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Preparation C-Carbon Composite Using Natural Graphite and Novolac Resin

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ABSTRACT: Carbon composites are prepared by using natural graphite (NG) as raw material which has to be good at electrical conductivity and excellent corrosion resistance at low density of about 2 g/cm^3. NG comprises flake-like particles which provide better face to face contact rather than point to point contact in spherical ones. Reported Expanded Graphite (EG)/Novolac Phenolic Resin (NPR) needs optimisation for proper volumetric mixing of EG with Resin. Graphite is made up of well-known hexagonal phase which is more stable phase and the rhombohedral phase is thermodynamically unstable formed by ball milling. Lattice defects induced in graphite break down the hexagonal symmetry of the graphite lattice. It's get down to nano-crystalline regime of fine grains which increase the free energy and form amorphous structure after forming nano structures.Samples were prepared form graphite-carbon composites by uniaxial hot compression after ball milling of NG with NPR followed by curing. The temperature was characterised for physical and mechanical properties. The intrinsically insulating polymer resins gets filled with filler material (NG) so as to get better percolation and better conductivity.

KEYWORDS: EG/NPR, Carbon-Carbon composite, Natural graphite, Ball milling

I. INTRODUCTION

The polymer electrolyte membrane fuel cell (PEMFC) is oneof the most promising power sources for stationary and transportation applications in the future due to its high efficiency, high-power density, relatively low-operating temperature, convenient fuel supply and long-life time[1].Bipolar plates areimportant components in PEMFC, which account for approximately 80% of the fuel cell volume, 70% of the fuel cell weightand as much as 60% of the entire stack cost [2].The cost of thebipolar plate has become a major barrier to its commercialization.

Metal plates such as titanium and stainless steel exhibitgood mechanical and low gas permeation characteristics withhigh corrosion resistance due to the formation of protectivemetal oxide films on their surfaces. To prevent formationof electronically insulating oxide films and to make these platesconductive in fuel cell environment, a protective and conductive inorganic or organic coating must be used. [1, 2].PEMFC is an electro chemical cell which converts chemical energy of fuel into electrical energy. Fig.1 represents bipolar plates used in PEMFC. The chemistry for a fuel cell is as follows.

Anode side: $2H_2 \rightarrow 4H^+ + 4e^-$
Cathode side: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Net Reaction: $2H_2 + O_2 \rightarrow 2H_2O$

The PEMFC uses a solid polymer as the electrolyte and porous carbon electrodes containing a platinum catalyst. With a solid and immobile electrolyte, this cell is inherently very simple. PEMFC operates at relatively low temperatures, around 80 ºC. Thus it need very less time to start up or warm-up. However, PEM FC require a noble metal catalyst (typically platinum) to facilitate the dissociation of hydrogen molecules into protons and electrons[3, 4].

Earlier researchers have targeted US-DOS target valuesand our research is based on attaining those order to get ready with the plates to be stacked in to the fuel cell. DOS target values are tabulated in Table I.

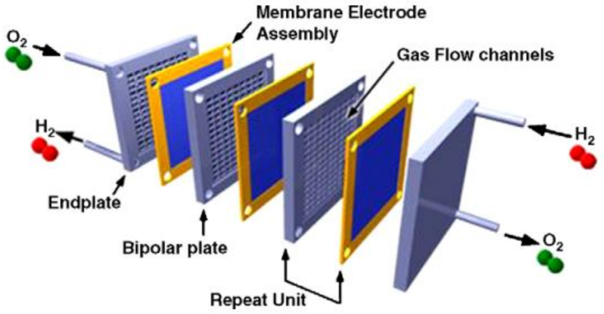

Fig.1-Bipolar plates used in PEM fuel cell stack.

TABLE 1
DOS TARGET VALUES.

Property	Value
Electrical Conductivity	>100 S/cm
Thermal Conductivity	>10 W/mK
Flexural Strength	>25 MPa
Shore Hardness	>50
Bulk Density	<5 g/cm^3

TABLE II
A COMPARISON BETWEEN A THERMOPLASTIC/FILLER COMPOSITE AND A THERMOSET/FILLER COMPOSITE FOR THE BIPOLAR PLATE MATERIAL

	Thermoset/Filler Composite	**Thermoplastic/filler composite**
Advantages	1.High-temperature operation than thermoplastic 2. fast life cycle-time 3.flow field introduced during moulding 4. Low-contact resistance.	1.Injection moulding lends itself to manufacture automation 2.fast cycle-time 3.flow field introduced during moulding 4.low-contact resistance
Dis-advantages	Relative low electrical conductivity	1.Low electrical conductivity when using standard thermoplastics 2.limited to low-temperature operation 3.injection moulding difficult at higher filler loading 4.generally less chemically stable then thermosets resin
Processing option	1.Compression moulding 2.post-moulding CNC milling of blank	1.Injection moulding 2.compression moulding 3. Post-moulding CNC milling of bank.

Both thermoplastic and/or thermosetting resins may be selected, depending on the criteria adopted by the designer. Table-II shows a comparison between a thermoplastic/filler composite and a thermoset/filler Composite for the bipolar plate material [6].Polymer not only plays a binder role in the bipolar plate fabrication process, but is also one of the main factors affecting performances of bipolar plate [7].The difference of surface energy between polymer and filler isanother critical factor for the conductivity of carbon-filled polymer composites. It is known that similar surface energies lead to betterwetting of the filler by the polymer. As a result, larger quantitiesof polymer coat the filler surface. Consequently, the percolationthreshold increases as more particles are required to form a conductive network in the structure of the composite [8].

II. PERCOLATION THRESHOLD THEORY

An important theory for understanding conductivity within thermoplasticcomposite materials, especially where the thermoplastic matrix and the fillers have very different characteristics, is the concept of percolation. Percolation processes were developed by Flory (1941) and Stockmayer(1943) to describe how small branching molecules react and form very large macromolecules [9].

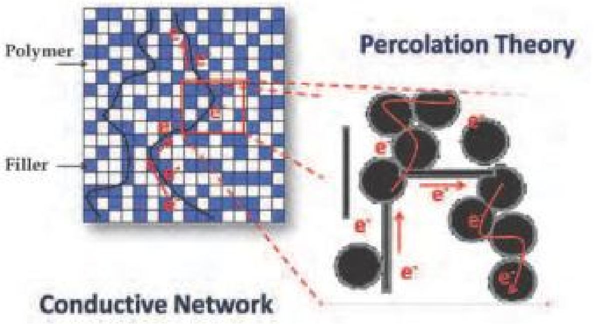

Fig2.-Schematics of percolation pathway

In a view of electrical conduction in a polymer matrix, electrons are free to flow through conductive filler particlesIf these filler particles contact one another, a continuous path is formed through the polymer matrix, which is an insulating material, for electrons to travel through.This path is called a conductive network, and the material with the conductive network turns into a conducting material, as illustrated in Fig.2

For the increase in conductive filler loading, three main regions define the relationship to the conductivity of conductive-filled-polymer composites as shown in Fig.3. At low fillerloadings (region A), the electrical conductivity value equals zero, since no path exists forelectron transport. The conductivity of the composite is still very close to that of the purepolymer matrix. At a certain critical loading, known as the percolation threshold, enough filler has been introduced so that it begins to form a continuous conductive network through the composite.

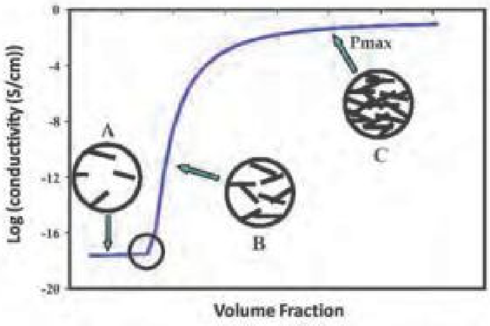

Fig.4 -Percolation S-Curve

Following the percolation threshold is a region that produces a significant increase in conductivity with very little increase in filler amount, as displayed by region B. After this region of drastic increase, the conductivity slows its increase, and approaches that of the filler material as increase happens because the conductive network through the sample is complete. This is depicted in area C of Fig.3. Eventually, P max is reached, at this point the addition of more filler does not increase the ease of electron movement. The addition of more filler will not enhance the conductivity to any significant degree. This paper reports different aspects of percolation phenomena of several polymer systems are reviewed. The information is closely related to the electrical performance of CPCs and it may be useful for the improvement of thermoplastic composite bipolar plates. To investigate the possibility of using conductive composite blends as bipolar plates in PEMFC, electrical conductivity and fuel cell performance must be characterized [10].

III. EXPERIMENTAL RESULTS

A. *Materials:*

The natural flake graphite, with a purity of 99.9% was obtained from metachem Pune. Novolac phenolic Resin was obtained from Abline polymers Mumbai. Novolac Resin-PF grade A-15

B. *Preparation of the composite materials:*

Ball milling was carried out in a conventional planetary ball mill. Pure graphite (99.9%, average particle size less than 200 µm) powder and Novolac resin powder was put into a Tungsten carbide ball bearing steel vial under a dry air atmosphere. To achieve better performance, a fixed volume fraction of 70:30 of NG/Novolac were ball milled. Hue et al. [11] experimented with NG/Novolac resin mixed in a Kinder for 2 hrs obtained better and void free samples for samples contains 30% Novolac epoxy resin. It was noticed that higher concentration of graphite is needed to create conductive path throughout the composite [11]. The ball milling was performed with a ball-to-powder weigh ratio of 10:1 with respect to which the total weight of the conductive powder to novolac powder was 11.2:4.8 i.e. 19g in total in a vial. The rotation rate of the vial was set for 250 rpm. The ball-milled powder was analysed by x-ray diffraction (XRD).Compression Moulding (CM) is best to manufacture bipolar plates. The plates are made up of thermosetting resin matrix of high electrical conductive by mixing 'solid' epoxy resin with the filler powder. Making graphite particles with longer aspect ratios is expected to resolve the problem of low electrical conductivity and flexural strength of CM manufactured bipolar plates. CM along with ball milling has been incorporated which gives both the required aspect ratio and proper mixing of natural graphite and novolac resin for 2 hrs., Samples were prepared by the varying pressure at constant curing temp of 150°c and varying curing time.

IV. CHARACTERIZATION

A. *Thermo-Gravimetric Analysis (TGA):*

TGA is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with a constant heating rate)performed by PerkinElmer with 10°c/min rate at National Chemical Laboratory Pune.

B. *Theoretical Density:*

Densities of all the composite samples were calculated by the dry bulk density measurement method. Weight of the samples were measured with the help of digital balance ρ- Theoretical density measured by using following equation

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

Mass is measured by taking weight of the sample and volume is measured by multiplying cross sectional area to thickness of the sample. The diameter of sample is 30 mm.

C. *Shore hardness:*

Shore hardness of the composite were measured by D type durometer (i.e. ASTM D2240-04). D-scale at our dept. Coep Pune. Hardness values mentioned in DOS target were by Shores D-scale stating a hardness of 50.

D. Electrical conductivity:

The electrical conductivity (σ) is characterised by both the methods of in-plane and through plane methods as described in Fig.5 and 6.The in-plane conductivity (σ) was measured using KEITHLEY four-point probe instrument (COEP. Pune). Through plane conductivity was measured using KEITHLEY instrument (National Chemical Laboratory Pune).Actual resistance=Observed resistance-Contact resistance (Contact resistance=2.05Ω)Conductivity=1/resistivity(R)

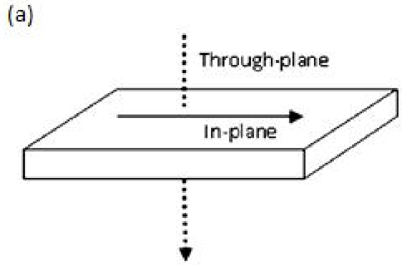

Fig. 5- Description of characterising conductivity in plane and through plane.

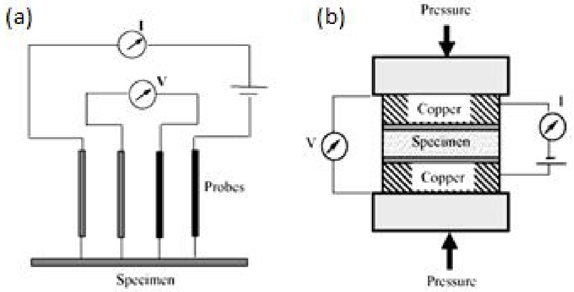

Fig. 6- Experimental setup for measuring (a) in-plane conductivity and (b) through-plane conductivity with four-point probe method. The applied voltage and measured current are respectively V and I.

E. X-ray diffraction (XRD):

Peak broadening obtained from XRD can be exploited to draw much information about the materials.XRD patterns were recorded using Rigaku-micromax 007HF equipped with Cu Kα target ranging from 2^{o}to 60^{o} with an interval of 4^{o}/min. High intensity micro focus rotating anode X-ray generator with R-axis IV $^{++}$ detector.

V. RESULTS AND DISCUSSION

A. Experimental results:

TABLE III
EXPERIMENTAL DETAILS OF SAMPLES OBTAINED

Composition	Temp (°c)	Curing time(t)	Pressure (MPa)	Remarks
NG	150	15	14.14	Crumbled into pieces
NG/Novolac 70:30 balll milled	150	15	14.14	Proper samples obtained
NG/Novolac 70:30 Manual mixing.	150	15	10	Porous sample

Table III and IV gives the experimental details with parameters and visual remarks which have been processed for sample preparation. The curing temp analysed as 150°C by the TGA of Novolac phenolic resin data as shown in Fig.7 and also from previous literatures. Varying curing time of 10 min and 15 min for 10 MPa hot compaction pressure at 150°c temperature as shown above.

TABLE IV
EXPERIMENTAL DETAILS OF SAMPLES OBTAINED

Samples	T **(min)**	P **(Mpa)**	**Hardness Shores-d**	**Resistivity ohms-cm**	**σ**	**P**
NG: Novolac **(70:30**	10	10	**52**	.005739	**174.23**	**1.76**
NG: Novolac (70:30	15	10	**43**	.006752	**148.11**	**1.94**

(T- Curing time, P-Pressure applied, σ- conductivity, ρ-density.)

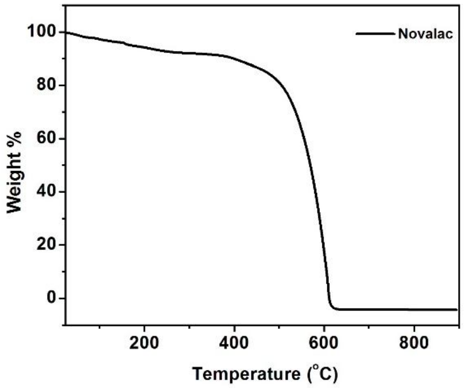

Fig. 7- TGA graph of Novolac Phnolic resin.

B. X-ray diffraction (XRD) analysis:

It is well known that the planetary-type mill favours the cleavage of the graphite sheets because the shear component of the applied stress is dominant, as shown in Fig. 8.

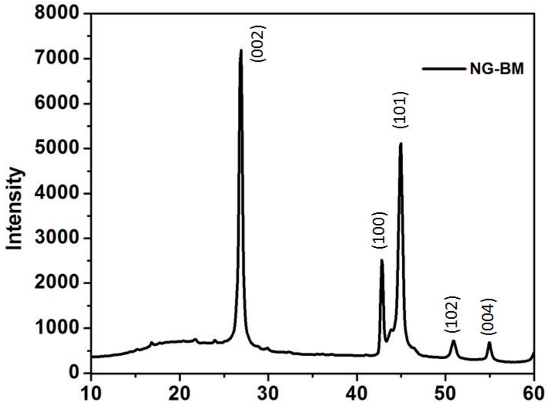

Fig. 8-. XRD graph of 2 hrs Ball milled NG/Novolac

For natural graphite, planetary ball mill is an effective method for the cleavage of the graphite sheetsIt can be seen that the diffraction of the NG is dominated by the high intensity (002) peak. It is well known that the hexagonal phase is the more stable phase and that the rhombohedral phase is thermodynamically unstable. The (101)peak at 43.7◦is attributed to the rhombohedral phase of graphite of graphite which is present with the hexagonal phaseThe presence of the latter phase in the natural graphite could have been caused by the milling operation used during its comminution possesses additional peaks at 2h = 43.4°, 46.2° and 56.6°.The main difference between the two phases relates to the stacking order of the graphene planes. It is ABABAB... for the hexagonal phase and ABCABC...for the rhombohedral phase. During the milling process, the graphite peaks become broadened. The (002) peak is shifted toward lower angles gradually, suggesting the widening of the d_{002} spacing caused by the destruction of the structure as well as the generation of defects. The asymmetric broadening of the (002) peak may relate to the reduction in the crystalline size, or the introduction of disordered graphene planes. The average interlayer spacing of the raw natural flake is0.3357 nm. The raw graphite powders featured interlayer spacing values close to that of the ideal single crystal graphite. The graphite composites showed larger average interlayer spacing (i.e.0.3364–0.3371 nm) than the raw graphite powders. This is attributed to Defects introduced during the milling of the green compound and the high pressure moulding process used to make the samples. [11, 13, 14].

C. Role of pressure in hot compaction:

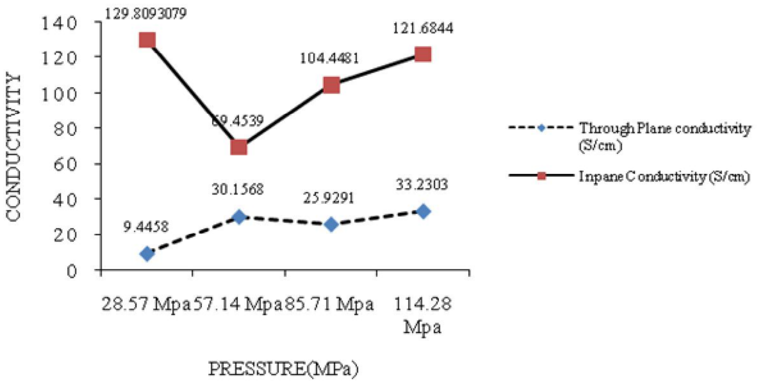

Fig.10-Plot of in-plane and through plane conductivity values with varying pressure for a curing temperature of 10 min.

The effect of pressure in hot compaction is significant .The increas in mold pressing pressure leads to reduction of the gap between particles, thereby causing increase in electrical conductivity [15]. By lowering the pressure, the porosity increases. Pressure also have a mojor role to play in percolation threshold in both through-plane and in-plane electrical conductivity. A considerable decrease in the composite electrical resistivity is observed by increasing the filler loading above the percolation threshold. Electric conductivity measured through plain and in plane which indicated by one in parallel to pressure and the other perpendicular to pressure. Ongoing to higher pressure values from 28.57 to 114.28 MPa an increasing trend in through plane conductivity from 9.4458 to 33.2303 S/cm. On the other hand in plane conductivity as shown in comparative graph of in-plane and Through Plane conductivity results show a steep decrease at 57.14 MPa there after the conductivity increased to 121.6844 S/cm. The resultsindicated in Fig.10 thatthe electrical conductivity of the samples had thesame change trend with decreasing particles size and widening granularity distribution. [15]

VI. CONCLUSIONS

(1) The graphitestructure is a layer-to layer one. Therefore, the electrical conductivity in parallel with graphite layer direction is much higher than that perpendicular to it.

(2) The hot compaction probably causesthe graphite layers to be oriented in a direction perpendicular tothe induced pressure direction ie found as in case of attaing 174 S/cm in plane conductivity.
(3) Ball milling could provide broadening of the graphite layers which get branch the resin to it and the polymer branches and eliminate the vacant spaces among the branched polymer network.

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