



Structure and Thermal Behaviour of BSCF-SDC-Ag Composite Cathode for Solid Oxide Fuel Cell

U.A. Yusop, K.H. Tan, H.A. Rahman

Abstract: Solid oxide fuel cell (SOFC) component has always under development to enhance catalytic activity. Components such as anode, cathode and electrolyte must have better structure and behavior for good SOFC performance. Traditional $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) cathode in solid oxide fuel cell application has been deterred several inappropriate circumstances such as high thermal expansion coefficient (TEC) and chemical instability. $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolyte and Silver (Ag) are added into BSCF to overcome the problem and has better material characterization and thermal stability. The composite cathode powder BSCF-SDC was prepared by high speed ball milling technique with mixture of 50wt% BSCF and 50wt% SDC commercial powder. The powders were then dried and calcined at 950°C for 2 hour. Silver (Ag) with 1wt%, 3wt% and 5wt% were milled respectively with BSCF-SDC by low speed ball milling technique. The developed composite cathode was then examined by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), dilatometer and Thermogravimetric Analysis (TGA). The vivid distinct phase of BSCF, SDC and Ag and absence of additional secondary phase was confirmed by XRD analysis indicating good phase structure compatibility. This also assured that less chemical reaction was happened during low speed milling process for BSCF-SDC-Ag as minor secondary phases are detected. However, milling process at high speed and high calcination temperature did destruct single phase of BSCF in BSCF-SDC composite cathode. However, Ag obtains its role to retain back the BSCF crystalline phase. The higher the percent of Ag added, the higher the BSCF peak retain. The absence of addition bonding in FTIR analysis demonstrating excellent structure compatibility of BSCF, SDC and Ag during milling process. There was no significant additional bonding appeared in BSCF-SDC-Ag after milling process. The thermal expansion coefficient (TEC) were determined using dilatometer, manifesting closer TEC mismatch between BSCF-SDC-Ag cathode composite and SDC electrolyte compared to BSCF-SDC. TEC is essential to be matched as it could prevent spallation during elevated operation temperature of SOFC. TGA analysis indicated cathode composite experiencing very less changes of weight when it was heated up 1000°C. BSCF is revealed of decomposition occurring

after 800°C. Result revealed that Ag exhibited desirable thermal and structure compatibility with BSCF-SDC as promising SOFC cathode which beneficial from medium scale automobile to high scale power plant application.

Keywords: BSCF composite, Cathode, SOFC

I. INTRODUCTION

Solid Oxide Fuel Cell (SOFC) is an environment friendly electric generator devices comprising anode, electrolyte and cathode. Oxidation process takes part at cathode to deliver oxygen ions for hydrogen anode reduction in solid oxide fuel cell [1]. Substantial studies on cathode performance and materials compatibility has always been a practical issue to settle down when operating temperature of SOFC is lowered down from over 1000°C. Co based perovskite materials are ultimate candidate for cathode in SOFC because of its mixed ionic and electronic conductor (MIEC) which possesses high conductivity and good catalytic activity such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $(La_{0.85}Sr_{0.15})_{0.9}MnO_{3-\delta}$ (LSM). In MIEC cathode, the catalytic reaction extends from traditionally triple phase boundary (TPB) to entire electrode gas interface [2]. Recently, $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ (BSCF) has been presented as new developed cathode material which is having consistent electrochemical satisfactory at both single and dual chamber [3]. BSCF attracts great research attention from its remarkable low area specific resistance at low to intermediate compared to others MIEC perovskite cathodes and outstanding electrochemical performance [4]. However, BSCF is suffocating thermal expansion mismatch and instable material compatibility in oxygen environment [5, 6]. One approach to improve those issues is incorporating electrolyte material into cathode. $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ - $Ce_{0.8}Sm_{0.2}O_{1.9}$ (LSCF-SDC) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ - $Ce_{0.9}Gd_{0.1}O_{1.95}$ (LSCF-GDC) were developed with proved material properties and electrical performance improvement [7, 8]. BSCF-SDC had been rarely studied and reported that the thermal expansion coefficient (TEC) and electric conductivity were improved slightly and it was still open up for further investigation. Developed BSCF-SDC indicating 30.1% TEC difference from SDC electrolyte which did not fulfill 10-20% acceptable range [9, 10] In this paper, BSCF-SDC was modified by incorporating several amount of silver (Ag) to generate series composite materials of BSCF-SDC-Ag in order to achieve better material characterization and thermal behavior. Optimization of cathode composite material was investigated in comparison with BSCF-SDC.

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II. METHODOLOGY

- (1) BSCF-SDC composite cathode powder were developed by mixing 1:1 ratio of commercial BSCF powder (Sigma Aldrich) and commercial SDC powder (Sigma Aldrich) ball milling method. The milling process was taken at 550 rpm for 2 hours in ethanol [10].
- (2) The slurry was dried in oven for overnight. The process follows the previous study parameters. Then dried powder was grounded in an agate mortar and calcined at 950°C for 2 hours [11].
- (3) Incorporating of 1%, 3% and 5 % of Ag powder was obtained from total weight of BSCF-SDC powder. The mixing as done by 150 rpm dry milling technique for 0.5 hour obtaining BSCF-SDC-Ag composite cathode.

Purity phase and each crystalline structure of composite cathodes were conducted by X-ray powder diffractometer, XRD (Shimadzu XRD-6000, D8-Advance, Bruker, German) with Cu K α radiation ($\lambda=0.15418$). The weight loss of composite cathode as function of temperature were carried out by thermogravimetric (TG) measurements up to 1000°C in air at heating rate of 5°C/min (TGA/SDTA, Linseis, Germany). Fourier Transform Infrared Spectroscopy (FTIR) machine (Perkin Elmer Spectrum 100, USA) was applied to analyse the chemical bonding of BSCF composite cathode powders. The BSCF composite cathodes were made into cylindrical sample and tested in dilatometer (Netzsch DIL 402C, Germany) upon heating from room temperature to 900°C at 5°C/min.

III. RESULT AND DISCUSSION

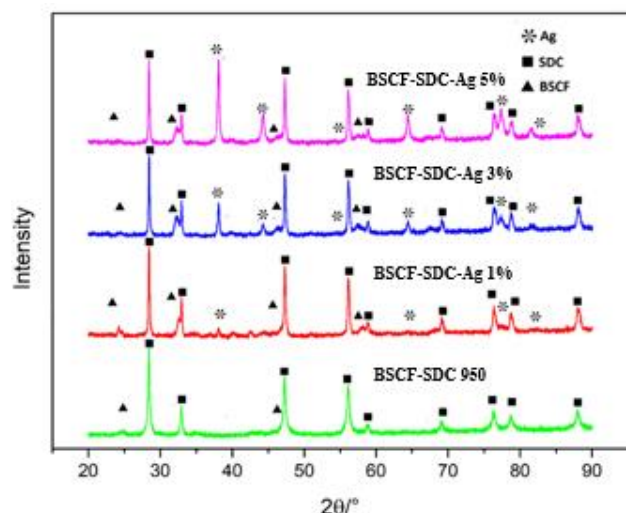


Fig. 1: XRD spectra for BSCF composite cathodes

Fig. 1 displays XRD patterns of BSCF-SDC after calcined at 950°C and addition of 1%, 3%, and 5% of Ag into BSCF-SDC. BSCF and SDC was accorded to the XRD BSCF JCPDS No. 79-5253 and SDC JCPDS No. 75-0158 while Ag was accorded XRD JCPDS No. 04-0783. BSCF exhibited cubic lattice, SDC and Ag exhibited face center cubic lattice. SDC lattices was apparently demonstrating its distinct crystalline phase for all composite cathode after BSCF-SDC was calcined at 950°C. Moreover, BSCF-SDC phase crystalline phase was not affected by Ag addition through the milling process. Adding of Ag did not generate

secondary phase or impurities in the BSCF composite. Furthermore, it can be observed that higher the amount of Ag addition, higher the intensity of Ag XRD intensity. However, it was vividly judged that serious interaction between BSCF-SDC composite and heat treatment environment had occurred when heat treatment was conducted on 950°C. The BSCF lattice lowered down its intensity which probably A-site Ba²⁺ ions chemically reacted with CO₂ in air which had been reported in previous studied [11]. It formed impurity phases of BaCO₃. These minor impurity could be observed much in BSCF composite cathode. However, BSCF-SDC after calcined at 950°C had removed the secondary phase and recover BSCF crystalline phase at minimum 900°C [12]. The introduction of Ag into BSCF-SDC had also assisted retaining BSCF crystalline phase especially peaks at 33.6° and 47.2°. The BSCF peaks was more apparent when Ag incorporation was increased. Secondary BaCO₃ phase was slightly appeared in all BSCF composite cathode as can be proved in FTIR analysis.

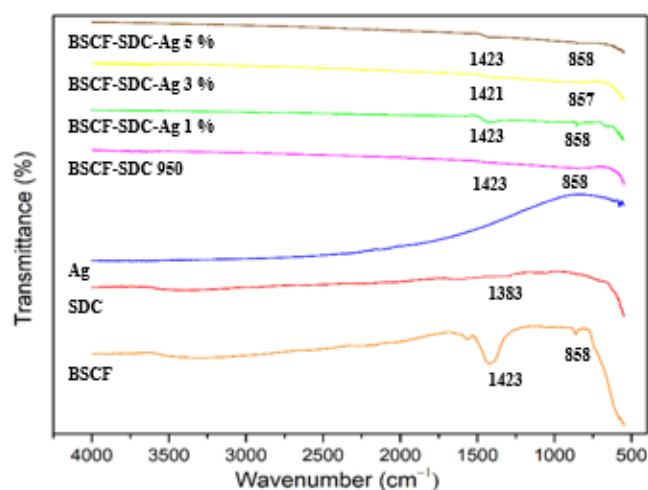


Fig. 2. FTIR spectra for BSCF composite cathodes

Fig.2 shows the present of carbonate bond in BSCF-SDC composite. Carbonate phase was observed in BSCF commercial powder in wavenumber of 1424 cm⁻¹ and 858 cm⁻¹. It assured that there were impurities in pure BSCF powders. This could be interaction between BSCF and CO₂ even in ambient temperature or a prolonged time. Commercial SDC presented no carbonate bond found in the FTIR spectra. Also, BSCF-SDC composite cathode assembled no others organic bond except of very insignificant carbonate bond shown in spectra 1423 cm⁻¹ and 858 cm⁻¹. This was contributed to calcination at high temperature which had been removing all impurities that appeared in BSCF-SDC including BaCO₃ during the milling process. It could be seen that milling process of BSCF-SDC-Ag had created slight carbonate spectra observed in the same wavenumber for all 1%, 3%, and 5%. This was owing to low speed milling process, also generated heat which provoked reaction between BSCF and SDC.

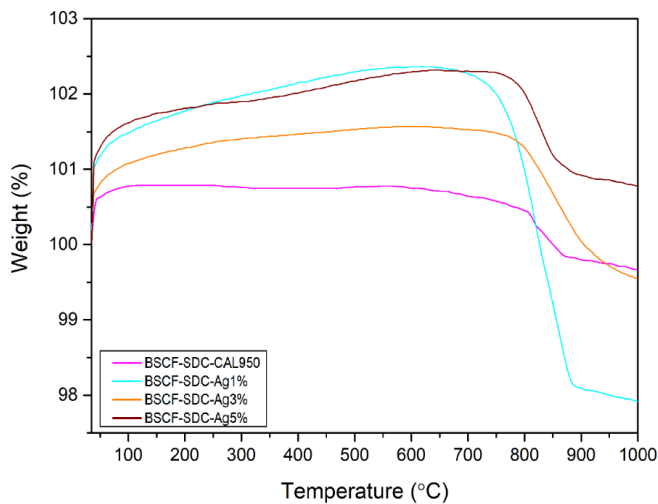


Fig. 3: The weight change of various BSCF cathode composites as function of temperature

The weight change of BSCF cathode composites was recorded versus temperature heating up from room temperature to 1000°C as shown in Fig. 3. The graph illustrated weight increment for all BSCF composite cathodes. The weight increment was obvious for BSCF composite cathodes with Ag incorporation. The weight increased from 30°C to 800°C which denoted slight weight increment from 0 to 2 % increment. BSCF-SDC weight had been increased but it was very insignificant below than 1% and then, the weight persists the same until temperature reached 800°C. Upon elevated temperature heating, BSCF was chemically interact with carbon dioxide in air and form minor secondary metal carbonate. After 800°C, the weight loss back to approximate original weight it was the temperature where secondary metal carbonate was removed. Moreover, the weight loss after 800°C also indicated the starting crystalline phase recovery of BSCF as reported in previous study no matter it was heating in conventional method or in microwave [13]. This was investigated that BSCF cathode composites were appropriate utilized in low and intermediate temperature application.

Table 1: Average TEC value for BSCF composite cathode at variant temperature

Samples	TEC ($\times 10^{-6}/K$)		
	(30°C-600°C)	(30°C – 800°C)	(30°C- 900°C)
SDC	12.7	12.8	12.8
BSCF-SDC	9.9	10.5	7.7
BSCF-SDC-Ag1%	10.2	11.8	6.3
BSCF-SDC-Ag 3%	9.5	11.0	7.4
BSCF-SDC-Ag 5%	8.6	9.3	3.4

Table I tabulates the TEC values of all SBCF composites. Assembling TEC value at 30°C – 600°C from Table 1, all BSCF composites cathode indicated huge mismatch of TEC with SDC electrolyte. All BSCF composite cathode had TEC value 20% higher than SDC electrolyte. High different must be avoided as delamination could be happened during SOFC operating and lead to degradation of SOFC electrode

component [14]. Demonstrating from 30°C – 800°C, TEC for BSCF-SDC-Ag 3% was 14.8% different from SDC electrolyte. BSCF-SDC-Ag 1% manifested the best match TEC with electrolyte with only 7.8% different from SDC TEC and this was complete within coverage of 10 % different which was reported the best TEC difference [10]. However, 10%-20% was an acceptable range for electrode component mechanical compatibility. The average TEC values from 30°C – 900°C for all BSCF composite cathode were not within the acceptable range as owing to decomposition of BSCF at after 800°C as mentioned in TGA discussion. Ag had been reported having capability to lower down the TEC of cathode composite [15-16]. Higher the amount of Ag added, lower the TEC was obtained. This is similar to Ag addition to BSCF-SDC in this study.

IV. CONCLUSION

In conclusion, Ag was successfully incorporated into BSCF-SDC cathode by milling, showing good outcome of crystalline phase distinction, no significant existing of additional bonding and stable thermal behavior determination. Generally, BSCF-SDC-Ag 1% and 3% was exhibiting the best cathode characterization which having stable BSCF, SDC and Ag crystalline phase, no impurities formed, enhance thermogravimetric analysis and less than 10% thermal expansion coefficient toward electrolyte. Hence, BSCF-SDC-Ag is proved promising for SOFC cathode application which exhibits excellent material properties. Good material properties is crucial for efficient cathode catalytic activity and conductivity.

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