Sealing glass system for molten carbonate fuel cells (MCFC)

M. J. Pascual, A. Durán & L. Pascual
Instituto de Cerámica y Vidrio (CSIC), Arganda del Rey, Madrid, Spain

Commercial development of molten carbonate fuel cells (MCFC) requires the production of sealing materials for the gas manifolds in order to ensure the tightness of the cell. Up to now, the most employed sealing material has been zirconia felt but it has a weak mechanical resistance to overpressures and sliding and, due to its porous structure, electrolyte migration takes place limiting the life of the cell. Glass is an ideal material for this application since it matches the relevant thermal properties such as thermal expansion coefficient, viscosity and transformation temperature and it constitutes a non-porous and tight seal. Glass compositions in the alkaline borosilicate system have been studied and optimised to fill the requirements for sealing MCFC, including a high resistance against molten carbonate corrosion at 650°C. The optimised glass shows good chemical, thermal and electrical behaviour but the corrosion rate at high temperature is still too fast. To increase the corrosion resistance, ZrO2 fibre was added to the borosilicate glass. Corrosion tests carried out on the composite material with 20 wt% ZrO2 fibre showed a significant increase of corrosion resistance without large changes in thermal properties, enabling a good seal at 650°C. Nevertheless, lower sealing temperatures, around 500°C are required to ensure tightness during cell start-up. This problem can be solved employing an additional borosilicate glass with lower softening temperature. Finally, a two-step sealing procedure has been developed through the combination of the glass fibre composite with a ‘softer’ borosilicate glass. The accomplishment of all the objectives presents a glass sealing system as an appropriate alternative to zirconia felt for sealing the gas manifolds of MCFC. The new system allows enhanced cell performance avoiding gas leaks and electrolyte migration, thus both improving the electrical efficiency and elongating the working life of the MCFC up to levels that make them attractive from the commercial point of view.

MCFCs are made up of a stack of cells whose lateral faces are closed by gas manifold plates. Cell tightness is achieved with a joint or seal located between the dielectric isolator of the manifold, an alumina frame, and the stack, the materials to be sealed being alumina and stainless steel. The seal must be specially joined to the alumina frame since they must slide together during the dimensional changes produced on heating the cell.

To date, zirconia felt under mechanical pressure has been the most employed sealant for this kind of cell since it shows good resistance against molten carbonate corrosion and has a low resistance to overpressure and sliding. However, due to its high porosity, it has low gas tightness and electrolyte migration to the pores occurs, generating voltage differences between the cells and decreasing the system efficiency. Taking into account these problems and the critical requirements of the seal at the working temperature (650°C), the main conditions for the sealing material are:

1. High resistance against electrolyte transport.
2. High thermal resistance (650–750°C) and thermal cycling.
3. Compatibility of thermal expansion coefficients.
4. Resistance to overpressures and sliding. Sliding caused by dimensional changes due to compaction of porous components during heating depends on the number of cells. Sliding is usually between 20 and 30 mm.
5. Gas tightness.
6. Perfect fitting to irregular profiles.
7. High electrical resistance.
8. High chemical resistance against molten carbonate corrosion.
9. The seal should work during 40 000 h without significant loss or modification of its properties.

The objective of this work was the development of new glass sealing materials to seal the gas manifolds of MCFC. Glasses have a series of advantages for this application. A glass is a non-porous that softens at high temperatures and fits well to the shape of the elements to be sealed ensuring a hermetic close. The viscosity and thermal expansion coefficient, TEC, can be quite easily adjusted but the most difficult requirement to fulfill is a high resistance against molten carbonates.

The specific requirements for sealing are TEC between 7 and 8×10^-6 K^-1, close to that of Al2O3 (α=8.3×10^-6 K^-1); sealing temperatures lower than 500°C, the melting temperature of the electrolyte: logn (η in dPas)=6–10 in the temperature range from 650 to 750°C, a viscosity range in which the glass can seal by viscous flow allowing the stresses which are generated in the seal to be absorbed.
This study focuses on the alkali borosilicate system in which compositions with high chemical resistance at high temperature and good sealant properties can be selected.\(^1\) Composite materials based on borosilicate glass/ZrO\(_2\) fibre were also characterised to enhance the corrosion behaviour at high temperature.

The studied properties were those of specific relevance to applications. The dilatometric properties, such as TEC, transformation temperature (T\(_g\)), softening temperature (T\(_s\)) and the viscosity temperature curve were analysed, since they are responsible for the mechanical stability and determine the performance of the seal. Phase separation and crystallisation processes that may take place during the start-up and throughout operation at the working temperature of the cell during long periods were characterised along with their influence on properties. The study of corrosion resistance was the key parameter for this application since it determines the long term survival of the seal. Finally, the sintering behaviour was studied since sealing involves the application and sintering of glass powder with agglomerant during cell heating.

**Experimental procedure**

Compositions with Na\(_2\)O or mixed alkali LiO\(_2\)/K\(_2\)O were prepared in the system R\(_2\)O–B\(_2\)O\(_3–\)SiO\(_2\), Figure 1.

In the case of Li/K glasses, the molar ratio was the same as in the electrolyte of the cell, corresponding to the eutectic mixture (Li\(_2\)O/K\(_2\)O = 62.5/37.5) which melts at 488°C.

The studied compositions are grouped in two series depending on the molar ratio B\(_2\)O\(_3\)/R\(_2\)O: series 50 with a ratio equal to 1 and series 40 with a ratio equal to 1:5. In both series silica is progressively substituted by boron and alkaline oxides from composition 1, with a SiO\(_2\) content of 75%, up to composition 4 with a content of 50%, Table 1. In this way it is possible to increase the TEC up to values similar to Al\(_2\)O\(_3\) and decrease T\(_s\) and T\(_g\) temperatures for sealing at temperatures around 650°C.

The glasses were prepared employing SiO\(_2\) sand, reagent grade Li\(_2\)CO\(_3\), Na\(_2\)CO\(_3\), K\(_2\)CO\(_3\), and vitreous B\(_2\)O\(_3\) melted from H\(_3\)BO\(_3\). The components were melted in air in an electric furnace at 1500°C, Figure 1 in the eutectic mixture (cell electrolyte) at 650°C. The tests were carried out from periods of 1 min to 10 days, always carbonate excess\(^5\).

Sintering behaviour was studied as a function of particle size. T and G glasses were crushed and milled in dry conditions. The powder glass was sieved and three size fractions were obtained: 40–60 µm (Fraction A), 20–40 µm (Fraction B) and <20 µm (Fraction C). Cylindrical samples (≈1 cm in height, ≈0.8 cm in diameter) from the different glass powder fractions were prepared by isostatic pressing at 200 M Pa.

The compacts were isothermally treated at temperatures between 600 and 750°C during times from 5 min to 24 h. The sintering process of the three powder fractions for each glass was examined in terms of density variations and dimensional modifications of the sample.

**Table 1.** Composition of glasses of series 50 and 40 (mol%)

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<td>24</td>
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The viscosity–temperature curve of the glasses has been determined by combining the rotation method, for viscosities in the range 10–10\(^{13}\) dPas, and the fibre elongation method, for viscosities in the range 10\(^{6}\)–10\(^{13}\) dPas. The viscosity measurements were performed with a Haake high temperature viscometer that allows the combination of the methods described in ISO 7884–2\(^2\) and ISO 7884–3\(^3\) standards using a Sensor System HE 1700. The viscosity data were fitted to the Vogel–Fulcher–Tamman (VFT) equation employing regressive calculus. The experimental procedure is described in detail in Ref. 4.

Corrosion tests were carried out by immersion of the glass samples in the eutectic carbonate mixture (cell electrolyte) at 650°C. The tests were carried out from periods of 1 min to 10 days, always carbonate excess\(^5\).

Figure 1. Ternary diagram indicating the borosilicate compositions studied
Results and discussion

Viscosity and dilatometric properties

Figure 2 gives the complete viscosity temperature curve of series 40 glasses with adequate dilatometric properties; Pyrex glass is also shown as a reference. The continuous lines represent the VFT fitting. The error corresponding to the measurements carried by the rotation method are smaller than the size of the points for the viscosity values.

As expected, a decrease in viscosity and higher glass fragility is observed when substituting silica by boron and alkaline oxide.

The mixed alkali glass SiBLiK403 with the same molar composition as SiBNa403 shows a minimum in viscosity at low temperatures due to the mixed alkali effect. SiBNa403 glass is maintained into the viscoplastic range (log $\eta$ = 6–10) between 650 and 750°C, the log $\eta$ at 650°C around 8 being high enough to resist overpressures.

Table 2 summarises the temperatures corresponding to the viscoplastic range and the viscosity value at 650°C. The combination of these data with dilatometric values of TEC and $T_g$ indicate that SiBLiK503 and SiBNa403 are the glasses that best fit the cell requirements. Since the mixed alkali glass, SiBLiK503, suffers complete devitrification during extended thermal treatment at 650°C it was discounted from further study.

Corrosion resistance

The thermal properties and rheological behaviour suggest that sodium glasses, especially SiBNa403 glass, are the most adequate for sealing. These glasses were therefore exposed to molten carbonates to simulate the working conditions in the cell and follow the corrosion behaviour.

Figure 3 shows the log-log plot of the weight loss results versus time for SiBNa403 glass and the corresponding glass with Li and K after immersion in the molten carbonate eutectic mixture at 650°C. Silica and Pyrex glasses are also shown as references. A strong corrosion viscosity dependence is observed.

For vitreous silica the weight loss depends on the square root of the time of the first corrosion steps thus suggesting an interdiffusion process. After some time, the slope becomes equal to 1 indicating that the glass network is in the process of dissolving.

For borosilicate glasses, two different slopes were observed corresponding to different corrosion mechanisms. At short and intermediate times, the slope is equal to 1 indicative of a dissolution mechanism; chemical and XPS analysis showed that this dissolution is congruent. At longer periods of time, however, the slope goes down to ½ or even less indicating a diffusion controlled mechanism. A layer attached to the glass containing the nonsoluble corrosion products is formed. This layer is mainly constituted of lithium metasilicate and acts as a protective barrier for the subsequent glass dissolution.

Considering these experimental results, a three-step corrosion mechanism for borosilicate glasses in molten carbonates is proposed, Figure 4.

1. First stage: interdiffusion. The carbonates diffuse into the glass and an ionic exchange with the glass modifiers takes place. This stage is mainly diffusion controlled and depends on the square root of time.
2. Second stage: network dissolution. The matrix dissolution converts into the dominant mechanisms and

![Figure 2](image-url)  
**Figure 2.** Viscosity temperature curve for some series 40 glasses and Pyrex glass.

![Figure 3](image-url)  
**Figure 3.** Weight loss as a function of time for some series 40 glasses and silica and Pyrex glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>log $\eta$ at 650°C</th>
<th>log $\eta$ at 500°C</th>
<th>$T_g$ (°C)</th>
<th>a$_{50–800}$ (x10$^{-6}$)</th>
<th>b$_{50–800}$ (°C)</th>
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<tr>
<td>Series 50</td>
<td>SiBLiK501</td>
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<td>8–3</td>
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<tr>
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<tr>
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<td>9–3</td>
<td>575·3</td>
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<td>576–678</td>
<td>6–9</td>
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<td>Series 40</td>
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<td>10–1</td>
<td>501·6</td>
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<td>SiBLiK402</td>
<td>656–719</td>
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Table 2. Viscoplastic range, viscosity at 650°C, $T_g$ and thermal expansion coefficient.
the first superficial layer of the glass structure starts to break at intermediate times.

The dissolution rate of the glass matrix is constant and the concentration of the network components such as silica and boron oxide in the melt will increase linearly with time in a diluted system. In this case, there is a low reaction products content in the melt and the concentration of the glass components is considerably under the saturation levels. It does not exist any barrier that limits the dissolution reaction in the glass surface. The reaction is governed by the attack of to Si-O-Si and B-O-B bonds by CO$_3^-$ ions.

If the dissolution rate of the corrosion products is slower than the rate for the corrosion reaction or the melt is saturated, the dissolution rate diminishes. This stage is reached very fast by the less resistant borosilicate glasses.

A similar mechanism has been observed for phosphate glasses in aqueous solutions, silicate glasses in basic solutions and quartz in molten carbonates. A after these stages, a superficial layer is deposited onto the glass over longer time intervals. Some of the soluble elements of glass dissolve into the solution while the other elements form insoluble compounds and precipitate on or over the lixiviated glass surface during intermediate and long times, this layer grows with time. These layers can contain a variety of precipitates from the glass components and can be constituted by high crystalline phases as well as by amorphous components. This precipitated layer has the potential to affect the later attack of the glass in which the components subsequently dissolved must go through this layer before being dissolved into the solution, so they act as protective barriers for a subsequent glass dissolution. The efficiency in the limitation of diffusion rate depends on the adherence, composition and microstructure of the layer.

The corrosion kinetic rate is equal to ½ for the attack in a diluted medium and significantly reduced when the medium saturates with the glass components. The slope tends to zero if total saturation and, consequently, equilibrium are reached.

The dissolution of many simple and complex glass systems can be described by a combination of diffusion and dissolution control processes. At the beginning of the eighties, Wallace & Wicks(12,13) developed a similar model for the attack of glasses for radioactive waste storage. This model insists on the formation of superficial layers and the effect of ions on the attack.

**Sintering behaviour**

SiBNa403 glass presents the best properties for sealing among the studied compositions, showing good devitrification resistance and a corrosion rate dependant on the fourth root of time $t^{1/4}$. However, its viscosity is rather high when the temperature is reduced, a value of logP (at 500°C) of 11.5 inhibiting sealing from temperatures below 500°C.

The sintering process of SiBNa403 glass has been studied as a function of temperature, time and particle size, Figure 5.

For isothermal treatment at 650°C (log$_{10}$ (dPaS)=9), the plots of density versus time show different sintering rates for different particle sizes, the fastest process corresponding to the smallest size. In all cases, a density equal to or greater than 95% was obtained.

Once the maximum densification is reached, longer thermal treatment leads to a decrease in density reduction due to quartz crystallisation. Although the density of quartz is higher than that of glass, the phase change involves a volume change of 15% which generates porosity around the quartz crystals, thereby reducing the overall density.
On reducing the sintering temperature by 25°C to 625°C, viscosity increases by one order of magnitude and it is possible to obtain good densification with a small particle size by employing longer sintering times. In this case, devitrification effects are not observed.

The results indicate that it is possible to seal even at high glass viscosity by increasing the sintering time and reducing the particle size. This information is significant for selecting the optimum sealing conditions.

**Simulation in a monocell**

The performance of SiBNa403 glass under working conditions was simulated in a monocell composed of 10 cells, with a total area of 100 cm² and 100 W of power. The configuration of the gas manifolds was of the external type with two manifolds for the entrance and exit of oxidant and two more for the fuel.

Firstly, the four alumina frames were enamelled with a perfectly dense glass layer, 2 mm thick, in order to improve the contact between the glass layers and the cells, then a further layer of powder glass mixed with agglomerant was applied. The frames were located in the cell and the manifolds were closed applying a closing pressure of 1.5 kg/cm². The system was slowly heated up to 650°C and kept at this temperature for 25 days after which the system was cooled and restarted in order to check the response on thermal cycling, Figure 6.

The test gave the following results: thickness reduction lower than 30% due to compression effects; voltage stability that indicates a high resistance against transport of the electrolyte; fit to cell profiles and sliding resistance; good gas tightness at 650°C; high electrical resistance; good chemical resistance; and small gas leakages between 450 and 600°C.

The last two results should be improved. In order to get better corrosion resistance, composite materials (SiBNa403/ZrO₂ fibre) were prepared and for sealing from lower temperature (~500°C) borosilicate glasses with lower softening temperature (‘softer’ glasses) were melted.

**Composite material (SiBNa403/ZrO₂ fibre)**

Results of the sintering and corrosion behaviour of the composite material are presented below.

Dense materials were obtained using 20 wt% fibre (9% in volume). The sintering kinetics for the composite material at two different temperatures, Figure 7. The figure shows that glass viscosity has the most pronounced effect on densification and on the maximum fibre concentration, it is the critical property that must be controlled when composite materials are designed and processed. With a high viscosity and low fibre concentration, good final densification can be obtained but to produce high density composite materials with a higher fibre concentration, lower viscosity must be used.

Densification is much faster at 650°C but once the maximum relative density is reached, longer treatment times case quartz crystallisation from the glass matrix, that causes the diminution of the density by new porosity generation due to gases originated during crystallisation.

Figure 8 presents the microstructure corresponding to a composite material when maximum densification is reached; the material presents similar thermal properties to the glass matrix.
The corrosion behaviour of the composite material in molten carbonates at 650°C for a period of up to 25 days has been evaluated. Figure 9 corresponds to a cross section of samples treated in molten carbonates at 650°C for 12 days for Na403 glass, Figure 9(a), and 25 days for glass with ZrO2 fibre, Figure 9(b). The photographs show that the corrosion behaviour of composite material is much better.

According to the corrosion kinetics, Figure 10, a glass layer of 2 mm should be attacked after 10 days for SiBNa403 glass while 150 days would be necessary in the case of samples containing fibre. On extrapolating the corrosion curve, it is found that a thickness of 2-7 mm would be necessary for a lifetime of 40000 h.

Soft borosilicate glass

Figure 11 shows the borosilicate compositions prepared in order to obtain a ‘softer’ glass for sealing from around 500°C. Table 3 presents the dilatometric properties of these glasses. SiB602Na shows the best thermal properties and better resistance in molten carbonates and was therefore selected for sealing.

Sealing system

In the light of these results, a two-step sealing process is proposed for sealing MCFCs: (1) enamelling of alumina frame with the composite material SiBNa403/ZrO2 fibre with a thickness of 2 mm and (2) applying a layer SiB602Na a glass powder of thickness 0.5 mm on the glass enamel and sintering during the start-up.

The sliding behaviour of the sealing system was tested in a monocell and a distance of 40 mm was obtained without breaking.

Conclusions

Borosilicate sealing glasses have been characterised according to the properties relevant for their application in MCFCs and those that best fit the cell requirements were selected.
A two-step sealing system has been developed: (1) enamelling of the alumina frames with SiBNa403/ZrO2 fibre composite and (2) sealing with ‘soft’ glass, SiB602Na, during cell start-up.

The glasses and composite materials and the design of the sealing system permit sealing from 480°C while maintaining cell tightness. Simultaneously, a sliding distance of 40 mm is supported without breaking and a high corrosion resistance is maintained suitable for a mean life of around 40000 h.

This system is adequate for sealing M C F C s of greater power. In particular it has been selected for a 500 kW M C F C for demonstration in the M O L C A R E - U E project.

Acknowledgements

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