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Compressive mica seals for SOFC applications

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Abstract

Muscovite and phlogopite micas have been assessed as SOFC seals at 800°C. Paper gaskets, composed of pressed mica platelets in an organic binder, proved ineffective seal materials predominantly because of their uneven surface. However, cleaved natural mica sheets (with no binder) indicated far superior sealing characteristics with leak rates lower than 0.1 sccm cm^{-1} at 800°C, and approximately 0.7 MPa (100 psi) compressive stress.

Keywords: SOFC; Compressive seals; Leak rate

1. Introduction

Planar SOFC designs have significant advantages when compared to tubular designs, including low cost processing methods and shorter current paths (and subsequently higher power densities). However, planar designs must overcome a significant challenge which does not apply to tubular systems: the need for effective, high temperature seals to prevent fuel leakage, and high temperature mixing of the reducing and oxidizing atmospheres. The requirements for the seal materials are extremely stringent. To avoid stresses due to thermal expansion mismatch with adjacent components, the coefficient of thermal expansion must be similar to that of the other components (typically, in the range of 10×10^{-6} to 13×10^{-6}°C^{-1}). Chemical compatibility with the stack components and the gaseous constituents of the highly oxidizing and reducing environments is also of primary concern. In addition, the seal should be electrically insulating to prevent shorting within the stack.

The majority of SOFC seal development has focused on bonded, rigid seals; primarily glasses and glass–ceramics, which essentially "glue" the stack components together. Many glass seals are designed to soften, and viscously flow above the SOFC operating temperature to provide hermetic seals by mechanical/chemical bonding. On cooling back down to the operating temperature, the glass crystallizes to form a rigid, bonded seal. A principal advantage of glass seals is that the glass composition can be tailored to optimize physical properties, such as coefficient of thermal expansion (CTE). However, several challenges remain with respect to the use of glass seals in SOFCs. The brittle nature of glasses below the glass transition temperature makes the seals vulnerable to crack formation, and glasses tend to react with other cell components, such as electrodes, at SOFC operating temperatures. Glass seals can affect electrode performance over a short range (via solid state diffusion or viscous flow) or over longer distances (via gaseous transport of glass constituents). The glass composition selected must also have good wetting behavior and sufficiently high viscosity (greater than $\sim 10^3$ Pa s) at the operating temperature to avoid deformation. In addition, some SOFC applications, such as auxiliary power systems, require frequent thermal cycling and short heat-up times, so the stack must be designed to withstand thermal shock. If bonded seals are used, the entire SOFC stack becomes rigid and is more prone to thermal shock.

All three of the primary glass forming oxides (B_2O_3, P_2O_5, SiO_2) have been investigated as potential SOFC seals. Ley et al. [1] reported promising results for high-B_2O_3 glasses in the SrO–La_2O_3–Al_2O_3–B_2O_3–SiO_2 system. However, the softening points for these glasses were too low for SOFCs operating above 700°C [2]. Also, glass compositions based on B_2O_3 tend to exhibit excessive volatilization in the SOFC environment. P_2O_5-based glasses can be adjusted to minimize volatilization, but their CTEs are too low, and they have low mechanical strength [3]. To date, the best results have been obtained using compositions based on silica. While alkali silicate glasses tend to be very reactive towards other SOFC component [1], alkaline–earth aluminosilicate glasses have yielded promising results [2,4–6]. Günther et al. [5] used a commercially available BaO–Al_2O_3–SiO_2–B_2O_3–As_2O_3

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glass (designated AF45) for sealing SOFC stacks operating at temperatures between 850 and 950°C. Substantial volatilization of B_2O_3 and As_2O_3 occurred, resulting in extensive crystallization and formation of pores. In a later study on glasses in the $BaO–MgO–Al_2O_3–SiO_2–B_2O_3$ system, annealing for 400 h at 850°C after bonding to a high Cr interconnect alloy resulted in reduction in strength due to the formation of a reaction layer of $MgCr_2O_4$ [7].

A possible alternative to glasses is the use of compressive, non-bonding seals. If the seals are non-bonding, the individual stack components are free to expand and contract during thermal cycling. Compressive seals utilize materials such as sheet-structure silicates, which do not bond to the SOFC components; instead, the sealing material acts as a gasket and the seal is achieved by applying a compressive force to the stack. The use of compressive seals brings several new challenges to SOFC stack design — a load frame must be included to maintain the desired level of compressive load during operation, and the stack components must be able withstand the compressive load required for adequate sealing for the lifetime of the stack. The research in this area is still in its early stages, and no significant studies have been reported in the open literature. A recent study by Kim and Virkar [8] indicates the use of compressed mica gaskets in a single cell SOFC set-up, though the effectiveness of such seals was not discussed. No additional studies have been reported in the published literature, and hence this present study has been designed to assess the potential of mica as a compressive seal for intermediate temperature (800°C) SOFCs.

Micas belong to a class of minerals known as phyllosilicates, and are composed of sheets of silicate tetrahedrons [9]. They are generally known for their high resistivity, uniform dielectric constant/capacitance stability, and low power loss (high Q factor), and consequently are used extensively in electronic devices. The general formula for micas is $AB_{2–3}(X,Si)_4O_{10}(O,F,OH)_2$. In most micas, the A ion is potassium. The B ion can be aluminum, lithium, iron, zinc, chromium, vanadium, titanium, manganese, and/or magnesium. The X ion is usually aluminum, but can also be beryllium, boron and/or iron. For this study, two types of mica were considered; muscovite (potassium aluminum silicate hydroxide fluoride, $KAl_2(AlSi_3O_{10})(F,OH)_2$), and phlogopite (potassium magnesium aluminum silicate hydroxide, $KMg_3(AlSi_3O_{10})(OH)_2$). Both have layered structures in which the layers are weakly bonded by potassium ions. These weak potassium ion layers enable perfect cleavage of the muscovite and phlogopite mica materials. Some relevant physical properties of the two micas are listed in Table 1 [10].

2. Experimental

Muscovite mica was evaluated in two forms: cleaved sheets (0.1 mm thick), and muscovite paper (0.5 mm thick). The cleaved sheets are essentially transparent, single crystal mica, whereas the mica paper consists of small mica platelets (<1 mm in diameter, ∼10 μm thick) bonded by an organic binder. Muscovite single crystal (muscovite SC) was tested as a single 0.1 mm sheet and also as 5×0.1 mm sheets laid on top of each other for direct comparison with the 0.5 mm thick mica papers investigated. Phlogopite was tested in 0.5 mm thick paper form only. All mica samples were purchased from McMaster-Carr supply company, USA.

A schematic of the compressive seal test set-up is illustrated in Fig. 1. The mica seal is placed between an Inconel 600 tube (ground to a 32G finish — roughness height 32 μin.) and Sr-doped $LaCrO_3$ disc (ground to a 16G finish — roughness height 16 μin.), and heated to 800°C. The Inconel tube is then lowered into contact with the mica seal, and a given compressive stress 0.69–6.20 MPa (100–900 psi) applied across the seal area via a mechanical testing machine (Applied Test Systems, Inc.) using a 4445 N (1000 lb) load cell. At the same time the Inconel tube and an external 200 cm^3 room temperature reservoir are pressurized to 13.8 kPa gauge pressure (2 psig) with high purity helium. The line between the helium source and the reservoir is then closed, and the resulting pressure decay in the reservoir and Inconel tube recorded with respect to time from 13.8 to 2.1 kPa (2.0 to ∼0.3 psig). From the pressure decay versus time data, leak rates can subsequently be established.

Thermal gravimetric analysis of as-received mica samples was carried out using a Cahn TG171 instrument from room temperature to 1250°C. SEM and EDX of post-fired and tested mica gaskets were performed using a JEOL JSM-5900LV, and an OXFORD INCA 200, respectively.

Table 1
Physical properties of muscovite and phlogopite micas

Property	Muscovite	Phlogopite
Color	Ruby/green	Amber/yellow
% Chemical water	4.5	3.0
Volume resistivity at 25°C (Ω cm)	40×10^{13} to 2×10^{17}	1×10^{12}
Tensile strength (MPa)	170	105
Compressive strength (MPa)	190–220	No data
CTE perpendicular to cleavage plane ($°C^{-1}$)	9×10^{6} to 36×10^{6}	30×10^{6} to 60×10^{6}
Thermal conductivity perpendicular to cleavage plane ($W\ m^{-1}\ °C^{-1}$)	0.52	0.43

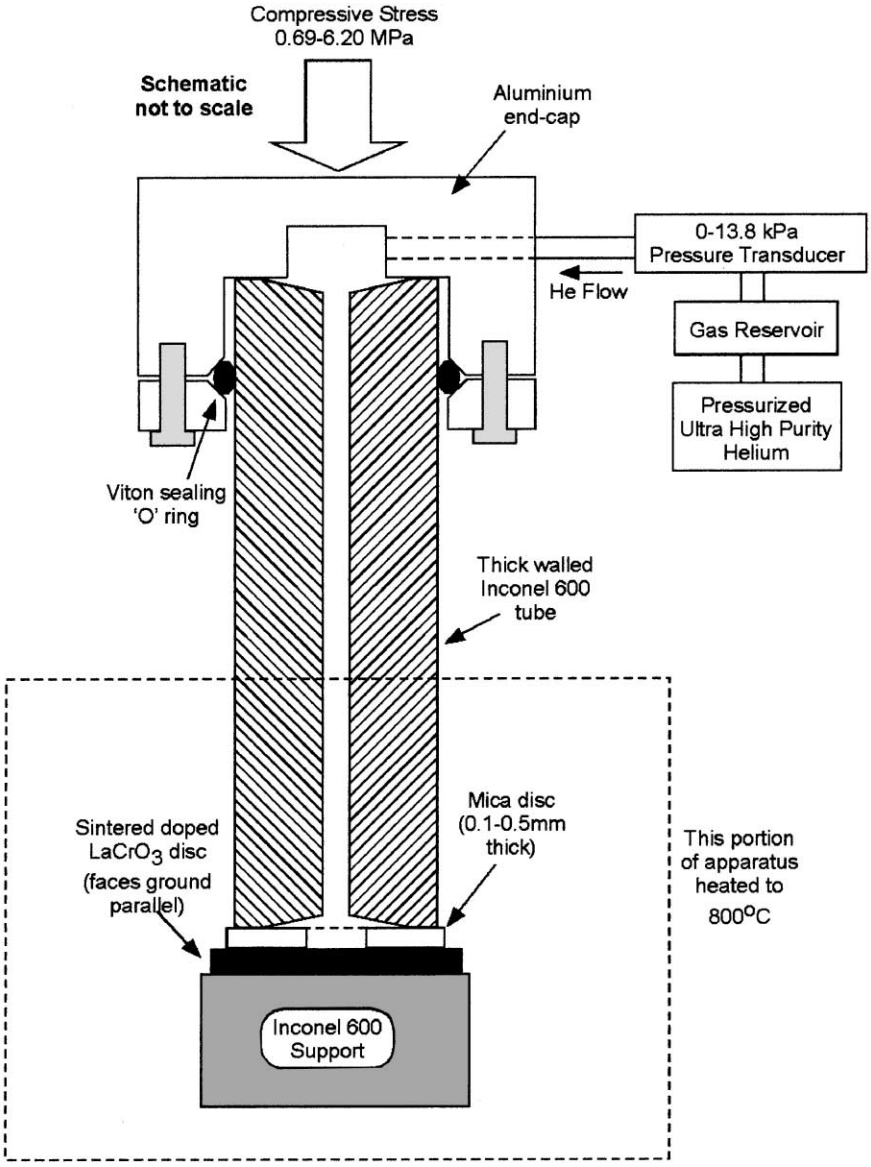


Fig. 1. Schematic of seal testing apparatus.

3. Results

TGA data for the muscovite single crystal, muscovite paper and phlogopite paper are presented in Fig. 2. Both mica papers indicate a significant weight loss from 400 to 550°C caused by organic binder burn-off. At ~600°C the muscovite materials (both paper and single crystal) experience a 4% weight loss, presumably the loss of chemical water. For the phlogopite paper, the loss of chemical water begins around 950°C. Two points should be noted. Firstly, the loss of binder in the paper micas makes them more fragile with respect to handling. Secondly, the loss of chemical water causes a swelling of the mica materials. However, these phenomena do not cause sample disintegration, and were not found to be problematic in terms of handling if the seals were placed in the test apparatus prior to organic binder burn-out, and chemical water release.

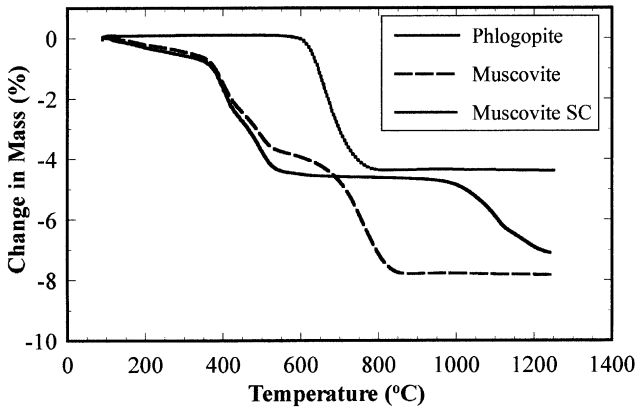


Fig. 2. TGA data for muscovite single crystal (SC), muscovite paper and phlogopite paper.

Table 2
Leak rates per inner seal length (sccm cm^{-1}) for compressive stresses 0.69–6.20 MPa, and gauge pressures 3.5–13.8 kPa[a]

Seal material and compressive stress, MPa (psi)	Gauge pressure, kPa (psig)			
	13.8 (2.0)	10.3 (1.5)	6.9 (1.0)	3.5 (0.5)
Leak rate (sccm cm^{-1})				
Phlogopite 6.20 (900) ($t = 0.5$ mm)	0.56	0.47	0.35	0.22
4.82 (700)	0.76	0.59	0.44	0.23
3.45 (500)	0.97	0.78	0.56	0.30
2.07 (300)	1.49	1.18	0.87	0.49
0.69 (100)	6.26	5.06	3.77	2.28
6.20 (900) pre-stress, 2.07 (300)	0.71	0.56	0.40	0.23
6.20 (900) pre-stress, 0.69 (100)	1.28	1.04	0.77	0.43
Muscovite 6.20 (900) ($t = 0.5$ mm)	0.68	0.54	0.39	0.20
4.82 (700)	0.85	0.67	0.49	0.24
3.45 (500)	1.15	0.92	0.68	0.33
2.07 (300)	1.91	1.54	1.14	0.57
0.69 (100)	6.94	5.58	4.17	2.54
6.20 (900) pre-stress, 2.07 (300)	0.70	0.57	0.42	0.23
6.20 (900) pre-stress, 0.69 (100)	1.51	1.18	0.86	0.44
Muscovite SC 6.20 (900) ($t = 0.5$ mm)	0.06	0.05	0.04	0.03
4.82 (700)	0.06	0.05	0.04	0.03
3.45 (500)	0.08	0.06	0.05	0.04
2.07 (300)	0.14	0.11	0.09	0.05
0.69 (100)	0.33	0.27	0.19	0.10
6.20 (900) pre-stress, 2.07 (300)	0.05	0.05	0.04	0.03
6.20 (900) pre-stress, 0.69 (100)	0.09	0.08	0.06	0.04
Muscovite SC 6.20 (900) ($t = 0.1$ mm)	0.13	0.10	0.08	0.05
4.82 (700)	0.19	0.15	0.11	0.06
3.45 (500)	0.28	0.23	0.16	0.10
2.07 (300)	0.42	0.33	0.24	0.14
0.69 (100)	0.65	0.51	0.37	0.20
6.20 (900) pre-stress, 2.07 (300)	0.15	0.13	0.10	0.06
6.20 (900) pre-stress, 0.69 (100)	0.43	0.35	0.28	0.18

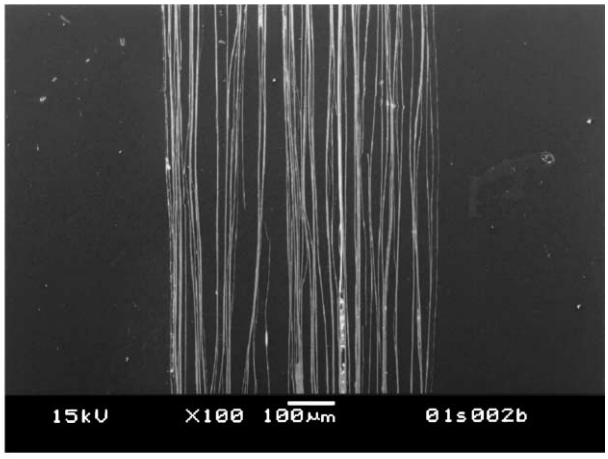
[a] 1 psi = 6.89×10^3 Pa.

Table 2 indicates leak rates for the phlogopite and muscovite mica materials. The leak rates are expressed as a function of the inner circumference of the Inconel compression tube.

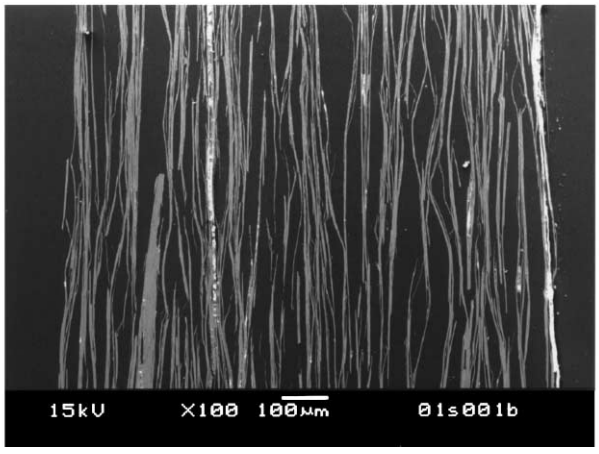
The results indicate a number of trends. Firstly, and most obviously, as the applied compressive stress increases so the leak rate decreases for all of the materials. This can be simply attributed to two phenomena: (1) a tighter (more hermetic) seal is achieved at the chromite–mica and Inconel–mica surfaces with higher compressive loads, and (2) individual sheets in the mica structures are pressed closer together with higher loads thereby reducing the volume of open pathways for gas escape (Figs. 3 and 4).

Secondly, the leak rates for the muscovite single crystal are typically 5–10 times lower than the paper micas at any given compressive stress or gauge pressure. SEM of post-fired samples reveals little difference between the cross-sectioned microstructure of the three tested seal-types. All have a layered structure with large open channels between the layers prior to the application of a compressive load; shown for muscovite SC and muscovite paper in Fig. 3(a) and (b), respectively. As expected, post-compression SEM indicates that the mica layers have been pushed together leaving less open volume between each layer: Fig. 4(a) muscovite SC, and (b) muscovite paper. The improved sealing characteristics of the muscovite SC might be explained by differences in the topography (roughness) of each seal surface (smoother surfaces will facilitate improved sealing characteristics). Fig. 5(a)–(c) show surface SEM images of muscovite SC, muscovite paper and phlogopite paper, respectively. The muscovite SC, Fig. 5(a), has a very smooth surface, with some cracks thought to be caused during the release of chemical water since no such cracks are observed in the material prior to heating. Such cracks are also observed in the muscovite paper, but not in the phlogopite material. The paper micas, Fig. 5(b) and (c), on the other hand, have much rougher surfaces purely due to the fact that the materials are composed of many small mica platelets randomly pressed together.

Finally, Table 2 also indicates leak rates for samples pre-stressed at 6.20 MPa (900 psi), and subsequently compressed at lower stresses of 2.07 MPa (300 psi) and 0.69 MPa (100 psi). The results show that pre-stressing the samples and then loading at a lower compressive stress improves the seal performance for a given applied stress.

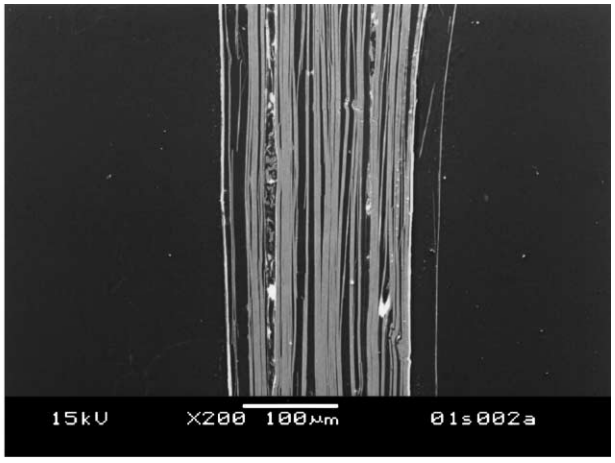


(a)

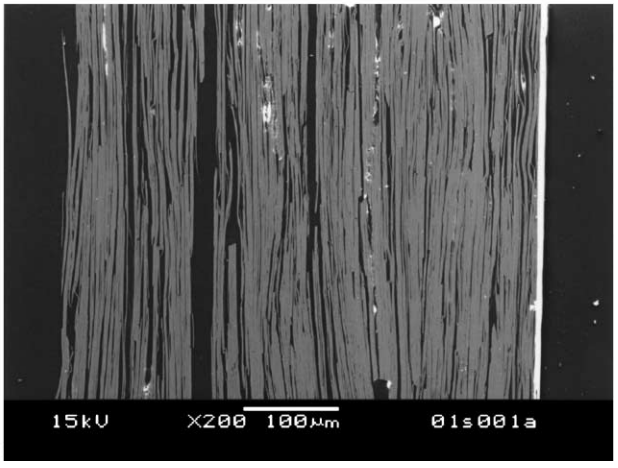


(b)

Fig. 3. (a) Cross-sectional SEM image of muscovite SC after heating to 800°C (prior to compression). (b) Cross-sectional SEM image of muscovite paper after heating to 800°C (prior to compression).



(a)

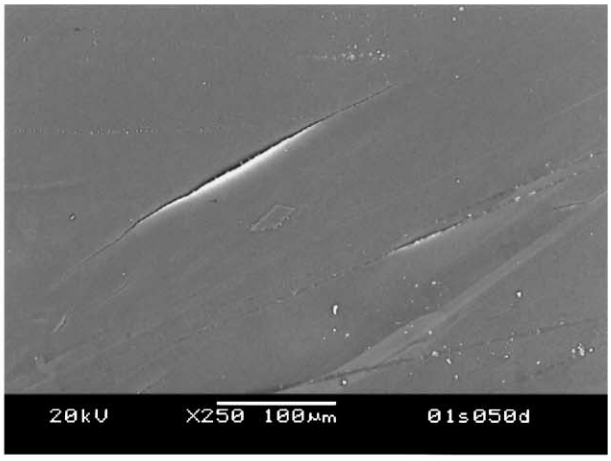


(b)

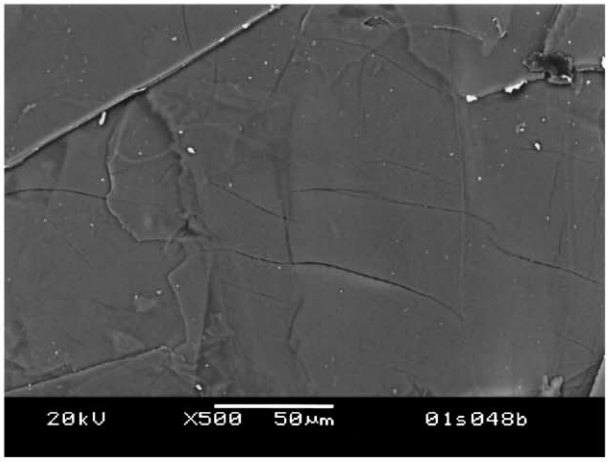
Fig. 4. (a) Cross-sectional SEM image of muscovite SC after heating to 800°C (post-compression). (b) Cross-sectional SEM image of muscovite paper after heating to 800°C (post-compression).

Fig. 6 compares leak rates from 2.1 to 13.8 kPa (0.3–2.0 psig) for a 0.1 mm muscovite single crystal sample. The dashed line represents a sample compressed at 2.07 MPa (300 psi), and the solid line the same sample pre-compressed initially at 6.2 MPa (900 psi), and then leak rates recorded at a reduced stress of 2.07 MPa (300 psi). At the higher gauge pressures, the pre-compressed seal exhibits leak rates three times lower than the seal compressed only at 2.07 MPa (300 psi). The observed improvement resulting from pre-compression at higher loads is presumably due to the fact that that the mica gaskets do not relax after release of the 6.2 MPa (900 psi) stress, and the individual sheets remain pressed together. This particular finding may be of some significance since it is possible that the mica gaskets could be initially compressed at high loads to give improved sealing, and the load then decreased to avoid creep of metallic cell components while still providing adequate sealing characteristics.

Low fuel leak rates are essential if SOFC stacks are to operate safely and economically. In an attempt to correlate the data from this study with stack sealing requirements, calculations were performed based on a ''generic'' stack containing cells with an active area of $10\,\text{cm} \times 10\,\text{cm}$ ($100\,\text{cm}^2$ active area). For simplicity, an exposed seal length of $4 \times 10 = 40\,\text{cm}$ per cell was assumed. Additional assumptions included reformed methane as the fuel (methane:water ratio of 1:3; reformed at 750°C), and an operating current density of $0.7\,\text{A}\,\text{cm}^{-2}$. At that current density, each cell consumes 730 sccm of reformate. Operation of a leak-free stack at 75% fuel utilization would then require a fuel flow rate of 975 sccm. Additional fuel penalties due to leakage through the compressive seals were calculated using data from Table 2. Assuming a 6.9 kPa (1 psi) pressure drop across the seal, a 0.5 mm thick muscovite SC seal compressed at 0.69 MPa (100 psi) would leak approximately 8 sccm per cell, requiring that the fuel flow rate be increased by only 0.8% to compensate for the leakage. While the scenario examined in this paragraph is very simplistic, it suggests that compressive seals could be viable alternatives to rigid, glass-based seals for SOFC stacks. It must be emphasized, however, that many challenges remain to be overcome, including



(a)



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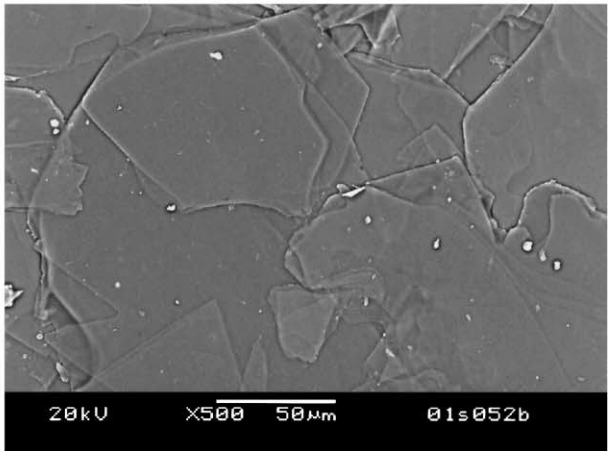

(c)

Fig. 5. (a) SEM image of muscovite SC surface after heating to 800°C. (b) SEM image of muscovite paper surface after heating to 800°C. (c) SEM image of phlogopite paper surface after heating to 800°C.

the design of inexpensive, compact, stable compressive load frames for the stacks, as well as the development of component materials and designs which are resistant to creep and/or fracture when subjected to compressive loads over the lifetime of the SOFC stack.

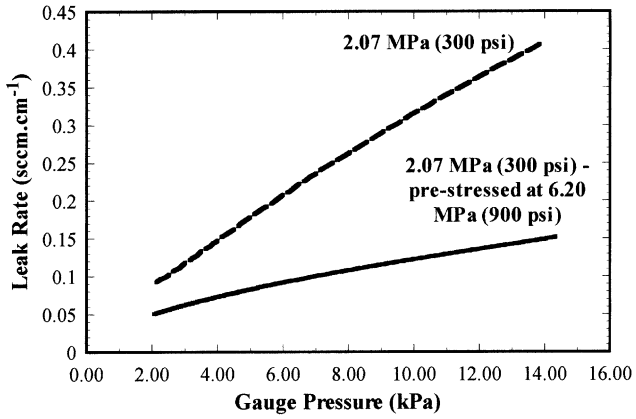

Fig. 6. Effects of pre-compression on leak rate for a muscovite SC sample.

4. Conclusion

In conclusion, mica papers indicate very poor sealing characteristics requiring extremely high compressive stresses primarily due to the surface roughness resulting from small mica platelets pressed together. However, single crystal mica materials with significantly smoother surfaces exhibit lower leak rates with a 0.69 MPa (100 psi) compressive stress than the mica papers achieve with a 6.2 MPa (900 psi) stress. As such, single crystal micas are potentially viable sealing materials, though their application to SOFCs requires rigorous testing in actual SOFC stacks to determine if the leak rates observed in this investigation are sufficiently low, and also to establish a maximum allowable compressive stress that can be supported by the stack without fracture or creep.

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