



Perspective ceria-based solid solutions $Gd_xBi_{0.2-x}Ce_{0.8}O_2$



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ABSTRACT

The series of Gd-Bi-Ce-O solid solutions were synthesized by co-precipitation method with sonication. These mesoporous nanocrystalline powders with the size of about 15 nm were used as precursors to ceramics formation, sintered at 1000 °C in air, for the application of materials as an electrolyte for IT-SOFC. The electrical conductivity of these materials was measured by AC impedance spectroscopy in the temperature range of 450–750 °C in air. It was showed that $Gd_{0.05}Bi_{0.15}Ce_{0.8}O_2$ ceramics, prepared through acetylacetonate complex, is the perspective system for this goal and has the conductivity of $5 \cdot 10^{-3}$ S/cm at 600 °C in air.

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1. Introduction

Materials based on ceria are of interest because they have a large oxygen storage capacity (OSC) and high mobility of oxygen, which can provide high catalytic activity and electrical conductivity. Thus, for the effective implementation of the process, the crystal structure with a sufficiently high oxygen vacancy defect concentration is required.

Selection of Gd is due to that the electrolyte based on gadolinium oxide-ceria $Gd_{0.2}Ce_{0.8}O_2$ (GDC) has a high ionic conductivity, low activation energy and good thermodynamic stability at 300–900 °C as compared with previously proposed electrolytes, such as YDC, YSZ, YScDC et al., however, the conductivity of GDC is somewhat lower than SmDC, but the cost of samarium oxide is greater than the cost of gadolinium oxide, and therefore only oxides of other rare earth elements are used as a small addition to GDC. To cut the cost, it is proposed to introduce alkaline earth metal oxides, but the electrical conductivity reduced more than doubled as compared with GSmDC [1–5]. The development of electrolytes based on ceria and bismuth oxide is proposed due to δ - Bi_2O_3 is the best ionic conductivity of all existing oxides. The increase in electrical conductivity occurs at increasing the content of bismuth oxide, respectively, but resulted in the formation of the additional tetragonal phase of Bi_2O_3 at $x \geq 0.2$ –0.3 in $Bi_xCe_{1-x}O_2$, and since cubic solid solution phase and formed bismuth oxide phase have different thermal expansion coefficients, so the stability of the electrolyte in the IT-SOFC is impeached [6–11]. The next

approach was proposed by doping of GDC by a small amount (1–5 mol%) of bismuth oxide, however, Bi_2O_3 (or Bi-Ca/Sr/Ba-O or Bi-Na-O) was used as a sintering additive to reduce the sintering temperature from 1500 to 1300–1200 °C [12–17]. Thus, it is necessary to investigate, synthesis, and study ceramics, based on ceria solid solution $(Gd_xBi_{1-x})_{0.2}Ce_{0.8}O_2$ as a promising electrolyte for IT-SOFC, which was carried out in this work.

2. Material and methods

$Ce(NO_3)_3 \cdot 6H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$ (Acros Organics) were used as metal precursors. Appropriate amounts of salts were dissolved in concentrated nitric acid (68%) with the concentration of salts of 0.667 M. After the dissolution of salts, this mixture was added to distilled water, giving the concentration of 0.1 M (in one experiment after dissolution acetylacetone was added). Then, the co-precipitation was carried out by addition of aqueous ammonia up to pH 12. Ultrasonic processing (35 kHz, 150 W) was used during all process at 30 °C under stirring. The resulting precipitates were filtered, washed with distilled water-ethanol solution ($H_2O/C_2H_5OH = 9$ vol), dried at 150 °C for 12 h, and calcined in static air by heating at a rate of 4 °C/min from room temperature to 500 °C and kept at 500 °C for 1 h in a muffle furnace.

The as-obtained powders were pressed into pellets (with 5 wt% binder made of 5% aqueous solution of polyvinyl alcohol) with 10 mm in diameter and 1 mm in thickness at 38 MPa. Then they were sintered at 1000 °C (T_{sint}) for 4 h in air with heating of 4 °C/min. To fabricate symmetric cells for the impedance studies (Elins Z-350 M impedance meter, the frequency range from 0.1 Hz to

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1 MHz at the amplitude of AC signal of 30 mV), platinum paste was brushed onto both sides of the electrolyte pellets, and were dried at 150 °C for 1 h and annealed at 900 °C for 4 h in air. A platinum wire was used as current conductors.

All powders and ceramics were characterized by XRD (Rigaku MiniFlex 600, CuK α radiation), nitrogen adsorption–desorption method (TriStar 3000 Micromeritics), TEM (Omega Leo-912AB), SEM (TESCAN VEGA II SBU with INCA Energy 300 energy dispersive spectrometers), TG–DSC (Netzsch STA449F3). The relative density of ceramics was determined by hydrostatic weighing.

3. Results and discussion

XRD pattern of powders (Fig. 1) shows that only single phase of solid solution was formed, and no peaks of other phases were detected. All peaks reflect the typical fluorite structure of ceria (Fm3m cubic unit cell). The unit cell parameter increases with increasing Bi content (Table 1) and correlates with Vegard's law, but these values are higher than calculated from the semiempirical equation for ceria solid solution [18] for ionic radii in eightfold coordination. Sample 2ac prepared by using acetylacetonate has a lower lattice parameter, which may be related to more homogeneity. The average crystallite size calculated using Scherrer formula was about 15 nm for all samples, and 8 nm for sample 2ac, which corresponds to the individual particles according to TEM.

It is known that pure ceria is a poor oxide ion conductor ($\sigma_{600^\circ\text{C}} \sim 10^{-5}$ S/cm), and the ionic conductivity can be significantly enhanced by increasing the oxygen vacancies, which can be created by the doping of ceria with about 20% concentration of dopant, because such systems achieve the highest conductivity, but a further increase in the dopant concentration results in decreasing one. Fig. 2 shows the temperature dependencies of a total conductivity of systems in Arrhenius coordinates. It has a thermal activation pattern and can be described by the Arrhenius–Frenkel equation. With increasing temperature the oxide ion mobility increased too, so the conductivity increased accordingly. The highest conductivity for intermediate temperature application ($\sigma_{600^\circ\text{C}} = 5 \cdot 10^{-3}$ S/cm) was found in Gd_{0.05}Bi_{0.15}Ce_{0.8}O₂ (sample 2ac), prepared by using acetylacetonate. The apparent activation energy (E_a , eV) of samples was almost the same (about 0.5 eV): 0.52 (sample 1), 0.49 (sample 2), 0.51 (sample 2ac), 0.49 (sample 3), 0.50 (sample 4), 0.49 (sample 5). However, the relative

density of the ceramics, calculated as the ratio of densities determined by hydrostatic weighing and XRD based cell parameter, was only 86% for sample 2ac, which may explain its better conductivity. These results demonstrate that co-doping with the optimum ratio can improve the conductivity of ceria based electrolytes, but in previous similar works (Sm–Bi–Ce–O systems) were claimed that optimal composition is Sm_{0.1}Bi_{0.1}Ce_{0.8}O_{1.9} [19]. The comparison with other data is indicated that our conductivity at 600 °C is higher than Bi_{0.2}Ce_{0.8}O₂ ceramics: $\sigma = 4 \cdot 10^{-3}$ S/cm [10] (hydrothermal method of powder preparation, $T_{\text{sint}} = 950$ °C), $\sigma = 2 \cdot 10^{-3}$ S/cm [8] (microwave sintering, $T_{\text{sint}} = 1050$ °C), but is lower than Gd_{0.1}Bi_{0.1}Ce_{0.8}O₂ ceramics: $\sigma = 2.7 \cdot 10^{-2}$ S/cm [15] (hydrothermal method of powder preparation, $T_{\text{sint}} = 1350$ °C), $\sigma = 2.25 \cdot 10^{-2}$ S/cm [13] ($T_{\text{sint}} = 1400$ °C), and Sm_{0.1}Bi_{0.1}Ce_{0.8}O_{1.9} ceramics: $\sigma \sim 2.5 \cdot 10^{-2}$ S/cm [19] (Pechini method of powder preparation, $T_{\text{sint}} = 1300$ °C). These three results mentioned are given rise to doubt. Firstly, the results [13,15] are approximately the same in [19], but it is well known that samarium doped ceria system has higher conductivity than GDC. Secondly, in these works the temperature of sintering is 1300–1400 °C, but it is clear proved that there is a concern of Bi evaporating process after 1000 °C (and almost completely evaporated at 1450 °C) [7,8,12,17], and our TG–DSC data are also confirmed (endo-effect and mass loss were observed at 1050 °C). So nominal chemical composition of initial powders and resulting composition of ceramics are different, and increasing the conductivity is due to only consolidation of ceramics without the same solid solution conservation. The ceramics based on sample 2, sintering at 1300 °C or using the hot pressing, has a lower conductivity than conventionally sintered samples 2ac, so the detailed changes of this system are then considered.

Impedance graph of the sintered sample at temperature 600 °C is shown in Fig. 3. In the frequency range from 0.1 Hz to 1 MHz, one impedance semicircle is observed, where low-frequency semicircle is attributed to the electrode polarization resistivity and can be included Warburg impedance due to the presence of diffusion processes of the reagent (oxygen) in the near-electrode layer of the electrolyte. In the case of electrodes on which some reversible Faraday process can occur in the presence of diffusion, the impedance and the equivalent circuit look like our scheme. In the temperature range of measurements the impedance diagrams show similar features and the electrode resistance decreases with the temperature increase.

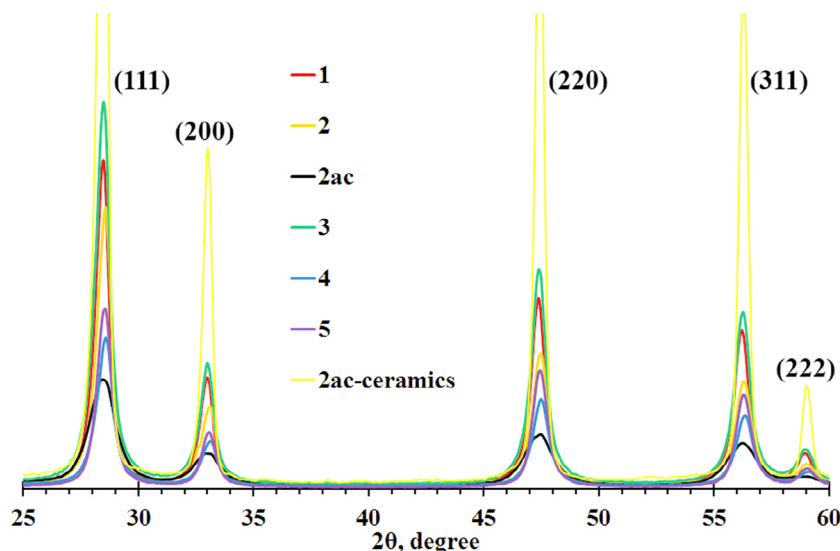


Fig. 1. XRD patterns of powders and ceramics 2ac.

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