Ni-Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-δ} Anode Composites for Proton Conducting Solid Oxide Fuel Cells (H-SOFCs)

Kalpana Singh¹, Ashok Kumar Baral¹ & Venkataraman Thangadurai¹

¹Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, T2N 1N4, Canada

Correspondence: Venkataraman Thangadurai, Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, T2N 1N4, Canada. Tel: 1-403-210-8649. E-mail: vthangad@ucalgary.ca

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Abstract

In this paper, we report the electrochemical properties of Ni-Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O₃₋₈ (BSCZGY) anode composites in 3% H₂O-H₂ for proton conducting solid oxide fuel cells (H-SOFCs). Ni-BSCZGY composites with volume ratio of 30:70, 40:60, and 50:50 were synthesised through mechanical mixing and combustion methods. In combustion method, auto-ignition step led to brown coloured ash, which was calcined at 1000 °C for 5 h to form NiO-BSCZGY powder. Screen-printing, co-firing and reduction process were used to prepare the symmetrical cell: Ni-BSCZGY/BSCZGY/Ni-BSCZGY. Ni50-BSCZGY anode exhibited the lowest polarisation resistance (Rp) of 0.8 Ω .cm² and 1.9 Ω .cm² at 710 °C under 3% H₂O-H₂, for both mechanically mixed and combustion methods, respectively.

Keywords: composite anodes, combustion synthesis, proton conducting solid oxide fuel cells, symmetrical cell, polarisation resistance, hydrogen oxidation reaction (HOR).

1. Introduction

Acceptor-doped ACeO₃ (A = Sr, Ba) perovskites show appreciable proton (H^+) conductivity under humid atmospheres in the temperature range of 500-700 °C (Iwahara, Esaka, Uchida, & Maeda, 1981; Iwahara, Uchida, Ono, & Ogaki, 1988). Ceramic proton conductors are being considered as alternative electrolyte materials to replace conventional oxide ion conducting yttrium-stabilised zirconia (YSZ) electrolyte in solid oxide fuel cells (SOFCs), which exhibits high conductivity only at very high temperatures (800-1000 °C) (Fergus, 2006). However, poor chemical stability of acceptor-doped BaCeO₃ under water and CO₂ containing atmospheres mars their widespread use as an electrolyte in SOFCs (Scholten & Schoonman, 1993; Bhide, & Virkar, 1999; Wu & Liu, 1997; Sneha & Thangadurai, 2007; Trobec & Thangadurai, 2008; Gill, Kannan, Maffei, & Thangadurai, 2013; Kan, Lussier, Bieringer, & Thangadurai, 2014). Recently, Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-δ} (BSCZGY) was reported to exhibit good chemical stability under water vapor and CO₂ containing atmospheres (Kannan, Singh, Gill, Fürstenhaupt, & Thangadurai, 2013). At 700 °C for H₂-air cell, BSCZGY electrolyte with an un-optimised Pt electrodes exhibited an OCV and power density of 1.15 V and 18 mWcm⁻², respectively (Kannan et al., 2013). Thus, appropriate anode and cathode materials are needed for its success as an electrolyte membrane for proton conducting SOFCs (H-SOFCs). Thus, aim of this work is to study the phase and microstructure of Ni-BSCZGY anodes, and to investigate the electrochemical processes occurring at the Ni-BSCZGY anodes under wet hydrogen through electrochemical ac impedance spectroscopy (EIS) (Singh, 2016).

By analogy with Ni-YSZ composite anode, most of the studies in H-SOFCs are also reported on Ni-proton conducting ceramic phase composites such as Ni-SrCe_{0.9}Yb_{0.1}O_{3- $\delta}$} (SCYb), Ni-BaCe_{0.9}Y_{0.1}O_{3- $\delta}$} (BCY10), and Ni-BaZr_{0.8}Y_{0.2}O_{3- δ} (BZY20) (Mather al., 2003; Essoumhi, Taillades, Taillades-Jacquin, Jones, & Rozière, 2008; Bi, Fabbri, Sun, & Traversa, 2011). Symmetrical cells studies on Ni33-SCYb (33 vol. % Ni), Ni35-BCY10 (35 vol. %) and Ni50-BZY20 (50 wt. % Ni) showed area specific polarization resistance (ASR) of about 10, 0.32 and 0.37 Ω .cm² at 600 °C under humid fuels (Mather et al., 2003; Essoumhi et al., 2008; Bi et al., 2011).

Mechanical mixing of the ceramic electrolyte with NiO powder and one-step nitrate-based combustion methods are being employed for preparing composite anodes for H-SOFCs (Mather et al., 2003; Essoumhi et al., 2008; Bi et al., 2011, Song et al., Moon, Lee, Dorris, & Balachandran, 2008; Mather, Figueiredo, Jurado, & Frade, 2003). Nitrate-based combustion method produce ultra-fine anode composite powders and possess a uniform distribution of NiO in the electrolyte matrix. This results in enhancement of the electrochemical performance towards fuel

oxidation, due to the increase in triple-phase boundary length for electrochemical reaction (Bi et al., 2011; Narendar, Mather, Dias, & Fagg, 2013). On the other hand, mechanical mixing method results in nonhomogeneous distribution of NiO and electrolyte phases, and thus, resulted in lower electrochemical performance (Bi et al., 2011). Here, solid state and combustion methods have been employed to prepare anode composites in Ni to BSCZGY volume ratio of 30:70, 40:60, and 50:50. Anode composites before reduction are labelled here as NiO-BSCZGY and after reduction as Ni-BSCZGY.

2. Materials Preparation and Experimental Procedures

NiO-BSCZGY anode composites with volume ratio of 30:70, 40:60 and 50:50 were prepared through mechanical mixing and combustion methods. The compositions of oxides were chosen, so that after reduction of NiO to Ni metal, the volume fraction of Ni would be about 30, 40 and 50% in Ni-BSCZGY. For the mechanical mixing, BSCZGY powders were first synthesized through a solid-state reaction (Kannan et al., 2013; Singh, 2016). Then, desired amounts of BSCZGY powders were mixed with commercial NiO (Alfa Aeser, 99.9%), and milled for 6 h with isopropanol, dried and used for making symmetrical cells (Singh, 2016).

In the combustion method, NiO-BSCZGY composite anodes were prepared in one step through auto-ignition. Stoichiometric amounts of high purity $Ba(NO_3)_2.6H_2O$ (>99%), $Sr(NO_3)_2.6H_2O$ (99.0%), $Ce(NO_3)_3.6H_2O$ (99.5%), $ZrO(NO_3)_2.xH_2O$ (99.9%), $Y(NO_3)_3.6H_2O$ (99.9%), $Gd(NO_3)_3.6H_2O$ (99.9%), and $Ni(NO_3)_2.6H_2O$ (98.0%) from Alfa Aeser were dissolved in distilled water. Citric acid monohydrate (99.5%, Alfa Aeser) as a complexing agent was added to the mixed solution in the molar ratio of 1:1.5 (metal ion: citric acid). The temperature of the solution was maintained at 90 °C throughout the stirring process until most of the water content evaporated and the gel was formed. Finally, the gel burnt into a brown colored ash through the auto-ignition process. The brown colored ash was calcined at 1000 °C for 5 h to get fine NiO-BSCZGY composite powders. Powder X-ray diffraction (PXRD) (Bruker D8 Powder X-ray diffractometer, $CuK\alpha$) was used to examine the chemical reactivity of NiO and BSCZGY powders (Singh, 2016).

BSCZGY discs for symmetrical cell measurements were prepared by pressing the as-prepared BSCZGY powders into pellets and calcining them at 1400 °C for 24 h. NiO-BSCZGY pastes were prepared by mechanically mixing the composite powders with appropriate amount of α -Terpineol and ethyl cellulose as solvent and binder, respectively. Symmetrical cell (NiO-BSCZGY/BSCZGY/NiO-BSCZGY) assemblies were fabricated by screen printing technique. The BSCZGY pellet was first screen printed with NiO-BSCZGY composite pastes on both sides. Then, it was fired at 1200 °C for 3h in air at the heating and cooling rate of 2 °C/min. The sintered symmetrical cells were painted with Au paste (LP A88-11S, Heraeus Inc., Germany), as the current collector during the symmetrical cell measurements. The symmetrical cells were reduced at 900 °C for 3 h in 3% H₂O/H₂ at the flow rate of 50 SCCM.

The electrochemical performance of the anode symmetrical cells was studied through electrochemical impedance spectroscopy (0.1 Hz to 1MHz) by using VersaSTAT 3 instrument. OTF1200X furnace was used to hold the cell at desired temperature. The morphology of anode composite before and after the reduction was analysed through scanning electron microscopy (Philips XL 30).

3. Results and Discussion

3.1 Phase and Microstructure

Figure 1 shows the PXRD patterns of mechanically mixed composite powders in 30:70, 40:60, and 50:50 ratio (volume ratio after the reduction), and the mixtures heat treated at 1200 °C for 3 h. The effect of high temperature firing on the phase and lattice parameters of BSCZGY in NiO-BSCZGY composites was investigated by PXRD. PXRD patterns of both the as-prepared NiO-BSCZGY composites and their respective heat-treated composite samples prepared by mechanical mixing show only the diffraction peaks corresponding to BSCZGY and NiO phases (Figure 1 (a-c)). It has been demonstrated that small amount of Ni might substitute the Zr due to the similar ionic radius ($r_{Zr(IV)} = 0.72$ Å, $r_{Ni(II)} = 0.69$ Å) during mixing through milling and high temperature firing process (Bi et al., 2011; Shannon, 1976; Babilo & Haile, 2005; Tong, Clark, Hoban, & O'Hayre, 2010). However, PXRD patterns did not show a shift in 20 peak positions, and the lattice constant for BSCZGY phase almost remained constant ~ 4.298 Å for all the three anode compositions (Table 1). This indicates that the stoichiometry of BSCZGY seems to be retained after mixing with NiO and firing at 1200 °C in air. Even if Ni substitution does happen into the BSCZY lattice, it will be beneficial for promoting anode reactions (hydrogen oxidation reaction, HOR), as it may introduce some electronic conductivity into the BSCZGY phase (Babilo & Haile, 2005).



Figure 1. Powder X-ray diffraction (PXRD) patterns of NiO, BSCZGY, as-prepared mechanically mixed composite powders, and the mixtures sintered at 1200 °C for 3 h. (a) NiO30-BSCZGY, (b) NiO40-BSCZGY, and (c) NiO50-BSCZGY

Composition	Lattice Constant (Å)	Lattice Constant (Å)
	as-prepared	after firing at 1200 °C
NiO30-BSCZGY	4.296 (2)	4.301 (8)
NiO40–BSCZGY	4.293 (2)	4.295 (2)
NiO50-BSCZGY	4.295 (7)	4.302 (8)
BSCZGY (as-prepared)	4.298 (9)	

Table 1. Variation of experimental lattice constants (Å) for BSCZGY in NiO-BSCZGY anodes prepared through mechanical mixing method.

Figure 2 shows the PXRD patterns of NiO-BSCZGY (30:70, 40:60, and 50:50) composites prepared by combustion method and calcined at 1000 °C for 5 h, 1100 °C for 5 h, and 1200 °C for 3h. The PXRD patterns of NiO-BSCZGY powders prepared by combustion method show impurity phases of BaY₂NiO₅ and SrY₂O₄ at all sintering temperatures, along with the NiO and perovskite BSCZGY phases (Figure 2 (a-c)). In combustion method, the lattice constants for the BSCZGY phase in all compositions are found to be higher than the lattice parameter of stoichiometric as-prepared BSCZGY (4.298 Å) (Table 2). Presence of BaY₂NiO₅ impurity phase indicates the potential loss of Ba and Y, and hence the deviation from nominal stoichiometry. One should expect a reduction in lattice parameter of BSCZGY phase in anode composite due to the loss of large ionic sized Ba²⁺ (1.35 Å) and Y³⁺ (0.9 Å) to form BaY₂NiO₅ (Shannon, 1976). Instead, increase in lattice parameter of BSCZGY phase was observed for combustion-synthesised composites. The higher lattice constant could be attributed to the formation of SrY₂O₄, in addition to BaY₂NiO₅, and former compound has smaller Sr²⁺ ions (1.18 Å) compared to Ba²⁺ (1.35 Å) (Shannon, 1976).

Table 2. Variation of experimental lattice constants (Å) for BSCZGY in NiO-BSCZGY anodes prepared through combustion method.

Composition	Lattice Constant (Å)	Lattice Constant (Å)
	after firing at 1000 °C	after firing at 1200 °C
NiO30–BSCZGY	4.333 (2)	4.320 (7)
NiO40–BSCZGY	4.340 (2)	4.309 (2)
NiO50-BSCZGY	4.330 (2)	4.328 (6)
BSCZGY (as-prepared)	4.298 (9)	

Literature studies have shown that the deviation from stoichiometry, presence of impurities, and Ba^{2+} and Y^{3+} loss results in a decrease of proton conductivity in doped-BaCeO₃ and BaZrO₃ (Narendar et al., 2013; Magrez & Schober, 2004; Yamazaki, Hernandez-Schanchez, & Haile, 2010). Also, the presence of BaY₂NiO₅ impurity phase was found during synthesis of Ni-BaZr_{1-x}Y_xO₃₋₆ composite anodes prepared through nitrate-based combustion method, and when Ni was used as a sintering aid for doped-BaZrO₃ (Bi et al., 2011; Babilo & Haile, 2005; Magrez & Schober, 2004; Tong, Clark, Bernau, Sanders, & O'Hayre, 2010; Bi, Fabbri, Sun, & Traversa, 2011). Literature studies have suggested that the impurity phase BaY₂NiO₅ form at temperatures above 900 °C, and remains even at high temperatures of 1500 °C (Tong et al., 2010). Some researchers have shown that BaY₂NiO₅ in the BaZr_{1-x}Y_xO_{3-δ} phases led to improved densification and enhanced grain-growth along with enhanced total electrical conductivity (Mather et al., 2003; Tong et al., 2010). However, subsequent work by Tong et al. showed that BaY₂NiO₅ impurity hampers proton conductivity and increases the activation energy for proton conduction (Narendar et al., 2013; Tong et al., 2010; Ricote & Bonanos, 2010).

Figure 3 shows the typical SEM micrographs after firing at 1200 °C for 3 h, of anode/electrolyte layer of the NiO40-BSCZGY symmetrical cells prepared by mechanical mixing and combustion methods. The thicknesses of the sintered anode layers were about 48 μ m and 26 μ m for mechanical mixing and combustion method, respectively. Also, proper attachment of anode layers on electrolyte was observed by the absence of delamination and cracks between composite electrode/electrolyte layers. The purpose of preparing anodes by combustion method was to obtain a uniform distribution of NiO in the BSCZGY. From Figure 3 (b), it can be seen that a better microstructure has been obtained by combustion method.



Figure 2. Powder X-ray diffraction (PXRD) patterns of NiO, BSCZGY, (a) NiO30-BSCZGY, (b) NiO40-BSCZGY, and (c) NiO50-BSCZGY prepared by combustion method and calcined at 1000 °C (5 h), 1100 °C (5 h) and 1200 °C (3h)



Figure 3. Typical SEM images of cross-section view of sintered NiO40-BSCZGY/BSCZGY anode interface prepared by (a) mechanical mixing and (b) combustion method before reduction. Different size meshes were used for screen-printing the mechanically mixed and combustion method synthesised anode pastes

3.2 Electrochemical Analysis

Figures 4 and 5 show the typical Nyquist plots of the Ni50-BSCZGY symmetrical cells measured in $H_2/3\%$ H_2O as a function of temperature for electrodes formed by the combustion and mechanical mixing methods, respectively. Electrochemical measurements were made in the direction of decreasing temperature after reduction of anode composites at 900 °C in H₂. At 500 °C, in the case of the symmetrical cells of Ni50-BSCZGY anode formed by the combustion method, three semicircles corresponding to the bulk contribution of BSCZGY electrolyte at high frequency, followed by two distinct electrode responses at low frequencies are visible (Figure 4 (a)). On increasing the temperature to 650 °C, the bulk response disappears from impedance spectra, and only two low-frequency electrode responses are visible (Figure 4 (b)). The increase in temperature resulted in a reduction of the diameter of both semicircles gradually. The total resistance of the cell can be extracted from the low frequency (LF) (0.1 Hz)intercept. Contributions from two arcs were separated by fitting the equivalent circuit, as outlined in the inset of Figure 4 (a-c). In the equivalent circuits at 710 °C, Rs is due to ohmic resistance, and R2 and R3 correspond to mid frequency (MF) and LF arcs, respectively due to the anode processes. The capacitance values in the range of 10^{-6} – 10⁻⁵ F for MF are associated with the resistance R2, suggests charge transfer between anode and electrolyte interface. LF arc with the capacitance in the order of $10^{-2} - 10^{-1}$ F related to the resistance R3 suggests surface electrochemical reactions at the anode (Bi et al., 2011; Narendar et al., 2013). The Nyquist plots of Ni30-BSCZGY and Ni40-BSCZGY anode composites showed similar Nyquist plots as Ni50-BSCZGY composite under the same conditions. The capacitance values obtained for the electrode process are in accord with the previous studies on Ni-Ba $Zr_{0.8}Y_{0.2}O_{3-\delta}$ and Ni-Ba $Zr_{0.85}Y_{0.15}O_{3-\delta}$ electrodes (Bi et al., 2011; Narendar et al., 2013). The ASR of LF arc could be due to dissociative adsorption of H_2 gas at anode with the following reaction steps (Bi et al., 2011; Narendar et al., 2013).

$$H_2(g) \rightarrow 2H_{ad} \text{ (Step 1)}$$
 (1)

$$H_{ad} \leftrightarrow H_{ad}^{+} + e^{-} (\text{Step } 2)$$
⁽²⁾



Figure 4. Typical Nyquist plots for the Ni50-BSCZGY/BSCZGY/Ni50-BSCZGY symmetrical cells (with anode prepared by the combustion method) in H₂/3% H₂O. (a) 500 °C, (b) 600 °C, and (c) 710 °C. Insets show the equivalent circuits used for fitting impedance data, and open symbols represent experimental data and solid lines represents fitted data. Porous Au was used as current collector during symmetrical cell measurements

For the symmetrical cells of Ni50-BSCZGY electrode prepared by the mechanical mixing method, only two responses due to electrode contributions are visible (Figure 5 (a-c)). Moreover, they also show the capacitance values in the range of $10^{-6} - 10^{-5}$ F, and $10^{-2} - 10^{-1}$ F for MF and LF arcs from 550 to 710 °C. Figure 6 (a-b) displays the variation of area specific resistance (ASR) as a function of temperature for Ni-BSCZGY anodes with different Ni contents. For anode composite prepared by the combustion method, ASR values of 1.9, 3.75, and 5.15 Ω .cm² were obtained for Ni50-BSCZGY, Ni40-BSCZGY, and Ni30-BSCZGY, respectively at 710 °C (Figure 6 (a)). The ASR values for anode composites prepared by the mechanical mixing method are found to be lower than the combustion method at all temperatures. At 710 °C the ASR values are 0.8, 2.6 and 2.1 Ω .cm² for Ni50-BSCZGY, Ni40-BSCZGY anodes, respectively (Figure 6 (b)). From the Figure 6 (a-b), it can be seen that among the samples investigated, the lowest ASR value for HOR, and hence, the best electrochemical performance is shown by Ni50-BSCZGY anode for both synthetic methods at all temperature ranges. Also, the electrochemical performances of the NiO-BSCZGY anodes prepared by the combustion method at all temperature for both synthetic methods at all temperature ranges. Also, the electrochemical performances of the NiO-BSCZGY anodes prepared by the mechanical mixing method are found to be better than those of the anodes prepared by the combustion method.

The presence of impurity phases and thinner anode layer might have contributed towards the lower electrochemical performance of investigated composites prepared by combustion method. Firstly, BaY_2NiO_5 impurity phase along with Ba and Y loss deviated the BSCZGY stoichiometry, which may have resulted in higher R2 resistance. The presence of impurity phase might have also increased the resistance of anode composite for proton conduction, especially in bulk and grain-boundary regions of BSCZGY phase, leading to a higher R2 and HOR ASR. Secondly, the thickness of the anode layer for Ni-BSCZGY anode composite prepared by the combustion method is smaller (~26 µm) than that of the anode layer prepared by the mechanical mixing method

(~48 μ m). In some literature work, enhancement in electrochemical performance of porous composite anodes for HOR has been achieved by increasing the anode layer thickness (Barbucci et al., 2008; Tanner et al., Fung & Virkar, 1997). By increasing the thickness of the anode layer, better electrochemical performance may be achieved. Additionally, the formation of BaY₂NiO₅ impurity can be avoided by employing a nitrate-free combustion method as suggested by Narendar et al. (2013).







Figure 6. Total ASR values as a function of temperature for the Ni-BSCZGY/BSCZGY/Ni-BSCZGY symmetrical cells formed by (a) combustion method and (b) mechanical mixing method with different Ni contents

4. Conclusion

Two synthetic routes for the synthesis of Ni-BSCZGY anode composites with different Ni to BSCZGY ratio were employed, and their electrochemical performance for HOR ASR was compared. Conventional mechanical mixing and nitrate based combustion synthesis methods were used for preparing the anode powders. PXRD analysis of as-prepared and heat treated anode powders revealed that the Ni-BSCZGY anodes prepared through the mechanical mixing route were free from impurity phases under the studied conditions. Conversely, anode powders prepared by the combustion route possessed BaY₂NiO₅ and SrY₂O₄ impurity phases along with NiO and BSCZGY phases. Among the compositions studied, Ni50-BSCZGY showed the lowest HOR ASR values for both the mechanical mixing and combustion methods. However, the combustion route synthesized anode composites showed higher HOR ASR (1.9 Ω .cm²) values than the mechanically mixed one (0.8 Ω .cm²) at 710 °C under H₂/3% H₂O for Ni50-BSCZGY. The formation of impurity phases and a thinner anode layer might have limited the electrochemical performance of anodes prepared by the combustion method.

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