Journal of Power Sources 260 (2014) 197–204

Contents lists available at ScienceDirect

Journal of Power Sources

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

Proton conducting intermediate-temperature solid oxide fuel cells using new perovskite type cathodes

Meiling Li [a,b], Meng Ni [a,*], Feng Su [b], Changrong Xia [b,1]

[a] Department of Building and Real Estate, The Hong Kong Polytechnic University, Hong Kong, China
[b] Department of Material Science and Engineering, University of Science and Technology of China, Hefei, Anhui, China

HIGHLIGHTS

- $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) is used as cathode for H-SOFC.
- SFM is compatible with BCZY electrolyte under 1100 °C.
- SFM–BCZY cathode is promising for H-SOFC at intermediate temperature.
- Good performance is achieved with SFM–BCZY composite cathode.
- Co-sintering temperature of 1000 °C is found optimal.

ARTICLE INFO

Article history:
Received 18 January 2014
Received in revised form
3 March 2014
Accepted 7 March 2014
Available online 16 March 2014

Keywords:
Composite cathode
Proton-conducting solid oxide fuel cells
Intermediate temperature
Symmetrical fuel cells

ABSTRACT

$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) is proposed as the electrodes for symmetric solid oxide fuel cells (SOFCs) based on oxygen-ion conducting electrolytes. In this work SFM is investigated as the cathodes for SOFCs with proton conducting $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) electrolyte. SFM is synthesized with a combined glycine and citric acid method and shows very good chemical compatibility with BZCY under 1100 °C. Anode-supported single cell (Ni–BZCY anode, BZCY electrolyte, and SFM-BZCY cathode) and symmetrical fuel cell (SFM–BZCY electrodes and BZCY electrolyte) are fabricated and their performances are measured. Impedance spectroscopy on symmetrical cell consisting of BZCY electrolyte and SFM–BZCY electrodes demonstrates low area-specific interfacial polarization resistance R_p, and the lowest R_p, 0.088 Ω cm^2 is achieved at 800 °C when cathode is sintered at 900 °C for 2 h. The single fuel cell achieves 396 mW cm^{-2} at 800 °C in wet H_2 (3 vol% H_2O) at a co-sintering temperature of 1000 °C. This study demonstrates the potential of SFM–BZCY as a cathode material in proton-conducting intermediate-temperature solid oxide fuel cells.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Solid Oxide Fuel Cell (SOFC) is a high temperature (600–1000 °C) power generator, which can convert the chemical energy of a fuel to electrical energy directly via electrochemical reactions [1,2]. The energy efficiency of SOFC is not limited by Carnot efficiency and is considerably higher than conventional heat engines. The high operating temperature enables direct internal reforming of hydrocarbon fuels or thermal decomposition of ammonia in the porous anode of SOFC, thus SOFC is capable of using various alternative fuels, including hydrogen, methane, natural gas, ammonia, and renewable biogas. Moreover, the waste heat from SOFC stack is of high quality and can be recovered by integrating SOFC with other systems for combined thermal (heating or cooling) and power co-generation, leading to high system efficiency. Due to these advantages, SOFC has received significant attention as a promising alternative power sources for a variety of applications with various fuels [3]. According to the type of electrolyte materials used, SOFC can be divided into two main types: proton conducting solid oxide fuel cell (H-SOFC) and oxygen ion conducting solid oxide fuel cell (O-SOFC).

Key issues that hinder the widespread application of SOFC include high cost and long-term performance degradation. It has been observed that performance degradation of SOFC is usually caused by coarsening of the catalyst particles, sulfur poisoning, or carbon deposition. In recent years, novel symmetrical fuel cell (SFC) has been proposed [4–6]. In an SFC, the use of same ceramic material as both the anode and cathode not only simplifies the

* Corresponding author. Tel.: +852 27664152; fax: +852 27645131.
E-mail addresses: bsmengni@polyu.edu.hk, memni@graduate.hku.hk (M. Ni), xiacr@ustc.edu.cn (C. Xia).
[1] Tel.: +86 0551 63607475; fax: +86 0551 63601592.

http://dx.doi.org/10.1016/j.jpowsour.2014.03.013
0378-7753/© 2014 Elsevier B.V. All rights reserved.

fabrication process, but also solves the carbon deposition problem as the deposited solid carbon can be removed simply by shifting the anode and cathode [7].

In addition, the high cost and catalyst coarsening can be solved by lowering the operating temperature of SOFC to an intermediate temperature (IT) range as low-cost materials can be used in SOFC and the sintering of porous electrodes at IT is greatly slowed down [8]. The performance of SOFC at reduced temperature with conventional materials is also low due to low ionic conductivity of the yttria-stabilized zirconia (YSZ) and high polarization loss of the LSM-based cathode. To improve the SOFC performance at IT, alternative electrolyte materials with good ionic conductivity and cathode materials with good catalytic activity towards oxygen reduction reaction (ORR) have been developed. BZCY is a potential electrolyte material for practical IT-SOFCs due to its good proton conductivity at a reduced temperature and good chemical compatibility with other SOFC components. In addition to its good proton conductivity, the use of proton conductor as electrolyte also leads to a higher Nernst potential (thus a higher maximum efficiency) since H_2O is produced in the cathode, which in turn increases the molar fraction of H_2 in the anode. With NiO–BZCY|BZCY|$Sm_{0.5}Sr_{0.5}Co_{3-\delta}$ (SSC)–BZCY configuration, an anode supported SOFC achieved a peak power density of 650 mW cm^{-2} at 700 °C [9] (detailed output performance data of SOFCs with different configurations or materials are listed in Table 1). In advanced H-SOFC with thin film electrolyte (about 10 μm), the polarization loss of the cathode could account for up to 50% of the total over-potential loss. To further improve the cell performance, new cathode materials have been developed by many researchers for H-SOFCs based on BZCY electrolyte, such as $La_{0.7}Sr_{0.3}FeO_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (LSF–SDC) [10], $Sm_{0.5}Sr_{0.5}Co_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SSC–SDC) [11], $Ba_{0.6}Sr_{0.4}Co_{0.9}Nb_{0.1}O_3$ (BSCN) [12], $GdBaCo_2O_{5+\delta}$ [13], and good performances have been obtained.

Due to the diverse conduction mechanisms, cathode materials of H-SOFCs can be classified into 3 main types [14]: (1) electronic conductor single phase cathode (i.e. Pt); (2) mixed electronic and oxygen ion conducting single phase (i.e. $La_{0.7}Sr_{0.3}MO_3$ [15], $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF) [16]) or composite cathodes (i.e. $Sm_{0.5}Sr_{0.5}Co_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SSC–SDC) [11], and $Sm_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_3$–SDC [17]); and (3) mixed electronic and proton conducting single phase (i.e. $BaCe_{0.5}Bi_{0.5}O_3$ [18] and $BaCe_{0.5}Fe_{0.5}O_3$ [18]) or composite cathodes (i.e. SSC-$BaCe_{0.5}Sm_{0.2}O_3$ (BCS) [20]). Many perovskite materials containing transition metal ions are known to be mixed ionic–electronic conductors (MIEC), which can be applied as both cathode and anode materials in IT-SOFCs, such as Sr-doped $LaFeO_3$ (LSF), Sr-doped $LaCoO_3$ (LSC), Sr-doped La (Co, Fe)O_3 (LSCF) [21]. The perovskite $Sr_2Fe_{1.5}Mo_{0.5}O_6$ (SFM) shows high redox stability and has been studied by many research groups for its possible use as SOFC electrodes. Due to its mixed Fe^{3+}/Fe^{2+} and Mo^{6+}/Mo^{5+} valences, SFM is proved to be a MIEC material [22]. Single fuel cells with the configuration of SFM|$La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_3$ (LSGM)| $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF) exhibits a remarkable electrochemical activity in H_2 and achieves a peak power density of 603 mW cm^{-2} at 800 °C [23]. Remarkable cell performances are also achieved using SFM and other material (i.e. SFM–SDC [24,25]) as composite cathodes for IT-SOFCs in humidified H_2. Compared with single phase SFM electrode fuel cells, nano-structured SFM electrode by infiltrating $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) nanoparticles onto the SFM backbone greatly decreases the interfacial polarization resistance of SDC electrolyte symmetrical fuel cells from 0.27 Ω cm^2 to 0.11 Ω cm^2 at 750 °C [26].

Despite of their potential for electrolyte and cathode materials in O-SOFC, the feasibility of BZCY–SFM composite cathode in H-SOFC has not been evaluated yet. To fill the research gap, this study is purposely designed to evaluate the feasibility of SFM as a cathode material for H-SOFCs. Anode-supported H-SOFCs are fabricated with the perovskite-type $Sr_2Fe_{1.5}Mo_{0.5}O_6$–$BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (SFM–BZCY) composite cathode, BZCY electrolyte, and NiO–BZCY anode. Symmetrical fuel cells are also made with SFM–BZCY as both electrodes. Both the single fuel cells and symmetrical fuel cells are characterized and tested. In addition, the effects of sintering temperature on the microstructure and cell performance are investigated.

Table 1
Output performance of fuel cells with different configurations (different cathode materials).

Fuel cells of different configuration with different cathode materials	Interfacial polarization resistance R_p (Ω cm^2)	Operating temperature t_{op} (°C)	Peak power density (mW cm^{-2})
NiO–BZCY|BZCY|SSC–BZCY [9]	NA	700	650
SFM|LSGM|BSCF [23]	NA	800	603
SFM infiltrated with nano-SDC| SDC [26]	0.27–0.11	750	NA
SFM|LSGM|SFM [32]	0.26	900	NA
LSCT|LSGM [5]	NA	800	220
BSCF–SFM|BZCY|NiO–BZCY [35]	0.46	600	NA
BCFN|BZCY|NiO–BZCY [12]	0.10	700	NA
BCBN|BZCY [18]	0.28	700	NA
$Pr_2NiO_4 + \delta$|BZCY [36]	2.76	600	NA
$Sm_{0.5}Sr_{0.5}FeO_{3-\delta}$–BZCY|BZCY [33]	0.10	700	341
SSC–BCS as cathode [20]	0.21	700	NA
$GdBaCo_2O_5 + \delta$|BZCY [13]	0.16	700	NA
$SmBaCo_0O_5 + \delta$|BZCY [37]	0.15	700	NA
$PrBaCo_2O_5 + \delta$|BZCY [38]	0.15	700	NA
LSF–SDC|BZCY [10]	0.074	650	542

2. Experimental

2.1. Material preparation and powder synthesis

$Sr_2Fe_{1.5}Mo_{0.5}O_6$ (SFM) was synthesized by a microwave-assisted combustion method using $Sr(NO_3)_2$ (AR), $Fe(NO_3)_3.9H_2O$ (AR) and $(NH_4)Mo_7O_{24}.4H_2O$ (AR, Sinopharm Chemical Reagent Co., ltd) as the starting metal materials. Glycine and citric acid were used to assist the combustion process. And the mixing process was conducted with continuous stirring and heating for 1 h to form first-step aqueous solution, which was subsequently heated to self-combustion, resulting in black ash. Then, the as-prepared ash was calcined at 1000 °C for 5 h to form dark SFM powders with perovskite structures, which were confirmed with X-ray diffraction (XRD) measurement.

The BZCY electrolyte powders were synthesized through a citric acid–EDTA sol–gel process. Y_2O_3 was dissolved in concentrated nitric acid, and the stoichiometric amounts of $Zr(NO_3)_4 \cdot 5H_2O$, $C_4H_6BaO_4$, $(NH_4)_2Ce(NO_3)_6$, and $Ce(NO_3)_3 \cdot 6H_2O$ (all in 99.9%, Sinopharm Chemical Reagent Co., ltd) were added into the aqueous solution sequentially with continuously stirring for 2 h. Then concentrated ammonia was applied to adjust the solution pH to ~6.0. A final viscous gel would be obtained after continuously heating and stirring, which would be pre-heated at about 300 °C for 3~4 h to get white ash-like material and be further calcined at 1000 °C in air for 5 h to obtain a BZCY perovskite.

2.2. Characterization

To investigate their chemical compatibility, SFM and BZCY were mixed, uniaxially pressed into pellets, and heated at 900 °C, 1000 °C and 1100 °C for 2 h. The phase structures of the heated pellets were analyzed using XRD (Riguku-TTR III) with Cu-Kα radiation under the scanning rate of 10 °C min^{-1}. The cross-section and detailed morphology of the single cell after electrochemical tests was

Download English Version:

https://daneshyari.com/en/article/1284136

Download Persian Version:

https://daneshyari.com/article/1284136

Daneshyari.com