Progress in the study of bipolar plates/conductive fillers

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Abstract. Proton exchange fuel cell (PEMFC) is an efficient, low-pollution and clean energy source that can directly convert chemical energy into electrical energy, and it has a broad application prospect in the future of on-board driving power supply, portable power supply and power station for home use. As one of the key components of PEMFC, the choice of material has a great influence on its performance. In order to find new materials for bipolar plates with excellent performance and low cost, this paper reviews the research progress of conductive filler/resin composite bipolar plates for PEMFCs, and summarizes the relevant properties of the current composite bipolar plates with different resins/different conductive fillers.

Keywords: proton exchange membrane fuel cell (PEMFC); bipolar plates; processing method; resin/conductive filler composites.

1. Introduction

The main role of bipolar plate in PEMFC is to support and connect each single cell to form a battery stack, and at the same time, separate the reactive gases, transport the reactive gases to the fuel cell through the flow channel, remove the water and heat generated by the reaction, and collect and export the electric current. Therefore, the bipolar plate must have low gas permeability, good electrical conductivity, thermal conductivity and corrosion resistance, as well as a certain degree of mechanical strength. In order to ensure that the bipolar has this excellent performance, the processing technology of bipolar plate plays a very important role.

For the processing of bipolar plates, thermoplastic injection molding and thermoset thermoset compression molding are the most common techniques. The most basic advantage of compression molding is that the viscosity of the final formulation does not need to be very low. Injection molding is highly productive, suitable for mass production, can be mechanized and automated, and results in products with precise dimensions and more complex shapes. Relative to injection molding, molding can be used in ordinary hydraulic presses, mold structure is simple, the products obtained are of high density, precise size, less shrinkage, good performance, at the same time can be molded with very poor fluidity of the material, in the bipolar plate molding, can take into account the performance, composition, molding process requirements, so that the bipolar plate products obtained are dimensionally stable, thermal stability, electrical conductivity, mechanical properties are relatively high. If the reasonable design of the mold and the organization of the molding process, can also achieve high productivity.

The injection molding of graphite/thermoplastic polymer composite bipolar plates was investigated at the University of Duisburg-Essen[1] , Germany. The results showed that the production cycle time of each plate was 30~60s, and the volumetric conductivity was 5~150 S/cm. Tongmin Cui et al.[2] prepared conductive composite plates as potentiostatic bipolar plates for a polymer electrolyte membrane fuel cell (PEMFC) by using expanded graphite (EG) as the carbon filler and polyimide (PI) as the binder of the thermo-compression molding method. 220°C was used for molding the plates to achieve conductivity above 160°C and flexural strength above 35MPa. molding was suitable for the composite plates to achieve conductivity above 160°C and flexural strength above 35 MPa.MinkookKim et al.[3] developed a continuous process for mass production of carbon/phenol composite bipolar plates using hot rolling. The results showed that the composite bipolar plates prepared by the optimized hot rolling process had a tensile strength of 400 MPa, which

was 33% higher than that of the compression molded samples.The ASR was 32% higher than that of the hot compression molded samples. And the permeability is absolute zero.

For other processing methods, based on the use of inexpensive and commercially available materials, it is possible to obtain materials that fully comply with the technical requirements in terms of electrical conductivity and permeability by appropriately altering the formulation and processing conditions of the composite material. The processability and productivity of the method can also be improved by reducing the molding time at the same time. E.A Cho et al.[4] Composite powders were made from 90% graphite powder, 10% unsaturated polymer and small amounts of organic solvents and additives. The volume resistivities of composite A and composite B were obtained as 16.85 Ω-cm and 131.1 Ω-cm, respectively.The flexural strengths of composites A and B were 394 kgf cm2 and 209 kgf cm2 . However, the performance of composite B bipolar plate was slightly better than that of composite A bipolar plate.Xiuping Zhang et al.[5] investigated a layer-by-layer method to prepare graphite/resin composite bipolar plates The interface contact resistance of the resulting composite was 9.0%. The resulting composite has an interfacial contact resistance of 9.2 mΩ-cm2 and a flexural strength of 44.3 MPa, which is better than that of the plates prepared by the single-layer method.

High-performance conductive filler-reinforced polymer composites are an ideal alternative to graphite and metallic materials in PEMFCs.Du et al.[6] obtained epoxy/CEG composite bipolar plates by three preparation techniques, and a comparison revealed that the compression-impregnation-compression method was the best method. The batteries with the best composite bipolar plates assembled by this technique showed excellent stability after 200 hours of endurance testing. Conductive polymer composites (cpc) with good density and corrosion resistance can be used as bipolar plates (BP) for PEMFC. HaEunLee et al.[7] Carbon felt reinforced PP/PE composites filled with MWCNTs were prepared as PEMFC bipolar plates by using sol-gel impregnation method and double penetration effect, which enhances impregnation state and improves the electrical conductivity of the composites. S. Raja et al. [8] The composites were successfully prepared by L16 orthogonal array (OA) using AquilaTaguchi optimization (ATO) method to control the mixing of the composites with the resin, whereas the composites were later poured into steel molds, and the curing time was maintained at 2 hr, curing temperature at 140°C, and curing pressure at 110 MPa during the casting process, based on carbon black, glass fiber, graphite, epoxy resin and silicone resin as raw materials for polymer composite bipolar plates.

Composite bipolar plates manufactured through various processing methods have a variety of characteristics, this paper focuses on the current application of resin-based carbon composite bipolar plates for PEMFC and comparing the proton exchange membrane fuel cell bipolar plates prepared with a single or multiple resins as the binder and a single or multiple carbon-based materials (carbon black, carbon fiber, carbon nanotubes, etc.) as the conductive filler.

2. Different carbon materials

Composite bipolar plates are made by molding and injection molding with polymer resin as binder and carbon material as conductive filler. Carbon black, carbon fiber, graphite, carbon nanotubes, etc. are often used as conductive fillers because of their good electrical conductivity and mechanical properties.

2.1 Single carbon material

2.1.1 Graphite/polymer composites

Graphite is the most commonly used material for PEMFC composite bipolar plates. It has good electrical and thermal conductivity, corrosion resistance and plasticity. Graphite in the crystal with sp2 hybridization between carbon atoms in the same layer to form covalent bonds, six carbon atoms in the same plane to form a positive hexagonal ring, stretching to form a lamellar structure. This

structure makes carbon and the layers (in-plane) with high conductivity, and in the vertical direction (through the plane) with low conductivity.

Polymer/graphite composite bipolar plates are prepared using graphite as conductive filler and polymer as binder. Many researchers have obtained polymer/graphite composite bipolar plates with very different properties by varying the graphite particle size, graphite content, controlling the graphite morphology, or by subjecting the graphite to a series of chemical reactions.

Zheng et al.[9] prepared graphite composite plates from flake graphite with different particle sizes and found that as the graphite particle size gets smaller, the graphite composite conductivity first decreases rapidly, then a relatively stable plateau occurs, and finally decreases slowly. When the graphite particle size was varied from 100 mesh to 2500 mesh, the flexural strength of graphite composites first increased rapidly and then maintained an equilibrium trend.OluwaseunA.Alo[10] team chose the maleic anhydride grafted polypropylene compatibilized polypropylene (PP)/ epoxy blends with a melting point of $156°$ C and a density of 0.934 g-cm−3 at $25°$ C, and by melt mixing and compression molding, the graphite composites were prepared. PP/epoxy/graphite composites with different graphite contents. The results obtained show that the in-plane and through-plane conductivity increases and the flexural strength decreases with increasing graphite content and conclude that in PP/epoxy/80 wt% graphite composites are the most promising combination of properties for bipolar plate applications.

Yao et al.[11] prepared compression-molded samples of SG, NG, EG and phenolic resin, respectively. When comparing the resulting samples, it was found that the EG/phenolic resin composite exhibited the best performance with a flexural strength of 109 MPa even at a high graphite loading of 80 wt% and a low plate thickness of 0.9 mm as well as an in-plane conductivity of 182 S/cm. Cui et al.[2] prepared conductive composites as PEMFC bipolar plates by hot compression molding method using expanded graphite (EG) as carbon filler and polyimide (PI) as binder. composites as PEMFC bipolar plates. It was found that increasing the expansion ratio of the EG used in the composites increased the flexural strength and electrical conductivity. The electrical conductivity was higher than 160 S-cm-1 and flexural strength was higher than 45 MPa when molded at $220°$ C. S.R. Dhakate et al.[12] developed expanded graphite-based nanocomposites by compression molding technique and obtained the samples with a packing density of 1.5-1.55 g/cm -3 . Compared with graphite resin-based composite (>12 GPa) plates, the Expanded graphite (3-8 GPa) composites have lower modulus values.Wei et al.[13] prepared graphite/PP/CCFs composites using two different types of graphite powders as primary conductive fillers and PP as binder. The experimental results showed that the NFG-containing composites had higher electrical conductivity than the SG-containing composites for the same graphite particle size. The electrical conductivity of NFG composites with a particle size of 106μm is 180.4% higher than that of SG composites with the same particle size. Since the NFG particles are in the form of thin sheets, the monolithic NFG particles are smaller in size and thinner in thickness compared to the SG particles with the same particle size having a block structure. In addition, these sheet-like particles are more easily compressed into oriented and laminated structures with higher density, which reduces the electrical resistance. Moreover, based on the XRD spectra of the NFG and SG powder samples, it can be obtained that the NFG powders and composites have a very small peak intensity in half of the maximum (FWHM) and a high degree of crystallinity, which results in a higher electrical conductivity.

2.1.2 Carbon black reinforced composites

Characterized by long-lasting and stable electrical conductivity, low cost, and wide sources, carbon black has also been used to improve electrical conductivity in composite bipolar plates in recent years.

R. Dhakate et al.[12] developed expanded graphite based nanocomposites as PEMFC bipolar plates by compression molding technique. EG-based composites having 40-45 wt% resin with addition of 5 wt% carbon black helped to improve the conductivity without compromising other

properties of the bipolar plates. Expanded graphite (3-8 GPa) composites have lower modulus values compared to graphite resin-based composites (>12 GPa) plates.ChenHui et al.[14] selected low-cost novel epoxy resins with natural graphite and carbon black to prepare graphite/polymer composite bipolar plates using an intrinsic molding composite process. The results showed that the composite bipolar plates had good corrosion resistance in 0.005 mol/LH2SO4+2×10-6 mol/LHF simulated solution.TGA results showed that the novel epoxy resin/NG composite had excellent thermal stability. Resin content of about 15 wt.%; molding pressure of 200 MPa; curing temperature of 180°C; and graphite particle size of -200 mesh were the optimum process conditions for the preparation of composite bipolar plates.Hendra Suherman et al.[15] 10 vol% carbon black (CB) as the second filler was mixed with synthetic graphite/epoxy resin (SG/EP) using an internal mixer After mixing, composite bipolar plates were prepared by compression molding.10vol% CB, 65vol% SG, 25vol% EP is the best combination of CB/SG/EP composites.The bipolar plates were obtained with an in-plane conductivity of 150S/cm, a through-plane conductivity of 55S/cm and a flexural strength of 38.8MPa.

The composite bipolar plate with carbon black added as the second conductive filler, due to the carbon black is easy to combine with the resin agglomeration, with the carbon black content of more thieves, the conductivity of the composite bipolar plate increases, but at the same time, it will make the strength of the bipolar plate decreased.

2.1.3 Graphene-reinforced composites

Graphene (GP) is an allotrope of carbon nanotubes. GP was chosen as one of the additives due to its high electrical conductivity (about 106 Scm-1), excellent mechanical strength (124 GPa), very good thermal conductivity (5.000 Wm K-1-1), very low gas permeability, inherent flexibility, high aspect ratio, and unique substrate structure.

M. Phuangngamphan et al.[16] developed highly conductive graphite/graphene-filled polybenzoxazine (PBA) composites for fuel cell bipolar plates.The thermal conductivity of the samples having the combination of 75.5 wt% graphite and 7.5 wt% graphene was increased to 14.5 W-mK-1 , and the electrical conductivity was increased to 323S-cm-1 , while the specimen's bending strength decreases with the increase of graphene content.

Kim et al.[17] Graphite nanoparticles (GNP) were used as secondary fillers to improve the electrical conductivity of polyphenylene sulfide (PPS)/graphite composites used as PEMFC bipolar plates. When 5 wt% GNP was added to the PPS/graphite (>80 wt%) composites, the in-plane conductivity was 1340 S/cm, the trans-plane conductivity increased from 19 to 54 S/cm, and the flexural strength was slightly reduced.

2.1.4 Carbon nanotube reinforced composites

Carbon nanotubes have also attracted extensive research in the field of composite bipolar plates in recent years due to their excellent mechanical properties and high electrical and thermal conductivity.

Liao et al.[18] prepared thin nanocomposite bipolar plates (1.2 mm thickness) consisting of multi-walled carbon nanotubes (MWCNTs), graphite powder and PP by compression molding method. The results showed that the bulk conductivity in the composite system with different MWCNT contents exceeded 100 S/cm. The optimal compositions were 4 phr-MWCNTs, 20 wt% LC-PP and 80 wt.% graphite.

Hu[19] et al. Polyvinylidene fluoride (PVDF)/ graphite/ multi-walled carbon nanotubes (MWCNTs) composite bipolar plates with isolated conductive networks were prepared by structural design and molding. When only one type of graphite was added as a conductive filler and the graphite content was increased to 60%, the in-plane conductivity was increased to 287.53 S/cm, and the ASR was reduced to 10.95 mΩcm2 . In addition, after the addition of MWCNTs, due to the presence of the conductive network, the conductivity of the composite bipolar plate containing 5 wt% MWCNTs and 35 wt% graphite was further reduced to 161.57 S /cm, with a flexural strength of 42.65 MPa and a corrosion current density of less than 1 μA/cm2 .

Li et al.[20] prepared reticulated carboxylated MWCNT, expanded graphite and resin were molded to prepare composite bipolar plates. The experimental results showed that when the carboxylation treatment time was 15 min and the filler content was 2.4%, the planar conductivity reached 243.52 S/cm and the flexural strength reached 61.9 MPa.Unlike the conventional composite bipolar plates with directly added MWCNTs, the carboxylated MWCNTs dispersed more homogeneously and the wettability with the resin was significantly improved. Both the addition of appropriate amount of MWCNTs and carboxylated MWCNTs are beneficial to the reduction of corrosion current density, and the corrosion resistance meets the DOE standard.

2.1.5 Carbon fiber reinforced composites

Carbon fiber has also been applied to composite bipolar plates by many researchers due to its advantages of low density, good electrical conductivity, mechanical properties and chemical stability. In order to replace the traditional graphite composite (GBP) and metal composite (MBP), the new bipolar plates are made of composite resin reinforced carbon fibers.

Zheng et al.[19] prepared composite bipolar plates using phenolic resin as a binder, natural flake graphite as a conductive substrate, and chopped carbon fibers with a length of 1 mm as an auxiliary filler. The changes in electrical conductivity and bending strength of graphite composite plates were investigated at 1%, 3%, 5%, 7% and 9% carbon fiber addition concentrations. After 3% addition concentration, the conductivity decreased slowly with the continuous increase of addition concentration. The addition of chopped carbon fibers significantly increased the flexural strength of the composite bipolar plates. With the increase of concentration, the flexural strength first increases and then gradually decreases after reaching the maximum value. In this case, the flexural strength of graphite composite plate is 60.46 MPa, which is 8.86 MPa higher than that of pure graphite composite plate.

T.S.K. Raunija et al.[21] Randomly oriented hybrid carbon fibers (T-800 and P-75) reinforced hybrid carbon matrix composites were successfully prepared. High electrical conductivity, high strength, sufficient density and savings in fabrication cost and time were achieved. The bulk density of the C/C composite bipolar plate with expanded carbon fibers was 1.75 gcm−3 , the flexural strength was 98 MPa, the compressive strength was 205 MPa, and the electrical conductivity was 595 S-cm−1 (in-plane), and the voltage difference was about 0.1 V at maximum power density at 65 ° C compared with the commercial graphite bipolar plate, which can be deduced that the bipolar plate has good electrical properties.

Minkook Kim et al.[22] developed a bipolar plate made of plain carbon fiber epoxy composites, and the experimental results showed that the volume resistance of the plain carbon composite bipolar plate is about 50% smaller than that of the carbon composite bipolar plate made of unidirectional carbon fiber epoxy composites of the same thickness.

BudsabaKaroonsit et al.[23] prepared laminated carbon fiber/epoxy composites for PEMFC bipolar plates. Two carbon fillers (COOH-MWCNT and COOH-GNP) reinforced with woven carbon fiber sheets (WCFS) were used. The prepared bipolar plates obtained volumetric conductivity of 214 S/cm and surface conductivity of 273 S/cm, flexural strength of 596 MPa, and compressive strength of 52.4 MPa.

According to the requirements of the U.S. Department of Energy for the performance of PEMFC bipolar plates[27] , the effects of four different conductive fillers (carbon black, graphene, multiwall carbon nanotubes, and carbon fibers) on the performance of graphite/resin composite bipolar plates can be derived. From the above, it can be seen that the electrical conductivity of the composites with the addition of carbon black, carbon nanotubes, carbon fibers, and multiwall carbon nanotubes increases in order, and the in-plane conductivity of polyphenylene sulfide (PPS)/graphite composites with the addition of GNP is as high as 1340 S/cm, and the flexural strength of the bipolar plates of the composites with the addition of graphene, carbon black, multiwall carbon nanotubes, and carbon fibers increases in order, and the mixed carbon fibers (T -800 and P-75) reinforced hybrid carbon matrix composites flexural strength up to 98MPa.

| Table 1 – Technical Targets for Bipolar Plates (adapted from ref. 13). | | | |
Characteristic	Units	2020 status	2025 target
Plate cost	$/kW	5.4	2
plate weight	kg/kW	< 0.4	0.18
plate H_2 permeability coefficient	std cm^3/s·cm^2·Pa @80 °C, 3 atm, 100% relative humidity	< $2 \cdot 10^{-6}$	< $2 \cdot 10^{-6}$
corrosion	$\mu A/cm^2$	< 0.1	< 1
electrical in-plane conductivity	S/cm	> 100	> 100
flexural strength	MPa	> 34	> 40

Figure 1 DOE technical targets for bipolar plated of PEMFCs[24]

2.2 Multiple carbon materials

2.2.1 Composite bipolar plates with two kinds of conductive fillers added

Hu et al.[25] prepared low filler highly conductive pvdf-34wt% graphite-6wt% carbon black composite bipolar plates with synergistic separation structure. Its in-plane conductivity was 177.87 S/cm, area specific resistance was 9.30 m Ω ·cm2 , and flexural strength was 26.14 MPa. The in-plane and through-plane conductivities were 256.78 and 9704.50 times higher than those of the randomly dispersed composite BP with graphite and CB, respectively. The maximum power density of the PEMFC monobloc cell of the composite bipolar plate was 646.08 mW/cm2 , which was higher than that of the conventional composite bipolar plate.FatihDarck et al.[26] investigated carbon fiber/epoxy composite bipolar plates with the addition of CNTs additives in the range of 0.25-1.25%wt. The experimental results showed that the electrical conductivity reached 120 S/cm at 1.25% carbon nanotube reinforcement.The flexural strength and flexural modulus of CF/BP were increased by 42% and 27%, respectively. Compared with aluminum alloy (AA3105) bipolar plates under the same conditions, the performance of carbon fiber/epoxy composite bipolar plates with 1.25% carbon nanotubes added is very close to it.

2.2.2 Composite bipolar plates with three kinds of conductive fillers added

MuhammadTariq et al.[27] Multi-filler conductive polypropylene matrix composites consisting of multi-walled carbon nanotubes (MWCNT) and carbon black (CB) were prepared by twin-screw extrusion technique. Compromises in flexural properties and electrical conductivity were observed in the case of synthesizing two different fillers, respectively. The most balanced PP/filler structure was observed in the case of 82.5 wt.% graphite and 2.5 wt.% carbon black, with conductivity and flexural strength of 25.7 S/cm and 34.8 MPa, respectively.R.K. Gautam et al.[28] added a fixed wt.% of carbon black (5 wt.%) and graphite powder (3 wt.%) in phenolic resin by varying the content of EG in phenolic resin (10 -35 wt.%) and preparing composite bipolar plates by compression molding. The experimental results showed that the composites with 35% expanded graphite 5% carbon black and 3% graphite powder by weight had in-plane and in-tank conductivities of 374.42 S/cm and 97.32 S/cm, respectively, a flexural strength of 61.82 MPa, a storage modulus of 10.25 GPa, a microhardness of 73.23 HV, and a water absorption rate of 0.22%. The maximum power density is higher compared to EG/phenol formaldehyde resin composite and commercial bipolar plates, and the synergistic effect of ternary carbon fillers provides excellent performance for the composite bipolar plates.A.Ghosh et al.[29] developed graphene reinforced carbon-polymer composite bipolar plates using monophenol formaldehyde resin and conductive reinforcement materials (natural graphite, carbon black and carbon fibers) by compression molding technique.The graphene-reinforced carbon-polymer composite bipolar plates were developed by using monophenol formaldehyde resin and conductive reinforcement materials (natural graphite, carbon black and carbon fiber) through compression molding technique.The in-plane Polar plate has an in-plane conductivity of about 409.23 S/cm, a through-plane conductivity of about 98 S/cm, a flexural strength of 56.42 MPa, and a Shore hardness of about 60.

2.2.3 Add four kinds of conductive filler composite plate

Aninorbaniyah Bairan et al.[30] PEMFC bipolar plates were prepared using compression molding technique using polypropylene (PP) as polymer matrix and graphite (G), carbon black (CB) and

carbon nanotubes (CNTs) as reinforcements. A synergistic effect on the electrical conductivity and mechanical properties was produced by adding a small amount of 1-10 wt% carbon nanotubes to the G/CB/PP composites. The results showed that the in-plane conductivity of the composites reached 158.32 S/cm when CNTs were used as the third filler in the G/CB/PP composites at a loading of 6 wt%.Meanwhile, the optimum value of flexural strength of 29.86 MPa was obtained at a CNTs mass fraction of 5 wt%.RomanBühler et al.[31] used the MWCNT containing 20% of Polypropylene was used as a masterbatch and natural flake graphite, carbon black, carbon fiber, and expanded graphite were added to prepare composite electrode plates by mixing and compression molding. It was shown that a concentration of 15 wt% was optimal and that the carbon fibers had no significant beneficial effect on either electrical or mechanical properties. On the contrary, a maximum electrical conductivity of 46 S/cm was achieved with expanded graphite as the fourth filler in addition to Gr, CB, and CNT.

The performance of composite bipolar plates with multiple conductive fillers is significantly better than that of composite bipolar plates with a single conductive filler due to the synergistic effect between them.

3. Different resins

3.1 Thermosetting resins

Thermoset resins include phenolic, epoxy, amino, unsaturated polyester, and silicone ether resins. Thermoset resin composites have high electrical conductivity and flexural strength, but poor toughness after curing, which can easily lead to impact failure.

3.1.1. Phenolic resins

MingYu Huang et al.[32] investigated the preparation of composite bipolar plates by molding and carburizing sintering process using PF, mesophase carbon microspheres (MCMB), graphite and CF as raw materials. The results show that the developed composite bipolar plates have better overall performance with 95% carbon content, compression strength of more than 100 MPa, bending strength of more than 30 MPa, volume resistivity of less than 50×10-6 Ω-m, and the assembled monocells are able to satisfy the requirements of the fuel cells under the harsh operating conditions and performance. Kang et al.[11] prepared the composite bipolar plates by compression molding with the raw materials of SG, NG, or EG and PF, and the composite bipolar plates are made from SG, NG, or EG and PF. Kang et al. used a compression molding process to prepare composites for bipolar plates of proton exchange membrane fuel cells using SG, NG or EG and PF as raw materials. With a high graphite loading of 80 wt% and a low plate thickness of 0.9 mm as well as an in-plane conductivity of 182 S/cm, the composites had a density of about 1.55 g/cm 3 , a flexural strength of 109 MPa, and a modulus of 24 GPa. WeiweiLi et al.[33] prepared a series of expanded graphite/phenol-formaldehyde composite bipolar plates with different phenolic contents by using a vacuum impregnation of the resins and a hot pressing method. The results showed that when the concentration of water-soluble phenolic resin solution was 25%, the bipolar plates had a flexural strength of 64.9 MPa, a resistivity of 8.9 mΩ-cm, a permeability of 3×10−7 cm3 cm s-2−1 , and the results of the single-cell test showed that the EG/phenol-formaldehyde resin composite BPs outperformed graphite BPs.

3.1.2 Epoxy resins

ChenHui et al.[34] prepared two types of composite bipolar plates, graphite/phenolic resin (PF) and graphite/epoxy resin (NE), by compression molding technique. The results showed that the bending strength of graphite/NE composite plates was higher than that of graphite/PF composite plates. Since the porosity of graphite/NE is smaller than that of graphite/PF, the conductivity and bending strength of graphite/NE composite bipolar plates are higher than that of graphite/PF composite bipolar plates. A current density of 1.56 A-cm2 corresponded to a maximum power density

of 611 mW-cm2 , using 15 wt.% NE, 4 wt.% carbon black and 74 μm NG particle size evaluation for single-cell testing.

3.2 Thermoplastic resins

Thermoplastic resins :: Polypropylene Polypropylene (PP)/ Polycarbonate (PC)/ Nylon (NYLON)/ Polyetheretherketone (PEEK)/ Polyethersulfone (PES), etc. Thermoset hardening requires a long curing time to vent the gases produced in the curing reaction, which is detrimental to productivity.PP is a commonly used thermoplastic resin with good mechanical properties, low cost and low density.

3.2.1. vinyl resin (VER)

Chengguo Wang et al.[35] used liquid vinyl ester resin as the binder and natural scaled graphite as the conductive aggregate, and adopted a mixing process combining kneading and then crushing to avoid the problems of resin agglomeration and poor uniformity that appeared in the traditional kneading and mixing.Chao Du et al.[36] Vinyl ester resin (VE) and expanded graphite sheet were selected as raw materials, and a new type of thin composite bipolar plate material by vacuum impregnation method. The results show that the composite bipolar materials have good gas tightness, mechanical strength, surface hydrophilicity/hydrophobicity and stability, and they have good performance in single cell test and 200h life test.

3.2.2 Polypropylene

PP is a non-polar and semi crystalline polymer It is characterized by its high chemical resistance and thermal stability, low density, good mechanical strength, excellent processability, and low cost. and low cost, it is widely used in the manufacture of composites.Oluwaseun AyotundeAlo et al.[10] prepared graphite-polymer composites by selecting polypropylene (PP)/epoxy blends as the matrix and using carbon black (CB) secondary filler. The PP/epoxy/graphite/CB composites with 80 wt% filler content exhibited the best in-plane conductivity (88.5 S/cm), through-plane conductivity (8.52 S/cm), and flexural strength (28.53 MPa) for BP applications.C.A. Ramírez-Herrera et al.[24] A melt blending method was used to prepare multi-walled carbon nanotubes (MWCNT)/polypropylene (PP) nanocomposites or polypropylene (PP) nanocomposites composited with different loadings of carbon nanofibers (CNFs).PP/20MWCNT, PP/21.5MWCNT, and PP/15MWCNT/15CNF nanocomposites met the Department of Energy (DOE) objectives.

3.2.3. Fluorinated ethylene propylene rubber (FEP)

KwangSang Park et al.[37] prepared bp consisting of fluorinated ethylene-propylene (FEP), graphite flakes (GFs), graphite nanoplates (GnPs), and graphite particles modified with silicon carbide particles silicon carbide (SiC) particles using the molten salt synthesis method for fuel cell applications. the SiC particles synergistically enhanced the flexural strength of the composites compared to the composites with no added SiC , the addition of SiC particles to large GFs and GnPs improved the flexural strength of the composites by 24% and 130%, respectively.

3.2.4. Polyphenylene sulfide (PPS)

Polyphenylene sulfide (PPS) has the advantages of high mechanical strength, high temperature resistance, corrosion resistance, good thermal stability, good processing and molding properties, excellent electrical properties, etc. PPS can be used for a long time under the condition of 250 ℃, and the heat distortion temperature is above 260 ℃. TaoYang et al.[38] used polyphenylene sulfide and intermediate-phase carbon microspheres as the main raw materials, and prepared the composite bipolar plates by molding under the condition of less than 400 ℃. It was shown that the best overall performance of the bipolar plates was achieved when the resin mass fraction was 20%. When the resin content was varied from 15% to 20%, the water absorption rate of the bipolar plates changed greatly, and the water absorption rate did not change much when the resin content was increased. With the increase of resin content, the bending strength of bipolar plate increases, especially when the resin content is below 20%, the bending strength of bipolar plate increases rapidly.

3.2.5. New resins

Shiyuan Zhang et al.[39] Graphite-based composite bipolar plates were prepared by mechanically mixing and hot press molding using polyaryl ethyl huan (PAA) and intermediate phase bitumen as binder and graphite as conductive filler material.Cui et al.[2] EG/PI composite plates with high thermal stability were prepared using conventional compression molding method. The EG/PI composite plates molded at 220 ° C with a PI content between 40-55 wt.% could meet the technological goal of composite bipolar plates

3.3 Multiple resins

Polymer blending is a simpler and more economical method than synthesizing new polymers to produce polymers with the desired combination of properties.Bo Lv et al.[40] prepared composite bipolar plates for proton exchange membrane fuel cells by molding process using polypropylene (PP), phenolic resin (PF), and natural flake graphite (NG) as raw materials.The flexural strength of the composite plates with a mass ratio of 2:1 for PF:PP was over When the mass ratio of PF:PP reaches 2:1, the flexural strength exceeds 25 MPa, and the composite plate shows hydrophobicity as a whole. As the main material of the composite plate, graphite, has excellent stability, the resin added in the experiment has good acid resistance, which makes the corrosion resistance of the composite plate under acidic conditions comparable to that of the graphite plate. When the mass ratio of PF:PP is 2:1 and above, the gas permeability of the composite plate has basically reached the requirements for use.

HuiChen et al.[41] Natural graphite and expanded graphite were used as fillers, and phenolic resin and epoxy resin were used as binders. Composite bipolar plates were prepared by solution insertion mixing, compression molding and curing. It was shown that the composite plates using epoxy and phenolic resins as binders had higher electrical conductivity and bending strength than a single resin. When the epoxy resin content was 20%, the electrical conductivity was >100 S/cm, the bending strength was >45 MPa, and the corrosion current density was only 1.8 μA/cm2 .

Yanwen Zou et al.[42] Composite bipolar plates were obtained by molding with P17-901 o-phenylene resin and 590 phenolic modified vinyl resin as binder and natural graphite, artificial graphite, and carbon black as conductive fillers, respectively. The conductivity of the materials decreased with the increase of the binder content; when the binder content was less, the conductivity of the 590 resin binder products was significantly better than that of the 901 resin products. However, when the mass fraction of the binder is higher than 20%, the conductivity of the two is comparable.

HaEunLee et al.[43] Carbon felt reinforced thermoplastic composite bipolar plates were prepared by solution impregnation method and double permeation effect. The solution impregnation consisting of isotactic polypropylene (i-PP) and polyethylene (PE) blends was used to introduce the double permeation effect, and MWCNTs were added to enhance the electrical conductivity of the carbon felt-reinforced PP/PE composites, and the conductivity will be improved based on the double permeation effect when the conductive MWCNTs form a network of connecting paths through the insulating PP/PE matrix.Lee et al.[44] Developed by the compression molding method a carbon fiber/polypropylene (PP)/polyethylene (PE) composite bipolar plate filled with multi-walled carbon nanotubes (MWCNTs). Carbon fiber/PP/PE composite sheets were prepared by sol impregnation method and double penetration effect.The results of the study surface that the viscosity of PP/PE blended sol is lower than that of PP sol at the same MWCNT content.The ASR results are inversely proportional to the conductivity results, and the ASR value tends to decrease after plasma treatment. The ASR values of PP/PE-sol_CNT5 samples with and without plasma treatment were below the DOE target of 30 mΩ-cm2 .

The composite bipolar plate prepared by two or more resins, due to the double percolation effect between the resins, after blending the polymer helps to form contact between the carbon filler, the formation of conductive network to further improve the electrical conductivity of the resin, thus reducing the ASR of the carbon matrix reinforced composite plate. with the same content of conductive filler, a variety of composites performance is significantly higher than that of a single

resin polymer, the conductivity has been significantly improved, other indicators Other indicators, such as permeability, density, etc., have also been improved to some extent.

4. Conclusions

This paper discusses and summarizes the different properties of bipolar plate materials in PEMFC and the effects of different conductive fillers and resin materials on the performance of bipolar plates. It is summarized that for resin-based carbon composite bipolar plates, the performance of bipolar plates composed of multiple carbon materials is better than that of single carbon materials, and the performance of bipolar plates prepared with the same two or more values is higher than that of single resins with the same content of conductive fillers, and the electrical conductivity is better as well. For the future manufacturing of bipolar plates in the PEMFC, a variety of carbon materials and a variety of resins manufactured by the bipolar plate or become the mainstream trend in the future development of a variety of high-performance, low-cost, low-power composite materials will be more attention.

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