Solid State Ionics 294 (2016) 67–72

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Synthesis and electrochemical performance of $Ce_{1-x}Yb_xO_{2-x/2}$ solid electrolytes: The potential of microwave sintering

Moisés R. Cesário *, Etienne Savary, Sylvain Marinel, Bernard Raveau, Vincent Caignaert

Laboratoire CRISMAT ENSICAEN UMR CNRS 6508, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex 04, France

ARTICLE INFO

Article history:
Received 2 April 2016
Received in revised form 8 July 2016
Accepted 12 July 2016
Available online 20 July 2016

Keywords:
Ytterbium-doped ceria
Microwave sintering
X-ray powder diffraction
Conductivity

ABSTRACT

Reaction-synthesized ytterbium-doped ceria ($Ce_{1-x}Yb_xO_{2-x/2}$; x = 0.2 and 0.5) ceramics have been prepared by microwave and conventional sintering approaches. X-ray powder diffraction confirmed the attainment of the fluorite-type structure with similar lattice parameter, regardless the sintering route used. Microwave sintering produces high-density $Ce_{1-x}Yb_xO_{2-x/2}$ ceramics with grain size (˜2 μm) lower than the conventional ones (5–10 μm). Electrochemical impedance spectroscopy carried out in air atmosphere revealed that microwave processed samples have higher bulk conductivity compared to conventional ceramics. The low activation energy of microwave sintered samples indicates that it is a very attractive process for obtaining solid electrolytes for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs).

1. Introduction

In a context of growing global industrialization that requires systems of production and distribution of electricity of high reliability and efficiency, solid oxide fuel cells (SOFC) emerged as a major technological promise for the production of clean energy. The development of novel functional electrolyte materials or even the microstructure optimization of conventional materials allows the decrease of the SOFC operating temperature to 600–750 °C or lower.

Cerium oxide (CeO_2) has been extensively studied as catalyst, a material of high refractive index, a hydrogen storage material, an oxygen sensor [1–4]. One of the most promising applications of CeO_2-based materials is the production of electrolyte material for IT-SOFCs. The choice of this material as electrolyte is due to its fluorite-type (AO_2) structure, which can be considered the prototype system for materials of high oxygen ion conductivity [5–8]. Its unit cell is face-centered cubic of tetravalent A-cation with oxygen anions occupying tetrahedral sites, leading to a large number of octahedral interstitial sites [5,9]. Thus, this structure can be considered open, with a large tolerance for high levels of atomic disorder, which may be introduced either by doping, reduction or oxidation. The addition of dopants as trivalent rare earth (RE) cations, Yb_2O_3 for example, to these fluorite-type oxides results in the creation of oxygen vacancy to maintain neutrality (Eq. (1), Kroger Vink notation of defects), which are responsible for the ionic conduction [5,9,10]. However, the mobility of oxygen ions will be dependent on the oxide crystal structure.

$$Yb_2O_3 \rightarrow 2Yb'_{Ce} + 3O_O^x + V_O^{\cdot\cdot} \quad (1)$$

where Yb'_{Ce} means an atom of Yb^{3+} that occupies a site of Ce^{4+}, $V_O^{\cdot\cdot}$ is an oxygen vacancy with doubly positive effective charge and O_O^x represents an oxygen ion.

The ionic conductivity of the electrolyte is strongly dependent on the dopant properties, such as concentration, formal charge and ionic radius [10,11]. Yb^{3+} ions are good candidates to replace Ce^{4+} due to their ionic radius, similar to that of Ce^{+4} (98.5 vs 97 pm). The conductivity of CeO_2 ceramics doped with various ions (Ca^{2+}, Sr^{2+}, Ba^{2+}, Y^{3+}, Ln^{3+}, Sm^{3+}, Gd^{3+}, Nd^{3+}) has been extensively studied [12–17].

An ideal electrolyte material for IT-SOFCs should have high densification to avoid the mixture of gaseous constituents of the anode and cathode compartments. However, the performance of the ceramic electrolytes is very much dependent on the ceramic processing route [18–20].

The present work reports the preparation of $Ce_{1-x}Yb_xO_{2-x/2}$ ceramics by microwave sintering. In recent years, microwave energy has been successfully used for processing many materials, including the synthesis of oxides or the sintering of materials [21]. This technology is known to be faster and greener than conventional technologies involving infra-red radiation heating sources (electrical or gas furnaces) [22]. It is also well established that considering the penetration depth of the microwave electrical field (E), which is a few centimeter in most oxide materials [23], the generated heat is volumetric. This is a great advantage over infra-red conventional heating since it also contributes to the high efficiency of the microwave thermal process. This method promotes a more homogeneous heating of green pellets, as a

---

* Corresponding author.
E-mail addresses: moises.cesario@ensicaen.fr, moisesrcesario@gmail.com (M.R. Cesário).

http://dx.doi.org/10.1016/j.ssi.2016.07.005

result of the interaction of microwave on a microscopic level with atoms, ions and dipoles in the materials [24]. This not only leads to a better homogeneity and purity of the final product but also an energy gain and time during the ceramic preparation. From an economic point of view, this process is very attractive for obtaining ceramics on an industrial scale. For comparison, $Ce_{1-x}Yb_xO_{2-x/2}$ ceramics were also prepared by conventional sintering.

The effects of sintering methods on specific grain boundary, grain and total conductivities were studied by electrochemical impedance spectroscopy.

2. Experimental

2.1. $Ce_{1-x}Yb_xO_{2-x/2}$ preparation

$Ce_{1-x}Yb_xO_{2-x/2}$ solid electrolytes ($x = 0.2$ and 0.5) were prepared by microwave and conventional sintering approaches. Firstly, stoichiometric amounts of cerium oxide [CeO_2 – Prolabo, France], and ytterbium oxide [Yb_2O_3– Alfa Aesar, Germany] were mixed by ball milling for 10 h with zirconia balls. Afterwards, powders were uniaxially pressed into pellets (10 mm diameter and 1–2 mm thick) using 200 MPa and then sintered in air atmosphere. Conventional sintering was performed at 1500 °C and 1600 °C with dwell time of 5 h and using a heating rate of 2 °C min^{-1}. As a second sintering approach, microwave sintering was performed only for the $Ce_{0.8}Yb_{0.2}O_{1.9}$ composition (Table 1). A 2 kW microwave generator, working at 2.45 GHz, was used (SAIREM 20 KSM). This generator delivers a microwave radiation through a TE10 rectangular wave guide (WR340). The circuit is ended by a TE10m single-mode cavity. The TE103 mode was excited, subjecting the sample to a maximum of the Electric Field (E mode). Details of the experimental microwave set-up can be found in reference [24]. The pellet samples were positioned into a thermal insulation box made of fibrous alumina-silica based material (Fiberfrax duraboard 1600). To avoid any contact between the sample and the thermal box, a small and thin rectangular alumina piece was used underneath the sample as a support. The sample surface temperature was measured by using an Infra-Red monochromatic pyrometer (Ircon modline 5). The incident power was tuned in order to achieve the target temperature (1500 °C) and the cavity length was also manually tuned to be in the optimal resonance conditions. The dwell time at 1500 °C was systematically 15 min, with a heating rate of roughly 2 °C s^{-1}.

$Ce_{0.8}Yb_{0.2}O_{1.9}$ ceramics, regardless the sintering route, exhibited >94% of the theoretical density (7.51 g cm^{-3}).

2.2. Structural and microstructural characterization

X-ray diffraction (XRD) patterns of the as-sintered sample were obtained with a Panalytical Xpert-Pro diffractometer using a Cu Kα radiation under a continuous scanning method in 2θ range of 10–100° for 1.5 h.

The powder and Ceramics samples polished mechanically and then polished using an Argon ion beam (JEOL SM – 09010 Cross section polisher) were subjected to microstructural characterization by Scanning Electron Microscopy (SEM, ZEIS SUPRA 55), coupled with an Energy Dispersive X-ray analyzer.

2.3. Electrical characterization

Platinum paste was applied to both sides of the pellets by firing at 1000 °C/1 h and electrochemical impedance spectroscopy (Princeton Applied Research –Model 1025) measurements were carried out in the 473–1073 K temperature range, with 100 mV AC test signal amplitude in the frequency range of 0.1 Hz–5 MHz under ambient atmosphere.

The impedance contributions ascribed to grain boundaries and grain interiors (bulk) were obtained after deconvolution of impedance spectra by fitting to conventional equivalent circuits using ZSimpWin software (version 3.1).

3. Results and discussion

The ball milled powders showed a clear mixture of CeO_2 and Yb_2O_3 phases in all compositions (X-ray diffraction pattern not given), as expected. X-ray diffraction patterns of as-sintered samples are shown in Fig. 1.

According to Fig. 1(a) and (b), $Ce_{0.8}Yb_{0.2}O_{1.9}$ materials prepared by solid state reaction using microwave or conventional sintering at 1500 °C showed single phase. The diffraction pattern was indexed using ICDD file number 75–0170, characterizing a cubic fluorite-type structure (Fm-3 m space group) with lattice parameter a = 5.39 Å. The $Ce_{0.5}Yb_{0.5}O_{1.75}$ composition was also heated at 1500 °C, a mixture of the fluorite type oxide and Yb_2O_3 was obtained, in good agreement with the lower solubility limit of Yb_2O_3 into the ceria lattice [25].

When the temperature of sintering was increased up to 1600 °C, the peak corresponding to Yb_2O_3 completely disappeared (Fig. 1d) and a single phase material can be assumed ($Ce_{0.5}Yb_{0.5}O_{1.75}$) from the pattern. The diffraction peaks for this phase were indexed using ICDD 75-0173 file number to the fluorite-type structure with lattice parameter a = 5.361 Å.

Fig. 2 shows the X-ray diffraction pattern from the Rietveld refinement of the CY02M sample. A comparative study between the crystallographic parameters of the materials is given in Table 2.

The refinement quality can be checked by the standard deviation ($\chi 2 = R_{wp}/R_{exp}$). The values of χ2 obtained in this work indicate that the data was successfully refined. Rietveld refinements confirm the Fm-3 m face-centered cubic symmetry and the lattice parameters obtained are in good agreement with reported ICDD and to those previously established [11,25].

The microstructures of the CeO_2 and Y_2O_3 powders mixture after ball milling and its sintered ceramics are shown in Fig. 3.

As can be seen, the powder microstructure exhibits apparent agglomeration with particles sizes in nanometer range (Fig. 3a). The grain average size of the starting powders was around 150 nm. This powder was easily densified using microwave or conventional sintering. According to SEM images (Fig. 3b and c) for all the different sintering procedures employed, the pellets sintered at 1500 °C showed a dense microstructure that is consistent with their relative densities. However, the ceramic obtained by microwave irradiation (CY02M) displayed lower grain size compared to CY02CF (~2 μm *vs.* 5–10 μm). The microwave sintering pellet showed lower grain size compared with the conventional method, because the densification is faster with

Table 1
Nomenclature, sintering conditions and sample densification after sintering.

Samples - Composition	Sintering conditions	Densification (%)	Nomenclature
$Ce_{0.8}Yb_{0.2}O_{1.9}$	Microwave RT to 1500 °C/15 min	96.54	CY02M
$Ce_{0.8}Yb_{0.2}O_{1.9}$	Conventional furnace RT to 1500 °C/5 h 2 °C min^{-1}	94.82	CY02CF
$Ce_{0.5}Yb_{0.5}O_{1.75}$	Conventional furnace RT to 1600 °C/5 h 2 °C min^{-1}	90.95	CY05CF

RT: room temperature.