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Theoretical calculations of the thermal expansion coefficient of glass-ceramic sealing materials in solid oxide electrolysis cell

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ABSTRACT

Three series of glasses, $BaO–CaO–SiO_2–Al_2O_3$, $SrO–SiO_2–Al_2O_3$ and $SrO–CaO–SiO_2–Al_2O_3$ were prepared. The coefficients of thermal expansion (CTE) of as-cast glasses were measured using dilatometer from room temperature to their glass transition. A new method — Average Field Strength Method was developed to accurately calculate the CTEs of all glasses and compared with traditional method (Appen method). Through comparison between calculated results and experimental results, the relation between the average field strength and the average field strength coefficient was found. With the increase of average field strength, the CTE of glasses calculated by the Average Field Strength Method of glass decreases smoothly. The CTE_F were very close to the experimental results. The errors between them were smaller than 3%. The error between the CTE of glasses calculated by traditional method and the experimental CTE was near 40%. The average Field Strength Method can be used to accurately calculate the CTE, and estimate the change trends of CTE.

1. Introduction

The solid oxide electrolytic cell (SOEC) has been actively studied as a hydrogen producing device. In planar SOECs (p-SOEC), gas-tight sealing is a basic requirement to prevent gases from mixing in the anode and the cathode. Many glasses and glass-ceramics have been used as sealants in the p-SOECs [1–3]. The seals must fulfill chemical requirements. The coefficient of thermal expansion (CTE) of a seal glass is one of the most important physical properties for SOFCs/SOECs, and it must match those of other cell components, such as connector [$(12–14)\times10^{-6}\ K^{-1}$] and electrolyte [$(10–12)\times10^{-6}\ K^{-1}$] [4–7]. Only under this condition can the cell withstand the deep thermal cycling (from room temperature to working temperature) for hundreds of times without degradation in the performance of SOEC. But in different cell systems, the sealant glass will seal the adjacent cell components whose composition will need to be changed to meet the different needs. Therefore, the CTE of the glass should be adjusted accordingly. It is necessary to find a very effective method to accurately calculate the CTE of the glass and reduce the workload of the experiment.

The CTE of a seal glass depends on cation field strength, bond-bending, structure symmetry, molar-free volume, and non-bridging oxygen (NBO) species which decrease the symmetry of the bonds, and increase the CTE in glasses [8]. There are several methods to calculate the glass properties based on glass composition. Appen (АППЕН) method is one of the best among these methods [9,10], which establishes the relationship between some properties of oxide and the content of oxide in the glass by accumulation of a large number of experimental data and analysis. However, the Appen method can only estimate the change trends of CTE, but cannot accurately calculate the CTE of glasses containing alkaline earth oxide glasses.

There are many factors which affect the structure, such as, composition, treatment process, non-bridging oxygen, structural symmetry. But for the thermal expansion coefficient of glass, the nature of the thermal expansion is the molecular thermal vibration deviate from the equilibrium position during the change of temperature. As the temperature raises, the thermal vibration amplitude of the glass particle is increased, and the dot spacing of the particle becomes larger correspondingly, which thus induce the expansion of glass. But the increase of the dot spacing is carried out against the force (the attraction) between cation (M: cations of the network former, network modifier, intermediate oxide, and additive) and oxygen anions. For the oxide glass, this force (the attraction) is the bond force between the cation and oxygen anions. Therefore, a new method is introduced to accurately calculate the CTEs of the glass: the Average Field Strength Method. From above, it is well known that the CTEs of the glass are caused by the thermal vibration of glass particle and the increase of the dot spacing with the increase of temperature. But the increase of the dot spacing is carried out against the force between cation and oxygen anions [11,12]. The force is the bond strength of M – O. So the CTE of glass exhibits a close relationship with the bond strength of M – O, but the bond strength of M – O is determined by the cationic field strength. So the CTE of glass must have a relation with the field strength of all cations in the glass. From above

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relations, it is clear that the cationic field strength is a major factor to determine the CTE of glass.

In this paper, the BaO–CaO–SiO_2–Al_2O_3-based seal glass (BCSA) [13,14], SrO–SiO_2–Al_2O_3-based seal glass (SSA) [15,16], and SrO–CaO–SiO_2–Al_2O_3-based seal glass (SCSA) [17,18] were used as sealants in the cells, because the three glasses and glass-ceramic systems show the best sealing performance with other cell components. The CTEs of the three glasses and glass-ceramic systems were calculated with the two methods, and then the calculated results were compared with the experimental results, where we found the relations between compositions, average field strength and the CTE. The CTE_A is the CTE of glasses calculated by the Appen method; the CTE_F is the CTE of glasses calculated by the Average Field Strength Method; and CTE_E is the actual experimental result. Some of the glasses in the three systems were selected for the following experiments.

2. Experimental procedure

2.1. Glass preparation

BCSA-based seal glass, SSA-based seal glass and SCSA-based seal glass were chosen as the starting materials because of their good glass-forming properties, chemical stability and thermal stability, especially their high coefficients of thermal expansion. The raw materials of the three series of glasses are shown in Table 1. All of the glasses were prepared by melting the thoroughly blended constituent compounds in a platinum crucible at 1500 °C for 2 h under static air. The constituents CaO, BaO, Al_2O_3, B_2O_3, La_2O_3, and SiO_2 were obtained from Chemical Company (Zhongguancun Chemical Company, Beijing, china) in analytical grade. Parts of the glass melts were poured into a graphite die, cooled, then annealed in air for 3–4 h to eliminate residual thermal stresses, and then were cut into rectangular blocks of 5 mm×5 mm×25 mm (for measurement of the CTE). The CTEs of each glass were measured with a dilatometer (DIL 402C, Nietzsche, Germany) on the rectangular blocks, with a heating rate of 10 °C/min (from room temperature (Tr) to glass transition (Tg)). According to instrumental error, LVDT sensitivity and operational error, the error of the CTEs was around of 0.5×10^{-7} K^{-1}.

2.2. Calculation of CTE

2.2.1. Appen method

According to the Appen method [9,10], the CTE of glass is given as:

$$CTE_A = \frac{\sum \alpha_i N_i}{\sum N_i} \tag{1}$$

where, CTE_A is the coefficient of thermal expansion of glass. α_i is the linear coefficient of thermal expansion of oxide. α_i of the oxide can be found in Table 2. N_i is the molar fraction of oxide i.

The α_{SiO_2} in formula (1) will change with glass structure because the glass network connectivity decreases gradually with the increase of alkaline earth oxides content in glass. The coefficient α_{SiO_2} of SiO_2 can be expressed by:when $N_{SiO2}>67$ mol%, α_{SiO_2} can be expressed as:

$$\alpha_{SiO_2} = [38.0-1.0(N_{SiO2}-67)]\times10^{-7} \tag{2}$$

when $N_{SiO2}<67$ mol%, α_{SiO_2} can be expressed as:

$$\alpha_{SiO_2} = 38.0\times10^{-7}. \tag{3}$$

When the glass contains B_2O_3, the calculation coefficient of B_2O_3 will become very complicated. α_{B_2O3} has a close relationship with the ratio ψ of metal oxide to B_2O_3.

$$\psi = \frac{N_{M_2O}+N_{MO}-N_{Al_2O_3}}{N_{B_2O_3}}. \tag{4}$$

M_2O represents the alkaline oxides: Li_2O, Na_2O, and K_2O and MO represents the alkaline earth oxides: CaO, BaO, and SrO.

And if $\psi>4$, the coefficient α_{B_2O3} of B_2O_3 is given by:

$$\alpha_{B_2O_3} = 50.0\times10^{-7}. \tag{5}$$

If $\psi<4$, the coefficient α_{B_2O3} of B_2O_3 is given by:

$$\alpha_{B_2O_3} = [12.5(4-\psi)-50]\times10^{-7}. \tag{6}$$

Therefore, the CTE of all glasses can be calculated with the above equations in the BCSA-based seal glass system, SSA-based seal glass system and SCSA-based seal glass system. The Appen method starts with glass constituents which have different CTE coefficients. Some CTEs of major constituents are listed in Table 2 [19].

2.2.2. The Average Field Strength Method

The CTE of the glass are caused by the thermal vibration of glass particles and the increase of the dot spacing with the increase of temperature. The increase of the dot spacing is carried out against the force between cation and oxygen anions [11,12]. The force is the bond strength of M−O. The bond strength of M−O is determined by the cationic field strength. So the CTE of glass must have a relation with the field strength of all cations in glass. From above relations, it is clear that the cationic field strength is a major factor to determine the CTE of glass. The relation between the coefficients of thermal expansion of oxide α_i and the force (the attraction) can be expressed in the Equation:

$$\alpha_i = A_i\frac{Z^-Z^+}{r^2} \tag{7}$$

where, α_i is the coefficient of thermal expansion of oxide; A_i is defined as attraction constant coefficient; Z^- and Z^+ are the valences of cation and

Table 1
Glass compositions (by mol%).

Glass no.	BaO	SrO	CaO	SiO_2	B_2O_3	Al_2O_3	La_2O_3
G1	20		20	24	24	8	4
G2	16		16	42	14	8	4
G3	28		16	30	15	7.5	3.5
G4	24		24	30	10	8	4
G5		36		41	13	8	2
G6		40		33	17	8	2
G7		40		25	25	8	2
G8		24	16	33	17	8	2
G9		28	16	31	15	8	2
G10		24	16	25	25	8	2

Table 2
Coefficient of thermal expansion of major compositions.

Compositions	SiO_2	B_2O_3	BaO	CaO	SrO	Al_2O_3	La_2O_3
CTE	5–52	−50–150	200	130	160	−30	60

Table 3
Field strength (F) and ionic radius (R) of cations of major compositions.

	Si^{4+}	B^{3+}	Ba^{2+}	Ca^{2+}	Sr^{2+}	Al^{3+}	La^{3+}
F	1.56	1.52	0.24	0.34	0.27	0.97	0.42
R	0.26	0.12	1.36	1.00	1.16	0.53	1.06