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Oxygen permeability, electrical property and stability of $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane

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Abstract

A typical dense membrane of perovskite $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ have been successfully prepared by citrate method using nitrate salts as cation source and citrate as an organic agent. Precursor of $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ was analyzed by thermal gravimetric analysis and XRD to investigate optimum calcination temperature. Organic compound and nitrate burned out below 400°C. Weight loss observed over 700°C is due to decomposition of $SrCO_3$. The recommended temperature for calcination of precursor is over 900°C at which single perovskite powder is obtained without impurities. The electrical property, oxygen permeation and stability of membrane were investigated in the range of 700 to 950°C. The electrical conductivity increased with increasing temperature but then decreased over 850°C (20% O_2) and 750°C (1% O_2) due to oxygen loss from the crystal lattice. The oxygen flux of $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane increased with the increasing temperature. The maximum oxygen permeation was measured to be 0.19 mL/min cm^2 at 950°C. The activation energy for oxygen permeation was calculated to be 78 kJ/mol. Perovskite structure and phase did not change even after permeation test of 40 h.

Keywords: Ceramic membrane; Perovskite; Electrical conductivity; Oxygen permeation; Activation energy; Stability

1. Introduction

Mixed conducting membranes possessing oxygen ionic and electronic conductivities have recently attracted attention and have been extensively investigated due to their oxygen separation ability. Especially, the ceramic dense membrane has a great potential to be applicable in chemical and petroleum industries for oxygen separation from gaseous mixture. It is very attractive technology economically and environmentally

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in industrial process with relation to oxy-fuel combustion. The dense membrane has been applied in membrane reactor on the partial oxidation of hydrocarbons upgrading natural gas to ethylene and ethane or syngas [1–3].

Among other dense ceramic membranes, perovskite type oxides, show high electrical conductivity and ionic conductivity when contain transition metals at B site and the partial substitution of A site cations by other metal cations with lower valences. Oxygen permeation of perovskite dense membrane has been studied by many researchers who reported permeation results for LaSrCoFe type perovskite compositions [4–9], since Teraoka et al. [10] reported first $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. Many researches have been dealt with the material properties with high oxygen permeation, oxygen flux and good stability at high temperatures and reducing conditions. In a feasibility test, Bredesen and Sogge [11] reported that a minimum oxygen permeation flux of ca. 10 NmL/cm^2 min is required to adapt commercially to viable processes, i.e. other traditional processes. However, there are no results with such a value up to now in the commercial scale process. Oxygen permeation of membranes can be improved by modification of many characteristics such as membrane material, membrane thickness, microstructure and temperature at the condition where the membranes should be applied. Among these properties, the membrane material and composition is intrinsic factor to obtain good enough oxygen flux to be applied.

It is well known that different composition can cause different oxygen permeation fluxes [12]. Oxygen vacancy formation, a major variable for high ionic conductivity, is also influenced by the membrane composition [8]. The influence of substitution of A site on oxygen permeation in the system of $La(A)CoFeO_{3-\delta}$ (A = Sr, Ba, Ca) was investigated by Stevenson et al. [13] and Tsai et al. [14]. Based on these results, although the oxygen flux is inclined to increase with increasing A-site substitution, the phase stability of composition with large substitution becomes unstable in the low oxygen partial pressure and high temperature environment.

In this work, $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite type oxides has been synthesized using citrate method and characterized by TGA and XRD. The purpose of this work was to investigate the fundamental properties of $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$, including electrical conductivity, oxygen vacancy and oxygen permeation. Phase stability was also studied by using SEM and XRD.

2. Experimental procedure

2.1. Sample preparation

Perovskite type powder has been synthesized by citrate method, a method resembling with the sol–gel method using citric acid as a complexing agent. Reagent grade $La(NO_3)_2 \cdot 6H_2O$ (99.99%, Aldrich, USA), $Sr(NO_3)_2$ (99%, Aldrich, USA), $Fe(NO_3)_3 \cdot 9H_2O$ (99%, Aldrich, USA), $Co(NO_3)_2 \cdot 6H_2O$ (98%, Aldrich, USA) and citric acid (99.5%, SAMCHUN, Korea) were used as starting materials. The schematic diagram of synthesis using citrate method was summarized in Fig. 1.

The nitrates were weighed according to the nominal composition of $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$. The nitrates were dissolved in deionized water and then a particular amount of citric acid was added into the nitrate solution. During the synthesis process, the mole ratio of citric acid to total metal cation content (abbreviated as C/M) was constant, C/M=1.2. The precursor solution was treated on hot plate with magnetic stirrer at 100°C for 4 h and then dehydrated at 80°C. Finally, a dark brown gel obtained was dried at 110°C for 24 h. As-prepared precursor was pulverized and calcined at 850–1100°C to prepare perovskite type oxide. The as-synthesized powders were compressed into disks of 20 mm