



Short Communication

Interaction between gadolinia-doped ceria electrolyte and sealing glass–ceramics

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Received 6 November 2014; received in revised form 14 January 2015; accepted 15 January 2015

Available online 7 February 2015

Abstract

The insufficient thermal–mechanical stability of sealing interface presents a challenge for the development of solid oxide fuel cells (SOFCs). Here we report for the first time that the presence of gadolinia-doped ceria (GDC) electrolyte leads to the formation of two hardystonite phases, $(\text{Ca}_{0.9}\text{Zn}_{0.03})_2(\text{Al}_{0.63}\text{Zn}_{0.37})(\text{Si}_{0.69}\text{Al}_{0.31})_2\text{O}_7$ and $\text{Ca}_2\text{ZnSi}_2\text{O}_7$, in the reaction couples between boroaluminosilicate sealing glass–ceramics and GDC powders held at 700 °C for 30 days. Similarly, the aggregation of these two hardystonite phases also occurs at the interface between GDC and sealing glass–ceramics under identical heat-treatment. In particular, $(\text{Ca}_{0.9}\text{Zn}_{0.03})_2(\text{Al}_{0.63}\text{Zn}_{0.37})(\text{Si}_{0.69}\text{Al}_{0.31})_2\text{O}_7$ becomes the dominant phase at the sealing interface when the heat-treatment time increases from 7 days to 30 days. Moreover, the sealing interface remains intact after thermal cycles for 100 times, indicating the excellent thermal–mechanical stability of hardystonite phases. Finally, the possible mechanism on the phase evolution of glass–ceramic at the sealing interface has been proposed.

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Keywords: Solid oxide fuel cells; Sealing glass–ceramics; Gadolinia-doped ceria; Thermal–mechanical stability; Phase evolution

1. Introduction

In recent years, considerable attention has been paid on the development of sealing glass–ceramics^{1–3} to meet the varied requirements of solid oxide fuel cells (SOFCs) sealants, *e.g.*, thermomechanical stability, thermal stability, chemical compatibility, and insulative ability.^{4–6} However, maintaining the stability of these sealing materials remains a challenge, especially for long-term SOFC operation.

In particular, the interfacial reactions occurring between the sealing glass–ceramics and the other SOFCs components present a challenge for sealing material development. For example, Jiang et al. reported that the reaction between boron vapor from borosilicate glass–ceramics and lanthanum-containing cathodes, *e.g.*, lanthanum strontium cobalt ferrite (LSCF), leads to the formation of LaBO_3 on the surface of cathode and thus the decomposition and degradation of cathode.^{7–9} Singh et al. also reported that the Zr diffusion

from the yttria-stabilized zirconia (YSZ) electrolyte to the borosilicate glass results in the formation of zirconates, *e.g.*, SrZrO_3 .¹⁰ Moreover, Misture et al. found that dissolved YSZ completely inhibits bulk nucleation and crystallization in the interfacial region between boro-galliosilicate glass and YSZ.¹¹ This indicates that the interfacial reaction between glass–ceramics and electrolytes plays an important role on the phase evolution at the sealing interface, which consequently affects the long-term performance of SOFCs stacks.

However, most works on the interfacial reaction between glass–ceramics and ceria-based electrolytes can only provide qualitative information on the chemical compatibility between glass–ceramics and ceria-based electrolytes.^{12–14} Wang et al. performed a XRD measurement on the mixture of glass and GDC powders (50:50 in wt.%) heat-treated at 850 °C for 1 h. The result revealed no chemical interaction between glass and GDC.¹³ Wei et al. investigated the morphology at the interface between glass and samaria-doped ceria (SDC) by SEM. The results showed that the glass remained good bonding with SDC after being aged at 650 °C for 100 h.¹⁴ To the best of our knowledge, there are no reports on the phase evolution at the sealing

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interface between glass–ceramics and ceria-based electrolytes in literature.

On the other hand, network modifiers are often employed to break the glass network and thus reduce the glass transition temperature (T_g) and softening temperature (T_d) of glass. For example, Wang et al. reported that ZnO dopant in $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--La}_2\text{O}_3\text{--SrO--ZnO}$ glass contributes to the decrease in T_g and T_d .¹² Therefore, ZnO-doped sealing glass has been regarded as a promising candidate for the application of intermediate temperature SOFC (IT-SOFC).^{13,15}

In this paper, ZnO was added gradually (from 2 to 10 mol.%) into a representative borosilicate glass system. Attention was focused on the following questions: (1) How does the reaction between glass–ceramics and GDC electrolyte change with ZnO dopant? (2) How does the crystalline structure at the sealing interface between glass–ceramics and GDC change with ZnO dopant? (3) How does the crystalline structure in the reaction couples between glass–ceramics and ceria-based electrolytes change with different electrolytes? The relationship between the glass–ceramics/ceria-based electrolytes interaction and the phase evolution at the sealing interface was then established to provide useful information for the development of reliable sealing material for SOFCs application.

2. Experimental

A 50-g sample of glass designated ‘glass#2ZnO’ was prepared from a batch mixture of reagent grade alkaline earth carbonates, boric acid, and various oxides to form the nominal glass composition (mol.%): $23.5\text{CaO--}23.5\text{SrO--}2.0\text{Bi}_2\text{O}_3\text{--}7.0\text{Al}_2\text{O}_3\text{--}8.0\text{B}_2\text{O}_3\text{--}34.0\text{SiO}_2\text{--}2.0\text{ZnO}$. Another composition designated ‘glass#10ZnO’ was prepared for comparison, with a nominal glass composition (mol.%) of $21.6\text{CaO--}21.6\text{SrO--}1.8\text{Bi}_2\text{O}_3\text{--}6.0\text{Al}_2\text{O}_3\text{--}7.0\text{B}_2\text{O}_3\text{--}32.0\text{SiO}_2\text{--}10.0\text{ZnO}$. The batches were melted in an alumina crucible in air at $1300\text{--}1350^\circ\text{C}$ for 1 h. The melt was quenched on a steel plate. Glass powders were then crushed and sieved to a particle size of $45\text{--}53\ \mu\text{m}$.

To accelerate the reaction between glasses and gadolinia-doped ceria (GDC) electrolyte, a mixture of glass and GDC ($\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$, Sinopharm Chemical Reagent Co., Ltd.) powders (50:50 in wt.%) was reacted in air at 700°C for up to 30 days. The crystalline phases of the reaction couples after reaction were identified by X-ray diffraction (XDS 2000, Scintag, Inc.). The crystalline phases in glass–ceramic powders after identical heat-treatment were also identified by XRD for comparison.

To further investigate the glass/electrolyte interaction, different ceria-based ceramics, including GDC, samaria-doped ceria (SDC, $\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$, Sinopharm Chemical Reagent Co., Ltd.) and CeO_2 (Sinopharm Chemical Reagent Co., Ltd.), were mixed with glass powders (50:50 in wt.%) and reacted in air at 700°C for 7 days, respectively. The reaction couples were also subjected for XRD measurement. The relative content of crystalline phases (in wt.%) in each species was then calculated by RIQAS software (Release 4.0.0.8, Materials Data, Inc., CA).

The onset crystallization temperature (T_x) of glass powders was determined using differential scanning calorimetry

(SDTQ600, TA, Inc.) at a heating rate of $10^\circ\text{C min}^{-1}$. The reaction couples between glass and GDC powders (50:50 in wt.%) were also subjected to DSC measurement.

In addition, the glasses were bonded to GDC substrates and the interfacial reactions were characterized. Glass pastes were prepared by mixing $\sim 50\ \text{mg}$ glass powder ($45\text{--}53\ \mu\text{m}$) with $\sim 50\ \mu\text{l}$ ethanol. The pastes were applied to the ultrasonically cleaned surfaces of GDC. The coated samples were subsequently held in air at 700°C for up to 30 days. The glass/GDC sealing couples were polished using SiC paper from 320 to 1200 grit, and then finished using an alumina suspension ($3\ \mu\text{m}$). The polished samples were analyzed using field emission scanning electron microscopy (Supra-55, Zeiss, Inc.) and energy dispersive analysis by X-rays (X-Max, OXFORD instruments, Inc.).

To evaluate the thermal–mechanical stability of sealing interface, thermal cycles were performed at the interface between glass#10ZnO and GDC. A single thermal cycle included heating sealing couple from room temperature to 700°C at a heating rate of $40^\circ\text{C min}^{-1}$, holding at 700°C for 30 min, and then quenching in air to room temperature for another 30 min. The interface after thermal cycles for 100 times was cross-sectioned and polished for SEM characterization.

3. Results and discussion

Fig. 1 shows the XRD patterns of glass–ceramics held at 700°C for 30 days. The XRD pattern of glass#2ZnO held at 700°C for 24 h is also included for comparison. The crystalline phases in glass–ceramics, held at 700°C for 30 days, include $(\text{Ca}_{0.9}\text{Zn}_{0.03})_2(\text{Al}_{0.63}\text{Zn}_{0.37})(\text{Si}_{0.69}\text{Al}_{0.31})_2\text{O}_7$ (referred to as ‘solid solution phase’), $\text{Ca}_2\text{ZnSi}_2\text{O}_7$, Sr_2SiO_4 and $\text{Bi}_4\text{B}_2\text{O}_9$; whereas, the diffraction peaks corresponding for two hardystonite phases, *i.e.*, solid solution phase and $\text{Ca}_2\text{ZnSi}_2\text{O}_7$, present in the glass#2ZnO sample held at 700°C for 24 h. This indicates that these two hardystonite phases are primary phases in glass–ceramics.

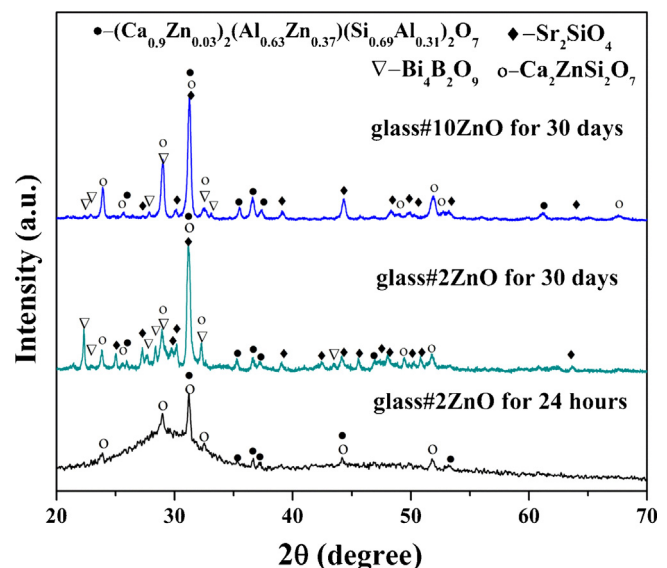


Fig. 1. XRD spectra of glass–ceramics held at 700°C for different time.

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