Solid State Ionics xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Solid State Ionics

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

Stability of LSCF electrode with GDC interlayer in YSZ-based solid oxide electrolysis cell

Sun Jae Kim, Gyeong Man Choi *

Fuel Cell Research Center, Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea

ARTICLE INFO

Article history:
Received 15 May 2013
Received in revised form 18 December 2013
Accepted 2 January 2014
Available online xxxx

Keywords:
SOEC
Co-firing
LSCF degradation
Delamination
Air electrode stability

ABSTRACT

The performance and stability of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) air electrode with $Gd_{0.2}Ce_{0.8}O_{2-\delta}$ (GDC) as an interlayer were tested in the Solid Oxide Electrolysis Cell (SOEC) mode. In order to study the stability and performance of the LSCF air electrode, an 8 mol% Y_2O_3-stabilized zirconia (YSZ) electrolyte supported on a Ni–YSZ fuel electrode was fabricated with and without a GDC interlayer, which was inserted between YSZ and LSCF. To determine the stability of the interlayer and find the optimum fabrication conditions, cells with the GDC interlayer were also co-fired at temperatures in the range of 1300–1500 °C and their performance was compared. Single cells were tested with an anodic polarization of 800 mA/cm^2 in 80% H_2O + 20% H_2 at 800 °C. The cell without an interlayer showed a large increase in Ohmic Area Specific Resistance (ASR) from 0.09 Ωcm^2 to 0.16 Ωcm^2 during 50 h of operation due possibly to the observed delamination between the LSCF and YSZ. On the other hand, the cell with the interlayer showed a slower increase in Ohmic ASR from 0.14 Ωcm^2 to 0.153 Ωcm^2 with little delamination. The electrode polarization ASR of the cell with the interlayer also had a similar slower change, from 0.16 to 0.185 Ωcm^2, compared to that of the cell without an interlayer, from 0.143 to 0.35 Ωcm^2, after 50 h. The cell co-fired at 1400 °C had the smallest and most stable value of the total ASR for 100 h.

1. Introduction

A steam electrolysis method using a Solid Oxide Electrolysis Cell (SOEC) is emerging as the state-of-the-art technology because water molecules are easier to split at high temperature into hydrogen and oxygen molecules than at low temperature. The SOEC has a variety of advantages due to its high operation temperature. First, electrodes in the SOEC have a cost advantage because they do not require expensive noble metal catalysis (Pt, Pd, etc.) for oxygen molecular desorption reactions. Second, the SOEC has a high hydrogen-generation efficiency from water steam at high temperature because the steam electrolysis reaction is an endothermic reaction [1]. In the SOEC electrochemical reaction, oxidation and reduction reactions take place in the reverse order from the reactions of the SOFC. The water steam reduced by electrons may produce hydrogen fuel at the fuel electrode (1). On the other hand, oxygen ions are oxidized to oxygen gas by giving out the electrons (2).

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \quad (1)$$

$$O^{2-} \rightarrow \tfrac{1}{2}O_2 + 2e^-. \quad (2)$$

Similar cell components are often used for the SOFC and SOEC [2,3]. Yttria-stabilized zirconia (YSZ) is usually used as an electrolyte. For the fuel electrode, Ni–YSZ cermet is generally used. (La,Sr)MnO_3 (LSM) or (La,Sr)(Co,Fe)O_3 (LSCF) has been used as an air electrode. These materials have been studied in the SOFC for a long time. However, the flow of oxygen in the opposite direction during SOEC operation requires an understanding of different electrochemical reactions. For example, LSM is stable in the SOFC mode. However, a LSM delamination phenomenon has been reported in the SOEC mode due to different oxygen ion movements [4–6]. Moreover, LSCF also shows degradation during SOEC operation as will be shown in this study.

SOFCs often utilize Gd-doped Ceria (GDC) as an interlayer for preventing the reaction between the air electrode and the electrolyte [7,8]. Although the GDC interlayer may effectively prevent the reaction, the insulation layer formed between the GDC and YSZ also contributes to increasing the Ohmic ASR of SOFCs and SOECs [9]. The interface between YSZ and GDC also shows instability under anodic current [10,11] which rapidly decreases the fuel-generation efficiency.

In this study, we selected $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) as an air electrode, a popular cathode material in the SOFC mode, and tested its stability in the SOEC mode. In order to study the LSCF stability, an 8 mol% Y_2O_3-stabilized zirconia (YSZ) electrolyte and Ni–YSZ composite fuel electrode were fabricated with and without a GDC interlayer and their performances were compared. In order to see the stability of the interlayer and find the optimum fabrication conditions, the cells with the GDC interlayer were also co-fired at various temperatures and their performance was tested with an applied anodic current.

* Corresponding author.
E-mail address: gmchoi@postech.ac.kr (G.M. Choi).

0167-2738/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ssi.2014.01.001

2. Experimental procedure

All the layers except the LSCF air electrode were fabricated using tape-casting and co-firing. YSZ paste for tape casting was prepared by ball milling YSZ (TZ-8YS, Tosoh, Japan) powder with organic solution (polymeric solution + binder) for 72 h with zirconia balls. NiO (99.97%, Kojundo chemical, Japan) and YSZ powders in a 6:4 weight ratio were mixed to prepare the fuel electrode by planetary milling with ethanol and zirconia balls for 4 h. To prepare the support layer, NiO-YSZ powder in a 6:4 weight ratio and 10 wt.% starch as a pore former were mixed by ball milling for 72 h with zirconia balls with ethanol. GDC powder was synthesized by mixing and ball milling 20 mol% Ga_2O_3 (99.9%, Kojundo chemical, Japan) powder with 80 mol% CeO_2 (99.9%, Kojundo chemical, Japan) powder for 72 h with zirconia balls followed by calcining at 1000 °C for 2 h. Tape casting of each layer was performed using a tape caster (Hansung system, Inc., Korea). Green tapes of the GDC interlayer, YSZ electrolyte, NiO-YSZ fuel electrode, and NiO-YSZ support were laminated with high pressure (650 MPa) at 60 °C for ~15 min. The laminated tape was cut into a circular shape (d = 24 mm) by a punch machine. Green circular tape was co-fired at 1300 °C, 1350 °C, 1400 °C, and 1500 °C for 5 h. LSCF (AGC Seimi Chemical Co., Ltd, Japan) pastes were prepared for screen printing by mixing the powders with an organic solution containing alpha-terpineol and ethylene cellulose. After co-firing the laminated circular tapes, LSCF as an air electrode was coated on top of the GDC interlayer by screen-printing and firing at 1040 °C for 2 h. The area of the air electrode was 0.502 cm^2. Platinum mesh as a current collector was in contact with the electrode using Pt paste and fired at 850 °C for 2 h. Fig. 1 shows the schematic setup for the SOEC test. The typical thicknesses of the layers are shown. The single cell was positioned on the alumina tube and sealed by ceramic sealant (Aremco Products, USA). The flow rate of fuel consisting of 80% H_2O + 20% was 150 cm^3/min and open air was used. The performances of the SOECs were tested and compared at 800 °C with an anodic current of 800 mA/cm^2 with typical voltage of 1.1–1.3 V. The impedance was measured by VSP (Bio Logic Science instruments, France) at open circuit conditions after stopping the anodic current. The microstructure and the phase change were examined after the SOEC test using a scanning electron microscope (FE-SEM, Philips electron optics B.V., Netherlands) and X-ray diffraction (XRD, Rigaku, Japan), respectively.

3. Results and discussion

Fig. 2 shows the impedance spectra of the cells with and without the GDC interlayer. Fig. 2a and b, respectively, show the impedance spectra with time for the cells with and without the GDC interlayer for 50 h. The

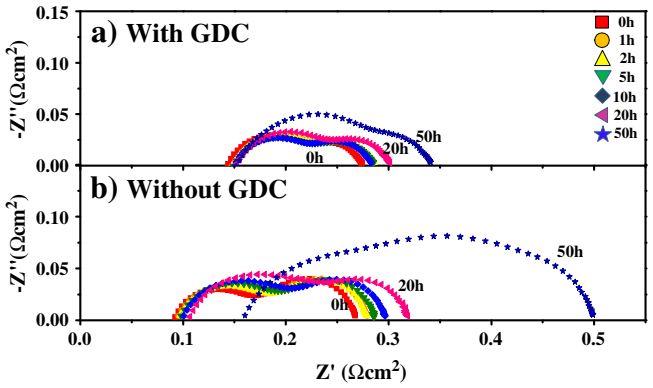

Fig. 2. Impedance spectra of cells co-fired at 1400 °C and measured at 800 °C for 50 h (a) with the GDC layer, and (b) without the GDC interlayer. Impedance data were recorded at the open circuit mode after interrupting the current at 800 °C with fuel gas of 80% steam + 20% H_2.

cells without GDC had lower initial Ohmic resistance values than the cells with GDC. The Ohmic resistance, ~0.09 Ωcm^2, was slightly larger than the calculated value (~0.05 Ωcm^2) from the known resistivity of the YSZ electrolyte and its thickness (~15 μm) due possibly to the contribution from the resistive layer formed between LSCF and YSZ [12]. The Ohmic resistance value of the cell without GDC increased slowly with time for first 20 h. There was a large increase after 50 h to 0.16 Ωcm^2 due possibly to the delamination between the air electrode (LSCF) and the electrolyte (YSZ). The electrode polarization ASR values exhibited similar behavior: a slow increase for the initial 20 h and a rapid increase after 50 h (~0.14 to ~0.35 Ωcm^2). The abrupt and simultaneous increase of the Ohmic resistance and the electrode polarization resistance confirms the possible delamination of LSCF from the YSZ electrolyte.

Fig. 2a shows the impedance for the cell with the GDC interlayer for 50 h. Initial Ohmic resistance was ~0.14 Ωcm^2, which was ~50% larger than that of the cell without GDC (~0.09 Ωcm^2). The high Ohmic resistance value is attributed to the insulating layer formed by the reaction between the YSZ and GDC layers. YSZ and GDC form a complete solid solution that has a minimum conductivity between the two fluorite materials [13]. Although the Ohmic ASR of the cell with GDC had a higher initial value than that of the cell without GDC, the value increased only slightly for 50 h, from ~0.14 Ωcm^2 to ~0.15 Ωcm^2. The increase of the electrode polarization resistance value was also relatively small for 50 h, 0.16 Ωcm^2 to 0.18 Ωcm^2. Thus the existence of GDC as

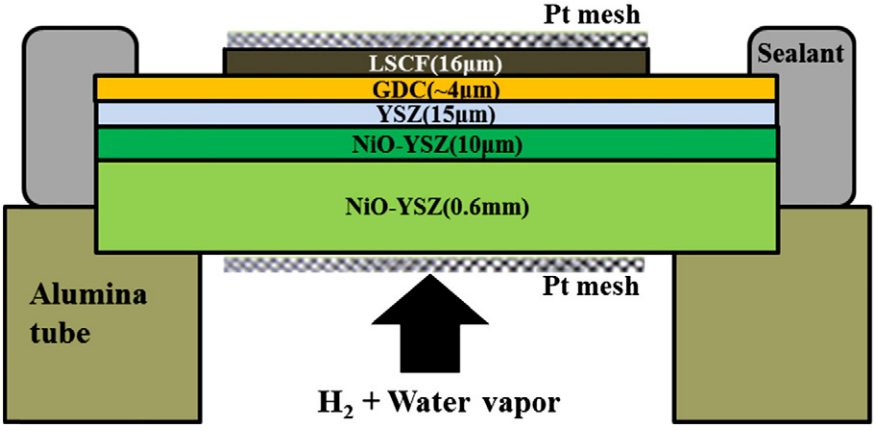

Fig. 1. A schematic figure of the experimental setup for the electrochemical test for the fuel electrode supported SOEC. All layers (GDC/YSZ/NiO–YSZ/NiO–YSZ), except the LSCF air electrode and Pt current collectors, are tape casted and their thicknesses are shown. A cell without the GDC interlayer was also tested.

Please cite this article as: S.J. Kim, G.M. Choi, Solid State Ionics (2014), http://dx.doi.org/10.1016/j.ssi.2014.01.001