Improving the interface adherence in solid oxide cell stacks
Glass seals and oxygen electrode contact layers

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Improving the interface adherence in solid oxide cell stacks

Glass seals and oxygen electrode contact layers

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Correction sheet

- Typo Page vii: Papers numbering fixed
- Page 12: the word interconnect was cropped during the PDF print, and fixed.
Abstract
Solid oxide cells (SOC) are electrochemical devices that allow an efficient conversion of electrical energy into chemical electrical energy, and vice-versa. The possibility of converting and storing excess energy from wind and solar energy production makes SOCs a promising solution for the future sustainable energy and transport sector. Notwithstanding, this technology is not fully commercialized yet due to economic reasons and a wish for higher durability. Production costs are still high and the lifetime is limited to some extent by the degradation of the different stack components.

The interfaces between the different components are the mechanical “weak spots” in SOC stacks. Here, reactions between the joined materials can occur or thermal expansion mismatches can create thermal stresses resulting in interface delamination. Especially two interfaces are contributing to the degradation of SOC stacks: i) the interface between the seal and the interconnect and ii) the interface between the oxygen electrode contact layer and the interconnect. The seal has to be gas tight and keep the gasses (fuel and air) separated, consequently, a delamination at this interface could lead to catastrophic stack failure. The contact layer is the “electrical link” between the electrodes and the interconnect, and a delamination at this interface would cause a contact loss and consequently a drop in performance, local heating and accelerated degradation. The goal of this PhD project was to improve the robustness of these two interfaces.

The first part of the project was focused on the seal-interconnect interface. An improved glass-ceramic seal was developed and characterized, and the chemical compatibility with relevant stack components/materials was investigated. Gadolinium doped ceria (CGO) and yttria stabilized zirconia (YSZ), materials used as the electrolyte in the SOC, and aluminized, pre-oxidized or MnCo₂O (MCO) coated Crofer 22 APU, materials commonly used as interconnect, were selected as joining partners. Characterization of the interfaces between these materials and the seal did not reveal any undesired reactions, even after long-term testing.
The interface adherence in terms fracture energy was measured for samples of the glass seal joined to aluminized, pre-oxidized or MCO coated interconnects. The results showed that the type of coating/pre-treatment of the steel had a strong influence on the measured toughness. The effective fracture energy of the glass seal was measured on the aluminized interconnect, and was as high as 23.7 J/m². In this type of assembly, the fracture occurred within the seal layer, showing that the seal/interconnect interface is no longer the weakest spot. When the glass seal was interfaced with MCO coated or pre-oxidized Crofer 22 APU, the fracture occurred within the oxide layers of the steel. In these cases, the fracture energies (13.6 J/m² and 15.9 J/m², respectively) were significant lower. Moreover, the fracture energy was measured again, but this time on an in-house alumina coating, and it resulted in an significantly higher fracture energy of approximately 100 J/m². In this test, the alumina coating was ripped off from the steel, in most of the fracture area. The tougher value obtained here is likely due to an optimization of the coating roughness.

The second part of the project was focused on the oxygen electrode-interconnect interface. Two spinels, Cu_{1.3}Mn_{1.7}O₄ and MnCo₂O₄, were selected as contact materials, based on their thermal expansion and high electrical conductivity. Cu-Mn and Co-Mn metallic powders were used as the starting materials. During heat treatment, the metallic powders oxidized and formed the conductive spinels. After 250 h at 750°C, the conversion from metallic powder to the oxide phases was completed. The electrical and mechanical properties of the contact layers were investigated by measuring the area specific resistance (ASR) and fracture toughness, respectively. After 3000 h aging at 750°C the ASR for an uncoated 441 interconnect with the Cu-Mn or Co-Mn contact layer was low (<25 mΩcm²) and stable. Moreover, the fracture energy measured for a contact layer-interconnect interface aged 250 h at 750°C was 6.0 J/m² and 3.9 J/m² for the Cu-Mn and the Co-Mn contact layer, respectively. The values obtained in this study are four times higher compared to state-of-the-art.
Preface

This thesis is submitted in candidacy for the Ph.D. degree from the Technical University of Denmark (DTU). It is the result of three years of work carried out from December 15\textsuperscript{th} 2016 to December 14\textsuperscript{th} 2019 at the Department of Energy Conversion and Storage of DTU. The project was supervised by Ragnar Kiebach and co-supervised by Henrik Lund Frandsen, Belma Talic and Karsten Agersted. The study was partly funded from the internal DTU SOC stack project and the LOWCOST-IC project (under the grant agreement No 826323).

The external stay was carried out at Politecnico di Torino, in collaboration with the Department of Applied Science and Technology (Prof. Federico Smeacetto, Prof. Monica Ferraris and Stefano De La Pierre) and the Department of Energy (Dr. Domenico Ferrero), and it was funded by Idella Foundation.
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Thanks to the SSC (former MIX) section, and to Peter Vang Hendriksen. Thanks to my colleagues, who made these three years of work enjoyable, having colleagues always open for discussions and help it was extremely valuable. Thanks to Lene, Karen and Kjeld, for helping me with the ceramic/processing issues and to Ebtisam for helping me with the sample preparation. Thanks to John, June and Jens, for all the technical assistance with RIGs and furnaces.

Thanks to Heidi, for helping me with all the bureaucracy, and for doing that always with the smile. Thanks to Philipp Zielke, working with you was always fun and constructive (sometimes destructive too). Thanks to Anders Christian Wulff for all the scientific discussions and the advices. Thanks to the people I collaborated with at Politecnico di Torino, especially thanks to Federico Smeacetto for being a reference point for the sealing work since four years now.

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Thanks to Risø, even though I'm writing these lines from my new office in Lyngby, I truly left a piece of heart there, and thanks to all the fridaybar-people.

A huge thank goes to Jessica, Sara and Silvia, for being always there for me from Turin, thanks to Paola, Berti and Luca. Thanks to Marco and Marco.

Thanks to my family, in particularly to my parents, for all the love and for always supporting me, all of this is would not have been possible without you.

And finally, I would like to thank my boyfriend, Björn, for the support, love and comprehension and especially for being you.
List of publications

Publications included in the thesis

**Paper 1**: A Ba-free sealing glass with a high coefficient of thermal expansion and excellent interface stability optimized for SOFC/SOEC stack applications


The Ph.D. student carried out all the experimental work and data analysis contained in this paper, except for the Leak test and the Rietveld refinement.

**Paper 2**: Improving the interface adherence at sealings in solid oxide cell stacks


The Ph.D. student carried out all the experimental work and data analysis contained in this paper.

**Paper 3**: High toughness well conducting contact layers for solid oxide cell stacks by reactive oxidative bonding interface stability optimized for SOFC/SOEC stack applications

I. Ritucci, B. Talic, R. Kiebach, H. L. Frandsen (Manuscript ready for submission)

The Ph.D. student carried out all the experimental work and data analysis contained in this paper.

**Paper 4**: Improved Robustness and Low Area Specific Resistance with Novel Contact Layers for the Solid Oxide Cell Air Electrode

From this paper only the results of the contact layers deposited on uncoated 441 are taken into account, as a follow-up of the results presented in Paper 3. The PhD student contributed to the sample preparation, testing, while the data analysis was focused only on the uncoated 441.

**Paper 5: Enhancing the Robustness of Brittle Solid Oxide Cell Stack Components**

H.L. Frandsen, I. Ritucci, P. Khajavi, B. Talic, L. Han, R. Kiebach, P.V. Hendriksen, ECS Trans. 91 (2019) 2201–2211. doi:10.1149/09101.2201ecst. (Published)

From this paper only the sections of the “Oxygen Electrode Contact Layer” and “Glass Ceramic Sealing” would be taken into account, as a follow-up of the results presented in Paper 3 and 2. The PhD student contributed to the sample preparation, testing and the data analysis of the sections mentioned above.

**Publications not included in the thesis**

**Paper 6: A Novel SOFC/SOEC Sealing Glass with a Low SiO 2 Content and a High Thermal Expansion Coefficient**


**Paper 7: Enhancing the long-term stability of Ag based seals for solid oxide fuel/electrolysis applications by simple interconnect aluminization**

Abbreviations

ASR  area specific resistance
CGO  gadolinium doped ceria
CL   contact layer
CTE  coefficient of thermal expansion
DCB  double cantilever beam
DSC  differential scanning calorimetry
DTA  differential thermal analysis
EDS  energy-dispersive X-ray spectroscopy
HSM  heating stage microscopy
LSC  \((\text{La, Sr})\text{CoO}_3\)
LSCF \((\text{La, Sr})(\text{Co, Fe})\text{O}_3\)
LSM  \(\text{La}_{1-x}\text{Sr}_x\text{MnO}_3\)
MCO  \(\text{MnCo}_2\text{O}_4\)
SEM  scanning electron microscope
SOC  solid oxide cell
SOEC solid oxide electrolyzer cell
SOFC solid oxide fuel cell
XRD  X-ray diffraction
YSZ  yttria stabilized zirconia
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1 Introduction

What an idea.
A crazy, mad, wonderful idea.
Alice in wonderland

It is not a hype.

Climate change and global warming are at the center of attention and worldwide, science, media and politics are focused on this problem. In 2015 the United Nations General Assembly agreed on a set of 17 Sustainable Development Goals with indicators and targets for 2030 with the aim of solving major problems such as poverty, inequality in health, education and economic growth, in a sustainable manner [1].

The need for the sustainable energy

Among the 17 Sustainable Development Goals, #7 is focused on Energy.

Sustainable development goal 7: Ensure access to affordable, reliable, sustainable and modern energy for all.

The demand for electricity is increasing worldwide, especially in developing countries. Renewable energies such as wind and solar power can play a major role in solving this problem, and these technologies are getting cheaper as more and more capacity is installed. The share of energy produced by renewable sources is expected to amount to 50% of the world energy production in 2050 [2]. Denmark is a first mover in this
1 Introduction

area, as 42% of the installed electricity was produced by wind power already in 2015, and by 2050 the country is planning to become completely independent from fossil fuels [3].

The challenge with wind and solar power is their intermittency, the energy production can vary during the day or during the seasons. Therefore, the energy production does not always match the energy demand. For example, solar panels can deliver the energy required during the day when the sun is shining, but the solar energy production decreases towards the evening, while the energy demand tends to increase. On the other hand, wind energy production peaks during the night. In principle coupling the two technologies could cover the daily energy demand, but still times with excess energy production or times with insufficient energy production (unavailability of both solar and wind energy production) can be expected in the future [4].

Therefore, it is clear that producing green energy is not enough; to overcome these obstacles it is also necessary to store the energy coming from renewable sources, in both short term and long term.

Energy can be stored in several ways: mechanical, thermal, electrochemical and chemical. Some of the storage technologies, such as alkaline electrolysis cells (AECs) and polymer electrolyte membrane (PEM) electrolysers, are already mature and on the market, while others, such as solid oxide electrolysis cells (SOECs), need further development [5]. Overall, a combination of these is necessary to reach the sustainable development goal. Especially storage technologies with a large storage capacity and long storage time are important to cover seasonal differences in energy production and demand. Energy storage in the form of hydrogen and synthetic natural gas (SNG) can fulfill these requirements.

In this context, solid oxide cells (SOC) are one of the most promising technologies. When operated as fuel cell (solid oxide fuel cell (SOFC)), hydrogen or hydrocarbons such as SNG can be converted to electricity with a high efficiency (> 60 %) [6]. When operated in the reversed mode as electrolysers (solid oxide cell electrolysis (SOEC)),


excess electricity can be used to produce hydrogen and/or syngas with an efficiency up to 90 % depending by the product [7]. The electrolysis products can easily be converted to fuel (Power-to-something (P2X)), which can be stored. In the following chapter, the basic principle, the possibilities and the challenges of this technology are described.
Solid oxide fuel cells (SOFC) are electrochemical devices which can convert fuels (e.g. hydrogen, gaseous hydrocarbons) into electricity [8]–[10]. These devices can operate in reverse/electrolysis mode (SOEC), and produce hydrogen, carbon monoxide, syngas and even more complex molecules as methane directly [11]. The gasses produced with a SOEC can be converted into liquid fuels or stored and eventually used to produce electricity in a SOFC or in a combustion engine [12]–[15]. SOCs can use the electricity produced in excess from renewable sources and produce various molecules, which can be stored or used as a fuel. As mentioned in Chapter 1, this technology does not directly classify as “renewable energy source” but it fits in the plan for lowering CO₂ emissions and providing the needed grid balancing in the production and storage of clean energy.

The basic core of a SOC consists of the three layers of solid-state materials that make up the cell: an ion-conductive and electronically insulating electrolyte in between two electrodes having both ionic and electronic conductivity.
The overall reaction taking place in the cell is:

\[ H_2O \leftrightarrow H_2 + \frac{1}{2} O_2 \]  \hspace{1cm} (2.1)

At the oxygen electrode:

\[ 2O^{2-} \rightarrow O_2 + 4e^- \]  \hspace{1cm} (2.2)

At the fuel electrode:

\[ H_2O + 2e^- \rightarrow H_2 + O^{2-} \]  \hspace{1cm} (2.3)

Since only small outputs can be achieved with a single cell, a stack of cells is used to increase the power output (SOFC) or the gas output (SOEC). Each repeating unit is then connected with the other ones using some extra components that will be described in the following section.
2 Solid Oxide Cells

**SOC components**

### 2.1 Stack

Stacking of SOC can be achieved with different configurations, tubular and planar being the most popular designs. The tubular design does not require high-temperature seals, leading to less chance of failure. The planar design requires the use of seals, but on the other hand they have a higher volumetric power density and can operate at a lower temperatures [17], [18]. Besides the cell there are some “linking” components in a stack. An overview of what it is typically present in a planar SOC stack is shown in *Figure 2.2*.

Each repeating unit is formed by a cell and an interconnect, which creates the electrical connection between cells and separates the gasses. To improve the adherence and the electrical conduction, contact layers are placed between the cell electrodes and the interconnect. Moreover, in between seals are used to link all the components mechanically.

*Figure 2.2 Sketch of a SOC stack, a single unit and a cell.*
2 Solid Oxide Cells

2.2 Electrodes

Fuel electrode

The fuel electrode must be an ionic and electronic conductor, have good catalytic properties and have a porous structure to allow for the gasses to diffuse in and out. The porosity also increases the surface area or triple point boundaries for the reactions to take place, and therefore increases the electrode's catalytic activity. The fuel electrode is typically a thick layer and supports the cell (for fuel electrode-supported cells), whereas the other layers are usually thinner. Ni-YSZ (Nickel-Yttria-stabilized zirconia) is the cermet that is commonly used as fuel electrode because of the good catalytic behavior of Ni, the high ionic conductivity of the YSZ and a coefficient of thermal expansion (CTE) in the range of the other materials for SOCs. The use of YSZ also helps lowering the CTE of the cermet and hinders the Ni-coarsening to some extent.

There are however some disadvantages with the use of Ni-YSZ as the fuel electrode:

- Long-term degradation: coarsening of the Ni particles and migration of Ni particles when operated in SOEC mode [19]
- Sulfur poisoning [20], [21]
- Carbon deposition when carbon-containing fuel is used in SOFC, or CO₂ is used in electrolysis mode and the stack is not operated correctly [22], [23]

Oxygen electrode

The oxygen electrode must be an ionic and electronic conductor and stable in an oxidizing atmosphere at the operative temperatures (600-900°C). Reactive sites in the electrode are needed for the reduction of the oxygen. Low reactivity and compatibility with the other components in the stack are required [24].

Sr-doped lanthanum manganites (La₁₋ₓSrₓMnO₃, LSM) mixed with YSZ were for a long time the most used materials for the oxygen electrode. The LSM acts as the electronic conductor and the YSZ as the ionic conductor [25].

Disadvantages with the use of LSM are:

- Ionic/electronic reactions only occur in the triple phase boundaries
Sr-doped lanthanum cobaltite ferrite ((La,Sr)(Co, Fe)O$_3$, LSCF) is now the most commonly used oxygen electrode material, having the advantage of being a mixed conductor (both ionic and electronic conductivity), thus providing a larger reactive area.

The main disadvantage with the use of LSCF is its tendency to react with YSZ [28]. However, the side reactions with YSZ can be prevented with the use of barrier layers, such as gadolinium doped ceria (CGO), between the oxygen electrode and the electrolyte [28], [29].

### 2.3 Electrolyte

The electrolyte material must be an ionic conductor and an electric insulator, since its main function is to conduct the ions that have been produced at the respective electrodes [30], [31]. Unlike the electrodes, the electrolyte structure should be dense, to prevent the gases to permeate and react directly. Stability in both oxidizing and reducing atmosphere are required.

8 mole doped Yttria-stabilized zirconia (YSZ) is the most common material used for electrolytes, where the role of the yttrium is to stabilize the cubic structure at room temperature. This material has a good ionic conductivity and is stable in the SOC environment. On the other hand, it can react with the sealing and electrodes [28], [32]. An alternative electrolyte for lower operating temperatures (<600°C) is gadolinium doped ceria (CGO) [33].
2.4 Interconnect

Interconnect materials are used to provide an electrical connection between the electrodes of two adjacent cells [34]. These materials should therefore be electrical conductive, and stable in both reducing and oxidizing atmosphere.

Few ceramic materials are suitable for this application, because of issues with sintering and processing. Instead, metals are widely used for this application, as they are cheaper, have an easier processing and can tolerate higher mechanical stresses [22], [35]–[37]. Chromia-forming alloys are a popular choice for interconnects, some examples are Crofer 22 APU, Crofer 22 H and AISI 441 [38]–[42].

Drawbacks of these materials are:
- Cr evaporation [41], [43]
- High temperature corrosion [40], [41]
- Creep [44]

Stainless steels tend to oxidize during operation at high temperatures forming an oxide scale of Cr$_2$O$_3$, which may limit the interactions between the interconnect and the glass-ceramic seals [45].

Some interconnect steels, e.g. Crofer 22 APU, Crofer 22 H, 441 form an oxide scale on the surface that consists of two layers: an inner layer of Cr$_2$O$_3$ and an outer layer of columnar (Mn, Cr)$_3$O$_4$ spinel [38], [46]. The outer layer helps to reduce the Cr vaporization by 60-70% compared to stainless steels that only form a chromia scale [47].

**Coatings for interconnects**

Protective coatings have been developed to mitigate the problem of Cr-evaporation, to limit high temperature corrosion and to improve the interface adherence on the interconnect [48]–[51].

For the oxygen side, a MnCo$_2$O$_4$ (MCO) coating is commonly used. This coating can reduce the Cr evaporation rate by 97% compared to uncoated steel [41]. Moreover, this coating has a good electrical conductivity, to keep an electrical path across the
stack. An alternative coating consists of reactive elements combined with Co, e.g. Ce-Co and La-Co. They both decrease corrosion and Cr-evaporation rate from the interconnect [40], [52].

Alumina coatings provide a barrier for Cr-evaporation, and high corrosion resistance, although their electrical conductivity is lower than for the above mentioned coatings [50], [53]. This makes them unattractive for the contact area, but suitable for the sealing area. Some alloys, such as Kanthal APM, form Al₂O₃ on the surface instead of Cr₂O₃. Otherwise, an alumina coating can be formed on the steel surface by reactive air aluminization. With this method it is possible to tailor the roughness and the final surface area of the metallic component [50], [51], [54]. Enhancement of interfacial adherence was also seen when applying an alumina coating between the interconnect and a glass-ceramic seal [49]. A commercial available example of this coating is AlumiLok from Nexceris [55].

For the fuel side, the interconnect encounters different problems, i.e. Ni diffusion from the Ni-YSZ electrode which leads to ferrite to austenite transformation in the steel [56], [57]. On the fuel side, the interconnect is usually either coated with Ni to improve the contact or left uncoated.
2.5 Seals

Seals in the SOC stack provide the mechanical bonding between the components. They are usually placed:

- between the cell (electrolyte or barrier layer) and the interconnect
- between the spacer and the interconnect

The seal must withstand an oxidizing and reducing atmosphere, mechanical stresses and must be gas tight. Since it serves as the mechanical bonding between the components, its coefficient of thermal expansion should match the other components [35], [58]. Different types of seals can be adopted, such as compressive, rigid and compliant seals (Figure 2.3)[59].

![Figure 2.3 Type of seals for SOC stacks. From the top: compressive seal, rigid seal and compliant seal.](image)

Compressive seals

An external load needs to be applied on the compressive seal in order to obtain gas tightness. Therefore, the compressive seal material needs to be soft and adapt to the interfaces that is supposed to seal. There is no chemical bonding at the interface, which means that this type of sealing can handle larger CTE mismatches and thermal stresses than other types of seals. Typically, compressive seals are metal- or mica-based [60]. It is challenging to keep a constant load in order to have low leak rates, and stack design should be planned accordingly [60].
Rigid seals
The seal, as suggested from the name, is rigid and is bonded at the interface with the joining components. A heat treatment must be performed in order to create the bonding, and the maximum temperature of this should be within the operation temperature of SOC stacks and the stability limit of the other components. Rigid seals are typically based on glasses and glass-ceramics [61].

The drawbacks of glasses and glass-ceramic seals are:

- Reactions with the Cr in the vapor phase and at the interface with the interconnect: delamination [45], [62], [63]
- Contamination of the electrolyte (see section 2.3)
- Thermal mismatch due to the CTE

Compliant seals
This category refers typically to brazes, although some no-devitrifying glasses can also be included. Compliant glasses, unlike the rigid seals, stay in a viscous state when heat treated, and do not devitrify.

Brazes can be deformed both at room and at the operative temperature with less thermomechanical drawbacks compared to the rigid seals [59]. Some examples of brazes are Ag, Ag-Cu, Ag-Al-Ti [51], [64], [65].

The drawbacks of metallic brazes are:

- Reactions at the interface with the interconnect and the electrolyte
- Formation of pores when exposed to dual atmosphere [66]
- Poor wettability of the surfaces [51]
2.6 Contact materials

Contact layers in the SOC stack are used to form a stable electrical conduction path between the cell and the interconnect. The conduction path can be provided by a rigidly bonded material or by a more flexible material kept in place by compression [67]. In both cases, a CTE matching with the other stack components, sufficient electrical conductivity, gas transport and good bonding to the adjacent layers are important requirements. In addition, the contact layer material should be stable in an oxidizing or reducing atmosphere, depending whether it is used on the air or fuel side of the stack, respectively. As illustrated in Figure 2.4, several different designs/configurations are possible: porous layers, mats, felts, foams or applying a solid contact material only onto the contact points [68], [69].

Fuel side

Ni paste, Ni foam or a Ni mesh are commonly used as the contact layer between the fuel electrode and the interconnect. The use of Ni ensures a strong metal to metal interface both with the Ni-YSZ fuel electrode and the steel interconnect. Since Ni is a relatively soft metal, a Ni-based contact layer can adsorb deformational mismatches due to differences in CTE and/or temperature variations in time and space [70]. The drawbacks are, as mentioned in Section 2.4 that Ni diffusion into the steel can lead to austenitization.

Oxygen side

The contact material used on the oxygen side should withstand an oxidizing atmosphere, which excludes the use of Ni. For single cells testing, noble metals such as Ag, Au, Pt or Pd are often used since they have a high conductivity, are ductile, easy to sinter and commercially available [67]. The main drawback of noble metals is the high costs. The exception to this is Ag, for which the main drawback is evaporation.
Perovskite and spinel oxides are widely used as the SOC cathode material and as coatings for the steel interconnect, respectively. The similar requirements for these components promoted their application also as contact layers [42], [67], [71]-[73]. Some examples of these materials are LSM, LSC ((La, Sr)CoO$_3$), LSF, LSCF (perovskites) and Cu$_{1.3}$Mn$_{1.7}$ and MnCo$_2$O$_4$ (spinels). All of the mentioned perovskite oxides have a high electrical conductivity, in the range of 320-1220 S cm$^{-1}$ at 800°C ([67]), while the conductivity of the spinel oxides is slightly lower: 225 S/cm at 750°C for Cu$_{1.3}$Mn$_{1.7}$ and 89 S/cm at 800°C for MnCo$_2$O$_4$ [74], [75].

The main drawback with using perovskite and spinel oxides as the contact material is related to their poor sinterability at low temperatures and consequently low densification and weak adherence to the electrode/interconnect [73].

In the case of the spinel oxides, improved densification may be achieved by doping, sintering in two steps (reducing+oxidizing) or using metallic precursors [41], [67], [76]. This will be discussed in greater detail in Chapter 5.
3 Improving the interface adherence in solid oxide cell stacks

One of the keys to developing viable solid oxide fuel cell (SOFC) systems is to first develop reliable and inexpensive stack sealing technology

-K. Scott Weil [59]

A lot of research and developments efforts related to SOC stacks has been carried out, but still they are not fully commercialized on large scale yet. The two key-reasons are mainly related to production costs and durability [59], [77], [78].

Production costs need to be decreased, and cheaper solutions in terms of materials and assembly would push SOC technology towards commercialization. Also, scaling-up the production would enable the use of cheaper manufacturing solutions, and significantly reduce costs.
3 Improving the interface adherence in solid oxide cell stacks

Today prototyping costs are still high. Due to the cost and time of producing and testing these stacks in order to demonstrate their durability, modelling and accelerated tests are more and more implemented as an alternative. Modeling and accelerated tests though need a large quantity of data regarding the degradation phenomena involved. Therefore, research should focus on single components, as well as on the interactions between these components to increase the accuracy of stack lifetime predictions.

What are the current challenges related to durability?

In order to have a reliable and durable product, the materials selection must be done meticulously. Interface reactions and thermal mismatches are the main factors affecting the durability of SOC stacks, since they often lead to leaks and/or loss of contact. The interfaces contact layer-interconnect and seal-interconnect were found to be the critical ones affecting the durability of SOC stacks [79]–[81]. Other factors influencing the durability of the individual components were listed in Chapter 2.

By searching for the term “SOFC” on webofscience.com¹ in connecting with the specific components (electrolyte, anode, cathode etc...), it is possible to obtain a qualitative distribution of the publications on the relevant components/topics (Figure 3.1).

The findings of these search are discussed below.

Electrolyte, anode and cathode, the individual layers forming the cell, are among the most studied, and account for ca. 40% of the results. Degradation and interconnect

¹ The values were obtained considering SOFC as the total (100%) and calculating the percentage of each.
covered 10%, while seal and the contact layer only account for 4% of the amount of available publications.

Considering the impact that the failure of the interfaces mentioned above can have, it is valuable to direct the research towards the improvement of those interfaces.

Glass-ceramic seals can delaminate (Figure 3.2a) or react at the interface with the interconnect, i.e. forming pores or chromates (Figure 3.2b), or the oxide scale on top of the interconnect can experience delamination while still bonded to the glass (Figure 3.2c).

Wherever cracks or delamination are occurring, the seal is not functioning anymore. The effects shown in Figure 3.2a-c are due to chemical reactions at the interface (glass-interconnect), and/or are caused by thermal mismatches between the different layers (cell-seal-oxide scale-interconnect).

Losses of contact can occur between the interconnect and the cell (Figure 3.3[82]), disabling the electrical path and decreasing the performance and robustness. Thermal expansion mismatches are one of the reason for contact losses, next to the poor sintering behavior of the contact layers resulting in a weak bonding at the interface.

Figure 3.2 SEM micrographs of the interface seal-interconnect. (a) Cracked seal. (b) Chromates formation at the interface. (c) Delamination of the oxide scale. [79] Copyright 2007, Fuel Cells.

Figure 3.3 SEM micrograph from [82], representing a loss of contact at the interface interconnect-cell. Copyright 2017, Journal of the European Ceramic Society.
Aim of the work
The aim of this work is to improve the two interfaces which are currently considered to be the weakest in SOC stacks, namely the interface between the seal and the interconnect, and between the contact layer and the interconnect. The focus of the work was on developing new materials and methodologies to ensure robust bonding between these components.

How to improve the sealing?
A glass-ceramic, V11, with a coefficient of thermal expansion (CTE) matching the fuel electrode and the interconnect material CTEs was developed. The seal was tested against relevant interfaces of the cell and coated or preoxidized interconnects, with the result that adherence in terms of fracture energy could be improved by more than 70% compared to state-of-the-art. Details are presented in Paper 1, 2 and Paper 5.

How to improve the contact layer?
The challenge in improving the contact component is not only limited to create a stronger mechanical bonding, but also to ensure a good electrical contact. As consequence, the minimization of the CTE mismatch and an increased fracture toughness are not the only factors to be considered. Additionally, factors that could increase the resistivity at the interface must be taken into account and avoided as well. Here materials that have a good electrical conductivity, matching CTE and act as a barrier against Cr-evaporation were chosen as starting point. Cu-Mn and Co-Mn contact layers, which form Cu$_{1.2}$Mn$_{1.8}$O$_4$ and MnCo$_2$O$_4$ spinels during stack assembly and operation, were chosen, and promising results were obtained. The interface adherence was tested, and results showed that measured fracture energies were 5 times higher compared to materials used today. Details are presented in Paper 3 and 4.
3 Improving the interface adherence in solid oxide cell stacks

3.1 SOC Materials used in this work

The materials used in this work are presented in Table 3.1.

Table 3.1 Materials for solid oxide cells used in this work.

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Suppliers/references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen electrode</td>
<td>LSC-CGO: ((\text{La}<em>{0.6}\text{Sr}</em>{0.4})<em>{0.99}\text{CoO}<em>x) Ce(</em>{0.9}\text{Gd}</em>{0.1}\text{O}_2)</td>
<td>In-house</td>
</tr>
<tr>
<td></td>
<td>LSM (\text{La}<em>{0.85}\text{Sr}</em>{0.15}\text{MnO}_3)</td>
<td>ULSA Rhodia, S.A., France</td>
</tr>
<tr>
<td></td>
<td>(see [83])</td>
<td></td>
</tr>
<tr>
<td>Barrier Layer</td>
<td>CGO Ce(<em>{0.9}\text{Gd}</em>{0.1}\text{O}_2)</td>
<td>ULSA Rhodia, S.A., France</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>8YSZ</td>
<td>Tosoh</td>
</tr>
<tr>
<td>Fuel electrode</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Active layer</td>
<td>40:60 vol% Ni:8YSZ</td>
<td>Sigma Aldrich, Tosoh</td>
</tr>
<tr>
<td>Support layer</td>
<td>40:60 vol% Ni:3YSZ</td>
<td>Sigma Aldrich, Tosoh</td>
</tr>
<tr>
<td>Interconnect</td>
<td>Crofer 22 APU</td>
<td>ThyssenKrupp [38]</td>
</tr>
<tr>
<td></td>
<td>Crofer 22 H 441</td>
<td>ThyssenKrupp [39]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sandvik group</td>
</tr>
<tr>
<td>Coating/surface modifications for interconnects</td>
<td>Alumina:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- AlumiLok</td>
<td>Nexceris [55]</td>
</tr>
<tr>
<td></td>
<td>- (\text{Al}_2\text{O}_3) in-house</td>
<td>Alfa Aesar (see section 2.4)</td>
</tr>
<tr>
<td></td>
<td>MCO (Mn(_2)CoO(_4))</td>
<td>Fuelcellmaterials, USA</td>
</tr>
<tr>
<td>Seal</td>
<td>Glass-ceramic (V11)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiO(_2)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td></td>
<td>MgCO(_3)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td></td>
<td>CaCO(_3)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td></td>
<td>NaCO(_3)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td></td>
<td>Al(_2)O(_3)</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td></td>
<td>ZrO(_2)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td></td>
<td>H(_3)BO(_3)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Contact materials</td>
<td>Cu-Mn (Cu(<em>{1.3})Mn(</em>{1.7})O(_4))</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>American Elements</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co-Mn (MnCo(_2)O(_4))</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>American Elements</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td></td>
</tr>
</tbody>
</table>
4 Glass and glass-ceramic seals

“Why did such an important discovery occur so late in the history of glass, and why was an accident necessary to bring it about?”

-Donald Stookey, 1977
Glasses and glass-ceramics are widely used in SOCs applications as sealants. The main role of the seals in SOC stacks is to ensure gas tightness, avoiding mix of the gasses, and furthermore to provide electrical insulation to avoid short circuits.

The word *glass* is familiar to most people, whereas *glass-ceramics* are generally still unknown. This class of materials was discovered by coincidence in 1957 by S. D. Stookey, who defined glass-ceramics as [85]:

“Glass-ceramics are made by first melting and forming special glasses containing nucleating agents and then causing controlled crystallization of the glass.”

An update of this definition was proposed in 2018 [86]:

“Glass-ceramics are inorganic, non-metallic materials prepared by controlled crystallization of glasses via different processing methods. They contain at least one type of functional crystalline phase and a residual glass. The volume fraction crystallized may vary from ppm to almost 100%.”

A large variety of properties desired for sealants used in SOC stacks can be covered by glasses and glass-ceramics thanks to their tunable composition. The process that transforms glasses to glass-ceramics is defined as *devitrification*, and consists in the partial crystallization of the glass during heat treatment.
Science behind glass-making

A glassy material can have different components: network former, network modifier, intermediate and additives [87]. The different positions, functions and compositions are briefly shown in Figure 4.1. By changing the composition and the heat treatment of the glass, it is possible to design a material with the desired properties and behavior.

Figure 4.1 Simplified sketch of a glass network structure (information about the components are adopted from [87]).
4 Glass and glass-ceramic seals

4.1 Properties and requirements of SOC seals

The properties that a seal should have were briefly presented in section 2.5, in this section these properties will be discussed more in more detail with the background of using glass or glass-ceramic materials for SOC applications.

4.1.1 Thermal properties

Coefficient of thermal expansion

Most glasses have a positive coefficient of thermal expansion (CTE), the volume increases with the temperature [88]. The CTE is usually measured in the linear part of the thermal expansion-temperature curve, before the glass transition occurs (Figure 4.2). The CTE of the SOC seal should match the CTEs of the components that it is joining, which are typically the interconnect to a steel frame (metal to metal) and the interconnect to the cell (metal to ceramic).

As a rule of thumb, the CTEs should not differ more than $1 \times 10^{-6} \, \text{K}^{-1}$ for the components of a SOC stack [35]. The CTE for some of the materials used as interconnects, electrodes and electrolytes are reported in Table 4.1.

The need of taking different CTEs into account is related to the different cell designs (electrode supported or electrolyte supported). Here, the thickest layer of the cell should be considered (e.g. the CTE of the electrode for electrode supported cells).

In principle, three situations can be envisioned for the seal:

- a) $CTE_{\text{seal}} = CTE_{\text{component}}$ no stresses in the seal
- b) $CTE_{\text{seal}} > CTE_{\text{component}}$ tensile stresses in the seal
- c) $CTE_{\text{seal}} < CTE_{\text{component}}$ compressive stresses in the seal
Situation (a) is the preferred, while among situations (b) and (c), compressive stresses are preferred over tensile stresses. This is valid when taking into account the bulk of the material, where tensile stresses could cause cracks through the seal. Considering the interface seal/component: both tensile and compressive stresses could cause delamination [35], [89].

The CTEs of glasses and glass-ceramics are commonly measured by dilatometry. Typically, the thermal expansion of a glass-ceramics is higher compared to its corresponding native glass. This can be explained by the fact that the formed crystalline phases generally have a higher CTE than the glass. Cells commonly used in the latest stack generations are fuel electrode supported, which means that the fuel electrode as the thickest layer should be considered when possible CTE mismatches are evaluated. CTE values for Ni-YSZ change depending on the Ni/YSZ phase fraction and the oxidation state of Ni (oxidized or reduced electrodes). Therefore, an average value was calculated, \(12.6 \times 10^{-6} \text{ K}^{-1}\), taking into account the CTEs reported in a literature study that collects CTEs measured between room temperature and 1000°C [90].

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>CTE (x 10^{-6} K^{-1})</th>
<th>Range</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel electrode</td>
<td>Ni-3YSZ</td>
<td>12.6</td>
<td>RT-1000°C</td>
<td>[90]</td>
</tr>
<tr>
<td>Interconnect</td>
<td>Crofer22H</td>
<td>11.8</td>
<td>RT-700°C</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>Crofer22APU</td>
<td>11.6</td>
<td>RT-700°C</td>
<td>[38]</td>
</tr>
<tr>
<td>Seal</td>
<td>V11</td>
<td>12.8</td>
<td>200-450°C</td>
<td>[84]</td>
</tr>
</tbody>
</table>

**Glass transition (T_g)**

The glass transition temperature (T_g) is defined as the onset of the glass transformation region [91]. It is typically reported for amorphous materials, and corresponds to a reversible transition from a brittle (T<T_g) to a viscous state (T>T_g). When the temperature of a SOC stack is above the T_g of the glass seal, the amorphous phase of the seal is viscous. Such a behavior could lead to self-healing of cracks, formed due to thermal stresses, via viscous flow [87].
4 Glass and glass-ceramic seals

**Softening temperature (T_s)**
At the softening/deformation point of a glass, also known as Littleton softening point, the viscosity of the glass is around \( \log \eta = 10^6 \) (dPa s). The \( T_s \) should always be above the working temperature of the SOC stack, to avoid an excessive viscous flow. One of the methods used to measure the \( T_s \) is heating stage microscopy (HSM) [92]–[95].

**Thermal stability**
The thermal stability is the resistance towards devitrification of glasses and glass-ceramics. Seals are required to be thermally stable up to the operation temperature of SOCs (650-1000°C). A high thermal stability indicates that the glass does not crystallize, or that the glass-ceramic does not undergo further crystallization during operation.

Thermal analyses, such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC) can be used to quantify the following parameters related to the thermal stability, see e.g. [96]:

- \( T_x \) onset of the devitrification (crystallization)
- \( T_P \) peak of the devitrification (crystallization)
- \( T_M \) glass melting point
- \( T_g \) onset of glass transition

With this information, it is possible to calculate the glass stability, which is defined by the Hruby parameter, \( K_H \):

\[
K_H = \frac{T_x - T_g}{T_m - T_x}
\]  

The higher \( K_H \) and the higher the glass stability, the lower is the tendency of the glass to crystallize.

Moreover, heating stage microscopy (HSM) can be used to retrieve information ([92], [94]) from the (changes in) sample shape:

- \( T_{FS} \) - Temperature of First Shrinkage: sintering of the small particles begins
- \( T_{MS} \) - Temperature of Maximum Shrinkage: the viscous flow allowed the larger pores to close.
4 Glass and glass-ceramic seals

- $T_D$ – Softening/deformation: first signs of softening can be observed (rounding of the sample corner).
- $T_b$ - Ball Temperature: the height/width ratio of the sample is between 0.9 and 1.
- $T_{HB}$ - Half Ball Temperature: the height of the sample is the half of its base.
- $T_F$ - Flow Temperature: the sample is melted, the height of the sample is 1/3 of the original height or the $T_{HS}$.

These temperatures are related to six fixed viscosity values of the glass. By plotting the viscosity as function of the temperature, it is possible to predict the viscosity values at the specific temperatures [92].

The combined results obtained from DTA and HSM measurements can be used for predicting the thermal stability, and for designing the sintering profile of a glass-ceramic seal. An example is shown in Figure 4.3. Several research groups ([84], [97]–[100]) have used this approach for designing the sintering processes.

The sinterability ($S_c$) is defined as [100]:

$$S_c = T_x - T_{MS} \quad (4.2)$$

This value corresponds to the temperature region marked in light green shown in Figure 4.3, i.e. the region between the maximum shrinkage and the onset of the crystallization. $S_c$ is a measure of the competition between sintering and crystallization while heating. At the $T_{MS}$ the sintering (and densification) is considered completed, and it is preferred that the crystallization ($T_x$) begins after the completion of the sintering. High values of $S_c$ indicates that the shrinkage and crystallization are independent from each other. Low values of $S_c$ implies that the crystallization occurs at a temperature (too) close to the $T_{MS}$, which hinders the viscous flow and results in a porous structure in the final seal.
4 Glass and glass-ceramic seals

Figure 4.3 Sinterability: Differential thermal analysis and heating stage microscopy of a glass (adapted from [84]).

4.1.2 Chemical properties

Seals should have no or limited reactions at the interface with other components. The chemical stability of the seal is related to its compositions and to the material that it is in contact with. To have a holistic understanding of the chemical stability, the stability of i) the bulk glass and the stability of ii) the interface should be taken into consideration.

Changes of the chemical composition in the bulk glass:

Several oxides in the amorphous phase of the glass seal, such as B₂O₃ or Na₂O, can be affected by vaporization at the SOC operating temperatures [35]. The weight loss from the glass network will affect the sealing properties. The formation of gaseous Si(OH)₄ is another issue that can occur in humid environments. The gaseous Si(OH)₄ species will be present in the vapor phase and eventually interact with the cell [13].

Stability of the seal-interconnect interface

As described in section 3.4, ferritic stainless steels used as the SOC interconnect material tend to form a chromia layer on the surface. One of the drawbacks of the chromia scale is Cr-evaporation. The vapor phase Cr-species tend to react with some of the components typically present in a glass-ceramic seal, such as Na, Ca, Ba, K, Mg [35], [62], [101]. Alkaline/alkaline earth chromates start forming on the exposed
surface of the seal and they will, after several thermal cycles, start affecting the interface between the seal and the interconnect, eventually causing delamination due to the different CTE between the seal, chromates and interconnect [63]. Also, the formation of conductive chromates on the surface of the seal has been reported to decrease the electrical resistance of the frame-seal-interconnect joint [62], [81]. Among the methods/strategies to solve this problem, the use of coatings to avoid Cr evaporation is popular for SOC stack applications.

**Stability of the seal-cell interface**

The seal is joined to the SOC towards the interface with the electrolyte (typically made of YSZ or CGO). For glasses Ba-containing have been reported that interactions with the YSZ can occur [102], e.g. leading to the formation of BaZrO$_3$ crystals which would lower the CTE of the glass [103]. As mentioned, the SiO$_2$ present in the seal could also influence the cell performance, silicate aggregations were found close to the interface electrolyte-oxygen electrode at the triple phase boundaries [13].

**4.1.3 Mechanical properties**

Temperature gradients in a joint comprising materials with different CTEs, such as glasses and metals/ceramics, can induce residual stresses at the interface between the materials and in the bulk. Therefore, it is necessary to investigate how strong an interface is and why.

There is no standard method for characterizing joined SOC stack interfaces [78]. However, considering that the seal typically is a thin layer compared to the thickness of the interconnect, the interfaces may be characterized using the methods developed for evaluating the adherence of coatings/thin layers. These methods will be discussed in the following.

There are two ways to characterize the adhesion of thin layers (including coatings): by measuring the strength or the interfacial fracture toughness. *Strength* or adhesion strength is measured considering the maximum load that a sample can hold before it fractures completely. The strength of brittle materials is influenced by flaws and
surface variation [104], [105]. Such defects can be reduced by polishing the edges of the sample, but on the other hand, the resulting surface will no longer be representative of the surface geometry in an SOC stack. To account for the variation of the flaw size and distribution, statistical methods are used to describe the resulting variations of strength measurements (i.e. Weibull theory) [106].

The *interfacial critical energy release rate*, also called the *fracture energy*, is a measure of the energy needed to initiate and propagate a crack, which can be related to the fracture toughness [107]. Unlike the strength, the fracture energy is an intrinsic property of the material, and therefore has the advantage of being independent of the sample geometry. Several methods can be adopted to measure the fracture energy of an interface. The most popular ones are the double cantilever beam test (DCB) and four-point bend test [108].

For DCB samples the thin layer (e.g. seal) is sandwiched between two bars of a substrate (e.g. interconnect) and is pre-cracked [109]. The method can be used to measure the mode I fracture toughness, and allows for an evaluation of the fracture energy. The crack growth rate can be controlled and several measurements can be obtained with the same specimen. The fracture energy is determined from the load at which the crack propagates, i.e. where the cantilevers bend without any increase of load.

The use of a four point bend test to evaluate the fracture energy of bilayered materials was proposed by Charalambides et al. [110], [111]. Sample preparation for this test is rather simple and the testing itself is fast and does not require any advanced equipment. The fracture energy is calculated from a steady state which appears as a plateau in the load-displacement curves. The sample geometry proposed by Charalambides was a bilayered structure where the thin layer is deposited on a thick substrate. For strong interfaces though, the formation of vertical cracks would disable the use of this method. Hofinger et al. modified the structure of the sample into a sandwich: the thin layer is placed between two thick substrates and the sample is pre-cracked [112]. Thereby delamination is promoted and vertical cracking is avoided. In
the four-point bend test the sample is exposed to something very close to a mode I type of fracture with a bit of mode II type of fracture. Also, the four-point bending allows for experiments to be carried out at high temperatures [113], which is challenging if not impossible with the DCB.

Considering a layered metal-seal-metal sample where the seal thickness is small compared to the metallic substrate allows for some simplifications to be made. The stiffness of the seal is negligible, therefore, the residual stresses within the seal do not influence the measurement (they are not released upon crack growth).

Some fracture energy values measured with the four-point bend test are presented in Figure 4.4. Malzbender et al. reported that the fracture energy of “Glass A”, joined on Crofer 22 APU, improved with time after due to crystallization of the glass and after 120 days reached 23 J/m$^2$ [114]. Measurements of this glass interfaced with YSZ showed a further increase in fracture energy for longer ageing (up to 1000 days, see Figure 4.4). The same glass interfaces with Crofer 22 APU had 50% lower fracture energy, due to oxide scale growth on this steel, and poorer bonding compared with YSZ. Lin et al. performed the four-point bend test at room temperature, on glass sandwiched between Crofer 22 APU, which resulted in a relatively low fracture energy (3 J/m$^2$) due to the delamination at the interface where Ba-chromate formed [115]. The same measurement, performed at different temperatures between 650-800°C, resulted in a significant increase of the fracture energy, probably due to the materials becoming tougher and softer at high temperature. The highest fracture energy was measured at 700°C (56 J/m$^2$) and was attributed to crack bridging.
4.1.4 Electrical properties

The electrical resistivity of a seal used for SOC stacks should be higher than $10^5 \ \Omega \text{cm}$ at the stack operating temperature, because an electrically conductive seal could cause a short circuit and lead to a failure of the stack [116]. The formation of conductive species, e.g. chromates, could lead to a decrease of the resistivity of the seal with time, as shown in [62]. Testing the seal under electrical load in dual atmosphere can give information about the electrical resistivity and chemical stability. Rost et al. [81] studied the degradation of seal glasses under electrical load and showed that under high potential (30V), the glass structure degrades: ZnO was found to react with Mn and Cr at the interface. The formation of large pores (> 100 μm) within the glass layer was also observed under high potentials, which had a negative effect on the gas tightness [81].

Figure 4.4 Fracture energy ($G_c$) of various glass-ceramic sealants reported in literature by Malzbender et al. [114] et al. and Lin et al. [115].
4.2 Workflow: design, production and characterization of glass seals used in this thesis

The tools to design and characterize a glass-based seal for SOC stacks were described in the previous sections. The workflow from producing the glass to the final application in SOC stacks is presented in Figure 4.7. This approach was used during the PhD study to design and develop the V11 glass-ceramic seal. The details and the results of the different steps described here are part of three publications: Paper 1, Paper 2 and Paper 5. Here, the different results and development steps will be linked together.

Step 1 Glass fabrication and characterization

This part of the process is focused on the glass preparation and characterization and it is presented in detail in Paper 1. Raw oxides are melted into glass, and thermal analyses are carried out in order to obtain characteristic temperatures, shrinkage information and the CTE. This information is combined together to design the heat treatment that will produce a glass-ceramic from the glass.

Step 2 Glass-ceramic characterization

This step focuses on the transformation from the glass to a glass-ceramic and its characterization (Paper 1). Taking into account the thermal properties of the glass, a sintering profile was designed. XRD\(^2\) analysis is performed to investigate the formation of crystalline phases, and complementary SEM/EDS\(^3\) analyses to evaluate the microstructure and the chemical composition of the phases are carried out.

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\(^2\) XRD X-ray diffraction
\(^3\) SEM scanning electron microscopy
EDS energy-dispersive X-ray spectroscopy
4 Glass and glass-ceramic seals

Step 3 Cell-seal-interconnect joint characterization

This step focuses on the joining of the seal towards relevant interfaces of the cell and the interconnect. Detailed results are presented in Paper 1 and 2.

Once the glass and the glass-ceramic are characterized, the glass powder is transferred into a slurry or paste, depending on the ceramic process that will be used to apply the final glass layer.

In this project, the glass paste was screen printed on small coupons (2x2 cm²) for preliminary characterization, and on full-size stack (15x15 cm²) components. Preliminary results were obtained by depositing a slurry of glass powder and ethanol by hand. As an alternative method, tape-casting was used for those applications where screen printing was not possible (e.g. complex 3D geometries of the substrate or in case thick layer of glass were required).

Deposited glass layers were quality checked by SEM to ensure the surface homogeneity of the layer, and by profilometry to check that the thickness of the print is consistent.

As a next step, the seal is tested in conjunction with the different components used in stacks. The interfaces of the joints are evaluated via SEM/EDS to investigate if any chemical reactions occurred at the interfaces.

How well the seal adheres to the components is evaluated via mechanical testing in terms of fracture energy tested on layered samples, the results of the testing are presented in Paper 2 and 5. In Appendix 1, preliminary strength measurements are presented.
Step 4 Stack assembly

Once the seal is characterized and optimized, a scale up to stack level can be done. The glass is then screen printed on the components, leak tests of the single assembly cell-to-frame are done to check the tightness before the stack can be assembled (Figure 4.6).

![Figure 4.6 Picture of the stack assembly from the DTU SOEC stack project: screen printed glass on steel frame.](image)

4 Glass and glass-ceramic seals
Figure 4.7 Workflow: design, production and characterization of glass seals used in this thesis
5 Contact layers

Different contact layer solutions were presented in section 2.6. Here, the focus will be on the perovskite and spinel oxides, which currently represent the most technologically relevant choice for the SOC oxygen side.

As mentioned in section 2.6, the critical challenge of using perovskite oxides as the oxygen side contact material is the high temperatures needed in order to sinter these materials. The SOC stack assembly/sealing temperature is typically limited to be below 900°C, in order not to damage the glass(-ceramic) sealant and steel interconnect and at this temperature the perovskite oxides only partially sinter, which results in non-adequate mechanical properties and a poor contact [117].

Spinel oxides on the other hand can be sintered at lower temperatures [118], thereby forming a denser and stronger bonding [75], [117], [119], [120]. As most of the previous work on spinel oxides has focused on their application as a coating for the interconnect, the following literature review will be referred to the spinel oxides both as the contact layer as well as the coating.

Spinels

The spinel unit cell is made up of 8 AB₂O₄ units, where the cations A and B typically are divalent and trivalent, respectively (Figure 5.1). The space group of most of the spinel compounds is Fd-3m. The 32 anions are arranged in a face centered cubic packing. Only 8 of the 64 tetrahedral cations sites are occupied and only 16 of the 32 octahedral sites are occupied.
Which spinel compositions are most suitable for SOC stack applications?

The thermal expansion and electrical conductivity of various spinel compositions have been investigated in order to identify the material having the best combination of desired properties [73], [74], [122]. Spinel oxides containing Co-Mn, Cu-Mn, Ni-Co and Ni-Fe are some of the materials that have been investigated for the use as coatings/contact layers [41], [42], [67], [68], [83], [123]–[125]. CoMn$_2$O$_4$ and Cu$_{1.3}$Mn$_{1.7}$O$_4$ spinels stood out among others, having an electrical conductivity of 89 and 225 S cm$^{-1}$, respectively [74], [75].

The CTE of these two compositions are $14.4 \times 10^{-6}$ K$^{-1}$ for CoMn$_2$O$_4$ and $12.2 \times 10^{-6}$ K$^{-1}$ for Cu$_{1.3}$Mn$_{1.7}$O$_4$ [74], [75]. Thus, Cu$_{1.3}$Mn$_{1.7}$O$_4$ is the more attractive choice in terms of CTE and electrical conductivity.

It should be noted that for the MnCo$_2$O$_4$ spinel a large range of CTE and the electrical conductivity values have been reported in literature [74], [75], [126]. The discrepancy between the values has been attributed to the presence of secondary phases, deriving from the sintering process [127]. The value reported here as a reference for the CoMn$_2$O$_4$ spinel, $14.4 \times 10^{-6}$ K$^{-1}$, was measured on a confirmed phase pure cubic spinel [75].
5.1 Properties and requirements of SOC contacting materials

5.1.1 Electrical properties

The performance measured on SOC stack level is typically lower than that obtained for single cells, and it has been shown that one of the reasons for this discrepancy is losses at the interface between the oxygen electrode and the interconnect [128]-[131]. Ensuring a low electrical resistance at this interface is required.

The electrical conductivity of contact materials, interconnects and coatings is often characterized in terms of the area specific resistance (ASR), which is a parameter that takes into account both the conductivity and the thickness of the different serially connected layers and is defined as:

\[
ASR = \tau_s I_s + 2\tau_c I_c + \tau_{CL} I_{CL} \approx \tau_{CL} I_{CL} + 2\tau_c I_c
\]

(5.1)

Where \(\tau\) and \(I\) are the resistivity and the thickness of the material, the subscript “s” indicates the steel, “c” the coating or the oxide scale on the steel, (multiplied by 2, as these layers are present on both side of the interconnect), and finally, “CL” indicates the contact layer. The resistivity of the steel (\(\tau_s\)) is typically negligible, thus, the ASR will be mainly dominated by the other layers.

ASR values for a SRU\(^4\) are typically in the range of ca. 300-500 mΩ cm\(^2\) at 750°C [11], [80], [132]), while an acceptable value for the interconnect is often quoted to be 100 mΩ cm\(^2\) [133]. The contact material should ideally not increase the ASR of the interconnect, but rather keep it stable.

The ASR can be measured experimentally with a four-point set up as shown in Figure 5.2. In this method, a Pt wire (probe) is welded to the interconnect (which may be coated), and the contact layer is placed on top. An extra layer is used on top of the contact layer to act as the current collector; this can be either a noble metal or a well-conducting oxide such as LSM or LSC. The latter is more representative measure of real SOC stack conditions, since the materials and microstructure are similar to the

\(^4\) SRU is the single repeating unit of a stack, i.e. one cell and one interconnect.
ones commonly used as the SOC oxygen electrode. Furthermore, some studies have shown that Pt used as the current collector may interact negatively with the steel interconnect during long-term measurements [40]. Therefore, noble metals are preferable for short-term testing, while LSC/LSM are more suited to monitor the ASR continuously over thousands of hours. It is important to keep in mind that the reported ASR values may differ according to the current collector used [40].

When comparing the results from ASR measurements it is important to take into account the different parameters:

- Applied current
- Temperature
- Material used for contacting

From an experimental point of view, ASR is calculated as:

$$ASR = \frac{\Delta V}{I} \cdot A_{contact} \quad (5.2)$$

$\Delta V$ is the voltage drop, $I$ is the applied current and $A_{contact}$ is the contact area between the current collector and the contact layer.

The current is supplied through gold plates placed in the bottom and in the top of the assembly (Figure 5.2).

Figure 5.2 Sketch of the four-point set up for ASR measurements, with LSM as current collector.
5.1.2 Chemical stability

Chromia-forming steels have the tendency of forming a layer of Cr$_2$O$_3$, which grows between the coating and the interconnect. The growth of the Cr$_2$O$_3$ layer has been reported to be the main contributor to an increasing ASR across the steel interconnect [134].

Contact layers, as well as coatings, can interact at the interface with the interconnect or oxide scale, forming an interdiffusion layer ([41], [73], [120], [123]). Especially Cr from the steel/oxide scale has been found to react with the materials commonly used as contact layers. For the (Co,Mn)$_3$O$_4$ spinel compositions, the formation of a Cr-rich spinel (Co,Mn,Cr)$_3$O$_4$ lowers the electrical conductivity and the CTE [127].

Chemical interactions at the interface could both be beneficial for forming a strong bond between the components or have the opposite effect, weakening the interface [49], [117].

5.1.3 Sinterability of the contact materials

Different approaches have been suggested for sintering spinel oxides into a dense layer at temperatures below 1000°C. [83], [120], [135]

When using spinel oxides as the interconnect coating, a common way to obtain a dense layer has been through a 2-step sintering process [41], [124], [136]. In this process, the spinel powders, e.g. MnCoO$_4$, are first heat treated in reducing atmosphere to reduce the spinel oxide into MnO and Co, and then in oxidizing atmosphere to reform the spinel oxide. This process results in improved densification via reactive sintering [135].

As an alternative to the 2-steps process, metallic powders or a mixture of metallic powders and metal oxide powders have been investigated [73], [125]. An example of metallic powders mixed with metal oxides was presented by Stevenson et al, where a mixture of Mn, Co and Cu, lead to the formation of a spinel single phase of Mn$_{1.5}$Co$_{1.2}$Cu$_{0.3}$O$_4$ when heat treated at 950°C [137]. The metal precursors can also be applied by electroplating, for examples, after heat treating plated layers of Cu-Mn and
4 Contact layers

Co-Mn, in air at 750°C spinel formation was observed [138]. Also in this case, reaction type sintering enhances a good densification of the material and moreover, a good bonding with the interconnect.

5.1.4 Mechanical properties

The fracture energy values for contact layers found in literature are mainly for perovskite oxides. As seen from the results from Tucker et al. and Han et al. ([71], [117], Figure 5.3), perovskite oxides typically lead to a weak bonding at the interface with the interconnect, due to insufficient sintering.

Tucker et al. showed that the fracture energy for a perovskite oxide contact layer can be improved from 1-1.7 J/m² up to 12.3 J/m² by embedding the perovskite (LSM) in a glass matrix (glass by Schott) to make a composite contact layer [71]. However, while this solution improved the mechanical adherence, it had a negative influence on the electrical conductivity of the contact layer. By instead mixing LSM with an inorganic binder (644A), a compromise was found between the mechanical and electrical properties, reaching a fracture energy of 5.4 J/m². Han et al. reported that the fracture energy when using metallic Cu-Mn foam as the contact layer was as high as 8.6 J/m² [117]. They also showed that the type of coating on the interconnect (Co-metal vs. MnCo₂O₄ spinel oxide) can influence the adhesion to the contact layer.

Further details on the method for measuring and calculating the fracture energy can be found in section 4.1.3 and [49].
4 Contact layers

Figure 5.3 Fracture energy (G) of various oxygen-contact layers reported in literature by Tucker et al. and Han et al. [71], [117]

5.2 Workflow: design, production and characterization of contact layers used in this thesis

The tools to design and characterize a contact layer for SOC stacks were given in the previous sections, and the workflow to combine these tools and obtain a functional contact layer are shown in Figure 5.4.

This approach was also used during the PhD project to design two compositions of contact materials: Cu-Mn and Co-Mn. The results are presented in Paper 3 and 4.

Step 1 Contact layer composition

The motivation behind the choice of Cu-Mn and Co-Mn were discussed earlier in this chapter. Step 1 is focused on the composition of the contact layers (Paper 3). Assuming that the contact layer would sinter in-situ during the sealing of the SOC stack, the sealing profile adopted for the V11 and presented in Paper 1 [84] was used. Therefore, the maximum sintering temperature was set at 800°C and the operation temperature at 750°C.

The phase diagrams were used to select the ratios of Mn-Co and Cu-Mn for forming MnCo$_2$O$_4$ and Cu$_{1.2}$Mn$_{1.8}$O$_4$ at the operating temperature [74]. In this project the contact layers were screen printed onto the metal plates representing the interconnect. The aim was to have an upscalble technique that in future applications
4 Contact layers

was suitable for printing the contact layer only onto the contact points between the interconnect and the oxygen electrode. Coupon samples were prepared as explained elsewhere (Paper 3), sintered at 800°C and then characterized in terms of XRD, SEM and EDS in order to investigate that the desired crystalline phases formed during the sintering.

Step 2 Short ageing

Once the initial characterization was completed, the samples were shortly aged in air at 750°C for 250 h to evaluate possible evolution of the structure/composition (Paper 3).

Step 3 Testing

Step 3 is focused on testing the electrical and mechanical properties of the contact layers in relevant conditions (air, 750°C). An evaluation of the resistivity and the interface adherence was performed.

The results of Step 1, 2, 3 (ASR until 2000 h) are part of Paper 3, while the second part of the ASR testing is part of Paper 4.
Figure 5.4 Workflow: design, production and characterization of contact layers used in this thesis
Paper 1

A Ba-Free Sealing Glass with a High Coefficient of Thermal Expansion and Excellent Interface Stability Optimized for SOFC/SOEC Stack Applications.
A Ba-free sealing glass with a high coefficient of thermal expansion and excellent interface stability optimized for SOFC/SOEC stack applications

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Abstract
A new glass-ceramic composition containing Si, Mg, Ca, Na, Al, Zr, and B is presented here as sealant for planar SOFCs/SOECs, with the aim of joining the metallic interconnect (Crofer22APU) to the solid oxide cell (YSZ electrolyte or CGO barrier layer). Characteristic temperature, thermo-mechanical properties, and compositional variations are reviewed and discussed by thermal analyses and in situ XRD, in order to design and optimize the sealing profile and reduce the residual porosity. The glass after heat treatment partially devitrifies into augite and nepheline with residual glass phase of around 64.3%; after crystallization the glass-ceramic sealant has a coefficient of thermal expansion of $12.8 \times 10^{-6} \text{ K}^{-1}$ and it is compliant with the other materials typically used for stack components. This work shows that the developed glass-ceramic can successfully join the ceramic cell with the Crofer22APU (preoxidized and alumina coating), proven by tests on small and large-scale samples. No signs of unwanted reactions at the glass-metal and the glass-cell interface are observed and sufficient gas tightness is achieved.

KEYWORDS
glass-ceramics, solid oxide fuel cell, synthesis, thermal analysis

1 INTRODUCTION

The rise in electricity consumption and the consequent need for sustainable energy is constantly driving research toward the development of new renewable energy conversion technologies. Solid oxide fuel/electrolysis cells (SOFC/SOEC) are considered as one of the promising choices for clean energy production because of their high efficiency and versatility for either mobile or stationary power production.1,2 SOFCs are electrochemical devices, which convert the chemical energy of a fuel (hydrogen or hydrocarbons) and an oxidant (air or oxygen) into electricity and heat without combustion and particle emissions. Nevertheless, the commercialization of SOFCs is still hindered by critical issues with durability and cost of installation. Durability issues stem from both moderate degradation rates of active electrodes and specific issues of material selection and combination of materials that can tolerate rapid fluctuations in operating temperatures.3 Cell and interconnect components in SOFC-stacks are commonly sealed using glass or glass-ceramic sealants, cf. Figure 1, for which the adhesion and more importantly thermal expansion have to be tailored to an almost perfect match with the joining partners to avoid a build-up of thermally-induced stress, when a stack is cooled down from sealing or operating temperature to room temperature (RT).

Glasses and glass-ceramics are relatively easily applied to the stack components by one of several techniques:
screen-printing, tape casting, or extrusion. The sealing process is normally carried out by a heat treatment at temperatures higher than the glass transition, which allows the glass-based sealant to flow and wet the parts to be sealed. This step, in controlled temperature-time conditions, determines the glass devitrification and the final properties of the sealant. Several glass compositions for sealing ceramic cells and metallic interconnects are reported in literature.4-10 In general, alkaline earth-containing glasses have a desirable high coefficient of thermal expansion (CTE), but, especially for Sr and Ba containing glasses, also a tendency to react with chromium (contained in the steel/interconnect) leading to the formation of chromates at the interface has been reported.11-15 These chromate layers have a very high CTE (\(>20 \times 10^{-6}°\text{K}^{-1}\))\(^{16}\) causing significant weakening of the seal and delamination. For this reason, the use of barium-free glasses is becoming popular to avoid the formation of chromates such as \(\text{BaCrO}_4\).\(^{17}\) The glass presented in this work contains both Na and Ca, which can as well lead to the formation of chromates at the interface. For that reason, a protective coating toward the steel will be included.

A suitable glass composition for this application is chosen according to (i) the CTE of the auxiliary stack components (the ceramic cell and the metallic interconnect) and (ii) the glass transition temperature of the glass. During the sealing process, glasses will normally react with metallic counterparts, for example, Crofer22APU, a high-temperature ferritic stainless steel by ThyssenKrupp VDM, Germany, through redox-type reactions. A typical counteraction is either to coat the metal or to select less aggressive glass compositions. The latter will add significant limitations to the choice of glass. Hence, 2 different surface modifications have been used in the present work; the formation of an oxide scale \((\text{Cr}_2\text{O}_3/(\text{Mn},\text{Cr})_3\text{O}_4)\) on the steel by preoxidation and a commercial alumina coating (AlumiLok\textsuperscript{TM}; Nexceris).

The glass presented here is designed to work in intermediate-temperature SOFCs stacks (700-900°C). The new glass composition, hereafter-labeled “V11 glass,” is an evolution of the V9 glass, which has been developed at Politecnico di Torino by Sabato et al\(^7\) and further optimized of the heat treatment described in this work were carried out at the Technical University of Denmark. The change in composition from V9 is motivated by the low value of its CTE, equal to 9.52 \(\times 10^{-6}\ °\text{K}^{-1}\) (300-500°C), resulting in a different quantity of Na and Ca proposed for the V11. This new system is designed to reduce the mismatch of the CTEs between the components and limit the consequent formation of thermal stresses during operation. The thermal characterization and the sintering behavior of the glass are presented; the compatibility with the different substrates was also studied and considered.

### 2 | EXPERIMENTAL

#### 2.1 | Materials and synthesis

The composition of the V11 glass in wt% is: 46.37% SiO\(_2\), 13% MgO, 14.34% CaO, 9.26% Na\(_2\)O, 8.34% Al\(_2\)O\(_3\), 2.92% ZrO\(_2\), and 5.76% B\(_2\)O\(_3\). The sealant, based on the V11, was produced as a glass by melting the precursors of the oxides (oxides and carbonates, Table 1) in a platinum crucible at 1300°C for 2 hours; the glass was then quenched in water. For the thermal characterization and use during application of the sealant smaller particles with a size of around 7 μm were produced using a planetary ball mill (Retsch PM 1000). The characteristic particle sizes were \(d_{10} = 1\ \mu\text{m}\), \(d_{50} = 7\ \mu\text{m}\), \(d_{90} = 25-30\ \mu\text{m}\), measured with a Beckman Coulter LS I3 320 Laser Diffraction Particle Size Analyzer. Larger drops of glass (“bulk”) were used for dilatometric measures.

For sealing tests, 2 relevant substrates were used, that is, sheet metal plates and solid oxide cells, to simulate the

<table>
<thead>
<tr>
<th>TABLE 1 V11 chemical composition</th>
<th>Raw materials for 100 g of glass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>46.37 SiO(_2)</td>
</tr>
<tr>
<td>MgO</td>
<td>13 MgCO(_3)</td>
</tr>
<tr>
<td>CaO</td>
<td>14.34 CaCO(_3)</td>
</tr>
<tr>
<td>Na(_2)O(_3)</td>
<td>9.26 Na(_2)CO(_3)</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>8.34 Al(_2)O(_3)</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>2.92 ZrO(_2)</td>
</tr>
<tr>
<td>B(_2)O(_3)</td>
<td>5.76 H(_3)BO(_3)</td>
</tr>
</tbody>
</table>

#### FIGURE 1 Exploded view of a repeating unit in a SOFC/SOEC stack
components presented in Figure 1. The metal plates were made of a ferritic stainless steel, Crofer22APU (ThyssenKrupp)\textsuperscript{18} with 2 different surface modifications: AlumiLok\textsuperscript{19,20} and preoxidation obtained at 900°C for 50 hours in air. The cells used were in-house produced multi-layer tape-casted anode-supported half-cells, which consisted of a NiO-YSZ (yttria-stabilized zirconia) support layer, a thin NiO-YSZ active anode layer, a dense layer of YSZ and in some cases a ceria-gadolinia (CGO) barrier layer.\textsuperscript{21}

2.2 Characterization of the glass and glass-ceramic

Differential thermal analysis (DTA) (Netzsch 404 PC) measurements were performed on the glass powder at 5°C min\textsuperscript{-1} from RT to 1300°C. The characteristic temperatures extrapolated from the measurements were evaluated at the onset and/or peak temperatures using the commercial Proteus software provided (Netzsch). The glass transition temperature \((T_g)\) was determined using the inflection of the relevant part of the DTA curve. Hot stage microscopy analyses (HSM) (TOMMI, Fraunhofer) were carried out on compacted glass powder pellets from RT to 1300°C at 5°C min\textsuperscript{-1} in static air. The pellets are typically cylindrical shaped, and the data recording is based on the projected image of the sample during the experiment. Dilatometry measurements (DIL) (DIL 402 PC/4; Netzsch) were performed on a drop of glass, as casted, and on a glass-ceramic pellet at a heating rate of 5°C min\textsuperscript{-1} to evaluate the CTE and the dilatometric softening point \((T_s)\). The measurements were carried out from RT to 1050°C with a “softening point detection” (set with the Netzsch Software) to avoid the melting of the sample in the instrument’s chamber. To obtain the devitrification of the pellet, a pressed bar of glass powder (4 mm length) is sintered with a specific thermal profile (see Section 3).

Chemical and microstructural analyses were performed using scanning electron spectroscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) (TM3000 Hitachi). The crystallization behavior was investigated by in situ XRD (XRD Bruker D8) from RT to 800°C with a 2theta range from 10 to 90°C to extrapolate the crystallization temperatures of the crystalline phases. The experiment was carried out on a platinum/rhodium stage in air.

Rietveld refinement of the XRD patterns of glass-ceramic powders was carried out in order to evaluate the content of amorphous phase and the proportion between the crystalline phases. The glass-ceramic powders were obtained by grinding a pellet of glass, which was sintered with the sealing profile presented in the Results section. As an internal standard 20 wt% of zincite (zinc oxide, Alfa Aesar) were added to the powders. Two measurements were carried out, one on pure zincite and another one on the glass-ceramic powder mixed with 20% of zincite.

All the XRD files were analyzed with X’Pert HighScore Plus (Panalytical) and the Rietveld refinement was carried out using the WINPOW software.\textsuperscript{22}

2.3 Sealing of the samples and characterization

The sealant was applied onto the metal substrates as a paste by screen-printing (DEK 248 CERD). The paste was prepared from 70% of glass powder and 30% of organic paste components (solvent, binder, surfactant and plasticizer; confidential composition). The powders needed to have a \(d_{50}\) particle size distribution lower than 10 \(\mu\)m for being suitable for screen-printing. After printing, the green paste was heat-treated at 120°C in air for 1.5 hours and at 300°C for 1.5 hours to burn out the organic compounds. The thickness of the layer was determined to be 55 \(\mu\)m (Cyberscan Vantage).

Surface modified metal plates were sealed to the cell in a furnace with a hydraulic piston used to apply a load of 16.7 N cm\textsuperscript{-2} to advice the sintering of the glass. These samples had a dimension of 2 cm \(\times\) 2 cm (metal substrate and half-cell), and were prepared for SEM analyses by vacuum embedding in epoxy resin (Epofix, Struers) and cut in the center to analyze the cross-sections and the interfaces between the glass and the joining partners. The samples were then ground with SiC paper with a polishing machine. While bigger samples with a cell of 11 \(\times\) 11 cm\textsuperscript{2} were then prepared with the same procedure to test the seal under conditions occurring in a stack of industrially relevant size.

2.4 Leak test setup

To determine the gas tightness of the seal, the pressure dependent diffusion of air through the glass seal was measured. An SOC half-cell (11 \(\times\) 11 cm\textsuperscript{2}) was sealed to an AlumiLok\textsuperscript{TM} coated Corfer 22 APU frame with the CGO layer facing the seal. The frame had an opening of 9 \(\times\) 9 cm\textsuperscript{2}. A 1 cm wide V11 seal was printed around the opening, resulting in a 40 cm\textsuperscript{2} seal area (Figure 2B). The assembly was then clamped into a test house forming closed cavities on both sides of the frame (Figure 2A). Each cavity had a gas in- and outlet. Silicon rubber gaskets were used to ensure gas tightness in the clamping area. By means of mass flow controllers (MKS GE50A-series, range: 500 SCCM) a defined flow of air (MFC 1) was fed to one cavity (air side) and nitrogen (MFC 2) to the other (nitrogen side). The outlets of the cavities were connected to a pressure gauge each (\(p_1\) and \(p_2\), Omega Engineering, absolute pressure transducer, 3500 mbar, 0.05% accuracy).
measuring the absolute pressure of the individual cavities and a differential pressure gauge (Δp, Omega Engineering, bidirectional pressure transducer, 350 mbar, 0.05% accuracy) measuring the pressure difference between the air and the nitrogen side. Downstream the pressure gauges metering valves (Swagelok, SS-4MG-MH) were installed to adjust the air and fuel side’s pressure. For measuring large leak rates > 5 SCCM 2 mass flow meters (MFM 1 and MFM 2, MKS GE50A-series) were installed. Small leak rates of air from the air to the nitrogen side were quantified by means of measuring the oxygen partial pressure of the nitrogen side outlet stream with an in-house built $p_{O_2}$-sensor. Assuming that the measured oxygen partial pressure equals

$$p_{O_2, measured} = \frac{p_{O_2}^0 \cdot J_{leak} + p_{O_2} in N_2 \cdot J_{N_2,inlet}}{J_{leak} + J_{N_2,inlet}}$$

the leak rate of air $J_{leak}$ can be calculated to

$$J_{leak} = \frac{(p_{O_2}^0 - p_{O_2} in N_2) \cdot J_{N_2,inlet}}{p_{O_2}^0 \cdot (1 - \frac{p_{O_2, measured}}{p_{O_2}^0})}$$

with $p_{O_2}^0$ as the oxygen partial pressure in the supplied air, $p_{O_2} in N_2$ as the oxygen partial pressure in the supplied nitrogen and $J_{N_2,inlet}$ as the inlet flow rate of nitrogen (MFC 2).

### 3 RESULTS

#### 3.1 Dilatometry analyses of the glass and glass-ceramics

The dilatometry curves of the amorphous glass and the glass-ceramic are shown in Figure 3, the CTEs to characterize the expansion of the glass-ceramic below the glass transition temperature, $T_g$, were extrapolated considering the linear part of the curve between 200 and 450°C. The CTE of the amorphous glass (as casted) resulted in $9.6 \times 10^{-6} \text{ K}^{-1}$ (200-450°C) and the curve shows a dilatometric softening point ($T_d$) at 635°C. The glass-ceramic pellet obtained from pressed glass powders was heat-treated at 800°C for 1 hour, and the displayed a CTE of $12.8 \times 10^{-6} \text{ K}^{-1}$ (200-450°C). Moreover, the dilatometric curve presents a deviation from linearity with an onset at 495°C and a softening at 999°C.

#### 3.2 HSM and DTA: sintering behavior

Sintering and devitrification behavior of the V11 glass were evaluated from HSM and DTA experiments, and the resultant graph is presented in Figure 4A.

A significant shrinkage of the specimen was observed at temperatures higher than 652°C (first shrinkage, $T_{FS}$). The volume decrease continued until reaching the first maximum shrinkage ($T_{MS1}$) at 700°C. At this temperature, the shrinkage corresponds to 18%. A second sintering maximum shrinkage is found at $T_{MS2} = 830^\circ C$, showing a volume decrease in 22%.

More information can be extrapolated from the HSM measure, the shapes of the sample (shown in Figure 4B) are related to some characteristic fixed points which correspond to a specific temperature (Table 2).

The method proposed by Pascual et al. was adopted to predict the viscosity of the glass at the characteristic temperatures. The data retrieved from the HSM curve (Table 2) can be plotted, as in Figure 5, in a viscosity-temperature curve. The fitting of these points gives a trend line for predicting the viscosity of the glass at a certain temperature.

In conclusion, the glass exhibited a 2-stage shrinkage behavior. The first shrinkage $T_{MS1}$ occurred before the crystallization peak (shown in the DTA, black curve in Figure 4A), while a second shrinkage, the $T_{MS2}$, occurred slightly before the onset of the crystallization. Moreover, a volume increase in the glass-ceramic can been seen after reaching 900°C (red curve Figure 4A), this should not influence the sealing process since it will be held at temperature below the crystallization peak.

FIGURE 2 (A) Sketch of the leak test setup; (B) Sketch of the cell sealed to Crofer22APU frame
3.3 In situ-XRD investigation

To investigate the crystallization behavior of the V11 glass during the sealing process, in situ XRD measurements were carried out. In these experiments, the glass powder was exposed to the same thermal profile used for sealing experiments described in Section 3.4.1. Here, the sample was heated up to 600°C from RT with a heating rate of 100°C h⁻¹, and was held at that temperature for 1 hour. Afterwards, the sample was heated up to 700°C with 100°C h⁻¹, further heating to 800°C was done with 50°C h⁻¹ and a final hold of 1 hour was carried out. XRD patterns were recorded at RT, after reaching 700°C, 750°C, and 800°C. Two additional XRD patterns were recorded at 800°C after a holding time of 30 and 60 minutes. The results are presented in Figure 6.

In the XRD measurements conducted up to 700°C (Figure 6F,E) only the diffraction peaks of the platinum substrate and the amorphous halo are recognizable, showing that the glass was still amorphous at these temperatures, as expected. The XRD measurement performed at 750°C (Figure 6D) shows the peaks corresponding to augite (Ca(Mg₃₀₇₀Al₀₃₀)(Si₇₀Al₀₃₀)O₆, Al-substituted diopside) and nepheline (NaAlSiO₄, sodium aluminum silicate) were identified. Further heating up to 800°C did not lead to the formation of new crystalline phases, but the peak intensity for the different phases increased, indicating ongoing crystallization going along with a disappearance of the glassy phase (Figure 6C). The patterns recorded at 800°C after 30 and 60 minutes (Figure 6A,B) gave similar results. Compared to the first measurements carried out at 800°C the characteristic peaks of the nepheline showed a higher intensity, while the intensity of the peaks corresponding to the augite were comparable for all measurements at 800°C.
In order to quantify the amounts of the crystalline phases, Rietveld refinements and reference intensity ratio methods using zincite as the internal standard were carried out. The details of the refinement of the glass-ceramic sintered at 800°C can be found in the Supporting Information (Table S1, Figure S1). Results indicate that the phase composition can be described as a mixture of an amorphous phase (64.3 wt%) and 2 crystalline phases (28.5 wt% augite and 7.2 wt% nepheline).

### 3.4 Joining of SOFC components

In this section, the results from using the V11 glass to join Crofer22APU to YSZ electrolytes and CGO barrier layer of nonreduced half-cells are described. The Crofer22APU used in these experiments was either preoxidized or protected by AlumiLok™ coating. All experiments were performed on samples with a size of 2 × 2 cm, the chosen joining setup of metallic and ceramic components (Figure 1) represents the most relevant configurations found in SOFC/SOEC stacks. In Section 3.4.1, the optimization of the sealing procedure, leading to a reduction in pores in the glass-ceramic sealing and a better adhesion at the interfaces to the joining partners, is presented, while the microstructure of the glass-ceramic seal and a detailed analysis of the different interfaces is presented in Section 3.4.2.

#### 3.4.1 Optimization of the sealing profile

In total, 3 different sealing profiles, pressure-temperature, were tested. The initial sealing profile was designed based on the insight gained from DTA and dilatometry experiments. Here, the joining assembly was heated up to 850°C with a heating rate of 1.67°C min⁻¹, held for 2 hours at this temperature, and then cooled down to RT with the same heating rate used during the heating up. During the complete sealing procedure, a constant weight load of 10 N cm⁻² was applied.

SEM images of the cross-sections of the sealed assemblies are shown in Figure 7A-C. On average, the obtained glass-ceramic sealant had a thickness of 90 μm. The light gray areas correspond to the crystalline phases formed during the sealing, while the darker gray areas represent the remaining amorphous glass. Both phases were evenly distributed. The adhesion to the YSZ electrolyte as well to the rough Al-coated Crofer22APU was good, that is, no crack formation or delamination was observed. The densification of the sealant was rather poor, and pores with different

| Table 2: Characteristic fixed viscosity points and related temperatures |
|-----------------------------|-----------------------------|
| Temperature (°C) | Log[η](Poise) |
| T FS 652 | 9.1 |
| T MS 700 | 7.8 |
| T d 769 | 6.3 |
| T B 825 | 5.4 |
| T HB 1110 | 4.1 |
| T F 1176 | 3.4 |

**Figure 5** Viscosity-Temperature curve for V11 glass

**Figure 6** XRD patterns of V11 amorphous powders at room temperature (F), 700°C (E), 750°C (D), 800°C (C), 800°C after 30 minutes (B), 800°C after 60 minutes (A)
sizes and shapes can be clearly observed throughout the complete seal (black areas in Figure 7D). A quantification based on the contrast of the different phases (Figure 7D) revealed a rather high porosity of 31%.

In a first attempt to reduce the porosity in the sealant, the sealing temperature was decreased down to 800°C, and the holding was reduced to 1 hour, while heating rates and weight load were kept constant, allowing the sample to remain in a temperature regime where the glass is viscous. The SEM micrograph of the cross-section is shown in Figure 7B. As for the previous experiment, the glass is partially devitrified, and a distinct separation of the crystalline phases and the residual amorphous glass can be observed. The good adhesion at interfaces was maintained and, most importantly, the porosity could be reduced by 40% down to a total of 18% (Figure 7E) using this sealing profile.

Further reduction in the porosity down to 8% could be achieved by increasing the weight load up to 16.7 N cm⁻² and following an optimized sealing profile: 20-600°C at 100°C h⁻¹, 1 hour holding, 600-700°C at 100°C h⁻¹, 700-800°C at 50°C h⁻¹, 1 hour holding and then cooling down. While the microstructure of the glass-ceramic and at the interfaces stayed unchanged, the thickness of the sealing was reduced to 75 µm, and only small, randomly distributed closed pores are present in sealant (Figure 7C,F).

3.4.2 | SEM-EDS analysis of the interfaces

In Figure 8, the SEM images of the interfaces of the V11 glass-ceramic and (a) preoxidized Crofer22APU, (d) AlumiLok™ coated Crofer22APU are shown. Comparing the cross-sections of the preoxidized and the AlumiLok™ Crofer22APU (Figure 8A and D, respectively), it is obvious that the surface roughness of the AlumiLok™ coated Crofer22APU is much higher. These results indicate that the used coating process heavily roughens the surface of the Crofer22APU alloy. Despite the different surface structure, both samples display a good adherence between the glass-ceramic and the (coated) Crofer22APU alloy, and no cracks, defects or delamination effects can be found (Figure 8A,B). Differences can be observed in the crystallization behavior of the V11 glass for the different substrates used. While for the Al₂O₃-coated sample, a random orientation of the crystals in the glass-ceramic was found, a more oriented crystallization was observed when preoxidized Crofer22APU was used as a joining partner. Additional EDS analyses were carried to investigate a possible Cr diffusion from the alloys into the glass-ceramic. The corresponding elemental maps and line scans are presented in Figure 8. For the AlumiLok™ coated Crofer22APU, a continuous layer of Al₂O₃ with a thickness of 0.6-0.9 µm separating the glass-ceramic seal and the Crofer22APU alloy was found after the sealing process (Figure 8B,G), indicating that the applied coating was chemically stable and no reactions occurred. Also, the Cr₂O₃/MnCr₂O₄ double layer with a thickness of 1.5-2.8 µm formed during the preoxidation of the Crofer22APU remained intact (Figure 8D,E), and no reactions with the V11 glass were observed. In both samples, no Cr enrichment in the glass-ceramic close to the Crofer22APU interface was observed in the elemental mapping (Figure 8C,F), indicating that no chromates (eg, Na₂CrO₄ or CaCrO₄) were formed. These results were confirmed by an EDS line scan.
performed on the sample with the preoxidized Crofer22APU (Figure 8H). A sharp drop in the Cr line indicated that no Cr diffused from the oxide scale into the sealant. Similar behavior it is shown in Figure 8G for the AlumiLok™ coated substrate, where the Cr line scan is decreasing sharply at the interface between Crofer22APU and the coating (peak in the Al line).

Figure 9A,B show the interface between the glass-ceramic and YSZ and CGO, respectively. In both cases, excellent adhesion was found, and no cracks or voids were present. In the elemental maps shown in Figure 9C, no diffusion from elements found in the YSZ electrolyte/CGO barrier layer into the glass or vice versa was observed, indicating a good chemical stability of the joining partners. In addition, an EDS point analysis of the crystalline phase in the glass-ceramic (light gray, marked “1” in Figure 9B) and the amorphous phase (dark gray, marked “2” in Figure 9B) was carried out. According to the point analysis (details can be found in the Supporting Information, Table S3) the amorphous phase is mainly composed of Na, Si, and, Al, while the crystals primarily contain Si, Ca, and Mg; hence this phase can be labeled, in agreement with the XRD result, as augite. It was not possible to identify any nepheline crystals by EDS analysis with the applied resolution, indicating that the crystals are either too small or the signal might overlap with the high content of augite.

3.5 Leak test on a cell with industrially relevant size

For proof-of-concept, a 11 × 11 cm² half-cell was sealed onto a Crofer22APU frame (AlumiLok™ coated). A compression force of 16.7 N cm⁻² was applied at RT and kept constant throughout the sealing procedure. The optimized temperature profile described earlier (see Section 3.4.1) was employed. After the sintering, the sealant was able to seal the cell onto the frame, and no cracks or signs of detachment were observed.
The gas tightness of the seal was investigated with the described leak test setup. First, the partial pressure of oxygen in the supplied nitrogen was determined to be $p_{O_2}^{\text{in N}_2} = 1.23 \text{ mbar}$. Afterwards, the cell assembly was mounted in the test house. The gas flows for the air and the nitrogen side were set to 500 standard cubic centimeter per minute (sccm). An initial differential pressure of $Dp = p_{\text{air side}} - p_{\text{nitrogen side}} = \sim 0.5 \text{ mbar}$ was set, with $p_{\text{air side}}$ at atmospheric pressure, and the setup was left to flush for 24 hours until the measured $p_{O_2}$ was constant. The differential pressure $Dp$ was stepwise increased to $\sim 20 \text{ mbar}$. At each step (9 steps) the setup was left to equilibrate and the $p_{O_2}$ of the nitrogen side’s outflow was recorded. Throughout the measurements, the measured oxygen partial pressure was constant at $p_{O_2} = 1.42 \text{ mbar}$ without showing any dependence on the applied differential pressure $Dp$. This behavior indicated a Knudsen diffusion process, which was expected for a leak through a low porosity seal. The oxygen partial pressure corresponds to a very low air leak rate of $1.2 \times 10^5 \text{ sccm cm}^{-1}$. It needs to be noted that this value is the combined leak rate through the seal, potential pinholes in the cell and leaks through the rubber gasket of the test house.

**FIGURE 9** Interfaces between the glass and the YSZ electrolyte (A) and the CGO barrier layer (B), EDS maps of some relevant elements: Si, Ca, Al, Na, Mg, Ni, Y, Ce

### DISCUSSION

As shown in Figure 3, the glass and the glass-ceramic have relatively high CTEs of 9.6 and $12.8 \times 10^{-6} \text{ K}^{-1}$, respectively. The increase has been ascribed to the presence of the nepheline and augite phases, but since the crystalline phases only account for $\sim 36$ wt% of the entire microstructure it indicates that the crystalline skeleton or network must be coherent and inter-grown. This hypothesis is supported by the lack of resiliency above $T_g$, as seen for the glass-ceramic in the Figure 4. The value for the technical coefficient of expansion (T-CTE) between RT and $800^\circ\text{C}$ is $13.6 \times 10^{-6} \text{ K}^{-1}$, which is in the desired range for SOFC sealing materials, and is compatible with other materials used in solid oxide cells (eg, YSZ electrolytes: $T$-CTE $= 10.8 \times 10^{-6} \text{ K}^{-1}$, Ni/YSZ electrodes: $T$-CTE $= 12.6 \times 10^{-6} \text{ K}^{-1}$) and auxiliary stack components like Crofer22APU ($T$-CTE $= 12.3 \times 10^{-6} \text{ K}^{-1}$). Compared to previously developed glasses with a comparable chemical composition (V9) a significant increase in the CTE of $3.3 \times 10^{-6} \text{ K}^{-1}$ was achieved by changing the Na:Ca ratio. The content of Na$_2$O in V9 and V11 is 10.3 wt% and 9.26 wt%, respectively. While the content of
CaO in V9 and V11 is 9.3 wt% and 14.34 wt%, respectively.

From the HSM curve (Figure 4) it can be seen that the first shrinkage sets on at 652°C ($T_{FS}$), indicating that the particles started sintering due to viscous flow since the temperature is above the $T_g$ (630°C). While passing the first sintering, which peaked at temperature $T_{MS1} = 700°C$, all the larger pores were presumably closed. Another interesting aspect of this graph is that a second shrinkage step, $T_{MS2}$ was also observed at higher temperatures probably due to the amorphous phase left after crystallization, but only the $T_{MS1}$ is considered when deciding on the sealing temperature of the stack. A two-stage shrinkage behavior is already known for glasses from literature.7-26 The $T_{MS1}$ occurred before the crystallization peak (shown in the black DTA curve, Figure 4), while the $T_{MS2}$ occurred really close to $T_x$. The red HSM curve shows a surprising increase in volume above 900°C, which is also evident in the dilatometry results presented in Figure 3. The exact cause for this has not been clarified yet, but it may due to the release of volatile species and consequent pores formation or stem from an additional crystallization from the glass in preferred growth directions, for example, formation of needle-shaped crystals at higher temperatures.

The combination of HSM and DTA can be used to determine the so-called thermal stability of the glass, which can be defined through the Hruby parameter $K_H = T_x - T_g / T_m - T_x$,27 where $T_x$ is the onset of the crystallization (850°C), $T_g$ = 630°C and $T_m$ = 1175°C. A $K_H$-value above 0.5 indicates a stable glass, and the value, $K_H = 0.68$, derived for the V11 glass indicates that the sealing process can be successfully undertaken. The sintering ability $S_C$, which is defined as $S_C = T_x - T_{MS}$ by Lara et al28,29 can also be used to characterize a glass for its sealing performance as it illustrates how independent crystallization and sintering are. The sintering ability for V11 is $S_C = 150°C$, which provides a temperature range below $T_x$ in which sealing can be successfully done. In the very same temperature range, nucleation processes exhibit maximum rates and by subsequently keeping the sealant at temperatures at or slightly above $T_x$, formation of the glass-ceramic microstructure will be as fast and efficient as possible. Concluding this discussion, sealing with a slow heating through the temperature range between 700°C and 850°C and subsequent annealing at 850°C, will provide the fastest route to a glass-ceramic sealant. It is however for practical reasons desirable to maintain a high degree of sealant resiliency during the sealing process for the various counterparts to attain optimum bonding and the final sealing temperature, chosen at 800°C, reflects how these arguments are brought together.

The sealing profile was optimized (see result section 3.4.1), and the porosity in the glass-ceramic was reduced from 31% to 8% by reducing the sealing temperature and increasing the weight load during the sealing process. In the first sealing experiments, a sealing temperature of 850°C was used. As shown in Figure 7D, the glass-ceramic sealant contained a relatively high number of pores, which can lead to gas leaks and reduce the overall bonding strength between the stack components. These nonspherical pores seen in Figure 7D could be a result of a relatively fast crystallization that hindered the viscous flow/distribution of the glass. Interestingly, this correlation is related to the sinter-crystallization behavior of the glass-ceramic. These results are in agreement with the observations from DTA/HSM and suggest that the sealing temperature was too close to the crystallization temperature (Figure 4).

By lowering the sealing temperature to 800°C, which is approximately half-way between the $T_{MS1}$ and before the $T_x$, a lower porosity of the glass would be expected, which was indeed confirmed by the observed microstructures demonstrating a more dense layer of glass visible in the SEM micrographs of cross-sections shown in Figure 7B,E. Based on data presented in Figure 5, it is possible to extrapolate the viscosity values, and the optimum value at the sealing temperature should be between 10^6 and 10^7 dPa s,29 from other sources is 10^6.6 dPa s.9,30 The extrapolated values of the viscosity are 10^6.3 and 10^6 dPa s at 800°C and 850°C, respectively.

Some pores are still present in the sealant, but the origin of these is not fully understood. It has been suggested that since the paste used for the screen printing contains an organic vehicle, not all the binders were fully oxidized during the heat-up and started to partly reduce the glass after an initial sintering and pore-closure between the glass particles, thus leaving entrapped CO₂ in pores. To avoid and solve this inconvenience, a step of 1 hour at 600°C, below the $T_g$ of the glass (630°C), was added in the heat treatment. The maximum temperature for the sealing was maintained at 800°C and to further force the viscous flow and sealant densification, a slightly higher load was applied at this temperature. Furthermore, limiting the maximum temperature to 800°C prevents an excessive crystal growth, which can potentially hinder the sintering by viscous flow, as previously showed. The resultant sealant is indeed thinner and with a lower porosity left, cf. Figure 7C,F.

The microstructure of the sealant, cf. the cross-sections in Figures 8 and 9, appears as a glass-ceramic with amorphous and crystalline phases. The point analyses (Supporting Information, Table S3) confirmed the presence of different phases, which were identified by the XRD analysis and the Rietveld refinement. The amorphous phase (64.3%) is the dark gray area in Figure 9 (Point 1 of the point analysis) compared to the initial composition of the glass, is rich in Na, Al, and Zr and poor in Ca and Mg, which are mainly retrieved in the augite, the predominant
crystalline phase according to the Rietveld refinement (28.5%). In accordance hereto, the dilatometric measurement of the glass-ceramic (Figure 3) exhibits the $T_g$ of the amorphous phase left at a lower temperature (495°C) than observed from the pristine glass. The presence of the augite, Al-substituted diopside, might indicate a certain stability of the glass, since the diopside “family” is known for being stable in terms of crystal growth and consequently not to influence the CTE after long time heat treatment,31 this will be evaluated with further experiments in future works.

The interfaces between the glass and the cell (both YSZ and CGO) and the surface modified (coating/preoxidized) Crofer22APU substrates were investigated and no particular signs of interface reactions were detected. The glass was providing a good adhesion and the efficiency of the surface modifications used for the Crofer22APU were proved. No chromates were detected at the interface or in the sealant, only at the edges of the substrates, where no coating/oxide scale provided protection.

By applying the latest sealing profile, a larger cell (~11 × 11 cm) was sealed onto a frame and tested for in the leak test setup as shown in Figure 2. A stably free-standing seal was achieved that even after weeks did not show any signs of delamination and exhibited a gas tightness, that is, low enough leak rate appropriate for application in SOC stacks.

5 | CONCLUSION

A barium-free glass-ceramic sealant (V11) containing Si, Al, Ca, Mg, B, Zr, and Na was designed and successfully tested for joining and sealing planar SOFC/SOECs components. The composition was optimized to achieve a CTE (12.8 × 10$^{-6}$ K$^{-1}$) complying with the other components in a SOFC stack. The final glass-ceramic seal was obtained after optimization of the sealing profile by means of the thermal (HSM, DIL, DTA) and in situ XRD analyses presented in this work. The glass-ceramic sealant exhibited a residual glass phase of around 64.3 wt% after sealing, shown by XRD and SEM/EDS analyses. The devitrification lead to the formation of 2 crystalline phases, augite (Al-diopside) and nepheline, which are responsible for the mechanical stability of the glass, also at higher temperatures. The interface reactions toward the metallic components, was tested on Crofer22APU substrates applying 2 different protective surface modifications, preoxidation and AlumiLok™ coating, for which neither chromate formation was detected in the glass or at the glass-metal interface, at least after the sealing process. Lastly, V11 was not only successfully tested on small test samples, but also by sealing a cell with industrially relevant dimensions (11 × 11 cm$^2$) to a AlumiLok™ coated Crofer22APU frame, which gave satisfactory results in terms of leak rates.

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**SUPPORTING INFORMATION**

Additional Supporting Information may be found online in the supporting information tab for this article.

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Paper 2

Improving the Interface Adherence at Sealings in Solid Oxide Cell Stacks
Improving the interface adherence at sealings in solid oxide cell stacks

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Thermal cycling of planar solid oxide cell (SOC) stacks can lead to failure due to thermal stresses arising from differences in thermal expansion of the stack’s materials. The interfaces between the cell, interconnect, and sealing are particularly critical. Hence, understanding possible failure mechanisms at the interfaces and developing robust sealing concepts are important for stack reliability. In this work, the mechanical performance of interfaces in the sealing region of SOC stacks is studied. Joints comprising Crofer22APU (preoxidized or coated with MnCo2O4 or Al2O3) are sealed using V11 glass. The fracture energy of the joints is measured, and the fractured interfaces are analyzed using microscopy. The results show that choosing the right coating solution would increase the fracture energy of the sealing area by more than 70%. We demonstrate that the test methodology could also be used to test the adhesion of thin coatings on metallic substrates.

Introduction

Solid oxide fuel cells (SOFC) are electrochemical devices that can efficiently convert fuels such as hydrogen and gaseous hydrocarbons into electricity [1, 2, 3]. If operated in the electrolysis mode (SOEC), they can be used to produce hydrogen or syngas, which can be stored or converted into liquid fuels for transportation [4, 5, 6, 7]. To advance the commercialization of solid oxide cell (SOC) technology, production and material costs need to be further decreased and long-term stability/reliability demonstrated [8].

Designing SOC stacks requires a careful selection of materials to provide the chemical and mechanical stability needed for several thousand hours of operation and to ensure robustness against thermal cycling. In this context, the sealings represent a critical issue, especially for planar SOC technology. Thermal mismatches between the sealing material and other stack components (e.g., interconnects and cells) can lead to delamination at the interfaces or formation of cracks inside the sealant, which may give rise to mixing of the fuel and the oxidant and, in worst case, lead to stack failure [9, 10, 11].

An ideal sealant for SOC stacks should adhere well to the joining components, remain chemically stable over time, provide high mechanical strength, have a low cost, provide electrical insulation, and have a coefficient of thermal expansion (CTE) that matches well with those of the other stack components [12, 13, 14]. Today, three main types of sealing materials are considered for SOC application: (i) compressive seals, typically based on mica, (ii) compliant seals, typically metal brazes and some glass-ceramics, and (iii) rigid seals, typically made of glasses or glass-ceramics [15, 16].

Compressive seals are deformable and thereby avoid the issue of stress build-up caused by thermal mismatches, but they contain cracks and pores and are therefore not as gastight as the other sealing types [17]. Compliant brazes are also deformable but consist generally of noble metals, which are typically more expensive than mica- and glasses-based sealants. Also, since metallic brazes are electrically conducting, additional insulating layers have to be introduced to avoid electrical short circuits between the electrodes [15]. Compliant glasses are known for being resistant against devitrification and having low glass transition temperature, which enable them to “self-heal” and release residual stresses [18].

Glass and glass-ceramic seals can be tuned in composition to reach the desired properties (e.g., CTE, melting point, degree of crystallization). The low viscosity, typically achieved during the sealing process, allows the seal to adapt to the surface of the joining components and thereby enables a hermetic seal [19, 20].
For these reasons, glasses and glass-ceramics are the most popular sealing materials for SOC stacks, and many different compositions with relevant properties have been reported in the literature, among which alkaline-earth alumina silicate-based glasses are the most common [21, 22, 23, 24, 25, 26, 27].

Despite many advantages, some critical challenges remain to be solved before glasses and glass-ceramic materials can be used as reliable sealants in SOC stacks. Some of the compositions have a low CTE compared to the structurally defining materials in the SOC stacks, which have CTE values in the range from 10.5 to 13.0 × 10⁻⁶ K⁻¹ [16]. In some cases, partial crystallization of the amorphous phase further decreases the CTE, with the consequence of crack formation due to the CTE mismatch [23, 24, 28].

Addition of barium is a popular way of increasing the CTE as well as the sintering ability of the sealants [19]. However, the main disadvantage of Ba-containing systems is the high reactivity between the Ba in the sealant and Cr in the metallic interconnect. Reaction at the steel–glass interface may lead to the formation of chromates having a high CTE that eventually cause interface delamination [22, 29]. These reactions may be diminished by coating the interconnects, as explained later. However, undesired interactions that lead to weakening of the interface can also be a challenge between the barium-containing glass-ceramics and the YSZ electrolyte [22, 26, 27].

Addition of boron oxide (B₂O₃) is a common way to decrease the viscosity and crystallization rate of the glass. On the other hand, borates are very volatile and form compounds that can lead to degradation of the sealing area. The problem can be solved by only adding a small amount of B₂O₃ [15, 16, 19, 30, 31].

From these perspectives, a promising new sealant was recently developed and used in this work: the V11 glass-ceramic [32]. The V11 glass-ceramic fulfills several of the requirements listed above. Its CTE (12.8 × 10⁻⁶ K⁻¹) matches the CTEs of the other stack components such as YSZ 10.8 × 10⁻⁶ K⁻¹ [15], Ni/YSZ 12.6 × 10⁻⁶ K⁻¹ [33], and Crofer 22 APU 12.3 × 10⁻⁶ K⁻¹ [34]. The V11 glass-ceramic adheres well to the joining components, results in a gas tight sealing (leak rate of 1.2 × 10⁵ sccm/cm²), and shows excellent long-term chemical stability [32].

In the SOC stack, the glass will typically be in contact with steel components such as the interconnect. Surface modifications and coatings are applied to the interconnect steel to reduce corrosion rates, lower the resistance for current collection, and reduce Cr evaporation [35, 36, 37, 38]. The latter phenomenon will cause poisoning of the oxygen electrode and lead to local formation of chromates [39, 40, 41]. Chromate formation directly affects the mechanical performance of the sealing area, since these compounds are brittle and have high CTE values (~18–20 × 10⁻⁶ K⁻¹ Ref. 42), which could lead to delamination [43, 44].

In this paper, the mechanical adherence of joints comprising the glass-ceramic sealant (V11) and Crofer 22 APU interconnects with three different coatings/surface treatments is investigated. The coating and surface treatments were chosen to represent interfaces that the sealing typically needs to adhere well to. They are: (i) preoxidized Crofer 22 APU; (ii) AlumiLok (Al₂O₃ coating, Nexcers, Fuelcellmaterials)-coated Crofer 22 APU; and (iii) MnCo₂O₄ (MCO)-coated Crofer 22 APU steel. (MCO coatings are commonly used to increase oxidation resistance and suppress Cr evaporation from interconnects.) [35, 45, 46].

Here, we evaluate the adherence by measuring the so-called critical energy release rate, also known as the fracture energy. The critical energy release rate describes the amount of energy needed to generate additional surface area at the propagation of a crack and relates to the fracture toughness (described below). The critical energy release rate is an intrinsic property of the material, which is not related to the geometry or surface treatment of the sample. This is in contrast to the strength of brittle materials, which depends on flaws stemming from sample production [47] or flaws/surface variations in the actual SOC stack. Some researchers polish the edges of the samples for strength testing, which reduces the variation from sample to sample, as described in Ref. 48. Nevertheless, such measurements will not be representative of the strength variations in a typical stack, as making a sample that replicates the geometry and flaws of the SOC stack is very difficult. Another disadvantage of strength measurements is that a large set of samples (≥30) is needed for a good description of the statistical variation (typically, Weibull variation) [49].

The steady-state critical energy release rate can be used as a criterion for failure. However, this parameter describes only the propagation of an already initiated crack, and not the critical energy for initiation of the crack. The energy release rate needed to initiate a crack is higher than the energy needed for steady-state propagation, as the initiated crack is sharp and the stress concentrations at the crack tip are correspondingly higher. Thus, using the steady-state critical energy release rate as a criterion for failure represents a conservative approach.

To measure the critical energy release rate, we here adopted a method in line with the one suggested by Charalambides and later modified by Høfinger for characterizing the glass–metal toughness. Charalambides proposed at first a simple design of a bilayered specimen to determine the energy release rate of a thin layer in a metal–ceramic interface using a four-point bending configuration [50]. This sample design was modified by Høfinger by adding a third stiffening layer on top of the thin layer, making it a trilayer [51]. The addition of the third layer helps to prevent vertical cracking and segmentation of the thin ceramic layer, which results in an increase in the probability of
delamination. Malzbender et al. [52] used the same geometry and a similar method to that of Hofinger for calculating the critical energy release rate, but neglected the strain energy contribution from the thin sealant layer. For thin sealant layers, this is a good approximation, but for thicker sealing layers, the strain energy contributes significantly to the total energy release (as compared to the substrate and stiffener layers). The analysis was further refined by Malzbender to describe a multilayer breaking apart [52]. As the samples in this study involve only a trilayer, we use the simpler formulation by Hofinger [51].

To identify the crack path, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were conducted on the broken pieces of the samples to identify the failing interface or material in the multilayer samples. Based on the results, we identify and predict weak interfaces in the sealing area of SOC stacks. Furthermore, measures for increasing the interfacial energy release rate in this area are suggested.

**Experimental**

**Sealing glass: preparation and properties**

The chemical composition of the V11 glass used in this study is (in wt%) as follows: 46.4% SiO2, 13% MgO, 14.3% CaO, 9.3% Na2O, 8.3% Al2O3, 2.9% ZrO2, and 5.8% B2O3. The glass-ceramic sealant was produced by mixing and melting the precursors at 1350 °C, followed by quenching in water. The obtained glass was ball-milled to powder and transferred to a paste for screen printing. Further details on the glass powder fabrication can be found in our previous work, where thorough characterization is also reported [32].

To summarize, the glass transition temperature (T_g) is 635 °C, and the glass devitrifies and forms a glass-ceramic material when heat-treated above 800 °C [32]. The glass-ceramic material is a composite material with an amorphous phase (64.3 wt%) and two crystalline phases: augite (28.5 wt%) and nepheline (7.2 wt%). The CTE of the glass-ceramic (after sintering at 800 °C) is 12.8 × 10⁻⁶ K⁻¹ measured between 200 and 450 °C.

**Metallic substrates and coatings: preparation and properties**

Crofer 22 APU (ThyssenKrupp, Essen, Germany [34]), a high-temperature ferritic stainless steel designed for the application as SOC interconnects, was selected as the substrate material, as it is relatively widely used steel for SOC.

Here, we investigate how some commonly applied coatings/surface modifications [preoxidation, AlumiLok (Nexceris, Fuelcellmaterials), MCO coating] influence the adhesion between the interconnect and the seal.

Preoxidation of the Crofer 22 APU was done by heat treatment in air at 900 °C for 50 h. The partial pressure of water vapor was not controlled during this preoxidation, but it is assumed to be in the range of 1–5% based on the typical humidity level and temperature of the laboratory. This preoxidation resulted in the formation of a dense 1.5- to 2-µm-thick oxide scale as shown in Fig. 1(a). This oxide scale is a combination of an inner layer consisting of Cr2O3 and an outer layer of columnar (Mn, Cr)3O4 spinel. This outer layer slightly reduces chromium evaporation from the steel compared to a surface of pure Cr2O3 [29, 42, 53, 54, 55].

AlumiLok™ is a commercial alumina coating (Al2O3) with a thickness of ~0.7 µm supplied by Nexceris (Lewis Center, Ohio) [Fig. 1(b)]. Details about the coating process can be found in Refs. 56 and 57.

The MCO coating was prepared by electrophoretic deposition. For this purpose, MnCo2O4 powder (Fuelcellmaterials) was mixed with isopropanol and ethanol (50:50 vol%) and iodine (0.5 g/L) to make a suspension. Deposition was carried out at 60 V for 1 min with 1 cm distance between the Crofer 22 APU substrate and the counter electrodes (stainless steel). The deposited coating was sintered in two steps: first in H2–N2 at 1000 °C for 2 h and then in air at 800 °C for 5 h. The final thickness of the coating is around 10 µm [Fig. 1(c)].

More details of the coating process are described in the literature [35, 36, 58].

**Sample preparation and assembly**

For the best possible replication of the actual geometry and possible manufacturing- and size-dependent effects, the sample design (materials and geometry) and processing were made to be comparable with the stack design and fabrication process at DTU Energy.

The samples fabricated for fracture energy measurement had a three-layered structure as shown in Figs. 2(a) and 2(b). This consists of two metallic layers (in black, Fig. 2, made of.

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**Figure 1:** The micrographs show 3 cross-sections with the oxidations and coatings: (a) preoxidation, (b) AlumiLok, and (c) MCO coating.
The first metallic layer, from the bottom, consists of two short “bars”/“strips” of Crofer 22 APU with dimensions of $3 \times 29 \times 0.3$ mm$^3$, and the second metallic layer, on the top, is one long slip (bar) of $3 \times 60 \times 0.3$ mm$^3$. All the components were cut from a larger sheet by laser cutting.

After cutting, the metallic strips were polished with SiC paper (grid size #500) to obtain smooth edges and then cleaned in acetone and ethanol for 10 min each in an ultrasonic bath. The polishing and cleaning procedure will remove the debris from the edges but not the flaws introduced by the laser cutting. However, these flaws are placed along the perimeter of the sample and only constitute a very small fraction of the fracture zone, where a sharp crack is running over the full width of the sample.

The V11 glass paste was applied by screen printing on the shorter metallic bars (29 mm). This ensures an 2-mm opening notch in the middle of the sample, where the crack will initiate during the test. With this procedure, it is possible to avoid extra machining for making a notch through the metallic and the ceramic layer, with the risk of damaging the samples. Having glass in the notch can make it hard to initiate the crack without deforming the metal substrates plastically and should therefore be avoided.

The sandwiched samples were heat-treated (“sealed”) under a load of 16.7 N/cm$^2$ applied by a hydraulic piston, with the sample placed between two alumina plates. The following heating profile was used: ramping from 20 to 600 °C at 100 °C/h, holding for 1 h, ramping from 600 to 700 °C at 100 °C/h, ramping from 700 to 800 °C at 50 °C/h, holding for 1 h, and then cooling down to room temperature. This heating profile was optimized according to the V11 glass-ceramic properties, obtained from thermal characterization, as described in Ref. 32. In this study, it was found that doubling the load level did not change the microstructure of the glass significantly, and the glass is thus relatively insensitive to load variations occurring over the stack height during sealing.

To ensure reproducibility and a representative value of the fracture energy, four samples of each type were tested.

**Test method**

Joint samples, as described in section “Sample preparation and assembly”, were tested at room temperature with a four-point bending fixture built in-house at DTU Energy [59, 60]. The setup is similar to a four-point bending test, with the sample placed between four loading pins [see Fig. 2(c)], two inner and two outer. The two inner pins can be moved up and down by an actuator, while the force of the two outer pins is recorded by force sensors [59, 60]. The distance is 25 and 50 mm between the inner and outer pins, respectively.

Before crack formation, the load increases linearly with displacement (constant stiffness). At crack initiation, there is a small drop in the load–displacement curve, as the resistance to crack propagation from a blunt (uninitiated crack) is higher than from a sharp (initiated crack). After crack formation, the two cracks propagate in a symmetrical manner (due to balancing of the two loads on the sample using a fulcrum [60]). When the crack length becomes larger than the thickness of the specimen, the energy release rate reaches a steady-state value [61].

During the steady-state stage, the displacement increases and the stiffness decreases, resulting in a constant loading plateau, $P$. In reality, the load varies slightly up and down

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**Figure 2:** (a) 3D sketch of the full sample geometry, (b) layers in each sample, (c) four-point bending loading configuration, and (d) failure mechanism during loading.
according to variations at the interface and dynamics of the crack propagation, including friction between sample and supports, etc., as shown in Fig. 3.

The plateau of the load is determined as an average of the recorded data after the initial crack initiation peak. The crack propagation occurs practically symmetrically to both sides of the initial notch and proceeds until it reaches the inner loading pins. The sample never reaches a complete failure, as the substrate (and stiffener) material here is made of Crofer 22 APU, which will deform plastically before failure. Here, we avoid plastic deformations, since the analyses presume that the stresses are in the elastic regime.

By ensuring crack propagation in the middle layer of a symmetric sandwich and having the glass adhering to a considerably stiffer substrate after failure, the release of residual stresses is negligible. This is further discussed in the discussion section.

**Microstructural characterization**

SEM and EDS (TM3000 Hitachi, Merlin ZEISS, Carl Zeiss AG, Oberkochen, Germany) were used to investigate the chemical compositions and the microstructures of the fracture surfaces.

**Analysis**

The load at the plateau, $P$, provides a constant bending moment, $M_{0\text{b}}$, between the inner pins in the four-point bending:

$$M_{0\text{b}} = \frac{Pl}{2b},$$

where $P$ is the total applied force (on both inner pins), $l$ is the distance between the outer and inner pins, and $b$ is the sample width. In this specific setup, $l$ is 12.5 mm and $b$ is 3.0 mm (as shown in Fig. 2).

The critical energy release rate, $G_c$, can then be estimated using the analysis made by Hofinger [51]:

$$G_c = \frac{M_{0\text{b}}^2(1 - v_2^2)}{2E_2}\left(\frac{1}{I_2} - \frac{1}{I_c}\right),$$

where $E_2$, $v_2$, and $I_2$, are the Young’s modulus, Poisson’s ratio, and second moment of area of the through-going substrate of Crofer 22 APU [see Fig. 2(a)], respectively. $I_c$ is the combined second moment of area of the stiffeners [d in Fig. 2(a)] and the glass-ceramic. The indexes 2 and d here refer to the glass-ceramic layer (sealant) and the substrate (long metal slip), respectively.

The second moments of areas are calculated as:

$$I_2 = \frac{h_2^3}{12},$$

where $h_2$ is the thickness of the substrate and $I_c$ is given by:

$$I_c = \frac{h_2^3}{3} + \kappa\frac{h_2^3}{3} + \mu\left(\frac{h_3^3}{3} + h_3^2h_1 + h_3^2h_d\right)$$

$$- \left[\frac{h_2^2 - \kappa h_2^2 - \mu(h_3^2 + 2h_1h_d)}{4(h_2 + h_1 + h_d)}\right]^2,$$

where the index 1 refers to the stiffener (the short metal strips). $\kappa$ is the ratio between the stiffness of the substrate and the stiffener (which are identical here):

$$\kappa = \frac{E_1(1 - v_1^2)}{E_3(1 - v_3^2)}.$$

and $\mu$ is the ratio between the stiffness of the substrate and the glass-ceramic layer

$$\mu = \frac{E_3(1 - v_3^2)}{E_3(1 - v_3^2)}.$$

Poisson’s ratios are specified as $v$ and they are assumed to be $v_1 = 0.3$, $v_2 = 0.2$. Values for the Poisson’s ratios of the glass and ceramic are scarce in the literature, but the results are practically insensitive to these values.

$E$ is the Young’s modulus. Values used for the calculations were: $E_2 = E_d = 220$ GPa [34] and $E_3 = 76$ GPa [52]. The latter value is taken from the literature as a representative number for the stiffness of the glass-ceramic. The results are practically insensitive to variations in the Young’s modulus of the glass-ceramic with the chosen geometry, and, e.g., assuming that $E_d$ has doubled the energy release rate changes by $0.0007\%$.

$h$ represents the different layer thicknesses. To obtain the exact thickness of each layer, one sample of each type was cast in epoxy, polished, and inspected in a scanning electron microscope (see section “Micro-structural characterization”). The thicknesses were measured at 10 locations for each layer, and results are summarized in Table I.
The fracture energy of the preoxidized Crofer 22 APU (15.9 J/m²) was comparable to the MCO-coated samples (13.6 J/m²). The highest G value (23.7 J/m²) was measured for the AlumiLok-coated sample, which is 74% higher than the preoxidized or MCO-coated samples.

**Fractography and microstructural analysis**

After mechanical testing, samples were manually taken apart to analyze the fractured surface, as shown in Fig. 4. The two fracture areas on either side of the tested sample (on the short and on the long bar), delimited by the red dashed lines in Fig. 4(a), were analyzed by SEM/EDS. Two samples of each type were analyzed to confirm that the results were consistent. Representative data from one of the samples is shown below in Fig. 4.

The elements shown in the EDS maps in Fig. 4 (EDS) are mainly present in one specific layer. This makes it possible to identify the interfaces or layers in which the crack propagation occurred. Si (yellow) represents the V11 glass-ceramic, a combined presence of Mn (purple) and Cr (red) the oxide scale of the (preoxidized) Crofer 22 APU, Al (green) the AlumiLok coating, and Co (blue) the MCO coating.

Figure 4(b) shows the fracture surface of the preoxidized Crofer 22 APU sample. The surface of the long bar, mainly Cr and Si are found. Similar results were found on the short bar, as shown in Fig. 4(c). The two distinct areas are separated by the yellow dotted line in the SEM images [Figs. 4(a) and 4(b)].

Two observations regarding the chemical characteristic of the fracture surfaces can be made: First, areas that are rich in Si have lower/no concentration of Cr and Mn and vice versa. Second, areas with a high Cr content on the long bar typically have a low Cr concentration on the short bar. The same trend can be found for Si, although this is not as pronounced. Based on these results, it can be concluded that crack formation and propagation mainly occurred within the thermally grown oxide scale and, to a much lower extent, within the glass-ceramic, as illustrated in Fig. 4(d). Comparing EDS maps of Cr and Mn in the stippled area of Figs. 4(b) and 4(c), it can be seen that Cr is present on both sides of the sample, while Mn is only present on one side (“bottom”). This indicates that the fracture within

**Results**

The critical energy release rates ($G_j$), here also referred to as fracture energy, for the different samples are reported in section “The fracture energy ($G_j$)”. Complementary analysis of the fractured interfaces is reported in section “Fractography and microstructural analysis”. Considering the complexity of the investigated samples (five layers and four interfaces [Fig. 2(b)]), all results are discussed in context in section “Discussion”.

**The fracture energy ($G_j$)**

Examples of the load-displacement curves measured for the different samples are shown Fig. 3. The plateaus in these curves were estimated by taking the average of the recorded loads, and $G_j$ was calculated as described in section “Test method”. Four specimens were tested for each combination to ensure reproducibility and to exclude possible errors due to sample preparation. An overview of the measured fracture energies is presented in Table II.

| TABLE I: Thickness values (mean ± standard deviation) of the Crofer 22 APU and the glass per each combination. |
|---------------------------------|-----------------|-----------------|
| Layer                          | Thickness (µm)  |
| Preoxidized samples            |                 |
| Crofer 22 APU                  | 310 ± 1         |
| V11                            | 48 ± 2          |
| AlumiLok-coated samples        |                 |
| Crofer 22 APU                  | 323 ± 6         |
| V11                            | 64 ± 5          |
| MCO-coated samples             |                 |
| Crofer 22 APU                  | 330 ± 8         |
| V11                            | 55 ± 1          |

The critical energy release rate relates to the mode I fracture toughness, $K_{IC}$, in plane strain stress, as follows:

$$K_{IC} = \sqrt{G \cdot E/(1 - \nu^2)},$$ (7)

where $E$ and $\nu$ are the elastic constants related to the failing material. If the failure occurs in the interface, then the approach by Hutchinson and Suo [62] can be used:

$$K_{IC} = \sqrt{G \cdot E^*},$$ (8)

where $E^*$ is defined as [62]

$$\frac{1}{E^*} = \frac{1}{2} \left( \frac{1 - \nu_1}{E_{11}} + \frac{1 - \nu_2}{E_{22}} \right),$$ (9)

where $E_{11}$, $v_1$, $E_{22}$, and $v_2$ are the elastic constants related to the two materials along the failing interface.

The curvature of the substrate was measured after testing to verify that the substrate was thick enough to keep the stresses within the elastic regime to avoid plastic deformation during the experiments.

The fracture energy ($G_j$)

Examples of the load-displacement curves measured for the different samples are shown Fig. 3. The plateaus in these curves were estimated by taking the average of the recorded loads, and $G_j$ was calculated as described in section “Test method”. Four specimens were tested for each combination to ensure reproducibility and to exclude possible errors due to sample preparation. An overview of the measured fracture energies is presented in Table II.

| TABLE II: Measured fracture energies and estimated fracture toughness for the three different interfaces with glass-ceramic and Crofer 22 APU with different coating/surface treatment solutions. |
|-----------------|-----------------|-----------------|
| Preoxidation    | AlumiLok        | MCO             |
| $G$ (J/m²)      | 15.9            | 23.7            | 13.6            |
| Std. dev.       | 2.1             | 3.5             | 3.0             |
| $E$ (GPa) (failing material) | 280 [72] | 76 [52] | 124.7 [73] |
| $K_{IC}$ (MPa m^1/2) | 2.5            | 1.6             | 1.6             |

*Estimated based on Eq. (7) and literature values for $E$. 

The elements shown in the EDS maps in Fig. 4 (EDS) are mainly present in one specific layer. This makes it possible to identify the interfaces or layers in which the crack propagation occurred. Si (yellow) represents the V11 glass-ceramic, a combined presence of Mn (purple) and Cr (red) the oxide scale of the (preoxidized) Crofer 22 APU, Al (green) the AlumiLok coating, and Co (blue) the MCO coating.
Figure 4: Overview of the SEM/EDS analysis of (a) sample sketch with highlighted analyzed area. V11 on preoxidized Crofer 22 APU (b) top bar SEM and EDS and (c) bottom bar SEM and EDS, and (d) sketch of the fracture mechanism. V11 on AlumiLok-coated Crofer 22 APU (e) top bar SEM and EDS and (f) bottom bar SEM and EDS (g) sketch of the fracture mechanism. V11 on MCO-coated Crofer 22 APU (h) top bar SEM and EDS and (i) bottom bar (l) sketch of the fracture mechanism.
the thermally grown oxide scale took place at the interface between the Cr$_2$O$_3$ and (Mn,Cr)$_3$O$_4$ layers of the scale.

Figures 4(e) and 4(f) show the fracture area of the AlumiLok-coated Crofer 22 APU sample. On both surfaces (long bar Fig. 4(e), short bar Fig. 4(f)), mainly Si and few spots that are Al rich were found. The yellow dashed line in Figs. 4(e) and 4(f) corresponds to the area in which the V11 glass was screen-printed.

As expected, the remaining area at the edge of sample corresponds to AlumiLok-coated Crofer 22 APU. Some iron-containing agglomerations are observed inside the yellow-line area, and those are visible on both sides. This may indicate that the crack propagates through the rough steel and coating surface. Overall, these results indicate that the fracture occurred in the middle of the glass-ceramic, as depicted in the sketch in Fig. 4(g).

The SEM/EDS images of the fracture area of the MCO-coated Crofer 22 APU sample are shown in Figs. 4(h) and 4(i). The center of the fracture area of the short bar [Fig. 4(i)] is rich in Mn and Co. A stripe of Si is found around this area, representing the glass layer underneath. Similar observations were made on the surface of the long bar [Fig. 4(h)]. In this case, the fracture occurred inside the MCO coating, part of the MCO remained attached on the glass-ceramic (short bar), while the other part remained attached on the steel (long bar).

Discussion

In this study, three different scenarios/assemblies of the SOC sealing areas were investigated. For all scenarios, the weakest interfaces were identified, and mechanisms of crack propagation postulated. Crack formation occurred in different layers or along interfaces in the investigated assemblies, underlining the importance of a complementary fractography analysis to supplement the mechanical measurements.

The weakest interface with the lowest energy release rate was found for the MCO-coated samples (13.6 ± 3.0 J/m²). From the EDS analysis [Figs. 4(h) and 4(i)], it can be concluded that the crack propagation for this type of sample occurs within the MCO layer, as Mn and Co are equally present in the sample pieces on either side of the crack. Accordingly, the critical energy release rate measured for this interface is characteristic of the MCO coating (and not for the glass-ceramic V11 sealant). This value is in reasonable agreement with the measurement by Akanda et al., who estimated a fracture energy of 10 J/m² by bending and detecting spallation of the coating [63]. As shown in Fig. 1(c), the glass partially penetrates the pores of the coating and probably enhances the energy release rate of the MCO.

The preoxidized samples showed a comparable, but slightly higher, critical energy release rate (15.9 ± 2.1 J/m²) than the MCO-coated sample. The elemental analysis of the interface [Figs. 4(b) and 4(c)] indicated that the fracture occurred between the Cr$_2$O$_3$ and the (Mn,Cr)$_3$O$_4$ layers of the oxide scale, thermally grown during preoxidation. Previous microstructural investigation of the oxide scale on Crofer 22 APU thermally grown in air at 900 °C has shown void formation between these two layers; thus, it seems plausible that this interface is the weakest region of the sample [36, 64]. In conclusion, the critical energy release rate measured for this sample relates to the interface strength between the Cr$_2$O$_3$ and the (Mn,Cr)$_3$O$_4$ layers of the thermally grown oxide scale.

The preoxidation process of 50 h at 900 °C used for the sample preparation results in a relatively thick oxide scale of ~1.5–2 μm. This is equivalent to the oxide scale thickness measured after 1000 h of aging at 800 °C [65]. The oxide scale will grow below either of the coatings (MCO and AlumiLok) used in the study, and the oxide scale may end up being the weakest interface independent of the type of coating applied. However, it is expected that the corrosion rate in the sealing area (below the sealing) is well below that in the active area, as the sealing also prevents oxygen from diffusing to the steel surface. According to the literature, the composition of the oxide scale does not change even after 23,000 h of aging at 800 °C [66]. On the other hand, interactions between the oxide scale and V11 during aging might cause changes in the fracture toughness. This is ongoing research.

With increasing oxide scale thickness, the residual stresses in the oxide scale also increase. However, these residual stresses are concentrated in very thin layers having negligible stiffness compared to the remaining SOC stack. The residual stresses are thus not released during crack propagation (the coating does not change shape—it is “frozen” onto the substrate). Consequently, increasing the oxide scale should not influence the integrity.

For the same reason, the residual stresses in the glass-ceramic layer do not influence the measurement significantly. The sandwich samples are symmetric with thick steel substrates as the stiffest layers. They contract equally, such that the only residual stresses being built up relate to the difference in thermal contractions between the steel and glass. Some of this residual stress is released as the crack grows (and the glass is primarily attached to one of the steel substrates). The most energy released is for the case where all the glass adheres to one of the metal substrates. In this case, ~50 μm of glass with a far lower stiffness (~76 GPa, see Table III) adheres to an ~300-μm steel substrate (~220 GPa, see Table III), with a stiffness ratio of ~1:18. Thus, the glass does almost not change shape during the failure, as it is
“frozen” onto the substrate. Using the classical laminate theory [67], this residual stress release can be estimated to be \(0.06 \text{ J/m}^2\), which is well below the uncertainty of the experiments and the magnitude of the critical energy release rates of 13–24 \(\text{J/m}^2\).

The highest energy release rate value (23.7 \(\pm\) 3.5 \(\text{J/m}^2\)) was found for samples with the AlumiLok coating. From the EDS analysis [Figs. 4(e) and 4(f)], it is clearly observed that the fracture in this case starts and develops inside the glass-ceramic layer. Taking into account that fracture occurs only in the glass-ceramic, the critical energy release rate measured for this interface reflects the mechanical properties of the V11 glass-ceramic.

Based on these results, three points should be highlighted: First, it is important to accurately identify in which layer crack propagation occurs, to correctly correlate the measured values with the right material/interface. Second, the strong interface adhesion achieved with the Alumilok allows for a quantification of the fracture properties of the V11 glass-ceramic. Third, the strong adherence of the V11 glass-ceramic to coatings and thermally grown oxide scales along with its high inherent toughness opens up the possibility to accurately characterize the adherence of other, weaker interfaces as here exemplified for preoxidized and MCO-coated Crofer 22 APU (Fig. 5).

The interface strength between the glass-ceramic/MCO coating and glass-ceramic/oxide scale is higher than one between the Crofer 22 APU/MCO coating/oxide scale, which were identified as the weakest interface in the sealing area. Consequently, to improve the overall strength in the sealing area, the stability of these interfaces must be improved (rather than the glass-ceramic itself). Our results show that this can be achieved by using the AlumiLok coating. The thin \(\text{Al}_2\text{O}_3\) layer (with high roughness) adheres very well to the Crofer 22 APU and drastically improves the interface fracture energy. The presence of a MCO coating in the sealing area, on the other hand, reduces the maximum achievable toughness in the sealing zone.

The critical energy release rate obtained for the V11 glass-ceramic (23.7 \(\pm\) 3.5 \(\text{J/m}^2\)) is comparable to values reported in the literature by Malzbender et al. [52]. In their work, an alumina silicate glass-ceramic sealant (glass 73) was tested with a comparable method, and an energy release rate of 12 \(\pm\) 6 \(\text{J/m}^2\) and 23 \(\pm\) 6 \(\text{J/m}^2\) before and after aging was found, respectively [52]. In this context, it is noticeable that the V11 glass glass-ceramic develops a high fracture energy already directly after the sealing process (no need for aging). Nevertheless, the energy release rate of aged V11 sampled needs to be investigated in the near future for a fair comparison.

The values here obtained for the V11 glass-ceramic (23.7 \(\pm\) 3.5 \(\text{J/m}^2\)) are comparable to the energy release rate of \(\text{NiO/3YSZ-based cells (25.2 \(\pm\) 3.2 J/m}^2\) [68]. The fracture energy thus balances well other brittle components of the stack, and there is no further need for optimizing the fracture energy of the glass-ceramic.

In literature, most studies on glass-ceramics are carried out with different materials at the interfaces. For example, Kuhn et al. [69] and Malzbender at al. [70] showed that sealants on steel with an interlayer of YSZ resulted in a fracture energy of 56 \(\pm\) 3 \(\text{J/m}^2\) after 500 days of aging at 800 °C. This interface is thus not the weakest one in a stack, and it shows that glass-ceramics are capable of becoming rather robust.

**TABLE III**: Poisson's ratio and Young's modulus of the Crofer 22 APU and glass.

<table>
<thead>
<tr>
<th>Material</th>
<th>(\nu)</th>
<th>(E) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crofer 22 APU</td>
<td>0.3</td>
<td>220 [34]</td>
</tr>
<tr>
<td>Glass</td>
<td>0.2</td>
<td>76 [52]</td>
</tr>
</tbody>
</table>

**Figure 5**: Fracture energy results of SOC stack components: V11, preoxidation, MCO coating, \(\text{NiO/3YSZ} [68]\), glass-ceramic 73 after sintering and after aging [52].
Conclusions

To understand the failure mechanisms occurring in the sealing area of SOC stacks, the critical energy release rate of several relevant interfaces was measured by four-point bending of notched sandwiched samples with the glass-ceramic adhering two layers of surface-treated Crofer 22 APU.

A recently developed glass-ceramic sealant (SiO2–MgO–
CaO–Na2O–Al2O3–ZrO2–B2O3) was joined to (i) preoxidized Crofer 22 APU, (ii) Crofer 22 APU with an AlumiLok coating, and (iii) Crofer 22 APU with a MnCo2O4 coating. The location of the fracture in the multilayer samples was determined by SEM and EDS.

It was found that the weakest interfaces are between the Crofer 22 APU and the oxide scale formed during preoxidation (15.9 J/m2) and between Crofer 22 APU and the MnCo2O4 coating (13.6 J/m2). Applying the AlumiLok coating to Crofer 22 APU significantly enhances the stability of the glass–interconnect interface such that the fracture occurred within the glass-ceramic. The critical energy release rate corresponding to the glass-ceramic was 23.7 J/m2. In absolute terms, the fracture energy characteristic of the V11 glass-ceramic is comparable to that of porous NiO/YSZ (~25 J/m2) and the interface with the AlumiLok is even tougher, i.e., the joint is in this configuration no longer the “weakest link.”

For the case of Mn–Co-oxide-coated interconnects, the fracture energy of the interface is only half the value characteristic of the cell, which should be accounted for in stack designs. In the testing of the Mn–Co-oxide, V11 served as a “glue” between two coated metal bars to test the mechanical properties of the coating.

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References


Paper 3

High toughness well conducting contact layers for solid oxide cell stacks by reactive oxidative bonding
High toughness well conducting contact layers for solid oxide cell stacks by reactive oxidative bonding

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Abstract

Looking into a future with an increased demand for large scale electrochemical conversion technologies, there is a desire for increasing the scalability of the solid oxide cell (SOC) technologies. The SOC technologies offers high conversion efficiency over the competing technologies, but the scalability is challenged by brittle ceramics needed for the stable high temperature operation. In this work we present a new type of high toughness contact layers to be used between the oxygen electrode of the cell and the interconnect, which is made by a cheap scalable processing route, i.e. screen-printing. The high toughness is achieved at moderate assembly heat treatment temperatures by using so-called reactive oxidative bonding, where metal particles (Cu, Co, Mn) are in-situ oxidized to well conductive spinels. The reactive oxidative bonding entails interdiffusion and higher sinterbility and eventually high fracture energy of the mechanical bond. We thus find fracture energies in the order of \(\sim 5\) times higher than those of conventional contact layers, while also maintaining low area specific resistance of the contact.

Keywords: Solid oxide cell; Fracture toughness, Interconnect, Contact layer; Coating
1 Introduction

Solid oxide fuel cells (SOFC) are electrochemical devices that can convert fuels such as hydrogen, ammonia or hydrocarbons into electricity with a high efficiency [1–3]. When operated in reversed mode as a solid oxide electrolysis cell (SOEC), the same device can be used to produce hydrogen or syngas. These gasses can be stored or converted into higher value chemicals [4–7]. In order for the solid oxide cell (SOC) technology to reach commercialization, long-term stability and reliability must be successfully demonstrated [8].

Establishing a robust contact between the oxygen electrode and the metallic interconnect is among the major durability challenges for state-of-the-art SOC stacks [9–11]. To improve the bonding between these two layers, a contact layer may be used. The contact layer material should ideally be chemically compatible with both the oxygen electrode and the coated interconnect, have a high electrical conductivity and high strength as well as having a thermal expansion coefficient matching the other cell components.

Ceramic perovskite oxides such as (La,Sr)MnO$_3$ (LSM), (La,Sr)CoO$_3$ (LSC), (La,Sr)FeO$_3$ (LSF), and (La,Sr)(Co,Fe)O$_3$ (LSCF) are currently the most common choice for this application [12–14]. The perovskite oxides offer a high electrical conductivity and a thermal expansion coefficient matching the other cell components [12,15]. The main drawback with using perovskite oxides as the contact layer is the high temperature (around 1100°C) required to sinter these materials well [16]. The contact layer is typically applied in the “green state” on the manufactured cell and sintered during stack assembly/sealing. Due to the use of steel interconnects and a glass(-ceramic) seal, the typical stack assembly/sealing temperature is limited to approximately 900°C [17]. This results in insufficient sintering of the contact layer and, as a consequence, a weaker bonding at the interface with an increased risk of contact loss during operation and thermal cycling.

Several suggestions to improve the perovskite oxide contact layer have been put forth. Sintering aids such as CuO have been added to enhance densification at a lower...
temperature [18] and glasses or inorganic binders have been mixed with the perovskite oxide to make a composite contact layer [13,19]. However, these solutions have been shown to have some drawbacks, such as limited long-term stability or poor compatibility with the oxygen electrode [18].

A promising method to achieve high density at a low sintering temperature is through the concept of “reactive oxidative bonding”, illustrated in Figure 1. In this approach, the contact layer is applied in the form of metal particles that oxidize during stack assembly/sealing. Due to the high enthalpy of the oxidation reaction, the driving force for sintering is greatly enhanced compared to the driving force during conventional sintering of oxide particles. This approach was previously used for fabricating contact layers based on Ni-Co [20], Co-Mn [21] and Ni-Fe [22].

In this study, we investigate the possibility of using mixtures of metallic Cu-Mn or Co-Mn particles deposited by screen printing to form the contact layer. The metallic particles are mixed in stoichiometric amounts to in-situ form the spinels $\text{Cu}_{1.2}\text{Mn}_{1.8}\text{O}_4$ [23] and $\text{MnCo}_2\text{O}_4$ [23,24] during a relatively mild heat treatment / sintering similar to those use in the assembly procedure of an SOC stack. The contact layers are characterized by measuring the area specific resistance and fracture toughness. The microstructural and compositional development of the contact layers is characterized by X-ray diffraction and electron microscopy.
2 Experimental

2.1 Contact layer preparation

Contact layer pastes for screen printing were prepared by mixing metallic powders with a solvent and organic binders to achieve a solid load of 70 to 72 wt.%. The CuMn contact layer was made with a mixture of 43 wt.% Cu (2 μm, Alfa Aesar) and 57 wt.% Mn (2 μm, American Elements), while the CoMn contact layer was made with a mixture of 66 wt.% Co (1.6 μm, Alfa Aesar) and 34 wt.% Mn (2 μm, American Elements). The specific Cu/Mn and Co/Mn ratios were chosen in order to form the spinel phases \( \text{Cu}_{1.2}\text{Mn}_{1.8}\text{O}_4 \) and \( \text{MnCo}_2\text{O}_4 \) after oxidation.

2.2 Chemical and microstructural characterization

For chemical and microstructural characterization the contact layers were screen printed on top of 2x2 cm\(^2\) coupons of Crofer 22 APU (VDM metals, Germany, [25]). The coupons were subsequently sintered in air following a representative SOC stack assembly/sealing procedure developed for a glass-ceramic sealant [26]. This procedure involved heating to 200 °C at 15 °C/h, holding for 2 h and heating to 400 °C at 15 °C/h, holding for 2 h (debindinging), heating at 600 °C at 100 °C/h, holding for 1
h, heating to 700 °C at 100 °C/h, heating to 800 °C at 50 °C/h, holding for 1 h and finally cooling down to room temperature at 120 °C/h. After this sintering procedure, some of the samples were subsequently aged in air at 750 °C for 250 h.

Chemical and microstructural analyses were performed by Scanning Electron Microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) (TM3000 Hitachi and Merlin ZEISS) either on the sample surface or on the sample embedded in epoxy resin (Epofix, Struers) to investigate the cross-section. X-ray diffraction (XRD) analyses were performed on the samples surface using a XRD Bruker D8 diffractometer with Cu Kα radiation. The spectra were collected from 15° to 75° 2θ with a step size of 0.02°, a collection time of 1 s per step and a v6 mm divergence slit.

2.3 Area specific resistance measurements

The electrical performance of the contact layers was evaluated by measuring the area specific resistance (ASR) in air at 750°C. The set-up for the ASR measurement was explained in detail in ref. [27]. The contact layers were screen printed onto 20 x 40 mm² plates of AISI441steel (0.3 mm thick) in a central area of 20 x 20 mm². The samples were dried at 90°C for 1 h to allow for handling. Pt wires were spot welded along the shorter edge of the steel plates to serve as voltage probes. Bisque-sintered 20 x 20 mm² La_{1-x}Sr_xMnO_3 (LSM) pellets spray coated with a mixture of LSM (90 wt.%) and Co_3O_4 (10 wt.%) were used as current collecting plates to mimic the contact the contact layer would have with an SOC air electrode. The screen printed steel samples and LSM pellets were stacked on top of each other as illustrated in Figure 5.

Gold foils were connected to gold wires and placed on top and bottom of the stack for a chemically inactive current supply. A load of 7 kg was applied on top of the stack, corresponding to a load of 17.5 N/cm². The stack was heated up to 800 °C following the sintering profile described in section 2.2. A 2 A current was applied, corresponding to 0.5 A/cm² considering the nominal contact area of 20 x 20 mm² between the steel plates and the LSM pellets. The stack was subsequently cooled down to 750°C at 120°C/h and the temperature was kept constant for 2000 h. The ASR was calculated
from the voltage drop measured between the Pt wires placed between the different components: 1) contact layer/LSM, 2) LSM/LSM and 3) AISI441/LSM (see Figure 5).

2.4 Fracture energy characterization

The adhesion of the contact layer to the steel interconnect was evaluated by measuring the critical energy release rate ($G_c$), here also referred to as fracture energy, of the interface between the contact layer and Crofer 22 H (VDM metals, Germany [28]). A detailed description of the measurement method and set-up can be found in the literature [29–32]. Here, the contact layers pastes were screen printed onto two 29 x 3 mm$^2$ Crofer 22 H bars (0.5 mm thick) and dried at 90°C for 1 h to allow for handling. The two bars were placed on top of a 60 x 3 x 0.5 mm$^3$ Crofer 22 H bar, and bonded by heat treatment described in Section 2.2. A load of 16.7 N/cm$^2$ was applied during the heat treatment.

Testing of the samples took place in air at room temperature using a four-point bending rig built at DTU Energy [30,33]. This test enables the measurement of the critical energy release rate for crack propagation at the interface of two layers [32,34,35]. It has also previously been used to test the adherence between steel and a glass-ceramic sealant [36,37].

The sample was placed between two inner pins, 25 mm distant, and two outer pins, 50 mm distant, and the bending was induced by a movement of the inner pins with a fixed displacement rate of 0.01 mm/s. During the measurement, both load and displacement were recorded. The fracture energy $G_c$ was evaluated following the method derived by Charalambides et al. and later modified by Hofinger [32,34]. The maximum loads $P$, which are achieved at the crack propagation, was used to calculate the bending moment, $M_b$, between the inner pin in the four-point bending rig:

$$M_b = \frac{P l}{2 b}$$

(1)

where $b$ is the sample width, 3.0 mm, and $l$ is the distance between the outer and inner pins, 12.5 mm.
was estimated, using the analysis made by Charalambides and then modified by Hofinger:

\[ G_c = \frac{M_b^2 (1 - v_2^2)}{2 E_2} \left( \frac{1}{I_2} - \frac{1}{I_c} \right) \]  

(2)

where \( E_2, v_2 \) and \( I_2 \) are the Young’s modulus, Poisson’s ratio and second moment of area of the through-going substrate of Crofer 22 H, respectively. \( I_c \) is the combined second moment of area of the stiffeners (metal bars) and the contact layer. The indexes 2 and \( d \) here refer to the contact layer, the substrate (long metal bar), respectively.

The second moments of areas are calculated as:

\[ I_2 = \frac{h_2^3}{12} \]  

(3)

where \( h_2 \) is the thickness of the substrate.

\( I_c \) is given by:

\[ I_c = \frac{h_2^3}{3} + \kappa \left( \frac{h_1^3}{3} + h_1^3 h_1 + h_1^2 h_d \right) \]

\[ - \frac{h_2^2 - \kappa h_1^2 - \mu (h_d^2 + 2 h_1 h_d)}{4 (h_2 + \kappa h_1 + \mu h_d)} \]^2 \]

(4)

where the index 1 refers to the stiffener (the short metal bars). \( \kappa \) is the ratio between the stiffness of the substrate and the stiffener:

\[ \kappa = \frac{E_1 (1 - v_2^2)}{E_2 (1 - v_1^2)} \]  

(5)

And \( \mu \) is the ratio between the stiffness of the substrate and the contact layer:

\[ \mu = \frac{E_d (1 - v_2^2)}{E_2 (1 - v_d^2)} \]  

(6)

where \( v \) are the Poisson’s ratios and \( E \) the Young’s moduli. In this specific case, stiffener and substrate were identical.

To ensure reproducibility and account for variations in sample preparation, four samples of each type were prepared and tested.
3 Results

3.1 X-ray diffraction

XRD patterns of the CuMn contact layer after sintering (at 800°C) and after ageing for 250 h at 750°C in air are shown in Figure 2a and b respectively. After sintering, three crystalline phases can be detected: Cu$_{1.2}$Mn$_{1.8}$O$_4$ (Figure 2c, cubic, Fd-3m), CuO (Figure 2d, monoclinic, C2c) and Mn$_2$O$_3$ (Figure 2e, cubic, Ia3). No additional phases were detected after ageing, but the intensity of the peaks assigned to Cu$_{1.2}$Mn$_{1.8}$O$_4$ increased.

XRD patterns of the CoMn contact layer after sintering (at 800°C) and after ageing at 750°C for 250 h are shown in Figure 2f and g. Three crystalline phases were identified after sintering: Co$_3$O$_4$ (Figure 2j, cubic, Fd-3m), Mn$_2$O$_3$ (Figure 2i, cubic, Ia3), and Co$_2$MnO$_4$ (Figure 2h, cubic, Fd3m). After ageing, no new phases were found, but the intensity of the MnCo$_2$O$_4$ peaks increased.
Figure 2 XRD patterns for the two contact layer compositions studied, CuMn-CL and CoMn-CL, after sintering at 800°C (black) and after ageing at 750°C for 250 h. 

- Cu$_{1.2}$Mn$_{1.8}$O$_4$ = PDF 01-071-1144
- CuO = PDF 01-089-2530
- Mn$_2$O$_3$ = PDF 01-076-0150
- Co$_2$MnO$_4$ = PDF00-023-1237
- Co$_3$O$_4$ = PDF 00-043-1003.
3.2 Microscopy

SEM micrographs and EDS maps of the CuMn contact layer on Crofer 22 APU after sintering at 800°C are shown in Figure 3a and b. At least two different phases can be distinguished on the top surface (Figure 3a), both from the contrast difference in the backscatter electron (BSE) image and from the EDS maps of Mn and Cu. According to quantitative EDS point analysis of the two areas, the lighter grey area is composed of mainly Cu (81.4 wt.%) and O (18.7 wt.%), while the darker grey area is composed of Cu (35.9 wt.%), Mn (36.8 wt.%) and O (27.2 wt.%). The latter is corresponds to the composition Cu\textsubscript{1.3}Mn\textsubscript{1.6}O\textsubscript{4.1}. Considering the XRD results (section 3.1) the light grey phase likely corresponds to CuO, while the dark grey phase corresponds to the spinel phase. The Mn\textsubscript{2}O\textsubscript{3} phase could not be detected on the surface based on the EDS results.

From the cross-section micrograph of the same sample (Figure 3b) it can be seen that the CuO phase (light grey) is manly present on the surface of the sample, in addition to the spinel phase. Based on the difference in contrast in the BSE image, the bulk of the contact layer consists also of two phases. According to quantitative EDS point analysis, the composition of the lighter grey phase is Mn 43.3 wt %, Cu 32.2 wt % and O 24.5 wt %, while the composition of the darker grey phase is Mn 69.8wt %, O 28.6 wt % and Cu 1.5 wt %. Based on this and the XRD results, the former is likely the spinel phase, while the latter is the Mn\textsubscript{2}O\textsubscript{3}.

Figure 3c and 3d show the SEM micrograph and EDS maps of the CuMn contact layer surface after ageing for 250 h at 750°C. The surface (Figure 3c) is now homogenous and composed of Cu (45 wt.%), Mn (34wt.%) and O (21 wt.%). No other phases can be detected. Inspection of the cross section (Figure 3d) confirms that the light grey layer of CuO has disappeared from the surface. The majority of the contact layer consists of a homogenous mixture of Cu (between 31-28 wt.%), Mn (between 44- 48 wt.%) and O (25-24 wt.%). A single CuO particle (Cu 83 wt % and O 17 wt %) was detected in the middle of the contact layer. This is likely due to insufficient mixing of the green powders in the screen printing paste.
Figure 3 SEM/EDS micrographs of CuMn CL after sintering, top view (a) and cross-section (b) and after ageing at 750°C for 250 h, top view (c) and cross-section (d). The EDS maps in (d) correspond to a small area of the micrograph which is limited by the red dotted frames.

SEM micrographs and EDS maps of the CoMn contact layer on Crofer 22 APU after sintering at 800°C are shown in Figure 4 a and b. The surface analysis (Figure 4a) indicates the presence of two phases. According to quantitative EDS point analysis, one phase is composed mainly of Co (75 wt.%), O (19 wt %) and a small fraction of Mn (6 wt %), while the other phase is composed of Co (39 wt %), Mn (39 wt %) and O (22 wt %). Taking into account the XRD results presented in section 3.1, the two phases are likely Co$_3$O$_4$ and (Mn,Co)$_3$O$_4$ spinel, respectively.

The cross section of the same sample (Figure 4b) shows that the CoMn contact layer after sintering at 800C consists of large, dense agglomerates with finer particles between. According to EDS analysis the larger agglomerates consist of a Mn-oxide core covered by a shell composed of 32 wt% Co, 37 wt% Mn and 32 wt% O. The finer
particles are composed of 73 wt% Co and 27 wt% O. The CoMn contact layer is clearly more porous than the CuMn contact layer (cf. Fig. 4).

SEM micrographs and EDS maps of the CoMn contact layer after ageing for 250h at 750°C are shown in Figure 4c and 4d. The top view micrograph (Figure 4c) shows that contact layer surface has not densified further with ageing compared to after sintering. The surface also remains inhomogeneous after ageing, as some areas with only Co (73 wt.%) and O (27 wt.%) can be detected in the area with the finer particles. The cross section of the same sample (Figure 4d), shows that the Mn found in core of the agglomerate after sintering at 800°C now, after ageing at 750°C, has fully interdiffused with Co and O. The composition according to EDS point analysis (39 wt% Co, 38 wt% Mn and 23 wt% O) indicates that the larger particles are the CoMn spinel. Also after ageing at 750°C, the CoMn contact layer is significantly more porous than the CuMn contact layer after ageing.
Figure 4 Overview SEM micrographs and EDS maps of CoMn after sintering, top view (a) and cross-section (b) and after ageing 250 h at 750°C, top view (c) and cross-section (d). The EDS maps in (b) and (d) correspond to a small area of the micrograph which is limited by the red dotted frames.
3.3 Area specific resistance

The ASR measured during ageing at 750 °C is plotted in Figure 5. The ASR of 441 steel increases throughout the whole measurement and reaches 54.4 mΩcm$^2$ after 2000 h of ageing due to corrosion. The ASR increase of the 441 steel is largest during the first 300 h of ageing, after this, the ASR increases almost linearly with time. With the addition of a CoMn or CuMn contact layer to the 441 steel, the ASR decreases slightly during the first 500 h, before it reaches a plateau and remains nearly constant for the next 1500 h. After 2000 h of ageing at 750°C, the ASR is 23 mΩcm$^2$ for the sample with a CoMn contact layer and 21 mΩcm$^2$ for the sample with a CuMn contact layer, i.e. less than half of the ASR measured for the 441 steel.

During the first 500 h the ASR measured over a single LSM plate shows similar trend as the ASR of the samples with contact layers. With further ageing, the ASR of LSM continues to decrease, but at a slower rate. The stack of samples experienced one unplanned thermal cycle around 450 h. This did not influence the results significantly as the ASR values followed the same trend before and after the thermal cycle.

Figure 5 a) ASR values of 441, LSM and the contact layers measured at 750°C in air, b) illustration of the set-up used for the ASR measurements.
3.4 The Fracture energy

Figure 6f shows a representative plot of the load and displacement recorded during the four-point bending test. While bending the samples at a continuous rate the load first increased to the point of the first crack growth and then continued in a saw tooth pattern. The jagged load response is the result of fast crack growth and arrestment. The fracture energy is evaluated using the load peaks, which corresponds to the load where the crack stopped propagating, as discussed further in Section 4.

The fracture energy, $G_c$, for each contact layer after sintering at 800°C and after ageing at 750°C for 250 h is reported in Table 1. Note that the $G_c$ after ageing decreased to 37 % and 65 % of the $G_c$ value after sintering for the CuMn and the CoMn contact layers, respectively.

<table>
<thead>
<tr>
<th></th>
<th>CuMn CL</th>
<th>After ageing</th>
<th>CoMn CL</th>
<th>After ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_c$ (J/m$^2$)</td>
<td>13.5</td>
<td>5.0</td>
<td>6.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Std. dev. (J/m$^2$)</td>
<td>3.2</td>
<td>1.6</td>
<td>1.6</td>
<td>0.9</td>
</tr>
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Table 1 Measured fracture energies for the two contact layers after sintering at 800°C and after ageing at 750°C for 250 h. CL= contact layer.

3.5 Fractography and microstructural analysis

After the fracture toughness test, the unbroken part of the sample sandwiches were manually broken apart to analyse the fracture surfaces by SEM/EDS. As illustrated by the sketches in Figure 6a and Figure 7a the analysis was made on the area closest to the notch of the sample, corresponding to the area fractured during the four-point bend test.

The different layers (i.e. steel, oxide scale, contact layer) of each sample contain elements that are unique to that layer. By comparing the EDS maps on each side of the fractured sample, the layer or interface where the crack propagation occurred can be identified. Specifically, the combination of Cu (green) and Mn (purple) in the same layer identify the CuMn contact layer, the combination of or Mn (purple) and Co (blue) in the same layer identify the CoMn contact layer, Fe (orange) identifies the Crofer 22 H substrate, while Cr (red) (without Fe) identifies the oxide scale of Crofer 22 H.
Figure 6b to 6e shows the fracture surface of the CuMn contact layer after sintering at 800°C. According to the EDS maps (Figure 6b) the majority of the surface of the top bar is composed of Fe, Cr and Mn. These elements can be assigned to the Crofer 22 H substrate and the oxide scale thermally grown on the substrate during the sintering heat treatment (i.e. \(\text{Cr}_2\text{O}_3\) and \((\text{Mn,Cr})_3\text{O}_4\)). The areas in Figure 6b highlighted by yellow dashed ellipses are rich in Cu and Mn, and can accordingly be assigned to the CuMn contact layer. On the equivalent area of the bottom bar (Figure 6c), Cu, Mn, and Cr are detected. The Mn and Cr can be assigned to the oxide scale formed on the Crofer 22 H during the sintering, while the Cu identifies areas covered by the CuMn contact layer.

A higher magnification image of the fracture surface is shown in Figure 6e. According to the EDS maps, in the fractured area there is a nucleus of oxidized Mn, covered by a shell of Mn, Cu and O.

The above analysis of the fracture surface indicates that the crack mainly propagates at the interface between the contact layer and the Crofer 22 H substrate, and to only a limited extent within the contact layer itself. The fracture pattern is schematized in Figure 6d.

Figure 6g to 6i shows the fracture surface of the CuMn contact layer after ageing at 750°C for 250 h. EDS analysis of the surface of the top bar (Figure 6g) shows that the majority of this surface is covered by Fe, Cr and Mn. All of these elements can be assigned to the Crofer 22 H substrate and thermally grown oxide scale. In addition, a smaller area of the surface has a relatively higher concentration of Fe. This area corresponds to the brightest contrast areas in the SEM-BSE image and may be assigned to the steel substrate (i.e. no oxide scale). The corresponding area of the bottom bar has two main compositions present, one rich in Cu and Mn and one rich in Cr. The Cr area corresponds to the Fe-rich area found on the top bar. Based on these results, as schematized in Figure 6i, it is possible to conclude that the crack propagates partly through the contact layer and partly through the \((\text{Mn, Cr})_3\text{O}_4\) corrosion scale on the Crofer 22 H, but primarily through the latter.
Figure 6 SEM micrographs and EDS maps of CuMn contact layer after sintering at 800°C (a) sketch of sample with the analysed area indicated by a stippled rectangle. (b) fracture surface, top bar and (c) bottom bar. (d) Schematic of the fracture mechanism (e) higher magnification SEM and EDS. (f) An example of recorded load-displacement curves (g). SEM micrographs and EDS maps of CuMn contact layer after ageing at 750°C for 250, top bar (h) bottom bar. (i). Schematic of the fracture mechanism.
Figure 7b-d show the fracture surface of the CoMn contact layer after sintering at 800°C. EDS maps from the surface of the top bar (Figure 7b) show that mainly Mn are present in the lighter contrast areas of the SEM-BSE image, the elemental analysis shows the presence of Fe and Cr, although the EDS maps are not reported in the figure. These elements can be assigned to the Crofer 22 H substrate. The darker contrast areas (highlighted by yellow dashed ellipses in Figure 7b) are rich in Co and Mn, and can accordingly be assigned to the CoMn-contact layer. EDS maps of the surface of the bottom bar (Figure 6f), show the presence of Co, Mn, and O, which can be assigned to the CoMn contact layer. Based on these results, it may be concluded that the crack propagates mainly at the interface between the contact layer and the Crofer 22 H, and only to a lower extent it propagates within the contact layer. This is schematically illustrated in Figure 7d.

Figure 7e-g show the fracture surface of the CoMn contact layer after ageing at 750°C for 250h. On the central part of the surface of the top bar (Figure 7e) mainly Co and Mn are detected, indicating the CoMn contact layer. The surrounding area is rich in Fe, Cr and Mn, indicating the presence of the Crofer 22 H substrate and a Cr$_2$O$_3$/(Mn,Cr)$_3$O$_4$ oxide scale. On the bottom bar (Figure 7f), the central part of the surface contains Co, Mn and O, while the surrounding area is Cr-rich. I.e. the central area corresponds to the contact layer while the surrounding area corresponds to the Cr$_2$O$_3$/(Mn,Cr)$_3$O$_4$ oxide scale. These observations indicate that the crack propagates within the CoMn contact layer in the central part of the fractured area. And in the outer part it propagates at the interface between the oxide scale and the Crofer 22 H.
Figure 7 Overview of SEM micrographs and EDS maps of CoMn contact layer after sintering. A sample with highlighted analysed area (a). CoMn on Crofer 22 H (b) top bar SEM and EDS and (c) bottom bar SEM and EDS. The sketch of the fracture mechanism in (d). Overview of SEM micrographs and EDS maps of CoMn contact layer after ageing at 750°C for 250h: CuMn on Crofer 22 H (e) top bar SEM and EDS and (f) bottom bar SEM and EDS. The sketch of the fracture mechanism in (g).
4 Discussion

4.1 Mechanical properties

For both, the CoMn contact layer and the CuMn contact layer high energy release rates of \(6.0 \text{ J/m}^2\) and \(13.5 \text{ J/m}^2\), respectively, were measured on the as-prepared samples. Also after 250 h of ageing at 800 °C, the fracture energies measured (3.9 J/m\(^2\) for CoMn and 5.0 J/m\(^2\) for CuMn) are still 4-5 times higher than in state-of-the-art contact materials like LSM and LSC [38], as illustrated in Figure 8.

Figure 8 Fracture energies for the two cathode contact layers: CuMn contact layer and CoMn contact layer, after sintering and after 250h at 750°C, and as a reference, the results from Tucker 2013 et al and Han et al 2019.

The reason for the decrease in fracture energy during the 250 h of ageing is believed to be due to changes in the microstructure and the associated changes in the crack paths. Based on SEM image analysis, it can be concluded that the as prepared sample consist of larger Mn\(_2\)O\(_3\) particles surrounded by more or less homogenously distributed Cu\(_{1.2}\)Mn\(_{1.8}\)O\(_4\) spinel (Figure 3a-b). This structure resembles a composite material consisting of Mn\(_2\)O\(_3\) filler material within a Cu\(_{1.2}\)Mn\(_{1.8}\)O\(_4\) matrix.
After 250 h of ageing, the microstructure is more homogenous. Also the microstructure in the SEM appears to be more homogenous and Cu, Mn and O appear evenly distributed in the elemental maps (Figure 3 c-d).

Possible crack paths in these two microstructures are expected to be different. In the as prepared sample, the crack path through the spinel phase/Mn$_2$O$_3$ particles composite is more tortuous as compared to the rather straight crack path expected in the aged sample with a more homogenous microstructure. The longer path, induced by the tortuosity, in the as prepared samples would result in a higher effective surface area and thus a comparatively higher surface energy. Furthermore, the crack also propagates through the corrosion scale for both the aged CoMn and CuMn contact layer, which is also a brittle ceramic layer. These hypothesis could explain the decrease in $G_c$ and the lower load measured to initiate and propagate the crack after ageing.

A comparable microstructural development was found for the CoMn contact layer. As observable in the SEM images for the as prepared sample (Figure 4), the MnCo$_2$O$_4$ spinel is forming on the surface of the Mn$_2$O$_3$ particles. Additionally, Co$_3$O$_4$ was identified as third phase in the XRD pattern (Figure 2). After 250 h of ageing, the fraction of the MnCo$_2$O$_4$ the microstructure is significantly homogenized, which again may be the explanation for the lower fracture energy measured in the aged samples.

Compared to the CuMn contact layer, the CoMn contact layer has a significant higher porosity. This can be explained with the higher sintering temperatures typically needed for the formation of a dense CoMn spinel (1100°C) [39]. The higher porosity is most likely also the reason for the measured lower fracture energy as compared to the CuMn contact layer.

The inhomogeneous microstructure also give rise to a more uneven crack propagation, which can be seen on the recorded load-displacement curve in Figure 6f. For a homogeneous material, the load would reach a plateau, due to a continuous crack propagation, when the displacement is at a continuous rate. The load plateau is usually used to determine the $G_c$ (using Eq. (2)). In this case of the inhomogeneous
microstructure the load does not reach a plateau, instead there are several peaks. Figure 6b-c show the inhomogeneous fracture surface with two distinct spots. A possible explanation is that the crack is stopped at these irregularities, where the fracture energy is built up. Once the fracture energy is high enough the crack propagates through these higher toughness areas but also propagates swiftly through the more homogeneous material behind (resulting in the drops after the peaks). The high toughness areas would thus stop a crack in real use and for this reason the peaks are used as the critical fracture energy, $G_c$, for the contact layer.

4.1.1  Comparison with state-of-the-art described in literature

As seen in Figure 8 other attempts to increase the interface adherence of contact layers have been researched in past studies. The highest value for the fracture energy reported is 12.3 J/m$^2$, which was achieved by mixing glass into the contact layer material to join Mn$_{1.5}$Co$_{1.5}$O$_4$ coated ASI441 steel at 1000 °C. Although the addition of glass improves the mechanical properties, insulating properties of the glass negatively influenced the electrical performance of the contact layer [35]. A compromise with a lower amount of glass added showed a sufficient high conductivity, but the fracture energy dropped down to 5.4 J/m$^2$. Furthermore, it should be pointed out that the high assembly temperature of 1000°C are used in the preparation of these samples, i.e. 200 °C more than in this study. As mentioned before, such high temperatures could be damaging to some components of the SOC stack.

Another study from Han et al. (see Figure 8 [38]) investigated the suitability of several materials as contacts between oxygen electrodes and coated metallic interconnects. The highest fracture energy (8.6 J/m$^2$) reported in this study is related to the use of metallic CuMn foam as contact layer. It should be noticed that all values reported in this study were for as prepared samples, the influence of ageing on the interface stability was not investigated in the study. Another interesting point mentioned in the study from Han et.al is that the coating of the interconnect can significantly increase the robustness of the interface. This finding indicates that the interface stability in the here reported system, i.e. bare steel without coatings, could possibly be further increased. Also in terms of up-scalability the here presented route (simple use of
metallic Cu and Mn or Co powder) is more promising because; i) the production cost of the CuMn foam is expected to be more expensive due to the complex processing route, ii) and the foam needs to be applied over the complete cell area while the CuMn powders can be selectively printed at the contact points between the interconnect and the oxygen electrode.

4.2 Electrical properties

The ASR measured for the 441 steel contacted to LSM increased rapidly during ageing at 750°C and reached 54.4 mΩcm⁻² after 2000 h. This behaviour is similar to the ASR values previously reported in literature when using a comparable measurement set-up. For example, Stevenson et al. [40] reported that the ASR of 441 after 2000 h at 800°C was ~ 35 mΩcm⁻² while Molin et al. [41] reported that the ASR of bare Crofer 22 APU was around 45 mΩcm⁻² after 40000 h of ageing at 750°C. The high resistance and increase in ASR with time can be attributed to the growth of poorly conductive oxide scales on the steel surface. In case of the 441 steel, formation of Cr₂O₃ and SiO₂ likely dominate the measured ASR [40].

By applying a CuMn or CoMn contact layer between the 441 steel and LSM contacting plate, the ASR is decreased to less than half and remains nearly constant with time. As discussed above, the CuMn and CoMn contact layers are oxidized during heat-up of the stack to form well-conductive Cu₁.₃Mn₁.₇O₄ (225 S/cm at 750°C [23]) and MnCo₂O₄ (89 S/cm at 800°C [24]), respectively. Since the electrical conductivity of these oxides is much larger than the conductivity of the native oxide scale formed on the steel (~0.01-0.1 S/cm for Cr₂O₃ at 800°C [42,43]) it may be concluded that the contact layers do not contribute significantly to the resistance of the interconnect. Instead, the results here show that the contact layers improve the ASR of the 441 steel contact layer assembly.

The improvement in ASR achieved with the application of the contact layers is similar to the improvements previously observed by application of protective coatings such as Mn₁.₅Co₁.₅O₄, MnCo₂O₄ and MnCo₁.₇Cu₁.₃O₄ [24,27,40]. This is not surprising considering that the composition and structure of the contact layers is very similar to
that of the protective coatings, i.e. Mn and Co/Cu-based spinel oxides. An important distinction is that the coatings tested in previous works were prepared by depositing an oxide power (by spraying or electrophoretic deposition) and subsequently heat treating the coating in two-steps in order to densify it [24,27,40]. Here, a comparable protection is achieved by in-situ sintering of the contact layer. An even greater reduction in ASR may be achieved by combining the contact layers with a CeCo coating on the 441 steel, as shown in [44].

The CuMn contact layer resulted in a slightly lower ASR than the CoMn contact layer, but the differences are almost within the uncertainty of this type of ASR measurement, where porous LSM is used as the contacting surface. As seen in Figure 5, the ASR measured over the LSM contacting plate alone decreases with time. This can be attributed to creep and sintering of the contacting plate, resulting in a change in the effective contacting area with time [27,45,46]. Although this somewhat masks the changes in ASR of the other samples, the use of lightly sintered LSM plates provides a more realistic measurement of the contacting between the cell and the interconnect in a real SOC stack compared to using Pt or other noble metals [47,48].

4.3 Conclusions

In this work a novel route for processing a robust and well conducting contact layer to join solid oxide cell air electrode and interconnect has been shown. The concept utilizes the reactive energy of the in-situ oxidation of metallic powders at high temperature to ensure interdiffusion into neighbouring surfaces and assisting the sintering to form a denser and better adhering contact layer. Metallic powders in a stoichiometric ratio were thus deposited onto the cells by screen printing to in-situ form well conducting spinels through the thermal treatment of the solid oxide cell stack assembly.

Two compositions of contact layers, containing Cu+Mn and Co+Mn, were synthetized, characterized and tested. The mechanical performances were tested in terms of fracture energy, resulting in very high fracture energies of 13.5 J/m² and 6.0 J/m² after sintering for the CuMn and CoMn contact layers, respectively, as compared to the
conventional perovskite contact layers of 1-2 J/m². The fracture energy did however drop down to 5.0 J/m² for the CuMn contact layer and 3.9 J/m² for the CoMn contact layer after ageing at 750°C for 250 h. Microscopy indicated that the failure after ageing was primarily occurring through the oxide scale and that the drop of the fracture energy in these measurements are thus primarily due to that the samples were uncoated and that the oxide scale formed on the 441 steel is comparatively weak.

The CuMn contact layers formed the denser contact layer, as Cu acts as a sintering aid, why the CuMn also became the stronger of the two investigated contact layers. The density of the CoMn contact layer, as shown from the SEM micrographs, could be improved resulting in a further improvement of both conductivity and fracture energy. Micrographs and EDS also showed that the failure primarily occurred in the interface between the contact layer and the steel substrate for both contact layers. The steels in this study were not protected by a coating. Literature and preliminary results indicate that coatings will further promote the adhesion of this new type of contact layers.

Relatively low area specific resistances (ASR) of the contact layer interconnect steel assembly of 21-23 mΩcm² were measured. The electric resistance of the corrosive scale was believed to provide the main contribution to the ASR. The contact layers were indeed found to reduce the ASR increase over time indicating that the contact layers also protected the steel as a coating.

Acknowledgements

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Paper 4

*Improved Robustness and Low Area Specific Resistance with Novel Contact Layers for the Solid Oxide Cell Air Electrode.*
Improved Robustness and Low Area Specific Resistance with Novel Contact Layers for the Solid Oxide Cell Air Electrode

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Stacking of solid oxide cells (SOC) requires that a robust and durable electrical contact between the cell and the interconnect is established. In this work we present a new contact layer solution for the SOC air side, based on the concept of reactive oxidative bonding. The contact layer consists of metallic Mn-Co and Mn-Cu particles that during initiation/operation are oxidized \textit{in-situ} to form well-conductive spinel oxides. The long-term (3000 h) stability of the new contact layers is evaluated by measuring the area specific resistance (ASR) during aging in air at 750 °C, and during thermal cycling. Both Mn-Co and Mn-Cu layers are found to be well compatible with the applied CeCo coated 441 steel, and do not significantly contribute to the resistance across the stack element, which is dominated by the coated steel.

Introduction

Stacking of solid oxide cells (SOC) requires that a robust and durable electrical contact between the cell and the interconnect is established. To achieve this, contact layers are applied during the cell fabrication process or the stack assembly. The contact layer material should have a high electrical conductivity, a suitable thermal expansion coefficient (TEC), be mechanically robust and chemically compatible with the adjacent electrode and interconnect materials. Most planar SOC stacks today employ perovskite oxides as the contact material on the air/oxygen side (1). The perovskites oxides are attractive due to their high electrical conductivity and suitable TEC, however, “hard” sintering of these materials requires high temperatures, (>1100 °C), which may have an adverse effect on other SOC stack components, such as the steel interconnects and the seals (2). As a result of poor sintering at lower temperature, the interface between the air electrode and the interconnect is among the weakest in the stack and the one most prone to loss of contact (3).

In this work we present a new contact layer solution for the SOC air side, based on the concept of reactive oxidative bonding. The contact layer is applied in the form of metal particles that during SOC stack operation (700-800 °C) are oxidized \textit{in-situ} to form well-conducting spinel oxides. The metallic precursors investigated in this work are Mn-Co and Mn-Cu, mixed in the stoichiometric ratio to form Mn\textsubscript{2}Co\textsubscript{3}O\textsubscript{4} and Cu\textsubscript{1.3}Mn\textsubscript{1.7}O\textsubscript{4}, respectively. Both oxides have an appreciable electrical conductivity (70 and 225 S/cm at 750 °C, respectively) and a TEC (14.4 and 12.2 K\textsuperscript{-1} between 25 °C and 800 °C, respectively) matching other typically used SOC materials (4, 5). Due to the high reactivity of the metallic precursors, a strong bond is created to both the coated...
interconnect and the air electrode. According to results presented elsewhere (6), the fracture energy of the interconnect-air electrode interface with this contact layer solution is almost a factor of 10 higher than with conventional perovskite oxide based contact materials.

Here, we evaluate the electrical conductivity and long-term stability of the new contact layers by measuring the area specific resistance (ASR) of a stack element comprising a steel interconnect, the contact layer and an air electrode. The ferritic stainless steel AISI 441 is chosen as the interconnect material due to its lower cost compared to more specialized steel grades developed specifically for interconnect application, such as Crofer 22 APU. Previous studies have indicated the potential of 441, but also several challenges, such as formation of insulating silica scales and a poor oxide scale adhesion (7, 8). However, coating the 441 steel with a thin layer of CeCo seems like a promising solution to these challenges (9).

The ASR is recorded during isothermal aging at 750 °C, as well as during thermal cycling. The thermal cycling was introduced to check the mechanical robustness (interface adherence) of the stack elements after the growth of an oxide scale and aging of a fully oxidized interface between the coupling components and the interconnect.

**Experimental**

A detailed description of the set-up for the ASR measurement can be found in (10). The ferritic stainless steel AISI 441 in 0.3 mm thickness served as the interconnect material. One side of the steel was coated with CeCo (Sandvik Materials) while the other side was left uncoated. The steel was cut into 20x40 mm\(^2\) coupons and a Pt wire was spot welded along one of the shorter edges of the uncoated side, to act as a voltage probe.

A contact layer (CL) paste for screen printing was prepared using Mn(32 wt.%) - Co(68 wt.%) and Mn(53 wt.%) - Cu(47 wt.%) metallic powders (American Elements), in the stoichiometric amounts to upon oxidation form MnCo\(_2\)O\(_4\) and Cu\(_{1.3}\)Mn\(_{1.7}\)O\(_4\), respectively. The pastes were screen printed onto a 20x20 mm\(^2\) area of the interconnect with a green thickness of 0.2 mm. The paste was dried at 90 °C for 1 h to evaporate the solvent before assembly.

Bisque-sintered La\(_{0.85}\)Sr\(_{0.1}\)Mn\(_{1.1}\)O\(_3\) (LSM) plates (20x20x1 mm\(^3\)) spray coated with a 50-60 µm layer of LSM and Co\(_3\)O\(_4\) slurry mixture was used as current collection plates. The LSM plates were stacked between the interconnect coupons as illustrated in Figure 1. Gold foil connected to gold wires was placed on the top and bottom of the stack to supply the current. A load of 7 kg was put on top of the stack. The stack was heated in stagnant air following a representative SOC stack heat-up profile used when employing glass-ceramic sealants, see reference (11). This involved heating to 600 °C at 100 °C/h, holding for 1 h, heating to 700 °C at 100 °C/h, heating to 800 °C at 50 °C/h, holding for 1 h and finally cooling to 750 °C at 120 °C/h. At 750 °C, a measurement current of 2 A was employed, corresponding to 0.5 A/cm\(^2\) considering the nominal contact area between the steel interconnect and the LSM plate.
The ASR was calculated according to Ohm's law, by measuring the voltage drop between the Pt-wire connected to the interconnect and a Pt-wire placed between two LSM plates. As illustrated in Fig. 1, the cross-plane resistance (ASR) is measured across five different configurations: a) LSM, b) 441/LSM, c) 441/CeCo/LSM, d) 441/CL/LSM, and e) 441/CeCo/CL/LSM. At least two interfaces of the same type were evaluated. After 3000 h of aging at 750 °C, the stack was thermally cycled 50 times between 750 °C and 200 °C (120 °C/h heating and cooling rate), with a dwell of 5 h at 750 °C between each thermal cycle.

Microstructural characterization after the ASR measurement was performed using a scanning electron microscope (SEM, Hitachi TM3000).

**Figure 1.** Illustration of set-up used for measuring the area specific resistance. CL = Contact Layer (Mn-Co or Mn-Cu).

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### Results and Discussion

#### Isothermal aging at 750 °C

The ASR recorded across the different interfaces during isothermal aging at 750 °C in air is shown in Figure 2. During the 3000 h period the samples were exposed to two unplanned thermal cycles (at ca. 400 h and 2100 h). For clarity, only one curve representative for each interface is plotted in Figure 2. The maximum difference between two ASR measurements of the same interface was ±3 mΩcm² for all but the 441/LSM interfaces, for which the scatter was greater (±16 mΩcm²). A summary of the average ASR values measured after 3000 h is given in Table I. A degradation rate (increase in ASR with time) was calculated by a linear fit of the ASR recorded the last 500 h of
isothermal aging. The results are presented in Table I. Note that the ASR is calculated on the basis of the nominal contact area (4 cm²), and that there likely is some difference in the actual contact area among the different samples, e.g. due to slight misalignment between the components and other unintended differences in the established area of contact. For this reason, the change in ASR with time provides a more important measure for comparison than the absolute values of the ASR.

For all but the 441/LSM interfaces the ASR decreased during the initial 1000-2000 h of aging due to improvement of the area of contact and improved conductance of the green and only mildly sintered layers. This is primarily due to creep and sintering of the LSM contacting plates, which are pre-sintered under mild conditions and coated with a LSM/Co₂O₃ layer. As a consequence, the ASR measured across a single LSM plate continues to decrease over the entire duration of the measurement (12).

The ASR of the 441/LSM interface increased rapidly from the start of the measurement and reached 70±16 mΩcm² after 3000 h of aging, which is above the acceptable limit for the interconnect ASR (50 mΩcm²) suggested in some papers (13). The high ASR can be attributed to the relatively faster growth of poorly conductive oxide scales (Cr₂O₃ and SiO₂) on the uncoated 441 steel (7). Compared to the uncoated steel, the ASR after 3000 h of aging is reduced by a factor of 2.6 with the CeCo coating. Previous ASR measurements have shown that a <1 µm thick CeCo coating does not contribute significantly to the cross plane resistance, instead, the ASR is dominated by the thermally grown oxide scale on the steel (14). Thus, the low and stable ASR for the 441/CeCo/LSM interface indicates a reduced growth rate and/or improved electrical conductivity of the oxide scale.

Comparing the ASR measured for an interface with the contact layer (e.g. 441/CeCo/Mn-Co/LSM) with the equivalent interface without the contact layer (e.g. 441/CeCo/LSM), it is clear that the contact layer does not contribute significantly to the cross-plane resistance. This is reasonable considering the much higher electrical conductivity (at 750 °C) of MnCo₂O₄ (70 S/cm) and Cu₁.₃Mn₁.₇O₄ (225 S/cm) compared to Cr₂O₃ (0.1-0.01 S/cm (15, 16)) and SiO₂ (10⁻¹⁰-10⁻⁸ S/cm (17)), which are the primary constituents of the oxide scale formed on the 441 steel. The contact layers may nevertheless indirectly have influence on the ASR through reactions with the coating, oxide scale and/or LSM plates. According to the degradation rates presented in Table I, the Mn-Cu contact layer results in a small improvement compared to the CeCo coating alone, while the Mn-Co contact layer slightly increases the degradation rate relative to the 441/CeCo/LSM interface.

Applying the Mn-Co or Mn-Cu contact layers directly to the 441 (i.e. no CeCo coating) also results in low and more stable ASR compared to the bare steel. This is not surprising considering that the oxidized form of the contact layers, i.e. MnCo₂O₄ and Cu₁.₃Mn₁.₇O₄, have been employed as interconnect coatings (18–20). Nevertheless, it is clear that the best performance in terms of ASR is achieved by combining the contact layer with a CeCo coating. The CeCo coating is furthermore beneficial for reducing the release of poisonous Cr(VI)-species from the interconnect (21).
Figure 2. ASR measured in air at 750 °C. Right side plot shows an excerpt of the ASR between 15 and 35 mΩcm².

TABLE I. ASR measured after 3000 h at 750 °C and degradation rates extracted from last 500 h of ASR measurement. Activation energy for ASR determined during cooling from 750 °C to 500 °C. Average and standard deviation of measurement of 2-4 interfaces of the same kind.

<table>
<thead>
<tr>
<th>Interface</th>
<th>ASR after 3000 h [mΩcm²]</th>
<th>Degr. rate [mΩcm²/1000h]</th>
<th>ASR after 50 thermal cycles [mΩcm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM (contact component only)</td>
<td>28</td>
<td>-0.7</td>
<td>29</td>
</tr>
<tr>
<td>441/LSM</td>
<td>70±16</td>
<td>8.8</td>
<td>80±29</td>
</tr>
<tr>
<td>441/CeCo/LSM</td>
<td>25±3</td>
<td>-0.3</td>
<td>24±3</td>
</tr>
<tr>
<td>441/Mn-Co/LSM</td>
<td>25±1</td>
<td>0.8</td>
<td>24±1</td>
</tr>
<tr>
<td>441/Mn-Cu/LSM</td>
<td>21±1</td>
<td>0.3</td>
<td>20±1</td>
</tr>
<tr>
<td>441/CeCo/Mn-Co/LSM</td>
<td>19±2</td>
<td>0</td>
<td>20±1</td>
</tr>
<tr>
<td>441/CeCo/Mn-Cu/LSM</td>
<td>18±1</td>
<td>-0.3</td>
<td>17±1</td>
</tr>
</tbody>
</table>

Thermal cycling

Figure 3 shows the ASR during 50 thermal cycles between 750 °C and 200 °C. For clarity, only the ASR recorded at 750 °C is plotted. The ASR measured after the 50th cycle is reported in Table I. In case of the uncoated 441 steel directly contacted to LSM, the degradation rate during thermal cycling is increased to 13.5 mΩcm²/1000 h, compared to the degradation rate during isothermal aging at 750 °C (8.8 mΩcm²/1000 h). The increased ASR during thermal cycling may be caused by a decrease in the effective contact area between the steel and LSM plate, due to partial oxide scale spallation. Oxide scale spallation typically occurs during thermal cycling due to stresses that develop from the TEC mismatch between the steel and the oxide scale and is a known challenge with the 441 steel (22, 23).

For the samples with a CeCo coating and/or Mn-Co/Mn-Co contact layer the degradation rate during the thermal cycles is similar to that measured during the last 500 h of isothermal aging at 750 °C, i.e., the thermal cycles do not accelerate the degradation. This can be attributed to the good TEC match and sufficiently strong bonding between the different layers, which is supported by the high values of interface toughness reported in (6).
Post-ASR microstructural analysis

SEM cross sectional images of selected interfaces after the ASR measurement are shown in Figure 3. Both the Mn-Co and the Mn-Cu contact layers, which were deposited as metallic particles, are fully oxidized after the > 3000 h of aging at 750 °C. On the non-coated 441 steel (Fig. 3a) an oxide scale of ca. 3.0-3.5 µm thickness has formed. On the CeCo-coated steel contacted with Mn-Co (Fig. 3b) the thickness of this oxide scale was reduced to ca. 2.0-2.5 µm, while on the CeCo-coated steel contacted with Mn-Cu (Fig. 3c) the thickness of this oxide scale was reduced to ca. 1.0-1.5 µm. These observations correlate with the ASR measurements, where interfaces with the Mn-Cu contact layer were shown to give the lowest ASR. In case of samples with the Mn-Cu contact layer, the interfaces between the oxide scale, coating and contact layer are difficult to distinguish due to interdiffusion of Cr and Cu at the interfaces. This interdiffusion likely contributes to the strong interface adherence achieved with the Mn-Cu contact layer, as presented in (6).
Conclusions

The metallic precursors Mn-Co and Mn-Cu have been evaluated as contact materials for solid oxide cell stacks by measuring the area specific resistance (ASR) during aging at 750 °C. The precursors are oxidized to well-conductive spinels during aging. The ASR was found to be dominated by the oxide scale thermally grown on the 441 steel and was significantly reduced by the application of a CeCo coating. The lowest ASR was measured for CeCo coated 441 with a Mn-Cu contact layer. Both Mn-Co and Mn-Cu were found to be well compatible with the CeCo coated 441 steel, and did not significantly contribute to the resistance across the stack element. These materials are thus promising for the application as SOC air side contact layers.

Acknowledgments

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Paper 5

Enhancing the Robustness of Brittle Solid Oxide Cell Stack Components.
For long-term durability and robustness to withstand thermal cycles, the planar solid oxide cell (SOC) stack technologies are challenged by the use of brittle components. With the current trend of increasing the footprint of the SOC stacks, even larger thermal gradients and thermal stresses can be expected. In this overview paper, we present recent advances from our group on improving the fracture energy of three critical materials/interfaces. The fracture energy of the fuel electrode support is increased by ~50 % by tailoring composition and further optimizing the phase transformation toughening. The fracture energy of the air-side contact layer is increased by a factor of ~10 by using metallic pre-cursors that are transformed to spinels through in-situ reactive oxidative bonding. Finally, the fracture energy of the seal-interconnect interface is improved by a factor of 5 by combining an optimized sealing glass with aluminum based coatings for the interconnect.

Introduction

In planar Solid Oxide Cell (SOC) stack technology the cells are either electrolyte or fuel electrode supported. By introducing an extra layer on the fuel electrode side, beyond the electrochemical active layer, the properties of the two fuel electrode layers can be optimized separately. The resistance towards in-plane crack propagation can thus be optimized by structural and material optimization of the separate fuel electrode support layer. This layer should allow for gas diffusion and conduction of electrons, but has no electrochemical function, as this is handled by the active layer close to the electrolyte.

The current state of the art for the support layer is a cermet of Ni and three mol% yttria doped zirconia (3YSZ) (1,2), which is considerably tougher (+ 60-70 %) than 8 mol% yttria doped zirconia (8YSZ) (3,4). The increased fracture toughness of 3YSZ stems from the martensitic phase transformation of metastable tetragonal zirconia to monoclinic zirconia. At crack propagation the high tensile stresses at the crack tip trigger the transformation, thereby inducing a volumetric expansion at the crack tip and in the wake of the crack, shielding the crack tip. The effectiveness of this toughening mechanism can be optimized by enhancing the transformability, which depends primarily on the amount of stabilizer, grain size and temperature, but also on porosity of the support to a small extend (5). Lowering the amount of yttrium substitution (serving as a stabilizer) might increase the fracture toughness, but the stability towards low and high temperature hygrothermal degradation is critically decreased (6).
Here, we will present how co-doping the zirconia with cerium and yttrium can increase the fracture energy of the fuel electrode support by ~50 % compared to the state-of-the-art NiO-3YSZ, without compromising the hygrothermal stability.

Other critical interfaces in planar SOC stacks are those between the cell and the interconnect. On the fuel electrode side Ni meshes or foams can be used to ensure good adhesion and current distribution (7–9). However, the adherence between the oxygen electrode and the interconnect is more challenging. Conventionally, contacting on the oxygen side is established by use of perovskite oxide contact layers, which are made of a composition similar to that of the oxygen electrode itself. This layer can be sintered in-situ during stack assembly to ensure a good contact to both the cell and the interconnect. The challenge is however to have sufficient sintering activity, as the temperature and hold time is limited by the other components of the SOC stack, primarily the metallic components (10). Lowering the grain size and addition of sintering aids have been attempted, with limited success (11,12). A loss of contact between the interconnect and oxygen electrode will result in redirection of current in less conductive materials, ohmic heating, and possibly a progressive development of failure due to the local higher temperatures. Therefore, the robustness of the oxygen electrode contact layer is critical in the SOC stacks.

Here, we show how application of reactive oxidative bonding, based on metallic precursors (Cu,Co,Mn) that in-situ form a well-conducting spinel oxide (13), can enhance the fracture energy of the interface approximately by a factor of 10 as compared to the in-situ sintered perovskite type contact layers.

The cells and different steel components in the planar SOC stacks are often joined by use of glass-ceramic seals. The gas tightness and integrity of the SOC stack depends critically on high robustness of the glass ceramic seals. Recently it was shown that the mechanical robustness of the sealing of SOC stacks not only depends on the glass-ceramic sealing material itself, but also on the adjacent interfaces, typically interconnect coatings and the zirconia of the cell (14). The choice of the coating material and its surface roughness significantly influences the adherence of the sealing to the steel components of the stack.

Here we show how the combination of an alumina based coating and a recently developed glass ceramic (15) can increase the fracture energy of the glass ceramic joint by more than a factor of 5, as compared to the adherence between the sealing and a pre-oxidized or Mn,Co-oxide (MCO) coated steel interconnect.

**Experimental**

**Fuel Electrode Support Layer**

Yttria doped zirconia powders 8YSZ (mixture of 16 mole % YO$_{1.5}$ and 84 mole % ZrO$_2$) and 3YSZ (mixture of 6 mole % YO$_{1.5}$ and 94 mole % ZrO$_2$) were acquired from Tosoh (Japan), and a ceria-yttria co-doped zirconia (1.5CeO$_2$ 4.5YO$_{1.5}$-SZ) (mixture of 4.5 mole % YO$_{1.5}$, 1.5 mole % CeO$_2$ and 94 mole % ZrO$_2$ powder) was specifically manufactured by Nanoe (France). The choice of the composition for the latter was found through a careful optimization, where the highest possible transformability is found while...
ensuring stability during processing (milling, sintering etc.) (16). The zirconia powders were mixed with NiO in the ratio of 45 wt% and 55 wt%, respectively. The fuel electrode supports were shaped by tape casting, such that they after sintering (~1315°C) had an average thickness of 200-300 μm. The sintered supports were cut by a laser into samples with in-plane dimensions of 40×20 mm². For the double torsion beam (DTB) experiment a slit of 10 mm was cut centrally (0.5 mm wide), with the last 2 mm cut as a notch, to concentrate stress and ensure a small resistance to crack initiation.

The testing was done with the double torsion beam method where the central loads were generated by a constant displacement rate of (0.6 mm/min). In the specified geometry the torsional moments do not increase with crack length, which ensures stable crack growth and a constant load through crack propagation. The constant load is used in the calculation of the critical energy release rate / fracture energy, $G_c$, for the crack propagation.

**Oxygen Electrode Contact Layer**

The oxygen electrode contact layers were made by mixing Cu, Co and Mn metallic particles (American Elements, USA) in stoichiometric amounts to form MnCo₂O₄ and Cu₁.₃Mn₁.₇O₄ spinel after in-situ oxidation.

The metallic powders were screen printed onto short coated interconnect (IC) steel pieces (29 mm x 3 mm) and consequently sandwiched with a twice as long interconnect piece (60 mm x 3 mm) to form the symmetric sandwiched samples, illustrated in Figure 1. The symmetric sandwiched configuration was chosen to avoid the energy release from residual stresses during crack propagation. This should otherwise have been estimated and subtracted from the measured fracture energy thereby introducing significant uncertainty.

The interconnects bars were made of 0.5 mm thick Crofer 22 H (C22) (VDM metals, USA) and "cut" to shape by a chemical etching process.

The samples were heat treated in air to ensure the bonding between interconnects and contact layer, in which process the metallic particles react and oxidize in-situ, forming spinel type oxides. The heat treatment procedure followed represents a typical SOC stack heat-up protocol: heating up from 20 to 600°C at 100°C/h, 1 hour hold, heating up to 700°C at 100°C/h, heating up to 800°C at 50°C/h and hold for 1 hour. The samples were loaded with 16.7 N/cm² to assist the bonding.
Glass Ceramic Sealing

The sealing material applied was an alumina-silicate-based glass (15). The powder used was prepared in-house at DTU Energy, (please see Ref. (15) for further details on the preparation). The powders were screen printed on the coated interconnect “bars” (shorter ones) subsequently sandwiched with the full length pieces (60 mm long), using the same procedure as for the contact layer. The geometry is the same as for the contact layer samples (see Figure 1) with the only difference that the contact layer is replaced by glass. During heat treatment the glass densifies, crystalizes and bonds with the adjacent surfaces (14). The samples are heat treated with an optimized heating profile (15), which corresponds to the one used for the heat treatment of the contact layers.

The interconnects bars were made of 0.5 mm thick Crofer 22 H (VDM metals, USA) “cut” to shape by a chemical etching. The interconnects were coated in-house with an alumina coating, where aluminum metallic powders are deposited on the steel, and heat treated to diffuse and partly alloy with the steel substrate and oxidize to form a thin (~1 µm) alumina (Al₂O₃) coating on the surface (18,19).

Analysis

Double Torsion Beam Test

The fracture energy for the double torsion beam test was deduced from the load according to (20):

\[ G_c = \left( \frac{PW_m}{t^2} \right)^2 \frac{3(1 + \nu)(1 - \nu^2)}{W\psi E} \]  \[ \text{[1]} \]

where \( P \) is the applied load, \( W_m \) is the moment arm, \( W \) and \( t \) are the width and thickness of the specimen, respectively. \( E \) and \( \nu \) are Young’s modulus and the Poisson ratio, respectively. \( \psi(t, W) \) is a correction factor for specimen thickness (21):

\[ \psi = 1 - 1.2604(t/W) + 2.4(t/W) \exp(-W\pi^2/2t) \]  \[ \text{[2]} \]

Four-Point Bending Using Charalambides Geometry

The critical energy release rate, \( G_c \), in the applied four point bending tests (used here for the IC/contact layer and IC/sealing samples) is determined by (22):

\[ G_c = \frac{M_F^2}{2E_2} \left( \frac{1 - \nu_2^2}{I_2} - \frac{1}{I_c} \right) \]  \[ \text{[3]} \]
where $E_2$, $\nu_2$ and $I_2$, are the Young’s modulus, Poisson’s ratio and second moment of area of the through-going substrate of Crofer 22 APU, respectively. The indexes 2 and $d$ here refer to that of the adhering layer (glass-ceramic layer/contact layer), and the substrate (long metal slip), respectively. $I_c$ is the combined second moment of area of the stiffeners and the adhering layer. The bending moment, $M_b$, at the load plateau, $P$, between the inner pins in the four-point bending is:

$$M_b = \frac{Pl}{2b}$$ [4]

where $l$ is the distance between the outer and inner roll, and $b$ is the sample width, $l$ is 12.5 mm and $b$ is 3.0 mm. The second moments of areas are calculated as:

$$I_2 = \frac{h_2^3}{12}$$ [5]

where $h_2$ is the thickness of the substrate. And $I_c$ as:

$$I_c = \frac{h_2^3}{3} + \kappa \frac{h_1^3}{3} + \mu \left( \frac{h_d^3}{3} + h_d h_1 + h_1^2 h_d \right) - \frac{\left[ h_2^2 - \kappa h_1^2 - \mu (h_d^2 + 2 h_1 h_d) \right]^2}{4 (h_2 + \kappa h_1 + \mu h_d)}$$ [6]

where index 1 refers to the stiffener (the short metal strips). $\kappa$ is the ratio between the stiffness of the substrate and the stiffener (which are identical here):

$$\kappa = \frac{E_1 (1 - \nu_2^2)}{E_2 (1 - \nu_1^2)}$$ [7]

And $\mu$ is the ratio between the stiffness of the substrate and the adhering layer

$$\mu = \frac{E_d (1 - \nu_2^2)}{E_2 (1 - \nu_d^2)}$$ [8]
Results and Discussion

Fuel Electrode Support Layer

In Figure 2, the results from the testing of the as-sintered fuel electrode supports are shown. The figure illustrates that a significant fracture energy gain of +\textasciitilde 200 \% is achieved by making the zirconia metastable such that phase transformation from the tetragonal to monoclinic occurs at the crack tip during crack propagation (going from NiO-8YSZ to NiO-3YSZ). This effect has been widely studied - for an overview please see Refs. (5,23,24). The effect is more pronounced at room temperature, which is closer to the Martensitic temperature. With increasing temperature, the susceptibility for the phase transformation decreases, and with this the transformation toughening effect, see e.g. Ref. (25). The fracture energy increase at 800°C is nevertheless \textasciitilde 100 \% for the NiO-3YSZ as compared to NiO-8YSZ.

![Fracture energy measurements for the three different NiO-SZ fuel electrode supports.](image)

Introducing Ce as a co-dopant to Y in ZrO$_2$ increases the fracture toughness of the fuel electrode supports even further, especially at room temperature (+\textasciitilde 50 \% as compared to the NiO-3YSZ samples). Ce doping is well known to induce an increased fracture toughness in ZrO$_2$ (23), however this has not previously been shown to be so for actual fuel electrode supports (meaning porous composites with NiO). The strength of ZrO$_2$ is on the other hand known to decrease with Ce doping (26). However, with the here chosen co-doping of the ZrO$_2$, the strength actually also increase slightly (27) compared to pure Y-doping.

We have also studied the hygrothermal stability of the metastable ZrO$_2$ compounds at both high temperature (800°C) and low temperature (100-200°C). Here it was found that the co-doped samples were more resistant to ageing (6) than those solely doped with Y. Nevertheless, an important finding was that all the metastable ZrO$_2$ compositions degraded fast at the lower temperatures (100-200°C) in humid atmospheres (27). This points to that the fuel electrode should be protected by a non-humid atmosphere during start-up and shut-down.
Oxygen Electrode Contact Layer

The fracture energies of different in-situ sintered perovskite contact layers were determined in Ref. (28). The results for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3-\delta$ (LSC), $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3-\sigma$ (LSM), and $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) are shown in Figure 3. The fracture energy of these contact layers are in the order of $1 \text{ J/m}^2$, which is far below those measured of the in-situ reactive bonded spinel contact layers (of CuMn and CoMn), as seen in Figure 3.

Of the two reactive bonded contact layers, the CuMn spinel forms the tougher contact ($12.6\pm2.0 \text{ J/m}^2$), but the CoMn spinel contact layer also results in a significantly higher fracture energy ($5.6\pm1.5 \text{ J/m}^2$) than those of the in-situ sintered perovskite contact layers. This is more than a 10 fold increase of the fracture energy over the state of the art contact layers (for similar temperature and hold time). The reason for the higher fracture energy of the CuMn contact layers are not fully known, and some studies are still in progress, but we speculate that it is due to the higher mobility of Cu, which ensures better diffusion into adjacent layers, anchoring and filling of gaps and flaws.

![Figure 3. Fracture energy of oxygen electrode contact layers made from in-situ sintered perovskites and in-situ reactive bonded spinels.](image)

The here applied bonding materials have also been tested for the electrical performance. Both the CuMn and CoMn contact layers result in a very low area specific resistance across the interconnect/contact layer/oxygen electrode interfaces, i.e. 18-22 m$\Omega$.cm$^2$ after 3000 hours of aging, and 50 thermal cycles – for further information on this please see Ref. (29).

Glass Ceramic Sealing

In Figure 4, the fracture energy of previously reported sealing assemblies from Forschungszentrum Jülich (FZJ) and DTU for solid oxide cell stacks are shown to the left (14,30). The fracture energy of the FZJ sealings develops with time due to crystallization, so the aged sealing is tougher than the as prepared one. The V11 glass, developed in a collaboration between Politecnico Turin and DTU, crystallizes faster and achieved a comparable fracture energy immediately after the assembly procedure (V11 on Al$_2$O$_3$ (Nexceris) -C22 APU) (14).
The lower fracture energy measured at DTU of the (V11 on MCO, -C22 APU (0.3 mm thick)) is due to the failure of the MCO interconnect coating (14), showing that the weakest link in this assembly is the interconnect coating not the glass. The same applied to the pre-oxidized samples (V11 on Pre-ox C22 APU), here the chromium oxide corrosion scale was delaminating from the steel. The alumina coating from Nexceris is in other words tougher, which make the glass-ceramic the weaker link.

![Figure 4. Fracture energy of sealing assemblies comprised of different steels, coatings and glass-ceramics.](image)

In more recent experiment, however, we have used an in-house alumina coating on a thicker (0.5 mm) Crofer 22 H substrate with smaller alumina particles of ~15 µm (17). This results in a lower surface roughness of 10-20 µm against the 40-50 µm of the alumina coating obtained from 45 µm particles (at Nexceris). For the recent experiments the fracture energy was measured to ~100 J/m² on 5 samples. As this appeared unexpectedly high, the preparation of samples and measurements were repeated yielding the same results, see Figure 4.

In these experiments the high toughness alumina coating was broken of the steel substrate (see Figure 6), in the majority of the fracture interface. Thus, the V11 glass was in this case not the weaker link anymore, but rather the tough alumina coating. The fracture energy of the alumina coating is thus relatively high i.e. ~100 J/m², but the porous V11 glass even tougher. Our current believe is that the higher fracture energy is due to the lower surface roughness, as the roughness on this length scale can be considered “flaws” or stress-concentrators, which could promote the crack propagation in the adjacent glass-ceramic layer. In this experiment the steel substrate was also changed from 0.3 mm Crofer 22 APU in Ref. (14) to a 0.5 mm Crofer 22 H in Ref. (17), but this we do not believe to have any influence.
Figure 5. Cross-section of broken sample, showing the delamination of the thin alumina coating and its presence on the porous glass sealing (closed pores).

Conclusions

In this paper we present an overview of research on increasing the fracture energy of critical brittle components of SOC stacks, i.e. the fuel electrode supports, the oxygen electrode contact layer and the glass-ceramic sealings. The main conclusions of the work are:

- In the fuel electrode support, the fracture energy was increased by 50% and 20% at room temperature and 800°C, respectively, over state of the art NiO-3YSZ by introducing Ce as a co-dopant to Y.
- In the oxygen electrode contact layer, the fracture energy was increased by a factor of 5-10 by using reactive oxidative bonding as compared to various in-situ sintered perovskite contact layers (LSC, LSM, LNF). For CuMn a ~10 fold, and for CoMn a ~5 fold increase was observed.
- CuMn was speculated to provide the better bonding due to the high mobility of Cu in its metallic phase, providing better integration with adjacent surfaces. More research is required to fully clarify this.
- A 5 fold increase of the fracture energy of the glass sealing/coated interconnect--assembly was achieved by depositing in-house manufactured V11 glass onto an in-house thin alumina coating on Crofer 22 H. The values compare favourably similar measurements on Crofer 22 APU with a commercial alumina coating and the same glass and with measurements from Forschungszentrum Jülich (30) on comparable sealing/steel-joints.
- The reason behind the significant gain of fracture energy was speculated to be the controlled surface roughness. More research is needed to fully clarify this.
Acknowledgements

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6 Conclusions

The main motivation for this work was to improve the durability of solid oxide cell (SOC) stacks by increasing the robustness and interface adherence between i) the seal and the interconnect, and ii) between the contact layer and the interconnect. The first part of the thesis was dedicated to the development of glass and glass-ceramic seals. A Ba-free sealing glass (V11) composed of SiO$_2$, MgO, CaO, Na$_2$O$_3$, Al$_2$O$_3$, ZrO$_2$, B$_2$O$_3$, was developed and successfully applied. The V11 glass showed promising results in terms of thermal properties, adherence and long term stability, making it a good candidate for the application in SOC stacks.

When joining different materials in SOC stacks the difference between the coefficients of thermal expansion (CTE) should not differ more than $1 \times 10^{-6}$ K$^{-1}$. The CTE of V11 was measured to $12.8 \times 10^{-6}$ K$^{-1}$ (200-450°C) after sintering as well as after ageing at 750°C for 5000h. This value is within the $\pm 1 \times 10^{-6}$ K$^{-1}$ requirement when the seal is joined to Crofer 22 APU (or H) and Ni-YSZ.

X-ray diffraction (XRD) analyses showed that the V11 glass partially crystallizes into two crystalline phases, Augite and Nepheline, during the heat treatment used for the sealing process. The same crystalline phases were found after ageing at 750°C. Moreover, no reactions occurred at the interface when the glass was tested with CGO, YSZ and pre-oxidized or AlumiLok coated Crofer 22 APU (Paper 1).

The adherence of the V11 glass seal towards the interconnect was investigated by measuring the fracture energy towards three relevant interfaces: pre-oxidized, AlumiLok (Al$_2$O$_3$) coated and MCO (MnCo$_2$O$_4$) coated Crofer 22 APU (Paper 2). The weakest interface (fracture energy 13.6 J/m$^2$) was found between V11 and MCO coated
6 Conclusions

Crofer 22 APU, in which case the fracture occurred in the MCO layer. The interface between pre-oxidized Crofer 22 APU and V11 was slightly stronger (fracture energy 15.9 J/m$^2$) and the fracture occurred mainly between the Cr$_2$O$_3$ and the (Mn,Cr)$_3$O$_4$ oxide layers formed on the steel. The strongest interface was between V11 and AlumiLok coated Crofer 22 APU, where a fracture energy of 23.7 J/m$^2$ was measured. In this case the fracture occurred in the glass-ceramic. Further testing on in-house alumina coating, showed that the interface adherence could be improved up to about 100 J/m$^2$, where the fracture occurred mostly at the interface between the alumina coating and the metallic substrate. The high toughness was attributed to a slightly lower roughness of the coating. The fracture energy obtained for the V11 glass-ceramic was in the same range as the best values reported in literature for glass-ceramic seals tested with the same method (Paper 2 and 5).

Coating the SOC stack steel components with AlumiLok (or equivalent alumina coating) seems the most promising solution to improve the interface adherence to the glass sealant. If this approach is used, the seal-interconnect interface itself is no longer the weakest part of the SOC stack, which is a significant improvement compared to state-of-the-art.

The second part of the thesis focused on new contact layers for the SOC air side (Paper 3). The contact layers investigated consisted of Cu-Mn and Co-Mn metallic powders that are oxidized to conductive spinels during the stack assembly heat treatment. XRD, scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) analyses confirmed the formation of the spinel phases, Cu$_{1.2}$Mn$_{1.8}$O$_4$ and MnCo$_2$O$_4$, after 250h at 750°C.

Area specific resistance (ASR) measurements were performed to evaluate the electrical conductivity of the Cu-Mn and Co-Mn contact layers deposited onto bare 441 stainless steel. After 3000h at 750°C, the ASR with the Cu-Mn layer was 21 mΩcm$^2$ and the ASR with the Co-Mn layer was 25 mΩcm$^2$. These values are significantly lower than the ASR measured for the bare 441 steel (70 mΩcm$^2$ after 3000h). The main contribution to the ASR was attributed to the corrosive scale that grew at the interface.
between the contact layers and the 441 steel. The ASR did not change significantly after 50 thermal cycles, indicating good adhesion at the interfaces (Paper 4).

The interface adherence was also quantified in terms of fracture energy. In this case, the contact layers were tested on bare Crofer 22 H after sintering and after aging for 250h at 750°C. The fracture energy after sintering of the Cu-Mn and Co-Mn contact layers was 13.5 J/m$^2$ and 6.0 J/m$^2$, respectively. After aging, the fracture energies decreased to 5.0 J/m$^2$ and 3.9 J/m$^2$, respectively, which is still 5 times higher than the state-of-the-art. These results demonstrate that Cu-Mn and Co-Mn are promising as contact layers (Paper 3).

6.1 Outlook

Promising results were achieved for both the glass-ceramic seals and the contact layers during the 3 years. Below ideas and suggestions for further investigations that could be performed in follow-up projects are listed.

Glass-ceramic seals

- **Long-term stability:** Information on the stability of the glass over time is extremely valuable. The data analysis of the V11 joined to relevant interfaces (i.e. aluminized or preoxidized Crofer 22 H) is ongoing, with the aim of retrieving information about changes in the thermal expansion, the crystalline phases and eventual interfacial reactions.

- **Testing aged, joined samples:** testing the adherence of steel/seal/steel joints after ageing would give valuable information on the reliability and robustness of the joints over time.

- **Degradation of the seal resistance when tested under electric load and dual atmosphere:** Studies of Na-containing glass seals indicated the degradation of the seal due to chromate formation and accompanying decrease in resistivity. Those studies were performed on bare or pre-oxidized steel. It would be interesting and relevant to perform similar experiments on samples with aluminized steel, which is expected to be better protected against Cr evaporation compared to pre-oxidized steels. Part of these
6 Conclusions

experiments are ongoing in collaboration with Federico Smeacetto (DISAT) and Domenico Ferrero (DENERG) (Politecnico di Torino).

- **Interface adherence:** Planned experiments in collaboration with DTU Wind are aiming to test the seal with a double-cantilever-beam set-up coupled with an environmental scanning microscope (ESEM). This combination would enable measuring the fracture energy of the seal and following the crack formation in the microscope at the same time. The need of further investigations comes from the extremely high toughness values presented in Paper 5, where the V11 fracture energy resulted about 100 J/m².

**Contact layers**

- **Optimized sintering:** the Co-Mn composition resulted in poorer densification compared to the Cu-Mn composition; improvement of the densification could lead to better adherence and lower ASR values. Infiltrating the porous structure could be a way to improve the densification of the Co-Mn composition, or increasing the temperature to 900-950°C.

- **Interface adherence:** the contact layers were tested only on bare Crofer 22 H. It would be valuable to test the materials also on coated steels, which would limit the oxide scale growth, and consequently lowering the ASR.
7 References


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Appendix 1

Strength measurements
Shear strength tests of glass-ceramic seal for solid oxide cells applications

Strength measurements using the torsional method are presented in this appendix.

This experimental part was carried out in collaboration with Stefano De La Pierre, under the supervision of Monica Ferraris and Federico Smeacetto at the Department of Applied Science and Technology (Politecnico di Torino).

The experimental plan
As a follow up of the results obtained in Paper 2, strength measurements of the joint V11-interconnect were desired. The relevant interfaces according to the experimental plan were preoxidized Crofer 22 APU and Alumina coated Crofer22APU as a comparison. The evaluation of the strength was planned after sintering and after ageing at 750°C, and six samples with the two types of contact layers were prepared. As these experiments are still ongoing, only the results on the aluminized Crofer 22 APU are presented in this appendix.

1 Materials and methods
Sample geometry
The test was carried out on hollow hourglass samples Figure 1.1, also called TDHG (torsion drilled hourglass [1]). The steel substrates was made of Crofer22APU (ThyssenKrup, VDM metals [2]) and joined with V11 glass, where the Crofer 22 APU was either preoxidized or aluminized in-house.

Screen printing on this type of samples was not possible because of their size and 3D structure. Therefore, the V11 glass powder (prepared as explained in Paper 1 [3]) were tape-casted. The tape was laser-cut in order to obtain the small sealing rings for the hour-glass Figure 1.2b.
Preoxidation of the Crofer 22 APU was carried out at 950°C for 2 h, 120°C/h. The aluminization process consisted in coating the Crofer22APU with an Al slurry and heat treating it at 1000°C for 1 h, 180°C/h, which results with the formation of a thin Al₂O₃ layer on top of the metal plate.

The samples were then assembled through an optimized sealing profile for V11 glass (Paper 1). Some samples were tested after sintering and some samples were aged for 700 h at 750°C in air.

The maximum of shear strength was calculated using:

$$\tau = \frac{TR}{J} \quad (1.1)$$

Where $\tau$ is the shear strength, $T$ the maximum applied torque, $R$ the external radius of the joined area and $J$ the polar moment of inertia of the cross-section.

$J$ is defined as:

$$J = \frac{1}{2}\pi(R_e^4 - R_i^4) \quad (1.2)$$

Where $R_e$ is the exterior radius and $R_i$ the interior, 2.5 mm and 1.5 mm respectively.

A universal testing machine was used for the torsion tests (Zwick 100, Zwick/Roell, Hertfordshire, UK).
2 Results and discussion

The fracture surfaces of the samples after sintering and after ageing are shown in Figure 2.1 a-b and a typical output of test is shown in Figure 1.2. The maximum of the torque is used to calculate the maximum shear strength. The strength after sintering resulted to 40 ±6 MPa and after ageing at 750°C for 700 h dropped to 33 ±6 MPa.

The fracture observed here, from the pictures, appears brittle, as expected from ceramic materials. The fracture occurs both at the interface glass/metal (e.g. adhesive fracture) and in the glass (e.g. cohesive fracture), mixed adhesive/cohesive fracture. The metallic substrates do not appear to be affected, but this should be further characterized by SEM/EDS to confirm the nature of the fracture.
In case of cohesive fracture, the measured strength is pure shear strength [4].

A comparison of the results obtained here with other shear strength values from literature [5], [6] is shown in Figure 2.3. The values from Greven et al. were obtained on a different geometry, THG (torsion hourglass, where the sample is not drilled in the middle. Smeacetto et al. measured the shear strength on both THG and TDHG, showing that no difference occurred between those values.

GlassH, tested by Greven, showed an increase in shear strength from 42 MPa to ~60 MPa after ageing for 500h at 800°C, due to a further crystallization of the glass [5]. Greven et al. investigated several composition of composites with the GlassH as a matrix, showing the possibility of reaching a shear strength up to 100 MPa after ageing when mixed with 20% Ni.

While V11, aged at 750°C will unlikely further crystallize at that temperature, the shear strength in fact slightly decrease after ageing.

KMBY glass, tested by Smeacetto et al. demonstrated a shear strength up to 71 MPa [6].
3 Conclusions
The results obtained here will be combined with the tests on preoxidized Crofer 22 APU, to investigate the effect of different interfaces at the glass/metal join.

And a microstructural analysis is also needed in order to have a detailed comprehension of the results and eventually explain the lower shear strength of the aged sample.

The presence of mixed adhesive /cohesive fracture proves that this sample geometry allows for pure shear strength measurement.

4 References


