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FABRICATION OF CARBON–POLYMER COMPOSITE BIPOLAR PLATES FOR POLYMER ELECTROLYTE MEMBRANE FUEL CELLS BY COMPRESSION MOULDING

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Fuel cells are considered as one of the most important technologies to address the future energy and environmental pollution problems. These are the most promising power sources for road transportation and portable devices. A fuel cell is an electrochemical device that converts chemical energy into electrical energy. A fuel cell stack consists of bipolar plates and membrane electrode assemblies (MEA). The bipolar plate is by weight, volume and cost one of the most significant components of a fuel cell stack. Major functions of bipolar plates are to separate oxidant and fuel gas, provide flow channels, conduct electricity and provide heat transfer. Bipolar plates can be made from various materials including graphite, metals, carbon / carbon and carbon/polymer composites. Materials for carbon–polymer composites are relatively inexpensive, less corrosive, strong and channels can be formed by means of a moulding process. Carbon–polymer composites are of two type i. e; thermosetting and thermoplastic. For thermosetting composite a bulk molding compound (BMC) was prepared by adding graphite, vinyl ester resin, methyl ethyl ketone peroxide and cobalt naphthalate. The BMC was thoroughly mixed, poured into a die mould of a bipolar plate with channels and hot pressed at a specific temperature and pressure. A bipolar plate was formed according to the die mould. Design of the mould is also discussed. Conducting polymers were also added to BMC to increase the conductivity of bipolar plates. Particle size of the graphite has also a significant effect on the conductivity of the bipolar plates. Thermoplastic composites were also prepared using polypropylene and graphite.

Keywords: Carbon-polymer composites, Mould, Bipolar plates, Fabrication, Properties

1. Introduction

Polymer electrolyte membrane fuel cells have potential applications in pollution free energy and particularly in the transport sector. Although significant developments have been done and fuel cell vehicles are technically competitive with the internal combustion engines, but due to the high cost of fuel cells these are not still commercialized [1] . Fuel cell costs can be reduced significantly as low as that of internal combustion engines and the key factor is mass production processes [2]. Development of new materials, stack technology innovations and system efficiency improvements are the drivers to achieve the cost target. A PEM fuel cell is a stack of electrochemical cell units placed in series. The stack consists of the membrane electrode assembly, the bipolar plate, seals, current collectors and end pates. Bipolar plate is one of the important and costly components in fuel cells. Bipolar plates distribute gases (fuel and air) and remove reaction products, provide electrical connection between the cells, remove heat through cooling channels and hold the membrane electrode assemblies. Bipolar plates should meet the standard criteria [3] . Bipolar plate should be conducting, transfer heat, non permeable, chemically inert, tough, light weight and cost effective. Mostly used materials for bipolar plates are graphite, C-C composites, metals, coated metals and polymer – carbon composites. Advantages and disadvantages of different materials for bipolar plates are discussed in the literature [3] . Carbon polymer composite materials are most promising for bipolar plates due to their good properties, easy manufacturing and particularly low cost [4-7]. Polymers used are of two types i.e.; Thermosetting (epoxy resins, phenolic resins, furan resin and vinyl ester) and thermoplastic (Polyvinylidene fluoride, polypropylene, polyethylene, polyesters etc) , fillers used are carbon/graphite, carbon black, coke– graphite and fibers used are carbon/ graphite, cellulose, glass and cotton flock .

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In this work bipolar plates were fabricated from materials developed using thermosetting (vinyl ester resin) and thermoplastic (polypropylene). Development of materials, fabrication of plates and their properties are discussed.

2. Experimental

2.1. Chemicals / Materials

All the chemicals/materials including polypropylene, polyethylene, vinyl Ester Resin (Methacrylated epoxy difunctional), glass wool, cobalt Naphthanate (CoNap), Methyl Ethyl Ketone Peroxide (MEKP) obtained from standard source suppliers, were of commercials grade and used without further purifications. Graphite powder used in this process was of reactor – grade, having different particle sizes ranging from 45 µm to 180µm after grading by sieve analyzer method. Poly (1-4 phenylene sulphide) (PPS), analytical grade, was supplied by sigma – Aldrich Chemie GmbH, Germany. Conductive filler polyaniline (PANI) was used of analytical grade, supplied by sigma-Aldrich Chemie GmbH, Germany. P-Xylene pure (BDH, 99%) was used in the solution blending method.

2.2. Bulk moulding compound (BMC) with vinyl ester resin (thermosett composite)

To vinyl ester resin, cobalt naphthenate (Co-Nap) was added and mixed thoroughly. Methyl ethyl ketone peroxide (MEKP) was then poured into the resin with intimate blending for catalysis. Conducting polymers, polyaniline and poly (1, 4-phenylene sulphide) were then added and mixed it thoroughly and finally graphite powder was gradually added to the formulated resin and the mixture was shaken to form a stiff paste of friable consistency. The paste was introduced into the mold and pressed in a preheated (80^{o}C) hot press by applying a force of 60 N. On raising the temperature of mold to 100^{o}C , the conditions were maintained for 15 minutes. The hardened plate was then removed from the mold while hot and air –cooled for half an hour.

2.3. BMC material with polypropylene (thermoplastic composite)

a) Melt compounding: The components of composite, polypropylene and conductive fillers (i.e., Graphite, poly (1,4 phenylene sulfide, polyaniline) were mixed manually in a small bucket before being melt compounded in furnace at temperature of 250oC along with manual shaking. The mixing time was set 15 minutes.

b. Solution blending: The polymer (polypropylene) was dissolved in xylene at 140oC and the conductive polymers polyaniline, poly (1,4 phenylene sulfice) were added to the solution and mixed it manually, graphite powder is then gradually added to the solution. After thoroughly mixing the fillers with the xylene – polypropylene solution for 20 minutes, the solvent – polymer solution containing the dispersed fillers was cooled to room temperature and left until the solvent was evaporated.

2.4. Compression moulding

The composites, which are obtained by melt compounding and solution blending, were grinded to form a powder. The powder was introduced to the mould, preheated in hot pressing machine for few minutes and then hot pressed into the plate of 10X10 mm and 3 mm thickness at a temperature of 200 ^{o}C. 50 kN force was supplied by the press for 5 minutes. The mould die was then removed from the hot press and allowed to cool it at room temperature; the hardened plate was removed from the mould. Different experiments were carried out to study the particle size effect, the polymer graphite composition, effect of the conductive polymer compositions.

2.5. Density measurement

The density of material was measured by water immersion technique (Archimede's principle) . The sample was weighed in air and value was named as X and it was reweighed as Y after completely immersing in water at 25^{o}C. The density of the specimen was evaluated as X/ (X-Y) . Density of vinyl ester resin composite plates was in the range of 1.62- 1.7 g/cm^{3}.

2.6. Conductivity measurement by Four – Probe Method

Conductivity was calculated by Four – Probe Method in which contacts were placed at four points on a specimen i.e., current and potential probes were mounted on a special holder (Fig.1) . The constant current was allowed to pass through the sample by digital multi meter.

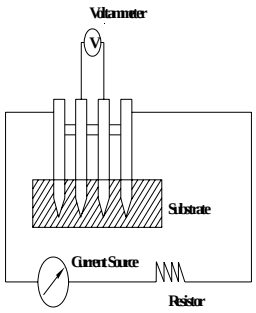

Figure 1. Four probe conductivity measurement set-up.

The potential drop was measured across the probes with a digital multi-meter at ambient conditions. The potential drop observed was the average value obtained for both directions of current flow. Conductivity was calculated by the application (8) of following equation:

$$EC = \frac{I * L}{V * W * T * K}$$

Where

EC = Electrical conductivity (S/ m)

I = Current (mA)

V = Voltage (mV)

L = Distance between two probes (mm)

W = Width of sample (mm)

T = Thickness of sample (mm)

K = 0.001

2.7. Thermal analysis:

Thermo analytical (TG) investigation of solid samples was carried out under atmospheric air using NETZSCH simultaneous thermal analyzer ST 409 with a temperature programmed furnace. The heating rate employed was 10^{o}C/min. All the experiments were performed in the temperature range of ambient to 1000^{o}C.

3. Results and Discussions

3.1. Thermosetting composites

3.1.1. Effect of contents of the conducting polymer

Different compositions were made by the varying contents of conducting polymers. It has been observed that as the contents of polyaniline increased the conductivity of the plate also increased and effect of poly(1-4 phenylene sulfide) was not significant. Table 1.

Table 1. Effect of conducting polymer.

Sample	Graphite (gm)	Resin (ml)	PPS gm	Polyaniline (gm)	Conductivity (S/ cm)
N-1	10.08	4.04	1.44	0.16	86.59
N-2	11.20	3.29	1.12	0.16	95.42
N-3	11.25	3.08	0.15	0.30	120.94

3.1.2. Influence of glass fiber

It is observed that as the percentage of glass fiber increased the conductivity of the plate increased(Table 2) as well as the mechanical strength increased. Increase in conductivity may be due to the better contact between graphite particles and presence of metals in the glass fibre. The glass fibers act as reinforcement fibers, addition of them dual purpose may be achieved i.e. increase in mechanical strength as well as in conductivity.

Table 2. Influence of glass wool addition.

Sample	Graphite (gm)	Resin (ml)	PPS (gm)	Glass Wool (gm)	Conductivity (S/ cm)
GF-2	10.2	3.5	0.75	0.30	101.79
GF-3	10.2	3.5	0.60	0.45	106.18
GF-4	10.2	3.5	0.45	0.60	124.31
GF-5	10.2	3.5	0.30	0.75	123.09

Table 3. Effect on conductivity of graphite content.

Sample	Graphite (gm)	Resin (ml)	Styrene (ml)	Conductivity (S/ cm)
GP-1	11.25	3.21	0.39	147.21
GP-3	10.5	3.86	0.47	126.57
GP-4	9.75	4.5	0.55	83.77

3.1.3. Effect of graphite content.

Graphite is conducting and increase in its content increases the conductivity (Table 3).

3.1.4. Addition of aluminium powder

Studies were done to see the effect of addition of aluminium. Initial studies show that addition of aluminium powder increases the conductivity of the composite (Table 4).

Table 4. Influence of Aluminium powder addition.Sample ID

Sample ID	Graphite (gm)	Resin (ml)	Al (gm)	Conductivity (S/ cm)
A1C-2	10.95	3.50	0.32	76.50
A1C-5	10.50	3.50	0.80	128.71
A1C-6	10.35	3.50	0.96	107.35
A1C-10	9.75	3.50	1.60	99.46

3.2. Thermoplastic composite.

3.2.1. Effect of solvent

Two methods have been adopted in forming the thermoplastic composites, namely melt compounding and solution blending to explore further mechanism of conduction in composites regardless the optimum formulation or conditions required to produce bipolar plates for fuel cells. Both methods have their own advantages and disadvantages: in melt compounding method the compositions can not be homogenized as in the solution blending method. Solution method produces very homogeneous material which is desirable for BMC.

3.2.2. Infuence of graphite

The values of the electrical conductivities of all the composites are tabulated in Table 1. The dependence of the electrical conductivity on the contents of graphite powder is shown in the Fig. 2. The graph trend shows that conductivity of the composite increases as the graphite contents increased.

3.2.3. Polypropylene/graphite/polyaniline composites

Composites containing a constant composition of polypropylene (20 wt %) and different compositions of graphite and polyaniline have been investigated and their conductivities are plotted in Fig. 3 as a function of polyaniline contents. Conductivity increases with the increase in polyaniline.

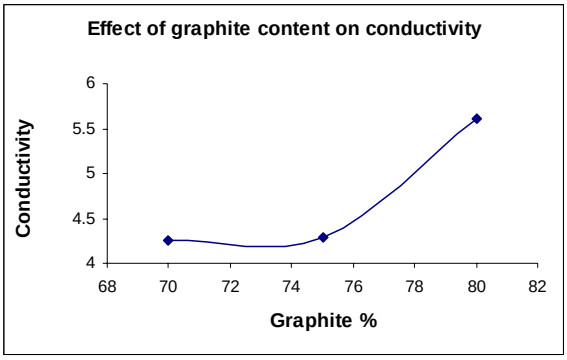

Figure 2. Effect of graphite on conductivity.

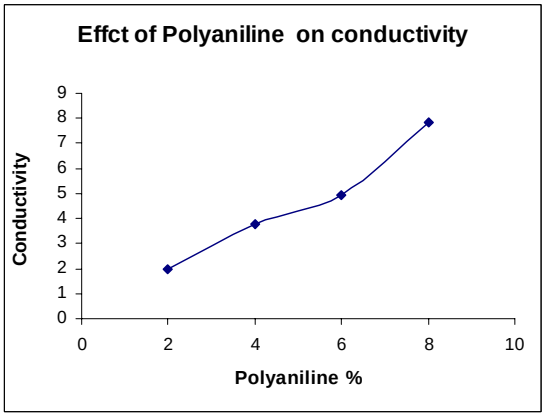

Figure 3. Influence of polyaniline.

3.2.4. Effect of particle size

Composites containing a constant composition of polypropylene (25%) and graphite (75%) but different particle sizes of graphite ranges from 45µm to 150 µm have been studied. The dependence of conductivities of PP/ G composites on particle size was plotted in Fig.4 as a function of particle size.

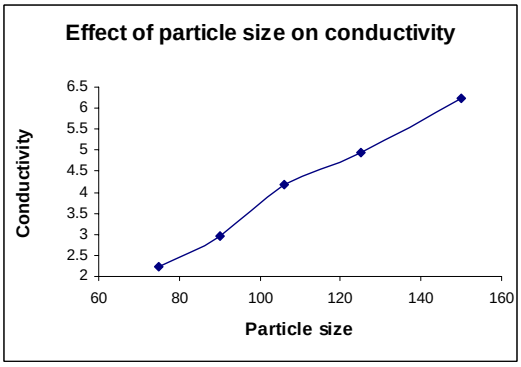

Figure 4. Effect of particle size on conductivity.

3.3. Preparation of mould

A mould was designed and fabricated for the preparation of bipolar plates. In this way a lot of time can be saved which is required for engraving channels on the plates for the flow of gases. Channels are of about 1-2 mm thickness and 1 mm of depth. It has inlets and outlets of hydrogen and air. It has also channel for flow of coolant through the plates. All these channel were engraved on the SS mould plates. When the plates were fabricated in the mould it produced plates with required channels. Plates produced were of 10 cm X 10 cm active area. Channels for air flow are given in Fig.5 and channels for hydrogen flow are given in Fig.6 Compression moulding technique can reduce the production costs many times and plates can also be produced quickly which will reduce the fuel cell costs significantly. After the success of compression moulding it can also be extended to injection moulding which will further reduce the production costs.

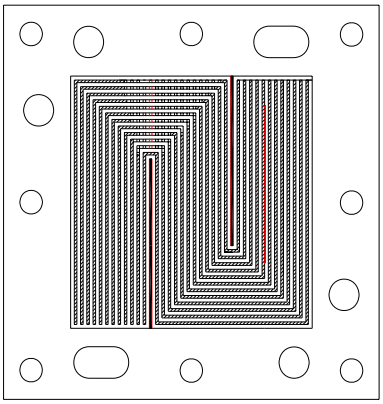

Figure 5. Channells for air flow.

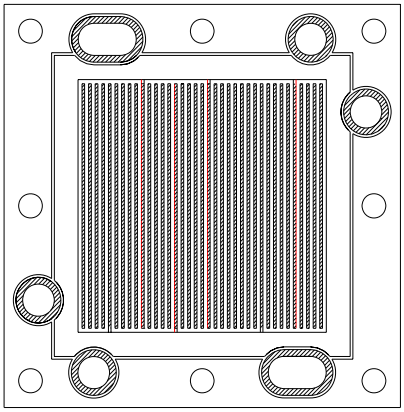

Figure 6. Channels for hydrogen flow.

3.4. Thermoanalytical analysis

Thermal analysis graphs of TG for thermosetting vinyl ester resin bipolar plate are given in Fig. 7.

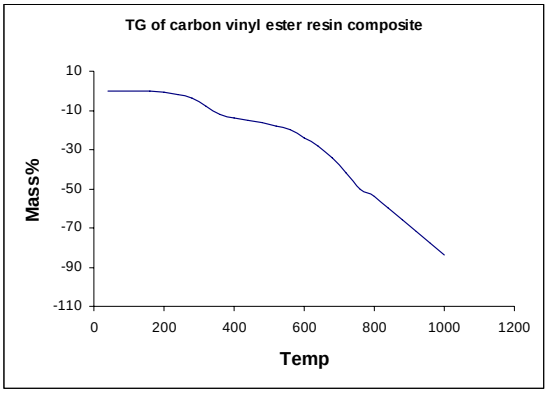

Figure 7. TG of thermosetting bipolar plate.

It can be seen that the plate is quite stable upto 200 ^{o}C. Which is much more than the operational temperature of the fuel cell i.e; 80-90 ^{o}C. Graphite is stable upto 700 ^{o}C . Partial degradation of polymer starts after about 200 ^{o}C.

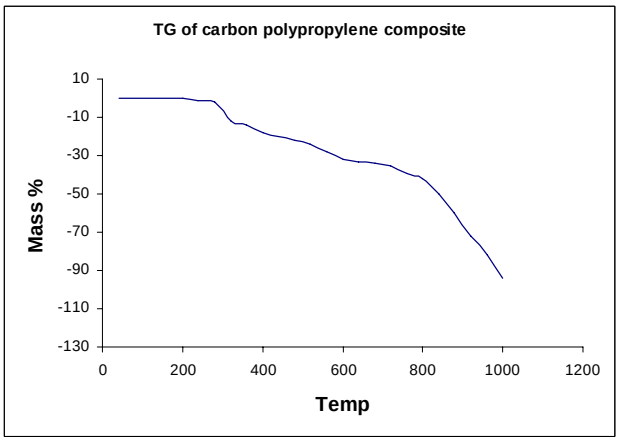

Figure 8. TG of thermoplastic composite.

TG graph of carbon polypropylene composite is shown in Fig.8 . Working range with this composite is higher than the thermosetting composite. This composite is stable upto more than 300 ^{o}C.

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