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Microtubular Solid Oxide Fuel Elements: Development and Testing

A. S. BAGISHEV^{1,2}, N. V. NIFTALIEVA^{1,2}, I. V. KOVALEV^{1,3}, B. V. VOLOSHIN^{1,2}, M. P. POPOV¹, N. V. LYSKOV⁴,
E. A. LEVCHENKO⁴, I. A. GVOZDKOV⁴, V. V. SINITSYN⁴, A. V. SIVAK⁴, A. P. NEMUDRY¹

¹*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia*

E-mail: popov@solid.nsc.ru

²*Novosibirsk State University, Novosibirsk, Russia*

³*Novosibirsk State Technical University, Novosibirsk, Russia*

⁴*NITs TOPAZ, Moscow, Russia*

Abstract

This paper presents the results on the development of microtubular solid oxide fuel cells (MT SOFC). A review of the literature data on solid oxide fuel cells (SOFC) is also presented. The procedure of MT SOFCs manufacture by means of the phase inversion technique and characterization methods are described. A measuring cell to determine the current–voltage characteristics of MT SOFC is described. The obtained data allow us to outline further routes to increase the capacity of MT SOFCs.

Keywords: MT SOFC, cathode, perovskites, oxygen exchange

INTRODUCTION

Solid oxide fuel cells (SOFC) that are able to convert the chemical energy of organic fuel directly into electric energy are especially relevant for Russia because two thirds of its territory (Far East, Siberia and Arctic) are poorly suitable for network generation.

Solid oxide fuel cells may be conventionally divided into *tubular* and *planar*, each group possessing their own advantages which are directly linked with application areas:

- *planar* structures are distinguished by the highest mechanical strength and are combined in stacks, which allows making stationary installations with high productivity. The start-up time for these installations reaches several days.

- *tubular* structures are characterized by shorter start-up time. Due to the geometric fea-

tures of the tubular shape, their productivity is directly dependent on the diameter of the element: the smaller is the diameter, the higher is the specific power of the element.

The studies of SOFC since 1990 have resulted in obtaining small-size tubular porous electrodes with thin electrolyte (the external diameter 1–3 mm, electrolyte thickness 5–15 μm). The small size promotes a decrease in the ohmic resistance of the element and hence helps increasing its specific power. This SOFC structure is called *microtubular* (MT) [1–4], and it has some features:

- a small diameter of the element, which allows achieving record specific power per unit mass and volume;

- high porosity of the supporting matrix, which provides the stability against thermocycling and a short time necessary to reach the operation mode

after switching on (less than 10 s for a separate element and 20 min for a generator);

- the ability to remain capable of working in the case of high temperature gradients along the element.

Foreign companies have made substantial progress within the two recent decades in the area of the development of electrochemical generators based on MT SOFC. Their advantages may be stressed:

- organization of fuel reforming inside tubular elements (AtrexEnergy, Inc.);
- the use of the methods of polymer extrusion and an increase in specific power up to the level required in pilotless vehicles (100 W/L) (AMI);
- production of relatively powerful generators with power intensity 850 (W · h)/kg and the time of reaching the nominal rating 25 min (Watt);
- the production of module systems based on MT SOFC distinguished by high specific power (starting from 2 W/cm³) at the working temperature of 500–600 °C and high resource parameters (up to 40 000 h) (TohoGasCo., Mitsubishi Heavy Industries and AIST [5, 6]).

Above-listed results were obtained mainly using the following materials [7]:

- thin layers of stabilized zirconium dioxide $Y_xZr_{1-x}O_2$ (YSZ), $Y_xSm_yZr_{1-x-y}O_2$ (YSmSZ), $Ce_xZr_{1-x}O_2$ (CSZ), etc. or stabilized cerium dioxide $Gd_xCe_{1-x}O_2$ (GDC), $Sc_xCe_{1-x}O_2$ (SDC), etc. were used as *solid electrolytes*;

- cermet Ni/YSZ with open porosity more than 40 % with respect to the volume was used as *the anode material*;

- $La_{1-x}Sr_xMnO_{3-z}$ (LSM) and $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-z}$ (LSFC) were used as *the cathode materials*.

Analysis of reviews shows that 38 % of publications on MT SOFC during the years 2003–2017 were made by authors from Japan, 23 % – from the USA and Canada, and 24 % – from the countries of the European Community [2–4]. By present, in Russia, the tubular SOFC based on YSZ manufactured with the help of extrusion or slip casting have been developed at the Institute of High-Temperature Electrochemistry, UrB RAS (Ekaterinburg). The preparation of MT SOFC with the help of phase inversion is carried out by our group in collaboration with InEnergy Group (Moscow) [8].

It is worth stressing that the development of the technology of MT SOFC is the necessary stage in making new efficient current generators for distributed generation and portable consumers (this area is an element of the start-to-finish

technology New and Mobile Energy Sources). The manufacture of MT SOFC possessing high specific power, strength and the possibility of rapid start-up will allow MT SOFC to be brought to the market of mobile and portable devices, the scale of which can hardly be overestimated (military technique, transport, electronics, etc.).

The procedure of obtaining MT anode cermets, the methods of deposition and formation of the layers of gas-tight electrolyte and porous cathode are presented in the paper, along with the measurements of the voltage-current characteristics of the manufactured one-off MT SOFC.

EXPERIMENTAL

The manufacture of MT anode blanks having the composition $NiO/Y_{0.08}Zr_{0.92}O_{2-\delta}$ (NiO/YSZ) in the stoichiometric ratio of 60 : 40 (mass %) was carried out by means of phase inversion. A stoichiometric mixture of NiO (chemically pure, Kh. Ch. reagent grade) and the electrolyte YSZ (chemically pure, Kh. Ch. reagent grade) was mixed with N-methylpyrrolidone (chemically pure, Kh. Ch. reagent grade) as a solvent and with polysulphone (chemically pure, Kh. Ch.) as a polymer in proportions 12 : 4 : 1, respectively. The polymer paste was extruded through a die into a bath with the coagulant, where the polymer suspension was subjected to phase separation. Thus prepared anode blanks were annealed at 600 °C in the air for 2 h to burn out the organic binder, and then agglomerated at 1150 °C in the air for 6 h.

Then the layers of the YSZ electrolyte (layer thickness 10 μm) and the cathode $La_{0.6}Sr_{0.4}MnO_{3-\delta}$ (LSM, Kh. Ch.) (layer thickness 20 μm) were deposited sequentially by means of dip-coating. The temperature of electrolyte/cathode sintering was 1400/1250 °C, respectively.

Determination of the phase composition of the resulting compounds was carried out with a D8 Advance diffractometer (Bruker, Germany) using the energy-dispersive detector Sol-X (Bruker, Germany) and a high-speed detector Lynx-Eye (Bruker, Germany). The recording was carried out within the range of 10–70° over 2θ with a step of 0.02°, signal accumulation time 0.5 s. The phase composition was determined with the help of the ICDD PDF-4+ database (2011). To refine the structures of the compounds under investigation, full-profile analysis over the integral intensities of diffraction peaks was carried out by

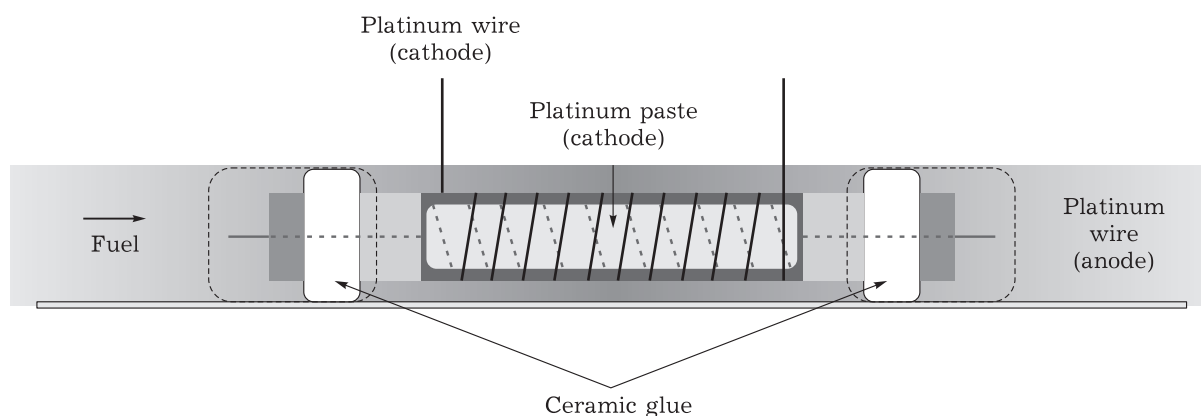


Fig. 1. Scheme of the reactor for the measurement of the voltage-current characteristics of the MT SOFC.

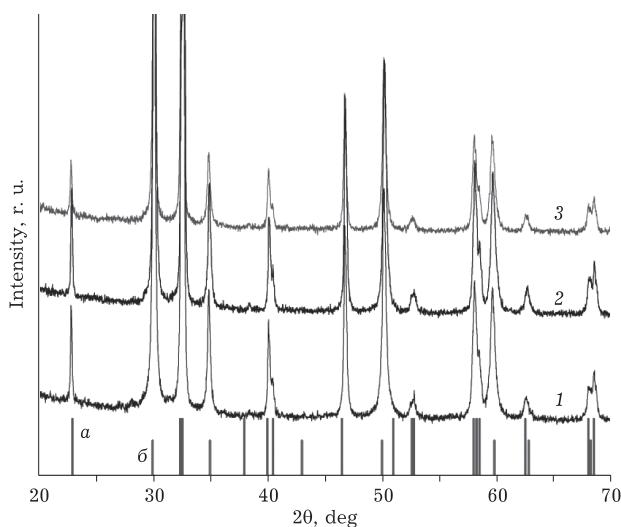


Fig. 2. Data of X-ray phase analysis at $T = 800\text{ }^{\circ}\text{C}$, $P_{\text{O}_2} = 0.21\text{ atm}$: 1 — initial mixture; 2 — after exposure for 120 h; 3 — after exposure for 340 h. Phases YSZ (a) and LSM (b) are presented in the form of a histogram.

means of Rietveld method with the help of DIFFRAC plus TOPAS 4.2 software.

To study the morphology and to carry out the elemental analysis of the resulting compositions, we used a Hitachi TM 1000 scanning electron microscope (Japan, accelerating voltage 15 kV, reso-

lution 30 nm) with the system of X-ray elemental analysis Swift ED-TM EDX (EDS).

The measurements of the voltage-current characteristics of one-off MT SOFC were carried out in the reactor shown in Fig. 1.

The anode and cathode of the SOFC cell were switched with the help of platinum wire (0.3 mm in diameter). For this purpose, a spiral made of this wire was placed in the inner part of the tube (anode), while the spiral made of the second wire was coiled (1.5–2 mm between the loops) on the outer part of the tube (cathode). To improve the contact between the coiled wire and the cathode, contact sites were covered with platinum paste (Heraeus, Germany). High-temperature airproofing of the cell was carried out with the help of ceramic glue. Then the cell was dried at $130\text{ }^{\circ}\text{C}$ for 30 min. Thus prepared cell was then placed into a gradient-free region of the furnace, and anode reduction was carried out at $550\text{ }^{\circ}\text{C}$ for 2 h in the flow of pure hydrogen, which was supplied inside the cell. Air was used as the oxidizer (flow rate $F = 80\text{ mL/min}$). Three types of gas were used as the fuel: 1) argon with 5 % hydrogen content (Ar/H_2); 2) pure hydrogen (H_2); 3) a mixture of gases Ar/H_2 and H_2 . Investigation was carried out at a temperature of $T = 750\text{--}850\text{ }^{\circ}\text{C}$.

TABLE 1

Characteristics of a single manufactured MT SOFC

Layer No.	Component	Chemical composition, mass %	Thickness, μm
1	Anode	$\text{NiO}/\text{YSZ} = 60 : 40$	250–300
2	Anode functional layer	$\text{NiO}/\text{YSZ} = 40 : 60$	10–15
3	Electrolyte	$\text{YSZ} = 100$	8–10
4	Cathode functional layer	$\text{LSM}/\text{YSZ} = 40 : 60$	10–12
5	Cathode	$\text{LSM}/\text{YSZ} = 60 : 40$	10–15

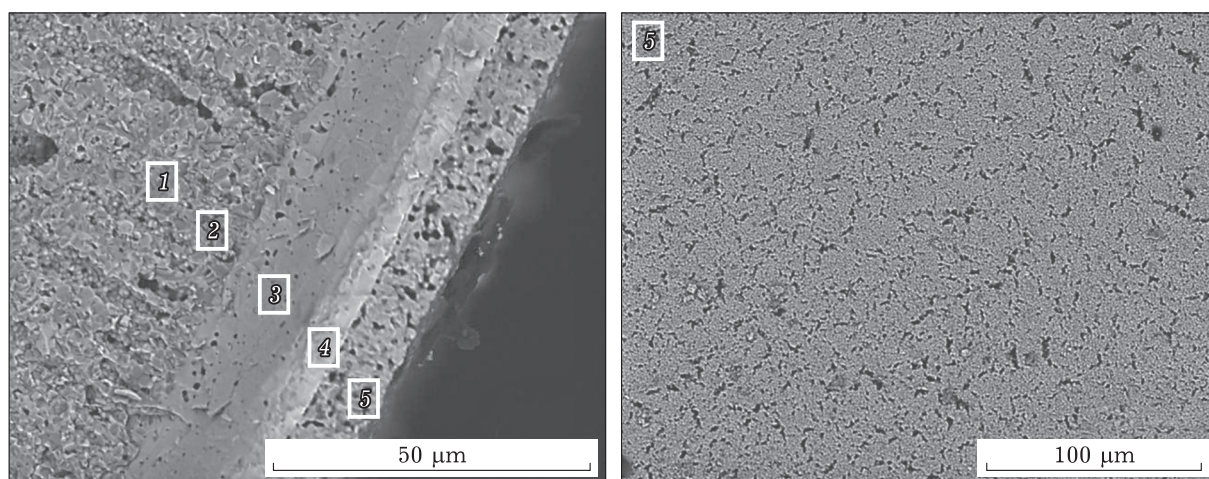


Fig. 3. Microstructure of MT SOFC: *a* – layer distribution 1–5 over components; *b* – porosity of the cathode layer. For layer designations, see Table 1.

Cell dimensions: inner/outer diameter = 1 : 2 mm, respectively; total length 80 mm; cathode length 50 mm; active area 3.1 cm². Gas flows were controlled with the help of a gas mixing device UFPGS-4 (SoLO, Russia).

RESULTS AND DISCUSSION

An essential factor for the development of SOFC was the absence of interaction between the electrolyte and electrode materials. Literature data on the interaction of the YSZ electrolyte and LSM cathode are contradictory. This may be connected with different purity and morphology of samples studied by each of the researchers. To de-

termine possible interaction between the cathode material LSM and electrolyte YSZ, an *ex situ* experiment was carried out under the SOFC operation conditions ($T = 800\text{ }^{\circ}\text{C}$, the partial pressure of atmospheric oxygen $P_{\text{O}_2} = 0.21\text{ atm}$) for a long time (340 h). A mixture of YSZ/LSM = 50 : 50 (mass %) was used as the sample.

The X-ray diffraction patterns (Fig. 2) exhibited no new reflections; no shifts of the reflections of initial phases were observed. These facts point to the high chemical stability of YSZ and LSM materials. So, the cathode material LSM is chemically inert with respect to the YSZ electrolyte.

Taking into account the obtained data, we manufactured a MT SOFC with the characteristics shown in Table 1.

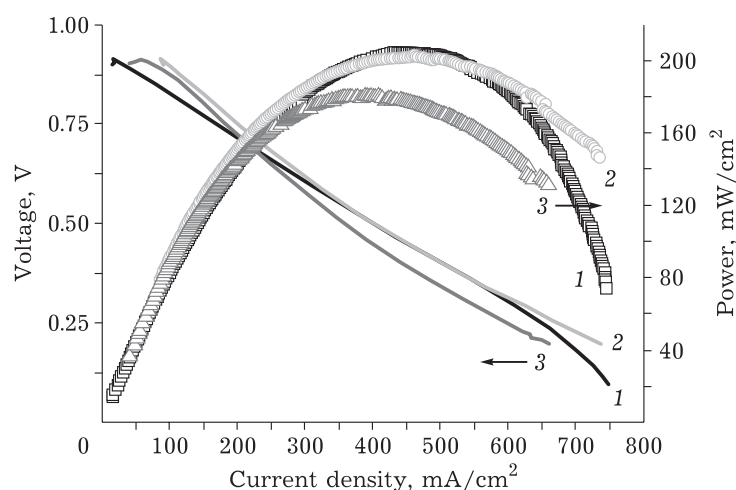


Fig. 4. Voltage-current characteristics of the MT SOFC based on YSZ electrolyte. Experimental conditions: $T = 850\text{ }^{\circ}\text{C}$, fuel: 1 – Ar/H₂ ($F = 80\text{ mL/min}$); 2 – Ar/H₂, H₂ ($F = 40\text{ mL/min}$); 3 – H₂ ($F = 80\text{ mL/min}$); oxidizer – atmospheric oxygen ($F = 80\text{ mL/min}$).

A section of the MT SOFC is shown in Fig. 3, *a*. One can see a gas-tight electrolyte layer located between the porous electrodes. The porosity of the cathode layer is clearly seen in Fig. 3, *b*. It should be stressed that additional layers between the electrolyte and the electrodes are necessary for levelling the thermal expansion coefficients.

Measurements of the voltage-current characteristics of the MT SOFC showed that the maximal peak power is 200 mW/cm² and is achieved under the following conditions: $T = 850$ °C, $F(\text{Ar}/\text{H}_2) = 40$ mL/min, $F(\text{H}_2) = 40$ mL/min (Fig. 4). One can see that the open circuit voltage (OCV) is lower than the theoretical value 1.1 V for MT SOFC with the YSZ electrolyte in the case when hydrogen is used as the fuel [9, 10], which is the evidence of non-ideality of the electrolyte layer. Further increase in cell power is connected first of all with the preparation of denser electrolyte layers, a decrease in the resistance of the electrode layers and contact resistance between them.

CONCLUSION

Relying on the *ex situ* experiment, it was demonstrated by means of X-ray diffraction that no chemical interaction occurs between the cathode material of the composition $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_{3-\delta}$ and the electrolyte of the composition $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_{2-\delta}$ either during the joint annealing at 1250 °C or during long-term interaction under the SOFC operation conditions for 340 h. Porous anode blanks were manufactured with the help of phase inversion. The layers of gas-tight electrolyte and porous cathode were obtained by means of dip-

coating. The voltage-current dependence for the manufactured element is presented, and the routes to increase the power of MT SOFC are outlined.

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REFERENCES

- 1 Kendall K., Sales G. A., Rapid Heating Ceramic Fuel Cell, Proceedings of the 2nd International Conference on Ceramics in Energy Applications, London, 1994, P. 55–63.
- 2 Lawlor V., Griesser S., Buchinger G., Olabi A. G., Cordiner S., Meissner D., *J. Power Sources*, 2009, Vol. 193, P. 387–399.
- 3 Jamil S. M., Othman M. H. D., Rahman M. A., Jaafar J., Ismail A. F., Li K., *J. Eur. Ceram. Soc.*, 2015, Vol. 35, No. 1, P. 1–22.
- 4 Wang W., Qu J., Juliao P. S. B., Shao Z., *Energy Technol.*, 2019, No. 7, P. 33–44.
- 5 Sumi H., Yamaguchi T., Hamamoto K., Suzuki T., Fujishiro Y., *ECS Transactions*, 2013, Vol. 57, No. 1, P. 133–140.
- 6 Kobayashi Y., Ando Y., Nishiura M., Kishizawa H., Iwata M., Matake N., Tomida K., *ECS Transactions*, 2013, Vol. 57, No. 1, P. 53–60.
- 7 Kendall K., Newton J., Kendall M., *ECS Transactions*, 2015, Vol. 68, No. 1, P. 187–192.
- 8 Popov M. P., Maslennikov D. V., Gainutdinov I. I., Gulyaev I. P., Zagoruiko A. N., Nemudry A. P., *Cat. Today*, 2019, Vol. 329, P. 167–170.
- 9 Noh H.-S., Yoon K. J., Kim B.-K., Je H.-J., Lee H.-W., Lee J.-H., Son J.-W., *J. Power Sources*, 2014, Vol. 247, P. 105–111.
- 10 Noh H. S., Hong J., Kim H., Yoon K. J., Lee J. H., Kim B. K., Son J. W., *J. Ceram. Soc. Japan*, 2015, Vol. 123, No. 4, P. 263–267.