



Fabrication of metal-supported solid oxide fuel cells by combining aerosol deposition and magnetron sputtering techniques

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Abstract

In the present study, the fabrication route, including combining the aerosol deposition method and magnetron sputtering, was demonstrated for the fabrication of metal-supported solid oxide fuel cells. Thick-film anode layers (approximately 45 μm) of 10 mol.% gadolinia-doped ceria (GDC) and nickel (57/43 wt% ratio) were deposited by means of the aerosol deposition method on porous metal (Cr-28 wt%, Fe) supports from softly agglomerated submicron powders. The half-cells with the anode layers were sintered at 1000 °C in vacuum. Thin-film membranes of gadolinia-doped ceria (approximately 4 μm) were deposited by magnetron sputtering. $(\text{La}_{0.80}\text{Sr}_{0.20})_{0.95}\text{CoO}_{3-\delta}$ (LSC) cathode layers were applied by screen printing with subsequent *in situ* sintering. The manufactured cells were investigated by scanning electron microscopy and electrochemical measurements. Depending on the manufacturing route and testing temperature, the cells with hydrogen as a fuel and air as an oxidant demonstrated open circuit voltages from 0.57 to 0.82 V. At 750 °C, the cell maximum power density was 0.3 W cm⁻².

Keywords SOFC · Aerosol deposition method · Nanostructured anode · Magnetron sputtering · *In situ* sintering

Introduction

Needless to say, effective energy production is necessary for robust human development. The technology of solid oxide fuel cells (SOFCs) will provide high-efficiency energy generation from traditional hydrocarbon fuel if problems associated with high-cost production and low time to failure are overcome. Metal-supported solid oxide fuel cells (MS-SOFCs) are based on metal supports instead of conventional ceramics, which provides the opportunity for fast start-up and sealing by welding of SOFC stacks [1]. MS-SOFCs have been on a radar of energy and material science for many years, but there are still relatively few successful examples of their implementation and testing in laboratories and even fewer in industry [2–4]. There are many reasons for their

slow progress, and there is no doubt that one of the main reasons is the lack of proper manufacturing technology. The easily oxidizable nature, challenging relief, and low hardness of metal supports make them uneasy supports in terms of functional layer manufacturing. One of the main problems is associated with the sintering of functional layers at elevated temperatures (> 1100 °C), as an air atmosphere leads to the oxidation of the metal support, and a reducing atmosphere leads to nickel coarsening [5].

All methods that are currently used for manufacturing the anode layer of MS-SOFCs are far from being called optimal for such tasks. Layers that were formed with organic inks (screen printing, inkjet spraying, etc.) need long and multi-stage sintering due to the necessity of removing organics and not oxidizing the metal supports [6–8]. Thermal spray technologies have problems associated with insufficient porosity of electrode layers, undesired phase formations, and high irregularities in the deposition of composites consisting of ceramics and metals [9–12].

Aerosol deposition (AD) is a method of fabrication of dense and porous films with a thickness of 0.1–100 μm from dry powder in low vacuum conditions without any external heat supply, which allows the prevention of any undesirable phase formations and minimizes heat-treatment steps. The deposited films consist of nanocrystallites and have a

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relatively high density [13]. The combination of AD for anode layer deposition with magnetron sputtering (MSP) for electrolyte membrane deposition can reduce the number of sintering steps with the possibility of one *in situ* sintering of the whole SOFC in a stack during the start-up procedure due to the possibility of depositing films by MSP onto an un-sintered AD layer [14].

In the present study, the first steps towards investigating MS-SOFC cells with anodes deposited by AD were taken: MS-SOFCs were formed by AD, MSP, and screen printing with one intermediate sintering step. The manufactured cells were investigated by scanning electron microscopy (SEM) and electrochemical measurements.

Material and methods

The steel substrates were made of metal powder (Cr-28 wt%, Fe) (Polema, JSC, Russia) by uniaxial pressing followed by vacuum sintering at 1200 °C. The porosity of the substrates equal to 30% was determined by weighing.

The anode functional layers were deposited by AD using a 5-mm² converging nozzle with axial symmetry. The absolute pressure in the deposition chamber was 200 Pa, and that in front of the nozzle was 0.1 MPa. Dry nitrogen was used as a carrier gas with a flow rate of 35 ± 15 NLPM. The sintering of the half-cells with the anode layer was conducted at 1000 °C in a vacuum furnace SNVE 1.3.1./16 (ThermoCeramics, Russia). The anode functional layers were deposited from loosely agglomerated nanoparticle powders: nickel (Ni) (surface area 8.1 ± 0.5 m² g⁻¹, IEP, UB RAS, Russia) and 10 mol.% gadolinia-doped ceria (GDC) (surface area 6.1 m² g⁻¹, Kceracell, South Korea) with a 50/50 wt% ratio (Fig. 1). Bonded particles with a size of approximately 1 µm, which are usually used in AD [13], can provide denser films. However, anode layers of SOFCs have to demonstrate

developed porosity, and layers with densities greater than 80% are not desirable [15]. Moreover, high-density particles of micrometer size have to be evenly broken to prevent defect formation during film sintering and do not erode the soft metal substrate and previously deposited film, which is a delicate balance. The soft agglomerates consisting of sub-micron particles are able to break down easily and provide submicron and evenly dense films, which is favorable for further sintering.

The GDC electrolyte was deposited by magnetron sputtering of a Ce_{0.8}Gd_{0.2} target with a diameter of 100 mm (Girmet Ltd., Russia) in an Ar and O₂ atmosphere [16]. The flow rates of Ar and O₂ were equal to 100 and 50 ml min⁻¹, respectively. The discharge power was 500 W, and the total pressure in the chamber was 0.6 Pa.

(La_{0.80}Sr_{0.20})_{0.95}CoO_{3-δ} (LSC) (Kceracell, South Korea) cathodes were formed by a screen-printing technique (area approximately 1.33 cm²) with subsequent *in situ* sintering at 750 °C or 1000 °C in a setup with nitrogen in the fuel chamber and air in the oxidant chamber.

Electrochemical measurements were conducted using a potentiostat/galvanostat/ZRA Reference 3000 (Gamry Instruments, USA) with air as an oxidant and hydrogen as a fuel. Impedance spectra were collected in a frequency range from 0.1 Hz up to 300 kHz at a 20 mV voltage amplitude.

The samples were studied using scanning electron microscopy (SEM) (Supra 50VP, Zeiss, Germany) with an installed energy-dispersive X-ray (EDX) spectrometer (Oxford Instruments, UK).

Results and discussion

Figure 2a–b show SEM images of the surface of the anode layer after aerosol deposition (Fig. 2a) and vacuum sintering at 1000 °C (Fig. 2b). Figure 2a demonstrates that the

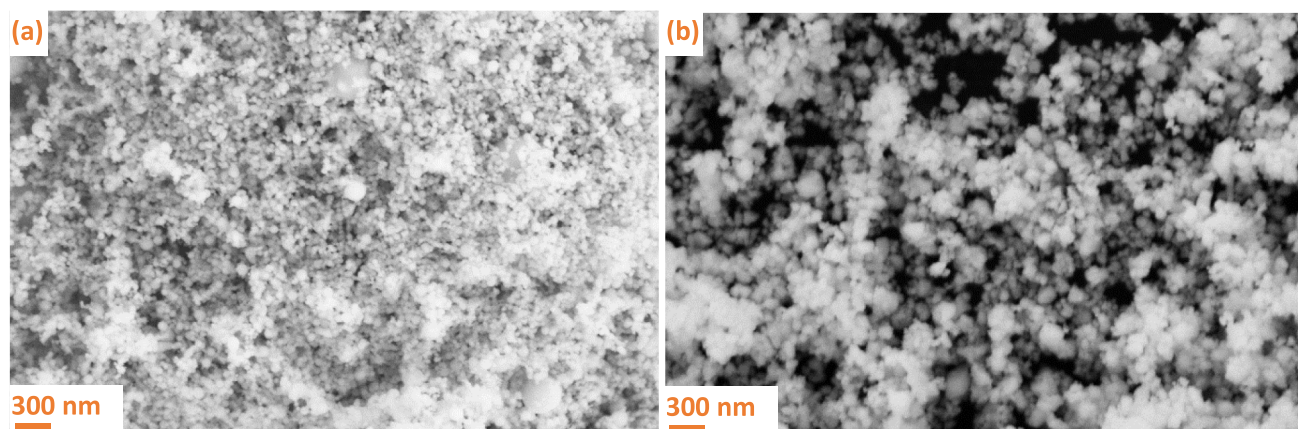


Fig. 1 SEM images of the Ni **a** and GDC **b** powders used for deposition of the anode

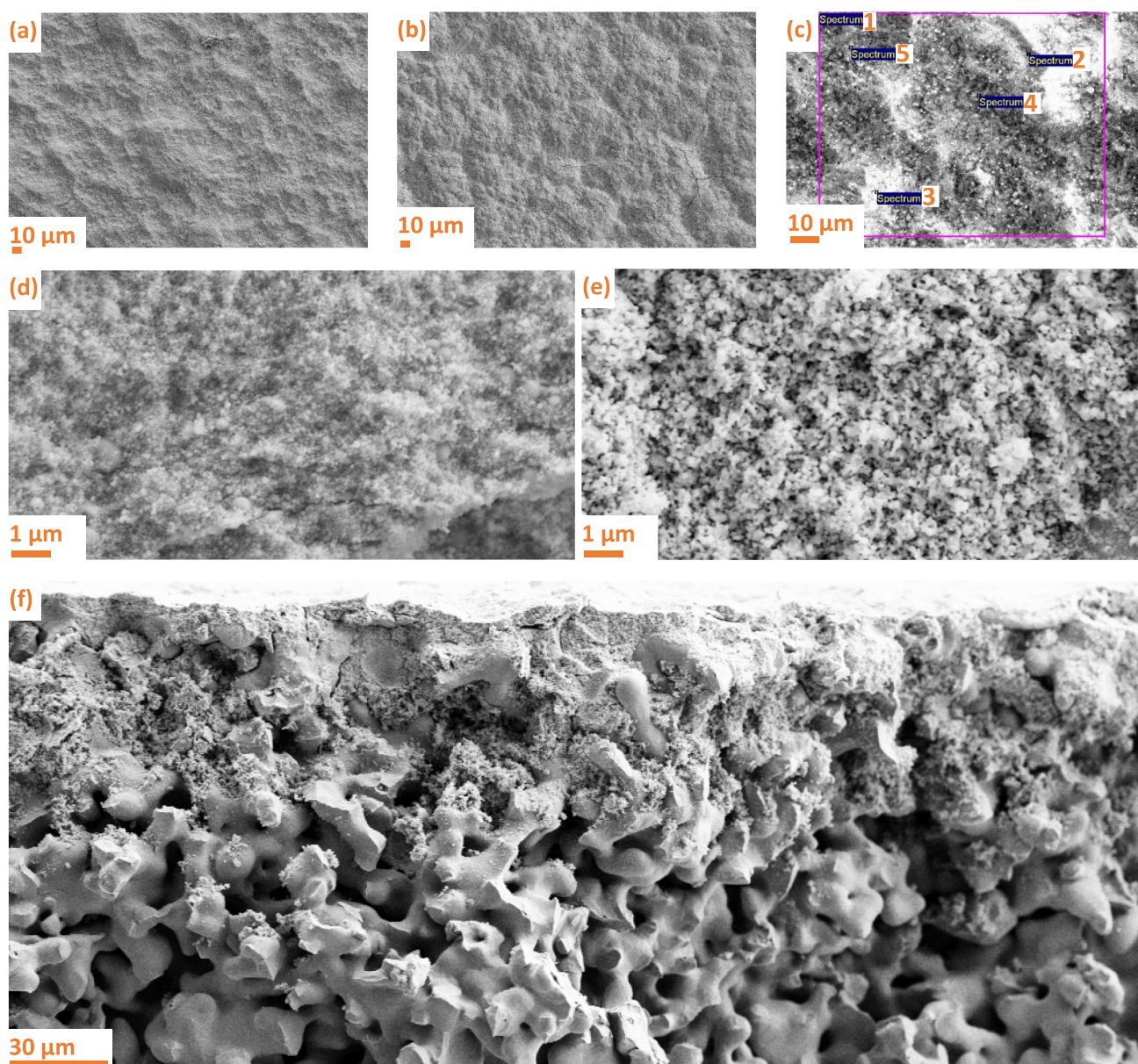


Fig. 2 SEM images of the surface of the anode layer after aerosol deposition (a) and after vacuum sintering at 1000 °C (b), surface of the anode from which information for EDX was collected (c), cross-

section of the anode layer before (d) and after vacuum sintering at 1000 °C (e), cross-section of the half-cell (f)

whole surface of the substrate is covered with the anode, and Fig. 2b shows that after vacuum sintering, the anode has not obtained any major defects. Figure 2c demonstrates a SEM image of the surface of the anode layer with marked areas from which information for EDX was collected. The Ni content varies from 24 wt% (spectrum 3) to 46 wt% (spectrum 4). The average ratio of Ni to GDC in the film is 43/57 wt% (spectrum 1), which is in the acceptable range of compositions of the functional anode of SOFCs [17]. Figure 2d–e show cross-sections of the anode layer before (Fig. 2d) and after vacuum sintering at 1000 °C (Fig. 2e). Figure 2d shows

that the anode layer is a sub-micron crystalline composite with a grain size of several dozens of nanometers and a relatively high density. Figure 2e demonstrates that the anode obtained a bonded microstructure with a grain size of less than 100 nm without any major defects or Ni coarsening. The low temperature of anode layer sintering results in the sub-micron particle size, which provides an additional thermodynamic stimulus, and does not impede the high density, which provides active diffusion. Figure 2f displays the SEM image of a cross-section of the half-cell with deposited and sintered anode. The thickness of the anode, taking into

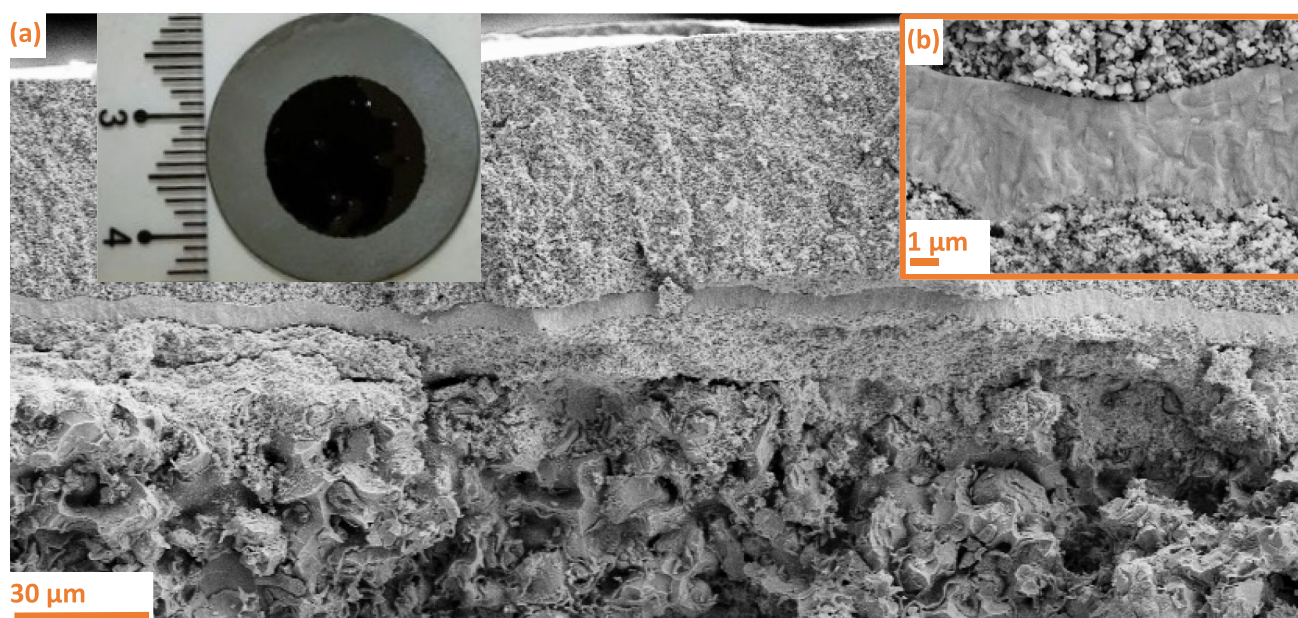


Fig. 3 SEM images and photo of the MS-SOFC after testing

account the anode deposited inside pores, is approximately 45 μm . The roughness of the surface of the anode layers is mostly determined by the relief of the metal substrate.

Figure 3 shows a photo and SEM images of the MS-SOFC with a diameter of 23 mm after testing. The thickness of the cathode layer is approximately 50 μm , and the thickness of the electrolyte membrane is approximately 3.5–4.5 μm . The structure of the electrolyte membrane is gas-tight, and bonding of the electrolyte membrane with the anode layer is present, which indicates good adhesion (Fig. 3b).

Figure 4 displays the current–voltage (j - U) and power (P) curves of the sample with hydrogen as a fuel and air as an oxidant after 750 $^{\circ}\text{C}$ *in situ* sintering. Figure 4 shows that the open-circuit voltage (OCV) was not higher than

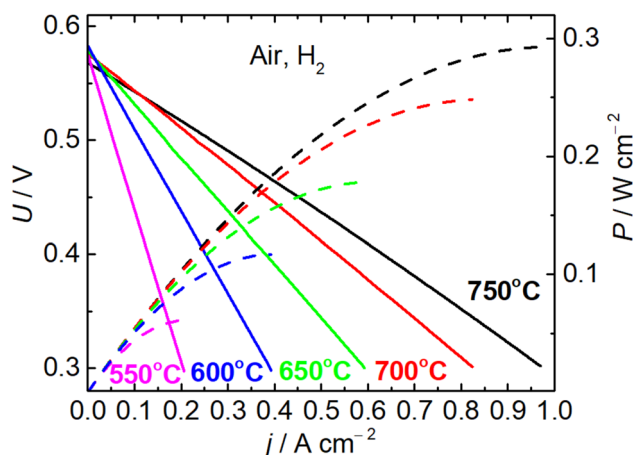


Fig. 4 Current–voltage and power curves of the SOFC after 750 $^{\circ}\text{C}$ *in situ* sintering

0.6 V, and the maximum power density was 0.29 W cm^{-2} at 750 $^{\circ}\text{C}$. Moreover, the dependence of the OCV on temperature is too weak for SOFCs with GDC electrolytes [18]. One possible explanation for these facts is the non-stoichiometric structure of the GDC electrolyte deposited by MSP, which was not able to stabilize at 750 $^{\circ}\text{C}$. The OCV of another MS-SOFC sample after 1000 $^{\circ}\text{C}$ *in situ* sintering is more than 0.8 V at 550 $^{\circ}\text{C}$ (Fig. 5), which is in good agreement with the literature data for the GDC electrolyte with a thickness of 3.5–4.5 μm ; that is, a temperature of 1000 $^{\circ}\text{C}$ was enough to stabilize the structure of the electrolyte [18].

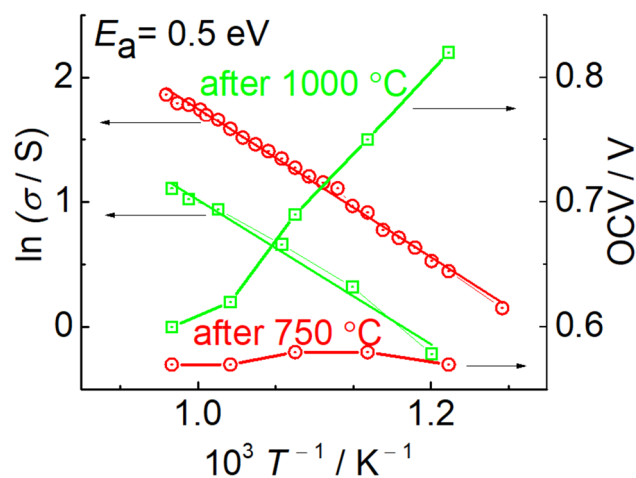


Fig. 5 Temperature dependence of the ohmic losses (left axis) and OCV (right axis) after 1000 $^{\circ}\text{C}$ or 750 $^{\circ}\text{C}$ *in situ* sintering of the SOFCs with the same screen-printed cathode area

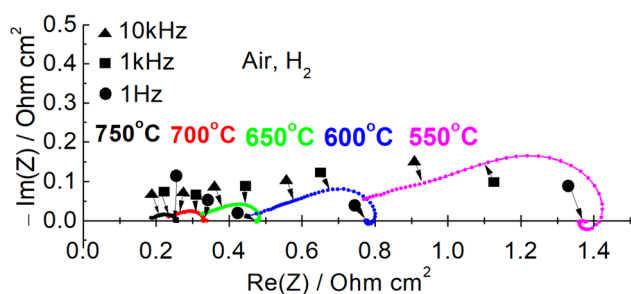


Fig. 6 Impedance spectra of the SOFC after 750 °C *in situ* sintering

Nevertheless, even after GDC stabilization, the OCVs are far from thermodynamic values (approximately 1.1 V). The thin layer of 8YSZ can solve this problem, which will be the goal of further research.

The impedance spectra (Fig. 6) demonstrate that the ohmic losses are more than half of the total cell resistance and rise from approximately 0.2 to 0.7 Ohm cm² as the temperature decreases from 750 to 550 °C. These ohmic losses are one order of magnitude higher than the expected resistance of the GDC electrolyte [19]. It should be noted that the ohmic losses show an exponential temperature dependence with an activation energy of approximately 0.5 eV (Fig. 5). This activation energy is close to the activation energy of the GDC electrolyte under similar test conditions [20–22] and may indicate the dominant role of the oxygen ion charge transfer through the GDC in the ohmic resistance of the cell. Therefore, one explanation for the high ohmic resistance is the insufficient electronic conductivity of the anode layer due to nickel agglomeration or diffusion to the metal substrate. On the other hand, the calculated activation energy is also close to the activation energy of electron transport in chromia films with different nickel contents [23], which may indicate oxide film formation on the “metal substrate–composite anode” interface. The higher ohmic losses of the SOFC after 1000 °C *in situ* sintering (Fig. 5) may come from partial delamination of the cathode due to a higher difference in the coefficients of thermal expansion, from stronger nickel coarsening/diffusion into the substrate or from more severe oxidation of the metal substrate, so further research is needed. Both problems of poor electronic conductivity of the anode composite and the interface between the metal substrate and the anode can be partially mitigated by Ni protective layer deposition on the metal substrate, for example, by electrodeposition technique [24]. The Ni layer deposited on the substrate will not only increase the conductivity of the oxide films [23] but also reduce nickel diffusion from the anode layer.

Conclusions

The fabrication route and electrochemical performance of the MS-SOFC with the anode functional layers deposited by AD from submicron powders were described. Microstructure investigation showed that the anode functional layer consisting of Ni/GDC (43/57 wt%) obtained a bonded microstructure with good adhesion to both the support and electrolyte membrane after vacuum sintering at 1000 °C. Electrochemical tests showed that for proper performance of MSP-deposited electrolyte membranes, they may need to go through a stabilization procedure in an oxidation environment. After 1000 °C *in situ* sintering, the 4-μm thick MSP-deposited electrolyte provided an OCV equal to 0.82 V. To achieve thermodynamic values of OCV (approximately 1.1 V), a thin layer of 8YSZ can be deposited by MSP, which will be the goal of further research.

Electrochemical measurements demonstrated that the ohmic resistance of the cells after 750 °C *in situ* sintering was in the range from 0.2 to 0.7 Ohm cm² in the temperature range from 550 to 750 °C, which is significantly larger than the expected ohmic resistance for the 4-μm GDC membrane. The temperature dependence of ohmic losses provided an activation energy, which was equal to 0.5 eV. The ohmic losses and the activation energy data indicated that the performance of MS-SOFC cells is probably limited by poor electronic conductivity of the anode layer, which may result from oxide film formation on the metal substrate or insufficient electronic conductivity of the anode layer due to nickel diffusion to the substrate or nickel coarsening. The problem of poor electronic conductivity can be partially mitigated by Ni protective layer deposition on a metal substrate, which will be implemented in future studies.

Author contribution I.S.E.: data curation, investigation, methodology, writing—original draft. M.N.L.: investigation, methodology. I.N.B.: data curation, investigation, methodology, writing—review and editing. D.V.Y.: data curation, investigation. E.A.S.: data curation, investigation. A.A.S.: data curation, investigation. S.I.B.: supervision, methodology.

Data availability Data will be made available on request.

Declarations

Competing interests The authors declare no competing interests.

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