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Short communication

Carbon deposition on patterned nickel/yttria stabilized zirconia electrodes for solid oxide fuel cell/solid oxide electrolysis cell modes

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HIGHLIGHTS

- Distribution and structural features of deposited carbon on patterned Ni stripes.
- Deposited carbon could directly participate in the electrochemical reaction $C(Ni) + O^{2-}(YSZ) \leftrightarrow CO(Ni) + (YSZ) + 2e^{-}$.
- Deposited carbon in crystal graphitic carbon structure.

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ABSTRACT

Carbon deposition on patterned nickel/yttria stabilized zirconia (YSZ) electrode of solid oxide cells operating in CO_2/CO mixture gas at 750 °C with different discharging voltages was studied. Patterned Ni electrode is a useful and effective tool for in-situ observation of the carbon distribution and structural features. The elemental analysis by energy dispersive spectrometer observed that the electricity significantly promoted the carbon deposition on Ni stripes for SOEC, but weakened the deposition for SOFC. Besides, the carbon content near TPB was obviously higher than that in the middle of Ni stripes for SOEC, but lower than that in the middle for SOFC. It is speculated that the deposited carbon could directly participate in the electrochemical reaction $C(Ni) + O^{2-}(YSZ) \leftrightarrow CO(Ni) + (YSZ) + 2e^{-}$ at TPB. The in-situ Raman spectra represented that the deposited carbon, produced or consumed by the carbon electrochemical reaction, was mainly in crystal graphitic carbon structure.

1. Introduction

Nickel/yttria stabilized zirconia (Ni/YSZ) is the most commonly used electrode material for solid oxide cells (SOCs) due to high electronic and ionic conductivity, high catalytic activity and good high-temperature stability [1,2]. However, one of the biggest drawbacks of Ni is the carbon deposition when exposed to the carbonaceous gas at 600–1000 °C, the working temperature of SOCs. The deposited carbon occupies the Ni surface reaction active sites, lead to catalyst deactivation, pore filling and an increase in polarization resistance [3–5]. It also causes irreversible damage, such as loss of the Ni by metal dusting and fracture of the cells by growing fibers [1]. These problems limit the utilization of hydrocarbon fuels in solid oxide fuel cells (SOFCs) [6] and the CO_2 electrolysis in solid oxide electrolysis cells (SOECs) [7]. Operating at higher current density, lower temperature or higher steam to carbon ratio (S/C) could be beneficial for the removal of carbon deposits to a certain extent in SOFCs [2,8–10].

At present, a lot of researches have been focused on the carbon deposition on Ni/YSZ anode of SOFC with CH_4 [2,5,10–14] and other types of hydrocarbon fuels [15,16]. Only few studies have paid attention to the carbon deposition in CO_2/CO atmosphere. Since the species and morphologies of deposited carbon highly depend on the temperature and reactants [9], the characteristics of CO carbon deposition should be quite different than that of CH_4. Therefore, the carbon deposition of CO/CO_2 gas on a Ni/YSZ porous button SOFC with different discharging time, temperature and components were investigated in our previous work [3]. As the reverse mode of SOFC, SOEC has attracted a great research attention in recent several years, which has been identified as one of the most promising and feasible routes to convert CO_2 and H_2O to the fuel, and as an effective way to storage the renewable energy [17]. Studies have noticed that although the materials of SOEC and SOFC are similar,

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the performances of the two modes are highly different, due to the opposite directions of mass and charge transport, heterogeneous reactions and electrochemical reactions [7,18–20]. Also, it was found that the characteristics of carbon deposition for SOEC are different from that for SOFC by the numerical simulation using an elementary reaction-based model of SOCs in our previous work [21]. The simulation results indicated that the carbon deposits more seriously close to the surface of Ni/YSZ electrode for SOFC, while close to the YSZ electrolyte for SOEC, which was primarily certified by the CO_2/H_2O co-electrolysis experiments of porous Ni/YSZ supported SOECs in Mogensen's group [22]. They believed that the H_2O gas steam could effectively depress the carbon deposits, and the carbon deposition close to electrolyte was mainly ascribed to the change in gas composition caused by the gas transport limitation.

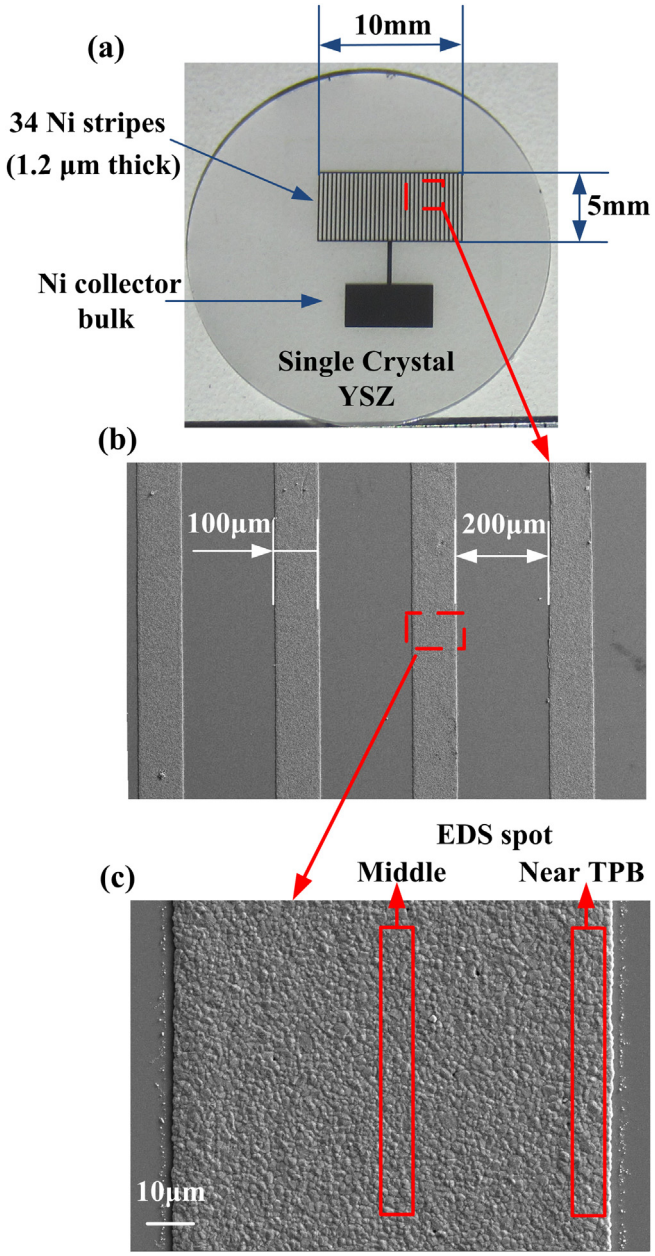

Fig. 1. (a) Picture of patterned Ni in single crystal YSZ, (b) SEM image after experiment and the width of Ni stripes, (c) The elemental analysis of two spots (Middle and Near TPB) on Ni stripes were tested by EDS.

And further experimental investigations on carbon deposition with CO_2/CO gas for both SOEC and SOFC will be significantly important especially without the effect of gas transport and interferential gas such as H_2O, H_2.

Patterned Ni electrode is an effective approach to avoid many complexities and gas transport associated with porous electrodes [23,24], easily characterize the surface topography and obtain a deeper understanding of the reaction mechanisms due to the well defined length of TPB for electrochemical reactions [25]. This kind of electrode has been successfully used to study the reaction mechanisms [23,26–28], degradation [29] and impurity effect [30] in SOFCs. In this study, button cells with patterned Ni electrode on single crystal YSZ electrolyte were utilized to in-situ investigate the distribution and structural feature of carbon deposition on Ni for both SOEC and SOFC modes in CO_2/CO atmosphere.

2. Experimental

2.1. Fabrication and design of patterned Ni button cell

The patterned Ni cell was supported by a single crystal YSZ electrolyte substrate with 13 mol% Y_2O_3, <100> in crystal orientation, 25 mm in diameter and 0.5 mm in thickness (Shanghai Institute of optics and fine mechanics, Chinese Academy of Sciences). One surface of the YSZ electrolyte is smooth and the other one is relatively rough. The surface roughness values of Ra (arithmetical mean deviation of the profile) are 0.69 nm and 540 nm respectively, tested by 3D profilometry (Phase Shift MicroXAM-3D, AEP Technology, USA). The patterned Ni (purity of 99.999%) was positioned in the center of the smooth surface, fabricated by the process of photolithography (SUSS MA6, Germany), etching (Sentech SI500, Germany) and magnetron sputtering (Denton Vacuum Discovery 365, USA). The other electrode was prepared from platinum paste (MC-Pt100, Grikin Advanced Materials, China) on the rough surface by silk-screen printing (120 mesh).

Fig. 1(a) and (b) show the design of the patterned Ni. Thirty-four 100 μm-wide Ni parallel stripes were distributed at intervals of 200 μm wide in an area of 5 mm × 10 mm. Two collector stripes with a width of 100 μm connected these stripes on both ends. A 3 mm × 6 mm Ni bulk was designed to be the current collector to attach the platinum net, which was connected with the pattern by a 300 μm-wide and 3 mm-long stripe. To achieve sufficient stability at high temperature [25], the Ni film with thickness of 1.2 μm was sputtered. The Pt electrode was printed in diameter of 16 mm, which covered the whole area of Ni pattern on the other surface of electrolyte. For each patterned cell, the length of TPB is 383 mm and the reaction area is 37.22 mm^2.

2.2. Test and characterization

A double chamber reactor for button cells and a test setup were used for evaluating the cell performance, which was described in details in our previous paper [31]. The patterned Ni cell was located at the end of two coaxial alumina tubes and strained by springs. The Pt electrode and the Ni collector bulk were both contacted with platinum nets (Shanghai Dingfu, China), and were fixed to the Au wires to collect the voltage and current. A borosilicate glass ring was used as a high-temperature sealant to separate the gas of two electrodes. A type-K thermocouple was mounted in an alumina tube and placed near the cell to measure the temperature. The reactor was enclosed in a quartz tube and placed in a vertical furnace.

Before the test, the patterned cell was heated from the room temperature to 800 °C over 10 h in Ar atmosphere for both two chambers. The temperature was kept at 800 °C for 1 h to sinter the