Research Article

Fabrication of a Microtubular $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ti}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Membrane by Electrophoretic Deposition for Hydrogen Production

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Microtubular type $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ti}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSTF) membranes were prepared by electrophoretic deposition (EPD). The oxygen permeation and hydrogen production behavior of the membranes were investigated under various conditions. LSTF green layer was successfully coated onto a carbon rod and, after heat treatment at 1400°C in air, a dense LSTF tubular membrane with a thickness of 250 μm can be obtained. The oxygen permeation and hydrogen production rate were enhanced by CH_4 in the permeate side, and the hydrogen production rate by water splitting was $0.22 \text{ mL}/\text{min}\cdot\text{cm}^2$ at 1000°C . It is believed that hydrogen production via water splitting using these tubular LSTF membranes is possible.

1. Introduction

Hydrogen is considered to be a next generation clean and efficient fuel that can be used in electrochemical devices, such as fuel cells or internal combustion engines, to power vehicles or generate electricity. Hydrogen is normally produced by methane steam reforming ($\text{CH}_4 + 2\text{H}_2\text{O} = 3\text{H}_2 + \text{CO}$) or the electrolysis of water because pure hydrogen does not occur naturally on Earth in large quantities. However, the methane steam reforming releases carbon dioxide into the atmosphere and does not help to decrease greenhouse gases. In addition, the electrolysis of water requires large amounts of electricity to decompose water and produce hydrogen.

Hydrogen production by high temperature water splitting ($\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + 1/2\text{O}_2$) is one of the most important long-term goals in hydrogen fuel production [1, 2]. Since the equilibrium constant of the water splitting reaction is very small, it generates very low concentrations of hydrogen and oxygen, even at high temperatures (0.1% hydrogen and 0.042% oxygen at 1600°C). This limitation of water dissociation can be overcome by controlling the thermodynamic equilibrium. If the produced oxygen or hydrogen can be removed from the reactor, the equilibrium is shifted towards the dissociation of water, thereby increasing the hydrogen production rate up to a realistic level.

Putting this in mind, water splitting via an oxygen transport membrane (OTM) is one of the most promising routes for sustainable hydrogen production without releasing carbon dioxide. Dissociated oxygen can be selectively transported outside the reactor through the OTM, and the hydrogen production rate depends on the rate at which oxygen is removed from the reactor. Therefore, an OTM with high oxygen permeability (i.e., excellent mixed ionic and electronic conductivity and good oxygen surface exchange kinetics [3, 4]) is required.

Perovskite-type oxides have been widely used as oxygen transport membrane materials because of their high oxygen permeability and good durability at high temperatures (both in oxidized and reduced atmospheres). Strontium and cobalt codoped barium ferrite (BSCF) are the most common materials for OTMs. Although BSCF shows excellent oxygen ionic and electronic transport properties, it suffers from a large thermal expansion coefficient and long-term structural and electrochemical instability, especially in atmospheres containing carbon dioxide.

Alternatively, lanthanum and iron codoped strontium titanate ($\text{La}_{1-x}\text{Sr}_x\text{Ti}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSTF)) has been developed as an OTM material by some researchers. Unlike cobalt, which exists at the B site of the perovskite ABO_3 , titanium is less likely to undergo valence changes and provides a more

FIGURE 1: Schematic diagram of the (a) EPD process and (b) sintering process.

stable crystal structure in a reducing atmosphere. The substitution of Fe by Ti is expected to improve durability and to lower the cost of materials. In addition, titanium-doped perovskite materials have been reported to catalyze the methane reforming reaction [5]. In this study, a dense microtubular $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ti}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSTF) membrane was fabricated by electrophoretic deposition (EPD). The microstructure and oxygen permeation behavior of this material were investigated.

2. Experimental Procedure

2.1. Preparation of a Microtubular Membrane by EPD. LSTF powders were synthesized from La_2O_3 (99.9%, YAKURI, Japan), SrCO_3 (99.9%, Sigma Aldrich, USA), TiO_2 (99.9%, High Purity Chemicals, Japan), and Fe_2O_3 (99.9%, High Purity Chemicals, Japan) by a solid state reaction technique. The starting materials were mixed using a planetary ball mill and then calcined at 1000°C for 5 h.

Microtubular LSTF membranes were fabricated using a sealless tube design by electrophoretic deposition (EPD), as shown in Figure 1(a). EPD is a colloidal deposition technique that has been proven to be simple and inexpensive for the production of many advanced ceramics bodies. EPD is recognized for its great potential to economically fabricate thin, dense, and gas-tight electrolytes, as well as porous electrodes for solid oxide fuel cell applications [6].

First, the LSTF powder was dispersed in acetyl acetone. After 15 min of ultrasonication, a stable slurry can be obtained. The LSTF slurry was stable for at least for 24 h. A graphite rod (10 mm in diameter and 50 mm in length), which was used as the substrate, was immersed in the LSTF slurry and 100 V of DC voltage was applied between the graphite rod and the nickel counter electrode for 10 min. The distance between the graphite rod and counter electrode was 13 mm. After the EPD process, a thin LSCF green layer was homogenously formed on the graphite rod. The dip-coating process was conducted using the same LSTF slurry to improve the strength of the membrane. The graphite tube, coated by the LSTF green layer, was finally fired at 1400°C

for 2 h in air to remove the graphite substrate and sinter the LSTF green body. The active surface area of the microtubular membrane was 1.85 cm^2 .

2.2. Characterization. The crystal structure of the microtubular LSTF membranes was analyzed by X-ray diffraction (XRD, RU-200B, Rigaku Co., Ltd., Japan) with Ni-filtered $\text{CuK}\alpha$ radiation. The microstructure was examined by field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan).

The oxygen permeability and hydrogen production rate were measured as a function of temperature by micro gas chromatography (micro-GC, Varian). The membranes were sealed and blocked using Pyrex glass rings on both sides of the alumina tube, as shown in Figure 2. Air or 50% $\text{H}_2\text{O}/\text{Ar}$ was supplied as a feed gas on the upper side of the alumina tube. Also, Ar or 1% CH_4/Ar was supplied as a sweep gas on the bottom side of the alumina. The gas flow rate was 100 mL/min. The oxygen permeability was calculated using (1) and (2), from the oxygen concentration measured by GC in the sweep gas.

In the case of the air || Ar/1% CH_4 system, the oxygen concentration was calculated with (3), using the CH_4 concentration. The overall oxygen permeation rate was also calculated with (1) and (2). The hydrogen production rate was calculated with (4) using the oxygen permeation rate

$$\begin{aligned} \text{O}_2 \text{ flow rate} &= \frac{\text{Ar flow rate} \times \text{O}_2 \text{ concentration}}{\text{Ar concentration}} \\ &= \frac{\text{Ar flow rate} \times \text{O}_2 \text{ concentration}}{1 - \text{O}_2 \text{ concentration}} \end{aligned} \quad (1)$$

$$\text{O}_2 \text{ permeability} = \frac{\text{O}_2 \text{ flow rate}}{\text{Membrane area}} \quad (2)$$

$$\begin{aligned} \text{O}_2 \text{ concentration} &= (\text{Inlet } \text{CH}_4 \text{ concentration} \\ &\quad - \text{Outlet } \text{CH}_4 \text{ concentration}) \times 2 \end{aligned} \quad (3)$$

$$\text{H}_2 \text{ production rate} = \text{O}_2 \text{ permeability} \times 2. \quad (4)$$

FIGURE 2: Characterization set-up for the oxygen permeability measurement and photo images of the microtubular membrane.

FIGURE 3: XRD pattern of the LSTF powder sample heat-treated at 1000°C.

3. Results and Discussion

XRD patterns for the powder sample heat-treated at 1000°C are shown in Figure 3. It was confirmed that the powder sample is $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ti}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and has a single phase of

cubic perovskite with a lattice parameter of 0.3950 nm, cubic lattice symmetry, and a space group of Pm3m [5, 7].

Cross-sectional images of the microtubular LSTF membrane are shown in Figure 4. These show that a uniform and dense LSTF microtubular membrane was successfully

FIGURE 4: Cross-sectional SEM images of the microtubular LSTF membrane.

fabricated; the thickness of the tube is estimated to be approximately $250\ \mu\text{m}$. Although some closed pores are observed in the membrane tube, it seems that these do not affect the gas tightness of the tube. In addition, LSTF particles, which were coated by dip-coating, were uniformly distributed on the tube surface.

Figure 5 shows the oxygen permeability of the LSTF membrane as a function of temperature. It was found that the oxygen permeation rate gradually increased as the operating temperature increased. This result is associated with the increase in the oxygen ion mobility at higher temperatures [8]. The oxygen permeability was higher in the $\text{Ar}/1\% \text{CH}_4 \parallel \text{air}$ system than in the $\text{Ar} \parallel \text{air}$ system. This can be explained by the difference in the oxygen partial pressure between the feed and permeated (sweep) sides. The oxygen partial pressure was much higher in $\text{Ar}/1\% \text{CH}_4$ than in Ar [9, 10]. However, the oxygen permeability was lowest in the $\text{Ar}/1\% \text{CH}_4 \parallel \text{Ar}/50\% \text{H}_2\text{O}$ system ($0.11\ \text{mL}/\text{min}\cdot\text{cm}^2$ at 1000°C). This suggests that hydrogen production should be possible because the permeated oxygen must be originating from the dissociation of water in the feed side.

Figure 6(a) shows the hydrogen production rate of the microtubular LSTF membrane and Figure 6(b) shows the methane conversion and hydrogen selectivity as a function of temperature in the permeated side (sweep) gas of $\text{Ar}/1\% \text{CH}_4$. In this study, hydrogen is produced in two ways: by splitting water in the feed side and by the partial oxidation of methane in the sweep side. Methane, which is supplied in the sweep side, is oxidized by oxygen permeating from the feed side and produces either hydrogen/carbon monoxide (partial oxidation) or water vapor/carbon dioxide mixtures (oxidation).

The open and closed circles indicate the hydrogen production rate, which is derived from water splitting and methane partial oxidation, respectively. The hydrogen production rate by water splitting is $0.22\ \text{mL}/\text{min}\cdot\text{cm}^2$ at 1000°C . Although hydrogen production by water splitting is modest and lower than the values previously reported in the literature, this observed phenomenon indicates that the catalytic thermal dissociation of water vapor can occur in the microtubular LSTF membrane and that the hydrogen

production rate is proportional to the oxygen permeability of the membrane. An interesting feature observed in Figure 6(a) is that the hydrogen production rate by water splitting is much higher than that by methane partial oxidation ($0.05\ \text{mL}/\text{min}\cdot\text{cm}^2$ at 1000°C). It appears that low hydrogen selectivity is responsible for this phenomenon.

The methane conversion and hydrogen selectivity were both low: 4.3% and 22.8% at 1000°C , respectively. However, it appears that these results are somewhat reasonable because the oxygen permeation was small in the $\text{Ar}/1\% \text{CH}_4 \parallel \text{Ar}/50\% \text{H}_2\text{O}$ system. The relatively low hydrogen selectivity might be associated with the poor catalytic activity for partial oxidation at low temperatures. The increase in the hydrogen selectivity at higher temperatures might be caused by the enhanced catalytic activity for partial oxidation at high temperatures.

4. Conclusions

Dense and crack-free microtubular type $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ti}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSTF) membranes were successfully fabricated by electrophoretic deposition (EPD) and dip-coating. It was confirmed that hydrogen production via water splitting is possible using these LSTF microtubular membranes. Oxygen that is produced by water splitting is transported to the sweep side through the LSTF membrane and reacts with methane to produce hydrogen. The oxygen permeability was much higher in $1\% \text{CH}_4/\text{Ar}$ than in Ar , which indicates that oxygen permeation can be significantly accelerated by the presence of CH_4 in the sweep side. Under the conditions of $10\% \text{H}_2\text{O}/\text{Ar}$ (feed side) and $1\% \text{CH}_4/\text{Ar}$ (permeate side), hydrogen was produced in both the feed side and in the permeate side. The total hydrogen production rate of the LSTF microtubular membrane was $0.26\ \text{mL}/\text{min}\cdot\text{cm}^2$ at 1000°C .

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

FIGURE 5: The oxygen permeability of the microtubular LSTF membrane as a function of temperature.

FIGURE 6: The catalytic properties of the microtubular LSTF membrane depending on temperature: (a) hydrogen production rate and (b) CH₄ conversion and H₂ selectivity.

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