



Short communication

Reduction of chromate formation at the interface of solid oxide fuel cells by different additives

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ABSTRACT

High temperature interactions between glass–ceramic sealants and ferritic interconnects used in solid oxide fuel cells (SOFCs) lead to the formation of detrimental chromate phases, such as BaCrO₄ or SrCrO₄, which lead to the mechanical failure of the cell. In present work, the interactions are characterized using model reactions between Cr₂O₃ and glass powders. It is found that the addition of MnO₂ reduces the formation of SrCrO₄ more significantly than that of ZnO and La₂O₃, in the SOFCs operational temperature range (e.g., 900 °C). In addition, the mechanism of the reduction of the chromate phase by different additives is discussed in terms of the possible competing reactions.

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1. Introduction

The design of sealing materials is driving the exploration of the planar solid oxide fuel cells (SOFCs), which possess much greater efficiency than that of tubular design, in the last two decades [1]. The glass–ceramics are known to be ideal for accomplishing the sealing task due to the unique viscoelastic flow above the glass transition temperature [2,3], which is desired to seal the interfaces at a relatively low temperature without ‘burning out’ the other components of SOFCs.

However, the reactions between the sealing glasses and Cr-containing stainless steel interconnects are often detrimental to the performance of SOFC stacks. In particular, the formation of chromate phases, such as BaCrO₄ [4,5] and SrCrO₄ [6], leads to the physical separation of the sealing glass and stainless steels due to the large CTE difference between these phases ($\sim 18\text{--}20 \times 10^{-6} \text{ K}^{-1}$) and that of glass–ceramic sealants ($\sim 12.5 \times 10^{-6} \text{ K}^{-1}$) or stainless steels ($\sim 13 \times 10^{-6} \text{ K}^{-1}$).

Many efforts have been made to reduce the interactions between glass–ceramic sealants and the ferritic interconnect alloys, but most are focused on the pretreatment of the interconnects, e.g., the pre-oxidation [7,8], deposition of the protective coatings [9], as well as the aluminizing of the Cr-containing ferritic alloys [10]. The design of glass composition for reducing the interfacial reaction is still a remaining challenge.

A recent work showed that the addition of ZnO (5–25 mol%) can reduce the formation of SrCrO₄, indicating by the decrease in the percentage of Cr⁶⁺ in the reaction couples between the sealing glasses and Cr₂O₃ powders [11]. Based on the competition mechanism between the chromate phase and other Cr-containing products, one can expect that the addition of La₂O₅ can reduce the interfacial reaction, with a negative Gibbs's free energy for the formation of LaCrO₃ [12]. In addition, a spinel phase, (Mn,Fe)Cr₂O₄, is often observed at the interface of SOFCs [11,13], implying another possible path to reduce the formation of chromate phase. In this paper, the effect of different additives on the formation of chromate phase was quantitatively analyzed using a UV/vis spectroscopy to provide instructive information for the design of the sealing glasses to reduce the detrimental interfacial reactions of SOFC.

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 an alumina crucible at a temperature of 1500 °C for 2 h in air and the melt was then quenched on steel plates. The nominal compositions of glasses (mol%) are shown in Table 1.

Glass powders were then crushed and sieved to a particle size of 45–53 μm. A ~15-mg mixture of glass and 10 wt% Cr₂O₃ was heat-treated in an alumina boat in air at 900 °C for different time periods. The crystalline phases in these mixtures were identified using X-ray diffraction (XDS 2000, Scintag, Inc.) analysis. After heat treatment, the mixture was dissolved into ~150 ml of deionized water and the

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Table 1
Composition of glasses (in mol%).

Glass ID	SrO	CaO	ZnO	MnO ₂	La ₂ O ₃	B ₂ O ₃	SiO ₂
1	26.0	26.0	0.0	0.0	0.0	4.0	44.0
2	23.4	23.4	10	0	0	3.6	39.6
3	23.4	23.4	0	10	0	3.6	39.6
4	23.4	23.4	0	0	10	3.6	39.6

absorption spectra were recorded using the UV–vis spectrometer (Optima 2000 DV, Perkin Elmer, Inc.). The detailed procedure of this quantitatively experiment by UV–vis spectrometer has been discussed elsewhere [14]. The concentration of Cr⁶⁺ in each solution was calculated by fitting the corresponding absorbance using the calibration curve derived from the K₂CrO₄ solutions. The total concentrations of Cr ions dissolved in each solution were determined by ICP-OES, and the percent of chromium present as Cr⁶⁺ in each sample is reported by comparing the absolute amount of Cr⁶⁺ determined by UV–vis with the total amount of Cr ions in each solution determined by ICP-OES.

3. Results and discussion

The UV–vis spectra of K₂CrO₄ solutions in DI water as a function of Cr⁶⁺ content are shown in Fig. 1. Two absorption peaks corresponding to the absorption by Cr⁶⁺ ions were present at 273 and 372 nm, in agreement with the previous studies (270 and 370 nm) [15,16]. The absorption intensity at a wavelength of 372 nm increased from 0.25 to 2 cm⁻¹ as the concentration of Cr⁶⁺ increased from 2.5 to 25 ppm. The absorption spectrum of DI water was also included in Fig. 1 for comparison. The concentration of Cr⁶⁺ in the K₂CrO₄ solutions was also measured using ICP-OES (not shown). The absorption intensity of Cr⁶⁺ as a function of measured Cr⁶⁺ concentration is shown in the inset to Fig. 1. The absorption intensity and Cr⁶⁺ concentration yielded a good linear fit ($R^2 > 0.99$). The slope of this plot was used to calculate the extinction coefficient (ϵ) for Cr⁶⁺, according to the Beer–Lambert law [17]

$$A = \epsilon \times c \times x \quad (1)$$

where A is the absorbance, x is the optical path length, and c is the concentration. In this study, the extinction coefficient for Cr⁶⁺ at

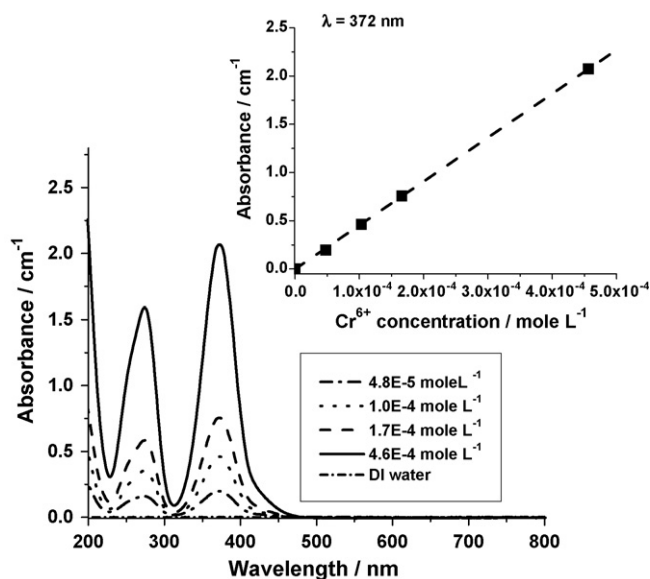


Fig. 1. UV–vis spectra of K₂CrO₄ solutions as a function of Cr⁶⁺ concentration. The absorbance of K₂CrO₄ solutions as the function of Cr⁶⁺ concentration at the wavelength of 372 nm in UV–vis spectra is shown in the inset.

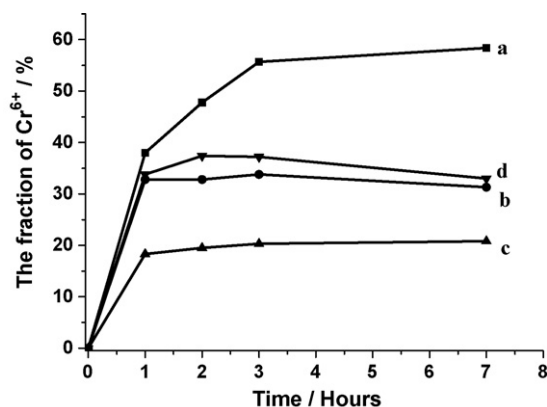


Fig. 2. The fraction of Cr⁶⁺, in the reaction couples between Cr₂O₃ and glasses, for (a) the base glass, (b) with 10 mol% ZnO, (c) with 10 mol% MnO₂ and (d) with 10 mol% La₂O₃, as a function of time in air at 900 °C. The solid lines are guides for the eye.

372 nm was $4264 \pm 79 \text{ L cm}^{-1} \text{ mol}^{-1}$, which was close to the value reported for Cr⁶⁺ in silicate glasses of $4218 \text{ L cm}^{-1} \text{ mol}^{-1}$ [18]. The concentration of Cr⁶⁺ in each solution of the glasses/Cr₂O₃ mixtures was then calculated by fitting the corresponding absorbance using the calibration curve, as mentioned above.

Shown in Fig. 2, is the percentage of Cr⁶⁺ presented in the glasses/Cr₂O₃ mixtures heated in air at 900 °C as a function of time. The presence of Cr⁶⁺ is an indication of the formation of SrCrO₄ in the glass/Cr₂O₃ mixtures, which is also confirmed by X-ray diffraction pattern (Fig. 3). The percentage of Cr⁶⁺ in the mixture of the base glass (#1 in Table 1) and Cr₂O₃ at 900 °C initially increased dramatically from 37 to 56% after the first 3 h, and then increased to 58% after the heat treatment for 7 h, which is in agreement with previous works [11,19]. In addition, the amorphous hump centered at the 2θ of about 30°, indicating the presence of the residual glass in the glass–ceramic after heat treatment, which imposes additional uncertainty on the intensity of the diffraction peaks and consequently the quantitative results for specific crystalline phases analyzed by Rietveld refinement. On the contrary, the measurement of absorption in UV spectra, depending only on the concentration of Cr⁶⁺ in the solutions, provides a more accurate and reproducible approach for quantitative analysis of the reaction products in the interfaces of SOFCs.

It is also worth noting that the percentage of Cr⁶⁺ in the mixture of glass and Cr₂O₃ decreased with any additives, indicating that the addition of additives in this work can reduce the formation of

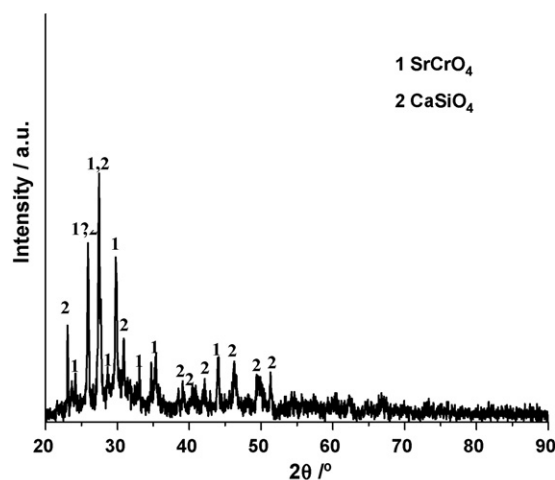


Fig. 3. XRD patterns from the base glass and Cr₂O₃ reaction couple after heating in air at 900 °C for 7 h; a.u., arbitrary units.

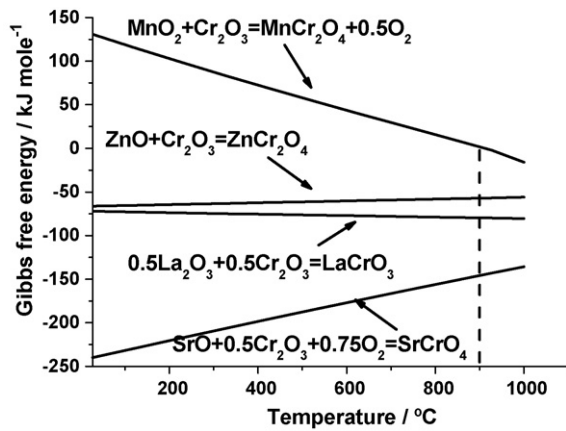


Fig. 4. Gibbs free energy for possible reactions as a function of temperature in air.

SrCrO₄. Furthermore, the effect of the additives on the reduction of the chromate phase is in the order of MnO₂ > ZnO > La₂O₃. For example, the percentage of Cr⁶⁺ decreased from 33 mol% for the glass containing 10 mol% La₂O₃ to 31 mol% for the glass containing 10 mol% ZnO, and to 21 mol% for the glass containing 10 mol% MnO₂ after heat-treated at 900 °C for 7 h. Considering the great difference between the softening temperature for all glasses in present work (750–800 °C) and the reaction temperature (900 °C), one can exclude the possibility of the oxygen-blocked effect caused by the softened glasses.

To explore the mechanism for reducing the formation of SrCrO₄, a thermal–chemical model was proposed, as shown in Fig. 4. It is clear that all of the four possible reactions are thermodynamically favored in air at 900 °C, since the Gibbs free energy for the formation of SrCrO₄, ZnCr₂O₄, LaCrO₃ and MnCr₂O₄ are –150, –57, –79 and –2 kJ mol^{–1}, respectively. Therefore, the reduction of SrCrO₄ in the glasses with additives can be caused by the formation of other phases, such as MnCr₂O₄, ZnCr₂O₄ or LaCrO₃, which supports the hypothesis of the competing reactions leading to the reduction of SrCrO₄ in present work. It is well established that the thermo-chemical models only can provide qualitative information on the possible reactions. The further verification of the hypothesis and the kinetics of the interfacial reactions is still a challenging subject for the future.

4. Conclusions

The measurement of Cr⁶⁺ content in the reaction products by UV–vis spectrometer provides an accurate and simple way for

the quantitatively analysis of the interfacial reactions of SOFCs. The effect of the additives on the reduction of the chromate phase is in the order of MnO₂ > ZnO > La₂O₃. The thermo-chemical model also provides evidences for the possible competing reactions, indicated by the negative Gibbs free energies in air at 900 °C, which result in the reduction of the SrCrO₄ in present work.

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