

Glass ceramics seals for solid oxide fuel cells

Montri Suklueng, Peter Hing^{*}, Nyuk Yoong Voo, Chee Ming Lim

Centre for Advanced Materials and Energy Sciences, Applied Physics, Faculty of Science, Universiti Brunei Darussalam,
Jalan Tungku Link, Gadong, BE1410, Brunei Darussalam.

Abstract:

In this paper, several silicate glass ceramics with thermal expansion coefficients ranging from about 5×10^{-6} to $12 \times 10^{-6}/^{\circ}\text{C}$ have been assessed as sealing for SOFCs. Glass ceramics with thermal expansions close to YSZ and GDC₁₀ solid oxide electrolytes were selected for electrical property measurement and development of hermetic seals. Small addition of zirconia up to 0.4 mole % to barium calcium alumina borosilicate glass compositions confers beneficial effect to the development of hermetic seals without covering the surface of the fuel cell element. This has enabled the power density of single fuel cell elements to be evaluated. The thermal expansion and the insulating behaviour of the sealing materials in moist oxidising and reducing environments are presented and discussed in relation to the microstructures evolved.

Keywords: Glass Ceramic, SOFCs, Sealing materials, Electrical Properties

*Corresponding author. Tel.: +673-8656626
E-mail address: Peter.ng@ubd.edu.bn

1. Introduction

For the two chambers planar solid oxide fuel cells, it is important to separate the fuel chamber from the oxidant one to avoid explosion between hydrogen and oxygen. This necessitates the use of sealing materials to effect hermetic seals. In the literature, several types of seals have been developed and evaluated. The use of glass ceramics materials for planar solid oxide fuel cells is, however, the most widely used to date [1-6]. This is because of the wide range of silicate glass ceramics with different thermal coefficients of expansions that can be developed by controlling the nucleation and crystallization of the glasses. Moreover, glass ceramics are cost effective, electrically insulating and can withstand strong oxidising and reducing environment without any adverse effect on the hermeticity of the seals.

2. Experimental

Chemicals from Sigma-Aldrich such as barium oxide, ferric oxide, cobalt oxide and yttrium oxide were used. Conventional ceramic powder fabrication and glass forming are used to process the materials. Some of the compositions studied are shown in Table 1. XRD using Shimadzu 7000 and DTA from Perkin Elmer have been used to identify the phases and the evolution of the glass ceramics. The electrical properties of the sealing materials are evaluated using the set up shown in Fig. 1. First the resistivity of the interconnect materials such as LSCF is first determined. Then the resistivity of the same interconnect is obtained after the ends are embedded in the experimental sealing materials. In this way the insulating nature of the sealing materials can be compared. The thermal expansion of the sealing materials has been studied using TMA from Setaram, France. The sample holder for evaluating the experimental fuel cells is shown in Fig. 2. The best sealing material is chosen to seal hermetically the SOFCs element to the sintered alumina tubes to form two separate chambers for hydrogen and oxidant respectively. The important criteria for choosing the best sealing materials are absence of cracking in the seals, minimal spreading of the barium alumino silicate glasses on the surface of the anode and cathode. The joints must be fully hermetic.

Table 1 Chemical composition of the sealing glass (mol %).

Composition	BCABS	BCABS-1Zr	BCABS-2Zr	BCABS -3Zr
BaO	35.00	35.00	35.00	35.00
CaO	15.00	15.00	15.00	15.00
Al ₂ O ₃	5.00	5.00	5.00	5.00
SiO ₂	37.00	36.60	36.20	35.90
B ₂ O ₃	8.00	8.00	8.00	8.00
ZrO ₂	-	0.40	0.80	1.10

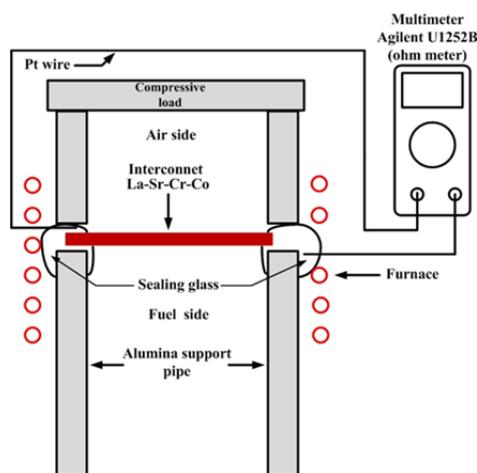


Fig. 1 Set up for the electrical stability testing of sealing materials

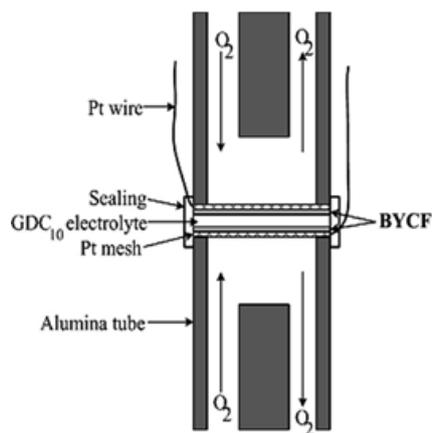


Fig. 2 Two chambers sample holder for SOFC elements

3. Results and Discussions

XRD of some sealing compositions with and without zirconia addition are shown in Fig. 3 and the phases identified are on the right side of the XRD spectrum. The DTA of the glass ceramic composition containing 1 mole zirconia is shown in Fig. 4. The resistivity of the interconnect materials shown in Fig. 5.

The thermal expansion of the glass ceramics developed from the addition of zirconia is particularly useful as it has eliminated the spread of the barium alumino silicate glass phase on the surface of the experimental fuel cell. XRD of the glass sealing compositions show that the glass compositions containing zirconia has formed additional crystalline phases identified as $\text{CaZr}(\text{BO}_3)_2$. The presence of zirconia, moreover, increases the softening temperature of the glasses as seen in the thermal expansion curves in Fig. 6. It is very likely that the presence of the calcium zirconium borate has eliminated or drastically reduced the residual barium alumino silicate glasses from spreading as seen in Fig. 8.

The addition of the zirconia results in a much finer and more uniform distribution of the crystalline phases in the glass ceramics as can be seen in Fig. 7(b). The fine grained glass ceramics is attributed to the formation of large number of crystal nucleus following the addition of zirconia which acts as nucleating agents in the glass compositions, followed by crystal growth. Such type of microstructure improves the refractoriness, enhances the mechanical and chemical stability. This is similar to the use of P_2O_5 for the crystal nucleation and crystallisation of glasses in the barium calcium aluminoborosilicate glasses [7] and lithium disilicate glass ceramics [8].

The glass ceramics are, moreover, free from microcracks and porosity. The highly crystalline nature of the glass ceramic seals containing zirconia addition and the well defined interface with the experimental BFCY cathode [9] can be clearly seen in Fig. 9(b). This is in sharp contrast with the microstructure of the glass ceramic without the addition of zirconia as shown in Fig. 9(a).

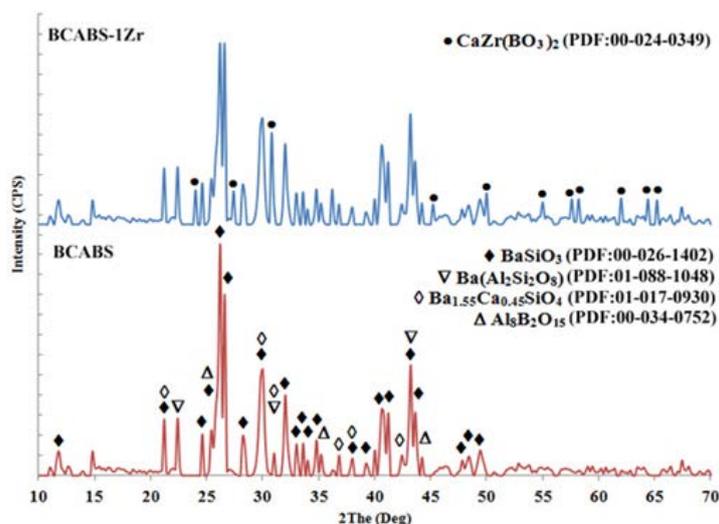


Fig. 3 Room temperature XRD of the glass sealing compositions with and without zirconium oxide. The phases identified are indicated on the right of the XRD pattern.

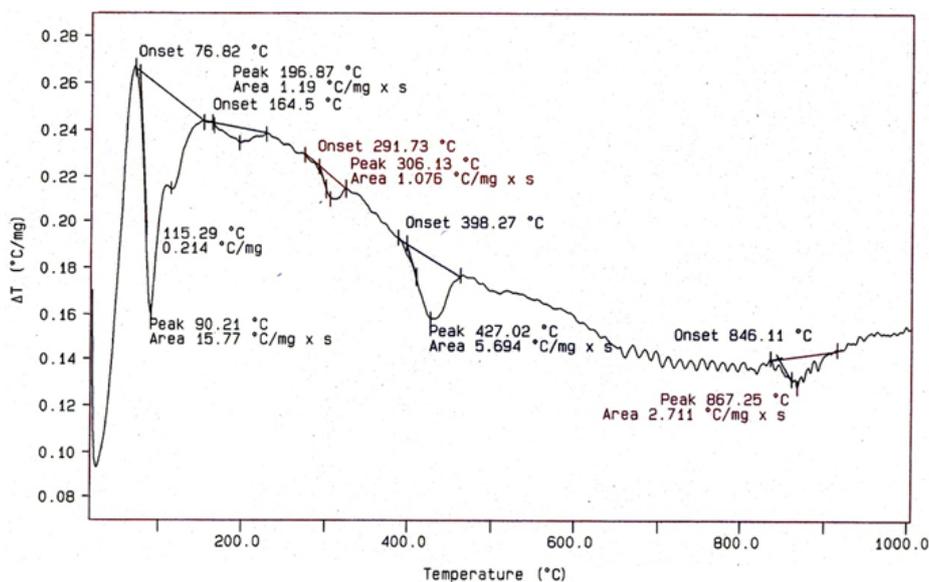


Fig.4 DTA of glass containing 1 mole % ZrO₂.

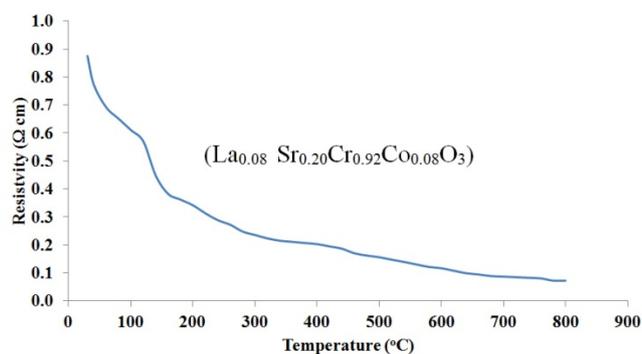


Fig. 5 Electrical resistivity up to 800°C

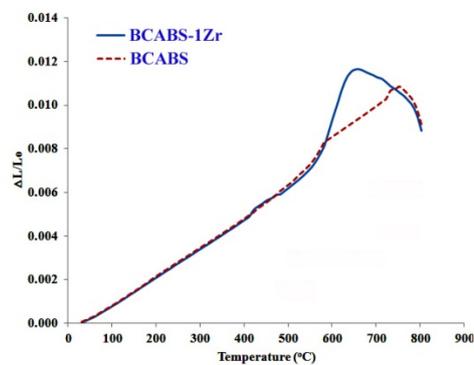


Fig. 6 Thermal Expansion of Sealing Materials

Table 2. Thermal Properties of Sealing Glass BCABS-1Zr and BCABS

Composition	Thermal Expansion Coefficient ($\times 10^{-6}/^{\circ}\text{C}$)			
	34-200 $^{\circ}\text{C}$	34-400 $^{\circ}\text{C}$	34-600 $^{\circ}\text{C}$	34-800 $^{\circ}\text{C}$
BCABS-1Zr	12.17	12.78	16.53	11.70
BCABS	12.20	12.81	12.54	12.40

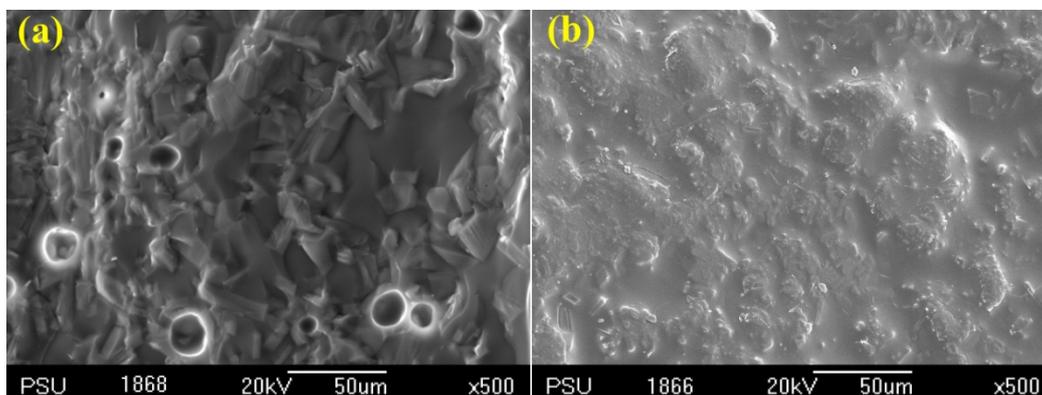


Fig. 7 Microstructure of refractory glass: (a) BCABS and (b) BCABS-1Zr on the surface.

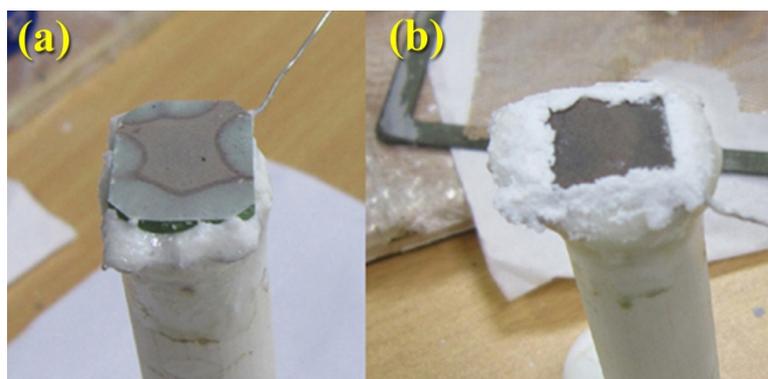


Fig. 8 LHS showing glass sealing composition without zirconia flowing over the surface of SOFC element. RHS: (a) Glass ceramic seals with addition of zirconia. (b) The glass ceramic seal does not flow on the surface of the SOFC element.

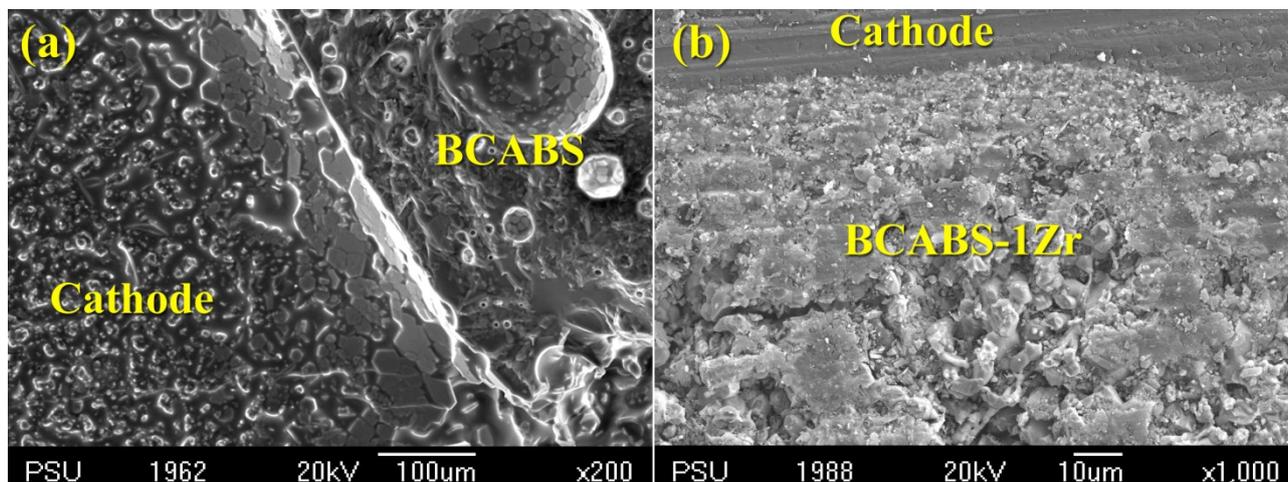


Fig. 9 Microstructure of cross-section between cathode materials and glass: (a) BCABS sealing glass without zirconia (b) BCABS-1Zr sealing glass containing 0.04 mole % zirconia.

Conclusion

The present study shows that the addition of 0.40 mole % of zirconia to a glass composition containing (mole%) 35%BaO,15% CaO, 5% Al₂O₃, 8%B₂O₃, 36.60%SiO₂ [BACBS] results in a fine grained glass ceramics. It is likely that the addition of zirconia acts as nucleating agents resulting in fine grained glass ceramics. The glass ceramics are insulating in moist oxidising and reducing environment rendering it suitable for the development of hermetic seals for not only the evaluation of the power density of the experimental SOFC using the two chamber design for the planar SOFC, but also for the fabrication of fuel cell stacksion.

Acknowledgement

The authors thank the Brunei Research Council (BRC) for the research grant. P. Hing would like to thank the Universiti Brunei Daussalam for a Graduate Research Scholarship.

References

- Chou, Y.-S. , Stevenson, J.W., and Choi, J.-P. 2014. Long-term evaluation of solid oxide fuel cell candidate materials in a 3-cell generic stack test fixture, part III: Stability and microstructure of Ce-(Mn,Co)-spinel coating, AISI441 interconnect, alumina coating, cathode and anode. *Journal of Power Sources*. 257(0): 444.
- Chen, J., Yang, H., Chadeyron, R., Tang, D., and Zhang, T. 2014. Tuning the interfacial reaction between CaO–SrO–Al₂O₃–B₂O₃–SiO₂ sealing glass–ceramics and Cr-containing interconnect: Crystalline structure vs. glass structure. *Journal of the European Ceramic Society*. 34(8): 1989.
- Hsu, J.-H., Kim, C.-W., and Brow, R.K. 2014. Interfacial interactions between an alkali-free borosilicate viscous sealing glass and aluminized ferritic stainless steel. *Journal of Power Sources*. 250(0): 236.
- Lin, S.E., Cheng, Y.R., and Wei, W.C.J. 2012. BaO–B₂O₃–SiO₂–Al₂O₃ sealing glass for intermediate temperature solid oxide fuel cell. *Journal of Non-Crystalline Solids*. 358(2):174.
- Ghosh, S., Das Sharma, A., Kundu, P., Mahanty, S. and Basu, R.N. 2008. Development and characterizations of BaO–CaO–Al₂O₃–SiO₂ glass–ceramic sealants for intermediate temperature solid oxide fuel cell application. *Journal of Non-Crystalline Solids*. 354(34): 4081.
- Chou, Y.S., Stevenson, J.W., Xia G.G., and Yang, Z.G. 2010. Electrical stability of a novel sealing glass with (Mn,Co)-spinel coated Crofer22APU in a simulated SOFC dual environment. *Journal of Power Sources*. 195(17): 5666.
- Ananthanarayanan, A., Kothiyal, G.P., Montagne, L., Tricot, G., and Revel. B. 2011. The effect of P₂O₅ on the structure, sintering and sealing properties of barium calcium aluminum borosilicate (BCABS) glasses. *Materials Chemistry and Physics*.130(3): 880.
- Hing, P. and McMillan, P.W. 1973. A Transmission Electron Microscope Study of Glass- Ceramics. *Journal of Materials Science*: 340-348.
- Suklueng, M., Yoong, V.N., Hing, P. and Ming, L.C. 2014. Optimization of a Novel Composite Cathode for Intermediate Temperature SOFCs Applications. *Walailak Journal of Science and Technology* (12).