

1. Introduction

Solid oxide fuel cells (SOFCs) are an electrochemical device that have been consistently developed due to their high efficiency, minimum impact on the environment, and ability to employ a range of fuels to produce power [1]. The device is widely used for future commercial implementation, making it simple to implement in a wide range of applications. This technology has been developed for both energy efficiency and building. [2], and a favourable economic evaluation of residential power systems [3]. Furthermore, it has been supported for fuel cell electric vehicles as a power plant with a 20 % increase in efficiency in SOFC-reforms by reducing energy destruction [4]. SOFC, on the other hand, is currently operating at high temperatures (800–1000 °C) [5]. Its temperature restricts the material options for cells and auxiliary components, accelerates the degradation of cell performance and interconnecting elements between components, and makes sealing more difficult. Some critical technical issues, particularly those related to reliability and durability, must be resolved before technology can be commercialized.

MIEC is widely promoted in intermediate temperature solid oxide fuel cells (IT-SOFCs) made of perovskite type oxides, which are represented by $ABO_{3-\delta}$ [6]. They can be used as electro-catalysts for solid oxide fuel cells (SOFCs), oxygen-permeable membranes, and oxygen absorbers, among other things. In some experiments, MIEC cathode has been shown to have good performance electro-catalytic activities, excellent oxygen transport and surface exchange properties, and thus high electrochemical activities [7, 8]. However, due to the high thermal expansion of the electrolyte, these cobalt-based MIECs have poor stability in practice for long-term applications, which has hampered the development of cathode IT-SOFCs [9]. Another factor to consider for successful use is the high cost of cobalt (Co) in comparison to other rare metals [10]. The analysis is required to discover a novel composite structure of free-cobalt cathode material for intermediate-temperature solid oxide fuel cells to address the numerous limitations mentioned above (IT-SOFCs).

There has been a lot of research into the free Co-based cathode to overcome the problems in the implementation of IT-SOFCs

STUDY ON THE COMPOSITE STRUCTURE OF CO-BALT-FREE OXIDES AS CATHODES FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS (IT-SOFCs)

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Summary: Solid Oxide Fuel Cells (SOFCs) represent a promising technology for efficient and clean energy conversion. This study focuses on the design and development of a novel cathode material for SOFCs, specifically exploring the use of a free-cobalt cathode within a composite structure. Investigating the structure of cobalt-free composites of $Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$ (BSF) and $Ba_{0.5}Sr_{0.5}Fe_{0.8}B_{0.2}O_{3-\delta}$ (B=Cu, Zn) (BSFB) have been prepared and evaluated as cathodes for IT-SOFCs. The solid-state reaction was employed for generating and modifying the composite structure of the model system. The decomposition reaction and the formation of perovskite structure have been observed using thermal gravimetric analysis and X-ray diffraction. The study encompasses experimental procedures, data processing using GSAS software, and the application of the Rietveld method to achieve precise analysis results. Rietveld analysis outcomes offer intricate details about the crystal structure, encompassing crystal unit parameters, and scale factors. The solid-state reaction led to the reduction in the weight of the composite during the heating process. The decomposition reaction of oxides was generated between 650 to 950 °C. The average of total weight loss during the period treatment was achieved up to 18 % and the perovskite phase formed in the composite structure. A single-phase perovskite from a cubic structure with space group Pm-3m was demonstrated by all composite's models. The lattice parameter and a unit cell volume were obtained from the model system of BSF, BSFC and BSFZ, respectively. This study explores the potential development of SOFCs technology with the hope of making a positive contribution to advancing clean and sustainable energy solutions in the future.

Keywords: solid oxide fuel cells, free-cobalt cathode, composite structure, single-phase perovskite, solid-state reaction.

up to this point [11]. As a result, the continuous development of a new cobalt-free cathode model was carried out [12]. Because of the strong electronic structure of Fe ions, the MIEC model with Fe in the B side on the composite structure of the cathode system as Fe-based composite oxides is expected to be low cost and more durable under SOFC operation conditions (500 to 800 °C and air atmosphere) [13, 14]. To date, the composite model in A side-based perovskite oxides has been constantly evolving to achieve excellent cathode performance. The use of the metal transition to strengthen the A-side perovskite structure has received a lot of attention [15, 16]. Barium (Ba) is a well-known element that is used in the A-side of composite structures as the BLF system for the cathode element [17, 18]. The excellent structure of the electro-catalytic activities for oxygen reduction, as well as the good operational stability. Furthermore, the substitution of samarium (Sm), Ba, and samarium (Sr) elements in the A-site demonstrates cathode elements' superior performance [9, 19, 20]. Unfortunately, the development of its composite, which uses Fe ions in the B-site, has not been completed. It was unusual to investigate the structure of a cobalt-free cathode using Ba combined with Sm and Sr in the A-site and Fe ions in the B-side of a composite structure.

The study aims to design a solid oxide structure on the composite cathode for IT-SOFC. This would make it possible to determine the calcination temperature related to weight loss and constructing the perovskite structure. To achieve this aim, the following objectives are accomplished by analysis the thermal gravimetry of the composite metallic oxide and characterization the structure of the composite model.

2. Materials and Methods

This study investigated the structure of a cobalt-free cathode of $Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$ (BSF) and $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (BSFC) and $Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ (BSFZ) composite materials as a possible cathode element for IT-SOFCs. The solid-state reaction method was used to modify the perovskite structure by incorporating a composite of Ba, Sr, Fe, Cu and Zn elements material. The characterizations will also be performed to learn more

about the cathode model's structure properties. Metallic oxide compounds, such as BaO, SrCO₃, Fe₂O₃, CuO and ZnO are used as raw materials in composites. The traditional solid-state reaction method is used to create BSF, BSFC and BSFZ cathodes. The method was used to prepare and synthesis the cathode material, which has previously been reported in our group's published papers [21–23]. For 12 hours, a stoichiometric volume of metallic oxide compound was mixed with zirconia balls in the presence of 96 % ethanol in solution. The powder mixture was then dried in an oven at 80 degrees Celsius for 24 hours. The powders were tested for thermal gravimetric analysis (TG). The temperature was increased to 1000 °C at a rate of 10 °C min⁻¹ before being cooled to room temperature. Further, the model precursor powders were calcined at 900 °C for 3 hours in an air atmosphere with a heating rate of 3 °C min⁻¹ and normal cooling in the furnace. After grinding with an agate mortar, the calcination powder was sieved through 200 mesh. The crystal

structure of the cathode powder was also determined using XRD characterization.

3. Results

Fig. 1 shows the thermal gravimetric analysis and differential thermal analysis (DTA) of BSFB composite oxide powders. The blue curve is related to the TG value of BSF, BSFC and BSFZ system composite, while the black curve is according to thermal behaviour during the calcination process. The thermal gravimetric was used to monitor the weight loss of the material due to either evaporation or decomposition reaction. This method can be employed to determine the next step of calcination and sintering temperature used.

Fig. 2 shows the XRD pattern of BSF, BSFC, and BSFZ composite structure respectively, calcined at 900 °C for 3 hours. The pattern has nine peaks with both sharpness and narrowness. The peaks in scale of 60 degrees in 2-theta present around 22°, 32°, 39°, 46°, 52°, 57°, 67°, 72°, and 76°, respectively.

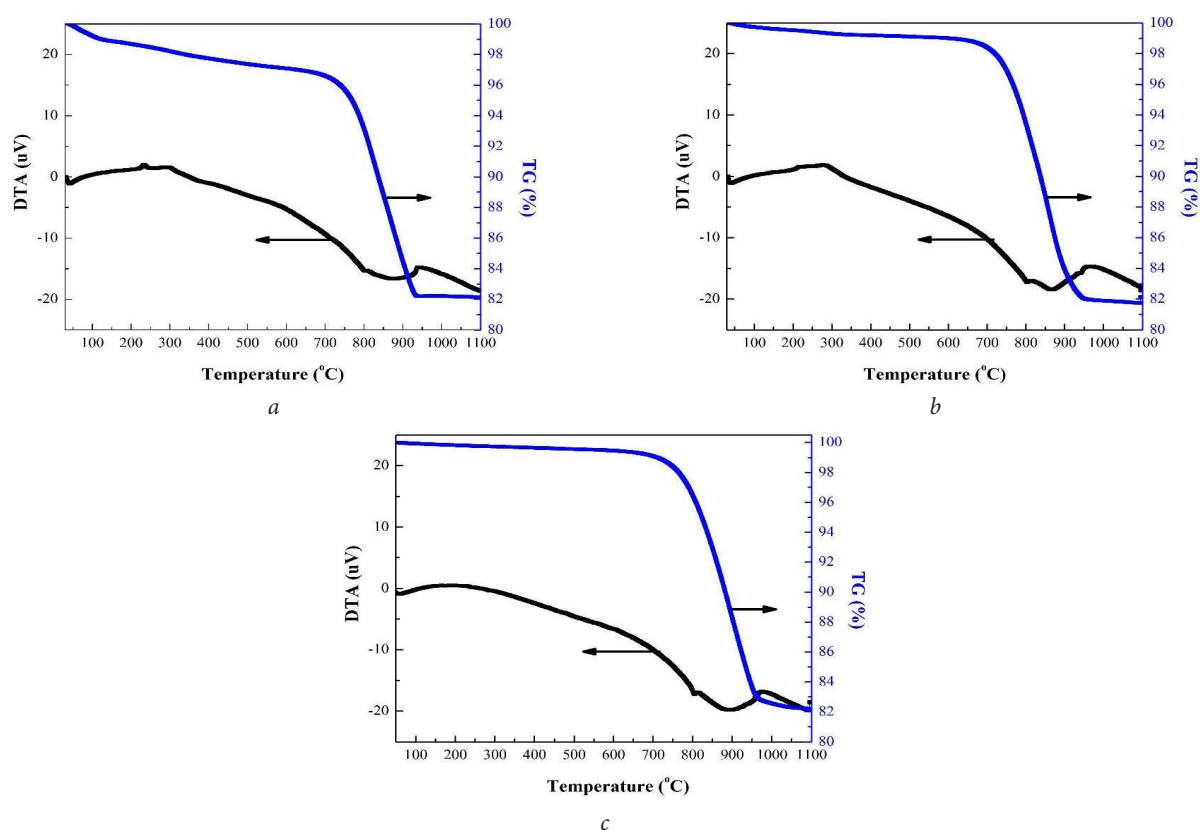


Fig. 1. Thermal gravimetric analysis (TG) and differential thermal analysis (DTA) of composite oxide powders: *a* – Ba_{0.5}Sr_{0.5}FeO_{3-δ} (BSF), *b* – Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-δ} (BSFC), *c* – Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-δ} (BSFZ)

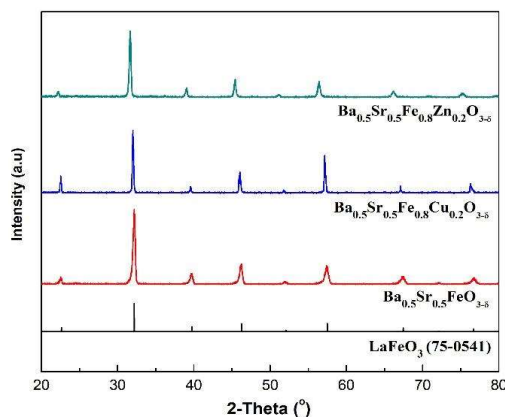


Fig. 2. XRD pattern of BSF, BSFC and BSFZ composite oxide powders

4. Discussion and scope of application

Based on the curve in Fig. 1, a for the BSF composite system, the decreasing blue line occurs linearly from room temperature to 120 °C due to both evaporation from H₂O and some impurities of the materials. While the drastic drop in curve related to decrease of weight loss occurred at 650 to 750 °C, suggesting that it was affected by generating the compound decomposition reaction from some elements of the system. Additionally, there are two steep valleys on the black curve at 60 °C, and 790 °C associated endothermic reaction on the sample. While two peaks of 235 °C and 950 °C are related to exothermic reactions from the sample as well. In the same way, the TG curve was formed, the decreasing curve was also created in the same spot. For BSFC and BSFZ composite system in Fig. 1, b, c, the DTA and TG results are similar to BSF system which is only small peak at 235 °C of SSFC related to exothermic reaction and no peak of SSFBZ. It indicates that the main degradation of weight loss of the composite system is because of decomposition reaction from material compound initiating between 650 to 750 °C.

According to the pattern displayed in Fig. 2, XRD pattern has nine peaks. Those peaks are like the perovskite structure as references for model composite in lanthanum ferrite (LaFeO₃). The single phase with different intensities at various theta positions is related to the crystalline perovskite structure from three samples which is constructed on the composite model system. The perovskite-phase was evident in crystalline form on the composite model framework. The arrangement of the phase is also similar to that of a nearly cubic LaFeO₃ structure [10, 15], implying that the single perovskite-phase crystalline structure built on the system cathode. The Ba and Sr component of the model system was used in the A-side of the model system, which was configured for the BA cathode materials in the perovskite phase. While Fe component doped with Cu and Zn played in the B-side. According to the XRD pattern, the stoichiometric of composite metal oxide for SSBF cathode materials could be developed as a crystalline structure with the single perovskite-phase using the solid-state reaction process.

To obtain more structural information, the crystal structure of the BSF, BSFC and BSFZ composite materials are further analyzed by Rietveld refinement (Rr) in this study, with the profiles shown in Fig. 2. It is seen that all model composite structures have a cubic structure with a space group Pm-3m. They have a lattice parameter ($a=3.919$ Å), ($a=3.939$ Å), ($a=3.987$ Å) and a unit cell volume of 60.203 Å³, (61.136 Å³), (63.394 Å³), respectively. The profile R-value (*Rp*), weighted-profile R-value (*Rwp*),

and the Durbin-Watson parameter of the refined structure parameters were 6.3 %, 8.5 % and 1.58, serially, indicating that the refinement results are acceptable. Based on Rr value, the BSFZ sample shows the largest unit cell volume, which may be attributed to the synchronous effect of the Zn atom in the B-side system.

5. Conclusions

The BSF and BSFB composite model system was successfully synthesized using solid-state reaction. The main weight loss on the model in TG analysis was dominated by the decomposition elements process during the solid-state reaction. The reaction process led to the construction of the new structure of crystalline phase in the free-cobalt system. The single-phase associated with the perovskite structure was built on the model which is demonstrated in detail by the XRD results. The stoichiometric structure of composite metal oxide for BSF and BSFB cathode materials could be obtained as a crystalline structure with the single perovskite-phase. The cubic structure with a space group of Pm-3m was detected by Rietveld refinement from GSAS analysis.

Conflict of interest

The authors declare that there is no conflict of interest in relation to this paper, as well as the published research results, including the financial aspects of conducting the research, obtaining and using its results, as well as any non-financial personal relationships.

Financing

The authors are grateful to the financial support provided by Unit Penelitian dan Pengabdian Masyarakat, Politeknik Negeri Jakarta (UP2M-PNJ) under contract number B.275/PL3.18/PT.00.06/2022 that made this work possible.

Data availability

Data will be made available on reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

Acknowledgements

Authors give expressing gratitude to Mr. Subardi and Mr. Maykel Manawan for their priceless collaboration and enlightening discussions during the entire research process.

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Received date 16.09.2023

Accepted date 18.11.2023

Published date 29.11.2023

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How to cite: Susanto, I., Jamhary, A. J., Permana, S. (2023). Study on the composite structure of cobalt-free oxides as cathodes for intermediate temperature solid oxide fuel cells (IT-SOFCs). *Technology transfer: fundamental principles and innovative technical solutions*, 31–34. doi: <https://doi.org/10.21303/2585-6847.2023.003198>