

Short communication

# Improvement of the performances of tubular solid oxide fuel cells by optimizing co-sintering temperature of the NiO/YSZ anode-YSZ electrolyte double layers

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## Abstract

The effects of co-sintering temperature on anode microstructure, electrolyte film microstructure, and final cell performance of tubular solid oxide fuel cells (SOFCs) were fully studied. The co-sintering of the NiO/YSZ anode-YSZ electrolyte double layers at temperature ranging from 1350 to 1400 °C for 5 h was carried out. Porosity and electrical conductivity were measured to examine the anodes microstructure, and the electrolyte films microstructure were characterized by scanning electronic microscope (SEM). A higher open current voltage (OCV) value of 0.99 V was achieved by co-sintering the cell at 1400 °C indicating denser electrolyte film, while the maximum power density of the cell co-sintered at 1380 °C was achieved with 322 mW cm<sup>-2</sup> at 800 °C, which was higher than that (241.3 mW cm<sup>-2</sup>) of the cell co-sintered at 1400 °C because of better anode microstructure.

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## 1. Introduction

As new type power generation devices, SOFCs have attracted wide attention. They are potentially used in many areas, such as residential, communicational, commercial, industrial, and military services. For intermediate temperature SOFCs, the anode-supported cell is a better alternative because the electrolyte can be easily and cheaply fabricated by several techniques, such as screen-printing [1], spin-coating [2], dip-coating [3,4], and tape-casting [5]. Anode-supported cells are usually prepared by co-sintering, which means pre-calcined anodes and electrolyte coats are sintered at the same temperature to form dense electrolyte films. The sintering shrinkage of anode supports would drive electrolyte coats sintering, which would affect electrolyte films directly. The sintering shrinkage of anodes is determined by several factors, such as anode materials, preparation process, pre-calcined temperature of anode supports, and

co-sintering temperature. In this paper, the effect of co-sintering temperature on electrolyte film was investigated. The studies about other factors are also ongoing and will be reported in the future.

Though the co-sintering of anodes and electrolyte coats may reduce preparation cost and improve the boundary between anodes and electrolytes, it brings some problems, such as mismatch of sintering shrinkage and different sintering temperature requirements between anodes and electrolytes. Ni/YSZ cermets are commonly used for anode materials owing to high electrical conductivity and electro-catalysis, and YSZ electrolyte films are well compatible with Ni/YSZ anodes for almost the same thermal expanding coefficient and good contact between them. High co-sintering temperature is required to form dense YSZ electrolyte films generally, but it would decrease porosity and electrical conductivity of Ni/YSZ anodes. Dense electrolyte films may increase the OCV value and reduce electrolyte ohmic loss. However, low porosity would increase the concentration polarization of anode, and low electrical conductivity would increase anode ohmic loss. So the co-sintering temperature of anode-supported cells influences

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cell performances greatly, as did not draw enough attention yet. Tubular anode-supported SOFCs were developed by some researchers [3,6–8], and the maximum power density was as high as  $1 \text{ W cm}^{-2}$  [8] which was comparable with that of the planar SOFCs. Du and Sammes [3] had studied the effects of co-sintering temperature from 900 to 1450 °C on tubular anode sintering shrinkage rate, porosity, and strength. In this paper, the effects of co-sintering temperature ranging from 1350 to 1400 °C on anode microstructure, electrolyte film and cell performance were fully investigated to achieve the best cell performance.

## 2. Experiment

### 2.1. Fabricating and characterizing Ni/YSZ tubes

The preparation process of anode tubes and cells are similar to the previous study [7]. NiO/YSZ green bodies were made by extrusion, and divided into two groups. One group of tubes were sintered at 1300, 1320, 1350, 1380, and 1400 °C for 5 h in the air, respectively, and the sintering shrinkage rates were tested. Next, the sintered NiO/YSZ anodes were reduced at 750 °C in  $\text{H}_2$  ambiance for 5 h. The porosity of Ni/YSZ anodes were measured by Archimedes method. DC four-probe method was used to measure the electrical conductivity. The other tubes were pre-calcined at 1000 °C for 2 h to prepare cells.

### 2.2. Preparing and testing cells

The pre-calcined tubes were dipped into fine-NiO/YSZ slurry whose powders were made by co-precipitation to form modifying coats. After drying, the tubes were sintered at 1100 °C for 2 h. The tubes with fine-NiO/YSZ coats were dipped into YSZ (fuel cell materials) slurry and sintered at 1350, 1380, and 1400 °C for 5 h to form electrolyte films, respectively.  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3/\text{YSZ}$  (fuel cell materials) cathode ink was brushed on YSZ electrolyte films, and sintered at 1100 °C for 2 h. The surfaces of YSZ electrolyte films were characterized by a SEM (a Hitachi X-650 Scanning Electronic Microscope). Current–voltage curves of the cells were measured at 800 °C with hydrogen on the anode side and with oxygen on the cathode side.

## 3. Results and discussions

### 3.1. Sintering shrinkage rate and porosity of anodes

NiO and YSZ powders have different sintering behaviors for their different physical properties. Clemmer et al. [9] found that NiO powders began to sinter at a lower temperature than YSZ powders. Fig. 1 shows that sintering shrinkage rate and porosity changed greatly in the temperature range of 1320–1350 and 1380–1400 °C, which corresponded to the sintering of NiO powders and YSZ powders. The sintering shrinkage of anodes has greatly affected electrolyte films made by the co-sintering of anode-electrolyte double layers. If the sintering shrinkage

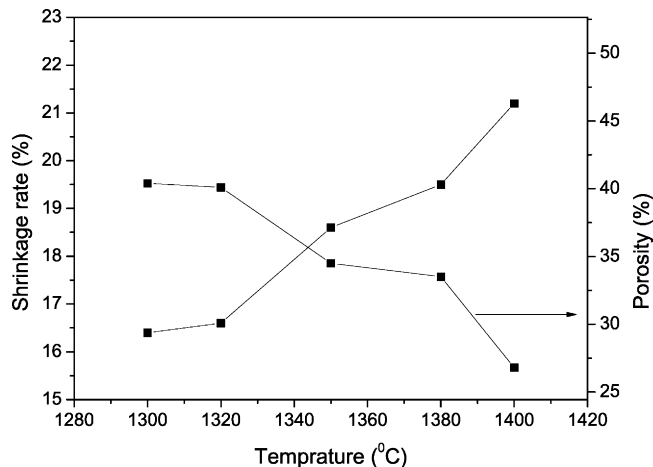


Fig. 1. The sintering shrinkage rate and porosity of Ni/YSZ anode sintered at different temperature.

rate of anode supports is lower than that of electrolyte coats, dense electrolyte films cannot be achieved because of cracks. On the contrary, the boundary between anodes and electrolytes will become poor. So the sintering shrinkage rates of anode supports and electrolyte coats should be matched. Bao et al. [10] found the sintering shrinkage rate of YSZ sintered at 1400 °C for 5 h was about 20.5%, so the sintering temperature of anode should be above 1380 °C, at which anode sintering shrinkage rate was 19.5%. More than 33.3% porosity in anodes is needed to form most open pores according to the theory of seepage flow. The porosity of Ni/YSZ sintered at 1380 and 1400 °C are 33.5% and 26.8%, respectively. Thus, the cells co-sintered at 1400 °C would show higher concentration polarization.

### 3.2. Electrical conductivity of Ni/YSZ anodes

Because the electrical conduction of Ni/YSZ anode mainly owed to Ni, it showed metal electrical conduction behavior in Fig. 2. As sintering temperature rose from 1320 to 1380 °C,

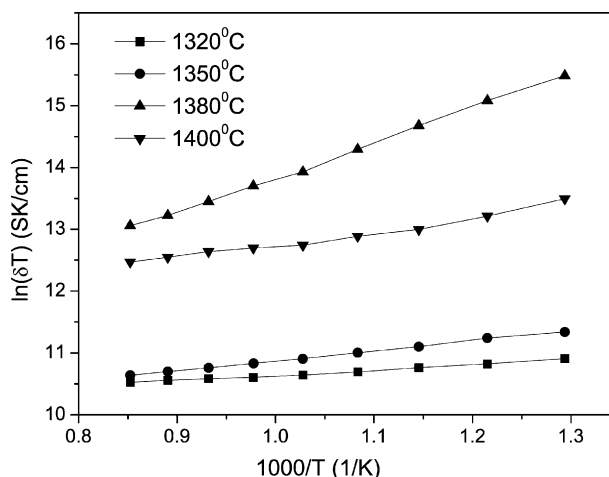


Fig. 2. Conductivity of Ni/YSZ anode sintered at different temperature.

the connection between Ni particles strengthened, which made electrical conductivity increased. However, when the sintering temperature rose to 1400 °C, the sintering of YSZ particles produced aggregated NiO particles, which weakened the connection and made anode electrical conductivity decreased. So the Ni/YSZ anode sintered at 1380 °C showed the highest electrical conductivity.

### 3.3. The surface of electrolyte films and cell performances

Fig. 3 shows the surfaces of YSZ electrolyte films co-sintered at different temperatures. At 1350 °C, the size of YSZ particles was only about 2 μm (Fig. 3a). There were many

cracks in the film because of the low sintering shrinkage of anode support, so it could not be made into cell. When co-sintering temperature rose to 1380 °C, YSZ particles grew into about 8 μm and formed a film with some pin-pores (Fig. 3b). YSZ particles fully grew at 1400 °C and formed a dense film (Fig. 3c). So just like Fig. 4 that shows current–voltage curves of cells measured at 800 °C, the OCV of the cell co-sintered at 1400 °C (0.99 V) was higher than that of the cell co-sintered at 1380 °C (0.88 V). However, thanks to lower concentration polarization and higher electrical conductivity of anode, the later cell produced a higher maximum powder density (322.2 mW cm<sup>-2</sup>) than that (241.3 mW cm<sup>-2</sup>) of the former cell.

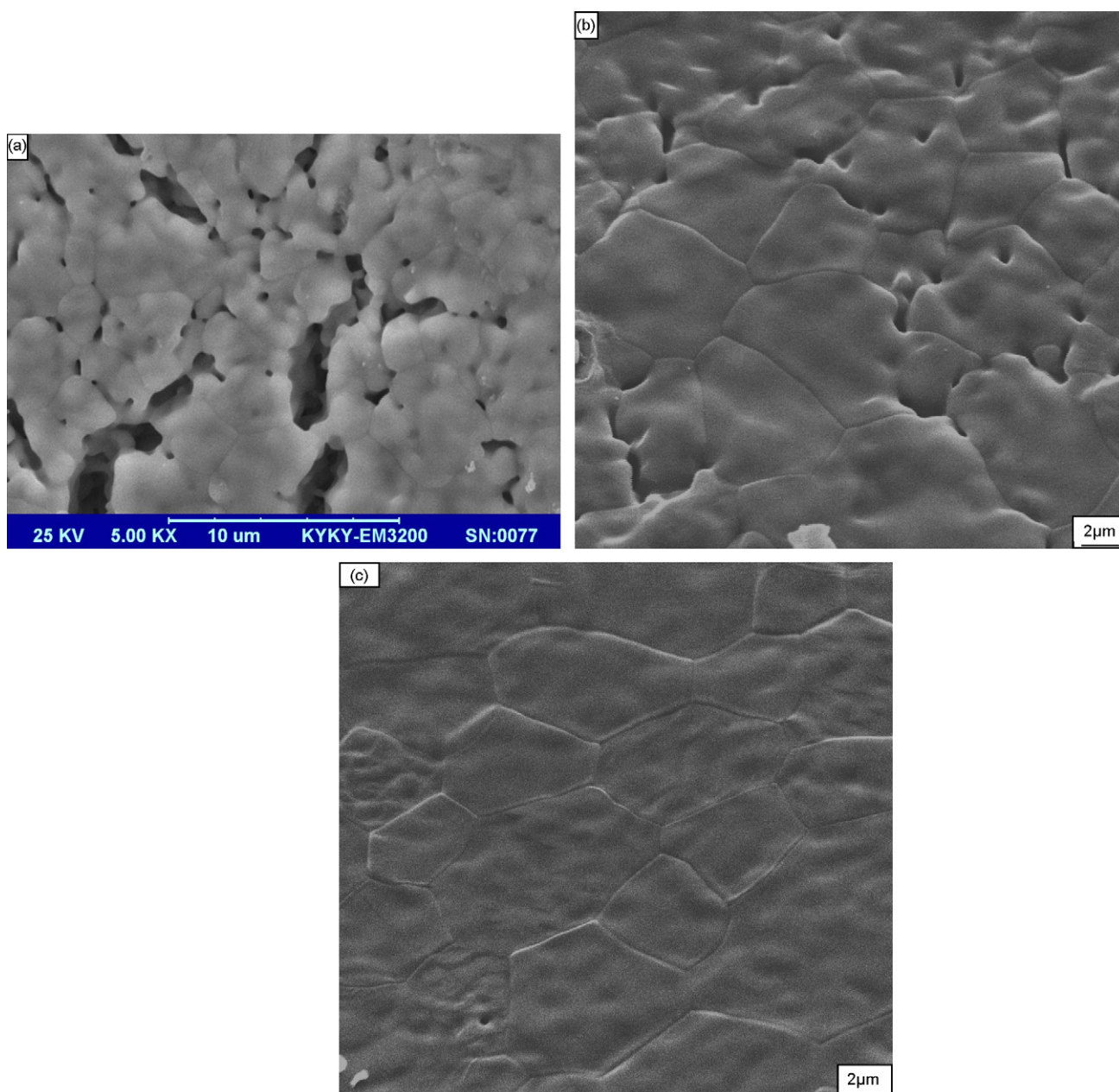


Fig. 3. The surface of electrolyte films sintered at different temperature: (a) 1350 °C; (b) 1380 °C; (c) 1400 °C.

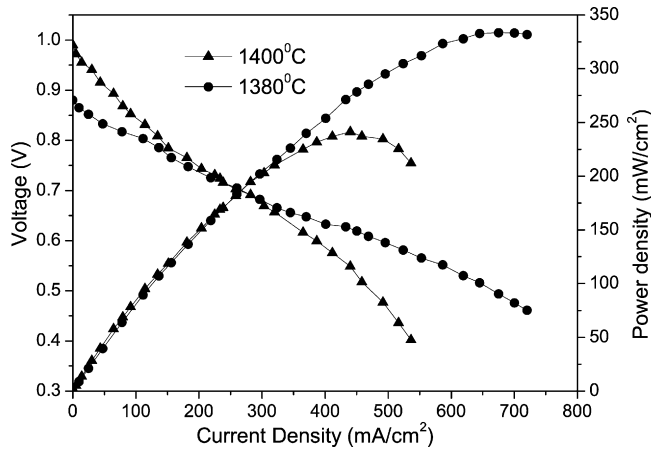


Fig. 4.  $I$ - $V$  curves of cells sintered at 1380 and 1400 °C.

#### 4. Conclusions

Co-sintering temperature affected on anode microstructure, electrolyte film microstructure, and cell performances directly. Sintered at 1380 °C, the anodes showed the highest electrical conductivity and lower concentration polarization, and the cells showed higher the maximum powder density ( $322.2 \text{ mW cm}^{-2}$  at 800 °C). But the OCV of it is lower for un-dense electrolyte films. Therefore, many ways to reducing the electrolyte sintering

temperature could be used to improve it, such as optimizing electrolyte powders [11] and adding sinter-aided additives [12].

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