

Structural features of the total electrical conductivity dependence of 1Ce10ScSZ solid electrolyte

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The influence of changes of structural components on the specific total electrical conductivity of different types of bulk 1Ce10ScSZ ceramics in the temperature range of 400—900 °C, which is working for intermediate-temperature solid oxide fuel cells, was studied. It is demonstrated that the dependence of the specific total electrical conductivity of different purity 1Ce10ScSZ ceramics on the porosity takes place in the temperature range μ a 600—700 °C and is practically absent at high temperatures. The effect of average grain size on the temperature-normalized porosity-modified specific total conductivity is not detected in the whole studied range or chemically pure ceramics 1Ce10ScSZ of type II. The influence of the average grain size on the temperature-normalized porosity-modified specific total conductivity is proportional at low-temperature range, is decreasing with increasing temperature and, is practically absent, at 900 °C in technically pure 1Ce10ScSZ ceramics of type I. In technically pure 1Ce10ScSZ ceramics of type III it was observed the inverse situation: no dependence at low temperature and inversely proportional dependencies with increasing temperature.

Keywords: specific total conductivity, structural dependence, solid electrolyte, ceramic fuel cell, stabilized zirconium dioxide.

Introduction

Oxygen-ion conductivity of ceramics based on zirconium dioxide, as of other the second kind conductors, is usually [1] described by the Arrhenius equation in logarithmic coordinates vs. temperature.

It describes of oxygen ions transport across the vacancy positions and vacancy complexes in the oxygen lattice, is fundamental in electrical conductivity theory of zirconium electrolytes:

$$\sigma T = A \exp\left(\frac{-E_a}{kT}\right), \quad (1)$$

where σ is the ionic conductivity; T — the absolute temperature; A — pre-exponential constant, and E_a is the activation energy of ions which moves through the lattice. Usually, the activation energy of the conductivity includes the energy of ion formation and the energy of ion migration through lattice defects. It is known that the energy of the formation of defect accounts for most of the activation energy of the conductivity. In this case, the activation energy can be described by the defect formation energy, that is, the free ion formation energy.

When a defective complex of oxygen ions is formed because in the same time occurs the significant increase in the distance between the boundary

vacancies of the complex in comparison with the case of unassociated uniform distribution of vacancies, so the dissociation energy of the ion complex is added to the activation energies of the conductivity. As a result, there are two ranges with different activation energies of the conductivity [2]. It has been shown previously that the transition temperature between low- and high-temperature ranges of oxygen-ion conductivity is independent of changes in the structure of the 1Ce10ScSZ ceramics of any type [3]. The transition temperature is the lowest for 1Ce10ScSZ ceramics with chemically pure powder (amount each of minor impurities less than 0,01% (mol.) and has the highest values for ceramics with technically pure powders (amount some of minor impurities more than 0,1% (mol.); moreover, it has different values for different impurity sets.

The equation (1) is general and correct for an ideal infinite single crystal. So it does not in any way take into account the influence of structural factors, such as grain size or porosity, which at the same time change with increasing sintering temperature of the ceramic. As a result, it is observing a deviation of the normal temperature dependence of conductivity [4]. However, it is clear that, in fact, the existence of boundaries, namely its distribution, purity, and perfection, has to change the electrical behavior [5]. The manifestation of boundaries changes observed into the material formation with energy influences, such as temperature and time, are simultaneous changes in the porosity and size of the structural component (grain or sub-grain) [6].

Based on the fact that the CFC is a complex macro-composite, and in fact, its “ideal” electrolyte should consist of thinnest gas-tight middle layer and perfectly connect with both porous skeletons parts of electrode layers. These skeletons are at the same time a continuation of the dense electrolyte and part of three continuous interpenetrating electrode phases (pore, ionic conductor, electron conductor) too. It is clear that the specific ionic conductivity, which is the limiting factor of reaction rate of fuel recovery, of both dense and frame electrolytes, probably will determine the maximum efficiency of the CFC as a whole.

Therefore, the study goal is analyzing the effect of changes of structural components on the total electrical conductivity of 1Ce10ScSZ ceramics in the temperature range, which is working area of the electrolyte of a ceramic fuel cell — a device that is capable of directly converting the chemical energy of fuel into electricity and heat with high efficiency.

Materials and methods

1Ce10ScSZ powders produced using technology [7, 8] and commercial powders of Daiichi Kigenso Kagaku Kogyo (DKKK), Japan and Praxair, USA were used as starting materials.

Specimens of 15 mm. diameters and 2 mm. thicknesses were compacted by oneaxial pressure at 30 MPa and sintered at different temperatures in the range 1250—1550 °C with a heating/cooling rate of 200 °/h during 1.5 h in the air.

Scanning electron microscopy (SEM) of fractures and surfaces of ceramics was performed by a JEOL Superprobe-733.

The dimensions of the visible elements of the structure (grains) were determined both by the Image Lab and ImageJ software and by the method of inclined sections with views of fractures and surfaces.

The porosity was determined by the hydrostatic weighing method with the separation of the contribution of closed and open porosity.

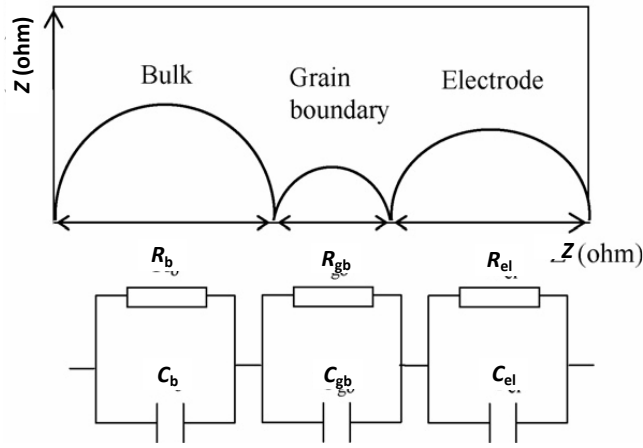


Fig. 1. Illustration of a typical impedance plot for a polycrystalline sample with equivalent circuits [10].

Specific total electrical conductivity was calculated by impedance spectroscopy plots (Fig. 1). The calculations were performed using the ratios [9]:

$$\sigma_b = \frac{H}{AR_b}; \quad (2)$$

$$\sigma_{gb} = \frac{H}{AR_{gb}}; \quad (3)$$

$$\frac{1}{\sigma_{tot}} = \frac{1}{\sigma_b} + \frac{1}{\sigma_{gb}}, \quad (4)$$

where H is the thickness of the specimen (tablet), A is the area of the specimen (tablet), R_b and R_{gb} are the electric resistance of nets of grain and the grain boundary respectively.

Results and discussion

Using of starting 1Ce10ScSZ powders of different purity with different morphological and chemical properties, namely, the primary particle size, agglomeration, content and internal distribution of the basic and non-basic impurities, has allowed, by different sintering temperatures, to obtain ceramics of different types with wide variations of structure: the structure components (grain/sub-grain), porosity and to realize all possible brittle fracture micromechanisms: interparticle, intergranular and transgranular. It should also be noted that the X-ray study of both the starting powders and the analyzed ceramics showed that all had fluorite structure [10].

The obtained materials can be classified taking into account changes in its structural features with increasing thermal impact, which can be detected during fracture surfaces study (Fig. 2). The material of I type is porous, not predisposed to rapid recrystallization and destroyed only by cleavage. Type II is a dense material, predisposed to rapid recrystallization and cleavage fracture. Type III material is predisposed to rapid recrystallization too and intergranular fracture.

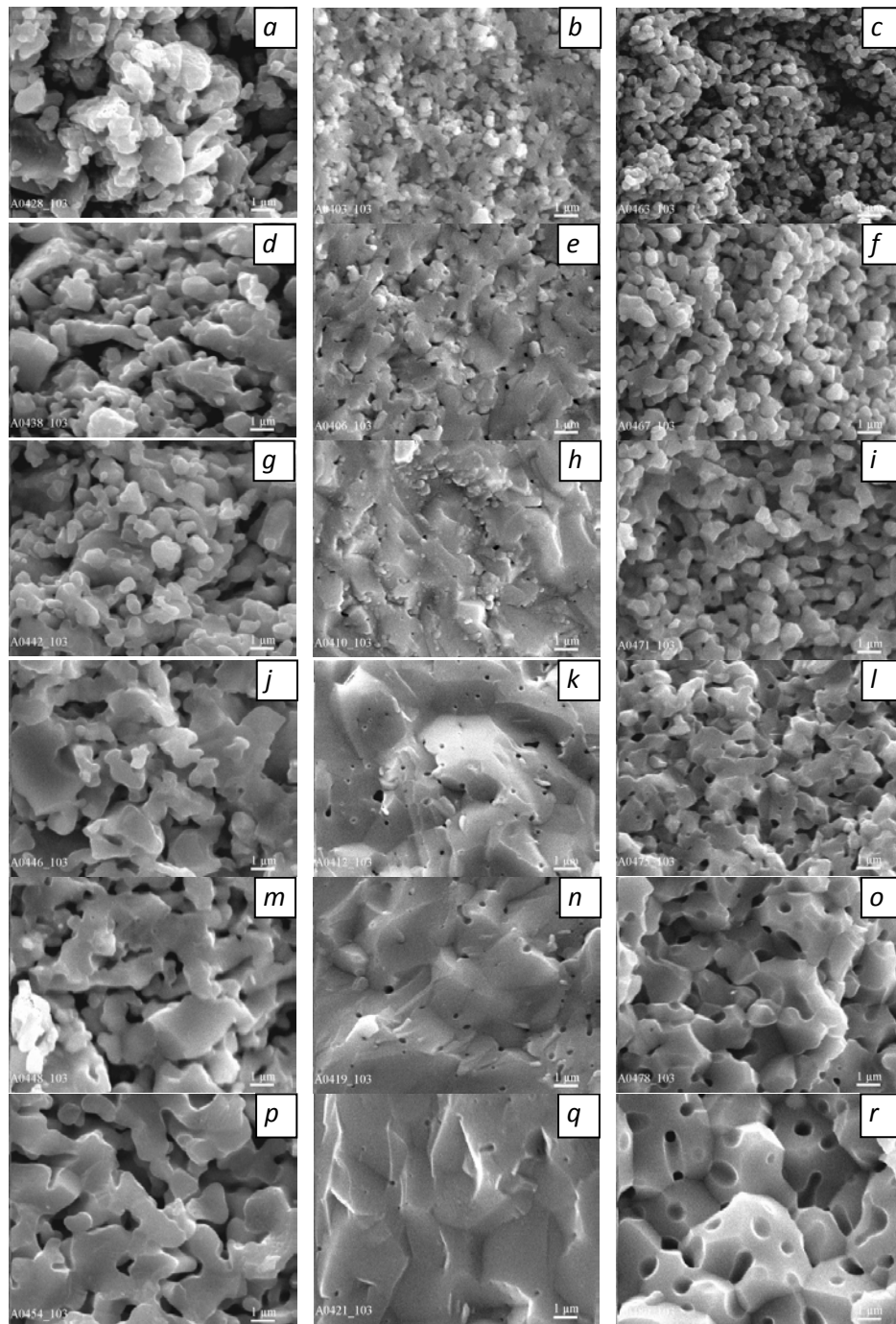


Fig. 2. The fracture surfaces (SEM) of 1Ce10ScSZ ceramics of different types (I — left column, II — middle column, III — right column) sintered at different temperatures 1300 (*a, b, c*), 1350 (*d, e, f*), 1400 (*g, h, i*), 1450 (*j, k, l*), 1500 (*m, n, o*) and 1550 °C (*p, q, r*) at 1,5 h. in the air.

The temperature dependences of the specific total conductivity of different types of 1Ce10ScSZ ceramics sintered at different temperatures, taking into account the testing temperature (Fig. 3), indicate that the conductivity of

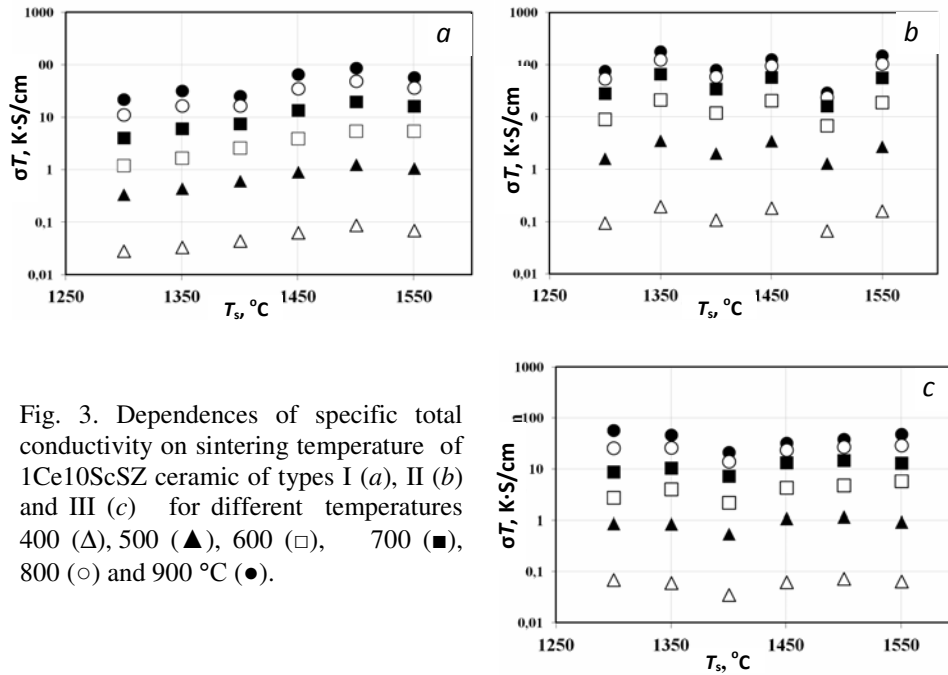


Fig. 3. Dependences of specific total conductivity on sintering temperature of 1Ce10ScSZ ceramic of types I (a), II (b) and III (c) for different temperatures 400 (Δ), 500 (\blacktriangle), 600 (\square), 700 (\blacksquare), 800 (\circ) and 900 °C (\bullet).

ceramics is visible depending on sintering temperature and shows different change dynamics of different types of ceramics.

It is known that increasing the sintering temperature leads to an increase not only in the density of ceramics, what, in turn, have to lead to increase the conductivity, the changes of which are the smallest in ceramics of type II, but also increase the average grain size, which is the largest in ceramics of type III, that usually lead to reduce total conductivity. The dependence of the conductivity on the sintering temperature of the ceramics of types I and II is almost linear up to the temperature of 600—700 °C. At higher temperatures, it becomes distinctly non-monotonic. Specimens of ceramics of type III, sintered at 1500 °C, have maximum conductivity at all testing temperatures.

It should be noted that the dependences of the conductivity and strength of ceramics [11] of type I and III (made from powders of technical purity) on the sintering temperature correlate with each other. In general, with increasing sintering temperature, there is an increase in total electrical conductivity. Moreover, increasing the temperature leads to a decrease in the slope of the dependence. The specific total conductivity of the type II ceramics (made from chemical purity powder) is almost independent of the sintering temperature. The reason for this difference in behaviors is probably the state of the boundaries, which is determined by the impurity concentration [12].

Traditional analysis of the dependence of specific total conductivity on the general porosity measured at different temperatures (Fig. 4, left column) of 1Ce10ScSZ ceramics with different degree of impurity contamination shows that the dependence takes place in the low-temperature range, decreases with increasing temperature and is practically absent at high measuring temperatures. (900 °C), which additionally confirms to different conductivity mechanisms at low- and hightemperature ranges. However, in fact the existence of such inverse dependence indicates need to take into account the effect of porosity in

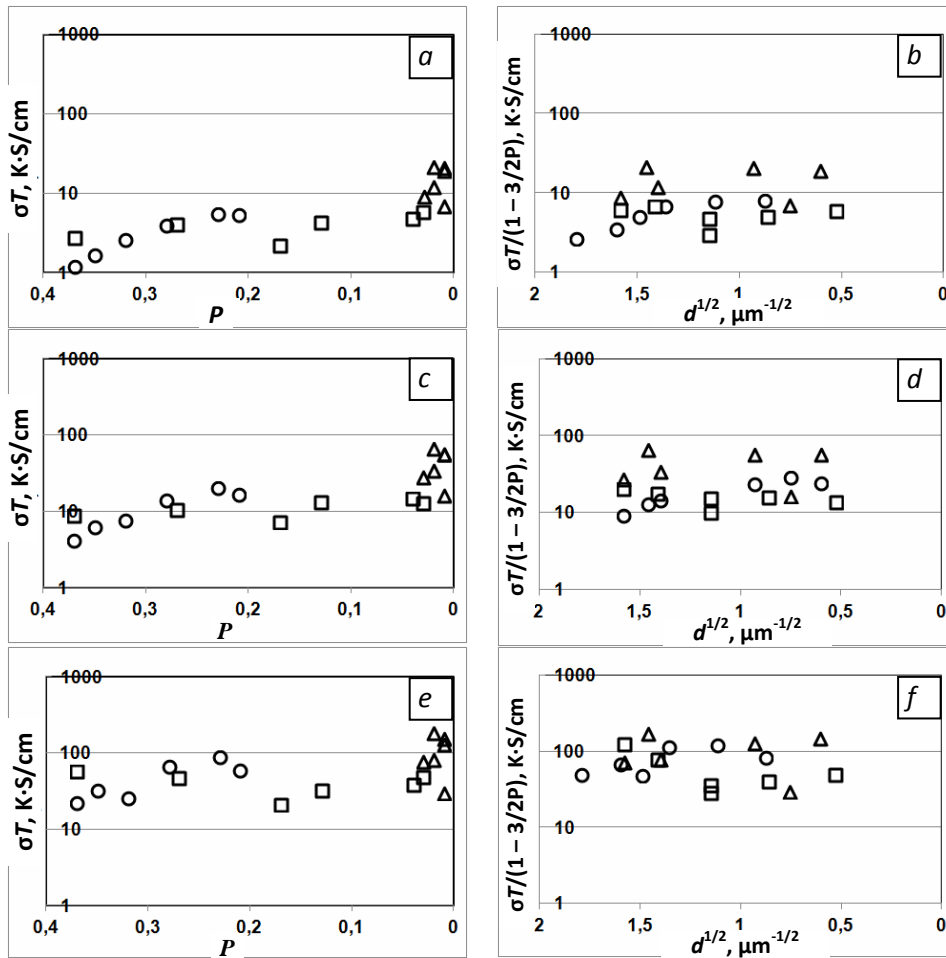


Fig. 4. Dependence of temperature-modified (right column) and additionally porosity-modified specific total conductivity (left column) measured at different temperatures 600 (a, b), 700 (c, d) and 900 °C (e, f) on average grain size (left column) and porosity (right column) of 1Ce10ScSZ ceramics of different types I (○), II (Δ) and III (□).

the analysis of the influence of the average grain size on the specific total conductivity.

Fig. 4 (right column) shows the dependencies of the temperature-normalized porosity-modified specific total conductivity measured at different temperatures on the average grain size of 1Ce10ScSZ ceramics of different types.

It can be seen that the effect of the average grain size on the temperature-normalized porosity-modified specific total conductivity isn't visible detect in the whole studied range of 400–900 °C in chemically pure 1Ce10ScSZ ceramics of type II (Δ). However, it should be noted that porosity and average grain size change ranges wasn't quite wide and the observed fluctuations of conductivity needs special research.

The effect of the average grain size on the temperature-normalized porosity-modified specific total conductivity of technically pure 1Ce10ScSZ ceramics of type I are proportional at low temperature, decreases with increasing temperature and are practically absent at 900 °C.

Conversely, it wasn't observed dependencies of the structural component size on the temperature-normalized porosity-modified specific total conductivity at low temperatures on technically pure 1Ce10ScSZ ceramics of type III. And it was detected emerging and increasing of inverse dependence with increasing temperature.

Conclusions

Traditional analysis of the dependence of specific total conductivity on the general porosity measured at different temperatures demonstrated that the dependence takes place in the temperature range (600—700 °C) and is practically absent at high temperatures. It can confirm of different conductivity mechanisms at low- and high-temperature ranges additionally.

The study of the influence of changes of structural components on the temperature-normalized porosity-modified specific total conductivity of different types of bulk 1Ce10ScSZ ceramics in the temperature range 400—900 °C showed the absolutely difference in the behavior at low- and high-temperature ranges.

It was observed proportional dependence at low temperature, which decreased with increasing temperature and were practically absent at 900 °C on 1Ce10ScSZ ceramics with >0,1% (mol.) content of silicon oxide. Conversely it wasn't observed any dependence on 1Ce10ScSZ ceramics with >0,1% (mol.) content of titanium oxide at low temperature. Inversely proportional dependences were detected with increasing temperature. Such difference was observed through possibly difference influences of impurity segregations kinds.

However, there wasn't detected similar dependence on chemically pure ceramics of type II, but the observed fluctuations of conductivity needs special study.

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Структурні особливості залежності загальної електричної провідності твердого електроліту ICe10ScSz

М. М. Бричевський

Досліджено вплив зміни структурних складових на загальну питому електропровідність різних типів масивної кераміки ICe10ScSZ в інтервалі температур 400—900 °С, який є робочим для середньотемпературних твердооксидних паливних комірок. Показано, що залежність питомої загальної електропровідності кераміки ICe10ScSZ різної чистоти від змін поруватості має місце в температурному діапазоні 600—700 °С і практично відсутня за високих температур. Для хімічно чистої кераміки ICe10ScSZ II-го типу вплив середнього розміру зерна на температурномодифіковану та нормалізовану поруватістю питому загальну провідність не виявлений в усьому дослідженому діапазоні. В технічно чистій кераміці ICe10ScSZ I-го типу вплив середнього розміру зерна на температурномодифіковану та нормалізовану поруватістю питому загальну провідність прямо пропорційний в низькотемпературному діапазоні, зменшується зі збільшенням температури і практично відсутній за температури 900 °С. У технічно чистій кераміці ICe10ScSZ III-го типу спостерігається зворотна ситуація: відсутність залежності за низької температури та обернено пропорційна залежність — із її підвищенням.

Ключові слова: *питома загальна електрична провідність, структурна залежність, твердий електроліт, керамічна паливна комірка, стабілізований двооксид цирконію.*

Структурные особенности зависимости общей электрической проводимости твердого электролита $\text{Ce}_{10}\text{ScSZ}$

Н. Н. Бричевский

Исследовано влияние изменения структурных составляющих на общую удельную электропроводность различных типов массивной керамики $\text{Ce}_{10}\text{ScSZ}$ в интервале температур 400—900 °С, который является рабочим для средне-температурных твердооксидных топливных ячеек. Показано, что зависимость удельной общей электропроводности керамики $\text{Ce}_{10}\text{ScSZ}$ различной чистоты от изменений пористости имеет место в температурном диапазоне 600—700 °С и практически отсутствует при высоких температурах. Для химически чистой керамики $\text{Ce}_{10}\text{ScSZ}$ II-го типа влияние среднего размера зерна на температурномодифицированную и нормализованную пористостью удельную общую проводимость не установлено во всем исследованном диапазоне. В технически чистой керамике $\text{Ce}_{10}\text{ScSZ}$ I-го типа влияние среднего размера зерна на температурномодифицированную и нормализованную пористостью удельную общую проводимость прямо пропорционально в низкотемпературном диапазоне, уменьшается с увеличением температуры и практически отсутствует при 900 °С. В технически чистой керамике $\text{Ce}_{10}\text{ScSZ}$ III-го типа наблюдается обратная ситуация: отсутствие зависимости при низкой температуре и обратно пропорциональная зависимость — при её повышении.

Ключевые слова: удельная общая электрическая проводимость, структурная зависимость, твердый электролит, керамический топливный элемент, стабилизированный диоксид циркония.