Journal of Power Sources 249 (2014) 270–276

Contents lists available at ScienceDirect

Journal of Power Sources

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

Single layer fuel cell based on a composite of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$–$Na_2CO_3$ and a mixed ionic and electronic conductor $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$

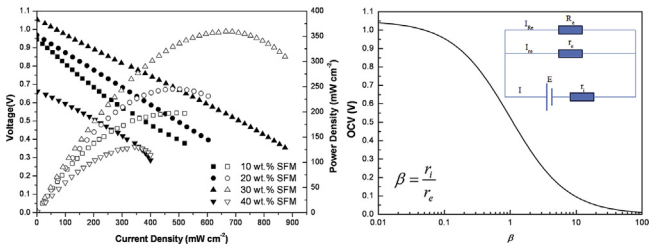
Xiao Dong, Li Tian, Jiang Li, Yicheng Zhao, Ye Tian, Yongdan Li*

Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin Key Laboratory of Applied Catalysis Science and Technology, State Key Laboratory of Chemical Engineering (Tianjin University), School of Chemical Engineering, Tianjin University, Tianjin 300072, China

HIGHLIGHTS

- Single layer fuel cells are fabricated with the mixture of SFM and SDC –Na_2CO_3.
- The fuel cell with 30 wt.% SFM gave the highest 1.05 V OCV and 360 mW cm^{-2} output.
- The single layer cell showed a comparable performance to the three-layer cell.
- The effects of the ratio between electronic and ionic conductions are elaborated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 July 2013
Received in revised form
12 October 2013
Accepted 12 October 2013
Available online 21 October 2013

Keywords:
Single layer fuel cell
Composite material
Mixed ionic and electronic conduction
Electrochemical performance
Intermediate temperature

ABSTRACT

A new kind of single layer fuel cell (SLFC) based on a composite material of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC)–Na_2CO_3 and $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) is successfully fabricated and characterized. As a mixed ionic and electronic conductor, SFM provides more reaction areas than the triple phase boundary provided by a simple mixture of ionic conductor and electronic conductor. SDC–Na_2CO_3 is used to adjust the ratio of ionic and electronic conductivities. The influence of the SFM content on the electrochemical performance of the SLFC is examined. The pellet made of 30 wt.% SFM and 70 wt.% SDC–Na_2CO_3 exhibits the highest open circuit voltage of 1.05 V and output of 360 mW cm^{-2} at 750 °C. Besides, by discussing influence factors of the OCV of the cell, the reason why the SLFC can give a similar OCV and output comparing with the conventional three-layer fuel cell, has been explained in detail.

1. Introduction

Fuel cells are electrochemical devices that directly convert chemical energy of fuels into electrical energy with high efficiency of power generation and low environmental impacts [1]. Solid oxide fuel cells (SOFCs) have received great attention for the potential of utilizing various fuels due to their high operating temperature, which benefits the reaction kinetics [2,3]. However, the high temperature also causes the mismatch of thermal expansion as well as inter-diffusion and interaction between electrolytes and electrodes, bringing serious mechanical and chemical problems [4–6]. Considerable efforts have been devoted to solve these problems, e.g. adding an interlayer between the electrolyte and the electrode [7–10], which would increase the complexity and the fabricating cost at the same time.

Recently, a single layer fuel cell (SLFC) was developed [11–14], and showed reasonable performance [15,16]. The fuel cell function is realized with one homogeneous layer based on a composite of

* Corresponding author. Tel.: +86 22 27405613; fax: +86 22 27405243.
E-mail address: ydli@tju.edu.cn (Y. Li).

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http://dx.doi.org/10.1016/j.jpowsour.2013.10.045

ionic and electronic conductors. Comparing to the conventional three-layer configuration, SLFC avoids the mechanical and chemical incompatibility between electrolytes and electrodes, and provides technical advantages of simplified fabrication, stack-design and operating requirements.

The basics and fundamental issues of SLFC, such as material choice, structure and morphology, reaction activity as well as working principle, have been intensively investigated [11–14,17]. In addition, Xia et al. [18] measured the overall conductivity of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC)–$Li_{0.15}Ni_{0.45}Zn_{0.4}O_x$ in air by adjusting the relative weight percentage of the ionic conductor and electronic semiconductor. Fan et al. [19] optimized the electrochemical performance of the SLFC by adjusting the ratio of ionic and electronic conductors as well as the pellet thickness. Liu et al. [20] developed a model to simulate the distribution of gases in the porous structure of a SLFC, and revealed that the electrode reaction depth of H_2 or O_2 was 1–2 orders of magnitude smaller than the thickness of a typical pellet, which was consistent with experimental results.

As the SLFC was occasionally discovered when testing a composite electrode material of conventional three-component fuel cell [15], the materials of SLFC tested up to now are mainly mixtures of an ionic conductor, e.g. doped ceria-carbonate composite materials (SDC–Na_2CO_3), and a semiconductor such as composite of metal oxides like NiO, CuO, ZnO and Li_2O [11–14,17–19]. Thus, the performance of SLFC has been limited by the volume of the triple phase boundary (TPB) in the electrochemical reacting region, similar to the conventional electrode materials such as Ni–yttria stabilized zirconia (YSZ), Ni–SDC anode and $La_{0.9}Sr_{0.1}MnO_{3-\delta}$–YSZ cathode [2,3,21–23]. In contrast, some mixed ionic and electronic conductors (MIECs), such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, have been developed as electrodes in recent years, which get rid of the restriction of TPB and enhance the cell performance [21,22,24]. Among them, $Sr_2Fe_{1.5}Mo_{0.5}O_{3-\delta}$ (SFM) double-perovskite is stable in both reducing and oxidizing atmospheres, and has been utilized as both the anode and the cathode of SOFCs [25–27]. However, due to the high electronic conductivity of SFM, it is not suitable to be used as the only material for composing a SLFC. Meanwhile, the doped ceria-carbonate composite materials with a promising ionic conductivity and negligible electronic conductivity, have been widely examined as electrolytes for fuel cells operating in intermediate temperature [28–32]. In this work, SFM is mixed with SDC–Na_2CO_3 [33] to obtain balanced electronic and ionic conductivities. The effects of SFM content on the electrical conductivity of the composite and the performance of the SLFC are investigated. By discussing influence factors of the OCV of the cell, the influence of the proportion of the ionic and electronic conductivities of the composite material on the performance of the SLFC is discussed.

2. Experimental

2.1. Material preparation

SFM powder was synthesized via a citrate-EDTA complexing method [34] with stoichiometric $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $Sr(NO_3)_2$ and $Fe(NO_3)_3\cdot 9H_2O$ (Guangfu corporation, China). The mole ratio of EDTA, citric acid and total metal ions was 1:1.5:1. EDTA was dissolved in diluted aqueous solution of ammonia to form EDTA–$NH_3\cdot H_2O$ solution, then $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was introduced under heating and stirring. $Sr(NO_3)_2$ and $Fe(NO_3)_3\cdot 9H_2O$ were dissolved in deionized water and then added to the previous solution, followed by stirring and introduction of citric acid. The pH value of the final solution was adjusted to 6 using $NH_3\cdot H_2O$. The solution was then heated to 95 °C to remove excess water and to form a yellow gel. The SFM powder was prepared by slowly decomposing the gel at 400 °C in air for 0.5 h and then calcination at 1200 °C in air for 5 h to obtain a pure double-perovskite structure.

SDC–Na_2CO_3 was synthesized by carbonate co-precipitation method as reported [35] using Sm_2O_3 and $Ce(NO_3)_3\cdot 6H_2O$ (Guangfu corporation, China) as starting materials. The precipitate was sintered at 800 °C for 4 h and ball milled to obtain the SDC–Na_2CO_3 powder.

The composite powders were obtained by mixing the as-prepared SFM and SDC–Na_2CO_3 powders with ratios of 10, 20, 30 and 40 wt.% SFM, respectively.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the composite powders were recorded at room temperature using a D8 Focus diffractometer (Bruker Corp., Germany) with Cu-Ka radiation, 40 kV and 200 mA, at a scanning rate of 10° min^{-1}. The surface morphology of the composite powder and the single cell was observed with a Hitachi S-4800 scanning electron microscope (SEM).

2.3. Conductivity test

The conductivity measurements were carried out using a DC four-probe method. Samples were pressed under 250 MPa and made into rectangular bars with a typical size of 2 × 10 × 18 mm and then calcined at 750 °C for the composite and SDC–Na_2CO_3 samples, and 1200 °C for SFM samples. Four silver wires acting as electrodes were connected to the bar with silver conductive paint. The measurements were carried out in H_2/N_2 and O_2/N_2 atmospheres, and the total gas flow rate was kept as 100 ml min^{-1} (STP). A constant direct current was supplied to the sample through the two outer wires, while the voltage drop between the two inner wires was recorded by the VERASTA2273 analyzer (Princeton Applied Research, Oak Ridge, TN, U.S.).

2.4. Fuel cell test

Composite powders were pressed under 250 MPa into pellets with a diameter of 13 mm and a thickness of 1.2 mm. For comparison, a traditional three-layer cell with the same size was also fabricated using composite with 30 wt.% SFM as electrodes material and SDC–Na_2CO_3 as the electrolyte material. For these cells, Ag paste was coated on both sides as the current collector.

Cells with the effective area of 0.64 cm^2 were tested from 650 to 750 °C. Hydrogen with a flow rate of 100 ml min^{-1} (STP) and oxygen with a flow rate of 30 ml min^{-1} (STP) were used as fuel and oxidant, respectively. The *I–V* and *I–P* curves of the cell were recorded using the aforementioned VERASTA2273 analyzer. Electrochemical impedance spectra (EIS) were performed in the frequency range from 1 MHz to 0.01 Hz using the same VERASTA2273 analyzer under OCV with the amplitude of 10 mV at various temperatures in both hydrogen and oxygen atmosphere.

3. Results and discussion

3.1. Structure and morphology

The XRD pattern of the composite powder shows a combination of the characteristic peaks of SFM and SDC–Na_2CO_3, as illustrated in Fig. 1, and no other phases can be found, indicating that there is no obvious interaction between the two materials. An intensity decrease of the peaks of the SFM phase can be observed, which may be caused by the existence of the other phases. However, Na_2CO_3 phase cannot be found since it forms an amorphous shell over the SDC core [35].