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Relationships between mechanical stability of the anode supports and electrochemical performance of intermediate-temperature SOFCs

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A R T I C L E I N F O

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A B S T R A C T

Mechanical strength and microstructure of the anode supports are among the most critical factors affecting the long-term stability and performance of the intermediate-temperature solid oxide fuel cells (IT-SOFCs). In this work, the anode supports made of Ni/NiO and 10 mol.% Sc_2O_3 and 1 mol.% Y_2O_3 co-stabilized zirconia (10Sc1YSZ) were fabricated by tape casting, followed by sintering and screen-printing of the anode functional layer of 10 mol.% Gd_2O_3 doped ceria (10GDC) and NiO. Then two dense solid-electrolyte layers, 8 mol.% Y_2O_3 stabilized zirconia (8YSZ) and 10GDC, were deposited by the reactive pulsed dual magnetron sputtering. Mechanical properties of as-sintered and reduced anode supports were estimated employing three-point bending technique. The power density of model anode-supported SOFCs, where mechanical stability of the support was kept after complete reduction in hydrogen, achieved 0.3 W/cm^2 at 800°C and 0.6 V under air/hydrogen gradient.

1. Introduction

Solid oxide fuel cells (SOFCs) provide an opportunity to directly transform chemical energy of various fuels into electrical power and heat with a high efficiency. Nowadays attention of numerous researchers and producers [1–3] is essentially centered on anode-supported SOFC architecture due to lower operating temperatures of 650–800°C [4] with respect to 850–1000°C necessary for electrolyte-supported SOFCs [5]. The most serious challenges which may hamper commercialization of this technology are associated with relatively low reliability and long-term stability [6]. These challenges originate from the use of metallic Ni as an electronic conductor in the supporting anode composite. In the course of anode support fabrication, NiO is embedded into the composite; its reduction into Ni during the SOFC operation leads to approximately 40 % volume changes [7–8], which is critical for the mechanical stability of the support. Therefore, frequent redox and thermal cycling is contraindicated for the anode-supported SOFCs that means, in turn, inability of frequent startups of any power plant based on the anode-supported SOFCs.

In previous work [9], the authors reported an optimization of pore-former content and thermal treatment protocol in order to obtain as-sintered bilayer anode supports with a sufficient mechanical strength. Continuing this research, the present work is centered on the search for optimum microstructures of the anode supports from the viewpoint of their reliability under different conditions, including reducing atmospheres. It was supposed that stability of the NiO/10Sc1YSZ (10 mol.% Sc_2O_3, 1 mol.% Y_2O_3, 89 mol.% ZrO_2) composite can be preserved when the particle sizes of electronically and ionically conducting phases have a substantial difference, namely, large grains of zirconia form a rigid skeleton and submicron-sized grains of Ni/NiO are located uniformly between the zirconia grains.

2. Experimental section

The anode supports were fabricated by the tape casting technique followed by stack lamination. NiO powder produced by T:SP company (Russia), $NiSO_4{\cdot}7H_2O$ (JSC Uralelektromed, Russia), 10Sc1YSZ powder (Neochem, Russia) and rice starch (BOT GAO, Vietnam) were used as starting materials. Table 1 lists the compositions and details of the slurry preparation.

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Table 1
Volume ratio of starting materials used for the composite support fabrication.

Sample designation	NiScSZ	NiOScSZ	NiOScSZ_10S
10Sc1YSZ	40 vol%	40 vol%	32 vol%
NiO	–	60 vol% (preliminary ball-milled)	48 vol%
$NiSO4 \cdot 7H_2O$	60 vol% in terms of NiO	–	
Rice starch	–	–	20 vol%
Technological route	Joint roll-milling during 24 h. Calcination at 1000 C for obtaining 60 vol% NiO/40 vol % 10Sc1YSZ composite. Subsequent preparation of slurry.	Joint roll-milling during 24 h. Subsequent preparation of slurry.	The procedure was similar to that reported in Ref. [9].

The slurries for tape casting comprised the organic additives listed in Ref. [9], in the same proportions. Tape casting procedure was carried out using Keko line (Slovenia) at NEVZ-Ceramics (Russia). The sintering procedures used to obtain ceramics with the thickness of 400–450 μm was also reported elsewhere [9]. The anode functional layers consisting of 40 vol% of NiO (supplied by T:SP, Russia) and 60 vol% of 10GDC (FuelCellMaterials, USA) were applied on one half of the sintered supports by screen printing and sintered at 1300°C. A half of the sintered single-layer supports were reduced in a tubular RHTC 80 furnace (Nabertherm, Germany) at 900°C during 1 h in flowing 6% H_2 - 94% Ar gas mixture.

Reactive pulsed dual magnetron sputtering was used to deposit two-layer 8YSZ/10GDC electrolyte (thickness of 5.0 and 1.75 μm, respectively) on the bi-layered anode supports. The procedure was described earlier [9]. The targets used for the magnetron sputtering, made of metallic Zr-Y (85:15 at.%) and Ce-Gd (90:10 at.%), were supplied by Girmet (Russia).

The cathodes made of $(La_{0.60}Sr_{0.40})_{0.95}Co_{0.20}Fe_{0.80}O_{3-X}$ (LSCF)/10GDC (KCeraCell, Korea) were deposited by screen printing using an EKRA E2 instrument (Asys, Germany) and then sintered at 1050°C in air. $(La_{0.80}Sr_{0.20})_{0.95}CoO_{3-x}$ (LSC) based paste from KCeraCell (Korea) was used to form contact layers between the model SOFCs and Pt current collectors.

Microstructure of the ceramic layers and model cells was studied using a Supra 50VP scanning electron microscope (SEM, CarlZeiss, UK). Mechanical stability of as-sintered and hydrogen-reduced anode supports was estimated using three-point bending method on a UTC111.2-50 machine for mechanical tests of construction materials (Russia). The flexural stress (σ) was calculated as [10]:

$$\sigma = \frac{3Fl}{2ah^2} \quad (1)$$

where F is the critical load; a, h and l are the width, thickness and length of the sample, respectively. The constant applied force was equivalent to 1 kg; the loading pin was moving with a constant speed of 0.5 mm/min. The high-temperature setup for the electrochemical measurements was described elsewhere [11]. The electrochemical testing was performed using a Reference 3000 potentiostat/galvanostat/ZRA (Gamry Instruments, USA).

3. Results and discussion

SEM images of the cross-section microstructure of as-sintered (left) and reduced (right) anode supports designated as NiScSZ, NiOScSZ and NiOScSZ_10S (see Table 1) are presented in Fig. 1. As expected, NiOScSZ_10S has a much higher porosity compared to other supports. Approximately 20 % porosity of the supports appeared during sintering due to the starch additive. Nevertheless, using of nickel sulfate instead of NiO also resulted in a microstructure with well-developed porosity even without use of pore-formers (Fig. 1a and 1b). The average pore size achieves approximately 3 μm in NiScSZ after reduction (Fig. 1b, d), whilst pore size in NiOScSZ is about 1 μm.

The results of mechanical tests by the three-point bending technique are displayed in Fig. 2. The levels of mechanical strength for all as-sintered supports are quite close to one another. The flexural stress varies from 40 to 50 MPa. The reduction leads, however, to an appearance of significant differences in the mechnical strength. The most porous supports (NiOScSZ_10S) became completely unstable after reduction; the corresponding flexural strength decreased by 93 %. On the contrary, the most gas-tight NiOScSZ supports showed an increase in avarage values of the bending stress and deflection (63 MPa instead of 48 MPa and 0.55 mm instead of 0.2 mm). In turn, NiScSZ supports exhibit an improved flexibility reflected by the substantially larger deflection, but the value of critical load became lower.

The electrochemical performance of model anode-supported SOFCs was studied at 800°C under air/ hydrogen gradient, with the fuel and oxidant flow rates of 200 ml/min. Fig. 3(a and b) presents the current–voltage (I-V) dependencies, power density and impedance spectra of the cells. The open-circuit voltage (OCV) in the case of NiScSZ support is higher than 1 V; for NiOScSZ, OCV is 0.98 V. These values indicate that the anode-supported electrolyte layers possess a sufficiently high density, in agreement with SEM analysis after testing (Fig. 3, c and d).

NiOScSZ_10S supported SOFC exhibited the maximum power density up to 1800 mW/cm^2 [9]. This level is associated with a relatively small contribution of gas diffusion to the overall cell resistance. The impedance spectra of both single cells where the anode supports were fabricated without pore-former, show that the gas diffusion contribution is a half of the entire cell resistance. This indicates that the support porosity is insufficient for fuel supply and should be increased. At the same time, the electrode polarization resistance of these cells is sufficiently low, 0.1 Ohm*cm^2 (Fig. 3b).

4. Conclusions

Anode supports for intermediate-temperature SOFCs were fabricated by tape casting technique. The best mechanical properties before and

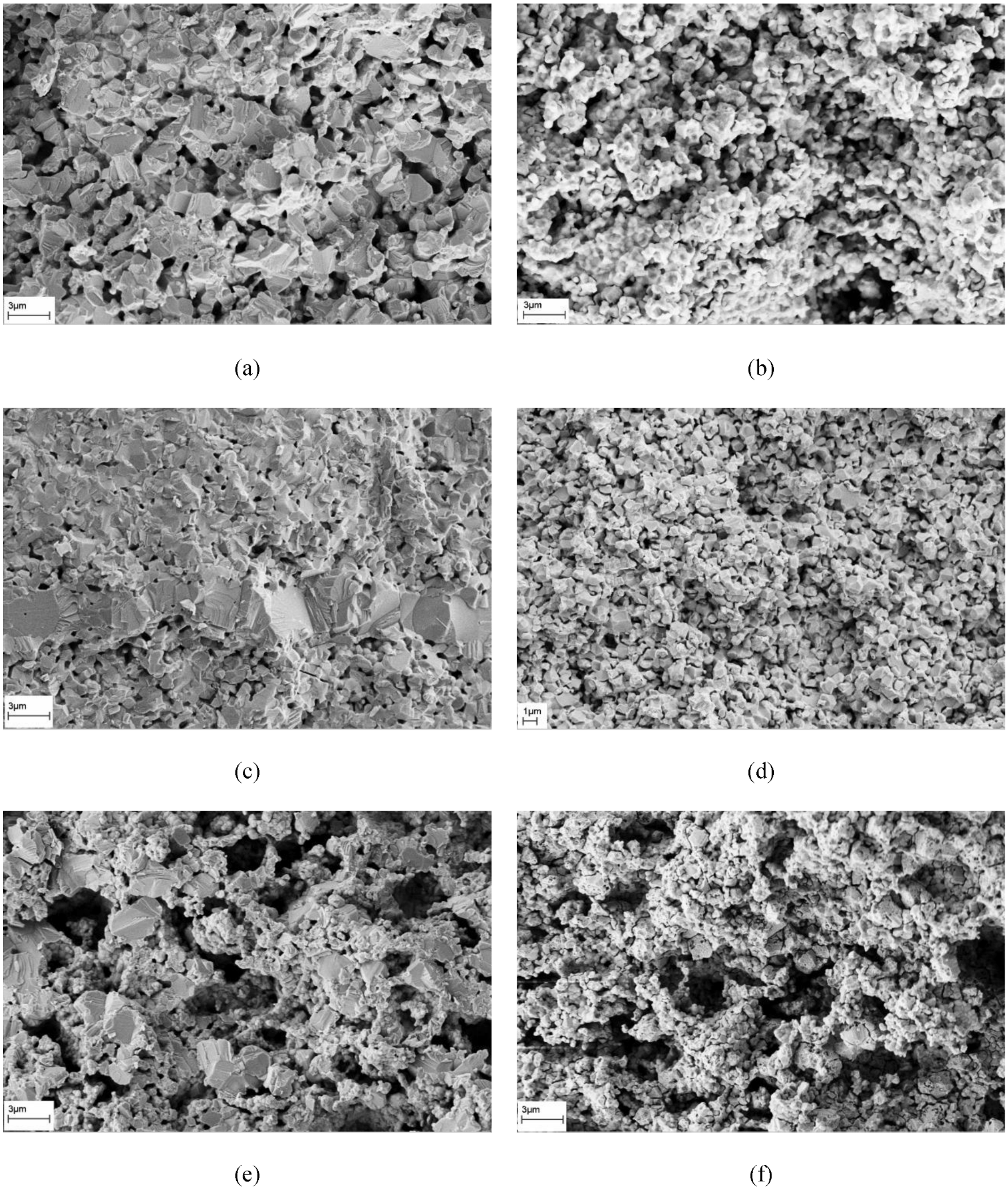

Fig. 1. SEM images of cross-sections of as-sintered (a, c, e) and reduced (b, d, f) samples of NiScSZ (a, b), NiOScSZ (c, d) and NiOScSZ_10S (e, f).

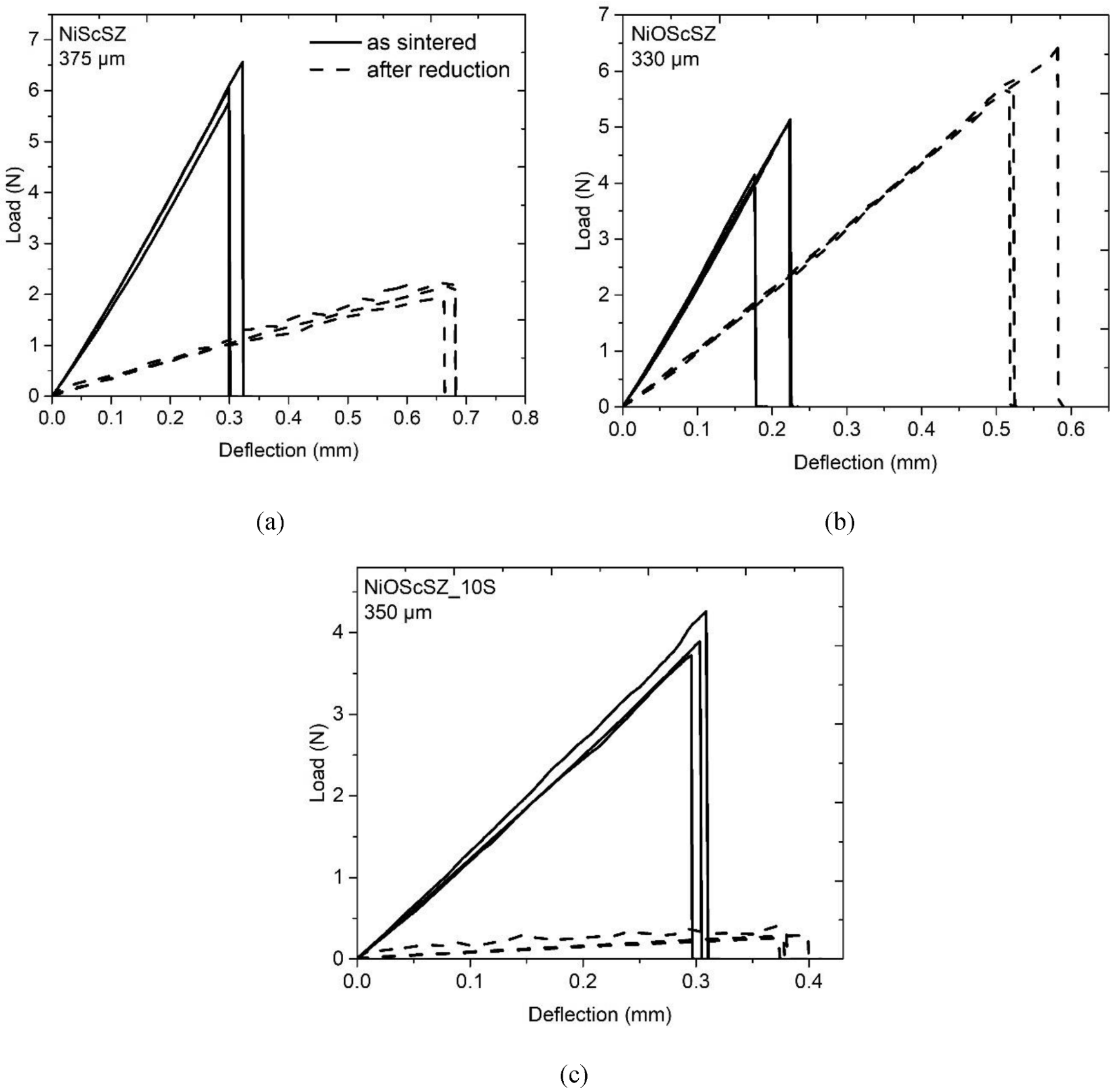

Fig. 2. Load curves of NiScSZ (a), NiOScSZ (b) and NiOScSZ_10S (c) supports tested by three-point bending technique.

after reduction were exhibited by the anode support fabricated without pore-former. The use of such supports results, however, in a worse electrochemical performance. The maximum output power obtained from the model anode-supported SOFCs is 300 mW/cm^2 at 800°C.

CRediT authorship contribution statement

E.A. Agarkova: Data curation, Investigation, Writing - original draft. **O.Yu. Zadorozhnaya:** Data curation, Investigation. **I.N. Burmistrov:** Investigation, Writing - original draft. **D.V. Yalovenko:** Investigation. **D.A. Agarkov:** Writing - original draft, Writing - review & editing. **S.V. Rabotkin:** Investigation. **A.A. Solovyev:** Data curation, Investigation. **Yu.K. Nepochatov:** Investigation, Writing - review & editing. **M.N. Levin:** Data curation. **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.

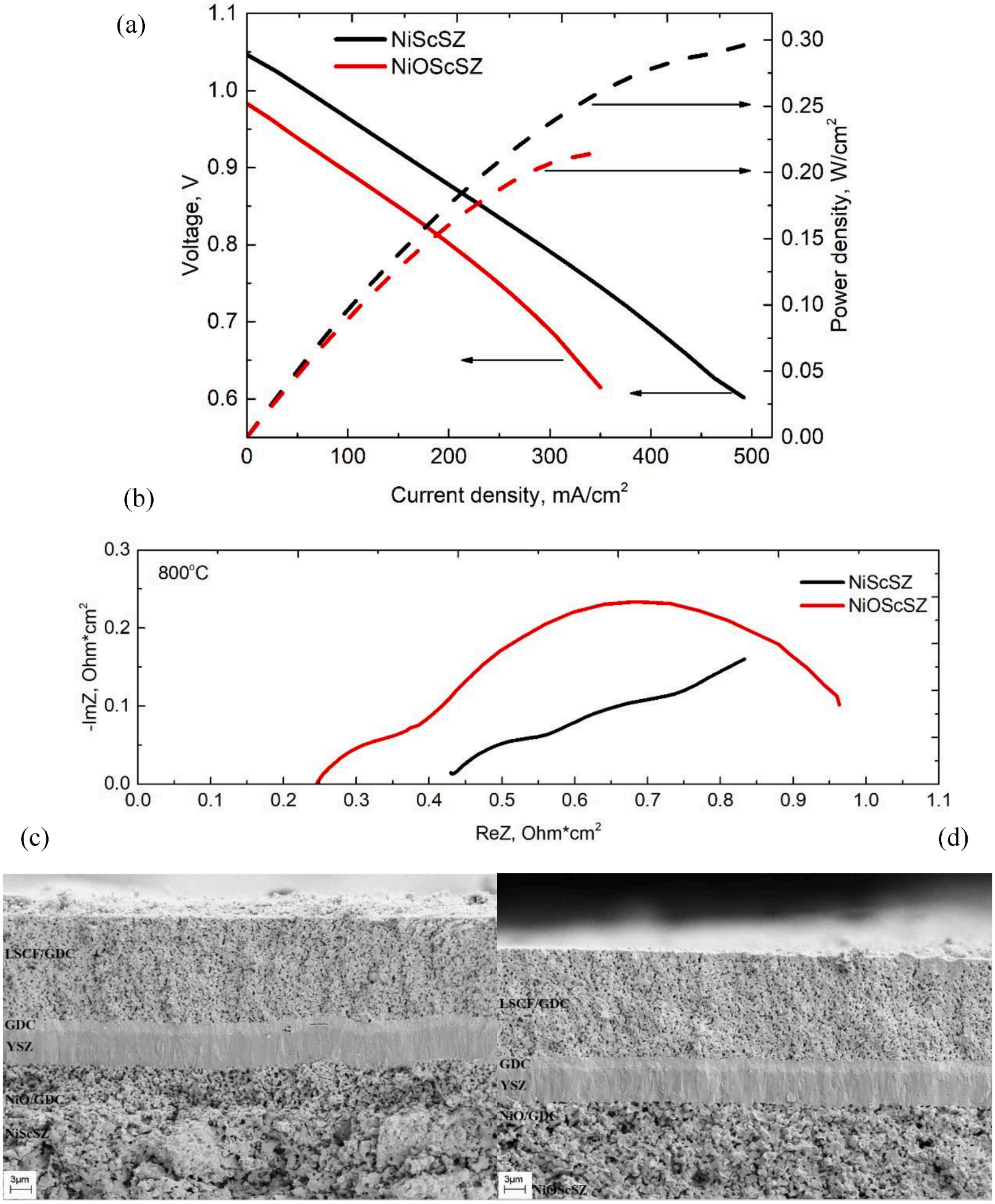

Fig. 3. I-V curves and power density (a) and impedance spectra (b) of model SOFCs with NiScSZ and NiOScSZ anode supports at 800°C, and SEM micrographs of cross-section of the cells based on NiScSZ (c) and NiOScSZ (d) supports after electrochemical testing.

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