

## Microstructural and Chemical Studies of Zirconia/Silicate Glass Interfaces Following Long-term Exposure to Solid Oxide Fuel Cell Environments

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Solid oxide fuel cells (SOFCs) are electrochemical devices with the unique ability to directly convert the chemical energy of a wide variety of fuels to electric power with a very high conversion efficiency [1]. Sealing of SOFCs in the flat plate configuration poses significant challenges for preventing the mixing of fuel and oxidizing gases. Seals need to be electrically insulating, chemically stable in oxidizing and wet reducing environments, chemically compatible with other cell components, and durable for tens of thousands of hours, which is the expected service life of SOFCs [2]. Crystallization-resistant glasses are one of the leading candidates for SOFC sealing application owing to their self-healing ability and because a wide range of compositions allows for tailoring of the physical and mechanical properties [3]. Here, we report results from the characterization of two barium-containing alkali silicate glasses, SCN-1 (SEM-COM, Toledo, OH) and G6 (Whatman Ltd., Piscataway, NJ), that were exposed to air at atmospheric pressure at 800°C for 40,000 hours while in contact with yttria-stabilized zirconia (8YSZ), which is widely used as an SOFC electrolyte. Scanning transmission electron microscopy (STEM) imaging and energy dispersive X-ray spectroscopy (EDS) were used to characterize the structural and chemical changes of the glass-8YSZ interface after long-term exposure.

The initial chemical composition of the glasses was quantified by inductively coupled plasma atomic emission spectroscopy (ICPAES) [2]. Both glasses had Si as a major element; the SCN-1 glass contained elements with decreasing concentration: K > Ba > Na > Ca > Al > Mg > Ti, while G6 contained elements with concentrations: Na > Ba > B > Zn > Al > Ca > K > Mg. After the 40,000 hour exposure, the samples were sectioned, metallographically prepared, and examined using scanning electron microscopy (SEM) (Fig. 1a-b). In the SCN-1/8YSZ sample, a high concentration of voids or bubbles was observed in the glass phase while in the G6/8YSZ sample, smaller bubble concentrations were found in the glass. The morphology of the 8YSZ substrates did not change during exposure. STEM samples were prepared from the interphase regions (areas marked in Fig. 1) by using focus ion beam (FIB) micromachining.

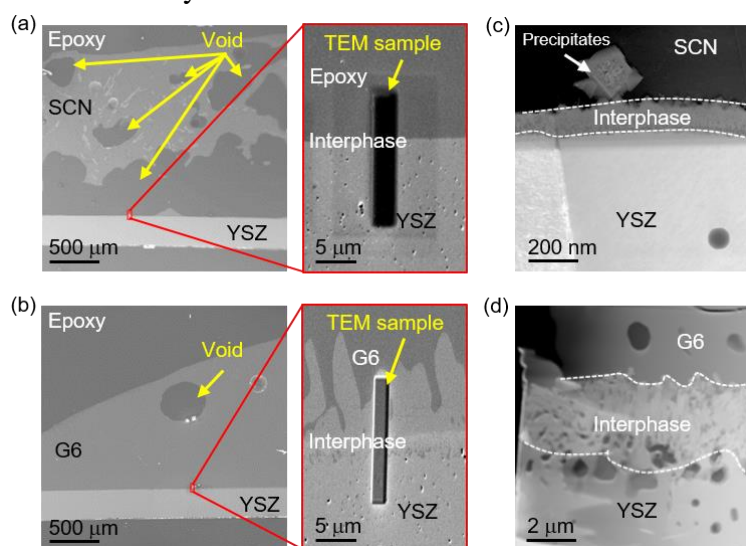
The structure and morphology of the interfaces formed after exposure for 40,000 hours were studied using Z-contrast STEM imaging (Fig. 1c-d) and EDS elemental mapping (Fig. 2). The interface formed between SCN-1/8YSZ (Fig. 1c) consisted of a  $114 \pm 19$  nm thick Ba-rich interphase layer; the 8YSZ substrate retained a homogeneous chemical composition, while crystalline precipitates formed within the glass near the interface, e.g., cube-shaped, Ba-rich precipitates (Fig. 1c). The G6/8YSZ interface was different than that of SCN-1/8YSZ (Fig. 1d) forming an interphase layer that was  $3.2 \pm 0.4$   $\mu\text{m}$  thick, nearly 30 times thicker than that formed in SCN-1/8YSZ. The interface compositions were non-homogeneous, as demonstrated by the EDS elemental maps (Fig. 2d-f) showing the formation of columnar-shaped Zr-rich grains near the glass with regions of higher Si and Ba concentrations between the Zr-rich grains. A small amount of Si and Ba were detected within the Zr-rich grains. Within the interface closer to the 8YSZ, 500-1,000 nm sized regions exhibiting Si and/or Ba segregation were observed, indicating elements from the G6 glass diffused through the interface to the 8YSZ substrate in this sample after 40,000 h exposure.

The functionality of glass seals for their expected service life depends on their resistance to crystallization

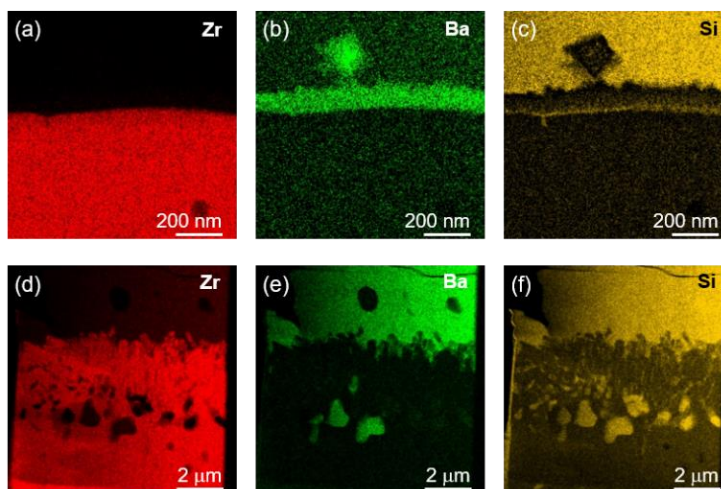
and formation of deleterious voids. This study provides information regarding the kinetics of precipitation and crystallization, interfacial reactions, and void formation of candidate glass seals for SOFCs [5].

#### References:

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**Figure 1.** SEM images of (a) SCN-1/8YSZ and (b) G6/8YSZ after 40,000 hours exposure to air at 800 °C. High-magnification SEM images (right) show location of TEM sample lift-out. STEM high-angle annular dark-field (HAADF) images of (c) ~ 200 nm thick SCN-1/8YSZ interphase and (d) ~ 2 μm thick G6/8YSZ interphase.



**Figure 2.** EDS elemental maps of SCN-1/8YSZ for (a) Zr, (b) Ba, and (c) Si correlated to STEM image Fig. 1(c). EDS elemental maps of G6/8YSZ for (d) Zr, (e) Ba, and (f) Si correlated to Fig. 1(d).