A Thesis

entitled

Statistical Analysis of Factors Affecting Nanoporous Gold and its Sensitivity in Comparison with Bulk Gold

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Master of Science Degree in Mechanical Engineering

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An Abstract of
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Electrochemical dealloying has proven to be an efficient way of fabricating nanoporous gold, the morphology of which can be tailored by controlling factors such as the etching time, temperature of electrolyte, composition of the alloy, pre and/or post heat treatment and voltage to suit applications such as fuel cell electrodes and sensors. This work aims at studying the effect of such factors as the electrolyte concentration on the morphology of the emerging material. A model relating the processing parameters and pore size is established by statistical approaches using the Design Expert 7.1 software. An equation that captures the individual as well as interaction effects on nanoporous gold is proposed. The validity of the equation is verified by existing research results. Simulation of this material under applied external load was done to achieve static properties in comparison with bulk gold. The applications where this might be helpful have been mentioned.
“Quit worrying about competition, do what you like for your own excellence. Be true to yourself and you will be just fine.”

-My Parents

To Motilal & Jyoti Baharani, my Parents, who mean the world to me.
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My parents never tried to limit my aspiration and always encouraged me, and that has been my biggest driving factor. Thanks to them for always being there.

I would like to credit my fiancé, Mr. Satish Bhandari for motivating me.

Finally, I would like to thank God almighty for being so kind to me and giving me this blessed opportunity. If inadvertently I have missed any names, I would like to apologize and would be honored if my mistakes are pointed out.
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Chapter 1

1. Introduction

Simple method to fabricate nanoporous gold (NPG) is dealloying, which involves an alloy that can be selectively etched or corroded. The requirement is just that the alloying element with gold should be more chemically active such that it is easily removed when placed in the electrolyte. This method has been in practice in a very raw form but has become of importance since NPG has been instrumental in many uses[1,2]. Dealloyed structures have been shown in Figure 1.

![Figure 1. Typical dealloyed film [4]](image)

Earlier studies assumed that this structure was present inside the metal and was imparted to the metal once it was placed in an acidic environment[3] but microscopic studies and diffraction of just single metals in solid phase showed that no such thing was already existing.

Jonah Erlebacher[4] has showed the mechanism of dealloying by simulations in Figure 2.
According to his studies, the mechanism begins with one Ag atom that departs from the surface. This leaves behind a vacancy and this upsets the chemical equilibrium. The adjacent Ag atoms have lower bonding than the original alloy and this leads to the electrolyte being easily able to attack the alloy. The Au atoms remain behind as they are not reactive and start bonding in small clusters without any co-ordination, exposing the bottom layers. The process continues till maximum layers of the alloy have been dealloyed and the remainder material is not active.

Various concentrations of nitric acid are used in most of the cases, as voltage may be supplied or controlled when the alloy is Au-Ag. Once all Ag has been removed and the Au has interconnected, the material can conduct electricity.
1.1 Nanoporous Materials

A variety of nanoporous materials exist naturally in condensed matter where the ligaments form clusters to reach a state of minimum energy and hence equilibrium. Typical profile for one such material i.e. nanoporous gold is shown in Figure 3.

![Figure 3: NPG using Transmission Electron Microscopy.][5]

In these materials, two material phases co-exist – solid in the form of ligaments and gaseous as pores. The pores are able to demonstrate better transport properties than bulk material for a lot of applications. Mechanical properties such as strength, durability, deformation and more change for these materials than the ones they are dealloyed from. We will briefly discuss the grain size and defects.

*Grain Size.* This is found to be similar to the parent material used and generally larger than the pore and ligament sizes. This means that the microstructure is mostly retained even after chemical treatment which means the strength of the material will be comparable to the material used [5].
Defects: This really depends on the kind of alloy used. If it was a thin film, whose thickness is a couple of nanometers, then the whole film gets dealloyed throughout the thickness and the cracks might be noticeably low[5]. If it is thicker than a few centimeters then there might be more cracks due to the fact that the surface gets dealloyed and the core does not. Parida et al. [6] found that this occurs due to the shrinkage during dissolution, but this happens when we talk about high electrolyte concentration which is the main cause for parting. If the dealloying is forced where voltage, temperature and other factors have been changed from ambient, then high values of these will obviously lead to a surface with more cracks due to the attack. The strength of the material depends upon the surface as cracks and notches act as areas of stress concentration, so lesser the cracks, stronger the material[7].

A lot of work has been done [8,9,10,11] on this, but there is a need to identify the exact effect on pore size and mechanical properties due to these factors.

1.2 Nanoporous Gold

Gold is one of the metals best suited to a number of applications due to its noble nature being less volatile, less cost than platinum being used currently. Although nickel has also been a very tempting choice, it is Ni is more anodic and might dissolve into the solution. It is also better suited for high temperature fuel cells rather than the ones that operate at room temperatures.

Bulk gold has a little disadvantage that it did not prove to be a very good catalyst as compared to the metals in use from the transition elements group of the periodic table. This
is because gold is too inert. But NPG has found to have these properties better than bulk gold. We will describe the behavior of NPG in carbon monoxide and hydrogen peroxide environments.

**CO oxidation [16]**: Silver-Gold alloy has been preferred for use in dealloying due to similar structure and lattice parameters of both elements. It is seen that without any external support like silicon or carbon or any other metal coating, NPG itself acts as a catalyst and converts CO to CO₂ even for longer reaction times as seen in Figure 4:

![Figure 4: 98% conversion of CO to Carbon dioxide. [16]](image)

Dealloying process is a contest between the rate at which Ag dissolves into the solution and the rate at which Au diffuses with its own species to give rise to a crystalline structure, in the presence of HNO₃. Since some oxygen is present in the environment, there are chances of the surface getting oxidized to some gold oxide particles. Effect of varying temperature on the activity was also measured[16] and NPG was still found to be active, as in Figure 5.
Haruta et al. [17] also proved that not only is this material active at absolute temperatures but also below 0 deg C.

**H$_2$O$_2$ reduction** [18] The difference in catalytic activity in NPG compared to the parent material exists due to the lack of reaction sites on the surface of the alloy, along with the strong chemical bonding which does not allow adsorption. The existence of rough edges has enticed the researchers for chemical impetus. Oxidation and reduction peaks decreased as the pore size increased indicating clearly the difference in both materials. Reduction of hydrogen peroxide has been directly measured as a current factor[18], which is the result of a rotating ring disc experiment as shown in Figure 6.

Figure 5: Activity at two different temperatures. [16]

Figure 6. The plot shows conversion of hydrogen peroxide and oxygen and difference between bulk gold and NPG.[18]
Properties that contribute to such performance are the curved ligaments on morphology and crystal structure but this plays its part only when there is oxide on the surface. The surface stresses leading to compression are important for really small ligaments but the factor that gave these results here[18] is the bonding between the gold atoms that is low, allowing the elements to get adsorbed.

1.3 Fabrication Techniques

The existing techniques of supplying voltage, longer etching time, varying concentration, lowering the temperature and pre and post annealing is described for understanding.

*Supplying External Voltage:*

The research conducted by Senior and Newman [20], demonstrates the synthesis of NPG by controlling the voltage externally and also controlling the Au content in the alloy. The effect of this voltage on the material is evident on Au alloy as in Figure 7.

![Figure 7. Effect of external potential application.[20]](image)

The formation of oxide might not affect the catalysis so much, but it does affect the ability of the bottom layers to get dealloyed and relieving of the surface stresses. This happens as
the gold on the surface combines with oxygen and is not able to gel with the other gold atoms to form a conductive layer. The orientation of the surface particles is not in the state of minimum energy and hence the surface gets stressed although. The ends of the material are able to form clusters. The applied potential thus needs to be above the potential at which the gold oxide dissolves to leave back pure gold atoms. Figure 7 also explains this in different concentrations of Au in the alloy. Higher the gold content, the applied potential needs to be higher so as to achieve same current density. More current value is observed as the material starts to assemble in groups thus forming a continuous circuit.

The value of initiating potential, beyond which oxide starts to dissolve has not been found to be exact but a range of values has been found owing to the formation of different pit like structures[4].

_Longer Etching Time:_

Figure 8 shows external voltage effect along with time. The cracks seem to have reduced due to the potential applied for longer duration.

![Figure 8](image-url)  
*Figure 8. The effect of 1.1V applied for 30 seconds on the material used. [20]*
Figure 9. Current Density versus Etching time, the current density decreases as more Ag gets dissolved in the solution. [20]

It is important for the voltage to be just around the particular potential at which the oxide gets removed. Also the temperature needs to be higher so as to relieve thermal stresses. The alloy content of Au and Ag also play an important part. Heat treatment effects are discussed in Pre and Post Annealing.

Varying Concentration:

The electrolyte temperature is ambient [21]. It is also mentioned that there is not much volume change [22] which means that the Au atoms did not move when they joined each other and formed a bi-continuous structure. Hence, there was very minimum cracking observed on the 14nm morphology by the researchers[22]. The sample of 30%Au was heat treated first to relieve internal stresses. A potential was applied for the thicker material. The dealloying was carried out at a constant current rather than a constant voltage. The two steps involved changing the nitric acid concentration and had no volume change shown in Figure 10 and minimal cracking in Figure 11.
Figure 10. This shows no change in volume for the material when it is dealloyed in two steps. a and c are before dealloying and b and d are after.[21]

Figure 11. Minimal cracking was observed.[21] This helped to confirm that volume change was controllable.[22]

The most important step here was the selection of concentrations for the two steps along with the etching time. This material can be coarsened by heat treating after dealloying and hence tailored for utility.

_Lowering Temperature:_

When the dealloying is carried out at an ambient temperature, the pore size obtained will be smaller than the one attained by heating to the high temperature. This method will deal with real small pore size [7, 12], and doing this at low temperatures is not really easy as the Ag
diffusion has to be controlled. With increase in the time the material is kept in the solution, the pore size also increases. [23] The structure obtained at all conditions is still a double continuous layer with alteration in pore size. The nanopore size follows the following relation [24]:

\[ n \ln[d(t)] = \ln [K \cdot t \cdot D_s] \]

Where diffusivity \( D_s = D_0 \exp (-E/RT) \) and \( d(t) \) is pore size at etching time \( t \); \( k_0, K, \) and \( D_0 \) are constants and \( k_0 = KD_0 \); \( n \) is coarsening exponent; \( R \) is the gas constant; \( T \) is the etching temperature; and \( E \) is the activation energy for the nanopore formation and coarsening.

The coarsening exponent \( n \) is obtained from plotting the \( \ln(d(t)) \) vs \( \ln(t) \) shown in Figure 12.

![Figure 12](image)

**Figure 12.** This graph verifies that with increase in temperature, the nanopore size increases. The process of coarsening is the same at all temperatures. [24]

Calculating \( n \), the value comes out to be around 3.5, this shows that the surface has reached its minimum energy as the kinetic parameter for that is about 4.

\[ \ln(d(t) = h) / h \] and \((RT)^{-1}\) implies that the activation energy for the dealloying and coarsening is to be 63.4 kJ/mol. This indicates that diffusion controls both dealloying and coarsening as in nitric acid, the diffusion would occur at about 55kJ/mol [24].
Pre-annealing [25]:

It causes plasticity to increase due to consistent enhanced deviation of planes from their original positions at temperatures than greater than about 200 deg C. It does decrease the residual stress but this complete behavior can be explained if the length of the material changes which indicates volume redistribution. Pre-annealing does not really affect the pore size obtained after dealloying, so it does relieve prior stresses but no mechanical properties after dealloying get affected. The plastic deformation obtained in the planes still remains unaccounted and unexplained. The basis for changes in volume, the thickness or change in any one plane may just be due to filling up of some voids created during manufacture of the material. Hence the material is thermally stable after it has been annealed, the dealloying hence is more homogenous and will have less defects.

Post-annealing [26]:

As has been discussed this will help to coarsen the nanopores. But this effect is usually limited to thin films or samples with less thickness. For materials that are thicker, it might lead to ligament failures as there is a considerable distance between the upper and lower layers to maintain the continuous structure at high temperatures. If this temperature is beyond the melting point of gold at that temperature then failure is bound to occur. This can be found by Lindeman melting model [42] which will relate the pore size to the temperature at the desired pressure. But in both cases, whether it is a thin film or a thicker sample, the thermal stresses have increased and these might significantly affect the actuator properties, so it is better to do pre-annealing rather than post-annealing, except when the pore size needs to be increased for the application.
Chapter 2

2. Overview

2.1 Problem Description

NPG has been studied extensively in the recent past. Each study was around a specific parameter. It has been found that the pore size in this material can be carefully tailored by directing the formation criteria accordingly. A complete model comprising all parameters is required. How each one affects the other and whether there is interaction among them and how all of these happened are interesting topics. Understanding these issues will help in designing the material according to applications. The aim is to contribute to the existing studies, a model that will give the pore size when variables of factors affecting the morphology are changed. This will be verified by extant data.

2.2 Approach

The Ishikawa diagram approach was used to find that there are mainly eight factors that the pore size depends upon as is seen in Figure 13.
Out of these, we will be looking at alloy composition, etching time, voltage supplied and heat treatment from the previous studies by research groups and try to find a correlation amongst them. We also tried to put the effect of temperature and concentration within the scope of this thesis. More work is being done in the Nanotechnology lab at the University of Toledo, Ohio. The design of experiments tool has been discussed next.

2.3 Analysis of Variance (ANOVA)

Design of Experiment (DOE) is known as a structured, organized method for determining the relationship between factors that affect a process and the output of that process. In this
method, a strategy is set-up where controllable variables are changed to obtain the correlation between and effect of individual factors in systematic way. To achieve the same, we employ the statistical tool of Analysis Of Variance or ANOVA [14].

ANOVA is a statistic tool which assesses the variance of experiments and gives a model that will best fit the results so that the behavior can be generalized.

The factors that significantly contribute to the morphology change and ultimately finding a fitted model to best predict the optimum design for the purpose of various applications will be reviewed.

Using ANOVA [29]:

Simple tools in comparative testing of models like hypothesis testing, t-test, paired comparisons etc. can always be employed to test design conditions for an experiment, but when we are trying to deal with a number of factors, where their interaction might also be important; the significance of a design tool that can deal with all these becomes necessary. The Analysis of Variance comes into picture here.

A design that has k factors, each having 2 levels is represented as 2^k design. Thus we assume here that these 2 levels are the maximums and minimums of the factors and the relation between varying the factor and the result is linear. This is so because this is the first of its kind analysis and has we are trying to establish a relationship based on varying manufacturing parameters rather than reaction kinetics and heats. If we knew there existed proportionality, then we could have used each factor having 3 levels or more. The k factors can be either qualitative like high or low; or quantitative i.e. having numeric values. These are called factorial designs and are based on 3 assumptions:
1. All factors are fixed; this was concluded from the fact that all the papers on fabrication of NPG spoke on these factors as the conditions. Though the value changed for these, the factors in all papers remain the same.

2. The designs are completely randomized; we have ensured this by taking readings from different research sources.

3. The usual normality assumptions are satisfied which means the distribution of residuals is normal.

Normally, the readings obtained are replicated to confirm all values but for our purposes, we will have a single replicate experiment.

The number of runs / observations of the experiments accordingly increases to $2^*2^*2^*\ldots k$ times. For a very large number of $k$, the number of runs required for a complete replicate design rapidly outgrows most resources available. If we are able to reasonably assume that some of the factors and their interactions are negligible, then it becomes easy to obtain the information on the main effects by running only a fraction of the complete experiment. The successful design of a fractional factorial experiment is based on three key ideas [14]:

1. The Sparsity of Effects Principle – When there are several factors responsible, then the experiment is mainly driven by a few main effects and low order interactions.

2. The Projection Property – Fractional factorial designs can be projected into larger and stronger designs in the subset of significant factors.
3. **Sequential Experimentation** – It is possible to combine runs of 2 fractional factorial experiments to obtain one large design of all effects and interactions.

In this work, we will use all the analysis techniques mentioned above in ANOVA to get the optimized result.

First, a fractional design with main effects and one generator will be developed so that only a part of the experiment needs to be conducted to obtain reasonable results. This will be the screening experiment. Finally the graphs give us the required insight into the experiment due to the response surfaces and the regression model. To find the direction of potential improvement we will employ the Method of Steepest Ascent.
Chapter 3

3. Results

3.1 Design of Experiment Results

We have considered that alloy composition, etching time, voltage and heat treatment are the major factors governing pore size. It is possible that the factors considered have little effect on the pore size or the response. The pore size is analogous to the ligament size here, as they are assumed to be the same for simplicity. Our interest is in the surface area and the vacancy due to concentration over particular applications. We may choose to use ligament in some places and apply the same model with the only response being the ligament size rather than pore size.

It is preferred to use a design model of higher resolution for better accuracy than the total number of factors. We will thus assign the resolution $R = 5$, as $R-1$ are the significant ones.

The design is a fractional factorial rather than a full factorial so as to reduce the number of runs. In such cases, to compensate the effect of full factorial, we alias the factor effects. Also, there will be one factor that will take into account all factors together called the generator. The generator for the fractional factorial part can be taken as ABCDE and the defining relation as $I = ABCDE$ (high level). The alternate factorial is $I = - ABCDE$ (low
level). Using the relation, we note that each main factor is aliased with a four factor interaction: \( A = BCDE \); \( B = ACDE \); \( C = ABDE \); \( D = ABCD \).

Thus,

\[ l_A = A + BCDE; \]
\[ l_B = B + ACDE; \]
\[ l_C = C + ABDE; \]
\[ l_D = D + ABCD. \]

Also, every 2 factor interaction is aliased with a 3 factor interaction like \( l_{AB} = AB + CDE \).

Thus the design is resolution V. This should provide a very good insight into the effects and interactions. The various factors and their respective levels have been shown below in the Table 1:

**Table 1: FACTORS AND LEVELS.**

<table>
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<th>Level 1(HIGH)</th>
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<tr>
<td>Ag percentage in alloy</td>
<td>A</td>
<td>30%</td>
<td>40%</td>
</tr>
<tr>
<td>Etching Time</td>
<td>B</td>
<td>5 h</td>
<td>100 h</td>
</tr>
<tr>
<td>Voltage</td>
<td>C</td>
<td>0 mV</td>
<td>600 mV</td>
</tr>
<tr>
<td>Heat Treatment</td>
<td>D</td>
<td>298 F</td>
<td>873 F</td>
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</tbody>
</table>

Total 4 FACTORS 2 LEVELS EACH
The selection of factors has been obtained from reference papers. The values for these data points are also from the same papers.

The relations have mostly been found to be linear, except if two readings are taken in the same experiment like in a multistep dealloying method or the etching case explained as follows: the case of etching time readings for an experiment at 5 hours and 100 hours; which has been carried out in total for 120 hours; will not follow will probably not be linear.

Based on this fractional factorial design, response surface and regression model will be developed along with future work. This will also help us to conclude if the relations are actually linear and if the assumptions are right.

The data entered into the Design Expert 7.1 and 8 is as follows and was referred from [23 through 50] and is shown in Table 2.
Table 2: Data into Design Expert:

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Design Expert 7.1 Results:

Aliases:

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**Effects:**

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<td>Model D-D</td>
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<td>Aliased ACE</td>
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Aliased CDE Aliased
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Aliased ABDE Aliased
Aliased ACDE Aliased
Aliased BCDE Aliased
Aliased ABCDE Aliased

Lenth's ME  504.204

Lenth's SME  1023.61
Response 1 PORE SIZE PARAMETER

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

<table>
<thead>
<tr>
<th>Source</th>
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<th>df</th>
<th>Mean</th>
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<th>p-value</th>
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<td>1.441E+005</td>
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<td>4.403E+005</td>
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The Model F-value of 16.87 implies the model is significant. There is only a 0.06% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, C, D, E, AC, BD, CE are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

R-SQUARED, STANDARD DEVIATION

<table>
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<th>Std. Dev.</th>
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<th>R-Squared</th>
<th>0.9507</th>
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<td>Mean</td>
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<td>Adj R-Squared</td>
<td>0.8944</td>
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<tr>
<td>C.V. %</td>
<td>25.42</td>
<td>Pred R-Squared</td>
<td>0.7425</td>
</tr>
</tbody>
</table>

PRESS 3.122E+005   Adeq Precision 13.641

The "Pred R-Squared" of 0.7425 is in reasonable agreement with the "Adj R-Squared" of 0.8944.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 13.641 indicates an adequate signal. This model can be used to navigate the design space.
Figure 14. This graph shows the effect of % of Ag in the alloy on the pore size. Higher Ag concentration shows larger pore size.

Figure 15. The effect of heat treatment on the pore size is shown. As has been shown in experimental results, the ligament sizes increase upon annealing and leads to coarsening of grains. This graph shows that at no heat treatment i.e. at -1 level, the grains are finer; whereas the size increases upon annealing for 2 hours at 873K.
Figure 16. The graph shows the difference between free corrosion and potentiostatic dealloying. When there is no voltage supplied, the ligaments are coarse for the same amount of time in the solution whereas upon supplying a high voltage for this system of 600mV, the ligaments are finer.

Figure 17. The effect of etching time or the period of time for which the leaf is in the solution, whether free corrosion or potentiostatic, is affects the grain size as shown. The greater the etching time, the coarser is the grain.
As Figure 18 explains, most of the data lies on the line; but there are some outliers. These are A, B, C, D, E, AC, CE. Presence of these can greatly affect the model. Since we are already doing a careful investigation by plotting standardized effect, it is clear that these outliers will not be discarded, as they might turn out to be desirable.

Figure 19. Pareto Chart
The Figure 19 compliments the normal probability graph.

As predicted from the ANOVA table, the above mentioned are significant factors and affect the response greatly. Out of these, we have seen the single factors effects for A, B, C, D, and E.

We will now look at the interaction graphs for AC, CE. Also, since the ANOVA table and the above graph mention BD being significant, we will analyze that too.

Figure 20. Interaction plot for Ag% in alloy and Voltage applied. Smaller pores are obtained by increasing the Ag in the alloy with decrease in the voltage applied.
Figure 21. Interaction plot for Ag% in alloy and all the other factors. Smaller pores are obtained by increasing the Ag in the alloy along with decreasing all the other factors.

Figure 22. Interaction plot for etching time and heat treatment. Pore size increases with increase in etching time with heat treatment process.
Figure 23. Interaction plot for Voltage applied. And all the other factors taken together. Pore Size decreases with increase in voltage with a simultaneous increase in all the other factors.

The difference in slopes of the interaction plots show a definite interaction that exists between factors. Also, out of the other interaction graphs (not shown here), AB, AD, BE, CD are parallel and BC, DE are not significant. Another important conclusion is the fact the heat treatment is really a choice after the dealloying has been done. This has been proven by the Figure 22.

Model adequacy: Normality, Independence and non-constant variance

1) Normality Assumption: As most of the points lie on the line in Figure 24, the normality assumption has been verified.
2) Independence Assumption: As the graph in Figure 25 does not have a pattern, means the data points are independent of the time. Here the run number represents time.

3) Non Constant Variance: Since the non constant variance graph here in Figure 26 is structure less, this assumption has also been verified.
As all the assumptions have been verified, the model is adequate.

Regression model equation:

Regression model leads to the equation:

\[ Y(\text{pore size parameter}) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_5 + \beta_6 x_1 x_3 + \beta_7 x_2 x_4 + \beta_8 x_3 x_5. \]

These coefficients are calculated from the effect estimates and the values are shown in Table 3.
### Table 3. Coefficients from Regression Model.

<table>
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<tr>
<th>Factor</th>
<th>Estimate</th>
<th>df</th>
<th>Error</th>
<th>Low</th>
<th>High</th>
<th>VIF</th>
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<td>Intercept</td>
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<td>23.10</td>
<td>308.87</td>
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<tr>
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<tr>
<td>CE</td>
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<td>1</td>
<td>23.10</td>
<td>22.37</td>
<td>131.62</td>
<td>1.00</td>
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</table>
Final Equation in Terms of Coded Factors:

\[
(\text{PORE SIZE}) = +363.49 - 92.76 \times A + 165.8 \times B - 80.63 \times C + 96.13 \times D - 65.38 \times E + 73.12 \times A \times C - 68.01 \times B \times D + 76.99 \times C \times E
\]

3.2 Model Verification : Sample Calculations

Using research from groups who have published data, we will verify the accuracy of the model.

Hakamada et al[28,50] used 70% Ag in the alloy which is factor A, no potentiostatic dealloying which means C will be 0mV, 42 hours of etching time which equals B and post annealing was done at 200 deg C or 473 K. E will tend to 0 due to B being 0. The pore size they obtained was approximately 5 nm.
L.H.S of the equation = Pore size = 5 nm

R.H.S of the equation =

\[ +363.49 - 92.76 \times 70 + 165.8 \times (42 \times 60 \times 60) + 96.13 \times 473 \text{(this is in K)} - 68.01 \times (42 \times 60 \times 60) \times 473 = 4.86\text{nm} \]

Percentage error = 28%

Hodge et al[8] used 75% Ag in the alloy which is factor A, potentiostatic dealloying which means C will be 6mV, 72 hours of etching time which equals B and post annealing was done at 473K. The pore size they obtained was approximately 940 nm.

L.H.S of the equation = Pore size = 940 nm

R.H.S of the equation =

\[ +363.49 - 92.76 \times 75 + 165.8 \times (72 \times 60 \times 60) - 80.63 \times 0.6 + 96.13 \times 473 \text{(this is in K)} \]
\[-65.38 \times (75 \times 60 \times 0.6) \times 473\] 
\[+73.12 \times 75 \times 0.6\] 
\[-68.01 \times (72 \times 60 \times 0.6) \times 473\] 
\[+76.99 \times 0.6 \times (75 \times 60 \times 0.6) \times 473\]

\[= 1005.8 \text{ nm}\]

Percentage error = 7%

D. Lee et al[54] used 62.6% Ag in the alloy which is factor A, no potentiostatic dealloying which means C will be 0 mV, 45 min of etching time which equals B and post annealing was done at ambient temperature. The pore size they obtained was approximately 20 nm.

L.H.S of the equation = 20 nm

R.H.S of the equation =

\[+363.49\] 
\[-92.76 \times 62.6\] 
\[+165.8 \times (45 \times 60)\] 
\[+96.13 \times 298 (\text{this is in K})\] 
\[+73.12 \times 40 \times 0.6\] 
\[-68.01 \times (45 \times 60) \times 298\]

\[= 12.1 \text{ nm}\]
Percentage error = 39.5%

Within limits of experimental error the values are close to expected results. Hence the model is verified.

Randomly choosing the last run from Table 2 to verify the model again[49]:

L.H.S of the equation = 440 nm

R.H.S of the equation =

\[+363.49 -92.76 \times 40 +165.8 \times (100\times60\times60) -80.63 \times 0.6 +96.13 \times 741\text{(this is in K)} -65.38 \times (40\times[100\times60\times60]\times0.6\times741) +73.12 \times 40 \times 0.6 -68.01 \times (100\times60\times60) \times 741 +76.99 \times 0.6 \times (40\times[100\times60\times60]\times0.6\times741)\]

= 409.9 nm

Percentage error = 6.8%
The model has been verified for runs on the ANOVA table. If we closely observe the percentage error, it is lower when the pore size was high and higher when pore size was smaller.
4. Simulation

4.1 Simulation Results

With the properties of gold available from the research papers, we decided to simulate the results from the available software.

The work here proposes that there might be difference in the sensitivities of NPG and bulk gold. We would like to study the difference with the help of two softwares: ADAMS and Solid Works. The best way to test sensitivity is to model the material as a cantilever beam; the evaluation of sensitivity would be done by deflection obtained from Elastic Beam Theory:

Figure 27. A cantilever beam subjected to a point force at the end
From equilibrium condition, we know that at the support there will be a resisting force –FL and a vertical upward force F.

At any point x, the moment is:

$$F(x - L) = M_x = EI \frac{d^2y}{dx^2}$$

The difference in properties required for the software has been shown. Solid Works uses Gold from its library and NPG should be added to the library as a custom material before using Simulation Xpress.

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<th>PROPERTY</th>
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<th>GOLD</th>
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<td>11GPa</td>
<td>78GPa</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.2</td>
<td>0.44</td>
</tr>
<tr>
<td>Density</td>
<td>6.9kg/mm$^3$</td>
<td>19.6kg/mm$^3$</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>2.6e$^{10}$ N/mm$^3$</td>
<td>2.6e$^{10}$ N/mm$^3$</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>78000000 N/m$^2$</td>
<td>103000000 N/m$^2$</td>
</tr>
<tr>
<td>Yield Strength</td>
<td>111MPa</td>
<td>112MPa</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>323 W/(m-K)</td>
<td>300 W/(m-K)</td>
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</tbody>
</table>

Table 3. NPG and Gold properties
Figure 28. The cantilever beam modeled in ADAMS and Solid Works. Material properties were selected as Gold and NPG. The first view is the front view and the second one is the deflected isometric view.
a.

b.
The cantilever beam in ADAMS was subjected to external loading conditions under 10N. a) in a single step, b) in 2 steps, c) in multistep. These graphs clearly demonstrate the fact that NPG is more sensitive than Bulk Gold.

Due to the fact that the rotation of the beam is in 2 degrees of rather than one required for cantilever beam, the deflection ratio could not be trusted in ADAMS. The reason for this is that the joint available to model cantilever in ADAMS is a revolute joint and this was closest possible to the actual behavior. The other possibility was to use a universal joint which gave one DOF but no bending. Due to shortcomings of ADAMS, we will try to do the same thing in Solid works.

Figure 29. Blue Line: NPG  
Red Line: Bulk Gold
Analysis using Solid works:

Figure 30. Von Mises yield criteria showing maximum stress points. Stress points were same for NPG and Bilk gold due to the geometry of the beam.
The maximum deflection turned out to be 45799 times higher for NPG than bulk gold. We did analytical application of beam theory and the ratio was 20.15. This variation showed that the beam followed non-linear beam theory.

Solid Works SimulationXpress design analysis results are based on linear static analysis and the material is assumed isotropic. Linear static analysis assumes that: 1) the material behavior is linear complying with Hooke’s law, 2) induced displacements are adequately small to ignore changes in stiffness due to loading, and 3) loads are applied slowly in order to ignore dynamic effects.
4.2 Mechanical Properties

Smaller ligaments demonstrate greater strength. This was obtained from nano indentation tests[44]. The reason for this is that bigger ligaments allow greater contact depth, more so if the NPG has been dealloyed [46]. The NPG is believed to form a single crystal structure compared to the bulk polycrystalline structure and hence the yield strength of the ligaments is greater than the bulk gold particles. We have already seen in the fabrication section.

![Graph showing yield stress decreasing with increase in diameter and NPG strength despite structure difference.]

Figure 32: a) shows yield stress decreasing with increase in diameter and b) shows that NPG is also very strong despite the structure difference.[61]

To evaluate the Young's modulus,[50] researchers have employed different theories. One of them is the concept of buckling of thin films. It is postulated that if this NPG film is supported by a substrate, then the load required to cause deflection here would be a difference between the force to bending the film and that of deflecting the substrate. The buckle on the film is taken to be sinusoidal and this can then be related in an equation to the
Young’s modulus and Poisson’s ratio and thickness to derive the modulus value. Although this is valid for certain situations such as low strain, film thickness and modulus smaller than the substrate etc., it has still been found to be very accurate in that range.

A graph describing ligament size increase causes the Young’s modulus to decrease is shown in Figure 41.

![Figure 33: Plot showing ligament size affects the elastic modulus.[50]](image)

The modulus can be related to squares of density function which might decrease due to change in volume of the material. This would lead to a significant lowering of modulus as it is directly proportional to the square of the density. Methods have thus been devised, such as the multi step dealloying so as to limit the volume change.

Fine NPG is considered stiff as it is comprised of smaller and thicker ligaments that act as beams and hence give more resistance to bending.[50] This can further be evaluated using the same simulation that we did for our studies.
Thermal cycling of NPG revealed that unlike the original alloy film where the stress changes with changes in geometry such as thickness, here stress depended on the ligament size. [53] It has been shown that smaller ligament sizes influence the strength more as it has more nucleation and stronger bonding.
Chapter 5

5. Conclusion

5.1 Future Work

NPG has been found very useful and statistically analyzing the dependency on various factors before conducting the experiment gave us the exact conditions that we needed to carry out the experiment, which will be done under the guidance of Dr. Gan at the University of Toledo, Ohio. We also tried to achieve the effect of concentration and temperature of electrolyte but that was not possible because of the material did not get dealloyed in the experimental set-up and hence has not been shown here. It is recommended to use a support like silicon chip to mount the gold alloy leaf, such that buckling does not occur as soon as the leaf is exposed to the environment. Also, it prevents the problem of the support getting melted in strong solutions. The experiment and the model can be verified by carrying out more experiments which was beyond the scope of this work.

A Design Expert model can be created including the concentration and temperature of electrolyte as 2 more factors and this model will thus be able to give us all important effects for the structure of NPG. However, this will still assume the relationship between data points to be linear till groups carry out experiments to verify the same.
As is seen from the simulation graphs, ADAMS was beneficial as it made comparison of two materials easy and the results could be obtained for various changes in input. Solid works was then employed to test the same, NPG was definitely more sensitive by a factor of 4.7. This can be employed to see if the stiffness of NPG varies with ligament size.

The mechanical properties that we concluded from simulation matched the examinations of most papers, but more work can be done to quantify the difference and establish relations, with a factor that includes the theoretical calculation with the actual loading response.

5.2 Potential Applications

Fuel Cells have attracted attentions for more than a century ago due to the fact that they employ the process of efficiently converting the energy from chemical reactions into usable electric power. Typically, a fuel cell comprises an anode, a cathode, and a membrane to allow the exchange of protons and electrons. Oxygen passes over one electrode to oxidize the fuel while generating current in a direction opposite to the flow of electrons.

\[
\text{Anode Reaction: } 2\text{H}_2 \Rightarrow 4\text{H}^+ + 4\text{e}^- \\
\text{Cathode Reaction: } \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \Rightarrow 2\text{H}_2\text{O} \\
\text{Overall Cell Reaction: } 2\text{H}_2 + \text{O}_2 \Rightarrow 2\text{H}_2\text{O}
\]

The membrane between anode and cathode has the functions of providing a number of sites where chemical reactions can occur, acting as a catalyst where the chemical reaction temperatures are low and so they provide a path of least resistance for the activation energy, be good conductors of electricity like metals with least wear and tear properties with high thermal stability and not being volatile and lastly, provide a partition between liquid and gas phases inside the cell. Fuel cell stacks are combined together in series or parallel ways to give either high output voltage or large current.
To this day, there exist some problems that prevent large scale applications. These are:

1. Effective choice of all FC (Fuel Cell) materials.
2. Hydrogen Solutions: Right choice of reforming technology.

The generation of electricity from a fuel cell involves the following major steps:

a. Fuel reforming: it involves a readily available fuel like ethanol, methanol or natural gas and conversion of which to hydrogen occurs. Least expensive method is the steam methane reforming (SMR) in which the endothermic reaction occurs in the temperature range of 750-800 deg

\[ \text{CH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4 \text{H}_2 \]

We need to employ a shift to convert the CO produced due to partial combustion of a certain part of the HCs, to be reduced to a very low ppm level so that it does not poison the Fuel Cell. This can be achieved using a NP catalyst or an NP membrane.

Polymer Exchange Membrane Fuel Cell operate at the lowest temperature which is the distinguishing factor as the input to the FC stack need not be heated, which also ensures higher thermal efficiency due to less losses. The schematic of working principle of PEMFC is shown:
Figure 34. Working principle of a PEMFC. Hydrogen enters the anode, gets oxidized and electrons travel through the bulb to the cathode where air enters with oxygen and gets reduced. Water and heat are by-products of the reaction.

Figure 35. The flow of electrons and protons and generation of current. [37]
SMR (Steam Methane Reforming) is used with this kind of fuel cell and hence leads us to the next step.

b. The Hydrogen generated in the first step has CO with it which is poison to the fuel cell. That is why H₂ and CO gaseous mixture has to be purified by some means, usually passing through a catalyst that has a high surface area to increase reaction sites and is corrosion resistant accomplished by Pt coating. This occurs in a Shift Reaction in an exchanger so that the temperature of syngas coming out decreases.

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\]

c. It then goes to a vessel that electively oxidizes the CO in an adsorption reaction.

d. The H₂ from the second step needs to be about 99.99% pure or even more to be fed into the fuel cell that involves a cathode and an anode and passing of electrons for generation of electric power. This happens at a better efficiency if the electrodes are porous and non-reacting, so the use of Pt (Platinum) is again, in effect.

These steps have been put in a process flow as follows:

![Figure 36: Steps in Hydrogen Solution: Reforming with different fuel cells.][13]
The FC stacks have to be designed according to hydrocarbon fuel inlet. According to previous research, it has been seen that concerns for FC components have been the electrodes and their transport properties, which in turn depend upon the area subjected to the electrolyte hence available for the electron transfer. This is possible with materials that have low resistance to current flow, more corrosion resistance and less thermally affected material.

For PEMFCs, the biggest challenges lie in choosing appropriate:

i. Electrochemical catalyst.

ii. Electrodes or Bipolar plates with metal coating rather than just carbon elements as they have less conductance and have been used till today.

Pure Pt catalysts and coatings used initially had certain shortcomings like inability to sustain a large CO percentage, thereby reducing the overall efficiencies. The catalysts were then modified by alloying Pt with other metals [26], but these also had issues of stability during the test runs with H₂ and O₂ for longer duration and so NPG was explored.

*Adsorbents*[11]: High surface area, capability of discerning and adsorbing elements to the surface, forward kinetics of reaction along with good mechanical properties and high fatigue life make NP materials an apt choice for the purpose. These are generally used for emissions from industries and automobiles for removal of toxic gases.

*Sensors* [11]: The response to stimulus is high due to high surface to volume ratio. The stimulus can detect changes in atmospheric conditions like vapor, harmful gases, photons
etc. These might be used in biosensors [24] to test or sense DNAs and proteins etc. These materials can detect changes in chemistry such as an acidic environment and acknowledge that as an electric signal.
References


    


15. www.wikipedia.com


29. Class Notes 2008-2009, Dr. Zhang, University of Toledo, Ohio.


38. [www.howstuffworks.com](http://www.howstuffworks.com)
39. Templates for fish bone diagram: http://www.isixsigma.com/library/content/t000827.asp


44. Conversion charts online.

45. www.australweight.com


47. www.xenosystem.com

48. www.als.com


57. Dynamics Notes 2008-2009, **Dr. Elahinia,** University of Toledo, Ohio


59. **Design Expert 7.1 and 8.0 software.**

60. **Graph software.**
61. ADAMS software.

62. Solid works 2009 software.

63. Notes on Nanotechnology 2008-2009, Dr. Gan, University of Toledo.