Chemical stability and hydrogen permeation performance of Ni−BaCe$_{0.7}$Y$_{0.3-x}$In$_x$O$_{3-\delta}$ cermet membranes

Chunli Yang[*], Xinyu Ma, Hong Chen, Qiang Lv, Kewei Sun, Jin Chen, Sining Yun[**]

Functional Materials Laboratory, College of Materials & Mineral Resources, Xi'an University of Architecture and Technology, Xi'an, Shaanxi, 710055, China

ARTICLE INFO

ABSTRACT

The Ni−BaCe$_{0.7}$Y$_{0.3-x}$In$_x$O$_{3-\delta}$ dense cermet hydrogen separation membranes were fabricated, and the hydrogen permeability and the stability in CO$_2$−containing atmosphere were measured. The In−doping level had a significant influence on the sinterability of the membranes and the sinterability increased with the In content increasing. The hydrogen permeation flux of the Ni−BaCe$_{0.7}$Y$_{0.3-x}$In$_x$O$_{3-\delta}$ dual phase membranes decreased with the In−doping level increasing, but the chemical stability against CO$_2$ increased. In wet 10% CO$_2$−containing atmospheres, the reaction between BaCe$_{0.7}$Y$_{0.3-x}$In$_x$O$_{3-\delta}$ and CO$_2$ made the hydrogen penetration flux decrease for the 10% and 20% In−doped membranes, while Ni−BaCe$_{0.7}$In$_{0.3}$O$_{3-\delta}$ membrane showed a good long−term stability, which was evaluated as a potential alternative for hydrogen separation.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Because of issues such as worldwide energy crisis and the increasingly intense air pollution, hydrogen may become more attractive as a sustainable and clean energy vector and fuel [1]. However, hydrogen is usually produced by coal gasification, reforming and partial oxidation of natural gas or water−gas shift reactions [2−6] with many byproducts. In this case, hydrogen separation and purification from other less desirable gases to obtain pure hydrogen is an important aspect of hydrogen production. Hydrogen separation based on a dense, mixed electronic and proton conducting membrane is considered to be more cost−effective than traditional gas separation technologies such as pressure swing adsorption and cryogenic distillation. No electrodes or external electrical circuit are necessary and the membrane uses the hydrogen chemical potential gradient as the driving force for the transportation of hydrogen. Therefore a simple and efficient hydrogen separator can be constructed [7,8]. This is because of their low energy consumption, the possibility of continuous operation, the dramatically lowered investment cost in plant and the ease in operation [6,9,10].

It has been reported that many perovskite oxides show excellent proton conductivity at elevated temperatures in a humid atmosphere, including BaZrO$_3$, SrZrO$_3$, SrCeO$_3$, and BaCeO$_3$ doped with a rare earth oxide [11−15], in which the trivalent rare earth elements are used as dopants to introduce oxygen vacancies [16]. However, high proton conductivity and stability seem to be antagonistic [17,18]. Though Y−doped BaCeO$_3$ possesses the highest proton conductivity among the high temperature proton conducting oxides, BaCeO$_3$ materials show poor chemical stability in the H$_2$O− and CO$_2$−containing atmospheres. The most popular approach to increase the chemical stability of doped BaCeO$_3$ is to replace any desired fraction of Ce with Zr at the cost of reducing proton conductivity and sinterability [19−23].

Up to now, many efforts aim to develop a new solid proton conductor which can show high proton conductivity and adequate chemical stability against H$_2$O and CO$_2$ [24−29]. It is found that indium behaved as an ideal dopant for BaCeO$_3$, which solved both the problems of the poor chemical stability and poor sinterability of the BaCeO$_3$−based materials [30]. However, the electrical conductivity of In-doped BaCeO$_3$ proton conductors is relatively low [16]. Further it has been recently reported that co−doping the B−site with In and Y while maintaining high Ce content (e.g., 0.7) can offer a unique composition with elevated proton conductivity and improved stability in CO$_2$ and H$_2$O−rich environments at operating temperatures [31,32]. These research results shed light on the concept of developing new mixed−conducting membranes. We can make a reasonable assumption that partially substitution of In at the Ce−site of Y−doped BaCeO$_3$ might develop a nickel/ceramic

---

* Corresponding author.
** Corresponding author.
E-mail address: yunsining@xauat.edu.cn (C. Yang).

composite membrane with high permeability and selectivity to hydrogen at elevated temperature. In this paper, we reported the effect of In−doping on the hydrogen permeation and chemical stability of Y−doped barium cerate−Ni cermet membranes under various conditions.

2. Experimental

$BaCe_{0.7}Y_{0.2}In_{0.1}O_{3−\delta}$, $BaCe_{0.7}Y_{0.1}In_{0.2}O_{3−\delta}$, $BaCe_{0.7}In_{0.3}O_{3−\delta}$ powders were synthesized by a modified Pechini method. This wet chemical route was also used to prepare the $BaCe_{0.7}Y_{0.3}O_{3−\delta}$ powder. Stoichiometric amounts of $Ce(NO_3)_3 \cdot 6H_2O$, In_2O_3, Y_2O_3 were dissolved in dilute nitric acid solution. Then an appropriate amount of $BaCO_3$ was slowly added to the solution under stirring. Subsequently, citric acid was added as complexation agent. Molar ratio of citric acid/metal set at 1.5 and the pH value was adjusted to about 8.0 using ammonia solution. The solution was heated under continuously stirring at about 353 K to evaporate water until it became a viscous gel and finally ignited to flame, resulting in a white ash. Finally, the powders obtained were calcined at 1273 K in air for 3 h.

The $BaCe_{0.7}Y_{0.3−x}In_xO_{3−\delta}$ powders were well mixed with Ni powder in a volume ratio of 60:40. The mixed powders were pressed uniaxially into pellets 15 mm in diameter and about 1 mm in thickness. Subsequently, the as−prepared pellets were sintered at 1593 K for 5 h in a 5% H_2 environment balanced with Ar. The phase composition was checked using X−ray diffraction (XRD, Philips X'Pert Pro Super, The Netherlands, Cu K_α) patterns. The microstructure was examined using a scanning electron microscope (SEM JSM−6700 F, JEOL, and Japan).

The hydrogen permeation flux measurements were carried out in a self−built apparatus. Both sides of the sintered pellets were polished and the thicknesses of all pellets was about 0.86 mm. The sintered pellets were sealed on a dense alumina tube using a glass ring as the seal. The upper surface was feed with wet 20%H_2/80%N_2 mixed gas, while the lower surface was swept with high purity Ar with a flow rate of about 20 mL/min. The hydrogen permeation through these pellets was measured by analyzing the effluent gas compositions with an online gas chromatograph (GC−14C, Shimadzu) using high purity Ar as the carrier gas. The hydrogen permeation was measured at different temperatures and in atmospheres with different concentrations of CO_2. Hydrogen leakage rate through the glass sealant was corrected by measuring the nitrogen concentration in the permeate stream. The leakage percentage was less than 5% during the measurements.

3. Results and discussion

Fig. 1 shows the XRD patterns of the Ni−$BaCe_{0.7}Y_{0.3−x}In_xO_{3−\delta}$ membranes sintered at 1593 K for 5 h. The membranes consisted of Ni and $BaCe_{0.7}Y_{0.3−x}In_xO_{3−\delta}$, and no other impurity diffraction peak was detected, indicating that the required phase composition had been achieved. Compared to the traditional Y−doped $BaCeO_3$, where the Y dopant solubility limit is less than 20% of the available Ce sites [31], the In solubility can reach to 30%, as reported by Giannici [33]. In addition, with the In content increasing, the peaks of the perovskite gradually shifted to the large angle side, implying that In^{3+} doping should lead to a smaller lattice parameter. The lattice parameters and unit cell volumes obtained by refining XRD patterns with the standard XRD card of barium cerate (PDF file no. 82−2372) are listed in Table 1. The lattice parameters and the unit cell volumes of $BaCe_{0.7}Y_{0.3−x}In_xO_{3−\delta}$ samples gradually decreased with the In content increasing. It's mainly because that the ionic radius of In^{3+} (0.80 Å) is smaller than that of Y^{3+} (0.90 Å), which leads to the reduction of lattice parameters as a function of the In

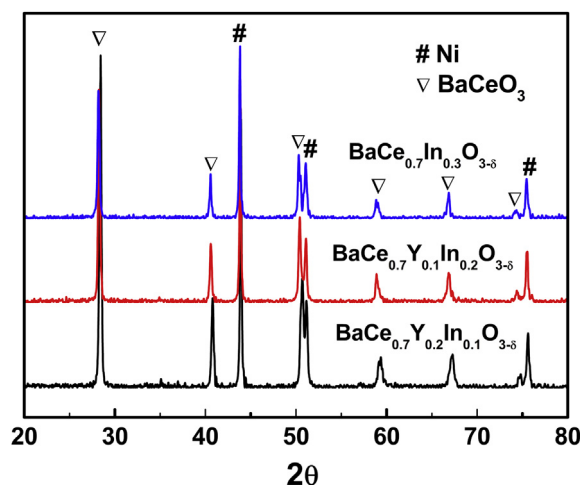Fig. 1. XRD patterns of the Ni−$BaCe_{0.7}Y_{0.3−x}In_xO_{3−\delta}$ membranes sintered at 1593 K for 5 h.

Table 1
Lattice parameters and unit cell volumes of $BaCe_{0.7}Y_{0.3−x}In_xO_{3−\delta}$ samples.

Samples	a (Å)	b (Å)	c (Å)	V(Å^3)
$BaCe_{0.7}Y_{0.2}In_{0.1}O_{3−\delta}$	8.809	6.216	6.208	339.880
$BaCe_{0.7}Y_{0.1}In_{0.2}O_{3−\delta}$	8.803	6.209	6.208	339.301
$BaCe_{0.7}In_{0.3}O_{3−\delta}$	8.789	6.206	6.205	338.472

content.

Fig. 2 shows the SEM micrographs of the Ni−$BaCe_{0.7}Y_{0.3−x}In_xO_{3−\delta}$ membranes sintered at 1593 K for 5 h. It can be clearly seen that the membrane was mainly composed of two phases and the minor metal Ni (dark region) was randomly distributed in the $BaCe_{0.7}Y_{0.3−x}In_xO_{3−\delta}$ ceramic matrix (white region). All the In−doped cermet membranes reached dense and little pores can be observed from images of the membranes. For comparison, Fig. 2 also shows the SEM image of the Ni−$BaCe_{0.7}Y_{0.3}O_{3−\delta}$ membrane after firing at 1593 K for 5 h. The Ni−$BaCe_{0.7}Y_{0.3}O_{3−\delta}$ membrane was still porous and the grain size of $BaCe_{0.7}Y_{0.3}O_{3−\delta}$ was quite small. Similarly, we also can see from Fig. 2 that the In−doped cermet membrane became denser and the grain size became larger with the increase of the In−doping level. These evidences strongly suggest that the In−doping has a significant influence on the sinterability of Ni−$BaCe_{0.7}Y_{0.3−x}In_xO_{3−\delta}$ membranes [31]. A dopant oxide with a low melting point and dopant ionic radius close to Ce cations are favourable to sintering [34]. In the present work, melting point of In_2O_3 is lower than that of Y_2O_3, which makes the Ni−$BaCe_{0.7}Y_{0.3−x}In_xO_{3−\delta}$ cermet membranes much easier to be densified than the Ni- $BaCe_{0.7}Y_{0.3}O_{3−\delta}$ membrane. For cermet hydrogen separation membrane, the high sintering temperature (>1673 K) would lead to the evaporation of metal Ni, resulting in the non−connection of metal Ni and then low electronic conductivity. Therefore, lowering the sintering temperature is beneficial to improve the performance of the hydrogen separation membrane.

Fig. 3 presents the temperature dependence of the hydrogen permeation flux using wet 20% H_2 (balance N_2) as the feed gas and high purity Ar as the sweep gas. The hydrogen permeation flux increased with increasing temperature as expected. Because of the exothermic water dissolution reaction, the concentration of protons decreases with increasing temperature [35]. Whereas, the proton defect transport mechanism is rotational diffusion and the diffusion process is thermally activated [36]. Thus, the proton