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Compression Properties and Leakage Tests of Mica-Based Seals for SOFC Stacks

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Abstract

Sealing properties and compression properties of two mica-based materials, Thermiculite 866 and Statotherm HT were measured. Thermiculite 866 was tested in two forms: as-made and precompressed (consolidated). Sealing tests were carried out at 800 °C with simulated fuel cell anode gas. Seals were pressed to a constant thickness, which represents the conditions in fuel cell stacks. Both seals showed stable leak rates over test periods of roughly 400 h. Leak rates of Thermiculite 866 samples were found to be independent of the hydrogen overpressure within the measurement accuracy in the pressure range of 10–100 mbar(g). However, a Statotherm HT gasket tested with lower compression stress compared to Thermiculite 866 gaskets showed roughly linear dependency on the overpressure. Compression tests were carried out at room temperature and at 800 °C. Compression properties of both materials were found to strongly depend on temperature. Both materials experienced swelling when heated to 800 °C and were more ductile compared to room temperature.

Keywords: Leak Rate, Mica, Seal, SOFC, Statotherm HT, Thermiculite 866

1 Introduction

A solid oxide fuel cell (SOFC) is an electrochemical device in which reactants are converted into electricity and heat. Main components of fuel cell stacks are cells, interconnects and seals. Seals should be stable, both in reducing atmospheres with high water vapour contents and in oxidising atmospheres. Chemical stability with interconnects in operating temperature and during thermal cycles is also required. A sealing failure in SOFC stack causes gas leakage which decreases the overall performance and the lifetime of the stack. Leakages can cause cell degradation by a number of mechanisms, e.g. increased thermal gradients [1], local shortage of fuel, oxidation of the anode and increased chromium evaporation [2] due to higher water vapour content at the cathode.

Seals in SOFCs are often either glass or glass-ceramics. Glass-ceramic sealants are rigidly bonded and thus may offer excellent sealing characteristics. However, using glass ceramics requires that all the stack components need to have matching coefficients of thermal expansion (CTE) to avoid mechanical failures. Typically, glass-ceramics also require a specific heat treatment in which binder is evaporated and a stable phase is formed. Chemical reactions have also been reported between glass-ceramics and other stack components. These reactions can include cross-diffusion [3] and excessive surface and internal oxidation at steel-sealant interface [4] as well as increased chromium evaporation from interconnect steels [5].

In order to mitigate the drawbacks of glass-ceramic sealants, a number of compressive sealing materials mainly based on mica have been proposed. Mica is a group of silicate minerals having a general structure of $AB_{2-3}(Al,Si)Si_3O_{10}(OH)_2$ in which A is either K, Na, Ca or Ba and B is either Al, Fe, Mg or Li [6]. Micas can also contain other elements such as F^- replacing some of the OH^- ions [7]. A few studies have been undertaken to assess the high temperature sealing properties of phlogopite ($KMg_3(AlSi_3O_{10})(OH)_2)$) and muscovite ($KAl_2(AlSi_3O_{10})(OH)_2)$) type micas. In temperatures exceeding 600 °C, muscovite mica has been reported to lose its constitutional water whereas phlogopite mica experiences the loss of constitutional water around 950 °C. This behaviour causes swelling of the mica material, which however might not necessarily affect the sealing properties [8]. It

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has been found that to achieve good sealing properties, mica papers comprising of discrete mica platelets require high compression stresses in excess of 6 MPa [8, 9]. Therefore, a number of hybrid seals have been proposed. Good sealing properties have been observed with hybrid sealing structures such as mica with glass-ceramic contact layers [10, 11] and mica with a corrugated metallic profile [9]. Thermal cycle capability of mica-based seals has been demonstrated with minimum drop in open-circuit voltage during 1,000 thermal cycles [12]. Some experimental compressive seals have also been developed based on ceramics [13] and fibre papers infiltrated with ceramic powders [14].

Considering stack-design, it is important to know the compression properties of the sealing materials. Sufficient mechanical stress on the cell and on the seals is required to achieve good electrical contact between cells and interconnects as well as to achieve good sealing properties. Compression stresses in the stack are limited by the material properties of seals, interconnects and cells. All the publications found on compressible mica seals were carried out with the sealing material compressed with a constant force. However, in a planar SOFC stack, this is often hard to achieve since the cell needs to have a good electrical contact to the interconnect and thus it needs to carry at least some of the load. Therefore, the seals around the cells are actually pressed into a constant thickness rather than with a constant force. This is illustrated in Figure 1a in which an anode-supported cell is pressed between two interconnects. Sealing is required between the electrolyte and interconnect and between the interconnects. In both cases, the cell acts as a spacer keeping the seals at constant thickness.

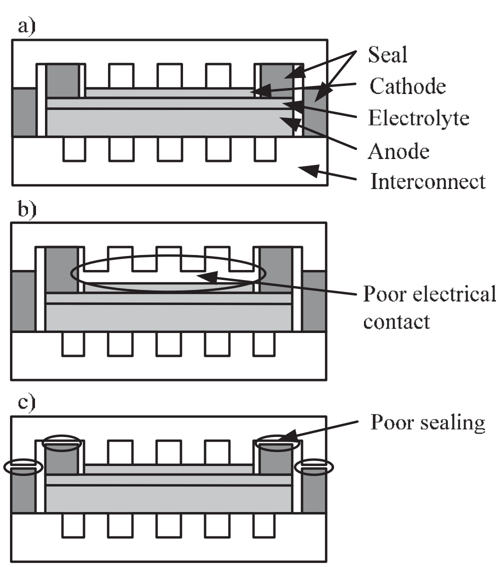

Fig. 1 (a) Simplified structure of a single repeating unit of a fuel cell stack based on an anode supported cell. (b) Poor electrical contact between cell and interconnect due to insufficient compressibility of the seals. Good sealing properties due to high surface stress on the seals. High mechanical stresses on interconnects. (c) Good electrical contact due to excess compressibility of the seals. Poor sealing properties due to low surface stress on the seals.

Figure 1b shows a case in which compression of the seals is insufficient. Thus, the seals experience most of the mechanical load on the stack and good sealing properties may be achieved. However, stresses on the interconnect are concentrated on a smaller area which can lead to mechanical failure. In this case, the cell experiences insufficient mechanical load, thus decreasing electrical contact. Figure 1c shows a case in which seals are either too thin or too compressible. This leads to insufficient compression stress on the seals and to poor sealing properties. However, electrical contact between cell and interconnect is maximised.

In this study, the long term sealing properties and compression properties of two types of commercial mica-based seals were studied. The sealing tests were carried out at 800 °C with seals compressed to a constant thickness. Compression properties of the materials were measured at room temperature and at 800 °C. Materials studied were Thermiculite 866 [15] and Statotherm HT [16].

2 Experimental

2.1 Materials

Thermiculite 866 (Flexitallic Ltd) [16] is a composite material consisting of chemically exfoliated vermiculite mica. Thermiculite 866 is available in two forms: as-made and consolidated, which were both tested. Consolidated form is a densified form of Thermiculite 866 and it is made by precompressing as-made material. Figure 2 illustrates SEM cross-sections of Thermiculite 866 samples. Images show horizontal vermiculite platelets (light-grey), steatite (grey) and voids (black). It can be noted that precompression diminishes the porosity of Thermiculite 866.

Statotherm HT (Burgmann industries) [4] is phlogopite mica with organic binder. Figure 3 illustrates the SEM cross-section of uncompressed Statotherm HT. Large voids between discreet mica platelets are seen.

2.2 Compression Properties

Compression tests were carried out with Instron 8801 fatigue system. Figure 4 shows a picture of the test setup. Round samples (12 mm diameter) were compressed between 13 mm diameter rods made of 253MA steel, and their thickness was measured with a strain-gauge. Tests were carried out at room temperature and at 800 °C. The high temperature tests were done by inductively heating the compression rods and measuring their temperature with thermocouples inserted into the compression rods.

2.3 Sealing Properties

Sealing properties were tested by compressing the seals to constant thickness and measuring the leak rates. Figure 5 shows the exploded view of the gasket holder setup. Gasket holder plates with circular groves for the seal-

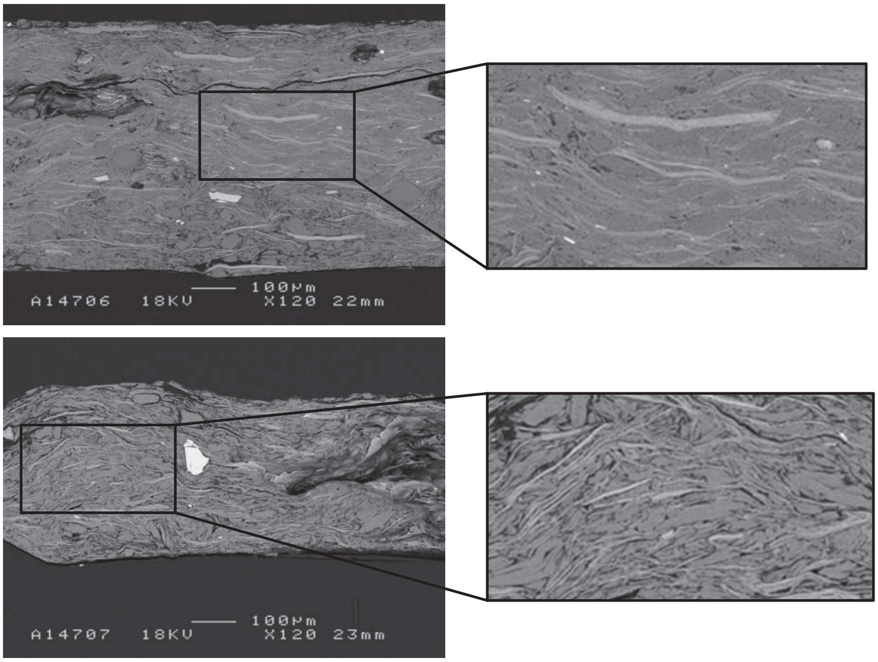

Fig. 2 SEM images of the consolidated (above) and as-made Thermiculite 866 cross-sections.

ing gaskets were manufactured of 3 mm thick 253 MA steel. The groves were manufactured by etching. The surface roughness of the sealing surfaces was measured to be around R_a = 40 nm with Taylor Hobson Surtronic 3+ surface roughness analyser. Radial groves were etched into the plates to allow leaked gas to evacuate. Inner diameter of the gaskets was 72.5 mm and width 5 mm. A gasket holder plate with a gasket was then pressed between two 253 MA steel plates, and the structure was tightened with 253 MA bolts. Bolts were fastened tight enough so that the seals compressed to accommodate the grove. Gas was introduced through a 6 mm Inconel 600 pipe welded to the endplate and gas outlet was via a 3 mm pipe welded to the gasket holder plate.

Flow diagram of the sealing tests is illustrated in Figure 6. Hydrogen feed to

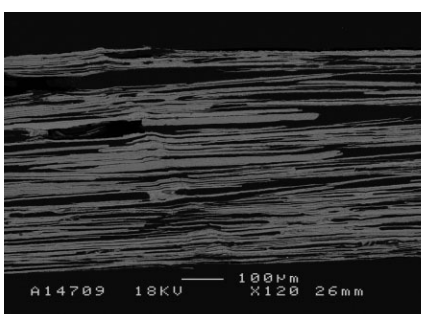

Fig. 3 SEM image of the uncompressed Statotherm HT cross-section.

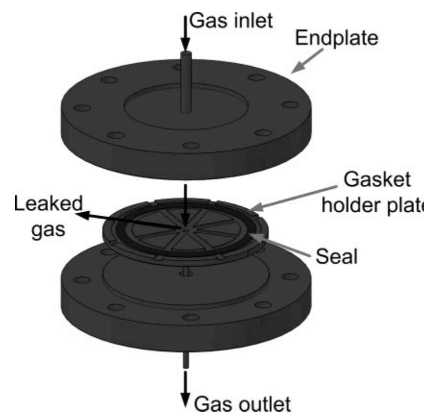

Fig. 5 Gasket holder setup.

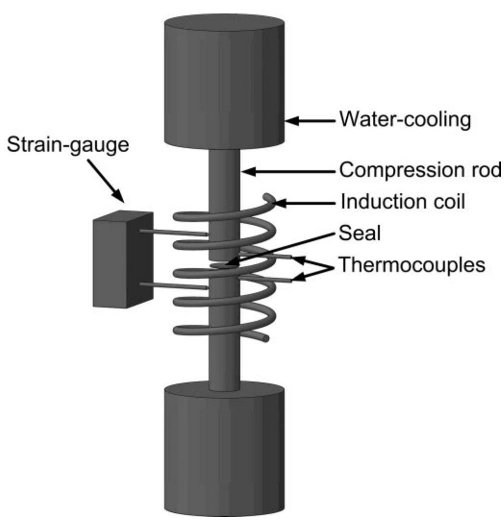

Fig. 4 Test setup for the compression tests.

the system is controlled with a Bronkhorst EL-FLOW-series mass flow controller. Inlet gas is fed through a humidifier (Fuel Cell Technologies) or through the by-pass line. The gas enters the furnace via a heated pipeline and exits the furnace through a pressure controller. Valves V2, V3 and V4 were used to change the inlet gas between dry and humidified hydrogen. Pressure upstream of the gasket was measured with pressure transducer and controlled by pressure controller V5. The pipeline between humidifier and the outlet was heated to avoid condensation. Inlet and outlet gas flows were measured with a Sensidyne Gillibrator II flow calibrator.

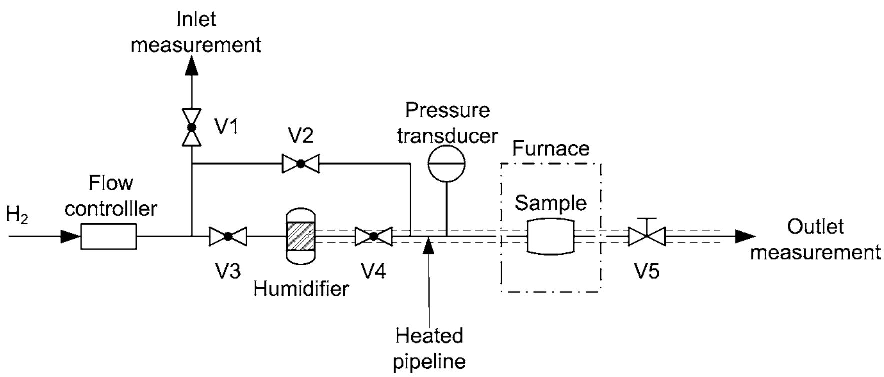

Fig. 6 Flow diagram of the leak measurements.

Sealing tests were carried out according to the following procedure.

(i) Heating up to 800 °C with 97% N_2 + 3% H_2.
(ii) Purging the pipelines with dry H_2 until water vapour content at the outlet dropped below 10 hPa.
(iii) Leak rate measurement with dry H_2.
(iv) Exposure with either 200 ml min^{-1} H_2 or 200 ml min^{-1} H_2 + 120 ml min^{-1} H_2O. Overpressure of the gas during the exposure was always 100 mbar.
(v) Cooling down to room temperature with 97% N_2 + 3% H_2.

Steps two to four were repeated periodically during the tests.

Table 1 summarises the tested gasket materials, test conditions and thicknesses of the compressed gaskets. Gasket holder grove depths for Thermiculite 866 samples were chosen so that the compressive stress on consolidated version would be lower (~4 MPa) than the compressive stress on the as-made version (~8 MPa). This was done because it was postulated that the smoother surface structure of the consolidated version would allow lower stresses. Since Statotherm HT consists of only discrete mica platelets with no additional filler, it was postulated that leak rates would be highly dependable on the compression stress. To test this hypothesis, two samples with different gasket holder plate grove depths, 290 and 230 μm, were tested.

Table 1 Samples used in the sealing tests.

Sample	Gas	Thickness of compressed gasket (μm)	Time (h)
Thermiculite 866, 0.5 mm, as-made	H_2	340	480
	H_2 + H_2O	340	480
Thermiculite 866, 0.5 mm, consolidated	H_2 + H_2O	460	360
	H_2 + H_2O	460	360
Statotherm HT, 0.4 mm	H_2 + H_2O	290	480
	H_2 + H_2O	230	480

3 Results and Discussion

3.1 Compression Properties

3.1.1 Thermiculite 866

Figure 7 shows thickness of consolidated Thermiculite 866 as a function of compression stress. It can be noted that at 800 °C, consolidated Thermiculite 866 compresses from 540 to 422 μm (118 μm/22%) between 1 and 8 MPa compared to compression from 497 to 464 μm (33 μm/6%) at room temperature. Figures 7–9 only show thicknesses of the seals above ~0.3 MPa because the ductile nature of the seals constricts measurement accuracy at lower compression stresses.

Figure 8 shows thickness of as-made Thermiculite 866 as a function of compression stress. It can be noted that at 800 °C, as-made Thermiculite 866 compresses from 444 to 346 μm (98 μm/22%) between 1 and 8 MPa compared to compression from 380 to 310 μm (70 μm/18%) at room temperature.

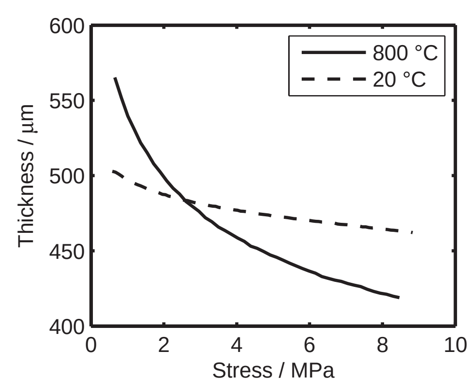

Fig. 7 Thickness of consolidated Thermiculite 866 as a function of compression stress.

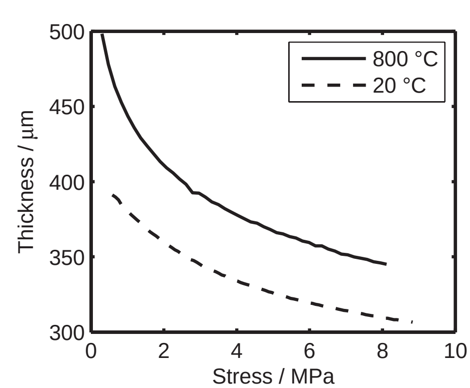

Fig. 8 Thickness of as-made Thermiculite 866 as a function of compression stress.

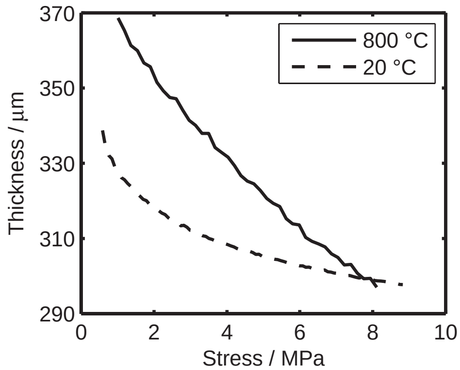

Fig. 9 Thickness of Statotherm HT as a function of compression stress.

Thermiculite 866 samples tested at elevated temperatures appeared to be thicker than those at room temperature. This might be accounted to the expansion of vermiculite mica at application of heat [6].

3.1.2 Statotherm HT

Figure 9 shows the thickness of Statotherm HT as a function of compression stress. It can be seen that at room temperature after the initial compression to 1 MPa the seal compresses from 328 to 299 µm (29 µm/8.8%) from 1 to 8 MPa. This behaviour accounts to the structure of Statotherm HT, consisting of phlogopite mica platelets. When stress is applied on the seal, the platelets are compressed together decreasing the porosity of the structure. At 800 °C, Statotherm HT also experienced swelling and became more ductile, compressing from 369 to 299 µm (70 µm/19%) from 1 to 8 MPa.

3.2 Sealing Properties

The leak rates of the samples were measured as a function of hydrogen pressure. Figure 10 shows leak rates of the samples at different pressure levels. The leak rate of Statotherm HT sample compressed to 290 µm seems to increase linearly with increasing pressure, which is in line with the leak rate model for micas developed by Sang et al. [17]. It is also notable that leak rate of Statotherm HT depends strongly on the compression stress. All other samples showed constant leak rates within the measurement accuracy. However, all the samples also showed significant leak rates, even at overpressures below 10 mbar(g).

Figure 11 shows the results of the leak rate tests at 100 mbar(g) H_2. As-made Thermiculite 866 samples show leak rates of 29 ml(m min)$^{-1}$ with humidified H_2 and 33 ml(m min)$^{-1}$ with dry H_2. Consolidated samples showed leak rates of 43 ml(m min)$^{-1}$ and 49 ml(m min)$^{-1}$. Statotherm HT sample pressed to 290 µm showed a leak rate of 90 ml(m min)$^{-1}$, and the sample pressed to 230 µm showed a leak rate of 22 ml(m min)$^{-1}$. Chou et al. [10] have measured leak rates of phlogopite mica to be around 200 ml(m min)$^{-1}$ (1 bar(g), air) at 800 °C and with compressive stress of 3.5 MPa. Simner and Stevenson [8] measured leak rates of 59 ml(m min)$^{-1}$ (103 mbar(g), He) for phlogopite samples compressed to 4.8 MPa load. These results are in good agreement with the results presented in this paper.

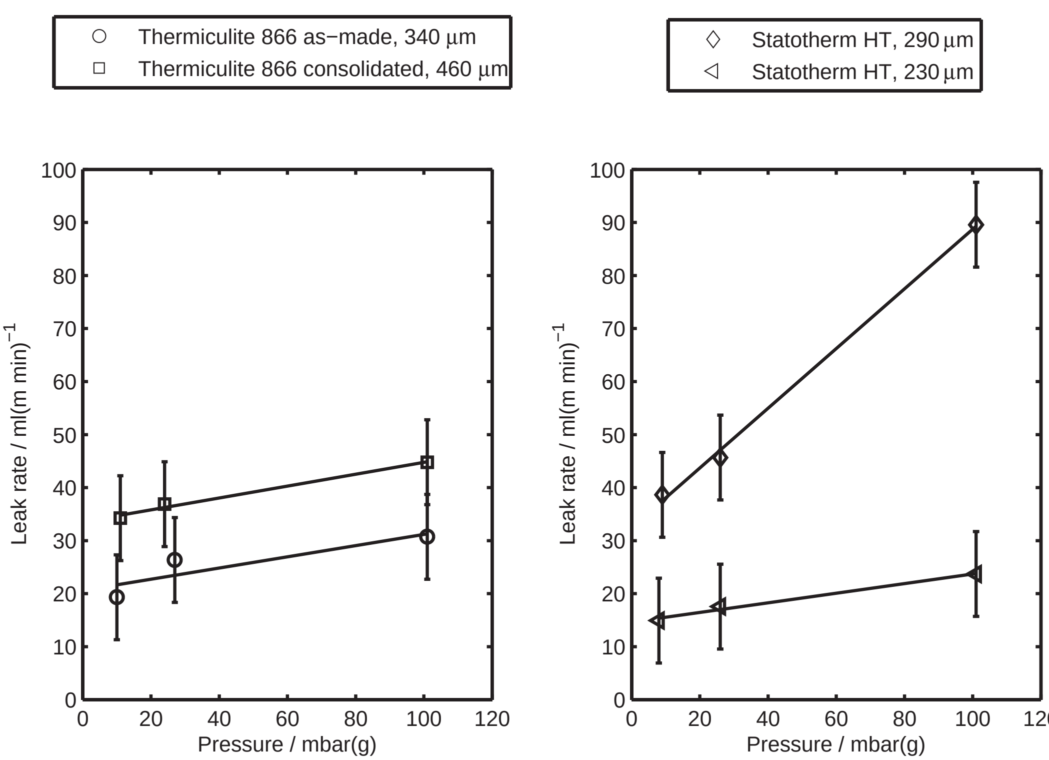

Fig. 10 Leak rates of the samples at different H_2 overpressures.

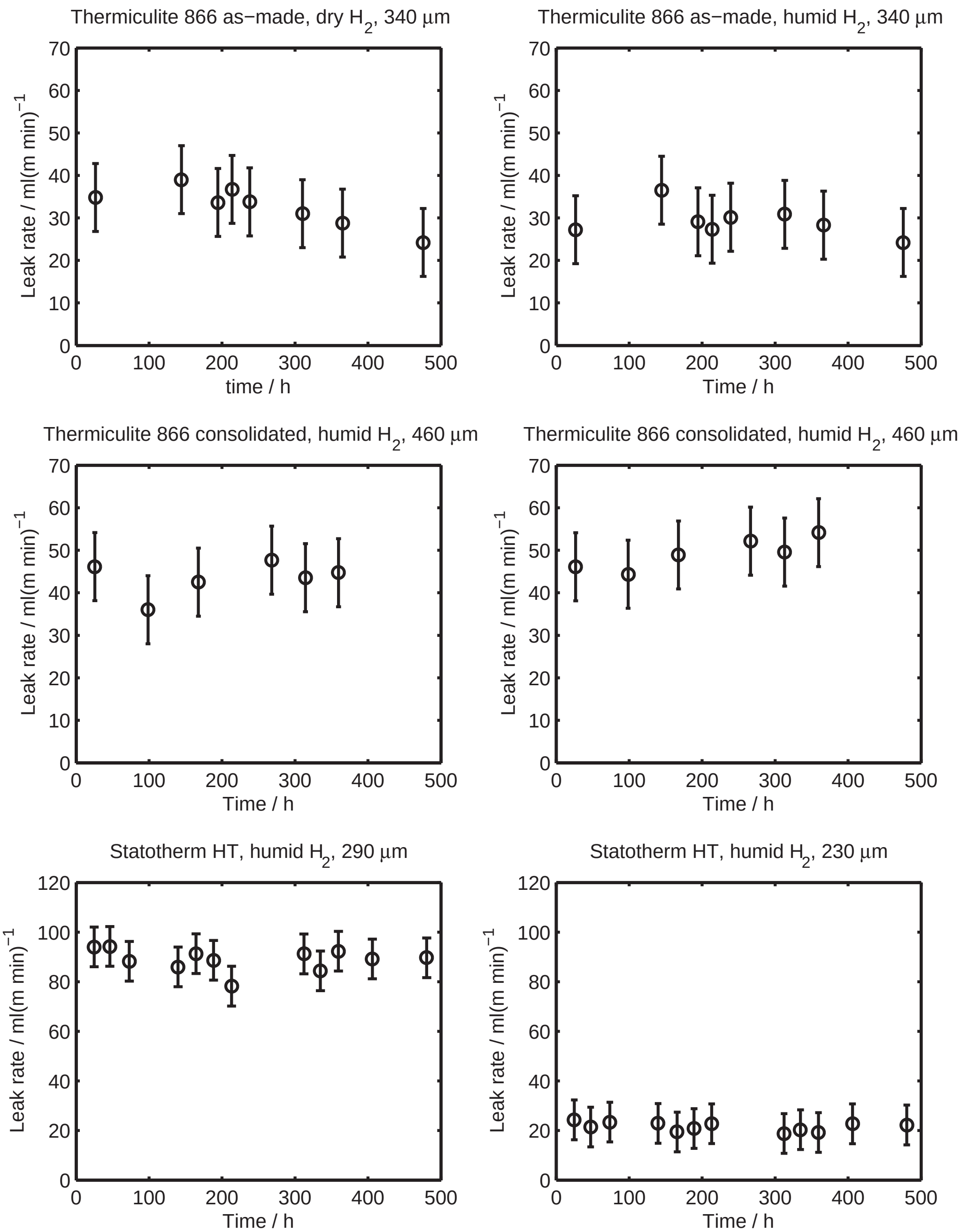

Fig. 11 Leak rates of the tested gaskets as a function of time.

Allowable leak rates of SOFC stacks vary greatly depending on design issues and materials used in the stack. For example let us consider a SOFC stack with 10 × 10 cm^2 cells (active area 9 × 9 cm^2) with sealing length of 1 m per single repeating unit. If the stack was used with 0.7 A cm^{-2} and 50% fuel utilisation, the fuel input would need to be 790 ml min^{-1} H_2. Therefore, Thermiculite 866 samples used in a stack, would lead to a stack leaking 4–6% of the input fuel flow. Statotherm HT samples would yield leak rates of 3 and 11%. If lower leakage levels in SOFC stacks are required, either lower pressure levels or higher compression stresses would need to be used. Another possibility is to minimise leakages through the contact interfaces of the seals. This has been discussed by Chou et al. [10], who measured leak rates of phlogopite mica with and without glass ceramic contact layers. In these measurements, samples without glass ceramic contact layers showed leak rates of the order of 100 times greater than those with glass ceramic contact layer.

4 Conclusion

Conclusion of the work presented here can be summarised into four items:

(i) Both Thermiculite 866 and Statotherm HT showed stable leak rates during the tests at 800 °C with simulated anode gas (62% H_2 + 38% H_2O, 100 mbar(g) overpressure).

(ii) Leak rates of as-made Thermiculite 866 samples were independent of the water vapour content in gas within the measurement accuracy.

(iii) Leak rate of Statotherm HT sample compressed to 290 μm was found to be roughly linear within the measurement range of 10 to 100 mbar(g). All other samples showed constant leak rates within the measurement accuracy.

(iv) Compression properties of both materials are very different at room temperature compared to 800 °C. Consolidated (precompressed) Thermiculite 866 and Statotherm HT showed similar compressibility (6.6 and 8.8%, respectively from 1 to 8 MPa) at room temperature, while as-made Thermiculite 866 compressed 18%. At 800 °C both Thermiculite types compressed 22% from 1 to 8 MPa. Also the Statotherm HT samples became more ductile at 800 °C compressing 19% from 1 to 8 MPa.

Further research needs to be done to assess the long term chemical stability of the sealing materials in SOFC operating conditions.

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