IMPROVEMENT OF POROUS GRAPHITE PLATE FOR PEM FUEL CELL BY ORGANO-IMPREGNANTS

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Porous graphite plates with improved properties for proton exchange membrane (PEM) fuel cells were fabricated from organo-impregnant materials such as styrene, epoxy resin and cyanoacrylate. The results revealed that porosity of porous graphite plate has been completely removed. However, the graphite plate impregnated with styrene was not thermally stable around the temperatures 80-100°C. The impregnated plates were also characterized to determine the properties such as density, mechanical properties, thermal stability and electrical conductivity. Study revealed that the graphite plates impregnated with cyanoacrylate was more suitable for PEM fuel cell applications.

Keywords: Fuel cell, PEM, Graphite plate, Impregnation, Styrene, Epoxy resin, Cyanoacrylate, Porosity

1. Introduction

Various types of fuel cells are being developed all over the world depending on the end users. Among these cells, PEM is the cheapest and easy to develop. Bipolar plates are a key component of PEM fuel cells with multifunctional character. They uniformly distribute fuel gas and air, conduct electrical current from cell to cell, remove heat from the active area, and prevent leakage of gases and coolant. They also significantly contribute to the volume, weight and cost of PEM fuel cell stacks [1-3]. Hence, great efforts are being made worldwide to find suitable materials for bipolar plates. The materials include non-porous graphite, coated metallic sheets, polymer composites etc. [4-6]. With respect to electrical and thermal conductivity, mechanical stability and machinability, metallic materials are preferred but weight and cost of the metallic bipolar plates is reasonably high [7-13]. Graphite materials are being preferred due to its corrosion resistance but due to weak mechanical properties and porosity they can not be used as such. However, composite materials of graphite with polymeric materials gave a reasonable solution at a little sacrifice of electrical conductivity [4, 14-24]. Naturally occurring graphite material possesses good attraction for bipolar plates of PEM fuel cells.

However, there is a need to improve the porosity and mechanical strength. Little efforts have been made to minimize the porosity and to improve mechanical properties of graphite powder by impregnation with different fillers and resins and subsequent compaction [25-27]. In the present investigation, work has been conducted to utilize the naturally occurring porous graphite by improving porosity and brittleness with organo-impregnant such as styrene, epoxy resin and cyanoacrylate. The porosity of the graphite and impregnated plates was measured with porosimeter and microstructure analysis. Thermal, mechanical and electrical properties were also measured to optimize the desired material for PEM fuel applications.

2. Experimental

2.1. Impregnation of graphite plates

An apparatus shown in Fig. 1 has been used to impregnate the graphite plates with styrene, a low viscosity resin (Palatal P5-801, BASF) and cyanoacrylate. To improve the contrast of impregnated material and graphite plate, dyes (green & red) were used during the impregnation process. The impregnate materials were mixed with the respective colored die, poured over the graphite plate and sucked through the graphite

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plate by vacuum pump. The carry over mixture was collected in the intermediate liquid receiver. After impregnation the plate was removed and heated in an oven at 100°C for 30 minutes to cure and stabilize the impregnated material. Then the top surface of the impregnated plate was cleaned (to avoid increase of contact resistance) to remove the deposited un-impregnated material.
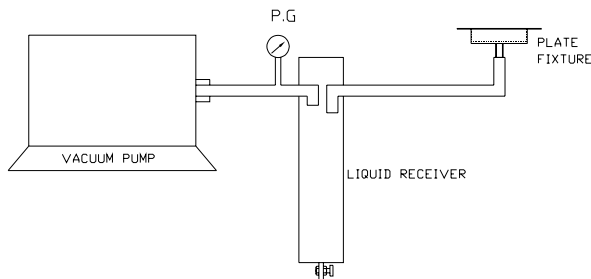

Figure 1. Assembly for graphite impregnation with liquid resins.

2.2. Measurement of porosity

The pore distribution, pore volume and pore size of raw graphite and impregnated plates were determined by using mercury intrusion porosimetry (Autopore 9220-II, Micromeritics, USA).

Metallographic technique was also employed to observe the existence of porosity under the optical microscope. For this purpose sample of each plate was initially ground and then polished down to 1 micron finished and micrographs were made under Nickon microscope.

2.3. Measurements of mechanical properties

The tensile test was performed on an Instron 8562 machine at ambient temperature in accordance with ASTM D638 standard. The flexural, bending and compressive strengths were conducted by using a universal testing machine (Instron 4468).

2.4. Thermal stability and analysis

Thermal stability of impregnated materials was investigated by heating the impregnated plates in the oven upto a temperature of 100°C. Thermogravimetry (TG) was carried out with NETZSCH simultaneous thermal analyzer (STA 429) in air atmosphere with heating rate of 10°C/min using alumina as reference material.

2.5. Measurement of electrical conductivity

Four probe method was used to measure the conductivity of raw graphite plate and the impregnated plates. The constant current was allowed to pass through the sample by constant current power supply Kyoritsu Model 1009. The potential drop was measured across the probes with a 195A digital multi-meter at ambient conditions where probe distance signifies the sample length. The potential drop observed was the average value obtained for both directions of current flow. Conductivity (δ) was calculated by the application of following equation [28]:

$$\delta = DI/VA$$

Where, "D" is the distance between voltage contacts, 'I' is current passing through current contacts, 'A' is the cross-sectional area of the specimen and 'V' is the voltage developed across voltage contacts.
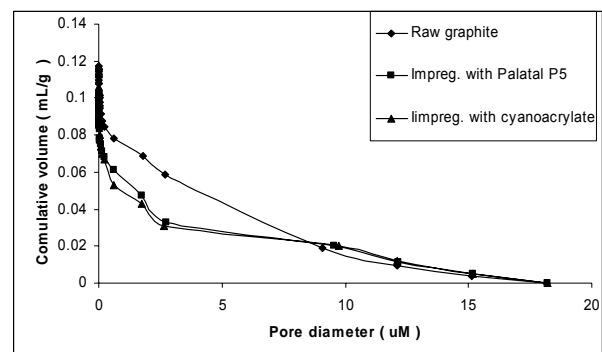

Figure. 2. Comparison of the porosity of raw and impregnated graphite samples.

3. Results and Discussion

3.1. Porosity measurement

It can be inferred from Fig. 2 that for the large pore diameters (9 μm to 18 μm) the number of pores are only 4 per sample. The intrusion of mercury into these pores is 0.02 ml/g and these pores are present only on the surface and not passing through the entire thickness of the sample. While considering the pore diameter ranging from 3 μm to 0.5 μm, the intrusion of mercury into raw graphite is more as compared to the impregnated graphite. Whereas the majority of the pores are of diameter less than 0.25 μm and in these pores the intrusion of mercury was 0.1 ml/g in case of impregnated graphite with Palatal P5 and this

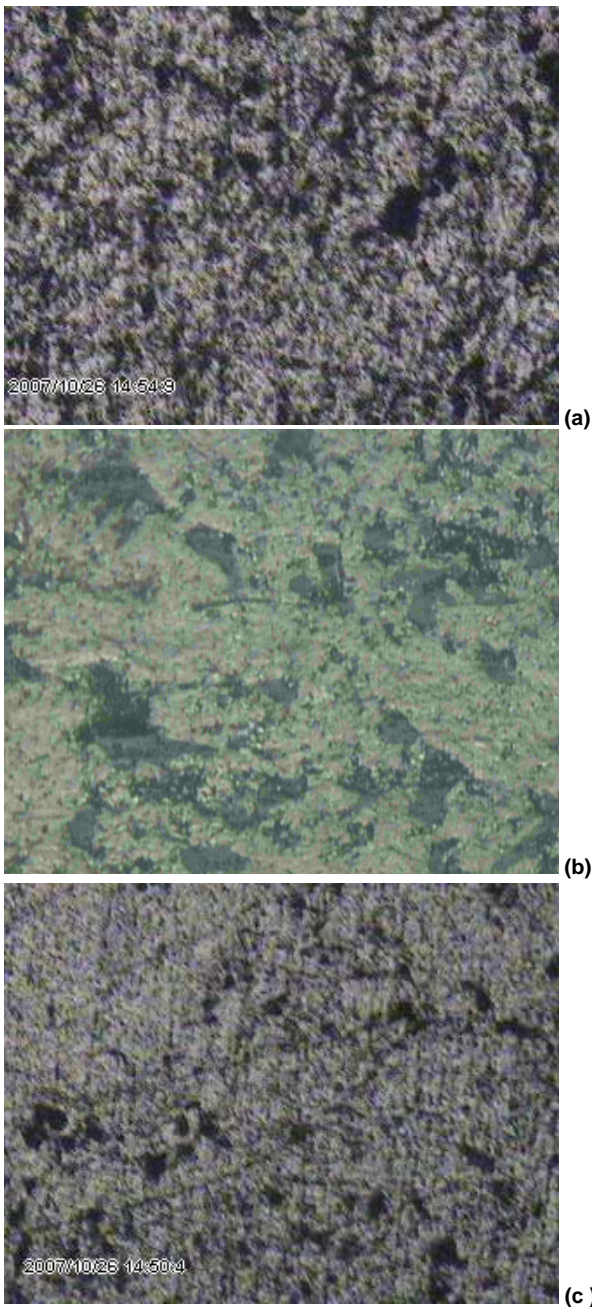M.N. Akhtar et al.

(a)

(b)

(c)

Figure 3a-c. Optical micrographs (a) Raw graphite (b) Impregnated graphite with palatal P5 (c) Graphite plate filled with cyanoacrylate.

value is 0.118 ml/g for the impregnated graphite with cyanoacrylate. From these results it can be concluded that majority of the pores are of very small diameter and also these are with closed/blocked end and may not pass through the long distance. Hence the impregnation was achieved only through the pores which extend from one side of the plate to the other side and these

pores were blocked by the Palatal P5 and cyanoacrylate. The density of the raw graphite was 1.887 g/cm^3 and the density of impregnated graphite plates with Palatal P5 and cyanoacrylate was found as 1.92 g/cm^3. It explains that 0.047 g/cm^3 of the impregnated material was intruded into the pores of the raw graphite to make it impermeable for nitrogen as well as hydrogen.

The existence of porosity was also confirmed in the samples by metallographic technique. The graphite plate when observed under the microscope revealed that the black area in Fig. 3a was not focused with the matrix, however, this area was focused by adjusting the microscope, which showed lot of porosity on the surface. To make the Palatal P5's and cyanoacrylate,s impregnation more prominent, green and red dyes are mixed in the resin, respectively. These dyes are visible in the pores (Fig. 3b&c) on both sides of the plate confirming the completion of impregnation process. In impregnated plates with Palatal P5 and cyanoacrylate (Fig. 3b&c) the black portion was fully focused with the matrix. This shows that the black area contains the impregnated material.

Table 1. Comparison of mechanical properties for raw graphite and impregnated graphite plates.

Material	Raw graphite	Impregnated with palatal P5	Impregnated with cyanoacrylate
Tensile strength (Kg / mm^2)	0.2035	0.2102	0.3569
Flexural strength (MPa)	7.58	7.59	12.85
Compressive strength (MPa)	23.97	25.39	29.66

3.2. Mechanical properties

The tensile, flexural and compressive strengths of the raw graphite and the impregnated graphite plates with Palatal resin and cyanoacrylate are given in Table 1. The tensile strength of raw graphite was 0.2035 (Kg / mm^2) and this was increased by impregnating the graphite with Palatal P5 and increased further by cyanoacrylate. These results showed that cyanoacrylate is the better material for increasing the tensile strength of the graphite by impregnation method. The flexural strength of the graphite plate (Table 1) is low enough (7.58 MPa) and it increases slightly by impregnating with Palatal P5 (7.59 MPa). The

major improvement in flexural strength comes after impregnating the raw graphite plate with cyanoacrylate (12.85 MPa). This is good enough to sustain the fuel cell assembling requirements. The compressive strength of the plate impregnated with cyanoacrylate was also high as compared to raw graphite and plate impregnated with Palatal P5 (Table 1). This increase in compression strength might have occurred due to the filling up of pores of the graphite with the impregnant. Bipolar plates must be strong enough to bear compressive load during assembly, so cyanoacrylate is quite suitable to improve compressive strength of porous graphite.
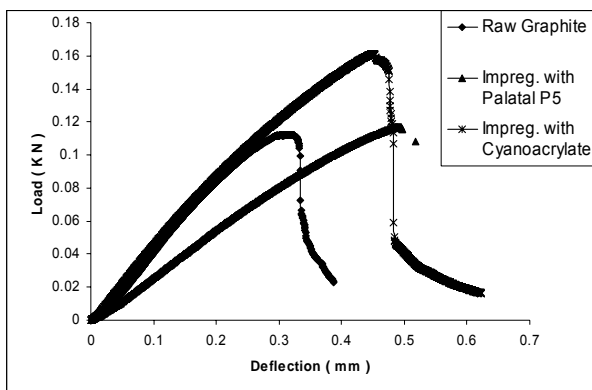

Figure 4. Comparison of the bending behavior of the impregnated samples with the raw graphite.

Bending behavior (Fig. 4) of the raw graphite plate is very poor because with the application of 1150 N bending force the deflection recorded was 0.35 mm. It was improved by impregnating with Palatal P5 which bears a deflection of 0.5 mm by the application of 1250 N. However, the graphite plate impregnated with cyanoacrylate presented the maximum bending strength (0.5 mm deflection for 1650 N force).

3.3. Thermal stability and decomposition

Styrene was partially solidified at 100°C and fully solidified with time (overnight). Thermal stability tests showed that when it was heated upto 100°C it became soft and converted into colorless gel. Hence this material is not suitable for this purpose because the PEM fuel cell normally operates at 60-80°C but the temperature may rise to 100°C or more. The impregnated material may come out of the pores of the graphite plate at high temperature due to gas pressure and plate may become permeable for hydrogen or oxygen. The

mixture of Palatal P5 and MEKP was solidified at once and crystal formation appeared after heating at 100°C. After cooling down to ambient temperature (30°C) it was again heated at 100°C. There was slight softening but remained stabilized in solid form. This result was encouraging for impregnation and stability at 100°C while using in the porous graphite plate materials for PEM fuel cell. Moreover, the cyanoacrylate was stable at 100°C even after sintering for 1 hour.
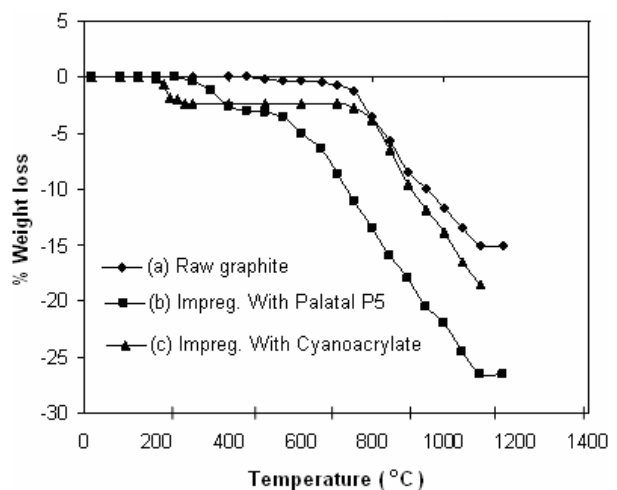

Figure 5a-c. TG curves (a) Raw graphite (b) Graphite impregnated with palatal P5 and (c) Graphite impregnated with cyanoacrylate.

Thermal curves (TG) of raw graphite and its composites are presented in Fig. 5a-c. The TG curve (Fig. 5a) for the graphite depicts weight loss (15%) in the temperature range of 660 to 1100°C, which might be due the evolution of CO_2 and shows thermal stability up to 660°C. The TG curve in Fig. 5b of the impregnated material (Palatal P5 + Graphite) exhibits two step weight loss. The first weight-loss (3%) in the temperature range (300-400°C) suggests a decomposition involving the evolution of organic material. The intermediate was not stable in this temperature range and when the temperature was raised, the material decomposed further. The second weight-loss (23.72) on TG curve was observed in the temperature range of (400-1100°C) which was due to the elimination of remaining organic matrix and carbon (in the form of CO_2) from the system. The material was stable upto 300°C. The impregnated material with cyanoacrylate also reveals two step weight losses (Fig. 5c). The first weight-loss (2%) in the temperature range of 200-260°C suggests a decomposition involving the evolution of organic

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matrix from the composite materials. The system was stable in the temperature range of 260-600°C. The second weight-loss (15%) in the temperature range of (680-1200°C) was due to the burning of carbon to carbon dioxide. The system was stable upto 200°C. While comparing the thermal stability of these systems on the basis of initial temperature of decomposition, raw graphite is stable upto 660°C, impregnated graphite with Palatal resin up to 300°C and impregnated graphite with cyanoacrylate upto 200°C. Since the operating temperature of PEM fuel Cell is about 60 to 80°C, both the systems (graphite impregnated with Palatal P5 and graphite impregnated with cyanoacrylate) are thermally stable over the required range of temperatures.

3.4. Electrical property

The electrical conductivity of the raw graphite calculated was 100 S/cm^2 and for impregnated graphite plates it was 95 S/cm^2 which is slightly less than the raw graphite but theoretically it should be unaltered because of the reason that graphite may be characterized as laminated structure of carbon, that is, consisting of superposed layers or laminates of carbon atoms joined together and during the impregnation process these layers and laminates of carbon remain intact and do not change while the impregnated material is introduced into the open pores which may not hinder the interconnects within the material structure. However, the value of electrical conductivity was within acceptable limits.

4. Conclusions

1. This impregnation of porous graphite plates is successful and useful for PEM fuel cells application.

2. Microstructural investigation reveals that the pores become closed on both sides of the plate in case of all the three impregnants.

3. The tensile, flexural and compressive strengths of the impregnated graphite plate with cyanoacrylate are higher as compared to the raw graphite and impregnated graphite plate with Palatal P5.

4. The raw graphite plates were successfully impregnated with styrene, Palatal P5 and cyanoacrylate. Among them the graphite plate impregnated with styrene was not suitable for PEM fuel cells due to its instability at 100°C.

5. The time of solidification of the cyanoacrylate is comparatively less than the Palatal P5 which can be managed for mass production scale.

6. Cyanoacrylate was found to be more suitable based on its physical and mechanical properties.

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