Journal of Power Sources 247 (2014) 243–248

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Glass coated compressible solid oxide fuel cell seals

M. Rautanen*, O. Thomann, O. Himanen, J. Tallgren, J. Kiviaho

VTT Technical Research Centre of Finland, Fuel Cells, P.O. Box 1000, Biologinkuja 5, Espoo, FI-02044 VTT, Finland

HIGHLIGHTS

- A novel sealing material for solid oxide fuel cell stacks: conformable Thermiculite 866 core with thin glass coating.
- A method to coat thin glass layers using an organic carrier.
- Leak test results of glass coated seals.
- Stack test results using glass coated seals.

ARTICLE INFO

Article history:
Received 8 May 2013
Received in revised form
23 July 2013
Accepted 21 August 2013
Available online 31 August 2013

Keywords:
SOFC
Seal
Thermiculite 866
Glass
Leak
Stack

ABSTRACT

With the growing footprint of solid oxide fuel cell stacks, there is a need to extend the operating range of compressible gaskets towards lower stress levels. This article describes a method to manufacture SOFC seals by coating a compressible sealing material (Thermiculite 866) with glass to obtain good sealing performance even at compression stresses as low as 0.1 MPa. Glass layer can be coated using an organic carrier consisting of terpineol, ethanol and ethyl cellulose. The coated seals can be heat treated by simply ramping the temperature up to operating temperature at 60 Kh^{-1} and therefore no extra steps, which are typical to glass seals, are required. Coated seals were manufactured using this route and evaluated both ex-situ and in a real stack. Leak rates of 0.1–0.3 ml $(m\ min)^{-1}$ were measured at 2–25 mbar overpressure using 50/50 H_2/N_2. A 30-cell stack was manufactured and tested using coated seals. At nominal operating conditions of 0.25 A cm^{-2} and 650 °C average cathode temperature, 46% fuel utilization and 20% air utilization the stack had a total hydrogen cross leak of 60 ml min^{-1} corresponding to 0.7% of the inlet hydrogen flow rate.

1. Introduction

Traditionally solid oxide fuel cell (SOFC) stack seals have been either bonding seals (glass/glass-ceramic or brazes) or non-bonding (compressible) seals [1,2]. Bonding seals wet adjacent surfaces forming a very gas tight structure with little interfacial leakages. The usual drawback is that the bonding seals are susceptible to thermo-mechanical stresses especially in thermal cycling. Properties of glasses or glass-ceramics, such as coefficient of thermal expansion (CTE), viscosity and porosity, often change over time. During long term operation these changes can create additional thermo-mechanical stresses leading to seal failure [3,4]. Non-bonding compressible seals are more resistant to thermo-mechanical stresses as they are not rigidly bonded to adjacent components. However, their leak rates are usually higher and dominated by the interfacial leak paths, especially at low compression stresses [5,6]. Compressible seals also require much higher compressive stresses compared to bonding seals, usually at least 2 MPa [7–9]. For example, in the results presented by Thomann et al. [10], with a cell footprint of 100 cm^2, the applied load on the stack was 2000 kg corresponding to roughly 4 MPa on the seals. If this stack was scaled up, the need for the applied load would naturally increase further complicating the mechanical design of the compression system.

Compressive stress is needed in SOFC stacks to ensure adequate sealing performance and to establish a good electrical contact between cells and interconnects. A general trend in SOFC stacks is towards larger cells and therefore towards larger stack footprints creating a need for higher compression on stacks, particularly the ones using compressible seals. This leads to heavier and more complicated compression systems. Compression rods usually need to go through the stack module heat insulation creating additional heat losses. Less compression would enable the use of thinner, less robust stack components. Therefore minimizing compressive stress required on the stack seals while maintaining the easy handling and assembly of the compressible seals would be beneficial.

* Corresponding author. Tel.: +358 405387552; fax: +358 207227048.
E-mail address: markus.rautanen@vtt.fi (M. Rautanen).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.08.085

In recent years, there has been some activity to develop composite seals combining properties from both compressible seals and glass-ceramic seals. The idea is to have a seal which would inherit its mechanical properties from the compressible core but, as opposed to standard compressive seals, would have very low interfacial leak rates because of the compliant surface coating. This would enable the compressible core to deform as a function of thermo-mechanical stresses without causing failure of the seal. Chou et al. have been experimenting with the hybrid sealing concept using different micas as substrates and glass or silver foil to seal the interfacial leak paths [5,6,11–15].

The hybrid seal developed at VTT Technical Research Centre of Finland is a composite structure consisting of compressible Thermiculite 866 [16] core coated with glass using an organic carrier. This method enables easy stack manufacturing as the seal can be coated beforehand and then cut and handled exactly in the same way as traditional compressible gaskets. The organic carrier is burned out in the first heat up and the remaining glass forms a thin conformable interlayer between the seal core and adjacent stack parts. The seal core is able to deform when subjected to stress and therefore can compensate e.g. differences in thermal expansion coefficients of adjacent components. A major advantage of the conformable core is also its ability to compensate for manufacturing tolerances of the adjacent components. Thermiculite 866 core is also less permeable compared to commonly used mica papers since voids between the platelets are filled with a fine grade of steatite. This paper presents a manufacturing method for the coated seals, ex-situ leakage test results and stack test results from a stack utilizing the sealing materials presented in this article.

2. Experimental

2.1. Seal manufacturing

Materials for the hybrid seals were chosen to target stack operation at around 700 °C. The chosen core material was Thermiculite 866 (Flexitallic Ltd) [16]. The glass layer was chosen to be relatively thin (<20 μm) so that the glass itself could be quite low in viscosity. The glass chosen for this study was a commercial glass material having a softening temperature of 650 °C.

Coating of the Thermiculite 866 seals was conducted using a mixture of glass powder and organic carrier. The organic carrier consisted of terpineol (mixture of isomers, Merck), ethanol (ETAX B, Altia) and ethyl cellulose (Fisher Scientific). Ethyl cellulose was mixed with terpineol and ethanol at 35 °C with a magnetic stirrer for 24 h. After that, glass powder was added and the mixture was stirred for 1 h. Table 1 presents typical compositions of the organic carriers and glass to organic ratios used in this study. When coating with brush/spatula/roller, a thicker coating paste proved easy to use and good coverage was achieved easily with a single layer. When using wet spraying, the carrier was diluted with more ethanol to achieve a lower viscosity of around 10–30 cSt which was suitable for the spray gun (U-POL Maximum HVLP mini with 1.0 mm nozzle). Several layers were sprayed from a distance of 10–20 cm.

Table 1
Typical composition of organic carrier and glass to organic ratio with different coating methods.

Coating method	Terpineol/w%	Ethanol/w%	Ethyl cellulose/w%	Glass to organic ratio/w/w
Brush/spatula/roller	81	15	4	2:1
Wet spraying	24	75	1	1:2

After applying the coating, the coated Thermiculite 866 sheets were dried at 75 °C for 2 h and then cut to the required shape. All the seals were heated from room temperature up to 700 °C using 60 Kh^{-1} ramp rate.

2.2. Ex-situ leak tests

Ex-situ leak tests were conducted on ring-shaped seals having 40 mm outer diameter and 5 mm width. The seal was placed on top of 20 mm thick Crofer 22 H (Thyssenkrupp VDM) plate. A 1 mm thick Crofer 22 H plate was placed on top of it and weight plates on top of the 1 mm plate. Gas was fed to the middle of the seal through the thick bottom plate. Fig. 1 presents the experimental setup for ex-situ leak rate measurements. Mass flow controllers fed a chosen gas mixture to the sample line and exhaust line. Sample pressure was controlled with a pressure controller which vents a sufficient flow of gas to the exhaust to keep the upstream pressure at a set level. During heat up, air was fed to the samples to ensure a complete organic burn off.

After heat up, samples were exposed to a 25 mbar overpressure using 50/50 mix of H_2/N_2 at 700 °C. Periodical leak rate measurements were conducted by shutting off the valve V 1 and measuring the pressure decay. A vessel of a known volume was connected to the sample enabling leak rate as a function of pressure to be calculated from the pressure decay curve. Based on the ideal gas assumption, the leak rate is proportional to the slope of the pressure decay curve and therefore the leak rate can be written

$$\dot{Q} = V\frac{T_{\mathrm{ntp}}}{Tp_{\mathrm{ntp}}}\frac{\mathrm{d}p}{\mathrm{d}t},$$

where V is the combined volume of the vessel and the sample, T is the average temperature of the gas in the volume and T_{ntp} and p_{ntp} are normal temperature and pressure. To calculate the leak rate one needs to evaluate dp/dt over the measurement data. If one wants to calculate leak rate at a specific pressure from the data which is a set of points taken at regular intervals, one could approximate dp/dt by

$$\frac{\mathrm{d}p}{\mathrm{d}t} \cong \frac{p_i - p_{i-1}}{t_i - t_{i-1}}.$$

If the sampling rate has been sufficient, the difference $p_i - p_{i-1}$ is bound to be small. As the uncertainty of dp/dt is proportional the uncertainty of the pressure measurement

$$\varepsilon\left(\frac{\mathrm{d}p}{\mathrm{d}t}\right) \propto 2\varepsilon(p),$$

this approach would yield very inaccurate results. To overcome this, a third degree polynomial was fitted to the $p(t)$ − data using least squares method thus minimizing the random uncertainty of the $p(t)$ measurement. Goodness of the fits were analyzed by calculating relative standard deviation of residuals and in case those were over

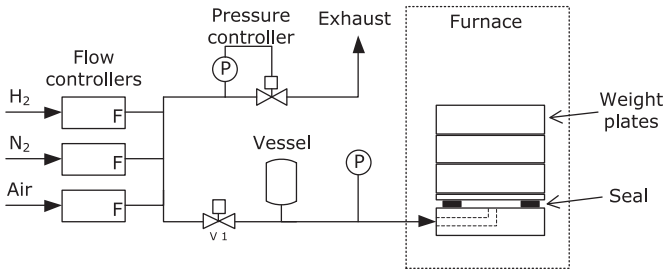

Fig. 1. Measurement setup for the ex-situ leak rate test. Four samples were tested simultaneously, although in here only one is shown for clarity.