INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–8

Available online at www.sciencedirect.com

ScienceDirect

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

Molybdenum substitution at the B-site of lanthanum strontium titanate anodes for solid oxide fuel cells

Jiang Li [a,b,1], Tianmu Lv [a,b,1], Nianjun Hou [a,b], Ping Li [a,b], Xueli Yao [a,b], Lijun Fan [a,b], Tian Gan [a,b], Yicheng Zhao [a,b,*], Yongdan Li [a,b]

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

ARTICLE INFO

Article history:
Received 18 January 2017
Received in revised form
21 March 2017
Accepted 27 March 2017
Available online xxx

Keywords:
Anode
Lanthanum strontium titanate
Solid oxide fuel cell
Molybdenum doping
Catalytic activity

ABSTRACT

The effects of Mo doping into the B-site of $La_{0.3}Sr_{0.7}TiO_{3-\delta}$ perovskite on its ionic conductivity and catalytic activity as an anode material of solid oxide fuel cells have been investigated. The partial substitution of Ti by Mo reduces the bond energy between metal and oxygen ions in the perovskite. The concentration of Mo^{5+}/Mo^{6+} redox couples increases with the rise of the content of Mo, while the oxygen ionic conductivity decreases simultaneously. The doping of Mo significantly reduces the anodic polarization resistance and improves the performance of the single cell. The cell with $La_{0.3}Sr_{0.7}Ti_{0.97}Mo_{0.03}O_{3-\delta}$ anode and $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ electrolyte exhibits a maximum power density of 135 mW cm^{-2} at 850 °C with hydrogen as fuel.

Introduction

Anodes of solid oxide fuel cells (SOFCs) catalyze the electrochemical oxidation of fuels and provide sufficient electronic and ionic conductivities for that reaction [1,2]. Conventional Ni-based cermet anodes, such as Ni-yttria stabilized zirconia (Ni-YSZ), exhibit excellent properties with hydrogen as fuel [3]. Ni provides outstanding catalytic activity for hydrogen dissociation and adequate electronic conductivity [4]. Meanwhile, the ceramic phase supplies oxygen ions to reacting sites, and mitigates the difference of thermal expansion coefficients between anode and electrolyte materials [5]. However, at the same time, Ni-based anodes faces a number of problems. Ni suffers from serious carbon deposition in a carbon-containing atmosphere, making it not a suitable anode for direct hydrocarbon SOFCs [6]. Besides, hydrogen from fossil fuels usually contains H_2S, which reacts readily with Ni and poisons the catalyst even at a low concentration [7]. In addition, the redox stability of Ni is quite poor, which results in mechanical degradation of the anode layer after several redox cycles [8]. Therefore, the exploration of novel anode materials is in urgency for the application of SOFCs.

---

* *Corresponding author*. State Key Laboratory of Chemical Engineering (Tianjin University), Tianjin Key Laboratory of Applied Catalysis Science and Technology, School of Chemical Engineering, Tianjin University, Tianjin, 300072, China. Fax: +86 22 27405243.
E-mail address: zhaoyicheng@tju.edu.cn (Y. Zhao).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.ijhydene.2017.03.189
0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Please cite this article in press as: Li J, et al., Molybdenum substitution at the B-site of lanthanum strontium titanate anodes for solid oxide fuel cells, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.03.189

Compared with cermet anodes, most oxide materials exhibit high resistance to carbon deposition [9]. In recent years, oxide anodes with various structures, such as fluorite [10], pyrochlore [11], rutile [12], tungsten bronze [13] and perovskite [14], have been extensively studied, in which perovskite anodes show the most promising properties. Perovskite with a general formula ABO_3 possesses a wide non-stoichiometric window, which shows excellent tolerance to dopants and lattice vacancies. Thus, the properties of perovskite oxides, such as electronic conductivity, ionic conductivity and catalytic activity, could be properly regulated [15]. Some perovskite oxides with high chemical stability and electrical conductivity in a reducing atmosphere, such as vanadate [16], chromite [17], titanate [18] and Mo-based double perovskite [19], have been investigated intensively as anode materials of SOFCs.

$SrTiO_3$ possesses high chemical stability in both reducing and oxidizing atmospheres and high tolerance to H_2S [20]. The electrical conductivity of pure $SrTiO_3$ is negligible in a wide range of O_2 partial pressure [21]. In 1997, Slater et al. [22] utilized $La_xSr_{1-x}TiO_{3-\delta}$ as an anode material of SOFCs for the first time. Partial substitution of Sr by La leads to the reduction of Ti^{4+} to Ti^{3+} in some degree, which decreases the band gap and increases the electrical conductivity of the titanate to about 250 S cm^{-1} at 700 °C in a reducing atmosphere [23]. The solid solubility of La in $La_xSr_{1-x}TiO_{3-x}$ is about 40 mol%. In addition, the coefficient of thermal expansion of $La_xSr_{1-x}TiO_{3-x}$ is about 10.4×10^{-6} K^{-1} between room temperature and 1000 °C, similar to that of the YSZ electrolyte (10.3×10^{-6} K^{-1}) [24].

The major hindrances of $La_xSr_{1-x}TiO_{3-x}$ to be the anode of SOFCs are its low catalytic activity and limited oxygen ionic conductivity. The former one is mainly attributed to the weak adsorption of H_2, which is considered as the rate determining step of the anodic reaction [25], while the later one is related to the limited oxygen vacancy concentration in $La_xSr_{1-x}TiO_{3-x}$ [26]. Yoo and Choi [27] mixed $La_{0.2}Sr_{0.8}TiO_{3-\delta}$ with $Gd_{0.2}Ce_{0.8}O_{1.9}$ as an anode, and the anodic polarization resistance decreased from 9.6 to 2.1 Ω cm^2 at 800 °C with wet H_2 as fuel. A single cell with the mixed anode and a 600-μm-thick $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ electrolyte layer exhibited a maximum power density (P_{max}) of 67 mW cm^{-2}. With further Ni (1 mg cm^{-2}) impregnation into the anode, the P_{max} increased to about 300 mW cm^{-2}. Doping of cations is another approach to improve the oxygen ionic conductivity and catalytic activity of the titanate anode. Vincent et al. [28] partially substituted Sr in $La_{0.4}Sr_{0.6}TiO_{3-\delta}$ with Ba, which resulted in the reduction of Ti^{4+} to Ti^{3+} and the improvement of catalytic activity. Aliovalent substitution of Ti by other transition metals, such as Co and Mn, could increase the oxygen ionic conductivity and reduce the anodic polarization resistance [23,29–31]. Cui et al. [7] found that Co in $La_{0.3}Sr_{0.7}Co_{0.07}Ti_{0.93}O_{3-\delta}$ could precipitate after reduction at 900 °C, which improved the catalytic activity of the anode. Tsekouras et al. [32] partially replaced Ti in $La_{0.4}Sr_{0.4}TiO_{3-\delta}$ by Fe and Ni. The A-site deficiency facilitated the exsolution of Ni and Fe nanoparticles, and the materials showed promising properties as cathodes for high temperature steam electrolysis. Ti in $La_{0.33}Sr_{0.67}TiO_{3-\delta}$ has been also substituted by other metal ions, such as Ga^{3+}, Al^{3+} and Mg^{2+}, while the anodic catalytic activity was not improved [33]. In recent years, Mo has been added into perovskite oxide and cermet anodes to modify their catalytic activity and resistance to carbon deposition [34,35]. In this work, Ti in $La_{0.3}Sr_{0.7}TiO_{3-\delta}$ (LST) is partially substituted by Mo as anodes of SOFCs with hydrogen as fuel. The effects of Mo content on the electrical conductivity and catalytic activity of the anode are investigated.

Experimental

Materials preparation

$La_{0.3}Sr_{0.7}Ti_{1-x}Mo_xO_{3-\delta}$ ($0 \le x \le 0.03$) powders were prepared through a EDTA-citrate sol–gel method [36]. A certain amount of EDTA ($C_{10}H_{16}N_2O_8$, Guangfu fine chemical, Ltd., 99.5%) was dissolved in an aqueous solution of ammonia (NH_4OH, Guangfu fine chemical, Ltd., 25%). Stoichiometric $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Guangfu fine chemical, Ltd., 99%), $La(NO_3)_3\cdot 6H_2O$ (Aladdin, 99.9%) and $Sr(NO_3)_2$ (Guangfu fine chemical, Ltd., 99.5%) were added to the solution. Then the solution was mixed with an ethanol solution of $Ti(OCH(CH_3)_2)_4$ (Alfa Aesar, 98%), followed by the addition of citric acid (Guangfu fine chemical, Ltd., 99.5%) as a complexing agent. The molar ratio of citric acid and EDTA to total metal cations were 1.5:1 and 1:1, respectively. The pH value of the solution was adjusted to 6 with the addition of $NH_3\cdot H_2O$. The solution was continuously stirred at 90 °C until a gel was formed, which was heated at 350 °C for 2 h and then calcined at 1050 °C in air for 5 h to form the anode powders. The obtained $La_{0.3}Sr_{0.7}Ti_{0.99}Mo_{0.01}O_{3-\delta}$, $La_{0.3}Sr_{0.7}Ti_{0.98}Mo_{0.02}O_{3-\delta}$ and $La_{0.3}Sr_{0.7}Ti_{0.97}Mo_{0.03}O_{3-\delta}$ were noted as LSTM1, LSTM2 and LSTM3, respectively. The synthesis procedure of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) cathode powder has been described elsewhere [37].

Characterization

The X-ray diffraction (XRD) patterns of the powders were recorded at room temperature with a D8 Focus diffractometer (Bruker Corp., Germany) with Cu-Kα radiation, 40 kV and 200 mA, at a scanning rate of 5° min^{-1}. Nitrogen adsorption/desorption isotherms were obtained with a Quantachrome Autosorb-1 analyzer. The specific surface area of each sample was calculated with Brunauer–Emmett–Teller (BET) method. H_2-temperature-programmed reduction (H_2-TPR) was performed with 10% H_2-90% Ar as the reductant using a Micromeritics Chemisorb 2720 instrument equipped with a thermal conductivity detector. The surface property of the reduced samples was measured with a PHI-1600 ESCA X-ray photoelectron spectroscopy (XPS) system with Mg-Kα radiation. The oxygen ionic conductivities of the samples in 700–850 °C were measured with the Wagner method in air by an electrochemical workstation (VersaSTAT 3, Ametek). A $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) (Fuel cell materials Co., USA) layer was used to block the conduction of electrons [23]. For the conductivity tests, the powders were pressed into pellets at 250 MPa, and then sintered in air at 1400 °C for 10 h.

Fuel cell test

The electrolyte-supported symmetric cells and single cells were fabricated with a screen-printing technique. LSGM powder (Fuel cell materials Co., USA) was pressed under

Please cite this article in press as: Li J, et al., Molybdenum substitution at the B-site of lanthanum strontium titanate anodes for solid oxide fuel cells, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.03.189