# The influence of the method of addition of Al<sub>2</sub>O<sub>3</sub> to 3YSZ material on its thermal and electrical properties

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Abstract The properties of tetragonal yttria-stabilized zirconia composites with the small addition of alumina (Al<sub>2</sub>O<sub>3</sub>- $Y_2O_3$ -ZrO<sub>2</sub> composite) obtained on two ways of synthesis were studied in terms of usability for anode materials in solid oxide fuel cell. Both methods were based on citric synthesis: in the first one, Al<sub>2</sub>O<sub>3</sub> was coprecipitated with the tetragonal ZrO<sub>2</sub> in the form of citrate by citric acid, while in the second Al<sub>2</sub>O<sub>3</sub> was impregnated in the form of aluminium nitrate precursor on tetragonal ZrO<sub>2</sub> matrix. The obtained materials were analysed by X-ray diffraction, dilatometry and impedance spectroscopy. The results of measurements show that regardless of synthesis method, the addition of Al<sub>2</sub>O<sub>3</sub> influences the conductivity of samples by increasing their grain boundaries conductivity as an effect of removing of SiO<sub>2</sub> and decreasing of conductivity activation energy. The impregnation of Al<sub>2</sub>O<sub>3</sub> on tetragonal ZrO<sub>2</sub> and sintering of this material above shrinking temperature cause, however, radical decrease of porosity of materials, which disqualifies these samples as anode materials. In the case of samples obtained by coprecipitation the significant decrease of porosity is not observed.

**Keywords** Composite materials · Thermal properties · Conductivity · Anode for SOFC · Synthesis of nanopowders

#### Introduction

Yttria-stabilized zirconia (YSZ) is the most known ceramicoxide material employed as a component of either solid

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Faculty of Materials Science and Ceramics, AGH University of Science and Technology, al. A. Mickiewicza 30, 30-059 Krakow, Poland e-mail: edrozdz@agh.edu.pl electrolyte or anode composite material for solid oxide fuel cell (SOFC). Both, cubic (8 mol%  $Y_2O_3$  in  $ZrO_2-8YSZ$ ) and tetragonal (3 mol%  $Y_2O_3$  in  $ZrO_2-3YSZ$ ) forms are commonly used, but while only 3YSZ has good enough mechanical and thermal properties to be a support for power cell, it reveals—due to so calling blocking effect on grain boundaries—too small ionic conductivity in comparison to that of the cubic type.

One way to improve the ionic conductivity of the 3YSZ can be an addition of alumina to zirconia matrix. This effect was analysed in the past several years mainly for dense composite materials, both 8YSZ [1–3] and 3YSZ [4–7] as the matrix for alumina. Al<sub>2</sub>O<sub>3</sub> addition can improve electrical properties of material by modification of surface conductivity of YSZ. Moreover, the uniform distribution of Al<sub>2</sub>O<sub>3</sub> in YSZ matrix can prevent abnormal grain growth and refine the matrix grains and as the consequence, control low-temperature degradation of mechanical properties [8].

It is commonly known that solubility of  $Al_2O_3$  in YSZ below 1,473 K is negligible. An experimental data presented by Bannister [9] and thermodynamic calculations [10] confirm this behaviour of  $Al_2O_3$ . This problem was, however, mainly examined for 8YSZ. Tekeli et al. [11] stated that the solubility of  $Al_2O_3$  is equal up to 0.3 mass% for materials sintered at 1,573 K. Feighery and Irvine [3] provided value 1.0 mass% in case of material sintered at 1,773 K. These authors explained also a mechanism of conductivity changes connected with the addition of  $Al_2O_3$  (Eq. 1). As they stated, on the one hand,  $Al_2O_3$  dissolved into  $ZrO_2$  can create the same amount of oxygen vacancies as the addition of  $Y_2O_3$  (Eq. 2):

$$Y_2O_3 \rightarrow 2Y'_{Zr} + V_0^{\bullet \bullet} + 3O_0^x \tag{1}$$

and

$$Al_2O_3 \to 2Al'_{Zr} + V_O^{\bullet \bullet} + 3O_O^x$$
<sup>(2)</sup>

which results in bulk conductivity increase. On the other hand, the grain boundary resistivity decreases because alumina acts as scavenger for SiO<sub>2</sub> impurities which are located on the grain boundaries [12]. Silica, which is a most common impurity in ZrO<sub>2</sub>, shows a tendency to form a glassy layer on the surface of zirconia grains, which causes decreasing of transport of oxygen ions across grain boundaries. As a result, the conductivity of grain boundary is drastically reduced [13]. For small amount of Al<sub>2</sub>O<sub>3</sub>, the bulk effect connected with alumina solubility is competitive to an effect on grain boundary. In case of 3YSZ, for which solubility of Al<sub>2</sub>O<sub>3</sub> is very small, the effect of removing SiO<sub>2</sub> is the main process.

It is commonly known that synthesis pathway of a given material can affect its microstructural properties (such as porosity, specific surface area, size and grain distribution) and in consequence—its thermal and electrical properties. The dense composite system  $Al_2O_3$ –YSZ is well-known, and the correlation of their microstructure with electrical conductivity was studied earlier [14]. Authors found the correlation between volume fraction of ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and conductivity of composite. A large volume of  $Al_2O_3$  (which is an insulator) significantly decreases conductivity of composite out that homogeneous distribution of composite elements decreases the percolation threshold for ZrO<sub>2</sub> oxygen vacancy conduction.

The properties of porous (the one of necessary feature for anode materials)  $Al_2O_3$ -YSZ composites are poorly examined. The basic widespread way for improving grain boundary conductivity of ZrO<sub>2</sub> at a synthesis stage is applying the method leading to samples with nanoscale grain size [15]. One of the most effective methods for obtaining 3YSZ porous nanopowders is citrate gel synthesis [16, 17], often named as Pechini process.

The main goal of this work was a preparation of porous Al<sub>2</sub>O<sub>3</sub>/3YSZ materials by two different synthesis methods based on classical citric method differing by way in which alumina is added to 3YSZ matrix and next the examination of thermal and electrical properties of obtained samples in order to determine the more efficient way of synthesis of materials on anode and electrolyte for SOFC technology.

#### Experimental

## Synthesis of the composite materials

In this paper, properties of materials composed with tetragonal  $ZrO_2$  (3YSZ) and the small addition of  $Al_2O_3$  (0.5, 1.0 and 2.0 mass%) obtained via two ways of synthesis were examined. The first one (named as MI) was the method which is well known as the citric method. The

second one (MII) was a deposition of aluminium nitrate as a precursor of  $Al_2O_3$  on 3YSZ nanopowder (obtaining by citric method) and next thermal decomposition of  $Al(NO_3)$ .

The solutions of metals yttrium nitrate and aluminium nitrate were prepared using analytically pure reagents  $[Y(NO_3)_3.6H_2O$  and  $Al(NO_3)_3.9H_2O$  provided by Sigma-Aldrich]. Only the solution of zirconyl nitrate was prepared differently: this one was obtained with zirconium(IV) oxychloride octahydrate (Beijing Chemicals Import and Export Corporation) by precipitation of hydrous zirconia gel with the use of ammonia. Next, this gel was calcinated at 973 K for 2 h, and obtained white ZrO<sub>2</sub> powder was then dissolved in concentrated nitric acid (analytical grade, Sigma-Aldrich).

The concentrated nitrate solutions of aluminium  $(0.556 \text{ mol dm}^{-3})$ , yttrium  $(0.955 \text{ mol dm}^{-3} \text{ per } Y_2O_3)$  and zirconyl  $(0.814 \text{ mol dm}^{-3} \text{ per } ZrO_2)$  were used in the synthesis. The composition of solutions was determined by classical gravimetric analysis. The citric acid was used in the form of monohydrate (analytical grade, provided by POCH).

#### MI

The solutions of aluminium, yttrium and zirconyl nitrates were mixed in the proper quantity in order to obtain assumed composition. The calculated amount of solid citric acid (with 10 mol% excess) was added to the nitrates solution. The final solution was heated on a hot plate (around 493 K) and stirred for about 12 h, till the solution turned into grey–white gel. Then, this gel was decomposed in laboratory dryer (at 513 K) until brown smoke (originated from the decomposition of nitrates groups) stopped liberate. In the next step, the grey powder was heated on the burner (at around 973 K) in the air for 5 h. As a result, materials with 0.5, 1.0 and 2.0 mass% of  $Al_2O_3$  in 3YSZ were obtained.

#### MII

Ethanol solution of aluminium nitrate was obtained by dissolving of  $Al(NO_3)_3 \cdot 9H_2O$  (Sigma-Aldrich) in 96 % ethanol (provided by POCH). The composition of this solution was equal to 0.499 mol dm<sup>-3</sup>, as determined by classical gravimetric analysis. 3YSZ powder was obtained by means of citric method (the same way of treatment as employed in method MI), i.e., the proper volume of water solutions of yttrium and zirconyl nitrates with citric acid was mixed, the final solution was heated on a hot plate (around 493 K) for about 12 h, and the resulting gel was decomposed in laboratory dryer (at 513 K) and heated on the burner (at around 973 K) in the air for 5 h.

The powder of 3YSZ was grinded in the mortar and then added in the proper ratio (in order to obtain the same composition  $Al_2O_3/3YSZ$  as in MI) to concentrated ethanol solution of aluminium nitrate. The suspension was stirred and simultaneously heated at around 333 K until the ethanol evaporated. The obtained (still wet) powder was initially warmed in the dryer (c.a. 353 K for 24 h) and then sample was calcinated in the furnace on air at 673 K for 1 h in order to decompose aluminium nitrate.

The same three compositions of materials were obtained by means of MI and MII methods. Next, the materials obtained by both methods were initially crushed in mortar, milled in atritor in isopropyl alcohol, dried in 513 K in air and calcinated at 673 K for 3 h in heater. Finally, disc pellets were pressed and sintered at 1,073 K or 1,473 K in air for 3 h. In case of MII, the ethanol solution of aluminium nitrate was applied in order to decrease the Al(NO<sub>3</sub>)<sub>3</sub> agglomeration on the surface of zirconia grains [18] and for fast evaporation of solvent.

## Apparatus

The X-ray diffractograms of fired and sintered powders were registered using a Philips X'Pert Pro diffractometer (CuKa = 1.5406 Å,  $2\theta = 20-90^{\circ}$ ). The crystallites size of materials was estimated from the ZrO<sub>2</sub> [011] peak broadening. The presence of aluminium in composites was confirmed by X-ray energy dispersive spectroscopy (EDAX company apparatus). Thermal analysis methods were used at two different stages of these studies. First one to determine conditions of thermal treatment of powders during synthesis (TG/DTA analysis), and the second one for setting thermal expansion coefficient for the composite materials (dilatometry method).

TG/DTA measurements with simultaneously evolving gaseous analysis (EGA) were performed on SDT 2960 TA instruments apparatus connected online with mass spectrometer ThermoStar QMD 360. All measurements were carried out in synthetic air with heating rate of 10 K min<sup>-1</sup>. The samples were placed in platinum crucible. The reference one was also platinum crucible. The mass spectrometer was operated with an electron impact ionizer with energy 0.112 aJ (70 eV). Mass spectra were recorded for M/z equal to 18, 44 and 46 which correspond to ions:  $H_2O^+$ ,  $CO_2^+$  and  $NO_2^+$ , respectively. M/q = 46 line was chosen to present the emission of nitrate groups in general (marked as  $NO_x$  in text).

Dilatometric measurements were carried out by means of NETZSCH DIL 402 C apparatus, equipped with linear displacement transducer. Cylindrical samples of diameter 10 mm and thickness around 1 mm were used in the experiments. The measurements were performed in the Ar atmosphere containing 5 %  $H_2$  with heating rate of 5 K min<sup>-1</sup> within the temperature range of 293–973 K.

The density of samples was determined on the basis of geometrical sizes and mass. The total porosity was determined by relative geometrical density measurements assuming that densities of  $Al_2O_3$  and 3YSZ are equal to 3.98 and 6.10 g cm<sup>-3</sup>, respectively.

Electrical measurements were carried out on Solartron SI 1260 Impedance/Gain-Phase Analyzer with the SI 1296 dielectric interface. A flowing gas atmosphere of 10 %  $H_2$  in Ar was used. The measurements were performed in temperature range 293–973 K at the frequencies from 0.1 Hz to  $10^6$  Hz with amplitude of the sinusoidal voltage 10 mV. The platinum paste was put on pellets as the electrode before conductivity measurements. The impedance spectra were analysed using software package (ZPLOT) enclosed by Solartron.

#### Results

#### TG/DTA/EGA analysis

The thermal treatment of precursors of composite materials is strictly connected with their application as anode in SOFC. The conditions of preparation should ensure the highest possible porosity of samples. For this reason, some of the following requirements should be fulfilled: (a) application of precursors which decomposed with generation of the large amount of gaseous products, (b) using of concentrated solutions and (c) proper thermal treatment. The last factor involves the use of relatively low temperature of calcinations of powders (it may prevent premature growth of grain). At the same time, it is very important to carry out the calcination process either in furnace with the flow of air or on the burner. This assures that material is still in contact with oxygen and simultaneously the gaseous products of decomposition and oxidation can naturally leave solid matrix. Conducting a process in closed oven can lead to pyrolysis process and as a consequence to formation of carbon as a residue.

Due to such significant role of calcination conditions, the thermogravimetric measurements for dry citrate gel originating from MI were performed. Additional registration of the mass spectra of the gaseous products involving during TG/DTA analyses was also helpful.

As one can observe in TG/DTA (Fig. 1) graphs, the process of dry gel decomposition goes on in the three stages. The first one, slight loss of mass (around 2.6 mass%) in the range 330–420 K is connected only with removal of adsorbed water. The second one (around 18.8 mass%), in the range 430–550 K, associated with evolving of water and a carbon dioxide from sample is a



Fig. 1 The example of TG/DTA/EGA curves decomposition of dry gel obtained in the method MI

result of first step of decomposition of metal complexes. Abakevičiene et al [19] attribute the loss of mass in this temperature range and corresponding strong endothermic DTA peak with maximum near 490 K to the removal of water from the coordination sphere of the metal complexes and/or chemisorbed water; however, in presented results (Fig. 1) there are no any clear peaks. The difference appears because of Abakevičiene's measurements were carried out on nitrate-citrate wet gel, while results presented in Fig. 1 were obtained for dry gel heated earlier at 513 K. The lack of peak is probably a result of compensation effect connecting with endothermic decomposition of metal complexes and simultaneously combustion of products. The third, main step of decomposition of citrate gel falls into temperature range 550-670 K. It is connected with around 49 mass% loss of mass of sample. The exothermic peak on DTA curve corresponds to this effect, which demonstrates that decomposition processes are closely associated with oxidation. The complete decomposition with simultaneous oxidation of organic remains is necessary from the point of view of potential application of synthesized materials. The analysis of mass spectrum registered during TG/DTA measurement at discussed temperature range shows the increase of ionic currents only, coming from water and carbon dioxide. This is in concordance with the results of TG/DTA curves analysis. There is another important information on the mass spectrum: the ionic current originating from  $NO_x$  does not increase and does not have any maximum. It means that the whole nitrate groups in the form of NO<sub>x</sub> (which was observed as brown smokes) were removed with gel during heating in laboratory dryer.

One can assume, therefore, that calcination can be carried out even in not much higher temperature than 670 K. On the other hand, temperature of drying wet gel— 513 K—was high enough for decomposition of nitric acid



Fig. 2 Thermal decomposition of aluminium nitrate in air atmosphere

which was created after adding of citric acid to the precursor's solution. The DTA peak with maximum around 633 K and corresponding water and carbon oxide ionic currents maxima are sharp. This demonstrates that both processes: decomposition of citrate groups and oxidation of carbon are fast, with big loss of mass.

From the point of view of method MII, the calcination conditions of nitrate–citrate gel should be the same as for gel obtained in the MI. It was important to apply similar conditions of synthesis of 3YSZ matrix as in MI method, in order to compare the influence of the way of addition of  $Al_2O_3$  on the properties of obtained composites.

For the MII, it was very important to determine the temperature of decomposition of aluminium oxide precursor in air. It follows from TG/DTA/EGA curves (Fig. 2) that the pure aluminium nitrate nonahydrate decomposes in a few steps. The first one, at temperature range 293-363 K corresponds to removal of adsorbed water and the first step of dehydration. The second one (much more complicated) in the range 393-653 K is related to two-step dehydration with simultaneous decomposition of nitrate groups. The first loss of mass (in the range 293-363 K) is about 3.7 mass%, while the main loss (393-653 K) is about 79 mass%. Theoretical calculations made on the basis of TG line indicate that the first step corresponds uniquely to dehydration. The second big loss of mass with accompanying endothermic DTA peak (with maximum around 438 K) seems to be a simple process. However, EGA analysis shows that the process is much more complicated. In this range of temperature, the ionic currents corresponding to water and NO<sub>x</sub> increase, as a result of dehydration and decomposition, which occur at the same time. Additionally, the both processes are not simple, what is clearly seen on the mass spectrum.



Fig. 3 X-ray diffraction pattern of 1.0 mass%  $\rm Al_2O_3\text{--}3YSZ$  materials after sintering at 1,473 K

The important conclusion, from the point view of preparation conditions is that aluminium nitrate is completely decomposed below 673 K. On the other hand, the temperature 513 K (which can be achieved in laboratory dryer) is too low for complete decomposition of aluminium nitrate in short period of time.

## X-ray analysis

Diffractograms of the powders after calcinations obtained in MI and MII methods (Fig. 3) confirmed that the final product is tetragonal ZrO<sub>2</sub>. As determined from the ZrO<sub>2</sub> (011) peak broadening, the crystallites of materials after calcination have nanometric sizes:  $15 \pm 3$  nm for MI and  $13 \pm 3$  nm for MII. As a result of sintering (in 1,473 K), crystallites grown and their sizes reach a range of  $110 \pm 10$  for MI and  $88 \pm 9$  for MII materials,

**Fig. 4** The EDS spectra for 2.0 mass% Al<sub>2</sub>O<sub>3</sub>-3YSZ samples obtained **a** with MI, **b** MII method

respectively. The identification of  $Al_2O_3$  on the basis of diffraction patterns analysis is not possible by this method due to too small amount of aluminium oxide in materials. The presence of aluminium was confirmed for all materials obtained with both, MI and MII methods, by means of EDS analysis (Fig. 4).

## Porosity

The powders described above were formed in pellets and then sintered at 1,073 K or 1,473 K. On the basis of geometrical measurements, the density of sintered body was determined for all tested compositions of samples. The calculated values are presented in Table 1. The respective values of density are similar for both series of materials sintered at 1,073 K in contrast to the values of density (and porosity) for materials sintered at 1,473 K. The latter forms two series of results. The density values obtained for samples synthesized with method of 3YSZ saturation by aluminium nitrate (MII) and then sintered at 1,473 K are much higher than those determined for samples obtained by means of MI method. As a result, samples synthesized with MII method demonstrate quite small porosity, which disqualifies these materials as potential anode material. In case when the sintering temperature was equal to 1,073 K, the method of synthesis does not have an influence on porosity of materials but in the temperature where ZrO<sub>2</sub> materials demonstrate a large contraction of volume, synthesis method turned out to be very important. It is known that the shrinkage of ZrO<sub>2</sub> observed in temperature range of 1,270-1,470 K leads to a considerable decrease of porosity [8, 20, 21]. However, our research showed that the 8YSZ materials obtained by citrate method and sintered at 1,573 K maintain a high porosity [22]. This result is connected with limitation of mass transport in porous samples being a result of empty spaces in the material.



 Table 1
 The density and total porosity samples after sintering

Sample	Sintering temperature 1,073 K		Sintering temperature 1,473 K	
	Density/ g cm <sup>-3</sup>	Total porosity/ %	Density/ g cm <sup>-3</sup>	Total porosity/ %
0.5 mass% Al <sub>2</sub> O <sub>3</sub> /3YSZ MI	2.37 ± 0.12	61.1	4.11 ± 0.21	32.3
1.0 mass% Al <sub>2</sub> O <sub>3</sub> /3YSZ MI	2.31 ± 0.13	62.0	3.87 ± 0.17	35.3
2.0 mass% Al <sub>2</sub> O <sub>3</sub> /3YSZ MI	2.29 ± 0.12	62.2	3.70 ± 0.16	38.6
0.5 mass% Al <sub>2</sub> O <sub>3</sub> /3YSZ MII	2.62 ± 0.11	56.9	5.61 ± 0.14	7.93
1.0 mass% Al <sub>2</sub> O <sub>3</sub> /3YSZ MII	$2.58\pm0.13$	57.6	$5.62\pm0.18$	7.54
2.0 mass% Al <sub>2</sub> O <sub>3</sub> /3YSZ MII	2.58 ± 0.15	57.4	5.53 ± 0.12	8.10

According to results presented in Table 1, the addition of a small amount of aluminium to the tetragonal zirconia system leads to densification of materials. This effect is highly connected with methods of addition of Al<sub>2</sub>O<sub>3</sub>. It is less evident in the case of materials sintered at 1,073 K than for materials sintered at 1,473 K. Moreover, as one can notice, the method of preparation of Al<sub>2</sub>O<sub>3</sub>/3YSZ materials strongly affects density of samples. Therefore, the hypothesis that density depends on a way of distributing Al<sub>2</sub>O<sub>3</sub> in 3YSZ matrix can be formulated. In the case of materials obtained in MI method, the particles of Al<sub>2</sub>O<sub>3</sub>, due to the coprecipitation with tetragonal ZrO<sub>2</sub> and coexistence of this species in the form (first sol and next gel), are uniformly distributed in 3YSZ matrix, while in materials synthesized by MII particles of Al<sub>2</sub>O<sub>3</sub> are distributed unregularly depending on a structure of open pores. In the material obtained by MI, the particles of Al<sub>2</sub>O<sub>3</sub> are located inside ZrO<sub>2</sub> grains, while in material from MII Al<sub>2</sub>O<sub>3</sub> created a layer on ZrO<sub>2</sub> grains. In effect, mass transport processes which occur on the grain boundaries can be much faster. Taking into account the mechanism of densification of ZrO<sub>2</sub> nanopowders in the presence of Al<sub>2</sub>O<sub>3</sub> proposed in literature (liquid phase sintering mechanism), it confirms that coating of ZrO<sub>2</sub> grains by Al<sub>2</sub>O<sub>3</sub> can decrease sintering temperature of these materials. Thus, we can draw the conclusion that the densification and simultaneously decreasing of porosity of materials obtained by MII result from a distribution of Al<sub>2</sub>O<sub>3</sub> on the surface of ZrO<sub>2</sub> grains. On the basis of the above results and



Fig. 5 Dilatometric plots of the  $Al_2O_3/3YSZ$  materials obtained by MI and MII methods

conclusions one can assume that the way of adding  $Al_2O_3$  to 3YSZ has significant influence on thermal and consequently electrical properties of testing samples.

The rest of this paper concerns with the results of measurements carried out for MI and MII materials sintered at 1,473 K, since a temperature equal to 1,073 K is not high enough for sintering of the materials good for anode and dense electrolyte.

#### Dilatometry

The dilatometric tests for samples obtained with MI and MII methods (the example for 1.0 mass% of Al<sub>2</sub>O<sub>3</sub> in Fig. 5) show that thermal properties of these materials are different from each other. Such conclusions can be drawn because of the different inclination angles on the curves of dilatation changes with temperature. The thermal expansion coefficients calculated for samples using the linear regression approximation are equal:  $(10.700 \pm 0.001) \times 10^{-6} \text{ K}^{-1}$  and  $(8.200 \pm 0.002) \times 10^{-6} \text{ K}^{-1}$  for samples obtained with MI and MII, respectively. In the case of material obtained by coprecipitation—they are similar to values of fully dense 3YSZ  $(10.5 \times 10^{-6} \text{ K}^{-1})$  and are much lower (like value for fully dense Al<sub>2</sub>O<sub>3</sub>=8.4 ×  $10^{-6} \text{ K}^{-1}$ ) in the case of material obtained with MII.

From the point of view of potential application of tested composites, in case of samples obtained with MII their thermal properties are too different from properties of pure 3YSZ in order to be used as anodes materials.

## Electrical properties

The electrical conductivity is another important property which has to be taken into account when considering the application of tested materials. In the case of both groups

**Fig. 6** The Nyquist plots determined at 973 K



of materials (for the samples synthesized by means of both methods), a characteristic behaviour for dielectric materials—the decreasing of electrical resistivity with increasing temperature was observed. Furthermore, the values of total resistivity of all examined samples are lower than resistivity of pure 3YSZ as can be noticed in Nyquist curve (Fig. 6). It means that all the samples with addition of  $Al_2O_3$  reveal higher conductivity than 3YSZ. While in the case of MI samples, the decreasing of resistivity with increasing of aluminium oxide content can be observed for all compositions, for MII materials this tendency is maintained—the sample 1.0 %  $Al_2O_3/3YSZ$  demonstrates the highest value of resistivity.

An analysis of the impedance spectra revealed that the equivalent circuit (Fig. 7) represents well the impedance data which are presented in Fig. 6. From the point of view of an Al<sub>2</sub>O<sub>3</sub> role, however, the most important are changes of grain interior and grain boundaries resistivity. The highfrequency part of impedance spectrum is related to the conductivity of zirconia grains ( $\sigma_{\rm b}$ ), whereas low-frequency part describes conductivity of grain boundaries  $(\sigma_{\rm gb})$ . The comparison of calculated values of conductivity  $\sigma_{\rm b}$  and  $\sigma_{\rm gb}$  versus temperature, for samples with the both synthesis methods, is presented in Figs. 8 and 9. The curves show that in the lower temperature, the values of bulk conductivity are slightly higher for the MII materials with the exception of composition 0.5 % Al<sub>2</sub>O<sub>3</sub>/3YSZ for which in the high temperature the values of  $\sigma_b$  are higher for MI sample. It can be seen from Fig. 9 that in case of all samples (obtained by the both methods), conductivity of grain boundaries increases with the temperature growth. When we consider the curves of dependence of energy activation ( $E_{act}$ ) versus Al<sub>2</sub>O<sub>3</sub> mass% (Fig. 10), it can be noticed that the addition of Al<sub>2</sub>O<sub>3</sub> reduces values of the activation energy of electrical conductivity of grain boundaries in case of the samples synthesized by the both tested methods. For the materials obtained by MI and MII, one can observe the lowest values of  $E_{act}$  for samples with

Fig. 7 Equivalent circuits used for interpretation of the impedance spectra

R<sub>ab</sub>

R<sub>b</sub>



Fig. 8 The comparison of bulk conductivities of samples sintered at 1,473 K. The measurements carried out at temperature range 773–973 K

the addition of 2.0 mass% of  $Al_2O_3$  to 3YSZ matrix. Generally, the values of  $E_{act}$  of  $\sigma_{gb}$  for MII sample are lower than for MI sample with the exception of samples with content of  $Al_2O_3$  equal to 2.0 mass% for which the values of  $E_{act}$  are similar one to each other.



Fig. 9 The comparison of grain boundaries conductivities of samples sintered at 1,473 K. The measurements carried out at temperature range 773-973 K



Fig. 10 The comparison of values of energy activation of grain boundaries conductivity for 3YSZ and samples with addition  $Al_2O_3$  obtained by MI and MII methods

It can be noticed, as we compare the bulk and grain boundary resistivity values for the bodies with the same contents of Al<sub>2</sub>O<sub>3</sub> sintered at 1,073 and 1,473 K, that MII samples demonstrate lower values of resistivity than MI ones, regardless of the sintering temperature (Fig. 11). The results in this figure coincide with values of  $E_{act}$ —the lower values of the energy activation of grain boundary conductivity for MII samples than MI sample, the higher values of grain boundary conductivity for MII samples in



Fig. 11 The comparison of values of bulk and grain boundary resistance for samples 0.5 mass%  $\rm Al_2O_3/3YSZ$  with MI and MII methods

comparison with MI samples. Furthermore, regardless of sintering temperature, for the same content of  $Al_2O_3$  in samples, values of  $R_b$  and  $R_{gb}$  for MII samples are lower than for MI samples.

#### Conclusions

The comparison of properties of the materials obtained by different methods of Al<sub>2</sub>O<sub>3</sub> incorporation in the 3YSZ matrix confirms how important is a way of synthesis of composite materials. The presented results show that methods of samples synthesis become very important especially above temperature where material shrinks. From the point of view of porosity, materials obtained by impregnation of Al<sub>2</sub>O<sub>3</sub> on 3YSZ framework using aluminium nitrate as precursor and sintered at 1,473 K reveals too low values of porosity in order to be applied as anode materials but at the same time they are very well sintered (the values of density) in such low temperature. These results suggest that these methods can be suitable for obtaining of electrolyte for SOFC. From the point of view of thermal properties, more useful for obtaining anode materials is synthesis on the way of citric method (with addition of Al<sub>2</sub>O<sub>3</sub> in 3YSZ framework by coprecipitation with the all precursors) with sintering at 1,473 K, but from the point of view of conductivity, the second method MII is definitely better regardless of sintering temperature of samples. The calculated values of activation energy of electrical conductivity of grain boundaries confirmed that applying of Al<sub>2</sub>O<sub>3</sub> as scavenger for SiO<sub>2</sub> impurities is an effective method for increasing of conductivity of materials.

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