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

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Abstract

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 $0.01 \text{ sccm.cm}^{-1}$ 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.

Key words: Solid oxide fuel cell, Ceramic-glass seal, Leakage rates, Thermal cycle stability, Deformability

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1. 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].

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 , $\text{AO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ glass system ($\text{A}=\text{Ba, Ca, Mg}$) [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 optimize the proportion of Al_2O_3 and glass.

2.Experimental

2.1. 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 :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 $9.2\times 10^{-6}/\text{k}$ 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.

2.2. 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 N₂ as testing gas. The leakage rates were tested under different compressive load and input gas pressure.

2.3. 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 Al₂O₃-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].

2.4. 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 mm², and the active area of cell was 90×90 mm². 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 tightness of the sealant. Furthermore, the tested cell configuration was disassembled to examine possible gas leakage paths.

3. Results and discussion

3.1 Design of flexible ceramic-glass seals

The ceramic-glass seals materials have excellent joint properties between metal and ceramic. Differing from regularly glass contained seals, a novel ceramic-glass seal structure was designed to provide lower leakage rates and reasonable deformation ability, as shown in Fig.5. The Al_2O_3 particles were chosen as support framework, and the relative fine glass powders were dispersed among Al_2O_3 particles as packing materials, in which the glass has relative low glass soften temperature (T_s). When the operation temperature is lower than T_s of glass, it is isolated and dispersed among Al_2O_3 particles. Similar with the compressive seals, the gas may be mainly leaked from the interface of seals [20-22]. With the temperature elevated to higher than T_s of glass, the initial low viscosity of the glass particle provides good fluidity to pores among Al_2O_3 particles, in which the Al_2O_3 particles is connected each other by the soften glass, so the inside pores of seals become much less. When the SOFC operation

temperature is reached, a glass can be wetted and bonded to generate well sealing interface, and eliminate the leakage paths of gas. Furthermore, the flexible seals can reduce the thermal stress, and improve long term thermal cycle stability.

3.2 Leakage rate and deformability of composite seals

The composite seals with different DT4 glass content were tested for leakage rates of gas under compressive load of 0.17 MPa at 750 °C. Different gas pressure requirement are desired for real stack operation to enhance the reliability of seals, thus the input gas pressure was increased from 3.4 kPa to 20.4 kPa. The results of the measured leakage rate were shown in Fig.6. The leakage rates basically remained stable with gas pressure varied from 3.4 kPa to 10.2 kPa which is usual gas pressure on SOFC operation. The initial leakage rate was 0.02 sccm.cm⁻¹ for AD10 seal, about 0.02 sccm.cm⁻¹ lower than the SECA standard with leakage rate of 0.04 sccm.cm⁻¹. When the glass content of seals reached to 30 wt% (AD30 seal), the leakage rates was gradually dropped to 0.01 sccm.cm⁻¹. Similar results were also observed on AD40 and AD50 seal. It is noted that improvement of gas tightness may have a limit with glass content increase in composite seals. Moreover, when the gas pressure was varied from 10.2 kPa to 21 kPa, the leakage rates were rapidly increased to higher than 0.04 sccm.cm⁻¹ for AD10, AD20 and AD30 seals. But different behavior in that the leakage rates maintained slowly increase, lowering than 0.02 sccm.cm⁻¹ for AD40 and AD50 seals. It is obvious that the presence of DT4 glass can enhance the gas tightness of Al₂O₃-glass composite seals in which the glass may eliminate some leakage paths by blocking pores and wet interface when tested temperature was higher than the T_s of the glass. The leakage characteristic of ceramic-glass seal can be described according to the model conducted by Fig.5.

Considering the fact that compressive load of the seals has effectively influence on gas tightness, the different compressive load was applied on the AD40 seals to measure the leakage rates at 750 °C, as shown in Fig.7. With the compressive load increased from 0.17 MPa to 0.54 MPa, the leakage rates were decreased from 0.01 sccm.cm⁻¹ to 0.005 sccm.cm⁻¹ with gas pressure of 10.2 kPa. The results illustrates

that the ceramic-glass seals present well interface combination with adjacent components under higher compressive load which has been proved on mica-based and Al_2O_3 -based compressive seals[23-25]. Because of the limitation from compressive strength of cell, the compressive load should be chosen on suitable range for seal.

Fig.8 is the microstructure of fracture surface for four seals under compressive load of 0.17 MPa after 750 °C heating treatment. It was concluded that DT4 glass becomes more soft and flowable at 750 °C, since its T_s temperature of this glass is around 620 °C. Based on the microstructural analysis, it could be seen that the seal was gradually densified with the glass content increased from 10 wt% to 50 wt%, flowable glass calked pores among Al_2O_3 particles. When the glass content was lower than 30 wt% in composite seals, the volume of glass was not enough to fill full of pores, thus the gas may be leaked from network of Al_2O_3 particles or interface. However, the microstructure of AD40 and AD50 have little difference and it was hardly observed on open pores in AD40 and AD50 seals, which is corresponded to good gas tightness. The proportion of glass and Al_2O_3 particles should be optimized to avoid excessive glass fluidity at high temperature, owing to low soft temperature of the glass. X-ray diffraction of five seals heat treated at 750 °C for 50 h are shown in Fig.9. It can be detected small amount of crystal phase Al_2SiO_5 and KAlSi_3O_8 belonging to rhombic crystalline system were appeared, besides Al_2O_3 phase in composite seals. Because the amount of crystalline phase originating from glass is little, the glass can keep relatively thermal stability under the high devitrification resistance, when operated at 750 °C. Generally, the kinetic of crystallization in glass should be suppressed because the crystalline phases may bring some problems such as thermal stability and CTE mismatch. The effect of crystalline phase on glass based seals has been discussed in some literatures [26-29]. As the result of phase identification and micrograph, the AD40 seal was considered as a suitable candidate for SOFC application.

It is desirable for seals to remain deformability under high temperature which can decrease the contact resistance between current collector and electrode of cell.

Fig.10 showed the deformation of different seals after heat treated for 2 h at 750 °C

under different compressive load of 0.17 MPa, 0.27 MPa, 0.54 MPa. When 30 wt% glass added into Al_2O_3 , the deformability of sample was obviously improved owing to the reduction of its high temperature viscosity. When the compressive pressure is overlarge, the glass would expand so the stress can't be calculated and compared especially the glass content is too much, so deformation for AD50 under compressive load of 0.27 MPa, 0.54 MPa at 750 °C is not provided. The soft glass can properly connect of adjacent components and release the thermal stress originating from CTE mismatch. This similar experimental result was also described on other ceramic-glass composite seals [18, 19]. It is noted that the seals showed similar deformability with compressive load increased from 0.17 MPa to 0.54 MPa, which imply that the framework of Al_2O_3 play the important role on maintaining deformability of composite seals.

3.3 Thermal cycling and interface characteristic of seals

The optimized composite seals AD40 were also tested for long term thermal cycles under different input gas pressure, and compressive load of 0.17 MPa at 750 °C. The relationship between leakage rates and number of thermal cycles was shown in Figure.11. The initial leakage rate was close to zero under input gas pressure of 3.4 kPa. The leakage rate was slowly increased to $0.005 \text{ sccm.cm}^{-1}$ after 10 thermal cycles. It is known from earlier studies that some micro crack may be produced in sealing interface because the thermal stress can be occurred during thermal cycling. But the leakage rate can be limited at a constant value which has been demonstrated by gas diffusion model [30]. It is important that the leakage rate maintained at relative low value even if the gas pressure was increased to 20.4 kPa for AD40 seals. The seals showed similar thermal cycle stability within 10 thermal cycles, but different behavior in that the initial leakage rate was gradually enlarged with gas pressure increased. However, the leakage rate of the seals was always lower than $0.03 \text{ sccm.cm}^{-1}$, even the gas pressure has reached to 20.4 kPa after 10 thermal cycles. The excellent gas tightness can be attributed to flexible glass interface seal layer which can effectively reduce the stress concentration.

Fig.12 showed the micrographs of AD40 seal interface adjoined with SUS 430

alloy and anode of cell, respectively. It can be observed that no obvious cracks and pore on interfaces or inside of seals. The relative low soften temperature could be considered as a potential reason for this glass. On the other hand, the Al_2O_3 framework can provide enough strength to maintain the shape of seals. Interface bondage also showed good agreement with low leakage rate measurement. Additional investigation was performed to determine the interface chemical compatibility. It is obvious that the seals have no elements diffusion and chemical reaction between the adjacent components by examining EDS line, suggesting that the AD40 seal was chemical stable operated on SOFC temperature. After dwelled 750 °C for 50 h, however, it cannot be observed on new crystalline phases in Fig.9 of seals. It may be explained that the alkali element in DT4 glass increase the difficult of crystallization [23]. Therefore, AD40 composite seal has the potential application at SOFC operation temperature.

The alkaline metals K, Na in DT4 play an important role of network modifiers, which can affect the glass T_g , T_s and CTE. But alkaline metal were reactive with stainless metal alloy including chromium and form much volatile species such as $\text{Na}_2\text{CrO}_4(\text{g})$ and $\text{K}_2\text{CrO}_4(\text{g})$ [6]. The presence of Na or K in sealants was noted to enhance the chromium vaporization from metallic interconnects and chromium ends up in the air electrode and blocks active sites[8]. This paper only discusses the sealing performance and mechanism of the ceramic-glass composite seals, the volatilization and poisoning effect on the stability of SOFCs need further study.

3.4 Investigation of cell performance by using AD40 seals

In order to evaluate the performance of AD40 seals on SOFC, single cell was configured when the seals was used on anode side. The current-voltage characteristics of single cell were measured at 750 °C, as shown in Fig.13. The open circuit voltage (OCV) in the test is 1.14 V which is close to theoretical voltage value of 1.23 V. According to the Nernst equation associating with gas partial pressure and voltage, the measured OCV could be used to estimate the leakage rates[31]. The power density of cell was nearly 0.7 W.cm^{-2} with current density of 1.2 A.cm^{-2} . The high performance of cell implied good interface contact because of high temperature

deformation of the AD40 seals. The gas leakage was main reason resulting to cell performance degradation. The time dependent degradation of cells used AD40 as anode seals was performed with the constant discharge current density of 0.37 A.cm^{-2} , the voltage degradation rate decrease steadily to 15 mV during the initial 50 h, then reaches a stable voltage value of 0.825 V for 50 h, as shown in Fig.14. The initial voltage degradation may mainly originate from thermal stability of interface contact layer, other than interface seal failure. From the results of post test analysis, there are no traces of hydrogen leakage on seal interface. Thus, it can be concluded that the AD40 seals can meet restrictive requirements for SOFC application.

4. Conclusion

An Al_2O_3 based composite seals were fabricated by tape casting technique. The effect of glass content was investigated on leakage rates and deformability. The optimized AD40 seals demonstrated an excellent gas tightness, thermal mechanical property and chemical compatibility, in which the leakage rates of $0.01 \text{ sccm.cm}^{-1}$ can be reached with gas pressure of 10.2 kPa at 750°C . The seals showed high thermal cycle stability after 10 thermal cycles of up to 750°C . Furthermore, with the seals adopted on cell test, it is also confirmed that the large size cell reached to OCV of 1.14 V and power density of 0.7 W.cm^{-2} , maintained stable voltages under current density of 0.37 A cm^{-2} for 50 h.

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Reference

- [1] Minh NQ. Solid oxide fuel cell technology—features and applications. *Solid State Ionics* 2004;174:271-7.
- [2] Singhal SC. Solid oxide fuel cells for stationary, mobile, and military applications. *Solid State Ionics* 2002;152:405–10.

- [3] Simner SP, Stevenson JW. Compressive mica seals for SOFC applications. *Journal of Power Sources* 2001;102:310-6.
- [4] Smeacetto F, Chrysanthou A, Salvo M, Zhang Z, Ferraris M. Performance and testing of glass-ceramic sealant used to join anode-supported-electrolyte to Crofer22APU in planar solid oxide fuel cells. *Journal of Power Sources* 2009;190:402-7.
- [5] Kumar V, Pandey O, Singh K. Thermal and crystallization kinetics of yttrium and lanthanum calcium silicate glass sealants for solid oxide fuel cells. *international journal of hydrogen energy* 2011;36:14971-6.
- [6] Fergus JW. Sealants for solid oxide fuel cells. *J. Power Sources* 2005;147:46-57.
- [7] Liu W, Sun X, Khaleel MA. Predicting Young's modulus of glass/ceramic sealant for solid oxide fuel cell considering the combined effects of aging, micro-voids and self-healing. *Journal of Power Sources* 2008;185:1193-200.
- [8] Lessing PA. A review of sealing technologies applicable to solid oxide electrolysis cells. *Journal of Materials Science* 2007;42:3465-76.
- [9] Punbusayakul N, Boonsiri K, Charojrochkul S, Fungtammasan B, Charoensuk J. Assessment on hermetic property and mechanical compatibility of various groove-gasket sealing designs for solid oxide fuel cell stack. *Journal of Power Sources* 2012;213:186-202.
- [10] Rautanen M, Himanen O, Saarinen V, Kiviaho J. Compression Properties and Leakage Tests of Mica-Based Seals for SOFC Stacks. *Fuel Cells* 2009;9:753-9.
- [11] Le S, Sun K, Zhang N, An M, Zhou D, Zhang J, Li D. Novel compressive seals for solid oxide fuel cells. *Journal of power sources* 2006;161:901-6.
- [12] Litzelman S, Hertz J, Jung W, Tuller H. Opportunities and challenges in materials development for thin film solid oxide fuel cells. *Fuel Cells* 2008;8:294-302.
- [13] Lin C-K, Chen J-Y, Tian J-W, Chiang L-K, Wu S-H. Joint strength of a solid oxide fuel cell glass–ceramic sealant with metallic interconnect. *Journal of Power Sources* 2012;205:307-17.
- [14] Chang H-T, Lin C-K, Liu C-K. High-temperature mechanical properties of a glass sealant for solid oxide fuel cell. *Journal of Power Sources* 2009;189:1093-9.
- [15] Lahl N, Singh K, Singheiser L, Hilpert K, Bahadur D. Crystallisation kinetics in AO-Al₂O₃-SiO₂-B₂O₃ glasses (A= Ba, Ca, Mg). *Journal of Materials Science* 2000;35:3089-96.
- [16] Bram M, Reckers S, Drinovac P, Mönch J, Steinbrech RW, Buchkremer HP, Stöver D. Deformation behavior and leakage tests of alternate sealing materials for SOFC stacks. *Journal of Power Sources* 2004;138:111–9.
- [17] Chou Y-S, Stevenson JW. Mid-term stability of novel mica-based compressive seals for solid oxide fuel cells. *Journal of Power Sources* 2003;115:274-8.
- [18] Wang X, Yan D, Fang D, Luo J, Pu J, Chi B, Jian L. Optimization of Al₂O₃–glass composite seals for planar intermediate-temperature solid oxide fuel cells. *Journal of Power Sources* 2013;226:127-33.
- [19] Ye Y, Yan D, Wang X, Pu J, Chi B, Jian L. Development of novel glass-based composite seals for planar intermediate temperature solid oxide fuel cells. *International Journal of Hydrogen Energy* 2012;37:1710-6.
- [20] Sang S, Li W, Pu J, Jian L. Novel Al₂O₃-based compressive seals for IT-SOFC applications. *Journal of Power Sources* 2008;177:77–82.

- [21] Sang S, Jian P, Jiang S, Li J. Prediction of H₂ leak rate in mica-based seals of planar solid oxide fuel cells. *Journal of Power Sources* 2008;182:141–4.
- [22] Dai Z, Pu J, Yan D, Chi B, Jian L. Thermal cycle stability of Al₂O₃-based compressive seals for planar intermediate temperature solid oxide fuel cells. *International Journal of Hydrogen Energy* 2011;36:3131–7.
- [23] Mahapatra M, Lu K. Glass-based seals for solid oxide fuel and electrolyzer cells—a review. *Materials Science and Engineering: R: Reports* 2010;67:65–85.
- [24] Chou YS, Stevenson JW, Singh P. Thermal cycle stability of a novel glass–mica composite seal for solid oxide fuel cells: Effect of glass volume fraction and stresses. *Journal of Power Sources* 2005;152:168–74.
- [25] Zhang W, Yan D, Duan J, Pu J, Chi B, Li J. Development of Al₂O₃/glass-based multi-layer composite seals for planar intermediate-temperature solid oxide fuel cells. *International Journal of Hydrogen Energy* 2013;38:15371–8.
- [26] Goel A, Pascual MJ, Ferreira JMF. Stable glass-ceramic sealants for solid oxide fuel cells: Influence of Bi₂O₃ doping. *International Journal of Hydrogen Energy* 2010;35:6911–23.
- [27] Reddy AA, Tulyaganov DU, Goel A, Sardo M, Wiper PV, Pascual MJ, Kharton VV, Kolotygin VA, Tsipis EV, Mafra L. Melilite glass–ceramic sealants for solid oxide fuel cells: effects of ZrO₂ additions assessed by microscopy, diffraction and solid-state NMR. *J.mater.chem.a* 2013;1:6471–80.
- [28] Rezazadeh L, Baghshahi S, Golikand AN, Hamnabard Z. Structure, phase formation, and wetting behavior of BaO–SiO₂–B₂O₃ based glass–ceramics as sealants for solid oxide fuel cells. *Ionics* 2014;20:55–64.
- [29] Ghosh S, Sharma AD, Mukhopadhyay AK, Kundu P, Basu RN. Effect of BaO addition on magnesium lanthanum alumino borosilicate-based glass-ceramic sealant for anode-supported solid oxide fuel cell. *International Journal of Hydrogen Energy* 2010;35:272–83.
- [30] Sang S, Jian P, Chi B, Li J. Model-oriented cast ceramic tape seals for planar solid oxide fuel cells. *Journal of Power Sources* 2009;193:723–9.
- [31] Chou YS, Stevenson JW. Long-Term Thermal Cycling of Phlogopite Mica-Based Compressive Seals for Solid Oxide Fuel Cells. *Journal of Power Sources* 2005;140:340–5.

Fig.1. SEM micro morphology of (a) Al_2O_3 powder and (b) DT4 glass used for fabrication of composite tape seals.

Fig.2. Thermogravimetric graph of the tape cast AD40 and AD30 samples.

Fig.3. The heat treatment schedule for leakage rates and thermal cycles test.

Fig.4. The schematic of the leakage rates test system.

Fig.5. The schematic of Al_2O_3 -glass composite seals operated at different temperature.

Fig.6. Leakage rates of the seals under different input gas pressure, compressive load 0.17 MPa at 750 °C.

Fig.7. Leakage rates of the AD 40 seals under different compressive load, input gas pressure from 3.4 to 20.4 Kpa at 750 °C .

Fig.8. Microstructure of fracture surface for seals under compressive load of 0.17 MPa at 750 °C, (a) AD 10, (b) AD 20, (c) AD 30, (d) AD 40,(e) AD 50.

Fig.9. XRD pattern of Al_2O_3 -based seals with different glass content, heat treated at 750 °C for 50h.

Fig.10. Deformation for Al_2O_3 -based seals with different glass content under compressive load of 0.17 MPa at 750 °C.

Fig.11. The relationship between leakage rates and thermal cycles for the AD40 seals, compressive pressure of 0.17 MPa and input gas pressure from 3.4 to 20.4 Kpa at 750°C

Fig.12. Interface micrograph and EDS line scan between seals and interconnect (a,c); interface micrograph and EDS line scan between seals and anode (b,d).

Fig.13. Cell performance used AD40 as anode seals, operated at 750°C.

Fig.14. The performance stability test result of cell under current density of 0.37 A/cm^2 at 750°C.

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