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EDITED BY
Xiaohu Yang,
Xi'an Jiaotong University, China

REVIEWED BY
Gouse Peera Shaik,
Keimyung University, Republic of Korea
Lindiwe Eudora Khotseng,
University of the Western Cape, South Africa

*CORRESPONDENCE
A. S. Alabi,
ayo.alabi@ymail.com

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Materials for electrocatalysts in proton exchange membrane fuel cell: A brief review

A. S. Alabi[1]*, A. P. I. Popoola[1], O. M. Popoola[2], N. R. Mathe[3] and M. Abdulwahab[4]

[1]Chemical, Metallurgical and Materials Engineering, Faculty of Engineering and Built Environment, Tshwane University of Technology, Pretoria, South Africa, [2]Center for Energy and Electric power, Electrical Engineering, Faculty of Engineering and Built Environment, Tshwane University of Technology, Pretoria, South Africa, [3]National Laser Center, Council for Scientific and Industrial Research, Pretoria, South Africa, [4]Metallurgical and Materials Engineering, Faculty of Engineering, Air Force Institute of Technology, Kaduna, Nigeria

Energy is a requisite factor for technological advancement and the economic development of any society. Currently, global energy demand and supply largely rely on fossil fuels. The use of fossil fuels as a source of energy has caused severe environmental pollution and global warming. To salvage the dire situation, research effort is geared toward the utilization of clean, renewable and sustainable energy sources and the hydrogen energy economy is among the most preferred choices. Hydrogen energy economy, which includes hydrogen production, storage and conversion has gained wide consideration as an ecofriendly future energy solution with a fuel cell as its conversion device. Fuel cells, especially, the proton exchange membrane category, present a promising technology that converts hydrogen directly into electricity with great efficiency and no hazardous emissions. Unfortunately, the current generation of proton exchange membrane fuel cells faces some drawbacks that prevent them from large-scale market adoption. These challenges include the high costs and durability concerns of catalyst materials. The main source of high cost in fuel cells is the platinum catalyst used in the electrodes, particularly at the cathode where the sluggish oxygen reduction reaction kinetics require high loading of precious metals. Many research efforts on proton exchange membrane fuel cells are directed to reduce the device cost by reducing or completely replacing the platinum metal loading using alternative low-cost materials with "platinum-like" catalytic behaviour while maintaining high power performance and durability. Consequently, this review attempts to highlight recent research efforts to replace platinum and carbon support with other cost-effective and durable materials in proton exchange membrane fuel cell electrocatalysts. Overview of promising materials such as alloy-based (binary, ternary, quaternary and high-entropy alloys), single atom and metal-free electrocatalysts were discussed, as the research areas are still in their infancy and have many open questions that need to be answered to gain insight into their intrinsic requirements that will inform the recommendation for outlook in selecting them as electrocatalysts for oxygen reduction reaction in proton exchange membrane fuel cell.

KEYWORDS

proton exchange membrane fuel cell, oxygen reduction reaction, platinum-based electrocatalysts, platinum-free electrocatalysts, alloy-based electrocatalysts, single atom electrocatalysts, metal-free electrocatalysts

1 Introduction

The ability of any society to evolve technologically and develop economically depends on the availability and effective utilisation of energy. The current global energy consumption mainly relies on fossil fuels (Abbasi et al., 2022; Shamoon et al., 2022). This state of global energy demand and supply is not sustainable considering the growth in global population, fast exhaustion of fossil fuel deposits and the environmental effects of using fossil fuels on the fragile ecosystem (Bogdanov et al., 2021; Schwanitz and Wierling, 2022). In addition, the increasing rate of fossil fuel utilization threatens to destabilise the environment because of the worsening greenhouse gas emissions and global warming that might result in unprecedented changes to human lives if nothing is done to prevent it (Chen et al., 2022a; Icaza-Alvarez et al., 2022). To address the situation, research effort is focused on utilising clean, renewable and sustainable energy sources and the hydrogen energy economy is among the most preferred choices.

The idea of a hydrogen economy was initiated by John Bockris in the 1970s. It was a dream to generate hydrogen *via* water electrolysis and channel it through pipelines to factories, homes, and fuelling stations where it would be harnessed and converted to other forms of energy (Oliveira et al., 2021). However, many challenges still need to be overcome in hydrogen production, storage and conversion to realise Bockris' dream of a global transition to a hydrogen economy. Such challenges include the high cost and poor reliability of the hydrogen energy conversion device known as the fuel cell. A fuel cell is an electrochemical device that converts chemical energy directly into electricity with great efficiency and no hazardous emissions (Wang and Jiang, 2017; Ioroi et al., 2019). It is a thermodynamic system that operates based on electrochemical reactions, which consumes reactants from external source (Rahaman and Islam, 2019). The fuel cell combines the best features of combustion engines and batteries. It can work continuously without any intermediate mechanical energy conversion if fuel is supplied constantly and also shows the characteristics of battery under load condition (Manoharan et al., 2019). Fuel cells are usually classified according to the electrolyte, fuel used, operating conditions, required load or the application for which they are used (Abdelkareem et al., 2021b). Diverse kinds of fuel cells are presented in Table 1 Although these fuel cells use different electrolytes and fuels, they all operate on a similar redox reaction principle and platinum (Pt) is the catalyst widely used for the cathodic and anodic redox reaction in proton exchange membrane fuel cell (PEMFC).

The PEMFC is promising for large-scale commercialisation because of its dynamic response, high efficiency, low operating temperature (60°C—80°C), high power density and quick start-up when compared with other fuel cells (Lucia, 2014; Jiao et al., 2021).

Despite the potential of PEMFC for widespread commercialisation, it needs to meet certain criteria about cost and reliability to gain end-user acceptance and compete favourably with other commercial energy conversion devices such as internal combustion engines and batteries (Wang et al., 2018a). The high cost of active electrocatalyst materials and their poor durability at PEMFC operation conditions are the major challenges facing the large-scale commercialisation of PEMFC (Borup et al., 2020). In addition, it has been reported that the membrane electrode assembly parameters have significant impact on the efficiency of the PEMFC stack (Majlan et al., 2018; Madheswaran and Jayakumar, 2021). Hence, improving the efficiency of PEMFC by rational selection of cost-effective materials is essential to achieve the hydrogen economy potential as an alternative to fossil fuel in electricity generation, fuel for vehicles and industrial processes (Egeland-Eriksen et al., 2021).

These could be achieved by deliberate attempt to improve the state-of-the-art electrocatalysts in PEMFC. The electrocatalyst is a vital component that performs a significant role in reaction kinetics involved in the effective functioning of PEMFC. It has to do with the surface adsorption of reactants, breaking the reactants bonds and formation of new bonds of intermediates and desorption of products (Figure 1) (Wacławek et al., 2018; Madheswaran and Jayakumar, 2021). The electrocatalyst in the PEMFC works as the cathode and anode, which conventionally uses Pt particles on carbon support (Wang et al., 2020b). Unfortunately, Pt-based electrocatalysts account for about half of the cost of the PEMFC stack and suffer degradation during prolonged PEMFC operation (Xie et al., 2020; Fan et al., 2022). The main degradation mechanisms have been identified as dissolution, migration and agglomeration of metal particles and carbon support corrosion that results in a loss in the electrochemical surface area (ECSA) (Wei et al., 2021b). In addition, Pt-based electrocatalysts are susceptible to carbon monoxide poisoning and requires highly active material loading at the cathode because of the cathodic sluggish oxygen reduction reaction kinetics. To address these challenges, two routes have been widely investigated to achieve low-cost electrocatalysts; which are lowering the loading of Pt and looking for substitutes (Ding et al., 2020b).

PEMFC energy conversion is achieved through hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) (Figure 2) (Cruz-Martínez et al., 2021). These reactions involve the transfer of charge (electrons) between an electrocatalyst and a chemical species. During the HOR, an external circuit transports electrons to the cathode while protons are transferred across the polymer exchange membrane. Meanwhile, ORR involves oxygen reduction with electrons and hydrogen protons at the cathode, leaving only water and heat as by-products (Cruz-Martínez et al., 2019). Research interest focus more on ORR because of its sluggish kinetics that is 4–6 times slower in order of magnitude when compared with HOR (Wang et al., 2018b; Wan et al., 2020).

The slow rate of ORR remains a major challenge in PEMFC (Kong et al., 2023). Significant progress has been made globally towards improving the-state-of-the-art electrocatalysts for ORR. As a result of these research efforts, commercial Pt/C remains the most widely used electrocatalyst among others because of its comprehensive evaluation and the superior activity of the Pt surface to other oxygen reducing surfaces (Ma et al., 2020a; Liu et al., 2022; Li et al., 2023). However, Pt high cost, scarcity and poor durability during prolong PEMFC operation hinder the widespread commercialisation of PEMFC, as the frequent cost of the replacement of the electrocatalyst significantly affects the overall cost of the fuel cell (Lv et al., 2019b; Meng et al., 2021; Xia, 2021). To this end, addressing the stability challenges, particularly at the cathode where the sluggish ORR kinetics require high loading of precious metal is imperative for its practical employment in PEMFC (Zhao et al., 2022). To overcome these challenges, research efforts

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TABLE 1 Types of fuel cells.

Type of fuel cell	Advantages	Disadvantages	References
Proton exchange membrane fuel cell	o Promising for large scale commercialisation	o Sluggish oxygen reduction kinetics	Abdelkareem et al. (2021a)
	o High efficiency	o Carbon monoxide poisoning	
	o Dynamic response	o Poor heat and water management	
	o Low operating temperature 40°C – 80 °C	o Costly catalysts	
	o Quick start-up		
	o High energy density		
Alkaline fuel cell	o Operates at low temperature 27°C – 70 °C	o Carbon dioxide intolerance	Ferriday and Middleton (2021)
	o Quick start-up		
	o High efficiency		
	o Low cost		
	o Good heat management		
	o Fast oxygen reduction kinetics		
	o High activity		
	o Can resist carbon monoxide poisoning		
Direct methanol fuel cell	o Quick start-up	o Fuel crossover that causes cathode poisoning	Alias et al. (2020)
	o Fuel can be obtained from wastes		
	o Cost effective	o Costly catalysts	
	o High energy density		
Phosphoric acid fuel cell	o High tolerance to carbon monoxide poisoning	o High cost of Pt catalysts	Stonehart and Wheeler (2005)
	o Comparatively lower Pt catalyst demand	o Sluggish start-up	
	o High activity	o Low ionic conductivity	
	o Good heat management		
Molten carbonate fuel cell	o High efficiency	o Susceptible to high temperature corrosion	Antolini (2011)
	o Can use carbon dioxide as oxidant	o Sluggish start-up	
	o Cost effective as its does not require precious metal catalyst	o Difficulty in handling molten carbonate	
Solid oxide fuel cell	o High efficiency	o Requires high temperature materials for effective functioning	Yang et al. (2020)
	o Good heat management		
	o Can function without precious metal catalysts		
	o Has long operational time		
	o Can use different types of fuels		
Reversible fuel cell	o Can operate both as fuel cell and water electrolyser	o Comparatively not cost effective	Wang et al. (2016), Lim et al. (2021)
	o High specific energy	o Relatively low efficiency	
	o Has energy storage capacity		
Direct ammonia fuel cell	o Runs at lower temperature	o Susceptible to ammonia crossover	Jeerh et al. (2021)
	o Cost effective	o Has low cell efficiency and power density	
	o Requires low-cost electrolyte and electrocatalyst		

(Continued on following page)

TABLE 1 (*Continued*) Types of fuel cells.

Type of fuel cell	Advantages	Disadvantages	References
Direct propane fuel cell	o Low-cost	o Generates carbon dioxide as reaction product	Mohammed et al. (2019)
	o Can be easily handle		
	o Requires simple infrastructure		
	o Has relatively higher power density		
	o Has the potential to work with low-cost membrane		
Microbial fuel cell	o Converts wastes to electricity	o Low power density	Do et al. (2018)
	o Can be used in wastewater treatment	o Current instability	
	oCan be used as biosensor	o Uses costly materials	
		o High internal resistance	

are on-going to develop durable electrocatalysts that are highly active and cheap (Batchelor et al., 2019).

1.1 Pt/C electrocatalyst degradation mechanism

Pt particles dispersed on carbon support remain the most widely used commercial electrocatalyst for PEMFC (He et al., 2022). This is due to the advance conductivity, flexibility and wide range of operable potentials that Pt offers for PEMFC application (Abbas et al., 2020). Unfortunately, under PEMFC operation conditions, Pt dissolves and breaks up and the carbon support also corrodes leading to the deterioration of the performance of the fuel cell (Kregar et al., 2020). The major degradation mechanisms were identified as dissolution, migration and agglomeration of metal particles and carbon support corrosion that results in a loss in the ECSA which causes overall decrease in the performance of PEMFC (Wang et al., 2021a; Wei et al., 2021b). Several studies have been conducted to investigate the degradation mechanism of Pt/C in PEMFC (Weber et al., 2018; Labata et al., 2021; Fan et al., 2022). The studies were aimed at understanding the degradation mechanism of Pt-based electrocatalyst to help researchers in developing mitigation strategies that could significantly reduce the cost of PEMFC (Lopes et al., 2020; Hersbach et al., 2021). Different perspectives exist in the literature on the cause of Pt-based electrocatalyst disintegration. Some researchers argued that Pt disintegrate due to change in cell potential, other researchers asserted that the discrepancy in anodic and cathodic charges is the cause of the disintegration (Okonkwo et al., 2021). With the disparity in the potential ranges at which Pt disintegration occurs in PEMFC operation, factors such as particles size and morphology play important role in the disintegration of Pt (Lopes et al., 2020; Hussain et al., 2022). To address these challenges, promising strategies (Figure 3) such as alloying Pt with transition metals has been suggested as an effective method to reduce the usage of the scarce and expensive precious metal as electrocatalyst without loss in its performance (Bhoyate et al., 2023). In addition, the use of mixed phases has been recommended as an effective strategy to optimise electrocatalysts activity and stability, thereby encouraging the development of electrocatalysts from binary, ternary, quaternary and high entropy alloys (Li et al., 2020c; Prabhu et al., 2020; Li et al., 2021; Du et al., 2022). The desired electrocatalyst activity and stability optimisation in alloy electrocatalysts is achieved by alloy compositional, morphological and particles size control (Zhang et al., 2021a; Loffler et al., 2021).

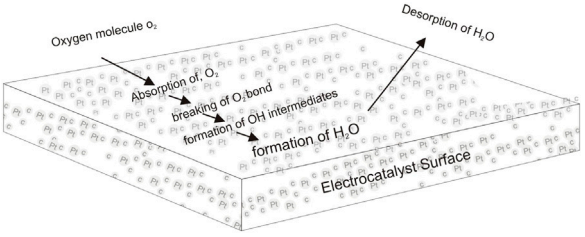

FIGURE 1
Schematic representation of electrocatalyst surface.

It is noteworthy that other electrocatalyst design strategies such as Pt-free alloys, single atom and metal-free electrocatalysts have been investigated (Bhatt and Lee, 2020; Han et al., 2020; Zhang and Guan, 2020; Wei et al., 2021a; Muhyuddin et al., 2021). Efforts have also been directed toward the development of other durable catalyst-support materials. Consequently, this review summarises recent research efforts to enhance or replace Pt and carbon support with other cost-effective and durable materials in PEMFC electrocatalysts application (Table 2). Overview of design strategies in developing alternative electrocatalyst using other cost-effective and durable materials to replace platinum and carbon support are highlighted with the activity and stability of various electrocatalysts for oxygen reduction reaction in PEMFC.

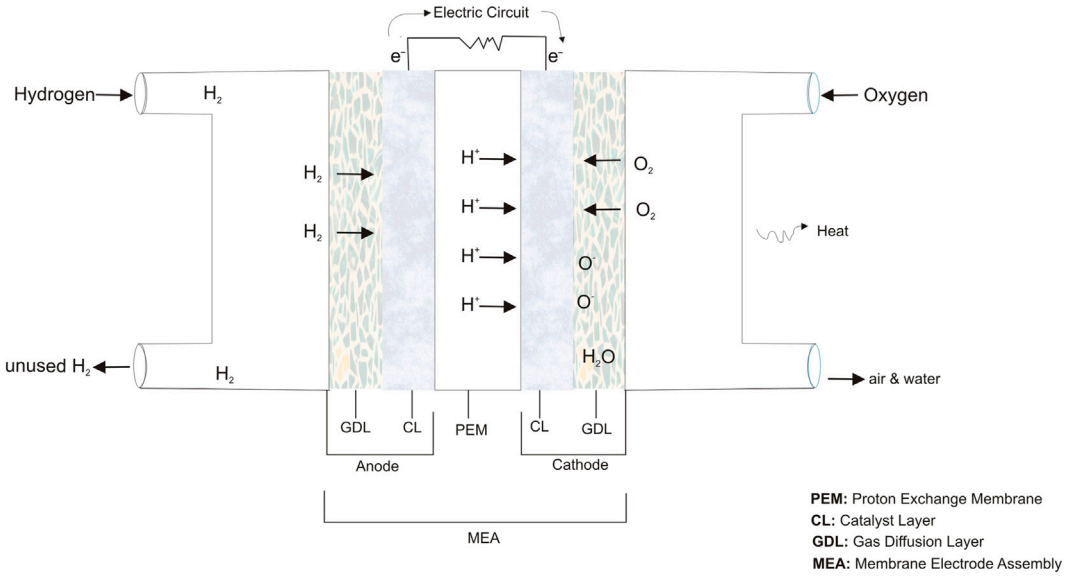

FIGURE 2
Representation of the role of electrocatalyst in HOR and ORR in PEMFC.

2 An overview of materials used as electrocatalysts in PEMFC

Herein research progress on electrocatalyst design strategies to address the drawbacks associated with the state-of-the-art Pt/C electrocatalyst for PEMFC were summarised. Pt-based electrocatalyst were discussed followed by alloy electrocatalysts. Emerging electrocatalysts such as high-entropy alloys, single atom and metal-free electrocatalysts were also highlighted.

2.1 Platinum-based electrocatalysts

Pt/C electrocatalyst remains the state-of-the-art catalyst for ORR in PEMFC because of its effectiveness in ORR kinetics (Tian et al., 2017; Huang et al., 2021; Kong et al., 2021). However, due to its high cost and durability concerns, research to enhance its performance and reduce its high Pt particle loading are on-going (Shao et al., 2018; Lopes et al., 2020; Kishida et al., 2021). According to Etesami et al. (2021), there are three major research areas for Pt-based catalysts, which are 1) reducing the particle size of Pt and increasing its dispersion in the carbon support in order to increase its active sites surface area 2) producing Pt-based catalysts with particles surface oriented in a specific direction and 3) dispersing Pt into other metals especially transition metals or modified carbon supports to form alloys or mixtures. Efforts have also been directed toward the development of other durable catalyst-support materials such as transition metal-based compounds (carbides, nitrides, oxides and chalcogenides) (Shang et al., 2020), carbon-based materials (carbon nanotube and graphene) (Liu et al., 2018), nitrogen doped carbon (Chen et al., 2021) and metal-organic-framework to address the carbon support corrosion challenge. On the other hand, Mukherjee et al. (2022) asserted that electrocatalysts that use only micro-sized Pt particles as their actives sites are no longer the state-of-the-art catalysts for fuel cell application. The authors claimed that high cost of electrocatalysts due to unrealistic Pt loading requirements and Pt particle susceptibility to carbon monoxide poisoning are the key reasons for the assertion. Along this line, research have evolved from using micro sized Pt on carbon supports to using Pt nanoparticles, Pt nanowires, introduction of porosity to increase catalysts surface area and bimetallic Pt electrocatalysts with other metals (Table 3) (Gilroy et al., 2016; Li and Sun, 2019; Shao et al., 2019; Xiao et al., 2021a).

2.2 Platinum-free electrocatalysts

To reduce the overall cost of PEMFC, researchers focus on the reduction or substitution of Pt in Pt-based electrocatalyst. Thus, research efforts have been directed towards the development of non-Pt-based electrocatalysts. Other Pt group metal-based electrocatalysts such as Pd-C, Ir-C, Rh-C electrocatalysts have been reported (Wang et al., 2022). Several Pt-free electrocatalysts have been developed using non-precious metals because of their low-cost, availability and abundance in nature (Etesami et al., 2021). Non-precious metal-based electrocatalysts have been widely investigated because of their excellent catalytic performance, durability and cost-effectiveness (Etesami et al., 2020). Such electrocatalysts include transition metal-nitrogen-carbon electrocatalysts, nitrides, carbides, chalcogenides and transition metal oxides (Gewirth et al., 2018; Xiao et al., 2021a). To achieve a Pt metal group-free electrocatalyst for PEMFC application Sanad et al. (2021) synthesised a non-precious metals Co-Cu metal organic framework bimetallic electrocatalyst by low-temperature hydrothermal strategy. The catalytic activity of the electrocatalyst was tuned by varying Co/Cu molar ratios. It was observed that the

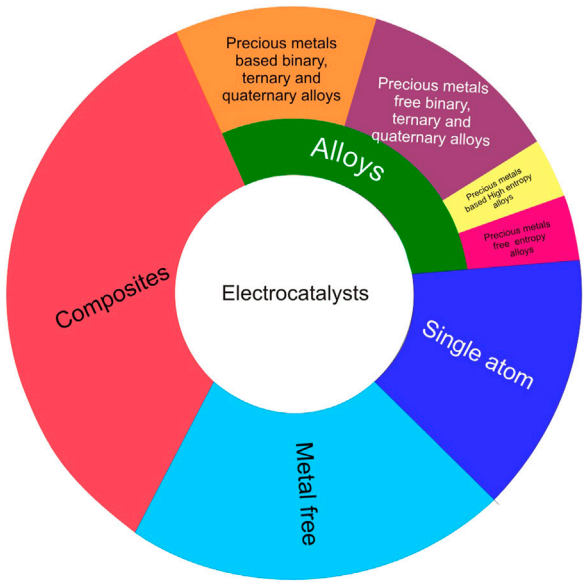

FIGURE 3
Electrocatalyst design strategies.

metal organic framework bimetallic electrocatalyst outperformed the electrocatalytic activity of commercial Pt–C catalyst for ORR in alkaline environment. It exhibited onset potential of 1.06V, half wave potential of 0.95 V and electrochemical stability of 30 mV after 1000 ORR cycles in 1.0 M sodium hydroxide solution. Chandran et al. (2018) adopted a single-step synthesis approach to develop Pd-Co alloy supported on reduced graphene oxide doped with nitrogen. The ORR activity of the electrocatalyst proceeded through the four-electron reaction pathway. The electrocatalyst showed 1.6 times enhanced mass activity when compared to the Pd-reduced graphene oxide doped with nitrogen. The electrocatalyst also recorded of power density of 68 $mWcm^{-2}$ with metal loading of 0.5 mg cm^{-2} at 60°C without any back pressure.

2.3 Alloy-based electrocatalysts

2.3.1 Bimetallic alloy electrocatalysts

Research findings have shown that alloying Pt with the d-block metals to form a bimetallic electrocatalyst could positively influence the stability and activity of Pt-C electrocatalyst in ORR of PEMFC (Seh et al., 2017; Sui et al., 2017). Literature also showed that the addition of a second metal to Pt-based electrocatalyst can prevent the adsorption of carbon-monoxide on the electrocatalyst's surface (Molochas and Tsiakaras, 2021; Lee et al., 2022b). In addition, such secondary metal addition could re-expose blocked sites on a poisoned Pt surface by oxidising the carbon monoxide thereby speeding up ORR kinetics (Zhang et al., 2021b; Lu and Elam, 2022). Owing to these characteristics, bimetallic electrocatalysts have been reported to exhibit comparatively better efficiency than Pt-C electrocatalyst due to their highly exposed surfaces (Bai, 2018; Huang et al., 2018; Wang and Spendelow, 2021). Guterman et al. (2018) prepared Cu_xPt-C electrocatalyst by successive deposition of copper and Pt on carbon support. The electrochemical performance of the Cu_xPt-C electrocatalyst was studied at ambient temperature in a three-electrode electrochemical cell with the help of CV using a rotating-disk as the working electrode. The results obtained were compared with that of commercial Pt-C catalyst. The study showed that the bimetallic electrocatalyst exhibited a combination of higher stability and mass activity values when compared with the commercial Pt-C catalyst with the same Pt loading. Ying et al. (2018) also developed a metal-organic framework Pt-Co bimetallic nanoparticles supported by hollow porous carbon capsules that were doped with nitrogen as highly active and durable electrocatalyst for ORR. The bimetallic catalyst was synthesised by wet chemistry method and was found to demonstrate outstanding ORR performance, with a mass activity that was 5.5 and 13.5 times better than those of commercial Pt/C and Pt/black catalysts respectively. Moreover, the catalyst exhibited better durability in terms of ECSA and mass activity when compared with commercial catalysts. The exceptional ORR performance of the catalyst was ascribed to the large surface area of bimetallic Pt-Co nanoparticles and hollow porous structure of nitrogen-doped carbon capsules. Although Pt has been widely alloyed with many transition metals and of recent lanthanides to form bimetallic electrocatalysts, they have not gain wide adoption for commercial application in fuel cell (Martínez-Hincapié and Čolić, 2022). However, it was reported that Pt-Co bimetallic electrocatalyst was recently use in commercial electric vehicle (Toyota Mirai) (Wang and Spendelow, 2021). The poor commercial patronage of Pt-based bimetallic electrocatalysts could be attributed to their susceptibility to poisoning by formic acid electrooxidation and dissolution into strong acids in working electrolytes, which lead to the loss of integrity of electrocatalysts and result in deterioration of catalytic performance. As a result, different electrochemical reaction pathways have different electronic structure requirements (Zhang et al., 2018; Mukherjee et al., 2022).

2.3.2 Trimetallic/ternary alloy electrocatalysts

To benefit from synergistic effect that can result from using three elements in trimetallic alloys, researchers have attempted to develop ternary alloy electrocatalysts for ORR in PEMFC (Wang et al., 2019c; Wang et al., 2020a; Zhu et al., 2020a). The introduction of a third element has proven to improve the lifespan of the parent bimetallic electrocatalyst at PEMFC operating conditions (Zhang et al., 2017). Hu et al. (2021) synthesised ternary platinum-based electrocatalyst using co-doping strategy. Cu and Co were co-doped into Pt-C to modulate the electronic structure of Pt in order to weaken the adsorption of deoxygenated species by Pt thereby enhancing the ORR kinetics. It was found that the trimetallic electrocatalyst exhibited better mass activity of 0.52 A mg_{pt}^{-1} and power density 1.15 Wcm^{-2}. Moreover, the mass activity of the ternary electrocatalyst only reduced by 8.3% after 30,000 cycles indicating comparatively good durability. Xiao et al. (2021b) reported a facile synthesis of carbon supported Pt-Cu-Fe nanoparticles trimetallic electrocatalyst for ORR in PEMFC. The authors found that the trimetallic electrocatalyst recorded a significant 0.99 A mg_{pt}^{-1} ORR activity at 0.9V potential and enhanced stability, losing only 7.6% of mass activity after 5000 durability cycles. Ma et al. (2022) developed a Pt-Ru-Te ternary electrocatalyst with only 11 at% of Pt for HOR in fuel cell. The electrocatalyst showed a current density of 30.6 $mAcm^{-2}$ at 50 mV and exchange current density of 0.426 $mAcm^{-2}$.

TABLE 2 Activities and durabilities of different electrocatalysts.

Electrocatalyst	Mass activity (A g^{-1})	Durability (Mass activity loss)	References
Commercial Pt/C	0.1	80% loss after 30,000 cycles	Liang et al. (2019)
Nanoparticle Pt/C	0.87	NA	Garlyyev et al. (2019)
$Pt_{26}Cu_{74}$ nanocrystals	0.74	21.2% after 1000 cycles	Huang et al. (2019)
Gallium-doped PtNi/C nanoparticles	1.24	12% after 15,000 cycles	Lim et al. (2018)
Pt supported on Mo-doped titanium nanotubes	0.10	No loss after 2000 cycles	Esfahani et al. (2018)
Nanoparticles Pt/TiO_2@CNT	0.36	No loss after 10,000 cycles	Kong et al. (2020)
$Ir_{23}Pd_{77}$/C	0.17	NA	Nguyen and Shim (2018)
Pt-Pd/C	0.15	Negligible loss after 10,000 cycles	Wu et al. (2019)
$Cu_{0.75}Fe_{0.25}$@Pt/C core-shell structure	0.91	11% loss after 10,000 cycles	Cao et al. (2020)
PtNiCo nanocage	1.03	NA	Ma et al. (2021)
PtNiRh nanowires	2.51	12.8% loss after 10,000 cycles	Li et al. (2018b)
AgCoCu oxides on reduced graphene oxide	0.04	No loss after 10,000 cycles	Madakannu et al. (2022)
$Pd_{59}Cu_{30}Co_{11}$ nanoalloy	1.01	No loss after 10,000 cycles	Li et al. (2018a)
Nanoparticle AlCuNiPtMn	3.47	No loss after 30,000 cycles	Li et al. (2020b)
Nanoparticle PtRuCuOsIr	0.86	50% loss after 15,000 cycles	Chen et al. (2015)
Nanoparticle PtPdCuNiCoAl	2.24	7.5% loss after 10,000 cycles	Qiu et al. (2019)

Furthermore, the electrocatalyst exhibited excellent stability with 5% loss in activity after 2000 durability circle.

The literature showed improvement in performance of ternary electrocatalysts in fuel cell application over their bimetallic counterparts, establishing the significance of ternary platinum based electrocatalyst in improving electrocatalytic performance. However, ternary electrocatalysts are also faced with the challenges of metal dissolution, agglomeration and carbon support corrosion. In addition, it is uncertain if the electrocatalyst will be able to replicate their excellent experimental activities in actual fuel cell operating conditions (Mukherjee et al., 2022).

2.3.3 Quaternary alloy electrocatalysts

Quaternary alloy has the potential to offer additional options that could improve electrocatalytic performance and durability than binary and ternary alloy electrocatalysts. However, it remains the least reported alloy-based electrocatalysts in literature (Du et al., 2022). Wang et al. (2019a) developed a quaternary structurally ordered Pt(Fe,Co,Ni) alloy electrocatalyst with equal proportion of constituent elements *via* a facile synthesis method that requires spray dehydration on a solid surface followed by annealing procedure. The electrocatalyst showed improved electrocatalytic performance towards ORR with mass activity 6.6 fold higher than that of commercial Pt/C with only 17% attenuation after 10,000 potential cycles at 0.9 V. Hornberger et al. (2022) synthesised an octahedral quaternary PtNi(RhMo) alloy electrocatalyst. The alloy electrocatalyst was prepared to control the shape of PtNi by co-doping it with Rh and Mo using solvothermal process. The electrocatalysts exhibited remarkable mass activity of 1.53 mg_{pt}^{-1}.

2.3.4 High-entropy alloy electrocatalysts

For centuries, alloying has been employed to impart desired material properties. It usually entails the addition of comparatively small quantities of secondary elements to the parent metal. However, for the past two decades, a new alloying approach has been in vogue that entails the combination of several key elements in high concentrations to create novel materials called high entropy alloys (HEAs) (George et al., 2019). HEAs have two definitions that are based on composition and configuration entropy, respectively. They are alloys that contain a minimum of five primary elements having respective atomic weight percentage between 5 and 35 based on composition. The entropic definition states that HEAs are alloys having configurational entropies at a random state greater than 1.5R, whether they are single or multiphase at ambient temperature; where R is gas constant (Yeh and Lin, 2018). HEAs have been recently used in catalysis because of their exceptional benefits, which include high tolerance, complex surface and adjustable composition (Li and Chen, 2021). They have gained wide acceptance as catalysts in electrochemical reactions due to their ability to catalyse different reactions. Such reactions include but are not limited to nitrogen reduction reaction (NRR), alcohol oxidation reaction (AOR), oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and carbon dioxide reduction reaction (CO_2 RR) (Zhang et al., 2022). HEA catalysts characteristics that distinguished them from other catalysts have been highlighted as their multiple combinations of elements located next to each other, which results in tailorable active sites. In addition, it was emphasised that their non-typical electrochemical behaviour made them a distinctive class of catalyst materials that are promising as a better alternative to other catalysts (Löffler et al., 2019). The application of HEAs in ORR is being researched to improve the

TABLE 3 Summary of recent works on Pt-based electrocatalysts for ORR.

Electrocatalyst	Research aim	Activity (A mg $^{-1}$)	Durability	Reference
Au@Pt nanoparticles	Development of nanoparticles Au@Pt core-shell structure to mitigate the instability of Pt nanoparticles electrocatalyst used in ORR.	0.35	Less than 5% loss after 10,000 potential cycles	Chung et al. (2020)
Pt/TiO_2@CNT nanoparticles	Synergistic combination of the high surface area of carbon nanotube, excellent conductivity and stability of TiO_2 nanoparticles and high activity of dispersed Pt nanoparticles for ORR.	0.36	No loss in activity after 10,000 potential cycles	Kong et al. (2020)
Pt/SnO_2-C nanocomposite	Modification of the electronic properties of Pt nanoparticles by selectively depositing it on SnO_2 nanoclusters formed on carbon surface	0.07	No loss after 2000 potential cycles	Hussain et al. (2019)
Pt@COF (covalent organic framework)	Development of Pt nanoparticles anchored on nitrogen-rich covalent organic framework for ORR.	Onset potential of 1.04V and half-wave potential of 0.89V	Current density drops by 4% of its initial values after 50 h of operation	Zhai et al. (2020)
Pt-N-S-pCNFs hybrid	Preparation of ultrafine Pt nanoparticles supported on sulphur and nitrogen codoped porous carbon nanonanofibers as electrocatalyst for ORR, OER and HER.	Recorded onset potential of 1.02 eV and half-wave potential of 0.83 eV	10.5% loss in current density after 10,000 s	Chen et al. (2022b)
PtM_3/C ordered intermetallic M = Fe, Co, Ni	Development of low-Pt ordered intermetallic on carbon support electrocatalyst	$PtCo_3$ exhibited mass activity of 0.74 A mg $^{-1}$	9% loss in mass activity after 10,000 potential cycles	Wang et al. (2019b)
Pt@CNT	Determination of effect of different particle sizes of Pt (1.5nm, 3nm and 6 nm) on the performance of Pt supported on carbon nanotubes electrocatalyst for HER and ORR.	The electrocatalyst with 3 nm particle size showed optimal ORR mass activity of 0.03 A g $^{-1}$	16% loss in initial value of current density after 15000s test	Ma et al. (2020b)
Pt/C nanoparticles	Investigation of effect of mesoporous carbon support on ORR activity and stability of nanosized Pt/C electrocatalyst	0.15	10.9% loss of ECSA in half cell test	Xie et al. (2022)
Pt/C nanoparticles	Study the effect of Pt(100) and Pt(111) orientations on the ORR properties of different nanosized Pt/C electrocatalyst (3 – 7 nm)	4.6 nm with Pt(100) crystallographic orientation exhibited the optimum ORR of 0.05 Ag $^{-1}$	NA	Erikson et al. (2022)
Pt_3Ni nanowires	Development of 1 nm thick bimetallic alloy nanowire as durable electrocatalyst for ORR.	0.55	67% mass activity loss after 50,000 potential cycles	Gong et al. (2019)
Pt_3Co-Mo nanowires	Preparation of Molybdenum doped Pt-cobalt bimetallic alloy nanowire as efficient electrocatalyst for ORR.	0.84	24% loss in mass activity after 50,000 potential cycles	Deng et al. (2022)

cathodic sluggish kinetics that limits the reliability of PEMFC. This is because HEAs emerged as materials that are capable of overcoming the limitation of Pt and Pt group metals (PGM) catalysts (Martínez-Hincapié and Čolić, 2022). Wu et al. (2020) studied the catalytic behaviour of the six PGM as self-supported HEA catalyst synthesised by wet chemistry method for ethanol oxidation reaction and found that the HEA exhibited variety of adsorption sites on its surface, which can catalyse many complex reactions. The PGM HEA catalyst's intrinsic mass activity was also compared with those of commercial palladium-C, palladium-black and Pt-C catalysts and found to be 2.5, 6.1 and 12.8 times higher than the intrinsic mass activity of the commercial catalysts, respectively. Lee et al. (2022a) synthesised IrPtPdRuRh HEA electrocatalyst by plasma ionic liquid reduction and showed excellent hydrogen evolution reaction catalytic performance with overpotential of 60 mV at a current density of 10 $mAcm^{-2}$. The electrocatalyst also recorded a Tafel slope of 42 mV dec^{-1} in alkaline electrolyte and demonstrated good stability for 6 h at a high constant current density of 100 $mAcm^{-2}$ without appreciable decay. The HEA nanoparticles were deposited on a carbon support. Qiu et al. (2019) synthesised senary AlNiCuPtPdAu octonary AlNiCuPtPdAuCoFe and senary all-non-noble metal AlNiCuMoCoFe nanoporous HEAs using a route that combined bulk melting and fast cooling followed by dealloying. The nanoporous HEA with low Pt loading exhibited 10 times mass activity when compared with commercial Pt-C catalyst for ORR and maintained 92.5% of its initial activity after 100,000 electrochemical cycles. It was also discovered that, unlike binary alloy system, HEAs exhibited high stability under electrochemical cycling conditions. An attribute that made them promising electrocatalysts for PEMFC. Furthermore, to explore catalytic potentials of PGM–free HEAs in ORR, Nandan et al. (2022) reported a facile method that combines wet chemistry and pyrolysis to synthesise FeCoNiMnCr HEA nanoparticles grafted on nitrogen-doped carbon nanotubes. The electrocatalyst designed for electrochemical ORR utilised the synergy between nitrogen-doped carbon nanotubes and HEA nanoparticles to promote improved performance in the ohmic polarization region of fuel cells when compared with commercial Pt-C electrocatalyst. Moreover, the FeCoNiMnCr-based catalysts exhibited better ORR performance compared to various newly reported transition metal-based conventional catalysts. In another research, Liu et al. (2021)

synthesised CoCrFeMnNi HEA nanoparticle-activated carbon nanocomposites electrocatalyst. The electrocatalyst was fabricated by impregnation–adsorption method of precursor salt solution followed by calcination. The HEA-activated carbon electrocatalyst performed excellently in the degradation of methylene blue at a comparable rate with those of other catalysts. The exceptional efficiency was because of the coupling effects of the solid-solution structure of HEA nanoparticles and the large specific surface area and considerable reaction channels of the activated carbon. In addition, HEA nanoparticles embedded in distinctive porous structure accelerated the mass transport and the electron transfer as nanoscale galvanic cells in the active bond splitting of methylene blue.

Most conventional alloys are made up of a single element with various alloying elements added to improve the properties of the principal element, forming an alloy family based on the principal element (Tsai and Yeh, 2014). HEAs were thought to be complex because they contained more than four primary elements and complex phase diagram systems that are often unavailable. As a result, the majority of HEAs earlier reported were created using the traditional trial-and-error method (Zhang et al., 2012). However, as the design of high entropy alloys progresses, several design routes have emerged which include the use of alloys design principles of materials science, building on promising binary or ternary alloy systems, the use of combinatorial material synthesis technique, Taguchi optimisation method and material science computational methods such as finite element, molecular dynamics, simulation, phase computation (PHACOMP) and calculation of phase diagram (CALPHAD) (Yeh, 2013). Wen et al. (2019) used material design strategy that combines machine learning model and experimental algorithms to determine high entropy alloys with high hardness in AlCoCrCuFeNi alloy system. Several alloys with hardness values that are 10% higher than the best original data set were fabricated using only seven experiments. In another study, Floriano et al. (2020) designed equiatomic TiZrNbFeNi and non-equiatomic $Ti_{20}Zr_{20}Nb_5Fe_{40}Ni_{15}$ high entropy alloys *via* thermodynamic calculations using CALPHAD. The alloys were fabricated by arc melting technique and showed small amount of cubic phases and C14 laves phases with $(Zr,Ti)_1$, $(Fe,Ni,Nb, Ti)_2$ constitution.

2.3.4.1 High-entropy alloy-based composites

HEA composites are emerging advanced materials that are produced by dispersing reinforcing phases (usually ceramics, whiskers or fibers) in multi-principal element metal matrix to improve their desired properties from the standpoint of dispersion strengthening mechanism (Liu et al., 2019; Zhu et al., 2020b; Wang et al., 2021b; Wang et al., 2021c). The reinforcing phase may be coated to prevent its chemical reaction with the matrix (Sharma et al., 2020). It is noteworthy that the use of HEAs as matrix in metal-based composites is still in the early stage (Sun et al., 2022). HEAs usually contain multi-principal elements in high concentration, thereby hindering their industrial application as bulk materials because of their higher cost compared to the conventional alloys (Fu et al., 2017; Wang et al., 2021b). However, their application as coatings have received considerable research interest because of the wide field of application and relatively cheaper cost of thin films (Li et al., 2018c). However, the hardness of HEAs coatings is usually relatively low, hence, their application as coatings requires enhanced hardness and wear resistance, which could be achieved by the addition of hard phases (Wang et al., 2021b; Guan et al., 2021). Wang et al. (2021b) prepared a HEA composite coating from titanium powder, C_3N_4 powder and $Cr_{20}Cu_{20}Fe_{20}Ni_{20}Al_{20}$ by plasma transfer arc cladding technique and studied the hardness, wear properties and microstructural features of the HEA composite coating using microhardness tester, dry wear test multifunctional tribometer, SEM, TEM and EDS. The results showed that the microhardness of the composite coating was 3.33 and 127.4 times higher than those of the Q235 steel substrate and the unreinforced HEA. The wear resistance of the composite coatings was 3.03 and 8.06 times greater than the monolithic HEA and the Q235 steel substrate. The coating exhibited good interfacial bonding with the substrate. Microstructural examination revealed that the coating contains body-centred cubic matrix grains with intergranular cuboidal nanoprecipitates that have face-centred cubic Ti(C, N) particles distributed along its grain boundary and a small quantity of face-centred cubic Cu–rich phase around the intergranular nanoprecipitate. A core-shell structure was observed in the nanoprecipitates, with the core rich in nitrogen and the shell found to be carbon-rich. Along the same line, Zhu et al. (2020b) developed TiN and Al_2O_3 reinforced CoCrFeNiMn HEA composite through the plasma cladding method. The reinforcements were prepared from high purity commercial Al, TiO_2 and BN precursors. The microstructure, chemical composition, hardness and wear properties were determined using field emission scanning electron microscopy, EDS, XRD, Vicker hardness tester and multi-functional tribometer. The microstructural examination revealed that the as-developed coating has a single face-centred cubic phase with TiN–Al_2O_3 as crystal dendrites associated with the Cr-B rich interdendritic phase. The hardness and wear resistance of the HEA composite coating were compared with those of the pure HEA and found to be 17.6% and 12.5% better. It was found that the reinforcing phases play significant roles in restricting the adhesive wear and encouraged the steady-state friction of the HEA composite coating throughout the sliding process. Cui et al. (2022) produced a corrosion resistance CeO_2 reinforced FeCoNiCrMo HEA composite coating by laser cladding technique. The composite coating was developed for TC4 titanium alloy surface coating. The morphology, microhardness and corrosion resistance of the composite coating were investigated using XRD, EDS, SEM, Vickers hardness tester and electrochemical workstation. The result revealed that the introduction of the CeO_2 powder to the HEA matrix reduced the coating sensitivity to crack. In addition, the introduction of the reinforcing phase to the HEA matrix did not change its body-centred cubic phase structure. Moreover, the microstructural examination showed that the CeO_2 was evenly distributed at the grain boundary, thereby refining the grains. This phenomenon improved the strength and toughness of the HEA composite coating. Due to this improvement, the microhardness of the coating increased 2.7 times than that of the TC4 titanium alloy substrate. The corrosion behaviour of the substrate, pure HEA and composite coating were examined, and

TABLE 4 Alloy-based electrocatalyst and their composites.

Electrocatalyst	Research aim	Fabrication method	Activity	Durability	Reference
CoNi@N-GCNT	Production of transition metal-based CoNi alloy supported on nitrogen-doped graphite carbon nanotube	Freeze drying	Onset potential of 0.9V and half-wave potential of 0.84V	No loss in current density after 10,000 potential cycles	Niu et al. (2021)
Ti_4O_7/Mxene	Development of non-precious metal-based nanocomposite electrocatalyst	Hydrothermal followed by carbothermal reaction	Onset potential of 0.91V and half-wave potential of 0.72V	35% loss in current density after 80,000 s	Wei et al. (2023)
PdNi nanowire	Synthesis of untrathin PdNi nanowire as electrocatalyst for ORR.	Hydrothermal reaction	Exhibited half-wave potential of 0.95V	29% ECSA loss after 200,000 potential cycles	Sahoo et al. (2022)
PdBP	Preparation of ternary alloy nanosphere as electrocatalyst for ORR.	Soft templating synthesis	Recorded mass activity of 1.45 mg_{pd}^{-1}	32.1% loss in mass activity after cycling for 5000s	Lv et al. (2019a)
MnO/CoMn@N-doped graphite composite	Fabrication of CoMn alloy coated with nitrogen doped carbon and MnO as composite electrocatalyst for OER and ORR.	Annealing of prusian blue analogue	Onset potential of 0.91V and half-wave potential of 0.76V	16% loss of its initial current density after continuous operation for 40000s	Deng et al. (2019)
$Fe_2Co_2Ni_2$/N-CNT	Development of ternary transition metal alloy embedded nitrogen doped carbon nanotube as electrocatalysts for ORR.	Solvothermal synthesis	0nset potential of 0.81V and half-wave 0.75V	4.5% loss in current density after 25000s cyclic test	Wang et al. (2021d)
Rh2.6Fe3Co2.6@NG	Synthesis of bifunctional rhodium, iron and cobalt alloy nanoparticles electrocatalyst anchored on nitrogen doped graphene for HER and ORR.	Sequential annealing and substitution reaction	Onset potential of 0.98V and half-wave potential of 0.82V	Positive shift in half-wave potential by 9 mV after 5000 cycles	Jiang et al. (2021)
$Pt(Fe,Co,Ni)_3$/C	Production of low Pt structurally ordered quaternary alloy electrocatalyst for ORR.	Spray dehydration and annealing process	Exhibited mass activity of 3.189 mA μg_{Pt}^{-1}	17% loss in mass activity after 10,000 potential cycles	Wang et al. (2019a)
PtNiRhMo nanoalloy	Preparation of octahedral shaped PtNi doped with rhodium and molybdenum as electrocatalyst for ORR.	Solvothermal synthesis	Recorded mass activity of 1.53 A g_{pt}^{-1}	NA	Hornberger et al. (2022)
PtFe/Pt intermetallic compound	Preparation of atomically ordered Pt-based intermetallic compound as electrocatalyst for ORR.	Wet impregnation method	Exhibited mass activity of 0.92 A mg_{pt}^{-1}	24% loss in mass activity after 10,000 potential cycles	Song et al. (2022)
$FeNi_3$@NC intermetallic compound	Development of intermetallic compound embedded in nitrogen doped carbon as bifunctional electrocatalyst for OER and ORR.	Freeze drying followed by annealing	Recorded 0.86V half-wave potential	Positive shift in half-wave potential by 6 mV after 3000 cycles	Chen et al. (2020)
Pt_5La intermetallic compound	Alloying Pt with early transition metal to produce intermetallic compound as durable electrocatalyst for ORR.	Solvothermal method	Exhibited mass activity of 0.49 A mg_{pt}^{-1}	Loss 6.1% of initial value of mass activity after 30,000 potential cycles	Zhu et al. (2022)
FeCoNiMnCr@N-CNT	Development of FeCoNiMnCr HEA nanoparticles grafted on nitrogen-doped carbon nanotubes as efficient electrocatalyst for ORR.	Solvothermal method	Onset potential of 0.95V and half-wave potential of 0.8V	10% loss in initial value of current density after 14 h of continuous operation	Nandan et al. (2022)
FeCoNiCuMn/NCNS	Utilization of the synergistic effect of HEA nanoparticles formed on nitrogen doped carbon nanosheet as bifunctional electrocatalyst of nitrite sensing and ORR.	Confinement growth method	Half-wave potential of 0.87V	Negligible loss in initial value of current density after 3000 potential cycles	Gao et al. (2022)
AlCuNiPtMn nanoparticles	Fabrication of self-supported AlCuNiPtMn nanoparticles HEA as durable electrocatalyst for ORR.	De-alloying method	Exhibited mass activity of 3.5 A mg^{-1}	No loss in mass activity after 30,000 potential cycles	Li et al. (2020b)

it was found that corrosion products were deposited on the TC4 titanium substrate. Pitting corrosion was observed in the pure HEA, however, the addition of CeO_2 enhanced the formation of higher density of stable passive film that significantly inhibited the pitting corrosion.

The use of HEA composites as coatings has been considerably explored, however, their application for catalytic purposes which are equally a surface phenomenon have not been well investigated. Hence, the authors of this review are currently investigating the potentials of HEA composites as self-supported electrocatalysts for ORR in PEMFC.

Table 4 summarises alloy-based electrocatalysts and their composites.

2.4 Single-atom electrocatalysts

This is a novel brand of electrocatalyst represented by the acronym M-N-C, where M is usually a transition metal and N-C is carbonaceous material doped with nitrogen (Xu et al., 2018). The electrocatalyst has shown promising optimum atomic efficiency, outstanding intrinsic activity, high electrical conductivity, large surface area, well-defined structure with composition and configuration that can serve as an alternative substitute to the pricy precious metal-based electrocatalyst for ORR in PEMFC (Han et al., 2020; Zhang et al., 2020; Zhang and Guan, 2020; Chen et al., 2021). Single-atom electrocatalyst is synthesised by the pyrolysis of transition metal with doped-carbonaceous materials, a process that covalently anchors well dispersed metal particles at an atomic scale on suitable support. The resulting electrocatalyst thereby exhibit exceptional activity and stability for specific reaction (Hou et al., 2020a). The multiscale tunability of a single atom electrocatalyst facilitates increasing active sites density with enhanced activity, stability, anti-poisoning properties and ultra-high affinity for oxygen (Zhu et al., 2018). (Yang et al., 2019) synthesised two-dimensional conjugated single atom electrocatalyst consisting of 10 wt% iron and 0.73 wt% cobalt atoms anchored on phthalocyanine macrocycles. The electrocatalyst was synthesised by pyrolysis-free one step ball milling of polyphthalocyanine and showed excellent ORR mass activity of 47 mAmg $^{-1}$ that was 6.4 times superior to that of commercial Pt/C with no appreciable loss in stability after 100 h of operation. Ding et al. (2020a) designed and synthesised an atomically dispersed Fe-N_4/C single atom electrocatalyst *via* an organic solution esterification process followed by melamine treatment to introduce nitrogen and restrict the migration of metal particles. ORR test was conducted on the single atom electrocatalyst and revealed a half-wave potential of 0.78 V. The electrocatalyst also showed a 17% loss in current density after 7 h of continuous polarization in acidic condition. (Xu et al., 2021). developed a single atom copper anchored on graphite foam doped with sulphur and nitrogen synthesised through underpotential deposition strategy. The single atom electrocatalyst showed outstanding ORR activity recording half wave potential of 0.862 V with calculated mass activity of 5.71 Amg_{Cu}^{-1}. The stability test revealed that the electrocatalyst retains 98% of its initial current density after 20,000s under continuous potential of 0.85 V. Chen et al. (2020) reported a single atom tungsten dispersed on nitrogen doped carbon nanosheet produced by modulated pyrolysis method. The electrocatalyst showed notable electrocatalytic activity with half wave potential of 0.88 V and mass activity of 0.63 Amg^{-1} at 0.9 V. The electrocatalyst only loss 13.9% of its mass activity after 10,000 sweeping cycles of cyclic voltammetry durability test. Wan et al. (2019) developed a concave Fe–N–C single-atom catalyst possessing an enhanced external surface area and porosity. The Concave-shaped Fe–N–C electrocatalyst was synthesised by preheating mesoporous SiO_2-coated ZIF-8 (Z8) metal-organic framework at 650°C under argon-controlled atmosphere, the silica layer was etched off to form a concave-shaped host having a negative zeta potential and larger micropores. The electrocatalysts displayed high current density of 0.047 A cm $^{-2}$ at 0.88 V under 1.0 bar H_2–O_2 that stems from the high density of active sites, which was achieved by exposing Fe–N_4 moieties and enhanced mass transportation of the mesoporous electrocatalyst. Furthermore, Zhu et al. (2021) reported a nitrogen doped carbon embedded rare-earth single-cerium-atom metal–organic framework electrocatalyst. The electrocatalyst was synthesised *via* hard–template approach and showed comparable ORR activity but inadequate stability to that of commercial Pt–C catalyst in PEMFC application. The result of the study revealed half-wave potential of 0.862 V in ORR and 0.525 W cm $^{-2}$ power density under 2.0 bar hydrogen–oxygen in fuel cell test.

2.5 Metal-free electrocatalysts

Heteroatom-doped carbon materials have demonstrated excellent ORR activity that is comparable or even better than that of commercial Pt-C electrocatalyst because of their extraordinary large specific surface area, good electrical conductivity and excellent durability under unfavourable conditions (Hu and Dai, 2019; Ma et al., 2019). Research progress have been made in developing highly stable and durable heteroatom-doped advanced carbon electrocatalysts such as iodine-doped graphene (Marinoiu et al., 2018), boron-doped carbon nanotube or graphene (Sawant et al., 2022), sulphur-doped graphene (Garino et al., 2021) and phosphorus-doped graphite layers (Shimoyama et al., 2015). It was also observed that doping advanced carbon materials with more than one heteroatom showed better ORR activity (Gao et al., 2019). For instance, Sun et al. (2018) co-doped carbon nanomaterial with boron and nitrogen to produce a very active, stable and inexpensive metal-free bifunctional electrocatalyst for ORR and OER. The catalyst was prepared by pyrolysis of precursors under ammonia atmosphere and exhibited excellent activity and stability for both ORR and OER. The catalyst showed an onset potential of 0.98 V for ORR in alkaline medium, which is similar to that of Pt-C catalysts. On the other hand, the onset potential recorded in acidic medium was 0.81 V for a 4–electron transfer process. The outstanding performance of the catalyst was attributed to the joint positive effect of rich carbon defects and the heteroatomic co-dopants. Duraisamy et al. (2022) synthesised a nitrogen-sulphur dual heteroatom doped mesoporous carbon electrocatalyst using 2D amorphous silica as support material and L-cysteine as nitrogen and sulphur precursor. The electrocatalyst showed high concentration of defective sites on the surface of the mesoporous carbon that favours improved ORR performance with onset potential of 0.78 V, half-wave potential of 0.68 V and current density of 2.8 $mAcm^{-2}$. Li et al. (2020a) co-doped porous carbon with nitrogen and sulphur for ORR and CO_2RR catalytic applications. The electrocatalyst was prepared by pyrolysis of glucosamine hydrochloride and thiocyanuric acid precursors using hard silica dioxide templates. The co-doped carbon electrocatalyst showed enhanced activity and selectivity with the porous structure exposing abundant active sites to reaction species which resulted in increased activity of the electrocatalyst. The authors reported that the electrocatalyst exhibited excellent ORR

activities in both acidic and alkaline media and is suitable for PEMFC application.

Despite the significant research progress in developing advanced carbon based electrocatalysts, the fundamental understanding of the doping effects and structural diversity of such catalysts remain unclear, particularly in terms of the molecular structures of active sites and the specific doping effects that control electrocatalytic reactions (Zhu et al., 2020c; Wu et al., 2021; Chattopadhyay et al., 2022). Many factors hinder the understanding of these phenomena, which include the sophistication of reactions at electrochemical interfaces; a lack of efficient strategies for precisely controlling the structures of active sites for directing catalytic reactions; and troubles inspecting and understanding the electrode-electrolyte interfaces through direct *in situ* observations. (Hu and Dai, 2019; Lai et al., 2022).

2.6 Catalyst supports

Most electrocatalysts used in fuel cell rely on support materials for mass transfer and water management (Ziv et al., 2018). Loading the electrocatalyst on high surface area support enhanced its catalytic activity and durability by increasing its electrochemical surface area (Hou et al., 2020b). Many carbon-based materials such as graphene, carbon nanotube, carbon black and mesoporous carbon have been used as catalyst supports due to their high surface area and electrical conductivity (Qiao et al., 2019). However, due to carbon corrosion that leads to the loss of ECSA, other electrocatalysts support materials such as transition metal oxides, carbides and nitrides have been adopted because of their excellent stability in harsh conditions (Samad et al., 2018). The presence of surface functional groups that promote catalyst support interaction, corrosion resistance, low surface poisoning, electrochemical stability, high electrical conductivity, a large surface area and a porous structure that improves the triple phase boundary are the characteristics of a good catalyst support material (Fashedemi et al., 2022). Asset et al. (2018) attempted to improve the ORR kinetics by investigating the effect of carbon supports' structure, texture and chemistry on the morphological properties, stability, and ORR activity of porous hollow Pt-Ni nanoparticles carbon black, carbon nanotubes, graphene nanosheets, and carbon xerogel. The nanomaterials had varying degrees of graphitisation, surface areas, and surface functionalisation. The inner and outer diameters of the supported porous hollow Pt-Ni/C nanoparticles were found to decrease as the surface area of the carbon mesopore increased. Despite their differences, the nanomaterials demonstrated comparable morphological properties and electrocatalytic activities for the ORR. The simulated electrochemical potential of PEMFC was used to evaluate the stability of the synthesised electrocatalysts. Identical location transition electron microscopy (IL-TEM) and electrochemical method showed that degradation in carbon nanotube, carbon xerogel and graphene nanosheet were by carbon corrosion to carbon dioxide while carbon black showed carbon surface oxidation to carbon monoxide. Souza et al. (2018) added niobium pentoxide (Nb_2O_5) and tungsten carbide (WC) separately to Pt/C electrocatalyst by impregnation method followed by heat treatment to modify its carbon content for improved stability. Both modified electrocatalysts were analysed by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), IL-TEM and cyclic voltammetry (CV). Results of the analyses were compared with those of commercial Pt/C electrocatalyst. The authors found two phenomena that led to ECSA loss in the electrocatalysts; which are Pt particle agglomeration and the loss of catalyst materials due to the degradation of carbon support. It was observed that WC addition increased the electrocatalyst particles' corrosion and detachment, however, the addition of Nb_2O_5 was more effective in improving the Pt/C electrocatalyst stability. More so, Yuan et al. (2022) synthesised a dandelion-like structured titanium nitride nanospheres as a non-carbon-based catalyst support for Pt nanoparticles, which were deposited on the dendritic structured titanium nitride by an electrochemical pulse deposition method. The catalyst recorded ORR mass and specific activity of 0.44 mA g^{-1} and 0.33 mA cm^{-2} at 0.9 V. At similar test conditions, the catalysts demonstrated superior stability to the commercial Pt/C catalysts recording 61% of the initial activity after 3000 repeated runs. In another study, Islam et al. (2019) attempted to address the carbon corrosion problem by developing a silica-coated carbon nanofibers catalyst support for Pt particles. Platelet-type carbon nanofibers were uniformly coated with silica using the hydrolysis method. Thereafter, the Pt was then deposited on the silica coating rather than carbon nanofibers. Accelerated degradation test was conducted on the silica-coated carbon nanofibers Pt catalyst and the result showed that the silica coated catalyst was more durable than Pt/C nanofibers catalyst under potential cycling. After 30,000 potential cycles, it was observed that silica coated carbon nanofiber catalyst lost 11% of its ECSA, while the loss of ECSA recorded by its uncoated Pt/C nanofiber counterpart was 21%.

3 Conclusion and recommendation

This review clearly showed that various authors asserted that the state-of-the-art Pt/C electrocatalyst typically impose cost ineffectiveness on PEMFC. In addition, Pt/C electrocatalyst suffers from rapid degradation during prolonged PEMFC operation, thereby, posing significant reliability challenge of the device. The rapid degradation is attributed to the dissolution, migration or aggregation of Pt as well as the carbon support corrosion leading to ECSA loss of the electrocatalysts and the eventual deterioration of electrocatalyst's activity during long-term operation. Many studies have been conducted to unveil other low-cost materials that can serve as active catalyst constituents to augment or replace the precious metal loading in the state-of-the-art electrocatalyst used in PEMFC. Efforts have also been made to modify or replace the carbon support with other corrosion resistance and highly stable materials. In the light of these, the following recommendations are made for further research in various emerging electrocatalysts:

1. Bimetallic, ternary and quarterly alloys electrocatalysts serve a pivotal role as emerging electrocatalysts for ORR in PEMFC. Significant progress has been made in the fabrication and characterisation of these alloys. However, the effective control of their composition, morphology and particle sizes could pave a

way for their commercial application in PEMFC. An understanding of the tunability of elemental composition, morphology and particles size could be used to control these alloys' microstructures thereby positively influencing their activity and stability towards ORR in PEMFC. Tuning alloy electrocatalyst composition has significant effect on its ORR activity and stability. Consequently, effect of elemental composition and ratios on various alloy electrocatalyst could be investigated. Some researchers have asserted that the ORR mass activity of alloy-based electrocatalyst is inversely proportional to its particle size, therefore, advancing design strategy to fabricate nanostructured alloy electrocatalysts could expose more active sites thereby improving catalytic mass activity. To investigate the assertion that alloy electrocatalyst activity has direct correlation to its particles shape, the effect of different particle shapes on various alloy electrocatalyst could be studied. In addition, considering a preferred crystallographic orientation for alloy particles in electrocatalyst can be a promising strategy for achieving its high performance for ORR in PEMFC.

2. HEA electrocatalysts have been suggested to be promising candidates that will address the existing limitations in the state-of-the-art electrocatalyst. However, their complex catalysts' structure-activity relationship still needs to be unravelled. In addition, only a small portion of the compositional space of HEAs has been investigated, therefore, there exist a vast possibility of HEA electrocatalysts to be explored. Understanding elemental interactions in HEAs is also necessary in order to predict suitable elemental combinations for PEMFC catalytic application. Research is required to determine the compositional limits of elemental choices needed for specific phase formation in HEA electrocatalysts. The effect of each element on the stability of HEA electrocatalysts need to be studied, as well as how to tune each element to achieve physical or chemical stability. Furthermore, the synergistic interactions between HEA and emerging electrocatalyst support materials can be investigated by developing their self-supported HEA-based composite electrocatalysts. More so, heteroatoms such as nitrogen, boron, sulphur and phosphorus could be introduced into the interstices of transition metals based high entropy alloys to offer the advantages of a self-supported electrocatalysts with surface that enhances accelerated electron transfer, high activity and stability that can meet PEMFC performance requirements at low cost.
3. Single atom electrocatalysts have the potential of offering high density of active sites that could speed up the sluggish kinetics of ORR in PEMFC. However, the research progress of this emerging electrocatalyst still needs to be consolidated in the areas of its synthesis and characterisation to achieve its commercial application in PEMFC. Synthesis of single atom electrocatalysts require expensive precursors and equipment, hence, there is a need to find alternative low-cost precursors and facile synthesis method for the large-scale commercialisation of the electrocatalyst. In addition, developing porous support materials that will enhance accessibility to single atom actives sites could greatly enhance the electrocatalysts activity and stability. More so, the support materials should possess high conductivity and corrosion resistance to address the undesired Fenton reaction that characterises single atom electrocatalyst in acidic medium. Designing and synthesising single atom electrocatalyst with dual adjacent metal atoms could result in synergistic effect that significantly improve the ORR activity and stability. Lastly, there is a need for *in situ* characterisation techniques for single atom electrocatalyst to identify and understand the central metal interactions with oxygen containing species at electrocatalyst working potential conditions.
4. The catalytic properties of metal-free electrocatalyst is based on doping carbonaceous materials with heteroatoms which serve as defects that enhance promising catalytic performance. Developing metal-free electrocatalyst with hierarchical porous structure could be beneficial in providing multiple active sites, however, there is a need for facile fabrication techniques for this structure due to the uncontrollability of the pyrolysis process currently used in its synthesis. Further research is required to understand the nature of the active sites in the emerging electrocatalyst to facilitate its future large-scale commercialisation and catalytic application in PEMFC. Sophisticated *operando* characterisation techniques such as the use of *in situ* equipment or on-line monitoring are required to unravel the nature of the active sites in this electrocatalyst in order to gain insight on the requirements for its structure-activity and stability correlations and the improvement strategies that will engender its commercial application in PEMFC.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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