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Modifying the electrode-electrolyte interface of anode supported solid oxide fuel cells (SOFCs) by laser-machining

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ABSTRACT

The NiO-yttrium stabilized zirconia (YSZ) anode substrates prepared by tape casting are modified via laser-machining technique in mesoscale for electrode-electrolyte interface modification. Two different surface processing methods are applied: (i) scanning the whole surface with continuous tracks to produce a "coarser" surface; (ii) engraving spots on the substrates surface forming "pits array". The microstructure and electrical performance of the cells based on these anode substrates are investigated. For the scanned anode, confocal laser scanning microscope (CLSM) images show that the surface roughness increases with the laser intensity. The scanning electron microscopy (SEM) images of single cells show that electrode-electrolyte interface contact area is increased. Compared with the unmodified cell, the maximum power density of the cells fabricated with "coarser" anode substrates is improved by 47% at 800 °C. For the second case, the SEM images of cross-section of single cells show that the electrode-electrolyte interface is wavy, resulting increase in the electrochemically active area. It's found that the degree of performance enhancement of the cells is related to the pits size, and a suitable diameter and depth of the pits are needed. The highest power density of the cells with "pits array" increases by 55% at 800 °C. In both cases, electrochemistry impedance spectroscopy (EIS) results show that ohmic and polarization resistances of single cells are decreased after modification.

1. Introduction

Solid oxide fuel cells (SOFCs) are sustainable energy devices which transform the chemical energy of a fuel gas directly into electricity [1–4]. They are regarded as future power generation systems due to their high chemical-to-electrical conversion efficiency, flexible fuel sources, and low emissions, rapid refueling capability [5–7]. The traditional SOFCs operate at high temperature (800–1000 °C) where the electrolyte YSZ has sufficient ionic conductivity [8,9]. However, this results in several barriers for wide applications, such as long activation time, large stress between various components due to differences of thermal expansion rates, as well as high materials and operation cost [10,11]. Consequently, reducing the operating temperature of the SOFCs to the intermediate temperature range (500–800 °C) while ensuring enough power output is an inevitable path to increase their marketability [12,13].

Currently, there are generally two strategies to lower the operation temperature of SOFCs. On one hand, extensive basic studies focus on the alternative materials as anode, cathode, and electrolyte [3,14–17]. For instance, high conductive electrolyte materials including doped CeO2, Sc-stabilized zirconia (ScSZ), Strontium- and magnesium-doped lanthanum gallate (LSGM) have been widely used to decrease the ohmic loss from YSZ electrolyte [1,2,18]. On the other hand, numerous studies on engineering the surfaces and microstructural of electrodes or the interface between the electrolyte and the electrodes have been performed to enlarge the three phase boundary (TPB) length [19]. It is widely assumed that electrochemical reaction occurs at the TPB, which is defined as the collection of sites where oxygen ion conductor, the electron-conducting phase, and the gas phase, all meet together. Considerable progress has been achieved in microstructural engineering aspects encompassing porosity, pore size, particle size, etc. [4]. Apart from the microstructure control of electrodes, many researchers concentrated on investigating the possibility of the electrode-electrolyte interface modification to increase the interface area. Cheng-Chieh Chao et al. [16] fabricated a micro-SOFC electrolyte membrane with a hexagonal-pyramid array nanostructure by nanosphere lithography and atomic layer deposition, achieving a 48.9% increase in maximum power density at 500 °C. Tsumori et al. [9] successfully fabricated thin electrolyte sheets with patterns on both sides by the micro powder imprint (μPI) method. To create corrugated YSZ electrolyte films, Su

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et al. [19] introduced a pattern transfer technique consist of deep reactive ion etching, low pressure chemical vapor deposition and atomic layer deposition technique. The peak power density of obtained corrugated fuel cell is 1.9 times that of the flat cell. Using the blasting method, Konno et al. [20] realized mesoscale-grooved structures on YSZ electrolyte surface, reducing the polarization and ohmic losses. However, almost all the modifications were carried out on the surface of electrolyte substrates. The complicated procedure and the cost of fabrication equipment may restrict their application to the manufacturing of large dimension cells [12].

Laser machining is a promising machining technique with the advantage of automation, high precision, able to efficiently produce repeatable periodic surfaces with excellent quality. In recent years, it has been widely used in processing ceramics in mesoscale and macroscale before and after sintering at competitive prices [21–25]. In our previous study, we used this technique to modify the electrolytes with a “windows” structure and a “dimples array” structure, significantly improving the cell performance [17,26]. Konno et al. [14] have also proved that surface enlargement by a wavy interface is most effective when the electrolyte is thin especially with anode-supported configuration via 2-D numerical simulation.

In this paper, laser-machining was used on the green NiO-YSZ anode substrates to enlarge the electrode-electrolyte interface. Using present fabrication techniques for anode supported SOFCs, the single cells with thin electrolyte were fabricated. The method is simple, not needing an extra change for application. The effect of the electrode-electrolyte interface modification by laser-machining on the performance of NiO-YSZ anode supported SOFCs is investigated and discussed.

2. Experimental

2.1. Preparation of the anode substrates

The NiO-YSZ anode substrates were prepared by tape-casting process, which is a well established industrial process to make large and flat anode substrate for anode-supported cells [4]. For the preparation of the anode-support slurry, commercial NiO (JINCHUAN Group Co., China) and $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ (YSZ, TERIO, China) powder, along with polymethyl methacrylate (PMMA) microspheres as pore former, and triethanolamine as dispersant were mixed with the mass ratio of 60:40:30:2.5 in solvents (ethanol and dimethylbenzene) for 24 h firstly. In the second step, the polyvinyl butyral as binder, polyethylene glycol as plasticizer, and dibutyl phthalate as plasticizer were added into the mixture, and it was ball milled again for 24 h to form homogeneous slurries. After evacuation under vacuum for 15 min, the slurries were subsequently cast onto a tape and dried in air. Finally, the tapes were around 560 μm thick and were punched into pellets with a diameter of 31 mm.

2.2. Laser processing of the anode substrates

A pulse optical fiber laser (IPG_YLP) operating at wavelength of 1060 nm with maximum power of 20 W and a beam quality factor $M^2 < 2$ was used in this work. Laser beam was controlled by the Computer Assisted Design (CAD) software to predefine the pattern and processing procedure. The laser spot diameter is 50 μm when focused on the green substrates surface. Detailed laser processing parameters used for experiments are listed in Table 1. During the experiments, the green anode substrate was fixed on a plate, and the focal length was held constant. A laser beam moves over the surface in accordance with the designed geometry at atmospheric conditions. The material is removed in the anode substrate attributed to the thermal ablation of organic matter compositions and the spallation of ceramic particles. For all experiments, the technics parameters listed in Table 1 were same.

In this study, two different methods were applied to modify the surfaces of anode substrates. For the first case, the laser scanned the whole surface in both X direction and Y direction with continuous tracks to produce “coarser” surface. The anode substrates modified with different laser power settings (1, 2, 4 W) were denoted as C1, C2 and C3, respectively. The green anode substrate without laser modification was noted as C0.

Table 1
Laser processing parameters.

Parameters	Value
Wavelength	1064 nm
Pulse width	1 μs
Repetition rate	20 kHz
Scan speed	340 mm/s
Scan line space	20 μm
Laser spot	50 μm
Processing numbers	1

For the second case, the laser engraved spots with 1 W power on the green substrates surface to form “pits array”. To study the impact of interface contact area on the electrochemical performance, patterns were devised by adjusting the diameter and separation distance of spots. The anode substrates with the pits designing diameter 0.08 mm separated by 0.08 mm and pits diameter 0.15 mm separated by 0.15 mm were named as P1 and P2, respectively. For every spot, the previously mentioned processing parameters such as laser beam separation lines (d = 20 μm) and the laser tracks were maintained.

2.3. Preparation of single cells

The modified anode substrates were pre-sintered at 1100 °C for 2 h. The NiO-YSZ anode functional layer (AFL) synthesized by the co-precipitation method [27] and the YSZ electrolyte layer were deposited onto anode substrate via drop-coating technique successively [28]. The volumes of the AFL slurry and YSZ slurry dropped onto the substrates were 1 and 0.5 ml, same for all samples. The anode/electrolyte half-cells were co-fired at 1450 °C for 2.5 h in air. The $La_{0.8}Sr_{0.2}MnO_3$ (LSM)-YSZ composite cathode was screen printed onto the top of the YSZ electrolyte layer, followed by calcination at 1100 °C for 2 h. The cathode slurry was prepared by mixing LSM (CNLTECH, China), YSZ powders and PMMA microspheres at a weight ratio of 6:4:0.5 with an organic binder. The effective area of the cathode was 0.5 cm^2. Ag paste was applied to the electrode surfaces as current collector.

2.4. Testing and characterization

The morphologies of the modified green anode substrates were determined by a confocal laser scanning microscope (CLSM). The CLSM images were obtained on an Olympus LEXT OLS 4000 microscope powered by a singer laser (λ = 405 nm) in the reflected light mode. The porosity of anode after sintering at 1450 °C was investigated using the Archimedes method in water. The anode supports present open porosity of about 30.2%. The cells fabricated with anode substrates C0-C3 and anode substrates P1-P2 in this work were denoted as cells C0, C1, C2, C3, P1 and P2, respectively. Microstructure morphologies of single cells were characterized by scanning electron microscopy (SEM, JEOL, JEM-6510).

The single cells were sealed to an alumina tube with conductive adhesive (DAD-87, Shanghai Synthetic Resin Institute, Shanghai, China), and silver wires were used as the lead wires. During impedance and power measurements, humidified H_2 (with 3% H_2O) at a flow rate of 70 ml min^{-1} was used as the fuel and ambient air as the oxidant, respectively. The temperature of the cells was stabilized at 800 °C. The electrochemical impedance spectra (EIS) was measured by an electrochemical workstation (CHI 604e) under open circuit condition with an AC amplitude of 10 mV and the frequency range of the measurement was from 100 KHz to 0.1 Hz. The EIS were fitted with the equivalent