PREPARATION AND CHARACTERISTICS OF A GLASS SEALANT FOR IT-SOFC

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ABSTRACT

Intermediate temperature plate type solid oxide fuel cells (IT- pSOFC) are operated at 500~850°C, and the working gases between the two sides of electrolyte, fuel in anode chamber and air in cathode chamber, must be separated, so that a hermetic seal between cell components is essential. In this paper, a glass system based on SiO2-B2O3-Al2O3-Na2O-PbO2-ZnO was prepared and the contents were optimized to determine the best material named T24. The softening point and viscosity at high temperature calculated based on thermal expansion curve are 840 K and 10^5 Pa.s (at 1198 K), respectively. The optimum sealing temperature range is between 1138 and 1173 K. The particle size distribution curves of powders ball-milled for different time were measured by laser light scatter method. After sealing, T24 glass sealant adhered with YSZ electrolyte well and there were no perforative pores in the sealant. The open circuit voltage of single cell sealed with this sealant was near theoretical value.

INTRODUCTION

Solid oxide fuel cell (SOFC) is a high efficiency and low pollution power device which can convert chemical energy into electrical energy directly (1). In planar solid oxide fuel cells (SOFCs), gas-tight seals applied along the edges of each cell and between the fuel cells stack and the gas manifolds are essential in order to prevent gas mixing during operation. The sealing materials must obey some strict requirements (2,3), including gas tightness, high stability to the fuel and cell components, electrically insulating, a thermal expansion coefficient matching other main SOFC materials, a suitable viscosity and good adherence to the components (mainly stainless steel, zirconia and Ni/YSZ). From consideration of these conditions, some noble metals (4) and glasses-ceramics (2,3) may be candidate materials. Considering the cost and long term chemical stability, glass ceramics seem the most appropriate materials for sealing SOFCs. In this paper, an investigation was carried out on the preparation and characteristics of a glass sealant for SOFCs. The basic physical properties, e.g. thermal expansion, electrical resistivity etc. and the performance concerning the sealing of SOFC were studied. The viscosity at high temperature was calculated from the analysis of thermal expansion curve.
Chemical purity powders of SiO$_2$, Al$_2$O$_3$, CaO, Na$_2$B$_4$O$_7$.10H$_2$O, PbO$_2$ and ZnO were used as starting materials to synthesize the glass sealant. The powders were weighed according to the composition listed in Table 1, and milled in an agate planetary ball mill for 4 h. The milled powders were calcined in a crucible at 600°C for 8 h to form an initial fused block. The fused block was milled for 4 h to grind it into a homogeneous mixture, and then calcining (at 650°C, 700°C, 750°C and 800°C for 8 h) and milling (4 h each time) were repeated in turn. After the last calcining, the fused glass was quenched into cold water and smashed into small pieces (less than 2 mm in size).

Table 1. Components ration of T24.

| components | SiO$_2$ | Al$_2$O$_3$ | CaO | Na$_2$B$_4$O$_7$.10H$_2$O | PbO$_2$ | ZnO |
|------------|---------|-------------|-----|--------------------------|---------|-----|
| weight%    | 54.6    | 10.3        | 2.1 | 23                       | 7.2     | 2.8 |

The small glass pieces were filtered with a screen (No. 10) and milled in an agate planetary ball mill for 0.5 h~8 h. The particle size distribution curves of the powder milled at different times were measured with a Malvern Mastersizer 2000 laser particle size analyzer using water as dispersant. The milled powders were pressed into a disk (13 mm in diameter and 2 mm in thickness) and a bar (6 mm in diameter and 6 mm in height) for electrical measurement. Thermal expansion curve was measured using a Netzsch DIL 402C/3/G dilatometer at 50~650°C in air. In the thermal expansion experiment, an alumina sample holder was used and the load on the sample surface by pushrod was 0.3N. The electrical resistivity of T24 glass was measured using Solartron 1260 impedance-gain analyzer combined with 1287 electrochemical interface between 400°C and 800°C with an interval of 50°C. In order to test the sealing effect, a single fuel cell was sealed using T24 glass at 900°C. An yttria stabilized zirconia (YSZ) disk with Ag electrodes on both sides was assembled on one side of a ceramic tube as a test cell, and the operating temperature range was 600-800°C.

RESULTS AND DISCUSSION

Particle size distribution

Fig. 1 shows the particle size distribution curves (PSDC) of T24 glass powder ball milled for different times. It can be seen that the ball-milling time affects the glass powders' particle size distribution. For the crushed powders filtered through screen (No. 10 mesh) without ball-milling, the size distribution range is from 1.23μm to 1760 μm, and the volume mean size is about 250 μm, so most glass particles are very big. However, after ball-milling even for a very short time, the bigger pieces got crushed into smaller ones; for example, upper size limit of the sample milled for 0.5 h became 178 μm, and at the same time, the lower limit retained the value of 1.23 μm. There are two peaks in the PSDC of milled samples: one position is less than 10 μm and the other is between 10 μm to 70 μm. As the milling time increases, there is no obvious movement on the lower limit and peak, while the upper limit and peak shift markedly. It means that the ball-milling process tends to crush and grind the bigger particles into small ones. After ball milling for...
8 h, there is only one peak (7.56 - 10 μm) on the PSDC. For general sealing application, glass powders with this size are acceptable.

Figure 1. The particle size distribution curves of T24 powders ball-milled for different times.

Thermal Expansion

Fig. 2 shows the thermal expansion curve of T24 glass. In the temperature range of 100-500°C, it expands linearly and the thermal expansion coefficient (TEC) is $10.12 \times 10^{-6} \text{K}^{-1}$ which is near to that of other SOFC components, e.g. TEC of YSZ is about $(10.2-10.8) \times 10^{-6} \text{K}^{-1}$. However, the curve inflects upward above 500°C and drops down at 584°C. This phenomenon is related to the transformation of glass and the following calculations are based on the analysis of this curve. In fact, the glass material becomes soft and flexible at temperatures above 500°C, so it is easy to match with other components nearby.

Calculation of Viscosity from the Thermal Expansion Data

Since the thermal expansion curve shows that T24 glass is a typical annealed glass, the softening temperature ($T_s$) can be obtained easily from the curve, the value of $T_s$ is 567.1°C (840.25 K). By fitting the two linear parts of thermal expansion curve, the transition temperature ($T_g$) can be obtained, and the value is 525.8°C. According to the simple liquid theory (Mott and Gurney), there is a relationship between pseudo-critical temperature ($T_k$) and the absolute melt point ($T_m$)[5]:

$$\frac{T_k}{T_m} = 2/3 \quad (1)$$

This rule can be applied on the glass systems of molecular compounds and polymers, it is also suitable for the inorganic compound glasses. Even sometimes when the glass is not a compound, this rule still can be used and the $T_m$ should be replaced with liquid temperature ($T_l$). Regarding $T_k$ as $T_g$, the rule can be presented as:
\[ T_g / T_l = 2/3 \]  

Figure 2. The thermal expansion curve of the glass T24.

Hence, the melt temperature can be calculated: \( T_m = 1198.425 \text{K} \), in Celsius scale, \( T_m = 925.3 \text{°C} \). Thus the three temperatures of glass point, softening point and melt point have been obtained. The viscosity values at \( T_g \), \( T_s \) and \( T_m \) are fixed and independent of materials:

\[
\begin{align*}
T_g &= 798.95K \rightarrow \eta_g = 4 \times 10^{14} \text{Pa} \cdot \text{s} \\
T_s &= 840.25K \rightarrow \eta_s = 4.5 \times 10^7 \text{Pa} \cdot \text{s} \\
T_m &= 1198.425K \rightarrow \eta_m = 10^5 \text{Pa} \cdot \text{s}
\end{align*}
\]  

Then, using Fulcher's empirical equation:

\[
\log \eta = A + \frac{B}{T - T_0} \tag{4}
\]

In this equation, \( A \), \( B \) and \( T_0 \) are all constant. Using the parameters in Eq. (3), the constants can be obtained by resolving coupled equations. Thus, the relationship of viscosity and temperature is obtained:

\[
\log \eta = 4.6 + \frac{184.4}{T - 780.6} \tag{5}
\]

Viscosity-temperature curve of the glass T24 calculated with eq. (5) is shown in fig. 3.
Figure 3. The viscosity-temperature curve of the glass T24.

Electrical Conductivity

Table 2 shows the resistivity data of T24 glass at intermediate temperatures. It can be seen that the resistivity of this material decreases with increasing temperature as most glasses. The resistivity is high enough at temperatures lower than 700°C for application in IT-SOFC (2), while it is appreciably low at 800°C. Fig. 4 shows the Arrhenius plot of the electrical conductivity for T24 glass. By fitting the InσT and 1/T data as a linear relationship, the activation energy of electrical conduction is obtained.

Table 2. Resistivity data of T24 glass at different temperatures.

| Temperature (°C) | 400  | 500  | 600  | 700  | 800  |
|-----------------|------|------|------|------|------|
| Resistivity (Ω·cm) | 1.10×10^6 | 1.24×10^5 | 1.59×10^4 | 2.90×10^3 | 9.16×10^2 |

Figure 4. Arrhenius plot of the electrical conductivity for T24 glass.
Fuel Cell Sealing and Testing

To examine the sealing effect of this material, a single fuel cell was sealed using T24 glass. As fig. 5 shows, the open circuit voltage (OCV) is between 1.042V to 1.086V in the temperature range of 600-800°C and there is no obvious change during a thermal cycle. It proves that the sealing is gas tight. To research the microstructure of sealing glass and electrolyte interface, an intersection SEM photo of T24 glass/YSZ interface has been taken as fig. 6 shown. It can be seen that the T24 glass contacts with YSZ well. Although the glass has been sintered relatively dense, there are still some closed pores filled with small glass particles in the glass region. It means that higher sealing temperature may be needed.

![Figure 5. Open circuit voltage of a fuel cell sealed with the glass T24.](image)

![Figure 6. SEM of the interface of glass T24 and YSZ electrolyte.](image)
CONCLUSIONS

In conclusion, T24 glass has a TEC near other SOFC components below 500°C and it becomes flexible above 500°C. $T_s$, $T_g$, $T_m$ can be calculated from the thermal expansion curve and the viscosity in high temperature range can be obtained using the Fulcher's empirical equation. The resistivity below 700°C is over $2.90 \times 10^3 \Omega\cdot \text{cm}$ which is sufficient for IT-SOFCs. The open circuit voltage of fuel cell sealed with T24 is near the theoretical value, so a gas tight sealing can be achieved using the T24 glass.

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