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Post-experimental analysis of a solid oxide fuel cell stack using hybrid seals

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HIGHLIGHTS

- Post-experimental analysis of a SOFC stack after 1800 h of operation.
- Microstructural analysis of the glass-coated hybrid seal.
- Materials interactions between glass-coated seals and Crofer 22 APU interconnects.
- Dual exposure of 0.2 mm thin Crofer 22 APU plates in stack operating conditions.

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ABSTRACT

A post-experimental analysis of a SOFC stack is presented. The stack was operated for 1800 h at 700 °C with air and hydrogen and contained hybrid glass-Thermiculite 866 seals. The goal of this work was to investigate the sealing microstructure and possible corrosion during mid-term operation. It was found that hybrid seals could effectively compensate for manufacturing tolerances of cells and other components due to the compliance of the glass layer. Additionally, different interfaces were investigated for corrosion. Corrosion was not observed at two-phase interfaces such as Crofer 22 APU/glass, glass/electrolyte and glass/Thermiculite 866. The three-phase interface between Crofer 22 APU/glass/hydrogen exhibited no corrosion. Some evidence of non-systematic corrosion was found at the Crofer 22 APU/glass/air interface. The possible reasons for the corrosion are discussed. Lastly, dual exposure to humid hydrogen and air of the 0.2 mm Crofer 22 APU interconnect had no detrimental effect on the corrosion compared to air exposure. Overall the hybrid seals used in combination with the thin interconnects were found to be a promising solution due to the low leak rate and limited material interactions.

1. Introduction

Currently, key challenges for successful commercialization of SOFC are to extend their lifetime and to reduce their cost. To achieve that, effective sealing solutions that address all the seals requirements are paramount [1,2]. Seals need to withstand simultaneous exposure to the air side and to the fuel side at temperature between 650 and 850 °C. In addition, they should withstand hundreds to thousands of thermal cycles for stationary and mobile applications respectively. Additionally, seal materials should be chemically compatible with the adjacent components like metallic interconnects and cell materials. Their electrical resistivity should also be high and stable. Lastly, the seals should also be inexpensive, easy to assemble and have to compensate for manufacturing tolerances of the other stack components. Presently, glass ceramic seals are widely used in SOFC stacks. Because they are rigidly bonded to the adjacent surfaces, their coefficient of thermal expansion needs to match closely the one of the neighbouring components. They exhibit very low leak rates [3] but can be prone to degradation with thermal cycling [4]. Compressible seals composed of mica-type paper have been investigated as an alternative [5–7]. The drawback of compressive seals is that in order to achieve acceptable leak rate, a compression stress of the order of several MPa has to be applied on the stack [5]. However, it was found that the leak rate remains significantly higher compared to glass ceramic seals and that the needed level of compression and the necessary compression system becomes technically challenging for large footprint stack. These inherent issues can be addressed by adding compliant layers of glass or metal on both sides of a compressible seal [3,8,9]. The compliant layers block the main leak

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path between the seal and the interconnects which leads to a leakage reduction of up to 90% [9]. Additionally, Rautanen et al. showed that a compression stress as low as 0.1 MPa can be used with hybrid seals [9].

Sealing material interaction studies have been previously published but most of the articles have been focusing on glass ceramic seals interaction. Batfalsky et al. performed post-experimental investigation on stacks that had undergone rapid performance degradation [10]. They found that the interconnects had so severely corroded in the vicinity of the glass ceramic seals that the corrosion product had formed electrical bridges between adjacent interconnects and caused short-circuiting after 200 h at 800 °C. They attributed the accelerated corrosion to the presence of PbO in the glass. Menzler et al. presented results of post-experimental investigation of a stack operated for 6400 h at 800 °C [11]. They showed that the corrosion of the interconnects was enhanced in the vicinity of the glass ceramic seals but that the extent of corrosion did not compromise the performance of the stack. Wiener et al. studied interactions between Thermiculite 866 materials (a composite of vermiculite and steatite [12]) and Crofer 22 APU at 800 °C in ex situ experiments [13]. They found that the Crofer 22 APU underwent accelerated corrosion and this was attributed to the decomposition of steatite at 800 °C and transport of Mg to the oxide layer. Bram et al. studied interaction of Thermiculite 866 with Crofer 22 APU in Ref. [14]. They found that the break-away corrosion of Crofer 22 APU took place at temperature as low as 600 °C in ex situ test. They attributed the accelerated corrosion due to the steam emitted by the Thermiculite 866 during heat-up. They found that such a corrosion reaction could be prevented by a pre-oxidation treatment of the interconnects. Interestingly, corrosion was most often found at the three-phase boundary between seal material, interconnect and gas (air or fuel) [10,11,13,14]. Only few material interactions studies have been published on hybrid seals. Chou et al. studied long-term interaction of hybrid seal materials in ex situ experiments [15]. They found that the phlogopite paper was reacting with the glass they used after 500 h at 800 °C, which compromised the performance of the seal during thermal cycling. Interactions between seal materials and ferritic stainless steel were not discussed in that paper. Chou et al. published the results of a post-experimental analysis of a 3-cell stack using hybrid seals operated at 800 °C [16]. They concluded that material interaction was limited and that their material selection for the seal and interconnect material was suitable for long-term operation. However, the three-phase interfaces between seal/interconnect/gases were not discussed.

Dual atmosphere exposure of interconnects has also drawn some attention in the literature. Skilbred et al. and Yang et al. studied the effect of dual atmosphere exposure at 800 and 850 °C on the corrosion of Fe–Cr–Mn steels and they showed that dual exposure affects the oxide scale composition with a higher concentration of Fe in the oxide scale on the air side. Exposure time was limited to 500 h and 300 h [17–19]. Holcomb et al. studied dual exposure of the austenitic steel 316L and found that heavy corrosion was taking place after 100 h at 700 °C. It was caused by the diffusion of oxygen and hydrogen in the alloy and the formation of steam in the metal alloy near the oxide layer, which formed a thick and porous oxide layer [20].

The amount of data available on dual exposure of interconnect steels is presently limited, which is partly explained by the fact that dual exposure tests are more complex than single atmosphere exposure tests. Additionally, the durations of the experiments are typically in the few hundred hours range. The hydrogen atmosphere is often lean with 5% hydrogen in argon for safety reason and the humidity restricted to 3%, whereas these values are typically higher inside a stack.

The thickness of the interconnects is also affecting their lifetime by decreasing the initial reservoir of Cr. Stainless steel alloys are protected from excessive corrosion by the formation of a Cr oxide layer. During operation, the Cr from the protective scale evaporates and is replaced by Cr diffusing from the bulk of the alloy. The Cr is consumed until it reaches a concentration of about 16% in the alloy, when break-away oxidation start to occur [21]. On the one hand, it is interesting to reduce interconnect thickness to reduce the cost associated with the interconnect steel, but on the other hand Asensio-Jimenez et al. showed that the corrosion rate of interconnect steel increases for thinner plate thickness [22]. Therefore data on the corrosion of thin interconnect are valuable.

This present paper contributes to the field with the results of the post-experimental analysis of a SOFC stack using hybrid seal consisting of a Thermiculite 866 compressible core with compliant glass layers. The seal cross-section has been extracted from a single-cell stack that was operated for 1800 h at 700 °C. The in situ nature of the experiment provides exposure conditions to the seals and interconnects that are closer to stack operation compared to ex situ experiments. For example, the steam content in this work was 20% at anode outlet, which is higher compared to ex situ seals (usually maximum 3%). However, even higher steam content is expected in a stack in an actual system environment (from 60 to 80% steam content).

The goals of the post-experimental analysis were: i) to investigate the microstructure of the hybrid seals, ii) to evaluate material interactions between the seal materials and the interconnects and iii) to investigate the effect of dual exposure on thin 0.2 mm interconnects. The stack presented here is a stack prototype developed at VTT Technical Research Centre of Finland in which hybrid seals were used. After this work, the hybrid seal design has been significantly improved by a 10-fold reduction of the amount of glass and the cost associated to it [9].

2. Experimental

The single cell stack used a co-flow configuration. Crofer 22 APU (ThyssenKrupp, Germany) was used for interconnects and end-plates. The interconnects were 0.2 mm in thickness. The anode-supported cell was manufactured by Elcogen AS (Estonia) and is 10×10 cm^2. Hybrid seals were used for all seals located between Crofer 22 APU plates and are made with consolidated Thermiculite 866 (Flexitallic LTd, the United-Kingdom) [12] between two glass tapes of 220 μm green thickness. The glass used belongs to the system MO (M = Mg, Ca)–Al_2O_3–BaO– SiO_2–B_2O_3 (GM31107, Schott, Germany [23]). The Thermiculite 866 is composed in nearly equal amount of vermiculite and steatite, which compositions are $[(K, Mg, Fe)_3(Si,Al)_4O_{10}(OH)_2]$ and $[(Mg_3Si_4(OH)_2]$ respectively. The seal between the cell electrolyte (yttria-stabilized zirconia (YSZ)) and Crofer 22 APU plate was made of glass without Thermiculite 866. 40 kg of weight was added on the stack, which corresponds to a compressive stress of ca. 0.1 MPa assuming that all the weight was carried by the seals and not by the cell.

Dry hydrogen and dry air were used as fuel and oxidant. Pure hydrogen was selected as fuel, which exposes the seals to a worst case condition as it has been shown that the leak rate through hybrid seal increases with the concentration of hydrogen [9]. The stack was operated at 700 °C for 1800 h. Average current density was 0.2 Acm^{-2} and fuel utilisation and air utilisation were 18%. The hydrogen cross leak value corresponded to a loss of 0.9% of the inlet hydrogen flow in these operating conditions, which is low. The cross leak value was calculated according to the method described in Ref. [9].

After the test, the stack was mounted in epoxy and a cross-section was extracted from the area close to the gas outlet for