A New Sealant Material for Solid Oxide Fuel Cells Using Glass-Ceramic

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1. Introduction

Solid oxide fuel cells are positioned to play an important role in electrical power generation in the near future because they efficiently convert the chemical energy of a fuel by electrochemical oxidation at 800–1000°C. They can provide the high energy conversion and low pollutant emissions necessary for meeting CO2 reduction targets. The basic unit of an SOFC consists of two porous electrodes (the anode and the cathode) separated by a dense electrolyte. SOFC configurations are generally divided into two types: the planar-type and the tubular type. Furthermore, the planar cell arrangement is electrochemically rational and suitable for manufacturing in stacks. When building planar SOFC stacks, the cells are separated from one another by a dense separator which contains channels for fuel and oxidant flow fields.

In practice, gas-sealing technology is critical to the performance of planar-type SOFCs. Gas-tight seals must be formed along the edges of each cell and between the fuel cell stack and gas manifolds. The sealant materials must maintain the gas-tight seal at high operation temperatures and under both highly reducing and oxidizing atmospheres. The chemical stability of these materials as well as their thermal expansion coefficients must also be compatible with the other SOFC components.

In general, melt sealing techniques are used when forming planar-type SOFCs, because they are expected to provide a strong gas-tight seal between SOFC components. Glass1-4 and glass-ceramic5-7 materials are commonly used as the sealant materials, but their softening temperatures are lower than or the same as the operating temperatures of the SOFCs. This causes difficulties because the melting glass readily reacts with the yttria-stabilized zirconia (YSZ) electrolytes and lanthanum chromite (LC) separators during operation.5,8 A new sealing method, therefore, has to be developed.

The present study reports a sealant which is able to keep the system sealed and retain high viscosity in comparison with the melt sealing method during operation of SOFCs by use of glass-ceramic materials. Our attention has been focused on the study of softening and crystallization behavior in glass-ceramics.9 In Fig. 1, the softening and crystallization temperatures of glass powder sealants is presented schematically. The glass particles before crystallization are formed in the gas-sealing area. During heating at a temperature of about 800°C, the glass softens and wets the SOFC components. As a consequence of this softening and wetting, the glass particles bond with the SOFC components and achieve a gas-tight seal. At higher temperatures, e.g., 900°C, bulk crystallization occurs and the viscosity of the residual glass phase also increases. This crystalline network within a glassy phase results in the being able to glass-ceramic seal gases and remain in a solid-like state during SOFC operation. The aim of the present study is to develop a new sealant material using a CaO-Al2O3-SiO2 glass-ceramic, and to show that it provides a good gas-tight seal and is chemically stable with the other SOFC components, e.g., YSZ electrolytes and LC separators.

2. Experimental

2.1 Glass preparation

Glass powder in the CaO-Al2O3-SiO2 system was made by a conventional glass-making technique. A composition of 19.6 mol% CaO, 9.5 mol% Al2O3, 63.6 mol% SiO2, 7.3 mol% R2O was selected, where R2O represents fluxes such as Na2O, K2O, BaO, B2O3, and Sb2O3. The commercially available raw materials were mixed, then melted and held at 1600°C for 2 h in a platinum crucible and finally quenched in the molds. The quenched glass was ground to fine powder for use as the sealant raw material.

2.2 Physical properties

The softening and crystallization temperatures of the glass were determined by differential thermal analysis (DTA). The powder samples were heated up to 1300°C with a heating rate of 10°C/min. The softening temperature of the glass-ceramic after crystallization was also determined by DTA. The softening behavior of the glass-ceramic...
before and after crystallization was observed by a high temperature microscope (Leitz). The cubic-shaped bulk samples were placed on top of a commercial YSZ plate and their shapes observed at various temperatures. The crystalline phases present in the sealant materials were examined by X-ray diffraction (XRD). Thermal expansion data were obtained with a thermal mechanical analyzer (TMA) using polished bar specimens after crystallization. Heating rate was set at 10°C/min.

2.3 Sealing tests

Figure 2 shows the arrangement of the sealing test system. The test was carried out at room temperature using air and helium gases. The sealing test piece was prepared as follows. The glass powder was uniaxially pressed into a pellet of 14 mm in diameter by applying a pressure of 30 MPa. The 5 mm thick pellet was placed on top of a commercial YSZ pellet of 13 mm in diameter and 1 mm in thickness. A hole of 3 mm in diameter was drilled at the center of the YSZ pellet to examine the sealing behavior of the glass-ceramic. This combined test piece was heated at 200°C/h (3.3°C/min) up to 1100°C without loading in order to join the glass-ceramic to the YSZ pellet and allow crystallization of the sealant. The holding time at maximum temperature was 2 h and the cooling rate was 200°C/h (3.3°C/min). The interface between the glass-ceramic sealant and YSZ was observed by a scanning electron microscope (SEM).

2.4 Chemical stabilities

Specimens for testing chemical stability were prepared as follows. The glass powder was uniaxially pressed into pellet using similar conditions to those described in Section 2.3.

One pellet each was then placed on top of the commercial YSZ and LC pellets. These test stacks were heated at 1100°C for 2 h without loading to allow joining and crystallization of the glass-ceramic. Heating and cooling rates were 200°C/h (3.3°C/min). The test pieces were further annealed at 1100°C for 500 h. The test bonds before and after annealing were embedded in epoxy resin and finely polished to observe the interface. The reactivity at the interface was evaluated using an electron probe microanalyzer (EPMA).

### Table 1. Softening and Crystallization Temperatures of the Glass and Glass-Ceramic

<table>
<thead>
<tr>
<th>Glass-ceramic</th>
<th>Softening temperature / °C</th>
<th>Crystallization temperature / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>750</td>
<td>1020</td>
</tr>
<tr>
<td>After crystallization</td>
<td>1160</td>
<td>—</td>
</tr>
</tbody>
</table>

3. Results and discussion

The physical properties of the glass-ceramic are listed in Table 1. Softening and crystallization temperatures of the glass were 750°C and 1020°C, respectively. Partial crystallization of the glass to form the glass-ceramic resulted in an increased softening temperature of 1160°C.

Figure 3 shows observations using the high temperature microscope of the glass material before crystallization at various temperatures. The shape began to deform at 900°C, as seen in Fig. 3(b). This behavior is as-expected, since the softening temperature of the glass is about 750°C. This state corresponds to the schematic shown in Fig. 1(b) and it is expected that at this temperature the glass will start to bond to the YSZ plate. Next, the interfacial energy of the glass decreased at 1000°C to a level sufficient for the glass to wet the YSZ pellet and form a seal. Crystallization started at about 1020°C; hence the shape of the glass pellet at 1100°C is not significant by different from that at 1000°C. After heat treatment of 1100°C for 2 h, the main crystalline phases embedded in the residual glass were anorthite (CaAl2Si2O8) and wollastonite (CaSiO3).

Heating-microscope observations of the glass-ceramic after crystallization at various temperatures are shown in Fig. 4. No deformation of the glass-ceramic can be seen in Fig. 4(b), although the original glass softened at 900°C. As shown in Fig. 4(d), the glass-ceramic maintained its shape even at 1100°C, since its softening is about 1160°C. Therefore, the glass-ceramic material is able to seal the system while remaining in an essentially solid state during operation of the SOFCs. This sealing method is expected to sup-
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Press reaction of the sealant with the SOFC components, because the high viscosity sealants seem to have superior stability than those with low viscosities.

Figure 5 shows results of the sealing test for the glass-ceramic material. After heat treatment at 1100°C for 2 h, the sealant material was well joined to the YSZ pellet. It was confirmed that the glass-ceramic material provides good sealing behavior, because no decrease in pressure caused by a gas leak was observed.

The microstructure of the interface between the glass-ceramic sealant and YSZ is shown in Fig. 6. This micrograph shows good connection without gaps between the two components. Some closed pores can be observed in the sealant material.
Fig. 7. SEM and EPMA images of the interface between the glass-ceramic and YSZ electrolyte.

Fig. 8. SEM and EPMA images of the interface between the glass-ceramic and LC separator.
Figure 7 shows the results of chemical stability tests for the glass-ceramic sealant with YSZ. As seen in Fig. 7(a), the interface between the glass-ceramic and YSZ after joining at 1100°C for 2 h is clean and free of any reaction products. It has been reported that silica reacts with YSZ to form ZrSiO₄ when using Pyrex glass as a sealant material.⁸ In the case of the CaO-Al₂O₃-SiO₂ glass-ceramic, however, the diffusion of Si into the YSZ pellet was not observed and the condition of the interface was unchanged even after annealing at 1100°C for 500 h, as shown in Fig. 7(b). Therefore, it can be confirmed that this sealant material possesses good chemical stability in contact with the YSZ electrolyte. It should be noted, however, that a difference in Si concentration in the glass-ceramic was observed. This is caused by nucleation of the crystalline phases.

Results of chemical stability tests for the glass-ceramic sealant bonded with LC is shown in Fig. 8. Although the glass-ceramic was well connected to the LC pellet, the interface after annealing at 1100°C for 500 h was as clean as that before annealing. Horita et al.⁹ reported that the silica in Pyrex glass easily reacts with LC to form calcium silicates, lanthanum silicates, and chromium oxides at the reaction zone. In contrast, diffusion of Si in the CaO-Al₂O₃-SiO₂ glass-ceramic into LC and precipitation of Cr at the interface were not observed in this study even after annealing. The chemical stability of silica with the SOFC components seems to be influenced by its viscosity. Horita et al.¹⁰ also reported that α-quartz did not react with LC at 1000°C, although the silica in Pyrex glass easily reacted with LC. The softening temperature of α-quartz (over 1600°C) is much higher than that of Pyrex glass (about 930°C).¹¹ Therefore, it is predicted that the stability of the sealant material is improved by increasing the viscosity of the silica phase. The softening temperature of the residual glass in the CaO-Al₂O₃-SiO₂ glass-ceramic after crystallization (about 1160°C) used here was also higher than that of Pyrex glass. Therefore, it is concluded that the high viscosity of the glass-ceramic depressed the reaction between the sealant and SOFC components.

The thermal expansion behavior of the glass-ceramic sealant after crystallization is given in Fig. 9. A small amount of deformation was observed at about 700°C, which is attributed to the glass transition of the residual glass. The average thermal expansion coefficient was 7.7×10⁻⁶/°C, which is a little lower than those for the SOFC components (9.5–11.0×10⁻⁶/°C). The matching of thermal expansion behavior with the SOFC components is one of the most important factors when assessing the suitability of sealing materials for use in SOFCs. Modification of the thermal expansion behavior of the glass-ceramic sealant is in progress. Preliminary results suggest that addition of ceramics such as YSZ is effective in increasing the thermal expansion coefficient of the sealant materials.

4. Conclusion
A glass-ceramic based on the CaO-Al₂O₃-SiO₂ system was used as the sealant material in an SOFC. The glass was formed in the area to be sealed, and subsequently softened and joined to the SOFC components during heating. At higher temperatures, bulk crystallisation occurred and the viscosity of the resulting glass-ceramic increased accordingly. This phenomenon enabled the glass-ceramic to remain solid-like state and impermeable to gases under conditions similar to those experienced during SOFC operation. Consequently, this new sealant material provided a good gas-tight seal and chemical stability to the YSZ electrolytes and LC separators.

References