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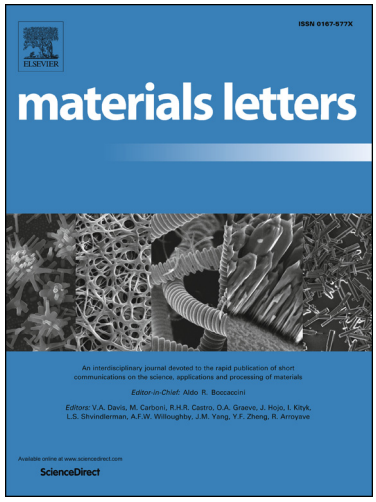

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Co-deposition of CuO and $Mn_{1.5}Co_{1.5}O_4$ powders on Crofer22APU by electrophoretic method: structural, compositional modifications and corrosion properties

S. Molin[1], A.G. Sabato[2], H. Javed[2], G. Cempura[3], A.R. Boccaccini[4], F. Smeacetto[2*]

[1] Department of Energy Conversion and Storage, Technical University of Denmark, Risø Campus, 4000 Roskilde, Denmark

[2] Department of Applied Science and Technology, DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

[3] AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Krakow, Poland

[4] Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Cauerstr. 6, 91058 Erlangen, Germany

* corresponding author, e-mail federico.smeacetto@polito.it, phone +39 011 0904756

Abstract

Co-deposition of CuO and $Mn_{1.5}Co_{1.5}O_4$ by single step electrophoretic deposition is used to produce ~15 µm coatings on Crofer22APU steel, which finds use as interconnect for high temperature solid oxide cells. Sintering of the green coatings in reducing and then oxidizing conditions led to formation of a mixed $(Cu,Mn,Co)_3O_4$ spinel. By the incorporation of Cu, the density of the coatings improved. Scanning and transmission electron microscopy observations, supplemented with energy dispersive spectroscopy, confirmed dissolution of Cu in the spinel phase. For the un-doped $Mn_{1.5}Co_{1.5}O_4$ both the tetragonal and cubic phases are detected at room temperature by x-ray diffractometry, whereas the addition of Cu seems to stabilize the cubic phase. Initial (~1000 hours) high temperature corrosion evaluation at 800°C in air showed promising properties of the mixed spinel coating.

Keywords: ceramics; corrosion; deposition; sintering;

Introduction

Mn-Co spinels have been suggested as the best candidates for protective materials for steel interconnects of Solid Oxide Cells [1,2]. They possess high electrical conductivity and thermal expansion coefficient (TEC) compatibility with metallic interconnect substrates. The doping of manganese cobaltite spinel with transition metals such as Fe and Cu has been previously evaluated [3]. Cu is an attractive dopant for increasing both the sinterability, the electrical conductivity of the spinel as well as the density of the obtained coatings with regard to the prevention of chromium volatilization [4,5]. The Cu/Fe doped spinel powders are typically prepared "ex-situ" (by soft chemistry or mechanochemical synthesis) in a separate process before the deposition, thus increasing the processing time and cost [6–8].

The novelty reported in this paper is the ability of using EPD to simultaneously co-deposit the Mn-Co spinel and the dopant (Cu) by adding a controlled amount of the second phase (CuO) to the suspension, thus in only one deposition step. Though the EPD has been used for preparation of protective coating in a few studies [9–13], co-deposition approach proposed in this work is a new and an interesting route.

Experimental

Crofer22APU (0.3 mm thick, VDM Metals, Germany) was used as substrate for EPD. Commercial $Mn_{1.5}Co_{1.5}O_4$ powder (mean particle size of 0.36 μm), purchased from American Elements (USA) was mixed with CuO (Alfa Aesar) obtaining suspensions with different CuO contents. In particular, 0 wt.%. 5 wt.% and 10 wt.% of CuO were used, maintaining constant the solid content of the ethanol and deionized water based (60/40 vol. of $EtOH/H_2O$) suspensions (37.5 g L^{-1}). The Crofer22APU substrates were cleaned in acetone prior to the electrophoretic deposition. A Crofer22APU substrate was used as the counter electrode in the EPD cell. The distance between both electrodes was 10 mm and a constant voltage of 50 V was applied for 20 secs. The samples were dried at room temperature for 24 h in air.

Un-doped and Cu-doped $Mn_{1.5}Co_{1.5}O_4$ coated Crofer22APU samples (labeled as 5CuMCO and 10CuMCO respectively) were processed with a two-step sintering procedure (first 900 °C for 2hrs in a Ar-4% H_2 and subsequently at 900 °C for 2hrs in air). For the x-ray diffractometry (XRD) studies, Bruker D8 Advance with CuKα radiation was used. For in-situ high temperature XRD measurements, an MRI attachment with Pt-Rh heating strip was used. Corrosion exposures of the samples were performed for 1000 hours in static air at 800°C in a chamber furnace. For each type of coated samples, 5 individual samples were used for reproducibility and an average weight gain values are presented. Area specific resistance (ASR) measurements have been performed according to the procedure presented in [14]. Metallographic cross sections of the coated alloys were prepared by embedding samples in epoxy and polishing to 1 µm finish (using Struers consumables). SEM analyses of sample surfaces and cross-sections were performed by using Hitachi TM3000 with EDS from Bruker (Quantax70 SDD). The sample obtained from the suspension containing the 5 wt% of CuO was submitted to STEM/EDS/SAED investigations. These analyses were performed with a FEI Tecnai G2 and a Titan Cubed 2 60-300 (STEM EDS) microscopes on a thin lamella prepared by focused ion beam (FIB using Zeiss NEON CrossBeam 40) at the steel/coating interface.

Results and discussion

Formation of Cu-doped spinel by a co-deposition process using commercial powders can be considered a new and promising route for spinel modification. As earlier works show [4,5,15], TEC and electrical conductivity might be matched to a desired level by doping of the spinel by Cu and/or Fe, thus tailoring for specific alloy and possible operation temperature.

Figure 1 shows SEM images of the coated alloy surfaces after the reduction (A, B, C) and subsequent re-oxidation step (D, E, F). Small metallic Co particles are observed in all reduced samples with larger Cu particles clearly distinguishable in the doped samples. After the re-oxidation, coating looks uniform and no residual CuO can be detected. Despite the large amount of

copper, no cracks were detected on the surface of the 10CuMnCo, as it can be observed in Figure 1F.

XRD patterns after the reducing heat treatment are shown in Figure 2 A. As expected, the MnCo spinel was decomposed into MnO and Co, while the CuO doped spinel decomposed to MnO, Co and Cu (the intense peaks of Pt are due to the sample holder). After the re-oxidation step (900°C 2hrs), re-formation of the spinel is visible. In the case of the un-doped MCO, both cubic and tetragonal phases are distinguishable, whereas for the Cu-doped, the peaks from the tetragonal phase are less intense. This is confirmed by HT-XRD (Figure 2 C). At high temperatures (>500°C) only a cubic phase is visible. Upon reaching 500°C, peak from the tetragonal phase is becoming visible, indicating formation of the new phase below this temperature. This is seen for the un-doped spinel. For the 5CuMCO spinel, much less of the tetragonal phase forms. This result may indicate that certain parts of the coating do not contain sufficient amounts of copper, allowing domains of the tetragonal phase to remain.

Furthermore, these measurements did not indicate any evidence of the presence of trace amounts of residual CuO in all coatings. These results provide thus further support for the hypothesis that copper becomes incorporated into the manganese cobaltite spinel lattice, thus stabilising the cubic phase.

The cross sections SEM images of the re-oxidized 5 wt.% and 10 wt.% Cu doped MnCo-based coatings, are shown in Figure 3 A and B. The coatings look dense since few residual pores in the coating appear all to be isolated and not interconnected. Furthermore, the Cu distribution appears to be uniform and well distributed throughout the MnCo coating.

The obtained coatings were compact and exhibited a good adhesion to the Crofer22APU substrate. The thickness of the Cu coatings was found to be 13 and 10 microns for the 5CuMCO and 10CuMCO respectively, thus highlighting a higher degree of densification with a higher amount of added Cu.

The corresponding FIB lamella with relative EDS mapping and SAED analyses are shown in Figure 3 C-D. STEM/EDS analysis, presented for the 5CuMCO sample (C) confirms that Cu is evenly distributed in the coating. The SAED patterns (Figure 3 D) were collected on two different grains on which Mn, Co and Cu seems to be present together, thus suggesting that Cu entered the spinel structure. The SAED identification revealed the presence of the $MnCo_2O_4$ cubic phase only.

The high temperature corrosion properties of the modified spinels were verified and compared with the un-doped spinel by weight gain (corrosion kinetics) and area specific resistance (ASR) measurements, presented in Figure 4 A and B. Comparing the weight gains of the coated alloys, the results are similar with only minor differences found. The addition of Cu to the spinel does not result in deteriorated corrosion protection capabilities. It is worth noting, that uncoated Crofer22APU has a corrosion rate of ~6×10^{-14} g^2 cm^{-4} s^{-1} in similar conditions [16]. The application of coatings reduces corrosion rate by a factor of ~10. In the ASR measurement, slightly lower values were found for the Cu-doped spinels, but up to 1000hrs of test the differences can be considered within the experimental uncertainties. Based on these initial corrosion examinations, it might be concluded that incorporation of Cu does not lead to deteriorated high temperature corrosion protective properties, and slightly improved the ASR behaviour, as studied for the 1000 hours period.

Conclusions

Cu-doped manganese cobaltite coated Crofer22APU samples were successfully processed by electrophoretic deposition. Single step co-deposition of the $Mn_{1.5}Co_{1.5}O_4$ and CuO is an effective way for the spinel modification since single phase materials has been obtained. The effect of Cu doping was reviewed and discussed with respect to structural, compositional changes and sintering behavior. Cu seems to stabilize the cubic phase of the spinel, decreasing the amount of the tetragonal phase. The addition of Cu improves the coating density, which should be beneficial for

blocking Cr vaporization. Good electrical and corrosion protective properties of the modified manganese cobaltite spinel were shown.

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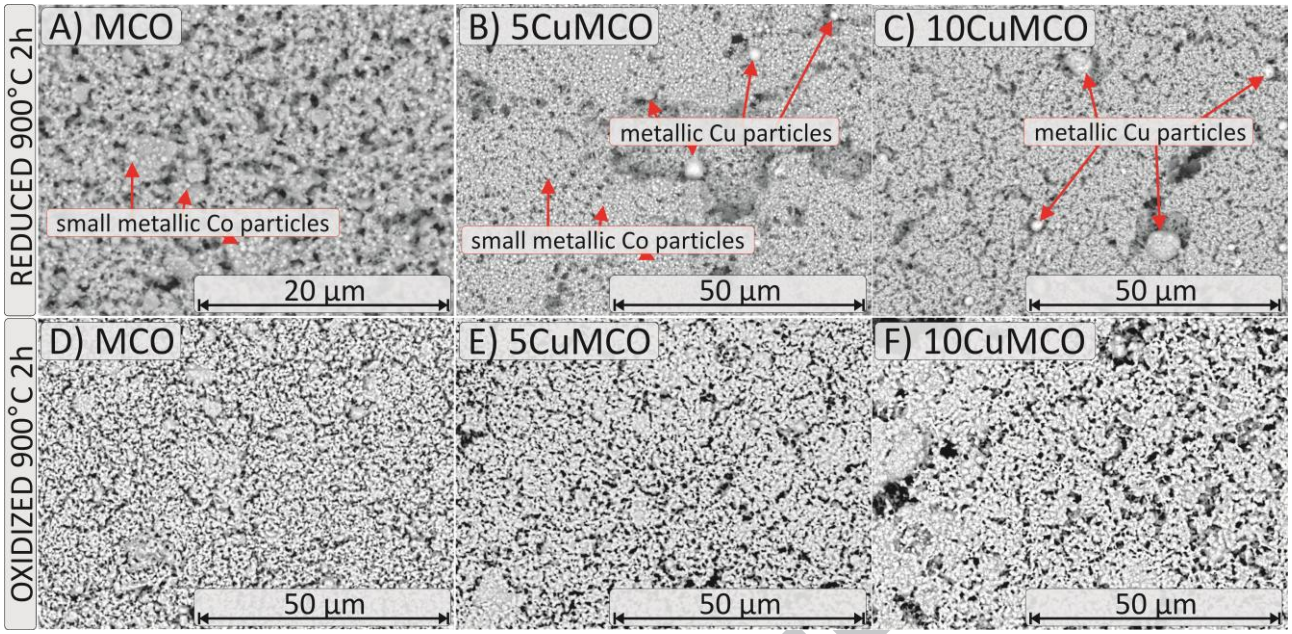
Captions

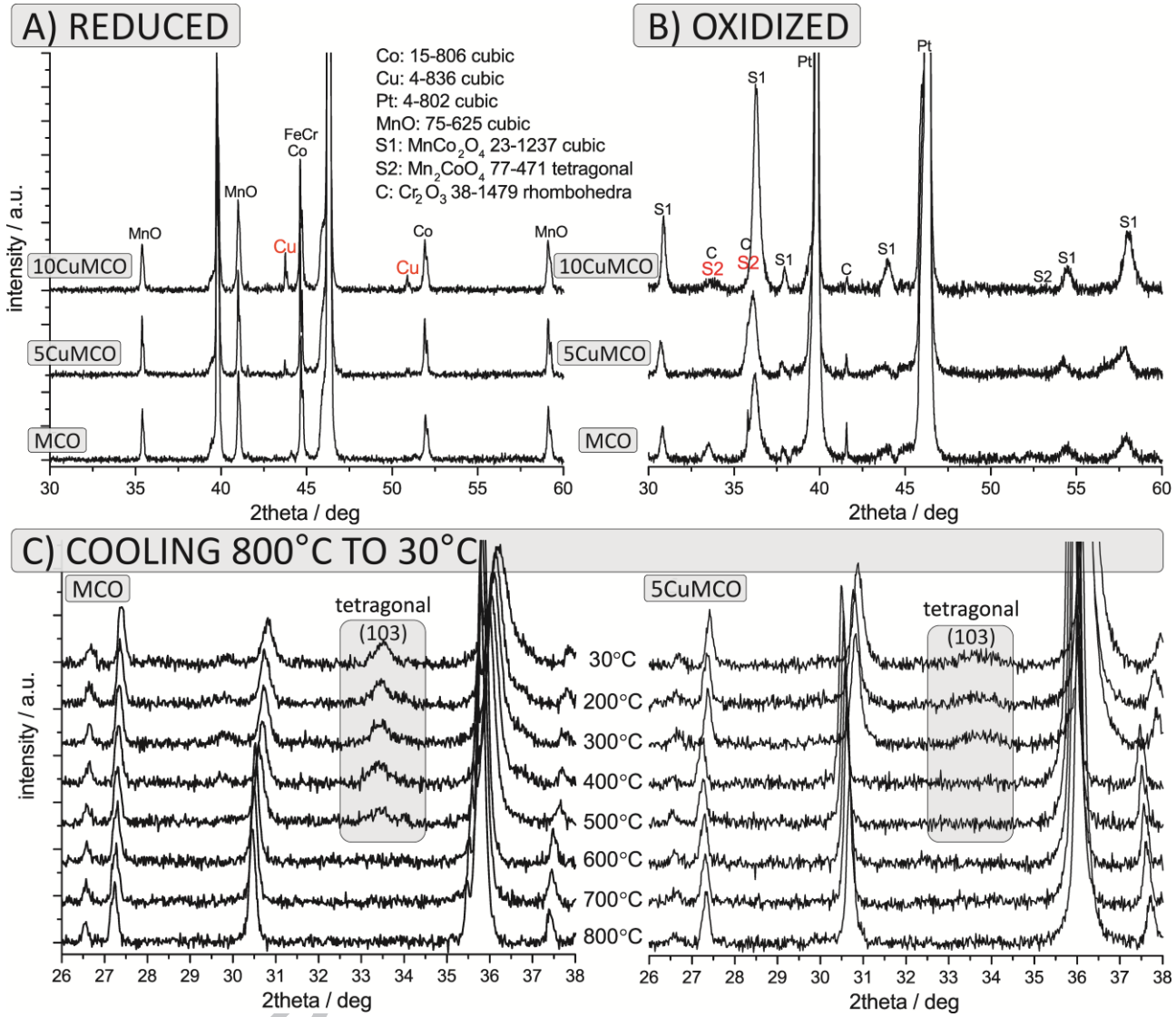
Figure 1. SEM surface images of reduced (top row) and re-oxidized (bottom row) coatings A,D) MCO, B,E) 5CuMCO and C,F) 10CuMCO and re-oxidized coatings.

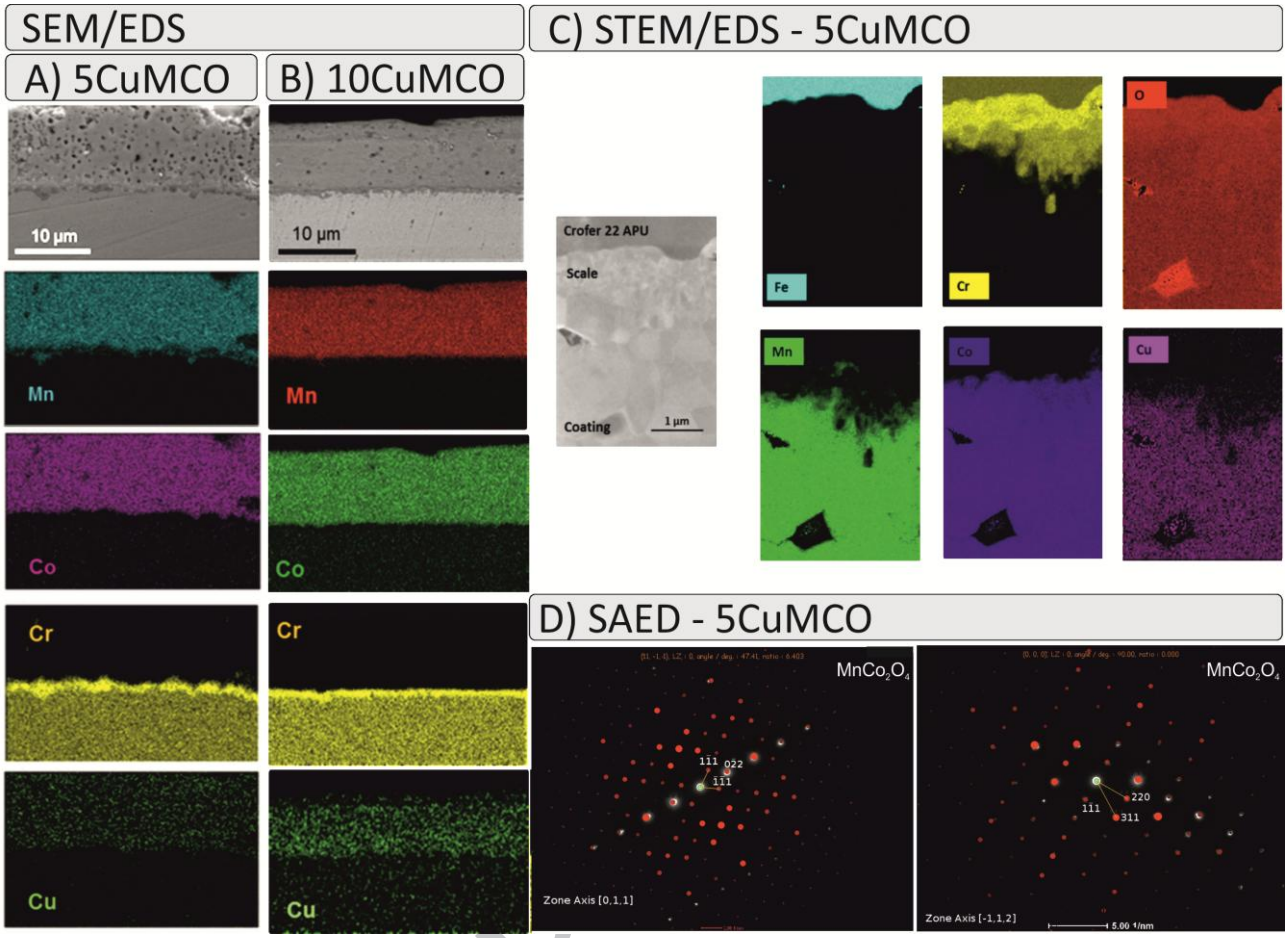
Figure 2. XRD study of the coated alloys. Spectra of: A) reduced coatings at RT, B) oxidized (800°C) coatings at RT, C) HT-XRD measured during cooling from 800°C to RT.

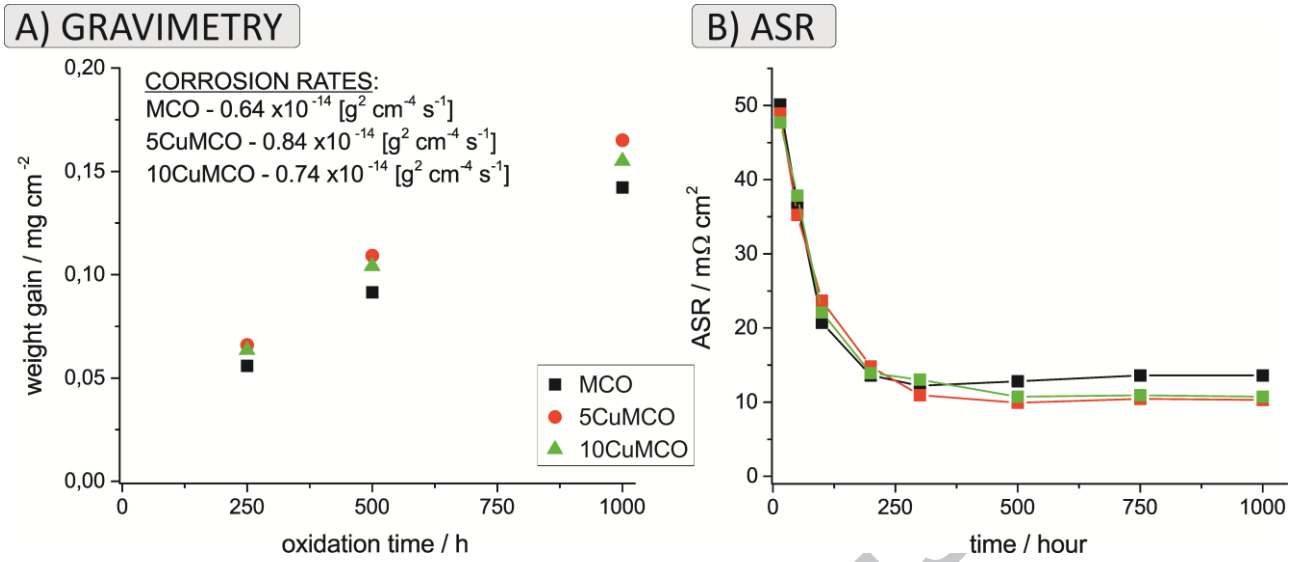
Figure 3. SEM (A,B) and TEM/SAED (C) cross-sections and elemental maps of A) 5CuMCO, B) 10CuMCO and C) 5CuMCO. D) experimental and superimposed theoretical SAED patterns.

Figure 4. Comparison of (A) cyclic thermogravimetric and (B) area specific resistance measurement (B) of the coated samples.




A) REDUCED
B) OXIDIZED
Co: 15-806 cubic
Cu: 4-836 cubic
Pt: 4-802 cubic
MnO: 75-625 cubic
S1: MnCo2O4 23-1237 cubic
S2: Mn2CoO4 77-471 tetragonal
C: Cr2O3 38-1479 rhombohedra
intensity / a.u.
10CuMCO
5CuMCO
MCO
MnO
Cu
FeCr
Co
S1
S2
C
Pt
2theta / deg
C) COOLING 800°C TO 30°C
tetragonal
(103)
30°C
200°C
300°C
400°C
500°C
600°C
700°C
800°C


SEM/EDS
A) 5CuMCO
B) 10CuMCO
10 µm
10 µm
Mn
Mn
Co
Co
Cr
Cr
Cu
Cu
C) STEM/EDS - 5CuMCO
Crofer 22 APU
Scale
Coating
1 µm
Fe
Cr
O
Mn
Co
Cu
D) SAED - 5CuMCO
MnCo2O4
111
022
111
Zone Axis [0,1,1]
MnCo2O4
111
220
311
Zone Axis [-1,1,2]
5.00 1/nm



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- Cu stabilized the cubic phase of the MnCo spinel
- Cu slightly improved the ASR behavior, as studied for the 1000 hrs period