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Carbon Based-Materials/Metal-Organic Framework for Catalytic Oxidation in Direct Borohydride Fuel Cell Application

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ABSTRACT

Metal-organic frameworks (MOFs), are known as novel types of crystalline materials formed by organic bridging ligands and coordination of metal ions. MOFs have unique characteristics such as high porosity, large surface area, and high structural durability. However, MOFs have some disadvantages such as having low stability, as well as electrical conductivity which causes their catalysis efficiency and application to be limited to a large extent. Thus, among the solutions made in previous studies, to overcome the disadvantages of this MOF is to combine it with carbon-based material to form a composite with better properties than pure MOF. This current review focuses on the performance of carbon-based material/MOF catalyst composites for direct borohydride fuel cell (DBFC) application. The catalytic oxidation of borohydride performance using carbon-based material/MOF catalyst is clearly and scientifically observed to enhance the catalytic activity in previous studies. There is no denying that carbon-based materials are widely used in fuel cell applications and have great advantages such as low toxicity, unique structure, good porosity properties, lightweight, controllable heteroatom doping, and easy processing, as well as excellent mechanical, chemical, and thermal properties. Thus, this review provides a summary of the application of carbon-based materials and MOFs with the properties and performance of this composite including the catalytic oxidation activity and DBFC potential for the entire system.

Keywords: Metal-organic frameworks; carbon, and graphene-based materials; direct borohydride fuel cell

INTRODUCTION

In this era, portable gadgets including notebooks, laptops, and cell phones are essential for new lifestyles. The durability of electricity through conventional batteries has limited portable device consumption (Shaari, Kamarudin & Zakaria 2019; X. Liu et al. 2012). Rechargeable batteries are a major source of energy for portable electronic devices. When using a rechargeable battery, has the disadvantage that the battery requires another source to recharge the electrical power. Therefore, it becomes a limitation to use rechargeable batteries because the energy source has a limited battery capacity (Velisala et al. 2015).

The disadvantages of this rechargeable battery have prompted many researchers to look for other alternatives and research to replace the battery technology with a more effective one. Batteries can be replaced with fuel cells because they are the most suitable source to power portable electronic devices. Fuel cells have practical benefits including being lightweight, greater energy density, compactness, and quick and easy to recharge with a replacement or a refilled fuel cartridge. Fuel cell technology has achieved high traction around the world (Velisala et al. 2015).

Direct liquid fuel cells (DLFC) are an attractive application. Many DLFCs are of concern to be studied in the literature, such as direct ethanol fuel cell (DEFC) and direct methanol fuel cell (DMFC). However, the fuel cell system has a poor kinetic reaction at the anode, causing the system to use many catalysts that can obtain catalysts of small power densities (Olu, Job & Chatenet 2016). Therefore, DLFCs have received much interest from researchers as it has some distinguishing characteristics, including high power density, low operating temperature, as well as high open circuit potential (Ma & Sahai 2018a).

Platinum (Pt)-based nanoparticle metals have offered a great deal of interest and are commonly used catalysts. It is also proved that Pt is an effective material for catalytic activity for borohydride oxidation (BOR) processes. Even so, the heavy price of Pt catalysts, poor kinetic oxidation, is impactful on single-metal Pt catalysts (Ramli and Kamarudin 2018). However, there is a reason why Pt cannot be used as a catalyst. This is because the reactions that take place in the hydrolysis activity have competed under certain conditions where 8 electrons per species of borohydride have been produced. In addition, fine Pt showed low potential direct oxidation of borohydride of 00.8 to 0.25 V vs Ag/AgCl where 7 electrons were generated resulting in the presence of hydride required on the surface of Pt. It is also proven to be an expensive material and has problems in kinetic reactions. Pt found in the system is also easily

poisoned by foreign species such as Carbon Monoxide (Ramli & Kamarudin 2018; S. Li et al. 2016). Carbon and graphene are widely employed as catalyst supports in a lot of fuel cells application. They appear to be appealing and functional additives due to the ability to design their qualities since it has great chemical and physical features, as well as large specific surface area (up to ~2,600 m^2g^{-1}), excellent electrical, mechanical, and thermal properties (Graś et al. 2021). Due to their highly customizable composition, pore size, and structure, metal-organic frameworks (MOFs) have proved a promising material in the creation of catalysts and precursors, attracting the interest of many researchers (Graś and Lota 2021). This review focuses on reviewing carbon and graphene-based materials/MOF as support catalysts to improve the catalytic activity in DBFC application.

BOROHYDRIDE ELECTROOXIDATION

Due to the great stability in a strong alkaline environment, direct borohydride fuel cells (DBFC) (Figure 1) were driven continuously through alkaline borohydride solution as anodic fuel. This potential anode is suitable for comparison with methanol oxidation reaction (MOR), ethanol oxidation reaction (EOR), and borohydride oxidation reaction (BOR), which is the fuel in DLFC. (Graś and Lota 2021; S. Li et al. 2016; Olu, Job, and Chatenet 2016). Besides, the DBFC system can convert the chemical energy found in oxygen ions (O_2^-) and borohydride ions (BH_4^-), which continue to be electrical through a process called the redox process (X. Liu et al. 2012; Ma & Sahai 2018b). Interestingly, in comparison to the hydrogen oxidation process, it causes a greater cell voltage, direct borohydride oxidation offers a far lower anode potential. DBFC is gaining popularity because of its low-temperature range and simple to recycle non-toxic materials (Graś and Lota 2021).

The borohydride oxidation process (BOR), which involves direct as well as complete 8-electron oxidation of the BH_4^- anion, is preferably the anodic reaction of the DBFC, as proposed in equation 1 below: (Olu, Job & Chatenet 2016)

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad (1)$$

The calculation of the standard potential of the BOR found in equation 1 is E_0 = -1.24 V and standard hydrogen electrode (SHE) at pH = 14. Practically, a perfect BOR competes with the hydrolysis reaction that occurs on heterogeneous and homogeneous BH_4^- ions where both the reaction happens on the surface of the catalyst, while oxygen is utilized as an oxidant (Olu, Job & Chatenet 2016). (Lafforgue 2020) concluded that the BOR mechanism takes distinct paths depending on the electrode potential: (i) at low potentials, -0.2 E 0.1 V vs. reversible hydrogen electrode (RHE), partial heterogeneous hydrolysis occurs, producing gaseous hydrogen (H_2) and BH_3OH^- (Equation 2), which is then electrooxidized according to Equation 3: (ii) at higher potentials, E > 0.4 V vs. RHE, direct BH_4^- electrooxidation occurs via a 6-electron reaction. The H_2 oxidation and direct BH_4^- oxidation events occur in parallel in the intermediate potential range (0.1 E 0.4 V vs. RHE).

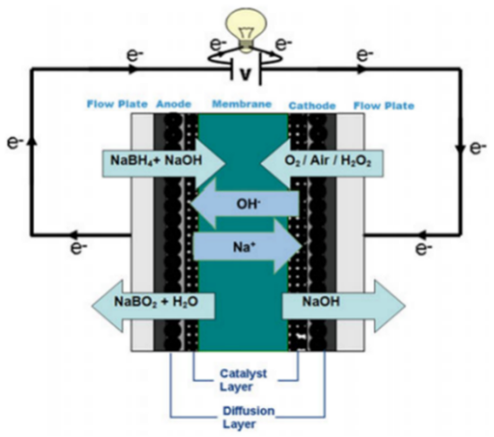

FIGURE 1. Schematic diagram of a DBFC (Ma and Sahai 2018a)

$$BH_4^- + H_2O \rightarrow BH_3OH^- + H_2 \quad (2)$$

$$BH_3OH^- + 3OH^- \rightarrow BO_2^- + 2H_2O + 3e^- \quad (3)$$

The predicted voltage of the DBFC is 1.64 V. The general reaction that occurs in the DBFC system is in equation 4 as below: (Olu, Job, and Chatenet 2016)

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O \quad (4)$$

Besides direct borohydride electrooxidation, hydrogen electrooxidation and borohydride hydrolysis also take effect. As a result, the BOR potential is mixed and the competition between these outcomes of the procedure in the creation of a large number of boron transitional species such as metallaboranes, carboranes, and metallacarboranes in terms of boron anode compound production, the electrochemical behavior of simple boron compounds, anodic and cathodic processes on boranes and boron anions, and electrochemical properties of compounds. In situ methods including rotating ring-disc electrode (RRDE), Fourier transformed infrared (FTIR), as well as on-line electrochemical mass spectrometry (OLEMS) have allowed the detection of BH_3^- based molecules including on a gold electrode, molecular hydrogen as BOR intermediates which is conforming to equation 5–7 as below: (Graś & Lota 2021).

$$BH_4^- + s + OH^- \rightarrow BH_{3,ads} + H_2O + 2e^- \quad (5)$$

$$BH_{3,ads} + OH^- \rightarrow BH_3(OH)_{ads}^- \quad (6)$$

$$BH_3(OH)_{ads}^- + 6OH^- \rightarrow BO_2^- + 5H_2O + 6e^- \quad (7)$$

MOF BASED COMPOSITE

Metal-organic frameworks (MOFs) (Figure 2) are a fascinating type of metal ion containing porous inorganic-organic hybrid materials or groups including polyfunctional organic ligands that have gained popularity in recent years due to major scientific interest as well as appealing applications. MOFs have been extensively studied as excellent precursors for the preparation of bi-transition metal phosphides because of their compositional diversity. In a carbonaceous matrix, the phosphating process is limited, and the regular holes of MOFs can successfully host nano-sized components while preventing agglomeration at high reaction temperatures (Lu et al. 2019). Furthermore, because of their distinctive qualities of modularly customizable structures, diverse functions, purity, high crystallinity, and customizable pore diameters, MOFs have been recognized as the most promising catalyst and precursors (X. Qin et al. 2019).

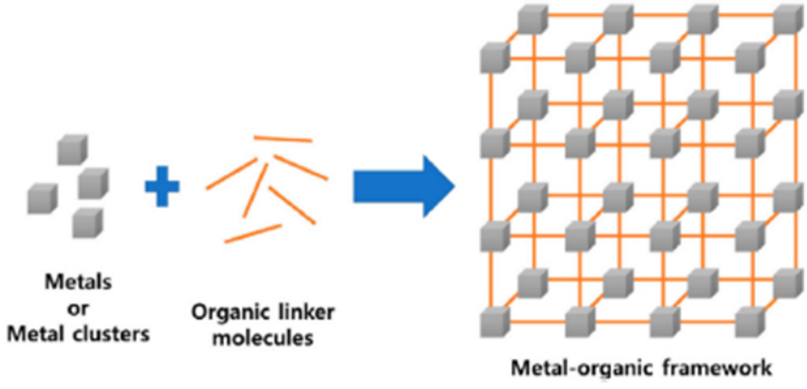

FIGURE 2. Structure of metal organic framework (Heo et al. 2020)

(X. W. Liu et al. 2016) stated the latter technique has piqued the interest of many scholars. In a comparison of previous with both procedures, the production of MOF-based composites with MOFs as well as other materials is as simple as it gets, where it is might combine the favorable features of the separate components while mitigating the undesirable downsides, resulting in synergistic action with new possibilities that the sole component would not ever have acquired to. MOF-metal nanoparticles, MOF-polyoxometalates, MOF-organic polymers, MOF-silica, and MOF-carbon composites have been successfully constructed.

CARBON AND GRAPHENE-BASED MATERIALS

MOF-carbon composites appear intriguing, which is MOFs are considered cutting-edge materials, but carbon-based materials are considered more traditional. (X. W. Liu et al. 2016). (J. Liu et al. 2014) produced the nanoporous carbon (NPC) via carbonizing of metal-organic framework-5 (MOF-5, $[Zn_4O(bdc)_3]$, bdc ¼ 1,4-benzenedicarboxylate) and carbon source which is furfuryl alcohol (FA), is applied as the anode catalyst provider in DBFC. Besides, using a modified $NaBH_4$ reduction technique, the NPC-supported Pt anode catalyst (Pt/ NPC) was synthesized. The outcomes proved Pt/NPC is composed of spherical Pt nanoparticles that are equally dispersed on the NPC's surface and have an average size of 2.38 nm, and Vulcan XC-72 carbon-supported Pt (Pt/XC-72) has a large recent density for directly borohydride oxidation. Furthermore, Pt/NPC electrocatalyst as anode exhibits a greater power density in DBFC.

(Xu et al. 2019) synthesized a mesoporous carbon-confined cobalt Co@C catalyst through pyrolyzing macroscale, which is a Co-metal organic framework (crystals) then utilizing it to stimulate $NaBH_4$ hydrolysis. Figure 3 depicts scanning electron microscope (SEM) pictures of the catalyst, whereas figure 4 depicts transmission electron microscopes (TEM) images of the catalyst. These findings indicate that the Co@C composite has remarkable morphological stability in alkaline reactant solution. In the conclusion, after the hydrolysis reaction, the Co nanoparticles preserve a high level of dispersion and crystallinity, demonstrating a good confinement effect of the MOFderived porous carbon to the metal nanoparticles. The carbon-confined cobalt Co@C composite also has remarkable morphological stability in the alkaline reactant solution. The novel cobalt spatial confinement of MOF-derived carbon matrix can reduce metal nanoparticle aggregation, resulting in good catalytic stability.

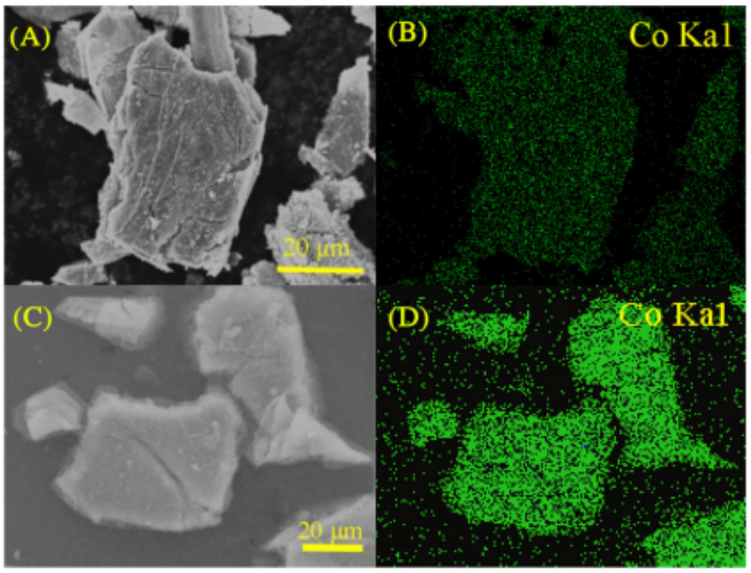

FIGURE 3. Carbon-confined cobalt SEM images and elemental maps: (A and B) fresh sample; (C and D) used sample (Xu et al. 2019)

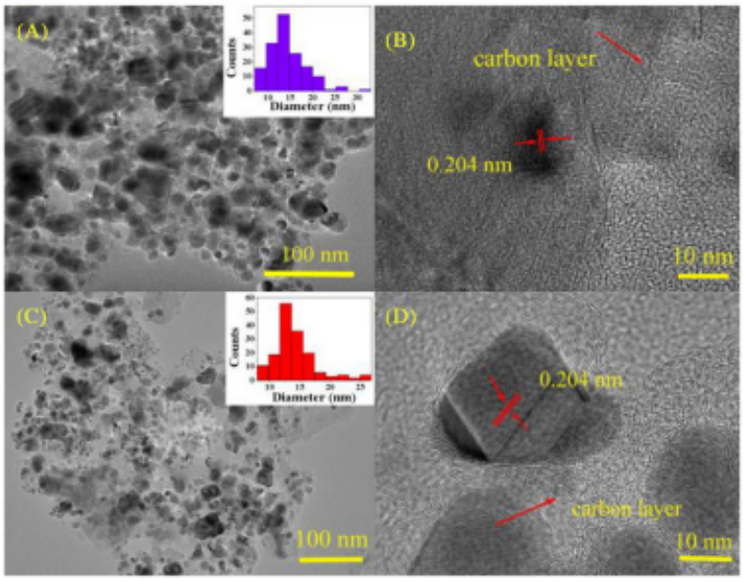

FIGURE 4. Carbon-confined cobalt TEM and HRTEM microscopic images: (A and B) fresh sample; (C and D) used sample (Xu et al. 2019)

(Ghasemi, Moghadas & Mohammadi 2020) stated that three Pd adorned Ni and Co catalyst nanoparticles were produced on reduced graphene oxide (rGO) substrates using a simple solvothermal technique. Borohydride oxidation reaction (BOR) activity and performance of produced electrocatalysts in the three-electrode and fuel cell configurations are examined using various electrochemical techniques. Pd_{10}-Ni_{45}-Co_{45}/rGO had the highest BOR activity among the produced catalysts. The findings of the DBFC test demonstrate that using Pd_{10}-Ni_{45}-Co_{45}/rGO nanoparticles as anodic catalysts increased the power density of the anode catalysts. These findings suggest that the competency of the operational technique for assembling nickel alloy electrodes can significantly improve the activity of the manufactured BOR catalysts. Figure 5 depicts the x-ray diffraction (XRD) pattern of Pd_{10}-Ni_{45}-Co_{45}/rGO indicating the formation of nickel and cobalt oxide, whereas Figure 6 depicts the transmission electron microscopy (TEM) image of the uniform distribution of Pd_{10}-Ni_{90}/rGO, $Pd_{10}Co_{90}$/rGO, and Pd_{10}-Ni_{45}-Co_{45}/rGO nanoparticles on graphene, respectively.

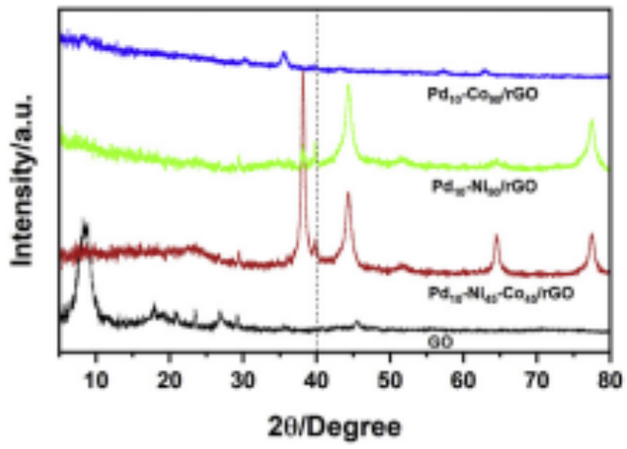

FIGURE 5. XRD patterns of the compounds (Ghasemi, Moghadas, and Mohammadi 2020)

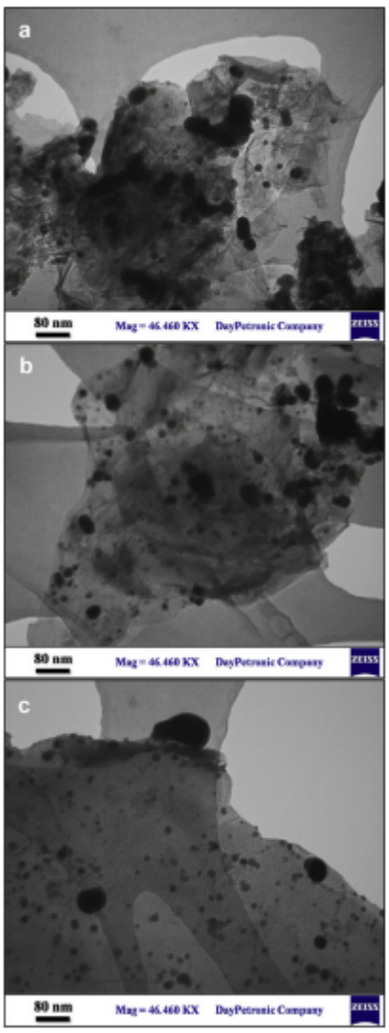

FIGURE 6. TEM images of the compound (Ghasemi, Moghadas & Mohammadi 2020)

CARBON AND GRAPHENE BASED MATERIALS AS SUPPORT CATALYST IN DBFC

Table 1 below shows a review of the comparative performance of different catalyst supports of the carbon and graphene-based materials in DBFC application including carbon black, activated carbon, carbon nanotubes, graphene, heteroatom-doped carbon, and MOF-derived carbon nanomaterials.

CARBON BLACK

Carbon blacks (CB) constitute spheroidal particles in distinct graphitic layer arrangements. This type of substance is often created through the pyrolysis of hydrocarbons. Commercially accessible carbon blacks which are Vulcan XC-72, black pearls 2000 are particularly common metal catalyst carriers in low-temperature FCs due to their excellent availability, conductivity, and low cost (Graś & Lota 2021). (Behmenyar& Akin 2014) used a modified polyol technique to create carbon-supported Pd with bimetallic Pd-Cu nanoparticles of variable compositional, functioning as anode catalysts in direct borohydride fuel cells (DBFC). The outcomes demonstrated that carbon-supported Pd-Cu bimetallic catalysts performed better catalytic activity for direct BH_4^- oxidation compared to carbon-supported pure nanosized Pd catalysts. (Duan et al. 2015) created carbon-supported Ni-Au with a core-shell nanoparticle's structure of (Ni@Au/C) via reverse microemulsion and two-step reduction. Ni@Au/C nanoparticles were produced and employed in direct borohydride-hydrogen fuel cells as anode electrocatalysts (DBHFCs). The particles have an average size which is around 10 nm. In direct borohydride electrooxidation, Ni1@Au1/C has the best catalytic activity among the resulting catalysts produced in this investigation. DBHFCs with an anode catalyst of Ni1@Au1/C and a cathode electrode of Pt mesh (1 cm^{-1}cm) produce a higher power density of 74 mW cm^{-2} as well as a density of emission current 130 mA cm^{-2} at 20 ^oC.

(Wang et al. 2012) fabricated carbon-supported Pt-Co nanoparticle catalysts (Pt-Co/C) with a crystallite size on average around 2 nm in ambient temperature aqueous solution using a modified $NaBH_4$ reduction process and applied as anode catalyst for direct borohydride fuel cell. The results demonstrate that Pt-Co/C as anode catalyst performs better than Pt/C catalyst in DBFC. For BH_4^- electrooxidation, the catalyst of Pt67Co33/C has the maximum catalytic activity amid as-prepared catalysts. At 25 °C, a single DBHFC with anode catalyst Pt67Co33/C with Pt/C as cathode catalyst achieves a higher power density of 79.7 mW cm^{-2}. In addition, (H. Qin et al. 2013) employed a wet chemical approach to creating carbon-supported silver nanowires, which is in DBFC, is employed as a cathode catalyst. Carbon supported silver nanowire catalysts outperform carbon-supported silver nanoparticles in the oxygen reduction process in alkaline conditions compared to commercial Ag/C. As a cathode catalyst, carbon-supported silver nanowires were used to improve cell performance and durability. Silver nanowires grow anisotropically with the open porosity. The microstructure has a role in structural stability, outcomes in enhanced electron transport characteristics, and fewer weak spots. It has benefits such as obtaining high durability and electrocatalytic activity. As a result, carbon-supported silver nanowire cathodes are attractive cathode catalyst options in DBFC.

ACTIVATED CARBON

All organic compounds containing elemental carbon could be utilized to make activated carbons, as is widely known as (AC). Natural leftovers produced by pyrolysis at high temperatures which is around 500 °C until 1000 °C as well as in an inert atmosphere, carbonaceous materials can be easily transformed. Furthermore, depending on the application, carbonaceous materials can be changed through physical or chemical activation. Physical activation at pyrolysis temperatures is performed whether by steam or CO_2. This approach is marked via low AC microporosity as well as a considerable reduction in raw material weight. Chemical activation enables the production of activated carbons with larger specific surface area (SSA) as well as at lower conversion temperatures, porosity increases. KOH is the most widely used activating agent. The chemical reaction of potassium compounds with carbon influences the activation mechanism. This approach is marked by low AC microporosity and a considerable reduction in raw material weight. Besides, it has been found that this method lowers the conductivity, as well as density of carbon electrodes, with the remaining reagents, must be removed (Graś et al. 2021) focused on enhancing hydrogen electrosorption by modifying anodes associated with multi hydrogen storage alloy with a low proportion of activated carbons derived from coffee waste. Pressure measurements showed their usefulness in terms of unconsumed hydrogen emission, which hampered fuel diffusion at first.

TABLE 1. A review of the comparative performance of different catalyst support of the carbon and graphene-based materials in DBFC application

Catalyst	Overview	Support catalyst	References
Carbon-supported Pt-Co nanoparticle catalysts	This paper focused on the production of carbon-supported Pt-Co nanoparticle catalysts (Pt-Co/C) with a crystallite size on average around 2 nm in ambient temperature aqueous solution using a modified $NaBH_4$ reduction process and applied as an anode catalyst for direct borohydride fuel cell. The results demonstrate that Pt-Co/C as anode catalyst performs better than Pt/C catalyst in DBFC.	Carbon black	(Wang et al. 2012)
Activated carbons differed in terms of their physicochemical properties due to the different coffee waste-to-KOH ratio (1 : 1–1 : 4)	This paper focused on enhancing hydrogen electrosorption by modifying anodes associated with multi hydrogen storage alloy with a low proportion of activated carbons derived from coffee waste in DBFC application.	Activated carbon	(Graś et al. 2021)
Monometallic CNT-supported Pd electrocatalysts (Pd/CNT)	This paper aims to produce monometallic CNT-supported Pd electrocatalysts (Pd/CNT) with different Pd loadings using the sodium borohydride ($NaBH_4$) reduction method to examine their $NaBH_4$ electrooxidation activities and resulting in increased $NaBH_4$ electrooxidation activity.	Carbon nanotubes	(Er et al. 2020)
Graphene-supported Pt (Pt/G) and NiPt (NiPt/G) nanoparticles	This paper aims to produce graphene-supported Pt (Pt/G) and NiPt (NiPt/G) nanoparticles through in situ chemical reduction of graphene oxide ions, Pt^{+4} and Ni^{+2}, and the anode catalyst was used to create direct borohydride-hydrogen peroxide (DBHPFC) fuel cells.	Graphene	(Hosseini et al. 2018)

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N-doped carbon-coated Co_2P-supported Au nanocomposite (Au/Co_2P@NC/C)	This paper focused on the production of N-doped carbon-coated Co_2P-supported Au nanocomposite (Au/Co_2P@NC/C) via a facile pyrolysis procedure. $Au_{(50)}Co_2P@NC_{(50)}/C$ exhibited the highest electrocatalytic activity for BOR.	Heteroatom-doped carbon	(Yi et al. 2011)
Nitrogen-doped carbon nanotubes with encapsulated cobalt nanoparticles	This paper focused on nitrogen-doped carbon nanotubes with encapsulated cobalt nanoparticles are manufactured here using co-pyrolysis of zeolitic imidazolate framework and nitrogen/carbon precursors with high N/C ratios and has the potential to be a cathode candidate for direct borohydride fuel cells (DBFC).	MOF-derived carbon nanomaterials	(Zhang et al. 2021)

Nonetheless, it has come to demonstrate the incorporation of activated carbons increased the anode's electrocatalytic activity, particularly during cyclic operation. Furthermore, X-ray photoelectron spectroscopy demonstrated that borohydride, a recognized reducing agent, reduced the carbon surface's oxygen functional groups over DBFC operation, this allowed for the elimination of one of the elements impacting BOR properties and, as a result, a more exact a review of the activated carbons was studied. In addition, (S. Li et al. 2011) demonstrated that carbon porosity composites generate hydrogen bubbles, which has a substantial impact on anolyte interaction on catalytic sites. It must be noted that surface chemistry, as well as pore size, have a major impact on the functioning of different types of fuel cells. Chemical and physical activation procedures allow the features of activated carbons (ACs) to be tailored to individual requirements.

CARBON NANOTUBES

Carbon nanotubes (CNTs) have a tubular three-dimensional (3D) shape that distinguishes them from other carbon compounds. They offer various qualities and advantages over other carbon materials, such as superior mechanical and chemical properties, high conductivity and particular surface area, and so on. As a result, carbon nanotubes have gradually replaced traditional carbon materials in fuel cells. Recent papers have proposed the use of carbon nanotubes as catalyst substrates in fuel cells (Y. W. Li et al. 2011). (Chen et al. 2015) demonstrated that N-doped hollow carbon nanospheres (HCNSs) can greatly increase the catalytic potential of CoO in a direct borohydride fuel cell (DBFC). Furthermore, (Er et al. 2020) produced monometallic CNT-supported Pd electrocatalysts (Pd/CNT) with different Pd loadings using the sodium borohydride ($NaBH_4$) reduction method to examine their $NaBH_4$ electrooxidation activities. According to the findings, 30 % of Pd/CNT catalyst had the maximum electrochemical activity. The catalyst surface electronic structure changes dramatically when the Pd loading is changed, resulting in increased $NaBH_4$ electrooxidation activity. As a result, Pd/CNT catalysts are promising anode catalysts for DBFCs. (Uzundurukan et al. 2021) used microwave-assisted synthesis to create carbon nanotube-graphene (CNT-G) supported PtAu, Au, as well as Pt catalysts to study the performance of direct liquid-fed sodium borohydride/hydrogen peroxide ($NaBH_4/H_2O_2$) fuel cells. At 50 °C, the PtAu/CNT-G catalyst outperformed the catalyst of Pt/CNT-G and the Au/CNT-G catalyst in terms of $NaBH_4/H_2O_2$ fuel cell performance. The improved $NaBH_4/H_2O_2$ efficiency increased due to the impacts of synergistic Au and Pt particles on the CNT-G support, which allows for higher catalyst utilization and interaction. These findings point to the produced PtAu/CNT-G catalyst as a potential anode catalyst for $NaBH_4/H_2O_2$ fuel cell applications.

GRAPHENE

Graphene is made up of a single layer of carbon atoms that form a two-dimensional (2D) sheet. Physical and chemical exfoliation methods, as well as epitaxial growth through chemical vapor deposition. As catalytic support, graphene outperforms in terms of stronger electrical conductivity, larger SSA, and extensibility. These nanocomposites are widely employed in various composites as electrocatalysts for the electrooxidation process of borohydrides (Graś & Lota 2021). (B. Li et al. 2019) established a novel anode material based on self-supporting graphene oxide foams for gold nanoparticles. Mechanism investigation revealed that the oxidation of $NaBH_4$ was a first-order reaction, with 7.2 electrons transferred at the constructed electrode. On the fuel cell that has been installed, a power density of 60 $mW \cdot cm^{-2}$ was reached in good stability. All of these findings suggest that the produced catalyst is an effective anode catalyst for DBFHCs. (Hosseini et al. 2018) produced graphene-supported Pt (Pt/G) and NiPt (NiPt/G) nanoparticles through in situ chemical reduction of graphene oxide ions, Pt^{+4} and Ni^{+2}. Due to the synergistic impact of Pt and Ni, the catalytic activity of PtNi/G against the electrooxidation of $NaBH_4$ is greater than that of Pt/G. Pt/G (0.5 $mgcm^{-2}$) as the cathode catalyst and NiPt/Gas as the anode catalyst was used to create direct borohydride-hydrogen peroxide (DBHPFC) fuel cells. The greatest power densities for 2 $mgcm^{-2}$ anodic loading were 64.9 $mWcm^{-2}$ at 60 ^oC, 1 M $NaBH_4$ and 2 M H_2O_2, with 60.4 $mWcm^{-2}$ at 60 ^oC, 1 M $NaBH_4$ and 2 M H_2O_2 for 1 $mgcm^{-2}$ anodic loading.

HETEROATOM-DOPED CARBONS

Conductive polymers which are known as electroactive conjugated polymers are becoming more popular since their potential in fuel cell electrodes as catalytic supports. In an inert atm, they carbonize and can produce certain carbon compounds, excluding polypyrol or polyyanillin, as well as nitrogen-containing carbon (Graś & Lota 2021). (Jin et al. 2016) used sol-gel synthesis to create nitrogen-doped carbon xerogels, which were then pyrolyzed in an ammonia 2 atm as well as post-treated. According to the findings, the catalyst with nitrogen-doped on the surface has an amorphous microstructure. Catalysts with and without post-treatment demonstrated nearly comparable oxidation-reduction reaction (ORR) electrocatalytic activity, demonstrating that metal removal does not effect on ORR performance. In an alkaline medium, post-treated catalysts demonstrated ORR activity equivalent to that of Pt/C, as well as better stability. It is also claimed to accomplish a greater power density of 115 mW cm^{-2} at 40 ^{o}C in a single cell using the catalyst manufactured as a cathode, demonstrating its application as a possible option for Pt-based electrocatalysts in direct borohydride fuel cells. (Yi et al. 2011) also stated that an N-doped carbon-coated Co_2P-supported Au nanocomposite ($Au/Co_2P@NC/C$) was synthesized via a facile pyrolysis procedure. $Au_{(50)}Co_2P@NC_{(50)/}C$ exhibited the highest electrocatalytic activity for BOR.

MOF-DERIVED CARBON NANOMATERIALS

A metal-organic framework (MOF) is a structure made up of metals and organic compounds that have recently been demonstrated to be an optimum sacrifice template for the fabrication of a variety of carbon-based nanomaterials, such as heteroatom-doped porous carbon, porous carbon, and metal-decorated porous carbon. Thermal breakdown of carbon/metal in a controlled environment (Shen et al. 2016; Graś & Lota 2021). The nanoporous carbon had a high specific surface area (3040 m^2g^{-1}) and homogeneous pores. Its structural characteristics can also be easily regulated during low-cost thermal breakdown. It is widely assumed that encapsulating metal nanoparticles in a carbon structure has a synergistic impact, as well as influences corrosion resistance. MOF-derived nanocatalysts are the most promising candidates, and they are commonly employed in the fabrication of electrode materials that act as catalysts for energy storage, conversion, and supercapacitors. Due to its exceptional qualities, it has also emerged as a promising catalyst (Graś & Lota 2021). (Luo et al. 2019) stated that the catalysis of $NaBH_4$ hydrolysis is studied utilizing single earth plentiful Co, Fe, Cu, as well as Ni nanoparticles supported by a metal-organic framework (MOF), ZIF-8. In this series, CoNPs@ZIF-8 seems to become the most discriminating as well as the effective catalyst. (Zhang et al. 2021) prepared nitrogen-doped carbon nanotubes with encapsulated cobalt nanoparticles using co-pyrolysis of zeolitic imidazolate framework and nitrogen/carbon precursors with high N/C ratios. These precursor-dependent materials are used as catalysts in the hydrogen peroxide (H_2O_2) and oxygen reduction reactions (ORR). The findings of electrochemical measurements indicate a substantial link between N-doped types and electrochemical performance. The proposed ZU catalyst (urea as an N-rich precursor) performs optimally in terms of ORR and H_2O_2 detection. Furthermore, this catalyst has the potential to be a cathode candidate for direct borohydride fuel cells (DBFC). The synthesis technique provides new insight into the development of effective non-noble-metal catalysts for electrochemical applications.

CONCLUSION AND FUTURE PERSPECTIVE

Liquid fuels such as borohydrides are among the materials that serve as fuel for DLFC without any renewal process. Even at room temperature, direct borohydride fuel cells produce electricity. The product's and reagents' safety makes it appealing for mobile applications. However, there are some drawbacks that prevent this type of FC from being commercialized, such as the reduction of high fuel performance due to the hydrolysis process. The development of anode catalyst electrocatalytic activity without diminishing the surplus potential for hydrogen evolution is critical to success. This is especially significant since catalysts with high excess efficiency for hydrogen evolution typically improve a strong anodic polarisation decrease during borohydride electrooxidation.

To summarize this research, it can be concluded that carbon-based materials/MOF get much attention to further development in fuel cell applications, especially in direct borohydride fuel cells. Because they have the option of customizing their possessions, they seem to be functional additives and attractive as it has extraordinary chemical and physical features including remarkable electrical, large specific surface area, mechanical and thermal properties. Furthermore, MOF has emerged as a promising material for the synthesis of precursors and catalysts. It has many positive characteristics, including a large specific surface area, high porosity, tunable architectures, tunable pore sizes, high crystallinity, and flexible functioning.

This review recommended carbon-based materials/MOF presented some information on this topic, including MOF-based composites and the role of carbon and graphene in DBFC, which is catalyst support. These materials work admirably as bi-functional electrocatalysts for DBFC applications. There are several types of support catalyst which is activated carbon, carbon black, carbon nanotube, heteroatom-doped carbons, graphene, and MOF-derived carbon nanomaterials. The incorporation between carbon and graphene with MOF also helps to create efficient and potentially useful catalysts. Furthermore, as a class comprising MOF design and exceptional crystalline characteristics, potential and produce efficient catalysts. Hence, as a class comprising MOF design and exceptional

crystalline characteristics, carbon and graphene-based materials/MOF should be investigated further because they have improved the efficiency of fuel cell applications. This review also suggests that integrating the two materials can be a potential candidate for electrode catalysts in direct borohydride fuel cells.

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DECLARATION OF COMPETING INTEREST

None

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