Surface reaction controlling hydrogen permeation through lanthanum-doped ceria membrane with asymmetric structure

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Received 2 July 2015

Abstract

A thin membrane (thickness = $\sim 10 \mu\text{m}$) made of a lanthanum highly-doped cerium oxide ($\text{La}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$, LDC) was fabricated on a mixed porous layer consisting of Ni and the LDC. Comparing the results of permeation experiments for hydrogen and helium gases confirmed that the asymmetric membrane acted as a mixed protonic and electronic conducting hydrogen separation membrane and that the thin LDC membrane was an almost dense layer. The most striking result of the permeation experiments was that the hydrogen permeation flux increased with increase in the crystal grain boundary length per unit area of the surface and increased in proportion to the square root of hydrogen partial pressure, showing that the flux is controlled by a surface reaction between the adsorbed hydrogen and proton at the crystal grain boundary.

Key words : Hydrogen separation, Surface reaction control, Protonic and electronic conductor, Lanthanum-doped ceria, Asymmetric membrane, Hydrogen permeation flux

1. Introduction

A lanthanum highly-doped ceria ($\text{La}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$, LDC) is an attractive hydrogen separation membrane at high temperatures. For example, when an internal reforming of hydrocarbon fuels is used in solid oxide fuel cells (SOFCs), a significant deposition of char (carbon) occurs on the anode, leading to reduction in output power, especially for SOFCs with anodes made of gadolinia-doped ceria (GDC). Using the LDC membrane, the synthesis gases produced by reforming process can be separated and only hydrogen can be simultaneously supplied into the anode side of SOFCs, leading to no deposition of char on the anode.

Recently, two types of hydrogen separation membranes have been investigated: (i) mixed protonic and electronic conducting membranes such as $\text{La}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ (LDC) (Zhu, et al., 2012), and (ii) metal-ceramic composite membranes such as $\text{Ni-BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (Zuo, et al., 2006, Yan, et al., 2010b, Zhu, et al., 2011) and $\text{Ni-La}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ (Yan, et al., 2010a, Fang, et al., 2010), in which the metal phase acts as a conductor for electrons only, while the oxide ceramic phase acts as a conductor mainly for protons. In both cases, the hydrogen partial pressure gradient across the membrane was the driving force for hydrogen transport involving the diffusion of protons and electrons in the membrane (Cheng, et al., 2005). The increase in the permeation flux is inversely proportional to membrane thickness. Hence, the fabrication of an asymmetric structure, in which a thin LDC membrane, for example, was fabricated on a mixed porous layer consisting of Ni and the LDC, has been attempted (Zhu, et al., 2012). The principle of mixed proton and electron transport for the LDC has been explained in detail elsewhere (Fang, et al., 2010). The electron conductivity was increased by adding Ni into the LDC membrane (Zhu, et al., 2015, Fang, et al., 2010), while, since an ordered structure of oxygen vacancy was destroyed and rearranged randomly by doping Sm into LDC, proton transport was enhanced (Yan, et al., 2010a). In addition, Ba, Zr, Y, and Yb were used (Zuo, et al., 2006, Yan, et al., 2010b, Zhu, et al., 2011) for further enhancing the hydrogen permeation flux. Among these, the BZCYYb ($\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$) membrane has the maximum permeation flux with good stability under the conditions of high humidity and high concentration of

carbon dioxide (Liu, et al., 2013). They also showed that the hydrogen permeation flux was controlled by surface reactions. However, it is not clear what is the most important issue that determines the hydrogen permeation flux in any types of membranes (such as, LDC and BZCYYb), though the permeation flux increases linearly with the square root of hydrogen partial pressure in the case of surface reaction control, while it increases with a logarithmic function in the case of bulk diffusion control.

In this study, a thin and dense membrane comprising LDC over the mixed Ni and LDC porous layer was fabricated, and its hydrogen permeation flux was investigated and discussed using a simple surface reaction model.

2. Experimental setup and procedure

2.1 Fabrication of membrane

A mixture of NiO and LDC powders with a weight ratio of 6:4 was prepared to fabricate the porous substrate layer consisting of Ni and LDC and was well mixed with ethanol for 1 h. After the ethanol was evaporated by an electric oven, the powdered mixture was pressed uniaxially at 50 MPa into a disk of diameter 20 mm, thus forming a green compact of NiO and LDC. The green compact substrate was covered by a thin LDC layer by dip coating using the LDC powder solution with ethanol. After the ethanol was evaporated, the bilayer compact was co-pressed at 300 MPa and was subsequently sintered at different temperatures such as 1400°C, 1450°C, and 1500°C. This procedure led to the formation of an asymmetric membrane consisting of a dense LDC layer with a thickness less than 10 μm and a porous Ni and LDC substrate layer with a thickness of about 500 μm . The resulting membrane was used for hydrogen permeation. The surface and cross section of the samples were observed through an FIB-SEM system to confirm the thickness of the top dense LDC layer and the microstructure of the crystal grains present on the surface.

2.2 Hydrogen permeation measurement

Figure 1 shows a schematic diagram of the experimental setup for hydrogen permeation. The bilayer membrane was fixed to the outer ceramic pipes of inner diameter 16 mm and outer diameter 21 mm by using a glass sealant. The inner pipes with inner diameter 6 mm and outer diameter 10 mm were arranged concentrically. In addition, for complete sealing, another ceramic pipe with inner diameter 22 mm and outer diameter 28 mm were used to cover the outer ceramic pipe at the location where the membrane was installed. Nitrogen, as a carrier gas with a flow rate of 100 mL/min, was introduced at both ends through the inner pipes and was impinged on both the porous Ni and LDC surface and the dense LDC surface. At the same time, hydrogen or helium gas with a flow rate of 20, 100, or 200 mL/min was introduced into the porous Ni and LDC surface, i.e., from the hydrogen-supply side. In the beginning of experiment, since some steam was produced by the deoxidization of NiO into Ni at the hydrogen-supply side, the exhaust gas was trapped by a gas bag after it flows through desiccant. The trapped gas was analyzed by a Thermal Conduction Detector (TCD) type gas chromatograph system using Molecular Sieve 5A as the column and argon as the carrier gas. The temperature of the membrane was controlled by an electric heater and measured by a K-type thermocouple near the membrane.

Fig. 1 Experimental setup for the measurement of hydrogen permeation flux. The isolated disc-shaped LDC membrane is fixed to outer ceramic pipes using glass seals. The inner ceramic pipes are arranged concentrically.

3. Results and discussion

3.1 Characteristics of membrane

Figures 2(a) and 2(b) show the SEM images of membrane cross sections before and after the experiment. As shown in Fig. 2(a), a 10- μm -thick dense LDC membrane covered with a dense mixed NiO and LDC layer was fabricated by using dip coating, co-pressing, and sintering processes. As shown in Fig. 2(b), after the experiment, the LDC membrane had many pores because NiO was deoxidized in the beginning of the experiment by hydrogen supply, resulting in a porous Ni and LDC layer.

Figures 3(a), 3(b), and 3(c) show SEM images of membrane surfaces sintered at 1400°C, 1450°C, and 1500°C. It can be seen that the LDC layer was almost dense, though the membrane sintered at 1400°C had some defects. On increasing the temperature, the crystal grain size on the surface became larger. As a result, the grain boundary length per unit area decreased with increasing temperature.

Fig. 2 SEM images of cross section of membrane before (a) and after (b) experiment at the sintering temperature of 1500°C. The top layer is a dense LDC layer with a thickness of about 10 microns. The bottom layer is a mixed NiO and LDC dense layer before experiment (a) and a mixed Ni and LDC porous layer after experiment.

Fig. 3 SEM images of the surface view of membrane sintered at (a) 1400°C, (b) 1450°C, and (c) 1500°C. The membrane has many crystal grains whose size increases with temperature. The grain boundary lengths per unit area are (a) $0.56 \mu\text{m}/\mu\text{m}^2$, (b) $0.29 \mu\text{m}/\mu\text{m}^2$, (c) $0.13 \mu\text{m}/\mu\text{m}^2$.

3.2 Hydrogen permeation flux

Figure 4 shows hydrogen permeation fluxes at 800°C for membranes sintered at 1400°C, 1450°C, and 1500°C. The horizontal axis shows the grain boundary length per unit area on the surface. For a comparison, helium permeation fluxes are also shown. At sintered temperatures of 1450°C and 1500°C, a dense and defect-free LDC layer could be fabricated because only negligible amount of helium was detected in the sweep side at these sintering temperatures. As a result, the hydrogen permeation flux is mainly caused by the mixed protonic and electronic conduction. In contrast, only a little permeation of helium occurred at 1400°C; the selectivity defined as the mole ratio of H_2/He in the sweep side is only 24.7. In this case, hydrogen permeation flux consists of molecular diffusion and mixed conduction.

Fig. 4 Variation of hydrogen permeation flux with crystal grain boundary length per unit area. The hydrogen permeation flux increases with grain boundary length, which is increased by reducing the sintering temperature. The permeation flux of helium is also shown. The results are for the operation temperature of 800°C and hydrogen supply rate of 100 mL/min, which results in hydrogen partial pressure of 50.7 kPa.

Fig. 5 Variation of hydrogen permeation flux with square root of hydrogen partial pressure at 800°C. The hydrogen permeation flux increases in proportion to the square root of hydrogen partial pressure at any sintering temperature.

Figure 5 shows the hydrogen permeation flux with respect to the difference in the square root of hydrogen partial pressures between the hydrogen supply and sweep sides at 800°C. It can be clearly seen from the figure that the increase in the hydrogen permeation flux is linearly proportional to the square root of hydrogen partial pressure. Here, if it is assumed that an exchange reaction between a hydrogen molecule and an adsorbed hydrogen, $H_2 + 2V \rightleftharpoons 2H_{ad}$, is much faster than a proton production reaction, $H_{ad} \rightarrow H^+ + e^-$, then the exchange reaction takes place under chemical equilibrium conditions, where V , H_{ad} , and e^- are an adsorption site, adsorbed hydrogen, and electron, respectively. As a result, the chemical equilibrium constant can be described using the hydrogen partial pressure P_{H_2} , hydrogen coverage θ_H , and adsorption site θ_V , as follows.

$$\frac{\theta_H^2}{P_{H_2}\theta_V^2} = K_H \quad (1)$$

Since $\theta_H + \theta_V = 1$, the coverage of the adsorbed hydrogen is expressed as follows:

$$\theta_H = \frac{\sqrt{K_H P_{H_2}}}{1 + \sqrt{K_H P_{H_2}}} \quad (2)$$

When the hydrogen coverage is very small, such as $\theta_H \ll 1$, Eq. (2) reduces to the following:

$$\theta_H \approx \sqrt{K_H P_{H_2}} \quad (3)$$

On the other hand, the reaction rate of proton production in the supply side, $r_{p,supply}$, is obtained as a product of the reaction rate constant k and the coverage of adsorbed hydrogen as follows:

$$r_{p,supply} = k\theta_H \approx k\sqrt{K_H P_{H_2}} \quad (4)$$

The net permeation flux r_p can be defined as the summation of the forward reaction in the supply side, $r_{p,supply}$,

and backward reaction in the sweep side, $r_{p,sweep}$, as follows:

$$r_p = r_{p,supply} - r_{p,sweep} \approx k\sqrt{K_H P_{H2,supply}} - k\sqrt{K_H P_{H2,sweep}} = k\sqrt{K_H} (\sqrt{P_{H2,supply}} - \sqrt{P_{H2,sweep}}) \quad (5)$$

According to Eq. (5), the permeation flux is linearly proportional to the square root of the partial pressure of hydrogen, as shown in Fig. 5. Hence, it can be concluded that hydrogen permeation is controlled by the surface reaction rate between the adsorbed hydrogen and proton.

In addition to the linear increase, as shown in Fig. 5, the hydrogen permeation flux also increases with the crystal grain boundary length, which increases with decreasing sintering temperature. It is known that oxygen vacancy contributes to proton conduction in the LDC. As a result, the interface between crystal grains might play an important role both in surface reaction and proton conduction; for example, there may be many oxygen vacancies around the interface between the crystal grains on the LDC surface.

4. Conclusions

A thin membrane (thickness = ~10 μm) made of a lanthanum highly-doped cerium oxide ($\text{La}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$, LDC) was fabricated on a mixed Ni and the LDC porous layer as a hydrogen separation membrane. By performing permeation experiments at 800°C, it was clarified that the hydrogen permeation flux increases with increase in the crystal grain boundary length per unit area on the LDC surface. This increase is also proportional to the square root of hydrogen partial pressure, which means that the permeation flux would be controlled by a surface reaction rate between the adsorbed hydrogen and proton at the crystal grain boundary.

Acknowledgements

The authors express their thanks to Hitachi High-Technologies Corporation for support related to the cross section analysis using an FIB-SEM system.

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