



A Review on Nature Inspired Non-precious Metal Catalyst for Oxygen Reduction Reaction in Proton Exchange Membrane Fuel Cell

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Received: 06.10.2025

Accepted: 20.12.2025

Published: 30.12.2025

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ABSTRACT

Proton exchange membrane fuel cell (PEMFC) is a promising alternative source of energy which has high efficiency and it's environmentally friendly. Commercialization of PEMFCs is hampered due to requirement of precious platinum-based catalysts for oxygen reduction reaction. Nature is a source of inspiration for developing alternative non precious metal catalyst which is highly active and durable. New catalytic materials can be designed and synthesized similar to enzyme oxygen reduction reaction (ORR) catalyst found in nature. These non-precious metal catalysts (NPMC) may help to reduce cost of the PEMFC. This review provides discussion on advancements in development of non-precious metal catalysts over the last decade. Nature inspired ORR catalyst involves transition metals coordinated with nitrogen rich ligand. Tremendous research work carried out in last few decades resulted in development of various non-precious metal catalysts with high activity and stability approaching closer to Pt group metals. These catalysts demonstrate significant promise as replacements for Pt-based catalysts in fuel cells. But their practical implementation in fuel cells is challenging due to the issues related to stability, activity, and integration. This review analyses various synthesis methods, electrochemical performance and future challenges in the development of catalysts for ORR.

Keywords: Electrocatalyst; Fuel cell; Oxygen reduction reaction; Renewable energy.

1. INTRODUCTION

The global demand for energy has been soaring, driven by population growth, industrialization, and technological advancements. Reliance on fossil fuels comes with numerous drawbacks, including environmental degradation and finite resources. This necessitates the exploration of alternative sources of energy which are more sustainable. Fuel cells, particularly proton exchange membrane fuel cells (PEMFC), have emerged as a promising alternative. PEMFC is a highly efficient electrochemical energy conversion device. It converts the chemical energy of a fuel into electrical energy. It offers many advantages. One of their significant advantages is its capability to function efficiently at relatively low temperatures. PEMFC operates at temperatures typically between 60°C and 80°C. This low-temperature operation leads to several benefits such as quick start up and safety. PEMFC can be used in wide range of potential applications. It can be used in small scale portable application or large stationary power systems. It has very high energy conversion efficiency. This results in contribution to overall energy savings. Another advantage of PEMFC is that, it produces electricity with lower emissions. This helps to mitigate environmental pollution and climate

change. Despite these advantages, there are still some challenges that need to be addressed. These challenges are in terms of cost, durability, and scalability to achieve widespread adoption of PEMFC technology.

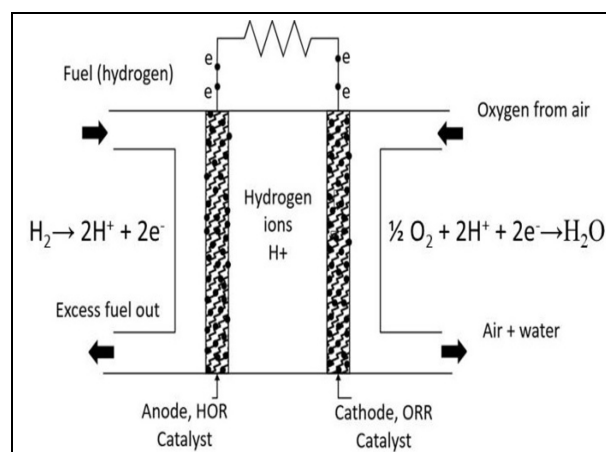


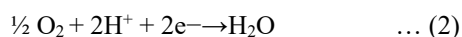
Fig. 1: Schematic Diagram of Fuel Cell

Ongoing research and development work is dedicated to enhance the performance and decreasing the cost of PEMFCs, making them even more competitive with conventional energy sources. Continued innovation

and investment in fuel cell technology are essential to realizing its full potential as a sustainable energy solution for the future. In proton exchange membrane fuel cells (PEMFCs), the fundamental reactions at the anode and cathode are indeed critical to their operation and efficiency. At the anode, hydrogen gas (H_2) is oxidized to produce protons (H^+) and electrons (e^-):



The protons move through the proton-conducting polymer membrane towards the cathode. The electrons travel through an external circuit as shown in Fig. 1. This creates an electric current that can be passed through the load in external circuit to accomplish various tasks. At the cathode, oxygen gas (O_2) is reduced by gaining electrons from the external circuit and combining with protons to form water (H_2O):



The presence of a catalyst is essential to facilitate these reactions. Catalysts lower the activation energy barriers, making the reactions proceed at practical rates producing sufficient current and power at normal temperature and pressure. Platinum (Pt) is the most effective catalyst for the hydrogen oxidation reaction (HOR) at the anode. It is also used as catalyst for oxygen reduction reaction (ORR) at the cathode. However, there are important differences in the way these reactions proceed.

The kinetics of hydrogen oxidation reaction (HOR) on Pt is relatively fast. HOR can take place efficiently in presence of lower catalyst loading. The kinetics of oxygen reduction reaction on Pt is considerably slower than HOR (Gómez-Marín *et al.* 2014). This sluggishness of ORR leads to the requirement of a much higher loading of platinum at the cathode to achieve acceptable reaction rates. Acceptable reaction rates sustain $0.5-1 \text{ A cm}^{-2}$ at cell voltage greater than or equal to 0.6 V (Cai *et al.* 2024). Several challenges emerge due to the use of platinum in PEMFCs. Platinum is an expensive metal, hence overall cost of PEMFCs increases tremendously. Since it is a rare element, it gives rise to problems about the sustainability and scalability of using it in large-scale applications. On-going research and development work is aimed at overcoming these challenges by reducing platinum loading or developing non precious metal catalyst. Platinum loading can be reduced by using platinum nanostructures. Another solution is to develop more effective catalyst supports. On-going research is also focused on improving catalyst performance and exploring alternative materials for commercializing PEMFC technology for widespread use. Developing highly active and stable electrocatalyst for PEMFC is a difficult task. The activity and stability issues of non-precious metal catalyst (NPMC) resulted in designing

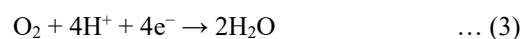
more sophisticated catalyst materials. Inspiration for the designing of highly durable and active NPMC can be obtained from nature. Drawing inspiration from nature and classical ORR catalysts, one can design new catalytic materials that incorporate key features found in enzyme ORR catalysts. Enzymes naturally excel in managing the ORR through various sophisticated strategies. These strategies include use of electron-donating functional groups, maintaining the appropriate separation of active sites, and employing a coordinatively unsaturated transition metal sites. By mimicking these strategies, it is possible to develop efficient and durable catalysts for practical applications.

2. ELECTROCATALYST IN PEMFC

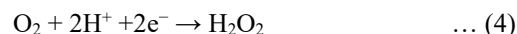
To be effective in PEMFCs, an electro catalyst must meet several criteria. The catalyst must exhibit high activity for the ORR to ensure efficient energy conversion. It must maintain its performance over a long period, resisting degradation in the harsh fuel cell environment. Efficient charge transfer is essential for the catalyst to operate effectively within the fuel cell. The catalyst should be inexpensive to produce and scalable for commercial applications. The search for non-precious metal catalysts (NPMCs) satisfying these criteria will replace platinum for the ORR in proton exchange membrane fuel cells (PEMFCs). Research efforts are driven by the need to reduce costs and overcome the limitations associated with platinum scarcity.

In the ORR, oxygen can be reduced via two primary pathways:

4-Electron Reduction Pathway: This pathway reduces oxygen directly to water (H_2O) and is preferred because it is more efficient and yields a higher energy output.



2-Electron Reduction Pathway: This pathway partially reduces oxygen to hydrogen peroxide (H_2O_2), which is less efficient and can be detrimental to the fuel cell components.



The substantial activation overpotential required for the ORR at the cathode significantly contributes to efficiency losses in PEMFCs. Overpotential is the extra voltage required beyond the theoretical potential to drive the reaction at a desired current density. Reducing this overpotential is important for enhancing the overall efficiency of PEMFC. To reduce the overpotential and enhance ORR performance, several strategies are employed. One way is to enhance the active site density and optimizing the electronic structure of the catalysts to enhance their intrinsic activity. Nanostructured catalysts tend to increase the

surface area and enhance the exposure of active sites. Hence creating nanostructured catalysts with a high concentration of active sites and large surface area is a key strategy to enhance catalytic activity. Nanostructures, such as nanoparticles, nanowires, and nanosheets, provide more exposed active sites and facilitate better mass transport.

Other approach is to develop advanced support materials that will enhance the dispersion and stability of the active catalyst particles. Combining non-precious metal catalysts with other materials can enhance their performance. For instance, integrating metal oxides, carbon-based materials such as graphene or CNTs, and conducting polymers can improve activity, stability, and conductivity (Tavakkoli *et al.* 2020). These structures consist of a core material (often a cheaper metal or alloy) coated with a thin shell of an active catalytic material. This structure helps to optimize the utilization of expensive noble metals. Development of nanostructured catalysts with high surface areas as well as high concentration of active sites are some of the innovations in catalysts synthesis. Techniques such as atomic layer deposition and various chemical synthesis routes are used to synthesize these structures. Hierarchical structures with multi-level porosity further improve mass transport and accessibility to active sites. Composites of metal phthalocyanines and other materials, such as carbon nanotubes, graphene, or metal oxides, help to create catalysts with superior performance. It is observed that, the synergistic effects between different materials in these composites results in enhancement of ORR activity, conductivity, and durability.

Metal-Nitrogen-Carbon (M-N-C) catalysts typically composed of transition metals such as Fe or Co coordinated with nitrogen and embedded in a carbon matrix. These catalysts illustrate significant potential in promoting the 4-electron reduction pathway. Certain metal oxides (e.g., manganese oxides) and metal phosphides have been studied for their ORR activity and stability (Yin *et al.* 2021) (Parra-Puerto *et al.* 2019). Significant research is already carried out in order to develop catalysts based on non-precious metals such as iron (Fe), cobalt (Co) and nickel (Ni) etc. These transition metals are more abundant and less expensive than platinum. Advanced characterization techniques (e.g., X-ray absorption spectroscopy, TEM) further provide insights into the structure and function of NPMCs at the atomic level. Computational modelling and theoretical studies will throw light on the ORR mechanism of these catalysts. This will further help in the design of more efficient and stable catalysts. Researchers are focusing on developing catalysts that facilitate the 4-electron reduction pathway of O_2 to H_2O , which will reduce the overpotential. It will enhance the overall efficiency of fuel cells. Continued advancements in catalyst design and novel materials in addition to mechanistic details are essential in case of fuel cell.

2.1 Biological Electro-catalysts in Nature

As observed in nature, transition metal macrocycles play an important role in biological systems in oxygen reduction reactions (ORR). It offers a promising approach for developing non-precious metal catalysts for PEMFCs. These macrocycles imitate the active sites for ORR found in natural enzymes. These compounds have shown potential in catalyzing ORR with high activity and durability.

Cytochrome c oxidase (CcO) is a thoroughly studied enzyme for its ORR mechanism (Yoshikawa and Shimada, 2015). It is known that it has the ability to catalyse the four-electron oxygen reduction reaction at very low overpotential (Pedram *et al.* 2021). It is located in the mitochondrial respiratory chain. CcO's active site comprises an iron (II)-porphyrin complex, also known as heme as shown in Fig. 2, it is bonded with copper centers. The sophisticated structure and high efficiency of CcO can become an excellent model for synthesizing bio-inspired, non-precious metal catalysts for PEMFCs. The active site of CcO comprises an iron (II)-porphyrin (heme) complex and a distal copper center. These two work cooperatively to efficiently reduce oxygen to water (Pedram *et al.* 2021). Heme-Copper Oxidase complex helps in the transfer of electrons and protons to oxygen. This reduces the formation of partially reduced oxygen species and enabling complete reduction to water. CcO act as catalyst for the ORR by accepting electrons from cytochrome c and transferring them to the oxygen molecule. Protons are simultaneously transferred to the

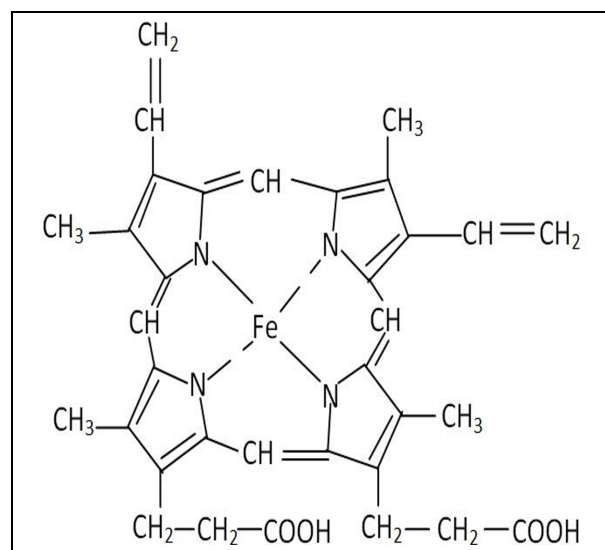


Fig. 2: Structure of heme complex

active site. It enables the reduction of oxygen to water. The enzyme operates at a very low overpotential, showcasing its highly efficient catalytic mechanism.

One principle for designing nature-Inspired ORR Catalysts is replicating the structure of heme with

iron or other transition metals coordinated within a nitrogen-rich ligand framework. Copper centres similar to those in CcO to facilitate efficient electron and proton transfer can also be considered. One has to ensure that the ligand framework is both chemically stable and electronically conductive, facilitating effective electron transport to the active sites. Fine-tuning the coordination of metal centers within the ligand has to be carried out to optimize the ORR activity and reduce overpotential.

It is possible to develop efficient and durable catalysts for practical applications by imitating enzyme structure. Enzymes use electron-donating groups to stabilize reaction intermediates and prevent the formation and release of harmful partially reduced oxygen species, such as superoxide or peroxide (Proshlyakov *et al.* 2000) (Grumelli *et al.* 2013). These functional groups play crucial role in smooth electron transfer during the ORR, ensuring efficient conversion to water. Bulky protein chains in enzymes keep the ORR active sites well-separated. This prevents active site overlap and potential catalytic deactivation due to site interference. This spatial separation is important for maintaining high catalytic efficiency and stability over time. Enzymatic active sites often involve first-row transition metals (e.g., iron, copper) that have coordinatively unsaturated sites, which are highly reactive and play a key role in catalytic transformations. These unsaturated sites enable strong adsorption of oxygen molecules and facilitate their reduction.

3. NATURE INSPIRED M-N-C ELECTROCATALYST FOR ORR IN FUEL CELL

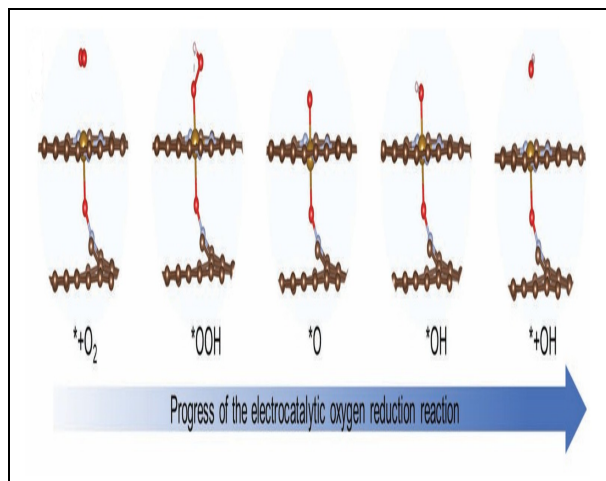


Fig. 3: Proposed ORR mechanism on FeN₄-O active site after DFT calculations (Peng *et al.* 2022). (figure reproduced from Peng *et al. advanced materials*, 2022, 34, 2202544, licensed under a creative commons attribution 4.0 international license)

The development of efficient and durable ORR catalysts for PEMFC remains a significant challenge due to the complexity of the ORR mechanism and the inherent limitations of alternative catalysts.

While nature-inspired non-precious metal catalysts offer a promising direction, several obstacles need to be addressed to achieve practical and commercial viability. The ORR involves multiple proton and electron transfer steps, which can proceed via two main pathways: the 4-electron pathway giving water and the 2-electron pathway leading to hydrogen peroxide formation. Understanding and optimizing these pathways at the atomic level is challenging due to the intermediate species and potential side reactions involved. As reported by Lishan Peng *et al.*, novel interface engineering was used to construct Fe-C-N catalyst (Peng *et al.* 2022). In catalyst synthesized, Fe-N₄ sites were modified by axial Fe-O bonds. Density functional theory calculations suggested that FeN₄-O structure offers lower energy and more selective 4 electrons ORR pathway as compared to FeN₄ sites. The progress of ORR with intermediates is shown in Fig. 3.

Many non-precious metal catalysts (NPMCs) often suffer from poor stability under fuel cell operating conditions, such as high potential, acidic environment, and prolonged use. Non-precious metal catalysts can be sensitive to changes in temperature and pH. It affects their performance and limiting their applicability in various environments. In the last five decades there have been significant advancements in the development of NPMCs for the ORR. These advancements have led to novel catalysts and innovative synthesis techniques. It aims to improve the efficiency and durability of catalysts for PEMFC. Transition metal macrocycles are inspired by biological systems where they function as efficient catalysts for ORR. Examples of such transition metal macrocycles are metal porphyrins and phthalocyanines. These macrocycles consist of a central metal ion coordinated to nitrogen atoms in a large ring-like structure. These macrocycles imitate the natural catalytic sites found in enzymes like cytochrome c oxidase and haemoglobin. These catalytic sites are highly efficient at reducing oxygen. Macrocycles can be synthesized with various transition metals (e.g., iron, cobalt, nickel) to optimize their catalytic properties. Transition metal macrocycles have shown promising activity and selectivity for the 4-electron reduction pathway of O₂ to H₂O, which is desirable for efficient ORR (Bhunia *et al.* 2018). They can be engineered to enhance their stability under fuel cell operating conditions. Iron porphyrins and cobalt phthalocyanines (Fig. 4) have been studied in detail. These catalysts can be modified to improve ORR performance. Modification is carried out by incorporating electron-donating or withdrawing groups to tune their electronic properties. Cobalt phthalocyanines (CoPc) are also similarly modified, where cobalt centers are embedded in a conjugated nitrogen ring system. These catalysts have been investigated for their ability to catalyze the ORR with high efficiency, benefiting from the electronic properties of the phthalocyanine ligand. Additional improvement in the activity and stability of transition metal macrocycles

is achieved by supporting them on high-surface-area carbon materials (Liu *et al.* 2016). This approach improves the dispersion of the active sites and improves the overall conductivity of the catalyst. Combining transition metal macrocycles with other materials, such as metal oxides or nitrogen-doped carbons, can create synergistic effects. It leads to higher ORR activity and durability. Using organic molecules with carefully designed molecular backbones allows for precise control over the coordination environment of the transition metal centers. Examples include macrocycles, such as porphyrins and phthalocyanines, or simpler nitrogen-containing molecules like pyridine derivatives. Incorporating functional groups that can donate electrons and stabilize intermediates (e.g., amine, hydroxyl, and carboxyl groups) enhances the catalytic performance (Navalon *et al.* 2017). Functional groups can be strategically placed to mimic the natural electron-donating groups found in enzymes.

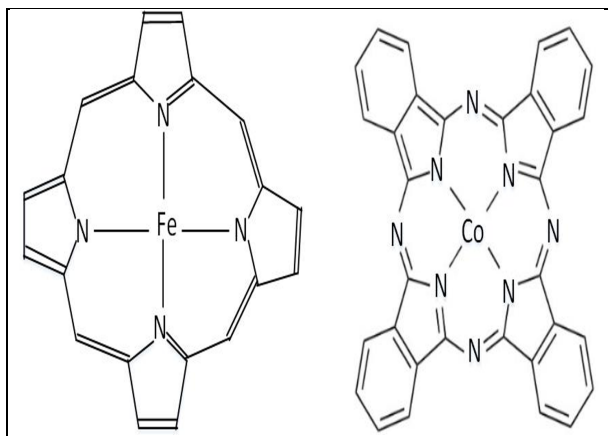


Fig. 4: Iron porphyrin and cobalt phthalocyanine structure

Nature inspired catalyst, mimicking CcO often use transition metals such as iron and copper. These transition metals are coordinated with nitrogen-containing ligands which creates structure similar to enzyme. These catalysts very often utilize porphyrin-like structures or other nitrogen-rich ligands. It helps to stabilize the metal centers and create a favourable chemical environment for ORR. Role of nitrogen atoms in the ligands is to coordinate with the metal centres to enhance the catalytic activity and stability of the catalysts (Wang *et al.* 2018). Commonly used ligands include porphyrins, phthalocyanines, and other macrocyclic compounds. These compounds provide a stable framework for the transition metals. Despite the promise of transition metal macrocycles, there are several challenges which need to be overcome. Traditional macrocyclic compounds like metal phthalocyanines and porphyrins are effective for ORR but the disadvantage of macrocyclic compounds is that these are expensive and complex to synthesize. Further optimization of the macrocycle structure and the choice of central metal ion is necessary to improve ORR activity and durability. It is

necessary to develop cost-effective and scalable synthesis methods for these macrocycles. Further, it has to be confirmed that these catalysts maintain high performance under the practical operating conditions of PEMFCs. It includes varying temperatures, humidity, and potential cycling. Researchers have found that small molecular precursors, such as simple organic molecules containing nitrogen, can be used to achieve similar catalytic properties. Use of these molecules will significantly reduce the cost and complexity of catalyst synthesis. These catalysts can be designed to promote the 4-electron reduction pathway efficiently. These catalysts incorporate transition metals (like Fe, Co) coordinated with nitrogen within a carbon matrix. These have shown promise in enhancing ORR activity and stability. There are many advantages of using small molecular precursors. Small molecular precursors are often more readily available and easier to handle as compared to complex macrocyclic compounds. This will make the synthesis process more scalable and suitable for industrial applications. The use of small molecular precursors allows for greater flexibility in modifying the nitrogen content and dispersion within the carbon matrix. This enables fine-tuning of the catalyst properties to optimize ORR performance. Use of these catalysts instead of expensive macrocyclic compounds will significantly reduce the overall cost of catalyst production, making NPMCs more economically viable for large-scale fuel cell applications.

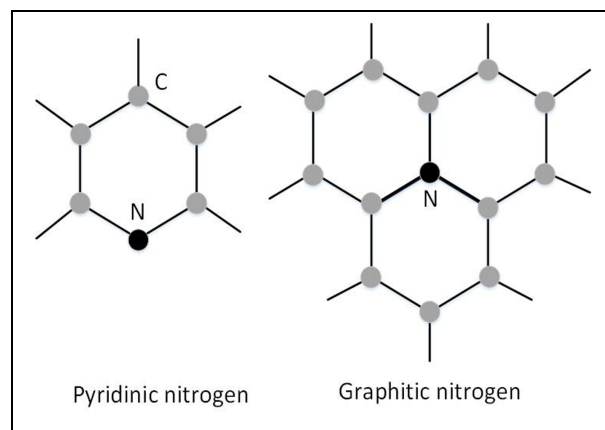


Fig. 5: Pyridinic N and graphitic N structure

The replacement of expensive macrocyclic compounds with small molecular precursors has been a major advancement in the development of non-precious metal catalysts for the ORR. Important nitrogen functionalities, notably pyridinic-N and graphitic-N (Fig. 5), have been identified as crucial for forming active sites that enhance the catalytic performance. This approach reduces the cost and complexity of catalyst synthesis and also allows for greater flexibility and scalability, paving the way for the broader adoption of NPMCs in fuel cells. There is important role of nitrogen Functionalities in NPMCs. In Pyridinic-N type, nitrogen atoms bonded

to two carbon atoms at the edge of graphene layers (analogous to nitrogen in a pyridine ring Fig. 4) play a crucial role in forming active sites. Pyridinic-N is known to enhance the ORR activity by facilitating the binding of oxygen molecules and promoting electron transfer. In graphitic-N, nitrogen atoms incorporated within the graphene plane (analogous to nitrogen in a graphite lattice) contribute to the overall electronic structure of the catalyst, enhancing conductivity and stability. Graphitic-N can improve the electron density around the active sites, boosting the ORR performance. The combination of pyridinic-N and graphitic-N creates a synergistic effect, where the different types of nitrogen functionalities complement each other, enhancing both the catalytic activity and durability of the NPMCs. Carbon support materials can enhance the dispersion of active sites and provide structural stability. Nitrogen-doped carbons, carbon nanofibers, and other conductive supports are being explored to enhance the performance of NPMCs. Advanced characterization techniques and computational modeling (e.g., density functional theory) are crucial for understanding the ORR mechanism and guiding the design of better catalysts. This investigation help identify the nature of active sites, reaction intermediates, and the role of various catalyst components in the ORR process. Synthesis of advanced materials and a thorough knowledge of ORR pathways will be a key to realizing the full potential of these novel catalysts in sustainable energy applications.

Transition metals are used as the central active sites in M-N-C catalysts. Most commonly used transition metals are Iron (Fe) and cobalt (Co). These metals are chosen due to their ability to facilitate the transfer of electrons and protons during the ORR. It is similar to the function of metalloproteins in biological systems. The transition metal centers are embedded within ligands that contain strongly conjugated nitrogen ring systems. Such systems are similar to porphyrins, phthalocyanines, and related macrocycles. These systems provide a stable chemical environment and support efficient electron transfer. It is crucial for catalytic activity. Bio-inspired catalysts for the ORR typically feature transition metal centers situated within chemically stable and electronically conducting ligands. These ligands often take the form of strongly conjugated nitrogen ring systems. These are designed to emulate the active sites found in natural enzymes. Such designs aim to balance the reactivity and stability requirements necessary for efficient catalysis. It helps to bridge the gap between theoretical predictions and experimental performance.

There are various advantages of nature inspired catalyst designs. These systems are chemically stable due to Conjugated nitrogen ring systems. It resists degradation under the harsh conditions of fuel cell operation such as acidic environment and high potential. Stability improvement is achieved due to the strong coordination between the metal centres and the nitrogen

atoms in the ligand structure. The extended π -conjugation in these nitrogen ring systems improves electronic conductivity to facilitate efficient charge movement to and from the active sites (Deng *et al.* 2017). This conductivity improvement maintains high catalytic activity and efficient fuel cell performance. The reactivity of metal centre is managed by the specific chemical environment provided by the nitrogen ligands. It ensures that the ORR proceeds via the desired 4-electron reduction pathway to produce water, rather than the less efficient 2-electron pathway leading to hydrogen peroxide. Nature inspired catalysts design is supported by theoretical studies, such as density functional theory (DFT) calculations. These studies predict the electronic structure and chemical activity of different catalyst configurations. It also gives optimal combinations of metal centres and ligand structures that should exhibit high ORR activity and stability. These theoretical predictions can be validated by synthesizing these catalysts and testing its performance in laboratory. Various characterization techniques such as X-ray absorption spectroscopy, electron microscopy, and electrochemical testing are used to characterize the catalysts and evaluate their performance. Insights gained from experimental data can be used to further refine theoretical models. It leads to the development of efficient and durable catalysts. In this iron atoms are coordinated with nitrogen within a carbon matrix. These catalysts utilize the stability as well as conductivity of the carbon support and the catalytic activity of the Fe-N sites. Extensive research has been focused on optimizing the synthesis conditions to increase activity. Parameters such as pyrolysis temperature and precursor composition are optimized to maximize the ORR activity and durability of Fe-N-C catalysts.

Bio-inspired catalysts for ORR are based on transition metal within strongly conjugated nitrogen ring systems. These catalysts offer a promising approach in achieving high activity, stability, and electronic conductivity. These are designed to control the reactivity of the catalytic process effectively, taking advantage of their chemical and electronic structures. The interplay between theoretical modelling and experimental validation is crucial in optimizing these catalysts. It makes them viable alternatives to precious metal-based catalysts in fuel cell applications. Continued research in this area aims to refine these designs further, enhancing their performance. This will bring them closer to commercial viability. Transition metals such as iron and cobalt can be coordinated with the organic ligands and anchored on conductive surfaces like carbon supports. Metal clusters can also be used to increase the number of active sites. It enhances catalytic activity through cooperative effects. There can be various synthesis strategies for non-precious metal catalyst. One way would be to synthesize organic ligands with desired functional groups that can effectively coordinate transition metals. Use techniques such as pyrolysis to

convert these molecular precursors into active NPMCs. One has to ensure proper integration of metal centres and functional groups into a stable carbon matrix. Another way is to functionalize conductive supports (e.g., carbon nanotubes, graphene) with organic ligands to create a platform for anchoring transition metals. Employ surface modification methods to enhance the interaction between the metal centers and the support, improving overall stability and activity. One more way could be fine-tune the coordination environment around the metal centers by adjusting ligand structures, pyrolysis conditions, and metal loading. Ensure the presence of coordinatively unsaturated sites that are important for high catalytic reactivity. Fe-N-C catalyst is already designed and synthesized using above strategies. Fe-N-C catalysts were designed using pyridinic and graphitic nitrogen as part of the carbon matrix to coordinate iron atoms. These catalysts were synthesized using a mixture of iron salts and nitrogen-containing organic precursors (e.g., melamine) on a carbon support (Ge *et al.* 2023). Functionalization was carried out by incorporating electron-donating groups to stabilize reaction intermediates and enhance ORR performance.

4. DEVELOPMENT OF FE/N/C ELECTROCATALYST

Non-precious metal catalysts (NPMCs) used in proton exchange membrane fuel cells (PEMFCs) encompass a range of materials designed to replace the expensive platinum group metals traditionally used.

4.1 Transition Metal Macrocyces

Synthesis of non-precious metal catalysts (NPMCs) based on macrocycles involves the preparation of catalysts using transition metal macrocyclic compounds. In this case, metal phthalocyanines and porphyrins, are used to coordinate with transition metals. These materials mimic the active sites of natural enzyme. It aims to enhance the ORR activity in proton exchange membrane fuel cells (PEMFCs). Transition metal macrocycles, such as metal phthalocyanines and porphyrins, are complexes where transition metals are coordinated with large, planar, nitrogen-containing ligands.

The pioneering work of Jasinski of using cobalt phthalocyanine marked a significant milestone in the development of non-precious metal catalysts (NPMCs) for ORR (Jasinski, 1964). Following this work, many transition metal macrocyclic N4-complexes were studied. For example porphyrins and phthalocyanines etc, were investigated for their electrocatalytic activity toward ORR. Among these, iron (Fe) and cobalt (Co) macrocyclic complexes have been extensively studied as promising candidates to replace expensive platinum (Pt) catalysts in polymer electrolyte membrane (PEM) fuel cells. These complexes have shown the highest

electrocatalytic activity. Iron Phthalocyanine (FePc) facilitates the ORR via a four-electron process but suffers from poor stability. Cobalt Phthalocyanine (CoPc) shows good electrochemical stability. But it tends to favor a two-electron pathway, producing hydrogen peroxide (H_2O_2), which is less desirable (Chen *et al.* 2014). In, (Jahnke *et al.* 1976) reported that pyrolysis at high temperatures enhances ORR activity of metal macrocycles (Jahnke *et al.* 1976). The following year, Bagotzky *et al.* furthered this research by demonstrating the pyrolysis of cobalt macrocycles impregnated on active carbon at 800–900°C in an inert atmosphere (Bagotzky *et al.* 1978). This work paved the way for the development of heat-treated Me/N/C (metal/nitrogen/carbon) catalysts, which have become a critical area of study in the pursuit of cost-effective and efficient catalysts for fuel cell applications.

To overcome the inherent drawbacks of macrocyclic compounds and make them viable as cathode catalysts in PEMFCs, researchers are focusing on developing methods to improve the durability of these materials, such as modifying the ligand structure or incorporating stabilizing agents. Focus is also on designing new macrocyclic compounds or composites that can achieve higher catalytic activity. High-temperature pyrolysis method is also used to create more stable and active metal-nitrogen-carbon (Me/N/C) catalysts. The development of advanced synthesis techniques and a deeper understanding of the relationship between structure and catalytic performance are essential for advancing the application of macrocyclic materials in PEMFCs. Liu *et al.* synthesized iron (II) phthalocyanine graphene composite as an efficient non precious metal catalyst for ORR. It was observed that the new composite was highly efficient because of its high conductivity and synergistic effect between iron(II) phthalocyanine and grapheme (Liu *et al.* 2013). Metal phthalocyanines, such as iron phthalocyanine (FePc) and cobalt phthalocyanine (CoPc), have been identified as effective catalysts for ORR. These macrocyclic compounds exhibit catalytic properties due to the presence of a metal center coordinated with nitrogen atoms, which can facilitate the reduction of oxygen.

The catalytic activity and stability of N4-chelates in acidic media can be significantly enhanced through thermal pretreatment in an inert gas atmosphere, such as argon (Song *et al.* 2020). This process, known as heat treatment, has gained substantial research interest and is considered an effective method for improving the catalytic performance of transition metal macrocyclic compounds. Pyrolysis at 500–700°C is optimal for achieving the highest catalytic activity of N4-chelates (Bron *et al.* 2002)(Song *et al.* 2020) (Faubert *et al.* 1996). For stable catalytic performance in PEMFCs, a temperature of around 800°C is required. Temperatures above 1000°C lead to a reduction in stability and activity. This is due to the formation and growth of metal particles

and a reduction in the nitrogen content on the catalyst surface (Li *et al.* 2010). Heat treatment enhances the dispersity of coordination compounds. It boosts catalytic activity by increasing the availability of active sites. During heat treatment, macrocyclic compounds may undergo polymerization. It results in maximum catalytic activity at lower temperatures (500–700°C). The heat treatment process facilitates the formation of metal-nitrogen (M–N₄) groups, which are known to be highly active and stable for ORR (Song *et al.* 2020). These groups are crucial for both the catalytic activity and long-term stability of the catalysts.

4.2 Metal-Nitrogen-Carbon (M–N–C) Catalysts

Non-pyrolyzed and pyrolyzed transition metal macrocyclic compounds demonstrate impressive oxygen reduction reaction (ORR) electrocatalytic activities. They also have several inherent challenges that limit their further development and practical application in PEM fuel cells (PEMFCs). The synthesis of these compounds involves expensive materials and complex procedures. It leads to higher overall costs. The multi-step processes required for synthesizing and activating these catalysts are intricate and challenging to scale up for commercial production. These compounds generally exhibit lower catalytic activity and stability in the acidic environments typical of PEMFCs. It is a significant drawback compared to platinum-based catalysts. To address the issues with catalysts based on macrocycles, researchers have focused on preparing metal-nitrogen-carbon (M–N_x–C) catalysts. It is synthesized using the pyrolysis of mixtures containing metal salts, nitrogen sources, and carbon supports under high-temperature conditions and specific gas atmospheres. Use of abundant and inexpensive transition metals (such as Fe, Co) and nitrogen sources can significantly reduce costs compared to noble metal catalysts. The preparation process, although involving high temperatures, can be streamlined into fewer steps, making it more scalable and feasible for large-scale production. Li *et al.* prepared atomically dispersed Fe–N–P–C catalyst using impregnate-pyrolysis method (Li *et al.* 2021). Carbon support stabilize the single Fe ions and dispersed them atomically during the pyrolysis process. Carbon was derived from phosphorous tri-doped wood briquettes. TEM image of the catalyst is shown in Fig. 6. Aberration corrected HAADF-STEM images of the catalyst and corresponding element mappings C, N, P and Fe are shown in Fig. 7. Uniformly distributed C and N and presence of Fe and P were easily verified by the images. Properly optimized pyrolysis conditions can lead to the formation of highly active and stable catalytic sites within the carbon matrix, improving performance in acidic electrolytes.

In M–N–C catalyst, active site is formed by metal atoms coordinated with nitrogen in a carbon matrix. Fe–N–C and Co–N–C are most widely studied NPMCs. Non-Nobel metal catalysts are usually obtained

by pyrolyzing transition metal and nitrogen precursors at high temperature which get adsorbed on carbon support. The synthesis of metal-nitrogen-carbon (M–N–C) catalysts involves three essential elements: carbon (C), nitrogen (N), and a transition metal (M).

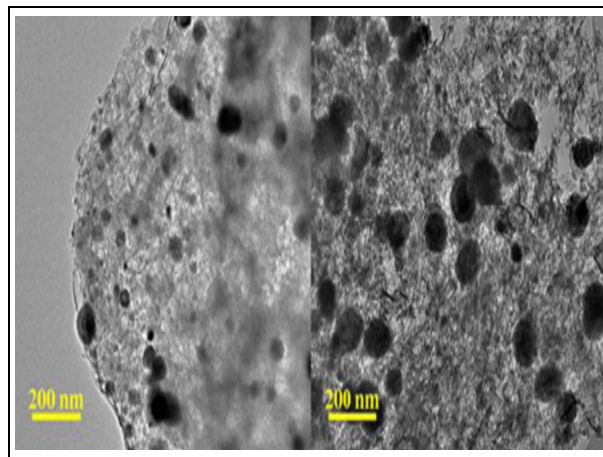


Fig. 6: TEM image of atomically dispersed Fe–N–P–C catalyst. (Li *et al.* 2021) (figure reproduced from Li *et al.* journal of energy chemistry, 2021, 55, 572–579, licensed under a creative common attribution 4.0 international license)

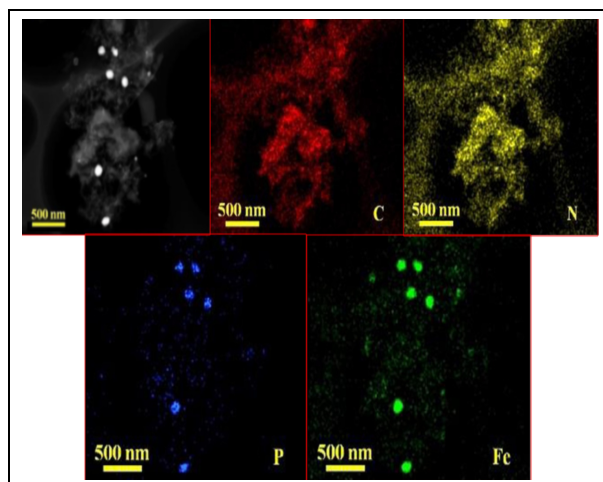


Fig. 7: HAADF-STEM Image of the Catalyst and Corresponding Element Mappings C, N, P and Fe. (Li *et al.* 2021) (Figure Reproduced from Li *et al.*, Journal of Energy Chemistry, 2021, 55, 572–579, licensed under a Creative Commons Attribution 4.0 International License)

These elements are typically derived from separate precursors. NH₃ is the primary nitrogen-containing gaseous precursor used in the pyrolysis process. It can either be the sole nitrogen source or used in combination with other nitrogen-containing molecules. Flowing NH₃ during pyrolysis is found to enhance catalyst activity. NH₃ aids in creating more micropores within the carbon matrix (Tran *et al.* 2018). The NH₃ content in the gas mixture during pyrolysis affects the incorporation levels of nitrogen and metal into

the carbon matrix. NH_3 can increase the incorporation of nitrogen into the carbon matrix, thereby enhancing the ORR activity of the catalyst (Meng *et al.* 2010). During the pyrolysis process, small molecular precursors containing nitrogen and carbon decompose and recombine to form the desired nitrogen-doped carbon structures. Transition metals (such as iron or cobalt) can be introduced during the synthesis to create metal-nitrogen-carbon (M-N-C) structures, which are critical for ORR activity. Transition metal salts are very often used as precursors. Most commonly used salts are chlorides, nitrates, sulfates, and acetates. Different metal salts can affect the final properties of the catalyst (Osmieri, 2019). For instance, chlorides and nitrates are effective in creating a uniform distribution of metal ions, whereas sulphates and acetates can produce different morphological and electronic properties of the catalyst (Woo *et al.* 2018). Carbon black, multiwall carbon nanotubes (MWCNTs), and graphitic carbons are commonly used carbon sources. These materials provide the necessary carbon matrix that supports the metal-nitrogen coordination sites. The choice of carbon source can impact the surface area, porosity, and overall structure of the catalyst. Carbon black provides a high surface area, while nanotubes and graphitic carbons offer excellent electrical conductivity and structural stability. The synthesis of M-N-C catalysts for PEMFCs involves carefully selecting and combining nitrogen, metal, and carbon precursors. By optimizing these precursors and the synthesis process, researchers aim to develop high-performance, durable, and cost-effective M-N-C catalysts that can compete with platinum-based counterparts. The effectiveness of M-N-C catalysts in catalyzing the oxygen reduction reaction (ORR) is largely determined by the nature and configuration of the active sites, which are typically metal-nitrogen (Me-Nx) complexes embedded within the carbon matrix.

Preparation of M-NxC Catalysts

Metals like Fe and Co are most commonly used due to their high ORR activity. Nitrogen atoms are essential for creating active sites by coordinating with the metal atoms. The carbon matrix provides a high surface area, electrical conductivity, and structural support. Researchers have developed various methods to prepare M-N-C catalysts by processing mixtures of individual metal salts, nitrogen sources, and carbon supports under high temperatures with specific gas atmospheres. In 1989, it was discovered that for the synthesis of M-N-C catalysts separate precursors of metal, nitrogen, and carbon can be used. These precursors after pyrolysis yield M-N-C catalysts. It opened the way to the use of various nitrogen compounds (Gupta *et al.* 1989). Lalande *et al.* reported novel catalysts synthesized using polyvinylferrocene (N-free) and carbon black. It was pyrolyzed in argon and then acetonitrile (Lalande *et al.* 1997). The catalyst demonstrated activity only after chemical vapor deposition (CVD) in acetonitrile. This

illustrates that simultaneous presence of metal and nitrogen during pyrolysis is essential for the catalytic activity. The 2008 work by Wood *et al.* involved heat treatment of nitro-aniline monomers and iron salt in inert atmosphere, followed by pyrolysis in NH_3 (Wood *et al.* 2008). This approach showed measurable current density, marking significant progress in Fe/N/C catalysts. Zelenay's group investigated polyaniline (PANI) as a dual carbon and nitrogen precursor (Wu *et al.* 2011)(Ferrandon *et al.* 2012). Their synthesis involved various steps. First aniline monomer was mixed with electron-conductive support high surface area carbon. Then addition of a metal salt and ammonium peroxydisulfate (APS). After polymerization first pyrolysis was carried out in 400–1000°C in N_2 atmosphere. Followed by acid leaching and again pyrolysis in N_2 atmosphere. Iron (Fe) and cobalt (Co) are the most promising metals for NPMC synthesis due to their abundance, low cost, and favourable catalytic properties. Fe-N-C and Co-N-C catalysts, where iron or cobalt is coordinated with nitrogen within a carbon matrix, have shown significant potential in ORR applications.

The development of advanced synthesis techniques, such as the polymeric approach and pyrolysis of metal, nitrogen, and carbon precursors, has led to significant improvements in their catalytic activity and stability. However, challenges such as complex fabrication, and lower performance in acidic environments remain, necessitating on-going research and optimization.

4.3 Zeolitic Imidazolate Frameworks (ZIFs)

Liu's group was pioneering in recognizing the potential of Metal-Organic Frameworks (MOFs) for the synthesis of metal-nitrogen-carbon (Me/N/C) catalysts. These MOFs offer several advantages for creating highly efficient ORR catalysts (Ma *et al.* 2011)(Goenaga *et al.* 2010). There are many advantages of using MOFs for Me/N/C Catalyst Synthesis. MOFs, especially Fe- or Co-based ones, provide a high density of metal-nitrogen (MeNx) active sites. The precursor's coordination chemistry can be precisely controlled before pyrolysis, ensuring optimal dispersion of metal centers. The well-defined dispersion of metal atoms within the MOF structure aids in creating uniformly active catalytic sites. ZIFs, a type of MOFs with imidazolate as the ligand, are particularly useful due to their nitrogen content. For example, a cobalt-based ZIF with CoN_4 pyramidal coordination has been explored as a catalyst precursor. Pyrolysis of this ZIF was carried out in an inert gas. Catalyst prepared using this showed half-wave potential of 0.68 V versus RHE in rotating disk electrode (with a loading of 0.6 mg/cm^2) (Ma *et al.* 2011). Significant advances in performance of NPMC was achieved by Dodelet's Group. During synthesis process Iron acetate, 1,10-phenanthroline, and a Zn-based ZIF (ZIF-8) were

milled together (Proietti *et al.* 2011). The mixture was first pyrolyzed in argon at 1050°C. A second pyrolysis was performed in ammonia at 950°C for an optimized duration. Initial pyrolysis step helped ZIF-8 transformed into an N-doped carbon structure porous structure, enhancing the catalytic properties. MOFs, particularly ZIFs, have proven to be highly effective precursors for synthesizing Me/N/C catalysts, due to their ability to provide a high density of well-dispersed and stable MeN_x active sites. The breakthroughs in synthesis techniques and the resulting high-performance metrics highlight the significant potential of these materials for replacing platinum-based catalysts in PEMFCs. There are many Fe-N-C catalyst incorporated into ZIF8 with the help of solid state reactions and analysed for their catalytic performance (Hou *et al.* 2020).

Pyrolysis is important step in the synthesis of these M-N-C catalyst. Pyrolysis involves the thermal decomposition of materials at high temperatures. It is usually carried out in an inert atmosphere. It has been employed to improve the durability of carbon-based NPMCs. Pyrolysis helps in creating a more stable structure, enhancing the bonding between the metal, nitrogen, and carbon, and increasing the overall catalyst robustness. The pyrolysis temperature is a crucial factor in the synthesis of NPMCs. It influences the formation of active sites, the degree of graphitization of the carbon support, and the overall stability of the catalyst. Systematic studies on the effect of synthesis conditions, such as pyrolysis temperature, precursor composition, and processing atmosphere, help in optimizing the catalytic properties of NPMCs. These optimizations aim to balance the trade-offs between activity, stability, and cost. The durability of these catalysts can be significantly enhanced through pyrolysis, with the pyrolysis temperature playing a critical role. Ongoing research continues to focus on optimizing catalyst design, understanding ORR mechanisms, and improving synthesis methods to achieve catalysts that are both effective and economically viable for large-scale fuel cell applications. The discovery that expensive macrocyclic compounds can be replaced by small molecular precursors for the synthesis of NPMCs has been a significant breakthrough in the field of catalyst development for oxygen reduction reactions (ORR). This finding has enabled the creation of cost-effective and efficient catalysts by focusing on the key nitrogen functionalities that contribute to the formation of active sites.

4.4 Metal Oxides, Carbides and Nitrides

Researchers have extensively analyzed the ORR performance, focusing on a broad range of metal and non-metal composites, including metal oxides, metal nitrides, and oxynitrides (Kiani *et al.* 2021). Hybrid nanomaterials have demonstrated significant enhancements in catalytic efficiency (Chen *et al.* 2015).

Recently, (Lang *et al.* 2020) conducted an in-depth analysis of metal-based electrocatalysts for ORR, emphasizing non-noble metal electrocatalysts that depend on transition metal complexes, such as transition metal oxides, carbides, and nitrides. These transition metal-based catalysts eliminate the need for noble metals, showcasing superior ORR electrochemical activity and stability. Although these electrocatalysts face challenges in acidic electrolyte media, they exhibit remarkable activity in alkaline environments. ORR kinetics is significantly improved in alkaline media compared to acidic electrolytes. With proper structural design, the efficiency of transition metal-based electrocatalysts can rival that of platinum-based electro catalysts. Recently, nitrides altered using non-precious metals have emerged as alternative ORR catalysts. In this context, molybdenum nitride (Mo₂N/C) and tungsten nitride (W₂N/C) were investigated (Zhong *et al.* 2006). A temperature-programmed reaction (TPR) was employed to synthesize Mo₂N/C. Manganese oxides (MnO_x) is also tested for its ORR activity. It is due to its low cost, easy availability and environmental friendliness. It was having notable catalytic activity in alkaline media, despite their insufficient stability in acidic environments (Morozan *et al.* 2011). For instance, Mn₃O₄ nanoparticles loaded on mesoporous carbon have demonstrated promising results. The crystallographic structure and morphology are key parameters influencing the catalytic properties of MnO₂-based nanostructures (Cheng *et al.* 2009). Similarly, titanium oxide (TiO_x) catalysts exhibit varying catalytic activities and stabilities in acidic media, which are influenced by annealing conditions that alter their oxidation state and crystalline structure. In addition to metal oxides, metal carbides can also act as alternative to platinum based catalysts. It is because of the similarity in electronic and catalytic behaviour with noble metal group. Tungsten carbides (WCs) also have garnered significant interest as electrocatalysts or catalyst support in PEMFC (Lee *et al.* 2004) (Chen *et al.* 2014). Various metal carbides have been investigated as catalysts in Hydrogen Oxidation Reaction (HOR) anodes and ORR cathodes in acidic PEM fuel cells. Due to the less ORR activity and stability issues in alkaline environments, significant advancements are necessary to make the practical use of metal carbides in alkaline fuel cells feasible. Tungsten carbides have metal-like conductivity, chemical stability, and high corrosion resistance. This makes them ideal candidates for using them as cathode supports in alkaline fuel cells or as electrocatalysts in alkaline media.

4.5 Composite Catalysts

Metal oxides, particularly manganese and cobalt oxides, demonstrate prolonged activity during oxygen reactions in alkaline solutions (Liang *et al.* 2012). However, their inherently low electrical conductivity is a significant drawback that limits their use as ORR cathodes in Alkaline Fuel Cells (AFCs). To address this

challenge, these metal oxides need to be mixed with materials having high electrical conductivity to create composite ORR electrocatalysts. The development of strongly coupled hybrid materials derived from transition metal oxides (Mn- and Co-based) and nanocarbon materials has become a focus for ORR catalysts in AFCs. One example of this is a graphene nanocomposite, CoO/rGO(N) catalyst. It was containing a high loading of cobalt oxide (24.7 wt% Co). It was synthesized by mixing CoO into nitrogen-doped reduced graphene oxide (He *et al.* 2013). In this process, nitrogen is doped into rGO prior to incorporating CoO. This may result in highly efficient incorporation of nitrogen as compared to other methods. In other methods the nitrogen source is added to metal precursor and graphene oxide (GO). Bio inspired graphene nanoplatelets based Fe/N/C ORR catalyst was synthesized by Yao *et. al* by ball milling and then pyrolysis (Yao *et al.* 2016). In addition to MnOx and CoOx, various types of metal oxides have been investigated. However, most nanocarbon/metal oxide hybrid catalysts still have less activity as compared to M–N–C catalysts. This reduced catalytic activity is due to the low inherent activity of these composites. Other factors contributing to low activity are the low conductivity of metal oxides and various interactions between carbon, metal, and nitrogen.

5. PERFORMANCE OF FE/N/C CATALYST

The Rotating Disk Electrode (RDE) method is widely employed for evaluating the Oxygen Reduction Reaction (ORR) activity of both Pt-based and non-precious metal catalysts. Its popularity stems from its speed and high reproducibility. However, when investigating ORR catalysts for Proton Exchange Fuel Cell (PEMFC) applications, it is crucial to recognize RDE's limitations. One major limitation is that RDE is not an in-device technique. Instead, the electrode is kept in a liquid electrolyte with dissolved O₂. It leads to mass transport limitations even at relatively low overpotentials. This results in current densities typically ranging from 1 to 10 mA·cm⁻². It depends on the electrode rotation speed, which are adjusted around 900 and 1600 rpm. These current densities are lower than those obtained in a real PEMFC operating with O₂ or air at the cathode (Osmieri, 2019). Consequently, RDE testing conditions differ significantly from those of an actual PEMFC system. Despite these limitations, RDE remains a robust technique for the rapid initial screening of ORR catalyst activity. If a synthesized catalyst demonstrates promising activity in RDE, it must then be tested in a real PEMFC to ensure its performance. Metal-nitrogen-carbon (Me/N/C) catalysts are much economical to synthesize than platinum (Pt)-based catalysts. Here Me is an inexpensive transition metal. They still need to meet stringent performance and durability criteria to be viable for PEMFC applications. Me/N/C catalysts should aim for power densities close to those achieved by Pt-based catalysts. While a slight

reduction might be acceptable, significant decreases would undermine their utility. Table 1 summarizes important electrochemical parameters for key NPMCs in ORR relevant to PEMFC. Zhang *et. al.* reported ORR parameters which are comparable to Pt catalyst (Zhang *et al.* 2018). This table highlights rapid progress in NPMC development with few catalyst even rivalling Pt/C. Pt-based catalysts typically achieve power densities around 0.7 W/ cm² at cell voltage of 0.68 V under operating conditions (Gasteiger *et al.* 2005). Me/N/C catalysts have achieved comparable current densities in certain optimized conditions. It should have comparable durability to Pt-based catalysts, which often exceed 5,000 hours of operation without significant degradation. At present, Me/N/C catalysts need to demonstrate improved resistance to degradation mechanisms such as metal leaching, carbon corrosion, and active site loss. When catalyst loading is considered, platinum based catalysts should be minimized to reduce the mass of Pt per watt of rated power. In case of non-precious metal catalyst, due to their lower cost, Me/N/C catalysts can afford higher loadings (e.g., 4 mg cm²) to achieve desired power densities without significant economic impact. Table 2 shows the performance of NPMCs with different catalyst loading. The relationship between catalyst loading and current density is crucial for optimizing NPMCs. Increasing catalyst loading generally increases current density. At higher loading improvement diminishes. Advanced Fe-N-C catalyst can achieve current densities of 1000 mA/cm² at 0.6 V and loading of 1-4 mg/cm². Non-precious metal catalysts (NPMCs) for PEMFCs have shown significant promise as cost-effective alternatives to platinum-based catalysts. While there have been notable advances in their performance, several challenges remain.

Table 1. Important ORR performance parameters for key NPMCs reported in the literature

Catalyst/System	Onset Potential (V vs. RHE)	Half-wave Potential (V vs. RHE)	Current Density (mA/cm ²)
Fe-N/Fe ₃ C/Fe/C-800 (alkaline) (Zhang <i>et al.</i> 2018)	1.00	0.82	6.23 (diffusion-limited)
Fe-N/Fe ₃ C/Fe/C-800 (acidic) (Zhang <i>et al.</i> 2018)	~0.95	0.62	5.48 (diffusion-limited)
Fe-doped C12A7:c/rGO (Khan <i>et al.</i> 2019)	1.03	0.89	~5.9
NPMC/Graphene Nanosheet (acidic) (Choi <i>et al.</i> 2011)	0.853	0.682	Not specified
FeSA-G (Fe single atom on graphene) (Cheng <i>et al.</i> 2019)	0.950	0.804	353 at 0.5 V (fuel cell, 230°C)
Pt/C (benchmark, acidic) (Zhang <i>et al.</i> 2018)	1.00	0.85	5.65

The catalytic activity of macrocyclic materials, such as phthalocyanines and porphyrins, is strongly influenced by the central metal ion and the ligand

structure surrounding it (Song *et al.* 2020) (Randin, 1974) (Zagal, 1992). The specific interactions between the metal center and the ligands affect the electron density and, consequently, the oxygen reduction reaction (ORR) activity (Song *et al.* 2020). The surface chemistry and the nature of catalyst support play a key role in catalytic activity of M-N4 chelates. In these metal based catalysts, metal support interactions are crucial in determining the activity (Morozan *et al.* 2011). The type of metal ion (e.g., Fe, Co, Ni, Mn, Cu) plays a crucial role in determining the catalytic performance. Different metals influence the ORR process differently, affecting whether it proceeds via a four-electron or two-electron pathway. The nature of the ligand and its electron-donating or withdrawing properties significantly impact the catalytic activity. Ligand modifications can tune the electron density surrounding the metal centres which alter the ORR efficiency. Alt *et al.* explored the ORR behaviour of many Co-ligand compounds in acidic electrolytes. This study highlighted the influence of the ligand environment on catalytic performance (Alt *et al.* 1971). Wiesener *et al.* demonstrated that the central metal atoms greatly affect the ORR process. This emphasize the impact of metal choice on the efficiency and pathway of the reaction (Wiesener *et al.* 1989). Despite their catalytic properties, macrocyclic materials face challenges in direct application within PEMFCs. These materials exhibit lower catalytic activity compared to platinum-based catalysts. Stability is a bigger issue, with many macrocyclic compounds showing poor long-term performance under fuel cell operating conditions.

Table 2. Current density for different NPMC loading in PEMFCs.

Catalyst/System	Catalyst Loading (mg/cm ²)	Current Density (mA/cm ²) at 0.6 V	Reference
Fe-Nx-C Polyhedron [H ₂ -O ₂]	1.0	1100	(Deng <i>et al.</i> 2019)
Fe-Nx-C Polyhedron [H ₂ -Air]	1.0	650	(Deng <i>et al.</i> 2019)
Fe/N/C NPMC	1.0	~600	(Banham <i>et al.</i> 2018)
Fe/N/C NPMC	2.5	~900	(Banham <i>et al.</i> 2018)
Fe/N/C NPMC	4.0	~1100	(Banham <i>et al.</i> 2018)
N-G-CNT + KB (metal-free)	0.5	30 (A/g) at 0.8 V (gravimetric)	(Shui <i>et al.</i> 2015)
VA-NCNT (metal-free)	0.16	35 (A/g) at 0.8 V (gravimetric)	(Shui <i>et al.</i> 2015)

Advanced NPMCs have demonstrated current densities approaching those of platinum-based catalysts. For example, the Fe/N/C catalysts have achieved current densities of around 1.25 A cm² at 0.6 V under certain conditions. Dodelet's group reported a maximum power density of 0.91 W cm² for their optimized Fe/N/C catalyst (Proietti *et al.* 2011). NPMCs typically exhibit half-wave potentials that are lower than those of platinum catalysts.

However, significant improvements have been made, with some catalysts achieving half-wave potentials around 0.76 V versus RHE (Mehmood *et al.* 2021). Wang *et al.* carried out Rotating Ring-Disk Electrode (RRDE) studies on catalysts synthesized by pyrolyzing Fe or Co salts at 900 °C (Wang *et al.* 2007). The catalysts consisted of polymerized phenylene-diamine and carbon. The study reported Peak Potential of 0.76 V versus SHE (Standard Hydrogen Electrode), approximately 0.8 V versus RHE (Reversible Hydrogen Electrode). Catalyst was 2 wt% Fe, 20 wt% polymerized monomer (phenylene-diamine) and 80 wt% carbon support. Electrolyte used was 0.5 M H₂SO₄. Pyrolysis temperature reported is 900° C in inert gas environment. This study highlights the necessity of optimizing the composition and synthesis conditions of non-precious metal catalysts (NPMCs) for achieving high ORR activity. The reported peak potential shows that the Fe-based catalyst is active in acidic conditions (0.5 M H₂SO₄), which is crucial for practical applications. In 2011, Dodelet's group achieved a notable breakthrough in Me/N/C catalyst performance, obtaining unprecedented power densities. The highest Current density of 1.25 A cm² at 0.6 V was observed. Maximum power density of 0.91 W cm² under H₂/O₂ conditions at 1 bar gauge pressure with a catalyst loading of 4 mg cm² was obtained (Proietti *et al.* 2011). This current density at 0.6 V was 2.3 times higher than any previous Me/N/C catalyst and approached the performance of a benchmark cathode with 0.3 mgPt cm², which achieved 1.7 A cm² at 0.6 V (Proietti *et al.* 2011). Bioinspired composite catalyst based on graphene platelets prepared by Yao *et al.* demonstrated high power density of 521 mW-cm². This material illustrates well defined controllability of specific surface area and microporosity (Yao *et al.* 2016). While the initial performance of NPMCs can be high, their long-term durability in acidic environments remains a challenge. In recent reported work, Mooste *et al.* synthesized silicon oxycarbide based, double transition metal doped and nitrogen functionalized NPMC. RRDE measurements reported were performed in 0.5 M H₃PO₄ solution. Fig. 8 shows the the ORR performance of the catalyst as compared to Pt/C and Fe-N-C. Authors have reported that the novel catalyst exhibits long term durability in H₃PO₄ solution and highest overall ORR activity during high temperature gas diffusion electrode testing in concentrated H₃PO₄.

The use of MOFs and ZIFs as precursors has significantly enhanced the performance of NPMCs. These materials allow for high-density, well-dispersed active sites. Optimized pyrolysis techniques, including controlled atmospheres (e.g., argon, ammonia) and multi-step pyrolysis processes, have improved both the activity and stability of NPMCs. Combining NPMCs with other materials, such as transition metal oxides or carbides, has shown potential for improving both performance and durability. Techniques such as atomic layer deposition and nanoparticle encapsulation have been employed to

enhance the stability and activity of NPMCs. Enhanced active site density and accessibility of active sites within the carbon matrix was achieved through the use of advanced precursor materials such as MOFs and optimized pyrolysis techniques. For example Liu's group leveraged MOFs to provide high MeNx site densities with controlled coordination chemistry (Goenaga *et al.* 2010). Another approach is to optimize synthesis process by Utilizing multi-step pyrolysis, templating techniques, and nanoengineering methods to enhance the catalyst's structural and chemical properties. For example Dodelet's group used a combination of planetary ball-milling and multi-step pyrolysis to achieve unprecedented performance metrics (Proietti *et al.* 2011). It is necessary to conduct detailed mechanistic studies to understand the ORR process at the atomic level, guiding the rational design of catalysts. Investigating the exact nature of active sites and the role of nitrogen coordination in enhancing ORR activity. This will result in developing scalable synthesis methods that can be economically viable for large-scale production. Streamlining processes such as pyrolysis and utilizing cost-effective precursor materials to reduce production costs further.

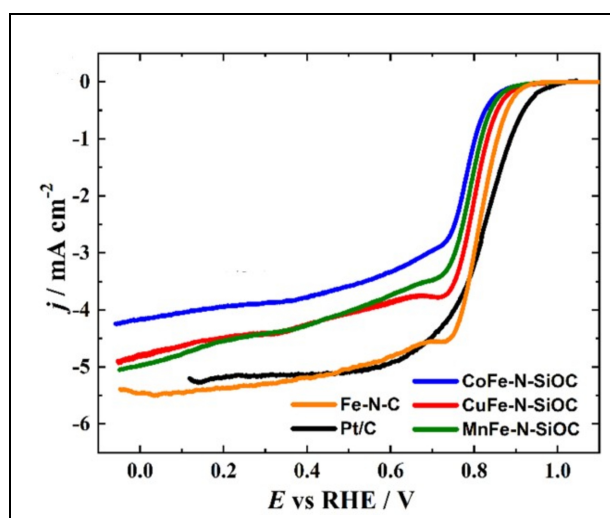


Fig. 8: ORR Curves for silicon oxycarbide based, double transition metal doped and nitrogen functionalized NPMC. (Figure reproduced from M. Mooste *et al.*, *electrochimica Acta*, 2025, 514, 145620, Licensed under a creative commons attribution 4.0 international license)

6. CHALLENGES

Mimicking the highly efficient catalytic processes of cytochrome c oxidase presents a promising pathway for developing noble metal-free ORR catalysts for PEMFCs. By focusing on transition metal complexes within nitrogen-rich ligand frameworks, researchers aim to replicate the enzyme's efficiency and stability. Despite the promising ORR activity results of bio-mimicking electrocatalysts, incorporating them into proton exchange membrane fuel cells (PEMFCs) remains a significant challenge. These catalysts have typically been

evaluated at the rotating ring-disk electrode (RRDE) level, which does not fully replicate the harsh conditions of a working fuel cell. Consequently, their activity and stability need further improvement to meet the practical requirements of PEMFCs. There are some critical challenges and potential strategies for advancing these bio-inspired catalysts. Non-precious metal catalysts can suffer from stability and durability issues under fuel cell operating conditions, such as high acidity and potential. Banham *et al.* reported highest performance for an NPMC based catalyst in membrane electrode assembly. In their study it was observed that higher catalyst loading resulted in higher stability. Fig. 9 indicates data for 60 hrs operation. Higher loading of 4 mg/cm² resulted in loss of 10 % of its initial activity where as 55% loss for loading of 1 mg/cm². Table 3 summarizes key parameters for various NPMCs. Some NPMC demonstrated comparable ORR activity to Pt/C in alkaline media. Durability is a challenge for NPMCs but under specific conditions it is approaching Pt/C. Pt/C still remains the benchmark for activity and durability in PEMFCs. Enhancing the density of active sites, optimizing the electronic properties of the catalysts, and improving the ligand design can help increase catalytic activity. Developing scalable and cost-effective synthesis methods for these bio-inspired catalysts is crucial for their practical application in PEMFCs.

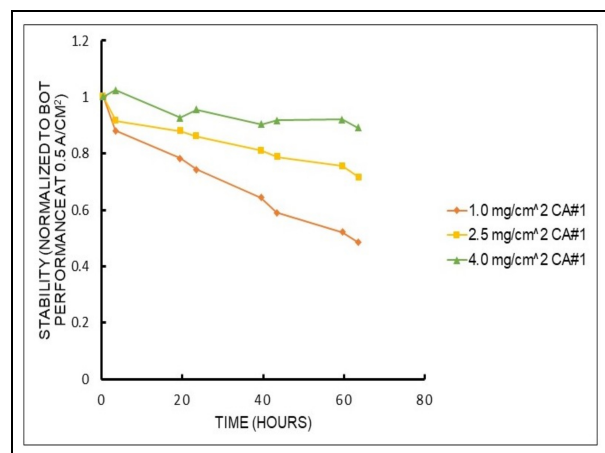


Fig. 9: Stability study of NPMC catalyst for various loadings (Banham *et al.* 2018) (figure reproduced from D. Banham *et al.*, *science advances*, 2018, 4, eaar7180, licensed under a creative commons attribution 4.0 international license)

While challenges remain in terms of stability, activity, and scalability, continued research and innovation in bio-inspired catalyst design hold the potential to create effective and sustainable alternatives to precious metal-based catalysts. Bio-inspired electrocatalysts often show poor durability when subjected to the high temperature, humidity, and acidic environment typical of PEMFCs. These catalysts can degrade due to factors such as corrosion of the carbon support, dissolution or agglomeration of metal centers, and loss of active sites. The high ORR activity observed in RRDE tests does not

always translate to membrane electrode assembly (MEA) performance, where mass transport and water management issues are more pronounced. The overpotential required for ORR may increase in MEAs, reducing overall efficiency compared to RRDE measurements. Integrating bio-inspired catalysts into electrodes that are compatible with existing fuel cell architectures can be challenging. This includes ensuring uniform distribution, adequate adhesion, and effective interaction with the ionomer.

Table 3. Comparison of ORR performance and durability for NPMC

Catalyst Type / System	Key ORR Performance Metrics (Acidic PEMFC)	Durability / Stability Results
N-doped Carbon Nanotubes (VA-NCNT) (Shui <i>et al.</i> 2015)	High gravimetric current density (35 mA mg ⁻¹); stable polarization over 5100 cycles; comparable to Pt/C	~20% current decay over 100 h (vs. ~75% for Fe/N/C)
N-doped graphene/CNT composite + carbon black (Metal-free) (Shui <i>et al.</i> 2015)	Excellent stability; small current decay over 100 h at 0.5 V	Superior to Fe/N/C; no significant acidic corrosion
Fe-N/Fe ₃ C/Fe/C (Zhang <i>et al.</i> 2018)	Onset potential: 1.00 V (alkaline), 0.82 V (acidic); half-wave: 0.82 V (alkaline), 0.62 V (acidic); peak current higher than Pt/C	Excellent methanol tolerance; good stability in both media
3D Porous Fe/N/C (Wei <i>et al.</i> 2017)	Activity: 1.91 mA cm ⁻² (Fe/N/C) vs. 0.32 mA cm ⁻² (Pt/C) at 0.9 V (alkaline); comparable in acid; better stability	No decay after 10,000 cycles (Fe/N/C) vs. 35 mV loss (Pt/C)
Calcinated FeNxC (Wang <i>et al.</i> 2019)	Max. power density: 140 mW cm ⁻² ; only 10 mV half-wave loss after 1000 cycles (vs. 27 mV for Pt/C)	High surface area, good durability

Although NPMCs have made significant strides, their activity still generally falls short of that of platinum catalysts, particularly at high current densities. Issues such as metal leaching, carbon corrosion and nitrogen loss need to be addressed. The synthesis processes for high-performance NPMCs can be complex and difficult to scale up for industrial production. While the raw materials are cheaper, the overall cost-effectiveness of NPMCs depends on achieving performance and durability comparable to platinum catalysts.

6.1 Strategies for Improvement

In past years' various strategies for improvement of performance of NPMC were tried. To Enhance Stability, advanced Supports materials were

used. Developing more robust support materials, such as doped carbon nanotubes, graphene, or metal-organic frameworks (MOFs), can improve the stability of the catalysts. Applying protective coatings or encapsulating metal centres within stable matrices can prevent catalyst degradation. Fine-tuning the coordination environment of metal centres and optimizing the distribution of nitrogen functional groups can enhance both stability and activity. Using bimetallic or alloy catalysts can leverage synergistic effects to improve ORR activity and durability. Ensuring proper integration of the ionomer with the catalyst layer is critical for efficient proton transport. This may involve optimizing ionomer content and distribution. Employing advanced electrode fabrication techniques such as layer-by-layer assembly or atomic layer deposition can enhance the uniformity and performance of the catalyst layer. Some stability issues can mitigate after optimizing fuel cell operating conditions, such as maintaining appropriate humidity and temperature. Incorporating additives that stabilize the catalyst and prevent agglomeration or dissolution can extend the operational life of the catalysts.

Conducting in-situ and operando studies to understand the behaviour of bio-inspired catalysts under real fuel cell conditions can provide insights for improving their design and durability. computational modelling can be utilized to predict and design new catalyst structures with enhanced stability and activity. Collaborating across disciplines, including materials science, chemistry, and engineering, will help to integrate bio-inspired catalysts into practical PEMFC systems effectively. It is necessary to develop methods to increase the density and accessibility of active sites within the carbon matrix. Investigating new materials and synthesis techniques to enhance the stability of NPMCs in acidic environments is necessary. Conducting detailed studies to understand the ORR mechanism at the atomic level can guide the rational design of more effective catalysts. Developing scalable and cost-effective synthesis methods is a key to enable the commercial production of NPMCs.

7. CONCLUSION

Non-precious metal catalysts have made substantial progress and hold significant promise for PEMFC applications. On-going research and development are focused on overcoming the current limitations in activity, stability, and synthesis complexity to realize their full potential as viable alternatives to platinum-based catalysts. Despite the promising ORR activity results of bio-mimicking electrocatalysts, incorporating them into proton exchange membrane fuel cells (PEMFCs) remains a significant challenge. These catalysts have typically been evaluated at the rotating ring-disk electrode (RRDE) level, which does not fully replicate the harsh conditions of a working fuel cell. Consequently, their activity and stability need further

improvement to meet the practical requirements of PEMFCs. While bio-inspired electrocatalysts show significant promise for ORR in PEMFCs, their practical implementation faces challenges related to stability, activity, and integration. Addressing these challenges requires a multifaceted approach, including enhancing catalyst stability, optimizing design, improving MEA integration, and conducting comprehensive research to understand and mitigate degradation mechanisms.

FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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