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ScienceDirect

Journal of Taibah University for Science 10 (2016) 381–385

Journal of Taibah University for Science

www.elsevier.com/locate/jtusci

Sintering temperature effect on density, structural and morphological properties of Mg- and Sr-doped ceria

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Available online 29 April 2015

Abstract

Strontium and magnesium doped ceria solid solutions ($Ce_{0.99}Sr_{0.01}O_{1.995}$ and $Ce_{0.99}M_{0.01}O_{1.995}$) were synthesized by a cost effective solid state reaction. The doped and un-doped CeO_2 samples were sintered at 1200 °C, 1300 °C and 1400 °C to investigate the effect of sintering temperature and doping on density, structural and morphological properties. The density was measured by Archimedes' method. It is observed that the density increases with increasing sintering temperature and with doping of strontium. The crystal structure and surface morphology have been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD and SEM reveals that the synthesized samples are single phase with a cubic fluorite structure, and the grains formed are of different sizes. The grain size depends on sintering temperature and type of doping. The lattice parameter increases with sintering temperature and substitution of Sr in ceria. The Grain size of Sr-doped ceria decreases, whereas that of Mg-doped ceria increases. EDS spectra show that the samples are free of contaminants. The $Ce_{0.99}Sr_{0.01}O_{1.995}$ shows a more open structure than un-doped ceria.

Keywords: Doped ceria; Relative density; XRD; SEM; EDS; SOFC

1. Introduction

Among various types of fuel cells, solid oxide fuel cells (SOFC) have multi-fuel capability, a high conversion efficiency of approximately 60% and flexibility in their operation. The electrolyte of an SOFC must be dense, have high ionic conductivity and zero electronic conductivity [1,2]. Yttria-stabilized zirconia (YSZ) can be used as an SOFC electrolyte, but the high operating temperature of ~1000 °C necessary for oxygen ion conductivity would decrease the efficiency and stability of the cell [3,4]. Cerium oxide has a peculiar function different from other rare-earth oxides, as it tends to consist of non-stoichiometric compounds with +4 and +3 oxidation states of cerium. The redox property of ceria leads to oxygen vacancies resulting in a very high oxygen ion conductivity when compared with YSZ, even at intermediate temperatures of 600–800 °C. Ceria doped with alkali earth metal oxides such as CaO and SrO

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Peer review under responsibility of Taibah University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jtusci.2015.04.003

has been studied extensively [5–7]. The conductivity of CaO-doped ceria is much greater than calcia-stabilized zirconia (CSZ) [8,9]. Ceria solid solutions with the formula $Ce_{1-x}M_xO_{2-\delta}$, where M is a rare earth metal or lanthanide, show more open structures, possess higher oxygen ion conductivities and are potential electrolytes for low temperature SOFCs (LT-SOFC) [10–12]. To achieve high ionic and zero electronic conductivity, an SOFC electrolyte requires high density and low porosity. The open structure of doped cerium oxides have high ionic conductivities and can be synthesized by various routes. The crystal structure and relative density of solid ceria electrolytes increases with increasing sintering temperature [13]. Alkali earth oxides such as MgO, CaO and SrO are soluble in the ceria lattice, and the resultant materials are suitable candidates for the electrolyte in LT-SOFCs. Mechanically mixed powders of CeO_2 and Sm_2O_3 have been studied extensively [14]. Gadolinium doped ceria (GDC) and samarium doped ceria (SDC) synthesized by the solid state reaction method have been studied extensively for the effects of sintering temperature on density, porosity, structural and electrical properties [15–17]. Ceria co-doped with rare earth and alkali earth metals have also been synthesized by the solid state reaction method. Their densities increased while their porosities decreased with sintering temperature yielding higher oxygen ion conductivities [18,19]. To explore simpler and cheaper synthesis methods for SOFC electrolytes and to study the effect of temperature on un-doped and Mg- and Sr-doped ceria, representative samples were prepared and investigated.

2. Experimental

2.1. Sample preparation

Commercially available powders of CeO_2, MgO and $SrCO_3$ (AR grade, Sigma Aldrich, USA, 99.9% purity) were used as starting materials. The powders of CeO_2 and $SrCO_3$ were mixed in the appropriate stoichiometric proportions (1 mole%) to make $Ce_{0.99}Sr_{0.01}O_{1.995}$. The mixture was ground in agate and mortar to obtain a homogenized powder. The powder was calcinated at 800 °C for 2 h to decompose the $SrCO_3$ and reground. Two mole% of polyvinylpyridine was added to the powder as a binder and was mixed thoroughly. The powder sample was uni-axially pressed by a pressure of 10 tons/sq inch to obtain disc-shaped pellets. $Ce_{0.99}Mg_{0.01}O_{1.995}$ and un-doped CeO_2 pellets were prepared in a similar manner. The prepared pellets were sintered at 1200 °C, 1300 °C and 1400 °C for 2 h in air, at a ramp of 2 °C/min and cooled to room temperature by the rate. The prepared un-doped CeO_2 pellets were identified as CE12, CE13 and CE14; Sr-doped pellets as SC12, SC13 and SC14; and Mg-doped pellets as MC12, MC13 and MC14, which were sintered at temperatures of 1200 °C, 1300 °C and 1400 °C, respectively. Additionally, bulk densities (d_B) were determined for the aforementioned samples. Finally, a total of six dense pellets (CE12, CE13 and CE14, Sr-doped pellets SC13 and SC14 and Mg-doped MC14) were used for characterization.

2.2. Characterization

2.2.1. Density

Bulk densities (d_B) of the sintered samples were measured by Archimedes' method. The theoretical densities were measured by the formula

$$d_{th} = \frac{4}{A^3 N_a}[0.99M_C + 0.01M + 1.995M_O] \quad (1)$$

where M_C, M_O and 'M' are atomic wt. of ceria; oxygen and the dopants Sr and Mg; and A is the lattice parameter.

2.2.2. Structure and morphology

The phase and structural properties of sintered pellets were studied by powder X-ray diffraction (XRD) using Cu Kα radiation (λ = 1.54 Å) as the radiation source at 40 kV and 30 mA. The crystalline size 'D' was measured by Scherrer's formula

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (2)$$

where β is FWHM of the peak and θ is Bragg angle. The lattice parameter was calculated by using the relation

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (3)$$

Surface morphology was characterized by scanning electron microscopy (ZEISS Evo series SEM) at an operating voltage of 15 kV. Grain size was measured from higher magnification SEM micrographs.

3. Results and discussion

The measured bulk densities, d_B, of samples are between 86% and 94% of their theoretical densities, d_{th}. Table 1 gives the relative densities of samples sintered at different temperatures. It is observed that the relative density increases with increasing sintering temperature, as shown in Fig. 1.

Substitution of Sr in ceria leads to an increase in density of the ceria solid solution. The relative density is