

Formation of a thin-layer electrolyte for SOFC by magnetic pulse compaction of tapes cast of nanopowders

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Abstract

From the analysis of the scientific and technical literature it is possible to determine the trend of development of technologies for preparation of thin films of solid electrolytes for SOFC as the most promising one. The use of powder compaction technologies and weakly agglomerated nanosized powders for this purpose has some advantages.

The present study deals with physicochemical properties of electrolytes based on zirconia and ceria and electrochemical cells loaded with these electrolytes. Weakly agglomerated nanopowders with particles about 15 nm in size were produced by laser sputtering. Films 15–25 μm thick were obtained from nanopowders of the electrolytes by butyral resin slip casting. Uniaxial and radial magnetic pulse compaction of the cast films was performed at 0.1–1.6 GPa. The apparent density of the compacts accounted for 0.5–0.7 of the theoretical value. Sintering at temperatures of 900–1250 °C provided electrolytes having the relative density of 0.92–0.98.

The analysis of the structure and the conductivity of the solid electrolytes, which was performed using samples shaped as flat thin disks 15–30 mm in diameter and 10 μm to 2 mm thick, and the examination of the electrochemical characteristics of the cells made of an ultrafine solid electrolyte in the form of tubes having the diameter of about 10 mm and walls 80–250 μm thick confirmed that the ceramic samples were gas-tight and had not laminations. The conductivity of, e.g. the YSZ electrolyte was 0.08–0.112 S cm⁻¹.

The electrochemical cells, which were tested in the regime of a fuel cell with a solid electrolyte synthesized using the proposed technologies, provided the specific power of about 1 W cm⁻² at 800–850 °C even without optimization of the electrodes. Thus, the ultrafine solid electrolytes met the requirements imposed on SOFC ceramics.

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1. Introduction

From the analysis of the scientific and technical literature it is possible to determine most promising directions of the development of SOFC compaction technologies. Designers most often use a solid electrolyte based on yttrium-oxide-stabilized zirconia (YSZ). One of alternative electrolytes is ceria doped with gadolinium or samarium oxide (GDC or SDC). The zirconia-based electrolyte has the largest mechanical strength among the electrolytes and, therefore, designers use it as

the bearing element having the minimum thickness of about 150 μm. If the thickness is smaller, the SOFC internal resistance decreases and the power at the external useful load rises. It is therefore reasonable to reduce thickness of the solid electrolyte to 10–15 μm. However, if the solid electrolyte is thin, it is necessary to ensure its mechanical strength by fitting a bearing electrode: a cathode based on lanthanum strontium manganite (LSM) or an anode based on nickel cermet (Ni + YSZ). The latter is assumed to be preferable. A promising design is the simultaneous formation of two “electrode–electrolyte” layers and subsequent sintering. However, simultaneous sintering of, e.g. LSM and YSZ can be reasonably realized at temperatures below 1300–1350 °C. Higher temperatures cause an unwanted solid-phase interaction and, as a result, lead to formation of

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intermediate layers having a high resistance. For this reason, the main problem in the development of a SOFC technology is how to synthesize a dense thin layer of the solid electrolyte at low temperatures.

It is known that processes of nanopowder sintering are much more intensive and provide dense materials having an ultra-fine structure. Solid YSZ electrolytes made of nanopowders are dense [1] if they are sintered 300–500 °C lower than the sintering temperature of micrometer-sized powders. However, an insufficient compaction of nanopowders requires the use of non-traditional high-energy methods for consolidation of particles in order to provide a high density of powder blanks [2]. It is a high starting density that allows producing sintered ceramics with an ultrafine structure at low temperatures and short heat treatments. The method of magnetic pulse compaction (MPC), which is developed at the Institute of Electrophysics (IEP), ensures a high (about 0.7) relative density of nanopowder compacts. Moreover, the sintering process is facilitated since powders undergo an additional mechanical activation during MPC [3]. Specialists at IEP currently develop a tape casting technology for preliminary formation of thin layers of a solid electrolyte made of nanopowders.

The present study had the following objectives:

- establish principles of a technology for preparation of thin films of a solid electrolyte 10–15 μm thick and thicker films (over 50 μm) using weakly agglomerated nanopowders;
- establish principles of a technology for compaction (solidification) of multilayered products by isostatic magnetic pulse compaction;
- synthesize a high-density nanostructured solid electrolyte in the form of a tube with walls less than 150 μm thick at low temperatures;
- analyze basic properties of this electrolyte and demonstrate the possibility of forming a thin-film tubular electrolyte, which would meet all requirements imposed on SOFC ceramics;
- test a fragment of a tubular fuel cell outfitted with traditional research electrodes and a traditional fuel and oxidizer ($\text{H}_2 + 3\% \text{H}_2\text{O}$, air).

2. Experimental

2.1. Starting powders

Nanopowders of 9.5YSZ (9.5 mol% Y_2O_3) and 15GDC (15 mol% Gd_2O_3) were prepared by laser evaporation (LEC) of a ceramic target and subsequent sedimentation in isopropanol for removal of coarse particles over 200 nm in size. The nanopowders and their production technology were developed at the IEP [4]. The powders were characterized by a weak agglomeration, the specific surface of $62 \pm 4 \text{ m}^2 \text{ g}^{-1}$, and the average size of YSZ and GDC particles equal to $16 \pm 2 \text{ nm}$ (Fig. 1) and $9 \pm 2 \text{ nm}$ (Fig. 2), respectively. Nanopowders, whose agglomerates were broken by the ultrasound, were referred to as weakly agglomerated ones.

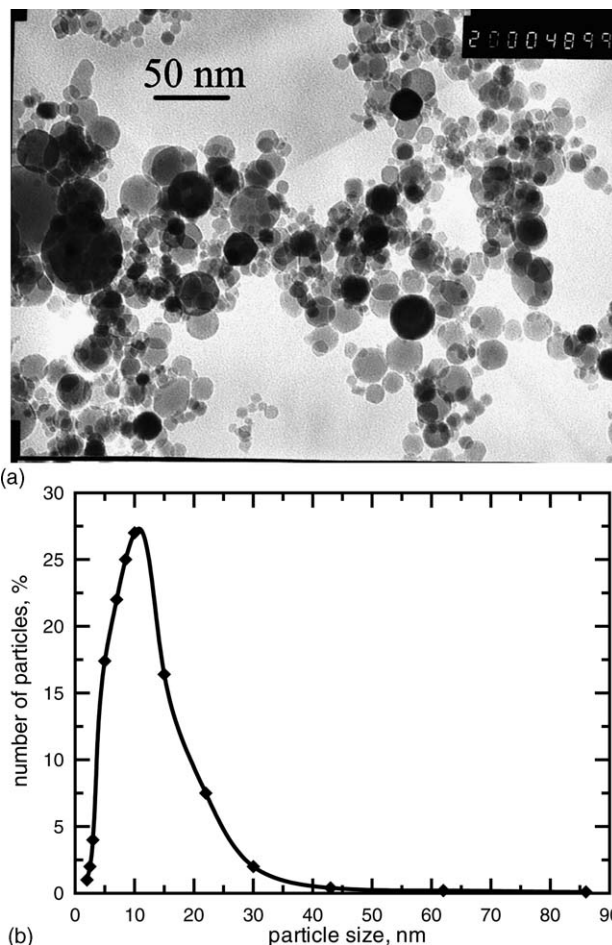


Fig. 1. (a) Particles of the 9.5YSZ nanopowder; (b) particle size distribution.

2.2. Tape casting

The technology of tape casting from butyral resin slips was not chosen by chance. It provides thin films with a reproducible stable thickness. This technology showed itself good in industrial production of ceramic capacitors [5]. It is used, along with extrusion, for formation of components of solid oxide fuel cells (Fig. 3) having a flat planar design [6]. Specialists at IEP made a film casting line and elaborated the appropriate technology. A slip (a suspension) was prepared for casting of films, for which purpose we took powders of necessary components of SOFC and a butyral resin (BR). Fig. 3 illustrates the transparency of a fresh cast film and a sintered ceramic shaped as a pellet. Being a thermosetting material, BR allowed forming from a set of films, similarly to production of capacitors, multilayered items of a simple flat or more complicated cylindrical shape. In combination with the radial magnetic pulse compaction (MPC), the film casting technology allowed forming a tubular fuel cell. A thin film 15–50 μm thick was wound on a steel rod to form a thin-walled tube of the solid electrolyte. The required stable thickness was achieved by winding a certain number of layers. The assembly was placed in a copper tube and was compacted using a pulsed current under isostatic conditions.

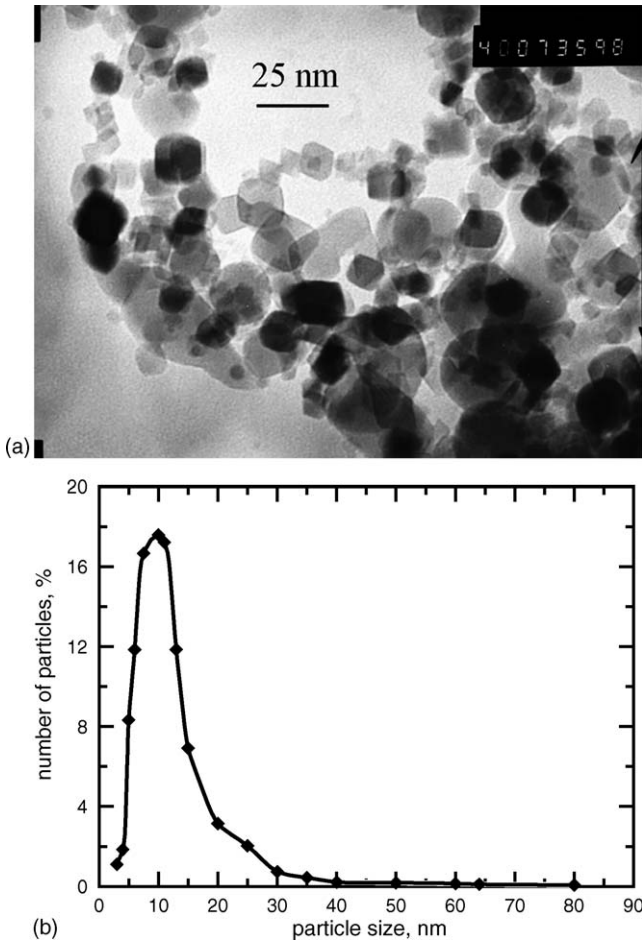


Fig. 2. (a) Particles of the GeGdO_x nanopowder; (b) particle size distribution.

2.3. Isostatic magnetic pulse compaction of the solid electrolyte films

2.3.1. Uniaxial magnetic pulse compaction

The required number of films (YSZ + 14% BR) was compacted using the uniaxial magnetic pulse method [7] under isostatic conditions to form disks 15 and 32 mm in diameter and up to 1–3 mm thick. Fig. 4 presents the dependence of the relative density of the compacts on the applied pulsed pressure. The circles refer to the powder taking into account BR, while the rhombus denote the density of the active powder only.

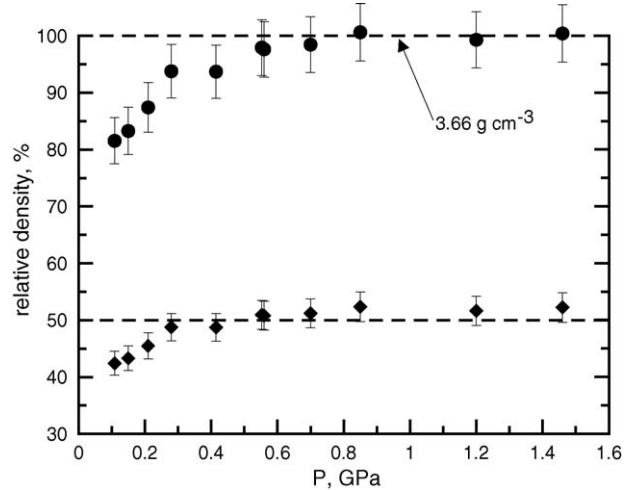


Fig. 4. Relative density of compacts depending on the uniaxial MPC force. For explanations refer to the text.

It should be noted that in the first case the density (3.66 g cm⁻³), which took into account the addition of 14% BR, was taken as the theoretical density. One can see that the half density of the compacts, which ensured sintering to the gas-tight state of the solid electrolyte, was achieved, within the experimental error, when the films were treated with a pulsed pressure of ~0.3 GPa. When BR was added less and the compaction force increased, the relative density of the compacts was improved, leading to the drop in the shrinkage percentage of the solid electrolyte during sintering. This is seen well from the dilatometric curves in Fig. 5. The obtained data also suggested that the sintering start temperature of the solid YSZ electrolyte, which was prepared from weakly agglomerated powders, was nearly 900 °C and was independent of the applied compaction force. Depending on the amount of the BR addition, MPC provided the apparent density of the compacts accounting for 0.5–0.7 of the theoretical density of the solid YSZ electrolyte. It should be noted that the sintering activity of our powders was such that the samples were sintered to the full density with a zero open porosity at the compaction density of the particles being over 0.35. The ceramic shrinkage factor could be adjusted during sintering by changing the compact density (Fig. 5).

Conditions, which were necessary and sufficient for synthesis of a dense solid electrolyte by uniaxial MPC, were taken as the

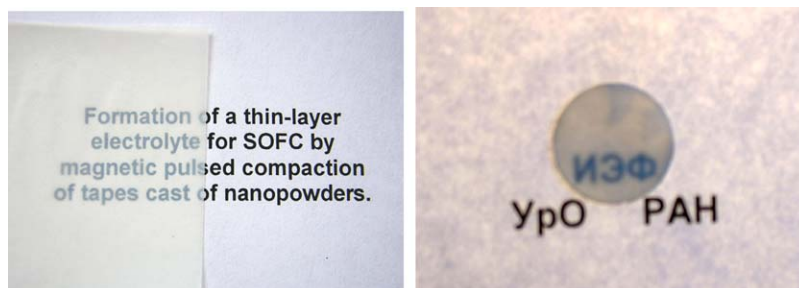


Fig. 3. Transparency of a cast fresh film and a sintered YSZ ceramic.

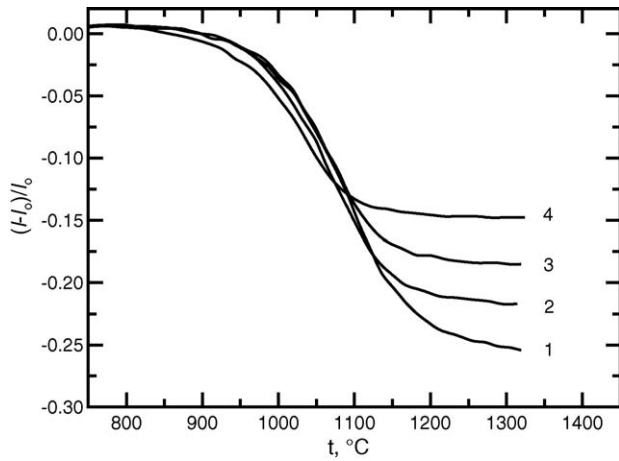


Fig. 5. Linear shrinkage curves for compacts of different green density: (1) 0.40; (2) 0.504; (3) 0.547; (4) 0.677; constant heating rate of $5^{\circ}\text{C min}^{-1}$.

basis for elaboration of regimes used for the radial magnetic pulse compaction of a thin-walled tubular electrolyte.

2.3.2. Radial magnetic pulse compaction

The radial isostatic magnetic pulse compaction was used to form thin-walled tubes ($80\text{--}200\ \mu\text{m}$) of the solid electrolyte in both the Z- and Θ -pinch regimes. A ceramic film preform was compacted in the Z-pinch regime by electrodynamic compression of a conducting sheath (most frequently, a copper tube) under the action of the magnetic field of a pulsed current flowing in the tube. In the Θ -pinch regime, the compaction of a ceramic film preform was realized thanks to the external magnetic field

of a spiral inductor carrying a pulsed current. Fig. 6 presents schemes of these regimes and a time scan of the currents.

The ceramic preforms were compacted using the electrodynamic method in both the Z-pinch regime (the storage charging voltage $U=13\ \text{kV}$ and the maximum compression pressure of about $0.28\ \text{GPa}$) and the Θ -pinch regime (the same compaction conditions were realized in this regime at the given charging voltage).

2.4. Sintering of ceramic samples

The preforms were sintered at $900\text{--}1250^{\circ}\text{C}$ in air and were held at the maximum temperature for $20\text{--}1600\ \text{min}$. The sintering regime provided monolithic samples of electrolytes having the relative density of $0.92\text{--}0.98$.

Physicochemical properties of the solid electrolytes were analyzed taking thin flat disks $15\text{--}30\ \text{mm}$ in diameter and $10\ \mu\text{m}$ to $2\ \text{mm}$ thick. Properties of electrochemical fragments of fuel cells were studied using cells with a solid electrolyte in the form of tubes about $10\ \text{mm}$ in diameter having walls $80\text{--}250\ \mu\text{m}$ thick. The analysis of the structure and properties of the solid electrolytes confirmed that the ceramic was a monolith and had a well-formed crystalline structure.

2.5. Methods and equipment

The phase composition, microscopic distortions and the size of the coherent scattering region (CSR) d_x were determined by the X-ray diffraction method (DRON-4). The size d_x was measured from widening of diffraction lines. The atomic-force

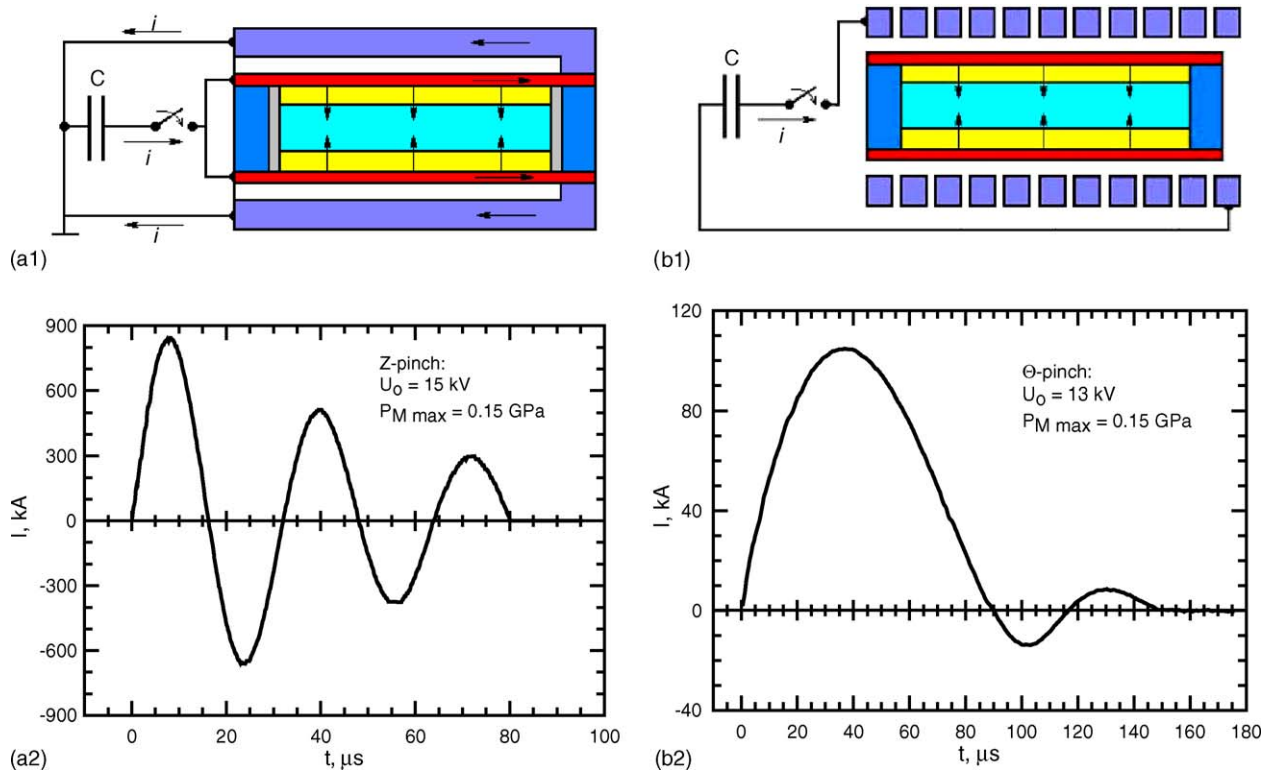


Fig. 6. Load unit of pulsed current generator: (a) Z-pinch, (b) Θ -pinch.

microscopy (Solver 47) and scanning electron microscopy (LEO 982) were used for analysis of the ceramic fracture structure. The average grain size was determined by the linear-intercept method from microscopic images of fractures. The Vickers microhardness (H_V) of the ceramics and the specific surface of the powders (S_{BET}) were measured using standard methods. The density of the samples was determined by weighing in water.

The conductivity of square samples (about 1 mm × 7 mm × 12 mm in size) was measured in air with silver electrodes deposited on the samples. The measurements were made by the two-probe four-wires method of impedance spectroscopy on a Im6 instrument (Zahner-Elektrik) at frequencies of 10^{-1} to 8×10^5 Hz and temperatures from 220 to 800 °C with a step of 20–50°.

An electrochemical cell with a partitioned gas space containing humid hydrogen, air and two symmetrical anodes and cathodes,

($H_2 + 3\%H_2O$), Pt, $CeO_2/YSZ/Pr_2O_3$, Pt, air,

was made from a tube of the solid YSZ electrolyte having walls 140 μm thick.

The surface area of the electrodes in each fuel cell was 1.2 cm². The end faces of a fragment of the tubular fuel cell

were connected with the constructional YSZ ceramic. In combination, they were made as a test tube. Two electrochemical transducers were fitted on the constructional ceramic at the gas inlet and outlet near the fragment of the fuel cell studied. Readings of the transducers showed the fuel utilization percentage. The gas flow rate was 10 l h⁻¹ for air and 4.5 l h⁻¹ for humid hydrogen.

The current–voltage curves of the fuel cell were measured by an ECI-1287 instrument (Solatron) working in the galvanostat regime (the electron load regime).

3. Results

3.1. Analysis of the ceramic microstructure

Fig. 7 presents typical microphotographs of fractures of ceramics sintered under different conditions.

By the MPC technology, it is possible to use a set of films cast of powders with particles of different fineness. For example, the middle set comprises films made of nanoparticles, while the outer films are prepared of microparticles. In this case, the SOFC electrolyte has necessary roughness of its working surfaces, which receive electrodes. The working surface of the

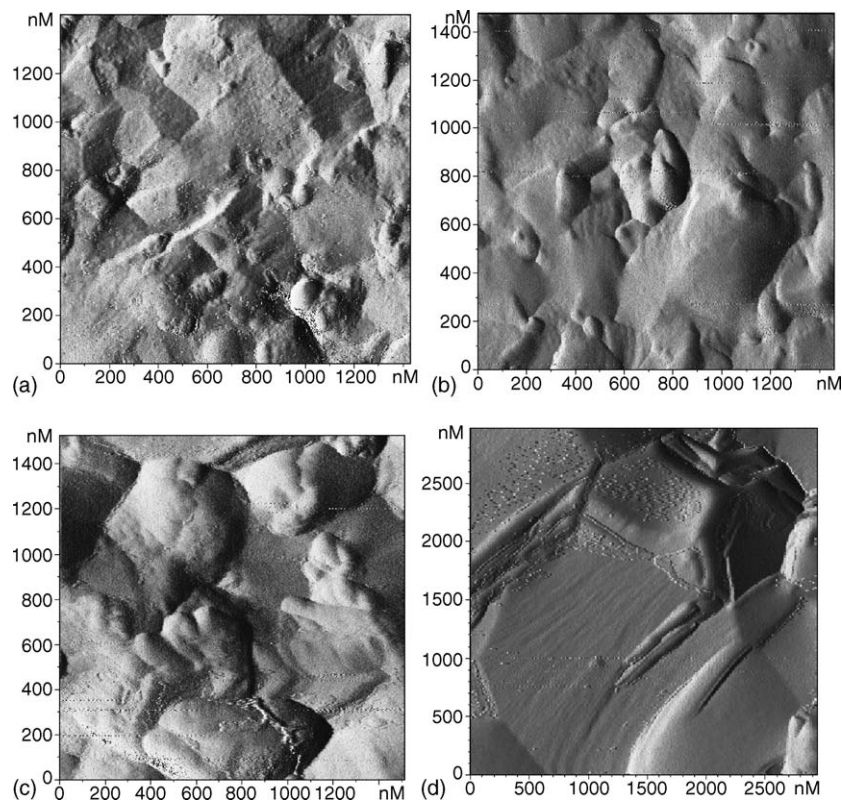


Fig. 7. AFM images of fracture surfaces of 9.5YSZ ceramic items, relative density of 0.984, sintered from compacts with different green densities.

Fig.	ρ_{green}/ρ_{sc}	t_{sint} (°C)	τ_{sint} (min)	d (nm)	ρ_{cer}
A	0.677	1150	60	170	0.981
B	0.603	1100	1600	160	0.984
C	0.541	1150	540	190	0.982
D	0.428	1250	180	460	0.987

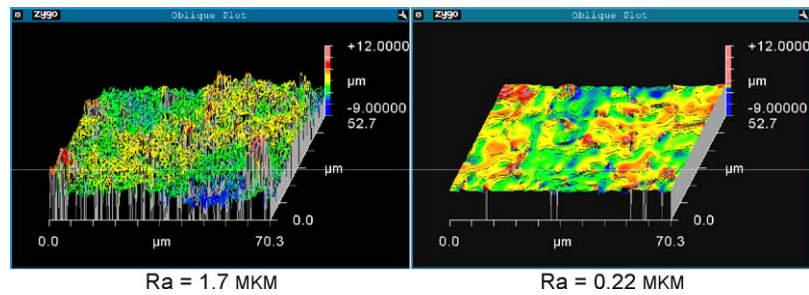


Fig. 8. Surfaces of a submicron solid YSZ electrolyte with and without microroughness.

electrolyte increases nearly by a factor of 1.5 relative to the visible surface. Images in Fig. 8 show surfaces of a submicron solid electrolyte and an additional microrough layer.

3.2. Examination of the electrolyte conductivity

The conductivity measurements revealed that the conductivity tended to increase with decreasing size of the electrolyte grains (Fig. 9). This tendency was observed over the whole interval of the temperatures studied [8].

Fractions of the bulk and boundary conductivities of the synthesized solid electrolyte were determined by the method of impedance spectroscopy. Fig. 10 presents conductivities of the bulk and boundaries of grains in the 9.5YSZ ceramic as a function of the grain size at a temperature of about 300 °C. The bulk conductivity of the ceramic grains depended little on their size, while the boundary conductivity (and resistance) of the grains considerably depended on the grain boundary size. The conductivity of the traditional ceramic, which was synthesized from micropowders, decreased as the grain size diminished from 75 to 5 μm . This fact was attributed [9] to the increase in the number of grain boundaries and, consequently, the growth of the boundary resistance. One could reasonably expect that in our case too the boundary resistance would rise further as the ceramic grain size decreased 50 times more. However, as the grain size decreased from 700 to 100 nm in YSZ samples having an ultrafine structure, the conductivity increased, i.e. exhibited an opposite tendency

[8]. The conductivity of the YSZ ceramic approached the conductivity of a single crystal and was equal to $0.057 (\text{Ohm cm})^{-1}$ at 900 °C. The activation energy of the ion transfer process was 1.10–1.18 eV.

It was already mentioned in the foregoing that the sintering shrinkage of the samples until they reached the dense state decreased with growing MPC pressure. A high density of the nanopowder compacts allowed a further decrease in the sintering temperature and, hence, ceramics with smaller grains could be synthesized. As ceramics are sintered, impurities, which are uniformly distributed over the bulk of particles, diffuse to the surface of ceramic grains and form their structure. Since precipitation of impurities on grain boundaries is a diffusion process, it progresses faster at higher temperatures. This increase in conductivity with decreasing grain size [8] can be explained by the decrease in the number of impurities at grain boundaries. The formation of a dense solid electrolyte at low temperatures ensures appearance of purer boundaries in ultrafine ceramics. In our opinion, the increase in the ceramic conductivity was due not to the nanosize of crystallites, but to the purity of the initial material and conditions (temperature and time) of formation of grain boundaries in the ceramics.

3.3. Electrochemical studies

The use of film casting and radial MPC technologies with subsequent sintering provided thin-walled tubes of an ultrafine solid YSZ electrolyte (Fig. 11).

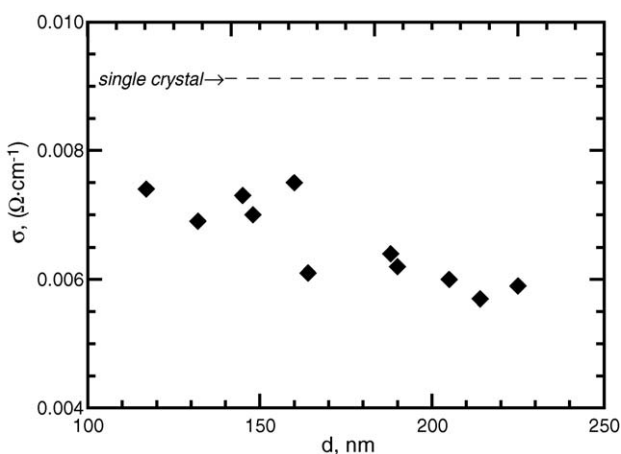


Fig. 9. Dependence of the conductivity on the average grain size in 9.5YSZ ceramics.

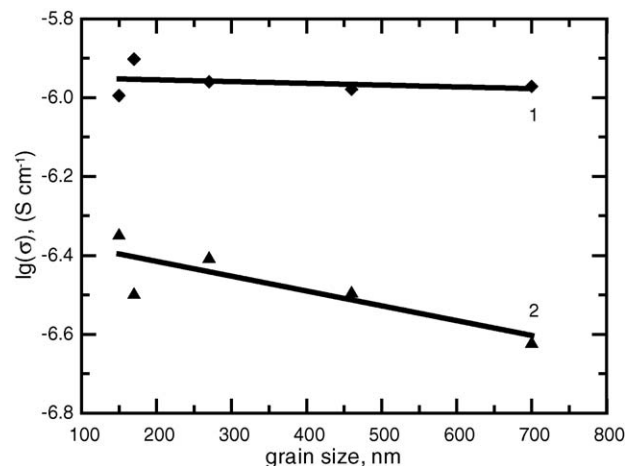


Fig. 10. Conductivity of the bulk (1) and grain boundaries (2) in 9.5YSZ ceramics vs. the grain size.

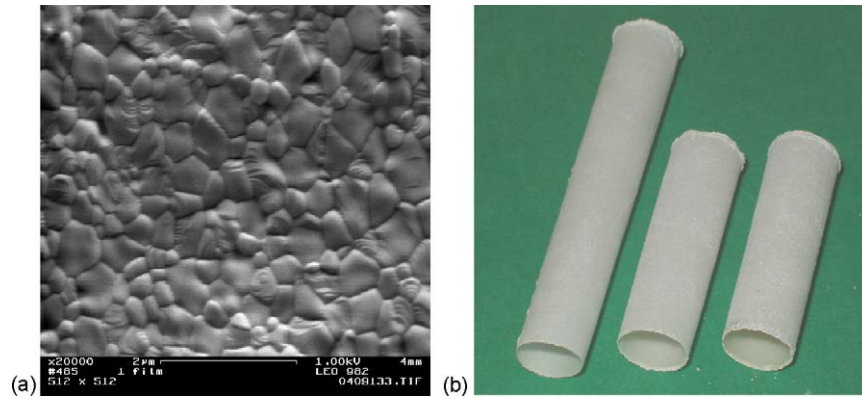


Fig. 11. (a) Surface of a sintered YSZ film 10 μm thick; (b) surface of a tube with walls 83, 170 and 250 μm thick made of an ultrafine solid YSZ electrolyte.

A tube with walls 140 μm thick was taken to make an electrochemical cell having a partitioned gas space outfitted with traditional research electrodes and gases (humid hydrogen and air):

(H₂ + 3%H₂O), Pt, CeO₂/YSZ/Pr₂O₃, Pt, air.

This cell was tested using the ultrafine solid YSZ electrolyte in the fuel cell regime. Fig. 12 presents current–voltage and power characteristics of a tested fragment of a tubular fuel cell. This fragment had the maximum specific power of about 0.3, 0.45 and 0.6 W cm⁻² at 785, 834 and 883 °C, respectively. The fuel utilization factor at the maximum power was 30%. It should be noted that the cell e.m.f. corresponded to thermodynamic values. This fact attested to gas tightness of the solid film electrolyte. The internal resistance of the cell, i.e. the electrolyte resistance, approached the value estimated from independent measurements. Thus, the ultrafine electrolytes, which were prepared using the proposed combination of technologies, met the requirements imposed on SOFC ceramics [10].

On the assumption that values of the specific polarization resistance of the electrodes were the same for cells having walls of different thickness, we calculated characteristics of the fuel

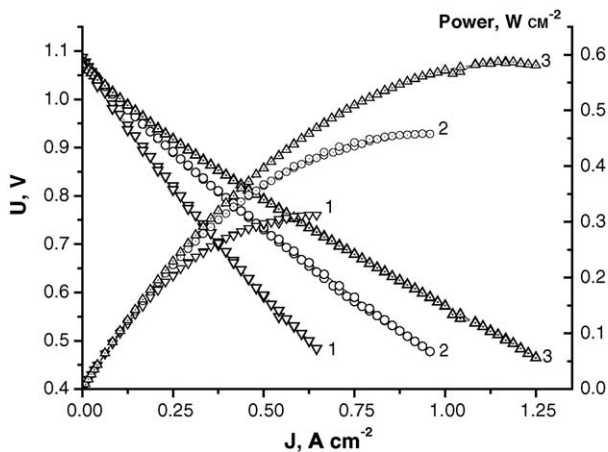


Fig. 12. Characteristics of a fragment of a tubular fuel cell with an ultrafine solid YSZ electrolyte having walls 140 μm thick. Temperature (1) 785 °C; (2) 834 °C; (3) 883 °C.

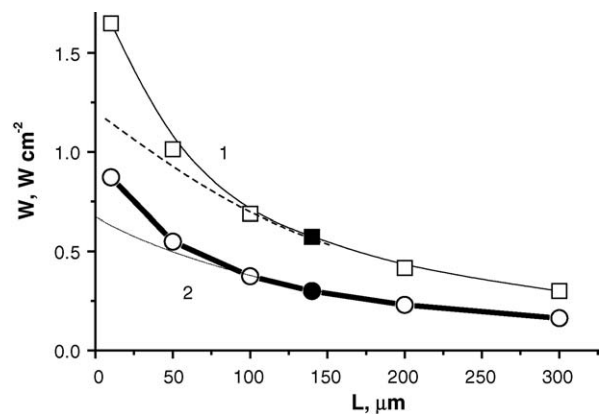


Fig. 13. Specific power of a tubular fuel cell with an ultrafine solid YSZ electrolyte at 883 °C (1) and 780 (2) vs. the electrolyte thickness (the dashed curves denote characteristics taking into account constructional losses).

cell depending on the solid electrolyte thickness. Fig. 13 presents the specific power of the fuel cell as a function of the electrolyte thickness. The solid lines denote power values disregarding the “constructional” resistance determined by the distribution of the current field lines near the electrode. The dashed lines show power values taking into account the contribution of the “constructional” resistance with the analogous current switching in the fuel cell. When the solid electrolyte is about 10 μm thick, one can expect that the tubular fuel cell will provide the specific power of nearly 1 W per square centimeter of the visible surface at 800–850 °C even without optimization of the electrode properties. This is in agreement with requirements imposed on SOFC ceramics [10].

4. Conclusions

1. Technological principles were established for synthesis of weakly agglomerated nanosized powders of electrolytes having particles about 16 nm in size for 9.5YSZ and 9 nm in size for 15GDC. The specific surface of the powders was nearly 62 m² g⁻¹.
2. Technological principles were established for casting of electrolyte films 10–15 μm thick and over 50 μm thick using weakly agglomerated nanopowders.

3. Technological principles were established for compaction (solidification) of multilayered articles by isostatic magnetic pulse pressing.
4. Technological principles were formulated for uniaxial (flat samples) and radial (tubular samples) MPC of solid electrolyte films.
5. Regimes were developed for radial MPC with the Z- and Θ -pinches to form tubular SOFC having necessary interface layers and the required micro- and macroscopic roughness of the surfaces.
6. Properties of samples of ultrafine solid electrolytes synthesized at the MPC pressure of 0.1–1.6 GPa were analyzed. When the apparent density of compacts accounted for 0.5–0.7 of the theoretical value and the compacts were sintered at 900–1250 °C, the relative density of the synthesized electrolytes was 0.92–0.98. Physicochemical properties of the ultrafine solid electrolytes were examined using flat disks 15–30 mm in diameter and 10 μm to 2 mm thick. The conductivity of the ultrafine (grain size 100–700 nm).
7. Solid electrolytes increased with decreasing grain size because, as we believe, the sintering technology improved the purity (the composition) of grain boundaries.
8. Electrochemical properties of cells with ultrafine solid electrolytes were studied using cells shaped as tubes about 10 mm in diameter having walls 80–250 μm thick.
9. A fragment of a tubular fuel cell ($\text{H}_2 + 3\% \text{H}_2\text{O}$, air) having walls less than 140 μm thick and traditional research electrodes was tested. The specific power was about 0.6 W cm^{-2} at a temperature of nearly 880 °C.
10. It was shown that even if the electrodes are not optimized, the specific power of about 1 W cm^{-2} can be realized at

800–850 °C at the achieved level of losses in the tubular fuel cell and thickness of the solid electrolyte equal to $\sim 10 \mu\text{m}$.

References

- [1] J.R. Groza, R.J. Dowding, Nanoparticle materials densification, *Nanostruct. Mater.* 7 (7) (1996) 749–768.
- [2] R.S. Mishra, C.E. Leshner, A.K. Mukherjee, Nanocrystalline alumina by high pressure sintering, *Mat. Sci. Forum* 225–227 (1996) 617–622.
- [3] V. Ivanov, S. Pararin, V. Khrustov, Yu. Kotov, S. Ivin, A. Nikonov, A. Medvedev, A. Shtol'ts, Application of magnetic pulsed compaction for sintering of nanostructured oxide ceramics, Part B, in: *Proceedings of 10th International Ceramic Congress, Florence, Italy, 14–18 July 2002*.
- [4] Yu.A. Kotov, V.V. Osipov, M.G. Ivanov, O.M. Samatov, V.V. Platonov, V.V. Lisenkov, A.M. Murzakaev, A.I. Medvedev, E.I. Azarkevich, A.K. Shtolz, O.R. Timoshenkova, Properties of YSZ and CeGdO nanopowders prepared by target evaporation with a pulse-repetitive CO_2 laser, *Rev. Adv. Mater. Sci.* 5 (2003) 171–177.
- [5] B.A. Rotenberg, *Ceramic Capacitor Dielectrics*, RFBR, 2000.
- [6] R.E. Mistler, E.R. Twiname, *Tape Casting (Theory and Practice)*, American Ceramic Society, 2000.
- [7] V.V. Ivanov, V.R. Khrustov, S.N. Pararin, A.I. Medvedev, A.K. Shtol'ts, O.F. Ivanova, A.A. Nozdrin, Stable zirconia nanoceramics prepared using magnetic pulsed compaction of nano-sized powders, *Book of Abstracts, ECERS Topical Meeting Nanoparticles, Nanostructures & Nanocomposites, 5–7 July 2004, S. Petersburg, Russia*, pp. 91–92.
- [8] V.V. Ivanov, V.R. Khrustov, A.S. Lipilin, S.N. Shkerin, Conductivity of zirconia and ceria electrolytes with sub-micrometer scaled grains, *Book of Abstracts, SSI-15, 17–22 July 2005, Baden-Baden, Germany*, p. 416.
- [9] A.I. Ioffe, M.V. Inozemtzev, A.S. Lipilin, *Phys. Stat. Sol. (a)* 30 (1) (1975) 87.
- [10] S. Baron, Intermediate Temperature (500–850 °C) Solid Oxide Fuel Cells (IT-SOFCs) explained, Imperial College http://www.fuelcelltoday.com/FuelCellToday/FCTFiles/FCTArticleFiles/Article_745_IT-SOFC0104.pdf, 21 January 2004.