# Synthesis and characteristics of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite cathode material by microwave assisted sol – gel method


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**ABSTRACT**

*In this study, LSCF 6428 was synthesized by microwave assisted sol – gel method. XRD and SEM analyses were used to determine the single-phase and nanocrystalline structure. Properties of this perovskite material including specific area, thermal expansion coefficient (TEC) and resistance of cathode were studied. The results showed that well-crystalline perovskite was obtained at microwaved of 500 W in 10 minutes, stirred at 90 oC in 2 hours and calcined at 900 oC in 1 hours. The surface area of the material was 13.384 m2/g. The properties of materials were also improved by mixing with Gadolinium doped ceria (GDC) at the ratio 7:3 (w/w). At this ratio, TEC of composite matched with electrolyte. The resistance of cathode was 0.17 – 0.2 Ω in the range of temperature from 580 – 700 oC. Microwave assisted sol – gel was an easy, economical and time – saving method to synthesis LSCF 6428 for Single Chamber - Solid oxide fuel cell (SC-SOFC) cathode application.*


***Keywords:*** *SC-SOFC, LSCF 6428, cathode, perovskite, microwave, sol – gel, TEC, GDC*

## 1. INTRODUCTION

Solid oxide fuel cells (SOFCs) are considered as a next generation power generating technology because of their fuel flexibility and high overall efficiency [1]. SOFCs operate at high temperature impose several challenges on reliability and long-term stability of these fuel cells [1]. Reducing their operating temperature is very important to commercialize SOFCs. Single Chamber - Solid Oxide Fuel Cell (SC-SOFC) is one kinds of

SOFC which can operate at intermediate temperature (600 – 800 $^oC$) in order to lower the cost and extend the lifetime [2]. In SC-SOFCs, both anode and cathode, are situated in a common gas chamber and are exposed to a mixture of fuel and oxidant. The working principle is based on the difference in catalytic activity of the electrodes for the respective anode and cathode reactions [1]. However, decreasing the operating temperature makes cell performance decrease due to less catalytic activity of the electrodes and poor conductive of the electrolyte. Most of the recent studies have focused on improving the electrochemical performance by searching new anode and cathode materials, electrolyte thickness... [1,2]. $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF 6428) is a mixed ion and electron conducting perovskite. This material is an attractive cathode for SC-SOFC because it has high catalytic activity as well as good ionic and electronic conductivities at intermediate temperature [1,2]. LSCF 6428 was synthesized by different methods such as solid state reaction, co-precipitation, combustion, hydrothermal, plasma spray decomposition... [2,3]. These methods generally require long reaction time and high calcined temperature (above 1000 $^oC$). In our previous works [4], LSCF 6428 was synthesized by sol - gel method, which was proved as a simple and economical method for making nano powders [5], with lower calcined temperature (900 $^oC$) in 1 hour. Recently, microwave synthesis is considered as a technology for high-purity, time-saving and energy-efficient [3,6]. Moreover, cathode materials require both matching of thermal expansion coefficient (TEC) with electrolyte and high conductivity [1,7]. Thermal expansion mismatches between components can lead to failure of the seals that separate anode, electrolyte, and cathode chambers [1,7]. To match TEC with electrolyte, LSCF 6428 can be mixed with Gd-doped ceria (GDC) at difference ratios. GDC is one of a class of ceria – doped electrolytes with higher ionic conductivity and lower operating temperatures (<700 $^oC$) compared to another electrolyte like YSZ [1]. Composite of LSCF 6428 and GDC matched with TEC will increase ionic conductivity [1,7]. In another research, LSCF 6428 has conductivity of $10^2$ - $10^3$ S/cm at 800 °C [1]. A thin layer of GDC between cathode and electrolyte is used to prevent chemical reaction of these materials [1]. The electrolyte application of LAMOX in SOFC appears very promising, it denotes the oxide ion conductor family based on its parent crystal $La_2Mo_2O_9$ [8]. This material exhibit high ion conductivity. Their conductivities are comparable with or slightly higher than those of the well-known oxide ion conductors of lanthanum strontium gallium magnesium oxide and Gd-doped ceria (GDC) at 600 - 800 $^oC$ [8].

In this paper, to improve synthesis process, nano-crystalline LSCF 6428 was synthesized by microwave assisted sol - gel method, which was not found in publication about LSCF synthesis at the ratio 6428. This research also focused on mixing LSCF 6428 with GDC at difference ratios to match TEC with LAMOX electrolyte and investigated the conditions which cathode has low resistance.

## 2. MATERIAL AND METHODOLOGY

### 2.1. Material synthesis process

The procedure to synthesize LSCF 6428 by sol-gel method was described in our previous work [4] using $La(NO_3)_3.6H_2O$ (99.9%), $Sr(NO_3)_2$ (99.0%), $Co(NO_3)_3.9H_2O$ (98.5%),

$Fe(NO_3)_3.9H_2O$ (98.5%), EDTA (98.0%), ethylene glycol (98.0%), ammonia solution (30%) and distilled water. The precursor solution was prepared by mixing individual nitrate salt solution in a molar ratio of 0.6:0.4:0.2:0.8 respectively for LSCF. EDTA was dissolved in $NH_4OH$ solution at the molar ratio of 1:1. This solution was added to nitrate solution in order to form complexes at defined the molar ratio of EDTA/$NO_3^-$ of 1.5:1. Ethylene glycol which was used to create dispersive environment was slowly added into the reaction mixture and the pH 8.0 of mixture was maintained by using ammonia. Then the mixture was heat and continuously stirred at 90 $^oC$ until a dark brown gel was formed. Gels were dried at 200 °C for 2 h, following by calcination at high temperatures from 700 - 1300 °C. After that, a ball mill in alcohol was occurred. Sample was dried at 105 ° C for 2 h.

The only difference here is the short time (5 minutes) microwave application during sol-gel ageing at 90 $^oC$ which lasts next 60 minutes, as indicated in Fig.1. Limited by the microwave oven in use, the microwave irradiation was either at 300W, 500W, or 700W. This step was repeated up to total 3 times.

A modified domestic microwave oven (Sanyo 700, China) was used. The frequency of the microwave irradiation was 2.45 GHz, and the maximum output power was 700 W. The modified microwave oven is shown in Fig.1.

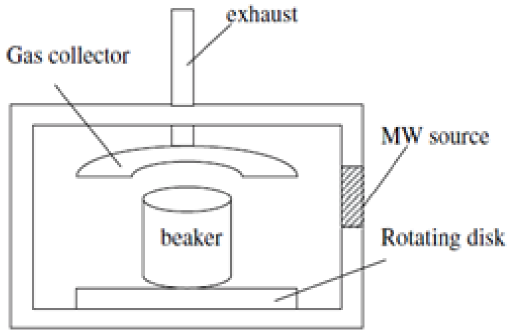


**Figure 1.** The modified household microwave oven (vessel size: 16 L, microwave power: 700 W, frequency: 2.45 GHz)

### 2.2. Characterization of LSCF 6428

#### *2.2.1 Characterization of synthesized materials*

The synthesized materials were characterized by XRD, SEM and $N_2$-BET methods, using a D8 advance Bruker equipped with a $CuK_\alpha$ source and scanning angle in region $2\theta = 20 \div 80^o$, a JEOL-JSM-7401F, and a BET NOVA 2200e, respectively.

#### *2.2.2 Preparation and characterization of cathode materials*

GDC was synthesized according to the sol-gel method described elsewhere [9]. The composites serving as cathode materials were prepared by ball milling the as-prepared LSCF 6428 with GDC at different ratios of 10:0; 8:2; 7:3 and 6:4 (w/w) in ethanol for 10 minutes.

The TEC of cathode materials in form of 5 mm x 20 mm cylindrical pellets (compressed at 7 MPa) were measured by a Netzsch Dil PC 402 in the range from room temperature up to 1000 $^oC$ at 10 $^oC$/minutes heating rate and under open air.

The electrical resistances of cathode materials in form of 15 mm x 1 mm pellets (compressed at 7 MPa) after 60 minutes calcining at 1000 $^{o}C$ in open air were measured in a home-made apparatus as described in Fig.2. The air mixing ration $CH_4/O_2$ ($R_{mix}$) was kept constant at 2 and the temperature was ranged from 400$^{o}$C÷700$^{o}$C. The electrical resistances of cathode were measured by a Wellink HL-1240 multimeter.

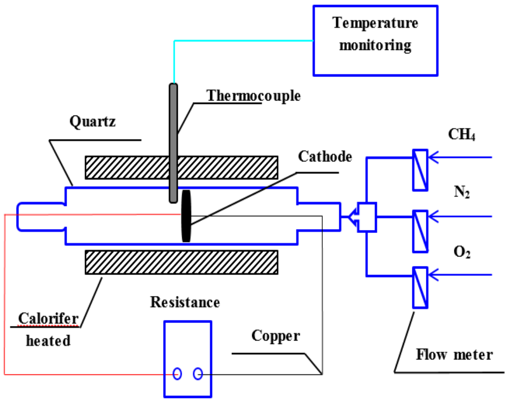


**Figure 2.** Schematic diagram of resistance measurement configuration.

## 3. RESULT AND DISCUSSION

### 3.1. Effects of power and time of microwave irradiation

The microwave irradiation made the temperature of the sol sample raised immediately. Within 1 minute of irradiation, the sol started boiling and then converted into a black solution. After every 5 minutes of irradiation, stirring was applied to maintain the temperature of solution at 90 $^{o}C$. Low heating supply to maintain because of the solution was boiled when irradiated.

The XRD pattern of LSCF 6428 cathode material synthesized at difference microwave powers (300, 500 and 700 W) is presented in Fig.3. The samples were microwaved for 5 minutes and stirred at 90 $^{o}C$ for 1 hours, this step was repeated up to total 3 times for every microwave power. The XRD results showed that at microwave power of 300 W, the perovskite structure was not clear because energy is not enough for reaction to occur. At 500 and 700 W, the perovskite structure became clearer, matched with standard peaks in both location and intensity. The difference between 500 W and 700 W was not clear because of sufficient energy supplied by both irradiations for the reaction. So the appropriate microwave power is 500 W. At this power, microwave assisted sol – gel method provided good condition that helps complexion reaction to occur completely. Compare with our previous work [4], the perovskite structure was obtained by stirring at 90 $^{o}C$ in 4 hours. In this experiment using microwave assisted sol – gel method, total time of microwave irradiation and stirring was 3 hours and 15 minutes. Total time was studied in next experiment. After sol – gel, both samples were calcined at 900 $^{o}C$ for 1 hour. In another study, LSCF was prepared by the Pechini method in which temperature of calcination was 1000 °C for 4 h to develop crystalline perovskite phase [2]. So both LSCF were synthesized by sol – gel method and microwave assisted sol – gel which reduced significantly the temperature and time of calcination.

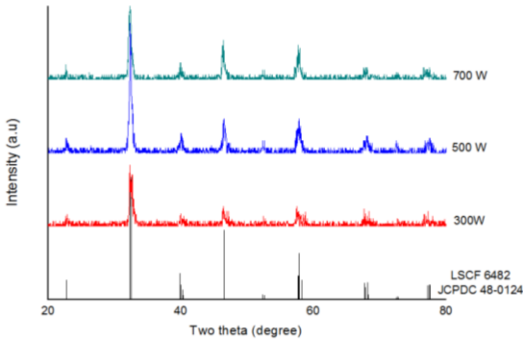


**Figure 3.** XRD of LSCF 6428 synthesized at difference microwave powers

The effect of difference microwave irradiation times on synthesis of LSCF 6428 cathode material is presented by XRD pattern in Fig.4. The microwave power was selected from the previous experiment at 500 W. The results showed that for one time of irradiation, the perovskite structure was not clear because energy is not enough for the reaction to occur. Two and three times, the difference was not much. In these cases, location and intensity of peaks matched with standard peaks. Because of sufficient energy for the reaction, providing higher energy does not make significant difference. Hence, the appropriate time in total for microwave irradiation is 10 minutes at the power of 500 W. At this condition, LSCF 6428 appeared in single phase with clear perovskite structure.

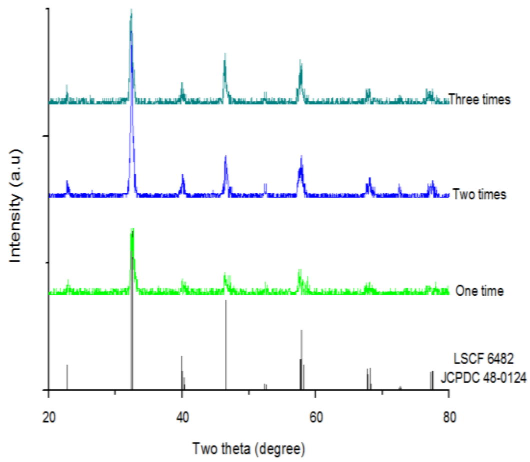


**Figure 4.** XRD of LSCF 6428 synthesized at difference microwave times (with the same microwave power of 500 W).

The comparison of XRD results between in this paper with LSCF synthesized only by sol – gel [4] is presented in Fig.5. The traditional sol – gel synthesis was conducted by stirring in 4 hours without microwave irradiating, while the microwave assisted sol – gel (MW sol – gel) synthesis was performed at 500 W in 10 minutes and stirring in 2 hours. Other conditions for preparation of two samples were kept the same. Both location and intensity of peaks in two samples were suitable with standard peak, but in the case of microwave assisted sol – gel synthesis, the peaks were much clearer, less interference, hence the material has better quality.

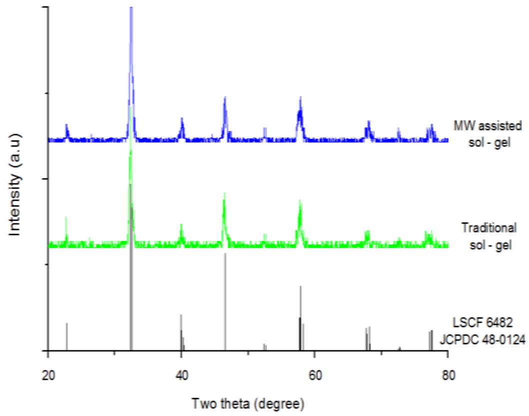


**Figure 5.** Comparison of XRD results of LSCF 6428 synthesized by traditional sol – gel and microwave assisted sol – gel methods.

In another study, LSCF 6428 was synthesized by sol – gel method that required stirring at 90 °C for 4 hours and after the sol-gel, calcination at 900 °C for 3 hours [5]. With LSCF synthesis processes at another ratio is 8255, material was also synthesized by sol - gel combined with microwave which required stirring at 90 $^{o}$C for 3 hours and microwave power of 700 W for 35 minutes [3]. In this study, the synthesis conditions were microwave power of 500 W for 10 minutes, stirred at 90 °C for 2 hours and calcined at 900 °C for 1 hours. The research results showed that well perovskite structure was obtained with the stirred time, calcined time, microwave power, microwave time were decreased. Because microwave assisted sol – gel help complexion reactions were effective, the consumption of energy decreased significantly and time – saving.

The crystallite size of LSCF 6428 synthesized at the intensity of microwave of 500 W for 10 minutes was determined by SEM as shown in Fig.6. The average particle size was in the range of 90 - 120 nm. In other studies, M. Ghouse et al [5] and Changjing Fu et al [10] reported that materials synthesized by sol - gel method also had nanosize in the range of 50 - 200 nm, with the surface area of 2.8 $m^2/g$. The synthetic material by sol - gel combined with microwave method obtained the smaller sizes compared to the one synthesized by the traditional sol – gel method, which could be due to good contact between the reaction and position $O_2$. BET results further showed that surface area of material was 13.384 $m^2/g$. Hence, comparing to the traditional sol–gel routes [5], the microwave sol – gel materials show smaller crystallite size and larger surface areas.

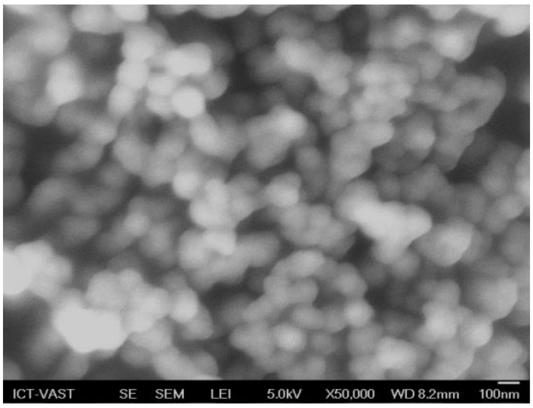


**Figure 6**. SEM result of LSCF 6428 microwaved at 500 W in 10 minutes.

### 3.2. Effect of the mixed ratio on TEC of composite made by LSCF 6428 and GDC

LSCF was mixed with GDC at difference ratios of 10:0, 8:2, 7:3 and 6:4 to match TEC with LAMOX. TEC results of these sample at 800 $^oC$ are presented in table 1.

At the ratio of 8:2, TEC of the composite was slightly higher than that of electrolyte α-$La_2Mo_2O_9$ (LAMOX). At the ratios of 7:3 and 6:4, TEC of the composites was matched with electrolyte. The reason is LSCF 6428 has TEC higher than electrolyte, on the other hand, TEC of GDC is lower than that of LSCF 6428 and LAMOX, according to table 1. So mixing with GDC can make TEC of the composite reduce and match with LAMOX. Matching with electrolyte will prevent cracking between cathode and electrolyte. Three ratios of 8:2, 7:3 and 6:4 were used to study in next experiments to find out the condition which has low resistance.

**Table 1.** TEC of materials

| Material | TEC ($10^{-6}/^oC$) |
|---|---|
| LSCF | 15.5 |
| LSCF:GDC = 8:2 | 15.1 |
| LSCF:GDC = 7:3 | 14.8 |
| LSCF:GDC = 6:4 | 14.5 |
| GDC | 12.3 [11] |
| α-$La_2Mo_2O_9$ (electrolyte) | 14 – 15 [8] |

### 3.3. Effect of the mixed ratio on the resistance of composite made by LSCF 6428 and GDC

Fig.7 shows the results of resistance of composite material of LSCF and GDC at the ratios of 8:2, 7:3 and 6:4 with $R_{mix}$ = 2, reaction temperature from 450 – 700 $^{o}$C. Sample LSCF 6428, which was not mixed with GDC (10:0), was used to verify.

Results showed that when the operating temperature increased, the resistance of cathode was decreased. From 550 $^{o}$C to 700 $^{o}$C, the resistance was higher because of poor conductivity of cathode materials at low temperature. From 550 $^{o}$C, the resistance of cathode materials was lower. So the suitable temperature for SC-SOFC operation is 550 - 700 $^{o}$C. According to another studies, the temperature is 600 – 800 $^{o}$C [12, 13]. Thus, this study has decreased operating temperature, which potentially lowers the cost while extends the lifetime of SC-SOFC.

The higher proportion of GDC in the mixture resulted in the higher resistance of cathode. So, the ratio 7:3 was chosen because of matching TEC with electrolyte and low resistance. In another research, this value of LSCF/GDC was 0.18 Ω at 800 $^{o}$C [12], or the lowest polarization resistance of 0.17 Ω $cm^2$ was achieved from LSCF–GDC (40:60 wt%) composite cathode prepared at 600 °C [13]. In this study, at the mix ratio of 7:3, the resistance of cathode is 0.17 – 0.2 Ω in range temperature 580 – 700 $^{o}$C and TEC is $14.8x10^{-6}$/$^{o}$C. Hence, the composite not only has suitable resistance for SC-SOFC but also has TEC matching with electrolyte.

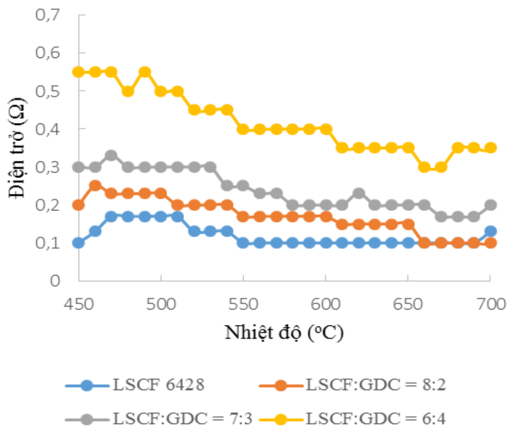


**Figure 7.** Resistance of cathode composite made by LSCF and GDC at difference ratios

## 4. CONCLUSION

LSCF 6428, with well single-phase and nanocrystalline structure, was successfully synthesized by sol – gel process combined with microwave method. Results in this study showed that the application of microwave assisted sol–gel route for the synthesis of LSCF 6428 is superior in terms of energy and time saving compared to the other methods. LSCF was then mixed with GDC at the ratio of 7:3 and the composite had TEC matched with electrolyte and low resistance in the range of temperature of 550 – 700 $^{o}$C. So it can be concluded that the mixture is suitable material for cathode fabrication in SC-SOFC.

# Tổng hợp và các tính chất của vật liệu catốt $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite bằng phương pháp sol – gel kết hợp với vi sóng


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**TÓM TẮT**

*Trong nghiên cứu này, LSCF 6428 được tổng hợp bằng phương pháp sol – gel kết hợp với vi sóng. Các phương pháp XRD và SEM được sử dụng để xác định tính đơn pha và cấu trúc tinh thể nano. Các tính chất của vật liệu perovskite này bao gồm diện tích bề mặt riêng, hệ số giãn nở nhiệt, và điện trở của catốt được nghiên cứu. Kết quả cho thấy cấu trúc perovskite thu được khi vi sóng ở 500 W trong 10 phút, khuấy từ 90 oC trong 2 h và nung ở 900 oC trong 1 h. Diện tích bề mặt riêng đạt 13.384 m2/g. Các tính chất của vật liệu cũng được cải tiến bằng cách phối trộn với GDC ở tỷ lệ 7:3 theo khối lượng. Ở tỷ lệ này, TEC của hỗn hợp tương thích với chất điện môi. Điện trở của catốt là 0,17 – 0,2* Ω *trong khoảng nhiệt độ 580 – 700 oC. Do đó, vi sóng kết hợp với sol – gel là phương pháp đơn giản, kinh tế và tiết kiệm thời gian để tổng hợp LSCF 6428 cho ứng dụng làm catốt trong pin SC-SOFC.*


***Từ khóa:*** *SC-SOFC, LSCF 6428, catốt, perovskite, vi sóng, sol – gel, TEC, GDC.*

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