Impact of Mn$^{4+}$ ion substitution on La$_{0.4}$Sr$_{0.6}$Fe$_{1-x}$Mn$_x$O$_3$ perovskite conductivity ($x = 0.2, 0.4$ and $0.6$) as a solid fuel cell cathode

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Abstract. The samples La$_{0.4}$Sr$_{0.6}$Fe$_{1-x}$Mn$_x$O$_3$ ($x = 0.2$, $0.4$, and $0.6$) as solid fuel cell cathodes have been successfully synthesized and characterized. Samples were made using the solid-state reaction method with the wet milling technique. X-ray diffraction is used to see the phases formed. Surface morphology in the form of particle shape and size is characterized using scanning electron microscopy, while electronic conductivity at room temperature is measured by measuring its resistivity. Sample $x = 0.4$ has a single phase, while two other samples, $x = 0.2$ and $0.6$ are still detected secondary phase. Surface morphology has a heterogeneous grain shape with a size between $63$-$250$ nm. The best electronic conductivity at room temperature is obtained at a composition of $x = 0.4$ of $3.39 \times 10^{-3}$ S.cm$^{-1}$ so that it can be used as a candidate material for a solid fuel cell cathode.

1. Introduction

The need for energy is increasing, while energy sources, especially from fossil fuels, are decreasing. Therefore, a new alternative energy source is needed. This new energy source should be more environmentally friendly because so far, the use of fossil fuels has been pointed out as one of the causes of air pollution and global warming. Therefore, an environmentally friendly energy source is a very urgent need. One of the renewable energy sources is solid oxide fuel cells (SOFC) consisting of cathodes, electrolytes, and anodes [1, 2].

Research on the cathode material in solid oxide fuel cells (SOFC) based on the structure of perovskite oxide ABO$_3$ (A = La, Sr, Ba, etc., B = Co, Mn, Fe, etc., and O = oxygen) attracted the attention of many researchers [1-4]. Some cathode materials developed for example, lanthanum strontium cobalt ferrite (LSCF) [1, 4], barium strontium cobalt ferrite (BSCF) [2], lanthanum strontium cobalt oxide (LSC) [3]. These materials are very promising as SOFC cathodes because they have good compatibility [1], high energy conversion [2], have high activity as an oxygen reduction catalyst [3], but there are also disadvantages, which are experiencing cathode degradation at temperatures high [4], the manufacture requires a high sintering temperature of $1400$ °C [5], and also requires a high...
operating temperature of ~ 1000 °C [3, 5-6]. To minimize this deficiency, SOFC was developed which operates at lower temperatures (low temperature/LT-SOFC or intermediate temperature IT-SOFC), which is around 500-800 °C. With lower operating temperatures, in addition to reducing component degradation, it can also reduce costs. In addition to the temperature factor, SOFC performance is also influenced by the morphology and composition of the electrodes and electrolytes. So that at low temperatures, these materials must have good conductivity, chemical, and mechanical compatibility [7].

Some methods used in the process of making SOFC cathode materials include co-precipitation [8], sol-gel [1, 9, 10], solid reaction [5], combustion of citrate–nitrate [11], and route of polymer precursors, based on the Pechini method [12]. But in general, of these methods, the easiest and cheapest method is the solid reaction, although it still requires a relatively high sintering temperature.

Dopant concentrations affect electronic conductivity. Sr doping on La (La$_{0.65}$Sr$_{0.35}$MnO$_3$) as well as, Co-doping at Fe (La$_{0.6}$Sr$_{0.4}$Fe$_{1-x}$Co$_x$O$_3$) has a higher electronic conductivity compared to without doping (LaMnO$_3$) [13]. However, under a temperature of 800 °C, LaSrMnO$_3$ material shows catalytic activity which is bad enough to reduce oxygen, and its electronic conductivity is significantly reduced [14]. Therefore, we tried to make samples La$_{0.4}$Sr$_{0.6}$Fe$_{1-x}$Mn$_x$O$_3$, where substitution is not only done at position A (position La with Sr) but at the same time at position B (Fe with Mn) to determine the electronic conductivity at room temperature.

In this paper, we will discuss the effect of Mn$^{4+}$ ion substitution on Fe$^{3+}$ ions on their structure, surface morphology, and electrical conductivity at room temperature. Samples La$_{0.4}$Sr$_{0.6}$Fe$_{1-x}$Mn$_x$O$_3$ (x = 0.2, 0.4, and 0.6) were prepared by the solid reaction method using high energy milling (HEM), then sintered at a temperature of 1000 °C.

2. Experiment
Synthesis of the precursor system La$_{0.4}$Sr$_{0.6}$Fe$_{1-x}$Mn$_x$O$_3$ with a stoichiometric composition (x = 0.2, 0.4, and 0.6) was prepared through a solid reaction of several raw materials La$_2$O$_3$, SrCO$_3$, Fe$_2$O$_3$, and MnCO$_3$, each of which has Merck products with the above purity 99%. The mixture of these ingredients was put into a stainless vial and given spheres of iron and ethanol liquid. Then with the solid reaction method using high energy milling (HEM), the material is ground for 50 hours with 750 rpm. To avoid contamination from iron balls, the milling time is set to 90 minutes of milling and 30 minutes of rest. Then the sample is heated in an 80 °C oven until all the ethanol has evaporated. Then it is sintered at 1000 °C for 5 hours in the air. Before being characterized, the sample was rounded with a diameter of about 1.5 cm with a pressure of 5 tons. To see the phase formation obtained using X-ray diffraction (XRD). Scanning electron microscopy (SEM) is used to characterize surface morphology in the form and shape of grain, while the conductivity of the sample is characterized using an LCR meter at room temperature conditions.

3. Results and Discussion
The diffraction patterns of the XRD results can be seen in Figure 1. For the substitution value x = 0.4 the sample is a single phase with an orthorhombic crystal structure, the Pbnm space group. For the substitution value x = 0.2 still detected two other phases, namely LaFeO$_3$ and La(OH)$_3$, while for the value of x = 0.6 still detected the second phase La(OH)$_3$. The complete results can be seen in Table 1. The secondary phase is still caused by the sintering temperature which is not high enough. This was also obtained by N. P. Bansal et al. (2011) which for temperatures < 1000 °C the sample was not in phase and would be in phase if the sintering temperature was > 1200 °C [9].

Refine the data was used the GSAS program and based on the Match program to obtain a crystallography information file (cif) that used as input for the GSAS program. The XRD data is then
fitted with a pseudovoigt model. The pseudovoigt model is expressed as the sum of the weights of the Gaussian and Lorentzian functions expanded by adding two other types of peak functions to increase accuracy when approaching the Voigt profile. Full width at half maximum (FWHM), the mixing parameters of Gaussian, Lorentzian and two other component functions in an extended model can be approximated by a polynomial of a parameter.

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(1)

Where \( \lambda \) is the wavelength (\( \lambda = 1.5406 \) Å) and \( \beta \) is full width at half maximum (FWHM).

Figure 1. (a) \( \text{La}_{0.4}\text{Sr}_{0.6}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3 \) sample diffraction patterns and (b-d) results of refining with the GSAS program for samples \( x = 0.2, 0.4, \) and 0.6, respectively.
Table 1. From the seven peaks in a single-phase sample (x = 0.4), crystallite sizes ranged from 6.1-12.5 nm.

| x   | Phase       | Crystal   | SG        | a (Å)   | b (Å)   | c (Å)   | ρ (g/cm³) | χ²   |
|-----|-------------|-----------|-----------|---------|---------|---------|-----------|------|
| 0.2 | LaMnO<sub>3</sub> | Orthorhombic | P b n m   | 5.532(1) | 5.451(1) | 7.705(1) | 6.620     |      |
| 0.4 | LaFeO<sub>3</sub> | Hexagonal | R -3 c    | 5.420(2) | 5.420(2) | 13.059(6) | 7.285     | 1.084 |
| 0.6 | La(OH)<sub>3</sub> | Hexagonal | P 63/m    | 6.520(1) | 6.520(1) | 3.850(1) | 5.443     |      |

(a) x = 0.2
(b) x = 0.4
(c) x = 0.6
Figure 2. Surface morphology of sample $\text{La}_0.4\text{Sr}_{0.6}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ (a) $x = 0.2$, (b) $x = 0.4$, and (c) $x = 0.6$

The results of observations using scanning electron microscopy indicate that the surface morphology of the sample appears to have a heterogeneous particle shape and size as shown in Figure 2. The particle size is determined by comparing the grain width to the length of the existing scale lines. Obtained grain size between 63-250 nm This shows that the granules formed are composed of one or several crystallines. The size of the grain is affected by the sintering temperature. The higher the sintering temperature, the larger the grain size will be. For a heating temperature of 700 °C, the grain size is around 15 nm [9]. Although the morphology of the grains is quite clear, agglomeration still appears. To reduce agglomeration can be done with a lower sintering temperature and preparing the sample [15, 16].

The particle distribution for $x = 0.4$ is better compared to the other two samples, $x = 0.2$ and 0.6. For sample $x = 0.4$, although not completely solid, the pores are not as much as compared to samples $x = 0.2$ and 0.6 as shown in Figure 2. The presence of this porosity can be observed directly from the SEM images. Porosity that occurs will greatly affect the conductivity of the sample [8]. However, the presence of these pores is also important for cathode materials for the insertion and removal of cations during the filling and discharging process [11].

Figure 3 is a characterization of conductivity as a function of frequency at room temperature. These results are not much different from those produced by Damena et. al (2019) where at room temperature for samples $\text{LaMnO}_3$, $\text{La}_{0.8}\text{Sr}_{0.1}\text{Co}_{0.1}\text{MnO}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.2}\text{MnO}_3$ electronic conductivity is $6.3 \times 10^{-3}$, $8.7 \times 10^{-3}$ and $5.8 \times 10^{-3}$ S.cm$^{-1}$, respectively [10]. Below 800 °C, $\text{LaSrMnO}_3$ material shows its electronic conductivity is significantly reduced [14]. In general, the material ($\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$) (Ln = lanthanide, A = Ca, Sr, Ba, Pb) ($\text{LaMnO}_3$) works well at operating temperatures above 800 °C due to high electronic conductivity [17]. To increase electronic conductivity can be done by supporting or making the particle size smaller. At a temperature of 800 °C, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ maximum conductivity is $1.1 \times 10^2$ S. cm$^{-1}$ and at 400 °C it drops to 0.1 S. cm$^{-1}$ [6]. Whereas L. J. Gauckler et al. (2014), obtained conductivity for $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.2}\text{Co}_{0.2}\text{O}_3$ were 102 S.cm$^{-1}$ and 302 S.cm$^{-1}$, respectively [13]. Smaller particle size gives lower resistance, so the conductivity will be better [1]. The electronic conductivity is 10-250 S.cm$^{-1}$ even at the same temperature of 800 °C [16].
Sample $\text{La}_{0.4}\text{Sr}_{0.6}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ with a composition of $x = 0.4$ has been successfully synthesized and produced a single phase. The surface morphology has a heterogeneous grain shape with a particle size between 63-250 nm and a crystallite size of about 6.1-12.5 nm. Besides that, this composition has the best electronic conductivity at room temperature of $3.39 \times 10^{-3}$ S.cm$^{-1}$ so that it can be used as a candidate for solid fuel cell cathode materials.

4. Conclusion
We have synthesized $\text{La}_{0.4}\text{Sr}_{0.6}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ samples ($x = 0.2, 0.4, \text{and} 0.6$) through the solid-state reaction method using high energy milling in wet conditions. Samples with $x = 0.4$ are single phase with orthorombic crystal structure, while the other two samples, $x = 0.2$ and 0.6 are still detected by the secondary phase, namely hexagonal. The particle size ranges from 63-250 nm. At room temperature, the electronic conductivity of the sample $x = 0.4$ is $3.39 \times 10^{-3}$ S.cm$^{-1}$, greater than the other two samples, $x = 0.2$ and 0.6, namely $1.48 \times 10^{-3}$ S.cm$^{-1}$ and $2.14 \times 10^{-3}$ S.cm$^{-1}$, respectively.
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