

ADVANCED PERFORMANCE OF $\text{LaBaCo}_2\text{O}_{5\pm\delta}$ DOUBLE-PEROVSKITE TYPE AS A LOW-TEMPERATURE SOFC CATHODE MATERIAL

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Received: July 19, 2018; Revised: August 18, 2019; Accepted: August 21, 2019

Abstract

A new double perovskite structure of $\text{LaBaCo}_2\text{O}_{5\pm\delta}$ was simply synthesized via a traditional solid state reaction. X-ray diffraction analysis of $\text{LaBaCo}_2\text{O}_{5\pm\delta}$ powder was conducted after calcination at $1,100^\circ\text{C}$ for 2 h in air indicated that a single phase of the double-perovskite type with a cubic structure. The electrical conductivity of $\text{LaBaCo}_2\text{O}_{5\pm\delta}$ was mixed between semiconducting and metallic conducting behaviors, with an operating temperature range of $100\text{--}800^\circ\text{C}$. $\text{LaBaCo}_2\text{O}_{5\pm\delta}$ exhibited the highest electrical conductivity, with a value of 320 S/cm at 240°C . Therefore, the $\text{LaBaCo}_2\text{O}_{5\pm\delta}$ cathode type can be utilized as a low-temperature SOFC cathode material.

Keywords: Double perovskite cathode, Mixed conductor, Solid oxide fuel cell, Electrical conductivity.

Introduction

Carbon dioxide (CO_2) is widely known as a primary greenhouse gas and emitted through human activities. Increasing atmospheric CO_2 gas concentrations has played a critical role in global warming and climate change. Concerns surrounding global warming has motivated intensive studies on the development of clean energy technologies (Gómez *et al.*, 2015). The attraction of solid oxide fuel cells (SOFC)

is based on a major aspect, including its clean conversion of chemical energy to electricity, low levels of noise pollution, the ability to operate with different fuels, and most of all its high efficiency (Minh, 1993; Liu *et al.*, 2006). Nonetheless, traditional SOFC operates at temperatures exceeding $1,000^\circ\text{C}$ to achieve a high electrical performance of the cell. The high operating temperature results in a quick

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degeneration of the SOFC's performance, resulting in high costs. One strategy to solve this issue is improving the long-term stability of its components and reducing the system costs. In an SOFC system, the cathode material is a highly important component due to its role in the electrochemical reduction of oxygen (Jin *et al.*, 2013). To resolve this issue, various researchers have developed new cathode materials to reduce the operating temperature to a low-intermediate temperature range of 200-850°C (Liu *et al.*, 2006; Chokkha *et al.*, 2013; Chokkha *et al.*, 2014). The conventional cathode for high temperature SOFCs is perovskite structure. The first conventional cathode materials included lanthanum manganite, cobaltite, and ferrite-based perovskite structures. However, LSM ($\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$) has been widely studied. The perovskite type is an interesting material for SOFC cathodes due to its compositional flexibility and its mixed ionic-electronic conductivity (MIEC) (Tarancón *et al.*, 2010; Wang *et al.*, 2015; Saccoccio *et al.*, 2017). Meanwhile, other structures have been studied as an alternative to simple perovskites, including Ruddlesden-Popper series (RP) and double perovskites. RP oxides present in the general formula of $\text{A}_{n+1}\text{A}'_2\text{B}_n\text{O}_{3n+1}$ consist of $n\text{ABO}_3$ perovskite layers between two A'O rock-salt layers along the c-axis. Among the materials with this particular structure, the RE_2MO_4 series (with RE = rare earths and M = transition metals) presents the best electrochemical performance for an intermediate temperature SOFC. Yet double perovskite type has attracted significant attention among the perovskite compositions. The general formula is $\text{AA}'\text{B}_2\text{O}_{5+\delta}$, where A is a lanthanide, A' is an alkaline earth element, and B is a transition metal. Double perovskites are made of stacked $\text{AO}_6|\text{BO}_2|\text{A}'\text{O}|\text{BO}_2$ layers along the c-axis (Kim *et al.*, 2007). In advanced, such a structure enhances the transportation of oxygen, while its high activity in match makes them particularly suitable for SOFC applications (Taskin *et al.*, 2005; Taskin *et al.*, 2007; Chen *et al.*, 2015; Gao *et al.*, 2015).

In the present study, the expected double perovskite structure of $\text{LaBaCo}_2\text{O}_{5+\delta}$ was

studied and synthesized by easily solid state reaction method. The reaction temperature, room temperature phase, microstructure, and electrical conductivity of the synthesized material were characterized by using Simultaneous Thermal Analyzer (STA), X-ray diffractometer (XRD), scanning electron microscope (SEM), and four-probe DC method, respectively.

Experimental

$\text{LaBaCo}_2\text{O}_{5+\delta}$ powder system was synthesized by a conventional solid state reaction. The stoichiometric amounts of starting materials, such as La_2O_3 (99.99% purity), BaCO_3 (99 % purity), and Co_2O_3 (99% purity) were weighed. The La_2O_3 was fired at 1000°C for 5 h in air to remove physically and chemically absorbed water and carbonate. After firing, the La_2O_3 was ground and the weight loss was measured in addition to the loss on ignition (LOI) prior to the next step. The starting powders were wet-milled in ethanol for 8 h. Next, the mixed slurry was placed and dried in an alumina crucible. After grinding, the dried powder was calcined in a furnace at 1,100°C for 2 h in air and held at reaction temperatures determined by Simultaneous Thermal Analyzer (STA), using the temperature range from room temperature to 1,100°C in air with a heating rate of 10°C/min. The room temperature phase of the calcined powder was investigated through X-ray diffraction using a Bruker D2 Advance with $\text{CuK}\alpha$ in the 2-theta range of 10°-80°. The single phase of the cathode material was weighed out to amounts of 2 g before being formed into a 6.5 mm × 32 mm × 2.5 mm bar steel mold using uniaxial pressing at 50 MPa. After forming, the sample was sintered at 1,100°C for 2 h in air at a heating-cooling rate of 5°C/min. The bulk density of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ specimen was determined using Archimedes' method. The electrical conductivity of the sintered sample was collected at 50°C to 800°C by a four probe DC method. All the data was measured in air with a heating rate of 4°C/min. Then the cross-section microstructure of the sintered

specimen was observed using a scanning electron microscope (SEM, Jeol JSM6010LV).

Results and Discussion

Material Preparation and Crystal Structure

The STA result consisted of TGA, Derivative-TGA, DSC, and Derivative-DSC of $\text{LaBaCo}_2\text{O}_{5+\delta}$ powder synthesized via a solid state reaction (Figure 1). The derivative curve presents the reaction temperatures in a form which is as visually accessible as TGA-DSC. The reaction peak temperatures occurred at 370°C, 720°C, and 1,050°C, so the powder was calcined and soaked at each of these reaction temperatures. Although the reactions of $\text{LaBaCo}_2\text{O}_{5+\delta}$ were completed at 1,050°C, the veritable calcined temperature at 1,100°C with a soaking period for 2 h in air was hired to obtain a single phase for $\text{LaBaCo}_2\text{O}_{5+\delta}$. Figure 2 (a) shows the x-ray diffraction (XRD) pattern of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ synthesized powder after calcination at 1,100°C for 2 h. All the peaks were well indexed with JCPDS no. 32-0480 as a cubic double perovskite structure,

with a lattice parameter of 5.4890(0) Å. These features indicated that the single crystalline phase of the double perovskite structure was successfully obtained after calcination in air. However, all the peaks slightly moved to lower 2-theta. Figure 2(b)

Electrical conductivity

The electrical conductivity (σ) of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ specimen as a function of the operating temperature measured in an air atmosphere is presented in Figure 3. The electrical conductivity value of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ specimen is shown in the range of 320-170 S/cm at between room temperature through to 800°C. During the simulated operating temperature, the electrical transition points were observed from $\text{LaBaCo}_2\text{O}_{5+\delta}$ after being sintered at 1,100°C for 2 h. In the present study, it is defined as the transition temperature from metallic conducting behavior to semiconducting behavior for T_1 , and the transition temperature from semiconducting behavior to metallic conducting behavior for T_2 . The electrical conductivity of $\text{LaBaCo}_2\text{O}_{5+\delta}$ synthesized sample decreased from room temperature to 140°C, indicating

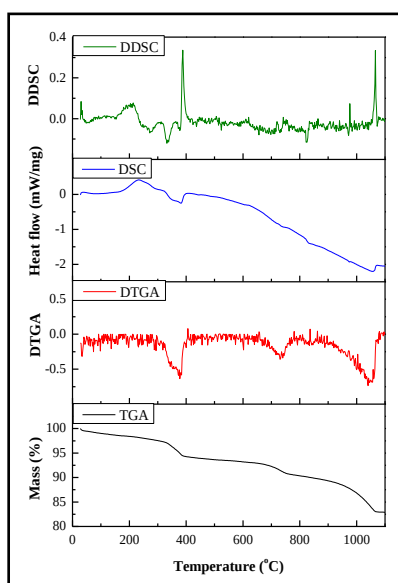


Figure 1. STA curves of $\text{LaBaCo}_2\text{O}_{5+\delta}$ residue composition

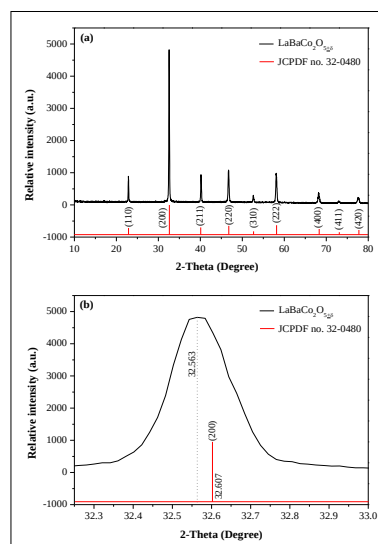


Figure2. XRD patterns of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ powder after calcination at 1,100°C for 2 h

Table 1. T₁ and T₂ and electrical conductivity values of LaBaCo₂O_{5+δ} cathode.

Composition	T ₁ (°C)	T ₂ (°C)	Electrical conductivity (S/cm)						
			T _{30°C}	T ₁	T ₂	300°C	400°C	600°C	800°C
LaBaCo ₂ O _{5+δ}	140	240	320	310	320	304	270	209	170

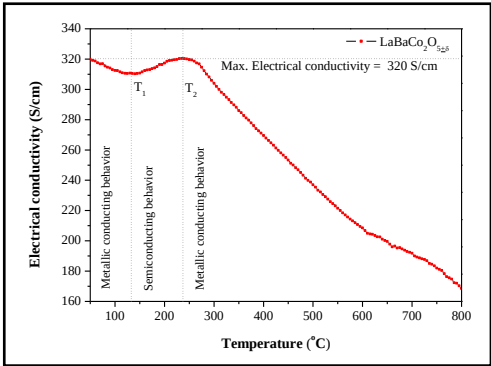


Figure 3. Electrical conductivity (σ) of LaBaCo₂O_{5+δ} measured at various temperature in air condition

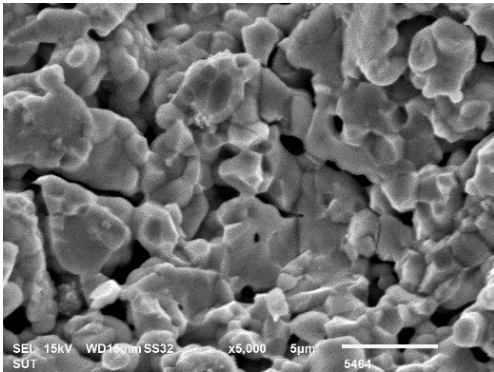


Figure 4. Cross-section scanning electron micrograph of LaBaCo₂O_{5+δ} cathode

that a metallic-like conducting behavior. Above $T_1 = 140^\circ\text{C}$, the electrical conductivity of the LaBaCo₂O_{5+δ} shows that the hkl peak of 200 of XRD index that occurred at 2-Theta of 32.607° clearly shifted to lower 2-Theta of 32.563° in the LaBaCo₂O_{5+δ} synthesized powder. To calculate the Bragg's law equation, a lattice parameter and unit cell volume of the LaBaCo₂O_{5+δ} synthesized powder were

$5.4951(4) \text{ \AA}$ and $165.9344(1) \text{ \AA}^3$. These results indicate that the lattice parameter and unit cell volume of the LaBaCo₂O_{5+δ} synthesized powder were higher than the XRD index. sample presented a semiconducting behavior, which increased along with rising testing temperatures until reaching $T_2 = 240^\circ\text{C}$. Between T_2 to 800°C , the electrical conductivity of the LaBaCo₂O_{5+δ} specimen decreased with increasing temperatures, indicating a metallic-like conducting behavior and related to other same structures such as GdBaCo₂O_{5+δ}, PrBaCo₂O_{5+δ}, and SmBaCo₂O_{5+δ} (Pelosato *et al.*, 2015). The highest conductivity in the present study was obtained from the LaBaCo₂O_{5+δ} synthesized-specimen with a value of 320 S/cm at room temperature and $T_2 = 240^\circ\text{C}$. The electrical transition temperatures of T_1 and T_2 including their conductivity values are included in Table 1. Although the electrical conductivity gradually reduced with temperature, it still shows that the high electrical conductivity value at temperatures below 800°C , compared with others cathode oxide such as some perovskite systems, some double perovskite systems, and the Ruddlesden-Popper (RP) structure (Sakaki *et al.*, 1999; Chokkha *et al.*, 2014; Wang *et al.*, 2016). These results demonstrate the high potential of the LaBaCo₂O_{5+δ} synthesized specimen for use as a cathode material in low and intermediate temperatures for solid oxide fuel cells.

Cross-Section Microstructure And Bulk Density

After the conductivity was tested using the 4-probe DC method, the cross-sectional micrograph was examined by SEM at a magnification of 3,000x. The average grain size of the LaBaCo₂O_{5+δ} sample was estimated to be in the range of $0.5\text{--}3.9\mu\text{m}$. The highly porous microstructure of the LaBaCo₂O_{5+δ}

cathode specimen is clearly seen. The bulk density of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ sample is a 69.89% theoretical density. In addition, the porosity of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ cathode specimen is 30 %. For a properly cathode designed, the SOFC cathode materials must have a porosity of 20 – 40% to ensure proper conduction of O_2 molecules to the reaction sites at the electrolyte interface (Conceicao *et al.*, 2011). The appropriate porosity is important for the SOFC cathode material to allow the rapid transportation of gaseous reactants and to achieve the perfect performance of the electrochemical reactions.

Conclusions

A $\text{LaBaCo}_2\text{O}_{5+\delta}$ double perovskite structure was successfully synthesized by a traditional solid-state reaction. The calcined powder at $1,100^\circ\text{C}$ presented a cubic double perovskite structure with higher lattice parameter and a unit cell volume greater than the XRD reference data. Moreover, a high electrical conductivity range of 170-320 S/cm was achieved when the cell was operated at a low-intermediate temperature SOFC range between room temperature to 800°C . In addition, the $\text{LaBaCo}_2\text{O}_{5+\delta}$ cathode specimen showed a high porosity in the cross-section micrograph. This indicates the proper use of the SOFC cathode is designed to allow rapid transportation of gaseous reactants and to achieve a perfect performance of the electrochemical reactions.

Acknowledgment

This work was supported by Suranaree University of Technology (SUT)

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