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Microstructure, conductivity and mechanical properties of calcia stabilized zirconia ceramics obtained from nanosized precursor and reduced graphene oxide doped precursor powders

Olga Yu. Kurapova^{a,b,*}, Oleg V. Glumov^a, Ivan V. Lomakin^a, Sergey N. Golubev^b, Mikhail M. Pivovarov^b, Julia V. Krivolapova^a, Vladimir G. Konakov^{a,b,c}

^a Saint Petersburg State University, Universitetskaya nab, 7/9, St. Petersburg 199034, Russia

^b Glass and Ceramics Ltd., 9th line V.O. 20 lit.A., office 2H, St. Petersburg 199004, Russia

^c Institute of Problems of Mechanical Engineering V.O., Bolshoj pr., 61, St. Petersburg 199178, Russia

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ABSTRACT

In the work 12CaO-88ZrO₂ (12CSZ, mol%) ceramics was manufactured both from nanopowder, obtained via cryochemical technique, and composite precursor 12CSZ + 0.25 wt% rGO (reduced graphene oxide). Via SEM, XRD and Raman spectroscopy the detailed investigation of the effect of the precursor type and intermediate processing on the microstructure and electrical conductivity of ceramics was carried out. It was shown that rGO is completely removed during the annealing at 1550 °C for 3 h in air with no effect on the high ionic conductivity of ceramics. The use of nanosized powder and the additional processing step results in vacuum dense solid electrolytes characterized by well-formed cubic zirconia based solid solution, thin discontinuous grain boundaries and rather high ionic conductivity. The addition of rGO leads to slight microhardness (HV) decrease comparing to ceramics manufactured from the nanosized precursor. As a result, a new technique for zirconia based solid electrolytes having both high electrical conductivity at high temperatures and sufficient mechanical properties was suggested.

1. Introduction

Along with Al₂O₃, CeO₂ based ceramics, spinel, perovskites and perovskite-like structures, cubic zirconia based ceramics is an important type of structural ceramics [1–3]. Due to the combination of great ionic conductivity at high temperatures, chemical and thermal stability, and sufficient mechanical characteristics, it is widely used as solid electrolyte (SE) in various electrochemical devices [3–7]. In particular, zirconia based SE are utilized in oxygen sensors for oxygen partial pressure measurement in the industrial gaseous mixtures [8] and pO value determination in oxide melts [9]. The working characteristics and lifetime of the sensors depend on chemical, transport and mechanical properties of zirconia based SE used as an ion-conducting membrane and temperature of the measurement. The requirements for zirconia based SE vary depending on the specific task of the investigation. However, the general requirements for oxygen-conducting SE application [1,10,11] can be summarized, as (i) fast oxygen ion transport; (ii) they should be oxygen conductors with the value of ion transport number close to one in broad temperature and P_{O2} range; (iii) solid

electrolytes should be chemically and thermally stable in that temperature and pressure range and exhibit low volatility of oxide dopant; (iv) under the exploitation conditions they should exhibit sufficient conductivity $\sim 10^{-2} - 10^3 \text{ S s m}^{-1}$; (v) to have coefficients of thermal expansion similar to those of the materials sensor is fabricated from, like alumina and steel; be vacuum dense; (vi) be chemically inert towards electrodes and the environment.

Despite the number of binary systems, e.g. Sc₂O₃-ZrO₂ [12,13], Yb₂O₃-ZrO₂ [14], Gd₂O₃-CeO₂ [15], Lu₂O₃-ZrO₂ [16], La₂O₃-ZrO₂ [17] etc., fit high conductivity condition (i), only Y₂O₃-ZrO₂ (YSZ) [1–3] is commercially used as a SE for oxygen sensors. It is mostly due to membranes degradation and limited availability of rare-earth oxide dopants. Calcia stabilized zirconia (CSZ) ceramics has rather high anionic conductivity at the elevated temperatures. Since early 1970th this system is of particular interest from the point of view of conductivity investigation [18,19]. That is why so far it is studied in details, i.e. phase relations and phase diagram [20], thermodynamic properties of solid solutions, [21,22], oxygen diffusion and transport properties of SE [20,23], temperature dependence of conductivity [23–26], the impacts

* Correspondence to: Universitetsky pr. 26, St. Petersburg 198504, Russia.
E-mail address: o.y.kurapova@spbu.ru (O.Y. Kurapova).

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of grain boundaries in conductivity [24]. However, the synthesis and application of calcia stabilized zirconia solid electrolytes is associated with certain difficulties as inhomogeneous compaction, high volatility of calcia at the elevated temperatures, and, as a result, low vacuum density of ceramics, low mechanical properties and instability of cubic solid solution [1,24]. That is why nowadays this system is mostly used as a model for the investigation of the new synthesis and processing techniques.

The control of microstructure on all the steps of ceramics manufacturing (as precursor synthesis, compaction and consolidation) is a key factor that determines the electrical, mechanical properties and performance of SE [26]. As it was mentioned in [1–3] the use of modern techniques of wet chemical synthesis with the respect to the thermal prehistory of the system allows to refine zirconia based ceramics microstructure, and, consequently, to enhance the conductivity of ceramics. Calcia stabilized zirconia with 16 mol% CaO content (16CSZ) was synthesized in [27] via citrate technique. Solid electrolyte obtained was characterized by mostly closed porosity and developed porous network in the bulk. Electrical conductivity of such SE was measured just at 466 °C. That did not allow to establish temperature dependence of SE conductivity and, consequently, the applicability of citrate technique to zirconia based SE manufacturing, in general. Also work [28] should be mentioned, where YSZ and CSZ ceramics were obtained by rapid combustion synthesis. Oxygen conductivity of 8YSZ solid electrolytes was shown to be comparable to commercial SE of the same composition. In case of CaO-ZrO₂ system the highest conductivity values were observed in case of 9CSZ ceramics. Nevertheless, the techniques of mild chemistry as, e.g., sol-gel synthesis [17,24], hydrothermal techniques [29–31], freeze-drying and freeze-casting [32,33] remain the most promising for zirconia based ceramics with required microstructure and conductivity manufacturing. In the recent work [33] it was shown that the use of freeze-dried powder during xCaO-(100-x)ZrO₂ ceramics synthesis results in SE having high ionic conductivity close to results obtained in [28] for commercial SE. The electrolyte with 12 mol% of CaO dopant possesses same conductivity values as the one with 9 mol% CaO in all temperature range.

Additional processing of ceramics is one of the most efficient ways for microstructural refinement of oxide solid electrolytes. In their work [28], Zhou et al. have shown that the additional thermal treatment of 15 mol% CSZ ceramics results in grain boundaries resistivity decrease due to crystallization processes. The introduction of Bi₂O₃ to zirconia based ceramics leads to sintering intensification [34]. At the same time the additive segregates on the grain boundaries. In the recent work [35] it was noted that alumina addition results in glassy phase formation on the grain boundaries that eliminates the negative effect of impurities on conductivity. However, both approaches do not allow to obtain sufficient conductivity level in zirconia based ceramics. The addition of graphene (Gr) or its derivatives as graphene oxide (GO) or reduced graphene oxide (rGO) is a novel path towards the microstructural modification of ceramics, its electrical and mechanical properties [36–39]. It is known that both Gr and rGO are excellent electronic conductors. So one can expect mixed electronic and ionic conductivity upon the introduction of graphene or its derivatives to ceramics, which is the case for graphene-YSZ composites obtained in [40] by spark plasma synthesis (SPS). However, for oxygen sensors application, solid electrolytes shall possess ionic conductivity only with no admixture of electronic one. At the same time, graphene and its derivatives effectively reduce the grain growth in metal and ceramic matrices resulting in microstructure refinement [41], i.e. during thermal treatment they are located into grain boundaries preventing the number of contacts of the grains.

Since graphene is unstable in the oxygen ambience it is expected to be removed from ceramic matrix during annealing with no segregation on the grain boundaries. Moreover, graphene derivative does not integrate into cubic solid solution structure and does not induce low symmetric phases formation, e.g. monoclinic zirconia and drastically

reduce the conductivity. In literature the amount of graphene addition to matrix (metallic or ceramic) is chosen according to simple rule of mixtures [40,41]. That approach turns to be not efficient for optimal composition determination. Thus the goal of the current work was the detailed investigation of the effect of the precursor dispersity, additional treatment steps and composite precursor 12CaO-88ZrO₂ + 0.25 wt% rGO on the microstructure, electrical and mechanical properties of 12 mol% CSZ ceramics.

2. Material and methods

2.1. Precursor powder synthesis

Based on recent studies [42,43] reversed co-precipitation technique with following freeze-drying was chosen for nanosized 12CaO-88ZrO₂ precursor synthesis. For that, nitrates hydrates Ca(NO₃)₂ * 4H₂O (Vekton Ltd., St. Petersburg, Russia, 99% a.c.s.) and ZrO(NO₃)₂ * 6H₂O (Acros organics, Geel, Belgium, 99.5%) were used to prepare 0.1 M aqueous solution. A decimolar aqueous ammonia solution (LenReactiv Ltd., St. Petersburg, Russia, c.p.) was used as a precipitant. A dilute salt solution was added dropwise to the ammonia solution at a rate of ~ 1–2 mL/min. The precipitation was performed at ~ 1–2 °C in an ice bath; the pH of the solution was kept at ~ 9–10 during the synthesis. To remove reaction byproducts, the obtained gel was filtered and rinsed using a water jet pump until neutral pH was reached. The washed precipitate of hydroxides was then freeze-dried (Labconco, 1 L-chamber, Kansas City, MO, USA; 293 K, 24 h, P = 0.018 mm Hg). The obtained powder was annealed at 700 °C for 3 h. In order to diminish powder agglomerate size, precursor was milled in a planetary mill (400 rpm, 12 reverse cycles of 5 min each, Pulverisette 6, Fritsch, Germany). Thus prepared powder is precursor 1.

2.2. Ceramics fabrication

Precursor powder 1 was compacted into the pellets with a diameter of 10.5 and ~ 4 mm thickness at P ~ 3.5 kg/cm² and annealed at 1550 °C for 3 h in air [33]. In order to reach microstructural refinement and prevent ceramics recrystallization, the annealed pellets were crushed, mixed with precursor powder 1 and milled once again (400 rpm, 15 reverse cycles of 5 min each). Thus prepared secondary powder (here and further precursor 2) was compacted into the pellets of the same size and finally annealed at 1550 °C for 3 h in air.

2.3. Composite precursor manufacturing

Reduced graphene oxide (rGO) was obtained according to modified Hammers technique with following reduction by thermal shock [44]. The formation of rGO was confirmed via Raman spectroscopy. In order to prepare composite precursor 3, ceramic precursor 2 was mixed with 0.25 wt% of rGO. Composite precursor homogenization was reached via milling in a planetary mill (400 rpm, 72 reverse cycles). Then ceramics was manufactured according to Section 2.2. Ceramic samples 1, 2 and 3 were obtained, respectively. Table 1 presents the numeration of the annealed ceramics with the respect with precursor powder properties [43].

2.4. Methods

The phase composition of powders and ceramics after the synthesis and consolidation was investigated by X-ray diffraction analysis (XRD, SHIMADZU XRD-6000, Cu-K, $\alpha = 1,5406 \text{ \AA}$). The phase identification was carried out using the Powder Diffraction File database (PDF-2, 2011) [45]. Mean crystalline size in ceramics was estimated using Sherrer's formula. Microstructure of ceramics was analyzed by scanning electron microscopy (SEM, Hitachi S-3400N, accelerating voltage 20 kV). Apparent density of consolidated ceramics was measured by

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