Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Short communication

The effect of NiO addition on the grain boundary behavior and electrochemical performance of Gd-doped ceria solid electrolyte under different sintering conditions

Dan Xu[a], Kehui Li[a], Yongjun Zhou[a], Yang Gao[b], Duanting Yan[c], Shifeng Xu[a,*]

[a] College of Science, Shenyang Aerospace University, Shenyang 110136, PR China
[b] Dalian Scientific Test and Control Technology Institute, Dalian 116013, PR China
[c] Center for Advanced Opto-Electronic Functional Materials Research, School of Physics, Northeast Normal University, Changchun 130024, PR China

ARTICLE INFO

Article history:
Received 5 February 2016
Received in revised form 22 June 2016
Accepted 21 July 2016
Available online xxx

Keywords:
Solid oxide fuel cell
Transition metal oxides
CeO_2
Grain boundary
Electrochemical performance

ABSTRACT

It has been reported that some transition metal oxides are effective aids both for the densification and the grain boundary behavior of ceria-based electrolytes. In the present work, NiO which is the most popular component of the anode of solid oxide fuel cells was added directly into the electrolyte ceramic, $Ce_{0.8}Gd_{0.2}O_{1.9}$, to investigate the effects of the presence of NiO on the properties of GDC electrolyte. All of the samples possess a single phase with cubic fluorite structure. The grain size is increased by the addition of NiO when the sintering temperature is 1400 °C. This modification in chemical composition also results in a decrease in activation energy and thus a tendency to enhance grain boundary mobility. The maximum power density of the composite electrolyte single cell is higher than that of a GDC single cell. Therefore, NiO can be used as an effective aid for ceria-based electrolytes.

1. Introduction

Solid oxide fuel cells (SOFCs) have been drawing great attentions due to its various potential advantages, such as a wide variety of available fuels, inexpensive technology, lower or zero emissions of pollutants (SO_2 and NO_x) and greenhouse gases and highly efficient in energy conversion [1–3]. Fluorite structure oxides such as zirconia and ceria have been studied as electrolyte materials for SOFCs. Compared with the conventional oxide ionic conductor yttria-stabilized zirconia (YSZ), rare-earth (RE) doped-ceria exhibits sufficiently high oxide ionic conductivity at lower operating temperatures (500–800 °C) and is considered to be a very promising alternative electrolyte material for intermediate/low-temperature SOFCs.

The grain boundary (GB) behavior usually dominates the total conductivity of RE doped-ceria electrolytes in intermediate temperature range. The grain boundary resistance is several orders of magnitude higher than the bulk resistance at the temperatures at which SOFCs are operated [4,5]. This is ascribed to the high activation energy of the grain boundary. There are two main factors known to contribute to the blocking effect of the grain boundary: one is attributed to the presence of SiO_2 or other impurities at the grain boundary; the other is the depletion of oxygen vacancies near the grain boundary due to the formation of the space charge layer [6–8]. These effects are strongly related to grain size and the associated grain-boundary area. In recent years, in order to reduce the grain boundary resistance, several transition metal oxides (TMOs), such as Fe_2O_3, ZnO and SrO have been used as additives. In our previous work [9], we found that Fe_2O_3 have a strong effect on the microstructure and grain growth of $Ce_{0.85}Sm_{0.15}O_{1.925}$ (SDC) ceramics; the power density of these single cell is improved with Fe_2O_3. Yifeng Zheng [10] found that the conductivity of $Ce_{0.8}Sm_{0.2}O_{1.9}$ can be improved with the addition of appropriate amounts of Fe_2O_3. Christoph Kleinlogel [11] reported that CeO_2 can be sintered at low temperatures to dense ceramics by the additions of Cu, Ni, and Co-oxide. TMOs could also be used as a grain boundary scavenger for ceria-based electrolytes [12].

NiO-a member of TMOs is most commonly used for the anode side of SOFCs. The main reasons for NiO/doped-ceria composite anode selection are in its relatively good ionic and electronic conductivity, acceptable catalytic activity for hydrogen or hydrocarbon electro-oxidation, and in its comparable thermal expansion coefficient with the doped-ceria electrolyte [13–15]. Since this kind of anode (NiO content of generally >40 vol%) and electrolytes are commonly co-fired at high temperature (>1200 °C) in SOFCs man-

---

* Corresponding author.
E-mail address: sfxu@sau.edu.cn (S. Xu).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.07.026

Please cite this article in press as: D. Xu, et al., The effect of NiO addition on the grain boundary behavior and electrochemical performance of Gd-doped ceria solid electrolyte under different sintering conditions, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.07.026

ufacturing, if NiO diffuses toward the electrolyte, the effects of the NiO on the properties of the electrolyte become relatively important. Chin-Yi Chen [16] has already added NiO directly into the electrolyte ceramic to investigate the effects of the presence of NiO on the related properties of yttria-doped ceria (YDC) electrolyte. The data revealed that the precipitated NiO may reduce the conduction activation energy of the YDC electrolyte, increasing the conductivity of the YDC composite. In this work, NiO was used as a sintering aid and the effects of NiO addition on the microstructure of GDC were investigated to clarify the role of the additive in the microstructure-related electrical conductivity of the solid electrolyte. The aim of the present study was to test the possibility of NiO as a grain boundary scavenger for ceria-based electrolytes and to find a way to reduce the grain boundary resistivity of ceria electrolytes. We decreased the content of NiO to a sufficiently low level so that the transportation of electron caused by NiO can be avoided. The relations between the transition metal concentration as well as the sintering conditions and the grain boundary resistivity of ceria were systematically investigated. $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) was chosen to be the base electrolyte because of its high grain conductivity and better stability at low oxygen partial pressure [17].

2. Experimental procedures

2.1. Synthesis of the GDC-NiO powder

For the GDC+ x mol% NiO (x = 0, 0.5,1, 2, 3) mixtures, $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) powder was synthesized by a co-precipitation method, to which NiO powder was added. Analytical reagent CeO_2 powder (99.8%), Gd_2O_3 powder (99.95%) and NiO (99.5%) powder were used as starting materials. Firstly, a mixed aqueous solution of 0.125 mol L^{-1} ($Ce(NO_3)_3$ and $Gd(NO_3)_3$) was prepared according to the stoichiometric ratio of $Ce_{0.8}Gd_{0.2}O_{1.9}$. NH_4HCO_3 was chosen to be the precipitating agent and the solution concentration was prepared to be 0.375 mol L^{-1}. The nitrates solution was poured in the precipitating agent one under vigorous stirring and co-precipitated by controlling pH about 8–9 using ammonia solution. The so formed suspensions were aged for 16 h at 50 °C to allow the equilibration of the precipitation process. The precipitates were filtered and washed by ultrapure water and ethanol three times, respectively. They were dried in an oven at 600 °C for 4 h. The dried precipitates were pulverized by alumina mortar and pestle to get GDC powder. The GDC and different amounts of NiO powders were mixed using zirconia balls for 6 h. Then the obtained powders were ground and die-pressed into disc pellets (13 mm in diameter, 0.5 mm in thickness) under a pressure of about 250 MPa. The pellets were subsequently sintered in air at 1200 °C, 1300 °C and 1400 °C for 10 h, respectively.

2.2. Cell fabrication

The cathode material $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) was prepared by a sol-gel method. The mixture of NiO and SDC by weight of 65:35 was used as anode. The cathode and anode materials were prepared as described in our previous report [18]. The anode slurry were painted on one side of each electrolyte pellet and sintered in air at 1250 °C for 5 h. The cathode slurry was painted on the other side of each electrolyte pellet with anode and sintered in air at 950 °C for 4 h. The pellet was attached to one end of an alumina tube with the anode inside by using silver paste for sealing. Finally, both anode and cathode surfaces were painted by silver paste as current collectors for fuel cell measurements.

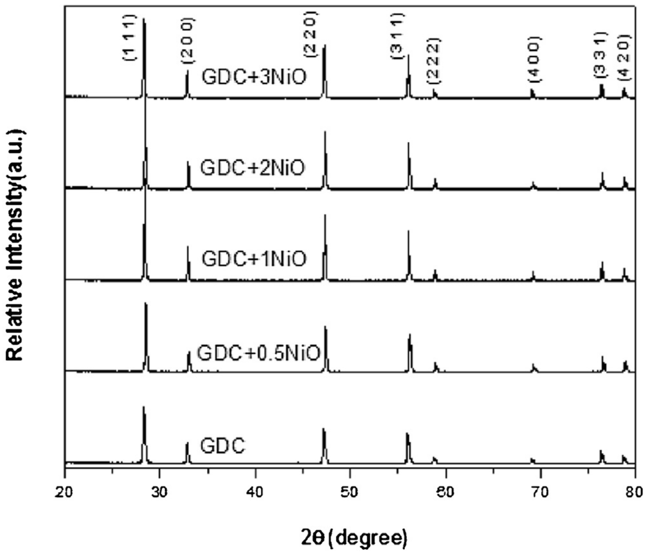

Fig. 1. X-ray diffraction patterns of GDC + x mol% NiO (x = 0, 0.5,1, 2, 3) sintered at 1400 °C for 10 h.

2.3. Characterization

The crystal structure and phase composition of sintered pellets were characterized by x-ray diffraction (XRD) in a Rigaku D/MAX2200PC diffractometer (Cu *Kα* radiation). Lattice parameters were evaluated from reflections appearing in the range 2θ = 20–80°, by means of the Unit-Cell program. The microstructure of the sintered samples was characterized using a Quanta FEG250 scanning electron microscopy (SEM).

Electrochemical impedance spectra (EIS) and the electrochemical performance of SOFC were obtained using an electrochemical instrument (CHI660E, CH Instruments Inc, China). The electrical conductivity of the electrolyte pellets was measured in air by A. C. impedance spectroscopy method in a temperature range of 400–800 °C. Frequency range for impedance measurement was 0.1 Hz–100 kHz.

The electrochemical performance of the fuel cells was tested between 600 and 800 °C. Hydrogen produced by TH-300 hydrogen generator (HP) was fed into the alumina tube as fuel with a flow rate of 350 ml min^{-1}, while oxygen in the air was used as oxidant.

3. Results and discussion

3.1. Phase analysis and crystal structure

The XRD patterns of GDC + x mol% NiO samples sintered at 1400 °C for 10 h are shown in Fig. 1. The ceria is cubic system with space group *Fm3m*. As seem from Fig. 1, all the characteristic peaks belong to cubic phase of CeO_2. No significant second phase is identified in the XRD patterns.

The effect of the NiO content on the lattice parameters is shown in Table 1. The lattice parameters of GDC + x mol% NiO samples are higher than that of GDC sintered at 1300 °C. The slight change of lattice parameter, demonstrates a very low solubility of NiO in GDC. Masashi Mori [19] reported that the solubility limit was <1 mol% for NiO after heating at 1200 °C. Most of the NiO take the interstitial lattice site of the GDC lattice or stay at the grain boundary. For the samples sintered at 1400 °C, NiO leads to the decrease of the lattice parameter of the based materials. Because of smaller radius of Ni^{2+} (0.083 nm) than that of Ce^{4+} (0.097 nm), substituting Ni^{2+} for Ce^{4+} can certainly induce the variation of lattice parameter. There is a slight increase in the lattice parameters with increase in the

Please cite this article in press as: D. Xu, et al., The effect of NiO addition on the grain boundary behavior and electrochemical performance of Gd-doped ceria solid electrolyte under different sintering conditions, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.07.026