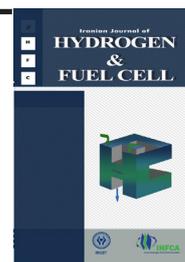


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Synthesis and characterization of Ag-Y co-doped Mn-Co spinel for solid oxide fuel cell application

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Abstract

Mn-Co spinel coating for solid oxide fuel cell interconnects shows a suitable thermal expansion match, acceptable electrical conductivity, and good structural stability. In this paper, the addition of different amounts of Ag and Y as dopants on the physical and electrical properties of the Mn-Co spinel is investigated to improve the coating performance. First, the doped and co-doped powders were successfully synthesized using the Pechini sol-gel method. The synthesized powders were then characterized using X-ray diffraction and field emission scanning electron microscopy. The results confirmed that Ag was not completely doped into the spinel structure and instead acted as an additive, whereas Y caused Mn₃O₄ impurity phase formation at higher mol%. Next, the powders were pressed and sintered at different temperatures (950 and 1050 °C) to evaluate the effect of dopants on the sintering and electrical behavior of the samples. Finally, the electrical conductivity of the samples was evaluated using a 2-probe direct current technique. Although results showed that room temperature electrical conductivity increased upon doping, adding Y had a better effect on conductivity than Ag.

1. Introduction

Solid oxide fuel cells (SOFC) are environmentally friendly energy-conversion devices that efficiently

generate electricity through an electrochemical reaction. SOFCs show promise to provide clean and pollution-free technology at high efficiencies of over 80% [1–3]. The advantages of these cells over traditional energy storage systems, such as fuel flexibility, long-

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term stability, low emissions, and relatively low cost, are due to their solid materials and high operating temperature [4]. All fuel cells have the same basic configuration (an electrolyte and two electrodes), but the different types of fuel cells are mainly differentiated by their electrolyte materials [5]. To increase the output power and voltage, SOFCs are connected in series by components called interconnects. The main function of the interconnect is to establish a proper electrical connection between the anode and the cathode of the cell. Another function of the interconnect is to separate the fuel and oxidizing gases. The interconnects can be either a metallic or ceramic layer. Although ceramic interconnects have shown long-term stability and are applicable for use at high-temperature, they have some drawbacks, like low electrical conductivity and manufacturing difficulties [6]. On the other hand, at lower operating temperatures (600–800 °C), metallic interconnects are more promising [7]. Ferritic stainless steel (FSS) interconnect, such as Crofer22APU and Crofer22H, have received extensive attention in SOFC stacks due to their high chemical stability, mechanical strength, thermal conductivity, and appropriate thermal expansion coefficient with other components [4, 8, 9]. Despite all the advantages of FSS, the performance of SOFCs is limited by its exposure to Cr_2O_3 oxide caused by the degradation of the FSS interconnect at typical SOFC operating temperatures [10]. Therefore, researchers are attempting to identify and coat the interconnects with appropriate materials to solve this problem. These coatings must perform well in terms of electrical conductivity, reduction of the electrical resistance of interconnects, and oxidation rate. Among the studied materials, $(\text{Mn},\text{Co})_3\text{O}_4$ spinel-based coatings offer a significant improvement against Cr vaporization [10, 11]. Based on the literature, various dopants can be added to enhance the structural and functional properties of SOFC. Different dopants, such as Ni, Cu, and Fe, provide different positive results, like a superior oxidation resistance and higher electrical conductivity [12, 13]. Previous studies have reported that Ag and Y exhibit excellent electrical properties, and they impressively decrease

Cr evaporation. Moreover, Ag-doped maintained in the Mn-Co spinel structure and adding Y demonstrated long-term stability [3, 8].

Therefore, in this study, different amounts of Ag and Y were doped in an Mn-Co spinel. The phase evolution of the doped materials was determined by X-ray diffraction (XRD) analysis before and after sintering. Then the microstructure of the powders was studied using field emission scanning electron microscopy (FESEM) analysis. Eventually, the powders were formed into a pellet, and their electrical conductivity and density were measured.

2. Experimental

The sol-gel Pechini method was used to synthesize $\text{Mn}_{1.5-x}\text{Co}_{1.5-x}\text{Ag}_x\text{Y}_x\text{O}_4$ ($x = 0, 0.15, 0.3$). Cobalt(II) Nitrate Hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Manganese(II) Nitrate Tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), Yttrium(III) nitrate Hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Silver Nitrate (AgNO_3), and Citric Acid ($\text{C}_6\text{H}_8\text{O}_7$) were purchased from Sigma-Aldrich and used without further purification. Stoichiometric amounts of nitrates were mixed in distilled water. After adding citric acid, the solution was stirred at 100 °C until a brownish gel formed. Then, the gel was dried in an oven at 250 °C. Afterward, the dried gel was calcined in ambient air at 800 °C for 5 h. To prepare 1.5 cm diameter pellets, 5 wt% PVB (Polyvinyl butyral) was added to the as-synthesized powders and pressed uniaxial (100 MPa). All pellets were sintered at two temperatures (950 °C and 1050 °C) for 5 h. Table 1 shows the prepared sample compositions and names used in this study. XRD analysis was performed on an XPERT-PRO diffractometer using Cu K_α radiation ($\lambda = 1.54060 \text{ \AA}$) to verify the phase evolution of the powders. The cross-section surfaces were examined by FESEM (TESCAN MIRA3) to investigate the morphology of the powders. Lastly, the powders' electrical conductivity and density were measured by a two-point probe electrical conductivity meter and the Archimedes method, respectively.

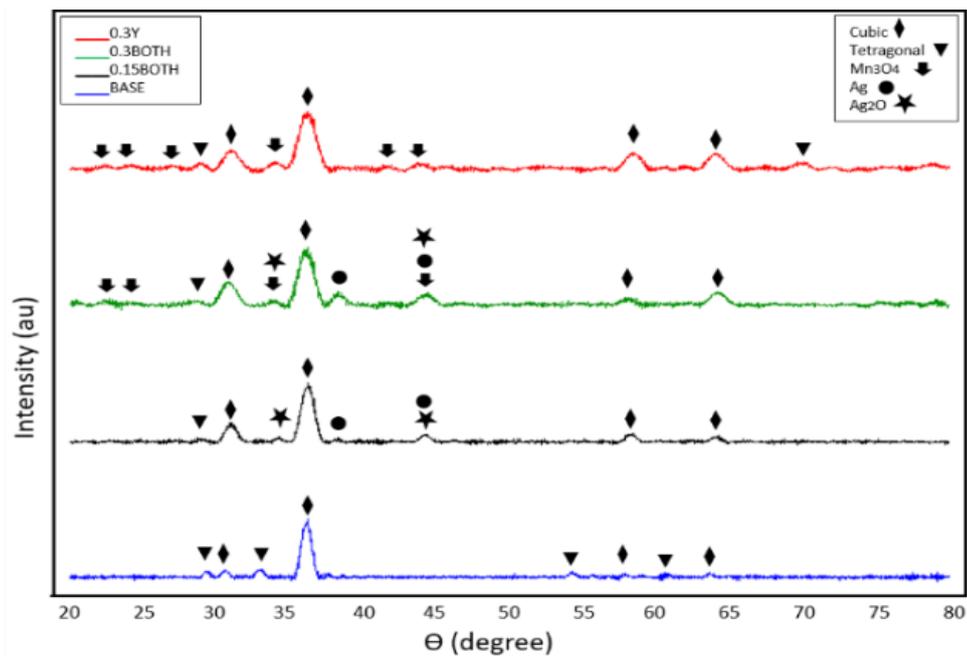
Table 1. Composition, sintering temperature, and label of the prepared pellets.

Pellet Composition	Sintering Temperature (°C)	Sample Name
$Mn_{1.5}Co_{1.5}O_4$	950	Base-9
$Mn_{1.5}Co_{1.5}O_4$	1050	Base-10
$Mn_{1.35}Co_{1.35}Y_{0.3}O_4$	950	0.3Y-9
$Mn_{1.35}Co_{1.35}Y_{0.3}O_4$	1050	0.3Y-10
$Mn_{1.35}Co_{1.35}Ag_{0.15}Y_{0.15}O_4$	950	0.15Both-9
$Mn_{1.35}Co_{1.35}Ag_{0.15}Y_{0.15}O_4$	1050	0.15Both-10
$Mn_{1.2}Co_{1.2}Ag_{0.3}Y_{0.3}O_4$	950	0.3Both-9
$Mn_{1.2}Co_{1.2}Ag_{0.3}Y_{0.3}O_4$	1050	0.3Both-10

3. Results and Discussion

Figure 1 shows the XRD patterns of all the synthesized powders after calcination at 800 °C for 5 h. All of the powders were composed of two spinel phases, the cubic and tetragonal phases, as reported by Yang

et al. [10]. They observed that the addition of both Ag and Y caused the Mn-Co spinel peaks to shift toward the lower angles. This can be explained by the doping of Ag^+ and Y^{3+} , which have larger ionic radiuses, in the spinel structure [3]. Although the Ag was not completely doped in the structure, Ag and the AgO phase formed as impurities for both amounts of Ag (0.15, 0.3). For the Y dopant, the sample with the lower amount of Y (0.15) did not contain any other impurity phases. However, new impurity peaks, related to the Mn_3O_4 phase, were observed in the samples with more mol% of Y. So it can be concluded that after the optimum mol% of Y is added, Mn ions exit the spinel structure and form the Mn_3O_4 phase. Xin et al. [14] reported the appearance of Y_2O_3 and MnO as impurity phases for Y-doped $MnCo_2O_4$ powders. A Mn_3O_4 phase was not observed in that study, which can be explained by the differences in the amount of Y dopant ($Mn_{0.9}Y_{0.1}Co_2O_4$), the spinel composition ($MnCo_2O_4$), or even synthesis parameters such as the time, temperature, and atmosphere of calcination (2h at 700 °C, reduction in hydrogen atmosphere).

**Fig. 1. XRD patterns of all samples after calcination.**

FESEM was used to study the effect of dopant on the microstructure evolution of samples. The results revealed that the amounts and the kind of additives had no significant effect on the size and morphology of the synthesized powders. As the microstructures were almost the same, only the micrograph of the 0.3Y sample after calcination is presented in Figure 2. As can be seen, the powders have a spherical morphology with an average particle size of 44 nm.

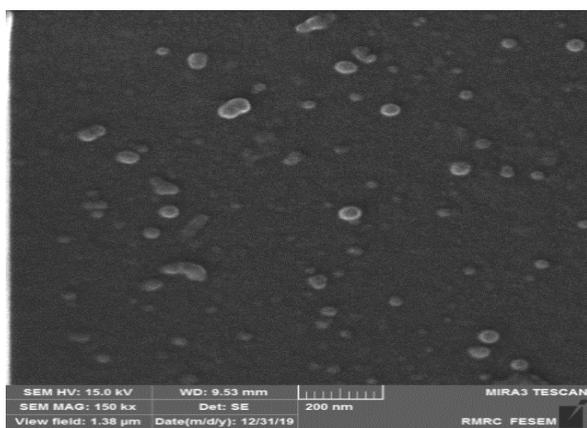


Fig. 2. The micrograph of 0.3Y sample after calcination.

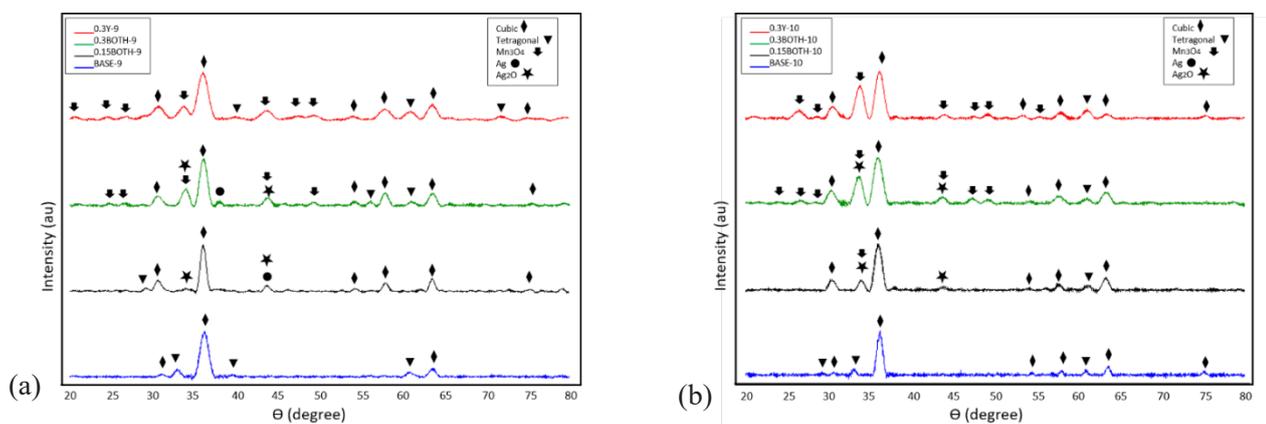


Fig. 3. XRD patterns of samples sintered at (a) 950 °C and (b) 1050 °C.

Figure 4 shows the micrographs of different samples sintered at different temperatures. As can be seen, the dopants did not affect the size or the morphology of the grains. Due to our previous study, we conclude that the addition of Ag and higher sintering temperature improved the densification [15]. Consequently, it seems the addition of Ag can facilitate the sintering of Mn-Co spinel. While the

Figure 3(a) and (b) exhibit the X-ray diffraction patterns of all the samples sintered at 950 °C and 1050 °C. As can be seen in the XRD patterns for the co-doped samples, the sintering temperature increased as the impurity peaks related to the metallic Ag and Ag₂O phases decreased. This was probably due to the rise of the solubility limit of Ag as well as the melting possibility of Ag-rich phases in the structure. For the co-doped samples sintered at 1050 °C, the Ag₂O phase still exists because while some part of Ag₂O has been dissolved, some Ag₂O has remained due to the solubility limit of dissolution in the composition. Moreover, for the samples with more Y dopant, the impurity peaks related to Mn₃O₄ increased with the sintering temperature, which means more Mn departed the spinel structure and formed the mentioned oxide. Peaks related to Mn₃O₄ appear after sintering at the higher temperature 1050 °C for both 0.15 samples, which means although the amount of Y did not increase, the formation of this oxide was due to the higher sintering temperature in the Mn₃O₄ forming procedure.

mechanism is not clear yet, this may be due to the formation of a low-temperature Ag-rich liquid phase, which limits XRD detection. Moreover, as can be seen in the FESEM images, the addition of Y decreased the densification, which is probably due to the Mn₃O₄ formation detected in the XRD results. Figure 5 illustrates the elemental map of the 0.3 both-10 sample.

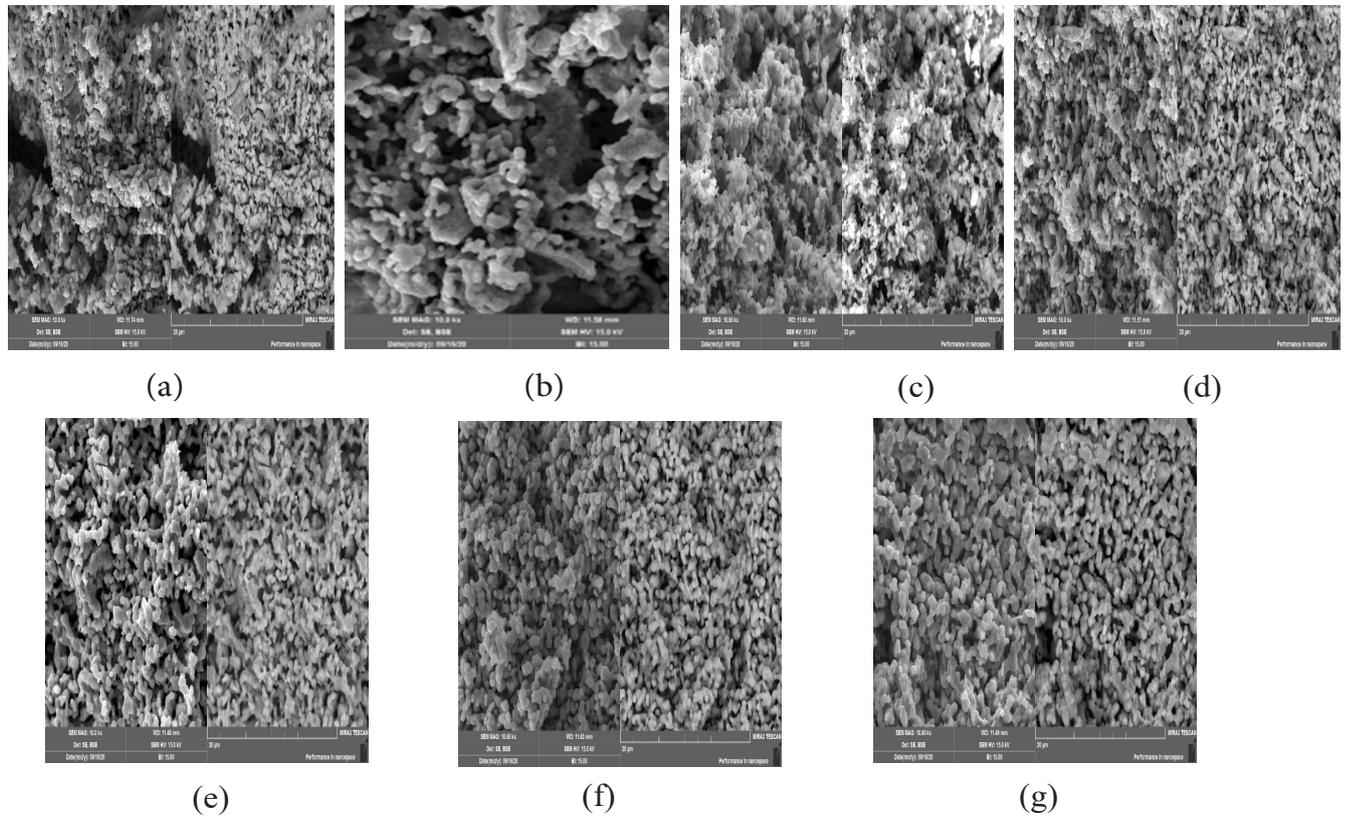


Fig. 4. The micrographs of different samples sintered at different temperatures: (a) Base-9, (b) 0.3Y-9, (c) 0.3Both-9, (d) 0.15Both-9, (e) 0.3Both-10, (f) 0.15Both-10, and (g) Base-10.

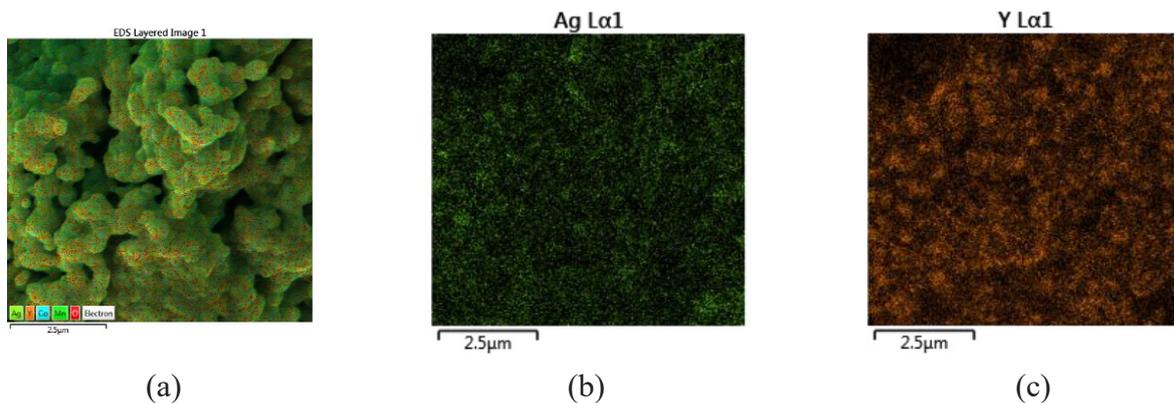


Fig. 5. SEM-EDS map of the 0.3both-10 sample: (a) Layered elemental mapping of Ag, Y, Co, Mn, and O element, (b) elemental mapping of Ag $L_{\alpha 1}$ element, and (c) elemental mapping of Y $L_{\alpha 1}$ element.

Table 2 presents the density of the samples sintered at different temperatures. As observed, a higher sintering temperature enhanced the density of the samples as expected. Although, it can also be seen that dopants type and mol% can affect densification. 0.3Y samples have the lowest density, probably due to the

Mn_3O_4 phase formation. In the case of co-doped samples, it is observed that the dopants mol% and sintering temperature, which can alter the type and amount of the impurity phases, have an important role in the densification of the samples. Co-doped samples sintered at 950 °C have higher densities compared with

the Base-9 sample, while co-doped samples sintered at 1050 °C have lower densities compared with the Base-10 sample. The reason for this is that higher sintering temperature caused a (more) Mn_3O_4 phase to be formed, and since there is no Ag metallic phase in the structure, the density decreased. The results of the density measurements are in good agreement with the FESEM results.

Table 2. The density of the pellets sintered at different temperatures.

Sample name	Density (g/cm ³)	Sample name	Density (g/cm ³)
0.3Y-9	2.86	0.3Y-10	3
Base-9	3.18	0.3Both-10	3.58
0.3Both-9	3.43	0.15Both-10	3.69
0.15Both-9	3.53	Base-10	3.82

Table 3 shows the electrical conductivity of all the pellets measured by the 2-probe technique at room temperature. All the samples with dopants have higher electrical conductivity than pure $Mn_{1.5}Co_{1.5}O_4$, which has also been reported by other researchers [3, 14]. For the doped samples with the same composition but different sintering temperature, the conductivity decreased as the sintering temperature increased due to the formation of oxides and enhancement of the Ag solubility limit (there was still an Ag metallic phase for pellets sintered at the lower temperature, which increases the electrical conductivity). Also, pellets sintered at higher temperatures had lower densities, which can also decrease the conductivity. Also, doping Y increased the conductivity. As mentioned above, adding Y caused the formation of Mn_3O_4 . The investigations of Bose et al. found that Mn_3O_4 conductivity increased by an order of 5 when annealed at higher temperatures, which enhanced the size of its particles and lowered its bandgap energy [16]. Finally, adding higher amounts of both elements created the best results in electrical conductivity.

Table 3. Electrical conductivity of all samples

Sample Name	Volume Conductivity (mS/cm) at 1050°C	Volume Conductivity (mS/cm) at 950°C
both 0.3	1.35E-02	7.47E-02
both 0.15	4.50E-03	2.62E-02
Y 0.3	4.18E-03	2.47E-02
base	1.35E-04	5.20E-06

4. Conclusions

In this investigation, the effect of the amount of Ag and Y dopants and sintering temperature on the Mn-Co spinel characteristics for coating applications in SOFC interconnects was studied. It was observed that Ag was not doped completely into the Mn-Co spinel structure and presented as some additional impurity phases (Ag and Ag_2O). Additionally, it was confirmed that the addition of Y caused Mn_3O_4 impurity phase formation. The reason for this behavior is thought to

be that doping Y makes the Mn stability in the structure weak, and as a result, the Mn exits the structure and forms Mn_3O_4 with oxygen. Moreover, the addition of Ag and higher sintering temperature improves the densification while doping Y decreased the densification due to the forming of Mn_3O_4 . It was concluded that the addition of Ag and Y enhanced the electrical conductivity of the Mn-Co spinel, while increasing the sintering temperature decreased the electrical conductivity. In conclusion, the best electrical conductivity was observed for the 0.3 Ag and Y co-doped samples.

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