

# Hydrogen production in zirconia membrane reactors for use in PEM fuel cells

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## Abstract

A yttria-stabilized zirconia (YSZ) membrane was formed on the surface of a porous  $\alpha$ -alumina support tube by a sol–gel procedure. The membrane was then impregnated with an aqueous solution of  $\text{H}_2\text{PtCl}_6$  or  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and calcined in air at  $500^\circ\text{C}$ , to produce a Pt- or Rh-loaded YSZ membrane. Methane steam reforming (MSR) over the Rh-loaded  $\text{Ce}_{0.15}\text{Zr}_{0.85}\text{O}_2$  catalyst was carried out in a membrane reactor using the Pt-loaded YSZ membrane. Methane conversion in the membrane reactor was 20% higher than that in a packed bed reactor due to the high permeation rate of hydrogen compared to the reaction rate. In addition, Pt- and Rh-loaded YSZ membranes were also examined for the selective oxidation of CO from a mixture of  $\text{H}_2$  and CO without any packed catalysts. When  $\text{O}_2$  was added to the feed, CO was oxidized in the Pt-loaded YSZ layer and the CO concentration of 10,000 ppm on the feed side was decreased to below 30 ppm (detection limit) at  $150^\circ\text{C}$ . Meanwhile the oxidation of CO was suppressed at higher temperatures because of the consumption of  $\text{O}_2$  as a result of the catalytic oxidation of  $\text{H}_2$ .

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## 1. Introduction

Application of membrane technologies to the production and purification of hydrogen for use in a proton exchange membrane fuel cell (PEMFC) promises to improve overall energy efficiency. The steam reforming of hydrocarbons, such as naphtha or natural gas is currently the most economic method for hydrogen production and is usually operated in a temperature range of  $750$ – $900^\circ\text{C}$ . A palladium-based membrane reactor can be used to shift the thermodynamic

equilibrium of methane steam reforming (MSR) [1–4]. As a result, it is possible to achieve practical methane conversion by MSR in a lower temperature range of  $500$ – $600^\circ\text{C}$ . However, palladium-based membranes are not always suitable for applications for membrane reactors because they are susceptible to damage by sulfur contaminants and coking during hydrogenation. Although porous silica ( $\text{SiO}_2$ ) membranes potentially offer a high selective permeation for hydrogen, the densification of  $\text{SiO}_2$  by exposure to water vapor leads to a decrease in gas permeation [5–7].

Carbon monoxide is formed as a byproduct of MSR and severely poisons the Pt electro-catalyst in the PEMFC. Hasegawa et al. [8,9] prepared a Pt-loaded Y-type zeolite

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Nomenclature	
$p$	partial pressure of methane, Pa
$v$	flow rate, $\text{m}^3 \text{s}^{-1}$
$X$	conversion of methane
Suffixes	
f	feed side
p	permeate side
r	retentate side

membrane (hereafter referred to as a Pt/NaY membrane) and investigated the selective oxidation of CO in hydrogen. The rates of oxidation of CO as well as the CO/H<sub>2</sub> selectivity were remarkably high, compared to the same reaction in a packed bed reactor. Thus the Pt/NaY membrane decreased CO concentrations to below 10 ppm from 10,000 ppm in the feed. A mathematical model of CO oxidation in Pt/NaY catalytic membrane has been reported [10]. Hasegawa et al. [11] also prepared a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membrane, which was loaded with rhodium and then coated with an additional hydrogen-selective SiO<sub>2</sub> layer (hereafter referred to as a SiO<sub>2</sub>/Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membrane) by a sol-gel technique. The H<sub>2</sub>/CO separation factor for the SiO<sub>2</sub> layer was in excess of 100, and the slight amount of CO that leaked from the SiO<sub>2</sub> layer was oxidized by the Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer. Thus, the use of this composite membrane led to a decrease in the CO content in hydrogen from 5% in the feed to 48 ppm in the product. The performances of the Pt/NaY and SiO<sub>2</sub>/Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membranes were compared, and the superiority of the catalytically active membrane reactors over packed bed reactors was discussed [12].

Zirconia and yttria-stabilized zirconia (YSZ) membranes were prepared on a porous  $\alpha$ -alumina support tube by a sol-gel procedure and then modified by impregnation with Pt or Ni to improve H<sub>2</sub> permselectivity [13,14]. The ideal H<sub>2</sub>/CO<sub>2</sub> selectivity at 500 °C through the Pt-loaded YSZ (Pt/YSZ) and Ni-loaded YSZ (Ni/YSZ) membranes was increased to 22 and 29, respectively [14]. Thus, it appears possible that noble-metal-loaded YSZ membranes with a high hydrogen permeability could be used as hydrogen selective membranes in a membrane reactor for MSR as well as the catalytic membrane for selective CO oxidation. We propose such a reforming process consisting of zirconia-based membrane reactors as illustrated in Fig. 1.

In this study, a Pt/YSZ membrane was used as part of a membrane reactor system for H<sub>2</sub> production in low-temperature MSR. The packed catalyst used in the membrane reactor was Rh-loaded Ce<sub>0.15</sub>Zr<sub>0.85</sub>O<sub>2</sub>, which showed a high activity with respect to MSR at 500–600 °C [15]. The conversion of methane and CO selectivity were determined. In the second part, the selective CO oxidation through Pt/YSZ membrane was investigated using a mixture of H<sub>2</sub>, O<sub>2</sub> and CO at 100–250 °C. The concentration

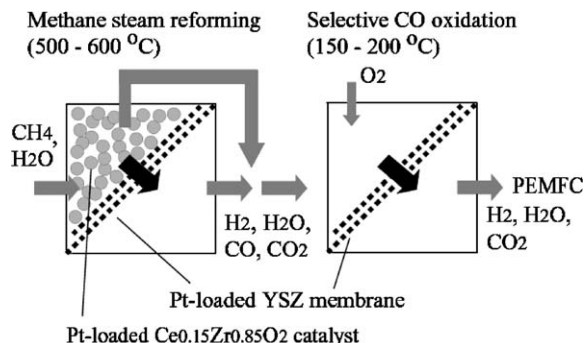


Fig. 1. Membrane reactor system for use in hydrogen production.

of CO in the feed was maintained at 10,000 ppm, and the concentration of O<sub>2</sub> in the feed was varied.

## 2. Experimental

### 2.1. Preparation of noble-metal-loaded zirconia membranes

A zirconia sol was synthesized in an atmosphere of dry nitrogen at room temperature [13]. A mixture of zirconium *n*-propoxide, 1-propanol, 1,5-diamino pentane and yttrium nitrate was stirred for 30 min, and glacial acetic acid was added to produce water via esterification. The stirring was continued for 40 h, and concentrated nitric acid was then added dropwise to complete the hydrolysis. The molar ratio of yttrium to zirconium in the zirconia sol was fixed at 0.08. A YSZ membrane was prepared on a porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support tube (NOK Corp., Japan, outer diameter = 2.1 mm, inner diameter = 1.7 mm, length = 200 mm, void fraction = 39%, average pore size = 150 nm). The outer surface, except for an area of 20 mm in the central region, was coated with a glass sealant. The support tube was immersed in the sol for 1 min, dried in air at ambient temperature for 12 h, and then calcined in air at 500 °C for 1 h at a heating rate of 1 K min<sup>-1</sup>. The dipping-firing process was repeated for a total of five times. The YSZ membrane was modified by immersing it in a solution of 0.10 mol L<sup>-1</sup> H<sub>2</sub>PtCl<sub>6</sub> or RhCl<sub>3</sub> · 3H<sub>2</sub>O for 30 min. The membrane was dried in air at room temperature for 12 h and then calcined in air at 300 °C. The metal loading procedure was repeated for a total of four times. The morphology of the membrane was observed by scanning electron microscopy (Hitachi, FE-SEM S-5200). The amount of Pt and Rh loading was determined by EDX (Kevex, Delta Class).

### 2.2. Permeation tests

The permeation properties of the membranes were determined through the use of H<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub> at 100 °C. The single-component gas and argon as the sweep gas were

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