Effect of Different Graphite Materials on Electrical Conductivity and Flexural Strength of Bipolar Plates Fabricated by Selective Laser Sintering

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Abstract

Graphite is an excellent material for bipolar plates used in Proton Exchange Membrane (PEM) fuel cell due to its great chemical resistance, but the brittle nature makes it difficult to manufacture. Selective Laser Sintering (SLS) based on layer-by-layer manufacturing technology can fabricate graphite bipolar plates with complex gas flow channels. To improve the performance of bipolar plates including electrical conductivity and flexural strength, different graphite materials (natural graphite, synthetic graphite, carbon black, and carbon fiber) were investigated to fabricate test samples. These samples then went through post processing including carbonization and infiltration. The results show that bipolar plates with electrical conductivity of 380 S/cm and flexural strength of 40 MPa are obtained from proper combinations of natural graphite and carbon fiber, which are higher than the target values set by the Department of Energy.

1. Introduction

Bipolar plate, which accounts for 40-50% cost and 60-80% weight of the whole fuel cell stack [1], is an important part in Proton Exchange Membrane (PEM) fuel cell assembly. The main functions of bipolar plate include carrying current away from each cell, distributing gas fuels within the cell and providing support for Membrane Electrode Assembly (MEA). The Department of Energy proposed a technical target of bipolar plates for the year 2010 [2], in which the main requirements are electrical conductivity >100 S/cm and flexural strength >25 MPa.

Compared with metal, graphite is a great material for bipolar plates due to its excellent chemical resistance and low weight. However, the brittle nature makes it difficult to manufacture. Recently, more and more researchers focus on graphite/polymer composite bipolar plate [3-7], which is easier to fabricate and has better mechanical strength but lower electrical conductivity compared to bipolar plates machined from bulk graphite. Two main fabrication methods for graphite composite bipolar plates are injection molding and compression molding [4,5], which are suitable for mass production but less effective in the research and development stage, e.g. optimization of materials and design.

Selective Laser Sintering (SLS), based on layer-by-layer manufacturing, has been applied to build graphite composite bipolar plates for PEM fuel cell [8-10]. The major advantages are its ability to build complex flow channels on the bipolar plates and the flexibility to investigate different materials and different designs. In this process, the mixture of graphite materials and

binder is scanned by laser and molten binder bonds graphite particles together to form 3D parts. Then the porous and weak green parts go through the post processes, carbonization and infiltration, to become gas impermeable, and to increase electrical conductivity and mechanical strength.

One of the big issues of bipolar plates fabricated by SLS process is the relative low electrical conductivity [8]. In this paper, different graphite materials including Natural Graphite, Synthetic Graphite, Carbon Fiber and Carbon Black, were studied in order to obtain good electrical conductivity and mechanical strength, fulfilling the requirements for bipolar plates. All these materials and their mixtures were used to fabricate bipolar plate with SLS process. The properties were measured and compared with those fabricated by compression molding [11].

2. Materials and Processes

2.1 Materials

Natural graphite (3610), synthetic graphite (4437), carbon black (5303) and carbon fiber (AGM99) were obtained from Asbury Graphite Mills, Inc. (New Jersey, USA). The properties of these materials were shown in Table 1. Phenolic powder (GP-5546, Georgia Pacific) having typical size of 15μm was used as the binder. After carbonization, porous brown parts were infiltrated by liquid epoxy resin (EPON^{TM} Resin 828) used as the matrix.

Table 1 Properties of graphite materials

Properties	Natural Graphite (3610)	Synthetic Graphite (4437)	Carbon Black (5303)	Carbon Fiber (AGM99)
Size (μm)	75-150	10-45	0.03	Diameter 7.4 Length 150
Surface Area (m^2/g)	1.27	11.46	254	1.87
Typical Conductivity (S/cm)	27.78	17.24	2.93	-

*Provided by Asbury Graphite Mills, Inc., NJ, USA.

2.2 Fabrication Process

First, graphite powders and phenolic binder was ball milled for 12 hours. Then, an SLS machine (Sinterstation 2000) was used to build green parts. The parameters used for the SLS process were: fill laser power (12W), outline laser power (4W), laser scan speed (60in/s), layer thickness (0.004in), laser scan spacing (0.003in). The part bed and feed bins were maintained at 60^{o}C and 40^{o}C respectively. For carbonization, green parts were heated to 1000^{o}C in the furnace filled with Argon gas, to convert the binder into carbon residue and get brown parts. The heating schedule was from room temperature to 200^{o}C with a heating ramp rate of 60^{o}C/h, followed by a slower rate 30^{o}C/h to 600^{o}C, and then a 50^{o}C/h ramp rate to 1000^{o}C, holding for 1h. For infiltration, brown parts were immersed into the liquid epoxy resin, after 20min getting them out and putting into oven at 80^{o}C for 1h to cure the resin.

2.3 Experiments

In the experiments, Synthetic Graphite (SG), Carbon Black (CB) and Carbon Fiber (CF) were mixed with Natural Graphite (NG) respectively in different volume ratios, then mixed with 35vol% binder (in all experiments), which was based on the previous experimental result and can ensure that the green parts have enough mechanical strength to go through the processes that follow. These mixtures of graphite materials and binder were used to fabricate bipolar plates with the process mentioned above. Then the properties of the final parts were measured.

2.4 Characterization of Properties

Electrical conductivity was measured by the Four Point Probe technique, following the ASTM C611 specification and using Keithley 2400 SourceMeter. Five $20\times3\times3mm^3$ specimens were tested and the average value was calculated. Flexural strength (dimension of samples: $3\times10\times60mm^3$) was measured with the three-point bending method, using Instron Model 4468. Microstructure of the samples was obtained by Hitachi S-4700 FE-SEM. Flowability of graphite powder was observed during the SLS building process.

3. Results and Discussion

3.1 Change of Microstructures

During the whole fabrication process, the microstructure changed from green part to brown part and then to infiltrated part, as shown in Fig. 1. Figure 1(a) shows the microstructure of a green part, in which the binder bonded graphite particles together. After carbonization, the binder was removed and lots of pores were left in the brown part (Fig. 1(b)). Finally these pores were filled with resin after infiltration and only few tiny voids were left (Fig. 1(c)).

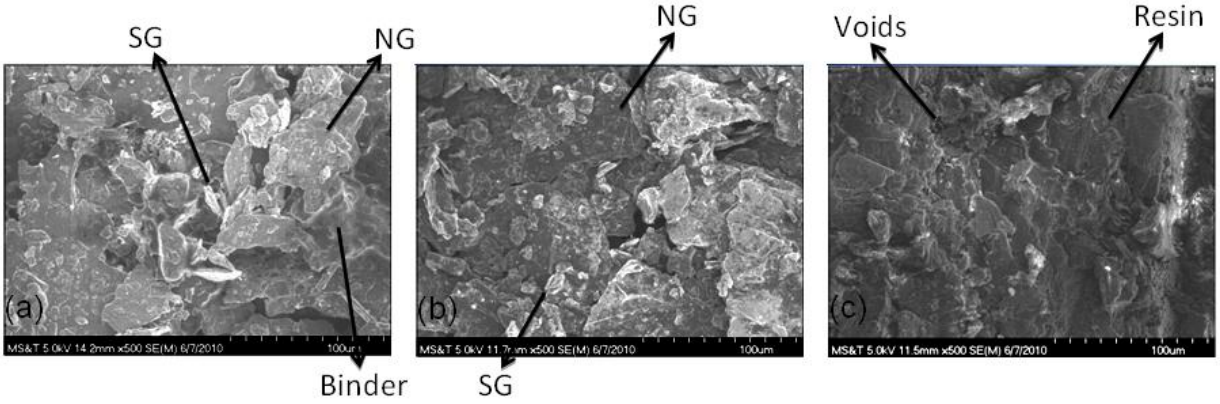

Fig. 1 Change of microstructures during the fabrication process: (a) green part; (b) brown part; (c) infiltrated part. The material composition is 15vol% SG, 50vol% NG and 35vol% binder.

After infiltration, the flexural strength of bipolar plates increased from 1.56MPa to 38MPa, as shown in Table 2. The material used here was 65vol% SG and 35vol% binder. Additionally, the result of electrical conductivity shows that infiltration with resin had no distinct negative effect on electrical conductivity. This is because the good connection between conductive filler (graphite particles) had been established in the green parts and brown parts (Fig. 1(a), (b)), which

was not broken by infiltration. This indicated that infiltration with liquid epoxy resin was a better way to increase the strength of fuel cell bipolar plate, meanwhile not impacting the electrical conductivity.

Table 2 Properties of bipolar plates before and after infiltration

	Electrical conductivity (S/cm)	Flexural strength (MPa)
Before infiltration	48.9	1.56
After infiltration	46.3	38.4

*The material used was 65vol% SG and 35vol% binder.

3.2 Effect of Synthetic Graphite

Figure 2 shows the microstructure of a brown part with SG and NG, in which the larger flaky particles are NG and the smaller sphere ones are SG. Electrical conductivity with various volume fractions of SG was shown in Fig. 3 (keeping binder at 35vol%, with the rest being NG). When only NG (65vol%) and binder (35vol%) was used, the electrical conductivity was 380S/cm. As the SG content increased, the conductivity decreased because the conductivity of NG particles is higher than that of SG. When SG particles were introduced into NG powder, these particles hindered the conduction of current among NG particles. The results show that several values of conductivity were higher than the target value of DOE (100S/cm).

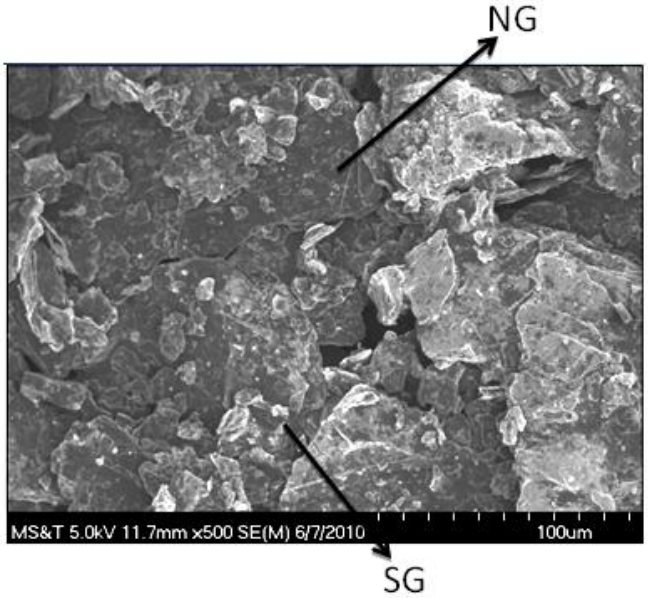

Fig. 2 Microstructure of brown part with 15vol% SG, 50vol% NG and 35vol% binder.

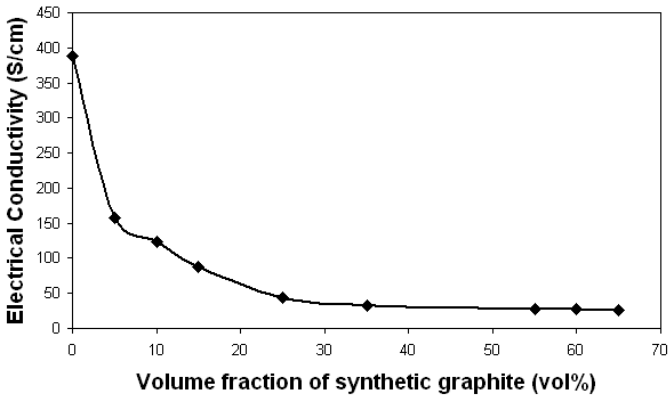

Fig. 3 Electrical conductivity varies with different SG fractions (keeping binder at 35vol%, with the rest being NG).

The effect of SG on flexural strength of bipolar plates was shown in Fig. 4. SG has slightly negative effect on the flexural strength. The strength decreased from about 37MPa to 33MPa when SG increased from 5vol% to 65vol%. Because the adding of smaller SG particles filled up the big voids among the larger flaky NG (as shown in Fig. 2), which reduced the porosity. Consequently a smaller amount of resin was absorbed after infiltration, thus less strength was established. But even so, all the results were still higher than the target value set by DOE (25MPa).

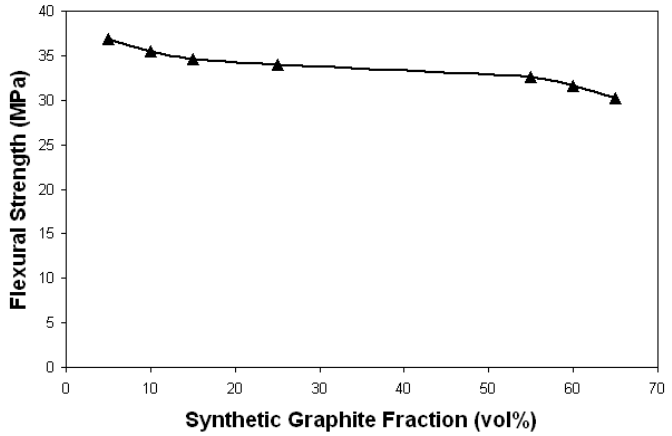

Fig. 4 Flexural strength varies with different SG fraction.

3.3 Effect of Carbon Fiber

Carbon fiber is widely used in composite materials to enhance mechanical strength. Figure 5 shows the microstructure of a brown part with CF and NG. It is shown that CF was uniformly mixed with NG particles.

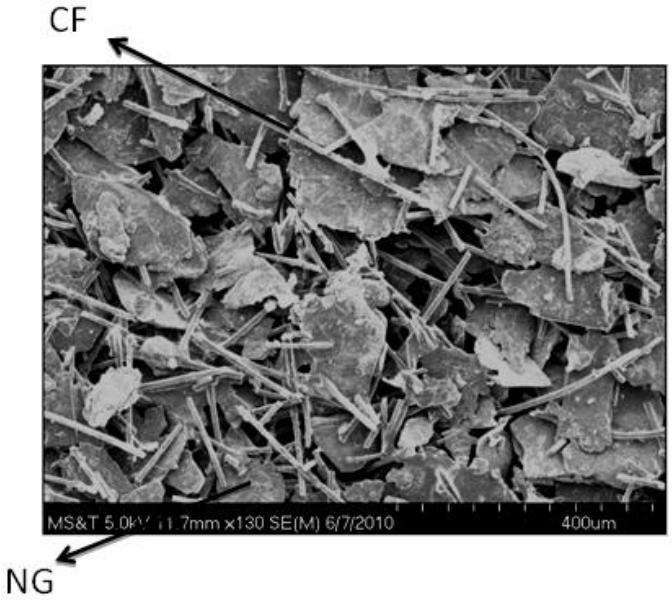

Fig. 5 Microstructure of a brown part with 25vol% CF, 40vol% NG and 35vol% binder.

Electrical conductivity with different volume fractions of CF was shown in Fig. 6. Electrical conductivity decreased as the fraction of CF increased. This is because the dispersion of CF among NG particles broke the contacts of NG particles and increased the electrical resistance.

Figure 7 shows that flexural strength varies with different CF fractions. Flexural strength increased greatly (35MPa to 40MPa) after introducing CF, and kept increasing with increase in the volume fraction of CF. When the content of CF was 25vol%, the flexural strength was almost 50MPa, which was 1.5 times of that without CF. It is obvious that the presence of CF can increase mechanical strength greatly.

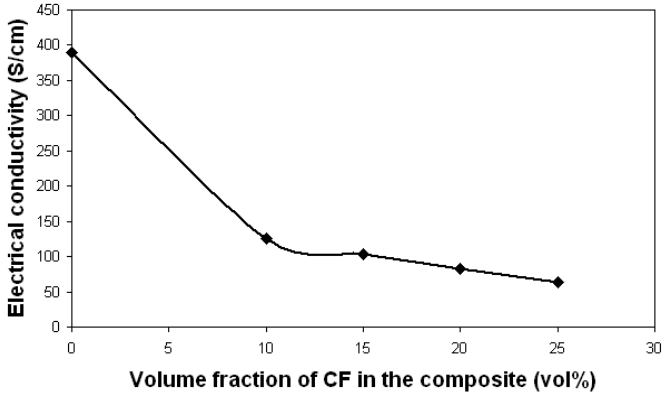

Fig. 6 Electrical conductivity varies with different carbon fiber fractions.

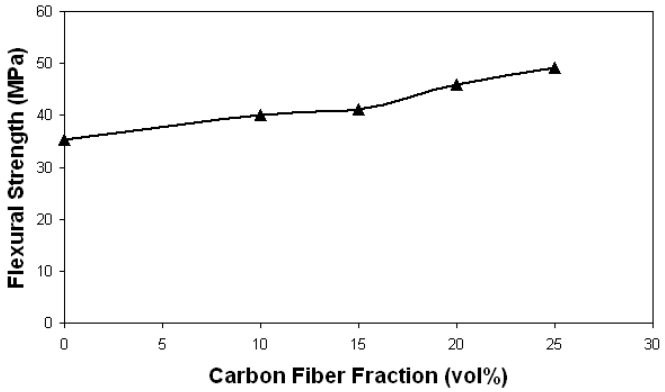

Fig. 7 Flexural strength varies with different carbon fiber fractions.

3.4 Effect of Carbon Black

It was reported that nano-size CB could be dispersed among NG particles to increase electrical conductivity for graphite composite bipolar plates made by compression molding [11]. Chen, et al. [10] also used epoxy resin containing carbon black to infiltrate bipolar plates made by the SLS process, to improve electrical conductivity. In this study, CB was directly mixed with NG to make bipolar plates with SLS. Figure 8 shows the microstructure of a brown part made from 16vol% CB, 49vol% NG and 35vol% binder. As shown in Fig. 8(b), the surface of NG particle was covered by these nano-size CB particles.

The variation of electrical conductivity with different volume fractions of CB was shown in Fig. 9. As the CB content increased, conductivity gradually decreased. After the fraction of CB reached 5vol%, electrical conductivity fell below 100S/cm. This is because CB has lower conductivity compared with NG. During the ball-milling process, CB particles with large surface area tended to agglomerate and cover on the whole surface of NG particles (as shown in Fig. 8), which hindered the contacts between NG particles. This is different from the case in compression molding [11], in which NG and CB were first mixed in liquid resin. CB was dispersed well and filled the small voids between NG particles rather than covered their surface, thus can enhance electrical conductivity.

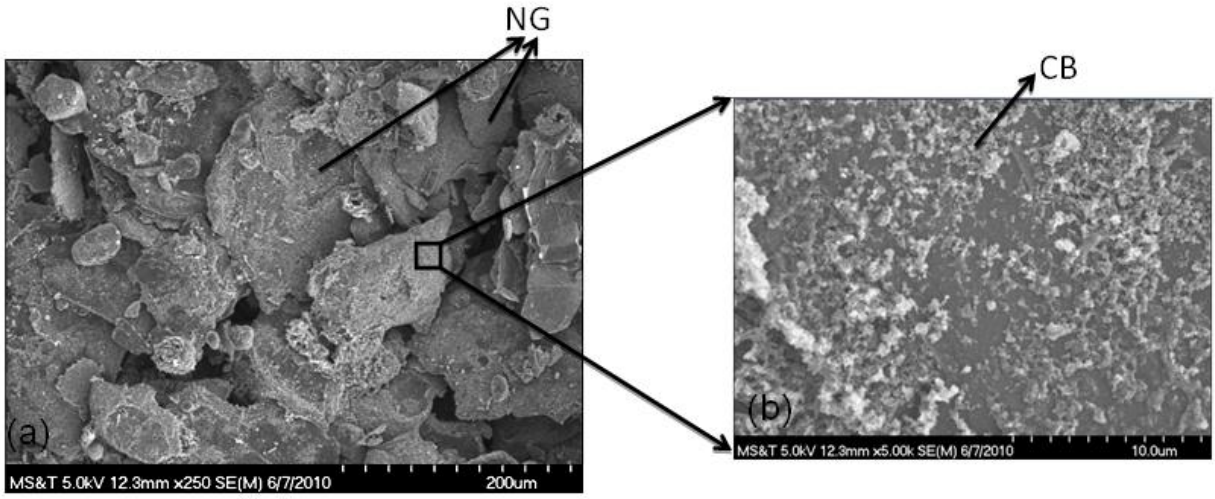

Fig. 8 (a) Microstructure of a brown part with NG and CB; (b) detail view of the surface of NG particle. (16vol% CB, 49vol% NG and 35vol% binder).

Figure 10 shows that flexural strength varies with different CB fraction. A similar result with SG was obtained in the case of adding CB into NG. The flexural strength slightly decreased with increase in the fraction of CB. A possible reason is that the coverage of CB on the surface of NG made it difficult for liquid resin (matrix) to fully wet the surface of NG particles (major filler), hence after the cure of resin the interface between the filler and matrix was impacted and the mechanical strength declined.

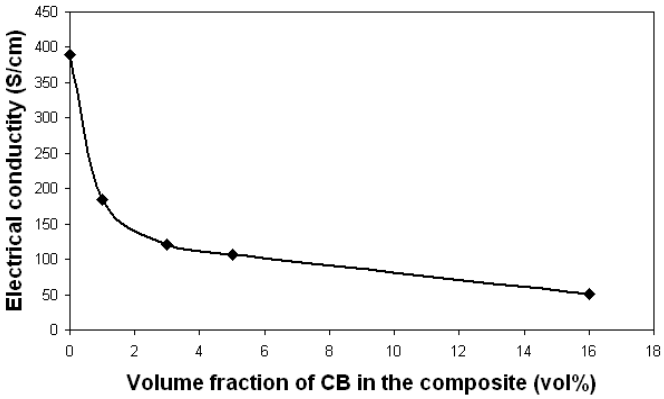

Fig. 9 Electrical conductivity varies with CB fractions.

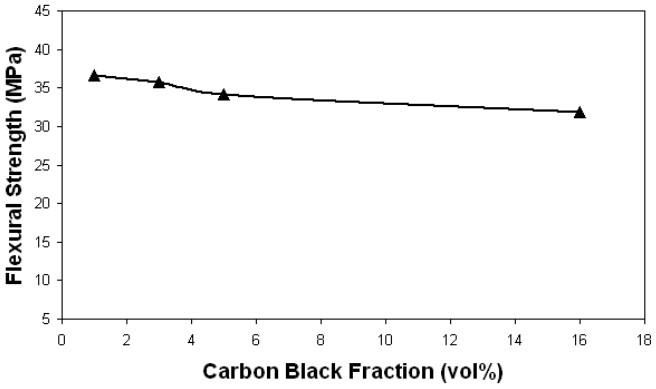

Fig. 10 Flexural strength varies with different CB fractions.

3.5 Flowability

As a powder based process, SLS requires powder to have good flowability in order to successfully build parts layer-by-layer. During the process after one layer is scanned, a new layer of powder is spread on the surface by a roller. Therefore, if the powder does not have a good flowability, the original position of the former layer will be moved by the new layer, due to the large friction between these layers.

Based on the experimental results, SG powder had better flowability than NG and CF powder, because the latter two have large size and irregular particle shape. For the mixture of NG and CB, the coverage of CB powder on NG surface increased the friction among the NG particles and also made it difficult to build parts with SLS. Hence in order to fabricate bipolar plates with complex and small channels, adding SG particles in the mixture was necessary in terms of improvement of flowability.

3.6 Comparison with Compression Molding

For electrical conductivity, the highest value of about 300S/cm was obtained from compression molding [11], and about 380 S/cm from the SLS process. The main reason is that for compression molding, graphite particles (conductive filler) were mixed with liquid resin (insulated matrix) at first. Thus the surface of graphite was covered by resin, reducing conductivity. However for the SLS process, only graphite powders were mixed together first and then green parts and brown parts were built in which all the particles contacted each other directly even after infiltration with liquid resin, so the conductivity was a little higher than that obtained from compression molding. For flexural strength, the value obtained from compression molding was around 45MPa [11] and from SLS was around 40MPa. So the SLS result was comparable to the compression molding result. This is because both of the strengths are mainly provided by solidified resin, which is hardly different with and without pressure.

Sample of bipolar plates fabricated using the process discussed above, was shown in Fig. 11. The material composition used was 45vol% NG, 10vol% CF, 10vol% SG and 35vol% binder. Electrical conductivity was about 120S/cm, and flexural strength was 40MPa. The feature dimensions are: active area $50\times50mm^2$, thickness 3mm, channel width 1.5mm and depth 1mm.

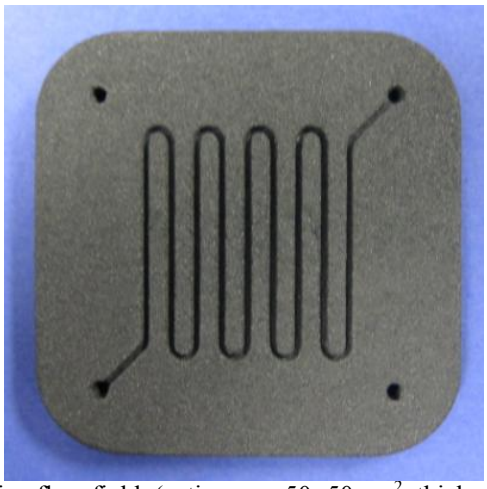

Fig. 11 Bipolar plate with a serpentine flow field. (active area 50×50mm^2, thickness 4mm, channel width 1.5mm and depth 1mm)

4. Conclusions

The SLS process was successfully applied to fabricate bipolar plates. Different graphite materials, NG, CF, SG and CB, were investigated in this process, and the corresponding electrical conductivity and mechanical strength were measured. NG was better for electrical conductivity and CF can greatly increase the flexural strength, but both of them were not good for flowability. Nano-size CB, covering the surface of NG particles, had negative effect on both conductivity and strength. Although adding SG decreased the conductivity and had slightly negative effect on strength, it was very good for flowability, which ensured the process had ability to build small and complex channels for bipolar plates. Finally, the material composition of 45vol% NG, 10vol% CF, 10vol% SG and 35vol% binder, was chosen to fabricate bipolar plates and the obtained properties satisfied the DOE requirements. The performance of the fabricated bipolar plates in a PEM fuel cell stack will be tested in the future.

Acknowledgement:

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