Expanded and Nano-Structured Carbonaceous Graphite for High Performance Anisotropic Fuel Cell Polymer Composites

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Abstract:

We disclose novel high pressure design, non-destructive structural analysis and fabrication of bipolar plate composites (BPC) that are highly conductive yet mechanically flexible. Here we report the highest electrical conductivity of 221 S.cm⁻¹ of a BPC by tailoring graphitic structure of carbon nanomaterials and their functional attributes through enhancement of in-plane conductivity as well as mechanical strength; another advanced BPC also displays a maximum flexural strength of 52 MPa. These key functional efficiency enhancements of hydrogen based electric power trains components became highly relevant for medium to heavy duty transportation. Evidently, tunable, expandable and expanded graphitic composites can play a major role in facilitating the fabrication of a light-weight high-performance plates for fuel cell application.

Keywords: Multifunctional composites; Graphene; Electrical properties; Mechanical properties; Fuel cell

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1. INTRODUCTION:

Proton exchange membrane fuel cell (PEMFC), the most used fuel cell in transportation sector, has advantages of low operating temperature, relatively fast start-up process, and high-energy density over other electrochemical devices. Hence, PEMFC becomes the most promising and vastly researched fuel cell. They have three main components, bipolar plates (BPP), gas diffusion layer (GDL) and membrane electrode assembly (MEA) (Fig. 1). BPP which can be made from graphite, metal or carbon polymer composite is a very important part because they can contribute up to 60-80% of the total weight as well as 30-40% of the total stack cost [1-4]. Their main functions include connecting the adjacent cells, distribution of fuel gas, removing heat and water, and supporting the MEA sustaining the clamp pressure [5].

Fig 1: Components of a PEM fuel cell and schematic diagram of reactants' delivery path

All three types of bipolar plates such as graphite, composite and metal plates are currently under investigation for improved properties. However, according to recent publications more focus has been given on composite as well as metal bipolar plate for fuel cell application. All of them has

43 advantages and disadvantages and researchers put their best efforts for decades to bring out the
44 spectrum of new materials and solutions to the existing problems. To this end, our research
45 covered the effect of advanced carbon composites on the key properties of bipolar plates,
46 especially electrical and mechanical attributes. From the history of fuel cell, it is noted that the
47 specification for Bipolar plate is driven by DOE target, which is often used by industry as the
48 gold standard. From the DOE target chart, the main criteria for bipolar plate are cost, weight,
49 corrosion tendency, electrical conductivity, H₂ permeation, areal specific resistance (interfacial
50 contact resistance) and flexural strength [17]. For the year 2020, DOE reduced the target criteria
51 for flexural strength compared to their 2015 target to strike a balance among the cost, electrical
52 conductivity and mechanical strength; the electrical conductivity is more of a desired criteria in
53 2020 and more important especially for composite bipolar plate as they have low electrical
54 conductivity issue due to presence of insulating resin matrix. (Table S1 in the supporting
55 document summarizes the merits and demerits of different BPP)

56 Graphite was once the mainstream BPP material, but due to its bulk weight and volume,
57 brittleness and expensive machining process the focus has shifted to composite and metal bipolar
58 plates. Graphite shows many advantages such as low contact resistance, high corrosion resistance
59 and good electrical conductivity. The graphite BPP has poor mechanical strength and more
60 porous structure due to their particle properties which increases H₂ permeability. Additionally,
61 the fabrication of channels becomes expensive, time consuming and barrier to mass production
62 because a computer numerical control machine is required [34-36]. Metal BPP is a potential
63 material due to its high electrical and thermal conductivity and good mechanical strength.
64 However, they are susceptible to corrosion and decomposition at fuel cell's harsh environment at
65 pH 2-4 and humid operating condition of 80⁰ C [6-10, 37,38]. Their greatest limitations are the

corrosion prone nature, hydrophilicity and high interfacial contact resistance (ICR) which can cause low power output and reduced efficiency of the cell; the membrane electrode assembly (MEA) may be affected, the expensive Pt catalyst can be damaged, and the evolved corrosion layer can increase the overall electrical resistance of the cell. Hence, the theoretical advantage values can be nullified with the long-term operation of the fuel cell system.

Polymer composite bipolar plates come into play to resolve these fundamental problems and show greater advantages in good pore tightening, improved mechanical strength, low contact resistance, eradication of machining problem and above all excellent corrosion resistance. However, they have low electrical conductivity issue due to non-conductive matrix and increasing electrical conductivity needs higher filler content which by default reduces the mechanical strength due to the brittle nature of the fillers [39,40]. This is a long-time ongoing objective of the research to achieve a maximum balance between the electrical conductivity and mechanical strength to provide a high-performance alternative of bipolar plate. Our research is following this trend to provide an optimized options which show both high electrical and mechanical properties well above the DOE target. (The specific comparisons are given in table S2 in the supporting document).

For electrochemical comparison, the main criteria are corrosion resistance and interface contact resistance which are two key factors for performance evaluation. The metal bipolar plates by nature lack in both these factors as they are very susceptible to generation of undesirable oxide layers, hence they cannot compete for higher life expectancy required by medium to heavy duty operations. From chemical stability analysis it was found that SS304 plate has redox peak at -0.2 V compared to graphite plate's 1.6 V [41]. This is an indication that the oxidation is predominant over the reduction and hence the corrosion can spontaneously occur for metal plates. Even with

different coating, the value comes close to 0-0.1 V [42] which is not sufficient to prevent corrosion. For interfacial contact resistance, a very high value of 239 mΩcm² was observed for SS316 metal bipolar plate which is much higher than the DOE target (<10 mΩcm²) and is a concern because 2-5% power loss can occur in PEMFC stack with an increase of 25 mΩcm² [43,44]. Even with the coating materials, ICR for most of the metal bipolar plates values exceed 10 mΩcm² [45]. On the other hand, most of the composite plates show ICR values <10 mΩcm². For example, Taherian et al 2011 [46] and Cho et al 2004 [47] achieved ca. 9 mΩcm² and 7.42 mΩcm² for composite bipolar plates which is within the DOE range. Due to the complex nature of multi-component design of composite plates, the results can vary between different filler-polymer pairs [11]. Nonetheless, very few literature on composite bipolar plate has undergone electrochemical tests due to their non-corrosive nature. Herein, two common corrosion resistant materials – carbon and epoxy are utilized which are well known for their chemical stability and non-corrosive nature. This is more confirmed from no-metal presence in EDX analysis as shown in fig 4b. An interesting option and potential future research can be using metal bipolar plate in the anode side only where the corrosion potential is less predominant. In essence, BPP can be fabricated with various materials and the commercialization of both composite and metal bipolar plates are underway to facilitate different requirements depending on the industry. Therefore, they are not really comparable rather parallelly moving forward and trade-offs between different properties must be critically assessed to achieve a good balance between processibility and high performances. Our main goal is to provide the scientific insight behind choosing different functional and nano-structured advanced materials to facilitate fabrication of high-performance bipolar plate composites.

111 For important factors determinant of composite attributes, roughness and porosity are important
112 properties which can affect gas permeation, water absorption, electrical conductivity and
113 mechanical strength [12-16]. . Although there are a number of examples citing design and
114 fabrication of composite plates with diverse light weight carbon materials, rarely with epoxy
115 matrix they achieve a desirable functional attributes up to US DOE standard, such as electrical
116 conductivity ($>100 \text{ S.cm}^{-1}$) and flexural strength ($>25\text{MPa}$) . Some of the key scientific
117 challenges need to be addressed are the intrinsic properties of fillers and polymers as well as the
118 interfacial interaction. Moreover, to increase the overall usage of the fuel cell, it is important to
119 enhance the cost-effectiveness and performance of BPP; herein the cost-effectiveness is
120 maintained by utilizing minimum amount of nanofillers with maximum improvement of
121 composite electrical and mechanical attributes. The main desired properties other than electrical
122 conductivity and mechanical strength are chemical stability and gas impermeability which is
123 ensured here with stable raw materials and a high pressure fabrication process to minimize
124 porous structures within the composites. There is also a lack of investigation on graphitic
125 structure of various carbon-based energy materials which possesses adaptive functional
126 properties. To addresses the most pressing challenges of specific functional attributes of
127 composite plates, the structure of diverse carbonaceous materials and their multi-layered
128 graphitic structures have been investigated here to better understand the electron transfer through
129 composite structure designed for fuel cell bipolar plate and correlate their structure-property to
130 BPP functions.

2. EXPERIMENTAL

2.1 Materials:

In this research, carbon-based particles such as graphite, carbon black, multi-wall carbon nanotubes, and carbon fiber were used as primary and secondary fillers (table 1 & fig. S1 in supplementary data) whereas epoxy resin-bisphenol A diglycidyl ether (West system 105; density 1.15 g/cm³, viscosity ~1000 cp) was used as the polymer matrix. For the fabrication process, direct mixing and hot compression molding were used with high pressure (55 MPa) which is unique and effective.

Table 1: Fillers and their properties

Material Name	Source	Density (g/cm ³)	Mean particle size	Surface Area (m ² /g)	Conductivity (S.cm ⁻¹)	Filler type (Filler content wt%)
Graphite 4012 (Gr)	Asbury carbon	2.2	~75 µm	1.27	~30	Primary (76%)
Graphite 4056	Asbury Carbon	2.18	~200 µm	1.27	~30	Primary (76%)
Carbon Black 5303 (CB)	Asbury Carbon	~0.1	~30 nm	254	~2.93	Secondary (1-3%)
Multiwall carbon-nanotube (MWNT)	Cheaptubes, USA	~2.1	~30 nm (length ~20µm)	110	>100	Secondary (2%)
Carbon Fiber (CF)	Zoltek PX35	1.81	Dia. ~7µm	1.87	~645	Secondary (1-2%)
Carbon Veil (CV)	Fiber Glast	Weight 4.8-6.5 g/yd	Thickness 50-100 µm	-	~2.85 S/cm ²	Secondary (1pc)
Expandable Graphite 3558 (ExG)	Asbury Carbon	2.2	~250 µm	23	~30	Primary (76%)

2.2 Methods:

2.2.1 Composite fabrication process: In this research, direct mixing and compression molding technique was used as the main process to fabricate the composite samples. The general method includes optimized mixing of carbonaceous materials and polymer matrix, fabricating composite

through hot molding process (fig. 2) and finally, characterization for conductivity, mechanical strength and morphological analysis for interface properties. In general, the carbon-based materials were mixed in a mechanical mixer (Caframo RZR1) at 200-300 rpm at ambient temperature. Primary fillers were placed first and the polymer resin and hardener or curing agent (polyamine based) were added dropwise with continuous mixing, then the secondary fillers were added intermittently at the end and mixing continued for more 15 minutes to ensure even dispersion of fillers in the matrix. Nanofillers and CF contents are kept within threshold to withhold the cost-effectiveness as well as high performance of the composites. For carbon veil, it was used in the middle of layers of filler-matrix mixture as a pre-preg system. The mixture was then compressed in the Carver hot press machine for 10-15 minutes at 110-120⁰ C and 55 MPa (8000 psi). In case of expanded graphite (EG), it was processed from expandable graphite (ExG) by heating up in muffle furnace at 950⁰ C for 30 seconds

Fig 2: Compression molding process for fabrication of bipolar plates

2.3 Characterization:

The following machines and processes were used for characterization of the carbon polymer composite (Details in the supporting document)

Conductivity: Conductivity was measured by 4-point probe method using high-precision Keithley 2450 source meter and Everbeing 4-point probe station. Results were averaged from 3 samples and 5 points in each sample. Sample size was 75×75×1.1 mm.

Flexural strength: Flexural strength was measured by 3-point bending test (ASTM D790-3) using Instron 3367. Support span length 25 mm and overhead speed was 1mm/min

Micro CT scanning: X-ray Micro-computed 3D Tomography-SkyScan 1172

Contact angle: Contact angle machine OCA 15EC (sessile drop method with water)

Morphology: Scanning electron microscope (JSM-6610LV) and Energy Dispersive Spectroscopy (Oxford, 20mm²)

XRD: Philips PW 3710 CuK α radiation ($\lambda = 0.15406$ nm) at 40kV and 30mA with 0.02⁰ step size, 2.5 s/step and 0.008⁰/s scanning rate.

Raman Spectroscopy: Senterra dual laser raman spectrometer with 532 nm wavelength

3. RESULTS AND DISCUSSIONS:

Functional fillers play a more important role in determining the electrical conductivity of the carbon polymer composites than the polymer matrix. Herein we report the effect of graphitic carbon structure and their dispersion on BPC performance.

3.1 Graphite and Graphitic structure:

In case of the graphite-epoxy composite particles, Raman spectra showed how the lattice can be varied with the addition of different materials. For Graphite composite (fig. 3), the D peak, G peak and 2D peaks were observed at 1350, 1580 and 2700 cm⁻¹ respectively. For composites with expandable graphite (ExG) and expanded graphite (EG) these peaks were not much shifted

as shown in fig. 4, however, peaks broadening in G peaks (6% for Graphite-EG and 27% for ExG), and splitting in 2D peaks were observed which indicates the presence of defects and more layered structure has been formed which induces more electrical conductivity in these composites.

Fig 3: Comparison of Raman spectra of the composites with various carbon materials

For expanded graphite, 27% increase in I_{2D} and I_G ratio signifies the layer expansion and presence of more graphene like structure (table 2). With introduction of MWNT and CB in the graphite-epoxy composite (fig 3), the broadened peaks were found with less intensity in graphitic bond (G peak) which indicates that the lattice is slightly distorted, and amorphous carbon became more dominant due to the more amorphous nature of these materials. This is evidenced from the increase and decrease in I_D / I_G and I_{2D} / I_G ratio respectively (table 2). It is possible that these changes in the band intensity is due to the de-bundling of nano fillers by penetration of polymer chains during composite melt mixing [18]. The resulting composite expects to show higher conductivity due to higher amorphous carbon content.

Table 2: Raman spectra data for different compositions of the composites

Sample	D peak	G peak	2D peak	I _D /I _G	I _{2D} /I _G
Gr-CB	1347	1582	2711	0.34	0.28
Gr-MWNT	1351	1578	2706	0.23	0.28
ExG	1351	1578	2700	0.2	0.48
Gr-EG	1353	1578	2701	0.3	0.56
Gr	1342	1582	2716	0.14	0.44

It is well known that in graphitic hexagonal lattice structure with layered planes, the interatomic distance is 1.42 Å and interlayer distance is 3.354 Å (fig 4a). One out-of-plane p-bond in each carbon atom contains delocalized electron which is responsible for high thermal and electrical conductivity. In a shear processed graphite as above intercalated and/or exfoliated layers are held adjacently by weak Van der Waals force and hence graphite layers can slip past one another leading to demonstrate lubricating behaviour and softness [19].

Fig 4: a) Graphitic structure [20], b) SEM/EDX analysis of graphite-epoxy composite

From the EDX analysis, the presence of carbon and oxygen and predominance of carbon molecules (ca. 15:1) are confirmed in the composition as shown in fig. 4b. In order to obtain deeper insight, graphitic crystal lattice along with the excitation states are determined by Raman spectroscopy which can be related to improvement of electrical conductivity (table 2). From the Raman spectroscopy data, the conformational changes were determined within the lattice of the graphite in the composite fabricated with epoxy resin and various carbonaceous materials which can be best described by the Brillouin zone (BZ) and phonon dispersion from fig. S2 (in the

supporting document) and table 2. The Raman spectra mostly show the sp^2 vibration as excitation that mainly resonates with the π states of the molecule and this is true even for highly sp^3 amorphous carbon. This is a well-established fact that the G peak in the spectra is caused by the stretching of sp^2 atoms in both rings and chains whereas the D peak by breathing modes of sp^2 atoms only in rings. The difference between D and 2D is that 2D band involves two TO (Transverse and Optical) phonon near the K point and D band originates from one TO phonon and one defect [21]. These are all caused by the Kohn anomalies for Γ - E_{2g} and K- A'_1 . However, for carbon nanotubes, stronger Kohn anomalies is present due to their reduced dimensionality. This gives phonon softening [22] and their presence make the Raman spectra different for the composites which can be observed from reduced I_D/I_G ratio in table 2.

3.2 Different sized Graphite Particles:

In general, functional fillers have more influence on the conductivity than the matrix. The conductivity can be improved by tuning fillers effectively. For example, if two fillers of different sizes are used, there can be less void space in between the round particles. As a result, the conductive path is formed easily, and the composite becomes more conductive. This can be explained from the equation 1 [23]

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

Where, R_c is the constriction resistance, ρ is the bulk resistivity, E is the young's modulus, F is the exerted force between the particles, ν is the poisson's ratio and r is the protrusion radius. From the equation 1, it can be found that the increase in protrusion radius r as well as force F can decrease the contact resistance. From our results, it has been found that using synthetic graphite (SG) with bi-modal size selection show better result than one-size filler (fig 5a) for both conductivity and flexural strength. Also, for composites containing a single size filler, fillers with bigger particles

when used in the same amount, show better conductivity due to the bigger protrusion radius (fig 5a). From our experiments, we found about 18% increase in conductivity for graphite with larger particle size. Two variables, namely aspect ratio and difference in diameters in this case contributes to increasing protrusion radius as shown from equation 1. As a result, the average distance between the filler particles decreases facilitating the electron hopping process (fig 5c) which can be also found in the one-way ANOVA result as the compositions are significantly different ($p < 0.05$). Hence, the increase in aspect ratio of carbon fillers increases conductivity at any particular loading [16, 24, 25]. We also found that 56% of 200 μm filler and 20% of 75 μm filler combination showed the best conductivity of 217 S/cm and flexural strength of 38 MPa (fig 5a). In most cases, flexural strength somewhat decreased with increasing electrical conductivity. This is due to the fact that the determinants for electrical conductivity and mechanical strength are different in nature. A more continuous electron flow path formation due to bi-modal distribution of carbon particles dominantly reflected in higher conductivity as schematically shown fig. 5c; however, brittleness of the carbonaceous fillers and weaker interface between carbon particles and resin led to lower ductility of the composite.

Fig 5: a) Effects of different composition with graphite of different particle sizes ($p=4.9 \times 10^{-6}$) fillers with primary filler and b) Comparison between synthetic and natural graphite filler - without and with Carbon veil ($p=0.0018$), c) Scheme of increased conductive network due to addition of different size or secondary fillers

Experiments were also carried out with the natural flake graphite (NG) and compared with the results of synthetic graphite (SG). NG based composite has 8% more conductivity than SG based composite which is shown by the one-way ANOVA result as they are significantly different ($p < 0.05$), however, flexural strength remained relatively indifferent (fig 5b). This may be because the difference in surface energies between filler and polymer matrix is greater for NG. Also, for natural graphite, its structural morphology differs between different sizes and also depends on the source of the graphite, their variations in production process and impurities present [26].

3.3 Effects of carbon nanomaterials:

Carbon black (CB) is a preferable nanofiller due to its lower cost and larger surface area. It also contains functional groups such as carboxyl, phenols, quinones and lactones that affect the blending with polymer matrix as well as the improved properties for the composite [10]. The main properties of carbon black that determine the electrical conductivity of the composite are particle size, structure, and degree of graphitization [27-30]. Multiwalled carbon nanotubes (MWNT) are the layers of graphene in rolled forms. They are more cost-effective than single-wall nanotubes (SWNT) and have high potential to enhance electrical conductivity due to their high aspect ratio [31]. From the experiments, both nano-sized CB and MWNT improved the electrical and mechanical performance of the composite which can be observed from the

ANOVA result as they are significantly different ($p < 0.05$). For CB, high electrical conductivity of 221 S/cm was observed when used with expandable graphite and high flexural strength of 52 MPa was achieved in a hybrid system with carbon fiber (fig 6a). For MWNT, the highest value of electrical conductivity of 201 S/cm was achieved with ExG and flexural strength of 50 MPa with CF in the hybrid system (fig 6b). However, CB shows better electrical conductivity in the non-hybrid system, whereas MWNT shows better performance when used along with carbon fiber or carbon veil. This may be because carbon black has more surface area than MWNT ($254 \text{ m}^2/\text{g}$ compared to $110 \text{ m}^2/\text{g}$). On the other hand, MWNT has less surface energy difference with carbon fiber, $5 \text{ mJ}/\text{m}^2$ compare to $14 \text{ mJ}/\text{m}^2$ for CB.

Fig 6: Electrical conductivity and flexural strength for different compositions a) for carbon black ($p = 0.00001$) b) for multi-walled nanotube ($p=0.0002$)

It can be inferred that both nano particles and fibrous fillers should be used below the threshold due to wettability issue. Agglomeration can occur if the wettability of multiple components is not optimized. From SEM pictures, it was found that CB particles are not as visible in the through plane surface and they are more dispersed in the in-plane direction (fig. S3c in the supporting

document); proper dispersion with high shear is required to get desired results as they tend to agglomerate when mixed at low shear such as an rpm below 100 (fig. S3b). Use of sonication and higher rpm (~400 rpm) improved the dispersion (fig. S3a); Nonetheless, an excessive rpm can cause damage to graphite particles and layers which affects the composite properties adversely.

3.4 Effects of expanded and expandable graphite/GIC:

Expanded graphite (EG) is an important modification of graphite layers to facilitate functionalization for electrical and mechanical properties. It comprises of 100-200 times expansion of the graphite layers initiated from graphite intercalation compounds (GIC) or expandable graphite (ExG), by the decomposition of intercalants present inside the graphite layers. ExG is also a potential material to increase the conductivity of the composite with low mass density at room temperature. It can absorb guest atoms between the graphene layers by forming ionic bonds which increase the conductivity of the graphite by adding electrons to its conduction band or holes to the valence band. Graphite is modestly conductive with a value of around 2×10^{-4} carriers/atom (2×10^{19} /cm³) [32]. The intercalation process provides injection of carriers from the intercalant layer, electrons for donors and holes for acceptors to the graphite layer and create a high mobile system. Hence, the graphite layer becomes charged and the released charge gives rise to the charge density in the graphite layers. McRae et al [33] concluded that the intercalant in the graphite layer stays in an ordered array and not as a statistical distribution. From the results for conductivity and flexural strength, it was observed that both expandable graphite and expanded graphite increase conductivity (fig. 7) up to 221 S/cm, but reduce the flexural strength up to 27 MPa as they have more layered structure with increased distance between the layers that lessens the bonding and wettability. Also, delamination may occur as found from the SEM pictures (fig 8).

Fig 7: Comparison of conductivity and flexural strength for graphite, expandable graphite and expanded graphite on the basis of density

Fig 8: SEM images of the fractured surface- a) layers from graphite intercalated compounds b) carbon fiber within the GIC layer

From the SEM pictures (fig. 8), it was also observed that with intercalated graphite there is more denser and visible layers of graphite, hence the density is reduced about 10% from 1.83 g/cm^3 to 1.64 g/cm^3 (measure as per ASTM D792) as shown in fig. 7. The average thickness is also reduced by 18% from 1.23 mm to 1.04 mm when the process parameters were kept same during fabrication (fig. 7). Above properties enable the fabrication of a light-weight high performance composite for fuel cell application which is important for US DOE's cost vs performance target. Raman spectroscopy provides a non-destructive and fast characterization of nanoparticles and their composites with maximum structural and electronic information which can be verified by

XRD. For graphene, in general, the 2D peak intensity increases significantly than the graphite and also in case of lesser number of graphene layers present, the G peak decreases.

Fig 9: Difference between Graphite, expanded graphite and expandable graphite from a) XRD of materials, b) XRD of composites and c) Raman spectroscopy of graphitic materials

Fig 10: Deconvoluted 2D peak analysis for a) expanded graphite and b) expandable graphite

Reduction in both (002) and (100) plane from fig. 9a and decreased intensity of D band peak as well as ~10% increase in (2D/G) ratio in fig. 9b and table 3 indicate reduction of defects and exfoliation of layers in the graphite lattice structure. After deconvolution, four sub-peaks were found at 2649, 2694, 2722 and 2739 for EG and 2651, 2682, 2716 and 2737 for ExG respectively (fig. 10) which indicates the change from graphite to graphene like layered structure contributing towards enhancement of electrical conductivity. From Table 4, it can be inferred that there is an increase between the spacing for EG and ExG compared to graphite as the d-spacing increases; it is true for both these carbon materials and their composites. There were also changes in crystallite sizes in the atoms, 55% and 17% reduction for ExG and EG respectively (table 4) which indicates change in crystallinity due to breakage of layers. From the XRD and Raman spectroscopy analysis (fig 9 & table 3,4), we concluded that the expanded graphite shows more graphene like structure than graphite and expandable graphite, as the distance between layers is expanded. However, in case of composite structure, the influence of graphite is more prominent due to low EG content (2-3%) as there is difference of Raman and XRD analysis between the carbon materials and their composites which is revealed for the first time in our research.

Table 3: Raman peak analysis

Sample	D	2D	G	I _D /I _G	I _{2D} /I _G
Gr	1351	2713	1581	0.14	0.41
ExG	1342	2716	1580	0.15	0.46
EG	-	2718	1578	-	0.45

Table 4: D-spacing and Crystallite sizes of different materials & composites from XRD

Sample	2 θ (002)	d-spacing, nm	Crystallite size, nm
Graphite	26.37	3.37	19.35
ExG	26.16	3.40	8.72

EG	26.05	3.42	16.12
Gr Comp.	26.27	3.39	18.04
Gr-EG Comp.	26.14	3.40	23.98
ExG Compo.	25.97	3.42	10.73

3.5 Pore effects on conductivity:

The presence of less porous structure in the BPP composite is an important criteria for target application of bipolar plates. This is important mainly because the porous structure can lead to H₂ gas permeability and thus reduce the efficiency of the fuel cell. To understand the pore effects on the performance of carbon polymer composite, the pore areas were calculated for various composition and a relation between the conductivity and the porous structure of the composites were investigated by a non-destructive test with x-ray Micro CT. There can be two kinds of micro-structures observed inside the composite in fig 11a, the dark grey structures indicate resin matrix whereas the bright white dots indicate pores or air voids in the samples. The analysis by 3D images from x-ray Micro CT scan showed that the composite with less porous structures have better conductive properties. For example, comparing between the 3D images of fig 11b,d,f and 11c,e,g, the later has bigger and denser pores (white dots) which is reflected in their conductivity values of 217 S/cm and 135 S/cm respectively. In our study, 10×15×1.1 mm samples were scanned by SkyScan 1172 with pixel size of 8-11µm. The projected images were acquired at 0.7 degree rotation increment over 360⁰ and with an exposure time of 600ms. After reconstruction and analyzing different composites by NRecon and imagej softwares and also from measured contact angles, we concluded that the porous structure is related to the increase or reduction of overall conductivity of the composite.

Fig 11: 3D images from X-ray μ Tomography showing pores in the internal structure of the

composite a-general sample showing pores and resin matrix, b,d & f- after reconstruction

From the table 5, it can be inferred that the less pore area and higher contact angle is incorporated to higher conductivity because of the established continuous conductive network enhancing electron transfer. For example, the introduction of carbon fiber or carbon veil increases pore area and decrease the hydrophobicity as shown in table 5. Similarly, the use of multiple secondary fillers as well as increase of resin matrix increases percentage of porous structure due to poor wettability. The pore area was calculated taking average of 50 layers reconstructed from X-ray μ Tomography and contact angle was measured by the sessile drop method. Further investigation is required to establish a relation between porosity and other composite properties. Anisotropically distributed advanced functional carbonaceous materials are difficult to analyze due to their complex nature of interaction in the composite, but the non-destructive techniques used in this paper can mostly capture their functional characteristics in terms of the desired properties of carbon polymer composite. Future research may include the

enhancement of mechanical properties by introducing novel materials such as continuous and functional fibrous materials without increasing the porous structure within the composite.

Table 5: Comparison between different composites showing the influence of porous structure on the conductivity of the composite

Materials*	Conductivity, S/cm $\pm$ SD	Pore area% (NPA ** $\pm$ SD)	Contact angle, degree $\pm$ SD
Gr56-ExG20	217 $\pm$ 5.6	1.3 (98.7 $\pm$ 0.6)	82.1 $\pm$ 1.0
Gr76	153 $\pm$ 4.6	2.1 (97.9 $\pm$ 0.6)	80.3 $\pm$ 3.8
Gr74-CF2	135 $\pm$ 4.2	2.3 (97.7 $\pm$ 0.8)	75.9 $\pm$ 1.5
Gr72-EG2-CB2	130 $\pm$ 3.8	2.9 (97.1 $\pm$ 1.1)	74.8 $\pm$ 1.1
Gr76-CV1(pc)	119 $\pm$ 3.8	3.6 (96.4 $\pm$ 1.1)	74.3 $\pm$ 2.0
Gr70	95 $\pm$ 4.5	4.1 (95.9 $\pm$ 1.1)	73 $\pm$ 3.2

Note: *Materials: Composition of fillers, the rest percentage is resin matrix, **NPA = Non-porous area%

4. CONCLUSIONS:

In this research, the functional properties of materials and graphitic structures were investigated to determine the pivotal elements for the improvement of carbon polymer composite in high-performance fuel cell application. The maximum electrical conductivity of 221 S/cm was achieved with ExG and CB and the maximum flexural strength of 52 MPa from hybrid composite with graphite, CF and CB which elucidate the importance of optimization for desired properties. The main findings are

- The high pressure fabrication process and use of functional hybrid materials improve both the electrical and mechanical properties of the composite.
- The main critical factor especially for the improvement of electrical conductivity of carbon-epoxy composites are types of raw materials, combination of different sizes and use of nanofillers tailored by functional graphitic structure

- Expandable graphite and expanded graphite can reduce the weight and thickness substantially by introducing layered structure which can incorporate to fabrication of a light-weight high-performance composite
- Porosity of the composite measured in a non-destructive way can be a very important factor which can be related to electrical conductivity, hence can be a determinant factor to the ultimate fuel cell performance

Overall, the fillers mainly control the conductivity through their graphitic functionalized structure whereas polymer matrix influences more to the flexural strength due to their inherent flexible properties. The electrical conductivity and mechanical strength need to be calibrated to achieve best targeted application requirements.

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Appendix A. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.compscitech.2021.108654>

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