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Morphological and Electrical Characterization of Nickel Oxide-Ytrria Stabilize Zirconia Thin Film Prepared Using Sol Gel Dip Coating Method

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Abstract: Considerable attention has been focused on solid oxide fuel cells (SOFCs) due to their potential for the most promising technologies for very high-efficiency electric energy. In the present work, the structure and electrical performance of NiO-YSZ anode, which were annealed at 600^{0}C were investigated. The dip-coating technique was used for preparing NiO-YSZ thin films on glass substrate. Atomic force microscopy (AFM) was used to observe the morphological structure and four point probe was used in order to analyze the electrical performance of the annealed films. The analysis showed that the NiO-YSZ anode annealed at 600^{0}C was successfully fabricated for SOFCs applications, due to minimum roughness and the minimum conductivity which is 0.05604, 0.02061, 0.01443 S cm^{-1} for the 1, 2 and 3 layers, respectively. Therefore, this NiO-YSZ anode is promising the future generation of SOFCs.

Keyword: Nickel Oxide-Yttria Stabilize Zirconia; dip coating; Atomic Force Microscopy; conductivity; solid oxide fuel cell.

1. Introduction

Solid oxide fuel cells (SOFCs) have pulled in extraordinary consideration in view of their high energy conversion efficiency, excellent fuel flexibility, and minimal pollutant emission. In any case, the general high working temperature (800– 1000˚C) of current SOFCs forces stringent prerequisites on materials that fundamentally increment the cost of SOFC innovation [1,2]. However, by reducing the operating temperature of an SOFC below 800˚C it gives merit to the cell which is it can reduce the degradation of cell components, improve flexibility in cell design, and lower the material and also for the manufacturing cost by the use of cheap and readily available materials [3,4]. Anode material requires being exceptionally electroconductive, adequately electrocatalytic, sufficiently permeable for proficient gas transportation, and thermal development perfect with other cell parts.

Considering cost and performance, the NiO-YSZ materials are still the most common anode for SOFC. This anode material is usually prepared by the mechanical mixing of commercial (Nickel Oxide) NiO and (Yttria Stabilized Zirconia) YSZ powders. Even though it is simple, it gives an appropriate rise to a non-uniform distribution of the Ni-phase in the cermets and hence poor performance.

Therefore, there are some options of wet chemical processes have been reported, such as sol-gel [5,6], complex formation with chelating agents, precipitation with buffer-solution of NH_4OH and NH_4HCO_3, coat-mix, liquid condensation process with thermoset polymer, combustion synthesis, spray pyrolysis of a slurry of YSZ in nickel acetate solution, and mechanofusion process. Other alternative processes such as vapor-deposition [7], a spray of wet powder were also reported. These efforts of methods have been focused either to prepare a homogeneous mixture of NiO and YSZ in nanoscale or to produce fine YSZ-covered submicron NiO composite powders.

In a previous study, nano-sized NiO conjugated on YSZ powder was composed of the NiO-YSZ composite powder. High performance and excellent tolerance for thermal and redox cycling were exhibited from the composite powder. Several of the recently investigated state that NiO and YSZ powders that being a homogenous mixture thus approach a promising characteristic for fuel cell electrocatalysts. Meanwhile, it is found

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that the presence of fine YSZ particles on the surfaces of NiO particles would significantly constrain the grain growth of NiO phase and show better homogeneity and performance than those by mechanical mixing, but has poor structural stability. In this paper, we present the roughness of the surface and the morphology of NiO-YSZ anode by atomic force microscope (AFM). The four-point probe also employed to study the conductivity of the deposited NiO-YSZ anode, annealed at 600˚C.

2. Materials and Methods

The substrate cleaning process is very important for thin film deposition. A glass with a dimension of 1 cm x 1 cm was cut and was placed in the beaker filled with acetone. The beaker was put into the ultrasonic cleaner (BRANSON 3510) around 20 minutes for the cleaning process. Next, the acetone was replaced with deionized water and again, the glasses underwent the cleaning process for 20 minutes. Finally, the glasses were dried using nitrogen gas or oven for the next step.

NiO-YSZ anode solution was prepared by the sol-gel method. 0.5 g Nickel Oxide – Zirconium (IV) Oxide Yttria stabilized (> 99%, Aldrich) was dissolved in 10 ml of acetylacetone. Among several solvents studied, acetylacetone was found to be the best in terms of stability of the suspension and deposition quality. The suspension was stirred on the hot plate for 2 hours before the processes of dipping begin.

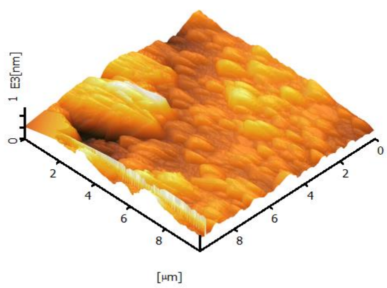
The treated glass substrate was placed in sample holder and dip into the solution for 2 minutes. The layer obtained on the substrate was dried at room temperature and the processes were repeated until 5 layers were deposited on the substrate. Finally, the sample underwent an annealing process at temperature 600°C for 1 hour using a furnace. The film morphology was characterized by using Atomic Force Microscopy (AFM) to find the surface roughness and grain size. Meanwhile, anode fabricated via sol-gel dip coating was tested in term of its electrical resistivity and conductivity performances measured using the four-point probe. A four-point probe was used to measure the sheet resistance and thus the resistivity and conductivity of the anode can calculate using the formula.

3. Results and Discussion

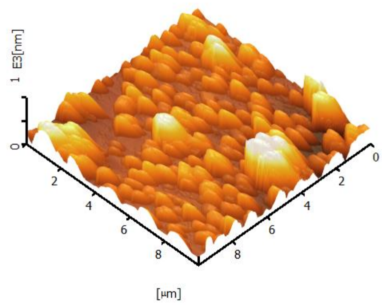
3.1 AFM Analysis

Fig. 1 shows the 3-dimensional images of NiO-YSZ films with different layer annealing at 600°C characterize from AFM. Morphological structure of the different thickness layer can be observed. AFM images of the anode surface revealed that the root mean square roughness for anode was slightly reduced if the film thickness increase, which is 159.8, 116.3, 108.1, 100.7 and 37.4 nm. The film becomes thinner as the more layers were deposited on the substrate. It shows that the surface roughness decreases if the thickness of the thin film increases.

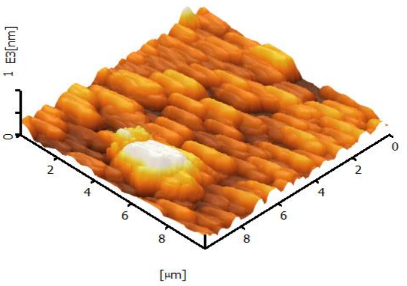
Table 1 shows the value of root mean square roughness (RMS) and grain size of the NiO-YSZ films measured by Nanonavi software for analyzing data from AFM. At an annealing temperature of 600°C, the grain size was decreased as the film layer increased. The findings regarding NiO-YSZ grain growth coincides with previously observed experimental trends showing that grain growth can be accelerated through an annealing process over temperature and time [8]. Therefore, to get the best surface, we also have to consider the thickness of the layer and the annealing temperature as we aim to produce the thin film SOFC.



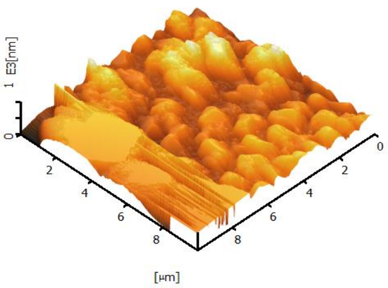
(a)



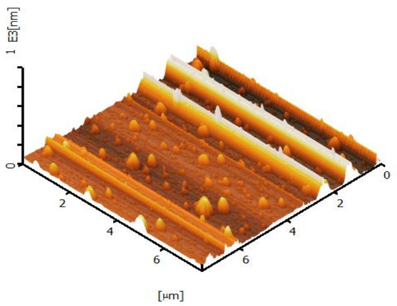
(b)



(c)



(d)



(e)

Fig. 1 3-Dimensional AFM images of NiO-YSZ thin film annealing at 600 °C with different layer (a) 1 layer, (b) 2 layer (c) 3layer, (d) 4 layer and (e) 5 layer.

Table 1 Root mean square roughness and grain size.

No of layer	RMS (nm)	Grain size (nm)
1	159.8	665.27
2	116.3	312.94
3	108.1	272.75
4	100.7	250.56
5	37.4	115.48

3.2 Electrical Analysis

There is another important characteristic of the anode material which is the conductivity. The conductivity of the samples was calculated using the formula:

$$\sigma = \frac{1}{\rho} \quad (1)$$

where ρ, is a resistivity and conductivity has SI units of siemens per meter (S/m).

The anode must have sufficiently high conductivity for electron flow in a reducing environment at the selected operating temperature. However, the conductivity of the NiO-YSZ anode coatings in fuel cells is also affected by the heat treatment and annealing temperatures of the anodes.

Table 2 Conductivity and the number of layers of NiO-YSZ thin film.

No of layer	Conductivity (S cm^{-1})
1	0.05604
2	0.02061
3	0.01443
4	0.02363
5	0.01769

Table 2 shows the conductivity and the layer of sample NiO-YSZ thin film. The conductivity of the anode annealed at 600^0C was only ~0.05604, 0.02061, 0.01443 S cm^{-1} for the 1, 2 and 3 layers, respectively. It is slightly increased at 4 layers with 0.02363 S cm^{-1} and dropped to 0.01769 Scm^{-1} at 5 layers as shown in Fig. 2. The electrocatalytic activity of the anodes for the H_2 oxidation response also expanded considerably with the expansion of the sintering temperature of the anodes. This effect of annealing temperature of NiO-YSZ on the conductivity behavior was also studied by Pratihar et., al [9]. According to Grahl Madsen et., al the initial reduction in temperature also affects the electrical conductivity [10]. The electrical conductivity is corresponding to the complementary of absolute temperature, which is the typical behavior of metallic solids, showing that the conductivity of the anode is controlled by the system of the Ni phase.

Perversely, isolated large Ni grains that may not participate in the electrical conductivity were observed in the anode that is made from the powder mixture. However, the electrochemical property of the anode, in which electron generated at the triple phase boundary (TPB) through the H_2 oxidation must be transferred to the current collector via Ni networks played an important role by Ni phase. Thus, it would say that the higher conductivity may be contributed to the better electrochemical performance of the anode made from the composite powder.

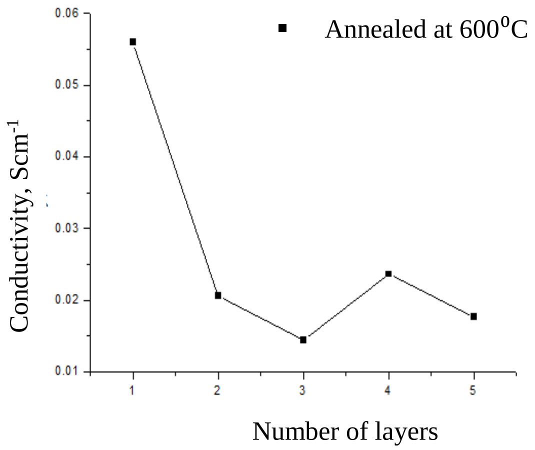


Fig. 2 the graph of conductivity versus number of layers.

4. Conclusion

In this paper, the morphology and the conductivity of NiO-YSZ thin film deposited by dip-coating method was analyzed by AFM and Four Point Probe respectively. The effect of annealing temperature and different layer were investigated. The four-point probe shows that the conductivity of all layers decreased. The first layer indicates the high reading of conductivity of NiO-YSZ at 600°C. Different layers of the thickness of the films investigated the roughness of the surfaces. It shows that the roughness decreases as the thickness layer increase. Therefore, we can conclude that thin layer will give a smoother surface. This experiment needs to be improved in term of annealing temperature and dip-coating timing parameter to achieve the phase of the NiO-YSZ smoother surface for better performance in SOFC.

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