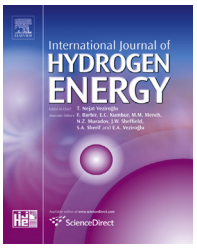
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–10

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Nanostructured $MnCo_2O_4$ synthesized via co-precipitation method for SOFC interconnect application

P. Lesani, A. Babaei[*], *A. Ataie, E. Mostafavi*

School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, P.O. Box 14395-553, Tehran, Iran

ARTICLE INFO

Article history:
Received 24 May 2016
Received in revised form
23 July 2016
Accepted 25 July 2016
Available online xxx

Keywords:
Manganese cobaltite
Spinel
Co-precipitation
Coating
Solid oxide fuel cell
Interconnect

ABSTRACT

Nanostructured manganese cobaltite spinel oxide ($MnCo_2O_4$) was successfully synthesized by co-precipitation method. X-ray diffraction (XRD) results revealed that the molar ratio of OH^-/NO_3^- = 1.5 in the precipitation stage is more appropriate for achieving $MnCo_2O_4$ phase. The results of thermal analysis (TGA/DTA) along with the XRD results revealed that the $MnCo_2O_4$ phase remains stable up to 1050 °C. Morphological studies show that by increasing the calcination temperature from 350 to 550 and 1000 °C, morphology of the particles varies from plate-like to quasi spherical and polyhedral shape, respectively. Density and porosity measurement of cold pressed and sintered samples showed that by employing un-calcined powder, a dense sample with 98% of the theoretical density could be obtained at the sintering temperature of 1000 °C. Selected synthesized powders were coated on the AISI 430 ferritic stainless steel coupons and the results demonstrated that using un-calcined powder, leads to the formation of a highly dense and adhesive coating layer due to the very high tendency of un-calcined powder for densification.

Introduction

Fuel cells with the ability of direct conversion of chemical energy to electricity offer a clean and renewable route with low emission for future power generation systems [1]. Among different kind of fuel cells, solid oxide fuel cell (SOFC) has attracted a great deal of attention in recent years because of its high conversion efficiency. SOFCs are also important as they can be used with a wide variety of fuels including not only hydrogen but also existing fossil fuels, and are affected less by impurities compared to polymer electrolyte membrane fuel cells (PEMFCs) [1,2]. Interconnects are vital components of a SOFC stack which connect adjacent cells electrically, while, separating the working atmosphere of the electrodes [3,4]. Stainless steels are usually utilized as the interconnect materials due to the similar coefficient of thermal expansion with other cell components, appropriate electrical and thermal conductivities, suitable formability and reasonable price [3,5,6]. However, using stainless steel as the interconnect material leads to the formation of chromia scales on the surface of ferritic stainless steel at the operating condition of SOFC electrodes and this can dramatically decrease the cell performance due to some unfavorable interactions between chromia scale with water and oxygen, resulting to the formation of volatile Cr species and condensation of solid Cr_2O_3

* *Corresponding author*. Fax: +98 21 88006076.
E-mail address: alireza.babaei@ut.ac.ir (A. Babaei).

http://dx.doi.org/10.1016/j.ijhydene.2016.07.216
0360-3199/

on the cathode electrode which causes devastating effects [7–9].

Recently, manganese cobaltite spinel with different molar ratios of Mn–Co has been used as the interconnect coatings [10]. Different synthesis methods including chemical routes and solid state methods have been reported for preparation of manganese cobaltite spinel [11–14]. Chemical routes, particularly co-precipitation method often result in almost pure phase with a uniform particle size distribution and high surface area without any subsequent milling in comparison to the solid state route [15]. Meanwhile, in the co-precipitation method, the phase formation and final microstructure of the particles are strongly depended on various factors such as pH of solution, process temperature, washing process of precursor, and calcination temperature [16]. Brylewski et al. [11] reported synthesis of manganese cobaltite spinel by co-precipitation method with the mean particle size of 0.1–1 μm after calcination at 800 °C for 10 h. Yoon et al. [17] reported that the relative density of 74% can be obtained by sintering of $MnCo_2O_4$ coupons at 1000 °C, while, Sharma et al. [13] reported that in order to achieve to 95% of the theoretical density of $MnCo_2O_4$, sintering temperature should be increased up to 1150 °C.

The impact of coating on chromium evaporation from the steel substrate has been discussed by many researchers. The results revealed that Mn/Co–O spinel coating can be considered as proper protective coating materials for SOFC/SOEC interconnect applications. Larring and Norby [18] reported that Cr diffusion from the substrate can be reduced by applying $(Co,Mn)_3O_4$ spinel coating. A $MnCo_2O_4$ spinel coating on Fe–21Cr was studied by Fang et al. [6]. The protective coating shows a good adhesion to the substrate and can successfully acts as a barrier to Cr outward transportation. Wu et al. [19] applied a Mn/Co–O coating on a T441 steel alloy and compared its behavior with uncoated samples after severe thermal cycles. They reported that coated interconnects not only show stable performance, but also act as a mass barrier to hinder the scale growth on the substrate and to prevent Cr from outward migration across the coating. Zeng et al. [20] applied Mn/Co (40:60) spinel coatings with different thicknesses on the AISI 430 stainless steel and investigated the surface morphology and cation distribution throughout the substrate and the coating and reported that faceted grains can be obtained after sintering of coated sample at 800 °C for 1000 h. The effect of pre-oxidation on the element distribution throughout the substrate and coating layer was investigated by Hoyt et al. [21]. The results indicated that by pre-oxidizing the coated samples, Fe transportation into the coating layer was inhibited. Also, the chromia oxide layer became thinner in comparison with non-preoxidized samples. It is also reported that doping of Cu into Mn/Co–O system can improve the sinterability and electrical conductivity of the coating layer [22]. In another study, the densification behavior of $MnCo_2O_4$ and $MnCo_2O_4$–MnO_2 composite material was studied. It was reported that a considerable amount of small pores were exist after sintering of $MnCo_2O_4$ at 1200 °C, while presence of MnO_2 causes formation of a quite dense micro-structure of spinel oxide material [23].

In the present work, manganese cobaltite spinel was successfully synthesized via co-precipitation method. The effects of different OH^-/NO_3^- molar ratios and calcination temperatures on the phase constitution and morphology of the products were systematically investigated. The influence of calcination temperature on the consolidation behavior of $MnCo_2O_4$ pellets was studied. Moreover, by applying uncalcined and calcined powders on the AISI 430 stainless steel coupons, the coating behavior of the synthesized powders was investigated.

Materials and methods

Materials and preparation

Manganese cobaltite spinel oxide ($MnCo_2O_4$) was prepared via co-precipitation method. In the synthesis process, an aqueous solution of stoichiometric amounts of $Mn(NO_3)_2{\cdot}4H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ (both from Merck) was prepared. Aqueous solutions of sodium hydroxide (NaOH) were added to the solution of metal nitrates in separate synthesis experiments while magnetic stirring at 25 °C to achieve different OH^-/NO_3^- molar ratios of 1, 1.5 and 2 in the solution. The resultant precipitates were filtered off, washed with distilled water and dried at 80 °C for 18 h. The dried precipitates were calcined in the temperature range of 300–1100 °C for 5 h in air. Table 1 summarizes the process conditions for powder preparation and the sample codes.

Polished AISI 430 ferritic stainless steel coupons was used as a substrate for the coating purpose [4]. The nominal composition of the steel substrate is reported in Table 2.

Selected powder samples were mixed with an Ink Vehicle (Fuel Cell Materials Co., USA) and screen printed on the steel coupons. The coated samples were sintered by a multistep regime for 17 h comprising dwelling at 1000 °C for 5 h.

Characterization

The phase composition of the calcined powders were analyzed by X-ray diffraction (XRD) technique at room temperature utilizing a Philips PW-1730 apparatus with Cu-K_α radiation ($\lambda = 1.5406$ Å) in the range of $10° < 2\theta < 70°$ and step size of 0.02°. The mean crystallite size of the powders was calculated by Scherrer's equation [24]:

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos\theta} \quad (1)$$

where D is the crystallite size in nanometer, λ is the wavelength of Cu K_α radiation, θ is the Bragg angles of the major diffraction peaks, and β is the full width at half maximum (FWHM) of XRD peaks in $2\theta = 36$, 58, and 64°.

Morphology of the synthesized powders were assessed by a field emission scanning electron microscope (FESEM, TESCAN MIRA3) equipped with an EDS analyzer. The mean particle size of powders was calculated using MIP software measuring more than 20 particles from FESEM images. The thermal behavior of the precipitate was investigated using a DTA/TGA LINSEIS L70/2171 apparatus in air, from room temperature up to 1200 °C at a constant heating rate of 10 °C/min.

Appropriate sintering temperature of the powder is selected based on density (ρ_{exp}) and relative porosity (%P) of

Please cite this article in press as: Lesani P, et al., Nanostructured $MnCo_2O_4$ synthesized via co-precipitation method for SOFC interconnect application, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.07.216