A Novel Design of a Planar SOFC with the Anode Supported on the Base Ceramic Structure

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Abstract

The paper presents the innovative design of a ceramic high temperature solid oxide fuel cell (SOFC) in which the anode consists of two parts: the bottom supportive part with microchannels for fuel distribution and the upper operating part which takes part in the electrochemical reaction in the cell. Both parts of the anode are made of co-fired yttrium-stabilized zirconia (Ni/YSZ) foils. Microchannels as well as the manifold for combustion products are engraved mechanically in the isostatic pressed stack of Ni/YSZ foils before their firing. The electrolyte and the cathode are performed on the upper functional part of the anode by successive screen printing and firing of the electrolyte paste and the cathode paste. The paper reveals details of the fuel cell processing, test fixture and measurement set-up for testing the cells as well as the results of open circuit voltage and short-circuit current measurements.

Keywords: planar SOFC, anode supported SOFC, Ni/YSZ foils, microchannels

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are highly efficient energy conversion devices that transform chemical energy to electrical energy through the electrochemical reactions. Typical SOFC cell essentially consists of three ceramic components: two porous electrodes separated by a dense oxygen-conducting electrolyte. Depending on which component serves as the support, the SOFCs are divided to anode supported, electrolyte supported and cathode supported. Fig.1 shows a typical design of the planar anode-supported fuel cell and illustrates the principle of its operation. On the cathode side, at the cathode/electrolyte interface oxygen absorbs electrons incoming from external load and as oxygen ions migrate through the electrolyte. On the anode side, at the anode/electrolyte interface fuel (hydrogen) is oxidized by incoming oxygen ions producing water and releasing electrons that flow through an external circuit to the cathode. Metallic interconnects serve as gas and fuel flow channels and charge collectors [1-6].

Microstructure of the cathode, anode and electrolyte is important for the proper fuel cell operation. The electrolyte should be dense, gas-tight and as thin as possible to ease the oxygen ions transportation. The electrodes should be porous due to the requirement of high transparency for fluids. In practical SOFC solutions, usually one of the ceramic layers is built-up with increased thickness to provide a sufficient mechanical strength for carrying the whole SOFC structure.

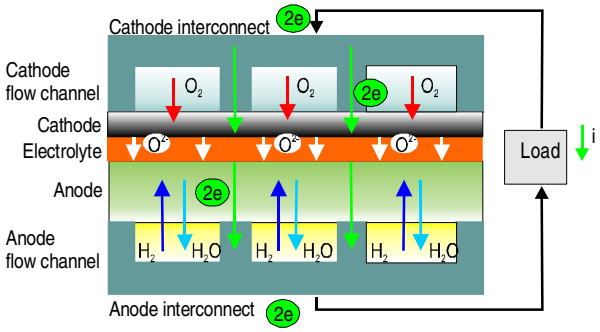

Fig. 1. Typical design of a planar anode-supported fuel cell

2. Fuel Cell Design

The paper presents the novel design of the double SOFC fuel cell. The core of the cell is the anode base structure with a large number of microchannels which distribute fuel just underneath relatively thin functional anode layers. The microchannels are arranged on both sides of the anode base structure and they are accompanied by internal fuel distributors and internal manifolds for combustion products. The anode functional layers are the inherent parts of the anode base structure. All components are made with the same commercially available ceramic foils. The electrolyte and the cathode layers are built-up successively on the both sides of the anode structure. The cathodes are in contact with the surrounding atmospheric air, drawing from it oxygen needed to produce oxygen ions. Fig. 2 presents the operating principle of the new design.

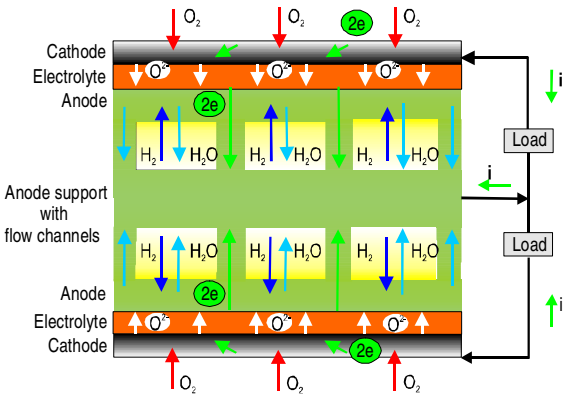

Fig.2. Operating principle of the new design.

The proposed design enables maintaining the relatively low thickness of the operating anode layer (100µm).

3. Experimental

3.1 Fuel Cell Fabrication

The commercial ESL ceramic tapes and thick-film pastes as well as processes typical for advanced thick film technology – tape co-firing and screen printing were used to perform the laboratory model of the cell. The set of materials included the anode foil ESL 42421 consisting of a mixture of nickel oxide and yttrium-stabilized zirconia (Ni /YSZ), the electrolyte paste ESL 4481 containing 8 mol% yttrium stabilized zirconia (YSZ) and the cathode paste ESL 4421 containing lanthanum strontium cobalt ferrite oxide (LSCF).

Fig. 3 presents the ceramic layers that constitute the entire monolithic fuel cell structure.

The anode base part consists of the six layers of ceramic foils Ni/YSZ of raw thickness 0,180 mm which were shaped into dimensions 80 x 25mm and pressed at 70 °C in the isostatic press under pressure of 7000 psi. A network of channels of width 350 µm and depth 500 µm with inlets for gas fuel and outlets for waste products are being cut in the stack of compressed unfired foils using a numerical machine tool. Fig. 4. shows the layout of the flow channels engraved mechanically in the support anode base.

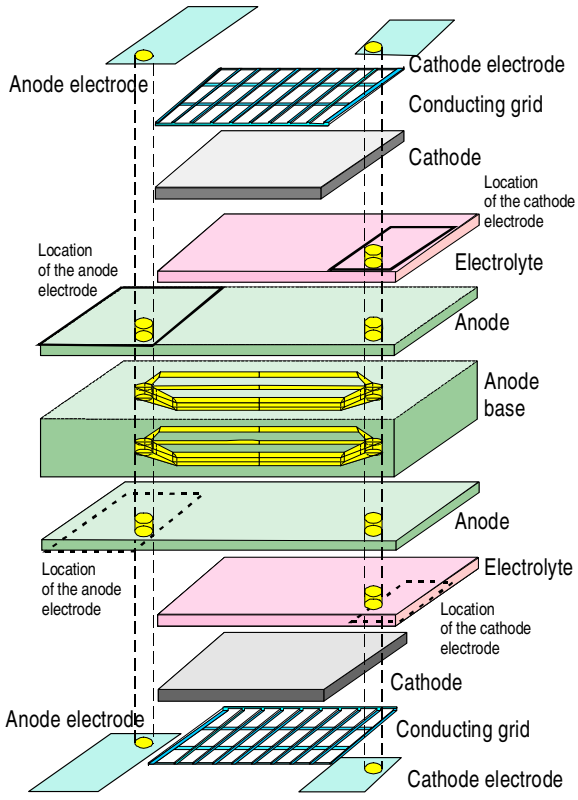

Fig. 3. Sequence of technological processes.

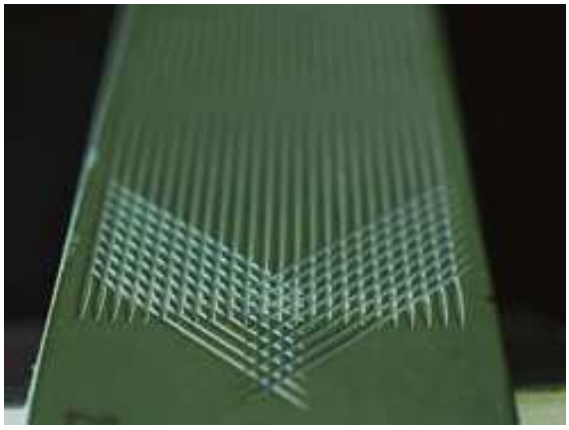

Fig. 4. layout of the flow channels engraved mechanically in the support anode base.

The walls of channels provide a support for the sheet of a Ni/YSZ tape which serves as an operating anode of a fuel cell. Fig. 5 shows the cross-section of the anode base structure with engraved mechanically channels.

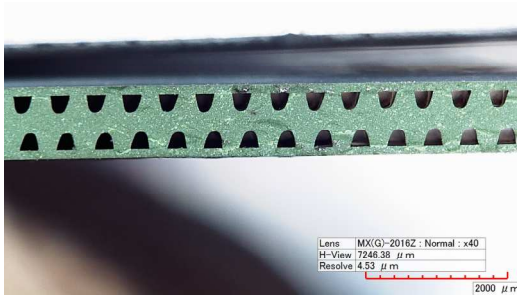

Fig.5. Cross-section of the anode base structure with engraved mechanically channels.

The entire structure is afterwards dried in an oven in the temperature range from 25°C to 350°C with a ramp 0.9°C/min., and then fired in the following sequence: temperature range from 300°C to 650°C with a ramp 1.5°C/min., temperature range from 650°C to 1550°C with a ramp 5°C/min., peak at 1550°C for 2 hours.

During the firing, the ceramic foils are shrinking to the dimensions of 60 x 19 mm in the X-Y plane and the thickness of 1.2 mm in the Z-plane. After firing, the channels width and depth diminish to 0.260 mm and 0.135 mm, respectively. The fired thickness of the functional layer of the anode is equal to 0.130 mm.

Once the ceramic structure of the anode is performed with the anode foils, the further functional layers of a fuel cell are deposited by screen printing. The electrolyte is screen printed twice first on the top surface of the anode structure through a 200 mesh screen with ESL 4481 electrolyte paste and dried at 900°C. Afterwards the electrolyte is printed twice at the bottom part of the anode structure and dried again 900°C. Finally both layers were co-fired at 1600°C for 3 hours. The thickness of the electrolyte after firing is 0.030 mm.

Fig. 6 shows the SEM of the electrolyte layer fired at 1600°C. This layer fired at lower temperature 1470°C is not dense enough (Fig. 7).

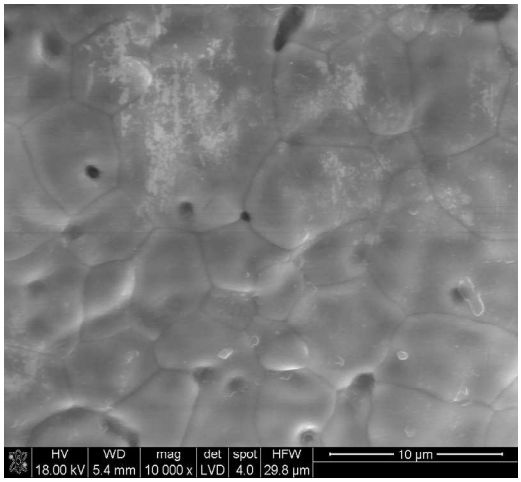

Fig.6. SEM of the electrolyte YSZ (ESL 4481) fired at 1600°C

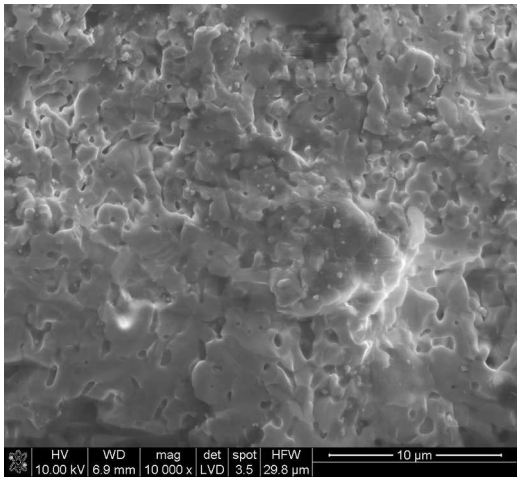

Fig.7. SEM of the electrolyte YSZ (ESL 4481) fired at 1540°C

The cathode paste ESL 4421 ($La_{0.80}Sr_{0.20}Fe_{0.8}Co_{0.2}$) is deposited on the surface of the electrolyte on both sides of the cell by a single pass of screen printing through a 200 mesh screen with separate drying. Both layers are than fired simultaneously at 1100°C. The thickness of the cathode layer after firing is 0.015 mm. Fig. 8 shows the cross-section of the anode, electrolyte and cathode layers in magnification x 350.

Afterwards, electrodes are screen printed with silver paste on top of the anode and the cathode and fired at 900°C. To increase the electrical conductivity of the cathode, silver grid is screen printed with the silver paste on the surfaces of the cathode.

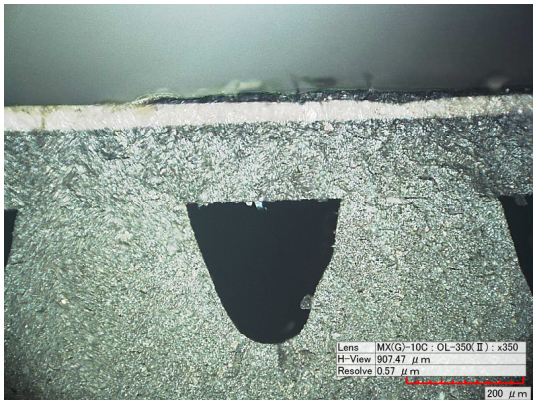

Fig.8. Cross-section of the anode, electrolyte and cathode layers

Finally, inlets for hydrogen and outlets for combustion products were drilled. The edges of the ceramic fuel cell were sealed with high temperature ESL glass C 129 at the firing temperature 950°C.

The final technological operation in the process of fuel cell fabrication is the reduction process of the complete cell structure in the atmosphere of hydrogen H_2. Reduction process is carried out in a tube furnace filled with hydrogen. The temperature of the process is 500°C and the process lasts for 2 hours. As a result, the particles of nickel oxide NiO deposited in a backbone of yttrium-stabilized zirconia are reduced to metallic nickel – Ni - forming a porous Ni-YSZ structure.

Fig. 9 presents the thick-film model of the fuel cell fabricated in the described technological processes. Top and bottom side of the model with silver grid printed on the surface of the cathodes as well as current collector electrodes (cathode and anode) can be seen.

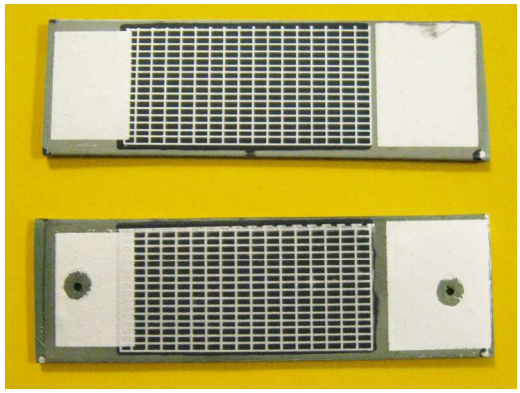

Fig. 9. Thick-film model of the double fuel cell

Materials and main technological processes of the cell fabrication are summarized in Table 1 and 2:

Table 1. Materials

Cell compo-nent	Material	Compo-sition	Firing cond. [°C]	Thick. after firing [mm]
Anode base	ESL 42421	Ni/YSZ foil	1550	0.780
Anode	ESL 42421	Ni/YSZ foil	1550	0.130
Electrolyte	ESL 4481	8YSZ paste	1600	0.030
Cathode	ESL 4421	LSCF paste	1100	0.015

LSCF: $La_{0.80}Sr_{0.20}Fe_{0.80}Co_{0.2}$
YSZ: yttria stabilized zirconia
Ni/YSZ: NiO/ yttria stabilized zirconia

Table 2. Technological processes

No.	Processes
	Anode base
1.	six layers of anode foils ESL 42421 (180 m thick) are laminated with iso-static press at 75°C and 7000PSI
2.	microchannels are machined on the both sides of unfired laminate
3.	both sides of engraved laminate are covered with ESL 44421

4.	drying: 25->350°C , ramp 0.9°C/min
5.	firing: 300->650°C, ramp 1.5°C/min; 650->1550°C, ramp 5°C/min, 1550°C, 2h
	Electrolyte
1.	screen print of electrolyte paste ESL 4481, 2 layers deposited on each side of the anode
2.	layers separately dried at 900°C, and finally fired at 1600°C, 3h
	Cathode
1.	Screen print of cathode paste ESL 4421 on each side of the ceramic structure, fired at 1100°C
	Electrodes
1.	Screen print of silver grid on the surface of cathodes, fired 900°C,
2.	Screen print of current collector electrodes for the anode and cathode, silver , fired 900°C
	Drilling inlets and outlets
	Reduction in hydrogen atmosphere at 500°C, 2h

3.2 Measurements and results

Fig. 10 shows the test set-up used in experiments. It consists of two flat platinum heaters deposited on the substrate of alumina nitrate AlN and embedded into thermal isolating foam. The heaters enable heating the cell up to 800°C. Hydrogen flow through the channels of the anode structure was maintained at 100 sccm. The active cell area is equal to 4 cm^2.

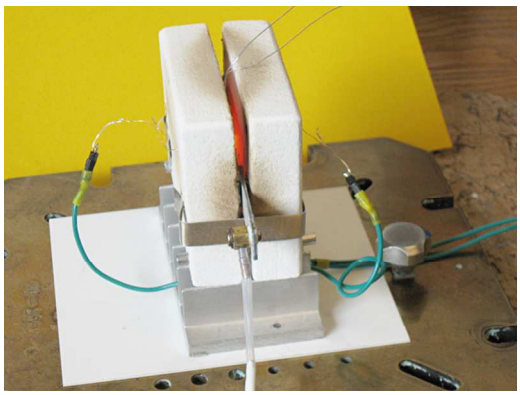

Fig. 10. Measurement set-up

The fuel is provided to hot fuel cell via ceramic intermediate connector, which thermally separates the fuel supply intake connector from the hot fuel cell. The combustion products are removed through the identical ceramic intermediate connector, which serves as a manifold. The connections between the manifolds and the fuel cell are sealed with mica gaskets. The both ceramic intermediate connectors are the basis for the reliable electrical wirings to the anode and the cathode.
Fig. 11 shows the ceramic intermediate connectors.

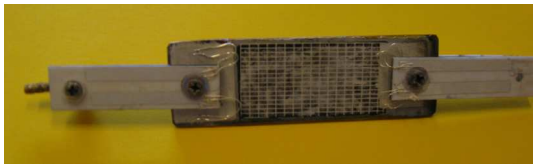

Fig. 11 Ceramic intermediate connectors

Each ceramic intermediate connector is provided with two silver paths which double the connection to the anode and the cathode. These doubled connectors are essential for accurate four probe electrical measurements of impedance spectra.

The performance of the SOFC as a voltage source can be specified by its basic electrical parameters, i.e. output voltage and output impedance. Electrical measurements were carried out during the cell operation.

The voltage-current (U-I)characteristics and power -current (P-I) characteristics of a single cell at temperature between 550°C and 800°C are shown in Fig. 12.

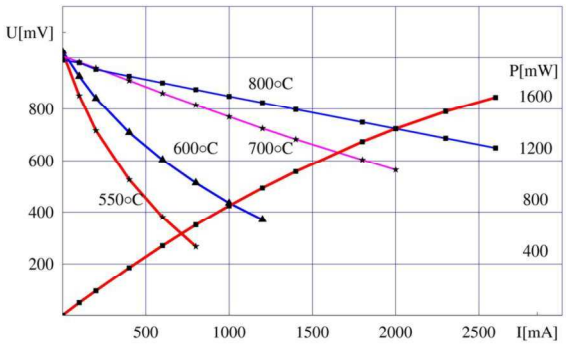

Fig. 12. Current-voltage (U-I)characteristics and current-power (P-I) characteristics of the cell

The cell exhibits the open circuit voltage (OCV) equal to 1.025V, and the power density equal to 400 mW/cm^2 at 800°C. The U-I characteristics enable to determine the total resistance of the cell R_t. For the temperature 800°C, this total resistance is equal to 130 mΩ. The results for other temperatures are collected in Table 3.

The impedance spectroscopy was carried out with the Quad Tech Impedance Meter Model 7600, which enables precision four probe measurements of low impedances with resolution of 0.1mΩ, and frequency swept within the range from 10Hz to 2MHz. Data collected for four operating temperatures (550°C, 600°C, 700°C and 800°C) are displayed in Fig. 13.

The further plots in Fig. 14 and Fig. 15 present magnifications of selected parts of plots from Fig. 13 to enable better data recognition. Fig. 14 shows for example the detailed data at temperatures 800°C and 700°C. Fig. 15 shows data collected at temperature 800°C which is the optimal temperature of operation for the tested fuel cell.

The low frequency intercept corresponds to the total polarization resistance R_t including ohmic resistance R_i, activation polarization resistance R_{act} and concentration polarization resistance R_{con} *[7]:*

$$R_t = R_i + R_{act} + R_{conc}$$

The high frequency intercept corresponds to the ohmic resistance of the cell R_i. Subtracting the high frequency intercept from the low frequency intercept enables to evaluate the sum of the activation polarization resistance R_{act} and concentration polarization R_{con}. Ohmic resistance R_i of the fuel cell includes ionic resistance of the electrolyte, electronic resistance of the electrodes and electronic resistance of current collectors [7-14]. Projection of the arc plot towards semicircle were made in order to read the resistance value at the low frequency intersection. Data measured by impedance spectroscopy are summarized in Table 3.

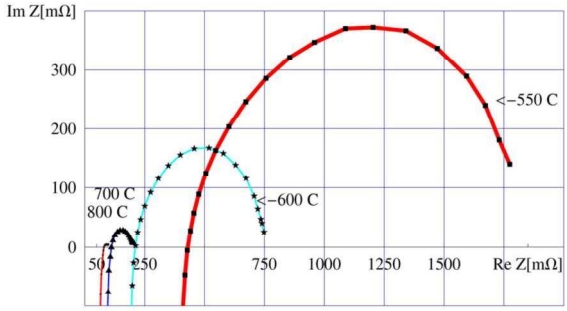

Fig. 13. Impedance spectra of the single cell measured in the open circuit state between 550°C and 800 °C

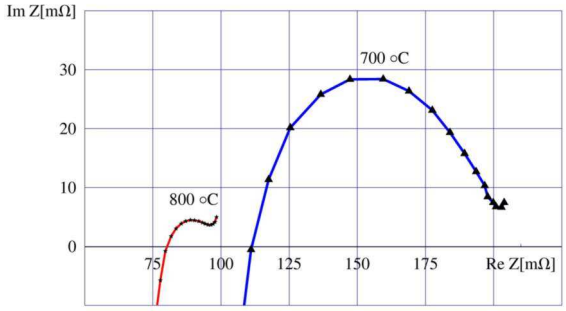

Fig. 14. Impedance spectra of the single cell measured in the open circuit at 800°C and 700°C.

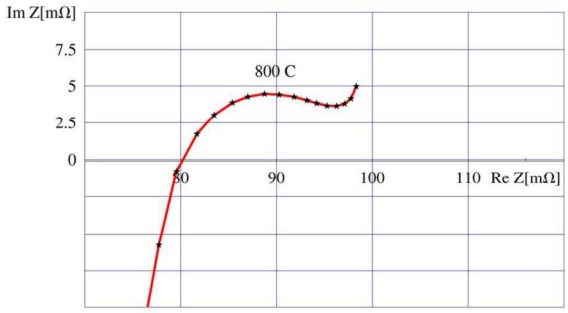

Fig. 15. Impedance spectra of the single cell measured in the open circuit at 800°C

Table 3. Results of electrical measurements

	Spectroscopy impedance			U-I curve at 100 mA
T[°C]	R_t [Ω]	R_{act}+R_{con} [Ω]	R_i [Ω]	R_t [Ω]
550	1.8	1.4	0.4	1.7
600	0.75	0.55	0.2	0.8
700	0.21	0.1	0.11	0.22
800	0.1	0.02	0.08	0.13

4. Discussion of results

4.1 Remarks on measurements

The voltage of the operating cell E_c is always lower than the open circuit voltage E_0 due to various polarization losses [7]:

$$E_c = E_0 - i \cdot R_i - \eta_{act} - \eta_{a,conc} - \eta_{c,conc}$$

where i is the current density (Acm^{-2}), R_i the area specific ohmic resistance of the cell (Ωcm^2), η_{act} the activation polarization (V), $\eta_{a,conc}$ the anodic concentration polarization (V) and $\eta_{d,conc}$ the cathodic concentration polarization (V).
The activation polarization η_{act} is caused by slow charge transfer reactions at the electrodes/electrolyte interfaces.
The concentration polarization of the cell η_{conc} is caused by the slow mass transport of gas-phase reactant and product species through the porous anode and cathode. The anodic concentration polarization with H_2-H_2O gas mixture as fuel can be expressed as [7]:

$$\eta_{a,conc} = -\frac{RT}{2F}\ln(1-\frac{i}{i_{as}}) + \frac{RT}{2F}\ln(1+\frac{p^{\circ}_{H_2} i}{p^{\circ}_{H_2O} i_{as}})$$

where R is the gas constant, F is the Faraday constant, $p^{\circ}_{H_2}$ and $p^{\circ}_{H_2O}$ is the partial pressure of hydrogen and water vapour in the anode bulk gas, and i_{as} is the limiting current density. When the current density is equal to the limiting current i_{as} , the interfacial hydrogen partial pressure is zero [7].

The thicker the electrode, the bigger the concentration loss. In proposed design of SOFC, the thickness of the operating part of the anode is about ten times smaller than in conventional anode supported SOFC. Due to that fact the polarization concentration losses should be decreased.

As seen in Table 3, the total resistance R_t of a cell at 800°C is equal to 0.1 Ω, the sum of activation polarization resistance R_{act} and concentration polarization resistance R_{con} is equal to 0.02 Ω and the ohmic resistance R_i is equal to 0.08 Ω.

Although we can't separate concentration polarization resistance R_{con} from the sum of R_{act}+ R_{con}, the overall low value of this sum points out that the reduced anode thickness of the anode supported cell affects positively on the level of polarization concentration losses in the cell.

The estimated from the Nyquist plot in Fig. 15, the total resistance of a cell at 800°C equal to 0.1 Ω is lower than resistance obtained on the basis of U-I plot in Fig.12 and equal to 0.125 Ω. But the discrepancy for estimations at lower temperatures are almost negligible (for example at 700°C the difference is less than 4%).

The ohmic resistance covers the electrolyte resistance, anode resistance, cathode resistance and resistance of the anode and cathode current collectors. Accurate separation of these partial resistances is difficult.

It has to be noted, that although the tested anode base structure consists of two flat SOFCs, measurements are confined only to the one cell. The second cell remained unloaded, although fueled. The core of the anode base structure operates as the anode current collector for two cells. It is possible to evaluate roughly the anode resistance on the basis of current measurement in the other cell. It was observed that switching on the current in the second cell causes voltage drop equal to 80 mV in the first tested cell. That enables to evaluate the resistance of the anode current collector on the level of 40 mΩ.

4.2 Remarks on technology

In the proposed design of the fuel cell, the anode functional layer is an inherent part of the anode base structure, which consists of the networks of micro channels arranged on the both sides of this central core. In this way a double sided anode base structure is accomplished, which includes internal fuel distributors and internal manifold for combustion products. The whole anode base structure is made with the same material and its embodiment was completed with commercially available ceramic tapes.

In contrary to majority of solutions, the processing of fuel cell is not a single step co-

fired process. After completing the anode base structure the following layers are deposited and fired step by step. That approach provides conditions for careful inspection after each technological step and enables repairing if required.

Deposition of the electrolyte layer on the base anode structure is the most critical and demanding step because the electrolyte must cover tightly almost the whole surface of the anode base structure enabling electrical access to the anode. Thanks to this solution, additional sealants are not required.

The other important issue is thermal processing. We have found that this approach requires a significantly higher processing temperature to achieve the required electrolyte density.

Our previous models, where the electrolyte layer were fired at 1470°C and 1540°C (Fig.7), displayed a poor performance, and the open voltages were respectively 450mV and 650mV. Acceptable fuel cell performance was achieved when the electrolyte was fired at temperature range 1600°C (Fig. 6). In both cases the electrolyte was deposited on previously fired rigid anode base structure.

For the last few years, we have investigated the issue of bonding of green tapes to rigid ceramic structures, and we have found, that if a ceramic composition is deposited on the other rigid structure and than fired, it does not achieve the same density as co-fired ceramics or ceramics fired separately. That fact can be attributed to the stretching of ceramics during the firing process. The stretching is a consequence of shrinkage obstruction of ceramics in two directions. Shrinkage of ceramics is allowed only in one direction, perpendicular to the rigid substrate. In order to achieve the sufficient ceramics density, increased temperature of firing is required.

5. Conclusions

A new design of tabular SOFC was successfully produced and experimentally verified.

The SOFC has been created on the basis of anode base structure which is provided with own fuel distributors and combustion products collector. The anode base structure comprises two 0.130 mm thick anode operating layers suspended on fine beams and permanently bonded with the central core of the base structure. Owing the low thickness of the anode functional layer the polarization concentration loses were significantly decreased.

The anode base structure is a carrier for two independent power sources provided with a common anode current collector. Each of the cells has an active area of 4 square centimeters, and provides more than 1,6 W of electric power. So, the single flat ceramic structure of SOFC of dimensions 19 mm x 60 mm and thickness 1.2 mm provides more than 3.2 Watts of electric power.

The flat ceramic structure of SOFC can be used as a power source separately or it can be easy connected into battery with application of mica gaskets.

Each cell is equipped with own electrodes for collection of charges from the anode and the cathode and therefore it is a complete independent device which might be useful for testing various alternative materials for fuel cells.

Acknowledgments

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