Journal of Power Sources 376 (2018) 100–110

Contents lists available at ScienceDirect

Journal of Power Sources

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

Mitigation of chromium poisoning of cathodes in solid oxide fuel cells employing $CuMn_{1.8}O_4$ spinel coating on metallic interconnect

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HIGHLIGHTS

- Performances of dense and porous Cu-Mn spinel coatings were compared in cell tests.
- Cr-poisoning occurs in open-circuit condition as well as under resistive load.
- Cr species diffuse into cathode via both gaseous and solid-state pathways.
- Porous Cu-Mn coating shows limited Cr gettering capacity and lifetime.
- Dense Cu-Mn coating shows distinct improvement in mitigating Cr-poisoning effects.

ARTICLE INFO

Keywords:
Solid oxide fuel cells
Cathode
Chromium poisoning
Copper manganese spinel coatings
Interconnects
Degradation

ABSTRACT

Chromium poisoning is one of the major reasons for cathode performance degradation in solid oxide fuel cells (SOFCs). To mitigate the effect of Cr-poisoning, a protective coating on the surface of interconnect for suppressing Cr vaporization is necessary. Among the various coating materials, Cu-Mn spinel coating is considered to be a potential candidate due to their good thermal compatibility, high stability and good electronic conductivity at high temperature. In this study, Crofer 22 H meshes with no protective coating, those with commercial $CuMn_2O_4$ spinel coating and the ones with lab-developed $CuMn_{1.8}O_4$ spinel coating were investigated. The lab-developed $CuMn_{1.8}O_4$ spinel coating were deposited on Crofer 22 H mesh by electrophoretic deposition and densified by a reduction and re-oxidation process. With these different Crofer 22 H meshes (bare, $CuMn_2O_4$-coated, and $CuMn_{1.8}O_4$-coated), anode-supported SOFCs with Sr-doped $LaMnO_3$-based cathode were electrochemically tested at 800 °C for total durations of up to 288 h. Comparing the mitigating effects of the two types of Cu-Mn spinel coatings on Cr-poisoning, it was found that the performance of the denser lab-developed $CuMn_{1.8}O_4$ spinel coating was distinctly better, showing no degradation in the cell electrochemical performance and significantly less Cr deposition near the cathode/electrolyte interface after the test.

1. Introduction

Lowering the operating temperature of solid oxide fuel cells to the intermediate range of 650–800 °C can not only improve the reliability and stability of SOFCs, but also enable the use of metallic alloys in interconnects and balance-of-plant (BoP) materials [1–5]. Compared with ceramic interconnects, metallic interconnects have higher electronic conductivity, higher thermal conductivity, better machinability and lower cost [1,4,6–8]. The most widely developed and studied metallic interconnect materials are the chromia-forming alloys due to their high thermal compatibility with other SOFC components, high oxidation resistance at high temperature, and the conductive chromium (Cr) containing oxide scale that forms on the alloy surface [3,4,7,8]. However, on the cathode side (oxidation environment), Cr-containing oxide scale can react with oxygen/moisture and form higher valent Cr-containing vapor species (e.g. CrO_3 and $CrO_2(OH)_2$) [9–13]. These Cr-containing vapor species can transport and deposit in the cathode and deteriorate its performance [1,2,14–24]. This degradation phenomenon, namely ‘Cr-poisoning’, is one of the major reasons for the performance degradation in the SOFC stacks.

To mitigate the Cr-poisoning effect, decreasing the amount of Cr-containing vapor species over interconnect becomes an obvious solution. Fe-Cr-Mn alloys such as Crofer 22 APU [25] and Crofer 22 H [26] (ThyssenKrupp VDM), Sanergy HT (Sandvik Materials Technology)

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https://doi.org/10.1016/j.jpowsour.2017.11.069
Received 2 October 2017; Received in revised form 21 November 2017; Accepted 22 November 2017

0378-7753/

[27] and ZMG 232 (Hitachi Metals) [28] have been widely developed for SOFC interconnect application. Due to the small amounts (0.3–0.5 wt%) of Manganese in the Fe-Cr alloys, these steels develop a well adherent $(Cr,Mn)_3O_4$ spinel top layer above the Cr_2O_3 layer at 800 and 850 °C, and Cr evaporation rate over them is 2–3 times slower than that over alloys with pure Cr_2O_3 scales such as Ducrolloy (Plansee), or with a noncontinuous $(Cr,Mn)_3O_4$ top layer such as E-brite (ATI Allegheny Ludlum) [29–32].

Although $(Cr,Mn)_3O_4$ top layer formed over the Fe-Cr-Mn alloys can effectively decrease the Cr evaporation rate, it has been shown that performance degradation caused by Cr-poisoning is still considerable when using these alloys as interconnect materials [13,20,21,23,33]. Thus, in order to mitigate the stack performance degradation, long-term stable protective coatings over the interconnect for minimizing the Cr vaporization are indispensable. Over the past 10 years, extensive efforts were made in the development of protective coatings for metallic interconnects [7,8]. Among various coating materials, composite spinel oxides appear to be the most promising candidate, due to their high conductivities and good capabilities in retarding oxidation of metallic interconnect and suppressing vaporization of chromium [8]. While $(Mn,Co)_3O_4$ spinels are the most studied to date [33–40], Cu-Mn spinels that have higher electronic conductivities and lower cost are recently receiving more attention [41–47].

In this paper, mitigation of Cr-poisoning employing a candidate $CuMn_{1.8}O_4$ spinel interconnect coating is demonstrated. $CuMn_{1.8}O_4$ spinel coating is deposited on Crofer 22 H mesh by electrophoretic deposition (EPD) and densified by a reduction and re-oxidation process. To evaluate the performance of the $CuMn_{1.8}O_4$ spinel coating, the spinel-coated Crofer 22 H mesh is employed in the electrochemical testing of anode-supported cell (ASC). To simulate the interconnect in the stack, the mesh is placed in direct contact with the SOFC cathode. For comparison, Crofer 22 H mesh with no protective coating and that with commercial $CuMn_2O_4$ spinel coating are also investigated. In addition to the electrochemical tests, microstructures of the different Crofer 22 H meshes and the corresponding cell cathodes are characterized and compared. The performances of two types of Cu-Mn spinel interconnect coatings, $CuMn_2O_4$ (commercial) and $CuMn_{1.8}O_4$ (lab-developed), in mitigating Cr-poisoning are evaluated, and the effect of coating density on degradation phenomena are discussed.

2. Experimental

2.1. Electrophoretic deposition (EPD) of $CuMn_{1.8}O_4$ spinel coating

A commerical ferritic stainless steel, Crofer 22 H with composition of 22.93 wt% Cr, 1.94 wt% W, 0.51 wt% Nb, 0.43 wt% Mn, 0.21 wt% Si, 0.07 wt% Ti, 0.02 wt% Al, 0.08 wt% La, 0.10 wt% Si, 0.07 wt% C, 0.015 wt% N and the balance in Fe, was used as the interconnect material in this study [26]. Crofer 22 H meshes with no coating and those with $CuMn_2O_4$ spinel coating were commercially available from Fiaxell SOFC Technologies (Switzerland) [48]. According to technical specifications, the $CuMn_2O_4$ coated mesh was sintered in air at 850 °C for 3 h. The meshes have opening of about 0.6 × 0.9 mm and thickness of 0.2 mm.

The uncoated Crofer 22 H meshes were used as the substrates for deposition of the $CuMn_{1.8}O_4$ spinel coating by the electrophoretic deposition (EPD) process in our laboratory (the substrates were ultrasonically cleaned in the mixture of acetone and ethanol prior to coating deposition). Powders of $CuMn_{1.8}O_4$ used for coating were synthesized by the glycine nitrate process (GNP). Propotional amounts of manganese nitrate ($Mn(NO_3)_2{\cdot}4H_2O$, Alfa Aesar, USA), copper nitrate ($Cu(NO_3)_2{\cdot}2.5H_2O$, Alfa Aesar, USA) and glycine (CH_2NH_2COOH, Alfa Aesar, USA) were dissolved in deionized water, stirred for 10 min, and heated on a hot plate at 100 °C for 25 min for evaporating the excess water. The temperature of the precursor was then raised until the auto-combustion occurred. After the combustion reaction was completed, the powders were calcined at 800 °C for 2 h to remove any unreacted reactants.

The synthesized spinel powders were ball-milled in ethanol for 4 h with 0.3 mm zirconia balls (Tosoh. Corp, Japan) to reduce the particle size. The $CuMn_{1.8}O_4$ powders were then mixed with desired amounts of acetone, ethanol and iodine, and the mixture was used as suspension media for the EPD. The EPD was performed for 10 min at a constant voltage of 20 V. Due to the irregular shape of the meshes, instead of conventional uniaxial compaction, the as-deposited coating was densified by subjecting the samples to a thermal treatment process: reduction at 1000 °C for 24 h in forming gas (2% H_2 + 98% Ar) and then annealing in air at 850 °C for 100 h.

2.2. SOFC fabrication

The cells used in this study were comprised of 5 layers: a Ni/8YSZ (8 mol% Y_2O_3–92 mol% ZrO_2) anode substrate, a Ni/8YSZ anode interlayer, an 8YSZ electrolyte, a LSM (Sr-doped $LaMnO_3$)/8YSZ composite cathode active layer, and a LSM current collector layer. As-sintered cell structures consisting of two anode layers and electrolyte were commercially purchased (Materials and Systems Research Inc., USA). Cathode active layer and cathode current collector layer were screen printed over the electrolyte. Slurry for the composite cathode active layer were prepared by mixing $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3\text{-}\delta}$ (Fuel Cell Materials, USA) and 8YSZ (Tosoh Corp., Japan) powders in a 1:1 wt ratio and ball milling the mixture for 10 h in alpha-terpineol (Alfa Aesar, USA) with the desired amount of pore former (Carbon lampblack, Fisher Scientific, USA) and binder (V6, Heraeus, USA). For preparation of slurry for the cathode current collector layer, LSM powders were ball milled for 24 h in alpha-terpineol with desired amount of pore former (Carbon black, Fisher Scientific, USA) and binder (V6, Heraeus, USA). After screen printing of each cathode layer, the structure was sintered at 1200 °C for 2 h. After the fabrication was completed, the thickness of cathode active layer and the cathode current collector layer were approximately 30 µm and 50 µm, respectively and the active cathode area was 2 cm^2.

2.3. On-cell tests employing interconnect meshes

On identical cells, Crofer 22 H meshes (a) with no protective coating, (b) with commercial $CuMn_2O_4$ coating, and (c) with lab-developed $CuMn_{1.8}O_4$ coating, were used individually as current collectors on the cathode side for electrochemical cell testing. Prior to the cell assembly, the Crofer 22 H mesh (bare/$CuMn_2O_4$ coated/$CuMn_{1.8}O_4$ coated) was cut into round pieces having the same area as the SOFC cathode (~2 cm^2), and was attached on the cathode with a LSM paste. A nickel mesh was also pre-attached on the anode with nickel paste (Fuel Cell Materials, USA). Fig. 1 shows the schematic of the cell structure and interconnect mesh during the cell testing. In the fixture for cell testing, a single cell was sandwiched between two alumina tubes. A gold gasket on the cathode side and a mica gasket on the anode side were used for sealing purpose. In addition, glass paste (Fuel Cell Store, USA) was applied outside the tube circumference to ensure gas tightness. Two silver wires on the cathode side and two nickel rods on the anode side were firmly pressed on the Crofer 22 H mesh and nickel mesh respectively, to ensure good contacts. On each side, one wire/rod was used for current application, and the other for voltage measurement. More details of the cell testing fixture have been previously published [23].

The cells were electrochemically tested at 800 °C. On the anode side, humidified hydrogen with 2% H_2O (obtained by passing hydrogen through a water bubbler at ~ 18 °C) was circulated at 300 cm^3/min, providing fuel under flooded condition and low fuel utilization. On the cathode side, dry air was used over at 1000 cm^3/min (with gas velocity of approximately 4.8 m/s at 800 °C), which also provided a flooded condition with negligible fractional oxidant utilization. The cell testing