

Available online at www.sciencedirect.com

ScienceDirect

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

A new, high electrochemical activity and chromium tolerant cathode for solid oxide fuel cells

Ling Zhao ^{a,b}, Yi Cheng ^b, San Ping Jiang ^{b,*}

^a Department of Material Science and Chemistry, China University of Geosciences, Wuhan, 430074, China

^b Fuels and Energy Technology Institute & Department of Chemical Engineering, Curtin University, Perth, WA 6102, Australia

ARTICLE INFO

Article history:

Received 13 April 2015
Received in revised form
3 September 2015
Accepted 3 September 2015
Available online 23 October 2015

Keywords:

Solid oxide fuel cells
Niobium doped cobalt ferrite
SSBCFN cathode
Chromium deposition and poisoning
Chromium tolerance
Stability

ABSTRACT

The commercialization of solid oxide fuel cell (SOFC) technologies requires the development of cathode materials not only with high electrochemical activity and stability but also with excellent tolerance and resistance towards contaminants such as chromium. Here, a new electrode, $\text{Sm}_{0.5(1-x)}\text{Sr}_{0.5(1-x)}\text{Ba}_x\text{Co}_{1-0.3x}\text{Fe}_{0.2x}\text{Nb}_{0.1x}\text{O}_{3-\delta}$ (SSBCFN with $x = 0.4, 0.5, 0.6$) is developed based on the combined composition of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) and $\text{Ba}(\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1})\text{O}_{3-\delta}$ (BCFN). SSBCFN with $x = 0.5$ (SSBCFN5) shows a high electronic conductivity of $128\text{--}221\text{ S cm}^{-1}$ in the temperature range of $500\text{--}900\text{ }^\circ\text{C}$, an essential requirement of SOFCs electrode materials and low electrode polarization resistance of $0.53\text{ }\Omega\text{cm}^2$ at $600\text{ }^\circ\text{C}$, significantly lower than $1.79\text{ }\Omega\text{cm}^2$ for the reaction on SSC and $0.64\text{ }\Omega\text{cm}^2$ on BCFN. SSBCFN5 shows cubic perovskite structure with a high oxygen non-stoichiometry, $\delta = 0.514 \pm 0.027$, based on chemical titration method. Compared to SSC and BCFN electrodes, SSBCFN5 shows better electrochemical activity for the oxygen reduction reaction and most importantly, it exhibits excellent stability and resistance toward chromium deposition and poisoning under SOFC operation conditions from $700\text{ to }900\text{ }^\circ\text{C}$. The results indicate that SSBCFN5 is a promising potential cathode of SOFCs with high activity, stability and high tolerance towards contamination by Cr.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

The demand for a clean and sustainable energy supply has stimulated a great interest in fuel cell technologies for direct conversion of chemical energy of fuels such as hydrogen, ethanol and natural gas to electricity. Among different types of fuel cells, solid oxide fuel cells (SOFCs) have the potential to be the cleanest and most efficient one with excellent fuel flexibility [1]. One of the technical hurdles to the

commercialization of SOFC technologies, however, is the development of cathode materials not only with high electrochemical activity and good stability but also with excellent tolerance to impurities, particularly volatile Cr species from the chromia-forming metallic interconnect, under SOFC operation conditions. To date, various cathode materials have been studied, including $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) [2,3], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) [4,5], $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) [6], $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) [7] and $\text{Ba}(\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1})\text{O}_{3-\delta}$ (BCFN) [8]. LSM perovskite is a traditional cathode material for

* Corresponding author. Tel.: +61 8 9266 9804.

E-mail address: s.jiang@curtin.edu.au (S.P. Jiang).

<http://dx.doi.org/10.1016/j.ijhydene.2015.09.091>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

high temperature SOFCs due to its high electrical conductivity, compatible thermal expansion coefficient, good structural stability and good chemical compatibility with yttria-stabilized zirconia (YSZ) electrolyte, however, the negligible ionic conductivity of LSM-based materials limits its application at intermediate temperatures of 600–800 °C [9]. Subsequently, mixed ionic and electronic conductors (MIECs), such as LSCF, SSC and BSCF, have been extensively investigated as potential cathodes of SOFCs for the oxygen reduction reaction (ORR) at intermediate temperatures due to their high surface exchange and oxygen ion diffusion coefficients.

On the other hand, chromia-forming alloys have been considered to be the primary candidates as the metallic interconnect materials of intermediate temperature SOFCs because of their low cost, easy processing properties, high electrical and thermal conductivities [10,11]. However, the chromium oxide, Cr₂O₃, formed in the cathode environment can further react with oxygen and/or moisture to form various gaseous hexavalent chromium species such as CrO₃ and/or CrO₂(OH)₂ under the operating temperatures of SOFCs [12–14]. The gaseous Cr species will react with the cathodes of SOFC, such as LSM, LSCF and BSCF, leading to the significant Cr deposition and rapid electrochemical performance degradation of the cathodes for the O₂ reduction reaction [15]. Therefore, in addition to the high electrochemical activity for the O₂ reduction reaction, cathode must provide high tolerance and resistance towards chromium deposition and poisoning for commercial and practical application of SOFC technologies [16,17]. We studied systematically the mechanism and kinetics of Cr deposition and poisoning on SOFC cathodes such as LSM, LSCF, BSCF, etc and demonstrated that the Cr deposition is most likely controlled by the chemical reduction of high valence Cr species, facilitated by the nucleation agents on the electrode surface, electrolyte surface, and/or at the electrode/electrolyte interfaces [15,18,19]. The driving force of the nucleation process is primarily related to the segregation and migration of cationic species on the surface of cathodes. The surface segregation and migration of cationic species such as Sr and Mn is a well-known phenomenon in the perovskite cathode materials under operation conditions of SOFCs [20,21].

There are various strategies to enhance the tolerance and resistance of electrode materials towards Cr deposition. For example, cathode materials can be modified with chromium inert phases, such as ionic-conducting Ce_{0.9}Gd_{0.1}O_{2-δ} (GDC). Our recent study [22] showed that GDC impregnation increases the electrochemical activities of LSCF cathode for the O₂ reduction reaction and enhances significantly its tolerant towards chromium deposition by reducing the direct contact between the LSCF and gaseous Cr species. Surface modification method works on the principle of physical separation of cathode surface and Cr species and largely depends on the structural stability of the impregnated protective phase. The second approach is to develop the Sr and Mn nucleation agents-free cathode materials, such as Nd₂NiO₄(NNO) [23] and La(NiFe)O₃ (LNF) [24,25]. However, NNO and LNF in general present relatively lower electrocatalytic activity for the O₂ reduction reaction at intermediate temperatures as compared to well-established MIEC cathodes such as LSCF and SSC. Adding Cr catcher or scavenger such as BaO has been proven to be effective to mitigate the Cr poisoning

problem [26]. A more effective strategy is to enhance structural stability of the MIEC cathode materials, thus reducing and inhibiting significantly the surface segregation of nucleation agents such as Sr. One good example is the development of (La_{0.24}Sr_{0.16}Ba_{0.6})(Co_{0.5}Fe_{0.44}Nb_{0.06})O_{3-δ} (LSBCFN) oxide as a highly active and Cr-tolerant cathode by direct mixing synthesis of LSCF and BCFN [27]. It has been shown that LSBCFN not only shows better electrochemical activity for the O₂ reduction reaction than either LSCF or BCFN in the temperature range of 600–900 °C but also exhibits excellent stability and tolerance toward chromium deposition and poisoning as a result of combining the structural stability and activity of BCFN and the high conductivity of LSCF [27].

In the present study, a new cathode material with composition of Sm_{0.5(1-x)}Sr_{0.5(1-x)}Ba_xCo_{1-0.3x}Fe_{0.2x}Nb_{0.1x}O_{3-δ} (SSBCFN, x = 0.4, 0.5, 0.6) was developed, based on the SSC and BCFN compositions. SSC is one of the best performed cathodes and offers higher electronic conductivity, higher surface exchange and oxygen ion diffusion dynamics, and better electrocatalytic activity for the O₂ reduction reaction than LSCF [6,28–31]. For instance, the electrode polarization resistance of SSC is very low, 0.10 Ω cm² at 700 °C [6], significantly lower than 0.24 Ω cm² reported on LSCF at 726 °C [29]. However, Sr from SSC is a potential nucleation agent for the Cr deposition. On the other hand, it has been reported that Nb doping at the B-site of lanthanum and/or barium cobalt-ferrite can significantly increase the structural stability of BSCF [32]. This implies that SSBCFN with the combined SSC and BCFN composition would be potentially a highly active and Cr tolerance cathode of SOFCs.

Experimental

Sm_{0.5}Sr_{0.5}CoO_{3-δ} (SSC), Ba(Co_{0.7}Fe_{0.2}Nb_{0.1})O_{3-δ} (BCFN) and Sm_{0.5(1-x)}Sr_{0.5(1-x)}Ba_xCo_{1-0.3x}Fe_{0.2x}Nb_{0.1x}O_{3-δ} (SSBCFN with x = 0.4, 0.5, 0.6) were synthesized by a sol-gel process [33–36]. SSBCFN with x = 0.4, 0.5, 0.6 was denoted as SSBCFN4, SSBCFN5 and SSBCFN6, respectively. In the case of SSBCFN, stoichiometric amount of Sm(NO₃)₃·6H₂O, Ba(NO₃)₂, Sr(NO₃)₂, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O and C₄H₄NNbO₉·H₂O (Sigma-Aldrich) were dissolved in distilled water to form an aqueous solution, the complexation agents of citric acid and EDTA were then added at a molar ratio of citric acid:EDTA:metal of 1:1.5:1. The pH of the solution was controlled at ~7 with the assistance of NH₃·H₂O. The homogeneous solution was heat-treated till self-combustion occurred. The as-synthesized powder was subsequently calcined at 1000 °C for 3 h to obtain fine SSBCFN powders. SSC and BCFN powder was prepared in similar ways.

Electrolyte pellets were prepared by dry-pressing gadolinium-doped ceria Gd_{0.1}Ce_{0.9}O_{1.95} (GDC, AGC SEIMI, Japan) powders, followed by sintering at 1500 °C for 5 h. The thickness of the sintered disks was kept as 1.00 ± 0.05 mm and the diameter was about 20 mm. The as-prepared cathode powders were then mixed with an ink vehicle (Fuel Cell Materials, USA) in a weight ratio of 1:2, to form an electrode ink. The electrode ink was applied onto the surface of GDC pellets using slurry coating technique, followed by sintering at 1000 °C for 3 h to form the working electrode. The thickness of the working

Download English Version:

<https://daneshyari.com/en/article/7713478>

Download Persian Version:

<https://daneshyari.com/article/7713478>

[Daneshyari.com](https://daneshyari.com)