



# **Review Recent Advancements in the Synthesis and Application of Carbon-Based Catalysts in the ORR**

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Abstract: Fuel cells are a promising alternative to non-renewable energy production industries such as petroleum and natural gas. The cathodic oxygen reduction reaction (ORR), which makes fuel cell technology possible, is sluggish under normal conditions. Thus, catalysts must be used to allow fuel cells to operate efficiently. Traditionally, platinum (Pt) catalysts are often utilized as they exhibit a highly efficient ORR with low overpotential values. However, Pt is an expensive and precious metal, posing economic problems for commercialization. Herein, advances in carbon-based catalysts are reviewed for their application in ORRs due to their abundance and low-cost syntheses. Various synthetic methods from different renewable sources are presented, and their catalytic properties are compared. Likewise, the effects of heteroatom and non-precious metal doping, surface area, and porosity on their performance are investigated. Carbon-based support materials are discussed in relation to their physical properties and the subsequent effect on Pt ORR performance. Lastly, advances in fuel cell electrolytes for various fuel cell types are presented. This review aims to provide valuable insight into current challenges in fuel cell performance and how they can be overcome using carbon-based materials and next generation electrolytes.

**Keywords:** oxygen reduction reaction; fuel cells; doped carbon; renewable energy; carbon catalyst; electrolyte; membrane

# 1. Introduction

A key issue for American society is the disparity of the supply and the demand of energy sources. For instance, the United States consumed 20.5 million barrels of petroleum per day (mbd) in 2020, which is significantly greater than the 16 mbd it produced [1]. This disparity leads to the importation of more petroleum each year to supply the growing energy demand. However, these fossil fuels are not sustainable. These nonrenewable products can cause detrimental environmental effects due to the production of greenhouse gas emissions such as carbon dioxide  $(CO_2)$ , methane  $(CH_4)$ , and ozone. This has led researchers to investigate alternative and more environmentally friendly methods for the production, storage, and conversion of energy. In order to avoid the rapid depletion of energy sources and continue towards a sustainable future, it is paramount that energy storage and conversion should primarily be performed by renewable means. In the last three decades, fuel cells have become a crucial technology for production of electrical energy from clean, renewable sources [2]. Fuel cells offer several advantages over other energy storage and generation devices such as lithium-ion batteries and flow batteries. Fuels cells offer a greater energy density compared to either type of battery [3]. In addition, while lithium-ion batteries are more portable, they suffer from short lifetimes, environmentally toxic waste products, and low utility at low or high temperatures [4]. Flow batteries offer significant versatility in that they can be used in a similar way to either fuel cells or rechargeable batteries. However, they currently utilize toxic or corrosive liquids and



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). rely on external loads to power their pump systems [5]. Additionally, their design is more complex than that of a fuel cell and utilizes expensive vanadium components.

In the past, the primary focus of fuel cell technology was on their application as energy generation devices to power vehicles or generators. As of late, fuel cells are finding utility as energy storage devices for intermittent renewable energy generation sources (wind, solar, etc.) as they can only generate energy under certain conditions (sunlight, wind conditions, etc.) [6]. Fuel cells require hydrogen fuel input to operate; this hydrogen is generated via electrolysis of water using an electrolyzer. By replacing fossil fuels with renewables as a source of electrolysis, fuel cells can act as a green method to store large amounts of energy.

The fuel cell is an electrochemical system, which is similar to an internal combustion engine, that directly converts energy from redox reactions into electrical energy [7] as long as the fuel source is being provided. Direct current is produced from this electrochemical process [2]. The common components of a typical fuel cell (Figure 1) consist of two electrodes (anode and cathode), the electrolyte for the electrons to be transported from anode to cathode [8], and the catalyst (usually platinum (Pt) for low temperature fuel cells) [9]. The anode and cathode receive a continuous supply of fuel and oxidizing agent respectively where the redox reaction takes place [9,10]. The hydrogen molecules are passed through the anode while the oxygen molecules (or air) are passed through the cathode. At the anode where the oxidation reaction occurs, the hydrogen molecule is split into electrons and protons by a catalyst. The protons or hydrogen ions  $(H^+)$  can pass through the membrane or the electrolyte to make their way to the cathode [9,10]. At the same time, in the cathode where the reduction reaction occurs, the oxygen molecule (or air) is split into oxygen ions  $(O^{2-})$ . Under the potential difference of the two electrodes, electrons from the anode flow through an external circuit to the cathode to equalize the charge in the cathode and produce water and heat as the product of the reaction [9–11].



Figure 1. Basic design of a fuel cell.

The cathodic oxygen reduction reaction (ORR) makes up one of the two half reactions necessary for fuel cell device operation. The ORR is kinetically very slow due to the high activation energy of oxygen double bond cleavage. This in turn causes the cathode to require enormous amounts of catalyst (traditionally Pt) to function efficiently [12]. This is approximately eight times greater than the amount of catalyst required for the anodic reaction [13]. Industrially, the required catalyst accounts for more than half of the total cost required to produce commercial fuel cells. Moreover, these Pt catalysts also suffer from long term degradation and instability [14]. Pt has other recorded shortfalls such as toxicity and methanol poisoning [15,16]. These disadvantages, coupled with the low utilization of Pt (0.25 g kW<sup>-1</sup>), make widespread economical application unfeasible, especially for transportation applications [17,18]. Considering the disadvantages of Pt catalysts for the ORR, research has been conducted to decrease the total amount of Pt used at the cathode

or to replace the precious metal completely. One promising replacement is carbon-based materials as they are inexpensive and readily available and have shown exceptional catalytic properties for the ORR.

Many efforts have been devoted to exploring alternative catalysts that can serve a similar purpose to conventional ones, owing to their abundance, their economic applicability, and their potential catalytic activity comparable to noble metals (Pt). Carbonaceous materials are widely available with excellent properties such as large surface area, the fact that they are environmentally friendly, great electrochemical activity, high conductivity, and tunability, which allows for great potential in both supercapacitors and fuel cell applications [16,19–21]. There are many existing carbon structures that have been used in the renewable energy area, some of which are highlighted in Figure 2.



Figure 2. Various carbon structures reported for use as ORR catalysts.

This review seeks to highlight advances in the implementation of these carbon-based materials by investigating the source materials, heteroatom and non-precious metal doping, surface characteristics, and synthesis methods' effect on their overall performance for the ORR. Similarly, advances in carbon-based support systems for Pt catalyst and next generation electrolytes are also reviewed for their impact on advancing fuel cell technology. This review encompasses a comprehensive report of many techniques used in the last three years to improve current fuel cell technology with a primary focus on the ORR

# 2. Carbon Sources for Electrocatalysts

Presently, carbon materials have become of great interest to many researchers and have been used in different applications, one of which is as electrocatalysts for the ORR [22,23]. Carbon is naturally abundant and can be obtained from different sources including biomass, naturally occurring materials, and chemically synthesized starting materials. Many renewable carbon sources have also been known to contain various heteroatoms, such as nitrogen (N), phosphorus (P), and sulfur (S), which can play a vital role in electrocatalytic activity of their resultant activated carbons. Additionally, their syntheses can be performed economically and with no harsh chemicals [16,22,24]. Current research works

have focused on developing next generation fuel cells by producing ORR catalysts from naturally abundant materials and waste which are less expensive compared to metal-based catalysts [16,25,26]. This section focuses on the recent use of these materials as carbon sources for highly efficient electrocatalysts.

## 2.1. Biomass

Currently, biomass such as agricultural waste, industrial waste, wood chips, and waste tires are utilized as potential carbon sources to prepare activated and doped carbon electrocatalysts [24–26]. An overview of these carbon sources is shown in Figure 3. Regarding used tires, approximately 1 billion tires are disposed yearly around the globe. The frequent disposal of used tires poses serious health and environmental concerns. With new methods to recycle tires, there are potential uses in many applications including as a carbon source for electrocatalysts [27–32]. Maurizio et al. [27] reported a novel approach tackling the recovery and valorization of chars, or the by-product of waste-tire pyrolysis. The tires are transformed into highly efficient ORR catalysts for use in alkaline fuel cells and metal air batteries. The samples exhibited an ORR onset potential of -90 mV (vs. reversible hydrogen electrode, RHE) and a  $4 e^{-}$  mechanism, which was attributed to the large specific surface area (72–296 m<sup>2</sup> g<sup>-1</sup>) and well-developed porosity, as well as the presence of a high concentration of zinc oxide (ZnO) particles embedded within the carbon matrix. Another synthesis using recycled tire rubber was conducted by Zachary et al. [28] in order to fabricate carbon-based support materials for electrocatalysts. They investigated three tire-derived carbons with different pore structures, crystallinity, surface area, and surface chemistry. Using the ORR as an example, they synthesized and deposited Pt nanocubes on tire-derived carbon with different textural properties and surface chemistries. Results showed that the Pt nanocubes were more effective toward the ORR when deposited onto tire-derived carbon with an increased electrochemically active surface area, a lowered average pore diameter, and good crystallinity. They compared their materials to a commercial carbon black support (Ketjen-300) and saw that the tire-derived carbon supports achieved greater performances. In another research study by Andrei et al. [29], non-condensable pyrolysis gases from waste tires were utilized as a source of carbon and S for heteroatomdoped carbon nanosheets (CNSs). The results showed tire waste is a good source for the growth of 2D porous carbon. They synthesized two different CNSs (O, S dual-doped and O, S, and N tri-doped CNS) via catalytic chemical vapor deposition (CCVD). N-doping of the surface was introduced by adding aqueous NH<sub>3</sub> solution to the non-condensable pyrolysis gas. Upon investigation of the electrocatalytic ORR activities, it was found that the CNSs had ORR peak reduction potentials of -0.217 V to -0.220 V (compared to -0.167 V for Pt electrodes) at a CCVD temperature of 700–750 °C. The materials showed high electrocatalytic activity and stability during the ORR, implying they can potentially replace expensive noble metals (Pt, Ir, Ru) for the construction of electrodes used in the ORR.

Another waste product that has been utilized as a carbon source for electrocatalysts is sewage sludge. It is an industrial waste that is collected from wastewater [33]. Although sludge has become an environmental issue, it is rich in carbon, N, and P [34]. It has been used as a carbon source to prepare heteroatom-doped porous carbon materials (PCMs) as a potential for use as an ORR electrocatalyst [33,34]. A recent study by Prabhsharan et al. [33] reported the synthesis of N-doped porous carbon via carbonization of dried sludge at 400, 500, 600, 700, 800, and 900 °C. The Brunauer Emmet Teller (BET) surface areas obtained for the resultant PCMs were 4.5, 127.9, 216.3, 310.8, 204.0, and 116.9 m<sup>2</sup> g<sup>-1</sup>, respectively. The rotating ring disk electrode (RRDE) voltammogram of the N self-doped carbon in an oxygen saturated 0.1 M KOH solution showed that, at -0.04 V electrode potential, a non-zero cathodic current began to appear, and it increased significantly with the increasing negative electrode potential. At even more negative potential (-0.30 V), it reached a quasi-plateau. This result indicates the effective electrocatalytic reduction of oxygen by porous carbon via a 4 e<sup>-</sup> mechanism.



Figure 3. Overview of carbon sources used for electrocatalyst syntheses.

#### 2.2. Naturally Occurring Materials

Naturally occurring materials include plants and crops, which are abundant in nature. Soybeans are one of the most important crops in the world because they are rich in fat and carbohydrates, which makes them useful as a source of carbon for electrocatalysts [35]. Soybeans are also rich in N and are among the naturally occurring materials that have been widely used as catalysts for ORRs due to their low cost and abundance in most parts of the world [36,37]. Wu et al. [37] utilized soybeans as the carbon and N source in synthesizing Fe-modified mesoporous N-doped carbons (Fe-N/C) through a SiO<sub>2</sub>-mediated templating method. They prepared four different materials with varying mass ratios of SiO<sub>2</sub> to soybean, of 1:4, 2:4, 3:4, and 4:4. The 3:4 mass ratio catalyst gave good stability and favorable ORR catalytic activity, as well as a high surface area of 1298 m<sup>2</sup> g<sup>-1</sup>. The onset potential and half-wave potential of the selected ratio were 0.890 V and 0.783 V (vs. RHE), respectively. In another study performed by Yong et al. [38], soybean straw was used as the precursor to synthesize a honeycomb-like Fe-N co-doped porous carbon material (Fe-N-PC). An Fe-N-PC catalyst with a BET surface area of 520.9  $m^2 g^{-1}$  was used as the electrocatalyst for the ORR in both alkaline and acidic media. The onset potential and half-wave potential in both acidic and alkaline conditions were recorded to be 0.886 V and 0.754 V, and 0.989 V and 0.854 V, respectively, indicating the exceptional ORR performance of Fe-N-PC. Jun-hong et al. [39] synthesized a series of Fe and N co-doped carbon composite ORR catalysts using carbon fiber (CF), soybean dregs, and graphitic carbon nitride SDs/g-C<sub>3</sub>N<sub>4</sub> (denoted as CS) as a complex carbon source. Three different mass ratios of CF:CS were prepared, and all samples exhibited a surface area above  $400 \text{ m}^2 \text{ g}^{-1}$ . The optimized Fe-N/CF-CS-2 (1:2) catalyst showed ORR activity comparable with that of commercial Pt/C. This catalytic performance was attributed to the combined effect of different carbon sources, leading to the formation of a hierarchical porous structure with large specific area and pore volume, as well as well-dispersed Fe–N and/or N–C active sites.

Pine needles, a naturally occurring material that has been seldomly used as a carbon source for preparing ORR catalysts, were used by Jian et al. [40] as a precursor to prepare P-doped porous carbon catalysts. They used pine needles due to their naturally high P content. The specific surface area for this material was around 621 m<sup>2</sup> g<sup>-1</sup>. Electrochemical tests showed that the carbon catalyst exhibited an onset potential of ca. 0.96 V vs. RHE and half wave potential of ca. 0.72 V vs. RHE. These results highlight pine needles as a promising precursor for developing heteroatom-doped carbon electrocatalysts.

#### 2.3. Chemically Synthesized Starting Materials

Chemically synthesized precursors such as polymers (materials comprising repeating structural units) and graphene-based materials have shown great utility in ORR catalysis. The use of polymers as starting materials for synthesizing carbon based electrocatalysts have gained particular interest in the research field of ORR [41]. Doping has been used as a method to incorporate heteroatoms such as N, P, and fluorine (F) into the active sites of the carbon matrix to improve its performance [42,43]. This process requires the mixing of carbon precursors with different heteroatom sources through multiple steps [42–44]. However, some research studies have been performed using a single precursor to prepare heteroatom-doped carbon as electrocatalysts for ORRs. Interestingly, some polymers have various heteroatoms (F, P, S) integrated into their carbon matrix, which allows them to produce self-doped materials [43,45].

Tianle et al. [42] used tricomponent polymers: polyacrylonitrile (PAN) as a carbon and N source, polyvinylidene fluoride (PVDF) as an F and carbon source, and polyvinylpyrrolidone (PVP) as a porogen to synthesize N and F co-doped microporous carbon nanofibers (N, F-MCFs) via electrospinning. The N, F-MCFs displayed an onset potential and half wave potential of 0.94 V vs. RHE and 0.81 V vs. RHE, respectively and a 4  $e^-$  transfer pathway for the ORR. They prepared two ratios of 1:1:1 and 1:1:1.5 for PAN, PVP, and PVDF, respectively. The surface areas obtained for the two samples were 709.8 and 621.5 m<sup>2</sup> g<sup>-1</sup>, respectively. Both materials showed exceptional stability and methanol tolerance, which are desirable for ORR catalytic activities. Yong et al. [43] also used a triazine polymer as a self-doping (containing carbon, N, P, and F elements) precursor to prepare N, P, and F tri-doped carbon nanospheres (NPF-CNSs) via an in-situ one step pyrolysis. The samples were prepared at three different pyrolysis temperatures of 800, 900, and 1000 °C to give NPF-CNS-1, NPF-CNS-2, and NPF-CNS-3, respectively. The optimum sample, NPF-CNS-2, which had the highest surface area and pore volume of 193.4 m<sup>2</sup> g<sup>-1</sup> and 0.145 mL g<sup>-1</sup>, respectively, exhibited high electrocatalytic activity and outstanding long-term durability for the ORR under a wide range of pH environments. The onset potential and half wave potential were found to be 0.93 and 0.81 V vs. RHE, respectively. In another research study by Shi-Bin et al. [44], metal-free electrocatalysts of N and S co-doped materials (N–S-DPCs) were prepared through the carbonization of thiazolothiazole based conjugated microporous polymer precursors (XWB-CMP). The XWB-CMP precursor was prepared through a condensation reaction of 1,3,6,8-tetrakis (p-formyl phenyl) pyrene (TFPPy) and dithiooxamide in the presence of DMF at 120 °C. The precursor was pyrolyzed at four different temperatures to determine the optimum condition. The sample prepared at 1000 °C showed the most optimal ORR results with a BET surface area of  $378.3 \text{ m}^2 \text{ g}^{-1}$ .

Other carbon materials such as graphene, graphene oxide (GO), and graphite have been widely used as catalyst support for the ORR [46]. Electrocatalytic activity of these carbon nanomaterials has been increased by doping the materials with heteroatoms [22,46,47]. Graphene, an allotrope of carbon, with high stability [47] and good catalytic loading, as well as remarkable electron delocalization properties [22], has gained attraction as an electrocatalyst support material for fuel cells. Both single doping and co-doping graphene with heteroatoms have shown to make it a better catalyst support material by preventing aggregation and enhancing the interactions between the graphene and metal [46–49].

N-doped nanocarbons using graphite, graphene, and GO as the carbon precursor in the presence of dicyandiamide (DCDA, N source) were prepared via ball-milling by Roberta et al. [46] to produce N-doped graphene (N-G), graphite (N-Gra), and GO (N-GO), respectively. Their results indicated that the ball-milling had a significant impact on the surface areas of graphite and GO (from 10 to 94 m<sup>2</sup> g<sup>-1</sup>, and from 19 to 50 m<sup>2</sup> g<sup>-1</sup>, respectively). Ball milling did not have any effect on N-Gra, and it possessed the highest surface area of  $415 \text{ m}^2 \text{ g}^{-1}$ . Qi Xue et al. [49] used graphene as the carbon source to synthesize N-doped graphene aerogel (N-GA) from the pyrolysis of graphene aerogel-polyallylamine (GA-PAA) hybrids. The optimized N-GA had a BET surface area of  $119 \text{ m}^2 \text{ g}^{-1}$ . They found that the electrocatalytic activity increased with an increase in surface N content (up to 2.07%). Roberta et al. [48] also used graphene as the carbon source to synthesize S and N co-doped graphene as ORR electrocatalysts using thiosemicarbazide and trithiocyanuric acid as S and N precursors. All doped materials exhibited better electrochemical performance compared to pristine graphene. Additionally, they found that dry ball-milling can enhance the 4 e<sup>-</sup> process for S and N co-doped carbons. Ruihong et al. [50] prepared a nickel phosphide/graphitic carbon (Ni<sub>2</sub>P/GC) composite as a support material by using Ni<sub>2</sub>P twisted together with graphite layers to study the effect of transition metal phosphides on the ORR at the cathode in acidic solution and the synergistic effect it has on the catalytic activity with low-Pt loading. They found that the composite support facilitated efficient O<sub>2</sub> adsorption at the surface via the introduction of active sites as well as effective mass transport due to the presence of mesopores. These qualities allowed exceptional ORR performance of the catalyst.

# 3. Doping Methods

One promising approach to improve the properties of these carbon materials is doping with heteroatoms or metals. The doping of these materials is advantageous because of the possibility of tuning the electrocatalytic performance of carbons that can serve as alternatives to existing high-cost Pt-based catalysts. Doped materials can show enhanced surface area, maximized exposure to active sites, and increased porosity compared to their undoped counterparts. These properties are essential for the development of superior ORR catalysts.

Various research groups have extensively studied the development of new catalysts via the incorporation of one, two, or more doping agents with carbon sources. Examples of doping atoms of interest are N, P, S, and B, which may be introduced with precursors via different methods [15,51]. In this way, various doped carbons can be synthesized by altering the ratio of the precursors to initial carbon source(s) [15]. These atoms alter the carbon matrix both physically and electrochemically (Figure 4). Reports show that upon doping of a material, the properties such as electrochemical activities, band gap, porosity, and density of the material were significantly changed [19] which resulted in improved electrocatalytic performance towards the ORR for fuel cell application due to the enhanced active sites contribution from the doping agent. In fact, many of the recently developed catalysts have been found to portray similar or superior activity upon comparison with commercial Pt/C catalysts [15,21,52].

#### 3.1. Nonmetal Heteroatoms

Heteroatoms are atoms that are non-carbon or hydrogen that can serve in the place of carbon in a molecular structure. The administration of heteroatoms into the unique structure of the carbon matrix causes alteration of physical and chemical properties that can positively contribute to the ORR. Examples of commonly used heteroatoms include N, P, S, F, and Si. These heteroatoms can influence surface area, porosity, and surface functional groups, which can impact their ability to reduce molecular oxygen. Furthermore, multi-doped carbons with multiple different heteroatoms have been shown to possess much higher catalytic activity than mono-doped analogues because of the synergetic effect from the two or more different atoms [51,53].



Figure 4. Carbon matrix when doped with one, two, or three atoms simultaneously.

# 3.1.1. N-Doping

N is the most commonly doped element in carbon-based materials. N is highly abundant in natural precursors and small enough to prevent excessive distortion of the carbon matrix. N may be introduced into the carbon matrix by use of various precursors such as dicyandiamide (DCDA) [15], polyaniline (PANI) [54], and 1,10-phenanthroline [55]. The resulting catalytic performance of N-doped carbon is greatly influenced by the choice of precursors. Most studies have demonstrated the enhancement of electrocatalytic performance for pyridinic N and graphitic N's [15,19,51,54,56]. Recently, the significance of large dimensions through holes have also been investigated. A recent study by Min Zhu et al. [54] observed that N-doped carbon materials with large hole structures such as hollow spheres and hollow tubes exhibit improved ORR catalytic capability and stability, as well as methanol resistance.

Lejian et al. [57] developed N-doped porous carbon in nanometer dimensions made from different plant biomass via a solvent-free approach showing great activity for ORR application. These inexpensive materials exhibited great porosity and surface area with 4 e<sup>-</sup> transfer pathway. These materials, interestingly, can also serve as universal-pH ORR catalysts with high stability within a wide pH range from alkalinity to acidity.

# 3.1.2. P-Doping

Another common doping element is P, which has a similar electronic structure to N, with a larger diameter and can distort the carbon matrix more intensely. Recently, Yang et al. [58] designed two structurally different P-doped carbon materials. Briefly, one was doped with an ordinary structure via pyrolysis and the other was prepared with a 3D hierarchical structure using a hard-templated method with silica NPs. Upon comparison of these two samples with commercial Pt/C activity, the sample with a 3D hierarchical porous structure showed enhanced electrocatalytic activity for the ORR in alkaline solution as compared to the ordinary P structure. The unique character portrayed by the hierarchical

porous carbon was ascribed to the presence of 3D-interconnected pores compared with the ordinary simple structure P-doped carbon. This abundance of pore structure (micro-, meso-, and macropores) allowed for multiple reactive sites and facilitated the transportation of both  $O_2$  and electrolytes. In addition, the material exhibited extraordinary methanol resistance and stability as compared to the commercial Pt/C catalyst. Previous studies have also emphasized the significance of 3D nanostructures in exhibiting better electrochemical activity [59,60].

Yuanyuan et al. [60] also worked on evaluating the significance of P when used in doping carbon materials for the ORR. The group developed P-doped carbon obtained via simple pyrolysis and double activation with sodium hypophosphite as the P precursor. The resultant material exhibited graphitized mesopores, revealing the effects of multiple defects introduced by the P precursor. The material portrayed a large specific surface area and underwent both 2 e<sup>-</sup> and 4 e<sup>-</sup> pathways. More so, the positive onset potential proved a promising result for the use of the material as a low-cost catalyst due to its high performance for fuel cell application.

# 3.1.3. S-Doping

Many studies have been performed to show the enhanced electrocatalytic effect when S is used as a doping agent for nanostructured carbon sources. Perazzolo et al. [55] proposed the synthesis of a high stability material for use as an electrocatalyst for the ORR in alkaline media. Upon evaluation of the activity of this material as compared to the non-doped nanostructured carbon source (carbon hollow spheres), there were significant differences between the materials: the S-doped material exhibited a more positive onset potential and a peroxide yield of less than 2%, and the number of electrons involved for the transfer process was approximately four [61].

#### 3.1.4. Co-Doped or Tri-Doped

The terms co- and tri-doped refer to the introduction of two or three different heteroatoms incorporated in the carbon source during synthesis. The introduction of more than one heteroatom in the carbon matrix has been shown to introduce synergistic enhancement of electrochemical performance between certain atoms. Song et al. [62] demonstrated the economical use of environmental waste, catkins, for the production of N and S codoped carbon electrocatalysts via the use of methylene blue dye as the N and S source. The material showed a positive onset potential, great stability, and limiting current as compared to the commercial Pt/C catalysts in alkaline media. Interestingly, the parent carbon microtubes (CMTs) may also be tuned by the introduction of other functional groups and heteroatoms in order to aid the enhancement of electrocatalytic activity.

Yinghua et al. [51] recently reported a noteworthy inexpensive and environmentally friendly electrocatalyst developed from a tri-doped carbon 2D material with prospective use for oxygen reduction and hydrogen evolution reactions. The newly synthesized electrocatalyst obtained via a 'mix-pyrolyze' method was derived by utilizing zinc pyrithione (ZPT) and phytic acid (PA) as precursors for the introduction of N, S, and P, respectively. Briefly, it was observed that the porosity of materials prepared independently with the various precursors varied from those made with both precursors together, signifying the role of the different doping agents. Furthermore, the tri-doped material, when compared to the commercial 20% Pt/C (0.87 V), exhibited excellent bifunctional ORR behavior with a half wave potential of 0.91 V (vs. RHE). This was attributed to the multiple active sites, large surface area, abundant porous structure, and excellent charge-transfer ability of the materials [51]. Upon evaluation of the electrocatalytic behavior of the material in both  $O_2$ saturated KOH [23,51] and HClO<sub>4</sub> electrolytes for ORR capability, the tri-doped material showed remarkable behavior with a more positive onset potential of 1.06 V and 0.94 V, respectively, as well as half-wave potential of 0.91 and 0.64 V, respectively. Interestingly, this behavior was found to exhibit electrochemical performance competitive with commercial 20% Pt/C (1.02 vs. 0.87 V). Due to the synergistic effect as earlier stated, the tri-doped

material showed a more efficient ORR than co-doped and mono-doped carbons, signifying the contribution of different heteroatoms in improving ORR character [16,51]. Interestingly, the tri-doped material shows the 4  $e^-$  transfer number in the reduction process as well as low peroxide yield. The material also displayed outstanding stability and selectivity towards the ORR, implying its excellent and promising use as an alternative to expensive metal catalysts [51].

Macchi et al. [16] also investigated the effects of the co-doping versus tri-doping of newly synthesized alternative non-Pt-based catalysts prepared via a renewable carbon precursor (molasses). For the tri-doped material, Si, P, and N were introduced using dimethylsiloxane and ammonium polyphosphate (APP) precursors, while only P and N were used to develop the co-doped material with APP alone. The simple and efficient microwave-assisted method was used to introduce an increased number of defects into the material as contributed by the doping agent(s). Various properties such as the electrochemical performance and conductivity bandgap were enhanced when compared to the parent compound. The tri-doped carbon material exhibited a greater positive peak potential and favorable reduction of oxygen, as well as a more favorable 4 e<sup>-</sup> process than the co-doped counterpart due to the incorporation of Si. Overall, the tri-doped material portrayed better ORR capability and stability which suggests its potential for use in fuel cell application [16].

Xiaowei et al. [19,23] reported the enhanced performance of a highly durable electrocatalyst carbon material, named NPSC-1000-1-3, for both energy storage and conversion via the incorporation of heteroatoms/tri-doped carbon material (N, P, and S), showing both ORR capabilities and high stability. Upon the investigation of the tri-doped/heterodoped electrocatalyst in oxygen saturated electrolyte, a more positive peak potential and higher current density was noticed for the material in KOH electrolyte. Furthermore, the electrons transferred reached a theoretical value closer to 4.0. Alternative evidence for the 4 e<sup>-</sup> transfer pathway is the low yield of hydrogen peroxide evidenced by RRDE studies. In addition, the computational density functional theory (DFT) calculations reveal the effect of tri-doping as it generates multiple active sites, as well as more positive and negative charges on surrounding carbon atoms than co-doped counterparts (the effect of multidoping was revealed via DFT). DFT methods were also used to characterize the possible reaction pathway of the material. Interestingly, the overall ORR performance of these materials was superior to other metal-free carbon materials [19].

Paul et al. [21] reported series of 3D-carbon nanomaterials doped with a series of heteroatoms such as N, S, P, B, F, and O that exhibited superior ORR catalytic performance of over 90% current density retention in alkaline electrolyte with positive onset potential value (0.93 V). Interestingly, this value surpasses the 81% retention observed by expensive Pt/C upon individual investigation after 10,000 s of reaction. Furthermore, DFT theory calculations were used to reveal the tri-doping effect due to a remarkable enhancement of charge localization. In this study, a series of samples were reported with different codoping/tri-doping agents introduced to the 3D material via various methods to reveal their ORR capability. These carbon nanomaterials were shown to have positive onset potentials, as well as 4 e<sup>-</sup> transfer pathways, in the reduction process. As explained earlier, all of these reported heteroatom-doped samples exhibited outstanding catalytic behavior due to various structural defects caused by the heteroatoms known as defect-induced ORR electrocatalysis as well as efficient charge transfer through intimate interfaces [21]. Furthermore, the presence of the heteroatoms in doped 3D carbon materials enhanced the performance due to an increase in charge redistribution and aided an increase in  $O_2$ adsorption and highly abundant sites in 3D.

# 3.2. Metal Doping

Non-precious metals such as Fe or cobalt (Co) are gaining popularity as doping agents for carbon materials due to their abundance, low cost, and stability. Transition metal hybrids combined with N-doped carbon obtained by heat treatment are relatively common due to their low cost and high electrocatalytic behavior [15]. To the best of our knowledge,

the electrocatalytic active sites in hybrids of transition metals supported on N-doped carbon are still debated [63]. Some agree that the presence of a transition metal is only required in order to form active sites during the chemical synthesis and that active sites consist of only N and carbon, while transition metal species do not remain in these sites [15]. However, others agree that the metal-N sites are the most active sites for the ORR [63]. To further enhance the electrochemical activity, two or more metals such as Fe and Co, most commonly used due to low cost and their excellent performance in acidic and alkaline media, may be used to form bimetallic-doped carbon electrocatalysts.

Kisand et al. [15] recently demonstrated the synthesis of a hybrid bimetallic (Fe and Co) electrocatalyst supported on N-doped graphitic carbon (FeCoNC) exhibiting better ORR activity than its single metal counterpart. Interestingly, these materials show comparable electrocatalytic activity to that of the Pt/C (20 wt%) catalyst. The bimetallic electrocatalyst exhibited improved ORR performance, compared to single element doping alone. The superior activity was attributed to high surface area (in the case of metals) and N contents.

## 4. Synthetic Methods of Carbon Materials

There are several synthetic routes used when developing carbon materials for use as energy materials (catalyst in fuel cells, electrode coatings for supercapacitors, etc.), each possessing its own distinct advantages and disadvantages. The most popular methods are microwave-assisted and thermal processes such as pyrolysis and hydrothermal carbonization [64]. These are advantageous in that they are relatively inexpensive and rapid techniques. Recent works have also investigated the use of template-guided synthetic methods, which can allow high specificity of pore structure and surface properties of catalyst materials. An overview of the primary advantages and disadvantages of these techniques are highlighted in Figure 5. This Section will focus on the recent advancements of these methods.



**Figure 5.** Primary synthetic methods and major advantages (green) and drawbacks (red) of those techniques.

#### 4.1. Microwave

Microwave-assisted approaches to generating carbonaceous materials have become popular due to their facile and cost-effective nature. These methods also allow a simple method for producing doped carbon materials often in only one step [16,23,35,65–67]. While there are many documented microwave-assisted protocols, researchers still often investigate the role of microwave irradiation time and temperature on the electrocatalytic performance of resultant carbon materials. Others have also investigated microwave irradiation in conjunction with other methods such as hydrothermal pretreatment and pyrolysis to achieve enhanced surface characteristics.

It has been recently explained that ORR performance can be enhanced by utilizing a core-shell catalyst, which is comprised of a non-precious metal, such as Fe, in the center and a carbon shell. Microwave-assisted processes have been shown as a facile way to synthesize these materials. Chen et al. [68] used microwaves to synthesize Fe encapsulated sulfur and N co-doped carbons. Microwave times of 2, 3, and 5 min were used to determine the most

optimal irradiation time (2 min). These materials have shown exceptional ORR performance compared to unencapsulated doped carbon, which was due to the enhanced charge transfer between the Fe core and the S and N functional groups in the carbon shell. Moreover, the Fe core allowed the materials to be highly stable in acidic and alkaline media. Liu et al. [69] also generated Fe core carbon coated nanomaterials using the direct microwave irradiation of Prussian blue dye, a coordinate complex with an Fe center, for 35 min. A second material was developed by adding an additional ultrasonic acid treatment to enhance the surface area and pore volume of the catalyst.

Microwave processes can also be utilized in conjunction with other methods to provide specific surface functionalities. Dai et al. [70] have reported for the first time an "uneven" microwave method to produce doped carbon. The synthetic route involves the hydrothermal pretreatment of glucose and doping agents (melamine and iron (III) nitrate, Fe(NO<sub>3</sub>)<sub>3</sub>), followed by 200 s of microwave treatment in air, and finally pyrolytic carbonization. The superior performance of this material is attributed to the uneven oxidation of carbon sites in close proximity to Fe due to the absorption of microwave energy by Fe, which generates mesopores and contributes to the overall surface area. Xu et al. [71] also investigated a rapid microwave-assisted thermolysis method to produce high performing catalyst materials. A microwave time as low as 30 s was found to convert PANI into an exceptional ORR material outperforming both pyrolyzed PANI and a Pt/C commercial catalyst in terms of half wave potential (from linear sweep voltammetry, LSV) and cycling (>98% retention over 7.5 h). The ultrafast microwave carbonization produced a high concentration of pyridinic and graphitic N and exceptional graphitization of carbon. Wang et al. [72] investigated the synthesis of N-doped nanocages using microwave plasma in tandem with chemical vapor deposition (MPCVD). They developed a homemade MPCVD apparatus, which synthesized doped nanocages in only 10 min at 450 W microwave power. These nanocages showed excellent cycling stability and methanol tolerance compared to Pt/C. From x-ray diffraction measurements, they found that N-doped nanocages showed greater interlayer spacing as compared to pristine nanocages, facilitating the ORR.

Other works have investigated the role of various microwave conditions such as temperature and power on the performance of the resultant carbon materials. Sudhakar et al. [73] investigated the role of microwave temperature (120–200 °C) on the ORR performance of N-doped graphene catalysts. The group utilized acetonitrile as a N source and GO as a carbon source with a microwave time of 10 min. The half wave potential of the ORR for the catalysts increased in the 120–180 °C prepared samples. The 180 °C sample showed the greatest performance due to having the highest surface area resulting from its enhanced N content. At an increased temperature of 200 °C, a sharp decrease in performance was observed, correlated to the disordered carbon matrix of graphene coupled with high boiling pressure of acetonitrile, which could lead to a breaking of C–N bonds, resulting in a reduction in N-doping. Xia et al. [74] investigated the role of microwave power in the electrocatalytic activity of N-doped carbons. It was found that greater microwave power correlated to both more pyridinic N and the enhanced ORR capability of the doped carbons. The rapid microwave process also allows the high surface area (186 m<sup>2</sup> g<sup>-1</sup>) and defined porosity to be retained even with high loading of N dopant at the surface (~19%).

## 4.2. Hydrothermal and Pyrolysis

Hydrothermal and pyrolysis are two of the most common methods of carbonization due to their facile and rapid nature. Pyrolysis involves heating carbon-containing precursors in an oxygen-free environment to a specific temperature, usually between 500 and 1000 °C, where thermochemical decomposition and carbonization occur [75]. Hydrothermal carbonization (HTC) utilizes milder temperatures (180–250 °C) and pressure to convert precursor materials into hydrochar in an aqueous environment [76].

While it is common to produce porous carbons from biomass directly, it has been shown in recent years that the carbonization of hydrogels can allow for more control over the resultant carbon surface characteristics such as surface area and porosity. Shi and Maimaitiyiming [77] generated hydrogels from renewable a chitosan precursor and carbonized them via pyrolysis to yield calcium-, N-, and P-doped carbon materials. The hydrogel structure allowed the formation of a 3D porous framework of the resultant material which gave them exceptional catalytic characteristics such as 4 e<sup>-</sup> pathway and an onset ORR potential similar to commercial Pt/C. The catalyst also showed great tolerance for methanol which is highly desired for practical application of these materials. Another group, Xiang et al. [78], developed a GO- and carbon nitride-based gel-like "hybrid" material via hydrothermal treatment, which was subsequently pyrolyzed to yield N-doped graphene nanosheets. Pyrolysis conditions were varied between 700 and 1000 °C to determine the optimum conditions for high performance materials. It was found that a temperature of 900 °C produced the best performing nanosheets due to the formation of pyridinic N at the surface evidenced by x-ray photoelectron spectroscopy. These materials displayed a more positive onset potential compared to the Pt/C catalyst and superior stability over 10,000 cycles (4 mV shift). Xu et al. [79] utilized biomass (egg whites) hydrogels which formed 3D networks under alkaline conditions as a framework for N and S co-doped carbons. Alkaline conditions are also commonly used in pyrolysis to generate porous structures in activated carbons. They show that increasing the pyrolysis temperature introduces greater porosity while sacrificing some dopant concentration. However, the optimum temperature of 900 °C yielded exceptional ORR catalysts with onset potentials (1.03 V vs. RHE) comparable to Pt/C (1.06 V).

N is the most common heteroatom used as a doping agent for carbon-based electrocatalysts due to its ease of introduction via pyrolytic or a combination of hydrothermal and pyrolytic synthesis methods [80]. Historically, a carbon precursor would be pyrolyzed under N<sub>2</sub> or ammonia gas in order to incorporate functional groups into the carbon matrix [75]. Recently, researchers have investigated new ways to synthesize N-doped carbon electrocatalysts. Hassani et al. [81] utilized ammonium acetate salt for the first time to produce N-doped graphene. They utilized various pyrolysis temperatures from 700 to 1000 °C and, in a similar manner to others, found that the optimum material is produced at a temperature of 900 °C. The ammonium acetate precursor allowed even distribution of N atoms across the carbon matrix, evidenced by energy dispersive x-ray spectroscopy. Likewise, the ORR performance of this material was exceptional with a 4 e<sup>-</sup> pathway and positive reduction potential. At as low as \*7 kg<sup>-1</sup>, ammonium acetate has been proven to be a cost-effective precursor for N-doped catalytic carbons. Liu et al. [82] developed doped carbon fibers using waste biomass sources for both a carbon source and a self-template, as well as a N source. The group utilized a hydrothermal pretreatment (120 °C, 5 h) followed by pyrolysis (optimal temperature = 900  $^{\circ}$ C). The resultant doped carbon retained the fibrous structure of the precursor catkin plant material and exhibited far superior recycling ability and methanol tolerance compared to Pt/C.

# 4.3. Templated Methods

Templating methods are often used when fabricating 3D porous carbon materials owing to the greater control allowed by the use of various templates such as metal organic frameworks (MOFs), zeolites, or carbon nanotubes [83]. These templates have inherent disadvantages such as cost and scalability. However, in recent years other strategies involving use of templates have been explored and show promising ORR performance, such as the utilization of dual templating.

The use of salts such as sodium chloride (NaCl) and zinc chloride (ZnCl<sub>2</sub>) as templates has become popular in recent years due to the control of porosity and elemental doping that they allow during synthesis. Shen et al. [84] proposed the use of eutectic NaCl and ZnCl<sub>2</sub> to generate 3D porous N, S, and Cl tri-doped carbons from a lignin biomass precursor. The NaCl acts as a sealant which regulates the decomposition of dopant materials, resulting in a greater doping percentage, while ZnCl<sub>2</sub> allows enhanced formation of pore structures, both micro and meso. The resulting carbon exhibited ultrahigh surface area (1289 m<sup>2</sup> g<sup>-1</sup>) and an exceptional maximum power density (779 mW cm<sup>2</sup>). Zeng et al. [85] saw a similar enhancement in surface area (938 m<sup>2</sup> g<sup>-1</sup>) of Fe, N, and S tri-doped porous carbon using NaCl. This group also utilized a dual-template method using NaCl as a primary template and iron (II, III) oxide (Fe<sub>3</sub>O<sub>4</sub>) NPs formed during pyrolysis (900 °C) as an in-situ secondary template. Following the first pyrolysis, acid leaching is used to remove the secondary template, and the material is pyrolyzed once more to yield porous tri-doped carbon. The product was shown to perform exceptionally well as an ORR catalyst with greater stability and half wave potential than Pt/C in acidic electrolyte.

Traditional templates such as silica nanomaterials and MOFs are also currently being utilized to prepare highly ordered porous carbon materials. Yan et al. [86] utilized silica NP templates to enhance the active sites of metal-free N and S co-doped carbon compared to non-templated materials. They prepared poly-(2-mercaptoethanol, dopamine) at the surface of silica nanospheres followed by carbonization and removal of silica by KOH treatment to yield porous doped carbon spheres and hemispheres. Templating produced a greater amount of N and S at the surface and increased the amount of ORR active pyridinic groups. Furthermore, templating enhanced the surface area from 447 m<sup>2</sup> g<sup>-1</sup> to 1326 m<sup>2</sup> g<sup>-1</sup>. Luo et al. [87] investigated using a dual-template strategy with silica nanospheres as a hard template and two different MOFs coated onto the surface as the self-sacrificing templates. Subsequent pyrolysis/etching of the dual template yielded porous Fe and N co-doped carbon with highly exposed active sites. This novel method could provide a route to develop even better carbon-based catalysts. A summary of templated methods and resultant sample performance towards the ORR is compiled in Table 1.

**Table 1.** Onset potential and electron transfer characteristics of doped carbon samples synthesized using various hard and soft templating methods.

Template	Sample	Onset Potential (V vs. RHE)	Electron Transfer	Electrolyte	Ref.
NaCl and ZnCl <sub>2</sub>	N, S, and Cl tri-doped porous carbon	0.892	3.93	HClO <sub>4</sub>	[84]
NaCl and Fe <sub>3</sub> O <sub>4</sub> NPs	Fe, N, and S tri-doped carbon	0.932	3.95	HClO <sub>4</sub>	[85]
NaCl and Fe <sub>3</sub> O <sub>4</sub> NPs	N and S co-doped carbon	0.878	3.9	HClO <sub>4</sub>	[85]
Silica	Porous N and S co-doped carbon spheres	1.00	3.94	KOH	[86]
Silica and MOF	Fe and N co-doped carbon	1.02	4	КОН	[87]

## 5. Physical Property Influence on Electrocatalytic Performance

Physical properties of the electrocatalyst and support materials play a huge role in the electrocatalytic performance of the fuel cell. It has been established that high surface area materials with abundant pores are the standard for the carbon support layer [88,89]. Recently, attention has turned to the elemental composition and morphology of the catalyst to further enhance performance. Figure 6 highlights the key physical properties of carbon catalyst and support materials.

#### 5.1. Surface Area

A major factor in the electrocatalytic performance of a fuel cell is the surface area of the carbon support. Pt is the commonly used active site for ORR catalysts but has several drawbacks. Pt is an expensive and rare metal and its large surface area causes lesser electrochemically active Pt sites to be used due to increased dispersion and agglomeration of Pt particles [90].

Maximizing the surface area of the carbon support is taken into consideration when producing a catalyst. On average, the surface area of the carbon supports ranges from 480 to 950 m<sup>2</sup> g<sup>-1</sup> [91–93]. Zhang et al. [90] created a chitosan-based carbon catalyst with an extremely high surface area of 1190 m<sup>2</sup> g<sup>-1</sup>, which showed excellent activity toward ORR. Interestingly, Mohanta et al. [94] investigated the effect of carbon catalyst support surface area at different current loads and discovered that the surface area may require tailoring to the specific conditions of the fuel cell. Their research showed evidence that, at low current loads, high surface area supports performed best, as expected. The unexpected result was

that, at high current loads, medium surface area materials (200 m<sup>2</sup> g<sup>-1</sup>) showed better performance due to mass transport losses and water accumulation in the smaller pores of the high surface area materials [94].



**Figure 6.** Summary of physical properties affecting carbon-based catalyst and support material ORR performance in fuel cells.

# 5.2. Pore Size

Another factor in electrocatalytic performance is the pore size of the material. Pore sizes are classified as macropores (>50 nm in diameter), mesopores (2–50 nm in diameter), and micropores (<2 nm in diameter) as shown in Figure 7 [95]. Mesopores are considered the most advantageous pore size because the ionomer cannot interact with the Pt particle inside micropores, essentially making them unavailable [95]. However, ORR kinetic activity can be poisoned by sulfate and phosphate anions, which are contained in the ionomer, meaning the ionomer must be in close proximity to the Pt without directly touching. Ideally, the pores should have small openings so the Pt can be enclosed in the pore, out of reach of the ionomer, but with access to the reaction of the fuel cell [2]. The material should not be devoid of micropores either. A hierarchal structure of pores allows full access to the active sites [92].

Zhu et al. [92] studied the micropore structure of catalyst materials to determine the effect on the ORR performance. In their work, the group concluded that a ratio of micropore volume to mesopore volume equal to 0.5 provides the best ORR performance and the least mass transport resistance through the synergistic effect of both sized pores. Ye et al. [96] further confirmed this idea in their work, which used a quantum-dot-level grain size carbon matrix that possessed a hierarchical pore structure, as well as high surface area. Because of the pore structure, the active sites were well distributed and showed excellent ORR performance.

As previously stated, the pores of the carbon support need to have small openings so the Pt can be protected from the ionomer but also stay within a close range to allow for the reactions needed in the fuel cell. Yarlagadda et al. [89] determined the ideal pore opening to be 4–7 nm to allow for highly efficient ORR activities and transport properties.



Figure 7. Example of hierarchical pore structure of a carbon-based material.

# 5.3. Elemental Composition

Elemental composition of the carbon support is also crucial in determining the performance of the fuel cell. Incorporating pyridinic-N has been shown to aid in ORR performance because it inhibits the 2 e<sup>-</sup> reactions and promotes the 4 e<sup>-</sup> reactions, thus accelerating the ORR reaction rate [90]. Further, the inclusion of different heteroatoms creates more active sites at the catalyst surface [91]. There is also a push to replace Pt as the active site due to the limited availability and the fact that Pt can contribute to intermediate product poisoning [90]. Currently, atomically dispersed single metal site M-N-C (M being any metal) catalysts show great potential to replace Pt in the cathodes for direct methanol fuel cells (DMFCs). DMFCs show a significant decrease in ORR activity in methanol concentrations above 4.0 M, due to strong adsorption of methanol [97].

Fe is a strong contender to replace Pt as the optimum ORR catalyst. Shi et al. [97] developed a dual-metal site Fe/Co-N-C catalyst. The Co atoms modify the porosity of the catalyst and provide more defects for stabilizing the active  $FeN_4$  sites. By using  $FeN_4$ sites, ORR activity in DMFCs is increased due to the weaker adsorption of methanol compared to pyridinic N, CoN<sub>4</sub>, and MnN<sub>4</sub> active sites. Chen et al. [98] were able to atomically disperse Fe atoms implanted in a M-N-C catalyst. The catalyst showed excellent ORR performance due to the Fe-N<sub>x</sub> atomically dispersed throughout the hierarchical pores. Razmjooei et al. [99] synthesized an Fe-N-C catalyst that was highly micro- and mesoporous. The material showed improved mass transfer and more efficient ORR active sites because of hierarchical porosity and the N contained in the carbon framework. The primary active sites were pyridinic N and Fe-N<sub>x</sub>. Aside from Fe, Mn has shown some promise as an efficient active site when used in tandem with S. Guo et al. [100] incorporated S into a Mn-N-C catalyst. The S atoms improved the activity of the MnN<sub>4</sub> sites by increasing the limiting potential and favorable ORR kinetics while also maintaining high active site density. S gives the added benefit of providing a repulsive interaction with the ORR intermediate species adsorbed on the MnN<sub>4</sub> active sites, which facilitates the desorption process.

Several attempts have been made to create a metal-free catalyst by incorporating N, S, and/or F into the carbon matrix. Kim et al. [91] incorporated thiourea into the synthesis of a bamboo-derived electrocatalyst to include S and N. N modulates charge distribution in the carbon matrix and S is involved in spin density distribution. The inclusion of both atoms in this material provided high ORR performance due to the synergistic effect from both. Akula et al. [93] used N and F in a silk-derived electrocatalyst. The N and F in the carbon support caused more open edge defect sites and increased the degree of disorder in the material. The two atoms synergistically enhanced the ORR activity. Akula et al. [101]

furthered this work by producing a graphitic carbon nanofiber framework with added N and F to modify the structure. N and F incorporation resulted in enhanced activity through the graphene-like structure, porosity of the material, and open edge active centers in the structure.

#### 5.4. Morphology

The last vital physical property that can influence the performance of the fuel cell is the morphology of the catalyst. This includes the thickness of the catalyst layer, the dispersion of the active sites, and the location of the active sites in the carbon support.

First, it is noted that highly dispersed active sites optimize the performance of the fuel cell. Zhan et al. [102] created a bamboolike carbon nanotube catalyst with highly dispersed Fe centered active sites. The catalyst shows high ORR activity because of the uniform dispersion of the active sites with the enhanced conductivity and mass/charge transfer properties. Hanifah et al. [103] deposited highly dispersed Pt-Pd alloy NPs on the surface of reduced GO. The catalyst showed high electrochemical surface area and electro-catalytic activity. Zhang et al. [104] used carbon black and Co-zeolitic imidazolate frameworks (ZIF) as templates to control the morphology, which revealed that the smaller catalysts had a more homogeneous distribution of catalyst and ionomer and a higher power density in alkaline fuel cells. Along with high dispersion, Kotaro et al. [105] determined that a monolayer of Pt on the carbon support allows for ultra-low Pt loading, high Pt utilization, and high tunability of the activity through the varying of the Pt shell.

As discussed with regard to the pore size, it has been determined that micro- and mesopores are necessary to achieve high performance [89,92]. To determine which had the stronger impact, Harzer et al. investigated the effect on electrocatalyst performance of Pt NPs deposited on the outer surfaces versus the inner surfaces. NPs externally deposited showed excellent high current density performance, but ORR mass activity was relatively low. Internally deposited NPs showed higher ORR mass activity but poor high current density performance. This finding indicates that the catalyst should have most of the active sites on the external surface to maintain good high current density performance, with a small fraction inside the pores for protection from the ionomer poisoning for high mass activity [106]. Further, Kaobayshi et al. [95] determined that catalysts with large nanopore capacities can utilize Pt in pores at an intermediate current density. There is a reduction in Pt poisoning because the number of Pt NPs not in contact with the ionomer increases.

# 6. Advances in Electrolytes/Membranes Used for Fuel Cell Applications

The choice of electrolyte or fuel cell membrane plays an essential role in the energy storage capacity for fuel cell applications. There have been many recent advancements in the electrolytes used for the optimization of fuel cells. The electrolyte/membrane moieties come in different forms—organic, inorganic, and ionic liquids. Fuel cells are mainly characterized by the electrolyte used, which makes any two fuel cells unique from each other.

## 6.1. Polymer Electrolyte

Most polymer electrolyte membrane fuel cells (PEMFCs) utilize Nafion as the polymer electrolyte of choice [107–109]. However, despite the polymer's high stability and performance as a fuel cell electrolyte, it is still high in cost, and proton exchange performance is limited at elevated temperatures (above 100 °C) [110]. This has driven researchers to look into alternative polymer electrolytes for PEMFC applications that are cost-efficient such as biochar [111] and polyvinyl alcohol (PVA)-based polymers [112], which present conditional durability.

Amongst the temperature-dependent performance limitations of Nafion as a PEM electrolyte are its decreasing proton conductivity rate at increasing temperatures [113,114]. Some research has focused on improving these Nafion membranes by developing composite membranes with inorganic components like  $TiO_2$  and  $WO_2$  [115]. Pineda-Delgado et al. [116]

investigated the incorporation of  $HfO_2$  as a filler in composite Nafion membranes. By using a sol-gel-like process they were able to integrate a low percentage of  $HfO_2$  (1–3 wt%) into the Nafion membrane. The lower percentage  $HfO_2$  (1.88%) achieved exceptional water uptake capability and power density at temperatures greater than 80 °C, as compared to a commercial Nafion membrane.

The temperature limitation of PEMFCs were addressed by Ahmadian-Alam et al. [117] by introducing a novel electrolyte composite which combined a cost-efficient polysulfone membrane with silica and aluminum MOF NPs. This moiety was shown to have an enhanced proton conductivity of 1712 mS cm<sup>-1</sup> at 70 °C which also demonstrated the direct proportionality of proton conductivity to concentration of membrane NPs. Al-Othman et al. [118–120] also aimed to enhance the high-temperature operation of PEMFCs by utilizing a novel electrolyte membrane which was a composite of zirconium phosphate and ionic liquid (imidazolium-based). This membrane demonstrated proton conductivity that was comparable to that of Nafion at room temperature, as well as at 80 °C, but which at 200 °C, greatly outperformed the Nafion membrane. Moreover, this composite exhibited ideal performance in completely anhydrous conditions, which also addresses the common water control issue with current PEMs and other types of fuel cells. This membrane setup shows great potential for use as a PEM fuel cell that can function at high temperatures, beyond the highest operating temperature of the widely used Nafion [121].

Additionally, polybenzimidazole (PBI) membranes have also been studied extensively for their usage in high-temperature (>100 °C) PEMFCs [122]. This is due to their excellent thermal stability, mechanical strength, and proton conduction due to the presence of the imidazole group [123]. Ghosh et al. [124] recently utilized a composite of PBI and reduced graphene oxide (rGO) as a PEMFC electrolyte membrane. They found that, even at low rGO loading, water and acid uptake, proton conduction, and charge transfer were enhanced due to the high surface area and crosslinking of rGO and PBI. Moreover, the composite achieved a high maximum power density (W/cm<sup>2</sup>) at a high operating temperature (170 °C).

#### 6.2. Solid Oxides

Solid oxide fuel cells (SOFCs) usually operate at high temperatures of 800 °C and above, which supports the need for thermal shielding to harness the heat being produced in order to improve device efficiency. Consequently, they present slow startup due to the need to reach high temperatures to be operational, and they are also costly. As a benefit of SOFCs, the current efficiencies achieved are over 60% in reference to converting fuel to energy [125,126]. The most commonly used electrolytes are those of yttria-stabilized zirconia (YSZ) [127,128] and gadolinium-doped ceria (GDC) [129,130], which are ionic conductors that are stable and functional at very high temperatures with an absolute minimum operating temperature of around 600 °C. The best way to improve SOFC restrictions is by way of electrolyte optimization.

One key focus in the current research is to lower operating temperatures and improve ORR efficiency. Jeong et al. [131] introduced a novel Pt GDC as a cathodic electrolyte interlayer that was shown to have improved the power of the SOFC at low temperatures (500 °C) by essentially enhancing the triple phase boundary (TPB) which occurs in SOFCs. This inherently enhanced the ORR, which usually has a slow production time and can limit the mechanical properties of SOFCs.

PVDF has been used as a shielding agent to prevent corrosion from SOFCs by Xu et al. [132]. This method shows that addition of a small amount of PVDF to the low temperature (up to 500 °C) solid oxide material used is an efficient way to fabricate a SOFC electrolyte that has enhanced power (max 505 mW cm<sup>-2</sup>) compared to other commonly used SOFCs, which exhibit maximum power of 200–400 mW cm<sup>-2</sup>. To add to the low temperature performance enhancement, Xu et al. [133] established a novel method for the synthesis of a SOFC electrolyte proton conductor, BaCe<sub>0.7</sub>Zr<sub>0.1</sub>Y<sub>0.2</sub>O<sub>3- $\delta$ </sub> (BCZY), by microwave sintering at temperatures that are lower than the normal protocol for synthesis

of this electrolyte. As a result, proton conductivity was increased, as was overall power density, with respective measurements of  $1.4 \times 10^{-2}$  S cm<sup>-1</sup> and 838 mW cm<sup>-2</sup> at 700 °C.

Another type of promising SOFC electrolyte is pyrophosphates, which have been shown to express high proton conductivity especially in anhydrous conditions [134,135], but low thermal stability at increasing temperatures. The novel ternary pyrophosphate synthesized by Shi et al. [136] exhibits an ideal proton conductivity ( $3.9 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ ) as well as an adequate power density of 167.1 mW cm<sup>-2</sup> at high temperatures of up to 800 °C in dry conditions.

For some promising SOFC electrolytes, very high sintering (solidification) temperatures are required. This poses several issues such as cost and the restriction of electrochemical properties [137–140]. The sinterability of electrolytes can be improved by the addition of a sintering aid such as bismuth oxide ( $Bi_2O_3$ ) [141] or nickel oxide (NiO) [142]. For example, the novel doping of samarium-doped barium cerate (SDC-BCS) with  $Bi_2O_3$ to make Bi-SDC-BCS demonstrated much improvement in intermediate temperature (IT) solid oxide fuel cell (IT-SOFC) applications. Sintering temperature decreased from 1300 °C to 1100 °C. With an exhibited thermal stability even at 700 °C, Bi-SDC-BCS demonstrated a power density of 352 mW cm<sup>-2</sup>, which is almost two times the compared power density of SDC-BCS alone [143].

# 6.3. Molten Carbonate

Molten carbonate fuel cells (MCFCs) have limitations that are very similar to that of SOFCs, which also traditionally operate at high temperatures (650 °C and up). There are some disadvantages that come with functioning at these temperatures including, most prevalently, a decrease in device lifetime due to temperature-induced degradation. Electrolytes utilized by MCFCs are liquid materials that are composed of a molten alkali carbon solution.

One way to address the degradation issue with MCFCs is to introduce a potential replenishing agent that would effectively elongate cell lifetime by replacing the components of the initial electrolyte that had been vaporized. Bae et al. [144] demonstrated the use of electrolyte precursors (EPs), which served as replenishing agents that have high vapor pressures and low melting points. It was concluded that lithium iodide (Lil) and potassium iodide (KI) have great potential as EPs in that that they can be injected into the MCFC system in either liquid phase at low temperatures (300 °C and below) or gaseous phase at high temperatures and can serve to replace electrolyte elements that are diminished through operation. Using this system, lifetime was increased, and users were able to obtain an additional 1000+ h of operation under extreme conditions with assistance from EPs. It was concluded that, with the consistent addition of EPs, operational longevity can be achieved. However, over-injection of EPs is possible and can cause adverse effects, but with adequate amounts of EP injection, use has been shown to be optimal.

## 6.4. Alkaline Electrolyte

Alkaline fuel cells (AFCs) are one of the more beneficial fuel cell types in that they have a high stability and performance in alkaline conditions (e.g., ethanol, methanol), fast startup, and are low cost. All things considered, they provide an optimal alternative energy source that can operate under ambient temperatures. However, they are very easily affected by CO<sub>2</sub> presence, which can affect overall mechanical and electrochemical function in very small amounts. They are also very exothermal, which affects the power density of the fuel cell.

With the many advantages of AFCs come a plethora of opportunities to further optimize the potential of this type of fuel cell. Zhao et al. [145] established a method to harness the heat output via a direct contact membrane and to further use it for water purification. Moreover, the results show that the efficiency and power density of this hybrid increased by over 140% compared to the AFC alone. The main explanation given for this phenomenon is that the parameters of the feedwater used within the system

(e.g., temperature, flow rate, and factors of heat transfer) are a pertinent feature in the operation of the hybrid fuel cell.

The dew point of a fuel cell is the point at which water vapor in the system is completely saturated to the point that the water condenses to liquid form. It signifies the full saturation of gas in the fuel cell system. This occurrence adversely affects fuel cell operation. Water management is a common effect of many different types of fuel cells such as the ones previously discussed. In such cases, water management occurred in the form of controlling dew points within the AFC system. With dew point expressed as a ratio of anode/cathode humidifying point, Mahmoud et al. [146] explored the maximum power density values for various imidazolium-based AFC membrane electrolytes at maximum dew points, as compared to standard vinylbenzyltrimethylammonium (BTMA)-based membrane electrolytes. With this, a power density of 710 mW/cm<sup>2</sup> was achieved using a sterically hindered imidazolium-based AFC membrane. This value is also the highest reported power density for an AFC thus far.

Functional properties of AFCs can further be enhanced by doping. PVA is a commonly used AFC electrolyte due to its cost-efficiency, chemical stability, and green features. However, its electrochemical properties are currently less than optimal. The proton conductivity has been enhanced for AFC applications by way of doping with compounds that will increase functional groups that are highly oxidative, leading to enhanced ion conductivity. The doping of PVA with sulfonated zirconia by Gouda et al. [147] for synthesis of a novel AFC membrane was shown to have an ion conductivity measurement of 22.3 mS cm<sup>-1</sup>, which is compatible with commonly used fuel cell electrolyte Nafion, which has a reported value of 34 mS cm<sup>-1</sup>. Hydrogen bonding between PVA and the doping agent further enhanced the thermal stability of the AFC membrane structure, as well as the ion conductivity and oxidative stability due to more functional groups having been formed as a result of doping. This group also focused on the enhancement of PVA as a direct borohydride AFC electrolyte by way of doping with sulfonated GO [148] and TiO<sub>2</sub> nanotubes [149], which in turn increased ion conductivity at stability.

The various fuel cell types discussed, as well as their improved electrolyte components, are summarized in Figure 8.



Figure 8. Summary of advancements in fuel cell electrolytes for common fuel cell designs.

# 7. Conclusions

Carbon-based electrocatalysts and support materials allow fuel cell technology to distance itself from Pt dependence by minimizing the amount of Pt needed or removing

it altogether. Recent advancements in carbonaceous precursor materials have been highlighted, including renewable and chemically synthesized sources. New ideas in synthetic methodology are also presented including microwave-assisted and templated approaches. Moreover, because doping has become commonplace for altering the band gap and electrocatalytic ability of carbon, the effect of various elemental doping has been extensively studied in relation to its effect on ORR performance. Likewise, other physical characteristics of carbon materials (surface area, pore size, etc.) have been investigated in regard to their role in carbon support and catalyst ability. Lastly, the advances in electrolyte systems of various fuel cell types have been covered. The reviewed carbonaceous materials are highly advantageous in that they are low cost and abundant, and their surface characteristics highly tunable. The strategies discussed for the enhancement of fuel cell performance possess unique advantages and limitations. Future researchers should keep these in mind when designing new methods and catalysts.

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