Recent Advances and Future Perspectives of Carbon Materials for Fuel Cell

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ABSTRACT:

Fuel cells in the near future are going to challenge the recent strong progress of the battery-based energy system. Despite many challenges, including material composition, storage and distribution, hydrogen fuel cell has demonstrated its potential in the trucking and fleet transportation energy systems due to its ability to be safely transported and used resulting in sharp drop in CO₂ and particulate emissions. Review works revealed that Proton Exchange Membrane Fuel Cell (PEMFC) technology is reaching a commercialization phase for the fuel cell electric vehicles (FCEVs). Study further disclosed the need for a more focused investigation into materials' properties and plate design to enhance the efficacy of composite bipolar plates (BPP), specially their electrical and mechanical properties, as one of the main components of PEMFC. Carbon fiber, expanded graphite and carbon nanotubes are promising functional materials that can be utilized to enhance the performance of bipolar plates further by addressing their critical challenges such as agglomeration and poor thermodynamic compatibility.

Conductive polymer embedded carbon nanomaterials showed high promise to improve the performance of PEMFC. Herein, the critical parameters affecting the introduction of carbon materials in fuel cell components are discussed with a focus on mechanical and durability performance of BPP. Recommendations are made related to cost vs performance for future development. This paper has also outlined the scope and future perspectives to fuel cell technology by reviewing the areas of recent developments with carbon based BPP as an attempt to highlight their potential commercial applications as high-performance bipolar plates for PEMFC.

Keywords: Carbon Materials; Bipolar Plates; Renewable Energy; Carbon Polymer Composites; Proton Exchange Membrane Fuel Cells; Electrical attributes; Mechanical Strength

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GRAPHICAL ABSTRACT:

41 Table of Contents

42

43	1. INTRODUCTION	4
44	1.1 PEMFC & BIPOLAR PLATES	6
45	2. IMPORTANT FACTORS EFFECTING THE PERFORMANCE OF BPP	8
46	2.1 EFFECTS OF VARIOUS MATERIALS ON THE COMPOSITE PROPERTIES	11
47	2.1.1 EFFECTS OF GRAPHITE	14
48	2.1.2 EFFECTS OF CARBON NANOTUBES	16
49	2.1.3 EFFECTS OF CARBON BLACK.....	17
50	2.1.4 EFFECTS OF CARBON FIBER.....	18
51	2.1.5 EFFECTS OF GRAPHITE INTERCALATION COMPOUNDS	19
52	2.1.6 EFFECTS OF EXPANDED GRAPHITE / GRAPHITE NANOPATELET	20
53	2.1.7 EFFECTS OF POLYMERS AND COMPATIBILIZERS.....	22
54	2.2 EFFECTS OF PROCESSING TECHNIQUES AND PROCESS PARAMETERS	24
55	3. ELECTRICAL CONDUCTIVITY OF THE COMPOSTIES FOR BPP	31
56	3.1 THROUGH-PLANE CONDUCTIVITY	32
57	3.2 PERCOLATION THEORY FOR CONDUCTIVITY	33
58	3.3 MODELS FOR CONDUCTIVITY.....	35
59	4. MECHANICAL PROPERTIES (STRENGTH AND MODULUS)	39
60	5. RESEARCH SCOPE AND FUTURE PERSPECTIVE.....	44
61	6. CONCLUSIONS	48

62

63

64

1. INTRODUCTION

With the increasing demand for renewable energy sources in the transportation sector and a shift in trends of vehicle-operation technologies, fuel cells for electric cars have become a hot topic of research as there are still many potential features to improve upon. Fuel cell is considered as a good alternative due to their high energy-density, excellent range, well response to varying loads, low-temperature operations, and quick start-up technology. PEMFC, the most common fuel cell, is used as one of the alternative renewable energy sources, which can contribute in reducing negative effects of climate change and air pollution caused by the consumption of fossil fuel [1]. One of the well researched subjects in this area is the BPP, which has important functions in the cell, such as distributing fuel gas and oxygen uniformly, collecting and conducting electric current from anode to cathode of the next cell to form a fuel cell stack with required voltage, proper water management within the cell, removing heat and supporting the membrane electrode assemblies (MEAs) by sustaining the clamp pressure [2-7]. The improvement of BPP is needed as it is responsible for 80% of the total weight and 40-60% of the total cost [8-11]. However, there are gaps in the research about critical factors that can help to improve the overall performance of the bipolar plates by implementing the synergistic effects of various parameters, such as effects of graphite structure and orientation, use of suitable polymer matrix on the mechanical properties and electrical performances. Other than these, dispersion of fillers, surface roughness, molding temperature, pressure and time are also important factors to be considered. In this paper, most recent researches are reviewed focusing on the progress and development in the performance improvement, especially for the electrical conductivity and mechanical strength of the bipolar plates.

Introduction of fuel cells in the transportation sector opens the tremendous opportunity of reducing non-renewable energy sources, which is important as the green house gas (GHG) emissions from this sector contributes around 14-17% globally [11,12]. Bipolar plates of the hydrogen fuel cell can be produced from various materials such as pure graphite, metal and carbon polymer composites. Among them, graphite-only plates are harder to work with due to their brittle nature and difficulties in machinability.

Metal plates offer advantages in cost and performance, such as excellent conductivity, less gas permeability, ease of mass production, less thickness and less weight than other materials. However, their corrosion tendency in the bipolar plate's harsh environment (presence of water and pH~4) make them ineffective as it may damage the expensive Platinum catalyst easily [13-17]. Hence, the carbon polymer composite may be the best option and a good alternative to metal bipolar plate. However, their performances need to be improved and cost to be minimized as per US DOE (Department of Energy) requirements. A significant amount of research has been undertaken for decades to improve the performance as well as to reduce the cost by decreasing the volume and weight. The main fillers that has been used are natural graphite (NG), synthetic graphite (SG), expanded or exfoliated graphite (EG), carbon nanotubes (CNT), carbon black (CB), and carbon fiber (CF) [18-22]. The main polymer matrix, on the other hand, has been used are phenolic, epoxy, polyvinyl ester (VE) from thermosets and polyvinylidene fluoride (PVDF), polypropylene (PP), polyethylene (PE), and polyphenylene sulfide (PPS) from thermoplastics family [23-27]. Overall, the fillers contribute more to the electrical conductivity and other electrochemical performances whereas the resin matrix contribute towards the mechanical properties and cost. Chemical, thermal, mechanical and the long-term stability of bipolar plates are the main criteria for the fuel cell to maintain long-term operation and hence, there should be greater focus on strength, corrosion resistance, easy mass production, less porosity and cost effectiveness. Research on these areas need to be critically reviewed and summarized to get an account of what has already been done and what need to be done. There are few review papers in this field and many of them are lacking in updated information as there have been a recent increase in demand of development and use of BPP. Moreover, potential applications of PEMFC are flourished in the transportation sector, electric vehicles for example, where these technologies can be harnessed. Therefore, latest important achievements need to be updated qualitatively and quantitatively. This paper has focused mainly on the recent developments and future perspectives as well as made an effort to bridge with the past achievement in this sector.

1.1 PEMFC & BIPOLAR PLATES

PEMFC is the most used fuel cell in transportation and stationary power generation sector and BPP are one of its key components. Pozio et al. [15] described PEMFC as a device that converts chemical energy of a renewable fuel into electrical energy. It depends on the continuous supply of external fuel and the theoretical conversion efficiency can reach up to 90% [28]. It is a potential energy source due to its high-energy density at low temperature (70-90 °C). The cells give an output voltage of 0.5-0.7 V individually, so they are stacked together in series connected by BPP [29] and overall efficiency depends on the single cells [30]. To increase the connectivity between the cells, the BPP need to be highly conductive. Also, to sustain the clamp pressure, they should have good mechanical properties such as flexural strength >25 MPa as per DOE requirement. The main US DOE requirements for bipolar plates are illustrated in the *Table 1* and the main components and functionality in the fuel cell stack are shown in Fig. 1.

Fig. 1: PEM fuel cell- a) Components and schematic diagram of reactants delivery path, b) fuel cell stack with external manifold (adapted from [31])

Table 1: The properties, testing standards and target values of BPP as per US DOE guideline

<i>Property</i>	<i>Testing Standard*</i>	<i>2020 Target Value*</i>
Electrical Conductivity (S.cm ⁻¹)	ASTM C611-98(2016) or 4-point probe method	>100
Flexural strength (MPa)	ASTM D790-03	>25
Corrosion resistance (μA.cm ⁻²)	Cyclic voltammetry/Potentiostatic measurement	<1
Areal specific resistance (ohm.cm ²)	ASTM D257-14 or both sides ICR measurement	<0.01
Thermal conductivity (W/m. K)	ASTM C714-17	>10
Weight (kg/kW)	Precise weighing balance method for specific thickness	<0.4
Plate H ₂ permeation coefficient (Std cm ³ /s cm ² Pa@80 C, 3 atm 100%RH)	ASTM D1434	<1.3×10 ⁻¹⁴

*Testing standards and target values are compiled as per US DOE guideline [32]

Kim et al. [33] described the advantages of using PEMFC in portable devices along with stationary and transportation applications over other devices. The main advantages are high efficiency, excellent specific energy, low operating temperature and hence, rapid start up. BPP are one of the most important parts of PEMFC as they largely contribute to stack volume, weight, cost and performance. Wang et al. [34] observed that the main phenomena of fuel cell operation are mass and heat transfer, electrochemical reactions and ionic or electronic transport whereas the main barriers to commercialization are its cost and durability which is largely dependent on BPP. Alaswad et al. [13] discussed the developments in fuel cell technologies for the transport sector. To reduce the harmful emission as well as to improve energy conversion efficiency, electric vehicles driven by fuel cells or batteries have been introduced and gained traction in the market nowadays. They are more efficient than internal combustion engine (ICE); their conversion rate is up to 90%, whereas ICE uses less than 25% of the energy produced. Their advantages include electric motors which if connected to wheels, make no energy consumption when the car is stopped. In addition to that, the regenerative braking system can return as much as half of the kinetic energy to the electrical cells [13]. The biggest advantage of electrical vehicles is the zero-emission factors compared to huge GHG emissions from conventional vehicles. PEMFC vehicles are considered as a better option for medium to heavy-duty vehicles because of the lightweight structure, low operating temperature, zero particulate emission, high energy-density, and high energy conversion efficiency.

2. IMPORTANT FACTORS AFFECTING THE PERFORMANCE OF BPP

The most desired properties of BPP for high level performances are electrical conductivity, chemical stability at high temperature, lightweight, cost effectiveness, gas impermeability and enough mechanical strength to sustain clamping forces. There are some important parameters that determine these characteristics of the bipolar plates. Among them, the orientation of fillers is the most important one; which can be controlled by regulating shear stress, die structure and filler aspect ratio [35]. To attain these parameters, the inherent properties of fillers and polymer matrix, their interfacial properties as well as processing conditions for both mixing and fabrication need to be looked carefully.

Boyaci San and Okur [36] investigated the parameters and their effects on the electrical and mechanical properties of bipolar plates using response surface methodology (RSM) and Design Expert software. They found that roughness is an important property that can be reduced by longer molding time and can affect the performance, especially electrical conductivity. Both roughness and electrical conductivity is influenced by pressure and temperature of the process (Fig. 2). However, minimum roughness can be achieved at mean temperature and pressure, whereas electrical conductivity is more affected by temperature than the pressure in the process. In most cases, molding temperature is more important as a parameter than molding time. Higher molding pressure, on the other hand, increases the electrical conductivity by suppressing the surface roughness [37-39]. **Table 2** shows some important parameters identified with different materials and fabrication methods.

a)

b)

Fig. 2: :Important factors affecting composite properties- a) Roughness as a function of pressure and temperature, b) Electrical conductivity as a function of pressure and temperature [36]

Table 2: Important parameters to consider for fabrication of composite

<i>Material</i>	<i>Process</i>	<i>Results</i>		<i>Parameters</i>	<i>Ref.</i>
		<i>Conductivity</i>	<i>Flexural Strength</i>		
Graphite/CB with Carbon-Epoxy prepreg	Prepreg-hot press	ASR* ~ 10 mΩ.cm ²	234 MPa	Content, morphology, processing techniques, size of added particles	[40]

Graphite/CF/EG/CF-cloth in phenolic matrix	Prepreg (CF cloth)- hot press	Power density ~ 812 mW/cm ²	65 MPa	Porosity, filler type, filler content, curing conditions (molding time, pressure and temperature)	[41]
xGnP ^{**} in PP	Coating in presence of solvent-injection or compression molding	Percolation < 0.1 vol%	51 MPa	Orientation, dispersion, interparticle spacing, filler aspect ratio, filler-matrix interaction and matrix crystallinity	[42]
Ti ₃ SiC ₂ in PVDF	Direct mixing-hot press	63.3 S/cm	45 MPa	Content, filler particle size, mold pressure, molding time	[43]
Graphite in Phenol formaldehyde resin	Dry ball milling-hot press	142 S/cm	61.6 MPa	Resin content, molding temperature, molding time	[44]

Note: *ASR-area specific resistance, **xGnP- exfoliated graphite nanoplatelets

Optimized production conditions, such as molding temperature, time and pressure, have greater influence in determining the electrical conductivity as well as mechanical strength of the plates. Cui et al. [45] fabricated composite plates with expanded graphite and polyimide (PI) and found the optimum electrical conductivity and flexural strength at molding temperature of 220⁰ C. Chaiwan and Pumchusak [46] compared between wet and dry methods to improve the dispersion of multiwall carbon nanotubes in phenolic resin; they found out the optimum electrical conductivity and mechanical properties only by the dry method. Other processes such as in-situ polymerizations [47] and resin vacuum impregnation [48] also yielded lower percolation and higher flexural strength. A high curing temperature can increase the conductivity of nanocomposites [49]. This is probably because of the reduced viscosity of the resin that increases the conductive filler mobility and hence forms a better conductive network. Air bubbles or voids occur during the fabrication process, a large applied pressure reduces these voids by letting the polymer to

penetrate and fill the micro-pores between the filler particles. Fig. 3 shows how the parameters such as secondary filler content, molding temperature, and molding pressure can affect the conductivity and flexural strength in the Graphite-CB-epoxy system.

Fig. 3: Effects of different parameters on in-plane and through-plane conductivity – a) & b) Carbon black (CB) effect on conductivity and flexural strength; c) molding temperature effect & d) molding pressure effect on electrical conductivity [50]

2.1 EFFECTS OF VARIOUS MATERIALS ON THE COMPOSITE PROPERTIES

The most common material used in the manufacturing of composite BPP is graphite because of its excellent corrosion resistance, abundance, chemical stability and high thermal conductivity. Kang et al. [52] developed light and thin bipolar plates using pre-preg method where graphite, epoxy and CF were used. They suggested that if only graphite and epoxy are used to fabricate bipolar plate, the thickness

would be increased, but if CF is used for improved mechanical strength, fabricating thinner bipolar plate with same strength is possible. However, the electrical conductivity can be decreased especially for using chopped CF. Other researchers also used CF to enhance the electrical and mechanical properties. For example, Hwang et al. [53] found high conductivity using CF, although for any secondary filler used, there is a critical threshold value. Suherman et al. [50] concluded that using both SG and CB in the same composite increases in-plane and through-plane electrical conductivity. However, CB loading above 10% by volume decreases both conductivity and flexural strength. Kakati and Mohan [54] suggested that fuel cells have a very strong acidic environment for metal to survive, so carbon polymer composite is a potential material to meet all the requirements in this hostile environment. However, the carbon polymer composite based bipolar plates comprised of large proportion of fillers can cause the wetting problem which should be minimized by reducing the difference between surface energies of polymer and fillers i.e., choosing the right type and right amount of materials. If the surface energy difference is low between the polymer and filler, the polymer wets the fillers efficiently and the filler concentration can be increased without sacrificing the physical properties of the composite.

Both thermosets and thermoplastics are used as resin matrix in the fabrication of bipolar plates. However, thermosets are more convenient as they have higher strength, creep resistance and lower toughness compare to thermoplastics. Despite being more brittle, they are commonly chosen because of their better dimensional and thermal stabilities especially at high temperature. However, some gases such as hydrogen, ammonia and water vapor formed during thermoset processing can be eliminated by higher molding pressure and longer molding time. Thermoplastics are also investigated in several literature, although thermosets are more favorable for commercial purposes. The main difficulty is that the thermoplastic polymers contain less amount of fillers than thermosets due to higher viscosity at higher temperature. To overcome this problem, a short cycle time and solvent free process can be applied. Taipalus et al. [55] tailored the conductivity value of thermoplastic compound by blending thermoplastics with conductive polymers such as polyaniline (PANI)-complex and observed that the conductivity

depends on the processing temperature, applied shear stress, viscosity of matrix polymer, the surface activity and content-of the PANI-complex. For injection molded samples, the high shear forces near the surface region lead to the formation of elongated PANI-droplets which causes a decrease in mechanical properties. To improve the mechanical strength, short and discontinuous long glass or carbon fiber reinforcement might be used. Planes et al. [9] stated that Polypropylene is the most researched thermoplastics that shows low cost, good processing conditions and mechanical properties [19, 24, 56]. PVDF is also used in many studies due to their good barrier properties, chemical inertness, good mechanical properties and moisture resistance [57-60]. PPS shows good mechanical properties and also incorporates high filler contents, but more research on thermoplastics needs to be done, especially to improve their electrical conductivity up to the DOE target and beyond [29, 61-65]. Dhakate et al. [66] suggested that the electrical conductivity can be improved by using polymers with polar groups which avail electrons to polarize or delocalize more easily [9,66].

Metallic bipolar plates although have superior conductivity, mechanical strength and less permeability to gases, they are harmful to the fuel cell because of the corrosive process metal goes through at the harsh fuel cell environment. Work carried out by Chen and Su [67] on PEMFC with stamped 304 stainless steel BPP reported that assembly torque on a PEMFC could play a big role in reducing overall weight as well as sealing performance. Their report concludes that compared to the traditional PEMFC, their proposed system reduced the overall weight by 37%. Moreover, the rate of pressure loss declined by 56% when the torque increased from 2 N-m to 7 N-m. They also cautioned that an excess torque decreases the power output due to a decrease in gas diffusion layer (GDL) porosity and hydrophobicity. A suitable alternative might be the graphite-polymer composite with an additional secondary filler such as CB, multi-walled carbon nanotube (MWCNT), single-walled carbon nanotubes (SWCNT), CF, EG etc. The secondary fillers have critical volume fraction, because after a certain percentage they are not properly wet by the matrix, creating incomplete compaction and thus reduce the electrical conductivity. Understanding the cohesive interaction between particles and matrix are of great importance as such the Brownian motion,

van der Waals and dipole-dipole interactions of the fillers can explain the percolation behavior of high aspect ratio particles [14].

2.1.1 EFFECTS OF GRAPHITE: Graphite is used as the most common bipolar plate material because of their superior corrosion resistance, high electrical conductivity and low specific gravity [68]. Graphite is a crystalline form of carbon that shows metallic properties such as thermal and electrical conductivities as well as non-metallic properties such as inertness, and high corrosion resistance. Sengupta et al. [69] reviewed the properties of graphite and modified graphite for carbon polymer composites. The graphite crystal lattice is made up of layers of two-dimensional graphene sheets with sp^2 hybridized carbon atoms tightly bonded in hexagonal rings as shown in Fig. 4. The $2p_z$ -orbitals between the layers overlap if they are parallel. There is a difference between in-plane and out-of-plane bonding of carbon atoms, so graphite is considered as anisotropic. Graphite is thermally and electrically conductive as the π orbital is distributed over the entire graphene sheet and adjacent graphene layers are held by weak van der Waals forces. **Table 3** depicts how different graphite sizes and shapes can affect various properties of bipolar plate composites. The compound with flake-like graphite showed higher conductivity than spherical compound [70,72,111], but the processability improved for spherical compound at least five to twelve times due to its ability of higher filler loading [70]. Another important aspect of graphite is that it is electrically conductive along with its crystalline layered structure, but perpendicular to the plane it is very less conductive which affects the conductivity of the composite in the through-plane direction. Kim et al. [71] investigated the synergy effects of hybrid carbon system with graphite powder and continuous CF fabric and observed the optimized electrical conductivity at the filler content of 70-75 vol%. Secondary fillers are commonly used with graphite for enhancing composite performance. For example, Kakati et al. [68] introduced 1 vol% graphene which yields 10% improvement in fuel cell performance. Kang et al. [72] varied different fillers such as natural and SG with different particles sizes. The plates with NG showed higher electrical conductivities, but lower flexural strengths than SG-based plates. However, it might vary due to the source of NG and its structure. Overall, there is a

good amount of literature to prove the efficacy of graphite in BPP, but very few have discussed about the carbon structure based functionality; more research in this area can improve the overall electrical attributes of the composite,

Fig. 4: Graphite structure showing sp² hybridized atoms and layers [69]

Table 3: Comparison between graphite materials with different sizes and shapes and their influence on different attributes of the composite

<i>Graphite Particle Size (μm)</i>	<i>Particle Shape</i>	<i>Resin-Process</i>	<i>Max. Conductivity (S/cm)</i>	<i>Other Attributes (Max. value)</i>	<i>Determinant Factors</i>	<i>Ref.</i>
5, 10 & 20	Flake like and Spherical	Polypropylene-Injection and compression molding	96.9 (Through-plane)	Output rate, 12 kg/h (during compounding)	Comparison between shapes and processability with output rate. Optimization required between the conductivity and process output	[70]
<53 - >177	-	Vinyl ester-Bulk molding compound	153.8	Porosity, 0.57%, Flexural strength, 31.23 MPa, Oxygen permeability 6.76×10 ⁻⁸ cm ³ /cm ² s	Comparison between conductivity, flexural strength, corrosion current and permeability for different sizes. The bigger particles yield better properties	[51]
10, 20 & 40	Flake and lumps	Phenolic resin-Compression molding	146	Flexural strength, 44 MPa	Comparison between shapes and types (SG and NG) Bigger flake type NG showed optimum properties	[72]

					due to higher aspect ratio and crystallinity	
≤150	-	Phenol formaldehyde-Compression molding	142	Flexural strength, 61.6 MPa	Moulding temperature and time are considered and optimized for conductivity and flexural strength	[44]
100-150	-	Polyphenylene sulfide (PPS)-Compression molding	168.8	Flexural strength, 62.4 MPa	Molding temperatures and holding times are considered with resin content for fluidity and degree of cross-linkage	[25]
7, 15 & 25	Sphere and flake type	Phenol powder-Compression molding	~250	Flexural strength, >50 MPa	Comparison between size, shape and molding pressure. Flake-type found to be superior	[111]

2.1.2 EFFECTS OF CARBON NANOTUBES: Although CNT is a very effective filler to improve the composite performance, dispersing CNT in a polymer matrix is a challenging job due to agglomeration. This happens because of their high surface energy and nano-sized diameter [49]. CNT being a capable filler, if dispersed properly, increases both flexural strength and conductivity (in-plane and through-plane) compared to a single-filler composite. However, there is a threshold concentration. For example, Suherman et al. [73] concluded that the critical weight percentage of CNT is 5 wt% as a secondary filler in 20 wt% epoxy matrix (Fig. 5). Above this threshold, a decrease in conductivity and strength was visible. There is more investigation needed to use different kind of CNTs in BPP based on their structural difference and cost effectiveness.

Fig. 5: Effects of CNT content on a) electrical and b) mechanical properties of the composite [73]

2.1.3 EFFECTS OF CARBON BLACK: CB is another form of elemental carbon that is synthetically

produced, mainly by furnace or acetylene process. This material is in the form of pellets from 100 nm to 2 mm in size, but upon mixing with polymer becomes agglomerate of 30-100 nm long. It might work as a secondary filler and generate high electrical conductivity at relatively lower filler loadings. It has a highly-branched and high surface area structure, so it can contact larger amount of polymer at low concentration. 'Carbon black' is a generic term for carbon based aggregate product and has unique complex configurations, colloidal dimensions and quasi-graphitic structure. The aggregate is made of spherical "particles" or "nodules" which has tiny graphite-like stacks, giving them a complex morphology [9]. Kakati et al. [68] showed that secondary fillers such as CB and CF have critical threshold contents. For example, above 5 vol% content of these fillers can largely reduce the electrical conductivity of the composite. The flexural strength is also optimum at this filler content (NG 60 vol%, CB 5 vol% and CF 5 vol%). Suherman et al. [50] investigated effects of CB (10 wt%) as small sized secondary filler and found that the porosity of the composite is largely reduced with high molding pressure during fabrication. However, being a cost-effective secondary filler, more investigation is required on CB's functionality and its interaction with different polymer matrix.

2.1.4 EFFECTS OF CARBON FIBER: CF, mainly produced from Polyacrylonitrile (PAN), has high aspect ratio and contains 90% carbon. It is used for strength and stiffness, although it has a lower intrinsic conductivity [9]. Ghosh et al. [74] found the optimum CF length is 1mm. CF increases the mechanical properties in the composite and sometimes the electrical conductivity. The increase in electrical conductivity due to using CF depends on the aspect ratio. The higher the aspect ratio, the less percolation threshold was observed for the composite. However, increasing aspect ratio has some disadvantages, such as an increase in porosity and hence the undesirable hydrogen permeability in bipolar plates. Also, the agglomeration of CF increases the bulk resistivity of the composite, hence optimization of CF content is required. Kim et al. [71] fabricated carbon polymer composite with plain weave CF and epoxy matrix and found that the bulk resistance is 50% less than the composite with unidirectional CF for the same thickness. Kang et al. [52] fabricated thin and light composite bipolar plates using pre-pregs with epoxy and CF, where flake like NG particles were 20 mm long and filler loading was 90 wt%. Fig. 6 shows the effects of NG, CB and CF contents on electrical conductivity and flexural strength of carbon polymer composite. However, there can be different attributes of CF which influence the composite properties. It is not broadly discussed in the literature how the CF strength can affect the composite in terms of interfacial properties.

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330 Fig. 6: Comparison between electrical and mechanical properties for composites with a) & b) NG, c) & d)
 331 CB and e) & f) CF [75]

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333 2.1.5 EFFECTS OF GRAPHITE INTERCALATION COMPOUNDS: Graphite intercalation

334 compounds (GICs) are formed by inserting different chemical molecules or layers between graphene

335 layers. In this process, graphite either accept electrons from or donate electrons to the intercalants. The

336 intercalants can be acceptor type such as halogens, halide ions and acids (e.g., nitric acid, sulfuric acid,

337 perchloric acid and selenic acid) or donor type such as alkali metals (e.g., potassium, sodium, etc.).

However, graphite bisulfate is the most common GIC and it is also used to prepare graphite nanoplatelets (GnPs) [69]. The reaction between graphite and concentrated sulfuric acid is shown in equation (1) [47]

Where [O] is the oxidant and [graphite. HSO₄] stands for the GIC. The stage number is expressed by n and it shows how many layers of graphene in between the adjacent intercalant layers. Polymerization of monomers such as dehydrated isoprene, 1,3-butadiene and styrene could also create expansion of graphite layers in c-direction [76,77].

Graphite flakes when intercalated by oxidizing agents to form Graphite Intercalation Compound (GIC) is called expandable graphite. It is then exposed to high temperature above 800⁰ C for a short period of time to produce expanded or exfoliated graphite. Heat can be applied to expandable graphite by using muffle furnace or microwave irradiation. The high expansion caused by heating modifies the spacing between graphite layers, reduce the density, increase the aspect ratio and so the conductivity increases. However, using expanded graphite might lead to decrease in mechanical strength at higher loading and another reinforcing filler such as CF should be added to compensate the strength. GIC can be a potential material possessing better efficacy than graphite, but their interaction with different nanofillers has not been thoroughly investigated.

2.1.6 EFFECTS OF EXPANDED GRAPHITE / GRAPHITE NANOPATELET: Planes et al. [9]

described the conversion of graphite flake into expanded graphite and then subjected to more exfoliation to generate GnP which contains no functional group on the surface similar to graphite. It shows improved properties such as a reduction in density (10⁻³ to 10⁻² g/cm³), increase in surface area (40 m²/g) and improved electrical conductivity (12,500 S/cm). However, not many literature is available and more research is needed for GnP. Taherian and Ghorbani [78] studied the expanded graphite system. This worm like form of graphite shows higher conductivity as the aspect ratio becomes higher with less bonding between layers and it forms better conductive network between the particles than the regular graphite.

They suggested that low purity of fillers brings lower conductivity in the composite, but aspect ratio can be more important than purity in case of conductivity. The inter-particle contact is ensured more from greater surface-to-volume ratio. For example, the increasing aspect ratio for CF and CB increases mobile carrier concentration and thus decrease the percolation threshold. The important parameter that determines distribution, dispersion and agglomeration condition of the fillers is the mixing method or the shear force exerted on the materials. Wang et al. [79] described the expansion process of graphite layers. At higher temperature such as 800-1000⁰ C or under microwave irradiation, the acid part decomposed and forced the graphite layer to be apart. They also suggested that the heated graphite emerge a loose and multi-pore structure whereas the unheated graphite consists of numerous sheets of nanolayers stacked densely layer by layer (Fig. 7). Overall, the expansion process destroys the crystal structure partially, makes graphite expand in the c-direction and causes more than hundred times increase in overall volume. The EG has nanosheet layers from 100-400 nm and shows good affinity towards organic compounds and polymers. Additionally, dispersed GnPs (~30-80 nm) can be obtained from EG by high speed shearing in presence of polymer after ultrasonication in solvents thinner [79]. Sykam et al. [80] worked with exfoliated graphite (EG) which shows excellent properties such as compressibility, resilience, and thermal stability alongside with its low density, high porosity and high electrical conductivity. Graphite flake of 20 μm are expanded even up to 2-20 mm in length [81]. The electrical properties are enhanced due to the increased aspect ratio. Dhakate et al. [66] found that expanded graphite based composite (up to 50wt% EG) can achieve high flexural strength of 54 MPa with acceptable electrical conductivity of $>120 \text{ S.cm}^{-1}$. The effects of using EG on the mechanical properties of the composite is yet to prove and more investigation is needed to optimize with other attributes.

Fig. 7: SEM images of a) Flake graphite and b) Expanded or exfoliated graphite [82]

2.1.7 EFFECTS OF POLYMERS AND COMPATIBILIZERS: Polymers, both thermoplastics and

thermosets play an important role to determine the properties of carbon polymer composites. They have more influence on the mechanical properties, but also contribute to the electrical properties by determining the wetting and dispersion of the conductive fillers. Moreover, they affect the processing method for bipolar plates. Their viscosity, curing temperature, cooling requirement, presence of polar groups work as determinant factors and suitable polymers ought to be chosen for achieving high-performance composites. Overall, thermosets are preferred due to their higher strength and creep resistance as well as better dimensional and thermal stability [5]. Also, they do not need cooling cycle after curing, so production process can be faster. Thermoplastics on the other hand need longer time to cool down and residual monomers need to be removed from the surface. This is detrimental to the electrical and mechanical properties of the composite. Another issue is that they cannot contain as much filler as the thermosets do due to their high molten viscosity resulting in a poor impregnation and inferior electrical and mechanical properties. However, Lee et al. [83] achieved better results in electrical conductivity as well as fiber connectivity for PP/PE/MWCNT composites by using sol-gel method, where solvent was used with polymer gel in the pre-impregnation process.

The presence of polar groups in the backbone of polymer resin contributes to homogenous dispersion of fillers and helps to improve electron transfer between the filler layers. For example, phenolic resins have polar groups and double bonds, so they are easy to polarize or delocalize [84]. Polypropylene on the other hand, has no polar group in its backbone and hence less effective to improve the electrical conductivity of the bipolar plates [85]. However, this challenge can be overcome by selecting the combination of high conductive fillers, low crystalline resin and proper processing condition to ensure good dispersion, compactness and least wetting problem [14]. The surface energy difference between the filler and the polymer matrix is another important factor to consider. If the difference is higher, the polymer can not properly wet the surface of the filler particles causing non-homogenous dispersion and hence create detrimental effects on the desired properties of the bipolar plates. Morphological analysis co-relates the filler-polymer matrix with electrical conductivity and porosity of the bipolar plates [86].

Using compatibilizer during fabrication might be an innovative way to enhance the performance of bipolar plates, but literature is scarce. In this context, Lee et al. [87] found that using maleic anhydride grafted polypropylene (MA-g-PP) as the main polymer and maleic anhydride grafted styrene-ethylene/butylene-styrene (MA-g-SEBS) as compatibilizers can help to improve the electrical conductivity of the composite. MA-g-PP yields strong hydrogen bonding between the hydroxyl groups and MA-g-SEBS yields aromatic rings in two ends that is compatible with CNT, whereas ethylene/butylene blocks are compatible with polypropylene. Hsiao et al. [88] also achieved improvement in flexural strength up to 70.9% and bulk electrical conductivity up to 473% by using a solution process with polypropylene grafted maleic anhydride (PP-g-MA) and MWCNT. Polymers are very much neglected in the research as no comparison has been compiled based on their functionality and interaction with different fillers in the composites. Most part of the research has been focused on the filler particles, but polymers have substantial contribution on mechanical properties as well as cost effectiveness of the composite.

2.2 EFFECTS OF PROCESSING TECHNIQUES AND PROCESS PARAMETERS

Processing techniques and parameters are very important as they help to determine the capacity of handling higher filler content by the polymer matrix in the composite. They determine whether an isolated polymer region is formed that hinders the transportation of electrons. They also control the orientation, aspect ratio, dispersion and interparticle distance for the fillers which are important to determine the overall electrical and mechanical properties of the bipolar plates. Fabrication methods also affect the filler-matrix interaction and can change the degree of crystallinity of the matrix [89-91].

Fig. 8: Compression molding process for bipolar plate [72]

The most common manufacturing method for bipolar plate is compression molding (Fig. 8**Error! Reference source not found.**). This process can handle the higher viscosity and exert less shear force during processing which prevents the breakage of fillers with high aspect ratio. Higher shear force damages the filler-polymer matrix interface, so there might be additional stages installed before compression molding, such as melt compounding or solution blending, especially for thermoplastic resins. Different pre-compression methods yield different results. For example, Dweiri and Sahari [24] stated that homogenous mixing is more difficult in melt compounding than solution blending. Hence, the solution blending favors better electrical conductivity by forming better conductive paths. The disadvantage in this case is the loss of materials such as organic solvents. Injection molding might be an alternative to compression molding, especially for the thermoplastics because of its higher production

rate. However, this method has many disadvantages that affects the properties of the bipolar plates. Higher loading of fillers increases viscosity which makes the injection process difficult. Also, the high shear can rupture the conductive filler particles, and adversely affect their size, shape and morphology [92]. The other problem with some conductive fillers such as CNT, graphite nanoplatelets, etc. is the agglomeration and non-homogenous dispersion in the injection process. There are some efforts with good results to overcome this problem such as coating and sonification [93] by which a uniform layer of polymer matrix can be achieved at the surface of conductive filler and the integrity of the aspect ratio and morphology can be maintained. Other innovative methods such as wet-lay method [64,94], prepreg method [52], solid-state shear pulverization (SSSP) method [95], vacuum resin-impregnation method [22], etc. may also be used (Fig. 9). The processing methods affect the electrical conductivity of bipolar plates as different methods show different orientation and dispersion quality for conductive fillers. Lee et al. [96] fabricated carbon polymer composite using non-woven carbon felt in the ‘soft layer’ method where a lower molding pressure is required, but a higher mechanical strength could be achieved.

Fig. 9: Different fabrication processes for BPP (a) laser-sintering process [97], (b) soft-layer method [96], (c) graphite pre-preg process [52], (d) vacuum resin impregnation process [22], (e) sol-gel method [83] and (f) wet-lay process [94]

The parameters of the manufacturing process such as molding time, temperature, and pressure are also important factors to determine the electrical and mechanical properties of the bipolar plates. For example, Yang and Shi [65] stated that the molding time influences in-plane electrical conductivity, 30 minutes is better than 10 minutes of highest temperature and pressure under compression. Yin et al. [44] also found the relation of both temperature and molding time with electrical conductivity and mechanical strength. This phenomenon occurs as curing of resin and higher degree of crosslinking is influenced by these process parameters; the three-dimensional network is also established at this time which facilitates the electron transportation between the conductive filler particles. Bin et al. [43] concluded that there is an increase in conductivity with the increase of molding pressure due to more compactness; a reduced porosity thus created can generate more conductive pathways. Process techniques and parameters are vital to achieve the additional benefit to the composite attributes, because they vary with filler-polymer matrix pairs and complement the enhanced properties contributed by the materials. **Table 4** depicts the electrical

474 and mechanical properties achieved by different filler-polymer pairs along with the used fabrication
475 processes as extracted from the literature.

476 **Table 4: Electrical and mechanical properties of composites with different carbon-polymer pairs**

<i>Polymer matrix</i>	<i>Conductive Fillers</i>	<i>Conductivity (S/cm)</i>	<i>Flexural Strength (MPa)</i>	<i>Fabrication Process</i>	<i>Ref.</i>
Epoxy	SG, CB	150.00 (in-plane) 55.00 (through-plane)	38.80	Compression molding	[50]
	SG, MCF*	70.00 (in-plane) 50.00 (through-plane)	36.00	Melt compounding	[98]
	Graphite, CF	172.00 (in-plane) 38.80 (through-plane)	-	Prepreg-compression	[52]
	EG	131.00	20.00	Solution impregnation-compression molding	[99]
	NG, SG	380.00	40.00	Selective laser sintering (SLS)	[98]
	Graphite, MWCNT	254.70	-	Compression molding	[100]
	EG	120.00	45.80	Resin vacuum impregnation with CEG sheet	[22]
	Graphite, CB	153.80	27.00	Compression molding	[18]
	EG, CB	500.00	40.00	Solution intercalation-Compression molding	[101]
	EG, NG, CB	416.70	49.00	Compression molding	[102]
Phenolic	EG	112.30	64.90	Resin vacuum impregnation-hot press	[48]
	EG, CB, Graphite	374.50	61.82	Compression molding	[103]
	Graphite, MWCNTs	197.00	57.50	Sonication-compression molding	[46]
	CF, CB, NG	282.00	54.64	Solution blending-compression molding	[74]
	NG, SG	146.00	44.00	Compression molding	[72]
	NG, GN**, CB, CF	319.40	62.35	Solution blending-compression molding	[74]
	EG, NG, CB, CF, GN	435.00	57.00	Compression molding	[68]
	NG, CB	120.00	38.00	Compression molding (bulk-molding compound)	[104]
	Graphite, CF, EG	74.00	74.00	Compression molding	[41]
	NG, CB, CF	286 (in-plane) 92 (through-plane)	55.28	Compression molding	[75]

	NG, MWCNT	178(in-plane) 30 (through-plane)	56.00	Compression molding	[105]
	EG	280.00	55.00	Compression molding	[106]
	EG, CB	285.00	52.00	Compression molding	[66]
	Graphite, CB	400.00	47.00	Compression molding	[20]
	Graphite, EG	390.00	51.00	Compression molding	[107]
	NG, MWCNT	145.20	68.60	Compression molding	[108]
	Graphite, CB, CF	263.00	75.00	Compression molding	[27]
	Graphite, EG	250.00	50.00	Compression molding	[109]
	Graphite, CB, CF	303.00	52.50	Compression molding	[110]
	NG	142.00	61.60	Compression molding	[44]
	Graphite	250.00	58.00	Compression molding	[111]
	NG, Montmorillonite Mesocarbon	260.00	50.10	BMC-compression molding	[112]
VE	NG, MWCNTs, Poly(oxyalkylene)-amines bearing maleic anhydride	641.00	41.44	Sonication-compression molding	[113]
	NG, MWCNT	744.00	41.55	BMC- Compression molding	[114]
PP	Graphite, CB, CNTs	158.00	29.86	Compression molding	[115]
	Graphite, MWCNT	548.00	29.46	Melt compounding-Compression molding	[19]
	Graphite, CB	36.40	-	Melt compounding-Compression molding	[24]
PPS	Graphite, CB, CF, MWCNT	73.00	35.00	Compression molding	[116]
	Graphite	118.90	-	Ball milling-Compression molding	[25]
	Mesocarbon microbeads	133.70 (in-plane) 21.37 (through- plane)	38.82	Compression molding	[65]
	Graphite, CF	325 (in-plane) 30 (through-plane)	95.80	Wet-lay lamination-Compression molding	[26]
PVDF	Ti ₃ SiC ₂	350.00	30.00	Compression molding	[117]

	Graphite, CF	292 (in-plane) 32 (through-plane)	54.40	Wet-lay lamination-Compression molding	[26]
PP/PE	Carbon Felt, MWCNT	ASR<20	>30.00	Prepreg-compression	[96]
PI	EG	149.00	47.26	Blending -compression molding	[45]
VE (methacrylated epoxy disfunctional), MEKP^{***}, PPS	Graphite, Cobalt naphthalate,	90.00	41.00	Solution blending-compression molding	[86]

477 Note: ^{*}MCF- Milled carbon fiber, ^{**}GN-graphene, ^{***}MEKP-methyl ethyl ketone peroxide

3. ELECTRICAL CONDUCTIVITY OF THE COMPOSTIES FOR BPP

Higher electrical conductivity is the first and foremost property required for any bipolar plate. Lee et al. [83] studied thermoplastic composite with carbon-felt reinforcement in sol-gel method and found that ASR was significantly reduced from the conventional film stacking method. Kim et al. [116] explained the conductivity of the composite by two mechanisms- inter-particle and intra-particle conductivity. The inter-particle conductivity depends on the connectivity between the particles and intra-particle conductivity is proportional to the particle conductivity, conductive path length and particle size. However, at higher filler loadings, distinctive difference can not be observed between these two. Hamilton and Pollet [118] discussed about the ICR which is more of a problem for metallic bipolar plates than graphite or composite bipolar plate. However, if the carbon polymer composite has rough surface and grow an insulating polymer skin during injection or compression process, ICR increases which decreases the bulk conductivity. This is influenced by the physical contact between the filler-matrix particles and compressive force. Mohd Radzuan et al. [119] reviewed different models that predict the conductivity. They also discussed about the orientation-based models along with the conventional models and concluded that the General Effective Media (GEM) model is the best and orientation is the most important factor to optimize the electrical and mechanical properties. Nonetheless, orientation can be optimized by controlling shear stress, changing filler dimension, and modification of die.

Nakamura [120] described the constriction resistance as the resistance of the conducting spots in any electric contact surface. This is important to determine to understand the problems and conductivity losses of electric contacts. The difference between constriction resistance is small if the spots have equal areas. This depends on the materials, their interaction and processing techniques. The surface properties of the fillers and polymer determines the interaction between them and how well the polymer can wet the fillers, which is important for achieving the desired electrical conductivity [41]. For example, the intrinsic graphite conductivity depends on the nature of the particles, degree of crystallinity, size and morphology. Wissler [121] stated that the degree of crystallinity influences the electrical conductivity and NG has

higher crystallinity than the synthetic product. However, this depends on the origin of the graphite. On the other hand, flake like particles make composites more conductive because of their high aspect ratio compared to the shorter spherical particles that enhance contact between neighboring particles explained by classical percolation theory.

Taherian et al. [41] stated that the smaller particle size lowers the percolation threshold in case of spherical particles, but for flake like particles with an aspect ratio greater than 1, larger aspect ratio lowers the percolation threshold. The main drawback of spherical particles is that they form point-to-point contact instead of surface-to-surface contact which reduces the conductivity as the void spaces are filled by insulating polymer matrix. Chunhui et al. [117,122] concluded that the contact resistance between conductive particles is the main determinant for the bulk conductive behavior of the composite. The pore volume and contact area between adjacent particles also play an important role in affecting the conductivity. Incorporating additional smaller particles in the mixture increases the conductive path and the resistivity of the composite decreases. However, incorporating too much of the small particles not only destroys the primary structure of large sized particles, it can also increase pore volume and decreases the conductive network. Hence, the additional fillers have critical threshold content above which the conductivity of the composite decreases.

3.1 THROUGH-PLANE CONDUCTIVITY

The through-plane conductivity is mostly neglected in the literature, albeit it is as important as the in-plane conductivity for improving cell-to-cell conductivity. Electrical conductivity in the through-plane direction is related to the operating conditions and materials used. Cunningham et al. [64] stated that through-plane conductivity is an important measurement because bipolar plates are stacked together in parallel and allowing electrons to travel in this direction can enhance the overall conductivity of an operating fuel cell. Lee et al. [96] described that the high resistivity in the through-thickness direction is one of the biggest limiting factors of the bipolar plate. The main reason for it might be the resin-rich area formed in layers during the manufacturing process especially for extrusion and injection molding. This

hinders the particle-particle contact between the carbon layers and creates high ASR. To reduce this barrier, some methods have been tried such as mechanical abrasion, plasma treatment, extra graphite layer attachment, and “soft layer method” by using non-woven carbon felt. However, the results are not convincing, and more research needs to be done in this area.

Kim et al. [71] reported high in-plane electrical conductivity and flexural strength for pre-preg composites with CF. However, the through-plane conductivity is much lower because of the uni-directional orientation of the CF. Kandare et al. [123] stated that the enhancement of through-thickness thermal and electrical conductivity depends on the concentrations and geometric aspect ratios, the degree of dispersion within the matrix and the polymer-filler interfacial properties. One probable way to reduce the effect of resin-rich pockets between adjacent layer impeding through-thickness conductivity is to use highly conductive nanofillers such as silver nanoparticles/nanowires that may form an integrated mesh with sheets of expanded graphite. The planar π - π stacking of expanded graphite may entrap silver nanoparticles between them. This may increase the number of physical contacts between filler particles and reduce the through-thickness resistivity. The geometric aspect ratio and filler concentration have substantial influence on the through-thickness electrical conductivity. More research is needed in case of through plane conductivity to decide how much it can affect the bulk conductivity of the composite and whether it affects the in-plane conductivity to some extent.

3.2 PERCOLATION THEORY FOR CONDUCTIVITY

According to the percolation theory, conductivity is predicted based on the probability of particle contacts within the composite. Before percolation, the composite has very low conductivity due to less particle-particle contacts, but at percolation, there occurs a sudden increase in conductivity as shown in Fig. 10. Bauhofer and Kovacs [124] explained percolation in two different ways, statistical and kinetic. For statistical percolation, filler particles are randomly distributed, forming conductive paths. For kinetic percolation, particles move freely forming conductive network at lower concentrations. These two phenomena substantiate the analysis of percolation phenomena. The results obtained by Bai and Allaoui

[125] can be explained by statistical percolation and the results by Martin et al. [126] through kinetic percolation where the increase of percolation threshold occurs with the decrease in CNT length. Carmona and Ravier [127] explained that the interaction between conductive particles and macromolecular chains depends on the processing conditions and dispersion of fillers within organic matrix. In case of CB, i.e., non-spherical particles, the percolation threshold decreases with increasing degree, which is explained in the Balberg's model considering the interaction between neighboring particles [128]. This is because the elongated particles of high-structure CBs have more contact area than spherical particles with the same volume. Also, electrical conductivity is higher for the composites with fillers of high-aspect ratio such as fibers or carbon sheet than the composites with spherical or elliptical particles because the conductive network formation occurs easily for elongated particles. Clingerman et al. [129] stated that the difference of surface energy between filler and polymer is an important factor for the conductivity of the composite as the fillers are better wetted by the polymer if they have close surface energy values. Overall, percolation theory is the basis to the introduction of conductivity in the composite which also determines the extent and efficacy of the contributions of different materials used in the composite.

Fig. 10: Percolation phenomenon for CF/CNT and CB: 1) before percolation, 2) at percolation and 3) above percolation concentration (adapted from [130])

3.3 MODELS FOR CONDUCTIVITY

There are various models to describe the relationships between the parameters and performance of the composite for bipolar plates, especially the electrical conductivity. Mohd Radzuan et al. [119] described modified fiber contact model (FCM) as a good model because it considers orientation factors, such as filler's volume fraction, diameter, conductivity and contact number and shows good agreement between the experimental results and modelling predictions. They also concluded that the parallel orientation of fibers provided better electrical conductivity compared to random orientation.

Strumpler and Glatz-Reichenbach [131] discussed about different models which can predict the conductive properties of the composite. The percolation theory is a statistical method that calculates the contact between particles in a specific environment. In this model, both the geometry factor and material factor are considered which can effectively predict the critical volume fraction of conductive composites. Other non-percolation models include thermodynamic models, geometrical and structure-oriented models. The structure-oriented models are the most promising ones as they consider microstructural data such as fiber orientation, length and packing arrangement. In the percolation theory, a large, preferably infinite regular periodic lattice was considered with a site assigned with probability P , which can be expressed as

$$\sigma(P) \propto (P-P_c)^n \quad (2)$$

The value of n is between 1.65 and 2 for any three-dimensional lattice [131]. At the critical probability P_c , there occurs an infinite conducting cluster forming in the infinite lattice. P_c is called percolation threshold. The percolation theory conventionally worked in a system where the insulating medium has zero conductance, or the filler has zero resistance. For real systems, percolation theory is used with the scaling factors and dependent on the shape of the filler [131].

For the effective media theory, a spherical or ellipsoidal grain is considered to be surrounded by a mixture with effective conductivity. This theory is applicable where sub-phases are well separated so that it is easier to predict and explain average values of electrical, thermal and diffusion properties. Effective

media theories are valid for two special cases, symmetric and asymmetric cases. In symmetric cases, it is assumed that all space is filled by a random mixture of two or more types of spherical or ellipsoidal particles. In the asymmetric cases, the surface of the one type particle is assumed to be always covered by the other type particles. McLachlan [132] proposed a generalized effective media equation which works as an interpolation between the symmetric and asymmetric effective media theories.

Weber and Kamal [133] proposed a new model named end-to-end model (EEM) that considered a perfect fiber-to-fiber contact to predict the volume resistivity of a composite. In the fiber-contact model (FCM) both fiber-to-fiber contact and fiber-length effects are considered for composite resistivity. They concluded that for carbon-fiber-reinforced composites, the conductivity depends on microstructural details, such as the fiber concentration, orientation, average length and length distribution. For example, samples with higher average fiber length become conductive at lower fiber loading because of the conductive network formation earlier than other systems. Taherian et al. [134] also investigated a new statistical-thermodynamic model with graphite, EG and CF by using sigmoidal function. They found good correlations between electrical conductivity and filler volume fraction considering the critical factors, such as filler conductivity, aspect ratio, wettability and interface contact resistance. Herein all the main models that explain the conductivity of carbon polymer composites are shown along with their limitations in **Table 5**. The main parameters considered in these models are conductivity, resistivity, diameter, length, volume fraction, orientation angle, elongation deformation, packing factor, volume fraction and width of percolation. There may not be a single model which can work as the silver bullet due to the wide ranges of materials used in the fabrication process. However, there could be a standard model for the individual filler-matrix pair which is a more realistic approach in this context.

616 Table 5: Summary of the conductive models (adapted from [119])

<i>Model</i>	<i>Equation</i>	<i>Limitation</i>	<i>Ref.</i>
Modified additive model	$\log(\sigma) = \log(\sigma_m) + \sigma_p(\varphi - \varphi_c)^{G/(\varphi - \varphi_c)n} + \sigma$	Not suitable for multiple filler system	[135]
Scarisbrick model	$\frac{\sigma_c}{\sigma_f} = \varphi x \varphi [\exp(\varphi^{-\frac{2}{3}})] x C^2$	Considered particles as spheres, not suitable for high aspect ratio fillers. Only showed better agreement with higher filler concentration	[130]
Percolation theory equation	$\sigma = \sigma_c + (\sigma_m - \sigma_c) [\frac{\varphi - \varphi_c}{F - \varphi_c}]^t$	Not fitted well below percolation concentration, not considered particle shape and polymer filler interaction	[136]
Model of Bruggeman	$\sum_i \varphi_i \int_0^1 dL \frac{\varphi(L)}{S_i + L} = 0 \quad S_i = \frac{\sigma_{eff}}{\sigma_i - \sigma_{eff}}$	Not considered particle shape and polymer-filler interaction	[137]
Effective medium model	$(1 - \varphi) \frac{\sigma_1 - \sigma_{eff}}{\sigma_1 - 2\sigma_{eff}} + \varphi \frac{\sigma_2 - \sigma}{\sigma_2 - 2\sigma} = 0$	Considered both electrical properties of the particles and matrix as isotropic, also considered particles in random ellipsoid shape	[138]
General effective media (GEM) model	$\frac{(1 - \varnothing)(\sigma_i^{\frac{1}{t}} - \sigma_m^{\frac{1}{t}})}{\sigma_i^{\frac{1}{t}} - A\sigma_m^{\frac{1}{t}}} + \frac{(1 - \varnothing)(\sigma_h^{\frac{1}{t}} - \sigma_m^{\frac{1}{t}})}{\sigma_h^{\frac{1}{t}} + A\sigma_m^{\frac{1}{t}}} = 0$	Not suitable for more than two fillers. Also, not considered filler orientation and shape factor	[139]
‘Pseudo-affine’ deformation model	$\tan\theta = \frac{\lambda_x}{\lambda_z} \tan\theta' \left[\frac{1 + \left(\frac{\lambda_y}{\lambda_x}\right)^2 \tan^2\varphi'}{(1 + \tan\varphi^2)} \right]^{\frac{1}{2}} \tan\varnothing = \frac{\lambda_y}{\lambda_x} \tan\theta'$	Considered fiber orientation only	[140]
Fiber contact model (FCM)	$\sigma_{c,longitudinal} = \frac{\pi d^2 \rho_f X}{4\varnothing_p d_c l \cos^2\theta}$	Difficult to measure experimentally, because it needed calculation from experimental data	[133]
McLachlan’s model (imaginary value)	$\frac{(1 - \varnothing)(\rho_m^{\frac{1}{t}} - \rho_f^{\frac{1}{t}})}{\rho_m^{\frac{1}{t}} + ((1 - \varphi_c)/\varphi_c)\rho_f^{\frac{1}{t}}} + \frac{\varnothing(\rho_m^{\frac{1}{t}} - \rho_p^{\frac{1}{t}})}{\rho_m^{\frac{1}{t}} + ((1 - \varphi_c)/\varphi_c)\rho_p^{\frac{1}{t}}} = 0$	Considered wetting angle, not surface energy which is not valid for all cases	[141]
Statistical-thermodynamic (Sigmoidal function) model	$\sigma_m = \sigma_p + \frac{\sigma_f - \sigma_p}{1 + \exp[-\frac{\varphi - PCP}{w}]}$	Considered DC electrical conductivity of nanocomposites. Not considered interaction among effective factors (aspect ratio, wettability, etc.). Not considered important parameters such as critical exponent of percolation, filler and matrix conductivity,	[141]

conductivity at max. packing fraction, conductivity at
percolation and width of percolation region.

Note: $\sigma, \sigma_1, \sigma_2, \sigma_c, \sigma_m, \sigma_p, \sigma_{eff}, \sigma_t, \sigma_h, \sigma_r$: conductivity, $\rho, \rho_f, \rho_m, \rho_p$: resistivity, X : function number of contact, d, d_c : diameter, l : length, $\varphi, \varphi_c, \varphi'$: volume fraction, θ : orientation angle, θ' : original orientation angle, $\emptyset, \emptyset_p, \emptyset_c$: percolation threshold, $\lambda, \lambda_x, \lambda_y, \lambda_z$: elongation deformation, L : spheroid depolarization factor, $\varphi(L)$: positive shape-distribution function, F : packing factor, t : critical exponential, C : geometric factor (function of φ), PCP: volume fraction of the filler in the midpoint of percolation, w : width of percolation, X : factor of fiber contact number, G, A, n : constant

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4. MECHANICAL PROPERTIES (STRENGTH AND MODULUS)

One of the other important requirements of DOE for Bipolar plates is the sufficient mechanical strength (>25 MPa) to withhold the clamping force from the stacking of the fuel cells. Moreover, they need to support the membrane and electrodes systems. However, higher filler loading to increase the conductivity is very common which introduce voids and defects causing a reduction in mechanical strength. Various works of literature have addressed the issue by applying a long list of polymers, both thermoplastics and thermosets, but optimization is always needed between the electrical conductivity and mechanical strength; it is an enormous challenge to achieve both the properties simultaneously.

Mechanical strength is mostly affected by the resin content, especially for low filler content, but at higher filler content, properties are mostly controlled by the extent of filler content, so the composite becomes brittle. Also, with the mixing of polymer and conductive fillers at lower filler loading, an increase in Young's modulus and tensile strength is observed along with a lower elongation at break and reduced toughness [90,142]. Around the critical loading i.e., percolation threshold, a significant decrease in the elongation at break occurs and the mechanical properties influence by the formation of a small continuous filler phase. Above the critical value and at higher loading, the density decreases because of porosity formation from the bad wetting of polymer. The mechanical strength decreases with increase in porosity. Hence, Planes et al. [9] concluded that the mechanical strength is largely dependent on the processing conditions. This porosity can also be minimized by using a mix of particles of different sizes to achieve a high compaction by reducing the void spaces between the particle-particle contact [9,143].

Mohd Radzuan et al. [35] stated that controlling the filler orientation achieved by shear stress, altering die and fillers aspect ratio improves the mechanical performance along with the electrical conductivity. Lee et al. [18] concluded that mechanical performance can be improved by using hybrid filler system, although after a certain level of filler content it deteriorates. Fig. 11 shows the flexural performance of composite without any reinforcement filler and with hybrid system; the load distribution is better for the later. There

is strong relationship between the shear stress and mechanical performance of the composite, especially when fibers are used to enhance the strength. Wang [74] and Kopplmayr [144] suggested that introducing higher shear stress in the fabrication process lowers the mechanical performance due to higher breakage. Overall, orientation of the reinforcing fillers in polymer matrix is the most important factor that determines the mechanical performance specifically for high filler content and in presence of fibers.

Fig. 11: Schematic diagram of flexural strength of carbon polymer composite a) without reinforcement b) with reinforcement fillers

Kalaitzidou et al. [42] discussed different fabrication techniques and suggested that in situ processing method help fabricating composites with better mechanical properties, because this method shows better dispersion, prevention of agglomeration and stronger interactions between the filler-polymer matrix system than the others. Antunes et al. [14] also stated that the mechanical strength depends on the content, morphology, processing techniques and size of added fillers. Addition of CF enhances the mechanical strength, but it can increase the hydrogen permeability, so a balance is required. Gojny et al. [145] investigated functionalization effects of CNT and suggested that mechanical performance is improved by functionalization. For processing of thermoplastics, it is important to keep the samples in the mold for proper cooling in order to gain the desired mechanical strength. For thermoset resins, on the other hand, mechanical property is enhanced if the molding time is increased to ensure the higher degree

of crosslinking. Overall, it is important to optimize the processing conditions to achieve better mechanical strength and less gas permeability [29, 42].

Strumpler and Glatz-Reichenbach [131] considered mechanical properties of the filler material to estimate the contact spot area for constriction resistance (Fig. 7) and established a relation between mechanical and electrical properties as illustrated through equations (3) to (5).

$$R_c = \rho_T / 2a \quad (3)$$

$$F = \frac{2}{3} \frac{E}{1-\nu^2} \frac{a^3}{r} \quad (4)$$

$$R_c = \frac{1}{2} \rho_T \left(\frac{2}{3} \frac{E}{1-\nu^2} \right)^{1/3} F^{-1/3} r^{-1/3} \quad (5)$$

Here, R_c is the interparticle constriction resistance, ρ_T is the bulk resistivity of fillers, a is the contact spot radius, F is the elastic force between the particles, r is the particle radius, E is Young's modulus and ν the Poisson's ratio. However, it is difficult to predict the contact forces between filler particles because of their irregular shape and distribution.

Meyer [146] stated that there is also an aging effect on the mechanical properties due to elevated temperature and environmental factors. This happens mainly because of the melting of crystalline areas and thus causes a reduction of crystallinity at higher temperature. Different commercial bipolar plates are compared in Table 5, which also depicts a comparison between different fillers in commercial scale.

Cunningham and Baird [26] stated that thermosetting polymers have advantages over thermoplastics in reduced fabrication time. For example, vinyl ester does not require cooling process as they are cured at high temperature during compression molding; however, results from the Los Alamos National Laboratories (LANL) showed that the composite with vinyl ester did not meet the DOE target for electrical conductivity (**Table 6**). Wet-lay method, a new approach investigated at Virginia Tech, yielded good electrical and mechanical attributes. In **Table 6**, electrical, corrosion potential and mechanical

properties were compared to conventional methods as well as commercial products such as BMC 940 and Dupont T8.

Table 6: Comparison between different commercial bipolar plates (adapted from [26])

<i>Source</i>	<i>Polymer</i>	<i>Graphite/ GF* or CF</i>	<i>Conductivity, S/cm</i>		<i>Mechanical strength, MPa</i>		<i>Ref.</i>
			<i>In-plane</i>	<i>Through-plane</i>	<i>Tensile</i>	<i>Flexural</i>	
GE**	PVDF	80/0	119	-		30	[147]
GE**	PVDF	64 /16 (CF)	109			42.7	[148]
LANL	VE	68/0	60		23.4	29.6	[149]
BMC 940	VE	70/0	100	50	30	40	[112], [150]
Plug Power	VE	68/0	55	20	26.2	40	[151]
Dupont T8	-	-	-	25-33	25.1	53.1	[3]
Virginia Tech	PET***	65/7 (GF)	230	18-25	36.5	53	[94]
	PPS	70/6 (CF)	271	19	57.5	95.8	

Note: *GF- Glass fiber, **GE- General electric company, ***PET- Polyethylene terephthalate

Guo and Leu [97] investigated laser sintering process using different raw materials and compared with other processes. They concluded that using CB can reduce the mechanical strength, whereas NG and CF can increase it which is also agreed upon by Wolf and Willert-Porada [152]. Kakati et al. [153] fabricated composites with graphite and phenol formaldehyde resin and found that graphite content above 75 vol% can reduce the mechanical properties due to the brittleness of the graphite particles. Du and Jana [101] investigated composite fabricated with EG and CB in epoxy resin matrix and found out that the mechanical properties deteriorate when EG content is higher than 65 wt%. It becomes fragile above 70 wt% of the filler content. Jiang and Drzal [154] implemented high-density polyethylene (HDPE)/WaxGnP-15 and HDPE/Wax MWCNT system to improve both the electrical conductivity and mechanical properties of the composite, however flexural strength was increased only at initial stage, but eventually showed downward trends for different wax contents. The increased percentage of the low-molecular weight polyethylene might be the reason of this lower strength. Allaoui et al. [155] investigated the effects of using MWCNT in epoxy matrix on the mechanical and electrical properties of the composite. They concluded that Young's modulus and yield strength was improved significantly with 1

wt% and 4 wt% of nanotubes content [156]. Onyu et al. [157] stated that injection molding process is cost effective and composites made of PP, graphene, NG, CB and CF showed improvement for mechanical properties (flexural strength 54 MPa to 57 MPa). Achaby et al. [158] concluded that the addition of graphene sheet into thermoplastics matrix improves the rheological and mechanical properties of nanocomposites as well. It was observed that the mechanical strength of flake graphene is higher than that of flake graphite. For PP composites, addition of graphene fillers improved the flexural performance, but hardness remained the same.

Kim et al. [33] investigated synergy effects of Graphite and continuous carbon fiber fabric (CFF) in epoxy matrix and achieved improvement in mechanical properties by applying several layers. They concluded that flexural properties of Graphite epoxy composite can be enhanced by introducing CFF. However, it only increases for filler content up to 65-70 vol% and above this a decreasing trend occurs. This may be because of the wetting problem caused by the difference in surface energy. Chatterjee et al. [159] investigated the effect of mechanical reinforcement by addition of GnPs and CNTs in epoxy matrix. They stated that the ratio of CNT and GnP has a synergy effect and is a controlling factor for the mechanical properties of nanocomposite. Kumar et al. [160] explained that CNT and GnP formed a co-supporting network by the platelet geometry shielding the tube-like fillers and protect them from fracture and damage during processing. They concluded that the larger flakes showed better reinforcement, proved by fracture toughness and three-point bending tests, although it is a challenge to disperse both GnP and CNT evenly without forming agglomeration. Overall, these materials promote crack deflection and crack bridging effectively and thus improve the mechanical strength. There are more aspects to work on for the mechanical attributes of the composite, because mechanical strength varies widely for different filler-matrix pairs and can be a main determinant for optimized parameters to achieve a high-performance cost-effective bipolar plate composite.

5. RESEARCH SCOPE AND FUTURE PERSPECTIVE

One of the major limitations found from the literature is that there is a lack of consistent results associated with similar materials and processing techniques. There are also big differences between the attributes of different filler-matrix pairs. The other limitation is that often the researchers have not necessarily considered the implication of the outcomes from commercial perspective, especially in terms of cost and processability. This can limit the feasibility of many conducted studies only in the lab scale.

Another less discussed aspect is the life cycle assessment (LCA) of BPP, which is a useful tool to evaluate the environmental impact. There is very few literature discussing the LCA of PEMFC [161,162]. Moreover, as far as the knowledge of the authors, there is no reported work discussing the LCA of bipolar plates particularly; nonetheless there are some LCAs of other distant related topics such as hydrogen production for fuel cell [163], fuel-cell fuels [164] and fuel cell vehicles [165,166].

Fig. 12: Lifecycle analysis process for fuel cell a) scope of LCA [166] b) Life cycle process flow diagram [7]

Fig. 12 depicts the life cycle process flow for PEMFC and the boundary conditions for LCA. It was concluded that extraction of platinum for fuel cell contributed as the largest environmental impact [166]. Pehnt 2001 [167] stated that the bipolar plate is the second most important component of fuel cell stack that also has a huge environmental impact, contributing 13% of the global warming potential and 17% of the electricity consumption (Fig. 13), especially from graphite production and resin impregnation. There is an on-going effort to reduce the weight of the bipolar plates to fabricate a light-weight high performance hydrogen fuel cell for transportation sector and hence, it is important to undertake a LCA of bipolar plate individually.

Fig. 13: Environmental impacts of different components of the fuel cell stack [167]

It is also necessary to do a cost benefit analysis for bipolar plate alone as one of the major targets of US DOE is the cost effectiveness (\$3/kW by 2020) of BPP [32]. Jayakumar et al. [168] reported cost benefit analysis for two types of commercial graphite plates used for 1 kW fuel cell stack system. They considered performance, configuration, and fixed costs for the repetitive units. One of the biggest contributors to the cost of PEMFC is the bipolar plate, although the overall cost factor is affected by production volume and operating conditions for rated output. They found that the cost of bipolar plate contributes up to 37% of the fuel cell assembly. However, if the component cost breakdown is considered for a 80kW_{net} automotive and high production volume of \$500,000 units/yr, the bipolar plates cost shows 28% of the fuel cell stack cost as shown in Fig. 14a [169]. Equation (6) was used for calculating the cost estimation by design for manufacture and assembly (DFMA) method [168]

$$C = N(C_e + C_s + C_c + C_p + XC_m) + Y C_{fc}(y_g + y_e + y_{b+n}) \quad (6)$$

Here, N is the number of cells, C_e is electrolyte cost, C_s is substrate layer cost, C_c is catalyst loading cost, C_p is bipolar plates cost, X is the number of sides of machining, C_m is the machining cost, C_{fc} is fixed cost of Y units which include y_g gas feed plate, y_e endplates, and y_{b+n} bolts and nuts. Nowadays there are more market focus for medium-duty vehicles (MDV) and heavy-duty vehicles (HDV) than light duty vehicles (LDV). The US DOE is considering two main plates, metallic plate with coating and flexible graphite composite bipolar plates to reach their cost target; the composite bipolar plates show much better cost

effectiveness closer to \$3/kW target for LDVs at 500,000 systems/yr [170]. So far, for the fuel cell system \$45/kW could be achievable (Fig. 14b with composite plate) which is still behind the target of 2020 (\$40/kW) and beyond 2025 (\$30/kW)[169] . However, there are very few literature available for the cost analysis of hydrogen fuel cell [171-174], especially considering the well researched materials for BPP and they need substantial update and more research initiatives to meet the DOE cost target for 2020. In our opinion, the overall cost might be reduced by increasing market share and production volume, reducing the fuel cell stack price by focusing on individual components, and improving recyclability and reusing options.

Fig. 14: Cost analysis of fuel cell a) cost breakdown of fuel cell stack for a production volume of 500,000 units/yr b) fuel cell system costs at two different system volumes by year [169]

In the near future, this domain of renewable energy research will become more intense with the increasing demand of electrical vehicle to reduce GHG emission and also to reduce dependency on the fossil fuel. Hydrogen fuel is more potential because they contain better chemical energy compared to conventional battery materials [175], although challenges prevail around cost and availability [176]. Fuel cells are especially attractive for cleaner, and more efficient power source showing most flexible chemical-to-electrical energy conversion [177]. Moreover, with the limitation of battery driven electrical cars, such as less abundant battery materials, longer time of refuelling, and climatic variations in efficiency, more research is encouraged on fuel cell as next generation technology for medium to heavy-duty electric vehicles. This can be fulfilled by achieving improvement in durability and cost of carbon materials-based components while maintaining high performance. Recent research advances in this field received much attention as the efficiency reaches up to 80% in co-generation of electrical and thermal energy as well as the hydrogen fuel cell enables >90% reduction in environmental pollutants compared to ICE [34,178]. However, the new technology needs to emerge with ease of manufacturing, higher efficiency and recyclability, which is possible by a greater co-ordination between the lab researches and industrial scale ups. There should be more focus on understanding of the recyclability of materials, their compositional balance based on filler-matrix interaction, manufacturing conditions and optimization of electrical and mechanical properties, especially maintaining strength and stiffness yet not sacrificing flexibility.

6. CONCLUSIONS

This paper has focused on the critical factors as described by recent research works affecting the improvement of properties and durability of the carbonaceous materials-based component of the fuel cell such as bipolar plates. How materials, manufacturing techniques and parameters influence the properties and performance of bipolar plates, have been discussed and presented connecting to the mechanisms for performance improvement. Also, the key application areas have been highlighted comparing the relevant

properties outlined by the different papers. The main goal was to elucidate the critical factors with updated research work for sustainable development of the bipolar plates in the fuel cell. The following important points were gathered from the literature

- The main parameters that affect the electrical property are type of fillers, orientation, dispersion and crystallinity of the polymer matrix and the parameters influencing the mechanical strength are type of polymer matrix, surface energy, filler-polymer interface properties, and use of fiber reinforcement
- External parameters that influence the electrical and mechanical properties are process temperature, pressure and molding time. However, these factors control the internal parameters and hence, different optimization for different filler-polymer pairs should be made for achieving maximum results
- CB, CF, CNT, and EG are potential filler materials that can enhance the performance of the bipolar plate, although they have individual critical threshold above which agglomeration can be an issue. For polymers, conductive polymers and use of compatibilizers can help to improve the electrical and mechanical properties
- Aspect ratio is an important factor to consider as elongated particles yield better result than round particles. However, fillers of two or more different sizes should be used to get additional conductive pathways and better load distribution by creating less void spaces between the particles. In this case, the agglomeration or proper dispersion can be the main issue for smaller-sized fillers and nanoparticles.

Conflicts of interest: No conflicts to declare

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