



# Review Recent Advances and Synergistic Effects of Non-Precious Carbon-Based Nanomaterials as ORR Electrocatalysts: A Review

Laksamee Payattikul <sup>1,2</sup>, Chen-Yu Chen <sup>3</sup>, Yong-Song Chen <sup>4</sup>, Mariyappan Raja Pugalenthi <sup>1,2,\*</sup> and Konlayutt Punyawudho <sup>1,2,\*</sup>

- <sup>1</sup> Department of Mechanical Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai 50200, Thailand; laksamee\_p@cmu.ac.th
- <sup>2</sup> Energy Harvesting and Storage Laboratory, Mechanical Engineering, Chiang Mai University, Chiang Mai 50200, Thailand
- <sup>3</sup> Department of Mechanical Engineering, National Central University, Taoyuan 320317, Taiwan; chenyuchen@ncu.edu.tw
- <sup>4</sup> Advanced Institute of Manufacturing with High-Tech Innovations, Department of Mechanical Engineering, National Chung Cheng University, Chiayi 62102, Taiwan; imeysc@ccu.edu.tw
- \* Correspondence: rajapugalenthi.m@cmu.ac.th (M.R.P.); konlayutt.p@cmu.ac.th (K.P.)

Abstract: The use of platinum-free (Pt) cathode electrocatalysts for oxygen reduction reactions (ORRs) has been significantly studied over the past decade, improving slow reaction mechanisms. For many significant energy conversion and storage technologies, including fuel cells and metal-air batteries, the ORR is a crucial process. These have motivated the development of highly active and long-lasting platinum-free electrocatalysts, which cost less than proton exchange membrane fuel cells (PEMFCs). Researchers have identified a novel, non-precious carbon-based electrocatalyst material as the most effective substitute for platinum (Pt) electrocatalysts. Rich sources, outstanding electrical conductivity, adaptable molecular structures, and environmental compatibility are just a few of its benefits. Additionally, the increased surface area and the simplicity of regulating its structure can significantly improve the electrocatalyst's reactive sites and mass transport. Other benefits include the use of heteroatoms and single or multiple metal atoms, which are capable of acting as extremely effective ORR electrocatalysts. The rapid innovations in non-precious carbon-based nanomaterials in the ORR electrocatalyst field are the main topics of this review. As a result, this review provides an overview of the basic ORR reaction and the mechanism of the active sites in non-precious carbonbased electrocatalysts. Further analysis of the development, performance, and evaluation of these systems is provided in more detail. Furthermore, the significance of doping is highlighted and discussed, which shows how researchers can enhance the properties of electrocatalysts. Finally, this review discusses the existing challenges and expectations for the development of highly efficient and inexpensive electrocatalysts that are linked to crucial technologies in this expanding field.

**Keywords:** carbon electrocatalyst; heteroatoms; single-atom metals; metal–organic framework; energy storage; oxygen reduction reaction

# 1. Introduction

It has become urgent to find new, efficient, clean energy sources due to the impact of environmental ruin and energy depletion caused by the use of fossil fuels [1]. Proton exchange membrane fuel cells (PEMFCs), which make electricity through an electrochemical process involving hydrogen (H<sub>2</sub>) and oxygen (air), have many benefits over conventional Liion batteries, including practically equivalent performance, a high energy/power density, rapid refueling, and a lack of CO<sub>2</sub> emission [2]. Researchers are becoming increasingly interested in the oxygen reduction reaction (ORR), which is a crucial electrode reaction that occurs in fuel cells and rechargeable metal–air batteries to convert chemical energy into electrical power [3]. However, the efficiencies of fuel cells and metal–air batteries are



Citation: Payattikul, L.; Chen, C.-Y.; Chen, Y.-S.; Raja Pugalenthi, M.; Punyawudho, K. Recent Advances and Synergistic Effects of Non-Precious Carbon-Based Nanomaterials as ORR Electrocatalysts: A Review. *Molecules* 2023, 28, 7751. https://doi.org/ 10.3390/molecules28237751

Academic Editor: Minghao Yu

Received: 18 October 2023 Revised: 8 November 2023 Accepted: 16 November 2023 Published: 24 November 2023



**Copyright:** © 2023 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/). severely constrained by the slow ORR reaction mechanism [3]. In the past, research has shown that there are two potential routes for the ORR process: a direct four-electron  $(4e^{-})$ pathway and a slow two-electron (2e<sup>-</sup>) process within standard potentials [4]. Direct fourelectron activity seems to exhibit superior activity over the use of unfavorable two-electron reactions, which indicates that designing efficient electrocatalysts is required to facilitate good ORR [4,5]. In view of the search for excellent electrocatalytic performance, platinum (Pt)-based nanomaterials show outstanding potential as ORR electrocatalysts [6]. However, significant efforts have been made to discover non-precious metal (Pt-free) electrocatalysts to replace Pt-based electrocatalysts due to the disadvantages of the cost, scarcity, and deprived stability of Pt [7]. Carbon-based electrocatalysts, including heteroatom-doped carbon electrocatalysts, [8] single-metal-atom-based carbon electrocatalysts (M-N-Cs), [9], and metal-organic frameworks (MOFs), have also been explored significantly in the past decades [10] due to their inexpensive cost and outstanding electrocatalytic efficiency. Since it alters the electron density of carbon atoms within the region of heteroatom dopants, the heteroatom doping of carbon has been accepted as a successful method to adjust the characteristics of carbon nanomaterials and augment ORR performance [11]. It may also alter the chemisorption of reactants and control the chemical properties of electrocatalysts. Via the strategy of doping heteroatoms, numerous groups have recently attempted to boost the ORR activity of carbon-based nanomaterials such as carbon nanotubes and graphene [12]. The structural, electronic, and electrochemical characteristics of carbon nanomaterials have been successfully modified via heteroatom doping [13]. Graphenedoped sulfur (S), boron (B), and nitrogen (N)-doped carbon nanotubes, as well as N-doped graphene, have all been the subject of extensive research in the past [14-17]. Additionally, N- and S-doped graphene has proven to be an extraordinary non-metal ORR electrocatalyst. Furthermore, heteroatom doping has produced exciting characteristics that have led to increased attention on the imperfections of carbon nanomaterials.

According to the second law of thermodynamics, natural carbon nanomaterials, such as carbon nanotubes, graphite, and graphene, have always exhibited numerous disordered structures or imperfections on their surfaces or the edges of carbon [18]. Such defects, which are caused by the absence of specific atoms or an adjustment within the crystalline structure, definitely disrupt the electron–hole pairs and increase the ORR activity. According to the results of physical characterization and density functional theory (DFT), heteroatom doping provides edge carbon atoms with a higher electron density than pure carbon atoms, which have a similar effect.

Because of their improved ORR performance, single-metal-atom-based carbon nanomaterials (M-N-Cs) have been found to be extremely good electrocatalysts for replacing Pt-based nanomaterials [19]. Due to the importance of reducing metal particle sizes and controlling their dispersion on carbon supports, a wide range of methods have been used to prepare relatively stable and superior ORR-active metal-based electrocatalysts. Such techniques enhance the interplay between supports through the formation of chemical bonds between the metal and its related interface and the carbon support interface as well as enhance the charge carrier between both the carbon framework and metal species. The precise active centers in the metal-enclosed electrocatalyst could alter ORR activity and stability and, finally, increase ORR [20]. Metal atoms are typically attached to nitrogen sites, which noticeably changes the electronic structure of carbon atoms. Because of their exceptional electrocatalytic activity, better selectivity, high stability, and maximum atom exploitation efficiency, single-atom electrocatalysts (SAECs) have a great potential for substituting Pt-based electrocatalysts in ORR, according to DFT and experimentation calculations [19]. Three crucial elements (N, C, and M) are simultaneously present in the metal–organic frameworks (MOFs), which are chemically and structurally distinctive. Researchers now exploring them as effective precursors present the single or bi-metallic active sites, which are atomically distributed within nitrogen structures and stabilized by carbon supports [21–23]. The M-N-C electrocatalysts have the notable performance improvement due to these unique features. Various scientific studies of SAECs show

their excellent ORR performance and comparability to the commercial Pt electrocatalyst, which have the outstanding catalytic reactions in the field of electrocatalysts. Additionally, there are significant efforts being made to create a wide range of electrochemical applications, such as fuel cells, metal–air batteries, electrochemical water splitting, solar cells, and supercapacitors [8,10,11,24].

In this review work, we start by discussing the active site mechanisms of non-precious carbon-supported or platinum-free electrocatalysts. In the second part, we briefly describe the most recent strategies for improving the ORR electrocatalytic activity of heteroatom doping, single-metal atoms (M-N-C), and MOF-based carbon electrocatalysts. Finally, we briefly go over the problems currently being experienced and the anticipated future of non-precious porous carbon-based electrocatalysts. The importance of non-precious carbon-supported electrocatalysts is highlighted and provides the pathway development of next-generation energy systems. Scheme 1 shows the advantage of carbon-based electrocatalysts.



Scheme 1. The advantages of various carbon-based electrocatalysts.

#### 2. Fundamentals of Electrocatalysis Kinetics

Electrochemical applied potentials have a significant impact on ORR reactions and their kinetics. The thermodynamic potential of 1.229 V vs. standard hydrogen electrode (RHE) for ORR is indicated as a specific potential in an electrochemical reaction. The least standard potential for the chemical reaction to take place while the reactant gas is delivered is regarded as the onset potential at the anode (small) and cathode electrodes (high). Overpotential ( $\eta$ ) is described as the additional potential present in addition to the standard potential during reactions. Figure 1a shows the ORR/OER polarization curves, which are very helpful for achieving a low over-potential with a high electrocatalysis current. Therefore, the main activity criterion in ORR reactions is half-wave potential (E half wave). For instance, the potential needed in the OER and HER reactions to achieve a current density of 10 mA cm<sup>-2</sup> (Ei) is a factor used to calculate the electrocatalytic activity. The reactions of electrodes might be optimized through charge transport, and the mass transfer parameter is not considered [25]. Such currents are dependent on the applied potential,

as explained by the Butler–Volmer equation. When  $\eta$  is greater (>0), the Butler–Volmer equation, which would be expressed in Equation (1), can be used to influence the cathode or anode reaction.

(a)  

$$(a)$$
  
 $(b)$   
 $(b)$   
 $(c)$   
 $(c$ 

$$\log(j) = \log(j_0) + \alpha z F / (2.303 \text{ RT})\eta$$
(1)

**Figure 1.** (a) Typical polarization curves for ORR/OER, (b) ORR reaction in alkaline (red line) and acidic (blue line); scheme adapted with permission from ref. [26] Copyright @ 2020, Elsevier B.V. (c) Pathway of oxygen reduction reaction as 4e<sup>-</sup> and 2e<sup>-</sup> pathway, where \* denotes an unoccupied active site.

In Equation (1), the term  $\frac{\alpha zF}{2.303 RT}$  is the Tafel slope. The smaller Tafel slopes contribute to the higher current density of electrocatalysis with the same  $\eta$ . The current density ( $j_0$ ) is calculated through the Tafel plot ( $\eta = 0$ ).

# 3. General ORR Mechanism

The ORR reaction is classified into two types: the four-electron (4e<sup>-</sup>) and twoelectron (2e<sup>-</sup>) pathways. During the four-electron pathway, O<sub>2</sub> is converted to H<sub>2</sub>O (4*H*<sup>+</sup> + 4*e*<sup>-</sup> + O<sub>2</sub> $\rightarrow$ 2*H*<sub>2</sub>O in acidic media) or OH<sup>-</sup> (2*H*<sub>2</sub>O + 4*e*<sup>-</sup> + O<sub>2</sub> $\rightarrow$ 4OH<sup>-</sup> in alkaline media). In another case, O<sub>2</sub> is converted to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) following the twoelectron (2e<sup>-</sup>) pathway that is not required for fuel cells application. Depending on the oxygen dissociation capability of the electrocatalyst surface, ORR took place via various mechanisms (dissociative or associative) in a four-electron pathway [24].

Dissociative mechanism:

$$1/2 O_2 + * \to O$$
 (2)

$$^{*}O + H^{+} + e^{-} \rightarrow ^{*}OH$$
 (3)

$$H^+ + e^- + {^*OH} \rightarrow H_2O + * \tag{4}$$

Associative mechanism:

$$O_2 + * \to ^* O_2 \tag{5}$$

$$^{*}O_{2} + H^{+} + e^{-} \rightarrow ^{*}OOH$$
(6)

$$H^{+} + e^{-} + *OOH \to *O + H_2O$$
 (7)

$$^{*}O + H^{+} + e^{-} \rightarrow ^{*}OH$$
(8)

$$H^+ + e^- + {^*OH} \rightarrow * + H_2O \tag{9}$$

The above reaction applies to acidic medium and \* represents active sites. In alkaline condition, the H<sup>+</sup> is substituted with water (H<sub>2</sub>O). For direct four-electron pathways,

$$O_2 + 4e^- + 2H_2O \to 4OH^-$$
 (10)

It is noted that the two pathways generate the <sup>\*</sup>O intermediate in the ORR reaction, as shown in Figure 1b.

The mechanism referred to as the series 2-electron pathway, or alternatively known as the indirect four electron (4e<sup>-</sup>) pathway, involves the formation of  $H_2O_2$  as an intermediary, as seen in Figure 1c. Hydrogen peroxide is first produced by a two-electron (2e<sup>-</sup>) route, which is followed by further reduction to  $H_2O$  with the addition of an additional two electrons.

Distinguished researchers Griffith, Pauling, and Bridge discovered the three distinct type of O<sub>2</sub> adsorption [27–29]. The Griffith model shows the existence of a strong bond between the atoms of an unfilled dz<sub>2</sub> orbital as well as the  $\sigma$  orbital causing the interaction of an oxygen molecule (O<sub>2</sub>) with a single atom on the surface of the metal substrate [30]. The necessary electron density in the  $\sigma$  orbital to the dz<sub>2</sub> acceptor orbital is created by end-on adsorption through the single-type bond of the oxygen molecule, according to the Pauling model. For the Pt-based electrocatalyst, the Bridge model describes how two strong bonds interact with two different active sites.

#### 4. Performance Analysis of ORR Electrocatalyst

The common approaches to investigate the potential of ORR electrocatalysts is the evaluation of power density through membrane electrode assembly (MEA). However, so much work is required to construct the improved electrodes for the intensive research of ORR electrocatalysts through MEA. As a consequence, the performance of the electrochemical cell has been examined using the two-half-cell method. Both rotating ring disk electrodes (RRDEs) and rotating disk electrodes (RDEs) enable the disk electrode to rotate at a great speed of 1600 rpm, which can be used to transfer mass [31–35]. The screen-printed carbon electrode (GCE) surface was shielded by a fine layer of electrocatalytic materials, confirming laminar flow during rotation and lowering the resistance of mass transfer via Nafion [36–38]. The atomically thin and homogeneous electrocatalytic can be coated on the GCE of RDEs to investigate the ORR reaction through polarization curves for accurate measurements.

#### 4.1. RDE and RRDE Method

The RDE and RRDE prototype is a useful tool for evaluating ORR electrocatalyst efficiency and also avoiding the insufficient oxygen transport [39]. Three distinct regions with a variety of reaction kinetics can be identified in the ORR polarization curve (diffusion, kinetic, and mixed kinetic diffusion controlled) of the RDE measurement. These associated ORR parameters were calculated via these equations (Equations (11) and (12)) with onset potential ( $E_{onset}$ ), limited current ( $J_L$ ), kinetic current density ( $J_K$ ), half-wave potential ( $E_{1/2}$ ),

hydrogen peroxide yield ( $H_2O_2$ –%), electron transfer number (n), double-layer capacitance ( $C_{dl}$ ), electrochemical surface area (ECSA), resistance (R), and so on.

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} \tag{11}$$

$$J_{\rm L} = 0.62 \, \rm nFC_0 (D0)^{2/3} \, \nu^{-1/6} \, \omega^{1/2} \tag{12}$$

In Equation (12), 'F' is the faraday constant; ' $\omega$ ' is the angular velocity (rad/s); 'D<sub>0</sub>' and 'C<sub>0</sub>' indicate the oxygen diffusion coefficient and oxygen bulk concentration, respectively. ' $\nu$ ' is the known kinetic viscosity.

# 4.2. Membrane Electrode Assembly (MEA) Test

The fuel cell test that contains the two-electrode and electrolyte system is shown in Figure 2a,b, which reveals how the electrocatalyst is used in actual devices [40]. Electrocatalytic layers, which have been composed of electrocatalysts, carbon black, and binder, are often needed for MEA analysis. The electrocatalyst-coated membrane (ECCM) or electrocatalyst-coated substrate (ECCS) techniques are presently used to produce MEA. In general, the US Energy standard equations were used to correct the fuel cells' current density [41–43]. The MEA methodology can display the real condition of fuel cells with electrocatalysts. However, its complicated fuel cell components, ambiguous electrocatalyst active sites, as well as slow mass transport in electrocatalyst layers describe the complexity associated to assessing the specific activity of electrocatalysts [44].





#### 5. Active Sites Engineering

# 5.1. Active Sites of Hetero Atoms Doped Carbon Electrocatalysts

To increase the ORR activity of the electrocatalytic site and also reduce its required amount of noble metals in electrocatalysts, the common strategy of alloying methods is employed to optimize the crystal phase and structure. These processes might alter the surface adsorption, and the electronic structures in electrocatalytic sites supports the features of electrocatalysis. Pure carbon exhibits a good OOR, but nanomaterials with various metals show strong electrocatalytic activity. N, P, B, O, and S within carbon resulted in active electrocatalysts for ORRs [47]. The doping atoms generate the efficient active sites in electrocatalytic materials by altering the spin density and charge distribution of adjacent carbon-supported atoms, thereby improving its overall adsorption/desorption property. This is possible due to the carbon atoms' distinct bond strength, electro-negativity and atomic sizes. It demonstrates that the carbon atoms in graphitic N-doped carbons that are close to nitrogen dopants contain pyridinic components that may function as electrocatalytic sites in ORR reactions [48]. Recently, both experimental and theoretical study indicate that doping creates natural carbon defect sites associated toward the material's ORR activity, as shown in Figure 3a [49]. According to studies, the N-doping strategy was not the only factor contributing the graphene mesh with an N-dopant to electrocatalyst ORR; topological defects were also a factor [50]. Significantly, edge effects (defect sites or dopants near the corner of the electrocatalytic material) also exhibit improved activity [51]. For carbon materials with an undoped structure, a defect mechanism creates the reactive groups and is used to release the electrons from the carbon materials for the electrocatalysis process. Recently, a few carbon materials with naturally defective sites and dopant-free structures had also demonstrated great electrocatalytic activity for ORR reactions [52]. The experimental and theoretical work revealed that the tetrahedral defects that were produced in pyrolytic graphite were not entirely accountable for the electrocatalytic active sites but rather showed higher activity than N-doped pyridinic graphite [53,54]. As a result of the effect, a crucial area for future research on defects, doping, and edge sites helps to create outstanding carbon-supported electrocatalysts with distinct structural characteristics.

#### 5.2. Active Sites of M-N-C Carbon Electrocatalysts

Due to atomically dispersed atoms on single-atom electrocatalysts (SAECs), usually the metal atoms contained in carbon support materials can function as effective active sites for ORR reactions. So many metal SAECs (Fe, Ir, Ru, and Mo) have been created for various electrochemical processes [54]. With the help of supporting materials like metal oxides and carbons, the created metal atoms might perform much better as electrocatalytic active sites (Figure 3b). Their improved electrocatalytic properties result in an effective interaction between both the metal and carbon support, which altered the intrinsic coordination structure of the support materials, enabling the electrons to transfer to the metal atoms and changing the adsorptive energies of the reaction products. The structural coordination and kinetics of various electrocatalytic reactions can be strongly affected by the characteristics of the support materials (nanostructure, composition, and preparation method). Likewise, the bonding of foreign atoms (S, B, and N) at preferential sites of carbon support might alter the materials' electronic characteristics and boost the activity of electrocatalysts. According to the findings, M-N-C sites on noble metal-free carbon supports outperform Pt-based nanomaterials in ORR activity [55]. The geometrical as well as edge defects sites in the carbon support have induced the beneficial effects in a variety of single-atom electrocatalyst. The defect sites might also immobilize the metal centers from creating more defect sites and improve the support's electrochemical and surface reaction properties [56].

#### 5.3. Mechanism of Reaction at ORR Active Sites of Metal-Based Carbon Electrocatalyst

In both zinc–air batteries and fuel cells, the ORR is a crucial cathode reaction. The efficient operation of fuel cells is hampered by the numerous protons and electron transfer processes and also involves a slow kinetics reaction. Because of its outstanding reaction, platinum (Pt) is typically recognized as an effective ORR electrocatalyst. However, due to its high cost and scarcity, efforts have been made to prepare Pt-free electrocatalysts. In particular, the carbon support comprises transition metal atoms (M-N-C) with an N-dopant, where M stands for Fe, Ni, Co, etc. [57–62]. It is also possible to improve the platinum activity by adding other inexpensive transition metals atoms through altering their surfaces. Most likely, the material to substitute Pt electrocatalysts is one which is made of Fe-N-C. The active sites are represented by an M-N<sub>x</sub> group as in standard nomenclature of M-N-C electrocatalysts. According to studies, the electrocatalytic activity of the M-N<sub>x</sub> group in the ORR reaction increases in the following order: Fe > Co > Cu > Mn > Ni [58]. Simultaneously, interest in carbon-supported electrocatalysts has increased as a result of the discovery of

N-doped carbon nanotubes in 2009, having the potential to function as extraordinary active ORR electrocatalysts [59]. The creation of electrocatalytic ORR adsorption sites is typically attributed to defects (carbon vacancies, local, and edges imperfections) in carbon support caused by heteroatoms [60]. However, recent research has not precisely pinpointed the active sites of carbon-supported materials and their instability in acidic environments. Additionally, the results obtained from the majority of studied electrocatalysts, including platinum-based electrocatalysts, reveal the necessity of high overpotential to activate the ORR. Because of the reaction intermediates, adsorption energies have a significant link. The optimization of intermediate adsorption reaction energies with another active site was not possible during an ORR [61]. Two reactions were able to establish the ORR processes at the metal site (M). The initial oxygen adsorption on the surface sites produces  $M-O_2$  species; afterwards, the different reactions occurred depending on the metal type or the  $M-O_2$ dissociation characteristics. By estimating the oxygen dissociation barrier of electrocatalysts, the ORR reaction mechanism can be classified as a dissociative or associative pathway. M-O<sub>2</sub> dissociates into two M-O groups via a neighboring metal atom in the dissociative type, and each M-O group later reacts with electrons as well as protons to yield  $H_2O$  as well as M-OH. M-O<sub>2</sub> reacted with an electron and proton in an associative type to produce M-OOH. After that, M-OOH leads to  $H_2O$  via a direct two-electron pathway (2e<sup>-</sup>) and to  $H_2O_2$  via a four-electron pathway (4e<sup>-</sup>), or it creates M-OH and M-O simultaneously within the active center. Because of its outstanding performance, the last route is beneficial for fuel cells and metal-air batteries. Distinct ORR mechanisms were suggested for the various kinds of O2 adsorption. If oxygen connects to the electrocatalyst sites end, an associative type of ORR was used. In another case, when  $O_2$  is attached to the electrocatalyst sites side because the bond between the O-O group is weakened due to a  $\pi^*$  orbital, the ORR became dissociative [62]. Researchers developed an appropriate theoretical model to analyze and examine the various parameters in the ORR reaction process (Figure 3b) [63–67].



**Figure 3.** (a) Two pathways of ORR on heteroatom-doped carbon electrocatalysts, scheme adapted with permission from ref. [68] Copyright @ 2021, Royal society of chemistry. (b) Doping, defect sites and atomic metal active sites in carbon materials, scheme adapted with permission from ref. [69] Copyright @ 2020, John Wiley & Sons, Inc.

#### 6. Recent Development of Non-Precious Metal Electrocatalyst

6.1. *Metal-Free Heteroatom Dopants Electrocatalyst* 

Promising electrocatalysts for ORR are thought to be metal-free or carbon-supported nanomaterial; the structures are doped with nitrogen (N), phosphorus (P), boron (B), and other carbon elements [40,70–78]. The carbon-supported nanomaterials are generally

acquired by biological systems. Advantages include a reduced cost and plentiful sources; they also have the ability to stop poisoning and corrosion, extending the lifespan of the transition metal group. The carbon structure (metal-free) and also its bonding with a heteroatom are thought to act as effective processing centers in the ORR reaction [40]. Here, we discuss the synergistic function of the heteroatom-doped carbon nanostructure for the ORR.

The charge and spin densities around at the carbon nanostructures could be altered by incorporating heteroatom dopants, which speed up the electron transport in ORRs. Numerous carbon-supported nanostructures, including graphene, carbon nanotubes, and graphene aerogel, have been thoroughly studied. An efficient ORR electrocatalyst based on carbon nanotubes was fabricated via modifying with an N-dopant. As shown in Figure 4a,b, a few of these electrocatalysts display excellent ORR activity in contrast to Pt/C in alkaline and acid media with long lifetimes [70,71]. The ability to create carbon electrocatalysis with a nitrogen dopant by carbonizing nitrogen-comprised groups [72–74] by heat treatment in ammonia [75,76] or nitrogen-comprised gas [77,78] would be made possible only by the good lattice similarity provided by N atoms, which has an equivalent radius to carbon atoms, as shown in Figure 4c. For instance, the pyrrole group and nitrogen were combined to create the N-carbon nanotube (N-CNT) aerogel. As shown in Figure 4d [79], XPS confirmed the N-doped carbon by detecting the presence of Npyrrolic (400.1 eV), N-graphitic (400.9 eV), and N-pyridinic (398.2 eV) groups. These demonstrated the exceptional ORR activity (0.85 V) in alkaline medium as well as current density and half-wave potential. The entire performance, which was examined using MEA, displays excellent polarization current density at 0.5 V (199.5 mA cm<sup>-2</sup>) and power density (103 mW cm<sup>-2</sup>). The polyacrylonitrile (PAN) organic resin serves as a carbon (C) and nitrogen (N) source and is used to fabricate the highly functional, three-dimensional carbon nanostructures. In acid media, these exhibit an excellent ORR activity and  $E_{1/2}$ value (0.755 V) [80].

Although the precise role of each carbon with N doping remains debated and needs to be meticulously studied in ORR electrocatalysts, the carbon with N doping is classified into various groups, including N-graphitic groups, N-pyridinic groups, N-pyrrolic groups, and others. To explore the contributions of nitrogen-doped groups, spectroscopy and molecule study were examined [81,82]. N-graphitic groups show superior thermal properties especially in comparison to both N-pyridinic and N-pyrrolic groups; the broad N groups are customarily easy to predict. As a result, the effect of various N doping within NGs on the ORR reaction was examined at varying temperatures. Such studies show that annealing could not change the NG morphologies and Raman spectra (Figure 4f), but it does encompass a range of oxygen contents (4.0% to 2.9%). Nevertheless, the nitrogen content gradually declines as the temperature rises. Specifically, N graphitic became increasingly prevalent while N amino and N pyrrolic were becoming less prevalent. As a consequence, the values of n and E<sub>onset</sub> were determined in the following sequence: NG-1000, NG-800, NG-400, and NG-600, in which x denotes the annealed heat, which decreases with a decrease in the quantity of amino moieties after increasing with a rise in the N-graphitic content [81]. These findings show that (i) the quantity of the N-graphitic and amino group substituent determines the ORR activity (E<sub>onset</sub> and n), and (ii) the amount of N-graphitic and N-pyridinic moieties determines the current density variability in the ORR, and (iii) additionally, N pyrrolic makes a negligible contribution to ORR activity. Moreover, an effective method for fabricating the carbon nanostructures with controlled nitrogen content (0 to 4.22 (at.%)) consisted of a single N-pyrrolic group (Figure 5a) [83]. To retain the N-pyrrolic group, the low-temperature carbonization treatment is crucial. Therefore, the fact that the pseudo-capacitance is entirely dependent on the N-pyrrolic content, offers a helpful suggestion for maximizing the N-dopants level and presents a novel model to investigate the ORR mechanism on nitrogen content in N-doped carbon.



**Figure 4.** (a) LSV (10 mV s<sup>-1</sup>, 1600 rpm) on NPC, edge-rich QMC, edge-rich QMNC, and Pt/C electrodes in 0.1 M KOH saturated with oxygen, reprinted with permission from ref. [70] Copyright @ 2018, American Chemical Society, (b) CVs of different composites with turnover current measured in the S. putrefacient CN32 cell suspension at 1 mV s<sup>-1</sup>, reprinted with permission from ref. [71] @ 2018, American Chemical Society, (c) TEM images of LIG-O, reprinted with permission from ref. [78] Copyright @ 2018, John Wiley & Sons, Inc., (d) XPS spectra of N 1s spectra of N-CNT, reprinted with permission from ref. [79] @ 2015, John Wiley & Sons, Inc., (e) LSV curves of NC-1:1:10, NC-1:0:10, NC-1:1:0 and NC- 1:0:0 in 0.1 M HClO<sub>4</sub> at 10 mVs<sup>-1</sup> and 1600 r min<sup>-1</sup>, reprinted with permission from ref. [80] Copyright @ 2019, Royal Society of Chemistry, (f) TEM image of AG and SAED pattern (inset), reprinted with permission from ref. [81] Copyright @ 2013, Elsevier B.V.



**Figure 5.** (a) Variations in the pseudo-capacitances with respect to pyrrolic nitrogen content in CMs (FPF), SPNCMs (F, 1/7), SPNCMs (F, 1/3), and SPNCMs (F, 1/1), reprinted with permission from ref. [83] Copyright @ 2020, NATURE, (b) the intensity of electron transfer on the ([NP]:[NG]) measured by XPS, reprinted with permission from ref. [82] Copyright @ 2018, Royal Society of Chemistry, This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY), (c) LSV curves of PG, Pt/C, PG/CB (5:1) and CB in 0.1 M KOH solution at 10 mV s<sup>-1</sup> and 1600 rpm. Inset shows the onset potential of PG, Pt/C, PG/CB (5:1) and CB, reprinted with permission from ref. [84] Copyright @ 2013, John Wiley & Sons, Inc., (d) N,S co-doped graphene, scheme adapted with permission from ref. [85] Copyright @ 2020, American Chemical Society, (e) polarization and power density curves of the NSHPC, reprinted with permission from ref. [86] Copyright @ 2020, American Chemical Society, (f) LSVs of different samples at a rotation rate of 1600 rpm; reprinted with permission from ref. [87] Copyright @ 2014, Scientific Report. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY).

The influence of nitrogen was investigated using spectroscopy analysis in addition to controlled fabrication techniques. For instance, the electronic molecule of 7,7,8,8-tetracyanoquinodimethane (TCNQ) was used to calculate the amount of transit electrons, confirming that the proportion of N pyridinic to N graphitic ([NP]:[NG]) determines the intensity of electron transfer [82] (Figure 5b). The NP: NG fraction and kinetic current density were both found to have a strong correlation. To summarize, the N-pyridinic and N-graphitic moieties may also be improving their ORR electrocatalyst performance, but their interaction may cause a decrease in the electron donation and could affect the ORR activity. The discovery provides more useful details regarding the impact of an N-doped carbon electrocatalyst on electronic and ORR activity. In addition, lighter elements such as boron, phosphorus, fluorine, and sulfur were used as carbon dopants in addition to N-doped carbon [87].

The addition of a heteroatom dopant with distinct electronegativity might rearrange the surface charge which could change the chemical and electronic properties of carbon. For instance, research was conducted on N-doped carbon with the dopant's electronegativity (3.0) being close to or greater than that of carbon (2.5). The phosphorus (P) exhibits a lower electronegativity (2.1) than carbon, allowing it to perform a significant electron-accepting function in carbon that has been doped with phosphorus. Hou's group created the first graphene structure doped with phosphorus using a low-cost pyrolysis method, which demonstrated superior ORR activity in alkaline media, as shown in Figure 5c [84]. The P graphene shows an excellent  $E_{onset}$  (0.92 V vs. RHE) and performance that is close to commercial electrocatalysis (20% Pt/C). In particular, graphene with P doping has better value for current density than graphene without P doping in the entire potential swiping. An investigation on developed boron (2.04)-anchored carbon could support the idea of boron-induced electron deficiency in the carbon network for an ORR reaction (Figure 5d) [85,88]. The heteroatoms of sulfur have similar electronegativity (2.58) and also experience synergistic interactions with carbon, making them a better alternative to carbon atoms [89,90]. Furthermore, this impact can significantly raise the ORR activity, particularly when adding multiple heteroatoms to carbon rather than a single heteroatom within the carbon structure. For instance, the pyrolysis-induced doping of S and N on the hierarchical carbon (NSHC) provides favorable results and motivates toward the synthesis of efficient ORR electrocatalysts. According to Figure 5e, the co-doping of S and N could significantly enhance the electrocatalytic process and afterwards induce cell performance for an ORR reaction. The co-doped NSHC structure possesses higher fuel cell performance than N-doped hierarchically carbon (NHC) in MEA conditions [86]. Additionally, MOF-5 (NPS-C-MOF-5) was used to create a ternary doping of carbon, which was then applied to ORR electrocatalysts. Dimethyl sulfoxide, triaryl phosphine and dicyandiamide were utilized as S, P and N-dopant sources during preparation. In comparison to single/binarydoped carbon electrocatalysts, derived ternary-doped NPS-C-MOF-5 has a greater positive onset potential (Eonset) and demonstrated the excellent synergistic activity of the dopants (Figure 5f) [87]. The oxidation of graphene nanoribbons in the simple hydrothermal synthesis produced co-doped B, N graphene nanoribbons. The calculations were made to determine the doping effects of boron and nitrogen on their morphologies, configuration, size, and associated electrochemical performance. This study indicates that  $H_3BO_3$  and  $CH_4N_2O$  in the hydrothermal process not only serve as B and N sources but also provide the active sites of electrocatalysts and enhance the synergistic effect of B and N dopant [91]. The outstanding ORR reaction is demonstrated by N-doped carbon nanosheets with a very high surface area (1793 m<sup>2</sup> g<sup>-1</sup>) and high edge defect sites [92]. Such electrocatalysts have been found to be durable in the ORR reaction; their performance level is similar to Pt/C in an acidic environment. The DFT was employed to probe the positions and configuration of N-dopant groups, including N-pyridinic, N-pyrrolic, and N-graphitic groups, which is a crucial requirement for ORR electrocatalysts. It was noticed that the edge atoms and N-graphitic carbon atoms were significant reactive sites for the ORR reaction. The findings show that heteroatom dopants like P, O, B, and S might be combine with N-doped carbon to produce promising effects for the ORR.

The thermal treatment of polyaniline on mesoporous silica (SBA-15) resulted in N and O co-doped carbons; they were subsequently etched to remove the silica, and the researchers demonstrated that the materials have outstanding ORR reaction activity [93]. The XPS findings suggest that O and N may exist as a N-O/C-O bond within pyrrolic/pyridine groups in the carbon structure. The following conclusions come from the above discussion: for the ORR reaction, boosting the number of N sites in the carbon structure helps to generate a four-electron reaction (4e<sup>-</sup>) instead of a two-electron reaction (2e<sup>-</sup>); for the ORR reaction, increasing the electrocatalytic activity through the doping of oxygen, creating heteroatom-doped carbon structures, is very much beneficial compared to using a metal-enclosed structure. In order to achieve effective ORR activity, the researchers compared ternary co-doping this carbon structure to single or double co-doping the carbon-supported electrocatalyst (Figure 6a–e) [92]. In addition, improving the activity of the electrocatalyst in the ORR reaction and the selectivity (producing useful products like H<sub>2</sub>O instead of H<sub>2</sub>O<sub>2</sub>) were also vital; these were accomplished by doping the various dopants on carbon-supported materials and investigating the effects on its synergism process.

The co-doping of S and N onto carbon aerogels was obtained by using the pyrolysis of carrageenan and urea [94]. The created carbon has a lot of interconnected mesopores and macrospores as well as a lot of surface area (up to 1307 m<sup>2</sup> g<sup>-1</sup>), which helps mass transport and forms the groups that are more reactive to the material. As a result, such materials demonstrated exceptional ORR activity in acidic media; the performance was comparable to that of commercial Pt/C electrocatalysts. Theoretical analysis suggests the

N-S-C defect sites within the carbon nanostructures might act as ORR active sites. High efficient electrocatalysts were developed in N-S-D-G-4 and N-S-D-G-6 carbon structures and we obtained the reduced ORR overpotentials, which were calculated in theoretical and experiential analysis. Thus, the researchers demonstrated the significance of polyhedral S defects and graphitic-type N dopant sites within materials, as they contributed to the ORR electrocatalytic activity. These investigations further demonstrate that the improved ORR activity of the carbon electrocatalysts was influenced by the dopant sites. The creation of more active species in a carbon structure was made possible by heteroatoms, porous structures, electronic structures, and defect sites. However, the specific roles played by active sites, including defect sites, pore edges, and dopants in electrocatalysts, are still unidentified [95]. To acquire a solid understanding of how different types of active sites contributed to ORR activity, sophisticated characterization methods with a combination of meticulous preparation and DFT analysis are necessary. Additionally, these electrocatalysts may be contaminated as a result of the synthesis vessel and precursor utilized; these must be potentially avoided to reduce the effect of contaminants on the electrocatalysts' final ORR activity. The various properties of heteroatom-doped carbon electrocatalysts are presented in Table 1.



**Figure 6.** (a) Synthetic procedures used to make NOSCs, schemes adapted with permission from ref. [92] Copyright @ 2014, American Chemical Society, (b) polarization curves of ORR over NOSC8-900 on RDE rotating at different speeds, (c) polarization curves of ORR over NOSC $_x$ -900 materials on RDE rotating at 1600 rpm, (d) electron-transfer number (n) and (e) % peroxide formed at three different potentials vs. amount of colloidal silica used as templates for a series of NOSCx-900 materials and NOSCB-900, reprinted with permission from ref. [92] Copyright @ 2014, American Chemical Society.

Heteroatom Doped	Metal Precursor	Catalyst Name	Metal Content	BET Surface (m <sup>2</sup> g <sup>-1</sup> )	Electrolyte	E <sub>onset</sub> (V)	E <sub>1/2</sub> (V)	Tafel Slopes (mV dec <sup>-1</sup> )	Electron Transfer Number	H <sub>2</sub> O <sub>2</sub> Yield	Reference
Nitrogen	-	Edge-rich QMNC (edge-rich quasi-mesoporous nitrogen-doped carbon)	-	1970	0.1 M KOH	1.05	-	-	3.9	-	[70]
Nitrogen	-	N-CNTs/rGO <sub>1:1</sub>	-	424	-	-	-	-	-	-	[71]
Nitrogen	Fe	m-GIC-HT(N-Fe)	-	-	0.1 M NaOH	0.82	0.72	-	3	-	[73]
				0.5 M H <sub>2</sub> SO <sub>4</sub>	0.8	-	-	-	-		
Nitrogen	Со	Co SAs/3D GFs	$\begin{array}{c} 1.16 \pm 0.03\% \ {\rm Co} \\ ({\rm XPS}) \\ 1.38 \pm 0.05 \ {\rm wt\%} \ {\rm Co} \\ ({\rm ICP}) \end{array}$	915.47	0.1 M KOH	1.032	0.901	71	3.99	-	[74]
Nitrogen	Zn, Co	2D-MCo3O4-NCNAs	-	161.6	0.1 M KOH	1.54	0.74	74	~ 3.9	3%	[76]
Nitrogen	-	LIG-O (oxidized laser- induced graphene)	-	246.8	0.1 M KOH	1.52	-	56	4.0 at 0.6 V	-	[78]
Nitrogen	Fe, Mn, Co, Ni	N-CNT-1030	198.1 ppm Fe 1452.4 ppm Mn 11.3 ppm Co 4.7 ppm Ni (ICP-AES)	Up to 869	0.1 M KOH	-0.055	-0.263	-	3.70–3.85	-	[79]
Nitrogen	-	NC-1:1:10	-	888.15	0.1 M HClO <sub>4</sub>	0.901	0.755	-	4.19-4.31	-	[80]
Nitrogen	-	N@CNTs	-	43-81	0.1 M KOH	-	-	70–105	2.2–4.2	-	[82]
Nitrogen,	-	NSHPC (N, S co-doped	_	1043.3	0.1 M KOH	1.04	0.89	62.5	3.8-4.0	<8.5%	[86]
Sulfur		hierarchically porous carbon)		101010	0.1 M HClO <sub>4</sub>	0.84	0.74	59.7	~4.0	-	
Boron	-	PN-B <sub>1</sub> G-GCE	-	108.3	0.1 M KOH	-	-	-	3.8-4.0	-	[85]
Boron, Nitrogen	-	BDD2 (boron-doped diamond)	-	-	0.1 M KOH	-0.634	-	-	2.65	-	
		NSCA-700-1000			0.5 M H <sub>2</sub> SO <sub>4</sub>	0.885	0.76	-	4	-	[88]
Nitrogen, Sulfur	-	(NSCA: N modified S-defect carbon aerogel)	-	1307.2	0.1 M HClO <sub>4</sub>	0.885	0.76	-	4	<3%	
		carbon actogery			0.1 M KOH	-	0.85	-	4	-	
Boron, Nitrogen	-	NB/C (B, N-doped Ultrathin Carbon Nanosheet)	-	1085	0.1 M KOH	-	0.8	69	3.89	18–22%	[94]
Boron, Nitrogen	-	NBGHSs (Boron and nitrogen co-doped hollow graphene microspheres)	-	512	0.1 M KOH	-	-	66	-	-	[96]
Nitrogen	-	N-doped HsGDY 900 °C		1754	0.1 M KOH	1.02	0.85	64.4	3.92	<4%	[97]
		graphdiyne)			0.1 M HClO <sub>4</sub>	0.86	0.64	76.7	3.88–3.95	<6%	[98]
Nitrogen	-	N-rich PDA-based carbon SMSs	-	422.4	0.1 M KOH	-0.1	-0.1	-	-	-	[99]

Table 1. Various parameters of heteroatom-doped carbon as ORR electrocatalyst.

# 6.2. M-N-C Carbon Electrocatalyst

The nitrogen is doped with carbon and then combined to form a single-atom or nonprecious metal nano-structure, resulting in an M-N-C structure with highly active sites used to evaluate the voltage in the ORR both in alkaline and acidic media [100–102]. Numerous non-precious metal atoms were studied in the M-N-C structure such as cobalt (Co), irons (Fe), manganese (Mn), copper (Cu), and nickel (Ni), zinc (Zn), and other elements (metal atoms indicated as 'M'). Additionally, the coordination number is altered by methods of synthesis, whilst the N and C components represent the bonding of metal atoms to nitrogen or carbon atoms. An in-depth investigation of the electrocatalysis based on the M-N-C structure revealed that the exhibited ORR reaction has high activity, selectivity, and longer life. Graphene substrates and Fe<sub>x</sub>N nanostructures have been developed. The resulting electrocatalyst shows superior  $E_{onset}$ , greater current density, and lower charge carrier resistance (R<sub>ct</sub>) in alkaline solution compared to that result obtained without Fe-N-C (Figure 7a,b) [103]. A Fe-N-C catalyst (P-FeMOF@ ZIF-8) that has been made using the pyrolysis method also exhibits excellent ORR activity in both alkaline and acidic media. The atomic-level analysis of Mossbauer spectroscopy and EXAFS (Figure 7c,d) [104] verified the occupation of Fe within Fe-N<sub>4</sub> coordination.

The core issue involves understanding the active sites of M-N-C single-atom structures because it is useful to gain knowledge about the reaction mechanisms and further encourage the ORR activity of electrocatalysts. Four elements, including transition metal centers with highly dispersed states, adjacent coordinated N atoms connected with carbon skeletons, heteroatom dopants as environmental atoms, and guest groups, are recognized as the M-N-C active sites in single-atom electrocatalysts (SAECs) [105]. The combination of a carbon-supported structure with transition metal nanoparticles is always considered as SAECs and nanoparticles (Table 2).



**Figure 7.** (**a**,**b**) RDE voltammograms and impedance spectra of Fe<sub>x</sub> N/NGA, Fe<sub>x</sub> N+NGA, NGA, free Fe<sub>x</sub> N and Pt/C in 0.1 M KOH at 10 mV s<sup>-1</sup> at 1600 rpm, reprinted with permission from ref. [103] Copyright @ 2014, John Wiley & Sons, Inc., (**c**) Fe Moössbauer spectrum and (**d**) FT-EXAFS fitting curve of P-FeMoF@ZIF-8, reprinted with permission from ref. [104] Copyright @ 2019, American Chemical Society, (**e**) synthesis of the micro-mesoporous Fe-N-C-Zn, scheme adapted with permission from ref. [106] Copyright @ 2019, American Chemical Society, (**f**) polarization curves of Mn–N–C-1100, Mn–N–C–HCl-1100, Mn–N–C–HCl-800/1100, and N–C, (**g**) steady-state ORR polarization curves of Mn–N–C–HCl-800/1100 before and after potential cycling tests (0.6–1.0 V, 30,000 cycles), (**h**) cell performance of different catalysts in H<sub>2</sub>-O<sub>2</sub>, reprinted with permission from ref. [107] Copyright @ 2020, American Chemical Society.

Metal Precursor	Catalysts Name	Metal Content	BET Surface (m <sup>2</sup> g <sup>-1</sup> )	Electrolyte	E <sub>onset</sub> (V)	E <sub>1/2</sub> (V)	Tafel Slopes (mV dec <sup>-1</sup> )	Electron Transfer Number	H2O2 Yield	Reference
Fe	Fe1/N,S-PC (Fe/N and S-co-doped hierarchical porous carbon)	2.6 wt.% Fe (ICP-OES)	998.5	0.1 M KOH	-	0.904	84.5	3.95	<9%	[101]
Fe	Fe-N-C (P-FeMOF@ZIF-8)	1.24 wt.% Fe (ICP)	785.0	0.1 M KOH 0.5 M H <sub>2</sub> SO <sub>4</sub>	1.01 0.85	-	-	- -	-	[104]
Mn	Mn-N-C-HCl-800/1100	2.00 wt.% Mn (XPS)	1511	0.5 M H <sub>2</sub> SO <sub>4</sub>	-	0.815	-	-	<3%	[107]
Fe	Fe/N-PCNs	3.89 wt.% Fe (XPS)	864	0.1 M KOH 0.1 M HClO <sub>4</sub>	0.96 0.88	0.86 0.79	-	~3.95 3.80	-	[108]
Мо	Mo/OSG-H	13.47 wt.% Mo (ICP-OES)	-	0.1 M KOH	0.78	-	54.7	2.1	-	[109]
Fe/Co	CAN-Pc(Fe/Co)	10.70 wt.% (ICP-OES)	84.11	0.1 M KOH	1.04	0.84	54	3.94	<5%	[110]
Zn/Co	Zn/CoN-C	0.33 wt.% Zn 0.14 wt.% Co (ICP-MS)	1343	0.1 M KOH 0.1 M HClO <sub>4</sub>	1.004 0.97	0.861 0.796	-	3.88	~5%	[111]
Zn	Zn-N-C	9.33 wt% Zn (EDX) 5.64 wt.% Zn (ICP-MS)	1002	0.1 M KOH 0.1 M HClO <sub>4</sub>	-	0.873 0.746	- -	-	<5%	[112]
Со	10Co-N@DCNF	0.649 wt.% Co (ICP-MS)	-	0.1 M KOH	-	0.83	56	-	<8%	[113]
Со	Co-N/S-DSHCN-3.5 (Co, N, and S co-doped hollow carbon nanocages)	-	429	0.1 M KOH 0.5 M H <sub>2</sub> SO <sub>4</sub>	0.989 0.84	0.878 0.754	-	3.9	<10%	[114]
Fe	FeCl1N4/CNS	1.50 wt.% Fe (ICP-OES)	-	0.1 M KOH	-	0.921	51	3.97-3.99	<1%	[115]
Fe/Co	M/FeCo-SAs-N-C	5.12 wt.% Fe 4.39 wt.% Co (ICP-MS) 3.32 wt.% Fe 3.33 wt.% Co (XPS)	1003.7	0.1 M HClO <sub>4</sub>	0.981	0.851	-	~4	<6%	[116]
Mn	20Mn-NC-second	3.03 wt.% Mn (ICP-MS)	715	0.5 M H <sub>2</sub> SO <sub>4</sub>	-	0.8	80	-	<2%	[117]
Со	Co-N-C-10	-	-	0.1 M HClO <sub>4</sub>	0.92	0.79	55.8	-	<2%	[118]
Cr	Cr/N/C-950	1.90 wt.% Cr (ICP-MS)	884.9	0.1 M HClO <sub>4</sub>	-	0.761	37	-	-	[119]
Fe	C-rGO-ZIF-2	4.29 wt.% Fe (ICP-OES)	650	0.1 M HClO <sub>4</sub>	0.89	0.77	-	3.8	<5%	[120]
Ce/Fe	Ce–Fe/NC	0.83 wt.% Ce 0.88 wt.% Fe (ICP-OES)	831	0.1 M KOH 0.1 M HClO <sub>4</sub>	-	0.913 0.791	55.55	3.98	~3%	[121]
Mn	Mn-N-C	-	1334.3	0.1 M KOH 0.5 M H <sub>2</sub> SO <sub>4</sub>	0.98	0.88 0.73	60.3	3.98	<2%	[122]
Mn/Co	MnCo <sub>2</sub> O <sub>4</sub> /N-C	-	630.5	0.1 M KOH	0.943	0.795	86	3.50-3.83	<10%	[123]

$\mathbf{I}_{\mathbf{I}}$	Table 2.	Various	parameters o	of singl	e-atom-based	ORR	electrocataly	vst.
---------------------------	----------	---------	--------------	----------	--------------	-----	---------------	------

The transition metal site center is considered to be the key factor in determining the active sites, which have a significant impact on the SAECs' intrinsic ORR activity. The interactions of metals (d-orbitals) with oxygen reactants species (p-electrons) modify their intermediates during the ORR process. These will aid the sorption process of oxygen molecules and facilitate the electron transport reaction [124]. Generally, transition metal groups with decent ORRs were created using cobalt (Co), iron (Fe), nickel (Ni), manganese (Mn), and zinc (Zn) [108–112,125]. For instance, Fe-N-C-derived carbon electrocatalysis has been created by the in situ polymerizing of iron, as shown in Figure 7e [106]. A high current density, excellent stability, and large positive  $E_{1/2}$  and  $E_{onset}$  values are accomplished in alkaline media by the Fe-N-C electrocatalyst. An atomically confined electrocatalyst with a Mn-N-C structure with closely packed Mn-N<sub>4</sub> active sites was designed; this is depicted in Figure 7f,g [107]. M-N-C generally contains an Fe metal center. Figure 7h shows that the produced Mn-N-C- electrocatalysts perform much better than Pt-free ORR electrocatalysts

in terms of their significant ORR activity and elevated power density ( $0.39 \text{ W cm}^{-2}$ ) in 1.0 bar of H<sub>2</sub>-O<sub>2</sub> gas in MEA. Discovering the ideal metal is of crucial importance and thus has been extensively examined. It was discovered that the electrocatalyst of various transition metals (Fe, Mn, Co, Ni, and Cu) had a serious influence on its structure as well as affected the ORR activity [58]. The ORR activities of different metal atoms improved in the following order: Fe > Co > Cu > Mn > Ni. The best choice of central metal in the M-N-C group can only be determined via experimental studies, since it is challenging to regulate different parameters, such as the degree of graphitic structures, morphologies, etc. Theoretical studies are an excellent option to assess the ORR activity of metal sites in M-N-C group with numerous central metals (M), the density functional theory (DFT) model seems to be an essential tool [126]. The crucial indicator of E<sub>onset</sub> activity was calculated and matched with \*OH adsorption energy to display a volcano slope (Figure 8a). The iron element, which is located just on slope of a volcano, exhibits an excellent ORR for M-N-C.



**Figure 8.** (a) Theoretical and corresponding experimental onset potentials for ORR versus the descriptor  $\varphi$ , (b) theoretical ORR overpotential as a function of  $\Delta_{ads}G(OH)$  and  $\Delta_{ads}G(O)$ , reprinted with permission from ref. [126] Copyright @ 2018, Nature, (c) observed correlation between the oxygen adsorption Gibbs free energy and the Bader charge on \*O for undoped (triangles, dotted line) and nitrogen-doped (circles, dashed line) systems, reprinted with permission from ref. [127] Copyright @ 2018, American Chemical Society, (d) ORR polarization curves for different catalysts treated at 900 °C, (e) potential cycling stability and constant potential stability at 0.6 V in O<sub>2</sub>-saturated 0.1m KOH, (f) polarization and powder density curves of primary Zn-air batteries using Pt- C and 10Co-N@DCNF as ORR catalyst and 6m KOH electrolyte, (g) the turnover frequency and the mass activity obtained at the potential of 0.8 V versus RHE for 1Co-N@DCNF, 10Co@DCNF, 1Co-N@CNF, 10Co@DCNF, 10Co@DCNF, 10Co@DCNF, 10Co.N@DCNF, 10Co.N.C.

The coordination sites atom (N) is directly combined with the carbon structure (C) and the central metal atoms (M), which connect the C and M sites. In the M-N-C active sites, the nitrogen atom (N) is typically bonded to the central metal of four atoms via d-p and  $\pi$ -bonds [105]. Because of the improved performance of the ORR reaction, the nitrogen atom that is present at the M-N-C active sites was investigated. DFT is employed to compare the ORR activity of N-graphitic and graphitic carbons (Fe<sub>3</sub>C/NG and Fe<sub>3</sub>C/G, respectively) (Figure 8b) [127]. Fe<sub>3</sub>C/NG demonstrates the superb stability of the \*O intermediate and reveals the critical function of the nitrogen element. Especially, the NG layer offers adequate support for Fe<sub>3</sub>C to display excellent ORR activity when compared to the Pt (111) surface, as verified by DFT study. Additionally, it is thought that the specific condition of the coordination atoms modifies their electronic structures and will affect the active M-N-C sites. By evaluating the oxygen adsorption ability using the Gibbs free energy (G) on the cobalt-anchored nitrogen-doped carbon nanosheets (Co/N-CNSNs), it was feasible to study the coordination atoms in specific chemical environments (Figure 8c). In contrast to the N-graphitic and N-pyrrolic sites, it has been demonstrated that the value of G in carbon sites close to pyridinic nitrogen exhibits the lowest G value. These demonstrate that N-pyridinic sites can absorb oxygen under favorable environmental conditions [128]. Another effective method for changing the electronic structure and M-N-C activity is to control the hierarchy of coordination atoms. These studies inspired the researcher to prepared the carbon structures with various types of defects, such as  $CoN_{4-x}C_x$ (x = 0-4). In order to comprehend the relationship between the activity and the active sites' structure, which corresponds to the  $CoN_{4-x}$  C<sub>x</sub> structure, DFT studies were used. The results of the acquired activity are as follows: CoN<sub>4</sub>, CoN<sub>2</sub>C<sub>2-3</sub>, CoN<sub>3</sub>C<sub>1</sub>, CoC<sub>4</sub>, CoN<sub>2</sub>C<sub>2-2</sub>,  $CoN_2C_{2-1}$ , and  $CoN_1C_3$  exhibit higher cyclic stability, mass activity, and excellent power density, as seen in Figure 8d–g. The improvement of the CoC<sub>4</sub> configuration in all seven investigation sites is a key finding, indicating that Co and C<sub>4</sub> had a greater impact than the other four coordinations that were only partially N doped ( $CoN_2C_{2-2}$ ,  $CoN_2C_{2-1}$ , and  $CoN_1C_3$ ) [113]. Additionally, the coordination of the central metal and dopant atoms had a crucial impact on the ORR properties, such as the two electron reactions and n, without experimental effects [129,130]. For instance, the two-electron process (2e<sup>-</sup>) was facilitated by the synthesized SAECs with high Mo loading (10 wt%), which contain S and O atoms and exhibit excellent hydroxide selectivity (95%) in alkaline solution, making them promising electrocatalysts for the ORR process (Figure 9a). As results, four-electron processes were facilitated by the particular coordination structure of MnN<sub>4</sub> groups, and it is clear that the specific active sites in the M-N-C structure play a crucial role in determining the reactions pathways and n.



**Figure 9.** (a) The calculated  $H_2O_2$  selectivity and electron transfer number (n) during the potential sweep in 0.10 m KOH, reprinted with permission from ref. [130] Copyright @ 2020, John Wiley & Sons, Inc., (b) synthesis process for Fe-NSDC, scheme adapted with permission from ref. [131] Copyright @ 2019, John Wiley & Sons, Inc., (c) LSV curves in  $O_2$ -saturated 0.1 m KOH, reprinted with permission from ref. [131] Copyright @ 2019, John Wiley & Sons, Inc., (d) ORR polarization curves in  $O_2$ -saturated 0.1MKOH, (e) ORR polarization curves before and after 5000 and 10,000 potential cycles for FeCl<sub>1</sub>N<sub>4</sub>/CNS in 0.1 M KOH, reprinted with permission from ref. [115] Copyright @ 2018, Royal Society of Chemistry, (f) ORR polarization curves of different catalyst, reprinted with permission from ref. [116] Copyright @ 2020, John Wiley & Sons, Inc., (g) power output, (h) 20 h cell durability test at 0.5 V of Z8-Fe-P and SA-3DNC in single cell PEMFC tests, (i) LSV plots of PAN-Fe-P, Z8-Fe-P, SA-3DNC, and 20% Pt/C before and after the 10,000-cycle durability test, reprinted with permission from ref. [132] Copyright @ 2019, American Chemical Society.

The atoms in the carbon structure that are not attached to M species (dopant atoms) and the N and S atoms that are linked to the central metal atoms (guest atoms) could impact the activity of M-N-C sites through the process of accepting and donating the electrons. Numerous heteroatom atoms (N, S, B, etc.) as dopant atoms were anchored within the carbon structure to alter the ORR activity [114,131,133]. The sulfur dopant was added to the Fe-N-C nanosheet in a unique way through the pyrolysis process (Figure 9b), and as a result, the Fe-N-C nanosheet exhibits superior ORR activity in the RDE method, which is thought to be due to the sulfur dopant inducing the active sites of Fe-N-C (Figure 9c) [131].

Some researchers looked at how guest atoms in the active sites affected ORR activity. By using a chlorine experimental setup, the influence of Fe-N-C active sites by chlorine atoms in alkaline media was investigated. This finding suggests that the short-range interaction of chlorine with an iron center might modify the electronic structure of active sites. As a result, as shown in Figure 9d,e [115], the ORR activity and cyclic stability of electrocatalysts in alkaline media were sufficiently improved. The active sites were stimulated, and the ORR activity was increased only when transition metal nanoparticles were combined with M-N-C. In particular, the anchored nanoparticles within M-N-C groups strongly motivate the interaction with carbon shell or sheet structures, which stimulates a synergistic interaction between M-N-C and nanoparticles that improved the ORR activity. For instance, it was suggested to investigate this effect by anchoring the cobalt within Co/N-CNSNs via DFT and a poisoning method [128]. The ORR process is aided by the conductive nature of the anchored metal nanoparticles, which are revealed by the higher  $\Delta G$  of M-N-C structures without metal content. The high electronegativity of carbon shells is caused by the Co component, which helps electrons flow on the outer layer of nitrogen-doped carbon materials. In a study conducted on M-N-C nanospheres decorated with  $Fe/Fe_3C$  in which researchers examined their electrocatalytic activity, the findings revealed the increase in the ORR activity. Such results demonstrated that the N-doped carbon and M-N-C might further modify the reactive groups in the carbon outer layer through the anchoring of iron atoms. Specifically, the connected iron atoms change the M-N-C active sites, especially on external carbon shells, which improves oxygen adsorption capacity and boosts ORR activity [134]. Further to that, it is well known that the influence of corrosion in acidic conditions leads to poor cyclic durability and inability. These cause make it difficult to identify the reactive groups in acidic media and create serious difficulties for metal nanoparticles. By creating the carbon-coated nanoparticles as depicted in Figure 9f, it is possible to increase the acidic stability of M-N-C sites. A novel strategy was successfully often used to develop a Fe-Co-N-C electrocatalyst (M/Fe-Co-SAs-N-C), wherein the carbon layer perfectly encompasses the metal atoms (Fe, Co) [116]. The synergism among nanoparticles (M) and Fe-N<sub>4</sub> sites modulates the oxygen adsorbs capacity and extended O-O bond, which could aid accelerating ORR in an acid medium, which was revealed by a DFT study. The O<sub>2</sub> dissociation barrier of M/Fe-Co-SAs-N-C electrocatalysts has been lowered during ORR, which may be advantageous for a four-electron reaction.

Exploring and understanding the electrocatalyst efficiency is crucial, especially for fuel cell technology and metal–air batteries because it entirely opens up the possibility of substituting with a commercial Pt electrocatalyst. The Fe-N-C groups are thought to be the most intensely investigated and highly active electrocatalysts utilized in fuel cell MEA. The isolated Fe-N<sub>4</sub> active site within a carbon network structure was created and employed as an efficient electrocatalyst to serve as the PEMFC cathode [132]. These demonstrate the excellent current density in PEMFC operations and the remarkable ORR activity of E<sub>onset</sub>, which was about 0.906 V through acid media (Figure 9g–i). However, the existence of Fe content induces the Fenton reaction, leading to the creation of free radical groups such as hydroperoxyl and hydroxyl. These radicals deteriorated the membranes' structure, and the poor stability was witnessed in PEMFC by Fe-N-C electrocatalysts. Mn-N-C and Co-N-C electrocatalysts are encouraging options for lowering the Fenton reactivity with satisfactory activity. The Mn-N-C electrocatalyst has effective active sites and demonstrates the better ORR activity of  $E_{1/2}$  (about 0.80 V in acid solution, which is significant compared

to the Fe-N-C group). The superior corrosion resistance of the Mn-N-C electrocatalysts obtained from the Mn metal created the effective carbon structure with strong active sites offer satisfactory efficiency and long-term durability (Figure 10a–j) [117].



**Figure 10.** (a) Atomically dispersed Mn-N<sub>4</sub> site catalyst synthesis, scheme adapted with permission from ref. [117] Copyright @ 2018, Nature, (b,c) HR-TEM images of a carbon particle in the catalyst, (d,e) STEM images of a carbon particle in the catalyst, (f–i) EELS elemental maps of C (f), N (g), O (h) and Mn (i) of the area in (e) and (j) aberration-corrected MAADF-STEM images, reprinted with permission from ref. [117] Copyright @ 2018, Nature.

# 6.3. Metal–Organic Framework (MOF) Carbon Electrocatalyst

It has been widely accepted that electrocatalysts made from metal–organic frameworks (MOFs) are more effective because they have large absorbent sites, uniform pore volume, controllable morphology, good electrochemical properties as well as a topographical scaffold. Brilliant competence is still needed for energy storage and transformation because it must satisfy specific requirements for industrialization. The various MOFs and their collection have been established as effective electrocatalysts for ORR reactions. Additionally, MOF-derived electrocatalysis offers beneficial methods for boosting ORR performance as well as provides the unique fabrication techniques that enable the large number of ORR active sites. The progress of MOF-derived electrocatalysts for ORR reactions has been recently analyzed, which covers the vital properties related to the mechanism of adsorption sites including the host sites, metal sites, dopant site and their synergistic interactions [135].

The porous polymer of MOFs is created by combining the metal clusters and organic precursors produced through the porous electrocatalysts. It is interesting to note that the MOF has a variety of qualities, including controllable porosity, adaptable morphology, and easy regulation of nanostructures, all of which are promising for electrocatalysis applications (Figure 11a) [136]. The most recent ORR development addresses the connection between structural property and interactions. Trying to combine the composition of inorganic heterogeneous and molecular homogeneous electrocatalysts, MOFs may contribute to achieving high performance and can be investigated as excellent electrocatalysts [137]. The hydrothermally produced MOFs had a well-crystalline nature, which act as effective bifunctional electrocatalysts. The resulting structure has a high surface area and a rich micro-porous composition, and it exhibits two electron reactions  $(2e^{-})$  at applied voltages between -0.30 and -0.50 V. It also reveals four electron reactions (4e<sup>-</sup>) at voltages between -0.50 and -0.95 V, respectively [138]. A metal electrocatalyst based on MOF has been synthesized that is made up of Pt free and exhibits the improved ORR efficiency in alkaline media. Compared to Pt-C, these electrocatalysts exhibit significant ORR efficiency at half-wave potentials (0.7 V) and onset potentials (0.85 V) as well as better stability and tolerance to methanol [139] (Figure 11b–d). By the pyrolysis of the zeolitic imidazolate framework (ZIF-9) with sulfur, the porous carbon structure was created. These notable mesoporous composites with porous carbon structures that enclose nanoparticles might enhance the ORR electrocatalytic performance and present the 4e<sup>-</sup> ORR pathway in alkaline media [140]. In recent years, the growth of electrocatalysts derived from MOF for energy storage as well as conversion technology has been evaluated and utilized in various applications including PEMFC, batteries, water splitting, supercapacitors, and ORRs. For extremely stable electrochemical technology application, the MOF-derived electrocatalyst with a unique structural design was carefully reviewed [141]. The electrocatalyst formed from the MOFs was found to have an effective porous structural morphology, which makes them a possible candidate for electrode applications with excellent performance. These materials provide a unique perspective to designing and creating novel electrocatalyst morphologies [142]. The fabrication and utilization of MOF-derived materials for energy storage and conversion, fuel storage, as well as hydrogen storage are covered in this study. It was explored how these materials might be used in energy applications. In comparison to commercial Pt-C, these MOFs have excellent methanol crossover barriers and long-lasting stability. This research laid the groundwork for fabricating new and relatively affordable electrocatalysts that function better in ORR [143]. There have been reports of carbon-derived materials with adjustable porous structures as well as a multidimensional core-shell structure. By subsequently surface polymerizing the identical monomers within carbon black XC-72 and silica nanoparticles, highly porous core-shell nanostructures were created. Carbon nanoparticles are like a substrate, and a spiro is like a twin monomer that might be employed to create a mesoporous carbon material core with a microporous shell structure. Moreover, applying the polymerizing effect of Spiro within silica nanoparticles led to a carbon material with hollow nanospheres featuring a double shell structure and a hierarchical arrangement [144]. A highly innovative electrocatalyst

for the ORR reaction has been obtained, which was created by pyrolyzing a Co-derived polymeric organic framework. This remarkable framework demonstrated the good ORR electrocatalytic activity in acidic solution through the 4e<sup>-</sup> route. Furthermore, this result is comparable to the available Pt-C without a methanol crossover. The study indicates the unique synthesis methods for creating new metal-free electrocatalysts with enhanced electrocatalytic activity for ORR in fuel cells as well as provides promising insight into ORR reactions that occurred at the M/N/C electrocatalyst. MOFs have vast surfaces because of their inner pores, but crystalline techniques could significantly identify their precise structures. However, the biggest problem with this electrocatalysis is really their lower chemical stability compared to MOFs because these reactions are carried out in electrolyte media, which typically required the highly acidic or basic condition [145]. As a result, research on MOF-based material has lagged far behind that of MOF-derived materials, including nanocomposites made of carbon, metal, and metal oxide [146–149]. Nevertheless, some MOFs exhibit improved stability in water as well as in extremely alkaline and acidic conditions [150,151]. Enhancing the interfacial adhesion between the metal and the ligand structure is crucial for designing efficient MOFs with improved electrochemical stability. Strong bond strength can be created only through the joining of metal ions with higher oxidizing states and carboxylate ligands in addition to joining soft metal ions of incredibly simple isolate ligands [152]. Dual-shelled nano-cages (DSNCs) contain an outer wall made of Co and N co-doped carbon (Co-NC) and an inner shell made of N-doped carbons, which were fabricated easily by a novel approach. The dual-shelled NC/Co-NC nano-cage is effectively constructed with Co-NC, performing more effectively and exhibiting excellent ORR properties, which are superior to those of Pt and RuO<sub>2</sub> ORR electrocatalysts in alkaline conditions. The improved performance of Co-NGC is attributed to the synergistic electron transport between the Co nanoparticles as well as the N-doped carbon, as revealed by first principles analyses (Figure 11f-h) [153].



**Figure 11.** (a) Synthesis of nano-MOFs by the coordination modulation method. TEM images of nanotubes, nanorods and nanowires of ZIF-8, scheme adapted with permission from ref. [135]

Copyright @ 2019, Royal Society of Chemistry, (b) RDE polarization curves on the different asprepared samples and Pt/C<sub>3</sub> in 0.1 M KOH at 1600 rpm, (c) K-L plots and electron transfer numbers at various potentials for Fe/Fe<sub>3</sub>C@NC electrode, (d) current–time chronoamperometric response of Pt/C and Fe/Fe<sub>3</sub>C@NC in 0.1 M KOH for 20,000 s in 0.1 M KOH solution at 1600 rpm, reprinted with permission from ref. [139] Copyright @ 2018, American Chemical Society, (e) synthesis of porous carbon materials with hierarchically structured porosity, scheme adapted with permission from ref. [144] Copyright @ 2017, Elsevier B.V, (f) ORR polarization curves of NC, Co-NGC, NC@Co-NGC DSNC, and Pt/C catalysts at 1600 rpm in 0.1 m KOH solution at 10 mV s<sup>-1</sup>, (g) ORR and volcano plots of overpotential ( $\eta$ ) versus adsorption-free energy of OOH\* and the difference between the adsorption-free energy OOH\* and O\*, respectively, (h) ORR pathways on Co-NGC in alkaline medium, reprinted with permission from ref. [153] Copyright @ 2017, John Wiley & Sons, Inc.

The fabrication of electrocatalysts (Fe/N<sub>x</sub>/C and N/Fe/Fe<sub>3</sub>C–C–RGO) to activate the ORR process by using the Co-based MOF, transition metal-based MOF, and Fe-based MOF were investigated [154–156]. Recently, one researcher investigated the shaft-like Fe-based MOFs with controllable dimensions and shapes, which were effectively made from components of Fe<sub>3</sub>O (H<sub>2</sub>N-BDC)<sub>3</sub> as well as 2-aminoterephtalic acid. The porous structure of MIL-B-NH<sub>3</sub> is unique in that it contains effectively distributed Fe and N atoms. The produced Fe-N<sub>x</sub>-C electrocatalyst showed enhanced ORR performance in comparison to Pt-C [157]. The electrocatalyst of the Co-Fe structure encased in N-graphene exhibits improved electrochemical characteristics, which was created through carbonizing a Prussian blue and cobaltocene/cobalt nitrate [158] (Figure 12a,b).



**Figure 12.** (a) Schematic representation for the synthesis of  $Co_xFe_{1-x}$  nano-alloy encapsulated in N-doped graphene layers, (b) HRTEM images of  $Co_xFe_{1-x}/N$ -G (X3), reprinted with permission

from ref. [158] Copyright @ 2018, American Chemical Society, (c) TEM images of Ni-NSPC-6 under different magnifications, (d) formation of Ni-NSPC-6 electrocatalyst, scheme adapted with permission from ref. [159] Copyright @ 2019, Elsevier B.V, (e) calculated electron transfer number (n) and peroxide percentage (HO<sub>2</sub><sup>--</sup>), (f,g) ORR polarization curves of the Ni-NSPC, Ni-NSPC-1, Ni-NSPC-6, Ni-NSPC-12 and commercial Pt/C for ORR on RDE in O<sub>2</sub>-saturated 0.1 M KOH aqueous solution at a scan rate of 10 mV s<sup>-1</sup> under 1600 rpm and different scan rates, reprinted with permission from ref. [159] Copyright @ 2019, Elsevier B.V, (h) SEM images of Ni<sub>2</sub>P/CoN–PCP, (i) ORR LSV curves for the studied catalysts, (j) ORR LSV curves before and after 2000 cycles, inset: CVs of Ni<sub>2</sub>P/CoN–PCP in O<sub>2</sub>-purged 0.1 M KOH with and without 1.0 M CH<sub>3</sub>OH, reprinted with permission from ref. [160] Copyright @ 2018, Royal Society of Chemistry.

Because of their outstanding electron permeability, porous structure, and variety of application areas, carbon materials made from MOFs had recently attracted a lot of interest from the scientific community. Researchers have attempted to modify the morphological and structure characteristics of the carbon materials obtained from MOFs in order to improve their own physical and chemical characteristics. A discussion of various kinds of carbon materials obtained from MOFs with an emphasis on energy applications has already taken place [161].

An efficient electrocatalyst for ORR has been satisfactorily developed and produced, which consisted of a one-dimensional (1D) carbon rod made of S and N gathered with Nibased MOFs [159] (Figure 12c–g). The fabrications of Ni<sub>2</sub>P nanoparticles anchored carbon polyhedrons (Ni<sub>2</sub>P-CoN/PCP) were obtained from MOFs. As a result, the Ni/P-CoN-PCP electrocatalyst exhibits exceptional functional electrocatalytic activity and promising cost-effective ORR electrocatalysts for fuel cells. This was attributed to a synergy between Ni<sub>2</sub>P particles and the strong active centers of Co-N<sub>x</sub> in Co-N-PCP electrocatalysts, which contain high electrical conductivity with a more disordered structure [160] (Figure 12h–j). In recent times, it has been noted that N-doped graphitic carbon materials are effective ORR electrocatalysts when operated in alkaline solution. Better ORR durability and efficacy have been found in carbon-based materials by utilizing carbon nanotubes and N-doped carbon nanotubes [162].

According to earlier research, the incorporation of extremely lightly coated carbon MOFs onto GO nanosheets could even produce a layer-by-layer structure with a huge surface area and exceptional electrical properties [162–164]. The ZIF/8/GO material was pyrolyzed at 800 °C in attempt to develop an emerging material (Figure 13a–c). Later, 2D carbon-graphene-carbon materials were developed, which significantly shows the better ORR results. A thin-layered N-doped carbon nanostructure maintains the necessary active sites and sustained the suitable stability between subsequent electrical conductivity, which is required for ORR. Therefore, the ORR output of nanocarbon, graphene, and nanocarbon is outstanding. An increased onset potential of 0.92 V as well as a high limiting current density of 5.2 mAcm<sup>2</sup> at 0.6 V was obtained in ORRs [160]. Many kinds of MOF precursors, including Zr-MOF, Cu-MOF, Cd-MOF, and polyoxometalate-MOFs, were extensively studied to generate unique metal-carbon electrocatalysts for fuel cells [165-169]. MoO<sub>3</sub> is a rare transition metal oxide with exceptional chemical stability and electrical conductivity. It will attract more interest in this field of study. The main reason for promoting the  $MoO_2$  as an ORR electrocatalyst in fuel cells was due to the efficient catalytically active sites, which generally provide a the molybdenum edge and the oxygen edge in the metal oxides [170]. Researchers also studied the MoO<sub>2</sub>-GO materials obtained from the polyoxometalate precursors [171]. The ORR reaction in the fuel cell is more favorable only when the carbon materials are doped with cobalt or iron and then doped with nitrogen. Pt-C based electrocatalysts are replaced by these novel doped electrocatalysts. Due to the synergistic interplay among two active metal sites, it is possible to even further increase the ORR activity as compared to single-metal doping (Figure 13d,e) [172]. Electrocatalysts based on MOFs have also made major advancements in the past few years. When compared with traditional electrocatalysts, MOFs usually display less electric conductivity. In order to take full advantage of MOFs, uncover the reaction mechanisms, improve the materials' ORR, and understand the depth of their electrochemical behavior, these electrocatalysts could be examined more. The development of MOFs-based electrocatalysts for ORR is still in its early stages, and many difficulties still need to be resolved before the fabrication of proficient MOFs-based electrocatalysts for ORRs will become a reality. Some of the studied MOFs are only available for definite applications. For instance, highly conductive and much more stable MOFs are preferred as pure electrocatalysts, and MOFs-based frameworks for metal-free materials seem to be effective electrocatalysts. The advancement from basic research to industrial growth and commercial application was severely constrained by the difficult preparation methods for some MOFs as well as the limited number of manufacturing methods. The synergistic effects stimulated the improved performance of electrocatalytic activity in the MOF composites. Based on the obtained reports, there are some pure MOFs that can be utilized as electrocatalysts. During the ORR process, the surface of the MOFs experiences an irreversible phase change. Therefore, it is necessary to identify these actual active sites using more inventive methods and the accurate controlling of active sites, particularly in MOF materials. Further theoretical research and experimental investigation are required to address the lack of knowledge regarding the process for converting MOFs into their different products with related mechanism.



**Figure 13.** (a) Different N-based functional groups of GNPCSs, (b,c) the contents and ORR polarization curves of N1, N2, and N3 in NG, NPC, GNPCSs-650, GNPCSs-800, and GNPCSs-950 at 1600 rpm, reprinted with permission from ref. [173] Copyright @ 2014, John Wiley & Sons, Inc., (d) synthesis of CoFeNi/NC, scheme adapted with permission from ref. [172] @ 2020, Elsevier B.V, (e) linear sweep voltammetry curves of the as-synthesized samples, reprinted with permission from ref. [172] Copyright @ 2020, Elsevier B.V, (f,g) the RDE polarization curves at 1600 rpm for Fe-N/GNs, FeNC/RGO, N/GNs, and Pt/C catalysts in 0.1 m KOH and 0.1 m HClO<sub>4</sub>, reprinted with permission from ref. [174] Copyright @ 2020, Elsevier B.V, (h) synthesis process of the Fe-N/GNs, scheme adapted with permission from ref. [174] Copyright @ 2020, Elsevier B.V.

Derivatives of zeolitic–imidazolate–framework-8 (ZIF-8) have been demonstrated as ideal precursors for making metal-based SAECs for ORRs. Scientists have just described a new ZIF-8 thermal treatment method to produce graphene nanosheets co-doped with Fe and N (Fe-N-GNs). This shows the half-wave potential of 0.903 V in a basic condition and 0.837 V in an acidic condition, in which the Fe-N-GNs SACs exhibit exceptional ORR activity similar to traditional Pt-C electrocatalysts (Figure 13f–h) [174]. Researchers have developed

a silica-based MOF template process for the fabrication of an elongated nanostructure decorated with single-atom Fe active sites for ORRs, which shows the outstanding efficiency in both basic and acidic solution (Figure 14a–g). These extraordinary electrocatalytic results are attributed to the presence of edge-rich nanostructures containing the three-phase boundary; they facilitate the reactants to connect the Fe-active sites of neighboring single atoms. These scenarios demonstrate the feasibility of the preparation method [175]. The various types of electrocatalyst were studied for ORRs in proton exchange membrane fuel cells (PEMFCs) and energy conversion applications (Table 3).



**Figure 14.** (a) Synthesis process of Fe/OES, schemes adapted with permission from ref. [175] Copyright 2020, John Wiley & Sons, Inc., (b) ABF-STEM, (c,d) HAADF-STEM images of Fe/OES showing the atomically dispersed Fe atoms, which are highlighted by yellow circles, (e,f) LSV curves of BCS, OES, Fe/BCS, Fe/OES and commercial Pt/C at 5 mV s<sup>-1</sup> with a rotating speed of 1600 rpm in 0.1 M KOH and 0.5 M H<sub>2</sub>SO<sub>4</sub>, (g) LSV curves of Fe/OES at different rotation rates, reprinted with permission from ref. [175] Copyright @ 2020, John Wiley & Sons, Inc.

Metal Precurs Co-Fe Fe Fe Fe Fe Co Fe

Co

Co-N-C @F127

or	Catalysts Name	Metal Content	BET Surface (m <sup>2</sup> g <sup>-1</sup> )	Electrolyte	E <sub>onset</sub> (V)	E <sub>1/2</sub> (V)	Tafel Slope (mV dec <sup>-1</sup> )	Electron Transfer Number	Reference
	MCF/NPCCNT-40 hybrid catalyst	-	74	1.0 M KOH	-	-	45.9	-	[176]
	MOF(Fe)	-	$1600\pm300$	1.0 M KOH	-	-	137	-	[138]
	Fe/Fe <sub>3</sub> C@NGL-NCNT	-	-	1.0 M KOH	-	-	-	3.6	[155]
	Fe/Fe <sub>3</sub> C@NC	-	107	1.0 M KOH	0.85	0.7	-	3.88-4.05	[139]
	N-doped Fe/Fe <sub>3</sub> C@C/RGO	-	34	1.0 M KOH	0.95	-	72	3.08-3.52	[177]
	PC-CoS <sub>1 097</sub> NCs	-	172	1.0 M KOH	-	-	-	3.8-4.0	[140]
	CNPs	-	326	1.0 M KOH	1.03	0.92	-	3.97	[178]
		1.38 wt.% Co							
		(EELS)							

0.5 M H<sub>2</sub>SO<sub>4</sub>

0.84

0.93

Table 3. Various parameters of MOF-based ORR electrocatalysts.

825

#### 7. Conclusions and Future Outlook

4.4 wt.% Co

(XPS) 6.2 wt.% Co (ICP-AES)

Technologically and scientifically, the development of high-performance Pt-free electrocatalysts is required to speed up the vast exploitation of feasible renewable power. It has been a main concern for many years to find a strong replacement for Pt electrocatalysts in fuel cells. Ingenious plans and designs have been developed to enhance ORR activity. The new carbon-based nanomaterials as ORR electrode materials in fuel cells have been revealed as excellent electrocatalysts. Electrocatalysts can be formed from carbon doping, metal-based carbon, and MOF nanostructures. Non-noble metal-based SAECs are interesting due their improved active sites, but more precise methods are needed to produce high-quality electrocatalysts. Currently, it is necessary to obtain ORR electrocatalysts with increased performance in an acidic medium compared to an alkaline medium. Thereby, the higher surface area and augmented active sites of materials are desirable, since they might lead to an improvement in the electrocatalyst's electrochemical properties. Despite the numerous difficulties throughout this area, the growing interest in electrochemical reduction by non-noble metal electrocatalysts indicates a positive future development. Additional investigations into the reduction mechanism as well as fabrications of effective electrodes are a crucial step to take in the future. The non-noble metal electrocatalysts may therefore find extensive exploitation in fuel cell systems and metal-air batteries for effective ORRs. One of the most important objectives is the improvement of the electrocatalyst for PEMFCs. The essential purpose of electrocatalysts is to maintain the stable continuous operation in fuel cells in order to make them viable for industrial fabrication. Nevertheless, safeguarding the electrocatalyst is indeed very challenging. The development of high-performance MOF-based SAECs will undoubtedly be delayed by the complex and time-consuming fabrication techniques. Therefore, straightforward, affordable design and manufacturing methods are required to achieve the electrocatalyst's massive scale and also satisfy the electrochemical test conditions. These will ultimately lead toward their practical applications in renewable technology [179,180]. It is necessary to overcome the current technical obstacles to fabricate useful nanostructures, which will require practical utility [181]. The theoretical calculation and simulation models reveal the hidden fact of ORR reaction mechanisms and inherent active sites, which will be evaluated further in on-going research. The experiment as well as measurement techniques have a significant impact on the creation of better ORR electrocatalysts [182,183]. In order to develop as well as prepare the ORR electrocatalysts for PEMFCs, detailed and consistent theoretical research must be implemented on nanomaterials.

# Future Efficient Carbon-Based Electrocatalyst

**Heteroatom-doped carbon electrocatalysts** contain the advantage of stability functioning in acidic environments due to the controlling of metal leaks and metal contamination. Using a co-doping model can generate active sites and quickly transfer charges. Although many metal-free electrocatalysts have been created over the years using a variety

[123]

of methods, there is still much to learn about the widespread use of ORR electrocatalysts in practical applications. Model electrocatalysts may provide additional evidence to establish effective materials. Developing carbon materials doped with nitrogen heteroatoms, which have numerous carbon defects, needs to be addressed. The model electrocatalysts with precise multi-doping produce extremely active materials for ORRs in an acidic medium.

**Single-atom carbon electrocatalysts** are broadly investigated and studied materials. A systematic assessment is highly required for ORRs in an acidic and basic environment. The synthesis method for diverse single-atom electrocatalysts is very difficult, so it is necessary to develop a standard fabrication method with improved techniques to prepare the wide range of SAECs for industrial utilization. Because of their superior characteristics and inexpensive nature, the advancement of SAECs through the non-noble metals is an exciting initiative, so further study is required for synthesis of non-precious SAECs, which provides an incredible direction for future electrocatalysis. To explore the non-precious SAECs as well as their active site mechanisms, advanced methodology and theoretical calculation are required. The unique structure of SAECs is investigated through a theoretical method, which is crucial for designing the new functional electrocatalysts. The SAECs with enhanced activity, excellent stability, and inexpensive natures have inspired extensive research. Investigating SAECs with improved characteristics is crucial for electrocatalysis especially related to energy storage applications

**Metal–organic framework (MOF)-based carbon electrocatalysts** could really provide stability to electrocatalysts. The enhanced electrocatalytic performance of MOF-based nanomaterials is highly required, particularly in acid medium. Electrocatalysts prepared from the MOFs are highly effective, and their stability is essential for energy storage and conversion application. In the future, it is important to design new SAECs for ORRs. In order to commercialize the MOF electrocatalysts, these novel materials should eliminate the above difficulty and also satisfy the following rules: (a) an inexpensive raw material and preparation technique is vital; (b) remarkable ORR activity, stability and also an upscale synthesis method for the electrocatalyst are highly essential. Consequently, significant effort will be needed in the upcoming studies.

The intrinsic ORR activity and reaction mechanisms of electrocatalysts can be effectively explored and tested using the half-cell methods. These primary factors are greatly influencing the PEMFC's efficiency, which is not studied in detail by RDE measurements nor in thin films. For the advancement of fuel cell technology with improved performance, the design and production process of electrode electrocatalysts is of utmost importance. Complex designs can increase the efficiency of active sites by encouraging the mass transfer property. Additionally, improving the reaction mechanisms can lead to enhancing the electrocatalyst activity and strengthening the performance of PEMFC technology. Overall, the development of Pt-free electrocatalysts by substituting the atomically distributed metal electrocatalysts within carbon supports is highly significant for fuel cell research and technology.

**Author Contributions:** Conceptualization, K.P. and M.R.P.; Methodology, L.P. and M.R.P.; Validation, K.P., C.-Y.C. and Y.-S.C.; Resources, L.P. and M.R.P.; Data curation, L.P. and M.R.P.; Writing—original draft preparation, M.R.P.; Writing—review and editing, K.P. and M.R.P.; Visualization, M.R.P.; Supervision, K.P., C.-Y.C. and Y.-S.C.; Project administration, K.P.; Funding acquisition, K.P.; All authors have read and agreed to the published version of the manuscript.

**Funding:** Energy Conservation and Promotion Fund Office: nmb.65-03-0002; National Research Council of Thailand: <code>nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: <code>nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: <code>nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: <code>nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: <code>nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: <code>nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: <code>nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: <code>nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: <code>nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand: nmb.05-03-0002; National Research Council of Thailand; <code>nmb.05-03-0002; National Research Council of Thailand; nmb.05-03-000; National Research Council of Thailand; nmb.05-03-000; National Research Council of Thailand; nmb.05-03-00; National Research Council of Thailand; nmb.05-03-00; National Research Council of Thailand; nmb.</code></code></code></code></code></code></code></code></code></code>

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data derived from public domain resources.

**Acknowledgments:** Thailand's Department of Energy provided financial assistance for this study via the Energy Conservation and Promotion Fund Office (ENCON). This project was also supported financially by the National Research Council of Thailand (NRCT) and the Electricity Generating Authority of Thailand (EGAT). Furthermore, the authors would like to thank Chiang Mai University for providing Post-doctoral Scholarships (PDF), as well as the facilities and financial support.

Conflicts of Interest: The authors declare no competing financial interest.

#### References

- Dou, S.; Tao, L.; Huo, J.; Wang, S.; Dai, L. Etched and doped Co<sub>9</sub>S<sub>8</sub>/graphene hybrid for oxygen electrocatalysis. *Energy Environ. Sci.* 2016, *9*, 1320–1326. [CrossRef]
- 2. Staffell, I.; Scamman, D.; Velazquez Abad, A.; Balcombe, P.; Dodds, P.E.; Ekins, P.; Shah, N.; Ward, K.R. The role of hydrogen and fuel cells in the global energy system. *Energy Environ. Sci.* **2019**, *12*, 463–491. [CrossRef]
- Wei, Q.; Xiong, F.; Tan, S.; Huang, L.; Lan, E.H.; Dunn, B.; Mai, L. Porous One-Dimensional Nanomaterials: Design, Fabrication and Applications in Electrochemical Energy Storage. *Adv. Mater.* 2017, 29, 1602300. [CrossRef] [PubMed]
- 4. Shi, H.; Shen, Y.; He, F.; Li, Y.; Liu, A.; Liu, S.; Zhang, Y. Recent advances of doped carbon as non-precious catalysts for oxygen reduction reaction. *J. Mater. Chem. A* 2014, 2, 15704–15716. [CrossRef]
- Zhang, Z.; Gao, X.; Dou, M.; Ji, J.; Wang, F. Biomass Derived N-Doped Porous Carbon Supported Single Fe Atoms as Superior Electrocatalysts for Oxygen Reduction. *Small* 2017, 13, 1604290. [CrossRef] [PubMed]
- Wu, R.; Chen, S.; Zhang, Y.; Wang, Y.; Nie, Y.; Ding, W.; Qi, X.; Wei, Z. Controlled synthesis of hollow micro/meso-pore nitrogen-doped carbon with tunable wall thickness and specific surface area as efficient electrocatalysts for oxygen reduction reaction. J. Mater. Chem. A 2016, 4, 2433–2437. [CrossRef]
- Wan, K.; Tan, A.-D.; Yu, Z.-P.; Liang, Z.-X.; Piao, J.-H.; Tsiakaras, P. 2D nitrogen-doped hierarchically porous carbon: Key role of low dimensional structure in favoring electrocatalysis and mass transfer for oxygen reduction reaction. *Appl. Catal. B Environ.* 2017, 209, 447–454. [CrossRef]
- Yu, H.; Fisher, A.; Cheng, D.; Cao, D. Cu,N-codoped Hierarchical Porous Carbons as Electrocatalysts for Oxygen Reduction Reaction. ACS Appl. Mater. Interfaces 2016, 8, 21431–21439. [CrossRef] [PubMed]
- Chen, Y.; Ji, S.; Wang, Y.; Dong, J.; Chen, W.; Li, Z.; Shen, R.; Zheng, L.; Zhuang, Z.; Wang, D.; et al. Isolated Single Iron Atoms Anchored on N-Doped Porous Carbon as an Efficient Electrocatalyst for the Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* 2017, 56, 6937–6941. [CrossRef]
- 10. Xia, W.; Zou, R.; An, L.; Xia, D.; Guo, S. A metal–organic framework route to in situ encapsulation of Co@Co<sub>3</sub>O<sub>4</sub>@C core@bishell nanoparticles into a highly ordered porous carbon matrix for oxygen reduction. *Energy Environ. Sci.* **2015**, *8*, 568–576. [CrossRef]
- Shi, P.-C.; Yi, J.-D.; Liu, T.-T.; Li, L.; Zhang, L.-J.; Sun, C.-F.; Wang, Y.-B.; Huang, Y.-B.; Cao, R. Hierarchically porous nitrogen-doped carbon nanotubes derived from core–shell ZnO@zeolitic imidazolate framework nanorods for highly efficient oxygen reduction reactions. J. Mater. Chem. A 2017, 5, 12322–12329. [CrossRef]
- 12. Dou, S.; Shen, A.; Tao, L.; Wang, S. Molecular doping of graphene as metal-free electrocatalyst for oxygen reduction reaction. *Chem. Commun.* **2014**, *50*, 10672–10675. [CrossRef]
- 13. Song, H.; Li, H.; Wang, H.; Key, J.; Ji, S.; Mao, X.; Wang, R. Chicken bone-derived N-doped porous carbon materials as an oxygen reduction electrocatalyst. *Electrochim. Acta* **2014**, 147, 520–526. [CrossRef]
- 14. Ma, Z.; Dou, S.; Shen, A.; Tao, L.; Dai, L.; Wang, S. Sulfur-Doped Graphene Derived from Cycled Lithium-Sulfur Batteries as a Metal-Free Electrocatalyst for the Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* **2015**, *54*, 1888–1892. [CrossRef] [PubMed]
- Liu, J.; Shen, A.; Wei, X.; Zhou, K.; Chen, W.; Chen, F.; Xu, J.; Wang, S.; Dai, L. Ultrathin Wrinkled N-Doped Carbon Nanotubes for Noble-Metal Loading and Oxygen Reduction Reaction. ACS Appl. Mater. Interfaces 2015, 7, 20507–20512. [CrossRef] [PubMed]
- 16. Wang, S.; Zhang, L.; Xia, Z.; Roy, A.; Chang, D.W.; Baek, J.; Dai, L. BCN Graphene as Efficient Metal-Free Electrocatalyst for the Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* **2012**, *51*, 4209–4212. [CrossRef] [PubMed]
- Wang, X.; Wang, J.; Wang, D.; Dou, S.; Ma, Z.; Wu, J.; Tao, L.; Shen, A.; Ouyang, C.; Liu, Q.; et al. One-pot synthesis of nitrogen and sulfur co-doped graphene as efficient metal-free electrocatalysts for the oxygen reduction reaction. *Chem. Commun.* 2014, 50, 4839–4842. [CrossRef] [PubMed]
- 18. Banhart, F.; Kotakoski, J.; Krasheninnikov, A.V. Structural Defects in Graphene. ACS Nano 2011, 5, 26–41. [CrossRef] [PubMed]
- 19. Yin, P.; Yao, T.; Wu, Y.; Zheng, L.; Lin, Y.; Liu, W.; Ju, H.; Zhu, J.; Hong, X.; Deng, Z.; et al. Single Cobalt Atoms with Precise N-Coordination as Superior Oxygen Reduction Reaction Catalysts. *Angew. Chem. Int. Ed.* **2016**, *55*, 10800–10805. [CrossRef]
- Bayatsarmadi, B.; Zheng, Y.; Vasileff, A.; Qiao, S. Recent Advances in Atomic Metal Doping of Carbon-based Nanomaterials for Energy Conversion. Small 2017, 13, 1700191. [CrossRef]
- Zhang, H.; Osgood, H.; Xie, X.; Shao, Y.; Wu, G. Engineering nanostructures of PGM-free oxygen-reduction catalysts using metal-organic frameworks. *Nano Energy* 2017, *31*, 331–350. [CrossRef]
- Barkholtz, H.M.; Liu, D.-J. Advancements in rationally designed PGM-free fuel cell catalysts derived from metal–organic frameworks. *Mater. Horiz.* 2017, 4, 20–37. [CrossRef]

- Zhang, H.; Li, J.; Tan, Q.; Lu, L.; Wang, Z.; Wu, G. Metal–Organic Frameworks and Their Derived Materials as Electrocatalysts and Photocatalysts for CO<sub>2</sub> Reduction: Progress, Challenges, and Perspectives. *Chem.—A Eur. J.* 2018, 24, 18137–18157. [CrossRef] [PubMed]
- 24. Seh, Z.W.; Kibsgaard, J.; Dickens, C.F.; Chorkendorff, I.; Nørskov, J.K.; Jaramillo, T.F. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **2017**, *355*, eaad4998. [CrossRef]
- Bard, A.J.; Faulkner, L.R. Electrochemical Methods: Fundamentals and Applications, 2nd ed.; Wiley: New York, NY, USA; Weinheim, Germany, 2001.
- 26. Wang, J.; Kong, H.; Zhang, J.; Hao, Y.; Shao, Z.; Ciucci, F. Carbon-based electrocatalysts for sustainable energy applications. *Prog. Mater. Sci.* **2021**, *116*, 100717. [CrossRef]
- Griffith, J.S.; Roughton, F.J.W. On the magnetic properties of some haemoglobin complexes, Proceedings of the Royal Society of London. Ser. A Math. Phys. Sci. 1997, 235, 23–36. [CrossRef]
- 28. Weiss, J.J. Nature of the Iron–Oxygen Bond in Oxyhæmoglobin. *Nature* **1964**, 203, 183. [CrossRef]
- 29. Yeager, E. Recent Advances in the Science of Electrocatalysis. J. Electrochem. Soc. 1981, 128, 160C. [CrossRef]
- Adžić, R.R.; Wang, J.X. Configuration and Site of O<sub>2</sub> Adsorption on the Pt(111) Electrode Surface. J. Phys. Chem. B 1998, 102, 8988–8993. [CrossRef]
- Du, C.; Sun, Y.; Shen, T.; Yin, G.; Zhang, J. Applications of RDE and RRDE Methods in Oxygen Reduction Reaction. In *Rotating Electrode Methods and Oxygen Reduction Electrocatalysts*; Elsevier: Amsterdam, The Netherlands, 2014; pp. 231–277. [CrossRef]
- 32. Biddinger, E.J.; von Deak, D.; Singh, D.; Marsh, H.; Tan, B.; Knapke, D.S.; Ozkan, U.S. Examination of Catalyst Loading Effects on the Selectivity of CNx and Pt/VC ORR Catalysts Using RRDE. J. Electrochem. Soc. **2011**, 158, B402. [CrossRef]
- Nagai, T.; Jahn, C.; Jia, H. Improved Accelerated Stress Tests for ORR Catalysts Using a Rotating Disk Electrode. J. Electrochem. Soc. 2019, 166, F3111–F3115. [CrossRef]
- Kocha, S.S.; Shinozaki, K.; Zack, J.W.; Myers, D.J.; Kariuki, N.N.; Nowicki, T.; Stamenkovic, V.; Kang, Y.; Li, D.; Papageorgopoulos, D. Best Practices and Testing Protocols for Benchmarking ORR Activities of Fuel Cell Electrocatalysts Using Rotating Disk Electrode. *Electrocatalysis* 2017, *8*, 366–374. [CrossRef]
- Mills, A.; O'Rourke, C. Wireless rotating disk electrode (wRDE) for assessing heterogeneous water oxidation catalysts (WOCs). Chem. Commun. 2016, 52, 7727–7730. [CrossRef] [PubMed]
- Martens, S.; Asen, L.; Ercolano, G.; Dionigi, F.; Zalitis, C.; Hawkins, A.; Bonastre, A.M.; Seidl, L.; Knoll, A.C.; Sharman, J.; et al. A comparison of rotating disc electrode, floating electrode technique and membrane electrode assembly measurements for catalyst testing. J. Power Sources 2018, 392, 274–284. [CrossRef]
- Bernt, M.; Hartig-Weiß, A.; Tovini, M.F.; El-Sayed, H.A.; Schramm, C.; Schröter, J.; Gebauer, C.; Gasteiger, H.A. Current Challenges in Catalyst Development for PEM Water Electrolyzers. *Chem. Ing. Technol.* 2020, *92*, 31–39. [CrossRef]
- Zhong, G.; Xu, S.; Liu, L.; Zheng, C.Z.; Dou, J.; Wang, F.; Fu, X.; Liao, W.; Wang, H. Effect of Experimental Operations on the Limiting Current Density of Oxygen Reduction Reaction Evaluated by Rotating-Disk Electrode. *ChemElectroChem* 2020, 7, 1107–1114. [CrossRef]
- 39. Ratera, I.; Veciana, J. Playing with organic radicals as building blocks for functional molecular materials, Chem. *Soc. Rev.* **2012**, 41, 303–349. [CrossRef]
- Kang, S.-F.; Chang, H.-M. Coagulation of textile secondary effluents with fenton's reagent. Water Sci. Technol. 1997, 36, 215–222. [CrossRef]
- Lefèvre, M.; Proietti, E.; Jaouen, F.; Dodelet, J.-P. Iron-Based Catalysts with Improved Oxygen Reduction Activity in Polymer Electrolyte Fuel Cells. *Science* 2009, 324, 71–74. [CrossRef]
- 42. Neyerlin, K.C.; Gu, W.; Jorne, J.; Gasteiger, H.A. Determination of Catalyst Unique Parameters for the Oxygen Reduction Reaction in a PEMFC. *J. Electrochem. Soc.* **2006**, *153*, A1955. [CrossRef]
- Jaouen, F.; Goellner, V.; Lefèvre, M.; Herranz, J.; Proietti, E.; Dodelet, J. Oxygen reduction activities compared in rotating-disk electrode and proton exchange membrane fuel cells for highly active FeNC catalysts. *Electrochim. Acta* 2013, *87*, 619–628. [CrossRef]
- 44. Gasteiger, H.A.; Kocha, S.S.; Sompalli, B.; Wagner, F.T. Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs. *Appl. Catal. B Environ.* **2005**, *56*, 9–35. [CrossRef]
- Jung, E.; Shin, H.; Antink, W.H.; Sung, Y.-E.; Hyeon, T. Recent Advances in Electrochemical Oxygen Reduction to H<sub>2</sub>O<sub>2</sub>: Catalyst and Cell Design. ACS Energy Lett. 2020, 5, 1881–1892. [CrossRef]
- 46. Li, X.; Yang, X.; Xue, H.; Pang, H.; Xu, Q. Metal–organic frameworks as a platform for clean energy applications. *EnergyChem* **2020**, *2*, 100027. [CrossRef]
- 47. Liu, X.; Dai, L. Carbon-based metal-free catalysts. Nat. Rev. Mater. 2016, 1, 16064. [CrossRef]
- Guo, D.; Shibuya, R.; Akiba, C.; Saji, S.; Kondo, T.; Nakamura, J. Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science* 2016, 351, 361–365. [CrossRef] [PubMed]
- Ortiz-Medina, J.; Wang, Z.; Cruz-Silva, R.; Morelos-Gomez, A.; Wang, F.; Yao, X.; Terrones, M.; Endo, M. Defect Engineering and Surface Functionalization of Nanocarbons for Metal-Free Catalysis. *Adv. Mater.* 2019, *31*, e1805717. [CrossRef]
- 50. Tang, C.; Wang, H.; Chen, X.; Li, B.; Hou, T.; Zhang, B.; Zhang, Q.; Titirici, M.; Wei, F. Topological Defects in Metal-Free Nanocarbon for Oxygen Electrocatalysis. *Adv. Mater.* **2016**, *28*, 6845–6851. [CrossRef]

- 51. Tang, C.; Zhang, Q. Nanocarbon for Oxygen Reduction Electrocatalysis: Dopants, Edges, and Defects. *Adv. Mater.* 2017, 29, 1604103. [CrossRef]
- Jia, Y.; Zhang, L.; Zhuang, L.; Liu, H.; Yan, X.; Wang, X.; Liu, J.; Wang, J.; Zheng, Y.; Xiao, Z.; et al. Identification of active sites for acidic oxygen reduction on carbon catalysts with and without nitrogen doping. *Nat. Catal.* 2019, 2, 688–695. [CrossRef]
- Jia, Y.; Zhang, L.; Du, A.; Gao, G.; Chen, J.; Yan, X.; Brown, C.L.; Yao, X. Defect Graphene as a Trifunctional Catalyst for Electrochemical Reactions. *Adv. Mater.* 2016, 28, 9532–9538. [CrossRef]
- 54. Wang, Q.; Huang, X.; Zhao, Z.L.; Wang, M.; Xiang, B.; Li, J.; Feng, Z.; Xu, H.; Gu, M. Ultrahigh-Loading of Ir Single Atoms on NiO Matrix to Dramatically Enhance Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **2020**, *142*, 7425–7433. [CrossRef] [PubMed]
- Zhang, X.; Zhang, S.; Yang, Y.; Wang, L.; Mu, Z.; Zhu, H.; Zhu, X.; Xing, H.; Xia, H.; Huang, B.; et al. A General Method for Transition Metal Single Atoms Anchored on Honeycomb-Like Nitrogen-Doped Carbon Nanosheets. *Adv. Mater.* 2020, 32, e1906905. [CrossRef] [PubMed]
- Chen, Y.; Ji, S.; Chen, C.; Peng, Q.; Wang, D.; Li, Y. Single-Atom Catalysts: Synthetic Strategies and Electrochemical Applications. *Joule* 2018, 2, 1242–1264. [CrossRef]
- 57. Tian, X.; Lu, X.F.; Xia, B.Y.; Lou, X.W. Advanced Electrocatalysts for the Oxygen Reduction Reaction in Energy Conversion Technologies. *Joule* 2020, *4*, 45–68. [CrossRef]
- Peng, H.; Liu, F.; Liu, X.; Liao, S.; You, C.; Tian, X.; Nan, H.; Luo, F.; Song, H.; Fu, Z.; et al. Effect of Transition Metals on the Structure and Performance of the Doped Carbon Catalysts Derived From Polyaniline and Melamine for ORR Application. ACS Catal. 2014, 4, 3797–3805. [CrossRef]
- Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Science* 2009, 323, 760–764. [CrossRef] [PubMed]
- 60. Zhang, L.; Lin, C.; Zhang, D.; Gong, L.; Zhu, Y.; Zhao, Z.; Xu, Q.; Li, H.; Xia, Z. Guiding Principles for Designing Highly Efficient Metal-Free Carbon Catalysts. *Adv. Mater.* **2019**, *31*, e1805252. [CrossRef]
- 61. Kulkarni, A.; Siahrostami, S.; Patel, A.; Nørskov, J.K. Understanding Catalytic Activity Trends in the Oxygen Reduction Reaction. *Chem. Rev.* 2018, *118*, 2302–2312. [CrossRef]
- 62. Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S.Z. Origin of the Electrocatalytic Oxygen Reduction Activity of Graphene-Based Catalysts: A Roadmap to Achieve the Best Performance. *J. Am. Chem. Soc.* **2014**, *136*, 4394–4403. [CrossRef]
- 63. Nørskov, J.K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J.R.; Bligaard, T.; Jónsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* 2004, *108*, 17886–17892. [CrossRef]
- 64. Vojvodic, A.; Nørskov, J.K. New design paradigm for heterogeneous catalysts. Natl. Sci. Rev. 2015, 2, 140–143. [CrossRef]
- 65. Liu, S.; Li, Z.; Wang, C.; Tao, W.; Huang, M.; Zuo, M.; Yang, Y.; Yang, K.; Zhang, L.; Chen, S.; et al. Turning main-group element magnesium into a highly active electrocatalyst for oxygen reduction reaction. *Nat. Commun.* **2020**, *11*, 1–11. [CrossRef] [PubMed]
- Liu, J.; Liu, H.; Chen, H.; Du, X.; Zhang, B.; Hong, Z.; Sun, S.; Wang, W. Progress and Challenges Toward the Rational Design of Oxygen Electrocatalysts Based on a Descriptor Approach. *Adv. Sci.* 2019, 7, 1901614. [CrossRef] [PubMed]
- 67. Huang, Z.F.; Song, J.; Dou, S.; Li, X.; Wang, J.; Wang, X. Strategies to Break the Scaling Relation toward Enhanced Oxygen Electrocatalysis. *Matter* **2019**, *1*, 1494–1518. [CrossRef]
- 68. Woo, J.; Lim, J.S.; Kim, J.H.; Joo, S.H. Heteroatom-doped carbon-based oxygen reduction electrocatalysts with tailored fourelectron and two-electron selectivity. *Chem. Commun.* **2021**, *57*, 7350–7361. [CrossRef] [PubMed]
- Chen, H.; Liang, X.; Liu, Y.; Ai, X.; Asefa, T.; Zou, X. Active Site Engineering in Porous Electrocatalysts. *Adv. Mater.* 2020, 32, e2002435. [CrossRef] [PubMed]
- Chen, L.; Chen, Z.; Kuang, Y.; Xu, C.; Yang, L.; Zhou, M.; He, B.; Jing, M.; Li, Z.; Li, F.; et al. Edge-Rich Quasi-Mesoporous Nitrogen-Doped Carbon Framework Derived from Palm Tree Bark Hair for Electrochemical Applications. ACS Appl. Mater. Interfaces 2018, 10, 27047–27055. [CrossRef] [PubMed]
- Wu, X.; Qiao, Y.; Shi, Z.; Tang, W.; Li, C.M. Hierarchically Porous N-Doped Carbon Nanotubes/Reduced Graphene Oxide Composite for Promoting Flavin-Based Interfacial Electron Transfer in Microbial Fuel Cells. ACS Appl. Mater. Interfaces 2018, 10, 11671–11677. [CrossRef]
- 72. Chen, Q.; Ding, R.; Liu, H.; Zhou, L.; Wang, Y.; Zhang, Y.; Fan, G. Flexible Active-Site Engineering of Monometallic Co-Layered Double Hydroxides for Achieving High-Performance Bifunctional Electrocatalyst toward Oxygen Evolution and H<sub>2</sub>O<sub>2</sub> Reduction. *ACS Appl. Mater. Interfaces* **2020**, *12*, 12919–12929. [CrossRef]
- Zhao, J.; Dumont, J.H.; Martinez, U.; Macossay, J.; Artyushkova, K.; Atanassov, P.; Gupta, G. Graphite Intercalation Compounds Derived by Green Chemistry as Oxygen Reduction Reaction Catalysts. ACS Appl. Mater. Interfaces 2020, 12, 42678–42685. [CrossRef] [PubMed]
- Zhou, H.; Yang, T.; Kou, Z.; Shen, L.; Zhao, Y.; Wang, Z.; Wang, X.; Yang, Z.; Du, J.; Xu, J.; et al. Negative Pressure Pyrolysis Induced Highly Accessible Single Sites Dispersed on 3D Graphene Frameworks for Enhanced Oxygen Reduction. *Angew. Chem. Int. Ed.* 2020, 59, 20465–20469. [CrossRef] [PubMed]
- Lou, Y.; Liu, J.; Liu, M.; Wang, F. Hexagonal Fe<sub>2</sub>N Coupled with N-Doped Carbon: Crystal-Plane-Dependent Electrocatalytic Activity for Oxygen Reduction. ACS Catal. 2020, 10, 2443–2451. [CrossRef]
- 76. Zhang, H.; Xu, J.; Jin, Y.; Tong, Y.; Lu, Q.; Gao, F. Quantum Effects Allow the Construction of Two-Dimensional Co<sub>3</sub>O<sub>4</sub>-Embedded Nitrogen-Doped Porous Carbon Nanosheet Arrays from Bimetallic MOFs as Bifunctional Oxygen Electrocatalysts. *Chem.—A Eur. J.* 2018, 24, 14522–14530. [CrossRef]

- 77. Zhang, Y.; Knibbe, R.; Sunarso, J.; Zhong, Y.; Zhou, W.; Shao, Z.; Zhu, Z. Recent Progress on Advanced Materials for Solid-Oxide Fuel Cells Operating Below 500 °C. Adv. Mater. 2017, 29, 17703452017. [CrossRef]
- Zhang, J.; Ren, M.; Wang, L.; Li, Y.; Yakobson, B.I.; Tour, J.M. Oxidized Laser-Induced Graphene for Efficient Oxygen Electrocatalysis. Adv. Mater. 2018, 30, e1707319. [CrossRef]
- Du, R.; Zhang, N.; Zhu, J.; Wang, Y.; Xu, C.; Hu, Y.; Mao, N.; Xu, H.; Duan, W.; Zhuang, L.; et al. Nitrogen-Doped Carbon Nanotube Aerogels for High-Performance ORR Catalysts. *Small* 2015, *11*, 3903–3908. [CrossRef]
- Wu, R.; Wan, X.; Deng, J.; Huang, X.; Chen, S.; Ding, W.; Li, L.; Liao, Q.; Wei, Z. NaCl protected synthesis of 3D hierarchical metal-free porous nitrogen-doped carbon catalysts for the oxygen reduction reaction in acidic electrolyte. *Chem. Commun.* 2019, 55, 9023–9026. [CrossRef]
- 81. Zhang, C.; Hao, R.; Liao, H.; Hou, Y. Synthesis of amino-functionalized graphene as metal-free catalyst and exploration of the roles of various nitrogen states in oxygen reduction reaction. *Nano Energy* **2013**, *2*, 88–97. [CrossRef]
- 82. 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.* **2018**, *10*, 1589–1596. [CrossRef]
- 83. Tian, K.; Wang, J.; Cao, L.; Yang, W.; Guo, W.; Liu, S.; Li, W.; Wang, F.; Li, X.; Xu, Z.; et al. Single-site pyrrolic-nitrogen-doped sp2-hybridized carbon materials and their pseudocapacitance. *Nat. Commun.* **2020**, *11*, 3884. [CrossRef] [PubMed]
- 84. Zhang, C.; Mahmood, N.; Yin, H.; Liu, F.; Hou, Y. Synthesis of Phosphorus-Doped Graphene and its Multifunctional Applications for Oxygen Reduction Reaction and Lithium Ion Batteries. *Adv. Mater.* **2013**, *25*, 4932–4937. [CrossRef] [PubMed]
- Yao, Z.; Hu, M.; Iqbal, Z.; Wang, X. N<sub>8</sub><sup>-</sup> Polynitrogen Stabilized on Boron-Doped Graphene as Metal-Free Electrocatalysts for Oxygen Reduction Reaction. ACS Catal. 2020, 10, 160–167. [CrossRef]
- Li, R.; Liu, F.; Zhang, Y.; Guo, M.; Liu, D. Nitrogen, Sulfur Co-Doped Hierarchically Porous Carbon as a Metal-Free Electrocatalyst for Oxygen Reduction and Carbon Dioxide Reduction Reaction. ACS Appl. Mater. Interfaces 2020, 12, 44578–44587. [CrossRef] [PubMed]
- 87. Li, J.-S.; Li, S.-L.; Tang, Y.-J.; Li, K.; Zhou, L.; Kong, N.; Lan, Y.-Q.; Bao, J.-C.; Dai, Z.-H. Heteroatoms ternary-doped porous carbons derived from MOFs as metal-free electrocatalysts for oxygen reduction reaction. *Sci. Rep.* **2014**, *4*, 5130. [CrossRef]
- Kahan, R.J.; Hirunpinyopas, W.; Cid, J.; Ingleson, M.J.; Dryfe, R.A.W. Well-Defined Boron/Nitrogen-Doped Polycyclic Aromatic Hydrocarbons Are Active Electrocatalysts for the Oxygen Reduction Reaction. *Chem. Mater.* 2019, *31*, 1891–1898. [CrossRef]
- Ai, W.; Luo, Z.; Jiang, J.; Zhu, J.; Du, Z.; Fan, Z.; Xie, L.; Zhang, H.; Huang, W.; Yu, T. Nitrogen and Sulfur Codoped Graphene: Multifunctional Electrode Materials for High-Performance Li-Ion Batteries and Oxygen Reduction Reaction. *Adv. Mater.* 2014, 26, 6186–6192. [CrossRef]
- 90. Chang, Y.; Hong, F.; He, C.; Zhang, Q.; Liu, J. Nitrogen and Sulfur Dual-Doped Non-Noble Catalyst Using Fluidic Acrylonitrile Telomer as Precursor for Efficient Oxygen Reduction. *Adv. Mater.* **2013**, *25*, 4794–4799. [CrossRef]
- Chen, L.; Feng, J.; Zhou, H.; Fu, C.; Wang, G.; Yang, L.; Xu, C.; Chen, Z.; Yang, W.; Kuang, Y. Hydrothermal preparation of nitrogen, boron co-doped curved graphene nanoribbons with high dopant amounts for high-performance lithium sulfur battery cathodes. J. Mater. Chem. A 2017, 5, 7403–7415. [CrossRef]
- Meng, Y.; Voiry, D.; Goswami, A.; Zou, X.; Huang, X.; Chhowalla, M.; Liu, Z.; Asefa, T. N-, O-, and S-Tridoped Nanoporous Carbons as Selective Catalysts for Oxygen Reduction and Alcohol Oxidation Reactions. J. Am. Chem. Soc. 2014, 136, 13554–13557. [CrossRef] [PubMed]
- Silva, R.; Voiry, D.; Chhowalla, M.; Asefa, T. Efficient Metal-Free Electrocatalysts for Oxygen Reduction: Polyaniline-Derived Nand O-Doped Mesoporous Carbons. J. Am. Chem. Soc. 2013, 135, 7823–7826. [CrossRef] [PubMed]
- Li, D.; Jia, Y.; Chang, G.; Chen, J.; Liu, H.; Wang, J.; Hu, Y.; Xia, Y.; Yang, D.; Yao, X. A Defect-Driven Metal-free Electrocatalyst for Oxygen Reduction in Acidic Electrolyte. *Chem* 2018, 4, 2345–2356. [CrossRef]
- Singh, S.K.; Takeyasu, K.; Nakamura, J. Active Sites and Mechanism of Oxygen Reduction Reaction Electrocatalysis on Nitrogen-Doped Carbon Materials. *Adv. Mater.* 2018, *31*, e1804297. [CrossRef] [PubMed]
- Zhao, R.; Li, Q.; Chen, Z.; Jose, V.; Jiang, X.; Fu, G.; Lee, J.-M.; Huang, S. B, N-doped ultrathin carbon nanosheet superstructure for high-performance oxygen reduction reaction in rechargeable zinc-air battery. *Carbon* 2020, 164, 398–406. [CrossRef]
- Jiang, Z.; Zhao, X.; Tian, X.; Luo, L.; Fang, J.; Gao, H.; Jiang, Z.-J. Hydrothermal Synthesis of Boron and Nitrogen Codoped Hollow Graphene Microspheres with Enhanced Electrocatalytic Activity for Oxygen Reduction Reaction. ACS Appl. Mater. Interfaces 2015, 7, 19398–19407. [CrossRef] [PubMed]
- 98. Lv, Q.; Si, W.; He, J.; Sun, L.; Zhang, C.; Wang, N.; Yang, Z.; Li, X.; Wang, X.; Deng, W.; et al. Selectively nitrogen-doped carbon materials as superior metal-free catalysts for oxygen reduction. *Nat. Commun.* **2018**, *9*, 3376. [CrossRef]
- 99. Ai, K.; Liu, Y.; Ruan, C.; Lu, L.; Lu, G. Sp2C-Dominant N-Doped Carbon Sub-micrometer Spheres with a Tunable Size: A Versatile Platform for Highly Efficient Oxygen-Reduction Catalysts. *Adv. Mater.* **2013**, *25*, 998–1003. [CrossRef] [PubMed]
- Sakaushi, K.; Eckardt, M.; Lyalin, A.; Taketsugu, T.; Behm, R.J.; Uosaki, K. Microscopic Electrode Processes in the Four-Electron Oxygen Reduction on Highly Active Carbon-Based Electrocatalysts. ACS Catal. 2018, 8, 8162–8176. [CrossRef]
- Wu, K.; Chen, X.; Liu, S.; Pan, Y.; Cheong, W.-C.; Zhu, W.; Cao, X.; Shen, R.; Chen, W.; Luo, J.; et al. Porphyrin-like Fe-N4 sites with sulfur adjustment on hierarchical porous carbon for different rate-determining steps in oxygen reduction reaction. *Nano Res.* 2018, 11, 6260–6269. [CrossRef]
- Kabir, S.; Artyushkova, K.; Serov, A.; Atanassov, P. Role of Nitrogen Moieties in N-Doped 3D-Graphene Nanosheets for Oxygen Electroreduction in Acidic and Alkaline Media. ACS Appl. Mater. Interfaces 2018, 10, 11623–11632. [CrossRef]

- Yin, H.; Zhang, C.; Liu, F.; Hou, Y. Hybrid of Iron Nitride and Nitrogen-Doped Graphene Aerogel as Synergistic Catalyst for Oxygen Reduction Reaction. *Adv. Funct. Mater.* 2014, 24, 2930–2937. [CrossRef]
- 104. Wang, Y.; Wang, J.; Wei, D.; Li, M. A "MOF-Protective-Pyrolysis" Strategy for the Preparation of Fe–N–C Catalysts and the Role of Fe, N, and C in the Oxygen Reduction Reaction in Acidic Medium. ACS Appl. Mater. Interfaces 2019, 11, 35755–35763. [CrossRef]
- 105. Zhao, C.; Li, B.; Liu, J.; Zhang, Q. Intrinsic Electrocatalytic Activity Regulation of M–N–C Single-Atom Catalysts for the Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* 2021, 60, 4448–4463. [CrossRef]
- 106. Yang, S.; Xue, X.; Liu, X.; Liu, W.; Bao, J.; Huang, Y.; Su, H.; Yuan, S.; Li, H.-M. Scalable Synthesis of Micromesoporous Iron-Nitrogen-Doped Carbon as Highly Active and Stable Oxygen Reduction Electrocatalyst. ACS Appl. Mater. Interfaces 2019, 11, 39263–39273. [CrossRef] [PubMed]
- 107. Chen, M.; Li, X.; Yang, F.; Li, B.; Stracensky, T.; Karakalos, S.; Mukerjee, S.; Jia, Q.; Su, D.; Wang, G.; et al. Atomically Dispersed MnN<sub>4</sub> Catalysts via Environmentally Benign Aqueous Synthesis for Oxygen Reduction: Mechanistic Understanding of Activity and Stability Improvements. ACS Catal. 2020, 10, 10523–10534. [CrossRef]
- 108. Zheng, L.; Yu, S.; Lu, X.; Fan, W.; Chi, B.; Ye, Y.; Shi, X.; Zeng, J.; Li, X.; Liao, S. Two-Dimensional Bimetallic Zn/Fe-Metal-Organic Framework (MOF)-Derived Porous Carbon Nanosheets with a High Density of Single/Paired Fe Atoms as High-Performance Oxygen Reduction Catalysts. ACS Appl. Mater. Interfaces 2020, 12, 13878–13887. [CrossRef] [PubMed]
- Tang, C.; Jiao, Y.; Shi, B.; Liu, J.; Xie, Z.; Chen, X.; Zhang, Q.; Qiao, S. Coordination Tunes Selectivity: Two-Electron Oxygen Reduction on High-Loading Molybdenum Single-Atom Catalysts. *Angew. Chem. Int. Ed.* 2020, 59, 9171–9176. [CrossRef]
- 110. Yang, S.; Yu, Y.; Dou, M.; Zhang, Z.; Dai, L.; Wang, F. Two-Dimensional Conjugated Aromatic Networks as High-Site-Density and Single-Atom Electrocatalysts for the Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* 2019, 58, 14724–14730. [CrossRef]
- 111. Lu, Z.; Wang, B.; Hu, Y.; Liu, W.; Zhao, Y.; Yang, R.; Li, Z.; Luo, J.; Chi, B.; Jiang, Z.; et al. An Isolated Zinc–Cobalt Atomic Pair for Highly Active and Durable Oxygen Reduction. *Angew. Chem. Int. Ed.* **2019**, *58*, 2622–2626. [CrossRef]
- 112. Li, J.; Chen, S.; Yang, N.; Deng, M.; Ibraheem, S.; Deng, J.; Li, J.; Li, L.; Wei, Z. Ultrahigh-Loading Zinc Single-Atom Catalyst for Highly Efficient Oxygen Reduction in Both Acidic and Alkaline Media. *Angew. Chem. Int. Ed.* **2019**, *58*, 7035–7039. [CrossRef]
- 113. Yang, Q.; Jia, Y.; Wei, F.; Zhuang, L.; Yang, D.; Liu, J.; Wang, X.; Lin, S.; Yuan, P.; Yao, X. Understanding the Activity of Co-N4–xCx in Atomic Metal Catalysts for Oxygen Reduction Catalysis. *Angew. Chem. Int. Ed.* **2020**, *59*, 6122–6127. [CrossRef]
- 114. Wang, T.; Yang, C.; Liu, Y.; Yang, M.; Li, X.; He, Y.; Li, H.; Chen, H.; Lin, Z. Dual-Shelled Multidoped Hollow Carbon Nanocages with Hierarchical Porosity for High-Performance Oxygen Reduction Reaction in Both Alkaline and Acidic Media. *Nano Lett.* 2020, 20, 5639–5645. [CrossRef] [PubMed]
- 115. Han, Y.; Wang, Y.; Xu, R.; Chen, W.; Zheng, L.; Han, A.; Zhu, Y.; Zhang, J.; Zhang, H.; Luo, J.; et al. Electronic structure engineering to boost oxygen reduction activity by controlling the coordination of the central metal. *Energy Environ. Sci.* 2018, 11, 2348–2352. [CrossRef]
- 116. Yin, S.; Yang, J.; Han, Y.; Li, G.; Wan, L.; Chen, Y.; Chen, C.; Qu, X.; Jiang, Y.; Sun, S. Construction of Highly Active Metal-Containing Nanoparticles and FeCo-N<sub>4</sub> Composite Sites for the Acidic Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* 2020, 59, 21976–21979. [CrossRef]
- 117. Li, J.; Chen, M.; Cullen, D.A.; Hwang, S.; Wang, M.; Li, B.; Liu, K.; Karakalos, S.; Lucero, M.; Zhang, H.; et al. Atomically dispersed manganese catalysts for oxygen reduction in proton-exchange membrane fuel cells. *Nat. Catal.* **2018**, *1*, 935–945. [CrossRef]
- Xiao, M.; Zhang, H.; Chen, Y.; Zhu, J.; Gao, L.; Jin, Z.; Ge, J.; Jiang, Z.; Chen, S.; Liu, C.; et al. Identification of binuclear Co2N5 active sites for oxygen reduction reaction with more than one magnitude higher activity than single atom CoN4 site. *Nano Energy* 2018, 46, 396–403. [CrossRef]
- 119. Luo, E.; Zhang, H.; Wang, X.; Gao, L.; Gong, L.; Zhao, T.; Jin, Z.; Ge, J.; Jiang, Z.; Liu, C.; et al. Single-Atom Cr–N<sub>4</sub> Sites Designed for Durable Oxygen Reduction Catalysis in Acid Media. *Angew. Chem. Int. Ed.* **2019**, *58*, 12469–12475. [CrossRef] [PubMed]
- Yang, L.; Shao, Z. Tunable and convenient synthesis of highly dispersed Fe–N<sub>x</sub> catalysts from graphene-supported Zn–Fe-ZIF for efficient oxygen reduction in acidic media. RSC Adv. 2019, 9, 42236–42244. [CrossRef]
- 121. Zhang, Z.; Zhang, H.; Hou, Y.; Liu, P.; Hao, X.; Liu, Y.; Xu, B.; Guo, J. One-step synthesis of CeFeO<sub>3</sub> nanoparticles on porous nanocarbon frameworks derived from ZIF-8 for a boosted oxygen reduction reaction in pH universal electrolytes. *J. Mater. Chem. A* 2022, *10*, 13013–13020. [CrossRef]
- 122. Fu, W.; Wang, X.-L.; Yang, X.-X.; He, X.-Q. MnCo2O4 Anchored on Nitrogen-Doped Carbon Nanomaterials as an Efficient Electrocatalyst for Oxygen Reduction. *ChemistrySelect* **2018**, *3*, 4228–4236. [CrossRef]
- 123. He, Y.; Hwang, S.; Cullen, D.A.; Uddin, M.A.; Langhorst, L.; Li, B.; Karakalos, S.; Kropf, A.J.; Wegener, E.C.; Sokolowski, J.; et al. Highly active atomically dispersed CoN4 fuel cell cathode catalysts derived from surfactant-assisted MOFs: Carbon-shell confinement strategy. *Energy Environ. Sci.* 2019, *12*, 250–260. [CrossRef]
- 124. Wang, X.; Li, Z.; Qu, Y.; Yuan, T.; Wang, W.; Wu, Y.; Li, Y. Review of Metal Catalysts for Oxygen Reduction Reaction: From Nanoscale Engineering to Atomic Design. *Chem* 2019, *5*, 1486–1511. [CrossRef]
- 125. Li, J.; Liu, H.; Wang, M.; Lin, C.; Yang, W.; Meng, J.; Xu, Y.; Owusu, K.A.; Jiang, B.; Chen, C.; et al. Boosting oxygen reduction activity with low-temperature derived high-loading atomic cobalt on nitrogen-doped graphene for efficient Zn–air batteries. *Chem. Commun.* 2019, 55, 334–337. [CrossRef] [PubMed]
- 126. Xu, H.; Cheng, D.; Cao, D.; Zeng, X.C. A universal principle for a rational design of single-atom electrocatalysts. *Nat. Catal.* **2018**, *1*, 339–348. [CrossRef]

- 127. Reda, M.; Hansen, H.A.; Vegge, T. DFT Study of the Oxygen Reduction Reaction on Carbon-Coated Iron and Iron Carbide. *ACS Catal.* **2018**, *8*, 10521–10529. [CrossRef]
- 128. Huang, X.; Zhang, Y.; Shen, H.; Li, W.; Shen, T.; Ali, Z.; Tang, T.; Guo, S.; Sun, Q.; Hou, Y. N-Doped Carbon Nanosheet Networks with Favorable Active Sites Triggered by Metal Nanoparticles as Bifunctional Oxygen Electrocatalysts. *ACS Energy Lett.* **2018**, *3*, 2914–2920. [CrossRef]
- 129. Zhou, R.; Zheng, Y.; Jaroniec, M.; Qiao, S.-Z. Determination of the Electron Transfer Number for the Oxygen Reduction Reaction: From Theory to Experiment. *ACS Catal.* **2016**, *6*, 4720–4728. [CrossRef]
- 130. Li, L.; Tang, C.; Zheng, Y.; Xia, B.; Zhou, X.; Xu, H.; Qiao, S.-Z. Tailoring Selectivity of Electrochemical Hydrogen Peroxide Generation by Tunable Pyrrolic-Nitrogen-Carbon. *Adv. Energy Mater.* **2020**, *10*, 2000789. [CrossRef]
- Zhang, J.; Zhang, M.; Zeng, Y.; Chen, J.; Qiu, L.; Zhou, H.; Sun, C.; Yu, Y.; Zhu, C.; Zhu, Z. Single Fe Atom on Hierarchically Porous S, N-Codoped Nanocarbon Derived from Porphyra Enable Boosted Oxygen Catalysis for Rechargeable Zn-Air Batteries. *Small* 2019, 15, 1900307. [CrossRef] [PubMed]
- Qian, Y.; Liu, Q.; Sarnello, E.; Tang, C.; Chng, M.; Shui, J.; Li, T.; Pennycook, S.J.; Han, M.; Zhao, D. MOF-Derived Carbon Networks with Atomically Dispersed Fe–Nx Sites for Oxygen Reduction Reaction Catalysis in Acidic Media. ACS Mater. Lett. 2019, 1, 37–43. [CrossRef]
- Wei, X.; Zheng, D.; Zhao, M.; Chen, H.; Fan, X.; Gao, B.; Gu, L.; Guo, Y.; Qin, J.; Wei, J.; et al. Cross-Linked Polyphosphazene Hollow Nanosphere-Derived N/P-Doped Porous Carbon with Single Nonprecious Metal Atoms for the Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* 2020, 59, 14639–14646. [CrossRef]
- She, W.; Xie, Q.; Huang, Y.; Xie, C.; Zhang, X.; Sun, M.; Wang, F.; Xiao, J. Microstructure Engineering of Fe/Fe3C-Decorated Metal–Nitrogen–Carbon Mesoporous Nanospheres via a Self-Template Method for Enhancing Oxygen Reduction Activity. ACS Appl. Mater. Interfaces 2020, 12, 28065–28074. [CrossRef]
- 135. Xiao, X.; Zou, L.; Pang, H.; Xu, Q. Synthesis of micro/nanoscaled metal–organic frameworks and their direct electrochemical applications. *Chem. Soc. Rev.* 2020, *49*, 301–331. [CrossRef]
- 136. Li, S.-L.; Xu, Q. Metal–organic frameworks as platforms for clean energy. Energy Environ. Sci. 2013, 6, 1656–1683. [CrossRef]
- 137. Liao, P.-Q.; Shen, J.-Q.; Zhang, J.-P. Metal–organic frameworks for electrocatalysis. *Coord. Chem. Rev.* **2018**, *373*, 22–48. [CrossRef] 138. Song, G.; Wang, Z.; Wang, L.; Li, G.; Huang, M.; Yin, F. Preparation of MOF(Fe) and its catalytic activity for oxygen reduction
- reaction in an alkaline electrolyte. *Chin. J. Catal.* **2014**, *35*, 185–195. [CrossRef]
- 139. Luo, Y.; Zhang, J.; Kiani, M.; Chen, Y.; Chen, J.; Wang, G.; Chan, S.H.; Wang, R. Synthesis of MOF-Derived Nonprecious Catalyst with High Electrocatalytic Activity for Oxygen Reduction Reaction. *Ind. Eng. Chem. Res.* **2018**, *57*, 12087–12095. [CrossRef]
- 140. Bai, F.; Huang, H.; Hou, C.; Zhang, P. Porous carbon-coated cobalt sulfide nanocomposites derived from metal organic frameworks (MOFs) as an advanced oxygen reduction electrocatalyst. *New J. Chem.* **2016**, *40*, 1679–1684. [CrossRef]
- 141. Yang, W.; Li, X.; Li, Y.; Zhu, R.; Pang, H. Applications of Metal–Organic-Framework-Derived Carbon Materials. *Adv. Mater.* **2019**, 31, 1804740. [CrossRef] [PubMed]
- 142. Zhu, S.; Ge, J.; Liu, C.; Xing, W. Atomic-level dispersed catalysts for PEMFCs: Progress and future prospects. *EnergyChem* 2019, *1*, 100018. [CrossRef]
- 143. Wang, Y.; Chen, L.; Hou, C.-C.; Wei, Y.-S.; Xu, Q. Multiple catalytic sites in MOF-based hybrid catalysts for organic reactions. *Org. Biomol. Chem.* **2020**, *18*, 8508–8525. [CrossRef] [PubMed]
- 144. Windberg, T.; Ebert, T.; Uhlig, D.; Schulze, S.; Spange, S. Hierarchically structured carbon/carbon nanocomposites with adjustable porosity fabricated by twin polymerization. *Microporous Mesoporous Mater.* **2017**, 246, 62–71. [CrossRef]
- 145. Ma, W.; Yu, P.; Ohsaka, T.; Mao, L. An efficient electrocatalyst for oxygen reduction reaction derived from a Co-porphyrin-based covalent organic framework. *Electrochem. Commun.* **2015**, *52*, 53–57. [CrossRef]
- 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. [CrossRef]
- 147. Wang, W.; Xu, X.; Zhou, W.; Shao, Z. Recent Progress in Metal-Organic Frameworks for Applications in Electrocatalytic and Photocatalytic Water Splitting. *Adv. Sci.* 2017, *4*, 1600371. [CrossRef] [PubMed]
- 148. Du, L.; Xing, L.; Zhang, G.; Sun, S. Metal-organic framework derived carbon materials for electrocatalytic oxygen reactions: Recent progress and future perspectives. *Carbon* 2020, *156*, 77–92. [CrossRef]
- Zeng, L.; Guo, X.; He, C.; Duan, C. Metal–Organic Frameworks: Versatile Materials for Heterogeneous Photocatalysis. ACS Catal. 2016, 6, 7935–7947. [CrossRef]
- Wang, B.; Lv, X.-L.; Feng, D.; Xie, L.-H.; Zhang, J.; Li, M.; Xie, Y.; Li, J.-R.; Zhou, H.-C. Highly Stable Zr(IV)-Based Metal–Organic Frameworks for the Detection and Removal of Antibiotics and Organic Explosives in Water. J. Am. Chem. Soc. 2016, 138, 6204–6216. [CrossRef]
- 151. Bai, Y.; Dou, Y.; Xie, L.-H.; Rutledge, W.; Li, J.-R.; Zhou, H.-C. Zr-based metal–organic frameworks: Design, synthesis, structure, and applications. *Chem. Soc. Rev.* 2016, 45, 2327–2367. [CrossRef]
- Solomon, M.B.; Church, T.L.; D'Alessandro, D.M. Perspectives on metal–organic frameworks with intrinsic electrocatalytic activity. *CrystEngComm* 2017, 19, 4049–4065. [CrossRef]
- 153. Liu, S.; Wang, Z.; Zhou, S.; Yu, F.; Yu, M.; Chiang, C.-Y.; Zhou, W.; Zhao, J.; Qiu, J. Metal–Organic-Framework-Derived Hybrid Carbon Nanocages as a Bifunctional Electrocatalyst for Oxygen Reduction and Evolution. *Adv. Mater.* 2017, 29, 1700874. [CrossRef]

- 154. Zhao, J.-Y.; Wang, R.; Wang, S.; Lv, Y.-R.; Xu, H.; Zang, S.-Q. Metal–organic framework-derived Co9S8 embedded in N, O and S-tridoped carbon nanomaterials as an efficient oxygen bifunctional electrocatalyst. *J. Mater. Chem. A* 2019, 7, 7389–7395. [CrossRef]
- 155. Li, J.-S.; Li, S.-L.; Tang, Y.-J.; Han, M.; Dai, Z.-H.; Bao, J.-C.; Lan, Y.-Q. Nitrogen-doped Fe/Fe3C@graphitic layer/carbon nanotube hybrids derived from MOFs: Efficient bifunctional electrocatalysts for ORR and OER. *Chem. Commun.* 2015, *51*, 2710–2713. [CrossRef] [PubMed]
- Ma, T.Y.; Dai, S.; Jaroniec, M.; Qiao, S.Z. Metal–Organic Framework Derived Hybrid Co3O4-Carbon Porous Nanowire Arrays as Reversible Oxygen Evolution Electrodes. J. Am. Chem. Soc. 2014, 136, 13925–13931. [CrossRef] [PubMed]
- 157. Banham, D.; Ye, S.; Pei, K.; Ozaki, J.; Kishimoto, T.; Imashiro, Y. A review of the stability and durability of non-precious metal catalysts for the oxygen reduction reaction in proton exchange membrane fuel cells. *J. Power Sources* **2015**, *285*, 334–348. [CrossRef]
- 158. Barman, B.K.; Nanda, K.K. CoFe Nanoalloys Encapsulated in N-Doped Graphene Layers as a Pt-Free Multifunctional Robust Catalyst: Elucidating the Role of Co-Alloying and N-Doping. *ACS Sustain. Chem. Eng.* **2018**, *6*, 12736–12745. [CrossRef]
- 159. Yan, W.; Cao, X.; Wang, R.; Sha, Y.; Cui, P.; Cui, S. N co-doped rod-like porous carbon derived from S, N organic ligand assembled Ni-MOF as an efficient electrocatalyst for oxygen reduction reaction. *J. Solid State Chem.* **2019**, 275, 167–173. [CrossRef]
- Sun, T.; Zhang, S.; Xu, L.; Wang, D.; Li, Y. An efficient multifunctional hybrid electrocatalyst: Ni2P nanoparticles on MOF-derived Co,N-doped porous carbon polyhedrons for oxygen reduction and water splitting. *Chem. Commun.* 2018, 54, 12101–12104. [CrossRef]
- 161. Li, D.; Xu, H.-Q.; Jiao, L.; Jiang, H.-L. Metal-organic frameworks for catalysis: State of the art, challenges, and opportunities. *EnergyChem* **2019**, *1*, 100005. [CrossRef]
- 162. Zhang, L.; Wang, X.; Wang, R.; Hong, M. Structural Evolution from Metal–Organic Framework to Hybrids of Nitrogen-Doped Porous Carbon and Carbon Nanotubes for Enhanced Oxygen Reduction Activity. *Chem. Mater.* **2015**, *27*, 7610–7618. [CrossRef]
- 163. Ge, L.; Yang, Y.; Wang, L.; Zhou, W.; De Marco, R.; Chen, Z.; Zou, J.; Zhu, Z. High activity electrocatalysts from metal–organic framework-carbon nanotube templates for the oxygen reduction reaction. *Carbon* **2015**, *82*, 417–424. [CrossRef]
- 164. Wei, J.; Hu, Y.; Liang, Y.; Kong, B.; Zhang, J.; Song, J.; Bao, Q.; Simon, G.P.; Jiang, S.P.; Wang, H. Nitrogen-Doped Nanoporous Carbon/Graphene Nano-Sandwiches: Synthesis and Application for Efficient Oxygen Reduction. *Adv. Funct. Mater.* 2015, 25, 5768–5777. [CrossRef]
- 165. Cichocka, M.O.; Liang, Z.; Feng, D.; Back, S.; Siahrostami, S.; Wang, X.; Samperisi, L.; Sun, Y.; Xu, H.; Hedin, N.; et al. A Porphyrinic Zirconium Metal–Organic Framework for Oxygen Reduction Reaction: Tailoring the Spacing between Active-Sites through Chain-Based Inorganic Building Units. J. Am. Chem. Soc. 2020, 142, 15386–15395. [CrossRef] [PubMed]
- 166. Zhao, C.-W.; Li, Y.-A.; Wang, X.-R.; Chen, G.-J.; Liu, Q.-K.; Ma, J.-P.; Dong, Y.-B. Fabrication of Cd(ii)-MOF-based ternary photocatalytic composite materials for H2 production via a gel-to-crystal approach. *Chem. Commun.* 2015, *51*, 15906–15909. [CrossRef]
- 167. Chen, C.; Kang, Y.; Huo, Z.; Zhu, Z.; Huang, W.; Xin, H.L.; Snyder, J.D.; Li, D.; Herron, J.A.; Mavrikakis, M.; et al. Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces. *Science* 2014, 343, 1339–1343. [CrossRef] [PubMed]
- Liberman, I.; Shimoni, R.; Ifraemov, R.; Rozenberg, I.; Singh, C.; Hod, I. Active-Site Modulation in an Fe-Porphyrin-Based Metal–Organic Framework through Ligand Axial Coordination: Accelerating Electrocatalysis and Charge-Transport Kinetics. J. Am. Chem. Soc. 2020, 142, 1933–1940. [CrossRef]
- 169. Wang, H.-F.; Chen, L.; Pang, H.; Kaskel, S.; Xu, Q. MOF-derived electrocatalysts for oxygen reduction, oxygen evolution and hydrogen evolution reactions. *Chem. Soc. Rev.* 2020, *49*, 1414–1448. [CrossRef]
- 170. Tang, Y.-J.; Gao, M.-R.; Liu, C.-H.; Li, S.-L.; Jiang, H.-L.; Lan, Y.-Q.; Han, M.; Yu, S.-H. Porous Molybdenum-Based Hybrid Catalysts for Highly Efficient Hydrogen Evolution. *Angew. Chem. Int. Ed.* **2015**, *54*, 12928–12932. [CrossRef]
- 171. Wang, X.; Liu, Y.; Zeng, J.; Peng, C.; Wang, R. MoO2/C hollow nanospheres synthesized by solvothermal method as anode material for lithium-ion batteries. *Ionics* **2019**, *25*, 437–445. [CrossRef]
- 172. Jing, Y.; Cheng, Y.; Wang, L.; Liu, Y.; Yu, B.; Yang, C. MOF-derived Co, Fe, and Ni co-doped N-enriched hollow carbon as efficient electrocatalyst for oxygen reduction reaction. *Chem. Eng. J.* **2020**, *397*, 125539. [CrossRef]
- 173. Zhong, H.; Wang, J.; Zhang, Y.; Xu, W.; Xing, W.; Xu, D.; Zhang, Y.; Zhang, X. ZIF-8 Derived Graphene-Based Nitrogen-Doped Porous Carbon Sheets as Highly Efficient and Durable Oxygen Reduction Electrocatalysts. *Angew. Chem. Int. Ed.* 2014, 53, 14235–14239. [CrossRef] [PubMed]
- 174. Liu, D.; Li, J.-C.; Ding, S.; Lyu, Z.; Feng, S.; Tian, H.; Huyan, C.; Xu, M.; Li, T.; Du, D.; et al. 2D Single-Atom Catalyst with Optimized Iron Sites Produced by Thermal Melting of Metal–Organic Frameworks for Oxygen Reduction Reaction. *Small Methods* 2020, 4, 1900827. [CrossRef]
- 175. Hou, C.-C.; Zou, L.; Sun, L.; Zhang, K.; Liu, Z.; Li, Y.; Li, C.; Zou, R.; Yu, J.; Xu, Q. Single-Atom Iron Catalysts on Overhang-Eave Carbon Cages for High-Performance Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* 2020, *59*, 7384–7389. [CrossRef] [PubMed]
- 176. Zhang, X.; Chen, Y.; Chen, M.; Yu, B.; Wang, B.; Wang, X.; Zhang, W.; Yang, D. MOF derived multi-metal oxides anchored N, P-doped carbon matrix as efficient and durable electrocatalyst for oxygen evolution reaction. *J. Colloid Interface Sci.* 2021, 581, 608–618. [CrossRef] [PubMed]

- Hou, Y.; Huang, T.; Wen, Z.; Mao, S.; Cui, S.; Chen, J. Metal–Organic Framework-Derived Nitrogen-Doped Core-Shell-Structured Porous Fe/Fe3C@C Nanoboxes Supported on Graphene Sheets for Efficient Oxygen Reduction Reactions. *Adv. Energy Mater.* 2014, 4, 1400337. [CrossRef]
- 178. Zhao, S.; Yin, H.; Du, L.; He, L.; Zhao, K.; Chang, L.; Yin, G.; Zhao, H.; Liu, S.; Tang, Z. Carbonized Nanoscale Metal–Organic Frameworks as High Performance Electrocatalyst for Oxygen Reduction Reaction. *ACS Nano* **2014**, *8*, 12660–12668. [CrossRef]
- 179. Niu, G.; Ruditskiy, A.; Vara, M.; Xia, Y. Toward continuous and scalable production of colloidal nanocrystals by switching from batch to droplet reactors. *Chem. Soc. Rev.* 2015, 44, 5806–5820. [CrossRef]
- 180. Zhang, L.; Niu, G.; Lu, N.; Wang, J.; Tong, L.; Wang, L.; Kim, M.J.; Xia, Y. Continuous and Scalable Production of Well-Controlled Noble-Metal Nanocrystals in Milliliter-Sized Droplet Reactors. *Nano Lett.* **2014**, *14*, 6626–6631. [CrossRef]
- 181. Xiong, Y.; Xiao, L.; Yang, Y.; DiSalvo, F.J.; Abruña, H.D. High-Loading Intermetallic Pt3Co/C Core–Shell Nanoparticles as Enhanced Activity Electrocatalysts toward the Oxygen Reduction Reaction (ORR). *Chem. Mater.* **2018**, *30*, 1532–1539. [CrossRef]
- Suntivich, J.; May, K.J.; Gasteiger, H.A.; Goodenough, J.B.; Shao-Horn, Y. A Perovskite Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles. *Science* 2011, 334, 1383–1385. [CrossRef]
- Estrada-Arriaga, E.B.; Guadarrama-Pérez, O.; Silva-Martínez, S.; Cuevas-Arteaga, C.; Guadarrama-Pérez, V.H. Oxygen reduction reaction (ORR) electrocatalysts in constructed wetland-microbial fuel cells: Effect of different carbon-based catalyst biocathode during bioelectricity production. *Electrochim. Acta* 2021, 370, 137745. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.