



# High-performance anode-supported solid oxide fuel cell with impregnated electrodes



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## HIGHLIGHTS

- The powders for bi-layer Ni-cermet anode was produced by combustion synthesis.
- High-performance SOFC have been produced using simple methods.
- Impregnation of the electrodes has increased power of SOFC by seven times.
- The SOFC with impregnation electrodes revealed the power of  $2.5 \text{ W cm}^{-2}$  at  $900 \text{ }^\circ\text{C}$ .
- Impregnation reduced resistances of all electrode reactions except the gas-diffusion.

## ARTICLE INFO

### Article history:

Received 12 February 2015

Received in revised form

7 April 2015

Accepted 16 April 2015

Available online

### Keywords:

Ni-cermet supported SOFC

Impregnation

CeO<sub>2</sub>

Combustion synthesis

## ABSTRACT

The 61%NiO + 39%Zr<sub>0.84</sub>Y<sub>0.16</sub>O<sub>1.92</sub> (NiO-YSZ) and 56%NiO + 44%Zr<sub>0.83</sub>Sc<sub>0.16</sub>Ce<sub>0.01</sub>O<sub>1.92</sub> (NiO-CeSSZ) composite powders have been prepared using two-steps and one-step combustion synthesis, respectively. The Ni-YSZ anode substrate with a low level of electrical resistance (less than 1 mOhm cm) and porosity of about 53% in the reduced state was fabricated. The functional layer of the anode with the high level of electrochemical activity was made of NiO-CeSSZ. The single anode-supported solid oxide fuel cell with the bi-layer Ni-cermet anode, Zr<sub>0.84</sub>Sc<sub>0.16</sub>O<sub>1.92</sub> film electrolyte and the Pt + 3% Zr<sub>0.84</sub>Y<sub>0.16</sub>O<sub>1.92</sub> cathode was fabricated. The power density and the U–I curves of the fuel cell at initial state and after impregnation of the cathode and anode by praseodymium and cerium oxides, respectively, have been measured at different temperatures. The maximum of power density of the initial fuel cell was  $0.35 \text{ W cm}^{-2}$  at conditions of wet hydrogen (air) supply to the anode (cathode) at  $900 \text{ }^\circ\text{C}$ . After the electrodes were impregnated, the value of power density increased by seven times and was approximately  $2.4 \text{ W cm}^{-2}$  at 0.6 V. It was suggested that after the electrodes impregnation the polarization resistance of the fuel cell was determined by the gas diffusion in the supported anode.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) are perspective sources of electric power [1–3]. One way to increase the power output of SOFC is to reduce the thickness of the electrolyte which is the main contributor of ohmic resistance. However, as the thickness of the electrolyte decreases, its mechanical strength also decreases and, when the electrolyte thickness is less than 200–300 μm, it can no longer function as a support. Consequently, the SOFC development has advanced by using cathode-supported [4–6] or, more frequently,

anode-supported [7–9] SOFCs with a thin film of electrolyte. The anode of the anode-supported SOFC should have the necessary level of thermal expansion coefficient (TEC), porosity, mechanical strength, electrical conductivity and electrochemical activity. These requirements can be achieved by using bi-layer anodes, the substrate of which possesses a high mechanical strength, porosity and electrical conductivity and the functional layer with a TEC value, possibly close to that of the electrolyte film, a high level of electrochemical activity and a level of porosity that is appropriate to the film electrolyte preparation.

Applying different synthesis methodologies for the preparation of the anode powders and methods for formation of the anode layers [1,10] could give the possibility for obtaining the necessary anode layers characteristics, but the majority of these techniques is

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complicated and requires specialized equipment. Combustion synthesis is the simplest and most perspective method to produce fine powders. Application of the combustion synthesis method implies the combustion of nitrate solutions with organic compounds such as: glycine, urea and others, which serve as a complexing agent and a fuel. Both simple and complex oxides and composite powders can be obtained using this method [11–16]. A high reaction rate and abundant gas emission prevent the growth of particles during the combustion process. A high level of chemical activity and the dispersion of powders obtained through this method make their use more profitable in the formation of SOFC components.

Other simple way to improve the SOFC power characteristics is the impregnation (infiltration) of the electrodes. Impregnating the porous electrode by nano-sized particles of the metals [17,18] or mixed conductors [19,20] leads to decreasing the electrode polarization resistance. This phenomenon is caused by several factors: improvement of the adsorption kinetic of the gas, increase of the triple-phase boundary length, improvement of the charge–transfer reaction and etc.

The purpose of this study is to reveal the possibility of producing the high-performance single SOFC by simple techniques. To achieve this goal, the combustion synthesis for preparation of the electrode powders, brush painting for applying the functional layer of the anode and electrolyte film, impregnation of the electrodes for improvement their electrochemical activity were used.

## 2. Experimental

### 2.1. Synthesis of powders

Hexahydrates of  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Y}(\text{NO}_3)_3$ ,  $\text{Sc}(\text{NO}_3)_3$ ,  $\text{Ce}(\text{NO}_3)_2$  and  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  (purity  $\geq 99\%$ ) were used as the initial substances,  $\text{C}_2\text{H}_5\text{NO}_2$  (glycine) was used as a fuel. The 61wt.%NiO + 39wt.%  $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$  (NiO-YSZ) composite powder have been prepared using two-steps combustion method. The YSZ powder was preliminary obtained by combustion synthesis. Then YSZ powder with the nickel nitrate and glycine solution was mixed and burned. The 56wt.%NiO + 44wt.% $\text{Zr}_{0.83}\text{Sc}_{0.16}\text{Ce}_{0.01}\text{O}_{1.92}$  (NiO-CeSSZ) powder was prepared by one-step combustion synthesis. After combustion the obtained powders were annealed at 900 °C in air for 5 h to remove carbon traces formed during the glycine combustion. Then NiO-YSZ and NiO-CeSSZ powders were grinded in a planetary ball mill PM100, Retsch for 2 h. The graphite powder (specific surface area is 12.4 m<sup>2</sup> g<sup>-1</sup>) in the amount of 10 wt.% was added to the NiO-YSZ as a pore-former. The graphite powder was obtained by grinding an industrial graphite electrode (with a purity of 99.9%) in a mill. Then the graphite- NiO-YSZ powder was grinded in a mill for 30 min.

### 2.2. Samples

The samples for measuring the TEC and electrical conductivity were prepared in the shape of bars by a dry isostatic pressing at 150 MPa cm<sup>-2</sup> for 10 s. The thin electrodes (thickness is 20 μm) for measuring the polarization resistance were applied by the brush painting onto the dense commercial  $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$  plates. All samples and electrodes were sintered for 2 h in air atmosphere at 1400 °C.

### 2.3. Fabrication of SOFC

The NiO-YSZ anode substrate was prepared in the shape of a disc with 12 mm diameter and 1 mm thickness by dry isostatic pressing at 150 MPa cm<sup>-2</sup> for 10 s and sintered for 2 h in air at 1400 °C. The slurry for functional layer was produced by mixing NiO-CeSSZ

powder with polyvinylbutyral and isopropyl alcohol. The slurry was applied by the brush painting onto one side of the sintered NiO-YSZ disk. When the slurry dried (thickness of functional layer about 20 μm) the first layer of the commercial  $\text{Zr}_{0.84}\text{Sc}_{0.16}\text{O}_{1.92}$  (SSZ) electrolyte powder was applied by painting onto the functional layer. Sintering of the half-cell was performed at 1390 °C with isothermal exposure for 2 h in air. After sintering the second SSZ layer was applied onto the first SSZ layer and then sintered at 1360 °C with isothermal exposure for 5 h in air. The total thickness of the SSZ electrolyte was approximately 30 μm. The self-made Pt + 3%  $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$  (Pt-YSZ) cathode paste was applied onto SSZ electrolyte and sintered at 1100 °C for 1 h. Thickness of the cathode was about 30 μm. The photos of anode-supported half-cell, single SOFC and sketch of SOFC are presented in Fig. 1.

To reduce the electrodes polarization resistances they were impregnated by the saturated water solutions of praseodymium (cathode) and cerium (anode) nitrates. After thermal decomposition of the nitrates (at 600 °C in wet hydrogen for 1 h) the weight of the electrode about 20% increased.

### 2.4. Measurements

The method of low-temperature nitrogen adsorption (by means of the SORBI N4.1 device) was used for measuring the Ni-cermet powders specific surface area. Before the measurement of the specific surface the degasification of powder in a helium atmosphere at 200 °C for 1 h was done. The powder diffractograms were obtained using the X-ray Rigaku D/MAX-2200VIPC diffractometer with Ni-filtered  $\text{CuK}\alpha$  radiation in the range of  $25^\circ \leq 2\theta \leq 70^\circ$  at angular scanning rate of 2° min<sup>-1</sup>. For micrographs the epoxy was used for filled the samples under for vacuum with subsequent polishing in the Struers Labopol device. X-ray spectral analysis was taken using the scanning electron microscope Jeol JSM 5900LV with INCA energy 200. The microphotographs were taken with the scanning electron microscope TESCAN MIRA 3 LMU. The TEC measurements were carried out by the automated set with the programmable “Thermodat-16” thermo regulator, quartz dilatometer and “Tesatronic TT-80” digital meter with the proper TESA GT 21HP measuring probe in the temperature range of 100–900 °C at the constant heating rate of 2 °C min<sup>-1</sup> in air.

The porosity ( $\epsilon$ ) of Ni-cermet bars was calculated as follows:

$$\epsilon = \left[ 1 - \frac{m}{V \cdot (x_1 \cdot \rho_1 + x_2 \cdot \rho_2)} \right] \cdot 100, \quad (1)$$

where  $m$  and  $V$  are the mass and volume of the sample,  $x$  and  $\rho$  are the mass and density of the fraction, respectively.

The  $\text{H}_2$  of high purity not less than 99.9 vol.% was used for the fuel gas mixtures preparation. The  $\text{H}_2\text{O}$  content in hydrogen was set by the temperature of the water evaporator, over which the  $\text{H}_2$  flow passed. The air compressor for supply of the ambient air as oxidizer on the cathode was used. Gases flow rate at the anode and cathode was 5 l h<sup>-1</sup>.

The electrical conductivity measurement was carried out by the DC four-probe method using the electrochemical interface EI-1287 (Solartron Instruments Inc.) in the current range of 0–750 mA cm<sup>-2</sup> (with step of 50 mA cm<sup>-2</sup>) at 700–900 °C. The SOFC electrochemical characteristics and thin electrodes were studied by means of impedance spectroscopy in the frequency range of 10<sup>5</sup>–10<sup>-2</sup> Hz using Frequency Response Analyzer FRA-1260 with the electrochemical interface EI-1287 (Solartron Instruments Inc.). AC measurements were carried out at galvanostatic mode with AC amplitude of 20 mA, the number of points per decade (log scale) was 20 at 700–900 °C. The electrochemical cell was connected to an electrochemical interface by two-electrode four-wire mode

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