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Controlling the redox reaction at the interface between sealing glasses and Cr-containing interconnect: Effect of competitive reaction

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HIGHLIGHTS

- The competitive reaction reduces the glass/metal interfacial reaction.
- The reaction also results in a stable Mn–Cr oxide scale at the interface.
- The Mn–Cr oxide scale acts as diffusion barrier at the glass/metal interface.

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ABSTRACT

In this paper, MnO_2 is added to CaO–SrO–B_2O_3–SiO_2 sealing system to control the redox glass/metal interfacial reaction in Solid Oxide Fuel Cells. The effect of MnO_2 dopant on the valance states of Mn ions in glasses, the glass structure and glass/metal interfacial reaction is systematically investigated. The quenched glasses contain Mn^{2+} ion only; whereas, the Mn^{3+} content in glasses, held at 600 °C for 9 h, increases with increasing MnO_2 dopant. The good bondage can be observed at the interfaces between Crofer 22APU and glass containing 6 mol % MnO_2, held at 700 °C for 500 h. The competitive reaction reduces the redox chromate formation by consuming the oxygen at the glass/metal interface. In addition, the competitive reaction results in the formation of a continuous Mn–Cr oxide scale at the glass/metal interface, which is helpful for reducing the further diffusion of Cr from metallic interconnect to glass.

1. Introduction

The direct operation of Solid Oxide Fuel Cells (SOFCs) on hydrocarbon fuels has attracted increasing attention in the last decade, due to the large amount of hydrocarbons as well as the highest conversion efficiency of SOFC among all types of fuel cells [1–3].

However, the long-term operation of SOFCs still faces many challenges, for example, the coke formation as well as the interfacial reaction between sealing glasses and other Solid Oxide Fuel Cell (SOFC) components. In particular, the chromate formation at the interface between sealing glasses and Cr-containing interconnect often leads to the generation of thermal stress and subsequently the physical separation of sealing glass from metallic interconnect [4–8].

Many efforts have been made on the modification of interconnects, including pre-oxidation [9–13], aluminizing [14,15] and protective coatings [16–21], in order to hinder the diffusion of Cr from the interconnect to the glass. However, few works on the improvement of the chemical compatibility of sealing glasses have been reported in literature, because of the difficulty in the quantitative analysis of the reaction in complex fixture of SOFCs. A recent work of our group has clearly demonstrated the effect of crystallization process on the interfacial reaction [22] using a quantitative approach developed by ourselves [23].

Considering the redox characteristic of the interfacial reaction (*e.g.*, $SrO + 0.5Cr_2O_3 + 0.75O_2 = SrCrO_4$) [7], ions with different valence states, such as Mn, Fe and Ce, in glasses might act as a competitive reaction for the interfacial reaction, by consuming the oxygen at the triple-phase boundary (TPB). In this paper, MnO_2 is added gradually, from 2 to 10 mol %, to a representative Sr-containing borosilicate sealing glass. Attention has been focused on the valence states of Mn ions in glasses and its effect on the glass/metal interfacial reaction to provide useful information on the control of redox-type interfacial reaction.

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Table 1
Nominal compositions (in mol %) of glasses.

Sample ID	SrO	CaO	B_2O_3	SiO_2	MnO_2	B/Si	Sr/Ca	Mn/Si
Glass#M1	25.48	25.48	7.84	39.2	2	0.40	1.00	0.05
Glass#M2	24.96	24.96	7.68	38.4	4	0.40	1.00	0.10
Glass#M3	24.44	24.44	7.52	37.6	6	0.40	1.00	0.16
Glass#M4	23.92	23.92	7.36	36.8	8	0.40	1.00	0.21
Glass#M5	23.4	23.4	7.2	36	10	0.40	1.00	0.28

2. Experimental

A 50-g sample of each glass was prepared by melting a homogeneous mixture of reagent grade alkaline earth carbonates, boric acid, and various oxides in a platinum crucible in air at 1500 °C for one hour. The nominal compositions of glasses (mol %) are shown in Table 1. Some of the melt was poured into stainless steel mold to obtain cylindrical shaped glass specimens (25 mm length and 6 mm diameter) and the rest of the melt was quenched on a steel plate. Glass powders were then crushed and sieved to a particle size of 45–53 μm. The final compositions of quenched glasses measured by XPS are shown in Table 2.

Raman spectra of quenched glasses powders were collected in 200–1600 cm^{-1} wave number range by Raman spectrometer (Renishaw invia). The light source was 514.5 nm argon laser with 10 s of exposure time. The spectra were analyzed by Gaussian fitting with Peak-Fit4.1 software. In addition, the crystalline phases in glass–ceramics powders, held at 700 °C for 100 h, were identified by X-ray diffraction (XDS 2000, Scintag, Inc.).

The onset crystallization temperature (T_c) of glass powders was determined using differential scanning calorimetry (SDTQ600, TA, Inc.) at a heating rate of 10 °C min^{-1}. The dilatometric characteristics of quenched glasses, including the coefficient of thermal expansion (CTE, between 200 and 600 °C), glass transition temperature (T_g) and dilatometric softening temperature (T_d), were determined by dilatometer (DIL402C, NETZSCH, Inc.) at 10 °C min^{-1} in air. Thermal properties of glasses, including T_c, T_g, T_d and CTE, are summarized in Table 4.

A ~10 mg mixture of glass and 10 weight % Cr_2O_3 powders was reacted in an alumina boat in air for different times. The reaction temperature was chosen to be 600 °C to exclude the effects of crystallization and softening processes (in Fig. 1 and Table 4). The reaction product was dissolved into ~50 ml of deionized water and the absorption spectra were recorded using the UV–vis Spectrometer (Optima 2000 DV, Perkin Elmer, Inc.). The fraction of Cr^{6+} was then calculated by fitting the measured absorption to the calibration curve. The detailed procedure of this analysis has also been discussed elsewhere [23].

The emission spectra of Mn^{2+} and Mn^{3+} ions in quenched glass powders were collected using the spectorfluorometer (Fluoromax-4, HORIBA Scientific, Inc.), after excitation at 420 nm and 490 nm, respectively. The valence states of Mn ions in glasses, held at 600 °C for 9 h, were determined by X-ray photoelectron spectroscopy (ESCALAB 250, Thermo Scientific, Inc.) using a monochromatic Al Kα source (10 mA, 15 kV).

The glasses were bonded to Crofer 22APU substrates and the interfacial reactions were characterized. Glass pastes were prepared by mixing ~50 mg glass powder (45–53 μm) with ~50 μl acetone. The pastes were applied to the ultrasonically-cleaned surfaces of Crofer 22APU. The coated samples were subsequently held in air at 700 °C for 100 h. The glass/metal sealing couples were polished using SiC paper from 320 to 1200 grit, and then finished using an alumina suspension (3 μm). 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.).

Table 2
Final compositions (in mol %) of quenched glasses measured by XPS.

Sample ID	CaO	SrO	B_2O_3	SiO_2	MnO_2	B/Si	Sr/Ca	Mn/Si
Glass#M1	26.0	25.6	7.3	39.6	1.5	0.40	0.99	0.04
Glass#M3	23.9	24.3	7.0	39.1	5.7	0.40	1.01	0.14
Glass#M5	23.5	24.0	6.7	36	9.8	0.41	1.02	0.27

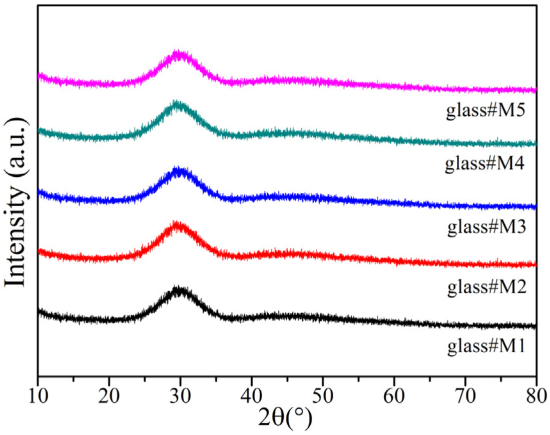

Fig. 1. XRD spectra of glasses held at 600 °C for 9 h.

3. Results and discussion

3.1. Valance states of Mn ions in glasses

Fig. 2 shows the photoluminescence spectrum of quenched glass#M5. It is clear that peaks corresponding for Mn^{2+} ion can be observed after excitation at 420 nm; whereas, no peak can be detected after excitation at 490 nm, indicating the absence of Mn^{3+} ion in present work. It is well known that the valance states of Mn ions depend strongly on the manganese content in glasses [24]. The Mn^{2+} ion is common in quenched glasses, while the Mn^{3+} ion can only be detected in glasses with great Mn content, *e.g.*, more than 10 mol % [25,26]. Therefore, the quenched glasses in present work contain Mn^{2+} ion only.

To clarify the change in valance states of Mn ions during the interfacial reaction, the XPS analysis was also conducted on the

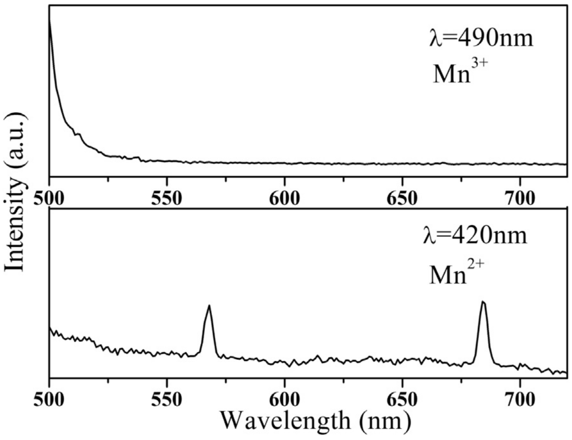

Fig. 2. Photoluminescence spectrum of quenched glass#M5.