Fabrication and Testing of Graphite Bipolar Plates for Direct Methanol Fuel Cells

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Abstract

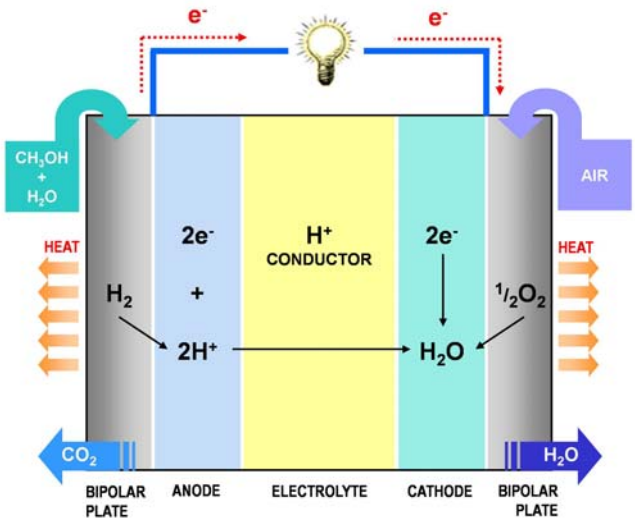
Bipolar plates made from graphite are highly desirable in fuel cell applications due to the properties of high electrical conductivity, low weight and resistance to corrosion that graphite possesses. However, the poor mechanical properties of natural graphite lead to prohibitive machining costs. Graphite parts are made by indirect SLS using graphite powder mixed with a phenolic resin binder which is subsequently burnt out. These parts fabricated using indirect SLS have poor green strength and electrical conductivity. The current work deals with the addition of carbon fiber to the graphite-phenolic mixture with an aim to improve green part strength and brown part conductivity. This research work also addresses fabrication of graphite bipolar plates for Direct Methanol Fuel Cells (DMFCs) with internal features and flow channels with different cross-sectional geometry that are difficult to produce using conventional machining processes.

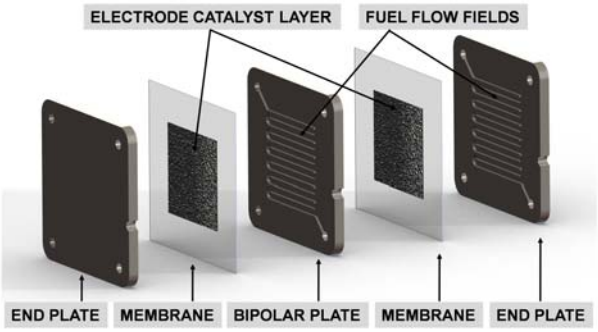
1. Introduction

Fuel cells are a clean energy technology with the benefits of high efficiency energy conversion and low power source emission. Most attractive is the high efficiencies achievable at temperatures under 100 ºC [1]. The basic operating principle of any fuel cell is the conversion of the chemical energy of the supplied fuel into electrical energy. Direct Methanol Fuel Cells (DMFCs) are a type of Polymer Electrolyte Fuel Cells (PEMFCs) that utilize methanol as a fuel. The energy density of methanol which is higher than that of Li – ion batteries coupled with the fact that methanol is a readily available liquid which is easy to store and transport, makes it an attractive option for fuel cell applications. However, DMFC technology is hampered by issues such as methanol crossover [2] from the anode to the cathode side of the fuel cell and unstable electrocatalysts [3].

In a DMFC the supplied fuel is a mixture of methanol and water which is oxidized into CO_2 and H^+ ions. The H^+ ions are transported across a polymer electrolyte membrane to the cathode side where they react with the supplied oxygen to form water. Figure 1 shows the schematic of a DMFC single cell, which comprises of membrane electrode assembly (MEA), sandwiched between bipolar plates that supply the fuel and provide structural support for the fuel cell stack. In a stack, bipolar plates serve the purposes of fuel distribution, current collection, separation of

the membrane electrode assemblies and bearing of the clamping force holding the fuel cell stack together. They are the most significant components of a fuel cell stack in terms of weight and cost of production [4]. Graphite has been the standard material of choice for bipolar plates due to its high electrical conductivity and low mass. However, machining fine features such as flow channels and fuel manifolds on graphite plates is expensive since graphite is brittle and has poor mechanical properties [5].





The performance of the fuel cell is dependent on factors such as the efficiency of the catalysis process, the electrical properties of the cell and the flow field design. Due to the difficulties in machining, testing of novel and complex flow field designs is an expensive, time consuming process. Indirect selective laser sintering (SLS) offers the benefit of producing graphite plates with features of significant complexity in a single step. Indirect SLS of graphite bipolar plates involves mixing graphite powder with a binder such as finely milled phenol formaldehyde (“phenolic”) powder and using a laser to scan individual layers of a .stl file into a solid 3-dimensional object. The ‘green’ SLS parts produced are porous and require post processing for the improvement of electrical properties and complete densification. The post processing steps include heating the green parts in a vacuum furnace to burn off the phenolic binder and infiltrating the porous ‘brown’ part with a suitable infiltrant to densify and strengthen the part.

Due to the presence of fine features in the flow field of the bipolar plate, there is a need for the green parts to be able to withstand the break out process without being damaged. The current work, investigates the suitability of carbon fiber as an additive to the graphite-phenolic mixture to improve green strength and overall conductivity. Three flow field designs are also evaluated for performance and verification of SLS as a process that can produce repeatable fuel cell results.

2. Experimental Process

2.1 Bipolar plate production by Indirect Selective Laser Sintering

The process of producing graphite bipolar plates by indirect SLS is shown in figure 2. It involves the production of a green part by the indirect SLS of a mixture of graphite (~ 70 microns, GS-150E, Graftech Inc) and phenolic (~ 11 microns, GP-5546, Georgia Pacific) powders in a 70 wt% to 30 wt% ratio, in a Sinterstation 2000 [6]. The porous green part is then heated in a vacuum furnace at temperatures greater than 1200 ºC to carbonize the phenolic binder, thus producing a 'brown' part. Phenolic is a "high ash" polymer, producing significant residual carbon after thermal dissociation. This carbon is effectively a high-temperature binder of the graphite powder. The parameters used for the SLS process are: fill laser power (10 W – 20 W), outline laser power (4 W), powder layer thickness (0.1016 mm), laser scan spacing (0.0762 mm), laser scan speed (1.524 m/s). Based on Differential Scanning Calorimetry (DSC) results of the phenolic powder, the part bed and feed bins were maintained at 65 ºC and 47 ºC, respectively, to ensure that the phenolic powder bed that was not laser sintered remained stable without being thermally affected. Post processing of this brown part includes infiltration with low viscosity cyanoacrylate glue [7] that seals the pores, thereby making the part fluid impermeable, and polishing of the surfaces to expose the underlying electrically conductive graphite matrix.

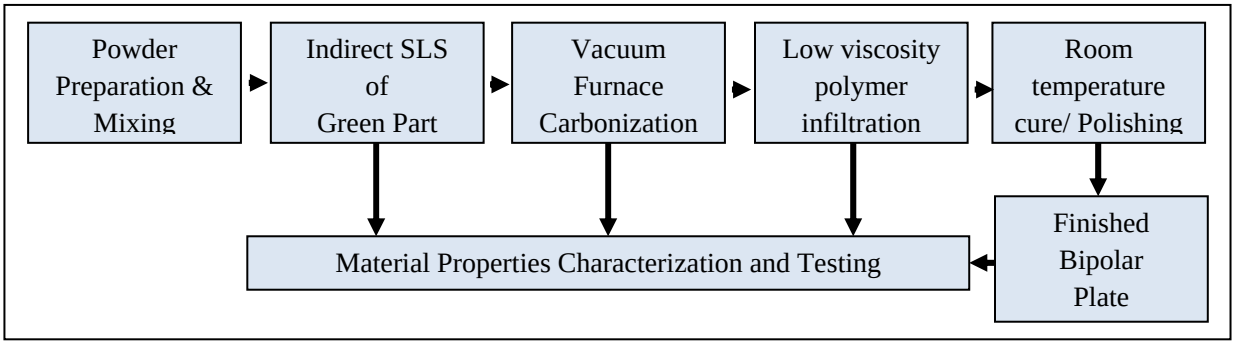


Figure 2. Flow chart of the experimental process of bipolar plate production by indirect SLS

2.2 Carbon fiber additive

Carbon fiber (length ~ 70 – 100 µm, diameter ~ 7 µm) was added to the graphite – phenolic resin mixture in three compositions, 10%, 20% and 40% by weight w.r.t the weight of graphite powder. The amount of phenolic binder was kept constant at 30% by weight. Three point bend specimens (127 mm x 13 mm x 3 mm) were built in an x-y orientation using the same SLS parameters as the regular graphite – phenolic mixture. The electrical conductivity of these specimens was first measured (ASTM C611) using a Cascade Microtech four point probe station in the green stage and the flexural strength of the specimens was then obtained using a three

point bend method (ASTM D790). Green parts were also burnt out in batches of three at temperatures varying from 400 ºC to 1200 ºC to produce brown parts whose electrical conductivity and flexural strengths were then measured.

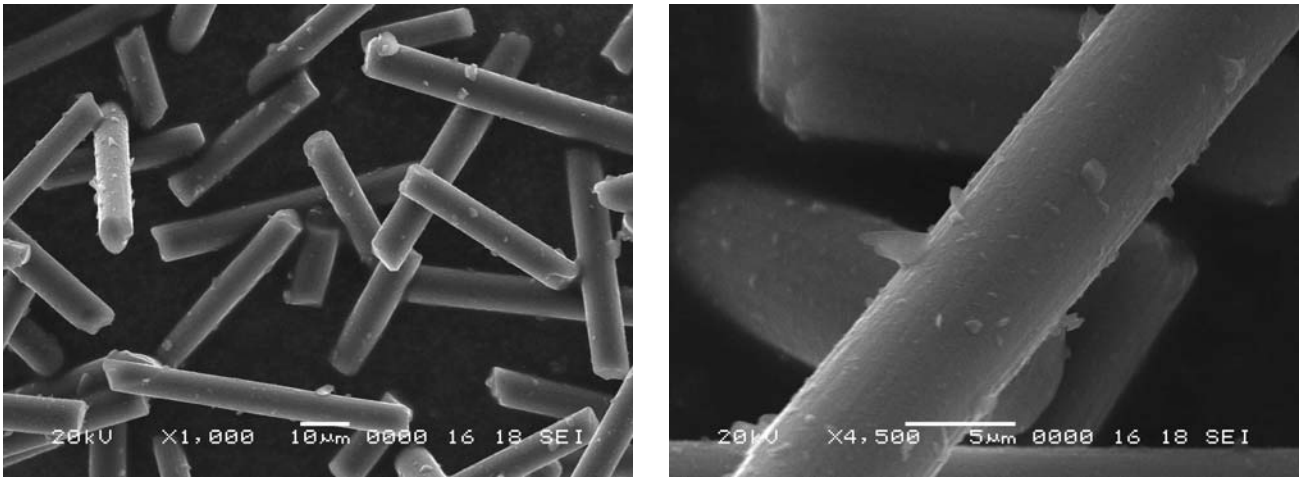


Figure 3. SEM images of the carbon fiber at a) 1000x and b) 4500x magnification.

2.3 Flow field designs for improved fuel cell performance

The design of the bipolar plate flow field has a significant impact on the various factors that affect the performance of the DMFC such as pressure drop across the cell, fuel absorption in the catalyst layers and transport of CO_2 and water out of the cell to name a few. Studies in flow field design [8, 9, 10] have shown that the cross-sectional geometry of the channel, aspect ratio of the channels (ratio of channel width to rib width) and the flow field pattern (serpentine, corrugated, interdigitated etc) all affect the performance of the fuel cell.

The electrochemical performances of the DMFC was evaluated with a single-cell fixture having active areas of 5 cm^2 and 10 $cm^2$and feeding a preheated methanol solution into the anode at a flow rate of 2.5 mL/min by a peristaltic pump without back pressurization and humidified oxygen into the cathode at a flow rate of 200 mL/min at ambient pressure [11]. Three basic shapes, elliptical, triangular and rectangular (figure 4) were chosen as the cross-sectional geometries of the flow field channel for comparative purposes. The flow field area was chosen to be 5 cm^2 and two sets of the geometries were made differing in the number of passes (10 and 15) of the flow field. One additional set of 10 cm^2 flow field area (10 passes) was made to verify the results on scaling up. These plates were post processed and tested in a Scribner Associates Inc. 850e fuel cell test station with the following commercially purchased MEA: Electrolyte Membrane: NaFion 117, Anode Catalyst: Pt/Ru/C, Cathode Catalyst: Pt/C, (4 mg/cm^2 loading). The performance of the plates made by SLS was compared to the performance of commercially purchased synthetic graphite plates with a rectangular cross-section and a serpentine flow field of 5 cm^2 making 15 passes.

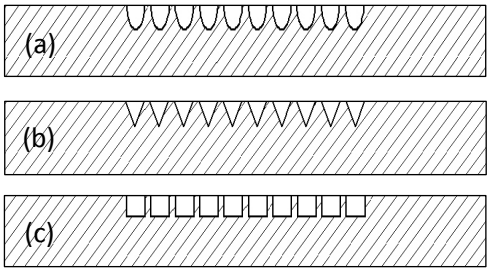


Figure 4 a) elliptical, b) triangular and c) rectangular flow fields with 10 passes.

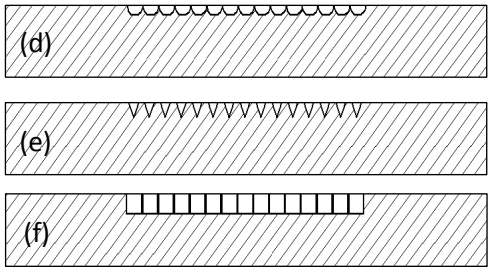


Figure 4 d) elliptical, e) triangular and f) rectangular flow fields with 15 passes.

3. Results and Discussion

3.1 Flexural strength of carbon fiber added parts

As seen from figure 5a, the flexural strength of the green parts increased with an increase in the percentage of carbon fiber added. An improvement in the strength of the green parts was not apparent with a 10% addition of carbon fiber. The difference in flexural strength values is small enough to be within the margin of error of the test process. Adding 20% to 40% of carbon fiber shows a significant increase (50% and 100% respectively) in the flexural strength of the green parts.

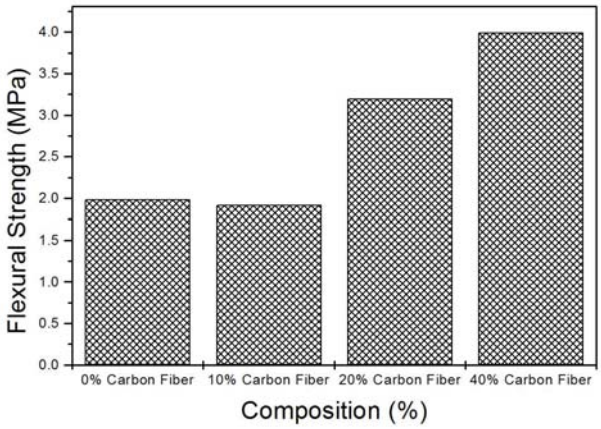


Figure 5 a) Flexural strength of green parts w.r.t addition of carbon fiber.

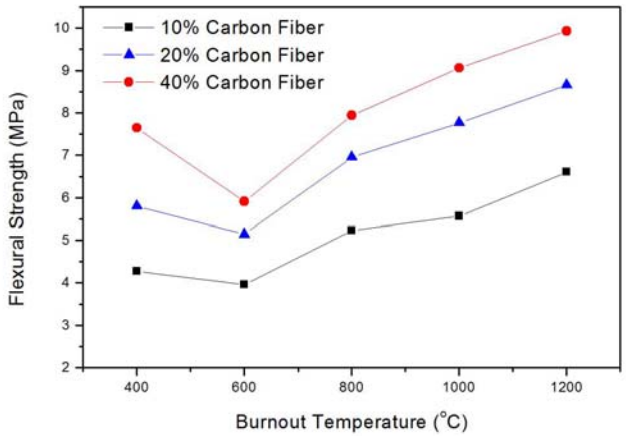


Figure 5 b) Flexural strength of brown parts w.r.t burnout temperature.

The flexural strength of the brown parts was found to dependent on the burnout temperature (figure 5 b). As in the green parts, the strength of the brown parts was found to increase with an increase in the amount of carbon fiber added. The flexural strength of the parts burnt out at 600 ºC was found to consistently lower than those sintered at 400 ºC. This could be due to incomplete dissociation of the phenolic binder. From 600 ºC to 1200 ºC, the increase in flexural strength is seen to be almost linear. There is almost a 90% increase in the strength of the brown

parts with 40% carbon fiber (9.933 MPa) burnt out at 1200 ºC compared to the brown parts without any carbon fiber (~ 5.27 MPa) burnt out at the same temperature.

3.2 Electrical conductivity of carbon fiber added parts

The electrical conductivity of the brown parts were found to increase with sintering temperature for the samples with 10% and 20% carbon fiber added (figure 6). For the samples with 40% carbon fiber, the conductivity increased as expected until 800 ºC and then decreased at temperatures above 1000 ºC. In general, compared to samples without the any carbon fiber, the electrical conductivity of carbon fiber added graphite parts is lower. This may be due to a lack of interconnectivity in the longitudinal fiber axis due to the small size of the fibers and also the percolation threshold. It has been shown that the electrical conductivity of carbon fiber filled composites is strongly dependent on the orientation of the fibers as well the percolation threshold [13, 14].

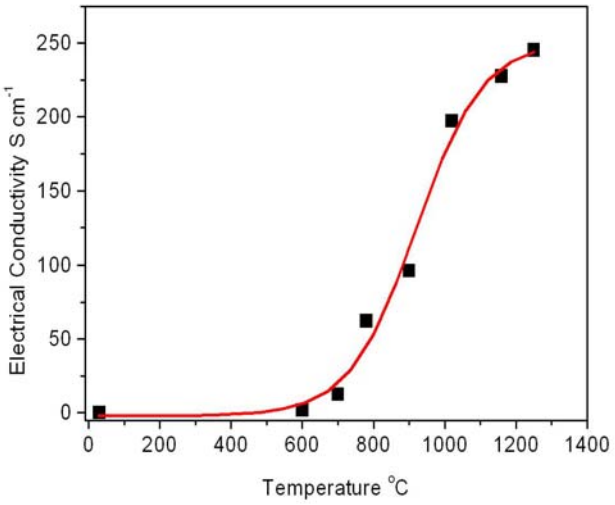


Figure 6 a) Electrical conductivity of graphite-phenolic parts w.r.t burnout temperature.

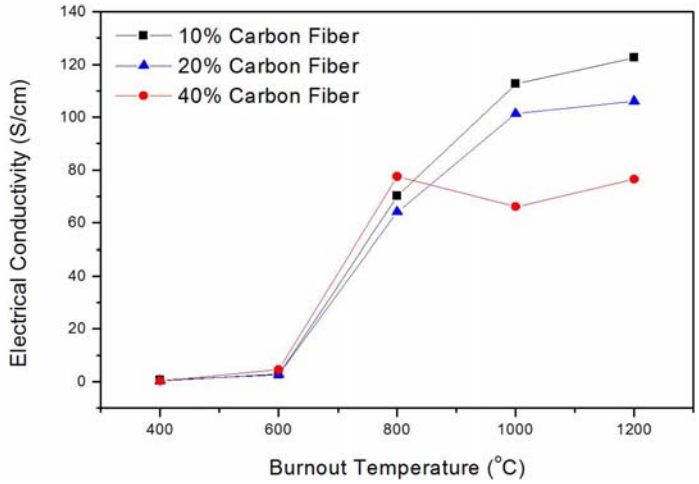


Figure 6 b) Electrical conductivity of carbon fiber added parts w.r.t burnout temperature.

3.3 Fuel cell performance tests

The performance of the 10 pass single serpentine plates with flow field areas of 5 cm^2 and 10 cm^2 was seen in general to be comparable to that of the commercially procured 15 pass single serpentine 5 cm^2 plates (figure 7a, 7b and 7c). Due to the superior electrical properties of synthetic graphite, the commercial plates showed better performance in the ohmic region of the polarization curve. The 5 cm^2 SLS plates with triangular and elliptical cross-sections, performed comparable to the commercial plates while the plates with a rectangular cross-section showed the poorest performance in both the ohmic and mass transport regions (figure 7a). This performance

was also seen with the 10 cm^2 plates, where the triangular and elliptical cross-sections outperformed the plates with the rectangular cross-section (figure 7b).

The performance of the SLS plates with 15 passes (figure 7c) was comparable to the commercial plates in the case of the rectangular cross-section. The rectangular cross-section plates showed similar performance against the triangular and elliptical cross-section as in the case of the plates with 10 passes. The plates with triangular and elliptical cross-sections outperformed the commercial plates in the mass transport region (higher current densities) while performing almost the same in the ohmic region. This suggests that the elliptical and triangular cross-sections enable the methanol to reach catalyst sites more readily than the rectangular cross-sectioned SLS and commercial plates.

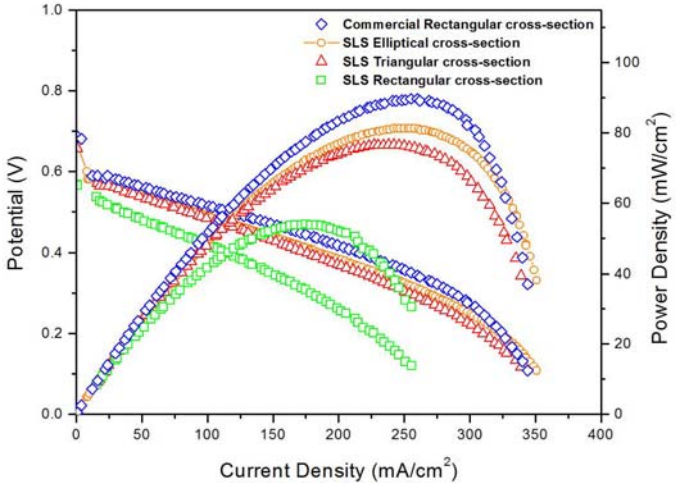


Figure 7 a) DMFC polarization curves of 5 cm^2 flow field area bipolar plates (10 passes)

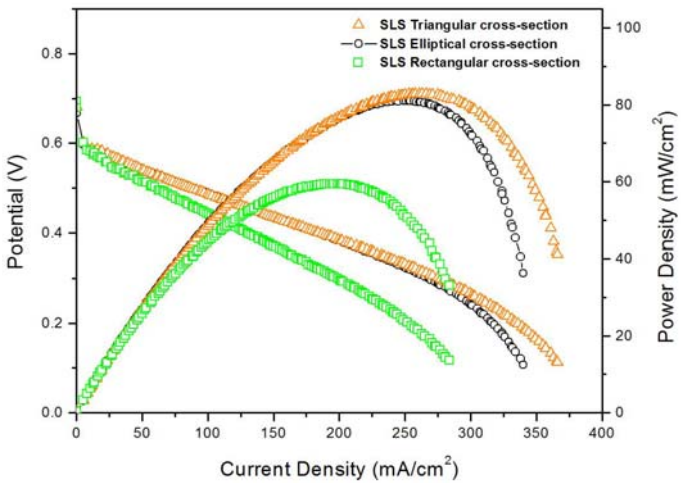


Figure 7 b) DMFC polarization curves of 10 cm^2 flow field area bipolar plates (10 passes)

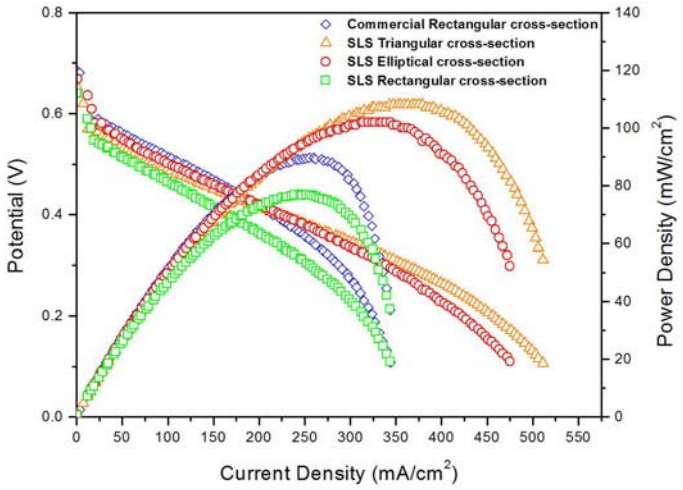


Figure 7 c) DMFC polarization curves of 5 cm^2 flow field area bipolar plates (15 passes)

4. Conclusions

Bipolar plates produced by indirect SLS were shown to perform comparable to and in some cases better than commercially produced synthetic graphite plates. It was found that flow fields with triangular and elliptical cross-sections showed better mass transport performance than flow fields with rectangular cross-sections. Carbon fiber was used as an additive in the SLS process and found to improve both the green part and brown part strengths. A 100% improvement in green part strength was obtained, while a part with 40% carbon fiber, sintered at 1200 ºC, was found to have almost 90% more flexural strength than parts made without carbon fiber. However, it was observed that adding carbon fiber reduces the electrical conductivities of the brown parts compared to parts made with just graphite and phenolic. This poses a tradeoff, in terms of optimum green part strength and brown part conductivity, which needs to be evaluated depending on the bipolar plate design.

Acknowledgement

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