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The effect of zirconia nanoparticles addition on thermal and electrical properties of BaO-CaO-Al₂O₃-B₂O₃-SiO₂ glass for solid oxide fuel cell sealant

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The objective of the present work is to study properties of a composite material consisting of zirconia nanoparticles in a glass matrix based on the system of BaO-CaO-SiO₂-B₂O₃-Al₂O₃. Zirconia nanoparticles are added by 0-20 vol.% into the glass matrix to prepare the glass composites. Coefficient of thermal expansion, glass transition temperature and dilatometric softening point temperature of specimens are determined by means of dilatometry analysis. Coefficient of thermal expansion of base glass is $10.38 \times 10^{-6} \text{ k}^{-1}$ and by increasing zirconia content to 10, 15, and 20 vol.%, coefficient of thermal expansion reduces down to 9.88×10^{-6} , 9.84×10^{-6} and $9.76 \times 10^{-6} \text{ k}^{-1}$ respectively. Sinterability of different specimens is studied by increasing zirconia nanoparticles. Electrical properties are measured in different temperatures, and results show that with increment of zirconia nanoparticles, temperature resistivity of specimens has been decreased. Microstructural investigation reveals a well-adhered bonding between the sealants and electrolyte.

Key word: Solide oxide fuel cell, Composites, Nano Zirconia, Thermal properties, Electrical properties, Sinterability.

Introduction

In order to obtain high voltage and high power from Solid oxide fuel cells (SOFCs), single cells are stacked together in different ways [1, 2]. Nowadays the dominant stack designs are of two main types; the tabular design and the planar design. The main advantage of planar designs over other concepts is the potential to achieve higher power densities due to the short transport paths across the cell. An additional advantage lies in the more simple fabrication technology, with the possibility to use low cost processes like screen-printing or tape-casting representing a large-scale production potential. The inconvenience of the planar design is the need of a high-temperature sealing [1-3]. The main functions of sealing materials for fuel cells are to ensure the gas separation between both gas atmospheres air on the cathode side and fuel gas on the anode side, and to guaranty electrical insulation between two successive interconnected plates [1-5].

Glass and glass-ceramics are suitable candidates as their properties can be tailored down to the specific requirement of this technology by choosing the adequate components of the glass and their proportions [6, 7]. The major advantages of glass-ceramics compared to glasses are a lower chemical reactivity and higher durability of their physical and mechanical properties.

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In particular a wide range of more stable thermal expansion coefficient can be obtained by controlling the crystalline phase content and their volume fraction [2].

Thermal expansion coefficient (CTE) of a seal glass is one of the most important thermal properties for SOFCs and should match with those of other SOFC components to avoid thermal stress. During cell operation, thermal stress arises due to the difference(s) in CTEs between the adjoined SOFC components and the seal glass. Both tensile (CTE component > CTE glass) and compressive (CTE component < CTE glass) stresses are possible at the interface. CTE difference(s) should not exceed $1 \times 10^{-6} \text{ k}^{-1}$ [3].

The CTE of a seal glass depends on the symmetry of vibrations in the glass structure, bond-bending, and molar-free volume. For example, pure SiO₂ glass has $0.6 \times 0^{-6} k^{-1}$ CTE due to its high symmetry of vibrations and B_2O_3 has $14.4 \times 10^{-6} k^{-1}$ CTE due to its low symmetry of vibrations. Modiers in silicate glasses create non-bridging oxygen which decrease the average symmetry of vibrations of the Si-O bonds, and thus increase the CTE [3-8]. Roles of different constituents on the CTE of a seal glass generally follow the opposite trend as on seal glass transition temperature (T_g) and softening temperature (T_s). Specic effects can be analyzed based on the functions of the glass constituents and the operating conditions and duration of a SOFC. $T_{\rm g}$ and $T_{\rm s}$ follow the conventional denitions. A seal glass is brittle below Tg but viscous above T_g. The stress between the seal glass and the adjoining SOFC components induced by thermal expansion mismatch during thermal cycling can generate

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cracks, which are potential paths for gas leakage. These cracks can "self-heal' by viscous ow of the seal glass above T_g [3, 4, 8]. At T_g and T_s points, the viscosity corresponds to $\sim 10^{11.3}$ and $\sim 10^9$ Pa.s, respectively. The viscosity of a seal glass should be greater than 10⁹ Pa.s to provide hermetic sealing at cell operating temperatures. This means hermeticity of a seal glass can be maintained by a $T_{\rm g}$ value slightly below the SOFC operating temperature while relieving thermal stresses and self-healing cracks. This temperature (T_g) for glasses which are suitable for sealant applications, must be generally between 650 °C and 800 °C. T_s should be higher than the SOFC operating temperature to avoid excessive glass ow but below 1000 °C to avoid excessive oxidation of the metallic interconnects during sealing. $T_{\rm g}$ and $T_{\rm s}$ of a seal glass depend on the glass composition [7].

As observed by several researchers, the particle size distribution of the glass powder has a strong inuence in controlling several properties, such as the crystallization behavior of the glass and viscosity of the paste. A large particle size of the glass powder will lead to a porous structure in the glass matrix during high temperature sealing that can cause gas leakage in the sealing condition during stack operation at elevated temperature [15]. Ionic charges contribute to ionic conductivity and electrons and holes contribute to electronic conductivity. Generally, conductivity is controlled by ionic charges in alkaline and alkaline earth oxide containing glasses and by electrons and holes in transition metal containing glasses. Both types of conductivity compromise seal glass resistivity. The electrical resistivity of a seal glass depends on the composition and the devitrication (phase separation and crystallization) of the glass as well as the operating temperature of the cell stack and should be greater than $10^4 \Omega cm$ in order to avoid electrical shunting [7, 9].

A glass-ceramic matrix composite seal, in which a crystalline ceramic phase is dispersed uniformly in a glass ceramic matrix, has many advantages over the traditional glass-ceramic seals. This priority refers to the more influence tailoring of the glass viscosity, coefficient thermal expansion, and thermal con-ductivity. These parameters can be controllable by changing of the volume fraction and particle size of the reinforcing ceramic phase. These composites sealant provide appropriate thermal, chemical and mechanical stability through stress relieving and self healing character of the viscous matrix and the interlocking nature of the reinforcing crystalline phases. Therefore, sealants must be flexible enough during fabrication as well as being rigid enough to prevent creep and stack collapse during application [3, 4, 9].

In the present work, 0-20 vol.% of zirconia nanoparticles was added to barium calcium aluminosilicate (BCAS) G18 glass matrix (for improving mechanical properties of glass. Mechanical properties of specimens were investigated in our prior article [4]. We found that addition of zirconia nanoparticles up to 10 vol.% improved mechanical properties but it is important that this improvement doesn't have negative effect on thermal and electrical properties, Thermal behavior and electrical properties of glass and composites specimens are characterized by zirconia nanoparticles in the present study.

Experimental

The starting materials were 3 mol.% yttria stabilized zirconia (Y_2O_3/ZrO_2) nano powder with particle size of 30-60 nm supplied by Advanced Materials and a barium calcium aluminosilicate (BCAS) glass G-18 powder of composition 56.4BaO-8.8CaO-5.4Al2O3-7.3B2O3-22.1SiO2 (wt.%) [8]. The raw materials used for the preparation of the glasses were SiO₂ (Sigma-Aldrich, S5631, 99%), Al₂O₃ (Merck, 101095, 98.5%), H₃BO₃ (Sigma-Aldrich, B6768, 99.5%), CaCO₃ (Merck, 102066, 98.5%) and BaCO₃ (Merck, 101714. 99%). The homogenized glass batch was melted in zircon crucibles (supplied by Material and Energy Research Center) at 1300 °C for 3 h. Then, the molten glass was rapidly quenched in distilled water to obtain frit. Fig 1 shows XRD pattern of glass frit. The glass frit was wet milled in acetone media for 6 h to reach mean particle size of 7.3 µm. The particle size of the glass powders was measured by a laser particle size analyzer (Analysette 22, Fritch, Idar-oberstein, Germany). Glass powders was mixed with 10, 15, and 20 vol.% of zirconia nanoparticles. The homogenization was performed in ethanol media for 3 h in zirconia jar-mill.



Fig. 1. XRD patent of untreated glass.

 Table 1. wt.% and vol.% zirconia nanoparticles in difference specimens.

Specimens	Wt.%	Vol.%
C10Z	19	10
C15Z	26	15
C20Z	33	20

Hereafter, they are referred to as C10Z, C15Z and C20Z, respectively. Table 1 shows wt.% and vol.% zirconia nanoparticles.

The glass powders were granulated by adding 5 wt.% polyvinyl alcohol solution. The granulated powders were pressed by a uniaxial hydraulic press into 5 mm \times 5 mm \times 50 mm parallelepiped specimens at the final pressure of 60 MPa. T_g, CTE, and T_s of the rectangular specimens were determined by dilatometric measurements. (Dilatometry 402E NETZSCH, heat rating of 10 °C/min).

Sinterability of the specimens was investigated according to Archimedes method (ASTM.C474-88) by using distilled water, and powder density of the samples was measured by a helium gas pycnometer (model Accupyc 1330, Micromeritics, Norcross, GA). The relative density of the sintered specimens was determined by dividing bulk density by powder density. Linear shrinkage of specimens is measured by difference between diameter of green specimens and fired specimens. An Impedance Analyzer (Autolab PG-STAT200) also was utilized to measure the electrical resistivity of sintered glass-ceramic pellets in temperature range of 600-800 °C and frequency range of 0.1 Hz to 1MHz. The microstructural analysis of heat-treated samples was performed by using X-ray diffraction analysis using a powder diffractometer (siemen SD500, Cu K_{α} radiation at 40 Kv). Silicon powder was used as the internal standard for semi-quantitative measurements.

To prepare thick film of sealants, the glass and composites powders were blended with a suitable organic media (Ethanol) to form a viscous paste. Then, the paste was spread between two YSZ disc (13 mm in diameter and 2 mm thickness). Afterward, this assembly was put into a furnace and sintered at 900 °C for 1 h in air under 100 g loads on the top of the assembly. After sealing, the furnace temperature was brought down to the SOFC operation temperature (~ 800 °C), and heat treatment was performed at that temperature for 30 h. Finally, samples were cooled down to room temperature with a cooling rate of 10 °C/min.

In order to examine the quality of the sealant at the interfaces (glass-YSZ) and to investigate the effect of heat-treatment on the corresponding microstructure, polished cross-sections of the specimens were monitored using scanning electron microscopy (VEGA/TScan, Scanning electron microscopy).

Results and Discussion

Thermal properties

In the Fig. 2 results of Dilatometry analysis is presented, also in the Table. 2 thermal properties of different specimens are summarized. The results of Dilatomerty analysis indicate T_g in all specimens to be lower than that of the SOFC application temperature

[1] Glass [2] C10Z [3] C15Z [4] C20Z [2] [3] [1] [1] [1] [1] [2] [3] [1] [1] [1] [2] [3] [1] [1] [1] [1] [2] [3] [1] [1] [2] [3] [1] [2] [3] [1] [2] [3]

Fig. 2. Dilatometry curve of difference specimens.

Table. 2 Thermal properties of different specimens.

sample	$\begin{array}{c} \text{Coefficiant thermal} \\ \text{expansion} \\ (\times \ 10^{-6} \ \text{K}^{-1}) \end{array}$	Glass transition temperature (Tg) (°C)	Softening point temperature (T _s) (°C)
Glass	10.38	626	678
C10Z	9.88	647	712
C15Z	9.84	671	743
C20Z	9.76	679	805

(800 °C). By adding 10 vol.% of zirconia nanoparticles to the basic glass, T_g and T_s increased 21 °C and 34 °C, respectively. With review of other specimens, it can be concluded that T_g and T_s increased with the amount of zirconia because of the effect of zirconia in increment of component melting point, T_g , and T_s by adding refractory phases to basic glass incresesed. For a composite seal, metal or metal oxide powders can be added to a seal glass powder to modify T_g and T_s . For example, for an alkaline oxide and ZnO containing silicate seal glass, 5-10 vol.% Al₂O₃ addition increases T_s by 20-60 °C [10]. For a MgO-borosilicate seal glass, 10-20 vol.% MgO addition (to form composite seal) increased T_g by ~25 °C [10]. For an alkaline earth borate seal glass, however, 5-20 vol.% addition of YSZ powder doesn't signicantly affect T_{g} [11].

It can be seen that CTE of specimens is partially decreased as a function of zirconia. The value of this reduction for 10, 15, and 20 vol.% of zirconia nanoparticles is $0.5\times10^{-6},\,0.54\times10^{-6}$ and 0.62×10^{-6} k^{-1} respectively. It is reported, in the similar work, that adding 2 mol.% of ZrO2 to BaO-borosilicate glass decreased the CTE by $\sim 0.5 \times 10^{-6} \text{ k}^{-1}$ [12], but it had no impact on a MgO-borosilicate glass [13]. This could be due to existence of Zr⁴⁺ions in 6coordination at eld strength 0.84 v/m and 8 coordination at eld strength 0.77 v/m. In the BaO-borosilicate glass, Zr⁴⁺ may be 6coordinated and the CTE decreases due to higher eld strength (0.84 v/m) [3]. Therefore, it can be concluded that with partial dissolution of nanozirconia particles in the glass and entering Zr⁴⁺ ions in the glass network which have 6 coordination with higher field strength, CTE decreases in composite specimens.



Fig. 3. Variation of linear shrinkage (a), bulk density (b) and relative density (c) of difference specimens versus firing temperature.

Sinterability

Linear shrinkage, bulk densities and relative densities of the specimens versus ring temperature are plotted in Fig. 3. By increasing the temperature, these parameters increased to the maximum values, and then decreased at higher temperatures. Achieving the maximum density was a criterion for determining the optimum sintering temperatures. Therefore, the temperatures of 720 °C and 800 °C were chosen for glass and C10Z, and 850 °C is chosen for C15Z and C20Z specimens as the optimum sintering temperatures. Both viscosity drop and better compressibility at elevated temperatures are reported elsewhere [14]. During operation of a glass sealant at high temperatures, it first wets the adjoining surfaces to make a bond followed by sintering to maximum densification before crystallization. The crystallization process also increases the viscosity of the glass. If crystallization occurs before complete wetting or sintering of the glass, it will result in poor adherence and porosity in the microstructure of the sealant glass-ceramics [15].

At higher temperatures, nucleation and formation of crystalline phases leads to increment of viscosity, and also because of the difference in the density of crystalline phases with based glass, porosity formation occur. On the other hand, according to the experimental observations, it seems that by sintering the surface of specimens, open porosities of specimens are closed and air is trapped into the porosities, and this phenomenon prevents the densification of the samples. To ensure this phenomenon, open and close porosities of different specimens are plotted in Fig. 4(a), (b), (c) and (d). As shown in Fig 4, in different specimens increasing the temperature, causes the volume fraction of total and



Fig. 4. variation of porosity in difference specimens versus firing temperature (a) glass, (b) C10Z, (c) C15Z and (d) C20Z.



Fig. 5. XRD pattern of difference fired specimens at optimum sintering temperature for 1 h, (a) glass, (b) C10Z, (c) C15Z, (d) (C20Z).

Table 3. sintering characterizes of different specimens.

Sample	Temperture (°C)	Linear shrinkage (%)	Relative density (%)	Bulk density (g/cm ³)
	680	9.16	87.66	3.14
	700	12.84	98.25	3.54
Glass	720	18.96	98.65	3.82
01055	750	15.04	97.6	3.79
	800	-	96.13	3.73
	820	-	95	3.5
	750	12.19	94.48	3.94
	800	15.08	97.88	4.081
C10Z	820	13.32	95	4.01
	850	11.1	93	4
	870	10.5	90	3.8
	750	8.84	90.02	3.78
	800	12.9	97.29	4.01
C15Z	820	12	96.1	4.055
	850	11.9	95.61	4.035
	870	10	93.89	4
C20Z	750	2.59	85.1	3.5
	800	8.68	91.12	3.9
	820	9.1	92.26	4
	850	10.39	95.12	4.16
	870	10.34	90.76	4.041

close porosities first to drop and then to increase while open porosities decrease continuously by temperature. Declining of density and shrinkage in different specimens can be due to the increase of close porosities by elevating temperature.

It can be interpreted from Fig. 3 that in the optimum sintering temperature, adding zirconia nanoparticles, bulk densities of base glass has increased while relative densities has decreased. Increasing crystalline phases and decreasing amount of glass phases yield to a lower viscous flow and consequently lesser sinterability. Effect of zirconia nanoparticles content on the bulk density can be attributed to high density of zirconia (zirconia density ~ 6-6.05 g/cm³ and glass density ~ 3.87 g/cm³). Therefore, reduced relative density means increased porosities. In the other words, presence of in-compressible secondary particles creates tensile stresses in the glass and prevents from densification of com-posites which observed in the other works [16].

XRD pattern of fired specimens at the different sintering temperatures is presented in the Fig. 5. In the optimum sintering temperature, there is no crystalline phase and densification occurs before crystallization. In the composite specimens, the presence of tetragonal ZrO_2 is noticeable. In the C10Z specimen, zirconia has dissolved partially in the glass phase, and as a result zircon (ZrSiO₄) phase forms while this phase has not seen in the C15Z and C20Z specimens. This can be due to the higher content of glass phase in C10Z where zirconia nanoparticles can dissolve in more than the other composites. By increasing vol.% of zirconia nanoparticles, amount of required glass phase for dissolution of zirconia and its reprecipitation as zircon decreases. Table 3 shows sintering characteristics of different specimens.

Electrical resistivity

Fig. 6 presents plots of the complex plane impedance of the glass and composites at different operating temperatures ranging from 600 °C to 800 °C. The similar resistivity values at different temperatures are given in Table 4. The resistivity decreases by the temperature and by zirconia nanoparticles. Seal glass electrical resistivity generally decreases with temperature because the diffusion of modier ions increases with temperature. In the barium-containing systems, declining



Fig. 6. Complex plane impedance plot of different specimens at different temperatures, (a) glass, (b) C10Z, (c) C15Z, (d) C20Z.



Fig. 7. XRD pattern of heat-treated specimens at 800 °C for various times (a) glass, (b) C10Z, (c) C15Z and (d) C20Z.

Table 4. Variation of electrical resistivity of the different specimens at different temperatures (Ω cm).

		Samples		
Temperature (°C)	Glass	C10Z	C15Z	C20Z
600	2.31×10^6	1.7×10^6	1.56×10^6	$1.15 imes 10^6$
700	3.47×10^{5}	2.2×10^{5}	2.17×10^{5}	1.01×10^{5}
800	4.7×10^{4}	3.7×10^{4}	4.21×10^{3}	3.7×10^{3}

of resistivity by temperature is because of Ba^{2+} ion migrations [17]. In the composites specimens, by partial dissolution of ZrO_2 in the glass phase and entering Zr^{4+} , electrical resistivity is reduced. Resistivity of glass and C10Z specimens are showed to be higher than $10^4 \Omega$ cm in 600-800 °C temperature

range which signposts that these specimens are suitable for SOFC application.

Microstructure investigation

In order to determine the type of crystallized crystalline phases in heat-treated specimens at SOFC application temperature for different times (1, 10, 30 and 50 h), x-ray diffraction and scanning electron microscopy analysis carried out. X-ray diffraction patterns of different heat-treated specimens are shown in Fig. 7. Using the XRD analysis, relative amounts of crystalline phases in each specimen is calculated. Also, variation of crystallization with time is exhibited in Fig. 8. As it can be seen, the main crystalline phases in the glass specimen after 10 h of heat-treatment are barium silicate (BaSiO₃) and barium calcium silicate (BaCaSiO₄). With



Fig. 8. Variation of crystallization with heat-treatment time for (a) glass, (b) C10Z, (c) C15Z and (d) C20Z.

Heat-treatment time (h)	Sample	Relative density (%)
1 h	GC	98.45
	C10Z	97.88
	C15Z	97.29
	C20Z	94.10
10 h	GC	98.10
	C10Z	95.69
	C15Z	95.36
	C20Z	93.30
30 h	GC	97.70
	C10Z	92.20
	C15Z	91.30
	C20Z	90.13
50 h	GC	95.10
	C10Z	91.00
	C15Z	90.80
	C20Z	90.03

Table 5. relative density of heat-treated specimens.

increasing heat-treatment time up to 30 h, hexacelsian phase (BaAl₂Si₂O₈), also, forms. In addition, tetragonal ZrO_2 and Zircon (ZrSiO₄) have crystallized in the composite specimens. By increasing heat-treatment time and crystallization of silica-rich crystalline phases, glass viscosity decreases while solubility of ZrO₂ in the glass matrix increases. It can be implied from figures that the crystallization of the samples increases with increasing heat-treatment time. Relative density of specimens is summarized in Table 5.

Fig. 9(a) exhibits crystallized crystalline phases in C10Z heat-treated specimen after 50 h. The area marked in Fig. 9(a) is show in greater magnification in Fig. 9(b). As the picture shows, crystalline phases have needle-shaped morphology. N.Bansal *et al* [14] have reported needle-shaped morphology of the barium



Fig. 9. SEM micrographs of polished cross-section of bulk C10Z heat treated at 800 °C for 50 h in different scale (a). 1 μ m, (b) 500 nm, and (c) EDS pattern of Fig (a).

silicate (BaSiO₃) and celsian (BaAl₂Si₂O₈) phases in their research. Thus, it seems all three phases identified by x-ray patterns are needle-shaped. We can find crystallization and growth of crystalline phases are two main factors lead to increase in amount of defect and porosities and decrease relative density.

To ensure the presence of ZrO_2 phase in specimens, EDS analysis of Fig. 9(a) (marked by circle) has carried out and the results are shown in Fig. 9(c). Due to the presence of the ZrO_2 peak in XRD pattern and



Fig. 10. SEM micrograph of the interface for based glass/YSZ (a) and C10Z/YSZ electrolyte (b) and C15Z/electrolyte.

the presence of sharp peak of Zr in comparison with Si peak in EDS analysis, it can be said that ZrO₂ is existed in the specimens. It seems that distributed white particles among the crystalline phases are related to the ZrO₂. To investigate the microstructure of sealing glass and electrolyte interface (sealed at 900 °C followed by heat-treatment at 800 °C for 50 h in air), a scanning electron microscopy (SEM) micrograph of sealant/YSZ interface is illustrated in Fig. 9. An acceptable adhesion of sealants to YSZ can be inferred from Fig. 8, also it can be seen that interface is free of cracks and pores and sealants is relatively dense.

Conclusions

According to mechanical properties in pervious article [4], we can find, adding zirconia nanoparticles up to 10 vol.% improves mechanical properties, therefore it is important that addition of zirconia doesn't have negative effect on thermal and electrical properties

By adding zirconia nanoparticles, T_g and T_s increased because of the effect of zirconia in increasing melting point of basic glass. Tg in all specimens to be lower than that of the SOFC application temperature (800 °C). CTE of specimens was partially decreased as a function of zirconia because of partial dissolution of nanozirconia particles and entering of Zr^{4+} with 6 coordination and higher field strength in the glass network. Also it is shown that resistivity decreased in elevated temperatures and higher zirconia nanoparticle contents because of Ba²⁺ and Zr⁴⁺ ion migration. The results show thermal and electrical properties of C10Z specimens are suitable for SOFC applications. By increasing temperature, linear shrinkage, bulk density and relative density of specimens increased to the maximum value because of reduction of viscosity. Further increase in temperature resulted in sudden drop in mentioned properties due to nucleation and formation of crystalline phases in higher viscosities.

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