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# Asymmetric anode substrate fabricated by phase inversion process and its interface modification for solid oxide fuel cells

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ABSTRACT

NiO/8YSZ anode supports for planar solid oxide fuel cells are prepared via phase inversion method. With the asymmetric anode structures, two approaches are applied to modify the interface active zones: One is eliminating the dense layer of the anode by mesh-assisted phase inversion process and laser ablation. The other is the introduction of an anode functional layer to further improve the electrolyte/anode interface. Furthermore, different anode structures fabricated by mesh mould and laser ablation are compared. The results show dense layers are effectively removed by mesh mould and laser ablation, and the peak power densities of the single cells all increase. Compared to the two methods on eliminating the dense layer, laser ablation is more effective way to modify the cell performance. For further improving interface active areas of anode support which is modified by laser ablation, an anode functional layer (AFL) is introduced to enlarge the three-phase boundary density. And the peak power density increases from 169 to 370 mW cm$^{-2}$ at 800 °C. These results imply that the effective structural modification and the introduction of the AFL may be promising approaches for enhancing the electrochemical performance for SOFCs.



## 1. Introduction

Solid oxide fuel cells (SOFCs) have gained considerable attention as clean and efficient power devices [1,2]. Tubular and planar SOFCs are two major configurations. In comparison with tubular SOFCs, planar supports have some advantages such as shorter current paths, higher power density and reduced manufacturing cost [3,4]. Currently, planar SOFCs are categorized into three types: electrolyte-, anode-, cathode-supported configurations. Among different supported substrates, anode-supported SOFC with thin electrolyte film which is able to effectively decrease the ohmic resistance has been extensively developed [5,6]. Since anode is the thickest part in SOFC, the gas transport will be hindered through the anode support [7]. To decrease the mass transport resistance, traditional tape-casting [8] and dry-pressing technique [9] adding fugitive pore formers are introduced. But the microchannels of as-formed pores are randomly distributed, imposing a large resistance to the transport of gaseous molecules [10].

In addition to decrease the resistance of mass transport, improving the active interface areas is also attractive because it can further improve the cell performance. Since electrochemical reaction can only occur at the triple phase boundaries (TPBs) where the gas phase, the electron-conductive phase and oxygen ion conductor all meet together [1], enlarging the areas of TPBs is crucial to enhance the electrochemical performance. Dai [11] introduced spherical pore former with the mean diameter of 20 μm to modify both sides of the electrolyte surface areas, and the active interface areas between the anode and electrolyte are improved. Tsumori [12] proposed a micro powder imprint technique to increase the active surface areas. Konno [13] prepared a corrugated mesoscale structure on the electrode-electrolyte interface to extend the density of TPBs. But most of studies have been based on electrolyte-supported SOFCs.

Recently, phase inversion technique without pore formers has been applied to fabricate asymmetric anode supports [14]. The team led by Li [15] reported the formation of the asymmetric structure is due to the unstable viscous fingering phenomenon that is influenced by the viscosity of anode slurry. When the slurry contacts with the non-solvent, the convection between the solvent in the slurry and the non-solvent will occur as the deep concentration gradient. With the increasing local viscosity, the polymer phase precipitates and a tendency for viscous fingering occurs [16].

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Since the phase separation rate decreases along the thickness direction of the precursor, a typically asymmetric structure consisting of a microvoid layer at the top, a thick highly porous finger-like layer in the middle and a dense layer at the bottom forms [16,17]. Therein, the highly porous finger-like layer in the anode is beneficial to gas transport and further increase the zones of TPBs. However, the detrimental dense layer has a lower porosity, which dramatically blocks the gas diffusion into the finger-like pores and decreases the active interface areas [6,10,18]. Therefore, optimizing the anode structure and further increase the zones of TPBs via eliminating the dense layer are essential. Wang [19] removed the dense layer using acids erosion. But this method suffers from complicated process and low mechanical strength as the thin hollow fiber wall. Meng [20] added the solvent into the internal coagulation to prohibit the formation of the inner dense layer. But this approach is not suitable for planar SOFCs to fabricate the asymmetric anode structure.

Currently, laser ablation is an industrial technique widely used in many materials such as metals, ceramics [21,22]. Compared with conventional microprocessing technique, laser engraving has the advantages in cutting, scribing and welding due to the non-contact and flexible process. Furthermore, laser ablation also has been applied for engraving thin ceramic film [23]. In the laser microprocessing method, the pulsed laser beam is focused on the target and material is removed from substrates by ablating the surface. But most of studies have been focus on modifying the anode or membrane surface. For example, J.A. Cebollero [24] tailored the anode surface by laser micro-patterning. Zhang [25] modified the ceramic membrane using laser microprocessing.

In this study, we report two different methods, namely, mesh-assisted phase inversion process and laser ablation technique to remove the dense layer. Furthermore, the different anode structures obtained by the two approaches and the corresponding morphological properties, electrochemical performance are compared. Additionally, the effect of a yttria-stabilized zirconia (YSZ)-NiO anode functional layer (AFL) is also investigated.

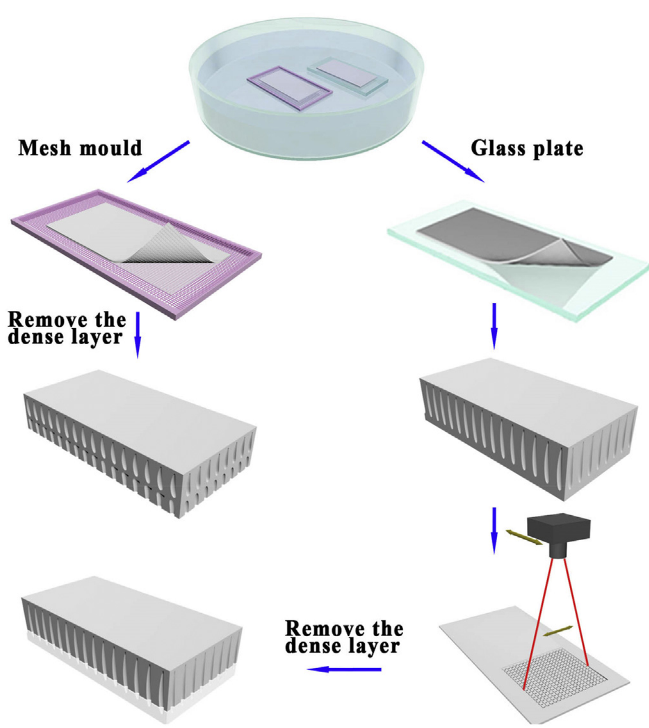


**Fig. 1.** Schematic representations of fabrication processes for anode templated with mesh mould and modified by laser ablation.

**Table 1**
Laser processing parameters of modifying anode substrate.

| Parameters | Value |
|---|---|
| Wavelength | 1064 nm |
| Repetition rate | 25–500 kHz |
| Laser scan speed | 340 mm/s |
| Laser power | 2 W |
| Scan line space | 20 μm |
| Laser spot size | 50 μm |
| Processing numbers | 10 |

## 2. Experimental

### 2.1. Preparation of anode slurry

Commercial NiO (JINCHUAN Group Co., China) and YSZ (TZ-8Y, Terio Co., China) powders at a weight of 55:45 were mixed by ball-mill with water for 24 h and dried at 100 °C for 24 h. 1.5 wt% polyvinylpyrrolidone (PVP, GR, SCRC, China) dispersant and 6.2 wt% commercial polyethersulfone (PESf) polymer binder were dissolved into the 30.8 wt% 1-methyl-2-pyrrolidone (NMP, AR, SCRC, China) to form the polymer solution, and the calculated NiO-YSZ powders were dispersed into the polymer solution for 48 h to obtain homogeneous slurry. Then the prepared slurry was degassed under vacuum for 1 h.

### 2.2. Preparation of anode substrates

Herein, mesh mould and glass plate were applied to tape cast the anode slurry, respectively. The detail fabricated schematic processes of anodes via different methods were shown in Fig. 1. On one hand, the degassed slurry cast on the mesh mould, parts of slurry penetrated the mould to form a thin layer at the bottom, and the phase inversion started from on the both sides of the slurry. After completing phase inversion process, the mesh mould was lifted off to eliminate the bottom layer. On the other hand, the degassed slurry was transferred into the glass plate, followed by immersing into the water for 24 h. And the phase inversion only started from on the top side of the slurry.

### 2.3. Modification of anode support by laser ablation

As shown in Fig. 1, when the anode slurry cast on the glass plate, a dense layer was formed at the bottom. For comparison, laser ablation was utilized to modify the anode precursor. Laser ablation was the removal of the bottom layer from the anode as the absorption of laser radiation [26]. The laser used was a Q-switched equipment (Daheng photoelectron technology Co., LTD) emitting at 1064 nm wavelength (normal power 2 W, quality factor $m^2 < 2$, repetition rate range 25–500 kHz). The focal distance of the laser lens was 100 mm, with which we reached a minimum laser spot of 50 μm and

**Table 2**
Abbreviations of different anode substrates.

| Structures | Abbreviations |
|---|---|
| Anode templated by mesh with 50 μm | TM50 |
| Anode templated by mesh with 25 μm | TM25 |
| Anode templated by mesh with 15 μm | TM15 |
| Anode casts on the glass plate | G |
| Anode modified by laser ablation | GL |
| Introducing an AFL for the anode | GL-A |