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Low-temperature co-firing process of solid oxide fuel cells by a trace of copper

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ABSTRACT

8 mol % yttria stabilized zirconia (8 YSZ) is widely used as an electrolyte material for solid oxide fuel cells (SOFCs) at high temperatures, but its poor sinterability causes complications of the cell fabrication processes, increasing manufacturing costs significantly. In this study, a low-temperature co-firing process for the YSZ-based SOFCs is developed by adding the small amount of Cu to each of YSZ electrolytes and anodes. The cells are successfully fabricated without any distortions or cracks. The cell is about 1.011 V at 850 °C in open circuit voltage (OCV), which is reasonable despite of the co-firing process even at 1250 °C. The maximum power density is 0.71 W cm⁻² at 850 °C, which has similar performance of a conventional cell fabricated by multi-step process. Overall, the co-firing process using Cu can become promising for cost-effective fabrication process of the SOFCs except the problems related to the cathode.

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Introduction

Solid oxide fuel cells (SOFCs) are an attractive power generation due to their high energy efficiency and fuel flexibility. However, different thermal expansion coefficient (TEC) among the materials for anodes, electrolytes and cathodes forces manufacturing steps to be divided into more than three steps; every step includes high-temperature sintering above 1000 °C. This multi-step fabrication process increases manufacturing costs of the SOFCs, which finally restricts their

commercialization [1]. One-step fabrication processes (co-firing) of the SOFCs has been studied by a number of researchers [2,3]. Mucke et al. reported that anode-supported cells were manufactured by co-firing anode and electrolyte films at 1300 °C [4]. However, the co-firing process was divided into two steps; anode supports were firstly fabricated, and then electrolytes and cathodes were co-fired on the anode supports. Moon et al. also reported that a one-step co-firing process using tape casting methods at 1300 °C [5].

For the co-firing processes, most of the studies have been focused on reducing sintering temperatures of the electrolytes

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because electrolyte materials are typically densified at significantly high temperatures above 1500 °C [6]. Ytria-stabilized zirconia (YSZ) has been widely used as an electrolyte material, and has stability of a widely range of temperatures. However, it should be also sintered above 1500 °C to obtain dense impermeable films due to its poor sinterability. K. Keizer indicated that YSZ was densified up to 1147 °C using 1–3 mol % Bi₂O₃ as a sintering aid [7]. However it has an extremely high resistivity in an impedance test. Lewis et al. also reported YSZ was sintered using 1 mol % cobalt oxides as low as 1330 °C [8]. In particular, Cu has been considered a good sintering aid to fabricate dense ceramic films at low temperatures. Y. Dong et al. showed Cu doped GDC synthesized with densification sintering temperature about 1000 °C and offered the possibility of the co-firing process [9]. In our previous study, we also found addition of Cu is effective to improve the sinterability of the YSZ electrolytes [10].

In this paper, a co-firing process was developed by addition of 5000 ppm Cu to the YSZ electrolytes and anodes. The co-firing temperature was about 1250 °C, which is significantly lower compared to multi-step fabrications with the sintering temperature above 1500 °C. The reasonable performances of 0.71 W cm⁻² at 850 °C in the co-fired cells where the fabrications of cathode layer were separated. However, the single-step cell performance was considerably degraded to 0.14 W cm⁻² at 850 °C due to the interactions between the YSZ electrolytes and the La_{0.8}Sr_{0.2}MnO₃ (LSM) cathodes at 1250 °C. The reasons for degradations of the cell performances were discussed below. Considering, it refers to possibility of the fabricating co-fired SOFCs at noticeably low temperature with improving the chemical properties of cathode material. The addition of 5000 ppm Cu to the electrolytes and anodes can be a promising method for low-temperature co-firing processes of SOFCs, reducing manufacturing costs.

Experimental

Powder preparation

NiO (J. T. Baker) and 8 mol % YSZ (8YSZ, LTC) were used as an anode material. The Ni-YSZ powders were prepared by ball-milling process in ethanol and the weight ratio of NiO to 8YSZ was 6:4. Cu(NO₃)₂·6H₂O (Sigma Aldrich) corresponding to 5000 ppm of Cu was added in the suspension as a sintering aid. The ball-milling was remained for 24 h, and then the powders were dried at 80 °C for 12 h. The 8YSZ slurry was also prepared by ball-milling process. The 8YSZ powders were ball-milled with EFKA 4340 as a dispersant in a mixed toluene/isopropyl alcohol (IPA) for 12 h. Di-n butylphthalate (DBP), Triton-X as a plasticizer, polyvinyl butyral (PVB) as a binder and Cu(NO₃)₂·6H₂O corresponding to 5000 ppm of Cu were added to the suspension. The slurry was ball-milled for 24 h in ethanol. The La_{0.8}Sr_{0.2}MnO₃ (LSM) powder was also synthesized by sol-gel method and mixed with the 8YSZ to prepare the cathode powders. The weight ratio of LSM to YSZ was 5:5. Stoichiometric amount of La₂O₃ (Sigma Aldrich), SrO (Sigma Aldrich), and MnO₂ (Sigma Aldrich) was ball-milled in ethanol for 24 h, and then dried at 60 °C for 24 h. The dried powders were calcined at 700 °C for 3 h.

Fabrication of single-cell

The Ni-YSZ powder was pressed at 50 MPa to fabricate disk-like pellets with diameter of 3.6 cm. The YSZ slurries with 5000 ppm Cu were coated on the Ni-YSZ anode by dip-coating method and the cathode paste was coated on the YSZ electrolyte side by screen printing. Then, the single-cells were sintered at 1250 °C according to the temperature profile for co-firing.

Characterizations

To measure the shrinkage of the 8YSZ electrolyte with different Cu contents from 0 ppm to 5000 ppm, the YSZ pellets with 12.7 mm of diameter, 2.5 mm of thickness, and 0.65 g of weight were prepared. The pellets were sintered at different temperatures from 1200 °C to 1400 °C. Gas permeability tests were conducted on the anode-supported half-cell (NiO-YSZ/YSZ) sintered at 1250 °C for 3 h and co-fired half-cell (NiO-YSZ-Cu/YSZ-Cu) sintered by temperature profile. To measure the performance of the co-fired cells, two Pt mesh were attached to each of the anodes and cathodes, and Pt paste was used only on the cathode side as a current collector. A Pyrex sealant adhered to the cell and a zirconia tube in a testing apparatus. The temperature was gradually increased to 850 °C, and then remained for 30 min to complete the glass sealing. The temperature was maintained at 850 °C, and then hydrogen gas was fed into the anode for 3 h to change nickel oxide to nickel metal. The electrochemical measurement was conducted in the flow rates of air of 400 sccm and hydrogen of 100 sccm, respectively. The electrochemical analysis was carried out by using a FC Impedance meter (Kikusii, KFM-2030 model) and versatile multichannel potentiostat (VSP, Biologic, VMP3B-10 model). The frequency range was varied from 1 Hz to 1 MHz with the applied AC amplitude of 20 mV.

Results & discussion

In our previous study [10], small amount of Cu contents can promote densification of the YSZ electrolyte at low temperatures. Fig. 1 shows the shrinkage of the YSZ electrolytes depending on sintering temperatures and Cu contents. The shrinkages of the YSZ electrolytes with 0 ppm Cu were about 41.4, 53.2 and 64.6%, respectively. Although the shrinkages of the YSZ electrolytes sintered at 1400 °C were similar regardless of Cu contents, they were significantly increased in the YSZ electrolytes sintered at 1200 °C as Cu contents were increased. The shrinkages of the YSZ electrolytes sintered at 1200 °C were about 41.4, 50.9, 57.3 and 60.7% at 0, 500, 1000 and 5000 ppm Cu, respectively. In particular, the shrinkage of the YSZ electrolyte with 5000 ppm Cu at 1200 °C was located on that of the YSZ electrolyte with 0 ppm Cu between 1300 °C and 1400 °C. It demonstrates that the addition of Cu to the YSZ electrolytes can reduce sintering temperatures of the YSZ electrolyte, which provides the possibility of co-firing processes, and further reduce manufacturing costs of the SOFCs.

For the first time, the co-fired cells were fabricated by adding 5000 ppm Cu only to the YSZ electrolytes to achieve co-firing at 1200 °C. However, the cells shrank as the initial status

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