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Fabrication of $Ni_{0.5}Cu_{0.5}O_x$ coated YSZ anode by hard template method for solid oxide fuel cells

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ABSTRACT

The fabrication of stereoscopic anode with high porosity is essential for the effective use of natural gas as fuel in solid oxide fuel cells. The tubular YSZ coated by $Ni_{0.5}Cu_{0.5}O_x$ was prepared by hard template method combined with wet impregnation method. YSZ electrolyte-supported single cell was fabricated by using $Ni_{0.5}Cu_{0.5}O_x$-YSZ as anode for the power generation performance test and the long-term stability test. The surface composition and microstructure of anode were further analyzed by SEM and EDS after 100 h test. The maximum power densities of 315.52 and 241.77 mW cm^{-2} were achieved under dry methane and wet methane (3% H_2O) at 800 °C, respectively. The voltage was stable even after tested for 100 h with the fuel of wet methane. The SEM observation of the tested anode showed that the tubular YSZ had hollow structure, in which both internal and external surfaces were coated by $Ni_{0.5}Cu_{0.5}$ alloy particles, resulting a stable structure.

1. Introduction

Hydrocarbon fuels such as methane can be applied for solid oxide fuel cells (SOFCs). However, at a temperature over 527 °C, methane decomposition reaction may occur which results in carbon deposition [1,2]. Therefore, coking problem should be solved when hydrocarbons are used as the fuel for SOFCs. It is reported that the preparation of anode with perovskite [3,4] and fluorite [5] structure materials or reducing the operating temperature are effective ways to avoid carbon deposition. Another good method is to change the microstructure of conventional anode to achieve a SOFC with a high performance. Rismanchian et al. [6] chemically plated Ni-based catalysts with Cu and used it as anode for SOFC and found that Cu had catalytic effect to hinder carbon deposition. Grgicak et al. [7] used Ni–Co and Ni–Cu alloy as anode materials and found that the alloy anode had great power generation ability and high sulfur resistance.

To solve the problems of carbon deposition and Ni sintering on Ni-based anode, it is necessary to optimize the microstructure of anode [8,9]. Sin et al. [10] tested long-term stability of a cell with NiCu-CGO anode working in dry methane at 1023 K for 1300 h and found that the porosity was declined due to the carbon deposition, which resulted in the decrease of power performance. Therefore, besides adding Cu at Ni-based anode for alleviating carbon deposition, it is also important to upgrade the microscopic pore structure of the anode. Zhang [11] demonstrated that the performance of the SOFC can be improved by optimizing the microstructure of anode with a higher porosity. An et al. [12] used YSZ nanoparticles coated spherical Ni as anode, which improved the properties of the fuel cell with good electrical conductivity and reduced polarization resistance. Li et al. [13] fabricated YSZ nano-fiber tubes by electrospinning and plated Ni layer on the fiber tube and used as anode material, and found that the performance of anode was improved to a great extent when comparing with the traditional Ni–YSZ milling anode. Low et al. [14] used Cu-coated Ni particles as anode material and found that the electronic conductivity and mechanical properties was promoted.

Anode porosity not only affects the power generation performance of fuel cell, but also has great effect on the anti-carbon deposition in the SOFCs [15]. Recently, the increase of the porosity in SOFC anode material has been pursued by many researchers [16,17]. It is well known that the porosity of anode can be improved by adding template materials such as polymers [18], graphite [19], or carbon dust [20] in the fabrication process. Srivastava et al. [21] added 15 wt.% graphite powder into NiO/YSZ to fabricate an anode with 32% porosity, which showed a high cell

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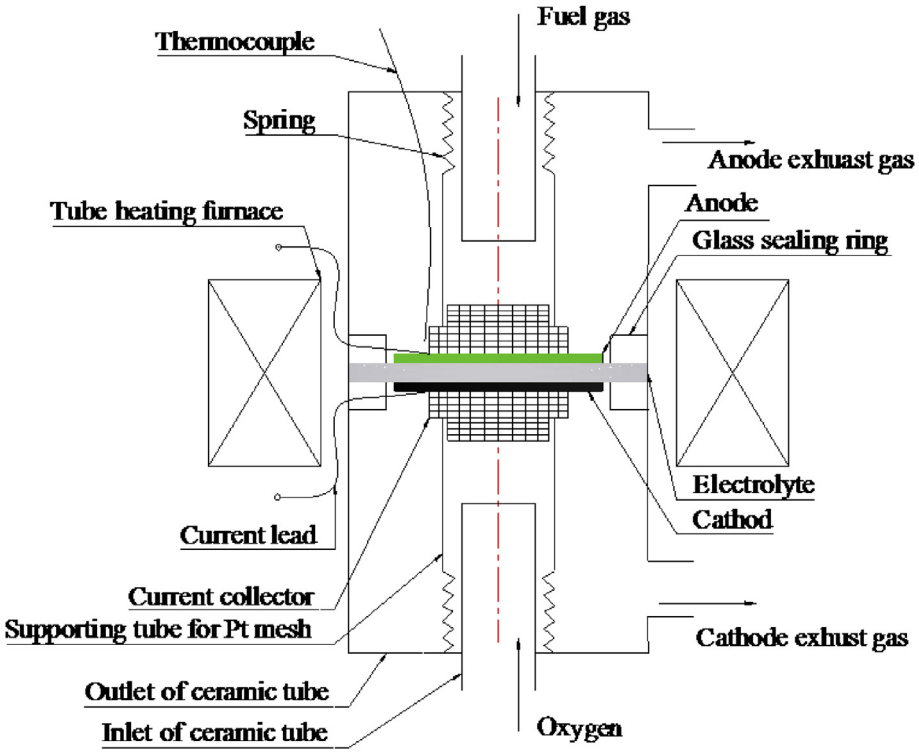

Fig. 1. The test rig for the performance of single cell.

performance. An et al. [22] prepared an anode-supported cell by adding different content of carbon powder as pore former, which also exhibited excellent performance.

Hard template method is an effective way to prepare porous microstructure material with high specific surface area [23]. In this study, activated carbon fiber (ACF) was used as hard template, tubular YSZ powders were prepared at first, and then dipped in salt solutions containing various concentrations of Ni and Cu species by wet impregnation method to fabricate $Ni_{0.5}Cu_{0.5}O_x$ coated tubular YSZ powders, which were used as anode materials. The performance of obtained SOFCs based on the obtained anode materials was tested under dry methane and wet methane (3% H_2O). It is expected to create a novel porous structure for general anode and obtain excellent cell performance with high anti-coking property.

2. Experimental

2.1. Preparation of anode materials

ACF(specific surface area of 1700 $m^2\ g^{-1}$) was employed as hard template to prepare tubular YSZ material. The process of fabrication was as follows. Y_2O_3 and $Zr(NO_3)_4 \cdot 5H_2O$ in a molar ratio of 23:2 were weighed and introduced separately into two beakers, A and B. The excessive concentrated nitric acid (HNO_3) was added into the beaker A to prepare a solution of $Y(NO_3)_3$, which was then poured into the beaker B. Afterwards, appropriate amount of deionized water was added into the beaker B for preparation of the saturated solution which use $Y(NO_3)_3$ as a reference. The calculated amount of ACF dried in an oven for 1 h at 120 °C, and added into the as-prepared saturated solution and stirred for 30 min. Then, the solution was evaporated at 100 °C for 4–5 h. Finally, the dried ACF was calcined at 1400 °C for 2 h, and the tubular YSZ powder was obtained.

The preparation process of the composite anode material of $Ni_{0.5}Cu_{0.5}O_x$ coated tubular YSZ was as follows. $Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 5H_2O$ in a molar ratio of 1:1 was dissolved in proper amount of deionized water and ethanol and an emerald green solution was obtained. The relevant amount of tubular YSZ power with a mass ratio of the calcined metal oxide to YSZ of 3:2 was introduced into the aforementioned solution, and heated at 50 °C for 6 h with stirring. Finally, the green and loose solid mixture was calcined in air at 750 °C for 2 h. As such, the composite anode material of $Ni_{0.5}Cu_{0.5}O_x$ coated tubular YSZ powder was obtained.

2.2. Fabrication and measurement of single cell

YSZ electrolyte-supported single cell was prepared as follows. Electrolyte substrate with a thickness of 0.5 mm and a diameter of 20 mm was prepared by pressing YSZ powders (8 mol% Y_2O_3–ZrO_2, Tosoh) with 3 wt% polyvinyl butyral (PVB, relative to YSZ), followed by sintered at 1400 °C for 4 h in air. Both anode and cathode were prepared by slurry coating method [24]. The mixture of α-terpineol and ethyl cellulose with a mass ratio of 4:1 was used as binders. LSM (CAS, China) and YSZ powders in a weighted ratio of 3:2 were mixed with 40 wt% binder (relative to LSM and YSZ) as cathode slurry, which was coated on the as-prepared electrolyte substrate and sintered at 1100 °C for 2 h in air. As-prepared composite anode material with 40 wt% binder (relative to anode material) was coated on the other side of the electrolyte substrate and sintered at 1000 °C for 2 h in air.

The fabricated single cell was measured in the test rig as shown in Fig. 1. Electrochemical performance test was performed at 650, 700, 750, and 800 °C, respectively using a CHI660C electrochemical workstation system (CHI604D, Shanghai Chen Hua Instrument Co., Ltd.) with HV–151 potentiostat constant current instrument. In the power generation performance tests with hydrogen, the flow rates of dry H_2 and O_2 were 80 $cm^3\ min^{-1}$ and 30 $cm^3\ min^{-1}$, respectively. Similarly, in the tests of power generation performance in