

Application of Yttria Stabilized Zirconia (8YSZ) and NiO Precursors for Fabrication of Composite Material for Anode-Supported SOFCs¹

E. A. Agarkova^{a, *}, I. N. Burmistrov^a, D. V. Yalovenko^a, O. Yu. Zadorozhnaya^b, Yu. K. Nepochatov^b, S. V. Rabotkin^c, A. A. Solovyev^c, and S. I. Bredikhin^a

^a Osipyan Institute of Solid State Physics RAS, Chernogolovka, 142432 Russia

^b NEVZ-CERAMICS, JSC, Novosibirsk, 630048 Russia

^c Institute of High Current Electronics SB RAS, Tomsk, 634055 Russia

*e-mail: stepanova.ea@issp.ac.ru

Received October 21, 2022; revised July 26, 2023; accepted October 3, 2023

Abstract—The optimization of technology for manufacturing bilayered anode supports for planar solid oxide fuel cells (SOFCs) using precursors was performed. The bilayered anode supports for the second-generation planar SOFCs were manufactured by the tape casting method followed by the lamination. Nickel sulfate heptahydrate NiSO₄·7H₂O was used to fabricate the composite material for the current-collecting layer containing 60 vol % NiO and the functional layer containing 40 vol % NiO (the chosen values are close to the first and second percolation thresholds). The 8YSZ/NiSO₄ composite mixture was calcined at a temperature of 1000°C. The use of this precursor resulted in fabricating durable anode support that retains mechanical stability during redox cycling. Finely dispersed NiO in a thin functional layer led to a high density of three-phase boundaries, which had a beneficial effect on the electrochemical activity of the anode. Based on these anode supports, the model samples of solid oxide fuel cells were manufactured. The samples were studied using conventional electrochemical techniques. The power density was 1 W/cm² at an operating temperature of 750°C.

Keywords: solid oxide fuel cells, SOFC, anode support, mechanical stability, microstructure

DOI: 10.1134/S1023193524030029

INTRODUCTION

The anode-supported solid oxide fuel cells (SOFCs) have an undeniable advantage over the electrolyte-supported SOFCs. The advantage is associated with a significantly thinner electrolyte film, approximately 5–10 microns. This significantly reduces the ohmic losses (for the first-generation SOFCs, the losses due to the anionic transport in the solid electrolyte membrane are about half the total internal resistance of the fuel cell) and enables one to obtain significantly higher power characteristics even at low operating temperatures [1–4].

One of significant problems that arise during the operation of anode-supported SOFC is a possible loss of cell mechanical stability during the operation [5]. The process is associated with possible mechanical and microstructural degradation of the anode during the redox cycling. Detrimental structural changes in the SOFC anode are caused by a significant volume

effect of approximately 42 volume percent that accompanies the oxidation of Ni metal to NiO and subsequent reduction process [6].

Various attempts have been made by researchers and developers to provide the mechanical stability of anode-supported SOFCs by optimizing the anode support microstructure. The main idea of the majority of approaches is to create the mechanically strong frame, which is formed by solid electrolyte grains [7–9]. In this approach, finely dispersed NiO, which in this case performs the electrochemical rather than mechanical functions, should be uniformly distributed over the entire electrode bulk.

Various ways of technical implementation of this approach are described in the literature. For example, in [7], first, a multilayer ceramic structure is formed. A gas-dense electrolyte based on lanthanum–strontium gallate–manganite (LSGM) is located in the center of the structure, and porous layers of LSGM electrolyte are located at its edges. The composite electrode is fabricated by impregnating porous LSGM layer with nickel nitrate aqueous solution followed by the calcination at a temperature of 700°C. This

¹ Based on the paper presented at the IX All-Russia Conference with international participation “Fuel Cells and Power Plants Based on Them,” Chernogolovka, Moscow region, Russia, 2022.

approach has several advantages. First, it enables one to form the structure framework at a high temperature; second, it enables one to form nickel oxide grains of as fine dispersion as is wished due to the absence of the need for high-temperature annealing after calcination (high-temperature annealing leads to a significant increase in the grain size).

In work [8], the surface of spherical $Zr_{0.92}Y_{0.08}O_{2-\delta}$ (8YSZ) particles was modified. Nickel oxide, nitrate and hydroxycarbonate were used as the precursors. Using the precursors, stable suspension based on NiO and 8YSZ was prepared. To form the powder of the correct morphology, the composite was calcined in two stages: first, the annealing at a temperature of 800°C; then, grinding to prevent rapid growth of NiO grains; and then, the second high-temperature annealing at a temperature of 1200°C. Cermet, sintered at a temperature of 1400°C, had a rigid frame composed of 8YSZ grains.

In the work, it is proposed to use nickel sulfate heptahydrate as the precursor for the production of the composite material. After the calcination, a homogeneous mixture containing large 8YSZ grains and finely dispersed nickel oxide was obtained. Correspondingly, when annealing ceramics made of this composite material, there is no danger of excessive increase in the NiO grain size. This approach allows the use of other Ni salts including nitrates. This approach also allows the use of conventional method for manufacturing the anode support, the tape casting method, with no additional techniques (such as impregnation).

EXPERIMENTAL PROCEDURE

The bilayered anode support was manufactured by the tape casting method followed by the lamination. The composite material was based on the 8YSZ powder (SOFMAN, China) and nickel sulfate heptahydrate $NiSO_4 \cdot 7H_2O$ powder (Uralektromed', Russia). The functional anode layer contained 60 vol % 8YSZ, and the current-collecting layer contained 40 vol % 8YSZ. The ratios between the components in the composite were chosen as the values close to the first and second percolation thresholds, which are accompanied by an abrupt change of the ambipolar conductivity of the composite material [10]. The powder mixture was ground in distilled water in a roller mill using grinding balls 10 mm in diameter made of partially stabilized zirconium dioxide. After homogenization of the mixture, it was calcined at a temperature of 1000°C. The suspension preparation and the casting procedure were described in detail in [11]. To provide the porosity of the support, the pore-forming agent, the rice starch (BOTGAO, Vietnam) with a typical particle size of 2–5 μm , was additionally introduced into the suspension for the current-collecting layer.

The bilayered 8YSZ/10GDC (10GDC = 90 mol % CeO_2 + 10 mol % Gd_2O_3) electrolyte was prepared using the reactive magnetron sputtering method. The sputtering was carried out using metal targets with the composition Zr–Y (85 : 15 at %) and Ce–Gd (90 : 10 at %) (Girmet, Russia). The deposition was performed in the atmosphere of Ar/ O_2 mixture at a working pressure of 0.2 Pa. The deposition rate of 8YSZ and GDC films was 0.72 and 2 $\mu m/h$, respectively. The deposition procedure was described in detail in [11].

The bilayered cathode (the functional and current-collecting sublayers) of the composition LSCF/10GDC–LSCF (LSCF = $(La_{0.6}Sr_{0.4})_{0.97}Co_{0.2}Fe_{0.8}O_{3-\delta}$) was manufactured on the basis of commercially available cathodic paste of this composition (KCeraCell, Republic of Korea) by the screen printing method using an Ekra E2 printer (Asys Group, Germany) followed by sintering at 1200°C in a high-temperature NaberTherm 40/16 furnace (Germany).

The microstructural study of the support and functional layers of fuel cells were carried out using a Supra 50VP scanning electron microscope with an INCA Energy+ microanalysis system (CarlZeiss, UK).

The mechanical properties of the anode supports were assessed using the three-point bending method using an UTS111.2-50 setup (Russia). The punch speed was 0.5 mm/min. The mechanical study was performed using a single-crystal sapphire insert, which was described in detail in [12]; the specimens were 24 by 9 mm in size. To estimate the mechanical strength of the supports during the SOFC operation, the supports were reduced in the Ar/ H_2 mixture at a temperature of 800°C for an hour followed by cooling in the hydrogen atmosphere.

The electrochemical characteristics of SOFCs were studied using the automated gas–temperature test setup, involving a high-temperature furnace, a measuring insert, a gas system based on the Bronkhorst gas flow controllers (Netherlands), and a Reference 3000 potentiostat/galvanostat (Gamry Instruments, USA).

RESULTS AND DISCUSSION

Figure 1 shows the images of the cross-sections of the sintered anode support that were obtained by the scanning electron microscopy. The upper images (Figs. 1a and 1b) show the cross-sections of the current-collecting layer, and the lower images (Figs. 1c and 1d) show the cross-sections of the functional layer. The left images (Figs. 1a and 1c) show the microstructure of the support after the fabrication prior to the reduction, and the right images (Figs. 1b and 1d), after the reduction. In the oxidized state (Fig. 1a), the 8YSZ grains are clearly seen, they are not more than 3 μm in size. In the reduced state (Figs. 1b and 1d), the Ni grains are more clear, they do not exceed 1 μm in size. The structure of the current-col-

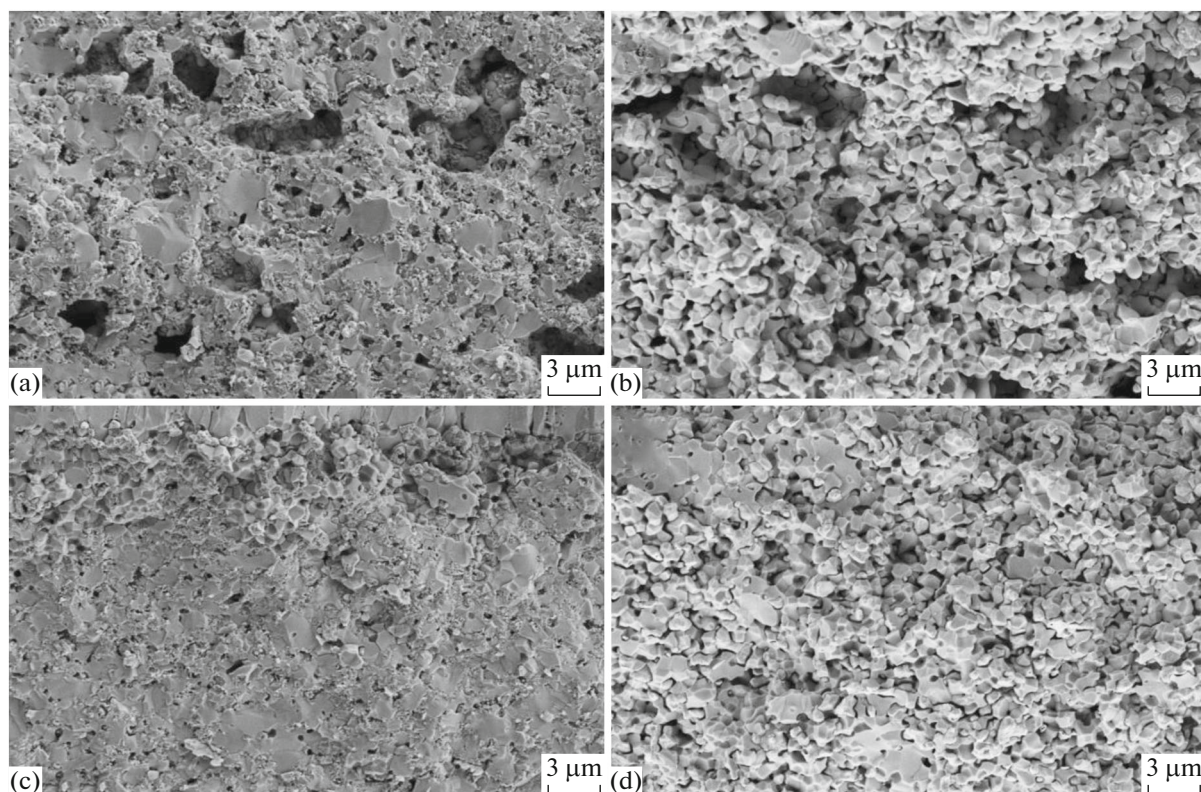


Fig. 1. Cross-sections of (a, b) current-collecting and (c, d) functional layers of the anode support (a, c) prior to and (b, d) after the reduction.

lecting layer contains open porosity formed by the introduced rice starch. After sintering, the anode support is 420 μm thick. The current-collecting layer, which is the mechanically supporting layer in the SOFC structure, is 400 μm thick. The functional layer is approximately 20 μm thick; a thicker functional layer is not required, because the reactive anode thickness is approximately 10 μm [10].

Figure 2 shows the load curves of the plates, which were measured prior to and after the reduction. It can be seen that an increase of the plate porosity, which is observed after the reduction (Figs. 1b and 1d), does not lead to a loss of the plate mechanical stability; by contrast, their flexibility increases. An additional porosity formed by starch leads to an increase in the limiting load, at which the destruction of the anode supports occurs, by 10–15% [13]. The limiting strength, which is required to destroy the support after its reduction, is approximately 1 kgf, and the corresponding deflection is approximately 0.45 mm.

Figure 3 shows the cross-sections of 8YSZ/10GDC bilayered electrolyte and LSCF/10GDC–LSCF bilayered cathode. The 8YSZ layer is approximately 5.4 μm thick and the 10GDC layer is approximately 2.4 μm thick. The functional (LSCF/10GDC) and current-collecting (LSCF) cathode sublayers are approximately 10 and 12 μm thick, respectively. It is

seen that the thickness of all functional layers is rather uniform and, as the internal interfaces of SOFC are well formed.

The electrochemical characteristics were studied on the samples 21 mm in diameter at the working temperatures of 700, 750, and 800°C with the air (oxidizer) and hydrogen (fuel) flow of 200 mL/min. The

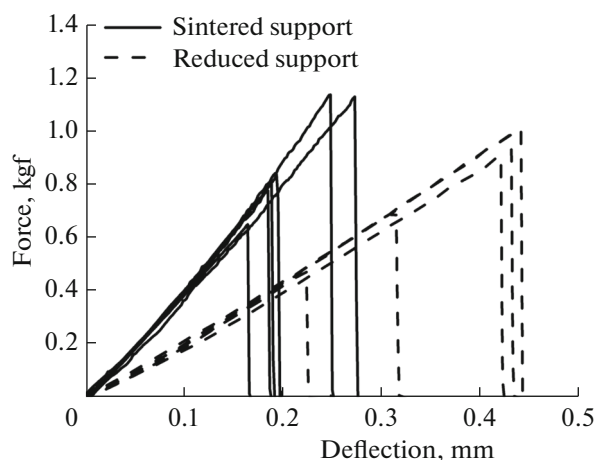


Fig. 2. Load curves of anode supports prior to and after the reduction.

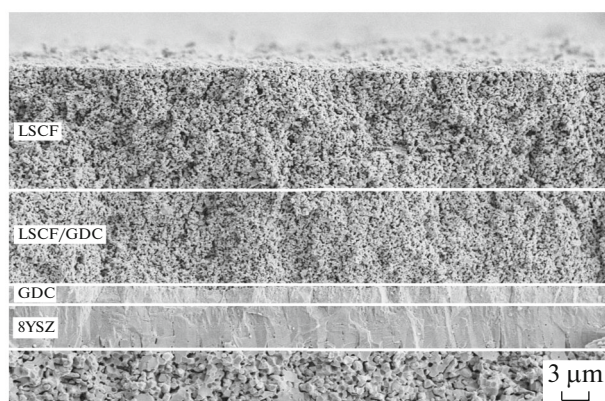


Fig. 3. Cross-sections of 8YSZ/GDC electrolyte and LSCF/GDC–LSCF cathode on the anode support surface.

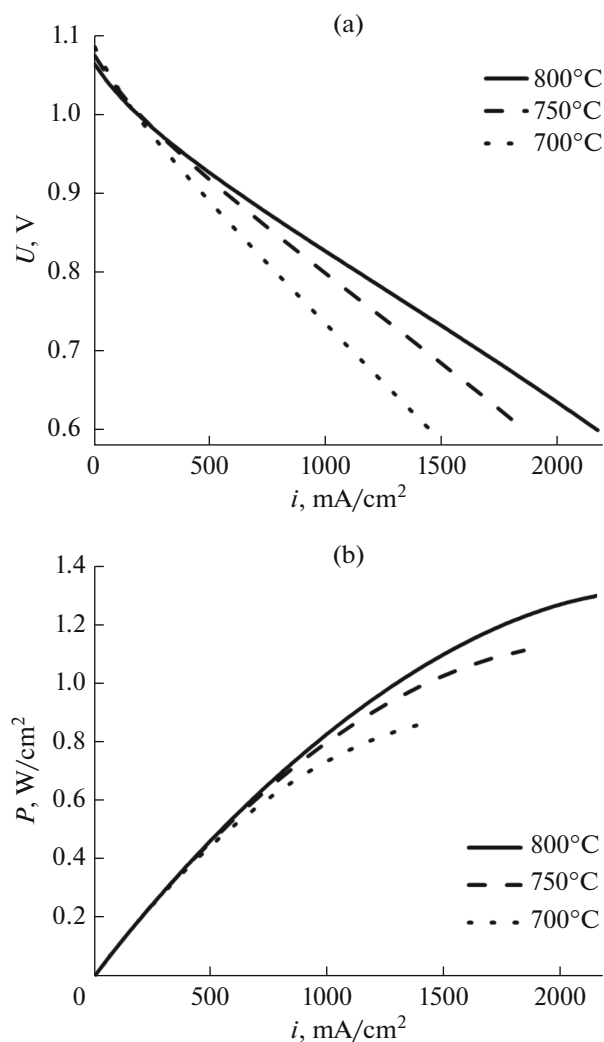


Fig. 4. (a) Voltammetric and (b) power characteristics of SOFC measured at 700, 750, and 800°C.

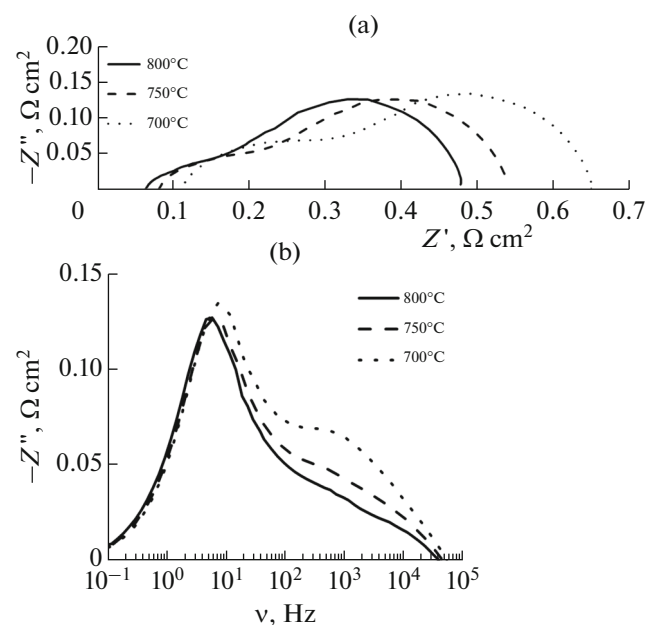


Fig. 5. (a) Impedance curves of SOFC and (b) their frequency dependences measured at 700, 750, and 800°C.

working area of the cell electrodes was 2 cm². The measured open-circuit voltage was higher than 1.05 V (Fig. 4a). This is the evidence for a high quality of cell sealing during the measurement and the absence of gas and current leaks. At the operating point at a voltage of 0.7 V, the power density was 0.78, 1, and 1.17 W/cm² for the operating temperatures of 700, 750, and 800°C, respectively.

From the impedance curves (Fig. 5a), it is seen that, with decreasing temperature, the cell resistance increases: the cell ohmic resistance increases, and the contribution of high- and medium-frequency processes also increases. This is seen more clearly in the frequency dependences of the imaginary part of resistance (Fig. 5b). A slight increase of the ohmic resistance (the high-frequency cutoff) from 44 to 94 mΩ cm² is associated with the thermo-activation nature of the temperature dependence of solid electrolyte resistance. It should be noted that the resistance of bilayered 8YSZ/GDC electrolyte with a total thickness of 7.8 μm at the temperatures of 800 and 700°C should be 20 and 53 mΩ cm², respectively. Consequently, the ohmic losses detected during the experiment contain not only the electrolyte resistance, but also an additional resistance of the contact areas. Its relative contribution decreases with decreasing temperature due to an increase of the electrolyte resistance.

An increase of the resistance in the middle-frequency impedance range (Fig. 5b) characterizes the degradation of the electrochemical activity of SOFC electrodes with decreasing temperature.

A fraction of losses associated with the electrochemical reactions does not exceed 30% in the entire temperature range. The fabrication of the composite material for the functional layer of SOFC anode using 8YSZ and nickel salt led to a high density of three-phase boundaries due to finely dispersed nickel oxide. In its turn, this is what prevented a large porosity in the functional layer, which probably had an effect on significant diffusion losses (Fig. 5).

CONCLUSIONS

It is shown that the use of nickel salt for fabricating a composite material based on 8YSZ/NiO has a beneficial effect on the quality of bilayered anode supports of planar SOFCs. Due to this approach, a supporting frame of large grains of anionic conductor forms in the current-collecting anode layer. At the same time, finely dispersed grains of nickel oxide, which provide the electronic conductivity, are uniformly distributed over the cermet structure and, due to their small size, their volume changes during redox cycling do not lead to the mechanical destruction of the structure.

On the other hand, in the functional layer, the same ratio between the grain sizes of the phases of electronic and anionic conductors leads to a high density of three-phase boundaries, which has a beneficial effect on the electrochemical activity of the anode during the SOFC operation.

FUNDING

This work was supported by ongoing institutional funding. No additional grants to carry out or direct this particular research were obtained.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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Translated by T. Kabanova

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