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CHARACTERIZATION OF NiO-BCZY COMPOSITE ANODE PREPARED BY ONE-STEP SOL-GEL METHOD

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ABSTRACT

NiO-BCZY composite anode has been proposed as a suitable anode material for the application in an intermediate temperature solid oxide fuel cell (IT-SOFC). Recent studies show that the microstructure of the anode region is critical factor affected to SOFC performance. In this paper, NiO-$BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ (NiO-BCZY) composite powders with different NiO-BCZY weight ratios (40:60 and 50:50 which are denoted as S1 and S2) were prepared by a one-step sol-gel method. The resultant powders were characterized by using X-ray Diffractometer (XRD) and Field Emission Scanning Electron Microscopy/ energy-dispersive X-ray (FESEM/EDX). A well- developed single-phase perovskite-type of BCZY was observed in S1 and S2. Peaks of NiO were matched to the JCPDs card no. 010780643 and peaks of BCZY can be indexed to the compound of $Ba(Ce,Zr)O_3$ (JCPDs card no. 010892485). The unit cell volume of BCZY in 40NiO-BCZY and 50NiO-BCZY composite were about 81.690Å^3 and 81.464Å^3 compared to standard $Ba(Ce,Zr)O_3$ (V''=81.950 Å^3). FESEM/EDX analysis shows a spherical shape powder with a uniform distribution of NiO and BCZY grains in S1 and S2. The elemental composition of both samples was not greatly deviated from their nominal stoichiometry.

Keywords: composite anode; microstructural properties; sol-gel; ceramic-metal

INTRODUCTION

A solid oxide fuel cell (SOFC) consists of two porous electrodes which is anode and cathode and a dense solid electrolyte separating the two electrodes. Among of the three parts, anode serves to provide electrochemical reaction sites for oxidation of the fuel. In order to permit the passage of electrons, the anode must be stable in the reducing environment of the fuel and should be electronically conducting. Other than that, it also must have sufficient porosity to allow the transport of the gas of fuel oxidation. Furthermore, an anode should exhibit high catalytic activity towards fuel oxidation [1,

2]. At the anode, the electrochemical oxidation is believed to occur at the regions which called triple phase boundary (TPB). The TBP is defined as the collection of sites where proton conductor (electrolyte), the electron-conducting phase, and the gas phase, all meet together.

Nowadays, one of the approaches used to reduce large anode over-potential at cell's surface affected by decreasing of the operating temperature in intermediate temperature solid oxide fuel cells (IT-SOFCs) is the application of composite anodes. Composite anodes for an example NiO- BCZY, demonstrates a longer triple phase boundary (TPB) as compares to anodes made of precious metals [3]. Recent studies show that the microstructure of the anode is critical to SOFC performance. The anode powders had produced using conventional mechanical mixing method which NiO and electrolyte materials were simply mixed together by ball milling. This may result in an inhomogeneous distribution of the two phases. In order to solve this problem, a wet chemical method for example sol-gel approach is regarded as effective ways to produce ultra-fine and uniform powders which can enlarge the length of TBP where electrochemical reaction occur [4]. Ni ceramic composite materials are widely used as anode materials for SOFC due to their capability to efficient electro catalyse the oxidation of the fuel. Moreover, chemical and mechanical stability, catalytic activity and cost, make a nickel a strong candidate as compared to other possible metals to be as anode material [5, 6]. As is generally recognized, Ni in the anodes is responsible for the oxidation of hydrogen and BCZY components play an important role in providing the ionic conductivity of the NiO-BCZY composite anode. Adequately controlling the volume ratio of Ni and BCZY allows the resulting electrode to benefit from optimum microstructure and excellent electrochemical performance.

Thus, in this work, the composition of the anodes will be modified by varying the weight ratios of NiO:BCZY composite by using one-step sol-gel method along with the microstructural studies of the composite anodes.

METHODOLOGY

In one-step sol-gel method, a stoichiometric amounts of $Ba(NO_3)_2$ (99%, ACROS), $Ce(NO_3)_3.6H_2O$ (99.5%, ACROS), $Zr(NO_3)_2O.xH_2O$ (99.5%, ACROS), $Y(NO_3)_3.5H_2O$ (99.9%, Aldrich) and $Ni(NO_3)_2.6H_2O$ (99%, ACROS) were dissolved in purified water under stirring process. As a complexing agent, citric acid was then added to the solution with molar ratios of soluble metal ions:citric acid of 1:1.5. NH_4OH was added to the solution to adjust the pH value around 7. The resulting solution was slowly evaporated on a hot plate at 120°C. The heating and stirring process were control accordingly. During the process, the browning gas (known as NOx) was released and a dark brown gel obtained. The gel was dried at 325°C in a furnace to yield black flakes. Then the sample was calcined at 1100°C with the heating rate of 10°C min^{-1} for 6 h to form fine NiO-BCZY powders. The samples were prepared such that the NiO-BCZY composite consisted of 40% and 50% by volume of NiO and these samples were labelled with S1 and S2 respectively.

The X-ray Diffractometer (XRD 6000 Shimadzu) using a monochromatic Cu-K_α radiation source (λ = 0.1540558 nm) with Ni-filtered was used to confirm the phase formation of NiO-BCZY powder. The XRD was operated at 40 kV and 30 mA using a step-scan procedure of 0.02º s^{-1} for 2 thetas (θ) ranging from 20º to 80º. The phase formation analysis was performed by using Eq. 1 as proposed by Swarts and Shrout [7]:

$$\text{Perovskite phase} = \frac{Ip}{Ip+Im} \times 100\% \quad (1)$$

where *Ip* refers to the maximum intensity of the perovskite phase and *Im* is the maximum intensity of the impurities phases.

The surface morphology and microstructure of the calcined powders were examined by Field Emission Scanning Electron Microscopy (FESEM, Nova NANO-SEM450) equipped with energy- dispersive X-ray (EDX, Oxford X-MaxN) analysis. The samples were coated with platinum to avoid charging as well as to get better resolution and signal quality. Imaging was performed using an accelerating voltage of 5kV.

RESULTS AND DISCUSSION

Phase Formation Analysis.
Figure 1 shows the XRD patterns of NiO-BCZY composite anode powders with a different weight ratio of NiO-BCZY after calcined at 1100°C. The XRD pattern showed a mixture of respective $Ba(Ce,Zr)O_3$, $BaCO_3$, and NiO. All the calcined samples exhibited a well-developed single-phase perovskite-type of BCZY with cubic lattice symmetry. The peaks of $BaCO_3$ that appeared in the XRD patterns are influenced by the high firing temperature and incomplete combustion. This occurred during calcination process due to the adsorption of CO_2 on the powder surface which is transformed to CO_3 [8]. The difference in the weight ratio between BCZY and NiO changed the relative intensity of the two phases in the XRD patterns.

The pronounced peaks of BCZY can be indexed to (110), (111), (200), (211), (220), (310) and (222), respectively, according to JCPDS card of $Ba(Ce,Zr)O_3$ (010892485). In addition, the peaks of NiO can be indexed to (111), (200) and (220) based on the JCPDS card of nickel oxide (010780643). The lattice parameter of BCZY in S1 and S2 after calcined at 1100°C were estimated and found to be a = 4.339 Å and a = 4.335 Å compared to pure $Ba(Ce,Zr)O_3$, a = 4.344 Å. Furthermore, the incorporation of NiO in BCZY by S1 and S2 induce a contraction in the unit cell volume of standard $Ba(Ce,Zr)O_3$. A summary of XRD analysis for S1 and S2 are given in Table 1. It is observed that the percentage of perovskite phase formed in S2 composite anode demonstrated the highest value compared to S1. It showed that the S2 were almost completely formed a single perovskite phase of BCZY rather than S1. This might due to the presence of the impurity peak with lower intensity than the impurity peak in S1.

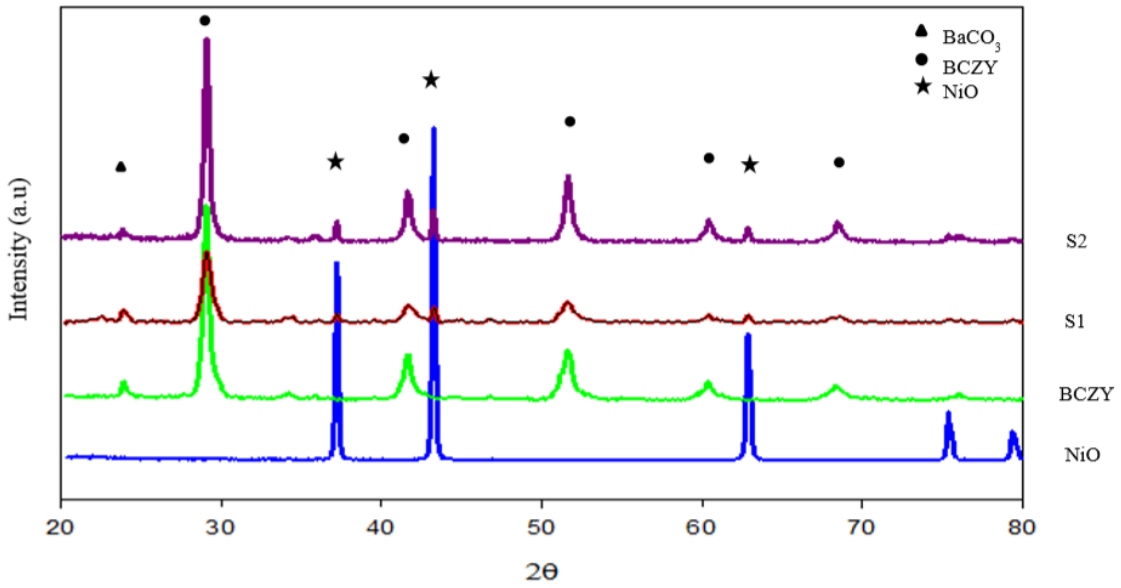

Figure 1: XRD patterns of NiO-BCZY composite anode powders after calcined at T=1100°C

Table 1: A summary of XRD analysis for BCZY in a composite of S1 and S2

Routes	Lattice parameters [Å]	Unit cell volume, *V* [Å^3]	Percentage of perovskite phase (%)
S1	4.339	81.690	86.10
S2	4.335	81.464	97.50
$Ba(Ce,Zr)O_3$ (JCPDS Card 010892485)	4.344	81.973	-

Microstructure Analysis.
Figure 2 shows the FESEM micrograph of the NiO-BCZY composite anode powders prepared by the one-step sol-gel method for S2 sample. The same morphology of particle was also observed for the S1 sample. S1 and S2 showed a spherical shape with a uniform distribution of NiO and BCZY grains. But there are some equiaxed shape particles showed in the samples. This is due to the sonication effect that had given for during the FESEM sample preparation. From the micrograph, it is observed that the ground of NiO particles are partially covered with BCZY fine particles. Similarly, Fukui et al [9] reported that the ground NiO particles are partially covered with YSZ fine particles. These results are comparable to that Ni– $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ which synthesized by wet chemical method [10].

Regardless to the different weight ratio of NiO to BCZY, one step sol-gel method was proven to produce a better distribution of particles rather that oxide powder mixture

method [9]. Shao et al [11] said that this method can produced a high phase purity, good compositional homogeneity and a high surface activity of the resulting powders. The EDX mapping was presented in Figure 3 order to show the distribution between the particles.

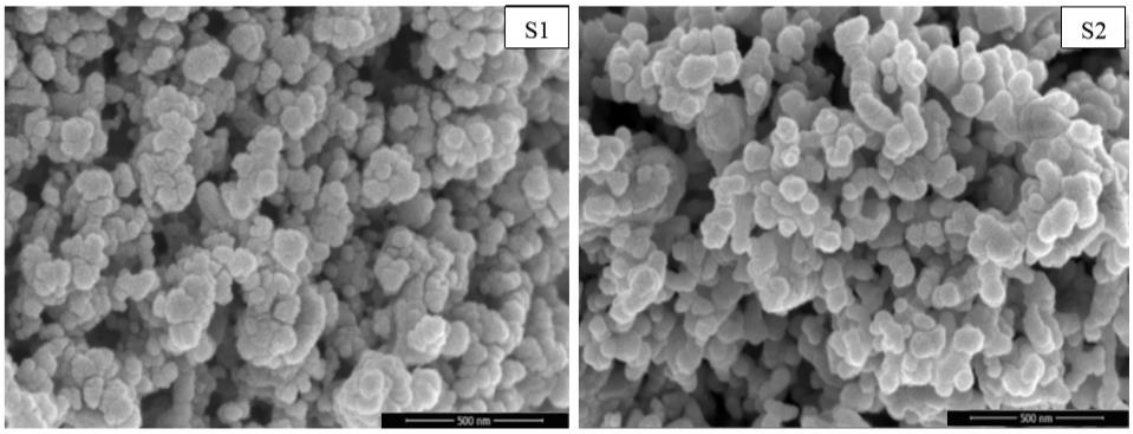

Figure 2: FESEM micrograph of the S1 and S2 composite anode powders after calcined at T=1100°C

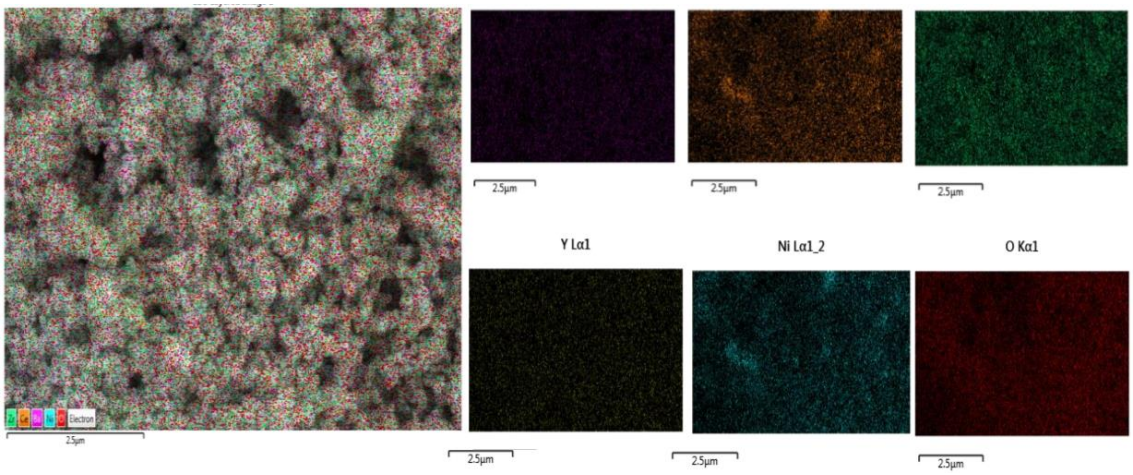

Figure 3: EDX mapping of the S2 composite anode powders after calcined at T=1100°C

Figure 4 shows the backscattered electron (BSE) FESEM micrograph of the NiO-BCZY composite anode powders after calcined at T=1100°C. The elemental analysis at the same location by EDX analysis confirm the present of Nickel (Ni), Oxygen (O), Barium (Ba), Cerium (Ce), Zirconium (Zr) and Yttrium (Y) in the calcined composite anode powders, S1 and S2. The results were tabulated in Table 2. The composition of the element for those two samples is almost the same. Its proved that the different ratio of NiO:BCZY does not really affect the elemental composition of the samples.

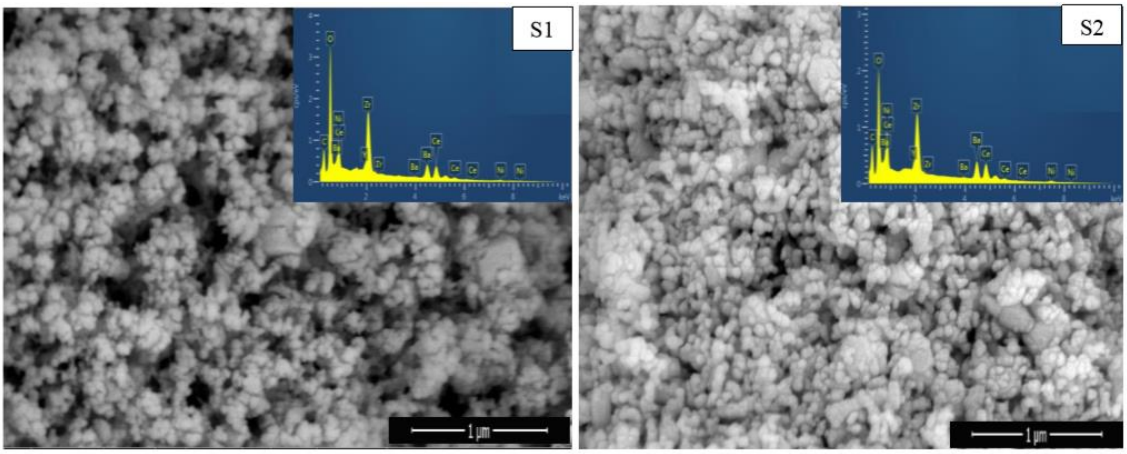

Figure 2: Backscattered electron (BSE) FESEM micrograph and EDX of the NiO-BCZY composite anode powders, S1 and S2 after calcined at T=1100°C

Table 2: Elemental composition of prepared samples

Element	Sample/ Elemental atomic percentage (%)	
	S1	S2
Ni	6.24	8.49
O	18.86	16.49
Y	2.97	2.71
Zr	23.45	20.69
Ba	30.66	33.95
Ce	17.82	17.67

CONCLUSION

A sample of NiO-BCZY was prepared via a one-step sol-gel method with a different weight ratio of NiO-BCZY. The XRD patterns for those two samples had shown a well developed single-phase perovskite-type oxides of NiO-BCZY composite. However, the incorporation of NiO in BCZY by all the samples with two different weight ratios of NiO-BCZY induces a contraction in the unit cell volume of $Ba(Ce,Zr)O_3$. FESEM/EDX analysis shows spherical shape powders with a uniform distribution of NiO and BCZY grains in S1 and S2. The elemental composition of both samples was not greatly deviated from their nominal stoichiometry.

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