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Featured Letter

Bilayered anode supports for planar solid oxide fuel cells: Fabrication and electrochemical performance

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ABSTRACT

Bilayered substrates for anode-supported solid oxide fuel cells (SOFCs), made of NiO and 10 mol.% Sc_2O_3 and 1 mol.% Y_2O_3 co-stabilized zirconia (10Sc1YSZ), were produced employing the tape casting technique. The optimization of the pore former (rice starch) content in the starting suspension and thermal treatment conditions provide necessary porosity, simultaneously maintaining sufficiently high mechanical strength of the composite measured by the three-point bending method. Bilayered gas-tight solid electrolyte films of 8 mol.% Y_2O_3 stabilized zirconia and 10 mol.% Gd_2O_3 doped ceria (8YSZ/10GDC) were deposited by magnetron sputtering, followed by annealing at 1200 °C. The area-specific power density of a model SOFC achieved 1.8, 1.4, and 0.9 W/cm^2 at 800, 750, and 700 °C, respectively.

1. Introduction

Solid oxide fuel cells (SOFCs), an important class of energy-conversion devices, are used to produce electrical power and heat from a variety of gaseous and liquid fuels [1,2]. Planar SOFCs have serious advantages over other types. Namely, this approach gives opportunity to conduct a full optimization of multilayered electrodes' composition and microstructure [3]; organization of current collection is easier than that for inner electrode in tubular design [4]; planar SOFC stacks have higher volumetric power density. One of the most promising architectures of planar SOFCs are anode-supported cells (ASC) [5]. The main technological challenges in the ASC production are related to mechanically stable porous anode supports [6] and gas tight thin-film solid oxide electrolyte [7]. In particular, the anode substrates should simultaneously have a sufficient mechanical strength and a minimum gas diffusion resistance provided by a well-developed network of pores.

In the previous report [8], tape casting technique was applied to fabricate three-layer electrolyte substrates. The optimized technological details were described in Ref. [9], including the production of electrolyte sheets of various compositions with their subsequent lamination into multilayer stacks and high-temperature treatment.

The present work was centered on the fabrication and characterization of highly efficient anode supports by tape casting. In this work full-size (100x100mm) bilayer (current-collecting, CCL and functional, FL layers) planar anode supports with bilayer thin-film electrolyte for SOFCs were manufactured combining the tape casting technique and magnetron sputtering [10]. To increase the efficiency, FL is introduced into the SOFC anode architecture. FL should have a finer structure to obtain a large triple-phase boundary (TPB) area. A fine porosity (pore size less than 1 μm) in FL, necessary to accelerate the electrochemical reaction, was formed during operation due to the 42% volume decrease caused by NiO reduction to metallic Ni. This made it possible to avoid use of pore-forming additives. To study the electrochemical performance, model SOFCs with lanthanum-strontium cobaltite (LSC) based cathode were manufactured.

2. Experimental section

Anode substrates were fabricated by tape casting technique followed by stack lamination. 10Sc1YSZ ($(Sc_2O_3)_{0.1}$–$(Y_2O_3)_{0.01}$–

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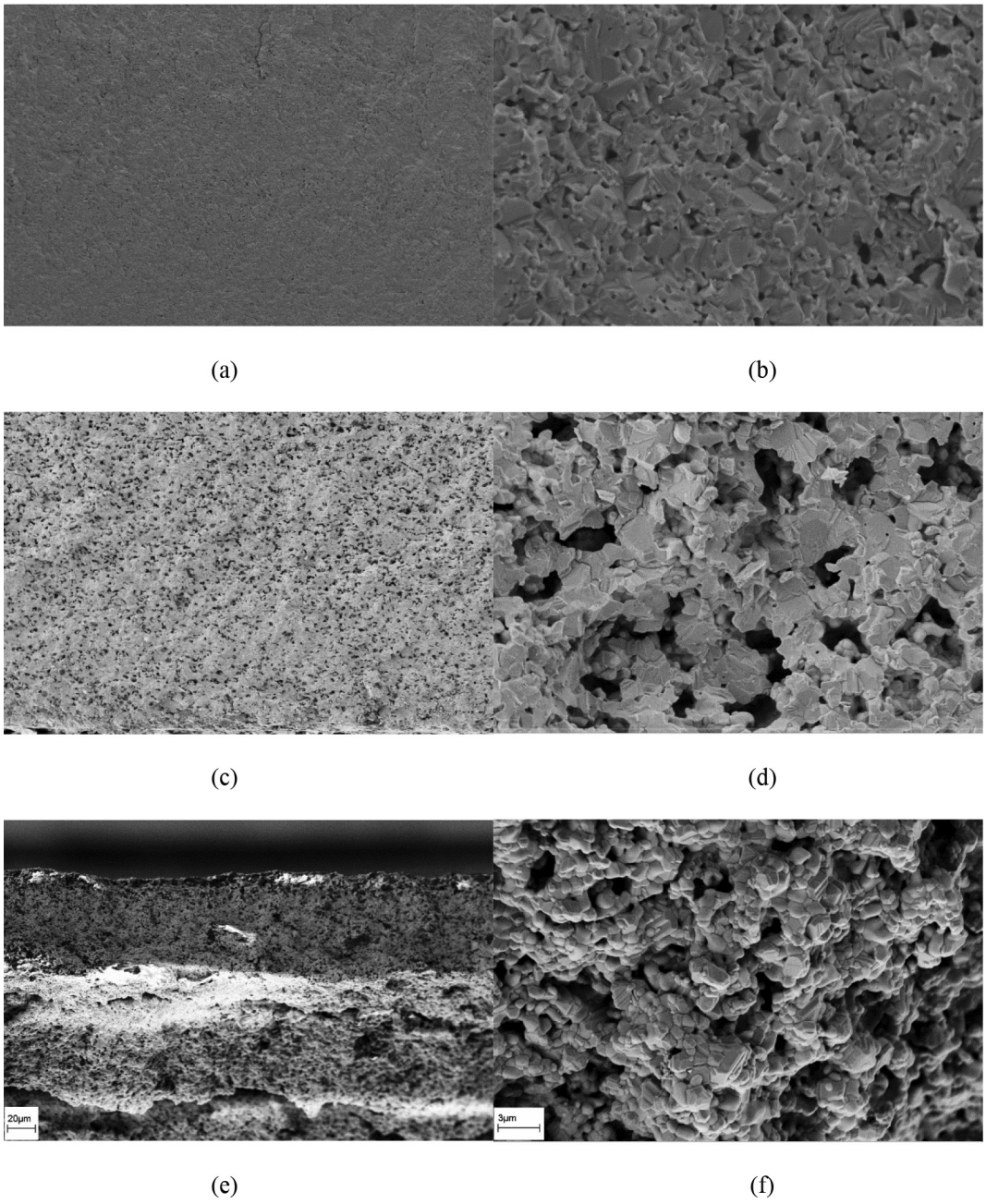


Fig. 1. Cross-section microstructure of single-layer anode supports (x1000 and x10000 magnifications on the left and right images respectively): a and b correspond to the suspensions without pore former; c and d – 10 wt% of the pore former; e and f – 20 wt%.

$(ZrO_2)_{0.89}$) powder produced by "Neochem" (Russia) and NiO powder produced by "T:SP" (Russia) were used. In addition to powders, the suspensions contained an azeotropic mixture of solvents (methyl-ethyl-ketone and isopropanol), PVB binder from Butvar (UK), PEG-2000 plasticizer from Sigma-Aldrich (USA), Santicizer from Valtris (USA), dispersant Menhaden Fish Oil from Sigma-Aldrich (USA), BOTGAO rice starch from Vinh Thuan (Vietnam). Mass content of components mentioned above (10Sc1YSZ:NiO:solvents:PVB:PEG-2000:Santicizer:dispersant:starch) for CCL was 21:35:26:5:3:3:1:6, and for FL it was 33:25:30:5:3:3:1:0.

The suspensions were prepared on a roller-mill in two 24 h stages with dry pre-grinding. For grinding and uniform mixing of the suspension, ceramic grinding balls made of ZrO_2 with a diameter of 10 mm were added. Before casting, suspension passed the degassing stage for 2–4 h. Casting took place on KEKO line (Slovenia).

To obtain bilayer 400–420 μm thick supports stacks from five "green" sheets (four of them contained pore former) were collected. The raw stacks were fired in air in a high-temperature furnace for 56 h with holding at 1350 °C for 2–4 h using high-temperature saggers from Conrad Liphard&Soehne (Germany) and Al_2O_3 setter plates with a protective zirconia coating from FuelCellMaterials (USA).

Reactive pulsed dual magnetron sputtering was used to deposit two-layer 8YSZ/10GDC electrolyte using metal Zr-Y (85:15at.%) and Ce-Gd (90:10at.%) targets from Girmet (Russia). The deposition was carried out in an atmosphere of Ar/O_2-mixture at operating pressure of 0.2 Pa. The samples were preheated to 400 °C and

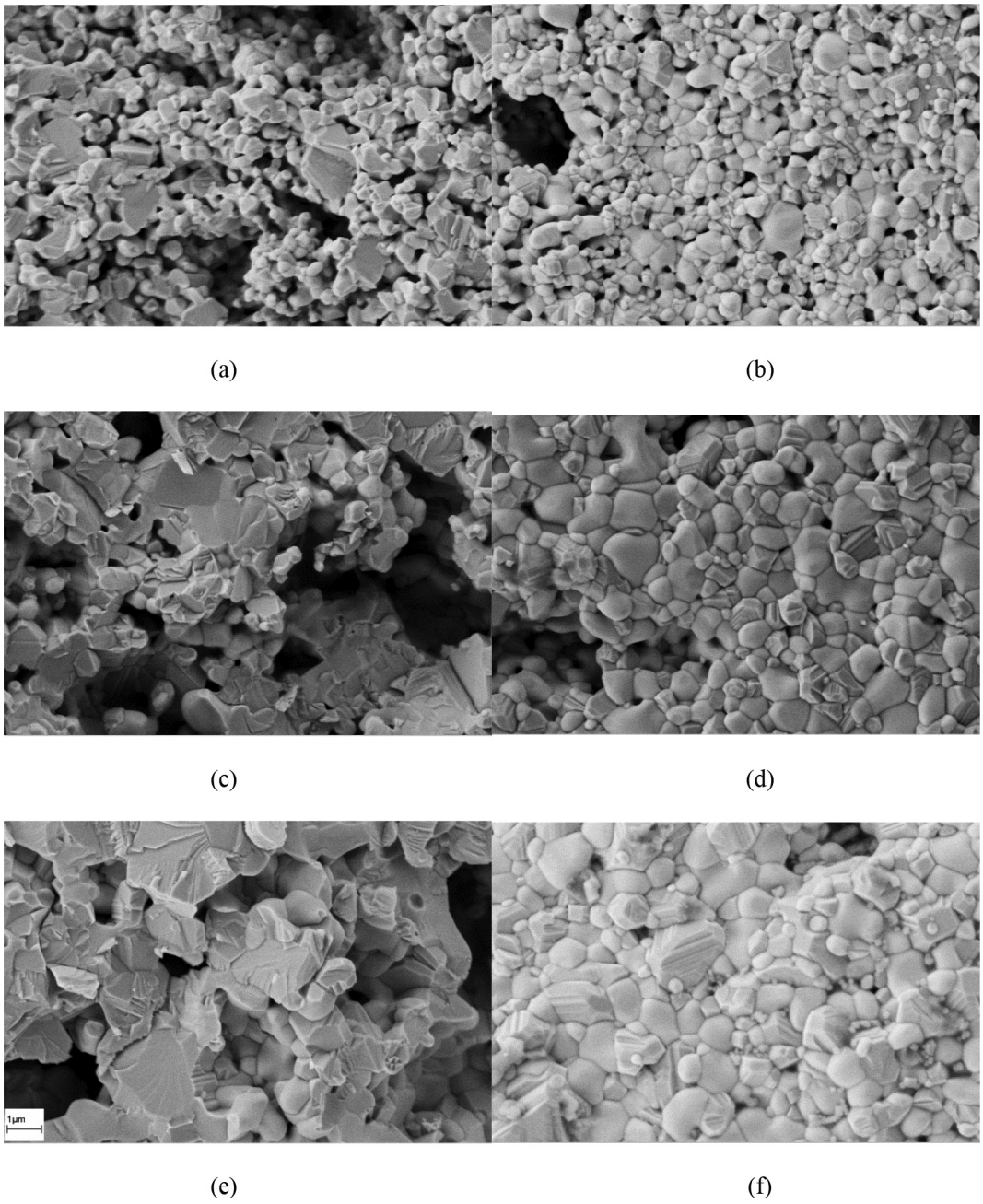


Fig. 2. Microstructure of the cross-sections (a,c,e) and surface (b,d,f) of single-layer anode supports (x25000 magnification): a and b – annealing at 1250 °C; c and d – 1300 °C; e and f – 1350 °C.

maintained at this temperature during deposition. Afterwards, ion-beam treatment of the substrate surface was carried out for 10 min using a source with a closed electron drift. The deposition rate of YSZ and GDC films was 0.72 and 2 µm/h, respectively.

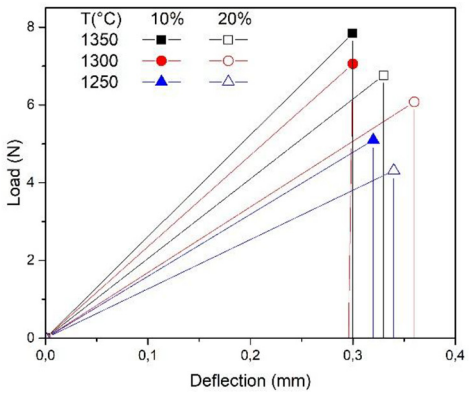
The cathode electrode was applied by screen printing using EKRA E2 (Germany) with paste based on $La_{0.8}Sr_{0.2}CoO_{3-d}$ from KCeraCell (Republic of Korea). The microstructure of the obtained multilayer ceramic plates was studied using a Supra 50VP scanning electron microscope (CarlZeiss, UK).

The mechanical properties of the substrates were estimated using the three-point bending method on an Instron 1195 setup. The measurement scheme and photograph of a single-crystal sapphire test-bed are given in [11]. The electrochemical performance was studied using PL-150 electronic load and Z-500P impedance spectrometer (Elins, Russia).

3. Results and discussion

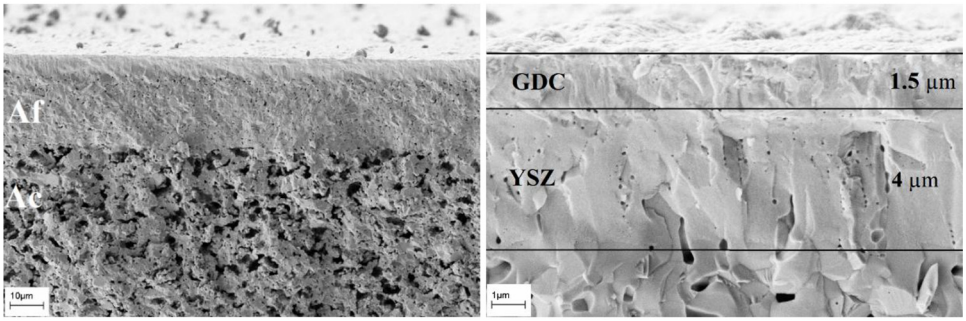
Influence of pore-forming agent content in the suspension on the microstructural and strength characteristics of the anode substrates was studied. For this, substrates were made using suspensions with different starch content. Fig. 1 shows SEM-images of the substrate cross-section with 0, 10, and 20 wt% starch content annealed at 1350 °C. Increase of the starch ratio in the suspension to 20 wt% leads to the destruction of the ceramic microstructure because of large (>45 wt%) ratio of organic materials in the green tape. The absence of a pore former in the slurry, in turn, results in almost 100% density.

The maximal firing temperature governs characteristic grain size and morphology of the substrate and its mechanical stability. Fig. 2 shows images of the cross-section and surface



(a)

(b)



(c) (d)

Fig. 3. a – critical load and deflection for different pore-former additions and firing temperatures. Photo (b) and cross-section microstructure (c,d) of bilayered anode support with bilayer solid electrolyte.

of plates with a starch content in the suspension of 10 wt%, fired at 1250, 1300 and 1350 °C. One can observe an increase in temperature leading to grain growth and, simultaneously, a decrease in the number of submicron pores. It should be noted that even at firing temperature of 1350 °C, the grain size of the structure does not exceed 1 μm, which is sufficient to create a highly efficient SOFC anode with developed triple-phase boundaries [6].

The results of mechanical characteristics studies are shown in Fig. 3a. The higher the firing temperature and lower the

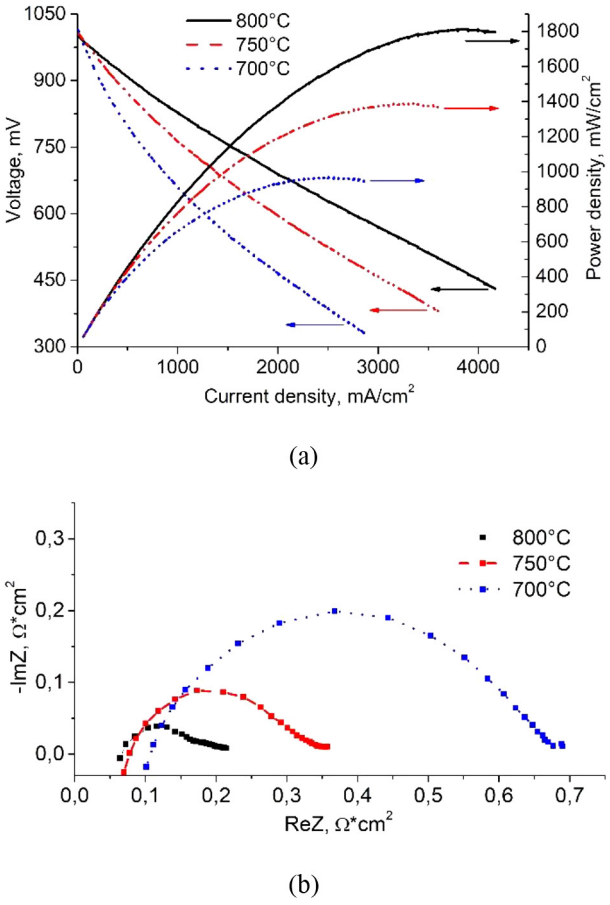


Fig. 4. I-V curves (a) and impedance spectra (b) of the model SOFC for 700, 750, 800 °C.

porosity, the higher mechanical load ceramic substrate can withstand. The substrate with a starch content of 10 wt% fired at 1350 °C has sufficient porosity and high mechanical stability and it is optimal for the manufacturing of a substrate for anode-supported SOFC.

A photograph and cross-sectional SEM-image for obtained two-layer plates with the bilayered solid electrolyte are shown in Fig. 3(b-d). The electrolyte layers exhibit a high density, complete absence of through porosity, and good adhesion both to each other and to substrate, and the thicknesses are 4 and 1.5 μm for 8YSZ and 10GDC, respectively.

Current-voltage characteristics were studied at temperatures of 700–800 °C at hydrogen and air flows of 150 and 450 ml/min, respectively. Fig. 4 shows that in all cases the open-cirquit voltage (OCV) exceeded 1 V, which indicates a sufficiently high quality of the electrolyte layers as well as sealing, providing a low level of gas leakage and local short-circuiting.

The maximum power density was 1.8 W/cm^2 at 800 °C, which indicates an extremely low value of the internal resistance of the fabricated SOFCs. Lowering the operating temperature to 700 °C leads to a decrease in the power density by almost 2 times (to 0.96 W/cm^2). From the impedance spectra (Fig. 4b) one can observe that the decrease in the characteristics is mainly caused by the increase in the contribution of electrode processes to the internal resistance. The polarization part of the resistance increased by more than 5 times with a decrease in temperature by 100 °C and became more than 0.55 Ω·cm^2. At the same time, the contribution of ohmic losses changed insignificantly and does not exceed 0.1 Ω·cm^2 even at 700 °C.

4. Conclusions

Anode supports with bilayer thin-film electrolyte for SOFCs were manufactured by tape casting and magnetron sputtering. Microstructure as well as mechanical strength were studied in order to optimize the preparation route. The output power obtained from the model anode-supported SOFCs reached the levels of 1.8, 1.4, and 0.9 W/cm^2 at 800, 750, and 700 °C, respectively.

CRediT authorship contribution statement

E.A. Agarkova: Data curation, Investigation, Writing - original draft. **I.N. Burmistrov:** Investigation, Writing - original draft. **D.A. Agarkov:** Writing - original draft. **O. Yu. Zadorozhnaya:** Data curation, Investigation. **A.V. Shipilova:** Data curation, Investigation. **A. A. Solovyev:** Data curation, Investigation. **Yu.K. Nepochatov:** Investigation. **S.I. Bredikhin:** Supervision, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2020.128752.

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