Electrochimica Acta 270 (2018) 9–13

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Archiving high-performance solid oxide fuel cells with titanate anode in sulfur- and carbon-containing fuels

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ARTICLE INFO

Article history:
Received 23 November 2017
Received in revised form
11 February 2018
Accepted 12 March 2018
Available online 13 March 2018

Keywords:
Solid oxide fuel cells
Doped $SrTiO_{3-\delta}$
Anode materials
Syngas
Natural gas

ABSTRACT

Yttria doped strontium titanate ($Y_{0.07}Sr_{0.89}TiO_3$, YST) material is synthesized using a conventional combustion method as anode for solid oxide fuel cells (SOFCs) in sulfur- and hydrocarbon-containing fuels. The YST perovskite exhibits good stability and chemical compatibility with yttria stabilized zirconia (YSZ) electrolyte in 0.5% H_2S-containing fuel at high temperatures. Moreover, the YST shows high electrical conductivity of 35 S cm^{-1} at 900 °C and the cell with this anode achieves a maximum power density of 200, 162 and 70 mW cm^{-2} when the anode is fed by 0.5% H_2S-containing hydrogen, syngas and methane fuels, respectively. More importantly, the cell shows negligible degradation in the sulfur-, carbon- and hydrocarbon-containing fuels. Thus, YST holds the promise as anode material for SOFCs, especially in high concentration sulfur-, carbon- and hydrocarbon-containing fuels.

1. Introduction

Solid oxide fuel cells (SOFCs), an electrochemical reactor which can directly and efficiently convert chemical energy stored in fuels into electricity without significant pollution, has attracted increasing attention in the past few decades [1,2]. Among all fuels, hydrogen is widely used in SOFCs due to its high energy conversion efficiency and environmentally friendly merit [3]. However, safety concerns and volumetric constraints compromise the energy and environmental advantages of pure hydrogen as fuel [4]. In addition, most of the hydrogen production methods are not mature, which makes pure hydrogen quite expensive up to date. In contrast natural gas and syngas are much more facile and cost-effective to obtain and they are being considered as fuels for SOFCs [5]. However, the direct utilization of conventional Ni-based anode in SOFCs will inevitably cause the carbon deposition due to the incomplete oxidation of alkanes (e.g., methane) and consequently deteriorate the cell performance [6–8]. Besides, the contaminations (e.g., H_2S) in the natural gas and syngas poison the Ni-based anode catalysts easily [9–11].

In an effort to alleviate sulfur poisoning and the build up of carbon, Ni-free anodes with high performance have been extensively investigated in the past few decades. Perovskite oxides, such as $La_{0.2}Sr_{0.7}TiO_3$ [12], $La_{0.33}Sr_{0.67}Ti_{1-x}Mn_xO_3$ [13], $(La_{0.75}Sr_{0.25})_{0.9}Cr_{0.5}Mn_{0.5}O_3$ [14], $Pr_{0.8}Sr_{1.2}(Co, Fe)_{0.8}Nb_{0.2}O_4$ [15] and $Sr_2MgMoO_{6-\delta}$ [16] have been considered as alternative candidates as Ni-free anodes. Among others, $SrTiO_{3-\delta}$ and $BaTiO_{3-\delta}$ have been demonstrated as sulfur- and coking tolerant anodes with excellent stability under various fuel conditions. However, the electrical conductivity and catalytic activity of these anodes are still inferior the conventional Ni-based anodes. Recently, Y doped $SrTiO_{3-\delta}$ (YST) perovskite materials have attracted increasing attention in SOFCs due to their intriguing advantages, such as high electronic conductivity in reducing atmosphere, good chemical and stability upon harsh redox cycling [17–19]. Despite the fact that YST exhibits a good tolerance to sulfur poisoning in H_2S containing hydrogen [20], However, its utilization in sulfur-containing syngas and hydrocarbons was has been not reported yet.

Herein, we prepare Y-doped $SrTiO_{3-\delta}$ perovskite fine powders as anode materials for SOFCs in sulfur-, carbon- and hydrocarbon-containing fuels. The electrochemical performance of this anode

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https://doi.org/10.1016/j.electacta.2018.03.078
0013-4686/

catalyst and its resistance against sulfur and carbon deposition are evaluated in high concentration sulfur- (0.5% H_2S) containing hydrogen, syngas and methane. More importantly, YST shows almost similar catalytic activity, and much better sulfur tolerance and coking resistance to Ni-based anodes.

2. Experimental

$Y_{0.07}Sr_{0.89}TiO_3$ powders were prepared using a combustion method [21]. Titanium isopropoxide and citric acid (CA) were dissolved in ethylene glycol (EG) in a mole ratio of Ti: CA: EG = 1: 4: 9.33 to make a Ti solution and heated at 90 °C in a glass beaker. The resulting solution was extracted into a crucible and calcined at 800 °C for 5 h to obtain an accurate Ti concentration of the solution. The Ti concentration of the solution was calculated from the weight of the residual TiO_2. Appropriate amounts of $Sr(NO_3)_2$ and $Y(NO_3)_3 \cdot 6H_2O$ were dissolved in the liquid titanium solution, and then heated further to dry the solution to form a gel on the hot plate. The resulting gel was then heated in the furnace at 600 °C for 5 h.

YSZ (8 mol% Y_2O_3 stabilized ZrO_2) powders were compacted into a 0.3 mm thickness disk samples under 200 MPa, the YSZ electrolyte membrane were sintered at 1500 °C for 6 h in air. The 50 wt% YST + 50 wt% YSZ compounds were screen printed onto one side of a YSZ electrolyte membrane with a 1 cm^2 area. LSM + YSZ paste was screen printed onto the opposite face of YSZ to form the cathode. Finally, the YSZ electrolyte supported membrane electrode assembly (MEA) was calcined at 1200 °C for 2 h in air.

X-ray diffraction (XRD) was employed to characterize the structures of the samples by an X-ray diffractometer (Rigaku Rotaflex X-ray diffractometer) using Cu Kα radiation, scanning angle 2θ range from 20° to 90°. The microstructures were determined using scanning electron microscopy (SEM, JEOL JAMP-9500F). Impedance measurements and current-voltage characteristics were determined using a Solartron 1287 electrochemical interface together with a 1255B frequency response analyzer. Anode and cathode feeds were 100 mL min^{-1} each of fuels and air, respectively. The electrical conductivity measurements were performed from 600 to 900 °C in air with a four probing DC technique on sintered YST using a Keithley 2400 source meter. YST pellets were prepared by pressing the YST powders at 5 tonnes in a 2.54 cm diameter die and sintering subsequently at 1300 °C for 5 h.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared YST powders firing at 600 °C in air (a) and reducing at 1300 °C in 5% hydrogen. It is found that pure YST is obtained without any impurities at lower temperature (600 °C) via combustion method as compared to the conventional solid state reaction. The combustion method involves the dissolution of the metal nitrates, which makes the metal salts distribute uniformly and chelate adequately with citric acid and thereby accelerate the formation of perovskite phase during the combustion process. The diffraction peaks show no obvious change, whereas the as-prepared YST powders experience increases intensity after reduction in 5% hydrogen at 1300 °C for 5 h. It is concluded that the YST has high structure stability and remains perovskite phase in redox atmosphere at high temperature. The enhancement of diffraction intensity could be ascribed to crystalline incensement of YST at higher temperature.

As seen from the TEM image in Fig. 2, the as-prepared YST powders shows a particle size of about 50 nm. At the initial stage of the combustion process, substantial gas bubbles formed from the decomposition of nitrates and the organic gel, this chelating strategy contributes to the formation of quite fine YST

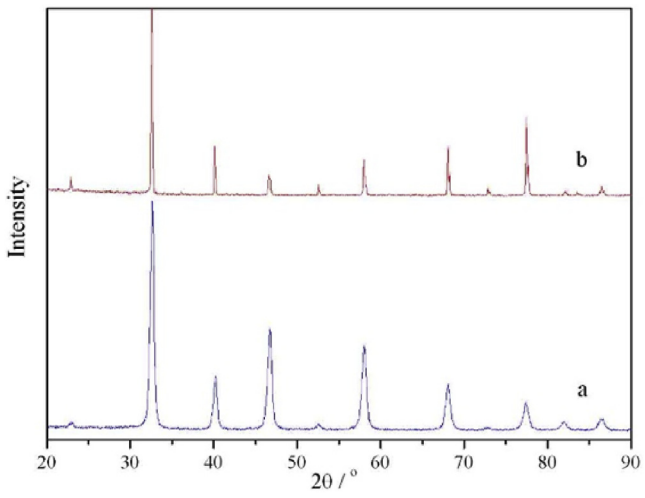

Fig. 1. XRD patterns of YST prepared from dry gel heated at 600 °C (a) and after reduction at 1300 °C in 5% hydrogen (b).

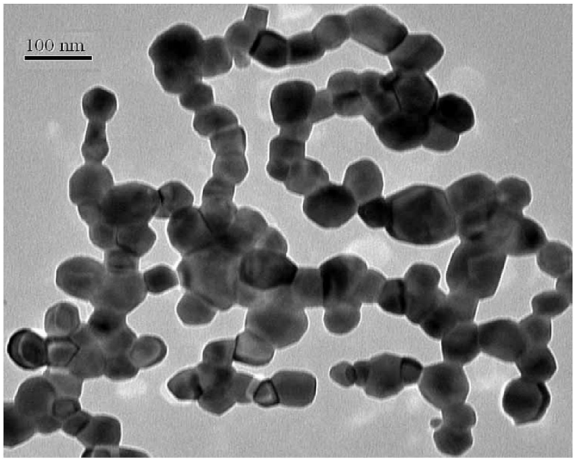

Fig. 2. TEM image of as-prepared YST powders.

nanoparticles. The YST powders prepared by the combustion method is, thus, more attractive as compared to the conventional solid state reaction since it brings more uniform morphology and smaller particle size.

Subsequently, the YST pellets are sintered at high temperature from 1200 to 1500 °C for 5 h in air. The cross-sectional SEM images of the sintered YST pellets are shown in Fig. 3. Apparently, substantial pores are interconnected in the YST pellet sintered at 1200 °C, indicating that dense YST is not preferred at this temperature. However, complete densification is observed when the temperature is increased to 1300 °C. Upon further increasing the temperature, such as 1400 and 1500 °C, the crystalline size gets larger for the sintered YST pellets.

The mixture containing YST and YSZ is pressed, and then fired at 1200 °C for 10 h in air for XRD measurement for the purpose of evaluating the chemical compatibility of YST and YSZ electrolyte. The result in Fig. 4 (a) shows both the diffraction peaks of YSZ and YST without impurities, suggesting that YST has good chemical compatibility with YSZ electrolyte during cell fabrication and operation, when utilized as anode material for SOFCs at high temperature. In the meantime, YST is also exposed to H_2S-containing hydrogen and methane at 900 °C for 10 h, XRD results in Fig. 4 (b) show that the YST remains perovskite and no significant