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Electrical conduction and hydrogen permeation investigation on iron-doped barium zirconate membrane

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ABSTRACT

Mixed conducting 10% Fe-doped $BaZrO_3$ (BZF10) membrane was investigated for electrical conduction and hydrogen permeation properties in the temperature range of 600–900 °C. A hydrogen permeation flux (J_{H_2}) as high as 0.75 mL/(min cm^2) was achieved at 900 °C using a 1.15 mm thick BZF10 membrane when 20% H_2/inert and Ar were flowed in the feed and sweep, respectively. J_{H_2} increases monotonically with the reciprocal of the membrane thickness, indicating bulk diffusion is the rate-limiting step in the examined thickness range (0.97–1.40 mm). At constant temperature, J_{H_2} increases with the feed side hydrogen partial pressure. In the range of 600–700 °C, hydrogen permeation is limited by the electronic transport with high activation energy 72–94 kJ/mol. While in the higher temperature range of 700–900 °C, hydrogen permeation is limited by the mixed protonic-electronic transport with low activation energy 18–23 kJ/mol. The addition of moisture did not influence J_{H_2} when the steam level was below 0.1 atm. While when the steam level reached 0.3 atm, hydrogen permeation process was promoted by the formation of extra protons. BZF10 membrane is found to be mechanically and chemically stable over dry and humidified hydrogen containing gas environments.

1. Introduction

Mixed ionic-electronic conducting electroceramic materials have received increasing interest as high-temperature hydrogen separation membranes for use in catalytic membrane reactors for natural gas conversion and as electrolytes in proton-conducting intermediate-temperature solid-oxide fuel cells (SOFCs) [1–4]. Since the first report of proton conduction in perovskite (ABO_3) type $SrCeO_3$ at high temperatures (≥ 600 °C) by Iwahara et al. [5] in 1981, several acceptor-doped barium cerates and barium zirconates ($BaCe_xM_{1-x}O_{3-\delta}$ and $BaZr_xM_{1-x}O_{3-\delta}$, M=Sc, Y, Nd, Gd, Yb, etc.) have been investigated as high-temperature protonic conductors in connection with hydrogen separation or SOFC applications [6–9]. The primary mechanism to produce protons in these materials has been identified as the interaction between water vapor and oxygen vacancies, the latter being generated in the oxide via charge compensation required by the presence of trivalent cations (M^{3+}) at the B-site (B^{4+}) [10]. Electronic conduction is introduced by doping with a multivalent cation (e. Graphomya transition metal), which enables free electron transport from a low-oxidation-state cation to a high-oxidation-state cation in its neighborhood, i.e. the “small polaron” mechanism [11]. The key advantage of the resulting mixed ionic-electronic conducting membrane is that no external circuit is needed, thus offering an economic solution in comparison to power-based technologies for hydrogen production [12].

Significant research has been conducted on mixed ionic-electronic conducting perovskite-type materials for hydrogen separation. Li et al. [13] measured the hydrogen permeation flux through $BaCe_{0.9}Mn_{0.1}O_{3-\delta}$ membranes with thickness 1.6 mm. The resulting flux was 0.011 mL/(min cm^2) at 900 °C and was shown to be controlled by surface kinetics. Qi et al. [14] studied electrical conductivity and hydrogen permeation on mixed conducting $SrCe_{0.95}Tm_{0.05}O_{3-\delta}$ membrane and its highest hydrogen flux was reported to be ~0.04 mL/(min cm^2) at 900 °C using 10% H_2 in the feed and 20%O_2 in the sweep. Effect of Zr doped Ni-$BaCe_xY_{1-x}O_{3-\delta}$ was investigated by Zuo et al. [15] in which hydrogen flux was promoted by addition of water vapor in the feed. Likewise, Cai et al. [16] showed that the hydrogen permeation flux under wet conditions was higher due to the increased proton concentrations. Hamakawa et al. [17] reported the H_2 permeation rates were proportional to the inverse of the membrane thickness even on a 2 μm thin film of $SrCe_{0.95}Yb_{0.05}O_3$, indicating that permeation is controlled by bulk diffusion and not by surface chemisorption or boundary transport. Song et al. [18] studied hydrogen permeation for Ni–$BaCe_{0.8}Y_{0.2}O_{3-\delta}$ and found the hydrogen permeation flux were due to ambipolar diffusion, which dominated over the entire examined temperature range

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(600–900 °C). Mather et al. [19] found that the hydrogen permeability could be largely improved by coating a porous Pt catalyst layer on the feed-exposed $Sr_{0.97}Ce_{0.9}Yb_{0.1}O_{3-\delta}$ membrane. Recently, Song et al. [20] investigated hydrogen permeation as well as oxygen permeation in Co-doped $BaCe_{0.85}Tb_{0.05}Co_{0.1}O_{3-\delta}$ (BCTCo) perovskite membrane (dual ion conducting membrane). The reported hydrogen flux reached 0.385 mL/(min cm^2) at 1000 °C under 50% H_2/inert and the oxygen flux reached 0.122 mL/(min cm^2) at 1000 °C under Air/He. In addition, a newly released finding showed a hydrogen flux as high as ~4.1 mL/(min cm^2) at 800 °C for the $Sr(Ce_{0.6}Zr_{0.4})_{0.85}Y_{0.15}O_{3-\delta}$ /Ni–$Sr(Ce_{0.6}Zr_{0.4})_{0.85}Y_{0.15}O_{3-\delta}$ hydrogen transport membrane, which increased the magnitude of reported H_2 permeation flux to a higher level [21].

In addition to hydrogen permeation rates, membrane chemical stability is a key factor in identifying suitable hydrogen separation materials and electrolysis cell components. Specifically, suitable materials must exhibit high chemical stability not only under reducing (H_2) environments, but also in the presence of gaseous species that are commonly associated with hydrogen containing mixture gasses (e.g. H_2O, CO_2, SO_2, and NO_x). Among similar chemical formulas, $BaCeO_3$ based materials showed high protonic conductivity under hydrogen containing environments [22], but their chemical stability under steam and CO_2 were reported to be poor [23–25]. A group of Zr-doped $BaCeO_3$ materials was investigated in order to mitigate the materials degradation pathways under CO_2-and steam-containing environments and the results showed that the chemical stability increased with increasing Zr amount in the doped materials [8,15,26–27]. However, hydrogen permeability data for $BaZrO_3$-based materials remains sparse.

Based upon the above reviews, a chemically stable, mixed ionic-electronic conducting ceramic material may be a good candidate for high-temperature hydrogen separating membrane application. Our recent findings confirmed high material stability under a full cycle of oxidizing and reducing environments expected for membrane reactor and electrolysis-cell applications at 600–800 °C for Fe-doped $BaZrO_3$ [28–29]. In this manuscript, we report the investigation of Fe-doped $BaZrO_3$ over a full study of hydrogen permeation with the hypothesis that transition metal doping of the proton conducting material $BaZrO_3$ would largely improve the electronic conductivity due to valence changes from Fe^{2+}/Fe^{3+}, thus higher hydrogen permeability could be expected. Results thus provide valuable insight into the underlying hydrogen permeation mechanisms present as well as the long-term materials stability of acceptor-doped perovskites over a broader range of temperatures, hydrogen and steam partial pressures than previously reported [29].

2. Experimental

2.1. Membrane preparation and characterization

10% Fe-doped $BaZrO_3$ (BZF10) membranes were prepared from metal nitrate precursors using conventional solid-state reaction method, as follows. High purity nitrate powders of $Ba(NO_3)_2$ (Sigma-Aldrich, 99+%), $ZrO(NO_3)_2 \cdot 6H_2O$ (Aldrich Chemistry, 99%), and $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich, ≥98%) were mixed and ground into powder. The blended powder was heat-treated at 1150 °C for 4 h with heating and cooling rates of 5 °C/min, followed by addition of acetone and grinding for 10 min to homogenize the partially calcined powder, followed by drying at 120 °C for 1 h. The resulting powder was subsequently heat-treated at 1600 °C for 12 h with heating and cooling rates of 5 °C/min, ground again, and uniaxially pressed into pellets using a 25 mm die (Carver, 4369) at 199.6 MPa. The pellets were sintered at 1700 °C for 4 h with heating and cooling rates of 3 °C/min and polished to remove any surface contaminants and to minimize surface rugosity. Relative density of the polished membrane was measured by Archimedes test, as detailed elsewhere [28]. The phase structures of the sintered disk were characterized by synchrotron XRD at Advanced Photon Source, Argonne National Lab (IL, USA). Microscopy analysis of fracture cross-section of the as-sintered BZF10 membrane and the membrane upon completion of all hydrogen permeation tests was investigated by scanning electron microscopy (SEM). An SEM (JEOL JSM-7500F) operated at 5 kV was used for conventional and analytical imaging of the sample.

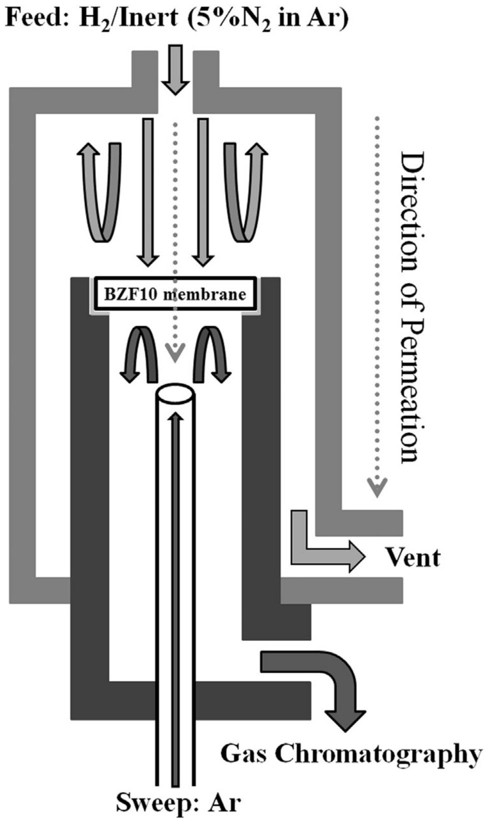

Fig. 1. Schematic of two-chamber gas permeation cell.

2.2. Hydrogen permeation

Hydrogen permeation experiments were performed in a vertical high temperature 2-volume permeation cell presented schematically in Fig. 1 and described previously [30]. Three polished dense membranes with thickness 0.97, 1.15, 1.40 mm were prepared for the permeation test. Each membrane was sealed onto a supporting ceramic tube by filling the gap between the membrane and the supporting tube with a sealing mixture, comprised of a well-ground wet mixture of glass powder (VIOX # 10584), BZF10 powder, and sodium aluminate (Riedel-de Haën # 13404) of mass ratio 5:4:1. The mixture was manually ground with appropriate amount of deionized water to form a sticky paste. After the sealing was dried in air at room temperature for 2 h, the supporting tube with attached membrane was sealed in the permeation set up and heated to 900 °C in air with heating and cooling rates 3 °C/min. After 30 min at 900 °C, residual air was purged from the system by introducing pure He (100 mL/min, 1 atm) to the volume between the outer quartz tube and the inner ceramic tube (feed side) and pure Ar (100 mL/min, 1 atm) to the volume inside the inner ceramic tube (sweep side) continually. The He content of the