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THE INFLUENCE OF THE WAY OF ALUMINA ADDITION ON PROPERTIES IMPROVEMENT OF 3YSZ MATERIAL

WPŁYW SPOSOBU WPROWADZENIA TLENKU GLINU NA POPRAWĘ WŁAŚCIWOŚCI MATERIAŁU 3YSZ

Yttria-stabilized zirconia (YSZ) is the best known ceramic-oxide material employed as a component of either solid electrolyte or anode cermet material for intermediate solid oxide fuel cell (IT - SOFC). The properties of traditionally produced (by mechanical mixing of oxides) Al_2O_3/3YSZ composite with the same composition materials obtained by citrate and impregnation methods and with properties of pure tetragonal zirconia (3YSZ) were compared. The materials were characterised by X-ray diffraction, SEM observations with EDX analysis, density and impedance spectroscopy measurements. The results shown that Al_2O_3/3YSZ composites reveals higher conductivity than pure 3YSZ and that addition of alumina (regardless of methods) improve electric properties of resulting materials. Taking into account application of this materials as anode in IT-SOFC the determined values of energy activation of conductivity and microstructural properties of composites show that materials obtained by citric method are the most promising.

Keywords: composite materials, ionic conductivity, tetragonal zirconia, IT - SOFC anode

Tlenek cyrkonu (IV) stabilizowany itrem (YSZ) jest jednym z najlepiej poznanych tlenkowych materiałów ceramicznych stosowanych jako składnik zarówno elektrolitów stałych jaki i materiałów anodowych dla stałotlenkowych ogniw paliwowych (SOFC). W pracy zostały porównane właściwości tradycyjnie produkowanego (poprzez mechaniczne mieszanie tlenków) kompozytu Al_2O_3/3YSZ z właściwościami analogicznych materiałów wytworzonych metodą cytrynianową oraz impregnacji oraz z właściwościami czystego 3YSZ. Otrzymane materiały badano metodami dyfrakcji rentgenowskiej, skaningowej mikroskopii elektronowej (SEM) z jednoczesną analizą EDX, spektroskopii impedancyjnej oraz wykonano analizę gęstości próbek. Wyniki badań pokazały iż niezależnie od sposobu wprowadzenia Al_2O_3 do układu, kompozyty Al_2O_3/3YSZ wykazują wyższe przewodnictwo niż czysty 3YSZ. Ponadto stwierdzono, biorąc pod uwagę możliwość zastosowania badanych materiałów jako materiał anodowy w IT-SOFC, iż najbardziej obiecujące właściwości mikrostrukturalne oraz elektryczne posiadają materiały kompozytowe otrzymane metodą cytrynianową.

1. Introduction

The effect of the alumina addition on properties of yttria stabilized zirconia (YSZ) materials has been extensively discussed in literature for many years. The studies concern cubic (6 to 10 mol. % of Y_2O_3) [1,2] as well as tetragonal (1 to 4mol.% Y_2O_3) grain structure[3,4]. The both forms of zirconia with addition of alumina can be applied in solid oxide fuel cell technology as an electrolyte [5] and component of anode nickel-cermet [6-8].The cubic zirconia shows high ionic conductivity but poor mechanical strength in comparison with tetragonal zirconia. On the other hand, tetragonal zirconia reveals too low conductivity to be commonly used in SOFC. The one way of improving its property is removing from ZrO_2 the natural contaminants that segregated on grain boundaries. The main contaminant of ZrO_2 is silica, which located between ZrO_2 grains and in consequence, hampers conductivity of oxygen ions on the grain boundaries. This blocking effect of SiO_2 on yttria stabilized zirconia (YSZ) materials has been studied for many years, especially in the context of dense, electrolyte material [2,9] but there is a little information about influence of alumina on properties of porous ZrO_2. It is very important issue – due to a possibility of using of porous zirconia as a component of nickel-zirconia cermet, which is a main anode material applied in intermediate-temperature SOFC anode. High porosity is one of the main requirements setting for anode apart from mechanical strength, thermal stability and high ionic-electronic conductivity. Only open porosity above 30 vol. % can ensure sufficient length of triple phase boundary (TPB) for catalytic oxidation of hydrogen on anode. It is well-known fact, that synthesis method can determine microstructure of materials. One of the common way for obtaining highly porous zirconia (even after sintering at 1200°C) is citric method [10,11]. Additionally, microstructure of material influences the ionic conductivity of materials [12], thus method of synthesis can determine the conductivity of resulting materials. However, it should be noted that addition of Al_2O_3 to zirconia matrix causes decreasing of sintering temperature of materials [13]. On the one hand, from energetic point of view, it is beneficial effect but on the other hand it can

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lead to decreasing of porosity of materials. For the electrolyte materials it is favourable effect but not for anode ones.

The main goal of this work was the analysis of influence of synthesis method on microstructural and electrical properties of composite – tetragonal zirconia stabilized in 3 mol. % byY_2O_3 (3YSZ) with addition of 0.5 wt. %, 1.0 wt. % and 2.0 wt. % of alumina.

2. Experimental

Preparation of materials

The modified citric method (described in detail in [6]) was applied for synthesis of 3 mol.% Y_2O_3-ZrO_2 samples. Alumina (in the quantity of 0.5 wt. %, 1.0 wt. % and 2.0 wt. %) was added to the zirconia matrix in three ways:

a) Al_2O_3 powder was obtained by citric method and subsequently mixed in the proper ratio with 3YSZ in propanol suspension in attritor grinder for 12hrs with rate of 350 revolutions per minute, using of 1 mm ZrO_2 balls. Then, Al_2O_3-3YSZ powders were calcinated in 600°C for 6h. In this paper this method was labelled as MM.
b) Aluminium nitrate solution was mixed with other nitrates solutions and treated according to citric method [6]. In this paper this method was labelled as CM.
c) The proper ratio of 3YSZ was mixed with ethanol aluminium nitrate solution in order to obtain the suspension. The latter one was stirred day and night and simultaneously heated at around 60°C until the ethanol evaporated. The obtained wet powder was heated in the dryer and calcinated in the furnace in air at 400°C for one hour (allowing aluminium nitrate to decompose. This method was labelled as IM.

As a result, materials with 0.5wt.%, 1.0wt.% and 2.0wt.% of Al_2O_3 in 3YSZ were obtained. Regardless of the preparation method, the Al_2O_3/3YSZ powders were pressed in pallets and sintered in air atmosphere at 1200°C for 3hrs.

Apparatus

The X-ray diffractograms of powders after calcination were registered using an Philips X'Pert Pro diffractometer (CuKa = 1.5406 Å, 2θ =20-90°). The energy dispersive X-ray spectrometer (EDS -Oxford Instruments) coupled with scanning electron microscopy was used to determine the presence of aluminum in the samples. The microstructure observations of fractures made for disk pallets were carried out on scanning electron microscope (Nova 200 NanoSEM, FEI Company. Density of investigated samples was calculated using geometrical method.

Electrical measurements were carried out on Solartron SI 1260 Impedance/Gain-Phase Analyzer with the SI 1296 dielectric interface. A mixture of 10% H_2 in Ar was used as a gas atmosphere. The measurements were performed at the temperatures: 500, 600, 700 and 750°C at the frequencies from 0.1Hz to 10^6Hz with amplitude of the sinusoidal voltage 10mV. The Pt- paste was applied as the electrode before conductivity measurements. The impedance spectra were analysed using ZPlot software package delivered by Solartron.

3. Results

Phase composition and microstructure analysis

X-ray diffraction patterns of powders obtained by three different methods described above are shown in Fig. 1.

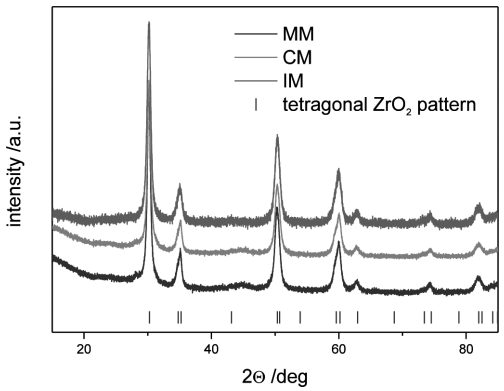

Fig. 1. X-ray diffraction pattern of 2.0%Al_2O_3-3YSZ materials after calcination

All peaks correspond to tetragonal ZrO_2. The identification of Al_2O_3 phase is not possible by this method because of too small amount of aluminium oxide in materials.

The presence of aluminium in the samples was confirmed by EDX analysis (Fig. 2). The crystallites size of materials after calcination, determined from the ZrO_2 (011) peak broadening, shows that crystallites obtained by MM, CM, IM methods have sizes: 13±2 nm, 15±3 nm, 13±3 nm respectively. These results are not surprising because zirconia matrix in each case was obtained in exactly the same way, *i.e.* citric method (CM). Besides, only in the CM process, aluminium was actually added to the system at the beginning of synthesis, when the zirconia matrix was not formed yet.

The SEM micrographs (Fig. 2) show that microstructure of each obtained sample after sintering at 1200 °C is totally different. The individual alumina grains cannot be detected in samples regardless of the method of Al_2O_3 addition employed. So, in the case of materials obtained by CM and IM methods, some similarity in the sizes of grains can be observed. Above materials contain big agglomerates, which are not visible in IM samples. The main reason of lack of agglomerates in structure of IM samples is additional process of suspension mixing in ethanol running around 24 hours and process of milling after decomposition of aluminium precursor (6 hours).

Just like in the case of samples obtained with IM method and samples from MM method, the milling process was carried out. However, the milling time was longer (12 hours). In consequence, MM samples shows similar (non-agglomerates) microstructure as IM samples. Theoretical density for dense ZrO_2 was 6.05 gcm^{-3} and 3.98 gcm^{-3} for Al_2O_3 but sintering temperature and synthesis methods used in presented analysis resulted in porous structure of materials. Analysis of density of samples after sintering (Table 1) show that samples obtained by all methods have lower density than theoretical value for dense material.

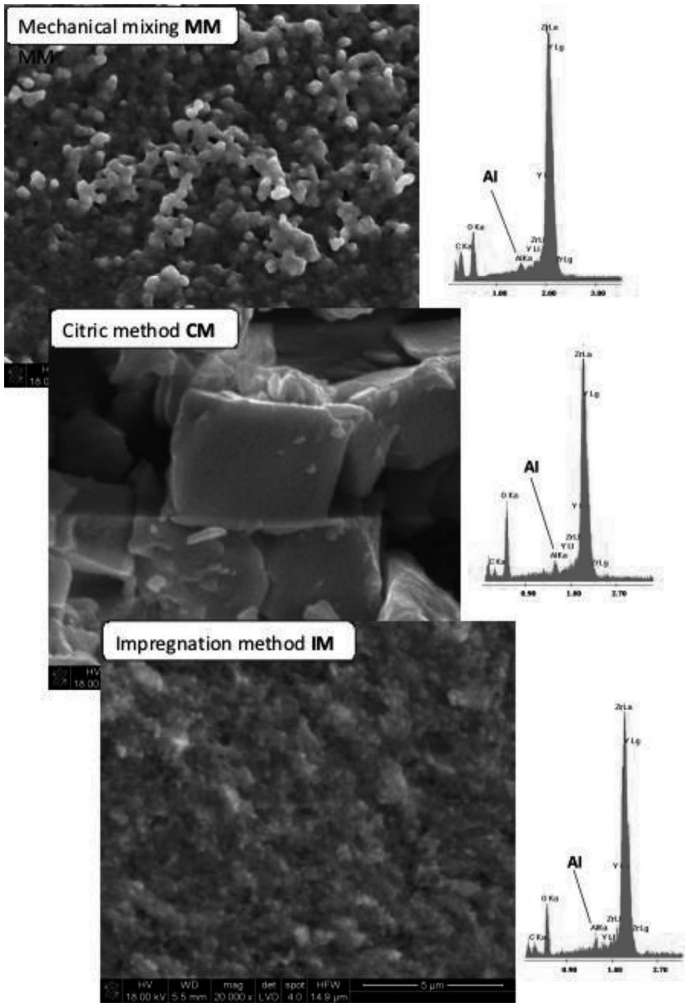

Fig. 2. SEM images and average EDX analysis for 2.0%Al_2O_3/3YSZ samples sintered at 1200°C

TABLE 1
Densities of Al_2O_3/3YSZ samples sintered at 1200°C

sample	density /g·cm^{-3}		
	MM	IM	CM
0.5% Al_2O_3	5.4±0.2	5.6±0.1	4.1±0.2
1.0% Al_2O_3	5.7±0.2	5.6±0.2	3.9±0.2
2.0% Al_2O_3	5.6±0.1	5.5±0.1	3.7±0.2

Non-agglomerated materials reveal significantly higher density than samples prepared by CM method. This is expected effect because citric method and their modifications are often use for preparation of porous materials, i.e. anode composite materials [10, 14]. Total porosity of CM samples was within the range of approx. 32-38 vol.%, which is a satisfactory results for anode materials.

Electrical properties

Impedance spectra registered for all samples (obtained by three presented methods) were analysed using equivalent circuit presented in Fig. 3.

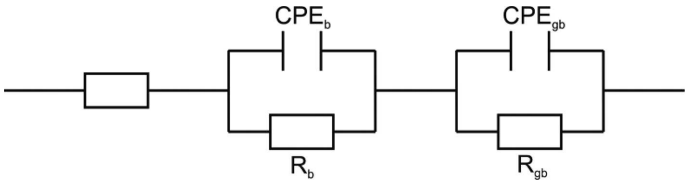

Fig. 3. Equivalent circuit used for interpretation of the impedance spectra

The high-frequency part of the spectrum is related to the specific electrical conductivity of zirconia bulk (σ_b) and the low-frequency semicircle describes electrical conductivity of grain boundaries (σ_{gb}).

The specific conductivity values of tested samples for bulk (σ_b) and grain boundaries (σ_{gb}) were calculated on the basis of determined R_b and R_{gb} values. Comparisons of conductivities of samples obtained by all methods and for basis (pure) tetragonal ZrO_2 as a function of temperature reverse, are show in Fig. 4, 5, 6. The analysed measurements were carried out in temperature range: 500-750°C.

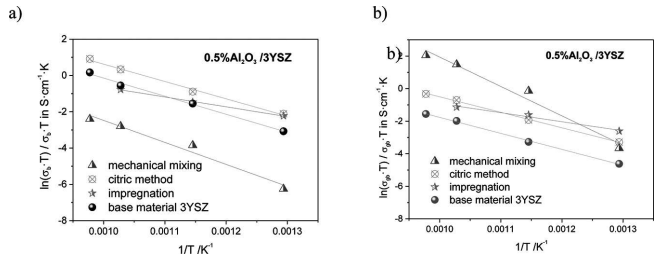

Fig. 4. The comparison of a) bulk (σ_b) and b) boundaries (σ_{gb}) conductivities of 0.5%Al_2O_3 /3YSZ and pure 3YSZ samples sintered at 1200°C

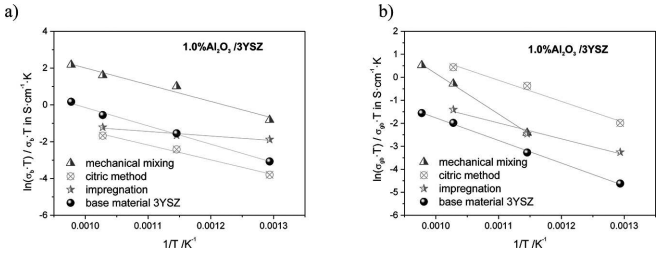

Fig. 5. The comparison of a) bulk (σ_b) and b) boundaries (σ_{gb}) conductivities of 1.0%Al_2O_3 /3YSZ and pure 3YSZ samples sintered at 1200°C

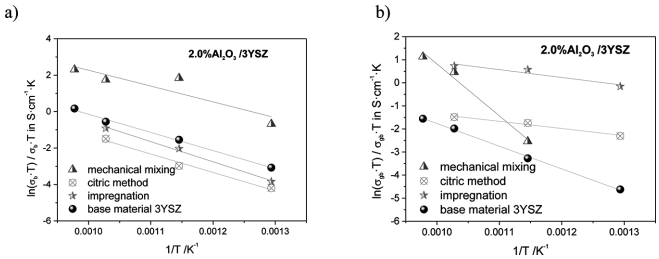

Fig. 6. The comparison of a) bulk (σ_b) and b) boundaries (σ_{gb}) conductivities of 2.0%Al_2O_3 /3YSZ and pure 3YSZ samples sintered at 1200°C

It can be observed that small addition of Al_2O_3 (0.5-2.0 wt. %) in the case of CM and IM samples have almost no influence on bulk conductivity of this materials. However, MM samples reveal considerable improvement of σ_b with an ex-

ception of 0.5%Al_2O_3/3YSZ sample, which shows above one orders of magnitude higher σ_b than non-modified (pure) 3YSZ sample. These results are in good agreement with values of densities presented in Table 1 – samples 1.0%Al_2O_3/3YSZ and 2.0%Al_2O_3/3YSZ reveal similar density but density of 0.5%Al_2O_3/3YSZ sample is insignificantly different.

The most important – from the point of view presented in this paper – is the influence of method of Al_2O_3 addition on grain boundaries conductivity of resulting samples. As can be observed in Fig. 4b, 5b and 6b, the addition of Al_2O_3, regardless of the method and amount of alumina, leads to improvement of boundaries conductivity on average one order of magnitude in comparison with values registered for non-modified samples. Citrate and impregnation methods are more efficient than mechanical mixing method, especially in the case of lower temperature – where, probably, homogenous distribution of alumina in zirconia matrix is particularly important. The comparison of activation energies (E_{act}) of electrical conductivity for all samples (Fig. 7) show that both citrate (CM) and impregnation (IM) methods leads to

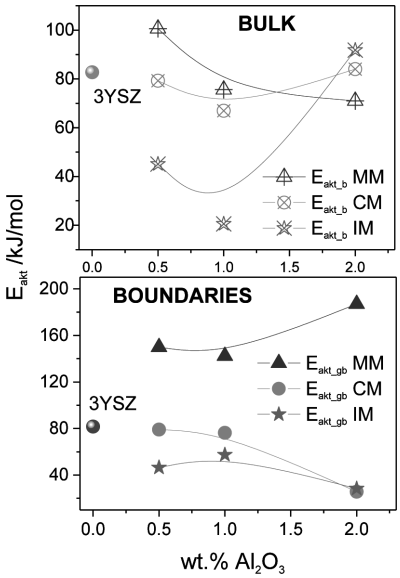

Fig. 7. The comparison of values of energy activation of bulk (top) and grain boundaries (down) conductivities for samples with addition Al_2O_3 and pure 3YSZ

decreasing of energy activation of grain boundaries conductivity (E_{act_gb}). In the case of samples obtained by mechanical mixing of oxides, the values of E_{act_gb} is much bigger than for pure 3YSZ. In the case of bulk conductivity, the values of energy activation (E_{act_b}) are the lowest for sample obtained by IM method for 0.5% and 1.0% of alumina samples but the highest for 2% of Al_2O_3 content.

4. Conclusions

The comparison of three series of Al_2O_3/3YSZ composite indicates that the synthesis methods strongly influences the microstructure of resulting materials. The addition of alumina in the 3YSZ matrix, regardless of method employed, improves grain boundaries conductivity of samples as well as bulk conductivity in the case of samples obtained by MM method. However, MM samples reached the highest values of activation energy of grain boundaries conductivities and very low porosity. Taking into account the results of ionic conductivity analysis and density of prepared samples it can be concluded that samples obtained by CM method reveal the better microstructure than IM and MM samples and sufficient electrical properties in order to be applied for anode materials.

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