Preparation and characterization of NiO-$Sm_{0.2}Ce_{0.8}O_{1.9}$ composite nanoparticles for solid oxide fuel cell anodes

Bo Xu, Dong Tian*

School of Chemical and Material Engineering, Huainan Normal University, Huainan 232001, PR China

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Abstract: An in situ reduction method has been used to synthesize NiO-$Sm_{0.2}Ce_{0.8}O_{1.9}$ (NiO-SDC) nanocomposites for SOFC anodes. The effect of NiO content on the crystalline phase, crystallite size, and average particle size is investigated. The anode-supported solid oxide fuel cells have been fabricated from the NiO-SDC nano-composite powders with NiO contents ranging from 40 to 60 wt%. Uniform pore structure of the anode is exhibited after testing although without adding pore former. The electrochemical performance of the anode-supported cells has been tested at 600-700°C using humidified hydrogen as fuel. The cell with 60 wt% NiO has an open circuit voltage (OCV) of 0.69 V with a maximum power density of 506 mW/cm^2 at 700°C.While at lower temperature (600°C), the cell with 50 wt% NiO has the maximum power density of 326 mW/cm^2.

Introduction

Solid oxide fuel cells (SOFCs) are the most promising electrochemical devices for power generation due to their high conversion efficiency, low environmental pollution and flexibility toward various fuels [1]. NiO-SDC composite anode has given rise to much interest recently due to its excellent performances. Under H_2 atmosphere, the NiO-SDC anode is reduced to Ni-SDC[2]. And the Ni-SDC extends the triple phase boundary (TPB) with oxide ions and electrons and avoid the coarsening of Ni particles, while the SDC in cermet must act as a supporting framework for the Ni particles. It is difficult to achieve a uniform distribution of NiO and SDC particles with simple mechanical mixing methods. To achieve high-performing SOFC anodes, researchers have lengthened the triple phase boundary (TPB) and redesigned the microstructure of the anodes. Various techniques were developed to synthesize NiO-SDC anodes with long TPB and controllable microstructures[3-5].

A soft chemical method is proposed to synthesize SOFC anodes. Herein, we developed a novel one-pot method to prepare porous NiO-SDC anodes composed of nanosized particles. The hexamethylenetetramine was used as the reducing agents. The NiO-SDC composite particles were synthesized successfully using an in situ chemical reduction at low temperature. As our knowledge, the mild and efficient reducing agent hexamethylenetetramine has been used to prepare metal or metal oxide nanoparticles. NiO-SDC nanoparticles were fabricated using a one-pot hydrothermal process, leading to a fine-grained powder. By comparing to previously reported methods, the hexamethylenetetramine reduction method is full of merits of simplicity and controllability.

Experimental

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

Sample preparation

$Ce(NO_3)_3 \cdot 6H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were used as starting materials to synthesize the NiO-SDC nanocomposite powders. The material was typically prepared as follows (50 wt% NiO-SDC): The appropriate proportion of $Ni(NO_3)_2 \cdot 6H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$

were dissolved in 60 mL deionized water to obtain a clear solution and stirred at 35°C for 1 h. Next the hexamethylenetetramine was added. Subsequently, the resulting mixture was loaded into a teflon link steel autoclave and heated to 110°C for 12 h. After cooling, the product was filtered, washed, dried (80°C) and calcined in air (300°C, heating rate 2 °C/min) for 10 h. The other composites with NiO contents 40 and 60 wt% were prepared using the similar procedure.

Characterization

Crystal phases of the synthesized powders were analyzed by an X-ray diffractometer (Philips X'Pert PRO SUPER) using nickel filtered Cu-Kαradiation. 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).

Results and discussion

Crystal structures

The powder XRD patterns of the NiO-SDC with various NiO contents are shown in Fig. 1. The NiO reflections became sharper as the NiO content increased from 40% to 60 wt.%, while the intensity of SDCs' diffraction peaks had not clear change. The nanocrystalline grain size for the SDC and NiO were estimated from their (111) peaks displayed in Fig.3 using the Scherrer equation which had similarly values (approximately 30 nm). The size of NiO-SDC nanoparticles prepared using this soft chemical method is easily repeated.

Morphologies(SEM) of cross-sectional areas of single cell

Fig. 2 presents the SEM images of the single cell with a 50 wt% NiO before and after testing. Fig. 2(a) displays a dense electrolytic layer and the anodic porosity is low. Additionally, the SEM images indicated that the anode layer adhered to the electrolyte surface without any apparent delimitation. Fig. 2 b shows the SEM images of the single cell after tested at 600-700°C under hydrogen atmosphere, thus demonstrated that the anode contained a uniform pore system. Large pores can be clearly observed from Fig. 2 b although without adding pore former, probably produced during the NiO reduction. Notably, these pores are orderly and uniformly distributed. It can also seen 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.

Electrochemical performances of single cells

To evaluate the electrochemical performance of the NiO-SDC powders, anode supported single cells were fabricated using NiO-SDC nanocomposite powders with various NiO contents, these cells were tested at 600-700°C. Every anode supported single cell demonstrated the electrical performance. Fig. 3 displays the I-V and I-P characteristics of single cells fabricated from NiO-SDC nanocomposite powders with 40-60 wt% NiO [14]. According to I-V characteristics, the open circuit voltages (OCVs) at 700°C were 0.74, 0.73 and 0.69 V for the anode-supported single cells with 40, 50 and 60 wt% NiO, respectively. In addition, the cell voltage of each single cell with a supported anode decreased linearly with increasing current densities. The maximum power densities at 700°C were 380, 459 and 506 mW/cm^2 for the cells with 40, 50 and 60 wt% NiO, respectively. While the cells were operated at 600°C, the maximum power densities were 208, 326 and 239 mW/cm^2 for the cells with 40, 50 and 60 wt% NiO, respectively. The maximum power density increased with increasing NiO content at 700°C. Finally, the maximum power density of each cell increased when the operating temperature increased from 600 to 700°C.

Generally, increasing the NiO content in the NiO-SDC powders increased the conductivity of the Ni-SDC cermets because the Ni content also increased. However, the electrochemical performances of the cells with supported anodes depends on the anodic composition and microstructure. This results agree with previous reports. Therefore, a single cell displays a maximum power of 506 mW/cm^2 at 700°C with 60 wt% NiO content, while a maximum power of 326 mW/cm^2 at 600°C with 50 wt% NiO content. The NiO is uniformly dispersed throughout the SDC due to the in situ reducing method so that it could decreased the Ni aggregation at high operating temperatures.

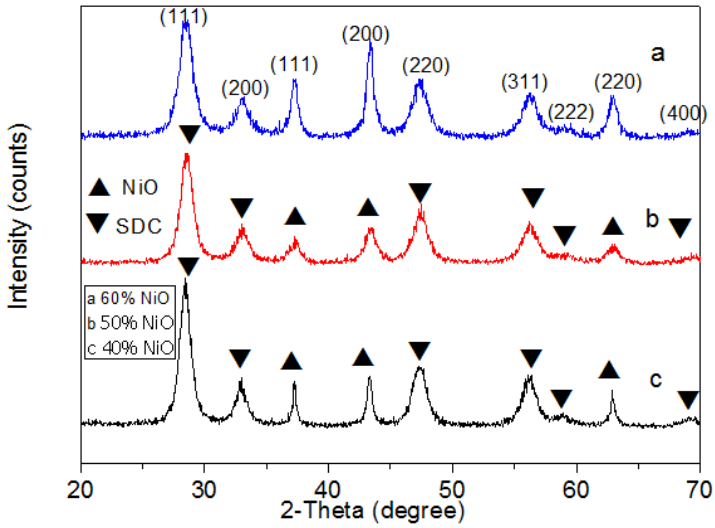

Fig. 1. XRD patterns for the NiO-SDC nanocomposite powders with 40-60 wt% NiO.(a 60%, b 50%, c 40%)

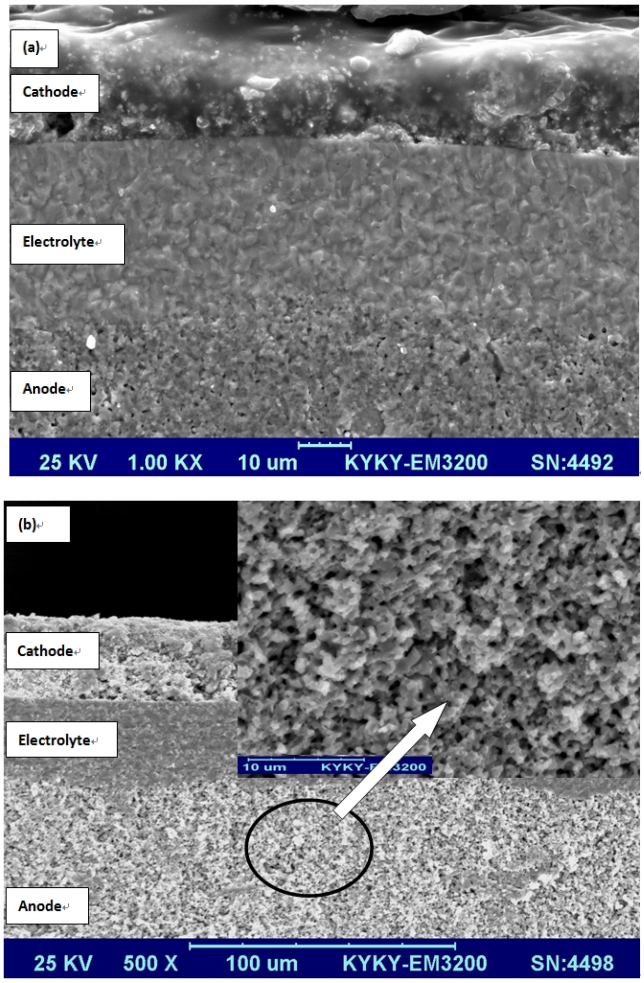

Fig. 2. SEM images of the single cell with a 50 wt% NiO. (a before testing, b after testing)

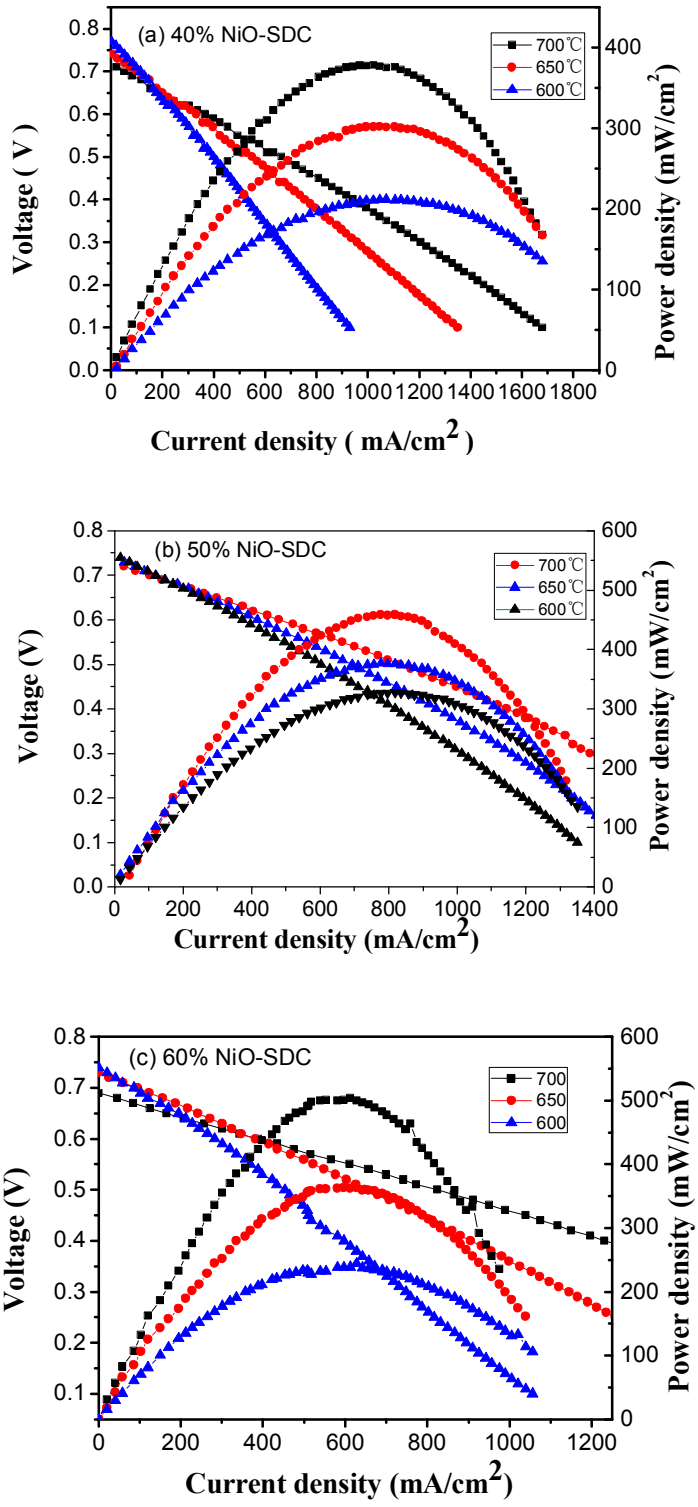

Fig.3. I-V and I-P characteristics of the anode-supported single cells fabricated from the NiO-SDC nanocomposite powders with different NiO contents: (a) 40 wt%, (b) 50 wt%, (c) 60 wt%.

Conclusion

NiO-SDC nanocomposite powders with different NiO contents were prepared using an in situ reduction with hexamethylenetetramine as the reducing agents. Using the NiO-SDC powder as precursors, anode supported cells were fabricated. The NiO-SDC nanocomposite powders exhibited a small size and uniform spherical morphology. The cell anode had a uniform pore distribution. An

OCV of 0.69 V was observed, and a maximum power density of 506 mW/cm^2 was generated by a cell with a 40-μm-thick SDC electrolyte at 700°C. Therefore, the NiO-SDC prepared using this method is suitable anodic material for SOFCs.

Acknowledgments

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