

Fabrication of Electrically Conductive, Fluid Impermeable Direct Methanol Fuel Cell (DMFC) Graphite Bipolar Plates by Indirect Selective Laser Sintering (SLS)

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Abstract:

Graphite bipolar plates are highly desirable due to their properties of high electrical conductivity and low weight but are associated with prohibitive machining costs arising from poor mechanical properties. Bipolar plates made by indirect Selective Laser Sintering (SLS) offer the advantages of complex part production in shorter times at lower cost. Due to the nature of the SLS process, the as-produced (green part) plates are porous and possess low electrical conductivity which can be improved by carbonizing the phenolic resin binder at high temperatures (brown part). It has been found that the electrical conductivity increases significantly (> 200 S/cm) with a corresponding increase in pyrolyzing temperature which correlates well with literature on the carbonization of phenol formaldehyde resins. The brown parts are subsequently infiltrated with low viscosity ($\sim 5 - 10$ cps) cyanoacrylate to seal up the open pores, rendering the plates fluid impermeable.

1. Introduction:

A Direct Methanol Fuel Cell (DMFC) functions by supplying methanol directly to the anode of the fuel cell where it is oxidized to CO_2 (Figure 1). The H^+ ions are transported across a polymer electrolyte membrane to the cathode where they react with oxygen to form water. A typical DMFC stack is comprised of repeating units of a membrane electrode assembly (catalyst coated electrodes on either side of a polymer electrolyte membrane), diffusion layers, sandwiched between bipolar plates that supply and distribute the fuel, methanol at the anode and oxygen at the cathode.

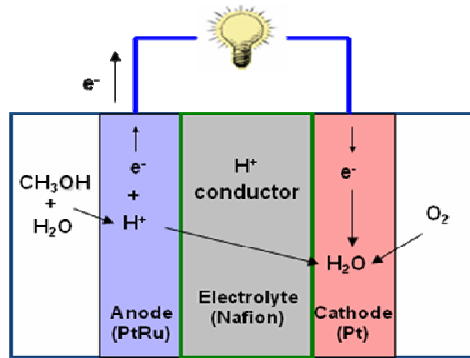


Fig 1. Schematic of DMFC working principle.

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 [1]. 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 [2]. Selective laser sintering (SLS) offers the benefit of producing plates with features of significant complexity at lower cost than machining. Indirect SLS of graphite bipolar plates involves mixing graphite powder with finely milled phenol formaldehyde powder and using a laser to scan individual layers of a .stl file into a solid 3-dimensional object. Due to the nature of the indirect SLS process, which involves the melting of the phenolic binder by the laser to hold the graphite powder together, the ‘green’ SLS parts produced are porous and require post processing for complete densification. Here, we have demonstrated a cost-effective method of producing bipolar plates by indirect SLS and subsequently carbonizing phenolic resin at > 1000 °C to obtain electrically conducting porous bipolar plates which are made liquid impermeable by cyanoacrylate infiltration.

2. Bipolar plate production

The process of producing bipolar plates by indirect SLS as shown in Figure 2, 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 [3]. The porous green part is then heated in a vacuum furnace to carbonize the phenolic binder, thus producing a ‘brown’ part. Post processing of this brown part includes infiltration with low viscosity cyanoacrylate glue that seals the pores, thereby making the part fluid impermeable, and polishing of the surfaces to expose the underlying electrically conductive graphite matrix. 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 °C and 47 °C respectively, to ensure that the phenolic powder remained stable without being thermally affected.

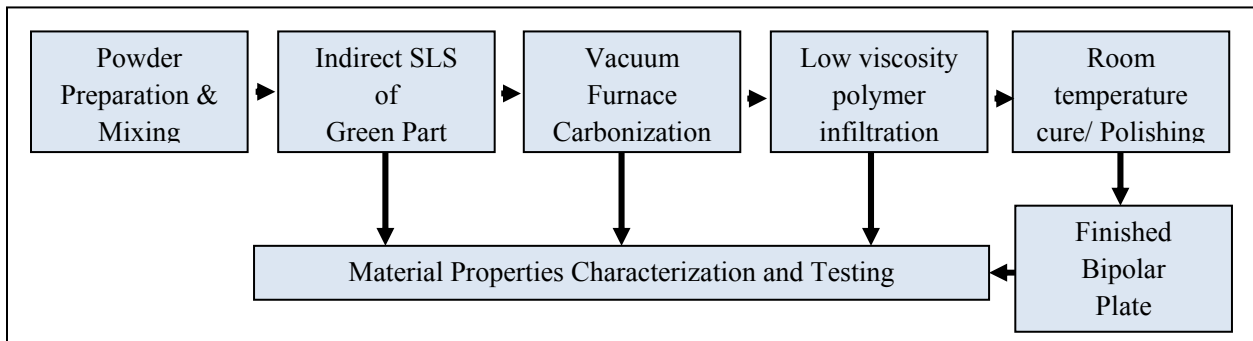


Fig 2. Flow chart of the experimental process of bipolar plate production by SLS

Post processing of the as-produced green parts was aimed at achieving the objectives of high fluid impermeability and electrical conductivity. Initial experiments were aimed at achieving both objectives in one step, viz. infiltrating the pores with a conducting material by electrochemical deposition and vacuum infiltration methods. Cubes of 15 mm side were produced for porosity measurements. The apparent and actual volumes of these porous structures were obtained by manual measurements and the use of a pycnometer, respectively. Conductivity

specimens of size 40mm by 5mm by 5mm were also made in the same builds and tested using a four probe conductivity setup according to ASTM C611 specifications.

3. Results and Discussion

3.1 Deposition and Infiltration of electrically conducting polymer:

Conducting polymers such as polypyrrole, polyaniline and polythiophene have been reported to show high values of conductivity [4, 5, 6] as well as chemical/thermal stability [7] in the operating conditions of a DMFC. The objective of the experiments was to synthesize the polymers *in situ* by:

- a) Chemical Synthesis: Conductivity and porosity specimens were soaked in a bath of aniline monomer in 1M dopant acidic solution (for conductivity) overnight so as to achieve complete infiltration. While maintaining the bath at 0 °C, an oxidizing agent such as ammonium persulfate was then slowly added to the bath to initiate polymerization. Upon oxidation, polyaniline separates from the solution and was found to coat the specimens in the solution. The samples were then removed from the solution, dried and then tested for both porosity and conductivity. It was the aim of the experiment to polymerize the monomer present within the porous matrix thereby tackling both issues of conductivity and porosity in one step. Results showed a slight improvement in the conductivity and a similar reduction of porosity in the samples. However, these results did not correspond to minimum standard expectations.
- b) Electrochemical polymerization: In this technique, the porous graphite specimen is used as the anode in a solution containing the required monomer, suitable solvent (electrolyte) and a doping salt, with a platinum counter electrode. Upon passing a current, electrochemical deposition of polyaniline layers occurs on the porous graphite anode. By initially soaking the graphite plate in the monomer solution, it was hoped to initiate polymerization of the conductive polymer (polyaniline, polythiophene) within the pores. SEM results (Figures 3a and 3b) show considerable deposition of the polymers on the exterior surface. However polymerization in the interior seems limited as a result of surface deposition which prevents access of fresh monomer to the internal pores.

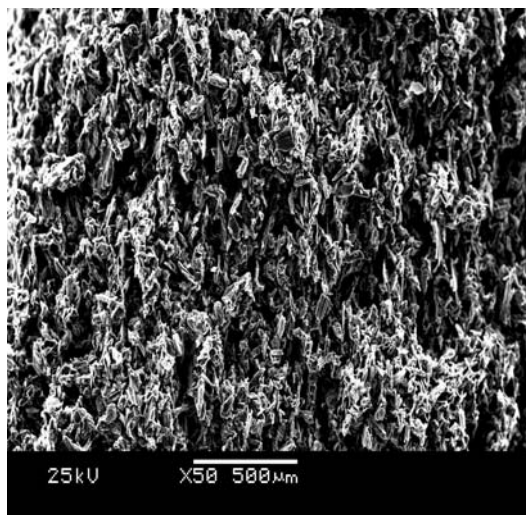
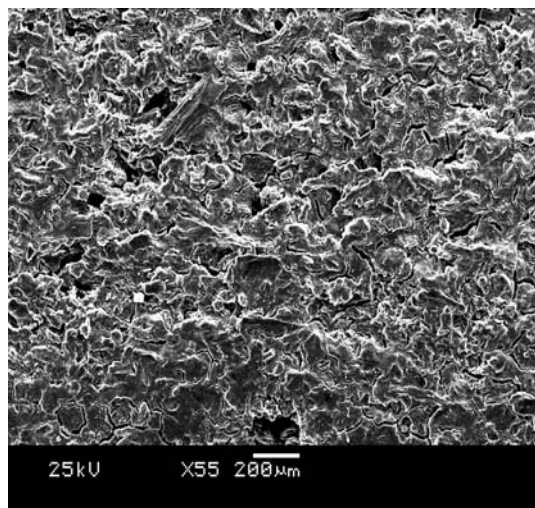


Fig 3a. Electropolymerized Polyaniline on exterior surface Fig 3b. Lack of interior deposition of Polyaniline

3.2 Electroless deposition of metals

Nickel metal was deposited onto the plate with the aim of infiltration of metal into the porous structure thereby increasing the conductivity of the plate. The electroless reduction was performed by placing activated SLSed graphite bars into a bath composed of nickel sulfate (source), sodium citrate (complexing agent), ammonium sulfate (buffering agent) and sodium hypophosphite (reducing agent) [8]. EDS results showed the presence of nickel on the exterior surfaces of the bars but negligible amounts in the interior, contrary to expected results. Furthermore, infiltration of metals into the graphite matrix was found to be infeasible, as the metals that would be stable in the environment of the DMFC, according to Pourbaix diagrams, are noble metals such as Gold, Platinum, Palladium, etc., that would be economically infeasible to use [9].

3.3 Infiltration using cyanoacrylate

Cyanoacrylate (ethyl-2-cyanoacrylate) was selected due to its availability in low viscosities (~ 5 cps) so as to achieve complete infiltration of the preforms. It possesses a large operating temperature range (-54 °C to 121 °C) and is stable in methanol. Its setting time is extremely rapid (on the order of minutes) and is enhanced by the presence of moisture. Due to its electrically insulating nature, an additional step for grinding off surface deposition is necessary to restore the electrical properties of the graphite matrix. It can be seen from pycnometric results (Table 1) that the graphite parts made by SLS are > 50% porous. Natural graphite has a theoretical density of 2.26 g/cm³. Upon infiltrating the porous brown part with low viscosity ethyl cyanoacrylate, the pycnometer measured volume (3.5709 cm³) of the part was about 95% of the apparent volume (3.6985 cm³) which shows that complete densification of the part is possible.

The cyanoacrylate was infiltrated into the porous specimen by a setup that applied a vacuum on one side of the bipolar plate while the infiltrant was manually dripped onto the other side. SEM images (Figures 4a and 4b) show charging of the regions containing the infiltrated cyanoacrylate indicating complete penetration into the interior pore structure and the bipolar plate before and after cyanoacrylate infiltration (Figures 4c and 4d). The white discoloration on the plate (Figure 4d) after infiltration is due to the setting of the polymer and is easily removed by polishing the surface. Impermeability to fluids was tested by applying the above infiltration method to liquids such as water and methanol and observing that no seepage from the top of the plate to the bottom occurred.

Porosity Measurement							
Green Part				Brown part			
Weight (g)	Apparent Volume (cm ³)	Measured Volume (cm ³)	Density (g/ cm ³)	Weight (g)	Apparent Volume (cm ³)	Measured Volume (cm ³)	Density (g/ cm ³)
3.101	4.1898	1.8497	1.6765	2.5695	3.3472	1.1646	2.2064
3.2397	4.2425	1.9129	1.6936	2.696	3.4419	1.3738	1.9624
3.206	4.2409	1.8183	1.7632	2.6765	3.379	1.1977	2.2348
3.287	4.4392	2.0072	1.6376	2.7347	3.5826	1.2248	2.2327
3.3097	4.4159	2.0201	1.6383	2.7528	3.34	1.2645	2.177

Table 1. Porosity measurements of SLSed graphite-phenolic parts, before and after phenolic pyrolyzation.

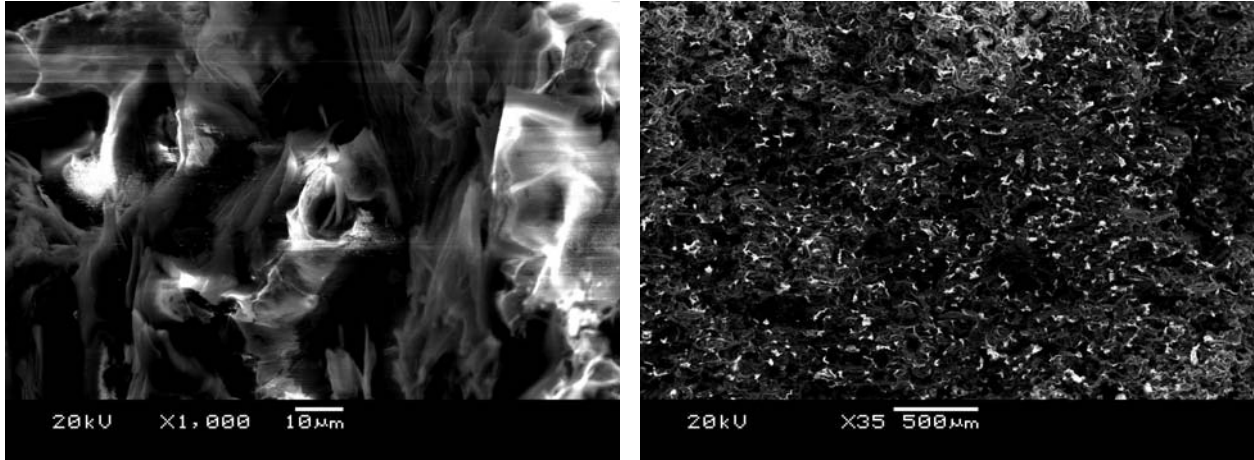
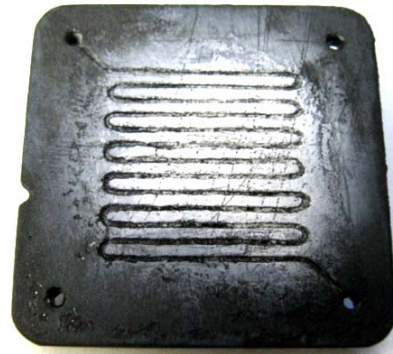


Fig 4(a). Charging of polymer coated graphite particles 4(b). Charging of midsection of bipolar plate.



Fig 4(c). Brown part before infiltration
(50mm by 50mm by 5mm)



4(d) Brown part after infiltration

3.4 Effect of carbonizing temperature on phenolic resin porosity

The Department of Energy (DOE) has set target parameters for the material properties of bipolar plates for which electrical conductivity is set to be > 100 S/cm. It is known that thermal and electrical conductivities of materials are affected by both porosity and non-conducting inclusions. Porosity has been derived by Koh and Fortini [10], to affect conductivity per the equation: $J/J_0 = (1-\epsilon) / (1+n\epsilon^2)$, where J/J_0 is the ratio of porous conductivity to fully densified conductivity, ϵ is the fractional porosity and n is the sensitivity to the presence of pores. Bhatia, et al [11], have shown that the open porosity in phenol formaldehyde resins increases with temperature. Above 800 °C, the porosity of the carbonized resin drops in a linear fashion with increasing temperature. This data in conjunction with the porosity vs conductivity studies suggests that the conductivity issue can be tackled by reducing the open porosity of phenol formaldehyde resin by carbonizing at high temperatures.

3.5 Effect of carbonizing temperature on conductivity

XRD was performed on the graphite and the phenolic resin before and after pyrolysis at 800 °C and 1200 °C (Figures 5a and 5b). The results show that the carbon product of the phenolic burnout at 800 °C is amorphous in nature and therefore may be contributing significantly to the drop in electrical conductivity of the part. The XRD result of the carbon produced at 1250 °C indicates a morphology change that suggests semi-crystallinity. Studies of phenol formaldehyde resin have shown that the electrical resistivity is highly dependent on the pyrolyzation temperature and that there is a change on the order of about 10^2 between treating at 800 °C and 1250 °C [11]. This was verified by measuring the electrical conductivities of selected brown parts and plotting them as a function of the pyrolyzation temperature (Figure 6, tabulated in Table 2). This increase may be due in part to the conversion of amorphous carbon into a semi-crystalline phase and also a reduction in porosity of the phenolic carbonization residue.

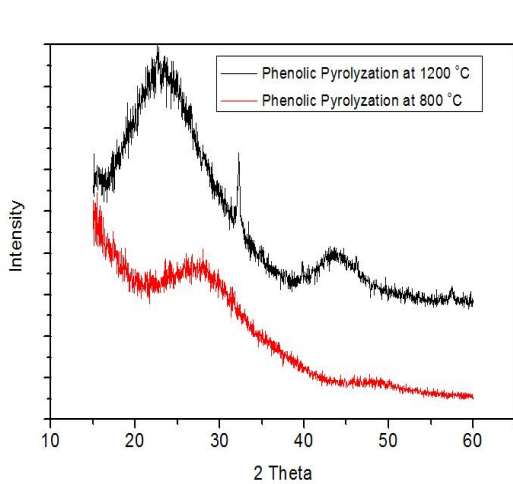


Fig 5a. XRD at different phenolic burnout temperatures

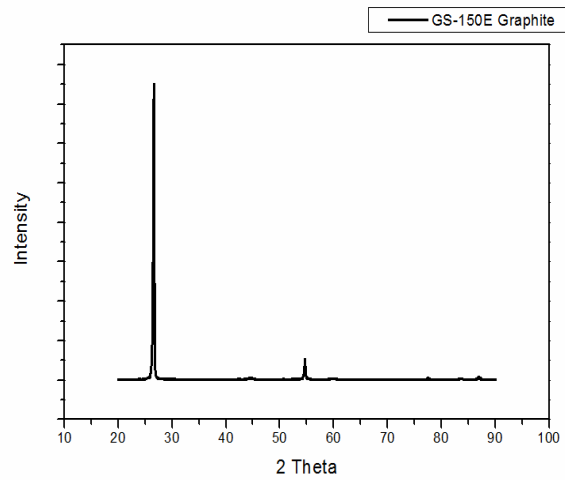


Fig 5b. Unprocessed graphite GS-150E

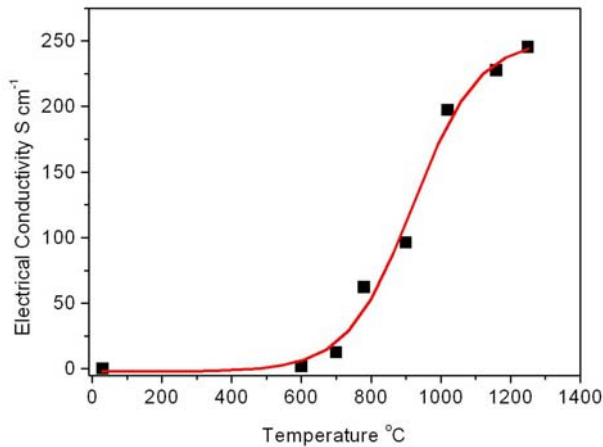


Fig 6. Measured conductivity vs temperature

Brown Part Electrical Conductivity							
Length (mm)	Breadth (mm)	Width (mm)	A/L	V (Volts)	V/I	Conductivity (S/cm)	Burnout Temperature °C
			(L=0.01 m)		(I = 0.1 Amperes)		
40.8	5.72	5.68	0.003249	1.846	18.46	0.1667339	30
33.54	5.97	4.4	0.0026268	0.205	2.05	1.857030905	600
40.14	5.84	4.16	0.00242944	0.032491	0.32491	12.66866185	700
33.54	5.8	4.08	0.0023664	0.00679	0.0679	62.23605688	780
39.64	5.15	4.93	0.00253895	0.00409	0.0409	96.29916993	900
40.54	5.54	4.33	0.00239882	0.002113	0.021127	197.3207372	1020
39.72	5.78	4.12	0.00238136	0.001845	0.01845	227.6033107	1160
40.32	5.5	4.74	0.002607	0.00156	0.01563	245.41437	1250

Table 2. Conductivity as a function of pyrolyzation temperature using a four point probe.

4. Conclusions

A process to make bipolar plates that are fluid impermeable and which possess acceptable electrical conductivity has been demonstrated. It has been shown that low viscosity ethyl cyanoacrylate polymer infiltrates the specimen completely under vacuum, producing a fully dense part whose electrical conductivity is maintained by grinding the surface to free it of cyanoacrylate. The electrical conductivity of the porous graphite matrix is observed as a function of the burnout temperature, and high values of conductivity (>200 S/cm) have been achieved by varying the same. Research into the change in materials properties (morphology, electrical conductivity and pore structure) of the phenolic resin is underway to better understand the results observed. Future work also includes the production of bipolar plates based on computational fluid dynamics models aimed at improving fuel distribution across the electrodes and reduction of methanol crossover which is a critical issue in DMFCs.

Acknowledgement

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