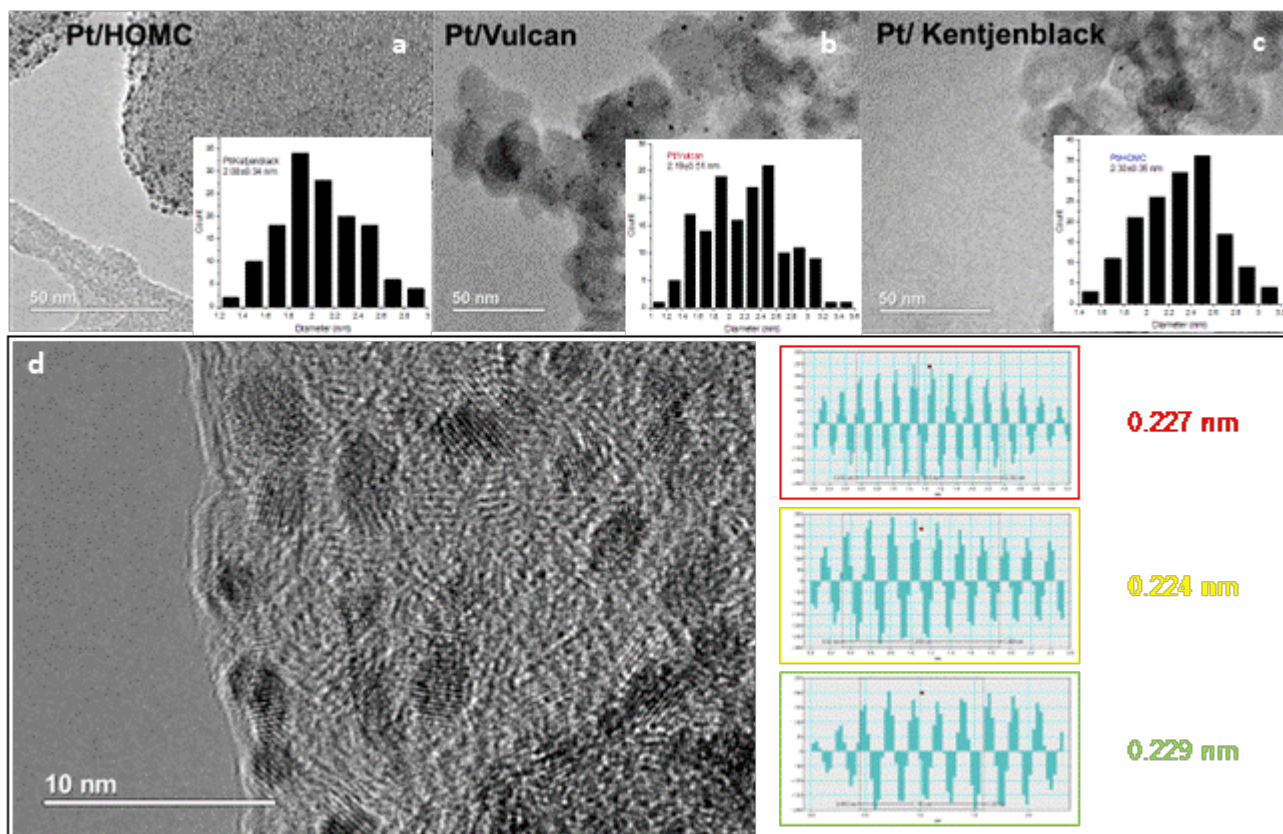


Figure 58. TEM images of Pt/HOMC (a), Pt/Vulcan XC-72 (b) and Pt/Ketjenblack (c) indicating similar particles sized obtained for 3 catalysts (insets: particle size distribution). d. HRTEM images reveal lattice fringe spacings corresponding to the Pt (111) plane.

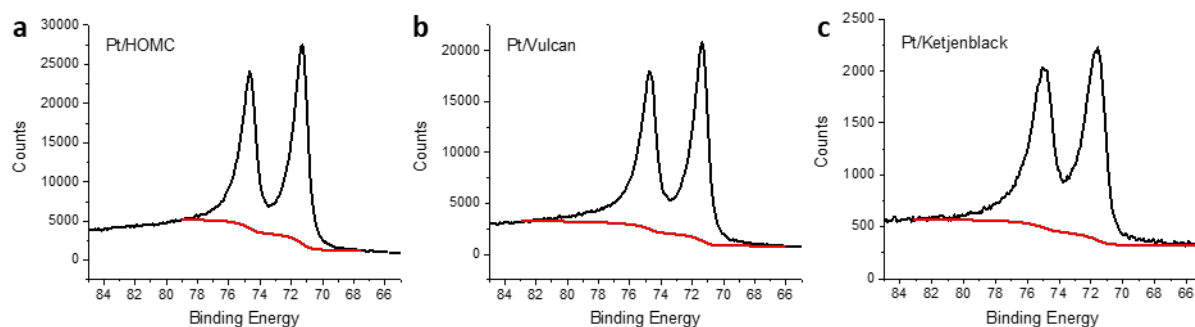


Figure 59. XPS Spectra of Pt/HOMC, Pt/Vulcan XC-72 and Pt/Ketjenblack indicating similar electronic properties of obtained Pt NPs.

1.17.3 ORR Performance Tested under Gas Diffusion Electrode Half-Cell

The evaluation of ORR performance via a RDE setup offers certain limitations, particularly given the low solubility of O_2 in the electrolyte. This consequently yields merely restricted data

concerning mass transport, a factor that becomes particularly pivotal at high currents. To scrutinize the impact of carbon support nanostructure, all ORR tests were executed in a GDE half-cell, procured from Gaskatel, and subsequently subjected to in-house modifications. Before proceeding to assess the catalysts developed within this study, we utilised a commercial Pt/C catalyst, HiSPEC4000 (which comprises 40% Pt on carbon black, manufactured by Johnson Matthey), as a reference point to benchmark the electrochemical cell. Comprehensive elucidation of the testing protocol utilising a GDE half-cell has been detailed in 0 of this dissertation.

Gas diffusion electrodes were prepared and tested to compare their performance, following the detailed protocol as described in Chapter 4. Among them, Pt/HOMC exhibited the best performance compared to Pt/Vulcan and Pt/Ketjenblack (Figure 60).

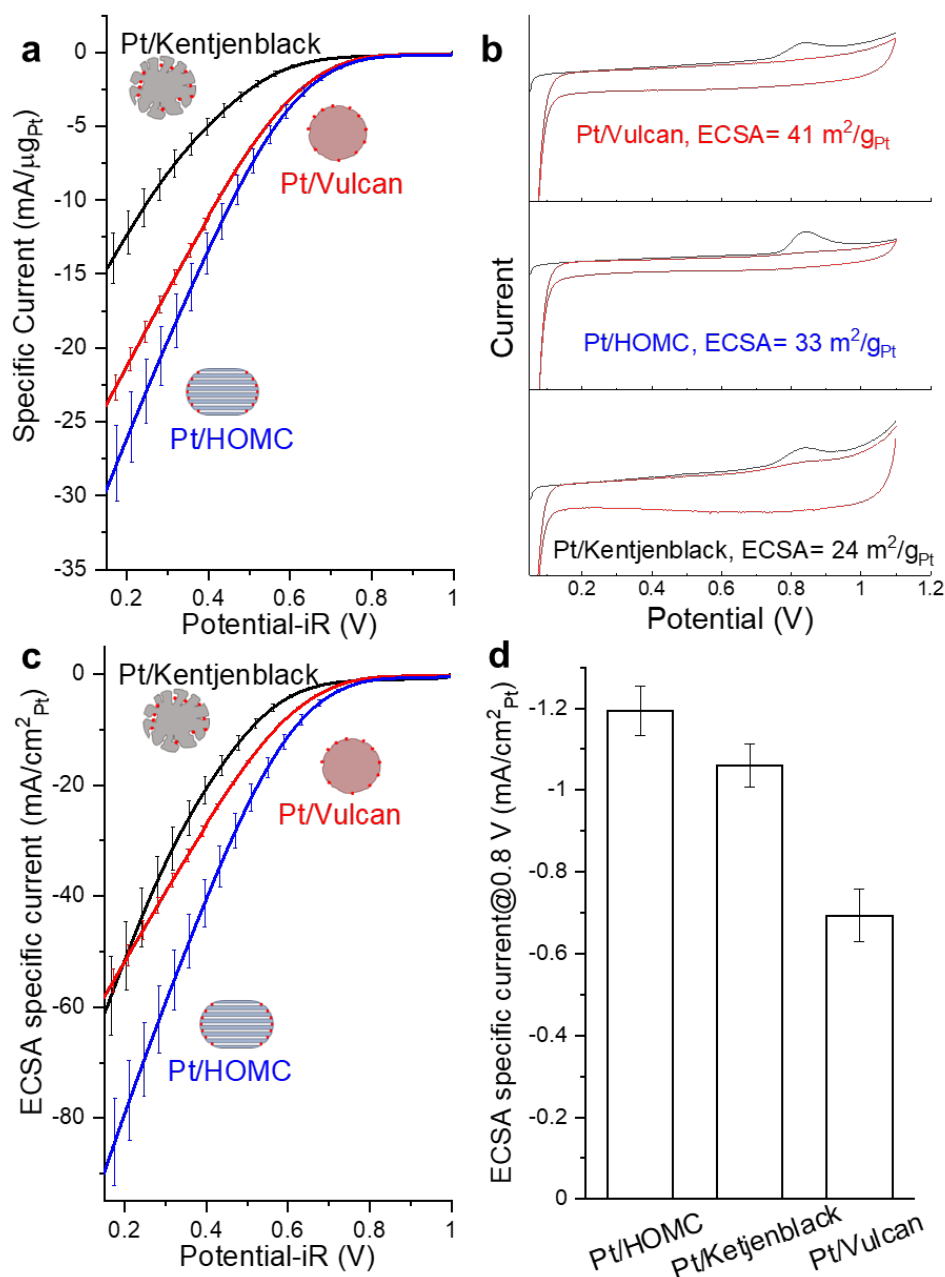


Figure 60. (a) ORR polarization curves measured in gas diffusion electrode half-cell. Measurements were done in 1M HClO_4 electrolyte at room temperature with 200 mL/min oxygen flow and 10 mV/s cathodic scanning rate. Pt wire was used as the counter electrode in the same electrolyte chamber without membrane separation, RHE was used as the reference electrode in a different electrolyte chamber connected with Luggin capillary. Potential was corrected for iR compensation. Two electrodes were prepared and measured with $\sim 10 \mu\text{g}_{\text{Pt}}/\text{cm}^2$ loading to generate the polarization curves. (b) ECSA determination via CO stripping for all three catalysts. CO stripping voltammogram (black line) and subsequent CV (red line) of the three Pt/C working electrode ($\sim 10 \mu\text{g}_{\text{Pt}}/\text{cm}^2$) recorded after the ORR measurements at a scan rate of 50 mV/s from 0.1 to 1.1 V RHE at room temperature. CO was

adsorbed for 5 min at 0.1 V RHE at a flow of pure CO (100 nccm) prior to the CV, followed by a 30 min purging procedure with N₂ while maintaining the potential at 0.1 V RHE. To obtain the ECSA, the CO stripping current was integrated using a linear baseline and converted to a corresponding Pt surface area using a specific capacity of 420 $\mu\text{C}\cdot\text{cm}_{\text{Pt}}^{-2}$. (c) ORR polarization curves normalised by ECSA measured with CO stripping. (d) ECSA specific current at 0.8 V for the three catalysts.

As depicted in Figure 60a, Pt/Vulcan and Pt/HOMC displayed similar behaviour at higher potential region (0.75 V – 1 V), with a slight lag observed for Pt/Vulcan; this lag was observed, and it could be attributed to catalyst poisoning by the ionomer. The exact numerical differences in this region, however, were marginal. The difference between Pt/Vulcan and Pt/HOMC emerged more substantial differences in the high current region, where mass transport effects dominated,

In contrast, Pt/Ketjenblack exhibited much slower kinetics compared to the other two catalysts, suggesting altered accessibility of active sites. This is corroborated by its relatively lower ECSA measured via CO stripping (Figure 60b).

The ECSA values, measured via CO stripping, were 41 $\text{m}^2/\text{g}_{\text{Pt}}$ for Pt/Vulcan, 33 $\text{m}^2/\text{g}_{\text{Pt}}$ for Pt/HOMC, but only 24 $\text{m}^2/\text{g}_{\text{Pt}}$ for Pt/Ketjenblack, respectively. The slightly smaller value of ECSA for Pt/HOMC is believed to be related to the location of the Pt NPs in mesoporous channels. A small amount of Pt atoms facing towards the inaccessible mesoporous channels could be inaccessible, thus decreasing the weight-normalized ECSA of Pt. However, this effect was not as pronounced as with Ketjenblack, whose structure leads to a much higher amount of Pt NPs being sealed in the microporous pores thus hardly accessible.

To further investigate the ionomer coverage across the three catalysts, the ORR current was normalized by the ECSA of each, illustrated in Figure 60c. Notably, Pt/HOMC consistently eclipses the other two catalysts in terms of ORR current density. In the context of lower potentials, both Pt/Vulcan and Pt/Ketjenblack manifest substantial mass transport limitations in comparison to Pt/HOMC. In contrast, at a higher potential of 0.8 V (Figure 60d), the current density of Pt/Vulcan markedly trails that of its counterparts, while the difference between Pt/Ketjenblack and Pt/HOMC can be neglected. This suggests that ionomer presence may impede catalyst performance via two distinct mechanisms: augmenting O₂ diffusion resistance and suppressing intrinsic activity. Subsequent sections will explore these two scenarios through gas sorption analysis and X-ray Absorption Spectroscopy.

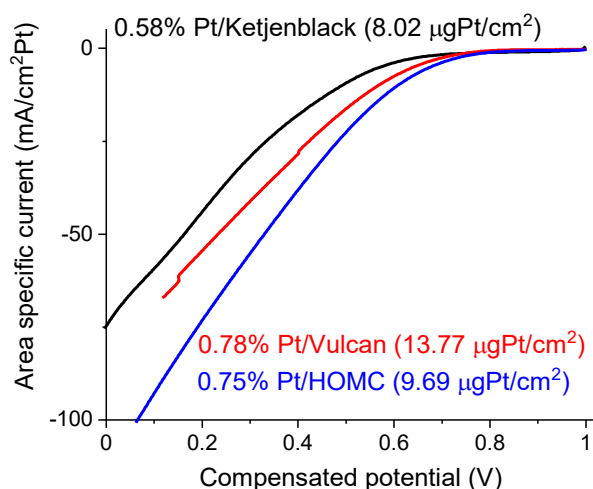


Figure 61. ECSA normalised ORR polarization curves measured in gas diffusion electrode half-cell. Measurements were done in 1M HClO₄ electrolyte at room temperature with 200 mL/min oxygen flow and 10 mV/s scanning rate.

1.17.4 Ionomer-Catalyst Interactions via Gas Sorption Analysis

One of the pivotal factors influencing mass transport effects pertains to local mass transport, which is intrinsically linked to the symbiotic interaction between ionomers and catalysts. Conventionally, the ionomer-to-carbon ratio is maintained within the ambit of 0.5 to 1.2.¹⁹¹ However, in the context of this research endeavour, an incrementally higher value of 1.0 within this range was chosen to expedite the elucidation of the associated effect.

A comparative analysis of N₂ sorption, both pre- and post-ionomer inclusion, was performed, facilitating a comprehensive understanding of ionomer coverage (Figure 62a-c). In the instance of Pt/HOMC, the inclusion of ionomer primarily impacted the microporosity. This conclusion is drawn from the comparative analysis which showed a reduction in adsorption at low P/P₀ (Figure 62a) and loss of pores smaller than 2nm (Figure 62d). This points to the inference that the ionomer film forms a protective layer on the surface, thereby obstructing a negligible number of surface micropores while the mesoporous aperture remains unaltered.

Upon examining Pt/Ketjenblack, post-ionomer blend porosity exhibited a dramatic alteration, underlined by a marked decrease in both micropores and mesopores suggested by the decrease adsorption over the whole P/P₀ range (Figure 62b) and changes in pore size distribution (Figure 62e). This can be ascribed to the superimposition of the ionomer film on the carbon support, thereby rendering the majority of its expansive surface area impermeable to N₂ molecules.

In the case of Pt/Vulcan, the alterations closely resemble those observed in Pt/HOMC with decreased adsorption at low P/P_0 (Figure 62c) and loss of pores smaller than 2nm (Figure 62f). The carbon's microporous structure was almost entirely obliterated due to the superimposition of the ionomer.

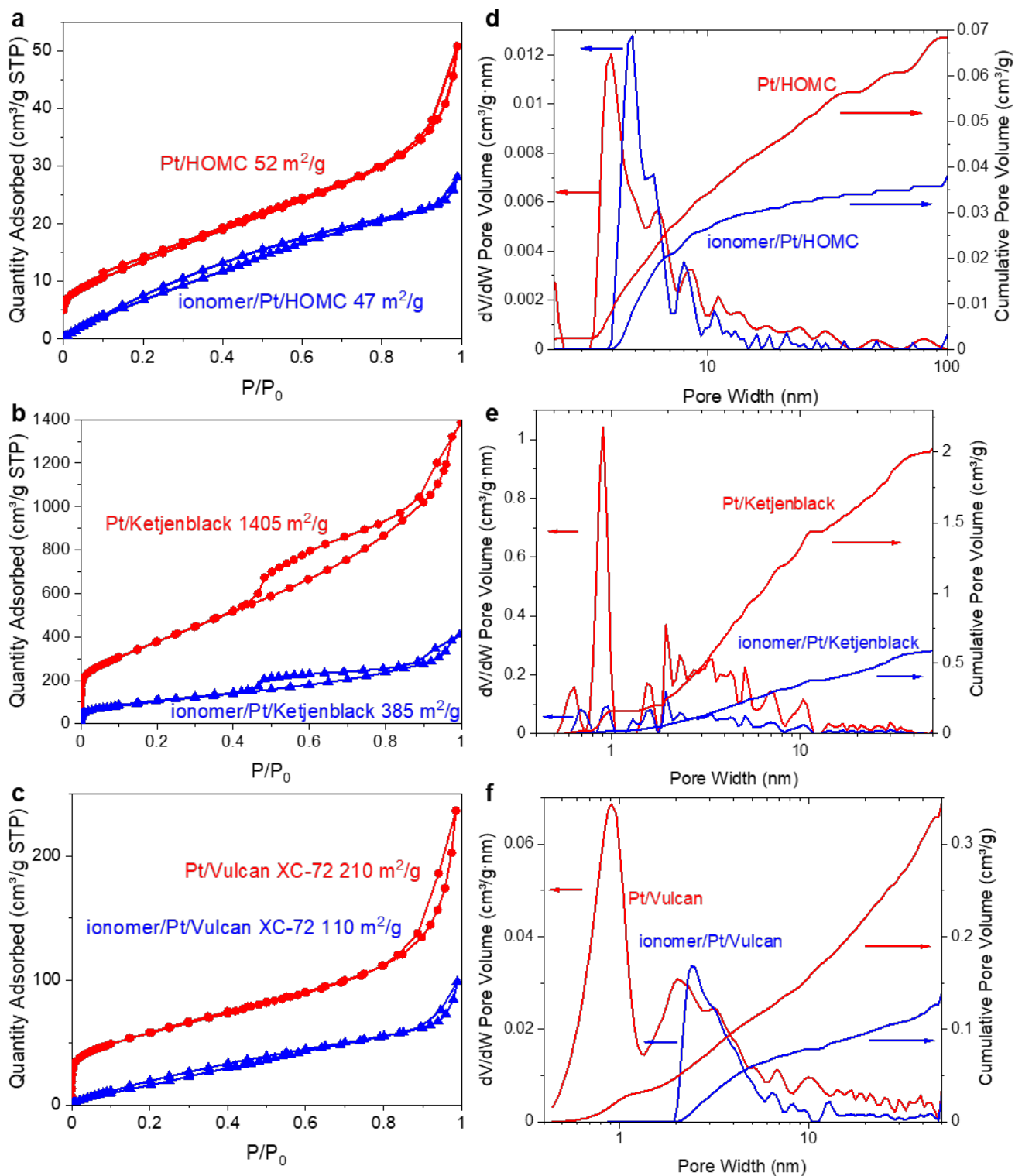


Figure 62. N₂ sorption isotherms for Pt/HOMC (a), Pt/Ketjenblack (b) and Pt/Vulcan (c) before and after the introduction of Nafion ionomer. NLDFT pore size distribution for Pt/HOMC (d), Pt/Ketjenblack (e) and Pt/Vulcan (f) before and after the introduction of Nafion ionomer.

1.17.5 Ionomer-Catalyst Interactions via Operando X-ray Absorption Spectroscopy

To reinforce the interpretation of the interaction between ionomers and Pt NPs under ORR conditions, an operando XAS analysis was performed. This aimed to scrutinise the unique adsorption properties of the ionomer under variable potentials across the three Pt/C variants. The corresponding shift in the electronic structure of Pt atoms occurs in response to anion adsorption under these potential states. The intensity of the 'white line' directly correlates to the quantity of anions adsorbed on the Pt surface, with increased intensity expected due to the formation of Pt-O bonds.

Kodama et al. observed that the adsorption of the NafionTM ionomer sulfonate group occurs at considerably lower potentials on Pt(111), around 0.5V versus RHE (Figure 63), compared to OH adsorption beginning at 0.8V versus RHE.⁸⁹ Although the exact adsorption potential would vary on the Pt NPs compared to this defined Pt(111) surface, it can be inferred that the sulfonate group adsorbs at a considerably lower potential than OH.

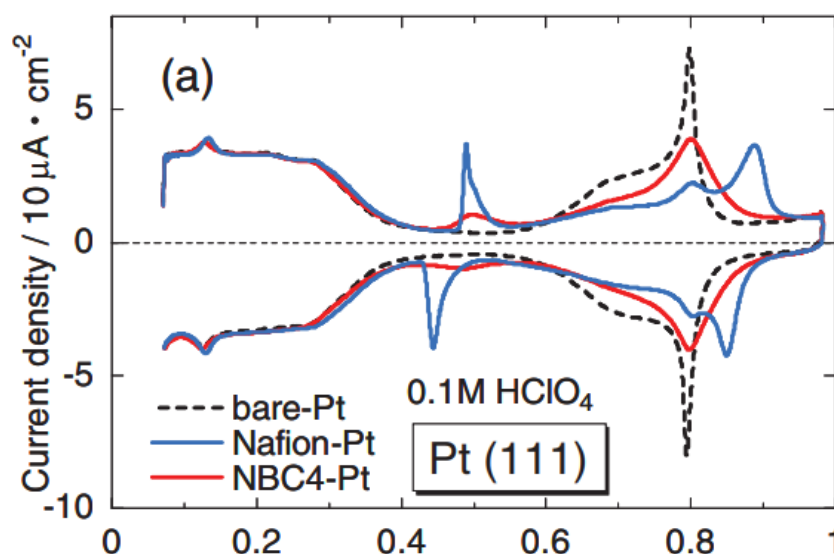


Figure 63. The CVs for Pt (111) surfaces covered with and without the ionomers revealing Nafion adsorption around 0.5V. Black dashed line: without ionomer coating (bare-Pt), blue solid line: with Nafion coating. Figure reproduced from ⁸⁹ with permission.

In a related study, Jonathan et al reported that sulfonate groups adsorption on step sites happens at potentials lower than 0.4 V vs. RHE, but only on those Pt electrocatalysts that possess the appropriate morphological features. These attributes include significant terrace ordering of (111), (100), or (110) facets and linear steps with a spacing of fewer than six atoms.¹⁹²

Conversely, on surfaces characterized by terraces wider than five atoms, all such electrochemical characteristics are entirely diminished, revealing only a broadened CV peak for the adsorption of sulfonate groups on Pt(111). When considering Pt NPs loaded on the three different carbon supports, which exhibit a predominance of Pt(111) facets as evidenced by HRTEM (Figure 58d), it's reasonable to anticipate observing sulfonate adsorption starting from 0.5 V vs. RHE, with OH adsorption occurring at higher potentials.

This differentiation permits the distinction of the increased 'white line' intensity instigated by sulfonate and OH adsorption. As illustrated in Figure 64a-c, the Pt L3 'white line' intensity elevated as the potential increased from 0.5 V to 1.0 V across all three Pt/C variants. A similar trend was detected at the Pt L2 edge (Figure 64d-f).

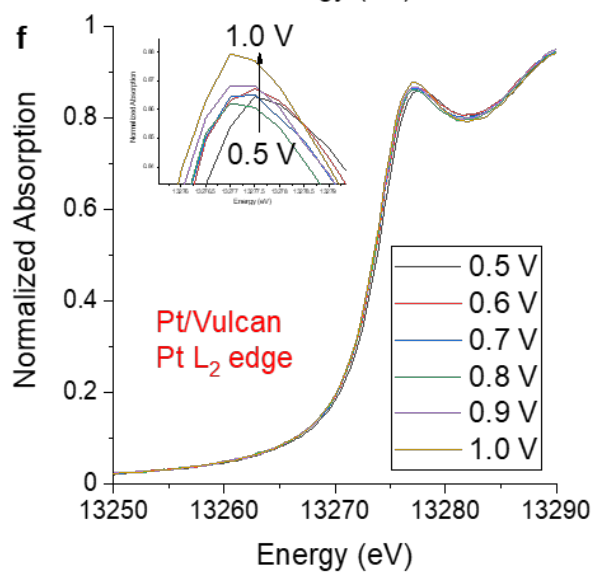
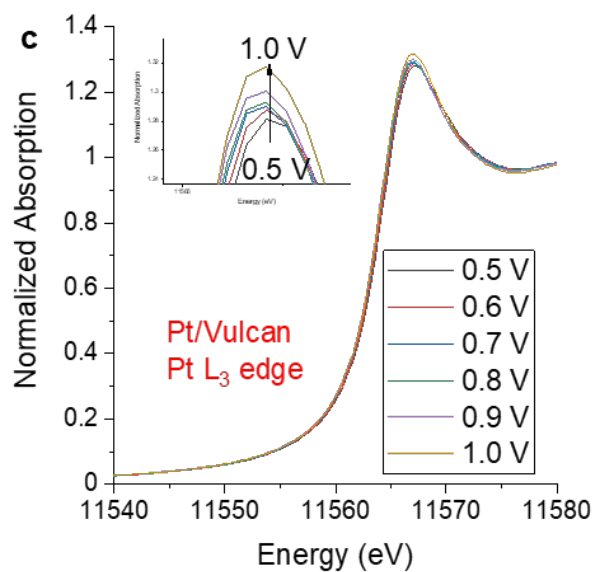
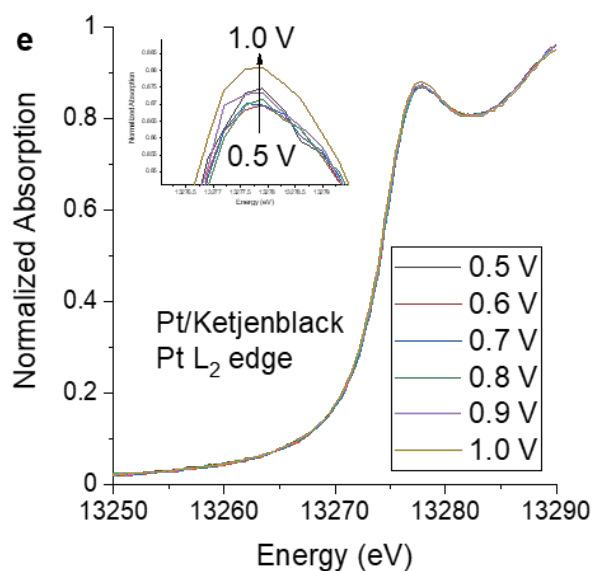
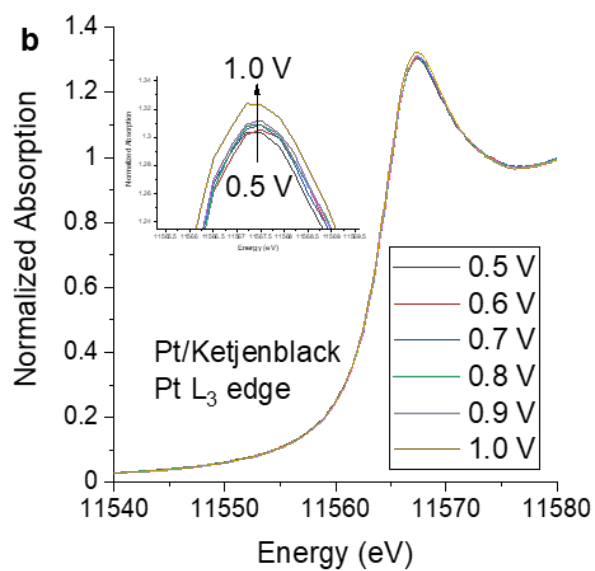
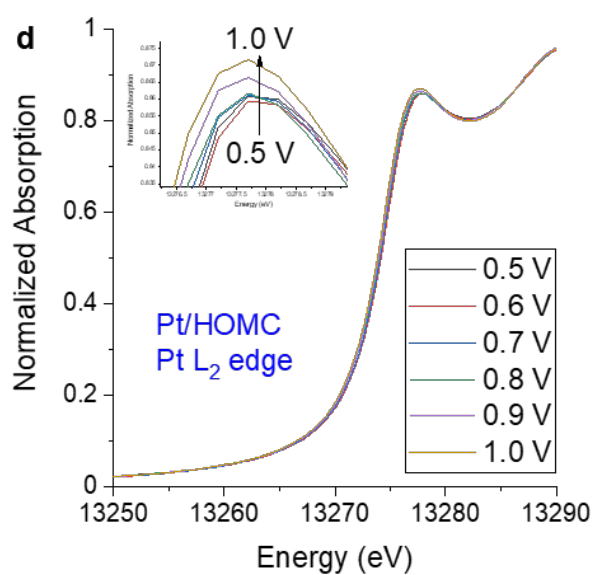
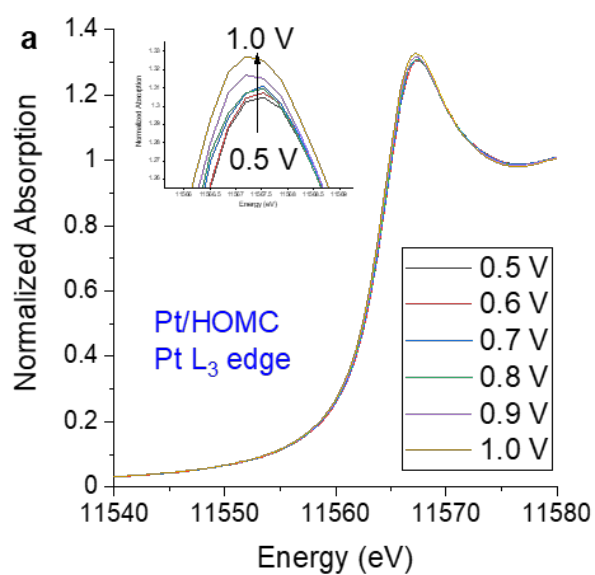


Figure 64. XANES spectra at Pt L3 edge for Pt/HOMC (a), Pt/Kentjenblack (b) and Pt/Vulcan (c); Pt L2 edge for Pt/HOMC (d), Pt/Kentjenblack (e) and Pt/Vulcan (f).

To demarcate the contributions of sulfonate and OH adsorption, the relative differences in the 'white line' are depicted in Figure 65b. A quantification method¹⁹³ was adopted to consider the near edge absorption differences against Pt foil reference at both L₂ and L₃ edges.

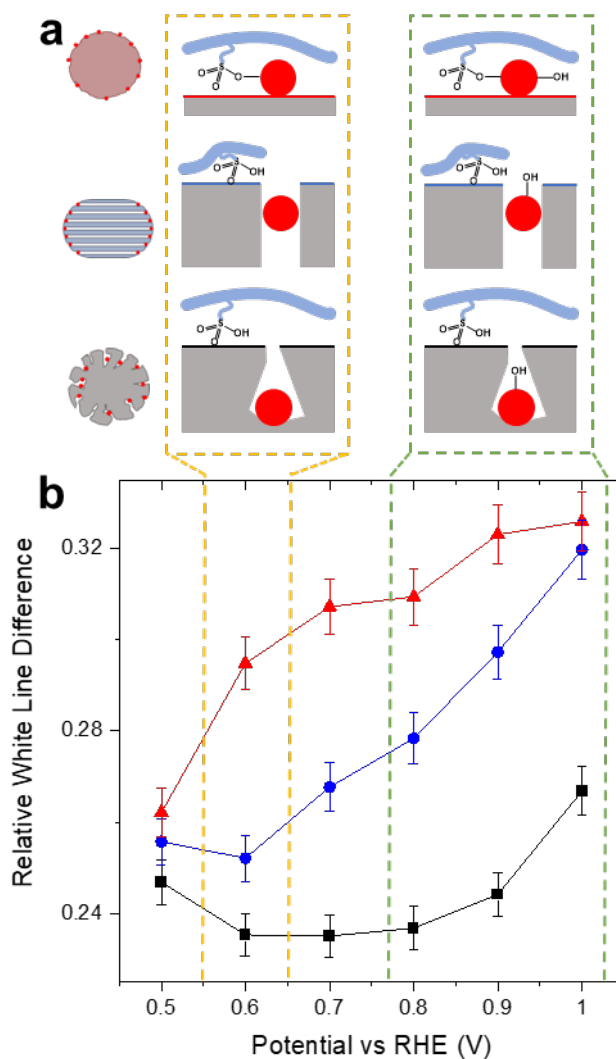


Figure 65. (a) Schematic illustration of different ionomer interactions of the 3 catalysts. (b) Relative white line difference against potential.

For Pt/Vulcan, a marked increase was detected as the potential rose to 0.6 V, signifying the adsorption of sulfonate, owing to the intimate contact between Pt NPs and ionomers. Contrarily, for Pt/Ketjenblack and Pt/HOMC, the 'white line' intensity exhibited a slight decrease as the potential ascended to 0.6 V. An increased 'white line' intensity was observed from 0.7 V onward, which can be attributed to OH adsorption and indicates an absence of sulfonate adsorption

within the lower potential range. This further corroborates that the majority of Pt NPs, whether located within the mesopores or at the mesopore mouths for Pt/Ketjenblack or Pt/HOMC respectively, were not in direct contact with the ionomers on the external carbon support surface. Notably, Pt/Ketjenblack showcased the lowest 'white line' intensity at 1 V, suggesting limited -OH accessibility for this particular catalyst. The proposed ionomer interactions were illustrated in Figure 65a.

In order to validate the above findings, a corroborative operando XAS analysis was executed at another synchrotron facility (Figure 66 a-d). The conclusions drawn mirrored those of the primary study, thus establishing a level of consistency in the results.

Shown in Figure 66e, observations concerning Pt/Vulcan revealed a notable uptick as the potential advanced to 0.5-0.6 V, which underscores the adsorption of sulfonate. This finding is attributed to the close proximity between Pt NPs and ionomers. On the other hand, when analysing Pt/Ketjenblack, there was a marginal decline in the 'white line' intensity as the potential was incremented to 0.6 V, which infers a lack of sulfonate adsorption within this lower potential threshold. As the potential progressed to 0.7 V and beyond, an escalation in the 'white line' intensity was discerned. This increase could be ascribed to the adsorption of OH. These observations provide further evidence supporting the notion that the majority of Pt NPs, which are predominantly situated within the mesopores for Pt/Ketjenblack, are not directly interfacing with the ionomers on the surface of the external carbon support. This lack of contact essentially prevents sulfonate adsorption from occurring in the initial potential stages.

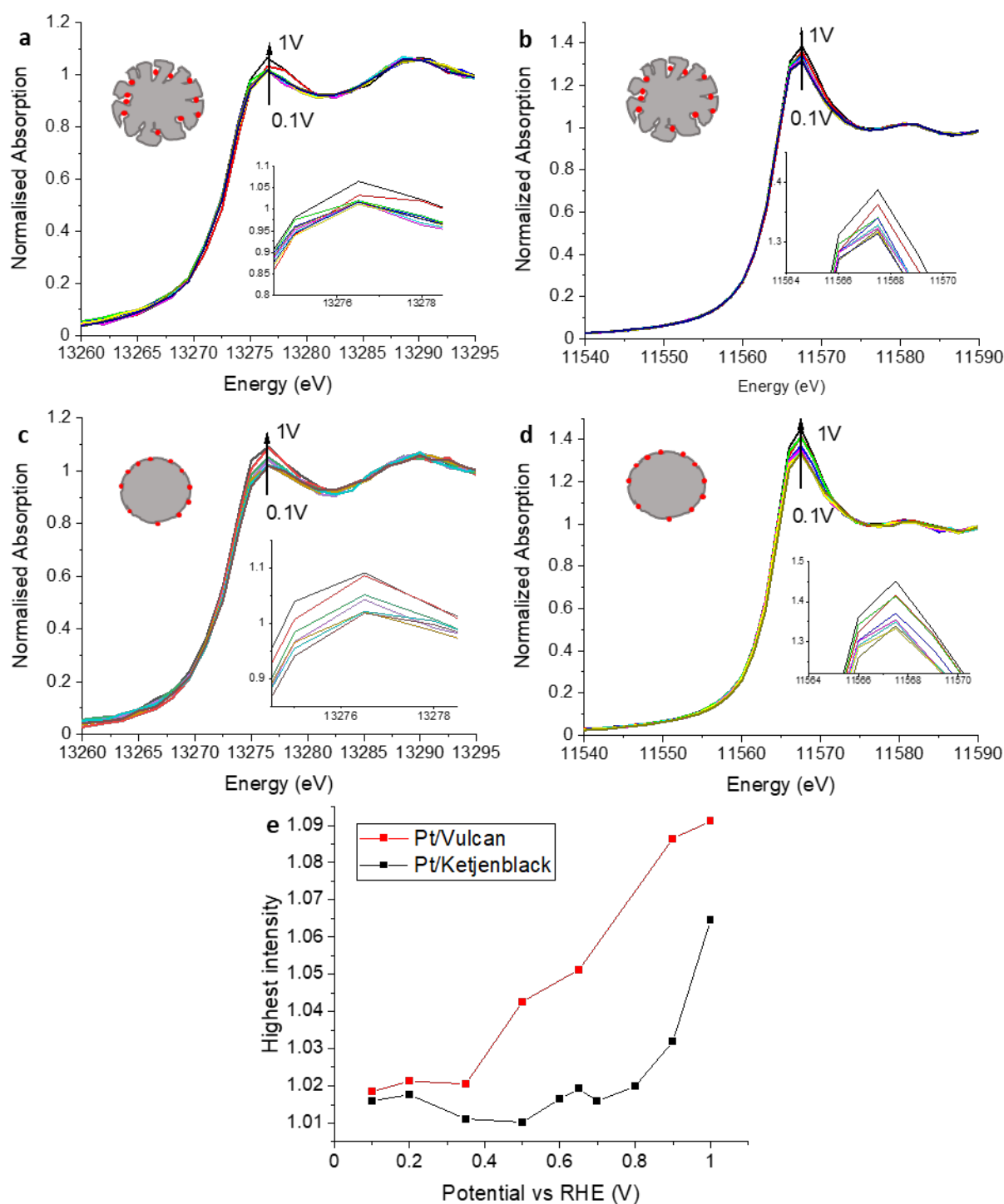


Figure 66. XANES results obtained from XMaS, ESRF showing the same observation for Pt/Vulcan and Pt/Ketjenblack.

Drawing upon comprehensive N_2 sorption and XAS analysis, catalyst models have been developed (as shown in Figure 57 and Figure 65) to represent the diverse interactions among ionomers, support materials, and nanoparticles. Further elaboration is provided in Figure 67. For each of the three support materials, the ionomers primarily accumulated on the external

surface, consequently obstructing the micropores, but the interiors of the mesopores remained unaffected. However, variances in the characteristics of mesopores and the localisation of Pt NPs led to differences among the three catalysts:

a) In the case of Pt/Ketjenblack, the reduction in mesoporosity could be ascribed to the obstruction of certain mesopores with micropore openings. Given that the volume loss of mesopores ($1.4 \text{ cm}^3/\text{g_catalyst}$) substantially exceeded the total ionomer volume ($0.3 \text{ cm}^3/\text{g_catalyst}$), the filling of mesopores by ionomers can be ruled out. The Pt NPs deep within the mesopores (as evidenced by XPS) were found to have limited access to O_2 and protons. Further obstruction of select mesopores hindered the transportation of O_2 , resulting in the least effective ORR performance of Pt/Ketjenblack among the three catalysts.

b) Regarding Pt/Vulcan, few mesopores were present, and the Pt NPs were identified on the surface, being in direct contact with ionomers. This was substantiated by the specific adsorption of sulfonate detected through XAS. However, this additional ionomer layer presented difficulties for O_2 diffusion.

c) For Pt/HOMC, the mesopore openings were large enough to remain accessible to N_2 (or O_2 under reaction conditions) despite the presence of ionomers. The absence of an elevation in white line intensity at 0.6 V, which is indicative of a lack of ionomer adsorption, suggests that the Pt NPs located at the mesopore openings are not directly covered by ionomers, thereby ensuring favourable O_2 accessibility. This distance was nevertheless not too far, making the Pt NPs still accessible to protons from the ionomers.¹⁹⁴

These favourable interactions contributed to the superior ORR performance exhibited by Pt/HOMC.

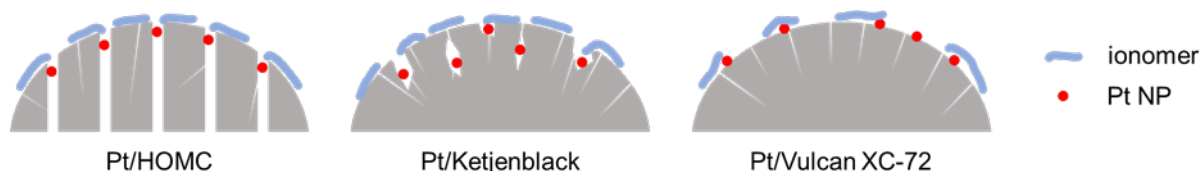


Figure 67 . Ionomer interaction models.

1.18 Summary

Mesoporous carbon nanospheres, sustainably synthesised from biomass, were employed as a substrate for the deposition of Pt nanoparticles using the polyol method. This ordered

mesoporous carbon (HOMC), alongside two other widely used commercial carbon supports (porous Ketjenblack and non-porous Vulcan XC-72), served as a comparison base. Characterisation of these catalysts via SEM, TEM, BET, ICP-MS, and XPS demonstrated that the Pt nanoparticles were equivalent in both geometric and electronic structure. This confirmed that disparities among these catalysts could be solely attributed to the differential support porosity - that is, the local environment of Pt NPs within the catalysts. Upon testing all the Pt/C catalysts under a gas diffusion half-cell configuration for their oxygen reduction performance, Pt/HOMC displayed the highest activity.

Operando X-ray absorption spectroscopy facilitated an evaluation of ionomer coverage on the Pt surface by tracking changes in the Pt white line intensity within a potential range of 0.5-1.0 V (vs RHE). Among the supports analysed, only Vulcan demonstrated sulfonate adsorption. These insights, coupled with a comprehensive structural examination via gas sorption analysis, contributed to understanding the platinum and ionomer distribution across the catalyst support.

Our findings indicate that on Vulcan, both platinum and Nafion are situated on the catalyst surface, facilitating effective accessibility to active sites and proton transport, albeit at the expense of ionomer poisoning. In stark contrast, platinum is lodged within the pores of Ketjenblack, while the ionomer resides on the surface. This configuration eliminates sulfonate adsorption but results in severe proton and oxygen transport limitations, thereby accounting for the inferior performance of this support.

In the case of the in-house synthesised HOMC, platinum is positioned at the entrance of the mesopores, with the ionomer in close proximity on the external surface. This arrangement explains the superior performance of HOMC, which optimises the interaction between Pt and NafionTM ionomer. Direct contact between these two components is avoided, yet accessibility of protons to Pt active sites is maintained.

Rationalisation of the Bulk Transport Through Hierarchical Architecture of the Catalysts Layer

1.19 Introduction

The evolution of advanced electrode materials is undoubtedly a critical aspect in the progress of electrochemical energy systems, due to its significant impact on the mass transportation of reactants and product removal. However, the attainment of desired levels of overall efficiency does not solely hinge on the quality of active materials in the electrodes. Equally important, if not more so, is the systematic organization and careful interfacing of these materials within the electrode itself. Striving towards enhanced catalysts utilisation, thus reducing stack size, promises significant reductions in capital cost. This strategy offers a two-fold advantage: not only it cuts down the cost of catalysts materials, but it also makes the device smaller and lighter, which brings its own set of advantages.

A meticulously designed electrode architecture, ensuring expedited transport and optimized material utilization, can be pivotal in achieving superior power density, enhanced durability, and increased efficiency. Such improvements, coupled with the potential for capital cost reductions, are clearly manifested in the work presented herein. Traditional PEMFC electrodes are formulated from an amalgamation of a carbon-supported platinum catalyst and an ionomer. These components are combined to form an ink slurry that is subsequently deposited onto a membrane or a gas diffusion layer, resulting in a porous electrode structure. This 'top-down' methodology produces a stochastic electrode architecture, characterized by a network of ionomer and pore channels with a high degree of tortuosity. Such a configuration poses considerable challenges for mass transport, and consequently, results in sub-optimal catalyst utilization.

Remarkably, the structure of the conventional electrode deployed in contemporary commercial PEMFCs remains fundamentally unaltered from the original design introduced by Wilson and Gottesfeld over three decades ago.¹⁹⁵ This persistence of conventional designs, despite their inherent limitations, underscores the challenge of implementing radical innovations in electrode architecture. In response to these challenges, a number of investigations have been dedicated to advancing alternative electrode structures.

Enabled by breakthroughs in microfabrication and nanofabrication techniques, these studies exemplify the ongoing efforts in pioneering innovative electrode designs that could surpass traditional MEA architectures. One significant family of such structures developed is inverse opals, which offers outstanding interconnected structures and low tortuosity. However, this kind of structure usually suffers from the lack of a hierarchy to host and protect the active catalytic site, as well as to facilitate the multi scale transportation. Hence, the development of a hierarchical structure within the electrode catalysts layer holds great importance. As discussed previously in Chapter 5, mesopores with a diameter of 4nm have been proven to facilitate optimal ionomer interaction, thereby governing efficient local transport. By introducing a higher level of macropores, the catalytic sites can be effectively interconnected, ensuring rapid delivery of reactants and swift removal of products.

In this chapter, a strategy involving dual templating was discussed with the aim of crafting a hierarchical structure, employing lignin as the carbon precursor.. Emphasis is put on the diversity of templating approaches and the comparison of two structures with and without hierarchical organization. Following this, an in-depth analysis of the structure of carbon supports was undertaken. The objective of this investigation was to comprehend the implications of the structure on electrochemical accessibility and how it might influence performance. Moving forward, characterization of the catalyst layers after the introduction of Pt NPs catalysts was carried out. This includes an exploration of various aspects such as the morphology, nanostructure, and chemical properties of the catalysts, offering a multifaceted understanding of their unique attributes and behaviours. The chapter is concluded with a performance evaluation of the three aforementioned catalyst layers. Operating under a GDE half-cell configuration, the intent was to accentuate the efficient mass transport capabilities governed by the hierarchical structure. The outcome of this comparison was to provide insightful data to aid the understanding of the influence of the hierarchical structure on the overall efficiency and effectiveness of the catalyst layers.

1.20 Results and discussion

1.20.1 Polystyrene Nanospheres Development

In an evolution from the mesoporous materials described in Chapter 5, which demonstrated 4 nm pores as optimal hosting sites for the Pt NPs, this research further explored the integration of macropores within the catalyst layer. These macropores are designed to facilitate bulk mass transport, offering protection to the Pt NPs from ionomer intrusion without compromising their

accessibility. Among the potential candidates for macropore templating, polystyrene particles emerged as particularly suitable due to its wide-ranging size availability and ease of removal through thermal decomposition in the pyrolysis process.

The synthesis of polystyrene was undertaken employing an emulsion method, utilizing a 5% styrene solution in water. Following synthesis, the resulting emulsion was subjected to DLS measurements and SEM imaging after drying. Figure 68 conspicuously illustrates that the synthesized polystyrene has narrow distributed size, exhibiting a polydispersity of merely 1.4%. This controlled synthesis underscores the suitability of polystyrene as a macropore template, aligning with the targeted design criteria for enhanced mass transport within the catalyst layer.

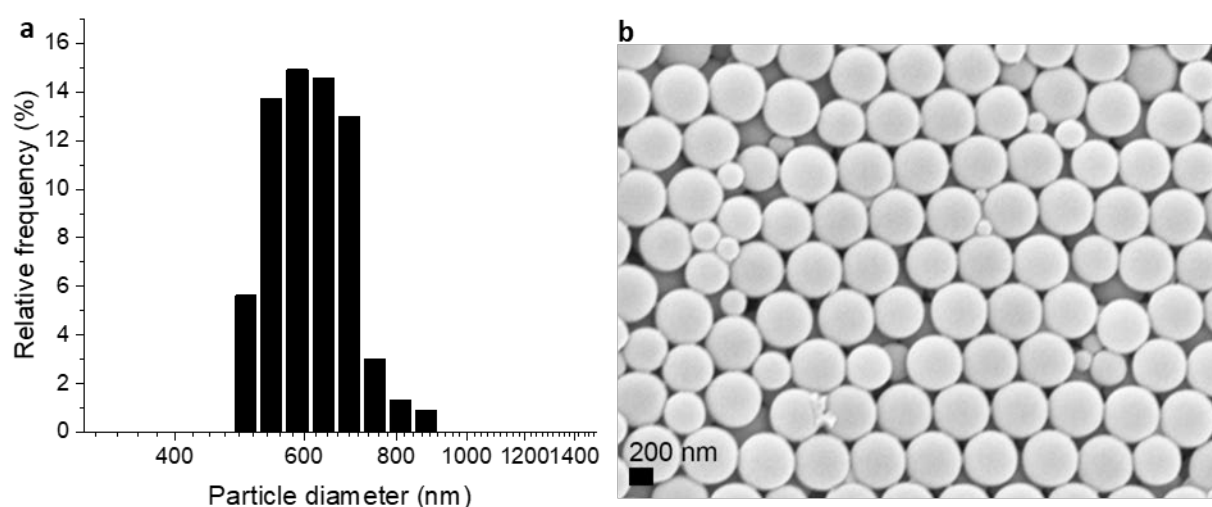


Figure 68. (a) DLS diameter distribution and (b) SEM images of the synthesised polystyrene particles showing particles size around 500nm.

1.20.2 Nanostructure Development

In the quest to develop nanostructured carbons, the study employed a dual templating process involving two distinct techniques to introduce mesoporosity and macroporosity in the carbon structure. (Figure 69)

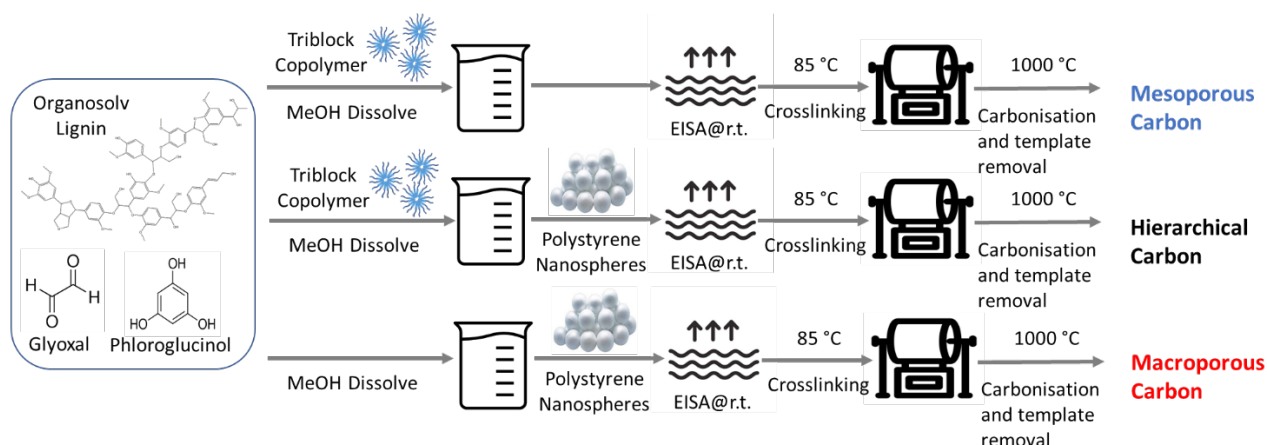


Figure 69. Schematic synthetic procedure for lignin derived carbon with mesoporous, microporous and hierarchical structure.

Soft templating, using block copolymers, was adopted to induce mesoporous structures into the synthesized carbons. Leveraging Pluronic™ F127 as the template, as done in Chapter 5, guaranteed the formation of mesopores of consistent size. These mesopores are pivotal for facilitating optimal interactions with ionomers, as previously demonstrated. The process commenced with dissolving the polymer template in methanol, followed by the addition of organosolv lignin, phloroglucinol, and glyoxal to the dispersion. These carbon precursors, replete with hydroxy moieties, interact non-covalently with the PEO sequence of the template via hydrogen bonding, governing the ensuing organic-organic self-assembly process. Ensuing formation of micelles is guided by the incompatibility between hydrophilic and hydrophobic polymer blocks, with the hydrophobic sequences constituting the micelle core in the hydrophilic solvent, methanol. The evaporation induced self-assembly (EISA) process fosters microphase separation within the block copolymers. Subsequent thermopolymerization at 85 °C stabilizes this ordered mesophase through cross-linking reactions with glyoxal, creating a three-dimensional network of covalently bridged phenols. This robust network supports the successful removal of the template, without compromising the structural integrity of the mesopores. The process concludes with pyrolysis at 1000 °C to yield the final mesoporous carbon.

Polystyrene nanospheres were employed as hard templates to introduce macroporosity (> 50 nm) and to create an inverse opal structure. The process involved dissolving carbon precursors in methanol and then dispersing in-house synthesized polystyrene nanospheres into the solution using probe sonication. This technique yielded a stable and homogenous

suspension, ready for the cross-linking and carbonization stages that eventually lead to the formation of carbon with macropores.

The synthesis of hierarchical carbon necessitated a hybrid approach that combines the two templating techniques described above. By combining Pluronic™ F127 and polystyrene nanospheres, a bimodal templating system was established to create a hierarchical structure comprising interconnected meso- and macropores. This novel methodology facilitated the formation of a sophisticated porous structure, thereby setting the stage for comprehensive characterization and performance analysis.

It's important to highlight that the carbon film, post-carbonization, is rather brittle. Consequently, it is not amenable to further sizing processes required for our electrochemical measurements. To address this issue, we attempted reinforcement with multi-walled carbon nanotubes (MWCNT), incorporating 5 wt% - 20 wt% MWCNT (with a diameter of 110-170 nm and length of 5-9 μm) into the precursor suspension. However, this did not yield a more manageable carbon film as we expected. In light of this, we opted for an alternative approach. We introduced a carbon paper as a back layer onto which the precursor suspension was evaporated, resulting in a monolithic polymer film. This strategy was designed to provide the necessary mechanical strength to the resultant carbon film, enabling its successful testing in the gas diffusion electrode half-cell configuration. Thus, this intervention ensures that despite the innate brittleness of the carbon film, it can be effectively utilized for our purposes.

1.20.3 Characterisation of the Carbon Film

Gas adsorption analysis using N_2 was applied to evaluate the porosity of the three different carbon structures. From the results shown in Figure 70, it was observed that all three carbon structures shared a similar microporous volume, for pores smaller than 2 nm. This commonality underlined a consistent formation of microporosity across the various templating processes employed. A noteworthy distinction emerged when studying the mesoporosity. The pore size distribution plots, complemented by the characteristic isotherm hysteresis, clearly delineated the presence of ~ 4 nm mesopores for both the hierarchical carbon and the mesoporous carbon. These features are consistent with the previously identified optimal pore size for ionomer interactions, as discussed in Chapter 5.

While the BET method could not resolve macropores explicitly, indirect evidence of their existence was inferred from the adsorption trends observed at high relative pressures (P/P_0). This observation hinted at the presence of macropores within the carbon structure, specifically

for the hierarchical and microporous carbon. However, further characterization techniques, such as SEM, would be required to verify this suggestion. Through these findings, the BET results demonstrated the successful creation of varying porous structures within the carbon substrates, thus setting the stage for subsequent catalytic performance testing.

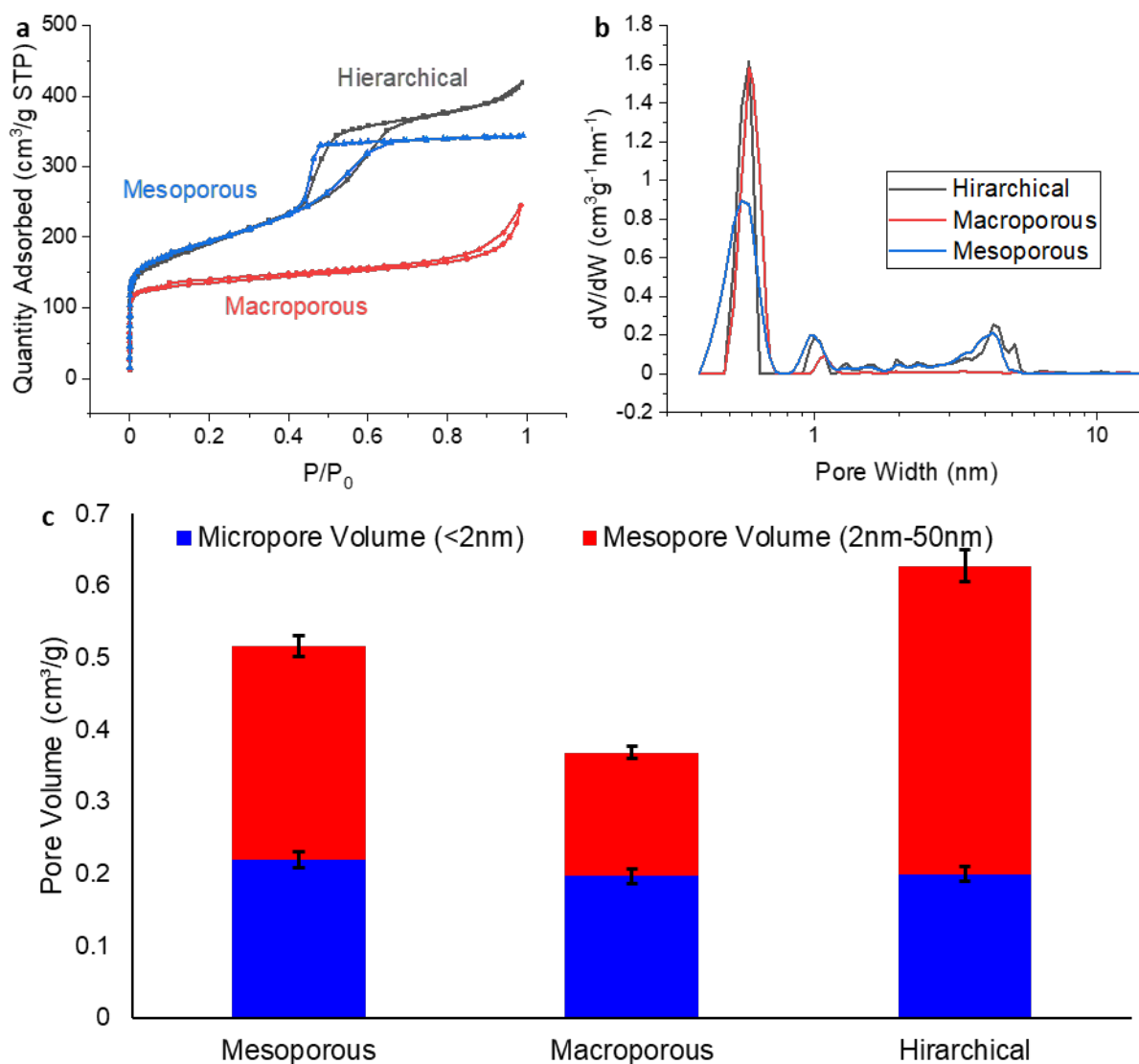


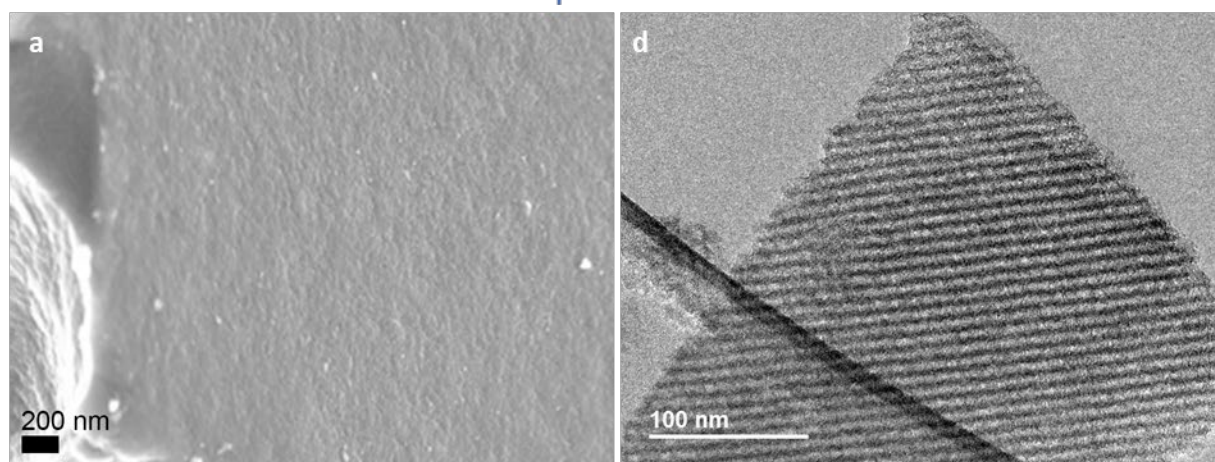
Figure 70. (a) N₂ sorption isotherm, (b) NLDFT pore size distribution and (c) micro-, mesopore volume comparison for the three different carbon film.

To verify the meso- and macropore structure established with the gas sorption results, SEM and TEM were used to image the morphology of the carbon materials (Figure 71).

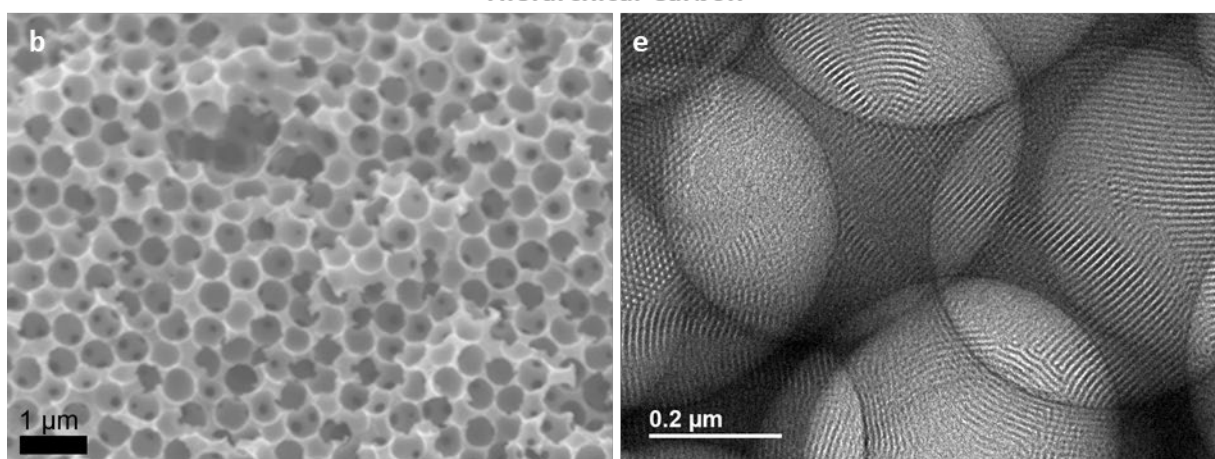
Mesoporous channels are clearly shown on the TEM images for hierarchical (Figure 71e) and mesoporous sample (Figure 71d), while macropores with size of about 400nm are observed in the SEM images for hierarchical (Figure 71b) and macroporous carbon (Figure 71c),

supporting the conclusions from gas sorption analysis. It is worth noting that for the hierarchical materials, the bimodal porous structure is interconnected to form a continuous architecture, posing great potential for the mass transportation.

Mesoporous Carbon



Hierarchical Carbon



Macroporous Carbon

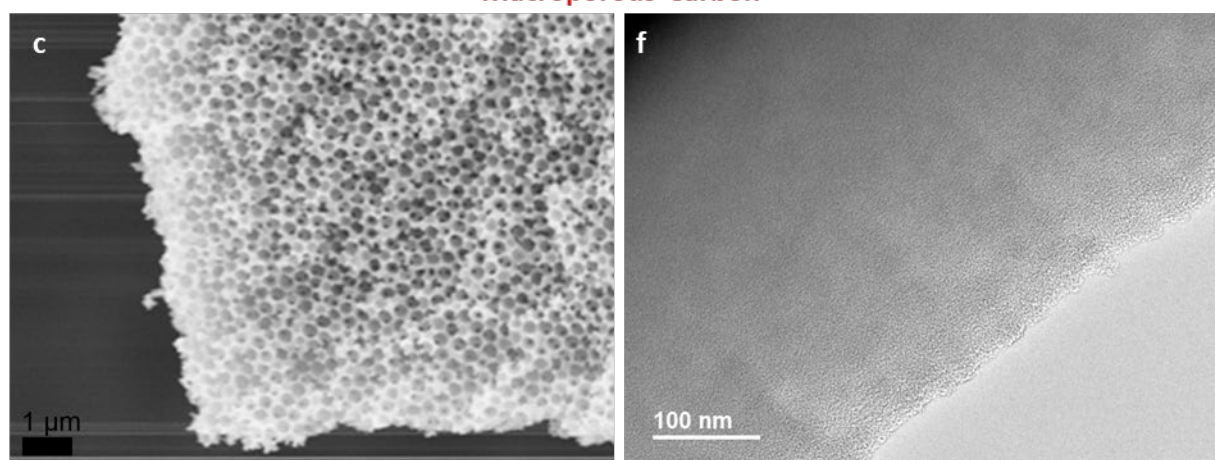


Figure 71. (a-c) SEM and (d-f) TEM images display yielded carbons after pyrolysis at 1000 $^{\circ}\text{C}$

1.20.4 Understanding the Electrochemical Accessibility of the Carbon Film

To further probe the electrochemical attributes of the distinct carbon structures developed in this research, we employed CV analyses using the carbon films as gas diffusion electrode, in a 1M HClO₄ solution. As depicted in Figure 72a, CV currents were normalized to the mass of each specific nanostructured carbon substrate. This standardization enables an effective comparative assessment between our carbon samples and benchmark data from the existing body of literature. An interesting observation emerged from the analysis - both the hierarchical and mesoporous-only carbon structures displayed comparable capacitance values. Contrarily, the material with only macroporous structure demonstrated a notably diminished capacitance.

In a further effort to explore the electrochemical accessibility of these materials, we scrutinized the capacity retention at high scan rates, an investigative approach commonly employed within the field. Significantly, materials incorporating macroporous structures, namely, the hierarchical and macroporous-only materials, exhibited outstanding capacity retention. A marginal loss of 20% (Figure 72b) implies a swift ion transport rate within the macropores, a testament to the advantageous characteristics intrinsic to macroporous structures.

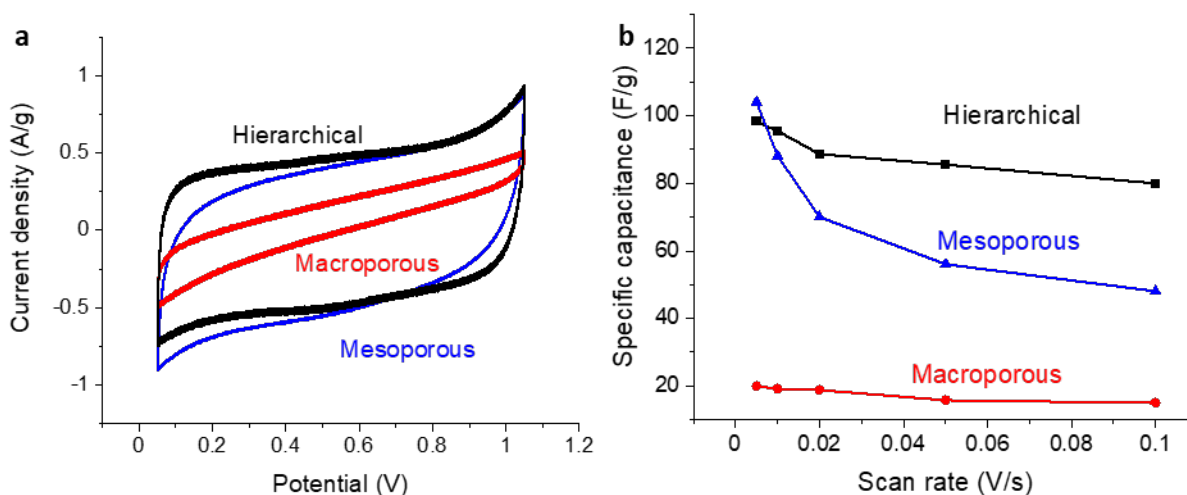


Figure 72. CVs (10 mV/s) of various carbon materials (a) and their capacitance retention as a function of the scan rate (b).

Attempting to correlate capacitance to surface area for these materials, a definitive conclusion remained elusive when employing the BET surface area (Figure 73a). Conversely, upon eliminating the microporous surface area, a strong correlation was achieved with an r^2 of 0.998. This result concurs with extant literature, which suggests that electrochemical accessibility can be challenging for microporous structures below 2 nm.¹⁹⁶

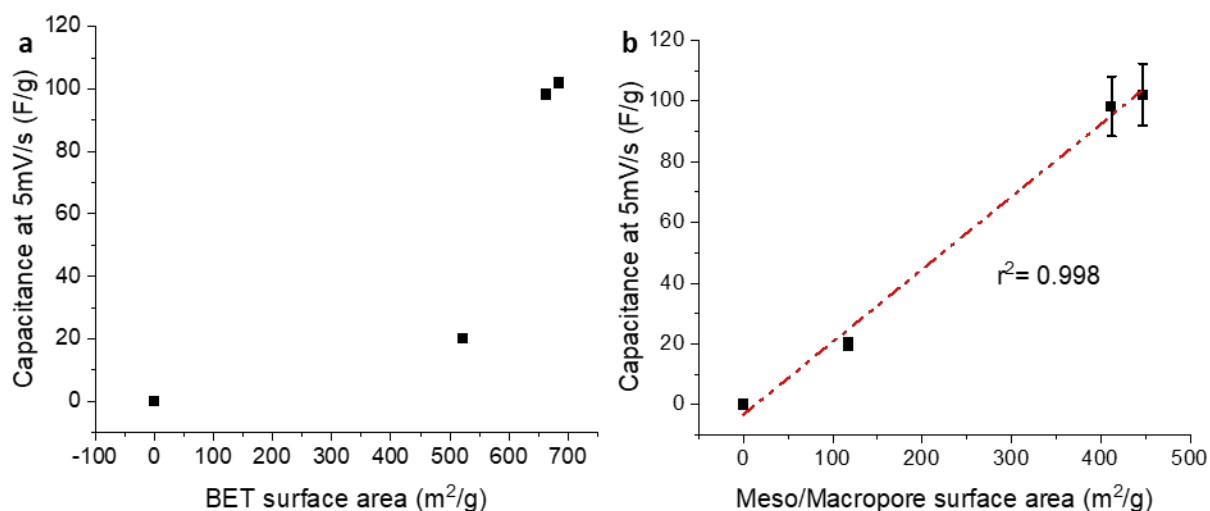


Figure 73. Correlation of the capacitance and surface area for the various carbon materials.

In conclusion, our investigations suggest the potential of hierarchical carbon materials for future applications. These materials boast an ideal, ultra-low tortuosity microstructure, devoid of binders, and exhibit superior electrochemical accessibility. The findings of this study highlight the promise of these carbon materials as effective substrates for the deposition of Pt NPs, heralding a significant leap forward in the development of innovative catalyst layers for use in PEMFCs.

1.20.5 Preparation of Catalysts Layer by Introducing Pt NPs

After a comprehensive characterization of the nanostructure of the carbon materials, the subsequent phase of our research involved the integration of active catalytic sites, specifically Pt NPs. For structures with continuous morphology such as ours, gas-phase synthesis methods like atomic layer deposition (ALD) are conventionally the optimal choice. However, the practical limitations of our experiment precluded the utilization of ALD.

The specifics of our investigation necessitated a sizable carbon film of 3x5 cm, which had to fit within the electrochemical half-cell configuration for later assessments of ORR performance. This requirement led to an incompatibility with the available ALD apparatus, which could not accommodate such a large carbon film size.

Given this constraint, we had to explore alternate approaches for the deposition of Pt NPs. The first alternative we turned to is physical method such as spark ablation or sputtering. Spark ablation, as illustrated in Figure 74, involves applying a high voltage across two metal electrodes to generate a spark. This spark incites a region of elevated temperature and pressure, leading to the ablation of the target material - in this context, platinum - and the formation of a

plasma composed of atomic particles. As this plasma expands and cools, it fosters the nucleation and growth of nanoparticles, which can subsequently be collected downstream. It was anticipated that the size of these particles could be manipulated by adjusting process parameters such as spark energy, flow rate, and carrier gas composition. Regrettably, in our initial trials, we could not secure a stable stream of Pt NPs. Instead, we observed the presence of random-sized Pt clusters exceeding 100 nm on the test substrate, which deterred us from further pursuing the application of spark ablation for our purposes.

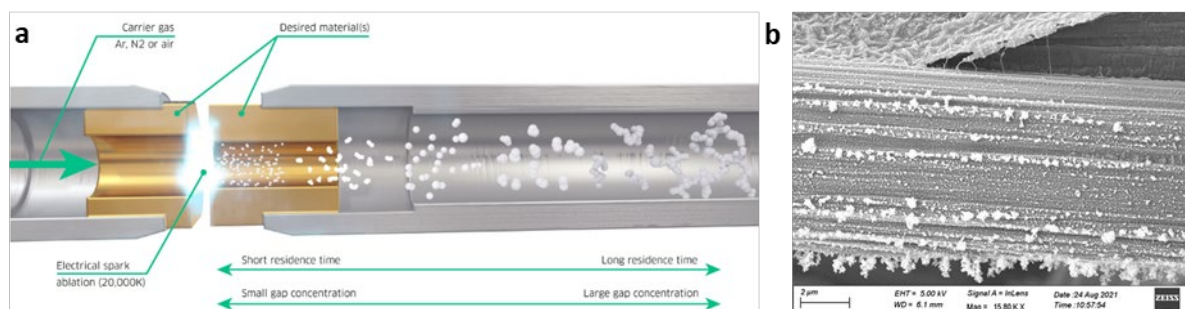


Figure 74. (a) Spark ablation technology diagram from VS Particles. (Extracted from <https://vsparticle.com/about/technology>) (b) SEM image of Pt clusters deposited on testing carbon paper.

Reflected upon this, the need for a stable carrier gas and a more uniform and controlled deposition becomes apparent. Consequently, sputtering was explored as a potential method. In contrast to spark ablation, sputtering involves bombarding a target material with ions. Typically, high-energy ions such as argon ions are directed towards the target material, which in this case is platinum. Upon impact, these ions cause the ejection or 'sputtering' of atoms from the surface of the target material. These sputtered atoms then accumulate onto the substrate located opposite the target. Not surprisingly, given its operational principle, a thin film of Pt nanoparticles was formed on the external surface rather than infiltrating the monolithic structure. As depicted in Figure 75, where a hierarchical carbon film served as the substrate, it is evident that most of the carbon structure lacked Pt nanoparticles, except for a minimal presence at the edges of the structure. The sputtered Pt was subsequently observed as thin films that had become completely detached from the substrate during the transmission electron microscopy (TEM) sample preparation.

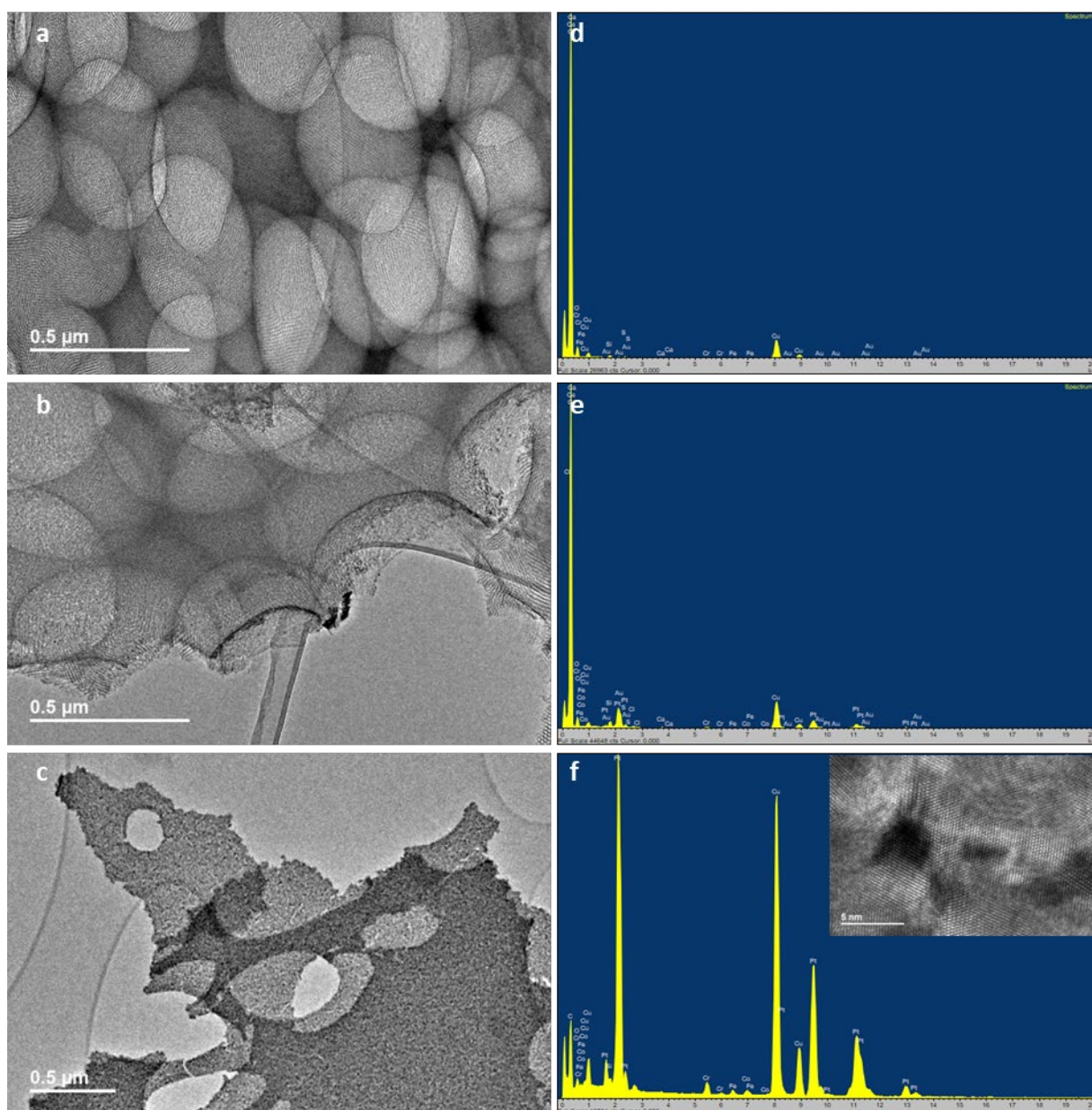


Figure 75. TEM images and EDX spectra of (a,d) majority of the carbon substrate without Pt NPs signal, (b,e) minimum Pt NPs observed on the edges of the carbon substrate and (c),f Pt thin film totally separately from the carbon substrate.

Faced with the limitations of physical methods that failed to deposit Pt as desired, the focus was reverted to chemical methodologies. The monolithic character of the carbon materials presented in this chapter precluded the use of conventional glycol methods that necessitate a stirring suspension during synthesis. The wet impregnation method could be employed, but this demands a detailed operation procedure to assure an even distribution of the precursors within the carbon matrix.

In this study, a platinum precursor solution (1 mg/mL H_2PtCl_6) was meticulously sprayed onto the carbon film, ensuring comprehensive penetration and drying of the precursor with each application. Following the precursor's impregnation, the carbon films were subjected to a reduction process at 350°C for 2 hours, using a 5% H_2 in N_2 gas flow. The resulting catalyst layers, with their deposited Pt, were then analysed via TEM, demonstrating successful preparation of Pt NPs on all three carbon substrates. The findings presented in Figure 76 reveal that the Pt NPs, when deposited onto the hierarchical carbon material, exhibit remarkable dispersion. Meanwhile, a moderate degree of aggregation is observed on the alternative carbon substrates. These observations further underscore the beneficial influence of the hierarchical structure in enhancing diffusion phenomena.

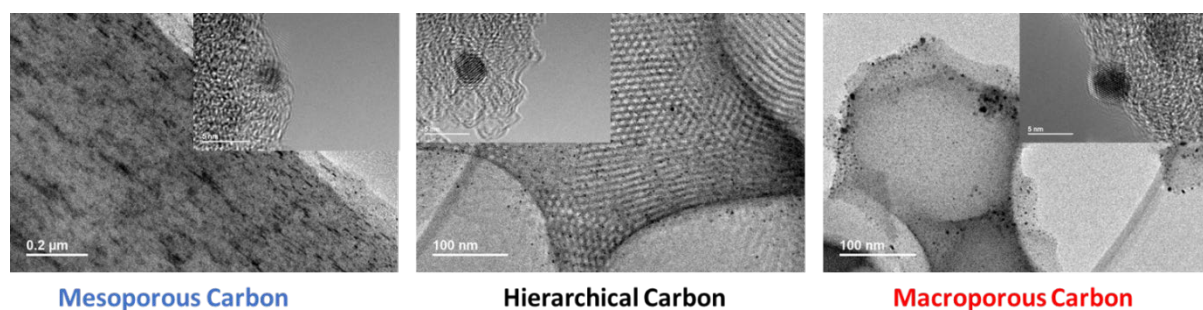


Figure 76. TEM images of the three catalyst layers with Pt nanoparticles deposited.

The loading of Pt was regulated by the volume of precursor solution applied to the carbon film. The precise Pt loading was determined by extracting a circular 0.5cm^2 sample from the catalyst layer, followed by microwave-assisted digestion using aqua regia, with subsequent quantification via ICP-MS.

1.20.6 Improved ORR Performance for Catalysts Layer with Hierarchical Architecture

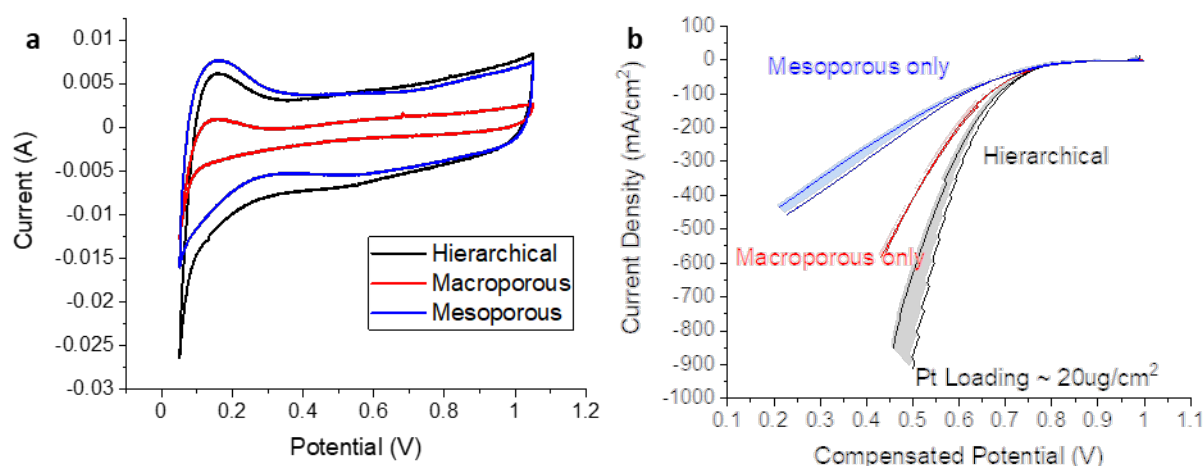


Figure 77. (a) CV for all three catalyst layers under N_2 measured in gas diffusion electrode half-cell. (b) ORR polarization curves for all three catalyst layers. Measurements were done in 1M $HClO_4$ electrolyte at room temperature with 200 mL/min oxygen flow and 100mV/s scanning rate for CV and 10 mV/s scanning rate for LSV. RHE is used as reference electrode and Pt wire is used as counter electrode. Two electrodes were prepared and measured with $\sim 20 \mu gPt/cm^2$ loading to generate the polarization curves.

Prior to incorporating the previously characterized catalyst layers into the GDE half-cell, the electrode preparation entailed the application of a dilute ionomer solution (0.05 wt% in IPA) onto the catalyst layer, achieving a balanced 1:1 ionomer to carbon mass ratio. Subsequently, polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) was dispensed onto the rear of the supporting layer (carbon paper). This treatment endowed the support layer with hydrophobic properties, an essential feature that boosts the overall performance of the catalyst layer.

When subjecting the prepared electrodes to the GDE half-cell under N_2 , the CV curves presented in Figure 74a displayed distinct H_{UPD} peaks for all three catalysts representing the successful loading of Pt. The double-layer capacitance aligns with that of the pristine carbon film without Pt introduction, suggesting that the integration of Pt did not significantly alter the accessibility of the nanostructures. Furthermore, Figure 74b delineates the ORR performance of the various catalyst layers, highlighting pronounced disparities in the polarization curves.

Upon analysing the figure, one can observe that the hierarchical electrode exhibits superior performance in terms of the ORR. The design of hierarchical structures, incorporating both meso- and macropores, promotes superior ion and mass transport, thereby enhancing electrochemical performance. On the other end of the spectrum, the electrode composed solely

of mesoporous structures displayed pronounced transport limitations at high current region, exhibiting the least efficient ORR activity. The mesoporous structure likely poses hindrances to ion transport and the accessibility of Pt, essential for catalysing the ORR. The restrictive nature of the mesopores, coupled with their higher length-to-diameter ratio, may slow down the diffusion process and impede effective contact with the catalyst sites.

It is noteworthy, however, that despite the substantial disparity in the polarization curves and ORR activity, all the electrodes exhibited a similar kinetics behaviour with alike onset potentials. This suggests that the same fundamental mechanisms govern the ORR in each case, but the differences in performance can be primarily attributed to transport effects within the distinct porous architectures of the carbon materials.

1.21 Summary

This research has successfully demonstrated the development of a hierarchical structure within the electrode catalyst layer, a significant advancement in the field of electrochemical energy systems. Lignin was employed as the carbon precursor to construct this hierarchical structure utilizing a dual templating strategy. The study underscores the importance of meticulous electrode architecture in achieving enhanced efficiency.

Two distinct templating techniques were employed to introduce mesoporosity (2-50 nm) and microporosity (>50 nm) into the carbon structure. The presence of mesoporous channels and macropores was confirmed through SEM and TEM images, corroborating the conclusions drawn from N₂ sorption analysis. The hierarchical materials, characterized by their bimodal porous structure, demonstrated significant potential for efficient mass transportation.

The electrochemical properties of the distinct carbon structures were examined where both the hierarchical and mesoporous-only carbon structures exhibited comparable capacitance values, while the material with a solely macroporous structure demonstrated a notably diminished capacitance. Moreover, the two materials incorporating macroporous structures exhibited outstanding capacity retention, suggesting a swift ion transport rate within the macropores. Upon eliminating the microporous surface area, a strong correlation was observed between double layer capacitance and surface area, indicating that electrochemical accessibility can be challenging for microporous structures below 2 nm.

After successfully introducing the Pt NPs as catalytic sites using a modified wet-impregnation method, performance evaluation of the catalyst layers was conducted under a GDE half-cell

configuration, highlighting the efficient mass transport capabilities facilitated by the hierarchical structure.

In conclusion, this research represents a significant contribution to the development of advanced electrode materials for electrochemical energy systems. The findings underscore the potential of a hierarchical structure in enhancing the overall efficiency and effectiveness of the catalyst layers. Future work should continue to explore and optimize these structures, with a particular focus on improving the homogeneity of the catalytic sites and enhancing the electrochemical performance.

Conclusion and Outlook

The research conducted in this thesis addresses some of the most pressing challenges in the field of PEMFC, contributing to the global effort to combat climate change through sustainable energy solutions. It has been a journey of discovery, analysis, innovation, and application, systematically identifying and tackling three critical obstacles in PEMFC catalyst layer development.

1.22 Development of a Suitable Testing Platform:

By constructing a GDE and benchmarking it against commercial electrocatalysts, this thesis has provided a robust and realistic platform for ORR measurements. This lays the foundation for future research and development in the field.

1.23 Understanding Local Transportation Dynamics:

Mesoporous carbon nanospheres, sustainably synthesized from biomass, were employed as a substrate for the deposition of Pt nanoparticles, alongside two commercial carbon supports, for comparison. Characterisation techniques like SEM, TEM, BET, ICP-MS, and XPS confirmed that disparities among these catalysts could be attributed solely to differential support porosity. The in-house synthesized ordered mesoporous carbon (HOMC) displayed the highest oxygen reduction activity when tested under a gas diffusion half-cell configuration. Operando X-ray absorption spectroscopy facilitated an understanding of ionomer coverage on the Pt surface, with insights showing distinct differences in platinum and ionomer distribution across the supports. Low surface area carbon Vulcan demonstrated sulfonate adsorption, contributing to ionomer poisoning, while high surface area carbon Ketjenblack's configuration resulted in transport limitations, explaining its inferior performance.

In contrast, the superior performance of the HOMC was explained by the strategic positioning of platinum at the entrance of the mesopores, with the ionomer in close proximity on the external surface. This arrangement optimized the interaction between Pt and Nafion™ ionomer, avoiding direct contact but maintaining accessibility of protons to Pt active sites. The findings of this study provide valuable insights into the role of support porosity in catalysis, highlighting the importance of the local environment of Pt nanoparticles within the catalysts. The innovative use of biomass-derived carbon, coupled with the nuanced understanding of catalyst structure

and performance, offers promising avenues for further research and potential applications in sustainable energy technology.

1.24 Constructing Efficient Catalyst Layer Architecture:

The thesis's development of a freestanding carbon film with a hierarchical architecture represents a leap forward in catalyst layer design. This research has successfully utilised lignin as the carbon precursor and employed a dual templating strategy to create both mesoporosity (4 nm) and macroporosity (400 nm). The study underscores the importance of meticulous electrode architecture in achieving enhanced efficiency. Both hierarchical and mesoporous-only carbon structures exhibited comparable capacitance values, while the solely macroporous structure showed diminished capacitance. However, materials incorporating macropores exhibited outstanding capacity retention, indicating swift ion transport and challenging electrochemical accessibility for microporous structures below 2 nm.

After successfully introducing Pt NPs as catalytic sites, performance evaluation of the catalyst layers highlighted the efficient mass transport capabilities facilitated by the hierarchical structure. In conclusion, these findings represent a significant advancement in the development of advanced electrode materials for electrochemical energy systems, with potential to enhance the efficiency and effectiveness of the catalyst layers. Future work should continue to explore and optimize these structures, focusing on improving the homogeneity of the catalytic sites and enhancing the electrochemical performance.

1.25 Outlook

As the world grapples with the urgency of mitigating climate change, the work presented in this thesis has timely and far-reaching implications. It not only contributes to the existing body of knowledge in PEMFC technology but also sets the stage for future advancements in several ways:

Operational Stability:

One of the foremost challenges in realizing the full potential of the nanostructured catalysts layer in PEMFCs is ensuring their operational stability, especially over extended periods of use. Central to this concern is the corrosion of carbon supports. The long-term stability of PEMFCs is compromised when carbon supports corrode, leading to decreased catalytic activity, loss of conductivity, and eventual cell failure. Thorough investigations into the mechanisms of carbon

corrosion, as well as the development of corrosion-resistant carbon materials, are essential. This would not only enhance the lifespan of the fuel cells but also improve their overall efficiency and reliability. Accelerated Stress Tests, either under the GDE configuration or within a single-layer MEA, would be valuable. Furthermore, future research that integrates ORR testing with GC for gas emission analysis will prove advantageous for understanding the oxidation of carbon.

Additionally, concerns regarding the oxidation and aggregation of the Pt NPs present another stability challenge. These concerns can be addressed through X-ray photoelectron spectroscopy in conjunction with an electrochemical cell and advanced imaging of the electrocatalysts before and after use.

Adaption of the Materials in Real PEMFC Devices:

In addition to corrosion concerns, the operational environment of PEMFCs can vary widely, especially when considering diverse applications ranging from stationary power sources to vehicular propulsion. Thus, understanding how these fuel cells perform under a spectrum of environmental conditions becomes paramount. Testing the materials in a real PEMFC device under varying humidity levels is crucial because water management within the cell directly affects proton conductivity and overall performance. Overhydration can flood the cell and obstruct the gas diffusion layers, while underhydration can diminish proton conductivity, leading to a drop in performance.

Temperature also plays a vital role. Extreme temperatures can affect the physicochemical properties of the cell components, especially the interaction between catalysts and the ionomer. As such, evaluating the materials under a wide range of temperatures will provide insights into their thermal resilience and help in designing cells that can operate optimally across different climatic conditions.

Environmental Impact and Lifecycle Assessment:

Beyond the direct benefits of employing sustainable materials, it's imperative to consider the entire lifecycle of the biomass derived catalysts supports in PEMFC. Comprehensive Life Cycle Assessments would offer insights into the environmental footprint of these systems, from raw material extraction to end-of-life disposal or recycling. This holistic view can identify further opportunities for reducing environmental impact and ensuring sustainable manufacturing processes.

In conclusion, this thesis represents a significant contribution to the field of PEMFC technology. By identifying and addressing key challenges, it offers tangible and actionable insights that can shape the future of sustainable energy. The innovations and discoveries made herein are more than academic achievements; they are vital steps towards a cleaner, more sustainable future for all. The path forward is filled with opportunity, and the work conducted in this thesis serves as both an inspiration and a guide for those committed to advancing the global pursuit of efficient, renewable energy solutions.

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