



SrFe_{0.75}Mo_{0.25}O_{3-δ} impregnated 430L alloys for efficient fuel oxidation in metal supported solid oxide fuel cells



Yucun Zhou, Xie Meng, Chun Yuan, Ting Luo, Xiaofeng Ye, Junliang Li, Shaorong Wang*, Zhongliang Zhan*

CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS), 1295 Dingxi Road, Shanghai 200050, PR China

HIGHLIGHTS

- Novel SFMO-430L composite anode is prepared for MS-SOFCs.
- Low polarization resistance of 0.11 Ω cm² at 800 °C is obtained.
- Promising power density of 0.81 W cm⁻² is obtained at 800 °C for the MS-SOFC.

ARTICLE INFO

Article history:

Received 4 April 2014

Received in revised form

16 June 2014

Accepted 17 June 2014

Available online 7 July 2014

Keywords:

Metal-supported solid oxide fuel cell

Impregnation

Anode

Molybdenum doped strontium ferrite

ABSTRACT

Here we report a novel SrFe_{0.75}Mo_{0.25}O_{3-δ} (SFMO)-430L composite anode for the application in the metal supported solid oxide fuel cells. Such an anode is prepared by coating a thin nano porous and mixed electronic-ionic conducting SFMO layer onto the internal surface of a micron porous 430L alloy backbone. The area specific polarization resistance of the composite anode for hydrogen oxidation can be as low as 0.11 Ω cm² at 800 °C. The electronic conductivity of the 430L alloy support is found to be critically important for promoting rapid hydrogen oxidation kinetics and attaining such a low polarization resistance as the fuel cell anode. A metal-supported fuel cell with the SFMO impregnated 430L composite anode exhibits outstanding power densities at 800 °C, e.g., 0.81 W cm⁻² in hydrogen and 0.31 W cm⁻² in *iso*-octane. Preliminary results show that the present SFMO-430L composite anode exhibits much higher tolerance for coking formation than the traditional Ni-based anode.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The solid oxide fuel cell (SOFC) is an electrochemical reactor directly converting fuels into electricity and exhibits attractive advantages over the conventional power generation technologies, including high energy efficiency, low pollution emission and wide fuel flexibility [1]. Currently, the common SOFCs consist of yttrium-stabilized zirconia (YSZ) electrolytes sandwiched between the Ni-YSZ anodes and the strontium lanthanum manganite (LSM) cathodes, mostly in the anode-supported configurations [2,3]. Nevertheless, extensive use of expensive and fragile ceramics in the SOFC architecture results in high materials costs and low mechanic reliability, which have been recognized as the main barriers for widespread implementation of the SOFC technology. The novel

metal-supported solid oxide fuel cell (MS-SOFC), where a porous alloy provides the mechanical support for thin functional anode–electrolyte–cathode layers, has gained increasing interest due to additional advantages over the common all-ceramic counterpart – including excellent structural robustness and stability, high tolerance toward rapid thermal cycling, easy stack assembling as well as low materials cost [4]. In particular, well-established joining techniques such as brazing and welding can be used for the MS-SOFC stack sealing that is able to withstand large thermal gradients and therefore allows for rapid start-up, making the metal-supported SOFC technology very competitive in the portable and transportation applications where frequent on–off cycling occurs and quick start-up is expected [5,6].

Despite these potential advantages of the MS-SOFCs as shown above, processing challenges should be addressed, especially the anode issues. Most developers of MS-SOFCs tend to co-fire the Ni-based anodes with the metallic supports at an elevated temperature (normally > 1200 °C) to densify the electrolyte layer. In order

* Corresponding authors. Tel./fax: +86 21 6990 6373.

E-mail addresses: zhouycwf@gmail.com (Y. Zhou), swang@mail.sic.ac.cn (S. Wang), zzhan@mail.sic.ac.cn (Z. Zhan).

to prevent the metallic support from serious oxidation, the sintering process should be conducted in the reducing atmosphere. However, the co-firing process in a reducing atmosphere would produce unacceptably large Ni particles with reduced surface areas available for fuel oxidation reactions and thereby decreased the fuel cell power densities [7,8]. Furthermore, metallic inter-diffusion occurring between the alloy substrates and the Ni-based anodes during the high temperature co-firing process and during the long-term operation at relative low temperatures is another problem, which would reduce the anode catalytic activity and alter the structural properties of the metallic substrate as well [9–11]. Introducing a barrier layer of ceria, gadolinium doped ceria or $\text{La}_{0.6}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{CrO}_3$ between the metallic support and the anode could prevent such metallic inter-diffusion, but could not address the issue of Ni coarsening during the co-firing process [9,10]. Low temperature thin film deposition techniques, including plasma spray method [12,13], and pulsed laser deposition (PLD) [14] have been used to form the functional ceramic layers on the metallic substrates to avoid excessive Ni coarsening and metallic inter-diffusion but would lead to high manufacturing costs. Alternatively, the anode catalysts could also be introduced into the pre-fired anode porous backbones at relatively low temperatures by the impregnating method [15–17]. Despite these extensive efforts, developing a durable and efficient anode catalyst for the robust metal-supported fuel cell remains a significant challenge.

As reported, $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SFMO) is a good electrode catalyst due to its good structural stability and important mixed ionic-electronic conducting behavior in both oxidizing and reducing atmospheres [18,19]. Here we report a novel robust, durable anode structure consisting of a nano porous SFMO catalyst coating supported on the internal surfaces of a micron porous 430L alloy backbone that exhibits impressive catalytic activity for fuel oxidation reactions and thereby yields low polarization resistances.

2. Experimental

For symmetrical anode fuel cells, the tri-layer structure of porous 430L|dense YSZ|porous 430L was produced by laminating three tape-cast green tapes, with 30 wt% ammonia oxalate used as the fugitive material for the two porous 430L substrates. The YSZ powders ($7 \text{ m}^2 \text{ g}^{-1}$) were purchased from Tosoh Corporation (Japan), and the 430L stainless steel powders (~ 400 mesh) were supplied by Jing-Yuan Powder Material (China). The slurry for tape casting was ethanol-based and consisted of acrylic resin dispersants, polyvinyl butyral binders, dibutyl phthalate plasticizer and other organic additives in addition to alloy or ceramic powders. Green tapes were obtained by casting appropriate slurries on the Mylar carrier on the tape casting machine (Lab-Cast Model TC-71LC Tape Caster, HED International, USA). The laminated green tapes were co-fired in a reducing atmosphere of 5% H_2 –95% N_2 at 1320 °C to produce the final structures. The SFMO catalysts were added into the porous 430L backbones by impregnating an aqueous solution containing $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and citric acid in a molar ratio of 1:0.75:0.0357:2, followed by calcinations at 850 °C in a reducing atmosphere of 5% H_2 –95% N_2 for 2 h to prevent oxidation of the 430L substrate. These salts were 99% pure and purchased from Sinopharm Chemical Reagent. The loadings of impregnated catalysts were controlled by a micro-liter syringe each time and a single impregnation–calcination cycle could yield an infiltrate loading of $\approx 3 \text{ vol}\%$. The ultimate catalyst loadings were tailored by increasing the impregnation–calcination cycles.

For single fuel cells, the tri-layer structure of porous 430L|dense YSZ|porous YSZ was produced by laminating three tape-cast green tapes, followed by co-firing at 1320 °C in 5% H_2 –95% N_2 [20]. Impregnation of SFMO catalysts was performed as described above,

yielding $V_{\text{SFMO}} = 16.0\%$ SFMO-430L composite anodes and $V_{\text{SFMO}} = 32.8\%$ SFMO–YSZ composite cathodes. A single impregnation–calcination cycle could generate an infiltrate loading of $\approx 6 \text{ vol}\%$ for the cathode.

The electrochemical properties of the SFMO-430L composite anodes were assessed on both symmetric anode cells and functional metal-supported cells over the temperature range of 650–800 °C. Silver ink was applied on the electrode surface as the current collector, and silver wires were used as the current leads. Current–voltage curves and electrochemical impedance spectra were obtained using an IM6 Electrochemical Workstation (ZAHNER, Germany). The frequency range for impedance measurement was 0.1 Hz–100 kHz with a 20 mV AC amplitude. Humidified (3% H_2O) hydrogen at a flow rate of 100 sccm, mixed with nitrogen in some cases, was used for measurement of the anode polarization resistance in the symmetric cells. The metal-supported fuel cell was tested with dry air at 100 sccm maintained in the cathode. The fuel in the anode was 97% H_2 –3% H_2O at 100 sccm or 6% *iso*-octane–94% nitrogen. Active area of the symmetric anode cell and the single cell was 0.64 cm^2 and 0.35 cm^2 , respectively.

For electrical conductivities test, SFMO powers were prepared by a combustion synthesis technique that used the corresponding metal nitrates and citric acid as the precursors. The as-synthesized SFMO powders were compacted into a bar and then fired in air at 1350 °C, yielding a relative density of 95% as measured by the

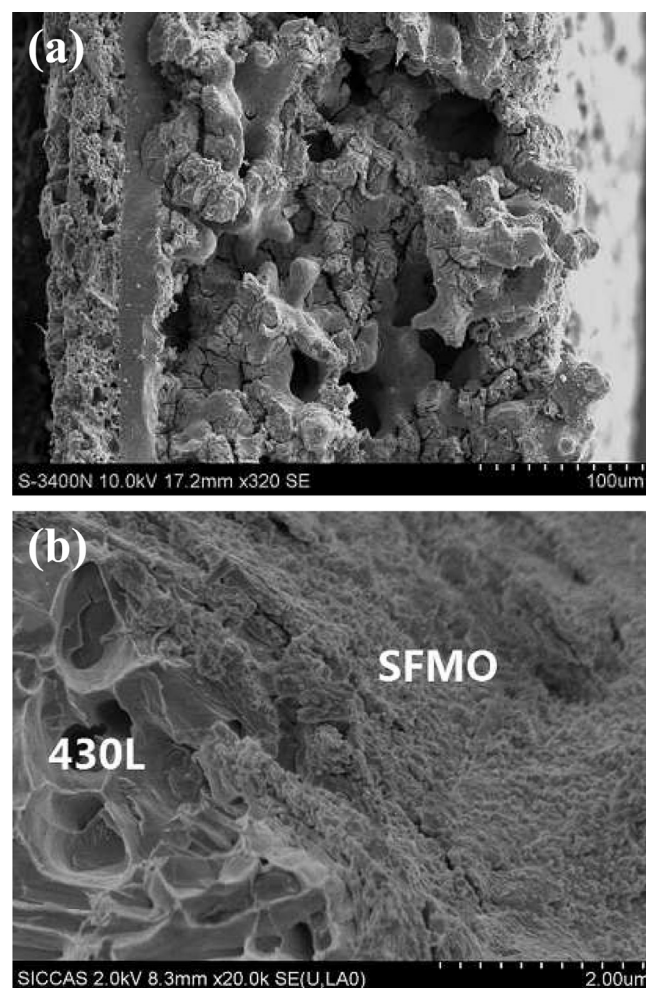


Fig. 1. (a) Cross-sectional scanning electron microscope (SEM) image of the MS-SOFC. (b) A higher magnification SEM image of the impregnated SFMO/430L anode.

Download English Version:

<https://daneshyari.com/en/article/7736045>

Download Persian Version:

<https://daneshyari.com/article/7736045>

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