ELECTRICAL CONDUCTIVITY STUDIES OF SCANDIA DOPED CERIA CERAMIC COMPOSITES

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In this paper electrical conductivity analysis of a new material, designed to be used as a solid electrolyte for intermediate temperature fuel cells (IT-SOFC) was performed. The material is based on a composite of scandia doped ceria (SDC) and yttria doped alumina (YA) which ensures higher mechanical stability. The initial powders were obtained by sol-gel method. The samples were prepared by cold pressing and sintering at 1500 ^{0}C. Materials with variation of the composition (SDC/YA = 95/5; 90/10, 85/15 mass %) were studied. The conductivity was determined by Electrochemical Impedance Spectroscopy. According of the electrochemical analysis the composites with 5 and 10 mass % YA exhibit better conductivity. The results are in correlation with morphological investigation, realized by SEM.

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1. Introduction

Current trend in solid oxide fuel cells (SOFC) research is to lower the operating temperature to 600-700 ^{o}C in order to benefit from reduced costs [1, 2]. Major problems are related to efficiency of materials (ionic conductivity and electrochemical activity) which tend to decrease at lower temperature and therefore need to be improved [3]. In the last decades a big effort has been devoted to searching for new materials for replacement of YSZ (yttria-stabilized zirconia) electrolytes and $(La,Sr)MnO_3$ (LSM) cathodes. A number of potential materials has been proposed but only few fulfil the severe requirements of the specific applications and are reliable enough. At present, in addition to the classical combination of YSZ/LSM, rare earth doped ceria (ReDC) electrolyte, where the dopant could be yttrium (Y), scandium (Sc), gadolinium (Gd), samaria (Sm) and dysprosium (Dy) have been proposed [4, 5] in combination with the alternative perovskites $La_{(1-x)}S_{rx}CoO_{3-\delta}$ (LSC) and $La_{(1-x)}$ $S_{rx}Co_{1-y}$ $Fe_yO_{3-\delta}$ (LSCF) cathodes. Therefore, the decrease of SOFCs operating temperature in the next years could rely on the improvement of existing materials by development of new microstructures and architectures starting from well accepted materials rather than on the development of new oxygen and mixed conductors, which will take a longer time.

In addition to the high conductivity, the electrolyte should have good mechanical stability, especially for the anode supported planar SOFC design, since the oxide ion conducting material gives the mechanical skeleton of the anode cermet.

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For improving the stability of ReDC a composite electrolyte based on scandia doped ceria (SDC) and low yttria doped alumina (YA) [10 Sc_2O_3: CeO_2 + (X%) (150 ppm) Y_2O_3: α – Al_2O_3], in which α - alumina percentage varies (X = 5 mass %, 10 mass % and 15 mass %), has been developed as new ceramic solid electrolyte for IT-SOFC [6]. Mechanical and microstructural studies determined these materials as promising in respect to their stability [6-10].

The aim of this paper is selection of the compositions with the best conductivity based on impedance spectroscopy.

2. Experiments

2.1 Materials

A new type of ceramic composite material consisting of scandia doped ceria (the matrix phase) and yttria (150 ppmY_2O_3) doped α-alumina (the reinforcement phase) in which the α - alumina percentage is 5, 10 and 15 mass %, were selected for electrical investigation. The three composite materials are marked as S1, S2 and S3.

The samples were prepared by mechanical mixing of the two nanopowders, synthesized by sol-gel method in the appropriate ratio, followed by cold pressing at 10 MPa and sintering at 1500 ºC for 2 h [6].

The samples are with diameter of 10 mm and thickness of 1.2 mm.

For the electrochemical measurements symmetrical electrolyte supported half cells with Ag electrodes deposited according to the procedure of the producer were fabricated (Fig. 1).

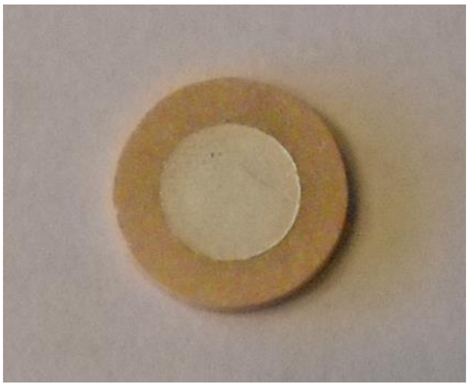

Fig. 1. Sample with silver electrodes used for electrochemical investigation

2.2 Equipments

The impedance measurements were performed on Solartron 1260 Frequency Response Analyser in a temperature interval of 500 – 700 ºC at frequency range from 10 MHz down to 0.1 Hz and density of 5 points/decade. The experiments were carried at amplitude 50 mV.

Morphological characterization (porosity and average grain diameter) of the samples was performed by a scanning electron microscope (SEM) type TESCAN LYRA 3 XMU. Average grain diameter was obtained by measuring 100 grains with a software type ITEM (image analysis program obtained by electron microscopy). The porosity P of the sintered composite samples was determined microscopically following the relation [6]:

$$P = \frac{A_p}{A_g} \cdot 100, \tag{1}$$

where A_p is the pores area and A_g the grains area.

3. Results and discussion

Impedance spectroscopy is the main tool applied for testing and characterization of new materials for SOFC, since it is sensitive to samples configuration, fabrication quality and mechanical stability as well as to recognition and separation of the bulk and grain boundary conductivities. The impedance of a solid electrolyte is described with the so called Voigt's model structure, which consists of two time-constants (R/C meshes) connected in series corresponding to the bulk and grain boundary behaviour [11-15]. A principle equivalent circuit of the two time-constant Voigt's model structure is presented in Fig.2.

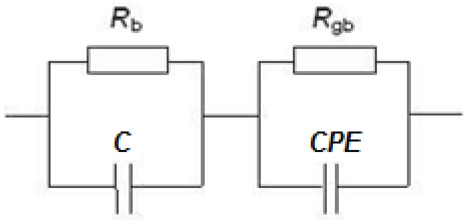

Fig. 2. Equivalent circuit of a two time constant Voigt's model structure

Impedance spectra of the three investigated electrolyte compositions at a constant temperature are presented in Fig. 3. The impedance diagrams consist of two typical highly mixed arcs. The high frequency one corresponds to the bulk behaviour, while the strongly depressed low frequency one represents the grain boundaries behaviour. For description of the frequency dependence the grain boundaries capacitance in Voigt's model is replaced with constant phase element CPE (Fig.2.). This behaviour can be related to the inhomogeneous microstructure of the samples (two phases with different grain size, orientation and porosity), which is confirmed by the microstructural studies (Table 1).

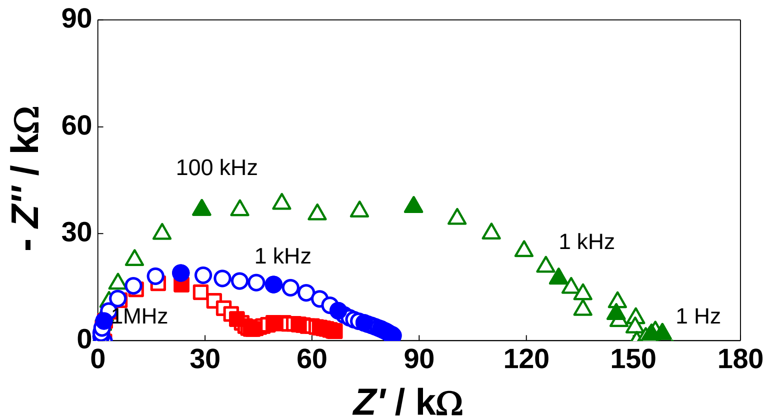

Fig. 3. Complex plane impedance diagrams of samples S1 (●), S2 (■) and S3 (▲) at temperature 500 ^{0}C

The resistance values obtained from the impedance measurements for the bulk and the grain boundaries at different temperatures were used for the construction of the corresponding Arrhenius plots (Fig. 4):

$$\rho = \frac{A}{T}\exp\left(-\frac{E_a}{kT}\right) \tag{2}$$

where ρ is the resistivity, A is the pre-exponential term, k is the Boltzmann constant, E_a is the activation energy and T is the temperature in K [16].

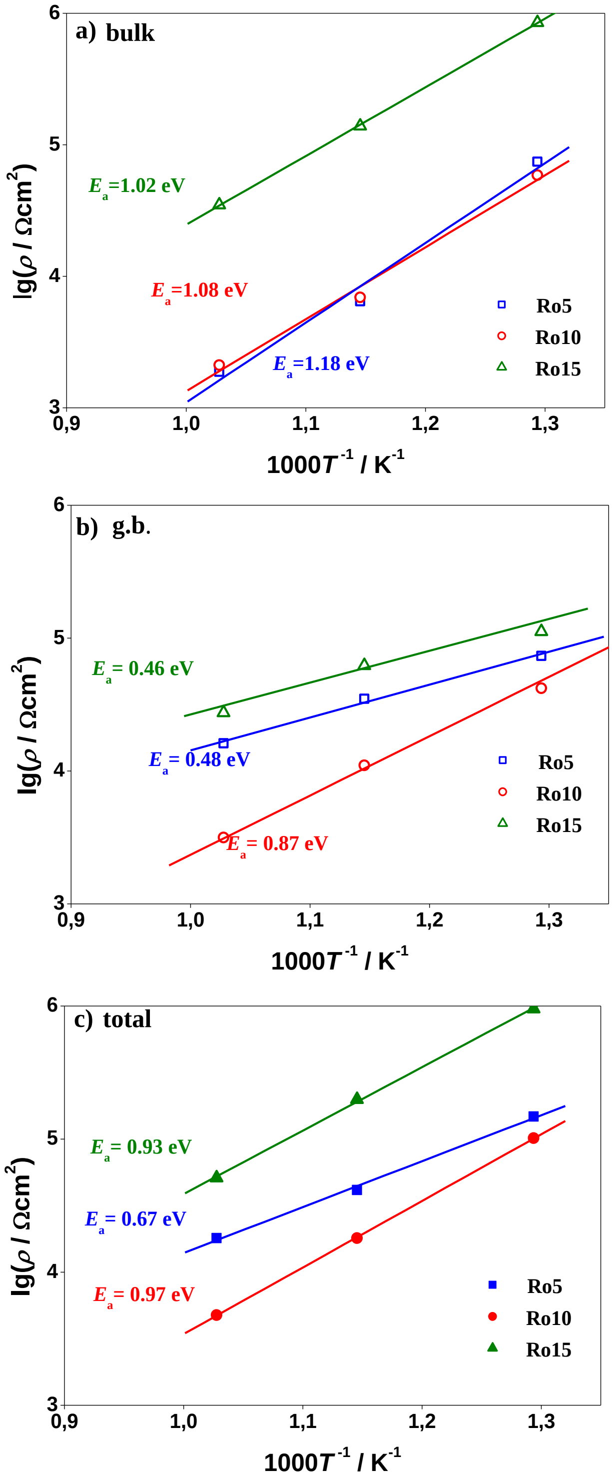

Fig. 4. Arrhenius plots for the total electrolyte resistivity (a), bulk (b) and grain boundaries (c) resistivity for samples S1 (■), S2 (●) and S3 (▲)

For sample S3 both the bulk and the grain boundary resistivities are higher than those for samples S1 and S2 (Fig. 4.a and Fig. 4.b). The results obtained for the bulk resistivity of S1 and S2 are similar which shows that the addition of alumina in the range 5-10 mass % does not influence the bulk conductivity of the composite. However it influences the microstructure and thus the grain boundaries behaviour. It is interesting to note, that the lowest conductivity is observed for sample S2 with 10 % YA second phase. As it can be seen in Table 1 and Fig. 5 the increase of the YA phase brings to increase of the grains size. For samples S1 and S2 the porosity is the same, while for sample S3 it is higher. Obviously the lower resistivity of sample S2 in comparison with S1 is due to bigger grain size. However in S3 this effect cannot compensate the higher porosity, which brings to increase of S3 grain boundaries resistivity and thus to the total resistivity (Fig. 4 b, c).

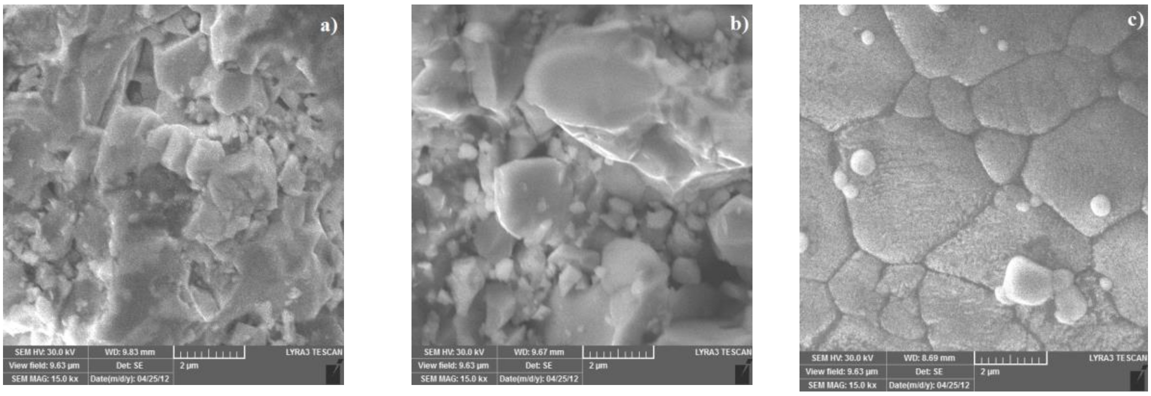

Fig. 5. SEM of samples S1 (a), S2 (b) and S3 (c).

Table 1. Porosity and grain size of samples S1, S2 and S3.

Samples	Porosity P [%]	Average grain diameter d_m [μm]	
		10 ScDC	150ppmYA
S1	0.2	0.59	2.05
S2	0.19	1.27	2.32
S3	0.31	1.57	2.71

The obtained results show that the conductivity of the composite SDC/YA electrolyte can be governed by the volume fraction of YA and the microstructure. Volume fraction of about 10 mass % is preferable.

4. Conclusions

The results obtained from the electrochemical analysis of the new composite SDC/YA electrolytes for IT-SOFC show that materials with 5 and 10 mass % YA have similar conductivity which is calculated to be $1.5 – 2\cdot10^{-4}$ S/cm. For higher YA concentrations, α - alumina has negative effects on the bulk and grain boundary resistivity and thus on the corresponding conductivity.

The investigated composite system SDC/YA can be successfully used as anode support in IT-SOFC with the high conductivity ceria based electrolytes due to their significant mechanical strength and stability and good chemical and thermal compatibility. Further studies will be performed for optimization of the composition and microstructure in respect to application for both dense electrolyte and porous anode support.

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