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Tape Casting of Bilayered Anode Supports and Electrochemical Performance of SOFCs Based on Them[1]

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Abstract—The bilayered supports for anode-supported solid oxide fuel cells (SOFCs) based on composites of NiO and ZrO_2 stabilized by 10 mol % Sc_2O_3 and 1 mol % Y_2O_3 (10Sc1YSZ) are synthesized by tape casting. The required porosity is attained by optimization of the content of pore-forming agent (starch) in the initial suspension and also by thermal treatment, on retention of the high strength characteristics of the substrate. The mechanical strength of supports is assessed by three-point bending method. The bilayered gas-tight electrolyte with the layers of ZrO_2 stabilized by Y_2O_3 (8 mol %) (8YSZ) and $Ce_{0.9}Gd_{0.1}O_{1.95}$ is obtained by magnetron sputtering followed by annealing at 1200°C. Studying the electrochemical characteristics of a SOFC with the $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ cathode has shown that as the working temperature decreases, the contribution of electrode processes into cell's internal resistance increases which induces the specific power decrease down to 1.8, 1.4, and 0.9 W/cm^2 at 850, 800, and 750°C, respectively.

Keywords: solid oxide fuel cell, anode support, bilayered solid electrolyte, electrochemical characteristics, mechanical strength

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INTRODUCTION

Solid oxide fuel cells (SOFCs) show promise as electrochemical generators of electric energy and high-potential heat [1]. To date, no technology more efficient than SOFCs is known for converting the chemical energy of oxidation of hydrocarbon fuels (natural gas, propane–butane, dimethyl ether, and even advanced diesel fuel) to the electric and high-potential thermal energies. In the largest part of the Russian Federation, the use of such power sources is economically justified because the Unified Energy System (UES) is still insufficiently developed and also due to the necessity of developing the hard-to-reach Arctic regions and the Northern Sea Route.

There are several SOFC types which differ in the component that imparts their mechanical strength, namely, electrolyte-supported, anode-supported, metal-supported SOFCs and also SOFCs with other supports (e.g., cathode or external ceramic supports) [1]. Their design determines the sequence of their fabrication, the microstructure and thickness of layers in individual SOFCs and, as a consequence, the working mode of the cell (working temperature, pressure of supplied gases, fuel composition and utilization percent, etc.). The anode-supported SOFCs (650–750°C) exhibit no drawbacks of their electrolyte-supported counterparts such as the high cost (due to the possibility of using the cheaper electrolytes containing no expensive scandium and also due to the more than 10-times thinner electrolyte layer) and the accelerated degradation of characteristics (due to the lower working temperature, because the working temperature interval for electrolyte-supported SOFCs lies within 800–1000°C). The metal-supported SOFCs operate at 500–600°C and exhibit the highest electrochemical characteristics (power density) as compared with the other types; however, their fabrication is a highly laborious task because the standard colloid methods can hardly be used in preparation of functional SOFC layers. Thus, the methods used in production of anode-supporting structures turn out to be the easier realizable and economically sound.

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The fabrication of an individual SOFC is started with the preparation of support. For the anode-supported structure, the support should, on the one hand, be mechanically strong and, on the other hand, exhibit the minimum gas resistance, i.e., have the well developed network of through pores. To increase the efficiency and improve the structure of the SOFC anode, an additional functional layer is introduced. This functional layer should have the fine structure in order to provide the well-developed three-phase interfaces on which the fuel is oxidized. The presence of coarse pores is undesirable because the functional layer thickness usually does not exceed 20 μm and coarse pores decrease the useful electrode volume in which the electrochemical reactions proceed. The well-developed fine (less than 1 μm) porosity in the functional layer appears during the cell operation due to the volume effect (about 42%) of the NiO reduction to metal Ni. For this reason, no pore-forming agents are added to the suspension used for casting the functional layer.

Tape casting is the most suitable method for fabricating ceramic supports for SOFCs [2]. We used this method earlier for fabricating the supports of three-layered electrolyte. In [3], the developed technology which involves the tape casting of electrolyte sheets with different composition followed by their lamination to multilayer packs and high-temperature treatment is described in detail. In the latter study, the suspension based on preliminarily ground powders and organic solvents which are also involved the binder, the plasticizers, and the dispersing agent was prepared in two 24 h stages. The structures were laminated on a hydraulic press at the elevated temperature. The multistep annealing of structures was carried out with the use of covering plates coated by a protective ZrO_2 layer for 56 h with the exposure at 1350°C for 2–4 h.

One of the most difficult tasks in the preparation of an anode-supported SOFC is the formation of a thin gas-tight layer on the porous anode support. As the electrolyte material, an anion-conducting material is used, most often zirconia stabilized by oxides of rare-earth elements: yttrium, scandium, cerium, ytterbium, etc. The thickness of such a layer does not exceed 10 μm and determines the working temperature of the cell, because as the temperature lowers down, the ohmic losses become largely associated with the ion-transfer current in the solid electrolyte [4, 5] the resistance of which depends on the working temperature according to the Arrhenius law. The fabrication of a thinner layer (<10 μm) is possible by the method of magnetron sputtering, which was used [6] in preparation of the protective CGO sublayer and the YSZ electrolyte layer on the anodic support with the composition NiO–YSZ, and also by the methods of "cold" aerosol deposition [7] and ink-jet printing [8].

Due to the lower working temperature as compared with electrolyte-supported SOFCs, the cathode for an anode-supported SOFC should be made of highly active cathodic materials with the high mixed conduction such as LSC ($La_{0.6}Sr_{0.4}CoO_{3-\delta}$) or LSCF ($La_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$). As for electrolyte-supported SOFCs, the cathode deposition is carried out most often by screen printing [4, 5, 7, 9].

In this study, we prepared and characterized the full-size (100 × 100 mm^2) planar anode-supported SOFCs. The bilayered supporting anode was tape casted and then laminated. The thus prepared multilayer packets were annealed. The magnetron sputtering was used for the deposition of thin dense layers of the 8YSZ electrolyte (8 mol % Y_2O_3, 92 mol % ZrO_2) and the GDC10 barrier layer (10 mol % Gd_2O_3, 90 mol % CeO_2). The electrochemical characteristics were studied on specially fabricated SOFCs with LSC-based cathodes.

EXPERIMENTAL

When fabricating the bilayered supporting anode, we used the powders of 10Sc1YSZ ($(Sc_2O_3)_{0.1}$–$(Y_2O_3)_{0.01}$–$(ZrO_2)_{0.89}$) (Neo Chem Ltd., Moscow, Russia) and NiO (T:SP Company, Gornyi Shchit, Yekaterinburg, Russia) as the starting materials.

The supports were prepared by tape casting followed by lamination. Besides the powders, the suspensions contained the azeotropic mixture of solvents (methylethylketone (reagent grade) and isopropanol (reagent grade)), a PVB binder (Butvar, Showiningan, UK), plasticizers PEG-2000 (Sigma-Aldrich, USA) and Santicizer (Valtris Specialty Chemicals, USA), and a dispersing agent Menhaden Fish Oil (Sigma Chemical Company, USA). To obtain the porous current-collecting layer, rice starch BOTGAO (VinhThuan, Vietnam) was added to the suspension.

Suspensions were prepared on a roll-miller in three stages of 4, 24, and 24 h. In the first stage, the powders of 10Sc1YSZ and NiO were dry milled; in the second stage, the powders were mixed in solvents in the presence of the dispersing agent; in the third stage, the binder and the plasticizers were added to the suspension. For easier grinding and uniform mixing, the ceramic grinding balls of ZrO_2 with the diameter of 10 mm were used. Immediately before casting, the suspension was degassed for 2–4 h. The tape casting was carried out on the KEKO line (Slovenia).

Insofar as the thickness of the current-collecting structure after the annealing should be within 390–410 μm, the casted tape before its shrinkage and the removal of solvents should be no thinner than 1.5 mm. The tapes of such a thickness are difficult to be dried uniformly and crack in the drying stage. This is why to obtain the bilayered structure with the current-collecting layer of about 400 μm thickness and the functional layer of about 20 μm, we used 4 raw current-collecting sheets with the thickness of 200 μm (after drying) and 1 functional sheet.

The raw stacks were annealed in air in a high-temperature furnace with the use of fireproof saggers (Conrad Liphard & Soehne, Germany) and fireproof

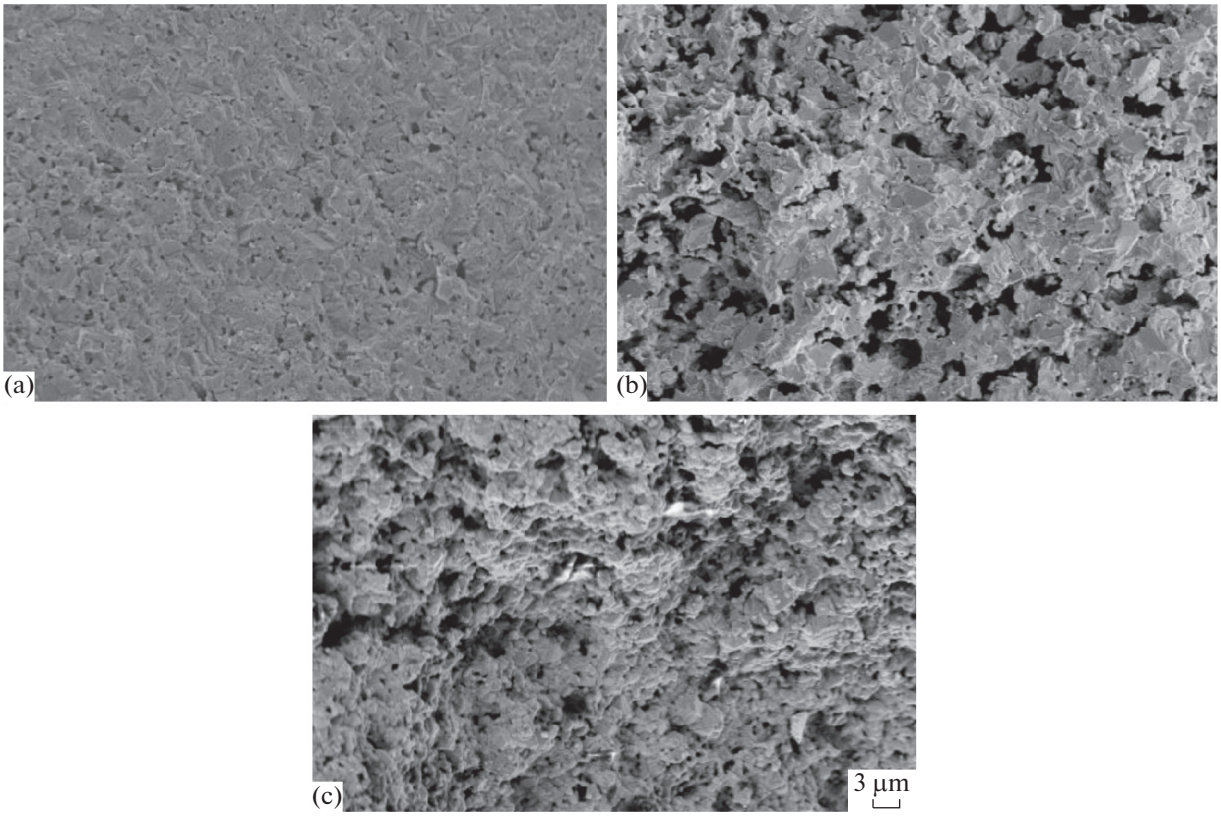

Fig. 1. Microstructure of cross-sections of one-layer supports annealed at 1350°C (magnification 5000). Suspension contained (a) no starch, (b) 10 wt % starch, (c) 20 wt % starch.

plates made of Al_2O_3 with the protective zirconium coating (Fuel Cell Materials, USA).

For the deposition of the bilayered 8YSZ/GDC10 electrolyte by the method of reactive pulse dual magnetron sputtering, we used metal targets of Zr–Y (85 : 15 at %) and Ce–Gd (90 : 10 at %) (Girmet, Moscow, Russia) with the size of 100 × 300 mm and 99.5% purity. The deposition was carried out in atmosphere of Ar/O_2 mixture at the working pressure of 0.2 Pa. The supports were fixed on the rotating barrel in order to obtain tapes with the uniform thickness over the whole surface. Before the deposition, the supports were cleaned by supersonic sequentially in pure isopropanol, acetone, and distilled water. The vacuum chamber was evacuated down to the baseline pressure of 10^{-3} Pa before the sputtering. The samples were preliminarily heated to about 400°C, this temperature was maintained during the sputtering. After this, their surface was subjected to the ion-beam treatment for 10 min (discharge voltage 2 kV, discharge current 100 mA) from an ion source with the closed drift of electrons. The discharge power was 4 kW on Zr–Y targets and 3 kW on Ce–Gd targets. After the deposition of the YSZ layer with the thickness of 4 μm, the GDC layer of 1.5 μm was deposited. The deposition rates of YSZ and GDC films were 0.72 and 2 μm/h, respectively.

The cathode was deposited by screen printing (EKRA E2, Germany) with the use of a paste based on $La_{0.8}Sr_{0.2}CoO_3$ (Kceracell, Korea).

The microstructure of multilayered ceramic plates was studied under a scanning electron microscope (SEM) Supra 50VP (CarlZeiss, UK).

The mechanical properties of supports were assessed by three-point bending method on the setup Instron 1195. The procedure of measurements and the photograph of the single-crystal sapphire tool can be found in [9]. Sample dimensions were 24 × 9 mm^2. The distance between the points of the sample-tool contact was 21 mm. The point of force application was at the equal distance from the contact points. The deformation was carried out at room temperature with a rate of 0.5 mm/min.

The electrochemical characteristics of elements were studied by using PowerLoad PL-150 electronic load and Z-500P impedance meter (Elins, Russia).

RESULTS AND DISCUSSION

First of all we studied how the concentration of the pore-forming agent in the suspension affects the microstructure and strength characteristics of anode supports. For this purpose, we prepared supports from suspensions containing from 0 to 20 wt % starch in the dry mixture. To obtain the required thickness

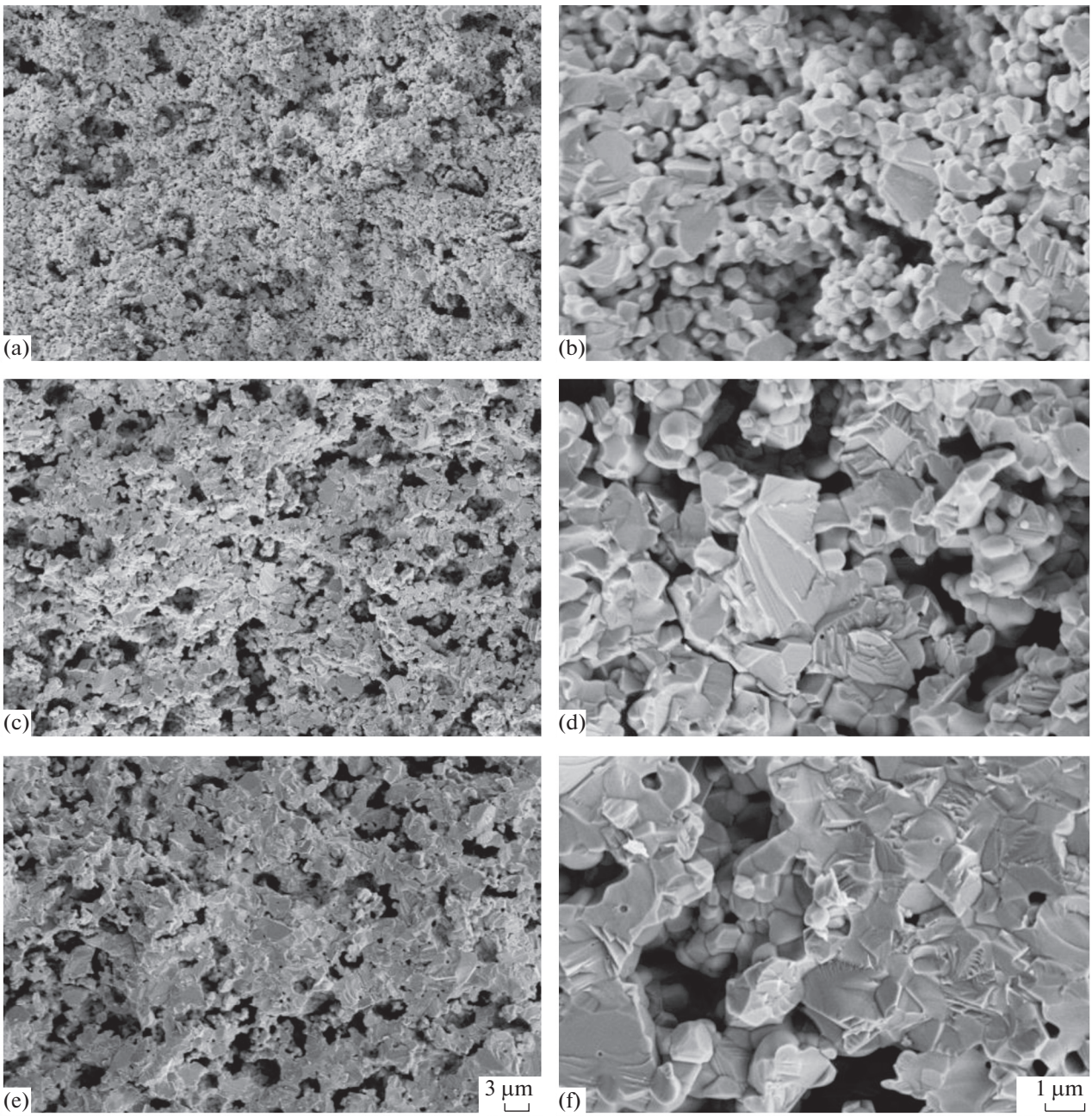

Fig. 2. Microstructure in cross sections of one-layer supports prepared from suspension containing 10 wt % starch (magnification 5000 and 25000): (a, b) annealing at 1250°C; (c, d) annealing at 1300°C; (e, f) annealing at 1350°C.

(420 μm), the samples were laminated to produce multilayered packets and then annealed in the temperature interval of 1250–1350°C.

Figure 1 shows the SEM images of the cross section of supports with different content of starch (0, 10, and 20 wt %) annealed at 1350°C (magnification 5000). Increasing the starch fraction in the suspension to 20 wt % led to destruction of the ceramic structure which included layering of multilayered packets along the inner lamination planes and the appearance of large voids. Such a behavior was explained by the large fraction of organic materials in the raw tape, namely, more than 45 wt %. In turn, in the absence of the pore-forming agent in the suspension, the plates with the almost 100% density were produced. Thus, it was shown that the addition of 10 wt % rice starch to the dry mixture makes it possible to obtain the ceramic structure of the required porosity on retention of the high strength characteristics of the support.

The maximum temperature of annealing controlled the characteristic size of support's granular structure and,

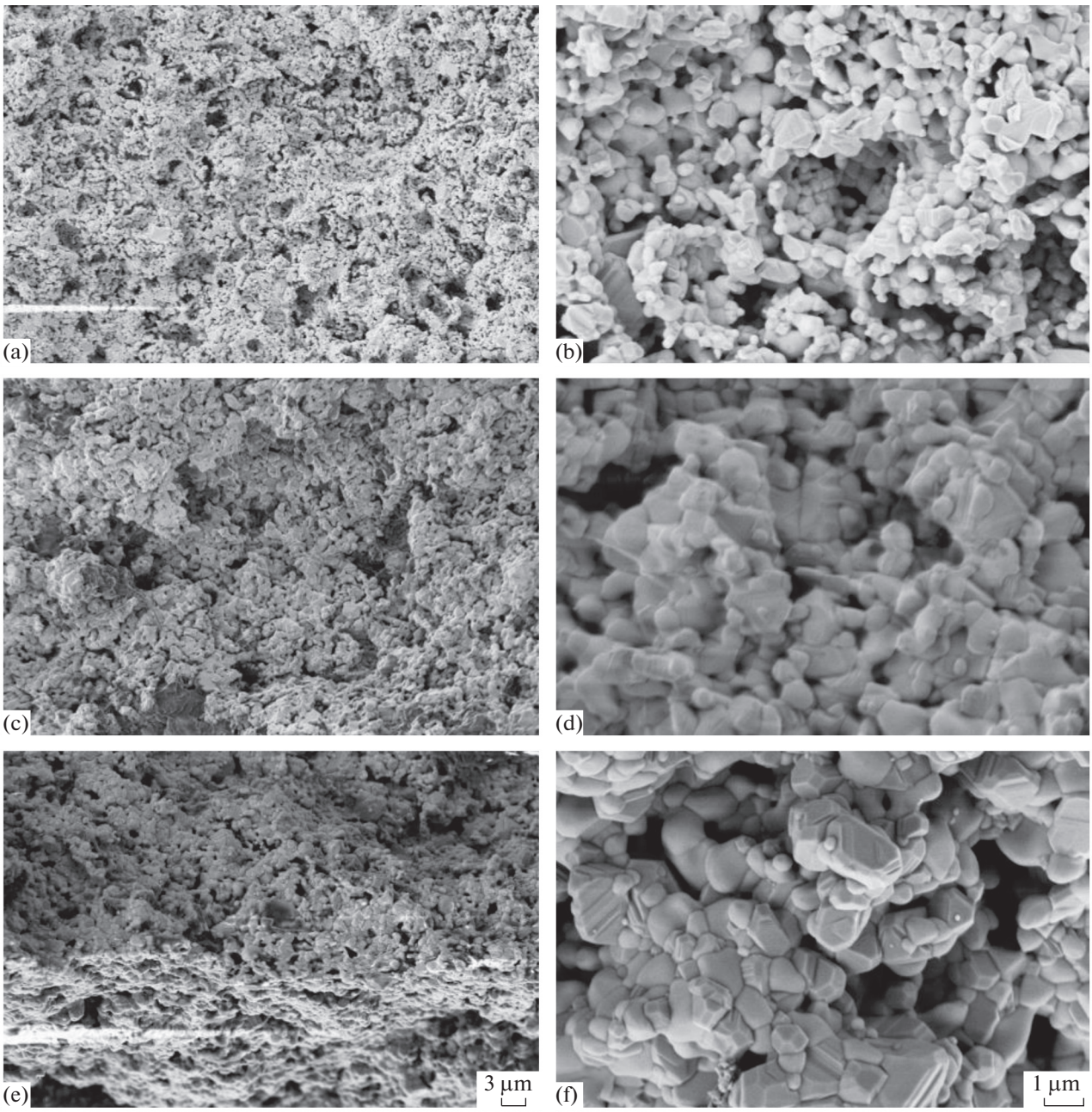

Fig. 3. Microstructure in cross sections of one-layer supports prepared from suspension containing 20 wt % starch (magnification 5000 and 25000): (a, b) annealing at 1250°C; (c, d) annealing at 1300°C; (e, f) annealing at 1350°C.

hence, its mechanical strength. Figures 2 and 3 show the images of the cross section of plates produced from suspensions containing 10 and 20 wt % starch and annealed at 1250, 1300, and 1350°C. It is seen that as the temperature increased, the grains grew and simultaneously the number of submicrometer pores decreased. It deserves mention that even at the annealing temperature of 1350°C, the grain size in the structure did not exceed 1 μm, which was sufficient for fabricating the highly efficient SOFC anodes with the well-developed three-phase interface [4].

Figure 4 shows the results of testing the mechanical characteristics of supports. At the higher temperature and the lower porosity, the ceramic support can sustain the higher mechanical loads. The support fabricated from the suspension containing 10 wt % starch at 1350°C exhibited the sufficient mechanical stability being the optimal choice for fabricating the supporting substrate for individual SOFCs of the anode-supported design.

To obtain the bilayered anode support with the current-collecting and functional layers of the necessary

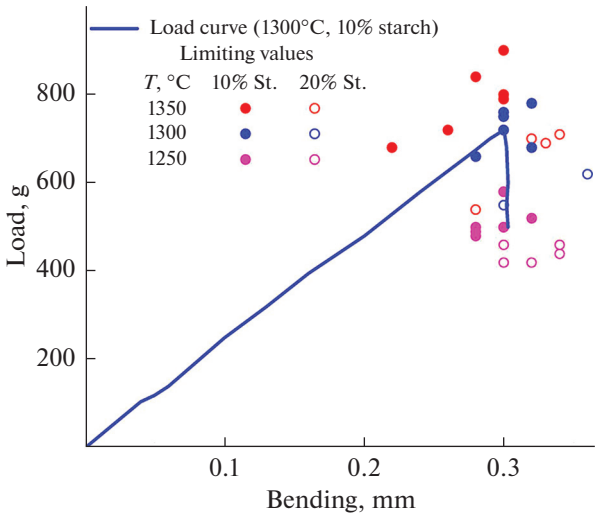

Fig. 4. The limiting values of bending and load found by the three-point method in the tests for mechanical strength of one-layered supports prepared from suspension containing 10 and 20 wt % starch and annealed at 1250, 1300, and 1350°C.

thickness, the tapes were laminated to produce multilayered packets which were cut into plates and sintered at 1350°C. Figure 5 shows the SEM images of the surface and the cross section of these bilayered supports. As seen, the adhesion between the layers was good, the functional layer was well sintered and contained no through pores on retention the grain size below 1 μm.

To study the electrochemical characteristics of our bilayered anode supports, we prepared a model SOFC. For this purpose, by magnetron sputtering (followed by annealing in air at 1200°C) the bilayered electrolyte of the following composition was deposited onto support's surface: the main 8YSZ layer and also the barrier GDC10 layer required to prevent the formation of nonconducting phases at the cathode/electrolyte interface. It should be noted that the method of magnetron sputtering imposes high requirements upon the quality of supports. Figure 6 shows microimages of cross-section of the anode support with the deposited bilayered electrolyte after annealing at 1200°C. It is seen that the electrolyte layers are characterized by the high density, the complete absence of through porosity, and good adhesion both with one another and with the anode support, and also have the

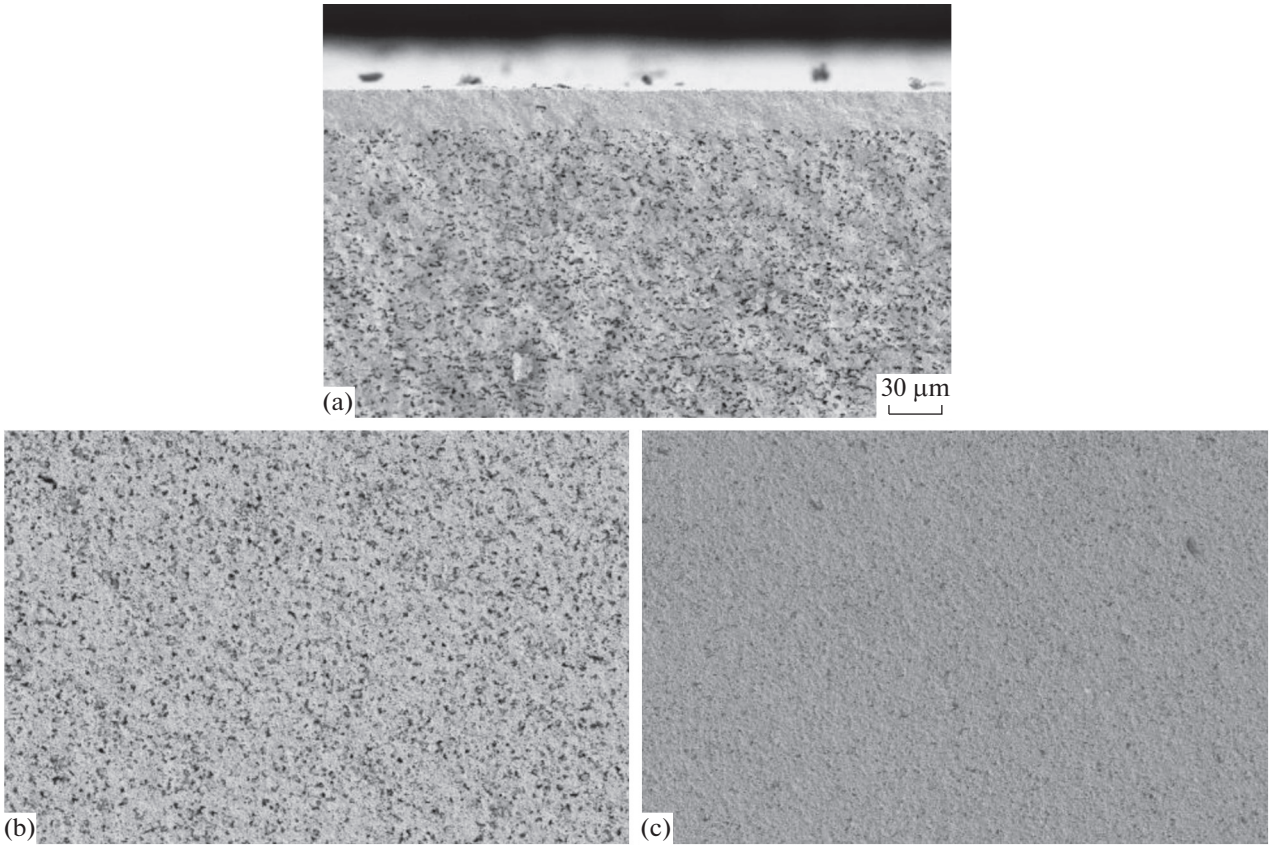

Fig. 5. Microstructure of (a) cross-section and (b) the surface of the current-collecting layer and (c) the surface of the functional layer for bilayered supports annealed at 1350°C (magnification 1000).

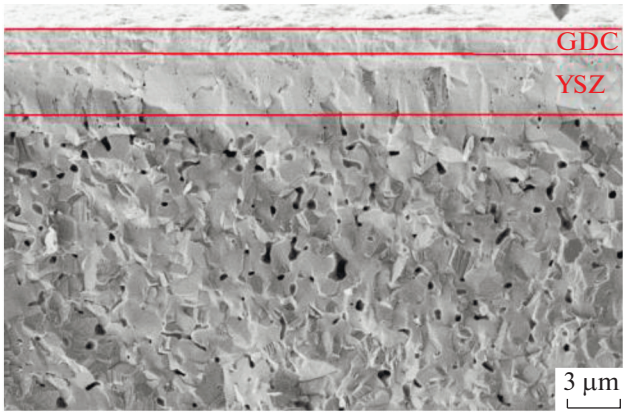

Fig. 6. Microstructure of a cross section of bilayered electrolyte supported by bilayered anode (magnification 10000).

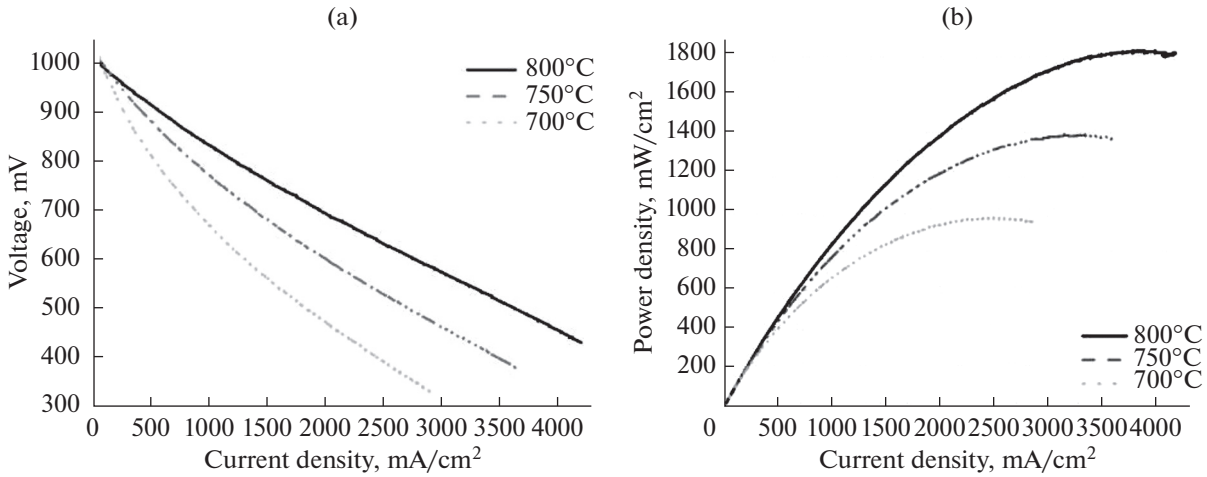

Fig. 7. (a) Voltammetric and (b) power characteristics determined at 700, 750, 800°C.

thickness of 4 and 1.5 μm for 8YSZ and GDC10, respectively.

The cathode based on lanthanum-strontium cobaltite was prepared by screen printing. The sintering of the cathode was carried out in the course of testing the characteristics of the model SOFC. Figure 5c shows the image of a cross section of such model SOFC on the cathode side.

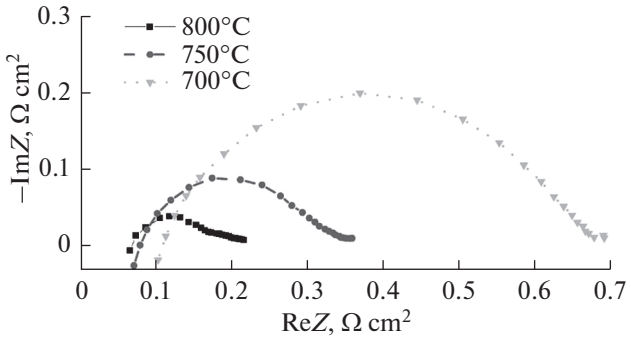

Fig. 8. Impedance spectra obtained at the temperature of 700, 750, 800°C.

The power and current–voltage characteristics were studied at the temperature of 800, 750, 700°C in the hydrogen flow of 150 mL/min and the air flow of 450 mL/min. Figure 7a shows that in all three cases, the open circuit voltage was 1 V which suggests that the electrolyte layers were of sufficiently high quality, which guaranteed the low level of gas and charge leakages.

The maximum effective power density reached 1.8 W/cm^2 at 800°C (Fig. 7b), which suggests the extremely low value of the internal resistance of the model SOFCs. It deserves mention that decreasing the working temperature to 700°C almost halved the power density (0.96 W/cm^2). The impedance spectra (Fig. 8) show that the deterioration of characteristics of the anode-supported SOFCs was preferentially caused by the increased contribution of electrode

processes to the internal resistance of the cell. The polarization part of the resistance increased more than 5-fold as the temperature decreased by 100°C and was higher than 0.55 Ω cm^2. At the same time, the contribution of ohmic losses changed insignificantly and did not exceed 0.1 Ω cm^2 even at 700°C.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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