CHAPTER I

INTRODUCTION

During the past decade, ceramic oxides with mixed electronic and oxygen-ionic conductivity have received considerable attention due to their versatile properties. For example, they can be used as cathodes or anodes for solid oxide fuel cells, and catalytic materials. Fabricated into dense ceramic membranes, particularly the mixed ionic-electronic conducting perovskite membrane (MIECM), the mixed oxides can be used for oxygen separation at high temperatures. MIECM also hold promising application in petrochemical process. One of the important applications of MIECM is the partial oxidation of methane to syngas process.

Methane partial oxidation to syngas is an important way for natural gas utilization. Methane was used as a valuable raw material for several industrial processes, including the synthesis gas (a mixture of CO and H_2) production. It is an important intermediate in the production of hydrogen and in conversion of methane to a range of value added products including paraffins, olefins and alcohols [1]. In addition, syngas play the important roles in hydrogen production for ammonia synthesis and methanol synthesis [2]. Technologies available for converting methane to higher hydrocarbons or liquid fuels are classified as either direct or indirect routes. Direct conversion of methane requires direct partial oxidation to methanol, formaldehyde, or others, or oxidative coupling to ethylene. However, the direct conversion processes have not yet been successful because the desired products are more reactive than methane. Therefore, low product yield is normally encountered [3].

Traditionally, indirect conversion to syngas is produced by steam reforming of methane as presented in Equation 1.1, which is the main component of natural gas [4].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H_{800\,^{\circ}C} \ +225 \text{ kJ/mol} \qquad (1.1)$$

This is a strongly endothermic reaction high temperatures and pressures are required for methane conversions exceeding 95 %. And a H_2/CO mole ratio of 3.0 is

obtained, which is not the desired stiochiometry of some chemical reactions such as methanol and Fischer-Tropsch synthesis requiring H_2/CO mole ratios of 2.0.

Another approach for syngas production originates from the energy demand of the steam reforming reaction, as this process requires energy input. The partial oxidation of methane to syngas is a mildly exothermic reaction that is free from the limitations of the above steam reforming reaction and would be more energetically efficient, equation 1.2. In fact the partial oxidation of methane, having a H_2/CO mole ratio of 2.0, would be a viable alternative reaction to the methane steam reforming reaction for syngas generation [5]. However, the most significant cost associated with the partial oxidation is the oxygen supply.

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \Delta H_{800°C} \ -23 \text{ kJ/mol} \qquad (1.2)$$

Dense ceramic membranes (MIECM) [6], perovskite for instance, perovskite represented by the general formula ABO_3, offer potential solutions to eliminate the need for constructing 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 selectivity, employing air as the source of the oxidant while eliminating N_2 contamination in the product, circumventing flammability limits due to diffusion-limited operation, reduce costs of gas compression in downstream processing, and avoiding the formation of environmental pollutants (NO_x) during high-temperature reactions [7].

Since Teraoka et. al. [8] reported high oxygen permeate through several $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ perovskite membranes, appreciable progress has been made in development of synthesis methods, and understanding of electric, structural and oxygen permeation properties of these materials. The $LaGaO_3$ based perovskite has been recently considered a membrane to separate oxygen from air. Since it exhibits high oxygen permeation at high temperature, and the structure of this composition is very tolerant to the incorporation of foreign cations. Then a large number of cations can be used to partially substitute for either La or Ga [9].

Oxygen transport through the membrane is known to occur *via* hopping oxygen ions to neighboring vacant sites in the crystal lattice. Accordingly, overall oxygen permeation flux is determined by the ionic diffusion through the bulk and

the oxygen molecular-ionic exchange reaction at the surface of the membrane. While the factors that determine the diffusion process in MIECM are relatively well understood, the factors controlling the surface-exchange reaction have been investigated.

The surface morphology of the membrane can affect the oxygen permeation flux if the permeation process is limited by the surface-exchange kinetics [10]. Deng and Abeles [11] showed that the oxygen permeation flux could be significantly increased if thin and dense membranes were coated on either one or both surfaces with porous layer. Besides controlling the surface porosity, the oxygen permeation flux could also be enhanced by coating of specific perovskite oxide to improve the surface activity for oxygen dissociation.

In this study, the dense perovskite, $La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_{3-\delta}$ (LSCF8264), $La_{0.6}Sr_{0.4}Ga_{0.3}Fe_{0.7}O_{3-\delta}$ (LSGF6437), and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582) were selected to be a model substrate because of their attractive properties: pure perovskite phase, high density membrane, and high oxygen permeation flux. The effects of surface modification by $La_{1-x}Sr_xCoO_{3-\delta}$, $La_{1-x}Sr_xFeO_{3-\delta}$, $Ba_{1-x}Sr_xCoO_{3-\delta}$, and $Ba_{1-x}Sr_xFeO_{3-\delta}$ with x = 0.2 - 0.6 were chosen to be the catalytic perovskite compounds for the coating layer. The oxygen adsorption-desorption of the coating layer was investigated.

1.1 The objectives of the thesis

1. To improve the surface exchange reaction of dense membranes to enhance the oxygen permeation flux.
2. To study the effects of Sr amounts substituted with x = 0.2 - 0.6 in the catalytic perovskite compounds.
3. To study adsorption-desorption of oxygen by using TGA and O_2-TPD measurement which correspond to oxygen vacancy in the perovskite structure.

1.2 The scope of the thesis

1. Synthesis of the single-phase perovskites by using the modified citrate method.

2. Selecting the single-phase perovskite compounds to coat on membrane perovskites.
3. Study the effect of the synthesis conditions, such as calcination and sintering temperatures.
4. Study the oxygen adsorption-desorption of coated membrane by using thermogravimetric analysis (TGA) and oxygen temperature programmed desorption technique (O_2-TPD).