1. Introduction

A solid oxide fuel cell (SOFC) is an electrochemical device developed continuously due to its high performance, low environmental effects and fuel flexibility for generating electricity [1]. The device is applied extensively to be used for future commercial purposes, which makes it easy to implement in a wide range of applications. The use of this...
technology has been developed for both the energy efficiency building [2], and the satisfying of economics evaluation for residential power system [3]. Moreover, it has also been supported for fuel cell electric vehicles as a power plant with an efficiency increase of up to 20% in SOFC-reformer by reducing energy destruction [4]. However, SOFC currently operates at high temperatures (800–1,000 °C) [5]. Its temperatures limit material choices for cells and auxiliary components, increase the degradation of cell performance and interconnecting elements between components, and increase the difficulty of sealing. Some critical technical problems, especially those related to reliability and durability, need to be resolved to move technology to commercialization.

Mixed ionic and electric conductors (MIEC) are widely promoted in intermediate temperature solid oxide fuel cells (IT-SOFCs) made of perovskite-type oxides, which are symbolized by ABO3–δ [6]. They are suitable for a variety of uses, including electrocatalysts for solid oxide fuel cells (SOFCs), oxygen-permeable membranes, and oxygen absorbers. MIEC cathode has been stated to have good electrocatalytic activities, excellent oxygen transport and surface exchange properties, and hence high electrochemical activities in some experiments [7, 8]. However, in practice for long-term applications, these cobalt-based MIECs have poor stability due to the high thermal expansion of the electrolyte, which has hampered the development of IT-SOFC cathodes [9]. Furthermore, the high cost of cobalt (Co) in comparison to other rare metals is another factor to remember for successful use [10]. To address the numerous limitations mentioned above, the analysis is needed to discover a novel composite structure of cobalt-free cathode material for intermediate-temperature solid oxide fuel cells (IT-SOFCs).

2. Literature review and problem statement

Up to now, there has been a lot of studies on Co-free cathodes as a way to overcome the problems in the implementation of IT-SOFCs [11]. So, the development of a new model of cobalt-free cathode was carried out [12], 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) due to the strong electronic structure of Fe ions [13, 14]. The composite model has been continually evolved in the A-side-based perovskite oxides in order to achieve excellent cathode performance up to now. Using the metal transition to strengthen the perchovskite structure on the A-side has received a lot of attention [15, 16]. Barium (Ba) is one of the famous elements that is applied in the A-side of the composite structure as a BLF system for the cathode element [17, 18]. The excellent structure is related to 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 shows the great performance of the cathode element [19, 20]. The development of its composite has not been complete as a composite using Fe ions in the B-site. The investigation of the structure into a cobalt-free cathode employing Ba combined with Sm and Sr in the A-site and Fe ions in the B-side of a composite structure was rare.

3. The aim and objectives of the study

The aim of the study is to design a solid oxide structure on the composite cathode for IT-SOFCs. This would make it possible to determine the calcination temperature related to weight loss, constructing the perovskite structure, and improving both oxygen content and conductive properties of the SSBF composite.

To achieve this aim, the following objectives are accomplished:
- to analyze the thermal gravimetry of the composite metallic oxide;
- to characterize the structure of the composite model;
- to test the conductivity properties of the cobalt-free cathode.

4. Materials and experimental methods

This work investigated the structure and properties of a cobalt-free cathode based on Sm, Sr, Ba, and Fe composite materials as a candidate for possible use in the cathode element of IT-SOFCs. The solid-state reaction method was employed to modify the perovskite structure using the composite of Sm, Sr and Ba elements into the A-side, resulting in a composite cathode of the SSBF system. Characterization will also be carried out in order to learn more about the cathode model related to the structure and conductivity properties.

The raw materials used as a composite are metallic oxide compounds, namely Sm2O3, SrCO3, BaO and Fe2O3 (SSBF model). The solid-state reaction method is used to make the SSBF cathodes in the traditional way. The method was used for preparing the cathode material, which has been reported in our group’s previous papers [21–23]. Using zirconia balls, a stoichiometric volume of metallic oxide compounds was mixed in the presence of ethanol 96% in solution for 12 hours. The powders blend was then dried in an oven at 80 °C for 24 hours. The SSBF precursor powders were calcined at 1000 °C for 4 hours in an air atmosphere with a heating rate of 3 °C min⁻¹ and normal cooling in the furnace. The calcination powder was sieved through the 400 mesh after being ground using an agate mortar. The powders were tested by thermal gravimetric (TG) analysis for checking the oxygen content. The temperature was raised up to 900 °C with a heating rate of 10 °C min⁻¹ and cooled to room temperature. While other powders were then pressed into a square bulk measuring 5x7x10 mm. The cathode bulk was sintered for 4 hours at 1200 °C with a heating rate of 3 °C min⁻¹ and natural cooling in the furnace. Further, the XRD was used to determine the crystal structure of the cathode powder, and the electrical conductivity bulk samples were determined from 200 °C to 800 °C.

5. Research results on the design of solid oxide structure on the composite cathode for IT-SOFC

5.1. Thermal gravimetric analysis

What do you try to find in this analysis, if as you wrote “The SSBF precursor powders were calcined at 1,000 °C” and “The bulk was sintered for 4 hours at 1200 °C with a heating rate of 3 °C min⁻¹ and natural cooling in the
furnace”. All the interesting data was lost due to your previous step.

Fig. 1 shows the thermal gravimetric analysis and differential thermal analysis (DTA) of SSBF composite oxide powders. The blue curve from number 1 to 5 is related to the TG value of the SSBF composite, while the black curve with the point of A, B and C corresponds to the thermal behavior during the calcination process. The thermal gravimetric analysis 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. Based on the curve, the numbers 2 and 3 are associated with a reduction of the sample weight due to the evaporation of H$_2$O and some impurities of the materials. While the points 4 to 5 are related to a decrease in weight due to the compound decomposition reaction.

![Fig. 1. Thermal gravimetric analysis (TG) and differential thermal analysis (DTA) of precursor SSBF powders](image)

The DTA and TG curves of SSBF oxide powder heated from room temperature to 1,200 °C are shown in Fig. 1. For points A, B, and C of DTA, there are three steep valleys on the curve: 289 °C, 422 °C, and 899 °C. In the same way that the TG curve was formed, the decreasing curve was also created in the same spot.

Fig. 2 demonstrates the TG analysis of the composite structure of the model system after the calcination process.

![Fig. 2. Thermogravimetric analysis of the SSBF composite cathode powders](image)

The thermal gravimetric analysis of the SSBF cathode material from room temperature to 1,000 °C is shown in Fig. 2. During the heating phase, the thermal gravimetric curve demonstrated the conduct of weight in percent TG. The curve began at 25 °C and remained steady until it reached 150 °C. At 380 °C, the curve will continue to decrease until it reaches 0.03 percent TG (point B to C). Finally, as the temperature reached 900 °C, the curve dropped dramatically along points C-D, with a decrease of 0.17 percent TG.

![Fig. 3. Oxygen content of SSBF composite cathode powders](image)

During the calcination process, the oxygen content in the SSBF composite material was monitored. The model’s oxygen content was calculated using O$_{3-\delta}$ in the perovskite structure. The curve slope was close to that of the TG study shown in Fig. 2. The stable curve was found in the A’ to B’ range. The decreasing curve of 0.02 O$_{3-\delta}$ was found at point B’ to C’.

5.2. Structure characterization

The XRD pattern of the composite SSBF structure (B) calcined at 1,000 °C for 4 hours and the perovskite structure (A) of lanthanum ferrite (LaFeO$_3$) as a reference is shown in Fig. 4.

![Fig. 4. SSBF cathode XRD diffraction pattern](image)

The single phase of the SSBF structure is constructed on the composite model system. The sequence in Fig. 4 showed the peak’s sharpness and narrowness in detail (B). The
pattern has nine major peaks with a scale of 60 degrees in 2-theta. 22.98°, 32.74°, 40.66°, 46.88°, 52.52°, 57.98°, 67.72°, 72.78°, and 77.44° were the peak positions. Those peaks are similar to the perovskite structure references (4).

5. Electrical conductivity properties

Fig. 5 displays the electrical conductivity curve for SSBF cathode composite products. The testing was carried out from 200 °C to 800 °C under atmospheric air pressure, with an oxygen concentration of 0.21 atm (21 percent O₂).

![Conductivity graph](image)

Fig. 5. SOFC cathode composite materials of electrical conductivity

The parabolic curve was visible in the conductivity value at the start of 3.25 S cm⁻¹ at 200 °C. The conductivity increases gradually as the temperature rises, peaking at 10.20 S cm⁻¹ at 502 °C in point P, and decreasing simultaneously to 7.25 S cm⁻¹ at 800 °C.

6. Discussion of experimental results on the design of solid oxide structure on the composite cathode for IT-SOFC

The weight loss of composite material compound was analyzed in detail by the thermal gravimetric analysis. The decrease of the curve in the first step of TG shown in Fig. 1 occurred at 289 °C and 422 °C, which was attributed to the weight loss of SSBF powders. The first step was due to the heat energy provided by the device, the water in the SSBF powders could be evaporated. The other way, the samarium powder element was contributed by the weight loss in the temperature range [24], also showed the evaporated water quality. It was also shown by the endothermic peak at the same temperature caused by substance dehydration. The second step at 422 °C, the weight loss was thought to be dominated by evaporation due to samarium content impurity. Since strontium carbonate decomposes into SSBF oxide compounds, the rate of weight loss accelerates. The decreasing curve at the third step at point 4 started at 710 °C to 899 °C was initiated by some elements reacting to form the new structure in the system. In this step, the solid-state reaction mechanism was playing to form the perovskite structure. According to the TG analysis, the calcination temperature could be employed enough up to 1,000 °C. The endothermic reaction will also demonstrate the formation of the perovskite matrix, as seen by XRD characterization.

7. Conclusions

1. The weight loss on the SSBF composite model in the TG analysis was dominated by the elements decomposition process related to the solid-state reaction for constructing the new structure in the cobalt-free system.

2. The single phase associated with the perovskite structure was built on the SSBF composite system demonstrated in detail by the XRD results. The stoichiometric structure of the composite metal oxide for the SSBF cathode materials could be obtained as a crystalline structure with the single perovskite phase. Based on the XRD pattern above, the stoichiometric structure of the composite metal oxide for the SSBF cathode materials could be developed as a crystalline structure with the single perovskite phase using the solid-state reaction process.

3. The compounding of Ba element to the Sm and Sr system in the A-side improved the electronic conductivity in Fig. 4. Besides, the system’s heat energy influences the decrease in oxygen content shown in Fig. 3. The reduction reaction for the perovskite structure in the SSBF cathode could be aided by heat energy as oxygen levels drop to 2.98 of O₃δ. Unless the temperature rises, the volume of oxygen in the air decreases, making it possible to transfer mobility oxygen in the cathode system, which was used in the IT-SOFC system.
properties in the SSBF cathode systems. The metallic element led to the generation of the conductive behavior at the low temperature, while the ionic structure acted as elevated temperature. The SSBF composite material might well be promising as an alternative cathode for IT-SOFC based on these studies.

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