Asian J. Energy Environ., Vol. 9, Issue 1 and 2, (2008), pp. 101-119

Preparation of high surface area $LaCrO_3$ for later application in Solid Oxide Fuel Cell (SOFC)

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Abstract: Perovskite-related solid solution based on lanthanum chromite, $LaCrO_3$, is of considerable interest for high-temperature electrochemical applications, such as intermediate-temperature solid oxide fuel cells (IT SOFCs), oxygen separation membranes and sensors etc. The structure, magnetic, electrical, synthesis and thermal properties of

$LaCrO_3$, as well as its solid solutions formed by doping with Sr, Ca, Ba on A site were extensively investigated. Since the high oxygen ion conductivity of doped $LaCrO_3$ perovskite has been reported, a considerable number of studies, such as the crystal structure, the mechanical property, the chemical stability, the oxygen ion and electrical conductivity, as well as the preparation technique of $LaCrO_3$ doped not only with Ca but also with Ni-, Cu-, Fe- and other transition elements can also be found in literature.

The major limitation of $LaCrO_3$ is its low specific surface area and consequently results in the high deactivation proportion due to the thermal sintering impact when operated under SOFC stack conditions. The use of high surface area (HSA) $LaCrO_3$ would be a good alternative procedure to improve the material performance. Several methods have recently been described for the preparation of high surface area (HSA) $LaCrO_3$ solid solutions. In the present work, high surface area (HSA) $LaCrO_3$ were synthesized by 3 processes including the surfactant-assisted, (co)precipitation and Sol-Gel methods. The specific surface area, stability, and activity of synthesized materials were then studied. Also, the effect of doping Ca and Ni on the specific surface area and properties of $LaCrO_3$ was also investigated. It was found from the work that,

after calcinations, $LaCrO_3$ prepared by the surfactant-assisted method provided significantly higher surface area than others.

Keywords: Solid Oxide Fuel Cell, Perovskite, high surface area.

Introduction

Global energy consumption is rising considerably, and is likely to continue accelerating; however, the forecasted production of energy resources, especially petroleum, is not keeping pace with consumption. This trend justifies urgency with respect to the need for more efficient, as well as alternative, energy conversion devices. The fuel cell is a leading candidate for alternative power due to its high efficiency and environmental friendly. Fuel cells are similar to batteries in term of produced electricity via electrochemistry, but fuel cells are open systems such that their reactants are externally stored.

Several types of fuel cells have been developed for different purposes including mobile, stationary, and portable applications. For mobile application, nowadays, Proton Exchange Membrane Fuel Cell (PEMFC) is used to power the vehicles. For stationary application, the Phosphoric Acid Fuel Cell (PAFC) is used currently to produce the energy for residential buildings. The Solid Oxide Fuel Cell (SOFC) is expected to be applied in big and high-power applications i.e.

for power plants (300 MW_{el}) or as combined heat and power generation [1]. SOFC is also being investigated whether it can be used as an auxiliary power unit (APU) in mobile applications and for portable systems [2].

SOFC is normally operated at high temperature, between 700ºC to 1100ºC [3]. This type of fuel cell has a solid-state electrolyte, which could reduce corrosion and electrolyte management problems. The most interesting fuel for SOFC is natural gas consisting mainly of methane (i.e. 80-95% CH_4). As SOFC is operated at such a high temperature, methane can be reformed effectively by either catalytic steam reforming or partial oxidation to produce a H_2/CO rich gas, which is eventually used to generate the electrical energy and heat.

Normally, hydrogen is the main fuel for SOFC. In order to supply this component to the fuel cell, the steam reforming reaction is always used to reform hydrocarbon fuels such as natural gas. Due to the high operating temperature of SOFC, the steam reforming occurs very efficiently. Practically, SOFC therefore consists of two main sections: a reformer part where the reforming reaction takes place and a fuel cell part where the electrochemical reactions occur. There are two possible reforming operations: external reforming and internal reforming. In external reforming, the reformer and the fuel cell are operated separately in the different units, and there is no direct heat transfer between both unit operations. In contrast, for internal reforming, the endothermic reaction from the steam reforming reaction and the exothermic reaction from the oxidation reaction are operated together in the single unit. Therefore, the requirement for a separate fuel reformer is eliminated, and this configuration is expected to simplify the overall system design, making SOFC more attractive and efficient means of producing electrical power. There are two internal reforming concepts; these are referred to as Direct Internal Reforming (DIR) and Indirect Internal Reforming (IIR). For DIR operation, the reforming reaction takes place at the anode of the fuel cell. Heat and steam are supplied directly from the electrochemical reaction, which also helps to complete the reforming reaction by removing and using of hydrogen. The main advantage of this type of operation is that the hydrogen consumption by the electrochemical reaction could directly promote the conversion of methane at the anode side of the fuel cell. For IIR operation, the reforming reaction takes place at the reformer, which is in close thermal contact with the anode side of fuel cell. IIR gives the advantage of good heat transfer between the reformer and the fuel cell. The heat transfer between these two reactors is expected to provide an autothermal operation. In the part of reformer unit, it requires the optimized catalyst that should be high effective properties such as not too high reducing reaction, high thermal stability and high carbon formation resistance. In this paper, catalyst for IIR is considered in term of methane steam reforming.

The steam reforming of methane is normally carried out over Ni catalysts. However, the endothermic reforming reaction over this catalyst is predicted to be too fast for indirect internal reforming operation requiring very large dilution [4], and carbon deposition always occurs [5]. A novel reforming catalyst with less activity and more resistance to carbon formation is required in order to improve the heat management in SOFC [4,6]. The interesting catalyst in this research is lanthanum chromite-based perovskite material ($LaCrO_3$) due to its good stability under strongly reducing conditions, and high electrical conductivity [7]. However, the weakness of this material is its low specific surface area, therefore, the one of the presently focusing research and development for this material is to increase its specific surface area.

Experimental

1. $LaCrO_3$ Preparation

Figure 1 presents all preparation methods of $LaCrO_3$ in the present work. First method, conventional $LaCrO_3$ was prepared by the precipitation of lanthanum (III) nitrate and chromium (III) nitrate. Both chemical were dissolved by stirring in excess of deionized water. After complete dissolution the mixture obtaining dark-green solution was then added ammonium hydroxide until pH ≥ 11. To acquire the blue-gray residue, the precipitate mixture was filtrated using glass microfiber filter from Whatman. This was further cleaned with deionized water and ethanol to remove the free ammonia until the neutral was achieved. After that, it was dried overnight in an oven at 110°C, and finally with calcinations sample at 900°C for 3 h.

According to the method used by S. Bilger and co-work (1996) [8] in synthesizing $LaCrO_3$ by sol-gel method, lanthane (III) nitrate and chromium (III) nitrate were mixed by large excess methanol corresponding to a ratio of $CH_3OH/(La+Cr) \approx 150$. After complete dissolution the mixture was refluxed for 30 min at the boiling point of the solvent (65°C) obtaining a dark green alcoholic solution. The exothermic precipitation of lanthanum-chromium methoxide occurred by adding ammonium hydroxide to pH ≥ 11. Then the precipitate was washed NO_3-free by methanol. The blue-gray methoxide residue was hydrolyzed in deionized water and peptized by adding nitric acid to stabilize the sol. the sol was directly dried at 110°C in oven for 2 days. Calcination of the green dried powder followed at 900°C for 3 h. For this research, the surfactant-assisted was separated in term of precipitation sol – gel method, furthermore, cationic surfactant have been used. Both above mentioned method, cetyltrimethylammonium bromide were directly added into the central solution which composed of lanthanum and chromium. The molar ratio of substance: surfactant is 5:4. Then the next step followed by main selected method.

As expected, catalysis calcination is vital parameter effecting to physical properties, especially surface area and crystalline structure. Dried catalysts from all methods have to be annealed at 900°C for 3 hr. in order to obtaining stability catalysts. To study of calcined catalyst in different conditions, the perovskite calcinations in air-atmosphere, N_2-atmosphere and H_2-atmosphere were considered. Dried samples are heated at room temperature to 900°C (rate 30°C /min). Controlling reaction gases including hydrogen and nitrogen gas were then fed continually in furnace. The obtained lanthanum chromites powder was characterized.

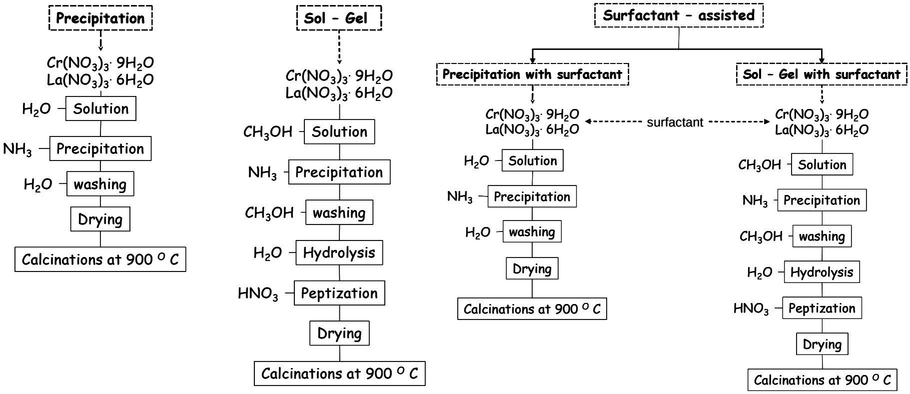

Figure 1. Perovkite preparation method: Precipitation, Sol-Gel and surfactant-assisted method.

2. Characterization

The surface area of all production was determine by using N_2 adsorption / desorption BET instrument. The crystalline phase of $LaCrO_3$ powder was determined by X-ray powder diffraction (XRD) analysis. SEM was also used for surface analysis.

3. Experimental Setup

Experiments were carried out in a flow reactor setup containing an ANSI-316 stainless steel reactor tube of 1/2 inches internal diameter. The auxiliary equipment installed completely system: such as non-return valves, three-way valves, elbows, reductions, expansions and on-off valves were also stainless steel from Swagelok Company. The commercial gases consisting of helium 99.99%, methane 5%, oxygen 10% balanced in helium and hydrogen 10% balanced in helium were supplied from TIG Company, and they were used without further purification. The pressure regulators were installed at the outlet of each gas cylinder in order to set the constant pressure to the mass flow controllers which were used for adjustment the flow rate of inlet gases. In order to study steam reforming, DI water was introduced into the system via a syringe pump. The syringe pump by Cole Parmer ™ Company was used to feed and control the flow rate liquid through the inlet stainless steel tube heated by the cable heater for 110°C in order to evaporate and supply steam to the reactor. It was fixed at the flow rate of 0.2 ml/hr. The reactor was filled with 100 mg of the catalyst to several layers on quart wool, feed H_2O in 0.2 ml·h^{-1} and balance CH_4 10% in helium to 100 mlmin^{-1}. The reaction was continually started at 200°C to 900°C (rate 20°C·min^{-1}) after which temperature was raised up to 900°C, hold on 10 h. The outlet gas composition was measured online with an online mass spectrometer (MS).

The result of methane conversion from the steam reforming could be obtained from the chromatogram data, which are the area under peak of each component including methane, carbon monoxide, and carbon dioxide. The conversion of methane was calculated according to following equation

$$X_{Methane} = \frac{100\,(\%Methane_{in} - \%Methane_{out})}{\%Methane_{in}}$$

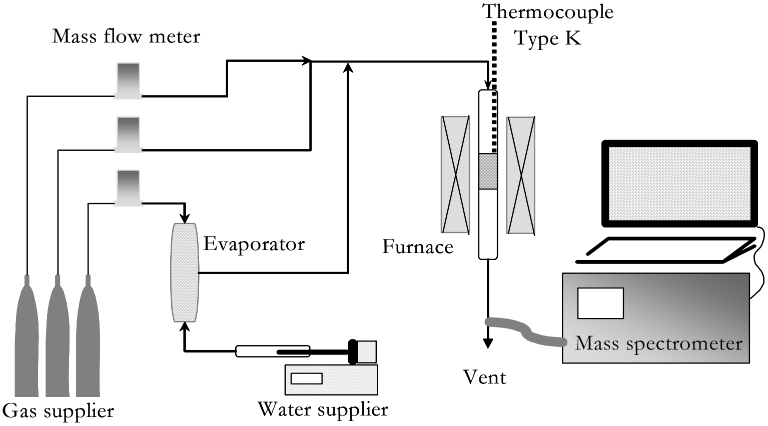

Figure 2. Schematic of the experimental set-up for methane steam reforming.

Results and Discussion

1. Surface area analysis of $LaCrO_3$

For all preparation methods, The BET - analysis of $LaCrO_3$ was carried out after the calcinations in order to determine the specific surface area. The values are presented in Fig. 3a. After calcinations in 900°C, the average surface areas of 1.44, 1.49 and 2.53 m^2g^{-1} were observed for $LaCrO_3$ by precipitation, sol-gel and surfactant assisted method, respectively. From the result, $LaCrO_3$ prepared by surfactant assisted method is the high specific surface area than the others.

In addition to increased the surface area, the treatment condition of $LaCrO_3$ after drying following by calcinations of 900°C in normal atmosphere and calcinations of 900°C in H_2-atmosphere was determined. As Fig. 3b, the surface area of 2.53 and 8.00 m^2g^{-1} were observed for $LaCrO_3$ after calcinations in air and hydrogen atmosphere respectively, and as expected, the surface area dramatically increased under high temperature of hydrogen atmosphere annealing. The specific surface area of $LaCrO_3$ after calcinations in H_2-atmosphere is ~ 4 times higher than surface area of $LaCrO_3$ after calcinations in air. It should be note that the calcinations in H_2-atmosphere is good method for increasing surface area.

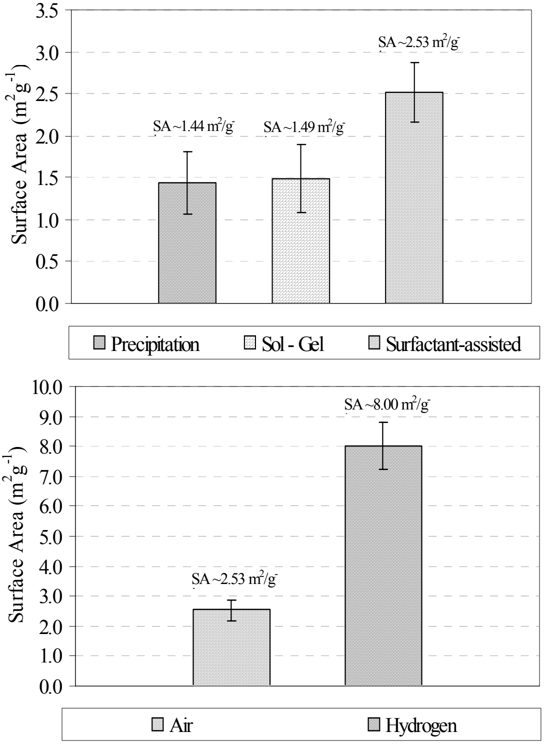

Figure 3. The specific surface area of lanthanum chromite by (a) different synthesis method and (b) effect of calcinations in air and in H_2- atmosphere.

In order to investigate the materials form each methods, the XRD pattern results was appeared in Fig.4. The X-ray diffraction patterns of $LaCrO_3$ powders single phase obtained by (a) precipitation method, (b) Sol-Gel method, and Surfactant-assisted method separated to (c) the $LaCrO_3$ calcinations in air- and (d) H_2-atmosphere. It is clear from the

XRD patterns that all samples prepared by different methods are $LaCrO_3$ (JCPDS #24-1016, Lanthanum Chromite oxide – Orthorhombic). Moreover, from the XRD patterns, it is also observed that all impurity compounds and surfactant agent disappeared after calcination.

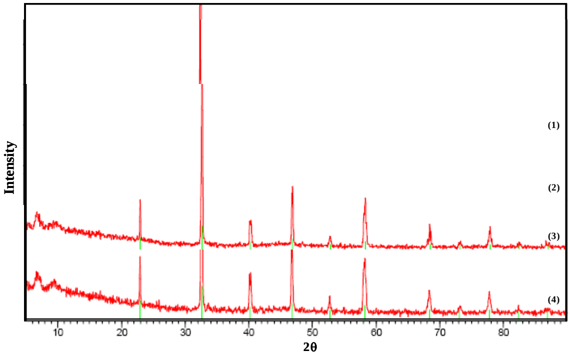

Figure 4. XRD patterns of $LaCrO_3$ with different precipitation method; (1) Precipitation, (2) Sol-Gel, and Surfactant-assisted method calcined in (3) air- and (4) H_2-atmosphere.

2. Reactivity of $LaCrO_3$ toward steam reforming of methane

At the isothermal condition (900°C), the methane steam reforming reaction was determined in term of methane conversion with time. As revealed in Fig. 5, the higher methane conversion was occurred on $LaCrO_3$ perovskite catalyst annealed in H_2-atmosphere (SA ~ 8.00) at initial state. In contrast, the $LaCrO_3$ prepared by surfactant-assisted after calcinations of

900°C in air (SA ~ 2.53) was small conversion of methane. At steady state reaction, the methane conversion of $LaCrO_3$ calcined in H_2-atmosphere was found to be equal the value of 12.9% conversion that is higher than the methane conversion of perovskite sample calcined in air (3.57% conversion). In addition, in term of stability, the $LaCrO_3$ catalyst calcined in H_2 reached the steady state faster than that calcined in air.

All these results noted that the specific surface area of lanthanum chromite is related to effectiveness of methane steam reforming. Following by methane steam reforming reaction (Eq.1), the high hydrogen gas producing come out the high methane conversion.

$$CH_4 + H_2O \gtrless CO + 3H_2 \quad \text{---------} \ (1)$$

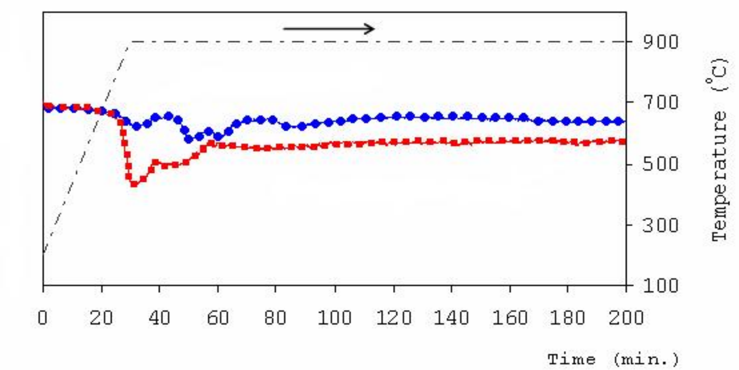

Figure 5. Catalyst performances toward steam reforming of methane: $LaCrO_3$ calcined in air (●) and $LaCrO_3$ calcined in H_2 atmosphere (■).

3. *Effect of the aging on the methane steam reforming reactivity of $LaCrO_3$*

The reactivity of $LaCrO_3$ (prepared by surfactant-assistant then calcinations of 900°C in air) was tested at different partial pressure of methane (0.04, 0.03, 0.02 and 0.01 atm). As shown in Fig.6, the testing result was indicated that the series of methane concentration was converted as 3.57%, 18.85%, 20.99% and 22.89% respectively at a temperature of 900°C. In order to improve the reforming reactivity of $LaCrO_3$, the effect of aging catalyst overnight with helium on the reforming reactivity of $LaCrO_3$ was then studied.

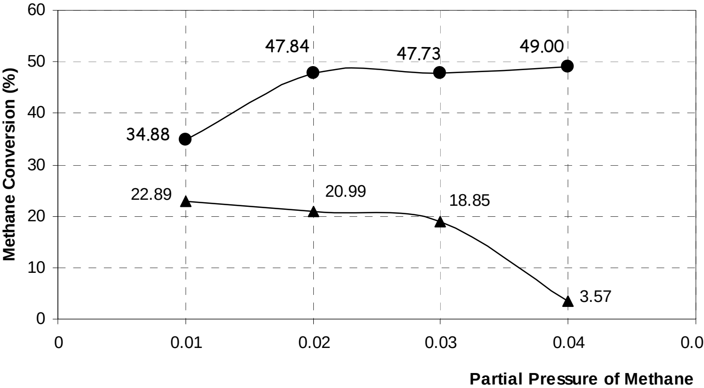

Figure 6. Comparison of the methane conversion activities due to aging and no-aging before start the reforming process at 900°C (aging (●) and no aging (▲)) form methane steam reforming.

According to the aging process, $LaCrO_3$ was left in the reactor at 900°C with the helium flow of 100 ml/min for 13 hr. Then, the catalyst with aging process was directly started the methane steam reforming as the same previous condition. From the results, the methane conversion significantly improves to 49.00%, 47.73%, 47.84% and 34.88% at the inlet methane partial pressure of 0.04, 0.03, 0.02 and 0.01, respectively. As expected, the activity of $LaCrO_3$ with aging was found to be higher. The increased activity of the $LaCrO_3$ catalyst may be related to surface modification during the aging process; possibly this is related to the loss of oxygen from $LaCrO_3$ surface. From the study, it can be concluded that the aging of catalyst provides strong impact on the reactivity of $LaCrO_3$ toward methane steam reforming.

4. Effect of steam content on the methane steam reforming reactivity of $LaCrO_3$

The effect of steam content on the methane steam reforming reactivity of $LaCrO_3$ was studied. According to all previous experiments, the flow rate of water was always kept constant at 0.2 ml/hr. In order to study the effect of steam, the flow rate of steam was steadily reduced from 0.2 ml/hr to 0 ml/min. The methane steam reforming reactivity, in term of methane conversion, was then measured using mass spectrometer, as shown in Fig.7.

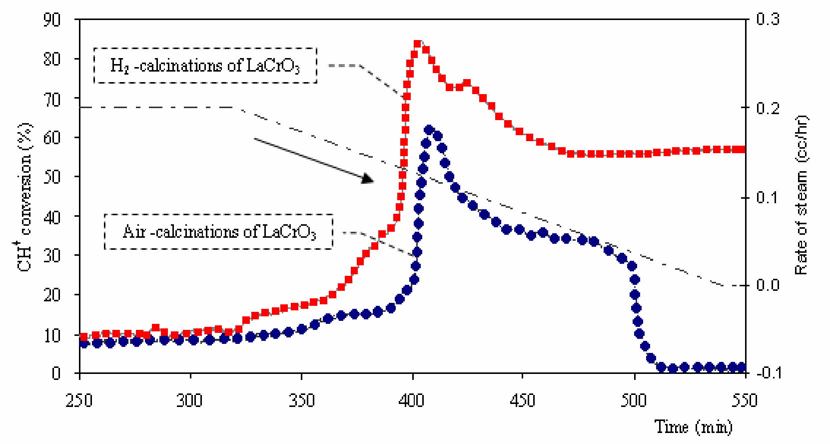

Figure 7. The steam effecting of catalytic activity toward methane steam reforming.

Interestingly, the methane conversion extremely increased to 59.07% and 85.14% both $LaCrO_3$ calcined in air and H_2 atmosphere, respectively. These results indicate that the $LaCrO_3$ reactivity is extremely increased under the low steam content or oxidant element. This behavior can be explained by the oxygen nonstoichiometry (δ) over perovskite material. The oxygen nonstoichiometry (δ) of the perovskite material can change as a function of oxygen (or steam) partial pressure and the catalyst can enter a different methane steam reforming regime, or the excess of water could adsorb on the catalyst giving rise to inhibition by H_2O.

Conclusions

In these experiments, $LaCrO_3$ sample which was prepared by cationic surfactant assisted method has much more surface area than those found from other preparation methods. The result suggests that no significant difference in surface area was found form this comparing. Moreover, the treatment condition at 900^{o}C which consisted of annealing in air and in H_2-atmosphere was shown the specific surface area of $LaCrO_3$ dramatically increases after calcined in H_2-atmosphere.

The stability and activity toward methane steam over synthesized $LaCrO_3$ were studied at 850-900°C. It was found that $LaCrO_3$ prepared by surfactant assisted method and with the heat treatment in H_2-atmosphere provided significantly higher stability and activity than other $LaCrO_3$. Furthermore, it was also observed that the aging and low inlet steam to methane content can dramatically improve the reactivity of $LaCrO_3$ toward methane steam reforming. These behaviors can be explained by the oxygen nonstoichiometry (δ) over perovskite material. The oxygen nonstoichiometry (δ) of the perovskite material can change as a function of oxidant (steam) presented in the system. The catalyst can enter a different methane steam reforming regime i.e., at the small oxygen deficiency, $LaCrO_3$ may perform like the metallic catalyst.

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