Understanding the phase formation and compositions of barium carbonate modified NiO-yttria stabilized zirconia for fuel cell application

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Abstract

A simple modification of a conventional nickel-yttria stabilized zirconia (Ni-YSZ) anode for a solid oxide fuel cell (SOFC) by BaCO₃ can enhance the coking resistance of the anode in carbon-containing fuels. In this study, X-ray diffraction, Raman spectroscopy, and thermo-gravimetric analysis are used to investigate the chemical reactions among BaCO₃, NiO, and YSZ to understand the phase formation and compositions during fabrication process. Our results indicate that BaCO₃ reacts readily with YSZ to produce a BaZr_{1-x}Y_xO_{3-δ} (BZY) phase at temperatures higher than 900°C. For the mixture of BaCO₃ and NiO, mixed phases of BaNiO₃-BaNiO_{2.36} are formed at 900 °C, but the mixed phases are unstable at elevated temperatures, or with the presence of YSZ, or under a reducing atmosphere. In line with previously

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published works, the obtained results imply that a BZY/YSZ-BaO/Ni anode can be easily created by a usual heat-treatment (cell fabrication condition) and subsequently reducing process (testing condition) for the mixture of BaCO₃, NiO, and YSZ.

Keywords: Solid oxide fuel cells; Nickel anode; Coking resistance; Barium carbonate; Catalyst modification

1. Introduction

Solid oxide fuel cells (SOFCs) powered by hydrocarbon fuels have attracted much attention because direct use of hydrocarbon fuels (rather than pure hydrogen) can reduce the costs of the SOFC systems by eliminating or minimizing the additional reforming and purification process [1-8]. Furthermore, the direct use of hydrocarbon fuels to generate electrical power has the potential to substantially accelerate the use of fuel cells in transportation and distributed power generation [1, 4, 5]. However, one of the major challenges for direct utilization of hydrocarbon fuels in SOFC is the deactivation of traditional nickel-yttria stabilized zirconia (Ni-YSZ) anode by coking under carbon contained fuels [1-8].

To improve the coking resistance of Ni-YSZ anode, substantial efforts have been devoted to two main directions: development of alternative Ni-free anode materials or modification of traditional Ni-based anodes. The search for alternative materials to Ni-YSZ has been mainly focused on Cu-based cermets [9, 10] and perovskite anodes including LaSr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} [11], Sr₂Mg_{1-x}Mn_xMoO_{6-δ} [12], doped (La,Sr)(Ti)O₃ [13, 14], and La_{0.4}Sr_{0.6}Ti_{1-x}Mn_xO_{3-δ} [15]. However, practical application of Cu-based cermets is hindered by their poor performance while the critical issues for perovskite anodes are poor electro-catalytic activity and limited chemical and thermal compatibility with YSZ electrolyte at high temperatures required for fabrication. On

the other hand, some catalysts such as SDC [5, 16] , $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ [17, 18], and Ru-CeO_2 [1, 19-21] have been applied to modify the Ni surface to promote reforming of hydrocarbon fuels before they reach Ni surfaces, which indeed showed different degrees of improved coking tolerance to various hydrocarbon fuels. It should be noted, however, that the performances of cells powered by hydrocarbon fuels are still much lower than those by H_2 fuel [21]. When a heavy hydrocarbon fuel such as iso-octane was used, a larger amount of CO_2 and/or O_2 must be co-fed to prevent coking [1, 5, 16], reducing the efficiency and increasing the complexity of the system [4]. In addition, the high cost of Ru [1, 19-21] may limit the practical application of SOFCs.

In recent years, surface-modified Ni-YSZ anodes have shown excellent coking resistance when they were directly exposed to hydrocarbon fuels, including methane, propane, and even octane fuels [2-4, 22, 23]. For example, a $\text{Ni-BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2-x}\text{Yb}_x\text{O}_{3-\delta}$ (BZCYYb) anode was reported to demonstrate superior tolerance to coking and sulfur poisoning due to strong water adsorption capability of the mixed ion conductor BZCYYb [2]. Later study indicated that the enhanced coking resistance might result from the BZCYYb phase modification of Ni surface during high temperature treatment [22]. Li et al. proposed that BZCYYb perovskite is a promising alternative anode material for direct hydrocarbon SOFCs with high activity and excellent carbon cracking resistance [24, 25]. In addition, a new anode with nanostructured barium oxide/nickel (BaO/Ni) interfaces *via* vapor deposition of BaO into Ni-YSZ was designed and investigated [3]. The obtained results indicated that these BaO/Ni interfaces indeed promoted a water-mediated carbon removal process and enhanced Ni resistance to carbon buildup and deactivation under carbon contained fuels [3, 26]. The cells with the novel anode demonstrated high power density and stability in C_3H_8 and gasified carbon fuels at 750 °C. Recently, we

adopted a simpler and cost-effective modification to fabricate a multi-functional composite anodes, derived from a conventional NiO-YSZ anode mixed with small amount of BaCO_3 [4]. The cell with BaCO_3 modified Ni-YSZ anode were operated on a transportation fuel (iso-octane) without the addition of excess amount of CO_2 and/or O_2 , demonstrating a peak power density of 0.6 W/cm^2 at 750°C . More importantly, at 750°C the cell showed a stable power output at a cell voltage of 0.7 V with wet iso-octane (6.5% in Ar) as the fuel over 100 h, indicating the great potential of BaCO_3 modified NiO-YSZ anode for direct utilization of transportation fuels. The unique properties were attributed to the formation of a unique microstructure: discrete nano-particles of BaO on Ni grain surface and a conformal coating of $\text{Ba}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ (BZY) BZY on YSZ grain surface, during the processes for fabricating the novel cells.

In those studies, different phases of Ba species have been detected in Ba modified NiO-YSZ anodes at different stages of the preparation and testing processes, including BaNiO_2 and BaNiO_3 on the NiO surface [3], BaO on Ni surface [3], and BZY on YSZ surface [4]. However, the details of the phase composition of a Ba modified NiO/YSZ anode during fabrication process are yet to be understood to gain deeper understanding of the coking resistance mechanism of the Ba modified Ni-YSZ anode. In the present work, we systematically study the chemical reactions in the system of BaCO_3 -NiO-YSZ using temperature-dependent X-ray diffraction (XRD), post-micro-Raman spectroscopy, and thermo-gravimetric analysis (TGA).

2. Experimental

BaCO_3 (Alfa), NiO (Alfa), and YSZ (yttria-stabilized zirconia, DaiichiKigenso, Japan) powders were mixed in a weight ratio of 4:3:3 (or mole ratio of 5:10:6) and represented as BaCO_3 -NiO-YSZ. In order to study the reactions between BaCO_3 and

YSZ or NiO, two mixtures, BaCO₃ and NiO (mole ratio 1:2) as well as BaCO₃ and YSZ (mole ratio 5:6), were also prepared, which were denoted as BaCO₃-NiO and BaCO₃-YSZ, respectively. These powders were mixed in an agate mortar and then pressed into pellets in a mold, followed by firing in ambient air at 800-1200°C for 5h. To determine the phase composition of sintered samples under fuel cell operating conditions, the BaCO₃-NiO samples were reduced in H₂ at 750 °C for 2h.

X-ray diffraction (PW1800 X-ray diffractometer, Philips Analytical) measurement using Cu K α radiation was employed to identify the phase of various BaCO₃-NiO-YSZ reaction products after different treatments. XRD data were obtained in the range of $2\theta = 20$ to 80° with a step size of 0.016° . A Raman spectrometer (Renishaw 1000, 40 mW) was also employed for phase identification of the samples. A Coherent Model Innova 90 argon laser with wavelength = 514.5 nm was used as an excitation source. The microstructure of the BaCO₃-NiO reaction products after different treatment was observed using a scanning electron microscope (SEM, Hitachi SU800, Japan). Thermo-gravimetric analysis (TGA) was performed using a TAQ600 DSC-TGA system in air to determine the mass change of these mixtures at various temperatures. The temperature program started from room temperature up to 1200 °C, holding at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ and an air flow rate of 100 ml min^{-1} .

3. Results and Discussion

Fig. 1a show the XRD patterns of BaCO₃-YSZ pellets after firing at 800-1200°C for 5h. To identify the new phase formation, XRD patterns of BaCO₃ and YSZ powder samples were first collected at room temperature. The main peaks appear at

23.7° and 34.1° for orthorhombic BaCO₃ [27, 28] and 30.2°, 50.3° and 62.1° for cubic fluorite YSZ. The reflection lines of BaZrO₃ (JCPDS no. 06-0399) are also presented. At low firing temperatures of 800–900 °C, there was little change in their peaks. Our isothermal TGA analysis of pure BaCO₃ at 900 °C for 2h under air showed that BaCO₃ underwent a weight loss of only ~0.5%, indicated its thermal stability under the process conditions. The results are also in good agreement with the thermodynamic calculation and Arvanitidis' reports that the decomposition temperature of BaCO₃ is above 1000°C under air condition [29]. Therefore, it can be concluded that at 800–900 °C BaCO₃ phase dose not decompose and have little reactions with YSZ. Increasing the firing temperature to 1000 °C, BaCO₃ phase almost disappear and some typical peaks of BZY are observed at 37.1°, 43.1°, and 53.5° as compared to the XRD patterns of BaZrO₃ [4, 27]. Taking account of the decomposition of BaCO₃ to BaO above 1000°C, the formed BZY are attributed to the reaction between BaCO₃/BaO and YSZ. It was reported that BaZr_{0.85}Y_{0.15}O₃ (BZY) electrolyte was prepared by the solid-state reaction of a gastight 8YSZ layer and a coated BaCO₃ layer [30]. The intensities of BZY phase grow gradually as the firing temperature was increased from 1000 °C to 1200 °C, while the intensities for YSZ phase decrease and finally disappear at 1200°C due probably to a conformal BZY coating formed on the YSZ grain surface. Somroop et al. also observed that the BYZ film would effectively form on the YSZ substrate, which may arise from the similarity in the crystal structures of YSZ and BYZ [31]. The observations are further confirmed by the corresponding Raman spectra of the BaCO₃-YSZ sample (Fig. 1b). The main Raman vibrations of BaCO₃ include 690 and 1059 cm⁻¹ [27], while the vibration of ~623 cm⁻¹ corresponds to YSZ [7, 32]. The chemical reaction between BaCO₃/BaO and YSZ is confirmed by a broad band of 720-730 cm⁻¹ for BZY [4] after a

heat-treatment temperature of 1000 °C. As expected, the intensity of BZY band increases with the firing temperature. It is noted that a weak peak at $\sim 1059\text{ cm}^{-1}$ of BaCO_3 is observable even after treatment at 1200 °C (as shown in Fig. 1b), indicating that a very small amount of BaCO_3 still exist, which might result from the reaction of BaO with CO_2 from air during cooling down process. Whereas, the BaCO_3 is under detection limits from XRD analysis, indicating that Raman spectroscopy has a better sensitivity to a trace amount of surface materials than conventional X-ray diffraction [7, 33]. Similarly, small BaCO_3 peaks were also visible in the Raman spectra for formation of $\text{Ba}(\text{Zr}_{0.8}\text{Y}_{0.2})\text{O}_{2.9}$ [27].

Fig. 2 are the XRD patterns and the corresponding Raman spectra of $\text{BaCO}_3\text{-NiO}$ after heat-treatment at 800-1200 °C for 5h, respectively. The XRD patterns of original NiO powder are also given in Fig. 2a and its main peaks appear at 37.2° , 43.3° and 62.8° . While, the two bands of 1090 cm^{-1} and 1490 cm^{-1} in Raman spectra correspond to NiO phase (Fig. 2b) [34, 35]. Both the XRD and Raman spectra of $\text{BaCO}_3\text{-NiO}$ suggest that chemical reaction between BaCO_3 and NiO started at 900°C. New phases of BaNiO_3 (main peaks at 26° and 31.7°) and $\text{BaNiO}_{2.36}$ (main peaks at 27.5° and 31.3°) are observed in the XRD spectra, and the color of $\text{BaCO}_3\text{-NiO}$ sample was changed from green to black. The formation of $\text{BaNiO}_3\text{-BaNiO}_{2.36}$ phase is further confirmed by the 415 cm^{-1} , 507 cm^{-1} and 600 cm^{-1} bands in Raman spectra (Fig. 2b), which are similar to the Raman features of BaCuO_2 [36, 37]. As temperature increases to 1000°C, BaCO_3 is fully converted to $\text{BaNiO}_3\text{-BaNiO}_{2.36}$, even trace amount of BaCO_3 could not be detected by Raman spectroscopy. However, the intensities of $\text{BaNiO}_3\text{-BaNiO}_{2.36}$ phase decreased slightly above 900°C, indicating that the formed mixture phase of $\text{BaNiO}_3\text{-BaNiO}_{2.36}$ is not stable at higher temperatures and will be decomposed gradually. Furthermore, it is noted that as the heat treatment

temperature increased from 900 to 1200 °C, the relative intensities of BaNiO₃ decreased whereas the relative intensities of BaNiO_{2.36} increased, indicating that the BaNiO₃ is less stable and undergo a phase transformation to BaNiO_{2.36} and O₂ at higher temperatures. Whereas, the intensity of the BaNiO_{2.36} phase also decreased above 1100°C, indicating the BaNiO_{2.36} is unstable and will be decomposed slowly to BaO and NiO at higher temperatures. The decomposition of BaNiO_{2.36} was further confirmed by XRD analysis (Fig. 2a). Only NiO phase was detected when the BaCO₃-NiO system was fired at 1400° C for 5h. Nevertheless, the formed BaO phase from decomposition of BaNiO_x has been proved to be amorphous by a high-resolution transmission electron microscopy image [3], which therefore could not be detected using conventional X-ray analysis

Fig. 3 shows the SEM images of surface of BaCO₃-NiO pellets after firing for 5h at (a) 800°C, (b)900°C, (c) 1000°C, (d)1100°C, and (e) 1200°C respectively. It can be seen that at 800°C the pellets consist of some irregular particles, which indicates the presence of BaCO₃ and NiO mixture. While, some dense and regular BaNiO_x grains with a number of NiO agglomerates (Fig. 3b) are observed at 900°C. As the sintering temperature rose to 1000°C, the amount of BaNiO_x grains increases (Fig. 3c). Meanwhile, a larger number of crevices between formed BaNiO_x grains are observed, which may due to the emission of CO₂ during the reaction process between BaCO₃ and NiO at 1000°C, which are also in good agreement with the XRD and Raman results in Fig. 2. The interesting morphology variation is that the grains of BaNiO_x continue to grow up and even formed dense film structure at 1100°C (Fig. 3d), which indicates their excellent sinterability. The melting phenomenon of BaCO₃-NiO pellets after firing at 1100°C was also observed. It was reported that NiO was an effective sintering additive for BZY, which can cause that its sintering temperature lowered

down from original 1600°C to around 1400 °C [38]. After firing at 1200°C some new rod structures extending from the BaCO₃-NiO pellets surface are observed (Fig. 3e), which indicates a phase transformation from BaNiO₃ to BaNiO_{2.36} or/and the further decomposition of BaNiO_x as shown in Fig. 2. Therefore, these morphological features of BaCO₃-NiO pellets also support both XRD and Raman results in Fig. 2

Shown in Fig. 4 (a) and (b) are the XRD patterns and Raman spectra of BaCO₃-NiO-YSZ mixture after heat-treatment at 800-1200 °C for 5 h, respectively. Compared with the mixture of BaCO₃-YSZ (Fig. 1) and BaCO₃-NiO (Fig. 2), the BaCO₃-NiO-YSZ mixture shows similar behaviors. There is no reactions take place at temperatures below 800 °C. When the temperature was increased to 900 °C, BaCO₃ is fully reacted with YSZ and NiO and converted to BaNiO₃-BaNiO_{2.36} and BZY. The results are consistent with the observations in the mixtures of BaCO₃-YSZ (Fig.1) and BaCO₃-NiO (Fig. 2). The only difference is that the mixture phase of BaNiO_x is less stable with the presence of YSZ. For example, the mixed phases of BaNiO₃-BaNiO_{2.36} disappear at 1000 °C, and only NiO, YSZ, and BZY phases could be detected, as confirmed by both XRD and Raman spectra. In contrast, BaNiO_x phase may still exist even after firing at 1200 °C of the BaCO₃-NiO mixture (Fig. 2), indicating that BZY is a more thermodynamically stable phase as compared to BaNiO_x at high temperature. Although the reactions among NiO, YSZ, and BaCO₃ are finished at 1000 °C from XRD analysis, the relative intensity of YSZ phase (Raman vibration at ~623 cm⁻¹) compared to BZY phase decreased significantly as the temperature increased from 1000 to 1200°C, indicating some microstructure or phase evolution at elevated temperatures. To systematically compare the three samples, the main components of BaCO₃-YSZ, BaCO₃-NiO and BaCO₃-NiO-YSZ after heat-treatment at different temperatures in air are summarized in Table 1.

To further understand the chemical reactions in these mixtures, TG analysis of BaCO_3 -YSZ, BaCO_3 -NiO, and BaCO_3 -NiO-YSZ was performed in air, as shown in Fig. 5(a). For comparison, the TG analysis of BaCO_3 is also plotted in Fig. 5(a). The samples of BaCO_3 -YSZ, BaCO_3 -NiO and BaCO_3 -NiO-YSZ show a progressive weight loss start after $\sim 800^\circ\text{C}$, and a fast weight loss happened at temperatures between 900°C - 1100°C . To compare the weight loss rate for those samples, Fig. 5b gave the derivative plots. Clearly, with the existence of YSZ and/or NiO, the BaCO_3 is more easily to decompose and give off CO_2 , causing the fast weight loss at relative lower temperatures as compared to pure BaCO_3 . The TGA results are consistent with the XRD and Raman results (Figs. 1, 2 and 4) that reactions between BaCO_3 and NiO/YSZ start at temperatures higher than 800°C , and the phase of BaNiO_3 - $\text{BaNiO}_{2.36}$ and BZY are formed at 900, accompanying the decomposition of BaCO_3 and emission of large amount of CO_2 . Finally the corresponding stable reaction products (NiO, BZY and YSZ) formed at temperatures above 1100°C . Here, the initial and final decomposition temperatures for pure BaCO_3 are $\sim 1000^\circ\text{C}$ and 1200°C , which keeps consistent with the Arvanitidis' reports that the decomposition temperature range of BaCO_3 was ~ 1200 - 1550K under Ar atmosphere [29]. Since the presence of NiO/YSZ would accelerate the decomposition of BaCO_3 , the final decomposition temperatures for these BaCO_3 mixtures are around 1150°C [28]. At 1200°C the maximum weight loss for BaCO_3 , BaCO_3 -YSZ, BaCO_3 -NiO and BaCO_3 -NiO-YSZ are 22.2%, 13.8%, 13.3% and 9.9%, which are very close to the theoretical weight of CO_2 loss associated with these compositions (22.3%, 12.8%, 12.8% and 8.9%), respectively, which further confirm that all the BaCO_3 has fully decomposed. Based on XRD, Raman, and TG analysis, the minimum heat temperature for BaCO_3 modified NiO-YSZ anode fabrication should be around 1200°C to create the right composition.

Since the BaCO_3 modified NiO-YSZ anode has to be exposed to a reducing atmosphere to reduce NiO to metallic nickel before electrochemical testing, we need to investigate the changes in phase composition upon exposure to H_2 . In some reports alkaline earth metal oxide BaO was infiltrated into the conventional Ni-YSZ for improving the coking and sulfur tolerance ability, and the final treatment temperature was usually below 1000°C [23, 39]. In these fabrication conditions, BaNiO_x phase might still exist in the anode. In addition, BaNiO_2 - BaNiO_3 phase were also observable in the BaO-NiO-YSZ anode before reduction when BaO was introduced into the NiO-YSZ structure by evaporation deposition [3]. The investigation of BaNiO_x phase stability under reducing condition will help understand the stability of the BaCO_3 modified anode. Since BZY phase is very stable under reducing condition [2, 40, 41], the sintered samples of BaCO_3 -NiO was used in this study. Fig. 6 shows the XRD of BaCO_3 -NiO pellets (firing at 800 - 1200°C for 5h) after exposure to H_2 at 750°C for 2h. Comparing with the data seen in Fig. 2b, it is clear that BaNiO_3 - $\text{BaNiO}_{2.36}$ are fully decomposed and only metallic Ni and BaCO_3 could be detected throughout the heat-treatment temperature ranges, suggesting that BaNiO_3 - $\text{BaNiO}_{2.36}$ compound is not stable in the reducing atmosphere and it will be decomposed to BaO. This is consistent with our previous observations using the more sensitive synchrotron-based X-ray analyses that BaNiO_x mixtures formed from the reaction between BaO and NiO can be reduced under H_2 atmosphere [3]. It is noted that the formation of BaCO_3 is likely caused by the reaction of BaO with CO_2 and moisture from air during the subsequent cooling process.

This study has helped us to gain a better understanding of the chemical reaction and phase transformation in a BaCO_3 modified Ni-YSZ anode. During the cell fabrication process, BaCO_3 reacts with YSZ and NiO to form BZY on YSZ surface

and $\text{BaNiO}_3\text{-BaNiO}_{2.36}$ on NiO surface at elevated temperatures. Furthermore, the formed $\text{BaNiO}_3\text{-BaNiO}_{2.36}$ subsequently decomposes at even higher temperature or under reducing condition.

4. Conclusions

We have systematically studied the reaction products of barium carbonate modified NiO-yttria stabilized zirconia heat treated between 800°C - 1200°C . Our results indicate that BaCO_3/BaO readily reacts with YSZ to produce stable $\text{BaZr}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ (BZY) on YSZ surface at 900°C , while BaCO_3 reacts with NiO to form $\text{BaNiO}_3\text{-BaNiO}_{2.36}$ on NiO surface during the initial firing step. However, the $\text{BaNiO}_3\text{-BaNiO}_{2.36}$ phases are unstable at high temperatures or under a reducing atmosphere (e.g., exposure to a fuel). Furthermore, the decomposition of $\text{BaNiO}_3\text{-BaNiO}_{2.36}$ is promoted by the presence of YSZ. Our obtained results helped us to gain a better understanding of the chemical reaction and phase transformation in a BaCO_3 modified Ni-YSZ anode.

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Table and Figure Captions

Table. 1 - Reaction products of the pellets of BaCO_3 -YSZ, BaCO_3 -NiO and BaCO_3 -NiO-YSZ mixtures after firing at 800–1200 °C for 5 h in air.

Fig. 1 - Temperature-dependent (a) XRD patterns and (b) corresponding Raman spectra of BaCO_3 -YSZ pellets obtained in air at room temperature.

Fig. 2 - Temperature-dependent (a) XRD patterns and (b) corresponding Raman spectra of BaCO_3 -NiO pellets obtained in air at room temperature.

Fig. 3 - SEM images of surface of BaCO_3 -NiO pellets after firing for 5h at (a) 800°C, (b) 900°C, (c) 1000°C, (d) 1100°C, and (e) 1200°C

Fig. 4 - Temperature-dependent (a) XRD patterns and (b) Raman spectra of BaCO_3 -NiO-YSZ pellets obtained in air at room temperature.

Fig. 5 - (a) TGA plot and (b) derivative plot of BaCO_3 , BaCO_3 -YSZ, BaCO_3 -NiO and BaCO_3 -NiO-YSZ powders from room temperature to 1200°C under air condition.

Fig. 6 - XRD patterns of BaCO_3 -NiO (sintering at 800-1200 °C for 5h) pellets after reduction in H_2 at 750°C for 2h

Table 1

Reaction products of the pellets of BaCO₃-YSZ, BaCO₃-NiO and BaCO₃-NiO-YSZ mixtures after firing at 800–1200 °C for 5 h in air.

Mixtures	BaCO ₃ -YSZ	BaCO ₃ -NiO	BaCO ₃ -NiO -YSZ
800 °C	BaCO ₃ and YSZ	BaCO ₃ , NiO	BaCO ₃ , NiO and YSZ
900 °C	BaCO ₃ , YSZ and BZY	BaCO ₃ , NiO, BaNiO ₃ and BaNiO _{2.36}	BaCO ₃ , NiO, YSZ ,BZY, BaNiO ₃ and BaNiO _{2.36}
1000 °C	BaCO ₃ , YSZ and BZY	NiO, BaNiO ₃ and BaNiO _{2.36}	NiO, BZY and YSZ
1100 °C	BaCO ₃ , YSZ and BZY	NiO, BaNiO ₃ and BaNiO _{2.36}	NiO, BZY and YSZ
1200 °C	BaCO ₃ and BZY	NiO, BaNiO ₃ and BaNiO _{2.36}	NiO, BZY and YSZ

Fig. 1 - Temperature-dependent (a) XRD patterns and (b) corresponding Raman spectra of BaCO₃-YSZ pellets obtained in air at room temperature.

Fig. 2 - Temperature-dependent (a) XRD patterns and (b) corresponding Raman spectra of $\text{BaCO}_3\text{-NiO}$ pellets obtained in air at room temperature.

Fig. 3 - SEM images of surface of BaCO₃-NiO pellets after firing for 5h at (a) 800°C, (b)900°C, (c) 1000°C, (d)1100°C, and (e) 1200°C

Fig. 4 - Temperature-dependent (a) XRD patterns and (b) Raman spectra of BaCO₃-NiO-YSZ pellets obtained in air at room temperature.

Fig. 5 - (a) TGA plot and (b) derivative plot of BaCO_3 , $\text{BaCO}_3\text{-YSZ}$, $\text{BaCO}_3\text{-NiO}$ and $\text{BaCO}_3\text{-NiO-YSZ}$ powders from room temperature to 1200 $^{\circ}\text{C}$ under air condition.

Fig. 6 - XRD patterns of $\text{BaCO}_3\text{-NiO}$ (sintering at 800-1200 °C for 5h) pellets after reduction in H_2 at 750°C for 2h