Laser based rapid manufacturing of metallic Gas diffusion layers for PEM fuel cells

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1.Abstract:

Gas Diffusion layers (GDL's) are an essential component of Polymer Electrolyte Membrane Fuel cells (PEMFC's) which aid in thermal & electrical conductivities, water management and act as backup layers for the membrane electrode assemblies. This paper summarizes the effort to prototype metallic GDL designs using a miniature laser deposition system developed at Missouri University of Science & Technology. The pore sizes are controlled by masking the diverging laser beam using stainless steel masks of varying sizes and shapes. The through pore feature and further treatment of the GDL's for hydrophobicity reduces the water management issue and thereby increases the performance of the fuel cells. The operational characteristics of the GDL can be optimized by understanding the effect of the key parameters like fluid permeability, porosity, hydrophobicity and the surface morphology.

2.Introduction:

PEM Fuel cells act as clean sources of energy .With low pollution it is a form of green energy. Even though it offers high efficiency, low noise and less pollution its cost is a major barrier for its commercialization. The crucial components of a fuel cell are the Membrane electrode assembly (MEA), bipolar plates and Gas diffusion layers (GDL's).The performance of the fuel cells depends on the functionality and durability of these components.

The GDL's mainly aid in the transport of the reactant gases from the electrodes to the MEA and to flush the water formed at the cathodic end and thereby avoid flooding of water [2]. Water management is an important issue which if left unattended degrades the performance of the fuel cell exponentially. The water accumulated in the GDL not only creates a barrier for the flow of reactant gases but also destroys the electrolyte membrane. Water accumulated in the membrane causes swelling of the membrane and its functionality.

Care needs to be taken to effectively remove water from the GDL. The commercially used materials for the GDL's are carbon cloth or Toray paper which have shown excellent performances. The main drawback of using the carbon cloth is their structure and their inability to handle water. The water which is formed at the cathodic end of the fuel cell needs to be drained as soon as possible before it gets accumulated in the pores. This is a major cause of concern in the GDL's [2,5].

The GDL which is either carbon cloth or paper has a weave like pattern allowing both in plane and through plane transport of water and the reactant gases. The reactant gases need to diffuse profusely over the entire catalyst surface, hence both the transport mechanisms aid in the thorough diffusion of the gases. On the other hand water needs to be removed in a short span of time. Hence, water needs to take a shorter path which in this case is the through plane transport. But because of the structure of the GDL there also exists in-plane transport of water, which makes it difficult to drain the water and hence it starts to accumulate in the pores causing performance degradation of the GDL. Hence the in-plane transport needs to be avoided to get rid of water quickly i.e., it needs to have only through plane transport or straight pore transport [4,5].

Commercially available GDL's are not robust structures and their performances decrease over time. Because the paper and cloth get worn off after continuous usage and also to improve upon the improper water handling capability metallic GDL's with straight pores have been introduced which are robust enough than the cloth that lasts longer and the straight pores drain the water quickly.

An initial laboratory based method attempted for the fabrication of the metallic GDL's is photo-lithography which mainly consisted of effectively transferring the pattern on the mask, on to the metallic foil (substrate) which in this case is copper (Cu110-99% pure copper). This process is a batch production process and replicates the pattern almost exactly on to the substrate with good surface quality and with no stress introduction in the substrate. But this process includes many steps and at the end of the process there are many etchants that need to be disposed off which are hazardous as well as expensive. The present study is an attempt to alleviate these issues and to come up with a green procedure for the fabrication of metallic GDL's [7].

Cu has been chosen as the material for the fabrication of metallic GDL's because of its good electrical conductivity and its resistance to acidic environments compared to carbon cloth. The electrical conductivity of copper is 20 times more than that of carbon cloth [1].

Porosity is one of the important parameters that characterize the property of the GDL. It determines the flow of the reactant gases and water in the fuel cell. Hence it needs to be controlled accordingly. In this laser based fabrication of the GDL's the pore size needs to be controlled so that there exists sufficient capillary pressures for the water to drain out and also for the flow of gases [1,3].

In the present case study blocking of the laser beam with stainless steel masks of varying sizes and shapes was attempted to control the size and shapes of the pores formed on the substrate. There are a large number of factors involved which impact the pore sizes and shapes. Statistical analysis is an appropriate tool which helps simplify the understanding of the effects of various factors. Design

optimization of experiments (DOE) is an important tool which determines the relationship between factors influencing the pore size and the response variable. DOE helps in performing a systematic set of experiments which gives a lot of information for minimal experimental runs. In the present case study DOE of experiments has been performed to determine the relation between the factors (dwell time, Power and Spacing) on the response variable (pore size).

3. Experimental setup:

A Mini Laser deposition system available with Missouri university of Science and technology has been used for this case. It has a 808nm diode laser as the main source of energy supply for the fabrication of metallic GDL's. The other equipment used for this purpose is a fixture to hold the GDL foil. The thickness of the copper foil used is 10 µm. Such thin foils need to be handled carefully and supported firmly. Fixtures have been used for this purpose to hold the substrate in position. After holding the foil in the fixture it should be provided a sufficient tension to avoid its up and down movement when the laser is turned On & Off. The foil behaves like it is breathing whenever the laser is turned On & Off due to the thermal stresses produced in the thermal cycle. In order to avoid this, a sufficient tension has been created in the foil by pulling the fixed ends of the foil firmly apart. Care needs to be taken to avoid tearing the foil due to excess tension.

The initial fixture which was tried for this purpose was made using a fused deposition modeling (FDM) machine. This picture frame-like fixture, as shown in the Fig 1., has a snug fit so that it can hold the foil in position. But the fixture failed to hold the foil under tension.
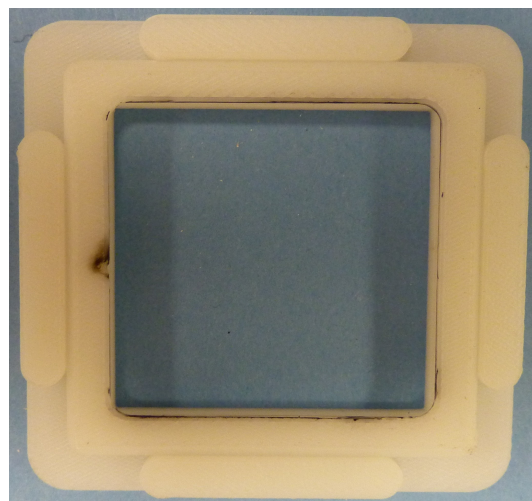

Fig 1. Picture frame fixture

In an attempt to increase the tension in the foil another fixture setup was implemented in which two metallic slabs hold down the foil on the jaws of a vice. Once the Cu foil is firmly held on the jaws, the handle on the vice is used to move

the jaws apart thus creating tension in the foil. Fig 2., shows the fixture that has been used for this purpose.
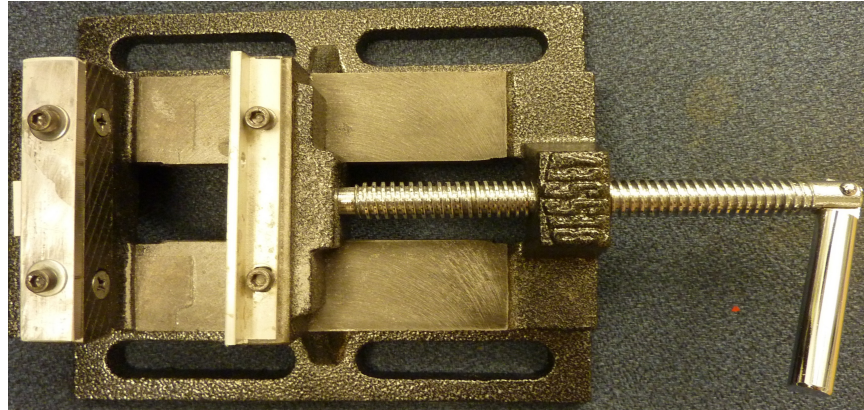

Fig 2. Vice as a fixture

The laser absorption coefficient of Cu110 (99.99% Cu) is very low. Hence the Cu foils were coated with thin layers of carbon black.

4.Results and Discussion:

This laser based fabrication technique for metallic GDL's is an attempt to obtain an eco-friendly manufacturing method. The method aims at obtaining performances comparable to the commercially available GDL's for which certain parameters like the porosity and permeability need to be controlled.

Table 1: Properties of commercially available carbon papers

Carbon cloth/Paper	Thickness(mm)	Porosity (%)	Density (g/cm^3)
Toray TGPH 090	0.3	77	0.45
Kureha E-715	0.35	60 to 80	0.35 to 0.40
Spectracarb 2050A-1041	0.25	60 to 90	0.4
Metallic GDL	0.01	9.3-12	8.913

The pore size as well as the spacing between the pores together seem to have a significant effect on the porosity of the GDL. Fig 3., shows the unit cell section of the pores of the GDL. Theoretically the porosity of the GDL as given by the area fraction is,

$$P = \pi \, r^2/s^2 \qquad (1)$$

Where,

r=Radius of the pore

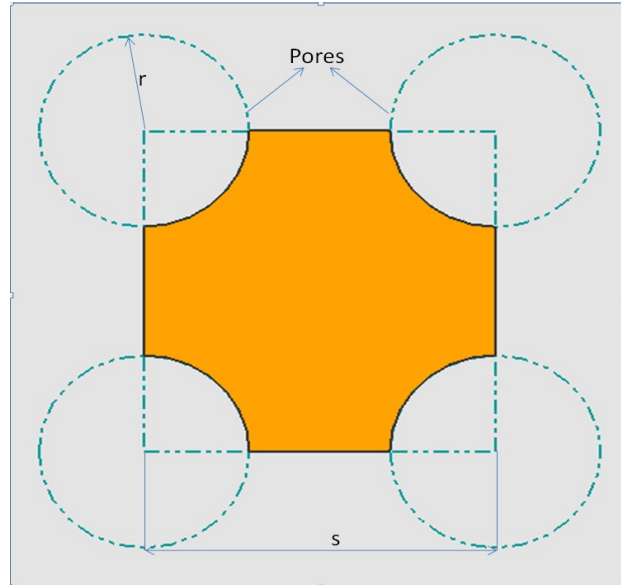s=Spacing between the centers of two adjacent pores.

Fig 3. Unit cell section of the GDL pores

Note: The pores were assumed to be circular theoretically, but in practise they were non circular when circular masks were used.

From the formula mentioned above it is clear that the porosity of the GDL depends on the pore size, which needs to be controlled. In order to achieve the variation in the sizes of the pores, maskings of the laser beam with stainless steel masks of various sizes was attempted.Initially circular masks were cutout form a stainless steel foil of thickness ~100 μm and were held in a fixture and the fixture was designed such that it fits to the end of the laser nozzle.

Circular masks of varying sizes have been attempted. The internal diameter of the masks were varied from 1" to 0.75" and down to 0.5" as shown in the fig.4 to see if the varying sizes of the masks had any effect on the pore sizes of the copper substrate.
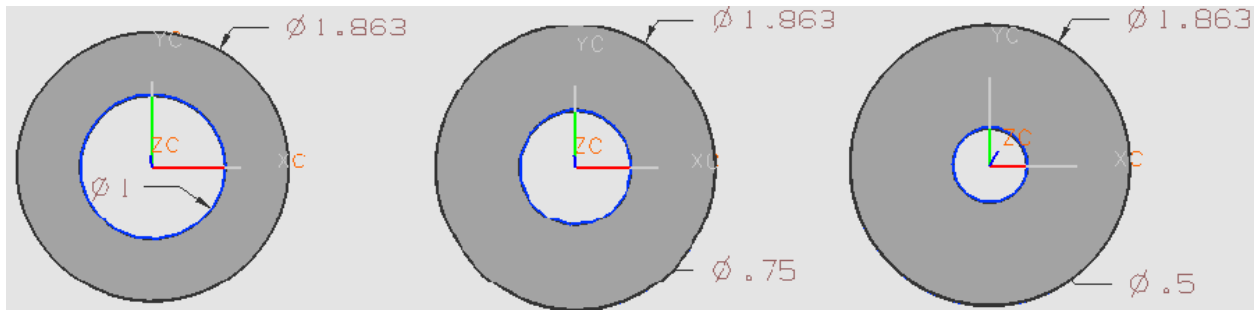
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Fig 4. Circular stainless steel masks

Changing the size of the masks from 1" to 0.5" has reduced the pore size from 170 μm – 110 μm at a power of 35Amps x 1.75Volts (~24W at the laser).The following fig. Shows the shapes of the pores that were formed using circular masks.
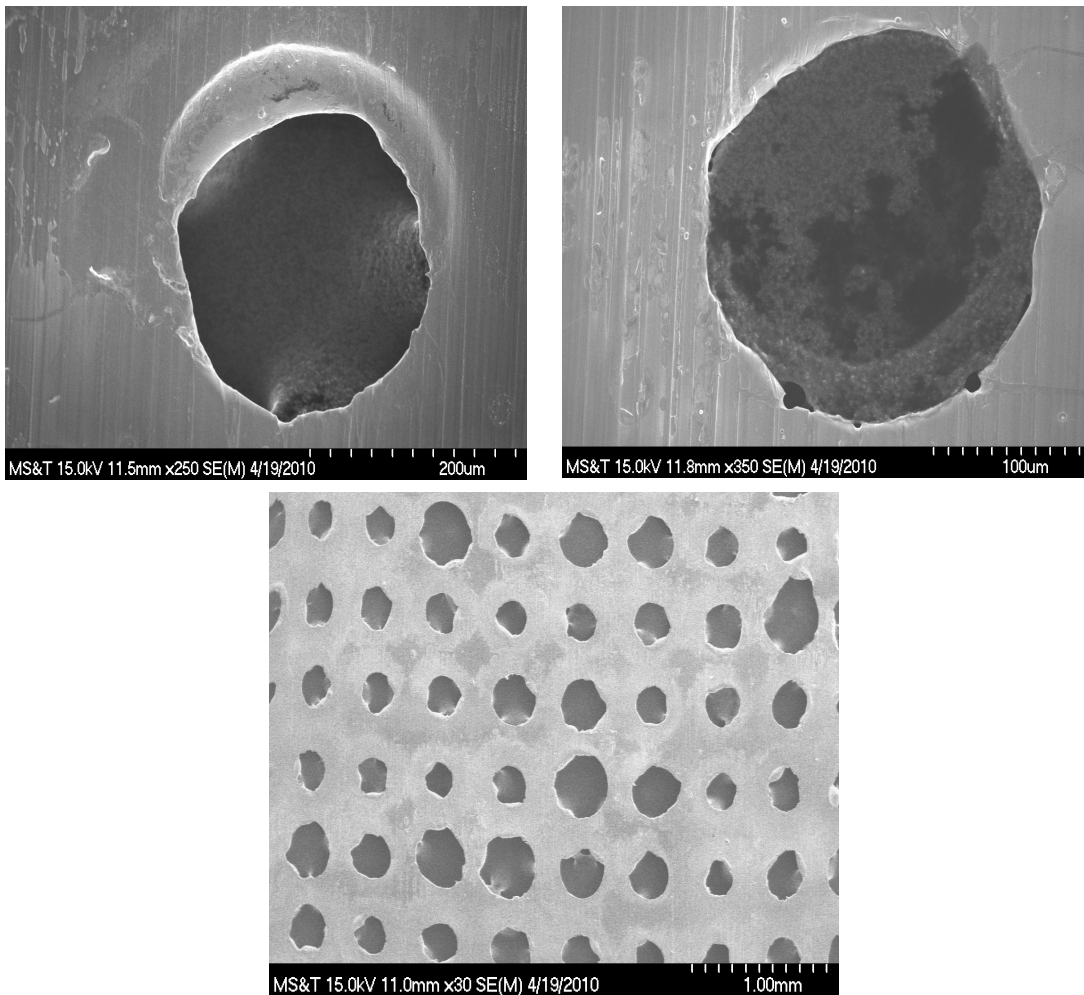

Fig 5. SEM images of pores formed due to circular masks

Elliptical masks were attempted to check whether different shapes of the masks had an effect on the shapes of the pores. Fig 6 shows the shapes and sizes of the elliptical masks that were attempted.
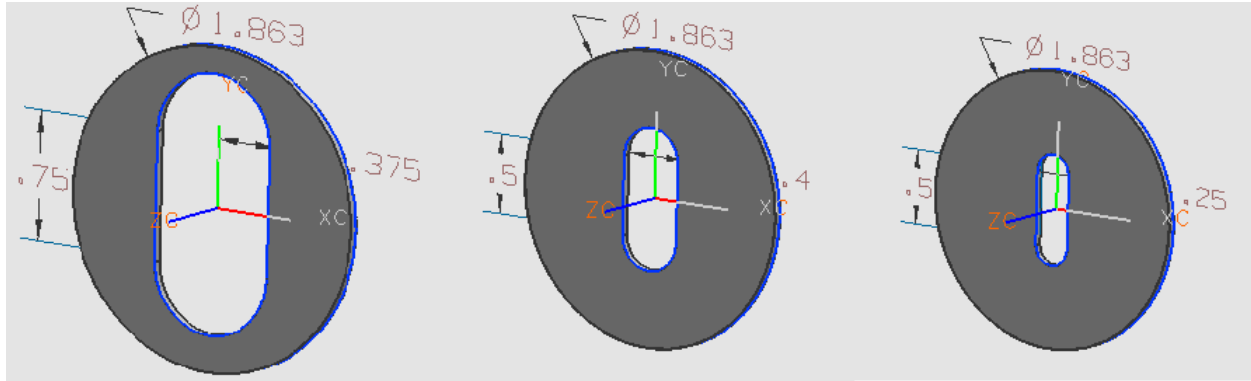
Fig 6. Elliptical masks of varying dimensions

A power of 35Amps x 1.75Volts(~24W at the laser) with a spacing of 0.02" and a dwell time of 3ms was appreciable. The smallest elliptical mask (0.75" x 0.25") was very small to create a pore and for the same parameters (Power density: ~24W), Dwell time: 3ms and spacing:0.02") the pores were interlinked and formed a continuous path when a bigger mask (1.5" x 0.75") was used. Finally a medium sized mask (0.9" x 0.4") gave optimum results. Fig 7., shows the shapes of the pores formed using the optimum sized elliptical masks).
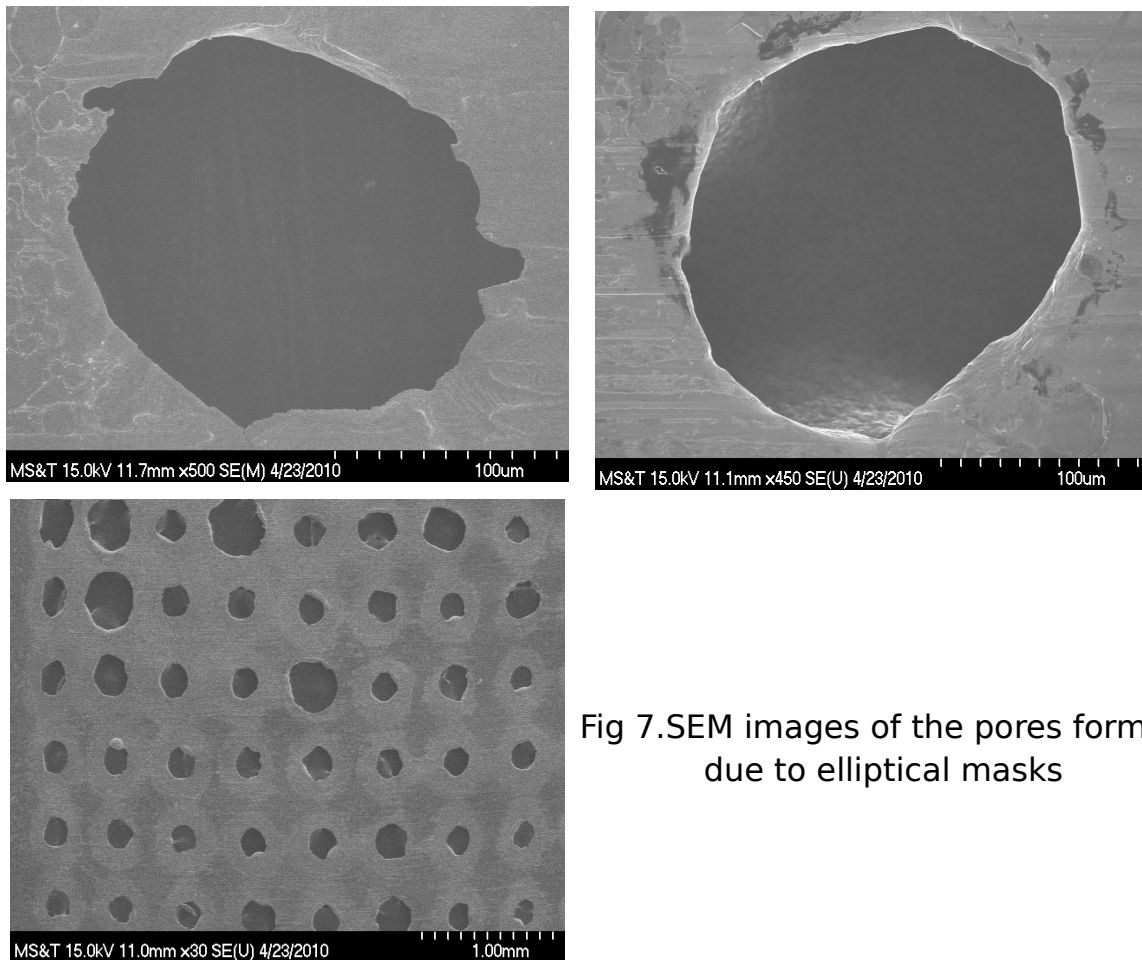

Fig 7.SEM images of the pores formed due to elliptical masks

Several experimental runs were performed to adjust the power density , dwell time and spacing which might optimize the pore size. A statistical analysis was performed to check the effect of various factors that might affect the pore size. A circular mask of 1" diameter was used throughout the experiment.

5. Statistical Analysis:

Planning the experiment systematically and analyzing the data statistically are the two important aspects of DOE. Planning includes the selection of the factors their levels which affect the response of the experiment, the response variable and finally the design procedure. The number of factors determines the number of experimental runs and the response variable is the output of these experimental runs. The ANOVA analysis of this statistical model determines whether or not these factors have any significant effect and which factors are more effective. Data for all the experimental runs needs to be available in order to have a balanced experiment.

As mentioned the three factors chosen for this analysis are Power (measured in terms of Amperage of the system), dwell time of the laser beam and the spacing between the centers of the pores that is desired, and the response variable (pore size). Two levels have been chosen for each factor and each run is replicated once. The factors and their levels are shown in the table below.

Table 2: Factors and their levels

Factor	Higher level	Lower level
Power (in terms of current)	40Amps (~29W)	33Amps(~24W)
Dwell Time (ms)	5ms	2ms
Spacing	0.06"	0.04"

A 2^3 factorial design with two replications has been used for this case, hence we have $16(2^3*2)$ experimental runs. These 16 runs were completely randomized by drawing these 16 experimental runs one after the other. This randomization order is similar to the one obtained from the randomization in SAS. The randomized order of the runs is shown in the appendix.

The pores that were obtained using the process mentioned above were not circular as desired. Hence image analysing software 'image J' has been used for this purpose. An ellipse was fit in to these non circular holes in order to obtain a major and a minor diameter of the pores. The circularity of the ellipse which is the ratio of the minor diameter to the major diameter is found to be approximately equal to

unity. Hence to obtain a balance of the data one dimensional measure has been chosen for this analysis which is the major diameter.

Table 3., shows the P-Values of the ANOVA results. The P-values signify the effect of each individual factor and also the effects of the interactions of these factors if any. If the obtained P-value is less than the significance level (α=0.05), then that effect is considered to be significant (i.e., it has a significant effect on the output/ response variable.

Table 3. ANOVA analysis, P-Values

SOURCE	P-VALUES
Power	0.02
Dwell time	0.914
Spacing	0.179
Power*Dwell time	0.225
Power*Spacing	0.420
Dwell time*Spacing	0.493
Power*Dwell Time*Spacing	0.687
R2 (%)	63.02 %
Standard Deviation	0.140637

From the ANOVA table it is clear that only power has a significant effect on the response (pore size) with 95% confidence level and no other factors or interactions are significant which is contrary to what has been assumed initially.

Fig 8., shows the plot of main effects i.e., power, dwell time and spacing on the response variable.It can be seen clearly from the plot that the change in the power has affected the pore size significantly which can be seen from its deviation from the mean. It was assumed that the spacing might have a significant effect on the pore size because of the preheating of the areas around the pore being formed. Whenever a laser pulses to burn a pore the adjacent areas of the pore are also preheated and this was assumed to have an effect on the adjacent pores every time the laser pulses, but contrary to the assumption the spacing had less significant effect. This can be attributed to the fact that the heat flux given to the substrate is

greater compared to the conduction of heat in the copper foil. This can be proved from the amount of energy absorbed by the foil and its final temperature.
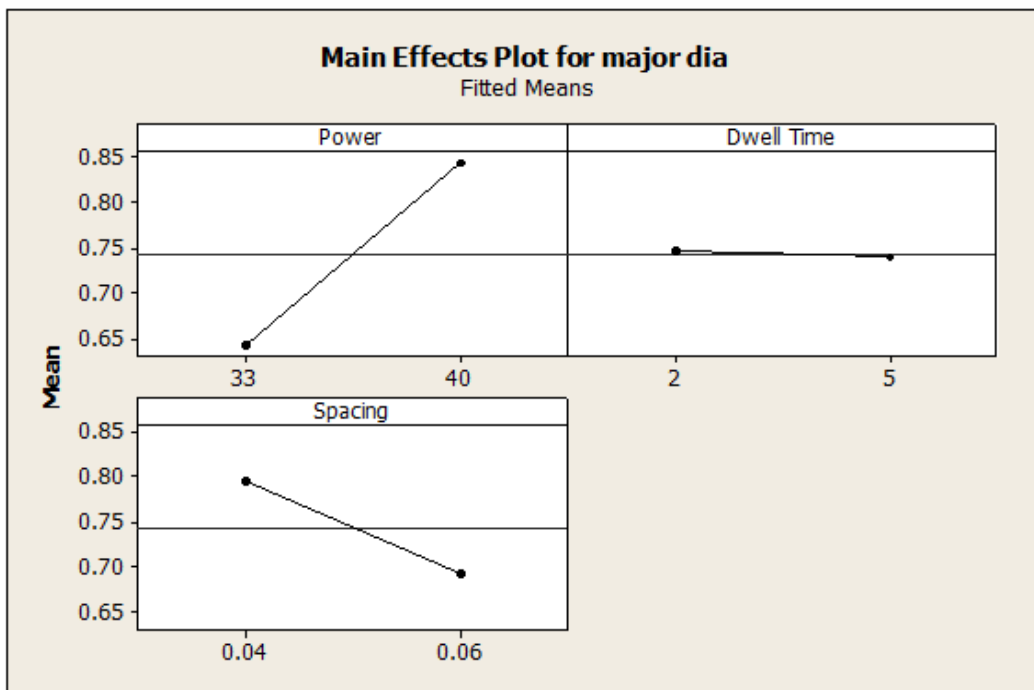

Fig 8. Main Effects plot

From the calculations of total energy absorbed by a 2" x 2" Cu foil it can be seen that even after burning 256 holes with all pores absorbing about .0.2121226J of energy the rise in the temperature of the foil is only 2.39°C which implies that most of the heat absorbed is lost in the form of convective losses to the atmosphere. This implies that the pre-heating temperatures of the foil adjacent to the burning pores are very less compared to the input temperature of the laser source. Hence spacing doesn't have any effect on the pore size.

The dwell time of the laser beam can be considered as an insignificant factor for affecting the pore size. This may be due to the fact that there is not a significant time difference between the levels of dwell time chosen for this experiment.

The Fig 9., shows the interaction plots of power*dwell time, dwell time*spacing and power*spacing on the response variable and none of these interactions were significant enough to effect the pore size. The interaction between spacing and Dwell time seems to be significant from the plot but it is not significant enough to affect the pore size as can be seen from the ANOVA table.
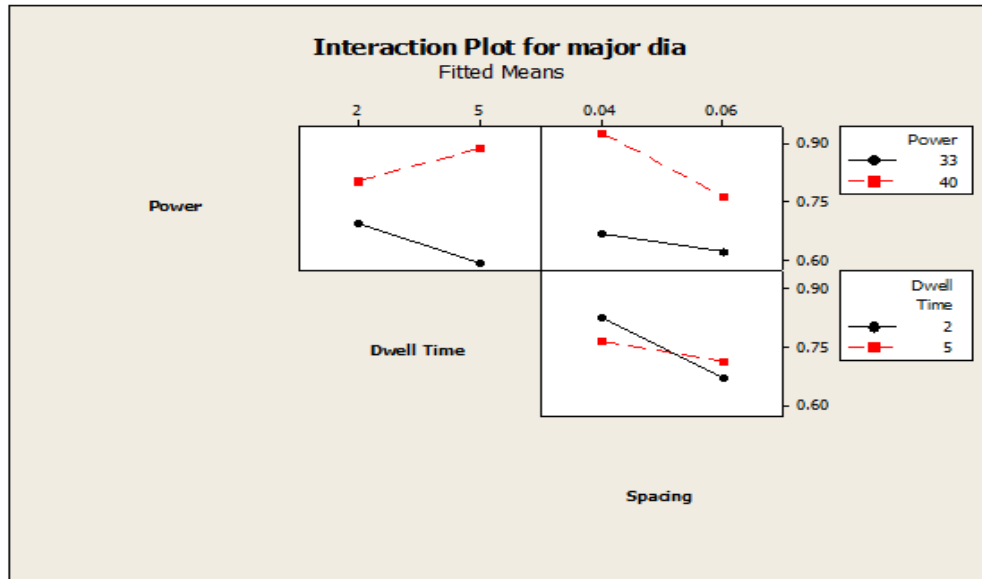
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Fig 9. Interaction plots

Fig 10., shows the residual plots. The normal probability plot shows the best fit possible with the experimental runs and the deviation of each run from the mean and the best fit curve for the major diameter from the regression analysis is given by,

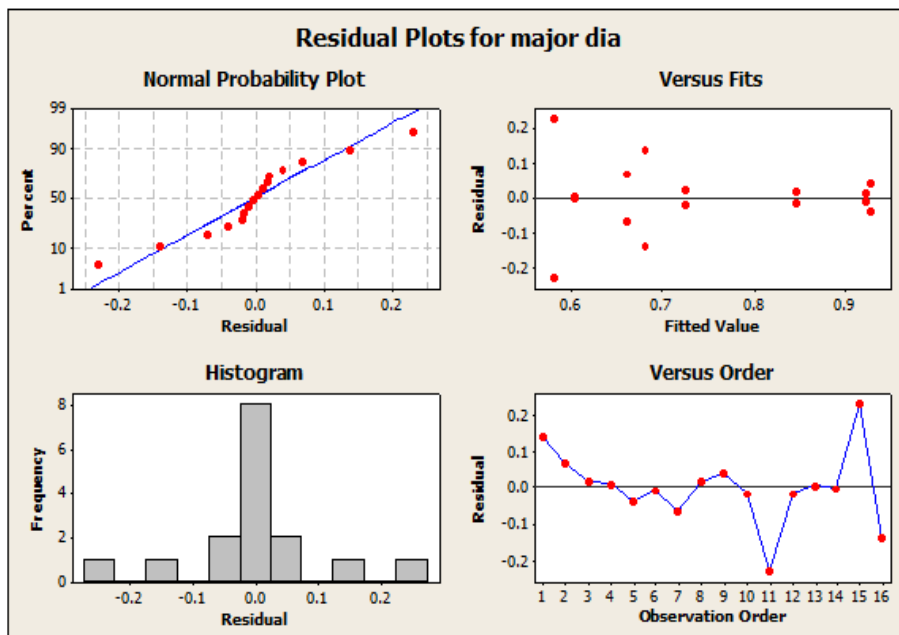$$\text{Major diameter} = -0.045 + 0.029 \text{ Power} \tag{2}$$

Fig 10. Residual plots

The versus order plot shows the distribution of readings around the mean and it can be seen that the 11th and the 13th experimental runs deviated from the mean significantly. This run corresponds to the readings taken from the followings factors and their corresponding levels.

Power: 33Amps (~24W)

Dwell time: 5ms

Spacing: 0.06"

The power was not sufficient for that particular dwell time to create a pore. Hence the readings deviated from the mean.

From the statistical analysis it is clear that the only power density of the laser has a significant effect on the pore size and no other factors nor their interactions showed any significant effect.

This paper deciphers an attempt to fabricate metallic gas diffusion layers for PEM Fuel cell using laser based rapid manufacturing techniques. However there are many future challenges to this form of fabrication technique like the scaling up of this process for it to be a mass production process and also the consistency in the results obtained during this process is very important for which the power density of the laser needs to be controlled. The method in which the foil is handled while loading it on to the fixture and while removing it from the fixture needs to be improved.

6.Conclusions:

A novel method for the fabrication of metallic GDL's using a laser based rapid manufacturing technique was attempted to improve the electrical conductivity, performance, and durability of a PEM Fuel cell. A copper foil of 10 μm thickness was used as a gas diffusion medium. In this attempt the laser beam was masked using stainless steel masks to obtain various sizes and shapes of the pores. Circular and Elliptical masks were used for this case study. A statistical analysis was performed to check the effect of various factors that influence the pore size. ANOVA analysis was performed to check the effect of power density, spacing and dwell time on the pore size. It was observed that only power had its effect on the response variable and no other factors nor their interactions showed any effective significance. This analysis helps gain thorough knowledge of the factors showing impact and simplifies the study.

References:

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APPENDIX:

Order of the experimental runs:

Current	Dwell time	Spacing
40Amps(~29W)	2ms	0.06"
33Amps(~24W)	2ms	0.06"
33Amps(~24W)	2ms	0.04"
40Amps(~29W)	2ms	0.04"
40Amps(~29W)	5ms	0.04"
40Amps(~29W)	2ms	0.04"
33Amps(~24W)	2ms	0.06"
40Amps(~29W)	5ms	0.06"
40Amps(~29W)	5ms	0.04"
40Amps(~29W)	5ms	0.06"
33Amps(~24W)	5ms	0.06"
33Amps(~24W)	2ms	0.04"
33Amps(~24W)	5ms	0.04"
33Amps(~24W)	5ms	0.04"
33Amps(~24W)	5ms	0.06"
40Amps(~29W)	2ms	0.06"