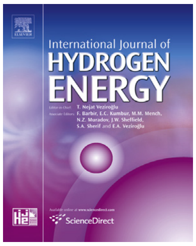
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 6036–6044

Available online at www.sciencedirect.com

ScienceDirect

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



Development of flexible ceramic-glass seals for intermediate temperature planar solid oxide fuel cell

Wei Zhang, Xiaopeng Wang, Yan Dong, JiaJun Yang, Jian Pu*, Bo Chi, Li Jian

School of Materials Science and Engineering, State Key Laboratory of Material Processing and Die &Mould Technology, Huazhong University of Science & Technology, Wuhan, Hubei 430074, PR China

A R T I C L E I N F O

Article history:
Received 2 December 2015
Received in revised form
22 February 2016
Accepted 22 February 2016
Available online 16 March 2016

Keywords:
Solid oxide fuel cell
Ceramic-glass seal
Leakage rates
Thermal cycle stability
Deformability

A B S T R A C T

The ceramic-glass was employed as the most commonly used seal materials in planar solid oxide fuel cell (SOFC). In this study, a novel glass with relative low glass soft temperature was added into Al_2O_3 powders to form ceramic-glass composite seals by tape casting technique. Based on the tested result of gas tightness and compressibility, it was found that the seals with 40 wt% glass exhibited excellent seal performance at the leakage rates of only 0.01 $sccm.cm^{-1}$ under gas pressure of 10.2 kPa, and compressive load of 0.17 MPa at 750 °C. The seals showed the desired thermal cycle stability at low leakage rates within 10 thermal cycles. It can be observed that the deformability of seals sharply increase when the glass contents was higher than 30 wt%. Microstructural analysis of the seals also exhibited very good interfaces bondage and chemical compatibility which was in good agreement with gas tightness prediction for the flexible ceramic-glass seals model. The seals have been applied in large size cell test to confirm its applicability in SOFC.

Introduction

Solid oxide fuel cell (SOFC) has been developed during the past decade for a wide range of application including stationary plant and portable power [1]. As one of two different SOFC stack designs, the planar SOFC provides higher energy conversion efficiency and low manufacture cost. However, it was also confronted crucial challenge on the leakage rate and thermal cycle stability under SOFC operation temperature [2–5]. The gas leakage may reduce fuel utilization, which directly results in the damage of SOFC stack. Many researchers have made a lot of efforts to develop sealing materials, which approximately includes compressive and rigid seals [3,6–8]. A principal advantage of compressive seals is to reduce the requirement for matching thermal expansion coefficients (CTE). Considering that the major leakage paths are locating on interface between the seals and cell/interconnect, the compressive seal should be able to achieve reliable sealing effect under extremely high compressive load [9–12]. For example, mica sheets can decrease leakage rates to lower than 0.1 sccm/cm under 0.7 MPa compressive loads [3]. Al_2O_3-based compressive seals also have been developed by tape casting and showed an excellent performance in SOFC application [13].

---

* *Corresponding author*. Tel./fax: +86 27 87558142.
E-mail address: pujian@hust.edu.cn (J. Pu).

http://dx.doi.org/10.1016/j.ijhydene.2016.02.120

Glass-based materials were considered as the most reliable seals because the chemical composition of glass was designed to meet most of seal requirements such as adherence, chemical stability, electrical insulation, and CTE match [5,6,13]. Additionally, a good glass-based seals should have suitable viscosity to maintain the mechanical strength at high temperature [14]. Two approaches have been employed for improving structural strength of seals. One of that is the volume fraction of crystalline phase was obtained from glass matrix such as BaO–CaO–SiO_2, AO–Al_2O_3–SiO_2–B_2O_3 glass system (A = Ba, Ca, Mg) [15]. But the crystallization kinetics of the glass is difficult to be controlled due to high temperature gradation inside of stack. Besides, it is also a problem that the formation of some crystalline phase can generate CTE mismatch. The other is that glass-ceramic seals are prepared by the addition of different oxides into glass powders including Al_2O_3, TiO_2, ZrO_2 to overcome inherent brittleness and crack growth from glass [16]. Recently studies have demonstrated that the leakage rate and thermal cycle stability have been significantly improved by adding glass into compressive seals materials such as mica and Al_2O_3 powders [17–19]. The leakage paths were minimized by infiltrating the voids volume with glass-based powders, and wetting the adjoining interface while ceramic powders provide the framework in sealant structure. It is very important that the glass has appropriate soft temperature and slow crystallization rate to obtain flexible seals at SOFC operation temperature.

In the present work, a special glass was chosen as seals because it has relative low soft temperature and high devitrification resistance after long time operation at 750 °C. The Al_2O_3-glass composite seals have been developed by tape casting technique. The purpose of this study is to lower the seals' leakage, improve the thermal cycle stability, deformability, and chemical compatibility of the sealant by optimizing the proportion of Al_2O_3 and glass.

Experimental

Materials and preparation

A glass was obtained in the form of powder from a commercial vendor (San Le Company, China), with composition: SiO_2: 64.74 mol%, Al_2O_3: 3.4 mol%, TiO_2: 6.66 mol%, K_2O_3: 9.8 mol%, Na_2O: 11.45 mol%, MnO: 3.95 mol%. This glass powder named as DT4 has an average particle size of 1–2 μm. Fig. 1 showed the micrographs of the glass and Al_2O_3 powder (average size 1–5 μm, Almatis, USA). The DT4 glass has soft temperature of 620 °C and CTE of 9.2×10^{-6}/k from room temperature to 300 °C. The Al_2O_3-glass seals were prepared by tape casting with different proportion of glass and Al_2O_3 mixture. The weight ratio of Al_2O_3 and glass was 50:50, 60:40, 70:30, 80:20, 90:10 which was named as AD50, AD40, AD30, AD20, AD10 respectively. The Al_2O_3-glass tapes with thickness of 0.3 mm were fabricated after drying at room temperature. Square window-frame with an outside dimension of 70 × 70 mm and inside 50 × 50 mm were cut from the seal tapes for leakage rates test.

Leakage rates measurement

Fig. 2 showed the graph of thermogravimetric analysis in air for AD40 and AD30 seals from room temperature to 800 °C with heating rate of 10 °C/min, which was carried out in the thermal analysis system (STA449F3, Retsch Inc, Germany). It can be seen that the mass of sample was gradually decreased from 200 to 450 °C, originating from some organic additives volatilized from the seals tape. The temperature program for leakage rates test was set as shown in Fig. 3 according to thermal analysis result. The heating rate was 2 °C/min, from room temperature to 200 °C, and dwelled at 200 °C for 90 min, then 1 °C/min from 200 °C to 450 °C, and also dwelled 90 min at 450 °C, followed by further heating at 2 °C/min up to testing temperature of 750 °C for 120 min. In order to evaluate the thermal cycle stability of seals, the sample was cooled to 300 °C to initiate thermal cycling, then rapidly heated from 300 to 750 °C with heating rate of 2 °C/min, dwelled at 750 °C for 120 min. The leak rates testing system used for seals as shown in Fig. 4, and the principle has been described in Ref. [20]. A precise flow meter with an accuracy of 0.001 $sccm.cm^{-1}$ was chosen to measure the leakage rates with N_2 as testing gas. The leakage rates were tested under different compressive load and input gas pressure.

Microstructural characterization

The samples were obtained from the tested seals for the observation of its surface morphology and cross section. The samples for the cross section examination were mounted in a Buhler epoxide and polished on a Buhler automatic polisher. A Quanta 200 scanning electron microscope (SEM) with energy disperse spectroscopy (EDS) attachment was used for the microstructural characterization of tested seals. The interconnect alloy (SUS 430) and cell anode (NiO + YSZ) were chosen as adjacent components to examine the joint interface and chemical compatibility of seal which was performed under compressive load of 0.17 MPa at 750 °C for 100 h. The crystalline phase of the Al_2O_3-glass seals was identified by X-ray diffraction (X'Pert PRO, PAN alytical B.V.) after dwelled 750 °C for 50 h. The relationship between deformability of the Al_2O_3-glass seals and the weight fraction of glass was determined at 750 °C under compressive load of 0.17 MPa, 0.27 MPa, 0.54 MPa using a cylindrical rod configuration (diameter of 25 × 10 mm). Detailed information about test principle and equipment was described in Ref. [18].

Cell performance test

The open circuit voltage (OCV) and performance of cell were tested as detector to investigate the applicability of sealant. The tape casting – screen printing–sintering processes were used for fabrication of anode supported planar SOFC cells with size of 110 × 110 mm^2, and the active area of cell was 90 × 90 mm^2. The cell was sealed at the periphery on anode and cathode sides by window-frame shaped AD40 seal tape and mica respectively which pure hydrogen and dry air were fed as the fuel and oxidant. The performance and degradation rate of cell were tested at 750 °C, associating with the gas