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Ultra-low leak rate of hybrid compressive mica seals for solid oxide fuel cells

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Abstract

A novel hybrid compressive mica seal was developed that showed a reduction of leak rate by about 4300 times (compared to simple mica seals) at 800 °C. The hybrid compressive mica seal is composed of 2 compliant glass layers and a mica layer. Three commercially available micas were tested in hybrid compressive seals for solid oxide fuel cell applications. The best results were obtained using Muscovite single crystal mica. The normalized leak rate for this seal at 800 °C was only 1.55×10^{-4} sccm/cm at a stress of 100 psi and a pressure gradient of 2 psi. Seals based on the other commercial micas (Muscovite and Phlogopite mica papers), also exhibited superior leak rates (~0.011 sccm/cm) compared to simple mica seals without the compliant glass layer (about 6–9 sccm/cm). The microstructure of the mica was examined before and after the 800 °C leak tests using scanning electron microscopy. The cause for the substantial reduction of the leak rate was discussed. In addition, the effect of the compressive stresses was also investigated.

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1. Introduction

Solid oxide fuel cells (SOFCs) are a new and fundamentally different way of making electrical power from a variety of fuels. The SOFC is an energy conversion device that produces electricity through the electrochemical reaction of a fuel (e.g. H_2) and an oxidant (e.g. O_2). Oxygen is transported via the vacancy mechanism through a dense ceramic electrolyte (e.g. fully stabilized zirconia), and then reacted with hydrogen electrochemically. Because the SOFC converts chemical energy without an intermediate thermal energy step, its conversion efficiency is not subject to the Carnot limit. Compared to the conventional power generation, SOFCs offer several advantages: substantially higher energy conversion efficiency, modular construction, minimal operating site restriction, and much lower air pollution [1].

Currently, there are two basic designs for SOFC applications: tubular and planar [1–4]. While planar designs are believed to potentially offer lower cost and higher power density per unit volume compared to tubular designs, planar designs face many challenges that must be overcome. In addition to the challenges in materials development for electrolytes, anodes, and cathodes, most planar SOFC designs require seals between each individual cell to prevent (or at least sufficiently minimize) leaking of gases from the stack as well as mixing of fuel and oxidant gases. The seal needs to have long-term stability at the elevated temperatures and harsh environments (oxidizing, reducing, and humid) typical of SOFCs during operation. Also, the seals should not cause degradation (e.g. corrosion) of the materials with which they are in contact (e.g. stabilized zirconia, interconnect, and electrodes). Approaches, such as glass seals, glass–ceramic seals, cement seals, brazes, and compressive seals have been proposed, though most of the work reported has focused on glass seals. Lahl et al. [5] studied aluminosilicate glass–ceramics as sealant in SOFC stacks. They investigated 13 glasses and examined the chemical interactions at the interface between the sealant and the SOFC component materials: anode, electrolyte and a metallic interconnect. Guidelines for the sealant development were given. Yamamoto et al. [6] studied the compatibility of mica glass–ceramics as gas-sealing materials for SOFC. The mica glass–ceramics were found to be chemically stable to the electrolyte (8YSZ) in that no severe chemical reaction was found at the interface in the temperature range of about 1000–1300 °C. Other glass systems (B_2O_3, SiO_2, and P_2O_5)

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have also been investigated as potential SOFC seals [7]. Glasses containing high B_2O_3 showed good results; however these glasses tend to exhibit extensive volatilization in the SOFC environment. P_2O_5-based glasses can be tailored to minimize the volatilization; however, the coefficients of thermal expansion are too low to match with the other stack components [8].

In comparison to the rigid glass seals, compressive seals potentially offer several advantages. Since they are not rigidly bonded to the cells, the need for matching coefficient of thermal expansion (CTE) of all stack components is reduced or eliminated. The cells and interconnects are allowed to expand and contract freely during thermal cycling and operation, thereby, greatly reducing structural degradation during thermal cycling and routine operation. Elimination of the need for matching CTE greatly expands the list of candidate interconnect materials, whether ceramic or metallic. The research in the area of the compressive seals is still in its early stages and very little data is available. Kim and Virkar [9] demonstrated the use of compressed mica in a single-cell SOFC set-up; however, the effectiveness was not discussed. Simner and Stevenson [10] studied the compressive mica seals for SOFC applications. They examined micas in paper form as well as the cleaved single crystal form. The results showed the cleaved natural mica sheets were far superior compared to mica papers; for the mica sheets, leak rates about 0.33–0.65 sccm/cm at 800 °C and 100 psi were measured on small test coupons. Though, the allowable leak rates for SOFC stacks at elevated temperature remains to be determined, a coupon leak rate of 0.33–0.65 sccm/cm is likely to translate to unacceptably high leak rates for actual stacks, in which multiple, full size components would be stacked together with the mica gaskets between each component. In this paper, we present a novel hybrid compressive mica-based seal in which the leak rate can be reduced ~4300 times by simply adding the glass interlayers between the mica and the adjacent stack components.

2. Experimental

2.1. Raw materials

Three commercially available micas were investigated in this study. Two of them were mica paper: Muscovite paper and Phlogopite paper, each with a thickness of ~100 μm. Those papers are composed of large mica flakes (<1 mm in diameter, ~10 μm thick) and an organic binder. The third one is cleaved Muscovite single crystal sheet, also with a thickness of ~100 μm (the cleaved Muscovite single crystal sheet is transparent whereas the other two paper-forms are not). For the hybrid compressive seal tests, a borosilicate glass filter paper was used as the compliant layers. The glass contains ~58% SiO_2, ~9% B_2O_3, ~11% Na_2O, ~6% Al_2O_3, ~4% BaO, and ZnO, CaO and K_2O.

2.2. Leak test

Mica samples were cut into 1.5 square inches with a 1/2 in. diameter central hole. The mica squares were then pressed between an Inconel tube (outer diameter = 1.3 in. and inner diameter = 1.0 in.) and a dense alumina substrate. For hybrid compressive seals, two extra glass interlayers were placed between the Inconel tube/mica and mica/alumina interfaces. For comparison, a test of a glass-only seal was also conducted using a single layer of glass without the mica sheet. Samples were heated in a clamshell furnace at a heating rate about 2 °C/min to 800 °C. The load was applied using a universal mechanical tester with a constant load control (Model 5581, Instron, Canton, MA). The experimental setup is shown schematically as in Fig. 1. A large known-volume (370 cm^3)

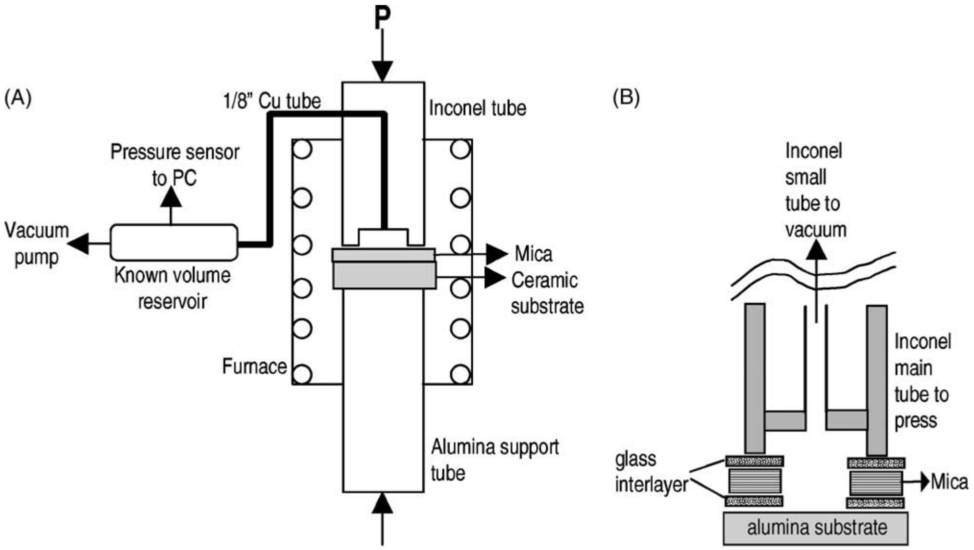


Fig. 1. Schematic showing (A) the experimental setup for the leak test and (B) a detail of the hybrid seal test.

reservoir was kept at ambient conditions and connected to the sample via a 1/8 in. Cu tube. By setting up a vacuum in the system (initially as low as ~100 mtorr), the leak rate was measured by monitoring the pressure change with time. The final pressure was about 2 torr. The pressure gradient across the seal therefore, could be considered to be essentially constant at 14.7 psi. Assuming the ideal gas law, the leak rate (L) was calculated by the equation:

$$L = \frac{\Delta n}{\Delta t} = \frac{n_{\mathrm{f}} - n_{\mathrm{i}}}{t_{\mathrm{f}} - t_{\mathrm{i}}} = \frac{(p_{\mathrm{f}} - p_{\mathrm{i}})V}{RT(t_{\mathrm{f}} - t_{\mathrm{i}})}$$

where n is the moles of the gas, T the temperature, V the reservoir volume, R the gas constant, t the time, and p the pressure. Subscripts f and i represent the final and the initial conditions. The calculated leak rate (L, in standard cubic centimeters per minute at STP, sccm) was further normalized with respect to the outer leak length (10.5 cm) of the Inconel tube and to a pressure gradient of 2 psi by the equation:

$$\bar{L} = \frac{L \times 2}{10.5 \times 14.7}$$

Before each run, the leak rate of the background (or the system without test samples) was also measured and subtracted from the actual test runs. To ensure a constant temperature, all leak tests were conducted at about 1/2 h after reaching the desired temperatures (800 °C).

3. Results and discussion

3.1. Concept of hybrid compressive seals

For a rigid glass seal, it was found that the leak rate was about 5×10^{-5} sccm/cm at 800 °C at a pressure gradient of 2 psi, using the current test setup. Ideally, the leak rate should be zero for a hermetic seal if the glass wets the surface in contact. In reality, the actual low leak rates were limited by the system's background since there were valves and tube connectors in the setup. As for the compressive mica seals, Simner et al. reported a leak rate of 0.65 sccm/cm at the same conditions and a compressive stress of 100 psi using the Muscovite single crystal sheet (~0.1 mm thick) [10]. It is appropriate to ask why the apparently flexible thin mica sheet allowed a leak rate about 10^4 times higher than that of a glass seal (the as-received Muscovite single crystal sheet, though relatively stiff in its as-received form, becomes flexible (and fragile) when heated to 800 °C). Looking at the compressed mica between the Inconel tube and the alumina substrate, one can imagine there are two possible paths for leaks. One is from the interface between the metal tube (or the ceramic substrate) and the mica. The other one is through the mica itself, since it cleaves into many sub-layers after losing its chemically bonded water at elevated temperatures [10]. Looking at the surfaces of the contact materials (dense alumina as the support substrate and the Inconel tube as the top pressing ram, Fig. 2), it was evident that many defects were present, including long grooves on the metal and the irregular grooves (voids) on the ceramic substrate. Therefore, it seemed likely that the major leaks for the compressive mica seal occurred through these interfaces. As a result, a "hybrid" compressive seal concept, in which a compliant glass interlayer is placed between the mica/component interfaces (to fill or block the surface defects), was developed. The concepts are shown schematically in Fig. 3. The results are reported and discussed in the following sections.

3.2. Raw materials characterization

Mica is a generic term applied to a group of complex silicate minerals having a sheet or plate like structure with a general composition of $AB_{2-3}(X, Si)_4O_{10}(O, F, OH)_2$. Three micas were used in this study: Muscovite ($KAl_2(AlSi_3O_{10})(F, OH)_2$) paper, cleaved Muscovite single crystal sheet, and Phlogopite ($KMg_3(AlSi_3O_{10})(OH)_2$) paper. All

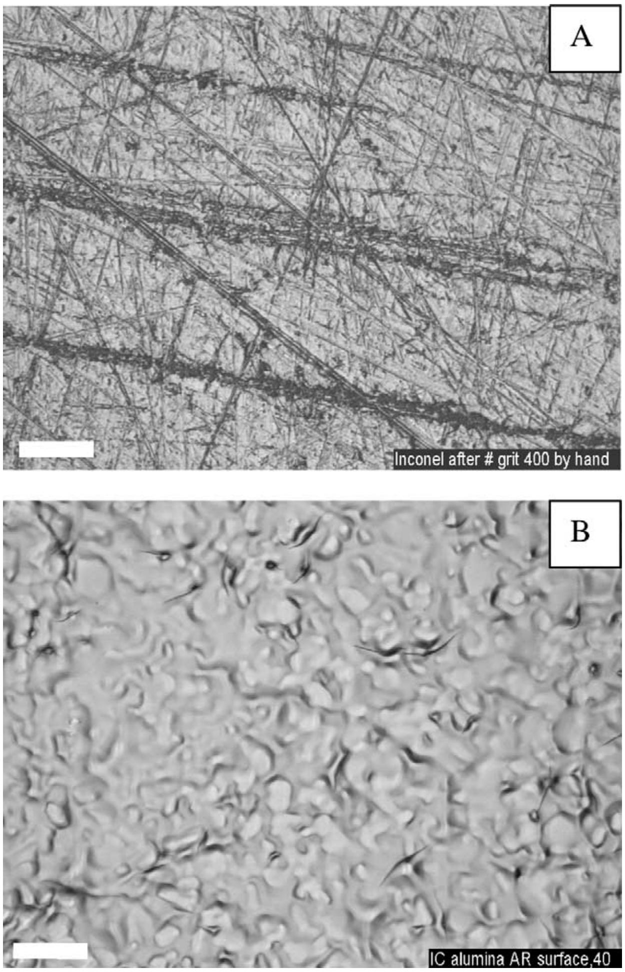
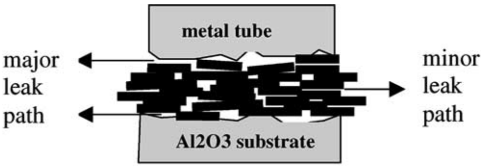
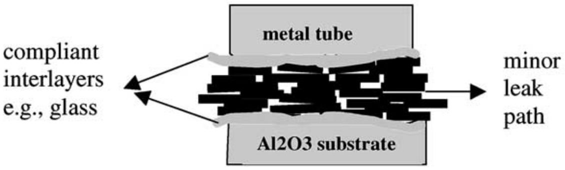


Fig. 2. Micrographs showing the surface morphology of (A) Inconel tube which was ground with a #400 grit paper (bar = 50 μm) and (B) alumina substrate (bar = 20 μm). Note the surface defects: continuous straight grooves (A) and irregular sintering grooves (B).



(A) conventional compressive mica seal



(B) hybrid compressive mica seal

Fig. 3. Schematics showing the conventional and the hybrid compressive mica seals; in the hybrid design, the major leak paths are filled/sealed by a compliant interlayer, such as glass.

three micas are about 0.1 mm thick. The Muscovite mica loses about 4% chemical water at ~600 °C. Phlogopite mica is more stable in high temperatures, losing its chemical water at ~950 °C [9]. The paper-type micas are composed of discrete large mica flakes bonded with organic binders, and pressed into thin sheets. Fig. 4 shows the typical surface morphology of the Phlogopite mica paper. It is clear that there are large voids (un-overlapped regions) and the surface is relatively rough. The Muscovite mica paper also shows similar surface features. On the other hand, the cleaved Muscovite single crystal mica sheets are transparent as received and have much smoother surfaces, though there are some scratches present (Fig. 5). After an 800 °C heat treatment, the single crystal sheets lost chemical water, which resulted in more defects on the surface (Fig. 6) and cleavage into many parallel sub-layers (Fig. 7).

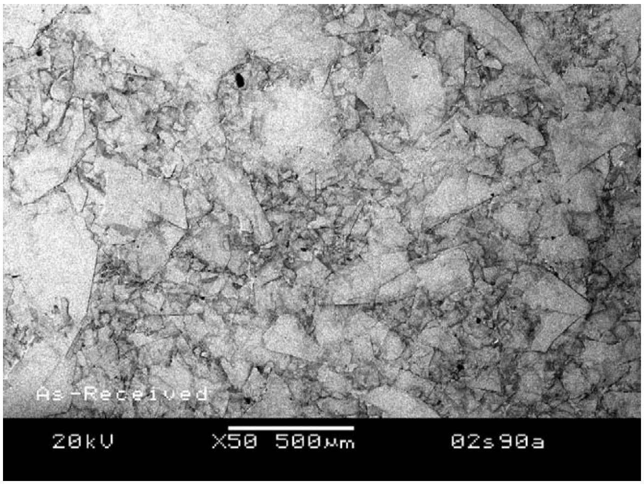


Fig. 4. Optical micrograph showing the surface texture of the as-received Phlogopite paper. It is clear the paper consists of large discrete Phlogopite flakes overlapping with each other.

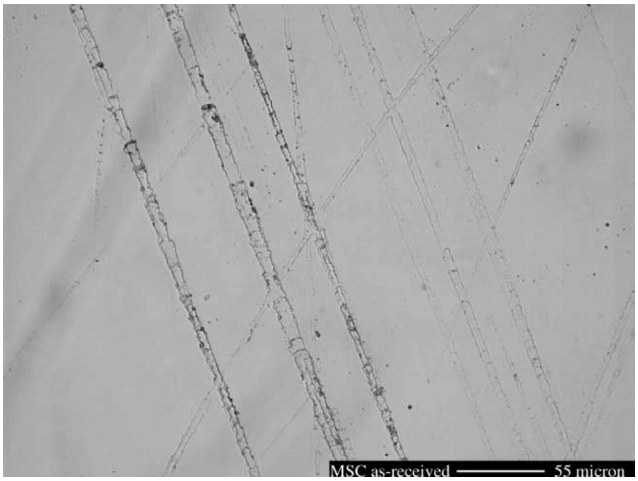


Fig. 5. Optical micrograph showing the surface texture of the as-received Muscovite single crystal. The material is transparent. The surface is very smooth and has less defects although some scratches are visible.

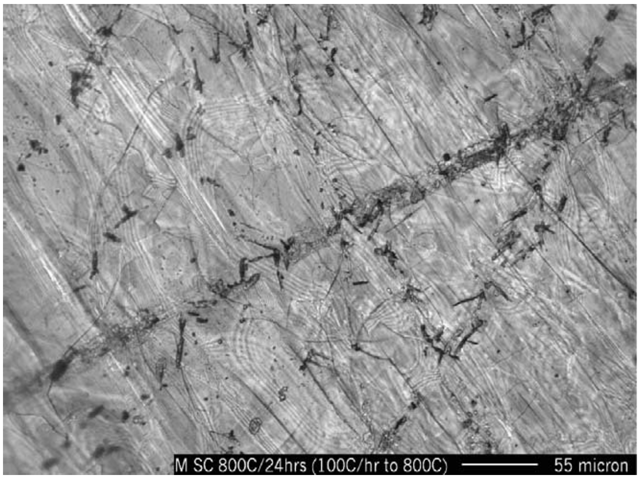


Fig. 6. Optimal micrograph showing the surface texture of the Muscovite single crystal after 800 °C heat-treatment. After heating, the material becomes opaque and also develops micro-cracks.

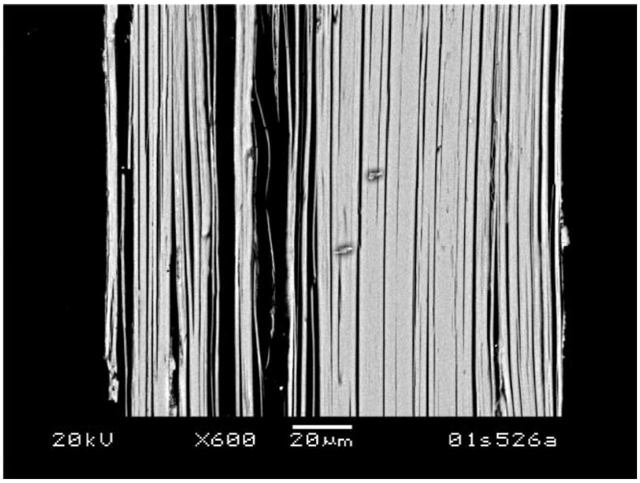


Fig. 7. Scanning electron micrograph shows the cleavage of Muscovite single crystal after heat-treatment at 800 °C.

Table 1
Normalized leak rate (sccm/cm) for the hybrid and plain compressive mica seals at 800 °C

Compressive stress (psi)	Muscovite single crystal		Muscovite paper		Phlogopite paper	
	Plain	Hybrid	Plain	Hybrid	Plain	Hybrid
25	–	0.000359	–	–	–	–
50	–	0.000243	–	–	–	–
100	0.65[a]	0.000155	5.77	0.0126	8.85	0.0108
200	–	–	–	0.0122	–	0.0105
300	0.42[a]	–	2.84	0.0115	2.97	0.0103
400	–	–	–	0.0107	–	0.0098
500	0.28[a]	–	1.92	–	1.68	–

Note that the leak rates were normalized with respect to the outer leak length (10.5 cm) and to a gas pressure gradient of 2 psi across the mica seals.
[a] Published data from [10].

3.3. Effect of stress on the leak rate

The 800 °C leak rates for the three micas are summarized in Table 1. The table includes data of the hybrid and the plain compressive mica seals. The results are also plotted as a function of the compressive stresses for Muscovite single crystal mica sheet (Fig. 8), Muscovite mica paper (Fig. 9), and Phlogopite mica paper (Fig. 10). It is evident that the leak rates were greatly reduced for hybrid compressive mica seals as compared to the plain compressive mica seals. For example, the Muscovite single crystal mica showed an extremely low leak rate of 1.55×10^{-4} sccm/cm at 800 °C and a compressive stress of 100 psi. As for the plain Muscovite single crystal mica, i.e. without the glass interlayers, the leak rates at the same test conditions were 0.65 sccm/cm [10], approximately 4300 times higher. Similar behaviors were observed for the paper type (discrete mica flakes bonded with organic binders) Muscovite and Phlogopite micas. For example, the leak rates for the hybrid Muscovite paper were 0.0126 sccm/cm, about 460 times lower than the plain Muscovite mica paper (5.77 sccm/cm) at 800 °C and a stress of 100 psi. The leak rates for the hybrid Phlogopite mica paper were 0.0108 sccm/cm, about 820 times lower than that of the plain Phlogopite mica paper (8.85 sccm/cm). The results clearly indicate that the major leaks occurred at the Inconel tube/mica and mica/ceramic substrate interfaces (Fig. 3).

It is also interesting to note that the effect of increasing the applied compressive stress was much weaker for the hybrid mica seals than for the plain mica seals. This is especially clear for the paper-type micas. For example, the leak rate

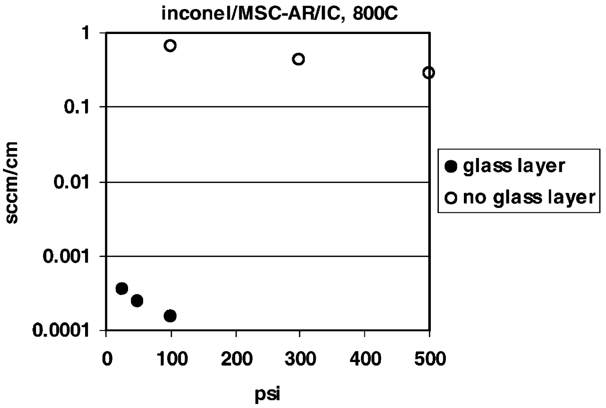


Fig. 8. Effect of the compressive stress on the normalized leak rate of Muscovite mica in the single crystal form at 800 °C. Data for the plain mica were from [10].

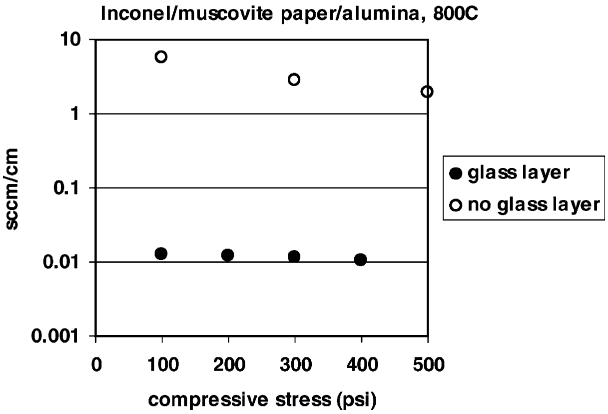


Fig. 9. Effect of the compressive stress on the normalized leak rate of Muscovite mica paper at 800 °C.

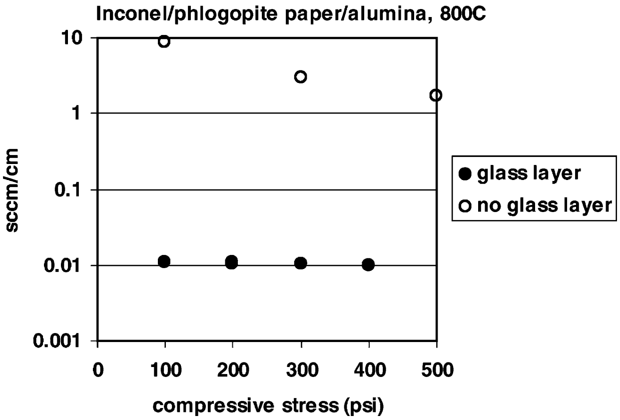


Fig. 10. Effect of the compressive stress on the normalized leak rate of Phlogopite mica paper at 800 °C.

reduced about 81% (from 8.85 to 1.68 sccm/cm) for Phlogopite mica paper when the compressive stress increased 400% from 100 to 500 psi (Table 1). For the hybrid form, the leak rate only reduced about 10% (from 0.0108 to 0.0098 sccm/cm) for a 300% increase in the stress from 100 to 400 psi. Similar results were also evident for the Muscovite mica paper. No substantial difference was observed between the Phlogopite mica paper and the Muscovite mica paper, though the former is more stable at higher temperatures than the latter. These results are consistent with previously reported data. Simner et al. reported a similar reduction for a thicker Phlogopite paper (0.5 mm) while using high purity helium at a 2 psi positive pressure gradient; in that study the leak rate dropped about 85% from 6.26 to 0.97 sccm/cm when the applied stress increased from 100 to 500 psi [10].

In the case of the Muscovite single crystal mica, there was a strong dependence on the applied compressive stress for both the hybrid and the plain mica seals. However, the stress range for the hybrid single crystal mica was only from 25 to 100 psi (at higher stresses the leak rates were close to the system's background, so tests were not conducted). It is expected that the hybrid single crystal mica would also show less dependence on stress at higher compressive loads since the sub-layers (after the loss of chemical water at elevated temperatures, Fig. 7) are more closely overlapped with each other. The fact that the hybrid seals were less dependent on the compressive stress is consistent with the fact that the major leaks occur at the interfaces between the mica and the metal tube (or the ceramic substrate, see Fig. 3). The glass used as the interlayer is a borosilicate glass which melts at around 600 °C and therefore, can fill and seal any surface defects, such as long grooves or voids.

Overall, it is clear that the Muscovite single crystal micas offer superior performance to the mica papers in hybrid seals; for example, the leak rate for a Muscovite hybrid seal was only 3.59×10^{-4} sccm/cm at a low compressive stress of 25 psi. This is likely due to the fact that the paper type micas are composed of discrete mica flakes/platelets, so that the leak paths are three-dimensional, whereas, the single crystal micas tend to have only two-dimensional leak paths (through the cleavage planes (Fig. 7)). Though, the single crystal mica sheets did form some defects after the loss of chemical water at elevated temperatures, these defects (micro-cracks) were minute in size compared to the connected voids which were prevalent in the mica papers.

3.4. Materials damage

There is a concern that the use of a low melting glass as the seal interlayer could damage the materials with which it is in contact (e.g. metal, ceramic, and the mica itself), especially under the compressive stresses. Though, long-term stability tests are underway, preliminary results showed no substantial corrosion or melting of the materials in contact. The corrosion at the glass metal/interface was limited to a depth of a few microns. This may result from the fact that the majority of the glass was squeezed out at elevated temperatures under the compressive stresses. If only a thin glass layer is left behind, only limited corrosion or melting would be likely to occur. As for the mica itself, degradation might be expected due to interaction between the mica (an aluminosilicate) and the borosilicate glass, but no significant degradation was observed. The mica remained intact except for a few surface sub-layers which bonded to the metal tube and the ceramic substrate when the test specimens were disassembled after testing.

3.5. Applications to SOFC

Low fuel leak rates are required if SOFC stacks are to operate safely and economically. Although, the allowable leak rates remain to be determined and will be somewhat design-specific, common sense points to the use of sealing materials offering leak rates as low as possible at a compressive stress as low as possible. The hybrid seal based on the Muscovite single crystal mica appears to be a viable candidate, considering the low leak rates reported above. For a 60-cell (14 cm × 14 cm active area per cell) stack, producing 0.5 W/cm^2 or 5.9 kW total gross power on steam reformed methane (steam to carbon mole ratio of 3.0), at 65% fuel utilization, 20% oxygen utilization, the total reformate gas flow rate entering the anode is estimated to be 1.36×10^5 sccm (STP). Assuming that the leak rate (per cm of seal length) measured in this study applied to full size stacks, the total leak rate for a 60-cell stack at 800 °C would be only 0.0019% of the total fuel rate for the hybrid Muscovite single crystal mica under a stress of 25 psi and a 2 psi pressure gradient (a leak length of 124 cm was assumed for each layer). While this assumption is somewhat simplistic, the current results clearly demonstrate the potential applicability of the hybrid-type compressive mica seals to SOFC applications. It must be emphasized, however, that other important aspects, such as thermal cycling and long-term stability in reducing and humid environments, must be evaluated. Results of studies examining these issues will be presented in the near future.

4. Conclusions

A novel hybrid compressive mica seal was developed that showed a reduction of leak rate by about 4300 times at 800 °C as compared to the conventional mica-only seals. The hybrid compressive mica seal is composed of a compliant glass layer on each side of the mica layer. Three commercial micas were tested as the compressive seals for solid oxide fuel cell applications. The best results were obtained using Muscovite single crystal mica. The normalized leak rate at 800 °C was only 1.55×10^{-4} sccm/cm at a stress of 100 psi and a pressure gradient of 2 psi. Hybrid seals based on mica papers also exhibited superior leak rates compared to the leak rates for mica papers alone. Microstructural examination revealed that the Muscovite single crystal mica appears to have two-dimensional leak paths compared to the three-dimensional leak paths for paper-type micas. Considerations of the potential corrosion or degradation of the materials in contact for the hybrid compressive seals were briefly discussed. Overall, the hybrid compressive mica seals based on Muscovite single crystal mica were found to be strong candidates for SOFC applications.

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