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Hydrogen Permeation Properties of Perovskite-type $BaCe_{0.9}Mn_{0.1}O_{3-d}$ Dense Ceramic Membrane

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Abstract: The electrical conduction properties of dense $BaCe_{0.9}Mn_{0.1}O_{3-\delta}$ (BCM10) membrane were investigated in the temperature range of 600-900°C. High ionic and electronic conductivities at elevated temperatures make BCM10 a potential ceramic material for hydrogen separation. Hydrogen permeation through BCM10 membranes was studied using a high-temperature permeation cell. Little hydrogen could be detected at the sweep side. However, appreciable hydrogen can permeate through BCM10 membrane coated with porous platinum black, which shows that the process of hydrogen permeation through BCM10 membranes was controlled by the catalytic decomposition and recomposition of hydrogen on the surfaces of BCM10 membranes.

Keywords: Hydrogen permeation, dense ceramic membranes, barium cerate, proton and electron conductivity.

In recent years, mixed-conducting oxides, in which both protonic and electronic charge carriers exist, have received increasing attentions[1]. Ceramic membranes made of such materials are semipermeable to hydrogen at elevated temperatures. In the early 1980s, Iwahara *et al*. first reported protonic conduction in $SrCeO_3$-based materials[2]. Later, $BaCeO_3$ system was extensively studied because of its higher conductivities. However, the electronic conductivity of rare earth doped-$BaCeO_3$ ceramics under hydrogen-permeation atmosphere is very low, which made them unsuitable for mixed- conducting ceramic membrane for hydrogen separation[3]. $BaCe_{0.9}Y_{0.1}O_{3-\delta}$, the most classical proton conductors, shows no observable hydrogen permeation in our previous experiments[4]. In order to promote the electronic conductivity, it is necessary to dope multivalent metal oxides into $BaCeO_3$. For this purpose, certain amount of manganese oxide was successfully doped into $BaCeO_3$, and its hydrogen permeation properties were studied.

BCM10 was prepared by a combined EDTA-citrate complexing method described in detail in Ref.5. With continual stirring and heating, stoichiometric amounts of the appropriate metal nitrates were dissolved in the EDTA-NH_3 solution, followed by the addition of citric acid. The mole ratio of EDTA acid: citric acid: total metal ions was controlled to be around 1:1.5:1. $NH_3 \cdot H_2O$ was added to keep the solution transparent. During stirring and heating, a flavescent gel was obtained with the continual evaporation of water. The gel was then heated at 150-200°C to make a precursor powder. The

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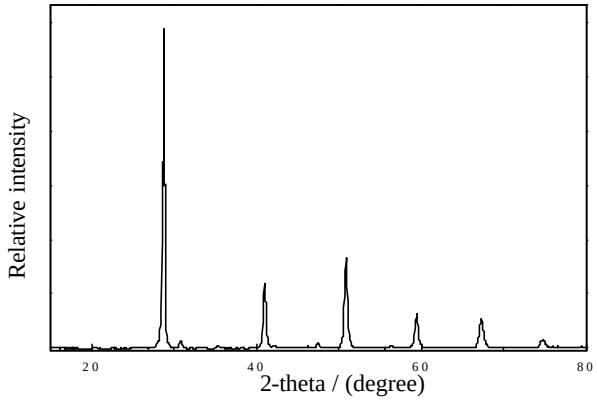
precursor was calcined at 950°C for 2 hrs to obtain the powder with final composition. The nonsupport disk sample of BCM10 was prepared by the conventional powder/sinter method. The pressed disks were sintered at 1500°C for 8 hrs. The densities of the sintered membranes were determined by the Archimedes method using ethanol. Only those membranes that had relative densities higher than 90% were used for electrochemical and hydrogen permeation studies. Porous platinum black was deposited on either side of sintered membrane (16 mm diameter, 1.6 mm thickness) by applying platinum ink and subsequent firing at 950°C for 2 hrs.

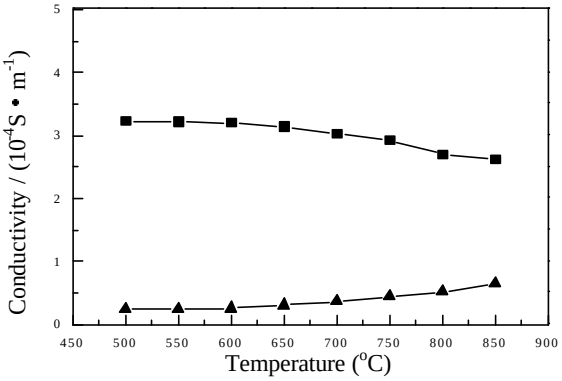
Figure 1 XRD pattern of $BaCe_{0.9}Mn_{0.1}O_{3-\delta}$ calcined at 950°C for 2 hrs



For electrical conductivity measurements, the 4-wires ac impedance technique was employed using an impedance analyzer in a frequency (f) range from 5 Hz to 100 kHz. The electronic and ionic conductivities of the samples were separated using open-circuit EMF method. The measurements were made in the temperature range of 873-1123 K, temperature being controlled within ±1 K. The ambient atmospheres were gas mixtures of selected ratios of N_2 and O_2. The oxygen partial pressure of the gas mixtures was controlled by the mixing ratio of O_2 and N_2 set by the mass flow controller within ±1%. The membrane sample was polished into 1.29×4.12×4.78 mm bar for measurement. More detailed procedure for conductivity measurement can be found elsewhere[6].

The hydrogen permeation experiments were performed in a vertical high-temperature gas permeation system[5]. The BCM10 membrane was sealed on the top end of the smaller tube with the glass powder. The membrane disk was set and pressed uniformly. After setting up the permeation cell, the temperature was slowly increased up to 100°C, kept for 60min, then increased to 1040°C and stayed for 10 min. At this temperature, the sealing powder melted and filled the gap between the membrane and the tube. During the hydrogen permeation experiment, a H_2/N_2 mixture gas was introduced into the chamber outside the small tube, while argon was used as the sweeping gas in the downstream. The downstream chamber effluent was intermittently sampled and analyzed by gas chromatography.

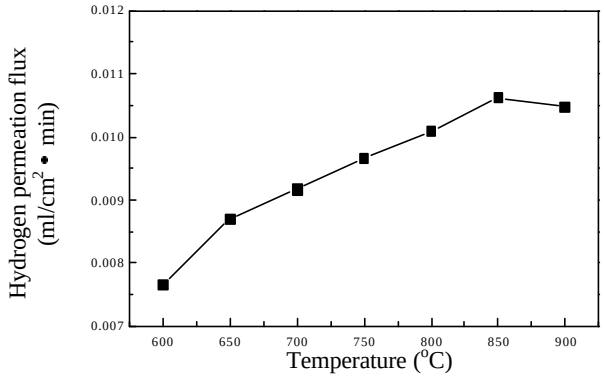
Figure 2 Ionic(—■—)and electronic(—▲—) conductivities of BCM10 membrane as a function of temperatures



Gas leakage through the sealant could be detected by monitoring nitrogen concentration in the downstream chamber. At each measuring temperature, the chamber was flushed by the permeation gas for about 30 min prior to collecting the permeation data in order to ensure the establishment of steady-state conditions.

Hydrogen permeation through BCM10 membrane with a thickness of 1.06 mm was measured in the temperature range of 600-950^{o}C. Throughout the entire temperature domain, little hydrogen could be detected at the sweep side. Similarly, hydrogen permeation experiments were done on a 1.64 mm thick BCM10 membrane coated with a porous thin film of platinum black. Hydrogen could obviously be detected at the sweep side. Hydrogen permeation fluxes in the temperature range from 600 to 900^{o}C were measured, which was shown in **Figure 3**. It can be shown that the hydrogen permeation fluxes increase with temperature in the temperature range of 600-850^{o}C. However, the hydrogen permeation fluxes decrease in the temperature range of 850-900^{o}C.

Figure 3 Hydrogen permeation flux through BCM10 coated with a thin film of platinum black



Probable reason is that BCM10 is a protonic-oxygen ion-electronic mixed conductor. Oxygen conductivity plays a big role in the ionic conductivity in temperature range of 850-900^{o}C. Keeping the membrane at 800^{o}C for 13 hrs, the hydrogen permeation flux increased a little from 0.0101 ml·cm^{-2}·min^{-1} to 0.0114 ml·cm^{-2}·min^{-1}.

BCM10 membrane shows appreciable electronic and protonic conductivities at elevated temperatures, and is potential used for hydrogen separation. Hydrogen permeation experiments on BCM10 membranes show that the hydrogen permeation process is controlled by surface kinetics.

Acknowledgments

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