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Fabrication of Membrane–Electrode Assemblies for Solid-Oxide Fuel Cells by Joint Sintering of Electrodes at High Temperature[1]

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Abstract—The results on optimizing the procedure of preparation of the electrode system within membrane–electrode assemblies (MEA) of solid-oxide fuel cells (SOFC) by joint sintering of electrodes at the enhanced temperature close to that of anode sintering are presented. The MEA are prepared based on membranes of the anionic conductor Hionic^{TM} (Fuel Cell Materials, USA); the cathode is formed based on cation–deficient lanthanum-strontium manganite $(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ with addition of activated carbon for optimizing its microstructure; the anode is formed on the basis of cermet NiO/10Sc1CeSZ (89 mol % ZrO_2, 10 mol % Sc_2O_3, 1 mol % CeO_2). The results of electrochemical testing of model MEA are also shown.

Keywords: solid-oxide fuel cells, membrane–electrode assemblies, joint sintering, electrodes, voltamperograms

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INTRODUCTION

Fuel cells are among the most promising technologies of direct conversion of the chemical energy of hydrocarbon fuels to the electric energy [1]. The efficiency of fuel cells as regards produced electric energy reaches 60% [2] and, in hybrid cycles with gas turbines, may reach 65–70% [3]. When thermal energy is utilized, the efficiency can reach 85–90% [4].

Solid-oxide fuel cells (SOFC) pertain to the most promising types of fuel cell [5]. They allow record-breaking efficiencies to be reached due to their high working temperature and also make it possible to use hydrocarbon fuels with minimum pre-reforming [6].

Among SOFC the closest to commercialization, mention should be made of planar electrolyte-supported SOFC [7]. Their planar geometry makes it possible to use the practically feasible methods of anion-conducting membrane preparation and multilayer-electrode application [8], while the use of a solid electrolyte membrane as the mechanical support makes it possible to avoid the expensive methods of preparation of thin layers thus removing the limitations on the sintering temperature of the next components.

The elaborators of the planar electrolyte-supported SOFC try, on the one hand, to increase the supporting-membrane area with the aim of decreasing the fraction of electrochemically inactive fields and, on the other hand, to decrease its thickness in order to reduce the contribution of this membrane to the total internal resistance of the cell. This brings about the problems of mechanical deformation [9] and even destruction of some membrane–electrode assemblies that arise when the membrane is sintered, multilayer electrodes are applied, or during the cell operation.

The main approach to solving this problem is to use the method of joint sintering of electrodes which allows compensating the mechanical stresses from the cathode and the anode. In this approach, the most pressing problem is associated with selecting the optimal temperature and the program for the joint high-temperature sintering, because this temperature should be suitable for both electrodes which substantially differ as regards the requirements imposed on them.

Earlier, we obtained the results on optimizing the procedure of fabrication of membrane–electrode assemblies (MEA) for solid-oxide fuel cells by using the methods of individual [10] and joint sintering of electrodes [11]. When the electrodes were sintered simultaneously, their high-temperature annealing was carried out at the temperature close to the value optimum for the cathode, i.e., 1170°C. Thus a planar MEA with the multilayer cathode and anode was obtained. Electrochemical measurements showed that the

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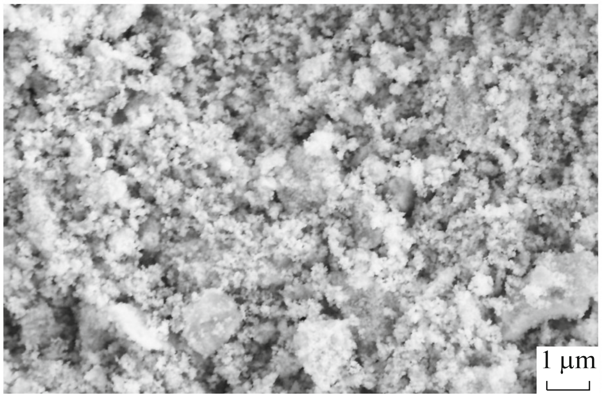

Fig. 1. SEM image of particles of anion-conducting GDC powder.

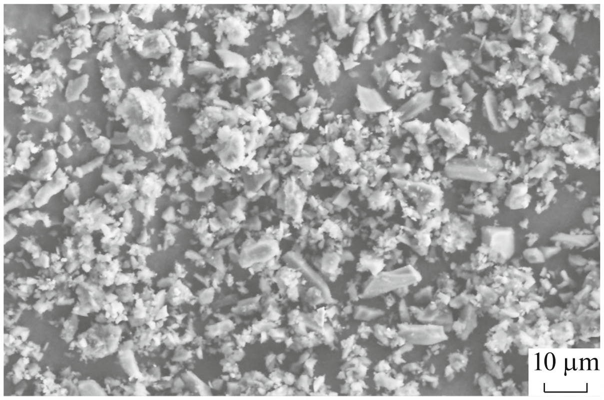

Fig. 2. SEM image of particles of pore-forming activated carbon.

power density produced at the working temperature of 850°C and the cell voltage of 0.7 V was 225 mW/cm^2 when the oxidative air mixture was used and also the fuel based on nitrogen and hydrogen with equal partial pressures. In this case, the mentioned cell characteristics were unstable for several days. This result was attributed to the insufficient connectivity of the composite anode obtained at insufficiently high temperatures of high-temperature annealing.

Below, we show the results on optimizing the procedure of preparation of membrane–electrode assemblies for solid-oxide fuel cells by the method of joint sintering of electrodes at temperatures close to the value optimal for the anode.

EXPERIMENTAL

The procedure of preparation of starting materials, the technological approaches, and the research methods used here were described in detail earlier [11–13].

The MEA samples were prepared based on anion-conducting membranes produced by Fuel Cell Materials (USA) with dimensions of 50 × 50 mm. The anodic layers were formed based on composites of NiO (Sigma Aldrich) and 89 mol % ZrO_2–10 mol % Sc_2O_3–1 mol % CeO_2 (10Sc1CeSZ) (DKKK, Japan). The original NiO powder was subjected to preliminary annealing in order to remove superstoichiometric oxygen and other adsorbed components [12]. The microstructure of the current-collecting anodic layer was controlled by introducing rice starch (Beneo, Belgium) [13].

The cathodic layers were prepared from cation-deficient lanthanum-strontium manganite $(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ (LSM) synthesized by the citrate method [14, 15]. To prepare the protective sublayer and the functional layer for the cathode, we used powder of anionic conductor $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) (Fuel Cell Materials, USA). Figure 1 shows the SEM image of this powder. It is seen that the average size of particles is about 100 nm. This size is suitable for preparation of homogeneous composites with the LSM material. The microstructure of the functional cathodic layer was optimized by activated carbon. Figure 2 shows the SEM images of powder particles. The particle size did not exceed 10 μm being in average 3–5 μm, which allowed the well developed system of pores to be developed.

Powder mixtures were subjected to multistage grinding procedures in a planetary mill Pulverisette 6 classic line (Fritsch, Germany) with cups of stabilized zirconia and balls of the same material. The grindings were aimed at preparing the composites and obtaining the homogeneous mixtures with pore-forming additives.

Screen-printing pastes were prepared based on an organic binder Heraeus V-006A (Germany). The powder/binder ratios were optimized in a separate study [16]. Homogenization and degassing of screen-printing pastes were carried out in a planetary mixer ARE-250 (Thinky, Japan). The pastes were screen-printed on supports by means of Mat S45 (Ekra, Germany) with the use of A-Design stencils (Russia). The printed electrodes had the geometrical surface of 40 × 40 mm.

The X-ray diffraction analysis of the structure and phase composition of original powders was carried out on D-500-Braun diffractometer (Siemens, Germany). Scanning electron microscopy studies were carried out on Leo Supra 50VP microscope (Oxford Instruments, Great Britain). Thermogravimetric studies were carried out on analyzer Setsys Evo 16/18 (Setaram, France).

The electrochemical characteristics of MEA were studied on a test bench TrueXessory-HT (FuelCon, Germany) and also on a gas-temperature bench. The impedance spectra were measured in the frequency range from 0.1 Hz to 1 MHz by means of a potentiostat-galvanostat Autolab PGSTAT 302N (Autolab,

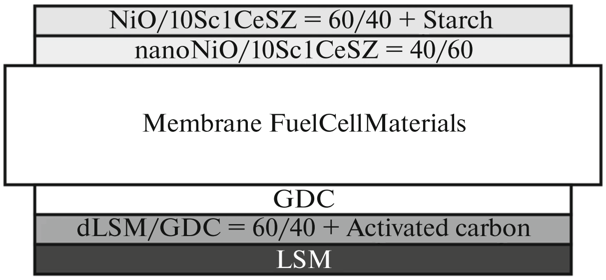

Fig. 3. Cross section of the membrane–electrode assembly prepared by joint sintering of electrodes at the enhanced temperature.

Netherlands) with a FRA32M module by the 2-electrode 4-contact method.

RESULTS AND DISCUSSION

We have shown earlier that the main drawback of MEA prepared by joint sintering of electrodes at temperatures close to the value optimum for the cathode (<1200°C) is the instability of electrochemical characteristics in time. According to impedance spectra and SEM images of SOFC electrodes, such degradation is caused most probably by the loss of connectivity of the electron-conducting cluster of the SOFC anode which leads to the simultaneous increase in the ohmic contribution into the total internal resistance and decrease in the effective surface area of cell electrodes. The reason for such behavior of the SOFC anode is the low density of anodes formed at the high-temperature annealing. During the operation in the fuel atmosphere, nickel oxide is reduced to metal nickel, which results in the further decrease in the density and connectivity of the electron-conducting subsystem of SOFC anode.

It is evident that to increase the stability of SOFC characteristics, one has to increase the initial density of electrode layers, which requires the higher temperature of anode formation.

When the sintering temperature is increased above 1200°C, it is necessary to avoid the direct contact between ionic conductors based on stabilized zirconia and strontium-lanthanum manganite. For this purpose, several modifications were introduced into the MEA design: an extra protective GDC layer was added (Fig. 3) and, in the functional cathodic layer, GDC was substituted for the anionic conductor 10Sc1CeSZ. After thermal treatment at temperatures above 1200°C, the diffusion of cerium to the anionic-membrane material was observed in the sites of contact between anionic conductors based on cerium and zirconium. It deserves mention that interaction between zirconium and cerium oxides yields intermediate the phases with the lower conductivity, which may decrease the total internal resistance of the cell [17]. To preserve the high porosity of the cathode functional layer, activated carbon was added to its composition. Such substitution allowed the temperature of electrodes' joint sintering to be increased to 1350°C. The procedure of preparation of precursors and anodic pastes was analogous to that described in [11].

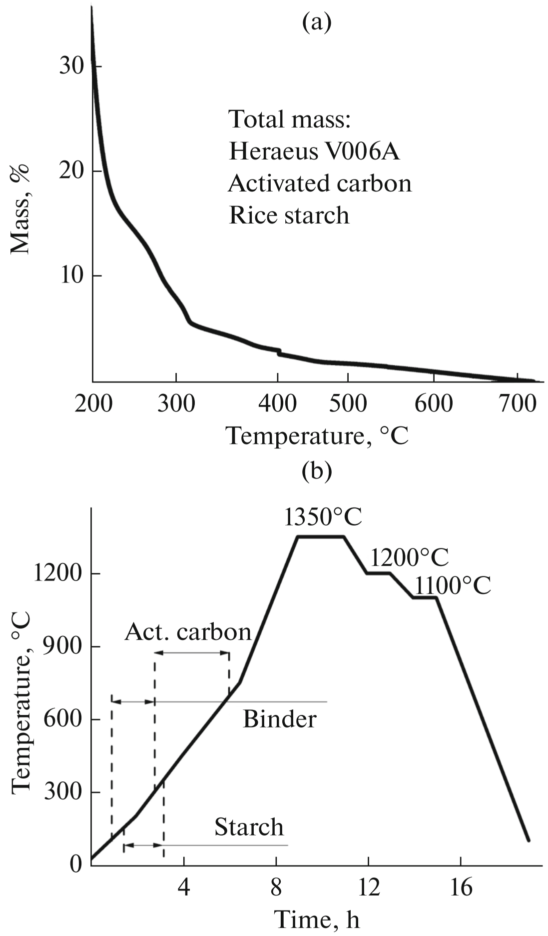

Fig. 4. (a) Mass loss of the combustible components of electrode pastes with regard to their ratio and (b) the program of high-temperature sintering of the SOFC electrode system.

The large number of organic substances used in preparation of electrode pastes necessitates that the special attention should be paid to the heating procedure at high-temperature annealing. Preliminary studies of the mass loss of the compounds during their heating in the air atmosphere were carried out. Figure 4a illustrates the overall mass loss of the combustible components with regard to their ratio in electrode pastes and the thickness of layers applied. The main mass loss (more than 80%) occurred below 200°C (is not shown) being associated with evaporation of terpineol used as a component in the electrode binder. The main volume of terpineol was removed during the intermediate technological procedures of drying the electrode layers. Figure 4b illustrates the heating of a membrane with the complete electrode

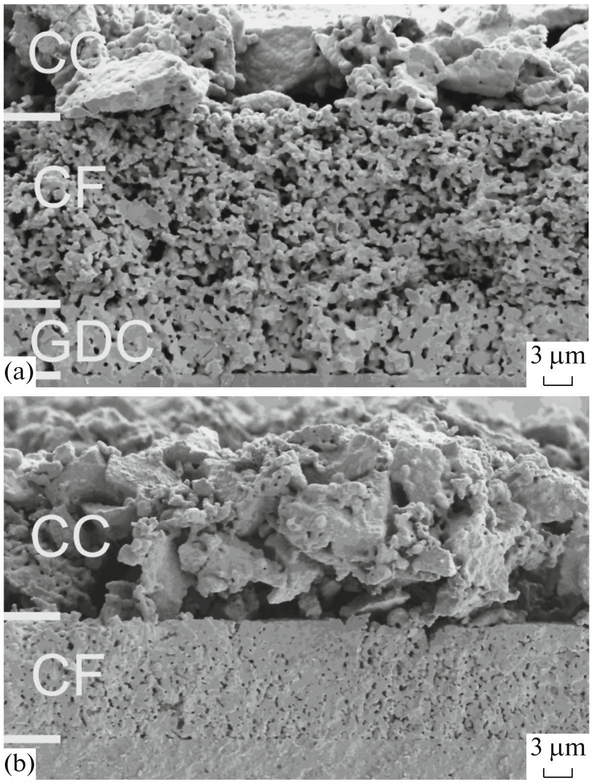

Fig. 5. SEM image of the cathode cross-section in a membrane–electrode assembly prepared by joint sintering at temperatures: (a) 1170°C and (b) 1350°C. CC is the cathodic current-collecting layer; CF is the cathodic functional layer.

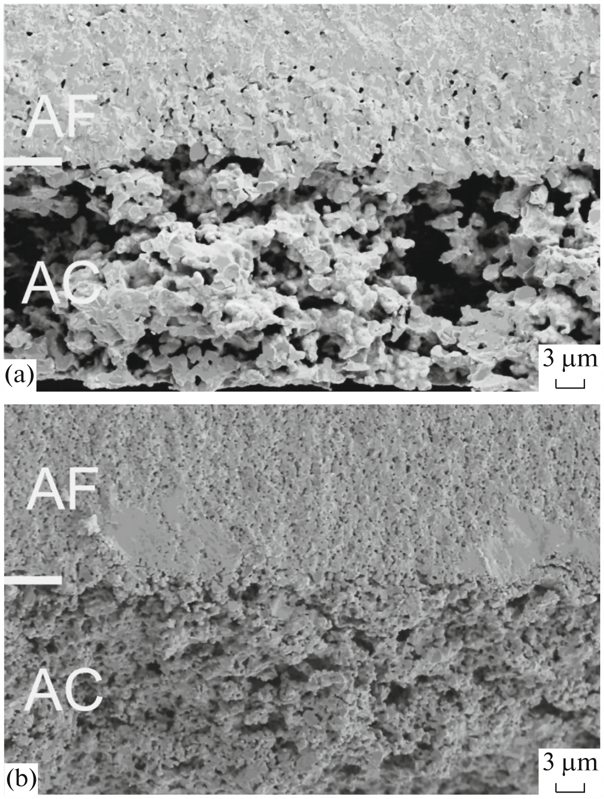

Fig. 6. SEM image of the anode cross-section in the membrane–electrode assembly prepared by joint sintering at temperatures: (a) 1350°C and (b) 1170°C. AC is the anodic current-collecting layer; AF is the anodic functional layer.

system. The vertical dashed lines outline the regions of predominant mass loss for components used.

By introducing the protective sublayer and changing the anionic conductor in the composite cathode, the joint-annealing temperature defined earlier [10, 18, 19] as the optimal for formation of anodes with the stable well-developed triple-phase boundary could be raised to 1350°C. It deserves mention that the program of high-temperature annealing was supplemented by 1-h exposures at 1200 and 1100°C during the cooling periods, which allowed the thermomechanical stresses associated with compacting of electrode layers to be eliminated.

Figure 5a shows a SEM image of the SOFC-cathode cross-section. On the supporting electrolyte (in the bottom), the following layers are applied sequentially: protective GDC layer, functional cathodic layer, and current-collecting layer. The protective GDC sublayer demonstrates the presence of open porosity and requires further treatment to increase its density. To compare the changes in the microstructure of the functional cathodic layer, the SEM image of its cross section is demonstrated for a cathode fabricated at 1170°C (Fig. 5b). The functional cathodic layer in the SOFC prepared at 1350°C has the much better developed triple phase boundary due to the presence of fine (<1 μm) pores in the absence of coarse agglomerates and with the average crystal size lower than 1 μm. The coarse-grain current-collecting layer of the cathode provides the high electronic conductivity of this layer at retention of through porosity. All internal interfaces demonstrate good adhesion, which is necessary for the charge transport in the transverse direction during the SOFC operation.

Figure 6 shows that as expected, raising the temperature of electrodes' joint sintering from (a) 1170°C to (b) 1350°C allows the density of the functional anodic layer to be substantially increased, which should improve the stability of SOFC electrochemical characteristics. Moreover, the current-collecting anodic layer retains its through porosity required for delivery of fuel and removal of gaseous reaction products.

The electrochemical characteristics of MEA were studied within a measuring cell TrueXessory-HT (FuelCon, Germany). The studies were carried out at 850°C. Figure 7 shows that the totality of modifications introduced made it possible to substantially improve the cell characteristics. Thus, at the working voltage of 0.8 V, the power produced by the cell

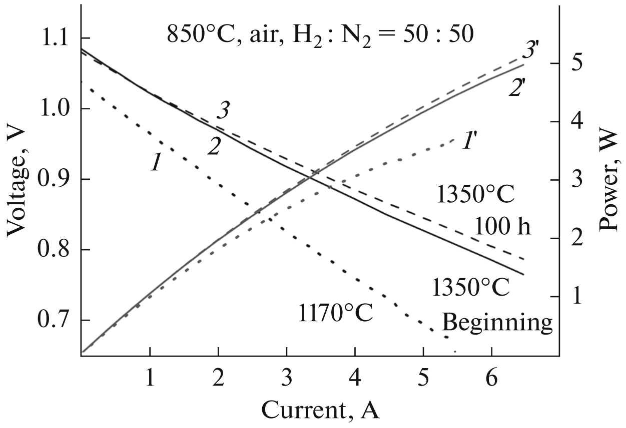

Fig. 7. (*1, 2, 3*) Voltammetric and (*1', 2', 3'*) power characteristics of SOFC MEA prepared by joint sintering of electrodes at temperature: (dotted line) 1170°C and (solid line) 1350°C immediately after the switching and also (dashed line) in 100 h from the beginning of the experiment.

increased virtually 2-fold, from 2.75 W for the cell with the final electrode-sintering temperature of 1170°C to 4.5 W for SOFC with the sintering temperature of 1350°C. Studying impedance spectra showed (Fig. 8) that the main contribution to the total internal resistance of the tested cell was made by the processes occurring on the SOFC electrodes, whereas the contribution of ohmic losses did not exceed 18 mΩ.

To elucidate which processes dominate in the interfacial part of the SOFC impedance spectrum, the measurements were carried out in the fuel and oxidative atmospheres of different composition. According to Fig. 8, increasing the oxygen pressure in the oxidation chamber of the experimental assembly induced substantial changes in the middle-frequency region of the impedance spectrum, which is usually associated with the changeover of the charge-carrier type. Hence, we can infer that the catalytic activity of the SOFC-cathode functional layer of is insufficient. At the same time, as expected, lowering down the hydrogen pressure in the cathodic chamber induced an insignificant increase in the contribution of the low-frequency impedance region reflecting the hydrogen-diffusion deceleration in the reaction zone. Thus, we can conclude that to improve the electrochemical characteristics of SOFC, the catalytic activity of the cathode must be increased.

To test the time stability, short-term lifetime tests were performed, in which the sample was kept at constant current of 5 A. Then, the repeat tests of SOFC, the electrochemical characteristics were measured in 100 h from the beginning of lifetime tests. It is evident (Fig. 7) that the voltammetric characteristics demonstrates a small decrease in its slope, which results in the higher power produced by the cell. Figure 9 compares the impedance spectra measured in the beginning of tests and after 100 h. It should be noted that the internal resistance decreases by ~9% which is associated with the decrease in both the ohmic contribution and the interfacial part of impedance spectrum. The ohmic-loss contribution is 16.5 mΩ, in agreement with calculated losses for the ionic current transfer

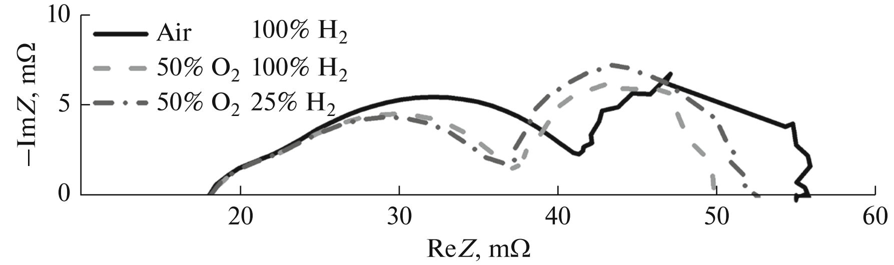

Fig. 8. SOFC impedance spectra measured for different compositions of the fuel and oxidative mixtures.

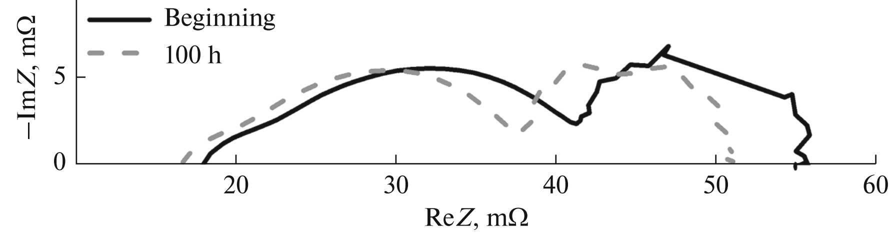

Fig. 9. SOFC impedance spectra measured immediately after reaching the working mode (850°C, air, $P(H_2) = 0.5$ atm) (solid black line) and in 100 h after the beginning of tests (dashed line).

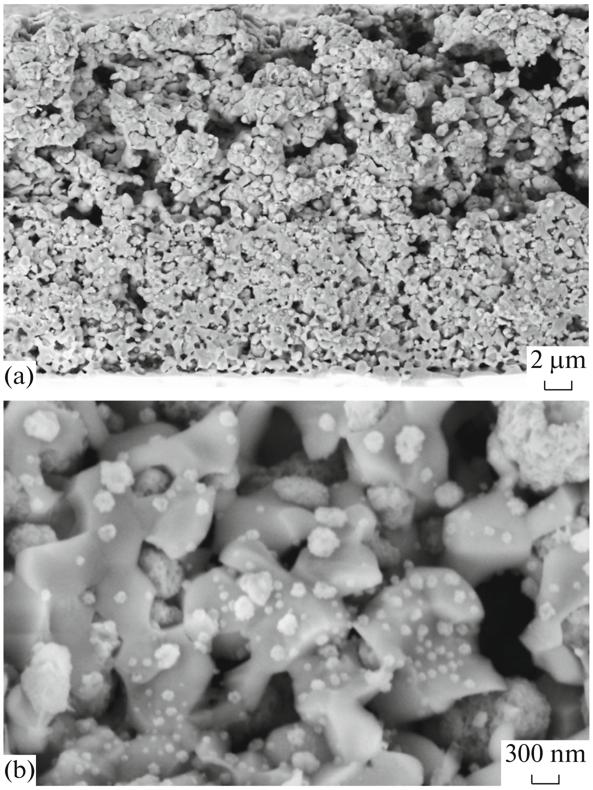

Fig. 10. SEM image of the SOFC anode cross-section after 100 h work.

through the anionic membrane of SOFC. It can be concluded that the effective working surface is well consistent with the geometrical surface of applied electrodes.

Thus, the impedance spectra show that the improvement in electrochemical characteristics of tested cells during short-term lifetime tests is associated both with the improvement of the electric contact on internal interfaces of the experimental assembly and with the increase in the catalytic properties of electrodes. Figure 10 shows the SEM image of the SOFC cross-section at different magnifications. It is seen that as a result of nickel oxide reduction, the functional layer of the SOFC anode acquired a well-developed system of fine pores. Moreover, the morphology of nickel particles was also modified, which induced the appearance of a large number of nanosized metal particles thus increasing significantly the reaction surface for fuel oxidation.

CONCLUSIONS

Results on optimizing the technology of preparation of membrane–electrode assemblies for solid-oxide fuel cells by joint sintering of electrodes at elevated temperatures close to the temperature of anode sintering are shown. The choice of the higher temperatures of joint sintering is explained by the fact that the electrochemical characteristics of SOFC MEA with the electrode system formed at lower temperatures proved to be unstable [11].

To prevent the chemical interaction between the cathodic materials and the anionic conductor based on stabilized zirconia, we introduced a protective sublayer into the system and changed the anionic conductor in the functional cathodic composite. Insignificant modifications were also introduced into the other parameters of the electrode system. As a result of this optimization, we obtained planar samples with multilayer electrodes of the optimized composition and microstructure. These MEA demonstrated the stable and high electrochemical characteristics. The power density produced by the cell was 280 mW/cm^2 for the working temperature of 850°C and the working voltage of 0.8 V. During short-term lifetime tests, the internal resistance of SOFC decreased by 9%, which can be explained both by the improved electric contact on the internal interfaces of experimental cells and by the increased catalytic activity of the anode. Studies of the impedance spectra obtained at different oxygen and hydrogen partial pressures showed that to improve further the SOFC MEA characteristics, attention should be focused on decreasing the contribution made by the reactions on the SOFC cathode into the internal resistance.

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