

The State-of-the-Art in Sealing Technology for Solid Oxide Fuel Cells

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One of the keys to developing viable solid oxide fuel cell (SOFC) systems is to first develop reliable and inexpensive stack sealing technology. Three general approaches are currently being pursued: rigid bonded sealing, compressive sealing, and compliant bonded sealing. This review highlights the advantages and limitations of each option, discusses some of the leading concepts, and outlines the future steps that need to be taken in their development.

INTRODUCTION

With crude oil prices soaring to record levels, many are concerned with how high energy costs will climb and what will be the economic and societal impact. Over the past 30 years, the consumption of energy has expanded at an alarming rate. Fossil fuels—crude oil, coal, and natural gas—are the sources of more than 85% of the energy consumed in the United States.^{1,2} Keeping up with the growing international demand for fossil energy has become an increasingly complex issue, fraught with innumerable factors both political and technical in nature. In particular, the environmental impact and geopolitical consequences of heavy reliance on fossil fuels will continue to be ever more conspicuous and problematic.

With the exception of reducing energy use—which is certainly a viable energy management strategy, but not one that has yet been followed with great collective enthusiasm—the most direct way to make resources last longer is to use them more efficiently, wringing more energy out of a given amount of fuel. One means of doing this is the fuel cell, which directly converts the chemical energy of the incoming fuel into electrical energy via an electrochemical reaction.³ Not only do fuel cells offer greater efficiency

than either gas turbines or diesel and gasoline combustion engines—in fact, they are three times more efficient—but they are also noiseless, low-maintenance, virtually pollution-free, and can be scaled from pocket portable to megawatt size.⁴

Of the various types of fuel cell technologies that have been developed, solid oxide fuel cells (SOFCs) are the least mature but offer a number of distinct advantages. Specifically, the SOFC is the only fuel cell constructed entirely from solid materials; all other types employ a liquid electrolyte and require a means of maintaining that liquid so the fuel cell will not dry out and lose function. In addition, because an SOFC stack operates at high temperature (on the order of 700°C or higher), fuel reformation can occur directly within the system. This potentially eliminates the need for an external fuel reformer and enables a wide array of commercially available hydrocarbon fuels to power the stack, including natural gas, methanol, and coal gas.⁵ The large amount of heat generated during operation is not only sufficient to carry out internal fuel reformation and keep the SOFC stack at its operating temperature, but can also be utilized to

increase the overall efficiency of the system. Even more intriguing, due to the temperature of operation and the type of electrochemical reactions that take place in an SOFC, carbon monoxide (a by-product of fuel reformation) will not poison the stack, but serves as an additional source of fuel. Among SOFC designs, the planar stack concept (pSOFC) has received attention because its compact nature affords high volumetric power density, an important design feature in transportation applications.

Solid oxide fuel cells typically function under an oxygen ion gradient that develops across the electrolyte⁵ and because of this, hermeticity across this membrane is paramount. Leaks, which form due to flaws that originate during stack manufacture or because of component degradation during stack operation, lead to reduced system performance, lower power-generation efficiency, and poor fuel utilization.^{6,7} They can also cause local hot spots or worse, widespread internal combustion within the stack, both of which induce accelerated degradation in the device.⁷ In a planar stack design, this means that the electrolyte layer must be dense and connected to the rest of the device with a high-temperature, gas-tight seal. One of the fundamental challenges in fabricating pSOFCs is how to effectively join the thin, electrochemically active ceramic cell to the metallic body of the device and thereby create a rugged, hermetic, and chemically stable seal. Typical conditions under which these devices are expected to operate and to which the accompanying seals will be exposed include: an average operating temperature of 750°C; continuous exposure to an oxidizing atmosphere on the cathode side and a wet reducing gas on the anode side; and an anticipated device lifetime

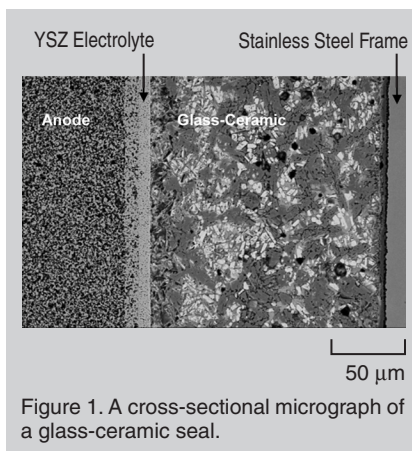


Figure 1. A cross-sectional micrograph of a glass-ceramic seal.

of more than 10,000 hours. A recent review by Fergus⁸ discusses many of the materials employed in pSOFC sealing. This paper will consider some of the stack design and performance issues.

See the sidebar for details on the functional requirements of pSOFC cells.

SEALING TECHNIQUES

The options for sealing and joining the ceramic and metal components in pSOFCs can be broadly classified into rigid bonded seals, compressive seals, and compliant bonded seals. Each offers advantages and limitations.

Rigid Bonded Seals

In rigid bonded sealing, the sealant forms a joint that is non-deformable at room temperature. Because the final joint is brittle, it is susceptible to fracture when exposed to tensile stresses of the type encountered during non-equilibrium thermal events or due to thermal expansion mismatches between the sealant and adjacent substrates.^{14,15} That is, the sealant must be tailored to match the coefficients of thermal expansion (CTE) of the adjacent substrates, which in turn must be selected to closely match each other.¹⁶ Even a modest degree of thermal expansion mismatch can cause substantial bowing in the cells, which can lead to fuel and air maldistribution in the stack and result in poor system performance.¹⁷ For these reasons, the metal stack components (i.e., frames, separators, and spacers) are typically fabricated from ferritic stainless steel (CTE of 12–13 $\times 10^{-6} \text{ K}^{-1}$) to approximately match the composite CTE of the cell (10.5–12.5

$\times 10^{-6} \text{ K}^{-1}$, depending on whether the cell is electrolyte- or anode-supported). Significant effort has been expended on developing sealing materials with CTEs in this range.

Glass and Glass-Ceramic Sealants

Among the first and still most important sealants employed in joining pSOFC stacks are high-temperature glasses and glass-ceramics. These materials tend to

display acceptable stability in the reducing and oxidizing atmospheres of the stack, are generally inexpensive, can be readily applied to the sealing surfaces as a powder dispersed in a paste or a tape cast sheet, typically exhibit good wetting behavior on both yttria-stabilized zirconia (YSZ) and stainless-steel surfaces, are electrically insulating, and can be engineered to exhibit a CTE matching those of the adjacent pSOFC components

FUNCTIONAL REQUIREMENTS FOR pSOFC SEALS

The selection of sealing material(s) used in the stack is dependent on the specific stack design and whether the device will be used in a mobile or stationary application. Numerous planar single oxide fuel cell (pSOFC) stack designs have been developed or are currently in development.^{5,9,10} The two generic examples shown in Figure A illustrate the impact of cell geometry on sealant considerations. In the cell-to-edge design of Figure Aa, the footprint of the cell matches that of the separator plate, each with the same pattern of gas manifold holes for the transport of fuel and air through the stack. Sealing is required along the interfaces between each cell and adjacent separator plate. If the cell is an anode-supported design, in which a thick anode layer serves as the support structure for the rest of the cell, the porous anode layer extends across the entire footprint of the stack and its exposed edges need to be sealed to prevent fuel from leaking outward and combusting with the ambient air. Sealing is also required along the edges of the manifold holes to preclude the fuel and air gases from mixing and reacting within the porous anode material.

In the window frame design (Figure Ab) the cell is smaller than the separator plate, contains no holes, and is joined to an intermediary component, a metallic window frame, which incorporates the necessary gas porting. Two seals are employed, one between the cell and window frame/separator plate assembly to form a cassette repeat unit and a second between each cassette in the stack. In both designs, the seal between each repeat unit must be electrically insulating to prevent internal shorting. In addition, a third seal, not shown, is required between the stack and the system gas manifold that supplies fresh fuel and air and allows the outlet gases to be exhausted. Typically, the system manifold consists of a base plate with the necessary gas connections or is a set of headers that

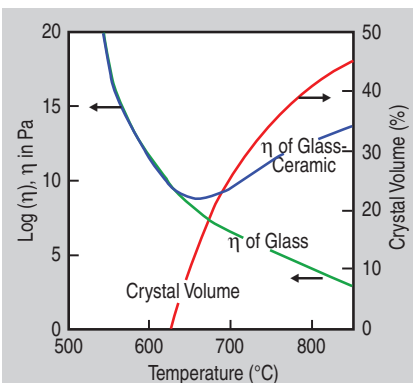


Figure 2. A plot of the general relationship between viscosity and temperature in a glass and in a glass composite undergoing incipient crystallization (courtesy of D.-S. Kim, Pacific Northwest National Laboratory).

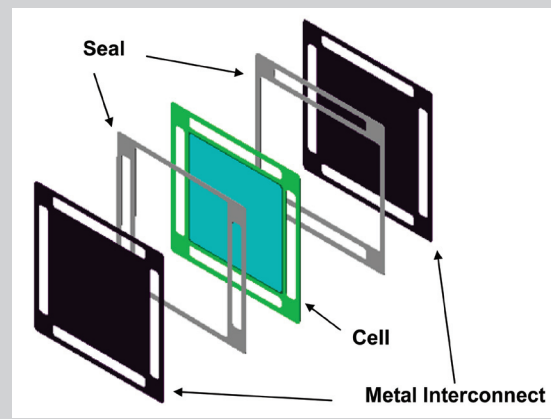
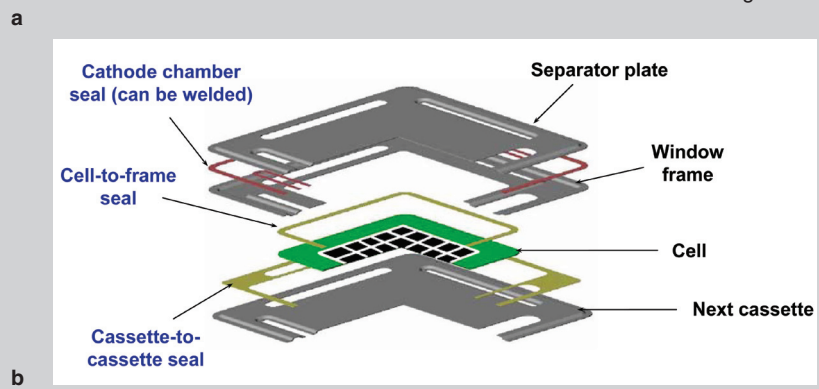


Figure A. Examples of two general cell geometries: (a) the cell-to-edge design and (b) the cell-to-frame design.



in the final joint. They are characterized by a glass transition temperature (T_g) above which the mechanical properties of the material change from brittle to elastic. However, the brittle nature of glasses below this temperature makes these seals vulnerable to cracking.

Many glass sealant formulations are designed to soften and flow at a temperature above that required for stack operation in order to form a hermetic

seal through a combination of mechanical and chemical bonding. When cooled to the stack operating temperature, the glass partially or fully crystallizes to form a rigid, bonded seal (Figure 1). Glass crystallization is advantageous for several reasons: the resulting material is typically stronger than the starting glass and by controlling the kinetics of crystallization and the product phases that form, it is possible to tailor the properties

of the resulting glass-ceramic sealant. Various glass-forming systems have been considered as pSOFC sealants, including those based on phosphates, borates, and silicates.¹⁸ However, prior work has shown that phosphate and borate glasses are not sufficiently stable in the humidified fuel gas environment, tending to undergo significant corrosion through the formation of volatile species as well as reacting with and degrading the various cell materials.^{19–21} To date, the best results have been obtained using compositions based on silica with various modifiers added to increase CTE and improve adhesion and joint strength. While alkali silicate glasses tend to interact deleteriously with the cell materials,²² the use of alkaline-earth silicates to form systems such as BaO-CaO-SiO₂²³ and BaO-Al₂O₃-SiO₂²⁴ yield glass-ceramics with much higher chemical resistance and far less reactivity toward other stack components.^{25,26}

There are several challenges in developing an acceptable glass-ceramic for pSOFC sealing. First is achieving the proper balance of material properties that results in a consistent and repeatable sealing process. The example in Figure 2 illustrates the importance of controlling material viscosity as a function of temperature. The starting glass must be fluid enough at the temperature of sealing to wet the sealing surfaces, yet not so fluid that it flows out from between the substrates and results in open gaps and subsequent leaks. By control of crystallization, the viscosity of the sealant can be slowly raised so that it attains the proper stiffness after wetting to minimize excessive flow or “squeeze out.” In addition to viscosity, several other key material parameters must be simultaneously controlled to achieve a robust sealing process, including T_g , T_s (the temperature at which the glass first softens), CTE, wetting behavior, and bulk strength. These factors can be optimized in one of two ways. The first involves tailoring the initial glass composition and the heating schedule employed during sealing^{27,28} to control the rate of crystallization, which primarily affects viscosity and wetting behavior, and the nature of the crystalline phases, which impacts CTE, T_g , T_s , and sealant strength. Listed in Table I are compositional modifiers that are commonly added to alter the initial bulk properties of the glass-

transport the gases to and from the stack.

A factor closely related to stack design that can have tremendous impact on seal selection is the stack assembly procedure. The ceramic cells are typically produced by traditional tape-casting, screen printing, and sintering processes, or more recently by large-scale coating techniques such as plasma spraying, forming a laminate structure that consists of a minimum of three layers: anode, electrolyte, and cathode. To mitigate interdiffusion and interfacial reactions between these layers, which can produce deleterious phases and/or microstructures,^{11,12} any processing steps to which the cell is subsequently exposed (e.g., joining/sealing) must be carefully controlled with respect to maximum soak temperature, soak time, and process atmosphere. For example, exposure to a high-temperature vacuum or inert gas environment can cause chemical reduction and substantial property degradation in many of the high-performance cathode materials used in pSOFCs.¹³ Additional considerations include processing and materials costs and the potential for mass manufacture. For these reasons, air-fired sealing processes are often favored because they maintain the proper oxidation state in the cell materials and are readily scaleable to low-cost, high-rate stack production.

The primary application in which the pSOFC system will be used also strongly dictates the type of seals employed in the stack. Systems used in mobile applications such as automotive or truck auxiliary power generation units require seals that can be subjected to repeated thermal cycling, thermal shock, and dynamic mechanical loading. Conversely stationary pSOFC stacks are generally exposed to less aggressive thermal and mechanical stress conditions, but are expected to operate at least an order of magnitude longer than their mobile counterparts. In both cases, the sealant material must exhibit minimal reactivity with the adjacent components (typically yttria-stabilized zirconia [YSZ] and ferritic stainless steel) and display high-temperature chemical stability in both air and wet fuel gas environments. Summarized in Table A is a generic set of requirements for SOFC seals broken down by functional category. Because sealant selection is closely tied to pSOFC stack design and system application, it is dependent on a number of design factors, including individual cell and stack materials and geometries, stack assembly sequence, thermal gradients expected across the seal and other stack components, maximum weight and/or volume of the power plant, anticipated external forces, and required system heating and cooling rates.

Table A. Functional Requirements for pSOFC Seals

<u>Mechanical</u>	<u>Design/Fabrication</u>
Hermetic Sealing or Marginal, Non-Localized Leak Rate	Low cost
CTE Matching or Mitigation of CTE Mismatch Stresses	Facile application/processing
Acceptable Bond Strength or Compressive Loading Requirement (i.e., Load Frame Design)	High reliability with respect to achieving initial hermeticity (seal conforms to non-flat substrate surfaces)
Resistant to Degradation Due to Thermal Cycling/Thermal Shock	Acceptable sealing environment/temperature (i.e., has little effect on the subsequent performance of the stack)
Robust under External Static and Dynamic Forces*	Design flexibility (e.g., allows use of Ni-based alloys in the interconnect)*
<u>Chemical</u>	<u>Electrical</u>
Long-Term Chemical Stability under Simultaneous Oxidizing/Wet Fuel Environments	Non-conductive (non-shorting configuration)*
Long-Term Chemical Compatibility with the Adjacent Sealing Surfaces	
Resistant to Hydrogen Embrittlement	

*These factors are stack-design specific.

Table I. Common Compositional Modifiers for Silicate-Based Glass-Ceramic Sealants

Modifier	Function
Al ₂ O ₃	Allows control over viscosity through the rate of crystallization
B ₂ O ₃	Reduces T _g , T _s , and viscosity and improves wetting
BaO	Reduces T _g and T _s , and raises CTE in the glass-ceramic
CaO	Reduces T _g and T _s , and raises CTE in the glass-ceramic
MgO	Reduces T _g and T _s , and raises CTE in the glass-ceramic
La ₂ O ₃	Used as a viscosity modifier and long-term CTE stabilizer
CuO	Improves surface adherence
MgO	Improves surface adherence

ceramic. This strategy has been used to prepare sealants that have been tested beyond 1,500 hours of continuous stack operation with no incipient leaking.^{29,30} In the second method, either an inert or reactive filler material (i.e., powder or fiber)^{31,32} is added directly to a fluid glass matrix to increase viscosity and raise the CTE of the resulting composite. The fillers also act as nucleation sites, thereby influencing the kinetics of subsequent crystallization. To date, this strategy has met with less success than the former.

The second key challenge in developing a useful glass-ceramic sealant is understanding how to stabilize the material's CTE as a function of time at temperature. As shown in Figure 3a, the devitrification process typically continues well beyond the sealing operation, which means that the thermal expansion properties of the sealant that were carefully engineered for initial sealing evolve during isothermal stack operation. If the CTE changes too much, the bonded joint becomes susceptible to cracking during thermal cycling. In the case of the barium aluminosilicate glass-ceramic shown in Figure 3b, the primary culprit for the time-dependent reduction in CTE is the transformation of a key crystalline phase, celsian, from its metastable, high-CTE structure (hexacelsian) to its stable, low-CTE form (monocelsian). It is possible to stabilize the long-term CTE properties of glass-ceramics by again modifying the starting glass composition or by incorporating filler additions.³¹⁻³³ Several glass-ceramic formulations prepared using the former approach have been reported to survive over 30 thermal cycles in full-scale stacks at slow-to-moderate heating/cooling rates (i.e., ~2–5°C/min.).^{30,34} Alternatively, there are new concepts to develop glass-based systems that can withstand some degree of thermally induced cracking by self-healing when re-heated.³⁵

The third and perhaps most critical challenge with glass-ceramic sealants is to control their reactivity with metal components. For example, barium aluminosilicate sealants generally adhere well to YSZ with little chemical interaction, but tend to form interfacial reaction products such as barium chromate (BaCrO₃) and monocelsian (BaAl₂Si₂O₈) with the oxide scales of the candidate stainless-steel alloys (Figure 4). With long-term exposure at the stack operating temperature, these phases thicken and become porous,^{36,37} yielding interfaces that are often weak and susceptible to thermomechanically induced cracking. Many of the glass-ceramic failures observed in full-scale stacks initiate along the metal/sealant interface.³⁸ It has been suggested that mechanically sound, chemically stable glass/metal interfaces can be formed in specimens that are sealed under an inert gas atmosphere that limits scale growth on the metal component. This environment is generally not compatible with the cell materials and therefore is not acceptable for stack manufacture, but the finding suggests that there may be merit in modifying the surface chemistry of the metal frames to reduce the amount of scale that forms during air-fired sealing. More recently, several patents report that geometric modification of the metal sealing surface can offer enhanced joint strength and long-term seal durability under steady-state and rapid thermal cycle conditions (~75°C/min.),^{39,40} which implies that crack deflection and blunting may be important strategies in combating weakened glass/metal interfaces.

Ceramic Seals

Other pSOFC joining techniques that have been considered include the use of high-temperature cements and sealants formed by reaction bonding. While ceramic adhesives such as Duco and Sau-

ereisen cements have been exceedingly useful in small-scale cell testing, they do not display the degree of CTE matching required for stack fabrication and often crack when cooled to room temperature. Ceramic sealants formed by in-situ reaction have also been investigated as an alternative method of rigid bonded sealing. Generally, reaction-based approaches require heat treatment at high temperatures. However, the use of pre-ceramic polymer precursors significantly lowers the temperatures required for joining.⁴¹ These precursors are typically organosilane polymers that convert to SiC or SiO_xC_y when heated to temperatures of 800–1,400°C.⁴² Lewinsohn et al. have recently reviewed the merits of this approach⁴³ and investigated its potential for pSOFC joining.⁴⁴ They found that the use of these polymeric precursors is no more difficult than applying a glass seal and that the resulting joining material is microstructurally and compositionally stable up to temperatures beyond that required for stack operation. However, the pyrolysis of these polymers is accompanied by the formation of gaseous reaction products and high volume shrinkage, which often causes pores and cracks to develop in the joint during processing⁴⁵ and leads to a reduction in joint strength. These problems can be overcome to some extent by incorporating suitable filler materials, which also allows the CTE properties of the sealant to be modified.⁴⁶ However, the technique requires further development.

Compressive Seals

Compressive seals employ deformable materials that do not bond to the pSOFC components but instead serve as gaskets. Thus, sealing results when the entire stack is compressively loaded. Because the sealing material conforms to the adjacent surfaces and is under constant compression during use, it forms a dynamic seal. That is, the sealing surfaces can slide past one another without a disruption in hermeticity and the individual stack components are free to expand and contract during thermal cycling with no need to consider CTE matching. This offers stack designers greater freedom in utilizing alloys other than ferritic stainless steels for the metal components. The gaskets are readily produced and easy to apply. Addition-

ally, they offer the potential for mid-term stack repair by releasing the compressive load, disassembling the stack, and replacing the damaged cell or separator components. However, to employ compressive seals in a pSOFC stack, a load frame is required to maintain the desired level of compression on the stack over the entire period of operation and the stack components must be capable of withstanding the sealing load. The load frame introduces several complexities in stack design, including oxidation of the frame material, load relaxation due to creep, and increased weight and thermal mass (and therefore reduced specific power and thermal response of the overall system). These factors increase system cost and seriously limit the use of compressive seals in mobile applications.

Metal Gaskets

The use of flat metal gaskets has been investigated for compressive sealing. Small-scale coupon testing indicates that non-oxidizing noble metals such as gold and silver may be viable in forming hermetic seals at pressures of ~25 MPa and higher due to sufficient deformation at stack operating temperatures.^{47,48} The key question is how durable these gasket materials are under prototypic long-term isothermal and thermal cycle conditions. Additional concepts include using stamped metal gaskets of the type employed in sealing pressure vessels.⁴⁹ In this case, oxidation-resistant alloys such as stainless steel and nickel-based superalloys are fabricated into gaskets with deformable C-shaped, corrugated, or hollow tube cross sections. A noble metal coating can improve hermeticity, particularly against a rough or uneven sealing surface. Again, little information is available as to the effectiveness of these seals. However, an obvious disadvantage is that the materials they employ are electrically conductive and therefore are subject to potential problems with internal shorting.

Mica-Based Seals

An alternative to metal-based gaskets is the use of mica-based materials. Micas belong to a class of layered minerals known as phyllosilicates and are composed of cleavable silicate sheets (Figure 5). These materials are well known for

their high resistivity and uniform dielectric constant. Of the forms of mica that have been investigated for use in compressive pSOFC seals, including muscovite paper, muscovite single-crystal sheets, and phlogopite paper, the cleaved muscovite sheet exhibited the lowest leak rates.⁵⁰ The commercial mica papers exhibited very poor sealing characteristics even under high compressive loads. Subsequent studies demonstrated that the primary leak paths in the compressed mica seal are along the interfaces with the ceramic and metal sealing surfaces and that sealing can be greatly improved by incorporating a compliant interlayer such as a deformable metal or glass at these interfaces (Figure 6a).^{51,52} Under equivalent loading conditions, the leak rates in these hybrid seals are several orders of magnitude lower than in the cleaved muscovite sheet (Figure 6b).

A separate study showed that the sealing characteristics of phlogopite paper can be greatly improved by infiltrating the mica particulate with a wetting or melt-forming agent such as $\text{Bi}(\text{NO}_3)_3$ or H_3BO_3 .⁵³ However, it was also found that care must be given to the reactivity of such infiltrates with the adjacent pSOFC components. More recent investigations have shown that hybrid seals prepared using phlogopite paper and barium aluminosilicate interlayers can undergo over 1,000 thermal cycles at a heating rate of $5.8^\circ\text{C}/\text{min}$. and a cooling rate of $3^\circ\text{C}/\text{min}$. with minimal seal leakage when compressed under a pressure of 0.34 MPa.⁵⁴ The next logical steps in the development of hybrid seals are to increase the seal footprint from the size used in coupon testing to that needed for full-size stack components and to test the seals in a stacked configuration prototypic of the actual pSOFC device. While there are potential concerns that the compressive sealing stress may not be uniform over the larger sealing area or from one end of the stack to the other, the incorporation of the compliant interlayers in the hybrid mica seal design may mitigate these issues. However, this remains to be demonstrated.

Compliant Bonded Seals

Unlike rigid bonded sealing, the sealant used in compliant bonded sealing forms a joint that can be plastically deformed at or above room temperature.

This mitigates the effects of thermal expansion mismatch stresses to some degree and lessens the requirements of CTE matching between stack components. However, there are still potential issues with cell bowing and the accompanying non-uniformities in gas distribution. In addition, all of the sealing concepts in this category are metal-based and electrically conductive. Thus, they cannot be used as the sole sealing solution for a pSOFC stack design without introducing the need for insulating layers to prevent internal shorting. However, they can potentially compliment a second sealing technique (e.g., glass sealing) in a multi-seal stack design.

Brazing

One of the most reliable methods of joining dissimilar materials is brazing. In this technique, a filler metal with a liquidus well below that of the materials to be joined is heated to a point at which it becomes molten and under capillary action fills the gap between the sealing surfaces. When cooled, a solid joint forms. Active metal brazing is a specialized version of this technique that employs a reactive element such as titanium to facilitate wetting between the filler metal and a ceramic sealing surface.⁵⁵ Unfortunately, active metal brazing is typically conducted in an inert or vacuum environment and therefore incurs the material incompatibility problems discussed previously. In addition, it has been shown that the ceramic-metal joint produced by this technique is not sufficiently resistant to oxidation and will degrade under exposure to high-temperature air.⁵⁶

Recently, an alternative brazing technique was developed specifically for use in fabricating solid-state electrochemical devices such as oxygen and hydrogen concentrators.⁵⁷ Referred to as air brazing, the technique employs a molten oxide that is at least partially soluble in a noble metal solvent to promote wetting of the ceramic sealing surface. One noble metal/oxide combination that has shown promise in air brazing is Ag-CuO, which displays high-temperature oxidation resistance, metallic ductility, and good oxide surface wettability. As little as 1.4 mol.% copper oxide in silver results in a good balance of wettability and adhesion on ceramic sealing sur-

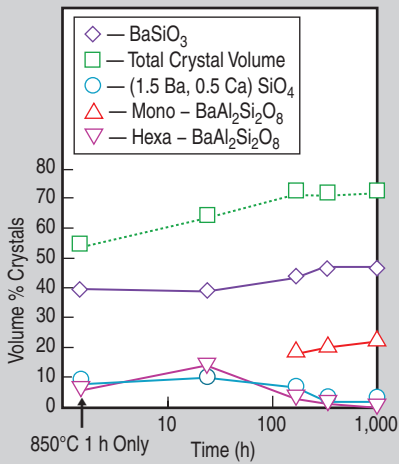
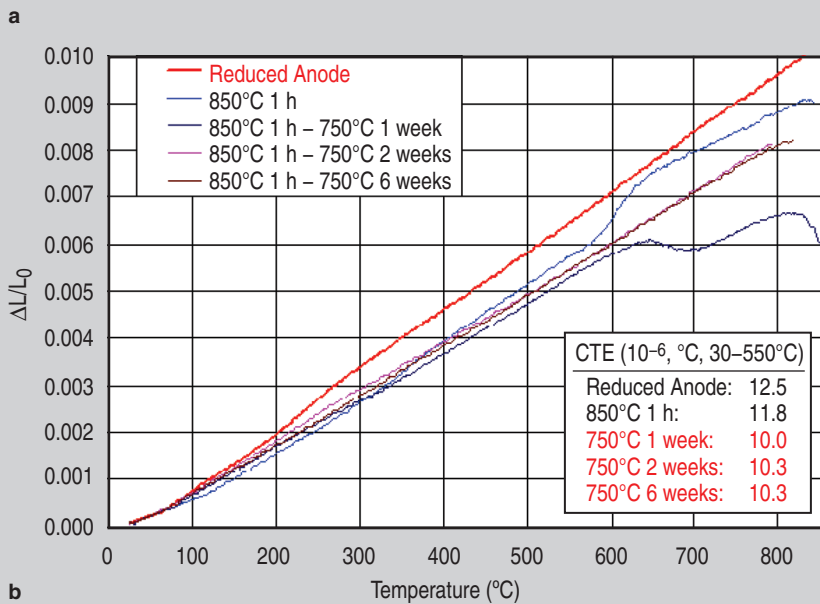


Figure 3. (a) The quantity of crystalline phases formed in a barium aluminosilicate sealant as a function of time held in air at 750°C and (b) thermal expansion of the sealant in Figure 3a as a function of temperature after thermal aging in air at 750°C (from Reference 33).



b

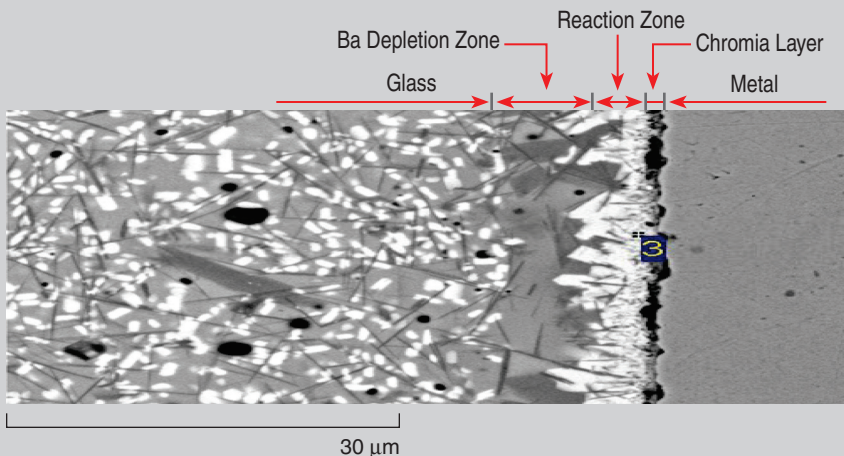


Figure 4. A cross-sectional micrograph of the interface between a barium aluminosilicate glass-ceramic and 446 stainless steel after 100 h of exposure in 750°C air (courtesy of Z.G. Yang, Pacific Northwest National Laboratory).

faces, thereby producing high-strength ceramic-metal joints of the type shown in Figure 7.⁵⁸ Recent work has shown that alloying agents such as palladium, aluminum, and TiO₂ can be added to Ag-CuO to modify its use temperature, oxygen solubility characteristics, and wetting behavior.⁵⁹⁻⁶¹

Like glass sealing, Ag-CuO braze filler metals can be used to join two components directly in air. However, unlike glass, the resulting joint is highly ductile and, when optimized, can be heated and cooled at a rapid rate through numerous cycles with no measurable degradation in either hermeticity or joint strength.⁶² Figure 8 compares the thermal cycling properties of joint strength specimens sealed by air brazing or by using a typical barium aluminosilicate glass-ceramic sealant. Note that the glass joints experience a substantial loss in strength beyond ten thermal cycles at 75°C/min., likely due to the compositional/microstructural changes that occur in the bulk glass and along the glass/metal interface. Conversely, the rupture strength of the air-brazed specimens remains constant as a function of thermal cycling.

There are, however, several concerns with using silver-based alloys in pSOFC applications, including silver volatility and degradation under dual atmosphere exposure (i.e., oxygen-rich air on one side and hydrogen-rich fuel on the other). Both oxygen and hydrogen are relatively soluble in silver, and at high temperature display rapid rates of diffusion in the metal. Klueh and Mullins observed that under certain dual-atmosphere conditions bubbles will form along the grain boundaries of silver, ostensibly due to a reaction between the two diffused species to form insoluble water vapor.⁶³ Recent

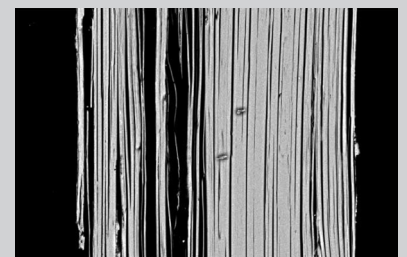


Figure 5. A cross-sectional micrograph of a cleaved muscovite mica sheet of the type employed in compressive sealing (from Reference 50).

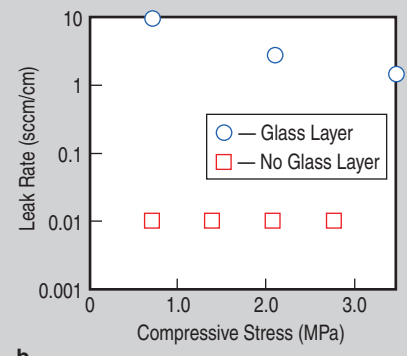
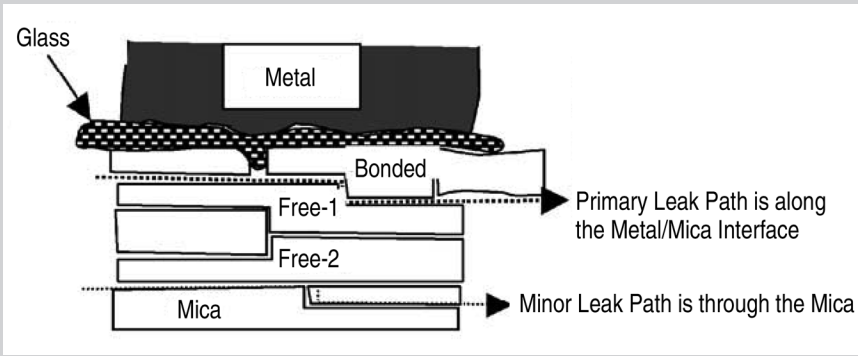


Figure 6. (a) The hybrid mica compressive seal concept (from Reference 51). (b) The difference in leak rate between a plain mica seal and a hybrid seal as a function of compression pressure. Both seals were prepared using phlogopite paper between an alumina substrate and an Inconel substrate as described in Reference 51.

studies of this phenomenon in ceramic-metal joints brazed with the Ag-CuO filler metal indicate that after 1,000 hours of dual-atmosphere exposure, some microstructural change occurs, but in general the joints remain mechanically and hermetically sound.⁶⁴ Based on these findings, air brazing was used to seal cells to frames in a full-size, three-cell stack. The stack was operated for 120 hours using simulated natural gas reformat with no loss in hermeticity and little change in the microstructures of the brazed joints.⁵⁷ While short-term testing of this type is encouraging, more extensive thermal cycle and dual atmosphere exposure testing is needed to fully evaluate the long-term merits of this sealing approach. If the test results prove promising, electrically insulating coatings may be incorporated on the metal components, extending the concept to broader use in the pSOFC stack.

Bonded Compliant Seal Concept

An alternative compliant sealing concept being developed is the bonded compliant seal (BCS). This method employs a thin stamped metal foil that is bonded to both sealing surfaces (Figure 9). Unlike a mica gasket, this seal is non-sliding. When properly designed, the foil yields or deforms under modest thermo-mechanical loading and limits the transfer of these stresses to the adjacent ceramic and metal components. Because the metal foil offers a greater degree of geometric deformation than the air-brazed seal, this sealing concept can accommodate a wider array of alloys for use in the pSOFC interconnect and/or frames. If high-CTE nickel-based

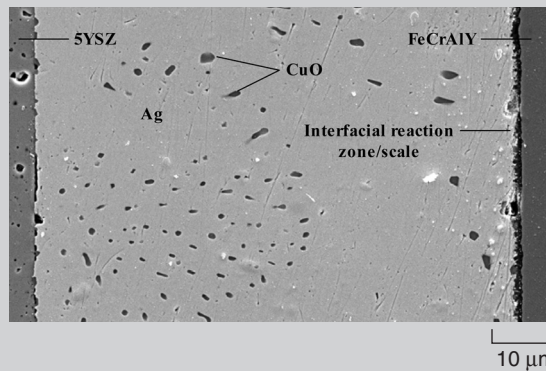


Figure 7. A cross-sectional micrograph of a joint between the YSZ electrolyte of a ceramic pSOFC cell and a ferralloy stainless-steel frame brazed using a 4 mol.% CuO in silver filler metal (from Reference 58).

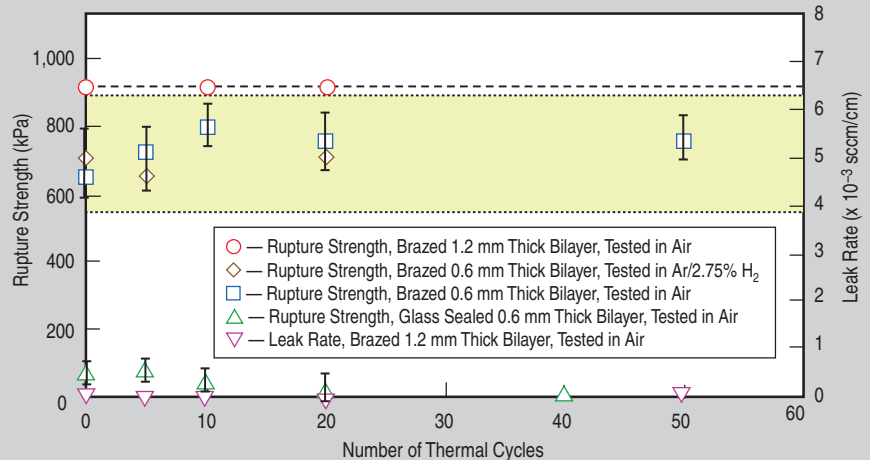


Figure 8. The leak rate and rupture strength of the bilayer/Ag4CuO/Crofer-22 APU specimens as a function of the number of thermal cycles between room temperature and 750°C (from Reference 62).

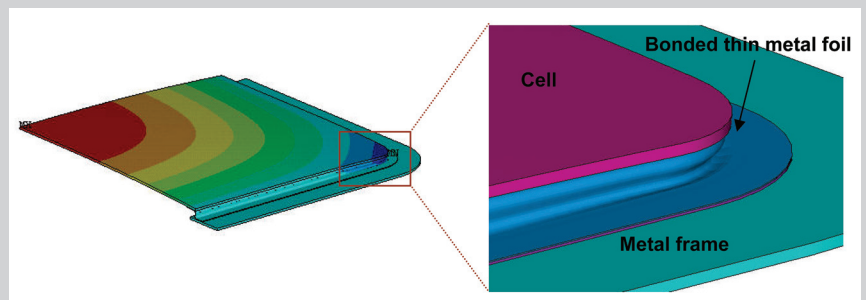


Figure 9. A schematic of the foil-based bonded compliant seal concept.

alloys could be used, for example, the mechanical, oxidation, and through-scale electrical properties of the interconnect would be significantly improved relative to those fabricated from ferritic stainless steel.¹⁶

As a proof-of-concept test, BCS rupture strength specimens were prepared using anode-supported seal coupons (CTE ~10.6 $\mu\text{m}/\text{m}\cdot\text{K}$), thick Haynes 214 washers (CTE ~15.7 $\mu\text{m}/\text{m}\cdot\text{K}$), and thin S-shaped ferralloy foils. The results from hermeticity and rupture strength testing conducted after thermal cycling the specimens at ~75°C/min. indicated no degradation in the seals out to 25 thermal cycles.⁶⁵ Computational analysis has subsequently been employed to identify the potential issues in scaling the BCS to full-size components and prototypic cell geometries. Initial findings indicate that the sealing concept appears to be scaleable, but that there may be some problems with bending of the cell depending on the radius of the corners. Refinements in foil geometry to mitigate the bending effect are being investigated using the established modeling code.

CONCLUSION

Planar SOFCs hold much promise for efficient, high-density power generation. However, to fulfill this promise, robust sealing technologies must be developed that can meet the functional requirements of both stack designers and manufacturers. No one sealing technique will likely satisfy all stack designs and system applications. Glass joining has proven to be effective in sealing stacks for short- and moderate-term operation, but questions remain concerning the long-term durability and thermal cycling performance of these seals. Recent efforts to address the interfacial weakness in the joint, which arises during long-term isothermal exposure suggest potential methods of extending the durability of these sealants. By comparison, the development efforts on compressive sealing have been more limited in scope but good progress has been achieved with hybrid mica seals. The concept needs to be tested on full-size components and test stacks to identify potential design and performance issues with scale-up. The use of air brazing also shows promise in small-scale coupon and short-term stack tests. However,

more extensive thermal cycle and dual atmosphere exposure testing is required to establish the durability of this seal over typical stack lifetimes. Additional progress on new concepts such as the BCS and self-healing seals is needed to determine whether they will truly be viable in pSOFC stack applications.

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