### Analysis of High Temperature Degradation of Alloys in Solid Oxide Fuel Cell

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par

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Non chiederci la parola che squadri da ogni lato l'animo nostro informe, e a lettere di fuoco lo dichiari e risplenda come un croco Perduto in mezzo a un polveroso prato. — Eugenio Montale

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### Abstract

Solid oxide fuel cells (SOFCs) are approaching commercialization to improve power production efficiency. Currently, cost and lifetime reliability limit their spread in the market. The SOFC is ceramic-based, but refractory metal alloys are in fact the majority materials present in SOFC systems. The lifetime behaviour of SOFC stacks, and of the metallic components in particular, remain in need of further investigation.

The degradation processes behind the possible failure of selected metal interconnect (MIC) and balance of plant (BoP) alloys were investigated. Samples were extracted from stacks operated for periods up to 18000 hours and analysed with scanning electron microscopy coupled with X-ray energy dispersion spectroscopy (SEM/EDS). Scanning transmission electron microscopy (STEM) coupled with EDS and electron diffraction was applied to identify corrosion products. Electrochemical impedance spectroscopy (EIS) analysis completed the characterization of the stacks. Degradation processes of steam generator BoP alloy were investigated with SEM/EDS as well.

Various protective coating solutions to limit interconnect and related cathode degradation were tested as small coupon samples. Area specific resistance (ASR) monitoring and evaluation of Cr evaporation blocking verified the effectiveness of these solutions. A special set-up able to test 8 small MIC samples simultaneously in different gas atmospheres was built and used to correlate operating variables to material degradation through a design of experiment (DoE) approach.

The results indicate that in commercial ferritic stainless steel, corrosion kinetics are fast in the first few thousand hours of operation and then tend to stabilize. The main influencing parameter is the initial density of the protective coating, independently of the steel and coating compositions. However, even porous coatings demonstrated to be viable for periods at least up to 2 years. The strong chemical interaction with the cell materials is their main drawback, but they present a competitive advantage in manufacturing cost.

The steam generator alloy used in the BoP suffered stress corrosion cracking induced by the strong thermal gradient between hot and cold gas and the aggressive hot outlet gas atmosphere. Aluminizing treatment of the alloy seems to solve the issue.

Key words: SOFC; corrosion; ferritic stainless steels; interconnects; refractory

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alloys, accelerated testing

### Riassunto

Le pile a combustibile ad ossidi solidi (SOFC in inglese) sono una tecnologia ad alta efficienza energetica, pronta per la commercializzazione. Costi ed affidabilità sul lungo periodo però ne frenano la competitività. Le SOFC sono a base di materiale ceramico, ma nel sistema basato su SOFC è il metallo ad essere presente maggiormente.

La durata delle pile ed in particolare dei componenti metallici al loro interno, necessita ancora di verifiche.

Nella tesi sono studiati i processi degradativi che portano al deterioramento delle leghe utilizzate per l'interconnettore (MIC) e il sistema ausiliario (BoP). Campioni di materiale sono stati estratti da sistemi che hanno funzionato fino a 18000 ore e sono stati analizzati tramite microscopio elettronico a scansione (SEM) e spettroscopia EDX. Inoltre, microscopio elettronico a trasmissione e analisi delle immagini di diffrazione hanno completato lo studio. Per certi sistemi, sono stati misurati anche gli spettri di impedenza elettrochimica (EIS). SEM e EDX sono stati ugualmente adoperati per l'analisi del BoP.

Su campioni di ridotte dimensioni sono stati testati molteplici rivestimenti per limitare la degradazione delle leghe usate per i MIC. Sono misurate sia la resistenza specifica di contatto (ASR), sia l'efficacia dei rivestimenti nel bloccare l'evaporazione del cromo dal substrato metallico. E' stato anche prodotto un banco prova speciale dove otto campioni possono essere testati simultaneamnte in condizioni atmosferiche differenti. Tale banco prova è stato utilizzato per correlare l'influenza delle condizioni di test con la degradazione dei material metallici tramite l'analisi statistica detta Design of Experiment.

I risultati mostrano che in acciai commerciali, a minore tenore di cromo, la cinetica di corrosione è elevata nelle prime ora di messa in opera nelle pile e poi tende a stabilizzarsi. Il parametro che piu' influenza questo processo è la densità del rivestimento, indipendentemente dalla sua composizione o da quella del substrato metallico. Ad ogni modo, anche i rivestimenti porosi hanno dimostrato di essere affidabili almeno per due anni di utilizzo ininterrotto. Le interazioni chimiche tra cella e substrato metallico sono il problema principale di questo tipo di acciai, ma il minor costo li rende comunque una scelta competitiva.

Le leghe di cui è fatto il generatore di vapore nel BoP hanno mostrato fratture di natura tensocorrosiva indotte dal gradiente termico tra fludi a temperatura differente. Un trattamento superficiale di alluminizzazione sembra essere la soluzione.

## Résumé

Les piles à combustible à oxyde solide (SOFCs), qui sont caractérisées par une haute efficacité énergétique, se rapprochent de la commercialisation. Actuellement, leur coût et leur durée de vie limitent leur diffusion sur le marché. Bien que les SOFCs elles-mêmes soient fabriquées à base de matériaux céramiques, les alliages de métaux réfractaires représentent la majorité des composants des systèmes de SOFCs. Le vieillissement des systèmes de SOFCs, et en particulier celui de leurs composants métalliques, doit être étudié de manière plus approfondie. Les procédés de dégradation, qui peuvent potentiellement causer la défaillance de certaines plaques bipolaires en métal (MIC) et des alliages présents dans les équipements auxiliaires (BoP), ont été étudié.

Des échantillons extraits d'empilements (stack) et d'empilements partiels (shortstacks), qui ont été opérés durant un maximum de 18000 heures, ont été analysés à l'aide d'un microscope électronique à balayage couplé d'un système de spectroscopie de rayons X à dispersion d'énergie (SEM/EDS). La microscopie électronique à balayage en transmission (STEM) combiné à l'EDS et l'imagerie diffractive cohérente ont également été utilisés pour identifier les produits de corrosion. L'étude par spectroscopie d'impédance électrochimique (EIS) complète la caractérisation de certains short-stacks. Les procédés de dégradation des alliages composant l'évaporateur des BoP ont aussi été examinés par SEM/EDS.

Plusieurs revêtements de protection, aillant pour but de limiter la dégradation des plaques bipolaires et son effet sur la cathode, ont été testés à échelle réduite. La mesure de l'ASR et l'évaluation de la capacité à limiter l'évaporation du chrome ont démontré l'efficacité de ces revêtements. Un banc d'essai, capable de tester simultanément 8 échantillons de MIC dans différentes atmosphères gazeuses, a été conçu et utilisé pour corréler les variables atmosphériques avec la dégradation des matériaux selon une approche basée sur la conception d'expériences (DoE).

Dans le cas de l'acier ferritique inoxydable commercial, les résultats indiquent que la cinétique des réactions de corrosion est rapide durant les milles premières heures de fonctionnement puis tend à se stabiliser. Le facteur principal influençant la dégradation est la densité initiale du revêtement de protection, indépendamment de la composition du revêtement et de l'acier. Toutefois, certains revêtements poreux ont démontré être de potentielles solutions pour des durées de vie allant jusqu'à 2 ans. La forte interaction chimique avec les composants de la cellule est leur inconvénient principal, mais ils représentent un avantage en termes de coût de fabrication.

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# Acronyms

AES	Auger electron spectroscopy
ALD	atomic layer deposition
APS	atmospheric plasma spray
ASC	anode supported cell
ASR	area specific resistance
ASS	austenitic stainless steel
BoP	balance of plant
CTE	coefficient of thermal expansion
DFT	density functional theory
DRT	distribution of relaxation time constants
ESC	electrolyte supported cell
EDS	energy dispersive X-ray spectrometry
FIB	focused ion beam
FSS	ferritic stainless steel
GDC	gadolinium doped cerium oxide
GGA	generalized gradient approximation
GIXS	grazing incidence X-ray scattering
HE	heat exchanger
IC	interconnect
IGC	intergranular corrosion
LEED	low-energy electron diffraction
LSC	lanthanum strontium cobaltite
LSCF	lanthanum strontium cobalt iron oxide
MCFC	molten carbonate fuel cell
MIC	metal interconnect
MIEC	mixed ionic-electronic conductors
мсо	manganese cobalt oxide (spinel)
MCF	manganese cobalt iron oxide (spinel)
ORR	oxygen reduction reaction
PEC	photoelectrochemistry
PEMFO	proton exchange membrane fuel cell
PVD	physical vapour deposition
SAED	selected area diffraction
SCC	stress corrosion cracking

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- **SEM** scanning electron microscopy
- **SCORED** steel coatings for reducing degradation in SOFC (EU Project)
- **SG** steam generator
- **SOFC** solid oxide fuel cell
- **SRU** single repeat unit
- **TEM** transmission electron microscopy
- **XPS** X-ray photoelectron spectroscopy
- **XRD** X-ray Diffraction
- YSZ yttria stabilized zirconia
- WPS wet powder spray

# Nomenclature

Latin letters	Description	Unit
A	Active area	$m^2/cm^2$ or $m^2$
D	Diffusion coefficient	cm²/s or m²/s
E	Nernst voltage	V
E <sup>0</sup>	Standard cell voltage	V
F	Faraday's constant	C/mol
G	Molar Gibbs free energy	J/mol
Н	Molar enthalpy	J/mol
i	Current density	$A/cm^2$ or $A/m^2$
Kp	parabolic rate constant	cm²/s
n	Number of electrons	_
Ν	Concentration	mol/cm <sup>3</sup> or mol/m <sup>3</sup>
p <sub>x</sub>	Species partial pressure	bar
q	electric charge	С
Q	Activation energy	J/mol
R	Universal gas constant	J/(molK)
S	Molar entropy	J/(molK)
Т	Temperature	K or °C
t	time	S
ν	stoichiometric coefficient	_
Y	Young's modulus	Pa or N/mm <sup>2</sup>
Greek letters	Description	Unit
ρ	Electrical resistivity	Ωm
σ	Electrical conductivity	S/m
Φ	Electric field	N/C or V/m

## **1** Introduction

SOFC energy conversion devices are still expensive and too short-lived for market application. Metal interconnects act in both of these limitations. Understanding the corrosion behavior of metal interconnects on the long-term and benchmarking of protective solutions will contribute to the success of the technology.

In this introduction, several sections were taken from the book chapter "Lifetime Issues for Solid Oxide Fuel Cell Interconnects", of which I am the first author, published in the book "Solid Oxide Fuel Cell Lifetime and Reliability".

### 1.1 Motivation

Since the 1992 UN conference on the Environment and Development and followed by the 1997 Kyoto and 2015 Paris key agreements, changes in the climate induced by anthropogenic greenhouse gas emissions is now a globally accepted issue. In the Paris 2015 agreement, all of the participating countries agreed on "holding the increase in the global average temperature to well below 2°C above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5°C above preindustrial levels, recognizing that this would significantly reduce the risks and impacts of climate change" [2]. As such, reducing the global consumption of fossil fuels should be the global energy policy for the next decades. Technologies using renewable energy sources such as hydro, solar and wind energy currently satisfy only 10% of the global energy demand [3]. Moreover, considering the lack of competitiveness of nuclear fission technology and long development time of nuclear fusion plants, the rapid reduction of fossil fuels consumption seems unlikely. The adoption of more efficient technologies is therefore a necessity to decrease or contain  $CO_2$  emissions on the short-medium term.

A solid oxide fuel cell (SOFC) is an electrochemical device, a galvanic cell, that is able to directly transform the chemical energy of a fuel into electricity. This allows for the

#### **Chapter 1. Introduction**

highest electrical efficiencies found in fuel-based energy conversion technologies. In addition, an SOFC can use different types of fuels ( $CH_4$ ,  $H_2$ ,  $NH_3$ ), both from fossil or renewable origin. Due to this high flexibility and efficiency, the use of SOFC power generator offers a viable option for accomplishing the Paris agreement goals. However, their costs and lifetime are currently limiting their commercialization. To convert useful amounts of energy, SOFC power generators must contain tens to hundreds of stacked ceramic cells separated by metal plates known as "interconnect" (IC). This component, compared to electrode and electrolyte materials, has received less consideration in research, despite accounting for a significant part of the total stack cost depending on the units produced [4, 5] and causing serious degradation phenomena, which reduces the device lifetime [6]. Obtaining a stable and long lasting (> 40000 h) interconnect is considered crucial for the wide-spread usage of this technology.

This thesis therefore focuses on the degradation phenomena affecting the lifetime of the SOFC interconnects. Because most interconnects are made of ferritic stainless steels, attention is given to the corrosion process at high temperature, on the interaction between the metal and the cell, and on the possible solutions to extend the IC lifetime.

Although extensive research has been performed regarding interconnects, including on the contribution of the steel substrate [7–12], coating composition/deposition technique [13? –24], or testing conditions [25–36], only modest correlation was seen between literature descriptions of the materials and post-test analyses of MICs operated in SOFC stacks. This is because the experiments in the laboratory are often performed in conditions different from those in stacks.

This thesis aims to integrate studies performed in controlled environment with metal tested in operative condition, i.e. inside SOFC stacks or short-stacks running for medium-long term. This chapter will first introduce the basic theory behind SOFC operation, then materials used as IC, and main degradation phenomena at high temperature and ceramic coatings will be explained in detail. Finally, a collection of MIC behaviour in real SOFC stack operative conditions will be presented as a table (Tables 1.3 and 1.4).

### **1.2 Fuel cell basic principles**

A fuel cell is composed of two electrodes, in which the reduction and oxidation semi-reactions take place, and an electrolyte to close the ionic exchange circuit. Although the invention of this galvanic cell has been attributed to W. R. Grove and C. F. Schönbein independently, in 1838, the concept was more advanced than the available materials at the time; the first example of practical use of fuel cell is in 1961, developed by NASA for spatial application. Fuel cells are classified according to their electrolyte materials. For example, the molten carbonate fuel cells (MCFCs) use a bath of sodium and potassium carbonate, polymer exchange membrane fuel cells (PEMFCs) use Nafion, and SOFCs use a thin ionically conduction ceramic (typically yttria-stabilized zirconia). The working principle is the same for all fuel cell types:

reduction of the oxidizing species at the cathode side, oxidation of the fuel at the anode side, and the electrolyte providing ionic conductivity and electronic insulation.



Figure 1.1 – Scheme of the working principle inside an SOFC

The working principle of an SOFC can be described with the help of Figure 1.1. Here, the oxygen flow passes through the porous cathode material where it is adsorbed on the surface, reduced, and ionized. The oxygen ions then cross the dense electrolyte membrane via solid diffusion and reach the anode. Fuel is sent to the porous anode, where it reacts with the oxygen ions coming from the electrolyte. The exothermic water formation reaction liberates heat and electrons. This heat can be recovered at the outlet of the stack, while the electrons will close the electric circuit. In the simplest case using only oxygen and hydrogen, the semi-reactions at the electrodes are:

$$H_2 + O^{2-} \to H_2O + 2e^-$$
 (1.1)

$$\frac{1}{2}O_2 + 2e^- \to O^{2-} \tag{1.2}$$

The total cell reaction therefore can be written as:

$$H_2 + \frac{1}{2}O_2 \to H_2O$$
 (1.3)

Reaction 1.3 contains: molecular hydrogen, molecular oxygen, and steam. Water vapour and oxygen are abundant in the environment, but pure hydrogen is present only in a few ppm. Meanwhile, it is impossible to observe a spontaneous reversal of reaction 1.3, because water production is thermodynamically favored over hydrogen

and oxygen alone. The spontaneity of the reaction can be quantitatively measured via the Gibbs free energy of the system.

$$\Delta G = \Delta H - T \Delta S \tag{1.4}$$

Enthalpy (H) provides information about the change in the internal energy of the system, whereas entropy (S) accounts for the work irreversibly lost as heat during the process. In an ideal reversible reaction, the Gibbs free energy matches the enthalpy, but in reality, there is always an irreversible loss. At atmospheric pressure and room temperature the enthalpy of formation for reaction 1.3 is  $\Delta H = -286 \ k/mol^{-1}$ , whereas the entropy change between the products and the reactants is  $\Delta S = 164 \ Jmol^{-1}K^{-1}$ ; at 298 K this gives  $\Delta G = -237 \ k/mol^{-1}$ . The reaction is thus energetically favored despite the decrease in the reaction's entropy. Furthermore, the Gibbs free energy of a system can be transformed into work. An SOFC can therefore theoretically transform the Gibbs free energy of a chemical reaction into electrical work; redox reaction 1.3 can provide a certain electrical potential difference, expressed as:

$$\Delta G = -nFE \tag{1.5}$$

Here n is the electrons exchanged per fuel molecule, F is Faraday constant (96486  $Cmol^{-1}$ ), and E is the cell potential. Returning to the practical example at standard condition, the maximum voltage obtainable with the reaction of hydrogen and oxygen is 1.229 V. The definition of standard condition is often misleading in literature. Standard thermodynamic conditions are usually P = 1 atm and T = 25 °C, but for Equation 1.5, the standard conditions are defined as P = 1 atm and species activity of 1. Temperature can change. Thus, the Gibbs free energy available for a certain reaction, changes with the temperature. Consequently, the theoretical maximum electrical work obtainable from the reaction changes with temperature. The standard Gibbs free energy is indicated as  $\Delta G^0$  and the standard cell potential as  $E^0$ . Equation 1.5 can be shown to relate to the Nernst equation:

$$E = E^{0} + \frac{RT}{nF} \ln \frac{\prod_{i}^{n} a_{p.i}^{vi}}{\prod_{i}^{n} a_{r.i}^{vi}}$$
(1.6)

Here R is the universal gas constant (8.314  $Jmol^{-1}K^{-1}$ ), T is the absolute temperature (K), n is the number of electronic species (electrons) involved in the reaction, F is the Faraday constant, a represents each activity coefficients of the product at the numerator and of the reactants at the denominator, and  $v_i$  each stoichiometric coefficient of the reaction. Equation 1.5 is a specific case of 1.6 because if all the activities are equal to 1 (standard condition)  $E = E^0$ . Because it is difficult to quantify activities in practise, it is common to use partial pressures if the species involved in the reaction are gases. Both equations 1.5 and 1.6 refer to the open circuit voltage (OCV) condition, i.e., when the two electrodes are not carrying current. Upon closing the circuit, *E* decreases due to dissipative phenomena present in the cell and circuit. These losses are typically categorized as activation, ohmic, and concentration losses. Activation losses depends on the kinetic of the redox reaction at the electrolyte interface. Ohmic losses are linearly linked with the material resistance to the flow of charged species. In SOFC devices, the largest ohmic contributors are the resistance of the electrolyte to the passage of ions and the oxide layers grown on the metal interconnect to the passage of the electrons. The concentration losses are related to the diffusion kinetics of the species involved in the process, e.g., if a reactant takes too long to reach the electrolyte interface, then there is a slowing down of the reaction. A detailed and precise explanation of activation and concentration losses can be found from many sources in literature, including [37, 38]. This thesis aims to focus on resistivity losses, as the corrosion undergone by the metals studied contributes to the increase of their electrical resistivity. Resistance is not an intrinsic material property, it depends on the material's geometry. Additionally, only a part of the cell and interconnect are in contact in SOFC devices. The resistance of the materials is usually measured as the area-specific resistance (ASR), where the measured ohmic drop ( $R_{mes}$ ) is multiplied by the electrical contact area ( $A_{cont}$ ). In turn, the ASR can be divided by the material thickness (L) to determine the resistivity:

$$\rho = \frac{R * A_{cont}}{L_{material}} \tag{1.7}$$

This measuring concept was largely applied in this thesis as 4-wire probe test to compare the electrical performances of different steel substrates and coatings solutions, especially in Chapter 2 and 7.

### **1.3 Materials**

The working conditions of SOFC are difficult to withstand for many materials. Operating temperatures are higher than 700°C, thermal cycles are likely to happen, and there is continuous chemical interactions. Each component has its specific challenges. The anode electrode, commonly made of yttria-stabilized zirconia (YSZ) doped nickel, - must resist RedOx cycles; it is initially in oxidized state and is reduced by the fuel while operating, but the presence of oxygen, very high steam partial pressure or unwanted device shut-down could re-oxidize the anode material, leading to mechanical stresses [39]. The Ni/YSZ must catalyze the hydrogen reaction with oxygen and be both an ionic and electronic conductor. The cathode material must catalyze the oxygen reduction reaction (ORR) and be a medium for the migration of the created oxygen ions towards the electrolyte. For the oxygen reduction, the cathode material must be also an electron conductor; hence, mixed ionic-electronic conductors (MIEC) are most often chosen. Perovskites are the common choice: because of their flexibilities in doping, the amount of oxygen vacancies can be increased to improve anionic conductivity. Currently, the most used cathode materials are  $La_{1-x}Sr_xCoO_3$  (LSC),  $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$  (LSCF) and  $La_{1-x}Sr_xMnO_3$ (LSM) [40–43]. Perovskite materials used in SOFC devices play an important role in the thesis; the chemical interaction occurring between these materials and the

#### **Chapter 1. Introduction**

interconnect is one of the main phenomena described in Chapter 2. A perovskite is a compound respecting the formula  $AMX_3$ , where A is an alkaline, an earth-alkalyne or a rare earth cation, M is a transition metal cation, and X is an anion, typically oxygen. The lattice of a perovskite can be idealized as compact cubic, with the oxygen ions shared among cations with different coordination.



Figure 1.2 – Qualitative representation of an ideal perovskite lattice for  $LaCoO_3$  and Sr doped- $LaCoO_3$ 

The schematic representation of  $LaCoO_3$  and Sr-doped  $LaCoO_3$  depicted in Figure 1.2 shows the unit lattice of the material, where the smaller M cations ( $Co^{3+}$ ) coordinate 6 oxygen anions and  $La^{3+}$  coordinates 12. Cations can easily be substituted in perovskite, allowing the electrical and mechanical properties of the material to be tailored. In Figure 1.2 for example, the  $Sr^{2+}$  ion is ca. 6% larger than  $La^{3+}$  and is one electron more negative. This implies both a lattice displacement and a charge imbalance inside the lattice. To reach a new equilibrium condition, oxygen ions might be expelled, creating oxygen vacancies. On the other hand, the introduction of alien ions in the structure leads to mechanical stress. The lattice will tend to relax expelling them. In an SOFC, this translates into strontium segregation on the perovskite surface, as demonstrated by Lee et al. [44]. The migrated strontium can react with the oxygen in the air, creating an insulating SrO oxide layer and therefore limiting the ORR. This could substantially decrease the voltage produced by the cell and even lead to its complete failure [45]. Alternatively, the SrO could react with the chromium hydroxide vapors originating from the interconnect and become SrCrO<sub>4</sub>. This compound is also unwanted because of its fragility and poor electrical conductivity [46]. Moreover, owing to its high thermodynamic stability, once it is formed, it is not possible to remove it without destructive methods. Strontium segregation is a diffusion-controlled phenomenon; the temperature influences the kinetics of the process according to an associated activation energy. Segregation is observed at high temperatures independently of the other testing conditions. Oxygen partial
pressure instead influences the perovskite lattice mechanically by expanding or contracting it. A higher oxygen partial pressure would contrast the oxygen vacancies, and therefore hindering relaxation of the crystal lattice. A more rigid and packed structure affects the  $Sr^{2+}$  doping cations, which are expelled towards the surface of the perovskite Lee et al. [44]. Cathodic polarization promotes oxygen vacancies, therefore opposing the formation of SrO at the cathode air side. Since cathodic A-site vacancies are already present in the material,  $Sr^{2+}$  and  $O^{2-}$  ions can accommodate in the perovskite lattice [40]. Mechanical stress are related to the dimensions of the dopant ions [47]. Studies on perovskite materials aged at high temperatures under stress have indicated a positive influence of compression stress in blocking strontium migration towards the air side [48]. Finally, the nature of the cation at the B site can also influence the perovskite behavior [43]. Although strontium diffusion preferentially takes place at the grain boundaries, compression stress can hinder this migration by closing the gaps among the grain boundaries. Perovskite with the same composition can have different properties according to sintering process, therefore experimental assessment of the perovskite materials used is still needed.

The electrolyte material must only be an ionic conductor only, to avoid an electrical short circuit between the anode and cathode. YSZ is the material typically used in SOFC as electrolyte. Oxygen ions migrates through the electrolyte via vacancy diffusion. Because of this, electrolyte thickness is a key parameter to determine the SOFC operating conditions. The substitution of electrolyte-supported cell type (ESC) with an anode-supported cell (ASC) was shown to decrease the operating temperature from 850-900°C to 700-750°C, as the electrolyte dimensions decreased from hundreds to tens of microns. Researchers have aimed to further decrease the electrolyte thickness [49]. Because of interaction between the YSZ electrolyte and an active cathode material, a Gd-doped Ce (GDC) oxide thin layer is applied in between them as compatibility layer. Like the cell materials, interconnect materials also have to fulfil precise features that will be discussed in detail in the next section.

### 1.4 Interconnects

Regardless of the geometry or material, an SOFC interconnect must be able to: divide the cathode (air) and anode (fuel) streams (gas impermeability), distribute gas flows to optimize fuel utilization (easy machining, stamping,..), collect electrical current generated by the cell (low electrical contact resistivity < 10  $m\Omega cm^2$ ), guarantee mechanical stability (creep resistance), show sufficient chemical stability and inertia with respect to the other components (low corrosion), avoid potentially damaging residual stress to the ceramic cell (coefficient of thermal expansion CTE compatible with the cell 12–13·10<sup>-6</sup> $K^{-1}$  [50]), and transfer heat from the cathode to the anode in case of fuel reforming (good thermal conductivity > 5  $Wm^{-1}K^{-1}$  [51]).

Balancing these criteria ultimately leaves a limited choice of potential materials:  $LaCrO_3$ -based perovskites [52], Cr-based alloy, and ferritic stainless steels (FSS) [53], listed from highest to the lowest operating temperatures. Yet, no material completely fulfills all the requested features. In addition, stationary applications

of SOFCs requires at least 40000 hours at operating temperature, thus leading to interconnect lifetime issues, such as mechanical deformation, corrosion, and surface spallation, which impact the stack lifetime. To mitigate such detrimental processes, metal interconnects have very specific chemical compositions and are combined with protective oxide coatings such as spinel or a perovskite layer deposited by different methods. The two main types of interconnect alloy used today in SOFC technology are ferritic stainless steel (FSS) and Cr-alloy CFY. Stainless steels are chosen because of their ability to grow a passivating oxide layer on the surface, preventing the formation of brittle and low electrically conductive hydrated iron oxide phases. The passivating film can be made of chromium and/or aluminium oxides. Both these oxides are effective in slowing down the corrosion kinetics, but the electrical insulating properties of aluminium oxide ( $\sigma_{Al_2O_3} \sim 10^{-10} \ Scm^{-1}$  @ 700°C [54]) leaves chromium oxide forming steel ( $\sigma_{Cr_2O_3} \sim 10^{-1} \ Scm^{-1}$  @ 750-800°C [26, 51]) as the best choice for an SOFC interconnect [55] (the conductivity values are not absolute because the oxides are extrinsic semiconductors at the IC operating temperature [56]). According to literature, the chromium content needed to ensure a continuous and homogeneous passivation layer is 18-19 wt.%, but, considering the risk of Cr-breakaway oxidation (depletion of the protecting element), 22-25 wt.% is considered a safer Cr content for the IC [53, 55]. Only austenitic (ASS) or ferritic (FSS) stainless steel can thus be used in an SOFC stack, as martensitic stainless steel contains an insufficient amount of chromium. The  $\gamma$ -austenitic phase is face-centred cubic, whereas the  $\alpha$ -ferritic phase is body-centred cubic. This difference causes different CTEs in the SOFC temperature range of 25-800°C:  $18 - 20 \cdot 10^{-6} K^{-1}$  for the  $\gamma$ -phase vs.  $11 - 14 \cdot 10^{-6} K^{-1}$  for the  $\alpha$ -phase. [55]. FSS is therefore more compatible with the ceramic cell CTE  $(10.5 - 12.5 \cdot 10^{-6} K^{-1} \otimes 30 - 800^{\circ} C [50])$ . On the other hand, ferritic stainless steel performs poorer than austenitic steel in creep resistance and high temperature mechanical strength. High Cr-alloy also creates a protective passivating surface layer, and its CTE value is close to that of the cathode (e.g. CFY produced by Plansee:  $8.9 - 10.5 \cdot 10^{-6} K^{-1} @ 300 - 800^{\circ} C [57]$ ).

Different alloy compositions have been tested and improved in an effort to meet property criteria mentioned above. The current state-of-the-art are specialized SOFC alloys: Crofer 22 APU or H, Sandvik Sanergy HT, Plansee ITM and CFY. Commercial FSS grade AISI441/K41 is also a widespread, SOFC non-specific alternative due to its lower cost, despite poorer corrosion resistance and mechanical properties. The compositions are specified in the Materials and Experiments chapter 2.

## 1.5 Corrosion

Corrosion and mechanical deformation are the most pronounced degradation phenomena affecting the SOFC interconnect. The first increases the electrical resistivity of the interconnect because of the lower electrical conductivity of the thermally grown oxide layer, whereas the second deforms the interconnect shape, potentially reducing the contact area with the cell. Among the different definitions of corrosion, the one by L.L. Shreir is taken into consideration [58]: "the reaction of an engineering

constructional metal (material) with its environment with a consequent deterioration in properties of the metal (material)". At the microscopic level, corrosion is a two-step nucleation and growth process: oxidative species are adsorbed and react with the metal surface, starting oxide nucleation, followed by two-dimensional lateral growth and finally three-dimensional growth. When the oxide layer is compact and continuous, growth becomes a diffusion-controlled phenomenon. Despite extensive research, no universally accepted description of the corrosion process yet exists. Depending on the oxide layer thickness, two approaches have been proposed. For initial-stage oxide layers and up to few nanometers in thickness, Cabrera-Mott's model is proposed [59]. This model is based on the assumption that the oxygen atoms adsorb on the surface, where they are ionized by an electronic exchange with the metal substrate. The fundamental simplification of the model is that the electron has no energy barrier that must be passed to access the oxygen in this phase. The gradient in the charged species generates an electric field at the metal/oxide interface, which then influences the ionic migration at the metal/oxide or oxide/gas interface. The generally accepted limit to the validity of these assumptions is at a thickness < 10 nm, which can be calculated as Eq. 1.8

$$X = \frac{(qa\Delta\Phi)}{(2kT)} \tag{1.8}$$

Here q is the electric charge of the charged species, a is the ionic jump distance,  $\Delta \Phi$  is the electric field, k is the Boltzmann constant and T the temperature [60]). However, this description is not helpful for the purposes of this thesis, as the materials described all underwent a pre-oxidation process, causing them to already have formed the first nanometers of oxide prior to the testing. Once the oxide layer is set and homogeneous, the corrosion growth process becomes diffusion controlled, with a gradient in a physical property (e.g. oxygen partial pressure) as driving force for the mass transport [61]. Wagner's diffusion-controlled model is the most known among these approaches [62]. The scale thickness growth ( $\Delta x_{ox}$ ) with time is proportional to a kinetic constant and follows a parabolic law:

$$\Delta x_{\rm ox} = \sqrt[2]{K_{\rm p}\Delta t} \tag{1.9}$$

Where  $K_p$  is the corrosion or parabolic rate constant, which is defined as:

$$K_{p} = k \int_{p'o_{2}}^{p''o_{2}} D_{M} d\ln p_{O_{2}}$$
(1.10)

Here k is a constant,  $D_M$  the diffusion coefficient for the dominant diffusive species,  $p'_{O_2}$  is the oxygen partial pressure at the metal/oxide interface, and  $p''_{O_2}$  is the oxygen partial pressure at the gas interface (for a detailed approach cf. [63–65]). Therefore, with a known  $K_p$  value obtained from a relatively short experimental period of 1000 h, the correlation presented in Eq. 1.9 would allow for the prediction of the oxide layer thickness for longer periods, e.g. years (>10000 h). 1000 hours of testing is a compromise between the need of short test and the need of results not

influenced by the initial transitory phenomena (e.g. change of the contact surface during the ASR test) [27]. In addition, for simple model in which the resistance of the MIC is directly proportional to the scale thickness, resistance forecasting is also possible. In reality, this is an oversimplification, as shown in Figure 1.3, where the fitted exponent n significantly deviates from purely parabolic behavior (n=0.5). Therefore, other parameters must be taken into account, such as scale morphology, oxide scale composition (always containing various impurities), and transient operating conditions (e.g., redox and thermal cycles).



Figure 1.3 – ASR trend obtained from a  $La_{1-x}Sr_xMnO_3$  (LSM)-coated CFY sample in air at 850°C. Reprinted with permission from "Solid Oxide Fuel Cell Lifetime and Reliability",2017

Comparing the evolution of the ASR in Figure 1.3, from conductivity measurements, with the evolution of the  $Cr_2O_3$  scale thickness, the trends are different and non-linear, with a much more pronounced variation at the beginning of exposure, i.e., for observation times < 5000 h. This behavior is related to the morphology of thermally grown oxide scales between the coating and the metallic substrate (on the cathode side). According to Ohm's law, the electrical current follows the paths of least resistance, i.e. through the bridges where the oxide scale is thinnest. These current bridges can lead to a significant reduction of ASR and provide local transversal electrical current pathways that amplify the bridging effect. Nevertheless, the impact of this bridging effect is time-dependent, as it depends on the overall scale thickness. With increasing scale thickness, the effect becomes less relevant. The Wagner equation also oversimplifies the corrosion process with strong basic assumptions: the oxide must be dense, the interfaces must be at equilibrium, there must be local space charge neutrality, and there can be no electric field involved [66]. The variable entity is the chemical gradient of the species, often only oxygen. In operating condition, these assumptions are not valid. The materials are constantly subject to an electric field and the system is not at equilibrium, as the interacting species is not only oxygen. Rather, the variables affecting the corrosion process in a SOFC interconnect include the alloy composition, material morphology, gas composition, surrounding materials, and polarization.

The aforementioned models give a general description of the oxidation process, but variables such as alloy composition, operating temperature, oxygen partial pressure, gas atmosphere composition, and chemical interaction with third components, make each corrosion process unique. Thus, the Wagner model often does not describe the scale growth in complex systems.

Ferritic stainless steel is the alloy class of interest for the present thesis. Even though this type of alloy has been studied for more than a century, the interpretations of the same oxidation process are still conflicting and incomplete. When a perfectly polished ferritic stainless steel surface comes in contact with an oxygen-containing atmosphere, the oxygen will adsorb on the metal surface, reacting with the exposed metal atoms. The chemical reaction between the oxygen and metal will occur, as the oxide phase is thermodynamically favored. Eq. 1.11 presents the simplest reaction between a pure metal and oxygen:

$$xM + \frac{y}{2}O_2 = M_X O_y \tag{1.11}$$

Considering the law of mass action and the Arrhenius equation, the reaction rate for Eq. 1.11 can also be written as Eq. 1.12:

$$\ln[(pO_2)^{\frac{y}{2}}] = \frac{-\Delta Q}{RT}$$
(1.12)

where  $p_{O_2}$  is the oxygen partial pressure, and  $\Delta Q$  is the activation energy for the oxidation process, notably the Gibbs free energy of the formation of the oxide. Eq. 1.12 therefore provides the oxygen partial pressure threshold, above which the metal will transform to oxide and vice versa. This specific oxygen partial pressure is called the dissociation partial pressure. The relation between oxide dissociation partial pressure and activation energy allows writing the Richardson Ellingham diagram. From this diagram, the following values of dissociation pressures have been extracted for 700°C:

Table 1.1 – Oxygen equilibrium partial pressures for some relevant compounds at 700°C. Values are expressed in atm

	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>3</sub> O <sub>4</sub>	FeO	<i>Cr</i> <sub>2</sub> <i>O</i> <sub>3</sub>	TiO <sub>2</sub>	H <sub>2</sub> O
<i>p</i> <sub>02(eq)</sub>	10-13	10-21	10-22	10-32	$10^{-40}$	$10^{-8}$

As shown in Table 1.1, at an SOFC operating temperature of 700°C: i) low oxygen are sufficient to oxidize the FeCr alloy and ii) if water is present, there will be oxidation agents in case of a reducing atmosphere. Studies on the first stages of alloy oxidation have been conducted on simple Fe-Cr systems at different atmospheric and temperature conditions and Fe/Cr ratio [67–70]. At temperatures up to 800°C and Cr contents  $\leq$  9 wt.%, the scale was constantly made of an inner chromium containing corundum phase and an outer iron oxide phase. The chromium-containing phase tends towards pure  $Cr_2O_3$  at higher chromium amounts in the starting alloy and with increasing oxidation time. Although a perfectly metallic stainless steel surface at the initial stage of oxidation may produce both chromium and iron oxides,  $Cr_2O_3$  is thermodynamically favored over hematite. As a consequence, the chromium oxide becomes the main phase and pushes the iron atoms towards the interface with oxygen. [71]. Experimentally, Srisual et al. confirmed this: at 850 °C the oxide grown on AISI441 samples in dry air was  $Fe_{1,2}Cr_{0,8}O_4$  after 5 minutes and  $Fe_{0,4}Cr_{1,6}O_4$ after 60 minutes [72]. The expelled iron cations react in turn with oxygen. In pure Fe-Cr alloys, a hematite phase top layer is constantly present.

In the Fe-Cr alloys enriched with different elements (Si, Mn, Ti, Nb), oxidation studies have reported an inner chromia layer and an outer  $(Cr, Mn)_3O_4$  layer as corrosion products. Iron is not usually reported as an element in the scale [73]. The most encountered explanation for this is that Mn is selectively oxidized in place of Fe. Like chromium, the Mn-containing oxidation products have lower Gibbs free energies than those based on iron. Furthermore, the description of the selective process is not coherent (cf. sources from Table 1.2). While one study did support simultaneous Mn and Cr oxidation with no iron involved in the entire oxidation process, another claimed than Mn transport towards the scale/gas interface and successive oxidation happens after the formation of a continuous  $Cr_2O_3$  film on the alloy surface. This latter hypothesis is more commonly encountered in literature. The absence of Fe in the description of the oxide layer is supported by material characterization techniques such as EDS and XRD, but when more precise methods are applied, iron is detected [25]. Hence, despite the preferential oxidation of Mn and Cr due to their lower enthalpy of formation than iron oxides, iron oxide nuclei also form. This initial nucleation and growth phase is referred to in the Cabrera-Mott model.

Table 1.2 helps to better understand the dependence between the scale composition and the oxidizing conditions.

Table 1.	2 – Summary c	of studies	on the fi	irst phases	s of scal	e formation on ferritic stainless steel and Fe-Cr all	oys.
Alloy	Experiment/ Model	Temp (°C)	Pre oxid.	Press (Pa)	H2O(g)	Corrosion products	Time
Fe-Cr (50:50) [74]	Model	1200	No	1.01E5 (air)	No	$(Fe_2O_3 + FeCr_2O_4 + Cr_2O_3 + CrO_2 + Fe_3O_4)/(FeCr_2O_4 + FeO)/Cr_2O_3$	Equilibrium
Fe-Cr (80:20) [74]	Model	1200	No	1.01E5(air)	No	$(Fe_2O_3 + Fe_3O_4 + FeCr_2O_4 + CrO_2 + Cr_2O_3)/(FeO + FeCr_2O_4)/Cr_2O_3$	Equilibrium
Fe-Cr (70:30) [68]	Experiment (XPS/GIXS)	600	No	1.01E5(air)	No	Fe rich oxide/Cr rich oxide Fe rich oxide/Cr rich oxide (higher Cr amount)	5 min 50 min
Fe-Cr (91:9) [69]	Experiment (AES)	400	No	1.01E5(air)	No	Fe2O3/Fe3-xCrxO4/Cr2O3	2 hours
Fe-Cr (82:18) [69]	Experiment (AES)	400	No	1.01E5(air)	No	Fe2O3/Fe3-xCrxO4/Cr2O3	2 hours
Fe-Cr (80:20) [70]	Experiment (LEED/AES)	476 to 677	No	1.3E-7 to 1.3E-5(air)	No	Fe3O4/Fe3-xCrxO4	2 hours
Fe-Cr-Mo (77:14:4) [70]	Experiment (AES)	25 to 800	Yes	1.3E-3 to 1.3E-5(air)	No	$Cr_2O_3$ for T > 700 °C Fe oxides for T < 700 °C	0.5-1 hours
AISI441 [75]	Experiment (EDS/XRD/PEC)	800	No	1E5( <i>CO</i> 2)	No	(Mn, Cr) <sub>3</sub> O <sub>4</sub> /(Fe, Cr) <sub>2</sub> O <sub>3</sub> (Mn, Cr) <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	25 h 200 h
				1E5 ( <i>αir</i> )→	No	Fe2O3/(Fe, Cr)2O3,Cr2O3 (Air, 650°C)	5 min
	Experiment (Raman/XRD/PEC)	850	:		N N	re1.2c10.8U3/C12U3 (MII, 03U C) (Mn, C1)304/Fe0.4C12.6O3/C12O3 (Air, 850°C)	60 min
AISI441 [72]			NO		20% in N <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub> /(Fe, Cr) <sub>2</sub> O <sub>3</sub> /Cr <sub>2</sub> O <sub>3</sub> (Water vapor, 650°C)	5 min
					20% in N <sub>2</sub>	(Mn, Cr) <sub>3</sub> O <sub>4</sub> /Fe <sub>0.4</sub> Cr <sub>1.6</sub> O <sub>3</sub> /Cr <sub>2</sub> O <sub>3</sub> (Water vapor, 850°C)	5 min
					20% IN N2	(MM, CT)304/FE0.4CF1.6U3/CF2U3 (Water Vapor, 85U C)	
Fe-Cr(80:20) [71]	Experiment (XPS)	25 25	No	2.5E4(air)	No	(Fe, Cr) <sub>2</sub> O <sub>3</sub> /FeCr <sub>2</sub> O <sub>4</sub>	46 h
Fe-Cr(82:17) [58]	Experiment (EDS, XRD)	650 750 850	oN	1.01E5(air)	o Z	$MnCr_2O_4/Cr_2O_3$ (for all the temperatures)	500h
AISI409 [60]	Experiment (EDS)	600	No	1.01E5(air)	No	$Fe_2O_3$ (No Cr detected) $Fe_2O_3/(Fe, Cr)_2O_3$	72 h 372 h
DIN50049 [61]	Experiment (EDS, XRD)	730 900	No	1.01E5(air)	No	<i>Mn</i> 1.5 <i>Cr</i> 1.5 <i>O</i> 4/Fe doped <i>Cr</i> 2 <i>O</i> 3	480 h

#### 1.5. Corrosion

Once the chromia scale is set, the oxide growth process would follow a diffusion behaviour. When considering the ferritic stainless steels in the context of Eq.1.10 the major diffusive species are  $Cr^{3+}$  and  $O^{2-}$  ions and their vacancies, with interstitial Cr-cations commonly accepted as the main diffusive species [64, 65]. The fastest and privileged diffusion path for the cations is the grain boundary. Because of the high operating temperatures of SOFCs, grain dimensions increase and thus diffusion paths reduce. In addition, the composition of the scale in aged interconnects cannot be simplified to  $Cr_2O_3$  as in the cited works. Predictions on the evolution of the scale are therefore not yet reliable and experimental observations are still necessary to validate the alloy corrosion behaviour.

Furthermore, no consensus has been formed on the effect of oxygen partial pressure on  $K_p$ . Although most researchers have considered the oxidation rate to be independent of  $p_{O_2}$  [62, 64, 76], others report an interdependence [65]. A correlation between  $D_{Cr}$  and  $p_{O_2}$  at high temperature actually does [62]. However, for small changes in oxygen partial pressure, like the condition existing at the SOFC cathode,  $D_{Cr}$  can be considered constant. The explanation for these different behaviors is not final and the lack of a common standardized test makes any comparison of results difficult. The scientific community agrees on the influence of water partial pressure on the growth kinetics of the corrosion process. In general,  $K_{\rho}$  has been shown to increase in the presence of humidity, both in anodic and cathodic conditions. Faster diffusion of ion hydroxide  $OH^-$  than  $O^{2-}$  (0.95 Å vs 1.4 Å ionic radius) through the scale is the prevailing accepted explanation [77]. Meanwhile, steam in the gas flows reacts with  $Cr_2O_3$ , producing the gaseous species  $CrO_2(OH)_2$  at SOFC operating conditions . This process then depletes Cr from the substrate and thins the scale. The rate at which the chromium cations diffuse towards the surface could be slower than evaporation. This could cause the formation of iron oxides on top of the alloy, in a process called iron breakaway due to the exponential shape of the growth oxide curve [78]. The predominance of one of the two concurrent processes is influenced by the deposition of a coating or by the alloy composition. For example, Mn migrates towards the alloy surface in the first stages of scale formation, forming a superficial  $(Mn, Cr)_3O_4$  spinel layer that decreases Cr evaporation. Water vapor also influences the structural scale properties: porosity in the thermally grown oxide layer has been found to be more homogenously distributed through the thickness when compared with a scale grown in a dry environment, where the pores were instead concentrated at the alloy/scale interface [77]. The aforementioned studies refer to samples studied in a single atmosphere. In a real stack, the ICs work in a dual atmosphere. Experiments conducted with FSS alloys placed between reducing and oxidizing environments found a raise in Fe concentration in the thermally grown oxide layer at the air side, attributed to H proton migration through the alloy from the fuel to the air side [13]. This behavior may be an important drawback for SOFCs working at temperatures near 550-600°C, as it has been demonstrated that AISI 441 exposed to dual atmospheres at 600°C suffered severe breakaway corrosion [79]. Different explanations have been proposed, e.g. hydrogen increased internal oxidation, reducing chromium supply and causing breakaway corrosion, but no theory

has been universally accepted. To accelerate the degradation kinetics and decouple the influence of coatings, most of the studies cited above used uncoated substrates.

In anode and electrolyte-supported SOFCs, glass sealants are used to ensure the gas tightness between the cell and the interconnects in the stacks. Barium-calciumaluminosilicate (BCAS)-based glasses are commonly used for this purpose [80]. To tune the glass properties, minor quantities of elements such as Pb, V, B, or Mg are added. Their presence may cause the acceleration of corrosion kinetics at the glass/steel interface. For example, in the stack failure described in [81] an electrical short circuit was experienced between metal plates after only a few hundred hours of operation at 800°C. The post-test characterization correlated the failure to the presence of iron oxide nodules at the cathode side. These bumps grew rapidly and electrically connected the interconnects; the electrical conductivity was further enhanced by the presence of metallic iron inside the nodules. This phenomenon appeared only at the triple phase boundary metal/glass sealing/gas (air or fuel). Another study helped to understand the corrosion process [80]: the reduction of PbO (contained in the glass) frees Pb, which reacts with the steel surface and scavenges chromium, increasing the oxidation kinetics. Fast  $Cr_2O_3$  growth continues until there is not enough Cr left and breakaway corrosion occurs. Eventually, iron oxides grow and form an electrically conductive pathway, leading to a short circuit. Ba also is an active element towards the chromium contained in the steel, which leads to the formation of  $BaCrO_4$ ; however, post-test analysis did not show a clear role for this compound in the stacks failure. A recent study analyzing the influence of polarization on the MIC/sealant interface degradation presented a clear picture of the barium chromate formation [82]: with increasing porosity accumulation at the seal/interconnect interface comes an increase in polarization. An alternative to glass sealing is phyllosilicates-based gaskets, which contain Mg, Fe, Al, Si and K, and provide a gas barrier if mechanically compressed. The interaction between a phyllosilicate material (Thermiculite XJ766) and Crofer 22 APU at 800°C for hundreds of hours revealed a corrosion behavior similar to that of glass/steel [7]. Cr corrosion kinetics at the steel/Thermiculite/air interface were faster than expected for Crofer 22 APU, with a scale thickness of 20-25  $\mu m$  vs. usual value of 2-3  $\mu m$ . In addition, Cr depletion from the steel substrate caused Mg/Mn/Cr-enriched Fe oxide to grow. At the steel/Thermiculite/fuel side, there was also an increase in corrosion , in the form of an 8-10  $\mu m$  thick Fe/Cr/Mg/Mn oxide, but no crack formation typical of the interaction with a BCAS glass seal was apparent at the anode side.

Post-test analysis showed that the most sensitive location for corrosion degradation was the triple phase boundary if alloy/sealant/gas (air or fuel) [80, 81, 83]. The use of a hybrid seal such as vermiculite-based materials, coupled with a BCAS glass, provided similar interactions at the three phase boundary [84].

### **1.6 Mechanical stresses**

Ferritic stainless steels were also selected as interconnect material because of their CTE compatibility with the ceramic components in an SOFC stack. Yet, the differ-

ence in lattice parameters between the steel substrate, thermally grown oxide, and protective coating can cause residual mechanical stresses during the heating or cooling of the stack and lead to spallation of the scale or protective layer. During heating and scale growth, the scale is subjected to tensile stresses because of the higher thermal expansion of the steel substrate compared than that of the scale. Conversely, compression stresses in the scale arise during cooling. Understanding of the thermal stresses in the stack components is of high relevance to meet the reliability requirements of SOFC systems. In addition, SOFC stacks have to withstand thermal cycling during their lifetime. Thermal cycling exposes the stack components to faster mechanical degradation, caused not only by the mismatch of thermal expansion between the materials, but also by thermal gradients during heat up/cool down. Researchers have approached this problem with different testing and simulation conditions; many have used the Griffith fracture approach, in which a certain energy (given by shear stress in this case) threshold must be overcome to cause the failure of the ceramic materials. The interfacial strength is measured experimentally using either an indentation test (e.g. Rockwell) or a four-point bending test. Knowing the other mechanical properties of the materials studied, it is possible to correlate this value to a certain oxide layer thickness, which in turn, coupled with a kinetic curve for oxide layer growth, could forecast the adhesion lifetime of the ceramic layers (oxide layer or protective coating). For example, Liu et al. forecasted the lifetime of  $MnCo_2O_4$  coated and uncoated Crofer 22 APU substrates [85]. The samples were first oxidized at 800 °C and cooled to room temperature to simulate the stress due to a turning off a system before a Rockwell indentation test was performed. Their results indicated that the strength at the metal/scale and scale/coating interfaces were the maximum shear stress tolerated by the samples. The experimental data were then used in an FEM model to obtain the interfacial strength as a function of the scale thickness. The model predicted a lifetime of about 4800 h for uncoated Crofer 22 APU and ca. 15000 h when coated with MnCo<sub>2</sub>O<sub>4</sub>. These results reflect a critical scale thickness of 11.4  $\mu m$  and 4.2  $\mu m$ , respectively.

Models such as these estimate the stress inside the MIC with finite element simulations. As an example, a temperature profile obtained from a combined thermoelectrochemical and fluid dynamics model was imported into an FEA model. The resulting Von Mises stresses in the metallic interconnect of an SOFC stack model simulated in co-flow configuration is shown in Figure 1.4. The center of the cassette was exposed to the highest temperatures, because of the electrochemical reactions occurring at the cell. Considering that stresses in SOFC stacks are by thermal gradients and thermal expansion mismatch between the components, among others, the highest Von Mises stresses in the IC was located at the central area of the cassette, as shown by Figure 1.4. The IC is likely to buckle in this area, especially if the material is relatively thin. Buckling may then provoke i) damage of the adjacent elements on one face, i.e. inelastic deformation of the GDLs (gas distribution layers) and ii) detachment of the interface, on the opposite face. As a result, stack reliability is affected also by the stresses in the IC. To investigate the thermo-mechanical reliability of SOFC stacks upon operation, scenarios of long-term operation, thermal



Figure 1.4 – Von Mises stress field at high temperature in a metallic cassette manufactured by SOLIDpower S.p.A. The stress field was calculated by FEA (finite elements analysis) simulating the stack production process steps, followed by co-flow operation. Operating conditions used to generate the simulated temperature profile were  $T_{fuel,in} = 700$  °C,  $T_{air,in} = 700$  °C, partial pre-reforming of 0.5, FU = 0.85, and  $T_{max,cell} = 827$  °C. Regions with high stresses indicate possible plastic deformation as well as risk of buckling.*Reprinted with permission from "Solid Oxide Fuel Cell Lifetime and Reliability"*, *Academic's Press*, 2017

cycling, and a combination of these have been simulated [86]. Using the stress states simulated by the FEA model, mechanical reliability analysis of SOFC stacks was then carried out either by applying fracture mechanics or by investigation of the contact pressure between the stack components. Contact pressure influences the electrical current pathways between the IC and cell and thus the stack performance and durability [86, 87].

Nonetheless, thermo-mechanical degradation of interconnects in real stacks appears less dramatic than that predicted by modeling: in a stack run for 35000 h containing Fe-doped  $MnCo_2O_4$  (MCF) coated Crofer 22 APU interconnects (same steel substrate as in [85]), no sign of delamination at the steel/scale or scale/MCF interface occurred, even though the average scale thickness was between 3-5  $\mu m$  [88] and the model of Liu et al. predicted delamination at 4.2  $\mu m$  scale thickness for coated surfaces. This difference supports the need for more validation test of interconnects in operative conditions.

## **1.7** Solutions to decrease IC degradation

One strategy that has been adopted to mitigate MIC degradation relies on tuning the alloy composition. The addition of reactive elements (e.g. small amounts of Ce, La or Y) in the alloy affects the oxygen and chromium diffusion coefficients in thermally grown  $Cr_2O_3$ , decreasing its kinetic growth [89, 90]. This technique also improves the

scale adhesion to the alloy substrate and therefore the resistance to thermal cycling. Another important alloying element is Mn; its fast diffusion across the chromia scale [65] and interaction with chromium leads to the creation of a preferred  $(Cr, Mn)_3O_4$  spinel phase at the gas interface of the thermally grown oxide scales. This spinel phase positively influences the electrical conductivity [51] and in addition reduces the undesirable Cr evaporation. However, alloy composition alone is not sufficient to achieve the desired IC lifetime. The deposition of protective coatings on the alloy surface has been established as a *sine qua non* for long-term SOFC applications. Spinel and perovskite coatings are commonly used. Their deposition techniques play an important role, as they lead to different microstructures, particularly the coating density. The effectiveness of a protective coating in improving the electrical contact is shown in Figure 1.5, where ASR results for coated and uncoated alloys substrates are compared. The difference is greater than one order of magnitude, and a similar result is shown for the same coating on different steels.



Figure 1.5 – ASR graph of alloys ITM (26 %wt. Cr) and Crofer 22 APU (22 %wt. Cr) with and without protective coating ( $MnCo_2O_4$ ). In air @800°C using 250  $mAcm^{-2}$ , in contact with LSCM5555 powder LSM tablet with Pt electrode (tablet and electrode resistance subtracted). Reprinted with permission from "Solid Oxide Fuel Cell Lifetime and Reliability", Academic's Press, 2017

Under the same coating material, high-coating-density deposition methods like PVD or atmospheric plasma spray (APS) give better results, as demonstrated in Figure 1.6 on Sandvik Sanergy HT steel substrates [91, 92]. The imaging of the microstructure of the thermal oxide layers formed, presented in Figure 1.7, help to partially explain these results. The  $MnCo_2O_4$  protective coating deposited by wet powder spray, shown in Figure 1.7 (a), remained porous, leading to a thicker  $Cr_2O_3$  scale grown on top of the FSS substrate, than either the APS or PVD deposited dense coatings, shown in Figure 1.7 (b) and Figure 1.7 (c), respectively. The  $\Delta p_{O_2}$  through a  $Cr_2O_3$  layer is very large going from metallic Cr at the metal/scale interface and air. Application of a dense coating (e.g. a spinel layer) therefore reduces the oxygen



Figure 1.6 – Electrical resistivity performances of FSS substrates coated with Fedoped MCO deposited by different methods. High-coating-density techniques (APS, PVD) produced the best results. Testing conditions: 700°C, 3%vol.,  $H_2O(g)$ , 0.4  $A/cm^2$ . WPS: wet powder spray, APS: atmospheric plasma spray, PVD: physical vapor deposition, ALD: atomic layer deposition. Results are presented in detail in chapter 3. *Reprinted with permission from "Solid Oxide Fuel Cell Lifetime and Reliability"*, Academic's Press, 2017

gradient over the  $Cr_2O_3$  layer significantly (from metallic Cr to the decomposition pressure of the spinel), lowering the gradient and oxygen transport in this layer. Adding a second protective layer (e.g. a perovskite) might then reduce the oxygen gradient over the spinel layer in the same way. These coatings have also different transport properties. Cation diffusion is predominant in spinels, whereas oxygen ions are often the predominant diffusing species in perovskites. The spinel thus limits the oxygen transport while a perovskite can limit cation diffusion. Although the total gradient is the same as for uncoated steel, but since the coating layers restrict diffusion efficiently, thus obtaining a protection that allows for several thousands of hours of operating time before Cr reaches the surface; since the Cr concentration in the surface is then very low and stabilized in a structure, only restricted Cr evaporation is expected.

The comparison between two cross sections taken from interconnects operated in short stacks for 10000 hours shown in Figure 1.8 depicts the Cr retention properties of spinels. Here, the denser coating, especially PVD-deposited, shows a thinner scale and excellent Cr retention. This can be qualitatively appreciated with the chromium element map showing no green areas in the cathode that has been in contact with the interconnect. In contrast, the perovskite material contacting the interconnect with a WPS coating underwent serious Cr contamination. After 10000 hours, the coating was no longer porous because of the Fe contamination due to enhanced corrosion. Iron contamination is also a drawback not experienced by dense coating.



Figure 1.7 – Thermally grown oxide on FSS substrates coated with different coating techniques depositing same protective layer ( $MnCo_2O_4$ ): a) wet powder spray b) atmospheric plasma spray c) physical vapour deposition. High-density coatings led to the best results in terms of minimum scale thickness, which in turn provided a lower contact resistive loss for the samples b) and c). Reprinted with permission from "Solid Oxide Fuel Cell Lifetime and Reliability", Academic's Press, 2017

On the other hand, wet-powder sprayed and other low density coatings, are cheaper and faster to deposit.

The next generations of protective coatings will likely be without cobalt [93], due to its cost, toxicity and handling/recycling. Recently copper and Fe have been used to substitute cobalt [94–98]. In addition to decreased cost and increased safety, these two elements are sintering aids, i.e., they help to increase the densification process at lower temperatures. Talic et al. demonstrated that Cu- and Fe-doped MCO had higher percentage of densified regions with respect to a pure MnCo spinel [99]. Additionally, the poor creep resistance of ferritic stainless steels was improved with the addition of a modest amount of Nb and/or W (0.5 to 2 wt.%). These elements lead to Laves phases, intermetallic compounds with the composition  $AB_2$  (e.g.  $Fe_2Nb$ ), which segregate at the grain boundaries and induce precipitation hardening [100]. An example of Laves phases in FFS is given in Figure 1.7: Crofer 22 H (cfr. Table2.1 chapter 2) segregates Nb-W containing precipitates at the grain boundary; these phases in the images are the small white particles and are clearly visible in the APS sample. The precise correlation between Laves phase precipitation and creep strengthening has not been determined, as other precipitates also strengthen the FFS microstructure. In addition, Ostwald ripening of Laves phases can decrease the mechanical properties of the material, leading to a ductile-to-brittle transition. The coarsening of the Laves phases must be delayed to ensure the long life of the interconnect [101]. Laves phases also segregate below the scale (Figure 1.7); this, together with their affinity for Si, may be another cause of interconnect electrical behavior degradation [92].

### 1.8 Metal interconnects operated in stacks

Many of the available studies on metal interconnects come from small samples tested in laboratory conditions; companies are often reluctant to disclose material degradation information under operating conditions. A collection of the available studies regarding MICs behavior in stack or short stacks is reported in Tables 1.3

#### **1.8.** Metal interconnects operated in stacks





and 1.4 along with operating conditions, cell and interconnect materials, and testing periods.

Table 1 phenor	L.3 – summa nena.	arizes lor	ng term results on	present state-c	of-the-art stacks, with a focus on the observed MIC degradation
	IC alloy & Coating	Testing Conditions	Cell	Stack degradation	Interconnect behavior
				Anode	supported
	Crofer 22 APU Mn <sub>2</sub> O <sub>3</sub>	17000 h	Anode: Ni-YSZ		- $Mn_2O_3$ allows Cr migration -> SrCrO_4 grown on LSCF -> progressive stack degradation - @ cathode side: 4 $\mu$ m scale thickness; local $Cr_2O_3$ breakaway with Fe-oxide spots
1 [102]	(SMPS)	700 °C 0.5 A/ <i>cm</i> ²	(H <sub>2</sub> /3%H <sub>2</sub> O) Cathode: LSCF (air)	ca. 1%/kh	(but no short-circuits between ICs). ( $\emptyset$ anode side: 2 $\mu$ m scale thickness; Ni diffusion into Crofer 22 APU -> austenite phase creation
	Crofer 22 APU	19000 h	Anode: Ni-YSZ		<ul> <li>minor cracks in MCF but no delamination</li> <li>thicker scale at the uncoated anode side (12 μm) than at the coated cathode side (3 μm)</li> </ul>
2 [103]	MCF (APS)	800 °C 0.5 <i>A/cm</i> ²	(H <sub>2</sub> /3%H <sub>2</sub> O) Cathode: LSM (air)	4 mV/kh	<ul> <li>accumulation of micropores in the MCF at the IC/MCF interface</li> <li>humidity present at anode side, lead to porosity in the anode side scale</li> </ul>
	Crofer 22 APU	35000 h	Anode: Ni-YSZ		- @ cathode side: 3-5 $\mu$ m thick Cr-Mn scale. No spallation at the steel/scale/MCF interface.
3 [88]	MCF (APS)	700 °C 0.5 <i>A/cm</i> ²	(H2/25%H2O) Cathode: LSCF(air)	0.3%/kh	<ul> <li>@ anode side: Ni diffusion (from contacting wires) lead to a 50-100 μm wide austenized zone. No brittle σ-phase found in the same area.</li> <li>No enhanced corrosion at the steel/sealing interface</li> </ul>
	Crofer 22 APU	6000 h	Anode: Ni-YSZ (1 NG 7 2 slm	0 3%/kh	<ul> <li>strong MCF adhesion on Crofer 22 APU</li> <li>no cracks penetrating through the coating</li> </ul>
4 [104]	I MCF (APS)	700 °C 0.5 <i>A/cm</i> <sup>2</sup>	H <sub>2</sub> 3.2 slm, H <sub>2</sub> O 15.2 slm) Cathode: LSCF (air)	for 4.5 kh	<ul> <li>MCF coating retained chromium</li> <li>MCF coating retained chromium</li> <li>melting of IC and sealing glass occurred in one cell because of a leakage in the sealant</li> </ul>
	AISI 441	5000h	Anode:		. @ cathode side: thicker scale on the IC ribs ( 5 $\mu$ m) than the valleys ( 3 $\mu$ m). Fe diffuses through Cr2O3 and Cr diffuses through MCO.
ۍ *	MCO (WPS)	780 °C	NI-Y5Z (N2/H2) Cathode:	0.4%/kh	<ul> <li>good adnerence: no coading or scale spallation</li> <li>densification of the MCO coating where the ribs are in contact with LSC.</li> <li>A possible reason is Fe diffusion into MCO from the steel substrate</li> </ul>
		0.4 A/cm <sup>2</sup>	LSC (air)		- no enhanced corrosion due to dual atmosphere - @anode side: no coating, yet corrosion was not aggressive ( $5~\mu m$ )

	IC alloy & Coating	Testing Conditions	Cell	Stack degradation	Interconnect behavior
				Anode supp	nted
	AISI 441	2600h	Anode:		$$ cathode side: scale thickness < 3 $\mu$ m where MIC not in contact with the cathode (rib),
			Ni-YSZ(N <sub>2</sub> /H <sub>2</sub> )		ca. 10 $\mu m$ where the MIC was in contact with the cathode (valley).
*9	Spinel	760 °C			Fe breakaway corrosion into the scale and the spinel coating
	(WPS)		Cathode:		No sign of delamination at the steel/scale and scale/protective coating interface
		124 thermal cycles	LSC(air)		despite the 124 thermal cycles
	AISI 441	6000 h	Anode:		@ AISI441/Ni-current collector interface corrosion is enhanced if Ni wires have
	Ce-MCO (Slurry)		Ni-YSZ		diameter < 100 $\mu$ m
7 [105]	on LSM	800 °C	$(H_2, N_2(1:1) + 3\% H_2O)$	1.4%/kh	@ cathode side: Cr depletion below the scale (16%at. instead of 20%at.)
	Al <sub>2</sub> O <sub>3</sub> where		Cathode:		No Cr traces in LSM. No spallation at scale/IC interface
	there is sealing	0.3 A/cm <sup>2</sup>	LSM-YSZ(air)		Si, Ti accumulation below the scale, but no continuous layer
				Electrolyte su	ported
			Anode:		Considering the IC ribs geometry, faster scale grows at the IC/cathode interface
	CFY	40000 h	Ni/CGO		than in the IC valley. This happens for both the cathode and anode.
8 [106][107]			(CPO +		Higher average scale thickness at anode with respect to cathode
	LSM(-)	D. 006	reformed natural gas)		Different CFY behavior at anode side: $\textcircled{O}$ the inlet valley, $Cr_2N$ compound is found
					$\oplus$ the center, the interaction of the oxide layer with the Ni-mesh is more intense;
		0.25 A/cm <sup>2</sup>	Cathode:		$\oplus$ the outlet valley, more pores in scale compared to the scale under the ribs
			LSM(air)		MIC-cell thermal mismatch lead to local stress peaks, which then boost crack propagation
				Metal supp	rted
		1100 h	Anode:	(single cell)	Increment in ohmic losses due to corrosion interlayer in between metal substrate
	FeCr alloy powders		CGO-Ni	5%/kh	and infiltrated CGO
9 [108]		650 °C	(H <sub>2</sub> /3%H <sub>2</sub> O)		
			Cathode:		
		0.25 A/cm <sup>2</sup>	LSCF/CGO (air)		
		500 h	Anode:		STN:FeCr half-cell showed better corrosion resistance than reference YSZ:FeCr reference cell
	FeCr powders		STN/FeCr		STN:FeCr (50:50) composition demonstrated a better oxidation resistance than STN:FeCr (70:30)
10** [109]	Ni-CGO	850 °C	$(p_{H_2O}/p_{H_2}=9)$		
			Half-cell**		

Table 1.4 - Continuation of Table 1.3

1.8. Metal interconnects operated in stacks

## 1.9 Interconnect carbon footprint

Steel making accounts for the 7-8% of the global carbon dioxide emissions. At the same time, steel demand has rapidly increased in the last 20 years, mainly due to China's manufacturing needs. National and continental associations for steel production have resolved to hinder further emission increase [110–113]. As described by the Intergovernmental panel for climate change, the emission of  $CO_2/t_{steel}$  depends on the type of steel produced, production energy efficiency, fuel mix, carbon intensity of the fuel mix, and electricity carbon intensity. India, for example, has a more consuming steel-making process than Korea (3.8  $t_{CO_2}/t_{steel}$  vs 1.6  $t_{CO_2}/t_{steel}$ ). Because this thesis has been carried out within the EPFL doctoral school of energy (EDEY), it is interesting to approximate how an understanding and solving of corrosion problems for SOFC MIC's may also directly mitigate CO<sub>2</sub> emissions. According to some forecasts, there will be ca. 1800 MW of SOFC devices installed [114] in 2025. For an interconnect made of AISI441/K41 with a weight of approximately 250 gr [5], 1 kg of steel produces 3.2 ICs, considering that ca.20% is lost during manufacturing. For 1 kW<sub>el</sub> produced with a SOFC system, about 45 interconnects, or ca. 14 kg/kW, are needed. If we consider the Chinese (the largest steel producer) value of 3.1  $t_{CO_2}/t_{steel}$ , the production of interconnects for 1800 MW generates ca. 63000 tons of carbon dioxide. Due to lifetime limitation, influenced in part by interconnect degradation, a SOFC stack for energy conversion has a lifetime of ca. 40000 hours. Doubling the lifetime, could therefore save 78000 tons of CO2. The savings would further increase if lifetime can be maximally extended and if SOFC deployment will further grow. Hence corrosion phenomena imply also the consideration for environmental reasons in addition to economics [115].

## 1.10 Concluding remarks

The publications of solutions to improve the SOFC interconnect performances, e.g. new coating compositions, is still variable and the absence of an established market encourages experiments on new materials.

On the other hand, the SOFC market players now focus on the consolidation of their technologies, pushing towards an extension of the lifetime and decrease of the cost. As a result, numerous interconnect solutions to extend stack lifetime have been proposed but not validated in real stack operating conditions, while real existing data are rare and often confidential (e.g., post operation-analysis of Ceres Power plc or Bloomenergy). This thesis contributes to fill this gap by comparing some of the most researched coating and alloy solutions for SOFC interconnects and testing the most promising ones in stack conditions. Experimental results are integrated with post-operational SEM/EDS observations to improve the knowledge of MICs behavior in SOFC stack operating conditions.

## 2 Materials and Experiments

This chapter describes the materials, the testing procedures and the characterization techniques that have been used during the thesis. The description of the adopted experimental procedures is needed to understand the results presented in the following chapters



## 2.1 Materials

The materials studied belong to metal (interconnect substrate) and ceramic (coatings, cell) classes. Notably for the metals: ferritic stainless steels(FSS), austenitic stainless steels (ASS) and nickel-chromium refractory alloys; for the ceramics: spinel oxides and perovskite oxides.

Different alloy compositions for interconnects have been tested. The current state-of-the-art alloys for SOFC are: Crofer 22 APU/H, Sandvik Sanergy HT, Plansee ITM and CFY. In addition, commercial FSS grade AISI441/K41 is a widespread SOFC

#### **Chapter 2. Materials and Experiments**

non-specific alternative due to its lower cost. With respect to Crofer 22 and Sanergy HT, AISI441/K41 is less resistant to corrosion and mechanical stresses. Table 2.1 gives the element weight composition for each of these alloys; those directly used in the thesis are highlighted in bold.

A part of the thesis is dedicated to balance of plant components of a SOFC power unit, Table 2.2 presents the composition of the alloys employed for that purpose. No steels have been directly purchased from steel manufacturers. SCORED2.0 and SOSLeM project partners provided all the testing samples.

	K41/AISI 441	Sanergy HT	Crofer 22 APU	Crofer 22 H	CFY	IT-11 or ITM
	[116]	[116]	[91]	[116]	[57]	[117]
Fe	Bal.	Bal.	Bal.	Bal.	5.0	71.8
Cr	18	21.2	20.0-24.0	20.0-24.0	94.0	26.4
Y	-	-	-	-	1.0	0.08
С	0.012	0.04	0.0-0.03	0.0-0.03	-	0.009
Mn	0.3	0.3	0.30-0.80	0.0-0.80	-	-
Si	0.35	0.12	0.5	0.1-0.60	-	0.01
ΑΙ	-	0.017	0.5	0.0-0.10	-	0.02
Мо	-	0.96	-	-	-	-
Nb	0.45	0.71	-	0.2-1.0	-	-
Ti	0.17	0.09	0.03-0.20	0.02-0.20	-	-
W	-	-	-	1.0-3.0	-	-

Table 2.1 – Chemical composition of the most used alloys for SOFC interconnects, weight percentage (wt.%)

Table 2.2 – Chemical composition of the most used alloys for balance of plant components, weight percentage (wt.%)

	Inconel 600	AISI 304
	[118]	[119]
Fe	6.00-10.00	Bal.
Cr	14.00-17.00	17.50-19.50
С	0.15 max.	0.07 max.
Mn	1.00 max.	2.00 max.
Si	0.5 max	1.00 max.
Ni	72 min.	8.00-10.50
Cu	0.5 max.	-
S	0.015 max.	0.015 max.
Ρ	-	0.045 max.

In Table 2.3 are listed the main mechanical, thermal and electrical properties of the ferritic stainless steel highlighted in Table 2.1.

During the period this thesis has been developed, Sandvik stopped producing Sanergy HT, substituted by 441 HT. This explains the difficulties in finding its material properties. Nevertheless, Sandvik Sanergy HT was one of the steel tested for the EU project SCORED2.0 (Chapter 3) and is therefore included in the studies.

Three spinel oxides:  $MnCo_2O_4$ ,  $MnCo_{1.8}Fe_{0.2}O_4$ ,  $MnCo_{1.6}Fe_{0.2}Cu_{0.2}O_4$  and one perovskite oxide  $LaFeO_3$  oxides have been tested as protective coatings. In addition

	<b>K41/AISI 441</b> [120]	Sanergy HT	<b>Crofer 22 APU</b> [91]	<b>Crofer 22 H</b> [121]
<b>Y</b> (GPa)	140 @600°C	-	183 @500°C	175 @600°C
<b>Rp<sub>0.2</sub></b> (GPa)	0.32	-	0.25	0.39
<b>R</b> <sub>m</sub> (GPa)	0.49	-	0.37	0.45
Hardness	78 (HRB)	-	160-200 (HV)	70-90 (HRB)
<b>CTE</b> (10 <sup>-6</sup> C <sup>-1</sup> )	12.1 (20-800°C)	12.9 (100-900°C)	11.6 (20-700°C)	11.4 (20-700°C)

Table 2.3 – Main physical properties for ferritic stainless steels described in this thesis. Sandvik did not disclose public information about Sanergy HT

to materials, also different techniques have been investigated. The spinels were applied with multiple deposition techniques, lanthanum iron perovskite only through dip coating. The next paragraph provides detailed information about these techniques.  $La_{1-x}Sr_xCoO_3$  (LSC) is the perovskite chosen as contact paste/chromium scavenging media. Figure 2.1 provides an example for both the structures. In all the small samples ASR tests, the LSC was provided by ELCOGEN. In the other tests when LSC is present, this was provided by SOLIDpower. In both cases, the material composition is proprietary information of the LSC supplier.



Figure 2.1 – (a) example of the of a spinel crystal structure (b) example of a perovskite crystal structure. These pictures are generated with the 3D visualization program for structural models VESTA

## 2.2 Coating deposition techniques

For a constant composition, the coating behaviour is mainly influenced by the deposition technique. SOLIDpower S.p.a., Turbocoating S.p.a., MIBA Teer Coatings Ltd, University of Birmingham, VTT Technical Research Centre of Finland Ltd, ENEA Italian National Agency for New Technologies, Energy and Sustainable Economic Development, AB Sandvik Materials Technology, produced the coatings. On demand of the

#### **Chapter 2. Materials and Experiments**

aforementioned partners, the deposition technique will not always be associated to the manufacturer and details of the deposition process can not always be disclosed. The information in this paragraph mainly concerns Chapter 3.

#### 2.2.1 Atmospheric plasma spray (APS)

With APS, an inert gas is forced to pass through the electric arc between two electrodes which ionizes the gas, creating a plasma on the order of thousands of degrees. This plasma is pushed outside a nozzle where it meets the coating powders which are eventually melted. The ceramic drops impact on the metal substrate creating the coating. Prior to the deposition, the material is sand-blasted to improve the mechanical adhesion between the drops and the material surface. The black alumina particles found during SEM/EDS observations at the steel/coating interface can be traced back to this practice (Figure 2.2).



Figure 2.2 – As deposited ferritic stainless steel sample APS coated with  $MnCo_2O_4$ ; SEM cross section. The surface is irregular because of a sandblasting pre-treatment

The coating layers obtained by APS are dense and with an average thickness of 50  $\mu$ m. The exact parameters (temperature, voltage, deposition time) used for the coating studied in the thesis are proprietary information and can not be disclosed.

#### 2.2.2 Atomic layer deposition (ALD)

The ALD technique is usually employed for high precision application at the nanoscopic level, e.g. semiconductors or batteries. ALD coatings are manufactured in reactors using metal organic precursors. The single atomic layers of these precursors are deposited on each other and then oxidized to evaporate the organic part and create the desired compound.

The result is a thin (hundreds of nm) but dense coating. Picosun's SUNALE R-200 reactor was used for the samples investigated in this thesis. The precursors were  $Mn(thd)_3$ ,  $Co(thd)_3$  (abcr GmbH and Co), ferrocene  $FeCp_2$  (Aldrich),  $Ce(thd)_4$ (Volatec Ltd) and ozone (thd=2,2,6,6-tetramethyl-3,5-heptanedionato and Cp=cyclopentadienyl). Before the coating application, the substrates were cleaned in an ultrasonic cleaner with ethanol, after which they were wiped with acetone. MnCo<sub>2</sub>O<sub>4</sub> coatings were manufactured as one homogenous layer but MCF and Ce/Co coatings were deposited in two phases. For the MCF coating, a 100 nm thick  $(MnCo)_3O_4$  layer was first deposited. Then, an approximately 10 nm thick layer of Fe<sub>2</sub>O<sub>3</sub> was added on top. For the Ce/MnCo coating, first an approximately 15 nm thick cerium oxide was deposited which was followed by a 130 nm thick  $(MnCo)_3O_4$  coating.

ALD is a stepwise process, the coating is made alternating layers of precursors and then making them react with ozone. This process continues until the desired thickness is obtained.

### 2.2.3 Physical vapor deposition (PVD)

PVD is the technique used by Sandvik to deposit their Ce/Co coating on Sanergy HT and by Teer Coating to deposit the spinels presented in Chapter 3. It has a good flexibility in terms of deposited thickness, from hundreds of nanometers to tens of microns. A target pellet and the surface to be coated are placed facing each other at the opposite poles of an electrical circuit. The material to be deposited is ablated from the target through different possible methodologies (e.g. thermal emission, sputtering) and the ions created and suspended in the atmosphere are oriented towards the surface to be coated by the electric field. Magnetron sputtering is the technique used for the tested samples. The resulting film is dense and its thickness varies from hundreds of nm (Sandvik Ce/Co) to 20  $\mu m$  of the MnCo based spinels.

### 2.2.4 Reactive dip coating

This technique has been used for the only perovskite coating studied. The deposition was performed by the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA). The sample to be coated is plunged in a molten carbonate salt bath, kept in this bath at high temperature and controlled atmosphere ( $CO_2$ ) for a period longer than 24h. The chemicals contained in the bath react with the steel substrate, growing a passivation layer whose thickness can be tuned to a few to tens of micrometers. For the  $LaFeO_3$  coating,  $La_2O_3$  is dissolved in a bath containing  $Li_2CO_3$  (53 % vol.) and  $Na_2CO_3$  (47% vol.) The steel samples are left for 48 hours in this solution at 595 °C with bubbling. The samples are then cleaned from salt residual in boiling water for 6 hours.

Based the experience with the first sample batches, the samples tested subsequently were firstly washed in boiling water for 6 hours and eventually aged for 100 hours at 800 °C prior to the ASR testing in order to eliminate possible chromium salts left after the coating process. While the composition of the coating did not change, a thin and thick type of coating were tested. Tuning the concentration of the precursors in the bath, the coating thickness can be adjusted from few to tens of microns .

### 2.2.5 Wet powder spray (WPS)

In WPS the powders are bound with a solvent in order to create a slurry. This dispersion is then sprayed at room temperature on the IC metallic surface. A post-sintering process is necessary to create adhesion of the sprayed layers. The result

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is a porous coating. As further step, a solution with other metal precursors can be infiltrated into the porous coating to improve the densification. Two types of WPS sprayed samples were tested, with one of the two procedures disclosed here. A conventional spray was applied with the suspensions that were prepared by ball milling (with zirconia balls) binder, solvent and commercial powders. The steel substrates of ASR samples were polished with SiC paper up to #1200 grit and then ultrasonically cleaned in acetone and ethanol respectively. The coating was sprayed with the following parameters: 3 mm of nozzle size (diameter), ca. 2.0 bar spraying pressure and 10 cm distance of nozzle to substrate. Sprayed samples were heattreated in 4% $H_2$ -Ar with 3%  $H_2O$  (100 ml/min) for 2 hours and subsequently in air (100 ml/min) for 10 hours at 800 °C. Coatings thicknesses are in the order of 20-30  $\mu$ m independently of the specific WPS method.

## 2.3 Plasma nitriding

This process is commonly used to harden the stainless steels surface and improve the erosion and corrosion resistance at room temperature. In the SCORED2.0 samples, nitriding was applied as a complementary process in addition to the coating procedure.

Plasma nitriding was performed using pulsed DC glow discharge plasma in a cylindrical vacuum chamber that used a conventional 4-magnetron close field configuration with a diameter of 550 mm and height of 600 mm. The substrate turntable had a diameter of 350 mm with single fold rotation. The total combined surface area of the biased rotation table was ca. 0.3  $m^2$ . Argon or Argon mixed with other gases were introduced into the vacuum chamber and the gas flow was adjusted to sustain a pressure of 1.33 Pa, maintained throughout the process. The process started with pure Ar plasma to clean the surface for about 20 min and then to introduce an Ar/ plasma with gas flow ratio of 1/3 and a pressure of 1.33 Pa. The turntable was biased by a pulsed plasma power generator (AE PinnacleTM Plus) with the following parameters: power up to 6.0 kW (equal to 2.0  $Wcm^{-2}$  or 3.3  $mAcm^{-2}$  on substrate), frequency up to 350 kHz, positive pulse width up to 1600 ns, implying a duty cycle of 44% (duty cycle means that out of 10 minutes the system can operate for ca. 4.5 min and then wait 5.5 min before applying the voltage again), and negative bias potential as low as -600 V (adjustable). The nitrided depth is dependent on time and power as applied in the plasma nitriding process.

## 2.4 Testing

Samples have been characterized either as small coupons of  $1 cm^2$  area or as metal interconnect, inserted in short stacks of six repeating elements, of 80  $cm^2$  of electrochemical active area. The remaining samples were obtained from SOFC systems which operated for different periods, up to 18000 hours (cf. Chapter 4). Experiments on short-stacks were performed on SOLIDpower's test-benches. Air was sent at the cathode side and a mixture of nitrogen/hydrogen at the anode with the ratio of 40:60 %vol. Gas flow rates were 33 NI/min at the cathode side and 3 NI/min

at the anode side (NI/min is normal liters per minute). The stack temperature was set between 720 and 780°C and the current density to 0.41  $Acm^{-2}$ .

#### 2.4.1 ASR and Cr retention

ASR characterization has the objective of measuring the resistance of different materials at specific operating conditions (temperature and controlled atmosphere) and to extract possible degradation trends, supposing that the contact area between the measured materials stays constant. Trying to measure the resistance of a material inside a furnace with an ohmmeter would lead to errors due to the leading wires resistance. To overcome this issue, the four probes technique uses a voltmeter and an ammeter to measure, given a certain current, the voltage drop and extract the resistance value by Ohm's law.

Figure 2.3 (b) sketches the four wires configuration adopted during the measurements. Two voltage leading sensing wires (K-type) are welded on the metal samples and two gold wires welded on gold meshes providing electrical current through the top and bottom area. Knowing the contact area, the voltage drop and the applied current, the area specific resistance is obtained through Ohm's law.



Figure 2.3 – On the left (a) ASR set up with samples compressed and current and leading wires (b) an example of the four wires testing method used to measure resistance. The grey wires represents the leading wires spot welded to the the steel samples, whereas the gold squares and wires represent the inlet and outlet of the electrical circuit.

As an example, Figure 1.6 reports some area specific resistance curves (for comparison, ASR reference values for the steels discussed in this thesis can be found here [122–124]).

A modification of the 4-probe technique was developed [125] to simultaneously characterize the contact resistance and the Cr blocking efficiency of each steel/coating sample combination. A 0.2 mm thick L-shaped FSS lamella with a 10\*10  $mm^2$  contact area coated with the desired protective layer was contacted to an identical L-shaped 0.5 mm thick Pd lamella screen printed on one side with a 20±2  $\mu m$  thick

lanthanum strontium cobaltite (LSC).

These two coupons were then assembled with the coated sides facing each other, simulating a SOFC cathode interface in contact with a coated interconnect. Such couples were then piled on top of each other into a tower usually made of 10-12 samples. Voltage lead wires were welded on the protruding smaller leg of the L-shape samples. Alternatively, a thin platinum wire was inserted through a hole drilled in the same leg and then tightened around the leg into a knot. Current was supplied through gold or palladium wires, and set to give 0.4 Acm<sup>-2</sup> current density through the samples. The samples tower was compressed under 0.4 MPa in a clamping set-up, heated up to 700°C and maintained for 1000 hours in humidified air atmosphere (3 vol.%). The air flow, controlled with a Vögtlin V-100 rotameter, was set to 1 NL/min. An alternative description of the testing method can be found in reference [116].

The testing procedure for small samples foresees the following steps: i) heating up in Rohde furnaces model TE 35 Q, ii) applying a current with a Tacussel PJT 35-2 Potentiostat or EA-PS 2042-20B power supply iii) data recording with Agilent 34970A Data Acquisition. In case of 3 vol.% of steam, the air was saturated with steam in a bubbler, filled with distilled water, at room temperature; for higher steam content, a selfmade alumina evaporator was used.

The testing condition of the samples involved in the design of experiment test, are specified in the dedicated chapter 7.

The LSC layer deposited on the palladium coupons absorbs the chromium coming from the steel substrate. It is thereby possible to estimate the effectiveness of the different protective coatings analyzing the chromium content inside it with SEM/EDS.

A specific set-up to test multiple small coupons in different gas condition was also designed and built in the frame of this thesis. Figure 2.4 presents the set-up as designed and under operation. There are 8 test positions each made of a two-pieces ceramic box. The upper part is attached to two 300 mm long alumina tubes that are the gas inlet and outlet. The bottom part of the ceramic cassette instead has a  $10*15*12 \text{ } mm^3$  hole to accommodate  $1*1 \text{ } mm^2$  samples. The alumina tubes are equipped also with holes of 0.6 mm diameter to let lead wires exiting the ceramic box. Gas tightness is ensured between the two ceramic parts with a silver gasket. Compression is given with a steel structure and spring system. Evaporators can be easily integrated to test the samples in higher than 3 vol.% steam environment. With this setup up to 8 different and independent gas testing condition can be applied simultaneously. Moreover, the set-up has the possibility to install a chromium trap at the outlet. This can be a denuder tube coated with  $Na_2CO_3$  or a SiC foam with open porosity, coated with  $Na_2CO_3$ . Currently, due to imperfect gas tightness at the ceramic cassette\alumina tube interface, the Cr capture system has not been fully validated yet.

#### 2.4.2 Real interconnects (short-stacks)

The degradation behavior of selected steel substrate/coating couples have also been evaluated in 6 short stack containing repeat units short stacks. The stacks, produced and assembled by SOLIDpower, contain AISI441/K41 interconnects (standard or



Figure 2.4 - (a) Design of a set-up fabricated in this thesis. Highlighted in yellow is a single test position unit repeated eight times. On the right (b) the set-up once it is realized and in operation. Metallic add-ons and alumina tissue are part of the evaporator system.

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nitrided) coated in pairs with different deposition techniques: WPS, APS or PVD. Each type of steel/coating coupling was applied on two repeat units to ensure repeatability of the measurements. The current density applied to the stack is  $0.41 Acm^{-2}$  (80 % FU); in case different current densities have been applied during a test, this will be indicated in the text for the specific test. Air is used as cathode flow and a 40/60 volume ratio of  $H_2/N_2$  at the anode side. The flow rates are 67 Nml/min/ $cm^2$  at the cathode side and 6 Nml/min/ $cm^2$  at the anode side. The polarization current was set through the Agilent 6060B Electronic load and the temperature and voltage data were acquired with an Agilent 34970A Data Acquisition. Tests on real interconnects were performed to validate the results obtained on small coupons and to observe the MIC behaviour for longer operating durations. The precise geometry of the MIC is property of the industrial partner, a sketch is given in Chapter 4 in the result section. Below the list of the stacks analysed and their testing conditions are given:

- #45: 6-cell stack, 45 hours operation at 720-780 °C, I-V characterized;
- #2700: 66-cell stack, 2700 hours operation at 720°C, 0.3 A $cm^{-2}$  current density;
- #4800: 6-cell stack, 4800 hours operation at 720-780 °C, 0.4 A $cm^{-2}$  current density;
- #10000: 6-cell stack, 10000 hours operation at 720-780 °C, 0.4 A $cm^{-2}$  current density;
- #18000: 2-cell stack, 18000 hours operation at 720-780 °C, 0.25 Acm<sup>-2</sup> first 12 000 hours and 0.05 Acm<sup>-2</sup> up to 18 000 hours;
- #124TC: 6-cell stack, 2600 hours operation, 124 thermal cycles between 25 °C and 750 °C, 0.4 Acm<sup>-2</sup> current density;

Gas flows are set with Vogtlin red-y or Bronkhorst EL-FLOW mass flow controllers. Rohde type TE 60 MCC furnaces are used to heat the stack. Air and fuel gases were preheated prior to be sent to the stacks.

## 2.5 Post-test characterization

#### 2.5.1 Sample preparation

In order to obtain microscopic information about the materials degradation, a polished surface is needed.

After the ASR or stack tests were completed, the sample pile is kept under pressure. This is needed to maintain the LSC/coating interface in place as it was during the test. For the same reason the samples are embedded in epoxy resin. Sigma-Aldrich epoxy resin is used for the small samples, Struers EpoFix epoxy resin for stacks. Once embedded, the small samples were cut in cross section with a diamond disc, while bigger short-stack samples underwent cutting in pieces of ca. 50\*50\*50 mm<sup>3</sup> with an Opus 400 SBF-4 vertical saw.

For the samples coming from the balance of plant component (cf. Chapter 6) instead,

electro erosion cutting was used. A difference in voltage is applied between a thin wires and the element to be cut. The joule effect melts few micrometers of the samples and a sharp and precise cut is obtained. This technique can be used only with electrically conductive samples and therefore could not be used for short stacks. The main drawbacks of this technique are the residuals of the cooling medium left on the samples. Like for the stacks sample, BoP components were embedded in the Struers epoxy resin.

All types of samples were successively manually polished on SiC papers, following a grit size sequence of: 320, 600, 1200, 2500, 4000 and finished with diamond paste of 6, 3 and 1  $\mu$ m on felt discs. Due to the difference in dimension, the definition of the interfaces for the small samples is sharper than the bigger ones coming from the stacks. This resulted in overall higher resolution images under the microscope.

The steps followed to produce a polished surface to be used for SEM observations are summarized in Figure 2.5. The samples (lamellae) for inspection with TEM were extracted from already polished cross sections by SEM-FIB microscope at the EPFL centre of microscopy (CIME) with a Zeiss NVision 40.



Figure 2.5 - (a) original tower of small samples that underwent ASR testing (b) The same tower after embedding in epoxy resin and removal of the clamping system (c) the block is cross sectioned with a diamond disc saw (d) one cross section of the block after manual polishing

#### 2.5.2 Microscopy characterization

The cross sections of the tested samples were analyzed using scanning electron microscopy (FEI TENEO) and energy dispersive x-ray spectroscopy (EDS) by Bruker, operating at a beam acceleration voltage of 15-30 kV. Such a high voltage is necessary for EDS analysis to avoid the overlapping of the Sr  $K_{\beta}$  peak with the Si peak. The chromium barrier property of the coating was assessed measuring the atomic chromium percentage along the LSC layer cross section with EDS linescan quantification. The EDS detecting error is between 0.5-1 %, a choice of 1 at.% threshold was adopted to judge the effectiveness of the coatings.

Transmission electron microscopy analysis was done with a FEI Tecnai Osiris at an acceleration of 200 kV. The instrument is coupled with a Bruker EDS detector for the chemical investigations. TEM was used also to obtain crystallographic information from the grains in the materials, through Selected Area Diffraction (SAED). A description of the technique and the working principle of the TEM are out of the scope of this chapter, the detailed theory can be found here. [126]

A JEOL TEM microscope equiped with the NanoMEGA ASTAR system was used to analyse two FIB lamellae. This system uses a nanobeam to probe the FIB lamella and acquire one diffraction spectrum at every impinged pixel. In chapter 5, this procedure will be referred to as nanoindexation.

The obtained set of diffraction spectra was then compared to a database of possible matching compounds through the softwares JEMS and ACOM -SIMAP NanoMEGAS SPRL. The CIF files used for the identification are taken from the FIZ Karlsruhe Inorganic Crystal Structure Database (ICSD).

Overall, considering the preparation of the samples for the ASR test, the sample embedding, the cutting plus polishing and the SEM/EDS analysis, obtaining microscopic information from each small sample described in Chapter 3 needs at least 10 hours of preparation work.

### 2.5.3 Data treatment

Data acquired during ASR testing have been treated and plotted with MathWorks Matlab. SEM/EDS images have been treated (e.g. image segmentation) with ImageJ, Adobe Illustrator and Adobe Photoshop. The oxide layer thicknesses have been extracted from segmented pictures via an own made Matlab routine. JEMS was used to simulate the crystal lattice for the indexing of diffraction images, ASTAR software was used for the indexation process. A portion of the thermodynamic data were obtained with Outotec's HSC v.7.

## 2.6 Density Functional Theory (DFT) calculation

Density Functional Theory (DFT) calculation is used in Chapter 5 to understand if strontium can migrate into  $MnCo_2O_4$  spinel through solid state diffusion. M.Sc. Michelle Liu from the Laboratory of Molecular Simulation at EPFL performed the calculation. DFT calculations were performed with the Vienna Ab initio Simulation Package (VASP) using projector augmented wave method potentials. Exchange-correlation energies were calculated using Perdew-Wang generalized gradient approximation (GGA) functionals. Geometry optimizations allowed both ionic positions and cell parameters to change and used a 520 eV energy cut-off and a 4x4x4 Monkhorst-Pack grid for the Brillouin zone. The Hubbard U correction values of 4.91 and 4.5 were used for Co and Mn, respectively. The geometry was relaxed until forces were less than 0.05 eV/Å.

# 3 Experimental Benchmarking of SOFC metal interconnect solutions (Results from the SCORED 2.0 project)

This chapter is structured in two parts. In the first, different solutions for metal interconnects are benchmarked with small ASR test samples, taking the Sandvik Sanergy HT Ce/Co coated as reference. In the second part, the most promising solutions of part I are tested in short-stacks for 10000 hours. EIS and SEM/EDS are used to characterize and understand the degradation phenomena taking place at the cathode side of these stacks.

An adapted version of this chapter has been prepared as manuscript for publication.

## 3.1 Introduction

It was introduced in Chapter 1 that metal interconnects with specific chemical compositions, such as Crofer 22 APU [91] or E-Brite [127], have been developed on purpose for use in SOFC power devices. Nevertheless the use of the bare steel as interconnect has proven to be insufficient because of chromium(VI) evaporation subsequently causing cathode poisoning [128]. For these reasons, ceramic protective layers are necessarily deposited on top of the metal interconnect (MIC). Literature about protective coating is vast, with a wide choice of materials regarding constituting elements, composition, crystal lattice, deposition technique etc. [53, 129, 130]. Taking into account common coating solutions and several steels in use recently, this chapter, based on the results of EU project Scored2.0, aims to contribute to identify suitable solution with a comparative study that covered 180 samples.

As benchmark state of the art, physical-vapor-deposited (PVD) Ce/Co protective coating on Sandvik Sanergy HT (SS HT) was taken, because of its industrial relevance

## Chapter 3. Experimental Benchmarking of SOFC metal interconnect solutions (Results from the SCORED 2.0 project)

and good properties in terms of low area specific resistance (ASR) and Cr-blocking. Two criteria have been chosen to define the performances of the studied samples because of their contribution to cathode side degradation in a stack: i) the ASR is indicative of the ohmic and contact losses of the layers representative of a stack environment, whereas ii) blocking the chromium evaporation reduce the poisoning of the cathode material. A disadvantage of the application of the PVD deposited Ce/Co coating and SS HT is their cost. This study aims to find, among the possible combinations of steel substrates, coating compositions and coating deposition techniques, if more economic solutions could emerge to match or even surpass the performance of SS HT Ce/Co reference samples. The chapter presents and compares data obtained experimentally on almost 70 steel/coating combinations (which led to observations of about 180 samples) . In the results and discussion section, a separated paragraph is dedicated to lanthanum iron perovskite based coatings. Finally, to validate the results obtained on small test samples, the most promising combinations have been transferred into industrial-like stacks and tested up to 10000 hours.

## 3.2 Materials and Experiments

Table 3.1 describes the types of steel/coating combinations evaluated in this study. To help to consult the table, they are embedded in this paragraph instead of in chapter 2. The first column lists the used deposition technology: wet powder spraying (WPS), atmospheric plasma spraying (APS), physical vapor deposition (PVD) and atomic layer deposition (ALD). Coatings were produced by SOLIDpower S.p.a., Turbocoating S.p.a., MIBA Teer Coatings Ltd, University of Birmingham, VTT Technical Research Centre of Finland Ltd and ENEA Agenzia Nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile. The reference Sanergy HT coated with cerium and cobalt was purchased from AB Sandvik Materials Technology [131]. Details of the coating procedures were reported in Chapter 2.

The steel substrates used are AISI441/K41, Sandvik Sanergy HT, and Crofer 22 H. Hereinafter AISI441/K41 will be referred to as K41.

Except for WPS, the deposition techniques leave dense coatings on the steel substrate surface. The deposition method strongly influences the coating thicknesses: tens of  $\mu m$  thickness (50-60  $\mu m$ ) for APS, few to several  $\mu m$  (1-20  $\mu m$ ) for PVD, between 10-20  $\mu m$  for WPS depending on the manufacturer, and nanometric thin barrier layers for ALD. The coating composition columns list the different protective layers applied:  $MnCo_2O_4$  (MCO),  $MnCo_{2-x}Fe_xO_4$  (MCF, x=0.2 or 0.1), and  $MnCo_{1.6}Fe_{0.2}Cu_{0.2}O_4$  (MCFC). Batches 2 and 5 have the same coating composition as 1 and 3 respectively, with the difference that the stainless steel substrates underwent a prior nitriding process. Details on steel substrates, coatings, testing methods and characterization techniques were reported in the Materials and Experiments chapter 2. The iron lanthanum perovskite are kept in a separate table because they are different from the spinel coated samples: the substrates were not nitrided and they were not tested as real interconnects. For the same reason, they are discussed also in the text in a separate subsection.

Coating	B/	TCH 1	BATCH 2	BAT	CH 3	BATC	CH 4	BATCH 5
Method	Coating	Steel	Coating Steel	Coating	Steel	Coating	Steel	Coating Steel
ALD	MCO	Crofer 22 H K41 SS HT		MCF	Crof 22 H K41 SS HT	Ce + MCO	Crof 22 H K41 SS HT	
APS	MCO	K41 SS HT	SAME COATING	MCF	Crof 22 H K41 SS HT			SAME COATING
PVD	MCO	K41 SS HT	COMPOSITION AS BATCH 1 WITH NITRIDED	MCF	Crof 22 H K41 SS HT	MCFC	Crof 22 H K41 SS HT	COMPOSITION AS BATCH 3 WITH NITRIDED
WPS 1	MCO	K41 SS HT	SUBSTRATES	MCF	Crof 22 H K41 SS HT	MCFC	Crof 22 H K41 SS HT	SUBSTRATES
WPS 2	MCO	K41 SS HT		MCF	Crof 22 H K41 SS HT	MCFC	Crof 22 H K41 SS HT	
PVD	CeCo	SS HT						
	Table 3	8.2 – Overvie	w of perovskite c	oated san	nples teste	ed in this co	mparative	study

Table 3.1 – = Cu and F

	Nitriding	NO	NO	NO
<b>BATCH 5</b>	Steel	Crof 22 H	K41	SS HT
	Coating		LareU3	(Thin)
CH 4	Steel	Crof 22 H	K41	SS HT
BAT	Coating	LaFeO3	thick	(podop)
CH 3	Steel	Crof 22 H	K41	SS HT
BAT	Coating		LaFeU3	thin
	Nitriding	NO	NO	NO
<b>BATCH 2</b>	Steel	Crof 22 H	K41	SS HT
	Coating	( ( 	LaFeU3	thin
Н 1	Steel		K41	SS HT
BATC	Coating	( (   	LaFeU3	thick
Coating		Dip	coat-	ing

## 3.3 Results and discussion

The ASR testing were performed at 700°C, in humid air (3 vol.%), with a current density of 0.4  $Acm^{-2}$  (cf. Chapter 2). Two samples for each substrate/coating combination are tested, but some combination have been tested more than once to confirm the results. Figure 3.1 gives an overview on the results, correlating the sample indications of Table 3.1 with the experimental results. The chromium barrier properties of the coating and the ASR values taken after 1000 hours of testing result to be a function of the steel type, the coating deposition technique, and the coating composition. The x-axis gives the contact resistance of the steel/coating couple in  $\Omega cm^2$ , the y-axis qualitatively represents the coating effectiveness in blocking chromium migration towards the LSC (by classifying the observed Cr presence in the LSC contact layer above or below the 1 at.% error threshold), and the z-axis indicates the deposition and/or steel pretreatment mentioned in table 3.1 (*N*+ indicates nitrided FSS substrates). The marks (cross, circle and diamond) are the fifth dimension, i.e. the type of steel substrate.



Figure 3.1 - Relations among coating deposition technique, steel substrate, coating composition, chromium retention properties and ASR performance. From a) to d) a progressive zoom on the ASR region of interest is plotted

As mentioned, the y-axis assesses the chromium retention effectiveness by the coating layer with three discrete values: samples deemed promising where the
presence of Cr in LSC was found (much) less than 1 at.% (<1%), samples deemed unsuccessful with a measured Cr content in the LSC layer higher than 1 at.% (>1%), and samples in the transition between these 2 cases, with detected chromium content around 1 at.%. Figure 3.1 a) shows all the values collected, while the Figures 3.1 b), c) and d) are progressive magnifications of the region with low chromium content in LSC and low ASR values (centre-bottom corner). The most promising combinations are included in this region. Because of the density of information in the graph, each variable will be treated separately in the discussion. Moreover, the same information reported in Figures 3.1 and 3.2 are represented in an alternative way in Figures 3.3 and 3.4. Figure 3.3 reports the values of the ASR testa at 1000 hours, while Figure 3.4 reports the chromium retention properties of the coating solutions. Each tile displays one coating deposition technique, the bar colors indicate the coating composition and the presence of nitriding substrates, and finally the bar patterns indicate the type of the steel substrate.



Figure 3.2 – ASR result of small steel/coating samples as a function of the coating deposition method, stainless steel substrate and coating composition. On the right a zoom on the lower ASR region of interest of the left hand side plot (<  $20 \text{ mOhmcm}^2$ )



Figure 3.3 – ASR results of small steel/coating samples after 1000 h of testing @ 700°C. Bar charts distribute the resistance value as a function of the coating composition and substrate processing. The error bars displays the range between the minimum and maximum values, typically of 2 tested samples



Figure 3.4 – Chromium retention properties of the ASR tested small steel/coating samples. The green line at 1 at.% indicates the EDS detection limit. Above this limit the coating is considered to fail in retaining chromium. Samples in the 1 at.% range are considered at risk. These values are calculated taking the averages of the chromium found in the perovskite materials in contact with the small samples.

### 3.3.1 Steel substrate

Focusing on Figure 3.2, Figure 3.3 and Figure 3.4 on the steel substrates behavior, no individual steel among K41, Crofer 22 H and SS HT proved consistently better than the others in terms of low contact resistance and high Cr retention. The influences of the coating is more significant and will be discussed later.

According to these results and testing conditions, commercial ferritic stainless steel with a chromium content of 17-18 wt.% (AlSI441/K41) can be an equivalent alternative to more alloyed steels (22-23 wt.%). This in spite of the fact that FSS like Crofer 22 (H or APU) and SS HT have originally been designed for use as SOFC interconnect. Specifically, high chromium content aims to grow a protective and stable  $Cr_2O_3$  layer at high temperature on the steel surface. Each alloying element improves a specific aspect of the FSSs. Manganese is added to lower the kinetic growth and electrical resistivity of the scale by forming (MnCr)<sub>3</sub> $O_4$  spinel on its top. Niobium to segregate Laves phases at the grain boundaries improving the creep resistance [100]. Addition of reactive elements such as lanthanum improves the oxide adhesion onto the steel substrate [62].

The production of these types of steel, currently at relatively small scale, is responsible for their high relative cost. Crofer 22 APU (similar to Crofer 22 H in this study) is about five times more expensive than K41 [5]. Because the cost of interconnects accounts for 10% to 30% of the total stack manufacturing cost [4, 5], using a cheaper lower alloyed steel would be significant in improving SOFC market competitiveness. On the other hand, this result must be taken with caution as 1000 hours is a short period compared to the desired operational time of the SOFC device. However, the interactions among the materials take place immediately after start, as chapter 4 will show. Therefore, even if the corrosion process continues over the lifetime, important interaction phenomena taking place at the interfaces are already visible at 1000 hours.

Among the different processes occurring at the MIC/cathode interface, most of the ohmic loss stems from the thermally grown oxide scale at the steel/coating interface because it is a semiconductor material (cf Introduction 1). Ideally, given the definition of ASR, it would be roughly sufficient to divide the ASR values by the average scale thickness in order to obtain the resistivity values of the scale. However, the resistivity values obtained with this method were not consistent. For example the resistivity values extracted from K41 WPS coated batches 2 (MCO coatings on nitrided substrates) and 3 (Fe-doped MCO on standard substrates) differed by orders of magnitude. The reason for this lack of homogeneity might be: i) the different scale composition and related low conductive values of the oxides or ii) the scale morphology, and irregularity.

The EDS analysis on the scale layer indicated that the main compound is  $Cr_2O_3$  with some discontinuous  $SiO_2$  segments in all the spinel coated samples and, in certain samples, also some Fe-Cr containing spinels. Since the inconsistence between resistivity values exists also among scale layers without iron oxides, the morphology factor is likely more responsible. Figure 3.5 Reports some steel/coating interfaces after 1000 hours of ASR test for different coatings on K41 samples. This figure is of

interest also for the comparison with the short stack results (cf. Figure 3.17). It is clearly visible how the PVD and APS deposited coating are dense - despite PVD leaves a significant amount of closed porosities - while the WPS deposited ones are always porous independently of the coating composition. In the K41 WPS MCO, a thick  $SrCrO_4$  layer at the interface between the coating and the perovskite denounces a failure in the chromium blocking properties of the coating. Regarding the APS coated samples, it is interesting to note how the real contact surface with the perovskite is different from the theoretical one, increasing the resistances of the material and limiting the advantages of this technique.



Figure 3.5 – SEM cross sections of the Steel/coating/perovskite interfaces coming from small samples which underwent ASR test for 1000 hours.

### 3.3.2 Coating

 $MnCo_2O_4$  spinel was the base reference coating material chosen for this study. This compound has been applied in SOFC for almost 20 years and proved to guarantee good electrical conduction and Cr-evaporation retention [22]. A partial replacement of cobalt was attempted during the project using a 1:1 Co:Mn stoichiometry instead

of 2:1. However, difficulties in producing powders with this composition hampered further developments [132].

As an **alternative to decrease cobalt content**, the MCO coating was doped with Fe or Fe+Cu in batches 3, 4, and 5. The addition of these elements should also be beneficial for increasing the spinel electrical conductivity [98, 133] and decreasing the sintering temperature[116].

Among all absolute **ASR values measured** after 1000 hours of testing, the lowest average was registered for Fe-doped MCO deposited by PVD on SS HT and Crofer 22 H: 5  $m\Omega cm^2$  (Figure 3.2, Figure 3.3). MCFC-coated samples showed the smallest dispersion of ASR values, i.e. the deposition technique had the lowest influence. On the other hand, APS and PVD depositions guarantee repeatability of results independently of the coating composition, with ca. 90% of the ASR values smaller than 20  $m\Omega cm^2$  and no Cr contamination detected in the LSC layers, when using APS or PVD. Doping of MCO with Fe and Cu demonstrated to decrease significantly the contact resistance for wet powder sprayed coatings. Based on SEM-EDS observations, this improvement in performance relates to the densification of the protective coating (Figure 3.5).



Figure 3.6 – On the left, WPS-deposited MCO coating containing open porosity, on the right WPS-deposited MCFC coating containing closed porosity, after 1000h at 700°C and humid (vol.%) air

It is again confirmed that **densification of the coatings** is a key aspect. Another example stems from the ASR results of MCO coatings. The ASR values of the samples with coatings deposited by PVD were in the 10-20  $m\Omega cm^2$  range, while WPS-deposited samples, ASR values were between 45-130  $m\Omega cm^2$ . Figure 3.6 shows the influence of Cu and Fe on the densification of the WPS-deposited coatings, leading from open to closed porosities. Coherently, the ASR values for WPS-deposited MCFC coatings are in the range 13-38  $m\Omega cm^2$ . This improvement was valid independently of the type of steel substrate.

A dense coating is a necessary condition, but it is not sufficient on its own. **ALD-deposited coatings** were homogenous but very thin and oxygen permeable, post-test characterization on ASR small samples revealed their failure in protecting the steel from Fe-breakaway corrosion (Figure 3.7). Presence of Cr into the LSC layer likewise demonstrated failure in chromium retention too.

Figure 3.7 shows ALD-deposited MCO coatings, on standard SS HT substrate (top in Figure 3.7) and on nitrided SS HT (bottom in Figure 3.7). The difference in image quality is due to the use of FIB ion milling for the cross section observation of the nitrided sample. In both cases, the coating failed to prevent iron breakaway. For the standard steel substrate this is apparent as exsolutions, while in nitrided samples the Fe oxide layer is between two cobalt layers. Chromium in both samples created an oxide layer below the Fe containing scale, while manganese is present both in the scale and in the original coating. For the standard steel substrate sample, the iron breakaway took place below the coating. The green cobalt EDS map helps to identify the coating. In the nitrided sample instead, the iron containing oxide is between two thin cobalt layers, as shown by the light-green element map.

The corrosion process in ALD-coated samples is probably a combination of chemical and mechanical iron breakaway. Considering the uniform thickness of Fe distribution in Figure 3.7 (b), the iron moved through a uniform migration process. In figure 3.7 (a) as well, where the scale is thinner, there is some iron contamination of the coating. This can be assumed to be the general corrosion process.



a) ALD deposited MCO on standard Sandvik Sanergy HT

STEEL ST

Figure 3.7 – On the top micrograph of SSHT/MCO interface in Batch1 sample with ALDcoated MnCo with clearly visible Fe breakaway regions. On the bottom FIB/SEM EDS of similar interface but on a batch2 sample (nitrided steel), also ALD MnCo-coated.

The enhanced corrosion attack regions shown in figure 3.7 (a) instead originate in precise locations, implying a coating failure at those locations. A first delamination and a consequent cracking of the thin protective coating is a potential explanation. The coating maker suggested an influence of the different CTE between the steel substrate and the thin layer, but for coating/substrate thickness ratio much smaller than 1 the film should follow the dilatation of the substrate. The as deposited coating could contain fabrication defects. The constant and generally thin scale formation ensured for all the coating compositions a reasonable resistance result, with ASR values contained in the 15-60  $m\Omega cm^2$  range. The chromium barrier function of the coating was instead only partially fulfilled (Figure 3.4). According to these results and for these temperature conditions, protective coatings for MIC steels deposited with the ALD technique appeared not to be entirely suitable for SOFC application. The 5<sup>th</sup> batch, MCF coating on nitrided stainless steel, hence does not contain samples coated with ALD (Table 3.1). As a reminder, the small samples coated through APS and PVD gave showed the best performances.

### 3.3.3 Nitriding

Comparing the results displayed in Figure 3.3 and Figure 3.4, the samples with the lowest contact resistances did not match those with the best Cr retention properties. Nitrided samples, in particular, present excellent Cr retention properties despite higher ASR values. Among all the nitrided substrates coated with MCO or MCF, only ALD MCO coated Crofer 22 H showed a potential Cr contamination risk (1 at.%). This was also confirmed by nitrided MICs operated in short stacks. The voltage degradations of single repeat units containing nitrided interconnects in short stacks are instead in line with those containing porous coatings and standard substrate. Later, it will be shown that the difference in voltage degradations between single repeat units containing standard and nitrided interconnects in short stacks is smaller than expected from ASR results (Figure 3.3).

In industry, nitriding is a process to harden stainless steel surfaces, for instance to improve the lifetime of drill bits. The enhanced mechanical properties are linked to the change in the **alloy microstructure** and in the formation of hard precipitates, such as  $Fe_4N$ . The Fe-Cr phase diagram indicates that chromium stabilizes the  $\alpha$ -phase (ferrite), which is a body centered cubic lattice. In Figure 3.8, the austenitic  $\gamma$ -phase exists in fact only for temperatures between 850°C and 1400°C together with low chromium weight percentage (<13 wt.%).

For example, at 950°C, if the chromium content is less than 10 wt.%, the atoms in the stainless steel solid solution will rearrange coordinating 12 atoms instead of 8. In other words, the smallest repeating unit in the lattice changes from bcc to fcc. As a result, the solubility of interstitial atoms changes too, with nitrogen and carbon atoms being more soluble in the austenite. For this reason, nitrogen and carbon expand the region of existence of the austenite in the phase diagram to the right, i.e. even for higher amount of chromium. However the starting temperature for the  $\alpha \rightarrow \gamma$  phase transformation is not affected by the increase of nitrogen and/or carbon content.



Figure 3.8 – Fe-Cr phase diagram [1]

According to the phase diagram, if the nitrided FSS at 950°C is cooled to room temperature, the lattice will return to the ferrite structure, expelling carbon and nitrogen atoms. On the other hand, phase diagrams are calculated according to thermodynamic equilibrium, which might not be reached in case of fast changes in surrounding conditions. If the steel undergoes a rapid quench, a metastable austenite phase will exist at room temperature too; in turn reducing the number of nitrided precipitates. With slow cooling, the nitrogen and carbon atoms can instead react with the other alloying elements and will segregate as interstitial compounds. The element diffusion kinetics is the reason for the different behaviors. Alloys guenched in water cool down at 280°C/sec, while in air they loose 4.6°C/sec in the 600-475°C interval [134]. In the first case, carbon and nitrogen atoms have not enough time to migrate from their interstitial position and segregate close to high energy defects (dislocations, grain boundaries). When cooling is performed in air or with a controlled temperature ramp instead, nitrides precipitate. Notably, nitrogen is forced out the ferrite lattice and reacts with the metal atoms creating  $Fe_4N$ , CrN or  $Cr_2N$ . Due to the rapid formation of  $Cr_2N/CrN$  segregates, the steel regions close to the precipitates are depleted in chromium. Since nitrides are likely to form at the grain boundaries, these regions risk intergranular corrosion (IGC). In practical applications, IGC is particularly problematic because it might eventually lead to the mechanical failure of the component. To prevent IGC, steel makers keep the carbon and nitrogen content in the alloy in the order of ppm. Another strategy is to add Nb and Ti, which form precipitates with nitrogen that are thermodynamically favored over those with chromium [135]. Yet, this requires a ratio (Nb+Ti)/(C+N) of around 9-10, based on

weight pct. Hence, this solution is valuable only for modest nitrogen content. As said, intergranular corrosion depends on deficiency of chromium in the neighboring of nitrides precipitates, but when chromium cations diffuse from the bulk of the grain towards the depleted regions, passivation properties are restored [134]. This process being diffusion controlled, at least 700°C is necessary to have sufficient chromium cations mobility. To summarize, the high content in chromium coupled with the high operating temperature (>700°C) decrease the time window during which the steel is prone to sensitization.

The samples underwent the following conditions: a) 800°C was the highest testing and operating temperature for ASR samples and MICs, and cooling has always been performed in furnaces; b) the coating processes were conducted < 900°C; c) the chromium content was always at least 17 wt.%.; d) the amount of nitrogen inserted during plasma nitriding is 4-5 at.% according to EDS measurement. Considering the Fe-Cr phase diagram (Figure 3.8), within these conditions, no austenite phases should have formed in the material. The nitrogen stabilization influence of austenite phases starts for higher temperature. The absence of  $\gamma$ -phase is important because the CTE difference with the cell could cause cell fracture. Fe-N-Cr phase diagram at 800°C predicts the presence of ferrite+ $Cr_2N$  at the thermodynamic equilibrium [136].

In Figure 3.9 the SEM cross section of a nitrided stainless steel substrate is compared with a standard stainless steel substrate.



Figure 3.9 – Cross sections of two not nitrided (left) and nitrided (right) stainless steel substrates (Sanergy HT), aged for eight hours at 750°C. The nitriding process led to refining of the steel grains.

Both samples have been aged for 8 hours at 750 °C. The nitriding process affected less than 70  $\mu$ m of the steel below the surface. Despite the noise in the image, the presence of smaller grains in the nitrided region is clear. The comparison with a standard steel substrate moreover confirms that the nitriding process refines the

alloy grains. In Figure 3.10 there are two cross sections from nitrided AISI441/K41 and Sandvik Sanergy HT substrates, both coated with MCF via WPS. Crofer 22 H is not reported, as its composition is similar to Sandvik Sanergy HT. In the steel substrate cross section, three areas with distinct morphologies can be observed in all the ASR and MIC samples. The layer immediately below the scale (belt 1) has spherical precipitates and no visible segregation at the grain boundaries. Below it, there is a region with a high density of small precipitates inside the grain and at the grain boundary (belt 2). Finally, in the core of the stainless steel the particles are the biggest and widest distributed (belt 3).



Figure 3.10 – Cross sections of nitrided FSS substrates aged for 1000 hours

Average particle size in belt 1 increases with exposure time: in nitrided K41 stainless steel substrate these were estimated to <0.005, 0.71 and 2.1  $\mu m^2$  in samples aged at 700°C for 1, 1000 and 10000 hours respectively. In addition, the thickness of belt 2 decreases too with the exposure to high temperature. This suggests an Ostwald ripening process for belt 1 [137]. The small particles size and their distribution inside the steel grains of belt 2 (Figure 3.10) suggest a nucleation process induced by dislocations. For particles to nucleate a defect point with high energy is needed. The milling of the steel sheets could have increased the dislocation density in belt 1 and belt 2 regions, unfortunately the precise history of the steel substrates is not known. As aging proceeds the particles merge; the doubling of the extension of belt 1 between 1000 and 10 000 hours support this hypothesis.

In belt 3 instead, the nitrides precipitate at the grain boundaries. In the paragraph describing the alloying of the steel substrates, it was mentioned that reactive elements are important for the steel microstructure evolution in presence of nitrogen. The analyzed samples revealed a modest content of TiN with respect to chromium containing nitrides and only few of the chromium nitride particles initiated close to TiN. The amount of nitroged inserted is therefore too high for the reactive elements to mitigate its reaction with chromium.

#### Figure 3.10 shows also **no sign of intergranular corrosion**.

EDS analysis found a Cr:N ratio of about 2:1 (Figure 3.10), suggesting  $Cr_2N$  precipitates as expected from thermodynamics. The absence of IGC can be explained with the combination of material and operating conditions. The temperature higher than 700°C increases the chromium diffusion rate, which in turn shorten the time needed to refill the depleted regions close to chromium-nitride segregates. Looking at the linescan in Figure 3.11 there is no sign of Cr depletion in the surrounding of a  $Cr_2N$  particle in a 1000 hours ASR tested FSS substrate.

According to J.J. Demo [138], already ten minutes after the beginning of the  $Cr_2N$  precipitation, at 700°C for AISI 446, the chromium diffusion rate is fast enough to refill the depleted surrounding of the nitrides. At 600°C on the other hand, chromium diffusion is delayed by hours, leaving the material exposed to possible IGC for longer period. This result is interesting for SOFC considering the generation of low temperature fuel cells aiming to work at temperatures around 500-600°C. Nitriding therefore appears to be an effective solution especially for IT-SOFCs working at around 700 °C.



Figure 3.11 – EDS Line scan over two  $Cr_2N$  particles and the surrounding area of a K41 nitrided steel substrate. Y axis reports at.%

The presence of a **coating** to avoid failure of the passivating layer is essential also in case of nitriding. Figure 3.12 presents the cross sections of the three nitrided substrates, without coatings, and analysed with a TEM; iron appears on top of nitrided stainless steel samples heated up to 700°C (Figures A.2 A.3 A.4). The oxide is made of a thin nitrogen containing phase at the steel/scale interface and subsequently a layer of manganese chromium oxide topped by a manganese iron layer. There is no difference between low and high chromium alloys. The element distribution is similar among all steels. Hence, considering the poor electrical and mechanical performances of the iron oxides, nitriding alone can not be an alternative to the coatings.

In nitrided substrates coated with porous MnCo oxide spinel, and ASR tested, the scale layers are similar to those on uncoated substrates, but iron cations infiltrated the coating. The presence of iron inside Mn-Co spinel (batch 2) is 3 to 4 at.%.

#### 3.3. Results and discussion



Figure 3.12 – TEM-EDS analysis of uncoated nitrided steel substrates heated up to 700  $^{\circ}$ C for less than 3 hours.

This value is modest compared to the iron contamination of the coating present in short stacks (cf. Chapter 4). This is in line with the hypothesis that the passivation properties of chromium were re-established after a short testing time. In coated samples, manganese accumulates close to the steel interface, while manganese cations on top of the scale cannot be distinguished from those in the coating. In the presence of dense coating (PVD, APS deposited) there is no iron outward migration. The scale is made of  $SiO_2$  particles and chromium oxide only.

Comparing the **ASR results** of nitrided and not nitrided batches, there is a significative difference mainly for WPS deposited samples (Figure 3.3). The 5<sup>th</sup> batch (MCF coatings on nitrided substrates) of the PVD in fact presents coating defects which are not dependent on the nitriding process.

The worsen results with WPS coatings might be explain by the accelerated corrosion kinetics at the beginning of the aging process, related to the chromium depletion action of nitrogen. The average scale thicknesses for these samples is in fact higher than for not-nitrided samples. On the other hand it was mentioned already that the oxide morphology factor is likely more influencing than the average scale thickness.

Looking at the existing **literature**, nitriding is already used in polymer electrolyte membrane fuel cell application (PEMFC). The MICs there are nitrided to form a continuous  $CrN \setminus Cr_2N$  layer on top of Ni-Cr alloys and demonstrated to improve the corrosion resistance and the electrical contact conductivity of the alloy [139].

Researches proved that nitriding is effective in decreasing the corrosion of vanadiumcontaining ferritic stainless steel [140] and austenitic stainless steel too [141]. Other than corrosion and erosion improvement at low temperature, CrN possess also a good electrical conductivity as a superficial contact layer. [142].

To summarize, nitriding limited the outward diffusion of chromium. Considering that the main limitation for porous coatings is the initial chromium leakage, nitriding could be taken in consideration also for industrial application. Regarding the influence on the electrical properties of the MICs instead the results are not final; according to small test samples, the ASR can be affected, while tests in short stacks (following paragraph) report degradation rates similar to some of the standard MICs.

### 3.3.4 Samples coated with lanthanum iron perovskite

Figure 3.13 summarizes the ASR and Cr retention results of the small steel samples coated with  $LaFeO_3$  perovskite coatings. The difference among the five batches lies in the coating thicknesses, in turn depending on the dip coating immersion duration. Batch 4 only presents a variation in the composition with a 0.2% addition of copper in the salt bath and it is a thick coating. Perovskite coatings have an opposite and complementary action with respect to the spinel based one. The perovskite structure in fact should stop cations migration and allow the transport of oxygen anions.



Figure 3.13 – ASR (a) and Cr retention (b) results of small samples dip-coated with  $LaFeO_3$  perovskite coatings after 1000 h of testing at 700°C. Bar charts distribute the resistance value as a function of the coating composition and substrate processing.

Despite this characteristic, the  $LaFeO_3$  coatings did not completely succeed in avoiding the presence of Cr in the LSC contact layers in 9 out of 14 samples (Figure 3.13). Incomplete washing of the salt bath, with chromium containing residuals on the surface might be a reason for this. Two samples from batch 1 were carefully washed in deionised water and no Cr was found this time. ASR tests consistently led to high loss values. The  $LaFeO_3$  coatings grow in a pyramidal shape, reducing the contact surface with the LSC layer. In addition, the oxide scale growing below the coating contains iron oxide. The use of a thinner coating, meaning less sharp crystals, improved the contacting and decreased the oxide layer thickness, but the comparison with the spinel coating results suggests the present dipcoated  $LaFeO_3$  coating to be unsuitable for SOFC interconnects.

# 3.3.5 Validation of small ASR test samples results on short stacks

While results on small coupons are of interest and relatively easy to obtain, they may on the other hand not be fully representative of the steel behaviour in a SOFC stack, for longer test duration. Hence, some of the steel/coating combinations tested as small samples were transferred to industrially sized and shaped interconnects and tested for up to 10000 hours in 6-cell stacks. The stainless steel substrates used for the interconnect was only AISI441/K41. Three short-stacks were tested, with the coating solutions reported in Table 3.3

	Substrate	Nitrided	Coating	Depostion tech.
STACK A	AISI441/K41	NO	MCF	WPS
STACK A	AISI441/K41	YES	MCO	WPS
STACK A	AISI441/K41	NO	MCO	WPS
STACK B	AISI441/K41	NO	MCF	APS
STACK B	AISI441/K41	YES	MCO	APS
STACK B	AISI441/K41	NO	MCO	WPS
STACK C	AISI441/K41	NO	MCF	PVD
STACK C	AISI441/K41	NO	MCO	PVD
STACK C	AISI441/K41	NO	MCO	WPS

Table 3.3 – Types of interconnects tested in three different short stacks for 10000h.

WPS deposited MCO was taken as reference and inserted in every short-stack to guarantee also robustness among data; MCF was the coating with the lowest contact resistance (Figure 3.3); APS and PVD were chosen because of the excellent Cr retention and electrical contact properties (Figure 3.3, Figure 3.4 ) and finally a nitrided substrate was added to the comparison to validate its improvement in blocking chromium (Figure 3.4). Voltage degradation of each stack is presented in Figure 3.14, Figure 3.15 and Figure 3.16. The stacks have been labelled A, B and C and their operational conditions were described in Chapter 2.

The voltage versus time graph for stack A presents multiple interruptions, due to unwanted power cuts. The degradation values obtained from this graph are therefore not reliable and can not be considered in the discussion. Still, the stack was analyzed by SEM/EDS to assess the enhancement of the chromium retention properties induced by the nitriding process. Stack B and C instead underwent controlled shutdowns, with the peaks in the graphs being mainly IV measurements to record the performances of the cells at different time intervals.

Table 3.4 reports the degradation rate for every single repeating unit. The SRUs are indicated with the type of the coating deposited (e.g. WPS MCO), but the losses also include the contribution of the cell. This nomenclature will be kept hereafter.



**Chapter 3. Experimental Benchmarking of SOFC metal interconnect solutions (Results from the SCORED 2.0 project)** 

Figure 3.14 – Voltage versus time curve of 6-cell short stack tested in a project partner facility. Multiple interruptions damaged the cells (stack A).



Figure 3.15 – Voltage versus time curve of the 6-cell short stack tested in a project partner facility (Stack B).



Figure 3.16 – Voltage versus time curve of the 6-cell short stack tested at EPFL. The peaks are mainly due to IV measurements (stack C).

The degradation rate is calculated taking the value at 1000 hours (when transition phenomena should have stabilized) as starting reference and the last recorded point as final one. The first 1000 hours are not calculated to exclude the influence of the transient phenomena taking place in the cell at the beginning of the stack operation. The more or less marked rise in the potential value in the first operation hours of certain SRUs, is due to the microstructural rearrangements taking place in the cell.

STACK B		STACK C	
MIC	Degradation (%kh-1)	MIC	Degradatior (%kh-1)
WPS MCO #1	0.72	WPS MCO #1	0.38
APS MCF #1	1.14	PVD MCO #1	0.4
APS N+MCO #1	0.34	PVD MCF #1	0.042
APS MCF #2	0.64	PVD MCO #2	0.059
APS N+MCO #2	0.45	PVD MCF #2	0.15
WPS MCO #2	0.67	WPS MCO #2	1.35

Table 3.4 – Degradation rates for stack B and C. Degradation rates have been measured between 1000 and 10000 hours

Less than  $0.5\%(kh)^{-1}$  of voltage degradation should be a target value for stack lifetime. In this sense, SRUs in stacks C are more promising. The SRU containing porous coatings, i.e. WPS deposited, show similar average degradation rate: 0.7  $\% kh^{-1}$  in stack B and 0.85  $\% kh^{-1}$  in Stack C, even if WPS MCO #2 in stack C clearly underwent an anomalous degradation process.

Other than APS MCF #1, the repeating units with porous coating present the highest degradation rates, coherently with what was observed on small test samples. On the other hand, the presence of an APS sprayed coating in the most degraded SRU is unexpected. Similarly, the low degradation rates of the SRUs containing nitrided substrate is unexpected if compared with the ASR test values. In addition, from the point of view of degradation rates, PVD coating deposition appears clearly to be the best option while from small samples test results the difference with APS coated samples was minor. PVD MCO SRU #2 reaches a value of 0.059 %( $kh^{-1}$ ) of degradation after 10000 hours, similar to the one of PVD MCF SRU #1 suggesting that small changes in coating composition, i.e. iron doping, are not meaningful for dense coatings.

From the V(t) curves proposed above it is not possible to distinguish the cell and the interconnect contribution to the ohmic losses, therefore the full stacks have been embedded in epoxy resin, cross-cut and SEM/EDS analyzed.

Stack A and B will be discussed together, while stack C will have a separate paragraph. This distinction is explained by a more detailed investigation of stack C and a better knowledge of its operational history as it was tested at EPFL whereas stacks A and B were tested by project partners.

### **STACK A and B**

Figure 3.17 provides observations for WPS-deposited MCO on regular and nitrided K41 substrates, as well as for APS-deposited MCF on standard K41 substrate. The EDS element maps are reported for chromium, cobalt, iron and manganese.

The APS deposited coating kept the original composition, the EDS map showing only Mn and Co in that region. The steel corrosion below the coating is uniform, the scale consists of  $Cr_2O_3$  and  $(CrMn)_3O_4$ . The coating barrier action is effective, no chromium is detected in any of the APS SRUs cathode contacting material and, at the same time, no third elements were detected in the coating, notably no iron and no strontium. The thick and dense coating slows down the migration of oxygen towards the stainless steel, keeping the oxide layer thin. As for the small ASR test samples, the presence of such a thick and dense coating hindered the influence of the nitriding process. The behavior of the WPS porous coating on standard stainless steel instead is the same as described in Chapter 4, with diffusion of strontium, iron and chromium ions across the metal/coating/perovskite interfaces. The SRUs containing iron doped coating (MCF) had a corrosion behavior in line with those coated in pure manganese cobalt spinel. In the nitrided interconnects coated with porous MCO instead, the reactivity at the MIC/coating/perovskite interface lays in between the cases mentioned above. In fact, the average scale in the standard MIC with WPS MCO is 11  $\mu$ m, on nitrided MIC with WPS MCO 7  $\mu$ m on average and on MCO-plasma sprayed standard K41 5.5  $\mu m$ . The standard deviation in the value of the scale thickness for the nitrided substrates is less than for the regular substrate. The inward corrosion front has been homogeneous all along the interface. This implies that the iron breakaway corrosion affected the whole interconnect/coating/perovskite interface until the passivation layer was established. In turn, the iron breakaway

corrosion confirms that nitrogen acts as a scavenger element for chromium in the first phase of the corrosion process. The evolution of the thermally grown oxide and the MCO coating is again very different from what was observed for small test samples (cf. Figure 3.5). At the same time, no chromium is found in the contacting perovskite, confirming the improvement brought by nitriding to the chromium barrier properties of the WPS deposited coating.



Figure 3.17 – Comparison of MICs tested for 10000 hours in a 6-cell short stack via MIC/cathode interface cross sections. Top: MCF deposited via APS showing no Cr migration towards the cathode. Middle: MCO deposited with WPS not blocking Cr diffusion. Bottom: WPS-deposited MCO on nitrided K41 substrate.

The difference in voltage degradation between single repeat units containing nitrided and not nitrided MICs (both coated with porous MCO) does not follow the results obtained with ASR small samples. In fact the voltage values of SRUs with nitrided MICs became lower than the ones with the corresponding standard MIC, only after 8000 hours . The long-term trend indicates a worsening in ohmic loss for nitrided substrates but stack A underwent disturbed testing which should be repeated for a more reliable result. In the case of APS deposited coating instead the two SRUs with nitrided MICs showed the lowest degradation rate, but the presence of a dense coating is more significant than the nitriding process itself.

Electrochemical impedance spectroscopies - reported in the Appendix - taken at different operating hours (0, 1000 and 10000) confirmed that the SRUs containing APS MCF #1 underwent aggravated degradation. The ohmic losses in fact increased of almost 0.2 *Ohmcm*<sup>2</sup> between 1000 and 10000 hours, while for the other APS coated SRUs, the increase of the ohmic losses is less than 0.1 *Ohmcm*<sup>2</sup>. The ohmic resistance values at the beginning of the test were markedly different among the SRUs, up to 0.15 (*Ohmcm*<sup>2</sup>) of difference between APS MCF #2 and WPS MCO #1. After 1000 hours of operation, the increase in ohmic losses of each SRU was less than 0.02 *Ohmcm*<sup>2</sup>. Excluding SRU APS MCO #1, which demonstrated to have a faster degradation of the cell, all APS containing SRUs had an ohmic starting resistance

of ca. 0.35 *Ohmcm*<sup>2</sup>. The WPS #2 starts at 0.41 *Ohmcm*<sup>2</sup> and the WPS #1 at 0.51 *Ohmcm*<sup>2</sup>. This difference at 0 hours of operation is partly related to the temperature distribution: WPS #1 was at the bottom of the stack and suffering higher thermal losses. Reported in the Appendix, the impedance plot indicates that chromium poisoning does not influence the polarization losses, in fact the responses at low frequencies do not change after different periods.

The comparison with MICs from Crofer 22 APU or H steels is unfortunately not possible, as few post test observations from stacks have been disclosed in literature and the testing conditions are different than those of the stacks presented here.

### STACK C

Two cross sections were extracted from this stack and analyzed by SEM/EDS. To assess the global degradation of the stack one sample was cut at the inlet and a second one at the outlet of the stack.

The impedance spectra for the six SRUs, taken at 10000 hours of operation, (Nyquist plot in Figure 3.18) confirm the degradation values of Table 3.3 with the WPS MCO #2 showing the highest value of ohmic loss.

The analysis of its spectrum through the Tikhonov regularization methodology (Figure 3.19 to obtain the distribution of relaxation time (DRT) constants, revealed that the main polarization losses, for this element, take place in the middle frequency range. This behaviour can be attributed to an imperfect contact between the cell and the IC. The DRT of the two WPS-MCO elements (#1 and #2) has been compared with another stack (tested in the framework of the European project SOSLEM) in which the RU 4 was purposefully assembled with an insulating material covering 11% of the interconnect area. The variation of the DRT peaks between the healthy and faulty element of this stack follow the same trend of the WPS MCO RUs (Figure 3.20). [143]. The other spectra instead revealed no particular defect of the corresponding SRUs.



Figure 3.18 – Impedance spectra of the SRUs tested in stack C.

Figure 3.22 compares the interconnect/perovskite interface at the inlet and the outlet of each single repeating unit. With PVD coated interconnects, iron breakaway corrosion takes place preferentially at the outlet and  $SrCrO_4$  passivation at the inlet; whereas with WPS coated ones the behavior is inverted. In addition, the kinetics of corrosion are accelerated at the outlet, showing a thicker average scale. In the WPS coated samples the corrosion process is characterized by iron-breakaway as will



Figure 3.19 – DRT treated spectra of the SRUs tested in stack C.



Figure 3.20 – Comparison of DRT spectra for the WPS MCO SRU in stack C and a SRU with a known contact defect (analysed in a parallel project).

be described in detail in Chapter 4. This means inwards corrosion with formation of different spinel oxides of Mn, Co, Fe and Cr in the scale and Fe migration in the porous coating densifying it. However in this case there is also another reaction product in WPS MCO #2, a 5  $\mu$ m thick layer of crystals found at the MCO/perovskite contact area. The EDS analysis of this phase detected Mn (22 at.%), Sr (20.5 at.%), Co (8.5 at.%) and oxygen (47 at.%), on top of this layer an accumulation of strontium is found as well. The values suggest a mixture of single oxides, containing also SrO. It would be important to identify the precise phase to estimate the influence on the electrical conductivity. If the species is, for example, *SrMnO*<sub>2</sub>, its contribution to conductivity would be of the same order as that of *Cr*<sub>2</sub>*O*<sub>3</sub> (0.5 *Scm*<sup>-1</sup> [144].

The PVD coated samples behaved differently than expected from the small ASR test samples behavior. The dense coating was expected to stop any strontium diffusion as for APS coatings in stack B. However, strontium chromate was regularly found below the original PVD coating and the coating itself presented porosity coalescence. A detailed analysis at high magnification revealed a strontium solid diffusion path through the PVD coatings, independently of their composition, as seen in Figure 3.21 with the example of PVD MCO #2.



Figure 3.21 – Quantitative element map of the perovskite/MIC interface for PVD MCO #2, Stack C. Element concentration in at.%.

Some enhanced inward corrosion regions were found in the small ASR samples coated with PVD coatings, but Fe breakaway was not present. In the stack, instead, in each MIC/perovskite interface there are regions where the passivation layer failed. This is visible in the densified and inward corrosion regions shown in Figure 3.22. Close to the regions where the oxides of chromium and strontium are formed in the PVD coated interconnect, there is also a third region where the oxide is the expected  $SiO_2/Cr_2O_3$  only. These oxide regions are also thinner than those where Fe breakaway takes place, therefore could also be preferential pathways for conduction. All six coatings failed to prevent chromium contamination of the perovskite material. This was expected for the WPS coatings but not for PVD. The white stains in figure Figure 3.22 indicate accumulation of strontium and chromium, likely  $SrCrO_4$ . At the same time, this layer is not continuous and it does not insulate electrically the stack. Paths where current can pass through still exist.

Correlating the voltage degradation of the SRUs and the microstructure observations is not straightforward because of the different sources of voltage losses.

### 3.3. Results and discussion



WPS MCO #2

Figure 3.22 – Comparison of the MIC/perovskite interface for all the 6 SRUs in stack C at the inlet and at the outlet. On the left column, the MIC/coating/perovskite interface at the inlet of the stack, on the right at the outlet. In WPS coated MICs there is Fe breakaway at the inlet and strontium chromate formation on the steel surface at the outlet. For PVD the trend seems inverted.

Regarding polarization losses, the comparison of impedance spectra of WPS MCO SRUs taken at different time lapses, up to 10000 hours of operation, indicates a stabilization. Hence, ohmic losses are the main responsible for voltage degradation with time. The difference in ohmic loss between WPS coated SRUs and PVD are bigger than expected from just the voltage degradation values. Because most of the resistive phases are semiconductors, the temperature gradient influenced the result. Unfortunately, it is not possible to separate the contribution of the cell from the MIC in the impedance spectra. The assessment of the cell degradation would sample preparation and analysis beyond the scope of this thesis.

The PVD and WPS steel/coating combinations tested in short stacks did not confirm the results obtained from ASR tests on small samples. Notably, iron breakaway corrosion and strontium migration towards the interconnect were not expected. In small samples a certain degree of inward degradation is observed but it never evolved in iron breakaway, and no strontium poisoning of the steel surface was detected. In WPS coated samples instead the iron breakaway corrosion was observed in the MCFC sample. Interestingly, the failed sample contains the Sandvik sanergy HT stainless steel while AISI441/K41 presented no such a failure. It follows that the adapted four probe ASR test developed for SCORED was partially representative of a stack. Nitriding steel treatment instead confirmed its positive effect on the chromium retention properties. Also APS coatings on standard substrates confirmed the good chromium retention properties.

The observations from stack B and C demonstrated that the ASR results are only partially representative of the degradation behavior of the MIC materials operating in a stack. Other than a different geometry and double atmosphere exposure, the use of a different type of perovskite influenced the result. The material simulating the cathode in the small ASR samples was provided by a different supplier and with a higher grade of densification. The activity of strontium in the cathode perovskite is key for the stability of the MIC/cathode interface

### 3.4 Practical application

In this chapter, we attempt to predict degradation of the short stack for 40000 and 80000 hours, based on the results of Table 3.4 and on the average voltage values of the SRUs at 10000 hours.

	PVD MCO #1	PVD average	APS average	WPS average
40000h	0.764	0.717	0.57	0.562
80000h	0.75	0.668	0.374	0.388

Table 3.5 – Voltage values for hypothetic SRU at 40000h and 80000h, based on the degradation rate values of Table 3.4.

Four cases of interest are considered: the lowest degradation performance (PVD MCO #1), PVD average, WPS average and APS average. The difference in composition between MCO and MCF was not taken into account. To calculate these values, the

voltage value of the cells at 1000h is taken as reference. Then the negative difference quotient between the voltage values at 1000 and 10000 hours was multiplied for 40000 and 80000 hours. The results were subtracted from the values at 1000 hours. These numbers are only crudely indicative, but from the results it can nonetheless be inferred that atmospheric plasma spray coating underperformed if compared to the small sample results. This result is even more surprising considering modest corrosion observed with SEM/EDS analysis and the good result obtained in different type of stacks [88]. Possible explanations are the reduced contact surface between the perovskite and the coating, caused by the hardness of the coating, and the thickness of the coating. The PVD coated units showed instead interesting results, confirming the expectations from the small samples.

As already mentioned in the introduction to this chapter, the EU project also aimed at assessing the economic feasibility of the different interconnect solutions. The MICs affect 10% to 30% of the stack cost [5], and, in turn, the raw materials are estimated to account for 40% of the MIC production cost. In this regard, APS and PVD techniques are more expensive because they over-spray more material than WPS. In addition, initial infrastructure investment is also higher for APS and PVD. Considering a production line of 1 MW/year, one interconnect coated via PVD and one via APS - with the same material - would cost respectively two orders and one order of magnitude more than one interconnect coated with WPS. Similar numbers are valid for the steel substrate: Crofer 22 H/APU or Sandvik sanergy HT would increase the MIC cost by one order of magnitude compared to AISI441/K41.

## 3.5 Conclusion

The chapter summarizes the outcomes of a comparison of more than 60 different combinations for coated metal interconnect materials for the use in solid oxide fuel cell stacks. Specifically, relations and comparisons between steel substrates, substrate preprocessing, coating composition and coating deposition techniques were observed and evaluated through their Cr retention and contact resistance properties, First as small coupons and later as real interconnect in short-stacks. The main results give new indications for the future choices of MICs and their coatings. Main findings are:

- The results of the modified four-probe ASR technique are strongly influenced by the perovskite contact material used to simulate the cathode. The presence of perovskites with different composition and sintering process introduced a discrepancy between small ASR test samples and the MICs tested in the stacks.
- Coating density is key: independently of coating composition and steel substrate composition, a dense coating is the most important parameter to ensure low corrosion.
- The best solution was obtained for Fe-doped MCO-deposited by PVD, with a performance compatible with the initial reference solution SS HT Ce-Co coating, i.e.  $\approx 5 m\Omega cm^2$ . No comparison in short stack testing could be done as Ce-Co

coated SS HT in the industrially shaped MIC was not available.

- Alloying influence: considering ASR and Cr retention results (Figures 3.1,3.2 and 3.3), commercial K41 (18 wt. % Cr) showed a comparable behavior to the higher alloyed steels Crofer 22 H and Sandvik Sanergy HT (23 wt. % Cr). No steel substrates outclassed the others for any coating composition or deposition technique. AISI441/K41 demonstrated to be a reliable solution also in short stacks.
- Nitriding of steel substrates is an effective solution to improve Cr retention properties of porous coatings.
- Composition influence: among the tested variations, no coating composition stood out with respect to the others. Hence, the change in coating composition is less influencing the performances than the coating deposition technique itself.
- Single repeating units containing PVD coatings shows the lowest degradation rates. Even though, the high production costs hamper the adoption of this technology for a realistic commercial stack production.

### **3.6 Acknowledgments**

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# 4 Degradation of Metals in SOFC stacks, Part I

This chapter is adapted from a manuscript submitted to a peer-reviewed journal. The details about materials and experiments can be found in Chapter 2. The aim is to describe and understand how commercial metal interconnects degrade during service life in a stack. The investigation covers a period of 18000 hours with steps at 45, 2700, 4800 and 10000 hours. The focus is on the cathode side and the interaction at the steel/coating/perovskite interfaces

### 4.1 Introduction

In the contribution to more efficient energy conversion to reduce  $CO_2$  emissions, solid oxide fuel cell (SOFC) electrochemical devices transform chemical energy from fuel and air directly into electric power with high efficiency [145]. Ceramic cells are stacked in series to add up voltage and obtain useful power outputs. In planar designs, each cell pair is separated by an interconnect plate in order to separate air from fuel, collect the electrical current, and ensure mechanical stability [51]. In the first generation of SOFCs stacks based on electrolyte supported cells operating at rather high temperature (>850°C), the interconnects were made of ceramic materials, with relatively low chemical inertia but high cost and limited mechanical properties. With the reduction of the electrolyte thickness achieved by transferring the mechanical support function to an electrode (typically the anode), the stack operating temperature could be decreased (<800°C) and iron metal based interconnects introduced. Nowadays, the state of the art material is ferritic stainless steel (FSS) which provides a reasonable coefficient of thermal expansion (CTE) match with the cell ceramics and good mechanical strength at the stack operating conditions. Specific ferritic stainless steels like Crofer 22 APU/H [53] or Sanergy HT have been produced for use in SOFCs, yet their still relatively high cost made

#### Chapter 4. Degradation of Metals in SOFC stacks, Part I

standard commercial K41/AISI441 FSS an attractive alternative.

During its use in a SOFC stack, the metallic interconnect (MIC) interacts with agents such as oxygen, steam, sealing materials and cell materials at high temperature and as such is subjected to harsher lifetime issues compared to common FSS applications. To evaluate the reliability of this material for SOFC application, K41 has been previously characterized ex situ [11, 79, 146]. Nevertheless, such studies are not fully representative of the use in a real stack; laboratory conditions usually focus on a few precise parameters, rarily considering all interactions within a stack. The existing publications regarding this topic are summarized in table 1.3.

This chapter adds a contribution to these aspects, through the analysis of SOFC stacks tested for 45, 2700, 4800, 10000 and 18000 hours. Hereinafter these stacks will be referred to in the text adding # before the number of testing hours. A history of degradation observed on K41 (MnCo)<sub>3</sub> $O_4$  coated MICs is presented, with particular emphasis given to the interaction between the MIC and the cell ceramics at the cathode side. The results of another stack, made of the same materials, which underwent 124 thermal cycles are also described.

Harmful phenomena affecting the steel lifetime are identified and discussed, both from the corrosion and mechanical point of view. A forecast on overall degradation is given.



### 4.2 Results

Figure 4.1 – Schematic not-to-scale representation of the interconnect in contact with the perovskite and the four distinct regions of relevance

In the analysis of the interconnects, four regions of interest (ROI) are defined based on the scientific and technological relevance (Figure 4.1):

- "cathode side rib" (oxidizing atmosphere, direct electrical contact with the cell, MIC is *coated*);
- 2. "cathode side valley" (oxidizing atmosphere, not in electrical contact with the

cell, MIC is coated);

- "dual exposure cathode side" (oxidizing atmosphere, not in electrical contact with the cell, MIC is *uncoated*);
- 4. "dual exposure anode side" (reducing atmosphere, not in electrical contact with the cell, MIC is *uncoated*).

### 4.2.1 Cathode side rib (Figure 4.2)

In this region, the coated MIC is in direct contact with the cathode perovskite material and thus subjected to the combined effect of elevated temperature, mechanical stresses, and polarization. Consequently, this interface underwent most of the changes observed in the stacks. Figure 4.2 gives the time evolution of this interface composed of steel/oxides/MCO/perovskite for 5 of the investigated stacks. A representative observation for each operating time is given. Note that among the different layers some void regions containing resin (black zones) appear; these originate from disassembling the stacks. Colors are superimposed to the pictures in Figure 4.2 to identify the evolution of the different layers. All the corrosion products are oxides or scales and indicated with green color; blue color represents the MCO densified coating; the reaction product  $SrCrO_4$  is associated to dark red; chromium-containing perovskite, finally, is colored with light red. Figure 4.3 displays the EDS chemical mapping of interfaces similar to those in Figure 4.2, but in different regions of interest. After 45 hours, isolated elliptical regions were discretely distributed along the steel/MCO interface (Figure 4.2 (a)). The hemisphere top is radially spreading into the MCO coating, densifying it; while the bottom half proceeds via inward corrosion - this behavior is comparable with Fe breakaway corrosion [31]. Where these bump-like protrusions are not present, the scale is thin and regular; at the interface with MCO,a thin dense oxide layer is formed. In Figure 4.2, 45h, this condition is obtained at the left and right of the inward corrosion area.

The densification of the first microns of porous MCO protective coating in contact with thermally grown oxide is a known phenomenon [19]. The scale composition is not homogeneous along the interface: when uniform corrosion is observed, it is made of discontinuous  $SiO_2$  and  $TiO_2$  [147] attached to a bulk  $Cr_2O_3/(MnCr)_3O_4$ double layer. In case of inward corrosion instead, the scale composition is not stoichiometrically defined among Cr, Fe, Mn and O (Figure 4.3, 45h). In the #45 stack, dense precipitations appear between the MCO protective coating and the cathodic perovskite material. EDS analysis revealed a Sr:Cr ratio close to 1, suggesting SrCrO<sub>4</sub> formation (Figure 4.3 45h). Some of these aggregates are observed also inside the MCO coating in stack #45. Strontium traces are found in proximity of the scale, but due to their small amount these are not visible in Figure 4.2 45h and Figure 4.3 45h. It should be noted that these traces are not represented by the strip at the steel/scale interface in the Sr map, this layer is instead due to the overlap with the Si EDS signal. The EDS peak at 14.14 KeV – specific of strontium – was always checked during the analysis to be certain of the presence of strontium and not to confuse it with silicon. At 2700 hours (3.5 months), the densification of the porous coating





(a) 45h

(b) 2700h



(c) 4800h

(d) 10000h



(e) 18000h

Figure 4.2 – Time evolution of the interface at the cathode side rib. Light red coloured regions indicate the chromium-poisoned perovskite, dark red the presence of  $SrCrO_4$  reaction product, blue the densified *MCO* coating and green the oxide layer.

propagated extensively (Figure 4.2, Figure 4.3). The densification is present inside the entire MCO layer in direct contact with the perovskite. Chemical analysis revealed that the densified coating is mainly made of MCO infiltrated by Fe, with presence of Cr and traces of Sr at the interface with the scale. In addition, Si, Ti and Nb precipitates are found at the scale/densified coating interface indicating the original steel/scale border. Inward corrosion further progressed into the steel substrate, and the corrosion front profile became irregular with the merging of single enhanced corrosion regions. Advancing towards 4800 hours (6 months) and 10000 hours (14 months) of stack operation, scale and densified coating show less morphological differences (cf. Figure 4.2, 4800h and 10000h). In both stacks strontium migration from the perovskite is confirmed. Figure 4.2, 4800h, presents a region of interest where  $SrCrO_4$  binds the densified coating and the perovskite, this interaction being strong enough to survive the stack disassembling. Moreover, Figure 4.3, 4800 h, highlights a phenomenon not observed in stack #45 and #2700: an intense steel inward corrosion with  $SrCrO_4$  as likely product. This type of corrosion was found in a few regions of interest in stack #4800.

In stack #10000, strontium confirmed its movement towards the steel, stopping at the interface with the scale or reacting directly with the chromium in the steel like for some regions of stack #4800 (cf. Figure 4.3, 4800h). If such regions with enhanced corrosion spots were rare to find in stack #4800, in stack #10000 they were frequently found. The strontium migration affected also the corrosion process in stack #18000. Indeed, strontium chromate is the main corrosion product on the steel surface. Densified coating is also a mixture of the original MCO and  $SrCrO_4$ . Minor amounts of regions presenting Fe breakaway corrosion behavior are present too.

Chromium is present in the whole perovskite zone in contact with the interconnect (Figure 4.2).



Figure 4.3 – EDS elemental map of regions similar to those of Figure 4.2. The presence of the Sr K $\alpha$  emission peak (14.14 keV) confirmed that strontium is not an artifact due to the Si X-ray Ka emission peak (1.74 keV).

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The microstructural aspects of the cathode side rib interfaces up to 18000 hours appear good. Randomly distributed cracks and porosities were found at the scale/densified coating interface in all stacks except for #45. Such regions match with deposits rich in Si, Nb and Ti oxides. The crack concentration at the scale/densified coating interface of the cathode side rib region was confirmed by the post-analysis of the stack which underwent 124 thermal cycles (discussed later, cf. Figure 4.7).

### 4.2.2 Cathode side valley (Figure 4.4)

In this region, the coated steel is not in direct electrical contact with the perovskite. Figure 4.4 illustrates the time evolution of this region. Two different behaviors exist below and beyond 10000 hours of operation. Up to 10000 hours, the MCO coating densified only in the first microns close to the steel/MCO interface. SEM/EDS analysis revealed traces only of Fe diffusion inside the protective coating.

The oxide layer has grown smoothly all along the steel/MCO interface, its composition being a discontinuous line of  $SiO_2$  and  $TiO_2$  precipitates followed by an uninterrupted  $Cr_2O_3/(Cr, Mn)_3O_4$  layer. Nb<sub>2</sub>Fe Laves phases are visible in the steel substrate too. Nb-precursors of Laves phases are inserted in the steel on purpose, to improve the mechanical resistance of the steel to creep [123]. Between 10000 and 18000 hours operation, the passivation layer failed, with Fe infiltrating the coating and densifying it. The oxide layer is now irregular due to inward corrosion. Thermal stress caused by the CTE difference between metallic and ceramic phases could potentially lead to adhesion failures, but as shown in Figure 4.4, at the metal/oxide interface the adhesion remains good. Instead, stress induced by disassembling and sample polishing caused most of the damage. The steel/coating interface (Figure 4.4) was damaged during the polishing process, hence it is not possible to assess if the delamination took place during the stack operation or because of the sample preparation process. Regarding chromium contamination, only <1at. % traces have been found in MCO up to 10000 hours by EDS chemical analysis (not shown). In the 18000 hours stack, chromium diffused into the coating together with iron. Iron was found to infiltrate the coating up to 30 at.%, this percentage not being constant. Chromium instead stays in lower amount (5 at.% max.). Figure 4.4 presents a small crack in the 2700h sample at the scale/MCO interface and a bigger delamination in the 45h sample between the steel substrate and the scale. These defects are actually not representative of the global status of the MIC; moreover, they could also be induced by sample preparation. In the observation of large areas of the MIC surface in fact, most of the MIC cross section was free from delamination.

### 4.2.3 Dual exposure region = anode side and cathode side (Figures 4.5 and 4.6)

In this region of the interconnect, uncoated steel is exposed simultaneously to the oxidizing and reducing environments, and is not in direct electrical contact with the cell. It can be thought of as a thin steel plate lapped on one side by air and on the other side by fuel. The behavior of ferritic stainless steel under dual atmosphere

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(a) 45h

(b) 2700h









(e) 18000h

Figure 4.4 – Time evolution of the steel/MCO interface at the cathode side valley.

operation has begun to be investigated carefully [79, 148], as hydrogen is suspected to hamper the steel passivation process at the air side. Figure 4.5 and Figure 4.6 describe the scale evolution at both sides of the dual exposure plate. Scale composition is the same for both sides: a thin  $SiO_2$  and  $TiO_2$  layer just above the steel substrate, followed by  $Cr_2O_3$  and  $(CrMn)_3O_4$  spinel. Other elements, notably Fe, are found only as traces. In Figure 4.5 and Figure 4.6, the white spots close to the steel/scale interface are Laves phases. In stacks #4800, #10000 and #18000 small and round TiN precipitates are observed too.

No spallation occurred in these two regions for any of the samples observed.

### 4.2.4 Stack that underwent thermal cycles

Figure 4.7 illustrates the interfaces at the cathode side rib and cathode side valley, for stack #124TC which underwent 124 thermal cycles (25°C-750°C) within 2600 hours of operation. SEM observations at different magnification did not highlight any failure between the metallic and ceramic layers. This is important because for the valley region, there is no stack compressive force acting that could prevent material spallation. The only region showing local cracks is the interface between the scale and the densified coating at the cathode side rib (red dotted rectangles). The same type of cracks was also observed in stacks #2700, #4800 and #10000, again at the scale/densified coating interface. The absence of material spallation is confirmed also by the consistency in scale thickness with the other analyzed stacks. Cross sections of the dual exposure regions did not present delamination nor cracks, like in Figure 4.5 and Figure 4.6). Stack disassembling and sample preparation caused some defects.

### 4.2.5 Summary

Merging the information of the six stacks described and analysed above, the following main observations apply:

- Fe diffuses into MCO principally where the coated MIC is in contact with the perovskite and densifies the MCO protective coating;
- Sr from the perovskite migrates towards the MIC and interacts with Cr contained in the steel to form *SrCrO*<sub>4</sub>;
- SrCrO<sub>4</sub> can form both at the coating/perovskite interface or on the steel surface;
- regarding dual atmosphere exposure and corrosion, the scale compositions present no Fe contamination or hematite-like zones;
- good adhesion of the ceramic layers to the steel substrate and absence of spallation is observed, but porosity at the interface between the scale and the densified coating may be present.

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 State
 Image
 Ident
 mode
 HV
 curr
 WD
 frame
 HFW

 5000 x
 T1
 A+B
 15.00 kV
 1.6 nA
 11.3 mm
 32.1 s
 41.4 µm

 (C)
 48000h





(e) 18000h

Figure 4.5 – Time evolution of uncoated steel surface at air side (cathode) of dual exposure region.
#### 4.2. Results



(a) 45h

(b) 2700h



(c) 4800h

(d) 10000h



(e) 18000h



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(a) Cathode side rib



(b) Cathode side valley

Figure 4.7 – Micrograph of the cathode side rib (a) and cathode side valley (b) regions of interest taken from a stack which underwent 124 thermal cycles.

### 4.3 Discussion

#### 4.3.1 Passivation layer failure at interconnect/perovskite interface (cathode side rib)

Not shown in Figure 4.3, silicon oxide presents a double occurrence in the regions affected by Fe breakaway: one line at the scale/coating layer interface and a second and thinner layer moving together with the  $Cr_2O_3$ /steel interface. The SiO<sub>2</sub> profile reflects the inward evolution of the steel/oxide interface confirming that there has been a corrosion inside the steel substrate. Also in stack #18000, Si presents a discontinuous distribution at the cathode side rib. This indicates that at least up to 18000 h, silica does not give rise to electrical insulation. The fragmented distribution of the  $SiO_2$  layer is a positive side effect of the inward corrosion. Literature describes the reaction between  $Cr_2O_3$  and MCO as an opposite interdiffusion of Cr-ions towards the spinel coating and Mn- and Co-ions towards the chromia scale. Two different reaction layers should hence be formed:  $(MnCo)Cr_2O_4$  close to  $Cr_2O_3$  and  $(MnCoCr)_3O_4$  close to the MCO protective layer [17, 19, 149]. This phenomenon has been commonly observed, while Fe-cation infiltration into MCO is not reported in any of the cited studies. The undesirable appearance of iron oxides on the stainless steel surface due to the failure of the passivation layer is known as iron breakaway. On the other hand, iron contamination of MCO spinel as such is not harmful, in fact improving the sintering of the coating and its electrical conductivity [116, 133, 150]; problems might arise if Fe segregates as oxide alone [80]. From a kinetic point of view, the Fe-diffusion coefficient inside  $Cr_2O_3$  is higher than the Cr self-diffusion coefficient [151], but  $Cr_2O_3$  is thermodynamically favored to form [33, 63, 152]. Iron breakaway originates from two possible causes: intrinsic chemical failure (InCF) or mechanically induced chemical failure [151]. In the first case, the Cr-ions supply from the alloy substrate is not fast enough to sustain the oxidation process. In practice, this translates into a minimum Cr concentration value  $(N_{Cr}^{min})$  at the metal/oxide interface to guarantee passivation. In order to assess if the InCF process occured in the investigated stacks,  $N_{Cr}^{min}$  was calculated using the approach given by Othman and co-workers [33], in turn derived from Wagner's theory [63].



Figure 4.8 – Elemental profile (wt. %) of cathode side valley and rib in stack #45 and #2700. The scanning starts in the bulk on the alloy substrate and ends in the thermally grown oxide layer. Note the Cr profile in proximity of the steel/scale interface.

For the calculation, two different diffusion coefficient values are taken into consideration: a more conservative  $2 \cdot 10^{-12} cm^2 s^{-1}$  [33] and a more optimistic  $7.4 \cdot 10^{-13} cm^2 s^{-1}$  [152]. The parabolic rate constant ( $K_p$ ) is taken from [149] after being converted from  $g^2 cm^4 s^{-1}$  to  $cm^2 s^{-1}$ . The result gives  $N_{Cr}^{min} = 8.9$  wt.% and 12.4wt.% for the 2 scenarios. These values are compared with the depletion profiles for stacks #45 and #2700 (Figure 4.8) at the cathode side rib and valley positions. Red lines represent the Cr content profile (% wt) and lila lines represent the Fe content profile (wt.%), while the black dotted vertical line indicates the steel/scale interface. In stack #45 the Cr depletion region starts 10-15  $\mu m$  below the steel/oxide interface with a marked decrease in the 8-10  $\mu m$  closest to the interface. The chromium content in the steel just below the scale is around 10 wt.% at the "cathode side valley" and less than 8 wt.% at the "cathode side rib" coherent with inward corrosion (matching with Fe breakaway cf. Figure 4.2, 45h). Additional chromium quantification in the steel beneath the inward corrosion region at the cathode side rib of stack #45 recorded ca. 6 wt.% of Cr. In stack #2700 instead, the corrosion kinetics slowed down, with a re-homogenization of the Cr content in the steel below the scale of ca. 15 wt.% in both the valley and the rib region. Even considering the limitation of the Wagner theory, the comparison of measured values at the cathode side rib with the calculated  $N_{Cr}^{min}$  values indicate that InCF could be a cause for passivation layer failure. The chromium profiles also indicate that the corrosion process tends to slow down and the Cr distribution in the steel to homogenize in the first months of operation. The difference in Cr wt.% between the standard and inward corrosion in stack #45 suggests the presence of an element or substance removing chromium. In ferritic stainless steel degradation studies, this could typically be steam, but the absence of Fe breakaway at the cathode side valley below 10000 hours of operation indicates that steam alone cannot explain all observations. Alternatively, strontium could be the chromium binding element. Gibbs free energy equilibrium values indicate SrCrO<sub>4</sub> to be a favored species over  $Cr_2O_3$  in the 700-800°C temperature range. Strontium chromate formation in SOFC operating conditions is harmful for the cell lifetime, as it is a poorly conductive phase ( $\rho_{SrCrO_4} = \sim 103 \ \Omega cm^{-1}$ ) [46] and decreases the oxygen surface exchange reaction sites [45, 153, 154]. Besides electrode poisoning, strontium chromate passivation on the steel surface is undesirable too due to the risk of electrical insulation. As shown in Figure 4.2, already in the first hours of stack operation, the perovskite is not stable and Sr moves towards the steel. EDS chemical analysis indicated the dense aggregates at the MCO/perovskite interface to be compositionally close to SrCrO<sub>4</sub> and found Sr and Cr inside the MCO coating too: traces of strontium close to the thermally grown scale were found already in stack #45 in coincidence with Fe breakaway regions. Segregation of strontium oxide on perovskite surfaces is a known degradation issue [155–157]. Strontium cations could have migrated from the perovskite through solid or gas diffusion mechanism. A study describing experimental conditions similar to ours proposed a solid diffusion mechanism for strontium contamination [15]. However, in different MICs containing dense barrier layer and tested in the same conditions reported here, there was no strontium diffusion through the coating. Notably, MCO was deposited via physical va-

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por deposition. In those SRUs, strontium cations accumulated at the perovskite/MCO interface are not passing this border. At the same time, Sr vapors are thermodynamically possible in our testing conditions. It can therefore be suggested that strontium moved through the gas phase and that steam in the air flow triggered Sr evaporation. Most of the vapor is carried away by the air flow and therefore not affecting the cathode side valley regions.

Regarding mechanically induced iron breakaway corrosion, it refers to random passivation failure due to machining. Some regions with enhanced corrosion could match this explanation, but final proof is lacking.

Chromium contamination is suspected to occur also via the gas phase, the perovskite is in fact chromium poisoned also where it is not in contact with the interconnect. The hypothesis of poisoning through the gas phase would also imply that after the complete densification of the coating, no more chromium vapors should leave the interconnect.



Figure 4.9 – Chromium profile evolution in the perovskite layers taken from stacks #2700, #4800 and #10000.

To assess this mechanism, the chromium profiles through three perovskite layers in contact with the interconnects are compared; notably these linescans are taken from the outlet region of stacks #2700, #4800 and #10000 (Figure 4.9). The element quantities are expressed in at.%. The evolution of the curves has a wave-like behavior, for the #2700 stack the chromium diffusion profile has its highest value at the interconnect/perovskite interface, the interconnect being the chromium source. After 4800h instead the maximum of the chromium diffusion profile moved towards the center of the perovskite, leaving a constant amount of chromium in the first layer close to the interconnect. Having the chromium peak not at the interface is confirming the idea of a complete densification of the coating before the 4800h of operation. The line scan from stack #10000 confirmed the spreading of the chromium and the fixed value of 2 at.% at the interface with the interconnect. Considering the fixed presence of  $SrCrO_4$  at the MIC/perovskite interface, the following process can be hypothesized: In a period between 0 to 4000 hours, part of the chromium oxide transforms into gas phase and passes through the porous coating reaching the perovskite, in the meantime the iron migrates from the steel substrate and reacts with the Mn and Co oxide. This process continues until the coating is completely densified, the chromium cations can not diffuse anymore and its profile in the perovskite homogenizes.

Analysis on PVD-coated MICs confirmed the absence of chromium contamination of the perovskite in the case of dense coatings. The distribution profile of iron and its ionic compatibility with Mn and Co suggest instead a solid phase diffusion process.

The literature on Fe-breakaway is rather scarce. Few papers described the MIC behavior in stacks over long operating periods; even less literature exists documenting operation at similar conditions to the stacks analyzed in this work. Haanappel et al. [80] found iron oxide formation on top of MICs, but the reacting element in this case was Pb contained in the sealing material. As another example, a 3-cell stack containing AISI 441 MICs coated with Ce-(Mn,Co) was run for 6000 hours, but no specific lifetime issues were found, notably no sign of Fe-breakaway even at the MIC/perovskite interface (LSM) [105]. Recently, uncoated SUS430 MICs have been employed in a 5-cell short stack [158]. Even if the test period was short, Fe-breakaway occurred with  $Fe_2O_3$  found at the steel/cathode interface. In the MICs analyzed in the present work instead, Fe substituted for Mn and Co, preventing the formation of pure iron oxide. Accumulation of Mn at the border of the growing densified coating suggests a preference for Mn-substitution. The fact that stacks #4800 and #10000 show similar average concentration values of iron may indicate a stabilization of the corrosion process. Regarding the long time reliability of stack operation, thermodynamic stability of Fe-infiltrated MCO should not be a problem as it is more stable than  $Mn_3O_4$ ,  $Fe_3O_4$  and  $Co_3O_4$  alone [159].

#### 4.3.2 Oxide growth

Figure 4.10 shows the scale thickness growth curves obtained by measuring the average scale thicknesses of the different regions of interest of the interconnects. The values of these curves consider the whole scale and not chromia alone; most of the literature curves refer to pure  $Cr_2O_3$  growth only. Values from stack #2700 are reported separately because this stack was operated at a lower average temperature than the others. This does not change the corrosion product composition, but slows down the kinetic growth, as corroborated from the data in Figure 4.10. High temperature corrosion processes are usually described with the model proposed by Wagner [63]. The oxide formation process is driven by diffusion of cations and anions through the growing dense scale, and the relation scale thickness/time on a plot would then assume a parabolic trend – the same as for Fick's law. Nevertheless, the



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theory is basic, leaving aside chemical interactions or the presence of alternative diffusion paths to lattice diffusion only. The curves extrapolated in Figure 4.10 in fact do not follow the parabolic trend. The "cathode side rib" curve shows a capacitance-like trend, with a sharp decrease in the growth rate after 5000 h, and the corrosion process being enhanced mostly during the first few thousand hours of operation. (cf. Figure 4.2, 45h and 2700h). It is interesting to note that the thickness value of the scale at the cathode side rib for the stack #2700, despite its lower average operating temperature, would nonetheless match the general trend, indicating that the materials chemical interaction may dominate the first stage of the corrosion process in this region of interest. Applying a trend line to the empirical curve of Figure 4.10, a forecast to longer operation time would give at 40000h an average scale thickness of 13.3  $\mu m$  and at 80000h of 14.4  $\mu m$ , not adding substantially to long term resistive loss compared to the situation after 5000-10000h.

The "cathode side valley" curve shows a different trend line than that of the "cathode side rib". This difference confirms the influence of the perovskite on the MIC oxidation degradation process. The corrosion behavior of this interface can be divided in two regions. Up to 10000 hours, a parabolic trend line with  $K_p = 3 \cdot 10^{-19}$   $cm^2sec^{-1}$  would fit the few data points. A validation of this value with data from literature is difficult, as the combination of materials and the operating conditions involved is difficult to find. Two compatible studies [18, 160] provide values of growth

rate 2-3 orders of magnitude bigger. The reasons for this difference are the higher temperature of their tests (800°C), the curve in Figure 4.10 does not follow exactly a parabolic trend and the longer period of oxidation of the MIC (the samples of the cited studied have been tested < 1000 h). In any case, the comparison is interesting because the growth rate at the cathode side is slower than expected from laboratory conditions. The elemental scale composition, however, is coherent with expectation:  $SiO_2$  precipitates followed by  $Cr_2O_3$  and  $(CrMn)_3O_4$  layers. After 10000 hours, iron breakaway occurs, as indicated by the curve rising again. A quantitative forecasting of the final scale thickness at the cathode valley side is not possible, even though a stabilization – similar to what happened at the cathode side rib- after the complete coating densification is likely to be expected.

The "dual exposure plate (anode and cathode side)" experienced simultaneous exposure to oxidizing and reducing atmospheres. This condition is potentially harmful for the steel as an iron oxide phase could form on top of the  $Cr_2O_3$  oxide at the cathode side [12, 161, 162]. EDS analysis at the cathode side of the dual plate instead revealed  $Cr_2O_3 + (CrMn)_3O_4$  oxides. In a recent paper, the appearance of iron oxides on top of the scale of uncoated AISI441 exposed to  $H_2$ /air dual atmosphere was associated to the change in testing temperature, i.e. this phenomenon occurs only at aging temperatures lower than 700°C [162]. This explanation is in contrast with a different study of AISI441 oxidation behavior, where, under similar dual atmosphere exposure at 800°C, on top of the scale grown of the stainless steel there is iron oxide [34]. The reason for this different behavior is that the AISI441 samples of the first study underwent a pre-oxidation process while that of the second study did not. It follows that for the dual plates observed in this thesis, the pre-operational aging that the stack underwent prior to operation resulted in a pre-oxidation process [28]. The deviation of the growth curve from the parabolic trend could instead be explained by hydrogen diffusion from the fuel side towards the air side. Hydrogen ions dissolved in the steel substrate would enhance metal vacancy formation in chromia and this in turn lead to faster transport of Cr-cations[163]. On the other hand, MIC pre-oxidation is likely to mitigate also this phenomenon [34]. Oxide growth at the "dual exposure anode side" follows a trend with slower kinetics than those obtained via experiments performed in laboratory conditions. The curve obtained through the average values becomes a plateau after 10000 hours, indicating a complete stabilization of the corrosion process. Realistically, the scale will still grow at a low rate; considering the curve passing through the maximum of each point the forecasted values will be 6.4  $\mu m$  and 6.9  $\mu m$  at 40000 and 80000 hours.

From the observations on the four regions of interest, the steel oxide growth is not expected to cause stack failure. Formation of a continuous  $SiO_2$  layer below the scale is the main concern in terms of maintained conductivity of the MIC. Nb addition and limited content of Si in the alloy composition should hinder the creation of such insulating layers, but the literature in this sense shows contradictory results [10, 123]. No long-term forecast could as yet be made, suggesting to look instead into real SOFC stack performances [10]. From the observations on the stacks in our study, Si oxidation appears to be stabilizing between 4800 h and 10000 h. Observa-

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tions on stack #18000 confirmed that no further changes in silica layer morphology or thickness were apparent. With the scale composition not exactly measurable, because of the nanometric thickness, it is not possible to precisely quantify the contribution of the interconnect scale to the stack degradation process in terms of ohmic losses. From the observations presented, however, this contribution will tend to stabilize after 5000 hours and therefore not present a main problem for long-term degradation. To counterbalance the initial increase of the scale ohmic resistance, the coating densification due to Fe-incursion in fact improves the conductivity of the spinel. Formation of  $SrCrO_4$  inside the perovskite cathode is also related to the initial stage of operation as, after coating densification due to Fe-breakaway, the Cr-migration will decrease. Merging the information from Figure 4.2 and Figure 4.10, the type of interconnect studied should not limit the stack lifetime. According to observations in stack #124 also a sudden shut down of the stacks should not lead to contact issues from the MIC side. The main risk for stack lifetime limitation originating at the cathode side therefore would be the complete covering of SrCrO4 on the steel underneath the protective coating.

#### 4.3.3 Mechanical behaviour

The adhesion between the oxide and the steel substrate was maintained even in presence of the stresses induced by the thermal cycling treatment. The coefficient of thermal expansion (CTE) for K41/AISI441 is  $12.8 \cdot 10^{-6} \text{ K}^{-1}$  in the 20-800°C range [120] while for  $Cr_2O_3$  it is 5.7.10<sup>-6</sup>  $K^{-1}$  in the 20-1000°C range [164]. In the presence of native scale prior to heating, as for the MICs studied here, this difference induces tensile stresses in the scale during heat up and compressive stresses during cooling. Hence, the repetition of thermal ramps could induce delamination between the oxide and the metal phases, eventually decreasing the contact surface between the MIC and the cell and triggering accelerated corrosion of the metal surface. In addition, another element of risk lies in the difference in CTE among ceramic phases too, i.e. the multiple oxide layers created. From the stacks observed, however, the difference in CTE values between metallic and ceramic phases did not lead to delamination. The densification of the MCO coating, instead, caused cracks, but in none of the observed cross sections these cracks lead to destructive failure. Similarly, small cracks at the scale/densified layer interface were commonly found. Again, none of these cracks caused mechanical issues. Pressures on the stack are thought to have a beneficial effect. Comparing these results with literature, few authors focused their attention on mechanical aspects of the MIC compared to that of the ceramic cell, but in all cases the energetic approach was used. A certain stress threshold must be reached for the cracks to propagate and the adhesion between layers to fail. In the specific case of metal interconnects the two interesting interfaces are the steel/scale and scale/protective coating. The parameter taken into account to determine whether the contact will resist is the scale thickness: Liu et al. for example measured the maximum shear stress tolerated by the steel/scale and scale/coating for MCO-coated Crofer 22 APU with a Rockwell indentation test [85]. According to their model, the predicted lifetime was 4800h for uncoated Crofer 22 APU (critical scale thickness

11.4  $\mu$ m) and 15000 h for coated Crofer 22 APU (critical scale thickness 4.2  $\mu$ m). Interestingly, the lifetime limit for the uncoated ferritic stainless steel matches the operating time of one of the stacks. However, stack #4800 showed no spallation of the oxide layer in the dual exposure (uncoated) region. It follows that the MIC is more reliable than what is predicted by the model, moreover accounting for the fact that K41 is a supposedly inferior steel to Crofer 22 APU. For the coated case, the comparison of the results is difficult as the scale grown on the MIC in the stack is not  $Cr_2O_3$  only; nonetheless, 11  $\mu$ m of scale thickness were reached after 10000 h of operation, yet no serious failure of the interface was found in this case either. Underestimation of the beneficial effect of compression against spallation could be a reason for the mismatch between model and operative reality. The observation on a stack run for 35000 hours at FZJ demonstrated the reliability of ferritic stainless steel for this long term operation [88].

# 4.4 Conclusion

Five short stacks tested for 45, 2700, 4800, 10000 and 18000 hours under air and  $H_2/N_2$  have been cross sectioned and observed by SEM/EDS to help understand the degradation behavior of AISI441/K41 metal interconnects coated with wet powder sprayed MnCo spinel. In addition, a stack that underwent 124 thermal cycles was post-test analyzed as well to focus on the mechanical behavior. The following conclusions are drawn:

- The electrical contact region between the MIC and the cathode perovskite is chemically the most active one. Strontium migrates from the first operating hours towards the steel. It reacts with chromium, affecting the  $Cr_2O_3$  passivation layer. This can lead to chemical failure-induced Fe-breakaway corrosion or formation of  $SrCrO_4$  on the steel surface.
- Iron breakaway triggers densification of MnCo-spinel which becomes infiltrated with Fe (> 30 at.%). This reaction, however, should not harm stack lifetime as (Cr,Fe,Mn) spinels are thermodynamically stable and will not separate into fragile and low conductive hematite phases.
- Spinel densification appears to have positive effects on the Cr barrier property of the coating on the long term.
- The main stack degradation risk is the formation of  $SrCrO_4$  on top of the stainless steel substrates, increasing ohmic losses. This phenomenon is in competition with Fe-breakaway and was found only in stacks #4800 and #10000.
- A discontinuous  $SiO_2$  layer forms in the electrical contact regions up to 18000 hours. From the observations it is not expected that silica for longer operating times should cause electrical insulation.
- Curves obtained from micrograph thickness measurements predict a stabilization in corrosion after ca. 5000 hours of operation for all the regions of interest

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but the uncoated steel at the cathode side of the dual atmosphere exposed plate region. According to the obtained empirical curves, average scale thicknesses at the cathode side ribs will be ~13.3  $\mu m$  and ~14.4  $\mu m$  respectively at 40000h and 80000h. The contribution of the MIC component to the ohmic losses at the steel/cell interface tends to stabilize.

- At the cathode side valley the passivation layer fails between 10000 and 18000 hours. This supports that Fe breakaway corrosion in AISI441/K41 is caused by intrinsic chemical failure process and that strontium is a catalyzer of this process.
- In the uncoated interconnect region, a scale made of discontinuous  $SiO_2$ , dense  $Cr_2O_3$  and  $(MnCr)_3O_4$  spinel on top is found on both anode and cathode exposed sides. No traces of hematite phases were seen at the cathode air side, contrarily to what was reported before from specific dual atmosphere tests on ferritic stainless steel. This may be due to the preoxidation of the MIC.
- No material spallation was found in the four regions analyzed. Overall, the adhesion between the different phases was good and any detachment found during observations was likely caused by the disassembling and polishing processes. The porosity found at the scale/densified coating interface is not considered to be harmful, as stack compression demonstrated to avoid delamination.
- In general, ex-situ tests on MIC materials demonstrated not always to be representative of the real degradation behavior of the ferritic stainless steel in a stack. Degradation in a stack was less negative than predicted from models found in literature for both the corrosion and mechanical resistance behaviors.

## 4.5 Acknowledgment

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# **5** Degradation of Metals in SOFC Stacks, Part II: Nanolevel Investigation

This chapter is complementary with Chapter 4. It investigates the interconnect/coating interface at the nano level to better understand the corrosion process and define the products.

# 5.1 Introduction

In the previous chapter, it was shown that the interconnect/coating/perovskite interface experience an intense chemical interaction, the inward corrosion products are mainly mixtures of chromium, cobalt, iron and manganese oxides. The necessity of the high energy beam (30 kV of beam acceleration voltage) to undoubtedly assess the presence of strontium with SEM/EDS analysis caused an interaction volume with the material bigger than the oxide crystals size to analyse.

To better identify the corrosion products, TEM crystallographic analysis through selected area diffraction (SAED) was performed. Two lamellae, about 10\*10  $\mu m^2$  were extracted by FIB from a pristine interconnect (Figure 5.1) and from stack #4800 Figure (5.5). Both samples were embedded before in epoxy resin. The pristine interconnect just underwent a sintering process above 800 C for less than 24 hours to improve adhesion to the protective coating.

The lamella extracted from stack #4800 was chosen to represent a region of inward corrosion and Fe breakaway. It originally contained a portion of the steel, the whole corrosion region and a portion of the  $MnCo_2O_4$  barrier coating. Because of the weakness of the bond between the steel and the corroded region, the steel portion detached from the sample after few hours of TEM observation. As in the previous chapter, the steel substrate is made of AISI441/K41 and the coating is deposited through wet powder spraying.

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## 5.2 Results

#### 5.2.1 Pristine interconnect



Figure 5.1 – (a) HAADF-STEM image of the lamella extracted from a pristine SOFC interconnect. The bottom light gray layer is AISI441/K41 ferritic stainless steel, while the porous phase is the  $MnCo_2O_4$  coating. (b) Detail of the interconnect/coating interface with an inward corrosion region. (c) the green arrow indicates the origin of an inward corrosion process

Figure 5.1 (a) shows almost the entire lamella extracted from the pristine interconnect and in (b) and (c) two magnified views of it at the steel/oxide/coating interface. In the lower part of the image is the AISI441/K41 stainless steel substrate, and above it a thin scale layer, while the rest of the picture is consisting of the porous coating. In the steel, the region immediately below the scale layer presents a band of well visible steel grains. Figures 5.1 (a), (b) and (c) are obtained with HAADF-STEM imaging, which is sensitive to the mass/thickness ratio of the material. The difference in contrast among the grains might depend on the crystal orientation or the chemical composition. EDS confirmed that all those grains have the same compositions, therefore in the image there are differences in the orientation of the grains. The average thickness of the grain belt in the steel is around 0.8  $\mu m$ . Rounded dark-gray particles segregated all around and inside the grains, highlighting the border with the rest of the steel substrate. The white thin whiskers that are also visible inside the grains are probably dislocations. The EDS analysis confirmed that the steel has a composition compatible with AISI441/K41 and detected high concentration of itanium inside the segregates, which are likely  $TiO_2$  (Figure 5.2) Above the steel grains there is the scale layer. The EDS analysis in Figure 5.2 helps to indentify this layer that is instead difficult to distinguish from the coating in Figure 5.1. It is mainly made of  $SiO_2$  and  $Cr_2O_3$ . In particular, the silicon traces helps to identify the steel/oxide interface. Silicon oxide is present as a discontinuous layer of few hundreds nanometers just above the steel substrate. In Figure 5.1 (b) Si might be confused with voids because of the very dark contrast. The  $Cr_2O_3$  is compact and about 350 nm thick, with the exceptions of isolated regions where it penetrates into the steel substrate. This area

(Figure 5.1 (b) and Figure 5.2) is inside one steel grain and it contains titanium as dispersed element. Silicon is partially spread inside this corrosion region as well; the process of inward corrosion growth disrupts the continuity of the silicon oxide layer. The coating is above this oxide layer. It is a not well sintered aggregation of square particles with a significant residual open porosity. Only the first nanometers in contact with the oxide layer show a better densification. The bright part in the top of the image is still presenting the protective coating, but the lamella is thicker and the electron beam has difficulty to pass it.

Note that despite the similar dark contrast, the black region in the coating area are voids while those at the steel/scale interface are made of silicon dioxide.





The TEM selected area diffraction analysis (SAED) (Figure 5.3) confirmed the nature of the compounds suspected after the SEM/EDS observations. All the indexed grains below the oxide layer are made of stainless steel (a). The identification of oxide layer and coating is made through diffraction rings because the beam impinged on multiple grains. Indexing of the coating provides a good matching with  $MnCo_2O_4$  (c) and to a lesser extent with  $Cr_2O_3$  too (b). Regarding the element depletion due to diffusion from the steel substrate, the iron and chromium profiles below the standard scale and the inward corrosion regions do not differ. In both cases, the level below the scale region is constant around 15 and 80 wt. % for chromium and iron respectively (Figure 5.4).

The silicon and titanium line profiles are instead different. Silicon presents a main peak before the chromium oxide layer in the standard corrosion condition while in the

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Figure 5.3 – Selected area diffraction analysis of regions in the pristine lamella.

inward corrosion its distribution is spreaded (black line). Neither silicon nor titanium diffuse in the MCO. Chromium on the other hand is not stopped by the spinel layer, a maximum of 15 wt.% of chromium is detected in the first micrometer of MCO in contact with the scale.

Finally, always comparing the two linescans, there is no difference in the iron contamination of the MCO. A higher iron content could have indicated a beginning of iron breakaway process.

#### 5.2.2 interconnect from stack #4800

The steel/oxide/coating interface of an interconnect operated for 4800h is more complex. The lamella is taken from the oxide layer as the one indicated with the green color in Figure 4.2 (c). Figure 5.5 (a) is the full lamella, and (b) is the area where nanoindexation took place.

These cracks are created during the FIB extraction process of the lamella. The brightest phase is the stainless steel substrate (labeled with 6), while there is no contrast difference between the corrosion layer (regions 1, 2 and 3) and the densified coating (region 5). Visually, only the vertical dark grey line starting from the bottom of the image helps to indicate this separation (region 4). In Figure 5.5 (b) the grain size helps to identify the different layers (note that the right part of the lamella is not present as it detached during the TEM observation). Porosities are found inside the corrosion layer and in the densified coating. The pores in the corrosion layer are mainly distributed at the interface between region 2 and 3 in 5.5.

Talking about the corrosion region, the titanium cations are spread between two necklaces of titanium oxide particles at the bottom of the corroded area (region 1), in a 2  $\mu$ m wide region (Figure 5.6. Their atomic concentration in region 1 is of about 2 %.

Similarly to the inward corrosion in the pristine interconnect, the silicon is distributed on different layers. The two regions of main accumulation are at the oxide/coating (region 4) and steel/oxide interfaces (border of regions 1/6) - silicon is ideally the



Figure 5.4 – Element linescans across the standard (a) and inward (b) oxide growing regions in the pristine MIC.

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Figure 5.5 – (a) HAADF-STEM picture of the lamella taken from stack #4800 (b) the nanoindexed region highlighted with the green rectangle in (a)

frame closing the corroded area - but there are independent particles inside the whole inward corrosion area (Figure 5.6).

Chromium is present in different amounts, its highest concentration being close to the steel substrate, region 1. This region contains also isolated manganese rich spots. Two other macro regions, identified with numbers 2 and 3 in Flgure 5.6, differ chiefly for the amount of Fe; table 5.1 provides the element concentration of these areas. These compositions are average values, corrosion products are in fact heterogenous inside the same corrosion region. For example in region 1  $Cr_2O_3$  co-exists with some spinel Fe-Cr compounds.

Moving towards the interface with the coating, there is an accumulation of strontium close the to silicon oxide layer (region 4). The source of these cations can only be the contacting perovskite material. In the same area niobium cations are detected too, but their origin is the steel substrate.

Finally, at the very left of the figure lies the protective coating, which did not maintain its pristine composition. Iron penetrated into it, with EDS quantification analysis indicating concentrantions up to 29 at.%.

Because of the limitation in the precision of the EDX results induced by the small grain dimensions and the interaction volume, to identify the corrosion products the TEM-SAED was used. Due to the vicinity of the grains, the standard diffraction acquisition might result in overlapped spectra, therefore nano beam indexation was used. With this technique one diffraction spectrum is associated to each pixel of the image (cf. Chapter 2). Figure 5.5 (b) presents the area analysed with this method. Despite the improvement in the diffraction spectra acquisition, just few

crystals gave a clear diffraction pattern. Merging the information of the EDS with the SAED analysis, the following compounds are likely to be part of the corrosion region:  $SiO_2$  (amorphous),  $Cr_2O_3$ ,  $Cr_2MnO_4$ ,  $Fe_2SiO_4$ ,  $Co0.5Nb0.5O_3$ ,  $FeCr_2O_4$ ,  $MnFe_{1.5}Cr_{0.5}O_4$ , and  $SrNb_2O_7$ . The identified diffraction patterns are presented in the Appendix (Figures A.5 A.6). Among these compounds,  $SrCrO_4$  is missing because the identification software was incompatible with the strontium chromate lattice database file. Its presence is therefore likely but still still requires validation. In Figure 5.5 (b), silicon containing grains are the brightest areas (excluding the bottom band made of carbon). Silicon oxide is found mainly in amorphous state, but some spectra matched with the trydimite structure or the fayalite ( $Fe_2SiO_4$ ). In the center of these peculiar phases there are always some black spots which are voids. However, no cracks originating from these voids have been observed.

 $Cr_2MnO_4$  is found close to the interface with the steel (region 1 close to 6), while iron containing phases are present only in regions 2 and 3 of Figure 5.6. Strontium chromate and strontium niobate are found in region 4.

These phases are coherent with the element distribution presented in table 5.1.



Figure 5.6 – Qualitative EDS mapping of the lamella in Figure 5.5

# 5.3 Discussion

Comparing the two lamellae, it could be thought that the corrosion process observed in Figure 5.2 (b) is the first stage of the iron breakaway corrosion, but the absence of outward iron migration assesses that the scale still protects the surface. In addition,

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Table 5.1 – EDS quantitative analysis of the regions indicated in Figure 5.6 with points 1, 2 and 3. Values in at.%

	0	Cr	Fe	Со	Мn	Si	Ті
1	48	44.3	<0.5	<0.5	5	<0.5	2.3
2	42	23.7	12	15.5	5.7	<0.5	<0.5
3	42	13.9	39.4	<0.5	2.2	<0.5	<0.5

there is no difference in the Cr concentration profiles below the standard and inward corrosion regions, with the chromium concentration below the inward corrosion too high for Fe breakaway (15 at. %) compared to the Cr threshold presented in Chapter 4.

On the other hand, Figure 5.1 (c) gives some hints on the initiation process of an inward corrosion area. In that region of interest, the process starts at the boundary between two grains (green arrow in Figure 5.1) but it continues preferentially inside one of the two grains. The reason for this might be in two concurring phenomena: the higher diffusion kineticsi of chromium cations along the grain boundary and then preferential corrosion in one of the two grains. Since the composition of the grains is about the same, the different grain orientation is the most likely explanation for the preferential grain corrosion [165].

The appearance of the silicon and titanium oxides presents instead similarities in the two lamellae.

The driving force resulting from the difference in oxygen concentration at the metal surface pushes the oxygen ions inside the steel. According to the Ellingham's diagram, the first oxide to form is titanium oxide. The nuclei of titanium oxides form preferentially in proximity of lattice defects because of the lowering of the nucleation activation energies. As a result, the particles are aligned along the steel grain boundaries or close to dislocations. Then, the high temperature favours the growth and the ripening of these nuclei.

When the oxidation front of chromium goes faster and bumps are formed (5.1 (b)), the titanium is dispersed inside the chromium oxide. This phenomenon has already been observed and it is speculated that  $Ti^{4+}$  might occupy the vacancies inside the chromium oxide layer [166]. In the #4800*h* lamella, the titanium oxide location is different, in fact the titanium rich chromium oxide layer lies between two rows of titanium oxide particles. The distance between the two titanium oxide particle rows changed (300 nm in the pristine lamella and 2  $\mu$ m after 4800*h*) and the distance from the original steel/coating interface changed as well (from 300 nm to 4  $\mu$ m). Thanks to their thermodynamically stability, the  $TiO_2$  particles can be viewed as probes and the change in distances suggests the counterdiffusion of cobalt cations from the coating and chromium cations from the steel substrate. The coating and the steel substrates are both sources of manganese ions moving towards the corroded regions; hence it is difficult to assess precisely the origin of the manganese inside the oxide layer.

Regarding the Laves phases, i.e. intermetallic precipitates such as  $Fe_2Nb$ , the EDS analysis in both the lamellae indicated a modest presence of them. Notably, in the sample taken from stack #4800*h*, niobium preferred to react with strontium rather than with iron, likely creating  $SrNb_2O_7$ . This reaction is confined at the interface and it should not interfere with bulk properties of the steels, i.e. the mechanical properties of the material. The presence of strontium niobate confirms once more the high chemical activity of strontium. The strontium chromate at the original steel/coating interface backs the supposition of an interaction of the perovskite material with the steel substrate, despite the protective coating. As a consequence, the idea of strontium as the scavenger element inducing chromium depletion and subsequent iron breakaway corrosion is realistic.

The source of the strontium contamination is clear, but the way it migrates, is not. In literature, the focus on high temperature behavior of perovskite is given to the demixing of the cathode material, while the interaction with the contacting material is less considered. Chen at al.[15] presented the idea of a solid migration of  $Sr^{2+}$  driven by the electrochemical potential difference between the perovskite and the coating. Nevertheless, their argumentation was not complete as problems due to ionic radius size and valence mismatches were not taken into consideration. Moreover, a gas diffusion controlled process can not be excluded *a priori*: at the stack operating temperature, the presence of SrO vapors is possible and they could pass through the porous protective coating. Finally, the migration of strontium through solid phase was also recently challenged by Menzler et al. [167]

To assess if the solid phase diffusion was indeed possible, a Density Functional Theory based simulation was performed in collaboration with the Laboratory of Molecular Simulation at EPFL. DFT was applied to a perfect  $MnCo_2O_4$  lattice to see if it can accommodate an atom of strontium.

Density functional theory (DFT) is an ab-initio method that computes the groundstate energy of a configuration of nuclei as a function of the electron density rather than the wavefunction. From this density, chemical and physical properties can be computed, such as bond energies, lengths and lattice parameters [168]. In a periodic DFT simulation, which is needed to describe solids, the periodic cell must be charge-neutral. If there is a net charge, a background charge can be introduced to compensate for the net charge. However, this approximation is inaccurate for most systems because charges are balanced by a discrete countercharge instead of a homogeneous background charge. It is also not known how or whether, for example, the net charge of a metal site vacancy could be compensated by a complementary oxygen vacancy. Since the charge compensation is not known experimentally, the structures are treated with a metal vacancy as charge-neutral, and thus the energy differences calculated correspond to the energy of removing a charge-neutral metal atom.

The defect-free  $Mn_xCo_{3-x}O_4$  crystal lattice was taken from Meena, Kumar and Sreenivas [169] as reference condition, with X set equal to 1. In this spinel, the

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Mn cations have valence (III) and occupy half of the octahedral sites, the other half of the octahedral sites are occupied by Co (III) cations and, finally, the tetrahedral sites contain the Co (II) cations. A stoichiometric material can contain different configurations of Mn(III) and Co(II) within the octahedral sites. Figure 5.7 (a) illustrates the structure.



Figure 5.7 – Representation of the spinel lattice used for the DFT simulation. (a) starting condition (b) a  $Co^{2+}$  missing in the tetrahedral site (c) with a strontium atom doping the lattice

In the DFT calculation, one atom at a time was removed from the lattice and the energy of the new relaxed structure was calculated. Two cases were considered: in the first case, an atom from the tetrahedral site was removed and, in the second case an atom from an octahedral one. DFT calculations indicate that creating both types of vacancies is energetically disfavored, with removing Co atom from the tetrahedral site being more unfavorable than from the octahedral site. From the relaxed, deformed lattice, a Sr atom was inserted in the tetrahedral and in the octahedral vacancies, respectively. This insertion was favorable for both vacancy types. Strontium has valence (II). As a consequence, in a neutrally charged lattice, it could occupy only the tetrahedral sites left by bivalent cobalt cations. Table 5.2 presents the new energies of the perfect spinel lattice before and after the insertion of the strontium cation. If the strontium atom is inserted in a octahedral position the energy difference is negative, i.e. the substitution is favorable. In contrast, a swap between the tetrahedral  $Co^{2+}$  and  $Sr^{2+}$  is energetically unfavorable.

Table 5.2 – Results of the DFT simulation on Sr doping of a perfect MCO lattice. The last column is the energy difference between the stoichiometric spinel and the one with one  $Sr^{2+}$  substituting either  $Co^{2+}$  or  $Co^{3+}$ 

Cation removed	Perfect lattice energy (eV)	Lattice with vacancy energy (eV)	LatticeSr- LatticeStoich (kJ/mol)
Co <sup>3+</sup>	-354.0023	-345.6111	-22.0804
<i>Co</i> <sup>2+</sup>	-354.0023	-345.8059	+72.406

On the other hand, this model has some limitations: the concentration of vacancy defects inside the material is not known, as well as if the hypothesis of charge neutrality is valid. The portion of the spinel considered is at the atomic scale, it does not take into consideration the interactions on the long range; manganese and cobalt can have other valence states than only II and III and the energetic change induced by the configurational entropy is not taken into account. More complicated and costly analysis would be needed to perform a more accurate round of calculations. Nevertheless, it is reasonable to consider that a  $Sr^{2+}$  cation would preferably occupy a tethreadral lattice site rather than an octahedral one because this would require the counterbalance charge of a half oxygen vacancy.

Overall, this calculation supports the idea of a strontium transport through the gas phase rather than through the solid phase, since there doesn't seem to be a likely route for  $Sr^{2+}$  to be inserted into the spinel lattice.

The SAED technique, together with the information from EDS analysis, helped to identify some likely as corrosion products candidates but not the precise ratio among them or the precise distribution pattern. It is established that the principal compound is  $Cr_2O_3$  oxide, whose properties have been already discussed in the introduction.  $FeCr_2O_4$ ,  $Co_{0.5}Nb_{0.5}O_3$ , and  $MnFe_{1.5}Cr_{0.5}O_4$  are more exotic oxides, whose modest application in industry produced rather scarce literature. These compounds (including also  $Cr_2MnO_4$ ) have the spinel structure, and depending on occupation of the d orbitals of the transition metals and the interaction with the oxygens atoms, can show metallic or semiconductive properties. More precisely they are Mott-Hubbard type semiconductors. Chromium, in particular, tends to shift the behavior of this compounds towards electrical insulation. Consequently, the electrical conductivity (at 1000 K) of the reported compounds is lower than of pure chromium oxide. Table 5.3 is based on data from [170] and [171].

Table 5.3 – Electrical conductivity values of corrosion products found in the inward corrosion region  $Scm^{-1} @ 1000 \ {\rm K}$ 

<i>Cr</i> <sub>2</sub> <i>O</i> <sub>3</sub>	FeCr <sub>2</sub> O <sub>4</sub>	Cr <sub>2</sub> MnO <sub>4</sub>	MnFe <sub>1.5</sub> Cr <sub>0.5</sub> O <sub>4</sub>	Fe <sub>2</sub> SiO <sub>4</sub>
10-1	10-3	10 <sup>-5</sup>	10 <sup>-4</sup>	10 <sup>-1.2</sup>

The distribution of the different compound crystals therefore influences the global electrical conductivity of the interconnect. Electrical conductivity takes place preferentially where the resistance is lower and this might be guaranteed by a thinner scale (morphological factor), by the presence of a network of more conductive phases (chemical factor) or by a mix of the two. From the results of the TEM diffraction pattern indexation previously presented, it is not possible to precisely define the position of the different phases because of the overlapping diffraction signal of the small grains. For a modeling of the electrical behaviour at the MIC/coating/perovskite interface of this type of interconnect, further studies - such as 3D FIB/SEM reconstruction - might be used, at least to find a pattern in the element distribution.

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In the results section, the presence of voids at the border between region 2 and 3 was shown. Looking closely, these voids have grown inside a silicon containing oxide. In Figure 5.5, these oxides are bright and surround the darker void. The TEM-SAED analysis of these regions produced patterns compatible with trydimite (a polimorph of silica) or fayalite, a Fe-Si oxide. According to the silicon oxide phase diagram, the trydimite forms at temperature above 870°C and is metastable also after a fast cooling to room temperature [172]. This temperature is reached during the sintering process of the coating but the larger part of the silicon oxide observed is in the amorphous state. Still according to the silicon should take place above 1400°C and, for the inverse transformation, the cooling rate should be very slow. In addition, the specific volume difference between amorphous silica and trydimite differs less than 1.5 %, a difference too small to explain the void formation. Consequently, it is not possible for trydimite to be the identified phase.

Fayalite -  $Fe_2SiO_4$  on the other hand is commonly found below the silicon oxide scale [173] in low carbon steel, due to the interaction between  $SiO_2$  and unstable wustite (FeO). The presence of fayalite would be another assessment that the passivation layer failure being chemically induced, the formation of wustite being possible in case of higher iron activity than chromium. The reason behind the voids formation is not clear, but considering the overall reaction

$$SiO_2 + 2FeO \rightarrow Fe_2SiO_4 \tag{5.1}$$

there is reduction of the molar volume from ca. 48  $cm^3$ /mol to 45  $cm^3$ /mol (ca. -6%). This voids could theoretically be the origin of destructive cracks, but Chapter 4 showed that also for stacks tested longer than two years, the fractures in the interconnect are located in region 4, where there is an important accumulation of amorphous silica. Thermal stresses could therefore be the cause for these voids. From the electrical conductivity point of view, the transformation would be positive, at 1000 K the electrical conductivity of fayalite being  $10^{-1.22}$  (table 5.3). However, considering the small quantity of fayalite produced, its impact on stack ohmic losses would be negligible.

# 5.4 Conclusions

This chapter aimed at better understanding the enhanced corrosion process at the MIC/cathode interface and to confirm some hypotheses from Chapter 4.

- The interaction of strontium with the interconnect is confirmed. *SrCrO*<sub>4</sub> and (likely) *SrNb*<sub>2</sub>*O*<sub>7</sub> are products of the reaction with species coming from the steel substrate;
- According to DFT simulations, the diffusion of strontium from the perovskite towards the MIC rather occurs via the gas phase because diffusion through the solid phase would be energetically unfavourable.

- Following the failure of the Cr<sub>2</sub>O<sub>3</sub> protective layer at the MIC/coating interface, heterogenous corrosion products form between the steel substrate and the protective coating: FeCr<sub>2</sub>O<sub>4</sub>, Cr<sub>2</sub>MnO<sub>4</sub>, MnFe<sub>1.5</sub>Cr<sub>0.5</sub>O<sub>4</sub> and Fe<sub>2</sub>SiO<sub>4</sub> are compounds that could be identified matching EDS information with the TEM selected area diffraction images;
- These compounds have different electrical conductivities; to model efficiently the ohmic losses of this type of MIC a 3D reconstruction of the connecting network of these phases would be needed;
- In case of Cr depletion, FeO is formed and could react with SiO<sub>2</sub> to fayalite. The different densities of the two phases create voids. From what is observed in the lamella, these voids did not initiate any mechanical failure.

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# 6 Degradation in Balance Of Plant (BoP) Components

For a successful (SOFC) power generator unit, an efficient stack is a necessary but not sufficient condition. All auxiliary systems - the balance of plant (BoP) contribute to the correct operation of the device integrating the heat, generating the steam, reforming the natural gas, etc. This chapter is dedicated in particular to potential issues with the steam generator.

# 6.1 Introduction

The stack is the core of the SOFC power system, but it needs a complex auxiliary system to deliver heat and power. For instance, the ceramic materials the cell is made of are sensible to thermal shock, hence a heating unit must heat the gases before they reach the stack. In case the fuel is methane, it must undergo steam reforming; therefore a steam generator is needed. The waste heat recovery system recycles the heat of the exhaust gases to improve the overall efficiency of the device. The ensemble of all these components is usually called balance of plant (BoP) and considering a commercial SOFC power generation unit, it is at least as voluminous as the stack.

Despite its role and dimension, relatively less interest has commonly been given to BoP components in research, compared to the stack. The presence of long-studied and well established materials such as Inconel  $600^{TM}$  or AISI 316L has probably shifted academic interest towards research on ceramic materials, i.e. towards the cell. Yet, failures in the BoP (and in the electronic system as well) can also cause more than once the shut-down of commercial SOFC systems, while the stack was still able to operate. This could mean that the operating conditions deviate these alloys from the expected behaviour based on existing literature. As a result, understanding the corrosion of BoP alloys is also necessary to assure the system lifetime reliability. The present chapter analyses the causes for the failure of steam generators operated

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in commercial SOFC systems and discusses some possible solutions to extend their lifetime.

In the steam generator (SG), liquid water is forced through thin channels, smaller than 1 mm, placed in between two thin refractory alloy plates. The SG can be thought as a metal rectangular parallelepiped with the height much smaller than the width and the depth (Figure 6.2). The precise dimensions are proprietary information of the supplier company. A hot flow of CO<sub>2</sub> (2.2 % vol.), nitrogen (73.7 % vol.), steam (8.6 % vol.) and  $O_2$  (15.5 % vol.) laps the two external sides of the SG at 2 atm. pressure, while water/steam counterflows in the inside. The two walls of the steam generator are therefore exposed to a dual atmosphere. The heat exchanger (HE) is a sequence of thin corrugated alloy sheets separated by flat metal sheets. The heat of the exhaust gas, both air and fuel, coming from the burner, placed after the stack outlet, is recycled as latent heat for the water evaporation. The precise heat profile inside the two systems is not measured. A simplified model (internal communication) based on heat and mass balance provides temperature profiles of the alloy in between the considered flows. For example, the trend named water/exhaust gas wall is the temperature inside the metal plate separating the water and the exhausted gas streams (Figure 6.1). On the x axis the distance is normalized on the SG length, at the very left is the inlet of the water and as soon as it enters the steam generator, the temperature dramatically rises. A reasonable estimation (Figure 6.1) is that at least 1/3 of the separator plate surface, starting from the water inlet, is below 400°C.

The evaporation takes place along the x direction before the water reaches half of the path on the x-axis. The biggest thermal gradient in the SG is therefore on this axis. Even if it is not visible in Figure 6.1, the water stream enters the SG at room temperature and leaves it hotter than 800°C.

The steam generator and the heat exchange unit are both made of Inconel  $600^{TM}$ , a refractory Ni-Cr:72-15 alloy whose precise composition is given in Chapter 2 Table 2.2. Hereafter, the merging of SG and heat exchanger (HE) will be called hotbop. In this discussion, two hotbops - hotbop #1 and hotbop #2 have been analysed. The former has no surface protective treatment and underwent 15960 hours of operation before failure. Three more hotbops of the same type of #1 also had problems with the steam generator, demonstrating a structural failure. The second hotbop instead had received an aluminizing treatment on the external wall of the steam generator; it experienced thermal cycles during an overall operation time of 18000 h.

To obtain samples for SEM/EDS analysis, electroerosion was used (cf. Chapter 2). The obtained samples refer to the alloy in between the exhaust gas stream and the water flow.

Infiltrations of surfactant containing solution revealed cracks passing through the steam generator wall. When present, these cracks are visible already with the optical microscope. To find out the degradation process, the samples were first observed from the top with SEM and later embedded in epoxy resin, cross-sectioned and polished down to 1  $\mu m$  grid diamond paste. Cross sections are studied through



Figure 6.1 – Temperature profile for three interface walls of the heat exchanger obtained through a simulation. Each trend represents the temperature in the middle of the alloy wall that is exposed to the double atmosphere indicated by the legend.



Figure 6.2 – Simplified and partial drawing of the steam generator/heat exchanger block





Figure 6.3 – Images of the steam generator from the heat exchanger side. (a) hotbop #1, (b) hotbop #2. The tube brings water to the steam generator but is not part of the heat exchanger



Figure 6.4 – Crack details on the separator plate of the steam generator (a) backscattered electrons mode, note the white area presenting the Ni-rich alloy substrate (b) SE mode, note the detaching scale

SEM/EDS as well. Figure 6.3 shows the external sides of the SG seen from the top. For both the hotbops, there are a dark and a bright area, hereinafter named black and grey surface. The red squares in the same figure indicate region regions where steam leaked.

# 6.2 Results

### 6.2.1 hotbop #1

Figure 6.4 presents a detail of the cracks present at point 2 in Figure 6.3 (a). The backscattered electrons image, Figure 6.4 (a) provides information about the element composition of the scale, bright zones represent heavier elements. The EDS element map (Figure 6.5) shows in fact that the white region of Figure 6.4 (a) is mainly containing nickel, whereas the darker areas of the oxide layer are predominant in chromium. A higher presence of iron and less of nickel is found close to the crack.

Silicon and manganese are homogenously distributed.

In some regions the scale detached from the metal substrate. In other areas there was delamination but no spallation, while on the rest of the surface an heterogeneous oxide layer is present.

The crack profile is not straight, the observations suggest it follows the material grain boundaries. The grain boundaries of the Inconel alloy are also well visible in the region where the oxide layer delaminated (bright area in Figure 6.4 (a)). Carbon debris are responsible for the black stains in the lower part of the channel. Note that this is only a portion of the crack, the full extension is ca. 5 mm.

The fins hindered partially the electron signal and the EDS analysis (Figure 6.5), causing the black belt at the bottom of each image; however, this is not affecting the results validity.

Figure 6.6 and Figure 6.7 show a second region of the same crack, the surface chemical analysis indicates a decrease in chromium content close to the crack. EDS analysis reported peaks from other elements (Al, Mo, S, Si), but without local enrichments of these elements.

In Figure 6.6 (b), the more intense green spots are chromium precipitates, while the black zones are carbon residuals. The other main elements in the steel are reported quantitatively in Table 6.1. The element concentration changes in proximity of the crack. It is confirmed that region 1, of Figure 6.6 (a), is poorer in chromium than in region 2, in addition SE mode image (Figure A.12) indicates a delamination process.

Figure 6.7 and Figure 6.8 provide the quantitative composition both in at% and wt% of the depletion profile around the cracks. The EDS linescan is indicated by the black arrow in Figure 6.6. From the surroundings to the centre of the crack, the nickel concentration decreases from 60 to less than 20 wt.% while iron increases three-fold from 10 to 30 wt.%. The weight percentage is used here to make a comparison with the as-produced chemical composition of the alloy to better understand the species depletion. Finally, on the dark surface, close to the steam generator entrance, nickel rich nodules were found (Figure A.10 in the appendix)

After the superficial analyses were completed, the sample was embedded in resin and finally cross-sectioned normally to the crack, zone number 2 in Figure 6.3 (a). The cross section does not represent the complete steam generator as the electro erosion cut it in two parts along the horizontal plane.

Table 6.1 – Element composition of the zone highlighted in green in Figure 6.6. Values in at.%

Zone	0	Ni	Cr	Fe	Мn	Si
1	47.4	19.9	8.8	19.2	<0.5	0.9
2	25	46.8	17.9	6.6	<0.5	1.1

In Figure 6.9 (a), the crack propagates from the external wall of the SG (the region observed so far) towards the water/steam flow channels. It does not follow a single



Figure 6.5 – EDS qualitative element map of the region of interest in Figure 6.4



Figure 6.6 - Electron backscattered image of a region of interest on the external wall of the steam generator. A crack is present and highlighted with white arrows. Green polygons indicate the region the chemical composition of which is given in Table 6.1



Figure 6.7 – EDS quantitative maps of region in Figure 6.6.



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Figure 6.8 – Linescan across the region indicated with the rectangle number 1 in Figure 6.6. Values are in wt. % .

direction, multiple cracks propagate in the center of the section, but the extreme one is at the top-left corner of the water channel.

The white shining regions are caused by electrostatic charges accumulated on regions filled with the non conductive epoxy resin, while the black and blurred halos on the surface are due to the carbon coating.

On top of the steel plate is a thick irregular scale layer of 8  $\mu m$  average, with peaks of 16  $\mu m$ . This layer resembles a multiple staged sedimentation. Figure 6.11 qualitatively displays the element distribution in this area. The quantitative analysis is given in the Appendix (Figure A.7) and the higher chromium and silicon content in the external part of the scale is appreciable. Chromium is present at 16 at.% on top of the scale and at 10 at.% inside the crack. Silicon and sulfur on the other hand are more present in the oxide grown inside the crack. The oxide on the surface and in proximity of the crack presents a different composition than the oxide commonly found in the black region: a bulk chromium oxide phase with a blurred irregular surface. The oxide on the grey surface is instead a double layer: an inner silicon oxide is followed by a thin chromium oxide. The blurred and flakes-like morphology of the surfaces of these two layers is similar (Figure 6.10). Regions with inward corrosion are also found during the investigation of this cross section. The oxides are thin and penetrating underneath the surface for some tens of microns, following a grain boundary. Their small dimension does not allow a reliable quantification through EDS, but the main constituent is chromium.



Figure 6.9 – (a) Cross section of the steam generator presenting the steam flow channel and the surface exposed to the heat exchanger (b) a detail (a crack) of this cross section after the etching

A quantitative linescan analysis across the oxide layer (Figure 6.8) revealed accumulation of iron cations at the two alloy/oxide interfaces inside the fracture. The weight percentage rises from 9% in the bulk of the alloy to 20% nearby the crack, or from 6 to 10 in at.%. The concomitant presence of oxygen indicates that this is an iron oxide.

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Figure 6.10 – Hotbop #1. (a) black surface (b) grey surface



Figure 6.11 – Beginning of the crack from the side exposed to the heat exchanger. The element quantification is in the table in the AppendixA.7


Figure 6.12 – Quantitative EDS linescan performed over the region indicated with a green arrow in Figure 6.11. Weight percentage

The scale composition in the left top corner (shown in Figure 6.9) of the steam flow channel is almost pure nickel oxide with few traces of chromium. The bulk alloy in this case has homogenous Cr, Fe and Ni distribution also close to the corroded region. Notably, the composition is close to nominal (wt.%): 73 Ni, 16 Cr, 9 Fe, 1.3 Si, 0.5 Ti+Nb, 0.5 Mn. The only exceptions are some Ti-Nb containing precipitates located close to the cracks.

Moving towards the channels where the water is evaporated, the scale grown on top of the SG channels has an inner layer made of Si and Ni in 1:1 ratio, opened and closed by a thinner NiO layer (Figure 6.13). The rounded corrosion region has the same composition but there is no a central NiO layer. Chromium is not detected. As said, the steam generator is composed of multiple water/steam flow channels; the observations of a dozen of them revealed big differences in the scale thickness from one channel to the other.

In order to better identify the precipitates grown in the alloy, etching was applied on the cross sectioned region containing the crack (Figure 6.9b). A solution of CuCl, HCl and ethanol (Kalling's reagent) was used. The surface was exposed to the acid for 10 seconds and subsequently rinsed with distilled water. The acid attack confirmed that the oxide mentioned before developed between two alloy grains. Globally, bigger precipitates appear at the grain boundaries and smaller whiskers distributing inside the grain. The dimensions of these particles are too small for a precise identification with EDS. The etching revealed also that, in the core of the





Figure 6.13 – Details of the scale grown in one of the steam generator flow channels

material, the fracture propagated inside the alloy grains. In Figure 6.9 (b) in fact the crack does not follow the grain boundary.

### 6.2.2 Hotbop #2

The detailed description of the hotbop #1 was motivated by the failure of the component, while hotbop #2 had no leakages. The two main differences with respect to hotbop #1 are: the steam generator geometry and an aluminizing process on the SG external surfaces.

As for hotbop #1, the steam generator external surfaces are two main areas, a dark one (referred to as black) and a bright one (referred to as grey) (Figure 6.4 (b)). The line dividing the two regions is not straight, but follows the parabolic profile of a laminar flow.

The effects of the aluminizing process are instead visible only with a cross section: in the first 15  $\mu m$  underneath the alloy surface (Figure 6.14) as the dark grey belt.

The cross section of this steam generator indicated again two different scale layers in terms of morphology and composition. Figure 6.14 (a) shows that the black surface in Figure 6.3 (b) is a mixture of bigger particles randomly deposited on the substrate and surrounded by a porous film that covers the whole surface. Upon a closer look this porous, fluffy-looking phase, is a disordered network of thin whiskers. The cross section of the bright surface shows a similar morphology but with a less pronounced flakes structure and no dark debris. The different magnification between the two images are necessary because the oxide on the dark surface is one order of magnitude thicker than that on the bright surface.



Figure 6.14 – Hotbop #2. (a) dark surface (b) bright surface. See Figure 6.4 (b)

EDS surface analysis revealed that the black surface is mainly composed of chromium oxide while on the grey surface the main elements detected are O, Si, Ni, Fe and Cr. However the analysis on the grey surface was influenced by the alloy substrate. The EDS surface analysis of hotbop #2 is reported in the Appendix (Figure A.8).

The chemical analysis identified the particles on the black surface as pure aluminium

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oxide while the surrounding film is a mixture of chromium and silicon oxide, with chromium by far as main element. The silicon oxide signal is more intense on the alumina debris and on the alloy surface (Figure A.9). The average scale thickness for the whole oxide layer on the alloy is about 5  $\mu m$ .



Figure 6.15 – Schematic representation of the different oxides grown on the two analysed surfaces. Concentrations are given in at.%

The quantitative profile in the first  $\mu m$  underneath the surface reveals a constant chromium concentration around 10 wt.%. The tabulated original concentration in the Inconel alloy is between 14-17 wt.%. The oxide grown on the grey section of the steam generator wall is thinner (ca. 2  $\mu m$ ) and composed mainly of silicon oxide. The dark gray spots in Figure 6.14 (b) are iron accumulation (Figure A.11). After the etching process, it is possible to observe thin scale protrusion growing from the alloy surface towards the inside (Figure 6.9 (b)) The enhanced inward corrosion detected in hotbop #1, with thin chromium oxides growing inside the alloy, inward growing of oxides is not observed on the surface of the hotbop #2. Small segregates inside the grains and longer ones along the grain boundaries are instead confirmed.

On the face exposed to the water/steam flow channel, the oxide is composed of nickel and silicon. While for the hotbop #1 the scale is clearly made of three different regions (Figure 6.13), in the hotbop #2 the ratio between nickel and silicon has no precise distribution. The scale thickness varied considerably from one flow channel to the other without any apparent relation to the chromia deposits observed at the fins side.

Figure 6.15 summarizes the information provided so far for the face of the two hotbops exposed to the heat exchanger side and the relative black and grey surfaces.

The extended region with the texture represents the dark surface, the big black dots on top of it are the Ni oxide-rich nodules, finally the light grey is silicon oxide covering the alloy substrate (represented in white). On schematization of hotbop #2 in Figure 6.15, the light grey debris are missing because they have not been observed.



Figure 6.16 – Oxide layer present inside one water/steam flow channel in the hotbop #2. (a) is the EBS SEM image (b) is the quantitative map for silicon (c) is the quantitative map for nickel. The quantities are expressed in wt.i% percentage.

# 6.3 Discussion

### 6.3.1 Oxide layer

The results section presented a complex aging history of the steam generator. There are multiple areas, differing by exposure conditions and corrosion products. The separator plate of the steam generator oriented towards the heat exchanger was exposed to a gas stream reaching temperatures up to 850°C. At the same time, during its flowing along the separator wall, the temperature undergoes a negative gradient because of the heat exchange with the cooling water on the other side of the plate. As a result, species with low vapor pressure can condensate.

The distribution of the black and grey region on the steam generator separator plate replicates a gas flow profile. The following observations suggest that a condensation process deposited the species creating the black surface: I) the two darkest regions are at the top and bottom extremes of the dark surface on the separator plate (Figure 6.3 hotbop #2) where the temperature gradients are highest. II) the shapes of the dark phases between hotbop #1 and #2.

Studies on the thermodynamic stability of  $Cr_2O_3$  and its vapours in high temperature and humid atmosphere assessed that  $CrO_2(OH)_2$  is likely to form and that starting from 400°C the condensation of the chromium hydroxide is possible [174]. The EDS analysis of the surfaces of hotbop #1 and hotbop #2 confirmed that there is a different composition between the grey and the black phase, but there is as well a difference between the regions of the same colour in the two hotbops.

The aluminization process causes the main difference between the hotbops: there is

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no chromium oxide growth on the bright surface of hotbop #2 but an accumulation of silicon oxide, <1  $\mu$ m thick. On the dark surface as well, the chromium oxide on top of the Inconel 600<sup>TM</sup> has a blurred texture, suggesting again a condensation process. Similarly, the alumina particles embedded in this oxide layer (cf. Figure 6.14) are deposits.

Inconel 600<sup>TM</sup> and related alloys have a strong niche in the research field because of their use in pressurised water steam generators for nuclear power plants [175– 178]. The operation conditions of these steam generators are different from those in this chapter: temperature between 350-400°C, high pressure and tubular geometry. There are only few tests performed at temperature >700°C and the information obtained from these case studies can be used only partially.

Tests performed at temperatures higher than 700°C and in humid atmosphere showed that the main corrosion products are  $Cr_2O_3$  and NiO in the initial phases (<500 hours) and NiO and  $NiFe_2O_4$  for longer exposure [175][179]. Notably, the iron nickel oxide is a consequence of the failure of the chromia passivation. These corrosion products are consistent with what is found on hotbop #1, especially the compounds found on the black surface.

Recalling Figure 6.15, the black surface in the hotbop #1 is mainly covered with chromium oxide. Figure 6.10 displays its bulk morphology, therefore it is a corrosion product of the alloys but at the same time the top is blurred and suggests a contribution of a condensation process as well.

Gas and steam streams are in counter-flow configuration, hence the water inlet matches also with the coolest segment of the external wall of the heat exchanger. This region is also where the nickel rich nodules appeared (Figure A.10). The nodules represent a form of breakaway corrosion. Abe at al. found a similar result for Inconel 600 samples aged for 500 hours in humid atmosphere at 800°C [175].

A mechanical failure of the passivation layer could introduce a crevice corrosion process, also considering the possible condensation of the alkaline species from the gas stream. However, the amount of steam in the flow (8 vol.%) would need a temperature of about 45°C for the condensation to take place. The thermal history of the SG indeed indicates a partial thermal cycles, but the temperature never went below 200°C.

A silicon oxide layer is the main oxide product found on both hotbops. The EDS quantitative analysis found a Si:O ratio of ca. 1:2. Figure 6.17 is a detail of the grey surface of the hotbop #1, the delamination of the oxide is evident. The spallation took place during the cooling of the component as suggested by the low percentage of oxygen in the substrate (white region in Figure 6.15).

The presence of the silica layer is the main difference with respect to the established literature on Inconel alloys used in steam generators. As mentioned before, the expected oxide is  $Cr_2O_3$ . Its absence can be linked to the chromium oxide condensation in the black surface. The steam in the gas flow, together with the high temperature, dissolved it and in the mean time the silicon oxidation process continued until  $SiO_2$  covered the whole surface.

In the result subsection, it has been shown that the scale in the surrounding of



Figure 6.17 – Detail of the oxide grown on the grey surface of hotbop #1

the crack presented differences in thickness and composition with respect to the rest of the dark surface. The accumulation of silicon striations in the EDS image indicates a continuous process of evaporation and solidification: the water coming from the steam generator channel leaked from the fracture and because of the higher temperature evaporates leaving just the dry residue. Since the dry residue is rich in silicon, it can be supposed that the water flowing in the steam generator channel contains elevated percentage of this element (Figure 6.11). The asymmetry in the shape of the final segment of the fracture hints to an erosion process.

### 6.3.2 Stress corrosion cracking (SCC)

For stress corrosion cracking to happen three factors must co-exist: susceptible metal substrates, aggressive environment and stresses.

The gas and the water flowing around and inside the steam generator were not sampled. Their presence and the quantification of contaminants are therefore not known. The EDS analysis constantly indicated peaks of sulphur, chlorine and alkaline elements such as sodium, calcium, potassium on the surface exposed to the gas stream and a significant amount of silicon in the water channel. The exhaust gas passes through and close to various elements, including glass sealing which contains the aforementioned elements.

Also the mechanical or thermal treatment that the material underwent before its operation is not known, for instance if it was solution annealed.

In a parallel with the analysis of the real MICs, in the investigation of real BoP components a most significative difficulty is that the complete history of the materials is not known.

Nevertheless, a history of the phenomena and some hypothesis can still be proposed

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according to other known elements. In his thesis, van Limpt [180] reported that the species containing sodium, sulphur and chlorine have the highest vapour pressure in glasses exposed to high temperature and humid atmosphere. Silicon instead is very stable also at high temperature. The trace elements are found along the whole black surface of the SG, and in higher concentration in the crack (Figure 6.11).

Looking at the position of the cracks, the failure in the steam generator plate took place around the same longitudinal position: in the dark surface close to the brightdark threshold, far from where the nodules are. The crack is supposed to start from the surface exposed to the heat exchanger because the second smaller crack existed without having an interaction with the water flow channel. The distribution of the gas and water streams causes a temperature gradient between the core and the external walls of the SG, the surface wall exposed to the gas tends to expand because it is exposed to higher temperature. This expansion is hindered by the wall exposed to steam, being colder and undergoing less expansion. As a result, the wall at the gas side would be under compression and the wall exposed to steam under tension. This in turn leads to thermal stresses through the wall thickness.

### 6.3.3 Fouling

The other relevant issue for the lifetime of the steam generator is the obstruction of the water/steam channels. Accumulation of material shown in Figure 6.16 was observed in other channels as well, with a different grade of obstruction. Instability of the steam flow was observed in hotbop #2 and in the long run there might induce complete obstruction of the steam generator. The EDS chemical analysis indicated that the deposits are composed of *NiO* and *SiO*<sub>2</sub>, with only few traces of iron oxide.

In the steam generators of nuclear power plants, the fouling of the channel in the SG is a recognized issue [181]. The balance of plant in that case is by far, more complex and bigger than in a SOFC device and different materials interact with the waterflow. As a result, the deposits found in the channel are typically hematite or iron hydroxides. The fast stream of the water in fact dissolves the corrosion product on the SG channel and then deposits them in other regions, for example in bends or where the water evaporates.

Moreover, there are different types of deposits, depending on their hardness. In nuclear power plant fouling, the crud is often a gel while in the SG observed in this chapter the material is hard (it resisted to polishing).

To extend the lifetime of the component, there are a chemical and a mechanical approach [182]. In the first case, the chemicals added to the water stream dissolves the oxides deposited and at the same time hinder the corrosion process inside the channel. This method is preferred because it is cheaper, but it applies to softer deposits than those observed in the water/steam channels of the SOFC BoP. The alternative is to send high pressure fluid through the channel and then to free the water stream from collected debris.

## 6.4 Conclusions

Lacking the complete details of the operating condition of the balance of plant components, the present chapter can not provide a full understanding of the steam generator failure in a SOFC system operated for 2 years. However, it can give useful insights and helps to better understand the behaviour of Inconel in operating conditions rarely encountered in scientific publications. Two systems composed of a planar steam generator welded to a heat exchanger have been compared. The first showed leakage while the second worked fine. The investigation brought the following results:

- The scale grown on the Inconel  $600^{TM}$  alloy, exposed to humid atmosphere and high temperature is mainly an inner  $SiO_2$  layer followed by  $Cr_2O_3$ ;
- Due to the gas flow, the chromia scale grown on the hotter side of the steam generator's external surface evaporates and then condenses in the colder regions of the same surface. This area takes a dark color and is close to the water inlet. Together with chromium oxides, also other species (S, Ca, Na, K) condense;
- The thermal gradient inside the material creates a state of tension which might cause failure of the passivation scale and mechanical stresses. The combination of these two phenomena likely lead to stress corrosion cracking in hotbop #1;
- This fracture originated on the SG surface exposed to the heat exchanger probably after an intergranular attack, as suggested by high sulfur percentage. The sulfur is likely coming from the glass sealing. The presence of multiple cracks indicates at the same time a stress condition.
- In hotbop #2 no fractures were found. This component underwent aluminization which protected the alloy substrate from the aggressive environment. Thinner scale is present on hotbop #2 compared to #1. The two hotbops differ also in a different water channel geometry. The influence of this parameter on the improved performance can not be assessed.
- Fouling of the water/steam flow channels is an issue for both hotbop designs. The clogging material is a hard mixture of silica and nickel oxide. According to the experience of steam generator for nuclear power plants, high pressure spraying of gas would be a possible maintenance method.

# 6.5 Acknowledgment

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# 7 Design of Experiment Approach Applied to Interconnects' Accelerated Testing

In this chapter the design of experiment method was applied to assess the influence of operating conditions (temperature, atmosphere, steam content, etc.) and their combined effects on the experimental results (ASR, chromium depletion). Taking a reference long-term testing condition, the aim is to understand if and how accelerated testing is possible.

## 7.1 Introduction

The diversity of the coating solutions developed in the last 15 years was the main motivation for the benchmark study presented in Chapter 3. That study could cover only a portion of the existing offers and new solutions will continue to appear in the future.

Each time a new product is released, its properties have to be tested to ensure its reliability: in the SOFC field this means ideally testing the interconnects for at least 40000 hours. Testing each new solution for 5 years is not reasonable in terms of costs, instruments and man power.

ASR testing on small coupons is then typically adopted to screen and compare new products. The shortest acceptable testing period for a reliable result is 1000 hours; after 1000 hours, the initial transient interactions between the materials start to stabilize. However, as already introduced in chapter 3, this compromise can only be a screening before the solution is tested in a real stack.

Accelerated test methods are therefore needed for industry and academic laboratories. So far, no successful accelerated test for SOFC materials has been developed.

To correlate the influence of the operating conditions with the degradation behaviour of materials for SOFC metal interconnects a design of experiment (DoE) approach is used.

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DoE was introduced by Sir Robert Fischer in the first quarter of the XXth century. It is a set of statistical rules applied to rationally choose how to organize the variables in a set of experiments and to determine their influence on the physical results. Among the various definitions of DoE, the following is concise and complete [183]: "Design of experiments (DOE) is a systematic, rigorous approach to engineering problem-solving that applies principles and techniques at the data collection stage so as to ensure the generation of valid, defensible, and supportable engineering conclusions. In addition, all of this is carried out under the constraint of a minimal expenditure of engineering runs, time, and money".

The classical way to perform an experiment is to take a set of variables, change one of them in each experiment and then perform the experiences. This approach is called one-factor-at-a-time (OFAT) and has two main limitations: there are no interactions among the variables and its matrix of experiments has exponential growth. On the other hand, in the full factorial and the fractional factorial design the matrix of the experiments can be built taking into consideration the interaction between the variables. For example in the matrix in table 7.2 the value in the last column is the multiplication of the previous three. The fractional factorial design has also the advantage of reducing the number of experiments to get a statistical model to describe the phenomenon.

In addition, the fractional factorial design can reduce the numbers of experiments. For example, considering an experiment with 4 variables with a classical approach where only one factor at a time (OFAT) is changed, 16 experiments would be needed. With a fractional factorial instead only 8 experiments are required.

The statistical analysis between the results and the variables will produce a vector of effects, that quantify how a certain variable affects the behavior of a result.

The effects later undergo the analysis of variance (ANOVA) to determine their statistical reliability, i.e. if the interaction values obtained are not just a random number. Finally, with the screen effects a model (in this chapter linear) is created and compared to the initial measurements from the experiments.

For a rigorous explanation of the DoE approach, see [184, 185].

The design of experiment terminology is adopted. The response (Y) is the manifestation of the observed phenomenon, the output. The factor (X) is the variable that can influence the response, the input. In this study the factors can assume two states, also known as levels; to generalize the discussion the factors are standardized in terms of [-1,1]. For example, if the testing temperatures were 700°C and 800°C (or 850°C), the first term is standardized as -1 and the second as 1.

### 7.2 1<sup>st</sup> Set of Experiments

### 7.2.1 Experimental procedure

The ASR tests of this chapter are performed in the same way as described in Chapter 2. Perovskite contact paste has been brushed on one face of eight steel coupons (four 0.2 mm and four 1 mm thick) and then sintered for eight hours at 800°C. This

sintering process is not part of the DoE test matrix. These eight coated coupons were eventually put in contact with other eight uncoated steel pieces. The furnaces used for the experiment are in both cases the TE 10Q SEV model produced by Rohde. Temperature, current density, sample thickness and compression force (indicated in the following as pressure) are the chosen variables, each variable may assume two values. Table 7.1 shows the values of the factors chosen for the experiments.

Factor	Factor number	Unit	Min value	Max value
Temperature	X <sub>1</sub>	°C	700	850
Current density	X2	Acm <sup>-2</sup>	0.4	1
Steel thickness	X <sub>3</sub>	mm	0.2	1
Pressure	X4	bar	4	10

Table 7.1 – Description of the values of the four factors

### 7.2.2 Design of experiment and results

Four factors were chosen to describe the trend evolution of ASR measurements. Since the experiments are time consuming (hundreds of hours) but there are four factors to test, it was decided to adopt a  $2_{IV}^{4-1}$  fractional factorial design, which involves 8 runs instead of 16 [185]. The generator for the fourth column ( $X_4$ ) is  $\pm 1 = X_1 X_2 X_3$ , as it is possible to observe in Table 7.2. Since the variables are assigned to each experiment following a scheme, when the data obtained are treated it is possible to understand the interactions between the variables.

Run	I	<b>X</b> 1	<b>X</b> <sub>2</sub>	<b>X</b> 3	$X_4 = X_1 X_2 X_3$
1	1	-1	-1	-1	-1
2	1	-1	-1	1	1
3	1	-1	1	-1	1
4	1	-1	1	1	-1
5	1	1	-1	-1	1
6	1	1	-1	1	-1
7	1	1	1	-1	-1
7	1	1	1	1	1

Table 7.2 – Matrix of the experiments

In Figure 7.1 are reported the results of experiments after more than 1000 hours. The temperature difference affects dramatically the trend of the curves; in particular, at 700°C the measured resistance increases during time, while at 850°C it decreases reaching a faster steady state value.

In order to analyze the interactions of the four factors over time, an empirical

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Figure 7.1 – Experimental results of the ASR test

model able to fit all the measurements has been used. The fitting curve is an exponential equation (Eq. 7.1), where "y" is the resistance, "t" represents the time and "a", "b" and "c" are three coefficients estimated and listed in the Table 7.3.

$$Y = a - b \cdot e^{-c \cdot t} \tag{7.1}$$

In particular, the coefficient "a" represents the steady state value (when the resistance measured reaches a plateau) and "b" is the pre-exponential factor which varies the sign according to the curve trends (positive at 700°C, negative at 850°C). The third coefficient "c" embodies a time constant. The parameter estimation process was realized with the software gPROMS and results are listed in Table 7.3.

A linear model with interactions has been chosen to understand the relation of each coefficient with the four factors adopted. During the analysis of variance the results of this model are compared with the responses from the experiments. Eq. 7.2 describes the linear model, where " $a_i$ " correspond to the main effects, " $a_{ij}$ " to the interaction effects and "Y" represents the set of the experimental results. Table 7.4 shows the model matrix, which includes the interaction effects. The effects, indicated with the letter a, quantify the relation between the responses and the normalized

	Run	а	b	С
1	0.2mm - 4bar - 0.4A - 700°C	0.2102	0.1261	0.0018
2	1mm - 10bar - 0.4A - 700°C	0.6450	0.5822	0.0006
3	0.2mm - 10bar - 1A - 700°C	0.1862	0.1538	0.0060
4	1mm - 4bar - 1A - 700°C	0.4081	0.4302	0.0033
5	0.2mm - 4bar - 4A - 850°C	0.0619	0.1714	0.0054
6	1mm - 4bar - 4A - 850°C	0.0264	0.0704	0.0039
7	0.2mm - 10bar - 1A - 850°C	0.0218	0.0613	0.0034
8	1mm - 10bar - 1A - 850°C	0.0232	0.046	0.0025

Table 7.3 – Coefficients "a", "b" anc "c" estimation

factors.

$$Y = a_0 + \sum_{i=1}^4 a_i X_i + \sum_{1, i \neq j}^4 a_{ij} X_i X_j$$
(7.2)

Table 7.4 – Matrix of the model

Run	Ι	<b>X</b> 1	<b>X</b> 2	<b>X</b> 3	<b>X</b> 4	$X_{12} = X_{34}$	$X_{13} = X_{24}$	$X_{14} = X_{23}$
1	1	-1	-1	-1	-1	1	1	1
2	1	-1	-1	1	1	1	-1	-1
3	1	-1	1	-1	1	-1	1	1
4	1	-1	1	1	-1	-1	-1	1
5	1	1	-1	-1	1	-1	-1	1
6	1	1	-1	1	-1	-1	1	-1
7	1	1	1	-1	-1	1	-1	-1
8	1	1	1	1	1	1	1	1

Thanks to the orthogonality of the fractional factorial design (Matrix X reported in Table 7.4), the vector of effects (A) can be estimated through Eq. 7.3 where "N" is the number of experiments (equal to 8).

$$A = \frac{1}{N} \cdot X^T \cdot Y \tag{7.3}$$

The sorted absolute values of the effects are reported in Figure 7.2 (a). As first analysis, it is possible to infer that coefficients "a" and "b" are linked because the main influence factors are the same, and in particular, the effect related to temperature is the most relevant. Similarly also the thickness has a big impact, as well as the interaction with temperature. Current and pressure do not appear as the most relevant factors. In addition, coefficient "c" does not present a clear





Figure 7.2 – (a) Sorted effects (b) Relative effects (c) Normal plot (d) DoE Model vs. experiment data

predominance of the effect of a single factor. Figure 7.2 (b) represents the relative effects, calculated as  $a_i/a_0$ . The same conclusions drawn from Figure 7.2 (a) can be confirmed also in this case.

Figure 7.2 (c) shows the half-normal plots which are useful to determine whether the effects may be assimilated to random effects. The effects are sorted on the x axis while on the y axis are the inverse of the standard cumulative distribution. Intuitively, the closer is a point to the blue line, the higher the probability that they are created by a random process. Concerning coefficients "a" and "b", temperature and thickness (with the interaction  $a_{13}$ ) are the effects that do not follow the normal distribution. Moreover, the majority of the effects related to coefficient "c" cannot be clearly distinguished from the experimental noise.

The second step of the investigation concerns the Anova analysis and the selection

of the linear model parameters that better fit the experimental results, to infer a more precise evaluation of the most important effects. Coefficients "a" and "b" present high values of relative effects, which does not allow to select any of them, since they are approximately higher than 10% (arbitrary threshold value, **P** in Table 7.5). For this reason, the ANOVA table and model are not reported because there is no clear evidence of predominance for one effect over the others. On the contrary, for coefficient "c" the effects  $a_4$ ,  $a_{13}=a_{24}$ ,  $a_{14}=a_{23}$  can be neglected. The ANOVA results (Table 7.5) show that the effects  $a_1$  and  $a_2$  exceed the imposed limit (more than 10% of the chance to arise from random processes). In the first column, the effects that are still considered after the screening with the relative effects distribution and the normal plot, plus the error, named residual are presented. The measured response can be approximated by the linear model of Eq. 7.4 and the difference between the real response and the one calculated with the model is the residual.

SS stands for "sum of square" (the effects are squared to avoid negative values); DF means degree of freedom; MS is the mean square and is rthe sum of squares normalized over the degree of freedom; F is the distribution of Fisher and P is its representation in probability percentage. The larger is P the higher the probability that this effect is random.

SS	DF	MS	F	Р
$9.02 * 10^{-5}$	1	0.0000902	273.9	0.04%
$1.5 * 10^{-6}$	1	0.0000015	4.5	12.34%
$1.6 * 10^{-6}$	1	0.0000016	4.8	11.73%
$5.1 * 10^{-6}$	1	0.0000051	15.4	2.95%
$1.32 * 10^{-5}$	1	0.0000132	40.2	0.79%
$1 * 10^{-6}$	3	0.000003		
$1 * 10^{-4}$	8			
	<b>SS</b> 9.02 * 10 <sup>-5</sup> 1.5 * 10 <sup>-6</sup> 1.6 * 10 <sup>-6</sup> 5.1 * 10 <sup>-6</sup> 1.32 * 10 <sup>-5</sup> 1 * 10 <sup>-6</sup> 1 * 10 <sup>-4</sup>	SSDF $9.02 * 10^{-5}$ 1 $1.5 * 10^{-6}$ 1 $1.6 * 10^{-6}$ 1 $5.1 * 10^{-6}$ 1 $1.32 * 10^{-5}$ 1 $1 * 10^{-6}$ 3 $1 * 10^{-4}$ 8	SS         DF         MS           9.02 * 10 <sup>-5</sup> 1         0.0000902           1.5 * 10 <sup>-6</sup> 1         0.000015           1.6 * 10 <sup>-6</sup> 1         0.0000051           5.1 * 10 <sup>-6</sup> 1         0.0000132           1.32 * 10 <sup>-6</sup> 1         0.0000033           1 * 10 <sup>-6</sup> 3         0.0000033	SS         DF         MS         F           9.02 * 10 <sup>-5</sup> 1         0.0000902         273.9           1.5 * 10 <sup>-6</sup> 1         0.0000015         4.5           1.6 * 10 <sup>-6</sup> 1         0.0000016         4.8           5.1 * 10 <sup>-6</sup> 1         0.0000051         15.4           1.32 * 10 <sup>-5</sup> 1         0.0000132         40.2           1 * 10 <sup>-6</sup> 3         0.0000033

Table 7.5 – ANOVA analysis for coefficient "c"

Therefore, the proposed model, able to reproduce the influence of the factors to coefficient c, is reported with Eq. 7.4 and in Figure 7.2 (d).

$$Y = a_0 + a_3 X_3 + a_{12} X_1 X_2 \tag{7.4}$$

The model reproduces the results fairly well ( $R_i^2 = 96.45\%$ ) but some differences can be appreciated. Therefore, the thickness seems to be the main factor that has an impact on the coefficient "c". In general, also temperature seems to have an important role, as well as the interactions with the other factors mostly for coefficients "a" and "b".

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#### Analysis of time derivative

The investigations realized up to now have not clarified the relations between the chosen four factors and the three coefficients that fit the experimental result. For this reason, a further study was conducted in order to understand the relation between the four factors and the time constants, i.e. when the trend curve approaches the extinction of the transient. Two different values arbitrarily chosen were used, as reported in Eq. 7.5 and Eq.7.6.

$$\frac{\Delta\rho}{h} \left[\frac{ohmcm^2}{h}\right] < 10^{-4} \tag{7.5}$$

$$E_r = \frac{E_A}{x_m} = \frac{\rho(t) - \rho(t+1)}{\left[\frac{\rho(t) + \rho(t+1)}{2}\right]} < 2 \cdot 10^{-5}$$
(7.6)

The first one concerns the calculation of the moment when the variation of the measured resistance after one hour is lower than an arbitrary value  $10^{-4}$ . The second one is based on the relative error, calculated as the ratio of the absolute error ( $E_a$ ) and the mean value ( $x_m$ ). The absolute value in turn is calculated as the variation of the ASR between two successive time intervals. In this case, the transient is extinguished when the error is lower than the arbitrary tolerance fixed at  $2 * 10^{-5}$ . Both calculations are based on the equation and the related coefficients previously described (that vary for each run). Figures 7.3 (a), 7.3 (b), 7.3 (c) and 7.3 (d) show graphically this procedure and, in particular, the violet line indicates the time when the imposed tolerances are met. The values of the obtained time constant are listed in Table 7.6.

	Run	time [h] @ $\triangle \rho$ /h [ $ohm * cm^2$ ] < 1 $e^{-4}$	time [h] @ <i>E<sub>r</sub></i> < 2 <i>e</i> <sup>-5</sup>
1	0.2mm - 4bar - 0.4A - 700°C	188.4	668.4
2	1mm - 10bar - 0.4A - 700°C	1256.7	1333.5
3	0.2mm - 10bar - 1A - 700°C	284.7	428.9
4	1mm - 4bar - 1A - 700°C	651.3	686.9
5	0.2mm - 10bar - 0.4A - 850°C	412	656.3
6	1mm - 4bar - 0.4A - 850°C	259	812.3
7	0.2mm - 4bar - 1A - 850°C	216.7	892.8
8	1mm - 10bar - 1A - 850°C	51.8	942.5

Table 7.6 – Results of the transient analysis

Similarly to what has been done in the former part of the analysis, the effects, the relative effects and the normal plot, were calculated (Figure 7.4 (a), Figure 7.4 (b) and Figure 7.4 (c)).

In the first case, all the effects and relative effects have a relevant role (apart for the interaction  $a_{12} = a_{34}$ ): it is not possible to distinguish a major contribution. Even in the normal plot the effects seem distributed along the same line, suggesting that the results are affected by experimental noise. On the other hand, time constants calculated with the relative error exhibit a better diversification on the effects. Figure



Figure 7.3 – Graphs representing the relation between the four factors and the time constants, i.e. when the ASR curve approaches the extinction of the transient.(a) $\frac{\rho}{h}$  calculations (b)  $\frac{\rho}{h}$  calculations(c)  $E_r$  calculations (d)  $E_r$  calculations





Figure 7.4 – (a) Effects sorted (b) Normal plot (c) Relative effects (d) Model vs experimental results for  $E_r$ 

7.4 (a) displays that thickness and its interaction with pressure  $(a_{12} = a_{34})$  are the dominant factors. The normal plot confirms that thickness does not follow the normal distribution, but it is not fully evident for the other effects. For this reason, an ANOVA analysis was performed for the " $E_r$ " case (Table 7.7). In particular, the effects  $a_1$ ,  $a_2$  and the interaction  $a_{14} = a_{23}$  were neglected for the same reason as explained in the previous paragraph.

Source	SS	DF	MS	F	Р
<i>a</i> <sub>0</sub>	5154618	1	5154618	250.5	0.01%
<i>a</i> <sub>1</sub>	59302	1	159302	7.7	4.96%
a <sub>12</sub>	196188	1	196188	9.5	3.66%
a <sub>13</sub>	64333	1	64333	3.1	15.17%
Residual	82303	3	20576		
Total	5656744	8			

Table 7.7 – ANOVA analysis for  $E_r$  case

From the ANOVA table results it is possible to eliminate the interaction  $a_{13}$ , whereas the contribution of pressure and interaction  $a_{12}$  remain in the confidence interval. Then, the model can be expressed with Eq. 7.7, which is the same obtained for coefficient "c" (Eq. 7.4).

$$Y = a_0 + a_3 X_3 + a_{12} X_1 X_2 \tag{7.7}$$

Experimental data and the results of the model are compared in Figure 7.4 (d). Also in this case the model reasonably reproduces the experimental results ( $R^2 = 98.54\%$ ). In general, the calculation of relative effects seems to be the best way to describe the stabilization of the resistance evolution during time. As for coefficient "c", thickness is the most relevant factor that directly affects the data.

#### **Final Considerations**

The activation of the material degradation is mainly influenced by the temperature and its thickness, but the other two factors (current and pressure) and all mutual interactions cannot be neglected. Although an exponential function with a time constant adequately represented the experimentally obtained results, the chosen fractional factorial method was found to be inconclusive. This unfortunate situation leads to three possible solutions: a) check if the measurements error influenced the experiment b) choose few points in the middle of the factors space and a second degree model c) replicate the eight experiments with a mirror strategy d) the factors chosen were not the most influencing.

Regarding the first hypothesis it is hard to believe that error measurements could have an important role: a highly precise 1 Ohm reference resistance (0.1% error) was inserted in series with the circuit, therefore it was possible to check precisely that the current passing through the sample was correct. The point b is interesting because it

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could de-aliased the results with less consumption of material; nevertheless, it is not the best choice because from the relative effects it was not possible to determine which factor is mostly influencing the system. Measuring, for example, new points in the middle of the temperature or pressure ranges would be like a bet. The third solution (c) is more reasonable: a new set of experiments might be performed with a mirror test matrix with respect to the one in Table 7.3. In this way, the advantages due to the fractional factorial design would be lost but, the factors will be de-aliased more precisely. The fourth solution (d), which is the one finally adopted, focuses the effort of the new round of experiment on introducing different variables that might be more impacting on the degradation process of the material.

# 7.3 2<sup>nd</sup> Set of Experiments

### 7.3.1 Experimental procedure

As in the first set of experiments, the samples are made of AISI441/K41 substrate, but in this case they are coated with a wet powder spray deposited  $MnCo_2O_4$  coating. In addition, the samples have a corrugated geometry, like in a real interconnect. The reason is to overcome the limitation of the flat design where no gas flows between the sandwiched samples.

A full factorial design is used in this set of experiments, where the factors are three: temperature, gas atmosphere and humidity. The temperature is chosen because of the influence on the diffusion process, the steam because it is supposed to boost the evaporation of the thermally grown oxide film, and a reducing atmosphere because it might accelerate the coating densification process. Each factor presents two levels, therefore there are 8 experiments ( $N = 2^3$ ). With respect to the  $1^{st}$  DoE attempt, the introduction of the steam and  $H_2/Air$  as factors was possible thanks to the set-up described in Chapter 2 (Figure 2.4): the independent ceramic boxes allow to simultaneously expose the samples to different gas atmospheres at the same temperature. The testing time in this case was 1500 hours.

Each pair of samples was sandwiched with the coated surfaces facing each other. To simulate the cathode and provide electrical conductivity, a LSC layer was applied in between the samples. As for all the other ASR tests on small samples described in this thesis, an electrical current was provided through two gold meshes touching the uncoated side of the samples. Similarly to the first set of experiments, the ASR curves should have been the responses. Contact issues in some samples challenged the measurments.

As a consequence, the response considered for this study was the amount of chromium (in wt.%) in the steel below the oxide layer. This value is calculated taking the average of three values of chromium weight percentage in the metal substrate adjacent to the oxide layer. Both corrosion and cathode poisoning are caused by chromium migration from the steel substrate, the differences in the depletion curves among the samples could therefore represent the degradation process.

Table 7.8 provides the level of the factors and Table 7.9 the matrix of experiments.

Factor	Factor number	Unit	Min value	Max value
Temperature	X <sub>1</sub>	°C	700	800
Gas atmosphere	X <sub>2</sub>	-	Air	H <sub>2</sub>
Humidity	X <sub>3</sub>	Vol. %	0	10

Table 7.8 – Description of the values of the three factors

Table 7.9 - N	Matrix of the	e experiments
---------------	---------------	---------------

Run		<b>X</b> 1	<b>X</b> 2	<b>X</b> 3
1	1	-1	-1	-1
2	1	-1	-1	1
3	1	-1	1	-1
4	1	-1	1	1
5	1	1	-1	-1
6	1	1	-1	1
7	1	1	1	-1
8	1	1	1	1

This matrix of the model corresponds to a linear model with interactions:

$$Y = a_0 + \sum_{i=1}^{3} a_i X_i + \sum_{i=1}^{2} \sum_{j=i+1}^{3} a_{ij} X_i X_j + a_{123} X_1 X_2 X_3$$
(7.8)

Run	<b>X</b> 0	<b>X</b> 1	<b>X</b> 2	<b>X</b> 3	<i>X</i> <sub>1</sub> <i>X</i> <sub>2</sub>	<i>X</i> <sub>1</sub> <i>X</i> <sub>3</sub>	<b>X</b> <sub>2</sub> <b>X</b> <sub>3</sub>	$X_1X_2X_3$
1	1	-1	-1	-1	1	1	1	-1
2	1	-1	-1	1	1	-1	-1	1
3	1	-1	1	-1	-1	1	-1	1
4	1	-1	1	1	-1	-1	1	-1
5	1	1	-1	-1	-1	-1	1	1
6	1	1	-1	1	-1	1	-1	-1
7	1	1	1	-1	1	-1	-1	-1
8	1	1	1	1	1	1	1	1

Table 7.10 – Matrix of the model

The sorted coefficients and the relative half effects (Figure 7.5 (a) and (b)) between the coefficient and the mean of the results reveal that the most relevant factors are the temperature and the steam. Notably, their interaction is influencing the mean response more than the temperature alone. On the other hand, the coefficients and the other relative effects do not differ significantly. The threshold of significance of





Figure 7.5 – (a) Sorted effects (b) Relative effects



Figure 7.6 – Half-normal distribution of the effects

the relative effects was arbitrarily set at 5%, only  $a_1$ ,  $a_3$  and  $a_{13}$  satisfy this cut-off.

The half normal plot Figure 7.6 (a) can assess the reliability of the measured effects, with those that are far from the normal distribution (green line) being the most significant. In other words, there is less probability for them to be random effects caused by noise.

According to the results of Figure 7.6,  $a_1$  should not be considered because it could just represent a random measurement. The coefficient  $a_{123}$  could be reconsidered lying far from the normal plot. Two possible models have therefore been taken into consideration:

$$Y = a_0 + a_1 X_1 + a_3 X_3 + a_{13} X_1 X_3 (Model1)$$
(7.9)

Source	SS	DF	MS	F	Р
<i>a</i> <sub>0</sub>	1626.7808	1			
<i>a</i> <sub>1</sub>	4.6208	1	4.6208	2.046684679	22.58 %
<i>a</i> <sub>3</sub>	8.4872	1	8.4872	3.759223989	12.45%
a <sub>13</sub>	7.0688	1	7.0688	3.130974	15.15 %
Residual	9.0308	4	2.2577		

Table 7.11 – Anova of model 1

Table 7.12 – Anova of model 2

Source	SS	DF	MS	F	Р	
<i>a</i> <sub>0</sub>	1626.7808	1				
<i>a</i> <sub>3</sub>	8.4872	1	8.4872	2.630181	18.02%	
a <sub>13</sub>	7.0688	1	7.0688	2.190619	21.3 %	
a <sub>123</sub>	0.7442	1	0.7442	0.230627	65.61 %	
Residual	12.9074	4	3.25685			

following the indication of the half-normal plot, and:

$$Y = a_0 + a_3 X_3 + a_{13} X_1 X_3 + a_{123} X_1 X_2 X_3 (Model2)$$
(7.10)

more oriented towards the results of Figure 7.5. Tables 7.11 and 7.12 report the results of the Anova analysis on the two models. For both models the P values are high, but for Model 2 the effect  $a_{123}$  must be undoubtedly discarded, considering that usually 10 % is a standard threshold.

Model 1 as well presented suspicious values. The comparison of model 1 with the experimental data (Figure 7.6 (b)) shows a good agreement in the 14-15 wt.% region, while the matching for lower values is poor.

The aim of these experiments was to understand if and how certain variables influence the corrosion behaviour of material used for metal interconnects. The statistical analysis of the parameters chosen to represent the corrosion process did not exclude any of the factors but indicates a preeminence of the steam and temperature effect. One of the limits of this analysis is probably linked to the chosen response and its measurement method. It was mentioned in chapter 3 that the detection error for chromium inside the perovskite was set at 1%. This limit is higher than what the EDS detector can measure, but the presence of a large number of elements and notably lanthanum - overlapping with the chromium x-ray signal - suggested this conservative solution. For the linescan inside the steel substrate instead the error limit can be decreased to 0.5%, as the only elements investigated are Cr, Fe, Mn, O, Si and Ti. However, six out of eight measured values of chromium stay in a range of 1.3 wt.%, being at risk of statistical error. Another response could have been

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the scale thickess measurement, but in that case as well the difference between samples could be smaller than the measurement error. Overall, the analysis of the interactions through the statistical approach unfortunately produced no final answer but confirmed the importance of steam in the depletion process of chromium.

# 7.4 Conclusions

To understand how some chosen variables (operating conditions) affect the corrosion behaviour of the materials used as metal interconnects, two rounds of experiments planned according to the design of experiments approach were performed.

In the first set, the variables, or factors, were temperature, sample thickness, compression pressure and current density while the macroscopic output chosen to describe the degradation behavior of the material was the ASR trend.

In the second set of experiments instead the factors were temperature, gas atmosphere (red/ox) and humidity and the response analysed was the chromium quantity in the steel below the thermally grown oxide layer. The sample materials were the same in the two rounds of experiments, while the geometry was different. In addition, the second set of samples was coated with MCO. The main results are:

- The first set of experiments indicate that temperature was the main variable affecting the ASR trends. Overall, the set of experiments demonstrated a limited practical interest.
- The second set of experiments found the presence of steam as the most influencing input, followed by temperature. On the other hand, the reducing or oxidizing environment is less influencing.
- The analysis of variance of this set of data indicated a relevant probability that these inputs are not statistically significant for the response. This result could also mean that the measurements of the response were not precise enough, or that another output (or other factors) should have been selected.
- Even though a precise correlation between input and output was not established, insisting on the presence of steam and temperature in the testing atmosphere could lead to a successful protocol to accelerate the degradation testing for MICs materials.

## 7.5 Acknowledgment

Vaibhav Singh and Giorgio Rinaldi are kindly thanked for their help in the data treatment of the first set of experiments. The fruitful discussion with Dr. Thierry Cornu from SOLIDpower was highly appreciated.

# 8 Conclusions and Future Work

This thesis is the sum of studies on the behaviour of alloy materials in use in SOFC energy conversion devices. Notably, ferritic stainless steels used for the metal interconnects and austenitic nickel-chromium based alloys for the balance of plant steam generator were investigated. The aim was to understand the degradation processes of these materials and their interactions with the surrounding environment inside a SOFC system operated for long durations. The outcome of the research, referring to the materials and the technologies tested, is summarized as follows:

 Results on small ASR test samples (tested for 1000 h) indicated that among steel substrate composition, coating composition and coating deposition technique, the last one is the most important parameter to obtain a protected interconnect with low corrosion rate and low evaporation of chromium. The reason is that dense coatings decrease or limit the interaction of the interconnect with the environment.

The result is industrially relevant in that it supports the substitution of chromiumrich ferritic stainless steels with cheaper variants, such as AISI441/K41.

• Still referring to the results on small ASR test samples, atmospheric plasma spray (APS) and physical vapor deposition (PVD) deliver the most performing coatings, independently of composition. Wet powder spray (WPS) leaves porous coatings, consistently performing worse in the ASR and chromium retention tests.

On the other hand, the former methods are at least ten times more expensive in terms of initial equipments investment (CAPEX) and material wasted during the deposition process (OPEX).

- Atomic layer deposition and dip coating have also been used to deposit, respectively, spinel- and perovskite-based protective coatings. The perovksite coating was low conductive but, if pre-oxidized, can block chromium evaporation. ALD deposited coating instead showed variable ASR trends performances, suffered from chromium evaporation and iron breakaway. In both cases, the modest results did not justify their application on real interconnects
- Real interconnects made of AISI441/K41 and coated through APS, PVD and WPS

were tested in short-stacks up to 10000 hours. The difference between dense and porous coatings over this test duration was less marked than expected from small ASR test samples results. Post-operation SEM/EDS analysis revealed that the WPS coating densified as well after thousands of hours of operation because of the infiltration coming from the steel substrate.

- A prior nitriding process applied to the steel substrates was effective to decrease chromium poisoning of the cathode by MICs coated via WPS. This positive influence is confirmed also for MICs operated in short stacks for 10000 hours.
- The corrosion history of MICs made of the industrially relevant combination of AISI441/K41 substrate coated with WPS MnCo<sub>2</sub>O<sub>4</sub> spinel was reconstructed observing the cross sections of samples from stacks operated for 45, 2700, 4800, 10000 and 18000 hours. At the MIC/cathode interface strong chemical interaction occurs. Strontium from the perovksite material interacts with the interconnect and can either trigger iron breakaway corrosion or massively react with chromium creating a SrCrO<sub>4</sub> layer on the alloy surface. In case of iron breakaway corrosion, the iron that migrated from the steel substrate densifies the coating, slowing down the FSS corrosion. Formation of a dense continous SrCrO<sub>4</sub> interphase may be the ultimate life- and performance-limiting factor in stacks where this process occurs.
- The observed phenomena are active but tend to stabilize within the first 5000 hours of operation. Also from the mechanical point of view, no significative cracks or delamination were found in MICs tested in stacks. There are no indications that these materials will fail for longer periods of operation.
- The corrosion products in the AISI441/K41 steel in case of Fe breakaway corrosion are heterogeneous; often spinels with a mixed stoichiometry are observed. TEM-SAED analysis indicated several likely corrosion species besides Cr<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>: Cr<sub>2</sub>MnO<sub>4</sub>, Co<sub>0.5</sub>Nb<sub>0.5</sub>O<sub>3</sub>, Fe<sub>2</sub>SiO<sub>4</sub>, FeCr<sub>2</sub>O<sub>4</sub>, MnFe<sub>1.5</sub>Cr<sub>0.5</sub>O<sub>4</sub>, SrCrO<sub>4</sub> and SrNb<sub>2</sub>O<sub>7</sub>. The presence of other species is not excluded.
- The same MIC materials were tested in different conditions of air atmospheres, steam content and temperature to understand how these variables could influence the degradation processes. The statistical analysis of variance of the results not yet unequivocally single out one variable over the others.
- Regarding balance of plant materials, the steam generator, made of Inconel600<sup>TM</sup>, is prone to stress corrosion cracking. Condensation of corrosion agents, such as sulfites, might be the cause. A surface treatment like aluminization seems to solve the problem, as a same BoP component with this treatment ran for 16000 hours without problems. On the other hand, obstruction of the steam generator channels is a serious issue risking to block completely the steam flow

Each time a problem is investigated, it is more likely to generate more new questions than answers. The broad approach of this thesis did not focus on one specific aspect. Suggestions for future researches are proposed as follows:

• Investigation of strontium interaction with the metal interconnect. The strontium segregation process is a well known issue, but systematic information on the influence of the sintering process, the gas atmosphere and the interaction with the contacting materials appears to be lacking. Whether the migration of strontium to the interconnect takes place via gas or solid diffusion is still a debatable question.

Finally, strontium reaction with the steel substrate might lead to iron breakaway or  $SrCrO_4$ , the reason behind this difference not being fully clarified.

• The corrosion product inside the inward oxide region following iron breakaway must be identify precisely. Notably, more regions of interest should be analysed by TEM/EDS and TEM-SAED. Once the phases are undoubtedly identified, a 3D reconstruction could define the shortest current paths as each corrosion product has a different resistivity.



# A.0.1 Experimental Benchmarking of SOFC metal interconnect solutions (Results from the SCORED 2.0 project)



Figure A.1 – EIS spectra for Stack B

### Appendix A. Appendix



Figure A.2 – TEM/EDS analysis of nitrided K41



**CROFER 22 H NITRIDED** 

Figure A.3 – TEM/EDS analysis of nitrided Crofer 22 H

### SANERGY HT NITRIDED



Figure A.4 – TEM/EDS analysis of nitrided Sanergy HT

### A.0.2 Degradation of Metals in SOFC Stacks, Part II: Nanolevel Investigation

The following images present indexing of the SAED spectra obtained on the lamella of Figure 5.5. The coloured points are the simulated diffraction spectra, the values are taken from a crystallographic database. The match between the points in the acquired spectra and those simulated tells the probability that the observed grain is the simulated phase.





(a) *Cr*<sub>2</sub>*O*<sub>3</sub>



(b)  $Fe_2CrO_3$ 





Figure A.5 – SAED images indexing



(a) *SiO*<sub>2</sub> amorphous



(b) *Co*<sub>0.5</sub>*Nb*<sub>0.5</sub>*O*<sub>3</sub>



(c) *SrNb*<sub>2</sub>*O*<sub>7</sub>

Figure A.6 – SAED images indexing

A.0.3	Degradation	in the	Balance	<b>Of Plant</b>	(BoP)	Components
-------	-------------	--------	---------	-----------------	-------	------------

2		0	Cr	Fe	Si	Ni	Mn	s
3	1	58.9	16.1	0.3	2.4	20.5	0.2	1.4
4	2	61.6	10	0.6	2.5	22.9	0.2	1.9
and the second sec	3	62.2	11.6	0.9	3.2	19.5	0.1	2.4
**	4	60.2	9.7	0.8	3.1	22.5	0.1	1.4
	5	58	10.7	2.4	3.7	21.5	0.3	2.1
2025 mag 8 dot mode HV WP fame HEW	6	-	15.7	8.9	2.1	70.2	0.5	0.3
				(1	o)			

Figure A.7 – Quantitative analysis of the scale on top and inside the crack in the steam generator



Figure A.8 – Quantitative analysis of the surface of hotbop#2


(a)

Figure A.9 – EDS element mapping of the dark surface on hotbop #2



(a)

Figure A.10 – EDS element mapping of the dark surface on hotbop #1 details of the nodules

# Appendix A. Appendix



(a)

Figure A.11 – EDS element mapping of the bright surface on hotbop #2



Figure A.12 – Detail of the cross section shown by Figure 6.9, after the etching. The cracks do not propagate along the grain boundaries

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# **List of Publications**

# **Book chapter**

M. Bianco, M. Linder, Y. Larring, F. Greco, J. Van herle. Lifetime Issues for Solid Oxide Fuel Cell Interconnects. Solid Oxide Fuel Cell Lifetime and Reliability. Academic Press. 2017.

# **Journal papers**

M. Bianco, J.P Ouweltjes, J. Van herle. Degradation analysis of SOFC interconnects in stacks operated up to 18000 hours. Journal of Applied energy. 2018. under revision.

M. Bianco, J. Tallgren, J.E. Hong, S. Yang, O. Himanen, J. Mikkola, J. Van herle, R. Steinberger-Wilckens. Experimental benchmarking of SOFC metal interconnect solutions. Manuscript close to finalisation.

S. Frangini, A. Masi, L. Della Seta, M. Bianco, and J. Van Herle; Composite  $Cu - LaFeO_3$  Conversion Coatings on a 18Cr Ferritic Stainless Steel for IT-SOFC Interconnects: Effect of Long-Term Air Exposure at 700°C on Cr Diffusion Barrier and Electrical Properties. J. Electrochem. Soc. 165(2). F97-F104. 2018.

# **Conference** papers

M. Bianco, M. Auchlin, S. Diethelm, J. Van herle. Evolution of oxidation of SOFC interconnect alloys in dry and wet air. Proceedings of the XII EFCF. B0513:98-137. 2016.

J. Tallgren, M. Bianco, J. Mikkola, O. Himanen, M. Rautanen, J. Kiviaho, J. Van herle. Comparison of different manganese-cobalt-iron spinel protective coatings for SOFC interconnects. Proceedings of the XII EFCF. B0619:114-124. 2016.

S. Pandiyan, M. Bianco, R. Tomov, M. Gálvez Sánchez, A. El-Kharouf, R. Steinberger-Wilckens. Evaluation of Inkjet Printed Protective Layer Coatings for SOFC Interconnects. Proceedings of the XII EFCF. B1302:93-105. 2018.

J. Tallgren, M. Bianco, O. Himanen, O. Thomann, J. Kiviaho, and J. van Herle. Evaluation of Protective Coatings for SOFC Interconnects. ECS Trans. 68(1): 1597-1608. 2015

J.E. Hong, A. Masi, M. Bianco, J. Van herle, R. Steinberger-Wilckens. Insight of Reactive Sintering in Manganese Cobalt Spinel Oxide of Protective Layer for Solid

Oxide Fuel Cell Metallic Interconnects. Proceedings of the XII EFCF. B0621:133-137. 2016.

J.E. Hong, M. Bianco, J. Van herle, R. Steinberger-Wilckens.Properties of Spinel Protective Coatings Prepared Using Wet Powder Spraying for SOFC Interconnects. ECS Trans. 68(1): 1581-1587. 2015

R. Steinberger-Wilckens, S. Yang, K. Cooke, J.Tallgren, O. Himanen, S. Frangini, A. Masi, M. Bianco, J. Van herle, J.E.Hong, M. Oum, F. Bozza, A. Dellai. Benchmarking Protective Coatings for SOFC ferritic steel interconnects – The SCORED 2:0 Project. Proceedings of the XII EFCF. B0605:41-50. 2016

S. Frangini, A. Masi, M. Bianco, J.E. Hong, M. Carlini, J. Van Herle, R. Steinberger-Wilckens. Thin film perovskite coatings and their application for SOFC ferritic steel interconnects. Proceedings of the XII EFCF, Lucerne. B0623:24-31. 2016.

# **Oral presentations**

High Temperature Corrosion of Stainless Steels in Solid Oxide Fuel Cell Energy Conversion Device, Corrosion Science Symposium, Leeds, 2018.

## **Poster presentations**

Nitriding influence on SOFC ferritic steel interconnects, EFCF XII, Lucerne, 2016.

Evolution of oxidation of SOFC interconnect alloys in dry and wet air, EFCF XII, Lucerne, 2016.

# **Manuel Bianco**

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٠	Specialist in materials engineering
٠	Five years of proactive collaboration in international projects
•	Determined, reliable and with a strong work ethics

# **EDUCATION**

Politecnico di Torino Master in material science and engineering	2013		
École Polytechnique Fédérale de Lausanne (EPFL) Master thesis on photocured polymer material charged with nanoparticles			
Politecnico di Torino Bachelor in material science and engineering	2010		
<b>Liceo Scientifico Vieusseux, Imperia</b> High school degree	2007		
PROFESSIONAL EXPERIENCE			
<b>Ph.D. assistant</b> EPFL doctoral school of energy (EDEY) Doctoral thesis on lifetime issues of metals used in high temperature energy conversion systems (SOFC). My collaboration with industrial partners inspired	2014-2018		

cheaper and long-lasting coatings to decrease corrosion

Internship	01.2014/	
Group of fuel and electrical materials (FUELMAT)	06.2014	
Stage dedicate to characterize the electrical and mechanical properties of		
different coating materials to choose the most performing one		

## **ADDITIONAL EXPERIENCE**

EU project SCORED 2.0	2014-2016
Project among 7 companies/universities. The project compared materials and	
technological solutions to contrast degradation in SOFC. I was the main	
responsible for microscopy observation and data interpretation	170

## **EU project SOSLEM**

*Industry oriented project, direct interaction between the company and me. My research led to the development of a new set of cheaper coatings.* 

## Start-up "MyBion"

2017-2018

Former member of this start-up project focused on genetic data analysis. The project won the Innosuisse Business Concept course, winter 2018 edition.

# **TECHNICAL SKILLS**

**IT:** Bruker ESPRIT , C/C++, Illustrator, Fiji (ImageJ), Outotec HSC, LabView, Matlab, Microsoft Office suit, Photoshop, SolidWorks.

**Material characterization**: Scanning Electron Microscopy coupled with Energy Dispersion Spectroscopy (SEM/EDS), X-ray Diffraction (XRD), Atomic Force Microscopy (AFM), Vickers hardness test.

**Materials synthesis and processes**: Metallographic preparation of samples for microscopy, Ink-jet printing of ceramic coating, Synthesis of nanoparticles, Metal etching, Design of Experiment (DOE) approach.

## LANGUAGES

	Understanding		Speaking		Writing
	Listening	Reading	Spoken interaction	Spoken production	
Italian	Mother t.	Mother t.	Mother t.	Mother t.	Mother t.
English	C2	C2	C1	C1	C1
French	C1	C1	C1	B2	B2

## **EXTRACURRICULAR ACTIVITIES**

- Sport is an important part of my life. I alternate swimming, running and cycling and when possible I love to organize football matches with colleagues and friends.
- I love gardening (on the balcony). Among all the plants I take care of, a four-wintersurvivor azalea is my greatest pride.
- I am the EPFL-Valais responsible for the EPFL Intermediate personal association (ACIDE): I collaborated with the direction to improve the working condition at EPFL Valais.
- Responsible for Switzerland for the Italian association called "UAAR". I am the reference person for the Italian expatriates here.

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