

Heat Treatment Effect on the Phase and Morphology of NiO-BCZY Prepared by an Evaporation and Decomposition of Solution and Suspension Method

(Kesan Rawatan Haba ke atas Fasa dan Morfologi NiO-BCZY yang Disediakan Melalui Kaedah Penyejatan dan Penguraian Larutan dan Mendakan)

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ABSTRACT

A nitrate-based nickel salt was used to prepare NiO-BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} (NiO-BCZY) composite powders by an evaporation and decomposition of solution and suspension (EDSS) method. The prepared powders with different weight ratios of NiO to BCZY (NiO:BCZY) were denoted as S1 (50:50) and S2 (60:40). The powders were characterized using Thermogravimetric analyzer (TGA), X-ray diffractometer (XRD) and scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectrometer. TGA results showed that the thermal decomposition of intermediate compounds in the dried powder ($T = 150^{\circ}\text{C}$) completed at $\sim 700^{\circ}\text{C}$. XRD analysis confirmed that the calcined powder ($T = 1100^{\circ}\text{C}$) of S1 and S2 did not show any crystalline peaks related to BCZY compound as the peaks associated to impurity phases of BaCeO₃ and BaZrO₃ were appeared in their XRD patterns. The impurity phases along with NiO still remained in the S1 sample after it was calcined at 1400°C . As the calcination temperature increased, the particles size of S1 also increased and Zr elemental composition deviates from the nominal stoichiometric of the NiO-BCZY as proven by SEM/EDX analysis. The results indicate that the formation of homogenize NiO-BCZY composite prepared using EDSS method was not favored even after calcined at high temperature ($T = 1400^{\circ}\text{C}$).

Keywords: Anode; composite; EDSS method; NiO-BCZY

ABSTRAK

Nikel berasaskan garam nitrat telah digunakan dalam penyediaan serbuk komposit NiO-BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} (NiO-BCZY) melalui kaedah penyejatan dan penguraian larutan dan mendakan (EDSS). Serbuk yang terhasil dengan nisbah berat NiO kepada BCZY (NiO:BCZY) yang berbeza telah dilabelkan sebagai S1 (50:50) dan S2 (60:40). Serbuk tersebut telah dicirikan dengan menggunakan penganalisis termogravimetri (TGA), pembelauan sinar-X (XRD) dan mikroskop elektron pengimbas (SEM) yang dilengkapi dengan spektrometer sinar-X sebaran tenaga (EDX). Keputusan TGA menunjukkan penguraian terma sebatian pertengahan bagi serbuk yang dikeringkan ($T = 150^{\circ}\text{C}$) telah lengkap pada suhu $\sim 700^{\circ}\text{C}$. Analisis XRD mengesahkan serbuk S1 dan S2 yang telah dikalsinkan ($T = 1100^{\circ}\text{C}$) tidak menunjukkan sebarang puncak fasa kristal sebatian BCZY disebabkan oleh kehadiran fasa bendasing BaCeO₃ and BaZrO₃ di dalam spektrum XRD. Kehadiran fasa bendasing ini dan juga NiO masih kekal di dalam serbuk S1 setelah dikalsin pada suhu 1400°C . Saiz partikel serbuk S1 bertambah apabila suhu pengkalsinan meningkat dan komposisi elemen Zr di dalam sampel menyimpang daripada stoikiometri sebenar NiO-BCZY seperti dibuktikan oleh analisis SEM/EDX. Keputusan daripada pencirian ini menunjukkan bahawa pembentukan fasa homogen komposit NiO-BCZY yang disediakan secara EDSS tidak dapat diperolehi walaupun selepas dikalsinkan pada suhu tinggi ($T = 1400^{\circ}\text{C}$).

Kata kunci: Anod; kaedah EDSS; komposit; NiO-BCZY

INTRODUCTION

An anode is one of the most crucial components of a solid oxide fuel cell (SOFC) as its properties such as porosity and conductivity play an important role in determining the SOFC performance. Ceramic-metal composite or 'cermet' such as nickel-yttria stabilized zirconia (Ni-YSZ) is frequently being employed as conventional or standard anode material, particularly for high temperature oxide ion conducting SOFC (O²-SOFC) (Aruna et al. 1998; Koide et al. 2000; Marinšek et al. 2000; Rojeck-Wockner et al. 2016). As nowadays research is focusing towards development

of intermediate temperature proton conducting SOFC (H⁺-SOFC), a cermet anode material that works compatibly with proton conductor electrolyte materials has been developed (Bae & Choi 2015; Coors & Manerbino 2011; Rainwater et al. 2012; Yamaguchi et al. 2016; Yan et al. 2010). One of them is composite anode based on nickel oxide and doped barium cerate-zirconate such as NiO- BaCe_{1-x}Zr_xY_{0.1}O_{3-δ}.

The cermet is commonly prepared by utilizing mechanical mixing method in which the nickel salts and an electrolyte powder are subjected to homogenization and sintering processes to form NiO-electrolyte cermet.

However, a problem with mechanical mixing is separation of NiO and electrolyte particles which resulting in a non-uniform distribution of NiO in the cermet anode material if the homogenization and grinding are not well performed (Marinšek et al. 2000; Yan et al. 2010). Thus, wet chemical methods are introduced to overcome the drawbacks of the mechanical mixing method. This technique enables mixing of precursors in the starting solution, resulting in a gel mixture with high degree of homogeneity (Aruna et al. 1998; Marinšek et al. 2000; Yan et al. 2010). Additionally, properties of the produced powders via the techniques are also affected by the metal salts precursor used, heat treatment profiles and composition of the cermet or electrolyte materials (Narendar et al. 2013; Ng et al. 2016; Osman et al. 2009; Yamaguchi et al. 2016; Zunic et al. 2014, 2011).

One of the wet chemical methods employed to produce cermet is via evaporation and decomposition of suspension and solution (EDSS). Usually, EDSS method is used to prepare cermet which consists of three metal elements in its ceramic compound or electrolyte parts such as Ni-BaCeYO₃ (Zunic et al. 2011), Ni-BaZrYO₃ (Narendar et al. 2013) and Ni-YSZ (Xi et al. 2014). However, there are scarce of works reported on the production of cermet which consists of four metal elements in its ceramic part such as NiO-BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} (NiO-BCZY) particularly by the EDSS method. Thus, in this present work, NiO-BCZY cermet powder was prepared via EDSS method using different ratios of nitrate-based nickel as starting material. Its thermal decomposition behavior, phase formation and powder morphology were observed and discussed, accordingly.

MATERIALS AND METHODS

The previous in-house developed BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} (BCZY) electrolyte powder was prepared via a modified sol-gel method as described elsewhere (Abdullah et al. 2012). The composite of NiO-BCZY was prepared via an evaporation and decomposition of solution and suspension (EDSS) method. The calculated amount of Ni(NO₃)₂·6H₂O (Bendosen, 98% assay) was first dissolved in 50 mL deionized water and stirred for an hour. Then, a single-phase powder of BCZY was mixed into the green nickel nitrate solution with 50:50 and 60:40 weight ratio of NiO to BCZY. They were respectively labeled as S1 and S2. The mixture was continuously stirred for another an hour and then dried at 150°C for overnight. The intermediate product obtained was ground and calcined at 1100°C and 1400°C with heating/cooling rate of 5°C min⁻¹ for 5 h, respectively. The steps involved in the preparation of NiO-BCZY composite via EDSS method is shown in Figure 1.

The pre-calcined powder dried at 150°C was analyzed by Thermogravimetric analyzer (TA) instrument model SDT-Q600 from room temperature up to 1400°C in the synthetic air (flow rate of 100 mL min⁻¹) with heating rate of 10°C min⁻¹. The calcined powders were characterized

by X-ray diffractometer (XRD 600 Shimadzu) using Cu-Kα radiation source for the 2θ range from 20° to 80° and Carl Zeiss SMT Supra 40VP scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectrometer. The SEM images were captured at 100000 magnification.



FIGURE 1. Steps for the preparation of NiO-BCZY composite powder by EDSS method

RESULTS AND DISCUSSION

Figure 2 shows the TG/DTG curves of the pre-calcined NiO-BCZY of S1 performed from room temperature to 1400°C. Few peaks were observed up to 700°C, temperature at which the weight loss was almost completed with the total loss of ~48%. TG/DTG profiles of S2 was also has similar pattern as the S1. The first peak in the DTG curve might be attributed to dehydration of water molecule and evaporation of physically adsorbed impurities. The second and the third peak, respectively at ~220°C and ~300°C is corresponded to decomposition of nitrates from Ni(NO₃)₂·6H₂O precursor material as the boiling point of

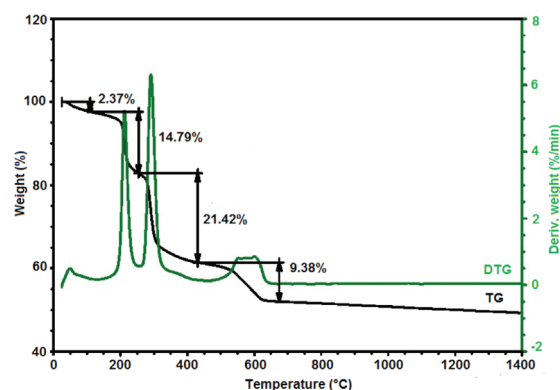


FIGURE 2. TG/DTG curves of the pre-calcined powder (S1) after heated at 150°C

this compound is about 160°C (Chevallier et al. 2009). The third peak may also be related to decomposition of nickel carbonate to nickel oxide as reported by Sheena et al. (2014). The last peak indicated the formation of oxide species of Ni. Above 700°C, the TG signal became plateau (no DTG peak), indicating that the required NiO-BCZY composite may form in this region and the decomposition process took about 140 min.

Figure 3 shows the comparison of XRD plots of the single-phase BCZY and the prepared composite powders (S1 and S2) after calcined at 1100°C. Single-phase of BCZY exhibits a cubic structure of perovskite-type oxide that matched to the JCPDS card no. 89-2485. XRD measurement confirmed that the calcined powder of S1 consists of two main secondary phases which are BaCeO₃ (JCPDS card no. 22-0074) and BaZrO₃ (JCPDS card no. 06-0399) and the required phase of NiO (JCPDS card no. 78-0643). Furthermore, XRD spectrum for S2 also did not show any crystalline peak related to the BCZY compound as the peaks associated to BaCeO₃ and BaZrO₃ were appeared in the XRD pattern. Figure 4 shows the XRD pattern of the single-phase of BCZY and S1 after calcined at 1100°C and 1400°C. The basic phases of the S1 are also the NiO and secondary phases of BaCeO₃ and BaZrO₃ at both temperatures. It means that even at high calcination temperature, the formation of homogenize NiO-BCZY composite cannot be achieved.

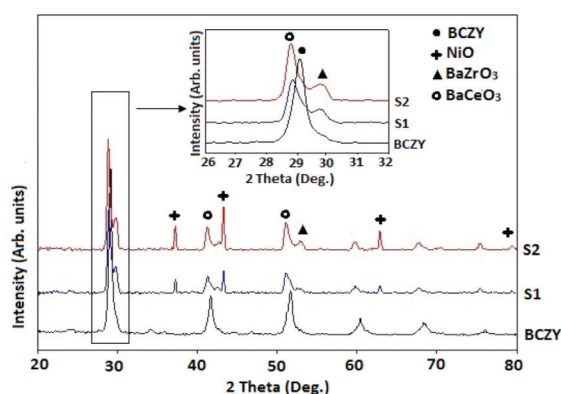


FIGURE 3. XRD patterns of single-phase of BCZY and the prepared composite powders after calcined at 1100°C

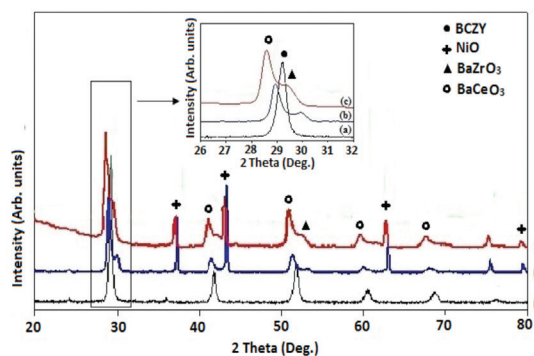


FIGURE 4. XRD patterns of (a) single-phase of BCZY and S1 powder after calcined at (b) 1100°C and (c) 1400°C

The use of Ni(NO₃)₂·6H₂O as the precursor material via EDSS method might contributed to the results of non-homogenize formation of NiO-BCZY composite anode due to the partial decomposition of the pre-prepared BCZY phase (Narendar et al. 2013). The results is in line with the work done by Yan et al. (2010) which also employed the nitrate-based nickel as the precursor material in preparing composite anodes of Ni-BCZY via a mechanical mixing powder method. Furthermore, detailed literature survey showed that homogenize composite anode prepared via EDSS method can only be formed if the ceramic part of the anode has three metal elements such as BaZr_{0.8}Y_{0.2}O_{3-δ}-NiO (BZY-NiO), Ni-BaZr_{0.85}Y_{0.15}O_{3-δ} (Ni-BZY) and Ni-BaCe_{0.9}Y_{0.1}O_{3-δ} (Ni-BCY) as respectively reported by Bi et al. (2011), Narendar et al. (2013) and Zunic et al. (2011). All their prepared samples were calcined at T = 800°C to 1100°C. For ceramic consisting of four metal elements such as BCZY, the higher calcination temperature up to T = 1400°C is still not suitable and sufficient enough to produce the desired composite anode of NiO-Ba(Ce_{0.6}Zr_{0.4})_{0.90}Y_{0.1}O_{2.95} (NiO-BCZY). The ratio of NiO to BCZY employed in this work might contributed to the results as an optimum or a proper ratio is required to produce a homogenize NiO-BCZY composite anode (Yamaguchi et al. 2016). Addition of less NiO may result into the production of non-homogenize composite anode due to incomplete reaction between NiO and the ceramic part of the composite anode and addition of more NiO may result into decomposition of ceramic part of the desired composite anode. Besides, composition of the BCZY ceramic part might also contributed to the formation of non-homogenize formation of NiO-BCZY composite anode. Composition of dopant in the ceramic part plays a significant role to allow the diffusion of NiO into the ceramic part during heat treatment process to form a homogenize composite anode (Yamaguchi et al. 2016; Zunic et al. 2014). Therefore, further improvement of the crucial conditions in the EDSS method along with modification technique using a modified sol-gel method to produce a composite of NiO-BCZY phase will be applied in our future work.

SEM images of the S1 powders after calcined at 1100°C and 1400°C, respectively, are shown in Figure 5. A significant increment in particle size was observed as the calcination temperature increased. These results obey the calcination theory which states that the particle growth increases with the increase in calcination temperature (Kishimoto et al. 2014; Rahman et al. 2012). The non-homogenize phase of the desired NiO-BCZY composite anode also resulted in the non-homogenize distribution of elements as shown in the EDX mapping spectrum in Figure 6. The analysis of elemental composition of the calcined powder of the S1 at 1100°C is shown in Table 1. The weight percent (wt. %) of each element obtained from EDX analysis was used to calculate mole fraction. The mole fractions were calculated assuming pure ABO₃ perovskite with Ba only on A-site and Ce, Zr and Y on the B-site. From the table, it can be seen that the elemental fraction of Ba/Ce/Y in the compound was close to the nominal

fraction of NiO-BCZY. However, the fractions of Zr in the powder are deviated from their nominal fraction. At >30%-mole Zr content, the cerate-zirconate sample tends to form Zr-rich clusters and it became relatively higher than the amounts of Ce cluster as previously reported by Osman et al. (2010). As a result, the Zr element were not homogenizely distributed in the sample giving rise to the fluctuations of chemical composition.

CONCLUSION

Nickel nitrate salt as precursor material and two different heat treatments profiles were used in the preparation of

NiO-BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} (NiO-BCZY) composite powders with different weight ratios of NiO:BCZY (50:50 and 60:40). XRD analysis revealed that the calcined powders at 1100°C of S1 (50:50) and S2 (60:40) consists of three phases which were NiO, BaCeO₃ and BaZrO₃, respectively. A NiO-BCZY composite still cannot be achieved even after the calcination temperature increased up to 1400°C. The sample tends to form Zr-rich clusters generating to the non-stoichiometric composition as proven by EDX analysis. The results indicate that the used of nitrate-based salt of nickel was not favored in the synthesis of composite anode which consists of four metal elements in its ceramic part such as NiO-BCZY by EDSS method without providing

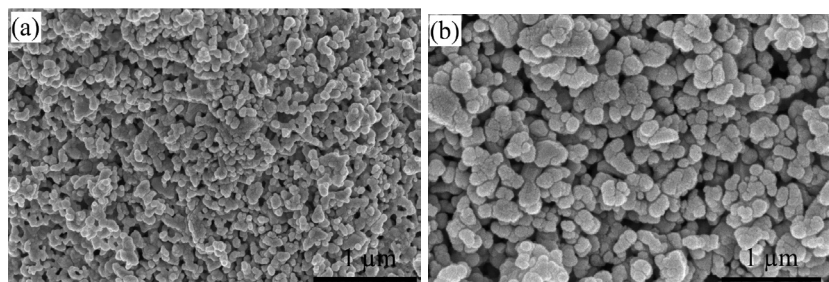


FIGURE 5. SEM images of the prepared S1 powders after calcined at (a) 1100°C and (b) 1400°C

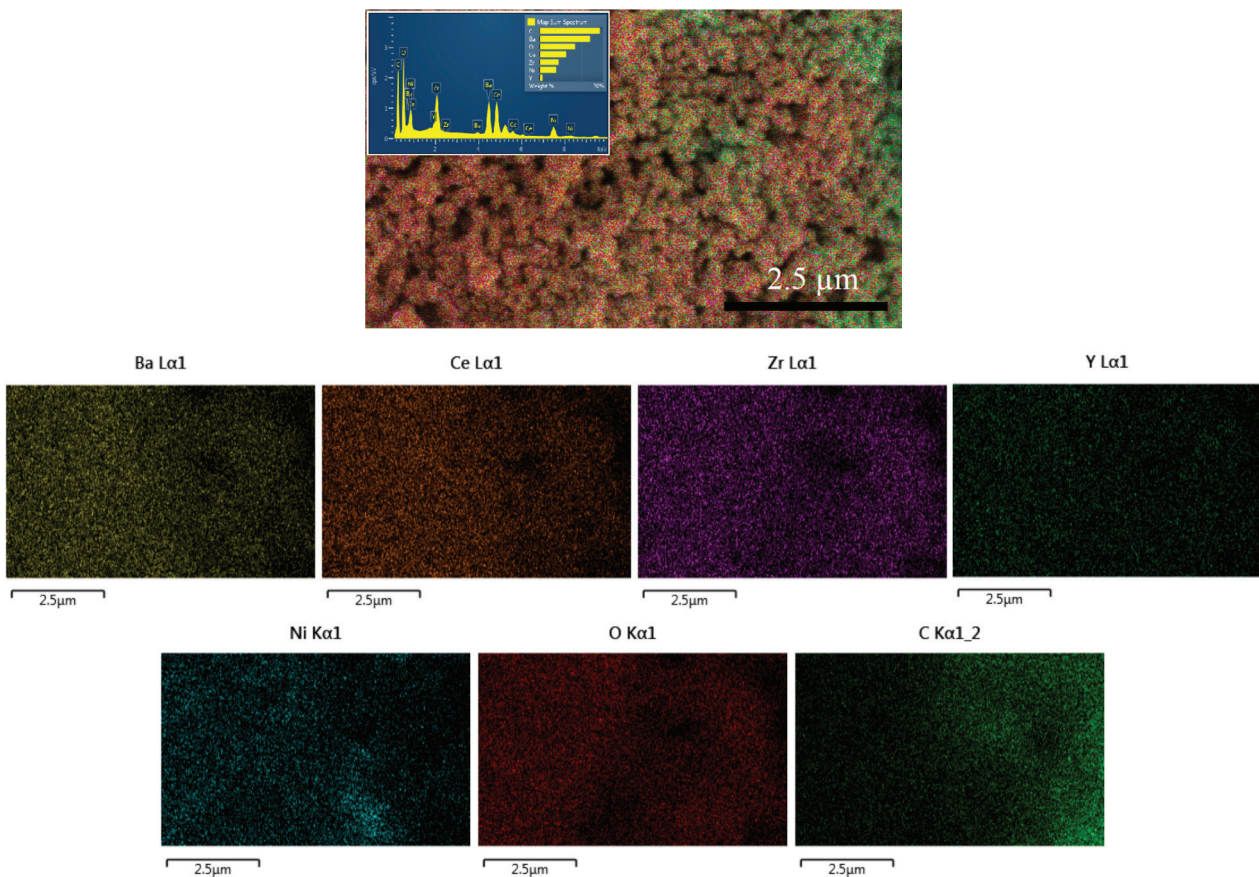


FIGURE 6. EDX mapping spectra of SEM image of the S1 powder after calcined at 1100°C

TABLE 1. EDX data of elemental composition of S1 powder after calcined at 1100°C

Element	wt. %	A _w	Mole	Calculated mole fraction	Nominal mole fraction
Ba	23.77	137.33	0.173	1.000	1.000
Ce	12.65	140.12	0.090	0.520	0.560
Zr	8.99	91.224	0.099	0.572	0.340
Y	1.47	88.906	0.017	0.098	0.100
			Total	1.766	2.000
Ni	7.78	58.693	0.133		
O	16.86	15.999	1.054		
C	28.47	12.0107	2.370		

proper amount of NiO and composition of ceramic. Further modification of the method is in progress and will be reported elsewhere.

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