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OBTAINING OF POROUS NICKEL ANODE BY HOT PRESSING AND ETCHING METHODS FOR SOLID OXIDE FUEL CELL APPLICATION

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The work represents a simple fabrication method of a porous nickel anode for thin film solid oxide fuel cells. The porous nickel anode is fabricated using a metal/pore-former mixing method with different ratios of powder followed by pressing and heat treatment. The process of obtaining a porous nickel anode by pressing of nickel and aluminum powders is shown. Further sintering of the samples and etching of aluminum from the obtained anode structure. The electrolyte layer was sputtered by pulsed laser deposition. Scanning electron microscope and energy-dispersive X-ray spectroscopy analysis are represented in article.

Keywords: thin-film solid oxide fuel cells, porous anode, electrochemical etching, electrolyte, pulsed laser deposition.

Introduction

Solid oxide fuel cells (SOFCs) have the potential to be one of the cleanest and most efficient energy technologies for direct conversion of chemical fuels to electricity. Economically competitive SOFC systems appear poised for commercialization, but widespread market penetration will require continuous innovation of materials and fabrication processes to enhance system lifetime and reduce cost [1].

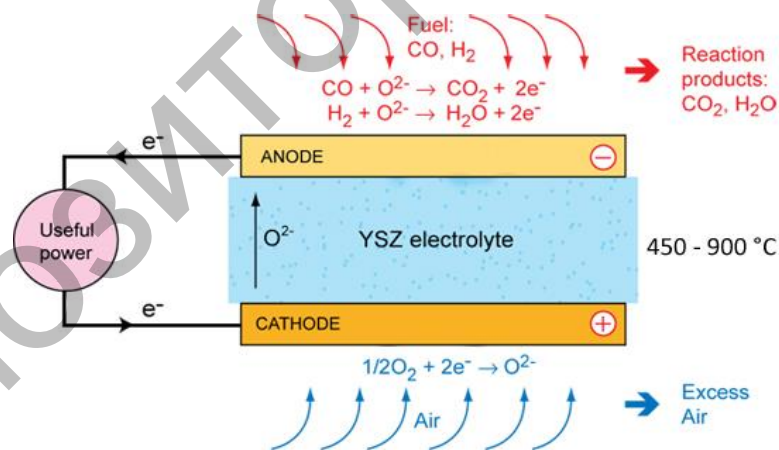


Fig.1. Scheme of an SOFC illustrating also the working principle

SOFCs convert chemical energy with high efficiency directly into electricity and heat. It can operate on a variety of fuels such as natural gas or hydrogen [2]. As shown in figure 1, the fuel supplying H_2 is fed into the anode compartment where it is oxidized, and the electrons released as a result are conducted to an external circuit [3, 7]. The reaction products on the anode side of an SOFC are mainly water and CO_2 . Air enters on the cathode side and oxygen is reduced here to O^{2-} by reaction with electrons from the external circuit. The O^{2-} ions can travel through the ion-conducting and gas-tight electrolyte, which separates the anode compartment from the cathode compartment [4]. Once on the anode side the O^{2-} joins with hydrogen to form water. Open circuit

voltage (OCV) is the voltage obtained at zero current that ranges from about 0.8–1.1V and is a measure for the gas leakage or electronic leakage through the electrolyte [5, 6].

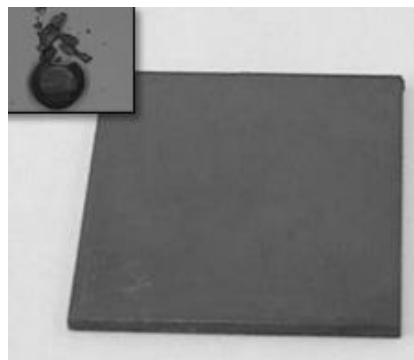
1. Experimental technique

The porous nickel anode is fabricated using a Ni and Al powders mixing method followed by pressing and heat treatment. Very pure Ni and Al powders of 99.99% purity were used in the work. The percentage of Ni and Al components is 60: 40%. The anode basis possesses a high porosity which is required for efficient delivery of fuel to the cell. Hot pressing method was used for obtaining tablet from nickel and aluminum powders. Next two steps was sintering of the sample and etching out aluminum from the anode structure. The mixing and grinding of the smallest powder with uniform dispersion is achieved by means of a grinding process in a SPEX Sample Pre 8000M ball mill with carbide tungsten cylinders with a 5 mm ball diameter.

Full experimental process of fabrication a porous nickel anode with a flat nanoporous surface shown in figure 2a, by thoroughly mixing commercial nickel powder (particle size between 0,5-1 μ m) with an aluminum (particle size of from 100 to 300 nm) proppant. The mixing of the two components must be thorough; therefore, it is typically performed by mechanical mixing and ball milling procedures. The resulting mixture (nickel powder and proppant) is then pressed into a parallel faced \approx 1 mm thick square tablet at 5000 psi (see figure 2b). The tablets pressed into round shape form as shown in insert of figure 2b. The tablet of pressed nickel powder/proppant is then loaded into a high temperature tubular furnace and sintered at 800 °C for 2 h in an ambient hydrogen atmosphere.



a)



(b)

Fig.2. Schematic diagram for the porous nickel anode fabrication process (a);
The fabricated porous nickel anode 10x10 mm (b).

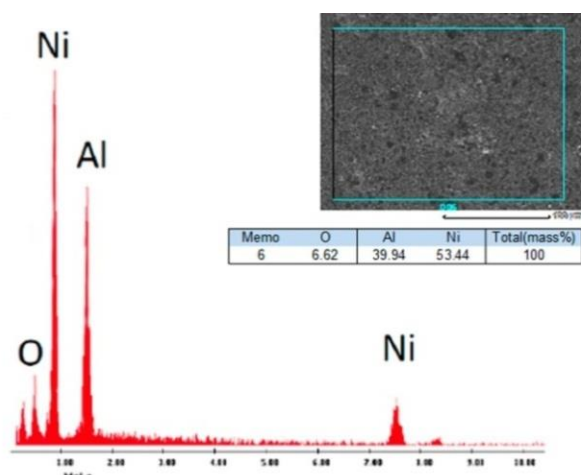


Fig.3. EDS analysis of anode after sintering

Next step of research was electrochemical dealloying of aluminum from the alloy of Ni-Al powders, as the potential increased, the amount of etched Al also increased. Passivation of nickel occurs with an increase in time, which contributes to the formation of NiO. The etching was carried out in a 30% KOH solution at room temperature. The process was carried out in two electrode cells, and under the action of ultrasound. A sample of Ni-Al alloy is used as a working electrode.

2. Results and discussion

Surface SEM images were carried out for the fabricated porous nickel anode after sintering (figure 4a, b). These images show clearly the surface and bulk porous structure of the nickel anode, with pore sizes of 100 nm – 1 μ m.

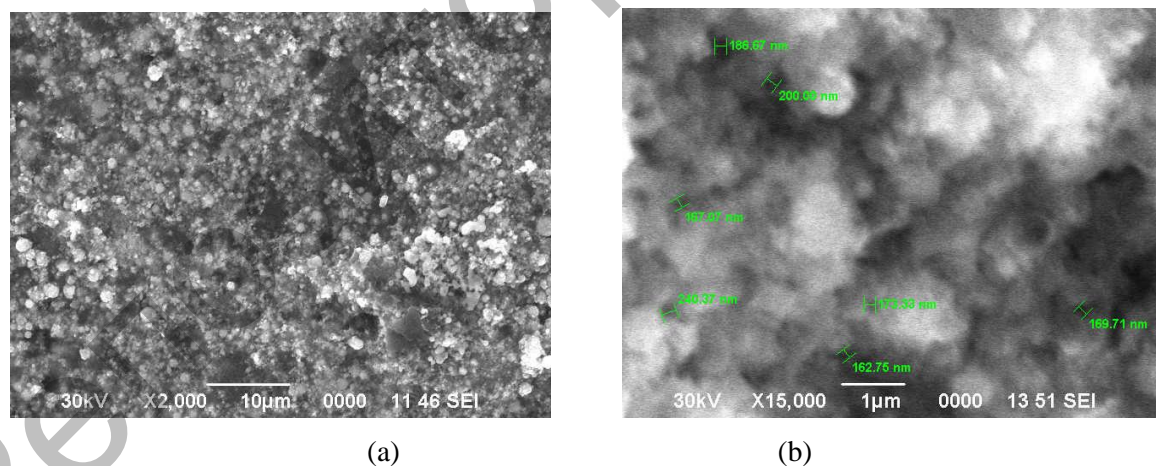


Fig.4. SEM images of the fabricated porous nickel anode: a) anode surface directly after sintering at 800 °C for 2 h.; b) anode surface after electrochemical etching.

This large pore size allows the fuel to readily reach the anode/electrolyte interface. The nickel surface treatments were applied to produce not only a flat surface, but also a surface with small pores (size < 500 nm) (see figure 5a, b) such that a continuous thin film electrolyte could be deposited and exhibit both gas and electrical hermeticity. The now smooth surface of the fabricated nickel anode will permit the deposition of a 3 μ m thick smooth, continuous electrolyte yttria-stabilized zirconia (YSZ) film, which is not only an electrolyte layer, but one that effectively blocks hydrogen from reaching the SOFC cathode.

Figure 3 shows the EDS analysis of the sample immediately after the annealing process in the tubular vacuum furnace. EDX analysis shows the correct ratio of components 60:40, which was originally set for the anode material.

The content of ~ 40% of aluminum compared with nickel makes it possible to vary the porosity due to a change in the concentration of the main component of nickel, but also it is impossible to forget the strength after etching. The dimensional content of aluminum can destroy the sample during electrochemical etching.

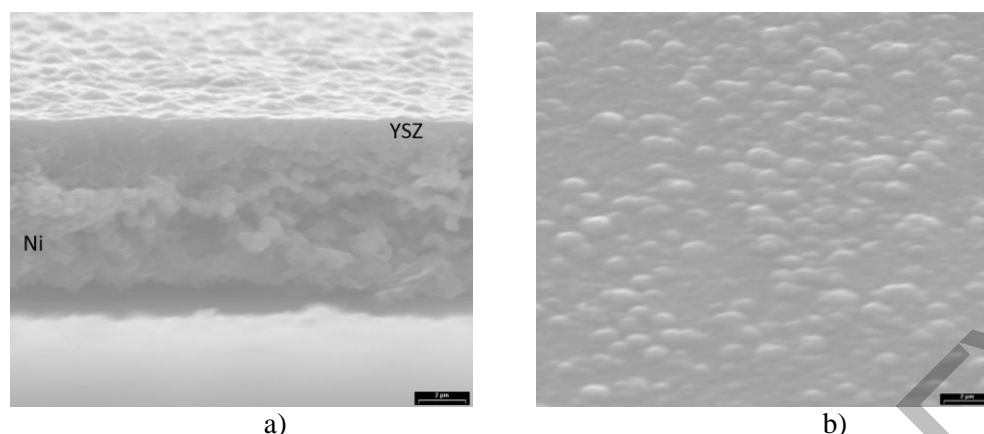


Fig.5. SEM cross-section images of the fabricated porous nickel anode with electrolyte layer, a) Anode cross-section after electrolyte deposition b) Electrolyte surface after deposition.

A 248 nm KrF Excimer laser at 7 Hz and 380 mJ was used to deposit the electrolyte layer on the porous nickel anode surface [2]. In this work, a dense YSZ electrolyte layer (about 1-2 μm thick) deposited at 150 mTorr and 650 $^{\circ}\text{C}$ in an atmosphere of 96% argon, 4% hydrogen to avoid nickel oxidation. Surface and cross-sectional SEM images were carried out for the fabricated porous nickel anode after pulsed laser deposition (figure 5a, b). As we can see from images the deposition of a thin (0.5–3 μm), smooth, and pore free electrolyte will not allow the diffusion of both fuel and air.

Conclusion

The porous nickel anode obtained by process of pressing nickel and aluminum powders, sintering and etching of aluminum from the obtained anode structure. The pore size between 100 – 500 nm, which allows for the H_2 to passage thru the anode to YSZ electrolyte layer. The thin YSZ electrolyte layer is sputtered by pulsed laser deposition. SEM and EDS analysis were obtained. Analysis shows the deposition of a thin (0.5–3 μm), smooth, and pore free electrolyte which will not allow the diffusion of both fuel and air. EDS analysis shows the correct ratio of the material after annealing in the furnace at 800 $^{\circ}\text{C}$, the presence of oxygen due to the interactions after discharge from the furnace.

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