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Review Heteroatom-Doped Carbon Materials as Support for Anode Electrocatalysts for Direct Formic Acid Fuel Cells

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Direct formic acid fuel cells (DFAFCs) are a viable energy source for electronic devices and transportation. The bottleneck in the commercialization of DFAFCs is the limited power-density output owing to the slow kinetics of electro-oxidation of formic acid at the anode. Platinum and palladium-based nanomaterials are found to be active for formic acid oxidation. However, they show limited mass activity and insufficient long-term stability. The structure-activity relationship for electrocatalysts is now well established. The large-scale synthesis of electrocatalysts containing well dispersed, optimum sized noble metal nanoparticles with desired surface properties is relatively challenging. The nature of the support of an electrocatalyst influences the morphology and structure (shape, size, and dispersion of the active noble metals) and chemical properties through interaction between the metal and support, as well as electronic effect. Materials with tailored physical properties such as surface area, pore structure, pore-size distribution, and electrical conductivity are deemed ideal supports for electrocatalysts. Introducing desired functional groups and defects can effectively tune the surface and electronic properties of the support further. Various novel carbon materials and their chemically modified forms have been explored as support materials for DFAFCs. In this review article, the latest developments in the synthesis, characterization, and performance of heteroatomdoped carbon materials as support material for anode electrocatalysts in DFAFCs are summarized. Directions for future research are presented based on the critical analysis of the present research in materials for DFAFCs.

Keywords: Nanostructured carbon materials; Heteroatom-doped carbon nanomaterials; Effect of support materials; Anode electrocatalysts; Enhancement mechanism; Direct formic acid fuel cells;

1. INTRODUCTION

The global energy demand has steadily increased over the last few decades owing to the increased population and the growing desire for an improved quality of life [1, 2]. Currently, the

energy demand has been primarily met by burning fossil fuels in solid (coal), liquid (petroleum), and gaseous (natural gas) state [3, 4]. Harvesting energy through fossil-fuel combustion has negatively affected the environment causing anthropogenic climate change, acid rain, global warming, and ozone hole [5-7]. Fossil fuels are known to have limited long-term availability. Remarkable advancements in environment-friendly and sustainable-energy sources called renewable energy have rendered them increasingly feasible and affordable for domestic and industrial applications. Nevertheless, the share of fossil fuels in transportation and electronic applications is expected to remain at 80% in the next decade because the cost per unit of energy from renewable sources is not yet competitive with those of the conventional sources of energy [8-10]. Renewable energy sources (solar and wind) are unpredictable and intermittent. Therefore, the continuous availability of energy at the point of application site by storing renewable energy as chemical energy and delivering the power to the application site by using batteries and fuel cells.

Fuel cells are especially attractive because chemical energy stored in liquid or gaseous fuel is converted directly into electric energy without emitting any harmful combustion products. Therefore, fuel cells are clean, highly efficient (independent of thermodynamic efficiency), and can ensure uninterrupted delivery of electrical energy at the point of application as long as the feed is supplied. Polymeric electrolyte membrane fuel cells (PEMFCs) are an attractive source of power for transportation and portable electronic devices as they operate at low temperatures and display good energy density [11-13]. A PEMFC has three major components: (1) an anode compartment, (2) a catalyst-coated proton-conducting membrane known as membrane-electrode assembly (MEA), and (3) a cathode compartment. Many low-chain molecules such as hydrogen [14], methanol [15, 16], formic acid [17], isopropanol [18], hydrazine [19], and ethanol [20, 21] have been investigated as anode feed for PEMFCs. Hydrogen or liquid feed enters the anode side of the cell to become oxidized at the anode electrocatalyst layer and generate electrons, whereas oxygen (air) reduction reaction occurs at the cathode. A liquid organic chemical is preferred over hydrogen as an anode feed because of easy storage and transport [22]. Widespread concerns exist regarding the safety and availability of hydrogen[4, 13, 23, 24]. Direct methanol fuel cells are popular because methanol shows high energy density (22 MJ/kg), relatively faster kinetics of electro-oxidation reaction, and ease of production from varied sources [25]. However, methanol suffers from chemical toxicity and high crossover through the perflourosulfonic acid-based conducting membrane Nafion®, which deteriorates the performance of fuel cells [26] [27, 28].

Direct formic acid fuel cells (DFAFCs) are PEMFCs using formic acid anode feed. The advantages of using formic acid over methanol as anode feed are as follows: (1) it is nontoxic and the United States Food and Drug Authority has approved it [29]; (2) it has a low crossover through the proton-conducting membrane, so high concentrations (up to 10 M) of formic acid can be used on the anode side [30-32]; (3) it has high open circuit potential of 1.48 V (versus 1.18 V for methanol-based dual cells); (4) it has faster kinetics; and (5) it can be easily produced commercially [33, 34]. Many industrial processes can produce formic acid [35-37]. Formic acid production from CO_2 is particularly attractive because CO_2 is harmful to the environment. Climate change and global warming have been associated with CO_2 , a greenhouse gas. The electrochemical reduction of CO_2 (ERC) is one such process that converts CO_2 directly into a range of products, including formic acid, with the help of

electrical energy from renewable sources at room temperature and atmospheric pressure. A DFAFC– ERC hybrid process generates electrical energy from CO₂, which can serve the dual purpose of chemical utilization of CO₂ and solar-energy storage [38, 39].

The working principle of a DFAFC is schematically presented in Figure 1. Electrical energy is produced by generating electrons by the oxidation of formic acid at the anode. Electrons flow through the external circuit to the cathode where they are consumed in the oxygen reduction reaction along with the protons. The electro-oxidation of formic acid at the anode is the most critical reaction in a DFAFC. A plethora of experimental and theoretical studies have been conducted to study the kinetics of formic acid oxidation (FAO). Despite tremendous progress in understanding the mechanism of FAO, details regarding the steps and chemical species involved in the reaction differ, so this topic remains a research hotspot [40-43]. However, researchers agree that FAO occurs via two mechanisms, namely, dehydrogenation or direct pathway and dehydration or indirect pathway [44, 45]. The equations for the two pathways are as follows:

Dehydrogenation pathway: $HCOOH \rightarrow active \ intermediate \rightarrow CO_2 + 2H^+ + 2e^-$ Dehydration pathway: $HCOOH \rightarrow CO_{ad} + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$



Figure 1. Schematic of the working of a DFAFC.

The power output and durability of DFAFCs primarily depend on the kinetics of FAO at the anode. An anode electrocatalyst aims to accelerate the kinetics of the electro-oxidation of the feed. Platinum- and palladium-based electrodes show activity for FAO. However, palladium-based electrocatalysts perform batter in terms of catalytic activity and long-term stability. The mechanism and nature of the intermediate species involved in the reaction over the Pt and Pd metals differ. FAO over Pt-based catalysts follows mostly the dehydration (indirect) mechanism. In the dehydration pathway, carbon monoxide is generated as an intermediate, and it is readily adsorbed on Pt catalyst. Thus, the active sites are blocked by the carbon monoxide adsorbed (CO_{ad}) species and cannot participate in the reaction any further, explaining the rapid deactivation of Pt-based electrocatalyst

during FAO. Moreover, platinum has limited availability and is prohibitively expensive [40, 46, 47]. Palladium is more abundant and costs lower than Pt. Moreover, FAO over Pd-based electrocatalysts occur primarily through the direct mechanism, which does not generate CO_{ad} as an intermediate [45, 48, 49]. Hence, Pd shows superior performance to Pt [50, 51]. Surprisingly, Pd-based catalysts also show slow deactivation by CO poisoning in FAO. Wang et al. investigated the origin of CO in the dehydrogenation pathway. They found that CO could be generated as a result of the ERC, which is the product of formic acid oxidation through the dehydrogenation mechanism [42, 52-54].

Recent research efforts have focused on establishing the structure–activity relationship in an electrocatalyst. The catalytic activity of an electrocatalyst depends on the morphology, structure, chemical composition, surface properties, physiochemical properties, and support materials. These properties depend on the catalyst synthesis (solvent, surfactants, acidity, heat treatment, and degree of reduction) and the nature of support materials. An ideal anode catalyst promotes the direct pathway for FAO, shows low onset potential, high peak-mass activity at a lower potential, and extended stability. Despite a large number of papers published on electrocatalysts for FAO over the last decade, only a few review papers on DFAFCs are available in open literature [17, 55, 56]. For example, Yu et al. discussed the effect of anode catalysts, supported and unsupported, on the performance of DFAFCs [29]. Rice et al.[57] summarized the fundamentals of the mechanism of FAO over Pt- and Pd-based catalysts and explained the reason behind the activity enhancement. Jiang et al. [51] published an excellent review paper where they discussed the mechanistic studies and recent developments in Pd and Pt-based electrocatalysts for DFAFCs.

2. ROLE OF SUPPORT MATERIALS FOR ELECTROCATALYSTS

Many researchers have used unsupported materials (platinum black) as electrocatalysts for wide-ranging electrochemical reactions. Many shape-controlled Pd nanoparticles have been reported for FAO [58]. However, unsupported electrocatalysts show excessive leaching of the active metals from the GDL during the fuel-cell operation, which affects the long-term performance of the catalyst and contributes toward deactivation [58-61]. Accordingly, for the effective utilization of expensive active metals and the lowering of metal loading, dispersing active metals throughout a high-surfacearea support material [62, 63], where the support material functions as an interface between the active metals and the MEA, is desirable. Thus, the support material is critical for the transfer of reactants and electrons to and fro the active sites. Figure 2 schematically describes the role of support material on the diffusion of reactants and products and electronic transport in an electrocatalyst. The support materials impart electronic and bifunctional effects to enhance catalyst activity owing to metal-support interaction. Depositing nanosized active metals onto highly porous support facilitates the electron transport and mass transport of feeds and reaction byproducts from the electrocatalyst layer of the MEA of a PEMFC. The prerequisites for good support material for electrocatalyst are as follows: (a) high electrical conductivity; (b) high porosity, well-defined pore structure, and surface area; (c) numerous anchoring sites (defects, edges, and dislocations) and functional groups for anchoring of noble metals and presence of high metal-support interaction; (d) high corrosion resistance in acidic environment; (e) large window of electrochemical stability; (f) availability (g) cost; and (h) high hydrophobicity for easy water management.



Figure 2. Schematic role of support material on the performance of catalysts.

Some review papers on carbon and non-carbon support materials for methanol oxidation and oxygen reduction have been published [63-67]. However, to the best of knowledge of the author, no review article on the application of heteroatom-doped carbon materials on the electrocatalytic performance of the FAO has been published yet. This review article aims to present the latest developments related to the applications of chemically modified novel nanostructured carbon materials as support for anode catalysts for DFAFCs.

3. NANOSTRUCTURED CARBON MATERIALS FOR DFAFCs

Carbon and its various forms are the most commonly used electrocatalyst support materials for PEMFC applications. They satisfy the criteria of an excellent support material, as described in the last section. They possess high surface area, excellent electrical conductivity, and stability for wide-ranging acid and alkaline environments. Carbon materials can also be produced economically at a mass scale. These features render them the most preferred support materials for electrocatalysts. Popular carbon nanomaterials used as support for PEMFCs include activated carbon, carbon nanotubes

(CNTs), ordered mesoporous carbon (OMC), carbon nanofibers (CNFs), and graphene (G) [65, 67]. Herein, the applications of various carbon materials for FAO are briefly discussed.

3.1 Activated carbon

Activated carbon is by far the most extensively used support for different types of PEMFCs, including DFAFCs [68-70]. Activated carbon is low cost, easy to synthesize on a commercial scale, possesses moderate electrical conductivity, and shows reasonably high surface area [71]. The physicochemical properties and purity of activated carbon are essential for the overall performance of electrocatalysts [72]. Vulcan carbon (XC-72) [73-76], carbon black [77], and carbon derived waste food material [78] are the most commonly used forms of carbon for FAO.

The most significant limitation of activated carbon is the presence of a large proportion of pores as micropores (<1 nm diameter) and their tortuosity. Small and tortuous pores become inaccessible for catalyst particles during the synthesis and the reactant and products [62]. Carbon-black support is also susceptible to corrosion in the oxidative and acidic environment of fuel cells, especially at high potentials. Corrosion of the support deteriorates the performance of the fuel cell owing to the loss of metal particles and particle agglomeration [66, 79]. Nevertheless, Pd/C remains the state-of-the-art catalyst and is extensively used as a standard for comparing the performance of prospective electrocatalysts for formic acid fuel cells [80, 81].

3.2 CNTs

CNTs are an immensely popular class of carbon nanomaterials for heterogenous catalysis. The tube-like cylindrical structure of the CNTs results from the rolling of single two-dimensional sheets. CNTs are classified as single-wall (SWCNTs) and multiwall (MWCNTs) CNTs depending on the number of the single layer of hexagonal carbon sheets in the structure [82, 83]. Single-wall CNTs consist of a single seamless cylinder, and MWCNTs are coaxial cylinders formed by multiple tubes [84, 85]. The processes for synthesizing CNTs have been described by Eatemadi et al. [86]. CNTs show superior surface area, electrical conductivity, surface-to-volume ratio, weight, mechanical strength, and chemical resistance over activated carbon [87, 88]. The chemistry and application of CNTs in PEMFCs have been extensively discussed by Luo et al. [89], Liu et al. [90], Akbari et al. [88], and Mukherjee et al. [91].

Synthesis of small, highly dispersed, and firmly bonded metal nanoparticles on the surface of CNTs is relatively challenging. CNTs are treated mostly with strong oxidizing agents such as HNO₃– H₂SO₄ mixture, KMnO₄, and H₂O₂ before being used as electrocatalyst support. This oxidative pretreatment removes amorphous carbon from the CNT structure and enforces tube-length cleavage and end opening. Moreover, oxidative treatment of CNTs introduces defects and carboxylic (-COOH), carbonyl (-C=O), and hydroxyl group (-OH) functional groups on their sidewalls [92, 93]. These functional groups serve as anchoring sites and improve electron transfer to attach small and well-

dispersed metal nanoparticles and achieve strong metal–support interaction [92, 94-96]. Figure 3 shows how metal or metal oxides are deposited onto CNTs.



Figure 3. Schematic of the synthesis of MWCNT-supported metal-alloy catalyst by ultrasonic-assisted chemical reduction [97].

Morgan et al. reported a current density of 0.18 over Pd/CNT for FAO compared with 0.082 mA cm⁻² for unsupported Pd black catalysts. The average size of the Pd particles was 13.2 nm. The Pd/CNT catalyst showed only a 33% loss in current density after 300 cycles [98]. Bimetallic PdIr supported on sonochemically treated CNT showed an exceptional mass activity of 3365 compared with 753 mA mg⁻¹ Pd for PdIr supported on untreated CNTs. The sonochemically treated CNTs could afford finer Pd particles (3.8 nm) than untreated CNTs (5.6 nm) [99]. Surfactants have also been used further to improve the dispersion and formation of small nanoparticles. For example, the modification of CNT surface with diallyldimethylammonium chloride (PDDA) [100] and phosphomolybdic acid–PDDA [101] lead to the anchoring of densely packed Pd particles onto the surface of CNTs. Our research group has reported high catalytic activity over cerium oxide- [102] and nickel oxide [103]-modified CNTs with catalytic activities.

In general, functionalization techniques and operating conditions should be cautiously selected. Extremely harsh oxidative procedures significantly damage the surface structure because of too many defects, thereby adversely affecting the electrical conductivity and corrosion resistance and hampering the performance of the metal electrocatalysts in fuel-cell operation [104, 105].

3.3 OMCs

OMCs have pore sizes ranging mostly within 2–50 nm according to the International Union of Pure and Applied Chemistry (IUPAC) [106]. OMC materials are considered as popular supports for PEMFCs because of their highly porous structure with large pore volume, surface area, and uniform pore sizes [107-111]. The large pore sizes of OMCs facilitate the mass transfer of the feed and products in catalysts. The synthesis and applications of OMCs have been discussed by Xu et al. [111], Li et al. [112], and Benzigar et al. [113]. OMC materials are classified based on the mesoporous silica

templates from which they are synthesized. For example, CMK-1, CMK-2, CMK-3, and CMK-8 are prepared from the silica templates MCM-48, SBA-1, SBA-15 and KIT-6, respectively [108, 112]. The structural features such as pore-size distribution, surface area, and pore shape of an OMC depend primarily on the method used for its synthesis. Hard and soft template methods are the most extensively used technique to prepare OMCs. The use of Pd or Pt supported on 3D mesoporous carbon [114], CMK-8 [115], CMK-3 [116], and mesoporous carbon-46 (MPC) [117] for FAO has been reported. The typical steps in the synthesis of metal supported on OMC by hard template method are shown in Figure 4.



Figure 4. Synthesis methods of mesoporous carbon materials [109].

Yang et al. synthesized a 3D mesoporous carbon matrix having large and interconnected uniform mesopores with a thin wall through a nano-CaCO₃ templated pyrolysis method. The Pd/OMC catalysts, with Pd particle size of 3 nm, showed a mass activity for FAO of 595.2 mA mg⁻¹ Pd, which is 1.9 times higher than that of Pd/C [114]. Mailyalagan et al. synthesized two types of Pd-nanoparticle-supported CMK-8, namely, CMK-8 I and II, prepared from the silica templates KIT-6 I and II, respectively [118]. The surface areas of CMK-8 I and II are 1060 and 1149 m²g⁻¹, and their pore diameters are 4.9 and 3.2 nm, respectively. TEM images show that Pd nanoparticles with sizes of 4. 1 and 3.6 nm are uniformly and homogenously dispersed on CMK-8-I and II, respectively. Electrochemical studies show that ECSA decreases in the order Pd/CMK-8-I (287) > Pd/CMK-8-II (256) > Pd/C (210 cm²mg⁻¹ Pd). Pd/CMK-8-I shows a mass activity of 486 mA mg⁻¹ Pd, which is higher than that of Pd/C (190 mA mg⁻¹ Pd). Pd/CMK-8 also shows excellent stability. The exceptional performance of Pd/CMK-8 for FAO reaction is ascribed to the high distribution of Pd nanoparticles,

excellent electrical conductivity, large BET surface area owing to the open continuous 3D structure, and large pore diameters that enable increased mass transfer of feed and product [115].

Chuntao Li (2012) explored platinum supported on CMK-3 as electrocatalysts for FAO and ORR. Pt nanoparticles 2.75 nm in size are uniformly distributed on CMK-3 support through the microwave-assisted polyol method. TEM results show that CMK-3 and Pt/CMK-3 possess well-defined, parallel pores with an average pore diameter of 8 nm [116]. The structural features and TEM images for CMK-3 and CMK-8 are shown in Figure 5.

The nitrogen adsorption-desorption isotherms and high-resolution TEM (HRTEM) images of the starting materials (MCM-41 and SBA-15) and CMK are shown in Figure 5b and 5c-5e, respectively.



Figure 5. (a) Structural features of CMK-3 and CMK-8. (b) Nitrogen adsorption isotherms MCM-41, SBA-15, and CMK-8. High-resolution TEM images of (c) MCM-41, (d) SBA-15, and (e) CMK-3 (d). (a) Reproduced with permission from reference [119]. (b–e) Reproduced with permission from reference [120].

MPC possesses well-defined 5–6 nm-wide channels with a small number of mesopores (2–3 nm). Zhang et al. (2012) reported that PtBi (1:1)/MPC shows one of the highest ever reported mass

activities for FAO of 5.63 Amg⁻¹ Pt at 0.57 V (vs. RHE). The catalyst shows high stability with a mass activity of 0.79 A/mg after 1800 s, which is 16.6 times higher than that of Pd black. The increased performance of the catalyst is owing to electronic, geometric, and third-body effects. The mesoporous structure also restricts the growth of PtBi nanoparticles, leading to the formation of highly distributed and smaller (3.1 nm) particles. The highly porous structure and the large pore sizes make the PtBi nanoparticles more accessible and facilitate superior mass-transfer features for reactants and products. The continuous carbon structure also enhances electrical conductivity [117]. Shim et al. prepared PtPb supported on large-pore (>30 nm) OMC/silicon dioxide materials.



Figure 6. (a) Steady-state cyclic voltammograms at 10 mV s⁻¹ scan rate. (b) Rotating-disk electrode voltammograms (10 mV s⁻¹ and 2000 rpm) of PtPb/OMCs and Pt/C in 0.5 M HCOOH+0.1 M mV s⁻¹ solution (c). Polarization curves (I-V) for PtPb/OMC. (d) Time dependence of power density at a fuel-cell voltage of 0.4 V. Reproduced with permission from reference [121].

Our research group has reported a high mass activity of 3.24 Amg^{-1} Pd for FAO reaction over Pd₃Pt₁/CeO₂-OMC [122]. Sun et al. (2009) used the anionic surfactant poly(sodium p-styrene sulfonate) during the microwave-assisted polyol method, which leads to well-dispersed Pd nanoparticles on carbon support. High loading is achieved with marginal enlargement of the nanoparticles from 5 nm to 5.4 nm [123].

3.4 Graphene

Graphene is an allotropic form of carbon having the thinnest 2D hexagonal single-layer structure. The ring consists of six sp²-hybridized carbon atoms that afford the presence of highly delocalized π electrons in the ring. G is an excellent support material for PEMFCs because of its superior electrical conductivity, 2D structure, tunable surface properties, large surface area (>2000 m²/g), and stability [124]. Its basic chemistry and structure have been discussed in reviews by Allen et al. [125] and Pumera et al. [126]. Choi et al. summarized the various synthesis methods for G [127]. Several reviews related to the application of G in fuel cells for MOR, ORR [128-131], and energy-storage devices [132] have been published in the last decade. For example, Iqbal et al. (2019) summarized the latest application of G-based materials for the different components of a PEMFC [133].

G, reduced G oxide (rGO), and G oxide (GO) have been reported as support for PEMFCs [134]. The three forms of G differ significantly in their chemical and physical properties owing to the difference in the extent of the oxygen functional groups. The three forms have different C/O ratios. The structure of the different forms of G is shown in (Figure 7).



Figure 7. Overview of the structure of graphene-based nanomaterials relevant for energy applications [135].

High-purity G can be synthesized by (1) chemical vapor deposition (CVD) using a volatile carbon source [136], (2) micromechanical exfoliation of graphite [137], and (3) epitaxial growth on SiC [138]. The chemical method of G synthesis uses low-cost graphite flakes as the starting material [139, 140]. In the first step, graphite is oxidized to GO by Brodie, Staudenmaier, Hoffmann, and Hummer's method. By far, Hummer or modified Hummer's method is the most popular synthesis route to large-scale GO production [138]. GO serves as the raw material to produce G and rGO depending on the extent of reduction. Sodium borohydride, hydrazine hydrate, and urea are the most commonly used reducing agents for the reduction of GO [141, 142].

GO is an almost electrical insulator but shows hydrophilicity, chemical tenability, and mechanical strength [64]. GOs contain basal and edge planes that are exposed to the surface. The oxygen functional groups are primarily alcohol (R-OH), epoxy (RC=O), and carboxylic (RCOOH) groups located at the basal and edge planes [143, 144]. The presence of the residual oxygen functional

group disrupts the π -bonding network in the hexagonal layer. These oxygen functional groups serve as active sites for the nucleation centers and anchoring sites for the growth of incoming metal nanoparticles [134]. Overall, GO is an unsuitable support material for electrocatalysts owing to its low electrical conductivity [145]. The electrical conductivity of GO increases upon reduction to resemble the G structure, which shows the highest electrical conductivity. During reduction, oxygen functional groups are removed, which is manifested by the increase in the C/O ratio from 2 to 4 to over 10 in rGO and infinity in pure G. The amorphous structure restacks into a more crystalline form. G sheets have the "perfect" and "thinnest" structure and thus shows the highest electrical conductivity (1000 Scm⁻¹) and electron-transfer rate. The high conductivity of rGO could be due to the increased d-spacing and the presence of corrugated surface resulting from the removal of oxygen functional groups and defects [146]. Nevertheless, G is not easy to disperse in solution owing to its hydrophobicity and tendency to agglomerate and precipitate because of the removal of the oxygen functional groups. rGO is a perfect combination of the properties of G and GO. It shows decent electrical conductivity caused by the proximity of its structure to G and the residual oxygen functional groups functioning as a nucleation point for incoming metals owing to electrostatic force [147-150].

In one of the first studies on Pd-supported G, Bong et al. prepared a high loading of Pd (80% by wt) over G by using G nanosheet as support. Narrowly distributed 4.6 nm-sized particles are deposited. The performance of G nanosheet as a support is better than that of carbon [151]. In another synthesis method of G, GO is first converted into G through a simple method where GO is placed in a vacuum overnight at 60°C and then quickly heated to 220°C. Palladium supported on G shows exceptional catalytic activity. The high performance is ascribed to the high surface area (402.9 m²g⁻¹), large proportion of macro and mesopores (3.65 nm), and strong metal–support interaction [152]. Yang et al. (2014) prepared shape-controlled cubic and spherical Pd nanoparticles supported on rGO using a two-step hydrothermal process. Cubic Pd/G shows superior performance compared with spherical Pd/G owing to a high percentage of the (100) plane and highly dispersed Pd particles. Notably, the most active plane of Pd for FAO is the (100) crystal plane [40, 153]. The presence of oxygen functional groups on GO also contributes to the oxidation of CO on Pd. The oxygen functional groups in rGO can be beneficial in the oxidative removal of CO. The rGO may form weakly adsorbs rGO-(OH)_{ad} species in water owing to the hydrophilic nature of the rGO. This rGO-(OH)_{ad} may oxidize Pd-CO_{ad} to Pd and CO₂ [154].

Zhang et al. reported the application of CuPd-loaded G for FAO. PdCu/G shows a high surface area 813.8 m²g⁻¹, four times higher than that of Pd/C (206.4 m²g⁻¹). The presence of mesopores and macropores leads to high a ECSA and promotes mass transfer and electron transfer in the catalytic process. The Tafel plot and EIS results confirm that charge transfer is favored in the presence of G [155]. PtNi nanoparticles have been loaded onto 2D G nanosheet by simple and one-pot-solution thermal decomposition using N-methyl-2pyrroidone as solvent and octadecylamine as solvent as well as reducing agent. PtNi/GO shows excellent catalytic activity and long-term stability for FAO. G favors the formation of highly dispersed smaller PtNi nanoparticles with an average size of $7.2 \pm \pm 1$ nm and high ECSA resulting from the strong synergistic effect owing to the strong metal–support interaction. The planar 2D structure, coupled with a large surface area of the reduced G nanosheet, leads to a high percentage of the active sites accessible for the reaction [156].

Venkatweshwara et al. (2011) prepared PtAu/GO and Pt/GO, with the mean diameter of Pt-Au alloy and Pt nanoparticles being 3.2 and 4.6 nm, respectively. Figure 8a shows that the cyclic voltammograms of Pt-Au/G in the presence of formic acid have two peaks (I and II) in the forward scan and another peak (peak III) in the negative scan. In the case of Pt-Au/G, the oxidation of formic acid occurs via dehydrogenation (peak I direct pathway) and the formate anion pathways (peak III). Peak II (dehydration pathway) is lower than peak I. Pt-Au/G shows better long-term stability than Pt/G, as shown in the chronoamperometry results obtained at 0.55 V (Figure 8b). The easier oxidative removal of CO over Pt-Au/G is responsible for the excellent stability of Pt-Au/G catalysts. The polarization curves of the prepared catalysts obtained in a single-cell DFAFC are shown in Figure 8c. Pt-Au/G shows the highest peak power density of 136.5 mWcm⁻² power density at 303 K [157]. The effect of the 3D G framework used to support Pd₂/PtFe is studied for FAO. Pd₂/PtFe nanowire network shows a mass activity of 740 mA mg⁻¹, which is 10 times the activity over Pt/C [158].

Zhang et al. (2011) synthesized PtAu/G with the addition of the cationic polyelectrolyte PDDA to improve the dispersion of PdAu on the hydrophobic G [159]. The rGO-based bimetallic PtNi [160], PdNi [161, 162], Pd-Fe [163], Pt-Au [147], Pd-Co [148], Pd-Bi [149], PtFe [150], and N-PtTe [164], as well as the trimetallic Cu-Fe-Pt [165], reportedly show excellent performance for FAO.



Figure 8. (a) Cyclic voltammetry of Pd-Au/G in 1.0 M HCCOH+0.5 M H₂SO₄ at different scan rates. (b) Current–time plot of Pt/G and Pt-Au/G in 0.5 M H₂SO₄ +1.0 M HCOOH at 0.5 V (NHE), (c) Current–voltage polarization curves of Pt/G and Pt-Au/G [157].

3.5 CNFs

CNFs have been used as carbon support materials for fuel cells [87]. The unique feature of

CNFs is their ability to form "embedded nanoparticles" rather than anchoring onto the active sites of the support. Qin et al. (2012) reported FAO over Pd particles of various sizes supported on CNF [166]. Pd nanoparticles with an average particle size of 3.76 nm and close particle-size distribution are loaded on the acid-functionalized CNF. Pd/CNF shows a current density of 40 mA cm^{-2,} primarily through the direct pathway. The corresponding mass activity is 0.56 Amg⁻¹ [167]. Nitze et al. used helical CNFs synthesized by CVD on C60 supported Pd with acetylene as a carbon source. The presence of defects and edge planes in CNF leads to the more robust anchoring of the Pd nanoparticles. Fuel-cell test results show that oxidized Pd/HCNF has the maximum power density, almost double than that of Pd/MWCNTs [168]. Liu et al. (2014) synthesized PdCo embedded into the CNF matrix. The resulting PdCo/CNFs show a mass activity of 1.5 Amg⁻¹ [169]. Palladium and gold nanoalloy supported on functionalized CNFs also demonstrate promising performance [170].

4. HETEROATOM-DOPED CARBON MATERIALS

Carbon nanomaterials are suitable supports for PEMFCs [171, 172]. The performance of carbon nanomaterials as support for electrocatalysts can be further improved by doping with a foreign element(s), which can modify their electronic and surface properties. The chemical structure, bonding (sp² and sp³), and presence of defects and edges in carbon materials render them eligible for chemical modification with various functional groups [173]. Many different strategies have been adopted for the modification of carbon nanomaterials, including the doping of carbon materials with heteroatoms [173-176], conducting polymers [177, 178], and transition-metal oxides [179-181]. This review deals only with the effect of heteroatom-doped carbon materials on the performance of DFAFCs. The most common dopant elements are boron, nitrogen, phosphorus, fluorine, and sulfur, as shown in Figure 9.

The introduction of one or more elements into the carbon network can be can performed in two ways: (a) noncovalent adsorption of species onto the edges and defects, and (b) substitution of carbon atoms with the heteroatoms in the carbon lattice via covalent bonding [182]. Heteroatom-doped carbon materials are more stable than the simple adsorption of species owing to the formation of high-strength chemical bonding. The surface energy and electronic properties of the host carbon material depend on the nature of the dopant and its concentration [183]. Functionalization of carbon materials (carbon, CNT, OMC, and G) with heteroatoms such as nitrogen, boron, phosphorous, and sulfur introduces a fascinating set of electronic, chemical, and mechanical properties into the carbon material. These properties change the nature of the interaction between active metal and the modified carbon material, leading to favorable adsorption characteristics of the active metals for catalytic applications.

The dopants B, N, P, and S, vary in their atomic radius, number of valence electrons, electronegativity, and electronic configurations [183, 184]. Irrespective of its nature and atomic size, a dopant modulates the electron distribution in the carbon structure and hence changes the electronic properties. It changes the Fermi energy level and bandgap without disturbing the structure of the carbon material [185, 186]. The synthesis and characterization of heteroatom-doped carbon materials have been discussed extensively in many review papers [183, 184, 187]. In this section, the latest

developments in the synthesis and application of heteroatom-doped carbon materials as support material for DFAFCs are analyzed.



Figure 9. Schematic of the positions and structures of heteroatom-doped carbons [186].

5. NITROGEN-DOPED CARBON MATERIALS

Nitrogen is abundant and close to carbon in the periodic table. It has readily available electrons owing to its electronic configuration $1s^2 2s^2 2p^3$. The electronic structure makes N-doped carbon materials unique compared with other dopants. Nitrogen can form a strong covalent bond with carbon, and their sizes are compatible [188]. As a result, nitrogen can easily replace carbon in the carbon network and creates active sites by creating defects. Moreover, nitrogen is more electronegative than carbon (3.04 for N vs. 2.55 for C on the Pauling scale), so introducing nitrogen to carbon network modifies the electronic and magnetic properties of the carbon material [189, 190]. The addition of a heteroatom (N, S, P) to carbon has been demonstrated to drastically improve the dispersion of the active metal, the formation of smaller nanoparticles, the current per unit mass, and the long-term stability of catalysts for fuel cells [174, 175, 191, 192]. The nitrogen dopant provides additional electron-rich active sites and modifies electronic properties of the noble metal atoms. Nitrogen-doped carbon materials have been used in supercapacitors [193], batteries [194], energy storage [195], and fuel cells [190, 196].

5.1 Nitrogen-doped carbon

Sun et al. (2017) used Pd supported on nitrogen-doped carbon for FAO. They used oxidized and non-oxidized carbon to introduce nitrogen by the hydrothermal method with ammonia as a nitrogen source. Preoxidation of carbon to produce functional groups and defects is essential to achieve high N content. Nitrogen in the carbon is primarily in the form of pyrrolic and pyridinic. XPS results shows the negative shift in the metallic Pd (0), and Pd (II) peaks for Pd/N-C compared with Pd/C. This shift confirms that N modifies the electronic properties of Pd acting as an electron donor. This electron transfer from N to Pd can alter the adsorptive characteristics of Pd, which can potentially help decrease CO or other species poisoning. Moreover, the presence of N in Pd/N-C is beneficial in producing small (3.6 nm) and well-dispersed Pd particles compared with Pd/C (4.22 nm). As a result, the ECSAs of Pd/N-C and Pd/C are 49.9 and 41.3 m^2g^{-1} , respectively. The peak mass activity for Pd/C-N is 1294 mA mg⁻¹ Pd, which is 2.23 times higher than that of Pd/C [197]. Chang et al. (2013) carried out nitrogen modification on acetylene carbon black by annealing acetylene carbon black with melamine under a nitrogen-gas environment at different temperatures. Pd/C-N formed by annealing at 900 °C shows an ECSA of 82.7, whereas Pd/C shows 56.6 m²g⁻¹. The peak mass activity is 1202 and 313 mA mg⁻¹ Pd, respectively, for Pd/C-N and Pd/C. The enhanced performance is primarily due to the formation of small and uniformly distributed Pd particles (3.5 nm) and strong electronic interaction between Pd and support [198].

5.2 Nitrogen-doped CNTs

Xin et al. (2015) studied palladium supported on nitrogen-doped CNTs as support material for FAO [199]. Nitrogen doping is carried out using a two-step process where pristine CNTs are treated with HNO₃, followed by the N functionalization with gaseous ammonia at 600 °C for 4 h. Pd nanoparticles supported on N-CNT are small (1.49 nm) and very well dispersed. Pd-N-CNT shows a negative shift in the Pd $d_{3/2}$ core level compared with Pd/CNT. XPS analysis confirms that N pyridinic, amino nitrogen, pyrrolic, and graphitic nitrogen are present in Pd/N-CNT. The Pd/N-CNT having low Pd content (2.4 wt% total content of Pd) showed a current activity of 550.5 mA mg⁻¹ Pd and an ECSA of 73.15 m²g⁻¹. After 50 cycles, it is able to retain around 70% of its initial peak current density. Therefore, nitrogen-doped CNTs increases the number of sites for anchoring the active metals and improves active metal dispersion and active metal–support interaction in electrocatalysts owing to the surface properties and electronic-characteristic modification of the support material.

5.3 Nitrogen-doped mesoporous carbon

Ray et al. reported nitrogen-modified 1D mesoporous carbon as a support material for Pd nanoparticles synthesized by the carbonization of palladium dimethylglyoximatre complex as a precursor at 400 °C for 1 h. TEM results confirm the presence of 20 nm-sized Pd nanoparticles dispersed in the mesoporous carbon support and a 3 nm-thick layer covering the Pd nanoparticles. Pd/N-C at 400 °C shows a surface area of 124.029 m^2g^{-1} with 1.82 nm pore size, whereas materials

carbonized at 300 and 500 °C have surface areas of 33.38 and 60.19 m²g⁻¹, respectively. ECSA for Pd/N-C 400 was 160.71 m²g⁻¹, which is higher than Pd/N-C300 (84.95) and Pd/N-C 500 (103.91). ECSAs over all catalysts are higher than that over Pd/C (59.4). Mass activity for FAO in alkaline medium is 525.7 mA mg⁻¹ Pd, which is almost five times larger than that of Pd/C with excellent stability. The improved performance is due to the high ECSA in the 1D porous structure and good donation of electrons from the nitrogen atom to the Pd atoms, as evidenced by the negative shift in the Pd3d_{5/2} peak of Pd/N-C-400 relative to that of Pd/C [200].

5.4 Nitrogen-doped G

G possesses a unique 2D structure of one-atom-layer thickness, having sp²-hybridized C atoms connected by conjugated C-C and C=C bonds. The conjugated single- and double-bond structure gives rise to delocalized π electrons over the sp²-hybridized carbons in the lattice [185, 186]. Doping of GO with nitrogen modifies the atomic charge density and the distribution of charges and spin density in the C-C sp²-hybridized G network to generate active centers. These active sites facilitate the anchoring of noble metals and the formation of a strong bond with the support [187, 196, 201-204]. Based on the C-N bonding configuration, nitrogen species in the G lattice are present primarily in three primary forms pyridinic, pyrrolic, and graphitic nitrogen [187]. The bonding arrangement and structure of the nitrogen species are shown in Figure 10. The three nitrogen species differ in the arrangement, bonding with the carbon atoms, and contributing to the π -delocalized electron in the carbon network. Pyridinic and pyrrolic nitrogen are bonded to two carbon atoms located at the edges or the vacancies. However, pyridinic N is joined to the hexagonal pattern, whereas pyrrolic N is bonded to the pentagonal ring. Graphitic or quaternary N is attached to the three sp²-hybridized carbon atoms of the ring [196, 205].

Several review papers dedicated to the synthesis and characterization of nitrogen-doped G, as well as its application for energy storage and conversion devices have been recently published [203, 204]. Moreover, the application of N-doped G for batteries [194], supercapacitors [193], and PEMFCs [128, 187, 206] have been reported.

Nitrogen doping of G can be carried out by CVD [207], thermal treatment [208], and chemical synthesis routes (hydrothermal [209], solvothermal [210], and microwave-assisted hydrothermal [211]). In the chemical process, nitrogen doping of G is carried out by treating GO with a nitrogen source such as ammonia [201, 206] and hydrazine hydrate [211, 212] through the hydrothermal process. GO undergoes partial reduction to rGO, and nitrogen is introduced to the structure simultaneously to result in nitrogen-doped rGO (N-rGO) in the one-pot hydrothermal synthesis. PtAg nanocrystals with hollow nanodendritic structure supported N-doped G has been synthesized by seed-mediated and galvanic replacement method. XPS characterization is carried out to identify the content of the different nitrogen species in the nitrogen-doped G. The XPS spectra of carbon, nitrogen, platinum, and silver are shown in Figures 11(a)–11(d). Deconvolution of the nitrogen peak shows three distinct peaks in Figure 11(b) associated with the nitrogen species on the G layer identified as pyridinic, pyrrolic, and graphitic nitrogen. Pyridinic. TEM images show highly dispersed nanodendrides with an average size of 53.8 nm dispersed over the nitrogen-doped G. The catalyst

shows excellent performance for FAO. The N-doped G support imparts synergistic and electronic effects from Ag, Pt, and N. Nitrogen doping also favors the adjustment in the electron transport of the support, thereby improving the support–metal interaction [213].



Figure 10. Various configurations of N atoms doped in the graphene layer [205].

Chowdhury et al. (2019) prepared PdCu bimetallic alloy nanoparticles (4 nm in size) supported on N-rGO by hydrothermal method. XPS analysis of Pd₇₅Cu₂₅/N-rGO confirms that oxygen and nitrogen are introduced into the structure of GO as a result of the synthesis process. Deconvolution of the nitrogen peak shows three distinct peaks associated with the nitrogen species on the G layer and identified as pyridinic, pyrrolic, and graphitic nitrogen. Pyridinic form of N is predominantly present with 63.7% of all the N species present. Pd₇₅Cu₂₅/N-rGO shows a high initial current density of 1738 mA mg⁻¹ Pd and is able to retain 70% of its original activity after 250 cycles. Chronoamperometry further confirms the high stability of Pd₇₅Cu₂₅/N-rGO [214].

Xu et al. (2018) synthesized nitrogen-doped G-supported PtAu intermetallic core with Pt dendritic shell using a novel synthesis route for the application as FAO electrocatalyst. The catalyst with composition Pt1Au1@Pt/NG shows the maximum mass activity of 1847.1 mA mg⁻¹ Pd, whereas unsupported Pt1Au1@Pt has the mass activity of 719.8 mA mg⁻¹ Pt. The excellent activity clearly shows the beneficial effect of the N-doped G as support material [215].



Figure 11. XPS spectra of (a) C 1S, (b) N 1S, (c) Pt4f, and (d) Ag 3d for Pt₁Ag₂/NG [213].

Jin et al. (2016) successfully prepared highly dispersed Pd and PdNi nanoparticles dispersed over G, carbon, and nitrogen-doped G. The average particle sizes for PdNi/NG, Pd/NG, and Pd/G are 1.6, 4.3, and 14.95 nm, respectively. XPS results confirm the formation of four types of nitrogen functional groups, namely, pyridinic, pyrrolic, graphitic, and oxidized N, with pyrrolic nitrogen having a significant contribution. The ECSA for Pd₁Ni₁/NG is 157 vs. Pd/G (72 m²g⁻¹). The highest current density for FAO is reported to exceed 709 mA mg⁻¹ Pd for Pd1Ni/NG. These results suggest that nitrogen-doped G support materials favor the formation of highly dispersed and narrow-sized small nanoparticles. Moreover, the addition of N atom to G leads to more zero-valent Pd and fewer Pd⁺⁺ in the catalyst during the catalyst synthesis owing to the transfer of an electron from N atom to Pd which modifies the electronic properties of the Pd nanoparticles to produce strong metal-support interaction. This modification results in enhanced resistance to CO poisoning of Pd and thus an improved performance [216]. Platinum and iron deposited onto N-rGO is prepared using a two-step process. The average size of PtFe nanoparticles is 3.7 nm. Electrochemical results show that the presence of nitrogen doping on GO makes FAO easier as indicated by the decrease in the oxidation peak potential [201]. Zhou et al. synthesized tungsten oxide-modified nitrogen-doped G supported Pd electrocatalysts. The catalyst shows excellent catalytic activity and stability for FAO, as shown in Figure 12 [217]. A similar performance has been reported for PdBi/NG [218].



Figure 12. (a) Cyclic voltammogram. (b) Stability of Pd/NRGO-WO₃ in 0.5 M HCOOH +1 M H₂SO₄ at a scan rate of 50 mV s⁻¹. (c) Chronoamperometry at 0.1 V in 0.5 M HCOOH +1 M solution [217].

The effects of nitrogen on the enhancement in the activities of Pd- or Pt-doped and nitrogendoped carbon materials for DFAFCs can be summarized as follows.

I. The electrical conductivity of nitrogen-doped G is superior to that of GO or G [200, 203, 208].

II. The nitrogen species in the nitrogen-doped G has been proven to control the nucleation and growth dynamics of noble metals to achieve small, well-dispersed nanoparticles [219, 220].

III. The proportion of zero-valent metal or metallic (M^o) species in the catalyst increases in the presence of nitrogen doping because of the electron-donating characteristics of N [221, 222].

IV. The synergistic interaction between the nitrogen-bearing support and metal modifies the electronic properties of the metal [219, 220, 222, 223].

V. The enhanced resistance to CO poisoning is due to the electron transfer from N to Pt, which decreases the energy density at the Fermi level, reduces the Pt-CO band energy, and weakens CO adsorption onto Pt [223, 224].

However, researchers are unsure which of the nitrogen species is responsible for the enhanced activity for oxidation reactions for methanol and formic acid. However, the pyridinic or graphitic

group may be responsible for the enhanced performance of catalysts containing more pyridinic N [223]. The electron-donating ability of the pyridinic N (having a lone pair of electrons) leads to the formation of Pt or Pd in the metallic form [224, 225].

6. PHOSPHOROUS-DOPED CARBON MATERIALS

6.1 Phosphorous-Doped Carbon

Phosphorous has the electronic configuration of $1s^22s^22p^63s^23p^3$ and the same number of valance electrons (five) as nitrogen. Phosphorous has a larger atomic size and lower electronegativity than nitrogen [176, 183, 185, 189]. Phosphorus-modified Pd supported on carbon has been synthesized using the self-redox method of sodium hypophosphite. The amount of P loaded carbon is low, and most of them are in the P₂O₅ states. Pd-P/C shows excellent stability compared with Pd/C [226]. Direct reduction of the precursor results in almost one-third elemental phosphorous. XPS results show that elemental phosphorous enters the lattice of Pd, thereby modifying the electronic structure of Pd. As a result, the phosphorus modification of carbon also shows enhanced FAO activity [226-228].

Jinfa et al. showed that nickel phosphide (Ni₂P) could effectively function as co-catalyst for Pd supported on carbon. Pd-Ni₂/C showed a high mass activity of 1.4 mAmg⁻¹. PdNickel phosphide has been experimentally shown to be not catalytically active for FAO. However, doping Ni₂P Pd can increase the activity manifold. The content of Ni₂P in the catalyst is crucial to achieving high performance. The optimum loading is found to 30 % Ni₂P on C. The polarization curves are shown in Figure 13a–13c. Pd–Ni₂P/C with 30% Ni₂P is found to exhibit the highest power density of 550 mW cm⁻², which is 3.5 times higher than the power density obtained for commercial Pd/C. Moreover, Pd–Ni₂P/C exhibits a more stable discharge ability at 0.35 V than other catalysts. Therefore, Pd–Ni₂P/C is a potential anode electrode material for DFAFCs [229].

Yang et al. studied the effect of synthesis temperature and the addition of phosphorous on the performance phosphorous-doped Pd/C catalysts [230]. Pd-P85/C catalyst synthesized at a higher temperature (85 °C) shows the maximum peak current density of 876.8 mA mg⁻¹ Pd with a -0.021 shift in the anode peak potential. The addition of phosphorus and elevated temperature during synthesis favors the long-term stability of the catalysts in chronoamperometry tests. Phosphorus can perturb the lattice structure of Pd and provide a bifunctional effect owing to PdP alloy formation. Conversely, higher temperatures tend to form smaller Pd nanoparticles, leading to increased ECSA and catalytic activity.



Figure 13. (a, b) Polarization curves and open-circuit voltage for Pd-Ni₂P/C catalysts in fuel cell. (c) Durability of the catalyst at 0.35 V [229].

6.2. Phosphorus-doped CNTs

Xin et al. (2016) doped CNTs with phosphorus by first treating it with HNO₃ followed by thermal treatment at 1000 °C in a H₂/He environment and in the presence of sodium hypophosphite. The metal loading Pd (3.2% wt) is low. Phosphorous partially replaces some of the oxygen functional groups. The strong interaction between palladium and phosphorous leads to the shift in the Pd $3d_{1/2}$ orbital binding. The peak current density is 694.6 mA mg⁻¹ Pd, which is 1.90 and 3.29 times higher than those of Pd/O-CNT and Pd/CNT. However, the catalysts loses 50% of its initial activity after only 50 cycles. Doping phosphorous to the carbon structure introduces a mismatch in the surface coordination owing to the different atomic sizes compared with the atoms in the vicinity, resulting in

defects and changes in charge distribution. The chemically and electronically changed surface leads to a stronger interaction with Pd nanoparticles. The low electron density on Pd caused by the electron transfer to phosphorous leads to weakened bond strength with COOH, so the surface coverage with (COOH)ad is reduced. Hence, phosphorous-doped CNT favors direct oxidation [228].

7. SULFUR-DOPED CARBON MATERIALS

7.1 Sulfur-doped CNTs

Sulfur shows electronegativity similar to that of carbon, so very little polarization of the S-C is observed. The defects in the network are due to the different bond lengths of S-C, and C-C [183, 186]. Ning et al. synthesized sulfur-doped CNTs through CVD by using thiourea as a sulfur source followed by annealing at high temperature 800 °C in an argon atmosphere. The data obtained from the XPS and Raman spectroscopy confirm the doping of S into the structure. The sulfur content of S-CNT is 0.95% (atomic). TEM results show that the Pt nanoparticles in Pt /S-CNT are less than 2 nm and have narrower size distribution than Pt/CNTs. The deconvoluted S spectra show the existence of thiophene (C-S-C at 164 eV) and C-SOX structure (168 eV). Thiophene interacts with Pt nanoparticles more extensively than does C-SO_X. The Pt4 $f_{7/2}$ peak shifts to higher values in Pt/SCNT. This higher shift is primarily due to the particle-size effect and not to the metal-support interaction. Smaller particles have higher binding energy for Pt4f_{7/2}. Pt supported on S-CNT prepared with a moderate amount of thiophene shows a current density of 9.06 compared with 0.75 mA cm⁻² for Pd/CNT. The promoting effect of sulfur is primarily ascribed to the activation and increase in the spin density of the neighboring carbon, which further improves the interaction with Pt and MSI, resulting in smaller and more finely distributed Pt nanoparticles, as well as a synergetic interaction between S-C-S and Pt nanoparticles [231].

7.2. Sulfur-doped mesoporous carbon

Ji et al. (2010) covered inner pores of OMC with a fine layer of sulfur through the meltdiffusion strategy. This strategy is used to modify CMK-3 with sulfur. The modified S-OMC is impregnated with Pt and PtBi by dissolving the precursors in aqueous ethylene glycol solution followed by heating in 7% H₂/Ar mixture for 4 h. The residual S is removed by the evacuation method at 300 °C for 6 h. TEM and XRD results confirm that Pt particles with mean atomic sizes ranging within 2.25 ± 0.5 nm are incorporated into the void space of S-OMC without damaging the welldefined pore structure of CMK-3. Moreover, the size and dispersion of the particles are sensitive toward heat-treatment temperature and duration. The cyclic voltammetry results in the formic acid solution for OMC-Pt-2nm (with S modification) show similar behavior to Pt/CMK-3. As expected, FAO over the monometallic Pt catalysts OMC-Pt-2nm and Pt/CMK-3 follows the dehydrogenation and dehydration processes, but the dehydration process is discouraged in S-OMC-Pt-2 nm. However, lower onset potential, lower peak potential, and higher mass activity have been reported for Pt/S-OMC-2 nm. The undesired dehydration process is entirely absent in FAO over PtBi/OMC catalysts. For PtBi/OMC with 3 nm particle size, a negative shift of 0.12 V in the onset potential compared with the Pt/OMC is observed. The catalyst PtBi/S-OMC-3 nm shows a mass activity of 770 mA mg⁻¹ Pt at a potential of 0.57 V and excellent stability [232].

7.3 Sulfur-doped G

Dual doping of nitrogen and sulfur incorporates dual functionalities into G. Nitrogen and sulfur are both doped simultaneously using 1,3,4-thiadiazole-2,5-dithol as a precursor and source of N and S through heat treatment at 700 °C in an inert environment, as shown in Figure 14 a. Nanosized Pd particles are anchored onto the composite support through a simple solvothermal process. Pd/N-SG shows mass activity of 501.8 mA mg⁻¹ Pd, which is about 3.5 and 2 times higher than those of Pd/C and Pd/G, respectively. The XRD and Raman spectra of the catalysts are shown in Figure 14 b and 14 c, respectively.



Figure 14. (a) Schematic of the synthesis of dual-doped G. (b) XRD patterns and (c) Raman spectra of the catalysts [233].

The higher performance of Pd/NS-G catalysts is ascribed to the following: (1) nitrogen and

sulfur favoring the formation of smaller and well-dispersed Pd nanoparticles, leading to more active sites and larger ECSA; (2) the large surface area and excellent electrical conductivity of G leading to high charge-transfer rate as evidenced by the low charge-transfer resistance in EIS; (3) nitrogen and sulfur electronically modifying the neighboring carbon atoms to increase spin density, leading to better electrocatalytic performance; and (4) the existence of S and N in the carbon network ensuring strong metal–support interaction [233].

8. FLUORINE-DOPED CARBON

8.1. Fluorine-Doped G

The atomic size of fluorine is smaller than that of carbon, but the former has higher electronegativity. Introducing fluorine into the G structure can change the electron distribution in the C-C network by strongly delocalizing the electrons. This modified charge distribution can influence the adsorption characteristics of the G and the active metal supported on it [234, 235]. Moreover, the interlayer distance in F-modified G is enlarged and new defect sites that can act as active sites are generated. It can also improve the corrosion resistance of the carbon support, thereby increasing the stability owing to the strong binding with the carbon atom of the highly electrophilic F atoms. Thus, the electrical conductivity and charge transport in fluorine-doped carbon nanomaterials increases. However, the greatest concern is the chemical hazards and toxicity associated with fluorine precursors and extreme process conditions [236, 237].

Shen et al. (2018) synthesized rhodium supported on fluorine-doped G using one-pot wet chemical approach with silicon nanowires as sacrificial template and 2% hydrofluoric acid under hydrothermal treatment. It is shown that catalyst with 4% by wt. F displays the best performance. The catalyst shows a negative shift in the onset potential for Rh/F-G (0.59) compared with Pt/C (0.83 V). The maximum mass activity is higher than that of 20% Pt/C. The increased catalytic activity is ascribed to the high surface area, abundant and uniformly distributed active sites, and strong metal–support interaction owing to the presence of F functional groups [238]. Electron-deficient Pd nanoparticles with twin structures are supported on semi-ionic fluorine-doped G. The twin structure is attractive as it contains defects, lattice strain, and high-energy atoms at the twin boundaries. The hydrothermal method is used to prepare surface electron-deficient Pd nanoparticles by using Si nanowires as a sacrifice template.

Figure 15 shows the details of the morphology of the twin structure.

Figure 15a shows the SEM image in which the characteristic ripple, like the structure of G, is evident, and metal nanoparticles are evenly dispersed. The TEM image and particle-size histogram of the catalyst (

Figure 15b–15d) show that the Pd nanoparticles have an average particle size of 17.5 nm.

Figure 15e and 15f show the theoretical model of the twin structure [239]. The misfit results from the improper superimposition of the 111 planes.

Table 1 summarizes the synthesis procedure, particle size, testing conditions, and electrocatalytic performance of the anode electrocatalysts based on different types of support materials for FAO in DFAFCs.



- **Figure 15.** (a) SEM image of Pd/F-GO–G. TEM image of Pd/F-GO at (b) low magnification, (c) high magnification, and (d) HRTEM. (e–f) Schematic of the twin structure [239].
- Table 1. Summary of the effect of support material on the performance of the electrocatalyst for DFAFCs

SN	Catalyst	Synthesis method	Particle size (nm)	ECSA (m ² g ⁻¹)	Peak current density/mass activity	Peak Potential	Ref.
1.	Pd icosahedra	Wet chemical reduction	17	11	$0.89 \mathrm{~A~mg^{-1}~Pd}$	0.6 V vs. RHE	[58]
2.	Pd/C (commercial)	_		13.3	237.6 mA mg ⁻¹ Pd	-	[80]
3.	Pt/C (40% wt. Pt) Commercial	-	3.5		173.7 mA mg ⁻¹ Pt	0.6 V vs. SCE	[81]
4.	Pt NPs/TPrA@VC- AC	Sonochemical double- reduction method	3.63	66.66	38.9 mA cm ⁻²	0.52 Ag/AgCl	[240]

5.	Pd/C	In situ synthesis	3.8	84.5	$1622 \text{ mA mg}^{-1} \text{ Pd}$	0.24 V vs. SCE	[76]
6.	Pd nanowires/C	Borohydride reduction method with PVP as surfactant	5 nm diameter	43.1 (49.8 for Pd/C commerc ial)	1.1 Amg ⁻¹ Vs 0.74 for Pd/C	0.2 V vs. Ag/AgCl	[74]
7.	Pd/CNT	Borohydride reduction method	13.3		0.18 mA cm ⁻² (33% loss after 300 cycles)	0.3 vs. RHE	[98]
8.	PdIr/CNT	EG-assisted NaBH ₄ reduction method	3.8		3365 mA mg ⁻¹ Pd	0.18V vs. SCE	[99]
9.	Pd/CeO2-CNT	Homogenous deposition precipitation followed by the borohydride reduction method	3.0	164.86	$2 \mathrm{A} \mathrm{mg}^{-1} \mathrm{Pd}$	0.3 V vs. Ag/AgCl	[102]
10.	Pd/HPMo-PDDA- MWCNTs	Impregnation method	3.1		945 mA mg ⁻¹ Pd vs. 373 for Pd/C	0.17 vs. Ag/AgCl	[101]
11.	Pd/MC	Nano-CaCO ₃ templated pyrolysis method followed by borohydride reduction method	3.0	18.9	595.2 mA mg ⁻¹ Pd	0.15 SCE	[114]
12.	Pd/CMK-8	Hard template method followed by the borohydride reduction method	4.5	287	486.4 mA mg ⁻¹ Pd	0.35 V vs. Ag/AgCl	[115]
13.	Pt-Bi/MPC	Impregnation	3.1		5.63 Amg ⁻¹ Pt	0.388 V vs. SCE	[117]
14.	Pd/CNF	Modified Turkevich method	3.67	-	$0.56~\mathrm{Amg}^{-1}~\mathrm{Pd}$	0.15 v vs. SCE	[167]
15.	PdCo/CNF	Electrospinning and thermal treatment	30	45.04	1.5 A mg ⁻¹ Pd	0.3 Ag/ AgCl	[169]
16.	Pd/G	Solution reduction using formic acid	4.3	56.0	$89.5 \text{ mA mg}^{-1} \text{ Pd}$	0.2 V vs. SCE	[152]
17.	Pd70Cu30@G	One-pot solvothermal method	2.3	64.1	1289.0	0.15 V vs. SCE	[155]
18.	PtAu/GO	Ethylene glycol reduction process	3.2	-	1.45	0.55 V vs. RHE	[157]
19.	Pd/N-C	Nitrogen-functionalized C by hydrothermal method with ammonia microwave-assisted ethylene glycol reduction process	3.6	49.9	1294 mA mg ⁻¹ Pd	0.22 V vs. SCE	[197]
20.	Pd/N-CNT	Impregnation method	1.49	73.15 m²/g	550.5 mA mg ⁻¹ Pd	0.38 V vs. SCE	[199]

21.	Pd/N-OMC	In situ carbonizing palladium dimethylglyoximate complex	20	160.71	525.7 mA mg ⁻¹ Pd	-0.38 V as Ag/AgCl	[200]
22.	PdCu/N-G	Wet chemical reduction process	4	73.39	1738 3.67 times higher than commercial Pd/C	0.15 V vs. SCE	[214]
23.	PtAu/N-G	An easy wet-chemical route	42 ± 6	12.35	1847.1 mA mg ⁻¹ Pd	0.2 V vs. SCE	[215]
24.	PdBi/N-G	Borohydride reduction method	4.64	26.83 m²/g	2025. 5 mA mg ⁻¹ Pd	0.3 5 V vs. SCE	[218]
25.	Pt/S-CNT	Chemical vapor deposition using thiourea followed by high-temperature annealing	2	390.3 cm ² /mg Pt	9.06 mA cm ⁻² compared with 0.75 for Pd/CNT	0.3 V vs. Ag/AgCl	[231]
26.	Pt-Bi/S-OMC	Melt-diffusion strategy	3		770 mA mg ⁻¹ Pd	0.57V vs. RHE	[232]
27.	Pd-P ₈₅ /C	Complexation–reduction method	3	44.38	876.8 mA mg ⁻¹ Pd	0.348 V vs. SCE	[230]
28.	Pd-P/O-CNT	Impregnation reduction with NaH ₂ PO ₂ as reducing agent	3-6	-	854.32 mA mg ⁻¹ Pd	0.097 V vs. SCE,	[241]
29.	Pd/NS-G	Thermal treatment process and solvothermal process	4.6	83.4	501.8 mA mg ⁻¹ Pd	0.1 V vs. SCE	[233]
30.	Rh/F-G	Sacrificial template metho	9.39		335.23 mA mg ⁻¹ Pt for 20% Pt/C	0.3 V vs. RHE	[238]
31.	Pd/F-G	Silicon wire template hydrothermal treatment	8-10	322	$0.697 \ { m A mg^{-1} \ Pd}$	0.55 RHE	[239]

9. CONCLUSION AND FUTURE OUTLOOK

Formic acid is a viable alternative to the hydrogen and methanol as anode feed for PEMFCs. The high cost of precious metals and the requirement of high loading hinder the commercialization of DFAFCs. Generally, supported electrocatalysts have been shown to improve the utilization of expensive precious metal-based catalysts. Apart from the active metals, support materials are a critical component of an electrocatalyst. The physical and chemical properties of support materials control the shape, size, electronic characteristics, amount of metal loading of the active metal, and the nature of metal–support interaction. Palladium supported on activated carbon is regarded as the state-of-the-art electrocatalyst for FAO. In recent years, many alternatives to activated carbon support have been explored in open literature because of their susceptibility to corrosion, limited porosity, and unsuitable surface properties.

CNTs, OMCs, and G are the most commonly researched carbon nanomaterials for FAO. The electrocatalytic performance of carbon nanomaterial-based electrocatalysts can be further improved by doping with a hetero atom, such as N, P, S, and F. Heteroatom-doped carbon materials increase the concentration of anchoring sites on supports for metals, enhance electrical conductivity, and show strong metal–support interaction s. The overall effect is to increase the mass activity, CO poison resistance, and long-term stability for FAO. Nevertheless, unresolved issues remain. First, the exact role and mechanism of activity enhancement of FAO reaction in the presence of heteroatom(s) are still not well understood. More theoretical and experimental studies should be conducted to improve the understanding of the mechanism of the reaction over heteroatom-doped carbon nanomaterials and thus identify the species that catalyze/s the oxidation reaction. Second, the optimum concentration of dopant in the support needs to be determined to achieve the highest performance. Third, the synthesis route to achieving the placement of doped metal on defects and edges should be developed.

Finally, more breakthrough works in synthesis and applied electrochemistry are required to completely exploit their potential as active electrocatalysts and supports for FAO. Metal–organic frameworks and perovskite are materials can also be explored as support materials for FAO electrocatalysts. Research and developments related to the support material must be conducted substantially to realize the large-scale deployment of formic acid fuel cells for mobile electronics and transportation applications.

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CONFLICT OF INTEREST

The author declares no conflict of interest in this manuscript.

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