

Ceramic Membranes Based on Scandium–Stabilized ZrO₂ Obtained by Tape Casting Technique¹

O. V. Tiunova^{a, z}, O. Yu. Zadorozhnaya^a, Yu. K. Nepochatov^a, I. N. Burmistrov^{b, z},
I. E. Kuritsyna^b, and S. I. Bredikhin^b

^aCeramic Engineering LLC, Krasnyi pr. 220, 630049 Novosibirsk, Russia

^bInstitute of Solid State Physics, ul. Akad. Osip'yana 2, 142432, Chernogolovka, Moscow Region, Russia

Received September 10, 2013

Abstract—Results of studies of solid–electrolyte membranes with the composition of 89 mol % ZrO₂–10 mol % Sc₂O₃–1 mol % CeO₂ obtained using the technique of slip casting on a moving tape are presented. Optimization of technological parameters of membrane casting and sintering allowed manufacturing parallel plane gastight plates with the thickness of 200–250 μm that were tested in model solid oxide fuel cells (SOFC) of planar design with standard electrodes based on nickel–containing cermets and lanthanum–strontium manganite. It is shown that though conductivity of such membranes is lower as compared to that of compacted and sintered compacted samples due to diffusion of the aluminum oxide admixture in the course of the manufacturing process, power density of SOFC is sufficiently high and reaches 430 mW/cm² at 850°C.

Keywords: solid oxide fuel cells, zirconia, slip casting, gastight solid electrolyte ceramic, voltammetric characteristics, ionic conductivity

DOI: 10.1134/S1023193514080138

INTRODUCTION

Materials based on zirconia stabilized by oxides of rare–earth metals can be used as solid electrolytes for solid oxide fuel cells, electrochemical oxygen sensors in oxide melts and gases, high–temperature electrolyzers of water vapor and carbon dioxide, and electrocatalytic reactors of different types [1–6]. Ceramic materials claiming the role of oxygen–ion–conducting electrolytes must fulfill many requirements [4, 5, 7]: (1) high values of ionic conductivity and minimum values of electron conductivity in the operating range of temperatures and chemical potentials of oxygen; (2) thermodynamic and thermomechanical stability under these conditions; (3) thermal and chemical stability; (4) gastightness; (5) high rate of oxygen interface exchange and absence of blocking effects at the interfaces between electrode materials and gas phase; (6) sufficient mechanical characteristics of the ceramic providing its integrity during the coating application, assembly of solid oxide fuel cells (SOFC), and their further operation.

The most widespread solid electrolyte is yttria–stabilized zirconia [3–5]. The highest ion conductivity can be reached by stabilization of the ZrO₂ cubic phase

as a result of simultaneous addition of Sc³⁺ and other cations with a comparatively small radius, such as Ce⁴⁺ or Y³⁺. Various techniques are used to manufacture articles of ceramic based on zirconia: compaction, thermoplastic slip casting, injection formation. The film casting technique is widely used to obtain ceramic plates with the thickness of up to 1.5 mm [8–11]. This method is preferable for manufacturing of relatively thin solid electrolyte membranes for SOFC, high temperature electrolyzers, and other electrochemical devices, in which the performance specifications directly depend on the thickness and quality of the ion–conducting ceramics [5]. The aims of this work were to develop the technology of manufacturing of high–density ceramics of stabilized zirconia using the slip casting technique on a moving tape, study transport properties of the obtained materials and the behavior of the manufactured solid electrolyte membranes in model SOFC.

EXPERIMENTAL

Manufacturing and Studies of Ceramic Membranes

Powder of stabilized zirconia with the composition of ZrO₂–10 mol % Sc₂O₃–1 mol % CeO₂ (10Sc1CeSZ) (Terio Corporation, China) was used to obtain gastight planar membranes. The process flow scheme is presented in Fig. 1. The ceramic tape was cast on a KEKO line (Slovenia). Removal of the binder

¹ This publication was prepared based on a lecture delivered at the All Russian Conference with international participation “Fuel Cells and Power Plants,” Chernogolovka, 2013.

^z Corresponding authors: tiunovaov@gmail.com (O.V. Tiunova); buril@issp.ac.ru (I.N. Burmistrov).

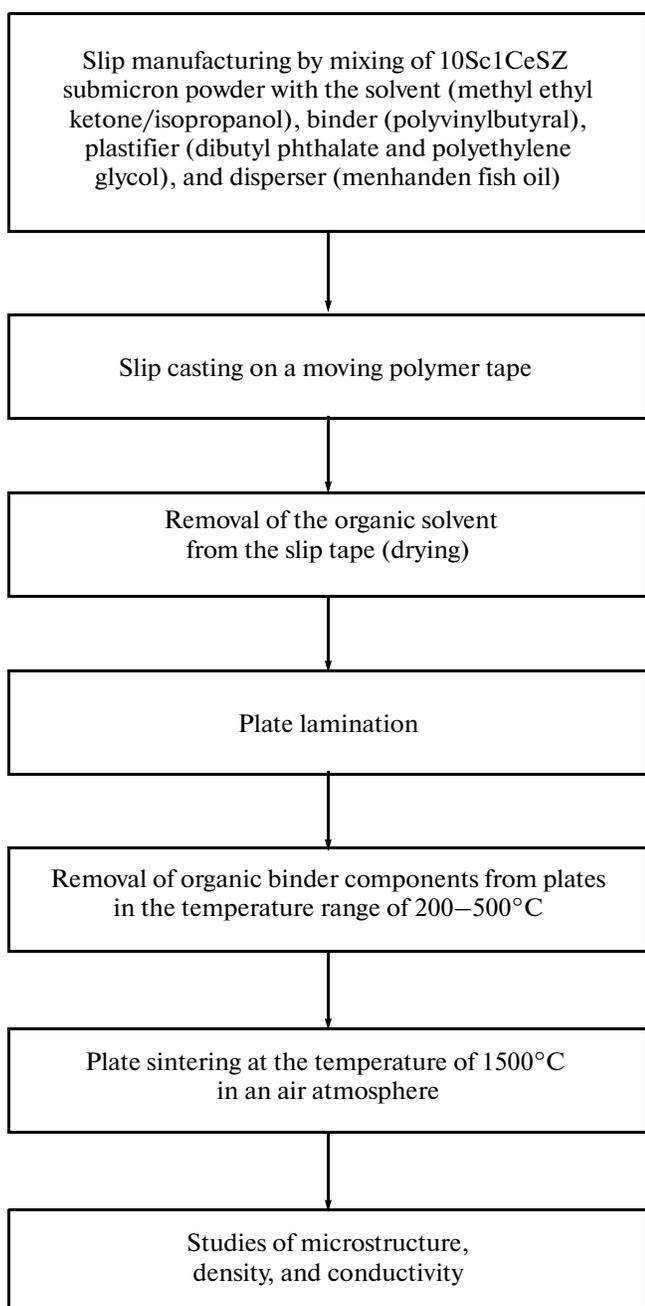


Fig. 1. Process flow scheme of manufacturing of gastight 10Sc1CeSZ solid electrolyte membranes using the technique of slip casting on a moving tape.

and sintering were carried out in Nabertherm furnaces (Germany) at 1450–1520°C.

Slips based on organic solvents (methyl ethyl ketone, ethanol, toluene, isopropanol) with the solid phase content of more than 60 wt % (viscosity range from 1500 to 4000 mPa s) were manufactured for casting. The solvent allows faster mixing of the organic phase components, obtaining organic phase of the required viscosity for a more complete homogenization with the ceramic filler powders, and imparting

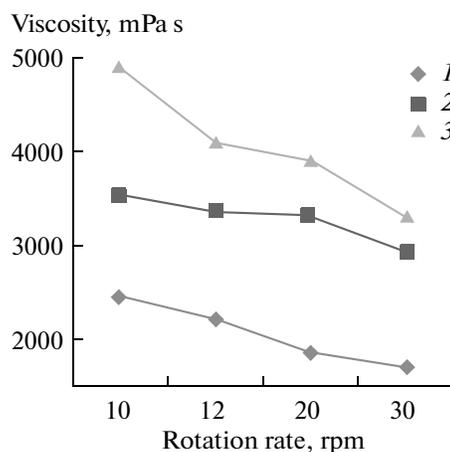


Fig. 2. Effect of organic solvents on slip viscosity. (1) methyl ethyl ketone/isopropanol, (2) toluene/isopropanol, (3) toluene/ethanol.

plasticity to the ceramic composition, which renders possible formation of a sheet material. Herewith, using a binary solvent provides the control of component solubility, rheological properties of the slip, and the tape drying rate. Azeotropic mixtures of methyl ethyl ketone/isopropanol, toluene/ethanol, and toluene/isopropanol were used in experiments. It was found that application of isopropanol allows obtaining suspensions with lower viscosity, while the methyl ethyl ketone additive provides better slip casting characteristics (Fig. 2). It is important to note that using toluene/isopropanol in the slip resulted in cracking of the whole film surface. Menhaden fish oil was used as a disperser allowing binding the particles of powder and organic binder via lipophilic and hydrophilic groups preventing aggregation. The choice of polyvinylbutyral as a binder was based on the necessity of providing the smooth mode of the further thermal treatment that was optimized on the basis of the results of thermogravimetric analysis and differential scanning calorimetry obtained using a Netzsch analyzer (Germany).

The density of ceramic tapes obtained by the film casting technique was measured using the hydrostatic weighing technique. X-ray phase analysis was carried out at the room temperature using a SIEMENS D-500-BRAUN, X02-1787 diffractometer with a position-sensitive detector and a primary monochromator for the $\text{CuK}_{\alpha 1}$ -radiation. The microstructure of sintered membranes and model SOFC was studied using a SUPRA 50VP high-resolution scanning electron microscope with a INCA Energy+ microanalysis system (UK). Ionic conductivity was measured by impedance spectroscopy technique using a Solartron SI 1260 impedance meter (USA) in the frequency range of 1 Hz to 10 MHz and at the temperatures of 300 to 900°C in air.

Manufacturing of Model Fuel Cells

Model SOFC were manufactured on the basis of the supporting solid electrolyte membranes with the diameter of 21 mm with a porous anode and cathode applied onto the opposite surfaces. Application of composite electrodes (surface area of 1.5 cm²) was carried out using the screen printing technique at an EKRA MAT S45 molder. The porous anode consisted of two layers: the functional one where the fuel oxidation reaction occurs and the collector one. Powders of a mixture of 60 vol % ZrO₂ solid electrolyte–10 mol % Sc₂O₃–1 mol % CeO₂ (Terio Corporation, China) and 40 vol % NiO (Aldrich, Germany) were used for manufacturing pastes for application of the functional anodic layer. Pastes of powders containing 40 vol % 10Sc1CeSZ and 60 vol % NiO were manufactured for application of the collector (outer) anode layer. The outer layer provides, in particular, uniform current distribution and electric contact of a platinum gauze current collector in the bilayer composite anode. Herewith, apart from the high electron conductivity, it must possess considerable porosity to provide gas diffusion to the inner functional layer of the anode. The required amount of the Heraeus V-006 binder was added to the mixture of component powders for preparation of electrode pastes; the Heraeus RV-372 dilutant was used to control viscosity of the obtained pastes. The anodic paste was mixed in a ThinkyMixer ARE-250 (Japan) until complete homogenization. After the functional and collector layers were applied, they were subjected to joint sintering at the temperature of 1380°C. By way of illustration, Fig. 3a shows an electron microscopy image of the cross section of the bilayer anode. The thickness of the functional and collector layers was 15 and 30 μm, accordingly.

The cathode of model SOFC also consists of the functional and outer collector layers. The functional cathode layer is responsible for the reaction of gaseous oxygen reduction reaction to O²⁻ anions. This layer was made of a composite containing 40 vol % of the 10Sc1CeSZ powder and 60 vol % (La_{0.8}Sr_{0.2})_{0.95}MnO₃ synthesized by the citrate technique to increase the density of the catalytically active three-phase interface. Pastes of the (La_{0.8}Sr_{0.2})_{0.95}MnO₃ powder were made for collector layer application. Electrode pastes were manufactured using the Heraeus V-006 binder and the Heraeus RV-372 dilutant. Bilayer composite cathodes were sintered in air at 1100°C. The cathode microstructure is shown in Fig. 3b. Same as in the case of anodes, the thickness of the functional and collector cathode layers was approximately 15 and 30 μm, respectively.

Model SOFC Testing

Electrochemical characteristics of SOFC were studied in a measurement cell with separate gas compartments at an automatic gas-temperature test

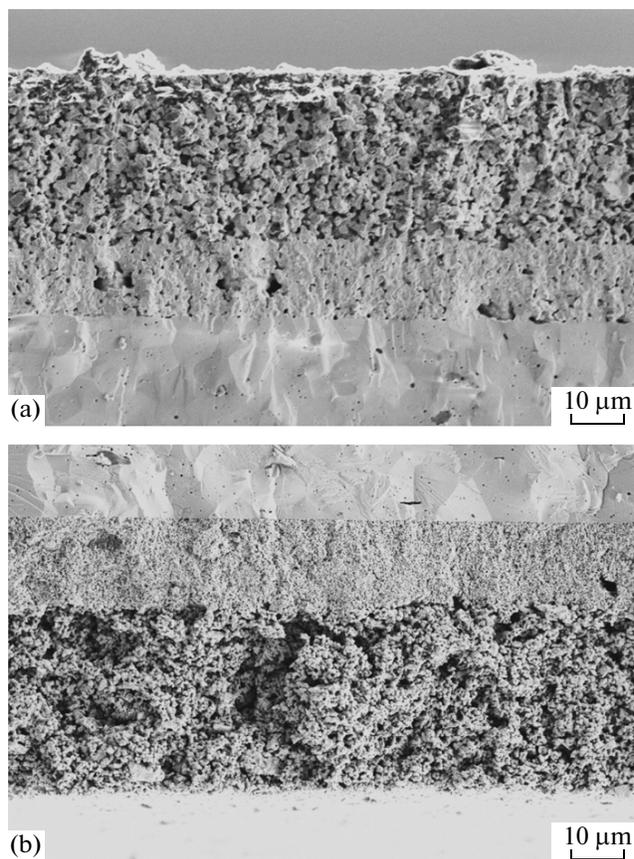


Fig. 3. Electron microscopy images of cross-sections of bilayer composite electrodes of model SOFC: (a) anode, (b) cathode.

bench. The composition and flow rate of the oxidant and reducing mixtures were regulated using Bronkhorst controllers (Netherlands). The ballast gas was nitrogen. The test bench allowed controlling the operating zone temperature (25–1000°C), the temperature of the fuel and oxidant gas mixtures, and also the rate of their supply (up to 1 L/min). Cell heating to operating temperatures was carried out at the rate of 200°C/h. Voltammetric characteristics of model SOFC were measured using the four-probe technique, for which a high-precision current stabilizer (Institute of Solid State Physics, Russian Academy of Sciences) controlled by means of a digital-to-analog converter was used. Measurements were carried out in the temperature range of 750–900°C. The oxidant mixture composition corresponded to artificial air (O₂/N₂ = 20/80). The fuel used was a mixture of hydrogen and nitrogen at the ratio of 1 : 1.

RESULTS AND DISCUSSION

The optimum sintering temperature of the 10Sc1CeSZ plates is 1500°C, as the maximum density is reached at this temperature (Fig. 4). When the temperature is enhanced, a decrease in density and an

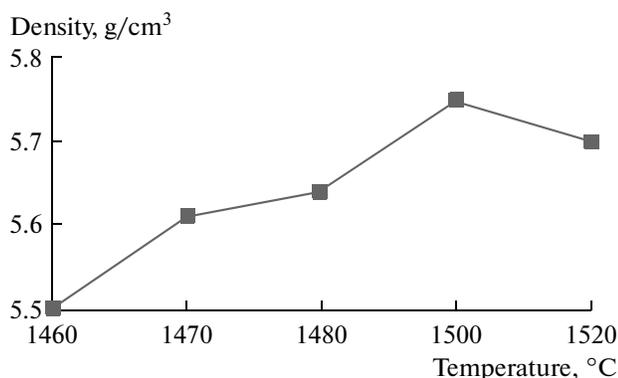
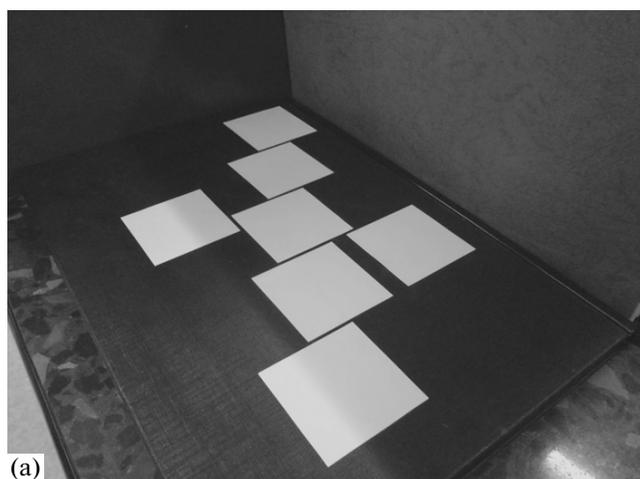
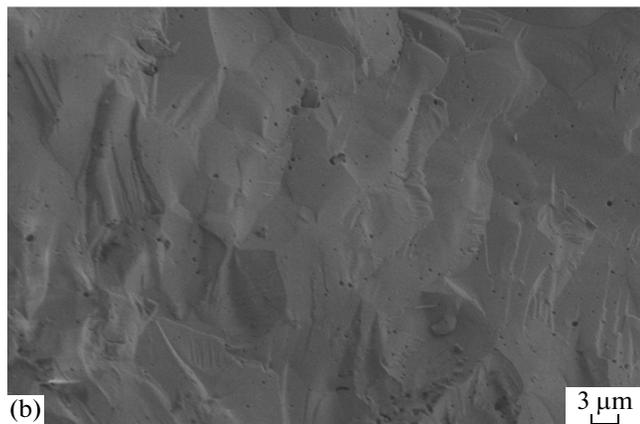


Fig. 4. Dependence of density of ceramic 10Sc1CeSZ membranes obtained using the technique of slip casting on a moving tape on the sintering temperature.



(a)



(b)

Fig. 5. (a) Samples of sintered ceramic 10Sc1CeSZ membranes with the size of $50 \times 50 \times 0.25 \text{ mm}^3$ and (b) their microstructure.

increase in porosity are observed due to intensive grain growth. After sintering, deviations from planarity were less than $40 \mu\text{m}$; 10Sc1CeSZ membranes had the density of 5.75 g/cm^3 and were gastight (Fig. 5). The thickness of ceramic membranes was varied in the

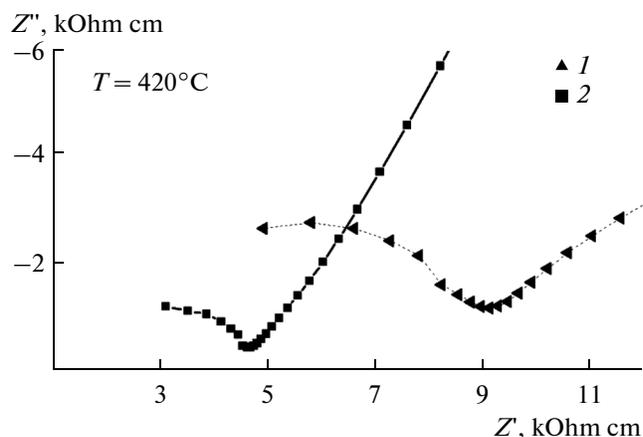


Fig. 6. Impedance spectra of the 10Sc1CeSZ ceramic manufactured using the techniques of (1) casting on a moving tape and (2) compaction with the further sintering at 420°C and atmospheric pressure of oxygen. The spectra are normalized by the geometric sample size.

range of $200\text{--}250 \mu\text{m}$. X-ray and electron microscopy studies confirmed the absence of impurity phases within the limits of sensitivity of these methods and also homogeneity of the microstructures of sintered plates and absence of cracks and other significant defects.

Microanalysis of the cation composition and impedance spectroscopy showed, however, the presence of a small Al^{3+} admixture that can be dissolved in the crystal lattice of the solid electrolyte and/or segregated on grain boundaries and results in a slight decrease in ionic conductivity. For example, Fig. 6 compares impedance complex plane plots obtained for two membranes at 425°C . The first membrane with the thickness of $220 \mu\text{m}$ was manufactured using the slip casting technique on the moving tape; the second one, with the thickness of $510 \mu\text{m}$, was compacted of the same powder and also sintered at 1500°C . The impedance spectra were used to calculate the specific resistance of ceramics. Thus, the intrinsic (bulk) resistance of the studied ceramics in the presented complex plane plot corresponds to a semicircle in the high-frequency region of the impedance spectrum and the low-frequency region corresponds to electrode processes. Obviously, ionic conductivity of the material manufactured using the compaction technique is approximately twice higher than that of ceramics manufactured by the slip casting technique. This trend is preserved in the whole studied temperature range (Fig. 7), while the ion transport activation energy is independent of the manufacturing technique within the range of the experimental error. The observed decrease in conductivity in the case of plates manufactured using the slip casting technique on a moving tape considerably exceeds the conductivity measurement error and is related to the presence of the Al_2O_3 admixture observed using the microprobe X-ray spectral

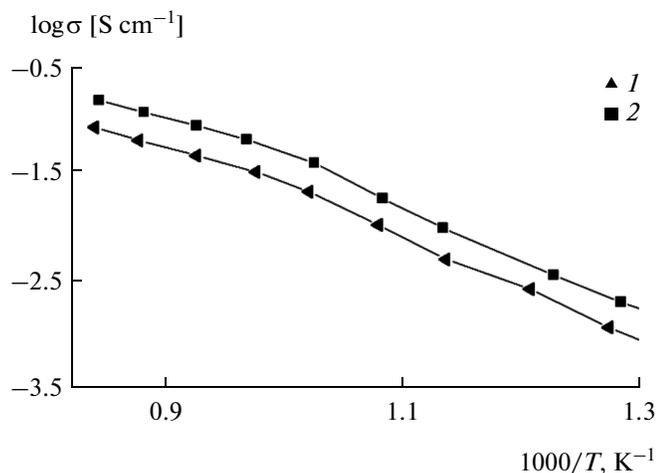


Fig. 7. Temperature dependences of specific conductivity of 10Sc1CeSZ solid electrolyte membranes manufactured using the technique of (1) casting on a moving tape and (2) compaction with the further sintering.

analysis (Fig. 8). The admixture source is diffusion from the support into a relatively thin tape in the course of its sintering. The amount of Al₂O₃ estimated according to the results of microprobe analysis is about 0.8 wt %. As follows from the phase ratios known for similar materials [4, 5], such an amount of aluminum oxide can be dissolved in the cubic ZrO₂ structure, though one cannot exclude significant segregation at the intergrain boundaries of the ceramics. In the case of formation of a fluorite-like solid solution, the concentration of Al³⁺ in the crystal lattice would be approximately 1 at %, which can result in a rather significant decrease in ionic conductivity [5]. A similar effect can also be expected in the case when aluminum oxide that is an insulator is segregated at the grain boundaries in the course of sintering and henceforth blocks ion transport

Irrespective of the presence of the admixture in solid electrolyte membranes manufactured according to the slip casting technique, model SOFC with these membranes demonstrated good characteristics. For example, the maximum power density at the tempera-

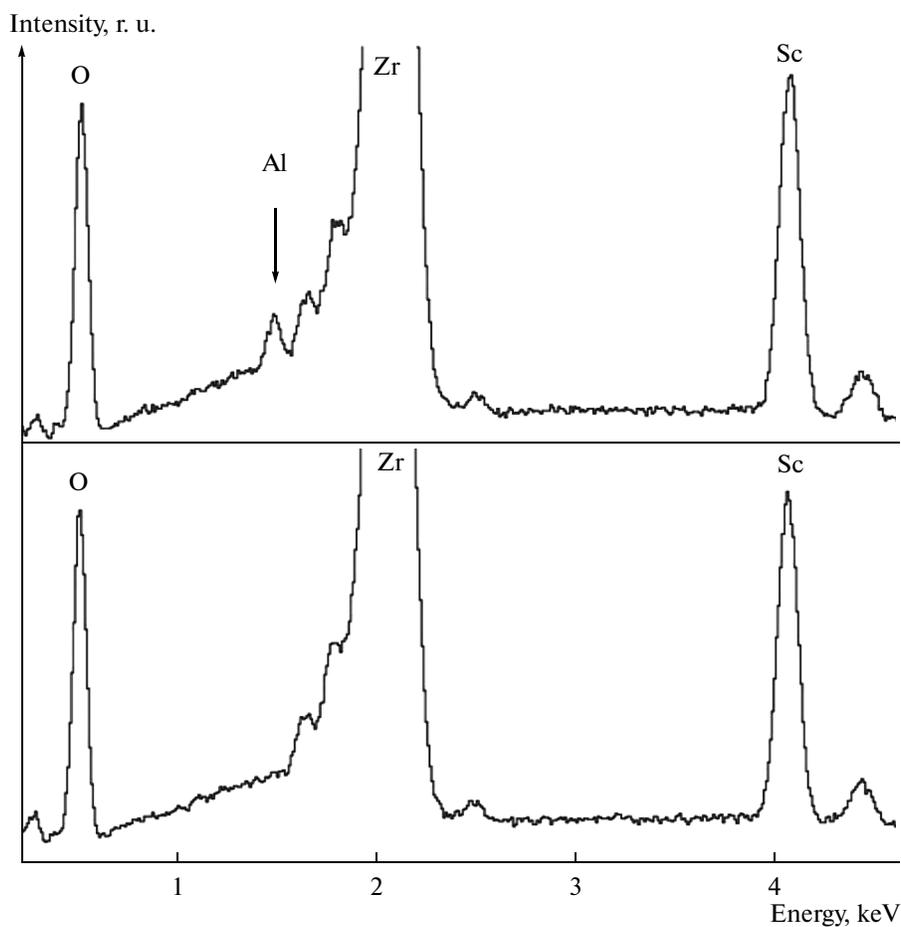


Fig. 8. Examples of X-ray fluorescent spectra of the 10Sc1CeSZ ceramic manufactured using the techniques of slip casting on a moving tape (top) and pressing with the further sintering (bottom). The arrow indicates one of the most intensive characteristic peaks of aluminum.

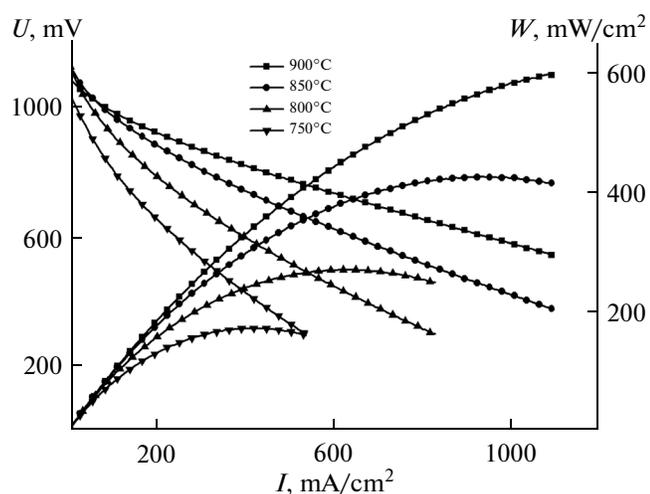


Fig. 9. Voltammetric and power characteristics of a model fuel cell with a 10Sc1CeSZ solid electrolyte membrane.

ture of 850°C and membrane thickness of about 250 μm was 430 mW/cm^2 (Fig. 9). This points to a sufficiently high quality of thin 10Sc1CeSZ plates, absence of cracking, and therefore sufficient mechanical strength, and also absence of blocking layers on the membrane surface and significant interaction with cathodes in the course of SOFC manufacturing.

CONCLUSIONS

Technological regimes of the manufacturing of solid electrolyte membranes with the composition of ZrO_2 –10 mol % Sc_2O_3 –1 mol % CeO_2 using the slip casting technique on a moving tape are developed, including the slip composition and conditions of thermal treatment. Plane parallel gastight plates with the density of 5.75 g/cm^3 , thickness of 200–250 μm , and sizes of 50 \times 50 mm^2 are obtained. It is found that diffusion of aluminum oxide into the ceramic solid electrolyte rape in the course of thermal treatment results in a decrease in ionic conductivity. This effect is of no critical importance for power characteristics of model fuel cells with a supporting membrane based on zirco-

nia that are determined primarily by the membrane quality and thickness. The maximum power density in model SOFC with standard cermet and manganese electrodes is 430 mW/cm^2 at 850°C with a mixture of 50% H_2 –50% N_2 used as a fuel. The further improvement of the membrane casting technique requires application of structural materials based on ZrO_2 at all stages of the technological process of the membrane manufacturing.

ACKNOWLEDGMENTS

The work was supported in part by the Ministry of Education and Science of the Russian Federation (Agreement No. 14.V25.31.0018).

REFERENCES

1. Evans, A.G. and Langdon, T.G., *Structural Ceramics*, Oxford: Pergamon Press, 1976.
2. Garshin, A.P., Gropyanov, V.M., Zaitsev, G.P., and Semenov, S.S., *Keramika dlya mashinostroeniya* (Ceramics for Engineering), Moscow: Nauchtekhlitizdat, 2003.
3. Mistier, R.E. and Twiname, E.R., *Tape Casting. Theory and Practice*, Westerville: Wiley. Amer. Ceramic Soc., 2000.
4. Zhuiykov, S., *Electrochemistry of Zirconia Gas Sensors*, Boca Raton, FL: CRC Press, 2007.
5. *Solid State Electrochemistry I: Fundamentals, Materials, and Their Applications*, Kharton, V.V., Ed., Weinheim: Wiley-VCH, 2009.
6. Tshipis, E.V. and Kharton, V.V., *J. Solid State Electrochem.*, 2011, vol. 15, p. 1007.
7. Chen, C.-C., Liao, L.C.K., Jung, G.B., and Chan, S.H., *ECS Trans.*, 2007, vol. 7, no. 1, p. 2161.
8. Timakul, P., Jinawath, S., and Aungkavattana, P., *Ceram. Int.*, 2008, no. 34, p. 867.
9. Hiroshi, K., Jpn. Patent JP63136677, 1988.
10. Barbashov, V.I. and Nosova, E.V., *Ogneupory Tekh. Keram.*, 2011, nos. 1–2, p. 3.
11. Hoffmann, C. and Grote, D., FRG Patent DE3809693, 1989.

Translated by M. Ehrenburg