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ORIGINAL PAPER

New glass-ceramic sealants for Na/S battery

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Abstract The sodium sulfur (Na/S) battery is one of the most promising candidates for energy storage applications developed since the 1980s. However, the seal between the alpha-alumina and beta-alumina in the Na/S battery presents a challenge. In this work, the new glass-ceramic sealants for the Na/S battery have been developed. The borosilicate glass was chosen as the basic glass and TiO_2 as the nucleating agent. The sintering behavior was evaluated by the shrinkage curves and the densities of the sintered samples. The sintering temperature of 750 °C was obtained. The thermal expansion coefficient (TEC) of the glass-ceramic sealants matched well with that of the alpha-alumina and beta-alumina. The thermal shock resistance and chemical stability of the sealants were also satisfactory. No microcracking was observed in the sealants after thermal shock for 100 times. The diffusion layer of about 10 μm was found between the glass and the substrate after 850 h. However, the densification of the sealants remained to be further improved. The factors influencing the densification of the sealants were clarified, and the possible solving means were proposed.

Keywords Glass-ceramics · Sealant · Sodium sulfur battery · Thermal expansion match

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Introduction

The Na/S battery is an energy storage technology that uses sodium and sulfur as the electrode active materials and beta-alumina as the electrolyte. The Na/S battery exhibits high power and energy density, temperature stability, moreover, low cost because of its abundant low-cost raw materials and suitability for high volume mass production [1]. However, the Na/S battery operates at a temperature of about 300 °C to keep the electrode materials in a molten state. For both safety and performance reasons, a satisfactory sealant between the beta-alumina and alpha-alumina is essential. The requirements of a suitable sealant include excellent TECs match, chemical stability, thermal shock resistance, gas tightness, and bonding behavior, etc.

Up to date, much effort has been devoted to develop an acceptable glass sealant [2–5]. However, the glass sealant has inherent disadvantage such as high brittleness, low strength, et al. The subsequent manufacturing processes of the Na/S battery further heat the sealant and tend to stress the glass sealant. Moreover, the densification of the glass sealant occurs at the operating temperature of the battery. This can again generate harmful stresses in the sealants. It is expected that the glass-ceramic sealants can be highly resistant to sodium. Additionally, the problems relating with stresses can be avoided [6], and the TEC of the glass-ceramics can be modulated to match with those of alpha-alumina and beta-alumina. Therefore, the systematic study on the glass-ceramic sealants for the Na/S battery was essential.

In this work, the borosilicate glass was chosen as the basic glass and TiO_2 as the nucleating agent. Y_2O_3 was doped to modulate the TECs, and CaF_2 was further added to decrease

Table 1 Compositions of the parent and doped glasses

No.	Compositions of the glasses (wt.%)									
	SiO_2	Al_2O_3	B_2O_3	Na_2O	K_2O	Li_2O	Bi_2O_3	CaF_2	TiO_2	Y_2O_3
G1	67.8	3.2	18.0	3.0	4.0	0.5	1.5	0.5	1.5	0.5
G2	67.8	3.2	18.0	3.0	4.0	0.5	1.5	0.5	1.5	1.0
G3	67.8	3.2	18.0	3.0	4.0	0.5	1.5	0.5	1.5	3.0

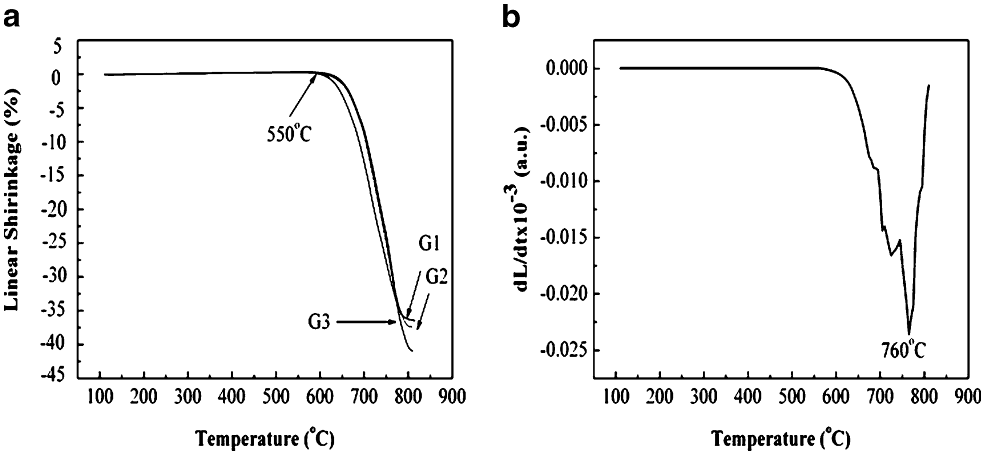


Fig. 1 **a** Sintering shrinkage curves of the investigated glass powder compacts and **b** Differential curve of the sintering shrinkage curve of glass G3 measured using dilatometer

the viscosity of the borosilicate glass. The properties of the glass-ceramic sealants for the Na/S battery were investigated in terms of the densification, thermal expansion match, thermal shock resistance, and chemical stability.

Experimental

The compositions of the studied glasses are listed in Table 1. Analytical grade SiO_2, Al_2O_3, H_3BO_3, Na_2CO_3, K_2CO_3, Li_2CO_3, CaF_2, Bi_2O_3, TiO_2, and Y_2O_3 were mixed at the given ratios listed in Table 1. The mixtures were heated to 1,400 °C to melt in an electric furnace. The glass melts were poured into the cold water. The obtained glass frits were further ground.

For the measurement of sintering behavior, the sample with a height of 5 mm was pressed. A dilatometer (NETZSCH DIL 402C, Germany) was used to observe the sintering behavior at a heating rate of 5 °C/min. Archimedes' method was used to measure the densities of the sintered samples [7].

The glass powders were shaped into $\varphi 5\times 5$-mm cylinders, which were sandwiched between the alpha-alumina and beta-alumina plates. The sealants were heated to the sealing temperature according to a given sealing process. For thermal shock resistance, the seals were heated at 350 °C for 60 min and then were cooled to room temperature immediately. This

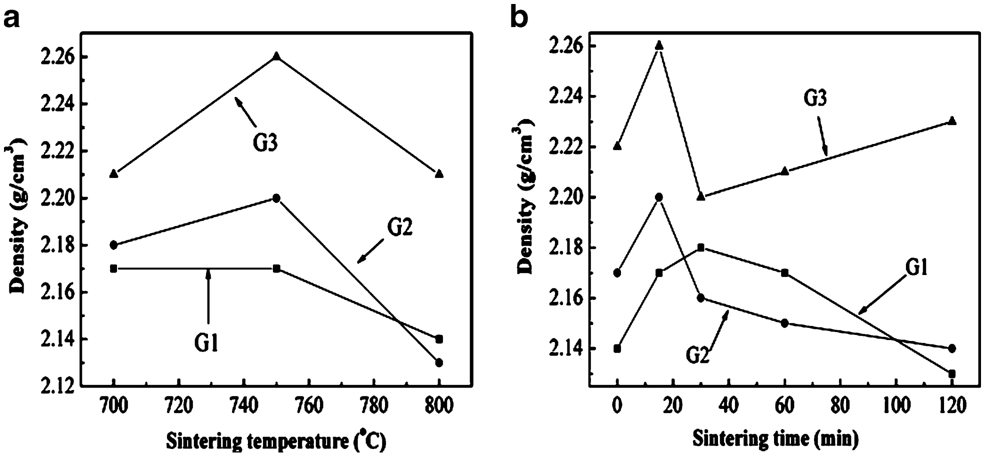


Fig. 2 Densities of the samples with different compositions vs. **a** sintering temperature and **b** holding time

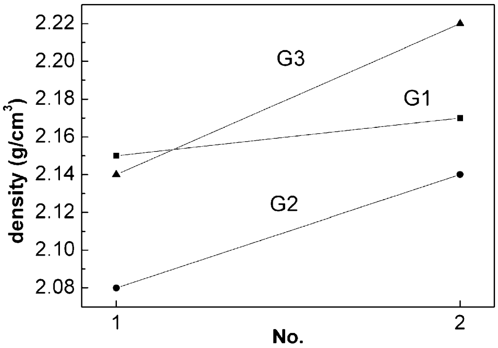


Fig. 3 Influence of the densification process on the density of the sealants. Series *1*: glass compacts were heated from room temperature to 1,000 °C directly; series *2*: glass compacts were heated from room temperature to 1,000 °C with a preheating step at 750 °C for 15 min

process was cycled for 100 times. The chemical stability of the sealants was measured at 350 °C for 850 h.

A differential scanning calorimeter (DSC; Netzsch STA 409PC, Germany) was employed to observe the glass crystallization temperature. The crystal phases in the glass-ceramic sealants were determined by X-ray diffraction (XRD; Rigaku RAD-C, Japan) at room temperature using Cu Kα radiation. The polished cross-section of the alpha-alumina/glass-ceramic sealants/beta-alumina joints were analyzed with an electron microscope (EPMA-8705QH$_2$, Japan).

Results and discussion

Densification behavior

Figure 1 shows the sintering shrinkage curves and the differential curves derived from the sintering shrinkage of the investigated glass pellets. As seen in Fig. 1a, all the glass pellets started to shrink at approximately 550 °C due to the viscous flow and ceased at about 800 °C due to the glass crystallization. This was consistent with the results of the DSC analysis (not given here). The level of the shrinkage was related to the glass softening point and the crystallization [8]. The shrinkage of the glass pellets increased with the doping of Y_2O_3, indicating that the doping of Y_2O_3 would improve the densification of the glasses. As seen in Fig. 1b, the differential curve of the sintering shrinkage of the glass G3 had the minimum value corresponding to the maximum shrinkage rate at about 760 °C. This temperature was taken as the sintering temperature of the glass G3. The sintering temperatures of the glasses G1 and G2 around 714 °C and 753 °C, respectively, were also obtained.

In order to understand the densification of the sealants, the sintering temperature and holding time were studied while the sealing temperature was temporarily fixed at 950 °C. The sintering behavior was investigated at 700 °C, 750 °C, and 800 °C, respectively. The glass pellets were heated slowly from 550 °C to the sintering temperature. The densities of the investigated glass pellets at the different sintering temperature and holding time were shown in Fig. 2. As seen in Fig. 2a, the maximum densities were observed at 750 °C. Thus, the sintering temperature was decided as 750 °C, which was coincident with the sintering shrinkage results of the glasses.

Besides the sintering temperature, the holding time also had a significant effect on the densification of the glasses. The glass pellets were heated to the sintering temperature 750 °C and held for 0, 15, 30, 60 and 120 min, respectively. Figure 2b shows the influence of holding time on the densification behavior. As seen, the maximum densities of the glasses G1 and G2 were reached at 750 °C for 15 min. The density of glass G3 sintered at 750 °C for 15 min was slightly lower than that sintered at 750 °C for 20 min.

The densification process of the investigated glass sealants was thus deduced according to Figs. 1 and 2. The starting and maximum sintering temperature was decided as 550 °C and 750 °C, respectively, while the maximum holding time was 15 min. Figure 3 shows the influence of the densification process on the densities of the sealants. The series 1 samples underwent an immediate heating step from room temperature to 1,000 °C and held for 7 min, while a preheating step at 750 °C for 15 min was carried

Table 2 Sintering processes and the TECs of the sealants

Glass	Sintering process	TECs (×10^{-6}K^{-1})	
		25–300°C	25–400°C
G1	Room temperature,550 °C–750 °C–1,000 °C, 1,000 °C for 7 min	6.5	6.7
G2	Room temperature, 550 °C–750 °C–1,000 °C, 1,000 °C for 7 min	6.3	6.5
G31	Room temperature, 550 °C–750 °C–1,000 °C, 1,000 °C for 7 min	5.1	5.7
G32	Room temperature, 550 °C–750 °C–1,000°C–800 °C, 1,000 °C for 7 min, 800 °C for 90 min	6.9	6.4
G33	Room temperature, 550 °C–750 °C–1,000 °C–700 °C–800 °C, 1,000 °C for 7 min, 700 °C for 120 min, 800 °C for 90 min	6.6	6.5

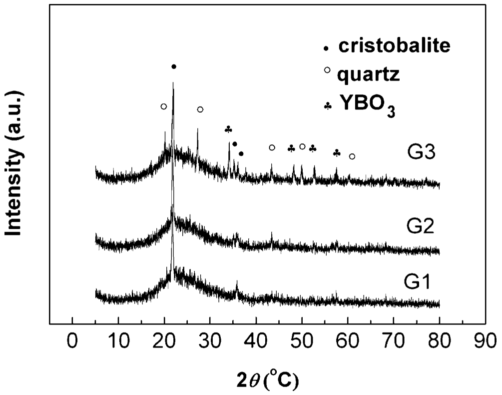


Fig. 4 XRD patterns of the glasses with various heat treatments. Glasses G1 and G2 were heated at 1,000 °C for 7 min; glass G3 was heated at 1,000 °C and then cooled to 700 °C and held for 120 min, and then was heated to 800 °C and held for 90 min

out for the series 2 samples. As seen, the densities of the series 2 samples were higher than those of the series 1 samples. It was indicated that the preheating step at 750 °C for 15 min increased the final densities of the sealants.

Thermal expansion match

An effective sealant should seal the different components with a slight thermal expansion mismatch between the sealant and the compartment. The sintering process and the TEC of the sealants are listed in Table 2. All the glasses were slowly heated to the sintering temperature 750 °C, and then to the sealing temperature 1,000 °C, additionally, the crystallization process was added for the glass G3. The nucleating and crystallization temperature is 700 °C and 800 °C, respectively. As observed, the TECs of the glass G1, G2, and G3 sealants were well-matched with those of the alpha-alumina and beta-alumina, which were 6.9×10^{-6} °C^{-1} and 6.6×10^{-6} °C^{-1} from room temperature to 300 °C, respectively. The TECs of glass G1 and G2 sealants were adaptive while sealed at 1,000 °C for 7 min, while the glass G3 sealant should be heated at 800 °C for 90 min to realize a satisfactory TEC match.

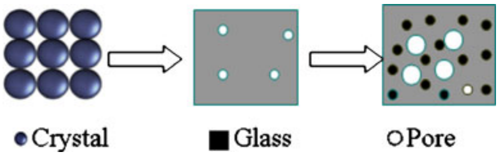


Fig. 6 Mechanism of the densification of the glass-ceramics sealants

Figure 4 shows the XRD patterns of the glasses under various heat treatments (sealing schedules). All the glasses were heated to 550 °C at 4 °C/min and to 750 °C at 1 °C/min and held for 15 min and then to 1,000 °C at 4 °C/min and held for 7 min. After that, the glasses G1 and G2 were cooled to room temperature, while the glass G3 was cooled to 700 °C at 2 °C/min and held for 120 min and then to 800 °C at 2 °C/min and held for 90 min. As seen in Fig. 4, all the glasses precipitated crystals after the heat treatment, indicating that all the glasses transformed to the glass-ceramics. This made the TEC of the glass-ceramic sealants matched with those of the alpha-alumina and beta-alumina. The glasses G1 and G2 precipitated cristobalite. The glass G3 precipitated not only cristobalite but also quartz and YBO_3 due to a great amount of Y_2O_3 doping. The amorphous diffraction in the XRD patterns of all the glass-ceramics suggested the existence of amorphous phase in the glass-ceramic sealants. The structural characteristics were in favor of wettability of the sealants on the alpha-alumina and beta-alumina plates.

Densification of sealing

Figure 5 shows the morphology of the sealing interfaces between the G3 glass-ceramics and alpha-alumina/beta-alumina. As seen, the glass-ceramic sealants were highly bonded with alpha-alumina and beta-alumina. However, lots of unexpected pores were visible through the sealants.

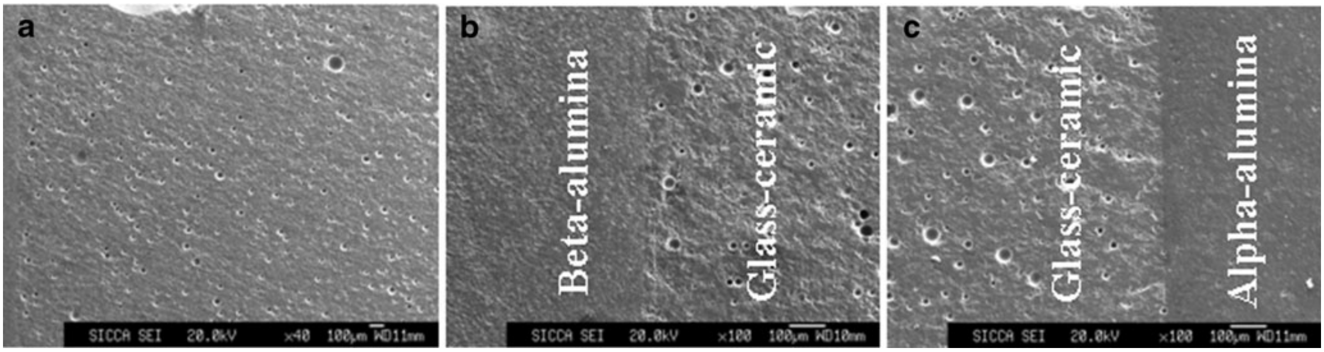


Fig. 5 SEM cross-sectional views of the G3 glass-ceramics sealant/alpha-alumina and beta-alumina interfaces held at 1,000 °C for 7 min followed by a heat treatment at 700 °C for 120 min and 800 °C for 90 min

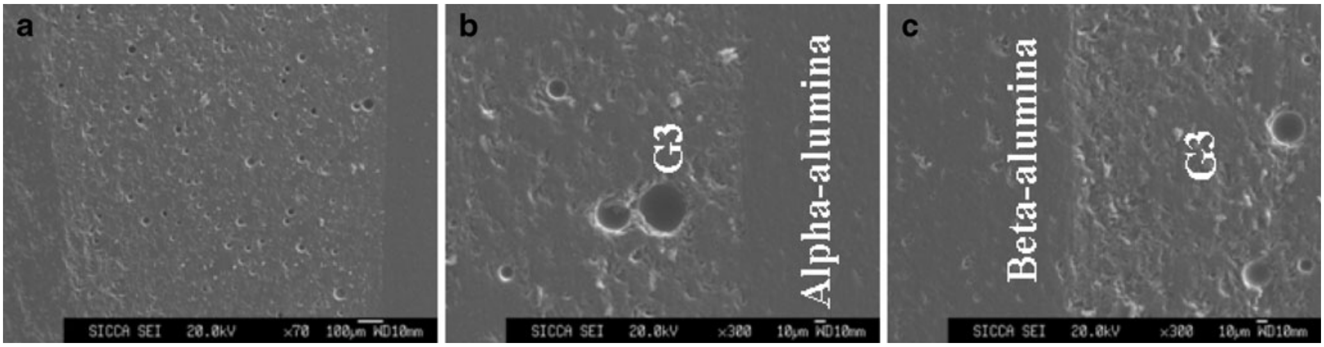
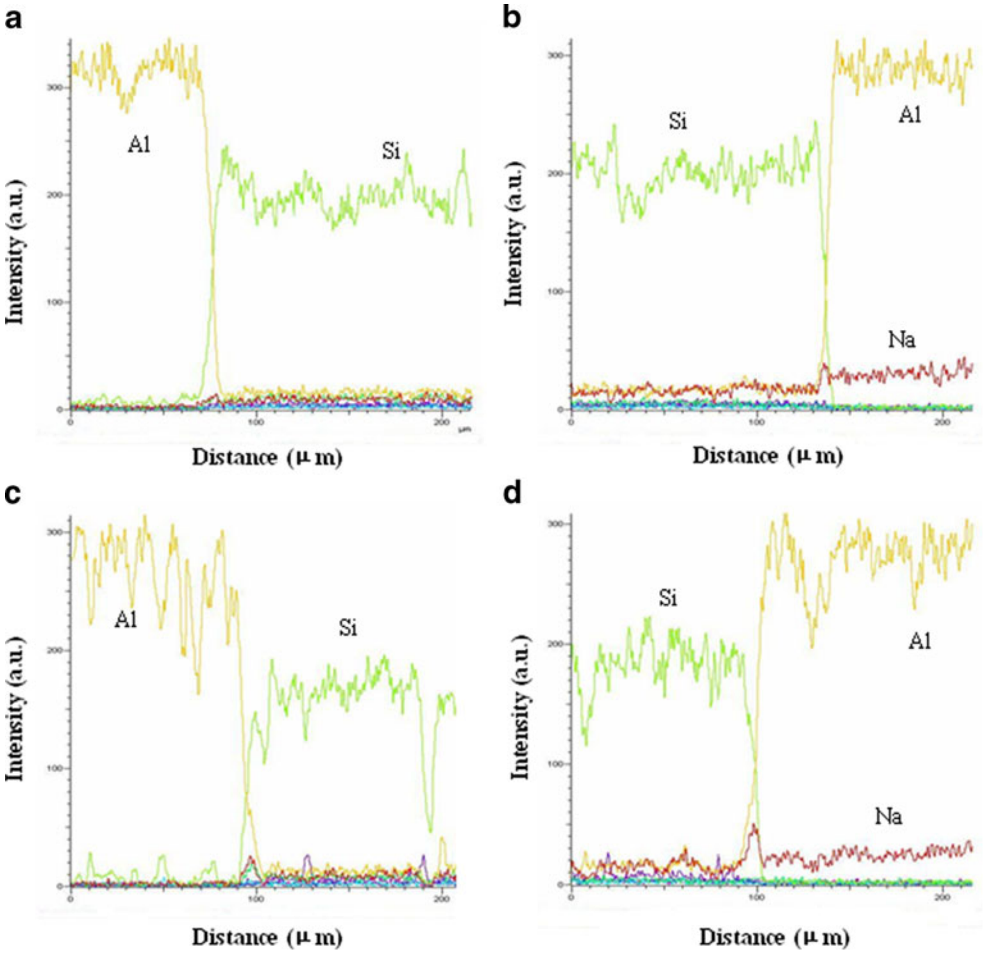


Fig. 7 Morphology of the interfaces of alpha-alumina/G3 glass-ceramics/beta-alumina after thermal shock for 100 times

The poor densification of the glass-ceramic sealants was mostly due to the glass crystallization at the sealing temperature. The densification of a glass is ruled by the mechanism of viscous flow [9–11]. The mechanism of the densification of the glass-ceramic sealants was deduced and shown in Fig. 6. As seen, a glass powder compact composed of the densely packed spheres would initially densify because of the viscous flow according to the Frenkel equation [9]. However, the increasing temperature caused the coalescence and expansion of small pores and led to the formation of large pores. As the temperature increased, the large pores would be vented out from the glasses and the final glass sealants were densified. However, for the glass-ceramic sealants, as the temperature increased to the sealing temperature, the crystallization occurred and depressed the viscous flow. Therefore, the large pores could not be vented to the outside of the glass.

Accordingly, in order to ensure the densification of the glass-ceramic sealants, the sealants could not precipitate crystal at the sealing temperature. Since the crystallization

Fig. 8 EPMA line analysis for the glass-ceramics sealants/alumina interfaces heat-treated at 1,000 °C for 7 min followed by a heat treatment at 350 °C for 850 h. **a** G1/alpha-alumina interface, **b** G1/beta-alumina interface, **c** G33/alpha-alumina interface, **d** G33/beta-alumina interface



enthalpy of cristobalite is only −8.2 kJ/mol [12] and the structure of amorphous SiO_2 is “cristobalite-like” [13], the borosilicate glasses easily precipitated cristobalite. It was thought that cristobalite was an unfavorable transformation product in terms of the thermal expansion behavior. Cristobalite transformed from α- to β-cristobalite at around 200 °C. This transformation caused a large volume change, sometimes resulted in microcracking during cooling, which made it difficult to reach densification [14]. Therefore, the precipitation of cristobalite should be avoided, especially at the sealing temperature. The SiO_2 would be replaced by some oxides like Bi_2O_3 in our next work. The decreasing SiO_2 contents would effectively depress the precipitation of cristobalite.

Thermal shock resistance

Figure 7 shows the morphology of the cross-section of the sealing of the G3 glass-ceramic and alpha-alumina/beta-alumina after thermal shock for 100 times. As seen, no microcracking was observed in the seals. It was indicated that the glass-ceramics improved thermal shock resistance because of the good TECs match and wetting, as well as the presence of plenty of the pores in the seals. It was ought to notice that the closed pores would relax the stresses in the seals and improve the thermal shock resistance.

Chemical stability

Figure 8 shows the EPMA line analysis for the glass-ceramic sealants/alumina joints heated at 1,000 °C for 7 min with the post-treatment at 350 °C for 850 h. The thickness of the diffusion layer was about 10 μm after 850 h. The minor diffusion related to the major components Si and Al. However, the diffusion layer formed after the long holding time was relatively thin, indicating a satisfying chemical stability of the glass-ceramic sealants.

Conclusions

In this work, new glass-ceramic sealants for the Na/S battery were studied. The sintering temperature of 750 °C and holding time of 15 min were decided as the formation conditions for the sealants. The TEC of the sealants was $6\sim 7\times10^{-6}$ $°C^{-1}$ after heat treatment, which well-matched with that of the alpha-alumina and beta-alumina. The thermal shock resistance of the seal was high, and no microcracking was generated after 100 times thermal cyclings. The thickness of the diffusion layer was only about 10 μm after heat treating at 350 °C for 850 h, indicating favorable chemical match of the sealants with alumina.

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