

SYNTHESIS OF NiO-SDC CERMET MATERIAL FOR LOW TEMPERATURE SOLID OXIDE FUEL CELL USING ONE STEP CO-PRECIPIATION PROCESS AND CHARACTERIZATIONS.

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ABSTRACT: Here in this work, we prepared Nickel oxide-Samarium doped ceria (NiO-SDC) cermet anode material by one step co-precipitation technique with $\text{Sm}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Ni}(\text{NO}_3)_2$ as starting precursors and Na_2CO_3 as precipitating agent. The co-precipitate powders were calcined at 600-900 °C for 3 hours separately, resulting in dry powders, which contain dual phase. X-ray diffraction (XRD) identifies the fluorite and cubic structure of CeO_2 and Ni. The sintering process at 750 °C under H_2 atmosphere reduced the NiO-SDC into Ni-SDC with porosity about 20-42%. The cermet material indexed the metallic behavior at temperature range from 450 to 600 °C measured with two probe method in CH_4 and H_2 atmosphere. The Ni-SDC seems to be well-suited cermet anode material for solid oxide fuel cells (SOFCs) application with SDC electrolyte having a healthier electric conductivity.

Keywords: Cermet, Co-precipitation, SOFC, X-Ray, Electrical conductivity, Dual phase.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are most desirable, promising and efficient organization for power generation with low material cost and minimum pollutant [1]. Though SOFCs operate at 800-1000 °C by using hydrocarbon fuel, scientist and researchers are taking interest to dropping SOFCs working temperature which becomes beneficial to upsurge period of cell [2]. SOFCs consist of three main parts (Electrolyte, Anode and Cathode). Electrolytes are only ionic conductor, but electrodes are both ionic and electronic conductor. In SOFCs fuel provides at anode side and oxygen at cathode sides. The electrochemical reaction take place at three phase boundary (TPB) that exist between the electrolyte and anode materials [3]. The electrochemical reaction causes the conversion of chemical energy into electrical energy with the addition of H_2O , CO_2 and heat [4]. Thermal compatibility, adequate porosity and better electronic conductivity are the basic necessities of anode for SOFCs. In past conductive oxides have been used for SOFCs anode materials. But now a day's scientist proposed the doped ceria materials for low temperature SOFCs anode. The composite ceria that based on the CeO_2 shows mixed electronic and ionic conductivity. Ceria materials have been considered an excellent catalyst due to oxygen vacancy migration and creation in the result of reduction associated of Ce^{4+} to Ce^{3+} [5].

Firstly, SOFCs developers have been used Co, Ni, Rh, Ru, Rd and Pd metals as possible anode materials. Until now, Cermet anode material (combination of metal and electrolyte material) is used for SOFCs anode materials instead of simply metals [6]. Anode material based on samarium doped ceria (SDC) has high performance than the yttrium based ceria (YDC), yttrium based zirconium (YSZ) and gadolinium doped ceria (GDC). Cermet anode material like Zn-SDC, Cu-SDC, Fe-SDC, Ru-SDC, Co-SDC and Ni-SDC etc. Ni-SDC propose to be appropriate anode material to attain high performance because better output for anode materials require large triple phase boundary (where chemical reaction take place), fine crystallite size and proper porosity [7]. Nickel is the choice for cermet anode material due to its high melting point, better power density, greater catalytic activity and precise composite structures enhance the performance of

anode than the other metals [8]. When hydrocarbon fuel is used nickel has become more attractive noble metal because of easily breakage of C- H bond [9].

i. MATERIAL AND METHODS

Hibino et al. Investigated the properties of Ru- Ni- GDC as cermet anode materials for SOFCs. They operated anode material at 600°C temperature with hydrocarbon as a fuel. Its power density with methane stretched to 750 mWcm^{-2} and on the other hand power density by hydrogen was 769 mWcm^{-2} [10]. Hibino et al. also studied Pd-Ni-SDC for low temperature SOFCs cermet anode material. For oxidation purpose they used Pd metal to encouraged electromotive force of 900 mV in the cell. At 550° C temperature its power density about 643 mWcm^{-2} by using samarium doped ceria as electrolyte having thickness about 0.15 mm [11]. Ahn et al. used Cu-ceria composite anode material in the replacement of CeO_2 with the solid solution of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$. They originated that $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ enhanced the thermal stability of SOFCs anode, which is assigned to the improved reducibility of the solid solution compared to that of pure ceria [12]. Ye et al. examined the Cu-CeO₂-ScSZ cermet anode material. They found that anode consist of Cu-CeO₂-ScSZ showed the stable performance at 800 °C after 50 hours operation [13].

ii. EXPERIMENTATION

NiO-SDC cermet anode material was synthesized by one step co-precipitation method using $\text{Sm}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Ni}(\text{NO}_3)_2$, as starting forerunners and Na_2CO_3 as the mineralizer. These materials (with a stoichiometric molar ratio of Ni: Sm: Ce: 5:2:8) were dissolved in distilled water to form a solution. This solution was stirred on magnetic stirrer for an hour to make it homogenous. Then Na_2CO_3 with the molar ratio of 1:1 mixed drop by drop to make the precipitates. A greenish black solution was obtained which was further filtered using suction system. The separated out the precipitates were dried at 150°C in an oven for 3 hours. After heating, this dry powder was minced in the motor pestle and calcined at various temperatures 600, 700, 800 and 900 °C for 5hour. After calcination the powder was again creased to get fine powder. The formed powder was examined using X-ray Diffractometer (XRD) and Energy Dispersive X-ray

analysis (EDX). The electronic conductivity was found using two probe method. For conductivity measurements the pellets were equipped using the hydraulic press and silver paste was applied on both sides of the specimen.

iii. RESULT AND DISCUSSIONS

Figure 1.shows the XRD pattern of specimens calcined at 600, 700, 800 and 900 °C. The planes (111), (200) and (311) belongs to CeO₂ and (111) for NiO which predicts that calcined samples contain dual phase. While, peak shifting of CeO₂ powder calcined at 600, 700, 800 and 900 °C indexed that samarium was doped into the lattice of cerium oxide. The crystallites size of each plane can be determined by Scherer’s formula which is given below.

$$D = \frac{K\lambda}{\beta \cos \theta} \tag{1}$$

where, D is crystallite size of XRD peaks, K represents to constant (0.9), λ belongs to X-ray wavelength (1.54 Å), θ The crystallite size of NiO specimen calcined at 600, 700, 800 and 900 °C was 13.4, 19.3, 29.7 and 35.5 nm and on the other hand crystallite size of SDC was 14.2, 16.5, 26.4 and 28.3 nm. Table.1 illustrated that crystallite size of SDC was slightly larger than the NiO at 600 °C but the crystallite size of SDC at 700, 800 and 900 °C gradually tends to decrease as compare to NiO. It means that crystallinity of NiO lands more rapidly than SDC with increasing the calcination temperature.

Figure 2 indexed the compositional structure of powder calcined at 700 °C. EDX reveals the elementary peaks of Ce, Ni, F and O that occur in the powder

diffraction angle and β denotes full width half maximum position.

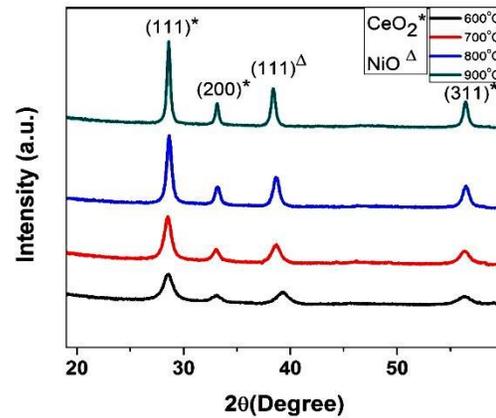


Figure 1: XRD Pattern of NiO-SDC calcined at 600°C, 700°C, 800°C and 900°C

Table 1. Particulate Crystallite sizes of as-formed NiO–SDC powders

Sample	Calcination Temperature (°C)	Crystallite size of NiO (nm)	Crystallite size of SDC (nm)
1	600	13.4	14.2
2	700	19.3	16.5
3	800	29.7	26.4
4	900	35.5	28.3

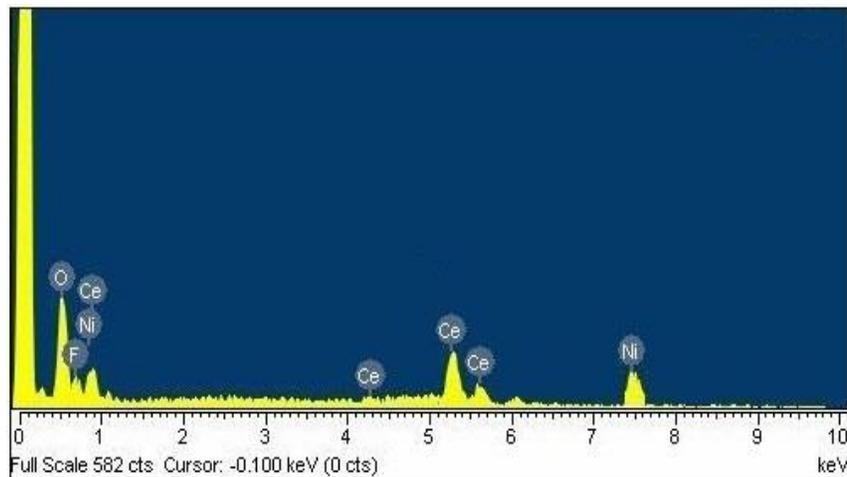


Figure 2: EDX Pattern of NiO-SDC calcined at 700°C

The phase formation of CeO₂ and NiO also confirmed from nickel, cerium and oxygen peaks. While existence of F was due to the usage of hydraulic press. No presence of samarium shows the doping of Sm into the lattice of CeO₂ which can be seen in XRD results.

The electric conductivity of cermet anode materials was measured by using two probe method. The grind powder

was compressed into pellet form. The pellets were made by using hydraulic press with 360 MPa pressure and using 13 mm diameter die. To collect electronic current silver paste was used on both sides of pellet. The conductivity measured by following expression

$$\sigma = \frac{L}{RA} \tag{2}$$

Where A is the effective area, L is thickness of prepared pellet and R is resistance. The sample density was calculated by using Archimedes method. The comparative densities of powder sintered at 600, 700, 800 and 900 °C is 80%, 71%, 62% and 58%. Hence porosity (100-density) in each case was 20%, 29%, 38% and 42% respectively. So the electric conductivity of material decreases with increasing calcination temperature. The sample calcined at 700 °C suitable for cermet anode material because its porosity was 29%, which shows better performance according to literature [14]. When NiO-SDC sintered at 750 °C in H₂ atmosphere, it reduced into Ni-SDC [15]. The Fig. 3 signifies the conductivity of cermet anode material calcined at 700 °C in the temperature range of 350-600 °C using hydrogen and natural gas as fuel. The electric conductivity of the sample calcined at 700 °C using natural gas ranges from 111-322 Scm⁻¹ in same temperature range. At the same temperature condition using hydrogen fuel, the electric conductivity varies from 183- 447 Scm⁻¹. The electric conductivity using H₂ was far too higher than the natural gas. The conductivity using one step co-precipitation method has greater value than the mechanical mixing method [16].

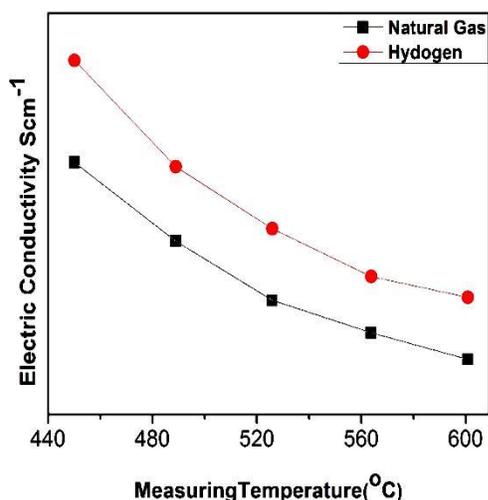


Figure 3: The electric conductivity comparison of NiO-SDC using Hydrogen and natural gas

iv. CONCLUSION

One step co-precipitation method was used to synthesize the NiO-SDC cermet anode powder. The specimens were calcined at 600-900 °C with the average crystallite size from 27.6 to 63.8 nm which indicates the rising trend of crystallinity with the calcination process. The porosity was also grown up with increasing temperature. In addition, the specimen calcined at 700 °C possesses conductivity closer to the theoretical value of NiO-SDC. The conductivity of sample calcined at 700 °C was found 322 Scm⁻¹ and 447 Scm⁻¹ under the atmosphere of natural gas and hydrogen respectively at measuring temperature 450 °C which is remarkably higher than the cermet anode fabricated by mechanical mixture method. Hence, 700 °C is the most favorable calcination temperature for the synthesis of NiO-SDC.

In future single phase cermet anode can be prepared which is consider more conductive than the dual phase cermet anode.

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