

Characterization of nio-bczy as composite anode prepared by a one-step sol-gel method

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Abstract

A high polarization resistance (R_p) at intermediate temperature (500–800°C) operation has become one of the major challenges in the development of proton-conducting fuel cells (PCFCs). R_p is the resistance of the cell that contributes by the electrodes parts which are anode and cathode as well as their interfacial components. The present study focused on the NiO-Ba(Ce_{0.6}Zr_{0.4})_{0.9}Y_{0.1}O_{3-δ} (NiO-BCZY) composite anode and its interfacial parts where the oxidation process takes place. The NiO-BCZY with a ratio of 50:50 was prepared by a sol-gel method and characterized by X-Ray Diffractometer (XRD), Field Emission Scanning Electron Microscopy/Energy Dispersive X-ray (FESEM/EDX), and Electrochemical Impedance Spectroscopy (EIS). At calcination temperature of 1100°C, NiO and BCZY oxides can preserve their phases to form composite anode as proven by XRD analysis. Morphology of the composite anode as observed by FESEM was spherical with particle size in the range of 30-70 nm. XRD analysis showed the formation of Ni-BCZY after undergoing reduction process under wet H₂:N₂ (10%:90%). As confirmed by the EIS data, the increased conductivity of the composite anode in wet H₂:N₂ (10%:90%) indicates that the NiO in the composite anode was reduced to Ni metal. The fabricated NiO-BCZY composite anode has shown a good potential to be a promising anode in PCFC application.

Keywords: Composite anode, sol-gel method, conductivity

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INTRODUCTION

High polarization resistance at intermediate temperature has become one of the major problems for the development of proton-conducting fuel cells (PCFCs). One way to overcome the high polarization resistance is to use composite electrodes that can increase the triple-phase boundary (TPB) length (Chevallier, Zunic et al. 2009). Nickel cermet is commonly used as an anode for PCFCs application due to its excellent catalytic activity towards hydrogen oxidation at specific temperature, offers significant cost saving as well as it provides a conduction path for electrons. Generally, the use of proton-conducting ceramic in the composite anode offers the extension of the TPB length to the whole anode volume and as a result, the electrochemical reaction occurred at the electrolyte/electrode interface is extended. In addition, the thermal expansion coefficient of the anode to the ceramic electrolyte can be adjusted (Fabbri, Pergolesi et al. 2010).

Owing to the qualities of proton-conducting ceramic, acceptor-doped BaCeO₃ compounds have been considered as electrolytes for PCFC since they show low activation energy and high proton conductivity at intermediate temperatures. Unfortunately, the compounds have poor chemical stability in the presence of CO₂ and water vapor at higher temperatures. To look for a compromise

between chemical stability and proton conductivity, the most effective technique is the partial substitution of Ce with Zr in acceptor-doped BaCeO₃. For example, yttrium doped barium cerate-zirconate (BCZY) reveals both adequate proton conductivity as well as sufficient thermal and chemical stability over a wide range of conditions significant to fuel cell operation (Zuo, Dorris et al. 2006, Zuo, Zha et al. 2006, Fabbri, D'Epifanio et al. 2008).

Despite growing interest received by the PCFCs system, more research has been conducted by tailoring the microstructure of the anode. A good dispersion of particles in the anode is required to improve cell performance. To the best of our knowledge, only a few methods have been investigated to prepare the anode powders based on protonic conductors which are mechanical mixing (Zuo, Dorris et al. 2006) and combustion method (Nasani, Ramasamy et al. 2014). The mechanical mixing method is very costly and leading to coarse and inhomogeneous powders while a pure crystalline phase of the anode cannot be easily obtained by combustion method (Chevallier, Zunic et al. 2009). By taking an account the effect of synthesizing method on the microstructure of the anode, several existing synthesizing methods need to be modified in preparing anode powder for a promising PCFC anode.

Thus, in this work, the NiO-BCZY composite anode was prepared by a one-step sol-gel method and the characteristics of the composite anode were examined.

EXPERIMENTAL

A stoichiometric amount of $\text{Ba}(\text{NO}_3)_2$ (99%, ACROS), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.5%, ACROS), $\text{Zr}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99.5%, ACROS), $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9%, Aldrich) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, ACROS) were dissolved in purified water under stirring process. The citric acid, which acts as a complexing agent was then added to the solution with molar ratios of soluble metal ions: citric acid of 1:1.5. The pH of the solution was adjusted to around 7 by adding the NH_4OH . The resulting solution was slowly vaporized on a hot plate at 120°C . The heating and stirring processes were controlled accordingly. The browning gas (known as NO_x) was released throughout the process and a dark brown gel was obtained. The black flakes were produced when the gel was dried in a furnace at 325°C . Then the obtained black flakes were calcined at 1100°C with the heating/cooling rate of $10^\circ\text{C min}^{-1}$ for 6 h to form fine NiO-BCZY powders.

To prepare the NiO-BCZY composite anode pellet, the NiO-BCZY composite anode powder was uniaxially pressed into a pellet under 365 MPa for about 1–2 minutes. Then, the anode pellet was sintered at 1300°C for 3 hours in an air atmosphere. The pellet was reduced at 700°C under a constant flow of a mixture containing 10% of H_2 in Ni gas. The composite anode pellet before and after reduction process was analyzed for its microstructure, phase verification as well as electrochemical studies.

The electrochemical performance of the composite anode pellet was measured by a lab-designed electrochemical system at a temperature ranging from $500\text{--}800^\circ\text{C}$ in humidified $\text{H}_2\text{:N}_2$ (10%:90%) and N_2 environment. The electrochemical impedance of the cell was evaluated by ZIVE SP2 Electrochemical Workstation (ZIVELAB WonATech) connected to a personal computer. EIS was recorded at the applied frequency range of 0.1 mHz to 1 MHz with an AC amplitude range of 1 mV to 10 mV. The obtained EIS curves were analyzed using ZMAN software.

RESULTS AND DISCUSSION

Fig. 1 reports the XRD pattern of the composite anode powder after calcined at 1100°C which showed the presence of NiO (JCPDS 78-0643) and BCZY phases (JCPDS 89-2485). The pronounced peaks of NiO can be indexed to their Miller index (*hkl*) of (111), (200) and (220) plane while the pronounced peaks of BCZY can be indexed to (110), (111), (200), (211), (220), (310), and (222), respectively. Traces of BaCO_3 also could be observed in the XRD pattern which were influenced by the high firing temperature and incomplete combustion of BCZY ceramic. According to Abdullah et al. (Abdullah, Osman et al. 2012), high temperature is needed to break the BaCO_3 bond once it formed during the processing stage.

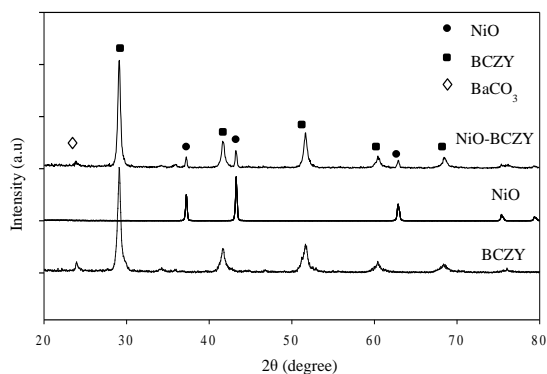


Fig. 1 XRD Patterns of NiO-BCZY Composite Anode After Calcined at $T=1100^\circ\text{C}$

Fig. 2 presents the FESEM image of NiO-BCZY composite anode powder after calcined at 1100°C for 6 h. The particle obtained was spherical in shape, size in the range of 30 to 70 nm, and with less agglomerates due to the presence of citric acid as a chelating agent. This agent binds the metal ions to form metal complexes and hindered the formation of aggregates in the composite anode. The chelating agent could enrich the interaction among the metal species through homogeneous dispersion of the metal-chelate matrix as it can effectively preserve the molecular level mixing of metal ions in the precursor.

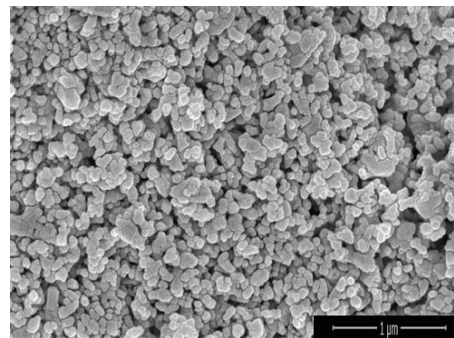


Fig. 2 Morphology of composite anode powder after calcined at $T=1100^\circ\text{C}$

In addition, the elemental composition of the prepared NiO-BCZY powder was investigated by EDX analysis and presented in Table 1. The percentage weight of each element obtained from EDX analysis was used to calculate the mole fraction. The elemental fraction of Ba/Ce/Zr/Y obtained in the NiO-BCZY composite anode was close to the nominal fraction of NiO-BCZY. The result indicates that the one-step sol-gel method used for synthesizing NiO-BCZY does not alter the elemental composition of the final product.

Table 1 Elemental composition of NiO-BCZY powder.

Element	Elemental Atomic Percentage (%)	Calculate Mole Fraction	Nominal Mole Fraction
Ba	23.77	1.00	1.00
Ce	12.65	0.54	0.54
Zr	8.99	0.38	0.36
Y	1.47	0.06	0.10
Ni	17.78	-	-
O	16.86	-	-

XRD analysis of the pellet before reduction confirmed the presence of the NiO and BCZY phases, while the existence of Ni metal (JCPDS 87-0712) and BCZY crystalline phases were detected after the reduction process as shown in Fig. 3. The pronounced peaks of Ni metal can be indexed to (111) at $2\theta = 44.5^\circ$ and (220) at $2\theta = 76.3^\circ$ as also observed by Chevallier et al. (Chevallier, Zunic et al. 2009).

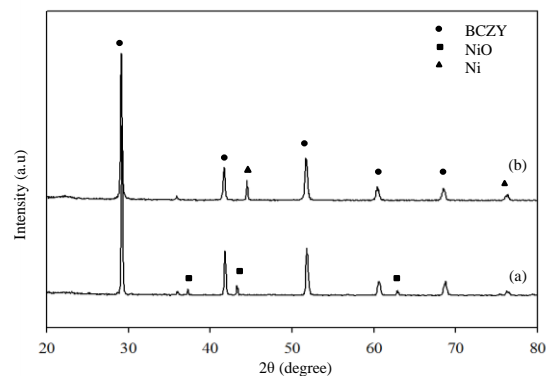


Fig. 3 X-ray Diffraction Pattern of (a) NiO-BCZY (before reduction) and (b) Ni-BCZY (after reduction)

The electrical anode performance of the NiO-BCZY pellet was studied using impedance measurement in different environments. Fig. 5 shows the Nyquist impedance plots of the NiO-BCZY composite anode pellet under N_2 gas and wet 10% H_2 :90% N_2 with temperature ranging from 400–700°C. It could be observed that when the increasing of the temperature, the size of the EIS spectrum decreased. This observation shows that the involved reaction is thermally activated process in which the increasing temperature provides extra thermal energy to overcome the energy barrier in order for the process to occur.

Furthermore, there was also clearly seen the size of arcs for NiO-BCZY in 10% H_2 :90% N_2 are smaller than the arcs for NiO-BCZY in N_2 gas. The smaller arcs for NiO-BCZY in 10% H_2 :90% N_2 revealed the low total resistance and high conductivity of the composite anode. The higher conductivity values of NiO-BCZY in wet 10% H_2 :90% N_2 are related to the microstructure of composite anode itself in the respective condition. In N_2 condition, the particle size of NiO in the composite anode is bigger than the Ni in wet 10% H_2 :90% N_2 condition as the NiO started to reduce to metallic nickel. Hence, the length of the triple-phase boundary increased, enhancing the kinetics of hydrogen oxidation and indirectly increases the conductivity of the composite anode with smaller Ni particle size.

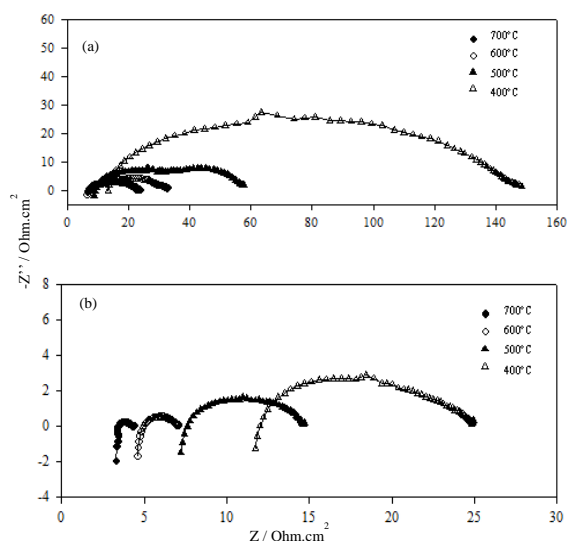


Fig. 5 The Nyquist Impedance Plots of NiO-BCZY Composite Anode Pellet Measured in (a) N_2 gas and (b) wet 10% H_2 :90% N_2 at Temperature Range of 400-700°C

CONCLUSION

A simple and low cost wet chemical method was developed to prepare NiO-BCZY composite anode powders for anode application in PCFCs. The XRD analysis of composite anode NiO-BCZY proved that the NiO and BCZY oxides could sustain their phases to form composite anode at a calcination temperature of 1100°C. Morphology of the composite anode as observed by FESEM was spherical in shape with particle size in the range of 30–70 nm. XRD analysis confirmed the formation of Ni-BCZY after undergoing the reduction process under wet H_2 : N_2 (10%:90%). Electrochemical measurement on the NiO-BCZY pellets showed that the increasing conductivity in wet H_2 : N_2 (10%:90%) verified that the NiO in the composite anode was reduced to Ni metal and showing appropriate electrochemical features for promising anodes in PCFCs application.

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