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Published in:
Solid State Ionics

Link to article, DOI:
[10.1016/j.ssi.2018.09.018](https://doi.org/10.1016/j.ssi.2018.09.018)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Talic, B., Hendriksen, P. V., Wiik, K., & Lein, H. L. (2018). Thermal expansion and electrical conductivity of Fe and Cu doped MnCo₂O₄ spinel. *Solid State Ionics*, 326, 90-99. <https://doi.org/10.1016/j.ssi.2018.09.018>

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Thermal expansion and electrical conductivity of Fe and Cu doped MnCo₂O₄ spinel

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Abstract. Manganese cobalt spinel oxides are promising coating materials for corrosion protection of metallic interconnects in solid oxide fuel cell stacks. This work investigates how Fe and Cu doping affect the crystal structure, thermal expansion and electrical conductivity of the MnCo_{2-x}M_xO₄ (M=Cu, Fe; x = 0.1, 0.3, 0.5) spinel oxides. Single phase cubic spinels were successfully prepared by spray pyrolysis. The electrical conductivity between room temperature and 1000 °C increased with addition of Cu and decreased with addition of Fe. The thermal expansion coefficient (TEC) between 50 and 800 °C decreased from 14.4 to 11.0×10⁻⁶ K⁻¹ going from MnCo₂O₄ to MnCo_{1.5}Fe_{0.5}O₄. The TEC of the Cu substituted materials did not follow any obvious trend with composition and was likely influenced by precipitation of CuO during heating. Based on their physical properties, the Fe doped materials are the most attractive for application as SOFC interconnect coatings.

Keywords: Solid oxide fuel cell; thermal expansion; electrical conductivity; spinel

1. Introduction

The lifetime and performance of solid oxide fuel cell (SOFC) stacks is today among other factors limited by degradation of the ferritic stainless steel (FSS) interconnect [1,2]. Under SOFC operating conditions the FSS is oxidized to form a continuous scale, typically composed of Cr₂O₃ and MnCr₂O₄ [3]. Due to the modest electrical conductivity of these materials [4,5], the resistance across the stack increases with time as the oxide scale grows thicker [6]. An additional challenge is the vaporization of Cr(VI) species from the scale surface by reaction with oxygen and water vapor present on the cathode side of the SOFC [7,8]. The volatile Cr(VI) species deposit on electrochemically active sites of the cathode, thereby causing significant performance degradation [9–11]. To mitigate these issues, the FSS may be coated with a protective material.

The protective coating should have a sufficiently high electrical conductivity, a thermal expansion coefficient (TEC) matching the FSS interconnect and other SOFC materials, and a low oxygen and chromium diffusion coefficient to limit growth of the oxide scale and vaporization of Cr(VI) [12]. The TEC target will be dictated by the thickest layer in the SOFC stack, which depends on the specific stack design. For a Ni-YSZ anode supported cell the TEC target will be 12.5×10⁻⁶ K⁻¹ while for an YSZ electrolyte supported cell the target will be 10.9×10⁻⁶ K⁻¹ (for the temperature range 25–900 °C) [13]. The TEC of Crofer 22 APU, a FSS commonly used as the interconnect material is 12.3×10⁻⁶ K⁻¹ (25–900 °C) [14].

Several materials have been investigated as protective coatings for SOFC interconnects, including rare-earth oxides [15,16] and various lanthanum-based perovskites [17–19]. (Mn,Co)₃O₄ spinel oxides were first suggested as a coating material candidate by Larring and Norby [20], and have received increasing attention over the last decade [21–28]. The most widely studied compositions in this system are Mn_{1.5}Co_{1.5}O₄ and MnCo₂O₄. Although these materials are not stable under the reducing conditions found on the anode side of the SOFC, they are considered promising coatings for the cathode side, where they limit Cr-volatilization and reduce the oxidation rate of the FSS [29–31].

The AB₂O₄ spinel structure (space group *Fd-3m*) adopted by MnCo₂O₄ can be described as a cubic close packed arrangement of oxygen ions where 1/8 of the available tetrahedral sites and 1/2 available octahedral sites are occupied by cations. The spinel structure is very flexible in terms of site occupancy and oxidation states of the elements, which makes characterization of the cation distribution complicated when transition metal cations are involved. Several suggestions for the cation

distribution in MnCo_2O_4 have been put forth [32–39]. Most of these agree that tetrahedral sites primarily are occupied by Co^{2+} , while there is more debate about the oxidation states of Mn and Co occupying the octahedral sites. It was early shown by Yamamoto et al. [32] that the lattice parameter of MnCo_2O_4 is lower when synthesized by a low-temperature (80 °C) method compared to when synthesized by solid-state reaction at 1000 °C. At the time, this was attributed to a higher fraction of the tetrahedral sites being occupied by Mn^{2+} when the material is prepared at a low temperature. More recently it has been shown that preparation of MnCo_2O_4 below ca. 500-600 °C yields a cation deficient spinel having a smaller lattice parameter compared to the stoichiometric material [34,40–44]. For convenience, the cation deficiency is often designated as an excess of oxygen, i.e. $\text{MnCo}_2\text{O}_{4+\delta}$, with δ up to 0.6 reported [40]. Upon heating above ca. 500-700 °C oxygen is released to form stoichiometric MnCo_2O_4 [40]. There are no reports about the process being reversible, i.e. that oxygen is taken up during cooling.

The small polaron hopping mechanism is generally accepted as the mechanism for electrical conductivity in spinel oxides containing transition metal cations [45,46]. Since the distance between octahedral sites is shorter than the distance between tetrahedral sites in the spinel structure, hopping takes place primarily between multivalent cations on the former [45]. For MnCo_2O_4 , hopping is believed to take place mainly between $\text{Mn}^{3+}/\text{Mn}^{4+}$ pairs on the octahedral sites, with a possible contribution due to hopping between $\text{Co}^{2+}/\text{Co}^{3+}$ pairs [47,48]. There is considerable scatter in literature regarding the magnitude of the electrical conductivity in this material, with values measured in air at 800 °C ranging from 34 to 132 S/cm [49–53]. There is also scatter in the reported thermal expansion coefficient of MnCo_2O_4 , ranging from $9.7\text{--}13.5 \times 10^{-6} \text{ K}^{-1}$ between room temperature and 800 °C [49–51,53,54].

There have been several attempts to improve the electrical conductivity and tailor the thermal expansion behavior of the $(\text{Mn},\text{Co})_3\text{O}_4$ spinels by partially substituting Co with Ti [55], Ni [56], Fe [57,58], Cu [59–62] or Bi [63]. There is consensus that doping with Cu increases both the electrical conductivity and the thermal expansion coefficient [60–62]. It has also been reported that Cu-doping lowers the sintering temperature relative to $(\text{Mn},\text{Co})_3\text{O}_4$ [56,58,59]. It is however not clear in all of the cases how doping affects the electrical conductivity and thermal expansion coefficient of $(\text{Mn},\text{Co})_3\text{O}_4$ spinels. For example, addition of Fe is reported to both increase [57] and decrease [51] the electrical conductivity.

The aim of this work is obtain better understanding of the electrical and thermal behavior of the spinel oxides by providing a thorough characterization of these properties in $\text{MnCo}_{2-x}\text{M}_x\text{O}_4$ ($\text{M}=\text{Cu}$, Fe ; $x = 0.1, 0.3, 0.5$). Iron and copper were chosen as substitutional elements based on an investigation of several binary spinels made by Petric and Ling [53], where it was shown that copper spinels exhibit appreciable electrical conductivities while ferrite spinels typically have TEC in the range of $11\text{--}12 \times 10^{-6} \text{ K}^{-1}$, thus providing a good match with other SOFC components.

2. Experimental

2.1 Powder synthesis

$\text{MnCo}_{2-x}\text{M}_x\text{O}_4$ ($\text{M}=\text{Cu}$, Fe ; $x = 0, 0.1, 0.3, 0.5$) powders were synthesized by spray pyrolysis using pilot-scale equipment. The details of this synthesis method have been described by Mokkelbost et al. [64]. Precursor solutions were prepared by dissolving metal nitrates, $\text{Mn}(\text{NO}_3)_2 \times \text{H}_2\text{O}$ (98 %, Aldrich), $\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ (97.7 % min., Alfa Aesar), $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ (> 98 %, Alfa Aesar) and $\text{Cu}(\text{NO}_3)_2 \times 2.5\text{H}_2\text{O}$ (Rectapur, VWR), in distilled water by stirring overnight. The precursor solutions were filtered and their exact concentrations determined by thermogravimetric analysis of the weight change after heating to 800 °C. They were then mixed in stoichiometric amounts according to the target compositions (Table 1) and stirred overnight. The mixed solutions were atomized by spraying through a two-phase nozzle at a rate of 10 L/h into a rotating furnace set to a target temperature of 1000 °C. The high temperature causes the atomized droplets to decompose instantly, forming the oxides. The resulting powders were collected at the furnace outlet and calcined in air at 650 °C for 10 h to decompose any remaining organics. The heating and cooling rate (HCR) during calcination

was 200 °C/h. The powders were subsequently ball milled overnight in 100 % ethanol (250 ml PE-bottles, Ø 10 mm YSZ milling balls), dried in a rotavapor, and sieved (250 µm).

The calcined (650 °C) powders were used for structural and thermogravimetric analysis. For measurement of the electrical conductivity and thermal expansion coefficient, the powders were pressed into bars/pellets and sintered in air at 1050 °C or at 1100 °C+800 °C, respectively. Details about the two sintering procedures are given in the following.

Table 1: Target compositions of prepared spinel powders and abbreviations used throughout this text.

Composition	Abbr.
MnCo ₂ O ₄	MC
MnCo _{1.9} Fe _{0.1} O ₄	Fe1
MnCo _{1.7} Fe _{0.3} O ₄	Fe3
MnCo _{1.5} Fe _{0.5} O ₄	Fe5
MnCo _{1.9} Cu _{0.1} O ₄	Cu1
MnCo _{1.7} Cu _{0.3} O ₄	Cu3
MnCo _{1.5} Cu _{0.5} O ₄	Cu5

2.2 Characterization

Structural characterization was performed on a Bruker DaVinci X-ray diffractometer (XRD) with Cu-K α radiation. Powder samples were mixed with ethanol and applied to a silicon single crystal sample holder while solid samples were mounted in a large-cavity sample holder using molding clay. The diffractograms were recorded on rotating samples from 15-75° 2 θ using a step size of 0.02° and a collection time of 1 s per step. Lattice parameters were refined by structure fitting of the diffraction patterns (Pawley method) using Topas software (Bruker).

Thermal expansion was characterized in a Netzsch DIL 402C dilatometer from 30-1000°C and reverse (HCR: 2 °C/min) under flowing (30 ml/min) synthetic air. All measurements were corrected against an Al₂O₃ standard. Dense pellets for the measurement were prepared by uniaxial pressing of the spinel powders in a Ø=5 mm steel die, sintering in air at 1100 °C for 5 h and subsequently annealing in air at 800 °C for 12 h (HCR: 2 °C/min). The annealing step was included to re-oxidize the spinel, which is partially decomposed when heated above 1050 °C in air [39,65]. The pellet ends were ground with #1200 SiC paper to make the surface planes parallel. Final pellet length was 8-11 mm. XRD was used to confirm that all materials were phase pure cubic spinels after the sintering procedure. For this purpose, larger pellets (Ø 20 mm) were prepared and sintered following the above described procedure. Before characterization, the pellets were ground with #500 SiC paper to remove 1-2 mm of the surface layer.

Thermogravimetric analysis (TGA) was performed using a TG 439 Thermo-Microbalance from Netzsch. The equipment consists of an electrically compensating symmetrical balance with two separate ovens for the sample and a counter weight, operating at identical heating and flow rates. The equipment has a resolution of 0.1 µm. Analysis was performed on ca. 15 mg of spinel powder with ca. 9.9 mg Al₂O₃ powder as the counter weight. Alumina crucibles containing the powders were suspended from the weighing beam using Pt30%Rh wires. The mass change was recorded between room temperature and 800 °C in flowing air (10 ml/min) at various heating and cooling rates. A background correction was made for each temperature program by measuring with empty alumina crucibles. In theory, buoyancy effects should be eliminated by the experimental set-up, however, a small influence was detected in the background measurement. The background data are provided in the Supplementary Material (Figure S1). After correcting for the background, the experimental results were fitted to a polynomial curve to reduce noise inherent to the measurement and improve readability of the figures. Details about the noise reduction procedure and the original data may be found in the Supplementary Material (Figure S2).

Electrical conductivity was characterized by the four-probe method on sintered rectangular bars. The bars were made by uniaxial pressing of the spinel powders in a steel die and sintering in air at

1050 °C for 5 h (HCR: 2 °C/min). The edges of the bar were cut to dimension (ca. 4×6×18 mm³) using a diamond saw and lightly ground with #1200 SiC-paper. Pt-wires were attached to the sides of the bars, which were painted with Pt-paste and then heat treated at 1000 °C for ca. 10 min in air (HCR: 2 °C/min) to ensure good electrical contact. The electrical conductivity was measured in flowing air between room temperature and 1000 °C with 1 h dwell time for each 100 °C (HCR: 1 °C/min). Temperature was monitored by a S-type thermocouple placed close to the sample surface. Current was supplied by a Keithley 580 micro-ohmmeter and varied between 10-100 mA depending on the resistance. The current direction was switched at a frequency of ca. 1 Hz and the average of the measured resistance in forward and reverse directions of passing current was used in order to eliminate any thermoelectric emf. The resistance was recorded every 10 min throughout the measurement. The measured resistance was used to calculate the electrical conductivity according to:

$$\sigma_m = \frac{1}{R} \cdot \frac{L}{A} \quad (1)$$

where R is the resistance [Ω], L is the distance between the voltage probes [cm] and A is the cross sectional area of the sample bar [cm²]. The Bruggeman asymmetric model was used to correct the measured electrical conductivity for sample porosity according to [66,67]:

$$\sigma = \sigma_m \cdot \frac{1}{(1 - p)^{\frac{3}{2}}} \quad (2)$$

where σ is the corrected conductivity, σ_m is the measured conductivity and p is the sample pore fraction. The porosity was determined by the Archimedes method according to ISO 5017:1998(E) using isopropanol as the solvent. The theoretical density of the spinel oxides was calculated using XRD results for the calcined powders. The phase purity of samples after the electrical conductivity measurement was checked by XRD of the crushed sample bars. Calculating the theoretical density based on XRD results of the sintered samples gives results in a difference of max. 4 % in density compared to using XRD results of the calcined powders.

3. Results

3.1 Crystal structure

X-ray diffraction patterns of the as-prepared spinel powders after calcination at 650 °C in air are shown in Figure 1. All materials are identified as single phase cubic spinels. The lattice parameters were determined by fitting the XRD patterns to the cubic $Fd-3m$ space group with the cation distribution set to¹ (Co²⁺)[Co³⁺Mn³⁺]O₄²⁻. Both iron (as Fe³⁺) and copper (as Cu²⁺) were added to the octahedral position in place of cobalt. There was no significant difference in the goodness of fit by placing Fe/Cu on the tetrahedral sites or with a different valence state. Lattice parameters obtained from the structure fit are plotted in Figure 2. Fe substitution increases the lattice parameter, while Cu substitution decreases the lattice parameter. This can also be seen in Figure 1 as a shifting of the diffraction peaks towards lower and higher 2 θ angles, respectively. Neither of the substitutions result in a perfectly linear change in lattice parameter with compositions starting from the parent (MC) material.

XRD patterns of ceramics sintered at 1100 °C and annealed at 800 °C indicated that all materials remained single phase cubic spinels (Figure S3, Supplementary Material). The diffractograms were characterized by sharper peaks compared to Figure 1, reflecting the enhanced crystallinity and increase in particle size after heat treatment at higher temperature. The lattice parameters determined

¹ In accordance with conventions for describing the cation distribution in spinels, the round brackets () designate cations in tetrahedral sites, while the square brackets [] designate cations in octahedral sites.

by structure fitting of these patterns are plotted in Figure 2. For nearly all of the materials, the lattice parameter after sintering at 1100 °C + 800 °C is higher than for the as-prepared powder (calcined 650 °C). The largest difference is for the Cu-doped materials, which after sintering show increasing lattice parameter with increasing Cu substitution, i.e. the opposite trend of what is observed for the calcined powders. For the Fe-doped materials, the difference between the lattice parameters measured for the calcined powders and the sintered ceramics decreases with increasing Fe substitution. For the sintered samples the lattice parameter scales linearly with the site fraction of Fe, in accordance with Vegard's law, i.e.:

$$a_{MnCo_{2-x}Fe_xO_4} = a_{MnCo_2O_4} + 0.15x_{Fe} \quad (3)$$

where $a_{MnCo_{2-x}Fe_xO_4}$ is the lattice parameter of the Fe-doped material, $a_{MnCo_2O_4}$ is the lattice parameter of MnCo₂O₄ and x_{Fe} is the site fraction of iron.

Figure 1. X-ray diffraction patterns of powders synthesized by spray pyrolysis after calcination at 650 °C in air. Individual patterns are normalized such that the highest intensity peak has the same intensity. The right-hand side of the figure shows an excerpt of the pattern between 63 and 65°.

Figure 2. Lattice parameters determined by structure fitting of XRD patterns for as-prepared spinel powders (calcined at 650 °C), and pellets sintered at 1100 °C and annealed at 800 °C. MC is indicated

by black symbols, Fe-doped by blue and Cu-doped by red. Stippled lines are added as guide to the eye.

3.2 Thermal expansion coefficient

Thermal expansion measured by dilatometry during heating in air is shown in Figure 3a. The thermal expansion decreases nearly linearly with increasing substitution with Fe. Substitution with Cu results in an overall increase in thermal expansion, however, the variation with composition is more complicated and does not follow any obvious trend. For all materials, the expansion between room temperature and 800 °C can be well fitted with two linear segments, as illustrated in Figure 3b for MnCo_2O_4 . The transition between the two segments varies with composition and is in the range of 300-500°C. The transition temperature for each material and the thermal expansion coefficients (TEC) calculated from the slopes of the curves in the different temperature intervals are summarized in Table 2. Measuring the same sample more than one time typically resulted in a difference of < 5 % in TEC (values reported in Table 2 are the first measurement of each sample).

There was a small negative hysteresis between the expansion measured during heating and cooling for all materials. For clarity, only the heating curves are shown in Figure 3 (full measurement in Figure S4, Supplementary material). The hysteresis decreases significantly when the measurement is performed between room temperature and 800 °C (Fig. S4 in the Supplementary Material), which indicates that the hysteresis is due to creep or possibly an onset of partial reduction of Co in the materials [39].

The material containing the highest fraction of copper, Cu5, displays a greater hysteresis compared to the other materials. A distinct change in the slope of thermal expansion above 800 °C can also be seen in Figure 3a. XRD of the crushed sample after testing, shown in Figure 4, reveals small amounts of CuO secondary phase. Thus, the change in slope for Cu5 is likely due to the transition from a single phase material ($\text{MnCo}_{1.5}\text{Cu}_{0.5}\text{O}_4$) to a dual phase mixture of $\text{MnCo}_{1.5+x}\text{Cu}_{0.5-x}\text{O}_4$ and CuO. The CuO secondary phase is not detected in the sintered pellet (also shown in Figure 4), possibly because it was under the detection limit of XRD (typically ~2 %) and/or this phase precipitated from the material with time at higher temperature.

Table 2: Thermal expansion coefficients (TEC) determined from linear fit of slopes in Figure 3a. Low temperature (LT) values are from 50 °C to the transition point, high temperature (HT) values are from the transition point to 800 °C. Sample density was determined by Archimedes method.

Comp.	LT-TEC [10^{-6} K^{-1}]	HT-TEC [10^{-6} K^{-1}]	Transition point [°C]	TEC 50-800°C [10^{-6} K^{-1}]	Sample density [%]
MC	12.9	15.3	410	14.4	91
Cu1	13.7	17.3	380	15.8	95
Cu3	12.7	16.3	330	15.1	95
Cu5	12.3	16.3	360	14.7	96
Fe1	11.4	14.8	350	13.6	95
Fe3	11.1	12.8	440	12.0	95
Fe5	9.9	11.2	440	11.0	96

Figure 3. (a) Thermal expansion measured by dilatometry during heating in air, (b) Thermal expansion curve for the MnCo_2O_4 (MC) material showing linear fit of curve at low (LT) and high (HT) temperatures.

Figure 4. X-ray diffractograms of the $\text{MnCo}_{1.5}\text{Cu}_{0.5}\text{O}_4$ (Cu5) material after sintering ($1100^\circ\text{C} + 800^\circ\text{C}$, air), after thermal expansion characterization, and after electrical conductivity characterization. The peak belonging to CuO is highlighted, all other peaks belong to the cubic spinel phase.

3.3 Electrical conductivity

Figure 5 shows the electrical conductivity measured during cooling in air as a function of temperature. The conductivity value was recorded every 10 min and the 1 h long isotherms every 100°C are visible from the higher density of points. The results have been corrected for sample porosity using equation (2). The conductivity increases nearly linearly with increasing site fraction of Cu and decreases nearly linearly with increasing site fraction of Fe. All materials exhibit semiconducting behavior. The temperature dependence can be described in accordance with the small polaron hopping model [68]:

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_A}{kT}\right) \quad (4)$$

where T is the temperature [K], E_A is the activation energy for hopping [eV], and k is Boltzmann's constant [eV/K]. The pre-exponential factor, σ_0 , is assumed to be constant. The slope of the $\ln(\sigma T)$ vs $1/T$ curve (Fig. 5) can be fitted to two linear segments in similar temperature intervals as the thermal expansion curves, i.e. one segment between room temperature and ca. 400°C and one at higher temperatures. The high temperature activation energy decreases nearly linearly from 0.53 eV to 0.41 eV with increasing site fraction of Cu, while Fe-substituted samples have the same activation energy as MC, namely 0.53 eV. The same trends are observed for the low temperature region, where Cu-substituted materials have activation energies in the range of 0.32-0.36 eV, while MC and the Fe-substituted materials have activation energies of 0.38-0.39 eV. The activation energy calculated from the slopes above 400°C , the conductivity measured at 800°C and the porosity of each sample are summarized in Table 3.

XRD of the crushed bars after measurement showed that all materials remained phase pure, cubic spinels. Unlike after TEC characterization, no CuO peaks could be detected in the diffractogram of the Cu5 material (see Figure 4). This is probably due to the different sintering procedures followed for

making samples for TEC (1100 °C + 800 °C) and for electrical conductivity (1050 °C). The lattice parameters of MC and Fe-substituted materials were equal to the lattice parameters obtained for the ceramics sintered at 1100 °C and annealed at 800 °C (see Figure 2). The lattice parameters for the Cu-substituted materials were in this case intermediate between those determined for calcined powder (650 °C) and sintered ceramic (1100 °C), decreasing from 8.286 Å for Cu1 to 8.274 Å for Cu5.

Table 3: Electrical conductivity (σ) measured at 800 °C, activation energy (E_A) and pre-exponential factor (σ_0) at high temperature (>400 °C) extracted from the Arrhenius plots. The conductivity values have been corrected for the measured sample density. σ_{uncorr} is the electrical conductivity at 800 °C before correcting for porosity.

Comp.	E_A [eV]	σ_0	σ (800 °C) [S/cm]	Sample density [%]	σ_{uncorr} [S/cm]
MC	0.53	17.2	89	72	55
Cu1	0.50	17.1	114	84	87
Cu3	0.44	16.7	142	95	131
Cu5	0.41	16.5	168	96	155
Fe1	0.53	17.1	77	77	52
Fe3	0.53	16.5	47	79	33
Fe5	0.53	16.2	31	81	23

Figure 5. Arrhenius plot of the electrical conductivity as a function of temperature, measured during cooling. Results are corrected for sample porosity (specified in Table 3).

In most cases, there was a negligible (< 1 %) hysteresis between the conductivity measured during heating and cooling. However, for the MC sample, the conductivity measured during the 1 h isotherm at 375 °C decreased considerably with time. When this sample was heated up to 1000 °C and cooled, the conductivity measured below 500 °C during cooling was higher than measured during heating, as seen in Figure 6a. Figure 6b shows that the electrical conductivity of the MC sample decreases more than 180 % over 40-50 h at constant temperature of 325 °C or 275 °C. The initial conductivity at both temperatures was re-established by heating the sample above 500 °C. In contrast, the electrical conductivity measured at 800 °C changes by less than 0.4 % over 25 h (Fig. 6b insert). A sample of the Cu1 material with 60 % density (sintered 10 h at 950 °C in air) also showed a hysteresis between the heating and cooling segments (Figure S5, Supplementary Material). This was not observed for the same material when the sample density was 84 % (sintered 5 h at 1050 °C in air), which suggests that the relaxation in electrical conductivity at low temperature is related to the sample's interaction with the atmosphere.

Based on several measurements on three different MC samples having similar density (70-73 %), the error in the electrical conductivity measurement is estimated to be ~ 1 %. The error when

correcting for the sample porosity is significantly larger. For the two Cu1 samples having a density of 60 and 84 % (Figure S5, Supplementary Material), the electrical conductivity at 800 °C differed by ~ 20 % after correcting for porosity. Accordingly, we consider the conductivity reported for the denser samples to be more reliable.

Figure 6. Electrical conductivity of MnCo_2O_4 (72 % density). The conductivity is corrected for sample porosity. (a) Hysteresis in electrical conductivity measured during heating and cooling. The plot is an excerpt from a measurement between room temperature and 1000 °C. (b) Conductivity as a function of time, measured at constant temperature

3.4 Thermogravimetric analysis

To investigate possible origins of the hysteresis in electrical conductivity, MC powder obtained from a crushed ceramic sintered at 1100 °C and annealed at 800 °C was analyzed by thermogravimetry. Figure 7 shows that the sample mass increases upon heating above ca. 200 °C, reaching a maximum at 370 °C before it decreases again. Between 510 and 800 °C the mass is nearly constant. Upon cooling, the same trends are observed, but the mass gain is shifted to a lower temperature. The mass gain around 400 °C is reproduced when the same sample is re-heated after cooling (Figure S6 in the Supplementary Material). TGA of the as-prepared (calcined 650 °C) powders of MC, Fe3 and Cu3 resulted in similar observations (Figure S7 in the Supplementary Material). Notably, for all of materials there is a peak in the mass change curve between 350 and 400 °C. Overall, the mass changes are considerably larger for the powder calcined at 650 °C than for the powder obtained from a crushed ceramic sintered at 1100 °C. The calcined powders experienced a continuous mass loss from the peak at 350-400 °C to 800 °C.

Figure 7. Thermogravimetric analysis of MnCo_2O_4 powder (obtained from a crushed ceramic sintered $1100\text{ }^\circ\text{C} + 800\text{ }^\circ\text{C}$) showing relative weight change as a function of temperature in air.

4. Discussion

4.1 Crystal structure

A smaller lattice parameter is measured for most of the materials after calcination at $650\text{ }^\circ\text{C}$ compared to after sintering at $1100\text{ }^\circ\text{C}$ (Fig. 2). This is consistent with the temperature dependence of the lattice parameter for MnCo_2O_4 reported in literature [32,44,69]. MnCo_2O_4 prepared below ca. $500\text{--}600\text{ }^\circ\text{C}$ is reported to be cation deficient, with a smaller lattice parameter compared to the stoichiometric material [34,40–44]. Comparing the value for the MC powder calcined at $650\text{ }^\circ\text{C}$ ($8.233\text{ \AA}$) with the value given in PDF 23-1237 for presumably stoichiometric MnCo_2O_4 prepared at $720\text{ }^\circ\text{C}$ ($8.269\text{ \AA}$) indicates that the as-prepared powder is slightly cation deficient. Nissinen et al. [40] reported $\delta = 0.1$ for $\text{MnCo}_2\text{O}_{4+\delta}$ calcined at $640\text{ }^\circ\text{C}$. With increasing Fe-substitution the difference between the lattice parameters after the $650\text{ }^\circ\text{C}$ and $1100\text{ }^\circ\text{C}$ heat treatments decreases, indicating that the as prepared Fe-doped powder has a lower cation deficiency.

Due to the similar scattering factors of the elements in MnCo_2O_4 , the cation distribution cannot be determined from XRD data. However, the most probable cation distribution may be estimated by comparing the lattice parameter determined by XRD with the theoretical lattice parameter for different cation distributions, following the method of O'Neill and Navrotsky [70]. The method is based on geometrical considerations of the spinel structure, described by Hill et al. [71], and assumes that the ions can be considered as hard spheres. The average ionic radius is used when multiple cations occupy the same site. Based on an extensive review of binary spinels, O'Neill and Navrotsky [70] derived a set of effective ionic radii for cations in the spinel structure, which are used in the calculation. These radii are in most cases slightly smaller than Shannon radii, which are derived as an average over a large number of different structures [72]. The theoretical lattice parameter, a , is obtained from:

$$a = R_{\text{oct}}(3u^2 - 2u + 3/8)^{1/2} \quad (5)$$

where R_{oct} is the octahedral cation-anion bond length and u is the oxygen anion parameter, given by:

$$u = \frac{R^2/4 - 2/3 + (11R^2/48 - 1/18)^{1/2}}{2R^2 - 2} \quad (6)$$

where R is the ratio of the octahedral to tetrahedral cation-anion bond length.

In the following, the calculated lattice parameters are compared to the lattice parameters determined for sintered samples (1100 °C + 800 °C), since the electrical conductivity and thermal expansion was measured on these samples.

For MC, Co^{2+} is assumed to be the only cation occupying tetrahedral sites, in accordance with the majority of the cation distributions previously suggested in literature [32–39]. The cation distribution resulting in the closest match with the lattice parameter determined by XRD (8.298 Å) is $(\text{Co}^{2+})[\text{Mn}^{3+}_{0.54}\text{Mn}^{4+}_{0.46}\text{Co}^{3+}_{0.54}\text{Co}^{2+}_{0.46}]\text{O}_4^{2-}$, which has a theoretical lattice parameter of 8.298 Å. This distribution is nearly identical to that suggested by Bordeneuve et al. [39] based on neutron diffraction data on a sample sintered at 750 °C and quenched to room temperature. The nearly 1:1 $\text{Mn}^{3+}:\text{Mn}^{4+}$ ratio accounts for the high electrical conductivity of MnCo_2O_4 in the series of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ spinels [47].

Addition of a third cation (Cu/Fe) complicates the calculation. However, taking the above suggested distribution for MC as the starting point, two possibilities with an almost equally good match between calculated and measured lattice parameters are obtained for the Fe-substituted materials. The first possibility is that Fe^{3+} (0.645 Å) replaces Co^{3+} (0.53 Å) on the octahedral sites, and the second is that Fe^{3+} (0.485 Å) replaces Co^{2+} (0.58 Å) on tetrahedral sites. The latter requires a charge compensation by reduction of Co and Mn on the octahedral sites, resulting in the distribution $(\text{Fe}^{3+}_{0.5}\text{Co}^{2+}_{0.5})[\text{Mn}^{3+}_{0.5}\text{Mn}^{4+}_{0.5}\text{Co}^{2+}]\text{O}_4^{2-}$ for Fe5. In both options for the cation distribution, the increasing site fraction of Fe reduces the site fraction of Co^{3+} on octahedral sites. This makes both cation distributions consistent with the electrical conductivity and thermal expansion results, as will be discussed in Sections 4.2 and 4.3.

Previous investigations of the cation distribution in $\text{MnCo}_{2-x}\text{Fe}_x\text{O}_4$ have suggested both a mixed occupancy of Fe on tetrahedral and octahedral sites [48], and that Fe mainly occupies the latter [73]. Crystal field theory predicts that both Mn^{3+} and Co^{3+} have a stronger preference for the octahedral site than Fe^{3+} [74]. It is therefore more likely that Fe^{3+} replaces Co^{2+} on tetrahedral sites in $\text{MnCo}_{2-x}\text{Fe}_x\text{O}_4$ and that the increase in lattice parameter is due to charge compensation by Co (and Mn) on the octahedral sites.

The lattice parameters of the Cu-substituted materials varied greatly with thermal history. The number of possibilities in terms of site occupancy and oxidation state of the elements are too numerous to use the method developed by O'Neill and Navrotsky to explain this variation. Investigations of MnCoCuO_4 have resulted in conflicting suggestions for the cation distribution. Brabers and Setten [75] suggested the distribution $(\text{Cu}^{+0.65}\text{Mn}^{3+0.35})[\text{Cu}^{2+0.35}\text{Co}^{3+}\text{Mn}^{4+0.65}]\text{O}_4^{2-}$, while others have suggested that both Cu^{2+} and Cu^{+} occupy tetrahedral sites and that octahedral sites are occupied by Co^{3+} and $\text{Mn}^{3+/4+}$ [76,77]. The different cation distributions are likely due to differences in thermal history of the samples. As discussed in Section 4.2, the electrical conductivity results suggest a mixed occupancy of Cu^{+} and Cu^{2+} on the octahedral sites.

4.2 Electrical conductivity

The electrical conductivity of MnCo_2O_4 determined in this work is in the upper range of the values previously reported in literature. For example, [49] reported 34 S/cm at 800 °C in air for a sample sintered at 1200 °C and [78] reported 40 S/cm for a sample sintered at 1300 °C. As previously discussed by Liu et al. [48] some of the discrepancies found in literature are most likely due to the high temperature at which many of the investigated samples have been sintered. According to the $\text{Mn}_3\text{O}_4\text{-Co}_3\text{O}_4$ phase diagram reported by Aukrust and Muan [65], the MnCo_2O_4 spinel is only stable up to ca. 1050 °C in air. Liu et al. [48] showed that MnCo_2O_4 sintered at 1200 °C had an electrical conductivity of 51 S/cm at 800 °C and contained significant amounts of rock salt secondary phases. When the same sample was annealed at 1000 °C for 72 h, the rock salt phases disappeared and the electrical conductivity at 800 °C increased to 87 S/cm. This is close to the value we obtained (89 S/cm) for the same material sintered at 1050 °C, which was confirmed to be phase pure by XRD.

The electrical conductivity decreases nearly linearly with increasing site fraction of Fe, without any changes in the activation energy. If hopping between $\text{Co}^{3+}\text{-Co}^{2+}$ pairs on the octahedral sites

contributes to the charge transfer in MnCo_2O_4 , as suggested by Rousset et al. [47], both of the above suggested cation distributions for the Fe-substituted materials would explain why the electrical conductivity decreases and there is no change in the activation energy. Irrespective of whether Fe^{3+} resides on the octahedral or tetrahedral sites in the spinel structure, the consequence of introducing Fe is a decrease in the concentration of Co^{3+} (see section 4.1). Thus, there are fewer available sites for hopping as charge transfer is limited to hopping between the Mn^{3+} - Mn^{4+} pairs.

With increasing Cu-substitution the electrical conductivity increases and the activation energy decreases. The change in activation energy indicates that copper ions participate directly in the charge transfer. Since small polaron hopping in the spinel structure is feasible only between equivalent sites, and the cation-cation distance is shortest between the octahedral sites, this implies that both Cu^+ and Cu^{2+} occupy the octahedral sites.

The decrease in electrical conductivity over time, as seen around 375 °C in Figure 6, has previously been reported for nickel and copper ferrite spinels and attributed to re-distribution of the cations between octahedral and tetrahedral sites [79,80]. Rousset et al. [47] investigated this so-called “aging” phenomenon in the $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ -system at 125 °C and also attributed a decreasing electrical conductivity with time to cation re-distribution. However, aging was only appreciable for the end members of the system ($2.8 < x < 1.5$); for MnCo_2O_4 the change in electrical conductivity was less than 0.1 % over 500 h at 125 °C. Here, we measured a considerable aging effect also for the MnCo_2O_4 composition. Since the effect only was observed for this particular sample (with 72 % density) and a Cu1 sample sintered to low density (60%), the effect is most likely connected to interactions with the atmosphere. The MnCo_2O_4 sample investigated by Rousset et al. was prepared by spark plasma sintering, resulting in a density of 95 %, which is significantly higher than the density of the MnCo_2O_4 sample measured here (72 %) [47].

The mass changes observed by TGA during heating (Figure 7) provide a basis to explain the time variation of the electrical conductivity. The sample mass increase between 200-370 °C is likely due to oxidation and formation of cation vacancies, which may be described in terms of Kroger-Vink notation as [81]:

where $\text{O}_0^{\times}$ represents an oxide ion on a regular oxide ion site, V_A'' represents an A-site vacancy with double negative charge, V_B''' represents a B-site vacancy with triple negative charge, and p^* represents an a hole with a positive charge. That is, oxidation results in the formation of a new unit cell by creation of cation vacancies on the tetrahedral (A) and octahedral (B) sites, and results in two electron holes. MnCo_2O_4 is a p-type conductor [82], so intuitively, it may be expected that the increase in hole concentration should result in an increase in electrical conductivity [45]. However, as discussed by Groen et al. [81], in this case the mobility of the charge carriers is more important than their concentration. The creation of cation vacancies reduces the number of available sites for hopping and consequently the mobility. When heated above 400 °C, oxygen is removed and cationic vacancies are annihilated, which results in an increase in the electrical conductivity.

Using X-ray absorption near edge structure (XANES) analysis, Bazuev et al. [69] demonstrated that the $\text{Mn}^{4+}/\text{Mn}^{3+}$ fraction in $\text{MnCo}_2\text{O}_{4+\delta}$ spinel increases with increasing δ . Accordingly, it may be inferred that the electron holes are localized on manganese cations, i.e. $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$ during oxidation. Above 370 °C the mass loss likely corresponds to reduction of Mn^{4+} to Mn^{3+} , as suggested previously for heating of cation-deficient $\text{MnCo}_2\text{O}_{4+\delta}$ [69]. For the calcined powders (650 °C), the mass loss continued to decrease upon heating to 800 °C. This is probably due to reduction of Co^{III} to Co^{2+} on the octahedral sites, considering that Co_3O_4 has the lowest decomposition temperature (900 °C) in the $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ series of spinels [39].

4.3 Thermal expansion

All materials exhibited a change in the slope of thermal expansion above ca. 400 °C. Similar behavior may be observed upon examination of several previously published thermal expansion curves for

MnCo₂O₄ and MnCo_{2-x}Cu_xO₄, although this was not explicitly discussed by the authors [49,50,83,84]. MnCo₂O₄ has no recognized phase transitions in the temperature interval where the TEC is observed to increase. Some calculated phase diagrams of the Mn-Co-O system suggest the coexistence of CoMnO₃ with MnCo₂O₄ below ca. 600 °C and precipitation of MnO₂ below ca. 400 °C [53]. However, as far as we are aware, this has never been observed experimentally. A magnetic transition can be excluded as the Curie temperature of MnCo₂O₄ is 180 K [63].

The most likely mechanism behind the increase in the TEC is a spin state transition of cobalt on the octahedral sites, which is responsible for the extra thermal expansion of Co₃O₄ observed above ca. 350 °C [85]. This can be described as Co³⁺(LS) (0.545 Å) → Co³⁺(HS) (0.61 Å), where the numbers in parentheses are the Shannon ionic radii. Three-valent cobalt residing in the octahedral sites of MnCo₂O₄ is believed to be in the low spin state at room temperature [39], so a transition to high spin with increasing temperature is feasible. A mechanism involving spin state transition of cobalt would explain why the thermal expansion becomes more linear over the whole investigated temperature range when cobalt is replaced by iron. As discussed above, both of the most probable cation distributions for Fe-substituted MnCo₂O₄ involve a lower concentration of Co³⁺ on octahedral sites. Mössbauer spectroscopy or a similar technique is required to confirm or falsify whether the observed TEC change can be related to a spin state transition, for now it must be considered a postulate.

The thermal expansion behavior of materials containing copper is more complicated and the TEC does not follow any obvious trend with composition. Furthermore, the lattice parameter varies significantly with the thermal history of the sample. This is most likely due to precipitation of CuO as a secondary phase, which indeed was observed for the sample containing the highest amount of Cu, namely MnCo_{1.5}Cu_{0.5}O₄. Precipitation of CuO may also have taken place in samples with a lower Cu substitution, but in a quantity below the detection limit of XRD.

4.4 Suitability as SOFC interconnect coating materials

As mentioned in the introduction, the most important criteria for selection of a suitable coating material for the protection of SOFC metallic interconnects are a close TEC match to the alloy and other SOFC components, a sufficiently high electrical conductivity and low oxygen and chromium diffusion coefficients through the coating. With respect to thermal expansion, the Fe-substituted materials show greatest promise. The average TEC of MnCo_{1.7}Fe_{0.3}O₄ (Fe3) between 50-800°C ($12.0 \times 10^{-6} \text{ K}^{-1}$) is very close to the TEC of Crofer 22 APU ($11.9 \times 10^{-6} \text{ K}^{-1}$ [14]) in the same temperature interval, which is one of the commonly used interconnect alloys today. A closer match in TEC leads to less build-up of stresses during thermal cycling, thereby reducing the risk of cracking and/or spallation of the coating. Although the electrical conductivity was reduced by doping with iron, the conductivity remains several orders of magnitude higher than the typical electrical conductivity of the oxide scale formed on FSS [4]. The area specific resistance (ASR) for a coated interconnect will scale with the thickness and resistivity of each layer. Assuming the scale is made of Cr₂O₃ with an electrical conductivity of 0.1 S/cm at 800 °C, and that the coating is a 20 µm thick layer of Fe5 (31 S/cm at 800 °C), the Cr₂O₃ scale will dominate the ASR once this scale grows thicker than 0.03 µm. This suggests that in order to lower the ASR reducing the oxidation rate of the alloy is more important than increasing the conductivity of the coating material. We have previously shown that the MC, Fe3 and Cu3 materials result in nearly the same ASR after more than 4000 h oxidation at 800 °C when applied as a coating on Crofer 22 APU [28,30].

5. Conclusion

Single phase MnCo_{2-x}M_xO₄ (M=Cu, Fe; x = 0.1, 0.3, 0.5) materials of the cubic spinel structure were synthesized by spray pyrolysis. The thermal expansion behavior of all materials is characterized by a lower TEC between room temperature and ca. 400 °C compared to between ca. 400 °C and 800 °C. It is suggested that a spin state transition of Co³⁺ from low spin to high spin is the most likely origin of the increased expansion at elevated temperatures. Substitution with Fe results in a more linear

expansion behavior in the whole temperature interval and an overall lower TEC. The thermal expansion behavior of Cu-substituted materials is likely influenced by precipitation of CuO secondary phases and the TEC values are generally slightly higher than that of MnCo₂O₄.

The electrical conductivity of MnCo₂O₄ (89 S/cm at 800 °C) decreases with increasing site fraction of Fe, reaching 31 S/cm for Fe₅, and increases with increasing site fraction of Cu, reaching 168 S/cm for Cu₅. The changes in electrical conductivity are almost in direct proportion with the number of sites available for polaron hopping and can thus easily be rationalized.

Based on the closest match in TEC to other SOFC materials, Fe doped MnCo₂O₄ is considered most promising for the application as a protective coating on SOFC metallic interconnects.

Funding

Financial support from the Faculty of Natural Sciences at NTNU is acknowledged.

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Supplementary material

Thermogravimetric analysis (TGA) was performed using TG 439 Thermo-Microbalance from Netzsch. The mass change of the sample is measured against a reference (Al_2O_3 powder) and in principle, this should eliminate any buoyancy effects. This means that a measurement with empty crucibles should result in no recordable mass change with change in temperature. In practice, this was not the case. Figure S1 shows the measurement with empty crucibles between room temperature and 800 °C, with heating and cooling rates of 10 K/min (first cycle) and 1 K/min (second cycle). All the results presented in the paper were corrected against this background measurement. Figure S1 also shows the measurement results of the MnCo_2O_4 powder before correction for background was made. It may be noticed that the mass change of the sample between 300-500 °C is significantly larger than the mass change in the background measurement. Furthermore, the characteristic peak in mass change in this temperature interval is reproduced with different samples and using different heating/cooling rates.

Figure S1. Background measurement for thermogravimetric analysis made with empty alumina crucibles and original measurement data for MnCo_2O_4 before applying the background correction.

To improve readability of the TGA results, the inherent noise of the measurement was reduced by fitting the experimental data to a polynomial curve. This was performed using the negative exponential function in Sigmaplot 13.0. The polynomial degree was set to 1 or 2 based on visual evaluation of best fit to original data. Figure S2 shows an example of the original data and polynomial fit for the MnCo_2O_4 material.

Figure S2. Polynomial fit of the experimental thermogravimetric analysis data of MnCo_2O_4 .

Figure S3 shows X-ray diffraction patterns for spinel ceramics in air at 1100 °C (5h) + 800 °C (12 h). These results were used to determine the lattice parameters, as described in the paper.

Figure S3. X-ray diffractograms of spinel ceramics sintered in air at 1100 °C (5h) + 800 °C (12 h).

Only the heating parts of the dilatometer measurements were shown in the paper. Figure S4 shows both the heating and cooling curve for the Fe1 composition, measured between room temperature and 1000 °C. A significant negative hysteresis is observed between the heating and cooling segments. Figure S4 also shows a new sample of the same material measured between room temperature and 800 °C. The hysteresis is seen to be considerably reduced, although not completely eliminated when the measurement is reversed at lower temperature. Based on this, the large hysteresis when the measurement is reversed at 1000 °C was attributed to creep or the onset of Co-reduction in the materials.

Figure S4. Heating and cooling curve for the thermal expansion data of the Fe1 material. Measurement reversed at 1000 °C (left) and 800 °C (right).

A hysteresis in the electrical conductivity of the MnCo_2O_4 material was observed between heating and cooling (Figure 6 in the paper). Figure S5 shows the electrical conductivity for two different samples of the Cu1 material. The sample with 60 % density displays hysteresis in electrical conductivity between heating and cooling (Fig. 6b). The sample with 84 % density does not display any hysteresis (Fig. 6a). The reason for the hysteresis in electrical conductivity is discussed in the paper.

Figure S5. Electrical conductivity of Cu1 measured during heating and cooling in air . Results for two samples with different sample density, (a) 84 % and (b) 60 %. The results are excerpts from measurements between room temperature and 1000 °C and are corrected for sample porosity.

Thermogravimetric analysis of MC, Fe3 and Cu3 powders is shown in Figure S6 and S7. The initial mass loss below 200 °C may be attributed to evaporation of adsorbed moisture. Upon further heating, all of the samples gain mass up to ca. 400 °C, before the mass decreases again. The results are discussed in the paper.

Figure S6. Thermogravimetric analysis of MC powder (obtained from a crushed ceramic sintered 1100 °C+ 800 °C) showing relative weight change during heating in air for two consecutive cycles. Heating and cooling rate 2 °C/min. Red solid lines = heating, blue stippled lines = cooling

Figure S7. Thermogravimetric analysis of MC, Fe₃ and Cu₃ powders (calcined 650 °C) showing relative weight change during heating in air. Solid lines = heating, stippled lines = cooling. (a) heating and cooling rate 10 °C/min, (b) second cycle of samples in a) with heating and cooling rate 1 °C/min. The curves have been shifted to start at 100 % mass.