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Short communication

Improvement of cathode–electrolyte interfaces of tubular solid oxide fuel cells by fabricating dense YSZ electrolyte membranes with indented surfaces

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Abstract

To improve cathode–electrolyte interfaces of solid oxide fuel cells (SOFCs), dense YSZ electrolyte membranes with indented surfaces were fabricated on tubular NiO/YSZ anode supports by two comparable methods. Electrochemistry impedance spectroscopy (EIS) and current–voltage tests of the cells were carried out to characterize the cathode–electrolyte interfaces. Results showed that the electrode polarization resistances of the modified cells were reduced by 52% and 35% at 700 °C, and the maximum power densities of cells were remarkably increased, even by 146.6% and 117.8% at lower temperature (700 °C), respectively. The indented surfaces extended the active zone of cathode and enhanced interfacial adhesion, which led to the major improvement in the cell performance.

Keywords: Cathode–electrolyte interfaces; Indented surfaces; Cathode polarization resistance; Interfacial adhesion; Tubular solid oxide fuel cells

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. Compared with the planar SOFC, the tubular SOFC is a better alternative because it is easier to be sealed, made into stacks and scaled up.

For industrialization, many researchers have devoted themselves to enhancing cells performance through improving preparation process. Anode-supported SOFCs are usually prepared by co-sintering anode–electrolyte double layers, with cathode layers deposited on electrolyte films subsequently. Therefore, a high co-sintering temperature is required to form dense electrolyte film, but it would make the surfaces of electrolyte film very smooth at the same time. In order to deposit cathode layers on the smooth surfaces, high viscosity cathode paste or sol is applied to be coated on electrolyte films by techniques, such as screen-printing [1,2], brushing [3], dip-coating [4] and painting [5]. Generally, the sintering temperature of cathode layers is lower than 1200 °C to insure cathode with sufficient porosity and electrochemical catalysis activity and avoid interfacial reactions between electrolytes and cathodes [6,7]. As a result, the rather poor cell performance reported in literature usually came from the high resistance of cathode–electrolyte interface that was probably due to the preparation process. Moreover, we found cells performance decreased rapidly with thermal cycles. And SEM photo (seen in Fig. 1) showed the cathode layer had broken away from the YSZ film after three times of thermal cycles. The tolerance of thermal cycles, which depends on the cathode–electrolyte interfacial adhesion, is an important performance of SOFCs in practical applications, especially for the tubular SOFCs, while the researches in laboratories always do not involve it. Several ways had been employed to improve the cathode–electrolyte inter-

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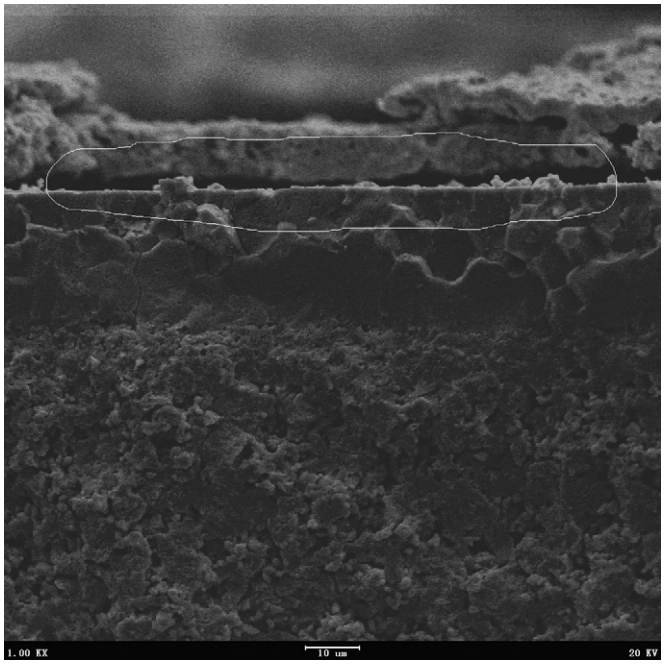

Fig. 1. The cathode–electrolyte interface of the cell made as usual after three times of thermal cycles.

faces, such as inserting graded layer [2,5,8] and impregnation method [5].

In this study, we improved cathode–electrolyte interfaces through fabricating dense electrolyte membranes with indented surfaces by two comparable methods. So far, there has been no such report.

2. Experimental

2.1. Fabricating NiO/YSZ tubes and electrolyte membranes

The preparation process of tubular anodes and cells is similar to the previous studies [9,10]. NiO/YSZ green bodies were made by extrusion or gel-casting [11], dried in air, and pre-calcined at 1000 °C for 2 h subsequently. Then, after being dipped into fine-NiO/YSZ slurry whose powders were made by co-precipitation, the tubes were sintered at 1100 °C for 2 h to form modified coats. For comparison, the tubes with fine-NiO/YSZ coats were divided into three groups. The first and second groups of the tubes were dipped into fine-YSZ (about 0.5 μm, Fuel Cell Materials) slurry as usual, and named tubes A and C; the third group of tubes were dipped into fine-YSZ and coarse-YSZ (about 4 μm, processed Fuel Cell Materials) slurry, and named tube B. All of them were sintered at 1400 °C for 5 h to form dense electrolyte membranes. Tube C was coated by coarse-YSZ powders and sintered 1400 °C for 5 h again. The surfaces and cross-section of YSZ electrolyte membranes were examined by scanning electronic microscopes (Hitachi X-650 SEM and Philips XL30 ESEM).

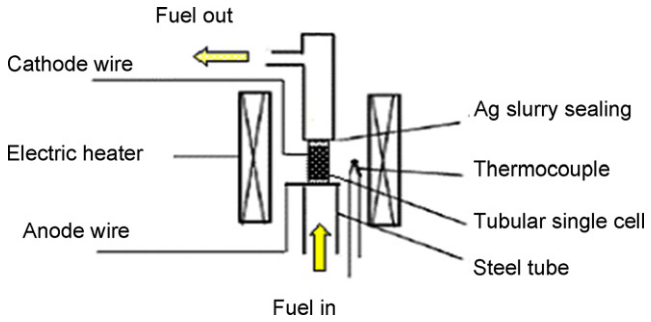

Fig. 2. The home-developed cell testing system.

2.2. Fabricating cathode layers and testing cells

To avoid reaction of La and Zr, $Pr_{0.35}Nd_{0.35}Sr_{0.3}MnO_3$/YSZ powders, synthesized by our lab and reported in another paper, were coated on YSZ electrolyte membranes and sintered at 1150 °C for 2 h to form cells. The cells made from tubes A, B, and C were named cells A, B, and C, respectively. The cathode–electrolyte interfaces of the cells were observed by the SEM (Hitachi X-650). EIS (Chi604a, Shanghai Chenhua) was performed on the cells under open-current condition at 700 °C. Current–voltage curves of the cells were measured from 700 to 800 °C in a home-developed cell testing system (seen in Fig. 2) with hydrogen as the fuel, air as the oxidant.

3. Results and discussion

3.1. The indented surfaces of electrolytes

In order to improve cathode–electrolyte interfaces, coarse-YSZ powders showed in Fig. 3 were employed to fabricate

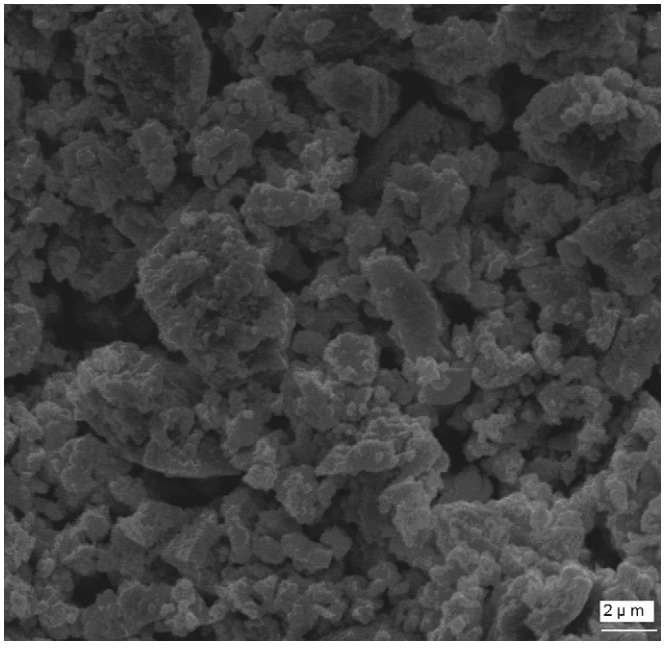

Fig. 3. The micro-photo of coarse-YSZ powders.

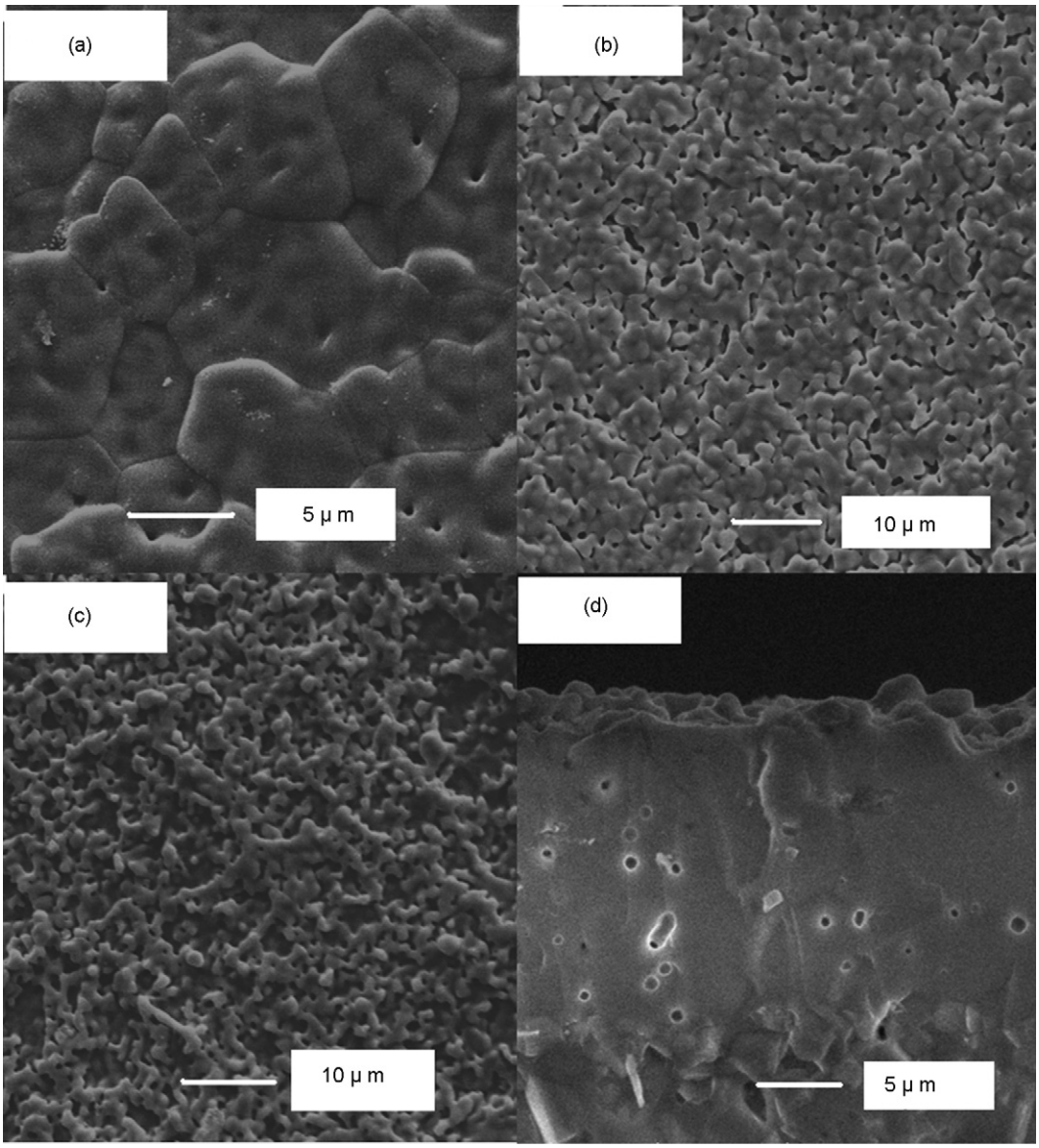

Fig. 4. The electrolyte membrane surfaces of tubes: (a) tube A, (b) tube B, (c) tube C, and (d) the cross-section of tube B.

electrolyte membranes with indented surfaces. The coarse-YSZ powders pre-calcined at 1200 °C had low sintering activity and packing density.

The electrolyte surfaces of tubes A, B and C were showed in Fig. 4a–c, respectively. Fig. 4a shows the smooth surface of electrolyte film composed of YSZ particles about 8 μm. Since the YSZ electrolyte film was sintered at 1400 °C to form the fully dense layer with larger particles, cathode powders could not bond it well by sintering below 1400 °C, which might be the reason why the cathode layer had broken away from the YSZ film after three times of thermal cycles. So the indented surfaces of electrolyte membranes showed in Fig. 4b and c were fabricated to improve it. The coarse-YSZ particles with low sintering activity were employed to fabricate rugged electrolyte surfaces, which could be seen from its cross-section in Fig. 4d, and named the indented surfaces. Compared with the smooth surface, the indented surface showed higher sintering activity and more bonding points with cathode layers for extending the cathode–electrolyte interfaces. Moreover, the indented interface helped to disperse stress produced during thermal cycles. So the indented surface enhanced the interfacial adhesion. The YSZ Particles in Fig. 4c had weaker contact with each other in comparison with the YSZ particles in Fig. 4b because the coarse-YSZ powders deposited on tube C had low packing density during coating and were supported on sintered electrolyte film without sintering shrinkage. But the indented surface had already been formed.

3.2. Characterization of cathode–electrolyte interfaces

The cathode–electrolyte interfaces of cells A, B and C were showed in Fig. 5. As can be seen in Fig. 5a, the contact between cathode layer and flat electrolyte surface was poor due to the low sintering activity of smooth YSZ surface. On the contrary,

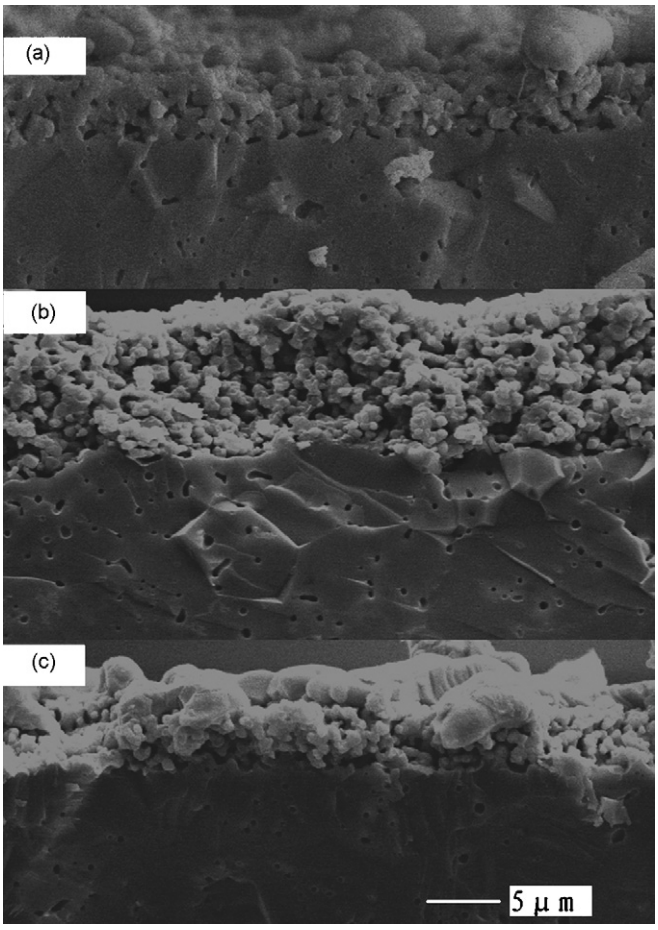

Fig. 5. The cathode–electrolyte interfaces of cells: (a) cell A, (b) cell B, and (c) cell C.

the contact between cathode layers and indented electrolyte surfaces in Fig. 5b and c was much well, especially in Fig. 5b. There were many YSZ particles protuberances (1–2 μm in height) on flat electrolyte surface in Fig. 5c, which were formed by sintering coarse-YSZ particles with smooth YSZ films at 1400 °C.

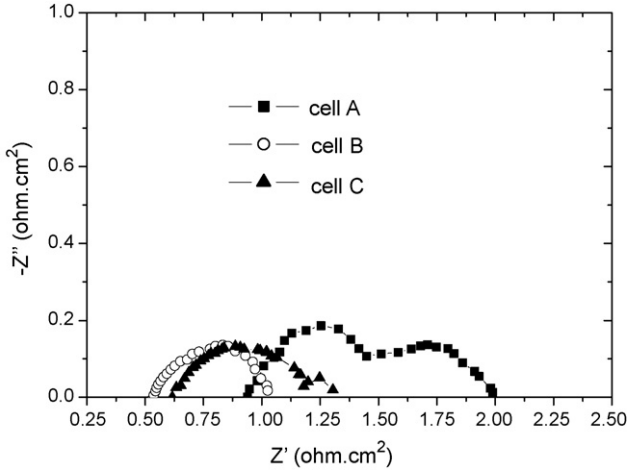

Fig. 6. The EIS of cells A, B and C tested at 700 °C.

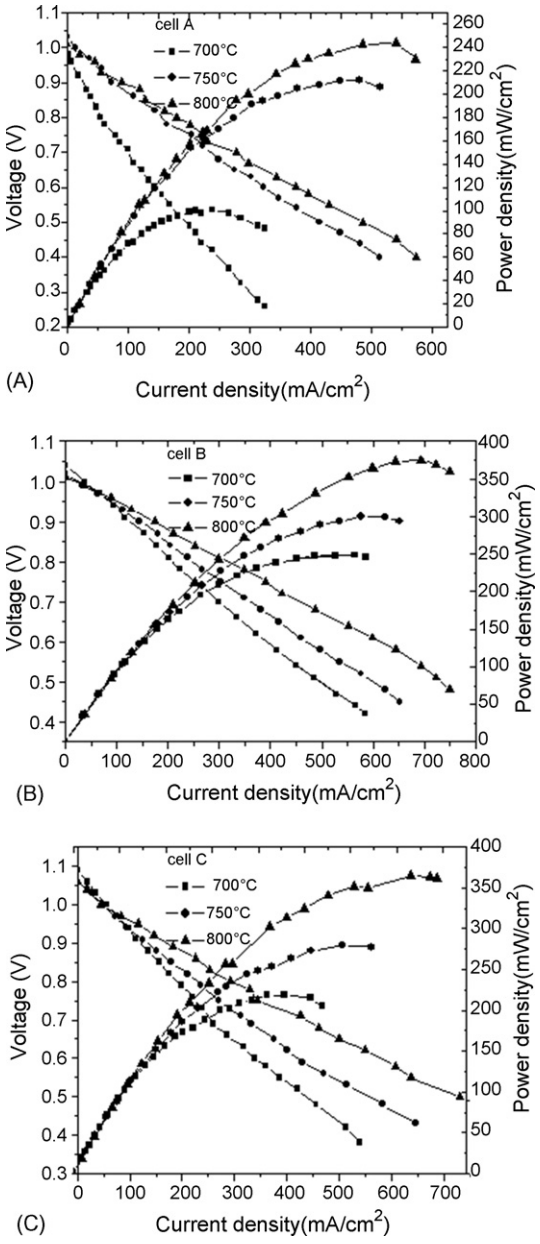

Fig. 7. The current–voltage and current–power curves of cells A, B, and C.

The same results could be concluded from the EIS and the power output measured at 700 °C, which were showed in Figs. 6 and 7. The electrode polarization resistances of cells A, B, and C were 1.07, 0.51, and 0.70 Ω cm^2, respectively. Since cells A, B, and C had the same anode–electrolyte interfaces, the difference in electrode polarization resistance must attribute to different cathode–electrolyte interfacial behaviors. The indented cathode–electrolyte interfaces formed by the indented electrolyte surface had more bonding points and larger triple-phases boundary (TPB) of cathode compared with the flat interface. Hence, the cathode–electrolyte interfaces were greatly improved in the cases cells B and C, and the electrode polarization resistances of cells with indented interfaces could be reduced by 52% and 35%, respectively. The ohmic

resistances of the cells A, B, and C, were 0.93, 0.52, and 0.6 $\Omega\,cm^2$, respectively. The cell ohmic resistances are made up of the ohmic resistances of anode, electrolyte and cathode and the interfacial resistances of anode/electrolyte and cathode/electrolyte. The cells A, B, and C had the same compositions with 1mm anode supports, about 20 μm electrolyte films and 5–10 μm cathode layers, so the difference in cells ohmic resistances must attribute to different cathode layers and cathode–electrolyte interfaces. The cell B showed lowest ohmic resistance though it had the thickest cathode layer, which indicated cathode ohmic resistances had little effect on the cells ohmic resistances. Therefore, the cathode–electrolyte interfacial behavior also affected the cell ohmic resistance greatly. Compared with the flat interface, the indented cathode–electrolyte interface had more bonding points and showed lower interfacial ohmic resistance. Owing to the reasons mentioned above, the maximum power densities of cells B and C were remarkably higher than that of cell A, which were showed in Fig. 7. The maximum power density of cells B and C were even increased by 146.6% and 117.8% at 700 °C compared with that of cell A. The cathode–electrolyte interfaces of the cells with indented interface did not change evidently in SEM photography after five times of thermal cycling, and the related study is going on.

4. Conclusions

The dense YSZ membranes with indented surfaces were successfully prepared on tubular NiO/YSZ anode supports by two comparable methods to modify cathode–electrolyte interface, and the performance of the modified cells were greatly improved. The cathode polarization resistances of it were reduced by 52% and 35%, respectively, and the maximum power densities of it were increased by 146.6% and 117.8% at 700 °C, respectively. The modified method employed in cells B is a better alternative for better cell performance and simple process. Compared with the smooth surface, the indented surfaces with higher sintering activity also enhanced the interfacial adhesion to resist thermal cycles in practical applications.

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