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A review of sealing technologies applicable to solid oxide electrolysis cells

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Abstract This article reviews designs and materials investigated for various seals in high temperature solid oxide fuel cell ''stacks'' and how they might be implemented in solid oxide electrolysis cells that decompose steam into hydrogen and oxygen. Materials include metals, glasses, glass–ceramics, cements, and composites. Sealing designs include rigid seals, compressive seals, and compliant seals.

Introduction

Research on hydrogen production using high temperature electrolysis methods has increased in the last few years [1–3]. One steam electrolysis method involves essentially reversing the polarity of a solid oxide fuel cell (SOFC) [4, 5]. Sealing is an ongoing concern for developers of solid oxide fuel cell stacks. However, sealing is an even greater concern for solid oxide stacks used in a high temperature steam electrolysis mode to generate hydrogen. Because hydrogen is the primary valuable product for electrolysis and due to hydrogen's small size, the gas molecules can quickly leak out of high temperature collection ducts. This review primarily covers sealing technologies that have been considered, are currently being used, or are now being considered for planar SOFCs. In many instances, an edge seal will be between zirconia electrolyte and a high-temperature metal frame (or housing) [6]. Seals can also be to a metal interconnect plate. Depending on the design, this seal will be exposed to operating temperatures of about 750–850 °C. But in fuel cells, this seal will always be exposed to an oxidizing atmosphere on the cathode side (e.g., air) and a wet fuel gas containing various ratios of hydrocarbons (e.g., CH_4), H_2, CO, CO_2, and H_2O on the anode side. For the steam electrolysis cell, the polarity is reversed; the cathode becomes the anode, and the anode becomes the cathode. The typical materials used for the electrodes will remain the same unless long-term endurance tests dictate a change in materials.

For steam electrolysis, the cathode will be exposed to a mixture of H_2O in the form of steam and H_2 where the ratio will vary depending on the position within the cell. The inlet will be high in H_2O. An example of an inlet ratio is 85 H_2O: 15 H_2. The H_2O will be depleted at the outlet. The outlet water might decrease to a ratio of 15 H_2O: 85 H_2. The H_2O/H_2 ratios will depend on the operating parameters of the electrolysis cell. Some H_2 must always be maintained in the cathode compartment (e.g., in the inlet) in order to prevent oxidation of the Ni to NiO (nonconductive). The anode (e.g., conducting perovskite) will evolve O_2 that might be collected for sale, or perhaps the O_2 will be swept with air to lower possible polarization at the anode. Therefore, electrode atmospheres are different for an electrolysis cell than for a fuel cell. The electrolysis cell's cathode chamber has a higher inlet steam content than the anode chamber of a fuel cell. These differences could affect the known long-term chemical stability of seal materials for SOFC studies, or influence chemical corrosion reactions or

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interdiffusion of elements of the seal with elements of the joined materials [7].

For fuel cells, a small amount of leakage does not cause a large drop in the stack efficiency. In the fuel cell application, DC electricity is the product, and any unconverted fuel, such as H_2 and CO, that is leaked out of the anode chamber is combusted and contributes heat to the cells. Therefore, some leakage in SOFCs is generally tolerated. In the electrolysis application, hydrogen is the primary product, and approximately 97+% of the hydrogen must be collected. Also, any gas crossover would negatively affect the hydrogen gas purity. Sealing is much less of a problem for tubular-type SOFCs. However, most tubular designs do use some high temperature seals to join single tubes (or flattened tubes) into bundles for attachment to a gas manifold, which is usually the fuel gas. For an electrolysis application, the same manifold structure would be used to collect hydrogen generated from single cells into a single gas stream. Many tubular designs are said to be ‘‘seal-less.’’ However, this only means that the gas seals can be located out of the high temperature areas and can be executed using fairly conventional metal seals. There are several very different tubular designs that are being developed. Their designed operating temperatures vary from about 700 °C to 900 °C, depending on the materials of construction.

Many developers of SOFCs hold critical details of their material compositions as proprietary. However, there was a recent review published [8] covering sealants for SOFCs. A short article on sealing SOFC stacks (specific to planar) was published by Weil [9] that provides a short review and then reveals two new, alternative, sealing methods that are covered below. Seal designs are fairly specific to a given developer and depend on cell and stack configurations. Figure 1 shows schematic drawings (typical) of a simple planar stack of cells. The upper drawing is an exploded view where the light-gray colored strips are the edge seals. The lower drawing of Fig. 1 shows a manifold seal in a stack that has a cross-flow configuration for the fuel and air gas streams. The external manifolds can distribute the fuel and the air gases across the face of the cell stack. An air manifold is shown in Fig. 1. Figure 2 is a schematic of seals typically found in a stack with metallic internal gas manifolds and a metallic bipolar plate. Common seals include: (a) cell to metal frame, which could include sealing of the edges of the cells and/or sealing to a particular cell layer; (b) metal frame to metal interconnect; (c) frame/interconnect pair to electrically insulating spacer; (d) stack to base manifold plate, and (e) cell electrode edge or electrolyte to interconnect edge. The schematic drawing illustrates features that are common to several specific designs. Some of the features, such as specific layers or current collectors, are only illustrative in nature and are not necessary to scale.

Most metals have thermal expansion values that exceed zirconia by at least 50% and do not afford a good expansion match. The thermal expansion of most metals is between 15×10^{-6} $K^{-1}$and 20×10^{-6} K^{-1} while that of zirconia is about 10.5×10^{-6} K^{-1}. In order to achieve lower thermal expansions, special high chromium alloys such as 95Cr4–5Fe (‘‘Plansee Alloy’’) or 94Cr–5Fe–1 Y_2O_3 were developed. However, these alloys experienced excessive high temperature Cr oxidation. The problem is primarily found on the cathode or air side of a SOFC. The Cr_2O_3 causes increased electrical resistance (planar design) and vaporization problems. The vaporization reaction is $Cr_2O_3 + 1/2O_2 \rightarrow 2CrO_3$ (high vapor pressure gas). Once in the vapor state, Cr oxide condenses in the LSM (strontium-doped lanthanum manganite) cathode and at the LSM/electrolyte and interferes with the electrode function. One proposed mechanism is for Mn^{+2} ion to remove the oxygen from the CrO_3, resulting in precipitation of Cr crystallites [10]. Kofstad and Bredesen [11] point out that a Cr problem may also exist at the anode or fuel side of a SOFC if high water vapor partial pressures spur the formation and evaporation of chromium oxyhydroxides (e.g., CrO_2OH). This could be a problem for the cathode during operation at high temperatures as an electrolyzer because of the high water content. As a result of the chromium problem, many SOFC developers have turned to using ferritic stainless steels that have greatly reduced the chromium content. However, Yang, et al. [12] present an evaluation of oxidation behavior that indicates electrically resistive chromia (Cr_2O_3) scales can grow tens of microns thick on ferritic steels after exposure for thousands of hours in the SOFC environment. This occurs even in an intermediate temperature range. Nonetheless, iron-based ferritic steels are presently in general use for the interconnect or metal frames because they have a reasonable coefficient of thermal expansion (CTE) match to zirconia, are less expensive, and are more easily fabricated than chromium-based alloys. Yttria stabilized zirconia (YSZ) has a CTE $\cong$ 10–10.5 × 10^{-6} K^{-1}. Typical ferritic alloys [13] investigated include: SS 410[1], SS430[2],

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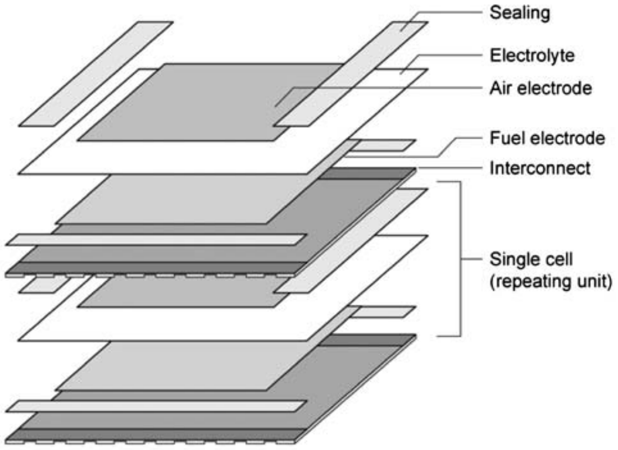
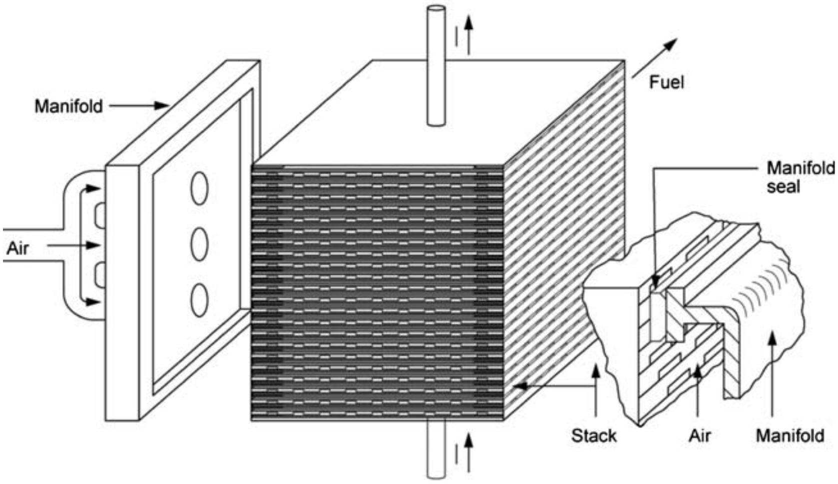
[1] AISI 410 Analysis: 11.5–13.5 Cr, 1 Mn, 1 Si, 0.04 P, 0.03 S, 0.15 C, Bal. Fe.

[2] AISI 430 Analysis: 16–18 Cr, 1 Mn, 1 Si, 0.045 Si, 0.030 S, 0.12 C, Bal. Fe.

Fig. 1 Schematics of edge sealing of planar cells (above) and external gas manifold seals (below) used for a simple cross-flow SOFC stack design



Exploded view, planar cross-flow stack concept.



External manifold and seals

Ebrite[3], Crofer22 APU[4], and ZMG232[5] (high surface electrical resistance due to Si content).

One solution to the interconnect oxidation problem has been developed at the Idaho National Laboratory (INL). The solution is to form a thin, electronically conductive ceramic coating of strontium-doped lanthanum chromite (LSC) on a porous NiAl plate [14, 15]. This approach entirely eliminates Cr_2O_3 in the interconnect. The NiAl is exposed to the fuel gas in a SOFC or hydrogen plus steam in an electrolyzer, while the ‘‘free’’ LSC surface is exposed to air. There is some concern that the NiAl structural component will be slowly oxidized in hydrogen/steam mixture. Oxidation studies are currently being conducted at the INL.

Glass seals

Historically, one of two techniques has typically been used to seal a planar SOFC stack: glass joining or compressive sealing. Glass was originally used because it is simple to make and apply. An important property for working with glass (an amorphous material) is viscosity. The viscosity varies with temperature and is categorized into ranges for melting, working, softening, and annealing. These ranges are shown for the common soda-lime–silica glass in Table 1. One normally takes a frit (powdered glass) and mixes it with an organic vehicle to make a paste. The paste is applied and then heated until the organic burns out and ultimately the glass melts, which is at least 1200 °C for soda-lime–silica glass, and flows to fill a gap. The glass also has to wet and adhere to the components to be sealed. Upon cooling, the glass gradually becomes more viscous until below the softening point temperature. At this point, it becomes

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[3] Ebrite Analysis: 26 Cr, 0.01 Mn, 0.025 Si, 0.001 C, Bal. Fe.

[4] Crofer 22 APU is a trademark of ThyssenKrupp. Analysis: 22.0 Cr, 0.005C, 0.5 Mn, 0.08Ti, 0.016 P, .002 S, 0.06La, Bal. Fe.

[5] ZMG is trademark of Hitcahi Metals, Ltd. Analysis: 22.0 Cr, 0.02 C, 0.5 M, 0.40 Si, 0.21 Al, 0.04La, 0.02Zr, Bal. Fe.

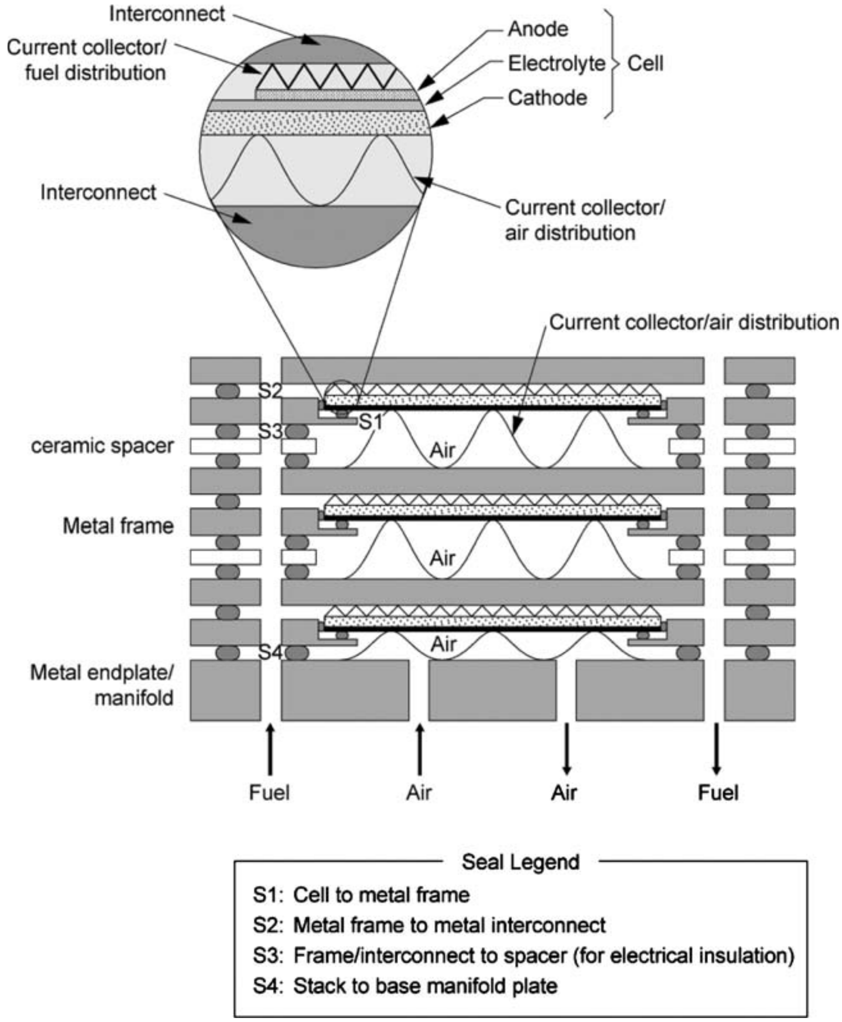

Fig. 2 Schematic of seals typically found in a planar design SOFC stack with metallic interconnect and metallic internal gas manifold channels (possibly for counter flow pattern of fuel and air gases)

Table 1 Viscosity of soda-lime–silica glass [16]

	Temperature range (°C)	Viscosity range (poise)
Annealing range	400–500	$10^{12.5}$–$10^{13.4}$
Softening point	700	$10^{7.6}$
Working range	700–950	10^{4}–$10^{7.6}$
Melting range	1200–1400	$10^{1.5}$–$10^{2.5}$

able to bear mechanical loads, and it can withstand some gas pressure as a seal.

The first requirement for a rigid seal is that the seal's thermal expansion should closely match the thermal expansion of cell components that it is joining. High stresses can result from thermal gradients or thermal expansion mismatches between the glass and cell materials during heating and cooling. Fully stabilized zirconia has a CTE of about 10–11 × 10^{-6} K^{-1}. The CTE and softening point of some silica-based glasses are shown in Table 2.

After melting and cooling, glass seals are brittle and non-yielding, making them very susceptible to cracking because of tensile stresses. The various silicate glasses are also easily fluxed by the perovksites (e.g., doped $LaMnO_3$ used as the cathode) if they are in physical contact. Even borosilicate glass, which has a low CTE, was successfully used on small single cells in Europe, but problems of cracking and inter-diffusion appeared when it was used to seal larger area cell stacks. However, if the sealing glass does not crystallize, then cracks that may form because of thermal cycling can self-heal if the glass seals are periodically heated to temperatures near the glass melting point.

Glass is relatively low in strength when compared to polycrystalline ceramics. The amorphous or ''vitreous'' structure of some glasses with high CTEs often tended to crystallize when held at high temperatures for a long time, and the CTE would change. This has led to the use of special compositions to form purposefully crystallized glasses, also known as glass–ceramics or

Table 2 Coefficient of thermal expansion for selected glass compositions

Code	Name	CTE (K^{-1}) (0–300 °C) × 10^{-6}	Softening Pt. (°C)
7740[a]	Pyrex	3.25	821
0080[a]	Soda lime	9.35	696
0139[a]	Potash soda alkali lead	9.70	658
1990[a]	Potash soda lead	12.4	500
7567[a]	Lead Zn borate	12.0	358
7576[a]	Zn boric lead	10.0	372
7580[a]	Pb Zn borosilicate	10.0	374
9048[a]	Alkali strontium	9.90	688
SP 712[b]	NA	9.70	628
SP 1360[b]	NA	12.4	632

[a] Corning Glass

[b] Speciality Glass Inc.

devitrified glass. Glass–ceramics are much stronger than glass and the designed, resultant crystalline structure will have a known CTE. Historically, the CTE of cell components have been matched to the CTE of the zirconia electrolyte. This CTE is relatively high for a ceramic, while relatively low for most common metals.

Glass–ceramic seals

Glass–ceramics are special compositions of glasses that are amorphous when melted but are specifically designed to partially or fully crystallize and become opaque when held in a high temperature range that is below the melting/solidification temperature range. The author also includes glass plus powdered crystalline ceramics (e.g., zirconia) in this category because they provide a similar "glass/ceramic" function. In general, glass–ceramic powdered "frits" with suitable CTE values are very difficult to obtain commercially, although a few compositions are available on a restricted basis. Most developers fabricate their own glass–ceramic compositions based on silica as the glass former. Larsen [17] reported problems with glasses purely based on phosphate as the glass former. At operating temperatures, the phosphate volatilized and reacted with the nickel–zirconia cermet anode to form nickel phosphide and zirconiumoxyphosphate. An additional problem is that the phosphate glasses usually crystallize to form metal or pyrophosphates, which can easily decompose at high temperatures in a humidified fuel gas atmosphere. Some glass–ceramic compositions reported in the sealing literature (based on SiO_2) are given in Table 3.

Many barium aluminosilicate-based compositions will eventually react with the chromium oxide or aluminum oxide scales on the metal interconnect or metal edge rails to form barium chromate or a celsian phase at the interface [18]. This can cause a mechanical weakness that is easily delaminated. Also, compositions that contain boron can react over time with water (steam) to produce $B_2(OH)_2$ or $B(OH)_3$ gas. This can decompose the glass and greatly limit the lifetime of the seal. Thus many of the new investigations have emphasized "low" or "no" boron glass compositions.

In Table 3, Argonne National Laboratory's formulation No. 14 (representing a family [19] of compositions) is high in boron (glass former) with a glass transition temperature[6] (T_g) of 740–780 °C and a CTE of 11.5×10^{-6} K^{-1} (25–600 °C). It has a minimum bonding temperature of 1,000 °C that corresponds to a viscosity of about 10^6 Pa s (in "working" range, see Table 1) that should limit "wicking." It exhibits crystals (needles) of Sr-doped $LaBO_3$ (approx. 40–60 vol%). The composition appears to be stable at 1,000 °C, but over time the presence of H_2O vapor likely will degrade the material due to vapor transport of the $B_2(OH)_2$ or $B(OH)_3$ gases as mentioned above.

Pacific Northwest National Laboratory (PNNL) has patents [20, 21] on its glass–ceramic sealing formulations and methods. This patent mentions composition No. 9 (Table 3) as an example, which contains no boron. It has a T_g of about 726 °C, with a CTE of 10.5×10^{-6} K^{-1} for the crystallized glass (with 9.4×10^{-6} K^{-1} for glass). This CTE was measured to be within 0.06% of the CTE of an 8-YSZ electrolyte. It was reported necessary to heat to about 1,150 °C to execute a seal. PNNL formulation No. 14 has boron. This reduces the T_g to 597 °C so that sealing would be possible at a lower temperature, and the CTE is reduced slightly to 9.48×10^{-6} K^{-1}. The addition of boron to glass will aid in wetting and flowability properties.

The Julich [22] No. 10 formula ("MASZ") in Table 3 has a T_g of 721 °C, and melts at greater than 1,100 °C with a crystallization (heat treatment) range of 741–859 °C (for times of 2–23 h, respectively). Julich's "BAS" composition in Table 3 is easy to crystallize with 100% crystals resulting after it is melted at less than 1,100 °C and then heat treated at 800 °C.

Three glass–ceramic compositions for sealing solid oxide cells [23] are available on a restricted basis from the AREVA T&C Technology Center (formerly ALSTOM) in the United Kingdom. These are BaO–

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[6] The glass transition temperature is the approximate midpoint of the temperature range at which there is a discontinuity in the curve when molar volume V is plotted against temperature. The glass transition manifests itself as a tremendous change in viscosity over a small temperature range.

Table 3 Representative glass–ceramic compositions

Source (Code)	BaO	MgO	SrO	La_2O_3	B_2O_3	Al_2O_3	SiO_2	Crystal aid
ANL (14)			24.56	20.13	40.29	6.92	8.11	
PNNL (9)	36.9					10.5	52.6	
PNNL (14)	30.0	10.0 CaO			20.0	10.0	30.0	
Julich (10)		38.0			5.0	10.0	45.0	2.0 ZrO_2
Julich (BAS)	45.0				5.0	5.0	45.0	

ANL = Argonne National Laboratory

PNNL = Pacific Northwest National Laboratory

$MgO–B_2O_3–SiO_2–TiO_2$ compositions with boron content less than 10% and zero alkali metal oxide. The minor oxides such as boric oxide, titanium oxide and zinc oxide are added to mediate wetting and viscous flow characteristics. TiO_2 obviously can have a role as a crystallization initiator. The exact chemical compositions are proprietary and are not revealed [24]. Three grades are available (NK2/4429/F, NK2/4414/M/27, NK2/4430/F) with CTE values of 10.5, 10.7, and 11.3×10^{-6} K^{-1} (25–900 °C), respectively, and volume electrical resistivities of $>1 \times 10^9$ Ω cm (700 °C). The maximum processing temperature is 1,100 °C in a neutral atmosphere with an intended service temperature of 800–950 °C. The materials are generally prepared by quenching high-purity melts, drying and ball milling to a powder with d_{50} in the range 5–30 µm. The powder is usually dispersed in an organic vehicle for application as green tape or paste, the precise mode of application depends upon the geometry of the assembly to be sealed. These glass–ceramics are attractive because their thermal expansion behavior can be tailored to match those of the assembly's end-members. Additionally, they can be made to be sufficiently refractory and inert for long-term service at elevated temperatures in reducing atmospheres.

High-temperature sealing is also required for some modern designs of tubular-type cells. An example is the Rolls-Royce IP-SOFC design which is a segmented cells-in-series concept in which the cells are deposited onto a flat, porous ceramic support tube. This support tube, which contains multiple channels, acts as the fuel gas delivery tube. In the IP-SOFC design, cells are only deposited on the flat surfaces of the tube, hence the edges of the tubes need to be sealed to prevent mixing of the fuel and air. For these seals Rolls-Royce Fuel Cell Systems Ltd (RRFCS) currently uses a glass–ceramic. In addition to sealing the tubes surfaces, glass–ceramics are also used in certain parts of the stack to create gas-tight joints between the porous support tubes and adjoining manifolds. For both locations long-term durability and mechanical stability under thermal cycling are required. The details of the glass–ceramic compositions are proprietary to RRFCS [25].

Long-term physical and chemical stability is very important for seals in both SOFC and high temperature electrolyzer devices. In addition to reaction with steam and vaporization, glass–ceramics will react with cell components. A series of 13 representative compositions in the $AO–SiO_2–Al_2O_3–B_2O_3$ (A = Ba, Ca, Mg) systems was evaluated by Lahl et al. [26] where the boron content was kept to less than 5%. During testing, the fuel gas was simulated using argon plus hydrogen and steam (with a H_2O/H_2 ratio of 4:1). In addition to boron volatility, the presence of Na or K in sealants was noted to enhance the chromium vaporization from metallic interconnects by the formation of very volatile Na_2CrO_4 (g) and K_2CrO_4 (g) species. This is a negative because the chromium ends up in the air electrode and blocks active sites. The BaO containing glasses showed significantly higher CTE, faster and more extensive crystallization, and lower T_g values when compared to the CaO and MgO containing glasses. MgO containing glasses were found to have significantly lower reactivity with component materials than those containing BaO or CaO. Investigation of MgO containing glasses with different Al_2O_3 ratios showed that the detrimental formation of $Mg_2Al_4Si_5O_{13}$ phases can be suppressed by using low Al_2O_3 concentrations and appropriate grain sizes and nucleating agents. Lahl et al. [27] also reported more details of crystallization kinetics for glass–ceramic compositions containing BaO, CaO, and MgO.

Eichler et al. [28] performed metal to metal joining experiment using four glass–ceramic compositions in the $BaO–MgO–SrO–Al_2O_3–B_2O_3–SiO_2$ system as the "solder." They found that many compositions containing MgO reacted with the interconnect alloy they used, CrFe5(Y2O3)1, to form the reaction phase $MgCr_2O_4$ spinel. This was in addition to formation of the oxidation barrier phase of $FeCr_2O_4$. Many joins showed enhanced leak rates after annealing at 850 °C for times up to 400 h and then cooling to RT. It was thought the leakage was a result of glass delamination (cracking) at the metal interface probably caused by the presence of the low CTE ($6.9 \times 10^{-6}\ K^{-1}$) $MgCr_2O_4$ spinel. Reduction of certain crystalline phases was also noted along with some phase transformation (e.g., hexacelsian to celsian or formation of quartz). Barium aluminosilicate sealing glass that is bonded to a chromia-forming alloy can react and deplete the protective chromia on the air side. Example reactions noted by Yang [29] are shown in Reactions (1) and (2):

$$2Cr_2O_3 + 4BaO + 3O_2 \rightarrow 4BaCrO_4 \tag{1}$$

$$CrO_2(OH_2)(g) + BaO(s) \rightarrow BaCrO_4(s) + H_2O(g) \tag{2}$$

It is thought that at seal edges where oxygen or air is accessible, reaction (1) proceeds. The formation of barium chromate often leads to the physical separation of the sealing glass and the metal alloy due to barium chromate's high thermal expansion. When some volume of glass is squeezed free during formation of the seal (and if a chromium-containing vapor specie is present), the freed glass surface can react according to reaction (2). Along interfacial regions where oxygen or air access is blocked, chromium or chromia can react with BCAS glass–ceramic to form a chromium-rich solid solution and a series of pores.

Based on the data published by Lahl and Eichler and Yang, it appears to be difficult to select a single glass–ceramic composition in the $BaO–MgO–Al_2O_3–B_2O_3–SiO_2$ system that would provide ideal performance in all the desired aspects as a sealant for SOFCs or high temperature electrolyzers for long periods of time. Therefore, other glass–ceramic compositions and other sealing options continue to be evaluated. These options are discussed below.

Recently, a new series of ''invert'' glass ceramic compositions have been developed/evaluated for SOFC sealing by the University of Missouri-Rolla (UMR) [30]. Significantly, the UMR compositions are BaO-free (they are ZnO-modified) in an attempt to avoid the chromia reaction problems associated with barium glass ceramics. An ''invert'' glass consists of discontinuous silicate tetrahedron groups tied together with modifying cations. The silicate tetrahedron can be bonded together as metasilicates ($[O]/[Si] \cong 3$) or polysilicates (short chains, $[O]/[Si] > 3.0$). The invert silicates are mixed with 45–55% CaO, SrO, ZnO, containing <45% SiO_2 ($[O]/[Si] > 3.0$) with minor additions of Al_2O_3, B_2O_3, and TiO_2. Representative crystalline phases in these glass ceramics are the pyrosilicates $CaSrAl_2SiO_7$ and $Ca_2ZnSi_2AlO_7$ and the orthosilicates Sr_2SiO_4 and Zn_2SiO_4. Test seals have been made at UMR using their invert glasses with both an interconnect alloy [E-bright alloy = Cr–ferritic steel with 26% Cr; CTE $11.7 \times 10^{-6}\ K^{-1}$)] and YSZ coupons (CTE $\times 10^{-6}\ K^{-1}$) at 850 °C. In the future, UMR plans to incorporate these seals into operating cells and stacks for testing and fully characterize the glass/metal interfaces for reactions, etc. after testing. Early results at UMR show invert glass compositions to have suitable CTE values and are stable in moist fuel gases at least for 30 days. However, some Cr-rich interfacial reaction products were found at the glass/E-bright interface after holding the seals at 750 °C for 14 days in air.

Compressive seals

The idea of a compressive seal is to place a compliant, high temperature material between the sealing surfaces. The material is then compressed using external forces to the fuel cell stack (e.g., using a load frame and springs or hydraulics to provide a constant pressure). The addition of a load frame adds complexity and cost to the SOFC. The best compressive seals allow the surfaces to slide past each other while maintaining a good (hermetic, if possible) gas seal. Using this seal, matching CTE values is not as important as with a solid (e.g., glass-based seal). Such seals in reducing or inert conditions have been made for some high temperature applications using materials such a pyrolytic graphite foil. Here the graphite planes can easily slide across each other. Other materials like nickel and copper have been considered but, like graphite, they are not oxidation resistant. High temperature compressive seals using various metals have been evaluated [31, 32]. These seals needed some improvement with mechanical behavior and gas tightness. Ceramic powders are oxidation resistant, and some have been used to form a compressive seal in SOFCs. But, ceramic oxide powders typically form a ''leaky'' seal.

Some success has been found using mica (even though its CTE is relatively low at approx. $6.9 \times 10^{-6}\ K^{-1}$) because it has internal slippage planes and is more oxidation resistant than metal powders. However, problems with through-seal leakage, interface reactions, and crystallization have been present [33]. Compressive seals using metal/mica sandwich composites have been developed as a proposed improvement to rigid glass-ceramics [34]. The metal layer (e.g. FeCrAl-Y-alloy) is presumably added to increase the overall CTE and plasticity of the seal. This approach did show reduced leak rates after five thermal cycles. A compressive hybrid mica seal is under development at

PNNL. Sheets of Phlogopite [$KMg_3(AlSi_3O_{10})(OH)_2$] (high temperature mica) have been layered between thin glass or silver layers [35] to form a seal between various metal components or metal to zirconia. The idea is that the mica will be compliant in two directions (2-D in x–y plane), and the thin silver or glass layers can more easily seal the uneven surfaces of the ceramic or metal (e.g., interconnect) and provide some compliance in the third (3-D) direction. Frictional damage is thought to be limited to the first several crystal sublayers below the mica surface. However, the slippage planes are due to waters of hydration, and the water can be lost at high temperatures and will destroy the crystal planes. Recent PNNL experimental results on the ‘‘hybrid mica’’ seal technology using Pholgopite[7] sandwiched between glass layers show promise [36, 37]. These experimental tests have involved joining Inconel 600 to 430 stainless steel using layers of modified G18 glass–ceramic[8] and Pholgopite mica sheet. The Inconel 600 has a high thermal expansion (16.7×10^{-6} K^{-1}) compared to the crystallized G18 glass ($11–12 \times 10^{-6}$ K^{-1}) and 430 SS (11.4×10^{-6} K^{-1}). Initially the G18 Ba–Ca–Al silicate glass layers showed severe reaction with the mica during aging at high temperatures. Therefore, the glass composition was modified by adding a nucleation agent (composition G18-M) or by lowering the B_2O_3 content (composition G18-M). The interlayer of G18-M glass showed good chemical compatibility with the mica for 1,000 h, but poor thermal cycle stability. The interlayer of G18-M (low B_2O_3) showed good chemical compatibility and good thermal cycle stability with a leakage rate of about 0.06 scc/cm over 35 thermal cycles using a 6 psi compressive stress. The interlayers of Ag foil exhibited good thermal cycle stability after 2,000 h with a leakage of about 0.04 scc/cm over 47 thermal cycles using a compressive stress of 12 psi. A calculation of vapor loss for silver at 790–800 °C showed a small (approx. 1 wt%) loss for 40,000 h. However, any effects of silver on electrochemical (I–V) performance need to be evaluated.

High temperature metal seals

The list of high-temperature metals useful for sealing that will not corrode in air is very short. Candidate metals include platinum (m.p. 1774 °C), gold (m.p. 1,063 °C), and silver (m.p. 961 °C). Gold and platinum are prohibitively expensive, while silver is only 1/100 the price of gold or platinum. Therefore, silver has been considered as a SOFC sealing material by several developers. Possible drawbacks are that silver has a high vapor pressure, and it has a high thermal expansion (CTE $\cong 20 \times 10^{-6}$ K^{-1}).

Duquette and Petric [38] recently developed and tested a method for sealing planar SOFCs (single cells only) using pure silver wire gaskets (sterling silver, containing 7.5 wt% Cu, was not sufficiently deformable) that are placed into channels machined into interconnect plates made from 430 grade stainless steel (430 SS). The seal was made using a compressive load. The idea is that sufficient compressive load is applied to deform the metal gaskets and prevent gas leakage. The combination of elastic and plastic deformation of the seal is intended to produce an increased tolerance of SOFC stack thermal expansion mismatches in addition to resistance to thermal cycling and vibration damage. A low leak rate was detected (75.8 Pa min^{-1} at 500 °C); however, many other problems were noted. These problems included (a) a need for flat interconnect plates, (b) a sealing of gas fittings, and (c) a need for a uniform load distribution (circular shape was recommended). The tests were not conducted over a long time period (just minutes).

Stevenson reported [39] that silver was unstable (developed large amounts of porosity) when exposed to a dual atmosphere of H_2–3% H_2O on one side and air on the other for 100 h at 700 °C. He found silver was stable when exposed to air or an air environment for 100 h at 700 °C in an identical configuration.

PNNL has been working on an Ag–CuO [40, 41] ‘‘fluxless’’ seal to ‘‘air’’ braze cells to metal frames [42]. Braze pastes are formulated by mixing silver and copper powders (4 mol%) with an organic binder. The copper oxidizes in situ to CuO during the brazing operation. In early tests, 5YSZ electrolyte (together with NiO-5YSZ anode in a ‘‘bi-layer’’ structure) was joined to thin-gauge FeCrAlY (22% Cr, 5% Al, 0.2% Y, Bal Fe) alloy at 1,050 °C in air. Hermetic seals were made with bond strength being maintained over 40 thermal cycles. The braze wets the YSZ well, with no reaction zone found at the interface (some CuO precipitates near the interface). There was a 2-mm-wide reaction zone between the braze and the FeCrAlY alloy. This region contained two mixed-oxide phases $CuO \cdot Al_2O_3$ and $2CuO \cdot Al_2O_3$. There also was a thick alumina-containing scale that was formed and

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[7] PNNL sources of Phlogopite mica paper made from agglomerated flakes, possibly with some high-temperature binder added: PH-‘‘A’’ = cogemica sheets from Cogebi Inc., Crosby Road Industrial Park, 14 Faraday Drive, Dover, NH 03820; PH-‘‘B’’: sheets from McMaster-Carr, www.mcmaster.com, Box 54960, Los Angeles, CA 90054-0960, p 3190 in Catalog 107.

[8] G18 composition : 35 BaO, 15 CaO, 5 Al_2O_3, 10 B_2O_3, 35 SiO_2.

maintained on the FeCrAlY alloy. If well dispersed, the copper oxide particles could be functioning as a strengthening agent (dispersed oxide) in silver at high temperatures. It also may be possible to form a silver-ceramic composite in which silver forms a three-dimensional network [43] and thereby reduces the high CTE of silver.

Ceramic-composite seals

Ceramic-composite seals are being investigated by Sandia National Laboratory [44] and NexTech Materials, Ltd. [45] Sandia's stated composite approach is to produce a deformable seal based on using a glass above its T_g with control of the viscosity and CTE modified by using ceramic powder additives. The composite is to be rigid enough to remain in the joint, but have a low enough viscosity to slightly flow to relieve stresses and heal cracks. However, they initially reported using BaO–CaO–MgO–Al_2O_3–B_2O_3 glass compositions mixed with ceramic powders such as YSZ. These types of compositions will crystallize, so the amount of deformation at high temperature will eventually be limited. Sandia found a reaction between BaO in the glass and YSZ to form $BaZrO_3$ (CTE of 7.9 × 10^{-6} K^{-1}) that increased with sealing temperature. However, this reaction reduced the amount of BaO available for reaction with monolithic YSZ electrolyte that might be joined. Also, there was an increasing dissolution of $MgCaB_2O_5$ crystals from the glass–ceramic at higher temperatures. The composite CTE of the seal was adjusted upwards by adding silver (CTE = 20.1 × 10^{-6} K^{-1}) to compensate for the formation of low CTE $BaZrO_3$.

NexTech report using BaO–CaO–Al_2O_3–SiO_2 candidate glass compositions (e.g., 15 BaO 25 CaO 7.5 Al_2O_3 45 SiO_2) together with powders of mica, talc, alumina, or zirconia fibers as an additive to increase the viscosity. Leakage rates were minimized by using 15–25 vol% glass with the various powders. In this approach, it is necessary to heat above the melting point of the glass in order to stimulate wetting and bonding. If these compositions were to contain sufficient glass that the seal was fully densified upon melting, then this approach would produce seals very similar to the dense, machinable mica-glass ceramics SOFC seals that were investigated in Japan during the 1990s. These composite seals consisted of micro-crystalline mica (fluoro-phlogopite, $KMg_3AlSi_3O_{11}F_2$) in a SiO_2–B_2O_3–Al_2O_3–K_2O–MgO–F glass matrix. However, the mica-glass composites were reported to react with the $La_{0.8}$ $Ca_{0.22}$ CrO_3 separator plate at high temperatures [46].

Glass–metal composite seals

Sandia National Laboratory scientists are experimenting with a glass–metal seal using ZnO–CaO–SrO–Al_2O_3–B_2O_3–SiO_2 glasses (glass–ceramic) in conjunction with adding powdered metallic nickel (5–30 vol%) [47]. Adding nickel adjusts the composite CTE to higher values, and the nickel appears to have low reactivity with the glass–ceramic. Recent experiments have been conducted using a "Brow 27" glass–ceramic composition. This composition evidently is the same as the G #27 "invert" glass–ceramic fabricated at the University of Missouri-Rolla and does not contain BaO and has low B_2O_3 (approx. 2 mol%). Early results show that the "Brow 27" invert glass shows no reaction with anode materials below 1,000 °C, and the interface maintains adhesion and structure after thermal cycling. The glass seems to have a low solubility for Cr_2O_3, with some precipitates containing Cr, Zn, Al, and O being formed after a sealing cycle of 10 min at 950 °C. Chromium was purposely added to the "Brow 27" glass to simulate the effect of Cr dissolution over a long time. Results suggest that once the glass matrix is saturated with Cr, no further dissolution will occur. Once saturated with Cr, the CTE of the glass was stable at 9.3 × 10^{-6} K^{-1}. These results indicate a compatibility with chromium containing alloys such as 430 or 440 stainless steel.

Compliant seals

Compliant seals might prove to be successful if they can be executed at high temperatures. Compliant seals might include: flexible metal "bellows," viscous glass that includes self-healing glass seals, or perhaps wet-seals (material system unknown). These require flexible seal designs, stable glasses that have the appropriate viscosity range (non-crystallized glasses), and some concepts may require an applied pressure.

PNNL [48] describes preliminary joining experiments using flexible foils made from an alumina-forming ferritic steel, DuraFoil[9]. This foil was brazed to Haynes 214 alloy[10] on the bottom side using BNi-2 braze tape[11]. The foil was also brazed to YSZ (component of a cell) on the top side using

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[9] DuraFoil composition: 22%Cr, 7%Al, 0.1%La+Ce, Bal. Fe. Manufactured by Engineered Materials Solutions Inc., Attleboro, MA.

[10] Haynes 214 has excellent oxidation resistant to temperatures over 1,000 °C, but has high CTE (15.7 × $10^{-}6$ K^{-1}).

[11] Wall Colmonoy Inc., Madison Heights, Michigan.

Ag–4 mol% CuO. The foil was in the form of a compliant/flexible edge seal (i.e., a single segment of a bellow). Good strength results were reported. In practice, this seal could be used around round gas manifold holes, which are incorporated into both the ceramic cell and the metal alloy separator plate. The foils are most applicable to provide thermal expansion relief to round holes and round structures. This is because side-expansion in a square or rectangular structure cannot be accommodated by flexing of the foil.

Cements

Historically, both alumino-silicate cements and alumino-silicate cements plus glass were used during the early 1990s by various developers. High temperature cements are easily available from a variety of commercial sources. However, after curing and firing, they are typically somewhat porous and lack good wetting/bonding with the metal interconnect and ceramic surfaces that are needed to produce hermetic seals. Therefore, in some cases, glass was added to the cement in an effort to fill the porosity and aid wetting. This combination then becomes a sort of ‘‘glass–ceramic’’ seal, assuming the mixture is fired to sufficient temperature to melt the glass.

Sealing cements can also be produced by combining ceramic powders (e.g., zirconia) with chemically bonded ceramics. An example is chemically bonded phosphate ceramics [49]. Phosphate bonded ceramics are formed like cements, but their resulting structure and properties are similar to ceramics. The ceramic powder provides a filler to help prevent cracking that results from shrinkage upon curing of the phosphate cement. The phosphate cements are formed by reaction of metal cations with phosphate anions. Typically, a cation donor (e.g., metal oxide) is mixed with and subsequently reacts with either phosphoric acid or an acid phosphate. As the reaction proceeds, the mixture then hardens into a reasonably dense ceramic. However, the end product generally is not completely hermetic. A classic example is $AlPO_4$ (SiO_2 type covalent phosphate structure) cement with a zirconia or alumina filler powder. Even more stable orthophosphate compounds [50] are known [51] (including $CePO_4$ and $LaPO_4$). These orthophosphate compounds have very high melting points that range from 1,920 °C to 2,072 °C in air. These compounds are thought to have reasonably high coefficients of thermal expansion (CTE for $LaPO_4 = 9.6 \times 10^{-6}\ K^{-1}$) [52]. Their crystal structure consists of a metal ion coordinated with eight phosphate tetrahedrons. When compared to the phosphate glasses, it is hoped that the very stable crystalline metal phosphates will exhibit reduced reactivity [53], volatility, and decomposition problems. However, reduced reactivity might result in insufficient bond strength between the metal–phosphate cements and zirconia electrolyte or metal (e.g., ferritic stainless steel) structures. This would prove to be detrimental to an effective seal. If there is no chemical reaction to provide bonding, adhesion strength would be limited to that provided by mechanical interlocking. The mechanical interlocking could be increased by enhancement of surface roughness.

Discussion and conclusions

A great number of materials and approaches have been investigated for sealing of planar type solid oxide fuel cell stacks. As noted above, the best of these approaches have been successful in sealing the cells to acceptable leakage rates. However, there appear to be significant problems with these seals during long-term service. This is due to corrosion effects or cracking associated with multiple thermal cycles. The long-term corrosion effects for solid oxide electrolysis cell seals are more unknown than for solid oxide fuel cell seals because of the difference in gas atmosphere compositions. The most obvious difference involves the H_2O/H_2 ratios. Many new sealing approaches seem to be promising, such as using ‘‘invert’’ type of glasses that do not contain BaO. However, testing histories have shown that the majority of promising approaches do not ultimately provide completely acceptable results.

Some of the newest approaches involve metal/glass composite seals. An example is the Sandia National Lab work on metal/glass composites. This approach brings with it the innate question of whether the glass component should be retained as amorphous glass or purposely designed to vitrify into a glass–ceramic. A second question is what metal composition should be used for the composite. And the third question is what design and fabrication techniques can be used to manufacture a complex composite geometry that provides for simultaneous plasticity and retention of the glass in the joint area. This would be considered to be a ‘‘soft’’ seal.

If the glass in a metal/glass composite seal de-vitrifies into a glass–ceramic, it loses its ability to relieve stresses and repair cracks via viscous flow during high temperature annealing or operation. The seal then becomes ‘‘hard’’. Therefore, an amorphous glass seems best as long as it does not overly react with the ceramic and/or metal end-members it is joining. For instance, a soda-lime glass (see Table 2) could be useful if it were isolated into micro-cells by metal walls in the composite seal. This could limit the reaction of the sodium and potassium with the protective chromium oxide coatings of ferritic stainless steel components. This would limit the chromium vaporization from metallic interconnects by suppressing the formation of very volatile Na_2CrO_4 (g) and K_2CrO_4(g) species. The metal to be used should be somewhat plastic. It should have a CTE that is close to that of zirconia, or be combined with the glass in a way to average out to a suitable CTE. One of the biggest requirements is the metal will be exposed to oxidation on one side and reduction on the other. The best choice for the metal component of a metal/glass composite seal is one that is highly deformable and oxidation resistant. Some metals that exhibit these traits are Au, Pt, or Pd. Silver is not as stable and has a high CTE. But, because of economic considerations, only Ag has being seriously investigated. Other metals have like Ni or Ni alloys or even ferritic stainless steels form oxide scales that can react with the glass component of the composite seal.

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