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Anode supported planar solid oxide fuel cells with the large size of 30 cm × 30 cm via tape-casting and co-sintering technique

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ABSTRACT

In this work, the NiO–8YSZ/8YSZ half-cells for planar ASCs with the large size of 30 cm × 30 cm are prepared by optimizing both the sintering characteristics and the sintering temperature. The shrinkage rates, open porosities and flexural strength of the half-cells are investigated systematically. The large size half-cells which are prepared by the tape-casting, co-sintering and two-step sintering method show the optimal comprehensive performances with the sintering temperature being 1350 °C. The NiO+8YSZ/8YSZ/LSM+8YSZ anode-supported single cells are obtained at the sintering temperature of 1050 °C. The maximum measurement power at output voltage of 0.8 V of the two cells and 1.6 V of the stack can reach 32.6 W, 34.7 W and 67.3 W, respectively. The two-cells stack is successively discharged under constant current of 5 A for 316 h with the degradation rate of 1.58% kh^{-1} and 30 A for 1161 h with no degradation at the temperature of 750 °C. The large size ASCs show the good mechanical strength and an acceptable degradation.

Introduction

Solid oxide fuel cells (SOFCs) convert the chemical energy from fuel directly into electrical energy have attracted much attention due to its high electrical efficiency, environmental friendly, and fuel flexibility [1,2]. SOFCs include the type of planar and tubular. Recently, the planar type SOFCs become the development trend for the commercialization application because of its high power density and low production cost [3]. However, the planar SOFCs are divided into the electrolyte-supported and anode-supported type [4]. The anode supported cells (ASCs) has higher powder density due to the thin electrolyte with the thickness of approximately 10 μm [5].

Though the tape casting and the co-sintering technology is a cost-effective technique for fabricating large-scale ceramic substrates and multilayered structures [6–10], it is still difficult to acquire a flat anode-supported half-cell, especially for the large-size ASCs. During the fabricating process, the mismatch between the material properties of the anode-support and the electrolyte causes the warpage of cells [11,12]. The different layers are already in strong tension and

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others in compression [13]. These high residual stresses can result in the single cell more fragile during the stacking process. Although there has been reported that a large-scale cell with the area of 22 cm × 33 cm was used to study the internal reforming on ASCs [14]. However, it is still necessary to research on the preparation of large-size flat anode-support fuel cells.

In this work, the tape-casting, co-sintering, two-step sintering, and screen printing technique have been used to fabricate the flat anode-supported planar SOFCs with the large size of 30 cm × 30 cm. Here, the large-size Ni-8YSZ/8YSZ/8YSZ-LSM ASCs with the electrolyte thickness of 10 μm were successfully fabricated. In addition, their sintering properties, microstructures, mechanical strengths, and electrochemical properties were investigated systematically.

Experimental

The material of 8 mol%Y_2O_3-stabilized ZrO_2 (8YSZ) and NiO was purchased from Qingdao Terio Corporation of China and Sinopharm Chemical Reagent Co. Ltd. of China, respectively. The powder of $(La_{0.7}Sr_{0.3})_{0.98}MnO_3$ (LSM) was prepared by the solid–liquid composite method [15]. For the preparation of the anode-support slurry, the mixture of 2-butanone and ethanol with a volume ratio of 2:1, polyvinyl-butyral (PVB) and dibutyl-phthalate (DBP) were used as the solvent, the binder and the plasticizer, respectively. Then the mixture of 8YSZ and NiO, solvent, binder and plasticizer with the ratio of 15:20:60:3:2 was ball milled for 24 h to obtain the uniform slurry. For fabrication of the NiO–8YSZ/8YSZ half-cell, the size of 38 cm × 38 cm anode-supports green tape were prepared by the conventional tape-casting method followed by multilayer lamination. The active anode layer with the thickness of 20 μm and the electrolyte with the thickness of 10 μm were prepared successively with the spraying, co-sintering and two-step sintering method. The half-cells were sintered by the two-step sintering process at the temperature of 1100 °C for 2 h and 1350 °C for 4 h, respectively.

To study the pyrolysis behavior and the phase evolution of the anode support green tapes dried at 40 °C, TG-DTA analysis was carried out with heating velocity of 5 °C min^{-1} in air. For studying the sintering behaviors of the anode-support green tape, the 5 cm × 5 cm samples were prepared with the same method, and then sintered at the different temperatures. The shrinkage rates of the half cells were measured by equation (1) with the formula as follows:

$$\text{shrinkage}(\%) = \frac{l_0 - l_1}{l_0} \times 100\% \quad (1)$$

where l_0 and l_1 are the lengths of the tape-cast green tapes and sintered half cells, respectively. For studying the flexural strength, the half cells with the dimensions of 4 mm × 1.4 mm × 36 mm were also prepared with the same method mentioned before. For each sintered temperature, 10 half-cell samples were selected and measured in a screw-driven universal testing machine (Instron4483, Instron, USA) with a span of 20 mm, at the cross-head moving velocity of 0.3 mm min^{-1}. The flexural strength values were obtained from the maximum load, according to the standard recommendations (ASTM-C1161, 1994). The microstructure of the single cell was observed by the scanning electron microscope (SEM, Hitachi T-1000).

The cathode slurry was prepared by mixing the powders of LSM (50 wt.%) and 8YSZ (50 wt.%) in terpineol solvent by ball milling. The cathode slurry was printed on the side of electrolyte by the method of screen printing. After drying at the temperature of 80 °C for 24 h, the single cells with the active areas of 625 cm^2 were sintered at the temperature of 1050 °C for 2 h, and the thickness of the cathode was approximately 20 μm.

Before the two-cell short stack performance tests, the NiO slurry and Ag paste were printed on the anode and cathode surface of the single cells for the current collection, respectively. The stack was reduced at 850 °C for 2 h and tested at temperature of 750 °C using the stainless steel 430 (SS430) as interconnect. Air and dry hydrogen were used as an oxidant and fuel, respectively. The two cells and stack performances were evaluated by the current–voltage (I–V) and current–-power (I–P) curves at the temperature of 750 °C. Lastly, the stack was successively discharged under constant current of 5 A for 316 h and 30 A for 1161 h at 750 °C.

Results and discussion

The TG/DTA curves of the half-cell green tape, the shrinkage rates of the half cells, and the photographs of the sintered half-cells are presented in Fig. 1. As can be seen in Fig. 1a, the loss in weight of approximately 21.4% for the TG curve is due to the thermal decomposition of the binder and plasticizer in the green tape accompanied by the sharp exothermic reaction in DTA curve. The exothermic peaks are approximately 380 and 450 °C. With an increase of temperature, no further changes in weight and heat are detected, indicating that the half-cell is in relatively stable state. The shrinkage rates of the half cells sintered at different temperature are showed in Fig. 1b. The shrinkage rates at the temperature from 100 to 900 °C are very small (less than 2%), and increasing rapidly from 2% to 20.5% from 900 °C to 1350 °C, then increasing slowly to 21.4%. The photos of the samples sintered at different temperatures show in Fig. 1c are also further confirmed the sintering process. It is the carbide and combustion process of the binder and plasticizer before the temperature of 500 °C, and then the sintering process of the NiO–8YSZ composite ceramic material from 900 to 1400 °C. Thus the two temperature range of 300–500 °C and 900–1100 °C are very important to fabricate anode-supported half-cells due to the combustion and sintering process. In addition, thermal behavior of the sample was characterized by a NETZSCH DIL 402C pushrod dilatometer from room temperature to 1450 °C with a heating rate of 3 °C min^{-1}. From the Fig. 1d, the analysis of the shrinkage rate curves of the sample pre-sintered at 1100 °C for 2 h revealed that the densification at the temperature of approximately 1150 °C and the maximum shrinkage rate was achieved at the temperature of 1225 °C.

Samples for the open porosity testing were also prepared with the same method, then sintered in air at different