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Hydrogen Permeability of BSCY Proton-Conducting Perovskite Membrane

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***Abstract*—**Perovskite-type membrane $Ba_{0.5}Sr_{0.5}Ce_{0.9}Y_{0.1}O_{3-\delta}$ (BSCY) was successfully synthesized by liquid citrate method. The hydrogen permeation and stability of BSCY perovskite-type membranes were studied at high temperatures. The phase structure of the powder was characterized by X-ray diffraction (XRD). Scanning electron microscopy (SEM) was used to characterize microstructures of the membrane sintered under various conditions. SEM results showed that increasing in sintering temperature, formed dense membrane with clear grains. XRD results for BSCY membrane that sintered in 1150 °C indicated single phase perovskite structure with orthorhombic configuration, and SEM results showed dense structure with clear grain size which is suitable for permeation tests. Partial substitution of Sr with Ba in SCY structure improved the hydrogen permeation flux through the membrane due to the larger ionic radius of Ba^{2+}. BSCY membrane shows high hydrogen permeation flux of 1.6 ml/min.cm^2 at 900 °C and partial pressure of 0.6.

***Keywords*—**Hydrogen separation, perovskite, proton conducting membrane.

I. Introduction

NOWADAYS, mixed ionic–electronic conductors (MIECs) with perovskite structure are applied in many different processes as they allow to selectively separate hydrogen from gaseous mixtures. Due to their possible applications such as hydrogen separation membranes, hydrogen pumps, hydrogen sensors, and electrolytes for fuel cells, they are great of interest for many industrial.

In the early 1980s, Iwahara et al. firstly reported proton conductivity in the doped $SrCeO_3$ perovskite materials in hydrogen-containing atmosphere [1]. Perovskite membranes with mixed proton and electron conductivity such as SrCeO and BaCeO which are doped with trivalent cations like Y, Yb, Gd have been identified to be appropriate for hydrogen separation [1]-[4]. In most cases for hydrogen separation, the A site is generally occupied by 2+ large alkali earth metals such as Sr, Ba, La, or their mixture. Zhan et al. [4] prepared $SrCe_{0.95}Y_{0.05}O$ perovskite membrane by a conventional and cost effective dry pressing method and reported a hydrogen permeation of 7.6×10−8 mol/cm^2.s at temperature of 950 °C with thickness of 50 μm towards a mixture of 80% H_2/He. Results for BaCeYO membrane with different method of preparation showed that it has high conductivity in temperature range of 700-1000 °C [5]-[7]. The choice of A-site cation is very important because it strongly affects the mobility of the oxygen ion (it is useful for create oxygen vacancy) in the bulk phase which results in conductivity; therefore, we decide to focus our attention in this field to see the effect of partial substitution of cation Ba in SrCeYO membrane for hydrogen separation [8]. Pressure, temperature, sweep gas (type, flow rate), and flow rate of the feed stream are important parameters of operating conditions that affect conductivity.

Results of partial substitution of Ba^{2+} instead of Sr^{2+} in SCFO for oxygen permeation show an improvement of structural stability and also the oxygen permeation flux through the membrane due to the larger ionic radius of Ba^{2+} [9]. However, there are no major reports for partial substitution in site A and their influence on stability and the permeation flux in hydrogen separation.

The present paper reports on synthesis and characterization of BSCY perovskite membrane. These membranes were prepared with liquid citrate method. Investigations of the microstructure were carried out by SEM. Phase stability of membrane was checked with XRD, thermal gravimetric analysis (TGA). Also the effect of sintering temperature on the microstructure and the hydrogen permeation behavior of the BSCY membrane were investigated.

II. Experimental

A. Membrane Preparation and Characterization

The BSCY powder was synthesized by liquid citrate method. Stoichiometric amounts of the nitrate powders, Barium nitrate ($Ba(NO_3)_2$, 99.9%, Fluka), strontium nitrate ($Sr(NO_3)_2$,99.9%, Merck) Cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$, 99.9%, Fluka) and Yttrium nitrate hexahydrate ($Y(NO_3)_3.6H_2O$, 99.9%, Merck) were dissolved in ammonium solution with EDTA (Ethylene diamine tetra acetic acid), while the solution was heated and stirred for several hours. The pH value was between 6 and 8 with addition of citric acid. The solution was dried in air for three days to obtain a yellow gel and was heated in oven at the temperature of 200 °C until all water was evaporated. To remove organic components, calcination of powder was carried out at 950 °C for 5h with a heating rate of 2 °C/min to get a pure perovskite phase. The powder was pressed into disks under a hydraulic pressure of 9 bars and sintered at temperatures between 1100 °C and 1200 °C to investigate the influence of sintering temperature on microstructure of the

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membrane.

SEM was used to evaluate the surface morphology of the perovskite membrane, which was also equipped with EDX. This test was carried out with Philips XL30 instrument. Density of membrane was calculated by Archimedes method.

B. Hydrogen Permeation

Fig. 1 shows the membrane permeation set up used in this work. The sintered membrane disk with thickness of about 0.8-0.9 mm and diameter of about 12 mm was mounted on a quartz tube using a Pyrex ring seal. A heating rate of 5 °C/min was used to increase temperature to 900 °C, and the assembly was kept in this temperature to insure the system was sealed. Experiment study for the membrane was carried out in temperature range of 650-900 °C. Mixture of H_2 and N_2 was used as feed gas and Ar with flow rate of 77 ml/min was introduced as sweep gas. The gas flow was regulated by mass flow controller (BronKhorst). The amount of H_2 permeated in sweep gas was measured with gas chromatographer (Agilent 7890A) equipped with a packed column and a TCD detector. The hydrogen permeation flux was calculated based on the total flow rate of the sweep gas and the hydrogen concentration in the effluents.

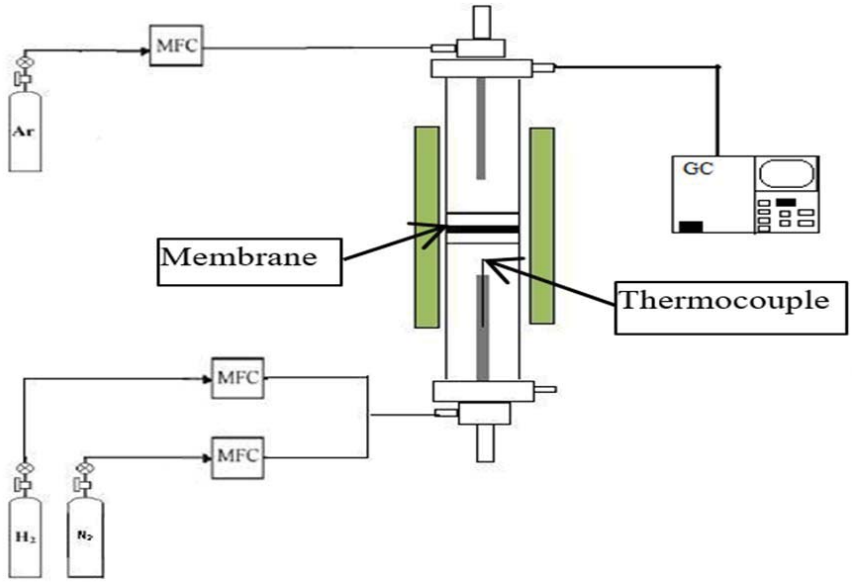

Fig. 1 Experimental apparatus for high temperature H_2 permeation test

III. Result and Discussion

Fig. 2 shows an X-ray analysis of the BSCY perovskite powders calcined at 950 °C for 5h. BSCY powders show pure perovskite structure with orthorhombic configurations. Reports indicated the same results for BaCeY membrane [5].

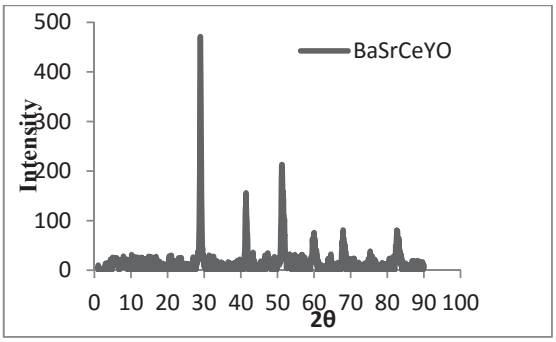

Fig. 2 XRD pattern for calcined perovskite powder of $Ba_{0.5}Sr_{0.5}Ce_{0.9}Y_{0.1}O$

The membrane was sintered in a temperature range of 1100-1250 °C and the best temperature was selected using SEM and density analysis. Fig. 3 shows the SEM image of the membranes surface. Table I reports average grain size and density of each membrane. According to the results, average grain size of BSCY membrane is between average grain size of BCY and SCY.

TABLE I
Sintering Temperature, Average Grain Size and Density for each Membrane

Sintering temperature (°C)	1100	1150	1200	1250
Average grain size(μm)	0.31	0.53	0.61	-
density (gr/cm^3)	4.2	6.3	6.35	6.4

Fig. 3 displays SEM images and corresponding grain size distributions of BSCY membranes after sintering at four different temperatures. As shown in the figure, the membrane sintered at 1100 °C does not show any significant formation of grained structure. At 1150 °C, a dense membrane with clear grain boundaries can be achieved. As the sintering temperature reaches 1200 °C, the grain boundaries start to disappear, and at 1250 °C, the grain size are melt and totally disappeared. Archimedes method was used to determine the densities of the sintered membranes. The results show that the density of disks

is sufficiently increased after sintering at 1150 °C with dwelling time of 10h which can be found from SEM images. The linear shrinkage can be defined as: Db-Da/Db×100% where Da is the diameter of the membrane after sintering and Db is the initial diameter of the membrane. It is clear that the linear shrinkage increases with increasing sintering temperature. The results show that BSCY membrane with average grain size of 0.53 µm has density of 6.3 gr/cm^3.

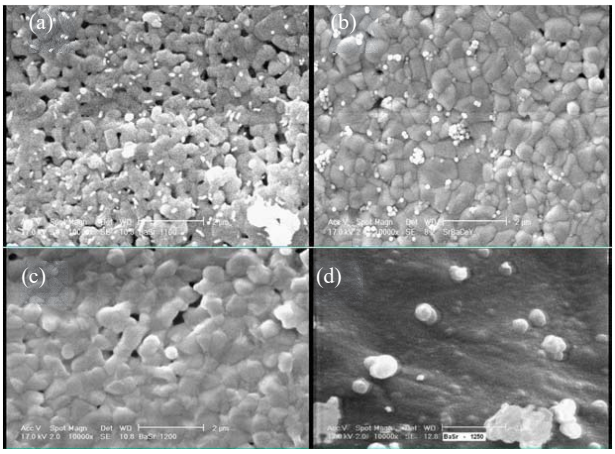

Fig. 3 SEM micrograph of the BSCY at 1100 °C (a), 1150 °C (b), 1200 °C (c), and 1250 °C (d) for 10h of sintering

Additionally, by TG analysis, the thermal behavior of powder at high temperature was investigated, which is shown in Fig 4. Zhang et al. [10] reported the TG analysis for $BaCo_{0.3}Fe_{0.7}Nb_{0.1}O_{3-\delta}$ that included two stages of weight loss. BSCY membrane includes one stage of reduction but a relatively slight weight loss at high temperature, suggesting more Ce^{+4} ions that have the higher value of the tolerance factor.

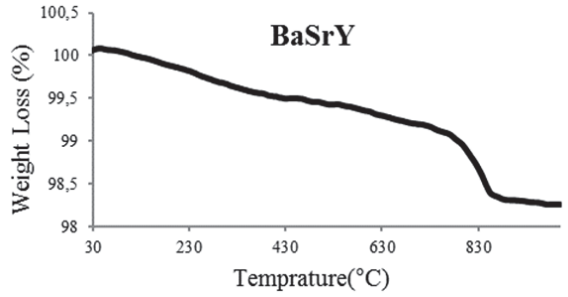

Fig. 4 TG curves for the membranes in N_2; with heating rate of 10 °C/min

Fig. 4 shows the effect of the operating temperature and membrane sintering temperature on the permeation fluxes in BSCY perovskite membranes at the constant Argon flow rate of 77 mL/min, feed flow rate of 120 ml/min and hydrogen partial pressure of 0.6. With increasing sintering temperature from 1100 °C to 1150 °C, hydrogen permeation flux was increased. Researchers found that the sintering temperature which affects the grain size, grain distribution and porosity of the membrane, has important effect on the oxygen permeation flux of membranes [11], [12]. With increasing temperature from 1150 °C to 1200 °C, that grain starts to melt, and hydrogen permeation sharply reduced. At 1250 °C with any grain, there is no permeation among membrane.

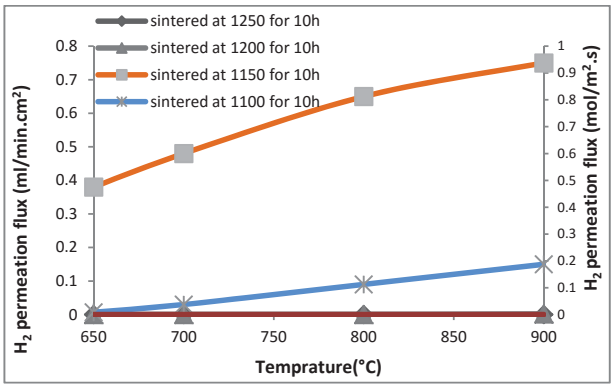

Fig. 5 Hydrogen permeation flux as a function of temperature for all the membranes with partial pressure of 0.6

Fig. 5 also shows that the permeation flux increases with increasing temperature due to the higher ambipolar conductivity at elevated temperatures. BSCY membrane that sintered at 1150 °C has maximum permeation flux at all temperatures, which is in agreement with values of the tolerance factor and the density. Permeation flux increases to 1.6 ml/min.cm^2 at 900 °C with partial pressure of 0.6. Zuo et al. [13] reported maximum flux of 0.805 ml/min.cm^2 for a dense Ni–BZCY membrane of 266 µm-thick at 900 °C using 100% H_2 as the feed gas and 100 ppm H_2/N_2 as the sweep gas.

Activation energy that calculated by Arrhenius equation equal to 20.8 (kJ/mol) for temperature range 650-900 °C

$$J = Aexp(\frac{-E_a}{RT}) \quad (1)$$

where A is the pre-exponential factor (mol/m^2.s) the activation energy is E_a (kJ/mol) and permeation flux, J (mol/m^2.s)

Guan et al. [14] showed that the electronic conductivity was much lower than the protonic conductivity for the SCY material. For the SCY membrane the activation energy of 132 kJ/mol corresponds to the activation energy of electronic conduction which indicated that the H_2 permeation is limited by electronic transport and surface kinetics in the temperature range 750-950 °C. Results show that improvement in protonic conductivity increases the hydrogen permeation flux [15]. The permeation flux of hydrogen increases more than two times whit the partial substitution of Sr with Ba. Moreover, the permeation flux is much higher with of CY oxide with Sr and Ba combination compared to the case of doping with Ba or Sr individually.

IV. Conclusion

BSCY was synthesized successfully by liquid citrate method. XRD and TGA analyses were used to characterize the

perovskite membranes. The influence of sintering conditions on microstructure of the membrane was studied by using SEM, and the hydrogen permeation flux was investigated through BSCY membrane. The grain growth leads to increase of permeation flux in membrane by bulk diffusion as the dominant controlling mechanism, and the grain melts due to high sintering temperature lead to decrease permeation flux in membrane. The influence of substitution cation in site A on the hydrogen permeation flux through the membrane was studied. Tolerance factor is known to largely control the stability of the perovskite, and BSCY perovskite membrane with tolerance factor about 1 has high stability and permeation flux.

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