



Recent advancements on non-platinum based catalyst electrode material for polymer electrolyte membrane fuel cells: a mini techno-economic review

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Abstract. The crucial component involved in a polymer electrolyte membrane (PEM) fuel cell stack is the catalyst electrode material which performs a significant role in reaction kinetics and subsequently on the performance. Recent days have given impetus to the advancements of a relatively cost-effective, yet high-performance electrocatalyst for PEM fuel cell application. Qualitative studies reveal that significant advancements in the stability and activity of non-platinum electrocatalysts were achieved that could make a significant contribution on commercializing the PEM fuel cells in a vast scale. The present paper reviews the non-platinum-based electrode materials used for PEM fuel cell in the past seven years (2015–2021) and also envisages on the role of novel cost-effective electrode materials. In addition, the paper also provides a critical snapshot on the advancements of the PEM fuel cell electrode materials in diverse operating environment.

Keywords. PEM fuel cell; electrodes; non-platinum catalysts; carbon; oxygen reduction reaction (ORR).

1. Introduction

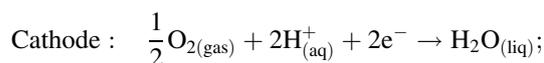
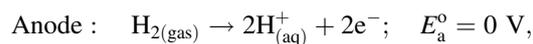
Energy and environment are mutually interdependent constituents that lead to a sustainable development [1]. A relatively highly efficient and sustainable energy system must be both cost-effective and must also produce minimal harmful emissions. The limitation with the most credentialed renewable platforms, such as solar and wind energy power systems, is because of the discrepancy between energy supplies and demands [2–6] due to their intermittent operation nature. Fuel cells are sustainable and reliable energy systems which operate on hydrogen (cleanest fuel) and are potential alternatives to the noxious fossil fuel-based [7,8] generators. Due to lack of combustion or emission, there is tremendous electrical efficiency than conventional generators of parallel size and rating [9–14]. Various types of fuel cell technologies are polymer electrolyte membrane fuel cell (PEMFC), solid oxide fuel cell (SOFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC) and molten carbonate fuel cell (MCFC) [15–17]. Among these fuel cell technologies, PEM fuel cells are widely used owing to their distinct features, such as quick startup, low-operating temperatures (60 to 80°C), dynamic response and high power density [18]. In addition, PEM fuel cell has significant implications on a nation's economy by reducing their rely on imported crude oils and thereby strengthening the energy security [19].

1.1 Components and principle of PEM fuel cell

PEM fuel cells comprise multiple layers of composite materials. Following are the key components of a PEM fuel cell illustrated in figure 1 [20].

1.1a *Membrane* The membrane (proton conducting) is a uniquely engineered material that appears to be modified Teflon used in home kitchen. The membrane conducts only the positive ions and blocks the electrons [21,22]. Being the integral PEM fuel cell component, the membrane allows only appropriate ions (positive ions) to flow from anode to cathode [23].

1.1b *Catalyst layer*: Catalyst layer (CL) is the core constituent in PEM fuel cell that drives the electrochemical kinetics and activity [24]. Hydrogen fed at anode catalyst-side is oxidized and generates electrons and protons (hydrogen ions). On the contrary, the oxidant is fed to cathode catalyst-side on another side where the reduction takes place. A PEM fuel cell's anode and cathode reactions are as follows:



$$E_{\text{c}}^{\circ} = 1.23 \text{ V}.$$

The optimal standardized potential (E°) for a PEM fuel cell at 298 K reaction kinetics is 1.23 V for liquid water as by-product and 1.18 V for gaseous water as by-product.

1.1c *GDL*: The gas diffusion layer (GDL) electrically interconnects with the current collector and the catalyst layer to facilitate the reactant transport to the electrocatalyst site. In addition, the GDL also aids in the removal of product water [25]. It usually comprises of two layers, namely hydrophobic layer made up of polytetrafluoroethylene (PTFE) and macroporous layer which is made up of carbon paper/carbon cloth concealed with the microporous layer. Reactant gases diffuse through the GDL pores. The hydrophobic PTFE held pores open, inhibiting the excess water accumulation [26,27]. The integration of GDL and catalyst layer is termed as electrode layer. Ironically, in case of the catalyst-coated membrane (CCM), the catalyst is coated directly onto the membrane.

1.1d *Bipolar plates*: Each cell within the stack is sandwiched across two bipolar plates, which separates it from nearest cells and provides the stack with electrical conduction and also provides robustness to the stack. The plates normally have a ‘flow field’ within them, that are machined/stamped with a set of channels which facilitates the gas flow evenly through membranes [28,29].

1.1e *Gaskets*: Membranes in each stack are sandwiched between couple of bipolar plates along with gaskets that are usually made of rubber polymers, around this membrane assembly that makes a gas tight seal [30].

Electrode is by far the most critical and expensive material among the various PEM fuel cell components discussed and its properties always said to have critical impacts on efficiency and durability of the stack [31–33].

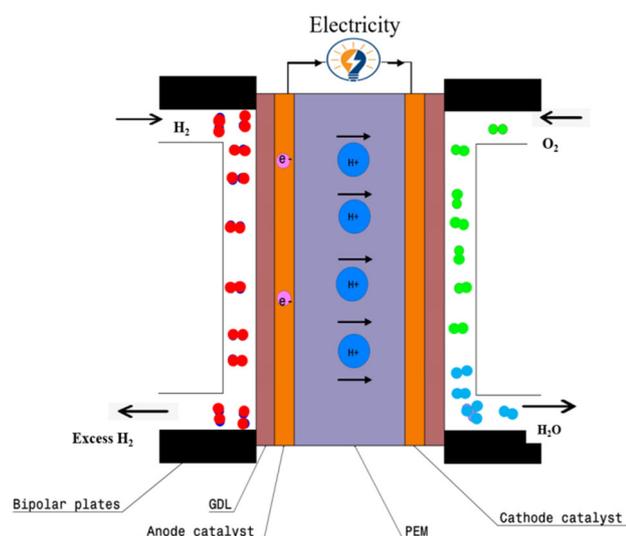


Figure 1. Basic components and working principle of a PEM fuel cell. Reprinted from reference [20]. Copyright 2019 with permission from Springer.

For instance, Ehelebe *et al* [34] reported that the effect of electrode parameters influences the stack performance. An electrode system should always be in contrast with the recent state-of-art developments to provide holistic insights [35].

Figure 2 represents the electrochemical reaction of PEM fuel cell electrode (cathode side) to produce water along with the proton and electron transport. It is still essential for the investigation of electrode materials for the PEM fuel cell applications, as the research on other components have already progressed much [36]. It is evident from figure 3 that the conventional electrodes (platinum group of metals) account to 43% of overall PEM fuel cell costs [37].

Although platinum is found to be a broadly employed electrode, it is attributed to its characteristics, such as reactant activity, chemical stability and high current density. Ironically, the limitation with Pt-based electrodes is its high cost and CO poisoning [38] which limit its commercialization. In recent days, numerous researches significantly contributed towards seeking optimal alternative electrode materials for PEM fuel cell application. A considerable number of literatures have already contributed to the optimized performance and durability of other key components of PEM fuel cell, such as GDL, membrane and bipolar plates [39–41]. In the present work, the review is limited to assessment on innovations in cost-effective non-platinum group of metal (PGM) electrodes for PEM fuel cell applications in the last seven years. Section 2 describes the required attributes for an electrode to be functionally effective and it also illustrates about the major challenges encountered for a PEM fuel cell electrode during operation i.e., critical losses. Section 3 provides short description on the conventionally used Pt and Pt-alloy electrode materials

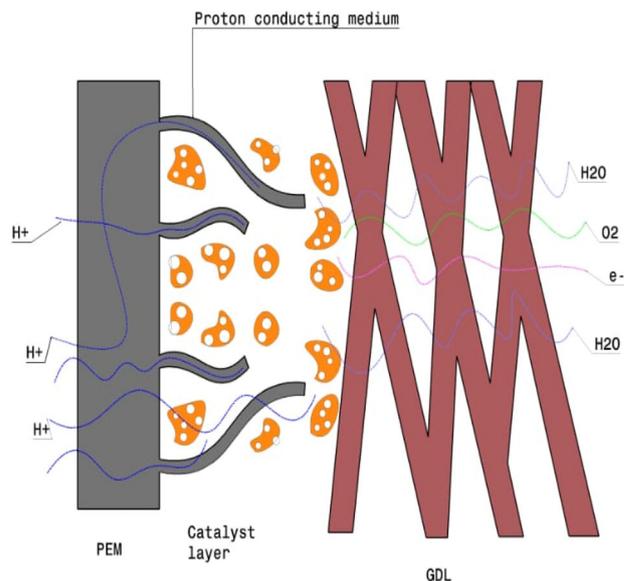


Figure 2. Electrochemical reaction of PEM fuel cell electrode (cathode side) to produce water.

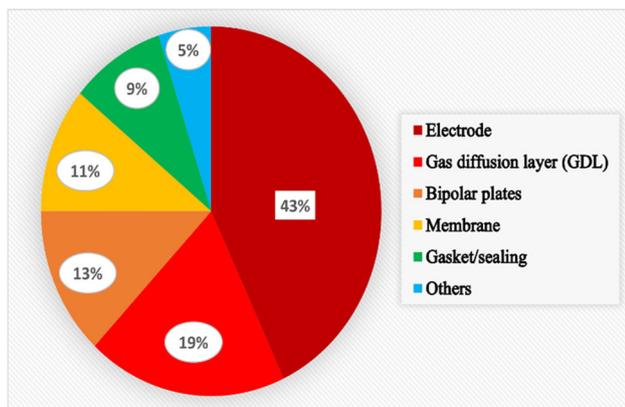


Figure 3. Cost contribution of PEM fuel cell stack components [37].

and their hurdles for not being much successful in commercial market. Followed by section 3, section 4 assesses researches attempted to develop inexpensive non-PGM electrode materials for PEM fuel cell. We describe the technology to adapt PEM fuel cell with electrode materials rather than PGM metals and their significance. Section 5 summarizes the overall review and the snapshot on the recent advancements in PEM fuel cell electrodes.

2. Functional attributes of a PEM fuel cell electrode

PEM fuel cell electrode is considered as the heart of the fuel cell stack and it indeed enables electrons to carry continually from the anode to cathode [42,43]. In compliance with this function, electrodes for PEM fuel cell are ought to have certain properties (table 1) to achieve overall better performance of the fuel cell stack. Researchers seek to develop a PGM-free catalyst and firmly focussed on meeting the crucial functional attributes at better performance and cost-effective [43].

In PEM fuel cell reaction kinetics, the oxygen reduction reaction (ORR) is sluggish compared to the hydrogen oxygen reaction (HOR) by a factor of 6–7 [52] and subsequently, the challenge is to develop a potential electrode for ORR [53]. In contrast with other electrode materials, Pt has the highest degree of activity for ORR and thus, often positioned at the top (peak) of the ‘volcano’ plot given in figure 4, which is described by the Sabatier theory [54].

The electrode performance is determined by the current at an obtained voltage (V_{fc}). i.e., normalized current density measured, also known as mass activity, which is most widely used figure to compare various electrodes [55]. The role of electrode is incredibly significant in minimizing the activation losses and subsequently, contributing towards a better performance [56].

The actual cell potential is computed from its ideal potential and is due to the various irreversible losses which are termed as polarization. Polarization curve given in figure 5 [57] is the fundamental kinetic law for fuel cells, which is a plot of current density and cell potential. With the help of polarization curve, the influence of three categories of loss is always easy to discern [58]. Multiple phenomena leading to irreversible losses in a PEM fuel cell are the activation polarization (V_{act}), the ohmic polarization (V_{ohmic}) and the mass transportation polarization (V_{con}) [59]. At the activation polarization region, the reaction kinetics are said to be sluggish. Ohmic polarization region is the liner region where the fuel cells predominantly operate, and at mass transportation region due to the inability of the fuel cell to match the reactant supply and demand. Activation losses (V_{act}) eventually lead from activation potential of the electrochemical processes that normally occurs at the electrodes i.e., sluggish electrode kinetics. The activation losses predominantly depend on catalyst material, microstructure, reactant activity and utilization, and current density [60]. The ohmic losses (V_{ohmic}) result from the ionic and electrical resistances of electrodes and also the contact resistances. These losses are directly proportional to the

Table 1. Functional attributes of a PEM fuel cell electrode.

Attributes	Functions	References
Activity	The reactant must facilitate the reaction kinetics of electrodes.	[44]
Selectivity	To develop intended product and minimize parasitic products at the output.	[45]
Stability, mechanical and chemical durabilities	To be robust and withstand the PEM fuel cell operational environment, such as strong oxidizing agents, reacting radicals, an acidified atmosphere and temperature rates which fluctuate faster at higher voltage. For reliable performance and durable life under oxidation.	[46]
Resistance to poisoning	Immune against impurities present in the fuel cell and in the feed gases.	[47]
Ionic and electronic conductivities	To carry charged ions and better electrical output.	[48]
High degree of porosity	For effective transportation of gases.	[49]
Design attributes	Low internal electric losses, low cost of electrode, constant composition electrolyte and ecologically acceptable fuels.	[50,51]

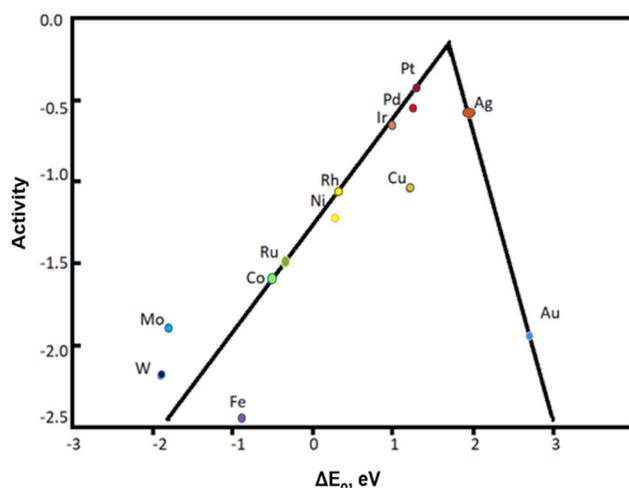


Figure 4. Volcano plot of key electrode materials for PEM fuel cell. Reprinted from reference [54]. Copyright 2014 with permission from licensee Beilstein-Institut.

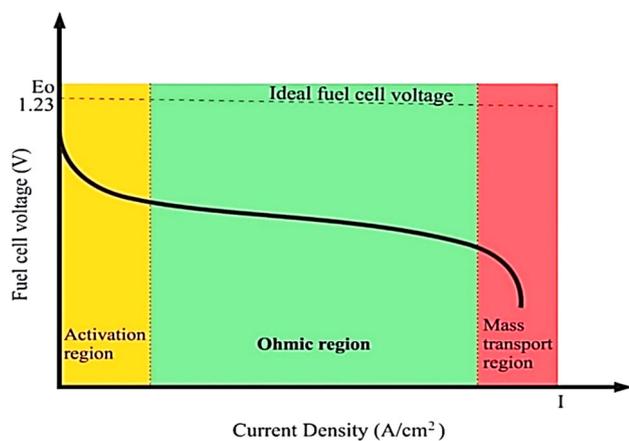


Figure 5. Polarization characteristics of a typical PEM fuel cell [57].

current density [61]. Mass transportation losses (V_{con}) are result of reactant rate limitations of finite masses occurred due to the reduction in concentration of the gas at the interface surface of electrode–electrolyte [62]. In addition to the activity of catalyst measurement cost and durability; overall efficiency must also be calculated to assess the commercial value, strength and stability of the electrode [63].

Following equation defines the fuel cell output voltage (V_{fc}) of single PEM fuel cell.

$$V_{fc} = E_o - V_{act} - V_{ohmic} - V_{con}$$

where E_o is the standard potential of fuel cell.

Numerous researchers have studied how expensive electrode materials can be substituted, while guaranteeing that the cells persist to augment primary efficiency metrics (durability and power density) [64]. Researchers eye to develop PGM free electrodes which not only contributed

towards economical material, but also towards an effective performance along with substantial robustness [65].

3. Platinum-based electrodes

Platinum (Pt) is the most effective electrode material for both HOR and ORR, where Pt nanoparticles are assisted by carbon nanosphere [66]. Since reactions of the PEM fuel cell are structural-sensitive reactions that are more concentrated on crystal facets, highly regulated morphological nanoparticles with highly active crystal facets are efficient in application of PEM fuel cell electrode [67,68]. Stability should also be considered in the electrode development, in addition to performance. The key cause of loss in electrode performance of PEM fuel cell is the Ostwald ripening [69–71] process which is accelerated by electrochemical dissolution and redeposition of dissolved Pt on the surface of electrode. Due to the disparity in the surface free energy, thermodynamic chances of agglomeration of smaller particles to larger particles being high; the larger particle sizes contribute to less efficient electrochemical surface area, thus, minimizes mass activity and catalytic efficiency [70,71]. The chemical synthesis of deposition of Pt nanoparticles into carbon, supports and ensures to obtain relatively small particles, thus, effectively eliminating Ostwald ripening of Pt nanoparticles [72–76].

Transitional metal alloy Pt has been found to greatly boost the slow ORR kinetics for the cathode due to geometrical and electronic attributes [77]. Pt–Co/C, Pt–Ni/C, Pt–Cr/C and Pt–Cu/C alloyed nanoparticles are few examples that are successfully prepared for fuel cell electrode application [78–81]. A comparative study demonstrated that although this form of alloying considerably enhances ORR operations, common alloy materials, such as Co, Ni and Fe are appeared to be leached from the electrode nanoparticles in a highly acidic PEM fuel cell environment [82,83]. ORR occurring at the PEM fuel cell cathode is catalysed by the Pt loadings to greatly minimize the over potential loss [84]. The standard loss is the activation of over-potential, on which their magnitude highly relies on the reaction kinetics, more precisely on the size of exchange current density [85]. Thus, the enhancement of kinetic reaction efficiency is accomplished by raising the current density that relies on the activation, reaction concentration and reaction sites, barriers and temperature. These variables inhibit large-scale marketing and have led to intensive research towards inexpensive, highly active and stable non-PGM electrodes [86].

4. Non-pt electrodes

PGMs are quite expensive, their cost is subjected to volatility, they are available from only very few sources and their cost does not scale with larger production volume.

Hence, for long-term accomplishment of fuel cells, PGM-free catalysts need to be developed. It is for this reason, researchers have strategically targeted their focus on their work on the eradication of PGM from the fuel cell system, and its replacement with a high-performance, durable PGM-free electrocatalyst for PEM fuel cells. Although substantial technological advancements have been made in various respects in developing Pt electrodes, there remain obstacles to commercialize fuel cells to compete with conventional sources, where the cost, efficiency and durability of fuel cells are yet to be enhanced [87]. This drives researchers to work on developing a substitute to address the criterion that PEM fuel cell electrode material demands [88]. Table 2 [32] provides the classification of various platinum and non-platinum electrode materials for PEM fuel cell.

The quest for developing low-cost, high-performance PEM-fuel cell electro-catalysts began approaching with two different strategies. The first way is to lessen the use of catalysts by enhancing Pt usage of the catalyst layers [89]. This could be executed by employing relatively cost-effective Pt alloys (such as Co, Fe, Mn, etc.) and/or through using unique supportive materials to enable deposition of Pt nanoparticles [90].

Over the past decades, although the Pt loading was reduced considerably to about 0.4 mg cm^{-2} [91], ironically, the overall cost of the electrode has not been reduced significantly, especially for the long-term way [92]. There is also an approach attempted to recycle the Pt electrodes to limit the large-scale production expenses. The attempt was made by Balva *et al* [93] to recycle platinum by leaching it via coupling with chlorine/ionic liquids. Though the recycled Pt electrode helps reducing large scale production cost, the sluggishness persist as a barrier on performance improvement. Those approaches were not found to be significantly contributed towards reducing the overall cost of PEM fuel cell. As a consequence, there has been an inclination towards research as a third approach on producing non-PGM electrodes. Developing high-performance, non-PGM-based electrodes thus, appear to be the key path to the sustainable manufacturing of PEM fuel cell applications. However, till date, activity and stability of non-PGM electrodes are inferior to Pt electrodes [94].

Table 2. Various PEM fuel cell electrode materials [32].

PGM-based	Platinum alloy-based	Non-PGM
<i>Electrode material</i>		
Pt	Pt–Cr/C	Fe–N–C
Pd	Pt–Ni/C	C
Rh	Pt–Co/C	Ionic liquids
Ru	Pt–Cu/C	Graphene
Ir		
Os		

4.1 Fe-based electrodes

Vinayan *et al* [95] developed an active, robust, non-platinum metal electrocatalyst that has been synthesized from a precursor of the electrode at high temperatures, which include Fe-, N- and S-charged salt co-doped with graphene that forms structured electrode made ideal for PEM fuel cell application. The material synthesized is an electrode of metal–nitrogen–sulphur group and has an open matrix structure (4 mg cm^{-2}) with Nafion 212 as electrolyte, regulated by the silica-templating process. The Fe–NSG electrode was shown to be sustainable, which at 0.5 V provides a peak power density of 225 mW cm^{-2} (80°C) with promising stability and high current density.

A hybrid Fe–N–C electrode from a bi-metal-organic frame (Zn/Fe-ZIFs) developed by Liu *et al* [96] was one of the best non-noble metal electrodes ever reported on ORR in acidic and alkaline environments. Fe–NC-20-1000 loaded with catalyst loading of 0.75 mg cm^{-2} and ZIF-7 precursor exhibited a half-wave potential ORR activity of 0.770 V which is close to that of the 0.827 V for Pt/C in acidic medium. The power density exhibited is 870 mW cm^{-2} at 130°C which is 10% positively higher than Pt/C's ORR.

Bhange *et al* [97] reported a Pt-free iron-based electrode doped with sulphur and scrolled graphene (P12-900) as a potential ORR electro catalyst. The single PEM fuel cell using Nafion with isopropyl alcohol (IPA) as electrolyte under catalyst ratio of 0.5 demonstration employed with P12-900 electrode (loading of 2 mg cm^{-2}) produced peak power density of 345 mW cm^{-2} and is equivalent to the state-of-the-art Pt/C cathode which is 322 mW cm^{-2} . Through its unrivalled propensity to accelerate electrode reaction, the prepared PGM free electrode can therefore, serve as a viable alternative to substitute expensive metal electrode for PEM fuel cell.

From last few decades, iron-based electrodes were found to be potential alternative for PGM-free electrode, in a research by Khan *et al* [98], Fe-doped C12A7 (a maynite electrode synthesized of nanoparticles) was developed with A201 Tokuyama as electrolyte membrane. The developed electrode was a composite, cost-effective, exceptionally durable, active and precious metal-free with catalyst loading of 0.1 mg cm^{-2} . The maximum power density reached up to 275 mW cm^{-2} at a potential of 1.03 V operated at 80°C , where for the conventional Pt/C electrode, the power density was 245 mW cm^{-2} at the same operating conditions. The results are evident that Fe-doped C12A7 would be an incredibly alluring precious metal-free electro catalyst.

In high-temperature polymer electrolyte membrane fuel cells (HT-PEMFC), the ORR activity of Pt-based electrodes is weak because of the poor resistance of Pt-based electrodes towards phosphate ions. Fe and N co-functionalized with carbon (Fe–N–C) exhibits resistance to phosphate ions and act as a potential option for PEM fuel cell [99–101].

Razmjooei *et al* [102] employed a silica sol optimized Fe–N–C electrode pyrolysed with organometallic acid resulted in an improved mass transfer which leads to improved ORR activity for a HT-PEMFC with phosphoric acid-based electrolyte (catalyst loading of 0.75 mg cm^{-2}). The developed electrode operated at 150°C offered an overall power density of 260 mW cm^{-2} and a current density of 1260 mA cm^{-2} at 0.2 V , which are superior to or comparable to the recently recorded values.

4.2 Carbon-based electrodes

High surface area carbons have been used as a worthwhile electrode for numerous electrochemical batteries and fuel cells [103,104]. In fuel cells, carbon indeed features its importance, particularly for PEM fuel cell electrodes [105]. Conventional platinum electrodes are often found to be supported with carbon and carbon nanotubes (CNT), especially with carbon black, due to its good electrically conductive property and easy availability [106]. However, carbon corrosion alongside the platinum dissolution and Ostwald ripening remains to be the primary cause for poor longevity of the electrocatalyst under large potentials [107]. As a result, researchers are devoted towards developing electrode using carbon entirely, rather than using carbon as a support material for expensive platinum electrode.

Centred on the fuel cell marketing criteria, a research study by Yang *et al* [108] identified the design and development of a durable fuel cell, based on carbon black (CB) and multi-walled carbon nanotubes (MWCNT), wrapped with polypyridine bibenzimidazole (PyPBI) electrolyte. Electrode developed with MWCNT/PyPBI/CB with catalyst loading of 0.45 mg cm^{-2} operated at 120°C showed extremely high reliability at a loss of just 5% from the original fuel cell potential in 500,000 realistic cycles, which demonstrated substantially greater stability and power density of 160 mW cm^{-2} at 0.8 V , which is comparatively higher to the traditional Pt-based electrode with a potential loss of 50%. In summary, the research is believed to be for the desired advantageous phase by the industries because of the high durability, economy and overall output of the produced electrode.

A study by Zamora *et al* [109] on non-PGM electrodes evaluated the use of carbon nanosphere (CNS) in microporous layers (MPL) with catalyst loading of 0.6 mg cm^{-2} using polybenzimidazole (PBI) as electrolyte and resonates the properties and efficiency against the traditional Pt-carbon black MPL for high-temperature polymer electrolyte membranous cell fuel (HT-PEMFC). A short fuel cell life test has been conducted at 120°C to determine efficiency under accelerated strain, showing that due to its high element stability and strong electrical conduction with peak power density of 380 mW cm^{-2} at 1.02 V , CNS is a viable alternative to conventional carbonaceous materials appropriate for use in this technology.

In a research by Zheng *et al* [110], an extremely effective and relatively low-cost mesoporous carbon octahedral electrode, synthesized with UIO-66-NH₂ by double-solvent diffusion-pyrolysis process, co-doped using finely splintered doping elements (Fe/N/S), has been developed, to decrease the sluggishness of the ORR reaction in PEM fuel cell, configured employing Nafion 211 polymer electrolyte with catalyst loading of 4 mg cm^{-2} . The electrode configuration is well-inherited by the mediated carbon content, exhibits excellent catalytic activity and ORR durability. The electrode exhibited with a maximum power density of 553 mW cm^{-2} at 0.6 V and at 80°C , rendering it one of the strongest electrode materials compared with that of any non-expensive metal electrodes.

A reference for economical and practical carbon paper engineering is reported by Waseem *et al* [111] for the requirements of commercialization of fuel cells. In the report, porous carbon fibre composite paper is used in fuel cell assembly as an electrode material, employed with Nafion 212 polymer electrolyte with catalyst loading of 4 mg cm^{-2} . Operated at 80°C , the composite electrode with fibre/matrix ratio of 65:35 delivered peak power density of 916 mW cm^{-2} at 0.99 V . The reliability of the overall equilibrated properties of the carbon composite electrode is a key factor in maintaining the much-required consistent high-power densities in a PEM fuel cell over expensive Pt electrodes.

Waseem *et al* [112] reported a PEM fuel cell assembly utilizing porous conductive carbon-composite paper as an electrode. Carbon paper is formed by patterning carbon fibres (through composite formation) in the form of sheets with high porosity, termed as preforms. With overall properties balanced (porosity, stability, electrical conductivity and electrochemical property) for single PEM fuel cell unit with standard calomel electrolyte (SCE), the pore formers are the urea and camphor with catalyst loading of 0.5 mg cm^{-2} . The prepared electrode operated at 55°C exhibited cell performance of 756.8 and 792.2 mW cm^{-2} at 0.9 V , which is more or less similar to that of commercial expensive Pt-based electrodes ($>750 \text{ mW cm}^{-2}$).

Catalysts based on Fe and N co-doped carbon (Fe–N–C) have exhibited a promising activity and stability. Wang *et al* [113] focussed to develop a Co–N–C catalyst for improved ORR activity in PEM fuel cells with Nafion 212 membrane. Experimental tests were carried out using a single PEM fuel cell with catalyst loading of 1 mg cm^{-2} , operated at 80°C , peak power density of 940 mW cm^{-2} was achieved at a potential of 0.5 V .

He *et al* [114] developed an effective surfactant-assisted confinement pyrolysis strategy to enable controlled synthesis of atomically dispersed CoN₄ sites with increased density, therefore, leading to significantly enhanced catalytic activity for the ORR in challenging acids for PEM fuel cell employing Nafion 212 as electrolyte and Co–N–C@F127 as catalyst with loading of 0.4 mg cm^{-2} . Co–N–C@F127 catalyst exhibited excellent ORR activity

with the most positive 0.84 V potential with peak power density of 870 mW cm⁻² operating at 80°C.

Wang *et al* [115] developed a thermodynamically decomposed hierarchical ordered porous carbon with atomically dispersed FeN₄ catalytic centres in the carbon matrix. The FeN₄/HOPC-C1000 catalyst with loading of 0.5 mg cm⁻² achieved a superior half-wave potential of 0.80 V (vs. RHE) in 0.5 M H₂SO₄, only 20 mV inferior to the 0.82 V of conventional Pt/C. Moreover, test results show peak power density of 420 mW cm⁻² at a potential of 0.57 V when operating at 80°C.

A new approach for carbon nanofibre paper-based PEM fuel cell electrode design was proposed and demonstrated by Ponomarev *et al* [116] for HT-PEMFC. Polybenzimidazole (PBI)/H₃PO₄ membrane is employed as electrolyte with carbonized electrocatalyst (polyacrylonitrile/carbon black Vulcan/Zr/Ni) loading of 1 mg cm⁻². Fuel cell tests were performed at 180°C. Maximum power density obtained was 342 mW cm⁻² at 0.9 V, and the performance is similar to that of conventional noble metal catalysts.

In recent times, hierarchically macro-/meso-/microporous 3D carbon materials have been given more interest due to their ingenious prospective in electrochemistry. With regard to this, Shen *et al* [117] reported a dual-template strategy using eutectic NaCl/ZnCl₂ melt as airtight and swelling agent to obtain 3D mesoporous skeleton structured carbon from renewable lignin. The prepared lignin-derived bio-carbon material was used as a cathode catalyst to assemble a H₂-O₂ single PEM fuel cell, and its excellent catalytic performance has been confirmed, while operating at 80°C with the maximum power density of 779 mW cm⁻² and potential of 0.7 V which is relatively better over conventional Pt/C electrocatalyst.

Xia *et al* [118] reported a novel synthetic strategy for the seeded growth of hierarchically branched CNTs with a high density of Fe-N_x active sites and toward durably high PEMFC performance using Nafion 211 ionomer as membrane with catalyst loading of 0.4 mg cm⁻². Single PEMFC test with the prepared Fe-N/C cathode was conducted at 75°C to evaluate their activity and durability under realistic conditions. Peak power density of 480 mW cm⁻² is obtained at 0.9 V.

Wu *et al* [119] reported their recent effort in developing carbon nanotube cross-linking MOF-derived Fe/N/C catalysts as oxygen reduction electrocatalysts for fuel cell. It is witnessed that the CNT cross-linking strategy effectively improve the activity and stability of fuel cell, proven with an experimental result of high power density of 732 mW cm⁻² at 0.7 V, achieved at 90°C.

4.3 Graphene electrode

As a viable option in contrast to expensive Pt electrodes, graphene contributes its best part as being universally

available at low-cost for various energy applications [120–123] including that of fuel cell.

In terms of graphene nanotubes, a research was undertaken by Unni *et al* [123] to develop an effective graphene nanotube hinged ORR electrode, procured from single-walled nano horns, confined with iron oxide graphene nanotubes (FeGNT) with catalyst loading of 2 mg cm⁻². FeGNT is reported to have high surface area amongst the metal-confined nanotubes, which the graphene encompassed. PEM fuel cells operated at 65°C using FeGNT as electrode, single cell polarization with Nafion 212 electrolyte, achieved power density of 200 mW cm⁻². Thus, FeGNT has the prospect of serving a promising non-Pt ORR electrode for PEM fuel cell applications.

Halogen-doped graphene oxide (GO) electrode developed by means of electrochemical exfoliation was reported by Kakaei and Balavandi [124] for ORR in alkaline media. With Nafion isopropanol as electrolyte, the catalytic activity of the GO electrode is 50 mA cm⁻² for a loading of 0.5 mg cm⁻², compared with a typical PT electrode that exhibited 30 mA cm⁻². Moreover, improved polarization efficiency with maximum power density of 320 mW cm⁻² at 1 V and 60°C with decreased resistance to electron transfer was achieved.

Marinoiu *et al* [125] synthesized iodine-intercalated graphene electrode for PEM fuel cell. Iodine-doped graphene was evaluated for electrochemical efficiency and compared to a standard PEM fuel cell configuration with loading of 0.2 mg cm⁻². The proposed cathode exhibited ORR activity of 90 m² g⁻¹ than the Pt/C of 38 m² g⁻¹ at 80°C. The hybrid cathode produced peak power density of 550 mW cm⁻² at 0.52 V

As grapheme-based materials already attracted extensive interest in energy devices and fuel cell technologies as a substrate for expensive electrodes, experiments are intended towards production of iodine-doped graphene electrode for PEM fuel cell [126–128]. Experimental results by Marioiu *et al* [129] on electrode based on I-doped graphene with Nafion 212 electrolyte and catalyst loading of 0.2 mg cm⁻² were of high electrochemical efficiency and long durability, demonstrating the potential of being an effective electrode material for PEM fuel cell. The overall durability test of 550 h showed that the initial voltage was just ~0.5% lost to 600 mA cm⁻² and at 1 V, the maximum power density achieved was 660 mW cm⁻².

The use of graphene is well-known as non-precious electrode for PEM fuel cell, for HT-PEMFC, the practical application of graphene is still curtailed because of their poor single atom catalyst (SAC) loading (<2 wt%) in acidic environment [130,131].

To address this challenge and subsequently to develop a PGM-free electrode, Cheng *et al* [131] reported the one pot pyrolysis technique of synthesized iron-based SAC on graphene (Fe SAC-G) electrode with catalyst loading of 0.3 mg cm⁻² for HT-PEMFC. The synthesized Fe SAC-G displays an onset potential and half wave potential of 0.95

Table 3. Snapshot on various non-PGM metals/alloy electrodes for PEM fuel cell.

Electrode material and loading	Electrolyte	Power density achieved @ operating condition	Results	References
Fe-N-C (1.6 mg cm ⁻²)	Aemion	420 mW cm ⁻² @ 0.6 V and 60°C	Improved stability in alkaline medium	[34]
Fe-N-S-G (4 mg cm ⁻²)	Nafion 212	225 mW cm ⁻² @ 0.5 V and 80°C	Rapid effect of catalytic parameters	[95]
Fe-N-C (20-1000) (0.75 mg cm ⁻²)	ZIF-7	870 mW cm ⁻² @ 0.7 V and 130°C	Improved stability and power density Excellent half wave potential in acidic medium	[96]
Fe-S (P12-900) (2 mg cm ⁻²)	IPA solvent Nafion	345 mW cm ⁻² @ 1.03 V and 80°C	Positive ORR activity Accelerated electrode reaction	[97]
F- doped C12A7 (nanoparticles synthesized mayenite electrode) (0.1 mg cm ⁻²)	A201 (Tokuyama)	275 mW cm ⁻² @ 0.2 V and 150°C	Improved power density Improved half wave potential and current density	[98]
Fe-N-C with organometallic acid (0.75 mg cm ⁻²)	Phosphoric acid	260 mW cm ⁻² @ 0.8 V and 120°C	Superior performance than conventional Pt/C electrodes	[102]
Carbon black with MWNT (0.45 mg cm ⁻²)	Polypyridine bibenzimidazole (PyPBI)	160 mW cm ⁻² @ 1.2 V and 120°C	Highly durable and stable	[108]
Carbon nanospheres (0.6 mg cm ⁻²)	Polybenzimidazole	380 mW cm ⁻² @ 1.02 V and 120°C	High electrochemical stability and electrode conductivity	[109]
Carbon octahedral configuration doped (U10-66-NH ₂) (4 mg cm ⁻²)	Nafion 211	553 mW cm ⁻² @ 0.6 V and 80°C	Excellent ORR durability	[110]
Porous carbon fibre composite paper (4 mg cm ⁻²)	Nafion 212	916 mW cm ⁻² @ 0.99 V and 80°C	Constant high power density output	[111]
Electrode material and loading	Electrolyte	Power density achieved @ operating condition	Results	References
Carbon composite paper preformed with urea and camphor pores (0.5 mg cm ⁻²)	Standard calomel electrolyte (SCE)	756. 8 mW cm ⁻² and 792. 2 mW cm ⁻² @ 0.9 V and 55°C	Similar performance to Pt/C electrode at reduced material cost	[112]
Co-N-C (1 mg cm ⁻²)	Nafion 212	940 mW cm ⁻² @ 0.5 V and 80°C	High power density Catalytic degradation is diminished	[113]
Co-N-C@F127 (0.4 mg cm ⁻²)	Nafion 212	870 mW cm ⁻² @ 0.84 V and 80°C	Improved ORR activity	[114]
Fe _N /HOPC-C 1000 (0.5 mg cm ⁻²)	H ₂ SO ₄	420 mW cm ⁻² @ 0.57 V and 80°C	Superior half wave potential	[115]
PAN/carbon black Vulcan/Zr/Ni (1 mg cm ⁻²)	PBI/H ₃ PO ₄	342 mW cm ⁻² @ 0.9 V and 180°C	Increased electron transfer Improved mass transportation	[116]
Lignin-derived biocarbon	Nafion 211	779 mW cm ⁻² @ 0.7 V and 80°C	Excellent catalytic performance Fascinating power density	[117]

Table 3. continued

Electrode material and loading	Electrolyte	Power density achieved @ operating condition	Results	References
Fe-N-CNT (0.4 mg cm ⁻²)	Nafion 211	480 mW cm ⁻² @ 0.9 V and 75°C	Improved ORR activity Improved H ₂ -O ₂ cell performance	[117]
MOF-derived Fe-N-CNT (0.6 mg cm ⁻²)	Nafion 211	732 mW cm ⁻² @ 0.7 V and 90°C	Improved stability	[119]
Graphene nanotubes (FeGNT) (2 mg cm ⁻²)	Nafion 212	200 mW cm ⁻² @ 0.87 V and 65°C	Highly active ORR	[124]
Halogen-doped graphene oxide (0.5 mg cm ⁻²)	Nafion isopropanol	320 mW cm ⁻² @ 1 V and 60°	Improvement in polarization efficiency	[125]
Iodine intercalated graphene (0.2 mg cm ⁻²)	Nafion	550 mW cm ⁻² @ 1.02 V and 80°C	Improved ORR activity	[126]
Iodine-doped graphene (0.2 mg cm ⁻²)	Nafion 212	660 mW cm ⁻² @ 1 V and 80°C	Long durability High electrochemical efficiency	[129]
Iron base graphene (Fe-SAC-G) (0.3 mg cm ⁻²)	Phosphoric acid	325 mW cm ⁻² @ 0.5 V and 230°C	Superior stability and tolerance	[132]
Nanoporous ionic ZnCoNC (2 mg cm ⁻²)	ZIF-ZnCo	210 mW cm ⁻² @ 0.7 V and 80°C	Highly porous for improved electrochemical reaction Improved power density	[134]

and 0.8 V in acidic medium of ORR, which is similar to that of Pt/C electrodes, however, with superior stability with high tolerance against phosphate anion. Moreover, at 0.5 V, the Fe SAC-G electrode provides peak power density of 325 mW cm⁻² at 230°C, which is higher than Pt/C electrode with 313 mW cm⁻². The findings of this study are evident that for HT-PEMFC, Fe-SAC-G electrode is a promising substitute for Pt/C electrodes.

4.4 Ionic liquid-based electrode

There are wide reports of non-PGM electrode for ORR enhancement in PEM fuel cell, but their reaction kinetics in acidic environment poses poor performance [133]. Hence, a potential solution to manipulate ionic liquids is to boost the operating efficiency of PEM fuel cell containing non-Pt ORR electrodes. Amendment shifts of ionic liquids of nanoporous ZnCoNC electrodes (sourced by ZIF-ZnCo) with catalyst loading of 2 mg cm⁻² is examined by Wang *et al* [134] in PEM fuel cells and to contextualize catalytic processes in practical condition. Since the O₂ solubility is high in ionic liquid, it enhances the active porous ZnCoNC, and their hydrophobic characteristic facilitates the transfer of water. Improvement in power density is given by the single cell measurement operated at 80°C reported 210 mW cm⁻² at 0.7 V.

5. Summary of recent advancements

The role of electrode is not only significant from the technical perspective, but also from the economical perspective as the electrode component/material contributes to around 50% of the PEM fuel cell stack. With a significant achievement of materials in the recent days, PGM-free electrodes are progressive for some commercial niche markets. The present assessment provides insights on recent electrode materials, their performance and durability for PEM fuel cell application experimented by range of researchers. An immense endeavour is vital to evaluate and refine the non-conventional electrodes to facilitate the adoption and validation of such materials. It is observed that there are potential non-Pt alloys that exhibited significant performance, and their related information are provided in table 3.

The global market size of PEM fuel cell is foreseen to soar by 47.60 billion USD by 2026 [135]; ironically, still there has been a major obstacle for PEM fuel cell mass production and commercialization. In specific, the costs of electrode remain a key constraint as it is an epochal contributor of the PEM fuel cell stack [136,137]. Identifying a non-conventional and cost-effective electrode material will be the key break-through in the PEM fuel cell commercialization. Based on the critical assessment, figure 6 illustrates the strength, weakness, opportunities and threats

STRENGTH	WEAKNESS
<ul style="list-style-type: none"> • Cost effective • Easy availability 	<ul style="list-style-type: none"> • Low performance / Slow kinetics, especially ORR • Durability at system level • High catalysts loading can impact power density
OPPORTUNITIES	THREATS
<ul style="list-style-type: none"> • Easily attain DoE cost target • Advanced hybrid electrode material or heteroatom for increased performance 	<ul style="list-style-type: none"> • Manufacturing protocol of electrodes need to be formed • Reliability • Recycling & environmental issues

Figure 6. SWOT analysis on the significance of non-PGM electrocatalyst.

(SWOT) analyses on the significance of non-PGM electrodes.

6. Conclusion and outlook

The limitation with platinum group metals (PGM) as an electrode material is its expensiveness that intensify the overall system cost, thereby limiting its mass commercialization. The proposed mini-review provides a recent insight on the summary of various non-PGM based electrode materials for PEM fuel cell application. There is a possibility of occurrence of hybrid composite catalyst electrode materials that provide an opportunity for material scientists. In addition, potential manufacturing process, such as additive manufacturing (3D-printing) can accelerate the electrode fabrication technique. This paper also provides data on the performance and power density attained with these cost-effective electrode materials which can provide information to fuel cell researchers to work on these alternate electrode materials.

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References

- [1] Jayakumar A, Chalmers A and Lie T T 2017 *IET Electr. Syst. Transp.* **7** 259
- [2] Nowotny J, Dodson J, Fiechter S, Gür T M, Kennedy B, Macyk W *et al* 2018 *Renew. Sustain. Energy Rev.* **81** 2541
- [3] Gielen D, Boshell F, Saygin D, Bazilian M D, Wagner N and Gorini R 2019 *Energy Strategy Rev.* **24** 38
- [4] Alizadeh M I, Parsa Moghaddam M, Amjady N, Siano P and Sheikh-El-Eslami M K 2016 *Renew. Sustain. Energy Rev.* **57** 1186
- [5] Hemanth Kumar D, Krishna R, Dinesh Kumar M, Pradhan R and Sreenivasan M 2020 *Mater. Today Proceed.* **33** 326
- [6] Hirth L, Ueckerdt F and Edenhofer O 2015 *Renew. Energy* **74** 925
- [7] Rahman M M and Velayutham E 2020 *Renew. Energy* **147** 399
- [8] Hosseini S E and Wahid M A 2016 *Renew. Sustain. Energy Rev.* **57** 850
- [9] Pethaiah S S, Sadasivuni K K, Jayakumar A, Ponnamma D, Tiwary C S and Sasikumar G 2020 *Energies* **13** 5879
- [10] Pethaiah S S, Arunkumar J, Ramos M, Al-Jumaily A and Manivannan N 2016 *Bull. Mater. Sci.* **39** 273
- [11] Ediger Volkan S 2019 *Energy Procedia* **156** 2
- [12] Chang Y and Fang Z 2017 *Energy Policy* **105** 493
- [13] Minh N Q and Shirley Meng Y 2019 *MRS Bull.* **44** 682
- [14] Ellamla H R, Staffell I, Bujlo P, Pollet B G and Pasupathi S 2015 *J. Power Sour.* **293** 312
- [15] Wilberforce T, Alaswad A, Palumbo A, Dassisti M and Olabi A G 2016 *Int. J. Hydrog. Energy* **41** 16509
- [16] Fuel cells: data, facts and figures. Available: https://energyeducation.ca/encyclopedia/Fuel_cell (Accessed on 8 February 2021)
- [17] Scherer G G 2013 in Kreuer K D (ed.) *Fuel cells: selected entries from the encyclopedia of sustainability science and technology* (New York: Springer) p. 97
- [18] Sohani A, Naderi S, Torabi F, Sayyaadi H, Akhlaghi Y G, Zhao X *et al* 2020 *J. Clean. Prod.* **252** 119567
- [19] Rosli R E, Sulong A B, Daud W R W, Zulkifley M A, Husaini T, Rosli M I *et al* 2017 *Int. J. Hydrog. Energy* **42** 9293
- [20] Jayakumar A 2019 *Front. Energy* **13** 325
- [21] Li Y, Zhou Z, Liu X and Wu W T 2019 *Appl. Energy* **242** 1513
- [22] Parts of fuel cells. Available: <https://www.energy.gov/eere/fuelcells/parts-fuel-cell> (Accessed on 11 February 2021)
- [23] Liu D, Xia S, Tang H, Zhong D, Wang B, Cai X *et al* 2018 *Int. J. Energy Res.* **43** 2571
- [24] Ioroi T, Siroma Z, Yamazaki S I and Yasuda K 2019 *Adv. Energy Mater.* **9** 1801284
- [25] Jourdani M, Mounir H and ElMarjani A 2017 *International Renewable and Sustainable Energy Conference (IRSEC)*, pp. 1–6
- [26] Jayakumar A 2018 *Appl. Phys. Chem. Multidiscipl. Approach.* **3** 23
- [27] Laoun B, Kasat H A, Ahmad R and Kannan A M 2018 *Energy* **151** 689
- [28] Lee D, Lim J W and Lee D G 2017 *Compos. Struct.* **167** 144
- [29] Shimpalee S, Lilavivat V, McCrabb H, Khunatorn Y, Lee H K, Lee W K *et al* 2016 *Int. J. Hydrog. Energy* **41** 13688
- [30] Pehlivan-Davis S 2016 PhD Thesis (Loughborough University)
- [31] Moreno N G, Molina M C, Gervasio D and Robles J F P 2015 *Renew. Sustain. Energy Rev.* **52** 897
- [32] Majlan E H, Rohendi D, Daud W R W, Husaini T and Haque M A 2018 *Renew. Sustain. Energy Rev.* **89** 117

- [33] Millington B, Du S and Pollet B G 2011 *J. Power Sour.* **196** 9013
- [34] Ehelebe K, Ashraf T, Hager S, Seeberger D, Thiele S and Cherevko S 2020 *Electrochem. Commun.* **116** 106761
- [35] Borup R L, Kusoglu A, Neyerlin K C, Mukundan R, Ahluwalia R K, Cullen D A *et al* 2020 *Curr. Opin. Electrochem.* **21** 192
- [36] Lee B, Kim J G and Pak C 2020 *Korean J. Chem. Eng.* **37** 2334
- [37] Leader A, Gaustad G and Babbitt C 2019 *Mate. Renew. Sustain. Energy* **8** 1
- [38] Wang Y J, Long W, Wang L, Yuan R, Ignaszak A, Fang B *et al* 2018 *Energy Environ. Sci.* **11** 258
- [39] Zheng Z, Yang F, Lin C, Zhu F, Shen S, Wei G *et al* 2020 *J. Power Sour.* **451** 227729
- [40] Stariha S, Artyushkova K, Serov A and Atanassov P 2015 *Int. J. Hydrog. Energy* **40** 14676
- [41] Stein T and Ein-Eli Y 2020 *Energy Technol.* **8** 2000007
- [42] Wang Y, Diaz D F R, Chen K S, Wang Z and Adroher X C 2020 *Mater. Today* **32** 178
- [43] Lee J M, Han H, Jin S, Choi S M, Kim H J, Seo M H *et al* 2019 *Energy Technol.* **7** 1900312
- [44] Guterman V E, Belenov S V, Alekseenko A A, Lin R, Tabachkova N Y and Safronenko O I 2018 *Electrocatalysis* **9** 550
- [45] Jung S M, Yun S W, Kim J H, You S H, Park J, Lee S *et al* 2020 *Nat. Catal.* **3** 639
- [46] Motz A R, Kuo M C, Horan J L, Yadav R, Seifert S, Pandey T P *et al* 2018 *Energy Environ. Sci.* **11** 1499
- [47] Narayanan H and Basu S 2017 *Int. J. Hydrog. Energy* **42** 23814
- [48] Barbosa R, Escobar B, Cano U, Ortegón J and Sanchez V M 2016 *Int. J. Hydrog. Energy* **41** 19399
- [49] Shojaeefard M H, Molaeimanesh G R, Nazemian M and Moqaddari M R 2016 *Int. J. Hydrog. Energy* **41** 20276
- [50] Rahman M A, Holby E F, Ahmed T, Chuang P Y A, Babu S K, Kort-Kamp W J *et al* 2020 *ECS meeting abstracts* (IOP Publishing) p. 2133
- [51] Wang X, Li Z, Qu Y, Yuan T, Wang W, Wu Y *et al* 2019 *Chem* **5** 1486
- [52] Holton O T and Stevenson J W 2013 *Plat. Met. Rev.* **57** 259
- [53] Wang X X, Swihart M T and Wu G 2019 *Nat. Catal.* **2** 578
- [54] Nørskov J K, Rossmeisl J, Logadottir A, Lindqvist L R K J, Kitchin J R, Bligaard T *et al* 2004 *J. Phys. Chem. B* **108** 17886
- [55] Kocha S S, Shinozaki K, Zack J W, Myers D J, Kariuki N N, Nowicki T *et al* 2017 *Electrocatalysis* **8** 366
- [56] Zhang H, Chung H T, Cullen D A, Wagner S, Kramm U I, More K L *et al* 2019 *Energy Environ. Sci.* **12** 2548
- [57] Jayakumar A 2018 PhD Thesis (Auckland University of Technology)
- [58] Bezmalinovic D, Simic B and Barbir F 2015 *J. Power Sour.* **294** 82
- [59] Goshtasbi A, García-Salaberrí P, Chen J, Talukdar K, Sanchez D G and Ersal T 2019 *J. Electrochem. Soc.* **166** F3154
- [60] Aghighi M, Hoeh M A, Lehnert W, Merle G and Gostick J 2016 *J. Electrochem. Soc.* **163** F384
- [61] Andronie A, Stamatini I, Girleanu V, Ionescu V and Buzbuchi N 2019 *Procedia Manufac.* **32** 810
- [62] Satjaritanun P, Hirano S, Zenyuk I V, Weidner J W, Tippayawong N and Shimpalee S 2019 *J. Electrochem. Soc.* **167** 013516
- [63] Scofield M E, Liu H and Wong S S 2015 *Chem. Soc. Rev.* **44** 5836
- [64] Thompson S T, Wilson A R, Zelenay P, Myers D J, More K L, Neyerlin K C *et al* 2018 *Solid State Ionics* **319** 68
- [65] Kiani M, Zhang J, Luo Y, Jiang C, Fan J, Wang G *et al* 2018 *J. Energy Chem.* **27** 1124
- [66] Duclos L, Chattot R, Dubau L, Thivel P X, Mandil G, Laforest V *et al* 2020 *Green Chem.* **22** 1919
- [67] Liu M, Zhao Z, Duan X and Huang Y 2019 *Adv. Mater.* **31** 1802234
- [68] Xiao W, Lei W, Gong M, Xin H L and Wang D 2018 *ACS Catal.* **8** 3237
- [69] Kregar A, Kravos A and Katrašnik T 2020 *Fuel Cells* **20** 487
- [70] Kregar A and Katrašnik T 2019 *Open Phys.* **17** 779
- [71] Neumann S, Schröder J, Bizzotto F, Arenz M, Dworzak A, Oezaslan M *et al* 2019 *ChemNanoMat* **5** 462
- [72] Antolini E 2016 *Appl. Catal. B: Environ.* **181** 298
- [73] Li L, Hu L, Li J and Wei Z 2015 *Nano Res.* **8** 418
- [74] Escaño M C S 2015 *Nano Res.* **8** 1689
- [75] Paul S, Choi S J and Kim H J 2020 *Energy Fuels* **34** 10067
- [76] Wang Y J, Zhao N, Fang B, Li H, Bi X T and Wang H 2015 *RSC Adv.* **5** 56570
- [77] Singh K, Tetteh E B, Lee H Y, Kang T H and Yu J S 2019 *ACS Catal.* **9** 8622
- [78] Sakhivel M, Radev I, Peinecke V and Drillet J F 2015 *J. Electrochem. Soc.* **162** F901
- [79] Lin R, Che L, Shen D and Cai X 2020 *Electrochim. Acta* **330** 135251
- [80] Rohendi D, Rachmat A and Syarif N 2018 *J. Phys. Conf. Ser.* **1095** 012007
- [81] Bele M, Gatalo M, Jovanović P, Ruiz-Zepeda F, Šala M, Šest E *et al* 2019 *Catalysts* **9** 544
- [82] Daş E, Gürsel S A and Yurtcan A B 2020 *J. Supercrit. Fluids* **165** 104962
- [83] Chiwata M, Yano H, Ogawa S, Watanabe M, Iiyama A and Uchida H 2016 *Electrochemistry* **84** 133
- [84] Zhang G R and Wöllner S 2018 *Appl. Catal. B Environ.* **222** 26
- [85] Latsuzbaia R, Negro E and Koper G 2015 *Fuel Cells* **15** 628
- [86] Ghanbarian A and Kermani M J 2016 *Energy Convers. Manage.* **110** 356
- [87] Cherevko S, Kulyk N and Mayrhofer K J 2016 *Nano Energy* **29** 275
- [88] Dewi E L 2019 *J. Sains Mater. Indonesia* **9** 57
- [89] Ayers K E, Renner J N, Danilovic N, Wang J X, Zhang Y, Maric R *et al* 2016 *Catal. Today* **262** 121
- [90] Chen J, Yang Y, Su J, Jiang P, Xia G and Chen Q 2017 *ACS Appl. Mater. Interfaces* **9** 3596
- [91] Lori O and Elbaz L 2020 *ChemCatChem* **12** 3434
- [92] Tian X, Luo J, Nan H, Zou H, Chen R, Shu T *et al* 2016 *J. Am. Chem. Soc.* **138** 1575
- [93] Balva M, Legeai S, Leclerc N, Billy E and Meux E 2017 *ChemSusChem* **10** 2922
- [94] Zhuang S, Shi X and Lee E S 2015 *International conference on fuel cell science, engineering and technology*, p. V001T04A005

- [95] Vinayan B P, Diemant T, Behm R J and Ramaprabhu S 2015 *RSC Adv.* **5** 66494
- [96] Liu T, Zhao P, Hua X, Luo W, Chen S and Cheng G 2016 *J. Mater. Chem. A* **4** 11357
- [97] Bhange S N, Unni S M and Kurungot S 2018 *ACS Appl. Energy Mater.* **1** 368
- [98] Khan K, Tareen A K, Aslam M, Khan S A, Khan Q U, Saeed M *et al* 2019 *Sci. Rep.* **9** 1
- [99] Martínez-Huerta M V and Lázaro M J 2017 *Catal. Today* **285** 3
- [100] Pavlicek R, Strickland K and Mukerjee S 2016 *ECS Meeting Abstracts* (IOP Publishing) p. 110
- [101] Wu N, Wang Y, Lei Y, Wang B, Han C, Gou Y *et al* 2015 *Sci. Rep.* **5** 1
- [102] Razmjooei F, Yu J H, Lee H Y, Lee B J, Singh K P, Kang T H *et al* 2020 *ACS Appl. Energy Mater.* **3** 11164
- [103] Pethaiah S S, Kumar J A and Kalyani P 2011 *Ionics* **17** 339
- [104] Rajalakshmi N and Dhathathreyan K S 2007 *Chem. Eng. J.* **129** 31
- [105] Pizzutilo E, Geiger S, Grote J P, Mingers A, Mayrhofer K J J, Arenz M *et al* 2016 *J. Electrochem. Soc.* **163** F1510
- [106] Ren X, Lv Q, Liu L, Liu B, Wang Y, Liu A *et al* 2020 *Sustain Energy Fuels* **4** 15
- [107] Garay-Reyes C G, Hernández-Santiago F, Cayetano-Castro N, Martínez-Sánchez R, Hernández-Rivera J L, Dorantes-Rosales H J *et al* 2014 *Bull. Mater. Sci.* **37** 823
- [108] Yang Z, Berber M R and Nakashima N 2015 *Electrochim. Acta* **170** 1
- [109] Zamora H, Plaza J, Cañizares P, Lobato J and Rodrigo M A 2016 *ChemSusChem* **9** 1187
- [110] Zheng L, Dong Y, Chi B, Cui Z, Deng Y, Shi X *et al* 2019 *Small* **15** 1803520
- [111] Waseem S, Maheshwari P H, Abinaya S, Sahu A K, Saini A and Dhakate S R 2019 *Int. J. Energy Res.* **43** 2897
- [112] Waseem S, Maheshwari P H, Maheshwari P, Sahu A K, Saini A and Dhakate S R 2020 *Energy Fuels* **34** 16736
- [113] Wang X X, Prabhakaran V, He Y, Shao Y and Wu G 2019 *Adv. Mater.* **31** 1805126
- [114] He Y, Hwang S, Cullen D A, Uddin M A, Langhorst L, Li B *et al* 2019 *Energy Environ. Sci.* **12** 250
- [115] Wang S, Qiao M, Wang Y, Wang Q, Hu G, Mamat X *et al* 2019 *Angew. Chem. Int. Ed. Engl.* **7** 2688
- [116] Ponomarev I I, Skupov K M, Naumkin A V, Basu V G, Zhigalina O M, Razorenov D Y *et al* 2019 *RSC Adv.* **9** 257
- [117] Shen Y, Li Y, Yang G, Zhang Q, Liang H and Peng F 2020 *J. Energy Chem.* **44** 106
- [118] Xia D, Tang F, Yao X, Wei Y, Cui Y, Dou M *et al* 2020 *Carbon* **162** 300
- [119] Wu Y, Huang J, Lin Z, Li L, Liang G, Jin Y Q *et al* 2021 *Chem. Eng. J.* **423** 130241
- [120] Tan R K L, Reeves S P, Hashemi N, Thomas D G, Kavak E, Montazami R *et al* 2017 *J. Mater. Chem. A* **5** 17777
- [121] Mitra S, Banerjee S, Datta A and Chakravorty D 2016 *Indian J. Phys.* **90** 1019
- [122] Ke Q and Wang J 2016 *J. Materiomics* **2** 37
- [123] Unni S M, Illathvalappil R, Bhange S N, Puthenpediakkal H and Kurungot S 2015 *ACS Appl. Mater. Interfaces* **7** 24256
- [124] Kakaei K and Balavandi A 2016 *J. Colloid Interface Sci.* **463** 46
- [125] Marinou A, Raceanu M, Carcadea E, Varlam M and Stefanescu I 2017 *Appl. Surf. Sci.* **424** 93
- [126] Ma R, Lin G, Zhou Y, Liu Q, Zhang T, Shan G *et al* 2019 *NPJ Comput. Mater.* **5**
- [127] Higgins D, Zamani P, Yu A and Chen Z 2016 *Energy Environ. Sci.* **9** 357
- [128] Zhu J, Yang D, Yin Z, Yan Q and Zhang H 2014 *Small* **10** 3480
- [129] Marinou A, Raceanu M, Carcadea E and Varlam M 2018 *Appl. Surf. Sci.* **456** 238
- [130] Wu J, Xiong L, Zhao B, Liu M and Huang L 2020 *Small Meth.* **4** 1900540
- [131] Cheng Y, He S, Lu S, Veder J, Johannessen B, Thomsen L *et al* 2019 *Adv. Sci.* **6** 1802066
- [132] Jiao L and Jiang H L 2019 *Chem* **5** 786
- [133] Arunchander A, Nishanth K G, Tintula K K, Peera S G and Sahu A K 2015 *Bull. Mater. Sci.* **38** 451
- [134] Wang M, Zhang H, Thirunavukkarasu G, Salam I, Varcoe J R, Mardle P *et al* 2019 *ACS Energy Lett.* **4** 2104
- [135] Proton Exchange Membrane Fuel Cell (PEMFC) Market. Available: <https://www.fortunebusinessinsights.com/industry-reports/proton-exchange-membrane-fuel-cell-pemfc-market-101708> (Accessed on 18 February 2021)
- [136] de Frank Bruijn A and Janssen G J M 2019 Lipman T and Weber A (eds) *Encyclopedia of sustainability science and technology series* (New York: Springer)
- [137] Zhang J 2019 Lipman T and Weber A (eds) *Encyclopedia of sustainability science and technology series* (New York: Springer)