Effect of Nb$_2$O$_5$ doping on improving the thermo-mechanical stability of sealing interfaces for solid oxide fuel cells

Qi Zhang, Xinhang Du, Shengwei Tan, Dian Tang, Kongfa Chen & Teng Zhang

Nb$_2$O$_5$ is added to a borosilicate sealing system to improve the thermo-mechanical stability of the sealing interface between the glass and Fe-Cr metallic interconnect (Crofer 22APU) in solid oxide fuel cells (SOFCs). The thermo-mechanical stability of the glass/metal interface is evaluated experimentally as well as by using a finite element analysis (FEA) method. The sealing glass doped with 4 mol.% Nb$_2$O$_5$ shows the best thermo-mechanical stability, and the sealing couple of Crofer 22APU/glass/GDC (Gd$_{0.2}$Ce$_{0.8}$O$_{1.9}$) remains intact after 50 thermal cycles. In addition, all sealing couples show good joining after being held at 750 °C for 1000 h. Moreover, the possible mechanism on the thermo-mechanical stability of sealing interface is investigated in terms of stress-based and energy-based perspectives.

Solid oxide fuel cells (SOFCs) are regarded as having great potential for fuel flexibility, high energy conversion efficiency and environmental friendliness. Glass and glass ceramic sealing materials are most intensively used in planar SOFCs, and they are required to have desirable chemical and thermo-mechanical stability under typical operating conditions. Especially, the thermo-mechanical stability is critical for the SOFC stacks since significant difference thermal expansion of glass and cell components can cause high residual stress as well as crack at the sealing interfacial, which consequently impairs the cell integrity.

However, there is a practical obstacle of developing reliable sealing glass because of the occurrence of interfacial reaction between the sealing glass and other components of SOFCs, leading to performance degradation of SOFC stacks. In particular, the interaction between glass-ceramics and Fe-Cr alloy interconnect is of a great concern. The transport of Cr from the metallic interconnect to form a Cr$_2$O$_3$ surface layer contributes to the formation of chromates, such as BaCrO$_4$ and SrCrO$_4$. These chromates possess a coefficient of thermal expansion (CTE) of 18–20 × 10$^{-6}$·K$^{-1}$ substantially higher than ~10.0–12.0 × 10$^{-6}$·K$^{-1}$ that of the sealing glass, leading to fracturing of the glass/metal interface. In general, the thickness of the reaction zone (or inter-diffusion zone) and the interfacial bond strength are an indicative of the thermo-mechanical stability at the glass/metal interface.

Previous studies have shown that strontium ions in an open glass network can react with the Cr$_2$O$_3$ layer and contribute to the sealing failure. Conversely, Nb$_2$O$_5$ falls within the intermediate class of glass-forming oxides. Part of Nb$^{5+}$ ions exist in NbO$_6$ octahedra as network formers, while the rest is present in NbO$_x$ octahedra. The NbO$_x$ will convert to NbO$_y$ when the Nb$_2$O$_5$ content is greater than 8 mol.%, causing an increase in non-bridging oxygen. On the other hand, the borosilicate glass with Bi$_2$O$_3$ shows excellent glass sintering ability for SOFC operating application. The borosilicate glass system with Bi$_2$O$_3$ dopant also stabilizes the B-O network, which is beneficial for reducing the detrimental interfacial reaction between sealing glass and cathode. Moreover, the B$_2$O$_3$-SiO$_2$-Bi$_2$O$_3$ glass system with ZnO dopant inhibits the chemical interaction between glass and interconnect. Therefore, appropriate amount of 8 mol.% Nb$_2$O$_5$ (2, 4 and 8 mol.%) is added to a B$_2$O$_3$-SiO$_2$-Bi$_2$O$_3$ glass system to condense the glass network structure in this work. And the effect of Nb$_2$O$_5$ on the chemical and thermo-mechanical stability of the sealing glass/metal interface is clarified using finite element analysis (FEA) and thermal cycling experiments.

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Results and Discussion

Mechanical properties. The interfaces of the sealing glass/cell components are required to withstand 70–200 kPa thermo-mechanical stress during cell operation. Therefore, the resistance to thermal cycling can be considered as an indicator for evaluating the thermo-mechanical stability of the sealing interface. The glass#4 Nb$_2$O$_5$ sample retains its good sealing ability after 50 thermal cycles (Fig. 1a), while fractures appear at the interface between Crofer 22APU and other glass. Microcracks are also observed between the needle-shaped phases (indicated by the arrows, Fig. 1b).

To investigate the changes in thermal-mechanical properties of the sealing glass, FEA was performed on the distribution of thermal stress at the glass/metal interface after 50 thermal cycles, as shown in Fig. 2a. The maximum thermal stress between the sealing glass and Crofer 22APU after the 50 thermal cycles increases from 7805 MPa to 20819 MPa as the Nb$_2$O$_5$ content increases from 0 to 8 mol.%. High stress mainly distributes at the corners, and the maximum stress is observed in the glass#8 Nb$_2$O$_5$ sample due to its most distinctive CTE mismatch with the interconnect (~38%).

Figure 2b shows the displacements for the sealing couple of glass/interconnect after thermal cycling for 50 times. It is clear that the maximum displacement appears at the corner of sealing couple and the maximum displacement increases from 9.10542 mm to 19.8688 mm with the Nb$_2$O$_5$ content increasing. In brief, the crack forms initially at the corner of sealing couples and sealing couple of glass glass#8 Nb$_2$O$_5$ is easiest to fail according to the FEA analyst.

We also stimulated in the case of one thermal cycle using the FEA model. The maximum thermal stress due to CTE mismatch between the sealing glass and Crofer 22APU for the glass without Nb$_2$O$_5$ is 64 MPa, and increases to 133 MPa for the glass doped with 8 mol.% Nb$_2$O$_5$. These stress values are in the same magnitude to those reported in the literature. For example, Lin et al. investigated the thermal stress distribution due to CTE mismatch of the sealing glass-ceramics and metallic interconnect of SOFC stacks. The sample was cooled from 800 °C to room temperature, and then heated to 600 °C followed by start-up for cell operation. The maximum thermal stress of sealing glass-ceramics after one thermal cycle is about 20~100 MPa. Jiang et al. also reported the maximum thermal stress for the sealing glass-ceramics is about 80 MPa at 754 °C and 60~80 MPa at 854 °C.

Figure 3a shows the XRD patterns of glass-ceramics held at 750 °C for 1000 h. Crystalline phases including SrAl$_2$Si$_2$O$_8$ (JCPDS card no. 70–1862), CaSiO$_3$ (JCPDS card no. 27–0088), Bi$_2$B$_2$O$_6$ (JCPDS card no. 25–1089).
Figure 2. (a) The stress distribution and its magnitude at the glass/metal interface after thermal cycling for 50 times. (b) The displacement for the sealing couple between glass and Crofer 22APU after thermal cycling for 50 times.

Figure 3. (a) XRD patterns of glass-ceramics held at 750 °C for 1000 h. SEM images and EDS elemental line scans of glass-metal interfaces held at 750 °C for 1000 h. (b) glass#2 Nb2O5, (c) glass#4 Nb2O5, and (d) glass#8 Nb2O5.
and Sr$_2$SiO$_4$ (JCPDS card no. 38–0271) appear in the glass without Nb$_2$O$_5$, whereas SrAl$_2$Si$_2$O$_8$, CaSiO$_3$, Sr$_2$SiO$_4$, CaNb$_2$O$_6$ (JCPDS card no. 11–0619), Bi$_2$O$_3$Nb$_2$O$_8$ (JCPDS card no. 33–0210), Ca$_2$B$_2$Si$_2$O$_8$ (JCPDS card no. 48–1885) and CaB$_2$Si$_2$O$_8$ (JCPDS card no. 72–2298) are present in the Nb$_2$O$_5$ doped glass.

Shown in Fig. 3b to d are the SEM images and EDS profiles at the glass/metal interface held at 750 °C for 1000 h. The EDS results are summarized in Table 1. Significant amounts of Ca and Nb are detected in the needle phase regions (point#1 in Fig. 3c and point#2 in Fig. 3d). In addition, the number of needle phases increases with increasing Nb$_2$O$_5$ content. The CaNb$_2$O$_6$ phase can be characterized with various morphologies including microneedles or ellipsoid-like shapes, depending on the processing conditions\textsuperscript{19,20}. This confirms the formation of a CaNb$_2$O$_6$ phase in Nb$_2$O$_5$-doped glass-ceramics, in agreement with the XRD results. It has been reported that the CaNb$_2$O$_6$ phase shows a low thermal expansion (\(\alpha_T = 2.80 \times 10^{-6} \text{ K}^{-1}\)), which explains the fact that the CTE decreases with the increase of Nb$_2$O$_5$\textsuperscript{21}.

Moreover, some microcracks are formed surrounding the needle phases (CaNb$_2$O$_6$) in glass#4 Nb$_2$O$_5$ (see Fig. 1b). Residual stresses can be released upon the formation of microcracks, which increases the fracture resistance of glass\textsuperscript{22–24}. Thus, the microcracks around the needle-shaped CaNb$_2$O$_6$ crystals are also beneficial to release the residual stress at the interface.

### Interfacial reaction

The formation of chromate phases is often observed at the glass/metal interface in the air side of SOFCs\textsuperscript{25}. Figure 4a shows the quantitative analysis of the Cr$_2$O$_3$/glass reaction couples held in air at 650 °C. The reaction decreases with increasing the Nb$_2$O$_5$ content. As demonstrated previously, the mobility of Sr\textsuperscript{2+} ions in the glass is reduced due to condensation of Sr in the glass network structure, which in turn reduces their reactivity with Cr\textsuperscript{6+}. Therefore, the improved chemical compatibility between the sealing glass and Cr$_2$O$_3$ is most likely due to the condensed glass structure by the Nb doping, as the glass remains amorphous at 650 °C (Fig. 1b).

Table 2 shows the thermal and mechanical properties of glass and glass-ceramics. Some previous articles have reported that the CTE, glass transition temperature \(T_g\) and glass softening temperature \(T_s\) are intimately associated with the connectivity of the glass network. The increase in non-bridging oxygen and decrease in glass network connectivity will result in the decrease in \(T_g\) and \(T_s\) as well as increase in CTE\textsuperscript{27,28}. Thus, in this work, the changes of \(T_g\), \(T_s\) and CTE of quenched glass indicate the condensed network structure of sealing glass by Nb$_2$O$_5$ doping. Similarly, it has been reported that some non-bridging oxygens in glass network reduces the connectivity of glass network and decreases the density of glass. The hardness of glass also increases as the glass network becomes rigid\textsuperscript{29–32}. Hence, the increase in density and Vickers hardness of glass also confirms the strengthened glass network in present work. Figure 5 shows the temperature dependent conductivity plots (\(\log \sigma\) versus 1000 T\(^{-1}\)) for as quenched glass and glass-ceramics, measured in air from 500 to 600 °C. The conductivity of glass and glass-ceramics meets the insulating requirement of sealing glass (<10\(^{-4}\)S cm\(^{-1}\)) for SOFCs application\textsuperscript{33}. The decrease in conductivity of glass with increasing Nb$_2$O$_5$ content further confirms the densification of glass network by Nb$_2$O$_5$ doping in present work.

The results of interfacial reaction between glass and metallic interconnect is consistent with changes in thermal, mechanical and electrical properties of the glass material with Nb$_2$O$_5$ doping.

In addition, the thickness of the interfacial reaction zone decreases from \(-4\mu\text{m}\) to \(-2\mu\text{m}\) with increasing Nb$_2$O$_5$ (Fig. 3b–d). The detected Cr contents also decrease from 60 at.% to 37 at.% at the interface (point#3 in Fig. 3b and point#4 in Fig. 3d) with increasing Nb$_2$O$_5$ content. This indicates that the addition of Nb$_2$O$_5$ significantly improves the chemical compatibility between sealing glass and Fe–Cr interconnect.

Fracturing occurs at the interface between the interconnect and the reaction zone (not shown here). Müller \textit{et al.} suggested that the sealing glass should be made as thin as possible, since the maximum energy release rate increases significantly with the increase in the thickness of sealing glass in an interconnect/sealing glass/interconnect diffusion couple\textsuperscript{34}. Regarding the reaction zone as a thin layer, the thinner reaction zone with Nb$_2$O$_5$ dopant should decrease the maximum energy release rate and improve the resistance to crack initiation.

There are two criteria including stress and energy for predicting crack initiation at the interface\textsuperscript{35}. Fracturing will be observed at an interface if the tensile stress is greater than the interface strength, whereas crack initiation will occur at the interface when the energy release rate exceeds the threshold value. Leguill\textit{on et al.} suggested that these two criteria must be considered together to provide a sufficient explanation of fracture conditions\textsuperscript{36}. In this work, the CTE mismatch between glass and interconnect increases with Nb$_2$O$_5$ amount, leading to increased thermal stress. This implies that fracturing is more likely to occur with increasing the Nb$_2$O$_5$ amount according to the strength criterion. On the other hand, Nb$_2$O$_5$ reduces the thickness of the reaction zone, which decreases the maximum energy release rate and thus improves the resistance to crack initiation. Therefore, the sealing couple of Crofer 22APU/glass#4 Nb$_2$O$_5$/GDC shows the best thermal-mechanical stability against the thermal cycling. Moreover, all sealing couples after heat-treatment at 750 °C for 1000 h showed good joining between the glass and the GDC electrolyte.

### Table 1. Quantitative EDS results in Fig. 3 (in at. %).

| Spot | Al | Si | Ca | Sr | Nb | Bi | Fe | Cr | Mn |
|------|----|----|----|----|----|----|----|----|----|
| #1   | 12 | 23 | 22 | 21 | 18 | 5  | 4  | 1  | 1  |
| #2   | 2  | 10 | 6  | 10 | 14 | 14 | 1  | 1  | 1  |
| #3   | 28 | 29 | 60 | 29 | 22 | 37 | 1  | 1  | 1  |
| #4   | 2  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  |

and Sr$_2$SiO$_4$ (JCPDS card no. 38–0271) appear in the glass without Nb$_2$O$_5$, whereas SrAl$_2$Si$_2$O$_8$, CaSiO$_3$, Sr$_2$SiO$_4$, CaNb$_2$O$_6$ (JCPDS card no. 11–0619), Bi$_2$O$_3$Nb$_2$O$_8$ (JCPDS card no. 33–0210), Ca$_2$B$_2$Si$_2$O$_8$ (JCPDS card no. 48–1885) and CaB$_2$Si$_2$O$_8$ (JCPDS card no. 72–2298) are present in the Nb$_2$O$_5$ doped glass.
Figure 6a shows the XRD patterns of glass-GDC powder couples held at 750 °C for 1000 h in air. The main phase in the glass and GDC reaction couples (50:50 w/w) is Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$. This implies that the glass is chemically compatible with the GDC electrolyte. On the other hand, there is observation of cation interdiffusion at the glass/GDC interface.

Figure 6b to d show the micrographs and EDS line scans of the glass/GDC sealing couples held at

![XRD patterns of glass-GDC powder couples](image)

| Sample ID | glass#0Nb$_2$O$_5$ | glass#2Nb$_2$O$_5$ | glass#4Nb$_2$O$_5$ | glass#8Nb$_2$O$_5$ |
|-----------|-------------------|-------------------|-------------------|-------------------|
| CTE($\times 10^{-6}$K$^{-1}$, 200–600 °C) |                      |                   |                   |                   |
| glass     | 12.2 ± 0.1        | 11.1 ± 0.1        | 10.6 ± 0.1        | 10.1 ± 0.1        |
| glass-ceramics | 10.1 ± 0.1  | 9.1 ± 0.1         | 8.7 ± 0.1         | 8.4 ± 0.1         |
| Measured by dilatometer (°C) |                      |                   |                   |                   |
| $T_g$     | 669 ± 5           | 684 ± 5           | 718 ± 5           | 726 ± 5           |
| $T_d$     | 722 ± 5           | 751 ± 5           | 779 ± 5           | 782 ± 5           |
| Density(g cm$^{-3}$) |                      |                   |                   |                   |
| glass     | 3.55 ± 0.01       | 3.56 ± 0.01       | 3.68 ± 0.01       | 3.83 ± 0.01       |
| glass-ceramics 750°C held for 1000 h | 3.31 ± 0.01   | 3.42 ± 0.01       | 3.48 ± 0.01       | 3.69 ± 0.01       |
| Vickers hardness(GPa) |                      |                   |                   |                   |
| glass     | 11.69 ± 0.01      | 12.98 ± 0.01      | 15.97 ± 0.01      | 16.48 ± 0.01      |

Table 2. Thermal and mechanical properties of glass and glass-ceramics.
750 °C for 1000 h, for glass#2 Nb_2O_5, glass#4 Nb_2O_5 and glass#8 Nb_2O_5. The EDS line scan reveals that the inter-diffusion zone is reduced from ~3 μm to ~1 μm with increasing the Nb_2O_5 content. This indicates that the Nb_2O_5 dopant enhances the chemical compatibility between the sealing glass and GDC.

**Conclusions**

In this work, the effect of Nb_2O_5 doping on the thermal-mechanical stability of sealing interfaces is investigated experimentally as well as using FEA simulations. The doping of Nb_2O_5 increases the CTE mismatch between the glass and the interconnect, leading to increased thermal stress. The Nb_2O_5 doping also condenses the glass.
network, reducing the interdiffusion between the glass and the interconnect. This decreases the maximum energy release rate, thereby improving the resistance to crack initiation. Moreover, some microcracks are form around the needle-shaped CaNb2O6 crystals. The presence of microcracks is beneficial to release the residual stress. The insights into the improved thermo-mechanical stability of sealing interfaces by proper addition of Nb2O5 will facilitate the development of reliable sealing materials.

Method
Preparation of glass. The base glass with nominal molar composition of 24.0CaO-24.0SiO2-8.0B2O3
-7.0Al2O3-35.0SiO2-2.0Bi2O3 was melted at 1350°C for 1 h in a platinum crucible, named glass#0 Nb2O5. The melt was immersed in water for quenching and the glass powder was crushed and sieved to a particle size range of 45–53 µm. The glass with Nb2O5 (2, 4, 8 mol.%) doped to the base glass was also prepared as above, and named glass#2 Nb2O5, glass#4 Nb2O5, glass#8 Nb2O5 respectively. Some glass powders were held at 650 °C for 20 h and 750 °C for 1000 h in air. The crystalline phases in the samples were identified using X-ray diffraction (XDS 2000, Scintag, Inc.) with a monochromator Cu Kα radiation (k = 1.54 Å).

Thermal cycling stability and finite element analysis. The Crofer 22APU/glass/Gd0.2Ce0.8O1.9 (Sinopharm Chemical Reagent Co., Ltd.) samples were prepared using a slurry technique, and the sandwiched samples were subjected to thermal cycles for 50 times after heat-treatment at 750 °C for 1000 h in air. A thermal cycle consists of heating the sealing couple from ambient temperature to 750 °C in 30 min, and then cooling in air in another 30 min. The micrographs of the sealing interface after 50 thermal cycles and after polishing were characterized by field emission scanning electron microscopy (FE-SEM; Supra-55, Zeiss, Inc.). FEA was selected to simulate the thermal stress distribution and the displacement caused by the CTE mismatch between different SOFC components in a uniform temperature field, in order to evaluate the thermo-chemical stability of the glass/metal interface.

Characterization of thermal properties of glass and glass-ceramics. The glass transition temperature (Tg), softening temperature (Td), and the CTE (at 200–600 °C) of quenched glass and species held at 750 °C for 1000 h (referred to ‘glass-ceramics’) was obtained using a dilatometer (DIL402C, NETZSCH, Inc.) at a heating rate of 10°C·min⁻¹ in air.

Characterization of interface reaction. A mixture of 10 wt.% Cr2O3 powder and 90 wt.% glass powder was reacted at 650 °C in air, to keep glass in amorphous state. The UV-Vis absorption spectra of the reaction products in aqueous solution were recorded using an Optima 2000 DV (Perkin Elmer, Inc.). The detailed procedure of this interfacial reaction has been described previously37.

The glass was bonded to Crofer 22APU and GDC substrates and held at 750 °C for 1000 h. Micrographs of the sealing interface were obtained using SEM equipped with energy dispersive spectroscopy (EDS; X-Max, OXFORD instruments, Inc.). Kaur et al. reported that the thermal stress is dependent on the thickness of sealing glass, and the deformation due to thermal stress decreases as the thickness of the sealing glass increases from 0.25 to 1.5 mm36. Therefore, the thickness of the sealing glass in this study was kept constant (~250 µm) in all samples as well as in the FEA model. A ~1 g mixture of glass and Gd0.2Ce0.8O1.9 powders (50:50, w/w) was reacted in air at 750°C for up to 1000 h. The crystalline phases in the glass/GDC reaction couples were also analyzed by XRD. The sealing interfaces between glass and GDC were also investigated by SEM.

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Author Contributions
Q.Z. prepared the samples and tested the properties. X.D. performed the finite element analysis. K.C. and T.Z. designed the research. Q.Z. and X.D. analyzed the data. All authors wrote the paper.

Additional Information
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