



Review Article

Recent trends in carbon support for improved performance of alkaline fuel cells

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Abstract

Alkaline Fuel cells (AFCs) are one of the emerging energy future energy sources and energy conversion systems. The use of the anion exchange membrane in alkaline fuel cells (AEMFCs) has made AFCs more versatile. It has also introduced the use of an abundance of catalysts, mostly non-Platinum group metals (PGMs), especially for its more favorable cathodic oxygen reduction (ORR). The benefits and importance of the presence of efficient porous carbon supports to enhance the electroactivity of these catalysts were highlighted. Apart from the well-known carbon allotropes used as catalyst supports, some new and innovative forms of porous carbon and their composites are discussed. Their performance as stand-alone catalysts or as support for non-PGMs for ORR in operating conditions of AEMFCs has given a further boost to the future availability of low-cost AFC-driven devices.

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Keywords

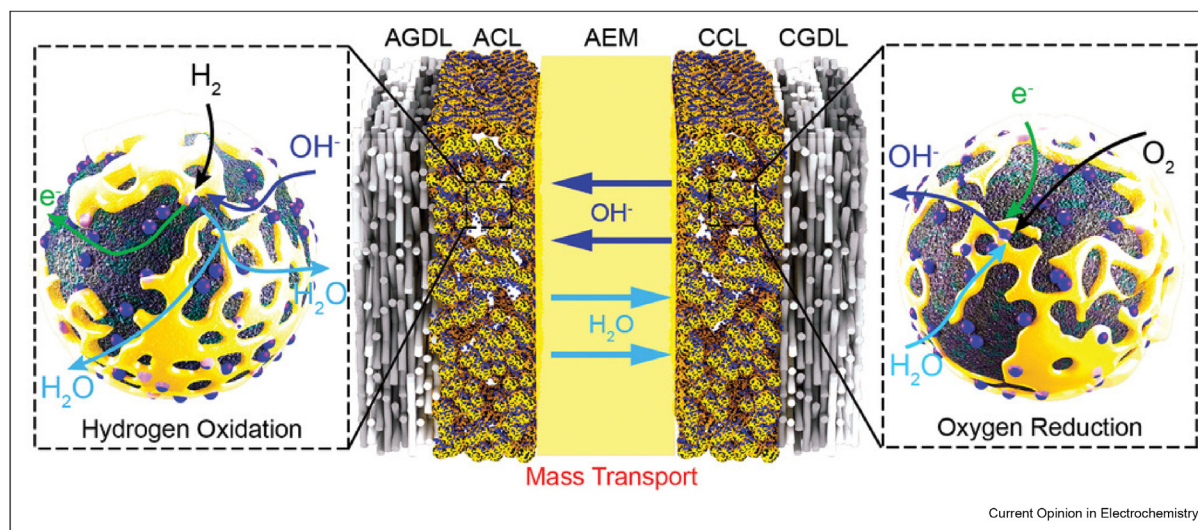
Alcohol alkaline fuel cells (AAFCs), Anion exchange membrane fuel cells (AEMFCs), ORR, Electrocatalysts, Carbon supports, Porous carbon materials, Nano carbon allotropes.

Introduction

Fuel cells (FCs) are promising new electrochemical and power generation devices that directly convert chemical energy into electrical energy. They are the best choice to replace batteries for delivering power for a wide range of applications due to their theoretical efficiency of more than 80%, continuous electricity to meet future clean energy generation without long-time charge, and lightweight [1]. Recent developments in fuel cell knowledge and technology have made it possible to utilize them as dependable sources of power. Low-temperature polymer electrolyte membrane FCs are the future of high-efficiency energy conversion for transportation [2]. The proton exchange membrane fuel cell (PEMFC) possesses a high peak power density operating on H₂ fuel with ambient air as the oxidant, even with low Pt loading (1.24 W/cm² at 0.125 mgPt/cm²) and stable operation for tens of thousands of hours [3]. However, PEMFCs have not yet achieved commercial success despite their great performance. The lack of H₂ distribution networks may have limited the adoption of these systems, but their high price tag has been the main hurdle to market acceptability and penetration in the transportation sector. The alkaline fuel cell (AFC) has certain advantages over its acidic counterpart. Among the most favorable attributes of AFCs are (i) the ability to utilize any catalyst, apart from the platinum group metals (PGM); (ii) the favorable thermodynamics of oxygen reduction in the alkaline media, (iii) the adoption of anion exchange membrane, and (iv) and the reduction in the corrosion problem faced by fuel cell stack hardware, [4,5]. These are mostly the main drawbacks of PEMFCs and demonstrate the potential of AEMFCs as an alternative to PEMFCs which have already been commercialized.

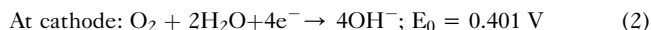
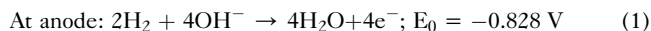
An AEMFC stack's structural design is typically similar to that of a PEMFC stack. Figure 1 depicts a typical AEMFC structure, which consists of an anode (AGDL and ACL) and cathode (CGDL and CCL) electrodes separated by an anion exchange membrane (AEM). A liquid electrolyte is used in AFC technology for ionic conduction between the two electrodes. Potassium hydroxide is the most conductive of all alkali metal hydroxides and the most commonly used electrolyte in this application. During operation, the anode electrode

Figure 1



The reaction and mass transfer processes of AEMFC [6].

receives $H_{2(g)}$ /fuel and water, while the cathode electrode receives O_2 gas and water. Equations (1) and (2) below describe the electrochemical reactions that occur at the catalyst surface in an AEMFC with a direct four-electron pathway. For the anode, much research has focused on exploring different materials to reduce the hydrogen binding energy (HBE) and increase the HOR activity. Since this is the region where water is generated, the anode catalyst layer (ACL) also faces problems of water management [6] and hydrogen gas transfer. For the cathode, the ORR occurs more easily in an alkaline environment than in acidic environment, allowing the use of non-PGM as the ORR active center [7]. In addition, ORR at the cathode is theoretically regarded as an important reaction in the energy conversion systems such as hydrogen FCs as well as other alcohol FCs [8–10].



For most electrocatalysts employed in FC devices, support materials play a critical role in determining catalytic activity and durability, as well as mass transfer and water management [11]. Pt-based catalysts, which effectively avoid the shortcomings of sluggish kinetics reaction in the ORR process, have been widely regarded as the most effective catalysts to make oxygen molecules undergo efficient reduction reactions at the cathode [12]. However, Pt-based catalysts have several disadvantages of high cost, low stability, and insufficient reserves, which bring huge challenges in practical applications and force the development of cheap, robust, and high-efficiency

non-precious metal catalysts [13]. An ideal ORR electrocatalyst should have an active surface responsible for catalyzing the ORR process and a conductive bulk to facilitate the charge transfer [14]. Due to their unique characteristics, such as being stable in both acidic and basic environments, meeting the majority of the desirable requirements for suitable support, and being removable from electrocatalysts by burning off, carbon materials have been used in heterogeneous electrocatalysts as a support for a long time [15,16]. Carbon materials are characterized by their very high surface area, high electrical conductivity, appropriate porosity, and presence of active sites (functionalized form) which can suitably disperse metal nanoparticles. They also have better electron transfer and adequate water management, resulting in enhanced performance of FC devices. Various carbon materials in diverse forms such as carbon black (CB), activated carbon, graphene (GR) [17,18], carbon nanotubes (CNTs) [19], nano carbons onions [20], carbon nanoribbons [21] reduced graphene oxide (rGO) [22], carbide-derived carbon (CDC) [23], carbon nanoions [24], nitrogen-doped hollow carbons (NHCs) [19], carbon-BP200 [25], carbon nanohorns (CNHs), carbon nanodots (CNDs) [26], and activated carbon (AC-) [27] have been employed in different electrocatalysts. Functionalizing some of these carbon supports like CNTs, and graphene, with organic groups like hydroxyl (OH), amines (NH_2), and acetyl (CO) via weak covalent π - π stacking has been seen to improve both their catalytic activity and hydrophilic nature in active FC operations [28]. As any large-scale and sustainable deployment of AEMFCs should minimize the use of both PGMs and even critical raw materials (CRMs) [29], recent studies have focused on the use of doped carbon

substrates as cathode catalysts in AEMFCs. Doping the different nano carbon forms with heteroatoms such as N, S, B, and O also improves electrocatalytic activity. N-doped carbon forms (N-C) and metal-nitrogen-carbon (M-N-C) are very well known as effective stand-alone electrocatalysts or electrocatalytic supports for ORR in FC applications [30]. The former was investigated by Biemolt *et al.* who utilized an ACL of Ni₇Fe/C and N-doped carbon as CCL in an AEMFC operation and thus, achieving a maximum power density of 56 mWcm⁻² at a current density of 138 mAcm⁻². According to the authors, this is among the highest values reported to date for CRM-free electrocatalyst systems [31]. It is believed that nitrogen dopants donate electrons to the π -orbital in carbon, which can then be transferred to the π^* -orbital of O₂, facilitating the splitting of oxygen bonds and increasing the ORR kinetics. As a result, non-PGM catalysts can be employed in the AEMFC cathode catalyst layers due to carbon support for nanomaterials, particularly single-atom catalysts. Thus, this article highlights some key research on carbon allotropes used as supporting materials for catalysts in AEMFC based on material design, catalyst fabrication, and FC test process. The goal is to provide an instructive perspective that scientists and researchers may utilize to better understand carbon supports and stimulate the use of such innovative materials in AFC technologies.

Anion exchange membrane fuel cells

Despite the efficiency and improved working performance of PEMFCs [32], it is yet to become commercially viable as a result of their relatively high cost. Cruz *et al.* suggested an effective way to circumvent this limitation by the modification of PEMFC cell chemistry [2] which can be carried out via acidic to alkaline membranes transition thus creating AEMFC. Thus, an obvious advantage of AEMFC over PEMFC is that the former operates at higher pH and therefore creates an environment that is less corrosive. Higher pH affords AEMFC the comparative advantage of using less expensive materials for cell components such as membranes, catalysts, and bipolar plates [2].

Thus, Cs are a specific type of FCs characterized by the alkaline electrolyte used in the cell. AFCs consist of typical FC components, including the anode, cathode, electrolyte, and catalysts [33,34]. Anion exchange membranes (AEMs) are gaining popularity for use in AFC technologies to replace traditional AFCs, creating the anion exchange membrane fuel cells (AEMFCs). Anion exchange membrane (AEM) is the core component of AEMFCs, which not only separate the cathode and anode catalyst layers (making up the membrane electrode assemble – MEA), but also plays a vital role in ion transport [35]. Being the main part of the MEA, the region where electrochemical reactions and mass transport occur, it plays an important role in power density

output. Therefore, it directly determines the performance of AEMFCs. Ideally, AEM should have high ionic conductivity, good alkali stability, and excellent mechanical strength. However, since the transfer coefficient of OH⁻ is only one-fourth of H⁺, the ionic conductivity of AEM is generally lower than that of proton exchange membrane (PEM).

Key characteristics and challenges

AFCs have a number of distinct characteristics as a result of the alkaline environment in the cell. One of the most important is the effect on the rates of reactions at the anode and cathode. The rates of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) at the cathode are higher in an AFC compared to an acidic cell due to the highly alkaline environment [36]. The slow ORR and OER rates in PEMFC typically necessitate the use of platinum catalysts to achieve adequate cell voltages. However, this increases the overall cost of the cell [37]. Because the ORR and OER rates are higher in an AFC [38], platinum catalysts are not as necessary, thus permitting the use of non-PGMs at the cathode with a large selection of cheap polymers and carbon supports with good durability [36]. On the other hand, hydrogen oxidation reactions (HOR) and hydrogen evolution reactions (HER) at the anode occur at a significantly lower rate in alkaline media when compared with acidic media [38]. The challenge (HOR) originates from the demand to maintain a partly oxide-free metal surface up to an anode potential of 0.1 V versus the reversible hydrogen electrode (RHE) and preferably higher, as required for the bonding of H_{ads} intermediates in the relevant potential range. This is a difficult requirement for a non-PGM catalyst; thus, appropriate catalysts need to be developed for hydrogen reactions in AEMFCs. Moreover, AEMFCs have low fuel crossover which means they can be operated with an extended use of alternative fuels to hydrogen-like alcohols (mainly methanol and ethanol, polyols-glycerol, glucose, and ethylene glycol and N-based fuels-hydrazine and ammonia). In contrast, classical AFCs are susceptible to CO₂ poisoning if the cell is exposed to air. AEM carbonation occurs when air instead of O₂ reacts with OH⁻ anions in the anion-exchange ionomers to form HCO₃⁻ and CO₃⁻ as CO₂ readily reacts with alkaline hydroxides which are the media for these fuels, to form negatively charged carbonate (CO₃⁻) and bicarbonate ions (HCO₃⁻), leading to cell performance losses [36,39]. This carbonation problem at the cathode not only reduces the conductivity of the electrolyte membrane but also leads to up to 50% performance reduction and a fast decrease in the ion conductivity [11]. Fortunately, as recent and ongoing development has shown, the use of solid membranes (alkaline anion exchange membranes) has minimized the carbonation and fuel crossover issues associated with aqueous hydroxides mainly, KOH [40,41].

In AEMFCs, water plays different roles: at the cathode, water acts as a reactant, whereas at the anode, it is a reaction product. The dehydration and flooding of the cathode and anode, respectively, are more prominent in AEMFCs than PEMFCs, which inevitably leads to poor cell performance. Thus, water management needs to be addressed in AEMFCs. The ionomer (which is mixed with the catalyst) content has a prominent effect on controlling the water management in both the electrodes in AEMFCs [42].

For example, the higher ion exchange capacity (IEC) of the ionomers at the cathode resulted in a reduction in OH^- ionic resistance and thus improved cell performance, while the relatively lower IEC of ionomer at the anode avoids detrimental effects such as ionomer dissolution and anode flooding. Also, too much ionomer content results in the blockage of the surface pores of catalyst supports and the shielding of the active catalyst surface of the electrode, thereby decreasing the efficiency of the catalysts' utilization. Generally, the formation of a proper TPB (three-phase boundary) formation is essential for maximum catalyst utilization. Thus, the utilization of ionomers should be such that it uniformly coats the catalyst but does not block the gas diffusion in the porous carbon substrates. Some authors have observed that the use of low-molecular-weight ionomers with hydrophobic blocks would lead to the promotion of systematic phase separation which create ion conduction and gas diffusion channels leading to better mass transport and improved FC performance [43].

Another drawback is the cell durability. According to a recent technical target provided by the U.S. Department of Energy, a viable single-cell AEMFC needs to operate above 60°C at a current density of over 600 mA/cm^2 for 2000 h with less than 10% voltage degradation [44]. Stability issues can be difficult to attribute to a single component in the integrated device, since electrocatalysts, catalyst supports, alkaline anion exchange membranes (AAEMs), anion exchange ionomers (AEIs), and their interfaces are all prone to degradation under AEMFC operating conditions [37]. However, regarding the catalyst layer (CL); the catalyst on the electrode surface can be easily detached during long FC operations. A stable catalyst support with highly exposed active facets, surface area, and strong corrosion resistance coupled with high mechanical stability will be desirable to maintain steady durability coupled with active performance [45].

Several PGM-free catalysts have shown ORR activity similar to platinum in preliminary liquid half-cell tests, reliable PGM-free catalysts with long-term high performance in an AEMFC are scarce. In particular, PGM-free electrodes generally require high catalyst loading due to their relatively low active-site density, which leads to thick electrodes that make oxygen and water transport

difficult. Therefore, in addition to the need for high ORR activity, achieving high-performance PGM-free cathodes in AEMFCs also requires mass transport to be more effectively managed. This can be overcome by use of appropriate supports in the form of carbon due its aforementioned properties. This will ultimately reduce the amount of catalysts required in building the catalysts layer. Moreover, obtaining a balanced pore structure (meso and macro) of such carbon supports will readily facilitate the mass transport in the system.

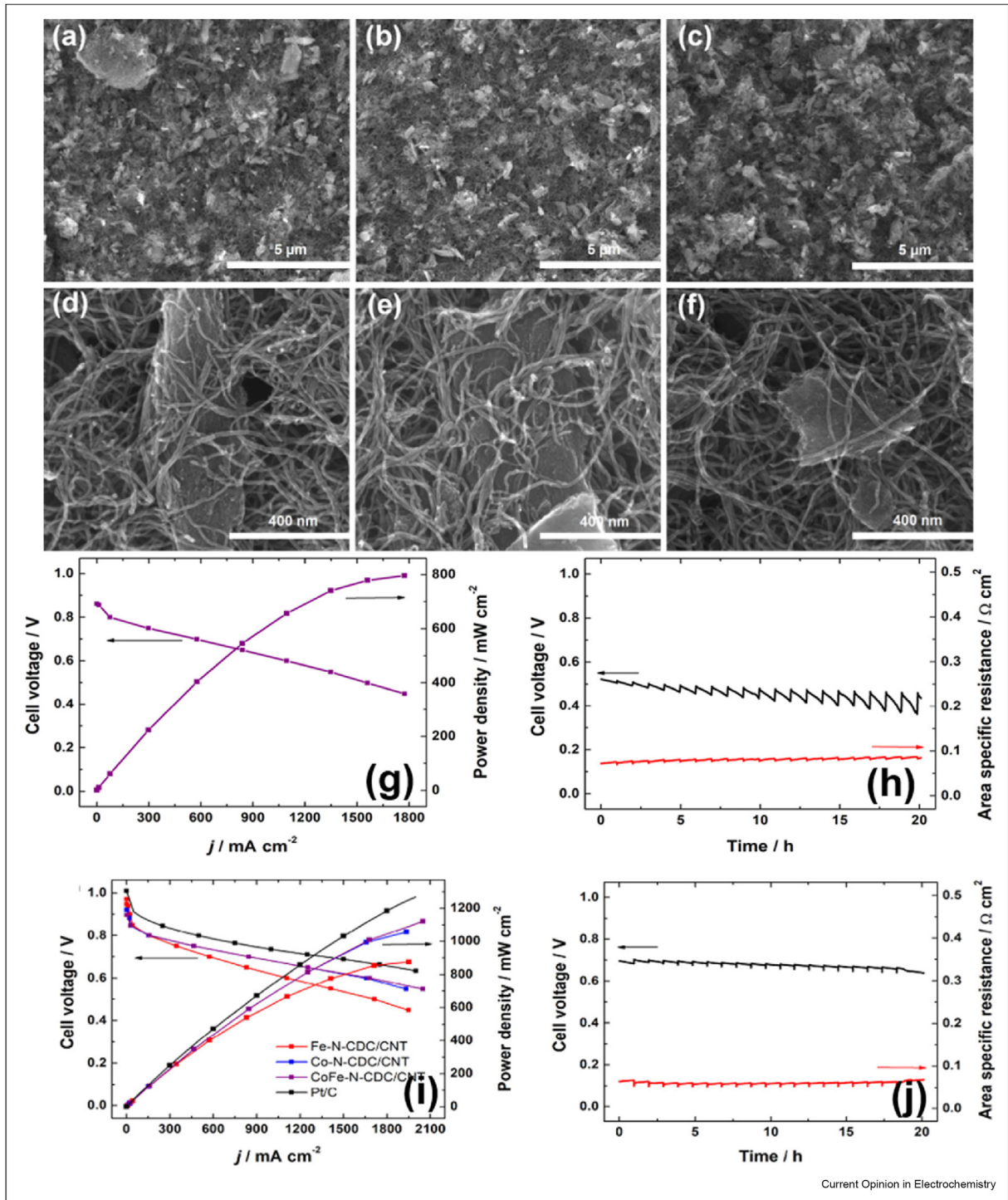
Main catalysts used in AFCs

Catalysts used in ORR

The general assertion is that ORR readily takes place in basic medium. This is because there is a change in thermodynamics as the pH of the solution increases thus changing the potential difference (acidic medium with 1.229 V and alkaline medium with 0.401 V). This reduction in potential difference causes the surface-free energy to increase, which then increases oxygen and its intermediates' adsorption by lowering free energy. However, only a few catalysts such as Pt in acidic medium have sufficient O_2 adsorption-free energy to allow efficient binding on the surface and occurrence of ORR. On the other hand, alkaline electrolytes allow surface reactions to occur, thus allowing other materials apart from Pt to be used as catalysts in ORR. Some of the other catalysts which have been used in ORR are PGMs-based catalysts including platinum alloys, and, PGM-free catalysts (non-PGM-based noble metals, carbon-based catalysts, and transition metal oxides) [33].

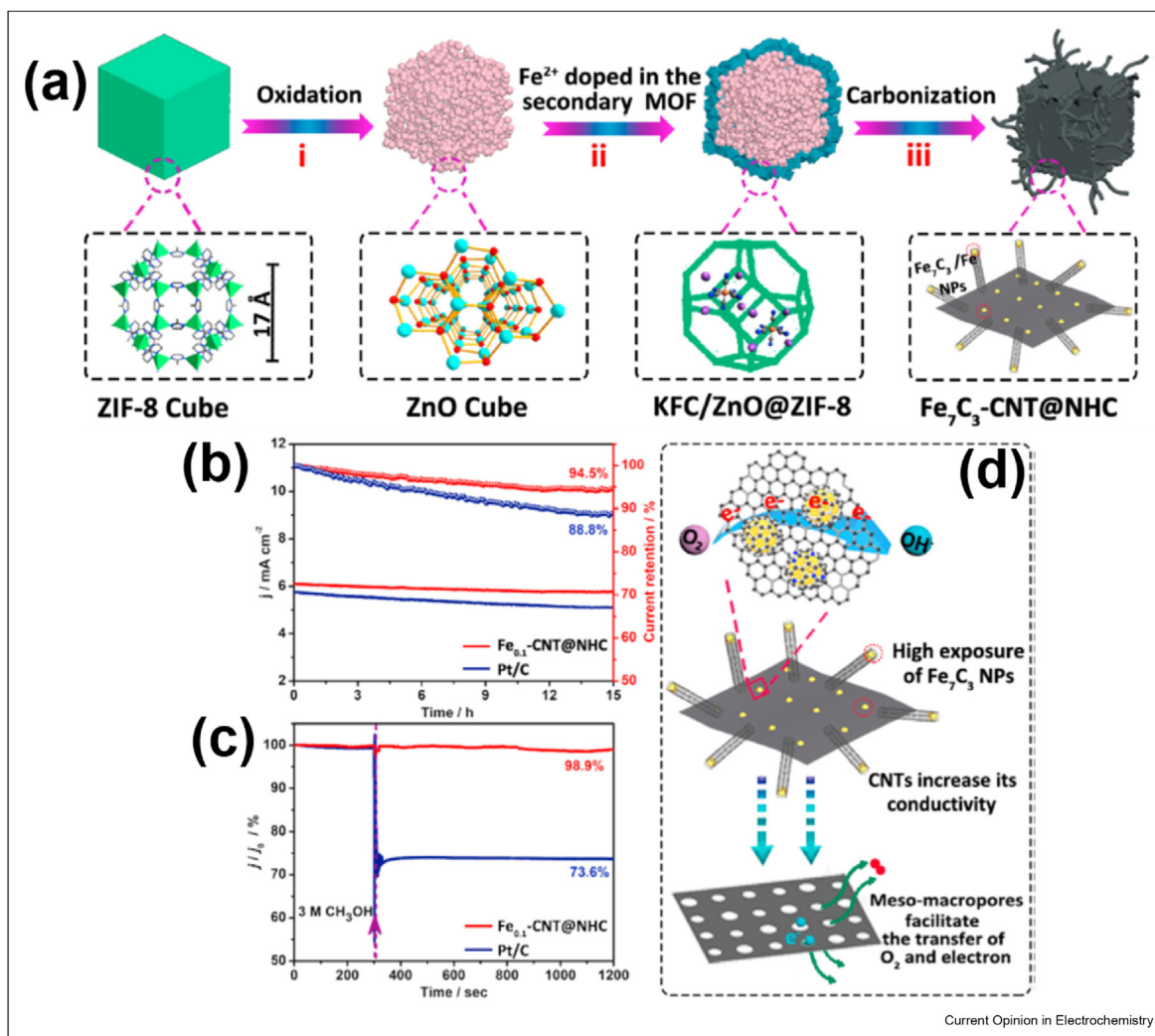
Adabi et al., 2021 [46] reported the use of Fe–N–C cathode electrocatalyst for AEMFCs and the result obtained showed a peak power density exceeding 2 W cm^{-2} with very good voltage durability for more than 150 h. Furthermore, a half-wave potential of 0.846 V was reported. Further tests carried out showed that H_2/O_2 integration gave a current density of $>7\text{ A cm}^{-2}$, while CO_2 -free air when integrated showed a current density $>3.6\text{ A cm}^{-2}$. When Fe–N–C cathode was used with low-loading PtRu/C anode, the total PGM loading of $0.125\text{ mg}_{\text{PtRu}}\text{ cm}^{-2}$ ($0.08\text{ mg}_{\text{Pt}}\text{ cm}^{-2}$) which gave power output peaking at $10.4\text{ W mg}_{\text{PGM}}^{-1}$ ($16.25\text{ W mg}_{\text{Pt}}^{-1}$), thus surpassing the highest DOE milestone performance reported for AEMFC reported in 2022. The use of non-precious transition metals (Co, Fe, and CoFe), N-doped carbide and CNT nanocomposites used as cathode catalysts for AEMFCs revealed that CoFe–N–CDC/CNT gave the best catalytic performance with a power density of 1.12 W cm^{-2} as compared with 1.06 W cm^{-2} and 0.88 W cm^{-2} respectively shown by Co–N–CDC/CNT and Fe–N–CDC/CNT. Furthermore, Co–N–CDC/CNT, Fe–N–CDC/CNT, and CoFe–N–CDC/CNT showed current densities of 0.47 A cm^{-2} , 0.35 A cm^{-2} , and 0.47 A cm^{-2} respectively at 0.75 V. These values are among the highest reported for precious metal-free cathode catalysts reported in literature [23].

Figure 2



SEM micrographs with lower (a–c) and higher magnification (d–f) for Fe-N-CDC/CNT (a, d), Co-N-CDC/CNT (b, e) and CoFe-N-CDC/CNT (c, f). With permission from Ref. [23] (g) Polarization and power density curves and (h) in situ stability operation at a constant current density load of 0.6 A cm^{-2} using CoFe-N-CDC/CNT as the cathode catalyst, (i) Polarization and power density curves using various cathode catalysts shown in the legend and (j) CoFe-N-CDC/CNT AEMFC in situ stability operation at a constant current density of 0.6 A cm^{-2} [19].

Figure 3



(a) Synthetic route to synthesize $\text{Fe}_x\text{-CNT@NHC}$ materials, Stability tests (b) MeOH crossover effect tests of $\text{Fe}_{0.1}\text{-CNT@NHC}$ (c) and the commercial Pt/C catalyst at 0.6 V vs. RHE at 1600 rpm. (d) Schematic illustration of the $\text{Fe}_{0.1}\text{-CNT@NHC}$ for efficient ORR electrocatalysis [8].

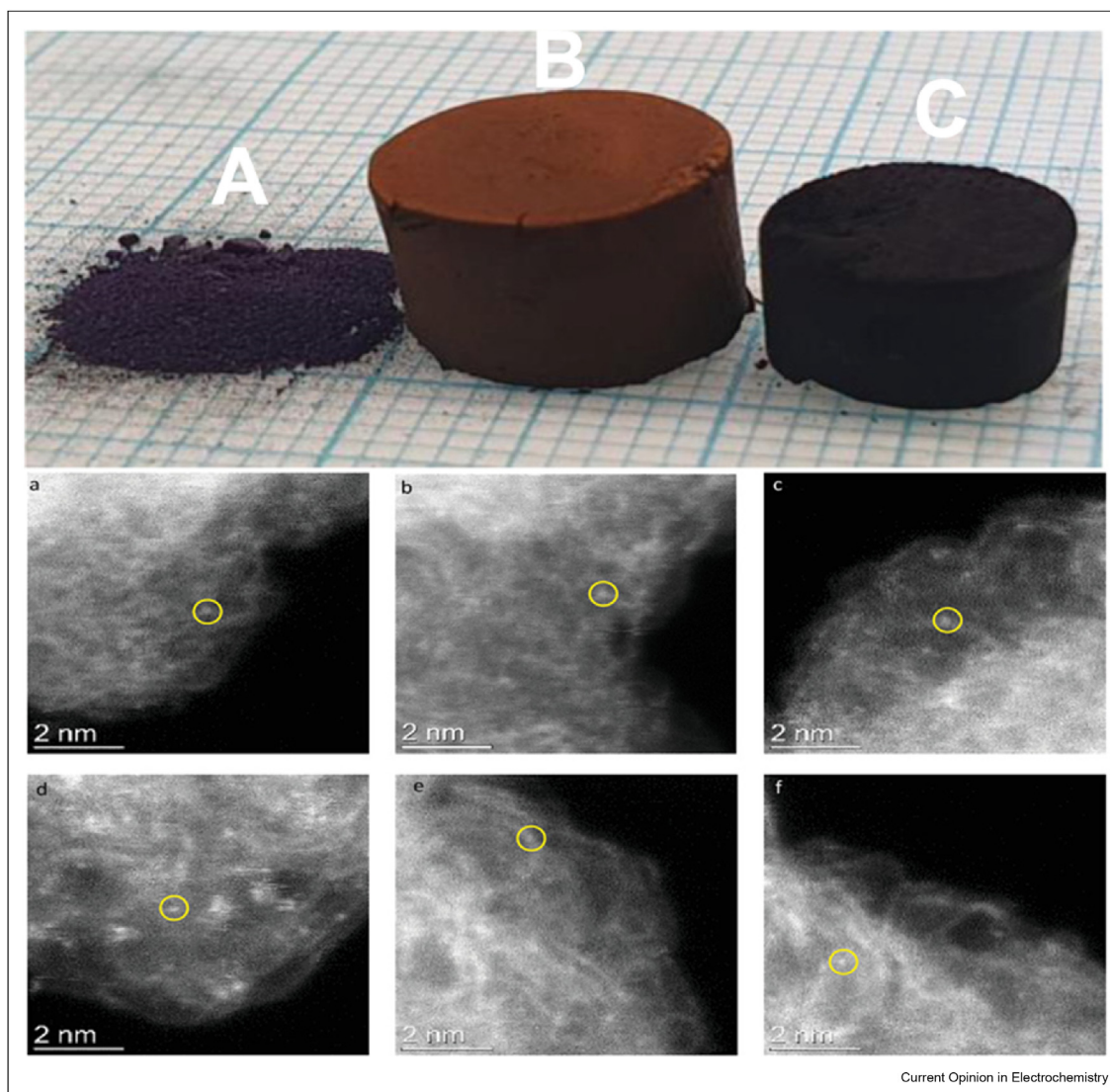
A similar study by Zeng et al., 2022 on the use of non-precious transition metal nitrides as ORR electrocatalysts for AFCs revealed that $\text{Co}_3\text{N/C}$, MnN/C , and $\text{Fe}_3\text{N/C}$ produced the best catalytic performance with $\text{Co}_3\text{N/C}$ being the highest with mass activity at approximately 170 A g^{-1} and $E_{1/2}$ 0.862 V vs RHE. The observed ORR activity is however lower than that observed for Pt/C with $\text{Co}_3\text{N/C}$ showing a lower Tafel slope value of 37 mV dec^{-1} while Pt/C showed a value of 66 mV dec^{-1} . This is an indication that ORR kinetics on Pt/C are controlled by the first proton transfer in alkaline medium.

Carbon supports for catalysts in AEMFCs

Microstructure and the fabricating method of electrodes associated with their transport resistances and

electrochemical kinetics are critical for the improvement of cell performance. Modern AEMFC electrocatalyst layers are usually composite structures of anion conducting ionomer material and noble or non-noble metal catalysts, usually supported on carbon. The characteristics of a good catalyst support material include the presence of surface functional groups that promotes catalyst–support interaction, a mesoporous structure that improves the triple phase boundary, electrochemical stability, high electrical conductivity, a high surface area, low surface poisoning, and corrosion resistance. The use of carbon-based support with various structural and morphological properties improves the stability and electrocatalytic activity of the catalyst. With the use of carbon support, mass transfer and electronic conductivity in the catalyst layer are found to be enhanced [34,47].

Figure 4



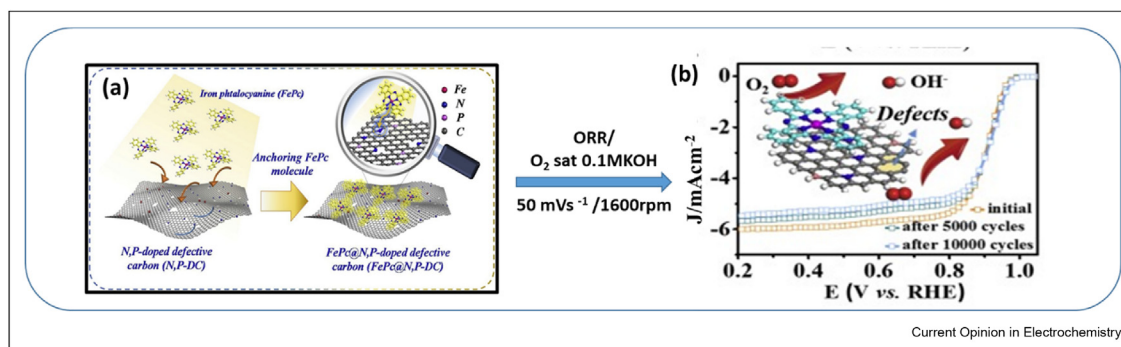
Photograph of porphyrin powder used for the synthesis of the FeP aerogel (a) FeP aerogel (b), and the aerogel after the heat treatment-HT800-FeP (c) and ADF-S STEM images of (a) pristine FeP aerogel, (b) HT600-FeP aerogel, (c) HT700-FeP aerogel, (d) HT800-FeP aerogel, (e) HT900-FeP aerogel, and (f) HT1000-FeP aerogel (yellow circles show examples of iron ions within the aerogel samples).

One of the basic prerequisites of catalyst supports is the high surface area that facilitates and promotes uniform dispersion of catalyst nanoparticles (NPs). Another factor is porosity, which impacts the mass transit of reactants, the homogeneity of the distribution of catalytic nanoparticles on supports, and the accessibility of embedded catalysts to the electrolyte. Thus, the presence of macropores and mesopores allows for easier gas flow and higher accessibility of electrolyte to the electrocatalytically active sites. The presence of a large surface-to-volume ratio and strong binding of the

nanoparticle catalyst on the support will enhance the catalytic activity of the electrochemical reaction while preventing detachment of catalysts during long runs of FC operations [45].

This section looks into the fabrication and development of new porous carbon supports and carbon composite supports that have been shown to assist the catalyst in enhancing their catalytic activities. These carbon supports have promoted selectivity, durability, surface area, and exposure of the active sites as well as

Figure 5



(a) The synthetic procedure of FePc@N,P-DC catalyst showing N,P-DC substrate and FePc and (b) ORR polarization LSV of FePc@N,P-DC measurement before and after 5000 and 10,000 cycles at the scan rate of 50 mV s^{-1} with the rotation speed of 1600 rpm. The inset figure indicates the two kinds of ORR active sites (the topological defect on N,P-DC and FePc) during ORR process. (Adapted and modified from original figures in Ref. [49]).

excellent conductivity especially for oxygen reduction catalysis in AEMFCs. Other carbon supports in view of being tested in active AEMFCs are also featured.

Carbide-derived carbon (CDCs)

It is widely known that CDCs are known to be one of the carbon materials which stands out due to the large specific surface area (higher than $1000 \text{ m}^2 \text{ g}^{-1}$), and easily tunable pore size [61]. CDCs also have other additional benefits, one of which is that they impart extremely high stability features to ORR catalysts. CDC materials can be produced from numerous carbide sources (e.g. SiC, TiC, ZrC, Mo_2C). Their porous structure can be easily modified, via the chlorination temperature and the initial carbide source. As a result, their composites could be used to make materials with both micro- and mesoporous pore sizes. Liloja et al. [23] developed some ORR catalysts with a combination of N-doped CDC and CNT. As shown in Figure 2. The carbon support N-doped CDC/CNT incorporated with CoFe(CoFe-N-CDC/CNT) showed no decline in current after 10,000 consecutive cycles, gave a power density of app 1120 mW cm^{-2} with H_2/O_2 FC operations.

N-doped hollow carbon cubes (NHCs)

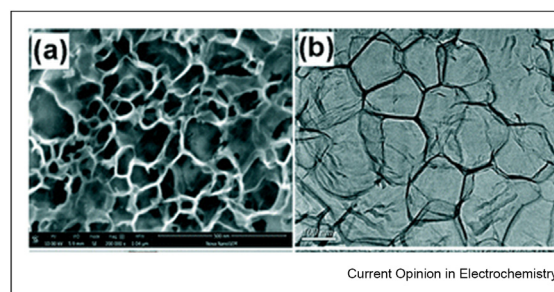
This was innovatively designed using MOF precursors and was incorporated with CNT grown with Fe in situ, to produce $\text{Fe}_x\text{-CNT@NHC}$ as shown in Figure 3. Chai et al. reported $\text{Fe}_{0.1}\text{-CNT@NHC}$ with a power density output of 105.9 mW cm^{-2} which is comparable to Pt/C with 134 mW cm^{-2} . A limiting current density of 164.8 mA cm^{-2} was also observed with a 73% current retention after 1200 s. The authors attributed this exceptional result with only Fe as the metal catalysts to: (i) presence of meso-macropores contained in the hollow structure which facilitates the transfer of O_2 and electron; (ii) the carbon network which provides effective support and exposure for highly active FeN/Fe₇C₃ species, and (iii)

the in situ grown CNT which greatly increased its conductivity to enhance its ORR activity.

Porphyrin-derived aerogels (FeHT800)

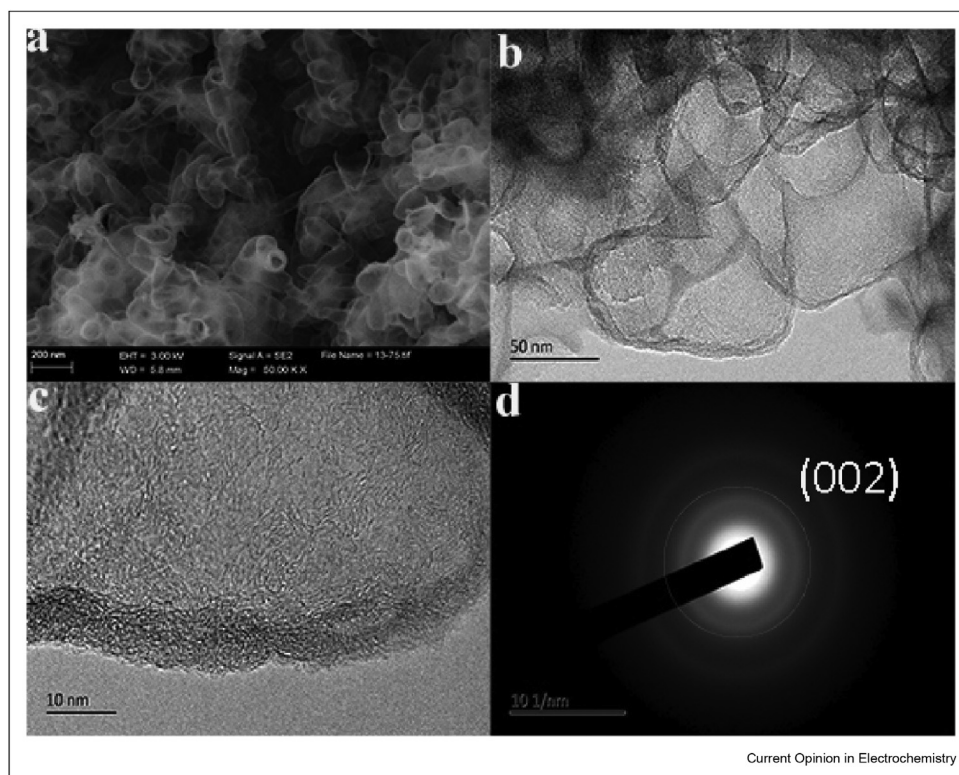
Porphyrin-derived aerogels were synthesized from Fe(III)-5,10,15,20-(tetra-4-aminophenyl) porphyrin (FeP) and heat treated from 600 to 1000 °C at intervals of 100 °C to produce a carbonaceous framework in form of FeP aerogels as shown in Figure 4. The pyrolysis temperature was optimized to ensure structural changes did not result in loss of activity due to the release of carbon and nitrogen from the aerogel matrix, especially at higher temperatures. FeP aerogel heat treated at 800 °C-FeHT800-(Figure 4 c and d) retained the highest catalytic performance (activity and selectivity) as cathode catalysts in AEMFCs reaching a peak power density of 580 mW cm^{-2} and a limiting current density of as high as 2.0 A cm^{-2} . Although a duration test was not included in this study, FeHT800 has been considered the state-of-the-art for PGM-free-based AEMFCs. It should also be noted that its performance was achieved with low catalyst loading of 1.25 mg cm^{-2} , which represents only 0.033 mg cm^{-2} of metal loading

Figure 6



SEM (a), and TEM (b) images of HSG, respectively (adapted from the original figure, reference [50]).

Figure:7



(a) SEM image, (b) TEM image, (c) High-resolution TEM image and (d) selected area electron diffraction of CeN-10% [51].

(based on 2.64 wt.% iron content). This catalyst loading was observed to be close to the average PGM-free M–N–C cathode loading reported in the recent literature [48].

N, P-doped defective carbon nanosheets (N, P –DC)

A facile non-pyrolysis strategy was used to synthesize high-effective well-define atomic-scaled metal-N-C catalysts by directly coordinating the metal (Iron) –N₄ organic macrocyclic molecules (FePc) to the N-doped sites of nitrogen phosphorus-doped defective carbon nanosheets (N, P-DC) to produce FePc@N,P-DC catalyst. FePc@N,P-DC was shown to exhibit enhanced catalytic ORR activities in terms of the half-wave potential, 0.903 V vs, a high kinetic current density (J_k) value of 7.64 mA cm⁻² in 0.1 M KOH with a very low tafel slope of 29 mV dec⁻¹ coupled with a catalytic durability of no-appreciable ORR current loss after 10,000 cycles.

It was seen that the ORR activity of FePc@N,P-DC was a result of the synergetic ORR activities on both the FePc surface and the topological defects on the N,P-DC as depicted in Figure 5 below:

A list of other factors given by the authors as the reason for the outstanding electroanalytical activity of the FePc@N,P-DC catalyst were attributed to the synthesized N,P-DC carbon substrate. The main qualities highlighted are: (i) the presence of the thin carbon, N,P-DC, nanosheets with high conductivity allow efficient electron transportation and mass transport during the electrochemical ORR process, favoring effective accessibility of the intrinsic active sites (enhancing ORR activity); (ii) the P-doped sites probably played an important role in modulating the charge distribution over the carbon skeleton and even the Fe–N₄ active center, leading to optimizing the adsorption behaviors of the reaction zone and thus tailoring the activity of the electrochemical catalysts; and (iii), due to the electron-withdrawing property of N and P substitutions, the FePc molecules with π electron can be firmly captured on the N,P-DC, and thus maintaining the structural stability during long-cycling test (enhancing ORR stability) [49].

3D porous graphene-doped Fe/N/S (FeNSG3)

A new type of graphene, 3D porous graphene-doped with Fe/N/S (FeNSG3) was synthesized, by

Table 1

Catalysts/Carbon-support composites and their performance in direct alkaline alcohol fuel cells.

Catalysts/Carbon support (Cathode catalysts)	Cathode Catalyst mass loading	Anode/mass loading	Fuel Cell test conditions	Open Circuit Voltage (V)	Peak power density (mW cm ⁻²)	Ref.
FeFPc@C-BP2000 (Fluorinated Iron Phthalocyanine)	2 mg cm ⁻²	Pt/C 0.6 mgPt cm ⁻²	80 °C H ₂ /O ₂ , 0.5 L min ⁻¹ , 500 sccm with 100% RH	0.98	165	[25]
N,P-SiCDC/CNT	2 mg cm ⁻²	Pt-Ru/C (0.8 mg Pt-Ru cm ⁻²)	60 °C H ₂ /O ₂	0.98	583 mWcm ⁻²	[62]
CoOx@CoNy/NCNF	1.26 mg cm ⁻²	Pt/C 0.2 mg cm ⁻² Pt	60 °C with H ₂ /O ₂	≈ 0.92	≈ 80	[52]
Fe/Co/IL-CNf-800b	2mgNPMC cm ⁻² (0.4 mg Pt cm ⁻²)	0.6 mgPt-Ru cm ⁻²	60 °C with H ₂ /O ₂		195	[53]
Fe-N-C	1 mg cm ⁻²	PtRu/C 0.6 mg cm ⁻²	60/60/60 °C, H ₂ /O ₂	0.9	2100	[46]
FeCoN-MWCNT	0.745 mg metal cm ⁻²	Pt/Ru 0.7 mg cm ⁻²	60/58/57 °C H ₂ /O ₂	0.98	692	[54]
Fe _{0.1} -CNT@NHC				1.46	105.9	[19]
N-GLC			H ₂ and O ₂		6	[55]
CF-VC	3.4 mg	0.7 mgPtRu cm ⁻²	70 °C, H ₂ /O ₂	0.85	1350	[56]
Ag/C	1.0 mg	0.8mgcm ⁻²	70 °C, H ₂ /O ₂	0.4	200	[57]
N-CDC/CNT	0.4 mgcm ⁻²	0.1 mgPt cm ⁻²	60 °C		260	[23]
FeMn-N-MPC	2 mgcm ⁻²	Pt-Ru 0.6 mg cm ⁻²	H ₂ /O ₂ /60 °C	1.0	474	[58]
Ag/MWCNT	1.0 mg cm ⁻²	Pt/C 0.8 mg cm ⁻²	70 °C with H ₂ and O ₂		356.5	[59]
NiCo/NCNTs	4.0 mg cm ⁻²	0.12 mg Pt cm ⁻²	H ₂ /O ₂ /100% RH	0.96	65	[60]

CNF-Carbon nanofibres; IL-ionic liquid; CNT-carbon nanotube; NHC-N-doped hollow carbon; N-GLC -nitrogen-doped graphene-like carbon; N-CDC-nitrogen-doped carbide-derived carbon; MWCNT-multi-walled carbon nanotube, NCNT-nitrogen-doped carbon nanotube N-MPC-n-doped mesoporous engineered catalyst carbon support, N,P-SiCDC/CNT-nitrogen and phosphorus dual-doped silicon carbide-derived carbon/carbon nanotube.

simultaneously introducing N, S, and Fe into honeycomb-like structured graphene (HSG) by using melamine formaldehyde resin (MFR), as a soft template and nitrogen supply, benzyl disulfide (BD) and the cheap Fe precursor ferric chloride. The 3D porous graphene doped with Fe/N/S (Figure 6) was further used as a substrate to incorporate with Fe₃O₄ nanoparticles (Fe₃O₄/FeNSG) by a pyrolysis method. HSG has been known to exhibit a distinct honeycomb-like porous architecture, with high conductivity, structural defects, and a desirable initial surface area, and it has been demonstrated to show great advantages in alternative carbon catalysts. With the added modification, Fe₃O₄/FeNSG exhibited a very high surface area (530.5 m² g⁻¹), the highest amount (74.4%) of active N species (pyridinic N and graphitic N) together with the highest content of S doping (2.11%), and homogeneously embedded Fe species (e.g., Fe–N–C, Fe₃O₄) in the graphene sheets, in comparison to the other prepared catalysts by the authors. It also showed the highest ORR performance, 1.70 A mgPt⁻¹, which was 14.2 times greater than the mass activity of commercial Pt/C (0.12 A mgPt⁻¹) among all of the counterparts tested. Furthermore, this novel Fe₃O₄/FeNSG electrocatalyst exhibited much better methanol resistance and stability than the commercial Pt/C catalyst in alkaline.

N-doped nano-hollow capsule carbon nanocage (CeN-800)

Nano-hollow capsules porous carbon was prepared in a simple and low-cost way with good morphology based on self-assembly of polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) three-block copolymer (F127), polyvinyl pyrrolidone (PVP) and Zn (OH)₂ which served as the carbon source, nitrogen source, and morphology retaining agent, respectively, in the self-template method to create a metal-free N-doped carbon nanocage via pyrolysis. The obtained porous carbon used as ORR catalyst not only presents the hollow capsule structure (as seen in Figure 7 a, b, and c) but also has high content of N. In an O₂ bubbled KOH experiment, the onset potential, limit current density, and half-wave potential of CeN-800 were 0.87 V, 5.45 mA/cm² @0.45 V, and 0.73 V, all of which are close to that of commercial 20% Pt/C catalysts. An efficient durability was observed after 5000 CV cycles, where the corresponding values dropped to 0.77 V, 5.34 mA/cm² @0.45 V, and 0.66 V. The retention rate of the limiting current density reached 88.25%. The initial potential and halfwave potential showed almost no loss and the authors attributed the slight reduction of limiting current density as a result of the oxidation of porous carbon at high potential. They further argued fabricating hollow capsule metal-free carbon-based electrocatalysts for ORR via block copolymer self-assembly is a promising direction towards fabrication of Carbon forms of non-PGM ORR catalysts [51].

Table 1 presents metal catalysts on other porous carbon nano supports not listed above and their performances in DAFCS.

Conclusion

Before the technology of AEMFCs can advance to the same extent as that of its PEMFC counterparts and earn a large percentage of the market for FC power, several important challenges need to be addressed, including the following:

At both electrodes, PGM-free catalysts must be used, as a result, more research and development is required to create new ground-breaking porous carbon supports with majority of the properties mentioned in the text.

Doping these carbon supports with mono and multi heteroatoms should be one of the essential properties of these new forms of carbon allotropes as creating additional mesopores (2–50 nm diameter) or macropores is expected to be an efficient approach to improving the mass transport of M-N-C cathodes. However, their porosity should not impair conductivity, so incorporating them with high electrical conducting carbon forms such as CNTs may be required. This will further promote their mechanical strength and durability.

Active FC test performances reported for most catalysts on porous carbon supports are qualitative as operating conditions used to differ. A more quantitative comparison can be achieved if testing is carried out under similar operating cell conditions for example testing with air instead of pure O₂ in order to consider such catalyst as useful for practical applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest

1. Perugupalli DH, Xu T, Cho KT: **Activation of carbon porous paper for alkaline alcoholic fuel cells.** *Energies* 2019, **12**:3207. <https://doi.org/10.3390/EN12173207>. 12 (2019) 3207.
2. Firouzjaie HA, Mustain WE: **Catalytic advantages, challenges, and priorities in alkaline membrane fuel cells.** *ACS Catal* 2020, **10**:225–234. <https://pubs.acs.org/doi/abs/10.1021/acscatal.9b03892>. Accessed 21 March 2022.
3. Verhage AJL, Coolegem JF, Mulder MJJ, Yildirim MH, De Bruijn FA: **30,000 h operation of a 70 kW stationary PEM fuel**

- cell system using hydrogen from a chlorine factory. *Int J Hydrogen Energy* 2013, **38**:4714–4724, <https://doi.org/10.1016/J.IJHYDENE.2013.01.152>.
4. Ge X, Sumboja A, Wu D, An T, Li B, Goh FWT, Hor TSA, Zong Y, Liu Z: **Oxygen reduction in alkaline media: from mechanisms to recent advances of catalysts.** *ACS Catal* 2015, **5**:4643–4667, https://doi.org/10.1021/ACSCATAL.5B00524/ASSET/IMAGES/MEDIUM/CS-2015-005246_0018.GIF.
 5. Yang W, Fellinger TP, Antonietti M: **Efficient metal-free oxygen reduction in alkaline medium on high-surface-area mesoporous nitrogen-doped carbons made from ionic liquids and nucleobases.** *J Am Chem Soc* 2011, **133**:206–209, https://doi.org/10.1021/JA108039J/SUPPL_FILE/JA108039_SI_001.PDF.
 6. Zhang Junfeng, Zhu Weikang, Huang Tong, Zheng Chenyang, Pei Yabiao, Shen Guoqiang, Nie Zixi, Xiao Di, Yin Yan, Guiver Michael D: **Recent insights on catalyst layers for anion exchange membrane fuel cells.** *Adv Sci* 2021, **8**:2100284, <https://doi.org/10.1002/advs.202100284>.
 7. Fu S, Zhu C, Song J, Du D, Lin Y: **Metal-organic framework-derived non-precious metal nanocatalysts for oxygen reduction reaction.** *Adv Energy Mater* 2017, **7**:1700363, <https://doi.org/10.1002/AENM.201700363>.
 8. Deng YP, Jiang Y, Liang R, Zhang SJ, Luo D, Hu Y, Wang X, Li JT, Yu A, Chen Z: **Dynamic electrocatalyst with current-driven oxyhydroxide shell for rechargeable zinc-air battery.** *Nat Commun* 2020, **11**:1–10, <https://doi.org/10.1038/s41467-020-15853-1>. 11 (2020).
 9. Jiang Y, Deng YP, Liang R, Fu J, Gao R, Luo D, Bai Z, Hu Y, Yu A, Chen Z: **d-Orbital steered active sites through ligand editing on heterometal imidazole frameworks for rechargeable zinc-air battery.** *Nat Commun* 2020, **11**:1–11, <https://doi.org/10.1038/s41467-020-19709-6>. 11 (2020).
 10. Zhao S, Wang DW, Amal R, Dai L: **Carbon-based metal-free catalysts for key reactions involved in energy conversion and storage.** *Adv Mater* 2019, **31**:1801526, <https://doi.org/10.1002/ADMA.201801526>.
 11. Ziv N, Mustain WE, Dekel DR: **The effect of ambient carbon dioxide on anion-exchange membrane fuel cells.** *ChemSusChem* 2018, **11**:1136–1150, <https://doi.org/10.1002/SSC.201702330>.
 12. Anandha Ganesh P, Prakrithi AN, Selva Chandrasekaran S, Jeyakumar D: **Shape-tuned, surface-active and support-free silver oxygen reduction electrocatalyst enabled high performance fully non-PGM alkaline fuel cell.** *RSC Adv* 2021, **11**:24872–24882, <https://doi.org/10.1039/D1RA02718B>.
 13. Qin S, Duan Y, Zhang XL, Zheng LR, Gao FY, Yang PP, Niu ZZ, Liu R, Yang Y, Zheng XS, Zhu JF, Gao MR: **Ternary nickel-tungsten-copper alloy rivals platinum for catalyzing alkaline hydrogen oxidation.** *Nat Commun* 2021, **12**:1–10, <https://doi.org/10.1038/s41467-021-22996-2>. 12 (2021).
 14. Zeng R, Yang Y, Feng X, Li H, Gibbs LM, DiSalvo FJ, Abruña HD: **Nonprecious transition metal nitrides as efficient oxygen reduction electrocatalysts for alkaline fuel cells.** *Sci Adv* 2022, **8**:1584, https://doi.org/10.1126/SCIADV.ABJ1584/SUPPL_FILE/SCIADV.ABJ1584_SM.PDF.
 15. Canda L, Heput T, Ardelean E: **Methods for recovering precious metals from industrial waste.** *IOP Conf Ser Mater Sci Eng* 2016, **106**:12020, <https://doi.org/10.1088/1757-899X/106/1/012020>.
 16. Messias S, da Ponte MN, Reis-Machado AS: **Carbon materials as cathode constituents for electrochemical CO₂ reduction—a review.** *C-J Carbon Res* 2019, **5**:83, <https://doi.org/10.3390/C5040083>. 5 (2019) 83.
 17. Su H, Hu YH: **Recent advances in graphene-based materials for fuel cell applications.** *Energy Sci Eng* 2021, **9**:958–983, <https://doi.org/10.1002/ESE3.833>.
 18. Selvaraj V, Thamilmagal R, Andal V, Arunkumar K, Murugan S: **Bio-based graphene sheet/copolymer composite as supporting material for nanocatalysts towards electrochemical studies and direct alkaline alcohol fuel cells.** *J Nanomater* 2022, **2022**, <https://doi.org/10.1155/2022/4598887>.
 19. Chai L, Hu Z, Wang X, Zhang L, Li TT, Hu Y, Pan J, Qian J, Huang S: **Fe₇C₃ nanoparticles with in situ grown CNT on nitrogen doped hollow carbon cube with greatly enhanced conductivity and ORR performance for alkaline fuel cell.** *Carbon N Y* 2021, **174**:531–539, <https://doi.org/10.1016/J.CARBON.2020.12.070>.
 20. Sikeyi LL, Ntuli TD, Mongwe TH, Maxakato NW, Carleschi E, Doyle BP, Coville NJ, Maubane-Nkadimeng MS: **Microwave assisted synthesis of nitrogen doped and oxygen functionalized carbon nano onions supported palladium nanoparticles as hybrid anodic electrocatalysts for direct alkaline ethanol fuel cells.** *Int J Hydrogen Energy* 2021, **46**:10862–10875, <https://doi.org/10.1016/J.IJHYDENE.2020.12.154>.
 21. Huang Q, Guo Y, Chen D, Zhang L, Li TT, Hu Y, Qian J, Huang S: **Rational construction of ultrafine noble metals onto carbon nanoribbons with efficient oxygen reduction in practical alkaline fuel cell.** *Chem Eng J* 2021, **424**:130336, <https://doi.org/10.1016/J.CEJ.2021.130336>.
 22. Irfan M, Liu X, Li S, Khan IU, Li Y, Wang J, Wang X, Du X, Wang G, Zhang P: **High-performance glucose fuel cell with bimetallic Ni–Co composite anchored on reduced graphene oxide as anode catalyst.** *Renew Energy* 2020, **155**:1118–1126, <https://doi.org/10.1016/J.RENENE.2020.04.016>.
 23. Lilloja J, Kibena-Pöldsepp E, Sarapuu A, Douglin JC, Käärik M, Kozlova J, Paiste P, Kikas A, Aruväli J, Leis J, Sammelseg V, Dekel DR, Tammeveski K: **Transition-metal and nitrogen-doped carbide-derived carbon/carbon nanotube composites as cathode catalysts for anion-exchange membrane fuel cells.** *ACS Catal* 2021, **11**:1920–1931, https://doi.org/10.1021/ACSCATAL.0C03511/SUPPL_FILE/CS0C03511_SI_001.PDF.
A simple high temperature pyrolysis method was used to design a nitrogen doped carbide derived carbon -N-CDC- incorporated with CNT. A PGM-free metal alloy catalysts (CoFe–N-CDC/CNT) embedded on this porous carbon-N- CDC/CNT gave excellent performance in an operational AEMFC with peak power densities of as 1120 and 800 mWcm⁻² H₂/O₂ and H₂/air, respectively].
 24. Butsyk O, Olejnik P, Romero E, Plonska-Brzezinska ME: **Post-synthetic treatment of carbon nano-onions: surface modification by heteroatoms to enhance their capacitive and electrocatalytic properties.** *Carbon N Y* 2019, **147**:90–104, <https://doi.org/10.1016/J.CARBON.2019.02.063>.
 25. Friedman A, Mizrahi M, Levy N, Zion N, Zachman M, Elbaz L: **Application of molecular catalysts for the oxygen reduction reaction in alkaline fuel cells.** *ACS Appl Mater Interfaces* 2021, **13**:58532–58538, https://doi.org/10.1021/ACSAMI.1C16311/SUPPL_FILE/AM1C16311_SI_001.PDF.
Both cheap commercially available molecular catalyst, fluorinated Iron Phthalocyanine (FeFPTc) and carbon support BP2000, were mixed in a solvent (with no post treatment) to produce one of the best molecular catalysts, FeFPC@BP2000, for ORR under alkaline conditions. The application of a molecular catalyst in fuel cell was demonstrated for the first time. This opens up for new avenues of investigations of molecular catalysts under real operating conditions in fuel cells instead of being limited to electrochemical experiments.
 26. Surprise Gwebu S, Nomngongo PN, Maxakato NW: **Platinum-based carbon nanodots nanocatalysts for direct alcohol fuel cells.** *Nanocatalysts*; 2019, <https://doi.org/10.5772/INTECHOPEN.82854>.
 27. Flores-Lasluisa JX, Quílez-Bermejo J, Ramírez-Pérez AC, Huerta F, Cazoria-Amorós D, Morallón E: **Copper-doped cobalt spinel electrocatalysts supported on activated carbon for hydrogen evolution reaction.** *Materials* 2019, **12**:1302, <https://doi.org/10.3390/MA12081302>. 1302. 12 (2019).
 28. Fashedemi OO, Mwonga PV, Miller HA, Maphanga RR, Vizza F, Ozoemena KI: **Performance of Pd@FeCo catalyst in anion exchange membrane alcohol fuel cells.** *Electrocatal* 2021, **123**:295–309, <https://doi.org/10.1007/S12678-021-00655-W>. 12 (2021).
 29. Asefa T, Huang X: **Heteroatom-doped carbon materials for electrocatalysis.** *Chem Eur J* 2017, **23**:10703–10713, <https://doi.org/10.1002/CHEM.201700439>.

30. Ning X, Li Y, Ming J, Wang Q, Wang H, Cao Y, Peng F, Yang Y, Yu H: **Electronic synergism of pyridinic- and graphitic-nitrogen on N-doped carbons for the oxygen reduction reaction.** *Chem Sci* 2019, **10**:1589–1596, <https://doi.org/10.1039/C8SC04596H>.
31. Biemolt J, Douglin JC, Singh RK, Davydova ES, Yan N, Rothenberg G, Dekel DR: **An anion-exchange membrane fuel cell containing only abundant and affordable materials.** *Energy Technol* 2021, **9**:2000909, <https://doi.org/10.1002/ENTE.202000909>.
32. Gukelberger E, Gabriele B, Hoinkis J, Figoli A: **MBR and integration with renewable energy toward suitable Autonomous wastewater treatment.** *Curr Trends Futur Dev Membr Renew Energy Integr Membr Oper* 2019:355–384, <https://doi.org/10.1016/B978-0-12-813545-7.00014-3>.
33. Ferriday TB, Middleton PH: **ScienceDirect Alkaline fuel cell technology - a review.** *Int J Hydrogen Energy* 2021, **46**:18489–18510, <https://doi.org/10.1016/j.ijhydene.2021.02.203>.
34. Hren M, Božič M, Fakin D, Kleinschek KS, Gorgieva S: **Alkaline membrane fuel cells: anion exchange membranes and fuels.** *Sustain Energy Fuels* 2021, **5**:604–637, <https://doi.org/10.1039/d0se01373k>.
35. Yang Z, Zhang M, Zhao Z, Zhang X, Fan M: **Construction of quaternized polysulfone/polyquaternium-10 anion exchange membrane with semi-interpenetrating network for alkaline fuel cell.** *Macromol Mater Eng* 2022, **307**:2100539, <https://doi.org/10.1002/MAME.202100539>.
36. Mandal M, Huang G, Hassan NU, Peng X, Gu T, Brooks-starks AH, Bahar B, Mustain WE, Kohl PA: **The importance of water transport in high conductivity and high-power alkaline fuel cells.** *J Electrochem Soc* 2020, **167**:54501. <https://iopscience.iop.org/article/10.1149/2.0022005JES>. Accessed 8 August 2022.
37. You W, Noonan KJT, Coates GW: **Alkaline-stable anion exchange membranes: a review of synthetic approaches.** *Prog Polym Sci* 2020, **100**, <https://doi.org/10.1016/j.progpolymsci.2019.101177>.
38. Wang H, Yang Y, Disalvo FJ, Abrunã HD: **Multifunctional electrocatalysts: Ru-M (M = Co, Ni, Fe) for alkaline fuel cells and electrolyzers.** *ACS Catal* 2020, **10**:4608–4616, <https://doi.org/10.1021/acscatal.9b05621>.
39. Vijayakumar V, Nam SY: **Recent advancements in applications of alkaline anion exchange membranes for polymer electrolyte fuel cells.** *J Ind Eng Chem* 2019, **70**:70–86, <https://doi.org/10.1016/j.jiec.2018.10.026>.
40. Xue J, Zhang J, Liu X, Huang T, Jiang H, Yin Y, Qin Y, Guiver MD: **Toward alkaline-stable anion exchange membranes in fuel cells: cycloaliphatic quaternary ammonium-based anion conductors.** *Electrochem. Energy Rev* 2021, **2021**:1–53, <https://doi.org/10.1007/S41918-021-00105-7>.
41. Das G, Choi JH, Nguyen PKT, Kim DJ, Yoon YS: **Anion exchange membranes for fuel cell application: a review.** *Polymers* 2022, **14**, <https://doi.org/10.3390/POLYM14061197>.
42. Dekel DR, Rasin IG, Page M, Brandon S: **Steady state and transient simulation of anion exchange membrane fuel cells.** *J Power Sources* 2018, **375**:191–204, <https://doi.org/10.1016/J.JPOWSOUR.2017.07.012>.
43. Ahlfield J, Huang G, Liu L, Kaburagi Y, Kim Y, Kohl PA: **Anion conducting ionomers for fuel cells and electrolyzers.** *J Electrochem Soc* 2017, **164**:F1648–F1653, <https://doi.org/10.1149/2.1341714JES/XML>.
44. Peng X, Omasta TJ, Magliocca E, Wang L, Varcoe JR, Mustain WE: **Nitrogen-doped Carbon-CoO_x Nanohybrids: A Precious Metal Free Cathode that Exceeds 1.0 W cm⁻² Peak Power and 100 h Life in Anion-Exchange Membrane Fuel Cells.** *Angew Chem Int Ed Engl* 2019, **58**:1046–1051, <https://doi.org/10.1002/anie.201811099>.
45. Karim NA, Alias MS, Yang H: **Recent developments for the application of 3D structured material nickel foam and graphene foam in direct liquid fuel cells and electrolyzers.** *Catalyst* 2021, **11**:279, <https://doi.org/10.3390/CATAL11020279>. 11 (2021) 279.
46. Adabi H, Shakouri A, UI Hassan N, Varcoe JR, Zulevi B, Serov A, Regalbuto JR, Mustain WE: **High-performing commercial Fe–N–C cathode electrocatalyst for anion-exchange membrane fuel cells.** *Nat Energy* 2021, **68**:834–843, <https://doi.org/10.1038/s41560-021-00878-7>. 6 (2021).
- A modified form of commercial Iron and Nitrogen co-doped carbon (Fe–N–C) synthesized via a silica template method coupled with two stage pyrolysis. With H₂/O₂ reacting gases, the cathode, the Fe–N–C AEMFC, a milestone power density of over 2100 mWcm⁻² (mass transport-controlled current density >3.6Acm⁻²). Pairing the Fe–N–C cathode with a low-loading PtRu/C anode electrode in a second AEMFCs configuration with a total PGM loading of only 0.125mgPtRu cm⁻² (0.08mgPt cm⁻²); a peak power output of 10.4WmgPGM⁻¹ (16.25WmgPt⁻¹), was achieved. This exceeds the DOE 2022 milestone for AEMFC initial performance.
47. Bandapati M, Goel S, Krishnamurthy B: **Platinum utilization in proton exchange membrane fuel cell and direct methanol fuel cell.** *J Electrochem Sci Eng* 2019, **9**:281–310, <https://doi.org/10.5599/JESE.665>.
48. Zion N, Douglin JC, Cullen DA, Zelenay P, Dekel DR, Elbaz L: **Porphyrim aerogel catalysts for oxygen reduction reaction in anion-exchange membrane fuel cells.** *Adv Funct Mater* 2021, **31**:2100963, <https://doi.org/10.1002/ADFM.202100963>.
49. Cheng W, Yuan P, Lv Z, Guo Y, Qiao Y, Xue X, Liu X, Bai W, Wang K, Xu Q, Zhang J: **Boosting defective carbon by anchoring well-defined atomically dispersed metal-N4 sites for ORR, OER, and Zn-air batteries.** *Appl Catal B Environ* 2020, **260**:118198, <https://doi.org/10.1016/J.APCATB.2019.118198>.
50. Li Y, Zhou Y, Zhu C, Hu YH, Gao S, Liu Q, Cheng X, Zhang L, Yang J, Lin Y: **Porous graphene doped with Fe/N/S and incorporating Fe3O4 nanoparticles for efficient oxygen reduction.** *Catal Sci Technol* 2018, **8**:5325–5333, <https://doi.org/10.1039/C8CY01328D>.
51. Qiu Z, Huang N, Ge X, Xuan J, Wang P: **Preparation of N-doped nano-hollow capsule carbon nanocage as ORR catalyst in alkaline solution by PVP modified F127.** *Int J Hydrogen Energy* 2020, **45**:8667–8675, <https://doi.org/10.1016/J.IJHYDENE.2020.01.112>.
52. Yoon KR, Hwang CK, Kim SH, Jung JW, Chae JE, Kim J, Lee KA, Lim A, Cho SH, Singh JP, Kim JM, Shin K, Moon BM, Park HS, Kim HJ, Chae KH, Ham HC, Kim ID, Kim JY: **Hierarchically assembled cobalt oxynitride nanorods and N-doped carbon nanofibers for efficient bifunctional oxygen electrocatalysis with exceptional regenerative efficiency.** *ACS Nano* 2021, **15**:11218–11230, https://doi.org/10.1021/ACS.NANO.0C09905/SUPPL_FILE/NNOC09905_SI_001.PDF.
53. Sokka A, Mooste M, Käärik M, Gudkova V, Kozlova J, Kikas A, Kikas A, Kisanid V, Treshchalov A, Tamm A, Paiste P, Aruväli J, Leis J, Krumme A, Holdcroft S, Cavaliere S, Jaouen F, Tammeveski K: **Iron and cobalt containing electrospun carbon nanofibre-based cathode catalysts for anion exchange membrane fuel cell.** *Int J Hydrogen Energy* 2021, **46**:31275–31287, <https://doi.org/10.1016/J.IJHYDENE.2021.07.025>.
54. Kumar Y, Kibena-Pöldsepp E, Kozlova J, Rähn M, Treshchalov A, Kikas A, Kisanid V, Aruväli J, Tamm A, Douglin JC, Folkman SJ, Gelmetti I, Garcés-Pineda FA, Galán-Mascarós JR, Dekel DR, Tammeveski K: **Bifunctional oxygen electrocatalysis on mixed metal phthalocyanine-modified carbon nanotubes prepared via pyrolysis.** *ACS Appl Mater Interfaces* 2021, **13**:41507–41516, https://doi.org/10.1021/ACSAMI.1C06737/ASSET/IMAGES/LARGE/AM1C06737_0007.JPEG.
55. Bosubabu D, Parthiban V, Sahu AK, Ramesha K: **Nitrogen-doped graphene-like carbon from bio-waste as efficient low-cost electrocatalyst for fuel cell application.** *Bull Mater Sci* 2021, **44**:2:1–7, <https://doi.org/10.1007/S12034-021-02367-9>. 44 (2021).
56. Kashyap Xiong Peng Varchaswal, Ng Benjamin, Wang Sree Kumar Kurungot Lianqin, Varcoe John R, William E: **High-Performing PGM-free AEMFC cathodes from carbon-supported cobalt ferrite nanoparticles.** *Mustain Catal* 2019, **9**:264, <https://doi.org/10.3390/catal9030264>.

57. Truong VM, Yang MK, Yang H: **Functionalized carbon black supported silver (Ag/C) catalysts in cathode electrode for alkaline anion exchange membrane fuel cells.** *Int J Precis Eng Manuf - Green Technol* 2019, **6**:711–721, <https://doi.org/10.1007/S40684-019-00123-3/TABLES/2>.
58. Lilloja J, Kibena-Põldsepp E, Sarapuu A, Kodali M, Chen Y, Assel T, Kaarik M, Merisalu M, Paiste P, Aruväli J, Treshchalov A, Rähn M, Leis J, Sammelselg V, Holdcroft S, Atanassov P, Tammeveski K: **Cathode catalysts based on cobalt- And nitrogen-doped nanocarbon composites for anion exchange membrane fuel cells.** *ACS Appl Energy Mater* 2020, **3**: 5375–5384, https://doi.org/10.1021/ACSAEM.0C00381/SUPPL_FILE/AEOC00381_SI_001.PDF.
59. Truong Van M, Duong NB, Yang H: **Comparison of carbon supports in anion exchange membrane fuel cells.** *Materials* 2020, **13**: 5370, <https://doi.org/10.3390/MA13235370>. 13 (2020) 5370.
60. Hanif S, Iqbal N, Shi X, Noor T, Ali G, Kannan AM: **NiCo–N-doped carbon nanotubes based cathode catalyst for alkaline membrane fuel cell.** *Renew Energy* 2020, **154**:508–516, [https://doi.org/10.1016/J.RENENE.\(2020\).03.060](https://doi.org/10.1016/J.RENENE.(2020).03.060).
61. Palm Iris, Kibena-Põldsepp Elo, Lilloja Jaana, Kaarik Maike, Kikas Arvo, Kisand Vambola, Merisalu Mado, Treshchalov Alexey, Paiste Päärn, Leis Jaan, Aile Tamm, Sammelselg Väino, Tammeveski Kaido: **Impact of ball milling on carbon derived carbons on the generation of hydrogen peroxide via electroreduction of oxygen in alkaline media.** *J Electroanal Chem* 2020, **878**:114690, [https://doi.org/10.1016/j.jelechem.\(2020\).114690](https://doi.org/10.1016/j.jelechem.(2020).114690).
62. Kibena-Põldsepp Elo, Mooste Marek, Kozlova Jekaterina, Kaarik Maike, Kikas Arvo, Treshchalov Alexey, Leis Jaan, Kisand Vambola, Aile Tamm, Holdcroft Steven, Atanassov Plamen, Tammeveski Kaido: **Nitrogen and phosphorus dual-doped silicon carbide-derived carbon/carbon nanotube composite for the anion-exchange membrane fuel cell cathode.** *ACS Appl Energy Mater* 2022, **5**:2949–2958, <https://doi.org/10.1021/acsaem.1c03627>.