Journal of Power Sources 353 (2017) 195–201

Contents lists available at ScienceDirect

Journal of Power Sources

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

Oxidation behavior of metallic interconnect in solid oxide fuel cell stack

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HIGHLIGHTS

- The growth of the oxide scale thickness is influenced by electric current.
- The oxidation rates vary greatly depending on its local environment.
- The value of ASR depends on the composition and thickness of oxide layer.

ARTICLE INFO

Article history:
Received 28 December 2016
Received in revised form
2 March 2017
Accepted 21 March 2017

Keywords:
Solid oxide fuel cell
Metallic interconnect
Current effect
Dual atmosphere
Stack

ABSTRACT

Oxidation behavior of integrated interconnect with bipolar plate and corrugated sheet made by ferrite steel SUS430 is investigated and compared in simulated environment and in a realistic stack. Electrical current is found to have a direction-related impact on the thickness of the $Cr_2O_3/MnCr_2O_4$ composite oxide scale. Oxide scale of the interconnect aged in the stack exhibits a dual-layered structure of a complex Mn-Cr oxide layer covered by iron oxide. The oxidation rates vary greatly depending on its local environment, with different thermal, electrical density, as well as gas composition conditions. By analyzing the thickness distribution of oxide scale and comparing them with the simulated test result, the oxidation behavior of interconnect in stack is described in high definition. ASR distribution is also conducted by calculation, which could help further understanding the behavior of stack degradation.

1. Introduction

Solid oxide fuel cell (SOFC) is considered to be an electricity-generation device that efficiently and environmental friendly converts the chemical energy into power and heat. Usually, cells are assembled into a stack to meet voltage and power requirement. For a planar stack, interconnect is an important component, which separates air and fuel and provides electrical contact and mechanical stabilization [1]. In recent years, traditional ceramic interconnects are replaced by metallic interconnects due to the reduction in SOFC operating temperatures to intermediate temperature (600–800 °C) [2–4]. Although, there can be found numerous experimental and theoretical studies in the literature about the oxidation behavior of metallic interconnects under simulation conditions [5–8], little has been done to reveal the metallic interconnects ageing in a real stack.

Being exposed in a dual atmosphere of an oxidative atmosphere (air) on one side while reductive atmosphere (fuel) on the other side is a challenge for metallic interconnects. The oxidation behavior of stainless steels under dual atmosphere condition totally differed from that under single atmosphere. Anomalous oxidation on the air side of AISI430 has been observed by Yang's team [9], they have found Fe_2O_3 nodules formed on the top of $MnCr_2O_4$/Cr_2O_3 layer only when the interconnect exposed in dual atmosphere and this phenomena was related to the rapid kinetics of hydrogen transport through the bulk alloy from the fuel side to the air side. And the hydrogen appeared to accelerate the iron transport in the oxide scale and eventually led to the formation of iron oxide nodules [10]. Zhao et al. investigated the effects of flow rate and humidity on the oxidation behavior of 430 alloys in dual atmospheres at 800 °C and found that the high hydrogen flow rate leaded to localized Fe-rich nodules [11]. Gannon et al. [12] also

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http://dx.doi.org/10.1016/j.jpowsour.2017.03.092
0378-7753/© 2017 Published by Elsevier B.V.

found the same phenomenon. Ageing at 800 °C and 300 h in dual atmosphere, Fe_2O_3 nodules were observed on FSS430 surface, while porous Fe_2O_3 layer was founded on FSS441 surface. The formation of Fe_2O_3 nodules on the alloys surface would break the continuum of Cr_2O_3 layer, causing severe oxidation [13,14]. And the electrical conductivity of Fe_2O_3 is poor [15], leading to the high resistance in SOFC stack and causing energy loss.

Besides, electrical current is an important factor that affects oxidation behavior of metallic interconnects. In an operating SOFC stack, electric current flow through interconnects from air side to fuel side. Liu et al. [16] reported that the oxide scale formed on the negative side was thicker than that formed on the positive side. This phenomenon was described as the consequence of accelerated outward diffusion of metal ions by the electrical field. And similar phenomenon was reported by Kawamura et al. [17], they founded that the oxide scale of Fe-25Cr at negative side is thicker than that without current flowing through.

Furthermore, the formation of oxide scale is influenced by a combination of dual-atmosphere effect and electric current effect. In a real stack, the oxidation behavior of alloys would be more complicated. Gas flow rate and temperature distribution could also affect the oxidation behavior of interconnects. Shong et al. [18] invested the cathode side oxidation behavior of nickel coated interconnect in a single-cell stack, and founded that oxide scale consisted of NiO, Fe_2O_3, and $(Fe,Ni,Cr)_3O_4$. The oxide layer offered an effective barrier to against chromium evaporation. But they didn't analyze the oxidation behavior at fuel side.

In previous study [19], we developed an integrated interconnect made of SUS430 stainless steel for the stack assembly. Bipolar plate separates the oxidation/fuel gases and corrugated sheet is applied as gas distributor and current collector at the cathode side. Therefore, this paper was mainly discussing the oxidation behavior of integrated interconnect in a 5-cells stack. In order to understand the electric current effect on the corrosion behavior of interconnect, contrast experiment (with and without electric current) were performed at 750 °C for 250 h.

2. Experimental

The oxidation behavior of interconnect with electric current flowing through was firstly investigated under simulating condition and compared with control group without current applied. Fig. S1 shows the photo of bipolar plate and corrugated sheet. The bipolar plate separates gases and corrugated sheet collects current from the surface of the SOFC cathode. Ferritic stainless steel SUS430, containing 16.76 wt% Cr, 0.69 wt% Mn, 0.75 wt% Si and 0.12 wt% C was used to fabricate both the plate and corrugated sheet. Bipolar plate and corrugated sheet were connected together by spot welding, and the whole unit was called integrated interconnect. Integrated interconnect was cut into 10 × 10 mm^2 coupons and total thickness was 1.9 mm (including 1 mm bipolar plate and 0.9 mm corrugated sheet). The coupons were polished with SiC abrasive papers up to #1200 grit and cleaned with ultrasonic in ethyl alcohol. It was then exposed at 750 °C in an ambient atmosphere furnace for 250 h with a current density of 0.5 A cm^{-2} to investigate the oxidation behavior. Electric current flowed from corrugated sheet to bipolar plate, simulating the actual condition in SOFC stack. For comparison, the current-free isothermal oxidation was also conducted at 750 °C in air for 250 h.

The oxidation behavior of interconnect in a 5-cell stack was then analyzed. Schematic diagram of the repeat unit with integrated interconnect in the SOFC stack is shown in Fig. S2. The cells used in this study were YSZ-NiO anode supported planar SOFC with squared shape. The details of cells fabrication can be found in our published paper [20]. The size of cells was 10 × 10 cm^2 and cathode active area was 8 × 8 cm^2. Integrated interconnect had the same size with cells. Air and fuel were cross-flow in this stack, as showed in Fig. S2. Air and hydrogen flowed rates were both 10 L/min. The stack operated at 750 °C for 250 h with a current density of 0.5 A cm^{-2}, followed by 5 thermal cycles.

Samples were taken at different places of interest as shown in Fig. 1. The thickness of oxide scale was measured at 6 typical spots in the cross-sectional marked *a~f* (Fig. 1a). Under the simulating conditions, electric current didn't flow through spot b, c and d, so we only focus on spot f. In the case of oxidation in 5-cells stack, the oxidation behavior of spots was affected not only by electric current but also dual-atmosphere effect, we analyzed the oxidation behavior at each spot. The 10 × 10 mm^2 coupons from the stack were taken from 4 typical regions on the interconnect and marked AOFI, AOFO, AIFI and AIFO, which represent four corners between Air In, Air Out, Fuel In and Fuel Out respectively, as shown in Fig. 1b. And they were used for ASR test and cross-sectional microstructure scanning.

The area specific resistance (ASR) reflects the electrical resistance of metallic interconnects. Four-probe DC technique was used to measure the ASR of integrated interconnect, schematically illustrated in Fig. S3. Interconnects with a dimension of 10 × 10 mm^2 were heated to 750 °C in nitrogen atmosphere for ASR test. The crystal structure of all phases was characterized by a PANalytical X'Pert PRO X-ray diffractometer (XRD) with Cu Kα radiation. Integrated interconnect cross-sectional morphology was revealed by an FEI Quanta 200 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) instrument.

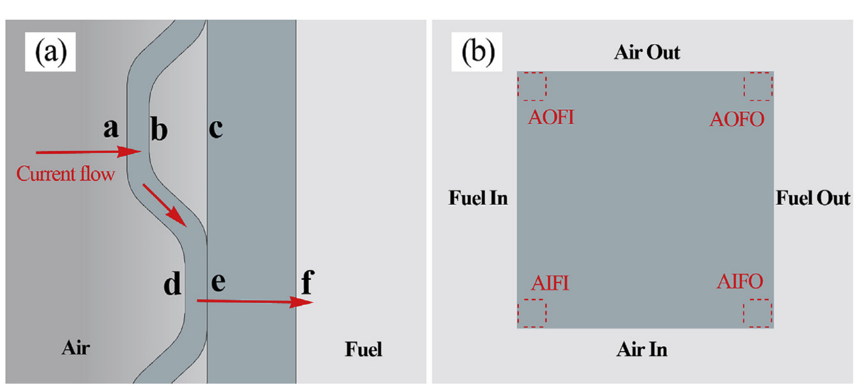

Fig. 1. Schematic representation of the cross-section view (a) and top view (b) of the integrated interconnect. Six typical cross-sectional spots were investigated marked as *a~f* in Fig. 1a. Four different samples were taken from corners between Air In, Air Out, Fuel In and Fuel Out and marked as AOFI, AOFO, AIFI and AIFO respectively in Fig. 1b.