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A robust NiO-Sm_{0.2}Ce_{0.8}O_{1.9} anode for direct-methane solid oxide fuel cellDong Tian^{a,b}, Wei Liu^{a,*}, Yonghong Chen^b, Weili Yu^c, Lianghao Yu^b, Bin lin^{b,c,*}

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Graphical abstract**Highlights**

- Robust NiO-SDC anode is synthesized by co-assembly for direct-methane SOFC.
- The cell performance was improved by 40%-45% with the new NiO-SDC anode.
- No significant degradation of the cell performance was observed after 60 hours.
- The double-pore NiO-SDC anode with higher TPB is promising for SOFC.

Abstract

In order to directly use methane without a reforming process, NiO-Sm_{0.2}Ce_{0.8}O_{1.9} (NiO-SDC) nanocomposite anode are successfully synthesized via a one-pot, surfactant-assisted co-assembly approach for direct-methane solid oxide fuel cells. Both NiO with cubic phase and SDC with fluorite phase are obtained at 550°C. Both

NiO nanoparticles and SDC nanoparticles are highly monodispersed in size with nearly spherical shapes. Based on the as-synthesized NiO-SDC, two kinds of single cells with different micro/macro-porous structure are successfully fabricated. As a result, the cell performance was improved by 40%-45% with the new double-pore NiO-SDC anode relative to the cell performance with the conventional NiO-SDC anode due to a wider triple-phase-boundary (TPB) area. In addition, no significant degradation of the cell performance was observed after 60 hours, which means an increasing of long term stability. Therefore, the as-synthesized NiO-SDC nanocomposite is a promising anode for direct-methane solid oxide fuel cells.

Keywords: Ceramics; Chemical synthesis; Thermogravimetric analysis(TGA); Electrochemical properties.

1. Introduction

Under the pressure of exhausting conventional fossil fuels and exploring safe renewable energy, solid oxide fuel cell (SOFC) keeps attracting extensive attention compared with various other types of power sources due to its high conversion efficiency, low environmental pollution and high flexibility to various fuels [1-3]. The advantages of direct-methane solid oxide fuel cells (SOFC) are high energy efficiency and relatively simple system design, which is a promising candidate for stationary power generation. However, there is a critical issue of deactivation of the conventional NiO-electrolyte composite anode that need to be solved. A perfect SOFC anode should meet some requirements of high electronic conductivity, proper porosity and thermal expansion compatible with other cell components [4, 5]. After some early bad experiences using single-phase anodes, NiO-electrolyte composite anodes (e.g. NiO-YSZ and NiO-SDC) have been the dominant SOFCs anodes for some fifty years [6]. The typical NiO-YSZ anode with excellent catalytic properties and good electrical

conductivity is deactivated during operation because of its sensitivity to carbon build-up from incomplete oxidation of methane, which can be improved through the substitute of ceria-based oxidation catalysts (e.g. SDC) [7-12]. Recently, some new microstructure for NiO-SDC anodes were investigated as alternative anode materials for direct use with methane fuels, such as surface modification of NiO-SDC anode by impregnation [9-11]. These results have indicated that the adjustment of NiO-SDC anodes are very effective in suppressing catalytic carbon formation by blocking methane from approaching the nickel, which is catalytically active towards methane pyrolysis [13-16].

The anodic microstructure depends mainly on the characteristics of the starting powders, which is relevant to the synthesis route [17, 18]. It is difficult to achieve a uniform distribution of NiO and SDC particles with conventional mechanical mixing methods [19]. To achieve high-performance SOFC, researchers have lengthened the triple phase boundary (TPB) and redesigned the microstructure of the anodes [20]. Techniques including the hydroxide co-precipitation [21, 22], urea-combustion [23], spray pyrolysis [24], self-assembling [25] and gel-casting methods [26] have been developed to synthesize NiO-SDC anodes with long TPB and controllable microstructures.

A soft chemical method is proposed to synthesize SOFC anodes. In this work, we developed a novel one-pot, surfactant-assisted co-assembly approach to prepare porous NiO-SDC anode. The triblock copolymer pluronic P123 and hexamethylenetetramine (HMT) were used as the surfactant and reducing agents, respectively. The NiO-SDC composite nanoparticles were synthesized using an in situ chemical reduction at 550°C. The development of alternative chemical approaches toward composite NiO-SDC materials, where the molecular for each phase are incorporated in a single step, may

prove to be successful in not only creating a homogeneous composite material, but also creating a nanostructure [25]. The use of the direct hydrocarbon fuels can lower their operation costs by eliminating the need for an additional external reforming process. In addition, such commercial natural gas can be more safely stored and more readily available than hydrogen, which can also reduce the operation costs of SOFCs and enhance the overall system efficiency. The codoping strategy functioned in a cooperative way was adopted to improve the ionic conductivity of doped ceria and the ability to resist deactivation by carbon coking, which appears linked to the collaborative mechanism of the rare earth elements for methane cracking and reforming [17]. In Yoon's report, a new microstructure for NiO-SDC anodes with the improved performance, in which the nickel surface of the anode is covered with a porous SDC thin film, was fabricated by traditional impregnation process and employed as an alternative to conventional NiO-electrolyte composite anodes [18].

In this work, the anode-supported single cells of NiO-Sm_{0.2}Ce_{0.8}O_{1.9}/Sm_{0.2}Ce_{0.8}O_{1.9}/Sm_{0.5}Sr_{0.5}CoO₃ (NiO-SDC/SDC/SSC) were fabricated based upon the nanocomposite anode powders. The electrochemical performance was tested using methane as fuel. The NiO-SDC composite anode shows high carbon coking tolerance ability and high electrochemical performance at operating temperatures.

2. Experimental

All reagents were purchased from commercial sources and used as received.

2.1. Sample Preparation

Ce(NO₃)₃·6H₂O (AR, Sinopharm Chemical Reagent Co.,Ltd), Sm(NO₃)₃·6H₂O (AR, Sinopharm Chemical Reagent Co.,Ltd) and Ni(NO₃)₂·6H₂O (AR, Sinopharm Chemical Reagent Co.,Ltd) were used as starting materials to synthesize the NiO-SDC

nanocomposite powders. The tri-block copolymer, pluronic P123 (AR, Sinopharm Chemical Reagent Co.,Ltd), and HMT (AR, Sinopharm Chemical Reagent Co.,Ltd) were used as templating and reducing agents, respectively. The material was typically prepared as follows (50 wt.% NiO-SDC): 2 g pluronic P123 was dissolved in 60 mL deionized water to obtain a clear solution. Next, The appropriate proportion of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added before the solution was stirred at 35°C for 1 h. Subsequently, HMT was added. The resulting mixture was loaded into a teflon lined steel autoclave and heated to 105°C for 24 h. After cooling, the product was filtered, washed, dried (80°C) and calcined in air (550°C , heating rate $2^\circ\text{C} \cdot \text{min}^{-1}$) for 5 h.

2.2. Cell fabrication

To evaluate the NiO-SDC nanocomposite powders as anode materials, two kinds of anode-supported SOFCs with different porous structure were fabricated. For the double-pore structure anode-supported cells, the NiO-SDC nanocomposite powders adding 10 wt.% starch as pore former were initially pre-pressed in a steel die. SDC powders (prepared using the citric acid combustion method) were added to the pre-pressed NiO-SDC substrates in the steel die. Subsequently, the SDC powders and NiO-SDC substrate were pressed together at 400 MPa and sintered at 1350°C for 5 h to denitrify the SDC membrane. Finally, the fine $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC, prepared by a sol-gel process) powder was mixed thoroughly with a 10 wt% ethylcellulose-terpineol binder to prepare the cathode slurry[27]. The cathode material was painted on the SDC membrane and fired at 1000°C for 3 h in air to form a single cell. The active cathode area was 0.237 cm^2 . Ag paste was applied as the current collector for both anode and cathode. The cell was in situ reduced at 700°C for 2 h with humidified H_2 . After cooling down, humidified methane ($\sim 3\% \text{ H}_2\text{O}$) was fed into the anode chamber at

approximately $30 \text{ mL} \cdot \text{min}^{-1}$, and the cathode was exposed to atmospheric air. The anode side was sealed with Ag paste. The single-pore structure anode-supported cell without using pore former was fabricated and tested with the similar process.

2.3. Characterization

The thermogravimetric (TG) analysis of the synthesized powders was carried out on thermogravimetric analyzer (Perkin-Elmer TGA7). Crystal phases of the synthesized powders were analyzed by an X-ray diffractometer (Philips X'Pert PRO SUPER) using nickel filtered Cu-K α radiation. The morphology and particle size of the synthesized powders were examined by transmission electron micrographs (TEM, JEOL-2010). The N₂ adsorption and desorption isotherms of anode powders were obtained at -196°C on an N₂ adsorption and desorption instrument (Omnisorp 100CX). The specific surface area was calculated using the BET model. The microstructures of the cell components after tested were investigated by a scanning electron microscopy (SEM, EDAX JEOL-JSM 840). Fuel cell performance was measured using a DC Electronic Load (IT8511). The electrochemical impedance spectra were measured under open circuit conditions using an impedance analyzer (CHI604B, Shanghai Chenhua)

3. Results and discussion

3.1. Thermal analysis

The thermogravimetric analysis (TGA) was used to compare the weight loss of the as-prepared NiO-SDC powders before and after calcination. The samples were heated to 1200°C at $10^\circ\text{C} \cdot \text{min}^{-1}$ in air, as illustrated in Fig.1. Before calcination, there is a gradual decrease in the mass of powders in the range $30\text{-}100^\circ\text{C}$, $100\text{-}550^\circ\text{C}$, and $550\text{-}1200^\circ\text{C}$ by 3.38, 45.07, and 4.21 wt.%, respectively. This mass change corresponds to desorption from the surface of the powder-free or crystal-bound water,

decomposition of remaining HMT or P123 surfactant species and coke calcinations, respectively. The remarkable change in mass is connected with the decomposition of remaining HMT or P123 surfactant species. It should be noted that the mass change of the calcined sample in the temperature range 30-1200°C was a minimal one (no more than 2.2 wt.%). This is due to the fact that the decomposition of remaining HMT or P123 surfactant species is almost complete in calcinations process, and a small change in mass appears because of the burning of C-containing residues and the thermally reduction to a non-stoichiometric state at high temperatures (Oxygen is released.). Therefore, the organic templates were almost completely removed after calcination at 550°C and the NiO-SDC composite was thermally stable at high temperatures.

3.2. Crystal structures and morphology

Fig. 2 shows the XRD patterns of the as-synthesized NiO-SDC before and after calcined at 550°C in air. It can be seen that the NiO peaks are inconspicuous in the as-synthesized sample, indicating that the organic block copolymer covers the NiO-SDC nanoparticles before calcination. This indicated NiO and SDC were not produced via the thermal decomposition process. After calcination at 550°C, the surfactant P123 and remnant reducing agent HMT were removed, and the reflections display increased intensity for both NiO and SDC. Six intense diffraction peaks, corresponding to the (111), (200), (220), (311), (222) and (400) lattice planes of the fluorite structure SDC are shown. Three lattice planes of (111), (200), and (220) confirm the cubic phase of NiO [28]. At the same time, the NiO-SDC composite powder is fine-grained with better crystallinity after calcination at 550°C. In addition, the low temperature N₂ adsorption and desorption isotherms indicated that NiO-SDC powder after calcination at 550°C had a large surface area (128.42 m²/g, calculated using the BET model).

Fig. 3 shows the TEM micrograph of the NiO-SDC powders calcined at 550°C. Obviously, highly monodispersed NiO-SDC spherical nanoparticles were fabricated using the in-situ reduction process. Additionally, this micrograph indicates that the spherical nanoparticle size is approximately 60 nm. Because the as-synthesized NiO-SDC anode after sintering at 1350°C exhibits perfect microstructure, it is possible to get some nice back-scattering electron microscopy images. In this paper, the energy selective backscatter (ESB) images for the sample of the fractured NiO-SDC composite anode are presented in Fig. 4, which is phase-contrast image. In backscattered imaging mode, as the incident beam scans across the sample's surface topography, backscattered electrons are emitted from the sample. A low atomic weight area of the sample will not emit as many backscattered electrons as a high atomic weight area of the sample. In reality, the image is mapping out the density of the sample surface. Therefore, black, light and dark gray particles are ascribable to pore, NiO (Ni atomic number: 28) and SDC (Ce/Sm atomic number: 58/62), respectively. The sample displayed uniformly distributed NiO and SDC phases in the micrograph, showing non-agglomerated well-developed grains. The NiO and SDC crystalline grains play a role as matrix for each other in the anode substrate, contributing to the lengthened triple phase boundary (TPB) [20]. High sintering temperature of 1350°C leads to the average grain size increases to about 1.5 μm . The pores produced by burning the pore former (starch) during sintering.

3.3. Morphologies of cross-sectional areas of single cells

Fig. 5 presents the SEM images of the single cells after testing with humidified H_2 and CH_4 . Fig. 5 displays a dense electrolyte layer and a porous anode substrate, which indicate that the anode substrate adhered to the electrolyte (40 μm thickness) without any apparent delimitation. The SEM images demonstrated that the anode contained a

double pore system (Fig. 5a). Many larger holes were disordered and mixed with the smaller pores. These large holes are produced by the starch, and the small pores were produced during the in-situ reduction of NiO to Ni. Notably, the small pores were orderly and uniformly distributed. The sizes of the large and small pores were approximately 5 μm and 0.3 μm , respectively. Fig. 5b shows the SEM images of the single cell without adding pore former, thus demonstrated a different pore structure from Fig. 5a. The pore can be also clearly observed which probably produced during the NiO reduction. Notably, these pores are orderly and uniformly distributed. It can also see from the inset, a well-connected network is observed on the anode cross section and the pore sizes on the network is approximately 0.3 μm .

3.4. Electrochemical performance of single cells

To evaluate the electrochemical performance of the NiO-SDC, the anode-supported single cells with different types of anode microstructure were fabricated and tested fuelled with humidified CH_4 at intermediate temperatures of 600-700 $^{\circ}\text{C}$. The voltages and the corresponding power densities as a function of current density are shown in Fig. 6. Fig. 6a displays the I-V and I-P characteristics of single cells with double pore structure anode. While the cell was operated at 700 $^{\circ}\text{C}$, 650 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$, the open-circuit voltages (OCVs) were recorded as 0.82 V, 0.85 V and 0.86 V, respectively. According to I-P characteristics, the maximum power density achieved at 700 $^{\circ}\text{C}$ was 297 $\text{mW}\cdot\text{cm}^{-2}$, and also achieved 165 $\text{mW}\cdot\text{cm}^{-2}$ and 73 $\text{mW}\cdot\text{cm}^{-2}$ when the testing temperature was 650 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$, respectively. Fig. 6b displays the I-V and I-P characteristics of single cells with single pore structure anode. According to I-V characteristics, the OCVs were 0.81 V, 0.83 V and 0.84 V while operated at 700 $^{\circ}\text{C}$, 650 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$, respectively. At 600 $^{\circ}\text{C}$, 650 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$, the peak power densities were 59 $\text{mW}\cdot\text{cm}^{-2}$, 149 $\text{mW}\cdot\text{cm}^{-2}$ and 204 $\text{mW}\cdot\text{cm}^{-2}$, respectively. In order to evaluate

the stability of the NiO-SDC anode, the as-prepared cell of NiO-SDC | SDC | SSC with double-pore anode microstructure was subjected to a long time (60 hours) measurement at 700°C. As shown in Fig. 6, the cell performance was improved by 40%-45% with the new double-pore NiO-SDC anode relative to the cell performance with the conventional NiO-SDC anode due to a wider triple-phase-boundary (TPB) area, where the electrochemical reaction takes place. In addition, no significant degradation of the cell performance was observed after 60 hours (Fig. 6), which means an increasing of long term stability. The two phases (NiO and SDC) with homogeneous distribution indicated that the new developed method could obtain nano-sized catalytic composite powders, which certainly benefits the cell performance [29]. The TPB is a region of contact between three different phases (an SDC electrolyte, a NiO electrode, and a methane gas fuel), which is a geometrical parameter that is of crucial importance for the performance of SOFC anode. High electrochemical performance required a high TPB in the anode, because increasing the TPB density will enhance the kinetics of the oxidation reaction that occurs between oxygen ions and methane fuel on the anode side of the cell, and thus increase cell performance. Using 3D imaging techniques like FIB-SEM[14, 30-33], the nanocomposite anodes with optimized electrode microstructure exhibit substantially higher TPB density, leading to higher cell performance and better stability[15, 16, 34-36]. Therefore, the new double-pore NiO-SDC anode with a wider TPB area is much more promising for direct-methane solid oxide fuel cells, compared with the conventional single-pore NiO-SDC anode.

4. Conclusion

In this works, a one-pot, surfactant-assisted co-assembly approach is developed to synthesize the NiO-SDC composite anode with new double-pore microstructure, which was investigated as an alternative anode for direct-methane SOFC and was compared

with the conventional mechanical mixed NiO-SDC anodes. As a result, the cell performance was improved by 40%-45% with the new double-pore NiO-SDC anode relative to the cell performance with the conventional NiO-SDC anode due to a wider triple-phase-boundary (TPB) area. In addition, no significant degradation of the cell performance was observed after 60 hours, which means an increasing of long term stability. Therefore, the as-synthesized NiO-SDC nanocomposite is a promising anode for direct-methane solid oxide fuel cells.

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Figure captions

Fig. 1 TG curves of the NiO-SDC anode powders before (a) and after (b) calcination at 550°C.

Fig. 2 XRD patterns of the NiO-SDC anode powders before (a) and after (b) calcination at 550°C.

Fig. 3 TEM micrograph of the NiO-SDC nanocomposite powders.

Fig. 4 Backscattered electron images of NiO-SDC composite anode after sintering at

1350°C for 5 h.

Fig. 5 SEM images of anode-supported single cells: (a) with adding the pore former, (b) without adding the pore former.

Fig. 6 I-V and I-P characteristics of the anode-supported single cells based upon the NiO-SDC nanocomposite powders ((a) double-pore anode, (b) single-pore anode); (c) The OCVs of the single cell with double-pore structure anode tested at 700°C as a function of time with methane (3% H₂O) as the fuel.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6