Recent advances in the development of carbon-based catalyst materials for fuel cells

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ABSTRACT

In recent years, the development of catalytic materials to enhance the efficiency of hydrogen energy conversion in fuel cells has become a primary focus in global scientific research. Platinum (Pt) and its alloys are widely used in fuel cells due to their superior catalytic properties; however, their high cost and scarcity limit broader application. Replacing Pt with carbon-based materials in fuel cell catalysts offers a promising pathway to reduce costs and enhance sustainability. Consequently, recent studies have shifted toward exploring non-precious metal catalysts based on carbon materials, which are of significant interest for their diverse applications and potential as viable alternatives to reduce amounts of Pt catalysts. This report presents and examines recent advancements in Pt-carbon hybrid catalysts for fuel cell applications, highlighting their synthesis, structural characteristics, and performance in hydrogen energy conversion.

Keywords: Catalysts; Fuel cells; Carbon-based materials; Electrochemical.

1. INTRODUCTION

Fuel cells are promising energy conversion devices that offer high efficiency and environmental benefits by generating electricity through the electrochemical conversion of fuels, such as hydrogen, into water. Central to their operation are electrocatalysts, which play a crucial role in driving key reactions, such as the oxygen reduction reaction (ORR) at the cathode and the hydrogen oxidation reaction (HOR) at the anode. Traditionally, platinum (Pt)-based catalysts have been the gold standard due to their unparalleled catalytic activity and stability. However, the high cost, scarcity, and susceptibility to degradation of Pt have spurred significant research into alternative materials to reduce dependency on this noble metal.

Carbon-based materials have emerged as a versatile and cost-effective class of electrocatalysts for fuel cells. These materials-ranging from activated carbons and carbon nanotubes (CNTs) to graphene and nitrogen-doped carbons-exhibit remarkable properties, including high surface area, electrical conductivity, and chemical stability. In addition to serving as supports for Pt nanoparticles, carbon-based materials can act as standalone electrocatalysts when properly functionalized. Their tunable structure and surface chemistry allow for the incorporation of heteroatoms (e.g., nitrogen, sulfur, boron) or transition metal species, which enhance their intrinsic catalytic activity for the ORR and other reactions.

The use of carbon-based materials for electrocatalysts in fuel cells offers several advantages, including reduced cost, improved sustainability, and the potential for enhanced durability. By replacing or partially substituting Pt with carbon-based catalysts, researchers aim to create affordable and efficient fuel cells that can accelerate the adoption of clean energy technologies. This field represents an exciting intersection of materials science, catalysis, and energy technology, with ongoing advances pushing the boundaries of performance and practicality. In the following, several types of carbon-based materials used to support the electrochemical reaction in fuel cells are introduced.

2. CARBON AEROGEL-BASED ELECTRODE MATERIALS

Carbon aerogel (CA) is considered a highly promising electrode material for energy storage and conversion applications in fuel cells, supercapacitors, and batteries due to its inherent properties, including a high specific surface area (SSA), large pore volume, excellent electrical conductivity, and outstanding chemical, mechanical, and thermal stability [1]. Additionally, it can be synthesized from bulk cellulose, which is a naturally abundant and low-cost biopolymer [2]. Yang and colleagues developed nitrogen-doped CA (NCA) via the pyrolysis of polyacrylonitrile at controlled temperatures ranging from 600 to 900 °C [3]. The resulting material was applied to ORR in microbial fuel cells (MFCs). In MFCs, organic waste is oxidized into electrons and protons at the anode by microbial activity, while oxygen is reduced to water at the cathode. The NCA catalysts served as cathode materials in the MFCs and demonstrated effective catalytic activity for ORR in a 0.1 M NaOH solution. Nitrogen doping created active sites and enhanced catalytic activity. The onset potential (E_onset) was recorded at +0.81, +0.82, +0.85, and +0.84 V for synthesis temperatures of 600, 700, 800, and 900 °C, respectively, with the best-performing catalyst synthesized at 800 °C (NCA-800). A maximum power density of 1048 ± 47 $mW\ m^{-2}$ was achieved using the NCA catalyst in MFCs, comparable to that obtained with commercial Pt/C catalysts (1051 ± 28 $mW\ m^{-2}$).

Porous NCA structures can be synthesized through two distinct methods using NH_4OH and NaOH as environments, via the pyrolysis of cellulose aerogels derived from coconut fiber [4]. Interestingly, these methods yield CAs with entirely different pore sizes, as shown in figure 1. SEM images clearly depict that the original material (cellulose fibers) has a cylindrical shape with numerous internal pores. The pore size and wall thickness of the raw material are approximately 3 µm and 3.2 µm, respectively (figure 1.1a). Under NaOH conditions, a relatively large internal pore is produced with a broken wall structure (figure 1b). In contrast, carbon aerogel derived from the NH_4OH system displays a stable structure with larger internal pores than those produced under NaOH pyrolysis (figure 1c). This suggests that ammonia not only contributes to cellulose dissolution but also induces defects within the carbon aerogel, resulting in aerogels with higher SSA and pore volume. The initial pore size of the cellulose aerogel was 200 µm, which decreased to 150 µm and 176 µm for carbon-NaOH and carbon-NH_4OH aerogels, respectively. Overall, the active SSA and pore volume increased from 70 to 3730 $m^2.g^{-1}$ and 0.54 to 4.20 $cm^3.g^{-1}$ when using NaOH and NH_4OH, respectively.

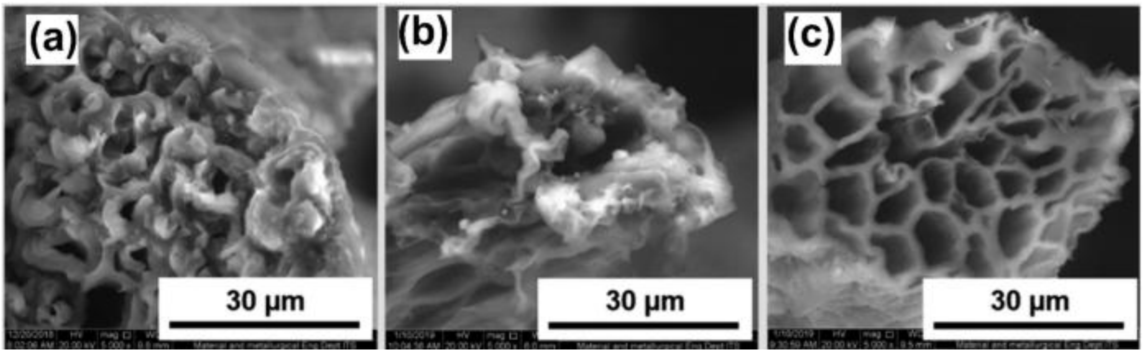

***Figure 1.** SEM images of aerogel (a) cellulose, (b) carbon-NaOH, and (c) carbon-NH_4OH aerogel [4].*

Another study [5] utilized similar precursors to synthesize carbon aerogels (CAs) for hydrogen storage applications. Na_2CO_3 is commonly used to dry wet catalysts, though it causes the catalyst to shrink. To prevent this issue, the study employed an organic drying agent, triethylamine (TEA). BET measurements indicated that the optimized catalyst (CA-1000) exhibited a specific surface area of 545.03 $m^2.g^{-1}$, a pore volume of 0.271 $cm^3.g^{-1}$, and a pore size of 1.96 nm, achieving a hydrogen storage capacity of approximately 4.0 wt%.

Cobalt atoms (Co-NCA@F127-1) were atomically dispersed on a chitosan template [6]. The polymeric material was synthesized by reacting p-aminophenol and F with hexamethylenetetramine (HMTA) under acidic and high-temperature conditions, after which the resulting polymer was coated onto the chitosan template. To obtain a Co^{2+} phenolic/hydrogel composite material, Co ions were chelated with the polymer containing functional groups such as −OH, $-NH_2$, and −COOH. The surfactant poloxamer (F127) was added to the mixture to improve mechanical stability and control the morphology and pore structure of the CAs. The morphology of the CA was analyzed by transmission electron microscopy (TEM), revealing a coral-like 3D structure. The ORR activity of the developed Co-NCA@F127-1 was investigated under alkaline conditions, and its catalytic performance was compared to that of commercial Pt/C as shown in figure 2. We can see that Co-NCA@F127-1 exhibits voltages of 0.935 V and 0.805 V versus RHE, respectively, which is nearly 128 mV higher than NCA. Moreover, regarding the limiting diffusion current density, Co-NCA@F127-1 (5.96 mA cm^{-2}) is better than commercial Pt/C (5.21 mA cm^{-2}).

3. CARBON NANOFIBER-BASED ELECTRODE MATERIALS

Nanoscale carbon materials, including zero-dimensional (0D) carbon dots and quantum dots, one-dimensional (1D) carbon nanotubes (CNTs), and two-dimensional (2D) graphene, have garnered substantial interest from researchers in recent years [7]. Previous studies have shown that the size, structure, shape, and functionality of carbon nanofibers (CNFs) play a crucial role in their applications across various fields, including materials science, nanotechnology, energy storage, biomedicine, tissue engineering, and environmental science [8]. Recent research has indicated that porosity significantly influences fuel cell performance, with high porosity facilitating the smooth passage of materials through fiber layers without obstruction [9]. CNFs are a promising alternative as their production technology can be readily scaled up for industrial applications. Moreover, CNFs are approximately 2 to 3 times more affordable than single-walled or multi-walled carbon nanotubes (SWCNTs or MWCNTs) [10]. Notably, CNFs are used as electrode materials in fuel cells [11], and have proven effective in microbial fuel cells (MBFC) [12], direct methanol fuel cells (DMFC) [13], direct ethanol fuel cells (DEFC) [14], membrane fuel cells (MFC) [15], and proton exchange membrane fuel cells (PEMFC) [16].

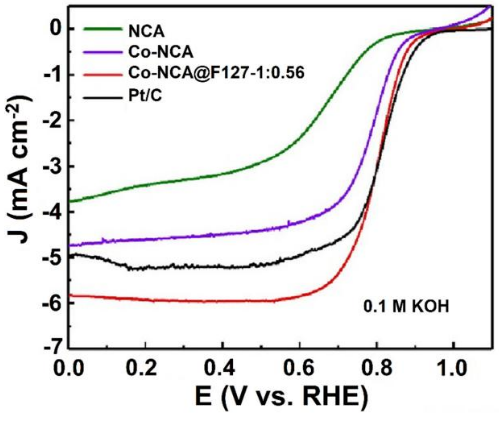

Figure 2. *Dependence of diffusion current density on the potential of NCA, Co-NCA, Co-NCA@F127-1, and Pt/C in 0.1 mol L^{-1} O_2-saturated KOH solution at a scan rate of 10 mV s^{-1} and a rotation speed of 1600 rpm [6].*

However, a limitation of CNFs is their restricted surface area (less than 200 $m^2.g^{-1}$), which poses challenges for dispersing metal nanoparticles (MNPs) on the CNF surface. A high metal concentration is required in practical fuel cell electrodes (20–60 wt%). The metal concentration must be sufficient to create a thin catalytic layer with a high density of active sites. However, maintaining a uniform dispersion of ultra-fine MNPs, along with strong resistance to corrosion, is critical for the catalyst's durability. Electrochemical corrosion is closely linked to surface area and the presence of defects in the graphite structure. Therefore, it is crucial to establish efficient preparation processes capable of achieving good metal dispersion on low-surface-area supports while enhancing the resilience of the metal phase.

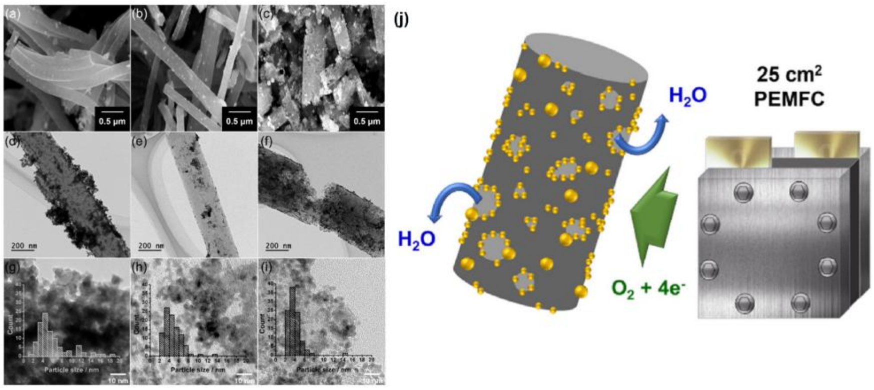

Figure 3. *(a – c) FE-SEM, (d – f) TEM, and (g – i) HR-TEM images of Pt/CNF, Pt/ GCF-HT và Pt/GCF- (Co), (j) Illustration of Pt catalysts on meso/macroporous graphitized in PEMFC cathode [17-20].*

Various CNF structures, such as porous [17], hollow [18], twisted [19], and stacked configurations [20], have been synthesized through different experimental methods. By adjusting the chemical composition of the combined or doped materials and modifying structural characteristics, it has been possible to create a wide range of multifunctional CNF-based nanomaterials with tailored chemical and physical properties. CNF materials have been produced using various techniques, including catalytic chemical vapor deposition (CCVD), arc discharge, and laser ablation. Among these, arc discharge and laser ablation produce high-purity CNFs, requiring large-scale operations and significant production costs. Since these technologies rely on carbon electrodes, they are not suitable for large-scale production in the long term. However, for many applications, reducing costs for mass production is necessary. Pt catalyst on graphitized CNF exhibits excellent catalytic activity and durability for ORR. Various Pt catalyst forms such as Pt/CNF, Pt/GCF-HT, and Pt/GCF-(Co) have been thoroughly studied in the context of ORR catalysis. By heat treatment, graphitized CNFs lead to the formation of unique porous structures. This can further expand the surface area, thereby providing more reaction sites. The morphology of the Pt catalyst was examined through high-resolution FE-SEM, as shown in figure 3(a – c). The Pt NP particles were clearly loaded on carbon supports made from fibers with a thickness of 250 nm. Morphological studies revealed that Pt was uniformly deposited on the Pt/CNF and Pt/GCF-HT material systems, while Pt/GCF-HT(Co) exhibited porous characteristics. Figures 3(d-f) demonstrate that Pt particles aggregated on CNF supports, while evenly dispersed on GCF-GCF-(Co). Compared to Pt/CNF and Pt/GCF-HT, the size of Pt NPs was reduced and dispersed on GCF-(Co) as evidenced by HR-TEM images. This is clearly shown in figures 3(g-i). The average particle sizes determined for Pt/CNF, Pt/GCF-HT, and Pt/GCF-(Co) were found to be 6.0, 4.7, and 3.9 nm respectively. Regarding PEMFC performance, Pt/GCF-(Co)-HT achieved a higher maximum power density of 0.85 W cm^{-2} in an active area of 25 cm^2 for a low loading of 0.1 mg Pt cm^{-2}. The Pt catalyst incorporated with graphitized carbon in the PEMFC cathode; the 25 cm^2 size of a single cell is schematically represented in figure 3(j).

4. GRAPHENE-BASED ELECTRODE MATERIALS (GR)

Among various nanomaterials, graphene (GR) and its compounds possess unique chemical, electrical, and mechanical properties, making them suitable catalysts for fuel cells. In recent years, numerous studies have focused on optimizing graphene-based materials for fuel cell applications. Graphene-based materials are excellent electrocatalysts as they increase the number of active sites and facilitate electron transport for both fuel oxidation and the oxygen reduction reaction (ORR).

Due to their high activity, superior corrosion resistance, and cost-effectiveness, non-metal graphene materials have emerged as promising candidates for ORR applications [21]. Structural modifications, such as electronic structure tuning, doping, heterostructuring, or functionalizing graphene, further improve fuel cell performance [22].

Incorporating graphene-based materials into polymer membranes can enhance ionic conductivity [23]. Polymer membranes containing graphene are regarded as fillers/additives due to their high proton conductivity and water resistance [24]. Beyond electrolytes and electrodes, GR-based materials can increase current density and maintain high stability [25]. Graphene has a unique atomic structure, consisting of a one-atom-thick layer of sp^2-bonded carbon atoms arranged in a hexagonal lattice [26]. Graphene-based materials include graphene oxide (GO), reduced graphene oxide (rGO), doped graphene, functionalized graphene, and three-dimensional graphene (3D). The use of graphene in fuel cells provides several advantages. Specifically, graphene-based materials offer high ORR activity, serving as electrocatalysts for fuel oxidation due to their high surface area and conductivity. Additionally, incorporating graphene into polymer membranes enhances ionic conductivity, tensile strength, and reduces fuel permeability [27].

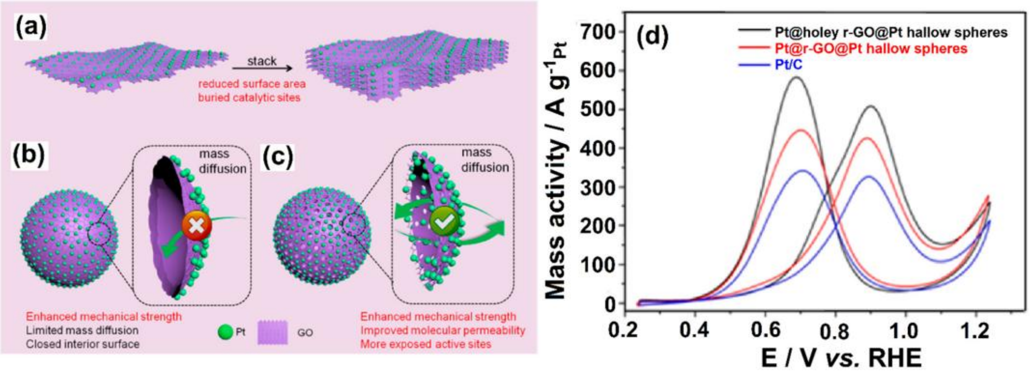

Figure 4. *Illustrative model of (a) 2D-GO/Pt NP, (b) 3D-GO Pt @ r-GO @ Pt hollow nanoparticles, and 3D-Pt @ rGO nanospheres, (c) @ Pt hollow nanospheres, and (d) Normalized Pt mass CV curve in 0.5 mol* L^{-1} N_2*-unpurged* H_2SO_4 + CH_3OH *solution with a scan rate of 50 mV.s*$^{-1}$ *from [28].*

The conductivity and corrosion resistance of electrodes can also be improved by combining graphene with other electrode materials. Qiu and colleagues [28] used spherical SiO_2 nanoparticles to create hollow 3D rGO nanospheres loaded with Pt nanoparticles inside and outside (Pt@rGO@Pt nanospheres) as shown in Fig. 4. The mass activity for the methanol oxidation reaction (MOR) was 1.3 and 1.7 times higher than that of hollow Pt@r-GO@Pt and commercial Pt/C, respectively, due to increased mechanical strength, enhanced mass diffusion, and improved contact sites. Notably, functionalizing graphene with additional atomic groups provides more contact sites for metal nanoparticles, significantly improving activity and durability in ethanol oxidation reaction (EOR). For instance, Yang and colleagues used a diazo process to produce aniline-functionalized graphene, which binds Pd nanoparticles for EOR. The mass activity of the aniline-functionalized catalyst (43.1 mA.mg^{-1}) was nearly five times higher than that of the non-aniline-modified catalyst (8.9 mA.mg^{-1}) after 7200 seconds of testing. This improvement was due to the well-dispersed Pd nanoparticles and enhanced bonding between the aniline groups and Pd. Additionally, 3D graphene structures can facilitate ethanol transport by reducing agglomeration and increasing catalyst activity.

5. CARBON NANOTUBE-BASED MATERIALS

Single-wall carbon nanotubes (SWCNTs) have become one of the most versatile materials due to their remarkable properties, including their unique structure, superior mechanical and electrical properties, low processing costs, high optical transparency, large specific surface area (SSA), and excellent catalytic capabilities. They typically have diameters ranging from 0.7 to 10 nm. Structurally, SWCNTs consist of a single graphene sheet rolled into a cylindrical tube. Thin Pt catalyst layers deposited on SWCNT substrates can facilitate better transport in direct methanol fuel cell (DMFC) applications. Composite materials like Pt-Ru/SWCNT and Pt-Mo/SWCNT are prepared using chemical reduction, in which the electrocatalysts are annealed for 2 hours at 400 °C in an N_2 atmosphere. The synthesized Pt-Ru/SWCNT composite exhibits improved current density and power output compared to Pt/SWCNT catalysts [29]. Rajala and colleagues fabricated Pt nanowires on SWCNTs (PtNWs/SWCNTs) [30]; these PtNWs/SWCNT catalysts were pretreated with ozone, introducing polar surface groups onto the SWCNTs. The synthesized PtNWs/SWCNT-O_3 composites were more hydrophilic than their non-ozonated counterparts, attributed to the increase in oxygen-containing groups in the catalyst during ozone pretreatment. Hu’s team found that encapsulating catalytically active iron and potassium metal nanoparticles in the SWCNT catalyst enhanced ORR electrocatalytic activity [31]. Furthermore, Wu and Xu demonstrated that, compared to Pt supported on MWCNTs and SWCNTs, the Pt-SWCNT/NAF catalyst displayed significantly enhanced power density, lower onset potential, higher CO-tolerance, and a higher abundance of oxygen-containing functional groups in methanol electrooxidation [32].

In recent years, electrode nanomaterials based on multi-walled carbon nanotubes (MWCNTs) have attracted significant research interest worldwide due to their intriguing electrical, mechanical, thermal, and optical properties. In 1991, Sumio Iijima developed carbon nanotubes from fullerene using the arc discharge method [33]. MWCNT-based electrocatalysts have contributed to a wide range of electrochemical applications, including electrochemical sensors, gas sensors, and energy storage devices. MWCNTs are cylindrical carbon-sp² structures, with diameters ranging from 3 to 30 nm and lengths of 40 to 50 nm. They consist of single graphene sheets wrapped in multiple layers, with an outer diameter of approximately 2 nm. MWCNTs remain highly promising candidates for advancing energy conversion and storage technologies.

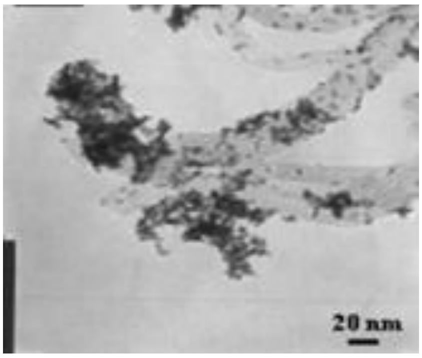

Figure 5. *TEM images of Pt/MWCNT [35].*

Recent studies have developed composite materials, such as porous polyaniline/MWCNT-based materials with Co_9S_8 (Co_9S_8 + PPANI/MWCNT), which can function as next-generation electrochemical hydrogen storage devices with a discharge capacity of 689.2 mAh.g^{-1} [34]. Dogan and colleagues synthesized hexagonal boron nitride-conjugated polymers with MWCNT (h-BN-Ph-NH-CO-MWCNT) through coupling, acylation, and oxidation processes. These electrode materials exhibit strong van der Waals interactions with hydrogen, and the acyl groups play a significant role in enhancing their quality. Tian and colleagues [35] successfully synthesized Pt nanoparticles on MWCNT composites (Pt/MWCNT) using intermittent microwave irradiation (IMT) with H_2PtCl_6 as a precursor. Figure 5 shows the TEM image of Pt/MWCNT; Pt nanoparticles are uniformly distributed on the MWCNT with a size range from 1.5 to 4.0 nm. The Pt/MWCNT nanocomposites demonstrated significantly enhanced methanol oxidation compared to the E-TEK 40% Pt/C catalyst under acidic conditions.

6. FULLERENE-BASED ELECTRODE MATERIALS

Buckminsterfullerene, or C60, is an anisotropic form of carbon found in various shapes such as spheres, tubes, and ellipsoids, first discovered by Kroto in 1985. Represented as a 0-D carbon material, fullerene (C60) has attracted research interest due to its high electron transport properties, excellent electron-accepting capability, and stable structural arrangement. Additionally, C60-based electrode materials have been used as effective electrocatalysts in diverse fields, including solar cells, batteries, biosensors, and fuel cells. Fullerene exhibits remarkable properties for direct methanol fuel cells (DMFCs), such as ease of use, low-temperature operation, and high energy density. Functionalized fullerene nanoplates (Pt/Ru/Sn/W fullerene) can enhance catalytic activity, improving fuel cell performance. Fullerene-based Pt electrocatalysts (Pt/C60(OH)24-27) were successfully synthesized using formic acid as a reducing agent. Pt fullerene catalysts are highly efficient in the electrochemical oxidation of ethanol. Rambabu and Bhat developed a sulfonated polyether ether ketone-based membrane, supporting a sulfonated fullerene composite membrane (SPEEK-Sfu) through a diazotization reaction [36]. The SPEEK-Sfu composite membrane substrate showed improved oxidation resistance and reduced methanol permeability in DMFCs.

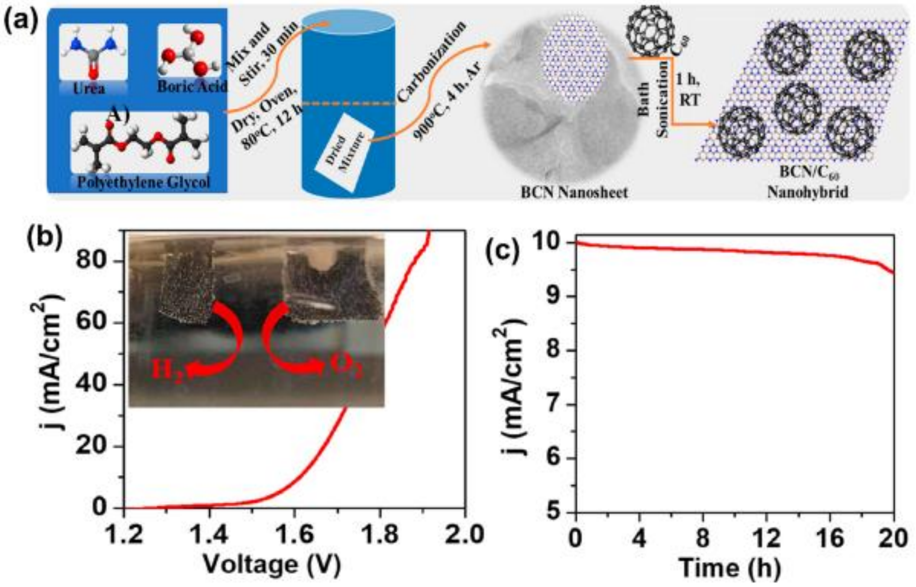

Figure 6*. (a) Schematic diagram of the nanohybrid F/BCN synthesis process, (b) LSV curve of the overall water splitting process using 10% F/BCN as both the cathode and anode in 0.5 M NaOH solution, (c) Digital images showing O_2 (anode) and H2 (cathode) gas bubbles generated on the 10% F/BCN-modified carbon cloth electrodes, and (d) Time-dependent current density measurements of the 10% F/BCN catalyst for H2O electrolysis at 1.61 V over 20 hours.*

A novel heterostructured layer of boron nitride nanosheets was functionalized with fullerene molecules to form multifunctional supramolecular structures based on 10% F/BCN (see Fig. 6). Using linear sweep voltammetry (LSV), the 10% F/BCN/10% F/BCN cell device exhibited a significant current density (10 mA cm^{-2}), with digital imaging demonstrating overall water splitting. The 10% F/BCN electrocatalyst displayed good electrode stability in time-dependent measurements over a 20-hour duration.

7. CONCLUSIONS

In conclusion, carbon-based catalysts have made significant advancements in developing energy storage technology in the form of hydrogen fuel cells. Numerous research groups have synthesized carbon-based catalysts with various functionalities to achieve higher surface area, uniform surface morphology, and homogeneous nanoparticle dispersion, thereby enhancing the electrocatalytic and durability properties. The future prospects of carbon-based materials for electrocatalysts in fuel cells are highly promising, driven by advancements in material design, synthesis techniques, and a growing emphasis on sustainable energy solutions. Emerging approaches, such as the incorporation of single-atom catalysts, heteroatom doping, and hierarchical nanostructures, are expected to enhance the catalytic activity and durability of carbon-based materials, making them competitive with platinum. Additionally, the integration of artificial intelligence and machine learning in catalyst development could accelerate the discovery of optimized materials. The gap between theoretical predictions and experimental results is gradually narrowing, and the understanding of operating principles and physicochemical properties is becoming clearer, facilitating future scientific research and application of these materials.

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TÓM TẮT

Một số tiến bộ về chế tạo vật liệu xúc tác nền carbon cho pin nhiên liệu

Trong những năm gần đây, tìm kiếm vật liệu xúc tác làm tăng hiệu suất chuyển đổi năng lượng hydro trong pin nhiên liệu là hướng nghiên cứu được các nhà khoa học trên thế giới đặc biệt quan tâm. Pt và các hợp kim của chúng là vật liệu điển hình trong pin nhiên liệu, nhưng chúng khan hiếm và đắt. Thay thế một phần Pt bằng các vật liệu nền không chứa kim loại quý là hướng nghiên cứu phát triển bền vững và chủ đạo trong lĩnh vực xúc tác pin nhiên liệu. Nhiều nghiên cứu gần đây tập trung vào vật liệu xúc tác không chứa kim loại quý nền carbon vì đây là họ vật liệu được quan tâm do có nhiều ứng dụng và tiềm năng giảm lượng xúc tác Pt trong ứng dụng thực tế. Trong báo cáo này, chúng tôi sẽ giới thiệu và phân tích một số tiến bộ về vật liệu xúc tác Pt nền carbon trong pin nhiên liệu.

Từ khóa: Xúc tác; Pin nhiên liệu; Vật liệu nền cacbon; Điện hóa.