

Improvement of Electrical Conductivity of SLS PEM Fuel Cell Bipolar Plates

Ssuwei Chen, David L. Bourell, Kristin L. Wood

Department of Mechanical Engineering, Laboratory for Freeform Fabrication
The University of Texas at Austin, Austin, TX 78712

Abstract

Reviewed, accepted August 3, 2005

Previous work in this research demonstrated the feasibility of fabrication of proton exchange membrane (PEM) fuel cell bipolar plates by an indirect selective laser sintering (SLS) route. Properties of the SLS bipolar plate, such as flexural strength, corrosion resistance and gas impermeability, etc. are quite promising and satisfactory. However, initial results showed that there was still room for the improvement in electrical conductivity. This paper summarizes the strategies investigated in an effort to increase the electrical conductivity, among which are: (1) infiltration of brown parts with conductive polymer (2) addition of a liquid phenolic infiltration/re-curing step prior to final sealing and (3) reduction of glassy carbon resistivity by curing process parameter control. Results show that the electrical conductivity value may be improved from 80 S/cm to around 108 S/cm, which is equivalent to a 35% jump, when the phenolic infiltration/re-curing step is applied before final epoxy sealing.

Background and Introduction

Fabrication of PEM fuel cell bipolar plates by indirect SLS has shown its feasibility based on previous experience [1]. To further increase the plate's electrical conductivity, three potential remedies were investigated. Since most of the strategies explored involved in using infiltration techniques for electrical conductivity improvement, their background and principle theories, Washburn and Young's equations, will be presented first.

The Washburn equation, which is commonly used to obtain pore size distributions by the mercury porosimetry approach, provides the required pressure P to infiltrate a pore of certain radius r . It is expressed as

$$P = (2\gamma_{LV} \cos\theta) / r \quad (1)$$

where γ_{LV} is the surface tension of liquid-vapor interface, θ is the contact angle between liquid and solid interface and r is the capillary radius. Equation (1) can further be modified to give a relationship between height of rising liquid front h and the corresponding time required t . [2].

$$h^2 = \frac{r\gamma_L \cos\theta}{2\eta} t \quad (2)$$

where η is the viscosity of the infiltrant.

In the case of pressureless and spontaneous infiltration of liquid phases into porous preforms, i.e. there is no aid expected from externally applied pressure or vacuum, one of the most critical issues is the adhesion or wetting characteristics of the infiltrant and

substrate. According to Young's equation, the surface energies at the three phase contacts are related to the equilibrium contact angle through:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (3)$$

where γ_{SV} , γ_{SL} and γ_{LV} are the surface free energies between solid and vapor, solid and liquid and liquid and vapor phase, respectively. For spontaneous wetting to occur, therefore, one of the rules relevant to effective bonding low surface energy substrates is:

$$\gamma_{in\ filtrant} < \gamma_{substrate} \quad (4)$$

Table 1 [3] lists surface energy of some of the common adhesive/infiltrant and substrate materials at room temperature. For obtaining best wetting behaviors and strong adhesion forces, the condition: $\gamma_{substrate} \gg \gamma_{in\ filtrant}$ is always desirable. It is evident from Table 1 that the surface energy of liquid epoxy resin is less than that of graphite. Thus spontaneous infiltration of liquid epoxy resin into a porous SLS brown part is expected to occur. Lastly, the time required for a complete infiltration of porous SLS bipolar plate with epoxy resin can be estimated from rearranging equation (2):

$$t = \frac{2\eta h^2}{r\gamma_L \cos \theta} = \frac{2 \times 10 \left(\frac{g}{cm.s}\right) \times (0.3cm)^2}{(50 \times 10^{-4} cm)(47 \frac{g}{s^2}) \cos 70^\circ} = 74.7(\text{sec}) \approx 1.24(\text{min})$$

where $h = 3mm$ is the thickness of the bipolar plate, $\eta = 1000cps = 10\text{poise} = 10 \frac{g}{cm.s}$ is the viscosity of epoxy resin used, $r = 50\mu m$ is the estimated pore radius and contact angle is reasonably assumed to be 70° . The estimated time value more or less matches our observed data for a complete infiltration.

Material	Surface Energy (dynes/cm= 10^{-3} J/m ²)
Silicone Oil	21
Liquid Epoxy Resin	47
Graphite	~70
Water	73
Mercury	470
Solid Aluminum	~500
Solid Copper	~1000

Table 1. Surface energy of selected materials [3].

Infiltration with Conducting Epoxy Resin

Infiltration of epoxy resin is one of the steps in the previous fabrication route. This necessary step was taken simply to make the porous brown part gas impermeable. It showed that with an adequate viscosity, epoxy resin was able to penetrate into the pore channels inside the part to make it gas tight upon curing. However, our attention at this point was focused on searching for an infiltrant capable of sealing the porous part as well as improving the electrical conductivity simultaneously. Based on the extensive literature survey, it is realized that epoxy resin containing carbon black makes up the greater

portion of conductive epoxy resins available since this additive is the most cost effective; even though some other fillers such as copper, silver and carbon fibril, etc. are available.

Theory

Electrically conductive compounds made of an insulating polymer matrix and conducting particles have been extensively used in antistatic materials, electromagnetic shielding and liquid crystal display (LCD) assembly industries. The electrical conductivity of such composites depends significantly on the concentration of the conducting phase and the extent of its continuity. Various mechanisms have been proposed to describe the electrically conducting behavior in polymeric composite materials [4, 5], among which percolation theory and the quantum mechanical tunneling effect are two popular models to illustrate the electron transport process [6]. The law of percolation theory states that a critical concentration or volume fraction, referred to as percolation threshold, of conductive filler is necessary to initiate the electrical conductivity in polymeric composite materials. The material behaves as an insulator when the filler concentration is too low to form a connecting network of conductive sites. On the other hand, the material undergoes a sharp transition from nonconductor to conductor when the filler concentration is above the percolation threshold, normally around 7% [7], allowing electrons to tunnel through or jump between closely distributed filler sites. Figure 1 [6] demonstrates an example of the experimental results of the relationship between electrical resistivity and carbon black (CB) fraction for CB filled high-density polyethylene (HDPE) compound.

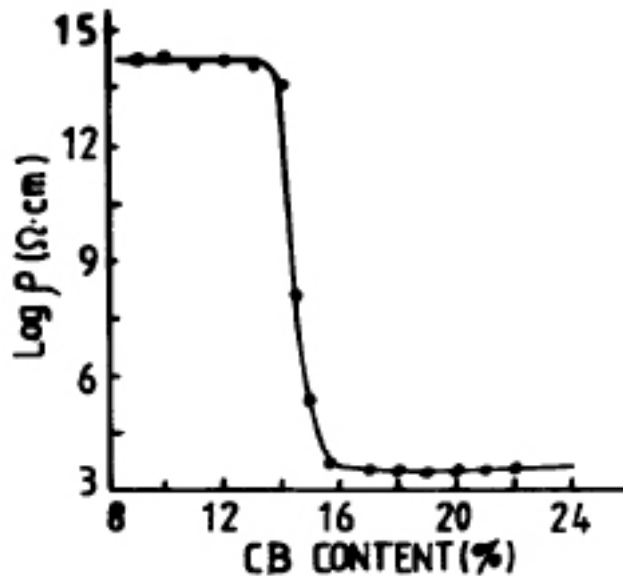


Figure 1. Electrical resistivity and carbon black fraction relationship for HDPE/CB compound. (adapted from Tang et al. [6])

Experimentation and Result

To assess the feasibility of electrical conductivity improvement on SLS bipolar plate by using conducting epoxy resin infiltration, we would like to first know the maximum achievable electrical conductivity value a cured conducting epoxy resin can

have. A commercially available epoxy resin and hardener obtained from System Three Resins, Inc. were mixed with carbon black powder purchased from Alfa Aesar Company. The epoxy was Clear Coat Epoxy Resin mixed with the hardener in a ratio of 2:1. The carbon black powder has an average particle size of 0.042 micron and a specific surface area of 75 m²/g. Ten cups of carbon black loaded epoxy resins were prepared and cured overnight in an oven to form ten solid samples. The carbon black loading level for each sample was 1, 2, 3, 5, 7, 10, 12, 15, 20 and 25 volume percent, respectively. Each cured solid sample was then cut into four 3 mm by 3mm by 30 mm test specimens, making a total of 40 specimens, for electrical resistivity testing according to ASTM D257 specifications. This four point probe technique measures electrical resistivity by applying a constant current over the test specimen and measuring the voltage drop across the specified distance. The electrical resistivity can subsequently be calculated by following Equation (5):

$$\gamma = \frac{\Delta V(t)(w)}{I(L)} \quad (5)$$

where γ is electrical resistivity, ΔV is voltage drop across a prescribed distance, t is specimen thickness, w is specimen width, L is the distance over which ΔV is measured and I is applied constant current. A Keithley 224 Programmable Current Source and Keithley 181 Nanovoltmeter were used to perform the tests. Figure 2 shows the average resistivity value for cured conducting epoxy resin versus its carbon black loading.

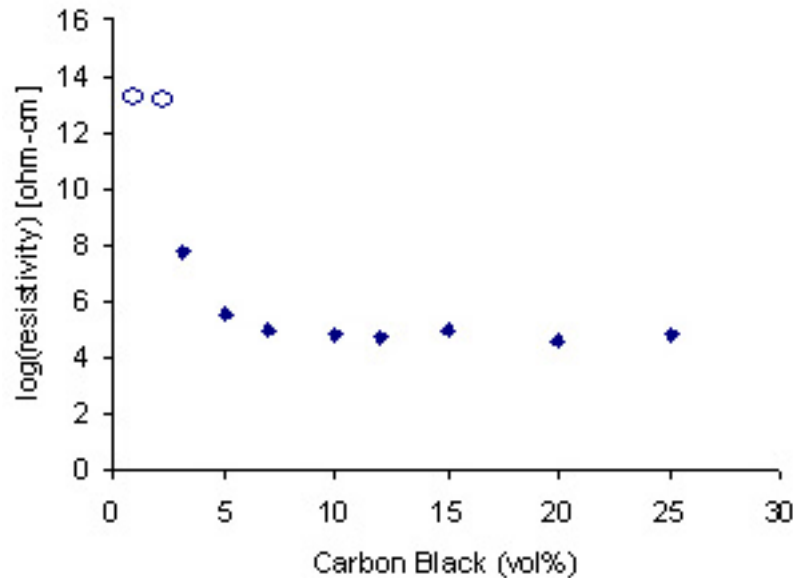


Figure 2. Resistivity of CB-filled epoxy resin versus CB content. The first two circle points are predicted values.

As can be noticed from the plot, the electrical resistivity curve is expected to drop dramatically from nonconductive to conductive behavior over a narrow range of carbon black loading due to the development of a network of closely-seated CB particles. The predicted very high electrical resistivity for 1 and 2 vol % CB specimens was not obtained due to the limits of our equipment. More importantly, the minimum resistivity

achieved is around $10^5 \Omega\text{-cm}$, which is equivalent to a maximum electrical conductivity value of 10^{-5} S/cm when CB loading is roughly above 8 vol. %. The result is very similar to what is reported elsewhere [8, 9]. However, the outcome is not promising for our application since it is far below our current conductivity value and does not seem to help in the overall conductivity improvement to a value of over 100 S/cm. What was even more disappointing is that the fine carbon black powder tends to agglomerate easily in the CB-filled epoxy resins and largely increase the resin viscosity. High resin viscosity and CB agglomeration can block CB powders from flowing into pores of the porous plate and limit the performance of infiltration. Figure 3 presents the photos showing that the agglomeration and sedimentation of carbon black powder in epoxy resin become more severe as CB loading increases. It is apparent, at this point, that infiltration of conducting epoxy resin will not be workable for the conductivity improvement of our SLS plates. Even many commercially available conducting epoxy resins exhibit much higher values of conductivity; most of them are in the form of “paste” instead of what is required here, a low viscosity infiltrant.

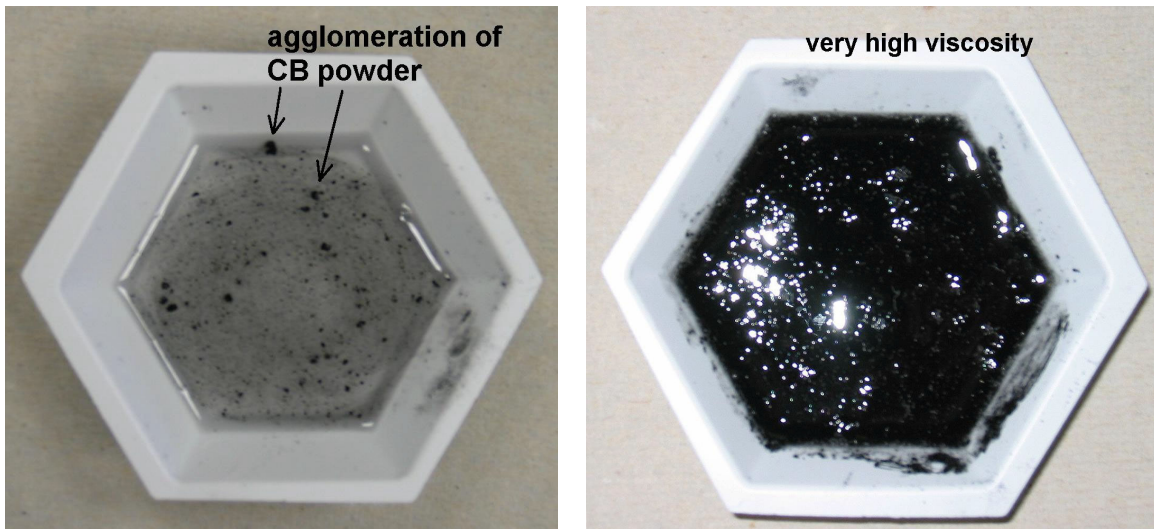


Figure 3. Agglomeration and sedimentation of CB powders in epoxy resins. (Left) 1 vol. % of CB loading. (Right) 15 vol. % of CB loading.

Liquid Phenolic Infiltration/Re-Curing

The electrical conductivity of powder metallurgy parts is affected by many variables, such as impurity, pore shape, and connectivity, etc, and one of the most significant factors is the amount of pores presented in the solids. Many models for thermal and electrical conductivity, based on theoretical or semi-empirical results, have been reported [10-13]. From these models, it is obvious that electrical conductivity increases as the percentage of porosity is reduced while the part becomes denser. This trend brought up the idea for improving electrical conductivity of SLS bipolar plate by increasing the glassy carbon residue level so as to replace portion of the porosity space that is originally occupied by the non-conducting epoxy resin when final epoxy sealing is completed.

Phenolic resin was previously chosen as one of the constituents along with graphite particles to make up the powder mixture for the requirements of this application. It is selected here as the intermediate infiltrant to elevate the carbon residue level when recuring process is executed. The phenolic resin GP5546 PARAC Powdered Phenolic Resin was obtained from Georgia Pacific Resins, Inc. and was dissolved in acetone at a temperature of 50 °C by using a magnetic stirrer for 30 minutes. The phenolic infiltrant was made of 60 vol. % of powdered phenolic resin and 40 vol. % of acetone for the first infiltration and the phenolic infiltrated brown part was placed back in the high temperature furnace for recuring. The recuring process was performed under inert gas atmosphere as the furnace chamber was filled with research grade argon gas from PraxAir Inc. The temperature profile for the recuring cycle started at room temperature and went up to 800 °C with a 1 °C/min heating ramp rate and was held for 1 hour before cooling back to room temperature naturally. The recured brown part was less porous compared to brown parts that did not receive such treatment. Electrical conductivity was improved to an average value of 108 S/cm. Following the same strategy, a second phenolic infiltration/recuring step was performed in an attempt to further increase the conductivity. The phenolic infiltrant was modified to a composition of 45 vol. % of powdered phenolic resin and 55 vol. % of acetone for reduced viscosity. The same temperature profile was implemented for the second time recuring process and the final electrical conductivity was increased to an averaging value of 117 S/cm. Figure 4a and Figure 4b are SEM micrographs of a brown part with and without a phenolic infiltration/recuring step, respectively. It can be seen that the amount of carbonized phenolic resin had increased by way of the addition of this fabrication step compared to that without phenolic infiltration/recuring treatment.

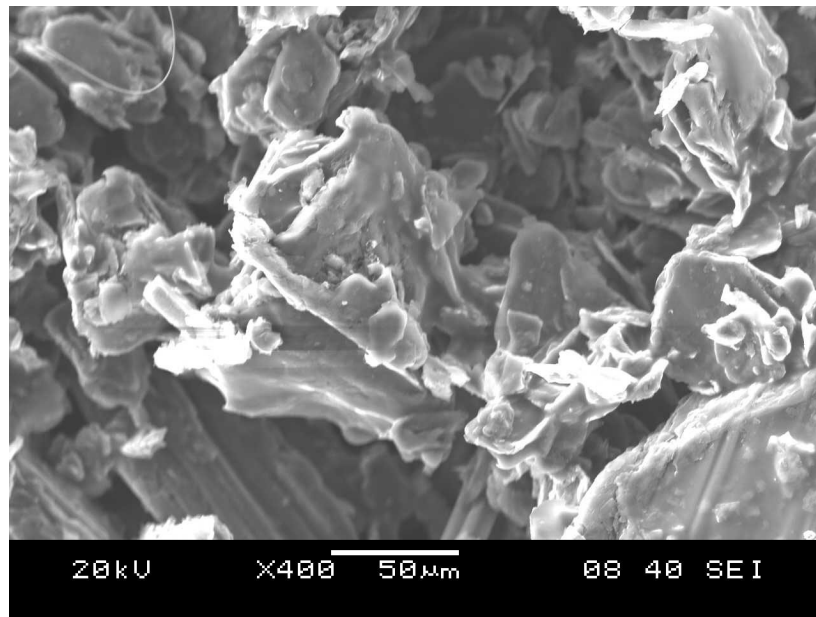


Figure 4(a). SEM micrograph of part with a phenolic infiltration/recuring step. The dendrite-like particles are glassy carbon while the larger flakes are graphite particles.

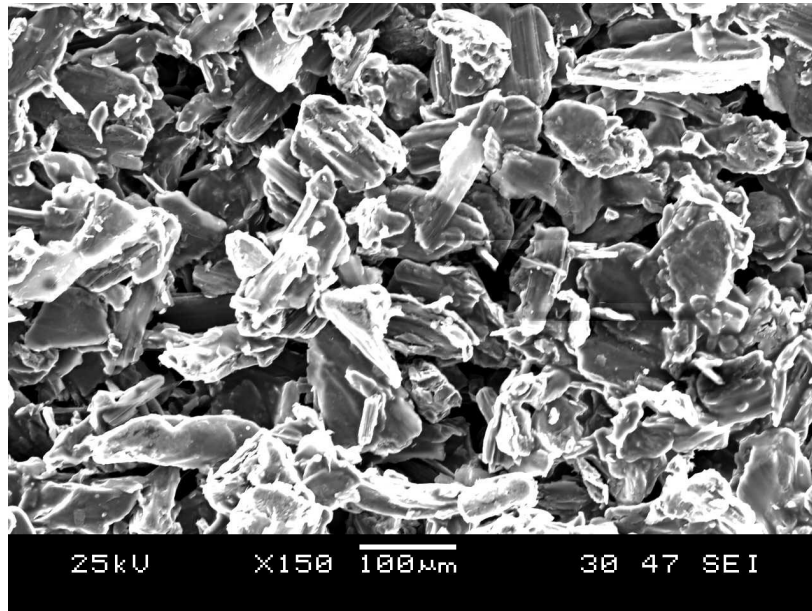


Figure 4(b) SEM micrograph of part without a phenolic infiltration/recuring step. Less glassy carbon residuals are able to be observed.

Figure 5 is a modified flow chart for SLS bipolar plate fabrication with added phenolic infiltration/recuring steps.

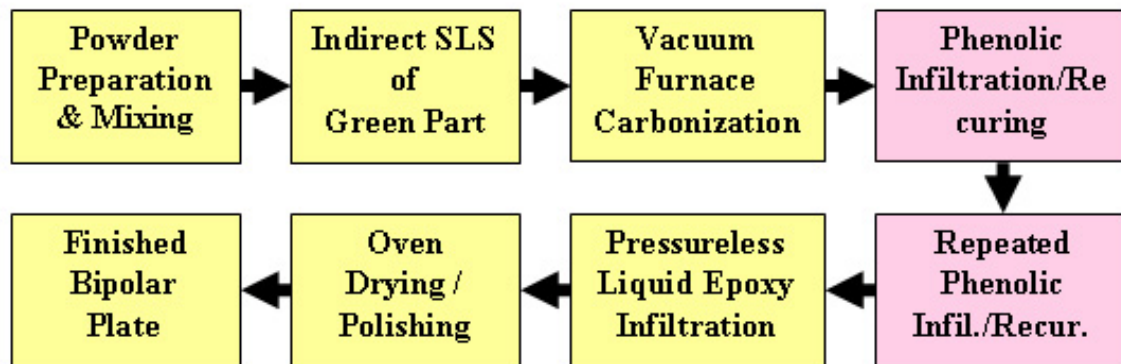


Figure 5. Modified flow chart for bipolar plate manufacturing using SLS.

In Figure 6, a bar chart for electrical conductivity with respect to each fabrication step is demonstrated. As can be seen, there is a 35% boost in electrical conductivity when the first phenolic infiltration/recuring step is employed and another 8.3% increase when the second phenolic infiltration/recuring step is done. The reduced rate in electrical conductivity improvement implies that less glassy carbon residues are deposited each time inside the brown part since the corresponding amount of porosity is lessened.

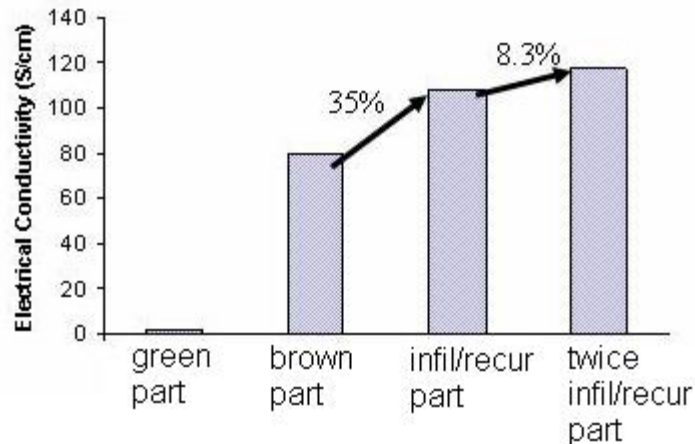


Figure 6. Electrical conductivity improvement of SLS bipolar plate with respect to corresponding fabrication step.

Curing Process Parameter Control

The brown part is composed of graphite particles and glassy carbon produced from carbonization of phenolic resin, and both ingredients contribute to its final conductivity. If the conductivity of glassy carbon were able to be significantly improved, it might be able to benefit the overall conductivity of brown part supposing that the conductivity of graphite particles is constant. Bhatia et al. [14] explored the variation of some physical properties of carbonized phenolic resin when increasing the curing temperature, one of which gives the relationship between its electrical resistivity and curing temperature as shown in Figure 7. It is evident from the curve that the electrical conductivity of pyrolyzed phenolic falls drastically in the range of 600° C to 800° C, beyond which the rate of fall in resistivity decreases gradually.

To examine the extent of the effect of conductivity increase from glassy carbon, the peak dwell temperature for brown part formation was raised from the original 800° C to 1000° C and electrical conductivity values were measured by using the four point probe technique described previously. Results showed, unfortunately, that the electrical conductivity of brown part does not exhibit significant improvement from the increase in final curing temperature. This may be attributed to the fact that only a relatively small portion of glassy carbon exists in the composition and the most critical factor dominating the electrical conductivity in powder sintered parts is its porosity level. Electrical conductivity of powder sintered parts normally follows a power law and is a strong function of porosity level inside the part [13, 15].

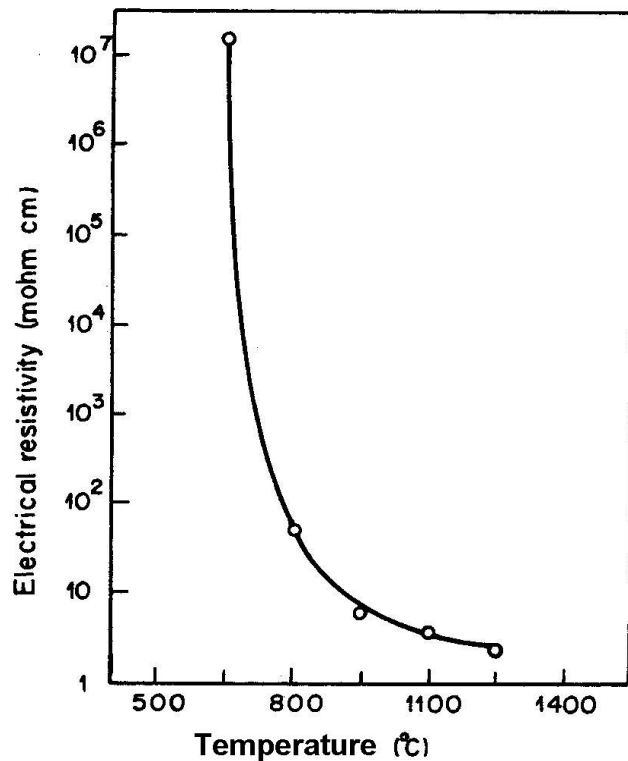


Figure 7. Variation of electrical resistivity of cured phenolic resin versus temperature. (from Bhatia et al. [14])

Conclusions

Three potential strategies were examined to ascertain the most appropriate method for improving the electrical conductivity of SLS bipolar plates. Inclusion of liquid phenolic infiltration/recuring steps to the fabrication route proved to be the most effective solution among others. This method is very similar to the way people used to make carbon/carbon or carbon/graphite composite materials where multiple cycles of thermosetting resin impregnation and curing are performed to form a gas-tight matrix. For our special application of fabrication of SLS PEM fuel cell bipolar plates, however, simply one or two times of liquid phenolic infiltration/recuring step are necessary to meet the electrical conductivity target value, especially when considering the lengthy and costly polymer pyrolysis process. The treated part is subsequently infiltrated with liquid epoxy resin to seal its surfaces. One other possible way to improve the electrical conductivity is chemical vapor infiltration (CVI) of carbon from hydrocarbon gaseous precursors into porous SLS brown parts. This technique is potentially capable of creating a hermetic skin on the plate surfaces as well as improving electrical conductivity due to the addition of elemental carbon.

References

- [1] S. Chen, D. L. Bourell and K. L. Wood “Fabrication of PEM Fuel Cell Bipolar Plate by Indirect SLS” The 15th Solid Freeform Fabrication Symposium Proceedings, August (2004), pp. 244-256
- [2] A. Siebols, et al. “Capillary Rise for the Thermodynamic Characterization of Solid Particle Surface” J. of Colloid and Interface Science, 186, (1997), pp. 60-70.
- [3] [Http://www.specialchem4adhesives.com/home/editorial.aspx?id=149&or=s11491_10](http://www.specialchem4adhesives.com/home/editorial.aspx?id=149&or=s11491_10)
- [4] John G. Simmons, “Generalized Formula for The Electric Tunnel Effect Between Similar Electrodes Separated by A Thin Insulating Film,” Journal of Applied Physics, Vol. 34, No. 6 (1963), pp.1793-1803.
- [5] Ping Sheng et al. “Fluctuation Induced Tunneling Conduction in Carbon Polyvinylchloride Composites,” Physical Review Letters, Vol. 40, No. 18 (1978), pp. 1197-1200.
- [6] H. Tang et al, “Studies on The Electrical Conductivity of Carbon Black Filled Polymers,” Journal of Applied Polymer Science, Vol. 59 (1996), pp. 383-387.
- [7] F. Bueche, “ A New Class of Switching Materials,” Journal of Applied Physics, Vol. 44, No. 1 (1973), pp. 532-533.
- [8] R. Schueler et al, “Agglomeration and Electrical Percolation Behavior of Carbon Black Dispersed in Epoxy Resin,” Journal of Applied Polymer Science, Vol.63 (13), (1997), pp.1741-1746.
- [9] J. A. Heiser et al, “Electrical Conductivity of Carbon Filled Nylon 6.6,” Advances in Polymer Technology, Vol. 23, No. 2 (2004), pp.135-146.
- [10] C. Argento, D. Bouvard. “Modeling the Effective Thermal Conductivity of Random Packing of Spheres through Densification” Int. J. Heat Mass Transfer, Vol. 39, No.7 (1996), pp. 1343-1350.
- [11] H. Fricke. “A Mathematical Treatment of The Electric Conductivity and Capacity of Disperse Systems” J. Physical Rev. 24 (1924), pp. 575-587.
- [12] J. C. Y. Koh, A. Fortini. “Prediction of Thermal Conductivity and Electrical Resistivity of Porous Metallic Materials” Int. J. Heat Mass Transfer, Vol. 16 (1973), pp. 2013-2022.
- [13] J. M. Montes, J. A. Rodriguez, E. J. Herrera. ”Thermal and Electrical Conductivities of Sintered Powder Compacts” Powder Metall. Vol. 46, No.3 (2003). pp. 251-256.
- [14] G. Bhatia et al, “Conversion of Phenol Formaldehyde Resin to Glass-like Carbon,” Journal of Materials Science, 19 (1984), pp. 1022-1028.
- [15] J. Koh and A. Fortini, “Prediction of Thermal Conductivity and Electrical Resistivity of Porous Metallic Materials,” International Journal of Heat and Mass Transfer, Vol. 16 (1973), pp. 2013-2022.

Acknowledgement

This research was funded by State of Texas Technology Development and Transfer Grant Number 003658 and by the US Office of Naval Research Grant Number N00014-00-1-0334.