Electrical Conductivity of Electroless Nickel/YSZ deposition for SOFC anode

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Abstract. The paper discusses on the electrical conductivity on nickel-yttria stabilized zirconia (Ni-YSZ) deposition for solid oxide fuel cell (SOFC) anode. The work measures the thickness of Ni-YSZ deposition onto substrate and the electrical conductivity of the anode of SOFC. The thickness of deposition is measured using digital micrometer while the conductivity is obtained by measuring resistance using Fluke multimeter. The factors in this work are particle size and particle condition and using Taguchi method to design the experiment in Minitab 19. It was found out that optimal parameter for high thickness of deposition and high conductivity is nano particle size and uncoated particle condition. The sample using optimal parameter were measured of its conductivity in SOFC environment using furnace up to 700°C. It shows that the optimum condition for SOFC anode is at 700°C to achieved high electrical conductivity. The electrical conductivity performance of Ni/YSZ anode fabricated by electroless nickel deposition was found out comparable to previous study.

1. Introduction
A fuel cell is a device that, through a chemical reaction, generates electricity. Each fuel cell has two electrodes, the anode and the cathode, respectively. The electricity-generating reactions take place at the electrodes. Each fuel cell also has an electrolyte that carries electrically charged particles from one electrode to the other, and a catalyst that accelerates electrode reactions. Solid oxide fuel cell (SOFC) can be divided into tubular and planar design [1].

Hydrogen is the main fuel, but fuel cells do require oxygen. One of the main appeals of fuel cells is that they generate electricity with very little emissions – much of the hydrogen and oxygen used to generate electricity eventually combine to create an innocuous by-product, namely steam. The chemical reactions that generate this current are the keys to how a fuel cell functions. Each type of fuel cell has advantages and disadvantages compared to the others, and none is yet cheap and efficient enough to widely replace traditional means of generating electricity, such as coal-fired, hydro-electric or even nuclear power stations.

A single SOFC cell is a construction layers of electrolyte, cathode and anode. In SOFC anode, the most vastly used material is Ni/YSZ. The typical working temperature for SOFCs is usually range between 600 °C to 1000 °C. However, operating on very high temperatures i.e. 800–1000°C, SOFC will reform used fuels inside the fuel cell itself without the need for external reforming or a metal catalyst [2].

Due to these high working temperatures most hydrocarbon fuels, including natural gas, biogas, and coal gas, etc., can be reformed directly within the SOFCs. These high operating temperatures,
however, often allow the carbon-containing compounds to break their reaction. In the case of natural gas-fuelled SOFCs, both methane cracking and CO disproportionation will result in carbon deposition on SOFCs' Ni/YSZ anode, resulting in degradation of quality and even SOFC damage [3]. Thus, most recent work on SOFCs are working on methodologies for inhibiting carbon formation in SOFCs due to the adverse effect of inhibiting carbon formation. It stated that criteria for anode SOFC is composition of synthesised Ni–YSZ cermet at 33wt% Ni and 67wt% YSZ with relative density of 70% and electrical conductivity $10^{-2}$ S/cm at 700°C [4].

In this paper, the purpose is to deposited Ni-YSZ anode of SOFC to test the electrical conductivity. Ni-YSZ are used as a material for anode to be prepared for the coating process by using appropriate bath agitation methods. The anode formed by co-deposition of electroless nickel was tested for its electrical resistance and conductivity output measured using a 2-point probe in simulated SOFC environment.

2. Methodology

8 percent yttria stabilized zirconia powder with micro and nano particle sizes used in this study. Both non-proprietary formulations are formulated with high purity deionized water and AR grade chemicals. Schloetter Company Ltd manufactured the electroless nickel chemicals under Slotonip's Tradename 2010 and developed a bright mid-phosphorous (6–9 percent) deposit of nickel. AlfaChimici developed the sensitisation and activator solutions under the tradename of Uniphase PHP. A 27 x 21 x 1 mm ceramic tile was used as a substrate. In order to increase its conductivity and catalytic characteristics, the anode needs pre-treatment to reduce NiO/YSZ to Ni/YSZ [5]. The substrate of ceramic tile is dipped into each pre-treatment solution for 15 minutes each with different temperature used as in Figure 1. This is followed by electroless co-deposition of nickel after the pre-treatment process sequence simplified in Figure 1.

![Figure 1. Schematic diagram of electroless nickel co-deposition.](image)

YSZ powder of 10 g/l was added to the electroless nickel solution and kept in suspension by mechanical stirring. The solution was warmed and the temperature was kept at 89°C for 60 minutes using the Fisher hotplate magnetic stirrer. All plating operations are carried out within 1 hour of the preparation of pre-treatment chemistries to mitigate the possible effects of chemical degradation. A set of 32 samples were used for Taguchi design of experiment. There are 2 factors at 3 level each giving to L9 orthogonal array. The 2 factors are particle size and particle condition. Particle size was varied from nano size (below 1 micron), micro size (10 micron) and mixed size (mixture of nano and micro size particle at a ratio of 1:1). Particle condition was varied from uncoated, single Ni-coated layer and double Ni-coated layers.

Then the sample is measured for resistance to get the conductivity as the resistivity is inversely proportional to conductivity. This is the simplest method of measuring resistivity is by using 2-point probe. In this method, voltage drop $V$ across the sample; current through the sample $I$; cross-section area $A$ of the sample and the length $L$ of the distance between the 2 probes are measured. Then the resistivity is given as Equation 1 below:

$$\rho = \frac{VA}{IL} \quad (1)$$
3. Results and discussion

3.1. Analysis of thickness deposition

The deposition thickness of Ni-YSZ coating was measured and the average thickness was 10 microns. Table 1 shows the analysis of variance (ANOVA) and the p-value of the thickness deposition. From the data, it can be seen that particle size has insignificant effect on thickness of deposition as its p-value is 0.082 is higher than 0.05. On the other hand, particle condition factor has p-value 0.032 is most influencing factor.

| Source            | DF | Adj SS    | Adj MS    | F-value | P-value |
|-------------------|----|-----------|-----------|---------|---------|
| Particle size     | 2  | 0.000030  | 0.000015  | 5.00    | 0.082   |
| Particle condition| 2  | 0.000055  | 0.000027  | 9.17    | 0.032   |
| Error             | 4  | 0.000012  | 0.000003  |         |         |
| Total             | 8  | 0.000097  |           |         |         |

By using Taguchi, the optimal control factor setting can be identified by making the process varied from the noise factor. The signal to noise ratio measures how the response varies relative to the target value which in this experiment, the target was set as ‘larger is better’ to maximize the response of thickness deposition. The software used S/N = −10 *log(Σ(1/Y2)/n) for larger is better. The response for signal to noise ratio by using Taguchi design experiment shows delta value for particle size and particle condition 7.23 and 9.93 respectively. Therefore, particle condition is at rank 1 and particle size at rank 2.

Main effect plot for S/N ratio are shown in Figure 2. They show the variation of individual response with two factors used, particle size and particle condition. In the plot x-axis represents the value of each process factor and y-axis is response value. Horizontal line indicates the mean of the response. It used to determine the optimal design condition to obtain the largest thickness deposition.

![Main Effects Plot for SN ratios](image)

**Figure 2.** Main effect plot for SN ratios for thickness deposition

Referring to Figure 2, particle size and particle condition have direct effect on thickness deposition which means the smaller particle size and uncoated YSZ powder is noted as optimal condition for the maximum thickness deposition.
3.2. Analysis of electrical conductivity

The analysis of variance (ANOVA) estimates the significance of factor on electrical conductivity test. Table 2 shows that both factor, particle size and particle condition have p-value higher than 0.05 which mean they are both insignificant effect on electrical conductivity. This may happen because some samples have very low thickness thus lead to high resistivity and low conductivity due to the probe of multimeter touches the ceramic surface.

Table 2. ANOVA table for electrical conductivity.

| Source          | DF | Adj SS | Adj MS | F-value | P-value |
|-----------------|----|--------|--------|---------|---------|
| Particle size   | 2  | 613.1  | 306.5  | 1.11    | 0.414   |
| Particle condition | 2  | 2754.4 | 1377.2 | 4.98    | 0.082   |
| Error           | 4  | 1107.1 | 276.8  |         |         |
| Total           | 8  | 4474.6 |        |         |         |

However, referring to signal to noise ratio on electrical conductivity the effect of factors can be identified. The target was set as ‘larger is better’ as quality indicator for S/N ratio. The delta value for particle size and particle condition are 13.8853 and 48.1653 respectively. Thus, the particle condition is ranked 1 and particle size is ranked 2. It is clear that particle condition plays important factor on the electrical conductivity followed by particle size.

Figure 3 shows main effect plot for S/N ratio respectively prepared by Minitab 19. It is present when the different level of factors affected the desire characteristic differently. The main effect plot presents the response mean for each factor level connected by straight line. If the lines connecting the levels are not horizontal, indicates the presence of the main effect and each level of factor affect the characteristic differently. The lines connecting level of factors are not horizontal means each factor affects differently. The minimum value of S/N ratio is observed at particle size of mix and single coat particle condition.

Figure 3. Main effect plot for SN ratios for electrical conductivity

It is found that particle size and particle condition have effect on electrical conductivity which indicate that the nano particle size and uncoated YSZ powder is noted as optimal condition for maximum electrical conductivity.

3.3. Verification of optimum condition

Samples were prepared at their optimum condition for thickness deposition and high electrical conductivity at nano size particle dan uncoated YSZ particle. There were 3 samples prepared for an electrical performance test that was conducted in SOFC environment range 100°C - 700°C. The three specimens had different coating deposition thickness. Specimen 1 and specimen 2 have thickness
deposition of 12 microns and specimen 3 has 15 microns. The resistivity and conductivity plots for the three specimens are given in Figure 4 (a) and (b).

![Figure 4. Plot of (a) resistivity (b) conductivity against temperature](image)

This test is to verify the optimum condition achieved for electrical conductivity in SOFC environment. It shown that the conductivity increase with temperature and the optimum condition is at 700°C to get higher electrical conductivity. This trend is comparable to the conductivity test obtained by the anode fabrication for SOFC with other research [6].

4. Conclusions
The study has successfully fabricated anode of solid oxide fuel cell based on electroless co-deposition of ceramic and metallic materials and tested for electrical conductivity of the anode. The ceramic was used as the substrate and the material to be deposited to the substrate is Ni-YSZ. Two factors were varied in this work which is the particle size and the particle condition. Particle sizes used were nano, micro and mixed of nano and micro particles. The particle condition was uncoated, single coated and double coated nickel. The DoE responses were thickness deposition and electrical conductivity. The DoEs were also analysed by Minitab 19 software and it was found out the optimum condition for high thickness of deposition and high electrical conductivity involved nano particle size and uncoated particle condition. Then the optimal condition which was nano and uncoated were fabricated for three specimens and were verified for its electrical conductivity in SOFC environment.

5. References
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