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

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Abstract

Direct Methanol Fuel Cells (DMFCs) are clean energy devices that convert chemical energy into electrical energy. The bipolar plate component of the DMFC is required to be fluid impermeable to prevent fuel leakage and electrically conductive to collect the electrons produced within the cell. Graphite possesses the properties of high electrical conductivity, low weight and resistance to corrosion that make it an attractive material for bipolar plates. However, the poor mechanical properties of graphite lead to prohibitive machining costs. The indirect Selective Laser Sintering (SLS) process, involving the laser sintering of graphite powders mixed with a phenolic resin binder, offers the advantage of complex part production and testing of prototype bipolar plates in short times. The current research deals with the production of bipolar plates for DMFC's by utilizing indirect SLS followed by post processing steps.

1. Introduction

Direct Methanol Fuel Cell (DMFC) technology is an attractive option as an alternative power source due to the theoretical energy density of methanol which is higher than current Li ion battery technologies and also hydrogen fuel cells. Moreover, methanol fuel is easy to handle and transport, making it a safe and viable means for portable energy solutions. However, issues such as methanol crossover [1] from the anode to the cathode side of the fuel cell and unstable electrocatalysts [2] hamper this technology from achieving widespread use.

A DMFC functions as a power source by converting chemical energy into electrical energy. This is accomplished 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.

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 [3]. 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 [4].
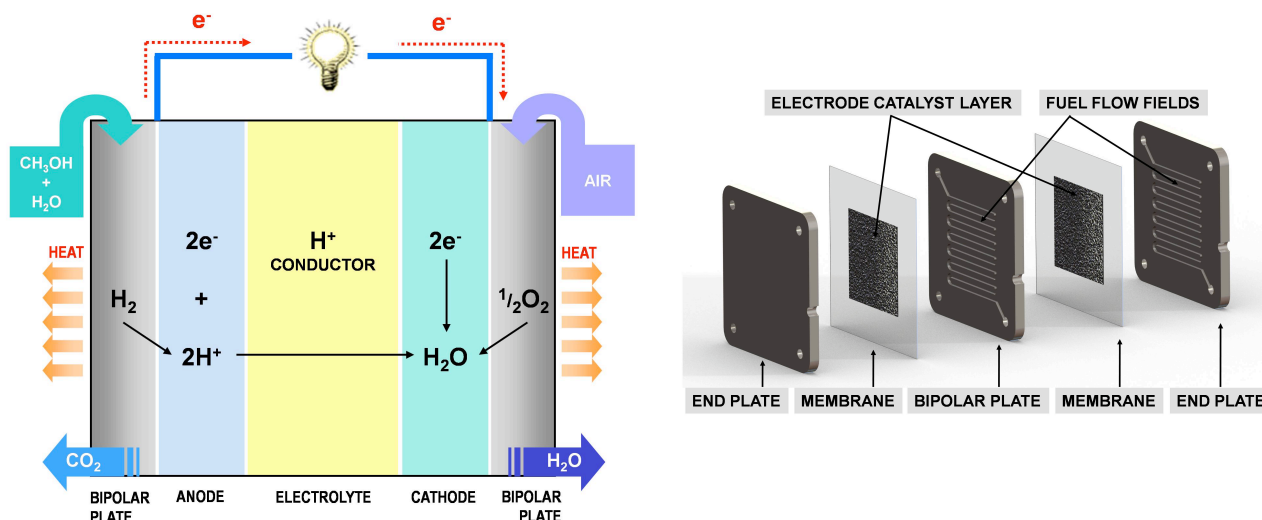

Figure 1. Schematic representation of DMFC working principle.

Selective laser sintering (SLS) is a rapid prototyping process that offers the benefit of producing plates with features of significant complexity in a single step. Indirect SLS of graphite bipolar plates involves mixing graphite powder with finely milled phenol formaldehyde ("phenolic") 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 bind the graphite powder together, 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. Bipolar plates made by indirect SLS offer the advantages of complex part production in a single manufacturing step. The functions of bipolar plates include distributing fuel and conducting electrons from the stack into the external circuit. However, due to the nature of the indirect SLS process, the as-produced (green part) plates are porous and possess low electrical conductivities.

The performance of the DMFC is dependent on optimal fuel distribution across the catalyst layer as well as the presence of detrimental processes such as methanol crossover which occurs when methanol from the anode side, permeates through the membrane to the cathode side where it poisons the catalyst sites, reducing the overall efficiency of the cell. Optimization of the flow field design in the bipolar plate has been shown to affect the efficiency of the fuel cell. The current research work deals with the issues related with the production of highly conductive, fluid impermeable graphite parts by indirect SLS and the optimization of the flow field design to improve the operating efficiency of the DMFC.

2. Bipolar plate production by Indirect Selective Laser Sintering

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 [5]. 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 [6] that seals the pores, thereby making the part fluid impermeable, and polishing of the surfaces to expose the underlying electrically conductive graphite matrix.
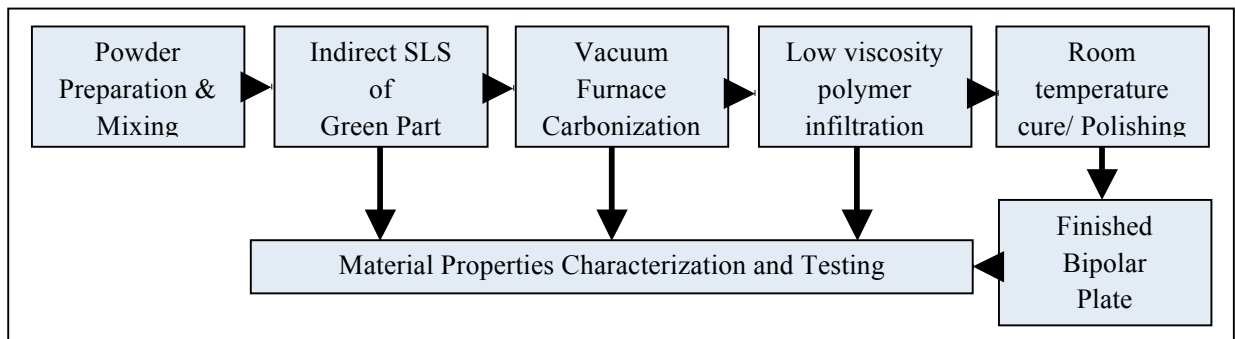

Figure 2. Flow chart of the experimental process of bipolar plate production by indirect SLS

3. Results and Discussion

### 3.1 Effect of Carbonizing Temperature on Electrical Conductivity

Though graphite has high electrical conductivity (~1000 S/cm), the phenolic powder used as a binder is electrically insulating, thereby rendering the green part produced by indirect SLS, a poor electrical conductor. 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 ºC and 1200 ºC [7]. XRD was performed on the neat graphite and phenolic resin before and after pyrolysis at temperature ranging from 600 ºC to 1200 ºC. The results show that the carbon product of the phenolic burnout at 600 ºC is amorphous in nature and therefore may be contributing significantly to the drop in electrical conductivity of the part. As the carbonizing temperature increases, a noticeable sharpening of the

peak at ~ 43º 2θ is observed (Figure 3), which implies an increase in graphitic order of the carbon product which in turn signifies an increase in electrical conductivity.
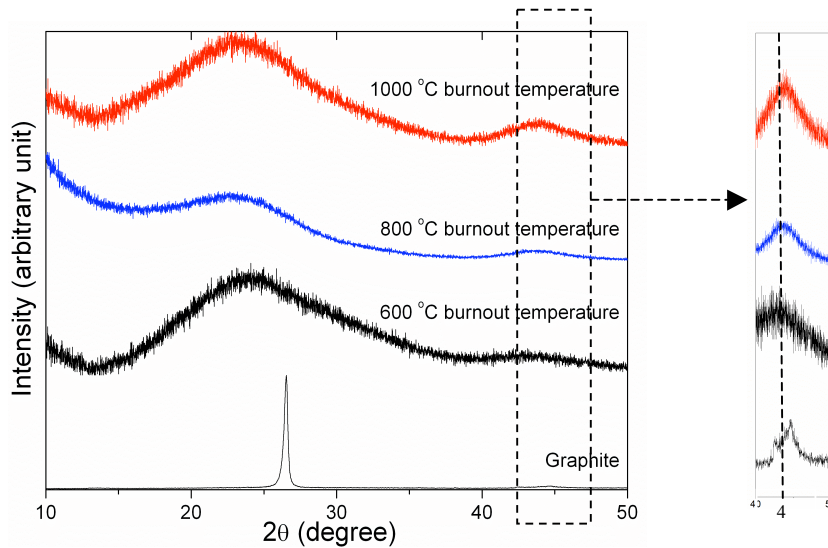
Figure 3. X-ray diffraction patterns of phenolic burnout and neat graphite powder at varying carbonization temperatures.

A four probe setup was used to measure the electrical conductivities of the heat treated brown parts and the results plotted as a function of the pyrolyzation temperature. The resulting graph (Figure 4a) corresponds to literature (Figure 4b) on the pyrolysis of phenolic resin [7]. This increase may be due in part to the conversion of amorphous carbon into a semi-crystalline phase and also a reduction in the porosity of the phenolic carbonization residue [6].
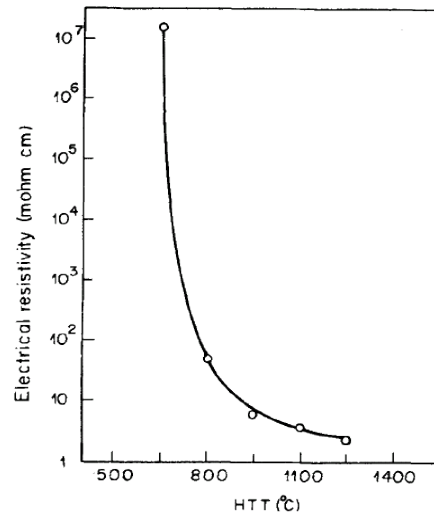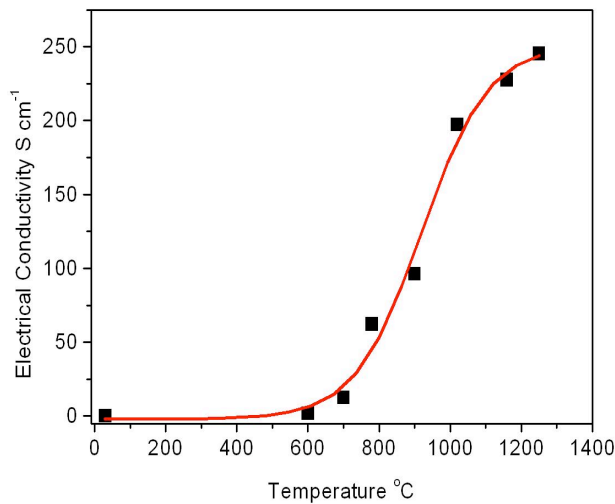
Figure 4. (a) Conductivity vs. Pyrolysis Temperature   **(b) Resistivity vs. Pyrolysis Temperature**

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3.2 Bipolar Plate Testing

For purposes of testing and comparison, 3 sets of bipolar plates (anode and cathode) with varying flow field patterns and active area of ~ 5 cm^2 were produced. Two of the sets with single serpentine flow field of uniform width channels, with 9 passes and 11 passes and a third set of 11 passes with the channel width varying from inlet to outlet (Figure 5). A fourth bipolar plate set with single serpentine, uniform width channels and active area of 5 cm^2, manufactured by Fuel Cell Technologies was used for comparative studies. The three sets were tested in a Scribner Associates Inc., 850C PEM Fuel Cell Test Station with the following Membrane Electrode Assembly (MEA):

Electrolyte Membrane: NaFion 117, Anode Catalyst: Pt/Ru/C, Cathode Catalyst: Pt/C, (2.5 mg/cm^2 loading).

9 Switchbacks Uniform Width Flow Field   11 Switchbacks Uniform Width Flow Field   11 Switchbacks Varying Width Flow Field

Fig 5. Bipolar Plate CAD models with varying flow fields

The electrochemical performances of the DMFC was evaluated with a single-cell fixture having an active area of 5 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 with a back pressure of 20 psi [8].

Methanol crossover was evaluated by a voltammetric method [9] in which methanol solution was fed at a flow rate of 2.5 mL/min into the anode side of MEA while the cathode side was kept in an inert humidified N$_2$ atmosphere. By applying a positive potential at the cathode side, the flux rate of permeating methanol was determined by measuring the steady-state limiting current density resulting from complete electro-oxidation at the membrane/Pt catalyst interface at the cathode side.

The performance of the single cells in the fuel cell tests was evaluated by plotting and comparing the scanned potential versus measured current density. As can be seen from figure 5a, the plates produced by indirect SLS worked without fuel leakage and produced expected polarization curves. The plate set with uniform width channels and 11 passes, exhibited

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performance comparable to the commercially manufactured plate set. The plate set with 11 passes of varying channel width and that with 9 passes of uniform width show diminished performance due to lesser active channel area and higher ohmic and mass transport losses.

Methanol crossover tests show that there is a direct correlation to the amount of methanol flowing in the channels to the amount of crossover observed. The larger the active flow area, more the crossover. The plate set with 11 passes of uniform width had the largest amount of methanol crossover, while that with 9 passes of uniform width had the lowest. The flow field of varying channel width showed methanol crossover comparable to that of the commercially produced plates. Since methanol crossover is largely a membrane related phenomenon, these results may be in part due to degradation of the MEA that was used in testing. Further tests need to be performed using a fresh MEA for each plate set in order to suitably study and compare the effect of the flow field on the amount of crossover observed.
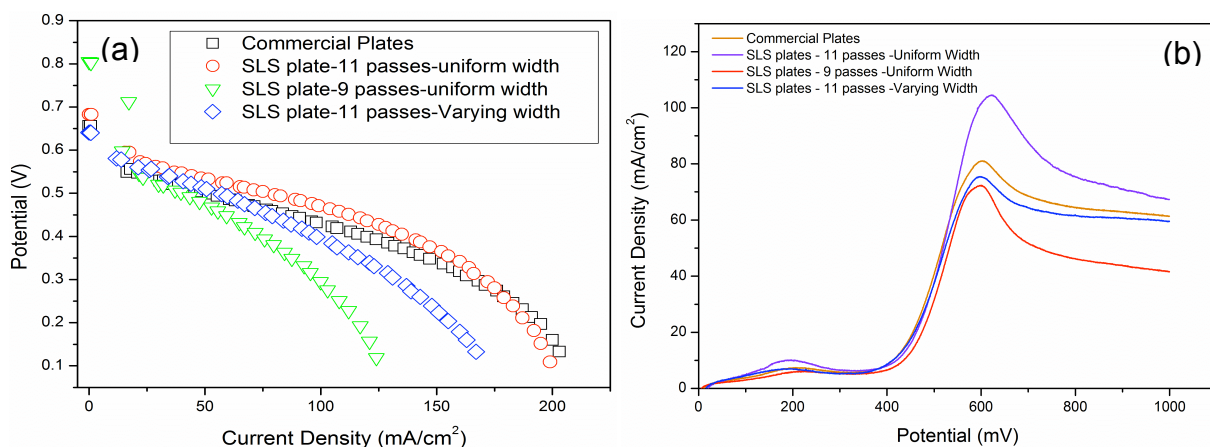
Fig 5. (a) Polarization curves of fuel cell test   (b) Comparison of methanol crossover

4. Conclusions

A process to produce fluid impermeable, electrically conductive graphite bipolar plates by indirect selective laser sintering has been implemented. Bipolar plates have been made using this process and tested in a fuel cell test station and compared with commercially produced plates for performance and methanol crossover. This production and testing process can be further enhanced by the implementation of Computational Fluid Dynamics (CFD) analyses in the design step to optimize the process of flow field pattern selection. This procedure can be useful in evaluating design concepts aimed at reducing methanol crossover and improving efficiency. Further studies on the effect of heat treatment on the conductivity of the brown part can also be performed. Complete mechanical and thermal characterization of the graphite-cyanoacrylate composite material needs to be performed in order to thoroughly understand the advantages and limitations of infiltrating with ethyl-cyanoacrylate.

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