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Study on the chemical stability of Y-doped $BaCeO_{3-\delta}$ and $BaZrO_{3-\delta}$ films deposited by aerosol deposition

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ABSTRACT

Barium cerate ($BaCeO_3$) has high proton conductivity but rather poor chemical stability in CO_2-containing atmospheres. Barium zirconate ($BaZrO_3$), in contrast, is a rather stable material, but exhibits poor sinterability. In the present work, powders of Y-doped $BaCeO_3$ and $BaZrO_3$ were synthesized via the solid solution reaction method, and dense ceramic membranes with $BaCe_{0.9}Y_{0.1}O_3$ and $BaZr_{0.85}Y_{0.15}O_3$ were prepared by the aerosol deposition method at room temperature. Aerosol deposition method is a technique that enables the fabrication of ceramic films at room temperature with a high deposition rate as well as strong adhesion to the substrate. The powders and aerosol-deposited membranes were characterized by X-ray diffraction, particle size analysis, scanning electron microscopy, and X-ray elemental mapping. The chemical stability of powders and aerosol-deposited membranes with $BaCe_{0.9}Y_{0.1}O_3$ and $BaZr_{0.85}Y_{0.15}O_3$ against water and carbon dioxide has been investigated, and it was found that $BaZr_{0.85}Y_{0.15}O_3$ materials showed a better chemical compatibility.

1. Introduction

Hydrogen is considered as one of the most prospective energy sources to lower fossil-fuel dependence, with beneficial effects for climate change, air pollution and energy security. Hydrogen separation and purification currently involves pressure-swing adsorption and cryogenic distillation, with membrane-based technologies in development as more economic alternatives. Types of membrane include polymers, Pd-based systems, and microporous inorganic materials. Among them, dense ceramic hydrogen-permeable membranes provide an analogue of the widely investigated oxygen-permeable membranes, which may be used for oxygen production, purification, and partial oxidation of hydrocarbons [1–6]. Recently, acceptor-doped $BaCeO_3$ and $BaZrO_3$-based ceramics have become of interest as protonic conductors [7–21]. Carrier doping is performed by partial substitution of A- and/or B-site atoms of the cubic perovskite-type ABO_3 structure. The development of dense ceramic membranes with these materials has received considered attention due to their possible applications in hydrogen-based energy, petrochemical process, fuel cells, separation membranes, and other technologies.

Although high proton conductivity has been reported for many perovskite-type oxides in humid atmospheres, the combination of high proton conductivity and stability, which is a prerequisite for the application of such electrolytes as conductive membranes in electrochemical cells and the IGCC (integrated gasification combined cycle) field, has not been satisfactorily addressed. $BaCeO_3$-based oxides with high conductivity generally show very poor phase stability with respect to formation of carbonate or hydroxide [1,13,22]. As their lattice energy (or Gibbs free energy) is higher, the crystal structure is intrinsically less stable. On the other hand, $BaZrO_3$-based ceramics show high stability towards water and carbon dioxide [22,23]. $BaZrO_3$ is an alternative protonic conductor that has been found to be chemically more stable than $BaCeO_3$. However, the poor sinterability of $BaZrO_3$-based ceramic leads to the presence of a large grain boundary surface, resulting in lower electrical conductivity than in doped $BaCeO_3$[13,14,24].

Dense mixed proton-electron conducting ceramic membrane has attracted increasing interest and is significantly dependant on the characteristics of membrane such as thickness, particle size, roughness, and adhesion with a porous support [25]. The several methods available for fabrication of ceramic films include sol–gel [26,27], sputtering [28], e-beam evaporation [29], metal organic chemical vapor deposition [30], and aerosol deposition [31–37]. In particular, the aerosol deposition (AD) method is a technique that enables the fabrication of ceramic films at room temperature with a high deposition rate as well as strong adhesion to the substrate. It is based on the impact adhesion of sub- or micron particles to a

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substrate. Oxide particles accelerated by gas up to a subsonic velocity impinge on the substrate, resulting in the formation of a dense ceramic layer without any additional thermal treatment (e.g. sintering). In addition, operation at room temperature of AD method makes it possible to fabricate a ceramic membrane without any phase change.

Thus far, research has been carried out to investigate the chemical stability and conductivity of powder- and bulk-form of $BaCeO_3$ and $BaZrO_3$ oxides, but few studies on chemical stability and phase transformation of $BaCeO_3$ and $BaZrO_3$ membranes in H_2–CO_2 mixed gas have been reported. With this in mind, we evaluated the chemical compatibility of powders and membranes of Y-doped $BaCeO_3$ and $BaZrO_3$ perovskite-type oxides, and here a dense ceramic membrane with these oxides was fabricated from micron-sized powder at room temperature by AD method. According to previous reports [10,18,19,21–23,38,39,42], yttrium doping within the composition range of $0.15 \leq x \leq 0.2$ of $Ba(Ce,Zr)_{1-x}Y_xO_{3-\delta}$ leads to a maximum protonic conductivity and then we have chosen $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ and $BaZr_{0.85}Y_{0.15}O_{3-\delta}$ as protonic conductors in this study.

2. Experiments

Polycrystalline Y-doped Ba-cerate and Ba-zirconate oxides, $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCYO) and $BaZr_{0.85}Y_{0.15}O_{3-\delta}$ (BZYO), were prepared by the conventional solid-state reaction method. High purity powders of $BaCO_3$ (99% up, High Purity Chemicals), CeO_2 (99.9%, High Purity Chemicals), ZrO_2 (99%, Aldrich Co.), and Y_2O_3 (99.9%, High Purity Chemicals) were mixed and ground in a ball mill with ethanol. Finally, BCYO and BZYO were calcined at 1473 K and 1723 K for 2 h in air, respectively. The calcined powders were then crushed and sieved through a mesh with a size of <45 μm. Fig. 1 depicts the X-ray diffraction (XRD) patterns of BCYO and BZYO powders after calcinations. As shown in Fig. 1, the XRD patterns of the calcined BCYO and BZYO powders confirm a single phase having a perovskite structure, and there are no diffraction peaks corresponding to either $BaCO_3$ or ZrO_2. To further analyze the size distribution of BCYO and BZYO powders synthesized using a solid solution reaction, a laser diffraction particle size analyzer (HORIBA LA-950 V2 model) was used; their geometric mean diameter, D_{50}, had an average value of 3 μm and 1 μm, respectively.

Fig. 2(a) shows a schematic diagram of the AD apparatus employed in this study. The AD apparatus consists of three parts: an aerosol generator, mass-flow controller, and deposition chamber. Aerosol formed in the aerosol generator with a carrier gas is transported into a deposition chamber, which is evacuated by a rotary pump with a mechanical buster, and accelerated through a nozzle to collide with a substrate. The deposition conditions of BCYO and BZYO films are given in Table 1. Yttrium-stabilized zirconia powders (TZ-8Y, TOSHO Co.) were used as porous substrate, pressed into pellets, and finally sintered at 1573 K for 1 h in air to afford disks with a porosity of 28%. The radius and thickness of the ZrO_2 porous substrate are 20 mm and 2 mm, respectively. In order to measure the density of aerosol-deposited ceramic membrane, a membrane disk was inserted into a stainless tube (pressure chamber) and associated gas flow tubes, as shown in Fig. 2(b). He gas was used as the feed gas with 200 kPa pressure on membrane side and pressure change was measured on the permeation side to check the density of aerosol-deposited membrane.

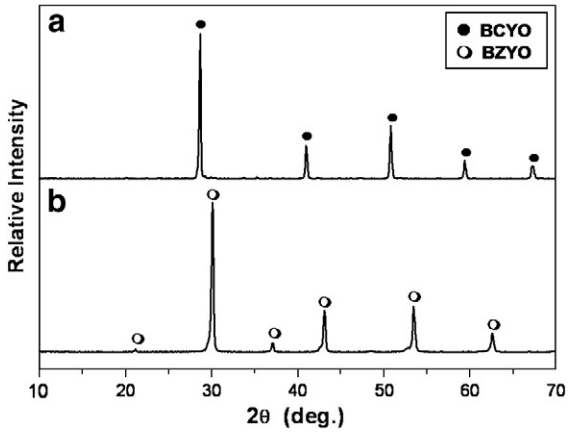

Fig. 1. XRD patterns of (a) $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ and (b) $BaZr_{0.85}Y_{0.15}O_{3-\delta}$ powders after calcinations.

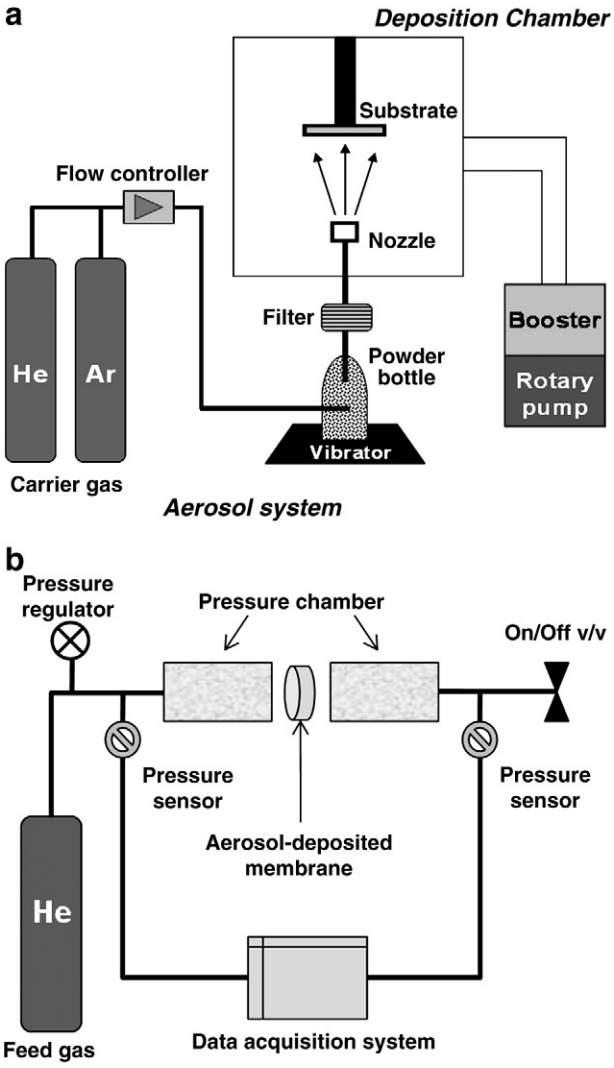

Fig. 2. Schematic illustrations of (a) aerosol deposition apparatus and (b) set-up used to measure the density of aerosol-deposited ceramic membrane.

Table 1
Deposition conditions of dense ceramic membrane by AD method.

Raw powder	BCYO and BZYO
Substrate	ZrO_2 porous disk (Dia. 20 mm, Th. 2 mm)
Carrier gas	He
Size of nozzle orifice	20×0.4 mm^2
Working pressure	<1.3 kPa
Consumption of carrier gas	4–5 L/min
Deposition area	10×10 mm^2