



Self-healing atmospheric plasma sprayed $\text{Mn}_{1.0}\text{Co}_{1.9}\text{Fe}_{0.1}\text{O}_4$ protective interconnector coatings for solid oxide fuel cells



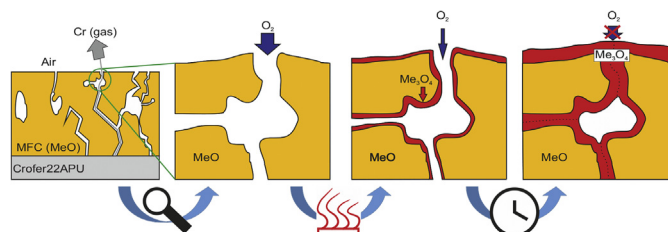
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HIGHLIGHTS

- Low chromium poisoning by self-healing APS- $\text{Mn}_{1.0}\text{Co}_{1.9}\text{Fe}_{0.1}\text{O}_4$ protective coatings.
- Intensive studies of microstructural and phase changes in APS- $\text{Mn}_{1.0}\text{Co}_{1.9}\text{Fe}_{0.1}\text{O}_4$.
- Self-healing coating by volume expansion related to phase transformation.

GRAPHICAL ABSTRACT



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ABSTRACT

Dense coatings on metallic interconnectors are necessary to suppress chromium poisoning of SOFC cathodes. Atmospherically plasma sprayed (APS) $\text{Mn}_{1.0}\text{Co}_{1.9}\text{Fe}_{0.1}\text{O}_4$ (MCF) protective layers demonstrated reduced chromium related degradation in laboratory and stack tests. Previous analyses revealed strong microstructural changes comparing the coating's as-sprayed and operated condition. This work concentrates on the layer-densification and crack-healing observed by annealing APS-MCF in air, which simulates the cathode operation conditions. The effect is described by a volume expansion induced by a phase transformation. Reducing conditions during the spray process lead to a deposition of the MCF in a metastable rock salt configuration. Annealing in air activates diffusion processes for a phase transformation to the low temperature stable spinel phase ($T < 1050^\circ\text{C}$). This transformation is connected to an oxygen incorporation which occurs at regions facing high oxygen partial pressures, as there are the sample surface, cracks and pore surfaces. Calculations reveal a volume expansion induced by the oxygen uptake which seals the cracks and densifies the coating. The process decelerates when the cracks are closed, as the gas route is blocked and further oxidation continues over solid state diffusion. The self-healing abilities of metastable APS coatings could be interesting for other applications.

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1. Introduction

In solid oxide fuel cell (SOFC) stacks interconnectors are used to establish electrical connection between single cells and separate the fuel and the oxidant gas. Chromium containing steels are

widely used for this purpose, as they fulfill the interconnector's demands, such as high electrical conductivity, mechanical and chemical stability, and easy manufacturing. The disadvantage of this material arises from chromium oxides formed under operating conditions. Those Cr-containing oxides tend to evaporate at the high temperatures at which SOFCs operate. The chemical and electrochemical interaction of these chromium species at the cathode layer leads to strong degradation of commonly used cathode materials [1–5]. The strength of this chromium poisoning

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effect strongly depends on the steel's oxide layer that is formed under oxidizing (air side) conditions. Simple chromium base alloys build up Cr_2O_3 layers leading to a high chromium oxide partial pressure at elevated temperatures. Adjusting the steel's chemical composition influences the growing oxide scale and thereby changes the amount of released gaseous chromium species. Adding manganese as dopant material leads to the buildup of an outer chromium manganese oxide spinel layer covering the inner Cr_2O_3 layer. Measurements reveal a strong reduction of the chromium evaporation rate by improved passivation layers [3,6–8].

Applying a chromium protection layer between interconnector and cathode further decreases the chromium evaporation rate and thereby reduces the cathode degradation. For the manufacture of these layers different materials can be applied by several coating technologies, protecting the cathode in different ways. One possibility is applying porous coatings, e.g. wet powder sprayed (WPS) manganese oxides, which chemically bind volatile chromium species. Additionally it supports the buildup of the chromium manganese oxide spinel at the interconnector surface. Despite the reduced degradation rate, chromium can still be found at the cathode after long-term operation [9]. In terms of long-term stability, this kind of protection layer entails a limited chromium absorption capacity. Another possibility is applying dense protective coatings that work in a different way by simply blocking the gas route for gaseous chromium oxides [5,10–12]. These kinds of coatings must provide the following properties: a) high electrical conductivity, b) high density, c) chemical stability under oxidizing (wet) environment up to about 900 °C, d) a thermal expansion coefficient that is adapted to the surrounding functional layers and the interconnector, e) adhesion on the interconnector's oxide scale, and f) low Cr-diffusion coefficient.

The effectiveness of dense chromium protective layers on metallic interconnects for solid oxide fuel cells induced a broad research on different material compositions applied by several coating techniques [5]. Hong et al. [13] achieved a densification of wet powder sprayed manganese-cobalt oxide coatings by reactive sintering. This cost efficient application technique faces the time and cost consuming sintering steps. Magnetron sputtering enables the deposition of very thin and dense protective layers [11] showing high conductivities but have to prove their stability in the long term and in stack tests. Further research on aerosol deposition [14], electrophoretic deposition [15,16], wet chemical methods [17] or several thermal spray techniques [12,18–20] revealed low chromium diffusion rates. Nevertheless, all protective coatings must exhibit minimum degradation for long-term operation within real stack tests. Atmospherically plasma sprayed (APS) $\text{Mn}_{1.0}\text{Co}_{1.9}\text{Fe}_{0.1}\text{O}_4$ (MCF) revealed its long-term stability and low chromium poisoning within real operation conditions. Fig. 1 shows the characteristic voltage-time behavior of two SOFC test stacks with different chromium protection coatings operated at Forschungszentrum Jülich [21]. The red line shows the recorded voltage of a still running stack with an operation time over 80,000 h, which keeps the world record in lifetime of planar SOFC systems. Its performance loss per 1000 h, called average degradation rate, is about 0.6%. The blue line illustrates the voltage curve of a four layer test-stack, which was shut down after more than 34,000 h of operation. The associated degradation rate of less than 0.3% per 1000 h is just half as the degradation rate of the other stack. The improved long-term stability is expected to originate from the difference between the integrated protection layers. In case of the stack showing a higher degradation rate, a manganese oxide (MnO_x) layer was applied by WPS, while the interconnectors of the other stack are coated with an MCF protective coating applied by APS. In contrast to WPS- MnO_x layers, it is known that APS-MCF layers are rather dense [19]. From these two stacks it can

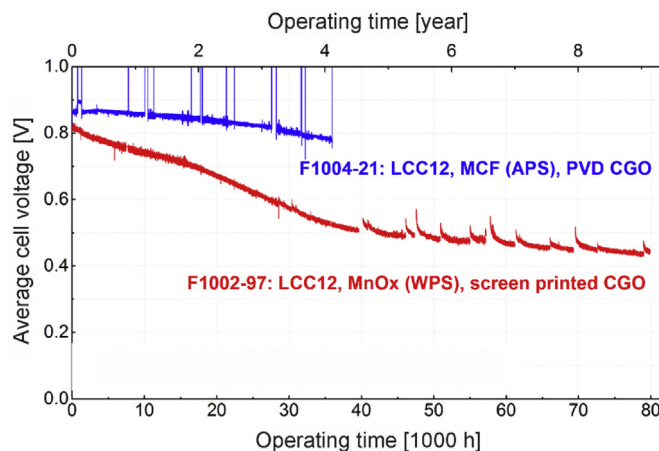


Fig. 1. Voltage degradation of two SOFC stacks operated at JÜLICH. Stack F1004-21 (blue) with APS-MCF protective coating and stack F1002-97 (red) with a WPS-MnOx coating. Modified after [21]. Reproduced with permission from J. Electrochem. Soc., 162 (9), F983 (2015). Copyright 2015, The Electrochemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

be concluded that APS-MCF coatings are promising candidates for chromium protection layers (assuming that most of the additional degradation originates from the chromium-cathode interaction).

Investigations of APS-MCF coated Crofer 22 APU interconnectors revealed a sufficient electrical conductivity, a good adhesion and remarkably low chromium evaporation rates [10,22,23]. Post-test analyses of stacks operated with APS-MCF layers and different studies of annealed thermally sprayed manganese-cobalt-(iron) oxide layers showed strong microstructural and phase changes between the as-sprayed and in air annealed condition [18,19,24,25]. A crack-healing effect during annealing is essential for the superior chromium-restraint in stack operation. Vaßen et al. assumed this crack-healing and densification to arise from a phase transformation [19]. The present work concentrates on this phase transformation giving a full description of the crack-healing on the basis of theoretical calculations, enabling long-term predictions of these layers.

2. Experimental

The ferritic steel Crofer 22 APU (ThyssenKrupp VDM GmbH, Werdohl, Germany) [26] is used as substrate material with the dimensions $25 \times 25 \times 2.5 \text{ mm}^3$. To mimic more realistic SOFC stack conditions, the substrates were laser cut from original interconnector components with linear channel structure. Before coating, the substrates were sandblasted with F150 alumina particles (size 63–105 μm). As coating material, a manganese-cobalt-iron oxide powder in spinel configuration (H.C. Starck, Laufenburg, Germany) was chosen with the following chemical composition: 23.5 wt% Mn, 47.6 wt% Co, 2.4 wt% Fe and 26.5 wt% O. The associated stoichiometry is $\text{Mn}_{1.00}\text{Co}_{1.89}\text{Fe}_{0.10}\text{O}_{3.88}$. Particle sizes were measured to $d_{10} = 14 \mu\text{m}$, $d_{50} = 27 \mu\text{m}$ and $d_{90} = 50 \mu\text{m}$ with a particle analyzer Horiba LA-950 V2 (Retsch Technology GmbH, Haan, Germany).

Atmospheric plasma spraying of the MCF powder was performed with a TriplexPro210 gun with a 9 mm nozzle within a multi coat facility (Oerlikon Metco, Wohlen, Switzerland). The parameters were set to a current of 500 A, a power of 49 kW and a plasma gas flow rate of 50 NLPM Argon and 4 NLPM Helium. To achieve a more homogenous layer thickness, three spray paths per coating were performed under different angles between substrate and

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