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ScienceDirect

Ceramics International 41 (2015) 9806–9812

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fe-doped YSZ electrolyte for the fabrication of metal supported-SOFC by co-sintering

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Received 1 April 2015; received in revised form 10 April 2015; accepted 10 April 2015
Available online 23 April 2015

Abstract

Considering Fe as sintering aid for Yttria Stabilized Zirconia (YSZ), studies have been conducted under conditions necessary for the fabrication of MS-SOFC by co-sintering. Pure and Fe doped YSZ was sintered at 1350 °C in air and in argon atmosphere and a comparative study has been performed. Structural characterizations were carried out using X-ray diffraction (XRD) techniques, while ionic conductivity was measured in air using four-probe impedance spectroscopy. It is found that Fe enhances the sintering rate of YSZ in both air and argon atmosphere. All samples sintered in argon atmosphere are characterized by better 'sinterability', larger lattice parameter, higher density, larger grain size and lower conductivity, as compared to samples sintered in air. Ionic conductivity is found to decrease with increase in Fe concentration for all sintered samples.

Keywords: A. Sintering; D. ZrO_2; E. Fuel Cells; Fe dopant

1. Introduction

Solid Oxide Fuel Cell (SOFC) is looked upon as promising technology to generate electricity with high efficiency and minimal environmental impact. This high temperature electrochemical device directly generates electricity through electrochemical oxidation of the fuel [1–3]. Although favorable, rapid commercialization of SOFC technology has however been slackened due to limited long term stability and, more importantly, high costs associated with starting materials and manufacturing techniques. Anode Supported-Solid Oxide Fuel Cell (AS-SOFC) represents a very typical design where electrolyte and cathode (with thickness between 10–50 μm) are supported on a comparatively thicker anode. Composite of Ni and Yttria Stabilized Zirconia (YSZ) is the most widely used material for anode in AS-SOFC. It is due to this anode material that AS-SOFC design suffers from drawbacks such as high starting materials cost, limited long term stability, and limited stability towards rapid thermal and redox cycling [4].

Metal Supported Solid Oxide Fuel Cell (MS-SOFC) is the latest SOFC design where the ceramic layers (anode, electrolyte and cathode) are supported on a cheap and more reliable metal substrate with thickness ranging between 400 and 1000 μm. Thus, MS-SOFC design promises to overcome the major issues which are usually associated with AS-SOFC [4–8].

For the successful commercialization of SOFC it is necessary not only to reduce the cost of starting materials, but also those associated with fabrication; the production of MS-SOFC by cost-effective co-sintering route can satisfy both requirements. In the co-sintering approach, green multilayers of metal support, anode and electrolyte are co-sintered at high temperature to obtain a gas tight dense electrolyte while the other layers remain sufficiently porous to allow gas diffusion. The cathode is usually applied after co-sintering and sintered in situ during operation [6,8,9]. 8 mol% Yttria Stabilized Zirconia (8YSZ) is the most preferred electrolyte material due to its excellent stability and pure ionic conductivity in fuel and air atmosphere at typical operating temperatures [10–12].

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http://dx.doi.org/10.1016/j.ceramint.2015.04.053
0272-8842/

However, the problem associated with YSZ as electrolyte material is that it sinters at temperatures as high as 1350–1400 °C, which have adverse effect on other cell components during co-sintering. In addition, it is usually difficult to obtain sufficient density for YSZ when co-sintered with other layers even at the cited temperatures (1350–1400 °C) [4]. It has been shown that the effect of high temperature can be reduced and complete densification can be achieved at lower temperatures by using film deposition techniques such as Pulsed Laser Deposition (PLD) [13] and Vacuum Plasma Spray (VPS) [14]. By these techniques, a nearly dense electrolyte layer is deposited which may be followed by a thermal treatment at relatively lower temperatures for complete densification. In any case such low temperature processes are multistep and expensive and therefore not suitable for production on an industrial scale. Therefore, the co-sintering of multilayer remains an attractive choice.

One important difference between the co-sintering route for fabrication of AS-SOFC and MS-SOFC is that the former is co-sintered in air whereas the second has to be co-sintered in inert or slightly reducing atmosphere to prevent metal substrate oxidation. As a matter of fact, fabrication of MS-SOFC at high temperature in inert or slightly reducing atmosphere by co-sintering encounters major issues such as Ni coarsening in the anode [9], over-sintering of the anode, and undesired interactions between anode and steel substrate [8,15,16]. Therefore, MS-SOFC fabrication by co-sintering route faces such extra problems in addition to the limited densification of YSZ electrolyte.

The use of sintering aids to facilitate the YSZ electrolyte densification has been proven for AS-SOFC [25,26]. The same can also be applied for MS-SOFC fabrication by co-sintering. Moreover, since a sintering aid reduces the required temperature to obtain complete densification, it will have a less severe effect on issues which are usually encountered in MS-SOFC fabrication by co-sintering as discussed above. The different sintering aids for YSZ include $Sr_2Ga_2O_5$ [17], Bi_2O_3 [18], CuO [19–20], Co [21,22], Al_2O_3 [23], MnO_2 [24] and Fe [25–28]. Out of these, Fe has been widely studied as it is most effective. Moreover, SOFC with Fe-doped YSZ electrolyte has been demonstrated to show enhanced performance [26,28]. In addition, Fe_2O_3 has also shown to exert scavenging effect on SiO_2 impurities in 'impure' YSZ. For YSZ containing SiO_2 impurities, Fe_2O_3 has been found to be beneficial for the total conductivity by significantly enhancing the grain boundary conductivity with little effect on grain interior conductivity [25].

All previous research works on Fe-doped YSZ concern anode supported-solid oxide fuel cells where the cell is fabricated by sintering in air atmosphere. With the goal to use it for MS-SOFC fabrication by co-sintering (i.e. in reducing or inert atmosphere), a comparative study of Fe-doped YSZ sintering in air and argon and on the obtained conductivity has been carried out in the present work.

2. Experimental procedure

$Fe(NO_3)_3 \cdot 9H_2O$ was used as source of Fe for the preparation of 0–3 mol% Fe-doped YSZ. 8YSZ (Baikowski, France), $Fe(NO_3)_3 \cdot 9H_2O$ (Farmitalia Carlo Erba, Italy), zirconia balls (Inframat Advanced Materials, USA) and water were put together in a plastic jar and mixed for 2 h by a planetary mixer (Turbula, Switzerland). The obtained slurry was dried overnight at 140 °C and the solid mass was then manually ground by mortar and pestle. The powder was then calcined at 600 °C for 2 h allowing the formation of Fe_2O_3 from the nitrate. The powder was mixed once again in the planetary mixer along with water and zirconia balls to ensure homogenization. The obtained slurry was dried overnight and finally ground manually to produce a fine powder.

In order to prepare the samples for sintering, 2.5 g of the powder was pressed in a cylindrical dye of 13 mm diameter at 75 MPa for 2 min. The pellets were sintered with a heating rate of 5 °C/min up to 1350 °C for 2 h in air or argon atmosphere in the dilatometer (Linseis GmbH, Germany). For sintering in argon, the dilatometer was first evacuated and flushed with argon, this procedure being repeated three times to ensure the complete replacement of air by argon. A flow rate of 100 mL/min of argon was used for dilatometric studies. A digital camera was used to take the picture of the sintered samples and compare their colors. The density of the samples was measured by Archimede's method.

For XRD and grain size analysis the sintered pellets were divided in two semicircle portions. XRD (Rigaku Geigerflex X-ray Powder Diffractometer-Japan) was carried on the flat surface between 20° and 80° with a step of 0.05° and a hold time of 8 s. For the grain size analysis the samples were polished up to 1μ with help of diamond paste, the polished samples were etched at 1300 °C for 20 min in air or argon and then observed under SEM (JEOL JSM 5500, Japan). The grain size was measured by the lineal intercept method.

For the conductivity measurements, pure and Fe-doped YSZ powders were first mixed with 5 wt% binder (B1000, Duramax, Rohm and Haas, France) and 1.5 g of such powder were pressed in a cylindrical steel mold with 20 mm diameter at 75 MPa for 2 min. The obtained pellets (thickness of ~1.7 mm) were heated at 600 °C for 30 min in air to remove the binder and then sintered with heating rate of 5 °C/min up to 1350 °C for 2 h in air or argon atmosphere in a tubular furnace (Gero, Hochtemperaturöfen GmbH, Germany). Again, care was taken for sintering in argon, the furnace being first evacuated and then filled with argon and flushed thrice before the thermal treatment, a flow rate of 100 mL/min was used for sintering in argon. The obtained samples were coated with a thin Pt paste layer on the circular surface and then cured at 1200 °C for 2 h in air or argon atmosphere. Ionic conductivity was then measured between 550–750 °C in air using four-probe impedance spectroscopy over the frequency range of 10° to 10^5 Hz with an amplitude of 150 mV. Before starting the conductivity measurements all the samples were first heated up to 750 °C in air for 24 h to stabilize the system.

3. Results and discussion

3.1. Dilatometric analysis

Fig. 1 shows the linear shrinkage (dL/L_o) as a function of temperature for Fe-doped YSZ samples sintered in air and in