Electrical and Mechanical Properties of $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ Composite Solid Electrolytes

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Abstract

Strategic priorities in the field of hydrogen energy include the design of intermediate-temperature solid oxide fuel cells capable of highly efficient operation in the temperature range of 573–973 K. Consequently, attempts are being made to replace the widely applied cubic zirconia electrolyte with an electrolyte consisting of tetragonal zirconia. The rationale for this approach is that 3Y-TZP exhibits higher mechanical strength and higher electrical conductivity at temperatures below 973 K. The addition of Al_2O_3 in an amount that exceeds its solubility limit in 3Y-TZP has been found to result in increased electrical conductivity and improved mechanical properties. The aim of the study was to synthesize 3-YSZ powder via co-precipitation and use it to obtain composites with a 3Y-TZP matrix and 0.5 mol.% or 1.0 mol.% of Al_2O_3 inclusions. The correlation between these samples' electrical conductivity and resistance to brittle fracture and their phase composition and microstructure was investigated by means of X-ray diffractometry, scanning electron microscopy, electrochemical impedance spectroscopy and Vickers indentation tests. For comparison, the properties of composites with an 8-YSZ matrix and Al_2O_3 inclusions were also investigated. It was determined that the composite based on the 3Y-TZP matrix and containing 0.5 mol.% of Al_2O_3 inclusions can be considered a viable alternative for 8-YSZ electrolytes in IT-SOFC applications.

Keywords Zirconia electrolyte · microstructure · electrical conductivity · mechanical properties

Introduction

In a balanced power system based on renewable energy sources, which are invariably characterized by fluctuations in power output, the ability to effectively store energy over longer periods is crucial. A frequently proposed solution for energy storage is the application of hydrogen as an energy carrier. Its advantages include high power density, suitability for long-term storage, and the fact that carbon dioxide is not released during its conversion to electrical energy. Furthermore, hydrogen obtained during the electrolysis of water conducted using surplus energy generated from renewable energy sources may be utilized not just to balance power systems, but also in industrial or transport-related applications.¹ The cornerstone of hydrogen energy is fuel cell technology. Fuel cells are electrochemical devices which directly convert

the chemical energy stored in the supplied fuel into electrical energy and heat with an efficiency ranging from 60% to 80%.² Solid oxide fuel cells (SOFCs), which are capable of efficient operation at temperatures from 1073 K to 1273 K, are currently one of the most popular types of electrochemical devices.^{2,3}

SOFCs feature a solid electrolyte; the function of this essential component is to transport oxygen ions between the cathode and the anode.^{2,3} Consequently, the prerequisites for an electrolyte material include conductivity that is purely ionic in character, gas-tightness, and morphological and chemical stability in atmospheres corresponding to the cathode and anode sides of the SOFC.^{2,3} To reduce ohmic resistance, anode-supported or cathode-supported cells (ASCs and CSCs, respectively) which feature a thin layer of the electrolyte are applied.⁴ For such cell types to exhibit high mechanical durability, an electrolyte with sufficiently high mechanical stability and resistance to cracking must be applied.

In recent years, a number of studies have focused either on the development of new electrolyte materials specifically designed for application in intermediate-temperature

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solid oxide fuel cells (IT-SOFCs)—a sub-type capable of high-efficiency operation at temperatures in the range of 873–1073 K^{3,5}—or the modification of existing ones. In this regard, materials based on tetragonal zirconia with a 3 mol.% addition of yttria (3Y-TZP) seem to be particularly promising. The advantages of this material, colloquially referred to as "ceramic steel", over the commonly applied fully stabilized cubic zirconia (C-YSZ) are its considerable mechanical strength and superior ionic conductivity below 973 K.⁶

3Y-TZP has nevertheless not seen widespread adoption as a solid electrolyte in fuel cells due to the high electrical resistance of grain boundaries in this material. One of the reasons for this disadvantage is the presence of impurities—mostly silica—which surround the ZrO_2 grains and inhibit the diffusion of oxygen ions.⁷ This is known as the blocking effect.⁸ Possible solutions include the development of a composite ionic conductor composed of tetragonal zirconia as the matrix and alumina inclusions. The research conducted on the subject thus far has shown that the introduction of alumina into zirconia fully stabilized with yttria removes the aforementioned impurities from grain boundaries in the latter. When Butler and Drennan conducted microscopic observations,⁹ they found that alumina undergoes a chemical reaction with the silica located at grain boundaries and acts as a scavenger of sorts, removing elements that adversely affect ion transport from grain boundaries. The results of impedance measurements presented in the cited paper indicate that an alumina addition has a positive influence on both grain boundary conductivity and—by virtue of modifying the microstructure—on the total conductivity of zirconia-based materials.¹⁰ These results provided an incentive for subsequent research on the effect of alumina on the physicochemical properties of zirconia in its role as a solid electrolyte. The most significant conclusions from experiments investigating $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ composite materials are as follows:

- The solubility of alumina in the interior of zirconia grains is very limited—for 8-YSZ at 1923 K, it is ca. 0.7 mol.%,¹¹ while at grain boundaries it is 10 times higher.^{9,12,13}
- When the alumina content in zirconia is below the solubility limit, the conductivity of both grain interiors and boundaries decreases slightly.^{12,14}
- 3Y-TZP with a 0.5 mol.% alumina content exhibits the highest grain boundary and grain interior electrical conductivity in comparison to unmodified 3Y-TZP and 3Y-TZP samples containing 0.25 or 1.0 mol.% of alumina.¹⁵
- The ionic conductivity of grain interiors in zirconia with a small number of alumina inclusions is similar or slightly lower, while grain boundary conductivity.

ity.^{12,16–18} Consequently, the aforementioned scavenger effect occurs and Al_2O_3 inclusions displace the impurities to grain boundary triple junctions.¹⁹

- When the solubility limit is exceeded significantly, a marked drop in ionic conductivity values for both grain interiors and boundaries is observed,^{11,12,20,21} which is explained via the effective medium theory.²²
- Alumina cations in the crystal lattice of ZrO_2 increase the activation energy of grain interior and grain boundary conductivity.^{12,16,18}

This short review of literature shows that adding alumina to $\text{ZrO}_2\text{-Y}_2\text{O}_3$ materials affects their transport properties in a complex way; whether the effect on electrical conductivity is negative or positive ultimately depends not only on the Al_2O_3 concentration, but also to a large extent on the microstructure and the procedure applied for the synthesis of the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ composite.

The function played by the electrolyte in a SOFC requires the material to exhibit not only high ionic conductivity, but also adequate mechanical properties. Electrolyte materials for SOFC applications must have a flexural strength of over 500 MPa and a tensile cracking strength of more than $3 \text{ MPa}\cdot\text{m}^{-2}$.²³ In order for these criteria to be met, inert corundum inclusions must be added to the zirconia material, which yields a particulate composite with areas characterized by different levels of mechanical stress. The increased resistance to brittle fracture and the concurrent inhibition of grain growth, which result in improved mechanical strength of composites composed of the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid solution and Al_2O_3 inclusions, are associated with two phenomena. The first of these is the removal of the glassy phase from phase and grain boundaries during the reaction with alumina, leading to the modification of these boundaries.¹⁹ The second phenomenon is related to additional mechanisms that absorb the elastic strain energy released due to the formation of Al_2O_3 inclusions. The most commonly observed mechanisms of this type are crack bridging and crack path deviation in a ceramic material.²⁴

The effect of alumina inclusions on the mechanical properties of cubic and tetragonal $\text{ZrO}_2\text{-Y}_2\text{O}_3$ has been studied extensively.^{17,25–32} Research on the subject has provided the following insights and results:

- Small amounts of alumina, such as 0.56 mol.%, intensify the densification of 3Y-TZP. In addition, Sakka et al. reported enhanced tensile deformation during the superplastic flow of nanocomposites.^{31–33}
- Adding small amounts of alumina (0.375–1.5 mol.%) to 3Y-TZP yields ceramics with improved toughness,^{34,35} while large amounts of alumina (23–65 mol.%) increase the strength and hardness of the material, but

also decrease fracture toughness (K_{Ic}) due to the growth of Al_2O_3 grains.³⁶

- A fully dense nanocrystalline 3Y-TZP/ Al_2O_3 composite was characterized by a hardness of 4.45 GPa and a toughness of $8.38 \text{ MPa}\cdot\text{m}^{1/2}$.³⁷
- A dense 3Y-TZP/ Al_2O_3 nanoceramic obtained using the colloidal method with a 3.08 mol.% addition of alumina exhibited increased average hardness and toughness at levels of 16.23 GPa and $7.86 \text{ MPa}\cdot\text{m}^{1/2}$, respectively.³⁰
- A freely sintered 8-YSZ composite with up to 23.6 mol.% of Al_2O_3 inclusions exhibited increased flexural strength. Increasing the alumina content beyond that value did not strengthen the material further.^{12,26}
- A cubic zirconia composite obtained via rapid free sintering at a rate of $1093 \text{ K}\cdot\text{h}^{-1}$ exhibited a significant increase in brittle fracture resistance (up to 480 MPa).³⁸
- A considerable improvement in the brittle fracture coefficient (K_{Ic})—from $1.5 \text{ MPa}\cdot\text{m}^{1/2}$ for the cubic zirconia matrix to $2.4 \text{ MPa}\cdot\text{m}^{1/2}$ for a composite containing 12.1 mol.% of Al_2O_3 inclusions was reported.²⁸

These observations lead to the conclusion that the effect of an alumina addition on the mechanical properties of tetragonal and cubic zirconia largely depends on the alumina content and the method applied to prepare the composites.

The objectives of the study were to obtain composite $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ sinters using powders prepared using the gelatin method, and to then investigate the influence of the added amount of alumina on the structural, microstructural, mechanical and electrical properties of solid electrolyte materials in the context of their application in intermediate-temperature solid oxide fuel cells (IT-SOFCs).

Preparation of Materials

This section described the procedures used to obtain two types of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid solution powders containing 3 and 8 mol.% of YSZ (3-YSZ and 8-YSZ) as well as 3Y-TZP, 8-YSZ, 3Y-TZP/ Al_2O_3 and 8-YSZ/ Al_2O_3 samples.

Co-Precipitation of Powders

Solid solution powders with 3 and 8 mol.% of YSZ (3-YSZ and 8-YSZ) were obtained via the calcination of partially amorphous gel consisting of co-precipitated hydroxides.³⁹

The precursors used for co-precipitation were zirconium oxychloride (ZrOCl_2) and yttrium oxide (Y_2O_3). An aqueous NH_3 solution was used as the precipitating reagent. All reagents were analytical grade and supplied by POCH-Gliwice.

In the first stage, ZrOCl_2 was dissolved in distilled water to obtain a solution with the concentration of $1.13 \text{ mol}\cdot\text{dm}^{-3}$. YCl_3 was prepared via the hot dissolution of the appropriate amount of Y_2O_3 in concentrated hydrochloric acid. The two

solutions were mixed at volume ratio corresponding to the desired nominal composition. The obtained mixtures were added dropwise to a vigorously stirred aqueous ammonia solution. The pH of the solution was maintained at 9 throughout the co-precipitation process.

The volume of the precipitating agent was ca. 10% higher than the volume corresponding to the stoichiometric ratios. The application of an alkaline medium made it possible to simultaneously precipitate zirconium and yttrium hydroxides and to obtain homogeneous gels. In the next stage, these gels were rinsed multiple times using distilled water, using decantation as a means of removing ammonium chloride, since its presence during sintering is undesirable. During this part of the process, the pH of the solution was maintained at 8, which accelerated the sedimentation of the gels. The gels were rinsed until Cl^- ions were no longer present, which was verified using an AgNO_3 aqueous solution. In the subsequent stage, the precursors were filtered using the Büchner funnel. The sediment was rinsed with an isopropyl alcohol solution, which prevented the formation of agglomerates.

The gels obtained in the above-described way were dried and calcined for 2 h in air at 1073 K. The prepared 3-YSZ and 8-YSZ powders were milled in an attritor mill with zirconia balls for 8 h.

Powder Impregnation

The obtained 3-YSZ and 8-YSZ powders were impregnated with an alcohol solution of aluminum nitrate to prepare four types of mixtures in total. Two mixtures (one for each type of powder) contained 0.5 mol.% of Al_2O_3 , while the other two contained 1.0 mol.%.

During impregnation, the powder placed in a glass container filled with an alcohol solution of aluminum nitrate was vigorously stirred for 24 h using a magnetic stirrer. The obtained mixtures were annealed for 1 h in air at 1073 K. For reference, certain amounts of unmodified 3-YSZ and 8-YSZ powders were heated under the same conditions in order to eliminate microstructural changes stemming solely from thermal treatment.

Sinter Preparation

To obtain dense sinters, two series of powders after calcination and impregnation were milled and then formed into pellets via preliminary uniaxial pressing under 100 MPa. The green bodies then underwent cold isostatic pressing under 250 MPa and free sintering. The green bodies were thermally treated in air at 1773 K for 2 h. The entire procedure yielded two series of sinters—one that included 3Y-TZP sinters with 0.5 mol.% and 1.0 mol.% of Al_2O_3 , and another with 8-YSZ sinters with 0.5 mol.% and 1.0 mol.% of Al_2O_3 . 3Y-TZP and 8-YSZ served

as reference samples in the first and second series, respectively. The pellets into which the sinters had been formed were ca. 7 mm in diameter and had a thickness of around 2 mm.

Research Methodology

The phase composition of the samples was evaluated by means of X-ray diffraction, using the PANalytical X'Pert Pro X-ray diffractometer and CuK_α monochromatic radiation. A 2θ angle range of $10\text{--}100^\circ$ was applied, with a step size of 0.008° and a time of 80 s per single step. The HighScore Plus software was used for phase identification and to perform Rietveld refinement, which allowed the lattice constants and mass fractions of the phases detected in the samples to be determined.

The microstructure of the powders and sinters was studied using an ultrahigh-resolution scanning electron microscope equipped with a Schottky field emission gun—the Nova NanoSEM 200 manufactured by FEI Europe.

Sample density was estimated using values of true density, apparent density and theoretical density. True density was determined with a helium pycnometer (AccuPyc HP 1340), apparent density was established via Archimedes' method with water as the immersion medium, while the theoretical one was computed from crystallographic data. To determine relative density, apparent density was divided by the theoretical density. Two equations were used to determine open (Eq. 1) and total (Eq. 2) porosities:

$$P_o = \frac{V_o - V_{\text{pic}}}{V_o} \cdot 100\% \quad (1)$$

$$P_c = \left(1 - \frac{\rho_a}{\rho_{\text{XRD}}}\right) \cdot 100\% \quad (2)$$

where: P_o —open porosity [%], P_c —total porosity [%], V_o —geometric volume [cm^3], V_{pic} —volume determined using the pycnometer [cm^3], ρ_a —apparent density [$\text{g}\cdot\text{cm}^{-3}$], and ρ_{XRD} —X-ray density of the sample [$\text{g}\cdot\text{cm}^{-3}$]. Closed porosity is understood as the difference between the total porosity and open porosity.

The specific surface area of the powders was calculated by means of the BET technique applied with the use of the ASAP 2010 v4.00 G apparatus manufactured by Micromeritics. Based on known surface area values, the mean diameter of BET particles (assuming their cubic shape) was calculated from the following equation:

$$d_{\text{BET}} = \frac{6}{S \cdot \rho_{\text{XRD}}} \quad (3)$$

where: d_{BET} —diameter of a spherical grain [μm], S —specific surface area of the sample [$\text{m}^2\cdot\text{g}^{-1}$].

The electrical properties of samples were investigated using electrochemical impedance spectroscopy (EIS), by means of a Solartron FRA 1260 frequency response analyzer coupled with the 1294 dielectric interface (also by Solartron). The measurements were conducted in air at temperatures ranging from 573 K to 1023 K, for a frequency range from 0.1 Hz to 1 MHz and an amplitude of 10 mV. The ZView application was used to fit the equivalent circuit and to determine the parameters of its elements. The established resistance values and the geometric dimensions of the samples were used to calculate the electrical conductivity of grain interior (σ_b) and boundaries (σ_{gb}), according to the formula:

$$\sigma_{b,\text{gb}} = \frac{L}{S \cdot R_{b,\text{gb}}} \quad (4)$$

where: L —sample thickness [cm], S —cross-sectional surface area [cm^2], $R_{b,\text{gb}}$ —electrical resistance of the grain interior (b) or grain boundaries (gb) [Ω].

As per the methodology described in,⁴⁰ the specific grain boundary electrical conductivity ($\sigma_{\text{sp,gb}}$) was determined. This parameter is usually computed from the brick layer model widely adopted for ceramic materials,^{10,41} according to the following equation:

$$\sigma_{\text{sp,gb}} = \frac{\delta}{d} \sigma_{\text{gb}} \quad (5)$$

where: δ —grain boundary width [nm], d —mean grain size [nm] and σ_{gb} —electrical conductivity of grain boundaries, expressed as $\sigma_{\text{gb}} = \frac{L}{S \cdot R_{\text{gb}}}$.

For these calculations, it was assumed that $\delta = 3$ nm.⁴² This value is close to the 2.9 nm reported by Martin and McCartney⁴⁰ for 8-YSZ. On the other hand, the mean grain size (d) for the studied specimens was determined based on the results of morphological observations presented in Figs. 4 and 5.

The Vickers hardness and fracture toughness of the samples were determined based on the results of measurements performed using the FV-700 hardness tester (Future-Tech Corp.) with a pyramidal indenter. Loads of 9.81 N, 49.05 N and 98.07 N were applied for 10 s. The Vickers hardness values were calculated from the following formula:

$$H_V = \frac{F}{S} \Rightarrow 1,8544 \cdot \frac{F}{d^2} [\text{GPa}] \quad (6)$$

where: F —the applied force [N], $d = (d_1 + d_2)/2$ —mean length of the indentation's diagonal [m].

The critical stress intensity factor (K_{Ic}) was estimated by measuring the length of cracks originating at the corners of the indentations made during the Vickers hardness test. The following formulae by Niihara et al.⁴³ and Anstis et al.⁴⁴ were applied:

Fig. 1 XRD pattern recorded for a 3-YSZ powder obtained after calcining co-precipitated gel for 2 h in air at 1073 K.

- for radial cracks—when $c/a > 2.5$:

$$\left(\frac{K_{Ic} \cdot \varphi}{H \cdot a^{1/2}} \right) \cdot \left(\frac{H}{E \cdot \varphi} \right)^{2/5} = 0.129 \left(\frac{c}{a} \right)^{-3/2} \quad (7)$$

- for Palmqvist cracks—when $c/a < 2.5$:

$$\left(\frac{K_{Ic} \cdot \varphi}{H \cdot a^{1/2}} \right) \cdot \left(\frac{H}{E \cdot \varphi} \right)^{2/5} = 0.035 \left(\frac{1}{a} \right)^{-1/2} \quad (8)$$

where a —one-half of the length of an indentation's diagonal, l —crack length, $c = a + l$, H —Vickers hardness, σ_y —yield point, E —Young modulus (a value of 345 GPa was assumed) and φ —safety factor ($\varphi = H/\sigma_y \cong 3^{43}$).

Results and Discussion

Physicochemical Properties of Powders

Figure 1 shows the XRD pattern recorded for the 3-YSZ powder obtained by calcining the co-precipitated gel for 2 h in air at 1073 K. Numerical analysis of the obtained XRD patterns, performed via Rietveld refinement, revealed that each of the analyzed powders had a dual-phase composition.

Table I lists the mass fractions of individual phases and their lattice constants. These data show that the tetragonal phase is predominant in the case of the 3-YSZ powder, the 8-YSZ powder contains a cubic majority phase, and the monoclinic phase of zirconia has the smaller mass fraction in both powders. These results are consistent with the literature data.¹⁵

Table II shows the values of specific surface area obtained via the BET method for the studied 3-YSZ and 8-YSZ powders and the mean particle size determined from these values using Eq. 3. In addition, it lists the respective crystallite size values calculated from the Scherrer equation.⁴⁵ Increased amounts of the Y₂O₃ stabilizer in zirconia are clearly associated with an increase in the specific surface area of the analyzed powders and a decrease in the size of crystallites of majority phases as well as the mean particle size determined via BET.

Figure 2 shows the SEM micrographs of the calcined 3-YSZ (Fig. 2a) and 8-YSZ (Fig. 2b) powders. The grains of the investigated powders have a roughly oval shape and a size ranging from 0.05 μm to 0.2 μm, and they have a tendency to agglomerate in clusters formed by numerous grains. The morphology of these powders suggests the presence of spherical grains embedded in one another and their dense

Table I Mass fractions of phases identified in 3-YSZ and 8-YSZ powders obtained after calcination and the corresponding lattice constants

Sample	3-YSZ		8-YSZ	
Phase	Tetragonal	Monoclinic	Cubic	Monoclinic
Mass fraction [%]	71.2	28.8	97.4	2.6
Lattice constants [nm, °]	$a = 0.360912$ $c = 0.517205$	$a = 0.515642$ $b = 0.521196$ $c = 0.531799$ $\beta = 99.1501$	$a = 0.513684$	$a = 0.519334$ $b = 0.525301$ $c = 0.526787$ $\beta = 98.7624$

Table II Crystallite size determined via XRD and the specific surface area and mean particle size estimated using the BET method for 3-YSZ and 8-YSZ powders prepared by calcinating co-precipitated gel for 2 h in air at 1073 K

Sample	3-YSZ		8-YSZ	
Identified phase	Tetragonal	Monoclinic	Cubic	Monoclinic
Crystallite size (XRD) [nm]	15	18	10	100
Specific surface area (BET) [m ² ·g ⁻¹]	23.39 ± 0.04		38.18 ± 0.12	
X-ray density [g·cm ⁻³]	6.0592		5.9978	
Mean particle size (BET) [nm]	4.2		2.6

Fig. 2 SEM micrographs of (a) 3-YSZ and (b) 8-YSZ powders obtained by calcining co-precipitated gel for 2 h in air at 1073 K.

Fig. 3 XRD pattern recorded for the 3Y-TZP sample with 0.5 mol.% of Al_2O_3 obtained through 2 h of thermal treatment in air at 1773 K.

agglomerates that do not have an overly developed surface. The size of individual agglomerates varies from 0.3 μm to 0.8 μm for 3-YSZ and from 0.2 μm to 1 μm for 8-YSZ.

Physicochemical Characteristics of Samples

Phase Composition

The phase composition of 3Y-TZP and 8-YSZ samples as well as those samples modified with either 0.5 mol.% or 1.0 mol.% of Al_2O_3 —all of which were obtained through 2 h of thermal treatment in air at 1773 K—was analyzed and was found to vary depending on the amount of the yttria stabilizer and the amount of alumina added in the form of inert inclusions in the zirconia matrix. Figure 3 presents the XRD pattern recorded for the 3Y-TZP sample with 0.5 mol.% of Al_2O_3 .

Table III lists the mass fractions and lattice constants of individual phases in the studied samples. The obtained data show that both the unmodified 3Y-TZP samples and the 3Y-TZP samples synthesized from the powders with alumina additions contained two phases—the tetragonal phase and the cubic one, with the former making up more than 94% of the total mass. The samples obtained after impregnation with alumina also contained the corundum phase. The lattice constants and the unit cell volumes of both the tetragonal and the cubic phase were very similar in all 3Y-TZP samples.

This indicates that the amount of introduced alumina does not affect the chemical composition of the two zirconia phases in the investigated samples. Furthermore, part of the added Al_2O_3 apparently does not segregate at grain boundaries in the 3Y-TZP material, and does not remove silica in this region. Based on the data shown in Table III, a drop in the lattice constant values—and subsequently the

Table III Mass fractions of the phases identified in the studied samples obtained through 2 h of sintering in air at 1773 K and the corresponding lattice constants (t- ZrO_2 —tetragonal zirconia, c- ZrO_2 —cubic zirconia)

Sample	Identified phase	Mass fraction (%)	Lattice constant (nm, °)	Unit cell volume (10^6 pm^3)
3Y-TZP	t- ZrO_2	95.5	0.360624 (7) 0.51788 (1)	67.35021
	c- ZrO_2	4.5	0.5125675	134.66450
3Y-TZP/0.5 mol.% of Al_2O_3	t- ZrO_2	94.7	0.360647 (7) 0.51803 (1)	67.37861
	c- ZrO_2	4.4	0.5125675	134.66450
	Corundum	0.9	0.47594 (3) 1.3002 (1) 120	255.06610
3Y-TZP/1.0 mol.% of Al_2O_3	t- ZrO_2	94.4	0.360695 (7) 0.51811 (1)	67.40692
	c- ZrO_2	4.4	0.5125675	134.66450
	Corundum	1.2	0.47594 (2) 1.30038 (6) 120	255.10270
8-YSZ	c- ZrO_2	100	0.59245	219.8400
8-YSZ/0.5 mol.% of Al_2O_3	c- ZrO_2	100	0.513958 (7)	135.76360
8-YSZ/1.0 mol.% of Al_2O_3	c- ZrO_2	100	0.513846 (7)	135.67480

unit cell volumes—can be observed for the single-phase 8-YSZ sinters obtained from powders after the addition of alumina.

This can be explained via the following defect reaction, which represents the process whereby zirconia is doped with alumina:

in which—in accordance with the Kröger-Vink notation— Al_i^{3+} stands for the tripositive aluminum ion in the interstitial position of the zirconia lattice, $\text{V}_{\text{O}}^{\bullet\bullet}$ is the fully ionized vacancy in the oxygen sublattice, and O_{O}^x represents an oxygen ion in the lattice site.

Taking into account the ionic radii of both zirconium ions ($r_{\text{Zr}^{4+}} = 98$ pm) and aluminum ions ($r_{\text{Al}^{3+}} = 67.5$ pm) as well as the noticeable change in the lattice constants and unit cell volumes of the zirconia phase, it can be suggested that aluminum ions incorporate at interstitial positions in the studied zirconia materials. This is consistent with the criterion for the formation of solid solutions.⁴⁶ According to this criterion concerning ionic radii, the formation of substitutional solid solutions is favored when the difference between the base ion (Zr^{4+} in this case) and the dopant ion (Al^{3+}) does not exceed 15%. On the other hand, for higher differences the formation of interstitial solid solutions is predominant. For the studied materials this can be represented as follows:

$$\frac{r_{\text{Zr}^{4+}} - r_{\text{Al}^{3+}}}{r_{\text{Zr}^{4+}}} \times 100 = 31\% \quad (10)$$

Morphology and Chemical Composition

The polished specimens of 3Y-TZP/ Al_2O_3 and 8-YSZ/ Al_2O_3 samples as well as the corresponding reference materials were examined via SEM in order to establish the influence of phase composition and alumina addition on the microstructure of these samples.

Figure 4 shows the cross-sectional morphology of samples with compositions of 3Y-TZP, 3Y-TZP/0.5 mol.% of Al_2O_3 , and 3Y-TZP/1.0 mol.% of Al_2O_3 . These observations showed that these samples had a fine-crystalline grain morphology with a small number of pores. All of the analyzed samples were practically homogeneous, and the dimensions of a large population of grains were approximately isometric. Grain size for the 3Y-TZP sample ranged from around 0.1 μm to ca. 1.2 μm , while the grain size ranges for its counterparts modified with 0.5 and 1.0 mol.% were 0.1–0.4 μm and 0.2–0.8 μm , respectively. It should be mentioned that samples from the 3Y-TZP series also contained a certain number of large, isolated grains with a size of 1.2–1.7 μm .

Figure 5 shows the SEM micrographs of the 8-YSZ samples without alumina addition and with either 0.5 mol.% or 1.0 mol.% of Al_2O_3 . The samples from this series were characterized by very large grains, some of which had a size in excess of 5 μm , surrounded by grains that were several times smaller (ca. 0.5 μm). These grains were irregular in shape. The differences in mean grain size between the reference 8-YSZ samples and those obtained after alumina addition are negligible. The cubic phase grains of this series of samples were surrounded by fine, black precipitates, which correspond to the corundum phase.

It is widely known that the main disadvantage of coarse-crystalline, tetragonal $\text{Y}_2\text{O}_3\text{-ZrO}_2$ solid solutions is the tetragonal-to-monoclinic phase transition that occurs at low temperatures (473–573 K) and is accompanied by significant changes in molar volumes.⁴⁷ The result is the deterioration of both mechanical properties and electrical conductivity.⁴⁸ This phenomenon is also observed when the size of grains in a 3Y-TZP material exceeds the critical value of ca. 0.3 μm .⁴⁸ In view of the above, it can be concluded that the 3Y-TZP/0.5 mol.% of Al_2O_3 is the most stable electrolyte material.

Fig. 4 SEM micrographs of the cross-sections of the following samples obtained through 2 h of sintering in air at 1773 K: (a) 3Y-TZP, (b) 3Y-TZP/0.5 mol.% of Al_2O_3 , (c) 3Y-TZP/1.0 mol.% of Al_2O_3 .

Fig. 5 SEM micrographs of the cross-sections of the following samples obtained through 2 h of sintering in air at 1773 K: (a) 8-YSZ, (b) 8-YSZ/0.5 mol.% of Al_2O_3 , (c) 8-YSZ/1.0 mol.% of Al_2O_3 .

Sample Density

The density of the investigated samples (3Y-TZP, 3Y-TZP/0.5 mol.% of Al_2O_3 , 3Y-TZP/1.0 mol.% of Al_2O_3 , 8-YSZ, 8-YSZ/0.5 mol.% of Al_2O_3 and 8-YSZ/1.0 mol.% of Al_2O_3) was determined based on the known true density values determined using the helium pycnometer as well as volumetric and theoretical density values.

Table IV lists the measured values of open, closed and total porosity as well as the relative and theoretical density of the studied samples. The listed values were calculated using Eqs. 1 and 2. The highest relative density and thus the lowest porosity was determined for the 8-YSZ sample obtained from the powder with a 1.0 mol.% addition of Al_2O_3 , whereas the lowest density—corresponding to a total density of 16.71%—was observed for its counterpart from the 3Y-TZP series.

Despite the fine-grained nature of the powders, which had been synthesized via co-precipitation, the samples obtained from them were characterized by fairly low relative density. Assuming that at a relative density of ca. 90% the porosity is almost entirely closed (with a very low fraction of open porosity), all studied samples with the exception of the 3Y-TZP sample with 1.0 mol.% of Al_2O_3 should be gas-tight and thereby suitable as electrolyte materials for application in IT-SOFCs.

Resistance to Brittle Fracture

The brittle fracture coefficient (K_{Ic}), which is a direct measure of a material's resistance to cracking, was estimated based on Vickers indentation tests.

Table V lists the lengths of the d_1 and d_2 diagonals measured for the two applied loads of 9.81 N and 49.05 N as well as the Vickers hardness values determined from dependence Eq. 6 for the studied samples. The presented data show that the H_V values measured at the lower load (9.81 N) do not differ significantly from those measured at the higher one (49.05 N). In the case of the 3Y-TZP series, the Al_2O_3 addition of 0.5 mol.% does not improve the hardness of the material, and for 1.0 mol.% of Al_2O_3 hardness actually decreases. This is a consequence of the low relative density of the sinter with the higher alumina content. A somewhat different tendency with regard to H_V is observed for the 8-YSZ samples, which had a cubic structure. The 8-YSZ material with 0.5 mol.% of Al_2O_3 has the highest Vickers hardness, whereas the hardness of the sinter with 1.0 mol.% of Al_2O_3 is lower, but nevertheless higher than that of the reference sample.

Table VI lists the lengths of fractures (l_1, l_2, l_3, l_4) caused by applying the load of 49.05 N and the brittle fracture coefficient (K_{Ic}) values calculated for the investigated samples. In the case of the 3Y-TZP series of samples, K_{Ic} values were calculated from dependence Eq. 8 proposed by Niihara et al. since for $c/a < 2.5$ Palmqvist cracks are observed, while for the second series (8-YSZ) dependence Eq. 7 derived by

Table IV Porosity and theoretical as well as relative density of the investigated samples, obtained through 2 h of sintering in air at 1773 K

Sample	Porosity [%]			Theoretical density [g·cm ⁻³]	Relative density [%]
	Open	Closed	Total		
3Y-TZP	1.59	8.23	9.82	6.0672	90.18
3Y-TZP/0.5 mol.% of Al_2O_3	0.27	10.06	10.33	6.0647	89.67
3Y-TZP/1.0 mol.% of Al_2O_3	7.12	9.59	16.71	6.0621	83.29
8-YSZ	0.69	9.34	10.03	5.9245	89.97
8-YSZ/0.5 mol.% of Al_2O_3	1.23	9.65	10.88	5.9258	89.12
8-YSZ/1.0 mol.% of Al_2O_3	0.55	9.18	9.73	5.9297	90.27

Table V Lengths of the d_1 and d_2 diagonals as well as Vickers hardness values measured at loads of 9.81 N and 49.05 N for 3Y-TZP and 8-YSZ samples obtained through 2 h of sintering in air at 1773 K

Sample	Load [N]							
	9.81		49.05					
	d_1 [μm]	d_2 [μm]	H_V	H_V [GPa]	d_1 [μm]	d_2 [μm]	H_V	H_V [GPa]
3Y-TZP	39.97	40.22	1174.9	11.51	84.07	85.04	1297.5	12.72
3Y-TZP/0.5 mol.% of Al ₂ O ₃	38.37	38.51	1259.5	12.35	86.23	86.21	1247.9	12.23
3Y-TZP/1.0 mol.% of Al ₂ O ₃	39.13	39.15	1210.4	11.87	90.79	91.01	1123.2	11.01
8-YSZ	38.39	39.22	1249.5	12.25	87.08	87.05	1124.4	11.02
8-YSZ/0.5 mol.% of Al ₂ O ₃	39.28	39.37	1210.6	11.87	84.87	85.55	1277.2	12.52
8-YSZ/1.0 mol.% of Al ₂ O ₃	38.46	38.53	1257.1	12.33	89.92	88.80	1159.9	11.37

Table VI Lengths of cracks (l_1 , l_2 , l_3 , l_4) caused by applying a load of 49.05 N and the brittle fracture coefficient (K_{Ic}) values calculated for 3Y-TZP and 8-YSZ samples obtained through 2h of sintering in air at 1773 K (a —one-half of the length of an indentation's diagonal, $c = a+l$)

Sample	l_1 [μm]	l_2 [μm]	l_3 [μm]	l_4 [μm]	c/a_1	c/a_2	K_{Ic} [MPa·m ^{0.5}]
3Y-TZP	30.86	30.00	20.39	25.79	1.72	1.54	6.61
3Y-TZP/0.5 mol.% of Al ₂ O ₃	23.47	23.95	25.09	25.10	1.55	1.58	7.50
3Y-TZP/1.0 mol.% of Al ₂ O ₃	19.31	19.30	20.24	18.10	1.43	1.42	8.22
8-YSZ	125.6	128.4	89.00	89.00	3.92	3.04	3.08
8-YSZ/0.5 mol.% of Al ₂ O ₃	111.9	112.1	120.1	110.8	3.64	3.70	3.45
8-YSZ/1.0 mol.% of Al ₂ O ₃	76.45	76.45	88.85	91.6	2.70	3.03	4.17

Anstis et al. was used, since in this case the c/a ratio was higher than 2.5. Based on these data, it can be concluded that the polycrystalline 3Y-TZP samples with a predominantly tetragonal structure are characterized by significantly higher K_{Ic} values than the samples based on cubic zirconia stabilized with 8 mol.% of yttria (8-YSZ).

These values are consistent with those reported in the literature, which range between 6 and 12 MPa·m^{0.5} for Y-TZP and Ce-TZP materials.⁴⁹ This confirms that polycrystalline tetragonal zirconia samples are suitable for both low- and intermediate-temperature applications. It is worth mentioning that the introduction of inert inclusions of alumina into the matrix of 3Y-TZP and 8-YSZ samples causes their K_{Ic} to increase systematically with the amount of this additive. In the case of 3Y-TZP samples, the addition of 1.0 mol.% of Al₂O₃ yields a 20% increase in K_{Ic} values compared to the reference sample. The increase in the 3Y-TZP and 8-YSZ materials' resistance to brittle fracture caused by the appearance of alumina inclusions in their matrix is generally attributed to the crack deflection caused by the residual stress field.⁵⁰ These stresses originate from differences in the Young's moduli of the two phases and their thermal expansion coefficients (TECs). Since the TECs of the 3Y-TZP and 8-YSZ are higher than that of the Al₂O₃ inclusions, ductile stress occurs in the matrix, whereas the inclusions are subjected to compressive stress. When a crack propagates through composite materials such as 3Y-TZP/Al₂O₃ or 8-YSZ/Al₂O₃, the stress field in the matrix "attracts" the

vertex of this crack to the inclusion, which presumably leads to cracking along grain boundaries to be more common than cracking across the grains of the matrix.⁵⁰

Electrical Conductivity

The total electrical conductivity of polycrystalline electrolyte materials has two components—the conductivity of grain boundaries and that of grain interiors. To measure each of these components, electrochemical impedance spectroscopy (EIS) was applied. The impedance spectra recorded for the 3Y-TZP sample obtained from the powder with a 0.5 mol.% addition of Al₂O₃ at temperatures in the range of 573–873 K are shown in Figs. 6 and 7 in the form of Nyquist plots.

Figure 6 illustrates the method used to determine both R_b and R_{gb} . The values of grain interior (σ_b) and grain boundary (σ_{gb}) conductivity were subsequently determined using Eq. 4. The impedance spectra recorded for all studied samples were interpreted by fitting the equivalent circuits appropriate to a given sample and temperature of measurement. These equivalent circuits are shown in Table SI (see supplementary data file).

The constant phase element (CPE) is an expression of the porosity and inhomogeneity of polycrystalline sinters and the imperfect electrode-electrolyte interface.⁴¹ The resistor (R), in turn, represents the resistivity of zirconia in a composite material. According to the conventional

Fig. 6 Impedance spectra recorded at 573 K for the 3Y-TZP sample with 0.5 mol.% of Al_2O_3 .

Fig. 7 Impedance spectra recorded at 673, 773 and 873 K for the 3Y-TZP sample with 0.5 mol.% of Al_2O_3 .

interpretation,¹⁰ semicircles in the impedance spectra can be attributed to the conductivity of zirconia grains (σ_b) for high frequencies, the conductivity of grain boundaries (σ_{gb}) for low frequencies, and to the transport properties of an electrode material in the case of very low frequencies.

As can be seen from Figs. 6 and 7, the parts of the impedance spectra corresponding to the bulk (high frequency) and grain boundaries (lower frequency) are well-separated. For other temperatures or samples, the determination of both parameters R_b and R_{gb} was likewise possible for temperatures below 973 K, and was performed using the proposed equivalent circuits listed in Table SI. On the other hand, based on the measurements conducted at temperatures over 923 K, it was only possible to determine the total electrical conductivity of the investigated samples (σ_{tot}).

Figure 8a and b show Arrhenius plots that represent the temperature dependence of grain interior electrical conductivity (σ_b) and specific grain boundary electrical conductivity ($\sigma_{sp,gb}$) for both unmodified and modified 3Y-TZP and 8-YSZ materials, respectively, whereas Fig. 9 shows the corresponding plots for total conductivity (σ_{tot}); the plots are shown for all investigated samples.

As can be seen in Fig. 8a, the specific grain boundary conductivity ($\sigma_{sp,gb}$) of 3Y-TZP is much lower than its grain interior bulk conductivity (σ_b). At 973 and 573 K the respective differences are 1.3 and 2.4 orders of magnitude. For 8-YSZ materials, the corresponding differences are 2.1 and 3.6 orders of magnitude. The observed significantly lower grain boundary conductivity indicates that their contribution as a limiting factor in oxygen transport should be the most significant. However, oxygen transport could also be hindered by a much smaller scale of diffusion through the grain boundaries than via the bulk. The differences observed in Fig. 9 are, therefore, essentially explained by the difference in the bulk conductivity of 3Y-TZP and 8-YSZ materials at high temperatures, while at lower temperatures this difference diminishes.

The presented plots show that the logarithm of the conductivity of components as well as the logarithm of the sample's total conductivity decrease linearly with the reciprocal of temperature, which indicates a thermally activated

Fig. 8 Temperature dependence of grain interior electrical conductivity (σ_b) and specific grain boundary electrical conductivity ($\sigma_{sp,gb}$) for unmodified and modified materials obtained through 2 h of sintering in air at 1773 K: (a) 3Y-TZP and (b) 8-YSZ.

Fig. 9 Temperature dependence of total electrical conductivity (σ_{tot}) for unmodified and modified 3Y-TZP and 8-YSZ materials obtained through 2 h of sintering in air at 1773 K.

Table VII Activation energy of total electrical conductivity ($E_{a(\text{tot})}$) as well as those of its grain interior ($E_{a(b)}$) and grain boundary ($E_{a(\text{gb})}$) components, as calculated for the studied samples obtained through 2 h of sintering in air at 1773 K

Sample	Activation energy [eV]		
	$E_{a(b)}$	$E_{a(\text{gb})}$	$E_{a(\text{tot})}$
3Y-TZP	0.85	1.15	0.92
3Y-TZP/0.5 mol.% of Al ₂ O ₃	0.86	1.11	0.96
3Y-TZP/1.0 mol.% of Al ₂ O ₃	0.84	1.15	0.95
8-YSZ	1.00	1.09	1.02
8-YSZ/0.5 mol.% of Al ₂ O ₃	0.97	1.23	1.03
8-YSZ/1.0 mol.% of Al ₂ O ₃	1.03	1.22	1.08

character of electrical conductivity, in accordance with the equation:

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{k \cdot T}\right) \quad (11)$$

where: σ —electrical conductivity [$\Omega^{-1} \cdot \text{cm}^{-1}$], T —absolute temperature [K], E_a —activation energy [eV], σ_0 —pre-exponential factor that accounts for defect concentration and other material-specific parameters [$\Omega^{-1} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$], and k —Boltzmann constant [$\text{eV} \cdot \text{K}^{-1}$].

Equation 11 was used to calculate the activation energy of total electrical conductivity ($E_{a(\text{tot})}$) as well as those of its grain interior ($E_{a(b)}$) and grain boundary ($E_{a(\text{sp.gb})}$) components. The error for these calculations did not exceed 0.01 eV. The corresponding values are listed in Table VII.

As can be seen, the activation energy of total conductivity of samples from the 3Y-TZP series is lower than that of

the 8-YSZ samples regardless of the concentration of Al₂O₃ inclusions. The activation energy of grain interior conductivity is lower than that of grain boundary conductivity across all studied samples. In the case of samples from the first series, the smallest difference between these values is observed for the samples with 0.5 mol.% of Al₂O₃, which is consistent with literature data.¹⁵

For the samples from the second series, the corresponding difference is smallest for the reference sample. As far as the influence of alumina inclusions is concerned, for the samples from the first series (3Y-TZP) it is negligible. It is, however, noticeable for the samples from the second series (8-YSZ)—in this case the addition of alumina increases the activation energy of grain boundaries in a more pronounced manner.

When discussing the impact of alumina inclusions in the zirconia matrices of both the cubic variant (8-YSZ) and the predominantly tetragonal one (3Y-TZP) on the total and specific grain boundary electrical conductivity, it can be noted that the alumina concentration does not have a pronounced effect on either of these conductivity values regardless of the temperature at which the measurements had been conducted. This is illustrated separately for each type of conductivity (Fig. 10a and b, respectively). The most pronounced effect is observed in the case of the specific grain boundary conductivity of the 3Y-TZP material—when measured at temperatures below 973 K, it was the highest for an Al₂O₃ addition of 0.5 mol.%. It is worth mentioning that in the case of the 8-YSZ series, the inert alumina inclusions reduced grain boundary conductivity to a greater extent than in the case of the 3Y-TZP samples (Fig. 10b).

The drop in the electrical conductivity of grain interiors associated with the addition of alumina, observed for both series of samples, may be attributed to a slight decrease in the concentration of free oxygen vacancies, which is consistent with Eq. 9. As far as the grain boundary conductivity of the studied composites is concerned, the presence of aluminum at grain boundaries in the matrix of the 3Y-TZP and 8-YSZ samples had an adverse influence on their conducting properties, despite the advantageous scavenging of silica impurities by alumina, which had been mentioned in the introduction to the present paper. The possible explanation is that aluminum ions increase the height of the Schottky barrier, in effect increasing the activation energy of conductivity in the space charge region.¹⁴

Taking into account the requirements set for electrolyte material for the construction of planar intermediate-temperature solid oxide fuel cells (IT-SOFCs), which include high ionic conductivity, gas-tightness and good mechanical properties, the composite based on the 3Y-TZP matrix and modified with 0.5 mol.% of alumina inclusions appears to be the most promising material of those investigated in the presented study.

Fig. 10 Dependence of (a) total electrical conductivity (σ_{tot}) and (b) specific grain boundary electrical conductivity ($\sigma_{\text{sp,gb}}$) on Al_2O_3 concentration at 573, 773 and 973 K for unmodified and modified 3Y-TZP and 8YSZ materials obtained through 2 h of sintering in air at 1773 K.

Conclusions

1. Fine-grained zirconia powders stabilized with 3 mol.% or 8 mol.% of yttria were synthesized via co-precipitation. It was demonstrated that tetragonal 3-YSZ and cubic 8-YSZ powders are suitable precursors for the preparation of dense composite samples containing inert alumina inclusions in a zirconia matrix.
2. The influence of alumina inclusion at concentrations of 0.5 and 1.0 mol.% on the structure and morphology of 3Y-TZP and 8YSZ samples obtained through 2 h of sintering in air at 1773 K was investigated. The 3Y-TZP and 3Y-TZP/ Al_2O_3 samples had fine-crystalline grains, and consisted of two phases—the predominant tetragonal phase with a fraction of over 94%, and a cubic one. Corundum was also found in this type of samples. The lattice constants of the tetragonal phase in the 3Y-TZP samples did not vary with alumina content. The 8-YSZ samples, which consisted solely of the cubic phase, had lattice constants that were affected by alumina content to a much higher degree, and they consisted of large grains with an irregular shape.
3. The highest values of the brittle fracture coefficient (K_{Ic}) were determined for the 3Y-TZP samples. The addition of alumina to both 3Y-TZP and 8YSZ samples was associated with improved fracture resistance.
4. At all applied measurement temperatures and for all sinter samples, grain interior conductivity was higher than specific grain boundary conductivity by ca. two orders of magnitude. Samples from the 3Y-TZP series exhibited higher specific grain boundary conductivity than the 8-YSZ samples at all measurement temperatures. A slight drop in total electrical conductivity was observed for the samples that contained alumina inclusions in their zirconia matrix.

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Conflict of interest The authors have no conflicts of interest to declare.

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