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# Corrosion Effects of Glass on YSZ Electrolytes

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***Abstract***

*This work reports on the microstructure and electrical properties of different yttria stabilized zirconia (YSZ) based cells using: (i) intimate mixtures of YSZ and a commercial soda-lime glass (up to 20 wt%), sintered at different temperatures; (ii) YSZ disks covered with a layer of glass on one side and fired in a clean laboratory furnace for two hours at different temperatures (1250–1350 °C); (iii) YSZ pellets exposed to the exhaust gases of one (industrial) glass melting furnace, at temperatures around 1300 °C. Microstructural observations and impedance spectroscopy measurements were used to demonstrate the potential of the latter technique in monitoring the electrolyte corrosion. The high-and intermediate-frequency impedance arcs showed a significant and coherent dependence on the progress of corrosion, due to the formation of glass–ceramic composites with large glass/ceramic interfaces. Similar results were obtained with laboratory scale and industrial experiments. EDS analysis showed an higher concentration of $Y_2O_3$ in the intergrain region and a corresponding concentration decrease in the electrolyte grains.* © *1999 Elsevier Science Limited. All rights reserved*

## 1 Introduction

The increasing demand by industry for materials which can perform under hostile conditions requires the design of materials tailored to suffer minimum degradation of their properties. A better understanding of the nature of interfaces and processes which occur within common ceramics and their effects on physical properties are key factors in improving their performance. Thus, the development of non-destructive techniques which are able to provide some insight on changes in bulk properties or interfacial conditions is highly desirable in materials science and engineering.

Several zirconia-based materials are commonly used in solid-state electrochemical devices such as oxygen sensors.[1] The use of these sensors is common in the glass-making industry for optimising combustion efficiency and controlling some glass properties such as colour.[2,3] Grain boundaries play a crucial role in the electrical and electrochemical properties of zirconia based materials, and are the most vulnerable points for chemical attack.[4] Glass penetration into zirconia sintered bodies is important for immersed sensors, but the corrosive action of dusts and volatile species in glass-making furnaces is not negligible.[5,6] A study on the correlation between microstructure of glass-ceramic composites and results obtained by impedance spectroscopy (to evaluate the development of new interfaces) is suggested, in order to test the potential of the latter technique as a simple diagnostic tool for the electrolyte degradation condition.

## 2 Experimental

Mixtures of electrolyte powder (YSZ, 8 mol% $Y_2O_3$, from Tosoh) with different amounts of glass (up to 20 wt%) were pressed as disks and sintered at 1500 °C in air. The soda-lime glass had the composition (cation wt%): Na-11·4, Si-68·8, K-3·1, Ca-15·6, Fe-1·2. The glass–YSZ composites with glass contents up to 5 wt% were sintered at 1500 °C during 2 h, and richer-glass compositions were sintered at 1300 °C. Characterisation of the sintered composites was carried out by scanning electron microscopy (SEM) and impedance spectroscopy (20 Hz–1 MHz) in air at various temperatures. All data resulting from electrical measurements were corrected for the different cell dimensions; for this reason the results will be shown as complex resistivity spectra. A simplified notation will be used to describe these glass-ceramic compositions '(**n**gYSZ' = **n** weight% glass).

Another set of YSZ samples was placed in the wall of a heat recovery chamber of an industrial

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glass furnace and kept in contact with the exhaust gas atmosphere for 17 days, at temperatures of around 1300 °C. For these samples, named 'IndYSZ' ('Ind' for industrial testing), characterisation was similar to that for glass–ceramic composites previously described.

Finally, a specific series of experiments was also performed with sintered YSZ disks (having over 96% densification) covered with a layer of glass on one side, and fired for 2 h at different temperatures (1250–1350 °C). These experiments were conceived to try to reproduce in closer detail the corrosion process of zirconia electrolytes when in direct contact with glass melts. After mechanical removal of the glass layer and a top layer of the ceramic with SiC sandpaper, disks were also electroded for electrical measurements (see scheme in Fig. 1). This process (removal of a thin ceramic layer and subsequent electrical characterisation) was repeated in order to study the dependence of the electrical response on the cell thickness. Microstructural characterisation of 'twin cells' (processed in exactly the same conditions) was also performed to confirm if changes in the electrical response could be related to the depth of glass attack.

## 3 Results and Discussion

### 3.1 Glass–YSZ composites

Figure 2 shows the complex-resistivity spectra of pure YSZ and three other samples with glass. Two of these were obtained by simple mixing of glass and YSZ (5 g YSZ and 20 g YSZ); the third was the result of long exposure to an industrial atmosphere (IndYSZ). As can be seen, the total resistivity of glass-containing samples is significantly higher than that of the glass-free electrolyte, mostly due to an enormous increase in the intergrain (intermediate frequency) contribution. This effect arises from the presence of glassy phases along the grain boundaries (Fig. 3), either as a result of the intimate mixture of both phases (5 g YSZ and 20 g YSZ) or as a result of attack by the gas phase (IndYSZ). This glassy phase is believed to block the transport of oxygen ions through the glass/ceramic interface, thus causing an enormous increase in interfacial polarisation.

Figure 3 shows similar microstructures for samples obtained in different circumstances (5 g YSZ and IndYSZ). In both cases the electrolyte grains are surrounded by a glassy phase. Only slight differences in microstructure confirm that high amounts of glass can be brought to the intergranular region by diffusion, after simple exposure to a corrosive atmosphere. For extreme conditions (long firing periods and/or high temperatures), formation of monoclinic zirconia was observed.[7] This indicates the need for a careful placement of the YSZ sensors in industrial furnaces, in order to increase their lifetime and minimise corrosion effects.

Figure 2 shows a significant increase in the magnitude of the high-frequency arc with glass content. At the same time, EDS analysis showed a higher proportion of $Y_2O_3$ in the intergrain region and a corresponding concentration decrease inside the YSZ grains, which may be responsible for a drop in the grain conductivity. The simple mixture of a

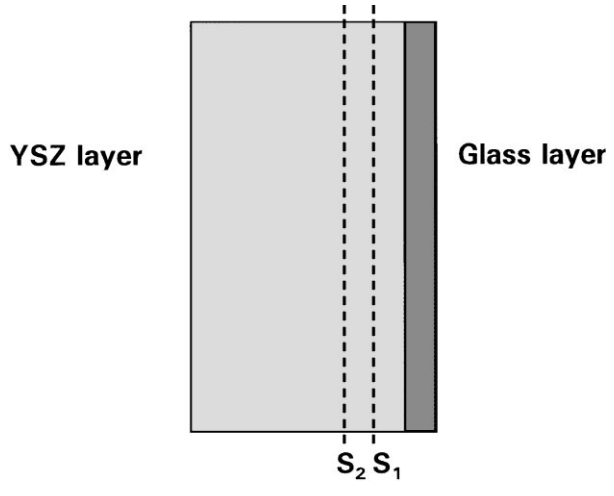


**Fig. 1.** Schematic view of cells used in corrosion experiments, performed with YSZ disks fired in direct contact with glass. Lines $S_1$ and $S_2$ indicate the relative positions of consecutive electroded surfaces used for impedance spectroscopy. These electrodes were deposited after mechanical removal of part of the electrolyte material. The second electrode was always deposited on the cell glass-free surface (left side of the cell).

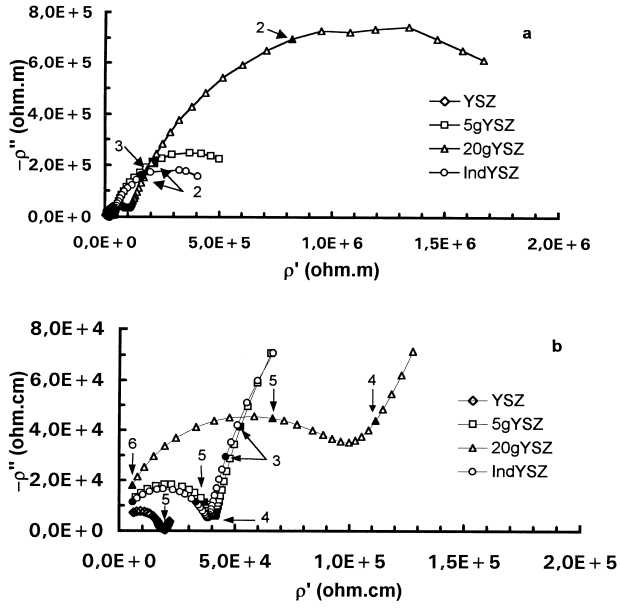


**Fig. 2.** Complex resistivity spectra obtained at 350 °C for YSZ, 5 g YSZ, 20 g YSZ, IndYSZ: (a) full frequency range; (b) high frequency range (roughly $10^3$–$10^6$ Hz). Numbers close to the arrows correspond to the logarithm of the frequency of the measurement (e.g. $2 = \log f$, with $f = 10^2$ Hz).

high resistivity glass with the electrolyte phase (relatively less resistive) should also cause an increase in the magnitude of the high-frequency arc.

Table 1 summarizes the effect on electrical properties of several glass additions. For comparison, the results of the IndYSZ sample are also shown. As discussed, the resistivity tends to increase with increasing glass content, and this effect is more pronounced in the intermediate-frequency contribution (usually ascribed to the grain boundary response). At the same time, both relaxation frequencies tend to decrease with increasing glass content. In particular, the intermediate frequency arc is seriously affected by glass incorporation, denoting a stronger influence of the presence of this phase on the electrical response of the intergranular region. For large glass contents, the relaxation frequency of the intermediate-frequency arc decreases by almost two orders of magnitude with respect to the glass-free electrolyte material. The magnitude of these values can thus be used as a measure of the corrosion condition and impedance spectroscopy can be exploited as a non-destructive technique to study solid electrolyte corrosion processes.

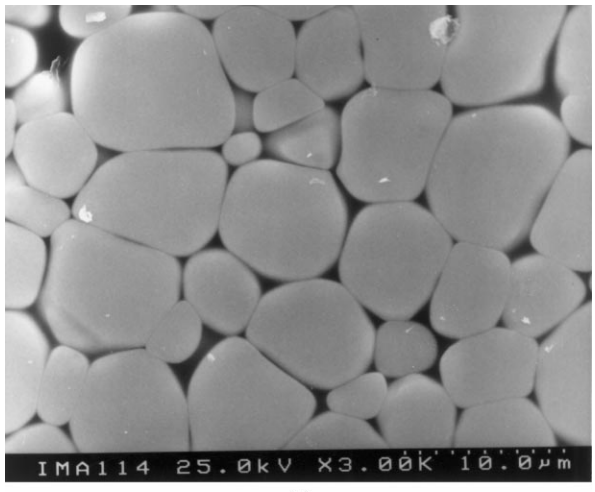


**Fig. 3.** Microstructures of glass containing YSZ samples: (A) 5 g YSZ, (B) IndYSZ.

**Table 1.** Resistivities and relaxation frequencies at 350 °C, obtained from the high frequency (HF) and intermediate frequency (IF) arcs for YSZ–glass composites (see text for the notation)

| *Sample* | *Frequency (Hz)* | | *Resistivity (Ωcm)* | |
|---|---|---|---|---|
| | *HF* | *IF* | *HF* | *IF* |
| YSZ | $6{\cdot}75\times10^{5}$ | $7{\cdot}75\times10^{3}$ | $1{\cdot}77\times10^{4}$ | $1{\cdot}70\times10^{3}$ |
| 1 g YSZ | $5{\cdot}16\times10^{5}$ | 463 | $2{\cdot}25\times10^{4}$ | $6{\cdot}46\times10^{4}$ |
| 5 g YSZ | $3{\cdot}90\times10^{5}$ | 50 | $4{\cdot}07\times10^{4}$ | $5{\cdot}91\times10^{5}$ |
| 10 g YSZ | $3{\cdot}22\times10^{5}$ | 39·5 | $6{\cdot}42\times10^{4}$ | $2{\cdot}37\times10^{6}$ |
| 20 g YSZ | $1{\cdot}61\times10^{5}$ | 45 | $9{\cdot}78\times10^{4}$ | $2{\cdot}30\times10^{6}$ |
| IndYSZ | $3{\cdot}38\times10^{5}$ | 49 | $3{\cdot}81\times10^{4}$ | $4{\cdot}45\times10^{5}$ |

The properties of the glass–ceramic composites being studied were shown to change quickly with increasing glass content, up to values of about 5 wt%. Above this limit the changes are less pronounced, as confirmed by comparison with data for 10 g YSZ and 20 g YSZ samples. Microstructural changes are also less pronounced when moving to 10 or 20 wt% glass additions, as a result of a complete coverage of YSZ grains.

### 3.2 Glass-covered cells

The successful use of impedance spectroscopy in monitoring the progression of the electrolyte corrosion process suggested to us the possibility of characterising the YSZ cells fired in direct contact with a glass layer by the same method, as shown in Fig. 1. As previously mentioned, the magnitude of the relaxation frequencies of the intermediate frequency arcs gave a good indication of the presence of glass throughout the electrolyte, because of a shift to low values.

Figure 4 shows the dependence of this relaxation frequency on the thickness of the removed electrolyte layer, obtained from the glass-covered cells. This thickness is in fact the distance to the original YSZ/glass interface, before firing the glass-covered cell. The results shown here were obtained from impedance measurements performed at 350 and 400 °C, after firing the glass-covered cells for 2 h at 1350 °C (see Fig. 1). The performance of a pure-YSZ sample (flat horizontal lines) is also shown in Fig. 4 as a reference. The onset in relaxation frequency with increasing distance can be used to estimate the depth of glass penetration throughout the electrolyte. From the impedance measurements at both temperatures, this depth was estimated to be in the order of 250 $\mu$m [see Fig. 4(A)].

Figure 5 shows the microstructure of one of these cells under different magnifications. The YSZ/glass interface is near the black separator between different magnifications in Fig. 5(a). The electrolyte phase corresponds to the light grey area,

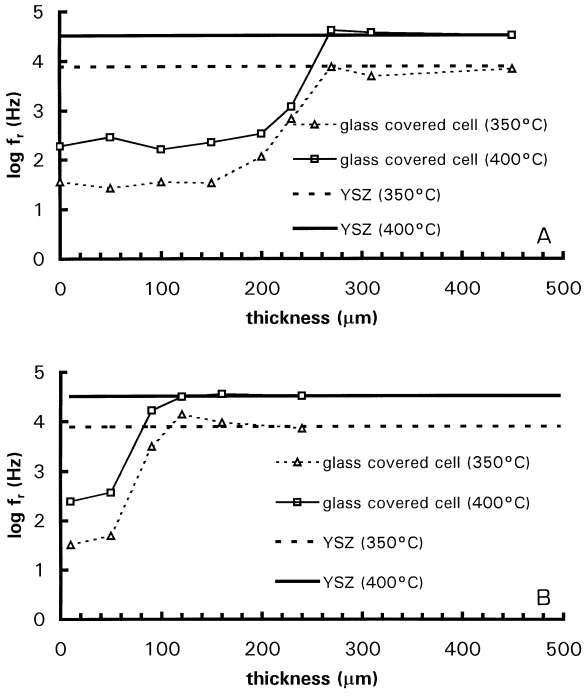


**Fig. 4.** Dependence of the relaxation frequency of the intermediate frequency arc of glass-covered YSZ cells on the thickness of the removed electrolyte layer (data obtained at 350 and 400 °C). For comparison, results of a glass-free YSZ sample are also shown (flat horizontal lines). The glass-covered cells were fired for 2 h at (A) 1350 °C and (B) 1300 °C (see Fig. 1 for experimental details).

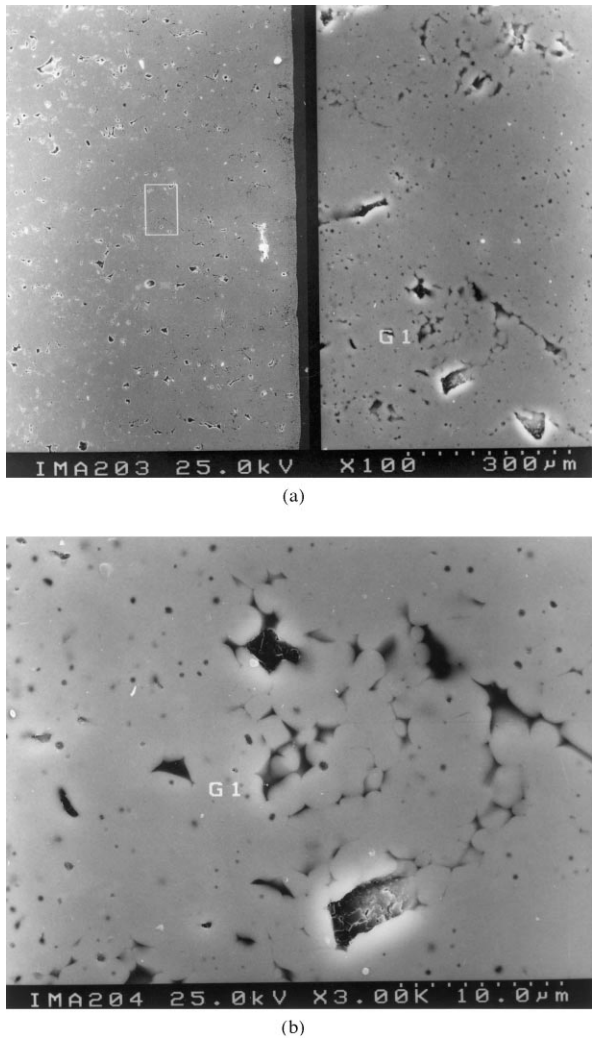


**Fig. 5.** Microstructure (cross section) of a glass-covered YSZ cell after 2 h at 1350 °C. Signed region in a (G1) is expanded in b to show the presence of glass (dark areas). EDS was used to confirm a glass penetration depth of about 300 $\mu$m (see text for details).

whereas the glass layer corresponds to the dark grey area, to the right of the YSZ area. Because of the preferential location of glass in triple contact points or in pores, compositional profiles obtained by EDS along a given line were invalid. However, from average compositions of consecutive areas of similar dimensions (thin and long), a glass-penetration depth could be estimated. The results were found to be in close agreement with data obtained from impedance spectroscopy. Additional firing treatments under less severe conditions (at 1250 and 1300 °C) were also performed. The predicted thickness of the corroded layer, obtained from impedance spectroscopy measurements, was about 100 $\mu$m for specimens fired at 1300 °C [see Fig. 4(B)]. These results were again in close agreement with microstructural and compositional analyses.

### 3.3 Final remarks

The results shown in Fig. 3 clearly indicate that exposure of zirconia-based electrolytes to an industrial furnace atmosphere at temperatures of about 1300 °C promote a strong incorporation of impurities into YSZ sintered bodies. A glassy phase formed between grains, with a composition similar to that of the glass produced in the furnace and now used in the preparation of glass–ceramic composites (mostly oxides of Si, Ca and Na). However, components like Na were present in smaller concentrations, together with significant concentrations of some of the fuel impurities (S and V). The location of this glassy phase along the intergranular region was similar to that obtained with glass–zirconia mixtures processed in the laboratory.

The similarity between electrical properties of the IndYSZ and 5 g YSZ samples (or even 10 g YSZ and 20 g YSZ) was remarkable, irrespective of the glass composition and different processing routes (see Table 1). Also, for cells with a non-uniform distribution of glass throughout their thickness (glass-covered cells), changes in glass content could be monitored by a significant shift in the relaxation frequency of the intermediate-frequency arc. This suggests that the development of oxygen ion blocking glass/ceramic interfaces is the major reason for the observed changes in electrical performance, namely in the intermediate-frequency

region. Lastly, the effect of exposure to conditions of practical relevance could be reproduced by simple direct incorporation of glass in the glass–YSZ composites prepared in the laboratory. Thus, laboratory-scale experiments can be used to evaluate the role of the materials characteristics (e.g. composition, microstructure, etc.) on corrosion kinetics, while impedance spectroscopy can be used to monitor the process.

## 4 Conclusions

Glass additions to YSZ (either intentional or as a result of chemical attack) cause significant changes on intergranular properties, with a strong increase in electrical resistivities and decrease in typical relaxation frequencies of the corresponding impedance arcs. The latter is a very sensitive parameter that can be used to monitor corrosion processes by impedance spectroscopy.

Industrial tests performed with YSZ samples exposed to the atmosphere of a glass-melting furnace showed strong corrosion effects. This points out to the need for careful placement of the YSZ sensors in the furnace, if corrosion is to be minimised.

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