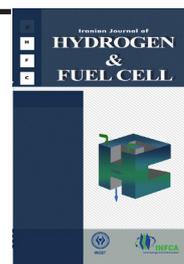


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## Synthesis and characterization of nanostructured $\text{Cu}_x(\text{Mn}_{1.5-x/2}\text{Co}_{1.5-x/2})\text{O}_4$ as an interconnect coating for solid oxide fuel cell

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### Abstract

Manganese-Cobalt Oxide (MCO) spinel oxide is a promising composition as a protective coating for the metallic interconnects of a SOFC. In an effort to reach better properties, such as suitable thermal expansion match, good electrical conductivity, and fine structural stability, various elements have been doped in the spinel structure. In this study, the effect of Cu addition as a dopant on the electrical properties of MCO spinel is investigated. Powders with a nominal composition  $\text{Cu}_x(\text{Mn}_{1.5-x/2}\text{Co}_{1.5-x/2})\text{O}_4$  ( $x=0, 0.15, \text{ and } 0.3$ ) were successfully synthesized based on the sol-gel Pechini method. The phase composition and microstructure of the synthesized powder were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The XRD results revealed that a pure phase with a spinel structure was obtained for different amounts of doped samples. The microstructural characteristics of the synthesized powders revealed that the average particle size of the powder decreased from about 84nm to 52nm with the introduction of Cu. To evaluate the effect of Cu on the sintering behavior of MCO, the powder was pressed and sintered at 1200°C for 2 h. The density measurement and FESEM results showed that the addition of Cu promotes the sintering mechanism, and the density was improved. In addition, the electrical properties of the samples were evaluated using the 2probe direct current technique at different temperatures. The results revealed that the addition of 0.3 Cu increased the electrical conductivity of the sample from 0.102 to 0.218  $\text{S}\cdot\text{cm}^{-1}$  at 800°C. This significant improvement can be attributed to the promotion of sintering and also facilitating electron flow by substitution of  $\text{Cu}^{+2}$  cations in the spinel structure.

## 1. Introduction

A Solid Oxide Fuel Cell (SOFC) is an electrochemical device that directly converts fuel to electricity. Electrochemical reactions occurred thermodynamically

at high operating temperatures (in the range of 600-1000°C). This high temperature could lead to the degradation of different parts of the device. In a planner high-power-density configuration, a series of anode-supported single cells are connected to make

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a stack of SOFCs [1-3]. Metallic interconnects are placed between single cells to collect current and construct the skeleton of the stack. Since the interconnect separates the oxidant and fuel gases, it must have good stability in both anodic and cathodic atmospheres. In the selection of materials used in interconnects, it is important to match their thermal behavior with other components. Failure to adjust the thermal expansion coefficient (TEC) at high temperatures will lead to the loss of performance and destruction of components [2, 3]. Various types of interconnects have been investigated over the last two decades, and currently, metallic interconnects, such as stainless steel alloys, are the best candidate due to their lower cost, better performance, and good thermal coefficient compatibility with single-cell components [4]. Briefly, research on commercial metallic interconnects, such as Corofer 22 APU, E-brite, ZMG 232, and AISI 430, has revealed that the presence of some alloying elements, such as Cr and Si, at SOFC operating temperatures led to degradation due to the formation of oxide scale on the surface of the interconnects [5-8]. One of the main solutions for this is to apply protective coatings on the surface of the interconnects to avoid the formation of unwanted oxide scales. Various studies have shown that spinel materials with the general structure  $((A, B)_3O_4)$ , and in particular  $(Mn, Co)_3O_4$ , function well as a coating material for metallic interconnects because they prevent the formation of chromium oxide scales [8-11].

Although the Mn-Co (MCO) spinel has shown effective results, it is interesting to see the effects of alternative elements. Rare earth and reaction elements have the most potential to add either a single dopant or co-dopant into the MCO spinels [10, 12]. The approach of adding a dopant to the spinel structure is to improve the adhesion of the coating, sintering temperature correction, increase the electrical conductivity, and reduce the oxidation rate. Among the reactive elements, Cu can improve electrical performance. Cu as a dopant improves the conductivity and matches the TEC with the Crofer interconnect [11, 13, 14].

The main goal of this study is to first synthesize a

Cu-doped MCO spinel using the sol-gel method and then to evaluate the effect of Cu content on MCO properties. The obtained powders were characterized by using X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). Afterward, the powders were isostatically pressed and sintered at 1200°C. The electrical conductivity and density of the samples were comparatively analyzed. Finally, FESEM analyses were conducted for further structural investigation.

## 2. Experimental

Cu-doped MCO spinel nanopowders were prepared by the citric acid-nitrate process. A desired amount of  $Mn(NO_3)_2 \cdot 4H_2O$  (MERCK 99%),  $Co(NO_3)_2 \cdot 6H_2O$  (MERCK 99%) as a base of spinel, and  $Cu(NO_3)_2 \cdot 2.5H_2O$  (MERCK 99%) as a dopant were dissolved with distilled water (as a solvent) on hot-plate stirrer to synthesize  $Mn_{1.5}Co_{1.5}O_4$  (MCO),  $Cu_{0.15}(Mn_{1.425}Co_{1.425})O_4$  ( $Cu_{0.15}$ MCO), and  $Cu_{0.3}(Mn_{1.35}Co_{1.35})O_4$  ( $Cu_{0.3}$ MCO) compounds. Table 1 shows the chemical composition of the synthesized powders.

The citric acid (>99.5%, Sigma Aldrich), as a chelating agent, was added to the solution with the molar ratio of 1.5 to metal nitrates under stirring conditions. Then the mixed solution was heated to 70°C and kept for 1 h. The resulting solution was again heated up to 150°C to form a viscose gel. The gel was dried in an oven at 250°C until it became ash. The ash was calcined in air at 800°C for 4 h with a heating rate of 10°C /min. The crystalline structure and phases were characterized by X-ray diffraction (Philips X'pert Pro) using Cu K $\alpha$  radiation in the  $2\theta=10-80^\circ$  range at a step size of 0.02° and count time of 1 s. The microstructure and composition of the synthesized nanopowders were characterized by a field emission scanning electron microscope (FE-SEM MIRA3 TESCAN) equipped with an energy dispersive spectroscopy (EDS). For evaluating the electrical behavior and density of the synthesized powder, a desired amount of powder was

pressed (100 bar) into disc shape samples with a diameter of 15 mm and thickness of 1~ 1.5 mm. The obtained discs were sintered at 1200°C for 4 h. After the sintering process, the density of the samples was measured by the Archimedes method conforming to ASTM B962-17. Afterward, the disc samples were prepared for electrical tests by applying a silver paste to both disk sides and curing at 800°C for 1h. Then, the electrical conductivity of the pellets was measured by using the 2-probe technique at operating temperature. In the final step, FESEM analysis was performed on a cross-section of the samples to study morphology, element distribution, interaction at the interface of the silver-paste substrate, and grain size.

**Table 1. Chemical Composition of Synthesized Powders**

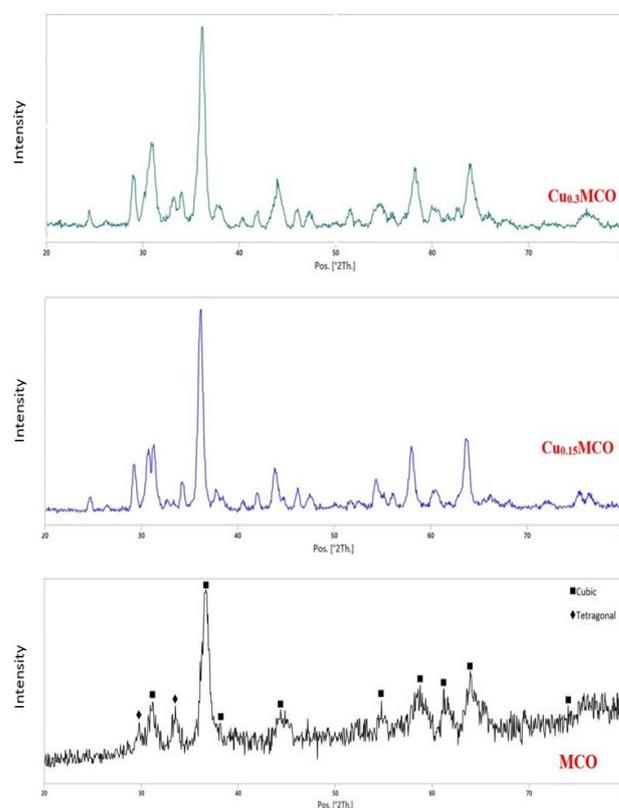
Chemical composition	Code
$Mn_{1.5}Co_{1.5}O_4$	MCO
$Cu_{0.15}(Mn_{1.425}Co_{1.425})O_4$	$Cu_{0.15}MCO$
$Cu_{0.3}(Mn_{1.35}Co_{1.35})O_4$	$Cu_{0.3}MCO$

### 3. Results and Discussion

Figure 1 shows XRD patterns of MCO,  $Cu_{0.15}MCO$ , and  $Cu_{0.3}MCO$  synthesized by the Pechini method. As can be seen, the diffraction patterns for all powders can be indexed to two compounds, mainly  $MnCo_2O_4$  and  $Mn_2CoO_4$ , with a cubic and tetragonal crystal structure, respectively. Thus, the synthesized  $Mn_{1.5}Co_{1.5}O_4$  spinel is a dual-phase material comprised of both cubic and tetragonal structures. The results obtained from the crystal structure are consistent with other research findings [12, 13]. No characteristics peak for secondary or impurity phases were observed. This means that doping Cu into MCO causes no significant change in the crystal structure, as was observed by other researchers [14]. Typically, a dual spinel oxide has the general structure  $A[B_2]O_4$ , where A is an oxygen-coordinated cation at the tetrahedral position and B is an oxygen-coordinated cation at the octahedral

position [15]. Cu cation expands the lattice structure [16]; therefore, as the amount of Cu dopant increases due to the larger Cu ions, and the peaks shift to smaller  $2\theta$ .

Despite the high compatibility of the diffraction peaks for the three samples,  $Cu_{0.15}MCO$  showed a new peak around the  $2\theta=32^\circ$ . This means that the addition of Cu to the MCO composition resulted in the formation of a spinel phase with a tetragonal crystal structure. The appearance of new peaks after adding Cu has been reported by many.



**Fig. 1. XRD patterns of synthesized powders after calcination at 800 °C (JCPDS card 23-1237 and JCPDS card 77-471).**

Figure 2 illustrates the micrographs of as-synthesized powders. Doping elements in the spinel structure lead to compaction of the crystal structure and the formation of finer grains [17, 18]. As can be seen, the powders are nano-scale particles with homogeneous distribution and average particle sizes of 84, 66, and 52 nm for MCO,  $Cu_{0.15}MCO$ , and  $Cu_{0.3}MCO$ , respec-

tively. Accordingly, the influence of doping Cu into MCO on the particle's morphology seems to be minor. The average particle size of the powder is inversely proportional to the amount of Cu dopant [10, 19, 20].

There is no clear theory explaining how doping Cu reduces particle size in spinels, but generally, it might be due to the increment of nucleation sites and reducing the energy for nucleation.

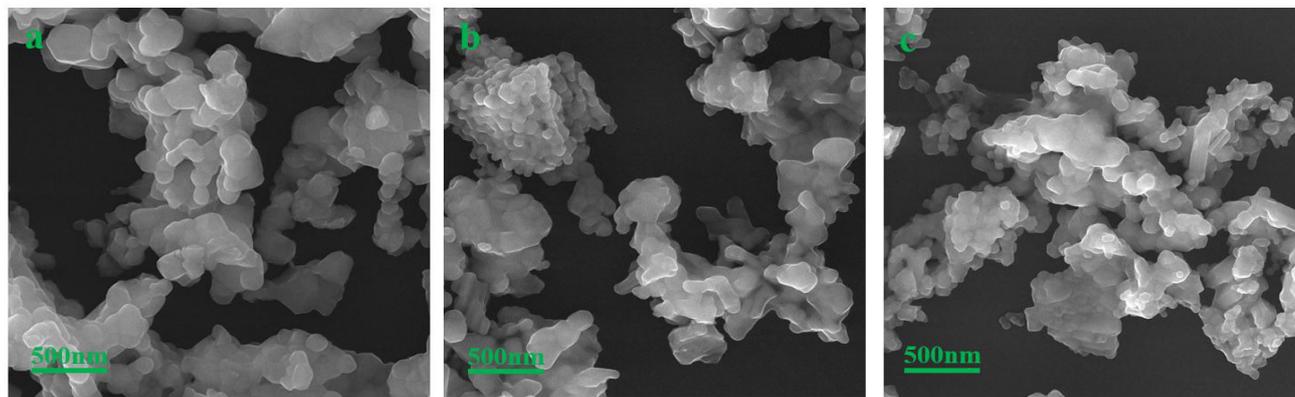


Fig. 2. FE-SEM photographs of nano-powders (a) MCO, (b)  $\text{Cu}_{0.15}\text{MCO}$ , and (c)  $\text{Cu}_{0.3}\text{MCO}$  synthesized by the sol-gel Pechini method.

The cross-section micrographs of sintered samples (MCO,  $\text{Cu}_{0.15}\text{MCO}$ , and  $\text{Cu}_{0.3}\text{MCO}$ ) are presented in Fig. 3. As can be seen, the grain size of  $\text{Cu}_{0.15}\text{MCO}$  is larger than the other two samples. It seems the addition of Cu to the spinel structure first leads to an increase in grain size, although the addition of 0.3 Cu

decreased the grain size. On the other hand, the density of the sample increased with the addition of Cu, which reveals that Cu promotes the sintering behavior of MCO. Improvements in spinel density with the addition of Cu have been previously reported [21-23].

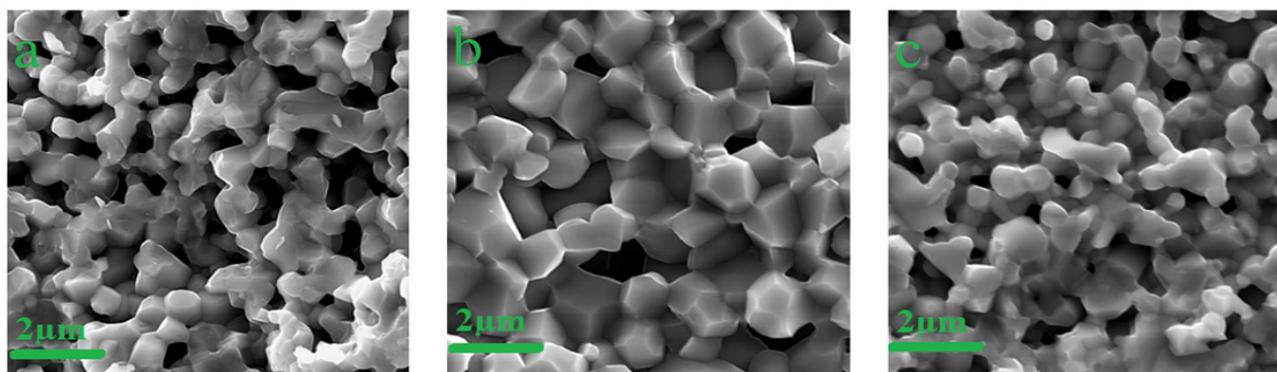


Fig. 3. Microstructure of MCO,  $\text{Cu}_{0.15}\text{MCO}$ , and  $\text{Cu}_{0.3}\text{MCO}$  from a cross-section perspective.

To investigate the effect of a dopant on the sintering behavior of the samples, the theoretical density of the discs was determined by the Archimedes method. The results showed that increasing the amount of Cu dopant can improve density in comparison with the bulk sample, which is in agreement with the FESEM re-

sults. Table 2 shows the density of discs sintered at  $1200^\circ\text{C}$ .  $\text{Cu}_{0.3}\text{MCO}$  has the highest density in comparison to the others, which was reported in other researches as well [24]. This improvement might be due to the presence of a Cu-rich area in the grain boundaries as well as a decrease in surface energy.

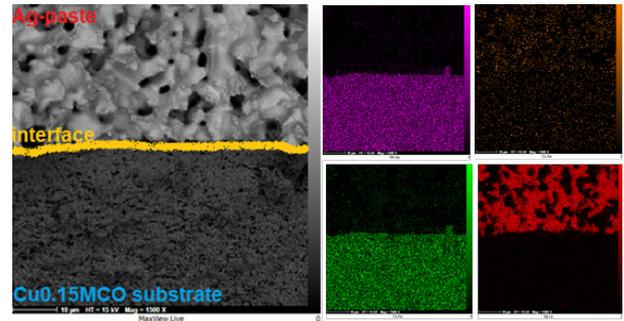
**Table 2. Density of Discs Sintered at 1200°C**

Sinter disc composition	(%)Density
MCO	88
Cu <sub>0.15</sub> MCO	91.3
Cu <sub>0.3</sub> MCO	92.1

The micrographs and EDS elemental maps of cross-sections of Cu<sub>0.15</sub>MCO after the electrical test are presented in Fig. 4. It might be informative to investigate the interactions of silver and MCO after the electrical test. Theoretically, we expect that self-diffusion occurs at the interface of the substrate and paste at high temperatures. But the microstructure of the Cu-doped compositions appeared homogeneous after prolonged annealing of the polished cross-section of the sintered pellets.

It worth mentioning that other samples were almost the same. The Cu map indicates that it is nearly fully dispersed in the as-synthesized powder, and no changes occurred after the electrical test. Although the Cu has been diffused in the Ag layer, there might have been some interphases formed that need further investigation to be clarified. Besides, the Ag paste has partially diffused in the structure at operating temperature, which can increase conductivity, as reported by other researchers [23, 24]. The Mn and Co maps are nearly the same due to the same stoichiometry; however, the migration of Mn to the interface is more than Co, which could be due to the lower manganese atomic radius.

The electrical conductivity ( $\sigma$ ) calculated for the spinel materials by measuring resistance against the temperature is presented in Table 3. The materials were sintered in the air at 1200°C. Then, the electrical conductivity of each disc sample was measured by the 2-probe technique at 600, 700, and 800°C. The results show that the addition of the Cu element into the spinel structure improves the electrical conductivity.



**Fig. 4. SEM image and EDS elemental mapping of a polished cross-section of Cu<sub>0.15</sub>MCO, where purple represent Mn, orange is the Cu, green is the cobalt, and red is the silver.**

Increasing the electrical conductivity is directly related to increasing the amount of Cu dopant. The electrical conductivity has been calculated via the following equation:

$$\sigma = \frac{L}{\rho} = \frac{L}{RA}$$

**Table 3. Electrical Conductivity of the Discs at Various Temperatures**

Disc code	$\sigma_{600}$ (S.cm <sup>-1</sup> )	$\sigma_{700}$ (S.cm <sup>-1</sup> )	$\sigma_{800}$ (S.cm <sup>-1</sup> )
Mn <sub>1.5</sub> Co <sub>1.5</sub> O <sub>4</sub>	0.041	0.059	0.102
Cu <sub>0.15</sub> (Mn <sub>1.425</sub> Co <sub>1.425</sub> )O <sub>4</sub>	0.07	0.091	0.16
Cu <sub>0.3</sub> (Mn <sub>1.35</sub> Co <sub>1.35</sub> )O <sub>4</sub>	0.153	0.17	0.218

As mentioned before, the Cu element has many benefits as a dopant in the MCO spinel. Many researchers have evaluated the performance of synthesized powders by coating metallic interconnect substrate and reported that the presence of enough Cu not only increases electrical conductivity but also makes it more compatible with the substrate due to its TCE Conformity [7, 24]. Homogeneous Cu dispersion in MCO could facilitate electron transfer pathways and thus improves electrical conductivity. Since the general composition of spinels is AB<sub>2</sub>O<sub>4</sub>, most likely, doping Cu in the structure of MCO and formation of copper compounds in the form of divalent and trivalent at tetragonal and cubic structures could also help improve electronic conductivity [23, 24]. It worth mentioning that as temperature increases, both the number of free electrons and lattice vibrations increase, while the former suppress the lat-

ter, and thus the conductivity increases. Thus, it seems the mechanism for improving the electrical conductivity is based on the placement of active Cu cations inside the spinel structure and improving the flow of electrons through this [25].

#### 4. Conclusions

1. Different amounts of Cu were successfully doped into Mn-Co-O spinel via the citric acid-nitrate method.
2. The cubic and tetragonal MCO spinel phases were characterized with no secondary phases for the doped samples. The average particle size of the produced nanopowder decreased after doping with Cu from 84nm for MCO to 52nm for  $\text{Cu}_{0.3}\text{MCO}$ , which might be due to the increment of nucleation sites.
3. The density of the samples was improved after doping with Cu, which means that doping Cu could promote sinterability.
4. Electrical conductivity measurements proved that doping Cu increased electrical conductivity about 2 times at the same temperature. The most important factor to improve electrical conductivity is the homogeneity of Cu dispersion at MCO, which facilitates electron flow.

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