

Preparation of $\text{BaCe}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\delta}$ asymmetrical membrane for hydrogen separation at high temperatures

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Abstract

A mixed proton–electron conducting perovskite was synthesized by liquid-citrate method and the corresponding membrane was prepared by pressing followed by sintering. The hydrogen permeability of $\text{BaCe}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\delta}$ was studied as a function of temperature and hydrogen partial pressure (PH_2) gradient. Using 100% dry hydrogen at 1173 K, the hydrogen permeation rate of dense membranes (1.63 mm thick) for a mixture of 60% H_2/He was 0.000293 mol/(m² s). The phase structure of powder was characterized by X-ray diffraction and thermogravimetry (TG). Scanning electron microscopy (SEM) was used to investigate the microstructure of sintered membrane. Activation energy estimated with Arrhenius equation was 29 kJ/mol.

Key words: Ceramic Membrane, BaCeYb , Electron/Proton Conductivity, Hydrogen Ppermeation.

Introduction

Ceramic perovskite membranes with mixed conducting materials are categorized into two types based on their different ion-transport properties: one exhibits mixed oxygen ionic and electronic conducting property and the other exhibits mixed proton and electron/hole conduction. Most researches have been focused on the oxygen conducting materials, but the mixed proton electron/hole conducting materials have also attracted such interest in recent years that for hydrogen separation application, the membrane material needs to have appreciable proton and electronic conductivity [1]. These membranes have received considerable attention due to high selectivity and low energy consumption.

In the early 1980s, Iwahara *et al.* [2] firstly reported proton conductivity in doped SrCeO_3 perovskite materials in hydrogen containing atmosphere at high temperatures. Later, protonic conductivity was also demonstrated in other doped perovskites.

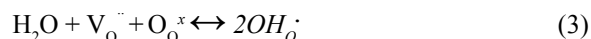
The introduction of protons into the perovskite ceramic is generally shown in terms of moisture containing gas streams as an acid/base equilibrium between water molecules and oxygen vacancies. Oxygen vacancies, $V_{\text{O}}^{\cdot\cdot}$, react with water to fill lattice positions with oxide ions, $\text{O}_{\text{O}}^{\cdot\cdot}$, and produce interstitial protons, H_i^+ , according to [3],



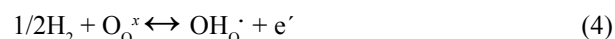
Protons are retained in the material by associating with oxide ions at normal lattice sites,



Thus, the net reaction demonstrating the interaction of oxygen vacancies with water vapor to produce proton charge carriers can be written as



However, in the absence of moisture, hydrogen in the gas stream is directly incorporated into the material as protons and electrons (e') through interaction with oxide ions according to [3]:



Considerable attention has been shown to the synthetic methods of perovskite materials due to their excellent electric, protonic, thermal, chemical and mechanical properties. Solid-state reaction [4-6] and wet chemical depositing such as water-soluble complex method, liquid-citrate method, glycine-nitrate process and EDTA/citrate acid complexing method [7-10] are two common methods that are being used in the synthesis of perovskite materials. Cheng *et al.* [11] synthesized the powders of $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\delta}$ via the liquid citrate method and Matsuka *et al.* [12] used solid state reaction for

SrCe_{0.95}Tm_{0.05}O_{3-α} membrane. Results show high permeation for first membrane prepared by liquid citrate method. Therefore, we used this method to prepare the membrane. Many researchers have done their research on the SrCeYbO [13-15] membrane but investigation on BaCeYbO for hydrogen separation is not available while the high conductivity of this membrane has been reported [16].

In this work, BaCe_{0.9}Yb_{0.1}O powder was synthesized by liquid-citrate method and the membrane was prepared by pressing followed by sintering. We studied the hydrogen permeability of BaCe_{0.9}Yb_{0.1}O as a function of temperature and P_{H₂}. Besides, the Influence of sintering temperature on density and morphology of membrane was investigated.

Experimental

Membrane preparation

The BaCe_{0.9}Yb_{0.1}O_{3-δ} (BCYb) powder was synthesized by liquid citrate method. Stoichiometric amounts of nitrate powders, barium nitrate (Ba(NO₃)₂, 99.9%), cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99.9%) and yttrium nitrate pentahydrate (Yb(NO₃)₃·5H₂O, 99.9%) were dissolved in an ammonium solution of EDTA (Ethylenediaminetetraacetic acid). The solution was then heated, stirred for several hours, dried in air for three days to obtain a yellow gel and heated in an oven at 250°C until all water had evaporated. To remove organic matter, calcination of powder was carried out at 950 °C for 5 hours at a heating rate of 2 °C/min to get a pure perovskite phase. X-ray diffraction was used to confirm the single phase of each calcined powder. The calcined powders were pressed into disks under a hydraulic pressure of 9 bars. The disks were sintered at 1200 °C for 10 h at a heating and cooling rate of 2 °C/min to give the final BaCe_{0.9}Yb_{0.1}O_{3-δ} membranes. All the membranes were 12 mm in diameter and 1-2 mm in thickness. The microstructure of sintered membrane was studied by scanning

electron microscopy (SEM).

Characterization of membrane

The crystal structure of membrane was identified by X-ray diffraction. X-ray diffraction (XRD) was conducted in $\theta/2\theta$ geometry on a Philips-PW model 1840 instrument using CuK_α radiation at 40 kV and 30mA in a step-scan mode with step width of 0.08° in the 2 θ range from 1° to 90°. SEM was used to evaluate the surface morphology of the perovskite membrane, which was also equipped with EDX. This test was carried out with a Philips XL30 instrument. Thermogravimetric analysis was carried out in a Perkin/Elmer TGA instruments in N₂. The sample was heated from 30 to 1000 °C at a heating rate of 10 °C/min under nitrogen with a flow rate of 20 ml/min.

Bulk density was calculated by using the modified Archimedes method [17,18]. Bulk density (density of samples containing pores), ρ_b , was calculated from:

$$\rho_b = \frac{W_d - W_w}{W_s} \quad (5)$$

Where W_d is the weight of the dry sample (kg), W_s is the weight of the ceramic suspended in water (kg) and W_w is the weight of the ceramic removed from water (kg).

The shrinkages of the membranes were calculated by measuring the diameter of the membranes before and after sintering using the following equation:

$$P(\%) = \frac{D_b - D_a}{D_b} \times 100 \quad (6)$$

Here, P is the shrinkage of the membrane, D_b is the diameter of the membrane before sintering and D_a is the diameter of the membrane after sintering.

Experimental Setup

Fig. 1 shows the schematic of experimental apparatus for the high temperature gas permeation tests. Two Pyrex rings, which were placed between membrane and quartz tube, were used as the sealing material.

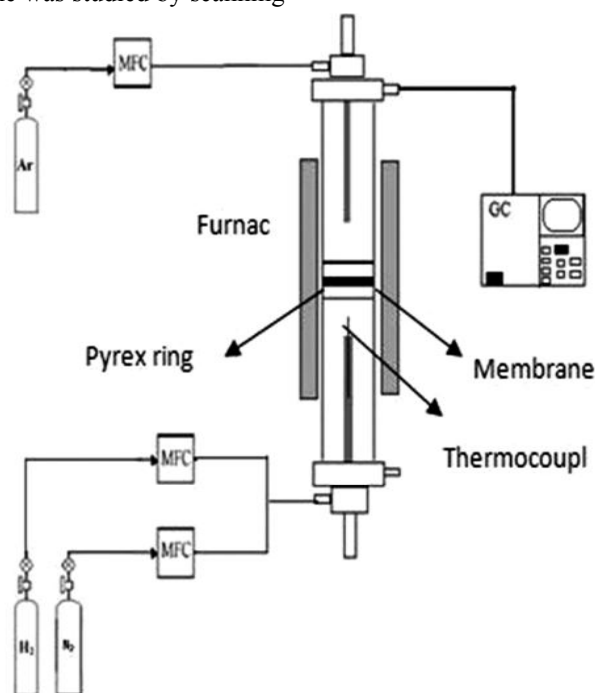


Figure 1.: Experimental apparatus for high temperature H₂ permeation test

The system was heated up to 900 °C at a ramping rate of 5 °C/min and kept at this temperature for 1 hr to ensure the softening of the Pyrex ring. H_2/N_2 mixtures were introduced to the feed side with Argon as the sweeping gas. The effluents were analyzed using a gas chromatograph (Agilent, 7890.A). The hydrogen permeation flux was calculated based on the total flow rate of the sweep gas and the hydrogen concentration in the effluents. The H_2 permeation tests were carried out in the temperature range of 650–1000 °C. During the permeation tests, the N_2 flux from the leak is constant. The component of the measured H_2 flux due to leakage was estimated from the detected N_2 flux assuming Knudsen diffusion for both species:

$$J_{\text{H}_2}^{\text{leak}} = J_{\text{N}_2}^{\text{leak}} \times \sqrt{\frac{m_{\text{N}_2}}{m_{\text{H}_2}} \times \frac{P_{\text{H}_2}}{P_{\text{N}_2}}} \quad (7)$$

The hydrogen flux (J_{H_2}) was calculated by

$$J_{\text{H}_2} = F \times \frac{C_{\text{H}_2}}{S} - J_{\text{H}_2}^{\text{leak}} \quad (8)$$

Where F is flow rate of the gas on the permeate side measured by a bubble flow meter; S is the effective surface area of membranes, C_{H_2} is the concentration of hydrogen in the effluents of the sweep side.

Results and discussion

Figure 2 shows the XRD pattern for $\text{BCe}_{0.9}\text{Yb}_{0.1}\text{O}$ powder

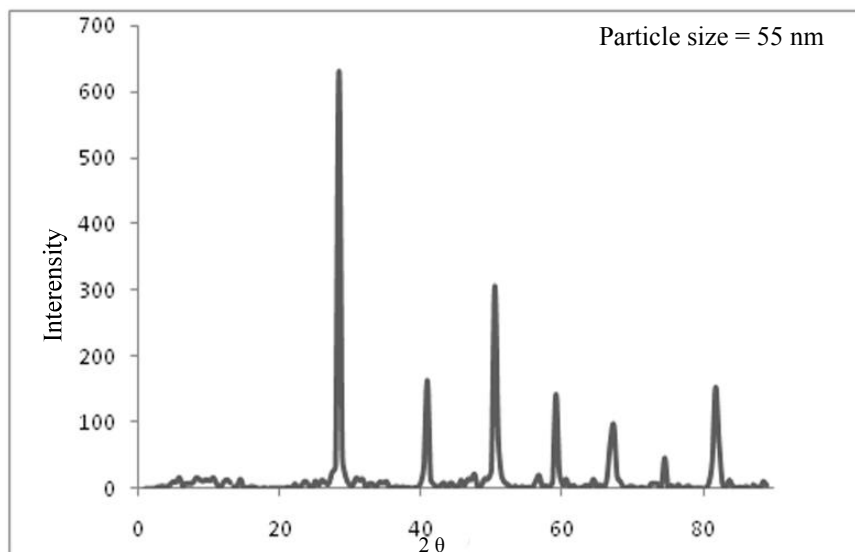


Figure 2. X-ray diffraction patterns of BCeYbO perovskite membrane calcined at 950 °C for 5hr

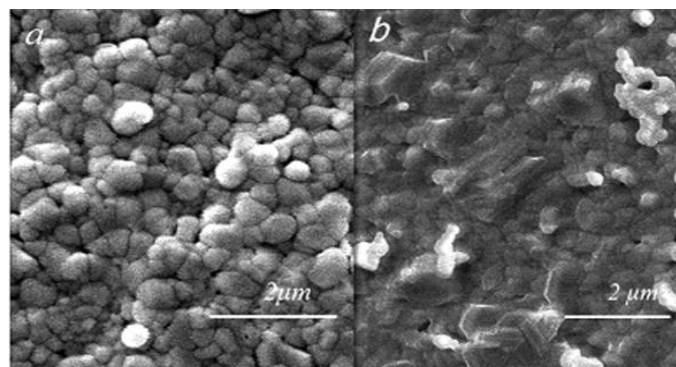


Figure 3. SEM micrograph of the BaCeYbO membrane sintered at a) 1200 °C for 10 hr, b) 1250 °C for 10 h

calcined at 950 °C for 5hr. As shown in the figure, a pure cubic perovskite structure can be observed. Microstructural improvement during sintering was investigated by SEM. Micrographs of BCYbO surfaces sintered at 1200 °C and 1250 °C temperatures are shown in Figure 3. A dense membrane with clear crystal can be observed at sintering temperature of 1200 °C. The compositions of the membranes after the preparation were determined using an energy-dispersive X-ray spectroscopy (EDXs).

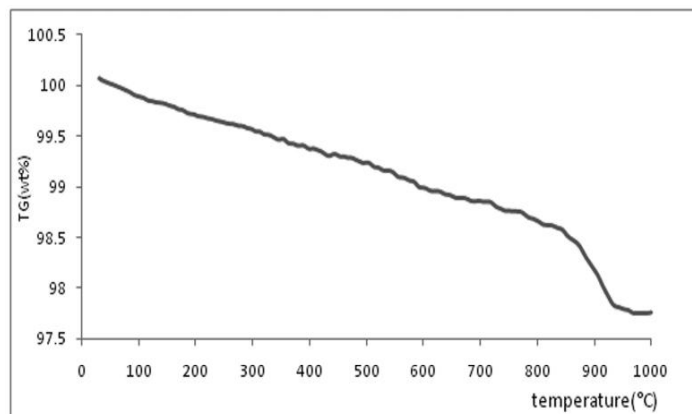
Table 1 shows the effect of sintering temperature on relative density. The shrinkage of BCYb membrane was about 8.9% after sintering at 1200 °C.

Fig. 4 shows that the material started to lose weight at a temperature of about 20 °C and with increasing the temperature, the loss of lattice oxygen uniformly decreasing monotonously the weight of BCYbO oxide material. TGA results showed a sharp decrease of the weight of the oxides at temperatures of 850–950 °C. The third stage is a gradual weight loss between 950–1000 °C.

Fig. 4 shows that the material started to lose weight at a temperature of about 20 °C and with increasing the temperature, the loss of lattice oxygen uniformly decreasing monotonously the weight of BCYbO oxide material. TGA results showed a sharp decrease of the weight of the oxides at temperatures of 850–950 °C. The third stage is a gradual weight loss between 950–1000 °C.

Table 1. Effect of sintering temperature on the shrinkage and relative density of BCYb membrane for dwelling time of 10h

Sintering temperature (°C)	Linear Shrinkage (%)	Relative density (%)
1150	6.09	89.2
1200	8.9	93.6
1250	9.2	94.5

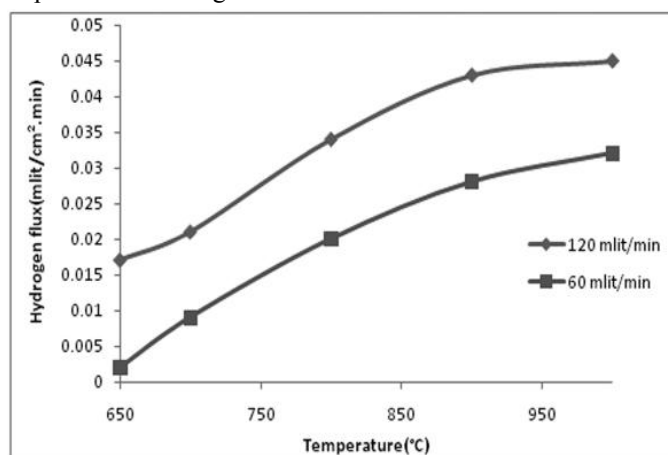
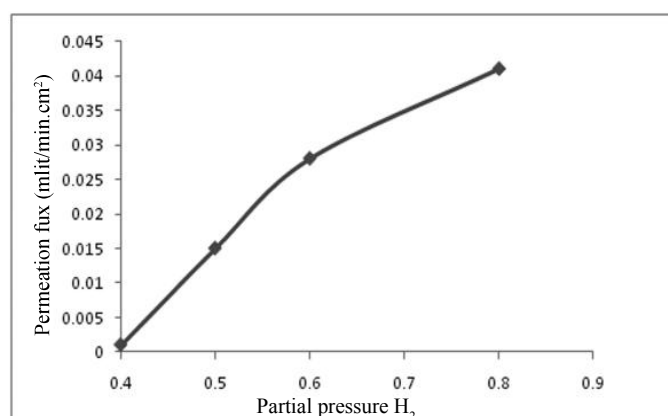
**Figure 4.** TG curve of precursor in nitrogen for BaCeYbO membrane. The heating rate is 10 °C/min

Hydrogen permeation

The hydrogen fluxes through the BCYb membrane with a thickness of 1.63mm and diameter of 12.02 mm were measured under dry conditions as a function of temperature and partial pressure of hydrogen, as shown in Fig. 5. Under dry conditions, the hydrogen fluxes increase strongly with temperature. At 1000 °C, the hydrogen flux reaches 0.043 ml/(min.cm²), which is higher than permeation through BCN

[19] (0.017ml/(min.cm²) at 925 °C) or BCM [20] (0.015 ml/(min.cm²) at 900 °C). The hydrogen permeation flux increases with raising hydrogen concentrations in the feed stream (Fig. 6).

To convert the flux values from mL (STP)/(cm².min) to SI units of mol/(m².s), the values in figure 5 should be multiplied by 0.00682.

**Figure 5.** Hydrogen permeation fluxes as a function of temperature at feed flow of 60 and 120 ml/min at $P_{H_2}=0.6$ **Figure 6.** H₂ partial pressure dependence of the H₂ permeation flux of BaCeYbO membrane at feed flow of 60 ml/min and temperature of 900 °C

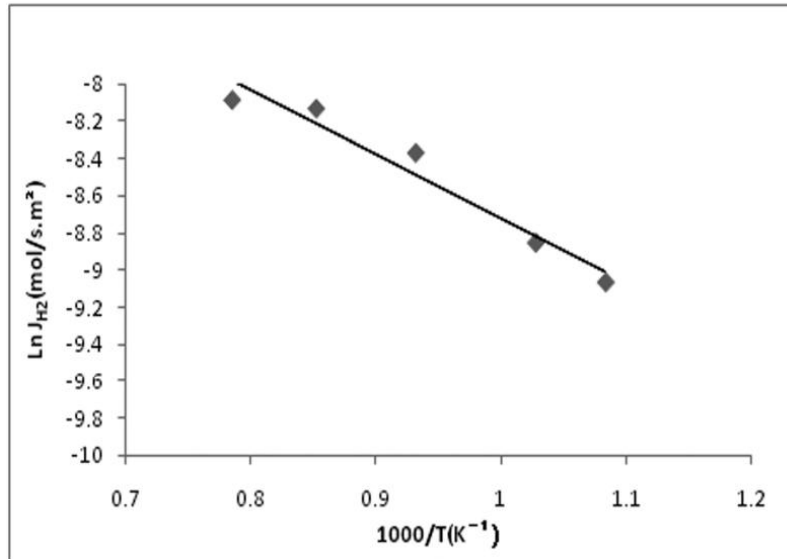


Figure 7. Permeation flux of asymmetrical BCYb membrane at partial pressure of 0.6 and feed flow of 120 mL/min

To convert the flux values from mL(STP)/(cm².min) to SI units of mol/(m².s), the values in figure 5 should be multiplied by 0.00682.

The activation energy, E_a , and preexponential factors, A (mol/m².s), are determined from a fit of the data to the Arrhenius equation.

$$J = A \exp\left(\frac{-E_a}{RT}\right) \quad (9)$$

The activation energy can be calculated from the slope of the Ln of hydrogen permeation flux versus the 1000/T. This value for BCYb membrane is determined from figure 7 to be 29 KJ/mol for SCYb membrane, the activation energies of the electronic conductivity and the protonic conductivity were reported to be 140 and 40 kJ/mol,

respectively, under asymmetric condition (feed side is exposed to reducing condition and sweep side is exposed to oxidizing condition) across the membrane [21]. These values should be comparable to the electronic and protonic activation energies of BCYb. The activation energy of 22 kJ/mol corresponds to the activation energy of the mixed protonic-electronic transport. For $\text{SrCe}_{0.9}\text{Eu}_{0.05}\text{O}_3$ (SCEu) membrane, the activation energy of the H₂ permeation was reported to be 80 kJ/mol and it remained constant in the temperature range of 600–850 °C [22].

Arrhenius plots of H₂ flux for BCYb membranes at feed flow of 60 mL/min are shown in Fig. 8. As seen in Fig. 8, the activation energy at lower temperature region (≤ 900 °C) is higher than its value at the higher temperature region (900–1000 °C).

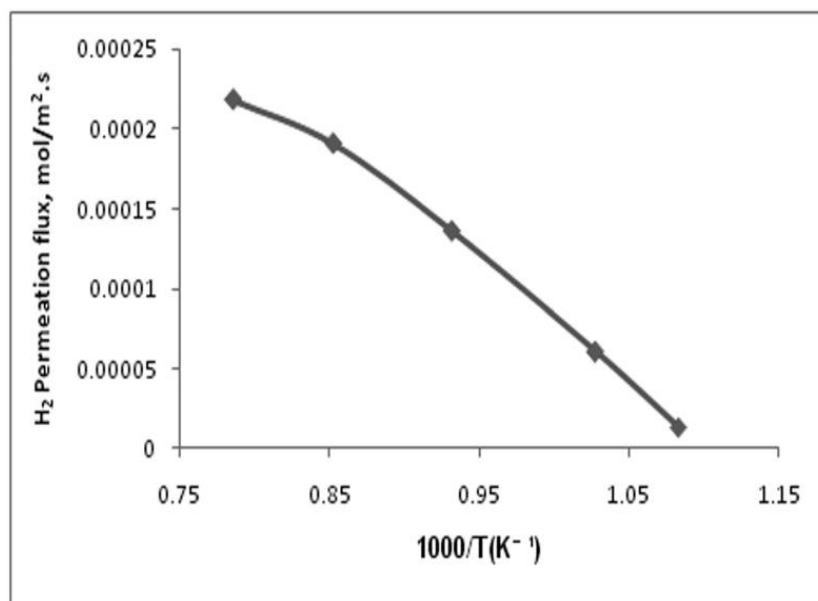


Figure 8. Permeation flux versus 1000/T of BCYb membrane at partial pressure of 0.6 and feed flow of 60 mL/min

Conclusion

Single phase $\text{BaCe}_{0.9}\text{Yb}_{0.1}\text{O}$ powders were synthesized by the liquid citrate method. XRD analysis was carried out to observe the structural phase of the membrane. Surface images obtained from SEM showed that dense membrane with clear crystal was in sintering temperature of 1200 °C. The H_2 permeation fluxes increased with temperature and with partial pressure of hydrogen in the investigated range of 650–1000 °C. A flux of 0.043 ml/cm².min was obtained at 1000 °C with a 1.63 mm membrane for 60% H_2/N_2 as the feed gas, which was a good flux compared with permeation flux of BCN membranes reported in previous works.

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