Solid State Ionics 324 (2018) 40–48

Contents lists available at ScienceDirect

Solid State Ionics

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

Effect of precursor materials on the performance of the $NiFe_2O_4$-based spinel layer for SOFC cathode-side contact application

Y.T. Yu, J.H. Zhu*, B.L. Bates

Department of Mechanical Engineering, Tennessee Technological University, Cookeville, TN 38505, USA

ARTICLE INFO

Keywords:
Solid oxide fuel cell
Contact layer
Spinel
Reactive sintering
Area specific resistance
Alloy powder

ABSTRACT

Simulated cathode/contact/interconnect cells are used to investigate the effects of different precursors on the microstructure and performance of the thermally-converted $NiFe_2O_4$-based spinel contact layer. The precursor materials include a mixture of NiO and Fe_2O_3 powders (NiO + Fe_2O_3), a mixture of pure Ni and Fe powders (Ni + Fe), an Fe-Ni alloy (Invar 36) powder, and an Fe-Ni-Co alloy (Kovar) powder. The isothermal area specific resistance (ASR) of the test cells is evaluated at 800 °C in air for 1000 h, which shows significant variation depending on the contact precursors. The cells with the metallic precursors exhibit much reduced ASRs compared to the one with the mixed oxides, due to the unique reactive sintering of the spinel layer with the metallic precursors. Furthermore, the cell ASR values with the alloy precursors are lower than that with the Ni + Fe mixture. While the cell ASR with the Invar 36 precursor decreases gradually with time, the Kovar precursor leads to the lowest ASR. Thermal cycling does not negatively affect the cell ASR performance with the Kovar-derived contact layer. Cross-sectional observation of the tested cells is conducted to assess the compatibility of the contact layer with adjacent components as well as its effectiveness in blocking Cr migration from the interconnect to the cathode.

1. Introduction

Solid oxide fuel cell (SOFC) is an electrochemical device that produces electricity and heat through electrochemical conversion of chemical energy of hydrogen and hydrocarbon fuels. One of the most difficult challenges in SOFC development is the power loss throughout the SOFC stack during its operation, due to high contact resistance between metallic interconnect and ceramic cathode [1, 2]. To address this issue, a cathode-side contact layer is usually applied to provide better electrical pathway to decrease the ohmic losses and compensate the dimensional tolerance between the interconnect and cathode [3–8]. As the state-of-the-art stack operates at an elevated temperature close to ~800 °C and its cathode side is exposed to air, the requirements for the cathode-interconnect contact material are quite stringent, including high thermal and chemical stability, adequate electrical conductivity, well-matched coefficient of thermal expansion (CTE) to other stack components, good Cr-blocking capability, reasonable sinterability and mechanical bonding with adjacent stack components, and low material/manufacturing costs [1, 8–10].

Various materials such as conductive perovskites, noble metals, and their composites have been studied for the cathode-side contact application. While perovskites with a formula of ABO_3 like $(La,Sr)MnO_3$, $(La,Sr)(Co,Fe)O_3$, $(La,Sr)(Co,Mn)O_3$ have been extensively evaluated for such application, it is difficult to find a perovskite phase that possesses overall balanced properties meeting all the material requirements for the contact layer [11–13]. Considering noble metals, Pt and Au have exceptional electrical conductivity and thermal stability; unfortunately, their costs are prohibitively high [1, 14]. In comparison, Ag is relatively cheap; however, its evaporation rate is unacceptable under the SOFC operating condition [15], and also the formation of the Ag-Cr-O compound(s) at the interconnect-contact interface could decrease the electrical conductivity of the contact zone [16, 17]. During the last decade, electrically-conductive spinels with an AB_2O_4 formula have been widely recognized as effective coatings to protect Cr-containing ferritic stainless steel interconnects, due to their adequate CTE and electrical conductivity [18, 19]. Some of them, for instance, $(Mn,Co)_3O_4$, $(Co,Fe)_3O_4$, $(Ni,Co)_3O_4$, $(Cu,Mn)_3O_4$ and $(Ni,Fe)_3O_4$, possess remarkable Cr-blocking ability and slow down the Cr_2O_3 scale growth on the metallic interconnect, thus significantly reducing the electrical resistance in comparison with the uncoated samples [20–24]. Due to the similar requirements, these spinels are also potential materials for SOFC cathode-side contact application.

Among all the potential spinels, the $NiFe_2O_4$-based spinel was chosen in the present study mainly due to the relatively lower cost of Ni

* Corresponding author.
E-mail address: jzhu@tntech.edu (J.H. Zhu).

https://doi.org/10.1016/j.ssi.2018.05.030
Received 8 February 2018; Received in revised form 17 April 2018; Accepted 28 May 2018

and Fe than that of Co. The $NiFe_2O_4$ spinel is normally prepared via solid oxide state reaction, citric acid-nitrate process, mechanochemical reaction, etc. [25–27]. However, these synthesis methods have the disadvantages of high sintering temperature, expensive starting materials, and/or complex experimental procedures. Since the spinel-forming reaction using Ni- and Fe-containing metallic powders as the precursor (i.e., $Ni + Fe + 2O_2 \rightarrow NiFe_2O_4$) releases a significant amount of heat which can raise the local temperature [27, 28], a lower sintering temperature might be realized. In this study, such unique reactive sintering mechanism was utilized to synthesize the spinel contact layer with different metallic powders as the precursor, including a mixture of elemental Ni and Fe powders, a binary Ni-Fe alloy (Invar 36) powder, and a ternary Ni-Fe-Co (Kovar) powder. Both Invar 36 and Kovar powders are commercially available; while Invar 36 has an atomic ratio of Ni/Fe close to 1:2 desirable for the $NiFe_2O_4$ spinel formation, Kovar has some additional Co which might be of interest for further modification of the final spinel composition and/or microstructure. The metallic powders were thermally converted to form the spinel contact layer at a temperature close to the initial stack firing temperature. The electrical performance of the converted spinel contact layer and its chemical compatibility with the adjacent components were presented and discussed. A mixture of NiO and Fe_2O_3 powders was also included in the investigation as the contact precursor for comparison.

2. Experimental

2.1. Material preparation and thermal conversion optimization

The interconnect used in this study was Crofer 22 APU (Crofer) coupons which had the following composition (in wt%): 22.74 Cr, 0.45 Mn, 0.06 Ti, 0.11 La, 0.002 C, 0.01 Al, 0.01 Cu, 0.02 Si, and balance Fe. The Crofer sheet was cut into 15 × 15 0.5 mm coupons, which was subsequently polished to a 600-grit finish. Dense $La_{0.8}Sr_{0.2}MnO_3$ (LSM) pellets to be used as the support for forming the interconnect/contact/cathode test cells were prepared as below. About 1.6 g of the LSM powder (NexTech Materials) was pressed at 150 MPa in a 19-mm diameter die to form a green body, followed by sintering at 1400 °C in air. These densified pellets of 16 mm in diameter and 1.2 mm in thickness were polished on both sides to an 800-grit finish. A porous LSM layer of approximately 14-μm in diameter was screen-printed onto the dense LSM support to simulate the cathode. The cathode layer was sintered at 1100 °C in air and its thickness was ~10–20 μm.

Three different metallic precursors for the $NiFe_2O_4$-based spinel contact layer formation were a mixture of pure Ni and Fe powders (i.e., Ni + Fe), a prealloyed Fe-Ni powder (Invar 36), and a prealloyed Fe-Ni-Co powder (Kovar). In addition, a mixture of NiO and Fe_2O_3 powders (i.e., NiO + Fe_2O_3) was also included in the evaluation for comparison. The oxide and pure metal powders were from Alfa Aesar, while both commercial Invar 36 and Kovar alloy powders were from Sandivk Osprey. As shown in Table 1, Invar 36 is a binary Fe-Ni alloy with about 36 wt% Ni, while the Kovar alloy is a ternary Fe-Ni-Co alloy with 29.2 wt% Ni and 16.5 wt% Co. These alloys were originally developed as low CTE materials for applications such as precision instruments [29] and glass-metal sealing [30, 31]. The average particle sizes of all the micrometer-sized precursor powders used in this study are shown in Table 2. The NiO and Fe_2O_3 powders had the smallest size, while the alloy powders had the largest size. The NiO + Fe_2O_3 and Ni + Fe precursor materials were obtained by hand-mixing the respective powders for 30 min using a mortar and pestle in the desired proportion (i.e., with the molar ratio of Ni/Fe equal to 1/2), followed by overnight tumbling. Upon drying, the mixed powders were brushed through a 200-mesh sieve. A 7 wt% carbon pore former and an ink vehicle were added to the powders to form a contact paste suitable for screen printing.

Table 1
Chemical compositions of the Invar 36 and Kovar powders (wt%).

	Ni	Mn	Co	Cr	Si	C	Fe
Invar 36	35.8	0.20	0.01	0.14	0.05	0.01	Balance
Kovar	29.2	0.45	16.5	0.03	0.20	0.01	Balance

Table 2
The average particle size of the precursor materials used in the investigation.

Powder	Fe_2O_3	NiO	Fe	Ni	Invar 36	Kovar
Particle size (μm)	1.0	0.8	3.0	2.6	3.5	5.2

The Invar 36 precursor layers screen-printed onto the Crofer coupons were thermally converted for 2 h in air at different sintering temperatures (i.e., 800, 850, 900, and 950 °C) to identify the proper conversion temperature. This temperature was then employed for the contact layer formation with different precursor powders for comparison. X-ray diffraction (XRD) was used to identify the phases in the sintered layers, while scanning electron microscopy attached with energy-dispersive spectroscopy (SEM/EDS) was used to investigate the microstructure and obtain compositional information.

2.2. Area specific resistance (ASR) evaluation

The different contact materials were incorporated into the test cells and evaluated with regard to the ASR changes during thermal exposure. For construction of each ASR test cell, the contact paste was applied between the Crofer coupon and the LSM cathode to form the Crofer/contact/LSM cell, and each cell was wired according to the four-probe method with Pt leads, as illustrated in Fig. 1. Two upper leads were spot-welded to the Crofer and two lower leads were attached to the Pt patch screen printed onto the LSM support for current collection. A DC power supply was used to apply a constant current density of 250 $mA{\cdot}cm^{-2}$ across the cell via one upper and one lower lead. A LabVIEW program was used in conjunction with a multi-channel Keithley 2700 multimeter to measure and record the voltage drop across each cell once every 2 min during testing via the other two leads. A compressive load of 0.16 $kg{\cdot}cm^{-2}$ was applied during the test to simulate a stack environment.

At the beginning of each test, the cells were heated to 900 °C and held for 2 h to facilitate the conversion/sintering of the contact pastes. The cell temperature was then dropped to 800 °C, followed by either isothermal or cyclic exposure in air. For the isothermal exposure, the overall cell ASRs were measured continuously at 800 °C for 1000 h. For the thermal cycling exposure, each cycle consisted of holding at 800 °C for 10 h, furnace cooling to 250 °C, and then re-heating to 800 °C. A total of 50 thermal cycles (or 500 cumulative hours of exposure at 800 °C) were completed for each test cell. Only the Kovar alloy powder was utilized as the contact precursor in the cyclic test. Multiple cells for each contact material were prepared and tested to verify the data reproducibility.

2.3. Microstructural evaluation of the tested cells

To investigate the microstructure in the contact layer and the potential interfacial interaction between the contact and the adjacent components, the ASR-tested cells were mounted, sectioned and examined with SEM/EDS. EDS line scans near the interconnect-contact and cathode-contact interfaces were obtained to identify possible interdiffusion and detrimental interaction between the different materials, while EDS mapping was used to observe the phase distribution before and after the ASR test. Cr migration throughout the cell during the thermal exposure was also assessed, which allowed for a rough estimate and comparison of the Cr-block capability of the different contact materials.