

Solid oxide fuel cell anode surface modification by magnetron sputtering of NiO/YSZ thin film

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Abstract. NiO/ZrO₂-Y₂O₃ (NiO/YSZ) anode functional layers (AFL) with 16-60 vol.% of NiO were deposited onto NiO/YSZ anode substrates by magnetron sputtering, followed by annealing in air at 1200 °C. The optimal deposition conditions for NiO/YSZ were determined. NiO content in the films was varied by changing the oxygen flow rate during the sputtering process. The microstructure and phase composition of NiO/YSZ anode functional layer were studied by SEM and XRD methods. Anode functional layers were fully crystallized and comprised of grains up to 500 nm in diameter after reduction in hydrogen. Anode-supported solid oxide fuel cells (SOFC) with the diameter of 20 mm including the magnetron sputtered AFL, 4-microns thick YSZ electrolyte and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃/Ce_{0.9}Gd_{0.1}O₂ (LSCF/CGO) cathode were fabricated and tested. Electrochemical properties of the single fuel cells were investigated as a function of NiO volume content in AFL and AFL thickness.

1. Introduction

A ceramic-metal (cermet) composite of Ni and yttria-stabilized zirconia (YSZ) is the most common anode material of solid oxide fuel cells (SOFC) operating at a temperature of 800-1000 °C. However, the desire to create a commercial SOFC requires to mitigate the problem, associated with a high operating temperature. In turn, the lower operating temperature would increase polarization of electrodes and ohmic resistance of electrolyte. The ohmic resistance can be decreased either by using ultra-thin electrolytes, or new materials with higher ionic conductivity at lower temperatures [1, 2]. Polarization losses of the anode can be reduced by creating new alternative materials or by nanostructuring commonly used NiO-YSZ cermet [3, 4]. The second approach seems to be the most promising for improving the SOFC characteristics. First, conventional NiO/YSZ cermet is cheaper than other materials, chemically stable in a reducing atmosphere at high temperatures and has thermal expansion coefficient close to that of YSZ electrolyte [5]. Second, it is known that the electrochemical reaction at the anode occurs at a three-phase boundary (TPB), the area of contact between the metal, the electrolyte and the working gas. Therefore, the electrode reaction rate and, hence, its efficiency is determined by the TPB length. The formation of nanoporous anode structure will significantly increase the TPB length. At that, the nanostructuring of the whole anode substrate is not required, since the coarse anode facilitates the rapid diffusion of fuel gas to the active reaction area and removal of reaction products out from the anode [6]. Formation of the nanostructured anode functional layer



(AFL) will lead to an increase of the TPB length of an anode and to a decrease of activation polarization of the anode [7].

Among many methods used to prepare the anode functional layer, the greatest success in terms of the nanostructures formation was achieved by methods of physical vapor deposition (PVD), such as pulsed laser deposition [8], magnetron sputtering [9, 10], electron beam evaporation [11] and others. Among all, magnetron sputtering is characterized by several advantages. By changing deposition parameters such as substrate temperature, working pressure, angle of incidence of the deposited particles, etc. both dense and porous coating structures can be formed. It is also possible to adjust the number, size and shape of pores in the deposited films.

In our recent work [12], we have used magnetron deposition technique to fabricate nanocomposite NiO/YSZ anode layer onto YSZ electrolyte support. As a result of nanocomposite NiO/YSZ anode deposition, the power density of the fuel cell was increased by two times, as compared to a cell with the anode fabricated by conventional screen printing technique. But such cells had high ohmic losses due to the large electrolyte thickness. Therefore, in the present work, we suggest forming the nanoporous AFL for the anode-supported SOFC with a thin electrolyte. AFL should also serve as an interface layer between the highly porous anode substrate and thin gas-tight electrolyte.

2. Methodology and materials

NiO/YSZ thin films were deposited onto NiO/YSZ substrates by reactive magnetron co-sputtering of Ni (99.995% purity) and Zr/Y (85/15 at.%, 99% purity) targets. The substrates with a diameter of 20 mm and 0.4-mm-thick were laser cut from commercial porous NiO/YSZ anodes for SOFCs (Ningbo SOFCMAN Energy Technology Co., China). The Ni and Zr-Y targets were inclined at an angle of 45° to the substrate holder. The vacuum chamber was evacuated to the base pressure of 0.01 Pa using a turbo-molecular pump. The substrates were heated up to 370 °C and the temperature was maintained during the sputtering process. Argon and oxygen were introduced into the vacuum chamber with the flow rate of 30 sccm and 9–16.5 sccm, correspondingly, at a working pressure of 0.2 Pa. To improve films adhesion before the deposition, the substrate surface was cleaned for 30 seconds by ion beam at 1000 V and 15 mA generated by an ion source with a closed electron drift. Prior to deposition, the targets were pre-sputtered for two minutes with a shutter covering the substrates in order to remove any contaminant on the surface of the targets and to ensure stable sputtering conditions. Ni target was supplied with a pulsed DC power supply (Applied Electronics, Ltd., Russia). The average power was 350–500 W at a frequency of 80 kHz. The bipolar pulse powering (Applied Electronics, Ltd., Russia) was used for Zr/Y target sputtering with pulse repetition frequency of 75 kHz, positive pulse duration of 4 μs and average power of 1500 W. After deposition, the samples were kept in the vacuum chamber until substrate temperature dropped to 150 °C.

The obtained samples were annealed in air at 1200°C for 1 hour to prevent Ni agglomeration in the film during subsequent use under hydrogen atmosphere. The heating/cooling rate was 200 °C/h. Undesirable massive metal phase agglomeration was observed after the reduction or thermal treatments of the cermet composites in the form of the thin film regardless of the deposition methods [13]. Ni agglomeration leads to the loss of connectivity and poor high temperature stability of electrodes. The method of suppression of Ni agglomeration in Ni/YSZ films by post-annealing was first used by Noh et. al. [14].

To study the electrochemical activity of NiO/YSZ, thin films SOFCs including YSZ electrolyte and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3/\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (LSCF/CGO) cathode were manufactured. 4 μm-thick YSZ electrolyte was deposited by reactive magnetron sputtering of Zr/Y target. Sputtering was also carried out using a bipolar pulsed power supply. We have previously shown that the bipolar pulsed magnetron sputtering can significantly increase the deposition rate of oxide coatings, as compared with unipolar pulsed DC or DC mode [15].

The LSCF/CGO cathode layer was prepared on the electrolyte surface by a screen printing technique using $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3/\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}$ paste (CERA-FC Co., Korea). The cathode area was 1 cm². Cathode was sintered at 800°C during the SOFC electrochemical test.

Electrochemical tests were performed using ProboStat™ device (NorECs, Norway). Details about the single cell test bench and testing procedures were given in our previous work [16]. The scanning electron microscope Quanta 3D 200 was used to study the cross section of the deposited films and to determine their thickness. The NiO content in the film was determined by X-ray diffractometry (XRD-6000 diffractometer with Cu K_α radiation). To minimize the contribution related to the substrate, the technique of X-ray diffraction at grazing incidence was used.

3. Results and discussion

In general, conventional SOFC anodes are made by mixing NiO and YSZ at a certain ratio. It is desirable to have NiO content as high as possible to improve the performance of the anodes. But high NiO content makes it impossible to match its thermal expansion to that of the YSZ. Change of the NiO content in the NiO/YSZ film deposited by co-sputtering of two targets is possible either by varying the power supplied to the Ni target (at constant gas flow rates and constant power to Zr/Y target), or by changing the oxygen flow rate (at constant power supplied to both targets). The second method was chosen in this work. The main problem of the simultaneous reactive sputtering of different targets consist in the fact that the increase in the discharge power at one of them results in a decrease in the partial pressure of oxygen in the chamber, which, in its turn, causes the change in the sputtering conditions of the other target. It is known that the deposition rate during reactive magnetron sputtering strongly depends on the target surface conditions. The target can become oxidized (poisoned) by the oxygen which reduces the amount of sputtered material. Therefore, the oxygen flow rate has to be precisely controlled for better results.

The deposition rate ($\mu\text{m/h}$) and NiO content in the film are highly dependent on the oxygen flow rate and deposition time at the growth conditions as shown in Figure 1. At oxygen flow rate of 9 sccm, the deposition rate of NiO/YSZ film is relatively high and is equal to 30 $\mu\text{m/h}$. This is transition region between metal and oxide sputtering modes. Above 9 sccm, deposition rate starts to fall abruptly but after 12 sccm the fall becomes slow. This means the process enters the oxide sputtering mode. In this mode, targets were oxidized, and the deposition rate was noticeably lower (3.6-8.6 $\mu\text{m/h}$).

NiO content in the film tends to decrease with increasing oxygen flow rate. A similar relationship was observed in [17] at sputtering of a single Ni/Zr/Y (68.8/26.6/4.6 wt.%) target. However, as can be seen from Figure 1, at the same oxygen flow rate and constant power, the NiO/YSZ film may contain different amount of NiO phase. This is because with increasing coating thickness, and, hence, deposition time there is a gradual decrease in the oxygen partial pressure in the chamber. This leads to the fact that the oxidation state of the sputtering targets is changed. In order to exclude this phenomenon, it is necessary to control the oxygen partial pressure, for example, by measuring the plasma composition by optical emission spectroscopy and controlling the oxygen flow rate by feedback control system [18].

Figure 2 presents XRD patterns of NiO/YSZ films with NiO content of 36, 45 and 62 vol.%. These samples were annealed at 1200 °C before measurements. The films exhibit a crystalline structure with clear indicated peaks. The intensity of NiO peaks increases with the decreasing oxygen flow rate, indicating an increase in the NiO content in the deposited films. According to data (curve 3) presented in Figure 2, the (400) YSZ reflection in X-ray pattern of the film with 62 vol.% NiO disappeared whereas the (311) NiO reflection intensity considerably increased. Interestingly, the increasing NiO content in the films leads to (111) YSZ reflection intensity increase, while intensity of YSZ (200) reflection decreases. Thus, textural evolution of YSZ phase is observed which is the transition from [200] out-of-plane preferential orientation to [111]. Lamas et. al. [19] showed that in magnetron sputtered YSZ films change of the orientation from [200] to a complete [111] out-of-plane orientation is due to the competition between the fastest growth direction and the lowest surface energy.

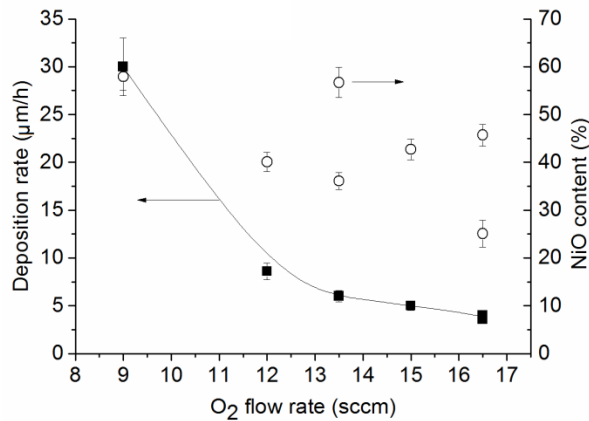


Figure 1. Effect of oxygen flow rate on deposition rate and NiO content of the NiO/YSZ films.

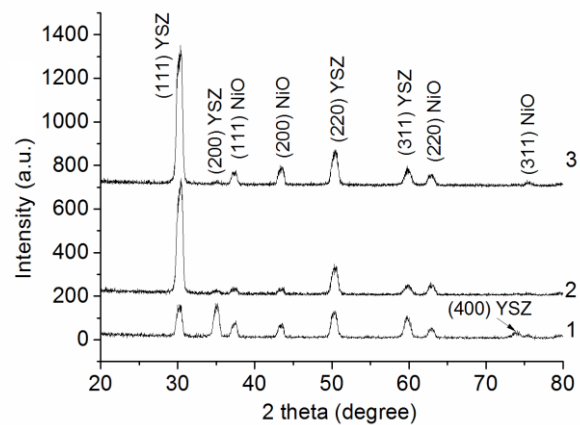


Figure 2. X-ray diffraction patterns of the magnetron sputtered NiO/YSZ films with different NiO content: 1) 36 vol.%, 2) 45 vol.%, 3) 62 vol.%.

The dependence of the NiO/YSZ film microstructure on the NiO content is shown in Figure 3.

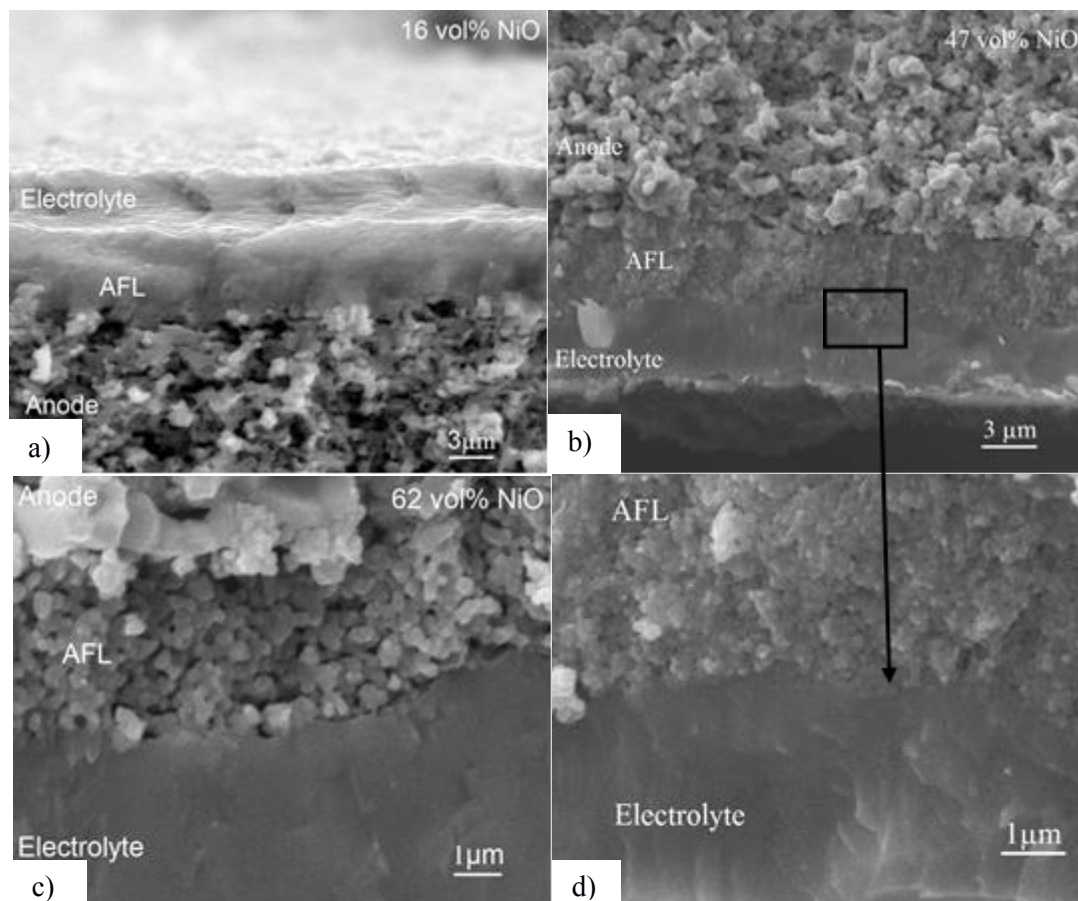


Figure 3. Cross sectional SEM images of the SOFCs with nanostructured anode functional layer with NiO content: a) 16 vol.%; b) 47 vol.%; c) 62 vol.% and d) is the magnified image of the electrolyte and anode interface marked in Figure 3b. SEM images were obtained after cells testing and NiO reduction in hydrogen.

It can be seen that AFL with the NiO content of 16 vol.% has the microstructure, which is slightly different from the microstructure of the YSZ electrolyte. A clear boundary between the NiO/YSZ film and the electrolyte is not distinguishable because AFL has quite dense structure. The porosity of NiO/YSZ layer, as expected, increases with increasing NiO content in the layer up to 62 vol.%. For the sample with 47 vol.% of NiO in AFL, the pore size is in the range of 50-100 nm, and the grain size is less than 200 nm. Pore and grain size for the sample with 62 vol.% of NiO is about 50-400 nm, and 150-600 nm, respectively. For all samples, there is a good contact of the AFL both with an anode substrate and an electrolyte layer. The change in anode substrate surface porosity and roughness by the formation of the NiO/YSZ AFL is clearly observable where the porous and rough anode surface (Figure 3) displays relatively large voids formed from large NiO and YSZ particles. AFL has a relatively smooth and uniform surface for subsequent deposition of a high quality YSZ electrolyte layer. The analysis of the microstructure of the YSZ electrolyte films showed that the nanoporous anode functional layer provides the conditions for the formation of thin homogeneous and dense YSZ electrolyte films without columnar grains (Figure 3), which is typical for magnetron sputtered films.

In order to estimate the impact of the anode functional layer on the fuel cell performance, the voltage-current (V-I) and power-current (P-I) characteristics of the anode-supported SOFC with different AFLs were measured at 700 °C (Figure 4). AFLs with different NiO content and thickness were used. The results presented in Figure 4 shown that power density increases almost twice with increasing of NiO content in the AFL from 16 up to 60 vol.%. Also, the thickness of AFL significantly impacts the fuel cell performance. The optimum thickness of deposited nanoporous layer from the point of view of power density is equal to about 4 μm . At the larger thickness of the AFL the diffusion losses begin to increase due to the small size of the gas transport channels. At the layer thickness of 1-2 μm the length of the three-phase boundary on the anode increases slightly and therefore, power density of the cells is significantly lower.

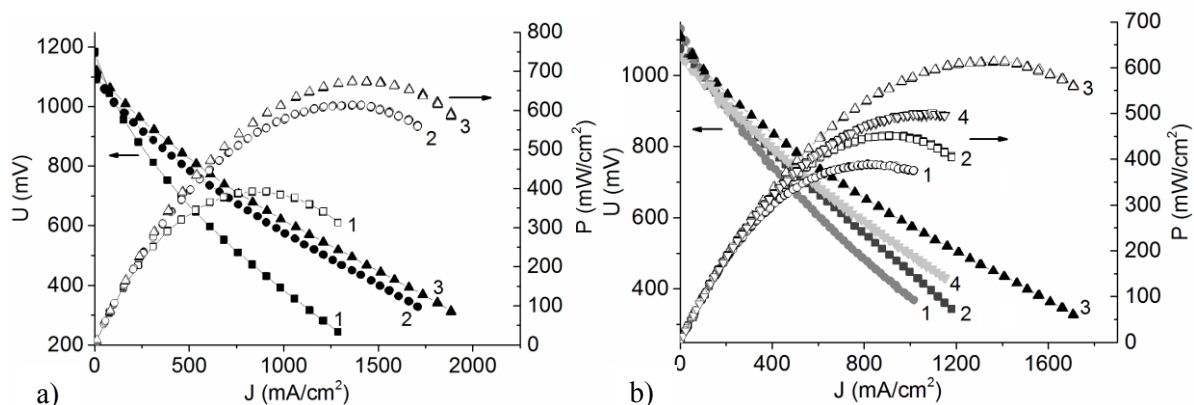


Figure 4. V-I and P-I characteristics of the anode-supported SOFC with magnetron sputtered NiO/YSZ AFL measured at 700 °C: a) AFL with different NiO content, 1) 16 vol.%, 2) 47 vol.%, 3) 60 vol.%, and thickness of 3.5 μm ; b) AFL with different thickness, 1) 1.3 μm , 2) 2.2 μm , 3) 4.3 μm , 4) 9.5 μm , and NiO content of 50 vol.%.

4. Conclusion

NiO/YSZ thin films with different NiO content and thickness were deposited by reactive magnetron co-sputtering of Ni and Zr-Y targets. The films were annealed at 1200 °C in air to prevent Ni agglomeration in hydrogen atmosphere. NiO/YSZ films with NiO content from 16 to 60 vol.% and thickness from 1.3 to 9.5 μm were deposited and tested as anode functional layers of anode-supported SOFCs. It was shown that the increase of NiO content in the film from 16 up to 60 vol.% leads to a nearly twofold increase of SOFC power density. It was also found that SOFC maximum power density was achieved at the NiO/YSZ film thickness of 4 μm .

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