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Comparison of iron and copper doped manganese cobalt spinel oxides as protective coatings for solid oxide fuel cell interconnects

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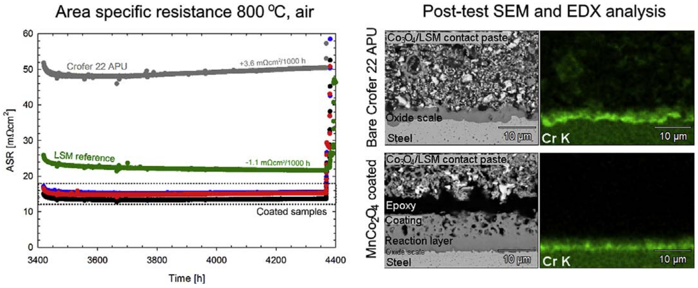
HIGHLIGHTS

- $MnCo_2O_4$, $MnCo_{1.7}Fe_{0.3}O_4$ and $MnCo_{1.7}Cu_{0.3}O_4$ compared as coating materials.
- All coating materials improve the oxidation rate and area specific resistance.
- All coatings effectively prevent Cr release from Crofer 22 APU.
- $MnCo_2O_4$ overall the most protective material.

GRAPHICAL ABSTRACT



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ABSTRACT

$MnCo_2O_4$, $MnCo_{1.7}Cu_{0.3}O_4$ and $MnCo_{1.7}Fe_{0.3}O_4$ are investigated as coatings for corrosion protection of metallic interconnects in solid oxide fuel cell stacks. Electrophoretic deposition is used to deposit the coatings on Crofer 22 APU alloy. All three coating materials reduce the parabolic oxidation rate in air at 900 °C and 800 °C. At 700 °C there is no significant difference in oxidation rate between coated samples and uncoated pre-oxidized Crofer 22 APU. The cross-scale area specific resistance (ASR) is measured in air at 800 °C using $La_{0.85}Sr_{0.1}Mn_{1.1}O_3$ (LSM) contact plates to simulate the interaction with the cathode in a SOFC stack. All coated samples have three times lower ASR than uncoated Crofer 22 APU after 4370 h aging. The ASR increase with time is lowest with the $MnCo_2O_4$ coating, followed by the $MnCo_{1.7}Fe_{0.3}O_4$ and $MnCo_{1.7}Cu_{0.3}O_4$ coatings. LSM plates contacted to uncoated Crofer 22 APU contain significant amounts of Cr after aging, while all three coatings effectively prevent Cr diffusion into the LSM. A complex Cr-rich reaction layer develops at the coating-alloy interface during oxidation. Cu and Fe doping reduce the extent of this reaction layer at 900 °C, while at 800 °C the effect of doping is insignificant.

1. Introduction

Solid oxide fuel cells (SOFC) are electrochemical devices that can covert the chemical energy of fuels such as H_2, CH_4 or CO to electrical energy at a high electrical efficiency. More than 10 000 domestic SOFC units are currently in operation in Japan [1], but high costs and a limited lifetime are impeding more widespread commercialization of the technology. One of the lifetime-limiting challenges is degradation of the ferritic stainless steel (FSS) used as the interconnect material [2,3]. Under SOFC operating conditions the FSS oxidizes, forming a several µm thick Cr_2O_3 and $(Mn,Cr)_3O_4$ scale on the surface. Because of the modest electrical conductivity of these oxides the resistance through a SOFC stack increases with time as the scale thickens, leading to a decrease in the power output [4]. Furthermore, the oxide scale is prone to

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form volatile Cr(VI)-species, that have been shown to degrade the SOFC cathode performance [5,6].

A way to mitigate these adverse effects is to coat the FSS with a protective, electrically conductive material. $(Mn,Co)_3O_4$ spinels are considered promising coating materials for the air side of the interconnect, demonstrated to reduce both the area specific resistance (ASR) across the interconnect [7,8] and the rate of Cr-evaporation [9]. The most extensively investigated compositions in this system are $MnCo_2O_4$ and $Mn_{1.5}Co_{1.5}O_4$. The former is a cubic spinel, while the latter is a dual phase mixture of cubic $MnCo_2O_4$ and tetragonal Mn_2CoO_4 that transform into a single phase cubic spinel above ca. 400 °C [10,11]. Both materials have appreciable electrical conductivity (60–90 $S\ cm^{-1}$ at 800 °C [11,12]) and an acceptable thermal expansion coefficient (TEC) ($11.4–14.4 \times 10^{-6}\ K^{-1}$ between 25 °C and 800 °C [13–15]). Attempts to improve the $(Mn,Co)_3O_4$ coating material by substituting some of the Co with Fe or Cu have been reported [13,16–21]. The TEC of $MnCo_2O_4$ is reduced by replacing some of the Co with Fe, which in some cases may be advantageous depending on what type of cell the interconnect is connected to [15]. Although Fe-doping also reduces the electrical conductivity, the conductivity measured for $MnCo_{1.7}Fe_{0.3}O_4$ at 800 °C (47 $S\ cm^{-1}$) is still several orders of magnitude higher than the typically reported electrical conductivity of Cr_2O_3 (0.1–0.01 $S\ cm^{-1}$) [22,23]. Substituting Co with Cu improves the electrical conductivity [15] and has been suggested to enhance densification of the coating [17]. Furthermore, diffusion couple studies indicate that both Cu and Fe substitution may be beneficial for reducing the formation of a moderately conductive Cr-rich $(Mn,Co,Cr)_3O_4$ reaction layer at the interface between the spinel coating and the thermally grown oxide scale [24,25]. The electrical conductivity of spinel oxides generally decreases with increasing Cr content and in case of $Mn_{0.5}Co_{0.5}Cr_2O_4$ the electrical conductivity at 800 °C is only 0.007 $S\ cm^{-1}$ [12,26]. Excessive growth of a Cr-rich $(Mn,Co,Cr)_3O_4$ reaction layer may therefore be negative for the interconnect ASR.

Most studies of the oxidation resistance and ASR of FSS coated with Fe and Cu doped $(Mn,Co)_3O_4$ are limited to relatively short exposure times (< 500 h) and do not provided a detailed investigation of the interaction between the coating and the FSS [16,17,27–30]. Furthermore, since the ASR has been measured using different set-ups and contact electrodes, it is difficult to compare the performance of the different coating materials and thus evaluate whether Fe or Cu doping offers any benefit.

In this work, we investigate the long-term (4000 h) oxidation behavior and cross-scale ASR of $MnCo_2O_4$, $MnCo_{1.7}Fe_{0.3}O_4$ and $MnCo_{1.7}Cu_{0.3}O_4$ coated Crofer 22 APU. The consequences of forming Cr-rich reaction layers between the interconnect and these spinel coatings are further discussed.

2. Experimental

2.1. Sample preparation

A 1 mm thick plate of Crofer 22 APU (Thyssen Krupp) with the composition given in Table 1 was cut into 20 × 20 mm coupons. A 3 mm hole was drilled in one of the corners to allow for hanging in the oxidation furnace. The coupons were ground with SiC-paper, polished down to 1 μm using diamond abrasive, and cleaned in acetone and ethanol for 10 min each in an ultrasonic bath.

Table 1
Composition of Crofer 22 APU alloy used in this study in wt.%. Analyzed by Optical Emission Spectroscopy at Force Technology, Denmark.

Alloy	Fe	Cr	Mn	Ti	La	C	Si	Al
Crofer 22 APU	Bal.	23	0.42	0.068	0.04–0.20[a]	0.003	0.049[b]	0.007

[a] La was not measured by OES. Typical concentration according to manufacturer's datasheet.

[b] Determination of Si content by OES is associated with large uncertainty.

$MnCo_2O_4$ (MC), $MnCo_{1.7}Fe_{0.3}O_4$ (MCFe) and $MnCo_{1.7}Cu_{0.3}O_4$ (MCCu) spinel powders were prepared by spray pyrolysis of aqueous based nitrate solutions as described in detail elsewhere [15]. The powders were calcined at 650 °C for 10 h in air, ball milled overnight in ethanol (Ø 10 mm YSZ milling balls), dried in a rotary evaporator, and sieved at 250 μm. The particle size of as-prepared powders was characterized using a Beckman coulter I/S particle size analyzer. Small amounts of each powder were dispersed in ethanol by ultrasonication before analysis. All powders had a bimodal particle size distribution, with median sizes (d_{50}) equal to 0.70 μm for MC, 0.63 μm for MCFe and 1.22 μm MCCu.

Electrophoretic deposition (EPD) was used to coat the Crofer 22 APU coupons with the spinel powders. The EPD set-up consisted of a 150 ml Teflon box and two 4 × 4 cm plates of Crofer 22 APU serving as counter electrodes. Suspensions were made by ball milling 5 wt% of powder in a 50/50 vol% mixture of isopropanol and ethanol for 2 days (Ø 10 mm YSZ milling balls, 500 ml PE-bottles). The steel coupon was connected to the negative terminal and mounted in parallel between the counter electrodes at a distance of 15 mm. Deposition was carried out at 35 V for 40–100 s. After drying in room temperature, the coated samples were heat treated in a tubular furnace at 900 °C for 2 h in N_2-9%H_2, followed by 2 h at 800 °C in air. The heating and cooling rates were 120 °C h^{-1}. Gasses were bubbled through water at 5 °C to give a moisture content of ca. 1%. Uncoated Crofer 22 APU was pre-oxidized under the same conditions to serve as a reference.

2.2. Characterization

The oxidation kinetics of spinel coated and bare pre-oxidized Crofer 22 APU were studied in air at 700 °C, 800 °C and 900 °C in a chamber furnace. There was no forced airflow to the furnace (i.e. nearly stagnant conditions). Three to five samples of each type were suspended vertically in the furnace. Every 250 h, the furnace was cooled to room temperature (180 °C h^{-1}) and the mass gain was determined by weighing the samples on a scale with 0.00001 g accuracy (XS205 Mettler Toledo). The coated and uncoated samples were oxidized separately to avoid any Cr(VI) (g) from the uncoated samples depositing on the coated samples.

The cross-scale/coating area specific resistance (ASR) was characterized in air using the set-up illustrated in Fig. 1, described in detail in Ref. [31]. For the ASR measurement, Crofer 22 APU was cut into 20 × 40 mm coupons and two 6 mm holes were drilled in the shorter ends for mounting purposes. Platinum wire (Ø 0.3 mm) was flattened on one end and welded to each coupon along the shorter edge. The spinel coatings were subsequently deposited and sintered as described above. Porous $La_{0.85}Sr_{0.1}Mn_{1.1}O_3$ (LSM) (20 × 20 × 1 mm) plates spray coated with a 50–60 μm layer of LSM (89 wt%) and Co_3O_4 (11 wt %) slurry mixture were used as contacting plates. The LSM plates were stacked between the steel samples as illustrated in Fig. 1. Gold foil (0.3 mm) connected to gold wires, was placed on the top and bottom of the stack to distribute the current, and a dead load of 7 kg was put on top.

The stack was heated up to 800 °C in a vertical furnace before a current of 2 A, corresponding to 0.5 A cm^{-2}, was applied. The current was monitored throughout the measurement by recording the voltage drop across an external resistor. Ohmic behavior was confirmed by varying the current between 0.1 A and 2 A during a short portion of the measurement.

The aging program consisted of 2000 h at 800 °C, followed by 30 thermal cycles between 800 °C and 100 °C and finally additional 2000 h at 800 °C. Temperature was monitored by two S-type thermocouples, one positioned close to the center of the stack and one positioned close to the bottom (see Fig. 1). The two thermocouples typically showed a difference of 10 °C at 800 °C. The area specific resistance was