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Study of an intermediate temperature solid oxide fuel cell sealing glass system

Kathy Lu*, Wenle Li [1]

Department of Materials Science and Engineering, Virginia Tech, Blacksburg, VA 24061, USA

HIGHLIGHTS

- A new sealing glass system is developed based on $SrO–La_2O_3–Al_2O_3–B_2O_3–SiO_2$.
- Atomic level microstructures and thermophysical characteristics are correlated.
- The most promising glass composition for solid oxide fuel cells is determined.

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ABSTRACT

This study investigates the effect of composition on the atomic level structure and thermal characteristics of sealing glass for solid oxide fuel cells (SOFCs). The glass systems studied contain varying percentages of SiO_2, Al_2O_3, SrO, La_2O_3, and B_2O_3; and the composition variables examined are SrO and B_2O_3. Atomic level parameters, including boron coordination number with silicon, the probability of boron coordination with silicon, and glass network connectivity are calculated. Thermal expansion coefficients, glass softening temperatures, and glass transition temperatures are measured by dilatometry. The glasses are then thermally treated at 700 °C for up to 1500 h in order to study their long term thermal stability at SOFC operating conditions. The resulting data show that the most desired glass composition is stable for at least 1500 h without devitrification and is a very promising sealant for solid oxide fuel cells.

1. Introduction

Solid oxide fuel cells (SOFCs) are an exciting prospect in the energy world due to their ability to cleanly generate electricity through the use of hydrogen or syngas fuels with high efficiency. Typically, SOFCs operate at temperatures of 800 °C and higher. However, stringent material requirements demand lower operating temperatures in order to ease cell degradation problems during cell operation [1,2].

In order to keep the fuels and air in a cell stack from mixing or leaking, a sealant material must withstand the cell operating temperatures and repeated cycles without cracking and without reacting with other cell components. This means sealing materials that have the desirable thermophysical properties (thermal expansion coefficient, glass transition temperature, and glass softening temperature) and thermal stability are a must. To be used as a seal, glass should meet a combination of several requirements [3–5]. Glass transition temperature T_g should be high enough but less than cell operating temperature; for intermediate temperature SOFC use, this temperature is around 700 °C. Glass softening temperature T_s should be reasonably low, such as less than 1000 °C. The glass transition and softening temperatures are critical for proper fuel cell operation because of the cell dependence on the glass to relieve thermal stress and avoid cracks during cell operation [6–8] while still being viscous enough to seal the SOFC components. Glass coefficient of thermal expansion (CTE) should be greater than $8.0 \times 10^{-6}\ K^{-1}$ to match with the CTEs of other cell components, which often include yttria stabilized zirconia, metallic interconnect, and lanthanum manganite electrode. More importantly, glass should not devitrify at SOFC operating temperatures for a long time (such as >40,000 h) in order to ensure cell stack durability.

BaO-containing aluminoborosilicate glass is the most common seal glass due to its excellent thermal properties [9–11]. This glass contains 35 mol% SiO_2, 10 mol% B_2O_3, 5.0 mol% Al_2O_3, 15 mol% CaO,

* Corresponding author. 211B Holden Hall, Materials Science and Engineering Department, Virginia Tech, Blacksburg, VA 24061, USA. Tel.: +1 540 231 3225; fax: +1 540 231 8919.

E-mail addresses: klu@vt.edu (K. Lu), wenle@vt.edu (W. Li).

[1] 127 Randolph Hall, Materials Science and Engineering Department, Virginia Tech, Blacksburg, VA 24061, USA. Tel.: +1 540 266 8020; fax: +1 540 231 5022.

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and 35 mol% BaO. The CTE of this glass is 11.8×10^{-6} K^{-1}; the T_g is intermediate, ∼630 °C. This glass is often used at >800 °C and is attractive mainly because of its high CTE. However, there are two major drawbacks for this system. First, it crystallizes at 800 °C, forming celsian ($BaAl_2Si_2O_8$) and its polymorph hexacelcian phases [10]. Both these phases have low CTEs. Also, the difference in the CTE values of the celsian phase (2.29×10^{-6} K^{-1}) and the hexacelcian phase (8.0×10^{-6} K^{-1}) develops thermal stress and degrades cell performance [12]. Second, the glasses based on this system interact severely with chromium-containing steel interconnect and other fuel cell components [13]. The most detrimental reaction product is $BaCrO_4$, which has a CTE of 22×10^{-6} K^{-1}. Poor thermal and chemical stabilities of the BaO-containing aluminoborosilicate glass prompt the need to search for new BaO-free glass systems.

Another system is the SCAN2 glass reported by Smeacetto et al. [14], which contains 40 mol% SiO_2, 10 mol% B_2O_3, 9.0 mol% Al_2O_3, 18 mol% CaO, and 23 mol% Na_2O. The CTE is 11.2×10^{-6} K^{-1}; the T_g is ∼545 °C. This is a low temperature seal glass for SOFCs with desirable CTE. However, it devitrifies extensively after thermal treatment at cell operating temperatures. The joining process with other cell components at 900 °C causes partial surface devitrification of the glass, resulting in a glass–ceramic seal.

A new glass system based on $SrO–La_2O_3–Al_2O_3–B_2O_3–SiO_2$ has been developed by us and possess excellent thermophysical properties and compatibility with other cell components [15–21]. It is a very desirable glass system for SOFC systems because of its high enough CTE (>10×10^{-6} K^{-1}) and superb devitrification resistance (stable for at least 2000 h at 800 °C). However, our previous efforts were mainly focused on 800 °C cell operating conditions. Therefore, the glass designs and thermophysical characterization were aimed for seal use at high temperatures. With the continuing efforts to decrease SOFC operating temperatures, there is a need to design new glass compositions for this glass system and re-examine the thermophysical characteristics and stability at lower temperatures.

In this work, $SrO–La_2O_3–Al_2O_3–B_2O_3–SiO_2$ glasses with different compositions are synthesized with the aim for a sealing system to be used at 700 °C. The glass atomic level bonding is calculated. The connectivity of the glass network and its relationship with the corresponding glass stability are discussed. The glass transition temperatures, softening temperatures, and CTEs are measured in order to characterize the thermophysical properties of the glass systems. Based on the above results, different promising glass samples are thermally treated at 700 °C for up to 1500 h. The most promising glass composition is identified.

2. Experimental procedure

Glass samples were prepared with conventional glass manufacturing process. $SrCO_3$ (99.9%, Sigma Aldrich, St. Louis, MO), La_2O_3 (99.98%), Al_2O_3 (99.95%), SiO_2 (99.8%), and B_2O_3 (99.98%) (All oxides were from Alfa Aesar, Ward Hill, MA) at designed compositions were mixed in a ball mill for overnight. The mixed oxides and carbonate were melted in a platinum crucible in a box furnace (Lindberg, Model No. 51314, Watertown, WI) at 1400 °C for 4 h. The heating schedule was at 10 °C min^{-1} heating rate from room temperature to 1100 °C; dwelling at 1100 °C for 1 h (for $SrCO_3$ to completely decompose); then heating at 5 °C min^{-1} to 1400 °C. Once the sample was sufficiently melted, it was poured into a graphite mold and all the excessive glass was poured into a bucket of water. The as-made glass samples were heated to 700 °C in a box furnace (Barnstead/Thermolyne Small Benchtop Muffle Furnace, 1400 Type). The samples were thermally treated at 700 °C for 1500 h in order to examine their thermal stability behaviors.

The glass samples were also cut with a diamond saw to about 25 mm long. The cylindrical glass sample end surfaces were polished with polishing papers and then different size alumina particle suspensions to optical finish (5 μm, 1 μm, 0.3 μm, and 0.05 μm) with flat, parallel ends. The flat ends were to ensure proper measurement of the thermal properties of the sealing glass. The glass transition temperature T_g, glass softening temperature T_s, and CTE were obtained by dilatometry (Orton Dilatometer Model 1000D, The Edward Orton Jr. Ceramic Foundation, Westerville, OH); the heating and cooling rates were 2.5 °C min^{-1}; the peak temperature was ∼20 °C after glass softening temperature T_s, depending on the glass composition. The devitrification resistance analysis for different glass samples was carried out by X-ray diffraction (XRD, X'Pert PRO diffractometer, PANalytical B.V., EA Almelo, The Netherlands); the scan speed was 0.02°s^{-1} with Cu Kα radiation ($\lambda = 1.5406$ Å). A Raman spectrometer (JY Horbia LabRam HR 800, Horiba Ltd., Japan) was used to study the glass network structural stability. The Raman spectra were collected on polished glass samples in the range from 200 cm^{-1} to 1600 cm^{-1}, with a 514.57 nm argon laser light source at 50 mW power and 400 s exposure time. Afterward, the Raman spectra were deconvoluted using a GRAMS/AI_7.02 software (Themo Fisher Scientific, Inc. Waltham, MA). The details of Raman spectrum measurements were reported in our previous work [22].

3. Results

3.1. Sealing glass design principles

As explained in the Introduction section, in our prior studies, glasses based on the $SrO–La_2O_3–Al_2O_3–B_2O_3–SiO_2$ system were investigated as sealant for SOFCs [22,23]. The study shows that as the B_2O_3:SiO_2 ratio increases, the $SrO–La_2O_3–Al_2O_3–B_2O_3–SiO_2$ glass micro-heterogeneity and the amount of non-bridging oxygen atoms increase. Correspondingly, the T_g of the $SrO–La_2O_3–Al_2O_3–B_2O_3–SiO_2$ glasses changes from 635 °C to 775 °C and the T_d changes from 670 °C to 815 °C. Glass thermal stability decreases with B_2O_3:SiO_2 ratio increase. As a result, even though the glass without B_2O_3 is thermally stable after being kept at 800 °C for 2000 h, the lower temperature thermal behaviors of the glass system have not been studied since the focus of the prior study was to find a suitable sealing glass system for cells operating at 800 °C.

Based on our prior work, B_2O_3 is a necessary component for lowering the operating temperatures of the sealing glass. In this study, Al_2O_3 and La_2O_3 are kept constant during our new glass composition design. Different SrO levels are studied. The relative contents between SiO_2 and B_2O_3 are changed so that the effect of glass network formers can be analyzed while the total amount of SiO_2 and B_2O_3 stays the same at a given SrO level. When the B_2O_3 content is increased, the SiO_2 content is decreased by the same amount.

Because of the configurational entropy difference between SiO_4 and BO_3 structural units, SiO_4 structural units should preferentially link with BO_4 instead of BO_3 structural units, in addition to the bonding among SiO_4 themselves. To understand the degree of bonding between SiO_4 and BO_4 units in the designed glass systems, two related parameters can be calculated: probability of silicon coordinated to BO_4 and mean number of silicon coordinated to BO_4. Taking X_{Si} as the molar ratio of silicon to total network formers (silicon and boron) and assuming no BO_4 units are linked with each other, the mean number of silicon coordinated to BO_4 $\langle l \rangle$ can be expressed as [24]:

$$\langle l \rangle = \frac{16X_{Si}}{0.62 + 4.38X_{Si} - X_{Si}^2} \quad (1)$$

The probability of silicon coordinated to BO_4 $P(l)$ becomes: