Investigation of Characteristics of the Anode-Supported Solid Oxide Fuel Cells with Thin-film Electrolyte Deposited by Electron-Ion-Plasma Methods†

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Abstract – Results of research of characteristics of anode-supported solid oxide fuel cells (SOFCs) with thin-film electrolyte deposited by the combined method including deposition of ZrO2:Y2O3 layers by reactive magnetron sputtering and their pulse electron beam processing are presented in this article. It is shown, that due to formation of a dense nanostructured electrolyte film with thickness about 5 microns working temperature SOFC can be reduced up to 650–750 °C without essential losses in generated power.

1. Introduction

In civilized countries big attention is attended to hydrogen energy, including the development of solid oxide fuel cells (SOFC) – one of the most perspective types of electrochemical generators for direct conversion of the chemical energy of the interaction of the hydrogen and oxygen in electric energy. The main elements of SOFC construction are porous electrodes (the anode and cathode) and located between them solid gas-tight electrolyte (yttrium stabilized zirconium oxide ZrO2:Y2O3 (YSZ) is most high-usage). Performance of SOFCs in most cases depends from such characteristics of the electrolyte as mechanical toughness and thermal stability, ion conductivity, gas-tightness.

Fabrication of commercial and efficient SOFC requires a solving of the actual problem – reducing of its working temperature from 800–1000 up to 500–650 °C. The way of the above-mentioned problem solving lies in reduction of main functional layers thickness, and electrolyte first of all [1].

It is important to note that reduction of electrolyte thickness must not be accompanied by deterioration of its gas-tightness in consequence of different defects arising such as cracks and pores, as well as films delaminating from substrate.

At realization of anode-supported SOFC design thin-film (thickness ~3–5 microns) gastight electrolyte is necessary to receive on a surface of porous substrate which is usual have porosity about 40% and the pore sizes from units up to tens micron for free pass of fuel gas to three-phase boundary at electrolyte surface. It is obvious, that for achievement of high gas tightness of ZrO2:Y2O3 coating it is appropriately to carry out preliminary surface processing of porous SOFC anodes with the purpose of creation of the modified and interface layers on their surface [2–4].

The purpose of the present work was research of characteristics of planar fuel cells of intermediate temperature solid oxide fuel cells by methods of voltammetry and impedance spectroscopy, and also revealing of the received characteristics connection with structure and parameters of synthesis of ZrO2:Y2O3 electrolyte. The YSZ electrolyte was formed on porous Ni/YSZ anodes by the combined method developed by us, including deposition of YSZ layers by reactive magnetron sputtering and pulse electron beam treatment.

2. Experimental

For the comparative analysis 3 samples of single cells with diameter of 20 mm have been selected. They were made by the following technology. Sample 1 represented the porous Ni/YSZ anode received as a result of high-temperature sintering (t = 1450 °C, 2 h of isothermal exposure) of a raw polymeric tape (ESL ElectroScience, USA) on which layer of electrolyte with thickness 5 microns had been deposited by the method of pulse reactive magnetron sputtering of the ZrO1.90Y0.14 cathode. Deposition of YSZ electrolyte was carried out in Ar/O2 atmosphere at pressure 0.2–0.3 Pa on the heated up to temperature 600 °C substrates. The pulse operating mode of a magnetron with frequency 50 kHz and discharge power of 1.5 kW was used. Thus growth rate of YSZ coatings was of 2.5 micron/h. The cathode was formed by a slurry coating and drying of paste from LaSrMnO3 (Fuel-cellmaterials, USA).

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At manufacturing of samples 2 and 3 the sublayer of YSZ electrolyte with thickness 0.35 and 1.5 microns, accordingly was deposited on the porous anode. After that samples were exposed to pulsed electron beam treatment (EBT) with the following parameters of a beam: electron energy of 10–12 keV, a beam current of ~15 kA, a pulse duration of 2–3.5 μs, density of beam energy of 0.8 J/cm², number of pulses 2–3. Then on the irradiated sublayer the basic electrolyte layer with thickness ~2.5 microns and pasted LaSrMnO₃ cathode were deposited.

The structure of the received samples was investigated on a scanning electronic microscope Philips SEM 515. Research of cells electric characteristics was carried out in device ProboStat™ (NorECs, Norway) in a range of working temperatures 550–800 °C (Fig. 1).

As fuel for SOFC hydrogen was used, as an oxidizer – air or oxygen. The flow rate of hydrogen changed in a range of 20–80 ml/min, and an oxidizer of 50–250 ml/min. The current-voltage characteristics of SOFCs were measured by potentiostate P-30 (“Elins”, Russia). Measurements of impedance spectra were spent with the help of impedancemeter Z-500P (“Elins”, Russia) in the frequency range of (1–3) × 10⁵ Hz with an excitation voltage of 10 mV.

The spectroscopy of electrochemical impedance is the method frequently used for the analysis of fuel cells and it is very important for the studying of charge transport in heterogeneous systems, including phase boundaries, electrode boundaries, elements of a microstructure. The impedance of electrochemical cell is measured in the present method as function from frequency. Full complex resistance (impedance) of a cell indicates as 

\[ Z^* = Z' - jZ'' \]

where \( Z' \) is the active (real), \( Z'' \) is the reactive (imaginary) components of an impedance. Graphic of dependence \( Z(\omega) \) in coordinates \( Z', Z'' \) is denoted as impedance hodograph, or its spectrum. Building of hodographs is used at interpretation of frequency dependences of impedance. In this case correspondence of hdefense form of investigated cell to hodograph of the concrete combination of the elementary electric elements (resistance, capacity, etc.) is analyzed. Each component of this chain characterizes some physical, chemical or electrochemical process existed in really investigated cell.

3. Results

Electronic microscopy has shown that YSZ coatings, deposited by magnetron sputtering, have dense but columnar structure (Fig. 2, a). Gas permeability of a sample 1 electrolyte was \( 2.1 \times 10^{-7} \text{ mole} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1} \).

Cross section image of the sample 3 is shown in Fig. 2, b. At its manufacturing on the anode surface was deposited sublayer of YSZ electrolyte and then it was processed by pulsed electron beam. It was observed recrystallization of surface layer as a result of high-speed heating and cooling. In result at deposition of the second layer of electrolyte on processed YSZ sublayer took place its formation with a dense pore-free structure. Gas permeability of electrolyte received by above mentioned method twice less and equal to \( 1.01 \times 10^{-7} \text{ mole} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1} \).
Figure 3 shows the voltage/power density versus the current density for cell Nos. 1 and 3.

![Graph of voltage/power density versus current density for cell Nos. 1 and 3.](image)

**Fig. 3.** The current-voltage characteristics of fuel cells No. 1 (a) and 3 (b) tested at different temperatures (where 1 – 550; 2 – 600; 3 – 650; 4 – 700; 5 – 750; 6 – 800 °C). Gases – H₂ and air.

The open circuit voltages (OCV) obtained for the single cells Nos. 1 and 3 tested at temperatures 600–800 °C were 0.84–0.96 V and 0.95–1.06, correspondingly. OCV of the sample with electrolyte deposited with use of EBT are close to theoretical (1.08 V). It says about good gas tightness of the received electrolyte that well correlates with measurements of gas permeability and structure of YSZ revealed by electronic microscopy.

Current-voltage characteristics of both elements have a nonlinear type. The first “fast” part of V-A characteristic (from 0 up to 40–400 mA, depending on temperature) is connected with the activation losses formed as a result of necessity of energy for realization of some processes. These are gaseous-phase diffusion of reagents to electrodes, adsorption, dissociation and ionization, surface diffusion to electrochemical active centers, entering of ion in the electrolyte and anode or cathode.

For cell 3 at the big current density (more than 1 A/cm²) the voltage decrease is accelerated, that is connected to formation of concentration losses.

This kind of polarization is caused by the fact that concentration of particles in a zone of reaction at passage of a current differs from concentration of agents in volume of electrode as the feed or removal of agents not keep pace with consumption of these agents on an electrode.

At 800 °C power densities in the range of 300 mW/cm² for sample 1 and of 600 mW/cm² for sample 3 are achieved at 0.4 V. At reduced operating temperatures down to 650 °C the power densities decrease to approximately 60 mW/cm² for sample 1 and 210 mW/cm² for sample 3, respectively. At decrease in temperature the difference between power density generated by cells 1 and 3 increases.

Hodographs of impedance received for cells 1 and 2 at temperatures 600–700 °C are shown in Fig. 4. Resistance of electrolyte was determined by a point of crossing of high-frequency part of the hodograph with the real axis of impedance.

![Impedance spectra of fuel cells 1 and 2.](image)

**Fig. 4.** Impedance spectra of fuel cells 1 and 2, measured at 600, 650, and 700 °C on air.

For a cell 1 electrolyte resistance increased from 0.25 up to 1.8 Ohm at temperature reduction from 800 up to 600 °C. For cells 2 and 3 in the same temperature range electrolyte resistance increases with temperature reduction from 0.27 up to 0.92, and 0.42 Ohm, correspondingly. Thus at temperature 800 °C electrolyte resistance of researched samples approximately identical and equal to 0.25–0.27 Ohm, but at temperature reduction samples with electrolyte sublayer processed by an electron beam have essentially smaller resistance of electrolyte. At the same time difference in YSZ layer resistance of cell 1 and cells 2, 3 increases with temperature reduction.

Lower resistance of electrolyte formed with use of EBT, evidently, is connected to an opportunity of pulsed melting to form layers with ultrafine-grained and nanocrystalline structure [5].

It is clear from Fig. 4, that cells 2 and 3 not only have smaller electrolyte resistance than cell 1, they also have smaller Faraday resistance (it is characterized by diameter of semicircles of impedance hodographs). Faraday resistance of a cell, as is known, characterizes process of charge transport through boundary electrode – electrolyte.

The analysis of impedance spectra of researched cells has shown that at high temperatures (near 800 °C)
hodographs represent semicircles with the center positioned below real axis impedance (Fig. 5).

Fig. 5. The equivalent circuit with CPE element and hodographs of impedance of cell 3 at $t = 750^\circ$C

For the description of such spectra usually apply equivalent circuits with constant phase element [6]. The constant phase element (CPE) is generalized and universal tool for impedance modeling of extensive class of electrochemical systems. It can represent exponential distribution of the electrochemical reaction parameters associated with overcoming of energy barrier at charge and mass transport.

At temperature reduction below 800°C for cell 1 and below 700–750°C for cells 2 and 3, hodographs start to be described by two partially overlapped half-rounds (Fig. 6).

As a rule, the impedance spectrum of polycrystalline materials in the complex plane, having two semicircles, suggest about the contribution to the total conductivity of grains volume material and their boundaries [7]. Such spectra are modeled by series connection of two parallel chains of capacity and resistance which time constant $\tau_1$ and $\tau_2$ differ insignificantly. Change of impedance spectra character with working temperature reduction, obviously, is connected to the fact that become more pronounced influence of electrolyte grain structure on conductivity. For cell 2 and 3 electrolyte grain structure starts to affect on conductivity at smaller temperatures owing to the smaller grain size of their electrolyte.

Fig. 6. The equivalent circuit and hodograph of impedance of cell 3 at $t = 550^\circ$C

4. Conclusion

In work the perceptivity of magnetron sputtering and electron beam treatment methods for formation of thin-film electrolyte of intermediate temperature fuel cells is shown. The power density of fabricated fuel cells at temperature 650°C is equal to 210 mW/cm$^2$ that is achieved due to reduction of formed YSZ electrolyte thickness and as consequence of its resistance reduction.

References