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Study on component interface evolution of a solid oxide fuel cell stack after long term operation

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HIGHLIGHTS

- The short stack ran for 4400 h with 1.5%/1000 h degradation and thermal cycles.
- Contact material and interconnect oxidant formed a dense layer.
- Oxidation on air side of bipolar plate contributes more oxidant thickness.

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ABSTRACT

A 5-cell solid oxide fuel cell (SOFC) stack with external manifold structure is assembled and underwent a durability test with an output of 250 W for nearly 4400 h when current density and operating temperature are 355 mA/cm^2 and 750 °C. Cells used in the stack are anode-supported cells (ASC) with yttria-stabilized zirconia (YSZ) electrolytes, Ni/YSZ hydrogen electrodes, and YSZ based composite cathode. The dimension of the cell is 150 × 150 mm (active area: 130 × 130 mm). Ceramic-glass sealant is used in the stack to keep the gas tightness between cells, interconnects and manifolds. Pure hydrogen and dry air are used as fuel and oxidant respectively. The stack has a maximum output of 340 W at 562 mA/cm^2 current density at 750 °C. The stack shows a degradation of 1.5% per 1000 h during the test with 2 thermal cycles to room temperature. After the test, the stack was dissembled and examined. The relationship between microstructure changes of interfaces and degradation in the stack are discussed. The microstructure evolution of interfaces between electrode, contact material and current collector are unveiled and their relationship with the degradation is discussed.

1. Introduction

Combining with high energy conversion efficiency, fuel flexibility, and low emission, solid oxide fuel cell (SOFC) is considered a promising next-generation power source [1]. Meanwhile, plenty of work has focused on the R&D of electrode and electrolyte materials and structures [2–6], which greatly improves the performance of SOFC. While, for commercialization of SOFC, durability is one of the superior considerations for developers, especially when the cells, sealant and interconnect are stacked together. An increase of the area specific resistance (ASR) of the cells [7], chromium poising of the cathode [8], oxidation of metallic interconnect [9], failure of sealant [10], as well as an increase of contact resistance between contact material and interconnect [11,12] will influence the long-term stability of the stack.

A world record operation time of 10 years on a 2-cell stack was reported by Forschungzentrum Jülich [13]. PLANSEE SE etc. have developed a robust and versatile stack structure which showed a degradation rate of 0.4%/10 system cycles approaching a total number of 90 cycles [14]. Osaka Gas has conducted a large number of long-term tests for stack, material, and SOFC generation units in order to establish 10 years lifetime, and has promoted the product commercialization for residential SOFC in Japan from the 2011 year [15]. Some other commercial companies, such as FuelCell Energy, Bloom Energy are aimed at large stationary power station for industrial needs [16,17].

Here, we are committed to developing an SOFC stack with the external manifold. The stack is composed of simple designed interconnects, anode-supported cells, external manifolds. Computer simulation has been used to analyze the gas and stress distribution in stack. The feasibility of the structure has been verified in previous work [18]. The typical anode-supported cell with a dimension of 100 × 100 mm (active reaction area of 90 × 90 mm) has an open circuit voltage (OCV) of 1.15 V and power density of 770 mW/cm^2 at a current density of

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950 mA/cm^2 at 750 °C [19]. A 1-cell stack has been tested for about 4000 h when temperature and current density were 750 °C and 370 mA/cm^2 and showed a degradation of 1.7%/1000 h. Also, a 10-cell stack was assembled and tested for 700 h. While the average degradation rate was 17.6%/1000 h at 750 °C and 370 mA/cm^2. Except for the oxidation of interconnect, the decomposition of cathode contact material caused by leaking contribute most of the stack degradation [20]. A layer of the cathode contact materials $LaCo_{0.6}Ni_{0.4}O_{3-\delta}$ (LCN) with novel structure was tested on a 1-cell stack, and the average degradation rate is 0.4% per thermal cycle from 200 °C to 750 °C [21]. The dimension of cells used above is 110 × 110 mm (active area: 90 × 90 mm).

To improve the stability of the stack and obtain a higher output, the dimension of cells was enlarged to 150 × 150 mm (active area: 130 × 130 mm), and the novel structure layer of cathode contact material was adopted. An improved 5-cell stack with the external manifold was assemble and underwent a long-term test for 4400 h with a degradation rate of 1.5%/1000 h. Two thermal cycles between 750 °C and room temperature were conducted at different stages which had little influence on the performance of the stack. After the test, the stack was dissembled and microstructurally examined. The relationship between microstructure changes of interfaces and degradation in the stack are emphatically discussed here.

2. Stack designing

The stack consists of core and manifolds, as shown in Fig. 1. The core is composed of five repeat units which include anode-supported cell, seal, interconnect, gas distributor. The dimension and components of the cells are illustrated in Table 1. The seal is composed of two parts: the ceramic tape and ceramic-glass slurry, both of which has the same solid content [22,23]. The slurry is used between cells and tape. The bipolar plate is made of SUS 430 alloy without a protective coating. Corrugated plate made of SUS 430 alloy is used as cathode gas distributor and current collector. Ni foam with an areal density of 1 kg/m^2 is used as anode gas distributor and current collector. The thickness of interconnect, corrugated plate, Ni foam, and the tape has been adjusted to assure the gas-tight of the stack. LCN and Ni paste are used as cathode and anode contact materials separately to keep the contact in the stack. Four manifolds including air-in, air-out, H_2-in, H_2-out manifold are mounted around the core to form a cross-flow structure. Bolts cooperated with ceramic tape are used to keep the gas-tight between manifolds and core. Two SUS 430 alloy plates (top & bottom plate) are used as supporters of the stack. Current and voltage wires are welded onto the supporters. A fixed compression load is applied on the stack by means of the cylinder.

Table 1
Dimension and components of the cells.

	Dimension (mm)	Thickness (μm)	Component
Anode supporter	150 × 150	1.1 × 10^3	Ni/YSZ
Anode functional layer	150 × 150	~5	Ni/YSZ
Electrolyte	150 × 150	~5	YSZ
Cathode	130 × 130	~5	YSZ based composite

3. Experiment

The stack was heated in test bench to 750 °C with a ramping rate of 2 °C/min before 500 °C and 0.83 °C/min after. Dry air and nitrogen with 5 vol% of hydrogen were supplied to anode and cathode manifolds respectively during the heating process. On reaching the operating temperature, pure hydrogen was supplied to anode manifold instead. The flow rate of air and hydrogen were 3 SLM/min and 1.67 SLM/min. After the anode was reduced completely, the voltage and power output as functions of current were tested. During the long-term test, the current density was set at 355 mA/cm^2. When the test came to 1000 h, the air supply system met a problem, so we reduced the flow rate of air and hydrogen, as well as the discharge current for 200 h. During the whole test, two thermal cycles between 750 °C and atmosphere temperature were conducted. Due to device faults and electricity interruption, the stack suffered frequent thermal shocks and re-discharges. The test was ended after the 4400 h test.

After the test, the stack was dissembled for post-test analysis. The macroscopic morphology of every interface was taken by optical equipment. The samples including cell, seals and metallic interconnect were characterized by field emission scanning electron microscopy (FE-SEM, FEI Sirion 200) with energy dispersive spectroscopy (EDS) attachment; surface oxide morphology, oxide thickness, and composition of the samples were analyzed using this method. The samples for the cross-section examination were mounted in Buhler epoxide and polished with a Buhler automatic polisher. An X-ray diffractometer (PANalytical X'Pert PRO) was used to identify the phases in the LCN powders under the conditions of 40 mA and 40 kV.

4. Result and discussion

Fig. 2 (a) shows the *i*-v and *i*-P curve of the stack. In the initial test,

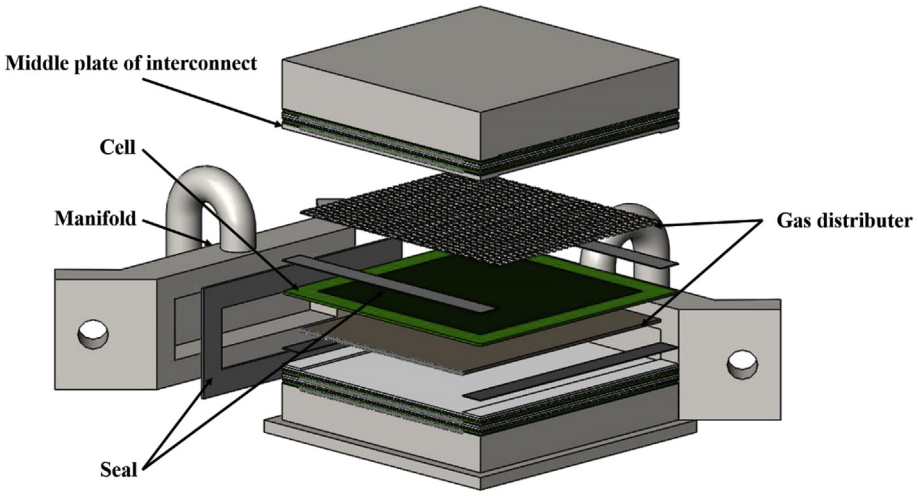

Fig. 1. Schematic diagram of SOFC stack with external manifold structure.