Transactions on Engineering and Technology Research
ISSN: 2960-1797, eISSN: 2960-2246 | Volume 2
AMMEE 2024

Advancements in Research on Composite Bipolar Plates for Proton Exchange Membrane Fuel Cells

HanJie Wu

International Elite Engineering School, East China University of Science and Technology, Shanghai, China.

21010480@mail.ecust.edu.cn

Abstract. In proton exchange membrane fuel cells (PEMFC), the bipolar plate is a crucial component. Positioned between the anode and cathode, it supports the electrode reactions and provides pathways for gas flow. Made of conductive materials, it boasts excellent conductivity and mechanical stability, capable of withstanding the current generated by electrochemical reactions and resisting the corrosive and oxidative environments within the system. Thus, to ensure efficient energy conversion, the bipolar plate must exhibit good conductivity, mechanical strength, and corrosion resistance. This thesis systematically categorizes the selection of resins and graphite, based on a graphite-resin composite system, and compares the performance of various composite bipolar plates against the Department of Energy (DOE) standards. By examining the microstructure, the thesis explores the reasons behind these performance characteristics, aiming to determine the optimal graphite-resin ratio and modification methods.

Keywords: Composite bipolar plate; PEMFC; synergy; dual percolation effect.

1. Introduction

1.1 New Energy

With the continuous increase in global population and economic development, the demand for energy is constantly rising. However, the large-scale use of fossil fuels has led to severe environmental problems, such as air and water pollution and climate change. To address these challenges, there is an urgent need to transition to more sustainable and environmentally friendly energy forms. Promoting the development and utilization of new energy sources, such as solar, wind, hydro, and biomass energy, can reduce dependence on limited fossil fuels, lower carbon emissions, and mitigate climate change. However, these energy sources have drawbacks, such as instability, geographical constraints, high initial investment, and difficulties in large-scale production. Various battery systems, like lithium batteries, sodium batteries, and fuel cells, have gained widespread attention due to their high energy conversion efficiency, abundant raw material resources, portability, and clean byproducts.

1.2 Fuel Cells

1.2.1 Definition and Principle of Fuel Cells

A fuel cell is essentially a large power generation system that can directly convert the chemical energy of fuel into electrical energy. Its working principle involves introducing hydrogen, methanol, or other gaseous fuels and oxygen between the anode (positive) and cathode (negative), where they undergo redox reactions catalyzed to produce electricity and water.

1.2.2 Advantages and Disadvantages of Fuel Cells

Fuel cells offer advantages such as high efficiency, cleanliness, low noise, and long endurance, aligning with the trends in clean energy development. However, their high cost, difficulty in fuel storage, low energy density, and the need for improved lifespan stability limit their large-scale commercial application. Overcoming these challenges is key to the widespread adoption of fuel cells.

1.2.3 Types and Applications of Fuel Cells

Fuel cells are primarily categorized into alkaline fuel cells (AFC), proton exchange membrane fuel cells (PEMFC), and solid oxide fuel cells (SOFC). Alkaline fuel cells, which use sodium hydroxide electrolytes and operate at low temperatures, are mainly used in aerospace. PEMFCs use proton exchange membrane electrolytes and are commonly used in vehicles and residential power supplies. Solid oxide fuel cells use solid oxide electrolytes and are suitable for large-scale power and industrial applications. As technology advances and costs decrease, fuel cells are poised to play a significant role in the transition to clean energy.

1.3 Proton Exchange Membrane Fuel Cell (PEMFC)

Following the discussion on the characteristics of fuel cells, we will delve into a typical type—PEMFC, a fuel cell system that uses a proton exchange membrane as its electrolyte.

1.3.1 Structure of PEMFC

The core components of PEMFC include the anode, cathode, proton exchange membrane, bipolar plate, electrolyte, and hydrogen-oxygen supply system (Fig. 1). The anode and cathode use precious metals such as platinum to catalyze the oxidation of hydrogen and the reduction of oxygen to produce water. The proton exchange membrane, made of polymer, transmits protons and blocks electrons, ensuring that the current only flows through the external circuit. The bipolar plate supports the reaction area and provides gas channels. Electrolytes such as ammonium phosphate enhance proton conductivity. The hydrogen-oxygen supply system provides gases and removes water, ensuring stable operation of the system. These components together enable the efficient energy conversion of the fuel cell.

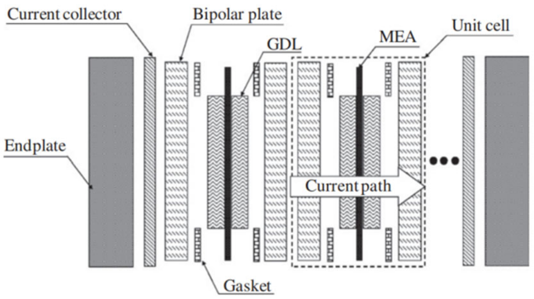

Fig. 1 Structure of PEMFC[1]

1.3.2 Working Principle of PEMFC

First, the oxidation reaction of hydrogen occurs at the anode. Hydrogen (H_2) molecules are split into protons (H^+) and electrons (e^-) by the catalyst.

$$2H_2 \longrightarrow 4H^+ + 4e^- \tag{1}$$

The catalyst causes the two hydrogen atoms in the hydrogen molecule to split into two protons and two electrons. Subsequently, protons from the anode migrate through the proton exchange membrane to the cathode. Meanwhile, electrons travel from the anode to the cathode through an external circuit, generating current and completing the power output. Finally, the reduction reaction of oxygen occurs at the cathode, where oxygen molecules combine with protons and electrons to form water.

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \tag{2}$$

Through these reactions, PEMFC converts the chemical energy of hydrogen and oxygen directly into electrical energy without environmental pollution.

1.3.3 Advantages and Applications of PEMFC

PEMFC has high energy conversion efficiency and performs excellently at low temperatures, reducing dependence on fossil fuels. Its quick start-up, adaptability to various hydrogen sources, and environmentally friendly byproduct of water make it widely used in vehicles, residential power supplies, stationary power sources, and portable power sources. PEMFC is considered a potential alternative energy source for driving electric vehicles, providing stable power in homes and industries, and meeting the power needs of mobile devices and outdoor activities. As the demand for clean energy increases, the application prospects of PEMFC will expand, contributing more to sustainable energy development.

1.4 Bipolar Plate

Within PEMFC, the bipolar plate accounts for 60-80% of the fuel cell stack's weight, 20-40% of its cost, and occupies almost the entire volume of the fuel cell stack, typically positioned between the anode and cathode.

1.4.1 Functions and Performance Standards of Bipolar Plate

Firstly, bipolar plates act as support structures, fixing and supporting the anode and cathode electrodes, ensuring they maintain proper spacing and positional relationships, thereby maintaining an effective reaction area and stabilizing the overall cell structure. Secondly, through a designed channel system, the bipolar plate guides hydrogen and oxygen to the reaction areas at the anode and cathode, facilitating the oxidation of hydrogen and reduction of oxygen. Excellent channel structures can efficiently distribute gases, improve reaction efficiency, and reduce gas flow unevenness. Lastly, the bipolar plate also helps the current collection, garnering and transmitting electrons to the external circuit by contacting the anode and cathode electrodes, forming a current and converting the electron flow generated by the electrochemical reaction into usable electrical energy. In summary, the bipolar plate in PEMFC has crucial roles in support, flow guidance, and current collection, providing essential support for the cell's normal operation and efficient energy output.

To achieve these functions, as such, the bipolar plate needs to have excellent conductivity, thermal conductivity, gas permeability, mechanical strength, corrosion resistance, hydrophobicity, and volume density. These properties must meet the requirements of the fuel cell system to ensure its efficient and stable operation. Additionally, these properties must comply with the standards set by the US Department of Energy (DOE) (Fig. 2).

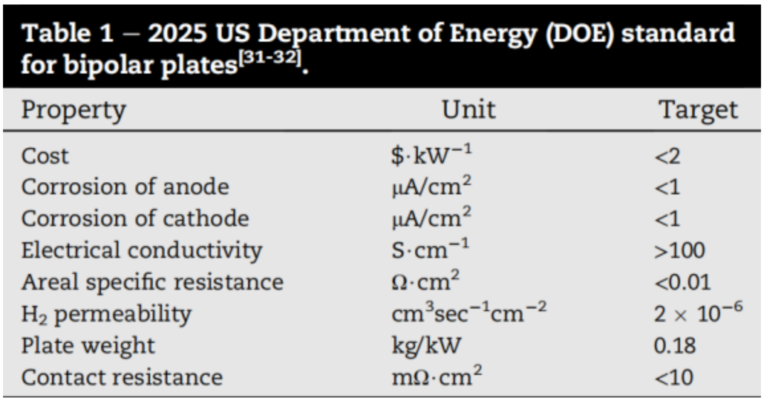

Table 1 — 2025 US Department of Energy (DOE) standard for bipolar plates[31-32].

Property	Unit	Target
Cost	$\$\cdot kW^{-1}$	<2
Corrosion of anode	$\mu A/cm^2$	<1
Corrosion of cathode	$\mu A/cm^2$	<1
Electrical conductivity	$S\cdot cm^{-1}$	>100
Areal specific resistance	$\Omega\cdot cm^2$	<0.01
H_2 permeability	$cm^3sec^{-1}cm^{-2}$	2×10^{-6}
Plate weight	kg/kW	0.18
Contact resistance	$m\Omega\cdot cm^2$	<10

Fig. 2 US department of energy requirements for bipolar plates in 2025

1.4.2 Classification of Bipolar Plates

Different types of bipolar plates have unique characteristics in PEMFCs. Graphite plates offer excellent electrical conductivity and chemical stability but are costly and complex to manufacture. Metal plates, such as those made from stainless steel or titanium alloys, provide high strength and conductivity, lower cost, and are widely used commercially. Composite bipolar plates combine the advantages of various materials to enhance performance and durability. Special types, such as polymer-based composites and carbon nanotube composites, may offer benefits like reduced weight and improved conductivity. Selecting a bipolar plate involves considering factors like mechanical strength, conductivity, corrosion resistance, and manufacturing processes to meet specific requirements.

1.4.3 Selection of Bipolar Plates

Graphite plates are commonly used as bipolar plates in PEMFCs. However, their smooth structure fails to meet strength requirements, typically necessitating high-pressure compression to increase density. Metal plates exhibit excellent conductivity and mechanical strength but are prone to corrosion in a proton exchange environment. Composite bipolar plates merge the strengths of different materials, such as the strength of metals and the conductivity of graphite, to optimize performance. A well-designed composite structure can enhance strength and stability, extend lifespan, improve conductivity, and increase efficiency, meeting comprehensive requirements. Therefore, composite bipolar plates have significant research potential and value.

2. Graphite Material

Graphite materials play a crucial role in PEMFCs. Firstly, graphite, as a conductive material, is used to manufacture bipolar plates, where its conductivity determines the efficiency of current transmission in fuel cells. Secondly, graphite is also used in the electrode catalyst layers within the proton exchange membrane, catalyzing the electrochemical reactions of hydrogen and oxygen, and facilitating proton conduction. Common graphite materials in PEMFCs include graphite powder, carbon fibers, graphene, and carbon nanotubes. Each of these materials has unique properties that support the efficient operation of PEMFCs.

2.1 Single Conductive Filler

2.1.1 Natural Graphite (NG)

Natural graphite offers significant advantages in PEMFCs. Firstly, its relatively low cost makes it an economical material choice, helping to reduce the overall cost of the fuel cell system. Secondly, as shown in Table 1, natural graphite has excellent conductivity, which effectively transmits current and improves the efficiency of the fuel cell system. Additionally, it has high corrosion resistance, maintaining stability in complex chemical environments and extending the system's lifespan. Overall, the application of natural graphite in PEMFCs not only reduces costs but also enhances system performance and stability, strongly supporting the development of fuel cell technology.

Table 1 Physical and chemical properties of natural graphite

Properties	Description	
Color	Gray-black or steel-gray	
Morphology	Crystalline Graphite	Flaky, with thin layers arranged in parallel
	Aphanitic Graphite	Earthy or powdery texture, gray or black
Particle Size	Aphanitic Graphiteparticle Size Irregular; Flaky, with thin layers arranged in parallel	
Thermal Conductivity	Approximately 1100-2000 W/mK	
Electrical Conductivity	1000~2000 S/m	
Application Areas	Thermal and electrical conductive materials	Batteries, thermal pads, heat sinks
	High-temperature refractory materials	Casting molds, electric arc furnace linings
	Lubricants	Additives for lubricating oils and greases
	Graphite Products	Pencil leads, carbon fiber-reinforced composites

Yin Qiang et al. [2] prepared conductive composite materials for bipolar plates using natural graphite powder and phenolic-formaldehyde resin powder. The study showed that as graphite particle size increased, both conductivity and flexural strength initially increased and then decreased, peaking at 105 μm with a conductivity of 142 S/cm and flexural strength of 61.6 MPa, meeting standards. The research revealed that PEMFCs containing natural graphite have improved conductivity and performance, with graphite particle size also affecting conductivity and flexural strength.

The thesis posits that smaller graphite particles form dense electron transmission paths with larger contact areas, enhancing conductivity and flexural strength. As particle size increases, although electron transmission paths lengthen, the number of particle contacts is still sufficient to maintain continuous increases in conductivity and flexural strength. However, with further increases in particle size, the electron transmission path extends, and the probability of particle contact decreases, leading to reduced electron transmission efficiency, causing conductivity and flexural strength to peak and then decline.

2.1.2 Synthetic Graphite (SG)

Synthetic graphite is an artificially produced carbon material that exhibits similar conductivity and thermal properties to natural graphite (Table 2). It also has excellent chemical stability and lubricity. Compared to natural graphite, synthetic graphite has a more uniform structure, and its physical and chemical properties can be precisely controlled and adjusted. In the research of composite bipolar plates, synthetic graphite is considered a potential filler due to its higher purity and more consistent particle size, which can lead to better performance in specific applications.

Table 2 Physical and chemical properties of synthetic graphite

Properties	Description	
Color	Gray-black or steel-gray	
Morphology	Flaky	Flaky, with a noticeable layered structure
	Granular	Irregular gaps between particles
Particle Size	Controllable, generally ranging from nanometers to micrometers	
Thermal Conductivity	Approximately 1000-2000 W/(m K)	
Electrical Conductivity	Approximately 1000-2000 S/m	
Application Areas	Battery manufacturing	Electrode material
	High thermal conductivity materials	Radiators, thermal pads
	Mechanical parts	Requiring both mechanical performance and conductivity

Compared to natural graphite, synthetic graphite's more uniform structure and controllable particle size make it easier to achieve precise control in composite material preparation. Its relatively consistent particle size allows for high dispersion, forming more effective electronic transport channels. Thus, by using synthetic graphite, researchers can better control the structure and performance of composite materials, enabling the efficient preparation of fuel cell bipolar plates.

2.1.3 Expanded Graphite (EG)

Expanded graphite is a carbon material obtained by subjecting natural graphite to high-temperature processing. Its structure is similar to that of natural graphite but features more micro-pores and expanded spaces (Table 3). These microstructures result in lower density and larger specific surface area, enhancing adsorption capacity and speed. In the study of composite bipolar plates, expanded graphite is also considered a filler due to its higher adsorption capacity and better dispersibility, improving the uniformity and stability of the composites.

Yao K et al.[3] conducted a comparative study on composite materials made from synthetic graphite, natural graphite, and expanded graphite with new phenolic-formaldehyde resin. The results indicated that the expanded graphite composite exhibited the best performance, with a density of approximately 1.55 g/cm^3, a flexural strength of 109 MPa, a modulus of 24 GPa, and an in-plane conductivity of 182 S/cm. This study highlighted that expanded graphite is the optimal candidate material, offering low density and excellent electrical, mechanical, thermal, and corrosion-resistant properties, which can reduce the weight and volume of fuel cell stacks.

Cui T et al.[4] used expanded graphite as a carbon filler and polyimide (PI) as a binder to fabricate conductive composite plates through hot press molding. The study discussed the effects of molding temperature and the expansion ratio of EG on the various properties of the EG/PI composite plates. The results showed that a molding temperature of 220°C was suitable for achieving satisfactory electrical conductivity and flexural strength in the composite plates. A higher EG expansion ratio was beneficial for improving electrical conductivity and flexural strength.

Wang X et al.[5] achieved breakthroughs in the electrical conductivity and corrosion resistance of graphite-resin composite bipolar plates (BPs) through HH-BP. The study found that high molding and impregnation pressure facilitated better connection and alignment among conductive fillers (such as graphite), and the interconnected layered structure of expanded graphite was well preserved. This optimized the conductive network structure, enhancing the electrical conductivity of the composite bipolar plates, reducing electrical resistance losses, and improving the energy conversion efficiency and power density of the cells.

Table 3 Physical and chemical properties of expanded graphite

Properties	Description	
Color	Dark gray to black	
Morphology	Sponge-like or porous structure with a large surface area	
Particle Size	Micrometer scale, irregular shapes	
Thermal Conductivity	Typically low, around 5-10 W/(m K)	
Electrical Conductivity	Typically low, around 100-200 S/m	
Application Areas	Insulating materials	For insulation and heat preservation
	Thermal fillers	For construction, automotive fields
	Chemical industry	Reactor fillers for adsorption and separation
	Electrode materials	For capacitors and other devices

2.1.4 Carbon Fiber (CF)

Carbon fiber is a high-strength, high-modulus material with excellent mechanical properties and chemical stability. It has a highly ordered crystal structure, where carbon atoms form a highly conductive network through π-π stacking between layers. In the study of composite bipolar plates, carbon fiber is used to enhance strength and rigidity. Carbon fiber has relatively high electrical conductivity but typically lower than natural graphite. The highly ordered crystal structure of natural graphite forms a high-conductivity network, resulting in higher electrical conductivity. The electrical conductivity of carbon fiber is influenced by the direction of fiber alignment, with higher conductivity in the horizontal direction and lower in the axial direction, generally ranging from several hundred Siemens per centimeter (Table 4).

Hwang IU et al.[6] manufactured a carbon fiber epoxy composite bipolar plate through compression molding. The study demonstrated that this composite bipolar plate exhibited excellent mechanical and thermoelectric properties, with a flexural strength of 195 MPa, far exceeding other candidate materials and the target value of 50 MPa. Its in-plane electrical conductivity was 300 S/cm, threefold the target value.

Additionally, to mitigate the issues of directional conductivity and thermal conductivity, researchers often use carbon fiber felt or carbon fiber cloth, which are mat-like or fabric-like materials composed of carbon fibers. These materials feature directionally distributed carbon fibers rather than random arrangements, providing high structural strength, stability, good thermal conductivity, and high-temperature resistance.

Kim M et al.[7] co-cured directionally distributed carbon fiber felt with composite bipolar plates using a pre-curing process to alter the surface structure of the composite bipolar plates, reducing the area-specific resistance (ASR). The study showed a tensile strength of 320 MPa; the area-specific resistance at 20°C was 101 $mX \cdot cm^2$.

Kuan YD et al.[8] used plain woven graphite fiber cloth as reinforcement for composite laminate materials. The study found that the uncarbonized bipolar plate’s average maximum flexural strength was 456.2 MPa. Although carbon black reduced its strength, the two-dimensional oriented arrangement of the graphite fiber cloth resulted in flexural strength exceeding the DOE’s 2020 target of 25 MPa.

Table 4 Physical and chemical properties of carbon fiber

Properties	Description	
Color	Usually black	
Morphology	Diameter	Micron scale, typically 5 to 10 microns
	Length	Typically a few millimeters to several centimeters, but longer fibers also exist
Thermal Conductivity	Approximately 500-700 W/(m·K)	
Electrical Conductivity	Extremely high; Approximately 10,000-20,000 S/m	
Application Areas	Aerospace	Used for manufacturing aircraft and spacecraft structural materials, composites, etc.
	Automotive Industry	Used for vehicle lightweighting and improving fuel efficiency, etc.
	Electrochemistry	It can serve as an electrode support for catalyst fixation and support.
		As one of the materials for electrochemical electrodes, it is used in various electrochemical reactions.
		It can be used to manufacture diaphragm materials for electrolytic cells, offering good conductivity and chemical stability, which aids in the transmission and separation of ions within the electrolytic cell.
		With excellent conductivity and surface activity, it can be used to manufacture various electrochemical sensors, such as pH sensors and oxygen sensors.

2.1.5 Carbon Nanotubes (CNTs)

Carbon nanotubes are tubular structures formed by carbon atoms arranged at the nanoscale, possessing excellent conductivity and thermal conductivity (Table 5), as well as good chemical stability. Compared to natural graphite, carbon nanotubes have a larger surface area, providing higher specific surface area and superior electrochemical performance. Researchers have also considered carbon nanotubes as an option in the study of composite bipolar plates.

Table 5 Physicochemical properties of carbon nanotubes

Properties	SWNTs	MWNTs
Color	Typically black, sometimes metallic	
Morphology	Single-layer carbon atoms rolled helically into a tubular form	Multiple concentric tubes held together by van der Waals forces
Particle Size	Diameter: 0.4 to 2 nm	Outer Diameter: 2 to 100 nm
Length	Tens to hundreds of micrometers	Hundreds of nanometers to tens of micrometers
Thermal Conductivity	Up to 3500~6000 W/(m·K)	Typically 3000~3500 W/(m·K)
Electrical Conductivity	Up to 10000~20000 S/m	Typically 1000~2000 S/m
Application Areas	Nanomaterials: for preparing nanocomposites, nanoelectronic devices, etc.	
	Battery Technology: as electrode materials for lithium-ion batteries, supercapacitors, etc.	
	Conductive Materials: for making conductive fibers, conductive coatings, etc.	
	Catalyst Support: used as a catalyst support to promote chemical reactions	

Madheswaran D K et al. [9] reviewed studies on carbon nanotubes as fillers to improve the electrical conductivity of composite bipolar plates for PEMFC. The study found that CNTs' high aspect ratio facilitates electron transport and charge carrier migration within the composites, forming more conductive pathways (Fig. 3), thereby enhancing conductivity. Experiments demonstrated that using CNTs as fillers can significantly improve the electrical conductivity of composite bipolar plates (BPPs), with 2 wt% MWCNTs achieving a notable electrical conductivity of 364 S/cm in PBA composite BPPs.

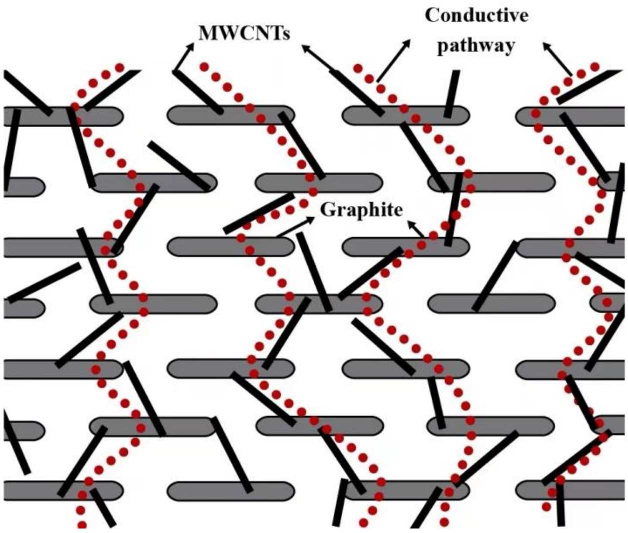

Fig. 3: CNTs Forming Conductive Pathways

In terms of mechanical properties, Ramírez-Herrera C A et al. [10] doped MWNTs into a polypropylene (PP) matrix, achieving up to 20 wt%, which enhanced microhardness, elastic modulus, and tensile and flexural strength by 71%, 47%, 56%, and 30%, respectively.

This thesis posits that multi-walled carbon nanotubes (MWNTs) with their nanoscale diameter and length, high specific surface area, and superior mechanical properties make them excellent reinforcing materials. When doped into a polypropylene matrix, their nanoscale structure can effectively enhance the microhardness, elastic modulus, and tensile and flexural strength of the composite materials.

2.1.6 Graphite Nanosheets (NanoG)

Graphite nanosheets are a type of carbon material with excellent conductivity and thermal conductivity similar to natural graphite (Table 6), along with good chemical stability and lubricity. Compared to carbon nanotubes, graphite nanosheets have a two-dimensional structure, appearing in sheet or flake form, which provides a larger surface area and more surface active sites. Consequently, researchers have also considered graphite nanosheets as an option in the study of composite bipolar plates.

Table 6 Physicochemical properties of graphite nanosheets

Properties	Description	
Color	Typically black	
Morphology	Single-layer graphite nanosheets with a planar structure, similar to the layered structure of graphite	
Particle Size	Generally a few nanometers to tens of nanometers	
Length	Generally tens to hundreds of nanometers, with a high aspect ratio	
Thermal Conductivity	Approximately 2000~3000 W/(m·K)	
Electrical Conductivity	Approximately 10000~20000 S/m	
Application Areas	Nanomaterials:	used in preparing nanocomposites, nanocoatings, etc.
	Battery Technology:	used as battery electrode materials, conductive fillers, etc.
	Thermal Management:	used in thermal interface materials, heat sinks, etc.
	Electronic Devices:	used in making conductive films, flexible electronics, etc.

Xiao M et al. [11] prepared POBDS/graphite nanosheet composites. The experiments revealed that a NanoG bipolar plate with 50% content demonstrated optimal potential, exhibiting a flexural strength of 32.05 MPa, an electrical conductivity of 158.7 S/cm, a porosity of 8.96×10^−2%, and excellent electrochemical performance.

This study also compared bipolar plates based on graphite nanosheets and expanded graphite within the same resin. It was found that graphite nanosheets in the composites resulted in fewer voids and better affinity, with smoother surfaces and better compatibility with POBDS, leading to less graphite sheet aggregation and fewer large POBDS blocks. In contrast, POBDS/EG composites showed more graphite sheet accumulation on the surface and less smooth surfaces.

Thie thesis posits that graphite nanosheets, compared to traditional expanded graphite, have a larger and smoother surface area, providing more contact area, which is beneficial for bonding with resin. Their nanoscale thickness, approximately 2-5 nanometers, and high aspect ratio allow for uniform dispersion within the composite materials, reducing voids and defects, improving flexural strength, and reducing water absorption.

2.2.1 Graphite Modification Methods

In PEMFC composite bipolar plates, to achieve better electrical conductivity and mechanical properties, researchers typically modify graphite materials with performance deficiencies. This improves compatibility with polymer matrices, enhances conductivity, and adjusts surface properties, thereby comprehensively improving bonding performance, electrical conductivity, overall performance, and stability.

One common modification method is grafting, which aims to change the bonding mode between graphite and resin, improving dispersion and electron transport capability in composite materials, thus significantly enhancing the mechanical and electrical properties of composite bipolar plates.

Liao S H et al. [12] grafted poly(oxyalkylene-amine) (POA) containing maleic anhydride (MA) onto the surface of MWCNTs. When mixed with VE, the grafted product demonstrated better dispersion within the VE matrix, connecting MWCNTs and enhancing interfacial interactions, thereby improving composite performance. Additionally, the double bonds of POAMA attached to MWCNTs formed a highly cross-linked covalent structure (Fig. 4).

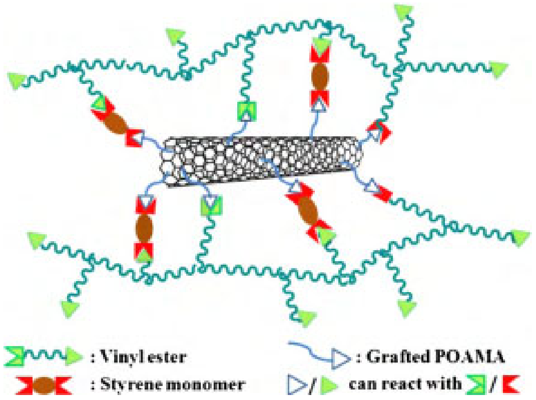

Fig. 4 Highly cross-linked structure

Apart from grafting maleic anhydride onto the surface of MWCNTs, Liao S H et al. [13] also linked poly(propylene glycol) diglycidyl ether oligomers with molecular weights of 400 and 2000 to the surface of MWCNTs (Fig. 5). The study found that introducing MWCNTs/POA400-DGEBA was more effective in forming more conductive pathways than MWCNTs/POA2000-DGEBA.

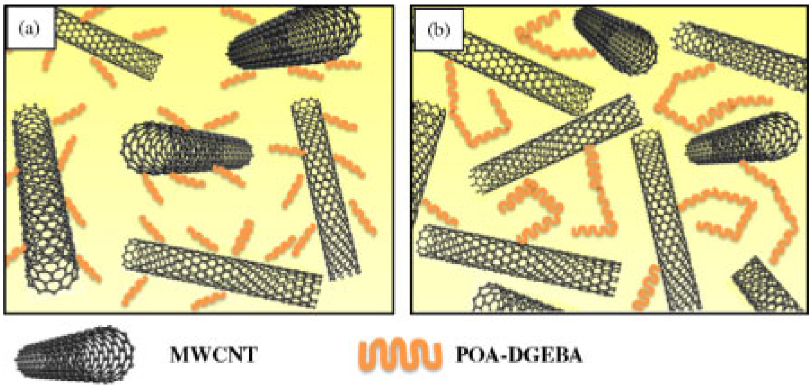

Fig. 5 (a) MWCNTs/POA400-DGEBA System (b) MWCNTs/POA2000-DGEBA System

This thesis posits that the shorter chain length of POA with a polymerization degree of 400, compared to 2000, more effectively disperses MWCNTs in the PP matrix of the nanocomposite bipolar plate. The shorter polyether amine chain length helps better encapsulate and disperse MWCNTs, promoting better contact between MWCNTs and forming more conductive pathways. This effective dispersion reduces MWCNT aggregation, thereby improving electrical conductivity. Consequently, introducing POA400-DGEBA better enhances the dispersion of MWCNTs in the PP nanocomposite bipolar plate, leading to the formation of more conductive pathways.

Besides grafting, carbonization and flame treatment are also common modification methods for graphite. Carbonization can enhance the conductivity and optimize electron transport of graphite composite bipolar plates, while flame treatment can significantly improve the flexural strength and gas permeability of carbon fiber/phenolic aldehyde composites, thus markedly enhancing the performance of bipolar plate materials.

The average surface resistance of graphite composite bipolar plates is relatively high. To address this issue, Kuan Y D et al. [14] compared the performance of bipolar plates that were not carbonized with those that underwent different levels of carbonization. The study indicated that after one round of carbonization, the average surface resistance decreased from 203.4 mΩ/sq to 130.6 mΩ/sq. This demonstrates that carbonization of the phenolic-formaldehyde resin in the bipolar plate removes part of the resin, facilitating electron transport.

Additionally, Hwang I U et al. [15] examined the effects of flame treatment on the surface of carbon fiber/phenolic aldehyde composite bipolar plates. They found that while flexural strength decreased with increased flame treatment time, a 5-second propane flame treatment resulted in a flexural strength of 48.6 MPa, which is double the Department of Energy’s target of 25 MPa. Gas permeability was also measured, and the composite met the Department of Energy’s targets after 5 seconds of propane flame treatment.

The thesis posits that the benefits of carbonization can be attributed to the removal of some of the phenolic-formaldehyde resin, which aids in improving electron transport efficiency. As the number of carbonization cycles increases, the performance of the graphite composite bipolar plate improves because more of the phenolic-formaldehyde resin is removed, reducing internal material barriers and facilitating smoother electron transport. Flame treatment, on the other hand, improves the surface properties of carbon fiber/phenolic aldehyde composites by inducing structural adjustments through thermal energy, enhancing flexural strength and gas permeability, thereby meeting higher performance requirements.

2.2 Synergy

“Synergy” refers to the cooperative interaction between different materials or structures to enhance the performance of composite materials. Researchers mix various conductive materials, leveraging synergy to amplify and complement the distinct characteristics of different graphite materials, thereby creating more interconnected conductive networks and enhancing the overall conductivity of the composites.

2.3.1 Synergy of Graphite Powder and Carbon Black

To achieve synergy and establish more conductive networks, researchers often use multiple conductive particles as materials for bipolar plates. Graphite powder is a preferred choice due to its excellent conductivity and thermal properties. Its layered structure allows for easy electron movement, providing superior conductivity and chemical stability. Meanwhile, carbon black, with its microporous structure and large surface area, is widely used as a filler, reinforcement material, and adsorbent. Although its thermal conductivity is not as high as graphite powder, it plays a crucial role in specific applications.

Kang K et al. [16] highlighted that flake natural graphite, as the primary conductive filler, facilitates the formation of conductive networks, improving the electrical conductivity of composite plates. Synthetic graphite, used as a secondary filler, enhances flexural strength due to its higher surface energy, which improves resin curing. The combined use of both graphite fillers achieves a synergy that enhances the electrical conductivity and flexural strength, thereby improving the overall performance of the composite plates.

In addition to enhancing conductivity, de Oliveira M C L et al. [17] discussed the corrosion behavior of PPS-carbon black-graphite composites in PEMFC bipolar plates and the factors affecting it. Their experiments showed that corrosion behavior is closely related to the carbon black content. As the carbon black content increases, corrosion resistance decreases due to the oxidation of carbon black particles at this potential, forming an oxide layer that prevents further electrochemical corrosion and improves corrosion resistance.

2.3.2 Synergy of Spherical Graphite

Spherical graphite is renowned for its excellent electrical conductivity and thermal conductivity. Due to its spherical structure, spherical graphite has a large surface area, making it widely applicable in electronic devices, thermal management systems, and lubricating materials. In composite bipolar plates, spherical graphite enhances electrical conductivity and thermal conductivity, improving the overall performance of the plates.

Chang F R et al. [18] added secondary conductive fillers, such as graphene and spherical graphite, to expanded graphite/polyimide composites. Tests showed that the composite achieved an electrical conductivity of 160.77 S/cm and a tensile strength of 64.62 MPa. Moreover, the results indicated that adding 5% spherical graphite increased the composite’s in-plane electrical conductivity and flexural strength by 29.8% and 17.3%, respectively.

The thesis posits that the addition of spherical graphite enhances the composite’s conductivity and mechanical properties due to its shape and structure, which help fill gaps between materials. This synergy with expanded graphite and graphene forms conductive networks, increasing the connectivity of conductive paths and thereby improving electrical conductivity. Additionally, the inclusion of spherical graphite improves the composite’s microstructure, strengthening internal interactions and making the material more uniform and stable under stress, thus enhancing its mechanical properties.

2.3.3 Synergy of Carbon Microspheres

Carbon microspheres typically have micron-sized particles and spherical structures. They have a large surface area and high specific surface area, making them widely used in catalyst supports, adsorbents, and electrode materials. One advantage of carbon microspheres is their uniform shape and size, which help improve material uniformity and stability. In composite bipolar plates, carbon microspheres are often used as catalyst supports or electrode material fillers, and their large surface area and uniform shape help improve reaction activity and electrode performance.

Wang J et al. [19] utilized carbon microspheres as the matrix and added carbon graphite fillers with different morphologies, such as natural flake graphite. The study revealed that when mesocarbon Microbeads (MCMB) were combined with natural flake graphite, the electrical conductivity reached 168.1 S/cm, and the flexural strength exceeded 25 MPa. This is attributed to the distinct layered structure of natural flake graphite, which facilitates efficient electron conduction and synergizes with carbon microspheres. By adding natural flake graphite with better conductivity and carbon microspheres with higher flexural strength, the overall performance of the bipolar plate was effectively improved.

2.3.4 Graphene Synergy

Graphene, composed of a single layer of carbon atoms arranged in a two-dimensional lattice, exhibits exceptional electrical conductivity and thermal properties. Its high electrical and thermal conductivities make it highly promising for applications in electronic devices and thermal management systems. Due to its excellent chemical stability and mechanical properties, graphene is also suitable for use in chemical engineering and materials science. In composite bipolar plates, graphene serves as a filler to enhance electrical conductivity and thermal transfer, thereby improving the overall performance of fuel cells.

Gautam R. K. et al. [20] prepared composite bipolar plates by varying the content of exfoliated graphite while keeping the weight percentages of carbon black and graphite powder constant. The study found that the exfoliated graphite/carbon black/graphite powder/resin composite bipolar plate performed better in fuel cells compared to the exfoliated graphite/resin composite bipolar plate. This improvement was attributed to the addition of carbon black and graphite powder, which created more conductive pathways (Fig. 6), thereby reducing resistance. Additionally, the incorporation of carbon black and graphite powder enhanced the mechanical properties of the composite plate, increasing its compressive and flexural strengths, and allowing it to maintain structural integrity under high pressure and high temperature conditions.

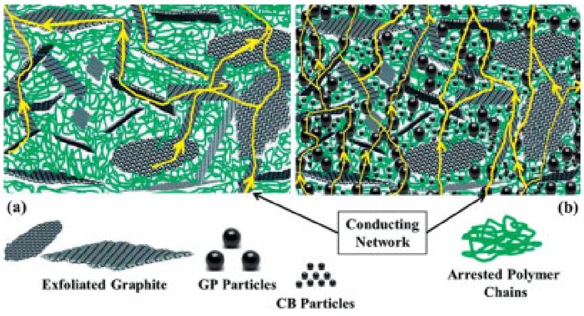

Fig. 6 (a) Conductive mechanism of a single carbon filler, (b) Conductive mechanism of multiple carbon fillers

Kakati B. K. et al. [21] used natural graphite, carbon black, carbon fiber, 1% graphene, and phenolic-formaldehyde resin (resole) in their composite material. Testing revealed that the addition of graphene significantly improved fuel cell performance, increasing the electrical conductivity of the composite bipolar plate by approximately 10%.

The thesis posits that graphene plays a crucial role in composites due to its unique two-dimensional structure and distinctive properties. Its planar structure offers excellent conductive pathways, reducing resistance and enhancing electrical conductivity. The strong covalent bond structure imparts high stability and strength, improving compressive and flexural strengths. The uniform load distribution reduces stress concentration, enhancing overall strength and toughness. The large specific surface area increases interaction with other materials, improving mechanical performance and chemical reactivity. Thus, graphene can significantly improve the electrical conductivity, mechanical properties, and chemical reactivity of composite materials, enhancing overall performance.

2.3.5 Carbon Fiber Synergy

Regarding permeability, polymer composite bipolar plates are more susceptible to gas penetration compared to metal bipolar plates due to their inherent molecular structure. Composite bipolar plates must meet electrical conductivity requirements and are typically thinner, making fuel gases more likely to permeate. Studies indicate that hydrogen permeability is related to composite plate thickness, carbon material content, and chemical aging. Influencing factors include thickness, graphite loading, and the barrier properties of the polymer matrix and filler dispersion quality.

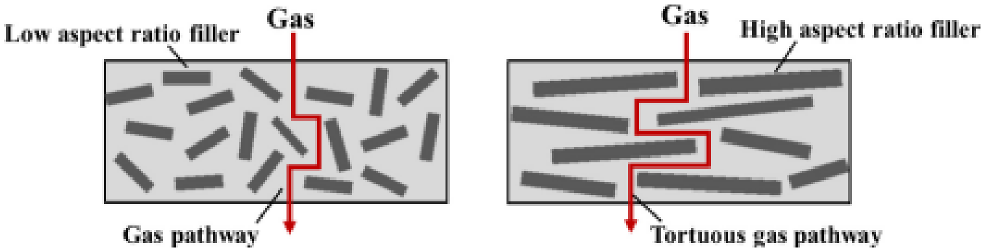

Fig. 7 Tortuous path of gas molecules[22]

High aspect ratio fillers, such as carbon fibers, can increase the tortuous path for gas molecules (Fig. 7), thereby hindering gas permeation through the composite film. These fillers have relatively long lengths, causing gas molecules to traverse more convoluted paths, increasing collisions and friction, and enhancing gas barrier performance.

You M M et al. [23] prepared composite materials with a flexural strength of 50.9 MPa and electrical conductivity of 376.8 S/cm by mixing natural and synthetic graphite of different particle sizes and adding an appropriate amount of ground carbon fiber. The ground carbon fiber, with its larger surface area, enhanced bonding with the resin and improved uniform dispersion, thereby enhancing performance. The rough surface increased mechanical locking and chemical bonding, further improving overall performance.

2.3.6 Carbon Nanotube (CNT) Synergy

Darıcık F. et al. [24] studied the effects of adding CNTs in various proportions on the performance of carbon fiber/epoxy laminates. Their results indicated that as the proportion of CNTs increased, the electrical conductivity of the non-conductive carbon fiber/epoxy plates also increased, reaching up to 120 S/cm. Notably, the performance of plates with 1.25% CNTs by mass was comparable to that of aluminum alloy (AA 3105) bipolar plates under the same conditions.

Yin Q et al. [25] examined the impact of CNT content on the properties of composite materials. It was found that within the experimental system, both the flexural strength and electrical conductivity of the composites increased with higher CNT content. The optimal performance was achieved at 5 wt% CNTs, with flexural strength and electrical conductivity reaching 81.2 MPa and 195.4 S/cm, respectively, representing increases of 36.0% and 14.1% compared to the unenhanced composites.

Dhakate S. R. et al. [26] incorporated 1% by volume of MWCNTs into graphite composite plates, resulting in a 100% increase in both electrical and thermal conductivity of the nanocomposite materials. This significant enhancement was attributed to the alignment of MWCNTs within the composite and the positive synergistic effect between the MWCNTs and axial heat transfer.

Witpathomwong S. et al. [27] used PBA composites filled with graphite, graphene, and MWCNTs. Testing revealed that the composite containing 2 wt% CNTs had a thermal conductivity of 21.3 W/mK, which was 44 times that of the composite without CNTs. Additionally, this composite exhibited an electrical conductivity of 364 S/cm, a flexural strength of 41.5 MPa, and a modulus of 49.7 GPa. Even at 0.5 wt% CNTs, the composite's thermal conductivity met DOE requirements.

The addition of CNTs significantly improved the thermal and electrical conductivities of the composites. This enhancement was due to the long length and small diameter of the tubular CNT structures, which could randomly orient within the composites and effectively combine with graphite and graphene to form more continuous pathways (Fig. 8), thereby greatly increasing the thermal and electrical conductivities of the composites.

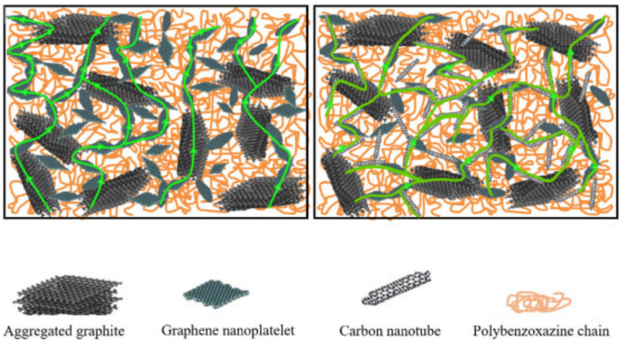

Fig. 8 Conductive pathways of CNTs and graphite

The thesis posits that the anisotropic orientation of MWCNTs in composites and the positive synergistic effect with axial heat transfer are key factors in enhancing composite performance. Due to their elongated nanostructure, MWCNTs exhibit anisotropic characteristics and can orient in various directions within the composite, fully leveraging their conductivity and thermal properties. The π-electron orbitals of CNTs provide excellent electron conduction channels, and their highly crystalline graphite structure ensures good thermal conductivity. MWCNTs form interconnected network structures that promote electron transport and interact with the matrix, improving the overall conductivity and thermal conductivity of the composite materials.

Lee J. H. et al. [28] prepared composites by mixing carbon black, MWCNTs, or carbon fibers with epoxy resin. Their experimental results showed that the addition of a small amount of MWCNTs significantly enhanced the electrical conductivity (by approximately 105%) and flexural performance (by approximately 173%) of the composites. For instance, a composite containing 73% graphite, 2% MWCNTs, and 25% epoxy resin demonstrated the highest electrical conductivity of 254.7 S/cm.

Hu B et al. [29] successfully prepared a high-performance polyvinylidene fluoride (PVDF)/graphite/MWCNTs composite bipolar plate by leveraging the distinct roles of graphite and MWCNTs within the composite: graphite provided conductive pathways and structural support, while MWCNTs offered additional conductive pathways, enhanced mechanical properties, and filled the voids within the graphite. The addition of MWCNTs resulted in the formation of a segregated conductive network, significantly enhancing the composite bipolar plate's conductivity, with electrical conductivity reaching 161.57 S/cm. As illustrated, a segregated conductive network formed between the graphite and MWCNTs (Fig. 9), where MWCNTs were selectively distributed at the PVDF interfaces, forming a continuous segregated conductive network, thus providing excellent electrical conductivity.

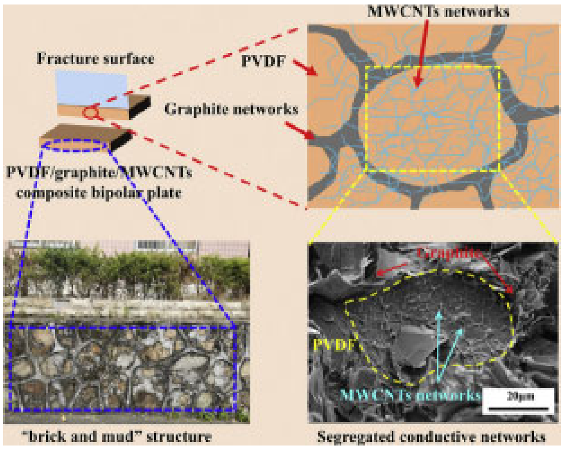

Fig. 9 Continuous segregated conductive network

3. Resin Materials

Resin materials, belonging to the category of polymeric compounds, serve as binders in composite bipolar plates by forming chemical bonds with graphite. Additionally, resins fill the gaps between materials, enhancing the compactness and mechanical strength of the bipolar plates (Table 7). Thermoplastic resins and thermosetting resins are two common types of synthetic resins, differing significantly in their properties and applications. Thermoplastic resins soften upon heating and harden upon cooling, a reversible process making them suitable for reprocessing and recycling. In contrast, thermosetting resins form a three-dimensional cross-linked structure upon initial heating and curing, rendering them irreversible and unable to melt upon reheating. Researchers employ both types of resins in composite bipolar plates to enhance mechanical strength.

Table 7 Physical and chemical properties of various resin materials

Material	Conductivity	Thermal Conductivity (W/(m·K))	Density (g/cm³)	Strength (MPa)
Phenolic-Formaldehyde Resin	Non-conductivity	Approximately 0.15	1.3 - 1.5	50 - 80
Epoxy Resin	Non-conductivity	Approximately 0.15	1.1 - 1.4	60 - 120
Polypropylene	Non-conductivity	Approximately 0.1	0.9 - 0.91	25 - 35
Polyethylene	Non-conductivity	Approximately 0.3	0.92 - 0.97	10 - 25
PEEK	Non-conductivity	Approximately 0.25	1.3 - 1.4	70 - 120
PPS	Conductivity at times	Approximately 0.15	1.3 - 1.35	50 - 100
Polybenzoxazine	Conductivity at times	Approximately 0.2	1.3 - 1.4	60 - 110
Polyimide	Non-conductivity	Approximately 0.2	1.3 - 1.4	80 - 150

3.1 Thermosetting Resin Materials

3.1.1 Phenolic-Formaldehyde Resin

Phenolic-formaldehyde resin is an excellent thermosetting resin, known for its outstanding mechanical strength, wear resistance, chemical corrosion resistance, and insulating properties. It finds extensive application in mechanical manufacturing, electrical equipment, the automotive industry, and construction materials. Researchers have introduced phenolic-formaldehyde resin into composite bipolar plates to improve their electrical performance. The addition of phenolic-formaldehyde resin as a filler can enhance mechanical strength and wear resistance, thus boosting the overall performance of fuel cells.

Li W et al. [30] prepared expanded graphite (EG)/phenolic-formaldehyde resin composite bipolar plates using a resin vacuum impregnation and hot pressing method, studying the performance of bipolar plates with varying phenolic-formaldehyde resin content. The study found that when the concentration of aqueous phenolic-formaldehyde resin solution was 25%, the bipolar plates exhibited better mechanical properties and resistivity. The BP impregnated with aqueous phenolic-formaldehyde resin showed a tensile strength of 33.2 MPa, a flexural strength of 64.9 MPa, a resistivity of 8.9 mΩ·cm², a gas permeability of 3×10^{-7} cm³/(cm² s), and a corrosion current density of 4.0 mA/cm².

Kim M et al. [31] used carbon cloth/phenolic aldehyde composites for mass production, as phenolic-formaldehyde resin cures much faster than epoxy resin. Because phenolic-formaldehyde resin becomes brittle upon complete curing, it was mixed with carbon black to increase its ductility. Experimental results showed that the composite bipolar plate achieved a flexural strength of approximately 195 MPa at both room temperature and an operating temperature of 80°C, far exceeding other candidate materials and well above the target value of 50 MPa.

Kakati B K et al. [32] compared the performance of phenolic aldehyde-type phenolic-formaldehyde resin and formaldehyde ester-type phenolic-formaldehyde resin as binders in bipolar plates using SEM microstructural analysis. The study revealed that regardless of the resin type, graphite particles aligned parallel to the plate surface, beneficial for conductivity. However, the natural graphite particles in phenolic aldehyde-type phenolic-formaldehyde resin were more evenly distributed due to its higher fluidity, facilitating uniform dispersion and forming a compact structure. In contrast, formaldehyde ester-type resin might form a linear structure with poorer fluidity, making it difficult to achieve the same level of dispersion and structure.

3.1.2 Epoxy Resin

Epoxy resin is a thermosetting resin characterized by its excellent mechanical strength, wear resistance, chemical corrosion resistance, and adhesive properties. It is widely used in aerospace, marine, electronics, and construction industries. In the study of composite bipolar plates, epoxy resin as a filler can enhance mechanical strength, wear resistance, and adhesive properties, thereby improving electrical performance. Compared to phenolic-formaldehyde resin, epoxy resin offers slightly better high-temperature resistance and adhesion properties, making it a suitable choice depending on the specific application environment.

Du C et al. [33] investigated the preparation of composite bipolar plates using a vacuum resin impregnation method on compressed expanded graphite sheets. The study revealed that the optimal composite material was epoxy resin (30 wt.%)/CEG, which exhibited an in-plane conductivity of 119.8 S/cm, a through-plane resistance of 17.13 $m\Omega \cdot cm^2$, a density of 1.95 $g \cdot cm^{-3}$, a gas permeability of 1.94×10^{-6} $cm^3/(cm^2\ s)$, and a flexural strength of 45.8 MPa.

3.1.3 Polyphenylene Sulfide (PPS)

PPS is a high-performance engineering plastic known for its high-temperature resistance, chemical corrosion resistance, and excellent mechanical strength, along with good insulating properties. It is widely used in automotive, electronics, aerospace, and chemical industries. Researchers have considered incorporating PPS into composite bipolar plates to enhance performance. PPS fillers can improve high-temperature resistance, corrosion resistance, and mechanical strength, thereby enhancing the overall performance of fuel cells.

Xia L et al. [34] prepared composite bipolar plates using PPS resin and graphite, finding that a 20% PPS resin content demonstrated favorable performance. When heated at 380°C for 30 minutes, the electrical conductivity was 118.9 S/cm, and the flexural strength was 52.4 MPa; at 390°C for 30 minutes, the electrical conductivity was 105 S/cm, and the flexural strength was 55.7 MPa, meeting the requirements of the US Department of Energy.

3.1.4 Polybenzoxazine (PBA)

PBA is a high-performance engineering plastic with excellent high-temperature resistance, chemical corrosion resistance, mechanical strength, and good insulating properties. It is widely used in aerospace, automotive, electronics, and chemical industries. Researchers have considered incorporating PBA into composite bipolar plates to enhance performance. PBA fillers can improve high-temperature resistance, corrosion resistance, and mechanical strength, thereby enhancing the overall performance of fuel cells. Compared to PPS, PBA has superior high-temperature resistance and mechanical strength, although it is slightly inferior in corrosion resistance.

Sirawit Witpathomwong et al. [27] prepared PBA composites containing graphite, graphene, and MWCNTs. Testing showed a flexural strength of 41.5 MPa and a modulus of 49.7 GPa, both of which exceeded the DOE requirements, indicating high application potential.

3.2 Thermoplastic Resin Materials

3.2.1 Polypropylene (PP)

Polypropylene is a common thermoplastic polymer known for its light weight, corrosion resistance, wear resistance, chemical stability, and high mechanical strength and stiffness. It is widely used in packaging, piping, automotive parts, and medical devices. Researchers have considered incorporating polypropylene into composite bipolar plates to enhance performance. Polypropylene fillers can improve mechanical strength and wear resistance, thereby enhancing the overall performance of fuel cells. However, compared to phenolic-formaldehyde resin, polypropylene is somewhat inferior in heat resistance and chemical stability.

Liao S H et al. [35] prepared thin nanocomposite bipolar plates composed of MWCNTs, graphite powder, and PP. They studied the effect of high, medium, and low crystallinity PP on the dispersion of MWCNTs. The results showed that MWCNTs dispersed better in low-crystallinity polypropylene due to its lower crystallinity, providing more amorphous regions (Fig. 10), which facilitated the uniform dispersion of MWCNTs, thereby improving volume electrical conductivity, mechanical properties, and thermal stability.

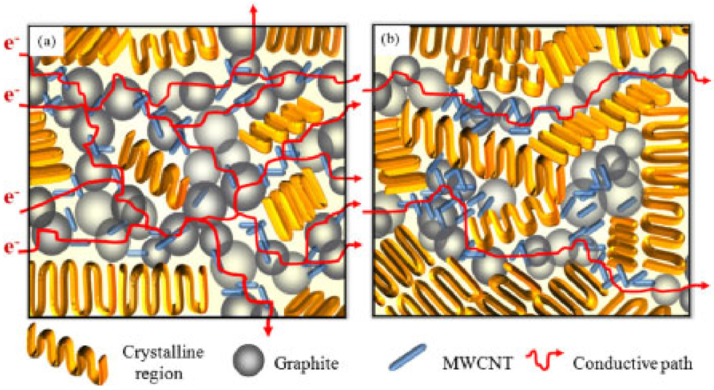

Fig. 10 Conductive paths in amorphous regions

3.2.2 Polyether Ether Ketone (PEEK)

PEEK is a high-performance engineering plastic with excellent mechanical properties, high-temperature resistance, and chemical stability, widely used in aerospace, medical, automotive, and electronics industries. Researchers have considered incorporating PEEK into composite bipolar plates to enhance performance. PEEK fillers can improve mechanical strength, wear resistance, and high-temperature resistance, thereby enhancing the overall performance of fuel cells.

Lim J W et al. [36] used the high-temperature thermoplastic polymer PEEK as a binder for carbon composite bipolar plates. Tensile and three-point bending tests verified that its flexural strength is twice the DOE target.

Zeng H D et al. [37] selected three resins—polyimide (PI), polyetherimide (PEI), and PEEK—to study the preparation and comprehensive performance of expanded graphite composite bipolar plates. The results indicated that among the different resin types, PEEK exhibited the best conductivity, with a maximum electrical conductivity of 200.4 S/cm. In contrast, PI and PEI had lower electrical conductivity under the same conditions, and as the resin content increased, electrical conductivity gradually decreased. This was attributed to the resin accumulating between graphite particles in the bipolar plate, forming non-conductive resin blocks that interrupted conductive pathways, resulting in lower in-plane electrical conductivity of the bipolar plate.

3.3 Other Resin Materials

Polyimide (PI) is a high-performance engineering plastic with excellent high-temperature resistance, chemical corrosion resistance, mechanical strength, good insulation, and dimensional stability. It is widely used in aerospace, automotive, electronics, and chemical industries. Researchers have considered incorporating PI into composite bipolar plates to enhance performance. PI fillers can improve high-temperature resistance, mechanical strength, and corrosion resistance, thereby enhancing the overall performance of fuel cells.

Chang F R et al. [18] prepared expanded graphite/polyimide composite bipolar plates. Test results showed that when the PI content was 30%, the in-plane electrical conductivity was 230.84 S/cm. The study indicated that polyimide (PI) resin has good thermal stability and corrosion resistance, suitable for high-temperature and strongly acidic environments.

3.4 Modification of Resin Materials

Researchers modify resin materials to improve their performance and stability under specific conditions. In high-temperature and high-pressure environments, resin materials may face challenges such as loss of mechanical properties or heat resistance, which can affect the reliability and long-term operation of equipment or systems. By modifying resin materials, their high-temperature resistance, mechanical properties, and stability can be enhanced, allowing them to adapt to more demanding working environments.

Lee D et al. [38] used cyanate ester-modified epoxy resin to withstand high-temperature and high-compressive pressure environments, showing excellent performance. During the curing process, the cyanate ester-modified epoxy resin forms an epoxy-aminoamide network structure, increasing the glass transition temperature and thermal stability, and enhancing compressive strength. Composite materials made from this modified resin have better heat resistance, mechanical properties, and stability, making them suitable for applications such as PEMFC.

Chen J et al. [39] improved the flexibility of phenolic-formaldehyde resin by introducing epoxy resin as an adhesive. Subsequently, they used a copolymerization method to embed flexible segments of epoxy resin into the PF resin structure, increasing the flexural strength of PF-EP-CBP to 46.20 MPa, a 156% improvement over the original PF-CBP, and surpassing the DOE target. Adjusting the flexible segments within the resin network structure was found to be an effective strategy, enhancing mechanical bonding between graphite and resin, improving overall performance, with potential for low-cost and large-scale manufacturing.

3.5 Dual Percolation Effect

The dual percolation effect describes the transmission processes of substances in complex networks, where different scales or mechanisms of percolation exist. This effect is also observed in biological or social networks, describing the spread of information and resources. In composite bipolar plates, the dual percolation effect forms dual conductive paths, enhancing electrical conductivity. Fillers or additives selectively position themselves in different phases or interfaces within polymer mixtures, forming conductive networks (Fig.11). This structure aids in electron transport, reduces resistance, and improves electrical conductivity, thereby enhancing the efficiency of fuel cell systems.

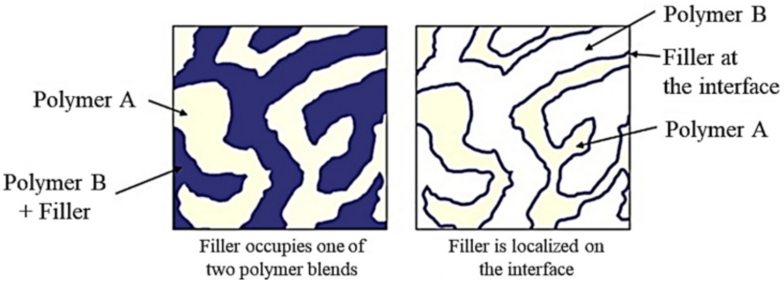

Fig. 11 Dual percolation effect

Lee H E et al. [40] improved the permeability state of thermoplastic polymers and the electrical conductivity of composite plates using solution impregnation and dual percolation effects. Through the dual percolation effect, MWNTs form an effective conductive network, reducing the area-specific resistance (ASR) of carbon felt reinforced PP/PE/MWCNT composites. This structure promotes electron transfer between conductive fillers, significantly enhancing the electrical conductivity of the composite, making its ASR approximately 59.4% lower than that of plates prepared by traditional methods.

Soares da Silva J P et al. [41] studied the dual percolation effect of PS/PBAT composites with carbon nanotubes. The electrical conductivity of PS/PBAT composites containing 0.66 wt.% carbon nanotubes reached 0.8 S/m, attributed to the dual percolation effect and the selective localization of CNTs in the PBAT phase. The preference of CNTs to localize in the PBAT phase and the continuous structure and selective localization of fillers are among the reasons for superior electrical performance.

Lee H E et al. [42] developed carbon fiber/polypropylene/polyethylene composites filled with MWNTs as bipolar plates. The study showed that the electrical conductivity of PP/PE mixed sol composites with 5 wt% MWCNTs significantly increased. At the same MWCNT content, the electrical conductivity of PP/PE mixed sol composites was higher than that of PP sol composites, attributed to the dual percolation effect where the selective distribution of MWCNTs improved conductivity without excessively increasing viscosity.

Ghosh P et al. [43] prepared PBI and phosphosilicate nanonetwork (PPSN) composite electrolyte membranes. They used the sol-gel method to prepare the PPSN nanonetwork, which was then compounded with PBI. Compared to the original PBI, the ultimate strength increased by 47.5%, and water absorption and acid doping levels significantly improved. The interaction between PPSN and PBI forms a structure of conductive channels, increasing proton conduction pathways (Fig. 12), enhancing conductivity.

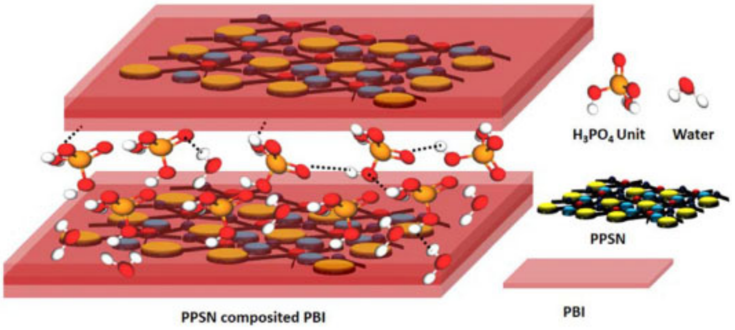

Fig. 12 Interaction of proton conduction channels in PPSN-PBI nanocomposite membranes

4. Summary and Outlook

The thesis emphasizes the importance of component regulation in understanding composite bipolar plates. By selecting two components—a graphite matrix and a resin binder—the study delves into material selection, formulation design, and modification methods. Additionally, the synergy and dual percolation effects among various materials were discovered. Performance comparisons were made against the Department of Energy standards for selected and modified composite bipolar plates. Through microscopic structural analysis, the reasons for achieving optimal performance were explored, summarizing the best graphite-resin ratios and modification methods for future reference.

In the years to come, further research can be conducted to explore the relationship between the performance and structure of various materials, aiming for more precise material design and synthesis methods. Emerging material science technologies, such as artificial intelligence and machine learning, can be integrated to accelerate material development processes, enhancing the performance of graphite-resin bipolar plates and expanding their applications in the energy field. Additionally, these research findings can be considered for applications in other fields, such as electronic devices and aerospace, to advance the development and application of material science.

References

[1] Kim M, Lim J W, Kim K H. Bipolar plates made of carbon fabric/phenolic composite reinforced with carbon black for PEMFC. Composite Structures. Vol. 96 (2013), p. 569-575.

[2] Yin Q, Li A J, Sun K N, et al. Preparation of high-performance phenolic-formaldehyde resin/graphite bipolar plate conductive composite materials. modern chemical industry. (2007) No. S1, p. 220-223.

[3] Yao K, Adams D, Hao A, et al. Highly conductive and strong graphite-phenolic resin composite for bipolar plate applications. Energy & fuels. Vol. 31 (2017) No. 12, p. 14320-14331.

[4] Cui T, Li P, Liu Y, et al. Preparation of thermostable electroconductive composite plates from expanded graphite and polyimide. Materials Chemistry and Physics. Vol. 134 (2012) No. 2-3, p. 1160-1166.

[5] Wang X, Wei S, Wu Y, et al. Achieving high electrochemical performance of PEMFCs with ultrathin and highly conductive graphite-resin composite bipolar plates. International Journal of Hydrogen Energy. Vol. 55 (2024), p. 654-664.

[6] Hwang I U, Yu H N, Kim S S, et al. Bipolar plate made of carbon fiber epoxy composite for polymer electrolyte membrane fuel cells. Journal of power sources. Vol. 184 (2008) No. 1, p. 90-94.

[7] Kim M, Lim J W. Surface modification of carbon fiber phenolic bipolar plate for the HT-PEMFC with nano-carbon black and carbon felts. Composite structures. Vol. 119 (2015), p. 630-637.

[8] Kuan Y D, Ciou C W, Shen M Y, et al. Bipolar plate design and fabrication using graphite reinforced composite laminate for proton exchange membrane fuel cells. International Journal of Hydrogen Energy. Vol. 46 (2021) No. 31, p. 16801-16814.

[9] Madheswaran D K, Thangavelu P. Reviewing carbon nanotube fillers for enhanced conductivity in proton exchange membrane fuel cell bipolar plates. Materials Letters. Vol. 358 (2024), p. 135838.

[10] Ramírez-Herrera C A, Tellez-Cruz M M, Pérez-González J, et al. Enhanced mechanical properties and corrosion behavior of polypropylene/multi-walled carbon nanotubes/carbon nanofibers nanocomposites for application in bipolar plates of proton exchange membrane fuel cells. International Journal of Hydrogen Energy. Vol. 46 (2021) No. 51, p. 26110-26125.

[11] Xiao M, Lu Y, Wang S J, et al. Poly (arylene disulfide)/graphite nanosheets composites as bipolar plates for polymer electrolyte membrane fuel cells. Journal of Power Sources. Vol. 160 (2006) No. 1, p. 165-174.

[12] Liao S H, Hsiao M C, Yen C Y, et al. Novel functionalized carbon nanotubes as cross-links reinforced vinyl ester/nanocomposite bipolar plates for polymer electrolyte membrane fuel cells. Journal of Power Sources. Vol. 195 (2010) No. 23, p. 7808-7817.

[13] Liao S H, Weng C C, Yen C Y, et al. Preparation and properties of functionalized multiwalled carbon nanotubes/polypropylene nanocomposite bipolar plates for polymer electrolyte membrane fuel cells. Journal of Power Sources. Vol. 195 (2010) No. 1, p. 263-270.

[14] Kuan Y D, Ciou C W, Shen M Y, et al. Bipolar plate design and fabrication using graphite reinforced composite laminate for proton exchange membrane fuel cells. International Journal of Hydrogen Energy. Vol. 46 (2021) No. 31, p. 16801-16814.

[15] Hwang I U, Yu H N, Kim S S, et al. Bipolar plate made of carbon fiber epoxy composite for polymer electrolyte membrane fuel cells. Journal of power sources. Vol. 184 (2008) No. 1, p. 90-94.

[16] Kang K, Park S, Ju H. Effects of type of graphite conductive filler on the performance of a composite bipolar plate for fuel cells. Solid State Ionics. Vol. 262 (2014), p. 332-336.

[17] de Oliveira M C L, Sayeg I J, Ett G, et al. Corrosion behavior of polyphenylene sulfide–carbon black–graphite composites for bipolar plates of polymer electrolyte membrane fuel cells. International journal of hydrogen energy. Vol. 39 (2014) No. 29, p. 16405-16418.

[18] Chang F R. Preparation and performance study of expanded graphite/polyimide composite bipolar plate (Master's thesis, East China University of Science and Technology, 2015).

[19] Wang J. Preparation and performance study of carbon microsphere-based bipolar plate composite materials (Master's thesis, Harbin Institute of Technology, 2017).

[20] Gautam R K, Kar K K. Synergistic effects of carbon fillers of phenolic resin based composite bipolar plates on the performance of PEM fuel cell. Fuel Cells. Vol. 16 (2016) No. 2, p. 179-192.

[21] Kakati B K, Ghosh A, Verma A. Efficient composite bipolar plate reinforced with carbon fiber and graphene for proton exchange membrane fuel cell. International journal of hydrogen energy. Vol. 38 (2013) No. 22, p. 9362-9369.

[22] Jeong K I, Oh J, Song S A, et al. A review of composite bipolar plates in proton exchange membrane fuel cells: Electrical properties and gas permeability. Composite Structures. Vol. 262 (2021), p. 113617.

[23] You M M. Preparation and performance study of fiber-reinforced resin/graphite composite bipolar plate (Master's thesis, Shandong University, 2011).

[24] Darıcık F, Topcu A, Aydın K, et al. Carbon nanotube (CNT) modified carbon fiber/epoxy composite plates for the PEM fuel cell bipolar plate application. International Journal of Hydrogen Energy. Vol. 48 (2023) No. 3, p. 1090-1106.

[25] Yin Q. Preparation and performance study of carbon nanotube-reinforced phenolic-formaldehyde resin/graphite composite bipolar plate (Master's thesis, Shandong University, 2008).

[26] Dhakate S R, Sharma S, Chauhan N, et al. CNTs nanostructuring effect on the properties of graphite composite bipolar plate. International Journal of hydrogen energy. Vol. 35 (2010) No. 9, p. 4195-4200.

[27] Witpathomwong S, Okhawilai M, Jubsilp C, et al. Highly filled graphite/graphene/carbon nanotube in polybenzoxazine composites for bipolar plate in PEMFC. International Journal of Hydrogen Energy. Vol. 45 (2020) No. 55, p. 30898-30910.

[28] Lee J H, Jang Y K, Hong C E, et al. Effect of carbon fillers on properties of polymer composite bipolar plates of fuel cells. Journal of Power Sources. Vol. 193 (2009) No. 2, p. 523-529.

[29] Hu B, Chang F L, Xiang L Y, et al. High performance polyvinylidene fluoride/graphite/multi-walled carbon nanotubes composite bipolar plate for PEMFC with segregated conductive networks. International Journal of Hydrogen Energy. Vol. 46 (2021) No. 50, p. 25666-25676.

[30] Li W, Jing S, Wang S, et al. Experimental investigation of expanded graphite/phenolic resin composite bipolar plate. International Journal of Hydrogen Energy. Vol. 41 (2016) No. 36, p. 16240-16246.

[31] Kim M, Lim J W, Kim K H. Ultra high speed curing bipolar plates made of carbon fabric/phenolic composite using acid catalyst for proton exchange membrane fuel cell. Composite Structures. Vol. 108 (2014), p. 1-8.

[32] Kakati B K, Deka D. Differences in physico-mechanical behaviors of resol (e) and novolac type phenolic resin based composite bipolar plate for proton exchange membrane (PEM) fuel cell. Electrochimica Acta. Vol. 52 (2007) No. 25, p. 7330-7336.

[33] Du C, Ming P, Hou M, et al. Preparation and properties of thin epoxy/compressed expanded graphite composite bipolar plates for proton exchange membrane fuel cells. Journal of Power Sources. Vol. 195 (2010) No. 3, p. 794-800.

[34] Xia L, Li A, Wang W, et al. Effects of resin content and preparing conditions on the properties of polyphenylene sulfide resin/graphite composite for bipolar plate. Journal of power sources. Vol. 178 (2008) No. 1, p. 363-367.

[35] Liao S H, Yen C Y, Weng C C, et al. Preparation and properties of carbon nanotube/polypropylene nanocomposite bipolar plates for polymer electrolyte membrane fuel cells. Journal of Power Sources. Vol. 185 (2008) No. 2, p. 1225-1232.

[36] Lim J W, Kim M, Yu Y H. Development of carbon/PEEK composite bipolar plates with nano-conductive particles for High-Temperature PEM fuel cells (HT-PEMFCs). Composite structures. Vol. 118 (2014), p. 519-527.

[37] Zeng H D. Preparation and performance study of graphite/polyimide-PEEK resin composite bipolar plate for PEMFC (Master's thesis, Central South University, 2022).

[38] Lee D. Carbon composite bipolar plate for high-temperature proton exchange membrane fuel cells (HT-PEMFCs). Journal of Power Sources. Vol. 327 (2016), p. 119-126.

[39] Chen J, Fan R, Peng Y, et al. Tuning the performance of composite bipolar plate for proton exchange membrane fuel cell by modulating resin network structure. Journal of Power Sources. Vol. 582 (2023), p. 233566.

[40] Lee H E, Chung Y S, Kim S S. Feasibility study on carbon-felt-reinforced thermoplastic composite materials for PEMFC bipolar plates. Composite Structures. Vol. 180 (2017), p. 378-385.

[41] Soares da Silva J P, Soares B G, Silva A A, et al. Double percolation of melt-mixed PS/PBAT blends loaded with carbon nanotube: Effect of molding temperature and the non-covalent functionalization of the filler by ionic liquid. Frontiers in Materials. Vol. 6 (2019), p. 191.

[42] Lee H E, Han S H, Song S A, et al. Novel fabrication process for carbon fiber composite bipolar plates using sol gel and the double percolation effect for PEMFC. Composite Structures. Vol. 134 (2015), p. 44-51.

[43] Ghosh P, Ganguly S, Kargupta K. Phosphosilicate nano-network (PPSN)-Polybenzimidazole (PBI) composite electrolyte membrane for enhanced proton conductivity, durability and power generation of HT-PEMFC. International Journal of Hydrogen Energy. Vol. 47 (2022) No. 75, p. 32287-32302.