

CHAPTER 1

INTRODUCTION

The efficient use of natural gas has been focused on the methane utilization. Methane is used as the starting material for the production of synthesis gas ($\text{CO} + \text{H}_2$) which acts as a feedstock for the synthesis of ammonia and methanol, and can be converted to higher hydrocarbons, alcohols and aldehydes by Fischer-Tropsch [1]. For converting methane to liquid fuels, there are two technologies classified as direct and indirect routes [2]. The direct-conversion process involves the oxidative coupling reaction to yield ethylene and ethane [3], and direct oxygenation to methanol and formaldehyde [4], to reduce the cost of the syngas preparation step in the direct route. However, these attempts have not yet been successful because the desired products are more reactive than methane. Low product yield is normally encountered.

In the indirect route for methane conversion to syngas, the partial oxidation of methane is a potential alternative to steam reforming process because this reaction is more mildly exothermic and more selective while obtaining lower H_2/CO ratio than this process [1]. This lower ratio is highly desirable for certain applications of syngas since it provides the suitable ratio for downstream processes, such as Fisher-Tropsch or methanol synthesis [5-6]. However, the most significant cost associated with the partial oxidation is the oxygen supply.

Dense ceramic membranes, particularly the mixed ionic and electronic conducting (MIEC) perovskite membrane, offer potential solutions to eliminate the need for the oxygen separation plant. The technology substantially reduces the cost of converting natural gas to syngas by 30%, and could save the oil and gas industry millions of dollars annually. Several advantages of using the oxygen-ion conducting membrane reactor include achieving high product selectivities, employing air as the source of the oxidant while eliminating N_2 contamination in the product, circumventing flammability limits due to diffusion-limited operation, reducing a large part of the cost of gas compression in downstream processing, and avoiding the formation of environmental pollutant (NO_x) during high-temperature reactions [7].

In recent years, the LaGaO_3 based perovskite has been considered as a membrane to separate oxygen from air. Since it exhibits high O^{2-} permeation at high

temperatures, and the structure of this composition is very tolerant to the incorporation of foreign cations and a large number of cations can be used to partially substitute for either La or Ga [8-11].

Ishihara et al. [9-11] reported that comparing with the undoped material, the Sr substitution increased the electrical and ionic conductivity of the LaGaO₃ based perovskite. It was found that the ionic conductivity, σ_i , increased with an increase in the amount of Sr additives and attained the maximum limit of the solid solution at $x = 0.1$ in La_{1-x}Sr_xGaO₃. They also concluded that iron was the most suitable dopant for LaGaO₃ due to its stability in a reducing atmosphere and the increase in the oxide ion conductivity. A high methane conversion rate was obtained when using La_{0.8}Sr_{0.2}Ga_{1-y}Fe_yO_{3- δ} where $y = 0.2-0.5$ as the oxygen-permeating membrane. Gharbage et al. [12] confirmed that Fe increased the chemical stability and the p-type conductivity in La_{0.9}Sr_{0.1}Ga_{1-y}Fe_yO_{3- δ} where $y = 0.05-0.2$ by the formation of Fe⁴⁺ ions under oxidizing conditions. Ming et al. (1994) [13] found that the perovskite oxide La_{0.5}Sr_{0.5}Ga_{0.2}Fe_{0.8}O_{3- δ} maintained its cubic structure from 20 to 860°C in a reducing environment with an oxygen partial pressure of about 10⁻¹⁷ atm. The perovskite La_{0.5}Sr_{0.5}Ga_{0.2}Fe_{0.8}O_{3- δ} was reported to have a higher oxygen permeation rate than the non-perovskite oxide SrFeCo_{0.5}O_{3- δ} [14]. Materials studied containing cobalt on the B site are normally not stable at low oxygen partial pressures. Iron based systems, in contrast, are more stable than cobalt compounds [10, 14]. Accordingly, LaGaO₃-based oxide doped with Sr and Fe could be a new candidate material for an oxygen permeation membrane, in particular, for air separation in the methane partial oxidation process.

The conventional method of solid state synthesis for producing ceramic powders involves the calcination of mixed metal oxides at high temperatures to obtain a single phase and mechanically milling the product to obtain the desired particle size. However, the high calcination temperature promotes crystal growth and resulting in a hard agglomeration [15]. Therefore, wet chemical syntheses have been developed to achieve the fine powder form. These methods include the citrate, spray-pyrolysis, and co-precipitation process [16]. It was reported that the membrane sample prepared by the co-precipitation method has a large strontium deficiency due to the filtration and aqueous washing steps involved in this method.

The spray-pyrolysis method requires a special chamber for spraying aqueous solution of raw materials into it.

For the synthesis of Sr and Fe doped LaGaO₃, the conventional method has been used by many investigators using the calcination of metal oxides at 1,000-1,100°C for 6-12 hours [10, 13, 17]. The powder was then pressed to form a disc, which was sintered at 1,500-1,600°C for 4-8 hours. Recently, Ming et al (1999) [13] reported a new method for the synthesis of La_{0.5}Sr_{0.5}Ga_{0.2}Fe_{0.8}O_{3.8}, using the self-propagating high temperature synthesis (SHS). They mixed metal oxide with NaClO₄, which acted as the internal oxygen for self-combustion, and then pressed into pellet. To increase the homogeneity, after combustion, the pellet was immediately transferred to a pre-heated furnace kept at 1,400°C and cooled at a controlled cooling rate. The pellet with the large particle size (up to 30 μm) was ground by mechanical milling to a fine powder before making the membrane, which was sintered at 1,380°C for 10 hours. Some other investigators used the sol-gel technique to synthesize this material by using metal acetates and forming a gel by ammonia solution. However, since three days for aging the gel and eight hours for dehydration and drying [18] were needed, the method required a large amount of synthesis time.

The citrate method has been chosen in this study for the synthesis of lanthanum based perovskites. The citrate method involves the complexing of metal ions with citric acid and the spontaneous combustion. The advantages of the citrate method include less energy consumption and potential to get fine particles and a single-phase powder.

The objectives of this study are as follows: (1) to synthesize fine particles of the single-phase LaGaO₃ based perovskites by using the modified citrate. Four series of oxide with the fixed components, La_{1-x}Sr_xGa_{0.4}Fe_{0.6}O_{3.8} (x = 0.4, 0.6, 0.8), La_{1-x}Sr_xGa_{0.2}Fe_{0.8}O_{3.8} (x = 0.2, 0.4, 0.5, 0.6, 0.8), La_{0.4}Sr_{0.6}Ga_{1-y}Fe_yO_{3.8} (y = 0.4, 0.6, 0.8), and La_{0.6}Sr_{0.4}Ga_{1-y}Fe_yO_{3.8} (y = 0.2, 0.4, 0.5, 0.6, 0.8), were selected in order to explore the influence of the amount of Sr and Ga for obtaining the single phase. The effects of the synthesis conditions, such as pH of the nitrate solution and calcination temperature, on the formation of a homogeneous product and on the particle size distribution were also studied., (2) to make the membrane discs, and (3) to test the oxygen permeation of LaGaO₃ based perovskite membrane.